ELSEVIER

Coordination Chemistry Reviews
164 (1997) 183–188

COORDINATION CHEMISTRY REVIEWS

Scandium 1995

Catherine E. Housecroft

Contents

---

1. Introduction

This review surveys the coordination chemistry of scandium published during 1995 and follows the corresponding survey for 1994 [1]. The literature has been searched using *Current Contents* and the Cambridge Structural Data Base. Structural figures have been redrawn using coordinates taken from the latter, implemented through the ETH, Zürich [2]. Organometallic complexes have been excluded.

2. Extraction

Extraction systems involving tributylphosphate (L, neat or 1 M in tetrachloromethane) and nitric acid (8–12 M) and being either scandium-containing or scandium-free have been investigated by use of IR spectroscopy. When scandium(III) is present, the species extracted were of the type $[Sc(NO_3)_3]\cdot nHNO_3\cdot 3L$ where $n=3$, 4 or 5 depending upon the concentration of nitric acid [3]. In related work from the same group, complexes of the type $[Sc(NO_3)_3].nL$ (L = tributylphosphate; $n=3.15$, 2.57 or 1.58) were prepared and characterised by IR spectroscopy. These results were compared with those obtained by preparing complexes of the type $[Sc(NO_3)_3]\cdot nHNO_3\cdot 3L$ where $n=1$ to 7 and the importance of hydrogen bonding interactions in these species was discussed [4].

2-Hydroxy-5-methylbenzaldehyde semicarbazone has been applied to the fluorometric determination of scandium(III) ions. Complex formation was rapid but the 1:1 cationic product was difficult to extract without careful choice of counter-ion;

PII S0010-8545(97)00029-5

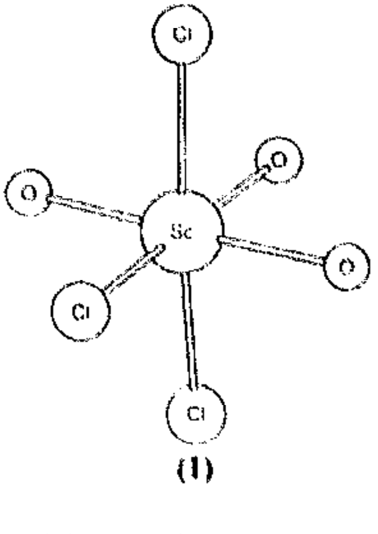
sodium dodecylbenzene sulfonate proved to be appropriate and the product was extracted into chloroform [5].

3. Catalysis

The uses of scandium(III) triflate, $Sc(OTf)_3$, as a catalyst have again been exemplified. The preparations of chiral acetals from carbonyl compounds and chiral diols and subsequent reactions with trimethylsilyl cyanide have been carried out in one-pot syntheses in the presence of $Sc(OTf)_3$ [6]. A report has appeared describing the reactions between imines and silyl enolates to give β-amino esters derivatives, and of Diels–Alder reactions between imines and dienes in the presence of catalytic amounts of $Sc(OTf)_3$ [7]. It has also been shown that scandium(III) trifluoromethanesulfonate is an active acylation catalyst [8].

4. Complexes with oxygen donor ligands

The preparation of the yellow complex $[ScCl_3(H_2O)_3][H_2L]Cl_2 \cdot 3H_2O$ where L = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane has been reported. This new complex has been characterised by IR and ^1H NMR spectroscopies and by elemental analysis, and these data indicated that protonation of ligand L had occurred during the synthesis. This was confirmed by the results of an X-ray crystallographic study which showed that $[H_2L]^{2+}$ ions were present in the solid state lattice. The scandium(III) centre was present in the form of the neutral species *mer*-$[ScCl_3(H_2O)_3]$, (**1**); average Sc–O and Sc–Cl bond distances were 241.7(7) and 212.2(14) pm, respectively. The solid state structure exhibited extensive intermolecular hydrogen-bonding [9].

