2.   Yttrium   1992

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CONTENTS

INTRODUCTION

This article surveys the coordination chemistry of yttrium for the year 1992 and is similar in format to the corresponding 1991 review [1], although organometallic complexes are no longer included in these articles. The literature has been searched, in the main, by use of *Current Contents*. Structural figures have been redrawn for this review by using crystallographic coordinates; hydrogen atoms have been omitted for clarity.


2.1   YTTRIUM(III)

2.1.1   Extraction

Several papers deal with various aspects of the extraction of yttrium(III). The extraction of yttrium(III) (and lanthanoid) ions from aqueous perchlorate solutions has been investigated by using a mixture of 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-thione (HBMPPT) and trioctylphosphine oxide (TOPO). The system provides a good means of separating trivalent actinoids from trivalent lanthanoids [2]. A new method for separating yttrium(III) ions from other rare earth metal ions has been developed. It relies on a non-equilibrium extraction procedure which uses diethylenetriaminepentaacetic acid and bis(2-ethylhexyl)phosphoric acid / kerosine. The isolation of yttrium(III) oxide (99.9% purity) from a state where it is only 60% pure can be achieved in fifteen steps — this is a relatively low number [3]. The separation of yttrium(III) from

terbium(III) ions can be achieved by using ion exchangers which are strongly basic. Of the exchangers tried (namely Dowex 1x4, Dowex 2x8 and Permutit SK in the acetate or NTA forms), the most efficient was found to be Dowex 1x4 in the NTA form [4].

2.1.2   Complexes with chloride and pseudo-halide donors

Crystallization of rac-[(thf)$_2$Li{LYCl$_2$}] (1) (where L^{2-} = bis(2-trimethylsilyl-4-$tert$-butylcyclopentadienyl)dimethylsilane) has yielded X-ray quality crystals and the results of a structure determination have been reported. The yttrium(III) environment is tetrahedral; each Cp moeity is regarded as occupying one site. The lithium ion is 2.35Å away from each of the chloride ligands; the Li$^+$ ion is also tetrahedrally sited with two thf molecules completing the coordination sphere [5]. A similar bonding situation is observed in [Cp*$_2$Y(μ-Cl)$_2$Li(thf)$_2$]. This bridged species is formed when [Cp*$_2$YCl(thf)] reacts with three equivalents of LiO^{t}Bu in toluene under reflux. A second product is [Cp*$_2$(Cl)Y(μ-Cl)Li(thf)$_3$]. The complexes [Cp*$_2$(Cl)Y(μ-Cl)Li(thf)$_3$] and [Cp*$_2$Y(μ-Cl)$_2$Li(thf)$_2$] co-crystallize and their structures have been determined by X-ray diffraction. In the dibridged species, the angle Cl$_{bridge}$-Y-Cl$_{bridge}$ is 84.8(1)° and is constrained by the bridging environment. On the other hand, in the monobridged complex, the corresponding angle (now defined as Cl$_{term}$-Y-Cl$_{bridge}$) is 95.4(1)°. The Cp* rings in [Cp*$_2$(Cl)Y(μ-Cl)Li(thf)$_3$] are almost fully staggered with a twist angle of 35.6°; exact staggering would be defined by an angle of 36°. In both complexes, the coordination environments about the yttrium and lithium centres are tetrahedral [6].


(1)
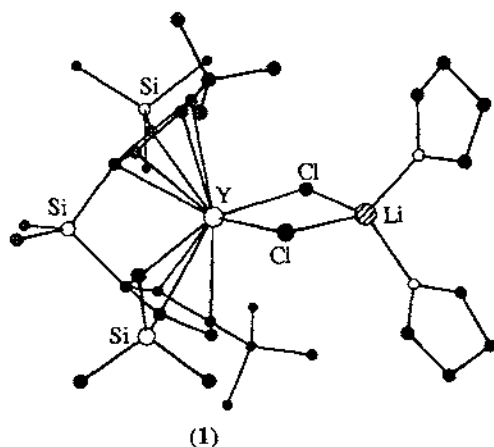
The formation of thiocyanate complexes of the type [Y(NCS)$_n$]$^{(3-n)+}$ (n = 1, 2, 3) has been studied by calorimetric methods in dmf solution (0.2M Et$_4$NClO$_4$ at 25°C). The systems have been studied by Raman and ^{89}Y NMR spectroscopies and results indicate that inner sphere complexes are present in dmf [7].

