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Jahn-Teller Distortions in Transition Metal Compounds, and their Importance in Functional Molecular and Inorganic Materials†

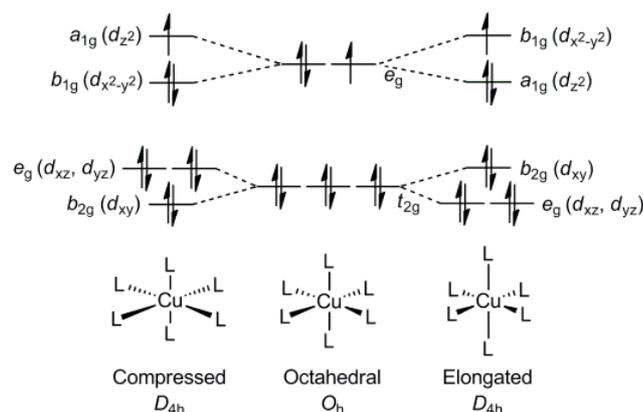
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This *tutorial review* discusses the structural and electronic consequences of the Jahn-Teller effect in transition metal complexes, focussing on copper(II) compounds which tend to be the most studied. The nature of a Jahn-Teller distortion in molecular complexes and extended lattices can be manipulated by application of pressure or temperature, by doping a molecule into a host lattice, or simply by molecular design. Many of these results have been achieved using compounds with a *trans*-[CuX₄Y₂] coordination sphere, which seems to afford copper centres that are particularly sensitive to their environment. Jahn-Teller distortions lead to some unusual phenomena in molecular magnetism, and are important to the functionality of important classes of conducting and superconducting ceramics.

Introduction

In 1937, Hermann Jahn and Edward Teller used symmetry arguments to demonstrate that a non-linear system in a degenerate energy state cannot be stable. It will spontaneously distort itself in some way so that its energy state will split, in such a way as to remove its degeneracy.¹ Such a distortion always has the effect of lowering the energy of the system to a small extent, and is thus energetically favourable (Scheme 1). This prediction has been borne out in practise in many areas of chemistry.²



Scheme 1. The two prototypical Jahn-Teller distortions of an octahedral copper(II) complex. Both distortions lower the energies of two electrons in the e_g subshell, while raising the energy of only one. Thus, there is a net reduction in electronic energy upon distortion of the complex. All Jahn-Teller distortions are driven by a comparable energy stabilisation.

Jahn-Teller distortions are most often associated with transition metal centres, either in molecular complexes or in ionic lattices. They are important, because Jahn-Teller effects strongly affect

the electron distribution within a material or molecule, as well as the arrangement of their atoms. Thus, Jahn-Teller distortions of the metal ions in a ceramic material can have large consequences for its conductivity, magnetism or other physical properties,² examples of which are described below. Jahn-Teller distortions also occur in several types of organic radical,² including some alkyl and aryl radicals and ions,³ fulleride anions⁴ and ionised carbon nanotubes.⁵ Although they are phenomenologically distinct, closely related effects (Peierls distortions) are also seen in linear chain structures including solid lattices,⁶ conducting polymers⁶ and chains of atoms on surfaces.⁷

In transition metal centres, the splitting of the *d*-energy levels in a ligand field can often lead to degenerate electron configurations, that are subject to Jahn-Teller effects. For example, in octahedral symmetry *d*¹, *d*², *d*⁴ (both spin-states), *d*⁵ (low-spin), *d*⁶ (high-spin), *d*⁷ (low-spin) and *d*⁹ transition ions all have orbitally degenerate electron configurations, that should be Jahn-Teller-active. In practise, ions with degenerate occupancy of the e_g subshell nearly always exhibit strong Jahn-Teller distortions, because of the M–L antibonding character of those orbitals. Thus, the Jahn-Teller effect is pronounced in six-coordinate complexes of high-spin *d*⁴ [chromium(II), manganese(III)], low-spin *d*⁷ [cobalt(II)] and *d*⁹ [copper(II)] ions. It is also important in less common oxidation levels of other transition ions with those *d*-electron counts. The other *d*-electron configurations on the above list show degeneracy in the t_{2g} subshell, which makes a much weaker, or zero, contribution to M–L bonding. In those cases, Jahn-Teller distortions are more subtle and can be so weak as to be unobservable using routine characterisation techniques (although not always – see below).⁸

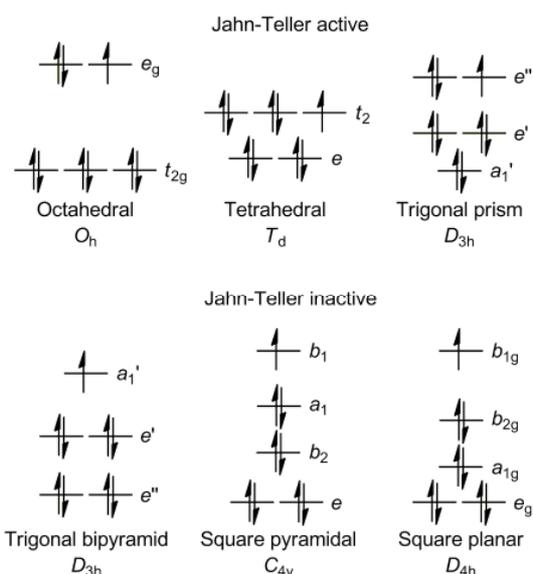
Nearly any other coordination geometry can also be subject to a Jahn-Teller distortion in principle, as long as its *d*-electron count leads to a degenerate ground state (see below). A notable exception are linear complexes, which are not treated by the Jahn-Teller theorem.¹ While open-shell two-coordinate compounds

often show bent coordination geometries, these reflect the formation of additional agostic M–L bonding interactions rather than Jahn-Teller phenomena.⁹

This article describes the measurement, manipulation and consequences of the Jahn-Teller effect in transition metal chemistry. Six-coordinate copper(II) compounds are by far the most common, and the most studied, molecular Jahn-Teller system so they will feature prominently in the discussion.¹⁰⁻¹² Systems containing other ions and coordination geometries will also be referred to where appropriate, however.²

Definitions of terms

A common point of confusion in copper chemistry in particular, is that not all copper(II) complexes are subject to the Jahn-Teller effect. Complexes with octahedral and tetrahedral geometries are well known to be Jahn-Teller active,¹⁰ while it has recently been pointed out that the rare trigonal prismatic coordination geometry also leads to a strong Jahn-Teller distortion in d^9 complexes.¹³ Notably, Jahn-Teller distortions in the two six-coordinate geometries are different. While octahedral copper(II) complexes exhibit the well-known *trans*-elongation along one L–Cu–L axis, trigonal prismatic examples instead undergo an elongation of two *cis* Cu–L bonds (Fig. 1). This can be understood as a consequence of splitting the degenerate e'' orbital pair (d_{xz} and d_{yz} , Scheme 2), which are oriented towards the donor groups in a trigonal prismatic ligand sphere.¹³ In tetrahedral examples, splitting of the t_2 orbital manifold is reflected in the bond angles about the metal ion, rather than its bond lengths, and leads to a flattening of the coordination sphere towards the square planar limit (termed a “tetragonal distortion”).^{10,14}



Scheme 2. Crystal field splittings for the common coordination geometries of copper(II) complexes, grouped according to whether they display Jahn-Teller distortions. The splittings between energy levels are indicative only, and are not drawn to scale.

In contrast, five-coordinate and square planar copper(II) complexes are not Jahn-Teller active, because the singly occupied

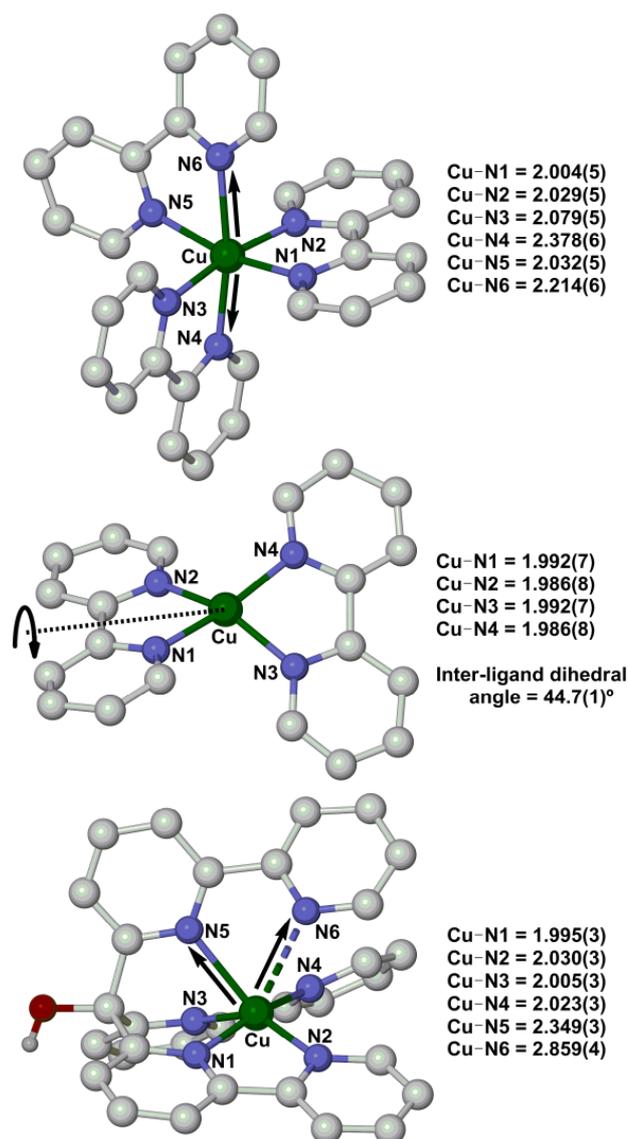


Fig. 1 Crystal structures of copper(II) complexes with 2,2'-bipyridyl ligation, with arrows illustrating different Jahn-Teller distortions that occur (Å, °). Top, octahedral $[\text{Cu}(\text{bipy})_3]^{2+}$;¹⁶ middle, tetrahedral $[\text{Cu}(\text{bipy})_2]^{2+}$;¹⁷ bottom, a trigonal prismatic complex of a *tris*-bipyridyl tripodal ligand.¹⁸ An undistorted $[\text{Cu}(\text{bipy})_2]^{2+}$ centre would show an inter-ligand dihedral angle of 90° .

d -orbital in those geometries is not degenerate (Scheme 2). In particular, the most common coordination geometry for copper(II) complexes is square-pyramidal, in which the apical Cu–L bond is longer than the basal ones by up to 0.5 Å. The lengthened apical bond is *not* a Jahn-Teller elongation in this case. Rather, it is simply a consequence of the double electron occupancy of the antibonding a_1 (d_{z^2}) orbital, and the single occupancy of b_1 ($d_{x^2-y^2}$), leading to increased antibonding electron density along the apical Cu–L axis.¹⁵ Second-order pseudo-Jahn-Teller effects (see below) can occur in five-coordinate complexes, however, leading to more subtle structural changes.

While Jahn-Teller elongations and compressions are both theoretically possible in octahedral complexes, in practise Jahn-Teller elongations are more common by far. This is particularly

elongation, that is disordered between the Cl(2)–Cu–Cl(2ⁱ) and Cl(3)–Cu–Cl(3ⁱ) axes (Fig. 2).