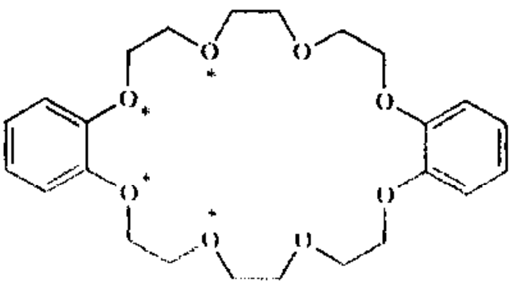


(**1**)

An X-ray diffraction study of the complex $[Sc(NH_3OH)(SO_4)_2] \cdot 1.5H_2O$ has been carried out. The solid state lattice consists of octahedrally sited scandium(III) centres connected into chains by the coordinated sulfate ions. Hydrogen-bonding exists between the chains and $[NH_3OH]^+$ cations and water molecules [10].

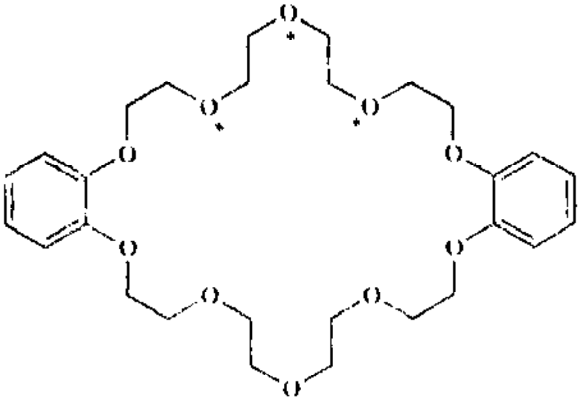
The reactions between $ScCl_3$, $SbCl_5$ and the crown ethers (**2**) or (**3**) in MeCN have been reported and two products have been characterised by X-ray crystallography. Ligand (**2**) binds to a $\{ScCl_2\}^+$ moiety such that the oxygen donor atoms shown in structure (**2**) occupy four the equatorial sites of the 7-coordinate scandium(III) centre (Sc–O lie in the range 218.4 to 229.7(7) pm). The fifth equatorial site is occupied by a water ligand (Sc–O = 213.0(8) pm). The complex cation was isolated and characterised as the hexachloroantimonate salt. Infrared and ^1H and ^{13}C NMR spectroscopic data were recorded. With the macrocyclic ligand (**3**), complex formation yields $[ScCl_2(\mathbf{3})(H_2O)_2]^+$ in which three of the oxygen donor atoms of the ligand bond to the metal centre. This cation has been structurally characterised as the yellow compound $[ScCl_2(\mathbf{3})(H_2O)_2][SbCl_6] \cdot MeCN \cdot H_2O$. Removal of chloride ion from the complex $[ScCl_2(\mathbf{2})(H_2O)][SbCl_6]$ by treatment with three equivalents of $SbCl_5$ in MeCN leads to the formation of a complex in which the macrocycle encapsulates a $\{ScCl(MeCN)\}^{2+}$ unit. When 10 equivalents of $SbCl_5$ are present, it is possible to remove all the scandium-bound chloro ligands; this system has been investigated by ^1H NMR spectroscopy [11].

Hydrated scandium(III) picrate, $[Sc(pic)_3]$, has been shown to react with ligand



* = coordination site

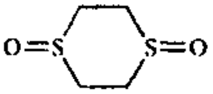
(**2**)



* = coordination site

(**3**)

(4) in water to give the complex $[Sc_6(pic)_6(4)_3(OH)_{10}(H_2O)_2](pic)_2(H_2O)_{10}$. This product has been characterised by IR spectroscopy and X-ray crystallography. In the solid state it consists of chains of centrosymmetric hexameric clusters connected by bridging molecules of (4). Of the six scandium(III) centres per complex dication, two have a coordination of seven and four are 6-coordinate. The Sc···Sc distances lie in the range 331.7–346.2 pm [12].



