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# Cobalt 1994

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**Contents**

## 1. Introduction

This review follows broadly the same format as that for 1992/93 [1], though this time it covers cobalt coordination compounds only for the year 1994. It excludes

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organometallic and cluster complexes. As in previous years the references are culled from a variety of sources including hand-searching of well-known journals and the use of electronic data bases. The number of references to cobalt in the literature continues to be very large, requiring extensive pruning to produce a review of the required size. Consequently the reviewer is responsible for those considered and those not included. This difficult task may inevitably result in some being left out which perhaps should be there.

There were a number of review articles in 1994 which contained relevant references to cobalt chemistry, including the review of cobalt coordination chemistry for 1991 [2] and of photoinduced intramolecular electron transfer reactions in donor-acceptor linked compounds in solution and in the solid state [3]. There have been two reviews of the health risks of cobalt compounds; one of the health of Danish pottery painters using cobalt blue dyes [4] and the other on the general effects of exposure to cobalt compounds by the general population from foods and a wide variety of other sources [5].

As in previous years the great bulk of the work on cobalt coordination compounds has been in cobalt(II) and cobalt(III) complexes, with the split between these being roughly equal and particularly for cobalt(III) a significant bias towards those ligands which coordinate through nitrogen in the ligand.

The structure of the review is based largely on the nature of the majority donor atoms in the ligands and this governs the overt sub-structure. However, throughout each section a looser attempt is made to treat complexes in terms of roughly similar ligands.

## 2. Cobalt(III)

### 2.1. *Complexes with nitrogen donor ligands*

The thermal decomposition of hexaamminecobalt(III) chloride has been studied using a variety of different techniques. The kinetics of the reaction and some thermodynamic parameters have been derived from the study [6].

There have been a number of investigations of the interaction of hexaamminecobalt(III) ion with DNA, involving co-condensation of mononucleosomal and plasmid DNA [7], conformational changes induced in DNA [8] and evaluation of electrostatic and hydrogen bonding involving hexaammine cobalt(III) ion and other amminecobalt(III) complexes with nucleic acids [9]. In this last work, a study using NMR line-shape analysis to determine apparent binding affinities of a series of complexes of metal ions $M^{n+}$(aq) and a series of Co(III) complexes $[Co(NH_3)_{6-z}X_z]^{n+}$ in which X = $NH_3$ or $NO_2^-$ with double strand nucleic has been used to compare $\Delta G_b$ (binding free energy) for $M^{n+}$(aq) with $\Delta G_{es}$ (electrostatic contribution) for the Co(III) complexes. Since in the latter case the bonding is largely electrostatic and the difference gives an estimate of the free energy of hydrogen bonding. The data show extensive hydrogen bonding to the nucleotide governs the exchange region for free and bound metal ions.

Fourier transform Raman spectroscopy is a particularly useful technique for examining adsorbed species and has been used to study the impregnation of $\eta$-$Al_2O_3$ with aquaamminecobalt(III) complexes [10]. This has allowed the assignment of Raman bands in the region of 522–537 $cm^{-1}$ to Co-OAl or Co-O(H)Al vibrational bands.

Once more the complex ion $[Co(NH_3)_5Cl]^{2+}$ has attracted the interest of a number of workers. The kinetics of the reaction:

$$[Co(NH_3)5H_2O]Cl_3(s) \rightarrow [Co(NH_3)_5Cl]Cl_2(s) + H_2O(g)$$

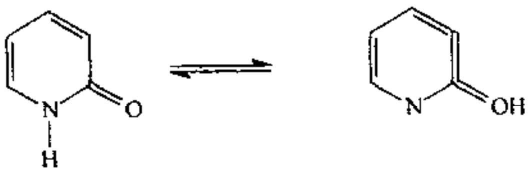
have been studied using thermogravimetric analysis [11]. This is found to be effectively a process of deammination and anation and the kinetic data, both isothermal and non-isothermal were treated using a wide range of different solid state rate laws. Isothermal data gave an activation energy of 97.0 kJ $mol^{-1}$.

The role of activated carbon in the preparation of cobalt(III) complexes from cobalt(II) species is well known but recently the kinetics and mechanism of the catalysis of the reaction of EDTA with $[Co(NH_3)_5Cl]^{2+}$ in the presence of activated carbon have been studied [12]. The quantitatively-formed product is $[Co(EDTA)]^-$ and the reaction was found to be first order in both complex and activated carbon, while being zero order in EDTA and independent of dissolved $O_2$.

The much-studied base hydrolysis kinetics of $[Co(NH_3)_5Cl]^{2+}$ ion have been investigated in the presence of sodium dodecyl sulfate (SDS) micelles with addition of alkyl-substituted ureas [13]. Increasing [SDS] reduces the rate of base hydrolysis but this effect is reduced by addition of 1.0 mol $dm^{-3}$ methylurea, 1,1′-dimethylurea, 1,1′,3,3′-tetramethylurea and tetrabutylurea caused by reduction of the binding constant of the cobalt complex to the SDS. It is concluded that an important feature of this is the hydrophobic nature of the additive.

The heterogeneous catalysis of the reaction of $[Co(NH_3)_5Cl]^{2+}$ with *N,N*-dimethyl-*p*-phenylenediamine at Ag, Au and Ag/Au discs has been examined electrochemically [14]. The formation of silver halide inhibited the reaction on Ag but on Au, iodide and organic compounds produced inhibition. All inhibition was prevented by use of Au/Ag discs because cobalt reduction occurs on the Ag surface and oxidation of the *N,N′*-dimethyl-*p*-phenylenediamine occurs on the Au surface. Rate constants for the reduction of two pentaamminecobalt(III) complexes attached to a mercury electrode by thiophenecarboxylate ligands have been determined over a range of temperatures [15] allowing the determination of the activation enthalpy. The rate constant was found to be decreased by the addition of acetone to the mixture. This is attributed to a decrease in the nuclear frequency factor produced by over-damped solvent friction.

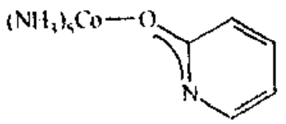
The linkage isomerism of thiocyanate bonded to cobalt(III) has been reviewed by Buckingham [16], including historical aspects involving the work of Werner and coworkers as well as the extensive work carried out by the author over many years. Linkage isomerism is also the subject of the paper on cobalt(III) pentaammine complexes of 2-pyridone (1) [17]. In aqueous acid solution after one week the



**(1)**

product of the reaction of the *O*-bonded complex is the aquapentaammine cobalt(III) ion and the rate constant $k_H = 1.3 \times 10^{-5}\ s^{-1}$. However, in aqueous TRIS a deep red solution is produced and a pale red-brown solid is isolated. This was found to be the deprotonated species (**2**). The reactions of the *O*-bonded species are summarised in (**3**), including the isomerism of the deprotonated *O*-bonded complex to the *N*-bonded species $k_{ON(1)} = 1.2 \times 10^{-5}\ s^{-1}$. The *N*-bonded complex was also isolated and its reactions are summarised in (**4**), where $k_{NO(2)} = 3.8 \times 10^{-6}\ s^{-1}$.

In a $^{15}N$ NMR spectroscopic study, the linkage isomerism reaction in water and



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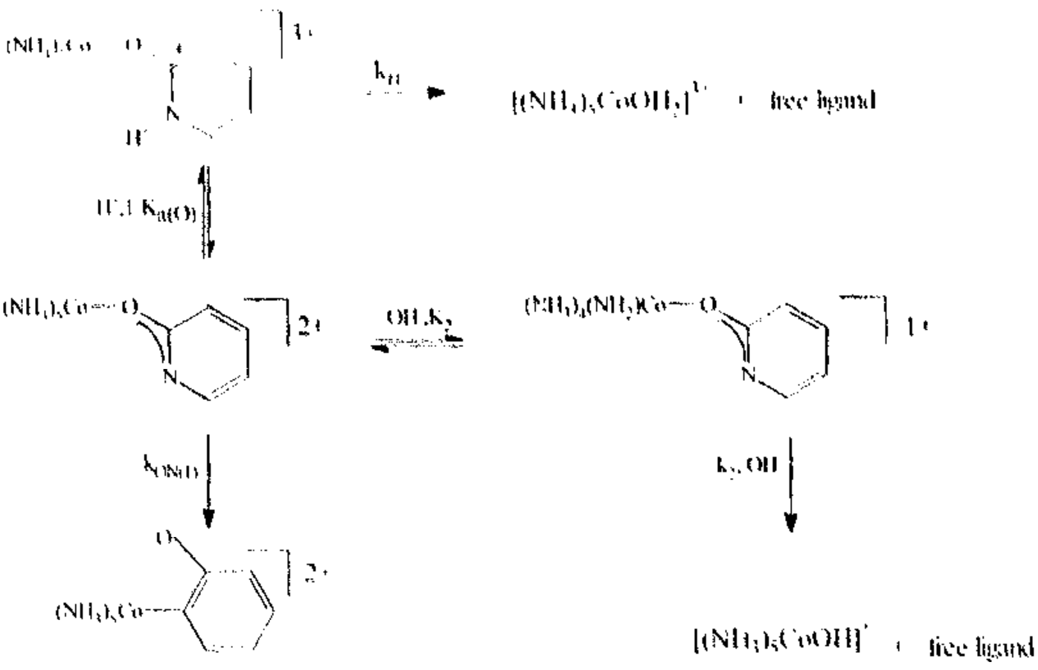

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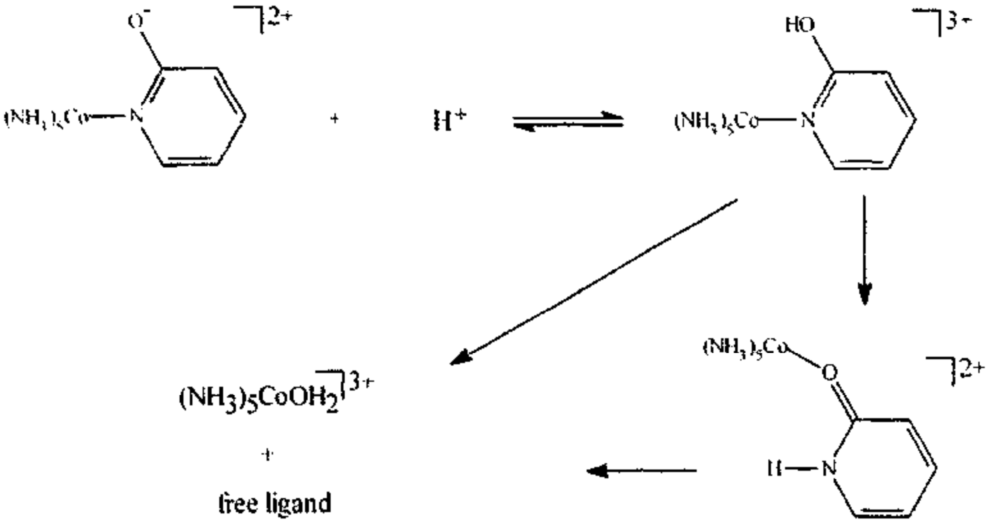
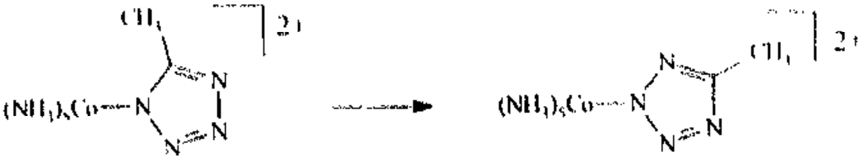


(4)

DMSO solution involving rearrangement in which Co moves from a position adjacent to the methyl group to that remote from the methyl group (5) has been investigated [18]. The results indicate that a $\eta^2$ $\pi$-bonded tetraazolato species is an intermediate in the process (6) which has a half life to about 3 h at room temperature. A slower N-2 to N-3 rearrangement was also observed and this too was an intramolecular process. The lower rate is attributed to the diminution of the methyl group interaction with the $NH_3$ groups arising from the remote configuration.

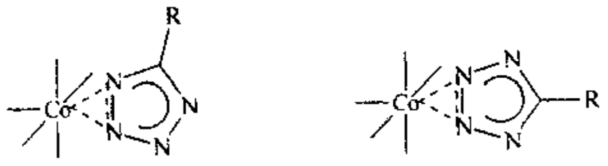


Adjacent to remote rearrangement for (5-methyltetraazolato)cobalt(III)

(5)

The X-ray crystal structure of the nitrito complex $[Co(NH_3)_5ONO]Br_2$ shows an orthorhombic space group Cmcm and $a = 10.8011$, $b = 8.9692$, $c = 10.6090$ Å and $Z = 4$ [19]. The change in the powder diffraction for the photoisomerisation reaction at room temperature of the conversion of the nitrito to nitro species showed that the lattice distortion was continuous throughout the course of the reaction but was anisotropic, while the cell volume varied linearly with the percentage of the nitro species present. The process was intramolecular and the powders monophasic.

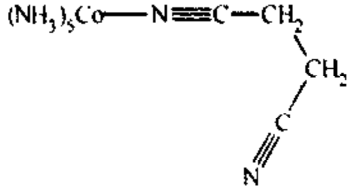
$^{1}H$ and $^{13}C$ NMR spectroscopies have been used to provide definitive evidence



$\eta^2$ $\pi$ intermediates

**(6)**

for the N to N rearrangement of the pentaammine (nitrile-amide)cobalt(III) complex (7) [20].



**(7)**

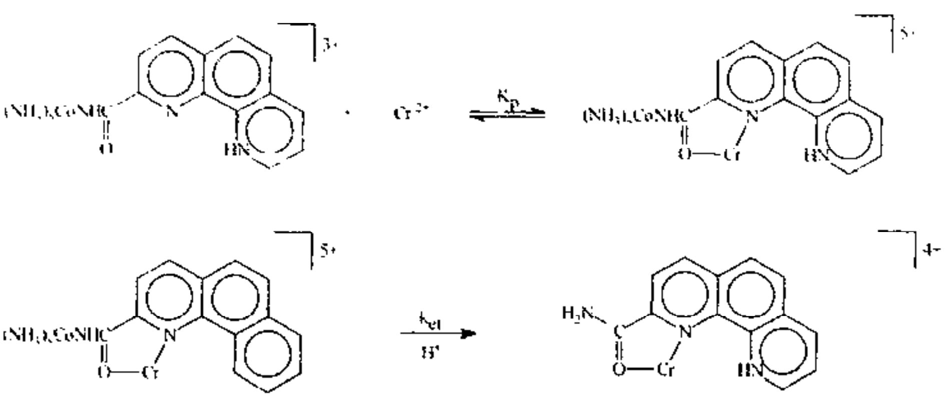
The solvolysis of $[Co(NH_3)_5Cl]^{2+}$ has been studied in mixtures of water with *tert*-butyl alcohol or 2-methoxyethanol [21] which have low and high hydrophobicities. When the kinetics were measured using 2-methoxyethanol as a co-solvent there was found to be a linear relationship between log *k* and the reciprocal of the dielectric constant of the solvent. This is to be expected for a reaction in which the $Cl^-$ in the transition state is sufficiently separate from the Co to be considered to behave like $Cl^-$ in the bulk solution. However, a similar linear relationship was not observed when *tert*-butyl alcohol was used. The authors apply a free energy cycle to the system and show that the solvated cobalt(III) species in the transition state is more stabilized in mixtures than $[Co(NH_3)_5Cl]^{2+}$ was in both co-solvents.

During the reaction of 2-cyano-1,10-phenanthroline with pentaammine (trifluoromethanesulfonato)cobalt(III) the major product is $[Co(NH_3)_5(NHCO\text{-}phen)]^{2+}$, while the minor product is $[Co(NH_3)_3(NHCO\text{-}phen]^{2+}$ [22]. The X-ray crystal structure of the latter shows that the 1,10-phenanthroline-2-carboxamido ligand is bonded meridionally in a tridentate fashion to the cobalt via the two ring nitrogens and the deprotonated carboxamide nitrogen. The kinetics of the chromium(II) reduction of the complex $[Co(NH_3)_3(NHCo\text{-}phen)]^{2+}$ were studied and a mechanism consistent with the rate law:

$$k_{obs} = kc_t K_p[Cr^{2+}]/(1 + K_p[Cr^{2+}])$$

is shown in (8). A chromium(II) catalysed reaction is also observed and the kinetics of this reaction were found to be consistent with the mechanism (9).

The reduction of pentaammine(phenanthroline-2-carboxamido-*N*)cobalt(III) by



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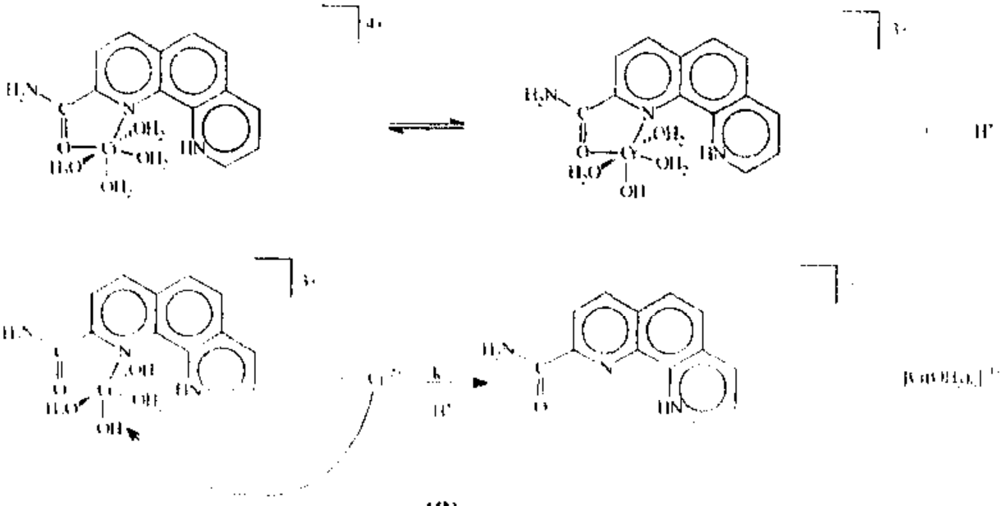


**(9)**

Ti$^{3+}$(aq) has been shown to occur in two steps involving first the formation of an intermediate species by chelation of the carboxamidooxygen and the nearest ring nitrogen to the Ti$^{3+}$ species [23]. The rate law for this step involves a [Ti$^{3+}$] and an [H$^+$] term (rate constants 240 and 6.7 s$^{-1}$, respectively). The other reaction involves outer sphere reduction of the above dinuclear species by [Ti(OH)]$^{2+}$. In a related study it was shown that reduction using V$^{2+}$(aq) also involved a two step process, though the second step was independent of [H$^+$].

A valuable method of examining intimate detail of mechanism in inorganic reactions is by investigating the effects of systematic but small changes in ligands attached to the metal ion but not actually involved in the reaction. Such a technique has been applied by Martinez, Pitarque and van Eldik to the reduction of [Co(RNH$_2$)$_5$(H$_2$O)]$^{3+}$ with [Fe(CN)$_6$]$^{4-}$ by examining the effects of pH, temperature and pressure on the reaction involving complexes having R=H, Me and Et [24]. The mechanism of the reaction is shown in (**10**). The variation of steric hindrance has a significant effect on the kinetics of the reaction and the formation constant, $K_{os}$ decreases with increasing size of R from 75 for H, 40 for Me and 23 $dm^3\ mol^{-1}$ for Et, while the electron transfer rate constant increases with increasing size of R from 0.11 for H, 9.3 for Me and 35 $dm^3\ mol^{-1}$ for Et. It is concluded that the major influence on the quantities obtained are the solvation changes during electron transfer.

$$[Co(RNH_2)_5(H_2O)]^{3+} + [Fe(CN)_6]^{4-} \overset{K_{os}}{\rightleftharpoons} \{[Co(RNH_2)_5(H_2O)]^{3+}, [Fe(CN)_6]^{4-}\}$$

$$\{[Co(RNH_2)_5(H_2O)]^{3+}, [Fe(CN)_6]^{4-}\} \xrightarrow{k} \{[Co(RNH_2)_5(H_2O)]^{2+}, [Fe(CN)_6]^{3-}\}$$

$$\{[Co(RNH_2)_5(H_2O)]^{2+}, [Fe(CN)_6]^{3-}\} \longrightarrow [Fe(CN)_6]^{4-} + Co^{2+} + 5RNH_2 + H_2O$$

R = M, Me or Et

**(10)**

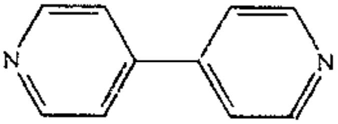
Photoreduction of the trinuclear complex $[(NH_3)_5Ru(III)(\mu\text{-}NC)Ru(II)(CN)_4(\mu\text{-}CN)Co(III)(NH_3)_5]Cl_2 \cdot 2H_2O$ results in the formation of $Co^{2+}$ [25]. For this process $\phi = 2 \times 10^{-4}$ at $\lambda_{(irr)} = 577$ nm and 0.18 at 366 nm. When the complexes $[(EDTA)Ru(III)LCo(III)(NH_3)_5]^{2+}$ (where L are the ligands shown in (**11**)) are reacted with ascorbic acid or dithionite ion, the Ru is preferentially reduced [26]. This gave the authors the opportunity of studying the intramolecular electron transfer from Ru(II) to Co(III) with the rate constants varying from 22.7 $s^{-1}$ for the pz to 0.039 $s^{-1}$ for 1,4-bis(4-pyridyl)butadiyne.

The X-ray crystal structure of $[cis\text{-}Co(NH_3)_4(OH)Cl)]Cl$ shows that it crystallizes in space group Pnma with $a = 13.295$, $b = 10.320$, $c = 6.732$ Å; $V = 923.63$ Å$^3$ and $Z = 4$ [27]. The complex $[Co(NH_3)_4(oxalato)]_2[trans\text{-}(NH_3)(OH)Co(oxalato)_2] \cdot 4H_2O$ has also been crystallographically characterised and the structures of the cation and anion are shown in diagram (**12**).

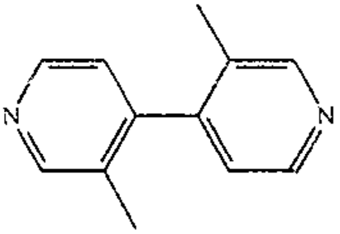
A range of tetraammine complexes of the type $[Co(RS)_2(amine)_4]^+$ (R = Me or Et and $(amine)_4 = (en)_2$, (trien) or (tren)) in which the $(en)_2$ and tren complexes were found to form the *cis* and *cis*-α isomers and were optically resolved [28]. It is interesting that oxidation using $H_2O_2$ of the $(en)_2$ and the (trien) complexes resulted in formation of the sulfinato species $[Co(RSO_2\text{-}S)_2]^+$. Ion exchange chromatography has been used to separate the *cis*-a, *cis*-$b_1$ and *cis*-$b_2$ isomers of the complex $[Co(opa)(trien)]^+$, where opa = 2-oxidephenylacetato (**13**) [29]. The *cis*-a complex was found to isomerize readily to the *cis*-$b_2$ in neutral or acidic aqueous solution.

The kinetics of the thermal dehydration of *trans*-dichlorotetraammine-cobalt(III) iodate dihydrate has been studied isothermally using thermogravimetry [30]. The reaction was found to be mostly second order with a rate governed by diffusion of

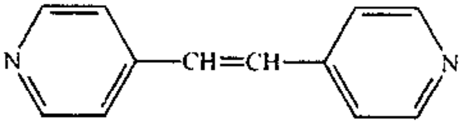
pyrazine



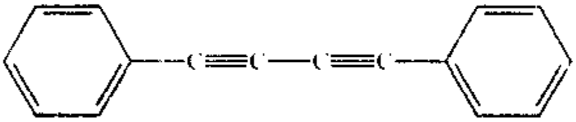
4,4'-bipyridine



3,3'-dimethyl-4,4'-bipyridine

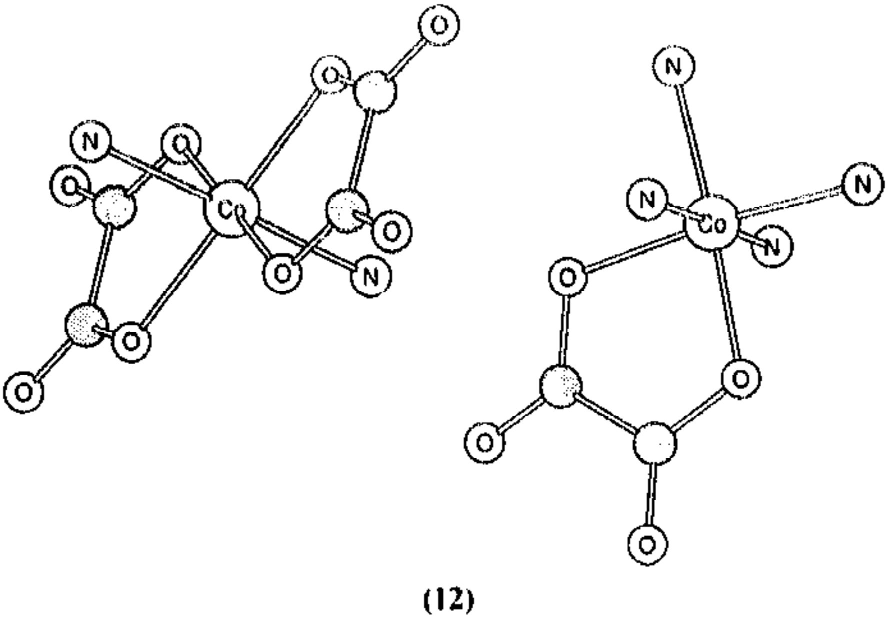


trans-1,2-bis(4-pyridine)ethylene



1,4-bis(4-pyridyl)butadiyne

**(11)**



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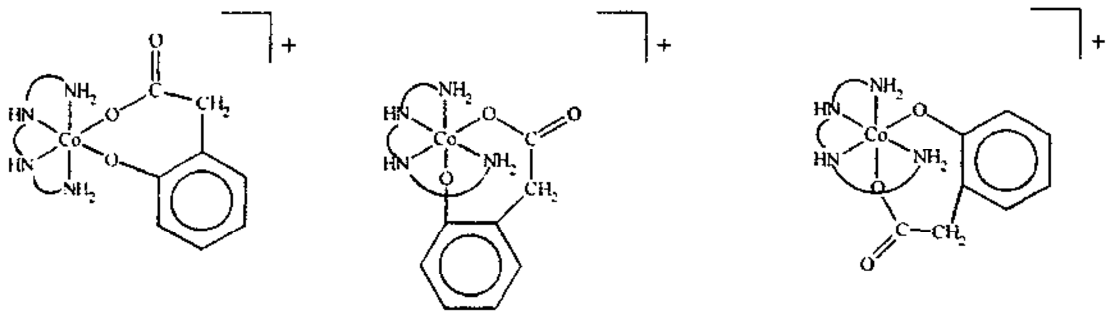


*cis* α   *cis* β₁   *cis* β₂

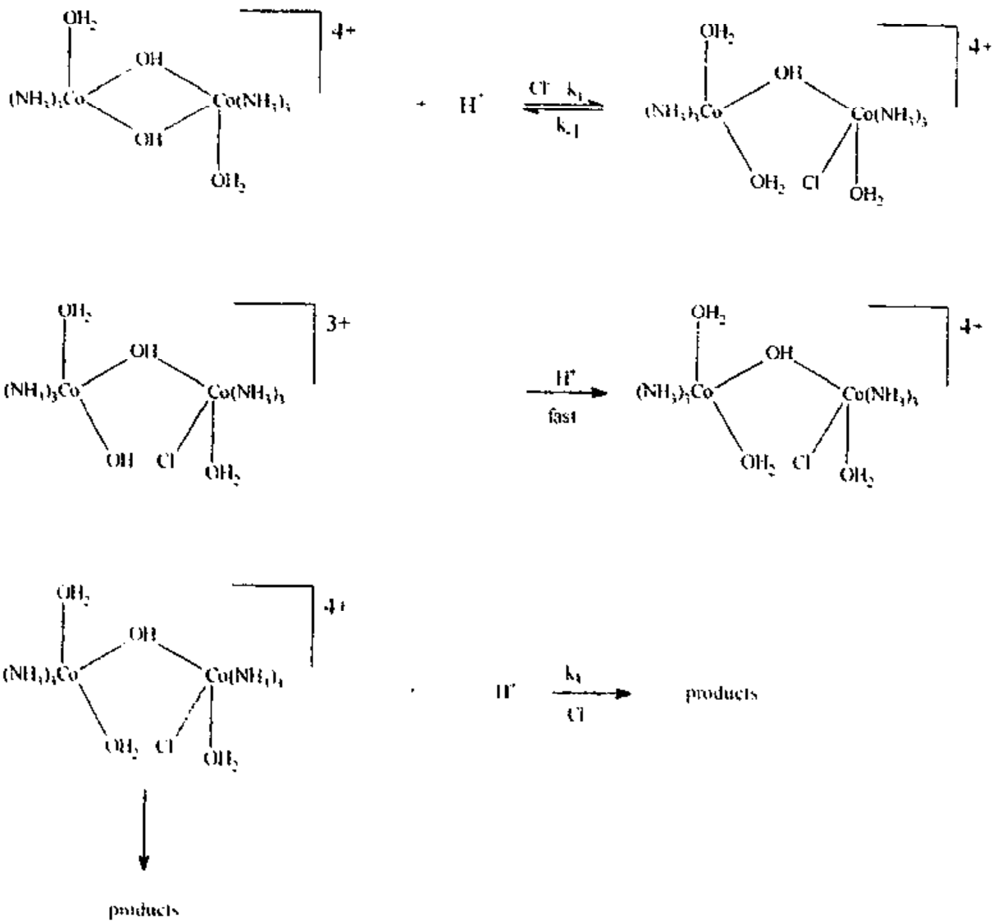
**(13)**

water occurring in the early stages. The overall activation energy was 103 kJ mol$^{-1}$ but in the early stages of the reaction an activation energy of 80 kJ mol$^{-1}$ was observed. The aquation of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in acidic chloride solutions results in a mixture of products consisting of $[Co(NH_3)_3(H_2O)_3]^{3+}$ and $[CoCl_2(NH_3)_3(H_2O)]^{+}$ [31]. The mechanism proposed for the reaction is shown in (**14**). At constant $[H^+]$ the reaction was found to be first order with respect to $[Cl^-]$ and $[Br^-]$. In aqueous methanol only the third was found to be significantly dependent on methanol concentration.

A set of resonances in the $^1H$ NMR spectrum for the non-exchangeable hydrogen atoms in d(CAATCCGGATTG)$_2$ dodecanucleotide which is a small segment of B-type DNA have been obtained for a number of ratios (0-11) of Λ-$[Co(en)_3]^{3+}$ to nucleotide [32]. It is shown that binding of the complex to the nucleotide is predominantly due to electrostatic reactions. The enantioselectivity is attributed to the formation of multiple hydrogen bonds from the en ligands to the nucleotide and also to the shape of the nucleotide.

The X-ray crystal structure of $[Co(en)_3]_3[FeCl_6]Cl_6 \cdot H_2O$ has been determined along with its chromium analogue [33]. Magnetic measurements showed that the Co Fe species was antiferromagnetic below $T_c = 1.43$ K. It is shown that magnetic ordering in the species studied involves hydrogen bonds in the propagation of magnetic interactions.

Osmotic coefficients of aqueous solutions of $[Co(en)_3]^{3+}$ salts at temperatures near to 273 K [34] have been determined. The kinetics of the aquation of *cis*-aquabromobis(ethylenediamine)cobalt(III) have been studied in aqueous mixtures with MeOH, EtOH, i-PrOH and t-BuOH [35]. The results of the study are compared with those for the corresponding chromium complex also investigated in this work. Comparison of plots of transfer functions for the complexes support the conclusion that there is a common mechanism.



(14)

$^{59}$Co NMR spectra in water, MeOH, propanediol-1,2-carbonate, dimethylsulfoxide, *N,N*-dimethylacetamide and hexamethylphosphoramide of $[Co(en)_3]^{3+}$, *cis*-$[Co(en)_2(N_3)_2]^+$ and *trans*-$[Co(en)_2(N_3)_2]^+$ show differences in linewidth which the authors attribute to co-solvent interaction [36]. A particular feature was the sensitivity of the Co chemical shifts and linewidths to the electronic structure of the oxygen in the solvents.

