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6. Yttrium

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INTRODUCTION

This review covers the coordination chemistry of yttrium for 1991 and is similar in layout to the corresponding survey of the 1990 literature [1]. Active interest in the field of superconductivity prompts the inclusion of a section which describes pertinent coordination complexes. The literature has been searched by use of *Currents Contents*. The Cambridge Crystallographic Data Base provided the coordinates for structures (3)-(6) and (9) which have been redrawn for this article.

6.1 YTTRIUM(III)

6.1.1 Complexes with halide and other simple ligands

The hydrothermal synthesis of yttrium hydroxide fluorides from Y_2O_3 and KF solution has been described. The product distribution obtained depends on the concentration of potassium fluoride. In solutions with a concentration [KF] less than 0.1 M, YOOH is formed; in 2.3 M KF solution, $Y(OH)_2F$ is produced. At values of [KF] > 6M, $K[YF_4]$ is formed in addition to the

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hydroxide fluoride. X-ray powder data are reported and changes in lattice constants as a function of fluoride content have been examined. The yttrium(III) complexes have been the subject of thermal decomposition studies [2].

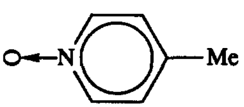
The complexation of halide ligands to yttrium(III) ions in dmf at 298 K has been studied by a method of precise titration calorimetry. Complexes observed include $[YCl]^{2+}$, $[YCl_2]^+$, YCl_3, $[YBr]^{2+}$ and $[YBr_2]^+$. Formation constants, enthalpies of formation, and entropies of formation have been determined. For the corresponding iodo complexes, the formation enthalpies are too small to be accurately measured. Trends in enthalpies of formation follow the order ΔH°_f Cl > Br > I which is unusual for a hard metal(III) ion. It is suggested that the bromide ion, in contrast to the chloride ion, forms outer sphere complexes with yttrium(III) ions in dmf solution. ^{89}Y NMR spectroscopic data are presented for the complexes $Y(ClO_4)_3$, YCl_3 and YBr_3 in dmf [3].

Amongst a series of isothiocyanate complexes of lanthanide metal(III) ions to be reported is the yttrium(III) compound $Y(NCS)_3.3L$ in which L = 4-picoline-*N*-oxide; see Section 6.1.2. Products have been characterised by elemental analysis, conductance measurements, and infrared, electronic and visible spectroscopy [4].

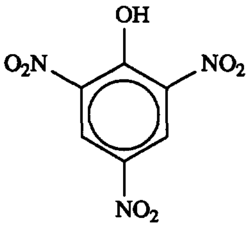
The new basic yttrium(III) nitrates $Y(OH)_{1.5}(NO_3)_{1.5}.H_2O$ and $YO_{0.75}(NO_3)_{1.5}$ have been characterised as a result of thermal decomposition studies of hydrated yttrium(III) nitrate. Infrared spectroscopic data and the results of X-ray powder diffraction studies are presented. The compound $YO_{0.75}(NO_3)_{1.5}$ is stable over the range 140-280°C [5]: The results of an X-ray diffraction study on 1M yttrium(III) nitrate and chloride solutions in dmso have been compared with data for the corresponding erbium(III) systems. The dmso ligands are coordinated to the yttrium(III) centres via the *O*-donor with $\angle Y\text{-}O\text{-}S \approx 130°$. For the nitrate system, there is an average of ≈ 1.5 NO_3^- ions coordinated in a bidentate fashion per yttrium(III) ion. In the case of chloride, approximately 1.3 Cl^- ions are in the inner coordination sphere of the metal ion [6]. The coordination of dmso to yttrium(III) ions is described in later sections [7].

6.1.2 Complexes with oxygen donor ligands

The complex $Y(NCS)_3L$ where L = (1) has been synthesised and characterised (see Section 6.1.1.) [4]. The reaction of YL_3 with dmso where HL = picric acid, (2), gives $YL_3.3dmso$ which is a non-electrolyte. Infrared spectroscopic data suggest that the dmso ligands are *O*-bonded to the yttrium(III) centre [7].

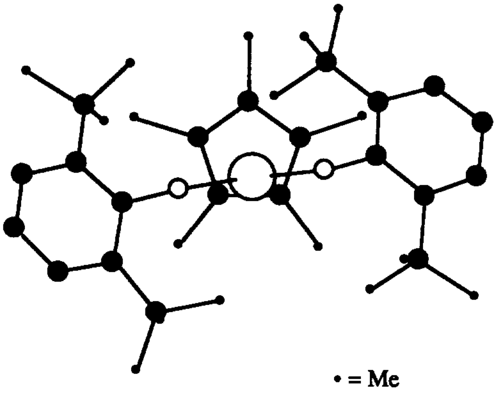


(1)



(2)

