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1. Cobalt 1992-1993

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CONTENTS

INTRODUCTION

This Cobalt Review for the years 1992-93 is rather different from those in the past because it covers two years. A consequence of this is that there are quite severe constraints on the number of references which it is possible to cite and consider within the space available. This results in an even more difficult choice among a much larger number of potential references. I have made the choice and for those that are left out I must apologize. As usual in this series, the review does not include either cluster or organometallic compounds.

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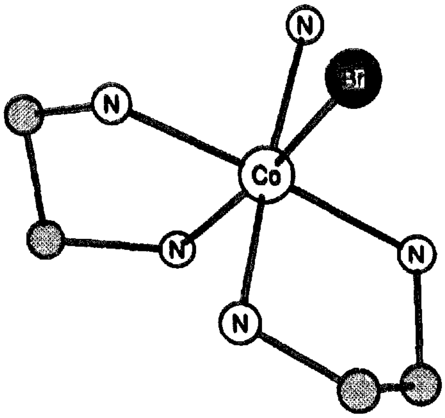
I have kept the format broadly the same as previously [1] based on the nature of the donor atoms in the ligands. In order to help in the limitation of the number of available references I have tended to leave out papers in which cobalt coordination compounds only make a comparatively small contribution to a work. I have also been somewhat selective in choosing papers which involve the preparation and characterization of complexes with new ligands without additional work other than conventional spectroscopic and analytical techniques which serve to identify the nature of the compounds. There has been a review of edta complexes with M(III) ions containing references to cobalt complexes [2].

The study of solid state reactions of transition metal complexes is comparatively rare. There have been a number of such studies for a variety of complexes of both cobalt(II) and cobalt(III) [3-7].

1.1 COBALT(III)

1.1.1 Complexes with nitrogen donor ligands

More than ninety years after the epic work of Alfred Werner, it is a tribute to him that there remains a deep interest in the very complexes that he prepared and their comparatively simple relatives. At that time he and his coworkers [8] resolved the complex [*cis*-$Co(en)_2(NH_3)Br]^{2+}$. This species and its resolution have been revisited [9] and the interaction of the ion with tetrathionate has been explored. The structure of a salt of $(+)_{589}$-[*cis*-$\Lambda(\delta\lambda)$–$Co(en)_2(NH_3)Br]^{3+}$ (**1**) shows that the hydrogen bonding exhibited between the anion and the cation is the same as that involved with the conventional resolving agent *d*-3-bromocamphorsulfonate. Another interesting feature is the intrinsic chirality of the $[S_4O_6]^{2-}$ ion arising from the helical nature of the S_4 chain and this is coupled to the chiral cation.



H atoms omitted

(**1**)

Careful measurement of conductivity of ionic species over a range of temperatures can furnish information about interactions between the ions and also about the interactions between the ions and the solvent [10]. The conductivities of the Cl^-, Br^-, I^-, NO_3^- and ClO_4^- salts of $[Co(en)_3]^{3+}$ measured over the temperature range 0-50°C allowed the determination of the ion association constant for each ion pair and these were found to exhibit a minimum value which increased in the order $Cl<Br<I<NO_3^-<ClO_4^-$. The authors deduce from these data and comparison with data for $[Co(NH_3)_6]^{3+}$ salts that the hydration around the $[Co(en)_3]^{3+}$ ion is relatively weak.

The molecular structure of the complexes $[Co(tn)(tmd)_2]Cl_3$ and $[Co(tn)_2(tmd)]Br_2$, where tn and tmd are $H_2N(CH_2)_nNH_2$ having $n = 3$ and 4 respectively, the former is found to be in the *lel lel*$_2$ form with the tn chelate ring being in the skew boat form [11]. In the latter the two independent cations have the *syn*-chair$_2$ *lel* configuration. The data are interpreted in terms of molecular mechanics calculations.

As part of a series of studies of the effect of the counter-ion on the crystallization of complexes of Co(III) [12], it has been found that the complex [*cis*-$Co(en)_2(NO_2)_2$]I, unlike its Cl^- and Br^- analogues, crystallizes in both a racemic and conglomerate fashion. The complex [*cis*$(-)_{589}$-$Co(en)_2(NO_2)_2$]I is $\Delta(\lambda\lambda)$. Hydrogen bonding is very important in determining the structure of these complexes and the cations in this system are found to form homochiral strings about a four-fold screw axis held together by hydrogen bonds. The iodide ions, and the hydrogens of the NH_2 groups form hydrogen bonds which result in helical strings alongside the cationic structure. In a similar way [13], the structure of the racemate $[H_3O][Co(en)_2ox]Cl_2.H_2O$ involves spiral strings of homochiral $[Co(en)_2ox]^+$ around the 2-fold screw axis of the crystal with adjacent spirals having opposite helicity. Hydrogen bonds are also important in determining the species present in crystallization of [*cis*-$Co(en)_2(NO_2)(SO_3)$]$.H_2O$ (i) [14]. In this case the X-ray data indicate that in (i) one of the en groups is in a higher energy conformation, and the authors suggest that this results from competitive hydrogen bonding between SO_3 and NO_2 for the hydrogen on the NH_2 group of the en ligand. Such competition between SO_3 and N_3 is of course not observed in [*cis*-$Co(en)_2(N_3)(SO_3)$]$.H_2O$ which was also studied in this work. *Cis*-amminebromobis(ethylenediamine)cobalt(III) is shown by an X-ray crystal structure determination to favour a structure in which the ethylenediamine configurations are $(lel)_2$-$\Lambda(\delta\delta)$ and $\Lambda(\lambda\lambda)$ [15]. In an attempt to prepare crystals of $[Co(NH_3)_4(oxalato)]Cl$ from $[Co(NH_3)(NO_2)_2][NO3]$, oxalic acid and NaCl, Bernal and coworkers actually obtained crystals of [*cis*-$Co(NH_3)_4(OH)Cl$]Cl (i) and $[Co(NH_3)_4(oxalato)]_2$[*trans*-$(NH_3)(OH)Co(oxalato)_2$]$.4H_2O$ (ii) [16] They obtained the X-ray crystal structures of these compounds and in the case of (i) were able to identify the positions of all the hydrogens and also those hydrogens in (ii) which were not in the anion which lies on an inversion centre; hence all the NH_3 and OH groups are disordered. From an examination of the products of the reaction, it is possible to make deductions about the nature of the ligand replacement reactions and this led to a study of possible *trans* effects which it is concluded could be present or else affected by charge compensation effects by ions in the crystal.

The kinetics of the base hydrolysis and solvolysis of *cis*-dichloro(1,2-ethanediamine)cobalt(II) has been studied in water mixtures with 1,2- or 1,4-butanediol, 1,2-ethanediol, 1-propanol, 1,2- or 1,6-hexanediol, or *tert*-butyl alcohol [17]. The kinetics of the base hydrolysis of the complex were also studied in methanol and ethanol-water mixtures. There was found to be a close correspondence between the rate constants and the transfer chemical potentials of the hydroxide and chloride ions and this is interpreted as evidence that hydration of the hydroxide or the complexed chloride is an important factor affecting reactivity within a given system. The kinetics and mechanism of the base hydrolysis of (αβs)(salicylato)(tetraethylenepentamine)-cobalt(III) in methanol + water and dimethylsulfoxide + water media have been investigated and it is found that there is both an OH^- independent path and an OH^- catalysed path [18]. It is concluded that the reaction involves $\mathrm{SN_1ICB}$ and $\mathrm{SN_1CB}$ mechanisms corresponding respectively to these pathways. The behaviour of the solvents is expressed in terms of stabilizing or destabilizing the transition state.

The kinetics of the redox reaction of $[Co(NH_3)_5(H_2O)]^{3+}$ with $[Fe(CN)_6]^{4-}$ or $[Mo(CN)_8]^{4-}$ has been examined over a very wide range of ionic strengths up to 5.0 mol dm^{-3} [19] using sodium nitrate or sodium perchlorate. The data are interpreted using dielectric continuum models.

The kinetics of the complexation of Fe(III) with (αβS)(tetraethylenepentaamine)-(salicylato)cobalt(III) and *cis*-(ammine)bis(ethylenediamine)(salicylato)cobalt(III) ions in aqueous anionic SDS micellar medium have been studied [20]. The reaction is believed to occur at the micellar surface in the water-rich zone to be found in the micellar-bulk aqueous interface. A heterodinuclear Co-Fe species is produced and unlike the situation in aqueous solution the dissociation of this moiety is not catalysed by H^+ in the micellar pseudo-phase. The formation of a similar dinuclear species $[N_5CoSalFe]^{4+}$ between *cis*-$[Co(en)_2(RNH_2)salH]^{2+}$ (where salH = salicylic acid) and Fe(III) ions has been investigated using stopped flow methods. An I_a mechanism is proposed when the active species are the phenol form of the cobalt complex and $[Fe(H_2O)_6]^{3+}$ and an Id mechanism when $[Fe(H_2O)_5(OH)]^{2+}$ is involved. The dissociation process was also studied.

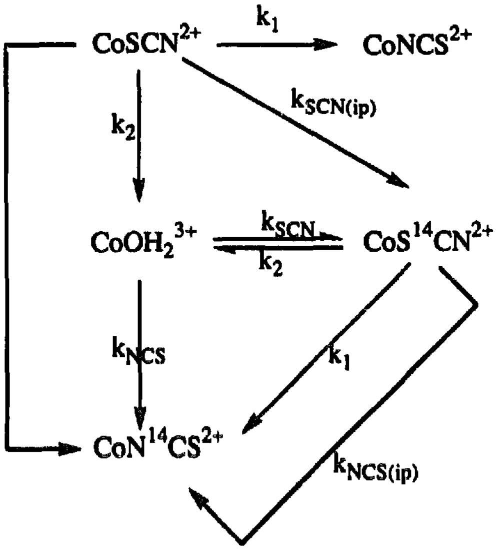
The *cis*-α complex [Co(sal)(trien)]Cl has been prepared and its properties investigated spectroscopically [22]. Activation volumes were determined for the reaction in 60% 1,4-butanediol.

The complexes ΔΛ–$[Co(aet)(en)_2][ClO_4]$ and Δ-$Na[Co(edta)].3H_2O$ or Na_2(D-tart)$.2H_2O$, (where aet = 2- aminoethanethiolate(1-), D-tart = (*RR*-tartrate(2-)) were crystallized together and the Δ aet complex always appeared in the first crop [23]. The ternary solubility isotherms were determined. The mechanism of the process is interpreted as involving a shift of the eutectic point from the racemic line into the optically active region and this is caused by the active cosolute. The authors conclude that for successful optical resolution in the conditions observed here the complex to be resolved must show conglomerate crystallization and the above shift of the eutectic point must occur and the larger the shift the better the resolution. The complex $Li[Co(III)\{Ltart(2\text{-})\text{-}O^1\}_2(en)_2]$ hydrate has been separated into its *cis* and *trans* isomers using a sephadex column and the crystal structure of the *trans* isomer has been determined [24]. The two tartrates are monodentate and the ethylene diamines are in the δδ gauche position. The environment around the Li^+ is tetrahedral being surrounded by oxygen atoms from the water molecules and the tartrate ligands.

A dissociative interchange mechanism is proposed for the mercury(II) promoted reaction of a series of *cis*-$[Co(en)_2(L)]^{2+}$ complexes in which L = NH_3, NH_2CH_3, $glyOC_2H_5$, $gluOCH_3$, dl-$alaOC_2H_5$, $NH_2CH_2CONH_2$ and NH_2CH_2CN. [25]. Reactions were followed in a number of different solvent mixtures and Grunwald-Winstein plots giving values of m and using Y, the solvent ionizing power as well as physical techniques such as CD spectra. The rate constants for the series in aqueous solution were related to the ligand field parameter. The rates were affected by NO_3^- ion added to the solution.

There is a phase transition in hexaamminecobalt(III) pentachlorocuprate at 280.8 K [26]. The X-ray crystal structure of this species above and below this temperature shows that moving through the phase transition changes the geometry of the $[CuCl_5]^{3-}$ from D_{3h} symmetry to approximately C_{2v} as a result of lengthening of one bond, shortening of the others in the equatorial plane and changing of the bond angles.

Buckingham and coworkers [27] have shown that in the isomerization of the complex $[Co(NH_3)_5(SCN)]^{2+}$ in the presence of $NaS^{14}CN$ the labelled ions are incorporated directly into the reactant and into the $[Co(NH_3)_5(NCS)]^{2+}$ product. The study shows that the process involved may be expressed as that in (**2**). The mechanism of the reaction which gives rise to these processes is believed to involve direct incorporation of the ions via the formation of the ion paired species $[Co(NH_3)_5(SCN)]^{2+}.N^{14}CS^-$. It is concluded that a similar mechanism applies to related reactions and that a D_n*Anint or D_nAn mechanism applies.



(**2**)

The acid dependence of the rate of anation reactions involving $[Co(NH_3)_5(H_2O)]^{3+}$ and $HCrO_4^-$ has been shown to be nonlinear [28]. The decrease reaches a limiting value between $[H^+] = 0$ and 2×10^{-4}M and an increase reaches a limiting value between $[H^+]$ up to 0.01M. It is concluded that the implication of the rate data is that the reaction proceeds essentially entirely via the protonated complex, $[Co(NH_3)_5HCrO_4]^{2+}$. The formation constant for the reaction between $[Co(NH_3)_5(H_2O)]^{3+}$ and $HCrO_4^-$ was found to be 1.55 M^{-1} and the acidity constant for the complex so formed is 4.43×10^{-3} M [29].

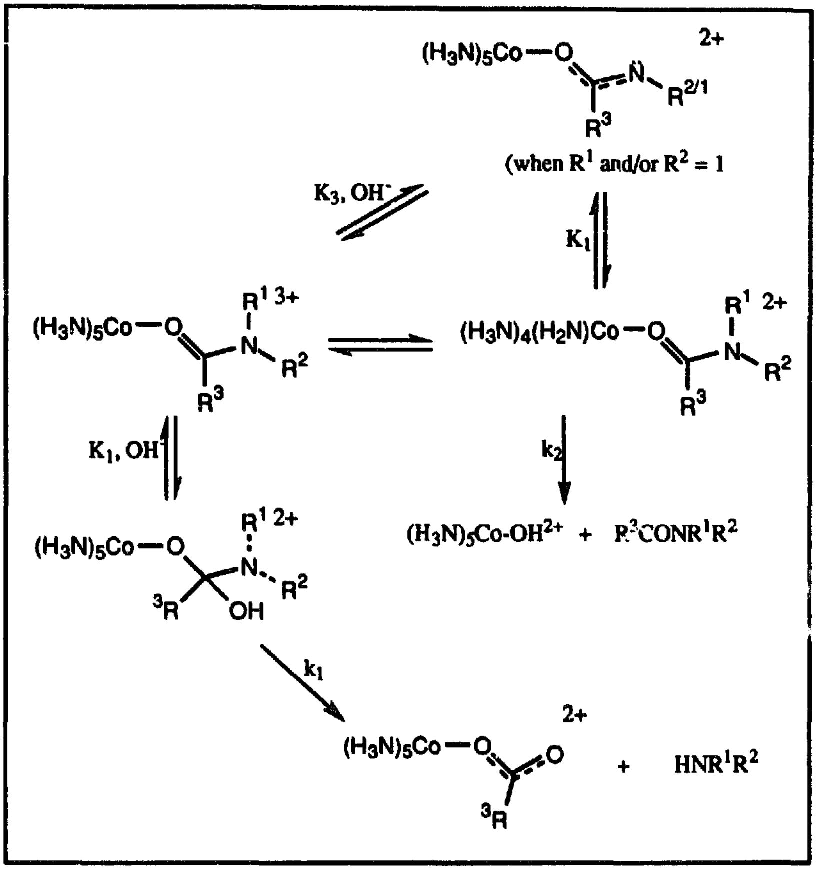
The chemistry of isomerization, base hydrolysis and oxidation reactions of the oxygen and sulfur-bonded complexes of the type $[(NH_3)_5Co(CH_3SO_2)]^{2+}$ have been explored [30]. The O-bonded isomer is readily obtained by reaction of the hydroxo complex with CH_3SOCl dissolved in

$PO(OCH_3)_3$ and then the *S*-bonded isomer is formed by the photolysis of this. Alkylation of the *O*-bonded isomer by MeI in dmso yields $[(NH_3)_5CoOS(CH_3)_2]^{3+}$ and oxidized by H_2O_2 to give $[(NH_3)_5CoOS(O)_2CH_3]^{3+}$, while oxidation by Cl_2 yields $[(NH_3)CoOS(Cl)(O)CH_3]^{3+}$. The *S*-bonded isomer does not undergo these reactions. The kinetics of the isomerization of the *O*-bonded species involving a base catalysed pathway have been studied as has also the base hydrolysis of this complex. A related study deals with the preparation and solution structures of a range of amide complexes of cobalt(III) with ligands (3) which are bonded through oxygen. The study also probes how reactions are affected by substituent groups on the amides [31]. The pink complexes were formed by the direct reaction of the amide with the complex $[Co(NH_3)_5CoOSO_2CF_3]^{3+}$ dissolved in the neat amide. In terms of structure, the occurrence of *Z*- and *E*-configurations was studied. The kinetics of solvolysis in dmso were investigated and the complexes of formamides were in general solvolysed more slowly than the C-substituted species. Base hydrolysis of formamide complexes results in the formation of the corresponding formato complex, while the C-substituted amido species produce the hydroxo complex. The kinetics of the base hydrolysis of a number of the primary and secondary amide complexes were interpreted in terms of the reaction scheme shown below (4) involving ligand protonation.

$HCONH_2$	CH_3CONH_2	$CH_2{:}FCONH_2$
$HCONH(CH_3)$	$CH_3CONH(CH_3)$	$CH_2{:}ClCONH_2$
$HCON(CH_3)_2$	$CH_3CONCH_3)_2$	$C_6H_5CONH_2$
$HCON(C_2H_5)_2$	$CH_3CON(C_2H_5)_2$	$CH_2{=}CHCONH_2$
$HCONH(C_6H_5)$		
$HCON(C_6H_5)_2$		

(3)

The kinetics and mechanism of the reduction of the superoxide complexes $[Co_2(O_2)(NH_3)_{10}]^{5+}$ and $[Co_2(O_2)(CN)_{10}]^{5-}$ by L-ascorbic acid has been studied [32]. The reaction of the ammine complex in the pH range 3.5 to 5.2 is concluded to be outer sphere, occurring through the reduction of the superoxo group to peroxo followed by rapid decomposition of the resulting product. The cyano complex reacts in the presence of copper(II) ions to form $[(CN)_5Co(H_2O)]^{2-}$. A change in the UV-VIS spectrum of the starting materials and the rate law strongly suggest that the reaction involves the initial formation of a copper(II)-cyanocobalt(III) complex. A mechanism incorporating these features is proposed scheme (5). In a related study [33] it has been shown that copper(II) catalyses the reduction of the complex cation $[Co_2(O_2)(NH_3)_{10}]^{5+}$ by 2-aminoethanethiol. The kinetic study of this reaction showed that under most circumstances there is not an accurately exponential loss of complex and that there is an almost linear loss over the early part of the reaction. These steps are in agreement with the kinetic behaviour shown in (6).



(4)

$$H_2A \rightleftharpoons H^+ + HA^-$$

$$Cu^{2+} + Ox \rightleftharpoons Cu(II)(Ox) \qquad K_{IP} > 10^7$$

$$HA^- + Cu(II)(Ox) \longrightarrow HA^{\cdot} + Cu(I) + Ox \qquad k = 3 \times 10^3\ M^{-1}\ s^{-1}$$

$$HA^- + Cu(II)Ox \rightleftharpoons Cu(II)(Ox)(A^{2-}) + H^+$$

$$Cu(II)Ox)(A^{2-}) \longrightarrow Cu(I) + A^{\cdot -} + Ox$$

$$HA^{\cdot} + Cu(II) \longrightarrow Cu(I) + A + H^+ \quad (Fast)$$

$$A^{\cdot -} + Cu(II) \longrightarrow Cu(I) + A \quad (Fast)$$

$$Cu(I) + Ox \longrightarrow Cu(II) + P \quad (Fast)$$

Where Ox = the oxidizing complex
P = the product

(5)

$$\mathrm{Cu^{2+} + RedH_2 \rightleftharpoons Cu(II)(Red) + 2H^+}$$

$$\mathrm{2Cu(II)(Red) \rightleftharpoons (Cu(II)Red)_2 \quad (inactive)}$$

$$\mathrm{Cu(II)(Red) + RedH_2 \rightleftharpoons Cu(II)(Red)(REDH) + H^+}$$

$$\mathrm{Cu(I)(Red)(RedH) \longrightarrow Cu(I)(RedH) + Red^{\cdot}}$$

$$\mathrm{Cu(I)(RedH) + RedH_2 \rightleftharpoons Cu(I)(Red)(RedH) + 2H^+}$$

$$\mathrm{Cu(I)(Red)(RedH) + Ox \rightleftharpoons Cu(II)(Red)(RedH) + prod}$$

$$\mathrm{2Red^{\cdot} \longrightarrow (Red)_2}$$

(6)

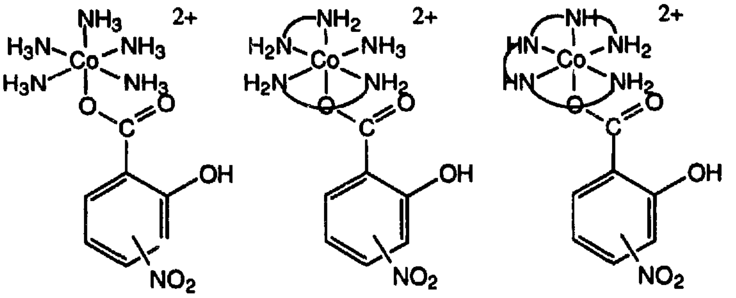
Single-crystal polarized absorption spectra of the *trans* planar cobalt(III) complexes; $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$ (NO_3CNS and CNS salt) $[(en)(dien)CoO_2Co(en)(dien)](ClO_4)_4$, $[(tren)NH_3CoO_2Co(tren)NH_3]^{4+}$ (CNS and SO_4 salts) [34] have been obtained using the data, ligand field transitions have been assigned. From the charge transfer transitions from the peroxide π^*-orbital to the cobalt *d* σ-orbital it was found that the HOMO of these complexes had peroxide π^*-character.

The reduction of diaquatetraamminecobalt(III) by L-ascorbic acid has also been studied [35]. The kinetics of the reaction were interpreted in terms of the usual reactions with HA^- and formation of $HA\cdot$ which subsequently reacts rapidly with another molecule of complex to produce the observed stoichiometry. The data are treated theoretically using the Fuoss model and the Marcus-Sutin cross relationship to calculate a self-exchange rate constant for diaquatetraamminecobalt(III)/(II) of 1.6×10^{-4} M^{-1} s^{-1} and the ion pair formation constant was estimated to be 4.9 M^{-1}. In the complex [(*S*)-alaninato]tetraamminecobalt(III) sulfate [36] the environment around the cobalt as determined by X-ray crystallography is distorted octahedral with didentate alanines bound through carboxyl oxygen and amine nitrogen and with Me groups equatorial to the Co-O-N plane.

The kinetics of the Cr(II) reduction of the cobalt(III) complexes; $[(NH_3)_5Co(SO_3)]^+$ (4.7×10^3), $[(NH_3)_5Co(S_2O_5]^+$ (2.1×10^4), $[(NH_3)_5CoSO_2C_6H_5]^{2+}$ (5.3×10^3) and $[(NH_3)_5Co(H_2O(SO_3)]^+$ (1.1×10^5] have been studied [37]. The second order rate constants are shown in parenthesis. It is noted that there is no linear correlation between the rate constants and the *trans* bond lengthening.

All three of the linkage isomers of the pentaammine(glycinamide)cobalt(III) complex have been prepared and characterized [38]. Also both the species $[(NH_3)_5CoNHCOCH_2NH_2]^{2+}$ and the protonated $[(NH_3)_5CoNHC(OHCH_2NH_3]^{4+}$ were isolated. An interesting feature of the latter is that it is a strong acid with $pKa< 0.5$. This readily isomerizes to the *O*-bonded species in acid solution and the $[(NH_3)_5CoOC(NH_2)CH_2NH_3]^{4+}$ complex loses the amine proton in the pH range 6 to 10 resulting in rearrangement to the amine-bonded isomer. Furthermore it hydrolyses rapidly in aqueous acid and at high pH undergoes base catalysed solvolysis without amide hydrolysis.

The kinetics of the complexation of Ni(II) ion with nitrosalicylato complexes of pentaaminecobalt(III) complexes such as for example (7), show that the nickel(II) is coordinated through the phenoxide form and that the kinetic data may be interpreted in terms of an I_d mechanism [39]. For the complex oxalatopentaamminecobalt(III) it is suggested that in MeOH/water mixtures, Ni^{2+} attaches itself to the end of the carboxylate group [40]. The rates of formation and dissociation of the dinuclear species are reported. The effect of anionic micelles of sodium dodecyl sulfate on the kinetics of the nickel(II) reaction and the similar iron(III) reaction with this complex have also been studied [41].



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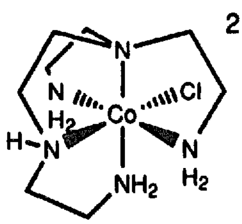


(8)

The structure of the complex *N*,*N*-bis(2-aminoethyl)diethylenetriamine(chloro)cobalt(III) chloride perchlorate hydrate, containing $[Co(trenen)Cl]^{2+}$ (8) [42] shows evidence of stronger binding of the secondary nitrogen with Co in that the bond is significantly shorter than the other Co-N bonds and this is related to the greater rate of base hydrolysis of $[Co(trenen)Cl]^{2+}$ compared with $[Co(NH_3)_5Cl]^{2+}$ and related complexes.

A series of complexes of the type $[Co(N_4)(CH_3CN)_2](ClO_4)$ in which $N_4 = (NH_3)_4$, $(en)_2$, $(tn)_2$, and tren has been prepared and characterized [43]. An I_d mechanism is proposed from the kinetics of acid hydrolysis of $[Co(tn)_2(CH_3CN)(H_2O)]^{3+}$ which is formed immediately when $[Co(tn)_2(CH_3CN)_2]^{3+}$ is dissolved in water.

The structures of *cis*- and *trans*-bis(ethylenediamine)isothiocyanato(thiosulfato)cobalt(III) have been determined [44] high-lighting the structural *trans* effect.

In the complex aniline(chloro)bis(ethylenediamine)cobalt(III) chloride the aniline ring has been found to tilt away from the chelate rings of the ethylenediamines [45]

Photochemical reactions may now be studied on the picosecond time scale and are beginning to reveal the earliest processes in chemical reactions [46]. One such is the study of the flash photochemical reaction of $[Co(NH_3)_4CO_3]^{+}$ in the picosecond to microsecond timescale. This reveals that the series of reactions which probably occur over this range is (9), with the last being rate determining and $k = 5.5 \times 10^5\ s^{-1}$.

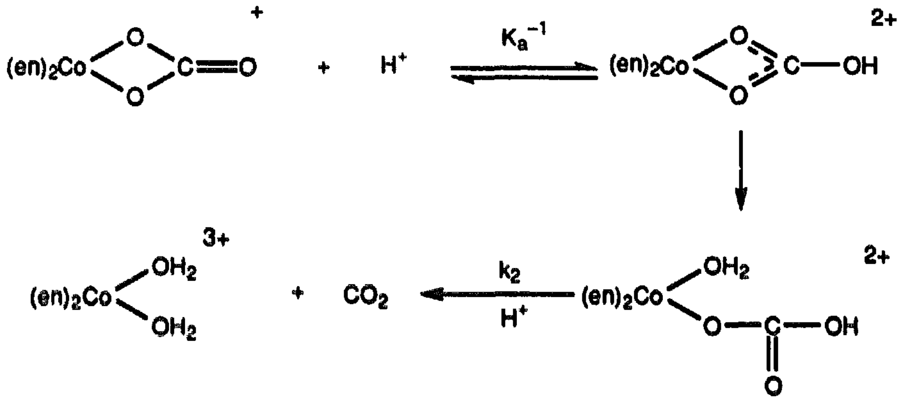
$$[Co(II)(NH_3)_4OC(O)O^{\bullet}]^+ + H_2O \longrightarrow [Co(II)(NH_3)_4(H_2O)OC(O)O^{\bullet}]^+$$

$$[Co(II)(NH_3)_4(H_2O)OC(O)O^{\bullet}]^+ + 2H_2O \longrightarrow [Co(II)(NH_3)_3(H_2O)_2OC(O)O^{\bullet}]^+ + [NH_4] + OH^-$$

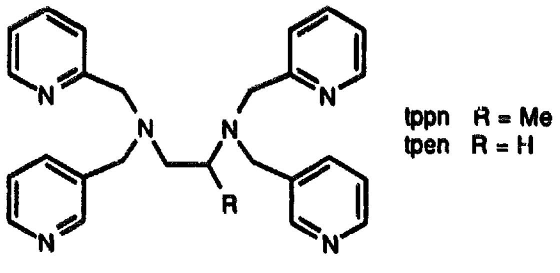
$$[Co(II)(NH_3)_3(H_2O)_2OC(O)O^{\bullet}]^+ + 2H_2O \longrightarrow [Co(II)(NH_3)_2]^{3+}\ CO_3H + [NH_4]^+ + 2OH^-$$

(9)

With the advent of the use of fast recording UV-VIS spectroscopy in cooperation with stopped flow techniques it is often rewarding to look at the early stages of slow reactions to see if there are any rapid reactions preceding the slower process. Buckingham and Clark [47] have examined again the acid catalysed hydrolysis of $[Co(en)_2CO_3]^+$ ion over the first second or so of the reaction. They detected a fast reaction [k_2 in (10)] which was independent of $[H]^+$ and a slower process which was pH dependent. The mechanism which is proposed based on the kinetic behaviour is shown in (**10**)



(10)

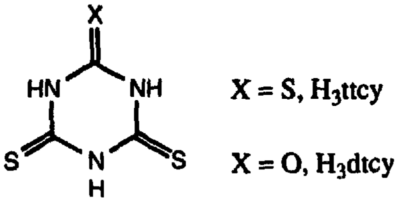


(11)

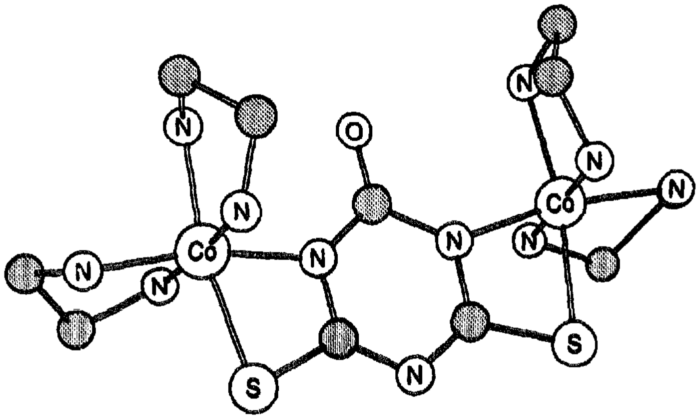
Excitation at a wavelength of 314 nm and for about 500 fs of the complexes $[Co(en)_3](ClO_4)_3$, $[Co(tpen)](ClO_4)_3$ and $[Co(tppn)](ClO_4)_3$ where tpen and tppn are shown in (**11**) shows relaxation kinetics in each a case which are biphasic [48]. The two τ values for the tpen complex are $t_1 = 4$ ps and $t_2 = 44$ ps and similar values are seen for the tppn complex. Somewhat different value of $t_1 = 2$ ps and $t_2 = 450$ ps were obtained for the en complex. The faster of these processes is assigned to the decay of the $^1T_1$ excited state and the slower to the $^5T_2$

state back to the ground state. By choosing a wavelength to carry out a kinetic study at which the extinction coefficients per cobalt of the starting material and the intermediate are the same, and by using chloride ion catalysis it has been possible to obtain valuable insight into the kinetics of the chromium(II) reduction of the complex, "Werner's hexol", $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ [49]. It was found that the reaction proceeded by a stepwise mechanism involving cobalt hydroxy complexes.

The brownish-red complex $[Cu\{(OH)_2Co(en)_2\}_2](S_2O_6)_2.2H_2O$ has been prepared and characterized [50]. Reaction of $[Co(en)_3]Cl_3$ with H_3ttcy /NaOH yields a number of complexes: *syn-(meso-* and *rac-*)[{Co(en)$_2$}$_2$(m-ttcy)]X_3 and (*meso-* and *rac-*)[{Co(en)$_2$}$_2$(m-dtcy)]X_3 [51] where the structures of the ligands are indicated in (**12**). The formation of the dtcy complex appears to involve replacement of sulfur by oxygen during the dinuclear complexation process. The structure of the complexes (**13**) and (**14**) were obtained by X-ray crystallography.

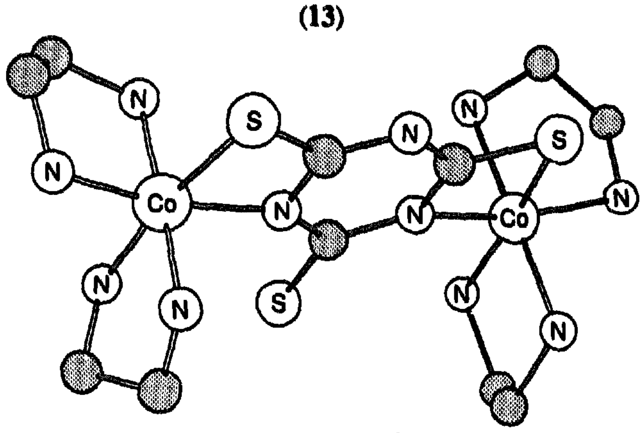


(**12**)



H atoms omitted.

(**13**)



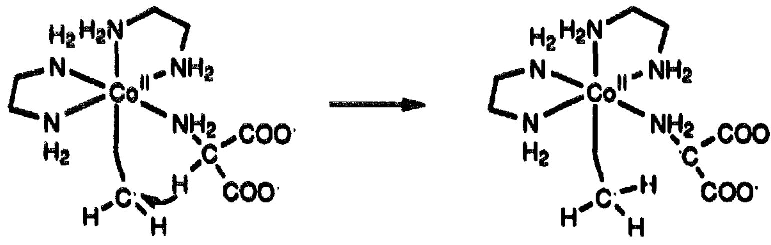
H atoms omitted.

(**14**)

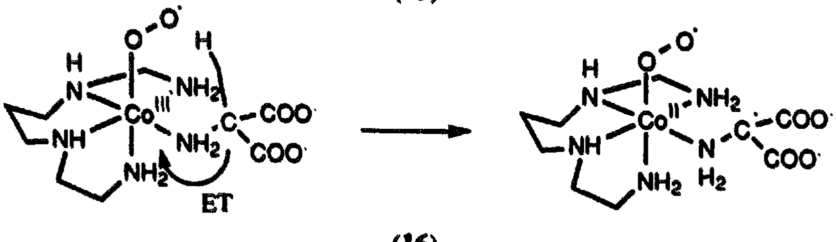
The kinetics and mechanisms of base hydrolysis of cobalt(III) amine complexes still attract the interest of kineticists and the generally accepted mechanism continues to be confirmed [52]. A study of the base hydrolysis of a number of chlorocobalt(III) (triamine)(diamine) complexes has shown that the stereochemistry of the ligands certainly influences the kinetics of base hydrolysis. The rather slower than expected rate for the macrobicyclic complex is interpreted in terms of the failure to attain the best geometry for the formation of the five coordinate intermediate.

The technique of polarized neutron diffraction (pnd) has been applied to a single crystal of $[Co(NH_3)_5(OH_2)][Cr(CN)_6]$ at two orientations at 1.5K under a magnetic field of 4.6T [53]. The results showed that there were significant amounts of spin to be found on both the cobalt and the ammine protons accounting for one third of the total spin of 3 electrons from the Cr^{3+} ion. Comparison using local density functional calculations on the $[Co(NH_3)_6]^{3+}$ cation and the $[Cr(CN)_6]^{3-}$ anion in model compounds were made with $[Co(NH_3)_5(OH_2)][Cr(CN)_6]$. A difference in spin density in the anion was found. A feature which is interpreted as a magnetic phase transition [54] has been observed at 3.925K from specific heat measurements over the range 1.6 to 40K of the complex $[Co(NH_3)_6][CuCl_5]$.

ESR spectroscopy has provided valuable information about the reactions of a number of complexes of the form *trans*-$[Co(III)Cl_2(N_4)]^+$ in which N_4 = $(en)_2$, 2,3,2-tet, 3,2,3-tet with α -aminomalonate [55]. The redox reactions crucially were carried out in solution in methanol. The routes by which the oxidation of the α–aminomalonate was oxidized to an iminomalonato intermediate were found to depend upon the nature of the cobalt(III)-coordinated amino group. When the amine grouping was en the process which occurred was (15) but for 2,3,2-tet the reaction was (16) which involves dioxygen to form a superoxo ligand attached to the cobalt(III). In the absence of dioxygen such complexes react by a process in which the cobalt changes spin state from low-spin d^6 to high-spin d^7.

