



This is a repository copy of *Estimation of the Thermochemical Radii and Ionic Volumes of Complex Ions*.

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/119570/>

Version: Supplemental Material

Article:

Simoes, M.C. orcid.org/0000-0002-6904-6280, Hughes, K.J., Ingham, D.B. et al. (2 more authors) (2017) Estimation of the Thermochemical Radii and Ionic Volumes of Complex Ions. *Inorganic Chemistry*, 56 (13). pp. 7566-7573. ISSN 0020-1669

<https://doi.org/10.1021/acs.inorgchem.7b01205>

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

Supporting Information for Inorganic Chemistry

Estimation of the Thermochemical Radii and ionic volumes of Complex Ions

Marcus C. Simoes, Kevin J. Hughes, Derek B. Ingham, Lin Ma, Mohamed Pourkashanian*

Energy2050, Department of Mechanical Engineering, University of Sheffield, Sheffield S10 2TN, United Kingdom.

Table S1. Comparison between calculated and reference values of the thermochemical radius of complex anions containing prevalence of ionic bond.

Anion	Ions	$r_{M_j}; r_{X_k}$ (Å)	$r_{MX_i}^{ref}$ (Å)	$r_{MX_i}^{calc}$ (Å)
AgF ₄ ⁻	Ag ³⁺ ; F ⁻	0.75; 1.33	2.31	2.14
AlBr ₄ ⁻	Al ³⁺ ; Br ⁻	0.54; 1.96	3.21	3.12
AlCl ₄ ⁻	Al ³⁺ ; Cl ⁻	0.54; 1.81	2.95	2.88
AlF ₄ ⁻	Al ³⁺ ; F ⁻	0.54; 1.33	2.14	2.12
AlH ₄ ⁻	Al ³⁺ ; H ⁻	0.54; 1.28	2.26	2.04
All ₄ ⁻	Al ³⁺ ; I ⁻	0.54; 2.2	3.74	3.50
AsF ₆ ⁻	As ⁵⁺ ; F ⁻	0.46; 1.33	2.43	2.42
AuCl ₄ ⁻	Au ³⁺ ; Cl ⁻	0.85; 1.81	2.88	2.90
AuF ₄ ⁻	Au ³⁺ ; F ⁻	0.85; 1.33	2.40	2.16
AuF ₆ ⁻	Au ⁵⁺ ; F ⁻	0.57; 1.33	2.35	2.43
BF ₄ ⁻	B ³⁺ ; F ⁻	0.27; 1.33	2.05	2.11
BH ₄ ⁻	B ³⁺ ; H ⁻	0.27; 1.28	2.05	2.03
Br ⁻	Br ⁻	1.96	1.90	1.96
Cl ⁻	Cl ⁻	1.81	1.68	1.81
CuBr ₄ ⁻	Cu ³⁺ ; Br ⁻	0.54; 1.96	3.15	3.12
F ⁻	F ⁻	1.33	1.26	1.33
FeCl ₄ ⁻	Fe ³⁺ ; Cl ⁻	0.65; 1.81	3.17	2.88
GaBr ₄ ⁻	Ga ³⁺ ; Br ⁻	0.62; 1.96	3.17	3.12
GaCl ₄ ⁻	Ga ³⁺ ; Cl ⁻	0.62; 1.81	2.89	2.88
H ⁻	H ⁻	1.28	1.48	1.28
I ⁻	I ⁻	2.2	2.11	2.20
IrF ₆ ⁻	Ir ⁵⁺ ; F ⁻	0.57; 1.33	2.42	2.43
MnO ₄ ⁻	Mn ⁷⁺ ; O ²⁻	0.46; 1.4	2.20	2.23
MoF ₆ ⁻	Mo ⁵⁺ ; F ⁻	0.61; 1.33	2.41	2.43
MoOF ₅ ⁻	Mo ⁶⁺ ; O ²⁻ ; F ⁻	0.59; 1.4; 1.33	2.41	2.45
NbCl ₆ ⁻	Nb ⁵⁺ ; Cl ⁻	0.64; 1.81	3.38	3.30
NbF ₆ ⁻	Nb ⁵⁺ ; F ⁻	0.64; 1.33	2.54	2.43
NbO ₃ ⁻	Nb ⁵⁺ ; O ²⁻	0.64; 1.4	1.94	2.04
OsF ₆ ⁻	Os ⁵⁺ ; F ⁻	0.58; 1.33	2.52	2.43
OsOF ₅ ⁻	Os ⁶⁺ ; O ²⁻ ; F ⁻	0.55; 1.4; 1.33	2.46	2.45
PaF ₆ ⁻	Pa ⁵⁺ ; F ⁻	0.78; 1.33	2.49	2.44
PtF ₆ ⁻	Pt ⁵⁺ ; F ⁻	0.57; 1.33	2.47	2.43

Table S1. Continued

Anion	Ions	$r_{M_j}; r_{X_k}$ (Å)	$r_{MX_i}^{ref}$ (Å)	$r_{MX_i}^{calc}$ (Å)
PuF ₅ ⁻	Pu ⁴⁺ ; F ⁻	0.86; 1.33	2.39	2.31
ReF ₆ ⁻	Re ⁵⁺ ; F ⁻	0.58; 1.33	2.40	2.43
ReOF ₅ ⁻	Re ⁶⁺ ; O ²⁻ ; F ⁻	0.55; 1.4; 1.33	2.45	2.45
ReO ₄ ⁻	Re ⁷⁺ ; O ²⁻	0.53; 1.4	2.27	2.23
RuF ₆ ⁻	Ru ⁵⁺ ; F ⁻	0.57; 1.33	2.42	2.43
SbCl ₆ ⁻	Sb ⁵⁺ ; Cl ⁻	0.6; 1.81	3.20	3.30
SbF ₆ ⁻	Sb ⁵⁺ ; F ⁻	0.6; 1.33	2.52	2.43
SbO ₃ ⁻	Sb ⁵⁺ ; O ²⁻	0.6; 1.4	2.05	2.04
TaBr ₆ ⁻	Ta ⁵⁺ ; Br ⁻	0.64; 1.96	3.51	3.57
TaCl ₆ ⁻	Ta ⁵⁺ ; Cl ⁻	0.64; 1.81	3.52	3.30
TaF ₆ ⁻	Ta ⁵⁺ ; F ⁻	0.64; 1.33	2.50	2.43
TaO ₃ ⁻	Ta ⁵⁺ ; O ²⁻	0.64; 1.4	1.92	2.04
UF ₆ ⁻	U ⁵⁺ ; F ⁻	0.76; 1.33	3.01	2.44
VF ₆ ⁻	V ⁵⁺ ; F ⁻	0.54; 1.33	2.35	2.43
VO ₃ ⁻	V ⁵⁺ ; O ²⁻	0.54; 1.4	2.01	2.03
WCl ₆ ⁻	W ⁵⁺ ; Cl ⁻	0.62; 1.81	3.37	3.30
WF ₆ ⁻	W ⁵⁺ ; F ⁻	0.62; 1.33	2.46	2.43
WOF ₅ ⁻	W ⁶⁺ ; O ²⁻ ; F ⁻	0.6; 1.4; 1.33	2.41	2.45
AmF ₆ ²⁻	Am ⁴⁺ ; F ⁻	0.85; 1.33	2.55	2.55
CdCl ₄ ²⁻	Cd ²⁺ ; Cl ⁻	0.95; 1.81	3.07	3.02
CeCl ₆ ²⁻	Ce ⁴⁺ ; Cl ⁻	0.87; 1.81	3.52	3.44
CeF ₆ ²⁻	Ce ⁴⁺ ; F ⁻	0.87; 1.33	2.49	2.55
CoCl ₄ ²⁻	Co ²⁺ ; Cl ⁻	0.75; 1.81	3.06	3.01
CoF ₄ ²⁻	Co ²⁺ ; F ⁻	0.75; 1.33	2.09	2.23
CoF ₆ ²⁻	Co ⁴⁺ ; F ⁻	0.53; 1.33	2.56	2.52
CrF ₆ ²⁻	Cr ⁴⁺ ; F ⁻	0.55; 1.33	2.53	2.52
CrO ₄ ²⁻	Cr ⁶⁺ ; O ²⁻	0.44; 1.4	2.29	2.32
CuCl ₄ ²⁻	Cu ²⁺ ; Cl ⁻	0.73; 1.81	3.04	3.01
CuF ₄ ²⁻	Cu ²⁺ ; F ⁻	0.73; 1.33	2.13	2.23
GeCl ₆ ²⁻	Ge ⁴⁺ ; Cl ⁻	0.53; 1.81	3.35	3.43
GeF ₆ ²⁻	Ge ⁴⁺ ; F ⁻	0.53; 1.33	2.44	2.52
HfF ₆ ²⁻	Hf ⁴⁺ ; F ⁻	0.71; 1.33	2.48	2.54
HgI ₄ ²⁻	Hg ²⁺ ; I ⁻	1.02; 2.2	3.77	3.66
IrCl ₆ ²⁻	Ir ⁴⁺ ; Cl ⁻	0.63; 1.81	3.32	3.43
MnCl ₆ ²⁻	Mn ⁴⁺ ; Cl ⁻	0.53; 1.81	3.14	3.43