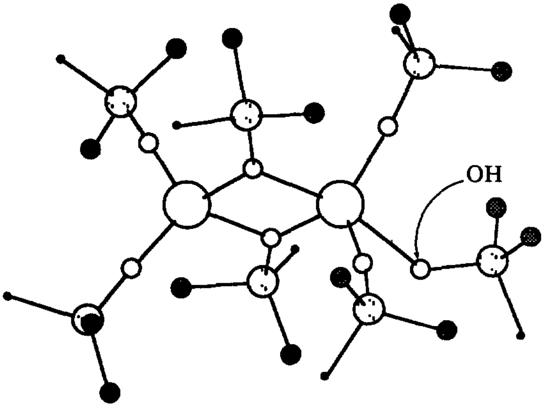
Interest in alkoxide and related complexes of yttrium(III) continues to be evident. Reactions of $Y\{N(SiMe_3)_2\}_3$ with an excess of various tertiary alcohols have been studied. With Me_3COH, the complex $Y_3(OCMe_3)_9(Me_3COH)_2$ is formed, and similarly with *t*-amyl alcohol (ROH), the product is $Y_3(OR)_9(ROH)_2$. With higher tertiary alcohols, the product complexes have the general formula $Y(OR')_3$ where R' = CMe_2CHMe_2, $CMeEtCHMe_2$, and CEt_3 and are dimeric. In $Y_3(OCMe_3)_9(Me_3COH)_2$, the coordinated alcohol molecules can be replaced by thf or py donors; trimethylamine does not displace Me_3COH. An X-ray diffraction study of the lanthanum analogue of $Y_3(OCMe_3)_9(Me_3COH)_2$ shows that the complex possesses a triangular Y_3-core which is capped by two μ_3-$OCMe_3$ groups and is supported by three edge bridging Me_3CO^- ligands. Evidence provided by NMR spectroscopy supports the fact that the yttrium(III) and lanthanum(III) complexes are isostructural [8]. The yttrium(III) oxo-complex $Y_5(O)(O^iPr)_{13}$ has been synthesised by a new method and has been characterised by mass spectrometry and ^1H, ^{13}C and ^{89}Y NMR spectroscopy [9]. The reaction of YL_3 with KCp* in toluene at 100°C yields Cp*YL_2, (3), where HL = 2,6-$^tBu_2C_6H_3OH$. The structure of (3) has been determined by X-ray crystallography. The Y-O distances are 2.096 (4) and 2.059 (3) Å and values of $\angle Y\text{-}O\text{-}C_{aryl}$ are markedly different (168.0 (3)° and 128.6 (3)°); the angle $\angle O\text{-}Y\text{-}O$ is 107.0 (1)°. The complex Cp*YL_2 reacts with $LiCH(SiMe_3)_2$ to give Cp*$YL(CH(SiMe_3)_2)$. The oxidative addition of dihydrogen to Cp*$YL(CH(SiMe_3)_2)$ leads to the dinuclear species $[Cp^*YL(\mu\text{-}H)]_2$; the bridging nature of the hydride ligands is apparent from a triplet resonance in the ^1H NMR spectrum (J_{YH} = 35.2 Hz) [10].



(3)

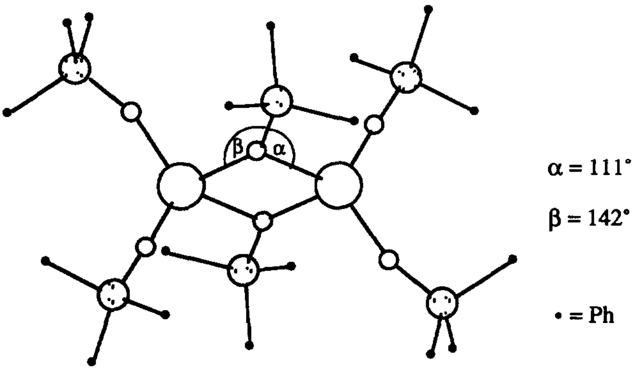
Treatment of $Y\{N(SiMe_3)_2\}_3$ with Ph_3SiOH in a 1:3 ratio leads to the homoleptic complex $[Y(OSiPh_3)_3]_n$ which forms monomeric Lewis base adducts $Y(OSiPh_3)_3L_n.xL$ with bases L (L = thf, $n = 3, x = 1$; py, $n = 3, x = 0$; OP^nBu_3, $n = 2, x = 0$). The structure of $Y(OSiPh_3)_3(thf)_3$.thf has been determined; the yttrium(III) atom is octahedrally sited and the ligands are in a *fac*-arrangement. Pertinent distances in $Y(OSiPh_3)_3(thf)_3$.thf are $Y\text{-}O_{Si}$ = 2.136 (17), 2.118 (18) and 2.138 (18) Å and $Y\text{-}O_{thf}$ = 2.406 (11), 2.462 (21) and 2.374 (20) Å. An X-ray diffraction study of

$Y(OSiPh_3)_3(OP^nBu_3)_2$ reveals a trigonal bipyramidal environment for the yttrium(III) centre; distances within the coordination sphere are $Y\text{-}O_{Si} = 2.121$ (3), 2.129 (3) and 2.118 (3) Å and $Y\text{-}O_{phosphite} = 2.261$ (3) and 2.266 (3) Å. With 3.5 equivalents of $HOSiMe_2{}^tBu$, $Y\{N(SiMe_3)_2\}_3$ reacts to give the dinuclear complex $[\{Y(OSiMe_2{}^tBu)_2(HOSiMe_2{}^tBu)\}\{Y(OSiMe_2{}^tBu)_2\}(\mu\text{-}OSiMe_2{}^tBu)_2]$, (4), which has been structurally characterised. This dinuclear species is degraded by thf to yield $Y(OSiMe_2{}^tBu)_3(thf)_3$. Related anionic complexes have also been prepared and characterised [11]. A solid and solution state study has been made of $[Y(OSiPh_3)_3]_n$ and, in solution, use has been made of ^{29}Si NMR spectroscopy. The spectroscopic data are consistent with an oligomeric species and a single crystal X-ray diffraction structure determination shows the presence of a dimeric complex, (5), in the solid state. The dimer is retained in $CDCl_3$ solution and any possible exchange between the bridging and terminal $OSiPh_3$-groups occurs either slowly on the NMR timescale or not at all [12].



