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5. Cobalt

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CONTENTS

INTRODUCTION

This review covers the coordination chemistry of cobalt for the year 1990. The most recent reviews of the coordination chemistry of cobalt in this series were for the years 1984 and 1985 [1]. One of the intentions of this series is to produce more rapid reviews than previously and no doubt the missing years will be covered later. The general format for the review is broadly that of previous ones in this series. This is strictly an account of coordination chemistry and consequently there is the problem of deciding what is coordination chemistry and in practice drawing the line with

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organometallic chemistry is often difficult. This review does not seek to cover organometallic chemistry and the well known definition of coordination chemistry being that which interests coordination chemists is broadly used here. A further limitation of the review is that in general it does not include cluster chemistry. Though again such chemistry may be included if it is thought relevant.

Interest in cobalt chemistry as measured by the number of publications in a given year continues to be extraordinarily high. Many new compounds of cobalt were made and the structures of hundreds of coordination compounds were determined in 1990. A feature of modern coordination chemistry is the increasing number, complexity and variety of new ligands which become available and this very much adds to the richness of the cobalt chemistry reviewed here.

5.1 COBALT(III)

As expected, the vast bulk of the references are to work carried out on cobalt(II) and cobalt(III) with about equal emphasis on each. Also for both oxidation states, much of the research was on complexes which involved nitrogen donor ligands in some form or another.

5.1.1 Complexes with pseudohalide ligands

The C-N stretch has frequently been used as a sensor for ligand outer cation interactions in cobalticyanides [2].

The crystal structure of the complex $Cs[Me_4N]_2Co(CN)_6$ with its mixed cation has been determined. There was found to be a cubic network of Co-CN-Cs units and there was hindered rotation of the CH_3 groups which were orientated towards the cesium ions [3].

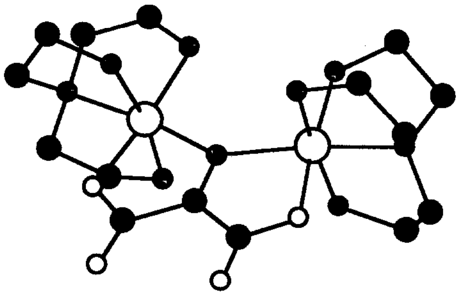
5.1.2 Complexes with oxygen donor ligands

The kinetics of the redox reaction between cobalt(III) ions and selenium(IV) in aqueous perchloric acid suggest a mechanism in which there is an initial reaction involving a complex between the oxidant and substrate and $[CoOH]^+$ and H_2SeO_3 are then reacting species [4]. Overall second order kinetics for the oxidation of oxalate when both bound and unbound to cobalt(III) by bromate ion has been reported [5].

A somewhat negative result from the point of view of cobalt(III) chemistry is that in the oxidation of malonic acid in the presence of a cobalt(III) malonato complex and malonic acid by potassium bromate, using cadmium acetate as a bromide ion scavenger, both bound and unbound malonic acid react at the same rate [6]. The mechanism proposed suggests that an ester is formed between the bromate and the enol form of malonic acid. The presence of small amounts of *tris*(acetylacetonato)cobalt(III) has been found to have a profound effect on the thermal degradation of polymethylmethacrylate [7]. The effects arise from complex formation with the unsaturated chain ends and attack from acetylacetonate radicals on the polymer.

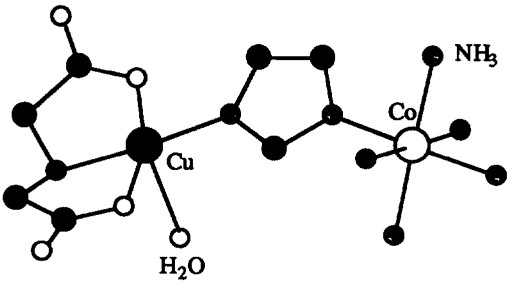
5.1.3 Complexes with oxygen-nitrogen donor ligands

An unusual imidomalonato-bridged cobalt(III) complex is produced when [$CoCl_2$(tren)]Cl.H_2O, ammonium α-aminomalonate and charcoal in methanol are reacted with triethylamine [8]. The complex which is formed is *p*-[Co_2(μ–imidomalonato)(tren)$_2$]$^{3+}$ in which the cobalt atoms are linked via the imido group nitrogen and two carboxylates. The structure is shown in (**1**).



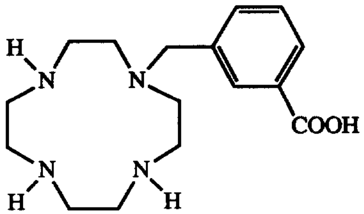
(**1**)

Two heteronuclear dinuclear complexes consisting of copper(II) and cobalt(III) centres united by an imidazolate bridge have been studied by X-ray crystal structure determination [9]. They are 2,2,2,2,2-pentaammine-1-aqua-1,2-(μ–imidazolato-*N,N'*)-1-(iminodiacetato-)-*O,O',N*)-cobalt(III)copper(II) perchlorate trihydrate (**2**) and 2,2,2,2,2,3,3,3,3-decaammine-1,2:1,3-di-(μ–imidazolato-*N,N'*)-1-(iminodiacetato-*O,O',N*)dicobalt(III)copper(II) perchlorate tetrahydrate.



(**2**)

Careful design of the groups attached to macrocyclic ligands can be used to control the nature of the products of reactions involving complexation by that ligand. Thus, the ligand (3) has a pendant group which allows the formation of the dimer $[\{CoL(H_2O)\}_2]^{4+}$ (4) [10]. The reactions which are involved in the formation of the dimer are shown in (5); the pink dimer has a structure involving a network of water molecules and some perchlorate oxygen atoms.



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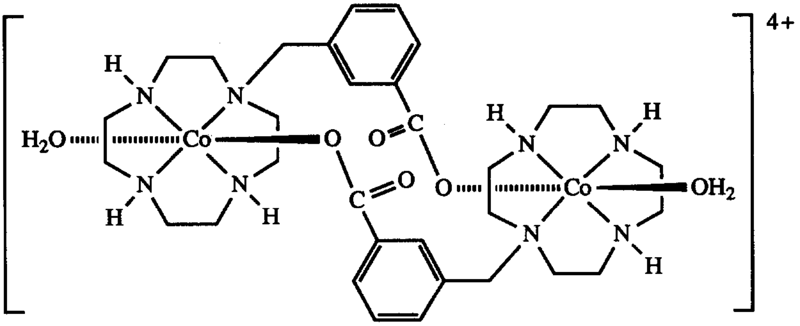

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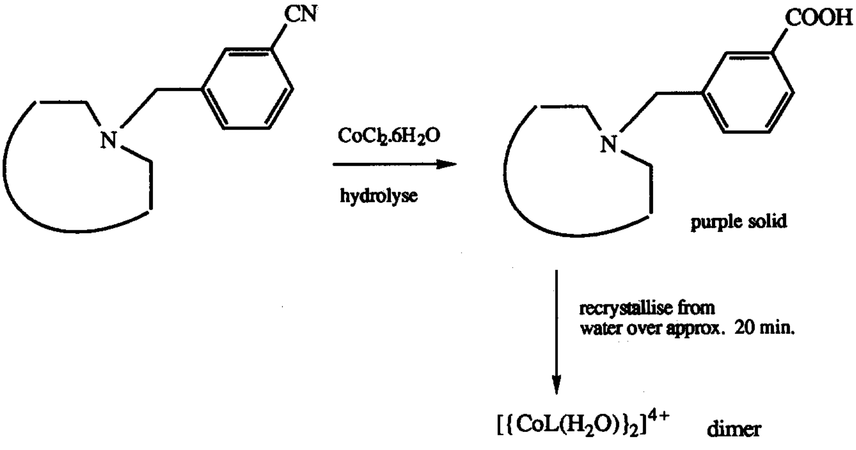
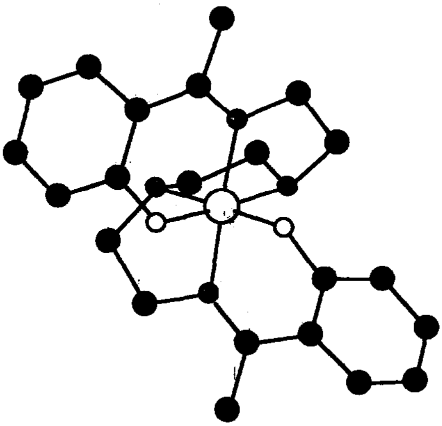


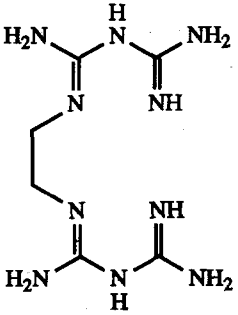
(5)

The ability of a ligand to wrap itself around a transition metal ion (which is so familiar to us with EDTA) is of course now known to be a very common phenomenon. The so-called facultative ligands [11] are ligands which wrap around the metal ion but have an external surface which has essentially organic properties. Such a species is the complex 7,7'-(ethylene-diiminodiethylene-dinitrilo)*bis*(7-methyl-*o*-cresolato-*O,N,N',N'',N''',O'*)cobalt(III) hexafluoro-phosphate which forms a 1:1 compound with acetone. The crystal structure shows the expected slightly distorted octahedral arrangement around the Co with all six donor atoms involved, *ONNNNO* (**6**).



(**6**)

New mixed-ligand complexes involving the ligand ethylenebiguanide (**7**) and DL- and L-methionine have been prepared [12]

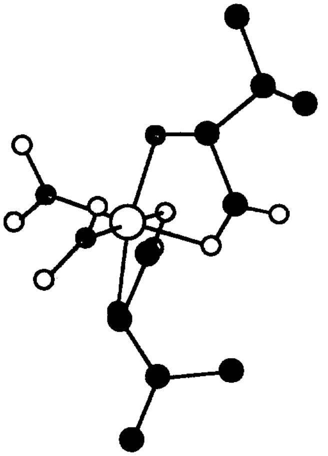


(**7**)

Methionine has also featured in a series of complexes which have been prepared involving dipeptides such as [Co(dipeptido)(diamine)]$^+$ and related species [13]. The peptides involved were L-methionyl-glycinate, glycyl-L-methioninate, L-methionyl-L-alaninate and L-alanyl-L-methioninate.

NMR spectroscopic and circular dichroism (cd) data are given and the cobalt(III) atom is coordinated by the NH_2 nitrogens, the COO^- oxygen and the CH_3S sulphur. The kinetics and mechanisms of the hydrolysis of the (*α*-*β*-*S*)-glycinato-*O*)(tetraethylenepentamine)cobalt(III) ion at pH 6.9 to 8.2 show a high rate of spontaneous aquation of the glycinato species and great inertness of the *N*-protonated form, suggesting an intramolecular conjugate base mechanism [14].

The structure of the complex silver(I)[*Δ*-*cis*(NO_2),*trans*(NH_2)-dinitro*bis*(*S*-valinato)cobaltate(III)] has been investigated in order to examine the effect of ligand conformation on the optical activity of the complex in solution [15]. The structure of the cobalt-containing anion is shown in (**8**).

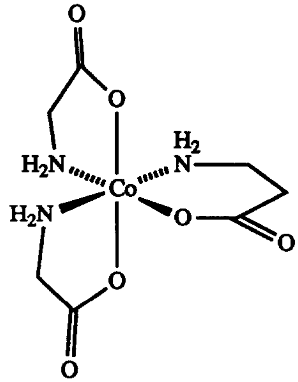


(**8**)

The proton NMR spectrum confirms that the solid state structure of the cobalt(III) anion is retained in solution. The authors conclude that in structures such as this, early branching of the side chain influences the axial positioning of a CH_3 group and that this explains much of the optical activity behaviour of this complex

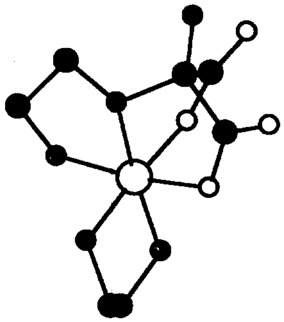
The crystal structure of the complex carbonato*bis*(histamine)cobalt(III) chloride shows that both the histamine and the carbonate act as bidentate ligands with the histamine imidazole rings coordinated in the *trans*-positions [16]. A wide ranging study has been carried out of *trans*(*O*5)-(*β*-alaninato)*bis*(glycinato)cobalt(III), (**9**) [17]. The structure was found to consist of enantiomeric pairs of complex molecules and water molecules. A new synthetic method is given, and the effect of magnetic anisotropy of the cobalt(III) on the NMR spectrum of the methylene protons is considered. In (**9**), coordination sphere around the cobalt atom is distorted octahedral and exhibits a twist-boat conformation of the chelate-ring and a puckered conformation in the five-membered ring.

The crystal and molecular structure of the complex (*α*-glycinato)(ethylenediamine-*N*,*N*′-diacetato)cobalt(III) dihydrate has been determined and simply consists of the neutral complex and water molecules [18]. Complexes of the amino acids, *S*-methylcysteine, methionine, aspartic acid and glutamic acid have been prepared by reaction of dichloro(*N*,*N′*-dimethylenediamine-*N*,*N′*-di-*α*-propionate)cobalt(III) [19] with the appropriate amino acid. The complex *sym*-*fac*-(1,5,9-triazonane)-(*R*,*S*)-asparto)cobalt(III), *sym*-*fac*-[Co(dpt)(*S*)-asp]$^+$ [20] consists of complex ions, ClO_4^- and H_2O held by hydrogen bonds. One of the two dpt fused chelate rings has a distorted chair formation which explains the optical activity behaviour of the complex. The complex *cis*-[Co(eddb)L], where H_2eddb is ethylenediamine-*N*,*N′*-di-α-butyric acid and HL is L-alanine has been prepared and characterised [21]. The X-ray crystal structure has been determined for $Na[Co(eddda)].0.5NaClO_4$ (where eddda is ethylenediamine-*N*,*N′*-diacetate-*N*,*N′*-di-3-propionate) and it is found to be a *trans* (*O*5) isomer with the two five-membered glycine chelate rings in the *trans* position [22].



(9)

The formation of transition metal complexes by carrying out reactions between the ligand attached to the metal and reagents in solution has been a feature of coordination chemistry for some years and has yielded many novel and interesting structures. The *α*-aminomalonate ion has been reacted with $[Co(en)_2Cl_2]^+$ in the presence of Et_3N to produce *α*-diamine and carbinolamine complexes. The structure of one of these, the complex [Co(*N*-(2-aminoethyl)-*α*,*α*-diaminomalonato)(en)]Cl.0.5H_2O has been determined (**10**) and the malonato-ligand H_2L is shown in (**11**). [23].



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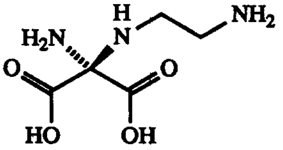
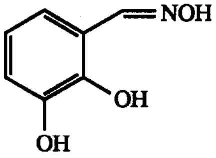


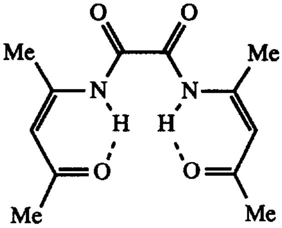
(11)

Octahedral cobalt(III) complexes of the bidentate ligand, *o*-vanillin oxime **(12)** have been synthesised and characterised [24].



(12)

A new ligand, L, which contains amido groups which are situated next to C=C double bonds has been synthesised [25] **(13)**. The cobalt(III) complex [CoLpy$_2$]ClO$_4$ is, unlike the cobalt(II) complex, a mononuclear species.

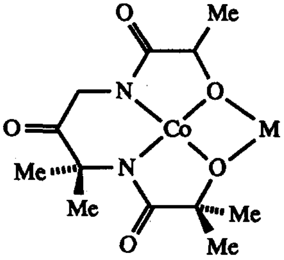


(13)

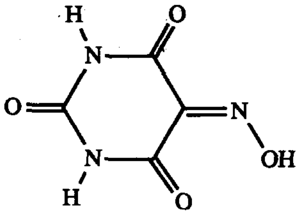
Perhaps one of the commonest reasons for studying reactions and structures of transition metal complexes is that they are, or may be, models for some biochemical process or other. The complex [(*S*)-2,5-di(salicylideneamino)-1-pentanoato(3-)](pyridine)cobalt(III) and related complexes are possible models for reactions catalysed by enzymes for which pyridoxal phosphate is the cofactor [26]. The complex is shown to have distorted octahedral symmetry with the above ligand coordinated stereospecifically at the nitrogens and the oxygens from the phenol and carboxyl groups. The expected distorted octahedral structure has been determined for the [*Δ*,*Λ*-racemic-(1-phenylenediamine-*N*,*N*,*N'N'*-tetraacetato)cobaltate(III) ion [27]. An azido bridge is observed between barium and cobalt in the complex barium (EDTA)cobaltate(III).5H$_2$O [28].

Occasionally transition metal complexes may themselves behave as ligands towards other metal ions. One such case is where square planar paramagnetic cobalt(III) complexes of acyclic polyanionic chelating ligands act as chelating ligands for other metals such as alkali or rare earth metal ions [29] **(14)**.

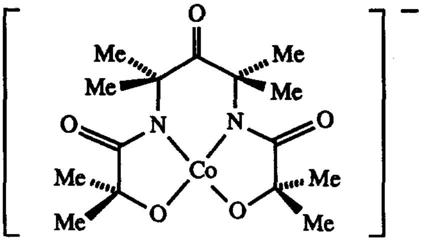
A number of cobalt(III) complexes of the dihydrogenviolurate ion, H$_3$vi = **(15)**, have been prepared and the crystal structure of K[Co(H$_2$vi)(nta)]2H$_2$O has been determined [30].


M = second metal

(14)



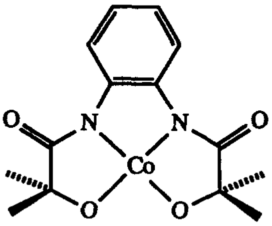
(15)



(16)

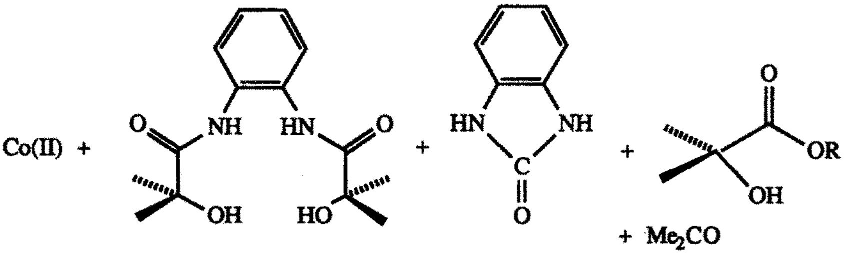
1,2,3- and 1,2,6-$CoL_3 3H_2O$, where HL is ethanolamine, are prepared by reaction in triethanolamine and KOH in iso-PrOH with ethanolamine with and without boiling respectively [31].

A number of chiral square planar cobalt(III) complexes based on ligands (–)2,4-*bis*[(*R*)-2-hydroxy-2-methylbutyramido]-2,4-dimethylpentan-3-one (L) [32]. The structure of (L) shown in (16) was confirmed by single crystal X-ray diffraction. Since square planar complexes similar to these had been shown to be active in the catalysis of the epoxidation of styrenes [33], these workers investigated the epoxidation of a number of styrenes in acetonitrile at –2 to 0°C. It was found that the yields were on the whole good, but that the asymmetric inductions were not very good and there was no obvious relationship between enantiometic induction and changing the phenyl group substituent on the styrenes.



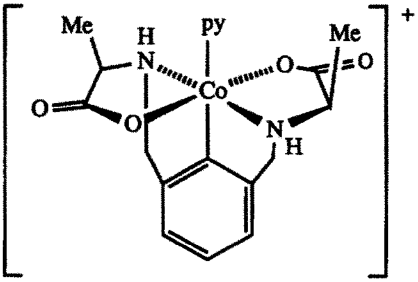
(17)

Most of what has been described above has been the preparation characterisation and structure determination of complex ions. However, in many ways cobalt is the archetypal element for the study of mechanisms of reactions using the tools of reaction kinetics and photochemistry. Photochemistry of the square planar cobalt(III) complex [34] (**17**) is only observed when radiation of wavelengths at the ligand to metal charge transfer bands is used and the products of the reaction are (**18**).

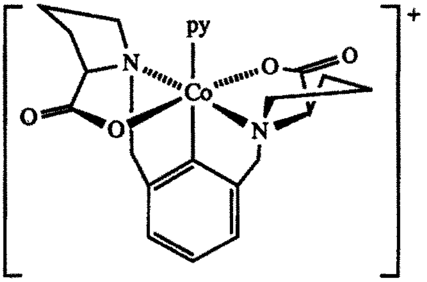


(18)

It has been pointed out that vitamin B_6 model compounds involving cobalt(III) have the advantage that the metal ion can be used to hold the bond angles in the ligand in specifically required positions which allow the study of steric effects in carbon-hydrogen bond-breaking reactions [35]. A series of twelve cobalt(III) complexes, *bis*(salicylideneglycinato)cobaltate(III) with substituents in various positions, have been prepared and the kinetics of the carbon-hydrogen bond breaking reactions of the *gem*-methylenic protons of glycine were found to be first order in [OH$^-$] with differing rates for the two protons indicating a reversal of stereoselectivity. The stereoselective isomerisation and racemisation of (*N*-methyliminodiacetato)(ethylenediamine-*N*-acetato)cobalt(III) in basic solution has been studied [36]. The kinetics of electron transfer between reduced spinach [2Fe-2S]-ferredoxin and the complexes shown in (**19a**) and (**19b**) were found to be stereoselective [37].

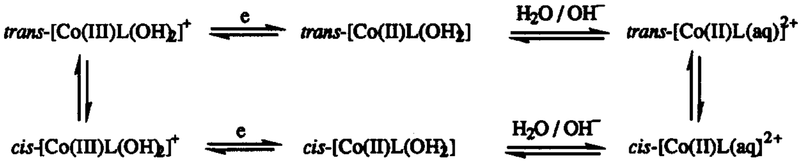


(19a)



(19b)

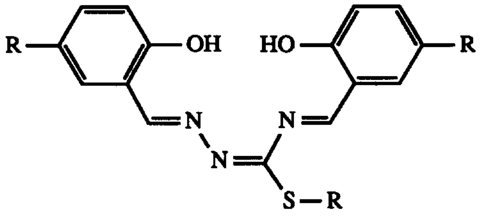
In basic solution, the redox behaviour of the Co(cyclam) complex involving the Co(III)/Co(II) couple is complicated by *cis-trans* isomerism and acid-base equilibria shown in scheme (**20**) [38].



(**20**) L = cyclam

5.1.4 *Complexes with nitrogen-sulphur donor ligands*

The synthesis of 1,3-*bis*(benzo-15-crown-5)-2-thio-*O*-4,5-*bis*(hydroxyimino)imidazole and its complexes with cobalt(III) and cobalt(II) have been described [39]. For the ligand (**21**), complexes of the form $Co(LRR')(NH_3)_2NCS.nH_2O$ are formed [40].