The strain-energy minimisation for 16 conformations of $[Co(en)(tn)(tmd)]^{3+}$ has revealed that the lowest energy conformation is en(*lel*), tn (chair(p,tmd)), tmd(*lel*) [37].

A series of carbonatotetraammine complexes in which the amine moiety was changed to give various stereochemical effects have been examined to investigate the effects of stereochemistry on the ring opening of the didentate carbonato ring. The complexes were all of the form $[Co(NN)_2CO_3]^+$, where NN = 1,1,2,2-tetramethylethylenediamine (tme) and dimethylethylenediamine (bmn) [38]. The rate law was:

$$\mathrm{Rate} = k_0 + k_1[H_3O^+]$$

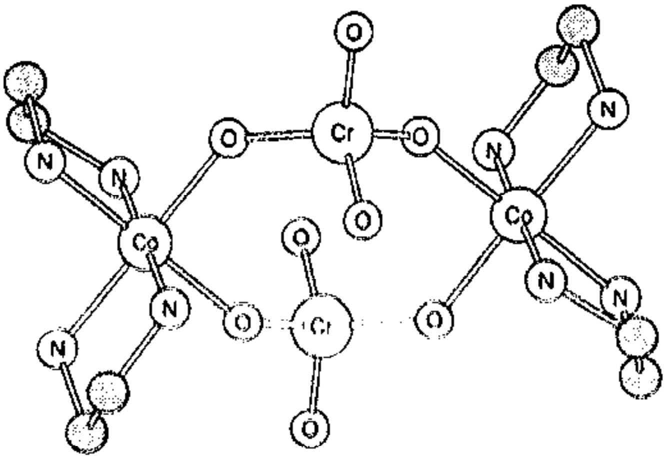
and the effect of various amine ligands on $k_1$ gives the series:

$$(en)_2 \cong (pn)_2 > (tme)_2 \gg (bmen)_2$$

showing the major effect of stereochemistry on the rate.

The mechanism of water exchange for the complex $[Co(CH_3NH_2)_5H_2O]^{3+}$ has been clearly shown to be dissociative in nature contrasting with an associative process for the corresponding chromium complex and a borderline situation for the rhodium complex [39]. When compared with the analogous ammine complexes there appears to be a shift towards a more dissociative mechanism with increasingly bulky amine ligands.

Reactions between $[CrO_4]^{2-}$ and $[Co(en)_2(OH)(H_2O)]^{2+}$ or $[Co(tren)(OH)(H_2O)]^{2+}$ each result in the formation of two different types of complex [40]. The first of these $M[Co(en)_2(CrO_4)_2] \cdot 0.5\ H_2O$ ($M = Li$ or K) has both the $CrO_4$ ligands in *trans* positions, while the second, $[Co_2(en)_4(CrO_4)_2]X_2$ (where $X = Cl^-$, $Br^-$ or $[ClO_4]^-$), has $CrO_4$ bridges involved in a cyclic structure. The X-ray crystal structure of the cation contained in the bromide species is shown in (**15**).



**(15)**

The X-ray crystal structure of the complex $[Co(en)_2(NH_3)Br]Br_2$ [41] shows that the preferred structures are $(lel)_2$ $\Lambda$ $(\delta\delta)$ and $\Lambda$ $(\lambda\lambda)$. The kinetics of the silver-catalysed oxidation of cis(diglycinato)bis(ethylenediamine)cobalt(III) by potassium peroxodisulfate have been studied in aqueous perchlorate [42].

A whole series of sixteen complexes, $[Co(hfac)L]^{n+}$, where hfac is hexafluoro-2,4-pentanedionato and L ranges from $(NH_3)_4$ through β-2,3,2-tet and edda to cyclam have been studied to determine the reaction volume at infinite dilution [43]. The nature of the ligand, L had a significant effect upon $\Delta V_{OH}$ and $\Delta V_{OMe}$ which was considered to arise from the change of electrostrictive volume of the reaction. The very large range of ligands allows the interpretation of the data in terms of properties of the ligands such as flexibility or formation of crevices in the surface of the complex which affects the intrusion of solvent into its structure.

The X-ray crystal structure of the complex *cis*-β-Δ-*S*,*S*-$[Co(CO_3)(trien)]$

$(ClO_4)\cdot H_2O$ shows a structure with the monoclinic space group $P2_1$ and $a = 7.410$, $b = 12.354$, $c = 8.676$ Å, $\beta = 108.88°$ and $Z = 2$, a didentate $CO_3$ ligand and an absolute configuration of $\Lambda(\lambda\lambda\delta)$ [44]. As predicted from earlier crystallization studies the complexes {[*cis*-α-Co(trien)ox]Cl}$_2$, [*cis*-β-Co(3,2,3-tet)ox]Cl·$4H_2O$, {[*cis*-α-Co(trien)ox]$NO_3$}$_2\cdot H_2O$ and [*mer*-Co(dien)ox($NO_2$)] all crystallize from aqueous solution as racemates [45]. They have been characterized by X-ray crystallography.

The re-examination of earlier work using new kinetic techniques often shows hidden complexities in processes which occasionally go a long way to solving long-standing problems. Such is the case in the study of the hydrolysis of a number of cobalt(III) carbonato complexes which exhibit a wide range of rate constants covering a span of $10^7$ [46] which has been difficult to explain from previous data in terms of the accepted mechanism (**16**). By examination of the kinetics of the hydrolysis of a number of complexes $[CoL(O_2CO)]^{n+}$ *viz* $[Co(NH_3)_4(O_2CO)]^+$, α- and β-$[Co(trien)(O_2CO)]^+$, $[Co(tren)(O_2CO)]^+$, $[Co(nta)(O_2CO)]^{2-}$, *cis*-$[Co(gly)_2(O_2CO)]^-$, $[Co(cyclen)(O_2CO)]^+$ and [Co(*N*-Mecyclen)$(O_2CO)]^+$ at suitable wavelengths it was found that a number of them exhibited biphasic behaviour involving consecutive first order reactions in the range $[H^+] = 0.1$ to 1.0M. The first process had the rate law:

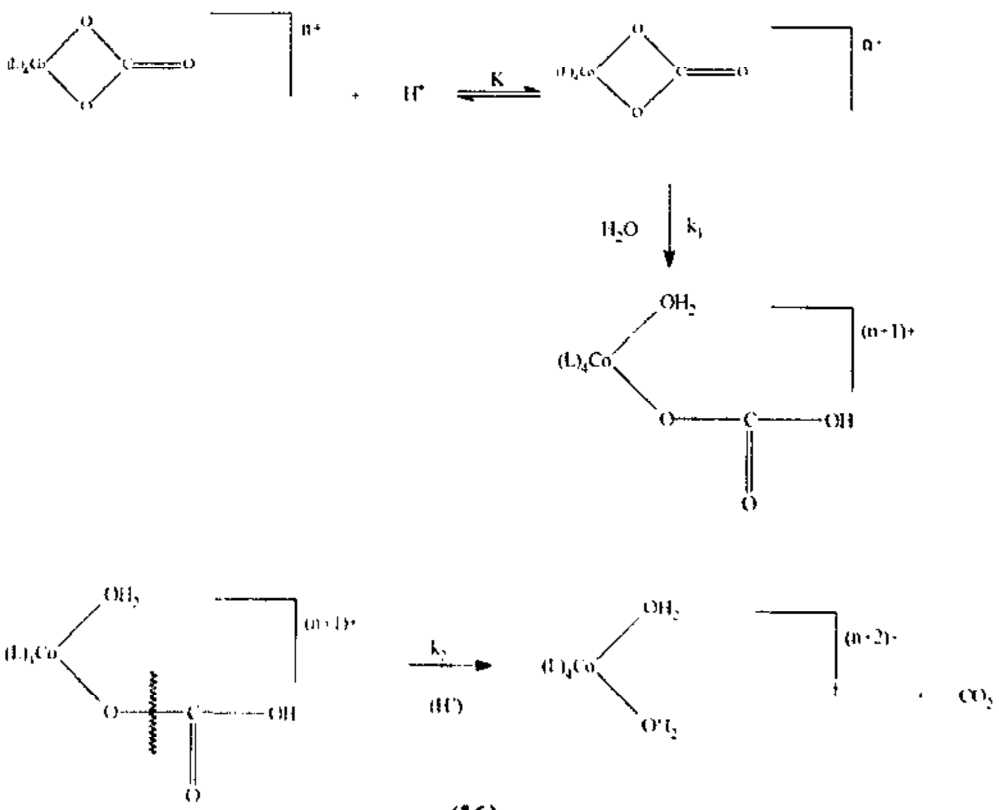
$$k_{\text{fast}} = \frac{k_1 K[H^+]}{1 + K[H^+]}$$

while the second step with $k_{\text{slow}}$ was independent of $[H^+]$. On the basis of the data, a more refined mechanism (**17**) is proposed which explains the very wide range of rates in terms of the variation in the ability of complexes to transfer the proton on the exo-O to the endo-O allowing a wide variation in $K_2$.

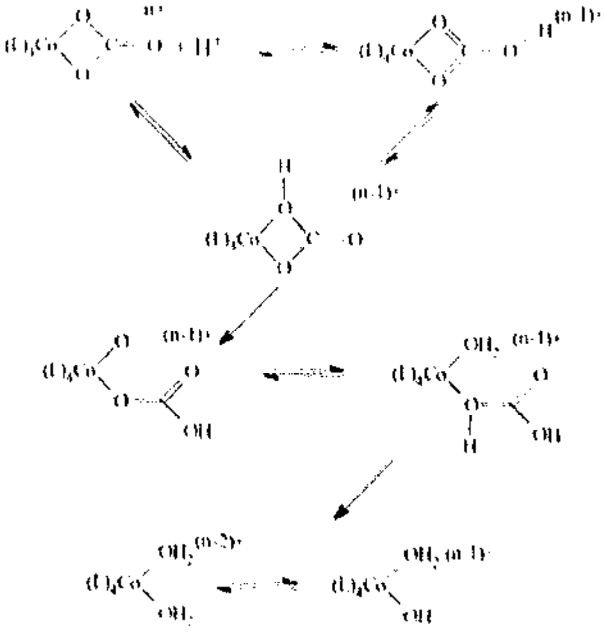
Because of the increasing interest in oxygen activation and specific oxidation of organic molecules a series of doubly bridged dinuclear complexes involving either $S_2O_3^{2-}$ $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}S_2O_3)Co(tren)]^{2+}$ or $SR^-$ $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}SR)Co(tren)]^{n+}$ where $SR^- = [SCH_2CH_2SO_3]^{2-}$, $[SCH_2CH_2OH]^-$, $[SC_6H_5]^-$ or $[SCH_2CH_2N(CH_2CH_3)_2]^-$ as one of the bridging ligands have been prepared [47]. The X-ray crystal structures of two of these species have been determined; the structure of $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}S_2O_3)Co(tren)]^{2+}$ is shown in structure (**18**).

The photochemical reaction (**19**) results in the 2-aminoethanesulfinato-*O,N* complex shown [48]. The X-ray crystal data confirm the structure and show that the geometrical configuration of the starting complex is retained in the product. The chiral sulfur centre in the complex confers optical activity and an optical isomer was chromatographically separated using $K_2[Sb_2\{(+)\text{-tartrate}\}_2]$ as the eluent; CD spectral measurements were obtained.

The complex $[(tren)Co(H_2O)_2]^{3+}$ reacts with hydroxyethylphosphate to form a monodentate complex [49]. However, in the complex $[(trpn)Co(H_2O)_2]^{3+}$ the phosphate species is didentate (trpn = tris(3-aminopropyl)amine. The kinetics of the hydrolysis of these two complexes show that the monodentate species is more readily hydrolyzed than the didentate phosphate. The rate of dephosphorylation of the complexes $[(tn)_2Co(ATP)]^-$ and $[(trpn)Co(ATP)]^-$ in the presence of added aqua-



**(16)**



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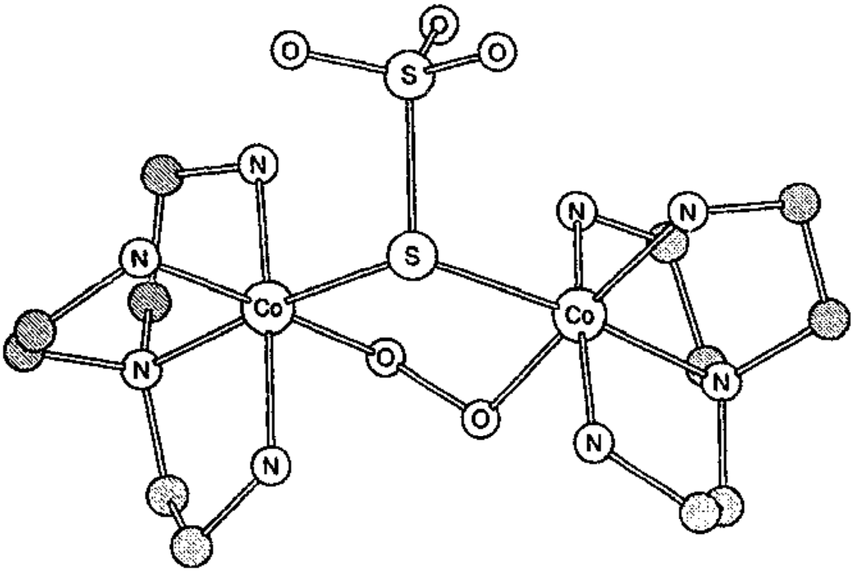

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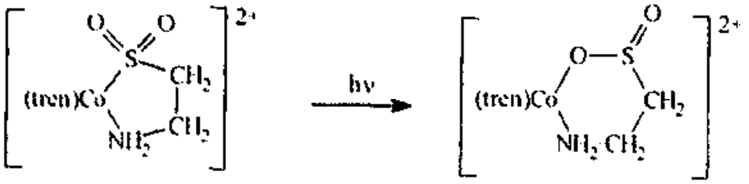
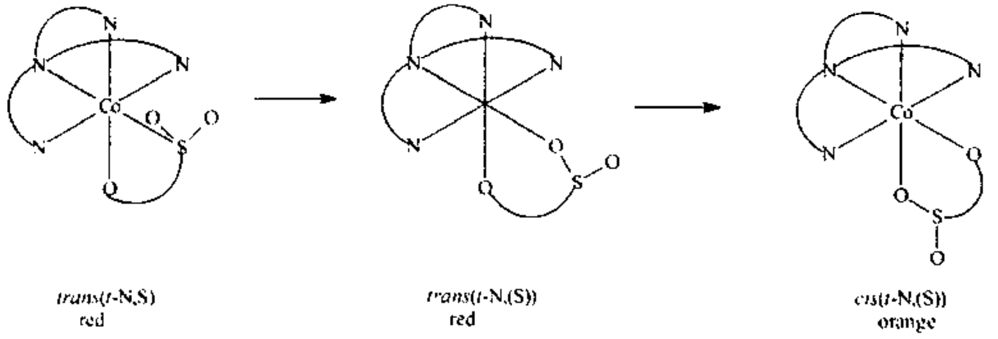


**(19)**

amine complexes has been used to demonstrate the effect of added species on ATP dephosphorylation [50]. The order of dephosphorylation was found to be trpn > dpt = cyclen > tn. The effectiveness is illustrated by the fact that the uncatalysed hydrolysis of ATP is over $10^6$ times slower than the hydrolysis occurring when $[(trpn)Co(aq)]^{3+}$ was added to $[(tn)_2Co(ATP)]$ and affected greatly by the nitrogen-containing moiety in the aqua complex but not to the $N_4$ ligand in the ATP complex.

Irradiation of the complex *trans*-(t-N,S)-$[Co\{S(O)_2CH_2COO$-*S,O*$\}(tren)]^+$ using a high pressure mercury lamp led to the reaction shown in (**20**) [51]. Both the product complexes were isolated and the X-ray crystal structure of the orange *cis*-(t-N,O(S)) species was determined. It was found to be monoclinic with space group $C2/c$ and $a = 23.326$, $b = 8.005$, $c = 18.631$ Å, $\beta = 108.03°$, $V = 3307$ Å$^3$ and $Z = 8$.

Dimethylglyoximato complexes, as usual, attract considerable attention, sometimes because of their role as models for vitamin $B_{12}$ behaviour but often because of their intrinsic interest. The photolysis of the complex $[(Hdmg)_2Co(III)_sBu(H_2O)]$ in the presence of 27 different nitrogen donor bases has shown that the products of the reactions are adducts of the bases with the



**(20)**

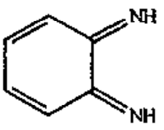
bis(dimethylglyoximato)cobalt(II) species [52]. The adducts which are produced differed according to the nature of the base. Thus for pyridine species substituted in the *ortho* position the ESR spectroscopic data showed only $[Co(II)(Hdmg)_2L]$ while for other pyridine or non-aromatic complexes the $[Co(II)(HdmgL_2]$ complexes were detected.

Using pulse radiolysis a number of bis(dimethylglyoximato)cobalt(III) complexes and also their alkyl derivatives have been reduced either by solvated electrons or by radicals in solution [53]. The complex $[(Hdmg)_2Co(III)Cl(py)]$ was found to lose $Cl^-$ and py on the formation of the cobalt(II) species within about 0.5 μs but the formation of the Co(I) complex involves the uptake of $Cl^-$. The rate of this reaction was measured to give $k = 4.6 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$. The alkyl substituted pyridine species $([(Hdmg)_2Co(III)(R)(py)])$ produces $[(Hdmg)_2Co(II)R]$ as a transient complex on reduction but this rapidly reacts with the starting material to produce the dialkyl product.

A series of complexes of the form $[(Hdmg)Co(III)(SBx)]$ or $[(Hdmg)(CO(III))(SBy)]$ in which SBx is the dianion of a tetradentate Schiff base and SBy is the monoanion of a didentate Schiff base, have been produced by reaction of an alcoholic suspension of the cobalt(III) dimethyl-glyoxime complex with the appropriate Schiff base [54]. A number of complexes of the form $[Co(DH2)(B)(X)]$, where DH2 = dimethylglyoxime, B = an imidazole base and X is an anion, $[Co(HL)X_2]$ and HL = $H_3Me_2em$, $HMe_2pn$, $H_2Me(Ph)en$ and $H_2Me(o\text{-}phen)$ as well as $[Co(L)(B)(X)]$ and $[Co(L)(B)_2](X)$ have also been prepared [55]. These are suggested as possible models for vitamin $B_{12}$.

A single crystal of the complex β-cyanoethylbis(dimethylglyoximato) (4-methylpyridine)cobalt(III) has been shown to produce a reversible crystal-to-crystal thermal phase transition at 343 K [56]. Irradiation of a single crystal with a powerful Xe source at > 343 K caused the β-cyanoethyl group to be isomerized to the α-cyanoethyl isomer. The authors propose a mechanism for this reaction. A large number of correlations of a variety of parameters of complexes of the type $[RCo(III)(Hdmg)_2L]$ where R is an alkyl group and L a range of pyridine or similar ligands have then been carried out in order to rationalize aspects of the solution and solid state properties of these complexes in relation to the electronic and steric properties of the alkyl species.

The X-ray crystal structure of the complex (bis[tris-(dimethylglyoximato) cobalt(III)]cobalt(II) fluoride octahydrate has been determined [57].



BQDI

**(21)**

The ligand s-BQDI (**21**) forms a series of square pyramidal cobalt(III) complexes with a wide variety of complexes of the form $[LCo(III)(s\text{-}BQDI)_2]^+$ [58]. A selection of kinetic and equilibrium data for the reaction:

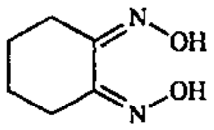
$$[(LCo(III))(s-BQDI)_2]^+ + L^1 \rightleftharpoons [L^*Co(III)(s-BQDI)_2]^+ + L$$

are shown in Table 1, where $k_f$ and $k_b$ are the forward and reverse rate constants for the reaction respectively and $n^{\circ}_{pt}$ is defined as in the reference [59]. In fact, data are available for 22 reactions in total which show a very large variation in $k_f$ from 14.5 to 0.009 $M^{-1}\,s^{-1}$ and the authors interpret this in terms of an $I_a$ mechanism. The data have been compared with the *trans* effect order in square planar Pt(II) complexes and shown to be similar and also give a reasonable linear relationship between log $k_f$ and log $k_b$ and $n^{\circ}_{pt}$.

A series of complexes $[CoD_3(SnBr_3)_2]^-$ have been prepared in which $H_2D$ are macrocyclic dioximes [60]. $^{59}Co$, $^{119}Sn$, $^{13}C$ and $^{1}H$ NMR spectra and $^{119}Sn$ Mössbauer spectra have been used to determine electron distributions in these compounds and the X-ray crystal structure of $[NBu_4][Co(Nx)_3(SnBr_3)_2]$, where Nx is the ligand (**22**), has been determined.

Table 1.

| Entering ligand, $L^1$ | $k_f/10^3\,M^{-1}\,s^{-1}$ | $k_b/10^3\,M^{-1}\,s^{-1}$ | $K$ | $n^{\circ}_{pt}$ |
|---|---|---|---|---|
| $L = Ph_3sb$ | | | | |
| $Ph_3P$ | 14.5 | 0.485 | 30 | 8.79 |
| $P(OEt)_3$ | 4.75 | 0.190 | 25 | 7.08 |
| SCN | 0.910 | 4.8 | 0.19 | 5.65 |
| $I^-$ | 0.055 | 2.04 | 0.027 | 5.42 |
| py | 0.035 | 1.29 | 0.027 | 3.13 |
| $L = Ph_3As$ | | | | |
| $Ph_3P$ | 3.68 | 0.720 | 5.1 | |
| $P(OEt)_3$ | 2.20 | 0.365 | 6.0 | |
| $SCN^-$ | 0.031 | 6.22 | 0.048 | |
| I | 0.009 | 1.70 | 0.0053 | |
| py | 0.019 | 2.34 | 0.008 | |



**(22)**

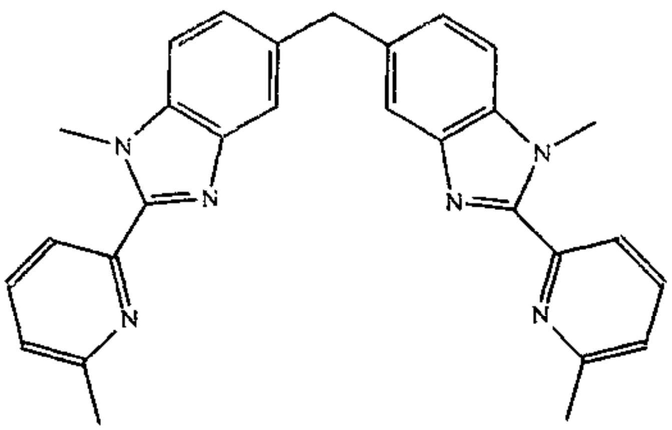
The X-ray crystal structure of tris(oxamideoxime-*N*,*N*′)cobalt(III)triiodide shows a trigonal structure with quasi-octahedral chiral cobaloxime cations and $I^-$ [61].

The kinetics of the reduction of a series of phenanthroline-type cobalt(III) complexes by $[Co(terpy)_2]^{2+}$ have been studied in the presence of aqueous surfactants [62]. The cobalt(III) complexes were $[Co(phen)_3]^{3+}$, $[Co(5\text{-Me-phen})_3]^{3+}$, $[Co(5,6\text{-Me}_2\text{-phen})_3]^{3+}$, $[Co(5\text{-Cl-phen})_3]^{3+}$, $[Co(5\text{-SO}_3\text{-phen})_3]$ and $[Co(dipic)_2]^-$ and the surfactants were dodecylsulfate (SDS), Triton X-100 ($C_8H_{17}C_6H_4(OCH_2CH_2)_xOH$, x = 9,10) and cetyltrimethylammonium bromide (CTAB). The effect of varying the concentration of the surfactant was to produce a rapid increase in rate at low surfactant concentration to a maximum followed by a rapid decrease resulting in an overall diminution in rate. This behaviour is interpreted in terms of the Berezin model. The rate data are compared with the electrochemical behaviour of the systems determined using cyclic voltammetry at various surfactant concentrations. The results show that changes in anodic and cathodic peak currents and half-wave potentials correlated with micellar binding.

The complex $[Co(dipic)_2]$ has also been the oxidant of choice in a series of kinetic and mechanistic studies of the oxidation of the Mo and W clusters $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$ [63], $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ [64], $[W_3S_4(H_2O)_9]^{5+}$ [65].

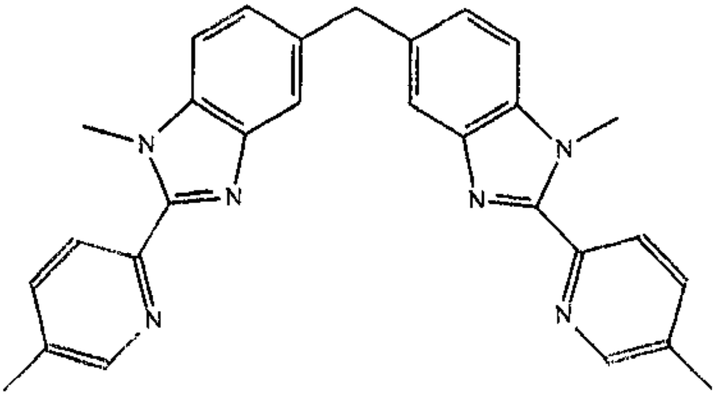
The X-ray crystal structures of the complexes $[CoCl(bpy)(dpt)]^{2+}$ and $[CoCl(phen)(dpt)]^{2+}$ (dpt = bis(3-aminopropyl)amine) as the perchlorate salts show them to be *mer-endo*(Cl NH) isomers with dpt forming two six-membered chelate rings [66]. The dpt ligand was disposed within the complex such as to produce chelate rings in the chair conformation. The analogous complexes containing *N*-(2-aminoethyl)-1,3-propanediamine were also prepared and characterized.

Following an earlier study of the reaction of the ligand 6-bismbmp (**23**) and cobalt(II) in which a cobalt(II) complex was formed which was not oxidized to a cobalt(III) species [67], a minor modification was carried out to the ligand to form the species 5-bismbmp (**24**), i.e. moving a methyl group from the 6 to the 5 position. A complete X-ray crystal structure of the previously studied complex $[Co_2(6\text{-bismbmp})_3](ClO_4)_4 \cdot 2.5CH_3CN$ is reported [68] as well as the crystal structure of $[Co_2(5\text{-bismbmp})_3](ClO_4)_4$. The cations $[Co_2(6\text{-bismbmp})_3]^{4+}$ and $[Co_2(5\text{-bismbmp})_3]^{4+}$ are (**25**) and (**26**) respectively. Both complexes show dinuclear triple-helical cations with the three didentate ligands wrapped around the pseudo-$C_3$ axis produced by the Co atoms. The formation of both these species in solution in acetonitrile followed by spectrophotometric titration showed a sharp end-point at Co:ligand = 0.7 and the presence of clear isosbestic points indicated the absence of any intermediate and hence the probability of a self assembly process.



6-bismbmp

**(23)**

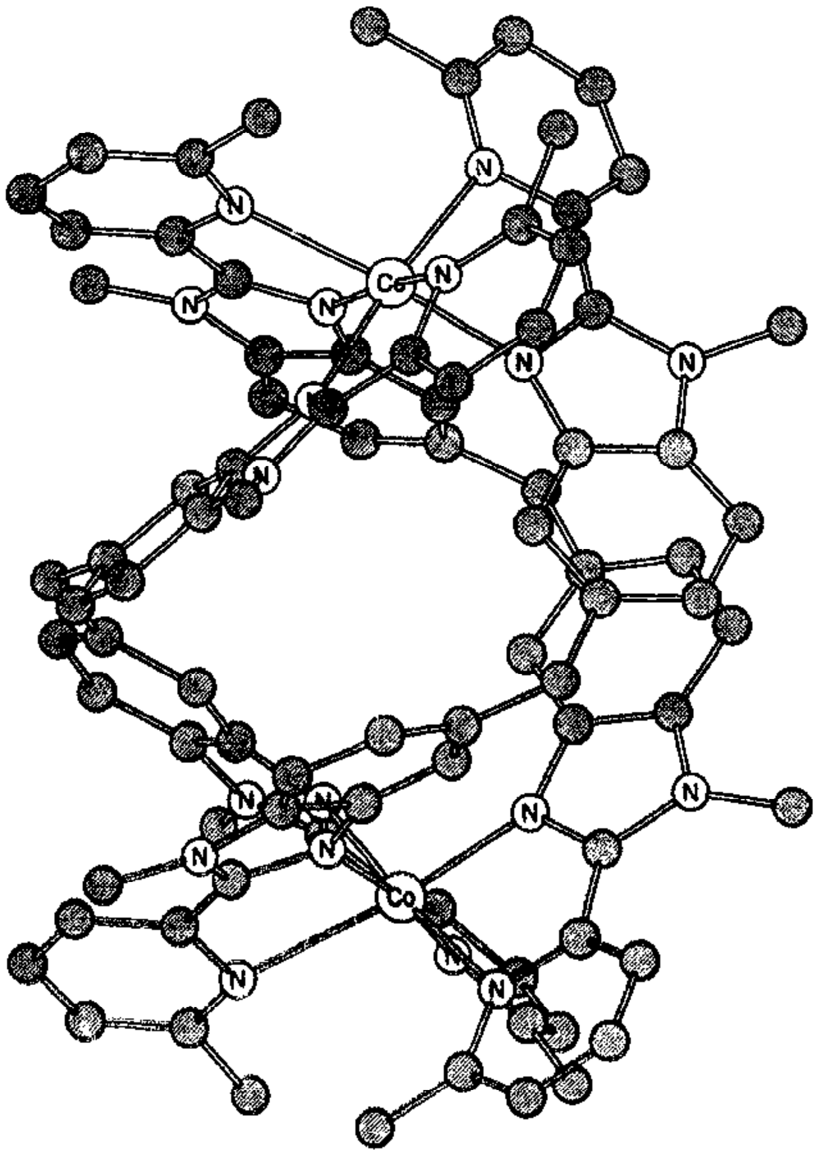


5-bismbmp

**(24)**

The electrochemistry showed that the 6-bismbmp complex showed no tendency to be oxidized to the cobalt(III) complex, while the 5-bismbmp complex is readily oxidized electrochemically. The oxidation of $[Co_3(5\text{-bismbmp})_3]^{4+}$ was carried out chemically using $Br_2$ in acetonitrile to produce red crystals of $[Co_2(5\text{-bisbmp})_3](ClO_4)_6 \cdot 4H_2O$ and the X-ray crystal structure determined; the cation is **(27)** [69]. The complex was also separated into two enantiomers. This is believed to be the first example of the separation of the helical dinuclear metal complex into enantiomers. The two species were characterized by $^1H$ NMR and circular dichroism spectra.