Table S1. Continued

Anion	Ions	$r_{M_j}; r_{X_k}$ (Å)	$r_{MX_i}^{ref}$ (Å)	$r_{MX_i}^{calc}$ (Å)
MnF ₄ ²⁻	Mn ²⁺ ; F ⁻	0.83; 1.33	2.19	2.24
MnF ₆ ²⁻	Mn ⁴⁺ ; F ⁻	0.53; 1.33	2.41	2.52
MoBr ₆ ²⁻	Mo ⁴⁺ ; Br ⁻	0.65; 1.96	3.64	3.71
MoCl ₆ ²⁻	Mo ⁴⁺ ; Cl ⁻	0.65; 1.81	3.38	3.43
MoF ₆ ²⁻	Mo ⁴⁺ ; F ⁻	0.65; 1.33	2.74	2.53
MoO ₄ ²⁻	Mo ⁶⁺ ; O ²⁻	0.59; 1.4	2.31	2.33
MoOCl ₅ ²⁻	Mo ⁵⁺ ; O ²⁻ ; Cl ⁻	0.61; 1.4; 1.81	3.34	3.32
NbCl ₆ ²⁻	Nb ⁴⁺ ; Cl ⁻	0.68; 1.81	3.43	3.43
NbOCl ₅ ²⁻	Nb ⁵⁺ ; O ²⁻ ; Cl ⁻	0.64; 1.4; 1.81	3.35	3.33
NbOF ₅ ²⁻	Nb ⁵⁺ ; O ²⁻ ; F ⁻	0.64; 1.4; 1.33	2.80	2.55
NiF ₄ ²⁻	Ni ²⁺ ; F ⁻	0.69; 1.33	2.11	2.22
NiF ₆ ²⁻	Ni ⁴⁺ ; F ⁻	0.48; 1.33	2.49	2.52
O ²⁻	O ²⁻	1.4	1.41	1.46
OsBr ₆ ²⁻	Os ⁴⁺ ; Br ⁻	0.63; 1.96	3.65	3.71
OsCl ₆ ²⁻	Os ⁴⁺ ; Cl ⁻	0.63; 1.81	3.36	3.43
OsF ₆ ²⁻	Os ⁴⁺ ; F ⁻	0.63; 1.33	2.76	2.53
PbCl ₄ ²⁻	Pb ²⁺ ; Cl ⁻	1.19; 1.81	2.79	3.06
PbCl ₆ ²⁻	Pb ⁴⁺ ; Cl ⁻	0.78; 1.81	3.47	3.44
PbF ₆ ²⁻	Pb ⁴⁺ ; F ⁻	0.78; 1.33	2.68	2.54
PdBr ₆ ²⁻	Pd ⁴⁺ ; Br ⁻	0.62; 1.96	3.54	3.71
PdCl ₄ ²⁻	Pd ²⁺ ; Cl ⁻	0.86; 1.81	3.13	3.02
PdCl ₆ ²⁻	Pd ⁴⁺ ; Cl ⁻	0.62; 1.81	3.33	3.43
PdF ₆ ²⁻	Pd ⁴⁺ ; F ⁻	0.62; 1.33	2.52	2.53
PoBr ₆ ²⁻	Po ⁴⁺ ; Br ⁻	0.94; 1.96	3.80	3.73
PoI ₆ ²⁻	Po ⁴⁺ ; I ⁻	0.94; 2.2	4.28	4.18
PtBr ₄ ²⁻	Pt ²⁺ ; Br ⁻ ; Cl ⁻	0.8; 1.96; 1.81	3.24	3.25
PtBr ₆ ²⁻	Pt ⁴⁺ ; Br ⁻	0.63; 1.96	3.63	3.71
PtCl ₄ ²⁻	Pt ²⁺ ; Cl ⁻	0.8; 1.81	3.07	3.01
PtCl ₆ ²⁻	Pt ⁴⁺ ; Cl ⁻	0.63; 1.81	3.33	3.43
PtF ₆ ²⁻	Pt ⁴⁺ ; F ⁻	0.63; 1.33	2.45	2.53
PuCl ₆ ²⁻	Pu ⁴⁺ ; Cl ⁻	0.86; 1.81	3.49	3.44
ReBr ₆ ²⁻	Re ⁴⁺ ; Br ⁻	0.63; 1.96	3.71	3.71
ReCl ₆ ²⁻	Re ⁴⁺ ; Cl ⁻	0.63; 1.81	3.37	3.43
ReF ₆ ²⁻	Re ⁴⁺ ; F ⁻	0.63; 1.33	2.56	2.53
ReF ₈ ²⁻	Re ⁶⁺ ; F ⁻	0.55; 1.33	2.76	2.78

Table S1. Continued

Anion	Ions	$r_{M_j}; r_{X_k}$ (Å)	$r_{MX_i}^{ref}$ (Å)	$r_{MX_i}^{calc}$ (Å)
ReH ₉ ²⁻	Re ⁷⁺ ; H ⁻	0.53; 1.28	2.57	2.78
ReI ₆ ²⁻	Re ⁴⁺ ; I ⁻	0.63; 2.2	4.21	4.16
RhF ₆ ²⁻	Rh ⁴⁺ ; F ⁻	0.6; 1.33	2.40	2.53
RuCl ₆ ²⁻	Ru ⁴⁺ ; Cl ⁻	0.62; 1.81	3.36	3.43
RuF ₆ ²⁻	Ru ⁴⁺ ; F ⁻	0.62; 1.33	2.48	2.53
S ²⁻	S ²⁻	1.84	1.89	1.91
Se ²⁻	Se ²⁻	1.98	2.09	2.06
SeBr ₆ ²⁻	Se ⁴⁺ ; Br ⁻	0.5; 1.96	3.63	3.71
SeCl ₆ ²⁻	Se ⁴⁺ ; Cl ⁻	0.5; 1.81	3.36	3.43
SeO ₄ ²⁻	Se ⁶⁺ ; O ²⁻	0.42; 1.4	2.29	2.32
SiF ₆ ²⁻	Si ⁴⁺ ; F ⁻	0.4; 1.33	2.48	2.52
SiO ₃ ²⁻	Si ⁴⁺ ; O ²⁻	0.4; 1.4	1.95	2.11
SmF ₄ ²⁻	Sm ²⁺ ; F ⁻	1.22; 1.33	2.18	2.33
SnBr ₆ ²⁻	Sn ⁴⁺ ; Br ⁻	0.69; 1.96	3.74	3.71
SnCl ₆ ²⁻	Sn ⁴⁺ ; Cl ⁻	0.69; 1.81	3.45	3.43
SnF ₆ ²⁻	Sn ⁴⁺ ; F ⁻	0.69; 1.33	2.65	2.53
SnI ₆ ²⁻	Sn ⁴⁺ ; I ⁻	0.69; 2.2	4.27	4.17
TcBr ₆ ²⁻	Tc ⁴⁺ ; Br ⁻	0.65; 1.96	3.63	3.71
TcCl ₆ ²⁻	Tc ⁴⁺ ; Cl ⁻	0.65; 1.81	3.37	3.43
TcF ₆ ²⁻	Tc ⁴⁺ ; F ⁻	0.65; 1.33	2.44	2.53
TcH ₉ ²⁻	Tc ⁷⁺ ; H ⁻	0.56; 1.28	2.60	2.78
TcI ₆ ²⁻	Tc ⁴⁺ ; I ⁻	0.65; 2.2	4.19	4.16
Te ²⁻	Te ²⁻	2.21	2.20	2.30
TeBr ₆ ²⁻	Tc ⁴⁺ ; Br ⁻	0.65; 1.96	3.83	3.71
TeCl ₆ ²⁻	Tc ⁴⁺ ; Cl ⁻	0.65; 1.81	3.53	3.43
TeI ₆ ²⁻	Te ⁴⁺ ; I ⁻	0.97; 2.2	4.30	4.18
TeO ₄ ²⁻	Te ⁶⁺ ; O ²⁻	0.56; 1.4	2.38	2.32
ThCl ₆ ²⁻	Th ⁴⁺ ; Cl ⁻	0.94; 1.81	3.60	3.45
ThF ₆ ²⁻	Th ⁴⁺ ; F ⁻	0.94; 1.33	2.63	2.56
TiBr ₆ ²⁻	Ti ⁴⁺ ; Br ⁻	0.61; 1.96	3.56	3.71
TiCl ₆ ²⁻	Ti ⁴⁺ ; Cl ⁻	0.61; 1.81	3.35	3.43
TiF ₆ ²⁻	Ti ⁴⁺ ; F ⁻	0.61; 1.33	2.52	2.53
UCl ₆ ²⁻	U ⁴⁺ ; Cl ⁻	0.89; 1.81	3.54	3.44
UF ₆ ²⁻	U ⁴⁺ ; F ⁻	0.89; 1.33	2.56	2.56
VO ₃ ²⁻	V ⁴⁺ ; O ²⁻	0.58; 1.4	2.04	2.12