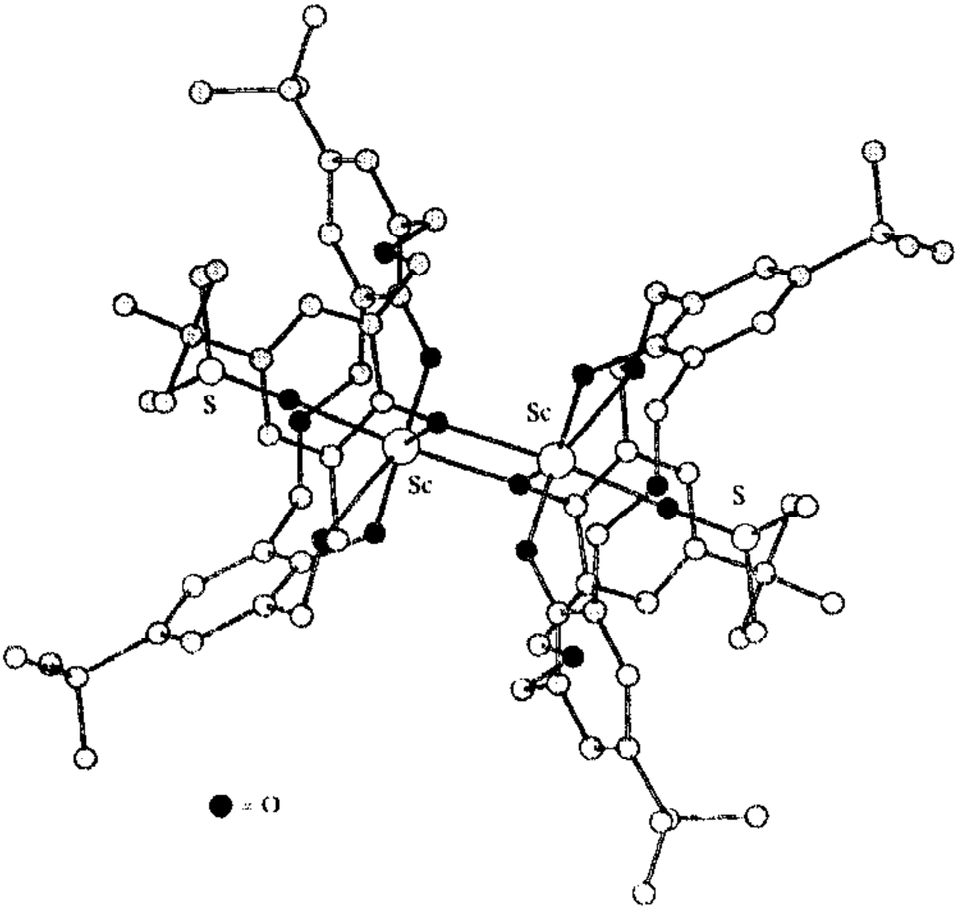
(4)

Complex formation between scandium(III) ions and oxacalix[3]arene macrocyclic ligands has been a subject for investigation. When scandium(III) trifluoromethanesulfonate reacted with 4-*tert*-butyloxacalix[3]arene, H_3L, in the presence of Et_3N, the product after work-up was found to be $[Sc_2L_2(dmso)_2]\cdot 2dmso\cdot Me_2CO$. This compound has been characterised by an X-ray diffraction study and the structure of $[Sc_2L_2(dmso)_2]$ is shown in (5). One aryloxo-group of each oxacalix[3]arene ligand is involved in a bridging interaction between the scandium centres which are 342.6 pm apart. Variable temperature ^1H NMR spectroscopic studies have indicated that a dynamic isomerisation process occurs in solution [13].

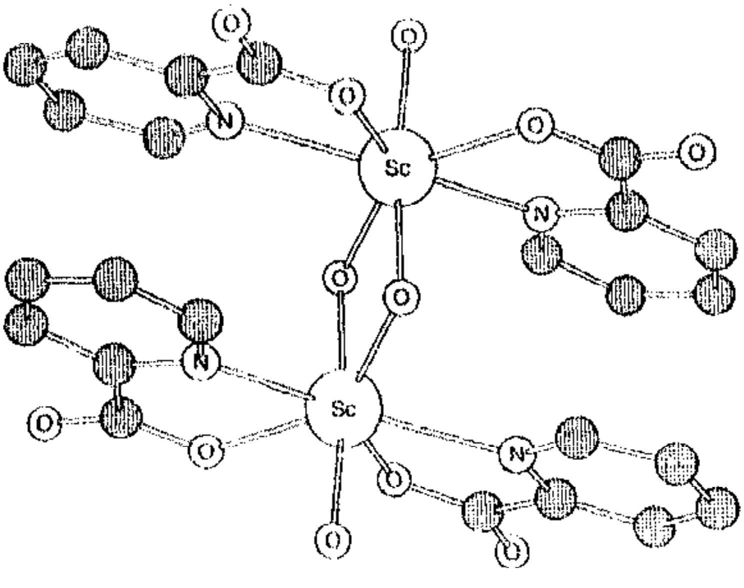
Both *O*-donor and *N,O*-donor ligands are exemplified in the final complex described in this section. The preparation and structural characterisation of the picolinato complex $[Sc_2L_4(H_2O)_2(\mu\text{-}OH)_2]$ (7) (HL = picolinic acid) have been described. Each picolinate ligand functions as an *N,O*-donor and each scandium(III) centre is 7-coordinate. Hydroxide bridges support the dinuclear core of the complex and the Sc···Sc separation is 331.6 pm [14].