(**21**)

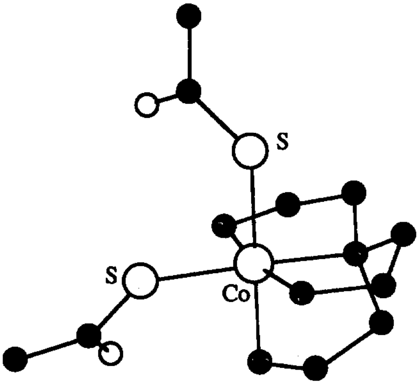
5.1.5 *Complexes with oxygen-sulphur-nitrogen donor ligands*

The kinetics of the thermal decomposition of polymer complexes of *N,N'*-*bis*(dithiocarboxyl)piperazine with cobalt(III) have been investigated under isothermal condition and interpreted using the Coates-Redfern, the Freeman-Carrol and the Horowitz-Metger equations [41].

5.1.6 *Complexes with sulphur, selenium and tellurium donor ligands*

Complexes of the type, $[CoMeSeCH_2CH_2SeMe]_2X_2]BH_4$, (X = Cl, Br, I) and $[Co\{o\text{-}C_6H_4(TeMe)_2\}X_2][BH_4]$ have been prepared by the reaction of the ligand, the anhydrous cobalt(II) halide and sodium borohydride in nitromethane [42]. ^{59}Co, $^{77}Se\text{-}\{^1H\}$ and $^{125}Te\text{-}\{^1H\}$ NMR spectra were used to characterise the complexes.

The complex *bis*(thioacetato-*S*)[*tris*(2-aminoethyl)amine]cobalt(III) perchlorate [43] has a cobalt atom which is octahedrally surrounded by four nitrogen atoms from $N(CH_2CH_2NH_2)_3$ ligands and the two sulphur atoms of the thioacetates, which are monodentate through sulphur (**22**).



(22)

The preparation of a number of complexes containing monodentate thioether ligands has been described [44]. Reactions involve the use of CH_3SCH_3 as shown in Eqn (i).

$$[(NH_3)_5\text{-}OSO_2CF_3](CF_3SO_3)_2 + CH_3SCH_3 \xrightarrow{(CF_3SO_3)_3} [(NH_3)_5Co\text{-}S(CH_3)_2]^+ \quad \text{Eqn (i)}$$

5.1.7 *Complexes with nitrogen donor ligands*

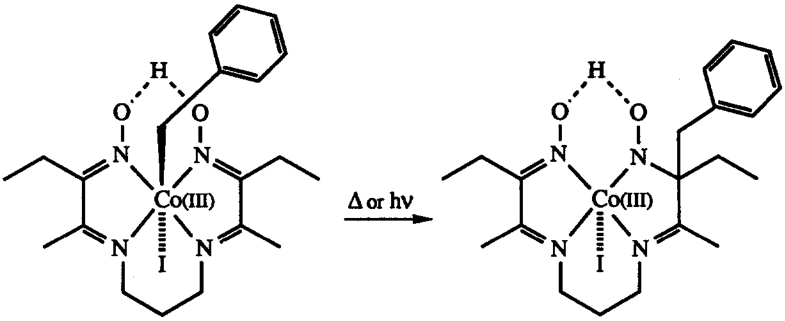
The whole history of cobalt chemistry has been dominated from the early days by the study of complexes with nitrogen donor ligands. Much of the kinetic and mechanistic data on reactions involving cobalt(III) complexes have been obtained from reactions of ammine and amine complexes and in more recent years structural information on macrocyclic ligands with many nitrogen donors has featured in a huge number of studies. It is not surprising therefore that 1990 saw the expected very large crop of publications in this area.

The complex methylmalonato-2,2',2"-triaminotriethylaminecobalt(III) chloride has been synthesised and the X-ray crystal structure determined [45]. The structures have been obtained for both the deprotonated and the protonated complexes. In the latter, the methylmalonate has a single negative charge and is bidentate.

There is much interest in the preparation, structure and spectroscopy of vitamin B_{12} model compounds and in the various manifestations of vitamin B_{12}. Cobaloximes are often cited as models for vitamin B_{12}. The X-ray crystal structure of the complex *trans*-(dichlorocyanomethyl)-

bis(dimethylglyoxime)(triphenylphosphine) cobalt(III) has been determined [46], showing an axial Co-C bond distance of 2.089Å and a Co-P bond distance of 2.371Å.

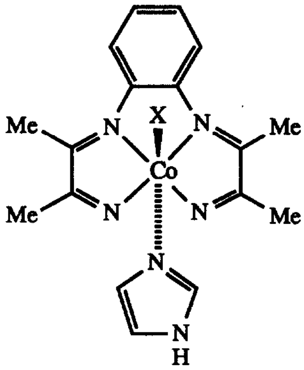
The structures of *bis*(aniline)*bis*(hexamethylglyoximato)cobalt(III) chloride and *bis*(aniline)-*bis*(methyloctylglyoximato)cobalt(III) chloride have been determined [47]. As expected the cobalt is octahedrally coordinated. The complex *trans*-diiodo*bis*(ethanedialdioximato(–1)-*N*,*N*)cobaltate(III) has also been shown to have a distorted (4+2) octahedral structure [48]. Electrochemical and ^{59}Co NMR spectroscopic studies of a series of cobaloxime-type compounds which contain O---BF$_2$---O or (CH$_2$)$_3$ instead of the more usual O---H---O have been carried out [49]. Plots of E$_{1/2}$(I) for the first Co(III)/Co(II) electron transfer against the ^{59}Co spectral chemical shifts showed that the two parameters had a similar sensitivity to the change in electroaffinity of the central metal atom produced by various organic groups bonded to cobalt in the axial position. Similar experiments involving Co(II)/Co(I) electron transfer did not show the same sensitivity to variation of the organic group. Exposure of crystals of dimethylglyoxime complexes to X-rays induces solid state racemisation of chiral cyanomethyl groups such as in the toposelective reactivity of the complex [(*S*)-1-cyanoethyl]-*bis*(dimethylglyoximato)(pyridine)cobalt(III) [50]. The authors used organic packing-energy calculations to examine reaction paths and differences in activation energies to give results compatible with experimental data.



(23)

The process (23) in which the vitamin B$_{12}$ model compound, $C_6H_5CH_2Co(III)[C_2(DO)(DOH)pn]$ (I) is converted into the isomeric compound (II) in a thermally (and not photochemically) reversible process has been facilitated by the development of a high yield reliable synthesis of (II) [51]. The structure of (II) was determined to be that shown above using X-ray crystallography. The compound is formally five-coordinate since the C(phenyl)-Co bond distance is much too great for there to be a formal bond between the two. The complex pyCo(Hdmg)$_2$[CF(CF$_3$)$_2$] has been prepared from Na[pyCo(Hdmg)$_2$] and (CF$_3$)$_2$CFI, where py = pyridine and Hdmg$^-$ is the monoanion of dimethylglyoxime [52]. The complex was characterised using ^{19}F NMR spectroscopy.

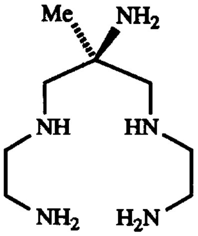
The reaction of 2,3-butanedionemonooxime with 1,2-diaminobenzene produces the ligand, 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime [53]. This ligand forms cobalt(III) complexes of the type [$CoLX_2$] and these then react with imidazole to form (24).



(24)

Raman spectroscopy would often be the technique of choice in examining metal to ligand bonds if it were not for the fact that it is frequently severely limited by the colour of the compound, any fluorescence which may be induced or if the compound is photochemically sensitive. Many of these difficulties are overcome by the use of near infrared Fourier transform Raman spectroscopy. This technique has been used to determine the frequency of the Raman active Co-C stretch in the notoriously photolabile methyl cobalamin to be $500cm^{-1}$ and $470cm^{-1}$ for methyl deuterated (CD_3^-) cobalamin [54]. Coenzyme B_{12} (adenosyl cobalamin) is, like its methyl counterpart, very photolabile and has been studied using nanosecond transient absorption spectroscopy; the nanosecond quantum yield was found to be 0.23 for the 'base on' variety and 0.045 for the more stable 'base off' species [55]. ^{15}N NMR spectroscopy has provided valuable information about cyanocobalamin and other monocyano and dicyano cobalt-containing corrins which have been enriched with ^{15}N and ^{13}C in the axial cyanide [56]. Alterations of the cobalt coordination sphere have the opposite effect on the ^{13}C and the ^{15}N spectral chemical shifts. From this it is inferred that there is a resonance structure $Co^+{=}C{=}N^-$ indicating that dπ-pπ metal to ligand back bonding is important.

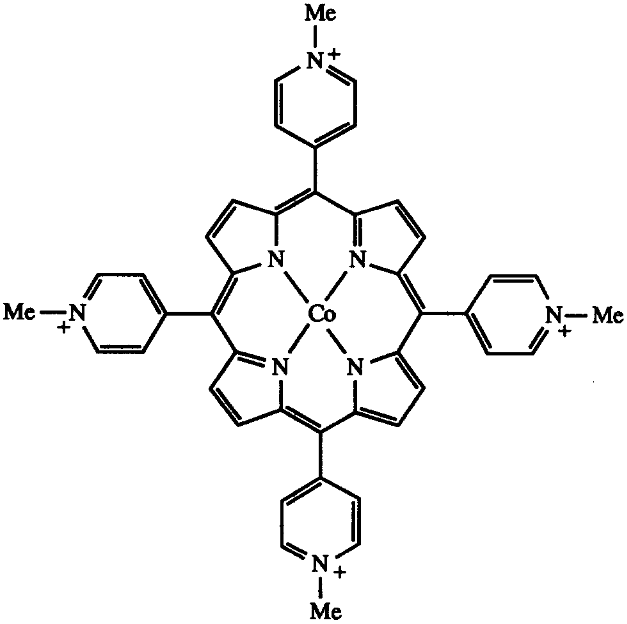
The ^{15}N NMR spectra of the axial nucleotide and amide side chains of cyanocobalamin and dicyanocobamides have been examined in some detail [57]. The comparisons allow conclusions to be drawn about the effects of the removal of the benzimidazole nucleotide on the chemical shifts of the various side chain amides, with a larger than expected effect on the downward projecting amides than on those projecting upwards. Electrochemical and ^{59}Co NMR spectroscopic studies have been carried out to investigate the electronic and steric influences of axial and equatorial ligands in cobaloxime complexes.



(25)

The ligand 1,5,9-triamino-5-methyl-3,7-diazanonane (**25**) forms quinquedentate complexes with cobalt(III) [58]. The complexes consist of both monomers, $[CoLX]_2^+$ ($X=Cl^-$, NCS^-, NO_2^-) and dimers, $[(CoL)_2O_2]^{n+}$ (n = 4 or 5) and both have been prepared and the structures of one of each determined. The rate of base hydrolysis of the chloro complex was determined and was found to be slow. Measurement of the Raman spectrum showed that the frequency of the vibration of the peroxo oxygen was at 40 cm^{-1}.

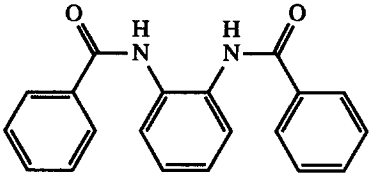
The variation in the oxidation state of the complex *meso*-tetrakis(1-methylpyridinium-4-yl)porphinato)cobalt(III) (**26**) has been studied in solution in DMF, DMSO and pyridine [59].



(26)

The oxidation of cobalt(II) to cobalt(III) was found to occur in the range +0.29V to −0.01V. The complex undergoes four electroreductions involving a total of six electrons giving a final product of $[(TMpyP)Co]^{2-}$. Thus, from −0.49V to −0.61V the species $[(TMpyP)Co(I)]^{2+}$ is produced and then an electron is added to the π-system to give $[(TMpyP)Co(I)]^{2+}$. Further reactions involving the four-electron reduction of the four *N*-methylpyridiniumyl substituents on the TMpyP of $[(TMpyP)Co]^{2+}$ are observed in the $E_{1/2}$ range −0.89V to −1.1V. The pyridine is bonded in the axial position and the bonding has been investigated electrochemically and using ESR spectroscopy.

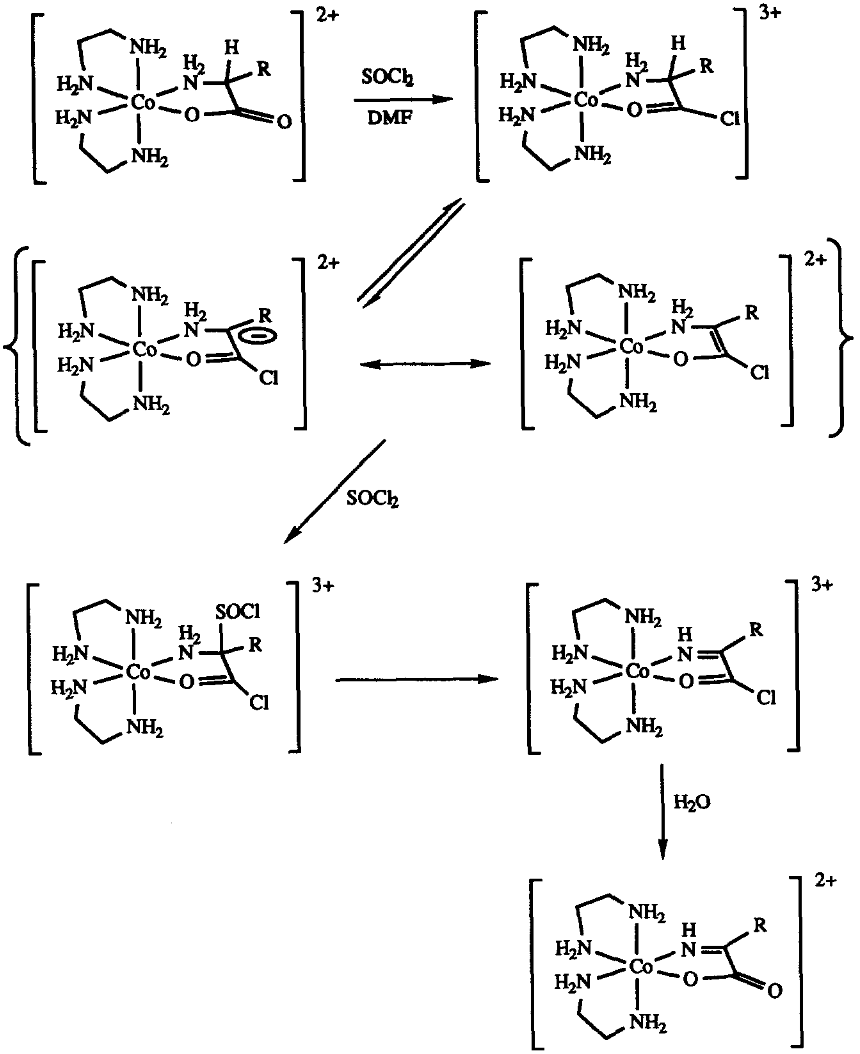
As part of a study of catalysts for the phosphate diester backbone of DNA, Chin, Drouin and Michel [60] determined the structure of the complex ion $[Co(tren)(NO_2)_2]^+$ (tren = *tris*(2-aminomethyl)amine). From this study it appears that the N-Co-N bond angle is crucial in determining the reactivity of these complexes in hydrolysing phosphate diesters.



(27)

Trans-bis(diethylenetriamine)cobalt(III) perchlorate dihydrate has all six nitrogen atoms in octahedral coordination around the cobalt [61]. The reaction of *N,N'*-dibenzyl-*o*-phenylenediamine (27) with cobalt(II) acetate in pyridine resulted in the formation of the complex pyridine-*bis*(*o*-benzosemiquinonediimine)cobalt(III) [62]. The deep red-purple product was found to contain five-coordinated cobalt arranged in a square pyramid of nitrogen atoms with pyridine occupying the axial position.

The presence of a metal ion in a complex often has a profound effect on the reactivity of the ligands attached to the metal. It has been pointed out [63] that there have been many studies of the reactions of nucleophiles with coordinated ligands, but less interest in the reactions of electrophiles, possibly because they were expected to react less readily. Thus, these workers have investigated the reactions of $SOCl_2$ with appropriate coordinated amino acid ligands. It was found that the treatment of α-amino acid complexes of *bis*(ethylenediamine)cobalt(III) with $SOCl_2$ dissolved in dimethylformamide resulted in the formation of the corresponding α-imino acidato species. The steps which occur in this reaction are proposed to be those shown in scheme (**28**) where R=CH_3, $CH_2(C_6H_4)OH$, $CH(CH_3)_2$, CH_2CH_2COOH, $CH_2CH_2SCH_3$, $CH_2CH_2CH_2CH_2NH_2$ as well as the complexes (**29**) and (**30**).



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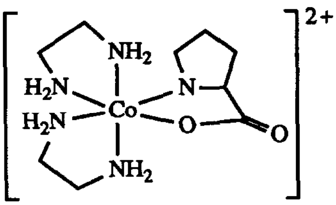

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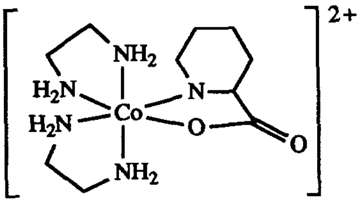
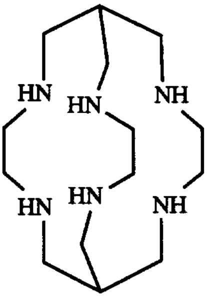


(30)

The redox potentials for some cobalt(III) complexes of the ligand 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane (**31**) with a variety of substituents have been determined [64]. A Hammett type of treatment was used, which allowed the authors to obtain polar substituent constants, the ^{1}H, ^{13}C and ^{59}Co NMR spectra are correlated with the redox potential data. Because changes in the redox potentials do not produce changes in the ligand field spectra of the complexes, it is concluded that the the effects of the nature of the substituent were not transmitted as a result of through-bond induction or through-space orbital overlap, but may be due to Coulombic interaction or via the σ-framework of the structure.



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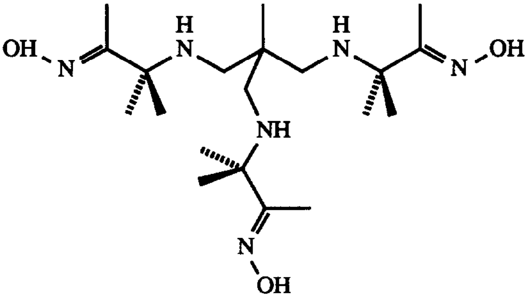

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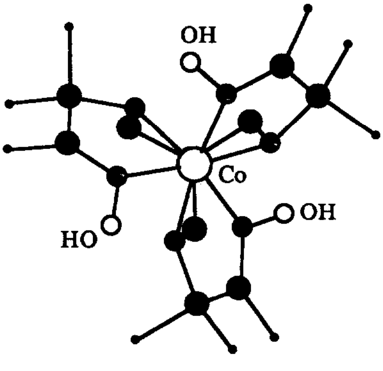


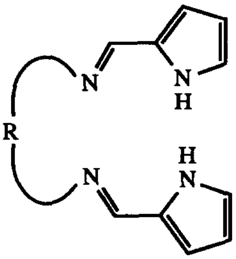
• = Me The CMe group of the tamox ligand is eclipsed by the cobalt atom.

(33)

A novel ligand tamox (32) (tamox = $CH_3C\{CH_2NHC(CH_3)_2C(CH_3)=NOH\}_3$) has been made from the reaction of 1,1,1-*tris*(aminomethyl)ethane and 2-chloro-2-methyl-3-nitrosobutane [65]. A deep yellow cobalt(III) complex is formed and the X-ray structure of the chloride has been determined; the cation is shown in structure (33). It will be seen from the structure that there are two different bonding nitrogen atoms, viz amide and oxime. The ligand is hexadentate, but the cobalt to nitrogen bond lengths for the two types of nitrogen atom are different; $Co\text{-}N_{amine}$ = 1.97Å and $Co\text{-}N_{oxime}$ = 1.92Å.

The complex (hemiporphyrazato)*bis*(1-methylimidazole)cobalt(III) triiodide also contains a hexacoordinated ligand and is prepared by the reaction of the complex $[Co(hp)(H_2O)_2]$, where hp = hemiporphyrazate, with 1-methylimidazole in the presence of molecular iodine [66]. The cobalt atom was found to be at the centre of a very nearly planar tetraaza ligand. A series of binuclear cobalt(III) complexes derived from the species $[(tren)Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(tren)]^{4+}$ (tren = *tris*(2-aminoethyl)amine) by replacement of OH by another ligand have been prepared [67]. The structure of the hydroxo-containing ion was determined. Aqueous solutions of cobalt(III) complexes of the ligands diethylenetriamine, triethylenetetramine, tetraethylenepentamine and cyclam, 1,4,8,11-tetraazacyclotetradecane have been studied using ^{59}Co NMR spectroscopy [68].

A series of cobalt(III) complexes of the four coordinate ligands (34) [69] have been prepared. When R is small it is believed that these complexes are monomeric. When R is $bn(PimH)_2$ or $pa(PimH)_2$ it is thought that the complex is dimeric.

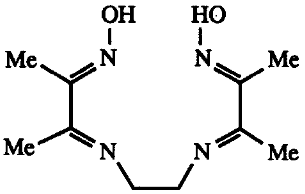


R = *o*-phenylene, ethylene, propylene, butylene, pentamethylene

(34)

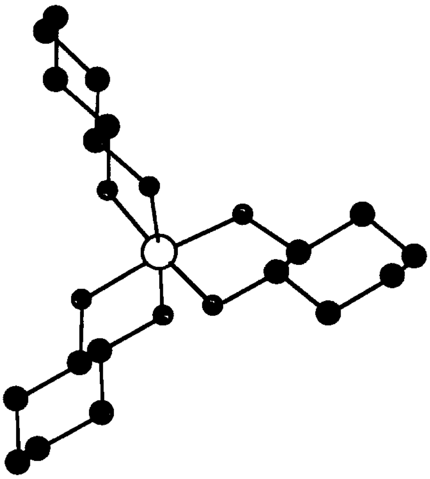
For $[Co(dien)(NO_2)_2NH_3]Cl$ the *mer*-configuration predominated. For cyclam *trans*-configurations predominate and for tetraen, all four possible isomers were present. The synthesis and structure of the complex *mer*-(diethylenetriamine)(4-hydroxybutyrato)phenanthroline-cobalt(III) has been determined [70]. The complex $[Co(trien)Cl_2]Cl$ reacts with $HSCH_2CH_2COOH$ (H_2L) and with sodium hydrazopyruvate (NaL') to produce, [Co(trien)L]Cl and [Co(trien)L']Cl respectively [71]. The coordination around the cobalt atom in [Co(trien)L]Cl is of the form N_4OS, while that in [Co(trien)L']Cl is N_5O. The reaction of *trans*-$[CoL_2Cl_2]Cl$ where L = ethylenediamine, 1,3-propane diamine or 1,4-butanediamine, diastereoisomers are formed [72]. In addition to 5-, 6-, and 7-membered rings, these diamines form monodentate species.