2.1.3   Complexes with oxygen donor ligands

The crystal structure of the aqua-complex [Y(H$_2$O)$_6$(TsO)]TsO.3H$_2$O (TsOH = toluene-4-sulfonic acid) has been determined. In the anion (2), the yttrium(III) ion is at the centre of a square prism of oxygen donors, six being water molecules and two being toluene-4-sulfonate ions. Dehydration in the solid state has been investigated. A group of related lanthanoid complexes has also been studied [8].

It has been found that concentrated aqueous solutions of yttrium(III) bromide and chloride appear to contain yttrium(III) hydrates as major solution species. Coordination to one metal centre by eight water molecules is evidenced. For aqueous solutions of between 0.6 to 2.1 M in yttrium(III) ions, EXAFS data give values of Y–O = 2.33 ± 0.02Å for the bromide species and 2.34 ± 0.02Å for the chloride species. Raman spectroscopic studies for the systems in which D$_2$O replaces H$_2$O have been carried out; the results support the presence of a relatively stable hydrate of yttrium(III) [9].


(2)
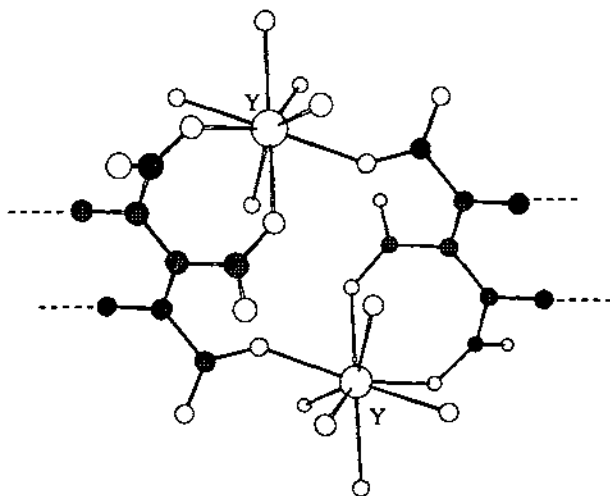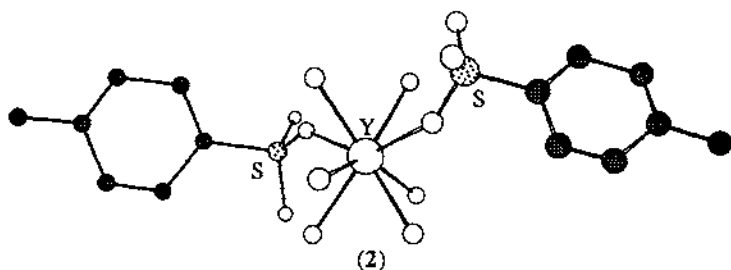
Structure shows part of each C$_6$-ring and indicates direction of infinte chain.

(3)

Colourless, monoclinic crystals of $[Y_2\{C_6(CO_2)_6\}].14H_2O$ have been grown from aqueous silica gel. An X-ray crystallographic investigation of the system reveals that the yttrium(III) centres are coordinated by five water molecules and three carboxylate ions to give a dodecahedral arrangement. The units are linked via the $C_6(CO_2)_6{}^{6-}$ ions to generate infinite chains. The compound formula is more usefully written as $[Y_2(H_2O)_{10}\{C_6(CO_2)_6\}]$ (3) plus lattice water molecules. Adjacent chains are connected together in the solid state by hydrogen bonding interactions [10].