• = t-butyl

(4)



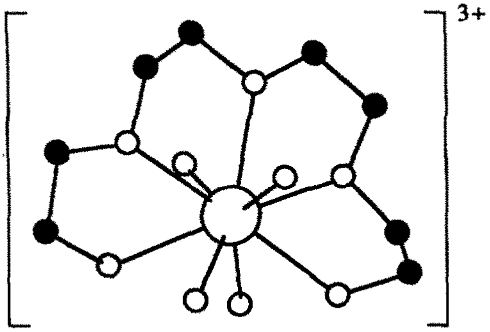
α = 111°

β = 142°

• = Ph

(5)

Yttrium(III) ions complex with tetraethylene glycol, L, in MeCN/MeOH solution to give $[YL(H_2O)_4]^{3+}$, (**6**). The chloride salt has been structurally characterised; the yttrium atom in trication (**6**) is 9-coordinate within a tricapped trigonal prismatic environment. Related lanthanoid complexes have also been reported. The glycol ligand provides a more hydrophobic environment than analogous crown ether ligands [13].



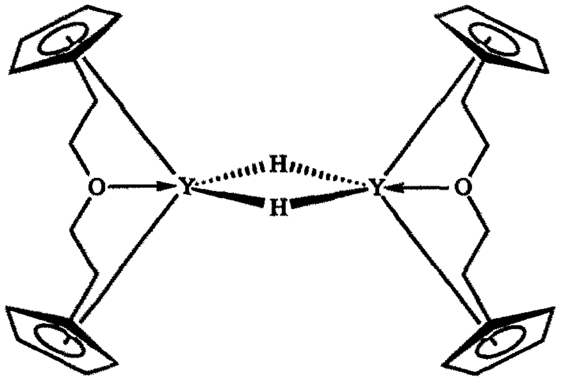
Y-OH_2 (prism) = 2.36 (1) Å

Y-Oether (prism) = 2.44 (1) Å

Y-Oether (cap) = 2.470 (3) Å

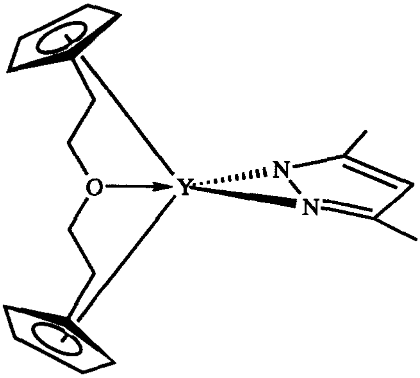
Y-Oalcohol (cap) = 2.43 (2) Å

(**6**)

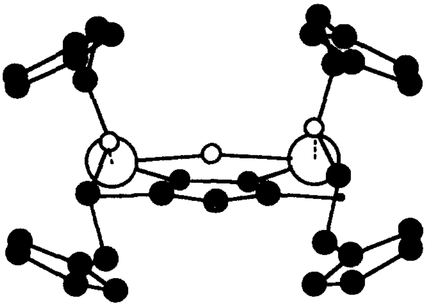


(7)

The reaction of $Y(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)Cl$ with NaH in thf at 45°C leads to the dimeric complex $[Y(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)(\mu\text{-}H)]_2$, (7). The method represents a convenient route to this type of yttrium hydride. The product has been characterised by elemental analysis, infrared and NMR spectroscopy. Analogous complexes with gadolinium, erbium, terbium and lutetium have also been prepared. The hydride complexes react with alkenes and alkynes [14]. When treated with $Na[N_2C_3HMe_2]$ in thf, $Y(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)Cl$ gives the mononuclear complex (**8**). Complex (**8**) hydrolyses to yield the hydroxy-bridged di-yttrium complex (**9**) which has been structurally characterised by X-ray diffraction. Important structural parameters in (**9**) are Y-$O_{\mu\text{-OH}}$ = 2.202 (2) Å, Y-O_{ether} = 2.662 (4) Å, Y-N = 2.445 (5) Å, N-N = 1.382 (9) Å and ∠Y-O-Y = 137 (2)°. Note the very long Y-O distance for the interaction between the ether-oxygen and the yttrium(III) atom; a shorter bond distance would have significantly influenced the positions of the other donor atoms in the coordination shell of each yttrium atom. At each yttrium centre, the two cyclopentadienyl rings are mutually staggered [15].