The cobalt(III) complexes, $[Co(H_2L)]X_2$ where H_2L is the *bis*(Schiff base) derived from the condensation of ethylenediamine with diacetyl monoxime (35) and X = Cl, Br, I, SCN, SeCN react with imidazole or 1-vinylimidazole to give [CoL(B)] where B = base [73].



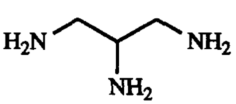
(35)

The same complex has been shown to react with $BF_3.Et_2O$ to form a macrocyclic dimer with an O-BF_2-O bridge [74]. The CD spectra of *bis*(*S*,*S*-1,3-diphenyl-1,3-propanediamine)cobalt(III) [75] in a number of different organic solvents show irregular changes at 540nm which are attributable to dissociated and associated species. Multinuclear NMR spectra have been used in a study of the crystal field strength of the nitro ligand and estimations have been made of the ^{59}Co NMR spectral chemical shifts of nitro complexes [76].

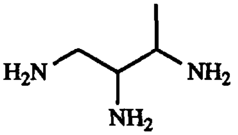


(36)

Ever since the discovery that d-tartaric acid and its salts have the ability of discriminating between cations having different chirality, the mechanism by which this occurs has been of great interest. d-Tartrate is particularly effective in discriminating the cations lel^3-$[Co(chxn)_3]^{3+}$ and lel^3-$[Co(pn)_3]^{3+}$, where chxn = *trans*-1,2-cyclohexanediamine and pn = 1,2-propanediamine. In order to throw light on this, the single crystal X-ray crystal structures of the diastereomeric pair Λ-lel^3-[Co(*S*,*S*-chxn)$_3$]Cl(d-tart).$2H_2O$ and Δ-lel^3-[Co(*R*,*R*-(chxn)]Cl(d-tart).$2H_2O$ were determined [77]. The structure of Λ-lel^3-[Co(*S*,*S*-chxn)$_3$]$^{3+}$ is shown in (36). Both structures have the d-tartrate anion with four of its oxygen atoms directed towards the cation and three of them are hydrogen bonded to the three amino protons parallel to the C_3 axis of the complex. The authors draw attention to the fact that the second complex has an unprecedented conformer in which steric repulsion by the bulky chxn groups forces the distal carboxylate group to be rotated. Also included are *ab initio* calculations on d-tartrate which show that the rotated carboxyl group confers considerable destabilisation producing the large solubility difference between the two isomers. A number of ligand systems which exibit chirality have been studied in cobalt(III) complexes in order to investigate the selectivity which they show towards additional coordination of racemic substrates [77, 78]. The equilibrium behaviour for the distribution of ions $[Co(L^3)_2]^{3+}$ and $[Co(L^3)(L^2)(X)]^{n+}$ when L^3 and L^2 were varied, were compared with theoretical data calculated from strain-energy minimisation. The ligand systems corresponding to L^3 are shown in (**37a-f**). The ligands corresponding to L^2 were ethane-1,2-diaminoethane, propane-1,2-diamine and $X = NH_3$, H_2O and OH^-. The distribution of the various species in the mixtures was determined using HPLC, a technique which is increasingly being used in transition metal coordination chemistry, but has yet to be exploited to the full. Systems with L = 1,2,4-trab were poorly discriminating. The authors predict from theory that Me substitution on the ligand 1,2,4-trab would lead to enhanced enantioselectivity at optimum site for substitution.



(37a)



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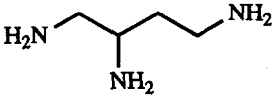

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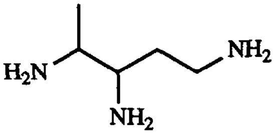
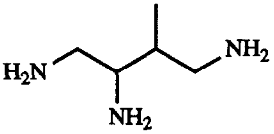


(37d)



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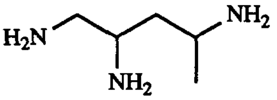


(37f)

A charge density refinement performed on X-ray diffraction data for $[Co(NH_3)_5(H_2O)][Cr(CN)_6]$ [79] shows charge flows from CN to Cr, σ-bonding, from NH_3 and H_2O to Co, σ- and back π-bonding and electron transfer from $Cr(CN)_6$ to $Co(NH_3)_5(H_2O)$ through 17 CN----H hydrogen bonds. A theoretical study based on the empirical reduction parameter introduced by Shimura [80] which allows the prediction of the first ligand field absorption band components has been used in a theoretical study of cobalt(III) and chromium(III) mixed ligand complexes [81]. Transition energies in good agreement with experimental data have been obtained using an NDDO method for calculating configuration interaction in $[Co(NH_3)_5L]^{n+}$, where $L = Cl^-$, OH^-, H_2O, CN^-, NH_3 [82].

Although Raman spectroscopy is not a very widely used technique, we saw above that valuable results can be obtained using it. One Raman technique with great potential is surface enhanced Raman spectroscopy; this has been used to probe the surface-induced substitution reactions of *tetrakis*(*N*-methylpyridinio)porphyrinatocobalt(III) in which silver(III) porphyrinato complexes are formed on a metallic silver surface [83]. The authors conclude that the reaction is not phonon assisted, but depends on sol activity and time.

The reduction reactions of the cyano- cobalt(III) complexes of TMpyP and *tetrakis*(4-sulphonato)porphyrin (TPPS) have been studied using radiolytic and electrochemical techniques [84]. The reactions occur in a stepwise manner forming in turn the cobalt(II) and cobalt(I) species and finally the phlorin. The complex $[(CN)_2Co(III)TMpyP]^-$ undergoes one-electron reduction of the porphyrin macrocycle to give the Co(III) π-radical anion, which then disproportionates to give the two-electron ring reduced cobalt(III) phlorin.

There is enormous interest on the behaviour of metal ions in a variety of geological situations because of the potential for migration of such ions in soils and rocks. The treatment of hectorite which had been exchanged with cobalt and which was treated by ligands such as 2,2'-bipyridyl, 1,2-diaminoethane and ammonia resulted in the formation of complexes of cobalt(III) [85]. Significant quantities of exchanged cobalt are displaced by groundwater ligands such as pentanoic and butanoic acids.

A study of the photochemistry and ligand to metal charge transfer spectroscopy of a series of complexes $[Co(RNH_2)_5X]^{2+}$, where R= methyl, ethyl or n-propyl, [86] shows that the solvent is less important than in the corresponding ammine complexes because of the hydrophobic nature of the alkyl groups on the coordinated nitrogen and the consequent interaction with the solvent.

The effect of the addition of a number of cobalt(III) amine complexes on the maximum absorbance of the complex $[Fe(phen)_2(CN)_2]$ has been studied in solution in dimethylformamide and nitromethane [87]. The σ-acceptor strength of the cobalt(III) complexes was found to decrease with increasing numbers of alkyl substituents:

$$[Co(NH_3)_6]^{3+} > [Co(en)_3]^{3+} > [Co(sep)]^{3+}$$

where sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane.

More than forty years after the study of the kinetics of the reactions of amine cobalt(III) complexes began to provide the data that became the basis for inorganic reaction mechanisms, there are still many papers published on a variety of substitution reactions of such complexes. The aquation of the complexes *trans*-$[CoLCl_2]^+$ and $[CoL(NO_2)Cl]^+$ for a range of tetraazamacrocycles, L, have been studied and a very wide variation in rates is found [88]. In a limited number of cases the rate variation may be attributed to the conformational strain energy. However, it is found that for large ringed macrocycles such as the 1,4,8,11-tetraazacyclohexadecane and 1,4,8,11-tetraazaheptadecane aquation occurs much more slowly than expected because of their curtailed ability to fold across a fold axis. There is also evidence that lower aquation rates may be influenced by the N----N bite distance. High rates of aquation in 14-member macrocycles are found if *gem*-dialkyl groups are present.

The rate law [89] for the hydrolysis in acid solution of both *cis*-*β*-carbonato(3,7-diazanonane1,9-diamine)cobalt(III) and *cis*-*β*-carbonato(4,7-diazadecane-1,10-diamine)cobalt(III) is given in Eqn (ii). The deuterium isotope effect suggests that the mechanism involves a rapid protonation equilibrium which is followed by slow opening of the carbonato ring.

$$-d(\ln[\text{complex}]) / dt = k_0 + k_1[H^+] \qquad \text{Eqn (ii)}$$

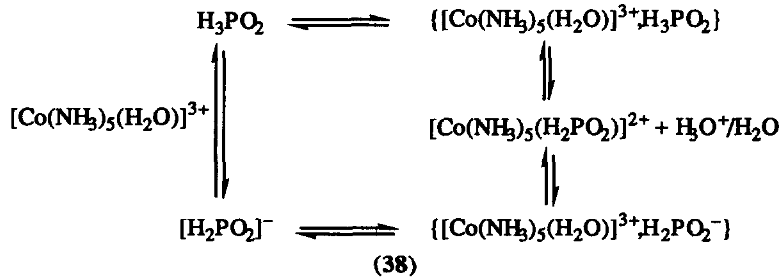
μ–Amido-μ–carbonato-*bis*-*bis*(ethylenediamine)cobalt(III) ion has been prepared from μ–amido-μ–carbonato-*bis*(*bis*(ethylenediamine)cobalt(III)) perchlorate and characterised [90]. The kinetics of the aquation of the compound were studied in acid solution and also the base hydrolysis was studied. The former were independent of $[H^+]$ and the latter was interpreted in terms of a rapid pre-equilibrium. The kinetics of the formation of the carbonato complex from the μ–hydroxo species indicate initial bridge cleavage

Iron(III) catalyses the aquation of *trans*-*bis*(Hmalonato)*bis*(trimethylamine)cobalt(III) ion in aqueous solution [91]. The rate law for the iron catalysed aquation is given in Eqn (iii).

$$\text{Rate} = \frac{k_0[H]^{+} + K_M K_M[\text{Fe(III)}]/[H^+]}{1 + K_M[\text{Fe(III)}/[H^+]} \qquad \text{Eqn (iii)}$$

The rate of aquation of *cis*-$[Co(en)_2LCl]^{2+}$, where L = alkylamines, imidazole, or *N*-methylimidazole, is decreased by sodium dodecyl sulphate because of binding to the micellar surface [92] and is very much affected by how hydrophobic the ligand L is. However, the addition of Triton X-100 to the reaction had very little effect on the rate for most of the complexes. Similarly, base hydrolysis reactions are slowed by anionic micelles of sodium dodecyl sulphate. In a similar study, the base hydrolysis of *cis*-(imidazole)(salicylato)*bis*(ethylenediamine)cobalt(III) and (*α*-*S*)-(sulphito)(tetraethylenepentamine)cobalt(III) was found to be moderately catalysed by cetyltrimethylammonium bromide [93]. The rate was decreased in the presence of sodium dodecyl sulphate and only slightly affected by Triton. Again the hydrophobic nature of the complex was believed to be a factor. The role of the hydrophobicity of cobalt-corrin complexes in the catalytic oxidation of quinols has been studied, with the possibility of using these complexes as active oxygen radical generators targetted at DNA [94].

An *Id* mechanism has been mooted for the anation reaction involving $[Co(NH_3)(H_2O)]^{3+}$ and the $H_3PO_2/H_2PO_2^{2-}$ system (38) [95].

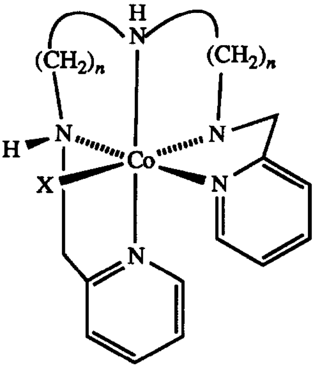


(38)

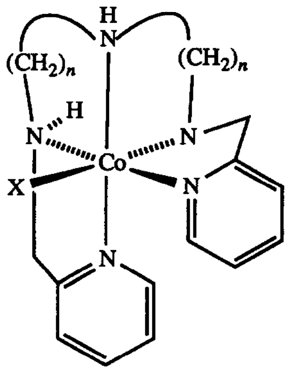
$$[Co(NH_3)_5OP(OR)_3]^{3+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + PO(OR)_3 \qquad \text{Eqn (iv)}$$

$$[Co(NH_3)_5OP(O_2)(OR)]^{+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + PO_3(OR)^{2-} \qquad \text{Eqn (v)}$$

An ion pair dissociative mechanism is proposed for the anation reaction of diaqua(3,6-diazaoctane-1,8-diamine)cobalt(III) with the amino acids, glycine, DL-alanine, L-proline, DL-valine and L-serine [96]. Rate data have been obtained for the reactions shown in Eqns (iv) and (v) [97]. For $[Co(NH_3)_5OP(OR)_3]^{3+}$ where R = Me, $k_{OH} = 78.3\ M^{-1}\ s^{-1}$, and where R = Et, $k_{OH} = 44.5\ M^{-1}\ s^{-1}$, for $[Co(NH_3)_5OP(O_2)(OR)]^+$ where R = Et, $k_{OH} = 5.0 \times 10^{-5}\ M^{-1}\ s^{-1}$. The hydrolysis always occurred at the cobalt(III) centre and not at the phosphorus(V) atom. Phosphate complexes of cobalt(III) were also the subject of a very thorough study of *trans*-$[Co(en)_2(OH_2)(OPO_3H)]ClO_4.{}^1/_2H_2O$ and its equilibrium and kinetic properties in aqueous solution [98]. The interest in this arose from the presence of an unknown complex detected in a ^{59}Co NMR spectroscopic study of alkaline aqueous solutions of $[Co(en)_2(O_2PO_2)]$. This newly characterised complex was found to have an electronic spectrum in which there were peak maxima at 570 nm ($E = 48\ mol^{-1}\ dm^3\ cm^{-1}$) and 359 nm ($69\ mol^{-1}\ dm^3\ cm^{-1}$). A single crystal X-ray structure determination showed that, as anticipated, this is indeed the *trans*-complex and contains a monodentate phosphato ligand. The pK_a values for the phosphato protons were determined to be pK_{a1} = 3.17 and pK_{a2} = 9.27 and for the aquo ligand, pK_{aaq} = 6.6. The neutral complex, [(dpt)Co(α,β,γ-HATP)], where dpt = $NH(CH_2CH_2CH_2NH_2)_2$, has been prepared and characterised [99] and the kinetics of formation from $[dptCo(OH)(H_2O)_2]^{2+}$ and $HATP^{3-}$ have been studied. The mechanism is believed to involve the initial rapid formation of the monodentate complex $[dptCo(H_2O)_2(\gamma\text{-}ATP)]^-$ followed by rate determining ring closure. It is found that $[dptCo(H_2O)_2]^{3+}$ at pH 4.9 is particularly effective in the hydrolysis of ATP.



(39a)



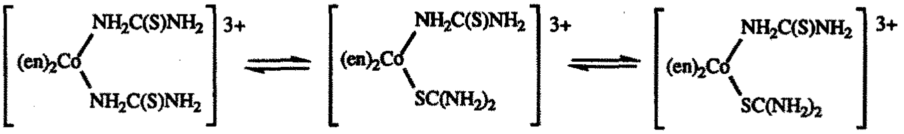
(39b)

The rates of base hydrolysis of cobalt(III) amine complexes usually show a first order dependence of the observed rate constant on hydroxide ion concentration. A departure from this behaviour has been found in the base hydrolysis of α,β-nitro, azido and isothiocyanato-[1,9-*bis*(2,2'-bipyridyl)-2,5,8-triazanonane] (picdien) and [1,11-*bis*(2,2'-bipyridyl)-2,6,10-triazaundecane]-

cobalt(III) cations [100]. The complexes *syn*- and *anti*-α,β-[Co(picdien)X]$^{2+}$ are shown as (**39a**) and (**39b**), respectively. It is found that the base hydrolysis of the complex for $X^- = NCS^-$ and NO_2^- shows saturation rate behaviour with increasing hydroxide ion concentration, while for $X^- = N_3^-$ there is strict first order behaviour. There are three non-equivalent acidic protons on the ligand and therefore the rate constant is very much a composite quantity involving the equilibrium constants of the three protons and the rate constant. When there are *i* different possible acid-base equilibria and the equilibrium constant K_i and the dissociation constant is k_2^i, then k_{obs} is given by Eqn (vi).

$$k_{obs} = \quad (K_2^i[OH^-] \,/\, (1+ \; K_i[OH^-]) \qquad\qquad \text{Eqn (vi)}$$

The reactions of a series of cobalt(III) complexes, *cis*-[Co(*N*-*N*)$_2$Cl$_2$]Cl, *cis*-*trans*-[Co(en)$_2$(H$_2$O)$_2$]Br$_3$ and [Co(CN)$_5$(H$_2$O)]$^{2-}$, where *N*-*N* is 2,2'-bipyridyl, 1,10-phenanthroline or ethylenediamine (en) with NO_2^-, SO_3^{2-} and thiourea have been investigated using ^{59}Co NMR spectroscopy [101]. The products of the reactions exhibited extensive linkage isomerism involving *O*,*N*-, *O*,*S*- and *N*,*S*-isomers in the case of the complexes of ethylenediamine, but no such behaviour in the bipyridyl or phenanthroline complexes. An example of such isomerism is the reaction of *cis*-[Co(en)$_2$(H$_2$O)$_2$]Br$_3$ with thiourea shown in (**40**).



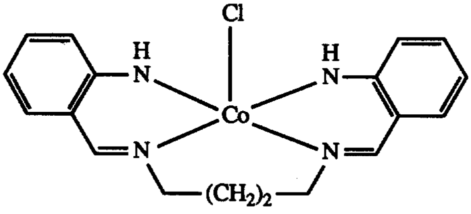
(**40**)

The reaction of sulphur dioxide in aqueous solution with *cis*-diaquo-*bis*(ethylenediamine)cobalt(III) and *cis*-diaquo*bis*(trimethylenediamine)cobalt(III) result in the formation of *cis*-[Co(L-L)(OSO$_2$)$_2$]$^-$ [102]. This complex is then shown to react through two kinetically identifiable steps consisting of the intramolecular reduction of cobalt(III) to cobalt(II) and the isomerisation to *O*- and *S*-bonded sulphito complexes.

It may be that now that so much work has been carried out on aquation and related reactions of transition metal complexes that there is nowhere else to go but into other solvents and a number of papers were published in 1990 on this theme. The solvolysis of the complex *cis*-chloro(1-aminopropan-2-ol)*bis*(ethylenediamine)-cobalt(III) in ethanol with methanol, propan-2-ol and ^{t}butanol as cosolvents produced the species, *cis*-[Co(en)$_2$(NH$_2$CH$_2$CHOHCH$_3$)]$^{3+}$ which is chelated through nitrogen and oxygen [103]. The rate of the reaction was reduced with increasing mole fraction of the added alcohols, though the effect became less marked with increasing hydrophobic nature of the alcohol. The question of the interaction of the solvent and the hydrophobic nature of the surface of complexes has been addressed in a study of the solvolysis of a series of complexes [Co(3-Rpy)$_4$Cl$_2$]$^+$ in water-rich water/methanol mixtures [104] where R = Me or Et. These complexes present a largely hydrophobic surface to the solvent mixture. Rate measurements allowed the determination of enthalpies and entropies of activation, while a free energy cycle was used to relate the free energy of activation in water to the free energy in the solvent mixture using the free energies of transfer of the individual ionic species from water to the solvent mixture. Changes in the solvent mixture stabilise the cation in the transition state rather than in the initial state. The application of proton NMR spectral line broadening techniques to aquation kinetics of cobalt(III) complexes [105] in mixtures of *N*-methylacetamide and water have shown that rates of aquation of *cis*-$[Co(en)_2Cl_2]^+$ depend on the fraction of the water molecules in the solvate shell around the complex as 1 or 2 water molecules participate in the transition state.

The aquation of *cis*-diacetato*bis*(ethylenediamine)cobalt(III) ion has also been studied in mixed solvents containing NaCl, NaBr and $NaClO_4$ as supporting electrolytes [106]. Another study in mixed solvents was on the solvolysis of *trans*-dichlorotetra-(4-^{t}butylpyridine)cobalt(III) ions in water/^{t}butyl alcohol mixtures [107]. There has also been a related study of chloropentacyanocobaltate(III) ion in water methanol mixtures [108]. When the solvent is varied from water to the various methanol water mixtures, the study suggests that in the transition state in going from $[Co(CN)_5]^{2-}$ to $[Co(CN)_5]^{2-}\cdots\cdots Cl^-$, the ion $[Co(CN)_5]^{2-}$ is stabilised by the changing solvent structure over the species, $[Co(CN)_5Cl]^{3-}$. The kinetics of the base hydrolysis of *cis*-chloro(benzimidazole)*bis*(ethylenediamine)cobalt(III) have been investigated in methanol-water and ethyleneglycol-water mixtures at isoelectric conditions [109]. The rate constant for the conjugate base of benzimidazole species was virtually unaffected by the composition of the solvent.

The effect of solvent on the kinetics of the solvolysis of *cis*-chloro(cyclohexane)*bis*(ethylenediamine)cobalt(III) ion in mixtures of water and acetone (in the range 0 to 50 wt% acetone) have been investigated [110]. Plots of log k_{obs} against reciprocal of the bulk dielectric constant were nonlinear, while plots of the same function against the mole fraction of acetone were linear with the same gradient at each temperature (–3.14). The authors conclude that this is in keeping with solvent structure effects and lack of preferential solvation of the substrate.



(41)

The complex chloro(1,2-*bis*(*o*-iminobenzylideneamino)ethane)cobalt(III) **(41)** is unusual in that it is a paramagnetic cobalt(III) complex. The equilibrium between this and the pyridine adduct when the reaction is carried out in pyridine has been reported [111] and the effect of variation of pressure and temperature on the position of the equilibrium in Eqn (vii) where L is shown in **(41)** has been studied [112]. This allowed the determination of a value of –21.8 $cm^3\ mol^{-1}$ for ΔV and a value of 51.8 $kJ\ mol^{-1}$ for ΔH. Also, the equilibrium constant, $K = 0.96\ M^{-1}$ and $\Delta G = 0.099$ kJ mol^{-1} and $\Delta S = -0.18\ kJ\ mol^{-1}\ K^{-1}$.

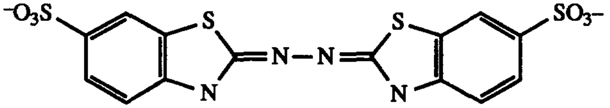
$$[CoLCl] + py \rightleftharpoons [CoLCl(py)] \qquad \text{Eqn (vii)}$$

The effect of increasing the pressure over the range 0.1 to 207 MPa on the self exchange reaction of $[Co(en)_3]^{2+}$ and $[Co(en)_3]^{3+}$ in aqueous solution at 65°C is that there is an increase in rate [113]. The interpretation of the data suggests that the reaction occurs largely via a homogeneous path with a small contribution from a heterogeneous path. The volume of activation, ΔV is -20 $cm^3\ mol^{-1}$ at 0.1 MPa and at -13 $cm^3\ mol^{-1}$ at 200 MPa. A non-adiabatic version of the Stranks-Hush-Marcus theory is used to interpret the data.