Some chemistry of yttrium complexes of the ligand (4), L^{2-}, was described in last year's review [1]; the ligand coordinates to the yttrium(III) centre via the two η^5-cyclopentadienyl groups and in addition has the option of utilizing the oxygen atom as a donor. This area of work has been further developed and the partial hydrolysis of $[(\eta^5-C_5H_4Me)YL]$ and $[CpYL]$ has been investigated. The products are $[LY(\mu-OH)_2YL]$ and $[Cp_3Y(OH_2)]$ respectively and these complexes have been characterized by elemental analysis, and IR and NMR spectroscopies. The crystal structure of $[LY(\mu-OH)_2YL]$ confirms the dimeric nature of the complex. The $Y-O_{OH}$ distances are 2.238(3)Å whilst the oxygen donor atom of each ligand L^{2-} is 2.500(3)Å away from an yttrium centre; this renders the metal coordination geometry in between being tetrahedral and trigonal bipyramidal. Preliminary crystallographic data for $[Cp_3Y(OH_2)]$ indicate that it is similar in structure to $[Cp_3Ho(OH_2)]$, the full crystal structure of which is reported [11].
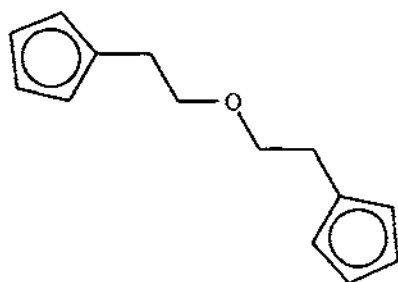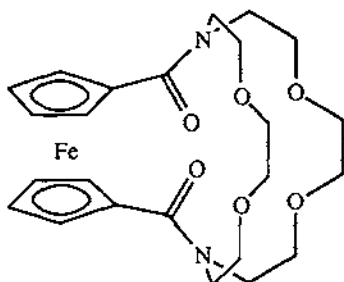

(4)   (5)

Complex formation between yttrium(III) ions and the macrocyclic ligand (5), L, has been studied by multinuclear NMR spectroscopy and single crystal X-ray diffraction. The reaction of yttrium(III) perchlorate, L and water gives rise to the complex cation $[YL_2(H_2O)]^{3+}$. The yttrium centre is within a face-capped trigonal prismatic array of oxygen donor atoms. This coordination shell is made up of the four amide carbonyl oxygen donor atoms of the two ligands L, two ether oxygen donor atoms from *one* of the ligands L, and the water ligand which occupies the capping site. The Y-O distances lie in the range 2.207(4) to 2.470(6)Å. The ^{89}Y NMR spectral studies illustrate the influence that coordination has on the chemical shift values [12].

The crystal structure of $[YL_3(H_2O)_3].3H_2O$ (where HL = 3-aminobenzoic acid) has been established. Within the complex $[YL_3(H_2O)_3]$ (6), the yttrium(III) centre is 9-coordinate and lies on a crystallographically imposed 3-fold axis. Each 3-aminobenzoate ligand acts in a didentate mode with the amino-group not being involved in coordination to the metal ion [13]. The reaction of YCl_3,

NaCp (2 equivalents) and $Li(CH_2)_3NMe_2$ in the presence of CO_2 leads to the formation of the complex $[Cp_2Y\{O_2C(CH_2)_3NMe_2\}]$ in which the carboxylate ligand acts as an O,O'-donor. The aminoalkyl chain is pendant. This has been confirmed by the results of an X-ray structure analysis; important bond parameters are Y-O = 2.42(2) and 2.40(2)Å and $\angle$O-Y-O = 54.4(7)° [14].


open circle = O

(6)
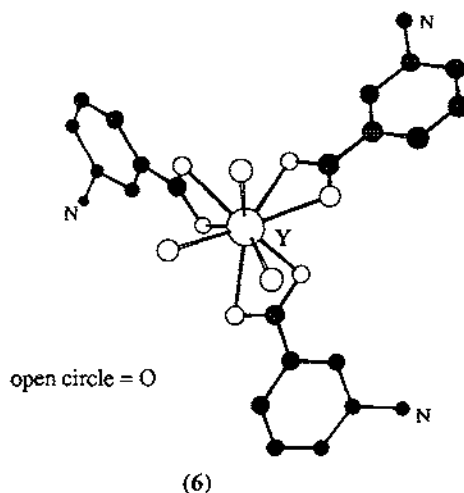
Reports of acetylacetonate (acac) complexes of yttrium(III) include a discussion of the kinetics of the thermolysis of yttrium, barium and copper acetylacetonates [15]. Copper(II) and yttrium(III) nitrates react with acacH in methanol in the presence of piperidine to yield the compounds $[Cu_3Y(acac)_5(OMe)_4].nMeOH$ and $[CuY(acac)_3(OMe)_2].nMeOH$. These species possess cubane-type structures with the methoxy groups in four of the eight corners of a cube and defining a tetrahedral arrangement. Two acac$^-$ ligands are coordinated to each yttrium(III) centre and one is attached to each copper atom. The complexes have been characterized by IR spectroscopy, crystallography, and magnetic measurements. The product of the thermal decomposition is $Y_2Cu_2O_5$ [16].