Table S1. Continued

Anion	Ions	$r_{M_j}; r_{X_k}$ (Å)	$r_{MX_i}^{ref}$ (Å)	$r_{MX_i}^{calc}$ (Å)
WBr ₆ ²⁻	W ⁴⁺ ; Br ⁻	0.66; 1.96	3.63	3.71
WCl ₆ ²⁻	W ⁴⁺ ; Cl ⁻	0.66; 1.81	3.39	3.43
WO ₄ ²⁻	W ⁶⁺ ; O ²⁻	0.6; 1.4	2.37	2.33
WOCl ₅ ²⁻	W ⁵⁺ ; O ²⁻ ; Cl ⁻	0.62; 1.4; 1.81	3.34	3.32
ZnBr ₄ ²⁻	Zn ²⁺ ; Br ⁻	0.74; 1.96	3.35	3.25
ZnCl ₄ ²⁻	Zn ²⁺ ; Cl ⁻	0.74; 1.81	3.06	3.01
ZnF ₄ ²⁻	Zn ²⁺ ; F ⁻	0.74; 1.33	2.19	2.23
ZnI ₄ ²⁻	Zn ²⁺ ; I ⁻	0.74; 2.2	3.84	3.64
ZrCl ₆ ²⁻	Zr ⁴⁺ ; Cl ⁻	0.72; 1.81	3.48	3.43
ZrF ₆ ²⁻	Zr ⁴⁺ ; F ⁻	0.72; 1.33	2.58	2.54
AlH ₆ ³⁻	Al ³⁺ ; F ⁻	0.54; 1.33	2.56	2.58
AsO ₄ ³⁻	As ⁵⁺ ; O ²⁻	0.34; 1.4	2.37	2.37
CdBr ₆ ⁴⁻	Cd ²⁺ ; Br ⁻	0.95; 1.96	3.74	3.88
CdCl ₆ ⁴⁻	Cd ²⁺ ; Cl ⁻	0.95; 1.81	3.52	3.59
CeF ₆ ³⁻	Ce ³⁺ ; F ⁻	1.01; 1.33	2.78	2.63
CeF ₇ ³⁻	Ce ⁴⁺ ; F ⁻	0.87; 1.33	2.82	2.74
CoCl ₅ ³⁻	Co ²⁺ ; Cl ⁻	0.75; 1.81	3.20	3.31
CoF ₆ ³⁻	Co ³⁺ ; F ⁻	0.55; 1.33	2.58	2.58
CrF ₆ ³⁻	Cr ³⁺ ; F ⁻	0.62; 1.33	2.54	2.59
FeF ₆ ³⁻	Fe ³⁺ ; F ⁻	0.55; 1.33	2.98	2.58
HfF ₇ ³⁻	Hf ⁴⁺ ; F ⁻	0.71; 1.33	2.77	2.73
InF ₆ ³⁻	In ³⁺ ; F ⁻	0.8; 1.33	2.68	2.60
MnCl ₆ ⁴⁻	Mn ²⁺ ; Cl ⁻	0.67; 1.81	3.49	3.57
N ³⁻	N ³⁻	1.8	1.80	1.92
NiF ₆ ³⁻	Ni ³⁺ ; F ⁻	0.6; 1.33	2.50	2.59
O ³⁻	O ³⁻	2.88	2.88	3.07
P ³⁻	P ³⁻	2.24	2.24	2.38
PaF ₈ ³⁻	Pa ⁵⁺ ; F ⁻	0.78; 1.33	2.99	2.86
PO ₄ ³⁻	P ⁵⁺ ; O ²⁻	0.38; 1.4	2.30	2.37
PrF ₆ ³⁻	Pr ³⁺ ; F ⁻	0.99; 1.33	2.81	2.63
TaF ₈ ³⁻	Ta ⁵⁺ ; F ⁻	0.64; 1.33	2.84	2.84
TbF ₇ ³⁻	Tb ⁴⁺ ; F ⁻	0.76; 1.33	2.90	2.73
ThF ₇ ³⁻	Th ⁴⁺ ; F ⁻	0.94; 1.33	2.82	2.75
TlF ₆ ³⁻	Tl ³⁺ ; F ⁻	0.89; 1.33	2.71	2.62
UF ₇ ³⁻	U ⁴⁺ ; F ⁻	0.89; 1.33	2.85	2.75

Table S1. Continued

Anion	Ions	$r_{M_j}; r_{X_k}$ (Å)	$r_{MX_i}^{\text{ref}}$ (Å)	$r_{MX_i}^{\text{calc}}$ (Å)
YF ₆ ³⁻	Y ³⁺ ; F ⁻	0.9; 1.33	2.75	2.62
ZrF ₇ ³⁻	Zr ⁴⁺ ; F-1	0.72; 1.33	2.73	2.73

Table S2. Comparison between calculated and reference values of the thermochemical radius of complex anions with higher covalent character.

