Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

On the relationship between structural and volumetric properties of solvated metal ions in O-donor solvents using new structural data in amide solvents

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Electronic Supplementary Information

Table S1. A selection of physical properties of different solvents

Solvent	Formula	Mp [a,b]	Bp [a,b]	D_S [c]	D_N [c]	ε_r [b,d]	μ [b,e]
Water	H_2O	0.0	100.0	17	18.0	78.5	1.85
Methanol	CH_3OH	-97.5	64.5	18	19	33.0	1.70
Ethanol	C_2H_5OH	-114.14	78.24	19	18.5	25.3	1.69
Dimethylsulfoxide	$(CH_3)_2SO$	18.5	189.0	27.5	29.8	46.4	3.96
N,N-Dimethylformamide	$(CH_3)_2NCHO$	-60.3	152.8	24	30.9	38.25	3.82
N,N-Dimethylacetamide	$(CH_3)_2N(CH_3)O$	-19	165.9	24	32.2	38.85	3.7
N,N-Dimethylpropionamide	$(CH_3)_2N(C_2H_5)O$	-19	165.9	24	32.2	38.85	3.7

[a] Melting points (Mp) and boiling points (Bp) given are in ^{o}C at atmospheric pressure (1 bar), unless noted.
[b] Data from Handbook of Chemistry and Physics, 96th Ed., Haynes, W. M. editor-in chief, CRC Press 2015-2016
[c] Donor strength (D_S) is a more complete quantitative measure of Lewis basicity, Sandström, M.; Persson, P.; Persson, I. *Acta Chem. Scand.* **1990**, *44*, 653-675, compared to the donor number (D_N) introduced by Gutmann. D_S is defined as ν_{HgBr_2}(g) - ν_{HgBr_2} (solv)
[d] The relative permittivity (ε_r) listed is relative to that of vacuum, $\varepsilon_o \approx 8.854 \cdot 10^{-12}$ F/m.
[e] The dipole moment is in Debye (1.00 D $\approx 3.335 \cdot 10^{-30}$ C·m).

Table S2a. Summary of M-O bond distances in solid alkaline earth metal ion hydrates listed in the Cambridge Structural Database (ref. f, letter codes) and the Inorganic Crystal Structure Database (ref. g, number codes).

Beryllium hydrates

Four-coordination

KIDREU	1.606	Robl, C.; Hentschel, S. *Z. Naturforsch., B: Chem. Sci.* **1990**, *45*, 1499-1502. $[Be(H_2O)_4]^{2+}$
417642	1.607	Massa, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2007**, *633*, 1366-1370. $[Be(H_2O)_4]^{2+}$
CADZIS	1.609	Fischer, N.; Klapotke, T.M.; Peters, K.; Rusan, M.; Stierstorfer J. *Z. Anorg. Allg. Chem.* **2011**, *637*, 1693-1701. $[Be(H_2O)_4]^{2+}$
KIQPEH	1.609	Klepov, V.V.; Vologzhanina, A.V.; Serezhkina, L.B.; Serezhkin V.N. *Radiokhimiya* **2012**, *54*, 500-504. $[Be(H_2O)_4]^{2+}$
MINKUP	1.616	Moers, O.; Friedrichs, S.; Blaschette, A.; Jones P.G. *Z. Anorg. Allg. Chem.* **2002**, *628*, 589-595. $[Be(H_2O)_4]^{2+}$
15858	1.616	Divjakovic, V.;Edenharter, A.;Nowacki, W.;Ribar, B. *Z. Kristallogr. Kristallgeom. Kristallph. Kristallch.* **1976**, *144*, 314-322 $[Be(H_2O)_4]^{2+}$
KIDREU01	1.617	Robl, C.; Hentschel, S.; McIntyre, G.J. *J. Solid State Chem.* **1992**, *96*, 318-323. $[Be(H_2O)_4]^{2+}$
INIMAU	1.618	Puchta, R.; Neumuller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2011**, *637*, 67-74. $[Be(H_2O)_4]^{2+}$
CICXOC	1.619	Yasodha, V.; Govindarajan, S.; Low, J.N.; Glidewell, C. *Acta Crystallogr., Sect.C* **2007**, *63*, m2720. $[Be(H_2O)_4]^{2+}$

Mean *d*(Be-O) = 1.613 Å/9 structures; $r_{Be(II)4}$ = 0.273 Å

Five-coordination

No five-coordinate beryllium(II) hydrates are reported.

Magnesium hydrates

Four-coordination

INSMGC	*n/a*	Blank, G *Acta Crystallogr.,Sect.B* **1973**, *29*, 1677-1683. *In reality a six-coordinate structure.*
SUKHUB	*n/a*	Egli, M.; Gessner, R.V.; Williams, L.D.; Quigley, G.J.; van der Marel, G.A.; van Boom, J.H.; Rich, A.; Frederick, C.A. *Proc.Nat.Acad.Sci.USA (1990),* **1990**, *87*, 3235-3235. $[Mg(H_2O)_4]^{2+}$?

Five-coordination

No five-coordinate magnesium(II) hydrates reported; ref. code KELDAC in CSD is erroneously listed as one, but is in reality six-coordinate.

Six-coordination

314 structures with hexaaquamagnesium(II) ions are listed in CSD, of which 249 have structural coordinates plus 69 structures from ICSD, including: AFEXEQ, AFEXIU, AHAKAX, AJIDUT, AJIDUT01, AMATIT, ANAPHS, APOJIZ, AQMEDA, AQOKEY, ASABAX, ASUNOT, ASUNUZ, ASUPAH, AVOLAA, AXIMOJ, AYIPII, BADTEX01, BADTEX10, BEKCID, BIHLIO, BIHNEM, BIKPUG, BIPQEY, BUVRAM, CADZEO, CAWCEK, CAWTID, CEBBUI, CIKYEC, CIPGIS, CIRVAA, CIRVAA01, CIVBUG, CUPRUB, CUPSIQ, CUPVEP, DABDEQ, DABDEQ01, DAMZAT, DANFUU, DAQMIT, DAWVED, DAWVON, DAWVON01, DEHMIN, DELBIH, DERJOZ, DOFXAY, DOFXIG, DUVNAL, DXMGHC10, EGAXIV, EKOYIO, EMEZAX, ENEFOT, EXUBOO, FADPEG, FAHJOQ, FAHSAI, FEDQUA, FEDQUA01, FETHAO, FUGCAM, FUJGOI, FURWIZ, FUYCOS, FUYCOS01, GADZAP, GAKPOY, GANVUO, GATLUI, GELTEX, GIJVEA, GIYCAT, GIYCEX, GIYCIB, GIYCOH, GOBSIA, GOLPIG, GUCSUU, GUHHOG, GUVJUE, HAGVOA, HAHWAO, HAZZIT, HAZZOZ, HAZZUF, HEBBAT, HETZUB, HONGOH, IBEMIM, IDIFEG, IFOYAE, IJIVED, IJIZIL, ILUXAO, IMAFOR, IRUYEB, IVOTET, IWOYEY, JAMQAQ, JEJTEY, JEYCEW, JOKQOQ, KAYQUY, KEQRAZ, KESVEL, KIDLUF, KIMNID, KURWOK, LAFYIB, LIFHEO, LONQIP, LUTVUS, LUZZUC, MAVDOD, MGCITD, MGEDTA01, MGHBZA10, MGHBZA20, MGNTSP, MINKOJ, MISXER, MODFAN, MOYTAV, MOYVOM, NEMRUU, NIMXOX, NIMXUD, NIQLIJ, NIQLIJ01, NIQLIJ02, NIQLIJ03, NOPPUE, NOQNIS, NUHROY, OBOHIY, OHUCEZ, OHUCID, OKOKOP, OKOKUV, OKOKUV01, OKUTUL, OKUTUL02, OKUVAT, OKUVAT01, OKUVAT02, OKUZIF, OLOKAD, ORAQOP, OROFEI, PICDUC, POHGIC01, PONGIJ, PONGIJ01, PONGUV, PUFYOF, QAJBOU, QERJIH, QEZKEM, QOFGID, QOFVIS, QOGYUI, RACBII, RAKYOR, RAKYOR01, RAMXOS, RARYUG, RATRIN, RATRIN01, REFTEC, RIHCOC, RIHFEV, RIRGEF, RIVCAA, RUMQUL, SEKKEZ, SEQQIQ, SIMZUJ, SUGKAI, TAHKUJ, TEHJUN, TEKBIU, TEZGOW, THIAMG10, TIZTIG, TOXDMG, TUCGII, TUGGEJ, TUHMOZ, UDIVIN, UDIVIN01, ULAQEE, ULAQEE01, ULULUK, UMANEB, UMANOL, UNATEI, UNEWEP, UNEVUE, UNUBAI, WABFOW, VAFKET, WANKUT, WIKXAP, VILLAE, VILLEI, VILLIM, VINFEF, WITMUJ, VOPCEI, WOPXOQ, VUKMIX, VUNFER, WUNWAF, VUYJIJ, XAGVAF, XAHFAQ, XECJIY, XECPEC, XEZCIP, XITDUZ, XOSPOL, YADGOB, YAQVUI, YIBROR, YIDVIR, YIGCOH, YIKKAG, YIKKEK, YIKKIO, YIKKOU, YIKKUA, YIKLAH, YIYBOZ, YOCGAA, YODWUK, YOHJAI, YORYOU, YOZTUE, YUNNAY, ZARMEK, ZURWIS, ZURWIS01, ZZZNLI01, and 1834, 2153, 2733, 10423, 35627, 61681, 63024, 63025, 65657, 68485, 69476, 69538, 69572, 74520, 79313, 80936, 81465, 86091, 87745, 89819, 95364, 96559, 151005, 155933, 158480, 162313, 163021, 166057, 170694, 172340, 181638, 181639, 188686, 190740, 191951, 192443, 236334, 236335, 248632, 248730, 250186, 250187, 250196, 250370, 252174, 252175, 260038, 260150, 260246, 281355, 281563, 401096, 409491, 409719, 409737, 409746, 409875, 409998, 413594, 413819, 415705, 416173, 419834, 419835, 419836, 419837, 710002, and 710008.

Excluded structures: 65 structures without crystal coordinates and AVEQUP, HMTMGC10, KIDLUF, LONQIP, NALFEO, 16007, 23220, 26040-26042, 28663, 49914, 74521, 78422, 79314, 79821, 185207, 188928, 192134-192137, 248633, 249107, 261110, 261581, 415688, 419421-419423, and 427801 (erroneous values).

Mean *d*(Mg-O) = 2.064 Å/318 structures; $r_{Mg(II)6}$ **= 0.724 Å**

Calcium hydrates

Five-coordination

No five-coordinate calcium(II) hydrates reported; ref. code WUZGAB in CSD is erroneously listed as one.

Six-coordination

RALHAO02	2.064 Å	Barnes, J.C. *private communication to CSD*, **2005**. $[Ca(H_2O)_6]^{2+}$
RALHAO	2.086 Å	Barnes, J.C. *private communication to CSD*, **2005**. $[Ca(H_2O)_6]^{2+}$
100329	2.248 Å	Rius, J.;Allmann, R. Fortschr. Mineral., Beiheft **1978**, *56*, 113-114. $[Ca(H_2O)_6]^{2+}$
FELWOK	2.297 Å	Torres, J.; Gonzalez-Platas, J.; Sanchiz, J.; Castiglioni, J.; Dominguez, S.; Kremer, C. *Inorg. Chim. Acta* **2013**, *394*, 196-202. $[Ca(H_2O)_6]^{2+}$
FELWIE	2.300 Å	Torres, J.; Gonzalez-Platas, J.; Sanchiz, J.; Castiglioni, J.; Dominguez, S.; Kremer, C. *Inorg. Chim. Acta* **2013**, *394*, 196-202. $[Ca(H_2O)_6]^{2+}$
FELVUP	2.305 Å	Torres, J.; Gonzalez-Platas, J.; Sanchiz, J.; Castiglioni, J.; Dominguez, S.; Kremer, C. *Inorg. Chim. Acta* **2013**, *394*, 196-202. $[Ca(H_2O)_6]^{2+}$
WANLII	2.306 Å	Rajbanshi, A.; Custelcean, R. *Supramol. Chem.*, **2012**, *24*, 65-71. $[Ca(H_2O)_6]^{2+}$
FELWAW	2.307 Å	Torres, J.; Gonzalez-Platas, J.; Sanchiz, J.; Castiglioni, J.; Dominguez, S.; Kremer, C. *Inorg. Chim. Acta* **2013**, *394*, 196-202. $[Ca(H_2O)_6]^{2+}$
FELVID	2.307 Å	Torres, J.; Gonzalez-Platas, J.; Sanchiz, J.; Castiglioni, J.; Dominguez, S.; Kremer, C. *Inorg. Chim. Acta* **2013**, *394*, 196-202. $[Ca(H_2O)_6]^{2+}$
FELVEZ	2.309 Å	Torres, J.; Gonzalez-Platas, J.; Sanchiz, J.; Castiglioni, J.; Dominguez, S.; Kremer, C. *Inorg. Chim. Acta* **2013**, *394*, 196-202. $[Ca(H_2O)_6]^{2+}$
67944	2.309 Å	Duhlev, R.;Brown, I.D. Z. Kristallogr. **1993**, *204*, 255-262. $[Ca(H_2O)_6]^{2+}$
WANLAA	2.311 Å	Rajbanshi, A.; Custelcean, R. *Supramol. Chem.* **2012**, *24*, 65-71. $[Ca(H_2O)_6]^{2+}$
WANLEE	2.313 Å	Rajbanshi, A.; Custelcean, R. *Supramol. Chem.* **2012**, *24*, 65-71. $[Ca(H_2O)_6]^{2+}$
RALHAO01	2.315 Å	Barnes, J.C. *private communication to CSD*, **2005**. $[Ca(H_2O)_6]^{2+}$
GAYLOH	2.316 Å*	Cini, R.; Marzilli, L. G., *Inorg. Chem.* **1988**, *27*, 1855-1856. $[Ca(H_2O)_6]^{2+}$?
FELWUQ	2.317 Å	Torres, J.; Gonzalez-Platas, J.; Sanchiz, J.; Castiglioni, J.; Dominguez, S.; Kremer, C. *Inorg. Chim. Acta* **2013**, *394*, 196-202. $[Ca(H_2O)_6]^{2+}$
NOGLEA	2.320 Å	Simonsen, O., *Acta Chem. Scand.* **1997**, *51*, 861-864. $[Ca(H_2O)_6]^{2+}$

FELWEA	2.321 Å	Torres, J.; Gonzalez-Platas, J.; Sanchiz, J.; Castiglioni, J.; Dominguez, S.; Kremer, C. *Inorg. Chim. Acta* **2013**, *394*, 196-202.. $[Ca(H_2O)_6]^{2+}$
FELVOJ	2.326 Å	Torres, J.; Gonzalez-Platas, J.; Sanchiz, J.; Castiglioni, J.; Dominguez, S.; Kremer, C. *Inorg. Chim. Acta* **2013**, *394*, 196-202.. $[Ca(H_2O)_6]^{2+}$
WITNAQ	2.327 Å	Rui Zhang, Yanxia Zhao, Jiamin Wang, Liguo Ji, Xiao-Juan Yang, Biao Wu, *Cryst. Growth Des.*, **2014**, *14*, 544-551. $[Ca(H_2O)_6]^{2+}$
RIHXIR	2.327 Å	L.Suescun, Jun Wang, R.Faccio, G.Peinado, J.Torres, C.Kremer, R.A.Burrow, Powder Diffr. 2012, 27, 232-242. $[Ca(H_2O)_6]^{2+}$
BIHNIQ	2.328 Å	Kennedy, A.R.; Kirkhouse, J.B.A.; McCarney, K.M.; Puissegur, O.; Smith, W.E.; Staunton, E.; Teat, S.J.; Cherryman, J.C.; James, R., *Chem.-Eur. J.* **2004**, *10*, 4606-4615. $[Ca(H_2O)_6]^{2+}$
DOXKUX	2.329 Å	Klapotke, T.M.; Stierstorfer, J. *J. Am. Chem. Soc.* **2009**, *131*, 1122-1134. $[Ca(H_2O)_6]^{2+}$
XEDFAO	2.342 Å	Cetin, A.; Ziegler, C.J. *Dalton Trans.* **2006**, 1006-1008. $[Ca(H_2O)_6]^{2+}$
DECDOE	2.396 Å*	Cini, R.; Burla, M. C.; Nunzi, A.; Polidori, G. P.; Zanazzi, P. F., *J. Chem. Soc., Dalton Trans.* **1984**, 2467-2476. $[Ca(H_2O)_6]^{2+}$?
EMETEW	2.464 Å*	Tamasi, G.; Berrettini, F.; Hursthouse, M.B.; Cini, R. *Open Crystallogr. J.* **2010**, *3*, 1-13. $[Ca(H_2O)_6]^{2+}$?
CICPUZ	*no coord.*	Cini, R.; Sabat, M.; Sundaralingam, M.; Burla, M. C.; Nunzi, A.; Polidori, G. P.; Zanazzi, P. F., *J. Biomol. Struct. Dyn.* **1983**, *1*, 633-637. $[Ca(H_2O)_6]^{2+}$
YADFEO	*n/a*	Zviedre, I. I.; Shvarts, E. M.; Bel'skii, V. K., *Latv. PSR Zinat. Akad. Vestis, Khim. Ser.* **1990**, 679. $[Ca(H_2O)_6]^{2+}$?