A series of new ligands **(28)** which exhibit optical activity have been synthesized

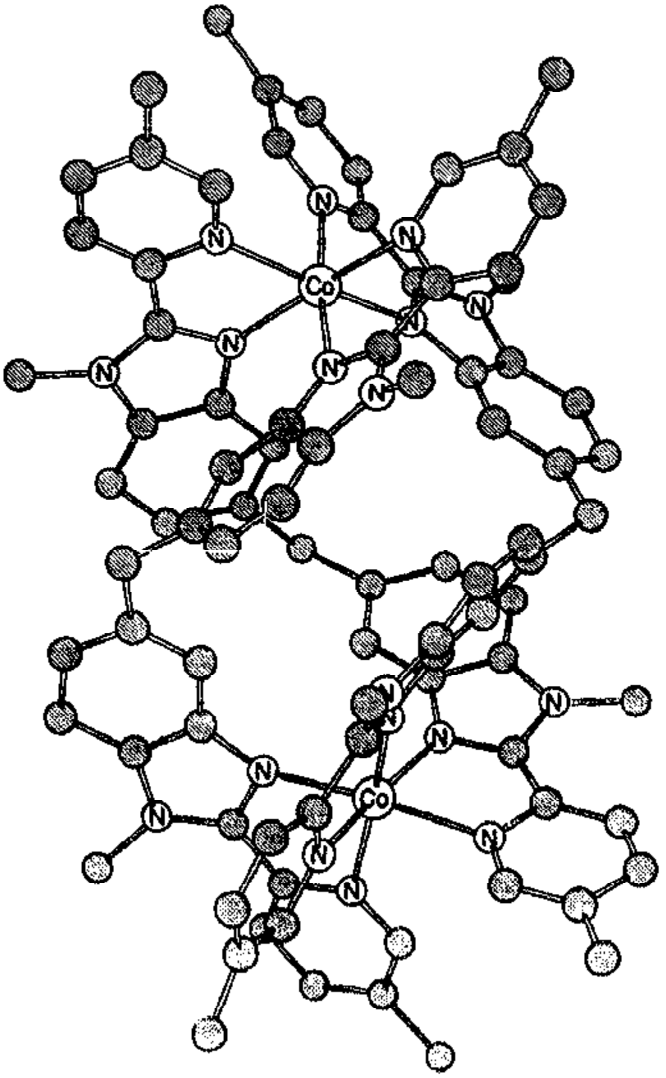


**(25)**

and their Co(III) complexes, $[Co(L)(H_2O)]^+$, prepared [70]. The kinetics of redox reactions of these species with optically active Fe(II) complexes {[Fe(S,S)-L], where L = promp or MeO-promp or *N,N'*-[(pyridine-2,6-yl)bis(methylene)bis[alanine]} show that the products lie in favour of the heterochiral diastereomeric pair such that $k_{DL}/k_{LL}$ was usually about 2.

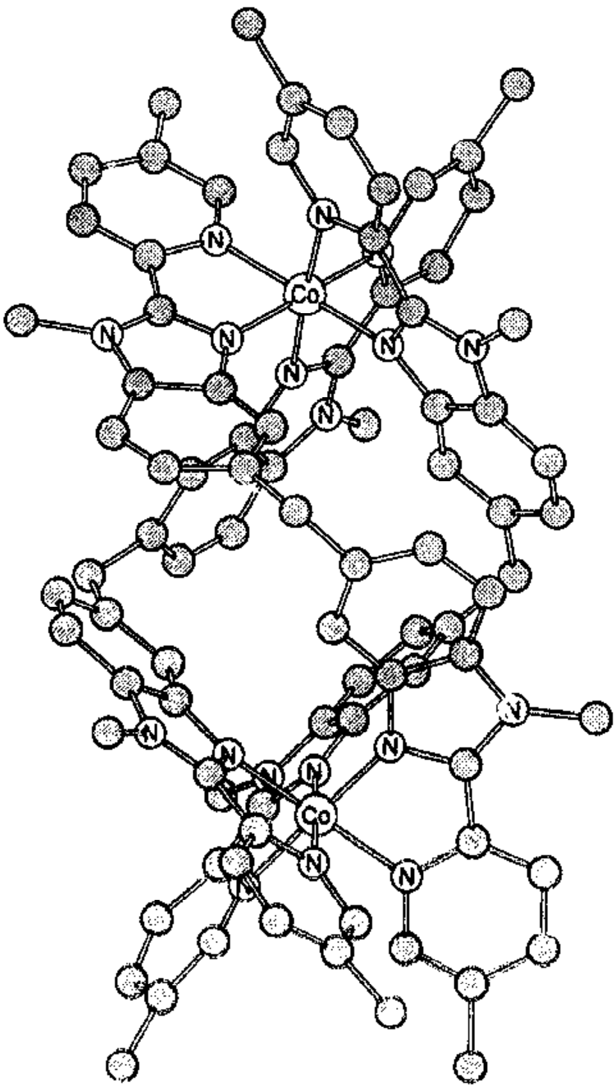
The X-ray crystal structures of the complexes $[Co(phen)_2(gly)]Cl_2 \cdot 4H_2O$ and $[Co(phen)_2(H_2O)_2](NO_3)_3 \cdot 2H_2O$ show them to have the expected six-coordination around the cobalt [71].

The activity of derivatives of the complex tetrakis(*N*-methyl-4-pyridiniumyl)porphyrin (TMpyP(4)) [72] has led Lin and Marzilli to examine



(26)

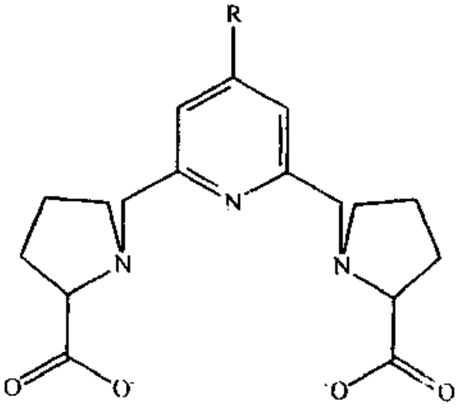
the bonding of a series of cobalt(III) complexes in water, DMSO and DMF [73]. They sought to prepare pure samples of the complexes (**29**) and found that a major problem in this was the presence of Co(II) species formed by reduction of the Co(III) complex by $I^-$ during the preparation. The compound [Co(TMpy(4)](ClO$_4$)$_5$·2H$_2$O was prepared as a crystalline solid, as the hexafluorophosphate salt. The use of NMR spectroscopy to examine solutions of [Co(TMpy(4)]$^{5+}$ species in solution in DMSO, DMF and H$_2$O showed that the order in which these bind to this moiety is DMSO > DMF > H$_2$O and that $Cl^-$ was found to bind more strongly in DMSO solutions than in H$_2$O. Bonding to DMSO was found to be through oxygen rather than sulfur. The nature of the *trans* ligand clearly influenced the rate of exchange of DMSO. Over the range of complexes studied, the extent of $Cl^-$ binding depended upon the porphyrin and was in the



**(27)**

order [Co(TMpyP(4))] > [Co(TCF3PP] > [Co(TPP)]. The complex Co(III)[5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin] (CoTPPS) has been shown to be an effective antidote to cyanide poisoning in mice when used alone [74]. Further protection is provided if it is used in conjunction with more conventional antidotes such as $NaNO_2$ or $Na_2S_2O_3$.

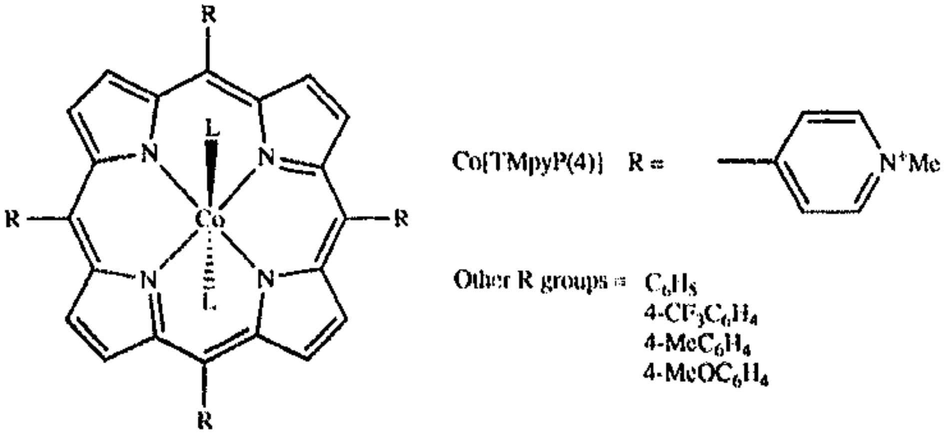
Metal ion porphyrin complexes have been widely used in the formation of sensor electrodes. The oxygen reduction properties of a cobalt diporphyrin polymer ligand system modified electrode has been studied [75] and a structural model of the electrode has been examined by augmented molecular mechanics. The oxygenation of octaethylporphyrinatocobalt(II) has been shown under appropriate conditions to produce octaethyloxaporphyrinatocobalt(III) [76]. The X-ray structure of this species has been obtained (**30**) and it is concluded that this is a verdoheme analogue.



R = H: promp

R = OMe: MeO-promp

**(28)**



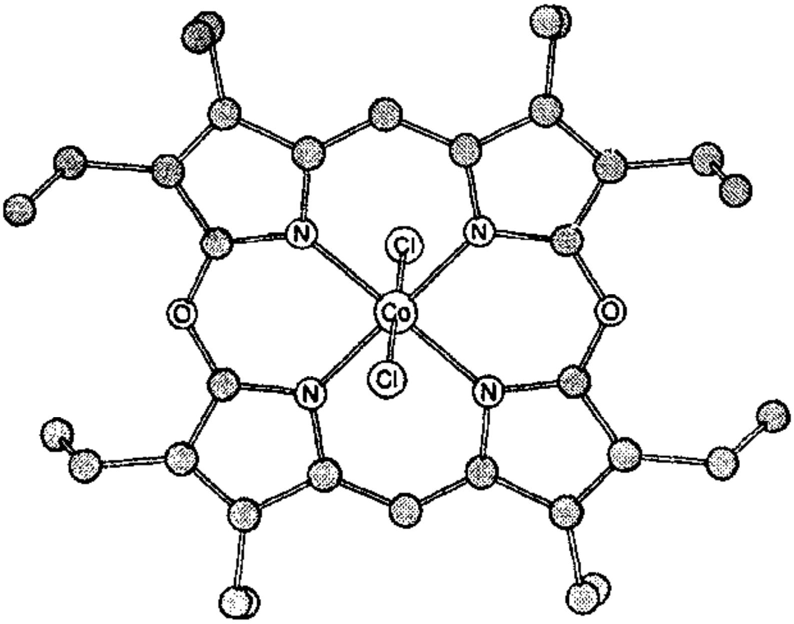
Co[TMpyP(4)] R =

Other R groups = $C_6H_5$
$4\text{-}CF_3C_6H_4$
$4\text{-}MeC_6H_4$
$4\text{-}MeOC_6H_4$

**(29)**

The crystal structure of the complex [Co(OEP)(DMAP] (31), where $OEPH_2$ = octaethylporphyrin and DMAP = 4-(*N*,*N'*-dimethylamino)pyridine has been determined along with others containing Co–C bonds allowing comparisons with similar vitamin $B_{12}$ systems [77]. It was found to have a distorted square pyramidal arrangement around the Co with a small displacement of the angle of the axial Co–N bond from the vertical.

EXAFS has been used to study the coordination around cobalt in the complexes



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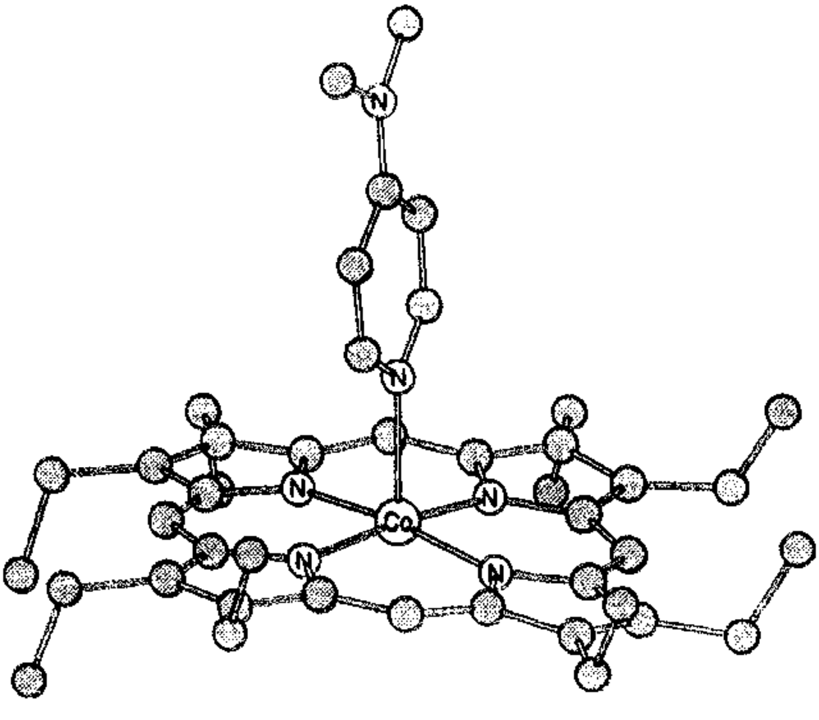
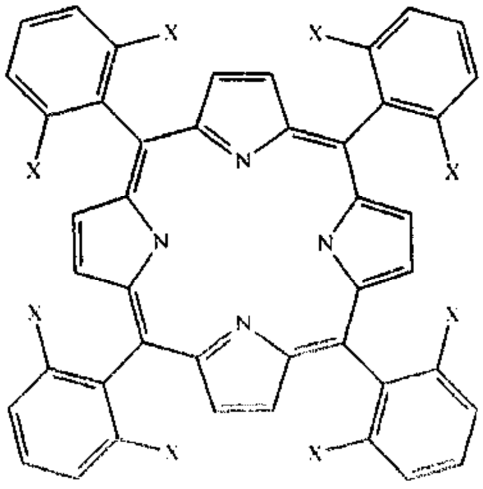


(31)

chloro(phthalocyaninato)cobalt(III) and chloro(pyridine(phthalocyaninato)cobalt(III) [78]. The data obtained have been used to investigate ring currents in the structure and to test the phthalocyanine ring current model. An EXAFS study has also been carried out on a series of porphinato cobalt(II) complexes dissolved in chloroform [79]. The complexes concerned were chloro(tetraphenylporphinato)cobalt(III) being complexed with the ligands py, isoquinoline or cyclohexylamine, chloro(tetra-*o*-dichlorophenylporphinato)cobalt(III) containing the ligand methylpiperidine and chloro(tetra-*o*-difluorophenylporphinato)cobalt(III) (**32**). In some of the species studied the Cl was coordinated and in others was the counterion. In addition, data for some similar Co(II) complexes were compared. The equatorial Co–N distances varied according to the conformation of the porphyrin rather than the oxidation state of the Co. There was good correlation between the crystal structure data for the complexes (tetra-*o*-dichlorophenylporphinato)cobalt(II) and (tetra-*o*-difluorophenylporphinato)cobalt(II) and the EXAFS data in solution.

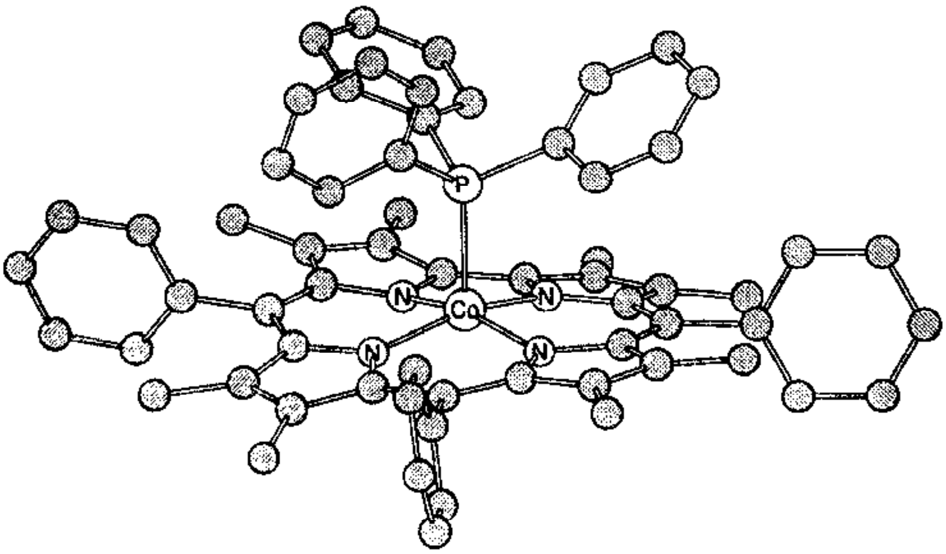


X = H TPPCoCl
X = F TFPCoCl
X = Cl TClPCoCl

**(32)**

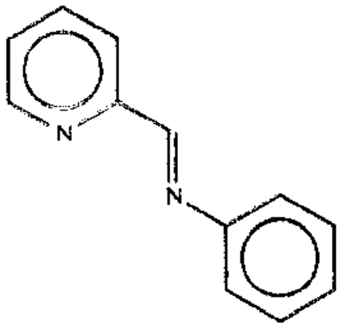
Starting with a monopyrrolic unit a self condensation to form a pyrrole ring has been achieved for the first time resulting in the complex (triphenylphosphine)(5,10,15-triphenyl-2,3,7,8,12,13,17,18-octamethylcorrolato)cobalt(III), [Co(OMTPC)PPh$_3$] [80]. The X-ray crystal structure of the complex in the form [Co(OMTPC)PPh$_3$]·CH$_2$Cl$_2$, (**33**)·CH$_2$Cl$_2$, has been obtained.

Two major products result from the reaction of L-b-[Co(*R*,*R*-picchxn)Cl$_2$]$^+$ with pyridine-2-carboxaldehyde-*N*-phenylimine (pcp) (**34**), where *R*,*R*-picchxn = *N*,*N*′-di(2-picolyl)-*R*,2*R*-diaminocyclohexane [81]. These were separated chromatographi-



**(33)**

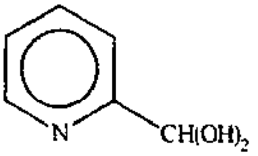
cally and the first fraction was a salt of L-b-[Co($R,R$-picchxn)pcp)]$^{3+}$, and was formed stereospecifically. The second was crystallized as L-b2-[Co($R,R$-picchxn)($R$-hpm)](ClO$_4$)$_2$ · H$_2$O and its crystal structure determined. The ligand hpm is shown in (**35**), and the crystallographically determined structure of the dication of the deep red complex is shown in (**36**).



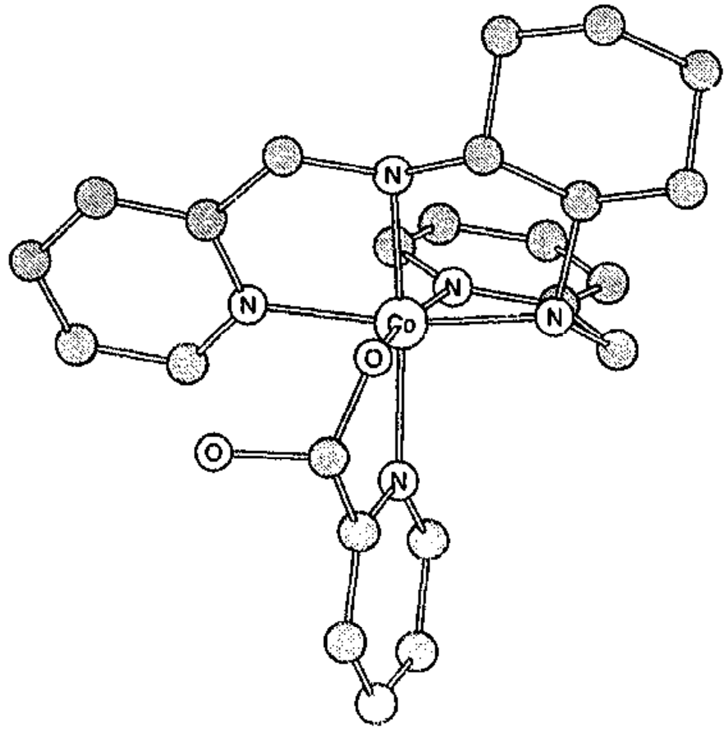
**(34)**

The X-ray structure of the complex [Co(ox)(cyclam)](NO$_3$) (H$_2$ox = oxalic acid) has been obtained [82]. It crystallises in an orthorhombic system, with $a = 8.583$, $b = 12.854$, $c = 14.944$ Å, $V = 1649.3$ Å$^3$, $Z = 4$. The structure shows a *cis* configuration for the oxalate ligand involving a folded cyclam configuration around the cobalt. It is suggested that cyclic voltammetry indicates that the complex would be a catalyst for reduction of carbon dioxide electrochemically.

Electrodes have been constructed using Nafion and bentonite clay coatings containing the photosensitizer [Ru(bpy)$_3$]$^{2+}$ [83]. This was then used in a photochemical



**(35)**

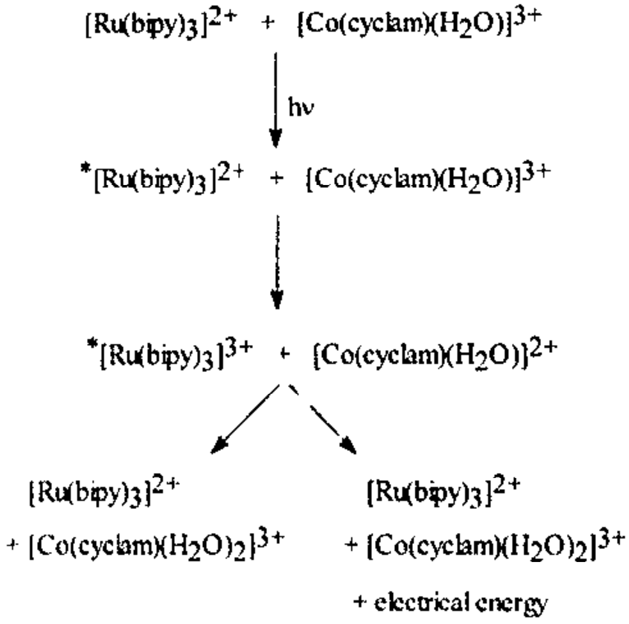


**(36)**

cell with Pt-nf-$[Ru(bpy)_3]^{2+}$ and Pt-bt-$[Ru(bpy)_3]^{2+}$ electrodes and having $[Co(cyclam)(H_2O)_2]^{3+}$ and $Fe^{3+}$ as electron relays. The photochemical behaviour observed indicates electron transfer reactions involving $[Ru(bpy)_3]^{2+}$ and $[Co(cyclam)(H_2O)_2]^{2+}$. On exposure to light the reactions which occur are shown in scheme (**37**).

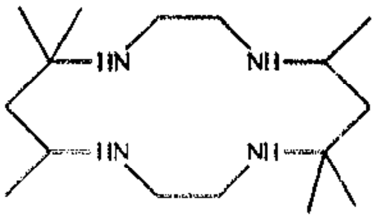
The cobalt(III) cyclam complex has also been used in a Nafion (R) film to catalyse the reduction of nitrate in concentrated NaOH solution and the rate constant for the electrocatalytic reaction determined [84].

Unexpectedly the reaction between $[(rac\text{-}Me_6[14]aneN_4)CoCl_2](ClO_4)$ where $Me_6[14]aneN_4$ is (**38**) and α-amino-α-methylmalonate(AMM) does not produce the AMM complex but for the 2-iminopropionato complex (**39**) [85], whether or not the 2-iminopropionato complex is produced depends upon the nature of the tetra-



**(37)**

amine ligand. Unsubstituted ligands do not appear to produce this species indicating stereochemical modification of the complex.

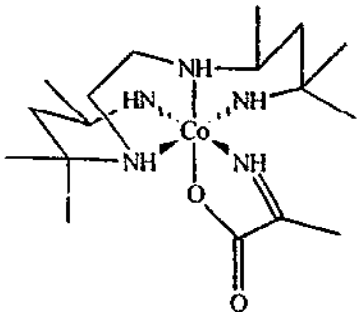


$Me_6[14]aneN_4$

**(38)**

A whole series of *cis* and *trans*-complexes of the form $[Co(3,2,3\text{-tet})XY]^{n+}$ in which 3,2,3-tet = 1,10,4,7-diazadecane and XY = $(Cl)_2$, $(Br)_2$, $(NO_2)_2$, $(N_3)_2$, $(CN)_2$, $(OCN)_2$, $(SCN)_2$, $(NH_3)_2$, $(NO_2)Cl$, $(NO_2)Br$, $(NO_2)(SCN)$, $(CH_3COO)_2$, $(C_6H_5CO)_2$, $(CO_3^{2-})$, $(C_2O_4^{2-})$, have been synthesized and characterized [86]. The $CO_3^{2-}$ and $C_2O_4^{2-}$ complexes were shown to be *cis* with the remainder being *trans*.

The X-ray crystal structure of the complex *trans*-dichloro [(2*RS*,5*RS*,9*SR*,12*RS*)-2,5,9,12-tetraazatridecane]cobalt(III) perchlorate shows that conformations of the alternate 5-,6- and 5-membered chelate rings are skew, chair and skew respectively [87].

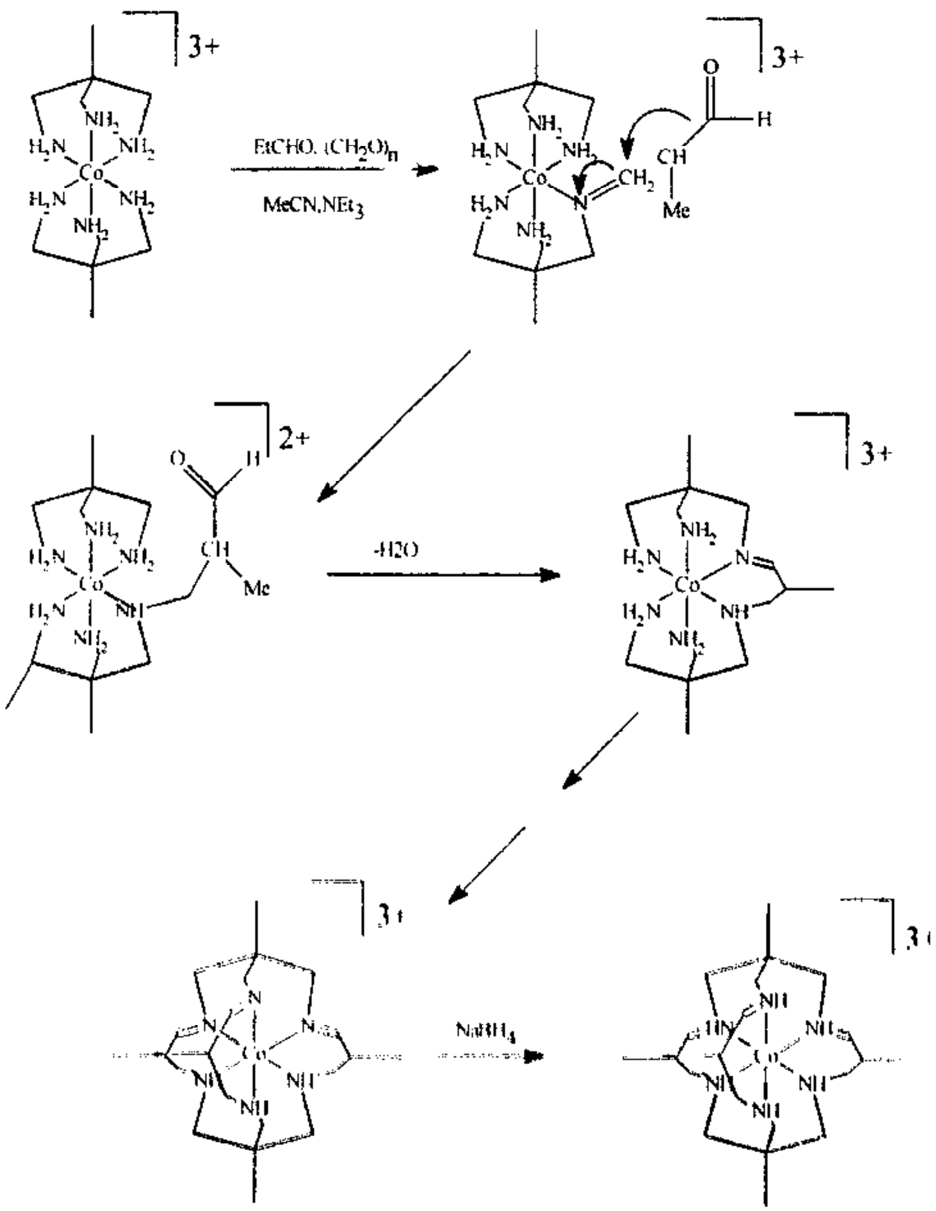


**(39)**

α-Imino acidato complexes have been found to be the products of the oxidation of a range of α-amino acidate (such as phenylglyanate, alaninate, valinate, *N*-methylalaninate, prolinate) Co(III) complexes of 2,3,2-tet (3,7-diazanonane-1,9-diamine) [88].

The base hydrolysis of the complex (αβS)-(*o*-methoxybenzoato)(tetren)cobalt(III) (tetren = tetraethylenepentamine) has been the subject of two studies involving the effect of mixed solvents [89] and of micelles [90]. In the former study the effect on the kinetics of variation of the ratio of water/solvent (solvent = methanol, ethanol, propan-l-ol, butan-1-ol, *tert*-butanol, ethyleneglycol, 2-methoxyethanol, acetone, acetonitrile, 1,4-dioxane and dimethylsulfoxide. All but the ethylene glycol/water caused an increase in the second order rate constant of the reaction which was nonlinear in mole fraction. The data are interpreted in terms of the solvation of the transition and initial states. The effect of micelles on the reaction was investigated relative to that of a number of anions of varying charge and basicity. These had either an accelerating or no effect on the rate of the reaction while the micelles (SDS, CTAB and Triton x-100) all showed the reaction in the order SDS > CTAB > Triton-100.

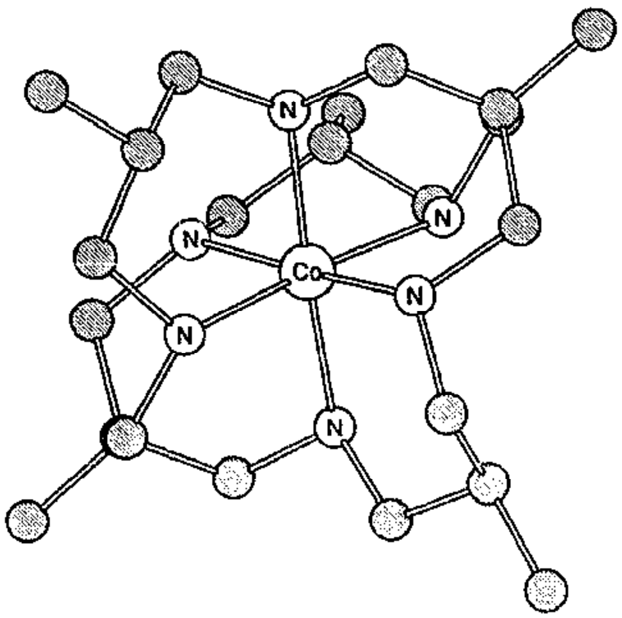
In an encapsulation which involved the process shown in (**40**) a product which had an enlarged cavity was produced by reducing the species containing Co(III)–N=CH– links [91]. The X-ray crystal structure of the final product of this synthesis, [Co{*fac*-(Me)$_5$-D$_{3h}$tricosaneN$_6$}](PF$_6$)$_3$ (where *fac*-(Me)$_5$-D$_{3h}$tricosane N$_6$ = *fac*-1,5,9,13,20-pentamethyl-3,7,-11,15,18,22-hexaazabicyclo[7.7.7]tricosane) was determined; the cation is shown in (**41**). The Co–N bonds were found to be significantly longer than similar complexes such as $[Co(NH_3)_6]^{3+}$ or $[Co(en)_3]^{3+}$ etc. The cation was readily reduced to the cobalt(II) complex and the rate of electron exchange was found to be $k_{ex} = 0.40$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 25°C. The favourable Co(III)/Co(II) reduction has been confirmed using molecular mechanics calculations to be due to destabilization of the Co(III) state [92]. In a related study the X-ray crystal structure of the complex (1-hydroxy-8-methyl-3,6,10,13,15,18-hexaazabicyclo[6.6.5]nonadecane)cobalt(III) trichloride hydrate, [(**42**)]Cl$_3$ · H$_2$O, which has a contracted cavity cage, has been determined [93]. The base hydrolysis of the complex was found to result in the deprotonation of one of the coordinated second-



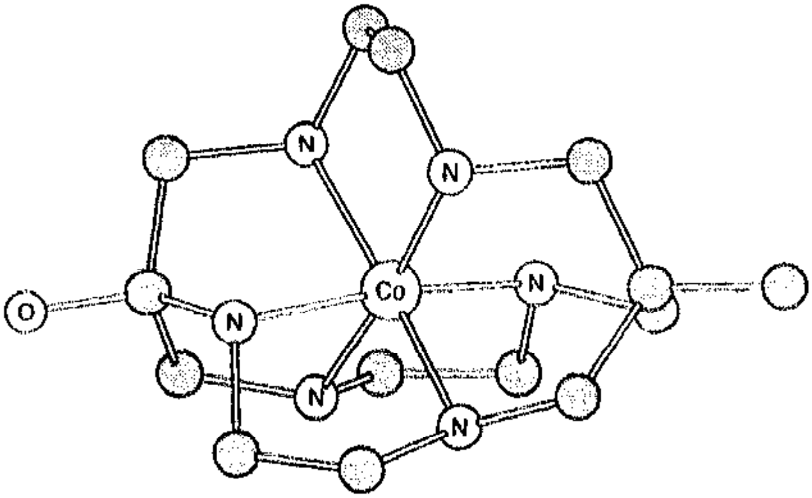
**(40)**

ary amine groups which then underwent a retro-Mannich type reaction and imine hydrolysis with intermediates consisting of two isomers with a pendant arm macrocyclic structures.

