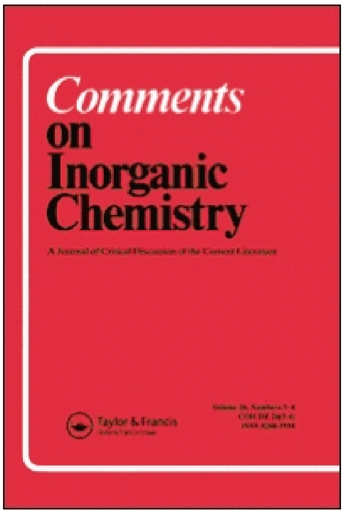

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

The Co-Ordination Number of Sc^3 (Aq)

S. A. Cotton[a]
[a] Uppingham School, Uppingham, Rutland, UK

To cite this Article Cotton, S. A.(1999) 'The Co-Ordination Number of Sc^3 (Aq)', Comments on Inorganic Chemistry, 21: 1, 165 — 173
To link to this Article: DOI: 10.1080/02603599908020421
URL: http://dx.doi.org/10.1080/02603599908020421

The Co-Ordination Number of Sc^{3+}(Aq)

S.A. COTTON*

Uppingham School, Uppingham, Rutland LE159QE, UK

(Received 10 August, 1998)

A consideration of the available evidence, drawn largely from X-ray diffraction data on crystalline scandium complexes, as well as aqueous solutions, points strongly to the co-ordination number of Sc^{3+} in aqueous solution being 7, an exceptional value for this region of the Periodic Table. Whilst the only $[Sc(OH_2)_n]^{3+}$ion isolated from solution has $n = 9$, *it is shown that this is an exceptional case*; consideration particularly of three dimers containing $[(H_2O)_5Sc(\mu\text{-}OH)_2Sc(H_2O)_5]^{4+}$ ions with seven co-ordinate scandium indicates that their Sc-OH_2 bond length of 2.18–2.19Å is close to that found from diffraction studies on solutions of Sc(III) salts, strong evidence for $[Sc(OH_2)_7]^{3+}$ being the principal species in aqueous solution.

Keywords: *Scandium(III), Lanthanide(III), Aqua ion, Co-ordination number, ionic radius, Raman spectrum*

1. OPENING REMARKS

It is remarkable that there has for many years been no concrete evidence for the co-ordination number of scandium in aqueous solution, it having been generally assumed[1-2] that the species present is $[Sc(OH_2)_6]^{3+}$,

---

* Correspondence Author.

Comments Inorg. Chem.
1999, Vol. 21, No. 1-3, pp. 165-173
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published by license
under the Gordon and Breach
Science Publishers imprint.
Printed in Malaysia

though increasingly evidence has pointed to a higher co-ordination number[3] and attention has been drawn to the resemblances between scandium and lutetium, the heaviest and smallest lanthanide, in many aspects of its chemistry[4]. With the publication[5] of X-ray diffraction and EXAFS studies on Sc^{3+} (aq), it is timely to review the evidence.

2. PREDICTIONS FROM IONIC RADII

The assumption of the existence of $[Sc(OH_2)_6]^{3+}$ is probably an unstated analogy with $[M(OH_2)_6]^{3+}$(M = Ti-Co), neglecting the point that since Sc^{3+} has an ionic radius (0.745 Å) intermediate between that of Ti^{3+} (0.670 Å) and the lanthanide ions (La^{3+} = 1.032 Å; Lu^{3+} = 0.861 Å), as shown in Fig. 1, a co-ordination number intermediate between 6 and 9 would be expected purely on steric considerations (values quoted are for six- co-ordination).[6]

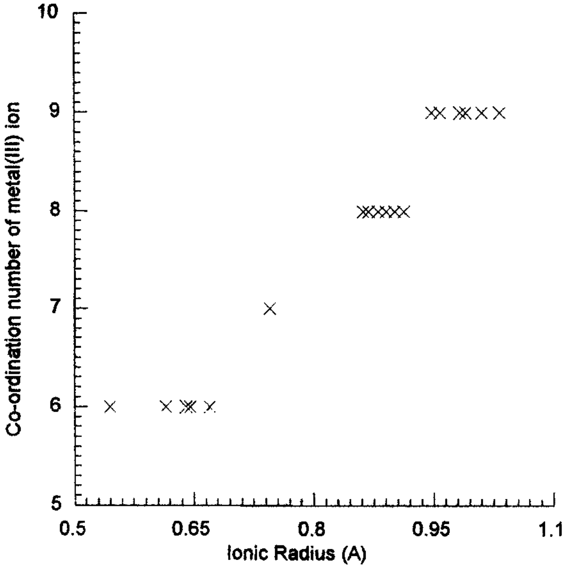

FIGURE 1 The dependence of co-ordination number upon the ionic radius of M^{3+} for a number of $[M(OH_2)_n]^{3+}$ ions in aqueous solution. A value of n =7 is assigned to scandium in the light of recent discoveries