(8)

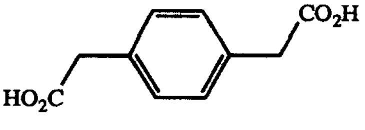


• = Me

Bridging O = OH

(9)

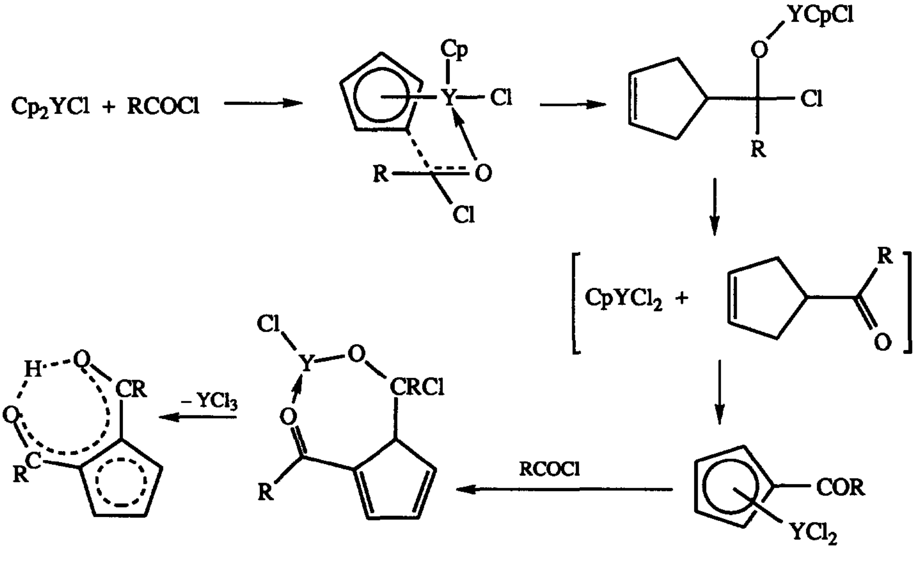
Large single crystals of $Y(HCO_2)_3.2H_2O$ have been grown from an aqueous solution containing an excess of methanoic acid at 70°C by controlled solvent evaporation. The electrooptic and electrostrictive properties of $Y(HCO_2)_3.2H_2O$ have been investigated [16]. The reaction of YOCl and HOAc yields $[Y(OAc)_2(H_2O)_3]Cl$. X-ray powder diffraction and thermal analytical data have been measured. The structure of the complex exhibits a cationic chain [17]. The crystal structure of $Y(O_2CMe)_3.4H_2O$ has been determined. The solid state structure of the complex is dimeric; each yttrium atom is 9-coordinate. The two yttrium atoms in the dimeric molecule are linked by acetate groups; each $MeCO_2^-$ ligand is bidentate with respect to one yttrium(III) atom and one of the oxygen atoms bridges between the two metal atoms. Infrared and ^{13}C MAS-NMR spectroscopic data have been reported for $Y(O_2CMe)_3.4H_2O$ [18].



(10)

The thermal decomposition in air of the complexes $Y_2L_3.nH_2O$ (n = 6-13) where H_2L = **(10)** has been studied. During thermolysis, the water of crystallisation is lost in a single stage. This is followed by complex decomposition to the oxide [19].

The reaction of Cp_2YCl with aromatic and aliphatic acid chlorides in thf solution at room temperature leads to the formation of 1,2-diacylcyclopentadienes (in a Zwitterionic form) and acylative ring-opening of a thf molecule. A mechanism for the reaction with the acid chloride, RCOCl, has been proposed and is shown in Scheme (i) [20].

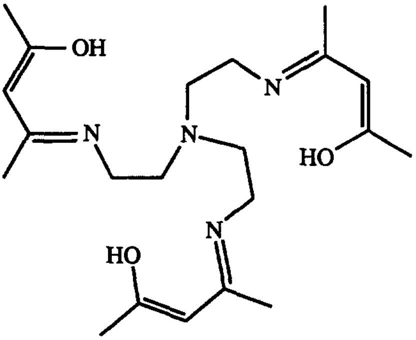


Scheme (i)

The complex $Y(acac)_2L$ where L = 1,10-phenanthroline-*N*-oxide has been prepared from $Y(acac)_3$ and L. A crystallographic study of $Y(acac)_2L$ shows that the yttrium(III) centre is 8-coordinate with a distorted square-antiprismatic geometry; see also Section 6.1.4 [21].

In Chapter 5 of this volume, the coordination of two phosphonato ligands to scandium(III) was described (see structures (6) and (7) in Section 5.1.2.5). The same ligands, the conjugate bases of ethylenediaminetetrakis(methylenephosphonic acid) and nitrilotris(methylenephosphonic acid), complex to yttrium(III) ions [22].

The preparation of $Y(H_3L)Cl_3$, where H_3L = **(11)**, has been reported along with related lanthanide complexes. The complex $Y(H_3L)Cl_3$ is synthesised from H_3L and hydrated YCl_3 in ethanol and is isolated as a diamagnetic, white solid (m.pt. = 212°C). ^1H NMR spectroscopic data have been recorded. No coordinated water molecules are present and this is in contrast to the results found for the lanthanide-containing species. It is proposed that **(11)** binds in a tridentate fashion to the yttrium(III) centre through the three *O*-donors [23]. The structure of the related ytterbium complex YbL illustrates the ability of L^{3-} to function as a hexadentate ligand.