5. Complexes with nitrogen donor ligands

A report has appeared of the template synthesis of a new macrocyclic ligand formed by the [1+1] cyclocondensation of 2,6-diacetylpyridine with 3,3′-diaminodipropylamine in the presence of scandium(III) salts $ScCl_3$ or $Sc(ClO_4)_3$. The dependence of the reaction pathway upon metal ion was illustrated by the observation that when the reaction was carried out in the presence of yttrium(III) ions, a [2+2] condensation product was obtained. The scandium(III) containing complex of the [1+1] product was characterised by elemental analysis, IR, UV–VIS and ^1H NMR spectroscopic data [15]. The same research group has reported the condensation of 2,6-diacetylpyridine with $1,3\text{-}(NH_2)_2C_6H_4$ in the presence of $Sc(ClO_4)_3$ to give the Schiff base complex $[ScL(ClO_4)_3]\cdot 4H_2O$ in which ligand L is the [2+2] cyclocondensation product [16].



(5)



(6)

References

[1] C.E. Housecroft, Coord. Chem. Rev. 152 (1996) 467.

[2] F.H. Allen, J.E. Davies, J.J. Galloy, O. Johnson, O. Kennard, C.F. Macrae, E.M. Mitchell, G.F. Mitchell, J.M. Smith, D.G. Watson, J. Chem. Inf. Comp. Sci. 31 (1991) 187.

[3] G.P. Nikitina, V.P. Egorova, A.A. Listopadov, L.B. Shpunt, Radiochemistry 37 (1995) 124.

[4] G.P. Nikitina, K.B. Papkov, A.A. Listopadov, Radiochemistry 37 (1995) 117.

[5] K. Watanabe, T. Kamagata, M. Itagaki, Bunseki Kagaku 44 (1995) 609.

[6] S. Fukuzawa, T. Tsuchimoto, T. Hotaka, T. Hiyama, Synlett (1995) 1077.

[7] S. Kobayashi, M. Araki, H. Ishitani, S. Nagayama, I. Hachiya, Synlett (1995) 233.

[8] K. Ishihara, M. Kubota, H. Kurihara, H. Yamamoto, J. Am. Chem. Soc. 117 (1995) 4413.

[9] G.R. Willey, P.R. Meehan, M.D. Rudd, M.G.B. Drew, J. Chem. Soc., Dalton Trans., (1995) 3173.

[10] A. Mirceva, L. Golic, Acta Crystallogr., Sect. C 51 (1995) 175.

[11] G.R. Willey, P.R. Meehan, M.D. Rudd, M.G.B. Drew, J. Chem. Soc., Dalton Trans., (1995) 811.

[12] J.D. Ayala, G. Vicentini, G. Bombieri, J. Alloys Compd. 225 (1995) 357.

[13] C.E. Daitch, P.D. Hampton, E.N. Duesler, Inorg. Chem. 34 (1995) 5641.

[14] J.F. Ma, Z.S. Jin, J.Z. Ni, Polyhedron 14 (1995) 563.

[15] W. Radecka-Paryzek, V. Patroniak-Krzyminiewska, Polish J. Chem. 69 (1995) 1.

[16] W. Radecka-Paryzek, E. Luks, Monats. Chem. 126 (1995) 795.