Alkoxide chemistry is a relatively well represented area of the yttrium(III) coordination studies reported in 1992. Two new methoxy complexes were mentioned above [16]. Caulton and coworkers have provided detailed results of NMR spectroscopic studies involving alkoxide, siloxide and acac complexes including aggregates. Of particular note are observations concerning the solution *vs* solid state structures and fluxional properties in solution. Amongst the compounds studied are $[Y(OSiPh_3)_3(thf)_3]$, $[Y_2(OSiPh_3)_6]$, *cis*-$[Y(OSiPh_3)_4(MeOCH_2CH_2OMe)]^-$, $[Y_3(acac)_4(OCH_2CH_2OMe)_5]$, $[Y_5(O)(O^iPr)_{13}]$ and $[Y_{10}(OCH_2CH_2OMe)_{30}]$. The ^{29}Si NMR spectrum of $[Y(OSiPh_3)_3(thf)_3]$ exhibits coupling between the ^{89}Y and ^{29}Si nuclei (J = 8.1 Hz) but this is only observed when exchange between the Ph_3SiO^- ligands and free Ph_3SiOH is not operating. The dimer $[Y_2(OSiPh_3)_6]$ is characterized by two ^{29}Si NMR spectral resonances in line with the discrete terminal and bridging sites of the Ph_3SiO^- ligands; ^{89}Y-^{29}Si spin-spin coupling is observed (J = 7.7 Hz) for the terminal environment only. For the complex anion *cis*-$[Y(OSiPh_3)_4(MeOCH_2CH_2OMe)]^-$, intramolecular fluxionality involving the inequivalent Ph_3SiO^-

ligands is observed in solution. For the decamer $[Y_{10}(OCH_2CH_2OMe)_{30}]$, a single signal is observed in the ^{89}Y NMR spectrum [17].


(7)
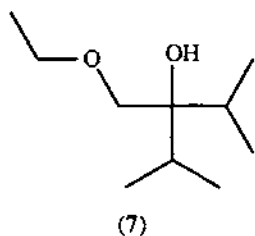
An interesting alkoxide complex of yttrium(III) has been prepared by reacting three equivalents of the bulky ligand (7) (HL) with $[Y\{N(SiMe_3)_2\}_3]$. The product is $[YL_3]$; this complex is volatile and is soluble in a range of aliphatic hydrocarbons. YL_3 has been characterized by elemental analysis and multinuclear NMR spectroscopy. In the ^{89}Y NMR spectrum, a signal at δ +277.1 (with respect to δ 0 for YCl_3 in D_2O) is observed. Related neodymium chemistry has also been investigated [18]. Volatile complexes of the type $[Y(OR)_3(thf)_3]$, $[Y(OR)_3(NH_3)_x]$ $(x = 0$–$3)$ and $[Y(OR)_3(Et_2O)_x]$ $(x = 0.33$ or $0.5)$ have been prepared starting from $[Y\{N(SiMe_3)_2\}_3]$ and the alcohols $(CF_3)_2CHOH$, $(CF_3)CMe_2OH$ and $(CF_3)_2CMeOH$ (ROH). The crystal structure of $[Y\{OCMe(CF_3)_2\}_3(thf)_3]$ has been determined. Related complexes of scandium and lanthanoids have also been prepared [19].