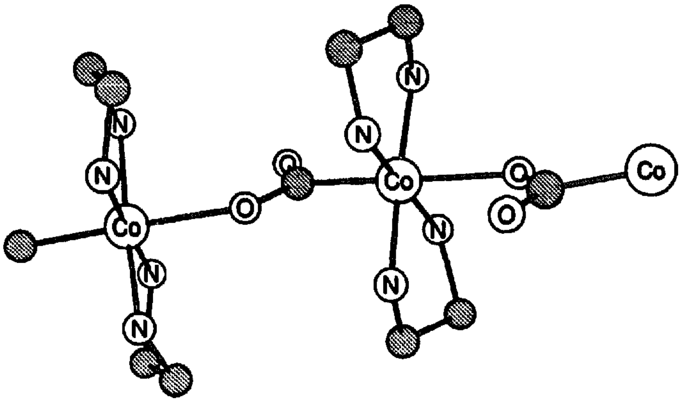


(15)



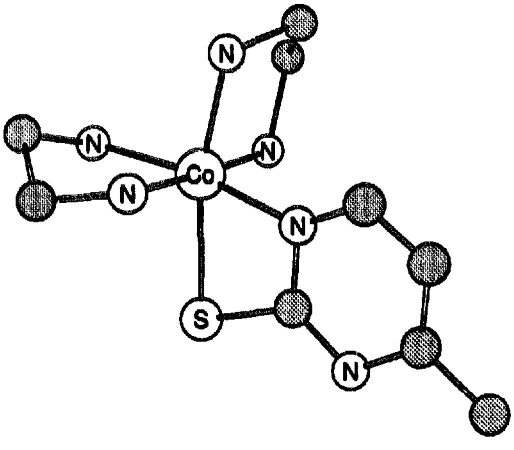
(16)

When crystals are grown from an alkaline solution of $Co(en)_2(OH)(CO_3)$ the product is $\{[Co(III)(en)_2(CO_3)](ClO_4).H_2O\}_n$ [56]. The crystal structure of this complex has been determined and the cation (**17**) contains the ethylenediamine groups in the equatorial planes of the octahedrally coordinated cobalt ion. Bridges are formed by the $[CO_3]^{2-}$ groups bonded to cobalt via the oxygen and the carbon and hydrogen bonds between the pendant oxygen of the bridging group and the amine hydrogens of the ethylenediamine. Improved structural data on the crystal structure of the complex carbonatobis(ethylenediamine)cobalt(III) chloride show the ethylenediamine having a λ chelate ring conformation in the Δ enantiomer which together with the Λ enantiomer constitutes the unit cell [57].



(**17**)

Photochemical irradiation using a halogen lamp of solutions of $[Co(en)_3]^{3+}$ in the presence of various pyrimidine-2-thiol derivatives produces the substituted species $[CoL_n(en)_{(3-n)}]^{(3-n)+}$ [58]. The X-ray crystal structure of $[Co(mpymt)(en)_2][ClO_4]_2$ was obtained and the structure of the cation is shown (**18**). Coordination is through the N and S atoms of the ligand.



(**18**)

The structure of the perchlorate salt of the complex cation bis(ethane-1,2-diamine)(*N*-methylethane-1,2-diamine)cobalt(III) $[Co(meen)(en)_2]^{3+}$ [59] is a racemate with one enantiomer being Λ–R–δ*λλ and the structure determined has been compared with that calculated using molecular mechanics.

The importance of correct labelling of bottles [60] is highlighted in a correcting publication in which the structure of the complex $[Co(en)_2(Cl)(benzimidazole)]Cl_2.1.3H_2O$ has been determined for the species whose structure had been described in an earlier paper [61] as that of bis(ethylenediamine)benzimidazole)chlorocobalt(III) perchlorate. There were no significant changes in the bond lengths published in the earlier paper.

The mechanism for the electron transfer reaction between $[Co(en)_2SQ]^+$ and Ti^{3+} [62] occurs in the following steps (**19**) resulting in a third order rate law involving the two types of Ti(III) species. Intramolecular electron transfer can be seen as well as intermolecular electron transfer. On the other hand the reduction of $[Co(en)_2Q]^+$ involves the steps (**20**) which account for the biphasic behaviour.

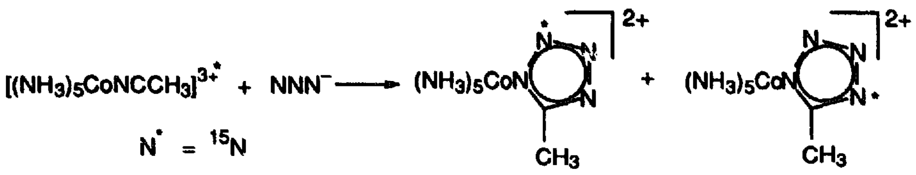
$$\boxed{\begin{aligned}
&Ti^{3+} \rightleftharpoons Ti(OH^{2+} + H^+\\
&Co(en)_2SQ^+ + Ti^{3+} \rightleftharpoons Co(en)_2(SQ)Ti^{4+}\\
&Co(en)_2(SQ)Ti^{4+} \rightleftharpoons Co(en)_2(SQ)TiOH^{3+} + H^+\\
&Co(en)_2(SQ)TiOH^{3+} \longrightarrow \text{products}\\
&Co(en)_2(SQ)TiOH^{3+} + TiOH^{2+} \longrightarrow \text{products}
\end{aligned}}$$

(**19**)

$$\boxed{\begin{aligned}
&Ti^{3+} \rightleftharpoons Ti(OH^{2+} + H^+\\
&Co(tren)Q^+ + Ti^{3+} \rightleftharpoons Co(trien)(Q)Ti^{4+}\\
&Co(trien)(Q)Ti^{4+} \longrightarrow \text{products}\\
&Co(tren)(Q)Ti^{4+} + TiOH^{2+} \longrightarrow \text{products}
\end{aligned}}$$

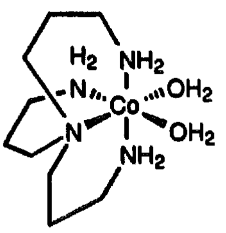
(**20**)

Insight into the nature of the transition state for any reaction is valuable, but such insight has proved particularly difficult in the case of ligand isomerization reactions [63]. The application of ^{15}N NMR spectroscopy to tetrazole complexes of pentaamminecobalt(III) has thrown light on the structures of such complexes and also on the nature of the transition state during their isomerization. By carrying out the reaction (**21**) using ^{15}N enriched sodium azide it was possible to produce the cobalt complex with ^{15}N enrichment at the N2 and N4 ring positions allowing assignment of the NMR spectroscopic signals to all the ring nitrogens. The isomerization was followed using ^{15}N NMR spectroscopy and from these data an η^2-mode for the transition state is deduced.

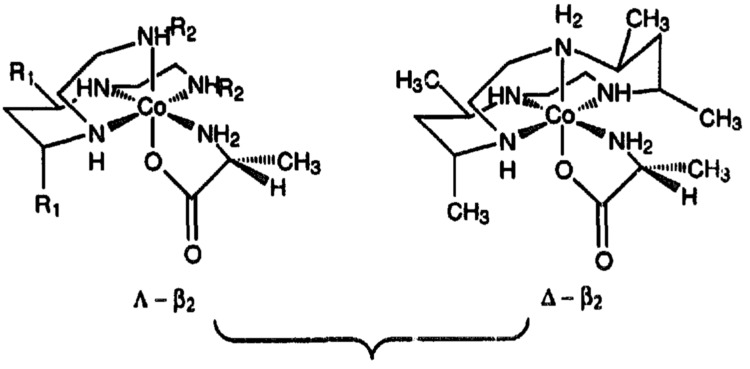


(21)

Unlike the corresponding tren complex , the complex $[Co(III)(trpn)(H_2O)_2]^{3+}$ (22) reacts quantitatively in acid aqueous solution by C-N bond cleavage to produce Co^{2+} and organic products [64]. The two major products are trpn (tris(3-aminopropyl)amine) and bpn (3,3'-iminobis(propylamine). The minor products were β-aminopropionaldehyde and its oxidation product β–alanine. The authors suggest that the process starts by a Co(III)-initiated intramolecular oxidation of the tertiary N atom. The structure of this cation has been determined and the sodium ion in diaqua[tris(3-aminopropyl)amine]cobalt(III) aquatetrakis(trifluoromethanesulfato)sodate monohydrate is found to be octahedrally surrounded by oxygen atoms and in the cation the cobalt is surrounded by one tertiary and three primary nitrogen atoms from the ligand and the two water molecules [65].



(22)



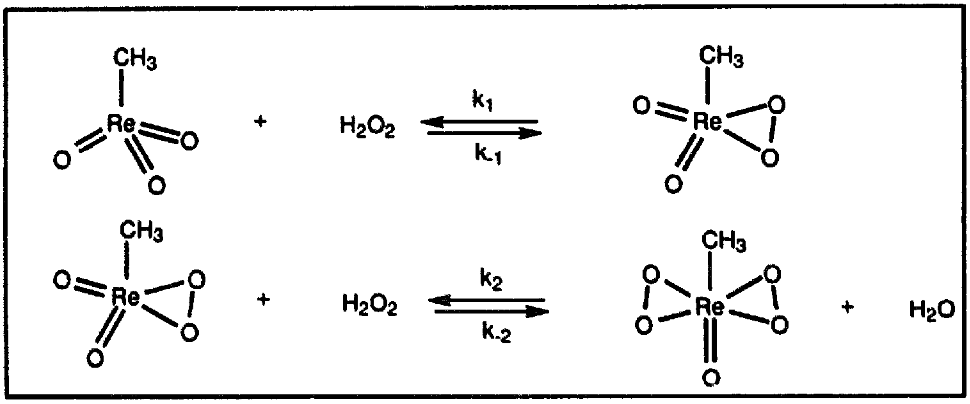
(23)

Cobalt-59 NMR and UV-VIS spectroscopies have been used to investigate the effect on the ligand field strength of substituting methyl groups into chelated tetraamine groups when attached to cobalt(III) to which alanine is also bonded (23) [66]. Increasing substitution reduces the ligand field strength with concomitant decrease in the stability of the alanine with regard to dissociation.

The importance of the presence of a pseudo-C_3 carboxylate face on the kinetics of certain electron transfer reactions has been discussed previously. Lappin and coworkers [67] have determined the X-ray and molecular structures of the diastereomeric pair [Λ-$Co(en)_3$][Δ-$Co(en)(ox)_2$]I2.$3H_2O$ and [Δ-$Co(en)_3$][Δ-$Co(en)(ox)_2$]$I_2.H_2O$ and for comparison of [Λ-$Co(en)_3$][Δ-$Co(gly)(ox)_2$]$I.H_2O$. The structures reveal extensive hydrogen bonding between the ions. Strong hydrogen bonds are essential to the propagation of chirality in this and other systems.

The mechanisms of the oxidations catalysed by CH_3ReO_3 are of interest because of the use of this catalyst in olefin epoxidation reactions. Espenson and coworkers [68] have chosen for such a study the complex $[(en)_2Co(SHCH_2CH_2NH_2)]^{2+}$ whose oxidation by hydrogen peroxide to

$[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ and $[(en)2Co(S(O_2)CH_2CH_2NH_2)]^{2+}$ in two clearly defined steps is catalysed by CH_3ReO_3. In the presence of small concentrations of the catalyst the reaction is initially zero order. The kinetic data are interpreted to include two equilibria involving the catalyst (**24**). However it is concluded that the 1:2 complex is not very kinetically active and that the important catalytic species is the 1:1 complex.



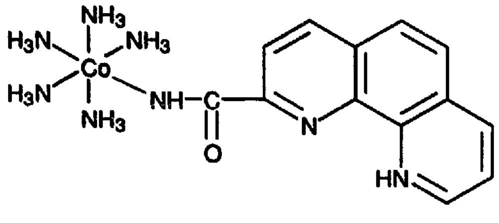
(**24**)

In the aquation of a series of complexes of the type $[Co(en)(tn)(A)Cl]^{2+}$ [69] in which tn = 1,3-diaminopropane while A = NH_3, $MeNH_2$, $EtNH_2$, $BuNH_2$, py, β and γ-pic and imidazole and $[Co(tn)_2ACl]^+$ in which A = py, β and γ-pic, 1-methylimidazole and 1,2-dimethylimidazole, it has been suggested that the intermediate in the process is a trigonal bipyramid and the rate of reaction is influenced by the nature of A and the effect it has on the structure of the intermediate.

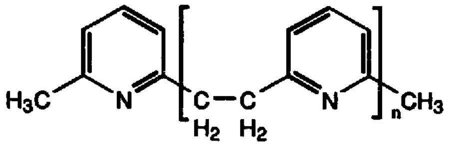
Cyanometallates of $Ru(bpy)_2(CN)_2$, namely $[(bpy)_2Ru((CN)Co(NH_3)_5)_2]^{6+}$, $[(bpy)_2(CN)Ru(CN)Co(tetraen))]^{3+}$ and $[(bpy)_2(CN)Ru(CN)Co(terpy)(bpy))]^{3+}$have been used in a study [70] to show that in such complexes electronic factors are able to inhibit thermally activated electron transfer. Irradiation of these complexes in the Ru(II) MLCT band produces no evidence of the expected ruthenium emission. It is concluded that a transient species produced by 18 ps irradiation at 532 nm and which decayed back to the substrates was due to photoinduced charge separation followed by back-electron transfer.

The complex (phenanthroline-2-carboxamide)pentaamminecobalt(III) (**25**) has a pendant phenanthroline which allows complexation with a number of other metal ions [71]. The kinetics and mechanisms of the reactions with aqua Ni^{2+}, Co^{2+} and Ni^{2+} have been studied. The initial reaction results in the formation of a species in which the metal ion is coordinated to the pendant phenanthroline through the carbonyl group and the nitrogen atom which is adjacent to it. In the case of iron(II) ions a further reaction occurs in which the iron becomes attached to both nitrogen atoms of the phenanthroline.

The complexes $[Co(endip)Cl_2]$, $[Co(endip)(NCS)_2]$, $[Co_3(entrip)_2Cl_6]$ and $[Co_2(entetp)Cl_4]$ where endip, entrip and entetp are shown in (**26**) have been prepared and characterized [72]. The complexes of the form $[Co(hfac)L]^{2+}$ in which L=$(MeNH_2)_4$, $(n\text{-}AmNH_2)_4$, *cis*-$(NH_3)_2$(en), (*R*-pn)(*S*-pn), cyclen, cyclam, *cis*-$(NH_3)_2$(bpy), (en)(bpy), (en)(phen), (tn)(bpy), (tn)(phen) (tn = 1,3-diaminopropane) and (bpy)(phen) have been prepared and the values of pK_{OH} and pK_{OMe} were determined respectively in water and methanol [73]. A number of complexes of the form $[Co(trpn)(halac)_2](ClO_4)$ in which halac is a number of halosubstituted acetates and $[Co(trpn)(L)](ClO_4)_2$ where L = OA^-, acac or hfac have been prepared and the field strengths of the ligands are compared [74].



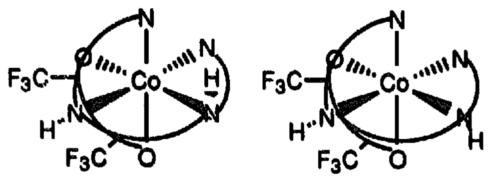
(25)



n = 1, endip, n = 2, entrip, n = 3, entetp

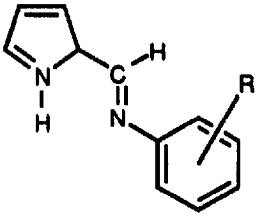
(26)

Fluorine-19 NMR spectra for the complexes of the *cis*-β-$[Co(hfac)L]^{n+}$ in which L = 1,8-diamino-3,6-diazaoctane, 1,9-diamino-3,7-diazanonane, 1,10-diamino-4,7-diazadecane and ethylene-*N*,*N*′-diacetate [75] show that in aqueous solution the complexes exist as two isomers Δ-β -*SS*- and Δ -β -*SS*-$[Co(hfac)L]^{n+}$ (27) with the relative quantities depending on the history of the solution.



Δ-β-SR Δ-β-SR

(27)



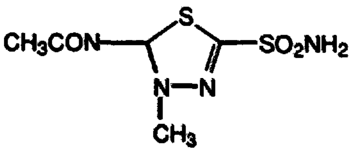
R = H, Cl, Br, CH_3, OCH_3, OC_2H_5, NO_2 in *ortho, meta or para* position

(28)

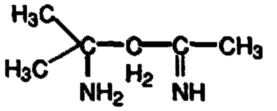
Data from the X-ray crystal structure of $[Co(EtNH_2)_5(H_2O)](ClO_4)_3.2H_2O$ show that additional steric hindrance results in a rate acceleration of anation compared with other similar complexes consistent with a dissociative process is observed [76]. The crystal structure of the complex $[Co(im)_4(H_2O)_2](C_6H_4OSO_2N)_2$ shows it to consist of repeated $[Co(im)_4(H_2O)_2]^{2+}$ cations and non-coordinated saccharin anions with an approximately octahedral arrangement involving 2 water molecules and 4 imidazoles around the Co(II) [77].

Cobalt(III) complexes of the ligand *N*-arylpyrrole-2-aldimine (**28**) have been shown using NMR spectroscopy to exist entirely in the *mer* configuration [78]

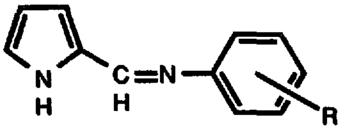
An aerated mixture of a Co(II) salt, the ligand methazolamide (**29a**), ammonia and acetone yields the complex ion $[Co(methazolamidate)(aib)_2(NH_3)]^+$, aib = (**29b**) [79]. The X-ray crystal structure of this shows a slightly distorted octahedral arrangement around the Co with the methazolamide coordinating through the sulfonamido nitrogen atom. Complexes of type CoL_3 in which HL is shown in (**30**) have been electrolytically prepared in acetonitrile [80]. When reacted with 1,10-phenanthroline and bpy, these yielded $[CoL_2(phen)]$ or $[CoL_2(bpy)]$. The X-ray crystal structure of tris{2-[(2-methylphenyl)iminomethyl]-pyrrolato}cobalt(III) showed that the CoN_6 unit only slightly departed from octahedral symmetry.



(29a)



(29b)

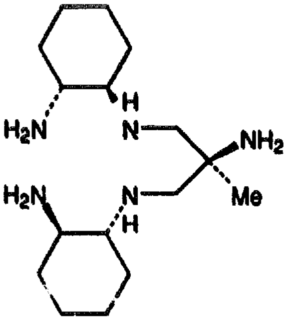


R = H, 2-CH_3, 4-CH_3, 4-Cl

(30)

Measurement of the apparent magnetic moment of the complex $[Co(phen)_3]^{2+}$ in aqueous solution over the temperature range 286 to 360 K [81] shows that it is entirely high-spin d^7 ($^4T_{1g}$). The self-exchange rate constant measured with variation of the counter ion (Cl^- and NO_3^-) is accounted for using the full Debye-Hückel equation with a size parameter of 520 pm for Cl^- and 360 pm for NO_3^-. The volume of activation $\Delta V^\ddagger$ for self exchange did not vary greatly with ionic strength but fitted Debye-Hückel-based theory. However when adiabatic electron transfer theory was applied to the determination of the volume of activation it predicted a rather less negative value ($-15 cm^3 mol^{-1}$) than that obtained experimentally and this and $[Co(en)_3]^{3+/2+}$ exchange volumes of activation are clearly anomalous amongst a wide range of complexes. The most likely explanation furnished by the authors is that it is due to non-adiabatic electron transfer between the Co(II) and Co(III) ground states.

The ligand *RR,RR*-1,3-bis(2'-aminocyclohexylamino)-2-amino-2-methylpropane (31) is a five coordinate in the complex $[Co(L)Cl]Cl[ClO_4].2H_2O$ with the chloride in the coordination sphere being *trans* to the central primary amine [82]. During base hydrolysis, the complex exhibits two reactions which are assigned to hydrolysis of the chloride and *cis-trans*-isomerism.

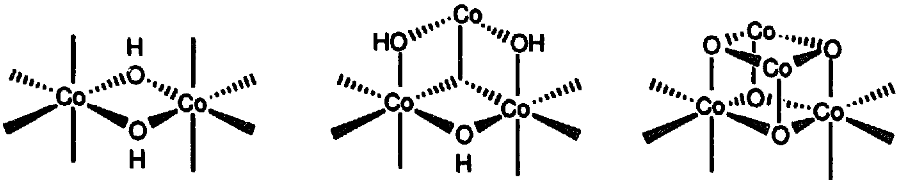


(31)

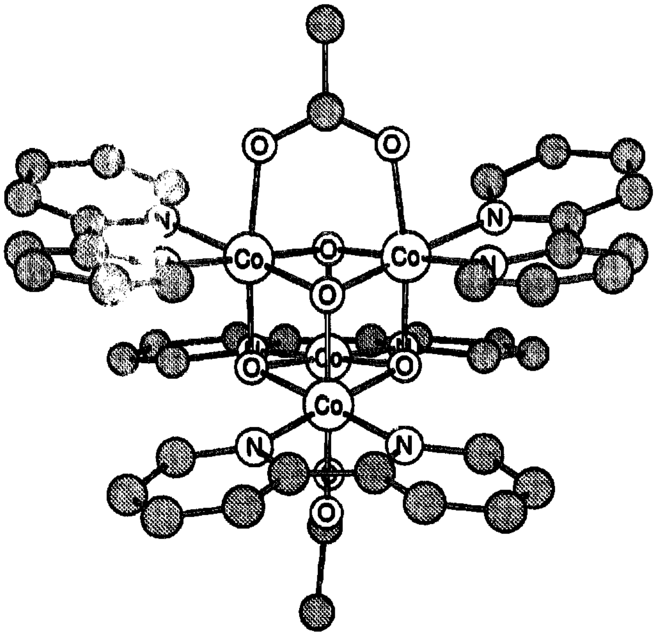
The reaction between $CoCl_2$, $[^nBu_4N]MnO_4$ and pyridine results in the novel complex $Co_2Cl_5(py)_5$ containing Co(III) and Co(II) [83]. The X-ray crystal structure of this species showed that it consists of a discrete octahedral cation, $[Co^{III}Cl_2(py)_4]^+$ and a tetrahedral anion, $[Co^{II}Cl_3(py)]^-$.

A series of complexes $[CoL_3(N_3)_3]$, where L = py, 4-amino-, 4-ethyl-, 4-methyl, 3-methyl-, 4-bromo-, 4-aldehyde-, 4-acetyl- and 4-cyano-py as well as Me, Et-nicotinate and isonicotinates has been prepared and characterized [84]. The X-ray crystal structures of *mer*-$[Co(py)_3(N_3)_3]$ and *mer*-$[Co(4\text{-}pic)_3(N_3)_3]$ been determined. In the complex cation 2,6-bis(aminomethyl)pyridine cobalt(III), the ligand is bis-tridentate in contrast to the corresponding Cu(II) complex [85].

The role of the Mn_4-unit in the process of photosynthesis is being widely studied. As part of such a study, Christou and coworkers [86] have investigated the formation of an analogous Co_4-structure. They have succeeded in isolating three complexes having 1, 2 or 3 cobalt atoms per molecule with skeletons (32) at their centres. The complex $[Co_2(OH)_2(OAc)_3(bpy)_2](ClO_4).H_2O$ (I) was first produced by the reaction of a $Co(OAc)_2$/bpy mixture with H_2O_2. From this mixture was also isolated $[Co_3O(OH)_3(OAc)_2(bpy)_3](ClO_4)_2$. Reaction of I with Li_2O_2 in dmso resulted in the formation of the complex $[Co_4O_4(OAc)_2(bpy)_4](ClO_4)_2$. The crystal structure of $[Co_4O_4(O_2CR)_2(bpy)_4](ClO_4)_2$ (RCO_2H = 4-methylbenzoic acid) has been determined and the cation (33) shows the cubane structure at its core.



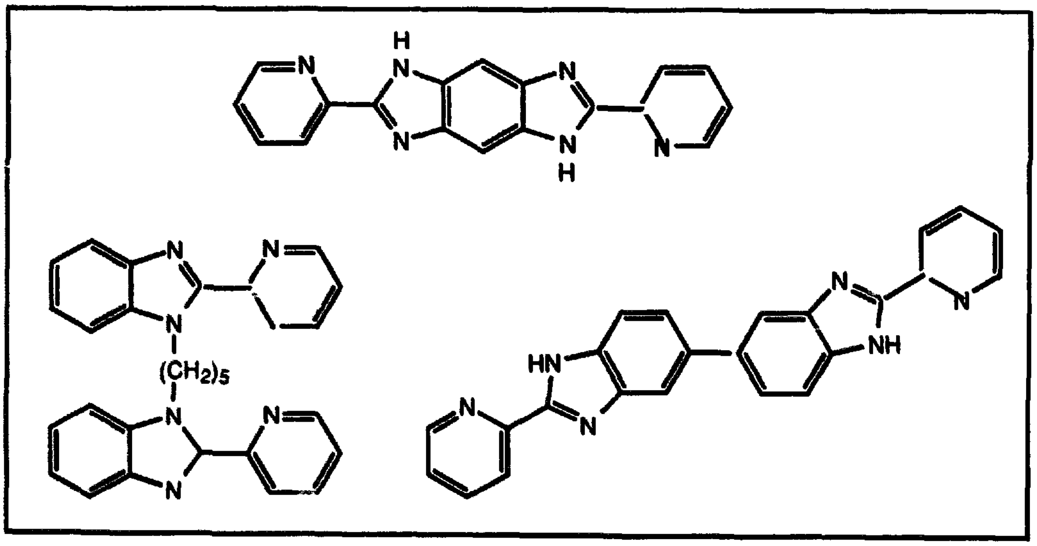
(32)



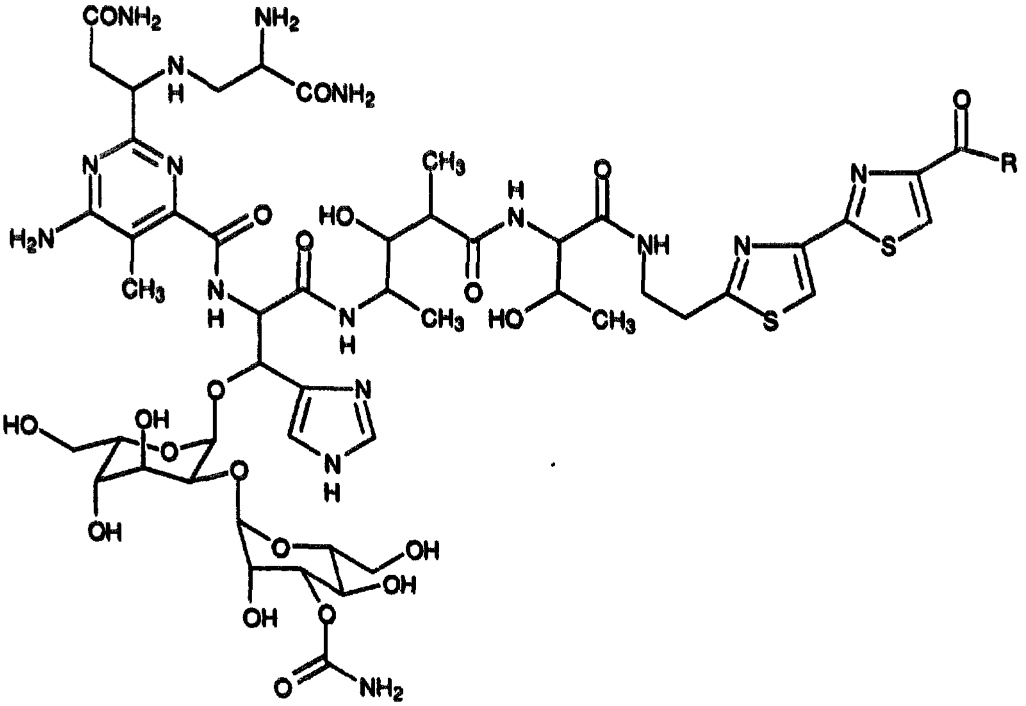
Only the ipso-C atoms of the 4-MeC_6H_4 are shown.

(33)

The photoinduced electron transfer reaction from Ru(II) to Co(III) has been studied in three complexes synthesized for the purpose [87]. These were all of the form $[(bpy)_2Ru(L\text{-}L)Co(bpy)_2](ClO_4)_5$ in which L-L has the structure shown in (34) for each one respectively. The rates of electron transfer determined were $k_{[1]} > 5 \times 10^{10}\ s^{-1}$, $k_{[2]} = 6 \times 10^{9}\ s^{-1}$ and $k_{[3]} = 1 \times 10^{8}\ s^{-1}$. The temperature dependence of the rates enabled a number of schemes for the electron transfer to be explored.

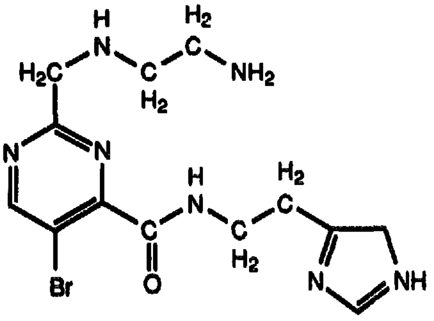


L-L (34)



(35)

Bleomycin (35) is an antibiotic which is used together with chemotherapy in the treatment of cancer [88]. An interesting feature of bleomycin is that iron and copper complexes are involved in DNA cleavage under aerobic conditions while cobalt(III) complexes show no DNA cleavage activity under these conditions and in fact only show DNA cleavage under the influence of UV light. In an effort to understand the mechanisms of these processes, Mascharak and coworkers have prepared models of bleomycin seeking to imitate the metal bonding section of the molecule delineated by the authors as in the above diagram. The ligand designed for this purpose was (36), HL, and the cobalt(III) complexes which were synthesized were $[CoL(H_2O)]X_2$, ($X = NO_3^-$ or ClO_4^-), $[CoL(N\text{-MeIm})](NO_3)_2.H_2O$ (*N*-MeIm = *N*-methylimidazole) and [CoLCl]Cl.EtOH. The X-ray crystal structure of the complex $[CoL(H_2O)](NO_3)_2$ (37) was determined. Like bleomycin these species cause DNA scission in the presence of UV radiation in the absence of dioxygen. The DNA cleavage reaction is attributed to the generation of $OH^•$ when the complex is attached to the DNA strand.



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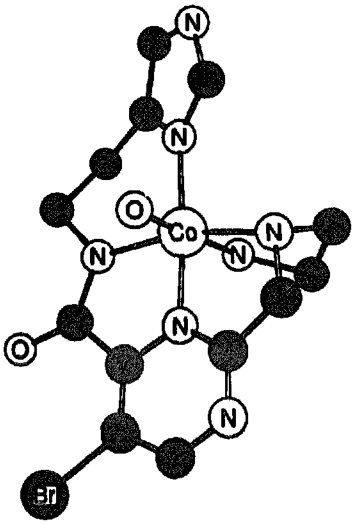
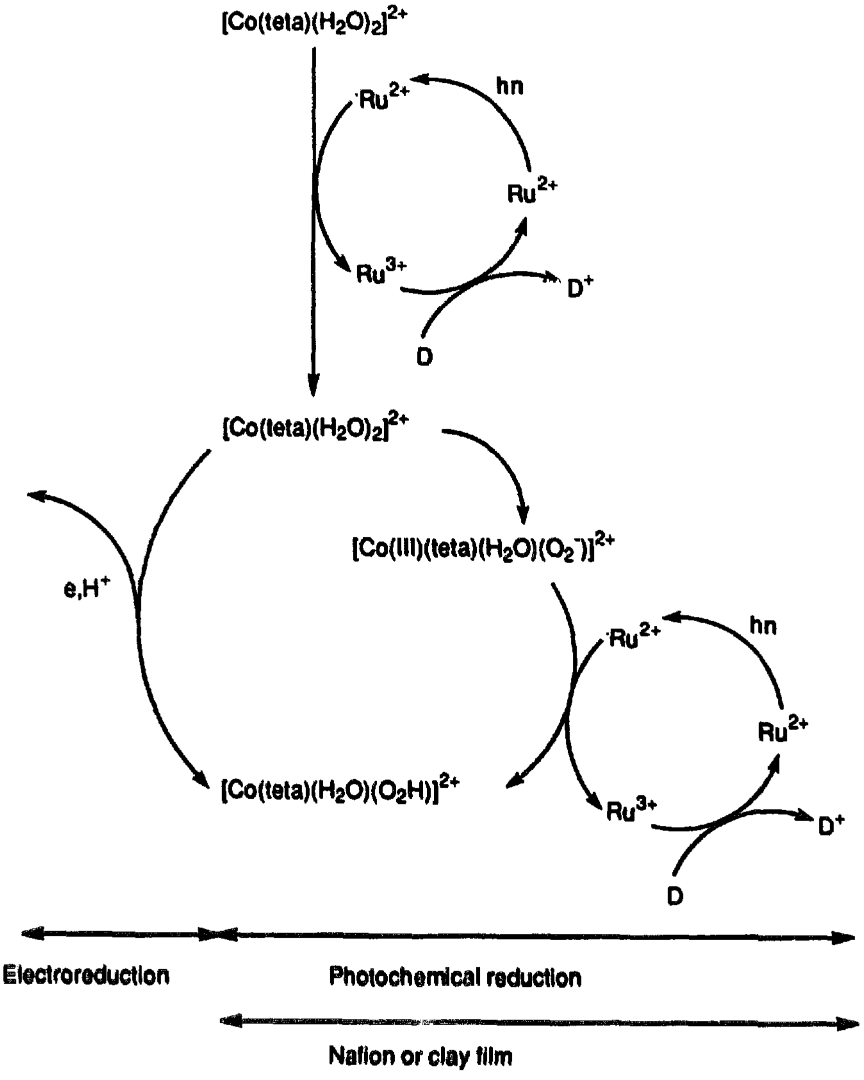


(37) *H atoms omitted*

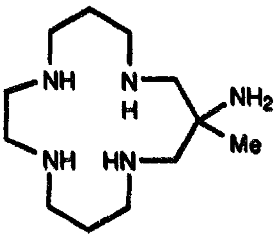
When a Nafion-$[Ru(bpy)_3]^{2+}$ coated electrode is dipped in $[Co(teta)(H_2O)_2]^{3+}$ {teta = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane}, hydrogen peroxide is produced and the yield of H_2O_2 is greatly increased by irradiation of the electrode from a xenon lamp [89]. The process involved in this increase in yield is suggested to be that shown in scheme (38). The macrocycle in the complex carbonato(*C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(III) is arranged in such a way as to produce a chair form for both of the six-membered rings, while the five-membered rings are in the skew form [90]. The structure of another carbonato complex of cobalt(III) has been determined *viz.* carbonatobis(1,10-phenanthroline)cobalt(III) perchlorate [91]. The Co-N bonds *trans* to the O atoms of the carbonate ligand are slightly longer than the *cis* bonds.



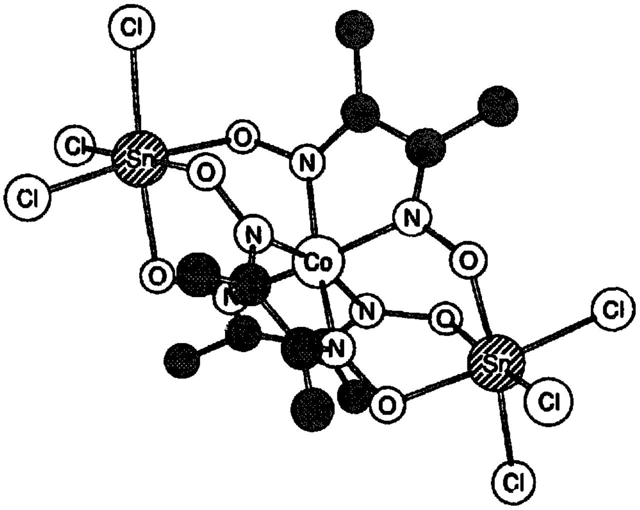
$Ru^{2} = [Ru(bpy)_3]^{3+}$ D = H_2O or ethylenediaminetetraacetic acid

(38)

The cobalt(III) complex of the macrocycle (39) $[Co(L)Cl]^{2+}$ has been prepared along with the corresponding Rh and Cr complexes [92]. A study of the base hydrolyses of these complexes shows that the activation volumes for the *cis*-Rh (+19.5 cm^3 mol^{-1}), *cis*-Co (+27.1 cm^3 mol^{-1}) and *trans*-Cr (+31.1 cm^3 mol^{-1}) complexes were in keeping with the conjugate base mechanism for the reaction.



(39)



(40) *H atoms omitted*

In the structure of *trans*-bis[dimethylglyoximato(1-)-*N*,*N′*]bis(pyridine-N)cobalt(III) [93] the two pyridine molecules occupy the axial positions of the cobaloxime distorted octahedron, while that of *trans*-[Co(Hdmg)$_2$I(py)] has I and py in the axial positions [94].

The structures of the clathrochelate acids H[CoD$_3$(SnCl$_3$)$_2$] in which D = the dianion of the corresponding dioxime have been ascertained by a variety of techniques including ^{119}Sn and ^{59}Co NMR and ^{119}Sn Mössbauer spectroscopies [95]. The oximes examined were glyoxime, methylglyoxime, dimethylglyoxime, α-benzyldioxime and nioxime. The X-ray crystal structure of H[CoD$_3$(SnCl$_3$)$_2$] (40) has also been obtained.

A series of papers has been published by Ohashi and coworkers investigating the effects of X-rays and UV-visible radiation on crystals of cobaloxime complexes. The dark red crystals of the complex [(*R*)-1-cyanoethyl]bis(dimethylglyoximato)pyrrolidine)cobalt(III) when irradiated by X-rays change their cell parameters while retaining crystallinity [96]. During this process the ordered cyanomethyl group changes to disordered racemates, a process which occurs despite the presence in the crystal of one molecule of water in the asymmetric unit which is hydrogen bonded to the cyanomethyl group. One of the polymorphs of the complex [(*S*)-1-cyanoethyl][(*S*)-phenylethylamine]cobaloxime is also racemized by exposure to X-rays [97] but also by visible light while retaining crystallinity. The other which has two molecules of water in an asymmetric unit is not reactive in these circumstances. The rates of racemization have been measured at four temperatures and it is demonstrated that the variation in the rate constant correlates with the size of the reaction cavity. The volume of the reaction cavity has also been invoked to explain the conformations of the cyanoethyl group in the three crystal forms, one produced by X-ray racemization and the other two from crystallization from different solvents [98], of the complex (*rac*-1-cyanoethyl)bis(2,3-butanedione dioximato)(pyrrolidine)cobalt(III). The crystal structures of the two forms produced by crystallization from different solvents were determined in this work. The crystal structures of the complexes [(*R*)-1,2-dimethoxycarbonylethyl]bis(dimethylglyoximato)(*R*)-phenylethylamine]cobalt(III) and [(*R*)-1,2-dimethoxycarbonylethyl]bis(dimethylglyoximato)(1-propylamine)cobalt(III) methanol solvate has been determined and this time there is no evidence for racemization of these complexes in either visible or X-ray radiation without the degradation of the crystal. It is suggested by the authors that the absence of a racemization process may be attributed to the small reaction cavity.