Mean *d*(Ca-O) = 2.316 Å/20 structures; $r_{Ca(II)6}$ = 0.976 Å

* incomplete coordination sphere

Seven-coordination

WIKXET	2.380 Å	Ojala, W. H.; Lu, L. K.; Albers, K. E.; Gleason, W. B.; Richardson, T. I.; Lovrien, R. E.; Sudbeck, E. A., *Acta Crystallogr., Sect. B* **1994**, *50*, 684-694. $[Ca(H_2O)_7]^{2+}$
NARKEY	2.384 Å	Yoshida, R.; Ogasahara, S.; Akashi, H.; Shibahara, T., *Inorg.Chim.Acta* **2012**, *383*, 157-163. $[Ca(H_2O)_7]^{2+}$
426335	2.390 Å	Hummel, T.; Glaser, J.; Stroebele, M.; Meyer, H.-J. Z. Anorg. Allg. Chem. 2013, 639, 2637-2642. $[Ca(H_2O)_7]^{2+}$
REMNAY	2.391 Å	Moers, O.; Blaschette, A.; Jones, P. G., *Acta Crystallogr., Sect.C* **1997**, *53*, 845-848. $[Ca(H_2O)_7]^{2+}$
HEPHOZ	2.392 Å	Shkol'nikova, L. M.; PoraiKoshits, M. A.; Poznyak, A. L., *Koord. Khim.* **1993**, *19*, 683-690. $[Ca(H_2O)_7]^{2+}$
WUKVEF	2.397 Å	Zhou,Q., Qian,J., Zhang,C., *J. Mol. Struct.* **2016**, *1119*, 340-345. $[Ca(H_2O)_7]^{2+}$
60773	2.401 Å	Faggiani, R.;Villella, M.;Brown, I.D. *Acta Crystallogr, Sect. C* **1986**, *42*, 773-774. $[Ca(H_2O)_7]^{2+}$
AHAKEB	2.403 Å	Baokuan Chen, *private communication to CSD*, **2015**. $[Ca(H_2O)_7]^{2+}$

CUPSUC	2.405 Å	Kennedy, A.R.; Andrikopoulos, P.C.; Arlin, J.-B.; Armstrong, D.R.; Duxbury, N.; Graham, D.V.; Kirkhouse, J.B.A., *Chem.-Eur.J.* **2009**, *15*, 9494-9504. $[Ca(H_2O)_7]^{2+}$
29437	2.407 Å	Takagi, S.; Mathew, M.; Brown, W. E., *Acta Crystallogr., Sect. C* **1984**, *40*, 1111-1113. $NH_4[Ca(H_2O)_7][PO_4]$.
20719	2.409 Å	Solntsev, K. A.; Kuznetsov, N. T.; Ponomarev, V. I., *Iz. Akad. Nauk SSSR, Neorg. Mater.* **1976**, *12*, 1044-1048. $[Ca(H_2O)_7][B_{12}H_{12}]\cdot H_2O$.
ZZZKVU10	2.411 Å	Brown, C. J.; Ehrenberg, M.; Yadav, H. R., *Acta Crystallogr., Sect. C* **1984**, *40*, 58-60. $[Ca(H_2O)_7]^{2+}$
187781	2.411 Å	Kampf, A.R.;Hughes,J.M.;Marty, J.;Nash, B. Can. Mineral. **2013**, *51*, 297-312. $[Ca(H_2O)_7]^{2+}$
RUMQOF	2.412 Å	Zasurskaya, L.A. ; Pozdnyak, A. L.; Polynova, T. N.; Rybakov, V. B.; Porai-Koshits, M. A., *Zh. Neorg. Khim.* **1996**, *41*, 1647-1655. $[Ca(H_2O)_7]^{2+}$
94430	2.415 Å	Tiritiris, I.; Schleid, T., *Z. Anorg. Allg. Chem.* **2001**, *627*, 1836-1845. $[Ca(H_2O)_7]^{2+}$
ZZZKVU	*no coord.*	Corbridge, D. E. C.; Brown, C. J.; Wallwork, S. C., *Acta Crystallogr.* **1966**, *20*, 698-699. $[Ca(H_2O)_7]^{2+}$

Mean *d*(Ca-O) = 2.401 Å/15 structures; $r_{Ca(II)7}$ = 1.061 Å

Eight-coordination

LIQRAE	2.417 Å*	Shibahara, T.; Yoshida, S.; Maeyama, M.; Kojima, M.; *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2271-2275. $[Ca(H_2O)_8]^{2+}$
32502	2.421 Å*	Thomas, R.; Moore, F. H., *Acta Crystallogr., Sect. B* **1981**, *37*, 2156-2159. $[Ca(H_2O)_8](I_5)_2$.
33874	2.428 Å*	Putzas, D.; Rotter, H.W.; Thiele, G.; Brodersen, K.; Pezzei, G., *Z. Anorg. Allg. Chem.* **1991**, *595*, 193-202. $[Ca(H_2O)_8]^{2+}$
YOHFIM	2.458 Å	Hennings, E.; Schmidt, H.; Voigt, W., *Acta Crystallogr., Sect.C* **2014**, *70*, 876-881. $[Ca(H_2O)_8]^{2+}$
30570	2.460 Å	Harr, T. E., *Thesis Univ. Syracuse (USA)* **1947**, 1-116. $[Ca(H_2O)_8]O_2$.
YOHGAF	2.463 Å	Hennings, E.; Schmidt, H.; Voigt, W., *Acta Crystallogr., Sect.C* **2014**, *70*, 876-881. $[Ca_2(H_2O)_{13}]^{4+}$
65087	2.464 Å	Thiele, G.;Putzas, D. *Z. Naturforsch., B: Chem. Sci.* **1988**, *43*, 1224-1234. $[Ca(H_2O)_8]^{2+}$
YOHFUY	2.466 Å	Hennings, E.; Schmidt, H.; Voigt, W., *Acta Crystallogr., Sect.C* **2014**, *70*, 876-881. $[Ca_2(H_2O)_{14}]^{4+}$
65085	2.466 Å	Thiele, G.;Putzas, D. *Z. Naturforsch., B: Chem. Sci.* **1988**, *43*, 1224-1234. $[Ca(H_2O)_8]^{2+}$
YOHFOS	2.467 Å	Hennings, E.; Schmidt, H.; Voigt, W., *Acta Crystallogr., Sect.C* **2014**, *70*, 876-881. $[Ca_2(H_2O)_{14}]^{4+}$
MINBOA	2.474 Å	Hammerl, A.; Holl, G.; Klapotke, T.M.; Mayer, P.; Noth, H.; Piotrowski, H.; Warchhold, M., *Eur. J. Inorg. Chem.* **2002**, 834-845. $[Ca_2(H_2O)_{14}]^{4+}$
30571	2.475 Å	Harr, T. E., *Thesis*, Univ. Syracuse (USA) 1947, 1947, 1-116. $[Ca(H_2O)_8]O_2$.
32548	2.476 Å	Leligny, H.; Monier, J.-C., *Acta Crystallogr., Sect. B* **1982**, *38*, 355-358. $[Ca(H_2O)_8]_2[Cd_3Cl_{10}]\cdot 2H_2O$.
2832	2.477 Å	Dickens, B.; Brown, W. E., *Acta Crystallogr., Sect. B* **1972**, *28*, 3056-3065. $K[Ca(H_2O)_8](AsO_4)$.
LIQREI	2.480 Å	Shibahara, T.; Yoshida, S.; Maeyama, M.; Kojima, M.; *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2271-2275. $[Ca(H_2O)_8]^{2+}$

POXKIW 2.481 Å Henke, K., Atwood, D. A., *Inorg. Chem.* **1998**, *37*, 224-227. $[Ca(H_2O)_8]^{2+}$

Mean *d*(Ca-O) = 2.470 Å/13 structures; $r_{Ca(II)8}$ = 1.130 Å

* incomplete or distorted coordination sphere

Nine-coordination

No nine-coordinate calcium(II) hydrates reported

Strontium hydrates

Five-coordination

No five-coordinate strontium(II) hydrates reported

Six-coordination

OPIFUQ 2.419 Å Yu Shen, Cong-Cong Fan, Yu-Zhen Wei, Jie Du, Hai-Bin Zhu, Yue Zhao, Dalton Trans. 2016, 45, 10909-10915. $[Sr(H_2O)_6]^{2+}$

USATEO 2.505 Å Yanmei Chen, Lina Zheng, Shixiong She, Zhou Chen, Bin Hu, Yahong Li *Dalton Trans.* **2011**, *40*, 4970-4975. $[Sr(H_2O)_6]^{2+}$

KOWFEJ 2.522 Å Savchenkov, A.V.; Klepov, V.V.; Vologzhanina, A.V.; Serezhkina, L.B.; Pushkin, D.V.; Serezhkin, V.N. *CrystEngComm* **2015**, *17*, 740-746. $[Sr(H_2O)_6]^{2+}$

Mean *d*(Sr-O) = 2.514 Å/2 structures; $r_{Sr(II)6}$ = 1.174 Å

Seven-coordination

No seven-coordinate strontium(II) hydrates reported; closest structure is EMUSUA, a monovalent hexaaquabenzoatostrontium(II) complex with a mean Sr-O bond distance of 2.537 Å, $r_{Sr(II)7}$ = 1.197Å

Eight-coordination

30572 2.578 Å Harr, T. E., *Thesis Univ. Syracuse (USA)*, **1947**, 1-116. $[Sr(H_2O)_8]O_2$

CUPRAH 2.599 Å Kennedy, A.R.; Andrikopoulos, P.C.; Arlin, J.-B.; Armstrong, D.R.; Duxbury, N.; Graham, D.V.; Kirkhouse, J.B.A. *Chem.-Eur. J.* 2009, 15, 9494. $[Sr(H_2O)_7L]^+$.

VOGDUQ 2.600 Å Hardie, M. J.; Raston, C. L.; Salinas, A., *Chem. Commun.* **2001**, 1850-1851.

35297 2.606 Å Thiele, G.; Brodersen, K.; Pezzei, G., *Z. Anorg. Allg. Chem.* **1982**, *491*, 308-318. $[Sr(H_2O)_8][HgI_4]$

65086 2.607 Å Thiele, G.; Putzas, D., *Z. Naturforsch., Teil B* **1988**, *43*, 1224-1234. $[Sr(H_2O)_8][CdI_4]$

XIJXEV	2.608 Å	Bazhina, E. S.; Nikiforova, M. E.; Aleksandrov, G. G.; Efimov, N. N.; Kiskin, M. A.; Ugolkova, E. A.; Minin, V. V.; Sidorov, A. A.; Novotortsev, V. M.; Eremenko, I. L. *Russ.Chem.Bul.* **2012**, *61*, 1426-1429. $[Sr(H_2O)_8]_n(VC_{10}H_{12}O_9)_n$
GETSII	2.609 Å	Zasurskaya, L. A.; Polyakova, I. N.; Rybakov, V. B.; Polynova, T. N.; Poznyak, A. L.; Sergienko, V. S. Crystallogr. Rep. **2006**, *51*, 448-458. $[Sr(H_2O)_8][Co(edta)]\cdot H_2O$
POXKOC	2.614 Å	Henke, K.; Atwood, A. T., *Inorg. Chem.* **1998**, *37*, 224-227. $[Sr(H_2O)_8](C_3N_3H_2S_3)\cdot H_2O$
16385	2.619 Å	Geller, S.; Dudley, T.O., *J. Solid State Chem.* **1978**, *26*, 321-328. $[Sr(H_2O)_8][Ag_2I_4]$.
94431	2.624 Å	Tiritiris, I.; Schleid, T., *Z. Anorg. Allg. Chem.* **2001**, *627*, 1836-1845. $[Sr(H_2O)_8][B_{12}H_{12}]$.
16430	2.630 Å	Lazarini, F.; Leban, I., *Acta Crystallogr., Sect. B* **1980**, *36*, 2745-2747. $[Sr(H_2O)_8][Bi_2Br_{10}]$.
200016	2.636 Å	Solntsev, K. A.; Kuznetsov, N. T.; Rannev, N. V.; Zavodnik, V. E., *Dokl. Akad. Nauk SSSR* **1977**, *232*, 1366-1369. $[Sr(H_2O)_7][B_{12}H_{12}]$.
87465	2.637 Å	Mathew, M., *J. Chem. Crystallogr.*, **1998**, *10*, 741-746. $K[Sr(H_2O)_8][AsO_4]$.
24775	2.645 Å	Vannerberg, N.-G., *Arkiv Kemi* **1959**, *14*, 17-30. $[Sr(H_2O)_8]O_2$.
250017	2.667 Å	Pushcharovskii, D. Yu.; Suleimanov, E. V.; Pasero, M.; Merlino, S.; Barinova, A. V.; Alekseev, E. V., *Kristallografiya* **2003**, *48*, 246-249. $[Sr(H_2O)_8][AsUO_6]$.

Mean *d*(Sr-O) = 2.616 Å/12 structures; $r_{Sr(II)8}$ = 1.276 Å

Nine-coordination

79713	2.660 Å	Abrahams, I.;Vordemvenne, E. *Acta Crystallogr., Sect. C* **1995**, *51*, 183-185. $[Sr(H_2O)_9]^{2+}$.
EFIZAV	2.685 Å	Murugavel, R.; Kuppuswamy, S.; Randoll, S. *Inorg. Chem.* **2008**, *47*, 6028-6039. $[Sr_2(H_2O)_{14}]^{2+}$.

Mean *d*(Sr-O) = 2.672 Å/2 structure; $r_{Sr(II)9}$ = 1.332 Å

Barium hydrates

Six-coordination

FABDEU	2.798 Å*	Jizhen Li; Chunyan Wang; Xiaoni Gao; Fengqi Zhao; Kai Zhao; Xuezhong Fan; Guofang Zhang; Weiqiang Zhang; Ziwei Gao, *Polyhedron* **2016**, *106*, 58-64. $[Ba(H_2O)_6]^{2+}$?. At least seven-coordinate, most likely eight-coordinate.
JUBXIP	*no coord.*	

* incomplete or distorted coordination sphere

Seven-coordination

VAWXOH	*n/a*	Erroneous structure

Eight-coordination

MUNKUC 2.813 Å Thuery, P. *Cryst. Growth Data* **2009**, *9*, 4592. $[Ba(H_2O)_8]^{2+}$.

Mean *d*(Ba-O) = 2.813 Å/1 structure; $r_{Ba(II)8}$ = 1.473 Å

Nine-coordination

195744 2.826 Å Thiele, G.; Vondung, L.; Donsbach, C.; Pulz, S.; Dehnen, S. *Z. Anorg. Allg. Chem.* **2014**, *640*, 2684-2700. $[Ba(H_2O)_9]^{2+}$

426703 2.827 Å Edhokkar, F.; Hadrich, A.; Mhiri, T.; Graia, M. *Journal of Molecular Structure* **2014**, *1059*, 260-264. $[Ba(H_2O)_9]^{2+}$

20539 2.828 Å Baturin, S.V.; Malinovskii, Yu.A.; Belov, N.V. *Doklady Akademii Nauk SSSR* **1982**, *266*, 624-627. $[Ba(H_2O)_9]^{2+}$

FEDWEQ 2.845 Å Harrowfield, J.M.; Sharma, R.P.; Skelton, B.W.; Venugopalam, P.; White, A.H. *Aust.J.Chem.* **1998**, *51*, 775. $[Ba(H_2O)_8NO_2\text{-}C_6H_4O]^{2+}$

EFIZEZ 2.849 Å Murugavel, R.; Kuppuswamy, S.; Randoll, S. *Inorg. Chem.* **2008**, *47*, 6028-6039. $[Ba_2(H_2O)_{14}]^{2+}$.

420481 2.901 Å Kazmiercak, K.; Heck, J.G.; Hoeppe, H.A. *Z. Anorg. Allg. Chem.* **2010**, *636*, 409-413. $[Ba(H_2O)_9]^{2+}$

ICEKAD 2.874 Å* Yuan-Fu Deng; Zhao-Hui Zhou; Hui-Lin Wan *Inorg. Chem.* **2004**, *43*, 6266-6273. $[Ba(H_2O)_9]^{2+}$?.