(8)
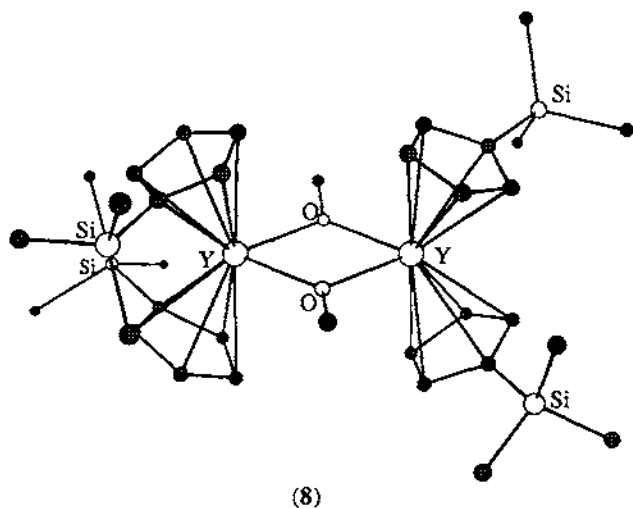
The reaction of NaOMe with $[Cp_2YCl(thf)]$ gives $[Cp_2Y(\mu\text{-}OMe)_2YCp_2]$ in high yield depending upon the method of work-up. Potassium methoxide can be used in place of the sodium salt. In this case, a second product is the anion $[\{Cp_2Y(\mu\text{-}OMe)_2\}_2\{Cp_2Y\}(\mu_3\text{-}O)]^-$ and the reaction can be turned in favour of this complex by altering the reaction conditions. Another product from this system is $[Cp_5Y_5(\mu\text{-}OMe)_4(\mu_3\text{-}OMe)_4(\mu_5\text{-}O)]$. The whole system is complicated and the pathway is critically dependent upon the conditions and choice of alkali metal methoxide. Related

chemistry using trimethylsilyl-substituted cyclopentadienyl ligands has been investigated. The crystal structures of [Cp$_2$Y(μ-OMe)$_2$YCp$_2$], [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Y(μ-OMe)$_2$Y(η^5-C$_5$H$_4$SiMe$_3$)$_2$] (8), [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Y(μ-Cl)$_2$Y(η^5-C$_5$H$_4$SiMe$_3$)$_2$], [Cp$_5$Y$_5$(μ-OMe)$_4$(μ_3-OMe)$_4$(μ_5-O)] and [{Cp$_2$Y(μ-OMe)$_2$}$_2${Cp$_2$Y}(μ_3-O)]$^-$ (as the [(thf)$_6$Na$_2$(μ-Cp)]$^+$ salt) have been elucidated. In each of the first three complexes, bent metallocene units are apparent. The Y$_5$O$_9$-core of [Cp$_5$Y$_5$(μ-OMe)$_4$(μ_3-OMe)$_4$(μ_5-O)] consists of a square-pyramidal arrangement of yttrium(III) centres (at nonbonded separations) with four oxygen atoms capping the triangular faces of the Y$_5$-unit and four oxygen atoms bridging the four edges of the square face. The final oxygen atom lies within the cavity defined by the yttrium atoms [20].


● = phenyl

(9)
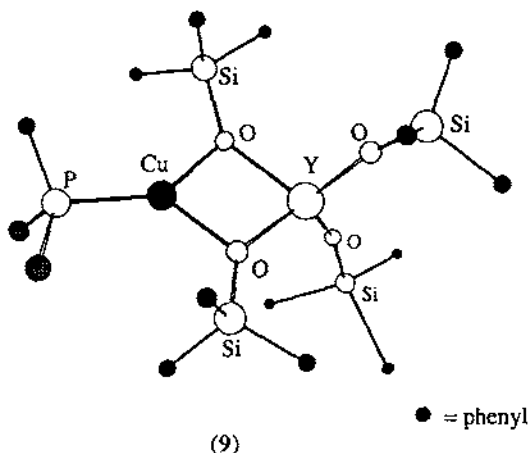
The reaction between [Y$_2$(OSiPh$_3$)$_6$] and [Cu$_2$(OSiPh$_3$)$_2$(PMe$_2$Ph)$_2$] (Y:Cu = 1:1) gives rise to the heterometallic complex (9). Spectroscopic and crystallographic data for (9) have been detailed. The yttrium(III) centre is in a distorted tetrahedral environment (Y-O = 2.170(3), 2.154(3), 2.071(3) and 2.080(3)Å) whilst the coordination sphere about the copper(II) centre is trigonal planar. The Y---Cu separation is 3.127Å and the authors indicate that this distance does not suggest any degree of Cu→Y interaction. In solution, ^{29}Si, ^{89}Y and ^{31}P NMR spectra have been recorded. The ^{89}Y NMR chemical shift (with respect to 3M YCl$_3$) in δ 300.7. The spectroscopic data indicate that the solid state and solution structures are consistent with one another [21].