The effect of variation of magnetic field on the rate of the outer sphere electron transfer reaction between $[Co(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{2+}$ has been investigated over magnetic fields, H, of between 0 and 9T [114]. The effect of the magnetic field on the rate may be summarised by Eqn (viii) where $k_{(H)}$ and $k_{(0)}$ are the rate constants at magnetic fields of H and 0 T respectively. A conclusion from these data is that the transition state is paramagnetic, probably from coupling of the magnetic dipoles of cobalt and ruthenium.

$$k_{(H)} / k_{(0)} = 1 - 0.295H + 0.157H^2 - 0.281H^3 + 0.001H^4 + \ldots , \qquad \text{Eqn (viii)}$$

The line between organometallic and coordination chemistry is perhaps at its most indistinct in the chemistry of coordination compounds involving vitamin B_{12} and its model compounds when they form carbon to cobalt bonds in the axial position. The reactions of such complexes, *bis*(dimethylglyoximato)(halo)cobalt(III), and others in the series $[Co(NH_3)_5X]^{2+}$, where X = halo, aquo, thiocyanato and azido, with $\bullet C_2H_5$ radical have been investigated using laser flash photolysis with $ABTS^{\bullet-}$ as a kinetic probe (**42**) [115]. In general, the products were C_2H_5X and C_2H_5CNS, confirming an inner sphere mechanism. In addition there were relatively small amounts of C_2H_4 produced and the authors interpret this as indicating a contribution from outer sphere oxidation of the $\bullet C_2H_5$ radical. Laser flash photolysis has also been used to study *bis*(*N*-8-(5,7-dichloroquinolyl)picolinamide)cobalt(III) chloride in solution [116]. The results indicated the presence of a long-lived transient species which lasted for about 2.5 s.



(42)

Reaction of the hydroxyl radical with a number of complexes including *tris*-(2,2,-bipyridyl)cobalt(III) have been studied in a nitrous oxide saturated medium [117]. The rate constant for the cobalt(III) complex was $2.7\times10^9\ M^{-1}s^{-1}$ and a major feature of the process is addition of hydroxide followed by the reaction shown in Eqn (ix).

$[Co(III)(bpy)_2(bpy(OH))]^{3+} + H_2O \longrightarrow [Co(III)(bpy)_2(OH)(H_2O)]^{2+}$ Eqn (ix)

The complex ion $[Co(N_4)(H_2O)_2]^{3+}$, where N_4 = Me_6[14]4,11-diene-*N*-4, has two substitutionally labile axial positions and the rate and equilibrium behaviour of the reaction of this complex with polymer-bound imidazole ligands, such as *N*-vinylimidazole-Co-vinylpyrrolidone, in aqueous solution at pH 6.5 have been studied [118]. Unlike corresponding nonpolymer systems, the reaction of the polymer-bound ligands proceeds by an intramolecular process and does not follow second order kinetics.

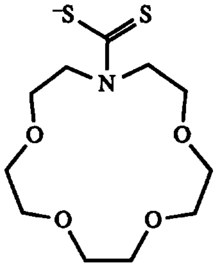
γ-Irradiation of hexaamminecobalt(III) chloride has been found to reduce the length of the induction period before the onset of decomposition [119]. It also increases the rate of thermal decomposition, largely because of a reduction in the activation energy from 46.82 kJ mol^{-1} to 20.22 kJ mol^{-1} upon γ-irradiation.

Weit and Kutal [120] have drawn attention to the fact that much of our current understanding of the reactivities of ligand to metal charge transfer (LMCT) excited states comes from earlier studies of the rather narrow group of compounds of the $[Co(NH_3)_5X]^{2+}$ type. These workers have therefore investigated the LMCT photochemical behaviour of complexes of the type $[Co(NMeH_2)_5X]^{2+}$. Photolysis of $[Co(NMeH_2)_5Br]^{2+}$ at 254 nm gave 5 mol $NMeH_2$ for each mol of cobalt, and flash photolysis gave Br• showing a reaction from the Br→Co charge transfer (CT) excited state. The process was independent of the amount of oxygen present in the solution. For $[Co(NMeH_2)_6]^{3+}$ and $[Co(NMeH_2)_5Cl]^{3+}$ on the other hand, the quantum yield and the $NMeH_2$/Co ratio depended on how much oxygen was present in the solution. This is interpreted as being due to the production of the radical $\bullet^{+}NMeH_2$ from the N→Co CT excited state. A further observation is that the replacement of NH_3 by $NMeH_2$ diminishes the involvement of the solvent in the photochemical process.

5.1.8 *Complexes with nitrogen-sulphur donor ligands*

The compound cobalt *tris*(aza-15-crown-5)dithiocarbamate, (ligand = (43)), was prepared in aqueous solution by reaction of two equivalents of sodium(aza-15-crown-5)dithiocarbamate with cobalt(II) sulphate under an atmosphere of nitrogen [121]; the product is a dark green powder. The structure involves trigonally distorted octahedral coordination around the cobalt with planar S_2CN.

The effect of variation of the substituent on the ligand field strength at the sulphur atoms of dithiocarbamate ligands has been studied using the complexes $[Co(S_2CN(CH_2)_4)_3]$, $[Co(S_2CNEt_2)_3]$, $[Co(S_2CNPr^i{}_2)_3]$ and $[Co(S_2CN(CH_2Ph)_2)_3]$, for which X-ray crystal structures have been determined or redetermined [122]. The results show that the substituents have an effect on the ligand field strength through intraligand S----H-C interactions, which in turn depend upon the bulkiness of the substituents. The same group has also investigated the crystal structure and the effect of phenyl ligands on cobalt(III) dithiocarbamate complexes [123]. The ^{59}Co spectral chemical shifts reflect the increase in the ligand field strengths of the ligands in the order $Me_2 < MePh < Ph_2$.



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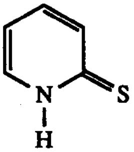
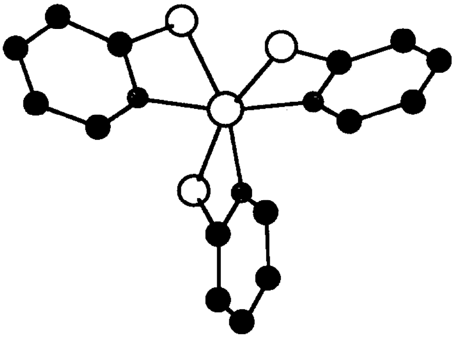


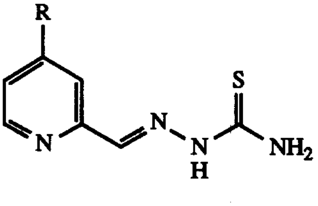
(44)

The ligand pyridine-2(1*H*)-thione (HL) (**44**) forms a wide range of complexes with a number of metal ions in which it may be monodentate through either the sulphur or the nitrogen atom or may be bidentate [124]. The reaction of $[Zn_4OL_6]$ with $[Co(H_2O)_6]Cl_2$ in methanol in an ultrasonic bath results in the formation of $[CoL_3]$ as intensely dark green crystals. The X-ray crystal structure confirms the expected meridional arranement of the ligands around the cobalt atom, (**45**).



(**45**)

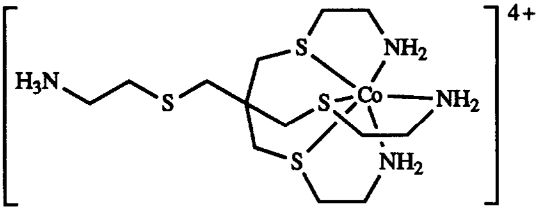
Two ligands, HL, which act as tridentate N---N---S ligands are 4-phenylpyridine-2-carboxaldehyde thiosemicarbazone and pyridine-2-carboxaldehyde thiosemicarbazone (**46**). These both form complexes $[Co(L)_2X].nH_2O$, where X = Cl or ClO_4 [125].



R = H or Ph

(**46**)

We saw earlier how the presence of a pendant arm on a macrocyclic ligand could modify the properties of the ligand, so that it became an even more versatile moiety. In a most interesting study of the cobalt(III) complex of 5,5-*bis*(4-amino-2-thiabutyl)-3,7-dithianonane-1,9-diamine (47) Gahan and coworkers [126] carried out the series of reactions shown in scheme (48) in which the encapsulation reaction is carried out with nitromethane and formaldehyde and then the NO_2 is reduced to the amine. Finally the cobalt is removed from the ligand thus produced. The structure of the species encapsulated via nitromethane has been confirmed by X-ray crystallography.



(47)

5.1.9 Complexes with nitrogen-phosphorus donor ligands

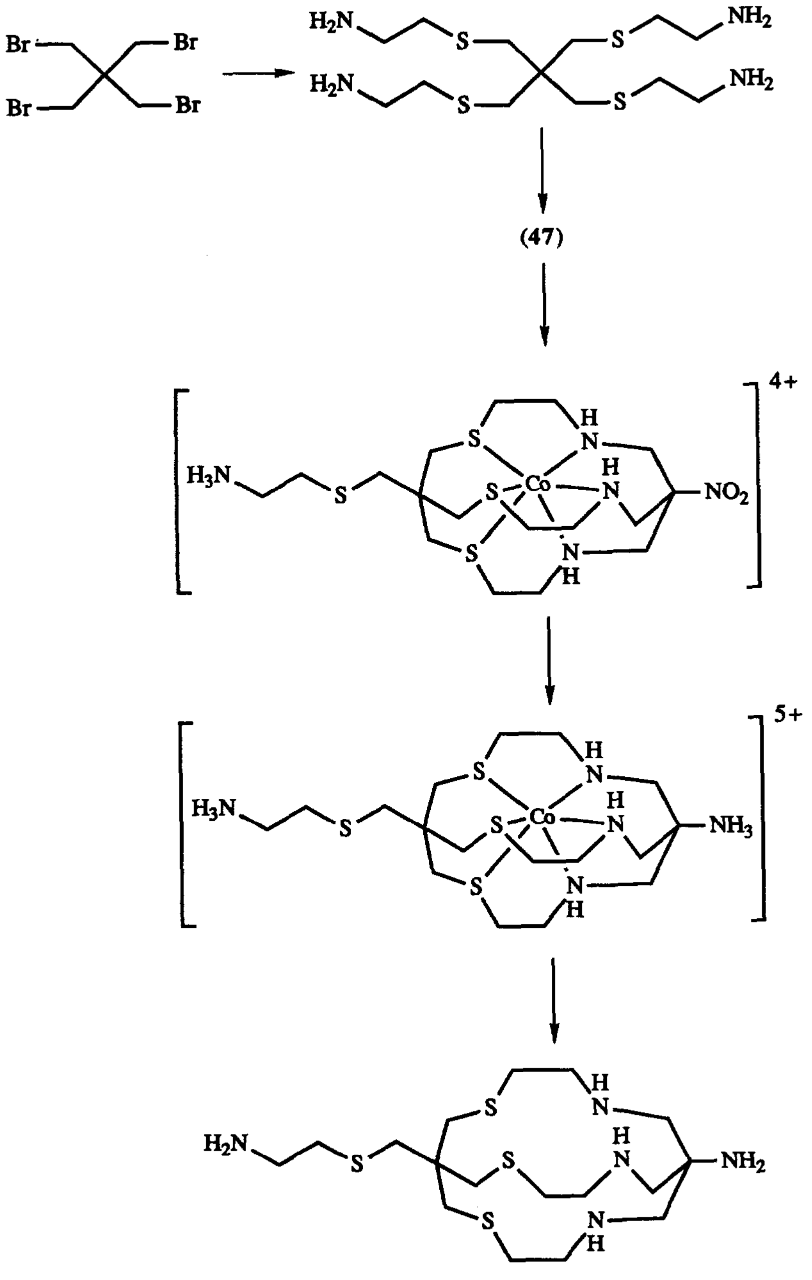
Cobalt(III) complexes of the ligands 3,7-diphenyl-3,7-diphosphanone-1,9-diamine, $NH_2CH_2CH_2P(C_6H_5)CH_2CH_2CH_2P(C_6H_5)CH_2CH_2NH_2$ (232NPPN) and $NH_2CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2NH_2$ (222NPPN) have been prepared and characterised using ^1H and ^{13}C NMR spectroscopy [127]. The complexes were *cis*-α-[Co(L)(*rac*-(P)-232NPPN)]$^{n+}$, L = pentan-2,4-dione or oxalate or ethylenediamine, *cis*-β-[Co(L)(*rac*- or *meso*-(P)232NPPN)]$^{n+}$, where L = acac or oxalate and *cis*-α–[Co(acac)(*rac*-(P)-222NPPN)]$^{2+}$ and *cis*-β-[Co(acac)(*meso*-(P)-222NPN)]$^{2+}$.

Five-coordinate cobalt(III) complexes are formed by the oxidation of $[Co\{Ph_2P(CH_2)_nPPh_2\}X_2]$, where n = 4 or 5 and X = Cl or Br in CH_2Cl_2 [128]. They are dark blue/black (X = Cl) or green/black (X = Br) crystals of formula $[Co\{Ph_2P(CH_2)_nPPh_2\}X_3]$. Measurements of the magnetic moments indicate that they each have two unpaired electrons. The authors suggest that the structure has C_s rather than D_{3h} symmetry.

5.1.10 Complexes with phosphorus-sulphur donor ligands

Twelve complexes of cobalt(III) containing the dithiocarbamato ligand (dtc) $((CH_3)_2(NCS)_2)$ and a variety of phosphorus containing ligands of the type $(CH_3)_2P(CH_2)_nP(CH_3)_2$, $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ and PR_3, R= C_2H_5 or C_6H_5 have been reported [128A]. The single crystal X-ray structure of the complex

$[Co(dtc)\{(CH_3)_2PCH_2P(CH_3)_2\}_2](BF_4)_2$ has been determined. In this the cobalt atom is surrounded octahedrally by four phosphorus and two sulphur atoms.



(48)

A number of complexes of the type $[Co(NO)(P\text{-}P)_2](BF_4)_2$, where $P\text{-}P$ is an alkyl or phenyl-substituted ditertiary phosphine, have been prepared and characterised [129]. In solution in the presence of halide or pseudohalide ions (X) it was found that the complexes containing the linear Co-NO system disproportionate to produce the dinitrosyl moiety $[Co(NO)_2(P\text{-}P)]^+$ and *trans*-$[CoX_2(P\text{-}P)_2]^+$ (Eqn (x).

$$2[Co(NO(P\text{-}P)_2]^{2+} + 2X^- \longrightarrow [Co(NO)(P\text{-}P)]^+ + trans\text{-}[CoX_2(P\text{-}P)_2]^+ + P\text{-}P \qquad \text{Eqn (x)}$$

5.2 COBALT(II)

5.2.1. Complexes with halide and pseudohalide donor ligands

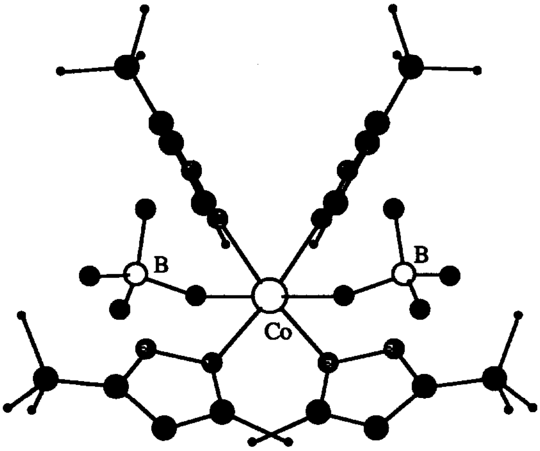
A spectrophotometric study of cobalt(II) thiocyanate systems has shown that both the monothiocyanato and dithiocyanato species exhibit a tetrahedral configuration and involve thiocyanate bonded to the cobalt through one nitrogen atom [130]. The study of the equilibrium between the tetrahedral complex $[Co(CNS)_4]^{2-}$ and the octahedral moiety $[Co(CNS)_4(H_2O)_2]^{2-}$ under the conditions of the experiment, 28% of the cobalt was present as $[Co(CNS)_4]^{2-}$. A thermodynamic and structural study [131] of a series of isothiocyanato complexes of cobalt(II) in *N,N'*-dimethylformamide indicates the formation of a series of mononuclear complexes, $[Co(NCS)]^+$, $[Co(NCS)_2]$, $[Co(NCS)_3]^-$ and $[Co(NCS)_4]^{2-}$. An octahedral to tetrahedral geometry change is demonstrated by the reaction shown in Eqn (xi).

$$\underset{\text{Octahedral}}{[Co(NCS)_2(DMF)_4]} + NCS^- \longrightarrow \underset{\text{Tetrahedral}}{[Co(NCS)_3(DMF)]^-} \qquad \text{Eqn (xi)}$$

The cobalt(II) complex $[Co(4\text{-}Etpy)_4(N_3)]$, where 4-Etpy is 4-ethylpyridine, obeys the Curie-Weiss law over the temperature range 5 to 300K with $\theta = 3.59K$ [132].

Using calorimetry and spectrophotometry in dimethyl sulphoxide, it has been found that the geometry of the solvated complex $[CoCl]^+$ is octahedral, while those of the complexes $[CoCl_2]$, $[CoCl_3]^-$ and $[CoCl_4]^{2-}$ are tetrahedral [133]. A related study has also been carried out, this time in dimethylformamide for the cobalt(II)/bromide system [134]. Similar species to those in the chloride study are indicated in the bromide study and again there is a change in geometry from $[CoBr]^+$ (octahedral) to $[CoBr_2]$, $[CoBr_3]^-$ and $[CoBr_4]^{2-}$ (tetrahedral).

Two coordinated tetrafluoroborate ions are found in the complex *trans*-tetakis(3-tert-butyl-5-methylpyrazole)*bis*(tetrafluoroborato)cobalt(II); the cation is shown in (**49**) [135]. The two $[BF_4]^-$ ions are both axially coordinated and the coordination causes lengthening of the B-F bond of the fluorine attached to the metal compared with the other three noncoordinated fluorines.



• = Me

(49)

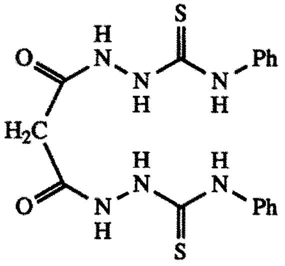
5.2.2. *Complexes with oxygen donor ligands*

There has been a study of mixed ligand complexes of *bis*(methylacetoacetato)cobalt(II) and *bis*(ethylacetylacetato)cobalt(II) with 8-hydroxyquinolinesulphonamides and pyrazole [136].

The oxidation of an olefin by atmospheric oxygen to the corresponding alcohol is a useful and important organic reaction. It is catalysed by transition metal complexes, in particular *bis*(1,3-diketonato)cobalt(III) complexes [137]. The solvent in particular had a very important effect on the yield, so that Co(acac)$_2$ catalysed the oxidation of 4-phenyl-1-butene in both 2-propanol and cyclopentanol, while there was no reaction when the same reaction was carried out in ^{t}butyl alcohol. Furthermore azeotropic distillation to remove water greatly improved yields when the complexes *bis*(trifluoroacetyacetonato)cobalt(II) or *bis*(2-ethoxycarbonyl-3-oxobutanalato)cobalt(II) were used as catalysts. In related work, Isayama [138] showed that the use of catalytic quantities of *bis*(1,3-diketonato)cobalt(II) complexes gave an efficient method for the direct peroxidation of olefinic compounds with molecular oxygen and triethylsilane. Thus, the reaction of 4-phenyl-1-butene with dioxygen and Et$_3$SiH at room temperature gave 1-phenyl-3-triethylsilylbutane. Similar results were obtained with styrene and ethylacrylate, which were readily peroxygenated giving 1-phenyl-1-triethylsilyldioxyethane and ethyl-2-triethylsilyldioxypropionate respectively in the presence of ^{t}BuOOH as initiator.

Infrared and proton NMR spectroscopy have been used to show that the structure of the cobalt(II) complex of the ligand 1-malonyl-*bis*(4-phenylthiosemicarbazide, **(50)**, is that shown in **(51)** [139].

The preparation, characterisation and thermal decomposition of the complexes [CoL$_2$nH$_2$O], where HL = 2-X-4-ClC$_6$H$_3$OCH$_2$COOH, X = Cl or Me, 2-Me-4-ClC$_6$H$_3$OCHMeCOOH, n = 6 and HL = $2\text{-X-4-ClC}_6\text{H}_3\text{O(CH}_2\text{)}_3\text{COOH}$, n = 1 are described [140]. The ligands are believed to be bidentate and after dehydration at 100-130°C, the complexes are stable up to 230 to 255°C.



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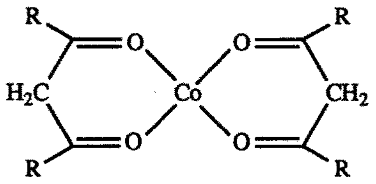


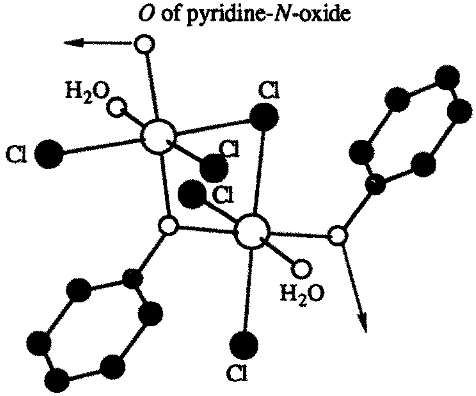
R = NHNHC(S)NHPh

(51)

The first chemical wave reported in a nonaqueous solvent has been discovered [141]. This was in the form of a propagating reaction front which was investigated in the closed system consisting of dissolved oxygen-$[\text{Co(Ac)}_2]^-$ benzaldehyde in glacial acetic acid. The measurements showed that the velocity of the front was increased by increasing the concentrations of both the dissolved oxygen and the benzaldehyde, but was decreased by increasing the concentration of the $[\text{Co(Ac)}_2]$.

Both the cobalt(II) and cobalt(III) complexes of dinitrosoresorcinol have been shown to be complexed through one of the hydroxy and one of the nitroso groups with the others remaining unbonded [142].

The X-ray structure determination of the red-violet complex $[\text{CoCl}_2(\text{pyo})(\text{H}_2\text{O})]_n$, where pyo = pyridine-*N*-oxide, has shown that the structure involves a polymeric chain in which the cobalt atoms are bridged by pyo and one chlorine atom. The coordination around the cobalt atom is essentially octahedral with the second chlorine atom and a water molecule occupying the other positions as indicated in structure **(52)** [143].

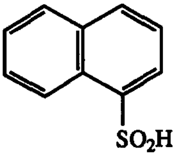


(52)

γ-Rays generate dislocations in the crystal lattice of cobalt(II) malonate [144]. One of the effects of this is that the peak temperatures of dehydration and melting as measured by thermal methods are decreased and the extent of the lowering is increased with increasing radiation dose. The kinetics of the reaction were found to be controlled by a phase boundary mechanism.

The thermal decomposition of tetrahydrated cobalt(II) methanesulphonate in argon occurred in two stages which are regulated by random nucleation [145]. The kinetics of the reaction were studied under both isothermal conditions and under conditions of linearly rising temperature and showed that the decomposition of the anhydrous salt was first order and that the rate determining step involved a nucleation process.