Such ambiguities can be resolved by EXAFS, whose short timescale yields true bond distances that are uncontaminated by disorder. In this case, an EXAFS study yielded a rhombic coordination sphere with Cu–Cl = 2.276(14), 2.377(18) and 2.83(5) Å at 10 K. The average of the two higher values, 2.60 Å, agrees perfectly with the two longer Cu–Cl distances from the crystallographic data above (Fig. 2).²⁵ The anomalous EPR data reflect the fact that g_1 and g_2 are averaged in the spectrum because of the disorder. The “true” g -values of the copper centres were obtained by replacing 80 % of the copper in the material with diamagnetic cadmium(II) ions.²⁶ The remaining copper ions in [3-ClC₆H₄NH₃]₈Cd_{0.8}Cu_{0.2}Cl₁₀ are well-separated and magnetically isolated, giving a higher resolution single-ion EPR spectrum with $g_1 = 2.30$, $g_2 = 2.09$, $g_3 = 2.04$. That maps perfectly onto the g -pattern expected for a Jahn-Teller-elongated, $\{d_{x^2-y^2}\}^1$ copper(II) centre ($g_1 > g_2 \geq g_3 > 2.0023$),²⁴ while the true g_1 and g_2 values agree well with the averaged g_{\perp} value (2.20) from the initial study.²³

A survey of copper(II) complexes that are known to show Jahn-Teller disorder is given in the ESI†. Most of these involve polyatomic organic ligands, which complicates the interpretation of the crystal structures. The size and direction of the ligand donor atom thermal ellipsoids (Fig. 2) are not a good indicator of masked disorder in that case, since they contain contributions from every covalent bond those atoms are involved in (not just the Cu–L bond). That issue can be resolved by a TLS analysis, which deconvolutes the thermal ellipsoids to provide a measure of the atomic displacements along each bond in the molecule.^{12,27}

TLS analyses are easily obtained using the program PLATON.²⁸ The Jahn-Teller disorder in [3-ClC₆H₄NH₃]₈CuCl₁₀ is static, and invariant with temperature. However, in many cases such disorder is dynamic and reflects fluxionality of the Jahn-Teller distortion in the molecule. This leads to temperature-dependent crystallographic and EPR behaviour, which show apparently “averaged” data at higher temperatures but where the true structure and g -values are slowly frozen out as the temperature is lowered.^{12,27} Analysis of the temperature dependence of Jahn-Teller disorder can yield the relative energies of the different orientations of the disorder axis, which depend on the steric properties of the crystal lattice as much as on the individual molecule (Fig. 3). The analysis in Fig. 3 was performed by modelling the metal/ligand vibrational potentials in isolated molecules,¹⁰ but more sophisticated treatments based on Monte Carlo simulations can reproduce cooperative Jahn-Teller fluxionality in an extended crystalline lattice.²⁹

Where Jahn-Teller disorder exists, placing a crystal under uniaxial stress can cause the Jahn-Teller elongation to order in an orientation parallel to the applied tension. This has been demonstrated in salts containing the [Cu(NO₂)₆]⁴⁻ ion.³¹

Such detailed studies of Jahn-Teller fluxionality have mostly been carried out using copper(II) complexes.^{10,27} However, comparable Jahn-Teller disorder has also been identified in six-coordinate complexes of other metal ions including vanadium(III),³² cobalt(II),³³ nickel(III),³⁴ rhodium(II)³⁵ and silver(II).³⁶

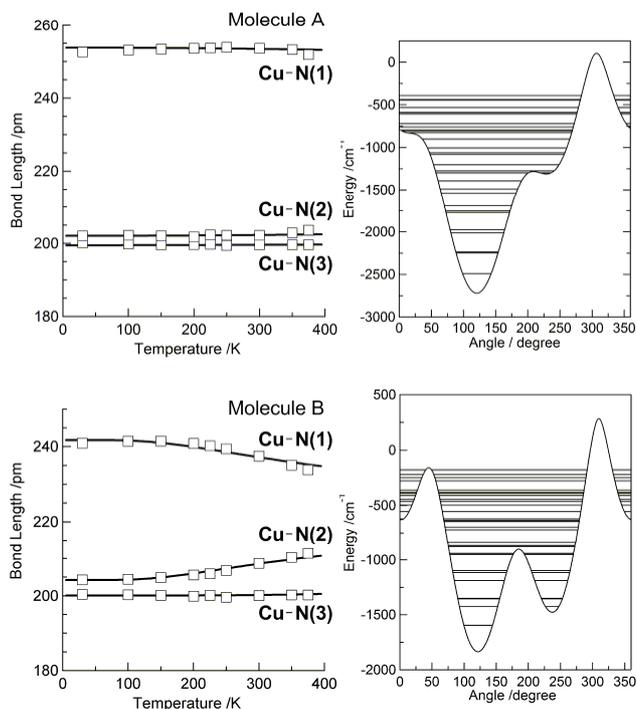
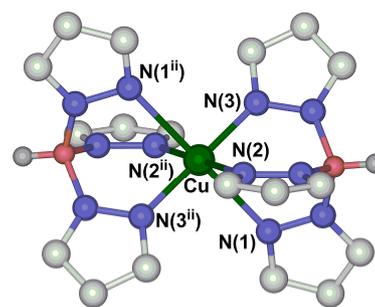


Fig. 3 Left: temperature dependence of the Cu–N bond lengths in two unique molecules in the crystal structure of [CuTp₂] (Tp[−] = hydrido-*tris*-pyrazolylborate). The lines show the fit of the data to a model based on the electronic and vibrational energies of the copper coordination sphere. Right: the results of that calculation, plotted as the electronic and vibrational energies of the molecules in different Jahn-Teller states. The minima in the plots correspond to orientation of the Jahn-Teller distortion along the three different N–Cu–N axes in the molecules, with N(1)–Cu(1)–N(1ⁱⁱ) being the most stable. Symmetry code (ii): 1– x , 1– y , 1– z .³⁰

Manipulating Jahn-Teller distortions under pressure

Most compounds of copper(II) behave similarly to those of other transition metal ions under hydrostatic pressure, in that a general contraction of M–L bonds is observed as the pressure is increased.^{37–39} This bond shortening tends to be more pronounced for the longer (weaker) Cu–L bonds in a Jahn-Teller elongated copper(II) centre, which can lead to a phase change under pressure,³⁹ or to the formation of new intermolecular Cu–L interactions as the atoms are forced together.^{40–42} No more notable structural changes are usually observed.

However, two copper(II) compounds are known where application of hydrostatic pressure leads to rotation of the Jahn-Teller elongation axis about the metal ion, from one L–Cu–L axis to another. First to be discovered was the deuterated Tutton’s salt,

[ND₄]₂[Cu(OD₂)₆][SO₄]₂. The Jahn-Teller elongation of the hexa-aqua copper(II) centres is disordered between different O–Cu–O axes at above *ca.* 150 K, but becomes crystallographically ordered in one position below that temperature. Interestingly, however, the orientation of the ordered elongation is different in the protio material [NH₄]₂[Cu(OH₂)₆][SO₄]₂, and deuterated [ND₄]₂[Cu(OD₂)₆][SO₄]₂.⁴³ The deuterated crystal reverts to the protio phase under pressure, so that the Jahn-Teller elongation axis switches from one O–Cu–O axis to another (Fig. 4).^{43,44} The critical pressure for this phase transition is *ca.* 500 bar (0.05 GPa[‡]) at room temperature, is temperature dependent, and shows a pressure hysteresis when cycled close to room temperature.⁴⁵ Hence, the high-pressure phase of [ND₄]₂[Cu(OD₂)₆][SO₄]₂ can also be obtained at 1 bar[‡], where it is metastable, if the crystal is kept below 297 K when the pressure is released.⁴⁶ A pressure-induced Jahn-Teller reorientation also occurs in the chromium analogue [ND₄]₂[Cr(OD₂)₆][SO₄]₂,⁴⁷ but not in M₂[Cu(OH₂)₆][SO₄]₂ (M⁺ = NH₄⁺, K⁺) or Rb₂[Cr(OD₂)₆][SO₄]₂ which behave normally under pressure.^{44,46,47}

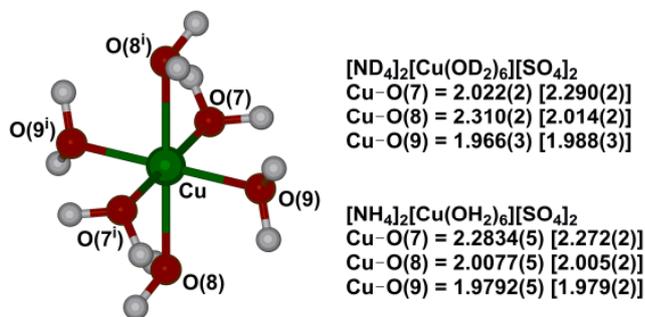


Fig. 4 Neutron diffraction structure of the [Cu(OD₂)₆]²⁺ ion in [ND₄]₂[Cu(OD₂)₆][SO₄]₂ at 15 K, with the Cu–O bond lengths for the deuterated and protio compounds at the same temperature, at 1 bar and [in square brackets] at 1.5 kbar[‡] (Å).^{43,46} Symmetry code (i): $-x, -y, -z$.

The other example is *catena*-[CuF₂(OH₂)₂(μ -pyrazine)], which crystallises as a 1D coordination polymer, with the co-parallel chains being linked into three dimensions by O–H...F hydrogen bonding (Fig. 5).⁴⁸ The centrosymmetric copper ions have a *trans, trans, trans* disposition of fluoro, aqua and pyrazine N-donor ligands, with a pronounced pseudo-Jahn-Teller elongation lying along the N–Cu–N axis at ambient pressure between 20 and 298 K. As the pressure is increased at 298 K, the compound undergoes two abrupt structural transitions at 0.9 GPa and 3.1 GPa. These were originally proposed to involve the consecutive reorientation of the Jahn-Teller elongation along the O–Cu–O and F–Cu–F directions.⁴⁹

A new, more detailed crystallographic study has partially borne out that proposal, in that the transition at 0.9 GPa does indeed involve migration of the Jahn-Teller elongation axis to the O–Cu–O axis, as described (Fig. 5).⁴² This is reflected in the material's magnetic response, which becomes more strongly antiferromagnetic in the intermediate-pressure phase. That is caused by reorientation of the copper $d_{x^2-y^2}$ magnetic orbital from being perpendicular to, to parallel with, the direction of the coordination polymer chain.⁴⁹ However, single crystal structures

above 3.3 GPa instead showed a new phase with a tripled unit cell, in which two out of every three coordination polymer chains become covalently linked through bridging fluoro ligands. Differences in the structural data for the highest pressure phase between this study and the earlier one were noted, however, and have still to be reconciled at the time of writing.⁴²

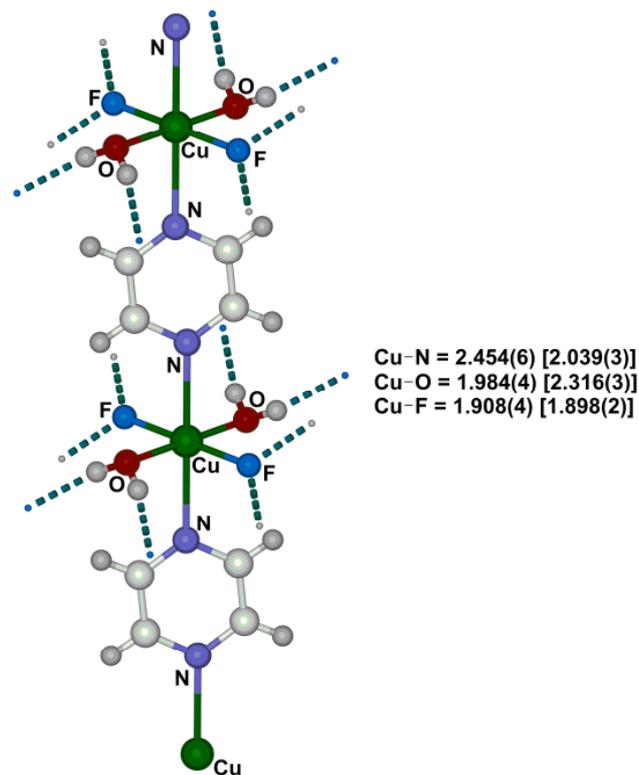


Fig. 5 Crystal structure of *catena*-[CuF₂(OH₂)₂(μ -pyrazine)] at ambient pressure, at 150 K.⁴⁸ Bond lengths are shown at ambient pressure, and [in square brackets] at 1.2 GPa (Å).⁴² The O–H...F hydrogen bonds shown link the co-parallel chains in the lattice into a 3D network.

