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Coordination Chemistry Reviews
172 (1998) 99–110

COORDINATION
CHEMISTRY
REVIEWS

Yttrium 1996

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Contents

1. Introduction

The properties of yttrium compounds have been the main interest in the literature in 1996 covering the majority of the 629 citations revealed by an SCI search and concentrating on the application of lasers in medicinal chemistry and the properties of ceramics and thin films in materials. This review covers the coordination chemistry of yttrium for 1996. It does not cover organometallic complexes. However, a few organometallic complexes could not be avoided, due to their mixed ligand nature featuring coordinatively interesting ligands. A section on superconductivity of yttrium complexes has not been covered this year as most of the respective literature described new methods rather than new coordination compounds; the synthesis of new ceramic and oxide films of yttrium is not covered as it is beyond the scope of this article. The literature was searched using both the Cambridge Crystallographic Data Base (CCDB) and the SCI. Crystal structures shown were redrawn using structural coordinate files from the CCDB.

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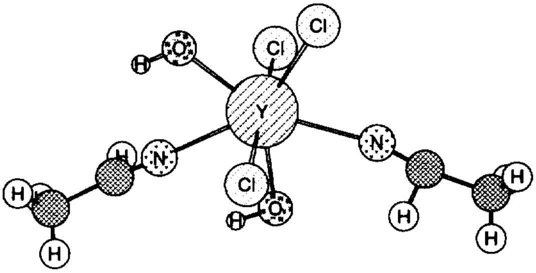
PII S0010-8545(98)00091-5

2. Yttrium(III)

2.1. Complexes with halide and other simple ligands

A series of yttrium and lanthanide hexacyanocobaltate(III) hydrate complexes {Y[Co(CN)$_6$]} was prepared for an investigation of the crystal structure and thermal dehydration of these complexes [1].

The molecular adduct [$YCl_3(H_2O)_2(MeCN)_2$] (**1**) was isolated by treatment of yttrium chloride with thionyl chloride in acetonitrile solution [2]. The X-ray crystal structure of (**1**) reveals a seven-coordinate, pentagonal bipyramidal geometry around the metal centre.



(1)

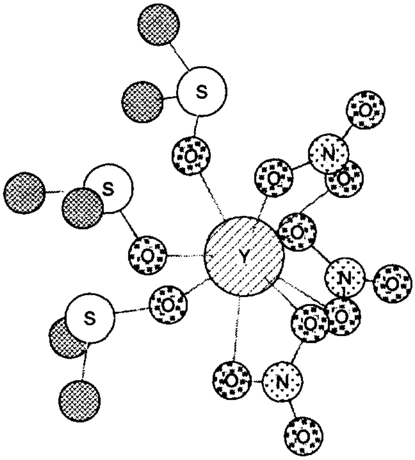
Adducts of yttrium and lanthanide nitrates with dmso obtained by crystallisation of the appropriate salt with excess of dmso have been studied by X-ray crystallography to define the manner in which stoichiometry and structure vary with change of metal ion radius [3]. The yttrium complex (**2**) is mononuclear and the monoclinic crystal structure shows the coordination of the didentate nitrate ions and three dmso molecules.

New methods have been developed for the synthesis of yttrium hydride films [4,5] and interesting optical switching properties have been reported [6,7].

2.2. Complexes with oxygen donor ligands

Complexes of a hexahomotrioxacalix[3]arene macrocycle with Group 3 and lanthanide metals have been prepared [8]. It is shown that trivalent metal ions are bound more strongly than alkali–metal ions. The crystal structure of the yttrium complex (**3**) reveals the dimeric nature of the complex in the solid state, which features bridged aryloxo units. The trianion ligand binds to a yttrium atom along with a dmso molecule.

A yttrium tartrate complex [$Y(C_4H_4O_6)(C_4H_5O_6) \cdot 2.5H_2O$] was synthesised and characterised by infra-red spectroscopy and X-ray crystallography [9]. The yttrium ion is nine-coordinate with four oxygens from the tartrate ligands and three from the water molecules. It is believed that one tartrate is monoanionic while the other one is dianionic.