Mean *d*(Ba-O) = 2.835 Å/5 structures; $r_{Ba(II)9}$ = 1.495 Å

***** incomplete or distorted coordination sphere

Ten-coordination

DAXCAI 2.851 Å Yu Hou; Rodriguez, M.A.; Nyman, M. *Cryst.Growth Des.* **2012**, *12*, 1422. $[Ba_2(H_2O)_{16}]^{4+}$.

Mean *d*(Ba-O) = 2.851 Å/1 structure; $r_{Ba(II)10}$ = 1.511 Å

Radium hydrates

No radium hydrates are listed in the CSD or ICSD.

Table S2b. Summary of M-O bond distances and M-O-C amide angle in solid alkaline earth metal ion amide solvates listed in the Cambridge Structural Database (ref. f, letter codes).

***Magnesium (homoleptic)*, CN = 6**

COBHOQ	2.046 Å	130.4 º	Rao, C. P.; Rao, A. M.; Rao, C. N. R. *Inorg. Chem.* **1984**, *23*, 2080-2085. Dimethylformamide, $[Mg(dmf)_6](ClO_4)_2$
KOLDAQ	2.050 Å	153.3 º	Ruben, M.; Walther, D.; Knake, R.; Gorls, H.; Beckert, R. *Eur. J. Inorg. Chem.* **2000**, 1055-1064. Dimethylformamide, $[Mg(dmf)_6][Zn_2Br_4(N_4(C_6H_5)_4)]$
KOLBIW	2.053 Å	158.4 º	Ruben, M.; Walther, D.; Knake, R.; Gorls, H.; Beckert, R. *Eur. J. Inorg. Chem.* **2000**, 1055-1064. Dimethylformamide $[Mg(dmf)_6][Zn_2Cl_4(N_4(C_6H_5)_4)]$
REHHES	2.054 Å	131.8 º	Barker, B. L.; Aubry, D.; Fronczek, F. R.; Watkins, S. F.; Stanley, G. G. *Acta Crystallogr., Sect. E* **2006**, *62*, m942-m944. Dimethylformamide, $[Mg(dmf)_6][MgCl_4]$
NALFAK	2.058 Å	137.4 º	Jinfang Zhang, Yuhang Liu, Linpei Gong, Guozhi Xu, Chi Zhang *Polyhedron* **2016**, *109*, 67. Methylpyrrolidinone, $[Mg(mp)_6]_n[AgS_4W]_{2n}.2n\ C_5H_9NO$
QOFGOJ	2.059 Å	126.6 º	Nitschke, C.; Kockerling, M.; Bernhardt, E.; Kuppers, T.; Willner, H. *Dalton Trans.* **2014**, *43*, 7128-7138. Dimethylformamide, $[Mg(dmf)_6](B(CN)_4)_2$
YEMNOT	2.059 Å	147.4 º	Pavanello, L.; Visona, P.; Bresadola, S.; Bandoli, G. *Z. Kristallogr.* **1994**, *209*, 946-949. Dimethylacetamide, $[Mg(dma)_6](MgCl_4]$
YURWUF	2.063 Å	125.8 º	Landmann, J.; Sprenger, J.A.P.; Hailmann, M.; Bernhardt-Pitchougina, V.; Willner, H.; Ignat'ev, N.; Bernhardt, E.; Finze, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 11259. Dimethylformamide, $[Mg(dmf)_6]B_2(CN)_6$
NMALIE	2.064 Å	142.3 º	Chakrabarti, P.; Venkatesan, K.; Rao, C.N.R. *Proc. R. Soc. London, Ser. A* **1981**, *375*, 127. N-methylacetamide, $[Mg(maa)_6]Cl_2$
PINFEX	2.067 Å	132.0 º	Pavanello, L.; Visona, P.; Marigo, A.; Bresadola, S.; Valle, G. *Inorg. Chim. Acta* **1994**, *216*, 261. Formamide, $[Mg(fa)_6]Cl_2$
GOGNAR	2.077 Å	132.3 º	Krautscheid, H.; Vielsack, F. *Z. Anorg. Allg. Chem.* **1999**, *625*, 562-566. Dimethylformamide , $[Mg(dmf)_6][Pb_2I_6]$
DOXKIK			Huang Liangren, Jiang Feilong, Lu Jiaxi *Huaxue Tongbao* **1984**, 14-3. $[Mg(dmf)_6][Fe_2OCl_6]$
Mean	**2.059 Å/11 structures**		**Mean Mg-O-C angle: 138.0 º**

***Magnesium (heteroleptic)*, CN = 6**

NOJCEW	2.053 Å	142.0 º	D.A.Kuznetsov, I.V.Fedyanin, K.A.Lyssenko, T.A.Bazhenova *Dalton Trans.* **2014**, *43*, 12876. Dimethylformamide/methanol/water, $[Mg(dmf)_3(MeOH)_2(H_2O)]_2C_{46}H_{126}Mg_4Mo_{22}N_6O_{82}$
ROHZUL	2.057 Å	140.1 º	Grepioni, F.; Wouters, J.; Braga, D.; Nanna, S.; Fours, B.; Coquerel, G.; Longfils, G.; Rome, S.; Aerts, L.; Quere, L. *CrystEngComm* **2014**, *16*, 5887. oxopropylpyrrolidinylbutanamide/water, $[Mg(oppba)_2(H_2O)_4]Cl_2$
ROJBEZ	2.057 Å	141.4 º	Grepioni, F.; Wouters, J.; Braga, D.; Nanna, S.; Fours, B.; Coquerel, G.; Longfils, G.; Rome, S.; Aerts, L.; Quere, L. *CrystEngComm* **2014**, *16*, 5887. difluorovinyloxopyrrolidinylbutanamide/water, $[Mg(dfvopba)_2(H_2O)_4]Cl_2$
KAGSAP	2.062 Å	140.2 º	Xi-Shi Tai, Wen-Hua Zhao *Res. Chem. Intermed.* **2015**, *41*, 3471. Dimethylformamide/water, $[Mg(dmf)(H_2O)_5]C_{10}H_6O_6S_2$
DURSAK	2.063 Å	141.8 º	Lewinski, K.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108*, 3693. Dimethylformamide/water, $[Mg(dmf)_2(H_2O)_4](NO_3)_2$
TOFKUU01	2.065 Å	129.2 º	Reiss, G.J.; Boldog, I.; Janiak, C. *Acta Crystallogr., Sect. E* **2011**, *67*, m1109. Dimethylformamide/water, $[Mg(dmf)_4(H_2O)_3]Cl_2$
BIPPAT	2.066 Å	134.9	Okamura, T.; Nakagawa, J. *Inorg. Chem.* **2013**, *52*, 10812. Dimethylformamide/water, $[Mg(dmf)_2(H_2O)_4][C_{11}H_{11}N_2O_4]_2$
LEVNIK	2.070 Å	140.5 º	Senkovska, I.; Kaskel S. *Eur. J. Inorg. Chem.* **2006**, 4564. Dimethylformamide/water, $[Mg(dmf)_2(H_2O)_4]C_{12}H_6O_4$
TOFKUU	2.071 Å	129.9 º	Pavanello, L.; Marigo, A.; Bresadola, S.; Valle, G. *Main Group Met. Chem.* **1995**, *18*, 9. Dimethylformamide/water, $[Mg(dmf)_4(H_2O)_3]Cl_2$
Mean	**2.063 Å/9 structures**		**Mean Mg-O-C angle: 137.8 º**
Total mean	**2.061 Å/20 structures**		**Mean Mg-O-C angle: 137.9 º**

***Calcium (homoleptic)*, CN = 6**

BASPUH	2.288 Å	148.8 º	Chen Ling, Yu Heng, Wu Liming, Du Wenxin, Gao Xiancheng, Lin Ping, Zhang Wenjian, Cui Chuanpeng, Wu Xintao *J. Solid State Chem.* **2000**, *151*, 286-293. Diethylacetamide, $[Ca(dea)_6]_n(Ag_6S_{16}W_4)_n$
ZOWKAX	2.290 Å	145.2 º	Kim, Y.H.; Calabrese, J.; McEwen, C. *J. Am. Chem. Soc.* **1996**, *118*, 1545. Dimethylacetamide/cyclotris(m-phenylenediamine-*N*,*N*′-isophthaloyl), $[Ca(dma)_4(ctpdip)_2](C_{12}H_{27}CaCl_3N_3O_3)_2$

JUWJUG	2.293 Å	143.1 º	Fenske, D.; Baum, G.; Wolkers, H.; Schreiner, B.; Weller, F.; Dehnicke, K. *Z.Anorg. Allg. Chem.* **1993**, *619*, 489-499. Dimethylformamide, $[Ca(dmf)_6]Te_4$
PAHRIA	2.297 Å	147.3 º	Xue-Jie Tan, Si-Xiu Sun, Jian-Ping Ma, Lian-Dong Liu, Yu-Bin Dong, Wen-Tao Yu, Dian-Xiang Xing *Acta Crystallogr., Sect. C* **2004**, *60*, m476-m478. Dimethylformamide, $(C_5H_3(CH_3)_2N)[Ca(dmf)_6][Mo_{12}O_{40}]$
MOBRIE	2.313 Å	144.4 º	Perruchas, S.; Simon, F.; Uriel, S.; Avarvari, N.; Boubekeur, K.; Batail, P. *J. Organomet. Chem.* **2002**, *643*, 301-306. Dimethylformamide, $[Ca(dmf)_6][Re_6Cl_8S_6]$
SIQYOG	2.313 Å	143.7 º	Heng Yu, Wenjian Zhang, Xintao Wu, Tianlu Sheng, Quanming Wang, Ping Lin *Angew. Chem., Int. Ed.* **1998**, *37*, 2520-2521. Dimethylformamide, $[Ca(dmf)_6][Ag_2Mo_2S_8]$
HECMAE	2.318 Å	145.7 º	Xi Liu, Li-Zhen Cai, Guo-Cong Guo, Qiang Li, Jin-Shun Huang *Jiegou Huaxue* **2006**, *25*, 90. Dimethylformamide, $[Ca(dmf)_6][Mo_6Br_8Cl_6]$
LARCOX	2.330 Å	131.0 º	Ya-Min Li, Sheng-Qing Xia, Jian-Jun Zhang, Xin-Tao Wu, Long-Sheng Wang, Wen-Xin Du, Sheng-Min Hu *Jiegou Huaxue* **2005**, *24*, 716. Dimethylformamide, $[Ca(dmf)_6][Ag_2W_2S_8]$
CUCNEU	*no coord.*		Kozhomuratova Z. S.; Mironov, Y. V.; Shestopalov, M. A.; Gaifulin, Y. M.; Kurat'eva, N. V.; Uskov, E. M.; Fedorov, V. E.; *Koord. Khim.* **2007**, *33*, 3. $[Ca(dmf)_6][Mo_6Cl_{14}]$
Mean	**2.305 Å/8 structures**		**Mean Ca-O-C angle: 142.3 º**

***Calcium (heteroleptic)*, CN = 6**

NMALID	*erroneous*		Chakrabarti, P; Venkatesan, K., Rao, C.N.R. *Proc. R. Soc. London, Ser. A*. **1981**, *375*, 127. Water/*N*-methylacetamide, $[Ca(H_2O)_2(nmaa)_4]Cl_2$
VEBGUE01	2.327 Å	168.9 º	Cole, L.B.; Holt, E.M Inorg. Chim. Acta 1989, 162, 291. Water/isonicotinamide, $[Ca(H_2O)_4(ina)_6]Cl_2$
VEBGUE	2.332 Å	167.7 º	Cole, L.B.; Holt, E.M Inorg. Chim. Acta 1989, 162, 291. Water/isonicotinamide, $[Ca(H_2O)_4(ina)_6]Cl_2$
Mean	**2.330 Å/2 structures**		**Mean Ca-O-C angle: 168.3 º**
Total mean	**2.310 Å/10 structures**		**Mean Ca-O-C angle: 147.5 º**

***Strontium (homoleptic)*, CN = 6**

OJINUR	2.451	153.7 º	Jinfang Zhang, Suci Meng, Yinglin Song, Huajian Zhao, Jianghua Li, Gaoju Qu, Liang Sun, M.G.Humphrey, Chi Zhang *Chem. Eur. J.* **2010**, *16*, 13946-13950. $[Sr(dma)_6]_2[Ag_4Mo_4S_{16}]$
OJIPAZ	2.445	147.5 º	Jinfang Zhang, Suci Meng, Yinglin Song, Huajian Zhao, Jianghua Li, Gaoju Qu, Liang Sun, M.G.Humphrey, Chi Zhang *Chem. Eur. J.* **2010**, *16*, 13946-13950. $[Sr(dma)_6]_2[Ag_4W_4S_{16}]$

OJIPED	2.458	156.5 º	Jinfang Zhang, Suci Meng, Yinglin Song, Huajian Zhao, Jianghua Li, Gaoju Qu, Liang Sun, M.G.Humphrey, Chi Zhang *Chem. Eur. J.* **2010**, *16*, 13946-13950. $[Sr(dma)_6]2[Ag_4W_2I_2S_8]$
Mean	**2.451 Å/3 structures**		**Mean Sr-O-C angle: 152.6 º**

***Barium (homoleptic, non-neutral)*, CN = 8**

RAZVIY	2.798 Å	141.1 º	Jingping Wang, Jie Li, Jingyang Niu *J. Coord. Chem.* **2005**, *58*, 1639-1651. $((CH_3)NH_2)[Ba(dmf)_6Mo_{12}O_{40}]$
MACLBA	2.725 Å	141.1 º	Lemoine, P.; Herpin, P. *Acta Crystallogr., Sect. B.* **1980**, *36*, 2608-2612. $Ba_2(dma)_8(H_2O)_2(ClO_4)_4$
XIHGEB	n/a*	n/a*	Jingping Wang, Jian Ru Ma, Jing Yang Niu *Chin. Chem. Lett.* **2006**, *17*, 817. $(C_{36}H_{88}Ba_3N_{12}O_{76}P_2W_{18})_n$

* incomplete or distorted coordination sphere

Mean	**2.762 Å/2 structures**	**Mean Ba-O-C angle: 141.1 º**

Radium

No radium amide solvates are listed in the CSD.

Table S2c. Summary of M-O bond distances in solid alkaline earth metal ion non-amide solvates listed in the Cambridge Structural Database (ref. f, letter codes).

Beryllium solvates

Four-coordination

TIZDAI	1.606 Å	Neumuller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2008**, *634*, 662. Dimethylsulfoxide/water, $[Be(dmso)_3(H_2O)]Cl_2$.
TIZDAI	1.615 Å	Neumuller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2008**, *634*, 662. Dimethylsulfoxide/water, $[Be(dmso)_2(H_2O)_2]Cl_2$.
MUZJEX	1.616 Å	Neumuller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2010**, *636*, 962. Tetramethylurea, $[Be(tmu)_4](I_3)_2$.
TIZCUB	1.619 Å	Neumuller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2008**, *634*, 662. Dimethylsulfoxide, $[Be(dmso)_4]Cl_2$.

Mean *d*(Be-O) = 1.614 Å/4 structures; $r_{Be(II)4}$ = 0.274 Å

Five-coordination

No five-coordinate beryllium(II) solvates are reported.

Magnesium solvates

Four-coordination

TUXHUR	1.897 Å	Blake, M.P.; Kaltsoyannis, N.; Mountford, P. *J. Am. Chem. Soc.* **2015**, *137*, 12352. Hexamethylphosphoric triamide, $[Mg(hmpa)_4][Fe(CO)_2(Cp)]$
FISSOQ	1.906 Å	Hursthouse, M.B.; Levason, W.; Ratnani, R.; Reid, G.; Stainer, H.; Webster, M. *Polyhedron* **2005**, *24*, 2867. Triphenylphosphine oxide, $[Mg(tppO)_4][SbCl_6]_2.CH_2Cl_2$
KIPBIW	1.917 Å	Tatarinov, D.A.; Kostin, A.A.; Baronova, T.A.; Dobrynin, A.B.; Mironova, E.V.; Krivolapov, D.B.; Buzykin, B.I., Mironov, V.F. *Zh. Org. Khim.* **2013**, *49*, 534. 4-(dipropylphosphoryl)-4-methylpentan-2-one, $[Mg(dppmp)_4]Br_2$
CABGIX	2.064 Å	Visseaux, M.; Terrier, M.; Mortreux, A.; Roussel, P. *Eur.J.Inorg.Chem.* **2010**, 2867. Tetrahydrofuran, $[Mg(thf)_4][Nd(BH_4)_2(Cp)_2]$

Mean 1.907 Å/3 structures; $r_{Mg(II)4}$ = 0.567 Å

Five-coordination

NUJRAN	2.002 Å	Popescu, A.R.; Rojo, I.; Teixidor, F.; Sillanpaa, R.; Vinas, C. *Chem.-Eur.J.* **2015**, *21*, 8613. 7,8-bis(diisopropylphosphino)-7,8-dicarbanido-undecaborane/water, $[Mg(dipp)_2(H_2O)].CH_3CN$.