3. VIBRATIONAL SPECTRA

Most of the evidence examined here is derived from diffraction results, but an important study by Japanese workers used vibrational spectroscopy.[7] Raman spectra of acidic ($pH < 2$) solutions and glasses of $Sc^{3+}(aq)$ and $Al^{3+}(aq)$ display significant differences in both the number and polarisation of bands. Glasses of $[Al(OH_2)_6]^{3+}$ show three bands (one polarised) in the region expected for metal-ligand stretching vibrations; three are predicted (ν_1 (a_{1g}), ν_2 (e_g) and $\nu_5(t_{2g})$). In contrast, glasses of $Sc^{3+}(aq)$ show four bands (two polarised) in the corresponding region, at 450 (p), 410, 375 and 310 (p) cm^{-1}. An octahedral $[Sc(OH_2)_6]^{3+}$ ion would be expected to have only three Raman-active metal-ligand stretching vibrations whereas a pentagonal bipyramidal D_{5h} ion would cause 5 bands, two with a_1' symmetry that would be expected to be polarised. At the pH of the measurements, significant amounts of a hydroxy-bridged dimer are unlikely, and in fact any species of lower symmetry would give rise to more bands. An important point is that spectra of $Sc(ClO_4)_3$ yield similar results to those obtained from the chloride, indicating that anion co-ordination is not responsible.

4. STRUCTURAL DATA CONSIDERED

Only one compound with solely water molecules in the co-ordination sphere of scandium has been studied by diffraction methods; the hydrated triflate $Sc(O_3CCF_3)_3.9H_2O$, synthesised by refluxing scandium oxide with triflic acid.[8] It was found to be isomorphous with the hydrated lanthanide triflates, containing tricapped trigonal prismatic scandium in the $[Sc(H_2O)_9]^{3+}$ ions, with Sc-O (vertices) = 2.171(6) A, Sc-O (face capped) 2.47 (2) Å, averaging 2.271 Å.

The fact that this structure is observed for all $M(O_3CCF_3)_3.9H_2O$ (M = Sc, Y, La-Lu), irrespective of ionic radius,[9] reflects the role of hydrogen-bonding between the co-ordinated water molecules and the triflate groups in stabilising the structure. In contrast, the $[Ln(H_2O)_8]^{3+}$ ions (Ln = Gd, Dy, Lu, Y) have been isolated[10] inside crown ether rings and it is salutary to recall that several perchlorate salts (Ln e.g. La, Sm, Tb, Er, Y) have been shown[11] to contain $[Ln(H_2O)_6]^{3+}$ ions. In contrast, in aqueous solution, early lanthanides (Ln = La-Sm) form $[Ln(H_2O)_9]^{3+}$, whilst the later lanthanides form exclusively the

$[Ln(H_2O)_8]^{3+}$ ions (Ln = Tb-Lu), the intermediate metals probably forming a mixture of eight and nine- co-ordinate species.[12,13] The isolation of the $[Sc(H_2O)_9]^{3+}$ ion in a solid salt has, therefore, no definite implications for the stoichiometry of the ion present in aqueous solution.

Hydrated scandium triflate is singular in featuring only water molecules in the co-ordination sphere of scandium. Other hydrated salts contain less than nine water molecules bound to Sc and probably involve additional co-ordination of an anionic ligand. They include[14] the very hygroscopic $Sc(NO_3)_3.nH_2O$ (n = 2, 3, 4), $Sc(ClO_4)_3.nH_2O$ (n = 6, 7) and $Sc(BrO_3)_3.3H_2O$. Though none of these compounds have been studied by X-ray diffraction, the encapsulation of $[Sc(NO_3)_3\ (H_2O)_2]$ and $[Sc(NO_3)_3\ (H_2O)_3]$ molecules, containing eight and nine-co-ordinate scandium respectively, with crown ethers, should be noted.[15] The Sc-OH_2 distances in the 9-coordinate $[Sc(NO_3)_3(H_2O)_3]$ complex with 18-crown-6 of 2.120(6), 2.221(6) and 2.303(15) Å, averaging 2.215 Å are relatively short compared with the average for $Sc(O_3CCF_3)_3.9H_2O$ and suggest that the nitrate group, with its small bite angle, allows closer approach of other co-ordinated groups than is otherwise found.

