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COORDINATION CHEMISTRY REVIEWS

12. Scandium 1994

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CONTENTS

INTRODUCTION

This review surveys the coordination chemistry of scandium reported during the year 1994 and continues the literature coverage from the 1993 review [1]. The literature has been searched by 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, in general, been excluded, although several complexes of interest to coordination chemists do possess cyclopentadienyl ligands.

A general article dealing with trends in metallo-organic chemistry of scadium, yttrium and the lanthanoids has appeared [3]. Fullerene chemistry has previously included endohedral compounds containing scandium, and recent ESR spectroscopic data have illustrated the existence of a C_x-cluster containing a non-equivalent Sc_3-unit. The data are compared with those for Sc@C_{82} and Sc_3@C_{82} and from HPLC retention times it has been concluded that the new species is larger than a C_{3v} C_{82} cage [4].

12.1 EXTRACTION AND ANALYSIS

The results of studies of scandium extraction using phenol formaldehyde resin oligomers have been reported [5]. Gravimetric determinations of scandium can be carried out by using di-(2-ethylhexyl)phosphate (L); optimal Sc:L ratios have been investigated [6].

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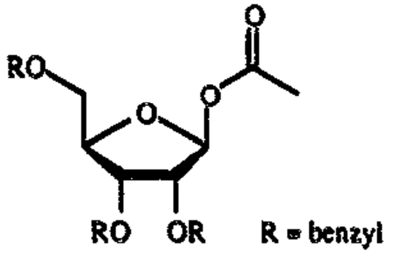
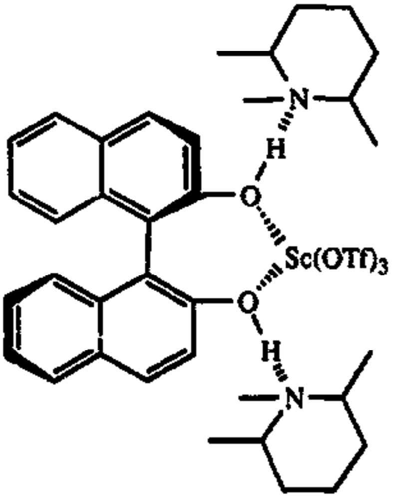
In the presence of $[NBu_4]^+$, scandium(III) may be extracted by hexafluoroacetylacetone (HL) into chloroform as the anionic chelate complex $[ScL_4]^-$. However, when the β-ketonate is 2-thienyltrifluoroacetate, no such anionic complex was observed. Scandium(III) has also been extracted in the form of the adducts $[ScL_3(topo)_n]$ (topo = trioctylphosphine oxide) [7].

12.2 CATALYSIS

Scandium(III) perchlorate (prepared from Sc_2O_3 and 70% aqueous $HClO_4$) has been shown to be an effective catalyst for the reaction between (1) and trimethylsilated nucleophiles to give α-D-ribofuranosides. The reactions proceed with good selectivities, and the catalyst was recovered and reused [8]. The allyation of various carbonyl compounds using tetraallyltin is catalysed by scandium(III) triflate [9, 10]. Scandium(III) triflate also catalyses the Friedel-Crafts acylation reactions of substituted benzenes with acid chlorides or acid anhydrides. The catalytic activity exceeds that of lanthanide triflates and $Sc(OTf)_3$ can be recovered and reused [11].



(1)



(2)

The chiral catalyst (2) has been prepared from $Sc(OTf)_3$, (*R*)(+)-binaphthol and *cis*-1,2,6-trimethylpiperidine. The structure of the catalyst has been proposed on the basis of ^1H and ^{13}C NMR spectroscopic data and hydrogen-bonds between the OH groups and tertiary nirogen atoms are important features. Catalyst aging processes have been investigated, and it has been found that the addition of 3-acetyl-1,3-oxazolidin-2-one stabilizes the catalyst. This catalyst is active for asymmetric Diels-Alder reactions [12, 13].