Anion	Ions	$r_{M_j}; r_{X_k}$ (Å)	$r_{MX_i}^{ref}$ (Å)	$r_{MX_i}^{calc}$ (Å)	Comments
Au(CN) ₂ ⁻	Au ⁺ ; C ²⁺ ; N ³⁻	1.37; 0.76; 1.8	2.66	2.47	
B(OH) ₄ ⁻	B ³⁺ ; H ⁺ ; O ²⁻	0.27; 0.3; 1.4	2.29	2.23	
Br ₃ ⁻	Br; Br ⁻	1.2; 1.96	2.38	2.22	Considering 2Br ⁰ + Br ⁻
BrF ₄ ⁻	Br ³⁺ ; F ⁻	0.59; 1.33	2.31	2.13	
BrO ₃ ⁻	Br ⁵⁺ ; O ²⁻	0.31; 1.4	2.14	2.02	
CF ₃ SO ₃ ⁻	C ⁴⁺ ; S ⁴⁺ ; F ⁻ ; O ²⁻	0.16; 0.37; 1.33; 1.4	2.30	2.48	
CH ₃ CO ₂ ⁻	H ⁺ ; C ³⁺ ; C ³⁻ ; O ²⁻	0.3; 0.76; 0.76; 1.4	1.94	1.86	covalent radius assumed for C ³⁺ ; C ³⁻
ClO ₂ ⁻	Cl ³⁺ ; O ²⁻	0.16; 1.4	1.95	1.76	Cl ³⁺ : Extrapolation using Cl ⁵⁺ (CN=3) and Cl ⁷⁺ (CN=4).
ClO ₃ ⁻	Cl ⁵⁺ ; O ²⁻	0.12; 1.4	2.08	2.02	
ClO ₄ ⁻	Cl ⁷⁺ ; O ²⁻	0.27; 1.4	2.25	2.22	
ClS ₂ O ₆ ⁻	S ⁵⁺ ; Cl ⁺ ; O ²⁻	0.33; 0.2; 1.4	2.60	2.55	Cl ⁺ : Extrapolation using Cl ⁵⁺ (CN=3) and Cl ⁷⁺ (CN=4); S ⁵⁺ : Interpolation between S ⁴⁺ (CN=6) and S ⁶⁺ (CN=6)
CN ⁻	C ²⁺ ; N ³⁻	0.76; 1.8	1.87	1.84	covalent radius assumed for C ²⁺
CNO ⁻	C ⁴⁺ ; N ³⁻ ; O ²⁻	0.16; 1.8; 1.4	1.93	2.05	
CNS ⁻	C ⁴⁺ ; N ³⁻ ; S ²⁻	0.16; 1.8; 1.84	2.09	2.29	
Cr ₃ O ₈ ⁻	Cr ⁶⁺ ; Cr ³⁺ ; O ²⁻	0.44; 0.62; 1.4	2.76	2.82	
H ₂ AsO ₄ ⁻	H ⁺ ; As ⁵⁺ ; O ²⁻	0.3; 0.46; 1.4	2.27	2.23	
H ₂ PO ₄ ⁻	H ⁺ ; P ⁵⁺ ; O ²⁻	0.3; 0.38; 1.4	2.13	2.23	
HCO ₂ ⁻	H ⁺ ; C ²⁺ ; O ²⁻	0.3; 0.76; 1.4	2.00	1.81	covalent radius assumed for C ²⁺
HCO ₃ ⁻	H ⁺ ; C ⁴⁺ ; O ²⁻	0.3; 0.16; 1.4	2.07	2.02	
HF ₂ ⁻	H ⁺ ; F ⁻	0.3; 1.33	1.72	1.68	
HSO ₄ ⁻	H ⁺ ; S ⁶⁺ ; O ²⁻	0.3; 0.29; 1.4	2.21	2.23	

Table S2. Continued

Anion	Ions	$r_{M_j}; r_{X_k}$ (Å)	$r_{MX_i}^{ref}$ (Å)	$r_{MX_i}^{calc}$ (Å)	Comments
I ₂ Br ⁻	I; Br ⁻	1.39; 1.96	2.61	2.35	Considering 2I ⁰ + Br ⁻
I ₃ ⁻	I; I ⁻	1.39; 2.2	2.72	2.52	Considering 2I ⁰ + I ⁻
IBr ₂ ⁻	I; Br; Br ⁻	1.39; 1.2; 1.96	2.51	2.29	Considering I ⁰ + Br ⁰ + Br ⁻
ICl ₂ ⁻	I; Cl; Cl ⁻	1.39; 1.02; 1.81	2.35	2.13	Considering I ⁰ + Cl ⁰ + Cl ⁻
ICl ₄ ⁻	I ³⁺ ; Cl ⁻	1.37; 1.81	3.07	2.97	I ³⁺ : extrapolation using I ⁵⁺ (CN=6) and I ⁷⁺ (CN=6)
IO ₂ F ₂ ⁻	I ⁵⁺ ; O ²⁻ ; F ⁻	0.95; 1.4; 1.33	2.33	2.23	
IO ₃ ⁻	I ⁵⁺ ; O ²⁻	0.95; 1.4	2.18	2.09	
IO ₄ ⁻	I ⁷⁺ ; O ²⁻	0.53; 1.4	2.31	2.23	
N ₃ ⁻			1.80		N ⁻ ionic radius is unknown
Nb ₂ F ₁₁ ⁻	Nb ⁵⁺ ; F ⁻	0.64; 1.33	3.11	2.98	
NH ₂ ⁻	H ⁺ ; N ³⁻	0.3; 1.8	1.68	1.81	
NH ₂ CH ₂ COO ⁻	H ⁺ ; C ³⁺ ; C ⁻ ; O ²⁻ ; N ³⁻	0.3; 0.76; 0.76; 1.4; 1.8	2.52	2.31	covalent radius assumed for C ³⁺ ; C ⁻
NO ₂ ⁻	N ³⁺ ; O ²⁻	0.16; 1.4	1.87	1.76	
NO ₃ ⁻	N ⁵⁺ ; O ²⁻	0.13; 1.4	2.00	2.02	
O ₂ ⁻			1.58		O ⁻ ionic radius is unknown
O ₃ ⁻			1.77		O ⁻ ionic radius is unknown
OH ⁻	H ⁺ ; O ²⁻	0.3; 1.4	1.52	1.40	
PdF ₆ ⁻	Pd ⁵⁺ ; F ⁻	0.47; 1.33	2.52	2.42	Pd ⁵⁺ : Extrapolation using Pd ³⁺ and Pd ⁴⁺
PF ₆ ⁻	P ⁵⁺ ; F ⁻	0.38; 1.33	2.42	2.42	
PO ₃ ⁻	P ⁵⁺ ; O ²⁻	0.38; 1.4	2.04	2.02	
S ₆ ⁻			3.05		S ⁻ ionic radius is unknown
Sb ₂ F ₁₁ ⁻	Sb ⁵⁺ ; F ⁻	0.6; 1.33	3.12	2.97	
Sb ₃ F ₁₄ ⁻	Sb ⁵⁺ ; Sb ³⁺ ; F ⁻	0.6; 0.76; 1.33	3.74	3.23	
SeCN ⁻	C ⁴⁺ ; Se ²⁻ ; N ³⁻	0.16; 1.98; 1.8	2.30	2.39	
SeH ⁻	H ⁺ ; Se ²⁻	0.3; 1.98	1.95	1.98	