The synthesis and characterisation of a number of groups of cobalt(II) complexes have been described. Complexes [CoL_2nB] of the ligands 2-formylcyclohexanone and 2-acetylcyclohexanone (L) with H_2O or py (B) as the other ligand have been described [146]. Complexes of the ligand (**53**) have been prepared and characterised [147]. Preparation of complexes of the ligands 1-(2-hydroxyphenyl)-3-(1-naphthenyl)-2-propen-1-one (**54**) and 1-(1-hydroxy-2-naphthenyl)-3-(1-naphthenyl)-2-propen-1-one (**55**) with cobalt(II) have also been described [148].



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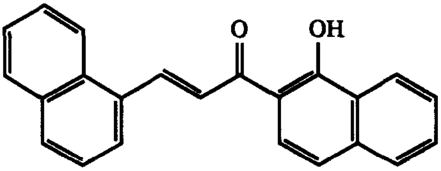

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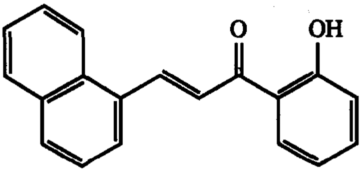


(55)

The nitrite ion may form complexes through the nitrogen atom or the oxygen atom. A potentiometric study of the nitrite complexes of cobalt(II) has been carried out [149].

Hydrometallurgical methods are becoming increasingly attractive low energy processes for metal extraction. Di(2-ethylhexyl)phosphoric acid (HDEHP, HL) has been widely studied as a potential extraction agent [150]. The distribution of cobalt(II) between an aqueous solution and a solution of HDEHP in kerosene has been found to reach an equilibrium, the position of which is affected by the extractant concentration, pH and the concentration of the cobalt(II) ions. The cobalt(II) in the nonaqueous phase was found to be present in the form of the complexes [$CoL_2(HL)_2$] and [$CoL_2(HL)_3$].

5.2.3. Complexes with oxygen nitrogen donor ligands

An elegant method of measuring rates of dissociation of labile complexes such as *tris*(glycinato)cobalt(II) is first to carry out a very rapid reduction of the inert cobalt(III) complex by pulse radiolysis, Eqn (xii), and the rate of this reaction is estimated to be about 2.5×10^{10} M^{-1} s^{-1} [151]. It was then possible to study the rate of loss of each of the glycinate ions over a range of pH values, since the rate constants are sufficiently different from each other. The rate law for these reactions is shown in Eqn (xiii).

$$[Co(gly)_3] + e_{aq} \rightarrow [Co(gly)_3]^- \qquad \text{Eqn (xii)}$$

$$k_{obs} = k_o + k_H[H^+] \qquad \text{Eqn (xiii)}$$

The values of the rate constant, k_o for the complexes with one, two and three glycinates were, respectively, 49, 350 and 4200 s^{-1} and the corresponding values of k_H were found to be 2.1×10^4, 8.1×10^5 and 2.7×10^7 $M^{-1}s^{-1}$ respectively. The reactions believed to take place are shown in scheme (**56**).

The first stage is:

$$[Co(gly)_3]^- \rightleftharpoons [Co(gly)_2] + gly^-$$
$$[Co(gly)_3]^- + H^+ \rightleftharpoons [Co(gly)_2] + glyH$$
$$gly^- + H^+ \rightleftharpoons glyH$$
$$glyH + H^+ \rightleftharpoons glyH^{2+}$$

The second stage is then:

$$[Co(gly)_2] \rightleftharpoons [Co(gly)]^+ + gly^-$$
$$[Co(gly)_2] + H^+ \rightleftharpoons [Co(gly)]^+ + glyH$$

And the third stage is:

$$[Co(gly)]^+ \rightleftharpoons Co^{2+} + gly$$
$$[Co(gly)]^+ + H^+ \rightleftharpoons Co^{2+} + glyH$$

(**56**)

The dipeptides L,L-Phe-Leu, Leu-Phe, Phe-Met and Met-Phe all contain weakly or non-coordinating side chains and the reactions of these dipeptides with cobalt(II) (as well as copper(II) and nickel(II)) have been studied [152] using ESR spectroscopy, electronic spectra, calorimetric and potentiometric measurements. The stabilities of the complexes varied and a number of different factors affected them depending on the chemical nature of the complex. Thus, increased stability was produced by hydrophobic interactions involving the non-coordinating side chains and also in species with a *C*-terminal Phe residue. The latter is interpreted as being due to the interaction between the metal ion and the aromatic ring and was not observed with *N*-terminal Phe residues. For cobalt(II) the major complex which is present in the pH range 7 to 8.5 was [CoL] in each case. The formation constants for the various complexes are shown in Table 1.

Table 1 *Formation constants for cobalt(II)-dipeptide complexes at 298K and ionic strength 0.2 mol dm^{-3} (KNO_3)*

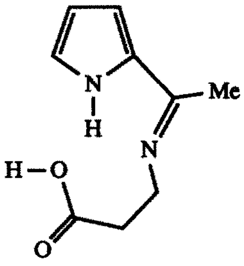
Complex	Formation Constant			
	L,L-Phe-Leu	L,L-Phe-Met	L,L-Leu-Phe	L,L-Met-Phe
[ML]	2.37	2.43	2.10	1.91
[ML_2]	3.28	3.82	3.93	3.57

A comparison has been made of the potentiometrically determined stability constants for complexes [Co(II)AL], where A = aminocarboxylic acid and HL = benzohydroxamic acid, with those of the complexes [Co(II)L] and [Co(II)L_2] [153]. The stability constants were compared by using the relationship given in Eqn (xiv). The complexes studied were those with A = iminodiacetic acid, *N*-methyliminodiacetic acid, anthranilatediacetic acid, nitrilodiacetic acid, nitriloacetic acid, 2,2'-bipyridine and *o*-phenanthroline. A similar study has been carried out on related systems with salicylaldoxime instead of benzohydroxamic acid as the secondary ligand [154].

$$\Delta \log K_M = \log K^{MA}_{MAL} - \log K^{M}_{ML} \qquad \text{Eqn (xiv)}$$

Equilibrium studies have also been carried out on complexes formed by cobalt(II) and L-cystine-dihydroxamate [155]. Complex formation constants and protonation constants were determined. It is concluded that the ligand is complexed to the cobalt atom via the nitrogen atom of the α-amino group and the deprotonated -NHO- group. The cobalt(II) complex which is formed with nitriloacetic acid, glycine and α-alanine has also been shown using NMR, infrared and electronic spectra and magnetochemistry to exhibit coordination of the amino acids through the α-amino nitrogen atom and the carboxylate group [156]. Preparation, characterisation measurement of stability constants, and magnetochemistry of cobalt(II) complexes of the ligand pyrrole-2-acetylideneamino)propionic acid, (**57**), have been described [157].

A series of novel binuclear cobalt(II) complexes containing the core, [Co_2(μ-X)(μ-carboxylatoxylato)]$^{2n+}$, where X = OH, Cl, Br and n = 1 to 3 have been prepared [158]. The crystal structures of the complexes [Co_2(II)(μ-O_2CCH_2Cl)$_2$(μ-Cl)L_2]PF_6, and [Co(II)Co(III)(μ-$MeCO_2$)$_2$(μ-OH)L_2[ClO_4]$_2$.0.5H_2O, where L = *N,N',N''*-trimethyl-1,4,7-triazacyclononane were determined and are shown in (**58**) and (**59**). The cobalt(II) atoms in the core is capped by the tridentate macrocycle. The Co(II)Co(III) species is produced by air-oxidation and a dicobalt(III) complex was also prepared. Complexes give cyclic voltammograms in which reversible and quasireversible one-electron transfer occur between the species containing Co(II)Co(II), Co(II)Co(III) and Co(III)Co(III). It is clear from the electronic spectra that in the mixed valence complexes the valencies are localised.



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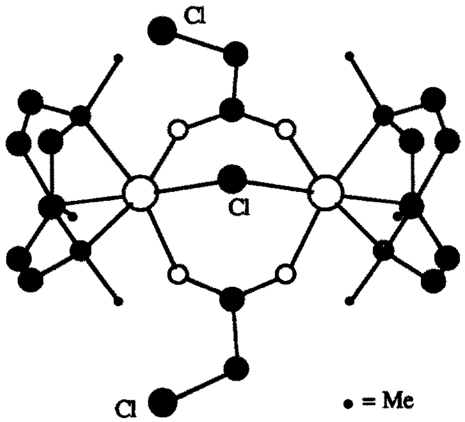

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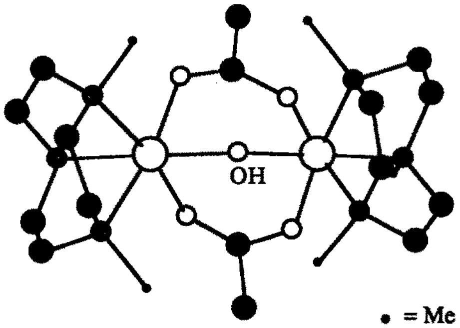
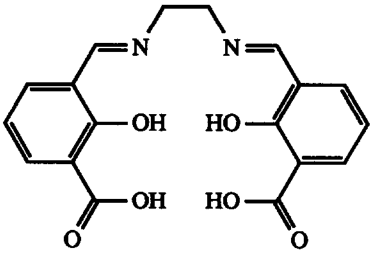


(59)

Cobalt(II) forms the complex $[Co(3,4\text{-dcp})(H_2O)_4]$, where dpc is pyridine-3,4-dicarboxylic acid containing octahedrally coordinated cobalt and which decomposes on heating in two stages, first losing water and then the ligand to form the metal oxide [159]. Complexes of hydrazides of 2,4-dichlorophenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid and γ-(2,4-dichlorophenoxy)butyric acid have been prepared [160].

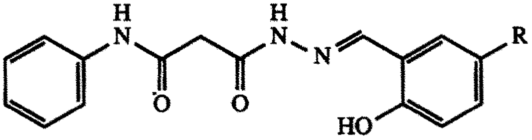
Proton NMR spectroscopic studies have been used to investigate the effects of substituents at the azomethine carbon atom on the electronic structure in the Schiff base complex *N,N'*-*bis*(ethylene)(salicylideneiminato)cobalt(II) [161]. Proton paramagnetic shifts of the H and CH_3 bonded to the azomethine carbon are interpreted as showing spin delocalisation through σ–interaction caused by the contact contribution to the paramagnetic shift. A whole range of stability constants of cobalt(II) complexes with Schiff bases derived from sulphapurazole, sulphapenazole, sulphadiazene, sulphadimethoxine and sulphamethoxpyridiazine with 5-nitrososalicylaldehyde in mixtures of dioxime and water [162, 163] has been prepared.

A series of new Schiff bases, H_2L (derived from reaction of benzoin with *o*-toluidine), L' (derived from reaction of benzil with *o*-toluidine), and L" (derived from reaction of benzil with diaminoethane) which form tetradentate complexes with cobalt(II) ions have been prepared and characterised [164]. The complexes are of the form $[CoL(H_2O)_2]_2$, $[CoL'(H_2O)_2]_2Cl_4$ and $[CoL''(H_2O)_2]Cl_2$. Physical measurements point to the expected octahedral geometry around the cobalt(II) atom.



(60)

An interesting series of complexes containing both cobalt(II) and a lanthanoid(III) have been prepared [165]. The complexes involved the ligand *N,N'*-ethylene*bis*(3-carboxysalicylideneimine) (H_4csalen) (**60**) and were $[CoLa(csalen)(CH_3OH)(NO_3)]$, $[CoNd(csalen)(H_2O)_2(NO_3)]$ and $[CoGd(csalen)(H_2O)(NO_3)]$. In these complexes, the cobalt atom is to be found in an N_2O_2 site, while the lanthanoid atom is at an O_4 site of the binucleating ligand. In solution in dimethylformamide or dimethyl sulphoxide, there is a planar arrangement around the cobalt atom at room temperature and this changes to a square pyramidal structure at liquid nitrogen temperature, when one of the solvent molecules occupies the axial position. With some of the ligands, the addition of pyridine produced a five coordinate arrangement around the cobalt atom at room temperature and this changed to six coordinate when the solution was cooled to liquid nitrogen temperature.



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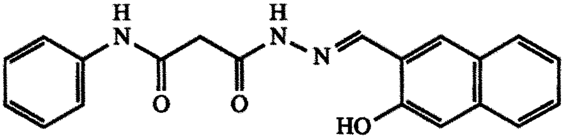
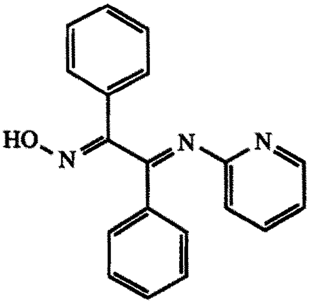


(62)

Cobalt(II)complexes of the ligands (**61**) and (**62**) have been prepared and characterised [166]. The ligands are dibasic and are tetradentate, and the geometry around the cobalt atom is octahedral. Violet-pink cobalt(II) complexes of the ligand 1-hydroxyimino-1,2-diphenyl(2'-iminopyridyl)ethane (**63**), of the form $[Co(HL)_2(H_2O)_2]X_2$, where X = Cl or Br and the red complex $[CoL_2]$ have been synthesised and characterised [167]. The dichlorocobalt(II) complex of pteridine (**64**) is believed to be tetrahedral [168]. On thermal analysis, the complex $[Co(C_6H_4N_4O)Cl_2]1.5H_2O$ loses the water in one step and this is followed by the exothermic loss of the ligand at 134°C to form Co_3O_4 as the final product.



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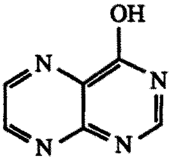
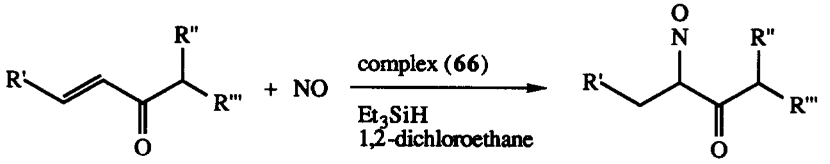


(64)

The X-ray crystal structure of the complex guanidinium diethylenetriaminepentaacetato(3–) cobaltate dihydrate $[LH][Co(H_2L')].2H_2O$ (where L = guanidine and H_5L' = $\{(HO_2CCH_2)_2NCH_2CH_2\}_2NCH_2COOH$) has shown that the complex has a trigonal prismatic distorted octahedral structure [169]. X-ray structure determinations have been performed on the complexes diaquo*bis*(isonicotinoylhydrazine)cobalt(II) [170] and *tris*(benzoylhydrazine)cobalt(II)· chloride [171]. The former is found to be orthorhombic, while the latter is tetragonal.

The ligand 4-(2'-oxobutylidene-2,2,5,5-tetramethyl-3-imidazolin-1-oxyl forms a complex with cobalt(II) ions in which the ligand is bidentate, coordinating through the oxo group and the imidazole nitrogen atom [172]. The structure is believed to consist of a distorted tetrahedral arrangement around the cobalt atom, in contrast to the square planar arrangement in the corresponding nickel complex. The cobalt(II) and copper(II) complexes show ferromagnetic exchange interaction.

Treatment of α,β-unsaturated carboxamides with nitric oxide produces the corresponding 2-nitrosocarboxamides regioselectively, (**65**), in the presence of catalytic amounts of the complex (**66**) ie. *N,N'*-*bis*(2-ethoxycarbonyl-3-oxobutylidene)ethylenediaminatocobalt(II) [173].



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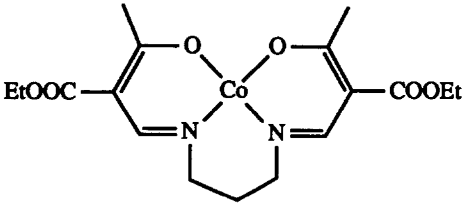
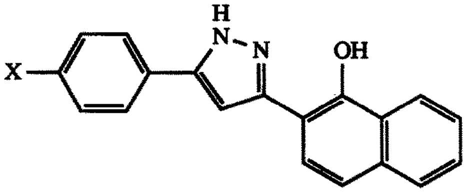


(66)

Complexes of the type $[Co(HL)_2].nH_2O$, where H_2L = pyruvylglycine oxime, pyruvyl-L-alanine oxime have been found to be polymeric with the ligands being bidentate and coordinating through the oxime nitrogen atoms and the amide oxygen atoms [174]. The ligand acetone *p*-bromobenzoylhydrazone forms complexes $[CoL_3X_2].nH_2O$, where X = Cl, Br, I, NO_3, $0.5SO_4$, in which the ligand is coordinated through the hydrazone nitrogen atom and the carbonyl oxygen atom [175].

The ligand 3-(1-hydroxy-2-naphthyl)-5-(4-X-phenyl)pyrazoline, HL = (**67**), where X = H, Me or MeO, forms complexes with cobalt(II) ions coordinating through the phenolic oxygen atom and the pyrazoline tertiary nitrogen atom [176].



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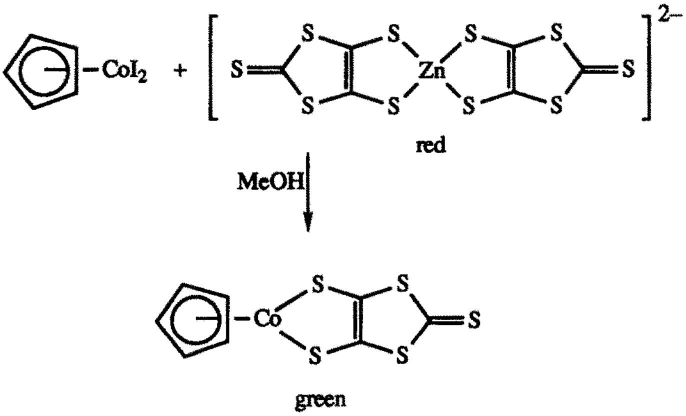
5.2.4 *Complexes with nitrogen-oxygen-sulphur donor ligands*

The formation constants of cobalt(II) complexes with thiodiacetic acid and various secondary ligands, imidazole, ethylenediamine, histidine, aspartic acid, phenylalanine, tryptophan, tyrosine, oxalic acid and sulphosalicylic acid have been determined using potentiometry [177].

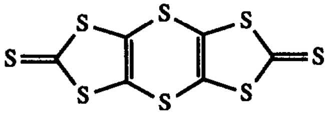
5.2.5 *Complexes with sulphur donor ligands*

A series of complexes members of which have the general formula M_4CoX_4, in which M = K or Na and X = S or Se has been prepared by reaction of the appropriate carbonate of metal M with cobalt in a stream of hydrogen charged with sulphur or selenium as appropriate [178]. Single crystal X-ray structure determination showed that the compounds crystallise in isotypic atomic arrangements in which there are isolated $[CoX_4]$ tetrahedra. A further series of ternary cobalt chalcogenides, M_2CoX_2, where M = Na, K, Rb, Cs and X = S, Se have been made by a similar reaction to that above [179].



(68)

Although cyclopentadienyl complexes would normally feature in a work dealing with organometallic chemistry, the complex (η^5-cyclopentadienyl)(1,3-dithiole-2-thione-4,5-dothiolato)cobalt(II) [Co(Cp)(dmit)] and the corresponding pentamethylcyclopentadienyl complex, [Co(Cp*)(dmit)], are of interest to coordination chemists because of the presence of the dmit which has been involved in superconductive behaviour as a ligand in some organometallic complexes [180] [181]. The complex is formed by the reaction shown in scheme (68). The cyclic voltammogram for both of these complexes revealed that they underwent one reversible reduction process at the cobalt atom and two reversible oxidation processes at the dmit ligand. Electrolytic oxidation of the pentamethylcyclopentadienyl complex resulted in the formation of a yellow solid on the working electrode which turned out to be C_6S_8, (69).



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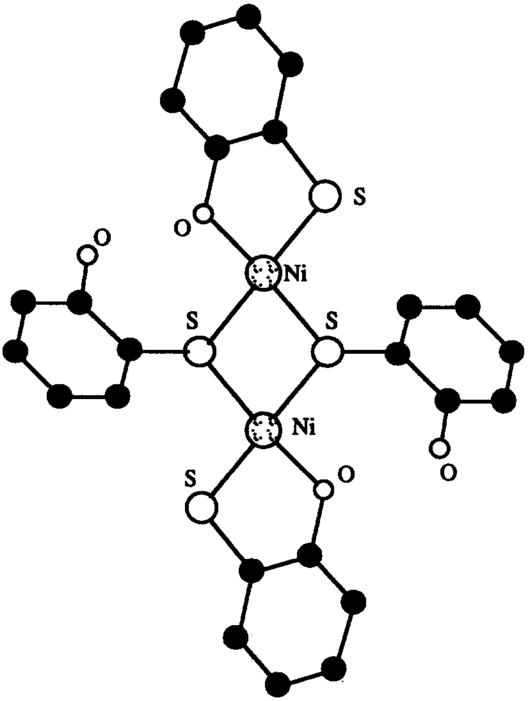

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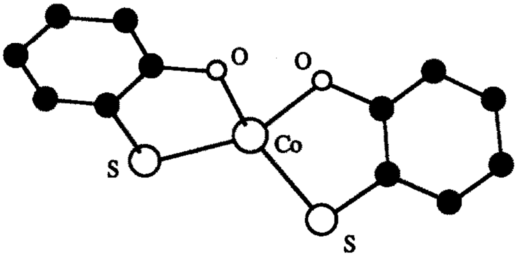


(71)

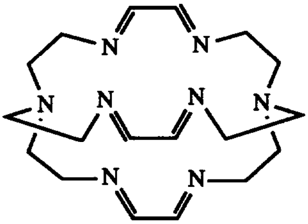
The reaction of cobalt(II) chloride with K[$S_2P(OMe_2)$] produced the complex [Me_4N][$CoCl\{S_2P(OMe)_2\}_2$] which contains a distorted trigonal bipyramidal five coordinate arrangement around the cobalt [182]. The structure of the cobalt(II) complex [$Co\{S_2P(p\text{-}C_6H_4Me)_2\}_2(DMF)_2$].2DMF [183] contains the two sulphur-containing ligands bonded to the cobalt atom through sulphur atoms in a bidentate fashion in the equatorial positions with the DMF molecules occupying the two remaining axial positions. Cobalt(II) unithiol complexes have been prepared and studied by spectrophotometry, indicating the presence of 1:1, 1:2 and 2:3 cobalt(II):unithiol complexes [184].

A deep red complex ([$Co(HL)_2$].H_2O) is formed when cobalt(II) ions react with captopril (1-[2(*S*)-3-mercapto-2-methyl-1-oxopropyl]-L-proline) and it is a potential drug for treating high blood pressure [185]. The complex is believed to consist of a structure involving S-Co-S bonds with the carboxylic acid group being uncoordinated.

A new cobalt(II) complex involving 2-mercaptophenolate (mp^{2-}) has been shown to have a dimeric structure consisting of $(Et_4N)_2[Co(mp)(Hmp)]_2$; the X-ray structure of the corresponding nickel(II) complex has been determined and confirms the dimeric array (**70**) [186]. In solution in dimethylsulphoxide the compound dissociates to form the monomer and this is very air sensitive, being readily oxidised to $[Co(mp)_2]^-$. The structure of the anion (2-mercaptophenolato-*O,S*)-(2-mercaptophenol-*O,S*)cobalt(1–), (**71**), has also been determined [186].