TMASOM	2.006 Å	Ng, Y.S.; Rodley, G.A.; Robinson, W.T. *Inorg. Chem.* **1976**, *15*, 303. Trimethylarsine oxide, $[Mg(tmao)_5](ClO_4)_2$.
Mean	**2.004 Å/2 structures; $r_{Mg(II)5}$ = 0.664 Å**	

Six-coordination

YADTOM	2.053 Å	Hoyer, M.; Hartl, H. *Z. Anorg. Allg. Chem.* **1992**, *612*, 45. Acetone, $[Mg(acetone)_6]Cu_2I_4$
SAHLOC	2.054 Å	Utko, J.; Sobota, P.; Lis, T.; Majewska, K. *J. Organomet. Chem.* **1989**, *359*, 295. Ethylacetate, $[Mg(EtAc)_6](AlCl_4)_2$
BIPPIB	2.057 Å	Okamura, T.; Nakagawa, J. *Inorg. Chem.* **2013**, *52*, 10812. acetamidooxoethylaminobenzoate/water, $[Mg(aaoeab)_2(H_2O)_4]$
BIPPUN	2.057 Å	Okamura, T.; Nakagawa, J. *Inorg. Chem.* **2013**, *52*, 10812. Methanol, $[Mg(MeOH)_6][C_{11}H_5F_6N_2O_4]_2$
DIYMOP	2.058 Å	Chen, X.; Liu, Y.-H.; Alexander, A.-M.; Gallucci, J. C.; Hwang, S.-J.; Lingam, H. K.; Huang, Z.; Wang, C.; Li, H.; Zhao, Q.; Ozkan, U. S.; Shore, S. G.; Zhao, J.-C. *Chem. Eur. J.* **2014**, 20, 7325. Methanol, $[Mg(MeOH)_6]B_{12}H_{12}$.6 MeOH
KAWWIO	2.061 Å	Antipin, M. Y.; Didenko, L. P.; Kachapina, L. M.; Shilov, A. E.; Shilova, A. K.; Struchkov, Y. T. *Chem. Commun.* **1989**, 1467. Methanol, $[Mg(MeOH)_6]C_{10}H_{34}Mg_2Mo_8O_{32}^{2-}$.6MeOH
YAGWUZ	2.061 Å	Langkilde, A.; Madsen, D.; Larsen, S. *Acta Crystallogr., Sect. B* **2004**, *60*, 502. Water/methanol, $[Mg(H_2O)_4(MeOH)_2](C_8H_5O_4)_2$
BURPEK	2.062 Å	Jaenschke, A.; Olbrich, F.; Behrens, U. *Z. Anorg. Allg. Chem.* **2009**, *635*, 2550. Dimethylsulfoxide, $[Mg(dmso)_6](C_9H_7)_2$
GEMDAF	2.063 Å	Frolova, E.A.; Palkina, K.K.; Kochetov, A.N.; Danilov, V.P. *Zh.Neorg.Khim.*. **2012**, *57*, 472. Urea/water, $[Mg(urea)_4(H_2O)_2](NO_3)_2$
EROQAD01	2.063 Å	Ullström, A.-S.; Warminska, D.; Persson, I. *J. Coord. Chem.* **2005**, *58*, 611. Dimethylsulfoxide, $[Mg(dmso)_6](ClO_4)_2$
OFUYET	2.065 Å	Dhungana, S.; White, P.S.; Crumbliss, A.L. *J. Biol. Inorg. Chem.* **2001**, *6*, 810. Water/ethanol, $[Mg(H_2O)_5(EtOH)][C_{25}H_{46}FeN_6O_8](ClO_4)_3$
SOMJEL	2.065 Å	Igawa, K.; Yoshinari, N.; Konno, T. *Chem. Commun.* **2014**, *50*, 15573. Water/methanol, $[Mg(H_2O)_4(MeOH)_2][C_{34}H_{30}Au_2NiO_8P_2S_2].nH_2O$
EROQAD	2.066 Å	Harrowfield, J. M.; Richmond, W. R.; Skelton, B. W.; White, A. H. *Eur. J. Inorg. Chem.* **2004**, 227. Dimethylsulfoxide, $[Mg(dmso)_6](ClO_4)_2$
CUPQOU	2.068 Å	A.R.Kennedy, P.C.Andrikopoulos, J.-B.Arlin, D.R.Armstrong, N.Duxbury, D.V.Graham, J.B.A.Kirkhouse *Chem.-Eur. J.* **2009**, *15*, 9494. 2-hydroxyethyl)amino)phenyl)diazenyl)benzenesulfonate/water $[Mg(H_2O)_4L_2].H_2O$.
UREAMG	2.068 Å	Lebioda, L.; Stadnicka, K.; Sliwinski, J. *Acta Crystallogr., Sect. B* **1979**, *35*, 157. Urea, $[Mg(urea)_6]Br_2.4(NH_2)_2CO$.

JADJED	2.069 Å	Valle, G.; Baruzzi, G.; Paganetto, G.; Depaoli, G.; Zannetti, R.; Marigo, A. *Inorg. Chim Acta* **1989**, *156*, 157. Ethanol, $[Mg(EtOH)_6]Cl_2$
NUQTAU (1)	2.069 Å	Antsyshkina, A.S.; Palkina, K.K.; Kuz'mina, N.E.; Orlova, V.T.; Sadikov, G.G. *Zh. Neorg. Khim.* **1997**, *42*, 1468. Dimethylurea/water, $[Mg(dmurea)_2(H_2O)_4][Mg(dmurea)_6](NO_3)_4$
NUQTAU (2)	2.070 Å	Antsyshkina, A.S.; Palkina, K.K.; Kuz'mina, N.E.; Orlova, V.T.; Sadikov, G.G. *Zh. Neorg. Khim.* **1997**, *42*, 1468. Dimethylurea, $[Mg(dmurea)_2(H_2O)_4][Mg(dmurea)_6](NO_3)_4$
NALGAL	2.071 Å	Marino, N.; Armentano, D.; De Munno, G. *Inorg.Chim.Acta* **2016**, *452*, 229-237. 4-aminopyrimidinone/water, $[Mg_2(ap)_4(H_2O)_2]Cl_2$
RIVCEE	2.071 Å	Geday, M.A.; De Munno, G.; Medaglia, M.; Anastassopoulou, J.; Theophanides, T. *Angew. Chem., Int. Ed.* **1997**, *36*, 511. methylcytosine/water, $[Mg_2(mcy)_2(H_2O)_4](ClO_4)_2.2C_5H_7N_3O$
LUVMUK	2.073 Å	Bremer, M.; Noth, H.; Warchhold, M. *Eur. J. Inorg.Chem.* **2003**, 111. Dimethylsulfoxide, $[Mg(dmso)_6](BH_4)_2.(CH_3)_2SO$
HUXRUN	2.077 Å	Jaenschke, A.; Paap, J.; Behrens, U. *Organometallics* **2003**, *22*, 1167. Dimethylsulfoxide, $[Mg(dmso)_6](C_5H_5)_2$
RIVCII	2.077 Å	Geday, M.A.; De Munno, G.; Medaglia, M.; Anastassopoulou, J.; Theophanides, T. *Angew. Chem., Int. Ed.* **1997**, *36*, 511. cytosine/water, $[Mg_2(cy)_2(H_2O)_4](ClO_4)_2.2C_5H_7N_3O.2H_2O$
JABHID	2.078 Å	Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1988**, *27*, 3596. Methanol, $[Mg(MeOH)_6]_2(C_9H_{27}Nb_2O_9)Cl_3$
MGBRME	2.078 Å	S.Halut-Desportes, S.; Philoche-Levisalles, M. *Acta Crystallogr., Sect. B* **1978**, *34*, 432. Methanol, $[Mg(MeOH)_6]Br_2$
SAVQAH	2.078 Å	Todorov, T.; Petrova, R.; Kossev, K.; Macicek, J.; Angelova, O. *Acta Crystallogr. Sect. C* **1998**, *54*, 1758. Urea, $[Mg(urea)_6]SO_4.½H_2O$
URMGBH	2.079 Å	Lebioda, L.; Lewinski, K. *Acta Crystallogr., Sect. B* **1980**, *36*, 693. Urea/water, $[Mg(urea)_4(H_2O)_2]Br_2$.
NUMYID	2.080 Å	Todorov, T.; Petrova, R.; Kossev, K.; Macicek, J.; Angelova, O. *Acta Crystallogr. Sect. C* **1998**, *54*, 927. Urea, $[Mg(urea)_6](ClO_3)_2$
YASKEI	2.081 Å	Di Noto, V.; Bresadola, S.; Zannetti, R.; Viviani, M.; Bandoli, G. *Z. Kristallogr.* **1993**, *204*, 263. Phenylmethanol, $[Mg(phMeOH)_6]Cl_2$
TAQPOQ	2.082 Å	Waters, A. F.; White, A. H. *Aust. J. Chem.* **1996**, *49*, 87. Methanol, $[Mg(MeOH)_6]I_2.2\ C_6H_{16}N_2$
NALFOY	2.098 Å	N.Marino, D.Armentano, G.De Munno *Inorg.Chim.Acta* **2016**, *452*, 229-237. 4-aminopyrimidinone/water, $[Mg_2(ap)_2(H_2O)_4]Cl_2$
MIYLUC	2.102 Å	Jing Zhu, Yan-Wei Song, Qian-Feng Zhang *Anhui Gongye Daxue Xuebao* **2007**, *24*, 146. Tricyclohexylphosphine oxide/water, $[Mg_2(tchpO)_4(H_2O)_6]Cl_4$

NALFUE	2.111 Å	N.Marino, D.Armentano, G.De Munno *Inorg.Chim.Acta* **2016**, *452*, 229-237. 4-aminopyrimidinone/water, $[Mg_2(ap)_4(H_2O)_2]Br_2$
NALFIS	2.125 Å	N.Marino, D.Armentano, G.De Munno *Inorg.Chim.Acta* **2016**, *452*, 229-237. 4-aminopyrimidinone/water, $[Mg_2(ap)_2(H_2O)_4]Br_2$
Mean	**2.068 Å/30 structures; $r_{Mg(II)6}$ = 0.728 Å**	

Tetrahydrofuran solvates (excluded)

WEQNOV	2.034 Å	$[Mg(thf)_6]^{2+}$	RARCOC	2.055 Å	$[Mg(thf)_6]^{2+}$
NUSREY (2)	2.071 Å	$[Mg(thf)_2(H_2O)_4]^{2+}$	UDAQUL	2.073 Å	$[Mg(thf)_6]I_2$
DOMSAZ (1)	2.073 Å	$[Mg(thf)_3(H_2O)3]^{2+}$	THFMGB01	2.073 Å	$[Mg(thf)_4(H_2O)_2]^{2+}$
DOMSAZ (2)	2.080 Å	$[Mg(thf)_2(H_2O)_4]^{2+}$	KODZOU	2.080 Å	$[Mg(thf)_6]^{2+}$
NUDXEP	2.086 Å	$[Mg(thf)_6]^{2+}$	NISQIQ	2.087 Å	$[Mg(thf)_6]^{2+}$
NEVFAV	2.088 Å	$[Mg(thf)_6]^{2+}$	VUSROR	2.088 Å	$[Mg(thf)_6]^{2+}$
NUSREY (1)	2.088 Å	$[Mg(thf)_4(H_2O)_2]^{2+}$	DABTEH	2.089 Å	$[Mg(thf)_6]^{2+}$
DAQFAD	2.090 Å	$[Mg(thf)_6]^{2+}$	BURPAG	2.091 Å	$[Mg(thf)_6]^{2+}$
DAQDUV	2.091 Å	$[Mg(thf)_6]^{2+}$	XAWYUQ	2.093 Å	$[Mg(thf)_6]^{2+}$
SUHWAT/01	2.094 Å	$[Mg(thf)_6]^{2+}$	WEGMUR	2.094 Å	$[Mg(thf)_6]^{2+}$
EFOKAL	2.095 Å	$[Mg(thf)_6]^{2+}$	EFOKEP	2.095 Å	$[Mg(thf)_6]^{2+}$
NUDXAL	2.095 Å	$[Mg(thf)_6]^{2+}$	UDAQUL01	2.095 Å	$[Mg(thf)_6]^{2+}$
JOKHOH	2.097 Å	$[Mg(thf)_6]^{2+}$	JOKHUN	2.097 Å	$[Mg(thf)_6]^{2+}$
RASHEY	2.099 Å	$[Mg(thf)_6]^{2+}$	TACQAQ	2.100 Å	$[Mg(thf)_6]^{2+}$
CUJGAQ	2.100 Å	$[Mg(thf)_6]^{2+}$	BUBQAQ	2.101 Å	$[Mg(thf)_6]^{2+}$
DAGZUH	2.102 Å	$[Mg(thf)_6]^{2+}$	ISETEH	2.103 Å	$[Mg(thf)_6]^{2+}$
NELCEM	2.103 Å	$[Mg(thf)_6]^{2+}$	XEKDIB	2.104 Å	$[Mg(thf)_6]^{2+}$
THFMGB	2.108 Å	$[Mg(thf)_4(H_2O)_2]^{2+}$	XAWYOK	2.109 Å	$[Mg(thf)_6]^{2+}$
YOTGET	2.111 Å	$[Mg(thf)_6]^{2+}$	JOKHUN	2.112 Å	$[Mg(thf)_6]^{2+}$
DIYLAY	2.113 Å	$[Mg(thf)_6]^{2+}$	WEGNEC	2.115 Å	$[Mg(thf)_6]^{2+}$
LIDKEO	2.162 Å	$[Mg(thf)_6]^{2+}$			
Mean	**2.094 Å/36 structures**				

Seven-coordination
No seven-coordinate magnesium(II) solvates are reported.

Calcium solvates
Five-coordination

GELVEA	1.989* Å	Shestopalov, M.A.; Smolentsev, A.I.; Kozhomuratova, Zh.S.; Fedorov, V.E.; Mironov, Yu.V. *Koord. Khim.* **2012**, *38*, 52. Triphenylphosphane oxide, $[Ca(tppO)_5]Mo_6Cl_{14}.C_{18}H_{15}OP$

Mean 1.989 Å/1 structures
** Severly disordered*

Six-coordination

VATPEL	2.275 Å	Paulus, E.F.; Frings, M.; Shivanyuk, A.; Schmidt, C.; Bohmer, V.; Vogt, W. *J. Chem. Soc., Perkin Trans.* **1998**, 2777. Dimethylsulfoxide/water, $[Ca(dmso)_4(H_2O)_2]C_{58}H_{42}N_4O_{16}.6(CH_3)_2SO$
IKEDOR	2.283 Å	Pilet, G.; Cordier, S.; Perrin, C.; Perrin, A. *Inorg. Chim. Acta* **2003**, *350*, 537. Dimethylsulfoxide, $[Ca(dmso)_6]Re_6S_8Br_8$
MOBRUQ	2.290 Å	Perruchas, S.; Simon, F.; Uriel, S.; Avarvari, N.; Boubekeur, K.; Batail, P. *J. Organometal. Chem.* **2002**, *301*, 643. Dimethylsulfoxide, $[Ca(dmso)_6]Re_6S_8Cl_8$
LAMDIN/01	2.303 Å	Ullström, A.-S.; Warminska, D.; Persson, I. *J. Coord. Chem.* **2005**, *58*, 611 & Marsh, R. E. *Acta Crystallogr., Sect. B* **2009**, *65*, 782. Dimethylsulfoxide, $[Ca(dmso)_6](ClO_4)_2$
XOMKAN	2.309 Å	Marino, N.; Armentano, D.; Zanchini, C.; De Munno, G. *CrystEngComm* **2014**, *16*, 8286. Water/cytosine, $[Ca(H_2O)_4(cy)_2](ClO_4)_2.2\ H_2O$
IXOJEK	2.315 Å	Wen-Xian Li; Hong-Sheng Wang; Rui-Jue Hu; Qi-Ge Qi *Wuji Huaxue Xuebao* **2005**, *21*, 1291. Acetylmethyl(phenyl)sulfoxide, $[Ca(ampso)_6](ClO_4)_2$
ZANPOV	2.320 Å	Zhang, J. *Acta Crystallogr., Sect. E* **2012**, *68*, m702. Dimethylsulfoxide, $[Ca(dmso)_6]W_6O_{19}$
MAYKAY	2.320 Å	Fromm, K.M.; Bernardinelli, G.; Mayor-Lopez, M.-J.; Weber, J.; Goesmann, H. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1685. Ethylacetate/water, $[Ca(EtOAc)_4(H_2O)_2]I_2$
RELFAP	2.325 Å	Huang, Q.; Wu, X.; Lu, J. *Inorg. Chem.* **1996**, *35*, 7445. Dimethylsulfoxide, $[Ca(dmso)_6]_{2n}(Ag_4S_{16}W_4)_n$
IPUROB	2.327 Å	Koch, E.C.; Klapotke, T.M.; Radies, H.; Lux, K.; Hahme, A. *Z. Naturforsch., B: Chem. Sci.* **2011**, *66*, 378. Methanol/water, $[Ca(MeOH)_4(H_2O)_2](C_3F_5N_4)_2$
CABRME01	2.334 Å	Boyle, T. J.; Ottley, L. A. M.; Alam, T. M.; Rodriguez, M. A.; Yang, P.; Mcintyre, S. K. *Polyhedron* **2010**, *29*,