Free sarcophagine and 1,8-diaminosarcophagine have been obtained by reduction of the Co(III) complex to the Co(II) species followed by treatment by $CN^-$; the crystal structure of the free bases have been obtained [94]. The reaction between zinc powder and the complex ion $[Co(III)(Cl_2Sar)]^{3+}$ in which $Cl_2Sar$ = 1,8-dichloro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane resulted in a series of complexes of the form $[CoCl_2(N_4)]$ ($N_4$ = 6,13-dimethylene-1,4,8,11-



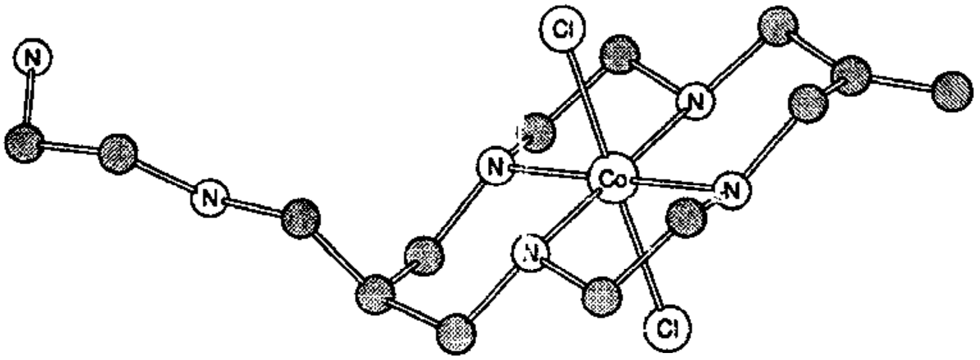
(41)



(42)

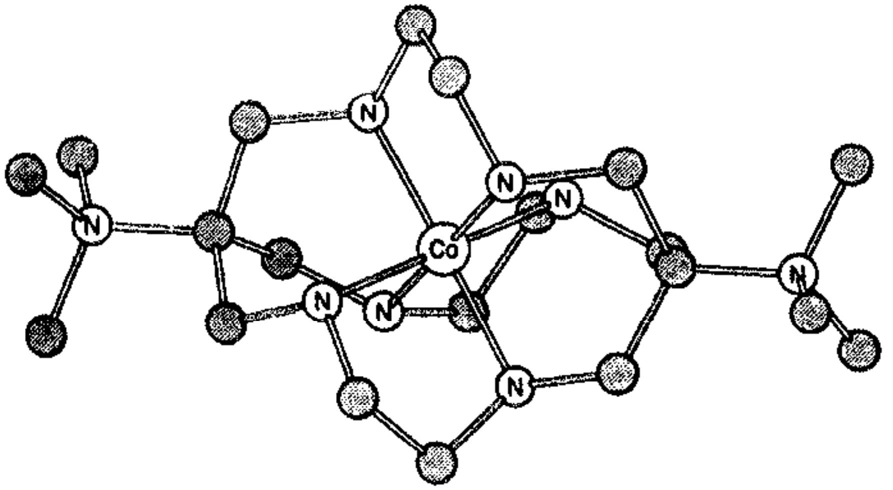
tetraazacyclotetradecane) [95]. Thus for the complex *trans*-[CoCl$_2$(N$_4$)] three different isomers were obtained which were shown using $^{13}$C NMR spectroscopy to be due to different configurations about the asymmetric *N*-donor centres. The X-ray crystal structure of the trichoride complex of *trans*-[CoCl$_2$(H$_2$L)]$^{3+}$ (**43**), in which H$_2$L$^{2+}$ = 6-(4-ammonio-2-azoniabutyl)-13-methylene-1,4,8,11-tetraazacyclotetradecane was also determined.

In a related study, cage complexes which contain dimethylamino substituents ([Co{(NMe$_2$)$_2$Sar}]$^{3+}$ and [Co{(NMe$_2$,Me)Sar}]$^{3+}$ {(NMe$_2$)Sar = 1,8-bis(dimethy-



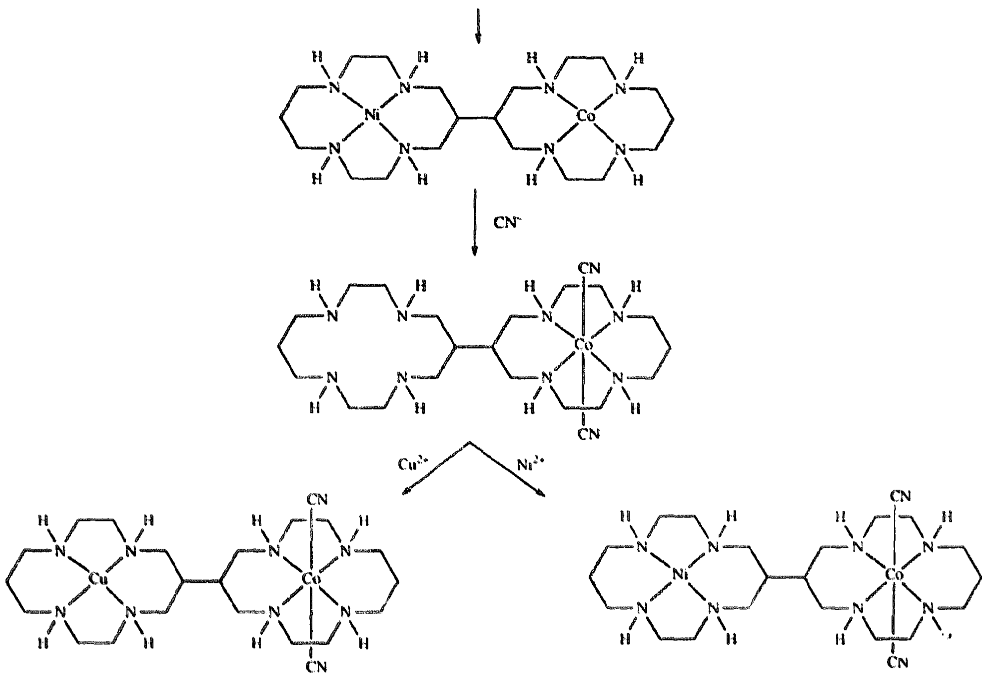
(43)

lamino)sarcophagine and (NMe$_2$,Me)Sar = 1-(dimethylamino)-8-methylsarcophagine} have been obtained in high yields by reacting the corresponding amino complexes with HCHO/NaNCBH$_3$/acetic acid in acetonitrile or refluxing with HCOOH/HCHO and when chiral precursors were used pure chiral forms were produced [96]. Further methylation was achieved using MeI and DMSO to give the trimethylammonium complex, and the X-ray crystal structure showed the ob$_3$ conformation; (**44**) shows the structure of [Co{(NMe$_3$)$_2$Sar}]$^{5+}$. The redox potential of the *ob*$_3$-[Co{(NMe$_3$)$_2$Sar}]$^{5+}$ is some 250 mV greater than that of *ob*$_3$-[Co{(NH$_3$)$_2$Me$_3$Sar}]$^{5+}$ while the electron exchange rate is much slower than that of any other hexaamine cage complex of this type, though faster than complexes of the type [Co(en)$_3$]$^{3+/2+}$.



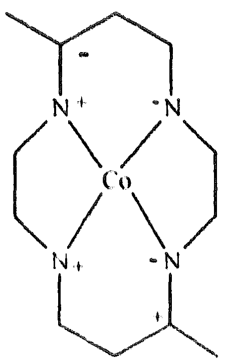
(44)

Two heteronuclear complexes containing Co(III)–Ni(II) and Co(III)–Cu(II), illustrated in the scheme shown in (**45**), have been prepared and characterized using mass spectrometry [97]. The last step in the process in each case utilizes a so-called "lariat" complex to take in the other metal ion.



(45)

The X-ray crystal structure of the complex *cis*-dichloro(*c*-*rac*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴)cobalt(III)chloride shows that the ligand is in a *cis*-folded conformation [98]. The corresponding *trans* diastereoisomer has also been prepared [99]. The structure of *trans*-dichloro(*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(III) ion (46) has been determined. The kinetics of the aquation of the complex are interpreted in terms of a dissociative activation resulting in configuration retention and a distorted square pyramidal activated complex is suggested.



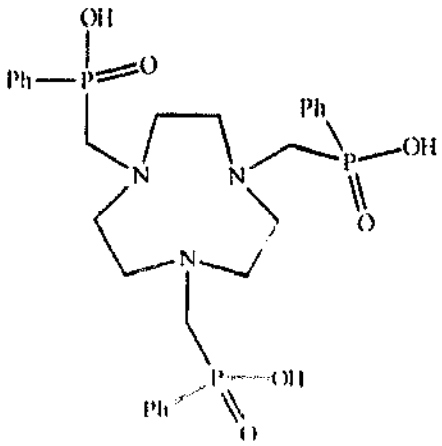
(46)

The Marcus-Hush theory has been used in the interpretation of rate data for the kinetics of the heterogeneous outer sphere redox reaction:

$$[Co(tacn)_2]^{3+} + e \rightarrow [Co(tacn)_2]^{2+}$$

(tacn = 1,4,7-triazacyclononane) and in which similar data are provided for the corresponding Fe, Ni and Ru complexes [100]. The reactions were carried out in NaF solutions and the variation of the standard heterogeneous rate constants varied with concentration of NaF in such a way that implies a combination of electrical double layer and ion-pairing effects with the electrical double layer being the most prominent. The contribution of the inner-shell to the process was determined by measuring the variation of the standard heterogeneous rate constants with temperature and subtracting 15 kJ mol$^{-1}$ for the outer-shell contributions.

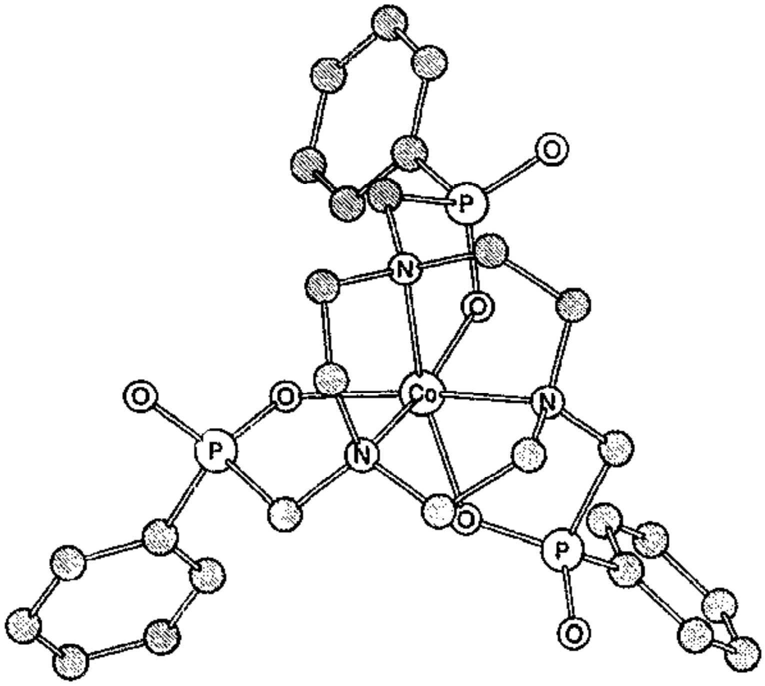
The pink complex $[H_3O][CoL]\cdot 4H_2O$, where L is shown in (**47**), slowly oxidizes in air or more rapidly by hydrogen peroxide to the blue complex $[CoL]\cdot 5H_2O$ [101]. The structures of these two rather unusual complexes are shown (**48**) and (**49**).



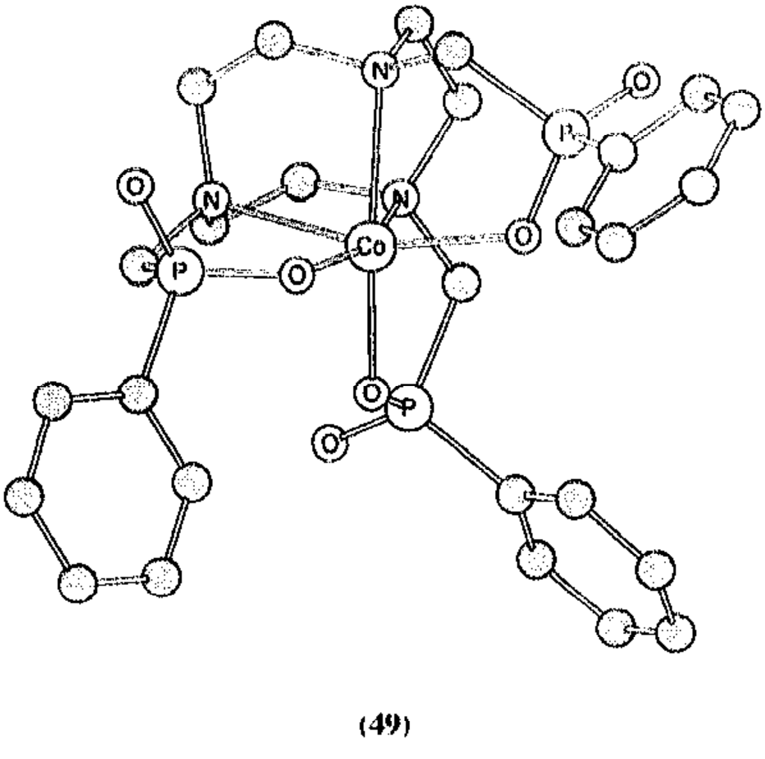
$H_3L^1$

**(47)**

The study of transition metal ion complexes with polyalcohols is notoriously difficult but a detailed study of reactions involving the complex $[Co(tach)]^{3+}$ (**50**) has provided valuable information on species involving *cis*-inisotol and its derivative 1,3,5-triacetamido-1,3,5-trideoxy-*cis*-inisotol (taino) (**51**) [102]. $[Co(tach)Cl_3]$ is a blue insoluble compound which when reacted with $AgNO_3$ produces the red complex $[Co(tach)(CH_3OH)_3]^{3+}$. This may then be reacted with *cis*-inisotol or 1,3,5-triacetamido-1,3,5-trideoxy-*cis*-inisotol to give the species shown in (**52**). $[Co(taino)_2]^{2+}$ crystallizes as the dinitrate tetrahydrate or the equivalent octahydrate. The X-ray crystal structures of all these complexes were determined and are shown

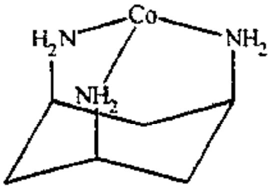


**(48)**



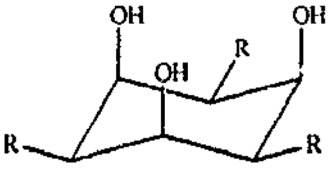
**(49)**

in (**53**), (**54**) and (**55**). NMR spectroscopic data, p$K_a$ values and molecular modelling studies of these systems are also reported.



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

**(50)**

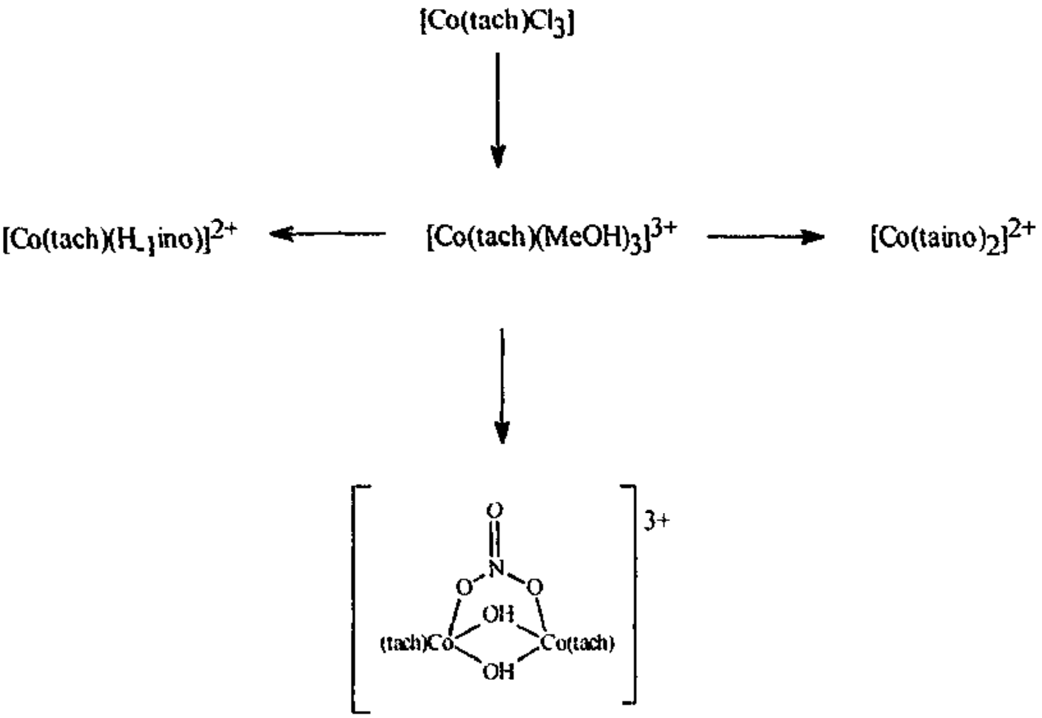


ino R = OH

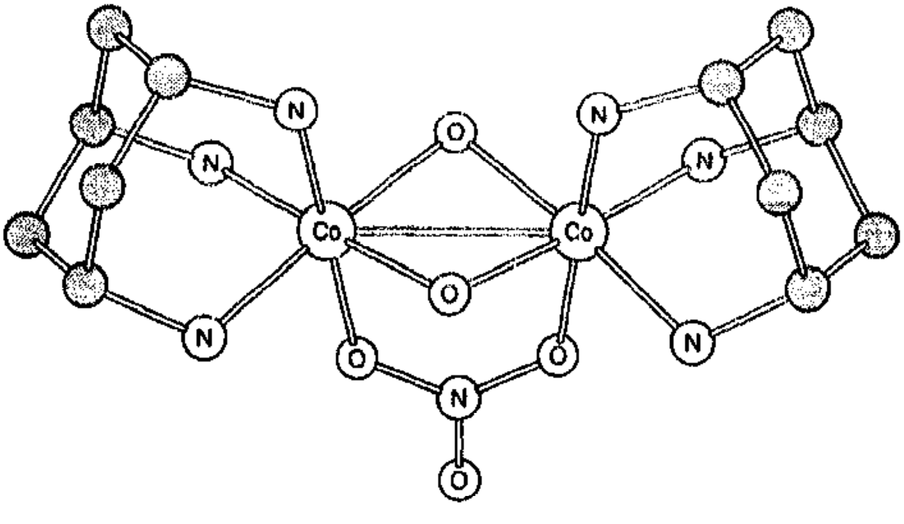
taino R = NHCOMe

**(51)**

The group of cancer-treating drugs called bleomycin attract particular interest to coordination chemists because their mode of action is believed to involve the scission of DNA strands in the presence of Fe(II) and $O_2$, while Co(III) bleomycin complexes cause DNA scission, not in the presence of $O_2$ but under the influence of UV radiation [103]. In the absence of X-ray crystallographic data the metal-bonding region in bleomycin is believed to be that shown in (**56**). Mascharak and coworkers have attempted to model this bonding area using the ligand PMAH (**57**) and have prepared a series of Co(III) complexes, most notably the dichloride of $[Co(PMA)(Int\text{-}A)]^{2+}$, the structure of which is shown in (**58**). These complexes also inflict DNA scission in the presence of UV radiation, but the Int-A species is significantly more successful in doing this. Using NOESY and COSY NMR techniques, these workers have investigated the extent to which the Int-A complex shows specificity in the DNA strand scission using the oligonucleotide $[d(GATCCGGATC)]_2$, which has a GG-N site. They found that the acridine part of the cobalt complex intercalates into the oligonucleotide and that while there it is usually to be found between G6 and G7; the DNA cleavage experiments show that

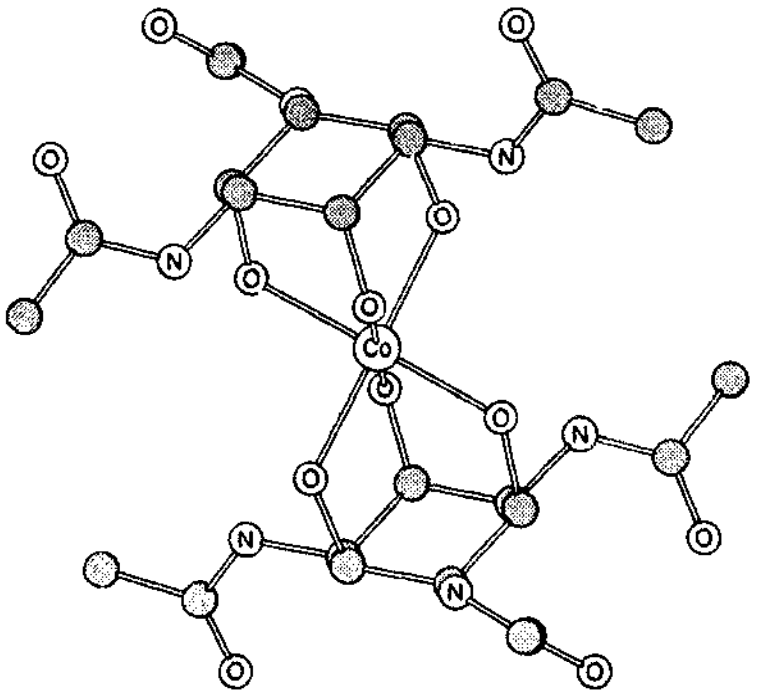


**(52)**

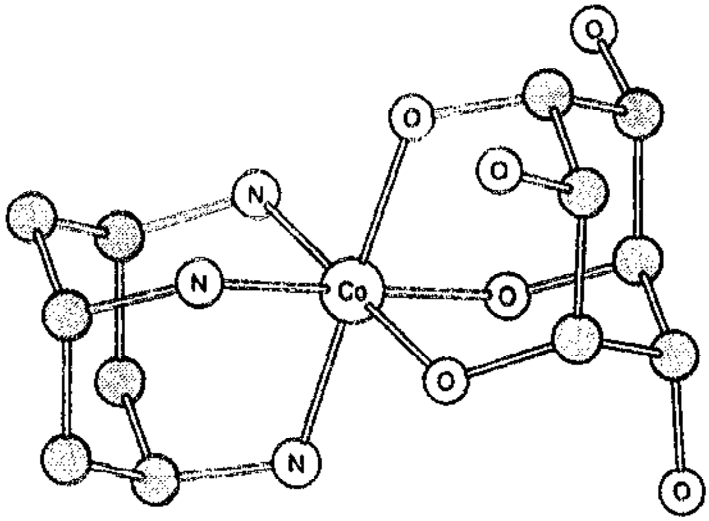


**(53)**

it is here that photo-damage occurs. It is inferred from the experimental data that the $[Co(PMA)]^{2+}$ adheres to the backbone of the oligonucleotide by electrostatic interaction. In a related study, empirical force field calculations have been applied to bleomycin bonding to Co [104] and these show that both the most recently



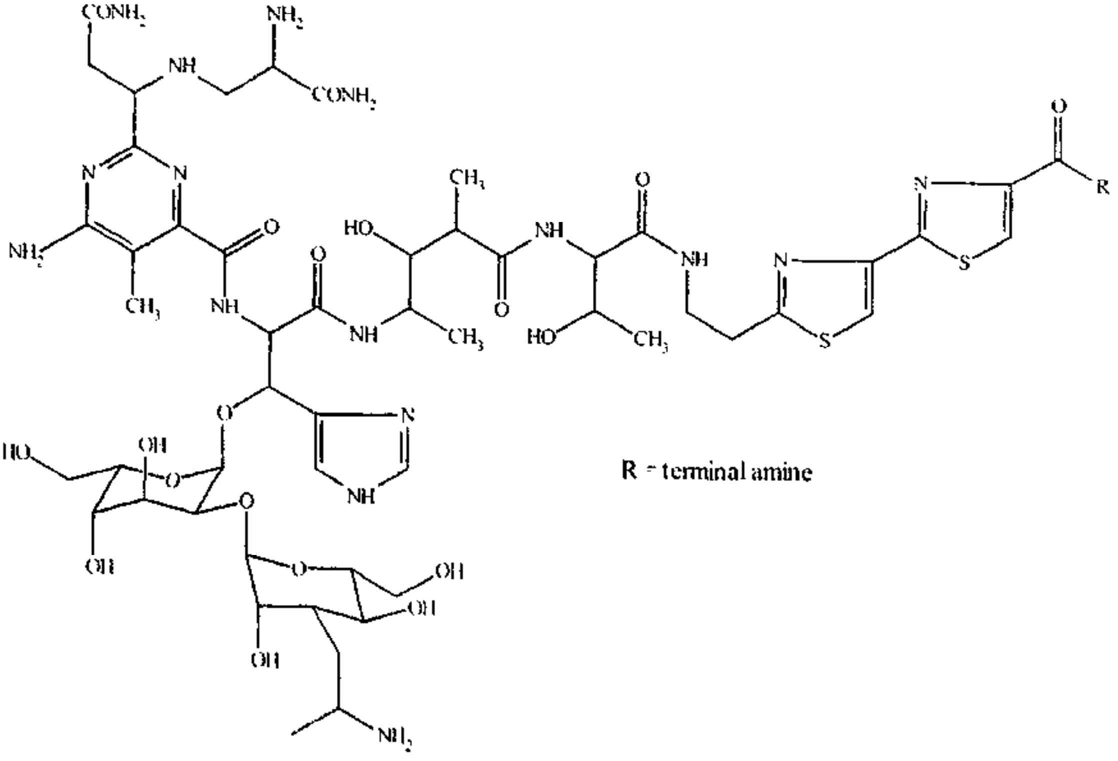
**(54)**



**(55)**

proposed coordination sites in bleomycin [105] were possible and that although varying the metal charge affected the conformation of the bleomycin this could not be as significant in conformational terms as the effect of the two different binding site.

The light activated scission of DNA by cobalt bleomycin has also been studied using a variety of synthetic DNA fragments which have (AT)n and (GC)n [106].



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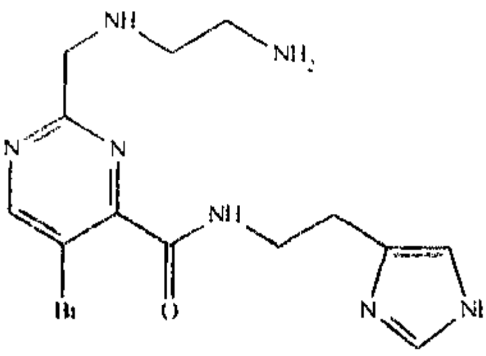
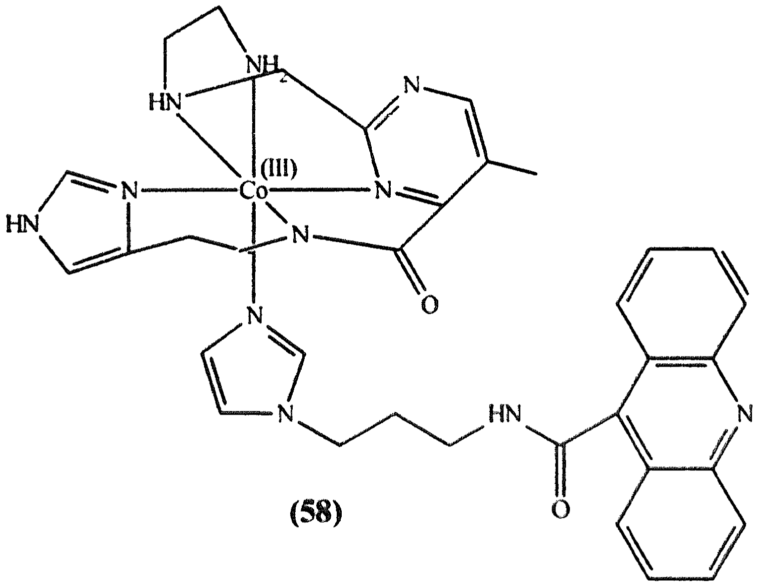


**(57)**

There are found to be differences in the cleaving ability of the Co-bleomycin depending on the amino acid sequence. Thus ApT is cleaved when there are alternating AT residues, but other sequences do not allow ready cleavage. It is suggested that bleomycin is bound more tightly to GpT than to ApT. The authors suggest that the process proceeds via a stoichiometric mechanism rather than a catalytic one and the binding site consists of a small number of base pairs, typically four and sometimes three.

It has been found that the oxidation of Co(II)bleomycin A2 by $O_2$ yields both

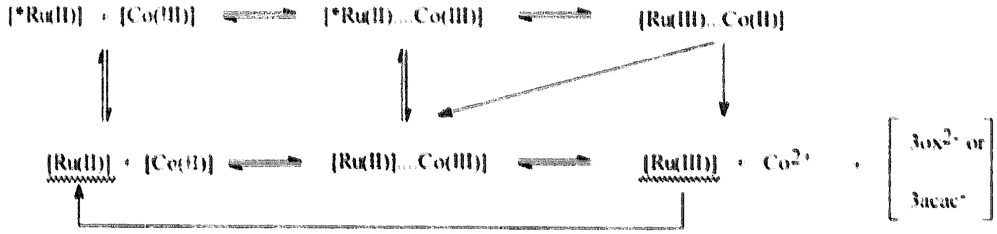


**(58)**

$HO_2^-$ Co(III)bleomycin A2 (form II) and Co(III)bleomycin A2 (form II) [107]. Using NOESY spectra and molecular dynamics calculations it was shown that in form I the bithiazole group is folded back across the square pyramid around the Co(III), a feature which does not appear to be present in form II, but in both forms the authors find significant folding of the peptide link between the Co(III) and DNA binding domains.

## 2.2. *Complexes with oxygen donor ligands*

When $[Co(ox)_3]^{3-}$ and $[Co(acac)_3]$ are decomposed by photoinduction in the presence of optically active $[Ru(bpy)_3]^{2+}$ it has been found that the process is stereoselective [108]. In the case of $[Co(ox)_3]^{3-}$ the preference was for Δ–Δ or Λ–Λ whereas for $[Co(acac)_3]$ there was a Δ–Λ heterochiral preference. The processes involved in the photosensitized decomposition are believed to be those shown in (**59**).



**(59)**

The homochirality of the $[Co(ox)_3]^{3-}$ reaction was found to change to a heterochiral preference on the addition of organic solvent to the aqueous solution whereas the $[Co(acac)_3]$ process remained heterochiral. The authors conclude that back electron transfer is the key factor in establishing heterochiral stereoselectivity and therefore the controlling features are the relative rates of back electron transfer and decomposition. The complex ion $[Co(ox)_3]^{3-}$ along with $[Co(ox)_2en]^-$ and $[Co(mal)_2en]^-$ have been investigated in various solvents using K-edge XAFS and XANES (X-ray Absorption Near-Edge Structure) [109]. It is concluded that the Co–O distance varies with different solvents in accordance with the variation of Gutmann's acceptor number and in a way which is in accord with the effect of solvent on the d–d absorption spectrum of $[Co(ox)_3]^{3-}$.

The complex ion $[Co(glyO)(ox)_2]^{2-}$, where glyO = glycinate, undergoes reduction by $[Co(phen)_3]^{2+}$ and related species such that the rate of electron transfer is faster than the racemization of the products, thus allowing a study of the possibility of chiral induction [110]. The kinetics of the outer sphere reactions show overall second order behaviour with values shown in Table 2. There was found to be a 37% enantiomeric excess of the Δ isomer in the $[Co(phen)_3]^{3+}$ product when Δ-$[Co(glyO)(ox)_2]^{2-}$ was the oxidant.