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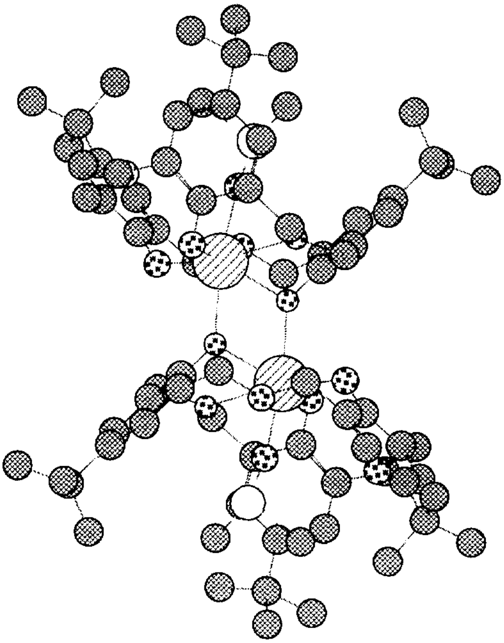
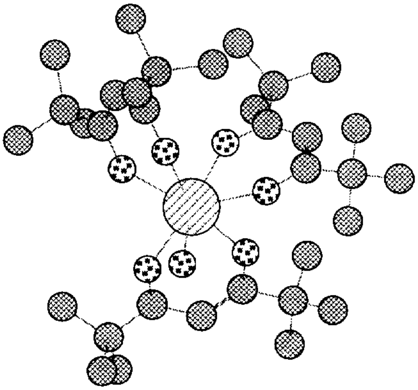


(3)

The preparation and chemical vapour deposition studies of yttrium tris(β-diketonate) complexes have been described [10]. The crystal structure of 2,2,6,6-tetramethylheptane-3,5-dionate complex with yttrium (**4**) shows the monomeric nature of the complex with three ligands and a water molecule to coordinate to one yttrium metal whereas the complex with 2,2,7-trimethyloctane-3,5-dionate crystallises as a dimeric unit (**5**).



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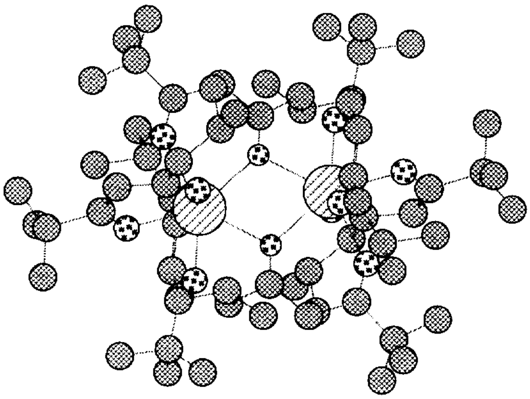
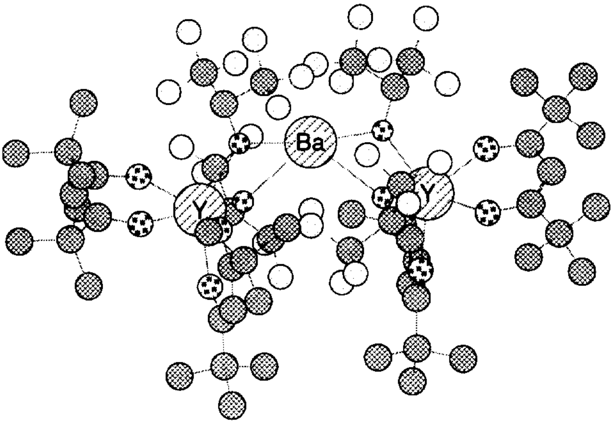


(5)

Mixed-metal diyttrium–barium and yttrium–copper complexes have been prepared and characterised by mass spectrometry, NMR spectroscopy and vapour pressure measurements [11]. The X-ray crystal structure of the diyttrium–barium complex (**6**) shows the coordination of the four hexafluoroisopropoxide groups along with the four dinucleating tetramethyl heptadiones which leads to the mixed-metal core.