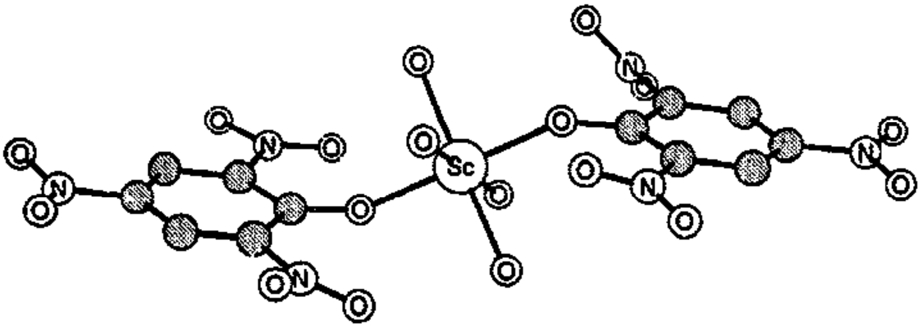
12.3 COMPLEXES WITH HALIDE LIGANDS

The results of a single crystal X-ray diffraction study of Na_3ScF_6 have been reported. In the solid state, both the scandium(III) and sodium centres are octahedrally sited with respect to fluorine atoms ($Sc{-}F_{av} = 2.007$ Å). The octahedral units are titled about 20° with respect to the axes of the perovskite-like cell and this structural observation has been discussed in relation to the structures of otehr cryolites and perovskites [14]. The electronic spectrum of scandium iodide has been recorded and the data analysed [15].

12.4 COMPLEXES WITH GROUP 16 DONOR LIGANDS

Several triflate complexes of scandium(III) were mentioned in section 12.2. The synthesis and characterization of $BaSc_2(SiO_4)_6$ have been reported. This compound represents a new structure-type in which tetrahedral silicate units are involved with a large group 2 ion and a large octahedrally sited metal ion — in the solid state, the Sc^{3+} ions are sited within O_6-octahedra whilst the Ba^{2+} ions are situated in interlayer sites [16].

Hydrated scandium(III) picrate has been crystallized from an excess of picric acid and the adduct that forms has been characterized as $[Sc(pic)_2(H_2O)_4](pic)(Hpic).{\approx}8.2H_2O$. The crystal structure of this complex has been determined and the octahedrally environment of the scandium(III) centre is shown in structure (3). The Sc–O_{pic} bond distances are 2.019(8) and 2.046(8)Å, and the Sc–O_{water} bond lengths lie in the range 2.100(9) to 2.121(8)Å [17].

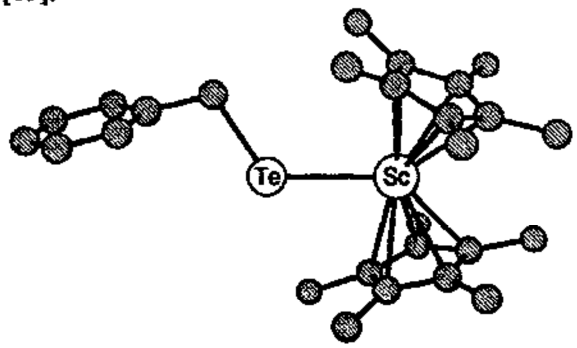


Hydrogen atoms omitted

(3)

The results of a ^{13}C and ^{45}Sc NMR spectroscopic investigation of the binding of scandium(III) ions to chicken ovotransferrin have been reported. The effects on the spectra of the presence of carbonate or oxalate ions have been discussed. The paper is the first report of a ^{45}Sc NMR spectroscopic study of a metalloprotein and also reinforces the use of quadrupolar NMR spectroscopy as a probe for metal ion binding sites in large proteins [18].

Piers *et al* have reported further results in their work on the heavier chalcogen derivatives of scandium(III). The reactions between $[Cp^*_2ScR]$ (R = Ph, CH_2Ph, CH_2SiMe_3) and tellurium or $^nBu_3P{=}Te$ lead to the formation of $[Cp^*_2ScTeR]$. For R = CH_2Ph, the crysal structure of the complex (4) has been determined; pertinent bond parameters are Sc–Te = 2.8337(14)Å and ∠Sc–Te–C = 121.61(21)°. When heated or subjected to photolysis, the compounds $[Cp^*_2ScTeR]$ eliminate TeR_2 and $[\{Cp^*_2Sc\}_2Te]$ is formed (see below). Reactivity studies of $[Cp^*_2ScTeR]$ have been carried out — the UV-VIS spectroscopic data and photochemical reactions illustrate that the primary photo-event during the reactions involves a Te→Sc ligand to metal CT transition. The reaction of $[Cp^*ScCH_2SiMe_3]$ with selenium yields $[Cp^*_2ScSeCH_2SiMe_3]$. When selenium or tellurium reacts with [Cp*ScD], D_2 is lost and the product is [{Cp*$_2$Sc}$_2$E] (E = Se or Te). In the case of E = Te, there is evidence for the intermediate species [Cp*$_2$ScTeD]. The crystal structures of both [{Cp*$_2$Sc}$_2$Te] and [{Cp*$_2$Sc}$_2$Se] (5) have been determined; (Sc–Te = 2.7528(12)Å and Sc–Se = 2.5424(16)Å) [19].