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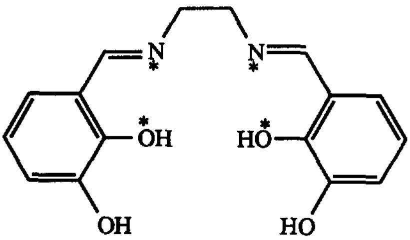


(12)

In the mixed copper(II)-yttrium(III) complexes CuLYX.*n*S (H_4L = **(12)**, X = NO_3 or Cl, and S = MeOH, dmso, or H_2O), the copper(II) is bonded within the N_2O_2-donor set, marked in structure **(12)**, and the yttrium centre is bound by the two remaining oxygen donor atoms. The complexes are discussed further in Section 6.4 [24].

6.1.3 Complexes with nitrogen donor ligands

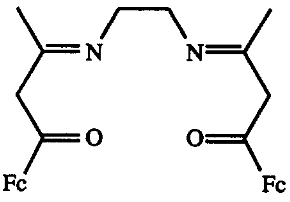
The reaction of hydrated yttrium(III) chloride with phenanthroline in MeOH yields the complex $[Y(OH)(H_2O)_2(phen)_2]Cl_2$. Infrared spectral data are presented as well as the results of a single crystal X-ray diffraction study. The compound is dimeric in the solid state and the tetracationic complex is centrosymmetric; uncoordinated chloride ions, two clathrated phen molecules and a methanol molecule are present in the lattice. Each yttrium(III) atom is 8-coordinate with a square-antiprismatic geometry, the donor atoms arising from two phen ligands, two water molecules and two bridging hydroxy-groups. The Y----Y separation is 3.651 (2) Å [25].

The incorporation of a pyrazole ligand in the complexes $Y(C_5H_4CH_2CH_2OCH_2CH_2C_5H_4)(N_2C_3HMe_2)$, **(8)**, and the hydroxy-bridged di-yttrium complex **(9)** was described in Section 6.1.2. The Y-N distance in **(9)** is 2.445 (5) Å [15].

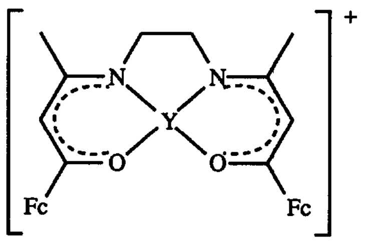
The porphyrinato-complex $Y(OEP)(OC_6H_3{}^tBu_2)$ reacts with methyl lithium in diethyl ether to yield a bright red product which is insoluble in ether. The complex has been characterised as $Y(OEP)(\mu\text{-}Me)_2Li(OEt_2)$. The latter reacts with $AlMe_3$ to give the deep red, hexane soluble complex $(OEP)Y(\mu\text{-}Me)_2AlMe_2$. ^1H NMR spectroscopic data are consistent with a rapid intramolecular exchange process in solution. The complex $(OEP)Y(\mu\text{-}Me)_2AlMe_2$ is oxidised by dioxygen to $(OEP)Y(\mu\text{-}OMe)_2AlMe_2$ [26]. The preparation from $Y(OAc)_3(H_2O)_x$, structure and magnetic properties of the phthalocyanine complex $YPc_2.CH_2Cl_2$ have been reported. The neutral yttrium(III) diphthalocyanine has a one-electron ligand oxidised sandwich structure. The N_4-macrocyclic ligands are stacked above one another in one direction in the solid state and are mutually staggered by 45°. The shortest distance between two adjacent Pc^{2-} ligands in a stack is 3.27 Å and between the ligands in adjacent stacks is 3.59 Å. The compound $YPc_2.CH_2Cl_2$ is a one-dimensional organic ferromagnet. The authors emphasise that this complex marks only the first step towards organic bulk ferromagnets [27]. Related work by the same authors has been reported separately [28].

6.1.4 Complexes with mixed oxygen and nitrogen donor ligands

In the complex $Y(acac)_3L$, in which L = 1,10-phenanthroline-*N*-oxide, the *N,O*-donor set of L forms part of the square-antiprismatic coordination sphere of the yttrium(III) centre [21].

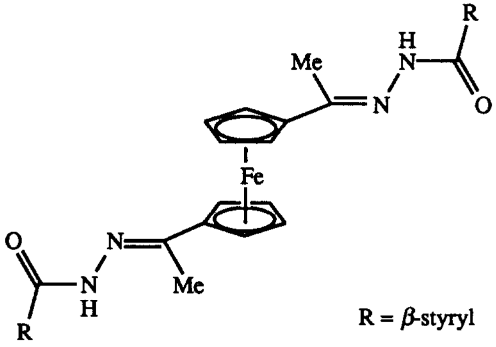


(12)