A comparable, *temperature*-dependent switching of a Jahn-Teller elongation axis, which leads to a magnetic transition in a family of copper(II) coordination polymers, is described below.

A different type of pressure-induced switching occurs in Rb₂CuCl₄·2H₂O, which contains layers of discrete *trans*-[CuCl₄(OH₂)₂]²⁻ octahedra linked by O–H...Cl hydrogen bonds, with a pseudo-Jahn-Teller elongation along one Cl–Cu–Cl axis. Consistent with this, a copper EXAFS study showed three distinct scatterers under ambient conditions at distances Cu–O = 2.00(5), and Cu–Cl = 2.25(5) and 2.85(5) Å. Application of hydrostatic pressure at first showed a typical gradual contraction of all these distances, before an abrupt transition at 16 GPa. Above this pressure, the Cu–O distance is unchanged at 1.96 Å, but all four chlorine scatterers in the copper EXAFS experiment are now equivalent at Cu–Cl = 2.25 Å. This indicates suppression, rather than reorientation, of the pseudo-Jahn-Teller distortion in the complex under pressure.⁵⁰

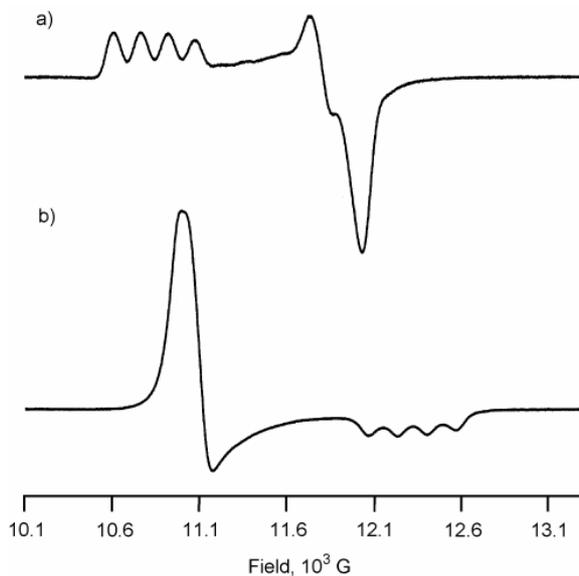
Comparable behaviour had been proposed for some layered perovskites of type M₂CuCl₄ (M⁺ = an alkali metal or primary

ammonium ion). These contain layers of *trans*-[CuCl₂(μ-Cl)₄]²⁻ octahedra, formed from pseudo-Jahn-Teller copper ions linked by alternating Cu...Cl-Cu bridges. Application of pressure leads to significant changes to their magnetic response, and vibrational and UV/vis spectra, which has been interpreted as indicating a disappearance (quenching) of the Jahn-Teller distortion when M⁺ = Rb⁺ or EtNH₃⁺.⁵¹ More recent structural studies under pressure, from diffraction or EXAFS methods, have not always been consistent with that conclusion however, and have shown that canting of the [CuCl₂(μ-Cl)₄]²⁻ layers can account for at least some of the magnetic and spectroscopic observations while retaining a pseudo-Jahn-Teller elongation at the copper centres. Currently it seems unlikely that Jahn-Teller quenching occurs in M₂CuCl₄ materials, at least at pressures below *ca.* 16 GPa.⁵¹

15

Manipulating Jahn-Teller distortions by molecular design

Some years ago, we showed that the EPR spectrum of [Cu(L^{Mes})₂][ClO₄]₂ (Mes = 2,4,6-trimethylphenyl; Scheme 4) is unprecedented for a six-coordinate copper(II) complex, and clearly indicates a {d_{z²}}¹ electron configuration at the copper ion (Fig. 6).⁵² The more usual disordered Jahn-Teller-elongated {d_{x²-y²}}¹ structure could be ruled out for two reasons. First, the same spectrum (with minor differences) is observed in solution as well as in the solid state, ruling it out as a crystallographic artifact. Second, the observed values g_⊥ = 2.20 and g_∥ = 2.01 (in frozen MeCN solution) agree well with the g_⊥ > g_∥ = 2.0023 pattern expected for a {d_{z²}}¹ radical.²⁴ In contrast, disordered Jahn-Teller elongated species with such an “inverse” pattern of g-values usually show higher-than-expected values of g_∥ (see above).^{12,27}

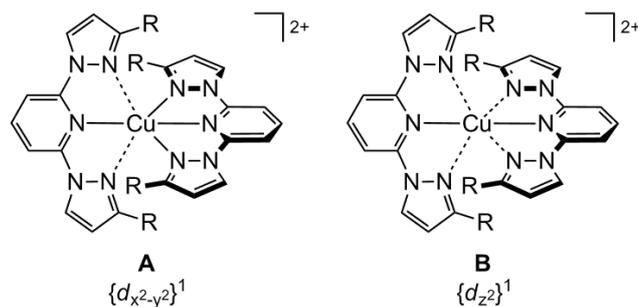


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Fig. 6 Q-band powder EPR spectra at 10 K of two complexes related to those in Scheme 4, with: a) structure A (without Jahn-Teller disorder); and b) structure B (Scheme 4).¹² The four-line splitting in each spectrum arises from hyperfine coupling to the Cu nucleus (^{63,65}Cu, I = 3/2).

35 The {d_{z²}}¹ electronic structure of [Cu(L^{Mes})₂]²⁺ corresponds to structure B in Scheme 4, with four long Cu-N{pyrazole} distances.⁵² Importantly this is not a Jahn-Teller compression,

because the e_g d-orbitals are not degenerate in the idealised D_{2d} symmetry of these complexes.¹² Rather, it corresponds to a suppression of the expected pseudo-Jahn-Teller elongation (structure A, Scheme 4). Similarly unusual EPR spectra are shown by salts of [Cu(L^{iPr})₂]²⁺ and [Cu(L^{Ph})₂]²⁺ in the solid and solution phases,¹² but not by the parent complex [Cu(bpp)]²⁺ which behaves like a typical Jahn-Teller elongated complex with this ligand type.⁵² Hence, the unusual electronic structures of [Cu(L^R)₂]²⁺ (R ≠ H) are probably sterically driven. The bulky distal substituents prevent any contraction of the Cu-N{pyrazole} bonds, forcing them all to be comparably long as observed.



Scheme 4 The structures and ground-state configurations adopted by [Cu(bpp)]²⁺ (R = H; structure A) and its derivatives [Cu(L^R)₂]²⁺ (R = *i*Pr, Ph or Mes; structure B). Short and long Cu-N bonds are indicated by solid and dashed lines, respectively].

55

Structure B can also be imposed on other related copper(II) complexes of linear tridentate ligands by steric hindrance (as above),⁵³ by ligand conformational strain,⁵³ and by tuning the basicities of the ligand donor atoms.⁵⁴ In the latter case, structure B is obtained in the absence of steric hindrance, if the distal ligand-donor groups are less basic than the central one. In the latter regard, we have also unexpectedly observed that [Cu(bpp)]²⁺ itself exhibits structure A as a pure compound, but transforms to structure B when doped into a host lattice, in [M_{0.95}Cu_{0.05}(bpp)₂][BF₄]₂ (M²⁺ = Fe²⁺ or Zn²⁺).⁵⁵ The lower basicity of the pyrazole donor groups in [Cu(bpp)]²⁺, compared to the central pyridyl donor, apparently makes structures A and B close in energy. The complex is therefore forced to adopt structure B in a rigid host lattice, that cannot undergo the local structural rearrangements required to accommodate a dopant site with structure A. Comparable phenomena have been seen in a small number of inorganic materials containing copper(II) dopant ions, like K₂Cu_xZn_{1-x}F₄ which also adopts a {d_{z²}}¹ electronic structure when *x* is small.¹²

75 There have been two recent observations of copper(II) complexes undergoing a temperature-dependent transition between structures A and B. In one example, a transition from structure B towards structure A was observed on cooling in a complex with a static Jahn-Teller structure, which was associated with the freezing out of anion disorder in the structure.⁵⁴ In the other, unusual EPR behaviour in a fluxional Jahn-Teller crystal implied that a fraction of the sample adopts a {d_{z²}}¹ configuration as the temperature is raised.⁵⁶ That situation is analogous to Fig. 3, but where one of the minima in the Jahn-Teller potential surface corresponds to an axial compression.

85

Structure B in molecular complexes has only been found in compounds with D_{2d} symmetry, like those in Scheme 4. Notably, these are stereochemically analogous to the *trans*- $[\text{CuCl}_4(\text{OH}_2)_2]^{2-}$ ion in $\text{Rb}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$, which undergoes Jahn-Teller quenching under pressure (see above).⁵⁰ Moreover, most of the copper(II) sites in inorganic materials that adopt $\{d_{z^2}\}^1$ ground states also have *trans*- $[\text{CuX}_4\text{Y}_2]$ coordination geometries.^{12,57} The electronic structure of copper(II) ions in D_{2d} symmetry seems to be unusually sensitive to their local environment.