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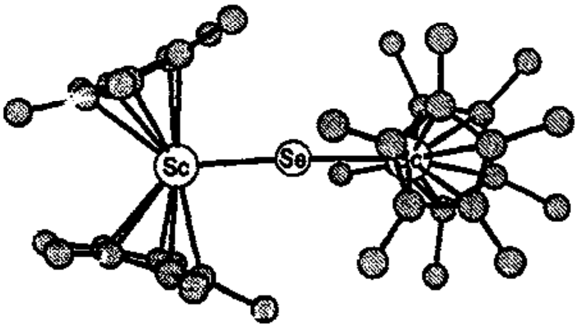

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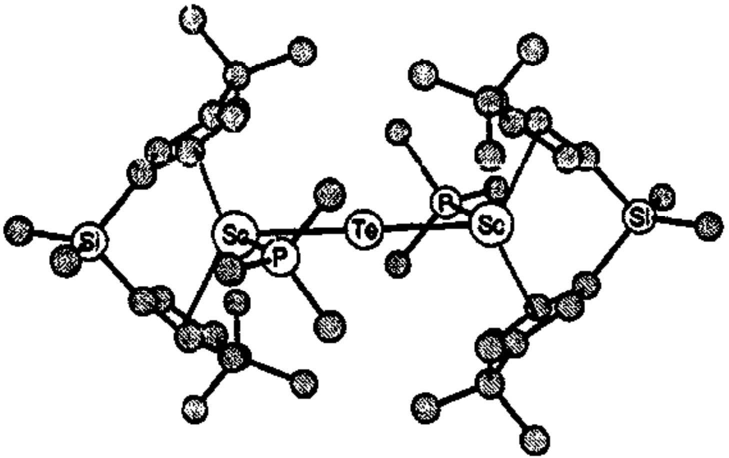


Interactions between Sc and C₅-rings shown by single lines

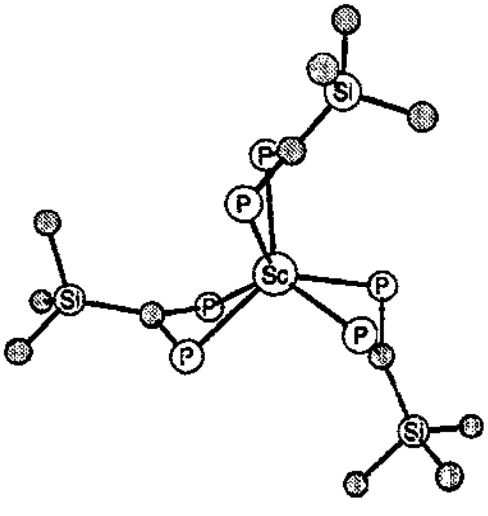
(6)

Tellurium inserts into the Sc-C$_{alkyl}$ bond in *meso*-[{Me$_2$Si(^{t}BuC$_5$H$_3$)$_2$}ScCH$_2$SiMe$_3$] to give [{Me$_2$Si(^{t}BuC$_5$H$_3$)$_2$}ScTeCH$_2$SiMe$_3$] in high yield. This complex can also be prepared from ^{n}Bu$_3$P=Te and [{Me$_2$Si(^{t}BuC$_5$H$_3$)$_2$}ScCH$_2$SiMe$_3$]. On heating the compound [{Me$_2$Si(^{t}BuC$_5$H$_3$)$_2$}ScTeCH$_2$SiMe$_3$], Te(CH$_2$SiMe$_3$)$_2$ is lost and the product is

$[\{\{Me_2Si(^tBuC_5H_3)_2\}Sc\}_2Te]$. This compound also forms when $[\{\{Me_2Si(^tBuC_5H_3)_2\}ScH\}_2]$ is treated with $^nBu_3P{=}Te$. With PMe_3, $[\{\{Me_2Si(^tBuC_5H_3)_2\}Sc\}_2Te]$ forms the adduct (6) which has been crystallographically characterized. The tellurium atom lies on an inversion centre and the Sc–Te–Sc unit is linear (Sc–Te = 2.875(5)Å) [20].