(**6**)

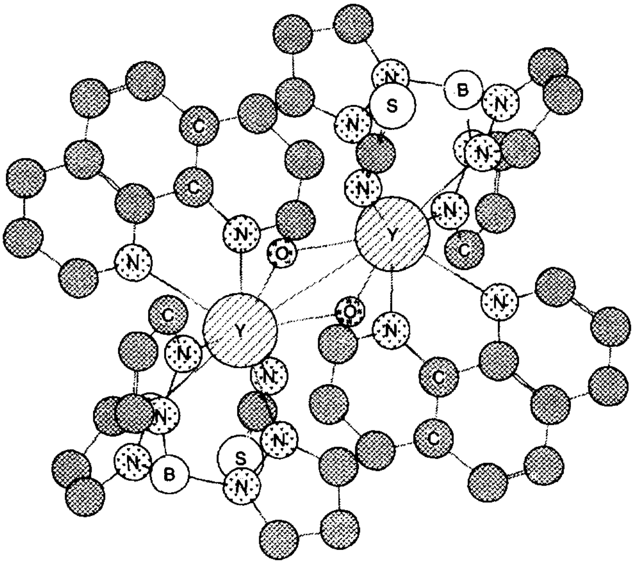
Reaction of $YMnO_3$ and BaO and MnO at 1000 °C for four days resulted in a ferrimagnetic compound, $YBaMn_2O_5$, with a layered perovskite structure [12]. The layered arrangement is due to the presence of oxygen vacancies in the yttrium plane leaving the yttrium eight-coordinate. The barium atoms show typical perovskite arrangement. The interesting magnetic properties arise from a manganese centre with mean oxidation state of 2.5.

A YBa_2 cluster was synthesised by reaction of $Y[(NSiMe_3)_2]_3$ and $Ba[NSiMe_3)_2]_2$ with t-butanol (^tBuOH) in ether [13]. The resulting complex $YBa_2(O^tBu)_7(^tBuOH)$ has a triangular structure with two μ_3-O^tBu and three μ_2-O^tBu ligands. The metals are five-coordinate and the crystal shows chains of triangles held together by hydrogen bonds between the terminal alkoxide units.

The synthesis and characterisation of a series of yttrium alkoxides has been described [14]. The chemistry of the oxo-alkoxides of metals is highlighted in a review article including synthetic procedure, structural features and potential applications [15].

2.3. Complexes with nitrogen donor ligands

Polypyrazolyl borate complexes of yttrium have been synthesised by two groups. Heteroleptic trispyrazolylborate complexes of yttrium were synthesised by reaction of $[Y(NCS)_3(phen)_3]$ where phen = 1,10-phenanthroline with $K(HBpz_3)$ where pz = pyrazol-1yl [16]. The resulting complex $[Y(HBpz_3)(NCS)(\mu\text{-}OH)(phen)]_2$ (**7**) is binuclear with a bridging hydroxide. The yttrium atoms are eight-coordinate with a distorted square antiprismatic geometry and a non-linear nitrogen-bonded thiocyanate ligand.



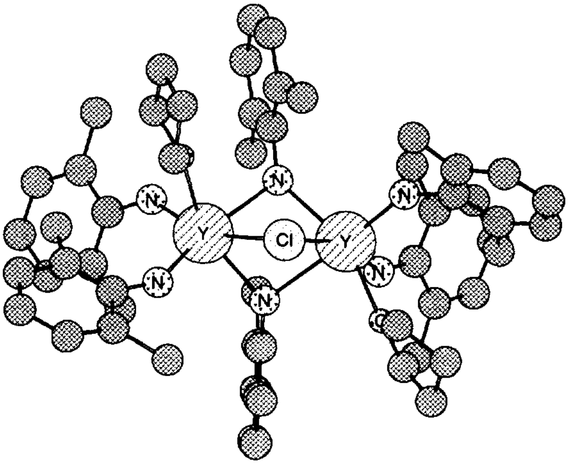
(7)

Lanthanoid chlorides were treated with K(HBpz$_3$) in thf at −78 °C to yield the bis(polypyrazolyl)borato complexes of several lanthanoids [17].