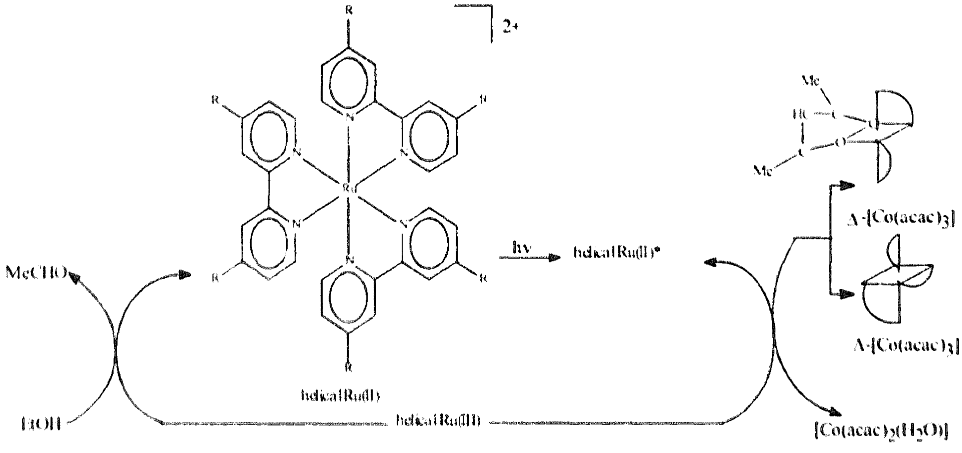
Boron difluoride β-diketonates [111] have been used in the preparation of cobalt(III) β-diketonates. The effects of γ-substitution by halogens in $[Co(acac)_3]$ complexes have been investigated in the vapour phase using X-ray emission spectroscopy [112]. Investigation of liquid secondary-ion mass spectrometry of six cobalt(III) β-diketonates in 3-nitrobenzyl alcohol [113] shows the presence of the molecular ion $[CoL]^{3+}$ and also $[Co_2L]^{4+}$ and $[Co_2L]^{3+}$. When two different cobalt(III) complexes were examined together mixed species ions were observed. Gas phase mass spectrometry has also been used in the study of chiral recognition in a number of diastereomeric cobalt(III) complexes [114]. Measurement of the kinetic energy release using the species produced by complexing four alkyl tartrate esters with $[Co(acac)_3]$ in the presence of *RR*- and *SS*- *threo*-hydrobenzoin showed different Ker values of the ion produced from $[Co(acac)_2$(D- or L-diisopropyltartrate)$]^+$ depending on the structure of the precursor ion. This chiral recognition only operates for an octahedral cobalt complex. The X-ray crystal structure of *cis*-$[Co(acac)_2(NH_3)_2]I \cdot H_2O$ shows that it crystallizes in space group $P1$ and has $a = 9.714$, $b = 9.885$, $c = 10.449$ Å, $\alpha = 69.12$, $\beta = 67.83$, $\gamma = 65.48$, and $Z = 2$, while $[Co(acac)_2(en)]ClO_4$ crystallizes in monoclinic space group $P2_1/c$ and $a = 12.756$, $b = 7.389$, $c = 19.76$ Å, $\beta = 102.55°$ and $Z = 4$ [115]. Structural data were calculated using molecular mechanics with good agreement with the experimental data allowing isomer ratios and solution structures of a series of β-diketone complexes to be determined.

A composite of L-tartaric acid and silica prepared using the sol-gel technique has been shown to be successful in distinguishing the chirality of $[Co(acac)_3]$ [116].

Table 2.

| Reductant | $k_2/dm^3\,mol^{-1}\,s^{-1}$ |
|---|---|
| $[Co(phen)_3]^{2+}$ | 0.14 |
| $[Co(4,7\text{-}dmphen)_3]^{2+}$ | 6.5 |
| $[Co(5,6\text{-}dmphen)_3]^{2+}$ | 2.3 |

Efficient stereoselective photoreduction of *rac*-[Co(acac)$_3$] (molecular helicities P(C$_3$) for $\Delta$ and M(C$_3$) for $\Lambda$) has been obtained using a series of diastereomeric Ru(II) photocatalysts *rac*- [Ru(L$^1$)$_3$]$^{2+}$ or $\Delta$-[Ru(L$^1$)$_3$]$^{2+}$ in which L$^1$=4,4$^1$di[(1R,2S,5R)-(-)-menthoxycarbonyl]-2,2'-bipyridine and also *rac*-[Ru(L$^{II}$)$_3$]$^{2+}$ or $\Delta$-[Ru(L$^{II}$)$_3$]$^{2+}$ or $\Lambda$-[Ru(L$^{II}$)$_3$]$^{2+}$ in which L$^{II}$=4,4'-di[(R)-(+){or(S)-(-)}-1-phenylethylaminocarbonyl) [117]. The species were shown using molecular mechanics to exhibit either P(C$_3$) or M(C$_3$) helical symmetry. The mechanism proposed for the photocatalytic process is shown in scheme (**60**).



(**60**)

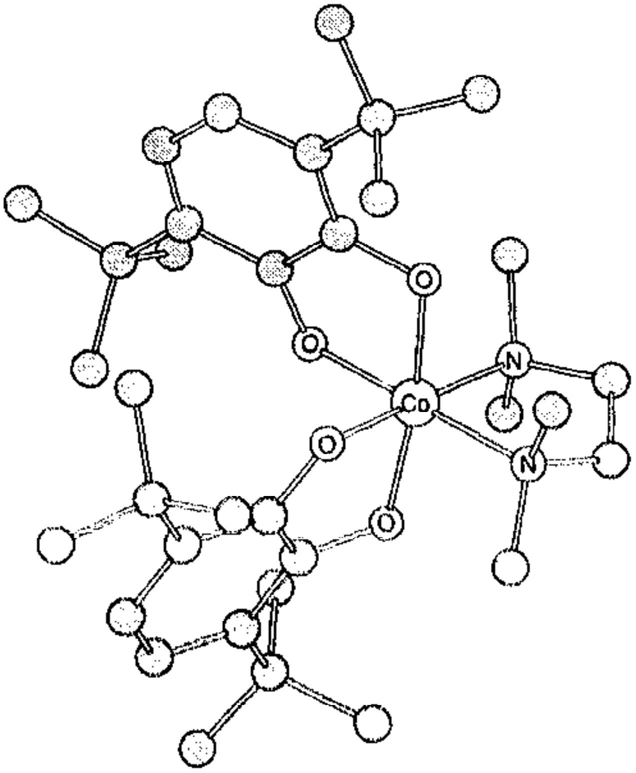
The X-ray crystal structure determination of tris(1,3-diphenylpropane-1,3-dionato)cobalt(III) [118] shows that it crystallizes in a triclinic system with space group P1 and $a=9.851$, $b=10.647$, $c=18.008$ Å, $\alpha=93.44$, $\beta=94.91$, $\gamma=107.14°$, and $Z=2$. The kinetics of the reduction of [Co(acac)$_3$] by aquatitanium(III) and acetatotitanium(III) ions in acidic aqueous solution have been studied [119].

Reaction of [Co(L)Cl$_3$]·H$_2$O with Na[acac] yields red crystals of [{CoL(acac)}$_2$($\mu$-H$_3$O$_2$)][PF$_6$]$_3$ [120]. The X-ray crystal structure of this complex shows that the structure is very similar to the corresponding Cr(II) complex even down to the packing of the PF$_6^-$ ions. However, unlike the Cr(III) complex, the Co(III) species did not show a solid state transformation to the mononuclear complex when heated to its melting point.

The X-ray crystal structure of the complex tris(3,6-di-*tert*-butylsemiquinonato)cobalt(III) [Co(DBSQ)$_3$] shows an octahedral structure having D$_3$ symmetry, monoclinic $C2/c$, $a=21.799$, $b=19.376$, $c=10.167$ Å, $\beta=9.4.99°$, $V=4278$ Å$^3$ and $Z=4$ [121]. In a comparison of the exchange interaction between radical ligands involving Al, Ga, Co and Zn it is concluded that d-orbital participation in metal-semiquinone $\pi$-bonding is important. In a related study Pierpoint and co-workers have investigated subtle co-ligand bonding effects in low-energy cobalt(III)-catechol electron transfer [122]. The complexes studied were [Co(N-N)(3,6-DBSQ)(3,6-DBCAT)] in which N-N=phen or 5-nitro-1,10-phenanthroline (NO$_2$phen) and DBCAT=di-*tert*-butylcatecholato. Pierpoint and co-workers have also investigated intramolecular cobalt-quinone electron transfer in similar complexes to those above in which N-N = 2,2′-bipyridine, *N,N,N′,N′*-tetramethylethylenediamine (tmeda), bis(2-pyridyl)ketone, dipyrido[3,2-a:2′,2′-c] phenazine, 4,5-diazafluoren-9-one as well as phen and $NO_2$phen [123]. In these complexes infrared absorptions in the region of 4000 $cm^{-1}$ are ascribed to cat→Co(III) charge transfer bands, while in toluene solution changes in the spectrum suggest the equilibrium:

$$\mathrm{Co(III)(N-N)(SQ)(Cat)} \rightleftharpoons \mathrm{Co(II)(N-N)(SQ)_2}$$

which in some complexes was also observed in the solid state and affected by the nature of the nitrogen donor ligand. The X-ray crystal structures of [Co(tmeda)(3,6-DBSQ)(3,6-DBCat)] **(61)** and [Co($NO_2$phen)(3,6-DBSQ$)_2$]·2.2toluene have been determined.



**(61)**

A study of the effect of variation of the optical spectrum of the polymer [Co(pyz)(3,6-DBQ$)_2$$]_n$ (3,6-DBQ = 3,6-di-*tert*-butyl-1,2-benzoquinone and pyz = pyrazine) with temperature revealed that internal electron transfer occurs producing a Co(III)/Co(II) shift, the former being increasingly favoured at temperatures below 350 K [124]. The transition may be induced by light and this produces a change in the Co–N bond length which when multiplied along the length of the polymer results in 0.06 mm change per mm of polymer length and is manifested as a reversible distortion of the crystal under irradiation from a tungsten–halogen lamp.

The kinetics of the oxidation of $(NH_2)_2CS$ and $(Me_2N)_2CS$ to the disulfides by $[Co(III)W_{12}O_{40}]^{5-}$ have been studied in acidic aqueous solution [125]. A mechanism involving free radicals is proposed. $[Co(III)W_{12}O_{40}]^{5-}$ has also been used as the oxidant in its reaction with ethylenediaminetetraacetic acid in which $CO_2$, $CH_2O$ and $(CH_2NH_2)_2$ were the major products [126] for which the kinetics have been determined.

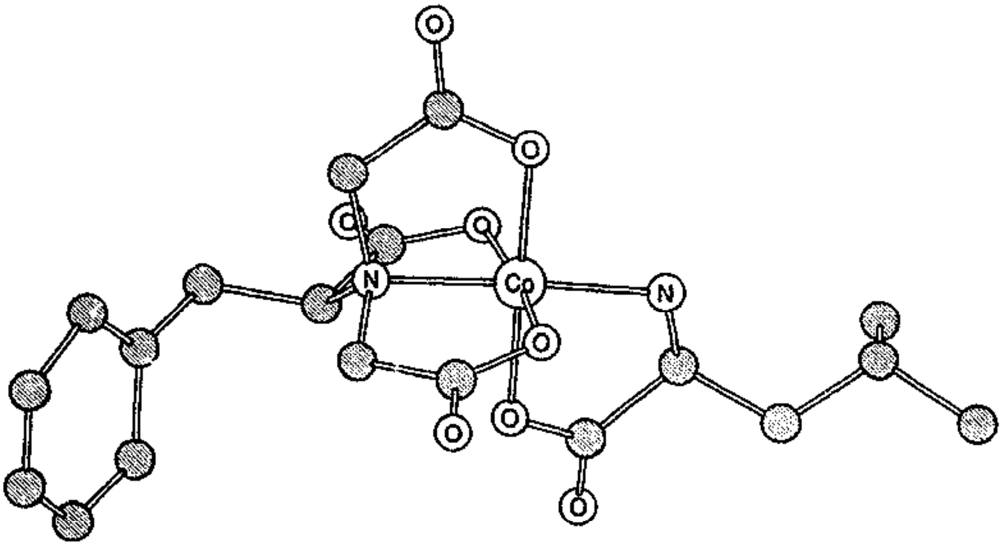
### 2.3. Complexes with nitrogen-oxygen donor ligands

An extremely efficient method has been developed for the resolution of the optical isomers of the complex *fac*-tris (b-alaninato)cobalt(III) [127] using cation exchange chromatography. The optically active *ob*$_3$ isomer of tris(*trans*-1,2-diaminocyclohexane)cobalt(III) was adsorbed onto the resin. It was observed that the Λ enantiomer became strongly bound to the D-*ob*$_3$ isomer.

The X-ray crystal structure and proton NMR spectrum of bis-(*N*-pyridoxy-L-phenylalaninato)cobalt(III) shows an unusual arrangement of the aromatic rings around the pyridoxy 2-methyl [128]. Comparisons of the $^{15}N$ NMR chemical shifts of *β*-alaninato and glycinato chelates of cobalt(III) show significant effects due to the presence of an amine group *trans* to oxygen compared to an amine group *trans* to a nitrogen [129]. The complex ion $[Co(AB)(AAUH)_2]^{2+}$ (AAUH = 1-amidino-*O*-alkylurea and ABH = glycine, alanine, valine or histidine) is produced by the reaction of *trans*-$[Co(NH_3)_2(AAUH)_2]^{3+}$ salts with the appropriate amino acid [130]. The X-ray crystal structure of the complex [Co(*α*-hydroxysalicylidene-*o*-hydroxybenzylamine)(terpy)]$^+$ which is prepared by the reaction of salicylidene-l-alanine with the terpy complex of cobalt(III) has been determined [131].

The ligand *N,N*-dicarboxymethyl-L-phenylalanine forms complexes involving an $(N)(O)_3$ tripodal tetradentate arrangement with cobalt(III) [132]. The X-ray crystal structure of the hydrate of potassium (*N,N*-dicarboxymethyl-L-phenylalanyl)-L-leucylcobalt (**62**) shows a *trans-N*-configuration rather than the expected *cis-N*-form. The $^{59}Co$ NMR spectra of a number of complexes involving L-histidine, imidazole, or histamine and another ligand have been examined to investigate the metal-ligand bond properties of cobalt(III) complexes [133].

The reaction of $[Co(edda)(H_2O)_2]^+$ with $[Co(gly)(en)(H_2O)_2]^{2+}$ in alkaline solution produces $[Co(gly)(en)Co(edda)(\mu\text{-}OH)_2]^+$ where edda = ethylenediamine-*N,N'*-diacetate [134]. Four geometrical isomers of the *μ*-hydroxo complex were isolated chromatographically. A mechanism for chiral discrimination is suggested to explain the network of hydrogen bonds found from an X-ray crystal structure of $[\Lambda\text{-}Co(en)_3][\Lambda\text{-}Co(edta)]_2Cl\cdot 10H_2O$ [135] by comparison with the nickel complex $[\Lambda\text{-}Ni(en)_3][\Lambda\text{-}Ni(edta)]\cdot 4H_2O$. The salt was found to crystallize in the orthorhombic space group $P2_12_12$ with $Z = 2$, $a = 21.046$, $b = 12.81$, $c = 8.158$ Å. The kinetics of the outer sphere reduction of $[Co(edta)]^-$ to $[Co(edta)]^{2-}$ by $[Ru(en)_3]^{2+}$ have also been studied and shown to be first order in each reactant with a rate constant of $6 \times 10^3$ $M^{-1}$ $s^{-1}$ at 25°C. The amount of chiral induction in the process is small producing only a 2% enantiomeric excess.

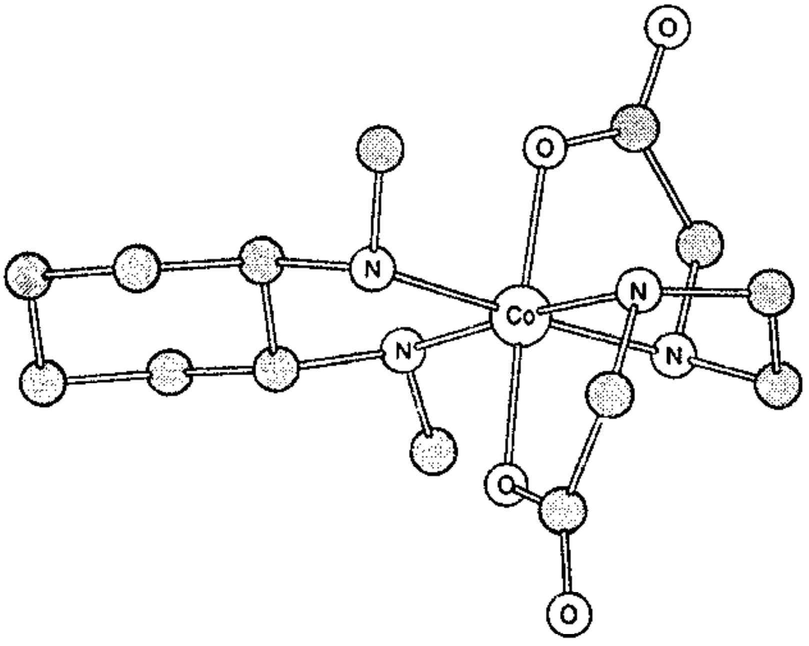


**(62)**

From a study of isomerization reactions of $[Co(edma)_2]^+$, [Co(ida)(edma)] and [Co(mida)(edma)] in weakly basic solution (mida = *N*-methyliminodiacetate, ida = iminodiacetate, edma = ethylenediamine-*N*-acetate), it has been concluded that where there were *fac* or *mer* coordinated ligands and the mechanism involved a deprotonated pentacoordinated intermediate which results from Co–O bond fission in the conjugate base [136].

Free radicals which were produced by γ-radiolysis of thymine have been shown to react with Co(III)(edta) and Co(III)(NTA) and electron transfer was detected for T· and TH· [137]. The crystal structure of (ethylenediaminetriacetato) aquacobalt(III) monohydrate has been determined [138].

The time-honoured method of reacting a cobalt(II) salt with the appropriate ligand in the presence of activated charcoal and bubbling air through the solution has been used to produce a series of mixed-ligand cobalt complexes: $[Co(edda)(2R,4R\text{-ptn})]^+$, $[Co(dmedda)(2R,4R\text{-ptn})]^+$ and $[Co(deedda)(2R,4R\text{-ptn})]^+$ in which 2*R*,4*R*-ptn is (2*R*)(4*R*)-pentane-2,4-diamine, $deeddaH_2$ = *N*,*N*′-diethylethylenediamine-*N*,*N*′-diacetic acid, and dmedda = *N*,*N*′-dimethylethylenediamine-*N*,*N*′-diacetic acid [139]. It was then possible to separate each of those using cation chromatography into diastereoisomers. All have *trans* $N_4O_2$ geometries.The crystal structures have been obtained for both of the diastereoisomers of *sym*,*cis* $[Co(edda)(2R,4R\text{-ptn})]^+$. Steric repulsion between the chelates is presented as the explanation for differences in the six membered chelate ring in the two species. In a related study, Yashiro and co-workers have determined the crystal structure of the compound $(-)_{550}[Co(edda)(R,R\text{-dmchxn})]ClO_4 \cdot H_2O$, in which *R*,*R*-dmchxn = *N*,*N*′-dimethyl-(1*R*)(2*R*)-cyclohexane-1,2-diamine; the cation is shown in **(63)** [140]. It is concluded that *N*-alkyl substitution in these complexes exerts a significant influence over chirality about the metal ion centre so that inclusion of methyl groups in the *R,R*-chxn structure produced predominantly the Δ form while substitution in the edda part of the complexes produced largely the Λ form.

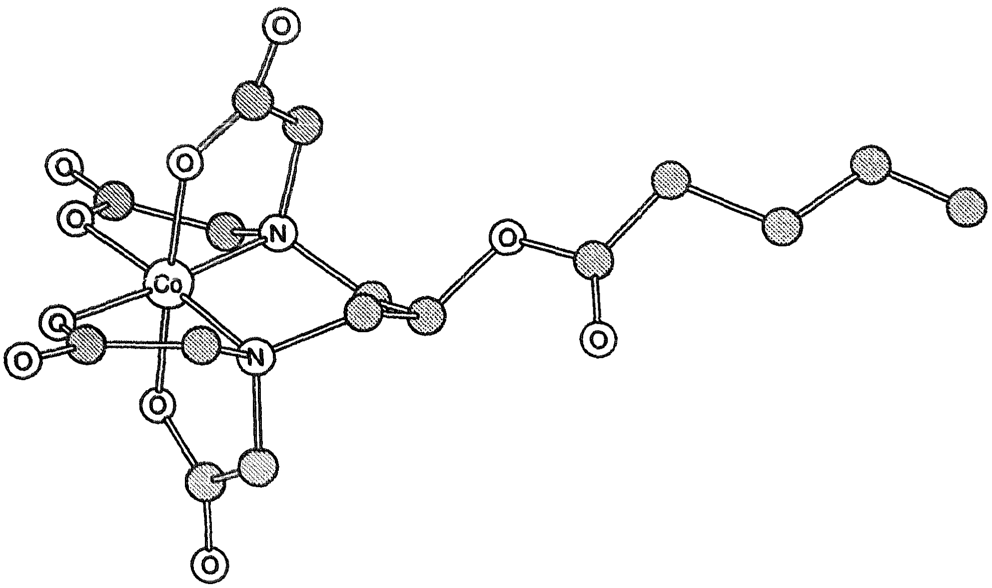


**(63)**

An attempt to esterify the free hydroxyl group in the anion of the complex K[Co(dhpta)] (dhpta = 1,3-diamino-2-hydroxypropanone-*N,N*-*N′,N′*-tetraacetate ion) was found not to work because the salt was insoluble in appropriate solvents [141]. In order to overcome this problem these workers used cryptand-222 to complex the potassium and thence to dissolve the complex in acetonitrile containing 4-(dimethylamino)pyridine (DMAP). This allowed a series of seven esterified complexes to be produced using acid anhydrides such as acetic, benzoic, octanoic, etc. The spectroscopic properties of these were investigated and the X-ray crystal structure of the complexes (DMAPH)[Co(Ben-dhpta)] and (STCH)[Co(val-dhpta)]·$6H_2O$ have been determined, where Ben-dhpta and val-dhpta are *O*-benzoylated dhpta and *O*-valerylated dhpta respectively, while STCH is the strychnine cation. The structure of [Co(val-dhpta)] is shown in **(64)**. Each complex has octahedrally coordinated cobalt with the dhpta bound to the carboxylic carbon through the oxygen atom of the hydroxy group which is not coordinated to the Co.

The Λ configuration has been assigned to one of the geometrical isomers of the cobalt complex of propane-1,3-diamine-*N,N,N′*-triacetate-*N*-3-propionate which has been isolated [142]. The complex ion $[Co(edbp)(H_2O)_2]^+$ (edbp = ethylenediamine-*N,N′*-bis-α-(β-phenyl)-propionic acid) produces only the *cis*-α isomer when prepared using $PbO_2$ as oxidant and involves an ONNO arrangement around the cobalt [143].

A range of compounds involving various salicylaldimine and salicylethylenediime complexes of both cobalt(III) and cobalt(II) have been prepared and their reactions



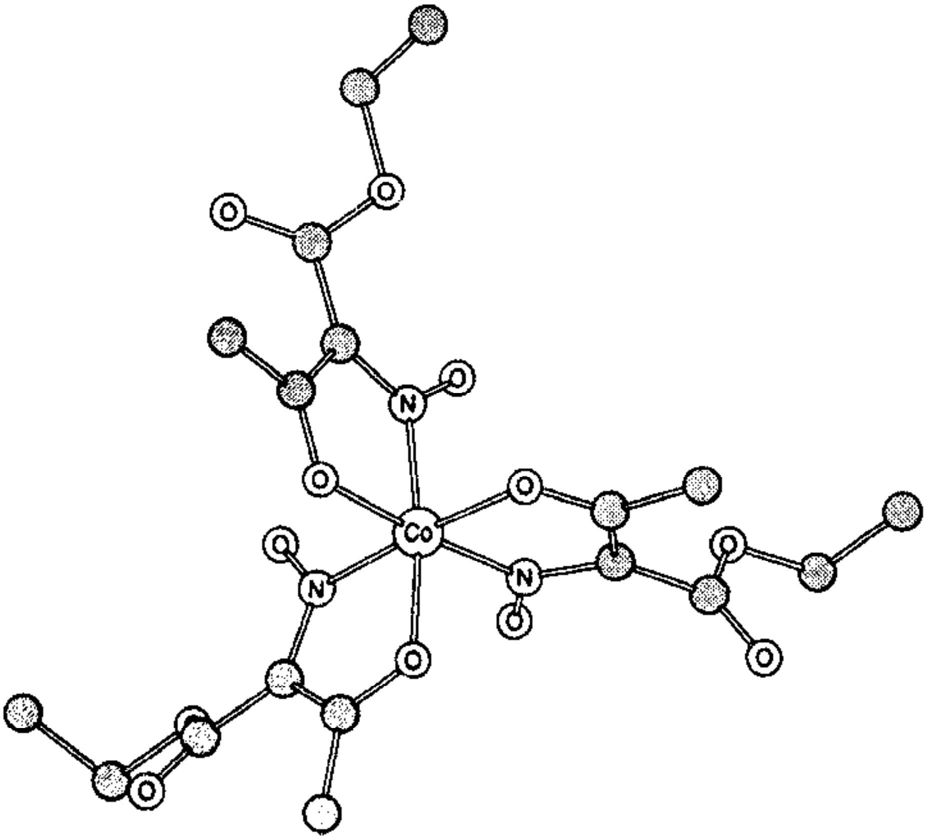
**(64)**

with various brominating agents such as *N*-bromosuccinimide have been investigated [144].

The crystal structure of (-)$_{552}$CD-Δ(*S*,*S*)-α-[Co(eddp)(en)]Br · 5H$_2$O(eddpH$_2$ = ethylenediamine-*N*,*N'*-dipropanoic acid) shows that it is monoclinic with space group $P2_1$ and with $a = 10.558$, $b = 8.523$, $c = 11.868$ Å, $\beta = 112.11°$ and $Z = 2$ while the corresponding (+)$_{536}$ CD-Δ(*R*,*R**) complex is orthorhombic with space group $P2_12_12_1$ and $a = 11.809$, $b = 16.144$, $c = 8.340$ Å and $Z = 2$ [145]. The structures of the racemic chloride and hexafluorophosphate complexes were also determined. An interesting feature is that two of the β-isomers turned out to be diastereomers due to the chirality around the two asymmetric nitrogen atoms. Photolysis of a range of cobalt(III) complexes of the type *trans*-[Co(N$_2$O$_2$)(N-ax)$_2$]$^+$ or *cis*-[Co(N$_2$O$_2$)(acac)] (in which N$_2$O$_2$ is a quadridentate Schiff base ligand, and N-ax is an axial nitrogen-donor ligand such as NH$_3$) results in substitution of one of the axial ligand by solvent in the case of the *trans* complexes while the *cis* complexes underwent reduction of Co(III) to Co(II) [146]. Photoreduction of Co(III) to Co(II) is however observed in the photo-substituted py complex when irradiated at 254 nm rather than 313 nm. Redox behaviour of [Co(salen)]$^+$ has also been investigated by determination of isopotential points of the Co(III) complex in DMF and pyridine [147].

The crystal structure of the complex [CoL$_3$] (**65**), in which L$^-$ = ethyl-2-(hydroxyimino)acetylacetate, shows that the ligands are coordinated through the ketone oxygen and the oxine nitrogen giving a facial configuration around Co [148].

The reaction between Co(II) and pyridoxylidene-L-amino acid Schiff base yields [CoL] by the process given in scheme (**66**) [149]. The X-ray crystal structure, $^1$H



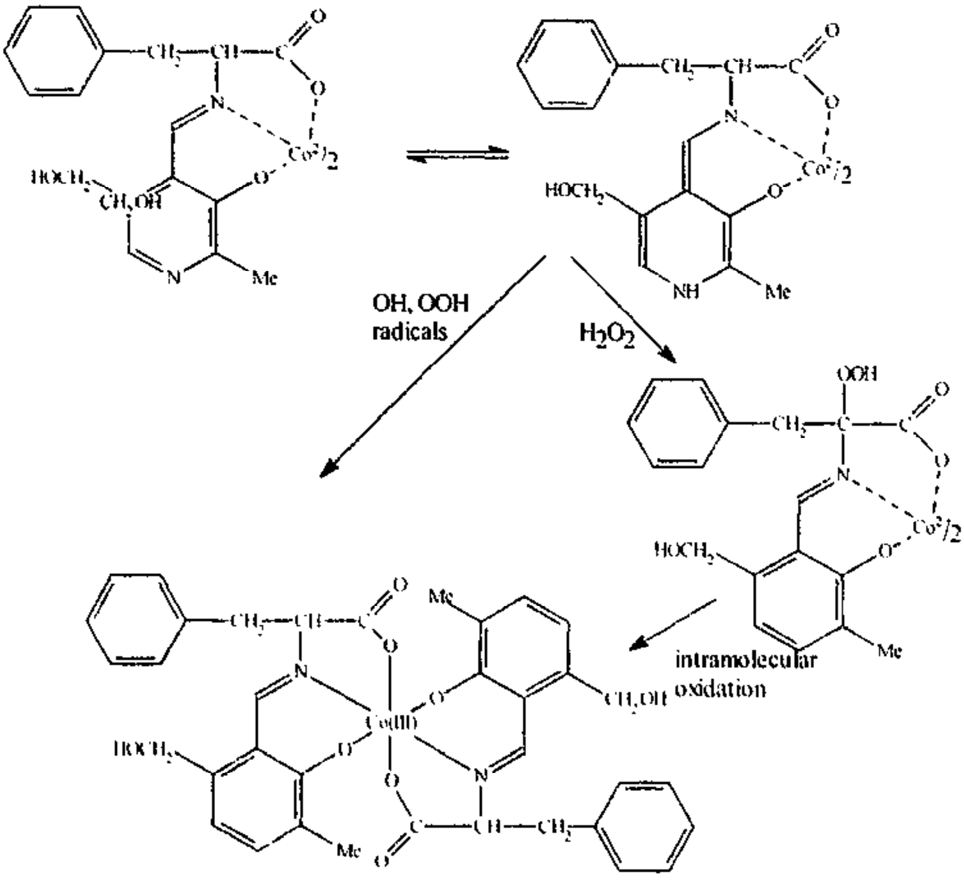
**(64)**

NMR and FAB mass spectrometry confirm the structure of the Co(II) complex with its *mer-trans* (N) configuration and with OH and OOH groups in the α-position of the 4-phenylalanine.

The di-μ-hydroxo-bis[bis(-1-aminocyclohexanecarboxylato-*N,O*)-cobalt(III) ion is shown by an X-ray crystal structure determination to have the expected dihydroxo-bridges and somewhat distorted octahedral arrangements around the cobalt atoms with the nitrogens *cis*-coordinated [150]. There is also a free molecule of 1-aminocyclohexanecarboxylic acid present in the structure as the Zwitter-ion which looks as if it is involved in the hydrogen bonding within the crystal.

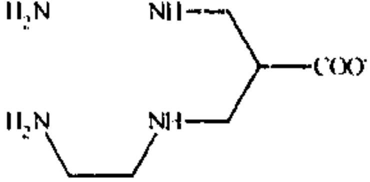
In the complex tris[*N*-(salicylidene)-2-aminoethyl]amino)cobalt(III) acetonitrile the X-ray crystal structure shows that there is a *fac* arrangement around the cobalt [151].