Exceptions to the rule

As always, there are rare exceptions to the rules discussed in the previous sections. Jahn-Teller distortions in six-coordinate complexes with degeneracy in the t_{2g} orbital manifold are usually small, because of the weak influence of those electrons on M-L σ -bonding.⁸ However, a few such complexes containing tridentate ligands related to terpyridine exhibit strong angular structural distortions away from the idealised D_{2d} symmetry (Fig. 7).^{58,59} Calculations have implied that this unusual stereochemistry is promoted by ligands imposing a narrow *cis*-bite angle on the metal.⁶⁰ For example, the iron(II) compound in Fig. 7 has an intra-chelate *cis*-N-Fe-N angle of 72° , much lower than the ideal value of 90° . Other unexpectedly strong Jahn-Teller distortions of t_{2g} -degenerate ions are also occasionally seen in oxide materials.⁶¹

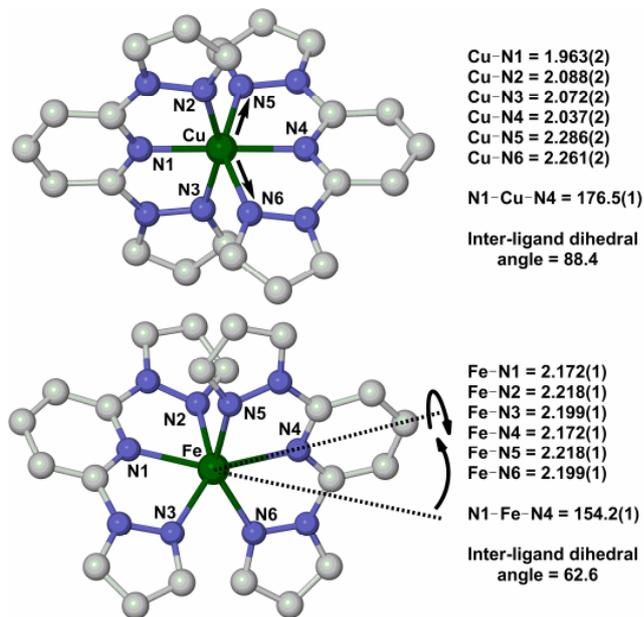


Fig. 7 Crystal structures of $[\text{Cu}(\text{bpp})_2][\text{BF}_4]_2$ (top)^{52,62} and high-spin $[\text{Fe}(\text{bpp})_2][\text{PF}_6]_2$ (bottom; $\text{bpp} = 2,6\text{-di}\{\text{pyrazol-1-yl}\}\text{pyridine}$),⁶⁰ showing their different Jahn-Teller distortions (\AA , $^\circ$). The copper structure is one of the three unique molecules in the low temperature polymorph of that compound.⁶²

Although the vast majority of square planar metal ions are low-spin, high-spin examples are known in a handful of iron oxide materials like SrFeO_2 . The first high-spin square-planar complexes have recently been obtained, in salts of $[\text{FeL}_2]^{2-}$ ($\text{LH}_2 = \text{meso-3,4-dihydroxy-oxolane}$). A high-spin d^6 ion with D_{4h}

symmetry is Jahn-Teller active. Although the crystallographic distortion in the compound is small, calculations imply that it has an important energetic role in stabilising the high-spin square planar site by reducing Fe-O covalency.⁶³

Jahn-Teller Effects in Molecular Magnetism

A bulk magnet retains its magnetisation when removed from a magnetic field. This requires strong coupling interactions between the electron spins in the material, whether they are localised electrons in an ionic or molecular solid, or itinerant electrons in a metal. Single molecule magnets (SMMs) are compounds whose individual molecules also retain magnetisation outside an applied field, albeit only at very low temperatures of <5 K.⁶⁴ They are of great current interest for quantum information storage applications,⁶⁵ and also for potential uses as magnetic refrigerants.⁶⁶

The best-known SMMs are polymetallic complexes with high-spin magnetic ground states, arising from ferromagnetic coupling of the individual metal ions in the molecule. The effect also requires a strong magnetic anisotropy in the molecule; that is, its magnetic moment must be different in different directions. Manganese(III) complexes meet the latter criterion particularly well, because the Jahn-Teller elongation exhibited by six-coordinate, high-spin d^4 manganese(III) ions lead to an anisotropic distribution of d -electron spins.

The most studied SMMs were also the first to be discovered, namely the “ Mn_{12} ” complex $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{MeCO}_2\text{H} \cdot 4\text{H}_2\text{O}$ and its derivatives (Fig. 8).⁶⁷ The acetate ligands can easily be replaced with other carboxylates or different oxanion ligands, leading to a large family of compounds that all show SMM behaviour. Their effectiveness as SMMs stems from their disk-like molecular structures, comprising a central $[\text{Mn}^{\text{IV}}_4\text{O}_4]$ heterocubane surrounded by a belt of eight Mn^{III} ions (Fig. 8). The Jahn-Teller elongations of the Mn^{III} centres are aligned approximately perpendicular to the plane of the disk, imparting a highly anisotropic magnetic structure to the molecule as a whole.

Unusually, Mn_{12} derivatives can adopt one of two different isomeric structures with different SMM properties. This is characterised by the effective energy barrier to the reorientation of their magnetisation in an alternating magnetic field (U_{eff}), which is *ca.* 60 K in one isomer (the high-temperature or slow-relaxing form) and *ca.* 40 K in the other (the low-temperature or fast-relaxing form).⁶⁷ The isomers differ in the orientation of the Jahn-Teller elongation in one Mn^{III} ion, which is perpendicular to the plane of the disk in the slow-relaxing isomer, but lies within the disk in the fast-relaxing form (Fig. 8). This makes the magnetic structure of the fast-relaxing molecule less anisotropic, thus lowering U_{eff} and reducing its effectiveness as an SMM.

In a small number of cases, both isomers of the same Mn_{12} derivative can be obtained in pure form.⁶⁸ In one such example, $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2t\text{Bu})_{16}(\text{H}_2\text{O})_4] \cdot \text{CH}_2\text{Cl}_2 \cdot \text{MeNO}_2$ (Fig. 8), placing crystals of the fast-relaxing isomer under hydrostatic pressure gradually converts it into the slow-relaxing form. This conversion occurs gradually as the pressure is raised, from ambient to 1.4 GPa.⁶⁹

A very different phenomenon is shown by some copper(II) complexes of nitronyl nitroxide (NITR) radical ligands. Adducts of type $[\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}]$ ($\text{hfacH} = 1,1,1,5,5,5\text{-hexafluoro-}$

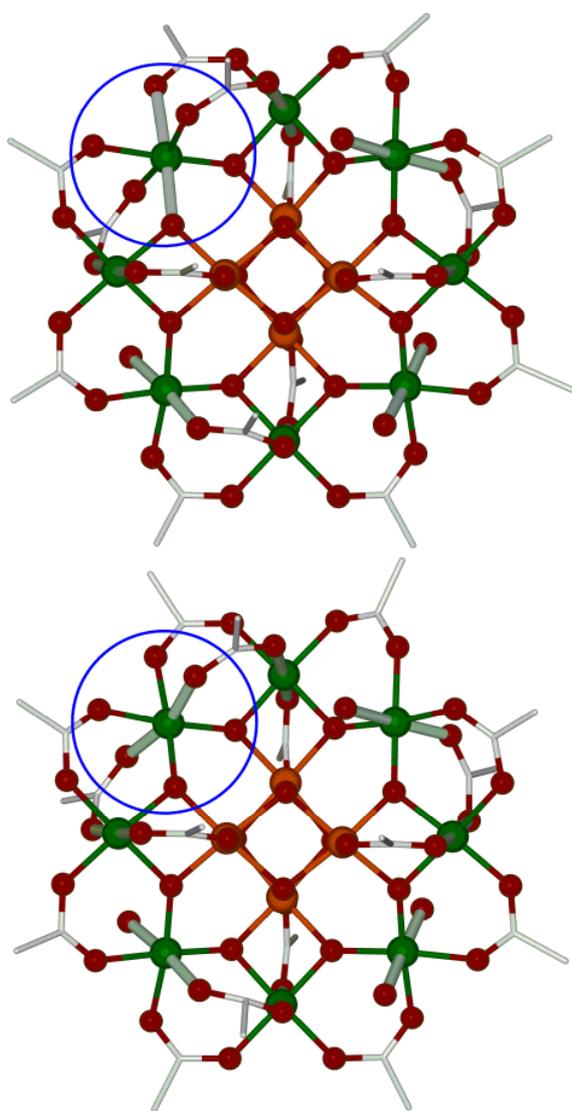
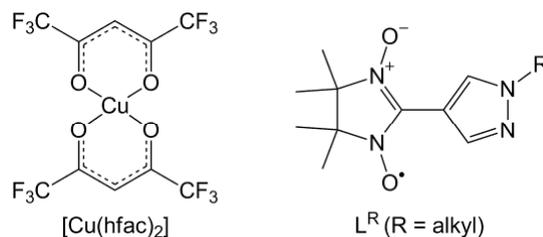


Fig. 8 The fast-relaxing (top) and slow-relaxing (bottom) isomers in differently solvated crystals of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{tBu})_6(\text{H}_2\text{O})_4]$. Methyl groups and H atoms have been omitted for clarity. Colour code: C, white; Mn^{III}, green; Mn^{IV}, orange; O, red. The Jahn-Teller-elongated Mn^{III}-O bonds are emphasised, and indicated in pale green. The isomers differ in the orientation of the Jahn-Teller distortion in the highlighted manganese ion.⁶⁸

acetylacetonate, and L^{R} is a 1-alkylpyrazol-4-yl-nitronyl nitroxide) have been particularly well studied. These are 1D coordination polymers with bridging L^{R} ligands, which can be obtained in “head-to-tail” or “head-to-head” isomeric forms.



The “head-to-head” isomers contain alternating $[\text{Cu}(\text{hfac})_2(\text{pyrazole})_2]$ and $[\text{Cu}(\text{hfac})_2(\text{NITR})_2]$ centres (Fig. 9). In the latter, the NITR radical donors coordinate to the copper axial sites, affording six-coordinate centres with a Jahn-Teller elongation along the $\text{Cu}-\text{O}\{\text{NITR}\}$ bonds at room temperature. This structure affords weak ferromagnetic coupling between the metal and ligand spins in the $[\text{Cu}(\text{hfac})_2(\text{NITR})_2]$ units, leading to a magnetic moment of $\mu_{\text{eff}} \approx 2.5$ BM per copper ion. Many of these materials undergo a magnetic transition on cooling, associated with a reduction in μ_{eff} to 1.8 BM per copper ion (Fig. 10).^{70,71} This reflects a temperature-dependent reorientation of the Jahn-Teller elongation in the $[\text{Cu}(\text{hfac})_2(\text{NITR})_2]$ centres, to lie along one of the two unique equatorial $\text{O}\{\text{hfac}\}-\text{Cu}-\text{O}\{\text{hfac}\}$ axes. This structural change in turn switches the Cu/NITR coupling, from weakly ferromagnetic to strongly antiferromagnetic, leading to the observed reduction in μ_{eff} at low temperature (Fig. 10). Comparable magnetic switching related to a pressure-dependent Jahn-Teller rearrangement is seen in *catena*- $[\text{CuF}_2(\text{OH}_2)_2(\mu\text{-pyrazine})]$ (see above).^{42,49} Although different in origin, these transitions resemble more conventional transition metal spin-crossover switching⁷² in exhibiting properties like thermal hysteresis⁷¹ and light-induced spin-state trapping.⁷³ Crystallographic order/ disorder transitions involving lattice solvent are important in propagating these cooperative phenomena through the bulk materials.⁷⁰ Although most work has been done on the $[\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}]$ system, comparable magnetic transitions have also been observed in some copper(II) complexes of other nitroxyl radical derivatives.⁷⁴

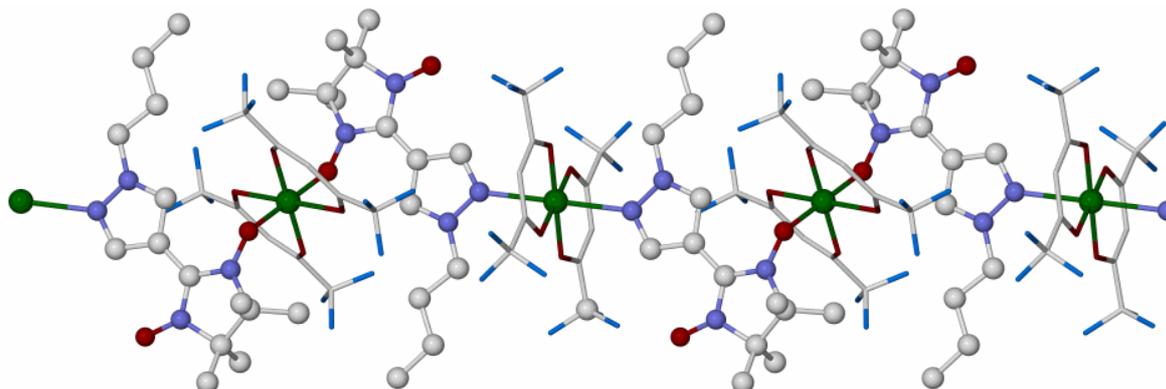


Fig. 9 Crystal structure of the head-to-head $[\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}]\cdot\text{C}_7\text{H}_8$ coordination polymer.⁷¹ The hfac⁻ ligands are de-emphasised for clarity, and H atoms and solvent molecules have been omitted. Colour code: C, white; Cu, green; F, cyan; N, blue; O, red.