Three other salts where water shares the co-ordination sphere of scandium with another ligand have been studied. In hydrated scandium picrate[16] (as a 1:1 adduct with picric acid), the scandium is part of a six-co-ordinate cation, *trans*-$[Sc(OH_2)_4(pic)_2](pic)(HPic)$. 8.2 H_2O (Hpic = $HOC_6H_2(NO_2)_3$-2,4,6), (Sc-OH_2 2.100(9), 2.102(9), 2.113 (9) and 2.121 (8); Sc-O 2.019 (8), 2.046 (8) Å). In contrast, hydrated scandium tosylate, $Sc(SO_3C_6H_4CH_3\text{-}4)_3$. 6 H_2O contains[17] *cis*-co-ordinated tosylate ligands in a six co-ordinate cation having the structure *cis*-$[Sc(OH_2)_4(SO_3C_6H_4CH_3\text{-}4)_2]^+$ with Sc-OH_2 2.097 (4), 2.118 (4), 2.119 (4) and 2.132 (4) Å ; Sc-O 2.021 (4), 2.067 (4) Å). (the later lanthanides form square antiprismatic $[Ln(OH_2)_6(SO_3C_6H_4CH_3\text{-}4)_2]^+$ (Ln = Sm, Gd, Ho, Er, Yb, Y) cations). $ScCl_3(H_2O)_3$ molecules have been encapsulated in a cryptand ligand, in a similar way to the isolation of hydrated scandium nitrate by crown ethers. In $[H_2L]$*mer*-$ScCl_3(H_2O)_3$.3 H_2O(L = cryptand-2,2,2)[18] the Sc-OH_2 distances are 2.078 (10), 2.132 (9) and 2.155 (9) Å. All these six co-ordinate compounds have Sc-O distances of around 2.11 Å. This is in keeping with a predicted value for Sc-O of 2.10–2.11 Å, extrapolating from the Ti-OH_2 distances of 2.018- 2.046 Å found in the tosylate salt of the $[Ti(OH_2)_6]^{3+}$ ion[19], making allowance for the radius of the scandium ion being 0.075 Å greater.[6]

The crystallographic characterisation of di-μ-hydroxy bridged species has been an important development. Attempted synthesis of scandium benzene sulphonate from $ScCl_3$and sodium benzene sulphonate led to the isolation of the dimer $[(H_2O)_5Sc(\mu\text{-}OH)_2Sc(H_2O)_5](C_6H_5SO_3)_4.4H_2O$. (Fig.2)

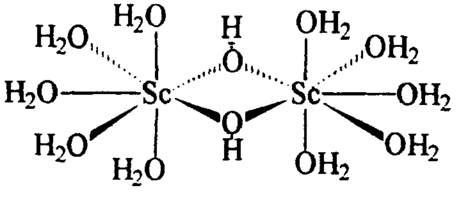

FIGURE 2

This contains seven co-ordinate scandium with an approximately pentagonal bipyramidal co-ordination geometry[20], the Sc-O bond lengths being given in Table I.

TABLE I Bond lengths in dimeric complex ions $[(H_2O)_5Sc(\mu\text{-}OH)_2Sc(H_2O)_5]X_4$ (in Å)

Compound	*Sc-OH_2 (Å)*	*Sc-OH (Å)*
benzene sulphonate	2.138 (4), 2.143 (6), 2.152 (6), 2.152 (4), 2.196 (5)	2.069 (4), 2.071 (4),
	2.200 (4), 2.228 (5), 2.230 (4), 2.249 (4), 2.256 (4)	2.072 (4), 2.076 (4)
chloride	2.175 (3), 2.175 (3), 2.175 (3), 2.175 (3), 2.189 (3)	2.066 (3), 2.066 (3),
	2.189 (3), 2.189 (3), 2.189 (3), 2.208 (3), 2.208 (3)	2.068 (3), 2.068 (3)
bromide	2.170 (7), 2.170 (7), 2.170 (7), 2.170 (7), 2.174 (6)	2.047 (6), 2.047 (6),
	2.174 (6), 2.174 (6), 2.174 (6), 2.207 (7), 2.207 (7)	2.076 (6), 2.076 (6)

The axial Sc-OH_2 bonds average 2.146 Å and the equatorial Sc-OH_2 bonds 2.227 Å, whilst the Sc-OH bridge distances of 2.072 Å are shorter than the terminal Sc-O distances of 2.111–2.125 Å in the $[Sc(OH)_6]^{3-}$ ion[21] and certainly do not give any evidence for congestion in the co-ordination sphere of scandium. Crystallisation of hydrated scandium chloride from *n*- and *iso*- propanol gives the related substance $[(H_2O)_5Sc(\mu\text{-}OH)_2Sc(H_2O)_5]Cl_4.2H_2O$ whilst the analoguous $[(H_2O)_5Sc(\mu\text{-}OH)_2Sc(H_2O)_5]Br_4.\ 2H_2O$ has been made from scandium bromide.[22] In these two compounds, the co-ordination geometry has been described as close to a monocapped trigonal prism, but most significantly the average Sc-OH_2 (Table II) and the Sc-OH bond lengths are similar in all three of these dimers.