Reaction of $CoCl_2$ with the ligand 3-[(2′-aminoethyl)amino]-2-[(2″-aminoethyl)-aminomethyl]propanoic acid [L =(**67**)] followed by oxidation, results in a single isomer of the cobalt(III) complex ion *trans*-$[CoLCl]^+$ [152]. The X-ray crystal structure of the complex shows that the chloro ligand is *trans* to the carboxylate with the secondary amines occupying an octahedral face in the manner shown in (**68**). Lawrance and co-workers have also studied the cobalt(III) complex of the



**(66)**

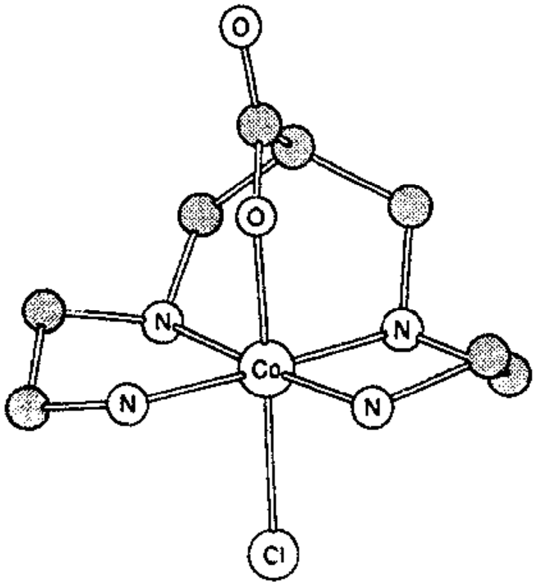
quinquedentate ligand (**69**) [153]. The cation in the resulting complex *SS*,*SS*-[CoL(Cl)](ClO$_4$)·0.75 HClO$_4$·2H$_2$O is shown in (**70**). The factors affecting the rate of base hydrolysis involving the length of the axial Co–Cl bond are discussed.



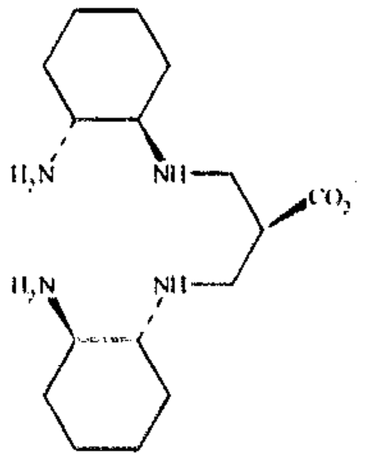
3-{2'-aminoethyl)amino}2-[(2''-aminoethyl)-aminomethyl]propionic acid

**(67)**

The reaction of the *S*-methylmethionine complex (**71**) in aqueous solution at pH > 12 has been found to yield a pink species, the X-ray crystal structure of which



**(68)**

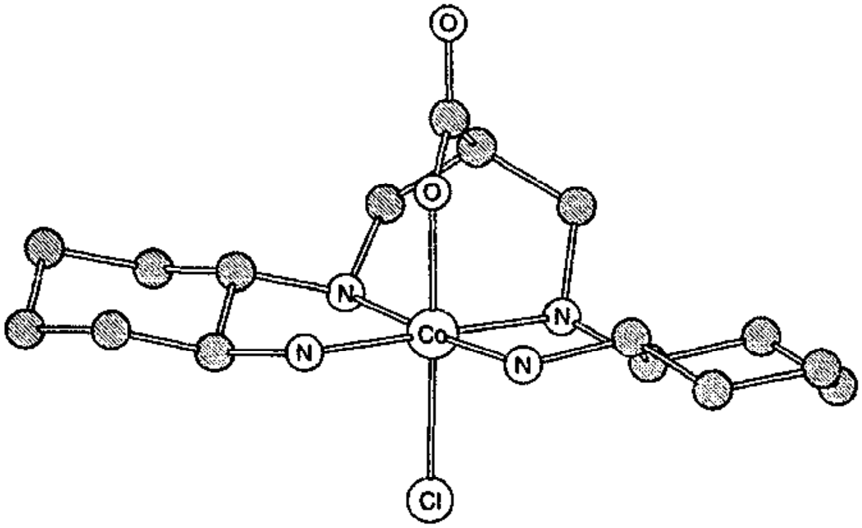


$L^1$

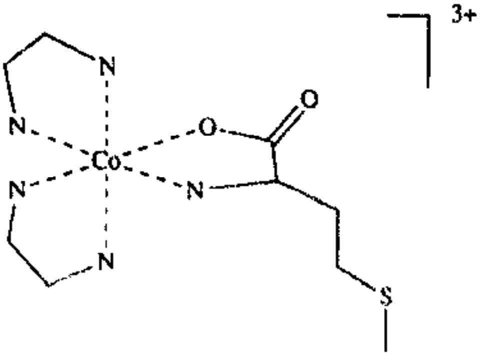
**(69)**

is shown in **(72)** [154]. A mechanism for the rather intriguing reaction in basic aqueous solution is proposed and is outlined in scheme **(73)**.

A range of complexes have been prepared involving the ligand *S,S*-cypim in which Co(III) occupies the closed site and a variety of $M^{2+}$ metal ions the open site **(74)** [155]. Examination of the UV–VIS absorption spectra of the complexes, $[Co(III)(S,S\text{-cypim})M(II)]^{2+}$, in which M(II) = Cu(II), Mn(II), Co(II) and



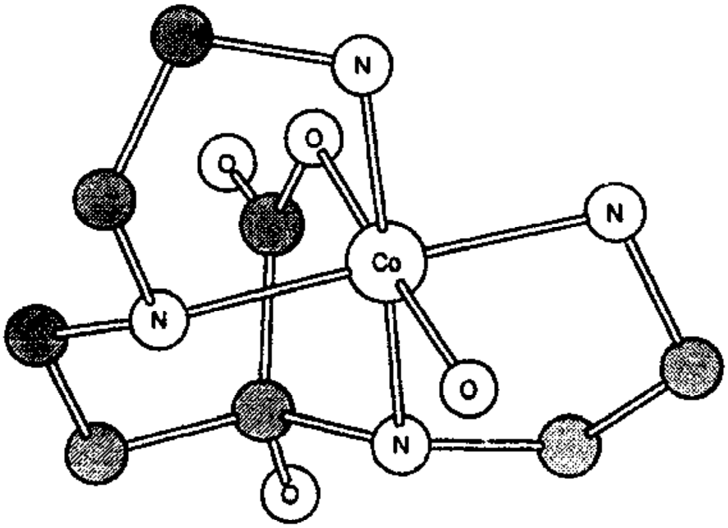
**(70)**



**(71)**

Ni(II), showed that the "open site" M(II) ion was situated in a distorted trigonal bipyramidal environment. The redox potentials for the Co(III)/Co(II) couples for $[Co(III)(S,S\text{-cypim})MCl(II)]^{2+}$ complexes varied between 0.32 V and −0.43 V, while those for, $[Co(III)(S,S\text{-cypim})M(II)]^{3+}$ were in the range −0.27 V to −0.44 V and it is clear that the redox potential involving the open site metal is affected by the other metal in the dimetallic complex.

The tetraphenolic macrocyclic ligand $L_xH_4$ (75) produces the Co(III) complex $[L_xCo_3(OH)(CH_3)CO_2)_3]BF_4 \cdot 3.83H_2O$ [156]. The X-ray crystal structure of this species has been determined; the cation contains at the centre three Co atoms bridged by an OH ligand and three acetato ligands.



**(72)**

The compound *N*-(phosphonomethyl)glycine (PMG) is also known commercially as glyphosate and is widely used as a horticultural herbicide. It has been shown for the first time to form 1:2 complexes with Co(III) and the structure of the red crystals of $Na_3Co(PMG)_2 \cdot 11H_2O$, $Na_3[(76)] \cdot 11H_2O$, has been determined [157]. It crystallizes in the triclinic space group $P\bar{1}$ and $a = 10.131$, $b = 11.316$, $c = 11.911$ Å, $V = 119.4$ Å$^3$, $\alpha = 97.21$, $\beta = 109.47$, $\gamma = 107.29°$ and $Z = 2$ and is the *fac-RS*-all-*trans* complex.

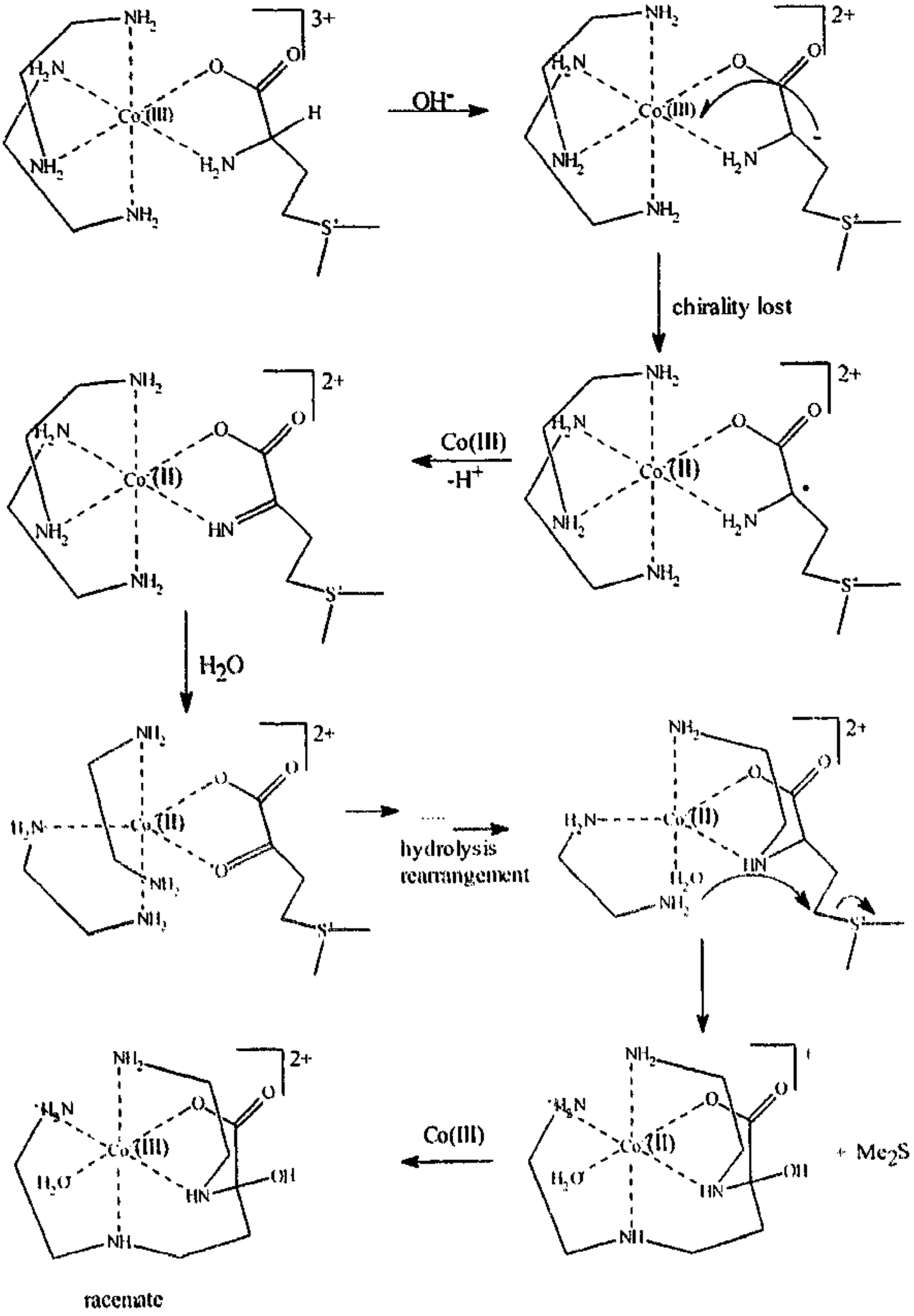
### 2.4. Complexes with sulfur or selenium donor ligands

Black needle like crystals of $[Hpy]_2[Co(L)_2]_2$, where L = 2,3-disulfanylmaleonitrile, have been prepared by the electrochemical oxidation of $[NBu_4][Co(L)_2(py)]$ [158]. The X-ray crystal structure shows that the Co in the anion (77) is coordinated via S atoms in a distorted square pyramidal arrangement. The structure involves an arrangement in which the cobalt complex ions are stacked with alternating rows of $[Hpy]^+$ sandwiched between.

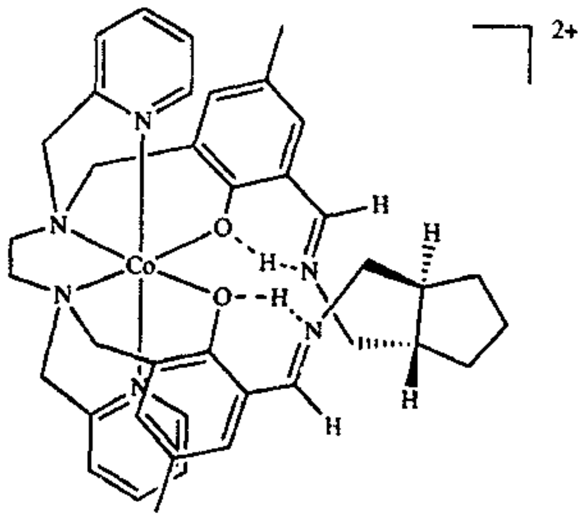
Tris(*N*,*N*-diethyl-*N*′-benzoylselenoureato)cobalt(III) has been found by X-ray crystal structure determination to have the ligand bound in a bidentate fashion via Se and O to the Co resulting in hexagonal channels in the structure [159].

### 2.5. Complexes with sulfur–oxygen donor ligands

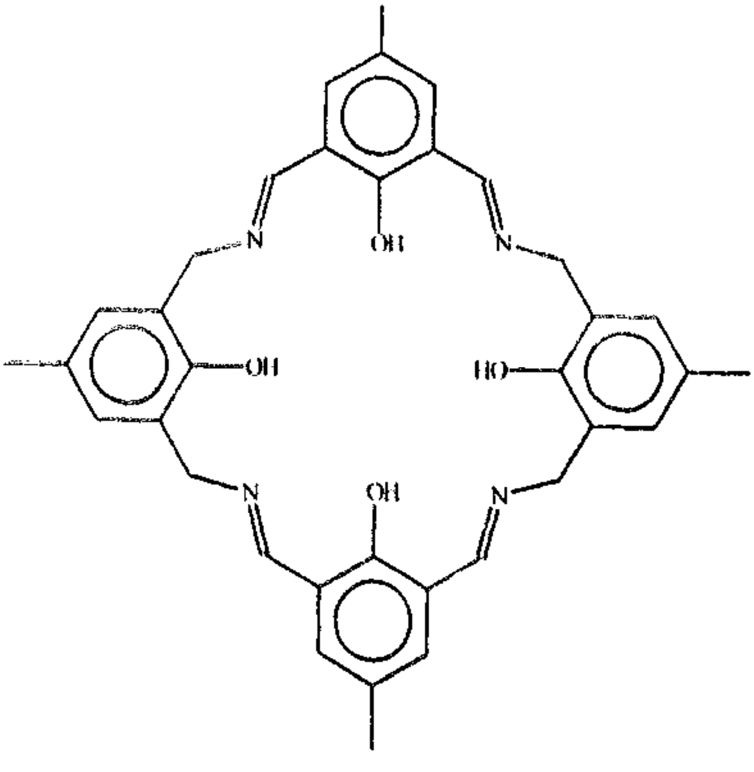
Very few studies were carried out on complexes in this category but cobalt(III) complexes have been prepared of 1-thio-β-D-glucose viz. $[Co(H_4tgS)_2en_2]^+$ and $[CoH_3tg\text{-}O,S\text{-}en_2]^+$. The crystal structure of $(+)_{330CD}$ -[Co(H$_3$tg-


3+
OH⁻
2+
chirality lost
2+
Co(III)
-H⁺
2+
H₂O
2+
hydrolysis
rearrangement
2+
+ Me₂S
Co(III)
2+
racemate

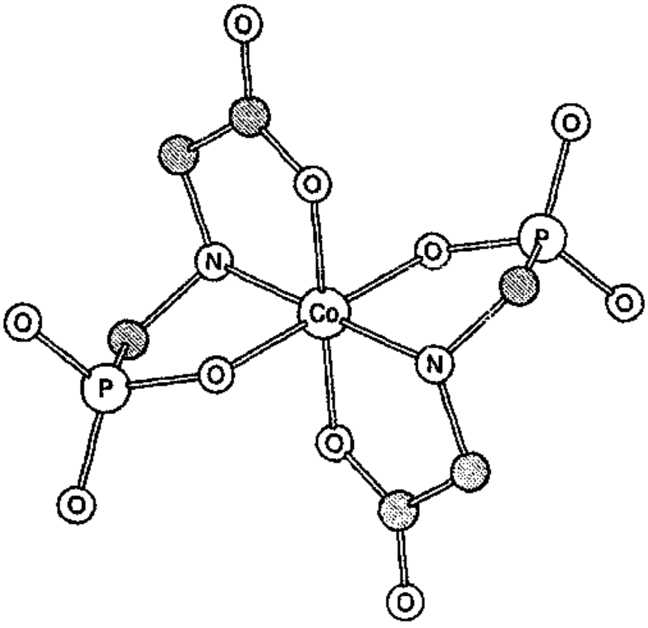
(73)



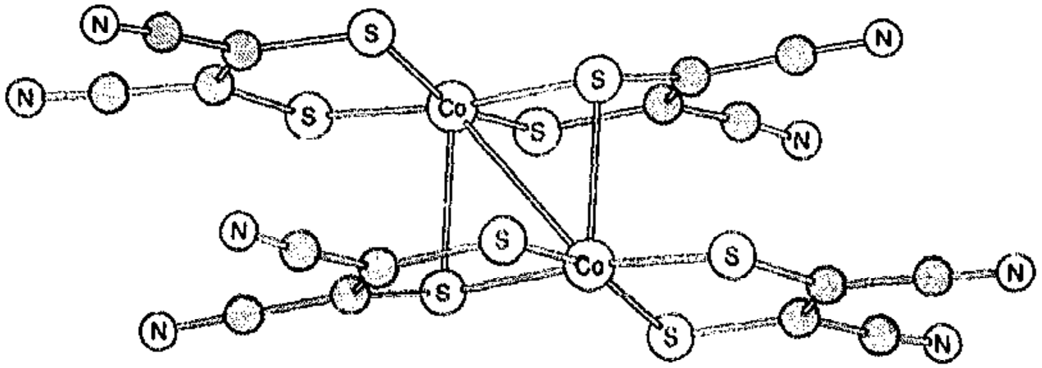
**(74)**



**(75)**



**(76)**



**(77)**

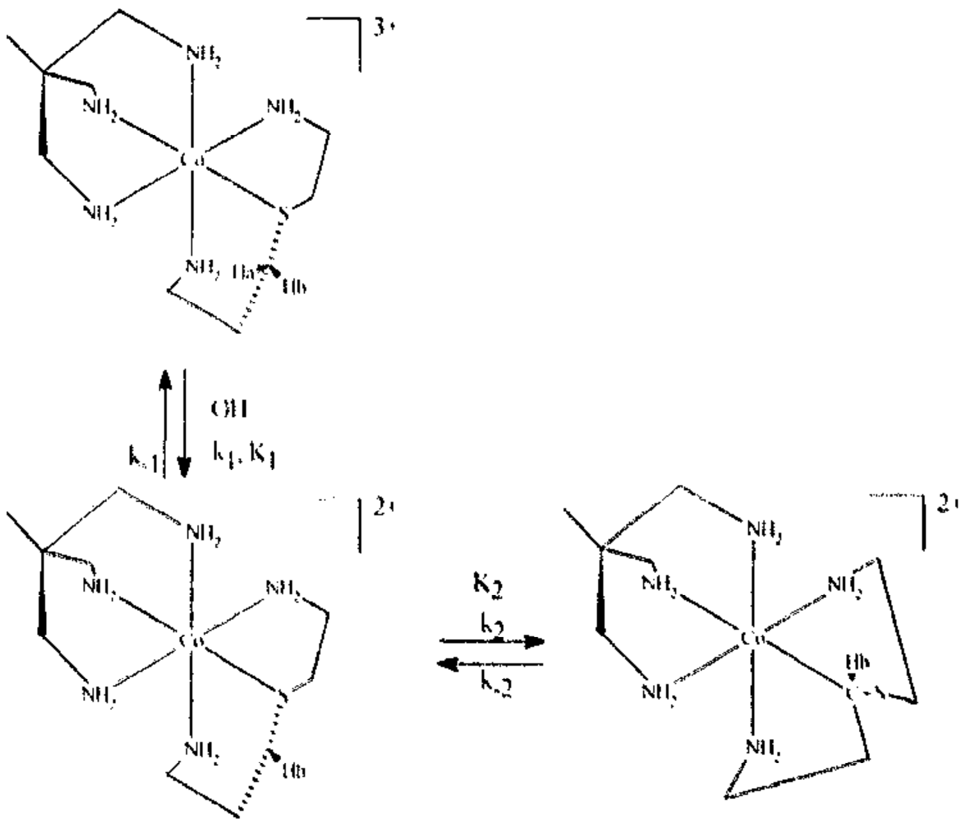
O,S)(en)$_2$]NO$_3$·H$_2$O has been obtained [160]. In this complex the 1-thio-$\beta$-D-glucose is coordinated through adjacent sulfur and oxygen atoms producing a cyclic chair arrangement. This complex is in the $\Lambda$ configuration and crystallizes in the space group $P2_12_12_1$ with $a = 14.328$, $b = 14.617$, $c = 8.605$ Å, $V = 1802.2$ Å$^3$ and $Z = 4$. Other complexes were also isolated and were characterized by spectroscopic methods.

### 2.6. Complexes with sulfur–nitrogen donor ligands

The reaction of the complex [Co(tame)$Cl_3$] (in which tame = 1,1,1-tris(aminoethyl)ethane) with the ligand aeaps (aeaps = 2-aminoethyl 3-aminopropyl sulfide) in solution in DMSO followed by purification using ion exchange chromatography results in yellow crystals of the complex [Co(tame)(aeaps)]$Cl_3 \cdot H_2O$ [161]. The ligand aeaps in this complex is bonded to cobalt via nitrogen and sulfur. However, when it reacted with hydroxide ion in aqueous solution, a nitrogen-carbon bonded complex is produced. The X-ray crystal structure of the latter confirms the formation of this species. A mechanism (**78**) involving the intermediacy of a carbanion-containing species is proposed for this process and kinetic data are presented for the reaction giving the rate equation:

$$k_{obs} = k_{-2} + [OH^-]k_2K_1$$

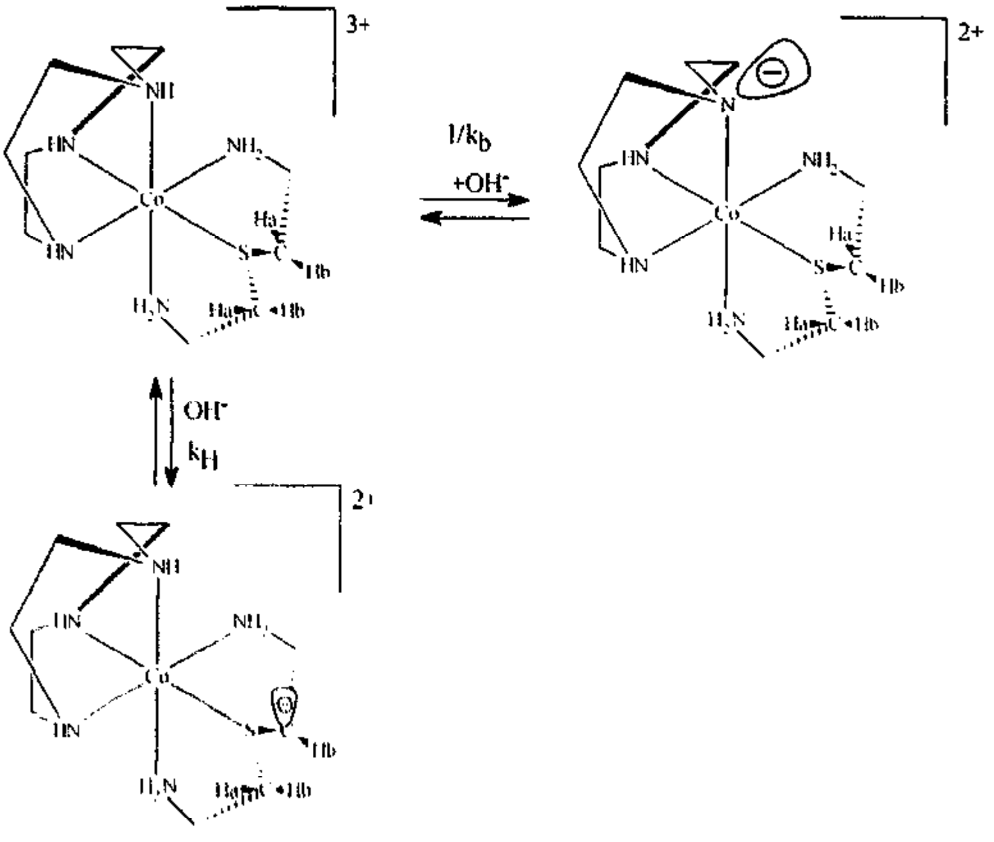
in keeping with the proposed mechanism (**78**).



**(78)**

In a related study, Kofod and co-workers have used $^{13}C$ NMR spectroscopy to measure the rate of deuterium-hydrogen exchange in the complex $[Co(tacn)(daes)]^{3+}$ (tacn = 1,4,7-triazacyclononane; daes = 3-thiapentane-1,5-diamine) [162]. The process involved in the deprotonation is believed to be that in

(**79**) in which $H_a$ was found to exchange about ten times faster than $H_b$. In basic solution the ligand daes was found to be lost fairly easily and a study by the same group [163] has outlined the important equilibria in 1.0 M NaOH solution. Crystals of $Na[(tacn)Co(OH)_3Co(tacn)](ClO_4)_2 \cdot 2H_2O$ were isolated and the X-ray crystallographically determined structure of the complex cation is shown in (**80**). In 4.0M NaOH, $[Co(tacn)(daes]^{3+}$ forms a triamido-bridged dicobalt(III) complex, the structure of which was determined using X-ray diffraction; the cation is shown in (**81**) [164].

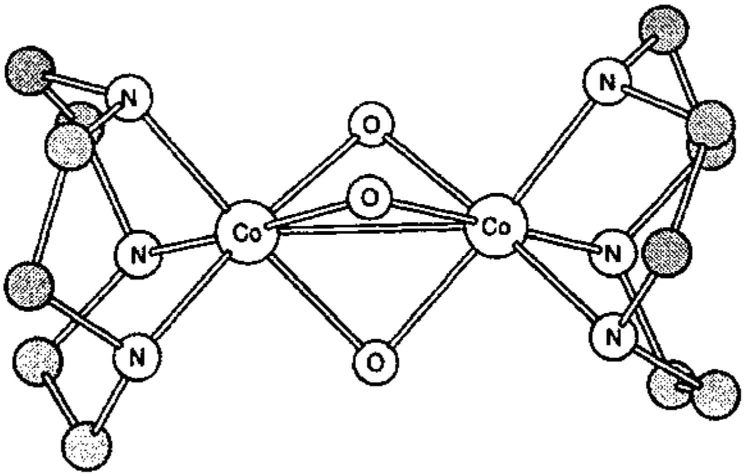


Deprotonation of $[Co(tacn)(daes)]^{3+}$

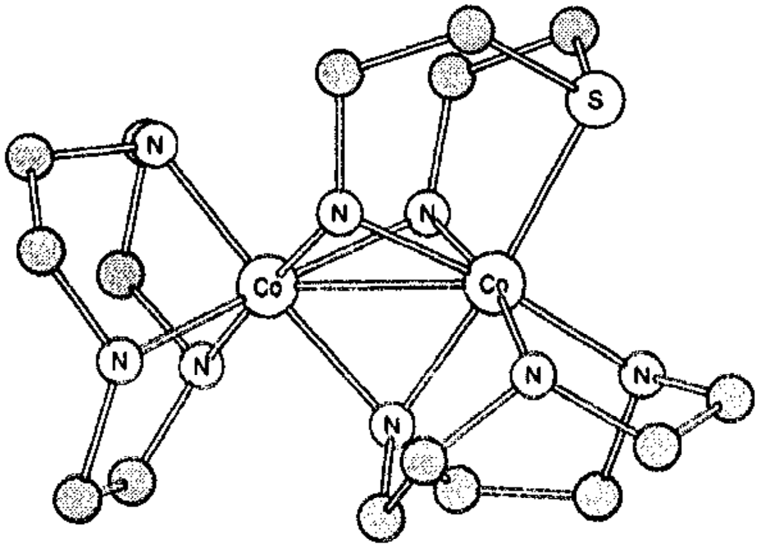
(**79**)

The crystal structures of two complexes of the form $[Co(L4M)_2]BF_4$ and $[Co(L4M)_2]BF_4$ have been determined [165] where L4M = 2-acetylpyridine 4-*N*-methylthiosemicarbazone and 4M = 2-formylpyridine 4-*N*-methylthiosemicarbazone. The crystal structure of the L4M complex cation is shown in (**82**); the 4M complex is very similar. The structures involve each of the thiosemicarbazones as tridentate ligands bonding to the Co through two nitrogen atoms and a sulfur to octahedral coordination.

The crystal structure of the complex $\Lambda$-*cis*-$[Co(Htsc)_3]Cl_3.3H_2O$ has been determined confirming the *cis* arrangement of the ligand around the cobalt [166]. The



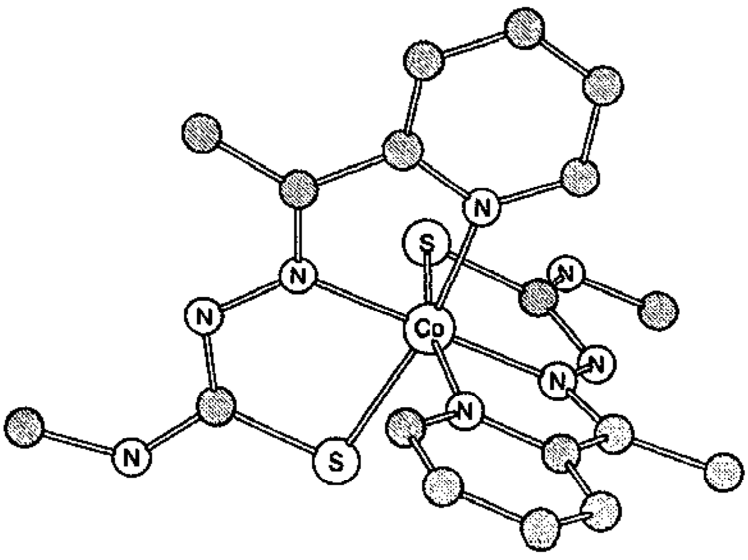
**(80)**



**(81)**

crystal structure of the cobalt(III) complex of 2-ketobutyric acid thiosemicarbazone shows that it contains two different forms of the ligand in which both the thione and the thiol forms are both present in the structure [167]. The arrangement around the cobalt involves the two terdentate ligands in a distorted octahedron producing a meridional conformation.

A highly distorted *fac*-octahedral arrangement is to be found around cobalt in the complex tris(4,6-dimethylpyrimidine-2-thiolato-*N,S*)cobalt(III) [168]. A series of cobalt(III) complexes has been prepared by the reaction of cobalt(II) acetate with pyrimidine-2-thione or its derivatives [169]. The nature of the product was



**(82)**

found to depend upon the substituents in the 4-position. Thus, when there was an alkyl substituent the species produced was $[Co(N\text{-}S)_3]$, while a 2-thiouracil substituent with O or S at the 4-position produced bis-type cobalt(II) complexes. A cyclic cobalt(III) tetramer is the unusual product of the reaction of $Co(CF_3SO_3)_2$ with a Schiff base from 2-thiouracil-4-aldehyde and dien [170]. The two complexes racemic *cis*-α-dinitro(1,8-diamino-3,6-dithiaoctane)cobalt(III) chloride and $(+)_{546}$-Λ(δ-λ-δ)[*cis*-α-dinitro(1,8-diamino-3,6-dithiaoctane)cobalt(III) perchlorate have a quadridentate ligand with the nitrogen atoms in axial positions and *cis* sulfur atoms having the two $NO_2$ groups *trans* to them as shown in (**83**) for the latter complex cation [171]. The absolute configuration of the $(+)_{546}$-Λ(δ-λ-δ) species allows the authors to deduce that complexes [Co(L)(XY)]A, ($L = C_6H_{16}N_2S_2$, X = Y = $NO_2$ or X = Y = Cl or X = Cl, Y = $H_2O$) which were used as precursors for the above complex must have consisted only of racemic Λ(δλδ) and Δ(δλδ) pairs with no *cis*-β or *trans*-isomers.