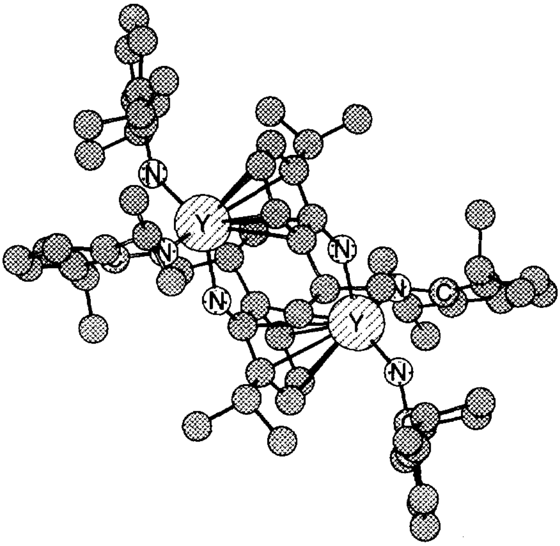
A diphthalocyaninate complex of yttrium(III) is obtained by reacting yttrium acetate with molten phthalodinitrile in the presence of potassium methylate and isolating with organic cations [18]. The redox properties are reported.

The complexation of arylamido ligands with yttrium and lanthanides has been investigated using either non-substituted arylamido reagents or the 2,6-dimethyl- or 2,6-di-isopropyl-arylamido derivatives [19]. A trimetallic ion pair was formed in the case of yttrium when the 2,6-dimethyl-arylamido was used whose structure was unequivocally established by X-ray crystallography. Only the anion is shown (**8**) for simplicity. The structure features a bridging chloride which was not observed in the case of larger metals. When bulkier ligands were used, such as 2,6-diisopropyl derivatives, neutral compounds were obtained. Yttrium forms a trigonal bipyramidal disolvated complex [$Y(NHC_6H_3{}^iPr_2\text{-}2,6)_3(thf)_2$]. Complexes free of thf could be obtained using $Y[N(SiMe_3)_2]_3$ as a precursor using a well-established technique in alkoxide chemistry. The crystal structure (**9**) reveals the yttrium dimer obtained.

Reaction of YCl_3 with $Li_3[N(CH_2CH_2NSiMe_3)_3]$ gave a novel Y_2Li_3O cluster (**10**) which introduces promising chemistry for rare earth azatrane complexes [20]. It is postulated that the other fragments, apart from the azatrane ligand, are due to facile cleavage of thf.



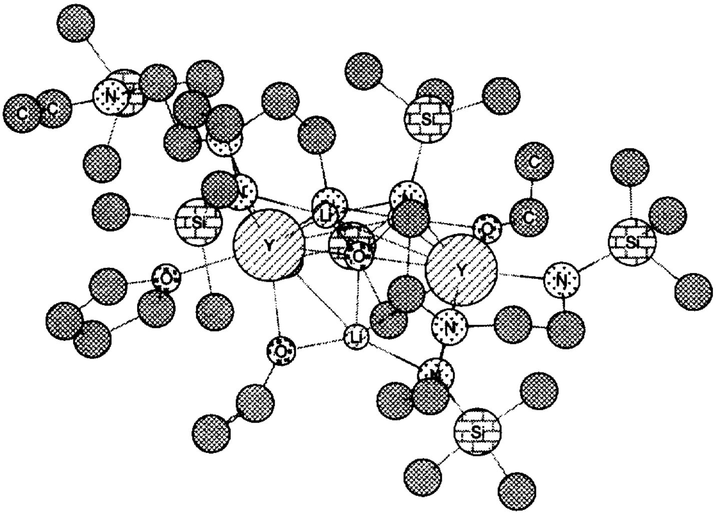
(8)



(9)