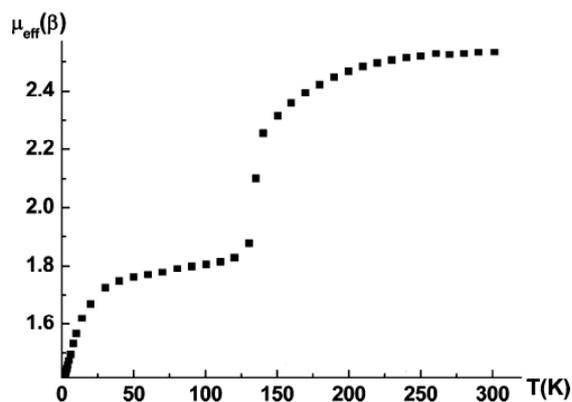


Fig. 10 Temperature dependence of the effective magnetic moment of $[\text{Cu}(\text{hfac})_2\text{L}^{\text{Bu}}] \cdot \frac{1}{2}\text{C}_7\text{H}_{16}$, showing the Jahn-Teller-induced magnetic transition near 150 K. Modified with permission from ref. 70. Copyright 2008, American Chemical Society.

Jahn-Teller Distortions in Conducting and Magnetic Materials

Superconductivity depends on the interaction between electron spins and lattice vibrations, which can promote strong pairing between electrons of opposite spin. If this coupling is strong enough, these electron pairs can be considered to be discrete particles in their own right with zero overall spin, which are termed Cooper pairs. These Cooper pairs can migrate through a solid lattice much more readily than isolated electrons, giving rise to superconducting properties.⁷⁵

The most important classes of high-temperature superconductors are cuprate materials, which can retain their superconducting properties at temperatures up to 130 K.^{76,77} A variety of such materials are known with varying elemental compositions and stoichiometries, but their lattices all contain CuO_2 sheets which are integral to their function (Fig. 11). These CuO_2 layers contain tetragonal copper(II) centres, with one or two longer $\text{Cu}\dots\text{O}$ distances to axial oxide ion donors.⁷⁷

Dynamic Jahn-Teller distortions occur in the CuO_2 layers,⁷⁷ which are coupled to $\text{Cu}-\text{O}$ vibrations (*c.f.* Fig. 3) and cause substantial changes to the local electron distribution (Schemes 1 and 3). This efficiently couples electronic structure to lattice vibrations, providing an alternative mechanism for electron pairing in cuprate superconductors that remains efficient at higher temperatures. Although the more detailed mechanism of superconductivity in these materials remains unclear, Jahn-Teller distortions in the cuprate layers are an important part of the process, and explain why these are still the most efficient superconductors known.⁷⁵

Another important class of magnetic materials are the manganites $[\text{Ln}_{1-x}\text{A}_x]_{n+1}\text{Mn}_n\text{O}_{3n+1}$ (Ln^{3+} = a lanthanide ion, A^{2+} = a group 2 metal). These are derived from the LaMnO_3 perovskite structure but have differing ratios of octahedral manganese(III) and manganese(IV), depending on the level of divalent cation doping x and the oxide stoichiometry n .⁷⁹ Differing compositions lead to strong changes in the conductivity and magnetic behaviour of these compounds, which partly arise because of the Jahn-Teller character of the manganese oxidation states. Manganese(III) (high-spin d^4) is strongly Jahn-Teller active and has an

anisotropic distribution of electrons (there is one e_g electron, whose orbital occupancy is determined by the direction and form of the Jahn-Teller distortion). Thus, magnetic coupling between a manganese(III) site and its nearest neighbour metal ions depends on its Jahn-Teller state, and is strongly directional. In contrast, manganese (IV) (d^3) is not Jahn-Teller active, and has an isotropic spin distribution with one unpaired electron in each orbital of the t_{2g} subshell. Thus, varying the manganese(III):(IV) ratio in manganite perovskites does not simply change their electron population, but has a much stronger effect on their electronic structure and magnetic ordering.⁷⁹

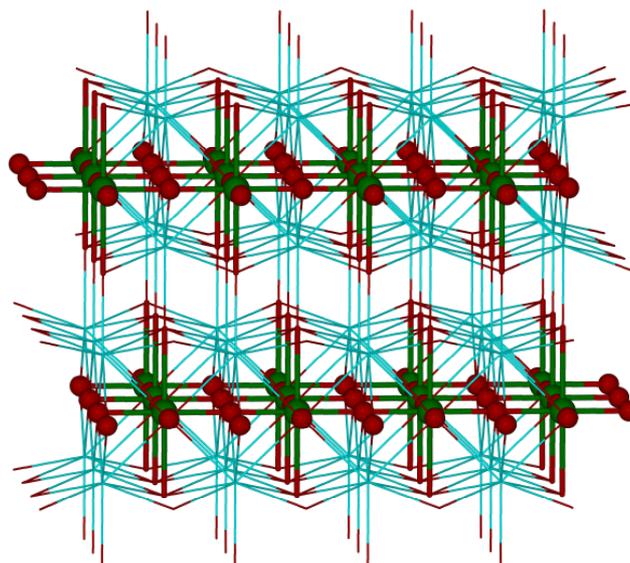


Fig. 11 Crystal structure of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, a superconductor with $T_c = 38$ K. Jahn-Teller disorder within the superconducting CuO_2 layers has been directly observed in this material.⁷⁸ The CuO_2 layers are highlighted, while the other atoms are de-emphasised for clarity. Colour code: Cu, green; La/Sr, cyan; O, red.

Manganite perovskites are particularly known as exemplars of the colossal magnetoresistance phenomenon, where the electrical resistance of a material increases by orders of magnitude inside a magnetic field at high temperatures.⁸⁰ Although its detailed mechanism is still under study, colossal magnetoresistance involves an interplay between three different types of transition, which can occur concurrently or independently in different materials. These are: magnetic ordering; charge ordering, between phases containing delocalised and localised manganese(III) and (IV) sites; and orbital ordering, involving a freezing out of Jahn-Teller disorder at the manganese(III) centres.⁸¹

Conclusions

Jahn-Teller phenomena in metal complexes continue to be discovered and developed, for new combinations of metal ion and coordination geometry.^{9,13,60,63,82} Temperature- and pressure-induced quenching or switching of Jahn-Teller distortions is now well-established in a limited number of copper(II) compounds,^{42-47,49,50,54,70-74} which can lead to functional materials with

switchable magnetic moments or low-temperature magnetic ordering.^{49,70-74} The Jahn-Teller structure of copper(II) compounds with tridentate ligands can also be manipulated by molecular design, or by doping into an undistorted host lattice.⁵²⁻⁵⁵ Many of these studies have involved compounds with a *trans*-[CuX₄Y₂] coordination geometry, which seems to give rise to a particularly plastic electronic structure. Other copper(II) complexes with *trans*-[CuX₄Y₂] ligation may also display novel Jahn-Teller structures or switching properties.

Important classes of magnetic and superconducting ceramics also contain Jahn-Teller ions. The functions of these materials are intimately connected to their Jahn-Teller distortions, which provide an efficient mechanism for coupling their electronic structures to lattice vibrations.^{78,81} Comparable effects can also be seen at the molecular level in some single molecule magnets, which depend on the strong magnetic anisotropy of the Jahn-Teller-distorted manganese(III) ion.⁶⁷⁻⁶⁹

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Notes and references

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† Electronic Supplementary Information (ESI) available: a list of copper(II) complexes that have been shown to exhibit dynamic or static Jahn-Teller disorder in the solid state. This is an updated version of the list given in ref. 12. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/#####.

‡ 1 bar = 0.98 atm = 0.1 MPa.

§ Strictly speaking, the electronic configuration of structure A (Scheme 4) should be written as $\{d_{x^2-y^2}\}^1$ rather than $\{d_{x^2-y^2}\}^1$, because the structural elongation occurs along the molecular *x*-axis, rather than the unique symmetry axis *z*.

¶ Quantum mechanical particles with integer spin, including $s = 0$, are bosons. Bosons have very different physics from half-integer spin particles (fermions), including individual electrons. In particular, bosons are described by delocalised wavefunctions, that are not centred on specific atoms or bonds. This allows Cooper pairs (which have effectively zero spin) to migrate freely through a lattice, without having to move between energy levels in a conduction band.

- 1 H. Jahn and E. Teller, *Proc. R. Soc. London, Ser. A*, 1937, **161**, 220.
- 2 H. Köppel, D. R. Yarkony and H. Barentzen (eds.), *The Jahn-Teller Effect: Fundamentals and Implications for Physics and Chemistry*. Springer Ser. Chem. Phys. vol. 97, 2009, p. 915.
- 3 See e.g. M. J. Molski, D. Mollenhauer, S. Gohr, B. Paulus, M. A. Khanfar, H. Shorafa, S. H. Strauss and K. Seppelt, *Chem. Eur. J.*, 2012, **18**, 6644.
- 4 K. Prassides (ed.), *Fullerene-Based Materials Structures and Properties. Struct. Bonding (Berlin)* vol. 109, 2004, p. 276.
- 5 P. Szakacs, D. Kocsis and P. R. Surjan, *J. Chem. Phys.*, 2010, **132**, 034309/1.