TABLE II Sc-OH_2 distance and co-ordination number

Compound	*average Sc-O (A)*	*Coord.No.*	*Reference*
Sc^{3+} (aq)	2.18		5
$[ScCl_3(H_2O)_3][H_2L].3H_2O$	2.122	6	18
$[Sc(OH_2)_4(\text{picrate})_2]^+$	2.109	6	16
$[Sc(OH_2)_4(\text{tosylate})_2]^+$	2.117	6	17
$[(H_2O)_5Sc(\mu\text{-}OH)_2Sc(OH_2)_5]^{4+}$			
benzene sulphonate	2.194	7	20
chloride	2. 187	7	22
bromide	2.179	7	22
$[Sc(OH_2)(\text{picolinate})_2(OH)]_2$	2.175	7	23
$[Sc(OH_2)_9(CF_3SO_3)_3$	2.271	9	8
$[Sc(NO_3)_3(H_2O)_3]$ 18-crown-6	2.215	9	15a

These $[(H_2O)_5Sc(\mu\text{-}OH)_2Sc(H_2O)_5]^{4+}$ ions are significant in that they are believed to be formed in the first stage of the hydrolysis of the scandium aqua ion, and the co-ordination geometry involving scandium bound to seven water molecules and hydroxide ions can clearly derive from a $[Sc(OH_2)_7]^{3+}$ ion, in the way that $[(H_2O)_4Fe(\mu\text{-}OH)_2Fe(H_2O)_4]^{4+}$ is related to the $[Fe(OH_2)_6]^{3+}$ ion. It is therefore possible to envisage a $[Sc(OH_2)_7]^{3+}$ ion with an average Sc-OH_2 bond length of ca. 2.18–2.19 Å.

The compound $[(\text{picolinato})_2(H_2O)Sc(\mu\text{-}OH)_2Sc(OH_2)(\text{picolinato})_2]$ shares with these compounds double hydroxy bridges and seven co-ordinate scandium[23]. Here the Sc-OH_2distance is 2.172 (2) Å whilst the Sc-O bridge distances are 2.063 (2) and 2.080 (1)Å, similar to those in the three hydroxy-bridged aqua species. The average Sc-OH_2 bond lengths in these four compounds that contain seven co-ordinate scandium lie in the range 2.175–2.194 A, significantly longer than in the six co-ordinate complexes. (Table II)

5. SOLUTION DIFFRACTION MEASUREMENTS

X-ray diffraction data for scandium perchlorate solutions indicate a Sc-O distance of 2.180(7) Å with a co-ordination number of 7.4(4); the XAFS data from scandium triflate solutions also indicate a Sc-O distance of 2.18(2) Å. No co-ordination number could be unambiguously obtained from the XAFS measurements, though the data were not consonant with a tricapped trigonal prismatic 9 co-ordinate structure. This Sc-O distance, some 0. 1Å longer than that found for 6 co-ordination, fits well with the Sc-water distances found in 7 co-ordinate species listed in Table II and shown in Fig. 3.

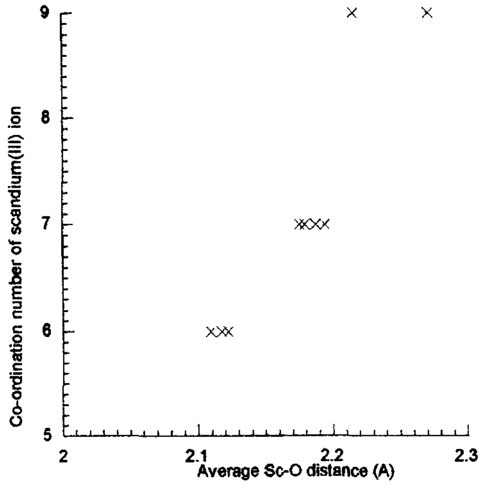

FIGURE 3 The relationship between co-ordination number of scandium and the average Sc-OH_2 distance

6. FINAL REMARKS

The X-ray diffraction studies[5] on solutions of scandium perchlorate and XAFS measurements on scandium triflate solution appear to be the final piece in the jigsaw. Although further structural studies on scandium salts of weakly co-ordinating anions would be interesting, their value is limited; further solution studies such as XANES measurements could give confirmation of a seven co-ordinate model, whilst molecular mechanics calculations could indicate which model for the $[Sc(OH_2)_7]^{3+}$ ion is likely to be favoured.