1784. Methanol, $[Ca(MeOH)_6]Br_2$

LITQEM 2.470 Å S.Orbisaglia, C.Di Nicola, F.Marchetti, C.Pettinari, R.Pettinari, L.M.D.R.S.Martins, E.C.B.A.Alegria, M.Fatima C.Guedes da Silva, B.G.M.Rocha, M.L.Kuznetsov, A.J.L.Pombeiro, B.W.Skelton, A.N.Sobolev, A.H.White *Chem.-Eur. J.* **2014**, *20*, 3689. Dimethylsulfoxide, $[Ca(dmso)_6](C_9HBBr_9N_6)_2.2(CH_3)_2SO$

Mean 2.309 Å/11 structures; $r_{Ca(II)5}$ = 0.969 Å

Tetrahydrofuran solvates (all excluded)

ESIDEQ	2.324 Å	$[Ca(thf)_6]^{2+}$	EFOJIS	2.328 Å	$[Ca(thf)_6]^{2+}$
GOJGAO	2.330 Å	$[Ca(thf)_6]^{2+}$	BEXZUA	2.334 Å	$[Ca(thf)_6]^{2+}$
AVEZAC	2.336 Å	$[Ca(thf)_6]^{2+}$	PUXCUH	2.336 Å	$[Ca(thf)_6]^{2+}$
EFOJUE	2.337 Å	$[Ca(thf)_6]^{2+}$	ESIDOA	2.338 Å	$[Ca(thf)_6]^{2+}$
HOJZUC	2.339 Å	$[Ca(thf)_6]^{2+}$	VEBJAB	2.339 Å	$[Ca(thf)_6]^{2+}$
FUDDAK	2.339 Å	$[Ca(thf)_4(hmpa)_2]^{2+}$	MOBROK	2.340 Å	$[Ca(thf)_6]^{2+}$
HOJZOW	2.341 Å	$[Ca(thf)_6]^{2+}$	VADPAT	2.342 Å	$[Ca(thf)_6]^{2+}$
MAYKEC	2.344 Å	$[Ca(thf)_4(H_2O)_2]^{2+}$	COFZED	2.345 Å	$[Ca(thf)_6]^{2+}$
PUXFIY	2.351 Å	$[Ca(thf)_6]^{2+}$			

Mean 2.338 Å/17 structures

Seven-coordination

UFOQIR (2) 2.390 Å Geier, M.J.; Bowes, E.G.; Lee, G.M.; Haoxin Li; O'Neill, T.; Flewelling, A.; Vogels, C.M.; Decken, A.; Gray, C.A.; Westcott, S.A. *Heteroat. Chem.* **2013**, *24*, 116. Water/isopropanol, $[Ca(H_2O)_4(iPrOH)_3][\underline{Ca(H_2O)_5(iPrOH)_2}](C_{20}H_{12}BO_4)_4.4\ C_3H_6O$

UFOQIR (1) 2.398 Å Geier, M.J.; Bowes, E.G.; Lee, G.M.; Haoxin Li; O'Neill, T.; Flewelling, A.; Vogels, C.M.; Decken, A.; Gray, C.A.; Westcott, S.A. *Heteroat. Chem.* **2013**, *24*, 116. Water/isopropanol, $[\underline{Ca(H_2O)_4(iPrOH)_3}][Ca(H_2O)_5(iPrOH)_2](C_{20}H_{12}BO_4)_4.4\ C_3H_6O$

YOPVIJ 2.409 Å Klapotke, T.M.; Sabate, C.M.; Welch, J.M. *Europ. J. Inorg. Chem.* **2009**, 769. Water/5-nitrotetrazolate, $[Ca(H_2O)_6(NO_2CN_4)](NO_2CN_4)$

YIWBOV 2.410 Å Lin Zhou-Bin; Chen Chang-Zhang; Gao Dong-Shou; Huang Xiao-Ying; Li Ding *Jiegou Huaxue* **1995**, *14*, 61. Water/cyanuric acid, $[Ca(H_2O)_6(cya)](C_3H_2N_3O_3)(OH)$

YIWBOV01 2.413 Å Chekhlov, A.N. *Zh.Neorg.Khim.* **2006**, *51*, 799. Water/cyanuric acid, $[Ca(H_2O)_6(cya)](C_3H_2N_3O_3).H_2O$; re-interpretation of YIWBOV as a monohydrate

CUPSAI 2.415 Å Kennedy, A.R.; Andrikopoulos, P.C.; Arlin, J.-B.; Armstrong, D.R.; Duxbury, N.; Graham, D.V.; Kirkhouse, J.B.A., *Chem.-Eur.J.* **2009**, *15*, 9494. Water/ bis(hydroxyethyl)amino)phenyl)diazenyl)methylbenzenesulfonate, $[Ca(H_2O)_6(bheapdmbso)](C_{17}H_{20}N_3O_5S).3\ H_2O$

FEDWIU 2.428 Å Harrowfield, J.M.; Sharma, R.P.; Skelton, B.W.; White, A.H. *Aust. J. Chem.* **1998**, *51*, 785. Water/nitrophenol, $[Ca(H_2O)_6(NO_2Ph)](C_6H_4NO_3)_2.C_6H_5NO_3.2\ H_2O$

Mean 2.409 Å/7 structures; $r_{Ca(II)7}$ = 1.069 Å

Eight-coordination
No eight-coordinate calcium(II) solvates are reported.

Strontium solvates
Six-coordination

EROQIL 2.445 Å J.M.Harrowfield, W.R.Richmond, B.W.Skelton, A.H.White *Eur. J. Inorg Chem.* **2004**, 227. $[Sr(OC(CH_3))_6]^{2+}$ *note: this structure includes one six-coordinate mononuclear species, and two dinuclear ones, where one has two seven-coordinate strontium(II) ions, and the other is seven-ccordinate in one end and eight-coordinate in the other; only the value of the six-coordinate is listed here.*

IXOJIO 2.453 Å Wen-Xian Li, Hong-Shneg Wang, Rui-Jue Hu, Qi-Ge Qi *Wuji Huaxue Xuebao* **2005**, *21*, 1291. $[Sr(OS(C_6H_5)CHCOCH_3)_6](ClO_4)_2$

FUDCIR 2.497 Å A.Verma, M.Guino-o, M.Gillett-Kunnath, Weijie Teng, K.Ruhlandt-Senge *Z. Anorg. Allg. Chem.* **2009**, *635*, 903. $[Sr(OP(N(CH_3)_3)_3)_6](B(C_6H_5)4)_2$

PUXFOE 2.499 Å J.Langer, S.Krieck, H.Gorls, G.Kreisel, W.Seidel, M.Westerhausen New. J. Chem. 2010, 34, 1667. $[Sr(OC_4H_8)_6](V(C_9H_{11})_4]_2\cdot 4C_4H_8O$

Mean 2.449 Å/2 structures

Tetrahydrofuran solvates (all excluded)

PUXDOC 2.566 Å Langer, J.; Krieck, S.; Gorls, H.; Kreisel, G.; Seidel, W.; Westerhausen, M. *New. J. Chem.* **2010**, *34*, 1667. $[Sr(OC_4H_8)_7](Al(C_6H_5)_4]_2\cdot C_4H_8O$

Seven-coordination

EROQIL 2.531 Å J.M.Harrowfield, W.R.Richmond, B.W.Skelton, A.H.White *Eur. J. Inorg Chem.* **2004**, 227. $[Sr_2(OC(CH_3))_{11}(H_2O)]^{4+}$ and $[Sr_2(OC(CH_3))_{12}]^{4+}$ *note: this structure includes one six-coordinate mononuclear species, and two dinuclear ones,*

where one has two seven-coordinate strontium(II) ions, and the other is seven-ccordinate in one end and eight-coordinate in the other; the mean value of the seven-coordinate ends are listed here.

EROQEH 2.598 Å Harrowfield, J. M.; Richmond, W. R.; Skelton, B. W.; White, A. H. *Eur. J. Inorg. Chem.* **2004**, 227.

Mean 2.564 Å/2 structures

Eight-coordination

EROQIL 2.587 Å J.M.Harrowfield, W.R.Richmond, B.W.Skelton, A.H.White *Eur. J. Inorg Chem.* **2004**, 227. $[Sr_2(OC(CH_3))_{11}(H_2O)]^{4+}$ *note: this structure includes one six-coordinate mononuclear species, and two dinuclear ones, where one has two seven-coordinate strontium(II) ions, and the other is seven-ccordinate in one end and eight-coordinate in the other; only the eight-coordinate end is listed here.*

Mean 2.587 Å/1 structure

Barium solvates

Six-coordination

UKUKOA/01 2.622 Å Teng, W.; Englich, U.; Ruhlandt-Senge, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 3661. Hexamethylphosporic amide $[Ba(OP(N(CH_3)_3)_3)_6][Ba(C_{12}H_{24}O_6)](Si(Si(CH_3)_3)_3)_4$.

UKUKIU/01 2.632 Å Teng, W.; Englich, U.; Ruhlandt-Senge, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 3661. Hexamethylphosporic amide $[Ba(OP(N(CH_3)_3)_3)_6](C_9H_{27}Si_4)_2$

PECDUY 2.633 Å Guino-o, M. A.; Torvisco, A.; Teng, W.; Ruhlandt-Senge, K. *Inorg. Chim. Acta* **2012**, *389*, 122. Hexamethylphosporic amide $[Ba(OP(N(CH_3)_3)_3)_6](CH(C_6H_5)_2)_2$

PECFAG 2.642 Å Guino-o, M. A.; Torvisco, A.; Teng, W.; Ruhlandt-Senge, K. *Inorg. Chim. Acta* **2012**, *389*, 122. Hexamethylphosporic amide $[Ba(OP(N(CH_3)_3)_3)_6](C(C_6H_5)_3)_2$

Mean 2.632 Å/4 structures

Tetrahydrofuran/trifluoromethanesulfonate (excluded)

TIRNOZ 2.647 Å Buchanan, W.; Ruhlandt-Senge, K. *Chem. Eur. J.* **2013**, *19*, 10708. $K[Ba(C_4H_8O)_3(OC(CF_3)_3].C_4H_8O$

TIRPER 2.678 Å Buchanan, W.; Ruhlandt-Senge, K. *Chem. Eur. J.* **2013**, *19*, 10708. $Na[Ba(C_4H_8O)_3(OC(CF_3)_3].C_4H_8O$

Eight-coordination

COZGIJ	2.750 Å	Shashank, M.; Jeanneau, E.; Ledoux, G.; Daniele, S. *Inorg. Chem.* **2014**, *53*, 11721. *Dimethylsulfoxide* $[Ba_2(OS(CH_3)_2)_{13}]Ag_{14}I_{22}$
COZGOP	2.762 Å	Shashank, M.; Jeanneau, E.; Ledoux, G.; Daniele, S. *Inorg. Chem.* **2014**, *53*, 11721. *Dimethylsulfoxide* $[Ba_2(OS(CH_3)_2)_{13}]Ag_6I_{11}H_3O^+.2OS(CH_3)_2$
EROQEH	2.785 Å	Harrowfield, J. M.; Richmond, W. R.; Skelton, B. W.; White, A. H. *Eur. J. Inorg, Chem.* **2004**, 227. *Dimethylsulfoxide/perchlorate* $[Ba_2(OS(CH_3)_2)_{10}(ClO_4)_2](ClO_4)_2$.
Mean	**2.756 Å/2 structures**	

Tetrahydrofuran solvate (excluded)

TASJEE	2.800 Å	Michel, O.; Kaneko, H.; Tsurugi, H.; Yamamoto, K.; Tornroos, K. W.; Anwander, R.; Mashima, K. *Eur. J. Inorg. Chem.* **2012**, 998. $[Ba(OC_4H_8)_8](B(C_6F_5)_4)_2 \cdot C_4H_8O$.

Nine-coordination

CUPREL	2.807 Å	Kennedy, A.R.; Andrikopolous, P.C.; Arlin, J.-B.; Armstrong, D.R.; Duxbury, N., Graham, D.V., Kirkhouse, J.B.A. *Chem.-Eur. J.* **2009**, *15*, 9494. $[Ba(H_2O)_8(C_{16}H_{18}N_3O_5S)](C_{16}H_{18}N_3O_5S).5.63\ H_2O$.
FEDWEQ	2.845 Å	Harrowfield, J.M.; Sharma, R.P.; Skelton, B.W.; Venugopalam, P.; White, A.H. *Aust. J. Chem.* **1998**, *51*, 775. Water/4-nitrophenolate, $[Ba(H_2O)_8(C_6H_4NO_3)](C_6H_4NO_3)$.
Mean	**2.826 Å/2 structures**	

Radium solvates

No radium(II) solvates are listed in CSD.

Table S3. Summary of solid state structures containing amide solvated alkali(I), manganese(II), cobalt(II), nickel(II), zinc(II), lanthanum(III), gadolinium(III) and lutetium(III) ions listed in the Cambridge Structural Database (CSD, ref. f.)

***N,N*-Dimethylformamide**

Sodium(I)

Six-coordination

XEPDOL	2.379 Å	Krautscheid, H.; Lode, C.; Vielsack, F.; Vollmer, H. *J. Chem. Soc., Dalton Trans.* **2001**, 1099.
XEPDIF	2.397 Å	Krautscheid, H.; Lode, C.; Vielsack, F.; Vollmer, H. *J. Chem. Soc., Dalton Trans.* **2001**, 1099.