- 6 J. S. Miller (ed.), *Extended Linear Chain Compounds* vol. 1, Springer, Berlin, 1982, p. 498.
- 7 P. C. Snijders and H. H. Weitering, *Rev. Mod. Phys.*, 2010, **82**, 307.
- 8 D. Reinen, M. Atanasov, P. Köhler and D. Babel, *Coord. Chem. Rev.*, 2010, **254**, 2703.
- 9 W. M. Reiff, C. E. Schulz, M.-H. Whangbo, J. I. Seo, Y. S. Lee, G. R. Potratz, C. W. Spicer and G. S. Girolami, *J. Am. Chem. Soc.*, 2009, **131**, 404.
- 10 M. A. Hitchman, *Comments Inorg. Chem.*, 1994, **15**, 197.
- 11 B. Murphy and B. Hathaway, *Coord. Chem. Rev.*, 2003, **243**, 237.
- 12 M. A. Halcrow, *Dalton Trans.*, 2003, 4375 and refs. therein.
- 13 J. Echeverría, E. Cremades, A. J. Amoroso and S. Alvarez, *Chem. Commun.*, 2009, 4242.
- 14 M. Atanasov, B. Delley and D. Reinen, *Z. Anorg. Allg. Chem.*, 2010, **636**, 1740.
- 15 A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 365.
- 16 B. Murphy, M. Aljabri, A. M. Ahmed, G. Murphy, B. J. Hathaway, M. E. Light, T. Geilbrich and M. B. Hursthouse, *Dalton Trans.*, 2006, 357.
- 17 C. Biswas, M. G. B. Drew, M. Estrader and A. Ghosh, *Dalton Trans.*, 2009, 5015.
- 18 J. C. Knight, S. Alvarez, A. J. Amoroso P. G. Edwards and N. Singha, *Dalton Trans.*, 2010, **39**, 3870.
- 19 Y. Sunatsuki, Y. Kishima, T. Kobayashi, T. Yamaguchi, T. Suzuki, M. Kojima, J. Krzystek and M. R. Sundberg, *Chem. Commun.*, 2011, **47**, 9149 and refs. therein.
- 20 M. J. Winter, *WebElements*. <http://www.webelements.com>.
- 21 D. A. Tucker, P. S. White, K. L. Trojan, M. L. Kirk and W. E. Hatfield, *Inorg. Chem.*, 1991, **30**, 823.
- 22 M. Wei and R. D. Willett, *Inorg. Chem.*, 1995, **34**, 3780.
- 23 H. Stratemeier, B. Wagner, E. R. Krausz, R. Linder, H.-H. Schmidtke, J. Pebler, W. E. Hatfield, L. ter Haar, D. Reinen and M. A. Hitchman, *Inorg. Chem.*, 1994, **33**, 2320.
- 24 B. A. Godman and J. B. Rayner, *Adv. Inorg. Chem. Radiochem.*, 1970, **3**, 135.
- 25 P. J. Ellis, H. C. Freeman, M. A. Hitchman, D. Reinen and B. Wagner, *Inorg. Chem.*, 1994, **33**, 1249.
- 26 B. Wagner, S. A. Warda, M. A. Hitchman and D. Reinen, *Inorg. Chem.*, 1996, **35**, 3967.
- 27 L. R. Falvello, *J. Chem. Soc., Dalton Trans.*, 1997, 4463.
- 28 A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7.
- 29 M. A. Hitchman, W. Maaskant, J. van der Plas, C. J. Simmons and H. Stratemeier, *J. Am. Chem. Soc.*, 1999, **121**, 1488.
- 30 C. A. Kilner, E. J. L. McInnes, M. A. Leech, G. S. Beddard, J. A. K. Howard, F. E. Mabbs, D. Collison, A. J. Bridgeman and M. A. Halcrow, *Dalton Trans.*, 2004, 236.
- 31 M. D. Joesten, F. D. Srygley and P. G. Lenhert, *Inorg. Chem.*, 1983, **22**, 1254 and refs. therein.
- 32 P. L. W. Tregenna-Piggott and G. Carver, *Inorg. Chem.*, 2004, **43**, 8061.
- 33 C. A. Kilner and M. A. Halcrow, *Dalton Trans.*, 2010, **39**, 9008.
- 34 E. Stephen, D. Huang, J. L. Shaw, A. J. Blake, D. Collison, E. S. Davies, R. Edge, J. A. K. Howard, E. J. L. McInnes, C. Wilson, J. Wolowska, J. McMaster and M. Schröder, *Chem. Eur. J.*, 2011, **17**, 10246.
- 35 R. T. Hamazawa, T. Nishioka, I. Kinoshita, T. Takui, R. Santo and A. Ichimura, *Dalton Trans.*, 2006, 1374.
- 36 J. L. Shaw, J. Wolowska, D. Collison, J. A. K. Howard, E. J. L. McInnes, J. McMaster, A. J. Blake, C. Wilson and M. Schröder, *J. Am. Chem. Soc.*, 2006, **128**, 13827.
- 37 J. Ruiz-Fuertes, A. Friedrich, J. Pellicer-Porres, D. Errandonea, A. Segura, W. Morgenroth, E. Haussühl, C.-Y. Tu and A. Polian, *Chem. Mater.*, 2011, **23**, 4220.
- 38 J.-S. Zhou, J. A. Alonso, J. T. Han, M. T. Fernández-Díaz, J.-G. Cheng and J. B. Goodenough, *J. Fluorine Chem.*, 2011, **132**, 1117.
- 39 M. Merlini, N. Perchiazzi, M. Hanfland and A. Bossak, *Acta Cryst., Sect. B*, 2012, **68**, 266.
- 40 S. A. Moggach, K. W. Galloway, A. R. Lennie, P. Parois, N. Rowantree, E. K. Brechin, J. E. Warren, M. Murrie and S. Parsons, *CrystEngComm*, 2009, **11**, 2601.

- 41 J. A. Gould, M. J. Rosseinsky and S. A. Moggach, *Dalton Trans.*, 2012, **41**, 5464.
- 42 A. Prescimone, C. Morien, D. Allan, J. A. Schlueter, S. W. Tozer, J. L. Manson, S. Parsons, E. K. Brechin and S. Hill, *Angew. Chem. Int. Ed.*, 2012, **51**, 7490.
- 43 C. J. Simmons, M. A. Hitchman, H. Stratemeier and A. J. Schultz, *J. Am. Chem. Soc.*, 1993, **115**, 11304.
- 44 W. Rauw, H. Ahsbahs, M. A. Hitchman, S. Lukin, D. Reinen, A. J. Schultz, C. J. Simmons and H. Stratemeier, *Inorg. Chem.*, 1996, **35**, 1902.
- 45 A. J. Schultz, R. W. Henning, M. A. Hitchman and H. Stratemeier, *Cryst. Growth. Des.*, 2003, **3**, 403.
- 46 C. Dobe, G. Carver, H.-B. Bürgi, P. L. W. Tregenna-Piggott, G. J. McIntyre, M. A. Augustyniak-Jablokow and M. J. Riley, *Inorg. Chem.*, 2003, **42**, 8524.
- 47 C. Dobe, T. Strässle, F. Juranyi and P. L. W. Tregenna-Piggott, *Inorg. Chem.*, 2006, **45**, 5066.
- 48 J. L. Manson, M. M. Conner, J. A. Schlueter, A. C. McConnell, H. I. Southerland, I. Malfant, T. Lancaster, S. J. Blundell, M. L. Brooks, F. L. Pratt, J. Singleton, R. D. McDonald, C. Lee and M.-H. Whangbo, *Chem. Mater.*, 2008, **20**, 7408.
- 49 G. J. Halder, K. W. Chapman, J. A. Schlueter and J. L. Manson, *Angew. Chem., Int. Ed.*, 2011, **50**, 419.
- 50 F. Aguado, F. Rodríguez, R. Valiente, J. P. Itié and P. Munsch, *Phys. Rev. B*, 2004, **70**, 214104/1.
- 51 F. Aguado, F. Rodríguez, R. Valiente, M. Hanfland and J. P. Itié, *J. Phys.: Condens. Matter*, 2007, **19**, 346229/1 and refs. therein.
- 52 N. K. Solanki, E. J. L. McInnes, F. E. Mabbs, S. Radojevic, M. McPartlin, N. Feeder, J. E. Davies and M. A. Halcrow, *Angew. Chem., Int. Ed.*, 1998, **37**, 2221.
- 53 J. M. Holland, X. Liu, J. P. Zhao, F. E. Mabbs, C. A. Kilner, M. Thornton-Pett and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 2000, 3316.
- 54 C. A. Kilner and M. A. Halcrow, *Acta Cryst., Sect. B*, 2010, **66**, 206.
- 55 R. Docherty, F. Tuna, C. A. Kilner, E. J. L. McInnes and M. A. Halcrow, *Chem. Commun.*, 2012, **48**, 4055.
- 56 C. J. Simmons, H. Stratemeier, M. A. Hitchman, D. Reinen, V. M. Masters and M. J. Riley, *Inorg. Chem.*, 2011, **50**, 4900.
- 57 Z. Mazej, I. Arcön, P. Benkič, A. Kodre and A. Tressaud, *Chem. Eur. J.*, 2004, **10**, 5052.
- 58 E. C. Constable, G. Baum, E. Bill, R. Dyson, R. van Eldik, D. Fenske, S. Kaderli, D. Morris, A. Neubrand, M. Neuburger, D. R. Smith, K. Wieghardt, M. Zehnder and A. D. Zuberbühler, *Chem. Eur. J.*, 1999, **5**, 498.
- 59 M. A. Halcrow, *Coord. Chem. Rev.*, 2009, **253**, 2493.
- 60 J. M. Holland, J. A. McAllister, C. A. Kilner, M. Thornton-Pett, A. J. Bridgeman and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 2002, 548.
- 61 E. Castillo-Martínez, M. Bieringer, S. P. Shafi, L. M. D. Cranswick, and M. A. Alario-Franco, *J. Am. Chem. Soc.*, 2011, **133**, 8552.
- 62 M. A. Leech, N. K. Solanki, M. A. Halcrow, J. A. K. Howard and S. Dahaoui, *Chem. Commun.*, 1999, 2245.
- 63 X. Wurzenberger, H. Piotrowski and P. Klüfers, *Angew. Chem. Int. Ed.*, 2011, **50**, 4974.
- 64 D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets*, Oxford University Press, Oxford, UK, 2006, p. 395.
- 65 D. Gatteschi, A. Cornia, M. Mannini and R. Sessoli, *Inorg. Chem.*, 2009, **48**, 3408.
- 66 R. Sessoli, *Angew. Chem. Int. Ed.*, 2012, **51**, 43.
- 67 R. Bagai and G. Christou, *Chem. Soc. Rev.*, 2009, **38**, 1011.
- 68 M. Soler, W. Wernsdorfer, Z. Sun, J. C. Huffman, D. N. Hendrickson and G. Christou, *Chem. Commun.*, 2003, 2672.
- 69 P. Parois, S. A. Moggach, J. Sanchez-Benitez, K. V. Kamenev, A. R. Lennie, J. E. Warren, E. K. Brechin, S. Parsons and M. Murrie, *Chem. Commun.*, 2010, **46**, 1881.
- 70 V. I. Ovcharenko, G. V. Romanenko, K. Yu. Maryunina, A. S. Bogomyakov and E. V. Gorelik, *Inorg. Chem.*, 2008, **47**, 9537.
- 71 G. V. Romanenko, K. Yu. Maryunina, A. S. Bogomyakov, R. Z. Sagdeev and V. I. Ovcharenko, *Inorg. Chem.*, 2011, **50**, 6597.
- 72 A. Bousseksou, G. Molnár, L. Salmon and W. Nicolazzi, *Chem. Soc. Rev.*, 2011, **40**, 3313.
- 73 M. Fedin, V. Ovcharenko, R. Sagdeev, E. Reijerse, W. Lubitz and E. Bagryanskaya, *Angew. Chem., Int. Ed.*, 2008, **47**, 6897.
- 74 See e.g. A. Okazawa, D. Hashizume and T. Ishida, *J. Am. Chem. Soc.*, 2010, **132**, 11516.
- 75 K. A. Müller and A. Bussmann-Holder (eds.), *Superconductivity in Complex Systems. Struct. Bonding (Berlin) vol. 114*, 2005, p. 394.
- 76 H. Keller, A. Bussmann-Holder and K. A. Müller, *Mater. Today*, 2008, **11(9)**, 38.
- 77 M. H. Whangbo and C. C. Torardi, *Acc. Chem. Res.*, 1991, **24**, 127.
- 78 A. Bianconi, N. L. Saini, A. Lanzara, M. Missori, T. Rossetti, H. Oyanagi, H. Yamaguchi, K. Oka and T. Ito, *Phys. Rev. Lett.*, 1996, **76**, 3412.
- 79 A. Maignan, C. Martin, S. Hébert and V. Hardy, *J. Mater. Chem.*, 2007, **17**, 5023.
- 80 C. N. R. Rao, *J. Phys. Chem. B*, 2000, **104**, 5877.
- 81 N. Mannella, C. H. Booth, A. Rosenhahn, B. C. Sell, A. Nambu, S. Marchesini, B. S. Mun, S.-H. Yang, M. Watanabe, K. Ibrahim, E. Arenholz, A. Young, J. Guo, Y. Tomioka and C. S. Fadley, *Phys. Rev. B*, 2008, **77**, 125134/1.
- 82 R. L. McNaughton, J. M. Chin, W. W. Weare, R. R. Schrock and B. M. Hoffman, *J. Am. Chem. Soc.*, 2007, **129**, 3480.