By treating anhydrous yttrium(III) chloride with two equivalents of NaL (HL = (10)) in thf and under aerobic conditions, it has been possible to isolate, in high yield, the novel compound [LY{CpCo{P(=O)(OEt)$_2$}$_2${P(=O)(OEt)(O)}}$_2$YL] (11). Complex (11) has been studied by NMR spectroscopy and the structure has been determined by X-ray diffraction methods. This provides proof of the unusual nature of the complex and the fact that the reaction has involved the cleavage of one O–C$_{Et}$ bond. Additional evidence for this comes from the observation of chloroethane as one of the products. In the solid state structure of (11), selected non-bonded distances are Y---Y = 5.645(2)Å and Y---Co = 4.339(2) and 4.243(2)Å; the Y-O distances are in the range 2.242(5) to 2.445(7)Å [22].

(10)

⊕ = P
○ = O

(11)
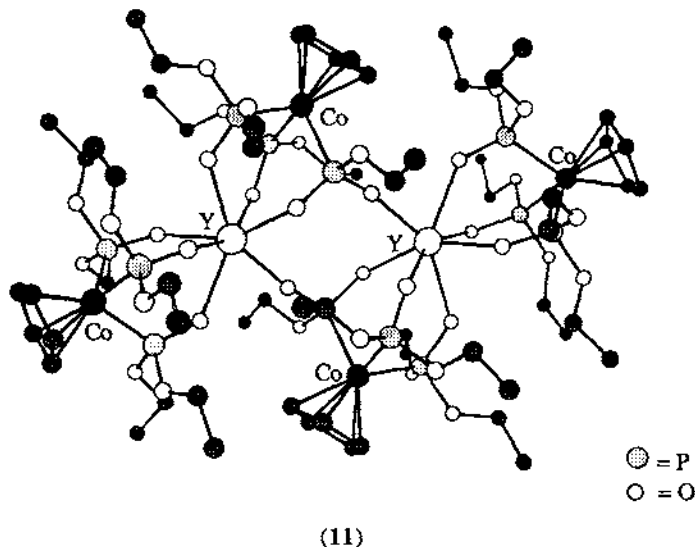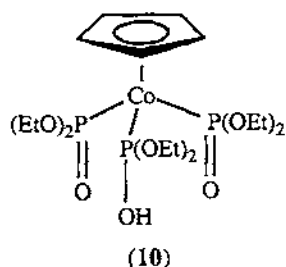
2.1.4   Complexes with nitrogen donor ligands

The use 2,2':6',2":6",2"'-quaterpyridine (qtpy) as a ligand in yttrium(III) chemistry is represented by the formation of the complex [Y(qtpy)(NO$_3$)$_2$(H$_2$O)](NO$_3$).H$_2$O. This compound is produced in the reaction of qtpy with yttrium(III) nitrate in methanol under reflux. An analogous reaction starting from YCl$_3$ has also been carried out and yields a complex formulated as [Y(qtpy)Cl$_3$(H$_2$O)$_6$]. The details of the organization of the chloride and water entities are not known, but in the FAB mass spectrum, an envelope assigned to the ion {Y(qtpy)Cl$_2$}$^+$ is observed. The crystal structure of the nitrate salt has been determined; NMR and IR spectroscopic data have been reported. In the cation [Y(qtpy)(NO$_3$)$_2$(H$_2$O)]$^+$ (12), the yttrium(III) centre is 9-coordinate with all four of the nitrogen donor atoms of the qtpy ligand bonded to the metal ion; Y-N bond distances are 2.464(8), 2.466(9), 2.469(9) and 2.465(10)Å. Two nitrate ions are O,O'-bonded and the ninth coordination site is occupied by a water molecule.
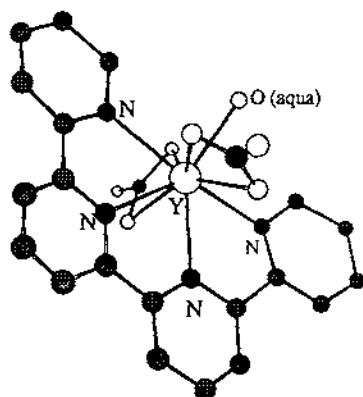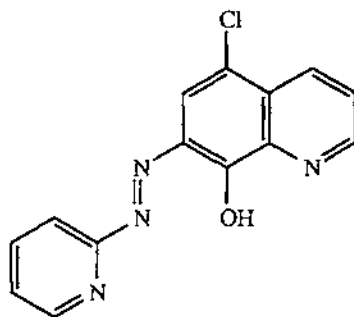
(12)   (13)