5.2.6 Complexes with nitrogen donor ligands

Complexes of ligands having nitrogen donor atoms continue to attract the attention of many researchers in cobalt(II) chemistry. An important category of such complexes, as in the case of cobalt(III) chemistry, is that of macrocyclic ligands and there is much interest in this area. The mechanisms of the reduction of cobalt(III) complexes have been widely studied over the years, but there has been less work done on kinetics and mechanisms of the oxidation of cobalt(II) complexes. A kinetic study has been carried out on the oxidation of cobalt(II) macrocyclic complexes involving the macrocyclic ligands, [14]aneN_4, *C-meso*-Me_6[14]aneN_4, [14]tetraeneN_4, [15]aneN_4 and 1,4,8,11-tetramethylcyclam [187]. The oxidising agent used was *tris*(bipyridyl)ruthenium(III) ion. The results of the kinetic measurements carried out using laser flash photolysis gave second order rate constants in the range 6.0×10^5 to 7.8×10^7 M^{-1} s^{-1} for the above cobalt(II) complexes. The rate constants were found to agree with those predicted by the Marcus theory. The complex of 1,4,8,11-tetramethylcyclam was also oxidised by $[Ru(phen)_3]^{3+}$ and $[Ru(4,7\text{-}Me_2phen)_3]^{3+}$, giving rate constants of $1.0\text{x}10^6$ M^{-1} s^{-1} and $3.2\text{x}10^4$ M^{-1} s^{-1} respectively. The authors also found that the cobalt(II) complexes quench emission of the excited state complex $^{*}[Cr(bpy)_3]^{3+}$ by electron transfer.



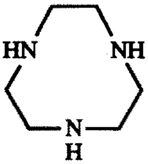
(72)

In order to avoid the preparative problems which arise because of the inertness of the template metal ions used in the preparation of macrocyclic ligands such as sepulchrate, a method has been designed to prepare a new mononucleating cage ligand (72) using labile group 2 ions as templates [188]. The preparation consists of the condensation of *tris*(2-ethylamino)amine with glyoxal in the presence of a group 2 ion such as Ca^{2+}. The main features of the structure of the cobalt(II) complex, $[CoL](ClO_4)_2$ have been determined using a preliminary X-ray structure determination. The cobalt atom is shown to be bonded to all six imino nitrogen atoms. The cobalt(II) ion is kinetically inert once it is inside the structure, so that attempts to react it with CN^- failed to produce any reaction. There is evidence that the cobalt(I) oxidation state may be stabilised by complexation with this ligand.

The single crystal EPR spectrum of the low spin macrocyclic cobalt(II) complex $[Co(C_{10}H_{20}N_8)]Cl_2$ which has been diluted by the analogous Ni(II) complex was found to be anisotropic with $g_x = 2.217$, $g_y = 2.681$ and $g_z = 1.966$ and $A_x = 44$, $A_y = 105$ and $A_z = 115G$ [189]. Attention is drawn to the fact that the observed orientational selectivity was very reminiscent of the stereochemical selection rules for carbocyclic reactions.

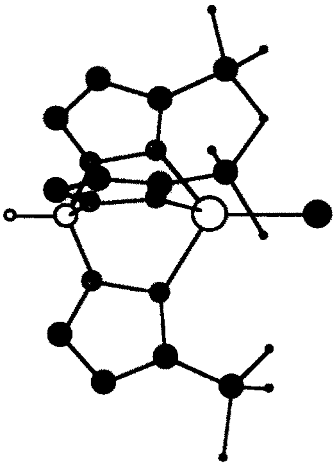
A theoretical treatment has been carried out to attempt to calculate energies, intensities and circular dichroism of *d-d* transitions in cobalt(II) complexes for the ligand $Me_2NCH_2CH(Me)N(CH_2CH_2NMe_2)_2$ (*S*-tan) [190]. This ligand is a tripodal triamine and in complex ions $[Co(S\text{-tan})X]^+$, where $X^- = NCS^-, Cl^-, Br^-$ or I^- it adopts a chiral conformation. The authors argue that the circular dichroism is produced because of slight bent bonding between the amines and the cobalt(II) ion.

The effects of a number of anions on the ultraviolet-visible absorption spectra of the complex $[Co(tacn)_2]ClO_4$, tacn = (73), have been used to study the second-sphere charge-transfer absorption bands of ion pairs [191]. The Cannon model [192] is used to interpret the relationship of λ_{max} and the second sphere charge transfer bands and the corresponding redox potentials.



(73)

An addition to the rather small number of alkyl complexes of cobalt(II) has been made in the preparation and crystal structure determination of the complexes [(TMED)CoR$_2$], where TMED = Me$_2$NCH$_2$CH$_2$NMe$_2$ and R = CH$_2$SiMe$_3$ or CH$_2$CMe$_3$ [193]. These complexes have a tetrahedral arrangement of donor atoms around the cobalt atom. An interesting feature of the complex [(TMED)Li]$_2$[Co(CH$_2$SiMe$_3$)$_4$] is that the CH$_2$SiMe$_3$ form a bridge between the lithium atom and the cobalt atom. In the complex [(TMED)$_2$Li][CoCl{CH(SiMe$_3$)$_2$}$_2$] there is a trigonal planar arrangement of donor atoms around the cobalt atom.



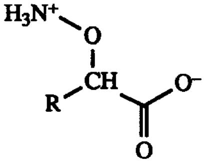
(74)

The crystal structure of the complex (*tris*(3-tert-butylpyrazoyl)hydroborato)cobalt(II), {η^3-HB(3-^{t}Bupz)$_3$}CoCl, (74), confirms the η^3-coordination mode of the *tris*(pyrazoyl)hydroborato ligand [194]. The complex was prepared by metathesis with Tl{HB(3-^{t}Bupz)$_3$}. An interesting feature of these complexes is the facile abstraction of chloride ion by AgBF$_4$, the product being the neutral fluoro complex, Eqn (xv). The authors ascribe this behaviour to the potent Lewis acidity of the presumed three coordinate intermediate in the reaction, {η^3-HB(3-^{t}Bupz)}$_3$Co]$^+$.

$$\{\eta^3\text{-HB(3-}^t\text{Bupz)}_3\}\text{CoCl} \xrightarrow{\text{AgBF}_4/\text{CH}_2\text{Cl}_2} \{\eta^3\text{-HB(3-}^t\text{Bupz)}_3\}\text{CoF} \qquad \text{Eqn (xv)}$$

Tris(ethylenediamine) complexes of cobalt(II) with $[B_{10}H_{10}]^{2-}$, $[B_{12}H_{12}]^{2-}$, $[B_9H_9CH]^-$ and $[B_{11}H_{11}CH]^-$ as counter ions have been prepared and characterised [195].

The crystal structure of the complex *bis*[4-amino-2-(1*H*)-pyrimidinone]dichlorocobalt(II) has been determined [196]. The cytosine molecules are attached to the cobalt atom via the nitrogen atoms of the pyrimidine rings. The two coordinated chlorine atoms complete the distorted tetrahedral arrangement around the cobalt atom. The two chlorine atoms also complete a pseudotetrahedral arrangement which is found around the cobalt atom in a number of complexes of 2-aminooxyacids (**75**) in which R = H, CH_3, C_3H_7, $CH_3CH(CH_3)CH_2$, $C_6H_5CH_2$ [197].

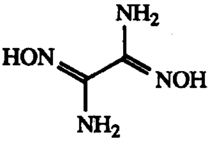


(**75**)

Equilibria of the formation of cobalt(II) complexes of DL-2-amino-*N*-hydroxy-^{n}butanamide have been studied and it is concluded that the cobalt(II) dinuclear species [Co_2L] is formed at pH 6.5 in addition to the complexes [CoL], [CoL_2] and [Co(OH)L] [198].

The paramagnetic relaxation rate and the shift of the CH_2 ligand protons for the complexes formed between cobalt(II) and ethylenediamine and malonate provide information about the formation rate constants [199]. The products of the reaction were shown to be $[Co(Hen)]^{2+}$, $[Co(Hmal)]^+$ and $[Co(mal)_3]^{4+}$.

The magnetic properties of cobalt(II) dioxime complexes have been investigated in relation to their stacked structures and the possible design of ferromagnetic organic compounds [200]. The compound studied was 2,3-diamino-1,4-diazabuta-1,3-diene-1,4-diol-*bis*(2,3-diamino-4-hydroxy-1,4-diazabuta-1,3-dien-1-olato)cobalt(II) ([$CoL_2(HL)$], dark purple crystals) and the ligand is (**76**). The structure was found to consist of chains made up of planar CoL_2 units stacked along the *b* axis. These stacked chains then form sheets in the *bc* plane. The variation in magnetic moment over the temperature range 2 to 100 K shows a rise in χ_mT below 50 K and the authors point out that this represents a change to a phase with dominant ferromagnetic interactions. This is confirmed by the application of the isotropic $S = {}^1/_2$ Heizenberg model based on the high temperature Pade expansion, which gives very good agreement with the experimental data.

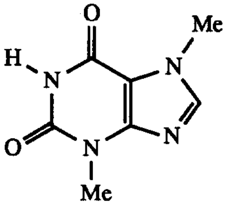


(**76**)

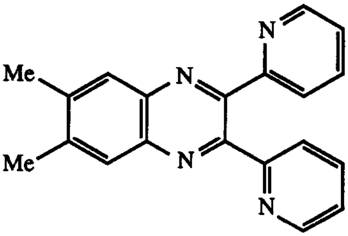
An electron spin resonance study of a frozen solution of the complex *bis*(dimethylglyoxime)cobalt(II) at both X- and Q-band frequencies, together with fourteen phosphines and phosphites has been carried out [201]. From the Q-band results a rhombic symmetry for all the adducts is unambiguously assigned. When the bases have identical substituents, 1:1 adducts are produced and when there are mixed substituents, 1:2 adducts are produced. It is suggested that the formation of phosphine and phosphite adducts, unlike the corresponding nitrogen donor adducts, cause the cobalt atom in the plane of the dimethylglyoxime nitrogen atoms to be pulled out of the equatorial plane and that this inhibits the formation of six coordinate species.

The complex *N,N'*-ethylene*bis*(isonitrosoacetylacetoneimine)cobalt(II) has been found to exist in two forms in which the chelate rings are five and six membered [202].

Although there is potential for bonding through oxygen and/or nitrogen atoms, the structure of *trans*-dichlorotetra(2-furaldehyde oxime)cobalt(II) was found to have the cobalt atom bonded to four nitrogen atoms with the two chlorine atoms in axial positions [203]. Similar coordination is found in the cobalt(II) complex of 2-hydrazino-4-hydroxy-6-methylpyrimidine with four square planar nitrogen atoms and water molecules occupying the remaining positions [204].



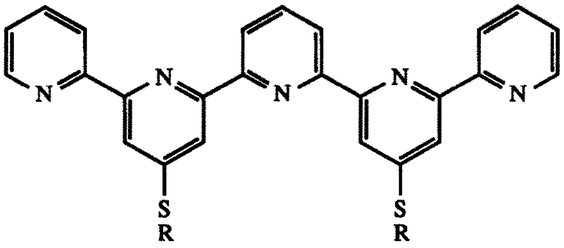
(77)



(78)

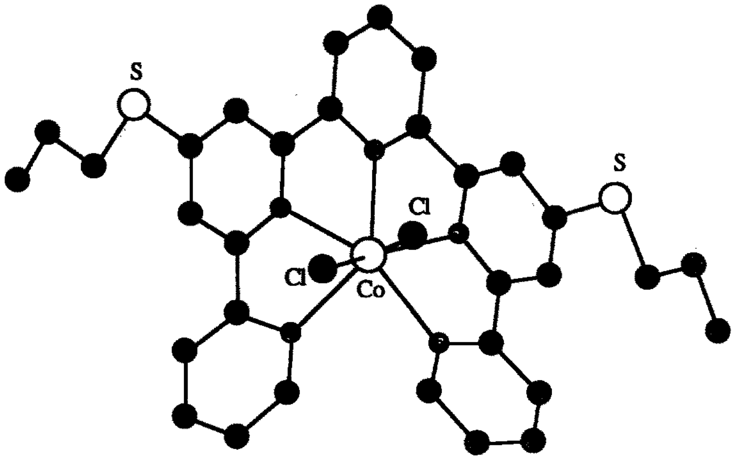
Theobromine (77) is commonly found in tea, coffee, and cocoa and its complexing properties are of some interest because of the metal ions, particularly aluminium, which are found in these beverages [205]. With cobalt(II) ions, theobromine forms complexes of the form CoL_2X_2 (X = Cl, Br) by refluxing the cobalt(II) halide with the ligand in a triethyl orthoformate-ethyl acetate mixture. It is believed that the complexes are distorted tetrahedral for X = Cl and Br, and five coordinate for X = I. A tetrahedral structure is also found for cobalt(II) complexes of the ligand (78), 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline [206]. The dark green complex $[CoLCl_2]$ decomposes without the formation of any intermediates to the metal oxide.

When 2,2'-dipyridylglyoxal is condensed with either one or two mol of 2-pyridylhydrazone the compounds 2,2'-pyridil-mono(2-pyridylhydrazone) or 2,2'-pyridil-*bis*(2-pyridylhydrazone) are produced [207]. These compounds were studied as potential solvent extraction agents from aqueous perchlorate media into methyl iso-butylketone. The extraction properties were very good in the pH range 4 to 6, where the efficiency of extraction was 80 to 99%. As well as comparisons with 1,2-diketonemono-2-azaarylhydrazone and 1,2-diketone*bis*-2-azaarylhydrazone, information is provided on equilibrium data such as stoichiometries, pH effect, ligand concentration and metal ion concentration on distribution coefficients.



(79)

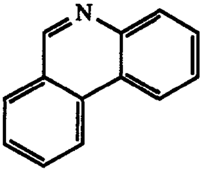
The synthesis of the ligand 2,2'-6',2"-6",2'"-6'",2""-quinquepyridine (L) derivitives (**79**) has been described [208]. Cobalt(II) complexes of these ligands have been prepared by the reaction of $CoCl_2.6H_2O$ with the ligand in absolute ethanol at 70°C for 2h. The structure of the dichloro-cobalt(II) complex of the 4',4'"-*bis*(^{n}propylthio) derivative of L is shown in (**80**). The five pyridine rings are arranged in an almost flat helix around the cobalt atom.



(80)

Some new pyrazole-derived ligands have been prepared [209]. These are 3,5-*bis*(2-pyridyl)pyrazole, (HL) 2-(6-methyl)pyridyl-2-pyridyl-3,5-pyrazole (HL') and 3,5-*bis*-2-(6-methyl)pyridyl-3,5-pyrazole (HL"). The complexes which have been made using these ligands were $[CoL(NO_3)].xH_2O$, $[CoL(NCS)].H_2O$, $[CoL'(NO_3)].H_2O$, $[Co_2L''(NO_3(OH)].H_2O$ and $[Co_2L'Cl_2(OH)]$. It will be seen that some of these are binuclear complexes and these were found to contain di-μ-pyrazole bridges in the nitrate and thiocyanate complexes with HL and HL' and mixed μ-hydroxo, μ-pyrazole bridged structures in the chloride complexes which are formed with HL' and HL".

A range of cobalt(II) complexes of the ligand acetophenone-5(3)-methylpyrazole-3(5)-carbohydrazone has been prepared with a variety of counteranions [210]. The infrared spectra indicate that the ligands are tridentate, bonding to the cobalt atom through an NON set of donor atoms.

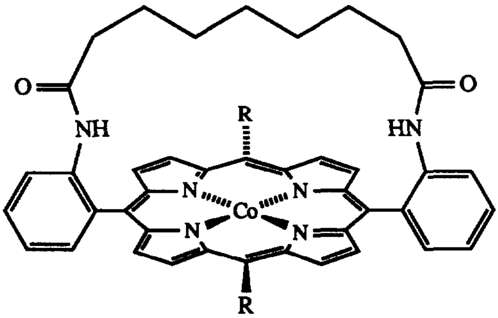


(81)

The complex $[Co(L)_2X_2]$, where L = phenanthridine, **(81)** are tetrahedral and thermal analysis shows that they undergo thermal decomposition according to Eqn (xvi) [211].

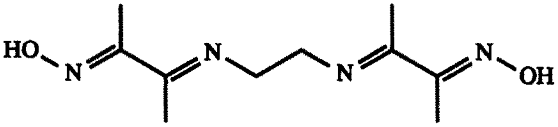
$$[Co(L)_2X_2 \xrightarrow[\text{Endo}]{} [Co(L)X_2] \xrightarrow[\text{Endo}]{} CoX_2 \qquad \text{Eqn (xvi)}$$

The porphyrins and related compounds are of course very important ligands in biological systems and have a vital role in processes involving the storage and transport of dioxygen in living systems. The conformational behaviour of the particular porphyrin system may have a profound effect on the uptake of dioxygen. A series of porphyrinatocobalt(II) complexes, the so-called "jellyfish" complexes, have structures in which the uptake of dioxygen varies with the fence structures [212]. The NMR spectra of a series of complexes **(82)** have been studied [213]. These proton NMR spectra show that when the cobalt atom is inserted into the porphyrin structure, there are distortions produced in the cavity structures in contrast to the behaviour of the corresponding zinc(II) structures, which showed no corresponding distortions.



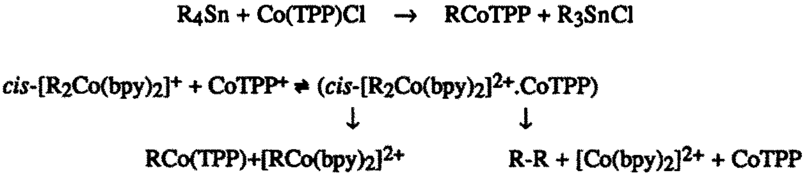
R = Ph or 2-NHC(O)^{n}Bu-C_6H_4 or 2-NHC(O)^{t}Bu-C_6H_4

(82)



(83)

Cyclic voltammetry and ESR spectroscopy have been used in order to show the presence of intermediates in the reduction of cobalt(II) tetraphenylporphyrin [214]. The reactions were carried out in the presence of alkyl bromide and during the reduction cobalt alkylporphyrin was found to be formed with the cobalt(I) porphyrin as an intermediate. It was found that the cobalt alkylporphyrin was reduced via Co-C bond cleavage at potentials more cathodic than the original porphyrin complex. Tetraalkyltin compounds, R_4Sn, where R = Me, Et, ^{n}Bu, ^{i}Pr and cobalt(III) complexes such as *cis*-$[R_2Co(bpy)_2]ClO_4$, where R = Me, Et, $PhCH_2$, *trans*-$[Me_2Co(DpnH)]$, where DpnH = 11-hydroxy-2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetra-1-olate, (83), and $[RCo(DH)_2py]$, where R = Me, Et, $PhCH_2$, (DH) = *bis*(dimethylglyoximato) and py = pyridine have been used to carry out reductive alkylation of cobalt(III) porphyrin [215]. Thus in chloroform [Co(TPP)Cl], where H_2TPP = tetraphenylporphyrin, is easily reduced by these species to yield alkylcobalt(III) porphyrins. The reduction and the use of *cis*-$[R_2Co(bpy)_2]^+$ as an alkylating agent are shown in scheme (84). The kinetics of the reductive alkylation reactions were also measured.



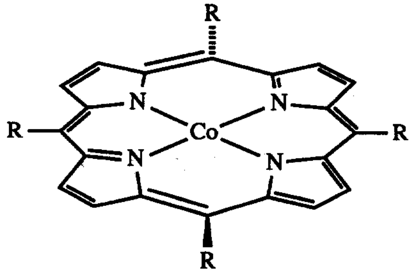
$$R_4Sn + Co(TPP)Cl \rightarrow RCoTPP + R_3SnCl$$

$$\begin{array}{ccc} cis\text{-}[R_2Co(bpy)_2]^+ + CoTPP^+ \rightleftharpoons & (cis\text{-}[R_2Co(bpy)_2]^{2+}.CoTPP) & \\ & \downarrow & \downarrow \\ & RCo(TPP) + [RCo(bpy)_2]^{2+} & R\text{-}R + [Co(bpy)_2]^{2+} + CoTPP \end{array}$$

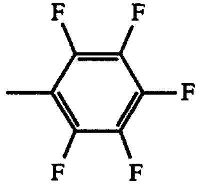
(84)

The products of oxidation by one and two electrons of the cobalt(II) octaethylporphyrin have been characterised by a variety of techniques but particularly optical absorption and magnetic circular dichroism spectroscopy [216]. It was found that oxidation of either the ring or the cobalt(II) occurred. Thus, the oxidation of [Co(OEP)] produces the species [Co(III)(OEP)]X in which the metal ion is oxidised or $[Co(II)(OEP^{+\bullet})]X^-$ in which the porphyrin ring is oxidised to the radical cation. The critical factor determining which of these reactions occurs is the counter ion, X^-. When X^- is Cl^-, Br^- or $SbCl_6^-$, it is the metal ion which is oxidised, while if X^- is ClO_4^-, then the porphyrin ring is oxidised. Two electron oxidation results in the species in which both the metal ion and the porphyrin ring are oxidised, i.e $[Co(III)(OEP^{2+\bullet})](X^-)_2$. The spectra of these two electron oxidised species are very much affected by the nature of the counter ion. The authors carried out deconvolution analysis of the spectral bands in order to obtain an understanding of the energies of the bands that contribute to the spectral envelope.

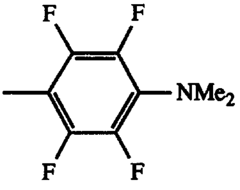
Metallation reactions of free porphyrins are often carried out in nonaqueous solvents such as acetonitrile or dimethylformamide. It has been observed that the reactions of cobalt(II) acetate with the porphyrin (TF$_5$PP)H$_2$, where TF$_5$PP is the dianion of *meso-tetrakis*(pentafluorophenyl)-porphyrin, yields different products when the reaction is carried out in dimethylformamide or acetonitrile [217]. In the latter, the product is that anticipated viz. [(TF$_5$PP)Co]. When the reaction is carried out in dimethylformamide, however, it is found that the cobalt(II) complex of the anion of *meso-tetrakis*(*o,o,m,m*-tetrafluoro-*p*-(dimethylamino)phenyl)porphyrin [T(*p*-Me$_2$N)F$_4$PP)Co] is formed. Both of these were characterised by the use of ^{1}H and ^{19}F NMR spectroscopy, UV-visible spectrophotometry and mass spectrometry. Reactions carried out in acetic acid result only in porpholactone or porphodilactone products. The authors draw attention to the fact that the species formed in dimethylformamide are the first examples of tetraphenylporphyrins in which all the phenyl rings are substituted with both electron withdrawing and electron donating substituents. The single crystal X-ray crystal structurs of both the cobalt(II) complexes, [(TF$_5$PP)Co] and [(T(*p*-Me$_2$)F$_4$PP)Co], were determined and are given in (**85**) and (**86**). As expected the coordination around the cobalt is square planar and the rings are essentially flat. Each porphyrin ring in the crystal is separated by two benzene rings of crystallisation.