The kinetics of the reduction by iron(II) of a series of complexes, *trans*-$[\mathrm{Co(Hdmg)_2L(X)}]$, where L = pyridine, nicotinamide (na) or isonicotinamide (isna) and X = Cl, Br or I in solution in a 1% dmso/water mixture has been studied [99]. A mechanism is proposed involving a pre-protonation of $[\mathrm{Hdmg}]^-$ ligand. The rate constants were in the order $\mathrm{Cl} < \mathrm{Br} < \mathrm{I}$ and $\mathrm{py} < \mathrm{na} = \mathrm{isna}$.

A range of complexes of the type $[\mathrm{LCo((DO)(DOH)pn)Cl]PF_6}$ in which (DO(DOH)pn = N2,N2'-propanediylbis(2,3-butanedione)-2-imine-3 oxime and L = py, 4-CNpy, 4-$\mathrm{CH_3O}$py and 4-($\mathrm{Me_2N}$)py and $[\mathrm{(py)_2Co(DO)(DOH)py}]$ [100] have been prepared.

Out of 17 cyano(ligand)cobaloximes in which the ligand varied from thiocyanate through a number of substituted pyridines, substituted anilines to ammonia, 14 show an excellent linear relationship between the $^{15}\mathrm{N}$ chemical shifts and the $^{13}\mathrm{C}$ chemical shifts [101]. These observations and others between chemical shifts and infrared absorptions and the basicity of the *trans* ligand lead the authors to conclude that there is significant amount of π-bonding involved in the Co-CN bond in these complexes.

The oxidation of cobalt(II) sepulchrate by copper(II) ions in aqueous solution is accelerated by the presence of both chloride ion and imidazole, but not by acetonitrile [102]. The acceleration is believed to be due to the formation of species of the form [Cu(II)Ln] which are also active as oxidants of the cobalt species. The data are explained by a reaction scheme such as that shown in (**41**). The reactions are considered to be outer sphere and Marcus theory is used to calculate self exchange rate constants. This allows the authors to conclude that the increase in rate produced by the presence of chloride ions arises from the enhanced driving force and the reduced charge for the $\mathrm{Cu(II/I)(Cl)_n}$ complexes. The process is complicated by the formation of copper metal and dioxygen had to be used as a scavenger for $\mathrm{Cu^+(aq)}$.

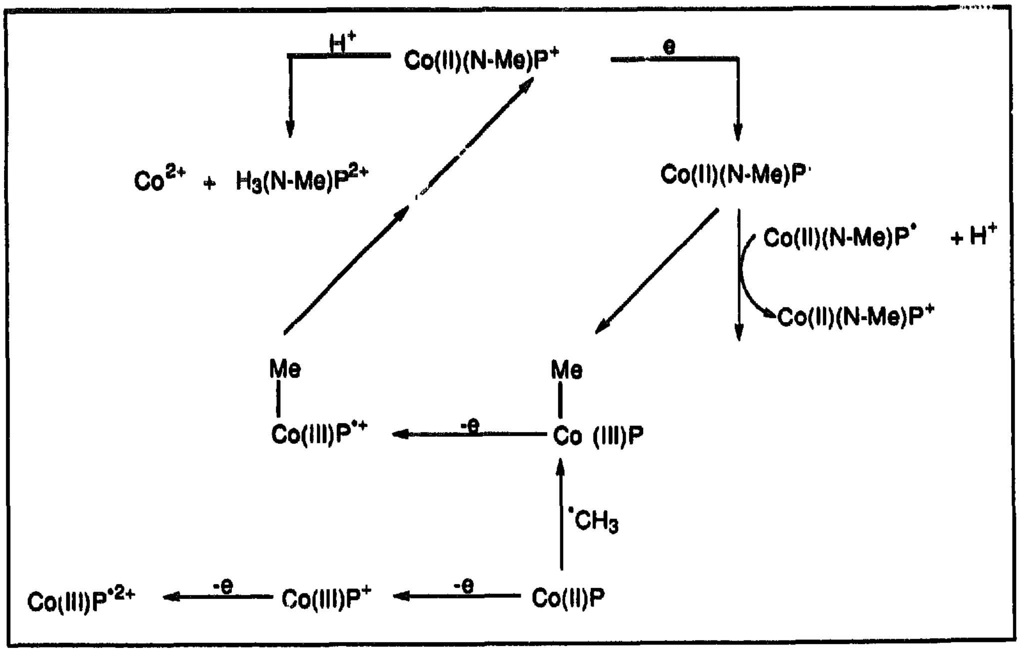
$$\left.\begin{array}{l}\mathrm{Cu(II)(L)_n + Co(sep)^{2+} \rightarrow Cu(I)(L)_n + Co(sep)^{3+}} \\ \mathrm{Cu(I)(L)_n + Co(sep)^{2+} \rightarrow Cu^0 + nL + Co(sep)^{3+}} \\ \mathrm{Cu(II)(L)_n + Cu^0 + nL \rightarrow 2Cu(I)(L)_n}\end{array}\right\} \quad (41)$$

The power of Fourier transform infrared spectrometry to go where dispersive infrared is unable is demonstrated by the application of this technique to the study of electrochemistry in a thin layer (10 -100 μm) of solution confined between an infrared transparent window and a platinum electrode [103]. The complexes studied were the Mn, Fe and Co complexes of 5,10,15,20-tetraphenylporphyrin. The spectra were obtained between about 1600 and 1000 $\mathrm{cm^{-1}}$. It was found that the cobalt(II) complex was oxidized in two steps, first forming the cobalt(III) species followed by the cobalt(III) π-cation radical complex. This type of study allows the possibility of distinguishing between ligand and metal ion-centred oxidation. Electron transfer from various substituted hydroquinone dianions to [Co(TPP)] in MeCN has been studied [104].

The temperature- and axial-ligand dependences of the EPR spectra of the cobalt tetraphenylporphyrin and octaethylporphyrin cation radicals have been re-examined [105]. The data show that there is significant mixing of the A_{1u} and A_{2u} states in the ground state and that the A_{2u} state contribution is increased as the axial ligand field increases. For the complex $[Co(II)OEP]^{\bullet+}$, Br^-, Cl^- and CN^- in the axial position produced line broadening attributed to locally excited triplet mixing.

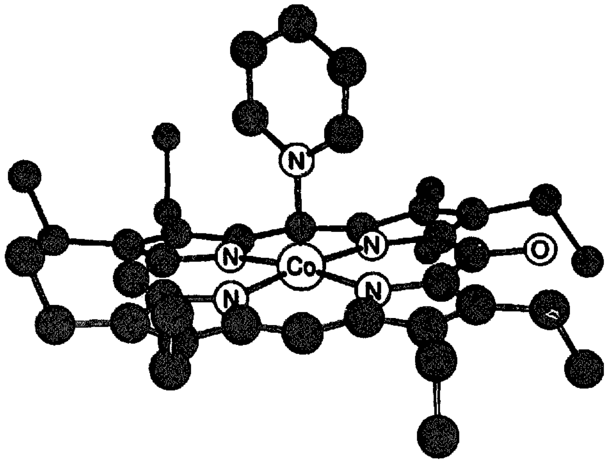
The sensitivity of ^{59}Co NMR spectra to small changes in the electric field near the metal in cobalt(III) porphyrins is illustrated in a study [106] which has been carried out on a number of sterically congested complexes of the type $[Co(por)(RIm)_2]^+$ in which RIm = imidazole or 1-methylimidazole and por = the dianion of tetramesitylporphyrin or tetrakis(2,6-dichlorophenyl)porphyrin (H_2TDCPP). The fact that there were *ortho* substituents such as the *ortho* chloro or methyl groups on the *meso* phenyl groups had a large effect on the line widths and the chemical shifts. The X-ray crystal structure of the complex $[Co(TDCPP)(1\text{-}MeIm)_2][BF_4]$ was also determined (monoclinic, $P2_1/n$, $a = 12.229$, $b = 21.344$, $c = 21.227$ Å, $\beta = 105.50°$, $V = 5339$ Å^3 and $Z = 4$) and this provided information about the steric effects observed in that the presence of the *ortho* chloro-groups in the structure blanked off the area above and below the porphyrin structure. The X-ray structure also served to provide an explanation for the fact that the effect of solvent on the NMR spectra is significantly different in the case of this hindered structure from that in unhindered structures in that solvation close to the metal does not readily occur because of the hindering groups.

γ-Radiolysis has been used to study the stable products of the reduction of [*N*-methyltetrakis(4-sulfonatophenyl)porphinato]cobalt(II) [Co(II)(*N*-Me)P] and its nickel(II) and copper(II) analogues [107], while the rates of formation and reactions of intermediates have been determined using pulse radiolysis. The product of the reduction was found to be [MeCo(III)P]· From this and the pulse radiolysis data, the overall progress of the reaction is proposed to be that shown in (**42**).

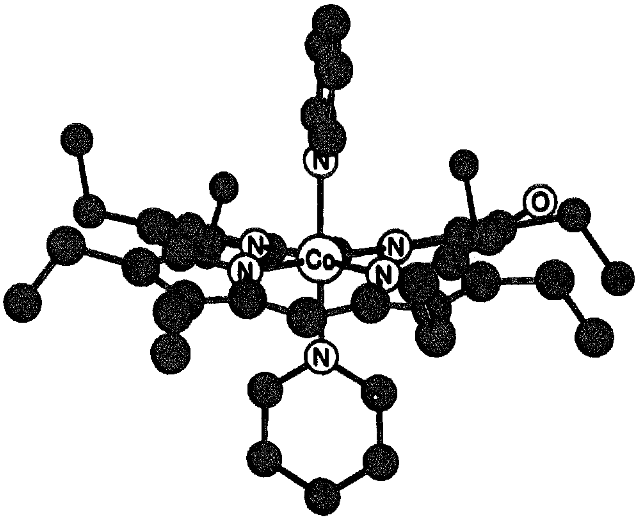


(**42**)

The bent apical nitroso group in the square pyramidal complex [Co(^{15}NO)(TPP)] in the solid state has been found using ^{15}N CPMAS NMR spectroscopy to be moving in a way which has been interpreted as a "swinging motion" [108]. The X-ray crystal structure of the deep orange 5-coordinate Co(II) complex of octaethyloxophlorin, [(py)Co(II)(OEPOH).py] (43).py has been determined along with that of the lime-green 6-coordinate Co(III) complex, [(py)$_2$Co(III)(OEPO)] (44) [109]. A series of complexes of basket handle porphyrins containing short *p*- or *m*-phenylenedimethylenedioxy chains of cobalt(II) and zinc(II) have been prepared and characterized spectroscopically and electrochemically showing significant distortion of the porphyrin skeleton [110].

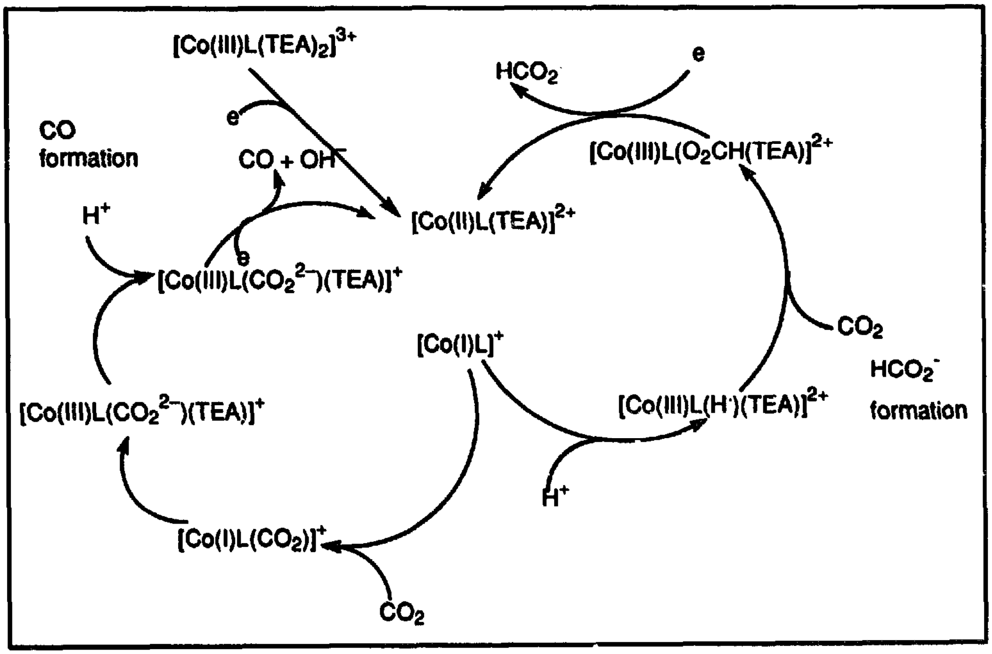


(43) *H atoms omitted*



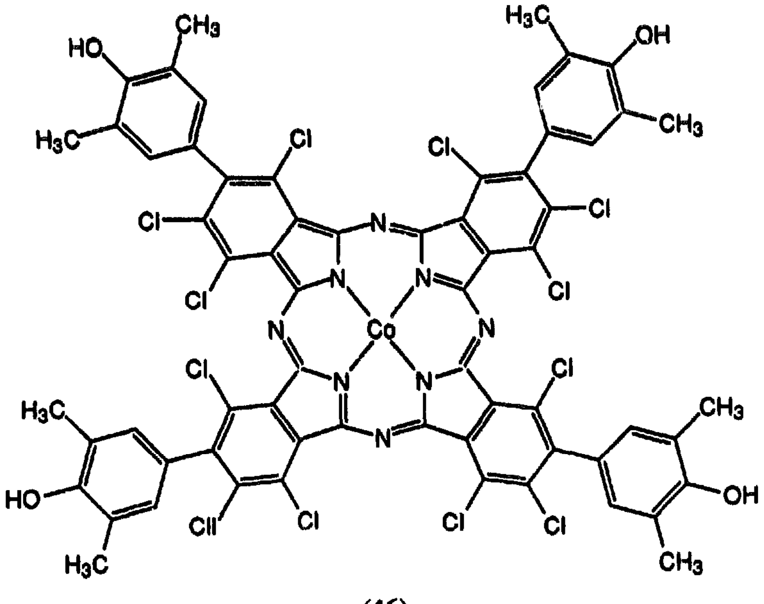
(44) *H atoms omitted*

Cyclam and related ligand complexes of cobalt(III) act as mediators for the highly efficient electron transfer involved in the photoreduction of CO$_2$ when *p*-terphenyl (OPP-3) is a photocatalyst and certain tertiary amines such as triethanolamine act as sacrificial electron donors in methanol/acetonitrile solution [111]. The stabilization of OPP-3 is enhanced by smooth electron transfer from [OPP-3]$^{\bullet-}$ to the cobalt(III) or (II) cyclam complex. The quantum yield in the presence of triethanolamine (TEA) of $CO/[HCO]^{2-}$ was 0.25 at 313nm. The selective reduction of CO_2 to CO benefits from the formation of intermediate species such as $[Co(I)L(CO_2)]^+$. A possible mechanistic cycle is shown in (45).



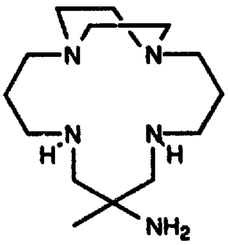
(45)

A spectrochemical study of the cobalt(II) tetraphenol-substituted phthalocyanine (46) showed that this organic soluble complex shows redox properties relating both to the metal ion and the ligand [112]. The yellow Co(I) and the pink reduced phthalocyanine complexes were observed on reduction, while the green Co(III) and red-brown oxidized phthalocyanine species were produced on oxidation.



(46)

The spectroelectrochemistry and electrochemistry of the complex (OMC)Co(PPh_3), (H_2OMC is 2,3,7,8,12,13,17,18-octamethylcorrole) in a range of solvents [113] shows the presence of three oxidations, which are reversible at rapid cyclic voltammetric scan rates and which involve the oxidation of the ligand system and two reductions which involve reduction of the metal ion and dissociation of the PPh_3 Co(III) complex which is 5-coordinate while the Co(II) complex is 4-coordinate though the situation varies according to the solvent used. The first examples of *meso*-substituted corroles in the forms of [triphenylphosphine(2,3,7,8,12,13,17,18-octamethyl-10-phenylcorrolato)cobalt(III)] and [triphenylphosphine(2.3,7,8,12,13,17,18-octamethyl-5,10,15-triphenylcorrolato)cobalt(III)] have been prepared and characterized, and each maintains a square planar corrole [114].



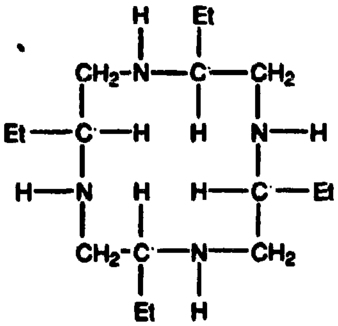
(47)

The ligand L (47) is one of a series of so-called reinforced macrocycles and it has a pendant amine group which is available for coordination with the metal [115]. Hancock and coworkers have prepared the complex [CoL(Cl)][$CoCl_4$].H_2O and determined its X-ray crystal structure. The complex forms green-black crystals (space group P21/c, $a = 8.778$, $b = 13.344$, $c = 19.380$ Å, $\beta = 98.48°$ and $Z = 4$). The structure does indeed show the amine nitrogen to be coordinated to the cobalt which is at the centre and coplanar with the other nitrogens of the ligand. The other position is occupied by the chloride. The coordination sphere is considerably distorted. The application of molecular mechanics to this structure succeeded in reproducing the distorted structure rather well, except for the Cl-Co-N bond angles; however, these are improved by using a different force constant for Cl-Co-N The C-C-C bond angles of the chelate rings were also not so accurately reproduced, since these too are considerably distorted from normal values. The authors suggest that this is due to disorder in the structure. The large thermal motion is suggested as being due to the presence of both boat and chair conformers of the six membered chelate rings, since the difference in the energy of these was found to be quite small. A study of the crystal structures of the complexes involving the cation (1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane[illegible]) with anions [ClO_4]$^-$, [S_2O_3]$^{2-}$ or Cl^- has been used to investigate conformation and packing in the crystals [116].

Very stable 1:1 "super-complexed" species have been demonstrated [117] using potentiometric and electrochemical methods between the complex anions, [$Fe(CN)_6$]$^{4-}$ and [$Co(CN)_6$]$^{3-}$ and the macrocyclic polyazaalkanes, 1,4,7,10,13,16,19-heptaazacyclohenicisane, 1,4,7,10,13,16,19,22-octaazacyclotetracosane and the open-chain species, 1,17-bis(methylamino)-3,9,12,15-pentaazaheptadecane and 1,20-bis(methylamino)-3,6,9,12,15,18-hexaazaicosane. The stability of the complexes formed are higher for the cyclic ligand than for the straight chain ligands.

The relationship between the topologies of the receptor and substrate species appears to be an important factor in the formation of these species.

The X-ray crystal structure of the complex 1,4,7,10,13,16-hexaazacyclooctadecane-cobalt(III) trichloride, *meso*-[Co(hexaen)]Cl_3 at 106 K has been shown to confirm the NMR spectroscopic assignment [118]. The electron density distribution in the complex showed that the aspherical 3d electron density was that expected for a low-spin complex. In the complex *meso*-chloro(1,4,7,11,14-pentaazacycloheptadecane)cobalt(III) chloride perchlorate [119] the nitrogen donor atoms are arranged in a distorted octahedron around the cobalt and the chiral nitrogen centres are in the conformation 1*RS*, 7*SR*, 11*SR*, 14*RS*. In order to throw light on the structure of one of the products of the reaction between $CoBr_2$ and the ligand (2*R*,5*R*,8*R*,11*R*)-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclodecane (L) (48), the structures of the complexes which are formed by reaction of the complex with the amino acids alanine (alaOH) and threonine (thrOH) have been studied using X-ray diffraction [120]. These complexes were found to be *cis* octahedral with the amino acid coordinated in a didentate fashion through oxygen and nitrogen. The configurations of the four asymmetric nitrogen atoms in the complexes were *RSRS*.



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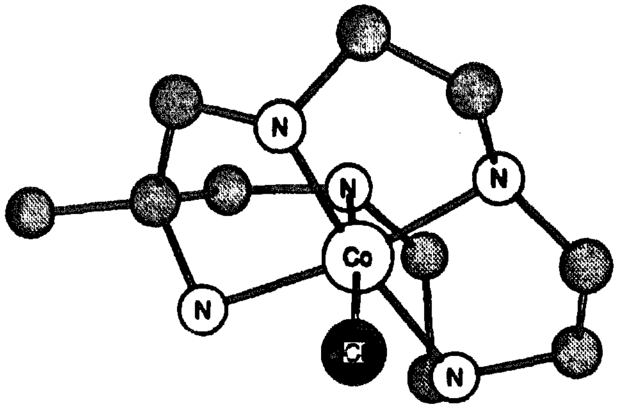
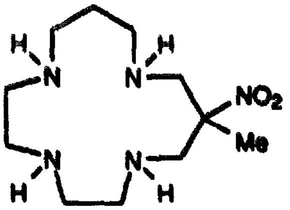


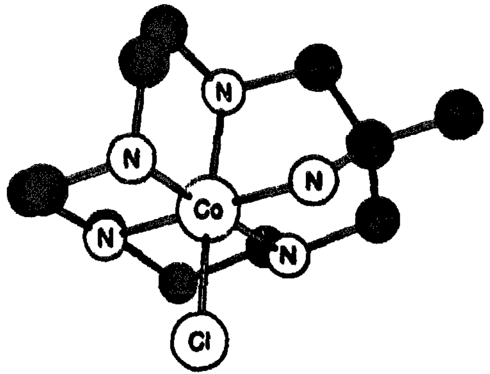
(49)

Reaction of the ligands (L1) (12-methyl-1,4,7,10-tetraazacyclotridecan-12-amine), (L2) (6-methyl-1,4,8,11-tetraazacyclotetradecan-6-amine) and (L3) (10-methyl-1,4,8,12-tetraazacyclopentadecan-10-amine) with aqueous cobalt(II) in the presence of activated charcoal and air followed by addition of HCl result in the formation of the *cis* complexes $[Co(L)Cl]^{2+}$ [121]. The single crystal X-ray structure of [Co(L2)Cl][ClO$_4$] gave the structure shown in (49). The structures of the other two complexes were also determined. The ligand is quinquedentate with the pendant primary amine and the two adjacent secondary amines occupying an octahedral face. The Cl is *cis* to the primary amine; *RRSS*-stereochemistries characterize the geometry of the secondary amines in the complex.

The *trans* isomers of the ligands L2 (3-methyl-1,5,9,13-tetraazacyclohexadecan-3-amine) and L3 (6-methyl-1,4,8,11-tetraazacyclotetradecan-6-amine) have also been isolated. The X-ray crystal structures of both of these species were determined [122]. The complex *trans*-[Co(L2)Cl][ClO$_4$]$_2$ belongs to the monoclinic space group (P21/c, $a = 9.107$, $b = 16.448$, $c = 13.898$ Å, $\beta = 99.16°$). The complex *trans*-[Co(L3)Cl][ClO$_4$]$_2$ belongs to the same space group but has the parameters $a = 16.868$, $b = 7.531$ and $c = 20.51$ Å, $\beta = 126.61°$. From molecular mechanics calculations it is deduced that the *cis*-L2 complex is 4.4 kJ mol^{-1} more stable than the corresponding *trans*-complex. The kinetics of the base hydrolysis of the three complexes was also studied. The usual SN1CB mechanism is assumed. There was a correlation for the *cis*-complexes between the observed rate constants and the macrocycle ring size and also the Co–Cl bond length suggesting that the ground state was an important factor in the hydrolysis reaction. In the case of the *trans* complexes, there was found to be a degree of insensitivity to changes in the ligand framework. Using $H_2N(CH_2)NH(CH_2)_2NH(CH_2)_3NH_2$, a copper(II)-directed synthesis of the asymmetrically substituted tetraazacyclotetradecane (50) has been carried out [123]. The X-ray crystal structure of the cation in the complex, *cis*-[CoL1(Cl)][ClO$_4$]$_2$ containing NH$_2$ instead of NO$_2$ is shown in (51). As in the previous cases the rapid rate of base hydrolysis is reflected in the rather long Co–Cl bond.



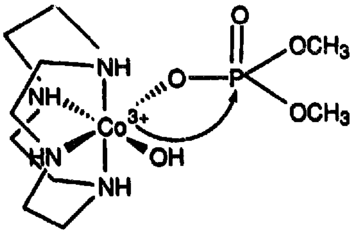
(50)



(51) *H atoms omitted.*

The reaction of cobalt(II) chloride with the ligand, HL (13-amino-13-methyl-1,4,8,11-tetraazacyclotetradecane-6-carboxylic acid) in air produced two complexes, the red *cis*-[CoL(Cl)][ClO$_4$]$_2$ and the orange *cis*-[CoL(H$_2$O)][ClO$_4$]$_3$ [124]. The X-ray crystal structure of the former was determined. The chloride was found to be *cis* relative to the pendant amine and the 4 secondary amines were coordinated in a folded geometry with *RRRR*-stereochemistry. The pendant carboxylic acid was not coordinated. When the above reaction mixture was heated with activated charcoal for 5 hours the complex *trans*-[CoLH][ClO$_4$].H$_2$O was produced, in which the ligand , L was now hexadentate with the pendant amine and carboxylic acid in the *trans* positions around the cobalt.

The complex $[(cyclen)Co(OH_2)_2]^{3+}$ has been found to hydrolyse dimethyl phosphate at 60°C with a rate constant of 6.2×10^{-7} M^{-1} s^{-1} [125] unlike $[(tren)Co(OH_2)]^{3+}$ which shows no tendency to hydrolyse the phosphate even after keeping at 100° C for a month. The reaction was followed by using ^{31}P and proton NMR spectroscopy. The mechanism proposed is (52). The same group has also studied the reaction sequence shown in (53) and the equilibrium constant (0.4 ± 0.1 M^{-1}) for the first stage was determined by using ^1H NMR spectroscopy; the second order rate constant for the second step was found to be $7.2 \pm 0.4 \times 10^{-5}$ M^{-1} s^{-1} [126]. The reaction proceeds at a measurable rate only as the pH approaches the pK_a of the water ligand. It is concluded that it is the hydroxide coordinated to the metal ion that produces the increased rate of hydrolysis.



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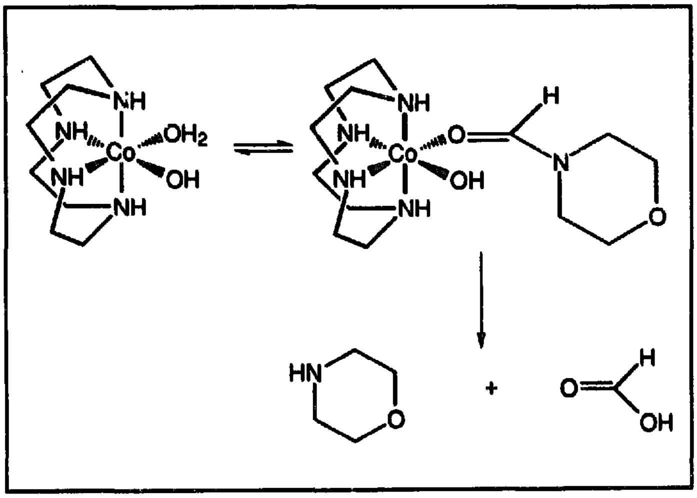
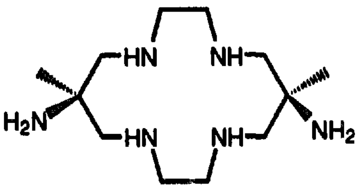


(53)

The yellow cobalt(III) complex of the macrocyclic ligand, *cis*-diammac (54) has been synthesized [127] along with its chromium(III) and nickel(II) analogues. The structure is compared with that of the corresponding *trans* complex and is found to be different — for example, the characteristic short M-N bond forced upon the *cis* complexes is not present in the *trans*-species.



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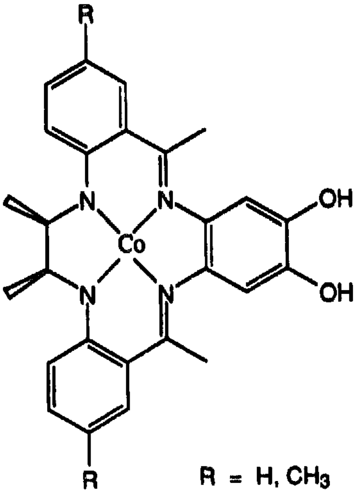
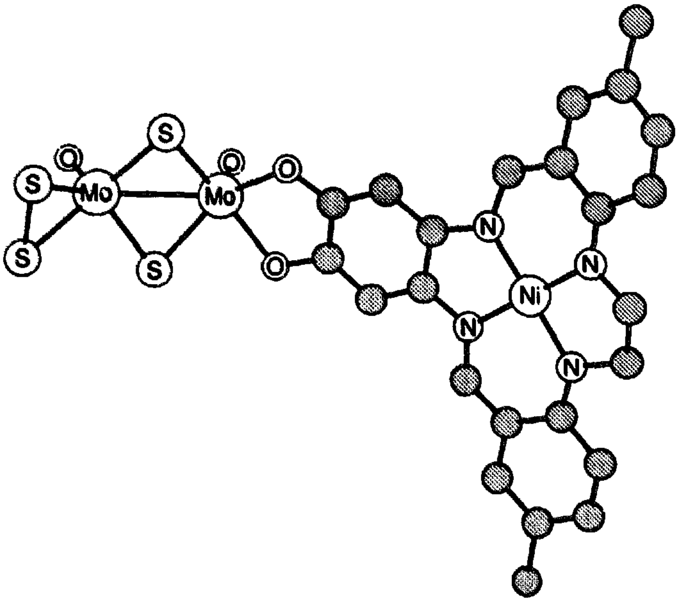


R = H, CH_3

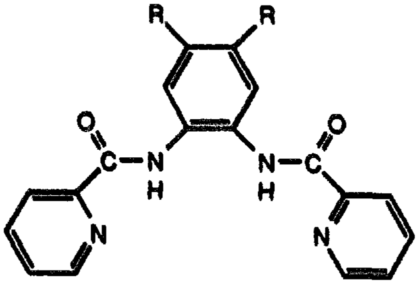
(55)

The complex (55) [128] containing a catechol group has been synthesized together with the dimeric antiferromagnetically coupled semiquinone derivatives. The structure of the cobalt(II) complex has been inferred from marginally insufficient X-ray data which are compared with the more accurate Ni(II) X-ray data. In a follow-up to their previous paper, Coucouvanis and coworkers have reacted the complex CoETC (above) in the presence of [^{n}Bu$_4$N]OH with the complex [(dmf)$_3$Mo$_2$O$_2$S$_2$(S$_2$)] to produce black crystals of [{CoETC}{Mo$_2$O$_2$S$_2$(S$_2$)}]$^{2-}$ [129]. The X-ray crystal structure of the corresponding Ni(II) complex (56) is reported.



(56)

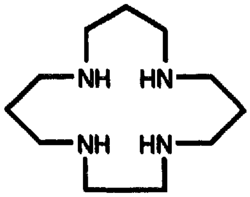
Cobalt(III) complexes of the ligands [bpb]$^{2-}$ and [bpc]$^{2-}$ (57) with a variety of axial ligands have been synthesized and shown by ^{1}H NMR spectroscopy to have a *trans*-geometry. A spectroelectrochemial study has been carried out, demonstrating the irreversible Co(III)/Co(II) couple [130].



(57)

H$_2$bpb, R = H

H$_2$bpc, R = Cl



(58)

The complex *trans*-[CoL(im)$_2$]ClO$_4$ in which L is (58) has been prepared and characterized [131].

Salts of $[Co(NH_3)_6]^{3+}$ have been used as oxidants for [2Fe-2S] isoferredoxins, FdI and FdII from spinach, parsley and *Anabaena variabilis* [132]. All the reactions showed saturation kinetics and are consistent with the scheme:

$$Fe(II)Fe(III) + Co(III) \rightleftharpoons Fe(II)Fe(III),Co(III) \qquad K$$

$$Fe(II)Fe(III),Co(III) \rightarrow Fe(III)_2 + Co(II) \qquad k_{et}$$

In fact, for the cobalt complex there was very little variation of either K or k_{et}. Using a tunnelling pathway model the authors have identified the most favoured electron transfer pathway in the system. In another related study application of the Marcus theory to the cross reactions of *Anabaena variabilis* plastocyanin and azurin with $[Co(phen)_3]^{3+}$ did not give self exchange rate constants in agreement with that obtained for reaction of ACu(I) with PCu(II) [133]. The cation $[Co(phen)_3]^{3+}$ has also been used as one of the oxidizing agents in a study of the reactions of five spinach plastocyanin PCu(I) mutants [134]

The kinetics of reduction of spinach plastocyanin and horse heart cytochrome c by Λ and Δ-$[Co((N(CH_3)_2\text{-sar})]^{4+}$ show significant stereoselectivity [135]. The reaction of $[Co\{(NH_2)_2\text{-sar}\}]^{2+}$, however, shows no stereo-selectivity. An extensive discussion is provided for use of cage complexes as metalloprotein redox mediators.

1.1.2 Complexes with oxygen donor ligands

The kinetics of the formation of the complex cation, $[Co(H_2PO_4)(H_2O)_5]^{2+}$ has been studied by following the reaction of $H_2PO_4^-$ and H_3PO_4 with $[Co(H_2O)_5]^{3+}$ over a range of acidities and ionic strengths [135,136]. As would perhaps be expected, the rates of reaction are of the order of 10^4 faster than for the reaction of the same species with $[Co(NH_3)_5(H_2O)]^{3+}$. The reactive species was found to be $H_2PO_4^-$.

In a study of the kinetics of the oxidation of arsenious acid by 12-tungstocobaltate(III) ion the stoichiometry of the reaction of 12-tungstocobaltate(III) ion with arsenious acid has been shown to be [137]:

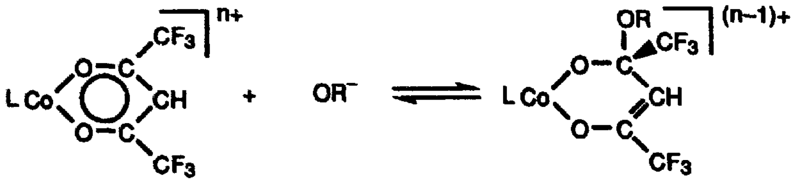
$$2[Co(III)W]^{5-} + H_3AsO_3 + H_2O \rightarrow 2[Co(II)W]^{6-} + H_3AsO_4 + 2H^+$$

The kinetics of the reaction are consistent with the rate law:

$$k_{obs}=2(k+k_1K_a[H^+]^{-1})[H_3AsO_3]$$

in which k and k_1 are rate constants for paths involving the species $As(OH)_3$ and $[AsO(OH)_2]^-$ respectively and K_a is the ionization constant for arsenious acid. Ion pairs involving the cobalt(III) moiety and the cations present are implicated in the reaction.

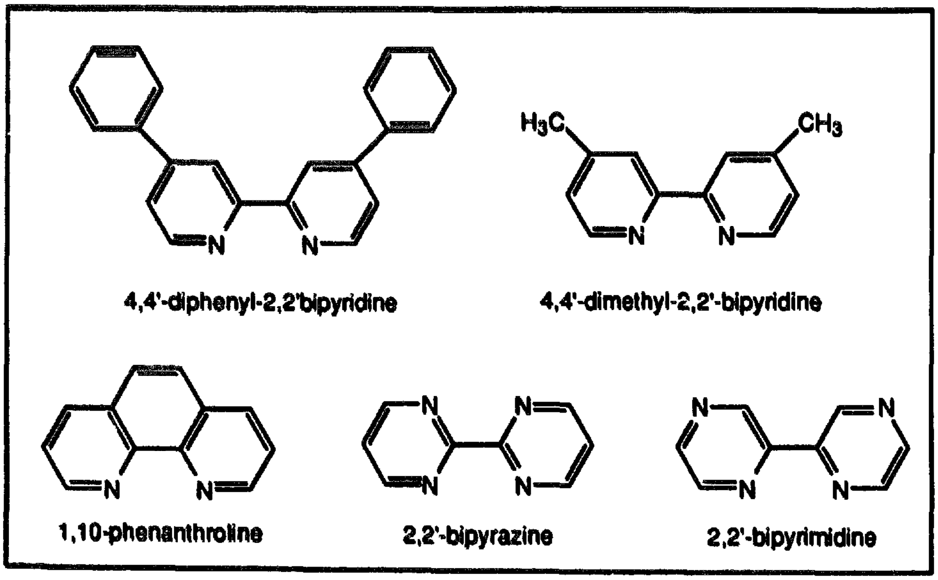
A range of 15 complexes of the form $[Co(hfac)]ClO_4$ have been investigated [138] to examine the pH dependent colour change which occurs in water or in methanol; pK_{OH} was in the range –7.4 to –4.8, and pK_{OMe} in the range –8.4 to –4.2. The reaction involved is shown in (59).



(59)

When some tris(β-ketoenolato)cobalt(III) complexes are treated with protic acids such as trifluoroacetic acid [139] the ESR spectra indicate that an electron transfer process has taken place giving a wide range of radicals depending on the nature of the β-ketoenolate. Thus, for example, the ESR spectrum of the complex $[Co(dbm)_3]$ (dbm = dibenzoylmethane) at –30°C shows a free radical in which spin delocalization is confined to one of the phenyl rings; on raising the temperature to –10°C, delocalization over all the ligand occurs. Many other examples are given of this phenomenon.