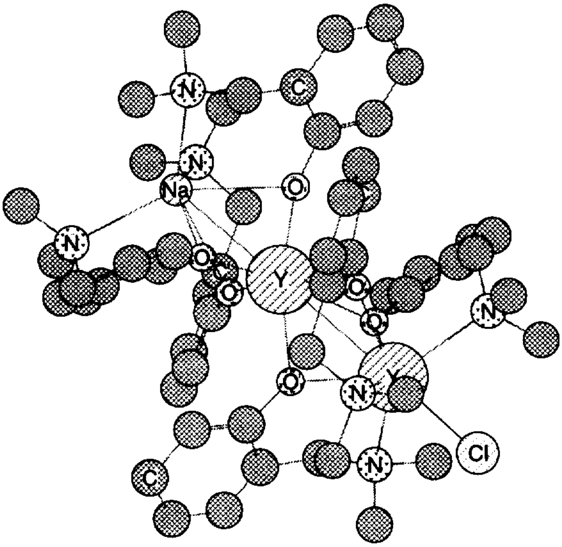
2.4. Complexes with mixed oxygen and nitrogen donor ligands

Novel heteropolymetallic complexes of yttrium have been prepared containing *o*-aminosubstituted phenolate ligands [21]. They have been characterised by NMR spectroscopy (^{1}H, ^{13}C and ^{89}Y) and X-ray crystal structure determination. The crystal structure of the diyttrium complex (**11**) shows that the chlorine, the two yttrium and sodium atoms lie on a pseudo-three-fold axis. There are two sets of



(10)

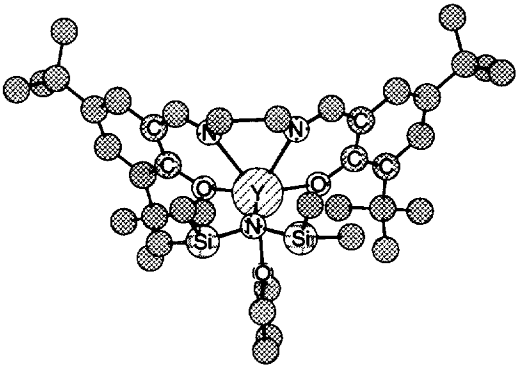
phenolate ligands around this axis. One bridges the yttrium atoms in an asymmetric fashion and the other bridges the yttrium and the sodium atom resulting in two shells of opposite screw type chirality. The NMR spectroscopic studies have confirmed that the same structure of the complex exists in solution. The ^{89}Y NMR spectroscopy showed two separate resonances at 202.5 and 132.4 ppm. The complexes



(11)

[ClM(OAr)$_3$Na] where M = lutetium or yttrium and OAr = [OC$_6$H$_2$(2,6-CH$_2$NMe$_2$)$_2$4-Me] were also prepared and fully characterised. It is claimed that their formation results from positive cooperativity between the anionic and cationic species that leads to complex preorganisation during its formation. This approach for the formation of the complexes may lead to synthesis of new coordination polymers.

A highly soluble yttrium complex with *N*,*N*′-bis(3,5-di-t-butylsalicylidene)ethylenediamine (L) was synthesised by reacting H$_2$L with {Y[N(SiHMe$_2$)$_2$]$_3$(thf)$_2$} in thf–hexane to afford monomeric [YL(thf)] (**12**) [22]. Its X-ray crystal structure reveals a six-coordinate yttrium atom with the ligand in distorted trigonal prismatic geometry. Attempted preparation by alcoholysis led to polymeric products.



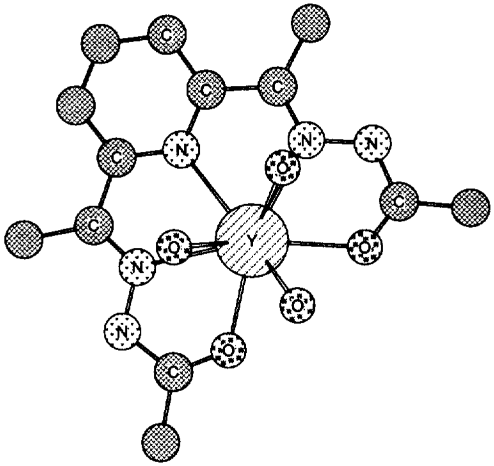
(**12**)

The synthesis and X-ray crystal structure of a yttrium complex with the neutral ligand 2,6-diacetyl pyridine diacetic acid hydrazone (**13**) was reported [23]. The complex was also characterised by ^{1}H and ^{13}C NMR spectroscopies. The pentadentate ligand leaves four available sites for the water molecules to coordinate, resulting in a nine-coordinate yttrium. Interestingly, the ^{89}Y NMR spectrum shows a very small chemical shift relative to the standard YCl$_3$.