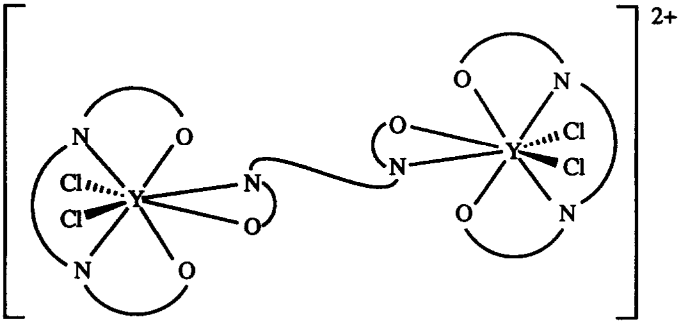
(13)

The *N,O*-donor ligand H_2L, **(12)**, and a series of lanthanide complexes have been prepared. Included in the series is [YL]Cl ($[YL]^+$ = **(13)**) which has been prepared by adding H_2L in ethanol to a hot ethanolic solution of YCl_3. The complex [YL]Cl is characterised in the IR spectrum by absorptions at 1595 cm^{-1} (ν_{CO}) and 1349 cm^{-1} (ν_{CN}). UV and ^1H NMR spectroscopic data are also recorded [29]. A related study reports the preparation of the ferrocene-derived ligand, L, **(14)** which was isolated as orange crystals. Yttrium(III) chloride reacts with ligand L to give the dinuclear complex $[Y_2L_2(\mu\text{-}L)Cl_4]Cl_2$ which has been characterised spectroscopically. Each yttrium(III) centre is 8-coordinate and the proposed structure of the dicationic complex is shown schematically in structure **(15)**. Infrared spectral absorptions for the new complex are 1645 cm^{-1} (ν_{CO}), 1581 cm^{-1} (ν_{CO}), 984 cm^{-1} (ν_{NN}), 555 cm^{-1} (ν_{YN}); these data support the coordination of the neutral ligand **(14)** in a keto-form via the carbonyl *O*-donor and the azomethine *N* donor atoms [30].



R = *β*-styryl

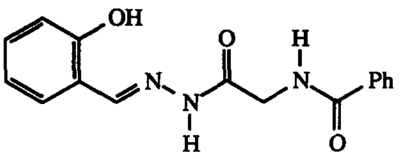
(14)



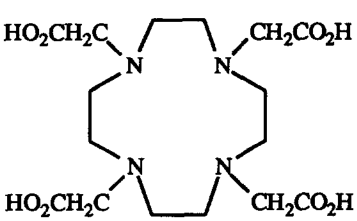
(15)

The synthesis, characterisation and complexation with lanthanide(III) ions of the ligand H_2L, **(16)**, have been reported. Infrared, and ^1H and ^{13}C NMR spectroscopic data are consistent with a dynamic equilibrium between two isomers of **(16)** over the temperature range 298-368K.

Complexation stabilises one ligand isomer. Amongst the complexes produced is $YL(OH)(H_2O)_2$; L^{2-} coordinates via the imidolic-*O*, azomethine-*N*, and phenolate-*O* atoms [31].



(16)



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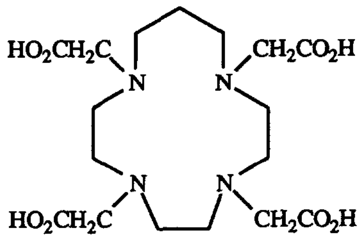

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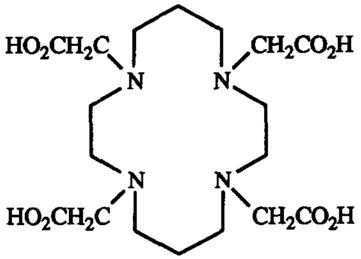

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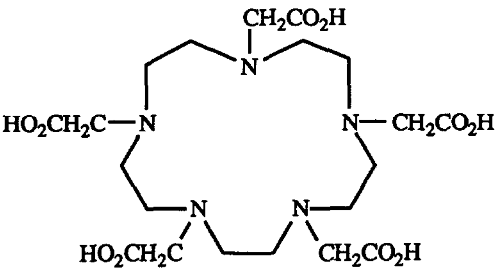
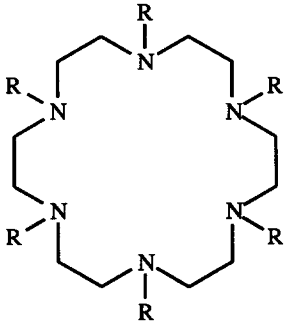


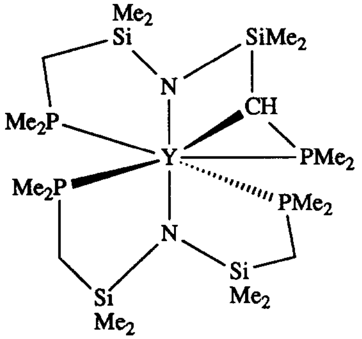
(20)