The solubilities and solvation of a range of β-diketonates including $[Co(acac)_3]$ and $[Co(acac)_2]$ have been determined in a variety of mixed water/organic solvents [140]. The data were interpreted in terms of solvation and preferential solvation by water and organic cosolvents. The molecular structures of a number of complexes of the type $[Co(acac)_2\{(CH_3)XCH_2CH_2NH_2\}][ClO_4]$, where X = N, P or As showed an arrangement around the cobalt which is a distorted octahedron made up of the O atoms from the acac, N and X [141]



4,4'-diphenyl-2,2'bipyridine

4,4'-dimethyl-2,2'-bipyridine

1,10-phenanthroline

2,2'-bipyrazine

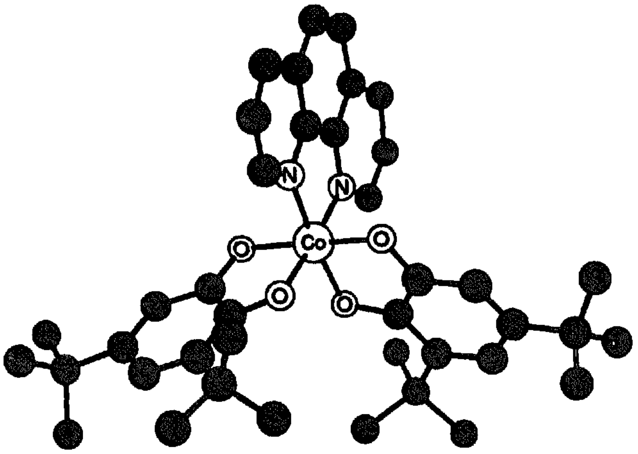
2,2'-bipyrimidine

(60)

$$[Co(II)(bpy)(3,5\text{-}DTBSQ)_2] \rightleftharpoons [Co(III)(bpy)(3,5\text{-}DTBSQ)(3,5\text{-}Cat)]$$

(61)

By preparing a series of complexes of the general type [Co(N-N)(3,5-DTBSQ)] in which N-N is one of the systematically varied ligands (**60**) and DTBSQ is 3,5-di-*tert*-butyl-1,2-benzoquinone, it has been found that the reaction typified by (**61**) can be controlled to occur at a variety of different temperatures [142]. Furthermore this "tuning" of the ligand structure allows the preparation of compounds in which this process occurs in crystals of the complex. Thus the toluene solvate complex [Co(phen)(3,5-DTBSQ)$_2$].$C_6H_5CH_3$ (**62**).$C_6H_5CH_3$ was found to be the first complex shown to undergo this reaction in the solid state, the reaction occurring at 220-260 K. This is clearly shown by the X-ray crystal structures of (**62**) determined at 238 K and 173 K.



(**62**) at 173 K; *H atoms omitted.*

A range of complexes of the form $[Co(tp)_2(Me_n\text{-}en)]^+$ (n=1 to 4, Me$_n$-en = methyl substituted ethylenediamine) containing the tropolonate ion (tp) as ligand have been prepared and the crystal structures of two of them determined [143]. The crystal structures of $[Co(tp)_2(Me_2\text{-}en)][ClO_4]$ and $\Lambda(R)\Delta(S)$-$[Co(tp)_2(Me\text{-}en)][ClO_4]$ were obtained and these data support the argument that the increase in the value of E° for Co^{3+}/Co^{2+} from -0.31V for $[Co(tp)_2(en)]^+$ to -0.09V for $[Co(tp)_2(Me_4\text{-}en)]^+$ is due to steric effects involving the $-N(CH_3)_2$ group. Another interesting result is that for these complexes there is a large increase (up to 10^3 times) in the hydroxide catalysed deuteration of the coordinated amine nitrogen atoms for these complexes compared with similar acac complexes.

The X-ray crystal structures of $[Co(pyo)_6][CoCl_4]$, $[Co(pyo)_6]I_2$ (where pyo = pyridine *N*-oxide), and $[Co(Me_3NO)_4]I_2$ have been determined [144]. The complexes $[Co(pyo)_6][CoX_4]$ form an isomorphous series when X = Cl, Br or I, although the iodo complex decomposes to form $[Co(pyo)_6]I_2$ in solution. The ionic nature of the complexes was confirmed; there is an octahedral arrangement around the cobalt centre in the pyo complexes and a distorted tetrahedral pattern in the case of the Me_3NO complexes.

Polarized single crystal Raman spectroscopy affords information which may be used to obtain unambiguous assignments of vibrational modes. Unexpectedly, in a study of the single crystal Raman spectroscopy of α–alums $CsM(SO_4)_2.12H_2O$ (M = Co or Ir) between 275 and 1200 cm^{-1} [145] it was found that the symmetric stretch of MO_6 was found to have a higher wavenumber for M = Ir (554 cm^{-1}) than for M = Co (548 cm^{-1}) in spite of the smaller size of $[Co(aq)]^{3+}$. This highlights a difference for the first row elements compared with the second and third row elements.

1.1.3 Complexes with nitrogen-oxygen donor ligands

The complexes $\Delta\Lambda[Co(aet)(en)_2][ClO_4]$ and Δ-$Na[Co(edta)].3H_2O$ or $Na_2(D\text{-}tart).2H_2O$, where aet = 2- aminoethanethiolate(1-), and D-tart =(*RR*-tartrate(2-) were crystallized together and the Δ aet complex always appeared in the first crop [146]. The ternary solubility isotherms were determined. The mechanism of the process is interpreted as involving a shift of the eutectic point from the racemic line into the optically active region and this is caused by the active co-solute. The authors conclude that for successful optical resolution in the conditions observed here the complex to be resolved must show conglomerate crystallization and the above shift of the eutectic point must occur and the larger the shift the better the resolution. The crystal structures have also been determined of the racemic crystals of K[*cis*-α-$Co(edda)(NO_2)_2].H_2O$, space group P_1 and the conglomerate crystals of K[*cis*-α-$Co(edda)(NO_2)_2$ also produced, orthorhombic space group P212121 [147]. The absolute configuration of the racemate is K[*cis*-α-Λ-(δλδ)-$Co(edda)(NO_2)_2].H_2O$. Both the conglomerate and the racemate form infinite strings, which in the case of the former are such that pairs of strings have opposite helical chirality while in the racemate, the strings are homochiral.

The four geometrical isomers of the complex $[Co(edma)(NH_3)(en)]^{2+}$, where edma = ammine(ethylenediamine)(ethylenediamine)-*N*-acetate, have been prepared [148] and the complexes with the edma facially chelated were resolved into optical isomers. NMR and CD spectroscopies used to determine the geometrical structures, but the X-ray crystal structure of one of the isomers was determined and this was found to have a ΛΔ configuration around the Co, and an *S* configuration around the secondary nitrogen atom. the related complex $[Co(eddp)(en)]^+$ in which eddp = ethylenediamine-*N,N'*-dipropionato, has been separated into three isomers which were optically resolved [149]. The rate of the reaction between the two β isomers was slow and was essentially an inversion reaction at the asymmetric secondary N atom, while the α to β change required the disruption of the Co-O bond to explain its stereoselectivity.

The preparation and subsequent determination of the X-ray crystal structure of the complex Λ-β_1-[Co(*R,R*-picchxn)[*S*-α-Me-trp)]$(ClO_4)_2$ has been described [150] as part of a study of inorganic synthetic means of synthesis and resolution of α-alkylamino acids.

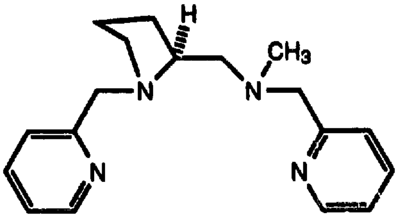
The crystal structure of the complex *trans*(N)-(1,10-phenanthroline)-bis(L-prolinato)cobalt(III) perchlorate hydrate [152] shows that the octahedral arrangement around the cobalt involves the L-prolinato ligand in bonding through oxygen and nitrogen in *trans*-*N*-N form.

The preparation of a series of aminocarboxylato(1,4-diaminobutane)dinitrocobalt(III) complexes has been described [153] and the crystal structure of the Δ-$(-)_{589}$-*cis*(NO_2), *trans*-(NH_2)-(*R*-alaninato)(1,4-diaminobutane)dinitrocobalt(III) diastereomer has been determined. A relationship between ring structural and pseudorotational parameters for five-membered rings has[154]. From this it has been possible to show that such rings prefer to have a Co-O-C-C torsional angle of about zero.

Both solution and solid state CD spectroscopic studies have been carried out to examine the vicinal optical activity of 4 classes of mono(*S*-aminocarboxylato)cobalt(III) complexes [155]. Replacement of the smaller ammine group by the more bulky nitro showed that axial orientation of the alkyl on the aminocarboxyl group was more effective in producing a larger negative dichroism at the first spin-allowed *d-d* band position.

The ligand 6-(2-hydroxyphenyl)-2,2'-bipyridine (HL) is tridentate and couples to metals as an *N,N,O*-donor [156] It has been synthesised by reaction of 2-lithioanisole with 2,2'-bipyridine followed by re-aromatization using potassium permanganate and the formation of a phenol from the anisole group using pyridinium chloride. The structure of the cobalt(III) complex $[CoL_2][PF_6].MeCN$ was determined using X-ray diffraction. it was found to contain *cis*-N_4O_2 coordination in an almost octahedral arrangement.

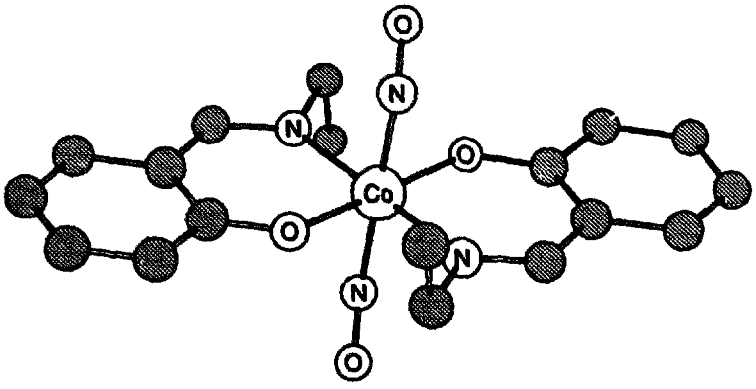
The use of a ring structure containing an *N*-atom to reduce flexibility in the ligand *N,N'*-di(2-picolyl)-*N'*-methyl-2*S*-aminomethylpyrrolidine (*S*-picpyrrMe) (63) allows the coordination specificity for Co(III) to be probed [157]. The X-ray crystal structure of the complex [Co(S-picmirrMe)(*R*-ala)]$(ClO_4)_2$ has been determined showing that the complex has a CoN_5O arrangement with *N,O*-didentate somewhat flattened *R*-ala and a_1 topology.



(63)

Complexes of the type $[Co(NO)(asal)_2]$ (where asal = *N*-alkyl or *N*-aryl-salicylidene-iminate, *o*-$OC_6H_4CH{=}NR$ with R = Me, Et (esal), ^nBu, Ph or CH_2Ph) have been prepared [158]. An X-ray structure of the esal complex (64) confirms a bent apical NO group. Solid state NMR spectra were obtained for $[Co(^{15}NO)(asal)_2]$ and also for the corresponding *o*-$OC_6H_4CMe{=}NOH$ complex. These show the large isotropic shifts which are characteristic of bent nitrosyls, as are the values of the ^{14}NO infrared stretching frequencies. The tensor components show great sensitivity to small changes in the MNO geometry. The magnetic behaviour of the complexes is that expected for complexes exhibiting van Vleck paramagnetism. Proton and ^{13}C spectra indicate that the structure of $[CoL_3]$ (L = 5-acetylamino-1,2-benzoquinone-2-oxime) consists of a mixture of the *mer* and *fac* isomers [159].

The ligand (65) has been synthesized [160] and when reacted with $CoCl_2$ in the presence of $NaO_2CCH_2CH_3$, it yielded the cobalt(III) complex ion $[Co_2L(O_2CCH_2CH_3)_2]^+$. The crystal structure of this species shows that the two cobalt atoms are bridged by the central phenolate of the ligand and all the other chelating positions in the ligand are attached appropriately to each cobalt (66).



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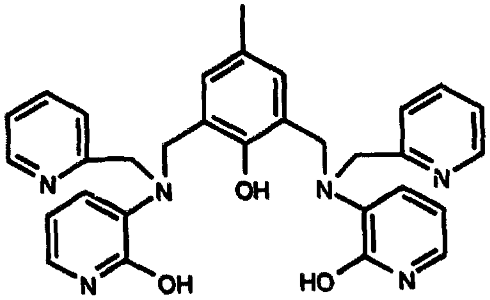

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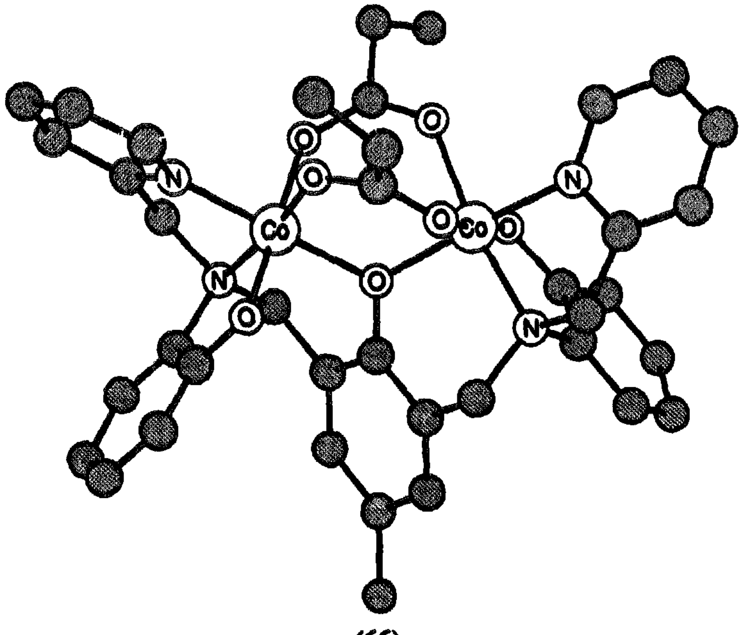
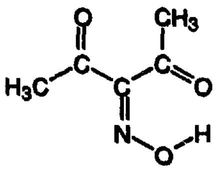


(66)

The ligand 3-hydroxyiminopentane-2,4-dione (HL) (67) forms the complex [CoL_3] [161] in which the N and O atoms are arranged in a distorted octahedron around the Co and in which an *N,N,O*-donor set occupies a *fac* position.



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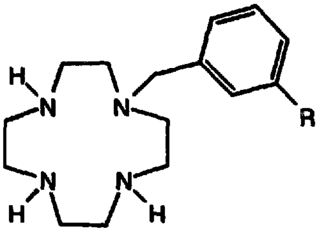


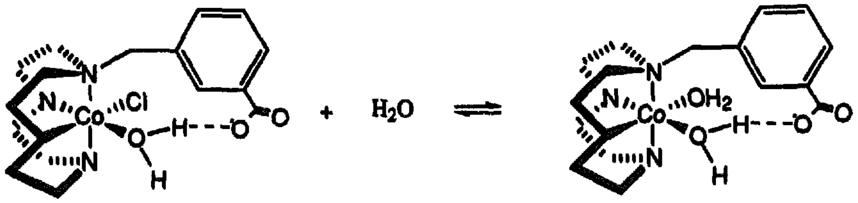
$L^{II}H$ R = CO_2H

L^{I} R = CN

(68)

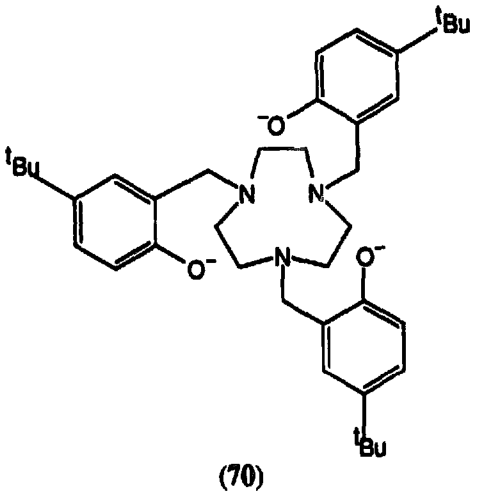
The ^{13}C NMR spectroscopy of some carboxylatocobalate(III) complexes in a variety of solvents [162] has shown that the shifts of the coordinated carboxylates in most cases were related in a linear fashion to the electrophilicity of the solvent except for oxalato species.A mixture of the *fac* and *mer* isomers of the complex tris(4-R-1,2-benzoquinato)cobalt(III) $[Co(RL)_3]$, where R = Me, Cl or Br is formed during preparation [163].

The kinetics of the aquation of cobalt(III) complexes, $[CoL_ICl_2]^+$ and $[Co(L_{II}H)Cl_2]^+$ of the carefully designed ligands L_I and $L_{II}H$ (68) have been studied [164]. For the $L_{II}H$ complex the reaction occurs in two stages with the first reaction in particular being much faster than for comparable species, though inhibited by acid. This is attributed to powerful intramolecular catalysis arising from a conjugate base mechanism (69).



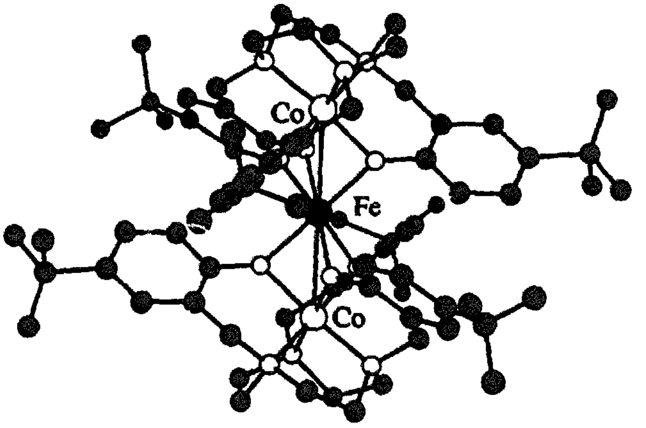
(69)

A number of mixed chelate complexes of cobalt(III) have been produced [165] by reacting acetylacetone, 8-hydroxyquinoline, picolinic acid, dipicolinic acid, iminodiacetic acid and dimethylglyoxime (H_nL) with $[Co(NH_3)_2L']^{3+}$ (L' = ethylenedibiguanide) to give $[CoLL']^{n+}$.



(70)

A number of complexes of the macrocycle 1,4,7-tris(5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (LH_3) (**70**) with first row transition elements [166] including cobalt(III) have been prepared. The last of these has been used in an elegant piece of work where the complex, [CoL] is reacted with hexaaqua metal cations to produce complexes such as $[(LCo)_2Fe](ClO_4)_n.2(CH_3)_2CO$ (n = 1, 2) [167]. These are trinuclear species confirmed by X-ray crystal structures (**71**) in which the iron centre is bonded by the three oxygen atoms of the ligand.



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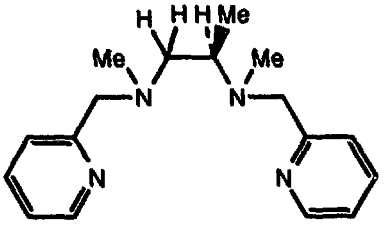
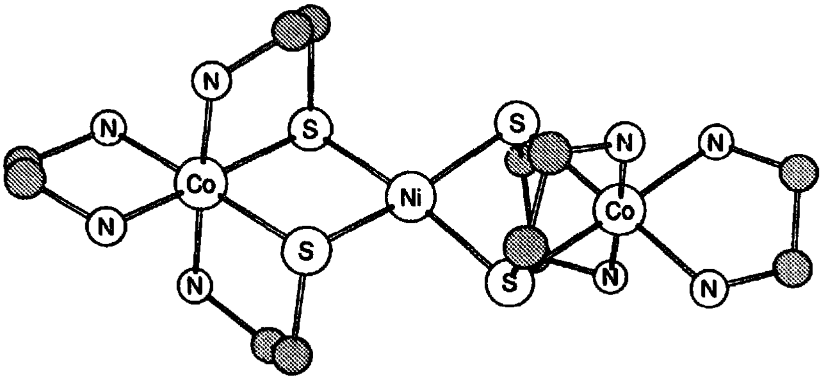


(72)

The ligand *R*-picpnMe$_2$ (*N,N'*-dimethyl-3*R*-methyl-1,6-di(2-pyridyl)-2,5-diazahexane) (**72**) by reaction of 3*R*-methyl-1,6-di(2-pyridyl)-2,5-diazahexane with sodium cyanohydride and excess formaldehyde in dmf [168]. From *R*-picpnMe$_2$ the Δ-*cis*-α-dichloro complex has been prepared and from this the alaninato complex. The X-ray crystal structure shows that this crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 10.502, b = 13.623, c = 18.655A and Z = 4. The expected octahedral configuration around the cobalt is such that the *R*-picpnMe$_2$ ligand is found in Δ-α topology. The *ci*-α_1 and *cis*-α_2 geometric isomers with different positions of the N and O atoms of the S-ala with respect to the N_4 ligand co-crystallize.

1.1.4 Complexes with sulfur donor ligands

The reaction between the compound $[Ni(aet)_2]$ (aet = 2-aminoethanethiolate) and the cation $[CoCl_2(en)_2]^+$ yields the complex $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (**73**) which consists of a nickel atom bridging between two *cis*-(*S*)-$[Co(aet)_2(en)]^+$ subunits [169]. The single crystal structure has been determined. The complex was optically resolved using antimonyl tartrate. The red-brown cuboidal crystals of $[Li(OEt_2)_3][Co_2(SC_6H_2Pr^i_3\text{-}2,4,6)_5]$ are prepared by reaction of $Li(SC_6H_2Pr^i_3\text{-}2,4,6)$ with $CoCl_2$ [170]; $[Li(OEt_2)_3][Co_2(SC_6H_2Pr^i_3\text{-}2,4,6)_5]$ contains the anion (**74**) which has proved to have an unusual structure involving two CoS_4 tetrahedra which share one face.



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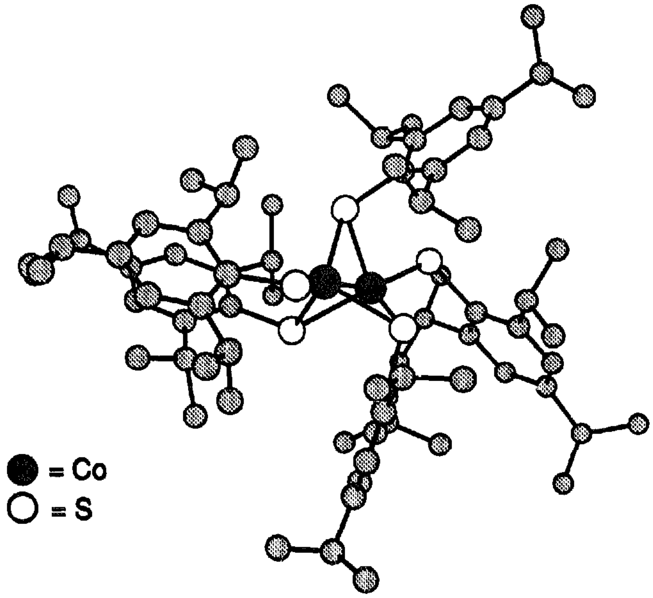
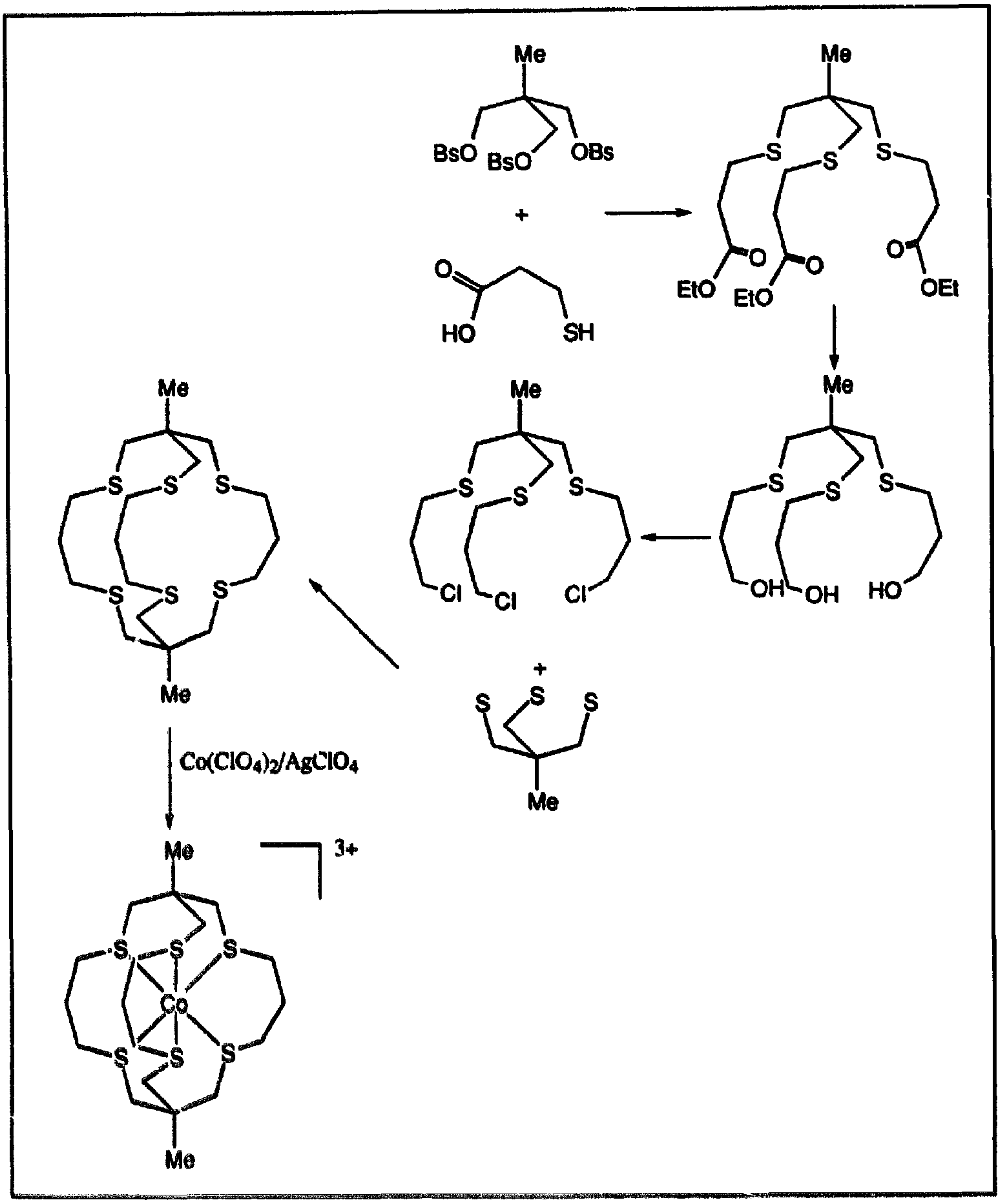


(74)

1.1.5 Complexes with sulfur-oxygen donor ligands

The kinetics of the Cr(II) reduction of the cobalt(III) complexes; $[(NH_3)_5Co(SO_3)]^+$ $(4.7 x 10^3)$, $[(NH_3)_5Co(S_2O_5]^+$ (2.1×10^4), $[(NH_3)_5CoSO_2C_6H_5]^{2+}$ (5.3×10^3) and $[(NH_3)_5Co(H_2O)(SO_3)]^+$ (1.1×10^5) have been studied [171], second order rate constants in parenthesis. There is no linear correlation between the rate constants and the *trans* bond lengthening.

An elegant synthesis of the species Me_2S_6tricosane has been achieved — the crude produc mixture from the last stage of the scheme shown in (75) is reacted with $Co(ClO_4)_2.6H_2O$ in the presence of $AgClO_4$ as oxidant to form a cobalt(III) complex from which the Co is removed by reduction to Co(II) and complexing with H_4edta. The properties of the Co(III) complex are explored [172].

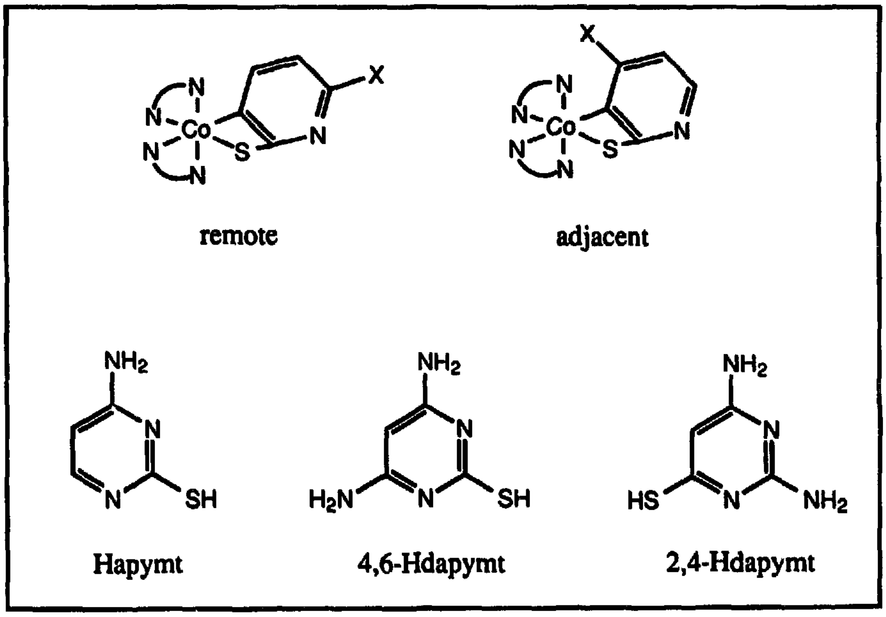


(75)

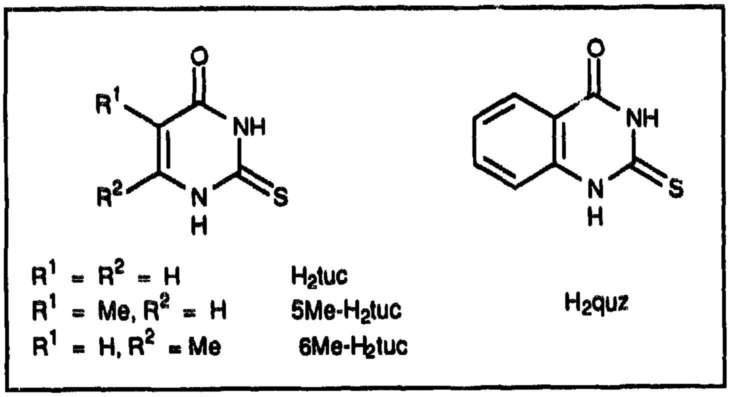
1.1.6 Complexes with sulfur-nitrogen donor ligands

Mixed ligand complexes containing ethylenediamine and *N*,*S*-chelates (76) have been prepared [173]. The crystal structure of the complex $[Co(apymt)(en)_2][ClO_4]_2$ shows that it has the amine group remote from the *N*,*S*-cobalt bonding system. An interesting feature of the *trans*-(S)-$[Co(4,6\text{-dapymt})(en_2)]^+$ and *trans*-(S)- $[Co(2,4\text{-dapymt})(en_2)]^+$ complexes is the formation of an intramolecular hydrogen bond between the amino group of one dapymt ligand and the coordinated sulfur atom of the other. In a related study Yamanari and coworkers [174] have looked at eight cobalt(III) complexes of the type $[Co(en)_2L]^+$ and $[Co(en)_2(HL)]^{2+}$ where H_2L are the ligands in

(77) which are bonded through nitrogen and sulfur. Again these were photochemically prepared, though with much longer photolysis times. The crystal structure of the complex $[Co(en)_2(tuc)][ClO_4]$ was determined and in this the bonding occurs via an adjacent linkage. An intramolecular hydrogen bond between the tuc oxygen atom and an amine nitrogen of the en was shown by both NMR spectroscopy and X-ray crystallography to be a feature of these complexes.

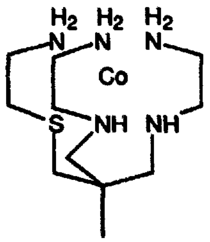


(76)



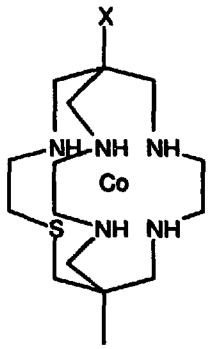
(77)

The reaction of the new ligand 5-methyl-5-(4-amino-2-thiabutyl)-3,7-diazanonane-1,9-diamine (N_5S) with a cobalt(II) salt in methanol with a stream of air produces mostly $[Co(N_5S)](ClO_4)_3.2H_2O$ (78). When this is reacted with nitromethane, a nitro-capped compound is formed; reduction leads to an amino-compound (79) and the X-ray crystal structure of this was determined. The absorption spectrum was measured at 11 K to separate the Co-S charge transfer band and octahedral ligand field parameters, $B = 565\ cm^{-1}$, $C = 3300\ cm^{-1}$ and $10DQ = 22900\ cm^{-1}$ were determined [175].



$[Co(N_5S)]^{3+}$

(78)

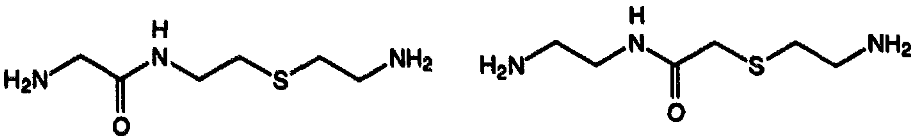


$[Co(XN_5Ssar)]^{n+}$

X = NO_2, NH_2

(79)

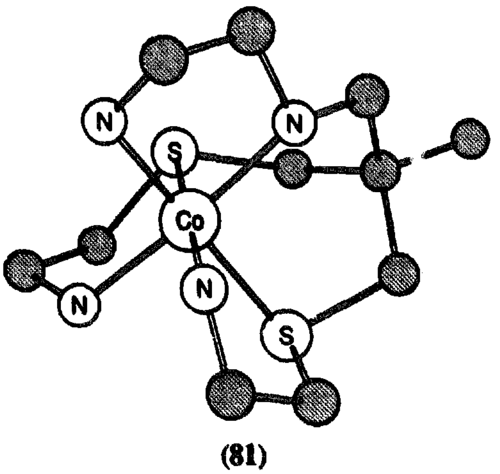
The complexes *cis*-β-$[Co(gee)(gly)]^+$ and *cis*-β-$[Co(ege)(AA)]^+$ (where geeH and egeH = (80); AA = gly, L-ala, L-leu and L-ile) have been prepared and shown by ^1H and ^{13}C NMR spectroscopies to be produced as only one geometrical isomer. The X-ray crystal structure reveals a β_1 configuration [176].



geeH egeH

(80)

Encapsulated complexes have been prepared [177] by the reaction of the cobalt(III) complex of the ligand 5-methyl-5-(4-amino-2-azabutyl)-3,7-dithianonane with formaldehyde and ammonia, or formaldehyde and nitromethane, to produce [8-methyl-6,10-dithia-1,3,13,16,19-pentaazabicyclo[6,6,6]icosane)cobalt(III)] perchlorate and [1-methyl-8-nitro-3,13-dithia-6,10,16,19-tetraazabicyclo[6,6,6]icosane)cobalt(III)]. The X-ray crystal structure of the latter has been determined along with that of the complex $[Co(N_4S_2)]Cl(ClO_4)_2$ which contains cation (81).



(81)

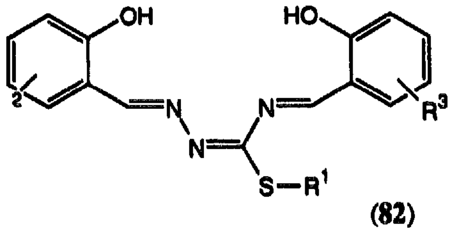
The X-ray crystal structure of *cis*-$[Co(atac)Cl_2]ClO_4.1/2H2O$ where atac = 6-methyl-6-(4-amino-2-azabutyl)-1-thia-4-azacycloheptane [178] shows that the atac coordinates through N_3S via a secondary amine and a thioether in the cyclopentane ring and the pendant primary amine and the chlorides in the *cis* positions. These structures were been determined for hfac complexes crystallized from basic solutions and are compared [179] with those of the complexes $[Co(hfac)(en)_2](ClO_4)_2$ and beta-$[(hfac)(trien)](ClO_4)_2$ The latter is rel-Δ-β -*R*,*R*.

The complexes $[Co(III)\{Ir(III)(aet)_3\}_2]^{3+}$ and $\Delta_{LLL}\Delta_{LLL}$-$[Co(III)\{Ir(III)(L\text{-}cys\text{-}N,S)_3\}_2]^{3-}$, where L-*cys*-*N*,*S* = L-cysteinate, have been prepared and the aet complex has been separated into the optical isomers, ΔΛ, ΔΔ and ΛΛ [180]. The crystal structure of the ΔΛ isomer shows that the environment around the Co consists of a trigonally distorted octahedron made up of the thiolato sulfur atoms.

1.1.7 Complexes with sulfur-nitrogen-oxygen donor ligands

The complex ammonium bis(pyruvic acid)thiosemicarbazone)cobalt(III) benzene has been found from its X-ray crystal structure to be the *mer* isomer with a very distorted octahedral arrangement around the cobalt [181].

ESR spectroscopic studies of low-spin [*N*1,*N*4-bis(salicylidene)-*S*-alkyl-isothiosemicarbazonato]cobalt(III) (**82**) complexes doped into lattices of the corresponding Zn(II) chelates, $[Co[R^1R^2R^3].H_2O$ show a six-coordinate structure involving the phenolic oxygen from a neighbouring molecule [182].