12.5 COMPLEXES WITH GROUP 15 DONOR LIGANDS

The kinetic stability of scandium(III) phthalocyanine complexes has been the subject of investigation [21]. The reactions of scandium(III) triflate with 3 equivalents of $Li[C(PMe_2)_2X]$ (X = PMe_2 or $SiMe_3$) in thf lead to the formation of the complexes $[Sc\{C(PMe_2)_2X\}_3]$. In solution, these have been characterized by ^1H and ^{13}C NMR spectroscopies, and $[Sc\{C(PMe_2)_2PMe_2\}_3]$ (7) has additionally been studied using solution ^{31}P NMR spectroscopy and X-ray diffraction methods. In the solid state, the Sc(III) centre is in a trigonal prismatic environment (Sc–P = 2.617(1)Å, Sc···C_{PCP} = 2.909Å). The ligands are described as functioning in a manner that is midway between σ-chelating and π-bonded [22].



P-bound methyl groups omitted

(7)

REFERENCES

1. C.E. Housecroft, *Coord. Chem. Rev.*, 146 Part 1 (1995) 37.
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 and D.G. Watson, *J. Chem. Inf. Comp. Sci.*, 31 (1991) 187.
3. A. Singh, *Proc. Indian Acad. Sci.-Chem. Sci.*, 106 (1994) 703.
4. S. Suzuki, Y. Kojima, Y. Nakao, T. Wakabayashi, S. Kawata, K. Kikuchi, Y. Achiba and T. Kato, *Chem. Phys. Lett.*, 229 (1994) 512.
5. S.A. Semenov, E.M. Valkina and A.M. Reznik, *Zh. Neorg. Khim.*, 39 (1994) 670.
6. K.W. Cha and E.S. Jeong, *Bull. Kor. Chem. Soc.*, 15 (1994) 9.
7. J. Noro and T. Sekine, *Bull. Chem. Soc. Jpn.*, 66 (1993) 3516.
8. I. Hachiya and S. Kobayashi, *Tetrahedron Lett.*, 35 (1994) 3319.
9. I. Hachiya and S. Kobayashi, *J. Org. Chem.*, 58 (1993) 6958.

10. I. Hachiya and S. Kobayashi, *J. Org. Chem.*, 59 (1994) 3242.
11. A. Kawada, S. Mitamura and S. Kobayashi, *Synlett*, (1994) 545.
12. S. Kobayashi, H. Ishitani, M. Araki and I. Hachiya, *Tetrahedron Lett.*, 35 (1994) 6325.
13. S. Kobayashi, M. Araki and I. Hachiya, *J. Org. Chem.*, 59 (1994) 3758.
14. P. Dahlke and D. Babel, *Z. Anorg. Allg. Chem.*, 620 (1994) 1686.
15. E.A. Shenyavskaya, *Zh. Fiz. Khim.*, 68 (1994) 85.
16. L.H. Wang, L.F. Schneemeyer, R.J. Cava and T. Siegrist, *J. Solid State Chem.*, 113 (1994) 211.
17. J.M. Harrowfield, B.W. Skelton and A.H. White, *Aust. J. Chem.*, 47 (1994) 397.
18. J.M. Aramini and H.J. Vogel, *J. Am. Chem. Soc.*, 116 (1994) 1988.
19. W.E. Piers, D.J. Parks, L.R. MacGillivray and M.J. Zaworotko, *Organometallics*, 13 (1994) 4547.
20. W.E. Piers, G. Ferguson and J.F. Gallagher, *Inorg. Chem.*, 33 (1994) 3784.
21. T.N. Lomova, L.G. Andrianova, T.N. Sokolova and B.D. Berezin, *Zh. Neorg. Khim.*, 39 (1994) 446.
22. H.H. Karsch, G. Ferazin, H. Kooijman, O. Steigelmann, A. Schier, P. Bissinger and W. Hiller, *J. Organomet. Chem.*, 482 (1994) 151.