Table S2. Continued

Anion	Ions	$r_{M_j}; r_{X_k}$ (Å)	$r_{MX_i}^{ref}$ (Å)	$r_{MX_i}^{calc}$ (Å)	Comments
SH ⁻	H ⁺ ; S ²⁻	0.3; 1.84	1.91	1.84	
SO ₃ F ⁻	S ⁶⁺ ; O ²⁻ ; F ⁻	0.29; 1.4; 1.33	2.14	2.20	
SNCl ₅ (CH ₃ CN) ⁻			2.90		Structure unclear, no reference that reports the structure of this anion was found
S ₃ N ₃ ⁻	S ²⁺ ; S ⁴⁺ ; N ³⁻	0.45; 0.37; 1.8	2.31	2.61	S ³⁺ : extrapolation using S ⁴⁺ (CN=6) and S ⁶⁺ (CN=6)
S ₃ N ₃ O ₄ ⁻	S ⁶⁺ ; S ⁴⁺ ; N ³⁻ ; O ²⁻	0.29; 0.37; 1.8; 1.4	2.52	3.06	
Bi ₂ Br ₈ ²⁻	Bi ³⁺ ; Br ⁻	1.03; 1.96	3.92	4.13	
Bi ₆ Cl ₂₀ ²⁻	Bi ³⁺ ; Cl ⁻	1.03; 1.81	5.01	5.20	
CO ₃ ²⁻	C ⁴⁺ ; O ²⁻	0.16; 1.4	1.89	2.10	
Cr ₂ O ₇ ²⁻	Cr ⁶⁺ ; O ²⁻	0.44; 1.4	2.92	2.79	
Nb ₂ OCl ₁₀ ²⁻	Nb ⁵⁺ ; O ²⁻ ; Cl ⁻	0.64; 1.4; 1.81	3.83	4.13	
NH ²⁻			1.28		It should be bigger than NH ₂ ⁻
Ni(CN) ₄ ²⁻	Ni ²⁺ ; C ²⁺ ; N ³⁻	0.69; 0.76; 1.8	3.22	3.06	covalent radius assumed for C ²⁺
O ₂ ²⁻	O ⁻	1.35	1.67	1.77	
Pt(NO ₂) ₃ Cl ₃ ²⁻	Pt ⁴⁺ ; N ³⁺ ; O ²⁻ ; Cl ⁻	0.63; 0.16; 1.4; 1.81	3.64	3.39	
Pt(NO ₂) ₄ Cl ₂ ²⁻	Pt ⁴⁺ ; N ³⁺ ; O ²⁻ ; Cl ⁻	0.63; 0.16; 1.4; 1.81	3.83	3.37	
Pt(OH) ₂ ²⁻			3.33		Structure unclear, no reference that reports the structure of this anion was found
Pt(SCN) ₆ ²⁻	Pt ⁴⁺ ; C ⁴⁺ ; S ²⁻ ; N ³⁻	0.63; 0.16; 1.84; 1.8	4.51	4.34	
S ₂ O ₃ ²⁻	S ⁶⁺ ; O ²⁻ ; S ²⁻	0.29; 1.4; 1.84	2.51	2.54	
S ₂ O ₄ ²⁻	S ³⁺ ; O ²⁻	0.41; 1.4	2.62	2.32	S ³⁺ : extrapolation using S ⁴⁺ (CN=6) and S ⁶⁺ (CN=6),
S ₂ O ₅ ²⁻	S ⁴⁺ ; O ²⁻	0.37; 1.4	2.70	2.50	
S ₂ O ₆ ²⁻	S ⁵⁺ ; O ²⁻	0.33; 1.4	2.83	2.65	S ⁵⁺ : interpolation between S ⁴⁺ (CN=6) and S ⁶⁺ (CN=6)

Table S2. Continued

Anion	Ions	$r_{M_j}; r_{X_k}$ (Å)	$r_{MX_i}^{ref}$ (Å)	$r_{MX_i}^{calc}$ (Å)	Comments
$S_2O_7^{2-}$	$S^{6+}; O^{2-}$	0.29; 1.4	2.75	2.79	
$S_2O_8^{2-}$	$S^{6+}; O^{2-}; O^-$	0.29; 1.4; 1.35	2.91	2.89	
$S_3O_6^{2-}$	$S^{5+}; S; O^{2-}$	0.33; 1.05; 1.4	3.02	2.71	S^{5+} : interpolation between S^{4+} (CN=6) and S^{6+} (CN=6)
$S_4O_6^{2-}$	$S^{5+}; S; O^{2-}$	0.33; 1.05; 1.4	3.25	2.77	S^{5+} : interpolation between S^{4+} (CN=6) and S^{6+} (CN=6)
$S_6O_6^{2-}$	$S^{5+}; S; O^{2-}$	0.33; 1.05; 1.4	3.82	2.88	S^{5+} : interpolation between S^{4+} (CN=6) and S^{6+} (CN=6)
$SbBr_6^{2-}$	$Sb^{4+}; Br^-$	0.68; 1.96	3.74	3.71	Sb^{4+} : interpolation between Sb^{3+} (CN=6) and Sb^{5+} (CN=6)
ScF_6^{2-}	$Sc^{3+}; F^-$	0.75; 1.33	2.76	2.54	Sc^{4+} : It was used the value tabulated for Sc^{3+} (CN=6)
$Sn(OH)_6^{2-}$	$Sn^{4+}; H^+; O^{2-}$	0.69; 0.3; 1.4	2.79	2.67	
SO_3^{2-}	$S^{4+}; O^{2-}$	0.37; 1.4	2.04	2.10	
SO_4^{2-}	$S^{6+}; O^{2-}$	0.29; 1.4	2.18	2.31	
$Th(NO_3)_6^{2-}$	$Th^{4+}; N^{5+}; O^{2-}$	0.94; 0.13; 1.4	4.24	3.84	
$ZrBr_4^{2-}$	$Zr^{2+}; Br^-$	0.72; 1.96	3.34	3.25	Zr^{2+} : It was used the value tabulated for Zr^{4+} (CN=6)
$ZrCl_4^{2-}$	$Zr^{2+}; Cl^-$	0.72; 1.81	3.06	3.00	Zr^{2+} : It was used the value tabulated for Zr^{4+} (CN=6)
$Co(CN)_6^{3-}$	$Co^{3+}; C^{2+}; N^{3-}$	0.55; 0.76; 1.8	3.49	3.57	covalent radius assumed for C^{2+}
$Co(NO_2)_6^{3-}$	$Co^{3+}; N^{3+}; O^{2-}$	0.55; 0.16; 1.4	3.43	3.42	
$Cr(CN)_6^{3-}$	$Cr^{3+}; C^{2+}; N^{3-}$	0.62; 0.76; 1.8	3.51	3.57	covalent radius assumed for C^{2+}
$Cu(CN)_4^{3-}$	$Cu^+; C^{2+}; N^{3-}$	0.77; 0.76; 1.8	3.12	3.14	covalent radius assumed for C^{2+}
$Fe(CN)_6^{3-}$	$Fe^{3+}; C^{2+}; N^{3-}$	0.55; 0.76; 1.8	3.47	3.57	covalent radius assumed for C^{2+}
$Ir(CN)_6^{3-}$	$Ir^{3+}; C^{2+}; N^{3-}$	0.68; 0.76; 1.8	3.47	3.58	covalent radius assumed for C^{2+}

Table S2. Continued

Anion	Ions	$r_{M_j}; r_{X_k}$ (Å)	$r_{MX_i}^{ref}$ (Å)	$r_{MX_i}^{calc}$ (Å)	Comments
$Ir(NO_2)_6^{3-}$	$Ir^{3+}; N^{3+}; O^{2-}$	0.68; 0.16; 1.4	3.38	3.42	
$Mn(CN)_6^{3-}$	$Mn^{3+}; C^{2+}; N^{3-}$	0.58; 0.76; 1.8	3.50	3.57	covalent radius assumed for C^{2+}
$Mn(CN)_6^{5-}$	$Mn^{+}; C^{2+}; N^{3-}$	0.76; 0.76; 1.8	4.01	3.69	covalent radius assumed for C^{2+}
$Ni(NO_2)_6^{3-}$	$Ni^{3+}; N^{3+}; O^{2-}$	0.6; 0.16; 1.4	3.42	3.42	
$Ni(NO_2)_6^{4-}$	$Ni^{2+}; N^{3+}; O^{2-}$	0.69; 0.16; 1.4	3.83	3.48	
$Rh(NO_2)_6^{3-}$	$Rh^{3+}; N^{3+}; O^{2-}$	0.67; 0.16; 1.4	3.45	3.42	
$Rh(SCN)_6^{3-}$	$Rh^{3+}; C^{4+}; N^{3-}; S^{2-}$	0.67; 0.16; 1.8; 1.84	4.28	4.44	
$Tc(CN)_6^{5-}$	$Tc^{+}; C^{2+}; N^{3-}$	0.78; 0.76; 1.8	4.10	3.69	covalent radius assumed for C^{2+}
$TiBr_6^{3-}$			3.15		It should be bigger than $TiBr_6^{2-}$ due to the extra electron

Table S3. Comparison between calculated and reference values of the thermochemical radius of complex cations with the highest covalent character.