$[R^1R^2R^3]$
R^1 = Me, Et, n-Bu
R^2 = H, 5-Cl
R^3 = H, 5-Cl, 3'5'-Cl_2, 3'-OMe

(82)

1.1.8 Complexes with phosphorus donor ligands

A total of 11 complexes of the form $[Co(S\text{-}S)P_4]^{2+}$ and $[Co(S\text{-}S)_2P_2]^+$ in which S-S = dimethyldithio- (dtc), diethyldithio- and piperidyldithiocarbamate and P = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane (etpb), trimethyl- (pome) or triethylphosphite, have been prepared [183]. The complexes of the form $[Co(S\text{-}S)_2P_2]$ possessed *cis*-geometries in the dark, but when they were exposed to light they changed to the *trans*-species. The crystal structures of two of these complexes were obtained; $[Co(dtc)_2(etpb)_2]^+$ and $[Co(pipdtc)(pome)_4]^{2+}$. A further series of dithiocarbamato complexes, this time containing 1,2-bis(dimethoxyphosphino)ethane, $[Co\{(CH_3)_2NC(S)S\}_{3-n}\{(CH_3)_2P(CH_2)_2P(CH_3)_2\}_n][BF_4]$, (n = 1, 2) have been prepared [184]. The X-ray crystal structure has been determined for the complex when n = 2 showing that both the chelate rings take the *gauche* conformation and there is evidence of *trans* labilization by the phosphorus ligands.

1.1.9 Complexes with halide and pseudohalide donor ligands

A study of the ^{13}C, ^{15}N and ^{15}N NMR spectra of 15 pentacyanocobaltate(III) complexes [185] has revealed a relationship between the chemical shift and the nature of the ligand which is changed and there is a linear relationship between the chemical shifts in these spectra and the ligand field parameters such as the nephelauxetic ratio.

Like cyclic polyimines, poly(ethyleneimines) have been found to offer protection against photoaquation for the complex $[Co(CN)_6]^{3-}$ [186], though over a much wider pH range. The process by which this occurs is believed to involve the formation of adducts between the Co complex and the polymer by the formation of hydrogen bonds between CN- and the NH groups of the polymers.

Copper(II) is a powerful catalyst for the reduction of the superoxo complex ion $[Co_2(O_2)(CN)_{10}]^{5-}$ to $[Co_2(O_2)(CN)_{10}]^{6-}$ by cysteine and 2-aminoethanethiol since in its absence the reaction is very slow [187]. The kinetics of the reaction show a first order dependence on copper(II) and as in many such reactions the activity of the catalyst is due to copper(I). The effect of added thiol is to cause inhibition at higher concentrations and this is attributable to the formation of copper(I) thiol species. The processes which are believed to be taking place are summarized in (**83**) to which the kinetic equations fit very well.

$$
\boxed{
\begin{array}{l}
RSH \rightleftharpoons RS^- + H^+ \\
RS^- + Cu^{2+} \rightleftharpoons [Cu(II)(RS)]^+ \\
[Cu(II)(RS)]^+ \longrightarrow Cu(I) + RS^{\cdot} \\
RSH + Cu(I) \rightleftharpoons Cu(I)(RSH) \\
Cu(I)(RSH) + Ox \longrightarrow Cu(II) + [Cu_2(O_2)(CN)_{10}]^{6+} \\
Cu(I) + Ox \longrightarrow Cu(II) + [Co_2(O_2)(CN)_{10}]^{6+} \\
2RS^{\cdot} \longrightarrow R_2S_2
\end{array}
}
$$

(**83**)

In a related study, the kinetics and mechanism of the reduction of the superoxide complexes $[Co_2(O_2)(NH_3)_{10}]^{5+}$ and $[Co_2(O_2)(CN)_{10}]^{5-}$ by L-ascorbic acid has been studied [188]. The reaction of the ammine complex in the pH range 3.5 to 5.2 is concluded to be outer sphere occurring through the reduction of the superoxo group to peroxo followed by rapid decomposition of the resulting product. The cyano complex reacts in the presence of copper(II) ions to form the complex $[(CN)_5Co(H_2O)]^{2-}$. The presence of a change in the UV-VIS spectrum of the starting materials and the rate law strongly suggest that the reaction involves the formation of a copper(II)-cyanocobalt(III) complex at the start. A mechanism containing this proposal is given (**84**).

$$\begin{aligned}
&H_2A \rightleftharpoons H^+ + HA^- \\
&Cu^{2+} + Ox \rightleftharpoons Cu(II)(Ox) \quad \text{ion-pair} \\
&HA^- + Cu(II)(Ox) \rightleftharpoons HA^\bullet + Cu(I) + Ox \\
&HA^-\ Cu(II)(Ox) \rightleftharpoons Cu(II)(Ox)(A^{2-}) + H^+ \\
&Cu(II)(Ox)(A^{2-}) \longrightarrow Cu(I) + A^{\bullet -} + Ox \\
&HA^\bullet + Cu(II) \longrightarrow Cu(I) + A + H^+ \quad \text{rapid} \\
&A^{\bullet -} + Cu(II) \longrightarrow Cu(I) + A \quad \text{rapid} \\
&Cu(I) + Ox \longrightarrow Cu(II) + P \quad \text{rapid}
\end{aligned}$$

(84)

The complex ion $[Co(CN)_6]^{3-}$ has been used in the more unusual role of a ligand for the replacement of water in the anation reaction involving the formation of the neutral complex $[Cr(NH_3)_5NCCo(CN)_5]$ from $[Cr(NH_3)_5(H_2O)]^{3+}$ [189]. The kinetic data are interpreted in terms of an I_d mechanism for the anation reaction.

1.2 COBALT(II)

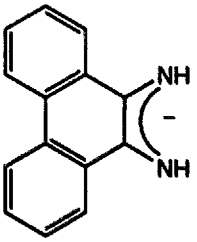
1.2.1 Complexes with nitrogen donor ligands

The products of the photolysis of complexes of the type $[Co(bpy)(Am)(AA)]^{2+}$ in which Am = ethylenediamine or propylenediamine and AA is an amino acid are cobalt(III) alkyl complexes [190]. The process has been studied by flash photolysis and the kinetics for the formation of the alkyl species have been determined. A reaction scheme is proposed which involves the intramolecular oxidation of a cobalt(II) centre and the formation of the alkyl complex followed by further reactions. In the case of the bis(bpy) complex, however the reaction produces a stable cobalt(III) alkyl complex. The complex cation $[Co(bpy)_2]^{2+}$ has been used [191] as the reducing agent in a study of the kinetics of a series of redox reactions involving Mn(III,IV) complexes a number of nitrogen donor ligands. The brownish-red complex $[Cu\{(OH)_2Co(en)_2\}_2](S_2O_6)_2.2H_2O$ has been prepared and characterized [192].

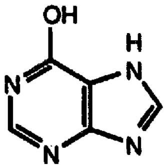
The kinetics of the electron transfer reaction of the complex $[Co(bpyO_2)_3]^{3+}$ (where $bpyO_2$ = 1,1'-dioxo-2,2'-bipyridine, which in these complexes forms a puckered seven-membered chelate ring) and a variety of reducing agents such as nickel polyazamacrocycles, $[FeL_3]^{n+}$ and $[OsL_3]^{2+}$, (where L = 2,2'-bipyridine or 1,10-phenanthroline) have been studied in MeCN solution [193]. The results are interpreted using the Marcus theory and compared with those from other relevant complex reactions.

The first crystal structure of a 2,2'-bipyrimidine cobalt(II) mononuclear complex, bis(2,2'-bipyrimidine-*N,N'*)dichlorocobalt(II), $[Co(bpm)_2Cl_2]$ [194] shows the bipyrimidine behaving as a didentate ligand and the chloride ligands in the *cis* positions.

The polymeric complexes $[CoL_2]_x$, in which L^- = pyrazolate, 3-methylpyrazolate and 4-substituted 3,5-dimethylpyrazolate have been shown to consist of one-dimensional chain structures which are held together by double pyrazolate bridges attached to the metal centres [195]. Magnetic studies were carried out and these detected antiferromagnetic exchange and anisotropic susceptibilities in all the complexes. Three related species, oligometallic 3,5-dimethylpyrazolate (dmpz) bridged Co(III) complexes have also been synthesized, namely $[Co(dmpz)_2(Hdmpz)]_2$ (i), $Co(dmpz)_2.0.344(Hdmpz)$ (ii) and $[Co(dmpz)_2Cl(Hdmpz)]_2Co$ (iii) [196]. Single crystals were available for (i) and (iii); (i) is orthorhombic, Fddd, a =17.022, b = 29.224, c = 13.575 Å, and (iii) is triclinic, P1, a = 11.742, b = 18.604, c = 8.950 Å, α = 99.76, β = 102.32, γ = 93.36°, Z = 2. These systems also exhibit antiferromagnetic behaviour.



(85)



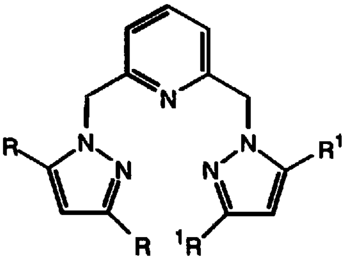
(86)

The crystal structure of the blue dinuclear complex $[Co_2(phda)_4$, in which pdha is **(85)**, shows a Co(II)-Co(II) bond with the ligands arranged in an eclipsed cofacial geometry [197]. The bridging water molecules in the complex $[Co_2(\mu\text{-hypoxanthine})_2(SO_4)_2(\mu\text{-}H_2O)_2(H_2O)_2$ **(86)** play a crucial role in stabilizing the structure of the complex via the formation of strong O-H····O bonds [198].

The question of the nature of the interaction between the reacting species in outer sphere electron transfer reactions has been addressed by Lappin and coworkers [199] by studying the effect of hydrogen bonding on the kinetics of such reactions. A series of cobalt(III) complexes were reduced by $[Cr(bpy)_3]^{2+}$, $[Co(en)_3]^{2+}$ and $[Co(en)_2]^{2+}$. The reactions with $[Co(en)_2]^{2+}$ were found to be inner sphere, while those with $[Co(en)_3]^{2+}$ and $[Cr(bpy)_3]^{2+}$ were inner sphere. The presence of an unhindered pseudo-C_3 axis in complexes C_1-*cis*(N)-$[Co(gly)_2(ox)]^-$ and C_1-*cis*(N)-$[Co(gly)_2(ox)]^-$ which allows easy hydrogen bonding when the oxidant and reductant come together enhances the free energies of activation of these reactions.

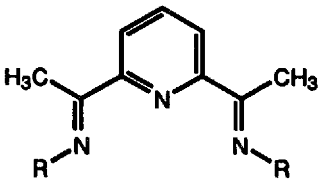
Kinetics of the outer sphere oxidation of $[Co(en)_3]^{2+}$ by $[Co(en)(ox)_2]^-$ and $[Co(gly)(ox)_2]^{2-}$ in several solvents [200] was found to be largely independent of the nature of the solvent. The data are, however amenable to fitting with the Gutmann donor number and acceptor number. Stereoselectivities for the reduction of $[\Delta\text{-}(+)_{546}Co(gly)(ox)_2]^{2-}$ and $[\Delta\text{-}(+)_{546}\text{-}Co(gly)(ox)_2]^{2-}$ by $[Co(en)_3]^{2+}$ interpreted in a similar way showed the importance of hydrogen bonding between reagents.

The X-ray crystal structures of the complexes $[Co(NH_3)_6][Hg_3Cl_9]$ and *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$ have been determined [201]. The octahedral complexes $[Co(L)_2]^{2+}$ in which L is (**87**) have been prepared; trends in anodic peak potentials are largely determined by steric rather than electronic effects as methyl group substitution occurs [202]. A series of high-spin Co(II) complexes of the tridentate ligands (**88**) have been prepared and characterized [203].



R = R¹ = H
R = H; R¹ = Me
R = R¹ = Me

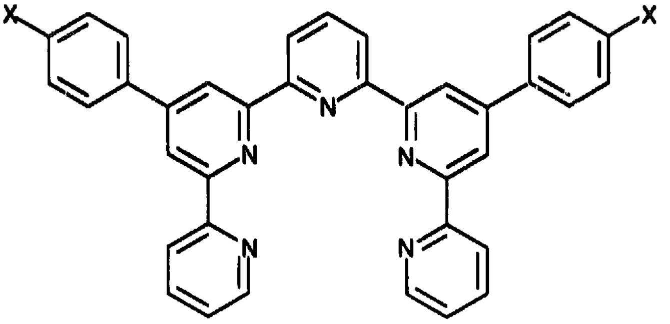
(**87**)



R = Ph, C_6H_4O-4, $(CH_2)_3Ph$

(**88**)

The cobalt(II) complexes of 4',4'''-disubstituted derivatives of qpy (**89**) have rather different structures in the solid state [204, 207]. The crystal and molecular structure of the complex aqua(methanol)[4',4'''-bis(4-chlorophenyl)-2,2':6',2'':6'',2''':6''',2''''-quinquepyridine]cobalt(II) bis-(hexafluorophosphate] $[Co(cp_2qpy)(MeOH)(H_2O)][PF_6]_2$ has been determined and shown to consist of a single helical arrangement around the cobalt with the ligand exhibiting 7-coordination as shown in the stucture of the cation (**90**). This contrasts with the structure of $[Co(qpy)_2(OAc)]^{3+}$ which has a double helical structure around two cobalt atoms [205]. A scheme for the interconversion of the single helix and the double helix is proposed. The interconversion of double and single helical cobalt(II) complexes of 2,2':6',2'':6'',2''':6''',2''''-quinquepyridines has been extended in a practical sense to allow the preparation of heterodimetallic complexes; the complexes $[CoML_2]^{3+}$ have been prepared in which M = Cu or Ag and L = Ph_2qpy or qpy [206].

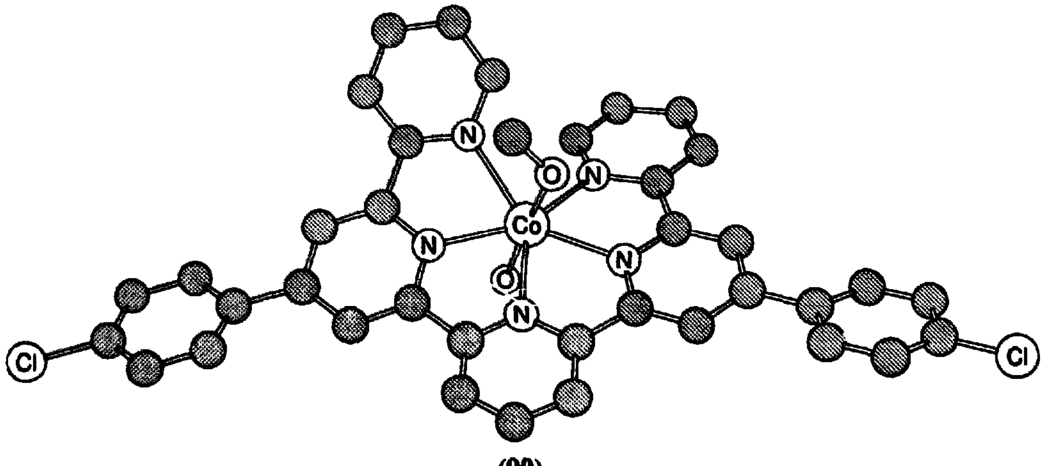


X = H, Me, Cl, HO, or Me_2N

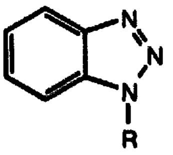
(**89**)

As part of an investigation of the anticorrosion properties of benzotriazole [208], the crystal structures of the complexes $[CoCl_2(Mebta)_2]$ (I), *trans*-$[Co(CNS)_2(Mebta)_4]$(II), *trans*-$[Co(NCS)_2(MeOH)_2(Mebta)_2]$ (III) and *cis*-$[Co(NO_3)_2(Mebta)_2]$ (IV) have been determined, in which Mebta = 1-methylbenzotriazole (**91**). The Mebta behaves as a monodentate ligand through

N. The geometry around the Co in (I) is tetrahedral, while in the other three complexes it is octahedral.

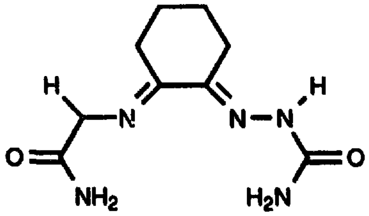


(90)



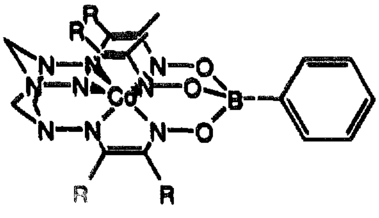
R = H, Me

(91)



(92)

The structure of dithiocyanato[(-)-spartein]cobalt(II) has been shown [209] to be similar to that of the dichloro complex [210] in which Fenton and Gerloch had to introduce so-called "bent bonding" to account for absorption intensities [211]. The dicobalt complex $[Co_2(H_2chds)_2(H_2O)_3(NO_3)][NO_3]$, where H_2chds = cyclohexane-1,2-dionebis(semicarbazone) (92), has been prepared and studied using infrared spectroscopy and the X-ray crystal structure has been determined [212]. This is triclinic, with space group P1, a = 13.616, b = 12.694, c = 11.537Å, α = 68.13, β = 77.71, γ = 70.01° and Z = 2. The ligand in the complex is almost planar tetradentate.



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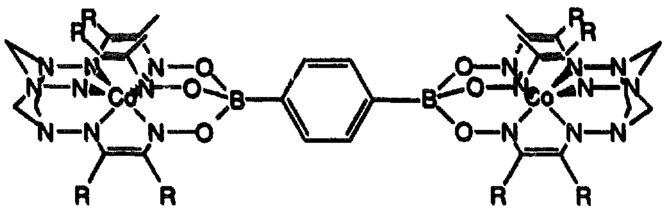
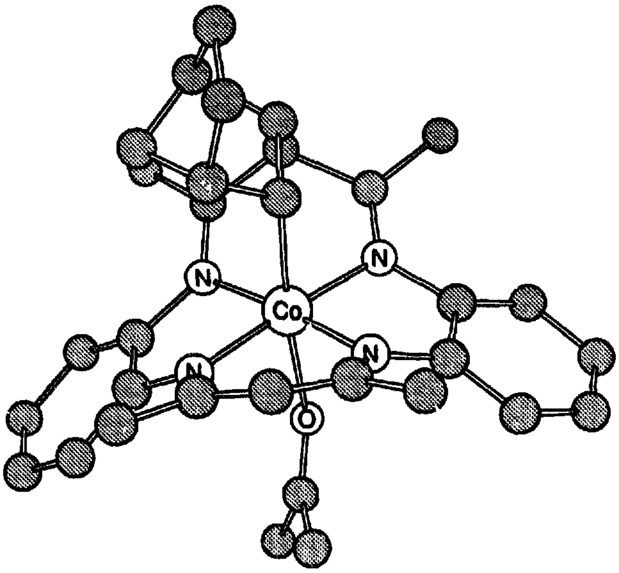


(94)

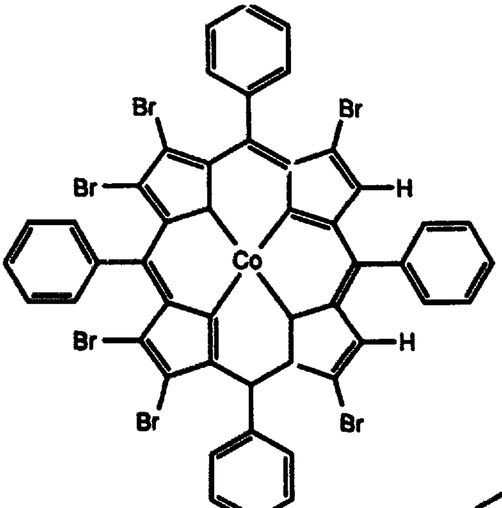
In a study of clathratochelate complexes in which a metal ion is entirely encapsulated within a ligand cage two new types of cobalt(II) complexes of the types shown in (93) and (94) have been synthesized [213]. Cyclic voltammetry on these show the possibility of +2 and +3 oxidation states.

Cyclam complexes showed no tendency to dissociate in aqueous perchloric acid [214], but when McIlvaine phosphate buffer was used to produce acid conditions the reaction proceeded readily. Complexation by the anions in the buffer is implicated in the catalysis of the dissociation. Dissociation of the trien and tren complexes occurred in perchloric acid solutions and mechanisms involving solvation and general and specific acid catalysis are invoked. The tetraazamacrocycle 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine has been chosen as having a closer resemblance to the corrin ring as a precursor for forming species with an intramolecular Co(III)-C bond. The reaction of norborane with this complex is reported along with the crystal structure of the product (95) [215].

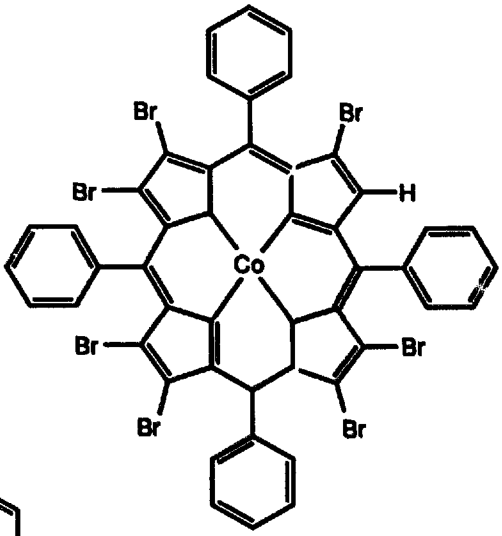


(95)

The structure of the complex [Co(tpb)I], where tbp = tetrabenzoporphyrinato, has been determined [216] to be essentially similar to other M(L)I molecular conductors in containing Co(tbp) cations which are surrounded by I_3^- anions in such a way that the cations are planar and are stacked metal over metal. Conductivity and thermoelectric power measurements show that oxidation occurs at the macrocycle and it is the holes in the five sixths-filled band which consists of the overlapping p-p orbitals in adjacent macrocycle rings. The tetraphenylporphyrinato cobalt(II) complexes (96)-(98) containing varying numbers of electron withdrawing bromine substituents have been prepared and characterized [217]. The application of electrochemistry and spectroelectrochemistry shows that they exhibit three one-electron oxidations of which the first is the formation of the Co(III) complex, while the first reduction results in the Co(I) complex, the effect of the Br atoms is to shift $E_{1/2}$ cathodically. The Br atoms also produce a red shift in the Soret and visible UV-VIS spectra. Stability constants have been obtained for the formation of complexes between cobalt(II) octaethylporphyrin, t-tetraethylchlorin, tct- and ttt-isomers of octaethylisobacteriochlorin with the base piperidine, py and substituted pyridines dissolved in toluene, cyclohexane and chloroform [218]. Reasonable linear correlations were found for the relationship between log K and the basicity of the ligand except for the 2-substituted pyridine species. As far as the macrocycle is concerned the stability constants were found to increase as the saturation of the macrocycle increases, but were unaffected by the steric effects.



(96)



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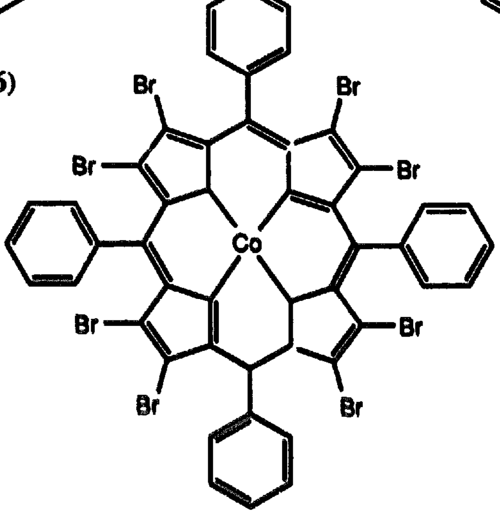
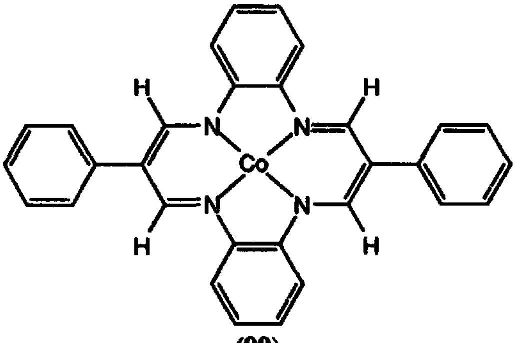
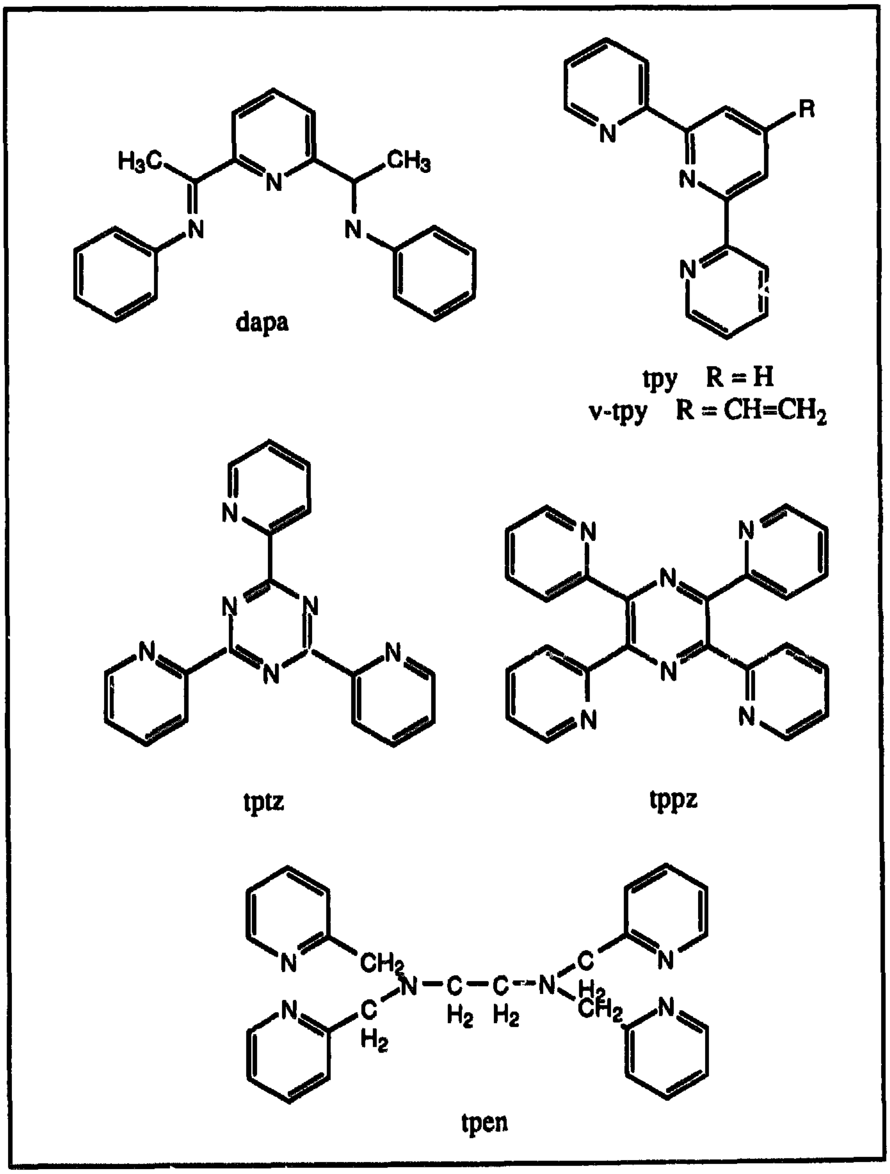


(98)

The temperature- and axial-ligand dependence of the EPR spectra of cobalt tetraphenylporphyrin and octaethylporphyrin cation radicals has been re-examined [219]. The data show that there is significant mixing of the A_{1u} and A_{2u} states in the ground state and that the A_{2u} state contribution is increased as the axial ligand field increases. For the complex $[Co(II)OEP]^+$, Br^-, Cl^- and CN^- in the axial position produced line broadening attributed to locally excited triplet mixing. The X-ray structure of the complex [CoL] (99) shows it to be almost planar except for the two phenyl groups which lie 30 and 38.1° with respect to the CoN_4 plane [220]. An X-ray crystal structure of the tetraimine complex $[Co(C_{10}H_{20}N_8)Cl(H_2O)]Cl.H_2O$ shows that unlike the corresponding Ni(II) and Cu(II) complexes which are square planar, the arrangement around the cobalt(II) is almost octahedral. FTIR spectroscopy shows the presence of NH····Cl hydrogen-bonds [221]. Among a range of complexes used in the study of the electrocatalytic reduction of carbon dioxide were the species $[Co(dapa)_2(PF_6)_2$, $[Co(tppz)_2](PF_6)_2$, $[Co(tpy)_2](PF_6)_2$, [Co(v-tpy)$_2$](PF$_6$)$_2$, [Co(tptz)$_2$](PF$_6$)$_2$, [Co(tptz)$_2$](PF$_6$)$_2$ and [Co(tpen)$_2$](PF$_6$)$_2$ in which the ligands are shown in (**100**). It was found that these complexes were particularly good catalysts for the process in which both metal-based and ligand based reactions are involved [222].

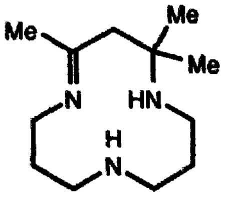


(**99**)



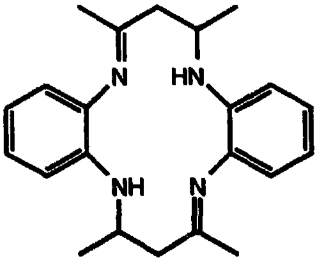
(**100**)

Complexes of the form $[Co(II)(L)(OH)]_2(ClO_4)_2$, where L is shown in (**101**) [223] are pentacoordinate complexes with di-μ-hydroxo bridges and show weakly ferromagnetic interactions in contrast to the strong antiferromagnetic coupling in the corresponding Cu(II) and Ni(II) complexes.



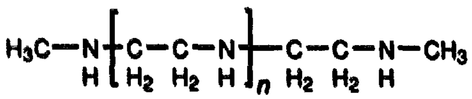
R = H, Me

(**101**)



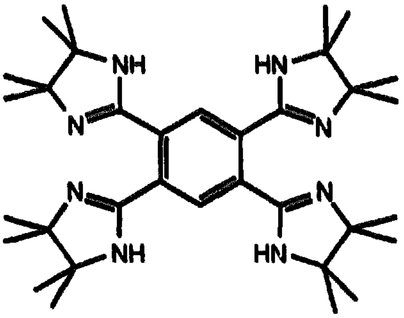
(**102**)

The superhyperfine structure in the ESR spectrum of the five coordinate complex of (**102**) in 3-methylpyridine has been observed for the first time. The data indicate that in this solvent a 1:1 adduct is formed between [CoL] and the 3-methylpyridine. Similarities between the ESR spectrum of the species studied here and that of vitamin B_{12r} are noted [224]. The stability constants of the Co(II) complexes of a series of open-chain ligands (**103**) have been determined and compared with their corresponding macrocyclic analogues; the "macrocyclic effect" giving rise to higher values in the macrocyclic ligand cases was only observed for $[18]aneN_6$ and $[21]aneN_7$ [225]. The X-ray crystal structure of the complex $[Co(macm)_2(py)_2(H_2O)_2]$ where macm = methazolamidato have been determined [226]. The arrangement around the Co consists of a square planar distribution of the two sulfonamidato and two pyridine nitrogens with axial water molecules completing an almost regular octahedron.



$$H_3C-\underset{H}{N}-\left[\underset{H_2}{C}-\underset{H_2}{C}-\underset{H}{N}\right]_n-\underset{H_2}{C}-\underset{H_2}{C}-\underset{H}{N}-CH_3$$

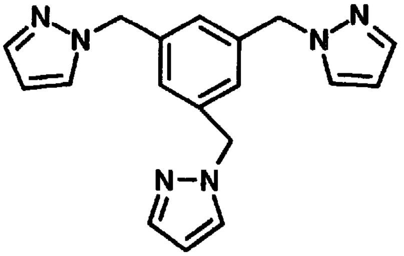
(**103**)



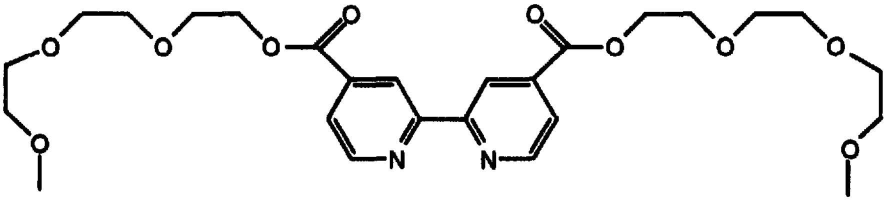
(**104**)

Two types of Co(II) complexes have been found to be formed with the ligand BTIM (**104**) [227], one with 1:1 stoichiometry and the other with 2:1 stoichiometry. The X-ray crystal structure of $[Co_2(BTIM)_2Br_2]Br_2$ shows that the complex involves didentate bonding by the ligand in metallocyclic manner so that an empty cavity is formed within the structure. The molecular structure of $[Co_2(BTIM)Cl_4]$ involves an open chain arrangement in which two tetrahedral Co(II) atoms form bridges with one ligand.

Along with several copper complexes, the complex $[\{Cu_2CoL_2Cl_6(H_2O)_3\}_n]$, where L is (**105**) has been prepared and its X-ray crystal structure determined [228]. The copper-containing structures are polymeric and bridged by cobalt(II) species. The complex $[CoL_3](ClO_4)_2$ in which L is the oligo(ethylene glycol) modified bpy ligand (**106**) [229] is found to be a liquid at room temperature unlike its crystalline parent bpy complex. This ionic liquid turns out to be a new electroactive molten salt having significant ionic conductivity. The liquid is extremely viscous. A cyclic voltammetric study at slow potential scan rates shows the 2+/3+ oxidation wave is nearly reversible.



(**105**)



(**106**)

There has been much interest in nitric oxide in recent years since its various roles in biological systems have begun to be recognized. The resonance Raman spectrum of nitric oxide adducts of cobalt(II) reconstituted myoglobin and haemoglobin have been studied [230]. It has been possible using isotopic substitution in NO to determine that $\nu(NO) = 1613\ cm^{-1}$, $\nu(Co\text{-}NO) = 576\ cm^{-1}$ and $\delta(Co\text{-}NO) = 367\ cm^{-1}$. It is concluded that comparison with similar data for the corresponding Fe(II)-NO complex that the Co(II)-NO bond is rather weaker than the Fe(II)-NO bond.

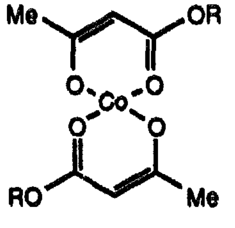
By replacement of copper by cobalt in the azurin *pseudomonas aeruginosa* the application of 2D NMR spectroscopy has allowed the assignment of the more important signals in the proton NMR spectrum [231]. A dinuclear cobalt(II) derivative of arthropod haemocyanin with spectral properties which indicate that the cobalt(II) environment is roughly tetrahedral has been prepared [232]. Up to two cobalt atoms per protein monomer are indicated. The EPR spectrum shows that there is coupling between the cobalt(II) species. The complex does not appear to bind dioxygen.

1.2.2 Complexes with oxygen donor ligands

There have been two X-ray crystal structure studies of $[Co(H_2O)_6]^{2+}$. In one, great similarity was been found [233] between the hydrogen bonding in the crystals of hexaaquacobalt(II) perbromate and that in the corresponding bromate salt. In the other the hydrogen bonding in the complex $[Co(H_2O)_6]$[hydrogen phthalate] was found to result [234] in an arrangement of layers -phthalate-$[Co(H_2O)_6]$-phthalate- involving anion-anion and anion-water bonds. The $[Co(H_2O)_6]^{2+}$ ion is octahedral. Using both X-ray and neutron diffraction data the electron density in monoclinic cobalt sulfate hexahydrate has been determined [235]. There are found to be significant polarization effects in the region of the lone pairs on the oxygen atoms of the water molecules depending on the coordination geometry of the water. There has been a related study of the crystal structure of cobalt formate dihydrate which shows an arrangement in which there is 3-D polymeric network throughout the crystal [236]. There are two different cobalt ions, one with 6 formate groups bonded to cobalt through oxygen and the other with 4 water molecules and 2 formate ions attached to cobalt, again through oxygen and the octahedra formed in this way are linked via formate through hydrogen bonds.

The reaction between the radicals Cl_2^-, Br_2^- and CO_3H^-, generated by flash irradiation with $[Co(H_2O)_6]^{2+}$, $[Co(NTA)]^-$ and $[Co(Me[14]dieneN_4)]^{2+}$ as a function of magnetic field intensities between 0 and 7 T has been studied [237]. The effect of the magnetic field on the rate of the reactions depended on the nature of the radical. In many cases there is a complex relationship between magnetic field and rate constant. Mechanisms are proposed to account for the kinetic behaviour. The reaction of citric acid with cobalt(II) is rapid and involves the intervention of the hydroxyl ion [238]. The kinetics of the rapid reaction between cobalt(II) ions and 3-nitro-, 4-nitrophthalate and phenylmalonate requires the use of pressure-jump relaxation methods [239]. The rate determining step proved to be ring closure during a dissociative interchange mechanism.

An interesting and apparently general method has been developed for the preparation of Co(II) complexes (**107**) of β-keto esters [240]. This involves the use of the Li enolate, the Cs enolate and the trimethylsilyl enolate of the β-keto ester in reaction with a Co(II) compound in tetrahydrofuran. The X-ray crystal structure of the complex $[Co(hfacac)_2.TCNE]_x$ [241] in which TCNE = tetracyanoethylene shows that it consists of a polymeric structure in which the long chains are produced by bridging between cobalt-containing species by TCNE.