The results of a spectrophotometric study of complexes formed between the ligand (13) and several metal ions including yttrium(III) have been reported. Yttrium(III) ions form a red complex (M:L) with this quinoline-based ligand under conditions of pH = 6.5 [24].

Porphyrin chemistry is represented by the reaction of YL_3 (HL = $CH_2(SiMe_3)_2$ or 2,6-$^tBu_2C_6H_3OH$) with $OEPH_2$ to give [YL(OEP)]; the corresponding lutetium complex for L = $CH_2(SiMe_3)_2$ has been crystallographically analysed. Protonolysis studies of the complexes [YL(OEP)] have been carried out using 2,6-$^tBu_2C_6H_3OH$, H_2O and $HC\equiv C^tBu$ (HX) as reagents. The products are of the type $[(OEP)YX]_n$ (n = 1 or 2). Amongst other reactions that have been reported is that of $[(OEP)Y(OC_6H_3^tBu_2-2,6)]$ with methyl lithium in ether to give the bridged species $[(OEP)Y(\mu-Me)_2Li(OEt_2)]$. A related complex $[(OEP)Y(\mu-Me)_2AlMe_2]$ has also been synthesized and characterized and has been found to activate O_2 yielding the methoxy-bridged compound $[(OEP)Y(\mu-OMe)_2AlMe_2]$ [25].

2.1.5   Complexes with mixed donor atom ligands

Complex formation between yttrium(III) ions and violuric acid (HL = (14)) has been investigated. Products with $Y:L^-$ stoichiometries of 1:2, 1:3 and 2:3 are evidenced. They are soluble in a range of common solvents including MeOH, dmf and dms, but are insoluble in EtOH, $CHCl_3$ and CCl_4. Complex characterization has been by elemental analysis, IR spectroscopy and molar electrical conductance measurements. It is proposed that the donor atoms involved vary with the $Y:L^-$ ratio but both O- and N-donors are involved [26].

Allyl magnesium chloride reacts with $[YL_2Cl]$ (HL = (15)) to generate the new dimer $[(\eta^3-C_3H_5)LY(\mu-Cl)_2YL(\eta^3-C_3H_5)]$, the structure of which has been elucidated. Each anion L^- acts as a tridentate ligand using the P,N,P'-donor set. The Y-P bond distances are 2.931(1) and 2.892(1)Å, and the Y-N distances are 2.292(4)Å . Of interest is the fate of the magnesium — the complex MgL_2 is formed [27].

(14)

(15)
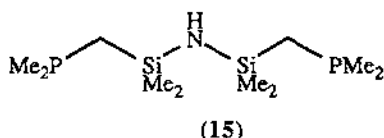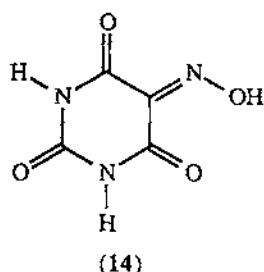
2.2 YTTRIUM(I)

This section is not well represented in the 1992 coordination chemistry literature and this one entry is perhaps misleadingly placed. Compounds which have previously been reported as 'YCl' and 'YBr' have now been found to be hydride halides of type $YClH_n$ and $YBrH_n$ with $0.7 \leq n \leq 1.0$. Significantly, dehydrogenation of these species did not yield the monohalides. Crystal structure data are reported. The bromide $YBrH_n$ crystallizes in a ZrBr-type lattice. The structure-type of the chloride however depends on n; for $0.7 \leq n \leq 0.8$, a ZrBr-type structure is observed but within the limits $0.8 \leq n \leq 1.0$, a ZrCl-type structure is favoured. The species $YClH_n$ and $YBrH_n$ are graphite-coloured. Hydrogenation leads to the formation of the colourless hydrides YXH_2 for both X = Cl and Br [28].

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