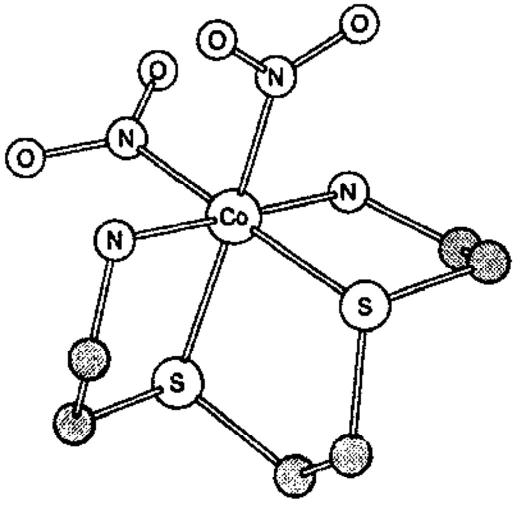
The crystal structure of the complex $[Co[18]ane\ N_2S_4][PF_6]_3.3H_2O$ has been determined with all six of the donor atoms of the macrocycle (**84**) being arranged in a distorted octahedron around the cobalt(III) [172]. Electrochemically two one-electron processes were identified for this complex involving Co(II)/Co(III) and Co(II)/Co(I) complex with spectroscopic evidence for significant stereochemical changes around the Co during the redox processes.

A complex series of reactions occurs when excess $OH^-$ is added to $[Co(NO_2)\text{-capten})]^{3+}$ (**85**) ($NO_2$-capten = 1-methyl-8 nitro-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6}icosane) consisting of:

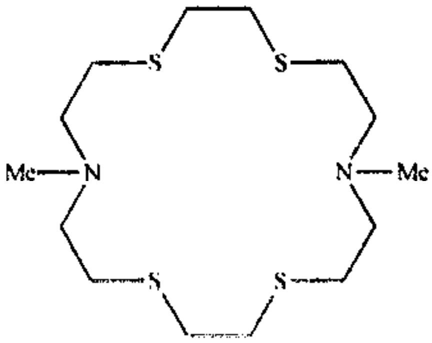
(i) loss of a proton from a secondary amine coordinated to cobalt,

(ii) a retro-Mannich-type reaction causing loss of a methylene from the cap,

(iii) intermolecular hydride transfer giving the complex carbanion: 13-(4-amino-



**(83)**



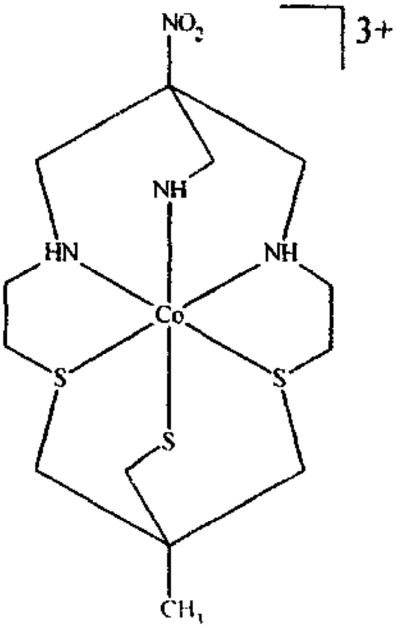
$Me_2[18]aneN_2S_4$

**(84)**

2-thiabutyl)-13-methyl-6-nitro-1,11-dithia-4,8-diazacyclotetradec-4-enato(6)cobalt (III)[173].

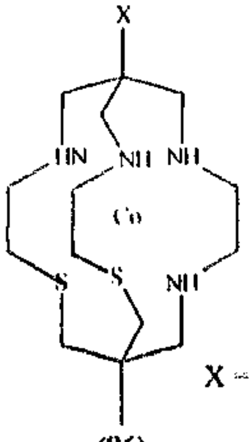
The redox behaviours of a range of complexes involving the ligand ($XN_4S_2sar$) **(86)** have been studied [174]. The kinetics of redox reaction of $[Co(SN_4S_2sar)]^{n+}$ with $[Co(AMMEN_6sarH)]^{3+}$ **(87)** were determined alongside the self-exchange rate data for $[Co(AMMEN_6sarH)]^{4+/3+}$ and self exchange rate constants for the $N_4S_2sar$ complexes deduced using the Marcus relationships.

Upon photolysis of the Co(III) complex $[Co(L\text{-}cysi\text{-}N,S)_3]^{3-}$, in which L-cysi = cysteinesulfinate(2-) ion, linkage isomerism takes place resulting in mixture of com-



$[Co(NO_2capten)]^{3+}$

**(85)**



X = $NO_2$, $NH_3^+$, Cl, H

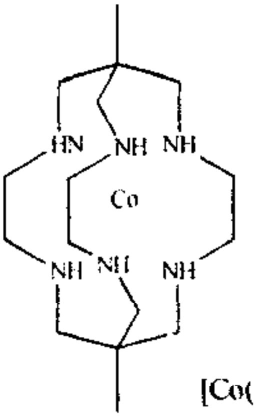
$[Co(XN_4sar)]^{n+}$

**(86)**

plexes, one of which was isolated and found to be [Co(L-cysi-*N,S*)$_2$(L-cysi-*N,O*)]$^{3-}$ [175].

## 2.7. Complexes with sulfur–nitrogen–oxygen donor ligands

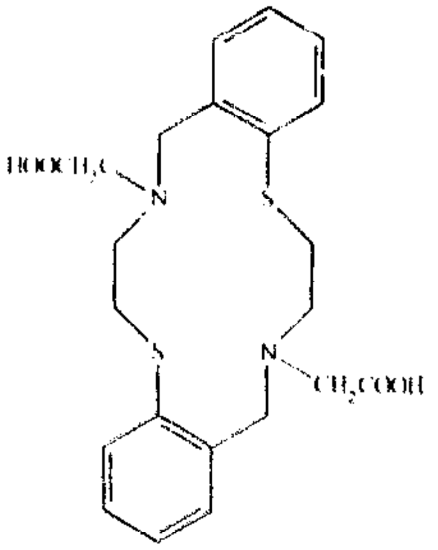
The 14-membered macrocyclic ligands 6,7,9,15,16,18-hexahydrobenzo[F,m][1,8]dithia[4,11]diazacyclotetradecine-8,17-diacetic acid, L1, (**88**) and 6,7,13,15,16,18-hexahydrodibenzo[e,m][1,4]dithia[8,11]diazacyclo-tetradecine-14,17,



$[Co(AMMEN_6sarH)]^{n+}$

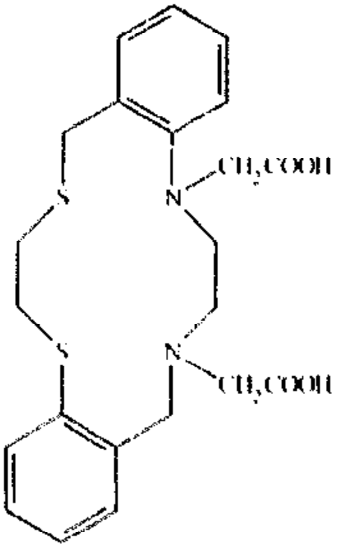
**(87)**

diacetic acid, L2, **(89)** contain a pendant acetato group and form hexadentate complexes with cobalt(III) $[CoL]^+$ **(90)** and **(91)** [176]. The X-ray structures show an arrangement in which the metal ions are to be found outside the cavity formed by the folded macrocyclic rings.



L1

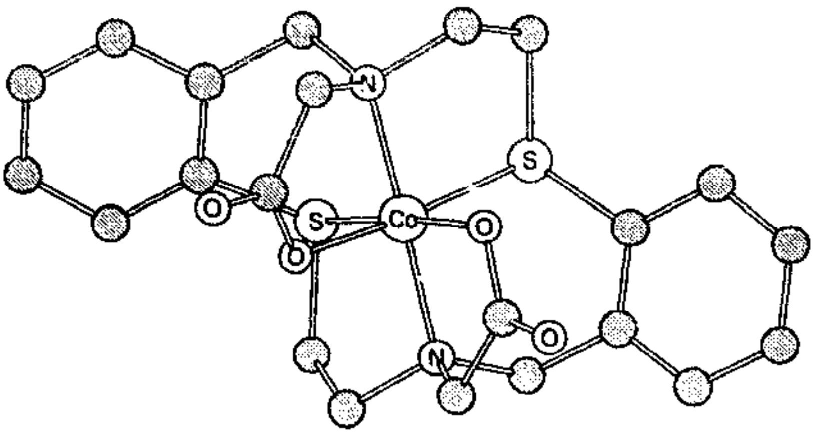
**(88)**



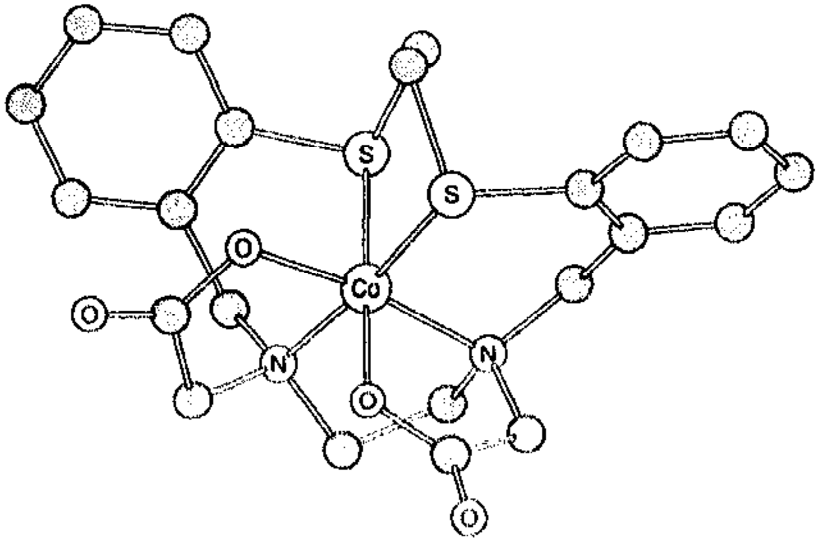
L2

**(89)**

A range of Co(III) complexes of the ligand $H_2Me_xL$ **(92)** have been prepared by the reaction of cobalt(II) acetate with the appropriate ligand followed by oxidation with $H_2O_2$ **(93)** [177]. The X-ray crystal structure of one of these is shown in **(94)**. A most interesting reaction occurs when $[Co(Me_3L)]$ is reacted in acetonitrile with KOH when cleavage of one of the C–S bonds occurs and the green complex **(95)** is produced. When the same reaction is attempted using $[Co(Me_3L)]$, then the complex **(96)** is formed in which one of the Co–S bonds is replaced by a Co–C



**(90)**

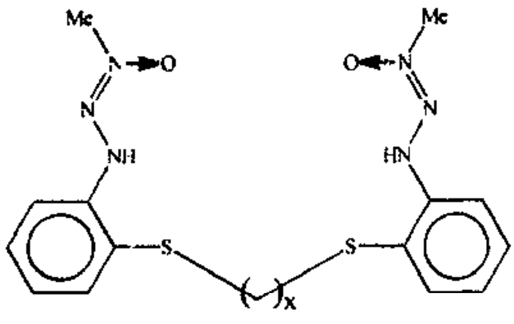


**(91)**

bond. The crystallographically determined structure of the complex [Co(MeL)(MeL$^1$)] **(95)** is shown in diagram **(97)**.

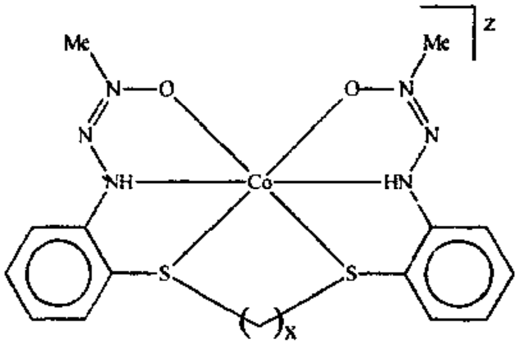
A series of Co(III) complexes of the ligand $H_2SxL$ (see scheme **(98)**) with various values of x have been prepared and some of their reactions studied; scheme **(98)** summarises some of the work [178]. The X-ray structure of one of the starting complexes in which x = 2 has been determined. The X-ray structure of the dinuclear product of the reaction of [Co(S2L)]$^+$ with OH$^-$ in acetonitrile confirms the very unusual structure shown in **(98)**.

The X-ray structure of the meridional isomer of the complex ammonium bis(phenylpyruvic acid thiosemicarbazone)cobalt(III) dihydrate shows that the S atoms are *cis* and the O and N atoms *trans* [179].



$H_2MexL$

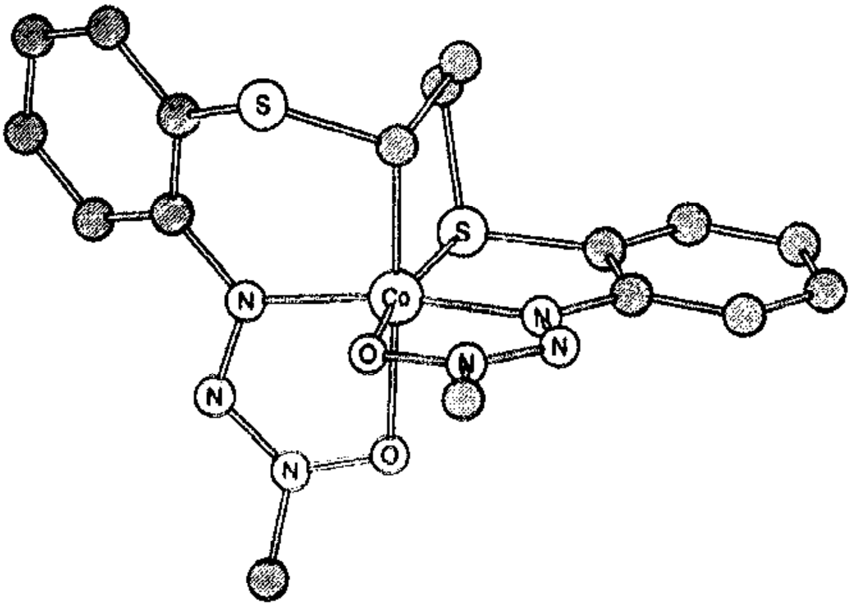
**(92)**



z = 0, [Co(MexL)]

z = +, $[Co(MexL)]^+$

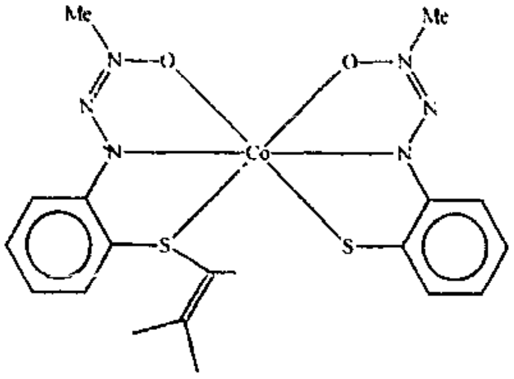
**(93)**



**(94)**

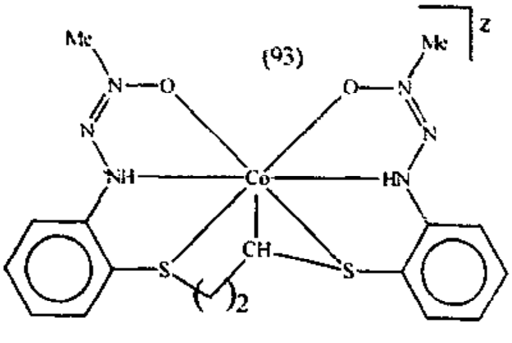
## *2.8. Complexes with phosphorus donor ligands*

It is suggested that the fact that the Co-P distances derived from the X-ray crystal structures of $[CoCl_3(mmtp)]$ and $[Co(CN)_3(mmtp)]$, in which mmtp = 1,1,1-tris(dimethylphosphinomethyl)ethane, are significantly shorter than in $[Co(mmtp)_2][Co(CN)_6]$ indicates a powerful *trans* effect by the phosphino groups [180]. The structure of the cobalt(III) complex $[(tripod)Co(o\text{-}(O)(S)C_6H_4)]^+$ containing the ligand which the authors refer to as tripod **(99)** involves 5-coordination around the cobalt in a structure which is described as lying between square pyramid



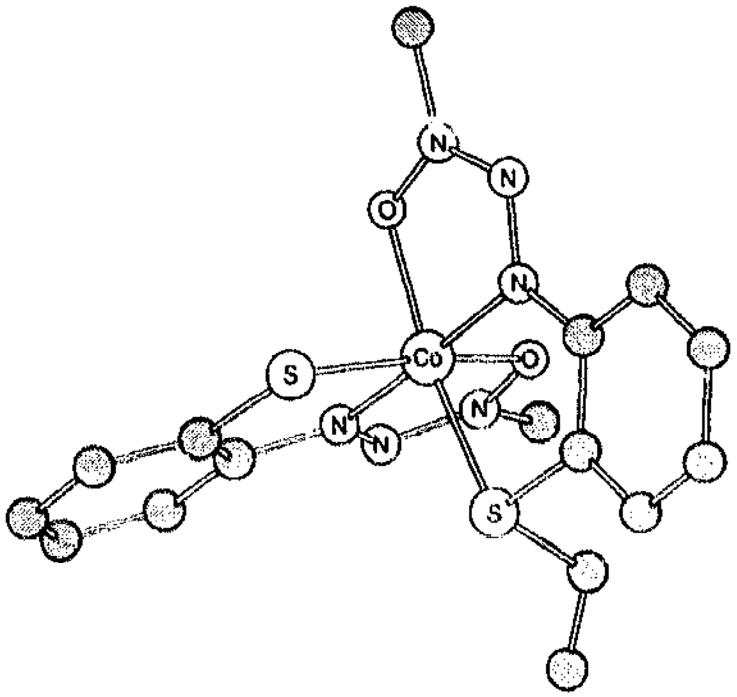
[Co(MeL)(MeL')]

**(95)**



[CoMeL']

**(96)**

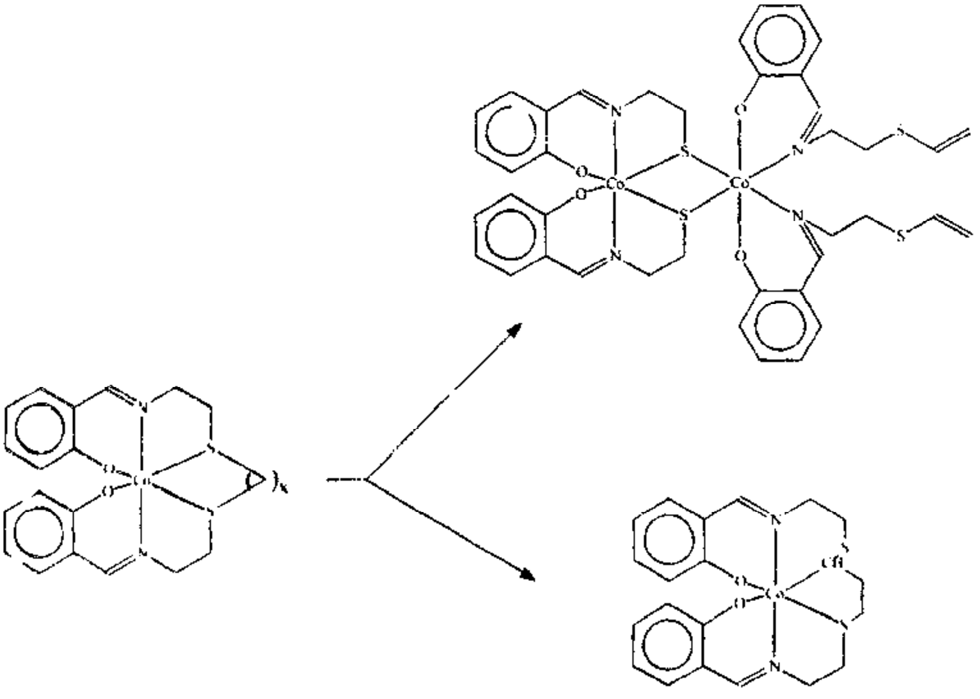


**(97)**

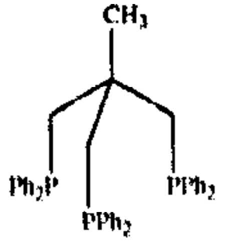
and trigonal bipyramid [181]. A similar structure is found for the corresponding Co(II) complex which is readily produced by reduction of the Co(III) species.

### 2.9. *Complexes with halide and pseudohalide donor ligands*

When the complex $Ag_3[Co(CN)_6]\cdot 16H_2O$ is heated at 60°C for 15 mins it is dehydrated and the infrared spectrum indicates that linkage isomerism has occurred in which the $Ag^+$–NC–$Co^{3+}$ arrangement in the original complex has changed to



(98)



(99)

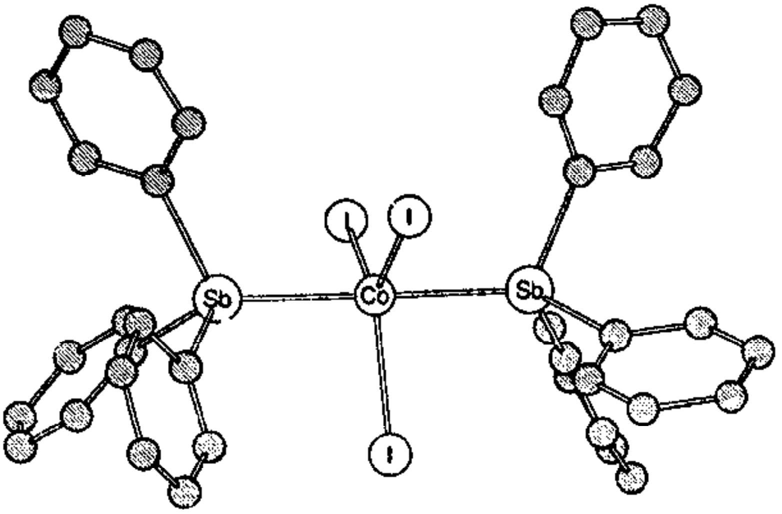
an $Ag^+$–CN–$Co^{3+}$ system [182]. When the kinetics of the process were studied using DSC, it was found that the Avrami rate law was followed giving an index of about 1.5. The X-ray crystal structure of the complex $[N(CH_3)_4]_2Cs[Co(CN)_6]$ shows that it is monoclinic, space group $I2/m$ with $a=8.855$, $b=8.926$, $c=12.599$ Å, $\beta=90.29°$, and $Z=2$ [183].

In a series of monoazido, diazido and triazido-amine-cobalt(III) complexes it has been confirmed that two strong infrared absorption bands associated with the azide ligands are to be found for the *cis*-diazido and the *fac*-triazido complexes [184].

Patience has been rewarded in the investigation of the remarkable reaction:

$$2Ph_3SbI_2+Co \rightarrow [Ph_3SbI][CoI_3(SbPh_3)]$$

since, after leaving for a further two weeks, green–black crystals were produced which subsequently turned out to be $[CoI_3(SbPh_3)_2]$ [185]. The crystal structure of the product shows it to be a trigonal bipyramid with the iodine atoms occupying the equatorial positions as shown in structure (**100**).



**(100)**

## 3. Cobalt(II)

As in previous years cobalt(II) is represented in the literature to approximately the same extent as cobalt(III). There have been studies of the Co(II) environment in large biochemical molecules. A study of the Co(II) reconstituted ribonucleotide reductase R2 from *Escheichia coli* has been carried out [186] and also the preparation and characterization of Co(II)-substituted rusticyanin [187].

### *3.1. Complexes with nitrogen donor ligands*

The effects of the presence of aqua complexes of Co(II) or Co(III) on the kinetics of the base hydrolysis of a number of methyl and ethyl esters of various amino acids have been studied [188].

In the complexes $CoCl_2(Me_2SiNPMe_2)_2$ and $CoCl_2(HNPMe_3)$, the X-ray crystal structure shows an arrangement which is monomeric and in which the phosphaneimine ligands are bound to the Co via their nitrogen atoms producing a distorted tetrahedral structure [189].

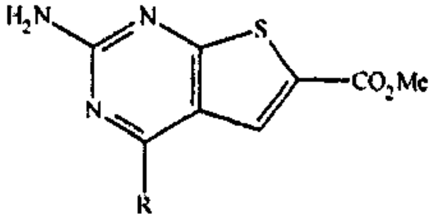
The Co(II) complex of hexamethylenetetramine with Wofatit KPS resin has been found to catalyse the decomposition of $H_2O_2$ [190].

A study of the low temperature magnetization and spectra of a series of Co(II) complexes involving the ligand α-furilglyoxime ([Co(Hafdo)$_2$X$_2$], X = O, S, P, As and Se) has been carried out [191]. The monodentate ligands occupy the axial positions in this complex which becomes subject to air oxidation to a Co(III) species when the axial X ligand exhibits a strong field, but there is no oxidation when water is the axial ligand.

$^1$H NMR and IR spectroscopic data for the Co(II) complex of three new substituted aminoglyoximes of *vic*-glyoximes (*o*, *m*, and *p*-chloroanilineglyoxime), show that the ligands occupy a square planar configuration with water molecules in the axial positions [192].

The kinetics and mechanism of the reaction between Co(H$_2$O) and (3-nitrosalicylato)(tetren)Co(III) has been shown to involve the phenoxide form of the Co(III) species [193]. It is concluded that the reaction mechanism may be described as I$_d$.

A series of complexes of Co(II) containing the ligands shown in (**101**) have been prepared and characterized [194]. Various physical measurements show the complexes to be coordinated through the N of the ligand and having a pseudotetrahedral arrangement around the metal.



LNMo, R = $\mathrm{N\overline{CH_2CH_2OCH_2CH_2}}$

LNEt$_2$, R = N(CH$_3$CH$_2$)$_2$

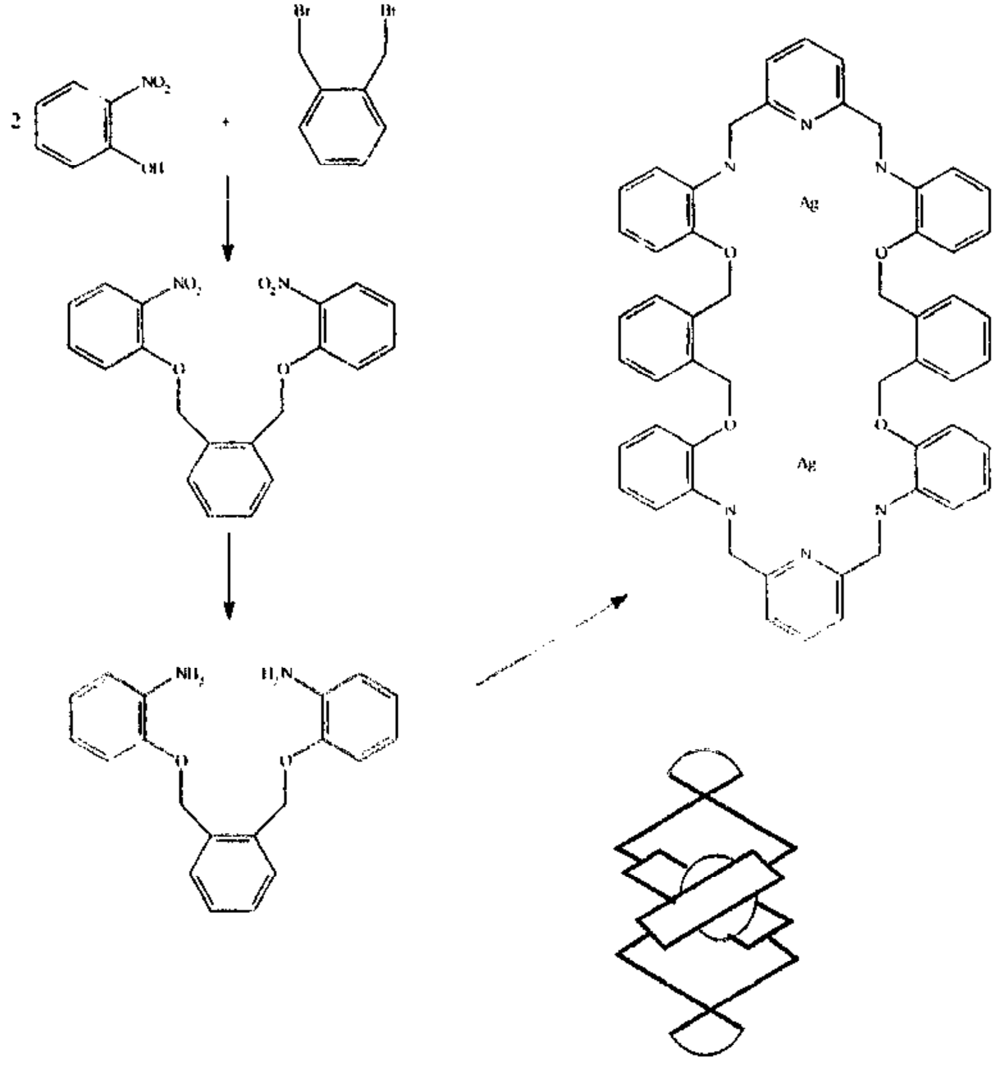
LNEtPh, R = NCH$_3$CH$_2$(C$_6$H$_5$)

**(101)**

The X-ray crystal structure of the complex difluorotetrakis(3,5-dimethylpyridine)cobalt(II)·n(hydrate) showed that it crystallizes with space group *P*4/mcc and with *a* = *b* = 9.352 and *c* = 17.264 Å and *Z* = 2 [195]. The geometry around the Co is tetragonally distorted octahedral. The complex [Co(BBP)Cl$_2$), in which BBP = 2,6-bis(benzimidazol-2′-yl)pyridine, has also been shown by X-ray diffraction studies to have distorted octahedral arrangement around the Co [196].

The X-ray structure of the complex dibromobis(2-bromopyridine)cobalt(II) has a 4-coordinate arrangement giving a somewhat distorted C$_{2v}$ symmetry around the Co [197]. Application of molecular mechanics and MO (SINDOI) calculations gave good agreement with the experimentally determined X-ray data. Thermal analysis of the complex showed that decomposition occurred at 200°C resulted in the loss of all the ligands in one step. The crystal structure of bis(tris(pyrazoyl-1-yl)methane)cobalt(II) nitrate has been determined [198].