References

1. F.A. Hart, Comprehensive Co-ordination Chemistry, ed. G. Wilkinson, R.D. Gillard and J.A. McCleverty, Pergamon, Oxford, **3,** 1064 (1987).
2. T. Mioduski, Comments Inorg. Chem., **14,** 263 (1993).
3. S.A. Cotton, "Scandium, Yttrium & The Lanthanides: Inorganic and Co-ordination Chemistry", Encyclopaedia of Inorganic Chemistry, R.B. King ed., John Wiley, 3597 (1994) ; D.T. Richens, "The Chemistry of Aqua Ions", John Wiley, Chichester, 173. (1997).
4. W.B. Jensen, J. Chem. Educ., **59,** 634 (1982).
5. T. Yamaguchi, M. Niihara, T. Takamuru, H. Wakita and H. Kanno, Chem. Phys. Letters, **274,** 485 (1997).
6. ionic radii from R.D. Shannon, Acta Crystallogr. Sect. A, **32,** 749 (1976).
7. H. Kanno, T. Yamaguchi and H. Ohtaki, J. Phys. Chem., **93,** 1695 (1989).
8. C.B. Castellani, O. Carugo, M. Giusti and N. Sardone, Eur. J. Solid State Inorg. Chem., **32,** 1089 (1995).
9. J.Mc.B. Harrowfield, D.L. Kepert, J.M. Patrick and A.H. White, Aust. J. Chem., **36,** 483 (1983).
10. R.D. Rogers, Inorg. Chim. Acta, **133,** 347 (1987) and references therein; R.D. Rogers, J. Coord. Chem., **16,** 415 (1988).
11. J. Glaser and G. Johannson, Acta Chem. Scand., **35,** 639 (1981).
12. E.N. Rizkalla and G.R. Choppin, Handbook on the Physics and Chemistry of Rare Earths, eds. K.A. Gschneidner, LeRoy Eyring, G.R. Choppin and G.H. Lander, North Holland, Amsterdam, **18,** 529 (1994).
13. S.F. Lincoln and A.E. Merbach, Adv. Inorg. Chem., **42,** 50 (1995).
14. for references see Gmelin., Handbook of Inorganic Chemistry, Syst. No. 39, **C2,** 226 (1974); **C5,** 98 (1977); **C6,** 94 (1978).
15. (a) Z. Jin, Y. Liu, S. Zhang, F. Yu and J. Li, Acta. Chim. Sin, **45,** 1048 (1987); M. Tan, X. Gan, N. Tang, J. Zhou, X. Wang and Y. Zhu, Wuji Huaxue Xuebao, **6,** 5 (1990), Chem. Abs., **115,** 221711 (1991);
    (b) X. Gan, N. Tang, Y. Zhu, Y. Zhai and M. Tan, Zhonggo Xitu Xuebao, **7,** 13 (1989); Chem. Abs., **112,** 150561 (1990); (c) M. Tan, X. Gan, N. Tang, J. Zou, Y. Zhu and X. Wang, Gaodeng Xuexiao Huaxue Xuebao, **9,** 1217 (1988); Chem. Abs., **111,** 125632 (1989).
16. J.M. Harrowfield, B.W. Skelton and A.H. White, Aust. J. Chem., **47,** 397 (1994).

17. Y. Ohni, Y. Suzuki, T. Takeguchii and A. Ouchi, Bull. Chem. Soc. Jap., **61,** 393 (1988).
18. G.R. Willey, P.R. Meehan, M.D. Rudd and M.G.B. Drew, J. Chem. Soc. Dalton, 3175 (1995).
19. M.A.S. Aquino, W. Clegg, Q-T. Lin and A.G. Sykes, Acta Crsyatllogr. Sect. C, **51,** 560 (1995).
20. F. Matsumoto, Y. Ohki, Y. Suzuki and A. Ouchi, Bull. Chem. Soc. Japan, **62,** 2081 (1989).
21. Th-J. Henning and H. Jacobs, Z. Anorg. Allgem. Chem., **616,** 71 (1992).
22. A.B. Ilyushin and S.P. Petrosyants, Zh. Neorg. Khim., **39,** 1517 (1994); Russ. J. Inorg. Chem., **39,** 1449 (1994).
23. J-F. Ma, Z-S. Jin and J-Z. Ni, Polyhedron, **14**, 563 (1995).