Jahn-Teller Distortions in Transition Metal Compounds, and their Importance in Functional Molecular and Inorganic Materials

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Supporting Information

Table S1 Six-coordinate copper(II) compounds that have show unusual crystallographic coordination geometries, and the techniques used to demonstrate their true structure as a disordered (pseudo)-Jahn-Teller elongated octahedron. Only compounds for which these additional experiments have been done are included in the table.

	Crystallographic Cu site symmetry and apparent structural distortion from an ideal octahedral geometry	Ref.	Technique	Ref.
α -M ₂ Pb[Cu(NO ₂) ₆] (M ⁺ = K ⁺ , Rb ⁺ , Cs ⁺ , Tl ⁺) ^a	T _h , undistorted	1-3	TLS analysis VT powder and single crystal EPR EXAFS	4 5 6
β -M ₂ Pb[Cu(NO ₂) ₆] (M ⁺ = K ⁺ , Rb ⁺ , Cs ⁺ , Tl ⁺) ^a	D _{2h} , tetragonal compression	4, 7-9	TLS analysis VT powder and single crystal EPR Single crystal UV/vis EXAFS	4 5, 10-12 12 6
K ₂ CuF ₄	D _{4h} , tetragonal compression	14	UV/vis and MCD measurements Susceptibility measurements Correction of incorrect space group	15 16 17
γ -Cu ₂ (OH) ₃ Cl, [Cu(μ_3 -OH) ₆] site	C _i , tetragonal compression	18	Reformulation of compound as Cu ₃ (Cu _{1-x} Zn _x)(OH) ₆ Cl ₂ (x > 0.5)	19
[NH ₄] ₂ [Cu(OH ₂) ₆][SO ₄] ₂	C _i , small rhombic elongation	20	VT crystallography VT powder and single crystal EPR Comparative UV/vis and EPR spectra of other M ₂ [Cu(OH ₂) ₆][SO ₄] ₂ salts	21-24 21, 23 25, 26
[Cu(pyO) ₆]X ₂ (X ⁻ = BF ₄ ⁻ , ClO ₄ ⁻ , NO ₃ ⁻) ^b	S ₆ , trigonal distortion	27-30	VT crystallography VT powder and single crystal EPR EXAFS	30 29, 31 32
[Cu(en) ₃]SO ₄	D ₃ , trigonal distortion	34	VT powder and single crystal EPR EXAFS VT crystallography	35 6 36
[Cu(dien) ₂][NO ₃] ₂ ^c	C ₁ , rhombical compression	37	VT crystallography and TLS analysis Single crystal UV/vis and EPR	38 39
[Cu(terpy) ₂]Br ₂ ·3H ₂ O, high-T phase ^d	C ₁ , rhombic compression	42	VT powder and single crystal EPR	42, 43
[Cu(terpy) ₂][PF ₆] ₂ , high-T phase ^d	S ₄ , tetragonal compression	44	VT powder and single crystal EPR	42
[Cu(terpy) ₂][BF ₄] ₂ ^d	C ₁ , rhombic compression	45	TLS analysis and VT powder EPR	45
[Cu(1,1''-dioxoterypy) ₂][ClO ₄] ₂	S ₄ , tetragonal compression	47	TLS analysis	47
[Cu(1-bpp) ₂][BF ₄] ₂	C ₁ , small rhombic elongation	48	VT crystallography and TLS analysis VT powder and single crystal EPR	49-51 50
β -[Cu(1-bpp ^{Mes}) ₂][ClO ₄] ₂ ·2CH ₃ NO ₂	C ₁ , small rhombic elongation	52	TLS analysis and VT powder EPR	52
[Cu(μ_3 -btz) ₆ (Cu{CNrBu}) ₄]	S ₄ , tetragonal compression	53	VT powder EPR	53
[Cu(tach) ₂][NO ₃] ₂ ^e	C _{2h} , small tetragonal compression	54	VT powder and single crystal EPR	54
[Cu(thch) ₂][CH ₃ C ₆ H ₄ SO ₃ -4] ₂	C _i , rhombic compression	55	VT crystallography	55
[H ₃ NC ₆ H ₄ Cl-3] ₈ [CuCl ₆]Cl ₄	C _i , tetragonal compression	56	VT crystallography EXAFS VT powder and single crystal EPR Single crystal UV/vis EPR of Cu-doped Cd(II) analogue	57 58 59 59 60
[Cu(ompa) ₃][ClO ₄] ₂	D ₃ , trigonal distortion	61	VT powder EPR Single crystal EPR	62 63
<i>trans</i> -[Cu(O ₂ CCH ₂ OCH ₃) ₂ (OH) ₂]	C _i , rhombic compression	64	VT crystallography	65
[Cu(HC{PPh ₂ O} ₃) ₂][ClO ₄] ₂	C _i , tetragonal compression	66	EXAFS VT crystallography and powder EPR	67 68
<i>cis</i> -[Cu(vanillinate)(OH) ₂]	C _{2v} , tetragonal compression	69	VT crystallography and TLS analysis	70
<i>trans</i> -[Cu(O ₂ NO) ₂ (tmbim) ₂]	C _i , rhombic compression	71	TLS analysis	71
[Cu([9]aneS ₃) ₂][BF ₄] ₂	C _i , small tetragonal elongation	72	VT crystallography VT powder EPR and powder UV/vis EPR of Cu-doped Fe(II) analogue	73 73, 74 73

Table S1 continued.

	Crystallographic Cu site symmetry and apparent structural distortion from an ideal octahedral geometry	Ref.	Technique	Ref.
[Cu([9]aneN ₃) ₂][Cu(CN) ₃].2H ₂ O ^f	C ₁ , small rhombic elongation	752	VT crystallography VT powder and single crystal EPR Powder UV/vis	75 74, 75 74
[Cu(MeTRI) ₂][BF ₄] ₂	D ₃ , trigonal distortion	78	TLS analysis	78
[Cu(NMe ₃ sar)][ClO ₄] ₄	S ₆ , trigonal distortion	79	VT powder EPR EPR of Cu-doped Zn analogue	79 79
<i>cis</i> -[Cu(ONO)(bipy) ₂][NO ₃] ₃ ^g	C ₁ , small rhombic elongation	80	VT crystallography	80
<i>cis</i> -[Cu(hat) ₂ (OH ₂) ₂][ClO ₄] ₂			VT powder EPR	82
[Cu(μ-dpp)(OH ₂) ₂] _n [BF ₄] _{2n} .2nH ₂ O ^h	C ₁ , small rhombic elongation	83	VT crystallography	83
[CuTp ₂] (molecule B) ⁱ	C _i , small rhombic elongation	85	TLS analysis VT crystallography and powder EPR	85, 86 86
[Cu(tpm) ₂][NO ₃] ₂	C _{3v} , trigonal distortion	87	EXAFS	87
[Cu(tpp) ₂]Br ₂ .8H ₂ O	C _i , tetragonal compression	88	VT powder and single crystal EPR	88

^aThe γ -phase of the same compounds exhibits a crystallographically ordered rhombically elongated octahedral Cu(II) centre.¹³ ^bThe solvated forms of these materials, [Cu(pyO)₆][NO₃]₂.2H₂O has a typical, static Jahn-Teller elongated geometry at 293 K.³³ ^cThe salts [Cu(dien)₂]Br₂⁴⁰ and [Cu(dien)₂]Cl[ClO₄]⁴¹ have a typical, static pseudo-Jahn-Teller elongated geometry at 293 K. ^dThe salt [Cu(terpy)₂][NO₃]₂ has a typical, static pseudo-Jahn-Teller elongated geometry at 298 K.⁴⁶ ^eThe salt [Cu(tach)₂][ClO₄]₂ has a typical, static Jahn-Teller elongated geometry at 293 K.⁵² ^fThe salts [Cu([9]aneN₃)₂][ClO₄]₂⁷⁶ and [Cu([9]aneN₃)₂]Cl₂⁷⁷ have a very similar, small rhombic elongated geometry at 293 K and so are also probably disordered although this was not studied. In contrast, [Cu([9]aneN₃)₂][CF₃SO₄]₂.H₂O has a static Jahn-Teller elongation in the crystal.⁷⁷ ^gSeveral other fluxional complexes of type [Cu(X)(bipy)₂]Y, [Cu(X)(phen)₂]Y or [Cu(X)(bipyam)₂]Y (X⁻ = NO₂⁻ or MeCO₂⁻; Y⁻ = NO₃⁻, BF₄⁻, ClO₄⁻, PF₆⁻ etc.) have also been studied by VT crystallography.⁸¹ ^hThe isomorphous ClO₄⁻ salt of the same compound also probably contains fluxional Cu centres, although this was not studied.⁸⁴ ⁱThere are two independent molecules in the crystal structure of this compound. The other molecule has a static Jahn-Teller elongated structure.