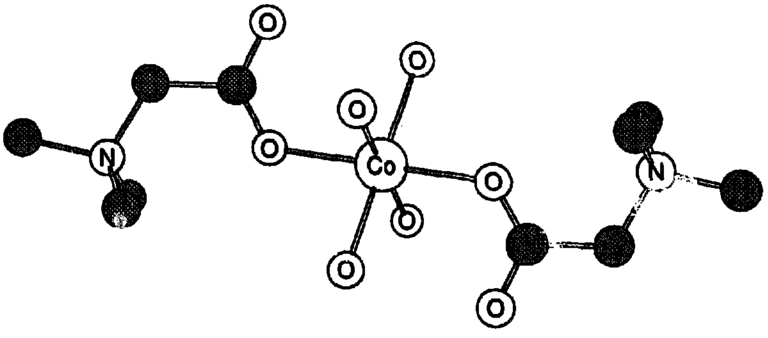


R = Et, $CHMeCH_2OMe$,

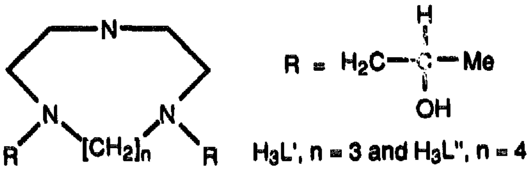
(107)

Linkage isomerization has been observed during the phenylisocyanation of unsubstituted and γ-halogenated β-diketonato and β-ketonimino complexes of Co(III) [242]. The nitro-nitrito linkage isomerism of cobalt(III) complexes has been revisited [243]. A study of the X-ray crystal structure of the complex pentaamminenitrocobalt(III) dichloride before and after irradiation with a xenon lamp for various times showed the way in which the structure changed during nitro-nitrito isomerism. This work indicated that as the isomerism proceeded it occurred in the original plane of the NO_2^-. This reaction has also been studied using the effect of high pressure on the infrared spectra of a number of nitropentaammine complexes of Co(III) [244]. For the nitro complexes a blue shift was observed in $\nu_{as}(ONO)$ and $\delta(NO_2)$ and this is interpreted as being the result of a decrease in the bond length of the N-O bond. For the nitrito complexes there was a red shift in $\nu_s(ONO)$ and $\nu_{as}(ONO)$ which in turn is interpreted as resulting from a decrease in the ONO bond angle as the pressure is increased.

The complex diaquabis(phenoxyacetato)cobalt(II) is shown by an X-ray crystal structure determination [245] to be polymeric and has centrosymmetric octahedral CoO_6 stereochemistry utilizing the 4 carboxylate oxygens and the two water molecules. The cation in the new complex *trans*-tetraaqua(bis(trimethylammonioacetato))cobalt(II) dichloride has the structure shown (**108**) [246]; the trimethylammonioacetato ligand (betaine) is coordinated to the Co in a *trans* fashion by the monodentate carboxyl groups. Monomeric complexes of Co(II) with the new ligands (**109**) have been prepared and characterized [247].



(**108**) *H atoms omitted.*



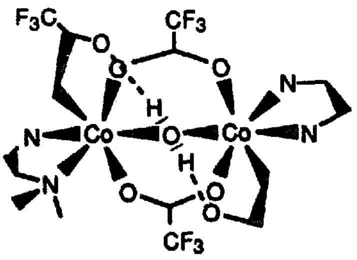
$$R = H_2C-\overset{H}{\underset{OH}{C}}-Me$$

H_3L', n = 3 and H_3L'', n = 4

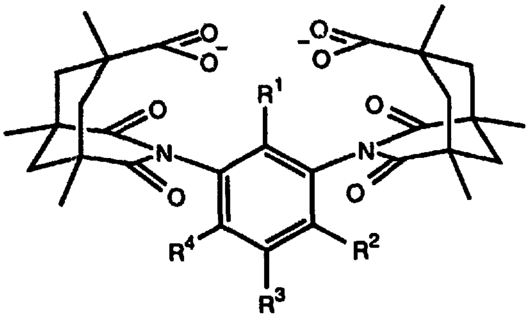
(**109**)

The polymeric complexes formed between Co(II) and 2,6-dimethoxybenzoic acid have been found to form adducts with added bases (py, 4-ethylpy, pyrazine, 2-methylpyrazine, imidazole and 1-methylimidazole) [248]. All form bis-adducts which are believed to contain a tetragonal arrangement around the Co in the hydrated form with 4 oxygens from carboxyls, solvent molecule and 2 nitrogens from the bases being involved

Reaction of the dicobalt(II) complex (**110**) with the ligand (**111**) yields the complex (**112**) [249], while the reaction of (**113**) is found to produce (**114**) which has been confirmed by an X-ray crystal structure determination. The structure of 4 in the scheme has also been determined in a related paper [250]. The effect of using these bulky ligands reduces the number of species found in equilibrium from ten when $Me_3CCO_2^-$ is used to only two when phenol-based ligands such as (**111**) are used.

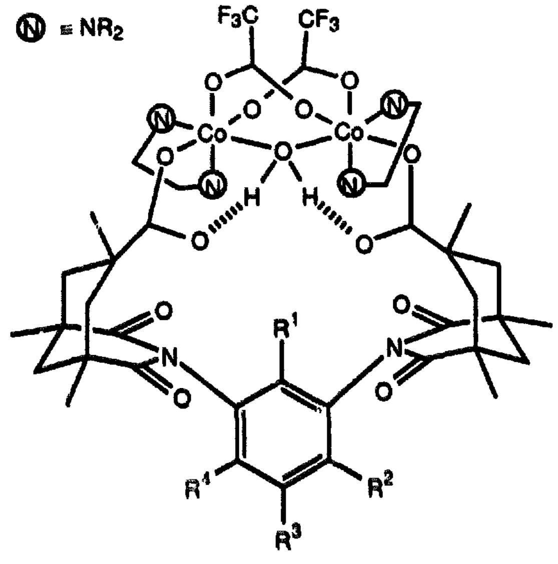


(110)

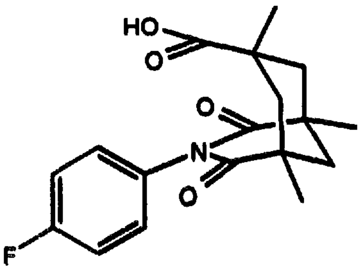


$R^4 = OH, R^3 = Me, R^1 = R^2 = H$
$R^1 = OH, R^3 = Me, R^2 = R^4 = H$

(111)



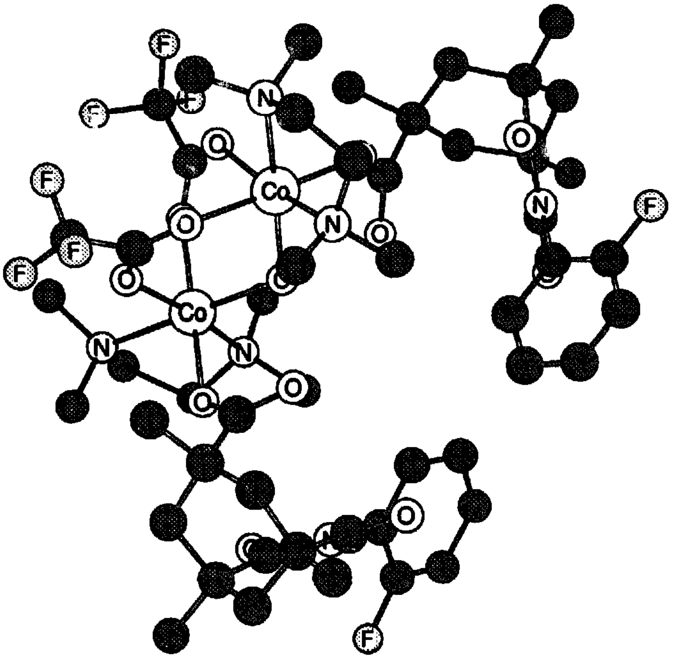
(112)



(113)

The effect of a micellar system on the kinetics of formation of complexes between 8-hydroxyquinoline and Co(II) was to decrease the rate by about a factor of 10 compared with the rate in aqueous solution [251].

The roles of so-called "blue" electrons and unpaired electrons on properties and structures in a range of mixed valence heteropoly tungsten blues have been investigated using magnetochemistry [252]. The complexes were derivatives of the Keggin structure α-$[XO_4W_{11}O_{35}ML]n^-$. X in this structure was a diamagnetic or paramagnetic hetero atom which occupies the central tetrahedral site. M is also a paramagnetic or diamagnetic atom which replaces a tungsten atom in an octahedral site. In addition the belt- and cap-octahedral site substituted derivatives of the Wells-Dawson structure, $[(XO_4)_2W_{17}O_{53}ML]^{n-}$ were also studied. As well as large spin-orbit coupling, electron delocalization, high distortion factors and high covalency are used to explain the observed properties of the paramagnetic (1e) blue electron systems. Antiferromagnetism is observed between the delocalized unpaired blue electrons and transition metal ions in octahedral and tetrahedral sites. In the 2e blues the diamagnetic blue electrons are antiferromagnetically coupled.



(114) *H atoms omitted.*

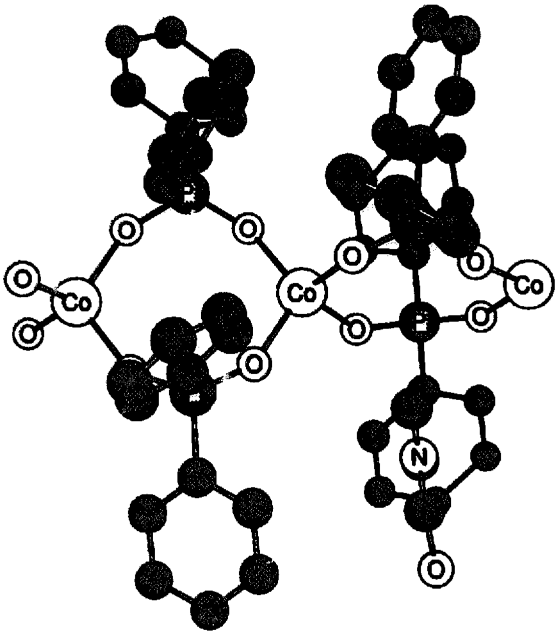
The application of fluorescent EXAFS to the investigation [253] of the structures of the Co(II) ion and its chloro complexes in dilute solutions (20 mM) in hexamethylphosphoric triamide (HMPA) shows that the coordination number of the cobalt is 4. The Co-O bond lengths in the complexes from $[Co(HMPA)_4]^{2+}$ to $[Co(HMPA)Cl_3]^-$ vary from 194 pm to 202 pm, while the Co-Cl bond lengths are in the range 224 pm to 229 pm, in both cases rather shorter than in similar complexes such as aqua complexes.

Two cobalt(II) diphenylphosphinate polymers have been prepared [254] by the reaction:

$$Co(OAc)_2.4H_2O + (C_6H_5)_2P(O)OH \rightarrow [Co(OPPh_2O)_2]_n + 4H_2O + 2AcOH$$

The crystal structures of these blue polymers have been obtained one of which is shown in **(115)**. The rate law for the catalysis of the loss of active oxygen from $[HOOSO_3]^-$ by cobalt(II) has been extended to pH 6 [255].

The synthesis of the complex $[Co(OPPr^n_3)_2X_2]$, where X = Br or I, has allowed a study of the uptake of SO_2 by this and related complexes [256]. When the complexes were exposed to gaseous SO_2 there was an increase in mass and measurements showed that this was equivalent to the absorption of two moles of SO_2 per mole of complex. The authors conclude that the resulting species which unlike the parent complexes are liquid, are formed by combination of the SO_2 with the ligand and the electronic spectrum shows that there appears to be little change in ground state or geometry (distorted tetrahedral) on the formation of the SO_2 species.

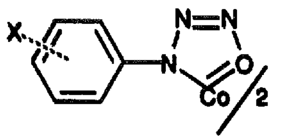


(115)

The crystal structure of diaquadichlorobis(piracetam)cobalt(II) shows that the Co atom is in an octahedral environment with the oxygen atoms of the two piracetam carbonyl groups of the pyrrolidine ring, two water molecules and two chlorides [257]. The nitrogen atom of the pyrrolidine ring is *cis* to the oxygen atom of the carbonyl. The X-ray crystal structure of [Co(15-crown-5)($CH_3CN)_2$][Cu_2Cl] [258] shows that the Co is inside the inner cavity of the macrocycle. On thermal decomposition this complex forms [Co(15-crown-5)($H_2O)_2$][$CuCl_4$] which similarly has the Co in the inner cavity.

1.2.3 Complexes with nitrogen-oxygen donor ligands

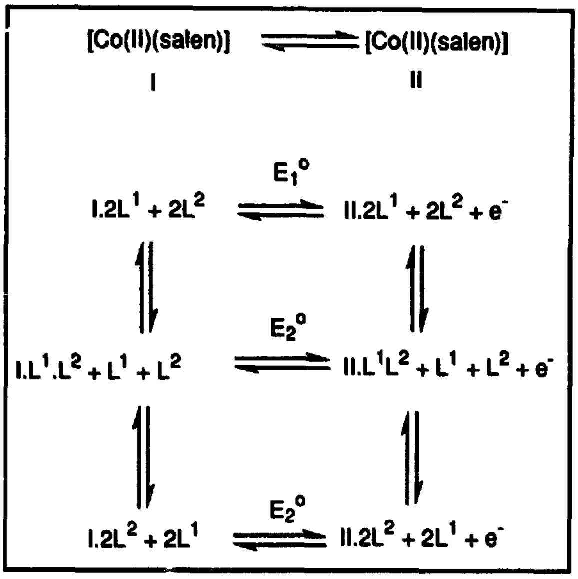
The structures of complexes (116) may be very markedly changed by altering range substituents in the ligand in the way shown [259]. The result is that high and low spin isomers of the cobalt(II) complexes may be produced so that in non-coordinating solvents the equilbrium between square planar and tetrahedral isomers may be observed with ΔH° values in the range 1–15 kJ mol^{-1} and ΔS° values between 5-30 J K^{-1} mol^{-1}.



R = Me, Et, Pr^n, Bu^t, or Ph
X = 4-H, 4-Me, 4-Et, 4-Pr^n,4-Bu^n, 4-OMe, 4-Cl, 4-Br, 4-CO_2Et, 4-NO_2, 3-Me, 2-Me,2,4-Me_2, 2,5-Me_2, 2,5-Me_2,2,6-Me_2 or 2-Me-4-NO_2

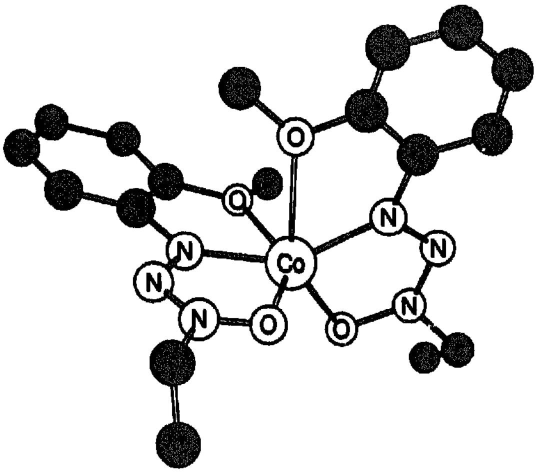
(116)

The ligand in [di-*tert*-butyl(dimethoxy)saien]cobalt(II) [260] is linked to the cobalt via two nitrogens and two oxygens to produce an almost planar arrangement around the cobalt. A complex series of redox reactions are observed in a cyclovoltametric study of the complex [Co(II)(salen)] dissolved in a mixture of dimethylformamide and pyridine [261]. It is demonstrated that if L_1 = dmf and L_2 + pyridine, then the following so-called ladder scheme explains the electrochemical behaviour as shown in (**117**).

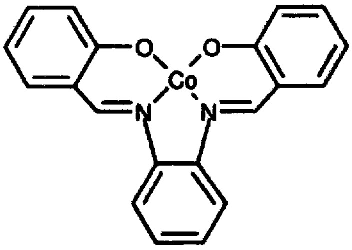


(**117**)

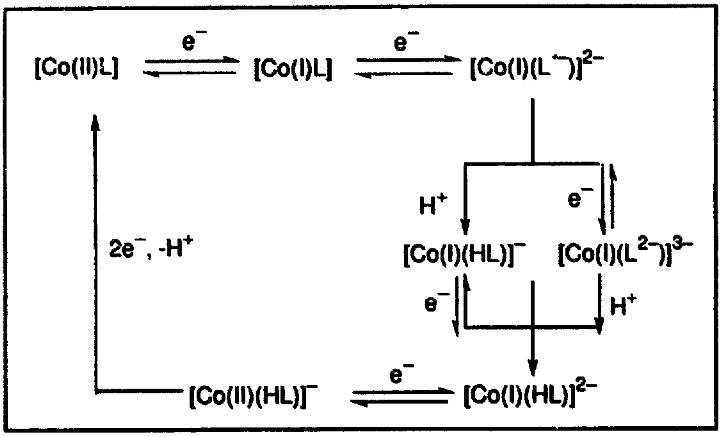
The X-ray crystal structure of the complex bis[3-(2-methoxyphenyl)-1-ethyltriazen-1-olato]cobalt(II) has been determined and is shown here (**118**) [262]. The geometry around the Co is a much distorted octahedron involving the methoxy oxygen atoms. Cyclic voltammetry and controlled-potential electrolysis applied to the complex (**119**) in dimethylformamide [263] have allowed the following sequence of redox reactions to be deduced (**120**). The highly unusual trigonal prismatic geometry is found [264] in the complexes $[(Co(H_3L'))_2(NO_3)_2][PF_6]$ and $[Co(H_3L'')](NO_3)$, in which L' and L'' are shown in (**121**). The former is a dimer in which two $[(Co(H_3L'))_2$ subunits are hydrogen-bonded NO_3^- ions.



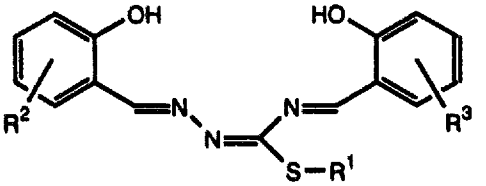
(**118**) *H atoms omitted*



(119)



(120)



R^1 = Me, Et, Pr^n, Bu^n
$R^2 = R^3 = H$

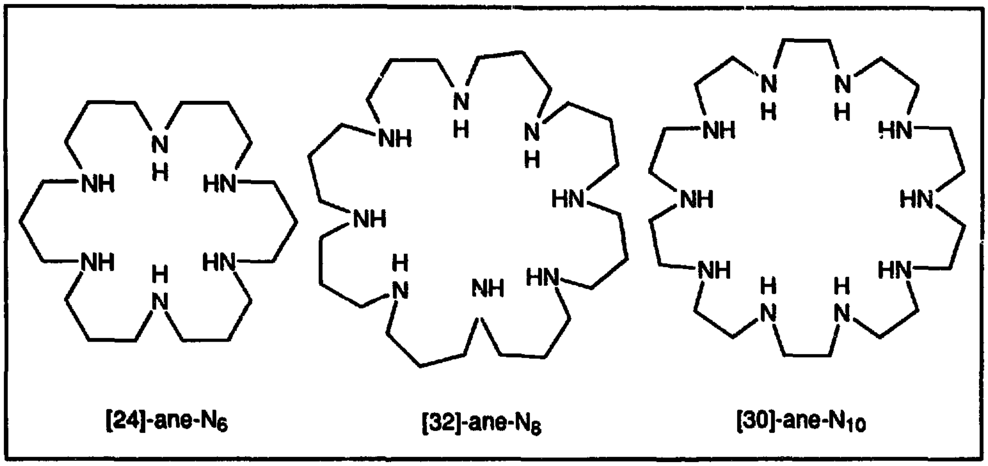
(121)

A single crystal EPR study of the ordered dimetallic chains in $Co_2(edta).6H_2O$ and $CoCu(edta.6H_2O$ has shown that there is dimerization of the chains and for the cobalt-copper exchange coupled pairs the exchange is anisotropic [265].

An investigation has been carried out on the reactions of a series of bis(peptide)nickel(III) $[Ni(H_{-1}PP)]^-$ complexes with $[Co(edta)]^{2-}$ in which the dipeptides ($H_{-1}PP$) were P = GH = glycine, AH = (S)alanine [266]. The electron transfer reactions were first order in both complexes and the rate constant showed a complicated dependence on the pH of the solution. Below pH8 the reaction pathway was as shown in **(122)**. Above pH 8 there is a decrease in rate followed by an increase up to about pH 11. Formation of $[Co(edta)OH]^{3-}$ above pH 10 is invoked to explain the increase. Above pH 8 an intermediate present in steady state concentrations is postulated, $\{[Ni(H_{-1}GG)_2]^-,[Co(edta)]^{2-}]\}$ in which its formation is H^+ catalysed. ¹H NMR relaxation studies have provided structural information on the intermediate.

$$\left.\begin{array}{l}[Co(Hedta)] \Leftrightarrow [Co(edta)]^{2} + H^{+} \\ [Ni(H-1GG)_2] + [Co(Hedta)]^{-} \rightarrow [Ni(H-1GG)_2]^{2-} + [Co(edta)]^{-} + H^{+}\end{array}\right\} \quad (122)$$

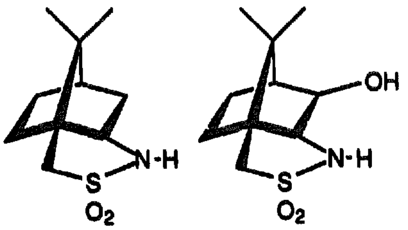
The effects on the photochemistry of $[Co(edta)]^-$ by the macrocycles **(123)** —1,5,9,13,1721 hexaazacyclotetraeicosane, [24]aneN_6, 1,5,9,13,17,2125,29-octaazacyclodotriacontane [32]aneN_8 and 1,4,7,10,13,16,22,25,28-decaazacyclotriacontane, 30[ane]N_{10} — have been studied [267].



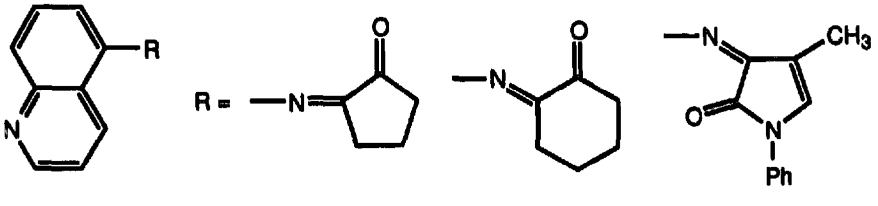
[24]-ane-N_6 [32]-ane-N_8 [30]-ane-N_{10}

(123)

The absorbance in the region of the ion-pair charge transfer band increased and there was an increase in the quantum yield for the intramolecular photo-oxidation reduction of the ion pair caused by an increase in the ion-pair association constant but with no increase in the intrinsic reactivity of the excited ion pair. The X-ray crystal structure of tetraaqua-4-chloro-1,2-phenylenediamine-*N,N,N',N'*-tetra-acetato-O^1,O^2,O^3,O^4,*N,N'*-cobalt(II) disodium shows the expected arrangement around the Co and each Na with six oxygens octahedrally arranged around them [268]. The cobalt(II) complex $[\{CoCl(H_2O\}_2(\mu\text{-}L)_2]$ where L is the ligand (1*S*,2*S*,3*R*)-3-hydroxycamphor sultam (**124**) [269]. Complexes with 8-hydroxyquinoline-5-iminoketones (**125**) bonded to Co(II) via *N,O* and believed to be polymeric are described [270]. Cobalt(II) complexes of 3-(1-imidazoyl)propionic acid and some nitro-substituted derivatives have been reported [271]. The dinuclear Co(II) complex (**126**) has been prepared and characterized [272].

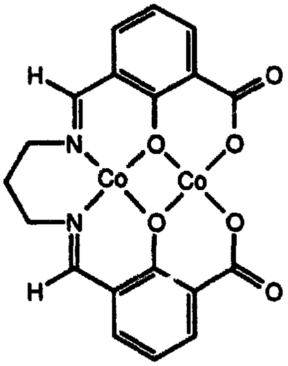


(124)

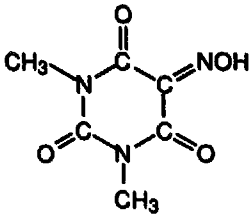


(125)

There are very few verified examples of low-spin octahedral complexes of cobalt(II) [273] The reaction of a cobalt(II) salt with dimethylvioluric acid (**127**) in the presence of phenanthroline yields [Co(dmvi)$_2$phen].2solv. The crystal structure of this complex shows the expected Jahn-Teller distortion in the axial ligands (positions occupied by the carbonyl oxygen of the dmvi) with a *trans*-N_4O_2 structure around the cobalt. The low-spin nature of the complex is confirmed by EPR and magnetic measurements. Values of ΔG, ΔH and ΔS in the temperature range 288 to 308K for reaction of cobalt(II) with 3,6-dihydroxypyridazine [274] have all proved to be negative and log K_1 and log K_2 had values of 7.70 and 3.74 respectively.



(126)

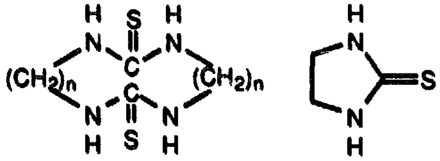


(127)

The X-ray crystal structure of the complex tris(*N*,*N*-dimethylaminomethyl)phosphine oxide)cobalt(III) perchlorate [275] shows that the ligand is coordinated to the cobalt via oxygen and nitrogen. The structure is significantly influenced by the two coordinated water molecules. The X-ray crystal structure of the complex dichlorobis(2-diphenylphosphoryl-cyclopentanone oxime)cobalt(II) showed that the complex was *cis* and had C_2 symmetry with the didentate ligand in a semi-chair configuration and bonding to the cobalt via nitrogen from the oxime and oxygen from the phosphoryl group [276].

1.2.4 Complexes with sulfur donor ligands

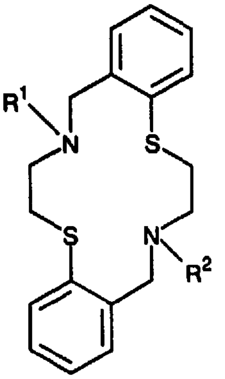
The X-ray crystal structures of the complexes [Co(mpo)$_2$L] (L = ^{n}Bu$_3$P or py, and mpo = mercaptopyridine-*N*-oxide) show that the cobalt atoms are surrounded by the ligands to produce a square pyramidal arrangement in which the two *trans* orientated mpo ligands occupy the basal plane and the other groups are in the axial position [277]. The stability constants for the cobalt(II) complexes of the ligands 1-thia-4,7-diazacyclononane, 1-thia-4,8-diazacyclodecane and 5-thia-2,8-diazanonane have been determined [278]. Polymeric complexes of cobalt(II) with the ligands (128) have been studied for antifungal activity [279]



(128)

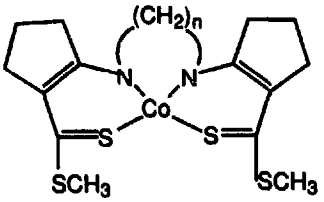
1.2.5 Complexes with sulfur-nitrogen donor ligands

The X-ray crystal structure of the complex $[CoL]^{2+}$, where L is **(129)** [280] shows that it has a trigonal prismatic arrangement around the cobalt with bonding through the sulfur atoms and both the amine and pyridine nitrogen atoms. A low spin Co(II) complex of the N_2S_2 ligand **(130)** has been prepared and characterized [281] as a different approach to the more usual N_2O_2-complexes which bind O_2. The ESR spectroscopic data are used to determine a possible ground-state configuration.



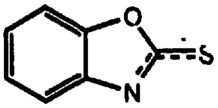
L = R^2 = R^1 = $CH_2C_5H_4N$-2

(129)



CoN_2S_3 n = 2, 3

(130)



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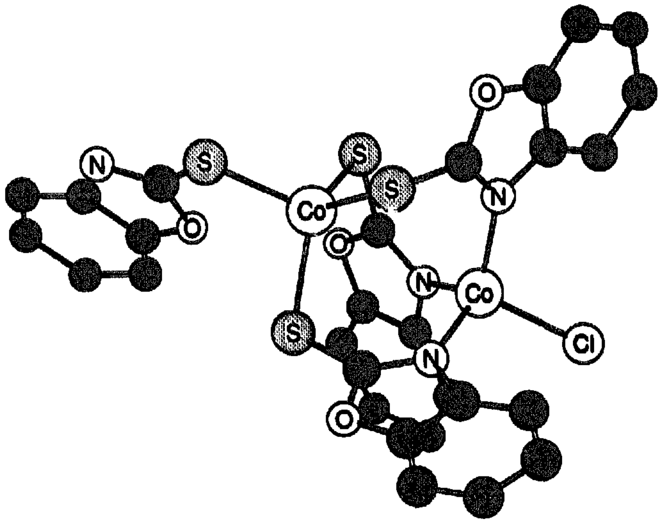
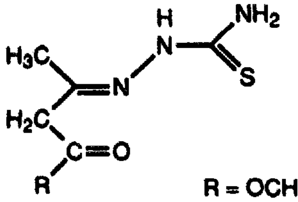


(132)

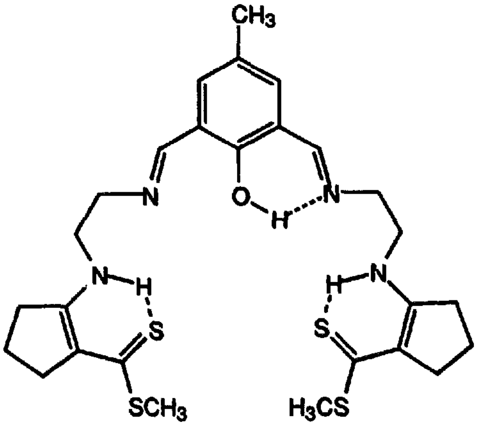
1.2.6 Complexes with nitrogen-oxygen-sulfur donor ligands

A most unusual complex is formed when solid $CoCl_2$ is heated with a solution of $L_2Ca.2HMPA$ in toluene, where L^- = **(131)** [282]. The X-ray crystal structure shows it to be $[LCa.4HMPA]^+[LCo\{\mu\text{-}L_3\}CoCl]^-$. The cation **(132)** has the two cobalt atoms in two quite different environments; one is coordinated to hard nitrogen atoms, while the other to soft sulfur atoms. The UV-VIS spectrum is characteristic of two Co(II) species rather than a Co(I) and Co(III) arrangement. The anti-tumour behaviour of $MatH_2$ and $EatH_2$ (**133**) has been investigated [283].

Mono- and dinuclear complexes of Co(II) and H_3L (**134**) have been synthesized and characterized [284].



R = OCH_3 ($MatH_2$)
R = OC_2H_5 ($EatH_2$)
(**133**)



(**134**)

1.2.7 *Complexes with halide and pseudohalide donor ligands*

A crystal structure of the complex $[emim]_2[CoCl_4]$ [285] and the corresponding nickel complex, where emim is (**135**) shows clearly that in the crystal there are there are hydrogen bonds formed between the cation and the anions such that all the ring protons and all the chloride ions are involved in a three dimensional network of hydrogen bonds.

(**135**)

In 1,3-propanediammonium tetrachlorocobaltate(II) the anion is tetrahedral [286] and arranged throughout the crystal with paraffinic chains bridging the tetrahedra in a zig-zag manner. The four complexes $[Co(dma)_{4-n}Cl_n]^{(2-n)+}$, n = 1 to 4 have been studied by calorimetry and spectrophotometry in the solvent *N,N*-dimethylacetamide, dma [287]. From the spectrophotometry the complex $[Co(dma)_6]^{2+}$ is assigned an octahedral structure, while $[CoCl(dma)_3]^+$, $[CoCl_2(dma)_2]$, $[CoCl_3(dma)]^-$, and $[CoCl_4]^{2-}$ have tetrahedral structures over the temperature range 278 to 318 K. Data are provided for formation constants. The high values of ΔH°_1 and ΔS°_1 are interpreted as being indicative of extensive desolvation in the formation of the monochloro complex indicating the early change in the geometry.

Inevitably the vast majority of complexes described in these reviews are in solution or in the solid state [288]. Occasionally a gaseous phase study is carried out. Such is the result when $[CoCl_2(py)_2]$ is heated between 290 and 420°C under a large excess of pyridine. The measurement of the visible spectrum of the gas shows that both $[CoCl_2(py)_2]$ and $[CoCl_2(py)_2]$ are present allowing comparisons of the solution and gaseous spectra and the determination of enthalpy and entropy data.

X-Ray crystal structure determination of the complexes [Co-(15-crown-5)$_2$CH$_3$CN][CoCl$_3$.CH$_3$CN].CH$_3$CN, [Co(15-crown-5)$_2$CH$_3$CN][CoCl$_4$].CH$_3$CN and [Co(15-crown-5)$_2$CH$_3$CN][Co$_2$Cl$_6$] [289] showed them all to be intracavital complexes with the cobalt being surrounded in a pentagonal bipyramid by donor atoms.

The crystal structure of the 2,6-dimorpholino-4-phenyl-1,3,5-oxadiazinium salt of the stable acetonitrile trichlorocobaltate(III) complex anion has been determined [290].

Once again, further insight into the structures of simple species has been sought in that the X-ray crystal structure of CoBr$_2$.4H$_2$O has been determined. It was found that around the cobalt the Br atoms were in the axial positions and the waters in the equatorial positions [291]. The cobalt(II) complexes [Co(N$_2$H$_4$)$_2$F$_2$].2H$_2$O, [Co(dmpz)F$_2$(H$_2$O)$_2$].2H$_2$O, [phenH][CoF$_2$(phen)].8H$_2$O and [(bpy)H][CoF$_2$(bpy)].6H$_2$O, where dmpz = 3,5-dimethylpyrazole have been prepared [292]. It is suggested that the complexes are generally polymeric with fluorine bridges.

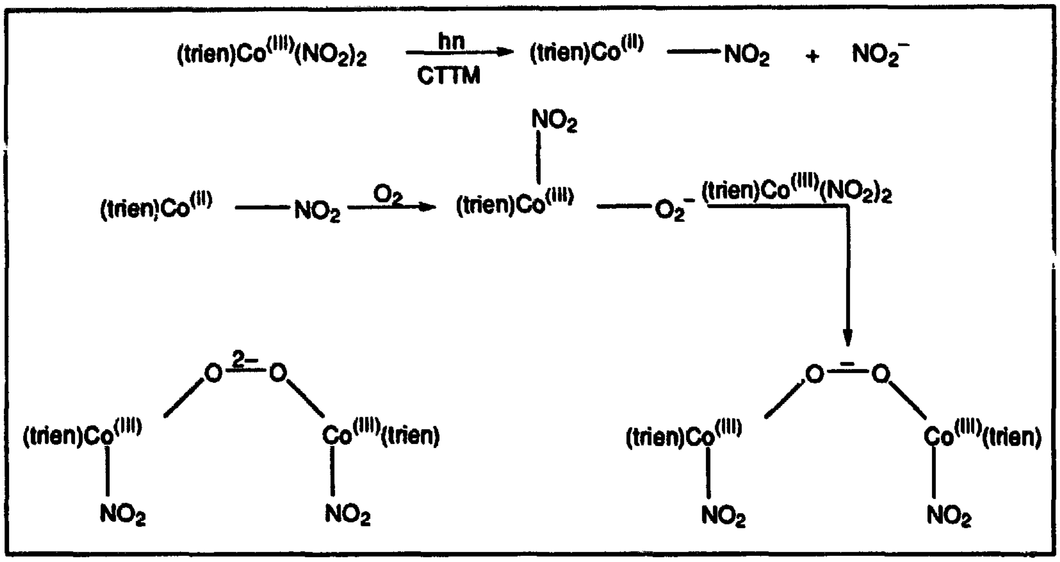
Most of us have used HgCo(SCN)$_4$ as a calibrant in magnetic susceptibility measurements [293]. It has recently been pointed out that confusion has reigned when the magnetic susceptibility is considered over the whole of the temperature range 1.7 to 300 K. This work has been carried out using single crystal measurements over the whole of the temperature range. It is found that in the temperature range 1.7 to 40K, the Curie-Weiss model does not fit the data well. It is concluded that the magnetic behaviour over the whole range can only be explained if temperature independent -paramagnetism, zero-field splitting and magnetic exchange are taken into account.

Infrared and fast atom bombardment mass spectrometry have been used to show that in the reaction of [Co(CN)$_5$]$^{3-}$ with NO, an intermediate was [Co$_2$(CN)$_{10}$(NO)$_3$]$^{6-}$ in which the authors suggest that the NO behaves as a bridge between the cobalt atoms [294].

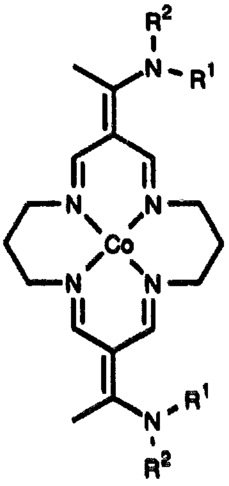
1.3 REACTIONS OF COBALT COMPLEXES INVOLVING DIOXYGEN

Irradiation of an aqueous solution of the orange complex *cis*-[Co(trien)(NO$_2$)$_2$]ClO$_4$ while bubbling oxygen through the solution results in a change in colour to dark green and the product is µ-superoxo dinuclear complex [295]. This forms part of a study of the oxygenation reactions which occur in oxygenated solutions of *cis*-[Co(trien)(NO$_2$)$_2$]ClO$_4$ and *cis*-[Co(tetraen)(NO$_2$)][ClO$_4$]$_2$ in water and CH$_3$CN using flash photolysis and steady radiation. The process involved in the reactions is illustrated below (**136**). This gives a new route to mononuclear dioxygen species using a cobalt(III) complex.