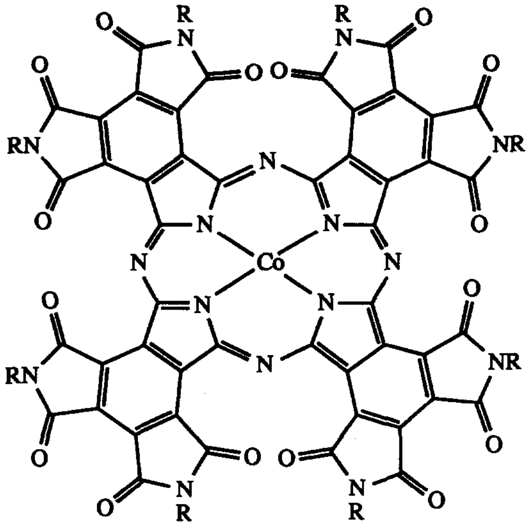
(**85**) R =



(**86**) R =



The shapes of the bands in the ultraviolet-visible spectra of cobalt(II)phthalocyanine complexes, (**87**) (R=H, C$_{10}$H$_{21}$), have been used to compare them with the corresponding iron(II) complexes with a view to producing the same four-electron reduction of dioxygen to hydrogen peroxide by the cobalt(II) complex as that produced by the iron(II) complexes [218]. In fact the absorption spectra of these phthalocyanines did have some unusual characteristics, such as strong hypochromism in the Q band region, produced by the strong perturbation by the eight amide groups and, indeed, they also reacted with oxygen in a four-electron reduction over the entire pH range to produce hydrogen peroxide.



(87)

The crystal structure of the complex dichloro(phthalocyaninato)cobalt(III) has been determined [219]. As expected the metal ion was in an octahedral environment with the chloride ligands in the axial positions. Electrical conductivity studies were carried out on single crystals and the behaviour was consistent with the observed structure. The solid behaved as a semiconductor.

Using reaction kinetics and inferring a mechanism from them, the effects of ionenes on the structure and catalytic activity of cobalt(II) phthalocyanine on the autooxidation of thiols has been investigated [220]. The mechanism which is suggested is shown in scheme (88).

$\mathrm{Co(II) + RSH \rightleftharpoons Co(II){-}{-}{-}RSH \rightleftharpoons Co(I){-}{-}{-}RSH}$

$\upharpoonleft\!\downharpoonright$

$\mathrm{Co(II) + RS^- + H^+ \rightleftharpoons Co(II){-}{-}{-}RS^- + H^+ \rightleftharpoons Co(I){-}{-}{-}RS\bullet + H^+}$

$\mathrm{RS\bullet{-}{-}{-}Co(I) + O_2 \rightleftharpoons RS\bullet{-}{-}{-}Co(I){-}{-}{-}O_2 \rightleftharpoons RS\bullet{-}{-}{-}Co(III){-}{-}{-}O_2{}^{2-} + 2H_2O \rightleftharpoons RS\bullet Co(III) + H_2O_2 + 2OH^-}$

$\mathrm{RS\bullet{-}{-}{-}Co(III) + RS^- \rightleftharpoons RS(S^-)R{-}{-}{-}Co(III)}$

$\mathrm{RS(S^-)R{-}{-}{-}Co(III) \rightarrow RSSR + Co(II)}$

(88)

The crystal structure of vitamin B_{12} as the cyano-complex has been known for many years [221] and is known to be six-coordinate with the cyano group in the axial position above the corrin ring. More recently the structure of the corresponding cobalt(II) complex (often called vitamin B_{12r}) has been determined [222] to be five coordinate with no ligand in the axial position. Vitamin B_{12} is involved in a number of enzymic reactions and it is believed that the cobalt(II) moiety is an intermediate in such reactions. It is of interest, therefore to know what the structure of the cobalt(II) complex is in solution. The structure has been determined in solution using EXAFS [223]. The cobalt(II) species was produced by two processes, the reduction of cyanocobalamin and the photolysis of adenosylcobalamin. As expected, the structures determined by EXAFS for these two compounds were very similar, with the cobalt-nitrogen distance in the corrin ring being 1.88±0.02 Å and the cobalt-nitrogen distance for the dimethylbenzimidazole being 1.99±0.03 Å. Like the complex in the solid state, the structure in solution was found to be five-coordinate. The results reported by these authors suggest that the cobalt-nitrogen bond to the dimethylbenzimidazole becomes much stronger after the cobalt to carbon bond is severed in the production of the cobalt(II) product, while the cobalt to nitrogen bonds to the corrin ring remain largely unaltered. The EXAFS technique was also used to determine the structure of the adenosylcobalamin. Another EXAFS study set out to determine the structures of cobalt(I,II,II) B_{12} derivatives and the cobalt(I) species. This showed that the 1*s*-3*d* transition was very small and this is interpreted as indicating that the structure consisted of a distorted square planar arrangement [224].

The first stage of the kinetics of the thermal decomposition of 1-benzyl-2-phenylbenzimisazole complexes of cobalt, $[Co(BPBI)_2X_2]$ where X = Cl, Br, I, NCS showed Coates-Redfern behaviour [225]. Decomposition occurred very quickly after melting and occurred in two stages, with the oxide being the final product.

The paramagnetic NMR spectroscopic shifts of cobalt complexes with alkylpyrazoles of the type $[CoX_2Pz_2]$ [226] were studied and when X is a halogen then the structure involved a pseudotetrahedral geometry and when $X = NO_3$ the geometry was distorted octahedral and with adducts of alkylpyrazole ligands with cobalt acetylacetonate.

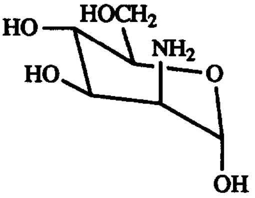
$$[CoCl_2(\alpha\text{-pic})_2](s) \rightarrow [CoCl_2(\alpha\text{-pic})](g) + \alpha\text{-pic}(g) \qquad \text{Eqn (xvii)}$$

$$[CoCl_2(\alpha\text{-pic})](s) \rightarrow [CoCl_2](s) + (\alpha\text{-pic})(g) \qquad \text{Eqn (xviii)}$$

The dynamic and isothermal thermal decomposition of the solid blue complex, dichloro*bis*(α-picoline)cobalt(II) [227] shows that the reaction occurs in two clearly distinguishable stages, Eqns (xvii) and (xviii). The first of these reactions obeys the contracting area model, $1-(1-\alpha)^{0.5} = kt$ and this gives $E_a = 116$ kJ mol^{-1} and lnZ = 29.82. The kinetics of the second reaction were more complex and several models were investigated.

An X-ray crystal structure determination of human serum transferrin has been carried out at medium resolution [228] and in the light of this the cobalt(II) derivative of human serum transferrin (Tf) has been investigated using proton NMR and electronic spectroscopy [229]. It is found that the cobalt(II) ion binds to the protein at the same binding sites as the iron(III) ion and the ratio of cobalt:protein of 2:1. The work finds significant differences in the absorption and CD spectra of $[Co(II)_2Tf]$ and those of $[Co(II)_2OTf)]$, where OTf = apo ovotransferrin. This is explained in terms of the coordination geometry and chirality. It is shown that proton NMR spectral data of the cobalt(II) derivitives provide selective detection of the isotropically shifted signals from protons in the residues which are coordinated to the metal and that this can be used as a very sensitive conformational fingerprint.

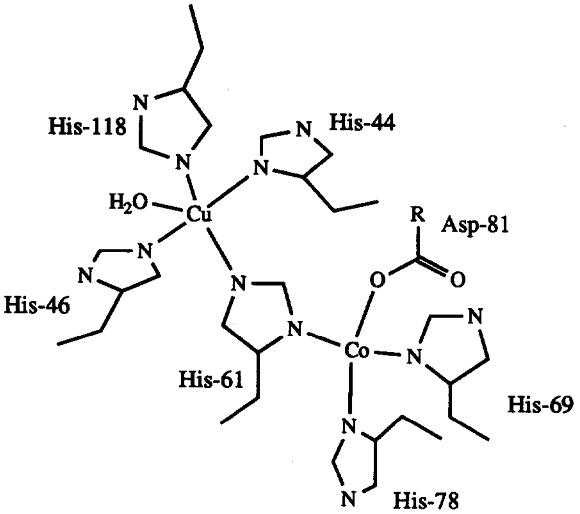
The stability constants of a variety of complexes of cobalt(II) with nitriloacetic acid (NTA) and iminoacetic acid (IMDA) as primary ligands and 2-aminophenol as a secondary ligand have been determined potentiometrically in 50% dioxane and compared with the complexes of copper(II), nickel(II) and zinc(II) [230]. With NTA as the primary ligand, the order of stabiity as measured by this technique is Cu > Co > Zn > Ni, while with IMDA as the primary ligand the order is Cu > Zn > Co > Ni. When the concentration of 2-aminophenol was increased in the presence of [Co(II)(IMDA)]-aminophenol systems, the products were [CoLA] and $[CoLA_2]$. Stability constants have also been determined for cobalt(II) complexes of D-mannosamine (**89**), this time using DC polarography [231]. Both the [CoL] and the $[CoL_2]$ structures were found to have been formed in which the amino nitrogen atom is believed to be the major binding site.



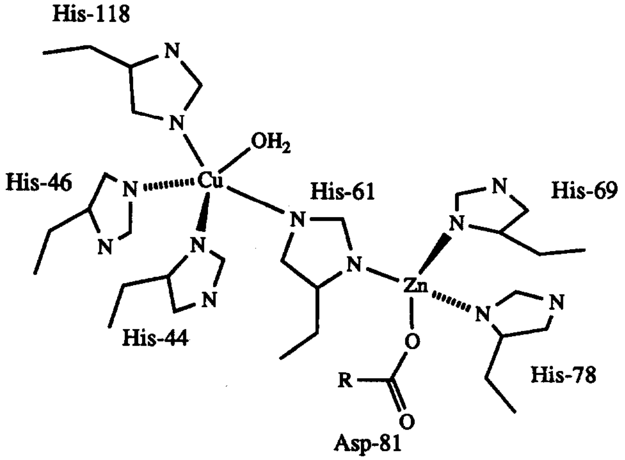
(89)

The enzyme erythrocyte superoxide dismutase may be represented as Cu_2Zn_2SOD. It is possible to prepare the two artificial derivatives of this enzyme, E_2Co_2SOD and Cu_2Zn_2SOD, and these allow the interpretation of the ^1H NMR spectrum of the protons in the enzyme in a cobalt domain to be investigated [232]. The structure of the enzyme around the cobalt is illustrated in (**90**). The proton NMR spectral signals are interpreted in the light of this and the spectra of bovine E_2Co_2SOD and $Cu(II)_2Co_2SOD$ are given and interpreted. Spectra are also given for human SOD expressed in *Escherichia Coli* (HECSOD) and prepared as $E_2Co_2HECSOD$ and $Cu_2Co_2HECSOD$ and the deuterated counterparts.

The dimeric metalloenzyme, bovine copper-zinc superoxide dismutase contains both copper(II) and zinc(II) ions in each of its subunits [233] and the effects of varying the pH conditions and the concentration of phosphate ions in aqueous solution has been investigated using electronic spectroscopy, isotropically shifted proton NMR spectroscopy and NMR relaxation. For the enzyme, Co_2Co_2SOD the electronic spectra and the isotropically shifted proton NMR spectra of the solutions in phosphate and acetate at pH 7 were found to be rather different. When the pH of the acetate solution was raised to 10, there was no significant change in the spectrum, but there were major changes in the spectrum in phosphate when the pH was changed in this way. The final spectrum in phosphate at pH 10 was very similar to that in acetate at pH 10. Similar experiments were carried out on Co_2Zn_2SOD (with cobalt in the copper site) and also on $Cu(I)_2Co_2SOD$ and $Ag(I)_2Co_2SOD$ (in which cobalt was in the zinc site). In addition, for the species E_2Co_2SOD, pH affects the migration of the cobalt from the zinc site to the empty copper site, so that there were subunits in which the cobalt occupied both the zinc and the copper sites. A general conclusion reached is that the phosphate binding affinity for cobalt in the copper site is affected by the pH and that conformational changes at the active site arise from the phosphate binding. In the parent enzyme, the copper and zinc sites are close together and are separated by a bridging imidazolate ring of histidine, (**91**). The results from this work show that the formation of this imidazolate bridge in derivatives of the type Co_2M_2SOD is dependent on the pH of the solution. The bridge is present at high pH but is absent at lower pH in phosphate solutions.



(**90**)

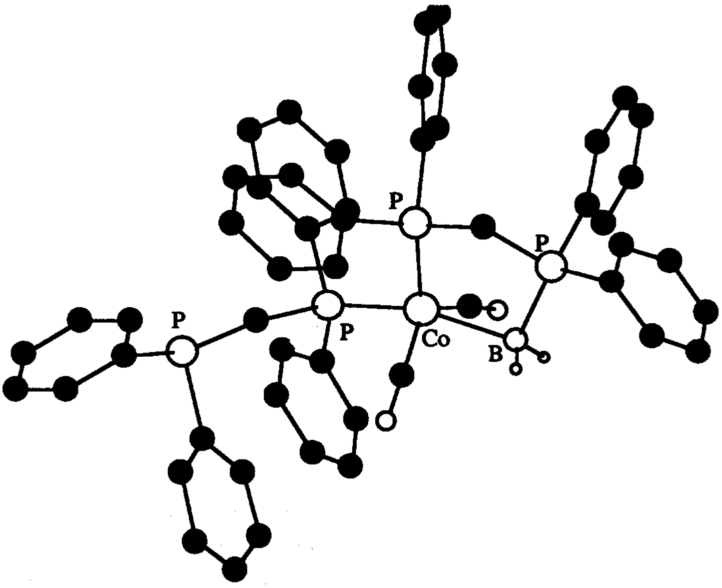


(**91**)

5.2.7 Complexes with phosphorus donor ligands

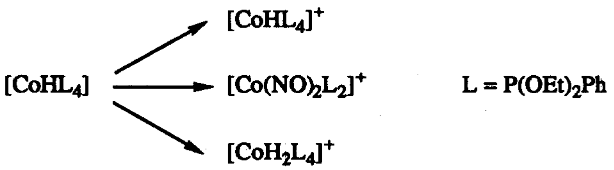
Much of the chemistry of cobalt(II) complexes with phosphorus donor ligands could be designated as organometallic chemistry. The following are felt appropriate by the author to be included amongst the coordination chemistry of cobalt(II).

The first structural characterisation of a transition metal complex containing a transition metal BH_2 complex has been carried out [234]. The complex which has been prepared containing this arrangement is $[(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})BH_2]$, in which dppm is $Ph_2PCH_2PPh_2$. The structure of this complex is shown in (**92**).

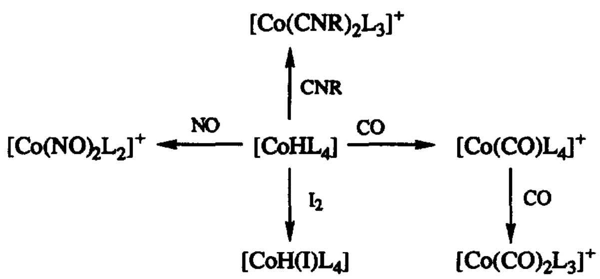


(**92**)

An extensive chemistry of the reactions of the complex $[CoH(P(OEt)_2Ph)_4]$ with a wide variety of reagents has been revealed [235]. Some reactions which have been observed are shown in schemes (**93**)-(**95**).



(**93**)



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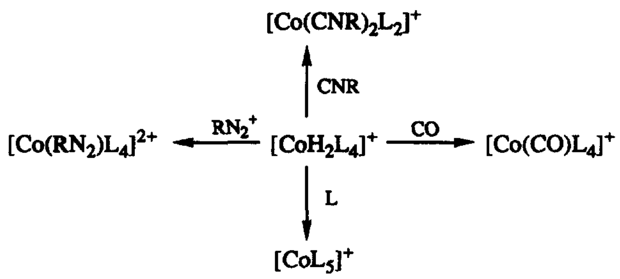


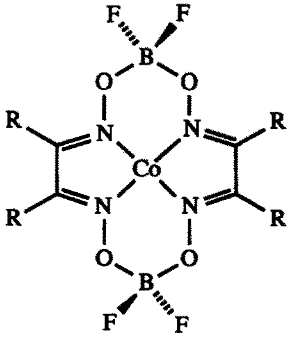
(95)

It is found that the complex $[CpCo(CO)I_2]$ will react with the species $Li_2[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]$ in tetrahydrofuran at a temperature between –78 and +25°C [236]. The product is $(NO)_2Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(Co,P)\text{-}\mu\text{-}Co(Cp)(CO)(PPh_2)Fe(NO)_2$ and the crystal structure was determined and showed that there was an unsymmetric triangular arrangement of the metal ions. The two PPh_2 groups bridged the Fe(1), Fe(2) and Co, Fe(2) pairs of atoms. When the system $Co(acac)_2\text{-}PR_3\text{-}R_nM$, where $PR_3 = PBu_3$ and RM = BuLi or PhMgBr was used to catalyse the hydrogenation of benzene, it was found that the introduction of carbon monoxide in to the system severely curtailed the catalytic activity [237].

The compound $[Co(HCONH_2)_2][H(C_6H_5)PO_2]_2$ and its cadmium and nickel counterparts have been synthesised and characterised [238]. The structure was found to consist of polymeric chains in which the phosphinate ligands formed double bridges between the metal ions. The two dimethylformamide ligands were found to be attached to the metal ions through the oxygen as donor atom. Magnetic studies showed that the cobalt compound was antiferromagnetic with a maximum in the temperature against magnetic susceptibility curve at 6.3K. The authors were unable to find an acceptable theoretical fit to the data over the whole temperature range between 2 and 80K despite using a variety of theoretical models. A reasonable fit below 30K was however obtained using both the Ising and Heisenberg models with effective spins of $S' = {}^1/_2$.

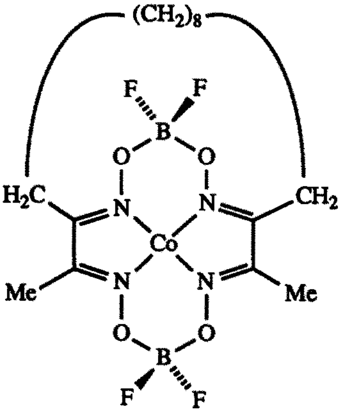
5.3 COBALT(II)/(III) COMPLEXES WITH DIOXYGEN AND RELATED COMPOUNDS

Much interest has developed in recent years in transition metal complex systems which are capable of absorbing and losing oxygen reversibly. A major driving force for this has, of course been the search for model compounds which will help to enhance our understanding of the behaviour of those oxygen transport proteins haemoglobin and myoglobin, which operate by the reversible taking up and releasing dioxygen molecules. The behaviour of the complexes of a number of transition metal complexes (those of iron being the most obvious) in relation to reverible uptake of dioxygen has been widely studied and the coordination chemistry of cobalt has been a particularly fertile area of investigation in this respect. The year 1990 saw a fairly large number of papers published on this topic and there were some quite interesting developments.



(96)

R = methyl, phenyl,
benzyl, mesityl

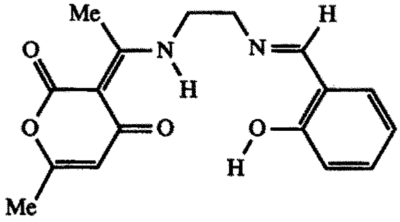


(97)

A number of new dioxygen carriers have been developed, including some compounds derived from dimethylglyoxime by replacing the hydrogen bonded protons linking the two dimethylglyoxime ligands in the molecule by BF_2^+ [239], (96) and (97). These turn out to be particlarly effective dioxygen carriers, forming 1:1 complexes of the Pauling type. A good test of dioxygen carriers is that they are able to repeat the oxygenation-deoxygenation processes over and over again. This is true for $[Co(Me_2GlyoxBF_2)_2]$ and $[Co(\textit{cis}\text{-}C_{10}GlyoxBF_2)]$ complexes which have been cycled through the oxygenation-deoxygenation process many times without becoming themselves oxidised. The following are the equilibrium constants for the formation of the oxygen adduct for $[Co(Me_2GlyoxBF_2)_2]$ and $[Co(\textit{cis}\text{-}C_{10}GlyoxBF_2)]$ over the temperature range –20°C to 0°C, also included are the thermodynamic parameters derived from these data, Table 2.

Table 2 *Equilibrium constants (273K) and thermodynamic parameters for O_2 adduct formation in acetonitrile*

Ligand	Axial Base	K_{O_2}/ Torr^{-1} (273K)	ΔH / kJmol^{-1}	ΔS/ JK^{-1}mol^{-1}
$(Me_2GlyoxBF_2)_2$	Pyridine	0.0019	–57.3	–257
	N-methyl-imidazole	0.025	–60.6	–265
(*c*-$C_{10}GlyoxBF_2)_2$	Pyridine	0.0036	–61.0	–272
	N-methyl-imidazole	0.052	–63.1	–287



(98)

Schiff bases have furnished many examples of reversible dioxygen uptake. The interaction of cobalt(II) complexes of the ligand (**98**) has been studied [240]. In the presence of air, the solid may be kept in a desiccator for days without any interaction with dioxygen and dissolved in nonpolar solvents such as chloroform little or no reaction occurs, but it was found that in the presence of pyridine even at –10°C reaction occurs and the products of the interaction with dioxygen are monomeric superoxo and dimeric peroxo adducts. When the complex is dissolved in pyridine in the presence of air, a brown-purple solution is produced, which becomes more purple when air is actually bubbled through the solution. When nitrogen is bubbled through the solution a brown colour is produced and the purple colour can be returned by bubbling air through the solution again. The cycle could be repeated many times.

The complex pentacyano(η^1-dioxygen)cobaltate(III) is readily prepared [241] and the structure has been determined [242]. The mechanisms of reactions in aqueous solution have been examined [243]. The complex, $[Co(CN)_5O_2]^{3-}$, reacts in aqueous solution to form the complex $[Co(CN)_5OH]^{3-}$ as well as the complex $[Co(CN)_5OOH]^{3-}$, the stoichiometry of the reaction being shown in Eqns (xix) and (xx).

$$[(CN)_5CoO_2Co(CN)_5]^{6-} + H^+ \rightleftharpoons [(CN)_5Co(OOH)Co(CN)_5]^{5-} \qquad \text{Eqn (xix)}$$

$$2[Co(CN)_5O_2]^{3-} + H_2O \rightarrow [Co(CN)_5(OH)]^{3-} + [Co(CN)_5(OOH)]^{3-} + O_2 \qquad \text{Eqn (xx)}$$

The kinetics of the reaction infer a mechanism which involves the formation of the five coordinate species $[Co(CN)_5]^{3-}$, which reacts with the initial complex to form $[(CN)_5CoO_2Co(CN)_5]^{6-}$. This is then hydrolysed to form the products of the reaction. The sequence of reactions is shown in scheme (**99**). The hydroperoxo complex is also produced by the reduction of $[Co(CN)_5O_2]^{3-}$ with a variety of reducing agents.