The complex of the hexadentate ligand 1,4,7-tris(carbamoylmethyl)-1,4,7-triazacyclononane with yttrium (**14**) has been synthesised and characterised by X-ray crystallography [24]. The yttrium ion is nine-coordinate with two bound trifluoromethanesulfonate ions and a water molecule filling in the coordination sphere. The lanthanide complexes dissociate completely in aqueous solution.

A 20-membered hexaaza macrocycle (**15**) has been synthesised by Schiff base condensation of 2,6-diformyl 4-methyl phenol with 2,6-diamine pyridine in the presence of the hydrated metal (yttrium and lanthanides) salts to yield the respective complexes [25]. This macrocycle differs from other Schiff base ones in respect of the combination of the rigid pyridine units with the relative flexible 2,6-diformyl phenols.

An yttrium complex of an 18-membered hexaaza Schiff base macrocycle was prepared using the yttrium ion as a template [26]. The complex is thermally stable up to 388 °C and is inert to release of metal ions in dimethylformamide. The yttrium


C
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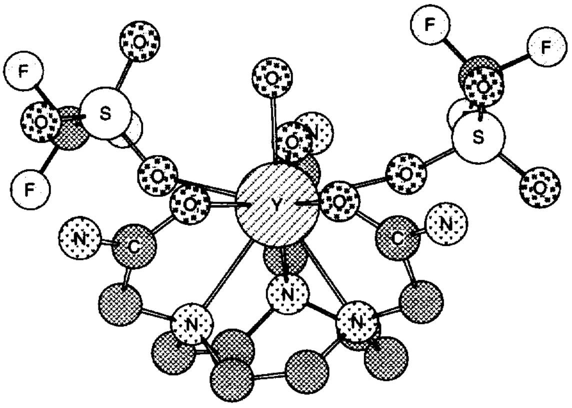
(13)


F
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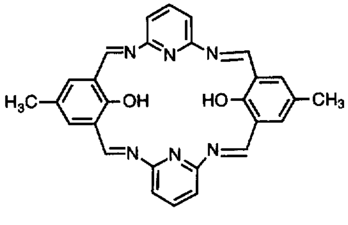
(14)


N
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H3C
OH
HO
CH3
N
N
N

(15)

complex with the Schiff base 1,2-(diimino-4′-antipyrinyl)ethane has been prepared and characterised by spectroscopic techniques and thermogravimetric analysis [27]. The iodide yttrium complex of 4-*N*(4′-antipyrylmethylidene)aminoantipyrine (L) $[Y(L)_2I]I_2$ was synthesised and characterised. Only one iodide seems to coordinate to the complex and the yttrium is seven-coordinate using the oxygens from the carbonyl groups and one azomethine nitrogen [28].

2.5. Complexes with chalcogenide donor ligands

The synthesis and characterisation of KYP_2Se_6 has been described. It was synthesised by the stoichiometric reaction of Y, P, Se and K_2Se_4 at 750 °C and crystallises in an orthorhombic space group [29]. The structure comprises a layered square network of yttrium centres that are bound to four distinct $[P_2Se_6]^{4-}$ units through selenium. The electrosynthesis of yttrium chalcogenide films and their characterisation by optical absorption, scanning electron microscopy and X-ray diffraction presents a new route for the synthesis of such films [30].

2.6. Complexes with mixed sulfur and nitrogen donor ligands

The structures of a series of nitride chlorides, nitride sulfides and nitride sulfide chlorides of yttrium and the lanthanides featuring $[NM_4]$ tetrahedra where M = metal have been described [31].

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