Manganese(II)

Six-coordination

IQOKEG	2.143 Å	Bosch, M.; Xing Sun; Shuai Yuan; Ying-Pin Chen; Qi Wang; Xuan Wang; Hong-Cai Zhou *Eur. J. Inorg. Chem.* **2016**, 4368-4372.
ACUBEH	2.149 Å	Semenaka, V.V.; Nesterova, O.V.; Kokozay, V. N.; Omelchenko, I. V.; Shishkin, O. V. *Acta Crystallogr., Sect. E* **2012**, *68*, m823-m823.
IHAZAS	2.152 Å	Khutornoi, V.A.; Naumov, N.G.; Mironov, Yu.V.; Oeckler, O.; Simon, A.; Fedorov, V.E. *Koord. Khim.* **2002**, *28*, 183-190. [Engl. transl.]
BETCUA	2.168 Å	Suzuki, R.; Chiba, Y.; Yamaguchi, R.; Yoshioka, D.; Mikuriya, M.; Sakiyama, H. *X-ray Str. Anal. Online* **2013**, *29*, 11-12.
YAFBIS	2.174 Å	Chygorin, E. N.; Petrusenko, S. R.; Kokozay, V. N.; Smal, Y. O.; Omelchenko, I. V.; Shishkin, O. V. *Acta Crystallogr., Sect. E* **2011**, *67*, m1563-m1564.
KUCQIK	2.174 Å	Dhifallah, F; Belkhiria, M.S. *Acta Crystallogr., Sect. E* **2016**, *72*, 841-844.
Mean	**2.160 Å/6 structures**	

Cobalt(II)

Six-coordination

IHAYUL	2.072 Å	Khutornoi, V.A.; Naumov, N.G.; Mironov, Yu.V.; Oeckler, O.; Simon, A.; Fedorov, V.E. *Koord. Khim.* **2002**, *28*, 183-190. [Engl. transl.]
QUWGOF01	2.075 Å	Light, M.E.; Edwards, P.; Gale, P.A. *CSD private communication*, **2016**
NACNEL	2.078 Å	Guo, Y.; Wang, X.; Li, Y.; Wang, E.; Xu, L.; Hu, C. *J. Coord. Chem.* **2004**, *57*, 445-451.
QUQNIB	2.078 Å	Filatov, A.S.; Anderson, J.S. *CSD private communication*, **2015**

ATAPOC	2.081 Å	Wenjiang Huang; Hongyang Wei; Longhua Li; Jun Qian; Chi Zhang *J.Cluster Sci.* **2016**, *27*, 1463
PUHLEK	2.084 Å	Eissmann, F.; Bohle, T.; Mertens, F. O. R. L.; Weber, E. *Acta Crystallogr., Sect. E* **2010**, *66*, m279-m280.
FIMDEM	2.087 Å	Suenkel, K.; Reimann, D. *Z. Naturforsch., Teil B* **2013**, *68*, 546-550.
WAYVID	2.088 Å	Abe, K.; Chiba, Y.; Yoshioka, D.; Yamaguchi, R.; Mikuriya, M.; Sakiyama, H. *X-ray Str. Anal. Online* **2012**, *28*, 65-66.
QUWGOF	2.089 Å	Thone, C.; Narro, N.; Jones, P. G. CCDC entry 767277.
WAYVID01	2.094 Å	Ridier, K.; Gillon, B.; Gukasov, A.; Chaboussant, G.; Cousson, A.; Luneau, D.; Borta, A.; Jacquot, J.-F.; Checa, R.; Chiba, Y.; Sakiyama, H.; Mikuriya, M. *Chem.-Eur.J.* **2016**, *22*, 724
Mean	**2.083 Å/10 structures**	

Nickel(II)

Six-coordination

NOHVEM	2.031 Å	Gong, Y.; Hu, C.-W.; Li, H.; Li, Y.-G; Wang, Y.-H. *J. Beijing Inst. Technol.* **2006**, *15*, 348.
FIMCUB	2.042 Å	Suenkel, K.; Reimann, D. *Z. Naturforsch., Teil B* **2013**, *68*, 546-550.
RASDOG	2.043 Å	Stieler, R.; Bublitz, F.; Lang, E. S.; de Oliveira, G. M. *Polyhedron* **2012**, *35*, 137-141.
NIDWUS	2.045 Å	Li, W. S.; Blake, A. J.; Champness, N. R.; Schroder, M.; Bruce, D. W. *Acta Crystallogr., Sect. C* **1998**, *54*, 349-351.
NACNIP	2.046 Å	Guo, Y.; Wang, X.; Li, Y.; Wang, E.; Xu, L.; Hu, C. *J. Coord. Chem.* **2004**, *57*, 445-451.
LAHNOZ	2.047 Å	Quail, J. W.; Paulose, T. A. P.; Foley, S. R. CCDC entry 739507
ZUZPEP	2.048 Å	McKee, V.; Metcalfe, T.; Wikaira, J. *Acta Crystallogr., Sect. C* **1996**, *52*, 1139-1141.
NASNUS	2.050 Å	Famengo, A.; Pinero, D.; Jeannin, O.; Guizouarn, T.; Fourmigue, M. *Dalton Trans.* **2012**, *41*, 1441-1443.
BAGGAT	2.054 Å	Yamaguchi, R.; Yamasaki, M.; Sakiyama, H. *X-ray Str. Anal. Online* **2011**, *27*, 71-72.
HIMSEB	2.055 Å	Hay, R.W.; Albedyhl, S.; Lightfootm, P. *Transition Met.Chem.* **1998**, *23*, 257
OQOHUZ	2.055 Å	Avdeeva, V.V.; Polyakova, I.N.; Goeva, L.V.; Buzanov, G.A.; Malinina, E.A.; Kuznetsov, N.T. *Inorg. Chim. Acta* **2016**, *451*, 129
Mean	**2.051 Å/11 structures**	

Zinc(II)

XUSQUZ	2.090 Å	Kaplan, P. T.; Xu, L.; Chen, B. McGarry, K. R.; Yu, S.; Wang, H.; Vicic, D. A. *Organometallics* **2013**, *32*, 7552-7558.
IMEBAF	2.093 Å	Ito, M.; Mitsuhashi, R.; Mikuriya, M.; Sakiyama, H. *X-ray Str. Anal. Online* **2016**, *32*, 21

HUXGUC	2.103 Å	Jing-Ping Wang; Qiang Wu; Jing-Yang Niu *Wuji Huaxue Xuebao* **2002**, *18*, 957
Mean	**2.095 Å/3 structures**	

***N,N*-Dimethylacetamide**

Potassium(I)

SEGSOM10	2.367 Å	Koz'min, P.A.; Kotelnikova, A.S.; Surazhskaya, M.D.; Osmanov, N.S.; Larina, T.B.; Abbasova, T.A.; Mekhtiev, M.M. *Koord. Khim.* **1989**, *15,* 1216.

Nickel(II)

PEGHAL	2.066 Å	Suzuki, H.; Ishiguro, S.-i. *Acta Crystallogr., Sect. E* **2006**, *62*, m505-m507.

Zinc(II)

TEDGUG	2.169 Å	Guang-Sheng Yang; Mei-Na Li; Shun-Li Li; Ya-Qian Lan; Wen-Wen He; Xin-Long Wang; Jun-Sheng Qin; Zhong-Min Su *J. Mater. Chem.* **2012**, *22*, 17947

***N*-Methylformamide**

Nickel(II)

KUSKEQ	2.041 Å	Sakiyama, H.; Mitsuhashi, R.; Mikuriya, M. *X-ray Str. Anal. Online* **2015***, 31*, 45-46.

Cobalt(II)

XUBXAV	2.088 Å	Yamaguchi, R.; Yoshioka, D.; Mikuriya, M., Sakiyama, H. *X-ray Str. Anal. Online* **2015***, 31*, 7.

Acetamide

Nickel(II)

VOCJED	2.051 Å	Savinkina, E.V.; Al'bov, D.V.; Buravlev, E.A.; Zamilatskov, I.A. *Zh.Neorg.Khim.* **2007***, 52*, 1133.

Propionamide

Zinc(II)

GUYKAN	2.087 Å	Savinkina, E.V.; Buravlev, E.A.; Zamilatskov, I.A.; Albov, D.V.; Kravchenko, V.V.; Zaitseva, M.G.; Mavrin, B.N. *Z. Anorg. Allg. Chem.* **2009***, 635*, 1458.

Acrylamide

Manganese(II)

LAMCUZ	2.170 Å	Kellett, A.; Rosair, G.; Devereux, M.; McNamara, M.; McCann, M. *Acta Crystallogr., Sect. C* **2010***, 66*, m358

Cobalt(II)

CEMGEH	2.090 Å	Girma, K.B.; Lorenz, V.; Blaurock, S.; Edelmann, F.T. *Z. Anorg. Allg. Chem.* **2006***, 632*, 1874
QAPKAU	2.093 Å	Girma, K.B.; Lorenz, V.; Blaurock, S.; Edelmann, F.T. *Z. Anorg. Allg. Chem.* **2005***, 631*, 1419

Nickel(II)

CEMGOR	2.057 Å	Girma, K.B.; Lorenz, V.; Blaurock, S.; Edelmann, F.T. *Z. Anorg. Allg. Chem.* **2006***, 632*, 1874

Zinc(II)

CEMHAE	2.091 Å	Girma, K.B.; Lorenz, V.; Blaurock, S.; Edelmann, F.T. *Z. Anorg. Allg. Chem.* **2006***, 632*, 1874
CEMGIL	2.095 Å	Girma, K.B.; Lorenz, V.; Blaurock, S.; Edelmann, F.T. *Z. Anorg. Allg. Chem.* **2006***, 632*, 1874

No *N,N*-dimethylpropionamide structures reported

Mean Na^+: 2.388 Å/2 structures – 6-coordination
Mean K^+: 2.367 Å/1 structure – 6-coordination
Mean Mn^{2+}: 2.161 Å/7 structures – 6-coordination
Mean Co^{2+}: 2.084 Å/13 structures – 6-coordination
Mean Ni^{2+}: 2.049 Å/15 structures – 6-coordination
Mean Zn^{2+}: 2.093 Å/6 structures – 6-coordination

Lanthanum(III)

8-coordination

KIKVIK	2.456 Å	Yarovoi, S. S.; Mironov, Y. V.; Solodovnikov, S. F.; Solodovnikova, Z. A.; Naumov, D. Y.; Fedorov, V. E. *Russ.J. Coord. Chem.* **2006**, *32*, 712-722.
KIKWIL	2.459 Å	Yarovoi, S. S.; Mironov, Y. V.; Solodovnikov, S. F.; Solodovnikova, Z. A.; Naumov, D. Y.; Fedorov, V. E. *Russ.J. Coord. Chem.* **2006**, *32*, 712-722..

HOXNIR	2.461 Å	Ling Chen; Xin-tao Wu; Xian-cheng Gao; Wen-jian Zhang; Ping Lin *J. Chem. Soc. Dalton Trans.* **1999**, 4303.
DIQHUG	2.466 Å	Ling, C.; Xintao, W.; Ping, L. *J. Chem. Cryst.* **1999**, *29*, 629-633.
CUZYIH	2.468 Å	Saha, S.; Jana, P.P.; Gomez-Garcia, C.J.; Harms, K.; Nayek, H.P. *Polyhedron* **2016**, 104, 58
KUDCIX	2.490 Å	Fuchs, A.; Lundberg, D.; Warminska, D.; Persson, I. *J. Phys. Chem. B* 2013, 117, 8502-8511.
Mean	**2.467 Å/6 structures**	

9-coordination

FEZCIX	2.549 Å	Liu, S.; Plecnik, C. E.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **2005**, *44*, 282-292.
BOWGIF	2.557 Å	Danjo, H.; Nakagawa, T.; Katagiri, K.; Kawahata, M.; Yoshigai, S.; Miyazawa, T.; Yamaguchi, K. *Cryst. Growth Des.* **2015**, *15*, 384
YEKMUX	2.560 Å	Berthet, J.-C.; Thuery, P.; Ephritikhine, M *Polyhedron* **2006**, *26*, 1700-1706.
Mean	**2.555 Å/3 structures**	

Gadolinium(III)

8-coordination

OGOJOJ	2.377 Å	Liu, S.; Meyers, E. A.; Shore, S. G. *Angew. Chem., Int. Ed.* **2002**, *41*, 3609-3611.
JAFKOR	2.382 Å	Umebayashi, Y.; Matsumoto, K.; Mekata, I.; Ishiguro, S.-i. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5599-5605.
IXOXOI	2.387 Å	Harrowfield, J. M.; Skelton, B. W.; White, A. H.; Wilner, F. R. *Inorg. Chim Acta* **2004**, *357*, 2358-2364.
Mean	**2.382 Å/3 structures**	

Lutetium(III)

8-coordination

KIKWEH	2.293 Å	Yarovoi, S. S.; Mironov, Y. V.; Solodovnikov, S. F.; Solodovnikova, Z. A.; Naumov, D. Y.; Fedorov, V. E. *Russ.J. Coord. Chem.* **2006**, *32*, 712-722.
KIKXAE	2.307 Å	Yarovoi, S. S.; Mironov, Y. V.; Solodovnikov, S. F.; Solodovnikova, Z. A.; Naumov, D. Y.; Fedorov, V. E. *Russ.J. Coord. Chem.* **2006**, *32*, 712-722.
Mean	**2.300 Å/2 structures**	

Table S4. Summary of solid state structures containing dimethylsulfoxide, methanol and ethanol solvated alkali, manganese(II), cobalt(II), nickel(II), zinc(II), lanthanum(III), gadolinium(III), and lutetium(III) ions.

Dimethylsulfoxide

Sodium(I)

Six-coordination

ITITAH	2.452 Å	Duarte-Ruiz, A.; Nunez-Dallos, N.; Garzon-Tovar, L.; Wurst, K.; Avella-Moreno, E.; Gomez-Baquero, F. *Chem. Commun.* **2011**, *47*, 7110.

Manganese(II)

Six-coordination

SEVRUG	2.152 Å	Chen M.-Q.; Zhu S.-S.; Gu Y.-D. *Chin. J. Struct. Chem.* **1990**, *9*, 26.
IPOGIF	2.167 Å	Glatz, M.; Schroffenegger, M.; Weil, M.; Kirchner, K. *Acta Crystallogr., Sect. E* **2016**, *72*, 904
GEPLUJ	2.169 Å	Migdal-Mikuli, A.; Szostak, E.; Nitek, W. *Acta Crystallogr., Sect. E* **2006**, *62*, m2581-m258x.
GEPLUJ01	2.176 Å	Szostak, E.; Migdal-Mikuli, A.; Kaczor, A.; Nitek, W. *Spectrochim.Acta A* **2011**, *79*, 1179-1186.
EVEQIF	2.180 Å	Niu, J.-Y. Duan, X.-Y.; Wang, J.-P.; Wu, Q. *Chin. J. Struct. Chem.* **2004**, *23*, 257-261.
SIZSEB	2.180 Å	Drachnik, A. M.; Kumari, H.; Barnes, C. L.; Deakyne, C. A.; Atwood, J. L. *CrystEngComm* **2014,** *16*, 7172-7175
Mean	**2.171 Å/6 structures**	

Cobalt(II)

DUPQOV	2.005 Å	*Cobalt(III)*
QUWQUW	2.049 Å	*Partially oxidized to cobalt(III)?*
SIZRUQ	2.056 Å	*Partially oxidized to cobalt(III)?*
WAJZAI	2.085 Å	Ciccarese, A.; Clemente, D. A.; Marzotto, A.; Valle, G. *J. Crystallogr. Spectrosc. Res.* **1993**, *23*, 223-229.
XUBDUT	2.088 Å	Comuzzi, C.; Melchior, A.; Polese, P.; Portanova, R.; Tolazzi, M. *Eur. J. Inorg. Chem.* **2002**, 2194-2021.
KEXDAU	2.094 Å	Sudo, R.; Yoshioka, D.; Mikuriya, M.; Sakiyama, H. *X-ray Str. Anal. Online* **2012**, *28*, 71-72.
FALVEU	2.095 Å	Chan, E. J.; Cox, B. G.; Harrowfield, J. M.; Ogden, M. I.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2004**, *357*, 2365-2373.
FALVEU01	2.099 Å	Chan, E. J.; Cox, B. G.; Harrowfield, J. M.; Ogden, M. I.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2004**, *357*, 2365-2373.
FALVEU02	2.100 Å	Chan, E. J.; Cox, B. G.; Harrowfield, J. M.; Ogden, M. I.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2004**, *357*, 2365-2373.

LIDNAO	2.101 Å	White, A. P.; Robertson, K. N.; Cameron, T. S.; Liengme, B. V.; Leznoff, D. B.; Trudel, S.; Aquino, M. A. S. *Can. J. Chem.* **2007**, *85*, 372-378.
YEWKUG	2.107 Å	Tkachev, V. V.; Lavrent'eva, E. A.; Rosschupkina, O. S.; Lavrent'ev, I. P.; Atovmyan, L. O. *Koord. Khim.* **1995**, *20*, 674-676.
SIZSAX	2.108 Å	Drachnik, A.M.; Kumari, H.; Barnes, C.L.; Deakyne, C.A.; Atwood, J.L. *CrystEngComm* **2014**, *16*, 7172
Mean	**2.097 Å/9 structures**	

Nickel(II)

CABPUR	2.059 Å	Blake, A. J.; Felloni, M.; Hubberstey, P.; Schroder, M.; Wilson, C. *Acta Crystallogr., Sect. E* **2001**, *57*, m556.
SAFMAP	2.059 Å	Niu, M.; Fan, S.; Liu, G. *Acta Crystallogr., Sect. E* **2012**, *68*, m67-m67.
YUSGUQ01	2.061 Å	Landmann, J.; Sprenger, J. A. P.; Hailmann, M.; Bernhardt-Pitchougina, V.; Willner, H.; Ignat'ev, N.; Bernhardt, E.; Finze, M. *Angew. Chem., Int. Ed.* **2015**, *54***,** 11259-11264.
YUSGUQ	2.061 Å	Landmann, J.; Sprenger, J. A. P.; Hailmann, M.; Bernhardt-Pitchougina, V.; Willner, H.; Ignat'ev, N.; Bernhardt, E.; Finze, M. *Angew. Chem., Int. Ed.* **2015**, *54***,** 11259-11264.
KAMYUT	2.061 Å	Cherkasova, T. G.; Tsalko, E. V. *Russ. J. Coord. Chem.* ***2004***, *30*, 888-891.
BAJXAM01	2.061 Å	Florke, U. *CSD private communication 2015*.
SEYKIS	2.061 Å	Sudo, R.; Yoshioka, D.; Mikuriya, M.; Sakiyama, H. *X-ray Str. Anal. Online* **2013**, *29*, 17-18.
LIDNES	2.063 Å	White, A. P.; Robertson, K. N.; Cameron, T. S.; Liengme, B. V.; Leznoff, D. B.; Trudel, S.; Aquino, M. A. S. *Can. J. Chem.* **2007**, *85*, 372-378.
RUZBAP01	2.064 Å	Chan, E. J.; Cox, B. G.; Harrowfield, J. M.; Ogden, M. I.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2004**, *357*, 2365-2373.
BAJWUF	2.065 Å	Bobicz, D.; Kristiansson, O.; Persson, I., *J. Chem. Soc., Dalton Trans.* **2002**, 4201-4205.
OQOJAH	2.069 Å	Avdeeva, V.V.; Polyakova, I.N.; Goeva, L.V.; Buzanov, G.A.; Malinina, E.A.; Kuznetsov, N.T. *Inorg. Chim. Acta* **2016**, 129.
BAJXEQ	2.070 Å	Bobicz, D.; Kristiansson, O.; Persson, I., *J. Chem. Soc., Dalton Trans.* **2002**, 4201-4205.
RUZBAP	2.072 Å	Kristiansson, O.; Persson, I.; Bobicz, D.; Xu, D. *Inorg. Chim. Acta* **2003**, *344*, 15-27.
BAJXAM	2.075 Å	Bobicz, D.; Kristiansson, O.; Persson, I., *J. Chem. Soc., Dalton Trans.* **2002**, 4201-4205.
TIRBEB01	2.077 Å	De-Liang Long; Huai-Ming Hu; Jiu-Tong Chen; Jin-Shun Huang, *Acta Crystallogr., Sect. C* **1999,** *55*, 339-341.
TIRBEB	2.083 Å	Reibenspies, J. H.; Kim, J. S., *Z. Kristallogr.* **1996**, *211*, 418-418.
Mean	**2.066 Å/16 structures**	