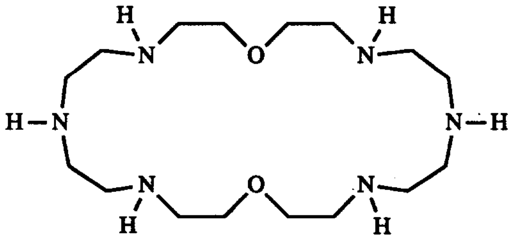
$$[Co(CN)_5O_2]^{3+} \rightleftharpoons [Co(CN)_5]^{3-} + O_2$$

$$[Co(CN)_5O_2]^{3-} + [Co(CN)_5]^{3-} \rightleftharpoons [(CN)_5CoO_2Co(CN)_5]^{6-}$$

$$[(CN)_5Co(OOH)Co(CN)_5]^{5-} + H_2O \rightarrow [Co(CN)_5OOH]^{3-} + [Co(CN)_5OH]^{3-} + H^+$$

(99)

Complexes of macrocyclic ligands with cobalt in many ways form obvious targets for the preparation of complexes which are capable of reversible dioxygen uptake. Such a complex is the species 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane (bisdien) (**100**) dicobalt dioxygen complex which reacts with catechol and tiron (1,2-dihydroxy-3,5-disulphobenzene disodium salt) which bridge the two cobalt atoms [244]. The resulting species are protonated and deprotonated to form the mono- and di- protonated complexes and also the mono- and di- hydroxo- complexes. The two bridging ligands, viz μ-peroxo and μ-catechol or μ-tiron are respectively oxidising and reducing and in the structure of this molecule, the authors point out that the two are in close proximity, so that easy oxidation of the substrates is expected. The structure which is proposed for the catecholate species is drawn in (**101**). Unlike catechol, the dianion of hydroquinone appears to be unable to bridge the two cobalt atoms and therefore it reacts in a monodentate fashion through one of its phenolic oxygen atoms to replace the dioxygen bridge in the (μ-peroxo)(μ-hydroxo)dicobalt bisdien dioxygen complex giving the inert binuclear cobalt(III) bisdien complex.



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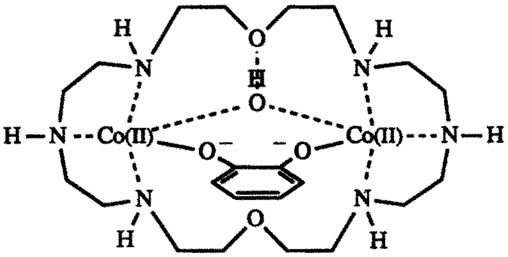
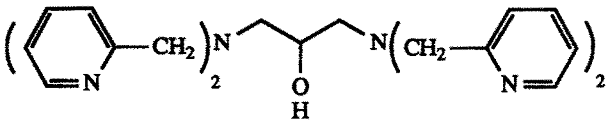


(101)

The two binuclear complexes $[Co_2(tpdp)(CH_3COO)].0.5H_2O$ and $[Co_2(tmdp)(CH_3COO)](ClO_4)_2.H_2O$, where Htpdp and Htmdp, **(102)** and **(103)**, react with dioxygen in dichloromethane and acetonitrile to produce the µ-peroxo complexes [245]. It is suggested that the steric effect of the dinucleating ligands is important in determining the oxygen affinities of these complexes.



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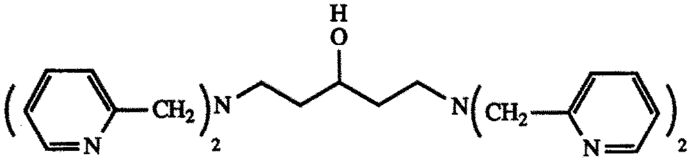


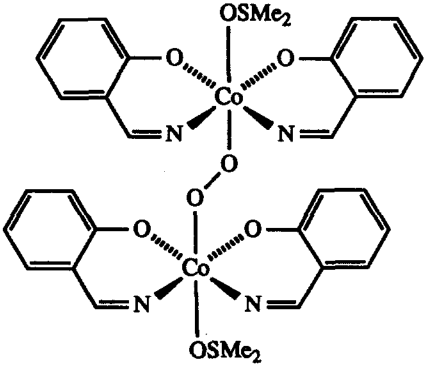
(103)

The mononuclear cobalt(III) complexes of $Me_6[14]aneN_4$ (L), $[(X)LCo]^+$, where $X^- = Cl^-$ or SCN^- react reversibly with dioxygen to produce $[(X)LCoO_2]^+$ and the kinetics and thermodynamics of the system have been studied in some detail [246]. When solutions containing $[LCo]^{2+}$, O_2 and X^- are subjected to laser flash photolysis they are partially bleached and then they return to the original absorbance. For the kinetics of the forward reaction and with $X^- = Cl^-$, $k = 1.80\times10^6\ M^{-1}\ s^{-1}$ and for $X^- = SCN^-$, $k = 7.29\times10^6\ M^{-1}\ s^{-1}$. These values resemble those of the diaquo commplex $[LCo(H_2O)_2]^{2+}$, where $k = 5.00\times10^6\ M^{-1}\ s^{-1}$. The structure of the complex $[LCo(ClO_4)]$ is also reported.

The oxygenation of the cobalt(II) complex of [14]aneN_4 in aqueous solution saturated with dioxygen produces an equilibrium, Eqn (xxi), between the μ-peroxo species and the mononuclear superoxo complex [247]. The mononuclear species was found to be stable at room temperature.

$$[\{Co([14]aneN_4)(H_2O)\}_2O_2]^{4+} + O_2 \rightleftharpoons 2[Co([14]aneN_4)(H_2O)O_2]^{2+} \qquad \text{Eqn (xxi)}$$

Cobalt(II) mixed ligand complexes with dipeptide and imidazole are dioxygen carriers and have been synthesised and characterised [248]. Reversible uptake of dioxygen results in the formation of a dimeric complex with a μ-peroxo bridge, while irreversible dioxygen uptake produces a complex with a μ-superoxo bridge.



(104)

Cyclic voltammetry on the dioxygen complex of salen, (**104**), shows that the release of oxygen may be achieved electrochemically [249]. The equilibrium involved is shown in Eqn (xxi).

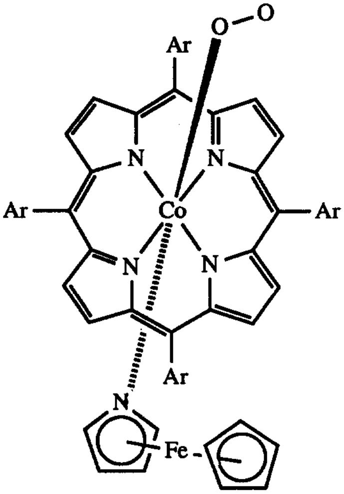
$$[Co(II)(salen)]_2O_2(Me_2SO)_2 \rightleftharpoons 2[Co(III)(salen)]Me_2SO + O_2 + 2e \qquad \text{Eqn (xxi)}$$

Flash photolysis and steady state photolysis of a variety of amine cobalt(III) complexes of the type $[Co(am)(NO_2)_2]^+$, where am = $(en)_2$ or trien, in acetonitrile in the presence of dioxygen showed the formation of a number of species [250]. During flash photolysis, the species formed sequentially were found to be mononuclear superoxo, dinuclear superoxo and dinuclear peroxo. Under steady state photolysis, the final result was found to consist of dinuclear peroxo complexes. A related system was studied electrochemically using a Nafion coated solid state three electrode cell [251]. The system studied was Co(II)-NH_3-O_2 at a glassy carbon electrode in a solid state Nafion coated cell and the reduction potential was found to be about 800 mV more positive than obtained for a glassy carbon-Nafion film electrode with the above system in water. The explanation offered for this is that they are due to two different electrode reactions, viz. reduction of $[(NH_3)_5Co-O_2-Co(NH_3)_5]^{4+}$ in the absence of a contacting liquid electrolyte and free oxygen in the cobalt(II) ammoniacal solution.

$$CoL + O_2 \rightarrow CoLO_2 \qquad \text{Eqn (xxiii)}$$

The thermodynamics and kinetics of the reaction between dioxygen and cobalt(II) derivatives of amino acids have been studied [252]. The kinetics of the reaction given in Eqn (xxiii) yielded enthalpies and entropies of activation. A similar study has been carried out on oxygenated cobalt(II) phenanthroline amino acid complexes in the pH range 9-10, this time yielding stability constants and from these thermodynamic equilibrium data [253]. The thermodynamic parameters (ΔH, ΔS and ΔG) tended to increase as the alkyl chain length and complexity of the coordinated amino acids increased.

Much of the work on the fixation of dioxygen has been carried out using complexes of ligands involving porphyrin or related ring systems. Dioxygen which has been complexed in the cobalt porphyrin (η^1-azaferrocene) complex (**105**) [254].

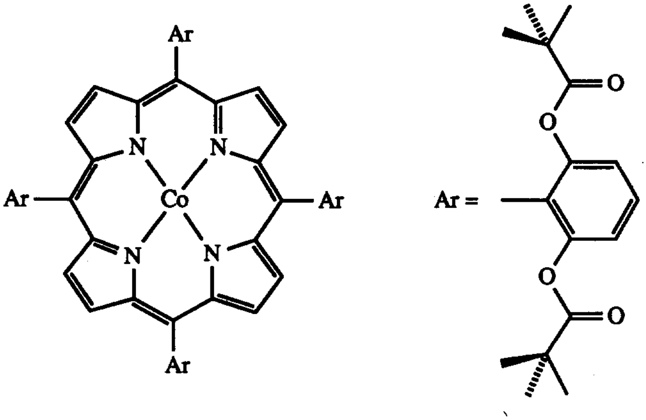


(105)

Irradiation of this with visible radiation was found to cause the dioxygen to be dissociated and the authors claim this to be the first example of photodissociation of dioxygen from a six coordinate (η^1-O_2)(η^1-amine) complex of cobalt(II) porphyrin in solution. The kinetics of the decay process show first order behaviour, with the rate constant being decreased by substitution of electron donating groups in the para position of the phenyl rings. The mechanism is thought to involve the homolytic scission of the Co-O bond to give CoPorphyrin(η^1-azaferrocene) and triplet oxygen.

Reversible uptake of dioxygen only occurred at temperatures below −66°C with the both-faces-hindered and highly symmetric complexes, 5,10,15,20-tetra(2',6'-dipivaloyloxyphenyl)-

porphyrinatocobalt(II) (**106**) which have no amide groups but have ester groups in the fence groups [255].

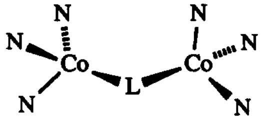


(106)

The copper atoms in the haemocyanine from the horseshoe crab (*limulus polyphemus*) may substituted with cobalt atoms and the cobalt atoms are then believed to be bonded to three imidazole nitrogens [256]. The complex hydroxo CoHcy takes up dioxygen and in doing so two very strong absorption bands at 320nm and 450nm are produced and these are assigned to the $O_2^{2-} \rightarrow \text{Co(III)}$ charge transfer process. The kinetics of the oxygen uptake were found to be pH dependent in the pH range 7.5 to 10. This is explained by a rapid pre-equilibrium in which OH^- reacts to form (OH)CoHcy and then the reaction with this species has a rate constant of 1400 M^{-1} s^{-1}.

The rotation of the dioxygen molecule in cobalt-porphyrin-dioxygen complexes studied by EPR spectroscopy has been extended to four hybrid haemoglobins [257]. The haemoglobins studied were $[\alpha(\text{Co})\beta(\text{Fe})]_2$, $[\alpha(\text{Fe})\beta(\text{Co})]_2$, $[\alpha(\text{Co})\beta(\text{Zn})]_2$ and $[\alpha(\text{Zn})\beta(\text{Co})]_2$ and it was concluded from the data that there was more restricted rotation of dioxygen in the T-state β-chain pockets than in the pockets of any other forms. Lacunar cyclidene complexes of cobalt(II) and nickel(II) have been synthesised as a new model for the T form of haemoglobin consisting of a pentadentate ligand bonded to cobalt(II) ion with the binding of the axial ligand being sterically inhibited [258]. The complexes contain a pyridyl group covalently attached to the macrocycle. The crystal structure has been determined for a nickel(II) isomer. The consequences of steric effects on the control of dioxygen affinity have been evaluated.

A form of *limulus polythemus* cobalt(II)-substituted haemocyanin has been prepared and characterised [259]. It was found that seven cobalt atoms were bound by the apoprotein and the cobalt atoms were distributed such that there were two situated in active sites and bound to three imidazole nitrogen atoms and an exchangable ligand, with the other five in peripheral positions. From the data the active site in the CoHcy is proposed as (**107**).



(107)

An equilibrium constant of $10^{9.34}$ M^{-1} was obtained for the cobalt in the active sites and $10^{4.13}$ M^{-1} for the cobalt atoms in the peripheral sites. The kinetics of the oxygenation of the cobalt(II) centre substituted haemocyanin showed that the reaction was first order in hydroxide ion concentration.

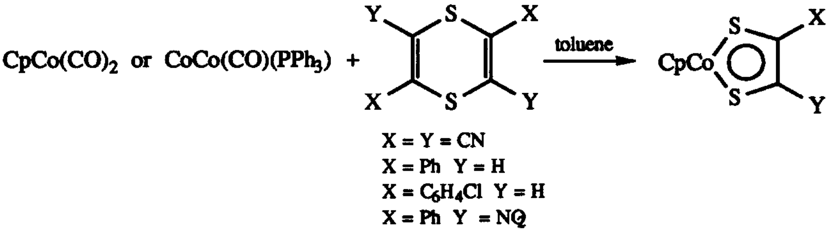
Resonance Raman spectroscopy is an obvious technique to use in the study of dioxygen bonded to transition metal complexes. The spectra of dioxygen in cobalt-substituted haem-proteins and model compounds are complicated and contain secondary bands and unexpected features for $\nu_{(O-O)}$ [260]. The interpretation presented by these authors is that vibrational resonance coupling occurs with the internal modes of the other axial ligand and are found to agree with those calculated using the Fermi resonance coupling scheme.

The complex [*bis*(salicylaldehyde)-*o*-phenylenediimato]cobalt(III), [Co(saloph)] and the related complexes, [Co(saloph)(py)] and [Co(saloph)(py)O_2], dissolved in dichloromethane were excited using a nitrogen laser, so that transient difference spectra could be obtained [261]. Photoinduced solvation at the phenolic oxygen atoms was thus observed.

Bilayers of electropolymerised cobalt and manganese *tetrakis*(*o*-aminophenyl)porphyrins have been used in the electrocatalytic reduction of dioxygen [262]. They are more efficient catalysts than cobalt porphyrin films in basic solution.

5.4 COBALT(I)

The complexes CpCo(cod), CpCo$(CO)_2$ and CpCo(CO)(PPh_3) (i.e. η^5-cyclopentadienylcobalt(I) complexes) have been found to react with 1,4-dithiins to form (η^5-cyclopentadienyl)(1,2-disubstituted 1,2-ethylenedithiolato)cobalt(III) complexes (**108**) [263].



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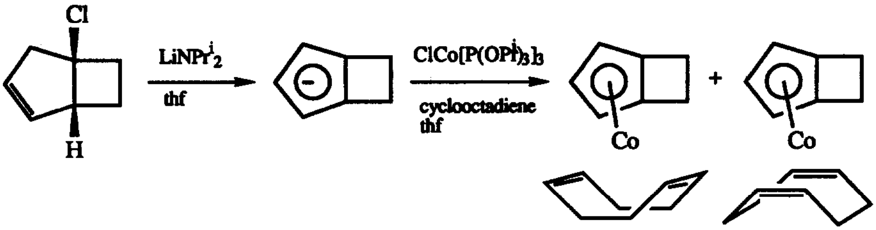
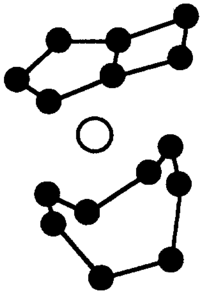


(109)

The preparation of (η^5-bicyclo[3.2.0]hepta-1,3-dienyl)-(η^4-cyclo-octa-1,5-diene)cobalt(I) has been described [264]. This is the first example of a cobalt(I) complex exhibiting this ligand. The complex was prepared by the reaction of $ClCo[P(O^iPr)_3]_3$ with bicyclo[3.2.0]hepta-1,3-dienyl at –20°C to 25°C for 16h and then with cyclo-octa-1,5-diene in tetrahydrofuran at 100°C for 4h; the reaction is summarised in scheme (**109**). The compound consists of brick red, slightly air-sensitive crystals. The crystal structure of the complex was determined and a notable feature of the structure, (**110**), is the somewhat distorted coordination-mode of the bicyclic ligand.



(110)

The reaction between thionyl chloride and cobalt thiocyanine has implications for $Li/SOCl_2$ batteries, since it has been found that when the carbon cathode has been doped with cobalt phthalocyanine the cell is greatly improved. These batteries were studied because they consist of a very high energy density system [265] and the system has been investigated using a number of techniques including cyclic voltammetry, differential-pulse voltammetry and electronic spectroscopy. The cell reaction is believed to be that shown in Eqn (xxiv). In practice, however the process is complex and involves a variety of intermediates; the cells themselves are prone to the possibility of explosion.

$$2SOCl_2 + 4Li \rightarrow S + SO_2 + 4LiCl \qquad \text{Eqn (xxiv)}$$

In fact thionyl chloride has been found to react with the complexes $[Co(I)TnPc(2-)]^-$ and $[Co(II)TnPc(2-)]$, (where TnPc is tetraneopentoxyphthalocyanine), to yield two-electron oxidised species and also a monoadduct with Co(II)TnPc(2-). A catalytic mechanism involving two electrons is proposed for the reduction of thionyl chloride in a $Li/SOCl_2/(CoTnPc,C)$ battery; the reaction scheme is shown in **(111)** where 'SO' is an initial reduction product of $SOCl_2$.

$$[Co(I)TnPc(2-)]^- + SOCl_2 \rightarrow [Cl_2Co(III)TnPc(2-)]^- + \text{'SO'}$$

$$2Li + [Cl_2Co(III)TnPc(2-)]^- \rightarrow [Co(I)TnPc(2-)]^- + 2LiCl$$

Overall, this then amounts to:

$$2Li + SOCl_2 \rightarrow \text{'SO'} + 2LiCl$$

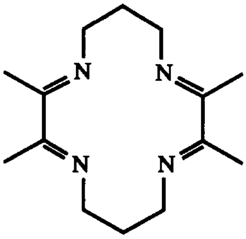
---

(111)

The ligand eHTP, $(Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2$ has been specifically designed to provide both bridging and chelation to two metal centres [266]. Indeed the authors have found that in every case tried, the addition of two equivalents of a mononuclear metal halide complex to the ligand has produced a bimetallic species in high yield. The 300 MHz and 500 MHz proton NMR spectra of the species $[Co_2(CO)_4(eHTP)]^{2+}$ were found to contain a number of solvent and temperature dependent shifts from the central methylene bridge and the chelate ring proton resonances. It is proposed that the shift changes for $P\text{-}CH_2\text{-}P$ proton resonances are caused by differing amounts of carbonyl shielding which are produced by the various rotational conformers in solution. Also, it is proposed that the shifts in the chelate ring resonances are produced by the equilibrium between trigonal bipyramidal and square planar geometries around the cobalt atoms. The species, $Co_2(CO)_2(eHTP)$ containing Co-Co bonding is produced by reduction of the above complex by naphthalenide ion.

The complex ion $[(TMpyP)Co(II)]^{4+}$, where TMPyP = *meso-tetrakis*(1-methylpyridinium-4-enyl)porphyrin, may be electrochemically reduced in dimethylformamide containing 0.1 M tetrabutylammonium perchlorate at $E^1/_2 = -0.49V$ to form the product, $[(TMpyP)Co(I)]^{3+}$, which was found to be stable under nitrogen, but which readily reacts with dissolved dioxygen to produce $[(TMpyPCo(II)(O^{2-})]^{3+}$ [267]. The cobalt porphyrin was a very efficient catalyst for the reduction of dioxygen or the electrocatalytic epoxidation of alkenes as witnessed by the fact that electrolytic techniques showed that for the reduction of $[TMpyPCo(II)]^{4+}$ in dimethylformamide containing benzoic anhydride under dioxygen gave turnover of 15 during 15 min.

The carbon dioxide binding constants for a series of complexes of cobalt(I) with a number of tetraazamacrocyclic ligands in solution in dimethyl sulphoxide have been determined and they showed a strong correlation with the cobalt(II) / cobalt(I) redox potential [268]. The macrocycles covered by this study were **(112)** to **(120)**.



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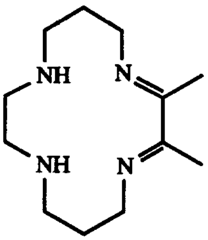
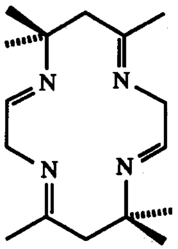
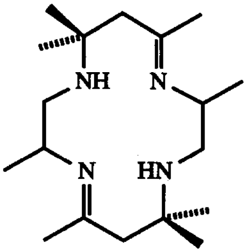


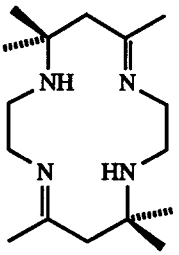
(113)



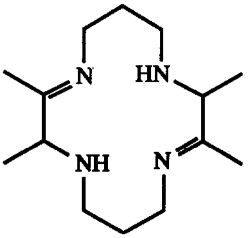
(114)



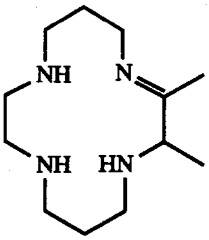
(115)



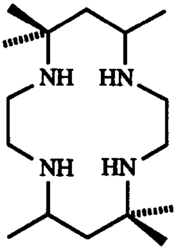
(116)



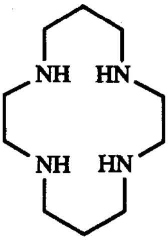
(117)



(118)



(119)



(120)

However, for the complex [Co(I)(Me$_6$-[14]-4,11-diene)]$^+$, the *meso* and d,l-stereoisomers had identical redox potentials, but the binding constants for carbon dioxide varied by a factor of 100; this is explained by invoking a large steric effect on the carbon dioxide binding. The other factor for which there was a slight correlation with binding constant was dielectric constant of the solvent for the complex d,l-[Co(Me$_6$-[14]-4,11-diene)]$^+$. The presence of different cations affected the binding constant for carbon dioxide for d,l-[Co(Me$_6$-[14]-4,11-diene]$^+$ in tetrahydrofuran, so that CO_2 was found to be more strongly held in solutions containing Li^+ than those in which tetrabutylammonium ion was present.

Cobalt(I) complexes, dodecylaminocarbonyl- and dodecyloxycarbonyl-cobalticinium chloride having a long-chain alkyl group attached have been prepared. It is found that they have abnormally low critical micelle concentration values [269].

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