Cation	Ions	$r_{M_j}; r_{X_k}$ (Å)	$r_{MX_l}^{ref}$ (Å)	$r_{MX_l}^{calc}$ (Å)	$V_{MX_l}^{ref}$ (Å ³)	$V_{MX_l}^{calc}$ (Å ³)
As ₃ S ₄ ⁺	As; S	1.19; 1.05	2.44	2.52	172	194
As ₃ Se ₄ ⁺	As; Se	1.19; 1.2	2.53	2.61	195	216
Br ₂ ⁺	Br	1.2	1.55	1.72	57	62
Br ₃ ⁺	Br	1.2	2.04	1.97	96	93
Br ₅ ⁺	Br	1.2	2.29	2.34	147	155
Cl ₃ ⁺	Cl	1.02	1.82	1.82	62	73
I ₂ ⁺	I	1.39	1.85	1.86	72	77
I ₃ ⁺	I	1.39	2.25	2.12	131	116
I ₄ ²⁺	I	1.39	2.07	1.95	132	129
I ₅ ⁺	I	1.39	2.63	2.52	210	193
IBr ₂ ⁺	I; Br	1.39; 1.2	1.96	2.03	95	101
N(S ₃ N ₂) ₂ ⁺	S; N	1.05; 0.71	2.58	2.64	197	223
NO ⁺	N; O	0.71; 0.66	1.45	1.30	10	27
NO ₂ ⁺	N; O	0.71; 0.66	1.53	1.48	22	39
O ₂ ⁺	O	0.66	1.40	1.28	15	25
P(CH ₃) ₃ D ⁺	P; H; C	1.07; 0.31; 0.76	1.96	2.11	138	114
S ₁₉ ²⁺	S	1.05	2.92	2.84	466	402
S ₂ (CH ₃) ₃ ⁺	S; H; C	1.05; 0.31; 0.76	2.33	2.23	147	134
S ₂ (S(CH ₃) ₂) ₂ ²⁺	S; H; C	1.05; 0.31; 0.76	2.30	2.17	206	177
S ₂ Br ₅ ⁺	S; Br	1.05; 1.2	2.67	2.57	217	206
S ₂ I ₄ ²⁺	S; I	1.05; 1.39	2.31	2.14	204	171
S ₂ N ⁺	S; N	1.05; 0.71	1.59	1.75	60	65
S ₃ (CH ₃) ₃ ⁺	S; H; C	1.05; 0.31; 0.76	2.39	2.36	157	160
S ₃ Br ₃ ⁺	S; Br	1.05; 1.2	2.45	2.41	169	169
S ₃ C ₃ H ₇ ⁺	S; H; C	1.05; 0.31; 0.76	1.99	2.32	145	152
S ₃ N ₂ ⁺	S; N	1.05; 0.71	2.01	2.05	97	104
S ₃ N ₂ ²⁺	S; N	1.05; 0.71	1.84	1.71	61	87
S ₃ NCCNS ₃ ²⁺	S; N; C	1.05; 0.71; 0.76	2.20	2.16	167	176
S ₄ N ₃ ⁺	S; N	1.05; 0.71	2.31	2.28	118	144
S ₄ N ₄ ²⁺	S; N	1.05; 0.71	1.86	1.96	123	132
S ₅ N ₅ ⁺	S; N	1.05; 0.71	2.57	2.54	215	198
S ₆ N ₄ ²⁺	S; N	1.05; 0.71	2.32	2.15	165	174
S ₇ I ⁺	S; I	1.05; 1.39	2.62	2.62	213	217
S ₈ ²⁺	S	1.05	1.82	2.13	174	169
SBr ₃ ⁺	S; Br	1.05; 1.2	2.20	2.14	123	119
SCH ₃ P(CH ₃) ₃ ⁺	S; P; H; C	1.05; 1.07; 0.31; 0.76	2.48	2.38	153	163
Se ₁₀ ²⁺	Se	1.2	2.53	2.45	256	258
Se ₁₉ ²⁺	Se	1.2	2.96	3.04	470	491

Table S3. Continued

Cation	Ions	$r_{M_j}; r_{X_k}$ (Å)	$r_{MX_l}^{ref}$ (Å)	$r_{MX_l}^{calc}$ (Å)	$V_{MX_l}^{ref}$ (Å ³)	$V_{MX_l}^{calc}$ (Å ³)
Se ₂ I ₄ ²⁺	Se; I	1.2; 1.39	2.18	2.18	204	181
Se ₃ Br ₃ ⁺	Se; Br	1.2; 1.2	2.53	2.49	185	186
Se ₃ N ₂ ²⁺	Se; N	1.2; 0.71	1.82	1.79	75	101
Se ₄ ²⁺	Se	1.2	1.52	1.81	94	103
Se ₄ S ₂ N ₄ ²⁺	Se; S; N	1.2; 1.05; 0.71	2.24	2.23	195	193
Se ₆ I ⁺	Se; I	1.2; 1.39	2.60	2.65	207	225
Se ₈ ²⁺	Se	1.2	1.86	2.28	214	207
SeI ₃ ⁺	Se; I	1.2; 1.39	2.38	2.30	159	147
SeN ₂ S ₂ ²⁺	Se; S; N	1.2; 1.05; 0.71	1.82	1.74	67	92
SH ₂ C ₃ H ₇ ⁺	H; C; S	0.31; 0.76; 1.05	2.10	2.08	109	109
SN ⁺	S; N;	1.05; 0.71;	1.58	1.48	32	40
Te ₂ Se ₂ ²⁺	Te; Se;	1.38; 1.2;	1.92	1.88	98	115
Te ₂ Se ₄ ²⁺	Te; Se;	1.38; 1.2;	2.22	2.12	177	167
Te ₂ Se ₈ ²⁺	Te; Se;	1.38; 1.2;	2.52	2.56	285	295
Te ₃ S ₃ ²⁺	Te; S;	1.38; 1.05;	2.17	2.09	162	159
Te ₃ Se ²⁺	Te; Se;	1.38; 1.2;	1.93	1.91	99	121

Table S4. Comparison between calculated and reference values of the thermochemical radius of complex cations with the lowest covalent character.

Cation	Atoms	$r_{M_i}; r_{X_j}$ (Å)	$r_{MX_L}^{ref}$ (Å)	$r_{MX_L}^{calc}$ (Å)	$V_{MX_L}^{ref}$ (Å ³)	$V_{MX_L}^{calc}$ (Å ³)	Comments
AsCl ₄ ⁺	As; Cl	1.19; 1.02	2.21	2.19	124	128	
BrClCNH ₂ ⁺	C; H; Br; Cl; N	0.76; 0.31; 1.2; 1.02; 0.71	1.75	1.98	92	93	
BrF ₂ ⁺			1.83		40		Should be smaller than BrF ₄ ⁺
BrF ₄ ⁺	Br; F	1.2; 0.57	1.72	1.81	44	72	
C ₁₀ F ₈ ⁺	C; F	0.76; 0.57	2.65	2.70	213	238	
C ₆ F ₆ ⁺	C; F	0.76; 0.57	2.28	2.34	136	155	
Cl(SNSCN) ₂ ⁺	S; C; Cl; N	1.05; 0.76; 1.02; 0.71	3.47	2.60		214	
Cl ₂ C=NH ₂ ⁺	C; H; Cl; N	0.76; 0.31; 1.02; 0.71	1.73	1.93		87	
Cl ₂ F ⁺	Cl; F	1.02; 0.57	1.65	1.69	34	59	
ClF ₂ ⁺	Cl; F	1.02; 0.57	1.47	1.55	32	45	
ClO ₂ ⁺			1.18		31		Should be bigger than ClF ₂ ⁺ , since O>F
Co ₂ S ₂ (CO) ₆ ²⁺	S; Co; C; O	1.05; 1.26; 0.76; 0.66	2.63	2.39	320	239	
FeW(Se) ₂ (CO) ₂ ²⁺	Fe; W; Se; O	1.32; 1.62; 1.2; 0.66	2.60	2.03	321	146	
I ₁₅ ³⁺			4.42		636		Not included, only cation with a 3+ charge
ICl ₂ ⁺	I; Cl	1.39; 1.02	1.75	1.93	83	87	
IF ₆ ⁺	I; F	1.39; 0.57	2.09	2.02	104	100	
Mo(Te ₃)(CO) ₄ ²⁺	Mo; Te; C; O	1.54; 1.38; 0.76; 0.66	2.34	2.35	221	227	