Two papers discuss complex formation between yttrium(III) ions and a series of derivatised-azacycloalkane ligands. Compounds (**17**)-(**19**) are potentially octadentate N_4O_4-ligands. An aqueous solution of yttrium(III) nitrate (at pH 4.0) was added to aqueous H_4L, (**17**). Crystals of YL were obtained; for YL, $\lg K = 24.9$ at 298 K. Related complexes with H_4L', (**18**), and H_4L'', (**19**), were also reported. The study also includes indium and gallium complexes of 1,4,7-triazacyclononanetriacetate; the interest is in pursuing kinetically stable complexes for application in imaging and radioimmunotherapy [32]. An independent piece of work investigates thermodynamic and kinetic aspects of a series of complexes between lanthanide(III) ions, including yttrium(III), and the ligands H_4L^4, **(19)**, H_5L^5, **(20)**, and H_6L^6, **(21)**, and L, **(22)**. The syntheses of **(20)** and **(21)** are reported. For yttrium(III), stability constant data at 298 K are $\lg K(ML^4) = 14.77$, $\lg K(ML^5) = 16.07$, $\lg K(ML^6) = 24.04$, $\lg K\{M(H_2L^6)\} = 15.93$, $\lg K(ML) = 8.52$. In some cases, complex formation (e.g. with **(17)** and yttrium(III) ions) is complicated by the precipitation of hydroxide-containing species and hence kinetic data were obtained via ligand displacement reactions rather than by direct reaction between ligand and Y^{3+} ions [33].



(21) R = CH_2CO_2H

(22) R = H



(23)

6.1.5 *Complexes with mixed phosphorus and nitrogen donor ligands*

The reaction of yttrium(III) chloride with $LiN(SiMe_2CH_2PR_2)_2$ in thf yields the complex $YCl\{N(SiMe_2CH_2PR_2)_2\}_2$ (R = Me, Ph, ^iPr). The N,P_2-ligand provides a hard NR_2^--donor which functions as an anchor point from which the two pendant phosphine groups are encouraged to coordinate to the metal centre; the syntheses of the ligands are reported. The new compounds have been spectroscopically characterised and ^1H, ^{13}C, ^{31}P and ^{89}Y NMR results are presented. Data indicate that, for example, in the complex $YCl\{N(SiMe_2CH_2PR_2)_2\}_2$ the yttrium(III) centre is

7-coordinate and the molecule is fluxional in solution. The complexes $PhY\{N(SiMe_2CH_2PR_2)_2\}_2$ and $PhCH_2Y\{N(SiMe_2CH_2PR_2)_2\}_2$ have also been prepared. These compounds are thermally unstable and thermolysis leads to cyclometallation. The kinetics of the cyclometallation process have been studied, and the cyclometallated product **(23)** has been structurally characterised by X-ray diffraction [34].

6.2 YTTRIUM(I)

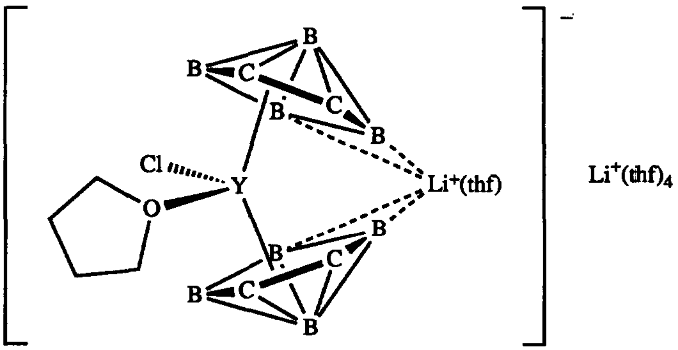
A high resolution spectroscopic study of YCl has been carried out. A band system in the near infrared corresponding to the theoretically predicted $B^1\Pi$-$X^1\Sigma$ transition has been observed. A detailed analysis of the band system is presented [35].

6.3 ORGANOMETALLIC COMPLEXES

Several complexes with organometallic features have been discussed in Section 6.1. Of particular note are the complexes $Cp^*YL(CH(SiMe_3)_2)$ and $[Cp^*YL(\mu\text{-}H)]_2$ (HL = 2,6-${}^tBu_2C_6H_3OH$) [10] and a series of complexes **(7)**-**(9)** involving the $\{(\eta^5\text{-}C_5H_4)CH_2CH_2\}_2O$ ligand [15]. These were discussed in detail in Section 6.1.2.

The organometallic complex $Cp^*{}_2Y(CH(SiMe_3)_2)$ is an active catalyst precursor for the oligomerisation of terminal alkynes. Corresponding lanthanum and cerium complexes have also been studied and it has been observed that the regioselectivity and extent of oligomerisation depends upon the metal present [36].

The first example of an yttracarbaborane cluster has been prepared and structurally characterised. $Li_2[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]$ reacts with YCl_3 in benzene at 0°C. After work-up with hexane and thf, the *commo*-complex **(24)** is isolated. The yttrium atom is bound within a bent-sandwich structure ($\angle C_2B_3$(centroid)-Y-C_2B_3(centroid) = 129.7°, Y-centroid = 2.36 and 2.39 Å), and is pseudo-tetrahedrally coordinated with the four sites being occupied by the two carbaborane cages, a chloride ligand and a thf molecule. ^1H, ^{11}B, ^{13}C NMR and IR spectroscopic data for **(24)** have been reported [37].