Cobalt(II) complexes of the lacunar cyclidene type (**137**) have been prepared [296]. These complexes were also incorporated into polymer matrices by coordination to pyridine in copolymers of 4-vinylpyridine with styrene, methyl methacrylate or butyl methacrylate. The reactions of the free complexes and the polymer-bound species with dioxygen resulted in spectra which indicated a 6-coordinate dioxygen adduct. A feature of the reactions was that the bridged species when free or polymer-bound react reversibly with the dioxygen. The dioxygen complexes bound to the polymer in general have half lives much longer than those of the free species.

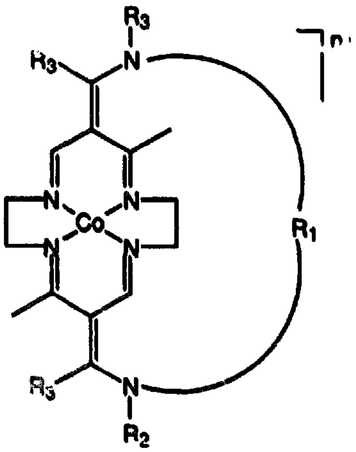


(136)



R^1 =	$^1/_2(CH_2)_6$	Me	CH_2Ph	CH_2Ph
R^2 =	Me	Me	Me	Me
R^3 =	Me	Me	Me	Ph

(137)



(138)

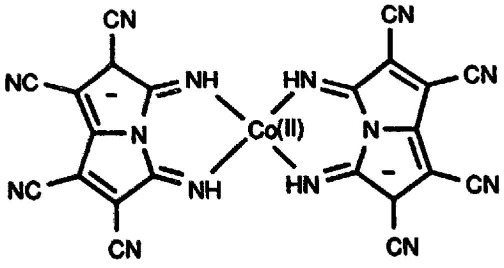
In order to investigate the effect of the nature of the cyclidene ring structure on the dioxygen affinity of metal ion complexes of lacunar cyclidenes, the cobalt(II) and nickel(II) complexes of a 14-membered cyclidene (**138**) have been prepared [297]. The X-ray crystal structure of the nickel(II) complex showed that the cavity was wide and low. Molecular mechanics calculations show very strikingly the differences in the geometry of the cavity in the 14-, 15- and 16- membered ring complexes. The cobalt(II) complex is shown to bind dioxygen reversibly and at −10°C auto-oxidation was found to be reasonably slow and the binding equilibrium constant at about 250 K was 0.11 Torr in CH_3CN with *N*-methylimidazole in the axial position. The more open cavity referred to above results in more rapid auto-oxidation compared with 16-membered ring analogues.

A range of complexes involving cobalt(II) triazine 1-oxide adducts with pyridine, imidazole and 1,2-dimethylimidazole have been prepared [298] and the crystal structure of bis[3-(4-chlorophenyl)-1-methyl triazine-1-olato]cobalt(II)-pyridine (1/1) has been determined. This is monoclinic with space group P2/c, a=18.39, b=12.553, c=9.827 Å, β = 105.65° and Z = 4. ESR spectroscopy was used to study reversible dioxygen binding. The addition of pyridine to CH_2Cl_2/pyridine solutions of $[Co\{(ORN_3C_6H_4X)_2]$ resulted in the disappearance of the ESR spectroscopic signal; bubbling dioxygen through the solution at 200 K produced ESR spectra characteristic of superoxo complexes. Subsequently bubbling argon through these solutions restored ESR silence. The authors were able to classify the complexes by their ability to take up dioxygen.

An investigation of the dioxygen uptake of some cobalt(II) tetraazamacrocycles showed that dioxygen, superoxo and peroxo species are produced [299]. The process involves, first the rapid formation of a superoxo complex and then the formation of the peroxo complex by reaction with another Co(II). The reactions of the superoxo complex with a variety of reducing agents is reported.

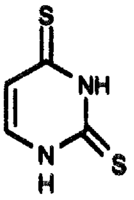
Against the background of the value of the electrochemical properties of dioxygen-active complexes, a study of the electrochemically controlled dissociation of dioxygen from the complex $[\{Co(III)(salen)(dmso)\}_2O_2]$ has been carried out (salen = *N,N'*-ethylenebis(salicylideneiminate)) [300]. Having established that the kinetically inert μ-dimer dioxygen adduct released dioxygen electrochemically, the system was studied using spectroelectrochemistry and this showed that during electrolysis, the spectrum changed to that of $[Co(III)(salen)(dmso)_2]^+$. Reduction of this species produces the cobalt(II) moiety which may then bind dioxygen. It has been found that reaction of [Co(salen)] and related complexes with Fe^{2+} resulted in the formation of heterodinuclear complexes which showed a much higher uptake of dioxide than the [Co(salen)] alone [301]. The enthalpies of reaction for the loss of dioxygen from a number of complexes of the type $[Co(3\text{-}X\text{-}salen)]_2O_2$, in which X = H, OCH_3, OC_2H_5 or NO_2 [302] have been determined. The values obtained using DTA vary from 88 kJ mol^{-1} (X =NO_2) to 120 kJ mol^{-1} (X = OCH_3). The kinetics of the reactions may be described in terms of a first order process.

The complex $[Co(L)_2].2A$, where L = 1,2,6,7-tetracyano-3,5-dihydro-3,5-diiminopyrrolizinide and A = 1,2-dimethoxyethane (**139**) has been prepared and characterized [303]. The X-ray crystal structure shows the square planar arrangement around the metal ion and two complex molecules lie axially to the plane to produce a tetragonally distorted tetrahedral arrangement about the cobalt. Magnetic data show that the complex is high spin with antiferromagnetic superexchange interactions. Polymeric superoxo adducts are produced when dioxygen is bubbled through a solution in MeCN. A centrosymmetrically dioxygen bridged structure is proposed for this polymer.



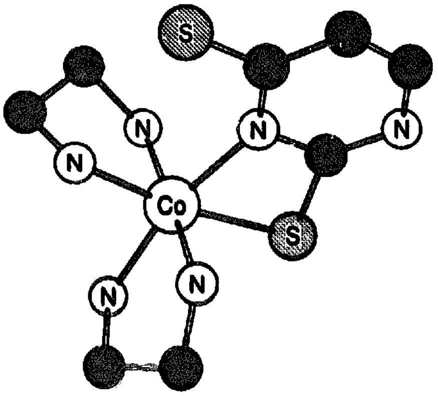
(139)

The ligand 2,4-dithiouracil (H_2dtuc) (**140**) presents some intriguing possibilities for the formation of linkage isomers. A series of such complexes has been prepared [304]. The X-ray crystal structure of one of these, $[Co(dtuc)(en)_2]ClO_4$ showed it to contain cation (**141**) and the structures of others were inferred from UV-VIS and NMR spectroscopies.



H_2dtuc

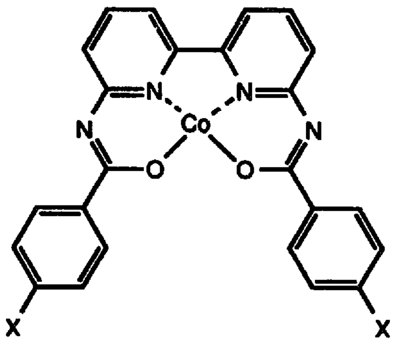
(140)



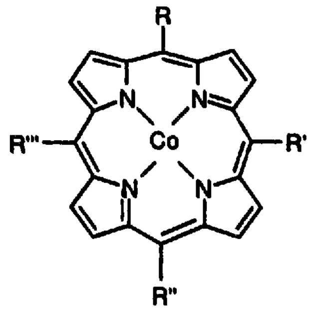
(141)

Earlier work by Araki and coworkers ([305]) has been extended to examine the dioxygen affinity and the properties of dioxygen complexes of cobalt(II) complexes of the ligand systems involving 6,6'-bis(*p*-substituted benzoylamino)-2,2'-bipyridines (**142**) [306]. Appreciable uptake of dioxygen was observed in the presence of a base such as 4-dimethylaminopyridine in dimethyl formamide. The affinity for dioxygen was particularly affected by the presence of *m*-substituted electron-donating substituents. The dioxygen affinity and the reactivity of the dioxygen adducts is related to the ability to oxidize 2,6-di-*tert*-butylphenol to the corresponding quinone.

When the cobalt(II) porphyrin complexes shown in (**143**), are reacted with pentaammineruthenium(II) complexes and adsorbed on pyrolytic graphite electrodes [307], it is found that complexes containing one or two Ru centres reduce dioxygen in a two-electron process to H_2O_2. However when there are three or four Ru centres present there occurs a four electron reduction of dioxygen to water. In related work, cobalt *meso*-tetrakis(4-pyridyl)porphyrin has been desorbed onto pyrolytic graphite electrodes and then reacted for several hours [308] with a solution of $[Ru(NH_3)_5(H_2O)](PF_6)_2$ to produce a complex system in which $Ru(NH_3)_5$ groups are attached to the pyridine sites. This electrode was found to act as an efficient catalyst for the four-electron reduction of O_2 to H_2O.


X = H, Cl, Me, Bu^t

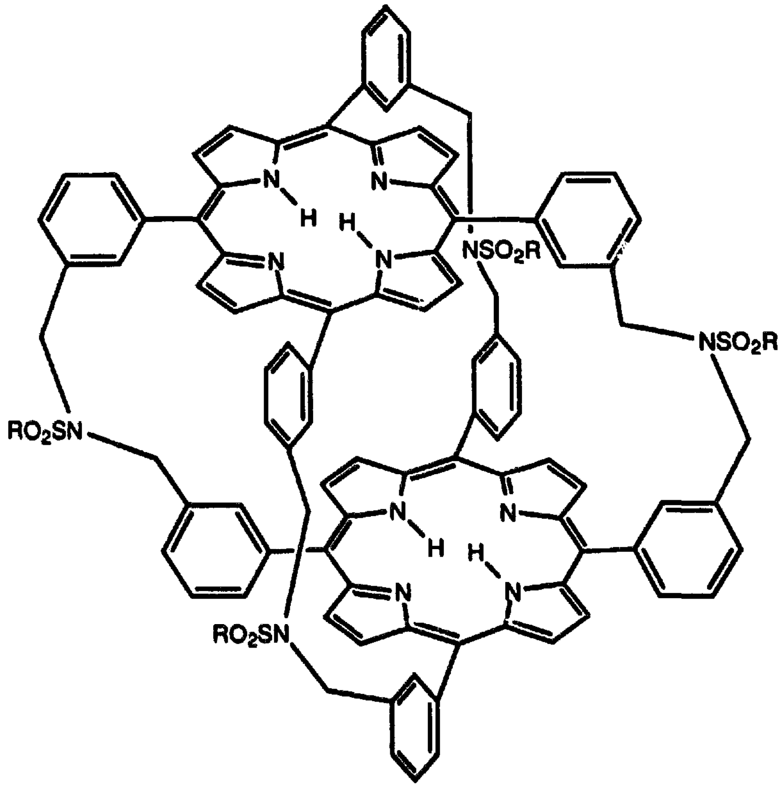
(142)

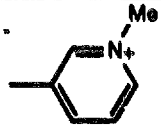
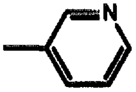
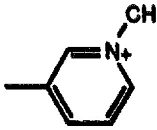
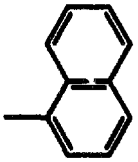


R	R	R"	R"'
4-py	Ph	Ph	Ph
4-py	4-py	Ph	Ph
4-py	Ph	4-py	Ph
4-py	4-py	$4-CF_3C_6H_4$	$4-CF_3C_6H_4$
4-py	4-py	4-py	Ph
4-py	4-py	4-py	4-py

(143)

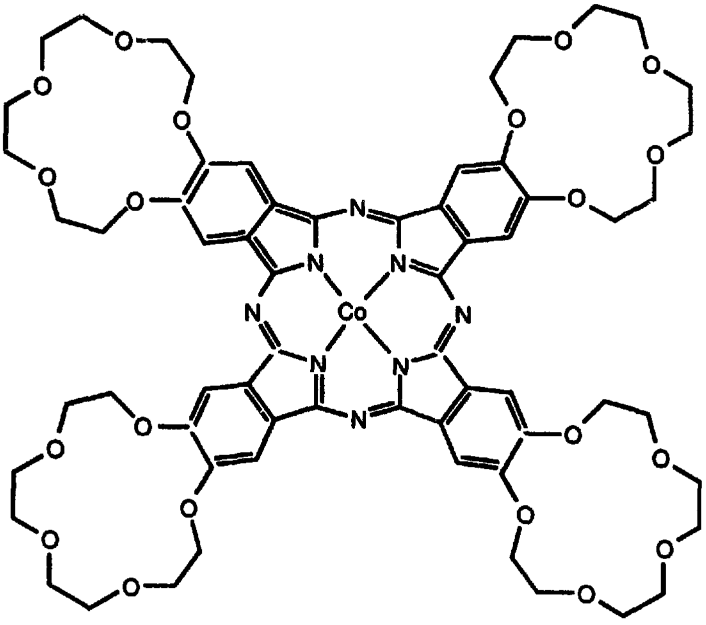
When the complex (*meso*-tetraphenyl porphyrinato)cobalt(II) is sublimed onto a sodium chloride plate it retains its structure [309] and may be reacted with MeIm by passing the latter mixed with Ar over the thin layer of the CoTPP. This system then reversibly absorbed O_2 at room temperature. Similar behaviour is found when CoTPP plasma films are used. It has also been found that this complex, when sublimed onto a substrate at -80 K, coordinates dioxygen, though the ability to do this depends crucially on the preparation of the film [310]. At temperatures below 200 K thin films of *meso*-(tetra-3-pyridylporphyrinato)cobalt(II) take up molecular O_2 [311]. The spectra of the films have been examined and the O_2 has a vibrational frequency of 1162 cm^{-1}. UV-Visible absorption spectra indicate that there is intermolecular interaction between the layers via the cobalt and the nitrogen atom of a neighbouring pyridyl. The Co(II) complex of the ligand 5-[*p*-[4-*m*-pyridyloxy)-butoxyl]-phenyl]-10,15,20-triphenylporphyrin (PyBPTPP) absorbs dioxygen reversibly in benzene solution at room temperature [312]. Infrared spectral data indicated that the O_2 was coordinated end-on to the cobalt. Synthesis of complexes of the type shown in (144) (with representative R groups shown) allows the effects of a wide range of subtle changes in the structure on behaviour such as the reduction of dioxygen to be investigated [313]. The structures were investigated using 2-D NMR spectroscopy and compared with the results of molecular modelling calculations for the [3-pyridyl]$_4$ dimer. For the cobalt(II) complexes, the ability to catalyse the 4-electron reduction of dioxygen to water was found to be more effective in the case of the 4+ complexes than the neutral complexes. A further factor was the number of bridges between the porphyrins, where it was found that there was a significant diminution in catalytic activity as the number of bridges decreased.



Ligand	R	Ligand	R	Ligand	R
[*N*-methyl pyridyl]$_4$	3- 	[3-pyridyl]$_4$		[methyl]$_4$	Me
[*N*-isopropyl 3-pyridyl]$_4$		[1-naphthyl]$_4$		[isopropyl]$_4$	CHMe$_2$

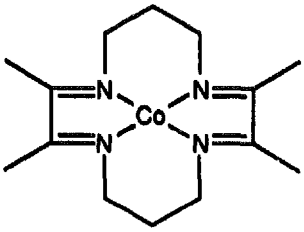
(144)

When cobalt(II) crowned phthalocyanine (**145**) is adsorbed on highly orientated pyrolytic electrodes, it is found to be an efficient catalyst of the cathodic reduction of oxygen and hydrogen peroxide [314]. Cobalt(II) phthalocyanine may be intercalated into a $Mg_5Al_{2.5}$-layered double hydroxide [315] and this species has been shown to be a very efficient catalyst for the auto-oxidation of 2,6-di-*tert*-butylphenol, a process which has considerable importance in the treatment of contaminated groundwaters. After more than 3200 turnovers, the catalyst was still fully active and readily recoverable in contrast to other catalysts and the homogeneous process.



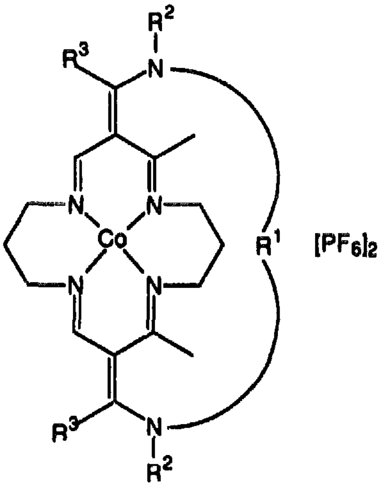
(145)

The reduction of O_2 by $[Co(tim)]^{2+}$, **(146)** catalysed by Fe^{2+} involves a four-electron process in which water is the product and does not involve the formation of H_2O_2 as an intermediate [316]. It is proposed that the process involves the formation of $[(tim)CoOOFe]^{4+}$ followed by $[(tim)CoOOH]^{2+}$.



$[Co(tim)]^{2+}$

(146)



(147)

The cobalt(II) complex, $[CoL][PF_6]_2$ where L is new macrobicyclic ligand **(147)** was prepared using the usual method for such complexes but reacting in methanol distilled into the Schlenk tube at room temperature. Reaction at higher temperatures resulted in other products. The complex was investigated by ESR spectroscopy and this shows that it consists of a mixture of 4- and 5-coordinated species, the latter being formed by intermolecular interaction of the cobalt(II) with the secondary amine group. A reasonably stable dioxygen complex is formed reversibly with dioxygen [317]. By examining the uptake of dioxygen by various concentration ratios in mixtures of $Co(NO_3)_2$ and 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontaine in aqueous solution [318] in the presence of various different anions it has been possible to demonstrate the formation of the dinuclear species, $[Co_2L(O_2)(OH)]$ and the mononuclear complex, $[Co(H_mL)(O_2)]$. The kinetics of uptake of dioxygen under a wide variety of conditions led to a series of equations (148) for the reactions involved. Phosphate (Y) ions take an active part in the reactions, being incorporated as $[Co_2L(O_2)Y]$ and $[CoL(O_2)Y]$.

[L]:[Co] low

pH 8 to 9:

$$2Co^{2+} + H_4L^{4+} + 5OH^- \longrightarrow [Co_2L(O_2)(OH)]^{3+} + 4H_2O$$

pH 11:

$$2Co^{2+} + HL^+ + 2OH^+ \longrightarrow [Co_2(O_2)(OH)]^{3+} + H_2O$$

[L]:[Co] > 1:1

pH 7.5 to 8.1:

$$Co^{2+} + H_nL^{n+}\ O_2 + 3OH^- \longrightarrow [Co(H_mL)(O_2)]^{(n-1)+} + 3H_2O$$

(148)

The kinetics of dioxygen uptake by the complex $[Co(hmc)(H_2O)_2]^{2+}$ to form $[Co(hmc)(OH)O_2]^+$ (hmc = c-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) have been shown to be substantially the same above pH 6, and also below until the reacting complex deprotonates ($pK_a = 11.68$). Then, the rate significantly decreases, while the rate of dissociation of dioxygen decreases by a factor 10^6 [319].

Mono and dinuclear Co(II) complexes of the ligand $[30]aneN_{10}$ (1,4,7,10,13,16,19,-22,25,28-decaazacyclotriacontane) have been found to bind phosphate in a cascade fashion affecting dioxygen uptake by the species [320]. A large number of complexes of Co(III), Rh(III) and Ir(III) of the form $[(triphos)M(Cat)]^+$, (cat = 9,10-phenanthrenecatecholate, 1,2-naphthalenecatecholate, 5-di-*tert*-butylenecatecholate, 4-methyl catecholate, 4-carboxycatecholate-ethyl ester and tetrachlorocatecholate) have been prepared and the reaction with dioxygen was studied [321].

The nature of the dioxygen which has been reversibly added to $[Co(L)(L')(H_2O)]^{2+}$, where HL = amino acid and L = bpy or phen has been investigated using already available literature results and from polarographic data [322]. It is concluded that if the O_2 is present in the peroxo form, then the reduction stage corresponding to peroxide will be at about 800mV.

The adducts formed by [*N*1,*N*4-bis(salicylidene)-S-alkyl-isothiosemicarbazoneato]cobalt(II) complexes (**148**) with a wide range of species having *N*-, *P*-, *As*-, *O*- and *S*- donor bases show that in most cases the ESR spectra indicate 5-coordinate low-spin complexes [323].

The exceptions are the complexes with adducts containing *N*-bases where 6-coordinate adducts are formed. The activity of the complexes towards dioxygen is also a feature of this work. The L-phenylalanyl-L-alanine dipeptide cobalt(II) complex has been shown to take up dioxygen in a highly reversible fashion, though other dipeptides having phenylanlanine as the *N*-terminal or C-terminal amino acid also showed a propensity to take up dioxygen [324]. The same group have also found that the Co(II) complex involving H-Gly-L-His-OH is as efficient dioxygen absorber [325].

1.4 COBALT(I) COMPLEXES

The complex *N*-rac-Co(I)L-CO_2, where L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, in acetonitrile exhibits thermochromism in that the solution is purple at room temperature and yellow at low temperatures [326]. By following the variation of the FTIR and ^1H NMR spectra of such a solution it is shown that the reaction involves the conversion of the purple five-coordinate complex to a yellow six-coordinate acetonitrile adduct. The situation is complex and there are in fact four types of CO_2 adduct involving hydrogen bonded and non hydrogen bonded 5- and 6-coordinate species.

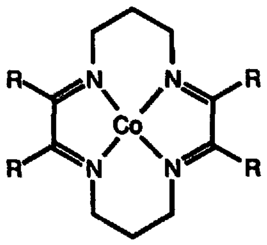
The protonation of cobalt tetraneopentoxyphthalocyanine as a function of oxidation state has been studied [327] for Co(I), Co(II) and Co(III) as well as the cobalt(III) cation radical species in dichlorobenzene using electronic spectroscopy and yielding stability constants. The basicity was found to decrease moving from Co(I) to the Co(III) radical species.

When membranes made from copolymers of 2-hydroxyethyl methacrylate and 4-methyl-4'-vinyl-2,2'-bipyridine are complexed with cobalt(II) and dipped into an aqueous solution of $NaBH_4$, H_2 is evolved and the membrane becomes an intense blue colour due to the formation of cobalt(I) [328]. This is fairly stable, having a half life in oxygenated water of about 47 min. Dehydration of this extends the life of the cobalt(I) to several days.

The crystal structure of the complex$[Co(NO)_2(py)_2]^+$ shows that the Co atom has a distorted tetrahedral environment [329]. The stability of the complex was affected greatly by the nature of the counter ion, so that for example in CH_2Cl_2 solution with BF_4^- as anion the complex was inert whereas with BPh_4^- the complex rapidly decomposed. Infrared spectroscopy revealed that this reaction involved a transient intermediate.

Reaction of $[Co(PPh_3)_3Cl]$ with $HSCH_2CH(OH)CH_2OR'$ (RSH) (R' = H, CH_3, C_2H_5) in tetrahydrofuran yields $[Co(PPh_3)_2RS]_2$ [330]

The complexes (**149**) readily undergo reduction to the corresponding Co(I) complexes and these behave as Lewis acids in acetonitrile solution [331]. The results of a study of the equilibrium constants for the formation of adducts between the Co(I) complexes and py, *N*-methylimidazole, triphenylphosphine and Br^- show that even in dmf which is not a π-acceptor ligand $[CoL]^+$ is still a good Lewis acid. This is interpreted as acknowledging that it is the nature of the macrocyclic ligand which governs the Lewis acidity of the species.



R = Me or Ph

(149)

1.5 REACTIONS INVOLVING VITAMIN B_{12}

The notion that the microenvironment in physiological situations in which vitamin B_{12} frequently operates is not always aqueous, but may sometimes be hydrophobic in character has motivated a study of the thermodynamics and kinetics of the reaction of iodide ion with aquacobalamin in solution in mixtures of methanol and water. The rates and equilibrium constants of the reaction were studied over a range of solvent compositions [332]. The results show that the reaction of iodide proceeds with the initial formation of an outer-sphere complex and that this species is more stable in methanol solution than in water.

An EXAFS study of aquacobalamin and cyanocobalamin has shown that the Co–(5,6-dimethylbenzimidazole) distance is rather long (2.14-2.15 A) and markedly affected by steric factors [333]. Reaction of the hydrolytic agent $[Co(L)(H_2O)_2]^{3+}$ [L = tris-(3-aminopropyl)amine)] with cyano- and aquo-cobalamin [334] in the hope of hydrolytically cleaving the 5,6-dimethylbenzimidazole group in the axial position has resulted in decomposition of $[Co(L)(H_2O)_2]^{3+}$ and the replacement of the water in the aquacobalamin by L. A similar reaction did not occur in the cyanocobalamin.

The technique of heteronuclear multiple-quantum coherence applied to cyanocobalamin [335] has allowed the observation of the B1 and B3 ^{15}N resonances at natural abundance providing a definitive assignment which is based on variation of the *trans* axial ligand. By using ^1H-^{13}C 2-D NMR spectroscopy a complete assignment has been carried out for the important B_{12} derivatives, hydroxocobalamin, azidocobalamin and cyanocobalamin [336]. The NMR spectroscopic techniques have also been used in this work to assess *trans* effects in alkylcobalamin species. The ability of neutron diffraction to locate hydrogen and deuterium atoms has allowed a preliminary investigation of the arrangement of water molecules in crystals of vitamin B_{12} coenzyme at 15K and 279K [337]. The unit cell was decreased in volume by some 2% on increasing the temperature and the coenzyme molecule itself was observed to have rotated by about 2°. The reaction between aquacobalamin and glutathione produced the complex glutathionecobalamin (GSCbl) by replacement of the axial water molecule [338]. The position of coordination of the glutathione has been in doubt. A complete unambiguous assignment of the proton and ^{13}C NMR spectra of GSCbl has been completed using a variety of two-dimensional NMR spectroscopic techniques. As a result of this and comparison with NMR spectroscopic data from free glutathione, it has proved possible to show that the glutathione is coordinated to the cobalt via the cysteine sulfur atom. There are now a number of complete NMR spectroscopic assignments for cobalamins and the authors have compared their spectra with these and concluded that corrin ring conformation varies considerably between the various base-on complexes.

The H-N connectivities of the peripheral amide groups in five 5'-deoxyadenosylcobalt corrinoids including coenzyme B_{12} [339] have been investigated using inverse detected ^1H and ^{15}N HMQC spectroscopy. All of these are related to vitamin B_{12} in that different groups occupy the axial positions. The application of NOESY spectra in dmso-d_6 allows the assignment of the ^1H and the ^{15}N NMR resonances for the side-chain amides.

Vitamin B_{12} and related complexes may exist in a base-on or a base-off configuration in which the benzimidazole nucleotide becomes detached from the cobalt [340]. Brown and Evans have arranged things so that the lower axial position (α) is occupied by an alkyl group, so that the pK_a of the uncoordinated nucleotide could be determined as being about 5.5. This study covers a range of temperatures and thermodynamic data are thereby obtained. The deprotonated benzimidazole species is believed to exist in the so-called "tuck-in" position.

In a kinetic study of the effect of pressure on Co-C bond fission reactions of methyl-, isopropyl-, neopentyl-, and adenosylcobalamin and adenosylcobinamide in water and 1-propanol/water mixtures, the reactions were found to occur in the temperature range 370-390 K with very little cage efficiency and with a large volume of activation [341]. Lowering the temperature caused the cage efficiency to increase. The volume of activation was not significantly affected by the nature of the R group.

EXAFS has revealed the first four-coordinate cobalt(II) corrinoid in the corrinoid/iron-sulfur protein from *Clostridium thermoaceticum*. [342]. This state is believed by the authors to be such that it has just the right stereochemistry for facile reduction to Co(I) which is required for the enzyme to carry out its task of transferring a methyl group from methyltetrahydrofolate to carbon monoxide dehydrogenase. The same group have also used EXAFS to show that cob(I)alamin has a distorted square-planar structure [343]. Data from this work and reference [103] are used to contribute to the debate about homolytic versus heterolytic bond cleavage. A low-spin cob(II)amide species has been detected from coenzyme B_{12} isolated from *Clostridium cochlearium* and is suggested as an intermediate in the coenzyme B_{12}-dependent glutamate mutase reaction [136].

REFERENCES

1. M.B. Davies, *Coord. Chem. Rev.*, 134 (1994) 195.
2. B.E. Douglas and D.J. Radanovic, *Coord. Chem. Rev.*, 128 (1993) 139.
3. L. Zheng, X. Xin and J. Shen, *Huaxue Xuebao*, 50 (1992) 145.
4. D. Jia and X. Xin, *Yingyond Huaxue*, 9 (1992) 1.
5. D. Jia, L. Changxiong, Y. Fu and X. Xin, *Huaxue Xuebao*, 51 (1993) 363.
6. X. Wang, L. Zheng and X. Xin, *Wuji Huazue Xuebao*, 8 (1992) 288.
7. J. Zhuang, Q. Cheng, X. Xin and L. Zheng, *Yingyong Hauxue*, 9 (1992) 33.
8. A. Werner, *Ber. Dtsch. Chem. Ges.*, 44 (1911) 1887.

9. I. Bernal, J. Cetrullo and W.G. Jackson, *Inorg. Chem.*, 32 (1993) 4098.
10. H. Yokoyama, T. Ohta and M. Iida, *Bull. Chem. Soc. Jpn.*, 65 (1992) 2901.
11. S. Kurachi and S. Ohba, *Bull. Chem. Soc. Jpn.*, 65 (1992) 3033.
12. I. Bernal, J, Myrczek and J. Cai, *Polyhedron,* 12 (1993) 1149.
13. I. Bernal, J. Cai and J. Myrczek, *Polyhedron,* 12 (1993) 1157.
14. I. Bernal, J. Cetrullo and W.G. Jackson, *Struct. Chem.*, 4 (1993) 235.
15. I. Bernal, J. Cetrullo and W.G. Jackson, *J. Coord. Chem.*, 28 (1993) 89.
16. I. Bernal, J. Cetrullo and J. Myrczek, *J. Coord. Chem.*, 30 (1993) 367.
17. S. Alshehri and J. Burgess, *Int. J. Chem. Kinet.*, 25 (1993) 113.
18. A.C. Dash and P.K. Das., *Int. J. Chem. Kinet.*, 24 (1992) 165.
19. M. Galán, R. Jiménez and F. Sánchez, *Ber. Bunsenges. Phys. Chem.*, 97 (1993) 16.
20. A.C. Dash and S.S. Mohammed, *Indian J. Chem. Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 31 (1992) 412.
21. G.C. Pradhan, *Transition Metal Chem. (London)*, 17 (1992) 104.
22. Y.Yamamoto, E.T. Kumon and H. Sekizaki, *Bull. Chem. Soc. Jpn.*, 65 (1992) 283.
23. K. Yamanari, *J. Chem. Soc., Dalton Trans.*, (1992) 1465 .
25. C.E. Oh, D.C. Yoon, B.J. Kim and M. Ki Doh, *J. Korean Chem. Soc.*, 36 (1992) 565.
26. T. Aoyama, S. Ohba, Y. Saito and I. Bernal, *Acta Crystallogr., Sect. C*, 48 (1992) 246.
27. D.A. Buckingham, C.R. Clarke and G.F. Liddell, *Inorg. Chem.*, 31 (1992) 2909.
28. M.R. Grace and P.A. Tregloan, *Inorg. Chem.*, 31 (1992) 4524.
29. M.R. Grace and P.A. Tregloan, *Polyhedron,* 11 (1992) 2069.
30. W.G. Jackson, S.S. Jurisson and M.A. O'Leary, *Inorg. Chem.*, 32 (1993) 445.
31. P.M. Angus, D.P. Fairlie and W.G. Jackson, *Inorg. Chem.*, 32 (1993) 450.
32. S.K. Saha, M.C. Ghosh and E.S. Gould, *Inorg. Chem.*, 31 (1992) 5439.
33. S.P. Ghosh, S.K. Saha, R.N. Bose, J.W. Reed, M.C. Ghosh and E.S. Gould, *Inorg. Chem.*, 32 (1993) 2261.
34. F. Tuczek and E.I. Solomon, *Inorg. Chem.*, 31 (1992) 944.
35. P. Martinez, J. Zuluaga, P. Noheda and R. van Eldik, *Inorg. Chim. Acta,* 195 (1992) 249.
36. B.Prelesnik, K. Andjelkovic and N. Juranic, *Acta Crystallogr., Sect. C*, 48 (1992) 427.
37. M.D. Johnson and R.J. Balahura, *Inorg. Chem.*, 31 (1992) 808.
38. P.M. Angus and W.G. Jackson, *Inorg. Chem.*, 32 (1993) 5285.
39. A.C. Dash, R.K. Nanda and A.N. Acharya, *J. Chem. Soc., Dalton Trans.*, (1993) 1023.
40. A.C. Dash and J. Pradhan, *Int. J. Chem. Kinet.*, 24 (1992) 155.
41. A.C. Dash and S.S. Mohammed, *Indian J. Chem., Sect A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 31A (1992) 166.
42. B.M. Gatehouse, R.L. Martin, G. McLachlin, S.N. Platts and L. Spiccia, *Acta Crystallogr., Sect. C*, 48 (1992) 271.
43. S.S. Massoud and A.M. Ismail, *Polyhedron,* 11 (1992) 1269.
44. K. Tang, M.E. Kastner, J.N. Cooper, M. Kanaskie and A. Monoski, *Acta Crystallogr., Sect. C*, 49 (1993) 1265.
45. R.J. Buthcher, H.H. Hayden and M.M.D. Deyrup, *Acta Crystallogr., Sect. C*, 48 (1992) 1122.
46. G. Ferraudi and M. Perkovic, *Inorg. Chem.*, 32 (1993) 2587.
47. D.A. Buckingham and C.R. Clark, *Inorg. Chem.*, 32 (1993) 5405.
48. J.K. McCusker, K.N. Walda, D. Magde and D.N. Hendrickson, *Inorg. Chem.*, 32 (1993) 394.
49. R.D. Cannon, S. Benjarvongkulchai, A. Gair and M.I.M. Ibrahim, *Polyhedron,* 11 (1992) 739.
50. J. Glerup, P.A. Goodson, D.J. Hodgson, M.H. Lynn and K. Michelson, *Inorg. Chem.*, 31 (1992) 4785.
51. K. Yamanari, Y. Kushi, M. Yamamoto, A. Fuyuhiro, S. Kaizaki, T. Kawamoto and Y. Kushi, *J. Chem. Soc., Dalton Trans.*, (1993) 3715.
52. B.R. Cameron, D.A. House and A. McAuley, *J. Chem. Soc., Dalton Trans.*, (1993) 1019.
53. B.N. Figgis, E.S. Kucharski and M. Vrtis, *J. Am. Chem. Soc.*, 115 (1993) 176.
54. R. Shaviv, M.E. Redmond and R.L. Carlin, *Inorg. Chem.*, 31 (1992) 1762.
55. T. Kojima, J.-i. Tsuchiya, S. Nakashima, H. Ohya-Nishiguchi, S. Yano and M. Hidai, *Inorg. Chem.*, 31 (1992) 2333.
56. D.J. Szalda, M.H. Chou, E. Fujita and C. Creutz, *Inorg. Chem.*, 31 (1992) 4712.