Table S4. Continued

Cation	Atoms	$r_{M_i}; r_{X_j}$ (Å)	$r_{MX_l}^{\text{ref}}$ (Å)	$r_{MX_l}^{\text{calc}}$ (Å)	$V_{MX_l}^{\text{ref}}$ (Å ³)	$V_{MX_l}^{\text{calc}}$ (Å ³)	Comments
$N(CH_3)_4^+$	H; C; N	0.31; 0.76; 0.71	2.01	2.15	113	121	
$N(SCl)_2^+$	S; N; Cl	1.05; 0.71; 1.02	1.86	2.11	115	114	
$N(SeCl)_2^+$	Se; N; Cl	1.2; 0.71; 1.02	2.46	2.18	277	125	
$N(SF_2)_2^+$			2.14		112		Should be smaller than $N(SCl)_2^+$
N_2F^+	N; F	0.71; 0.57	1.56	1.47	29	38	
$N_2H_5^+$	H; N	0.31; 0.71	1.58	1.59	28	49	
$N_2H_6^{2+}$	H; N	0.31; 0.71	1.58	1.36	75	44	
$NH(C_2H_5)_3^+$	H; C; N	0.31; 0.76; 0.71	2.74	2.43	177	173	
$NH_3C_2H_4OH^+$	H; C; N; O	0.31; 0.76; 0.71; 0.66	2.03	1.96		91	
$NH_3C_2H_5^+$	H; C; N	0.31; 0.76; 0.71	1.93	1.86	64	78	
$NH_3C_3H_7^+$	H; C; N	0.31; 0.76; 0.71	2.25	2.03	100	102	
$NH_3CH_3^+$	H; C; N	0.31; 0.76; 0.71	1.77	1.65	51	54	
NH_3OH^+	H; O; N	0.31; 0.66; 0.71	1.47	1.53	21	43	
NH_4^+	H; N	0.31; 0.71	1.36	1.36	21	30	
$O_2(SCCF_3Cl)_2^+$	C; S; O; F; Cl	0.76; 1.05; 0.66; 0.57; 1.02	2.75	2.74	237	248	
$ONCH_3CF_3^+$	H; C; N; F; O	0.31; 0.76; 0.71; 0.57; 0.66	2.00	2.06	89	106	
$P(CH_3)_3Cl^+$	P; H; C; Cl	1.07; 0.31; 0.76; 1.02	1.97	2.23	142	134	
PCl_4^+	P; Cl	1.07; 1.02	2.35	2.17		123	

Table S4. Continued

Cation	Atoms	$r_{M_i}; r_{X_j}$ (Å)	$r_{MX_l}^{ref}$ (Å)	$r_{MX_l}^{calc}$ (Å)	$V_{MX_l}^{ref}$ (Å ³)	$V_{MX_l}^{calc}$ (Å ³)	Comments
S(CH ₃) ₂ Cl ⁺	S; H; C; Cl	1.05; 0.31; 0.76; 1.02	2.07	2.06	103	105	
S(N(C ₂ H ₅) ₃) ₃ ⁺	S; H; N; C	1.05; 0.31; 0.71; 0.76	4.39	3.53		533	
S ₂ (CH ₃) ₂ Cl ⁺	S; H; C; Cl	1.05; 0.31; 0.76; 1.02	2.65	2.21	222	131	
S ₂ (CH ₃) ₂ CN ⁺	S; H; C; Cl; N	1.05; 0.31; 0.76; 1.02; 0.71	2.23	2.29	128	145	
S ₂ N ₂ C ₂ H ₃ ⁺	S; H; N; C	1.05; 0.31; 0.71; 0.76	2.11	2.16	106	123	
S ₂ N ₂ P ₂ ((C ₂ H ₅) ₃) ₂ ²⁺	S; P; N; C	1.05; 1.07; 0.71; 0.76	3.12	2.76		367	
S ₂ NC ₂ (PhCH ₃) ₂ ⁺	S; H; N; C	1.05; 0.31; 0.71; 0.76	3.10	3.16	333	380	
S ₂ NC ₃ H ₄ ⁺	S; H; N; C	1.05; 0.31; 0.71; 0.76	2.18	2.20	119	128	
S ₂ NC ₄ H ₈ ⁺	S; H; N; C	1.05; 0.31; 0.71; 0.76	2.25	2.36	131	160	
S ₃ C ₄ F ₆ ⁺	S; C; F	1.05; 0.76; 0.57	2.61	2.55	204	200	
S ₃ CF ₃ CN ⁺	S; C; F; N	1.05; 0.76; 0.57; 0.71	2.63	2.32	152	152	
S ₃ Cl ₃ ⁺	S; Cl	1.05; 1.02	2.33	2.31	146	149	
S ₃ N ₂ Cl ⁺	S; N; Cl	1.05; 0.71; 1.02	2.32	2.20		129	
S ₃ Se ²⁺			3.26		623		Should be smaller than S ₈ ²⁺ as well as smaller than Se ₁₀ ²⁺
S ₄ N ₃ (Ph) ₂ ⁺	S; H; N; C	1.05; 0.31; 0.71; 0.76	3.16	3.13	351	373	
S ₄ N ₄ H ⁺			1.78		139		Radius should be between S ₄ N ₃ ⁺ and S ₅ N ₄ ⁺
Sb(NPPh ₃) ₄ ⁺	Sb; P; N; C	1.39; 1.07; 0.71; 0.76	5.18	5.06	1540	1571	
SCH ₃ O ₂ ⁺	S; H; C; O	1.05; 0.31; 0.76; 0.66	1.83	1.87	64	79	

Table S4. Continued

Cation	Atoms	$r_{M_i}; r_{X_j}$ (Å)	$r_{MX_l}^{ref}$ (Å)	$r_{MX_l}^{calc}$ (Å)	$V_{MX_l}^{ref}$ (Å ³)	$V_{MX_l}^{calc}$ (Å ³)	Comments
SCH ₃ PCH ₃ Cl ₂ ⁺	S; P; C; Cl	1.05; 1.07; 0.76; 1.02	2.05	2.34	162	156	
SCI(C ₂ H ₅) ₂ ⁺	S; H; Cl; C	1.05; 0.31; 1.02; 0.76	2.07	2.33	167	153	
SCl ₂ CF ₃ ⁺	S; C; Cl; F	1.05; 0.76; 1.02; 0.57	2.07	2.15	105	120	
SCl ₂ CH ₃ ⁺	S; H; C; Cl	1.05; 0.31; 0.76; 1.02	2.04	2.03	95	102	
SCl ₃ ⁺	S; Cl	1.05; 1.02	1.85	2.01	96	98	
Se ₁₇ ²⁺			2.36		456		Should be between Se ₁₉ ²⁺ Se ₁₀ ²⁺
Se ₃ Cl ₃ ⁺	Se; Cl	1.2; 1.02	2.45	2.39	169	166	
Se ₃ N ²⁺			2.88		96		Should be smaller than Se ₃ N ₂ ²⁺
Se ₃ NCl ₂ ⁺			1.63		140		Should be similar in size to Se ₃ Cl ₃ ⁺
SeBr ₃ ⁺			1.82		114		Should be bigger than SeCl ₃ ⁺
SeCl ₃ ⁺	Se; Cl	1.2; 1.02	1.92	2.05	92	104	
SeF ₃ ⁺	Se; F	1.2; 0.57	1.79	1.72	53	62	
SeN ₂ Cl ⁺	Se; N; N; Cl	1.2; 0.71; 0.71; 1.02	1.96	1.90		84	
SeNCl ₂ ⁺	Se; N; Cl	1.2; 0.71; 1.02	1.57	1.98	129	94	
SeS ₂ N ²⁺			2.82				Should be smaller than SeN ₂ S ₂ ²⁺
SF(C ₆ F ₅) ₂ ⁺	S; F; C	1.05; 0.57; 0.76	2.94	2.99	300	325	
SF ₂ CF ₃ ⁺	S; C; F	1.05; 0.76; 0.57	1.98	1.97	88	92	
SF ₂ N(CH ₃) ₂ ⁺	S; H; F; N; C	1.05; 0.31; 0.57; 0.71; 0.76	2.10	2.12	105	116	