Zinc(II)

QUTYOU	2.075 Å	Qi Yue; Qian Sun; Ai-Ling Cheng; En-Qing Gao **2010**, *10*, 44
UXEMAN	2.100 Å	Sakiyama, H.; Abiko, T.; Ito, M.; Mitsuhashi, R.; Mikuriya, M.; Waki, K. *Polyhedron* **2016**, *119*, 512-516
EHIXAW	2.101 Å	Hammami, I.; Ghandour, Y.; Belkhiria, M.S. *IUCr Data* **2016**, *1*, x160406..
BIPMIW01	2.103 Å	Chan, E. J.; Cox, B. G.; Harrowfield, J. M.; Ogden, M. I.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2004**, *357*, 2365-2373.
BIPMIW	2.109 Å	Persson, I. *Acta Chem. Scand., Ser A* **1982**, *36*. 7-13.
MINGIB	2.111 Å	L.Garzon-Tovar, L.; Duarte-Ruiz, A.; Fanwick, P. E. *Acta Crystallogr., Sect. E* **2013**, *69*, m618-m618.
SAWTEQ	2.112 Å	Clegg, W; Elsegood, M. R. J. CCDC entry 283652.
Mean	**2.106 Å/6 structures**	

Lanthanum(III)

8-coordination

AZEBIQ	2.414 Å	Cherkasova, T. G.; Anosova, Yu.V; Shevchenko, T.M. *Zh.Neorg. Khim.* **2004**, *49*, 22.
KOPCIB	2.452 Å	Chunying Tang; Fang Wang; Dingxian Jia; Wenqing Jiang; Yong Zhang *CrystEngComm* **2014**, *16*, 2016
KOPDAI	2.470 Å	Chunying Tang; Fang Wang; Dingxian Jia; Wenqing Jiang; Yong Zhang *CrystEngComm* **2014**, *16*, 2016
YIHPAG	2.480 Å	Cherkasova, T. G. *Zh.Neorg. Khim.* **1994**, *39*, 1316-1319.
LITHOL	2.492 Å	Qian-Feng Zhang; Wa-Hung Leung; Xin-Quan Xin; Hoong-Kun Fun *Inorg. Chem.* **2000**, *39*, 417.
FAQMOB	2.493 Å	Ya-min Li; Da-gang Yang *Huaxue Yanjiu* **2010**, *21*, 8-3.
YIPKAK	2.494 Å	Abbasi, A.; Risberg, E. D.; Eriksson, L.; Mink, J.; Persson, I.; Sandström, M.; Sidorov, Y. V.; Skripkin, M. Y.; Ullström, A.-S. *Inorg. Chem.* **2007**, *46*, 7731-7741.
YIPKAK01	2.496 Å	Abbasi, A.; Risberg, E. D.; Eriksson, L.; Mink, J.; Persson, I.; Sandström, M.; Sidorov, Y. V.; Skripkin, M. Y.; Ullström, A.-S. *Inorg. Chem.* **2007**, *46*, 7731-7741.
Mean	**2.488 Å/6 structures**	

Gadolinium(III)

KOBCOV	2.357 Å	Tang, C.; Wang, F.; Jia, D.; Jiang, W.; Zhang, Y. *CrustEngComm* **2014**, *16*, 2016-2024.
YIPLAL	2.384 Å	Abbasi, A.; Risberg, E. D.; Eriksson, L.; Mink, J.; Persson, I.; Sandström, M.; Sidorov, Y. V.; Skripkin, M. Y.; Ullström, A.-S. *Inorg. Chem.* **2007**, *46*, 7731-7741.
PEMDEQ	2.393 Å	Klinga, M.; Cuesta, R.; Moreno, J.M.; Dominguez-Vera, J. M.; Colacio, E.; Kivekas, R. *Acta Crystallogr., Sect. C* **1998**, *54*, 1275-1277.

Mean **2.378 Å/3 structures**

Lutetium(III)

YIPLOZ 2.302 Å Abbasi, A.; Risberg, E. D.; Eriksson, L.; Mink, J.; Persson, I.; Sandström, M.; Sidorov, Y. V.; Skripkin, M. Y.; Ullström, A.-S. *Inorg. Chem.* **2007**, *46*, 7731-7741.

Methanol

Sodium(I)

Six-coordination

ZOVWIQ 2.368 Å Blake, A.J.; Grant, C.M.; Parsons, S.; Solan, G.A.; Winpenny, R.E.P. *J. Chem. Soc., Dalton Trans.* **1996**, 321

ZEBKIA 2.381 Å Blake, A.J.; Grant, C.M.; Parsons, S.; Rawson, J.M.; Solan, G.A.; Winpenny, R.E.P. *J. Chem. Soc., Dalton Trans.* **1995**, 2311.

JABHUP 2.383 Å Cotton, F.A.; Diebold, M.P.; Roth, W.J. *Inorg. Chem.* **1988**, *27*, 3596

JIDKOW 2.410 Å Brnicevic, N.; McCarley, R.E.; Hilsenbeck, S.; Kojic-Prodic, B. *Acta Crystallogr., Sect. C* **1991**, *47*, 315

ZOMWON 2.443 Å Thiele, K.-H.; Steinicke, A.; Dumichen, U.; Neumuller, B. *Z. Anorg. Allg. Chem.* **1996**, *622*, 231.

Mean **2.397 Å/5 structures**

Manganese(II)

Six-coordination

QESNUX 2.149 Å Harmjanz, M.; Scott, M. J. *Inorg. Chem.* **2000**, *39*, 5428-5429.

TUJTIC 2.167 Å Sterzik, A.; Gorls, H.; Spielberg, E. T.; Plass, W.; Imhof, W. *Z. Anorg. Allg. Chem.* **2009**, *635,* 1594-1599.

GELMUG 2.168 Å Coronado, E.; Galan-Mascaros, J. R.;Marti-Gastaldo, C.; Martinez, A. M. *Dalton Trans.* **2006,** 3294-3299.

QESNOR 2.170 Å Harmjanz, M.; Scott, M. J. *Inorg. Chem.* **2000**, *39*, 5428-5429.

Mean **2.164 Å/4 structures**

Nickel(II)

Six-coordination

AGEYAM 2.051 Å Goodgame, D. M. L.; Grachvogel, D. A.; Williams, D. J. *Inorg. Chim. Acta* **2002**, *330*, 13-16.

HUKMUV 2.071 Å Harrop, T. C.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chim. Acta* **2002**, *338*, 189-195.

Mean **2.061 Å/2 structures**

Zinc(II)
Six-coordination
CIRJIW 2.086 Å Sudbrake, C.; Muller, B.; Vahrenkamp H. *Eur. J. Inorg. Chem.* **1999**, 2009-2012.

Lanthanum(III)
Nine-coordination
LUSNET 2.558 Å Boyle, T. J.; Ottley, L. A. M.; Alam, T. M.; Rodriguez, M. A.; Yang, P.; Mcintyre, S. K. *Polyhedron* **2010**, *29*, 1784-1794.

Ethanol
Sodium(I)
Six-coordination
HOVDAX 2.368 Å Hubert-Pfalzgraf, L.G.; Miele-Pajot, N.; Papiernik, R.; Vaissermann, J. *J. Chem. Soc., Dalton Trans.* **1999**, 4127

Cobalt(II)
Six-coordination
KOBQUO 2.078 Å Crewdson, P.; Bryce, D. L.; Rominger, F.; Hofmann, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 3454-3457.
ETHCOB 2.084 Å Bkouche-Waksman, I.; L'Haridon, P. *Bull. Soc. Chim. Fr.* **1979**, 50-51.
COCLET 2.095 Å Bkouche-Waksman, I.; L'Haridon, P. *Acta Crystallogr., Sect. B* **1977**, *33*, 11-21.
Mean 2.086 Å/3 structures

Zinc(II)
Six-coordination
CIRKUJ 1.995 Å Sudbrake, C.; Muller, B.; Vahrenkamp H. *Eur. J. Inorg. Chem.* **1999**, 2009-2012.
CIRNIA 2.079 Å Sudbrake, C.; Muller, B.; Vahrenkamp H. *Eur. J. Inorg. Chem.* **1999**, 2009-2012.

Mean Na^{+}: 2.401 Å/7 structures – 6-coordination
Mean Mn^{2+}: 2.168 Å/10 structures – 6-coordination
Mean Co^{2+}: 2.094 Å/12 structures – 6-coordination
Mean Ni^{2+}: 2.066 Å/18 structures – 6-coordination
Mean Zn^{2+}: 2.100 Å/8 structures – 6-coordination

Difference between non-amide/amide mean bond distance, as listed above:
Na^{+}: 0.013 Å; Mn^{2+}: 0.007 Å; Co^{2+}: 0.010 Å; Ni^{2+}: 0.017 Å; Zn^{2+}: 0.007 Å

[f] Allen, F. H. *Acta Crystallogr., Sect. B* **2002**, *58*, 380-388; Cambridge Structural Database (CSD) ConQuest build 1.19

[g] Hellenbrandt, M. *Crystallogr. Rev.* **2004**, *10*, 17-22; *Inorganic Crystal Structure Database* (ICSD) 1.4.6 (release: 2017-1); FIZ/NIST.

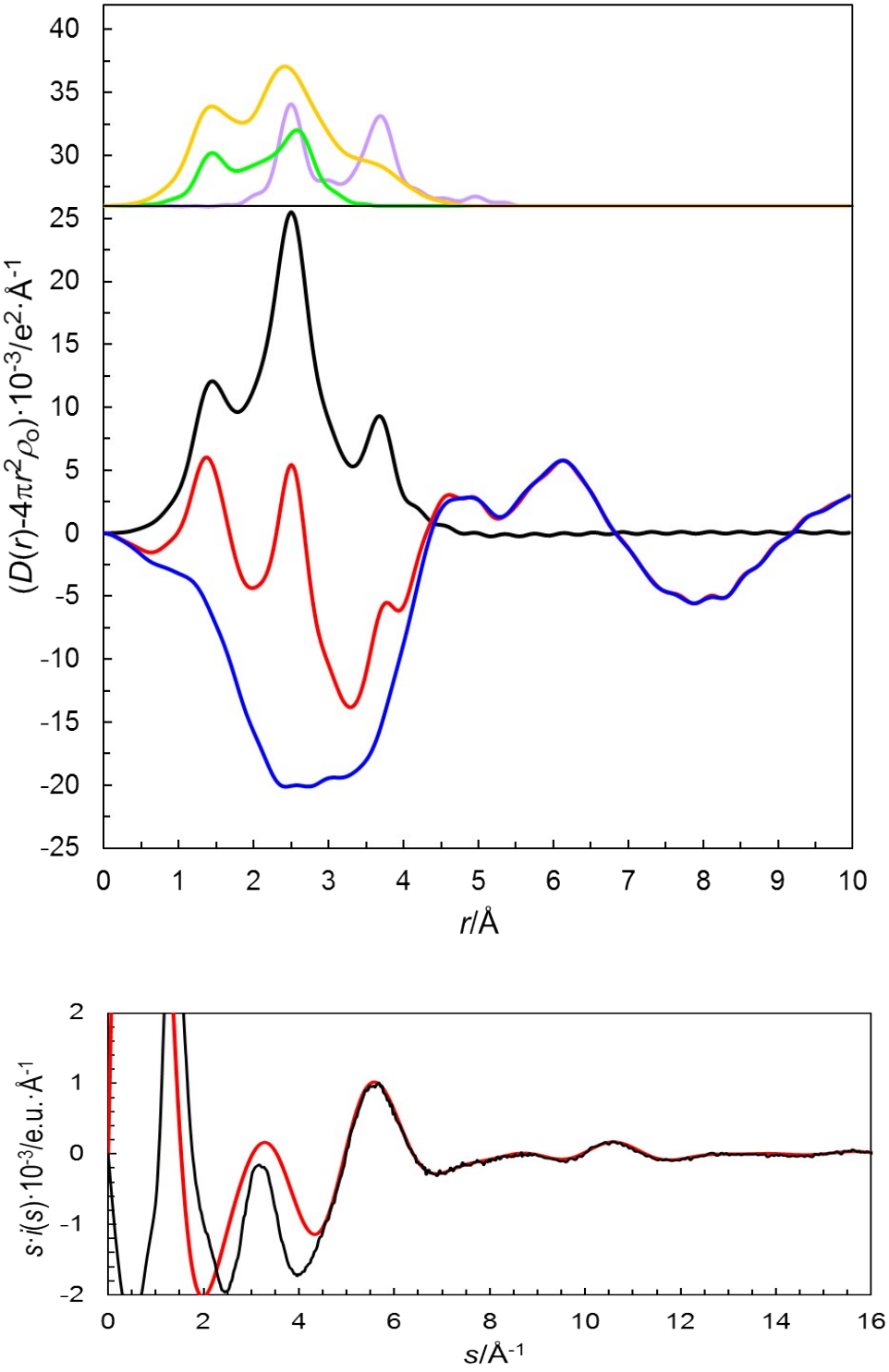

Figure S1. LAXS radial distribution function of $Sr(CF_3SO_3)_2$ solution in dma. Top, upper panel: Separate model contributions (offset: 27) of strontium ion solvated by *N*,*N*-dimethylacetamide (purple line), the trifluoromethanesulfonate ion (green line) and dma molecule (yellow line). Top, lower pane: Experimental RDF (red line); sum of model contributions (black line); the difference (blue line). Bottom: Reduced intensity function (experimental results - black line; model - red line).