57. S. Garcia-Granda, V. Calvo-Perez and F. Gomez-Beltran, *Acta Crystallogr., Sect. C*, 49 (1993) 322.
58. K. Yamanari, K. Okusako and S. Kaisaki, *J. Chem. Soc., Dalton Trans.*, (1992) 1615.
59. G.H. Searle, E.R.T. Tiekink, I.M. Atkinson and F.R. Keene, *Acta Crystallogr., Sect. C*, 49 (1993) 13.
60. R.E. Marsh, *Inorg. Chem.*, 31 (1992) 4890.
61. N. Rowan-Gordon, A.A. Nguyenpho, E. Mondon-Konan, A.H. Turner, R.J. Butcher, A.S. Onkonkwo, H.H. Hayden and C.B. Storm, *Inorg Chem.*, 30 (1991) 4374.
62. K. Lu and J.E. Early, *Inorg. Chem.*, 32 (1993) 189.
63. S. Hubinger, J.H. Hall and W.L. Purcell, *Inorg. Chem.*, 32 (1993) 2394.
64. A.M. Calafat and L.G. Marzilli, *Inorg. Chem.*, 32 (1993) 2906.
65. G.H. Rawji and V.M. Lynch, *Acta Crystallogr., Sect. C*, 48 (1992)1667.
66. M. Yashiro, S. Yoshikawa and S. Yano, *Inorg. Chem.*, 32 (1993) 4166.
67. A.G. Lappin, K.J. Haller, R.M.L. Warren and A. Tatehata, *Inorg. Chem.*, 32 (1993) 4498.
68. P. Huston, H.J.H. Espenson and A. Bakac, *Inorg. Chem.*, 32 (1993) 4517.
69. S.K. Chawla, A. Sandhu and S.S. Sandhu, *Polyhedron*, 11 (1992) 1679.
70. T. Buranda, Y. Lei and J.F. Endicott, *J. Am. Chem. Soc.*, 114 (1992) 6916.
71. M.D. Johnson and R.J. Balahura, *Inorg. Chem.*, 31 (1992) 1832.
72. K. Ida, H. Sakiyama, H. Okawa, N. Matsumoto, Y. Aratake, I. Murase and S. Kida, *Polyhedron*, 11 (1992) 65.
73. Y Kitamura and A. Shibata, *Inorg. Chim. Acta*, 203 (1993) 37.
74. S.S. Massoud and M.A. Haiza, *Polyhedron*, 11 (1992) 1443.
75. Y. Kitamura and A. Shibata, *Polyhedron*, 11 (1992) 2441.
76. G. Gonzalez, M. Martinez, X. Solans and M. Font-Bardia, *Inorg. Chim. Acta*, 203 (1993) 229.
77. L Jianmin, Z. Yugeng, L. Wenbin, L Shixiong and H. Jinling, *Polyhedron*, 11 (1992) 419.
78. A. Mohamadou, J.-P. Barbier and R.P. Hugel, *Inorg. Chim. Acta*, 196 (1992) 129.
79. G Alzuet, S. Ferrer, J. Casanova, J. Borras and A. Castineiras, *Inorg. Chim. Acta*, 205 (1993) 79.
80. J.A. Castro, J. Romero, J.A. Garcia-Vazquez, M.L. Duran, E.E. Castellano and J. Zuckerman-Schpector, *Polyhedron*, 11 (1992) 235.
81. M.R. Grace and T.W. Swaddle, *Inorg. Chem.*, 32 (1993) 5597.
82. B.L. Eliot, T.W. Hambley, G.A. Lawrance, M. Maeder and G. Wei, *J. Chem. Soc., Dalton Trans.*, (1993) 1725.
83. H. Xu, L.Z. Wu, J. Zou, Z. Xu, X. You and Z. Dong, *Polyhedron*, 12 (1993) 2261.
84. M.A.S. Goher, R.-J. Wang and T.C.W. Mak, *Polyhedron*, 11 (1992) 829.
85. P. Bonhote, M. Ferigo, H. Stoeckli-Evans and W. Marty, *Acta Crystallogr., Sect. C*, 49 (1993) 2102.
86. K. Dimitrou, K. Folting, W.E. Streib and G. Christou, *J. Am. Chem. Soc.*, 115 (1993) 6432.
87. A. Yoshimura, K. Nozaki, N. Ikeda and T. Ohno, *J. Am. Chem. Soc.*, 115 (1993) 7521.
88. J.D. Tan, S.E. Hudson, S.J. Brown, M.M. Olmstead and P.K. Mascharak, *J. Am. Chem. Soc.*, 114 (1992) 3841.
89. K.V. Goby and R. Ramaraj, *J. Chem. Soc., Chem. Commun.*, (1992) 1436.
90. T.-H. Lu, B.-H. Chen, and C.-S. Chung, *Acta Crystallogr., Sect. C*, 49 (1993) 1912.
91. C.A. McAuliffe, R.G. Pritchard, M.R. Bermejo, A. Garcia-Vazquez, A. Macias, J. Sanmartin, J. Romero and A. Sousa, *Acta Crystallogr., Sect. C*, 48 (1992) 1841.
92. G.A. Lawrance, M. Martinez, B.W. Skelton, R. van Eldik and A.H. White, *Aust. J. Chem.*, 45 (1992) 351.
93. D. Xu, L. Lei, Y. Xu, C. Cheng and J. Chen, *Acta Crystallogr., Sect. C*, 48 (1992) 1399.
94. M. Megnamisi-Belombe, G.N. Nlend and B. Nuber, *Bull. Chem. Soc. Jpn.*, 65 (1992) 612.
95. V.Z. Voloshin, V.K. Belsky and V.V. Trachevskii, *Polyhedron*, 11 (1992) 1939.
96. Y. Takenaka, Y. Ohashi, T. Tamura, A. Uchida, Y. Sasada, Y. Ohgo and S. Baba, *Acta Crystallogr., Sect. B*, 49 (1993) 272.
97. Y. Takenaka, Y. Kojima and Y. Ohashi, *Acta Crystallogr., Sect. B*, 49 (1993) 852,.
98. Y. Takenaka, Y. Ohashi, T. Tamura, A. Uchida and Y. Sasada, *Acta Crystallogr., Sect. B*. 49 (1993) 1015.
99. A. Dayalan and V.R. Vijayaraghavan, *J. Chem. Soc., Dalton Trans.*, (1992) 2491.
100. A. Gerli and L.G. Marzilli, *Inorg. Chem.*, 31 (1992) 1152.

101. K.L. Brown and S. Satyanarayana, *Inorg. Chem.*, 31 (1992) 1366.
102. M.J. Sisley and R.B. Jordan, *Inorg. Chem.*, 31 (1992) 2880.
103. D.H. Jones and A. S. Hinman, *J. Chem. Soc., Dalton Trans.*, (1992) 1503.
104. S. Fukuzumi and T. Yorisue, *Bull. Chem. Soc. Jpn.*, 65 (1992) 715.
105. M. Satoh, Y. Ohba, S. Yamanuchi and M. Iwaizumi, *Inorg. Chem.*, 31 (1992)298.
106. H. Bang, J.O. Edwards, J.Kim, R.G. Lawlor, K. Reynolds, W.J. Ryan and D.A. Sweigart, *J. Am. Chem. Soc.*, 114 (1992) 2843.
107. D.M. Guldi, P. Neta, P. Hambright and R. Rahimi, *Inorg. Chem.*, 31 (1992) 4849.
108. C.J. Groombridge, L.F. Larkworthy and J. Mason, *Inorg. Chem.*, 32 (1993) 379.
109. A.L. Balch, M. Mazzanti and M. Olmstead, *Inorg. Chem.*, 32 (1993) 4737.
110. D. Reddy and T.K. Chandrashekar, *J. Chem. Soc., Dalton Trans.*, (1992) 619.
111. S. Matsuoka, K. Yamamoto, T. Ogata, M. Kusba, N. Nakashima, E. Fujita and S. Yanagida, *J. Am. Chem. Soc.*, 115 (1993) 601.
112. E.R. Milaeva and G. Speier, *Inorg. Chim. Acta*, 192 (1992) 117.
113. K.M. Kadish, W. Koh, P. Tagliatesta, D. Sazou, R. Polesse, S. Licoccia and T. Boschi, *Inorg. Chem.*, 31 (1992) 23051.
114. R. Paolesse, S. Licoccia, M. Fanciullo, E. Morgante and T. Boschi, *Inorg. Chim. Acta*, 203 (1993) 107.
115. T.N. Mali, P.W. Wade and R.D. Hancock, *J. Chem. Soc., Dalton Trans.*, (1992) 67.
116. A. Bacchi, F. Ferranti and G. Pelizzi, *Acta Crystallogr., Sect.*, 49 (1993) 116.
117. J. Arago, A. Bencini, A. Bianchi, A. Domenech and E. Garcia-Espana, *J. Chem. Soc., Dalton Trans.*, (1992) 319.
118. M. Morooka, S. Ohba and K. Toriumi, *Acta Crystallogr., Sect. B*, 48 (1992) 459.
119. T.H. Tahirov, T.-H. Lu, B.-H. Chen, C.-Y. Lai and C.-S. Chung, *Acta Crystallogr., Sect. C*, 49 (1993) 1910.
120. S. Tsuboyama, Y. Shiga, Y. Takasyo, T. Chijaimatsu, K. Kobayashi, K. Tsuboyama and T. Sakurai, *J. Chem. Soc., Dalton Trans.*, (1992) 1783.
121. G.A. Lawrance, T.M. Manning, M. Maeder, M. Martinez, M. O'Leary, W.C. Patalinghug, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1992) 1635.
122. T.W. Hambley, G.A. Lawrance, M. Martinez, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1992) 1643.
123. G.A. Lawrance, M. Martinez, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.* (1992) 1649.
124. T.W. Hambley, G.A. Lawrance, M. Maeder and E.N. Wilkes, *J. Chem. Soc., Dalton Trans.*, (1992) 1283.
125. J.H. Kim and J. Chin, *J. Am. Chem. Soc.*, 114 (1992) 9792.
126. B.K. Takasaki, J.H. Kim, E. Rubin and J. Chin, *J. Am. Chem. Soc.*, 115 (1993) 1157.
127. P.V. Bernhardt, P. Coba and T.W. Hambley, *Inorg. Chem.*, 32 (1993) 2804.
128. D. Coucouvanis, S.G. Jonasdottir, D. Christodoulou, C.G. Kim and J.W. Kampf, *Inorg. Chem.*, 32 (1993) 2987.
129. S.G. Jonasdottir, C.G. Kim and D. Coucouvanis, *Inorg. Chem.*, 32 (1993) 3591.
130. M. Ray and R.N. Mukherjee, *Polyhedron*, 11 (1992) 2937.
131. M. S. Islam and M.M. Uddin, *Polyhedron*, 12 (1993) 423.
132. E. Lloyd, N.P. Tomkinson and A.G. Sykes, *J. Chem. Soc., Dalton Trans.*, (1992) 753.
133. D.G.A.H. de Silva, D. Beoku-Betts, P. Kyritsis, K. Govindaraju, R. Powls, N.P. Tomkinson and A.G. Sykes, *J. Chem. Soc., Dalton Trans.*, (1992) 2145.
134. P. Kyitsis, C. Dennison, W. McFarlane, M. Nordling, T. Vanngard, S. Young and A.G. Sykes, *J. Chem. Soc., Dalton Trans.*, (1993) 2289.
135. J.R. Pladziewicz, M.A. Accola, P. Osvath and A.M. Sargeson, *Inorg. Chem.*, 32 (1993) 2525.
136. U. Leutbecher, S.F.J. Albracht and W. Buckel, *FEBS Lett.*, 307 (1992) 144.
137. S. Dholiya, A. Prakash and R.N. Mehrotra, *J. Chem. Soc., Dalton Trans.*, (1992) 819.
138. Y. Kitamura and A. Shibata, *Polyhedron*, 12 (1993) 2143.
139. P. Diversi, C. Forte, M. Francheschi, G. Ingrosso, A. Lucherini, M. Petri and C. Pinzino, *J. Chem. Soc., Chem. Commun.*, (1992) 1345.
140. A. Al-Alousy and J. Burgess, *Polyhedron*, 11 (1992) 531.
141. M. Kita, K. Nemoto, K. Kashiwabara, J. Fujita, M. Goto, T. Miyamoto and S. Ohba, *Bull. Chem. Soc. Jpn.*, 66 (1993) 1687.

142. D.M. Adams, A. Dei, A.L. Rheingold and D.N. Hendrickson, *J. Am. Chem. Soc.*, 115 (1992) 8221.
143. M. Kojima, G. Ma and T. Miyamoto, *Bull. Chem. Soc. Jpn.*, 65 (1992) 1572.
144. S. Jin, M. Nieuwenhuyzen and C.J. Wilkins, *J. Chem. Soc., Dalton Trans.*, (1992) 2071.
145. S.P. Best, R.S. Armstrong and J.K. Beattie, *J. Chem. Soc., Dalton Trans.*, (1992) 299.
147. I. Bernal, J. Cetrullo, J. Myrczek, J. Cai and W.T. Jordan, *J. Chem. Soc., Dalton Trans.*, (1993) 1771.
148. T. Yasui, T. Ama, H. Kawaguchi, K. Okamoto and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 65 (1992) 1920.
149. H. Kawaguchi, N. Maruyama, T. Ama and T. Yasui, *Bull. Chem. Soc. Jpn.*, 65 (1992) 175.
150. P.D. Newman, F.S. Stephens, R.S. Vagg and P.A. Williams, *Inorg. Chim. Acta*, 204 (1993) 257.
152. B. Ye, T. Zeng, P. Han and L. Ji, *Transition Metal Chem. (London)*, 18 (1993) 515.
153. M.J. Malinar, M.B. Celap, R. Herak and B. Prelesnik, *Polyhedron*, 11 (1992) 1169.
154. N. Juranic, S. R. Niketic, K. Andjelkovic and I. Juranic, *J. Mol. Struct*, 271 (1992) 209.
155. N. Juranic, K. Andjelkovic, M.J. Malinar, M.B. Celap, M. Vucic, D. Vucelic and B. Prelesnik, *Polyhedron*, 11 (1992) 773.
156. J.C. Jeffery, E. Schatz and M.D. Ward, *J. Chem. Soc., Dalton Trans.*, (1992) 1921.
157. R.R. Fenton, F.S. Stephens, R.S. Vagg and P.A. Williams, *Inorg. Chim. Acta* 197 (1992) 23.
158. C.J. Groombridge, L.F. Larkworthy, A. Marecaux, D.C. Povey, G.W. Smith and J. Mason, *J. Chem. Soc., Dalton Trans.*, (1992) 3125.
159. H. Barjesteh, J. Charalambous and N.D. Pathirana, *Polyhedron*, 12 (1993) 883.
160. V.D. Campbell, E.J. Parsons and W.T. Pennington, *Inorg. Chem.*, 32 (1993) 1773.
161. H. Elias, D. Wiegand, K.J. Wannowius and H. Paulus, *Inorg. Chim. Acta*, 197 (1992) 21.
162. T. Taura, *Polyhedron*, 11 (1992) 1463.
163. P. Basu, *Polyhedron*, 11 (1992) 3037.
164. R. Zhang and D.H. Busch, *Inorg. Chem.*, 32 (1993) 4920.
165. R.K. Ray, *Polyhedron*, 11 (1992) 469.
166. U. Auerbach, T. Weyermüller, K. Wieghardt, B. Nuber, E. Bill, C. Butzlaff and A.X. Trautwein, *Inorg. Chem.*, 32 (1993) 508.
167. U. Auerbach, C. Stockhelm, T. Weyhermueller, K. Wieghardt and B. Nuber, *Angew. Chem.*, 105 (1993) 735.
168. R.R. Fenton, F.S. Stephens, R.S. Vagg and P.A. Williams, *Inorg. Chim. Acta*, 201 (1992) 157.
169. T. Konno, K. Okamoto and J. Hidaka, *Inorg. Chem.*, 31 (1992) 160.
170. K. Ruhlandt-Senge and P.P. Power, *J. Chem. Soc., Dalton Trans.*, (1993) 649.
171. M.D. Johnson and R.J. Balahura, *Inorg. Chem.*, 31 (1992) 808.
172. P. Osvath and A.M. Sargeson, *J. Chem. Soc., Chem. Commun.*, (1993) 40.
173. K. Yamanari, M. Yamamoto, M. Kida, T. Fujihara, A. Fuyuhiro and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, (1993) 1651.
174. K. Yamanari, K.-i. Okusako, Y. Kushi and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, (1992) 1621.
175. J.L. Bruce, L.R. Gahan, T.W. Hambley and R. Stranger, *Inorg. Chem.*, 32 (1993) 5997.
176. P. J. Toscano, K.A. Belsky, T. Nocholson and J. Zubieta, *Inorg. Chim. Acta*, 206 (1993) 77.
177. T.M. Donlevy, L.R. Gahan, T.W. Hambley and R. Stranger, *Inorg. Chem.*, 31 (1992) 4376.
178. T.M. Donlevy, L.R. Gahan and T.W. Hambley, *Polyhedron*, 12 (1993) 1593.
179. N. Azuma, T. Ozawa, A. Shibata and Y. Kitamura, *Polyhedron*, 12 (1993) 2291.
180. T. Konno, K. Nakamura, K.-i. Okamoto and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 66 (1993) 2582.
181. R. Chikate, P. Sonawane, A. Kumbhar, S. Padhye and R.J. Butcher, *Inorg. Chim. Acta*, 205 (1995) 59.
182. K. Drabent, J.A. Wolny, M.F. Rudolf and P.J. Chmielewski *Polyhedron*, 11 (1992) 271.
183. H. Matsui, M. Kita, K. Kashiwabara and J. Fujita, *Bull. Chem. Soc. Jpn.*, 66 (1993) 1140.
184. M. Kita, M. Okuno, K. Kashiwabara and J. Fujita, *Bull. Chem. Soc. Jpn.*, 65 (1992) 3042.
185. T. Fujihara and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, (1993) 1275.
186. M.F. Manfrin, L. Setti and L. Moggi, *Inorg. Chem.*, 31 (1992) 2768.

187. S.K. Ghosh, S.K. Saha, M.C. Ghosh, R.N. Bose, J.W. Reed and E.S. Gould, *Inorg. Chem.*, 31 (1992) 3358.
188. S.K. Saha, M.C. Ghosh and E.S. Gould, *Inorg. Chem.*, 31 (1992) 5439.
189. D.C. Gaswick and S. M. Mallinak, *Inorg. Chem.*, 32 (1993) 175.
190. E. Natarajan and P. Natarajn, *Inorg. Chem.*, 31 (1992)1215.
191. M.M. Monzyk and R.A. Holwerda, *Inorg. Chem.*, 31 (1992) 1969.
192. J. Glerup, P.A. Goodson, D.J. Hodgson, M.H. Lynn and K. Michelson, *Inorg. Chem.*, 31 (1992) 4785.
193. D.H. Macartney and S. Mak, *Can. J. Chem.*, 70 (1992) 39.
194. G. de Munno, F. Nicolo and M. Julve, *Acta Crystallogr., Sect. C*, 49 (1993) 1049.
195. M.K. Ehlert A. Storr and R.C. Thompson, *Can. J. Chem.*, 71 (1993) 1412.
196. M.K. Ehlert, S.J. Rettig, A. Storr, R.C. Thompson and J. Trotter, *Can. J. Chem.*, 71 (1993) 1425.
197. S.-S Chern, M.-C. Liaw and S.-M. Peng, *J. Chem. Soc., Chem. Commun.*, (1993) 359.
198. G. Hänggi, H. Schmalle and E. Dubler, *Acta Crystallogr., Sect. C*, 48 (1992) 1008.
199. R.M.L. Warren, A. Tatahata and A.G. Lappin, *Inorg. Chem.*, 32 (1993) 1191.
200. T. Tatehata, H. Oota, T. Fukagawa, R.M.L. Warren and A.G. Lappin, *Inorg. Chem.*, 32 (1993) 2433.
201. H. Wen, S.E. Miller, D.A. House, V. McKee and W.T. Robinson, *Inorg. Chim. Acta*, 193 (1992) 77.
202. S. Mahaptra, T.K. Lal and R.N. Mukherjee, *Polyhedron*, 12 (1993) 1477.
203. D.A. Edwards, S.D. Edwards, W.R. Martin, T.J. Pringle and P. Thornton, *Polyhedron*, 11 (1992) 1569.
204. E.C. Constable, J.V. Walker, D.A. Tocher and M.A.M. Daniels, *J. Chem. Soc., Chem. Commun.*, (1992) 768.
205. E.C. Constable, S.M. Elder, P.R. Raithby and M.D. Ward, *Polyhedron*, 10 (1991) 1395.
206. E.C. Constable and J.V. Walker, *J. Chem. Soc., Chem. Commun.*, (1992) 884.
207. E.C. Constable, M.A.M. Daniels, M.G.B. Drew, D.A. Tocher, J.V. Walker and P.D. Wood, *J. Chem. Soc., Dalton Trans.*, (1993) 1947.
208. J.C. Plakatouras, S.P. Perlepes, D. Mentzafos, A. Terzis, T. Bakas and V. Papaethymiou, *Polyhedron*, 11 (1991) 2657.
209. K.M. Jupp and P.R. Raithby, *Acta Crystallogr., Sect. C*, 48 (1992) 1214.
210. R. Kuroda and S.F. Mason, *J. Chem. Soc., Dalton Trans.*, (1977) 371.
211. N.D. Fenton and M. Gerloch, *Inorg. Chem.*, 30 (1990) 3178.
212. L.P. Battaglia, P.G. Bezolla, A. B. Corradi, C. Pelizzi, G. Pelosi and C. Solinas, *J. Chem. Soc., Dalton Trans.*, (1992) 3089.
213. J.J. Grzybowski, R.D. Allen, J.A. Belinski, K.L. Bieda, T.A. Bish, P.A. Finnegan, M.L. Hartenstein, C.S. Regitz, D.M. Ryalls, M.E. Squires and H.J. Thomas, *Inorg. Chem.*, 32 (1993) 5299.
214. H.A. Gazza, N.M. El-Guindi and A.A. El-Awady, *J. Chem. Soc., Dalton Trans.*, (1993) 2313.
215. P. Kofod. P. Moore, N.W. Alcock and H.J. Clase, *J. Chem. Soc., Chem. Commun.*, (1992) 1261.
216. K. Liou, T.P. Newcomb, M.D. Heagy, J.A. Thompson, W.B. Heuer, R.L. Musselman, C.S. Jacobsen, B.M. Hoffman and J.A Ibers, *Inorg. Chem.*, 31 (1992) 4517.
217. F. D'Souza, A. Villard, E.Van Caemelbecke, M. Franzen, T. Boschi, P. Tagliatesta and K.M. Kadish, *Inorg. Chem.*, 32 (1993) 4042.
218. J.S. Summers and A.M. Stolzenberg, *J. Am. Chem. Soc.*, 115 (1993) 10559.
219. M.Satoh, Y. Ohba, S. Yamanuchi and M. Iwaizumi, *Inorg. Chem.*, 31 (1992) 298.
220. J. Jubb, L.F. Larkworthy, D.C. Povey and G.W. Smith, *Polyhedron*, 12 (1993) 1179.
221. A. Ceulemans, B. Coninckx, M. Vanhecke, Th. Zeegers-Huyskens and G.S.D. King, *Inorg. Chim. Acta*, 202 (1992) 101.
222. C. Arana, S. Yan, M. Keshavarz, K.T. Potts and H.D. Abruna, *Inorg. Chem.*, 31 (1992) 3680.
223. A. Escuer, R. Vicente and J. Ribas, *Polyhedron*, 11 (1992) 453.
224. A. Pezeshk, *Inorg. Chem.*, 31 (1992) 2282.
225. A Bencini, A. Bianchi, V. Fusi, P. Paoletti, B. Valtancoli, A. Andres, J. Arago and E. Garcia-Espania, *Inorg. Chim. Acta*, 204 (1993) 221.

226. G. Alzuet, S. Ferrer, J. Boras, A. Castineiras, N. Solans and M. Font-Bardia, *Polyhedron*, 11 (1992) 2849.
227. S.S. Tandon, L.K. Thompson, J. Bridson and J.C. Dewan, *Can. J. Chem.*, 70 (1992) 2771.
228. W.-K. Chang, A.-C. Sheu, G.-H. Lee, Y, Wang T.-I. Ho and Y.-C. Lin, *J. Chem. Soc., Dalton Trans.*, (1993) 687.
229. C.S. Velazquez, J.E. Hutchison and R.W. Murray, *J. Am. Chem. Soc.*, 115 (1993) 7896.
230. S. Hu, *Inorg. Chem.*, 32 (1993) 1081.
231. J.-M. Moratal, J. Salgado, A. Donaire, H.R. Jimenez and J. Castells, *Inorg. Chem.*, 32 (1993) 3587.
232. L. Bubacco, R. S. Magliozzo, M. Beltramini, B. Salvato and J. Peisach, *Biochemistry*, 31 (1992) 9294.
233. A.C. Blackburn and R.E. Gerkin, *Acta Crystallogr., Sect. C*, 49 (1993) 1271.
234. B.M. Karuki and W. Jones, *Acta Crystallogr., Sect. C*, 49 (1993) 2100.
235. T. Kellersohn, R.G. Delaplane, I. Olovsson and G.J. McIntyre, *Acta Crystallogr., Sect. B*, 49 (1993) 179.
236. A. Kaufman, C. Afshar, M. Rossi, D. E. Zacharias and J. P. Glusker, *Struct. Chem.*, 4 (1993) 191.
237. G. Ferraudi, *J. Phys. Chem.*, 97 (1993) 11929.
238. E. C. Canaviri, M. R. Feliz and A.L. Capparelli, *Transition Metal Chem. (London)* 17 (1992) 446.
239. S. S. Yun, J. B. Doh and K. Y. Choi, *Bull. Korean Chem. Soc.*, 13 (1992) 659.
240. P.G. Harris, P.P. Houghton and P.L. Taylor, *Polyhedron*, 11 (1992) 2957.
241. A.G. Bunn, P.J. Carroll and B.B. Wayland, *Inorg. Chem.*, 31 (1992) 1297.
242. S.A. Samath, N. Raman, K. Jeyasubramanian and S. K. Ramalingam, *Polyhedron*, 11 (1992) 33.
243. M.Kubata and S. Ohba, *Acta Crystallogr., Sect. B*, 48 (1992) 627.
244. E.V. Boldyreva, L.P. Burleva, E.B. Burgina, V.P. Baltachinov, H. Uchtmann and V.E. Doulepov, *Ber. Bunsenges. Phys. Chem.* 96 (1992) 931.
245. G. Smith, D.E. Lynch, T.C.W. Mak, W.-H. Yip and C.H.L. Kennard, *Polyhedron*, 12 (1993) 203.
246. X.-M. Chen and T.C.W. Mak, *Acta Crystallogr., Sect. C*, 48 (1992) 1211.
247. I. Karadjova, S. Arpadjan and I. Shishkova, *Polyhedron*, 11 (1992) 2525.
248. Gulinati and F Cariati, *Polyhedron*, 11 (1992) 101.
249. K.S. Hagen, R. Lachicotte and A. Kitaygorodskiy, *J. Am. Chem. Soc.*, 115 (1993) 12617.
250. K.S. Hagen, R. Lachicotte, A. Kitaygorodskiy and A. Elbouadili, *Angew. Chem., Int. Ed. Engl.*, 32 (1993) 1321.
251. S. Tagashira, K. Onoue, Y. Murakami and Y. Saaki, *Bull. Chem. Soc. Jpn.*, 65 (1992) 286.
252. N. Casan-Pastor, J. Bas-Serra, E. Coronado, G. Pourroy and L.C.W. Baker, *J. Am. Chem. Soc.*, 114 (1992) 10380.
253. K. Ozutsumi, K. Tohji, Y. Udagawa, Y. Abe and S.-I. Ishiguro, *Inorg. Chim. Acta*, 91 (1992) 183.
254. S.-J. Liu, R.J. Staples and J.P. Fackler, *Polyhedron*, 11 (1992) 2427.
255. Z. Zhang and J.O. Edwards, *Inorg. Chem.*, 31 (1992) 3514.
256. S.M. Godfrey, C.A. McAuliffe, G. A. Ranger and D.G. Kelly, *J. Chem. Soc., Dalton Trans.*, (1993) 2809.
257. V. Kh. Sabirov, M.A. Porai-Koshits, Yu.T. Strutchkov and A.N. Yunuskhodzhaev, *Koord. Khim*, 18 (1992) 614.
258. B.M. Bulychev, O.K. Kireeva, V.K. Belsky and N.R Streltsova, *Polyhedron*, 11 (1992) 1809.
259. J.A. Wolny, M.F. Rudolf, Z. Ciunik, K. Gatner and S. Wolowiec, *J. Chem. Soc., Dalton Trans.*, (1993) 1611.
260. W. Hiller, A. Nishinaga, T. Tsutsui and A. Rieker, *Acta Crystallogr., Sect. C*, 49 (1993) 1357.
261. E. Eichhorn, A. Rieker and B. Speiser, *Angew. Chem., Int. Ed. Engl.*, 31 (1992) 1215.
262. M.F. Rudolf, Z.Ciunik, K. Gatner and J.A. Wolney, *Polyhedron*, 11 (1992) 2591.
263. A.A. Isse, A. Gennaro and E. Vianello, *J. Chem. Soc., Dalton Trans.*, (1993) 2091.
264. H. Al-Sagher, I. Fallis, L.J. Farrugia and R.D. Peacock, *J. Chem. Soc., Chem. Commun.*, (1993) 1499.

265. J.J. Borras-Almenar, E. Coronado, D. Gatteschi and C. Zanchini, *Inorg. Chem.*, 31 (1992) 294.
266. S.E. Schadler, C. Sharp and A.G. Lappin, *Inorg. Chem.*, 31 (1992) 52.
267. F. Pina, A.J. Parola, A. Bencini, M. Micheloni, M.F. Manfrin and L. Moggi, *Inorg. Chim. Acta*, 195 (1992) 139.
268. M. Hernandez-Padilla, S. Dominguez, P. Gill, A. Mederos and C. Ruiz-Perez, *Polyhedron*, 11 (1992) 1965.
269. M. Fernanda, N.N. Carvalbo, A.C. Consiglieri, M.T. Duarte, A.M. Galvac, A.J.L. Pombeiro and R. Herrmann, *Inorg. Chem.*, 32 (1993) 5160.
270. S.A. Ibrahim, *Polyhedron*, 11 (1992) 1349.
271. D.M.L. Goodgame, C.J. Page, D.J. Williams and I.J. Stratford, *Polyhedron*, 11 (1992) 2507.
272. X.Y. Zhou, Z.W. Yu, R.J. Tao, H.X. Han, D.M. Jin and D.Z. Liao, *Polyhedron*, 11 (1992) 3041.
273. J. Faus, M. Julve, F. Lloret and M.C. Munoz, *Inorg. Chem.*, 32 (1993) 2013.
274. P K Sahu, N R Bannerjee and S. Sengupta, *J. Indian Chem. Soc.*, 69 (1992) 184.
276. Yu. A. Simonov, A.A. Dvorkin, V.F. Shul'gin and O.V. Konnik, *Koord. Khim.*, 19 (1993) 899.
277. B.-S. Kang, Y.-J. Xu, J.-H. Peng, D.-X. Wu, X.-T. Chen, Y.-H. Hu, M.-C. Hong and J.-X. Lu, *Polyhedron*, 12 (1993) 871.
278. D.M. Wambeke, W. Lippens, G.G. Herman, A.M. Goeminne and G.P. van der Kelen, *Polyhedron*, 11 (1992) 2989.
279. L. Mishra and A.K. Pandey, *Polyhedron*, 11 (1992) 423.
280. D. Funkemeier and R. Mattes, *J. Chem. Soc., Dalton Trans.*, (1993) 1313.
281. R.D. Bereman, J. R. Dorfman and S.-N. Choi, *Inorg. Chim. Acta*, 202 (1992) 127.
282. M.G. Davidson, M. Gerloch, S.C. Llewellyn, P.R. Raithby and R. Snaith, *J. Chem. Soc., Chem. Commun.*, (1993) 1363.
283. S. Jayasree and K.K. Aravindakshan, *Polyhedron*, 12 (1993) 1187.
284. B. Adhikary, K.K. Nanda, R. Das, S.K. Mandal and K. Nag *Polyhedron*, 11 (1992) 347.
285. P.B. Hitchcock, K.R. Seddon and T. Welton, *J. Chem. Soc., Dalton Trans.*, (1993) 2639.
286. G. Ning, L. Yong-Hua, Z. Guang-Fu and X. Shi-Quan, *Acta Crystallogr., Sect. C*, 48 (1992) 542.
287. H. Suzuki, M. Koide and S. Ishiguro, *J. Chem. Soc., Faraday Trans.*, 89 (1993) 3055.
288. C. Daul, F. Emmenegger, M. Mlinar and M. Piccand, *Inorg. Chem.*, 32 (1993) 2992.
289. O.K. Kireeva, B.M. Bulychev, N.R. Streltsova, V.R. Belsky and A.G. Dunn, *Polyhedron*, 11 (1992) 1801.
290. J. Hartung, L. Beyer, E. Gutierrez-Puebla, V. Fernandez and B. Olk. *Z. Naturforsch., Teil B*, 47 (1992) 183.
291. C. Waizumi, M. Masuda and H. Ohtaki, *Inorg. Chim. Acta*, 192 (1992) 173.
292. D. Nelson and L.W. Haar, *Inorg. Chem.*, 32 (1993) 182.
294. V.V. Zhilinskaya, Yu.G. Gol'tsov, A.M. Glukhoi and E.N. Korol, *Teor. Eksp. Khim.*, 28 (1992) 176.
295. T. Dhanasekaran and P. Natarajan, *J. Am. Chem. Soc.*, 114 (1992) 4621.
296. J.H. Cameron and S. Graham, *J. Chem. Soc., Dalton Trans.*, (1992) 385.
297. J. Chen, N. Ye, N.W. Alcock and D.H. Busch, *Inorg. Chem.*, 32 (1993) 904.
298. M.F. Rudolf, J.A. Wolny, T. Lis and P. Starynovicz, *J. Chem. Soc., Dalton Trans.*, (1992) 2079.
299. M.A. Khalifa, *Bull. Chem. Soc. Ethiop.*, 7 (1993) 79 (*Chem. Abstr.*, 121 (1994) 164820k).
300. J.H. Cameron and S.C. Turner, *J. Chem. Soc., Dalton Trans.*, (1992) 3285.
301. Y. Abe, K. Shinguhara and S. Yano, *Chem. Lett.*, 6 (1992) 897.
302. K. Miyokawa, S. Kinoshita, T. Etoh and H. Wakita, *Bull. Chem. Soc. Jpn.*, 65 (1992) 3374.
303. M. Bonamico, V. Fares, A. Fiamini and N. Poli, *J. Chem. Soc., Dalton Trans.*, (1992) 3273.
304. K. Yamanari, Y. Kushi, A. Fuyuhiro amd S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, (1993) 403.
305. M. Yamada, K. Araki and S. Shiraishi, *Bull. Chem. Soc. Jpn.*, 65 (1992) 1220.
306. K. Araki, T. Kubcki, M. Otahata, N. Kishimoto, M. Yamada and S. Shiraishi, *J. Chem. Soc., Dalton Trans.*, (1993) 3647.
307. B. Steiger, C. Shi and F.C. Anson, *Inorg. Chem.*, 32 (1993) 2107.

308. C. Shi and F.C. Anson, *Inorg. Chem.*, 31 (1992) 5078.
309. J.M. Skelly, N.C. Morosoff, V.T. Stannett and A.L. Crumbliss, *Inorg. Chem.*, 32 (1993) 1306.
310. T.S. Kurtikyan, G.G. Martirosyan, A.V. Gasparyan and G.A. Zhamkochyan, *Zh. Priki. Spektrosk.*, 59 (1993) 452 (*Chem. Abstr.*, 121 (1994) 43940r).
311. T.S. Kurtikyan and V.N. Madakyan, *Koord. Khim.*, 18 (1992) 869.
312. L. Ji, X. Qin and J. Huang, *Zhongshan Daxue Xuebao, Ziran Kexueban*, 32 (1993) 1 (*Chem. Abstr.*, 122 (1995) 26581c).
313. S. Jeon, O. Almarsson, R. Karaman, A. Blasko and T.C. Bruice, *Inorg. Chem.*, 32 (1993) 2562.
314. N. Kobayashi, P. Janda and A.B.P. Lever, *Inorg. Chem.*, 31 (1992) 5172.
315. M. Chibwe and T.J. Pinnavaia, *J. Chem. Soc., Chem. Commun.*, (1993) 278.
316. A. Marchaj, A. Bakac and J.H. Espenson, *Inorg. Chem.*, 32 (1993) 2399.
317. J.H. Cameron and E.L. Scott, *J. Chem. Soc., Dalton Trans.*, (1993) 397.
318. A. Bencini, A. Bianchi, S. Cabani, N. Ceccanti, P. Paoletti and M.R. Tine, *J. Chem. Soc., Dalton Trans.*, (1993) 695.
319. A. Marchaj, A. Bakac and J.H. Espenson, *Inorg. Chem.*, 31 (1992) 4164.
320. A. Bencini, A. Bianchi, P. Paoletti, S. Cabani, N. Ceccanti, M.R. Tine and E. Garcia-Espania, *Inorg. Chim. Acta*, 204 (1993) 227.
321. P. Barbaro, C. Bianchini, K. Linn, C. Mealli, A. Meli, F. Vizza, F. Laschi and P. Zanello, *Inorg. Chim. Acta*, 198-200 (1992) 31.
322. D. M. Palade. *Ukr. Khim. Zh.*, 59 (1993) 510.
323. K. Drabent, J.A. Wolny, P.J. Chmielewski, K. Gatner and M.F. Rudolf, *Polyhedron*, 12 (1993) 651.
324. A Kufelnicki, *Pol. J. Chem.*, 66 (1992) 1077.
325. A. Kufelnicki and M. Swiatek, *Pol. J. Chem.*, 67 (1993) 1345.
326. E. Fujita, C. Creutz, N. Sutin and B. Brunschwig, *Inorg. Chem.*, 32 (1993) 2657.
327. P.A. Bernstein and A.P.B. Lever, *Inorg. Chim. Acta*, 198-200 (1992) 543.
328. A.L. Lewis and J.D. Miller, *J. Chem. Soc., Chem. Commun.*, (1992) 1029.
329. J.-L. Roustan, N. Ansari, Y. Le Page and J.-P. Charland, *Can. J. Chem.* 70 (1992) 1650.
330. M. Shakir, D. Kumr and S.P. Varkey, *Polyhedron*, 11 (1992) 2831.
331. N.K. Kildahl and W. J. Clarke, *J. Coord. Chem.*, 25 (1992) 291.
332. R. Moreno-Esparza, M. Lopez and K.H. Pannell, *J. Chem. Soc., Dalton Trans.*, (1992) 1791.
333. I. Sagi and M. Chance, *J. Am. Chem. Soc.*, 114 (1992) 8061.
334. A.M. Calafat and L.G. Marzilli, *Inorg. Chem.*, 31 (1992) 1719.
335. K.L.. Brown, D.R. Evans and G.-Z. Wu, *Inorg. Chem.*,(1993) 32 4487.
336. A.M. Calafat and L.G. Marzilli, *J. Am. Chem. Soc.*, 115 (1993) 9182.
337. J.P. Bouquiere, J.L. Finney, M.S. Lehmann, P.F. Lindley and H.F.J. Savage, *Acta Crystullogr., Sect. B*, 49 (1993) 79.
338. K.L. Brown, X. Zou, S. R. Savon and D. W. Jacobsen, *Biochemistry*, 32 (1993) 8421.
339. K.L. Brown and X. Zou, *J. Am. Chem. Soc.*, 115 (1993) 1478.
340. K.L. Brown and D.R. Evans, *Inorg. Chim. Acta*, 197 (1992) 101.
341. L.E.H. Gerards, W.G. de Bolster and S. Balt, *Inorg. Chim. Acta*, 192 (1992) 287.
342. M.D. Wirt, M. Kumar, S.W. Ragsdale and M.R. Chance, *J. Am. Chem. Soc.*, 115 (1993) 2146.
343. M.D. Wirt, I. Sagi and M.R. Chance, *Biophys. J.* 63 (1992) 412.