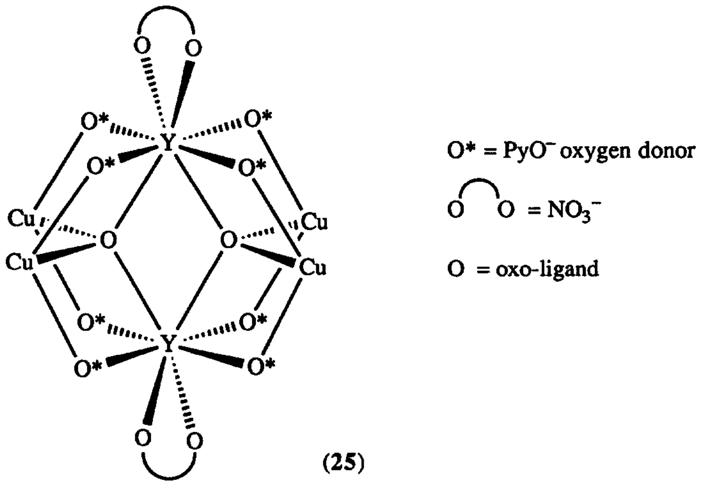


B = BH   C = C(SiMe$_3$)

(24)

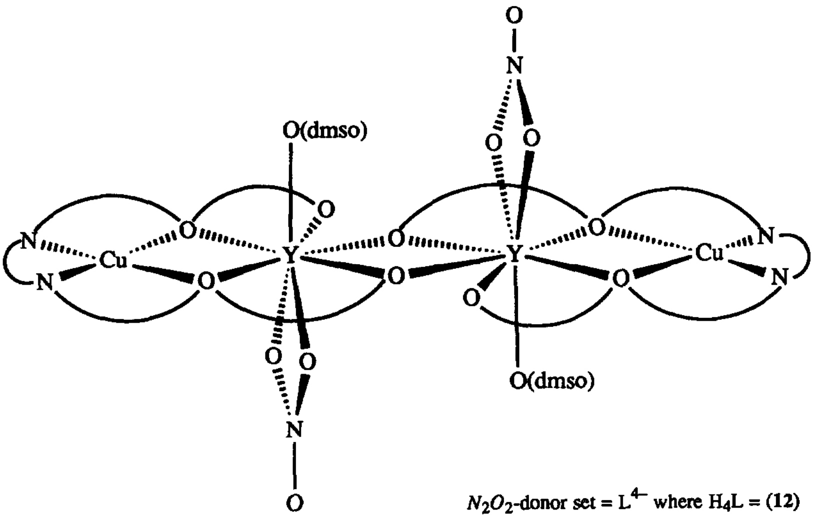
6.4 SUPERCONDUCTIVITY

The synthesis and properties of Y-Ba-Cu-O superconductors have been discussed [38]. Two complexes of importance with respect to modelling Y-Ba-Cu-O superconducting materials have been prepared and characterised. The first is $Y_2Cu_8(\mu\text{-pyO})_{12}(\mu\text{-Cl})_2(\mu_4\text{-O})_2(NO_3)_4(H_2O)_2.2H_2O$ in which pyO^- = deprotonated 2-hydroxypyridine. This complex has been synthesised by reacting $Y(NO_3)_3.4H_2O$ with $Cu(OMe)_2$ and 2-hydroxypyridine (1 : 4 : 6 molar equivalents) in thf. Green microcrystals constitute the major product but a second product (30% yield) crystallises as a dark green material. $Y_2Cu_8(\mu\text{-pyO})_{12}(\mu\text{-Cl})_2(\mu_4\text{-O})_2(NO_3)_4(H_2O)_2.2H_2O$ has been characterised by X-ray crystallography and the core structure is shown in (25); the Y----Y separation is 3.785 (8) Å. If a nitrate ligand were to be replaced by another Cu_4O_2-unit, the yttrium and copper environments would be similar to that in the oxygen-deficient perovskite structure of the $YBa_2Cu_3O_{7-x}$ superconductor [39].



(25)

The mixed copper(II)-yttrium(III) complexes CuLYX.*n*S (H_4L = (12), X = NO_3 or Cl, and S = MeOH, dmso, or H_2O), were mentioned briefly in Section 6.1.2 [24]. The complex CuLYX.*n*S is formed in the reaction of $Cu(H_2L)$ with YX_3 and lithium hydroxide. An X-ray diffraction study of $CuLY(NO_3)$.dmso shows that the complex is dimeric in the solid state. Each yttrium(III) centre is 8-coordinate and the authors state that it is almost impossible to approach a description of the coordination polyhedron in a classical way. The core of the dimeric complex centres upon an oxygen-bridged di-yttrium unit, **(26)**. The ligand L^{4-} (H_4L = **(12)**) contains an N_2O_2-donor set which surrounds the copper(II) ion and an O_4-donor set which forms part of the coordination sphere of the yttrium(III) ion. Note that one *O*-donor of L^{4-} (O* in **(12)**) bridges between the copper and yttrium atoms whilst the second *O*-donor bridges between the two yttrium atoms. The Y---Y separation is 3.781 (2) Å and the Y---Cu separation is 3.397 (3) Å. Thermogravimetric measurements have been carried out on $CuLY(NO_3)$.meOH and $CuLY(NO_3).H_2O$ [24].



N_2O_2-donor set = L^{4-} where H_4L = (12)

(26)

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