1. D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 1971, **10**, 1264.
2. S. Takagi, M. D. Joesten and P. G. Lehner, *Acta Cryst., Sect. B*, 1976, **32**, 326.
3. S. Klein and D. Reinen, *J. Solid State Chem.*, 1978, **25**, 295.
4. M. D. Joesten, S. Takagi and P. G. Lehner, *Inorg. Chem.*, 1977, **16**, 2681.
5. C. Friebel, *Z. Anorg. Allg. Chem.*, 1975, **417**, 197.
6. F. Villain, M. Verdaguer and Y. Dromzee, *J. Phys. IV*, 1997, **7**, 659.
7. S. Takagi, M. D. Joesten and P. G. Lehner, *J. Am. Chem. Soc.*, 1975, **97**, 444; S. Takagi, M. D. Joesten and P. G. Lehner, *Acta Crystallogr., Sect. B*, 1976, **32**, 1278.
8. R. Helmbold, D. Mullen, H. Ahsbahs, A. Klopsch, E. Hellner and G. Heger, *Z. Kristallogr.*, 1976, **143**, 220.
9. D. Mullen, G. Heger and D. Reinen, *Solid State Commun.*, 1975, **17**, 1249.
10. B. V. Harrowfield and J. R. Pilbrow, *J. Phys. C*, 1973, **6**, 755.
11. M. D. Joesten, S. Takagi and J. H. Venable jr., *Chem. Phys. Lett.*, 1975, **36**, 536.
12. D. Reinen, C. Friebel and K. P. Reetz, *J. Solid State Chem.*, 1972, **4**, 103.
13. S. Klein and D. Reinen, *J. Solid State Chem.*, 1980, **32**, 311.
14. K. Knox, *J. Chem. Phys.*, 1959, **30**, 991.
15. D. I. Khomskii and I. Kugel, *Solid State Commun.*, 1973, **13**, 763.
16. W. Kleemann and Y. Farge, *J. Phys.*, 1975, **36**, 1293; J. Ferre, M. Regis, Y. Farge and W. Kleemann, *Physica B+C*, 1977, **89**, 181; J. Ferre, M. Regis, Y. Farge and W. Kleemann, *J. Phys. C*, 1979, **12**, 2671.
17. R. Haegle and D. Babel, *Z. Anorg. Allg. Chem.*, 1974, **409**, 11; E. Herdtweck and D. Babel, *Z. Anorg. Allg. Chem.*, 1981, **474**, 113; D. Reinen and S. Krause, *Inorg. Chem.*, 1981, **20**, 2750.
18. M. E. Fleet, *Acta Cryst., Sect. B*, 1975, **31**, 183.
19. J. D. Grice, J. T. Szymanski and J. L. Jambor, *Canad. Mineral.*, 1996, **34**, 73.
20. H. Montgomery and E. C. Lingafelter, *Acta Crystallogr.*, 1966, **20**, 659; G. M. Brown and R. Chidambaran, *Acta Crystallogr., Sect. B*, 1969, **25**, 676.
21. N. W. Alcock, M. Duggan, A. Murray, S. Tyagi, B. J. Hathaway and A. Hewat, *J. Chem. Soc., Dalton Trans.*, 1984, **7**.
22. B. J. Hathaway and A. W. Hewat, *J. Solid State Chem.*, 1984, **51**, 364.
23. M. A. Hitchman, W. Maaskant, J. van der Plas, C. J. Simmons and H. Strateimer, *J. Am. Chem. Soc.*, 1999, **121**, 1488.
24. B. N. Figgis, A. N. Sobolev, C. J. Simmons, M. A. Hitchman, H. Strateimer and M. J. Riley, *Acta Cryst., Sect. B*, 2000, **56**, 438.
25. M. A. Hitchman and T. D. Waite, *Inorg. Chem.*, 1976, **15**, 2150.
26. T. D. Waite and M. A. Hitchman, *Inorg. Chem.*, 1976, **15**, 2155.
27. C. J. O'Connor, E. Sinn and R. L. Carlin, *Inorg. Chem.*, 1977, **16**, 3314.
28. D. Taylor, *Aust. J. Chem.*, 1978, **31**, 713.
29. J. S. Wood, C. P. Keijzers, E. de Boer and A. Buttavava, *Inorg. Chem.*, 1980, **19**, 2213.
30. C. P. Keijzers, R. K. McMullan, J. S. Wood, G. van Kalkeren, R. Srinivasan and E. de Boer, *Inorg. Chem.*, 1982, **21**, 4275.
31. D. Reinen and S. Krause, *Solid State Commun.*, 1979, **29**, 691.
32. J. S. Wood, C. P. Keijzers and R. O. Day, *Acta Cryst., Sect. C*, 1984, **40**, 404.
33. I. Persson, P. Persson, M. Sandström and A.-S. Ullström, *J. Chem. Soc., Dalton Trans.*, 2002, 1256.
34. D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 1970, **9**, 1858.
35. I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chim. Acta*, 1974, **11**, L17; I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem.*, 1977, **26**, 1973.
36. M. Lutz, *Acta Cryst., Sect. C*, 2010, **66**, m330; S. Smeets, P. Parois, H.-B. Bürgi and M. Lutz, *Acta Cryst., Sect. B*, 2011, **67**, 53.
37. F. S. Stephens, *J. Chem. Soc. A*, 1969, 883.
38. A. Murphy, J. Mullane and B. Hathaway, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 129.
39. B. J. Hathaway, M. J. Bew and D. E. Billing, *J. Chem. Soc. A*, 1970, 1090.
40. F. S. Stephens, *J. Chem. Soc. A*, 1969, 2233.
41. M. Duggan, B. J. Hathaway and J. Mullane, *J. Chem. Soc., Dalton Trans.*, 1980, 690.
42. J.-V. Folgado, W. Henke, R. Allmann, H. Strateimer, D. Beltrán-Porter, T. Rojo and D. Reinen, *Inorg. Chem.*, 1990, **29**, 2035.
43. W. Henke and D. Reinen, *Z. Anorg. Allg. Chem.*, 1977, **436**, 187.
44. M. I. Arriortua, T. Rojo, J. M. Amigo, G. Germain and J. P. Declercq, *Acta Cryst., Sect. B*, 1982, **38**, 1323.
45. R. Docherty, F. Tuna, C. A. Kilner, E. J. L. McInnes and M. A. Halcrow, *Chem. Commun.*, 2012, **48**, 4055.
46. R. Allmann, W. Henke and D. Reinen, *Inorg. Chem.*, 1978, **17**, 378.
47. A. J. Amoroso, M. W. Burrows, S. J. Coles, R. Haigh, R. D. Farley, M. B. Hursthouse, M. Jones, K. M. A. Malik and D. M. Murphy, *Dalton Trans.*, 2008, 506.
48. N. K. Solanki, E. J. L. McInnes, F. E. Mabbs, S. Radojevic, M. McPartlin, N. Feeder, J. E. Davies and M. A. Halcrow, *Angew. Chem., Int. Ed.*, 1998, **37**, 2221.
49. M. A. Leech, N. K. Solanki, M. A. Halcrow, J. A. K. Howard and S. Dahaoui, *Chem. Commun.*, 1999, 2245.
50. N. K. Solanki, M. A. Leech, E. J. L. McInnes, F. E. Mabbs, J. A. K. Howard, C. A. Kilner, J. M. Rawson and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 2002, 1295.
51. G. S. Beddard, M. A. Halcrow, M. A. Hitchman, M. P. de Miranda, C. J. Simmons and H. Strateimer, *Dalton Trans.*, 2003, 1028.
52. N. K. Solanki, M. A. Leech, E. J. L. McInnes, J. P. Zhao, F. E. Mabbs, N. Feeder, J. A. K. Howard, J. E. Davies, J. M. Rawson and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 2001, 2083.
53. G. F. Kokoszka, J. Baranowski, C. Goldstein, J. Orsini, A. D. Mighell, V. I. Himes and A. R. Siedle, *J. Am. Chem. Soc.*, 1983, **105**, 5627.
54. J. H. Ammeter, H. B. Bürgi, E. Gamp, V. Meyer-Sandrin and W. P. Jensen, *Inorg. Chem.*, 1979, **18**, 733.
55. J. Bebandorf, H.-B. Bürgi, E. Gamp, M. A. Hitchman, A. Murphy, D. Reinen, M. J. Riley and H. Strateimer, *Inorg. Chem.*, 1996, **35**, 7419.
56. D. A. Tucker, P. S. White, K. L. Trojan, M. L. Kirk and W. E. Hatfield, *Inorg. Chem.*, 1991, **30**, 823.
57. M. Wei and R. D. Willett, *Inorg. Chem.*, 1995, **34**, 3780.
58. P. J. Ellis, H. C. Freeman, M. A. Hitchman, D. Reinen and B. Wagner, *Inorg. Chem.*, 1994, **33**, 1249.
59. H. Strateimer, B. Wagner, E. R. Krausz, R. Linder, H.-H. Shmidtke, J. Pebler, W. E. Hatfield, L. ten Haar, D. Reinen and M. A. Hitchman, *Inorg. Chem.*, 1994, **33**, 2320.
60. B. Wagner, S. A. Warda, M. A. Hitchman and D. Reinen, *Inorg. Chem.*, 1996, **35**, 3967.
61. M. D. Joesten, M. S. Hussain and P. G. Lehner, *Inorg. Chem.*, 1970, **9**, 151.
62. M. D. Joesten, R. C. Koch, T. W. Martin and J. H. Venable jr, *J. Am. Chem. Soc.*, 1971, **93**, 1138.
63. R. C. Koch, M. D. Joesten and J. H. Venable jr, *J. Chem. Phys.*, 1973, **59**, 6312.
64. C. K. Prout, R. A. Armstrong, J. R. Carruthers, J. G. Forrest, P. Murray-Rust and F. J. C. Rossotti, *J. Chem. Soc. A*, 1968, 2791.
65. K. Prout, A. Edwards, V. Mtetwa, J. Murray, J. F. Saunders and F. J. C. Rossotti, *Inorg. Chem.*, 1997, **36**, 2820; C. J. Simmons, H. Strateimer, M. A. Hitchman, D. Reinen, V. M. Masters and M. J. Riley, *Inorg. Chem.*, 2011, **50**, 4900.
66. S.-J. Shieh, C.-M. Che and S.-M. Peng, *Inorg. Chim. Acta*, 1992, **192**, 151.
67. V. M. Masters, M. J. Riley, M. A. Hitchman and C. Simmons, *Inorg. Chem.*, 2001, **40**, 4478.
68. C. J. Simmons, H. Strateimer, G. R. Hanson and M. A. Hitchman, *Inorg. Chem.*, 2005, **44**, 2753.
69. B. Kozlevčar, M. Humar, P. Strauch and I. Leban, *Z. Naturforsch., Teil B*, 2005, **60**, 1273.
70. B. Kozlevčar, A. Golobič and P. Strauch, *Polyhedron*, 2006, **25**, 2824.
71. M. F. Belicchi, G. V. Gasparri, C. Pelizzi and P. Tarasconi, *Transition Met. Chem.*, 1985, **10**, 295.
72. W. N. Setzer, C. A. Ogle, G. S. Wilson and R. S. Glass, *Inorg. Chem.*, 1983, **22**, 266.
73. R. S. Glass, L. K. Steffen, D. D. Swanson, G. S. Wilson, R. de Gelder, R. A. G. de Graaf and J. Reedijk, *Inorg. Chim. Acta*, 1993, **207**, 241.
74. D. Reinen, A. Ozarowski, B. Jakob, J. Pebler, H. Strateimer, K. Wiegardt and I. Tolksdorf, *Inorg. Chem.*, 1987, **26**, 4010.
75. P. Chaudhuri, K. Oder, K. Wiegardt, J. Weiss, J. Reedijk, W. Hinrich, J. Wood, A. Ozarowski, H. Strateimer and D. Reinen, *Inorg. Chem.*, 1986, **25**, 2951.
76. A. D. Beveridge, A. J. Lavery, M. D. Walkinshaw and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1987, 373.
77. M. Kavana, D. R. Powell and J. N. Burstyn, *Inorg. Chim. Acta*, 2000, **297**, 351.
78. R. I. Sheldon, A. J. Jircitano, M. A. Beno, J. M. Williams and K. B. Mertes, *J. Am. Chem. Soc.*, 1983, **105**, 3028.
79. P. V. Bernhardt, R. Bramley, L. M. Engelhardt, J. M. Harrowfield, D. C. R. Hockless, B. R. Korybut-Daszkiwicz, E. R. Krausz, T. Morgan, A. M. Sargeson, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1995, **34**, 3589.
80. C. J. Simmons, B. J. Hathaway, K. Amornjarusiri, B. D. Santarsiero and A. Clearfield, *J. Am. Chem. Soc.*, 1987, **109**, 1947.
81. C. J. Simmons, *New J. Chem.*, 1993, **17**, 77.

82. H. Grove, J. Sletten, M. Julve, F. Lloret, L. Lezama, J. Carranza, S. Parsons and P. Rillema, *J. Mol. Struct.*, 2002, **606**, 253.
83. H. Grove, J. Sletten, M. Julve, F. Lloret and L. Lezama, *Inorg. Chim. Acta*, 2000, **310**, 217.
84. L. W. Morgan, K. V. Goodwin, W. T. Pennington and J. D. Peterson, *Inorg. Chem.*, 1992, **31**, 1103.
85. A. Murphy, B. J. Hathaway and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1979, 1646.
86. C. A. Kilner, E. J. L. McInnes, M. A. Leech, G. S. Beddard, J. A. K. Howard, F. E. Mabbs, D. Collison, A. J. Bridgeman and M. A. Halcrow, *Dalton Trans.*, 2004, 236.
87. T. Astley, P. J. Ellis, H. C. Freeman, M. A. Hitchman, F. R. Keene, E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 1995, 595.
88. T. Astley, H. Headlam, M. A. Hitchman, F. R. Keene, J. Pilbrow, H. Stratemeier, E. R. T. Tiekink and Y. C. Zhong, *J. Chem. Soc., Dalton Trans.*, 1995, 3809.