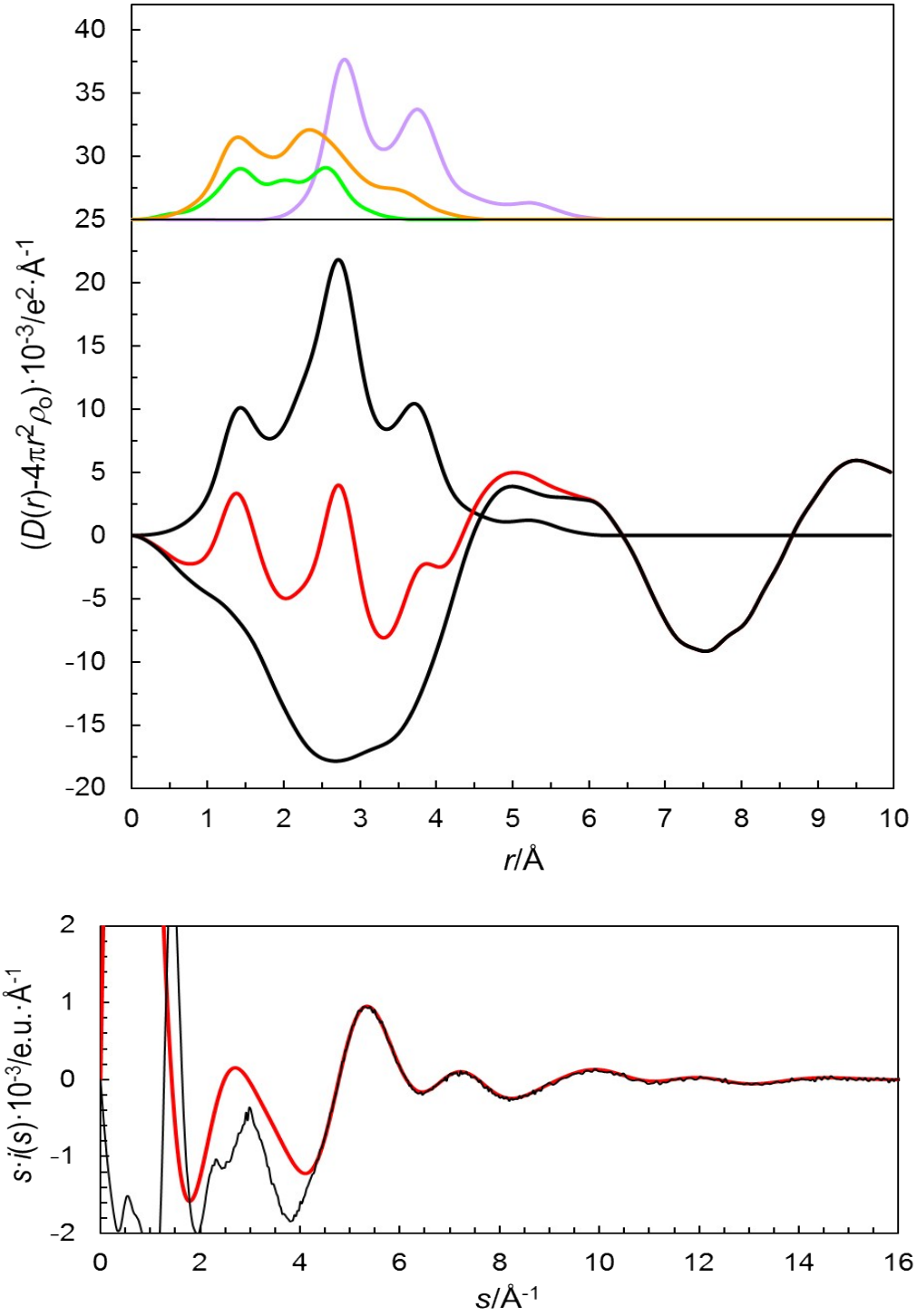

Figure S2. LAXS radial distribution function of $Ba(CF_3SO_3)_2$ solution in dmf. Top, upper panel: Separate model contributions (offset: 25) of barium ion solvated by *N*,*N*-dimethylformamide (purple line), the trifluoromethanesulfonate ion (green line) and dma molecule (yellow line). Top, lower pane: Experimental RDF (red line); sum of model contributions (black line); the difference (blue line). Bottom: Reduced intensity function (experimental results - black line; model - red line).

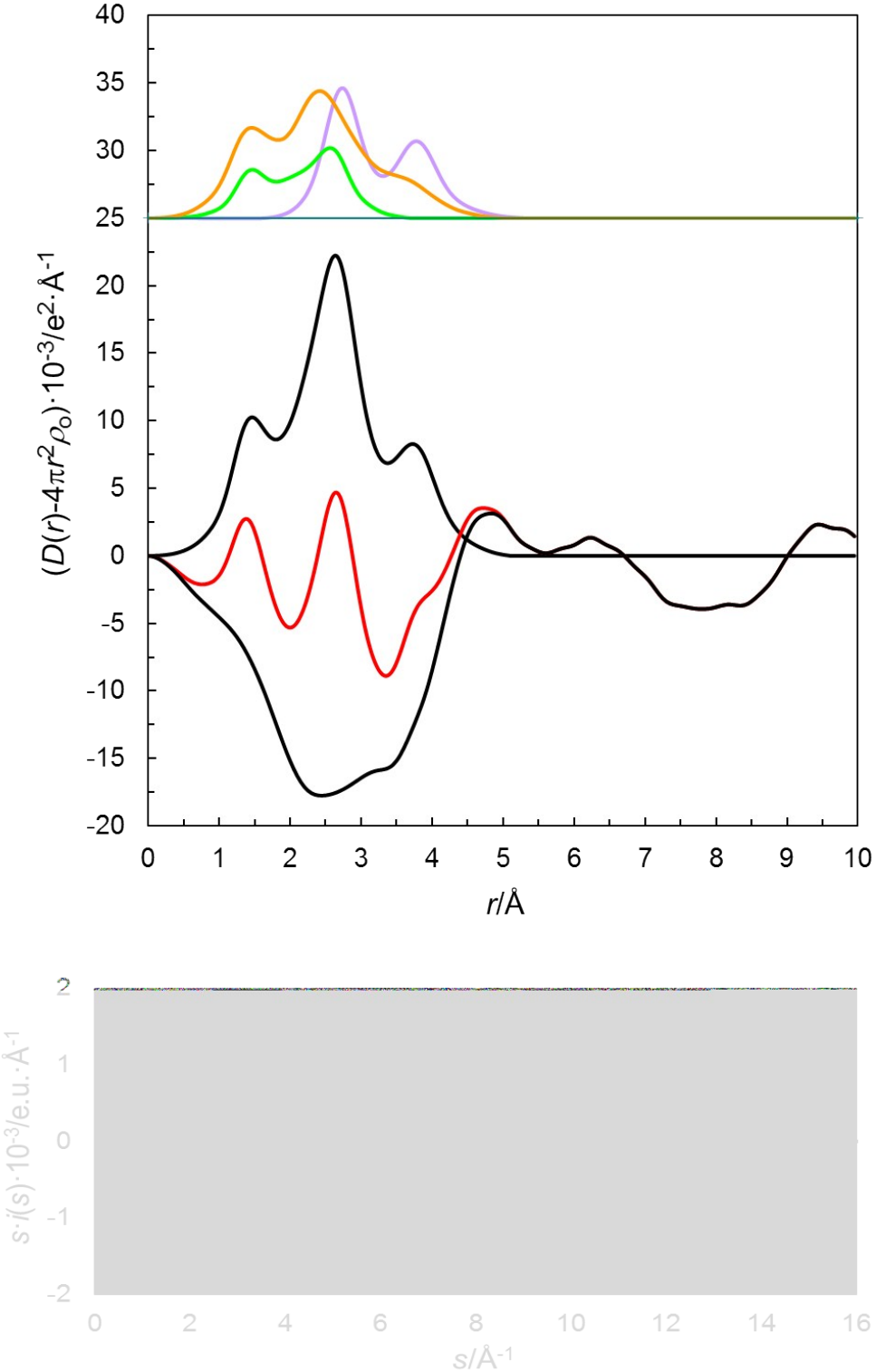

Figure S3. LAXS radial distribution function of $Ba(CF_3SO_3)_2$ solution in dma. Top, upper panel: Separate model contributions (offset: 25) of barium ion solvated by *N*,*N*-dimethylacetamide (purple line), the trifluoromethanesulfonate ion (green line) and dma molecule (yellow line). Top, lower pane: Experimental RDF (red line); sum of model contributions (black line); the difference (blue line). Bottom: Reduced intensity function (experimental results - black line; model - red line).

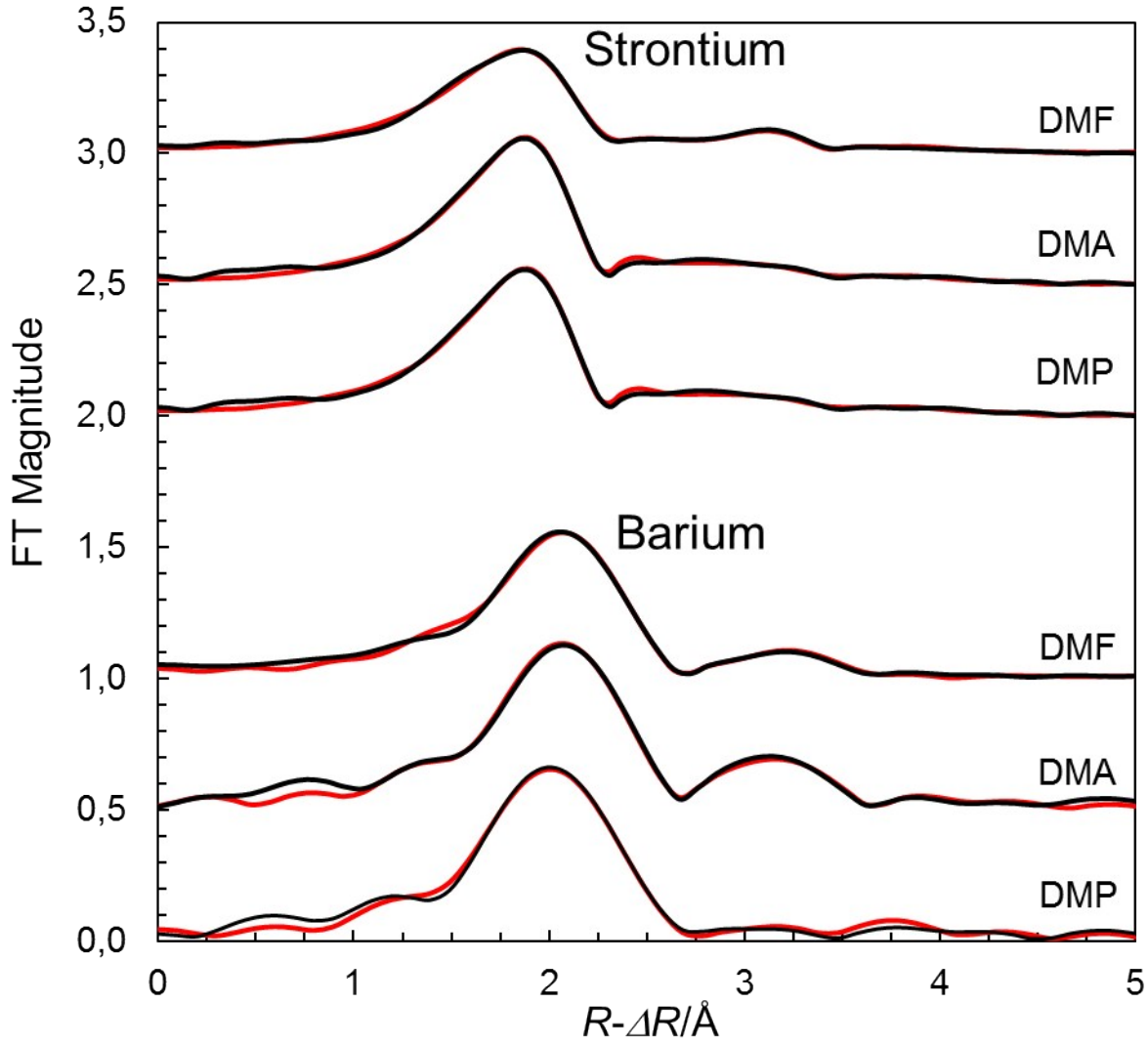

Figure S4. Fourier transformations non-phase corrected of the EXAFS functions of dmf, dma, and dmp solvated strontium and barium ions (dotted lines – experimental; red lines – model).

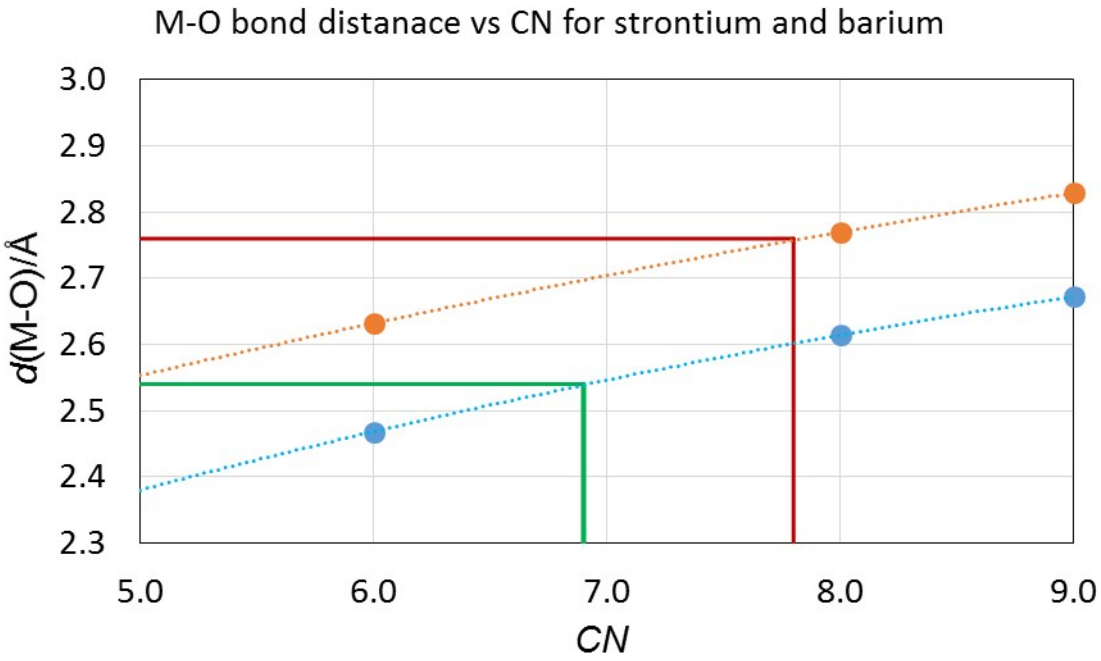

Figure S5. The relationship ionic radius (recalculated to expected M-O bond distance by adding 1.34 Å, the oxygen radius in most oxygen donor solvents, ref. 47-coordination number from solid state structures for the strontium and barium ions (blue and orange filled circles and calculated trend line as dashed line). The solid lines represents Sr^{2+}/dmso (green) and Ba^{2+}/dmso (dark red).

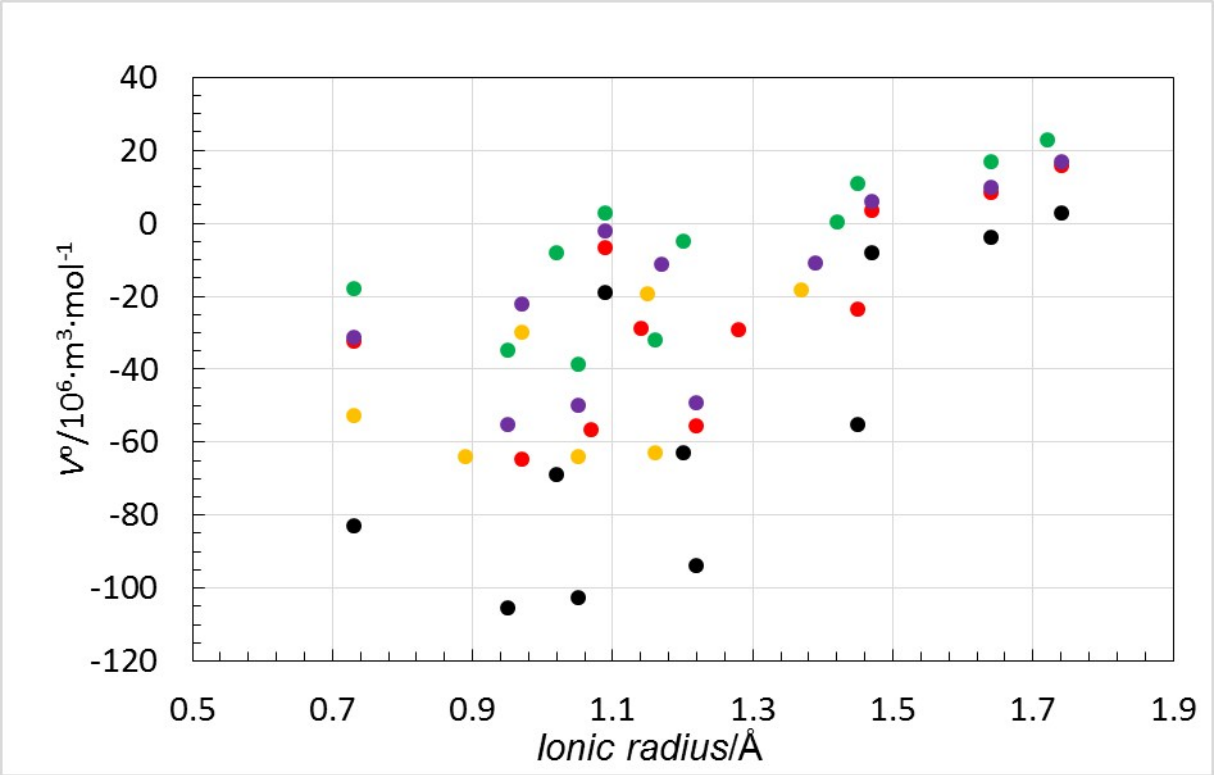

Figure S6. Scatter plot of standard partial molar volumes *versus* ionic radii of the alkali, alkaline earth, lanthanum(III), gadolinium(III) and lutetium(III) ions in water (red), methanol (black), dmso (green), dmf (purple) and dma (orange).