Table S4. Continued

Cation	Atoms	$r_{M_i}; r_{X_j}$ (Å)	$r_{MX_l}^{ref}$ (Å)	$r_{MX_l}^{calc}$ (Å)	$V_{MX_l}^{ref}$ (Å ³)	$V_{MX_l}^{calc}$ (Å ³)	Comments
SF ₃ ⁺	S; F	1.05; 0.57	1.72	1.67	53	56	
SFS(C(CF ₃) ₂) ₂ ⁺	S; C; F	1.05; 0.76; 0.57	2.75	2.84	248	277	
SNSC(CH ₃)N ⁺	S; H; N; C	1.05; 0.31; 0.71; 0.76	2.25	2.16	96	123	
SNSC(CN)CH ⁺	S; H; N; C	1.05; 0.31; 0.71; 0.76	2.09	2.21	103	130	
SNSC(Ph)N ⁺	S; H; N; C	1.05; 0.31; 0.71; 0.76	2.51	2.58	182	209	
SNSC(Ph)NS ₃ N ₂ ⁺	S; H; N; C	1.05; 0.31; 0.71; 0.76	3.27	2.96	267	313	
SNSC(PhCH ₃)N ⁺	S; H; N; C	1.05; 0.31; 0.71; 0.76	2.64	2.69	210	237	
Te(N ₃) ₃ ⁺	Te; N; N	1.38; 0.71; 0.71	2.26	2.39	139	165	
Te(trtu) ₄ ²⁺	Te; H; C; N	1.38; 0.31; 0.76; 0.71	3.28	3.17	595	555	
Te(tu) ₄ ²⁺	Te; H; C; N	1.38; 0.31; 0.76; 0.71	2.96	2.63	353	317	
Te ₂ (esu) ₄ Br ₂ ²⁺	Te; H; C; Br; N	1.38; 0.31; 0.76; 1.2; 0.71	3.56	3.12	596	532	
Te ₂ (esu) ₄ Cl ₂ ²⁺	Te; H; C; Cl; N	1.38; 0.31; 0.76; 1.02; 0.71	3.61	3.10	588	521	
Te ₂ (esu) ₄ I ₂ ²⁺	Te; H; C; I; N	1.38; 0.31; 0.76; 1.39; 0.71	3.42	3.15	612	545	
Te ₂ (su) ₆ ⁴⁺			4.53				Not included, only cation with a 4+ charge
Te ₄ ²⁺			1.69		115		Since Te>Se, Te ₄ ²⁺ should be bigger than Te ₃ Se ²⁺
Te ₄ Nb ₃ O ₇ Te ₂ I ₆ ⁺	Nb; Te; O; I	1.64; 1.38; 0.66; 1.39	4.07	3.72	602	623	
Te ₈ ²⁺			1.87		200		Since Te>Se, Te ₈ ²⁺ should be bigger than Te ₃ Se ²⁺

Table S4. Continued

Cation	Atoms	$r_{M_i}; r_{X_j}$ (Å)	$r_{MX_l}^{ref}$ (Å)	$r_{MX_l}^{calc}$ (Å)	$V_{MX_l}^{ref}$ (Å ³)	$V_{MX_l}^{calc}$ (Å ³)	Comments
TeBr ₃ ⁺	Te; Br	1.38; 1.2	2.35	2.21	117	131	
TeCl ₃ (15-crown-5) ⁺	Te; H; Cl; C; O	1.38; 0.31; 1.02; 0.76; 0.66	2.82	3.24	407	413	
TeCl ₃ ⁺	Te; Cl	1.38; 1.02	2.16	2.09	100	111	
TeI ₃ ⁺	Te; I	1.38; 1.39	2.43	2.34	168	154	
W ₂ (CO) ₁₀ Se ₄ ²⁺	W; C; O; Se	1.62; 0.76; 0.66; 1.2	2.90	2.89	447	420	
Xe ₂ F ₁₁ ⁺	Xe; F	1.4; 0.57	2.66	2.50	184	190	
Xe ₂ F ₃ ⁺	Xe; F	1.4; 0.57	2.21	2.08	123	109	
XeF ⁺	Xe; F	1.4; 0.57	1.74	1.60	45	49	
XeF ₃ ⁺	Xe; F	1.4; 0.57	1.83	1.79		70	
XeF ₅ ⁺	Xe; F	1.4; 0.57	1.86	1.95	77	90	
XeOF ₃ ⁺	Xe; O; F	1.4; 0.66; 0.57	1.86	1.89		82	

Table S5. Comparison between the thermochemical radii and the ionic radii in aqueous solutions for complex ions.

Ion	$r_{\text{MX}}^{\text{ref}}$ (Å)	$r_{\text{MX}}^{\text{calc}}$ (Å)	$r_{\text{MX}}^{\text{aqueous}}$ (Å)
$\text{N}(\text{CH}_3)_4^+$	2.01	2.15	2.80
NH_3CH_3^+	1.77	1.65	2.00
NH_4^+	1.36	1.36	1.48
UO_2^{2+}		1.63	1.75
$\text{Au}(\text{CN})_2^-$	2.66	2.47	3.20
AuCl_4^-	2.88	2.90	3.30
$\text{B}(\text{OH})_4^-$	2.29	2.23	2.30
BF_4^-	2.05	2.11	2.32
Br_3^-	2.38	2.22	2.70
BrO_3^-	2.14	2.02	1.91
CH_3CO_2^-	1.94	1.86	1.90
ClO_2^-	1.95	1.76	2.40
ClO_3^-	2.08	2.02	2.00
ClO_4^-	2.25	2.22	2.40
CN^-	1.87	1.84	1.91
CNO^-	1.93	2.05	2.03
CNS^-	2.09	2.29	2.13
H_2AsO_4^-	2.27	2.23	2.48
H_2PO_4^-	2.13	2.23	2.38
HCO_2^-	2.00	1.81	1.69
HCO_3^-	2.07	2.02	1.56
HF_2^-	1.72	1.68	1.72
HSO_4^-	2.21	2.23	2.30
I_3^-	2.72	2.52	2.85
IO_3^-	2.18	2.09	1.81
IO_4^-	2.31	2.23	2.50
MnO_4^-	2.20	2.23	2.40
NO_2^-	1.87	1.76	1.92
NO_3^-	2.00	2.02	2.00
OH^-	1.52	1.40	1.33
ReO_4^-	2.27	2.23	2.60
SeH^-	1.95	1.98	2.05
SH^-	1.91	1.84	2.07

Table S5. Continued.

Ion	$r_{\text{MX}}^{\text{ref}}$ (Å)	$r_{\text{MX}}^{\text{calc}}$ (Å)	$r_{\text{MX}}^{\text{aqueous}}$ (Å)
CO_3^{2-}	1.89	2.10	1.78
$\text{Cr}_2\text{O}_7^{2-}$	2.92	2.79	3.20
CrO_4^{2-}	2.29	2.32	2.40
MoO_4^{2-}	2.31	2.33	2.54
PdCl_6^{2-}	3.33	3.43	3.19
PtCl_6^{2-}	3.33	3.43	3.95
$\text{S}_2\text{O}_3^{2-}$	2.51	2.54	2.50
$\text{S}_2\text{O}_4^{2-}$	2.62	2.32	2.50
$\text{S}_2\text{O}_6^{2-}$	2.83	2.65	2.70
$\text{S}_2\text{O}_8^{2-}$	2.91	2.89	3.00
$\text{S}_4\text{O}_6^{2-}$	3.25	2.77	3.10
SeO_4^{2-}	2.29	2.32	2.43
SiF_6^{2-}	2.48	2.52	2.59
SiO_3^{2-}	1.95	2.11	2.14
SO_3^{2-}	2.04	2.10	2.00
SO_4^{2-}	2.18	2.31	2.30
WO_4^{2-}	2.37	2.33	2.57
AsO_4^{3-}	2.37	2.37	2.48
$\text{Co}(\text{CN})_6^{3-}$	3.49	3.57	3.75
$\text{Fe}(\text{CN})_6^{3-}$	3.47	3.57	3.80
PO_4^{3-}	2.30	2.37	2.38