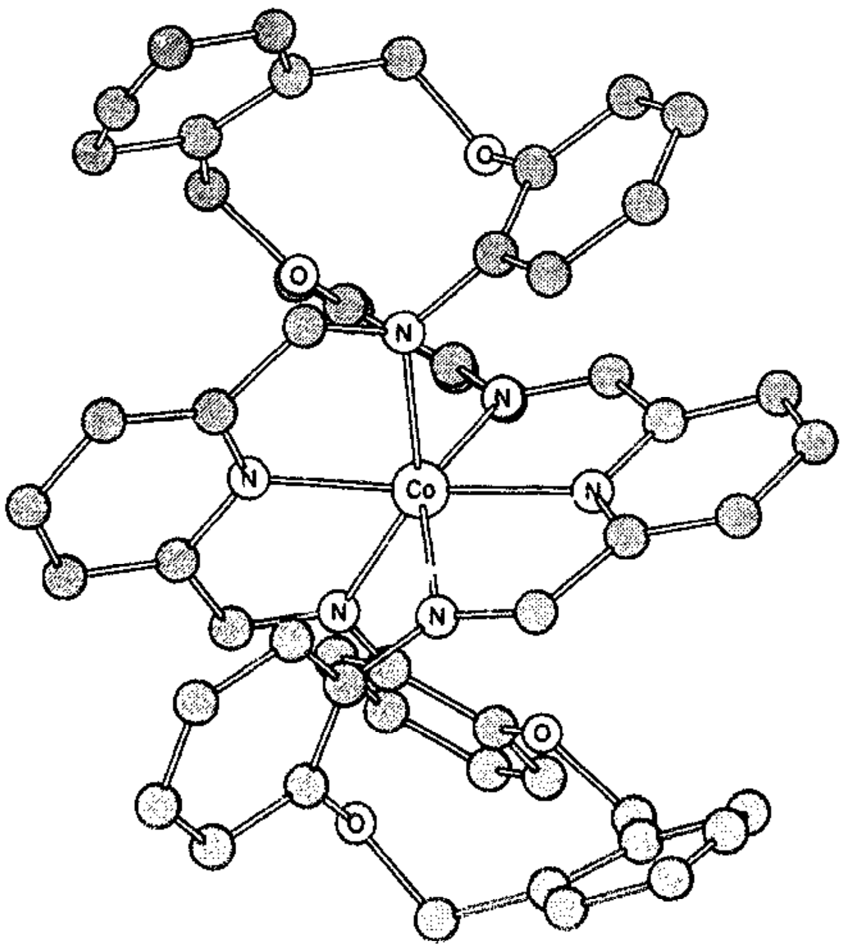
A fascinating feature of recent developments in inorganic chemistry has been the preparation of a variety of metal ion complexes in which the ligand "raps itself" around the metal to produce a helical arrangement. A recent novel example of these developments has been the preparation of a 34-membered Schiff-base macrocycle and its complexes by reactions such as that shown in **(102)** [199]. The X-ray crystal structure of $[CoL]^{2+}$ **(103)** shows the Co in a distorted octahedral environment with the ligand arranged in a helical fashion around it. The $^1H$ and $^{13}C$ NMR spectra of the approximately isostructural Zn complex show the characteristic resonances corresponding to a quarter of the molecule indicating the expected $D_2$ symmetry.



**(102)**

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

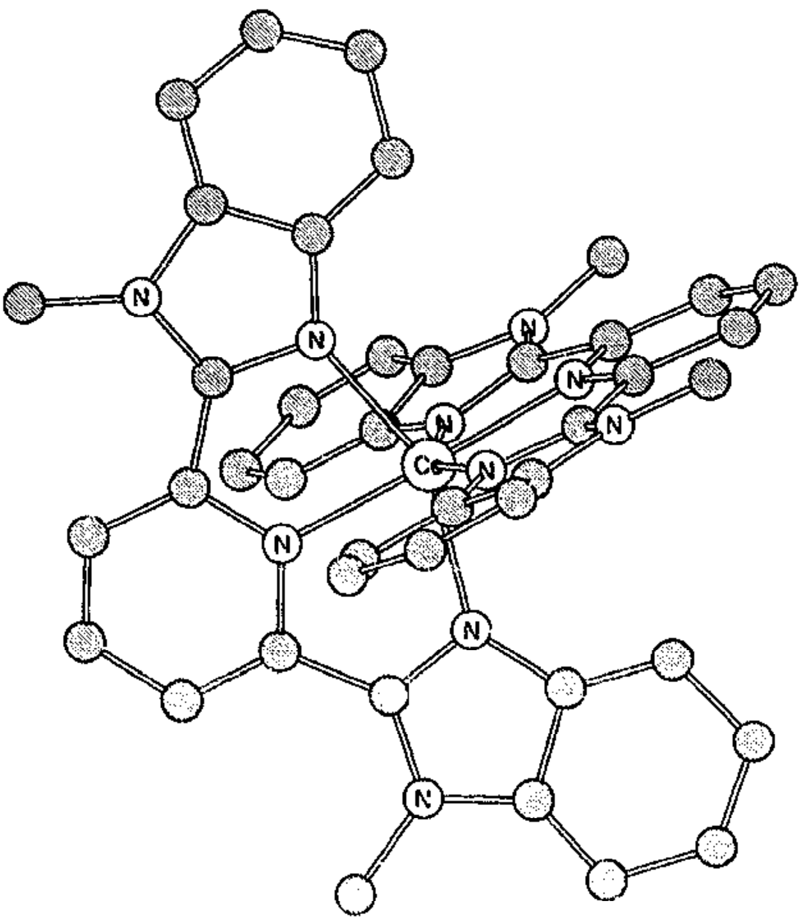
Reaction of 4′,4‴-bis(ferrocenyl)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (L) with a Co(II) salt resulted in the formation of the complex $[CoL(H_2O)_2][PF_6]_2$ in which



**(103)**

the Co is 7-coordinated [200]. Crystals of the complex $[CoL_2](PF_6)_2 \cdot 3C_4H_6O_3$, in which L = 2,6-bis(1′-methylbenzimidazol-2′-yl)pyridine and $C_4H_6O_3$ = 4-methyl-1,3-dioxolan-2-one, have two types of $(CoL_2)^{2+}$ ions each having similar geometry [201]; one cation is shown in structure (**104**). In these species each Co(II) is surrounded by six N donor atoms which the authors describe as a flattened tetrahedron with two pseudo axial Co–N bonds.

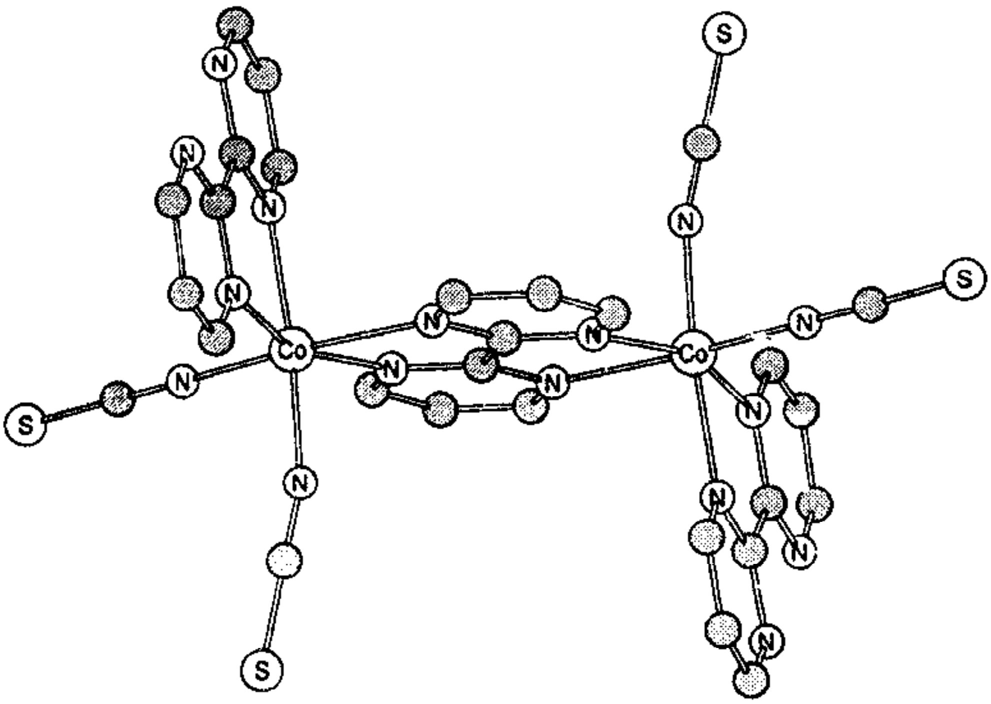
It has been found possible to describe the back donation in dichlorobis(2-chloropyridine)cobalt(II) and dichlorobis(2-methylpyridine)cobalt(II) by calculating the electronic structures of the two complexes and then comparing the valence electron densities of the pyridine ring atoms [202]. The similar complex dibromotetrakis(3-methylpyridine)cobalt(II) has been shown to have a square bipyramidal structure and molecular orbital and molecular mechanics calculations have been performed on it [203]. Three new bipyrimidine complexes of Co(II) have been prepared *viz.* $[Co_2(H_2O)_8(bipym)][NO_3]_4$, $[Co_2(H_2O)_8(bipym)][SO_4]_2$



**(104)**

and, $[Co_2(bipym)_3(NCS)_4]$ [204]. The structures of the first two of these involve dinuclear complexes in which each Co has a distorted octahedral arrangement around it consisting of water molecules and bridging bipyrimidine. The other complex (**105**) also has a distorted octahedral arrangement around the Co atoms, but as well as a bridging bipyrimidine each Co is surrounded by a bipyrimidine and two NCS ligands. A study of the temperature dependence of the magnetic properties of these complexes shows that they all exhibit antiferromagnetic exchange and the susceptibility maxima are found in the range 13.0 to 16.4 K. A distorted tetrahedral structure around the Co is to be found in the complex dichloro[2,2′-(2,5-diphenyl-3,4-pyrrolediyl)dipyridine-*N*,*N*′]cobalt(II) [205]. The organic ligand is didentate involving the N(13) and N(7) atoms.

Crystal structures of three dinuclear Co(II) complexes $[Co_2(Phth)(H_2O)(L)_4](ClO_4)_2$, in which $Phth^{2-}$ = phthalate and L = 2,2′-bipyridine, 1,10-phenanthroline or 5-nitro-1,10-phenanthroline have shown them to have structures involving extended phthalate bridges with each of the Co atoms being in a

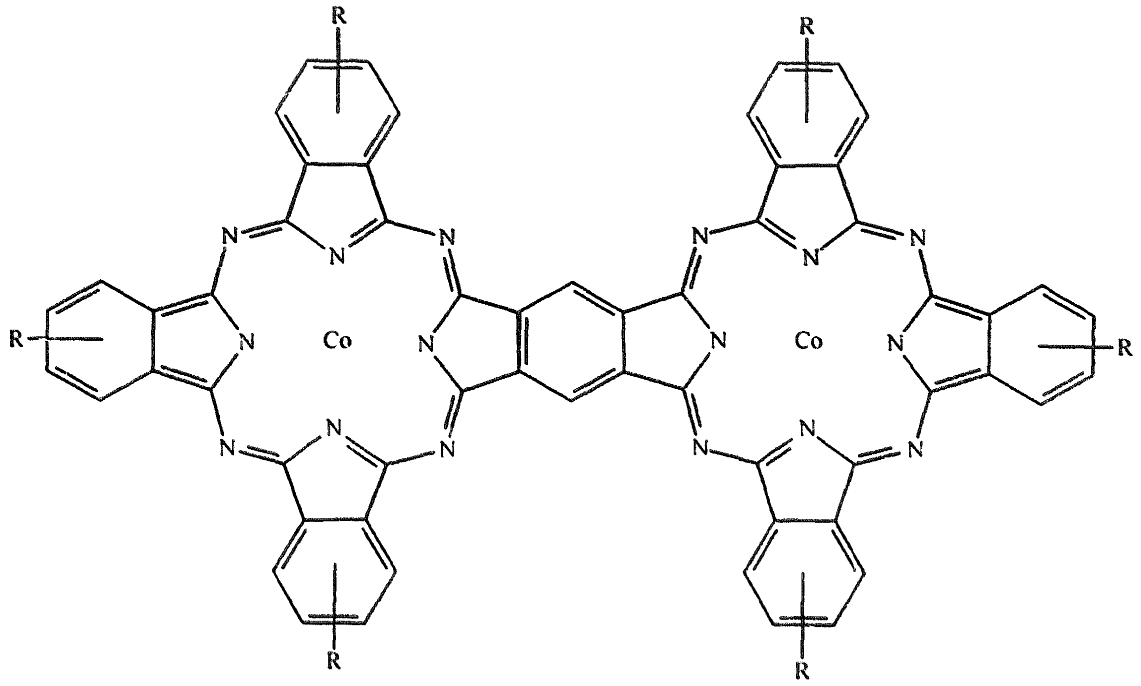


**(105)**

distorted octahedral environment [206]. There is a weak ferromagnetic interaction between the Co atoms.

In what is described as the first study in detail of a planar dinuclear complex there is a very thorough investigation of the electrochemistry using cyclic voltammetry and differential pulse voltammetry, spectroelectrochemistry and spectroscopy and Langmuir-Blodgett film formation of the dark blue complex [CoTrNPc]$_2$ **(106)** [207]. It is concluded from the electrochemical data that the two phthalocyanine planes in the complex do not exist in a completely planar arrangement in solution and show a variety of redox species and mixed valence oxidation states.

In an attempt to find out to what extent phthalocyanine and related complexes are ionic, what is the relative contribution of $\sigma$- and $\pi$- bonds in the structure, how does bonding occur in metals where d orbitals are not available and how do the structural and electronic properties relate to coordination, Rosa and Baerends have carried out a detailed investigation of the electronic structures of phthalocyanine complexes of a number of metal ions including Co(II) [208]. It was found that the $\pi$-bonding in such structures involving $Co^{2+}$, $Ni^{2+}$ and $Cu^{2+}$ is relatively weak and $\sigma$ bonding predominates. The authors compare the effect of the different hole size in porphyrin and phthalocyanine complexes and conclude that the larger hole size in the porphyrin species results in smaller orbital interactions, lower Pauli repulsion and larger electrostatic attraction. All this results in stronger bonding to the porphyrin ring system than to the phthalocyanine.

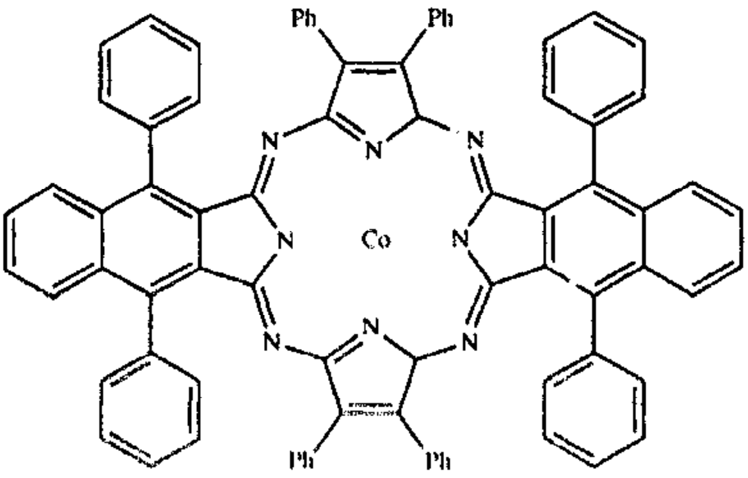


R = $OCH_2C(CH_3)_3$

**(106)**

Cobalt(II) phthalocyanines catalyse the oxidative decomposition of erythrosine by hydrogen peroxide [209]. A comparison of the relative ability of these porphyrin complexes in the solid state as particles and in solution to catalyse the reaction shows that the former are significantly better catalysts than the complexes in solution. This is attributed to reactions occurring on the surface of the particles involving dioxygen bonded to the cobalt and to erythrosine. A more unusual use of the catalytic ability of cobalt(II) phthalocyanines is in the incorporation of the complex into porous rayon where foul odours (for example from thiols) are conveniently removed by the "enzyme-like" catalytic activity of the phthalocyanine complex [210]. This group have also investigated the catalytic autooxidation of 2-mercaptoethanol using new water-soluble polymers which contained Co(II) phthalocyanine as a catalyst [211]. There has been a similar study of the autooxidation of mercaptoethanol by water-soluble cobalt(II) phthalocyanines [212]. A successful catalytic combination was found to be a mixture of [Co(II)Pc][$NMe_4$] and [Co(II)Pc]($NaSO_3$)$_4$. In this case it is suggested that the catalytic ability of the phthalocyanine system was aided by the formation of aggregates. In another development which takes advantage of the catalysing ability of Co(II) porphyrin complexes a study has been made of the synthesis of Co(II)$F_{16}$Pc ($F_{16}$Pc = perfluorophthalocyanines) inside synthetic faujasite zeolites [213]. The redox behaviour of the complex is clearly altered by the isolation within the zeolite structure, since the Co(II)/(I) process is readily observed by cyclic voltammetry in contrast to the situation obtaining in solution. This is attributed to some extent to the likely absence of aggregates of the complex in the zeolite system.

The cobalt(II) tetraazaporphyrin shown in (**107**) has been prepared by the reaction between $CoCl_2$ and diphenylmaleonotrile and 2,3-dicyano-1,4-diphenylnaphthalene [214]. One reason for interest in this complex is the fact that such compounds are structural isomers of phthalocyanines. In fact many of their spectroscopic and electrochemical properties are found to be significantly different from the Co(II) phthalocyanine complexes. Thus in the electronic spectrum of such complexes the $Q_{0\text{-}0}$ and Soret bands are split. Similarly cyclic voltammetry showed evidence of both oxidation and reduction of the Co within the seven redox couples for [CoDiNpTAP], of which two are assigned to Co(III)/(II) and Co(II)/(I) couples and the remainder to ligand redox behaviour. An electrochemical study of a number of metalloporphycenes including [Co(II)(TPrPc)] (**108**) showed only two redox steps, the first of which is established as the Co(II)/(III) redox reaction [215].



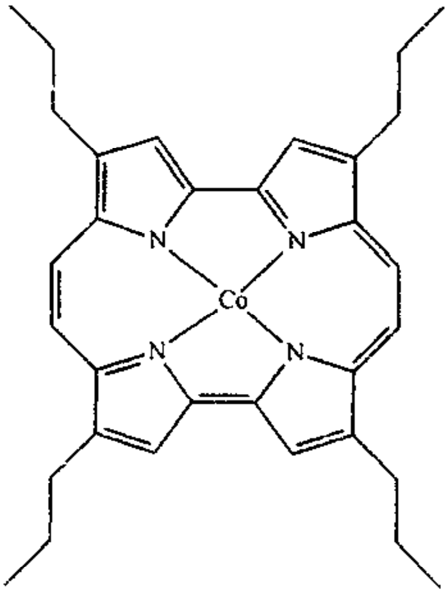
Co(DiNpTAP)

"Opposite form"

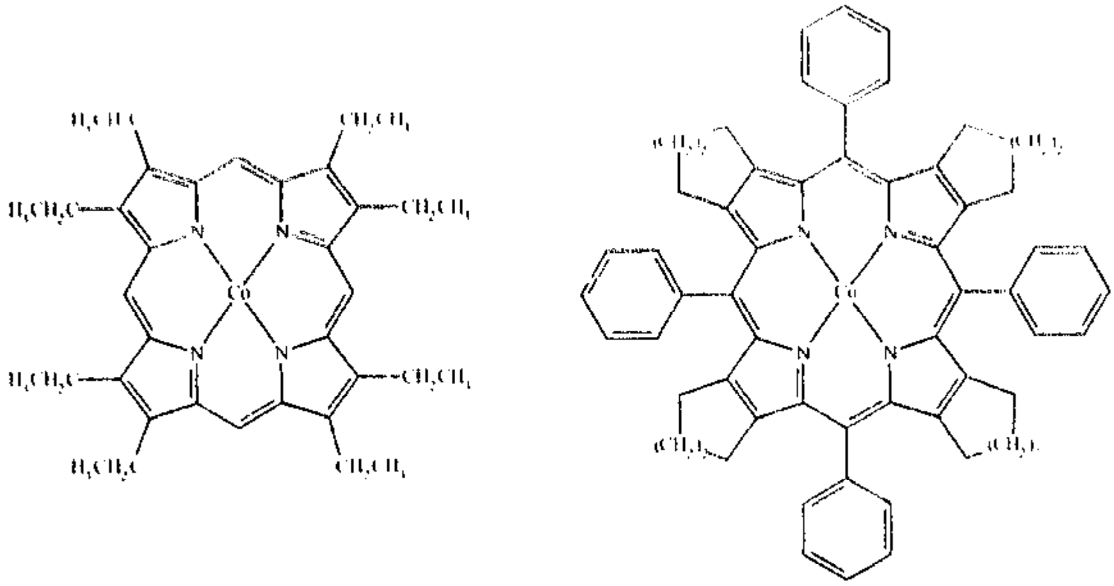
**(107)**

Cobalt(II) porphyrin complexes of the types shown in (**109**) have been investigated as part of a series of metal ion complexes studied using resonance Raman spectroscopy in order to examine correlations between the Raman frequencies and structural changes in the porphyrins resulting from systematic changes in the metal ion and substituent groups in the porphyrin [216].

The thermal decomposition, studied using DSC of the solid state of the complexes [Co(TPP)(L), [Co(Tp-$CH_3$ PP)(L)] and [Co(Tp-$OCH_3$PP)(L), in which $H_2$TPP = tetraphenylporphyrin, $H_2$Tp-$CH_3$PP = tetra(*p*-methylphenyl)porphyrin and $H_2$Tp-$OCH_3$PP = tetra(*p*-methoxyphenyl)porphyrin, and L = one of a number



[Co(II)(TPrPc)]
**(108)**



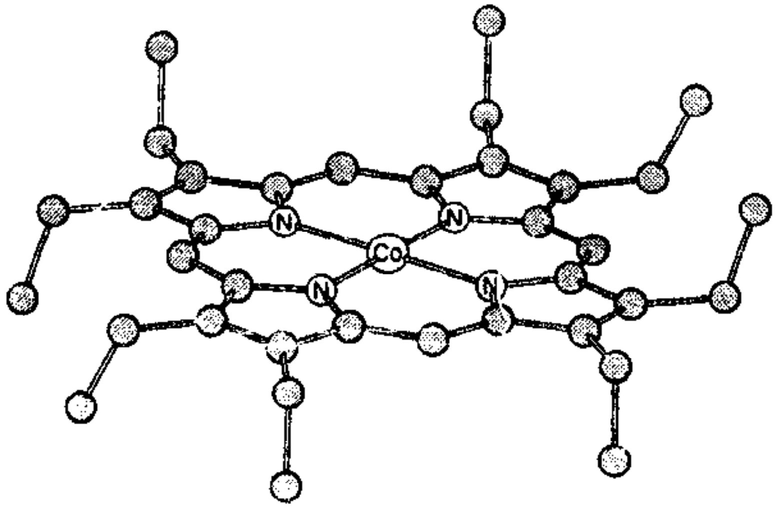
[Co(OEP)]

[Co(T6TPP)]

**(109)**

of 4-substituted pyridines, resulted in loss of the pyridine molecule [217]. The larger the size of the pyridine substituent or the more basic the moiety, the higher was the decomposition temperature in keeping with the variation of the Co-pyridine bond.

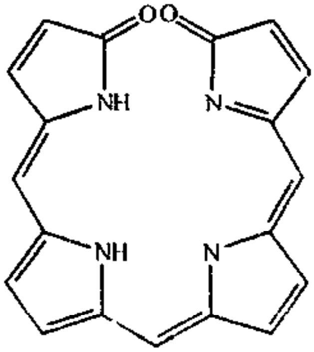
Developments in instrumentation in X-ray crystallography are demonstrated through the determination of the crystal structure of [CoOEP] (**110**) [218]. This completes the set of Fe, Co, Ni and Cu complexes of $OEP^{2-}$ whose structures have been obtained by X-ray crystallography and comparisons are made between the structures of these complexes.



(**110**)

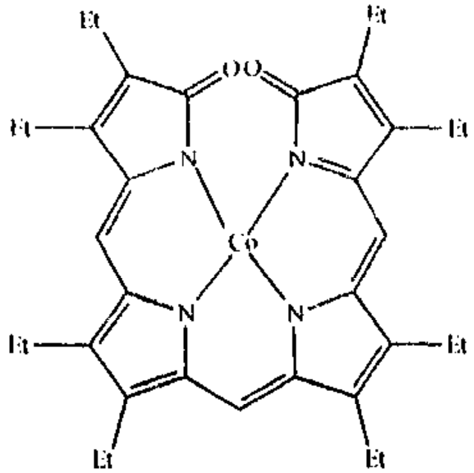
The spectroelectrochemistry and cyclic voltammetry of tetraphenylporphyrin in $EtCl_2$ the presence of $OH^-$ has been investigated [219]. Under the conditions studied, there remained only one coordinated $OH^-$. However the electrochemistry showed that electrochemical oxidation produced $[(TPP)Co(III)(OH)_2]^{2-}$. Porphyrin ring redox reactions were also observed. When the complex tetrakis(*N*-methyl-4-pyridiniumyl)porphyrinatocobalt(II) ([Co(TmPyP)]) is intercalated into the structure of crystalline negatively charged aluminosilicates and a layered hydroxide, it is found that it is orientated in such a way that the porphyrinic plane is parallel to the clay layers [220]. The ESR spectroscopic data suggest that the intercalated complex does not possess coordinated water in the axial positions but interacts with the oxygen atoms of the clay. The kinetics and mechanisms of the electro-oxidation of hydrazine by tetrakis(4-trimethylammonium phenyl)porphyrin, $H_2TMAP$, and the complex [CoTMAP] have been investigated [221]. Using electrospray ionization mass spectrometry organic dications have been observed from cobalt(II) octaethylporphyrin [222].

Bilverdins, a typical example of which is shown in (**111**), strongly resemble porphyrin ligands when complexed to a metal, but have an incomplete ring around the metal because of two terminal keto-groups [223]. A consequence of the open end is that these complexes, are not able to form the planar ring involving tetracoordination to the metal which is characteristic of porphyrin complexes. The structure of the cobalt complex [Co(OEB)] (**112**) has been determined and it is found to have a tetracoordinated cobalt in a structure in which there is a helical disposition of the ligand around the cobalt as shown in structure (**113**). Although this work is included here under the heading of cobalt(II) complexes, the formulation of the complex could be [Co(III)(OEB)] or [Co(II)(OEB·)] or a thermal equilibrium between the two species.



Bilverdins

**(111)**

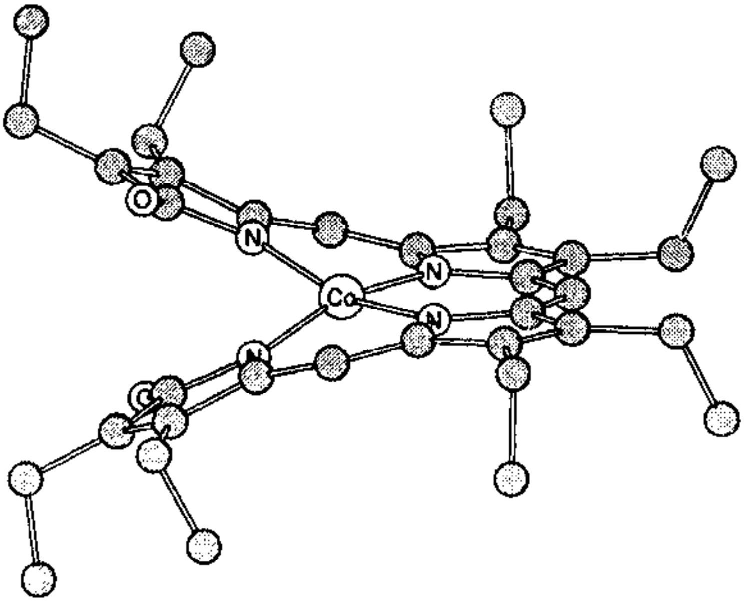


[(OEB)Co]

**(112)**

The synthesis and reactivity of a number of semicorrinate complexes of Co(II) have been studied [224].

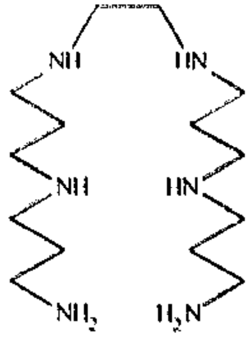
A distorted tetrahedral geometry is the arrangement around Co in the blue



**(113)**

complex dichloro(1,2-bis(pyrazolylmethyl)benzene)cobalt(II) [225]. The space group is monoclinic, $P2_1/c$, $a = 10.364$, $b = 11.617$, $c = 13.720$ Å and $\beta = 109.76°$, $Z = 4$.

The ligand 4,8,11,15-tetraazaoctadecane-1,18-diamine (**114**) has been synthesized and it has been found to form both mononuclear and dinuclear complexes with Co(II) [226].

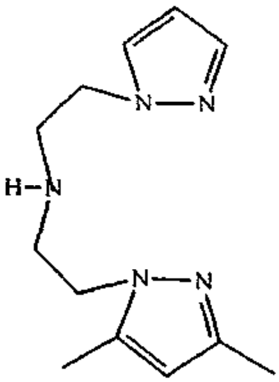


4,8,11,15-tetraazaoctadecane-1,18-diamine

**(114)**

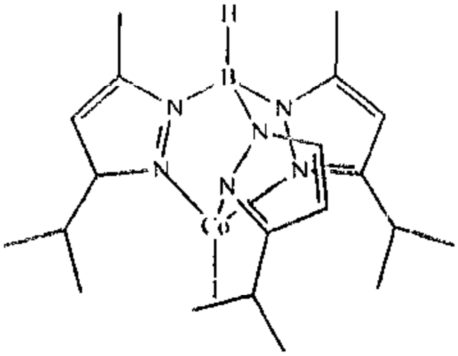
The ligand ddaH (**115**) forms the cobalt(II) complexes $[Co(ddaH)Cl]_2(CoCl_4)$ and $[Co(ddaH)Cl](BF_4)$ and the X-ray crystal structures of both of these have been determined [227]. The Co is in a distorted octahedral array made up of two azido N atoms, one amine N atom and the chloride.

An excellent yield of regiosymmetric cobalt complexes is obtained when a tris(pyr-



**(115)**

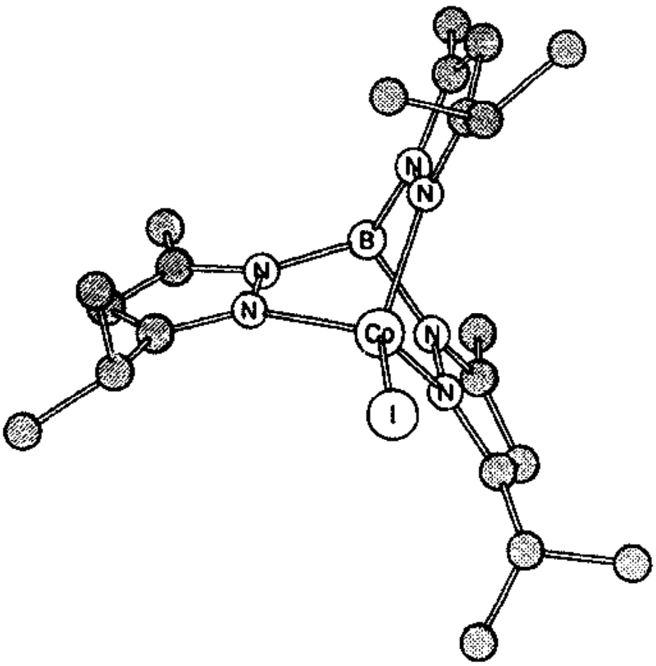
azolyl)borate is reacted with $CoI_2$ [228]. An interesting method of separation has been devised for these compounds by the authors which they term "inverse crystallization". Basically the method used was to produce a suspension of the crude mixture in $CH_3CN$, in which it could not be dissolved under normal conditions. They cooled this suspension down to −30°C, when dissolution occurred; they then rewarmed and allowed the blue crystals to be produced. This resulted in the complex shown in (**116**); the crystallographically determined structure of this is shown in diagram (**117**). A key feature of the unusual recrystallization procedure appears to be the formation of a complex $[(Tp)Co(NCCH_3)_3]I$ (Tp = ligand in (**116**)). Equilibrium studies were carried out on the formation of this species.



[Hydridotris(3-isopropyl-5-methylpyrazoyl)borato]iodocobalt(II)

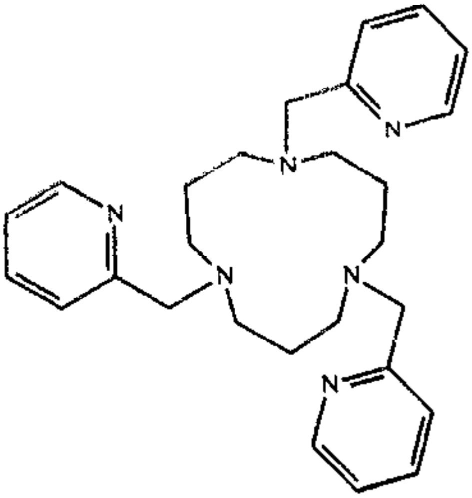
**(116)**

A rather more reliable process has been developed to make the ligand L (**118**) and its Co(II) complex has been prepared and characterized [229]. Although the two complexes only differ in triaza ring size, this was found to be oxidized less readily than the corresponding 1,4,7-triazacyclononane complex, redox potentials being Co(III)/Co(II) = 0.31 V and 0.09 V *vs* NHE respectively. The Co(II) complex of a tetraazamacrocyclic ligand made by condensation of 1,2-diaminoethane,



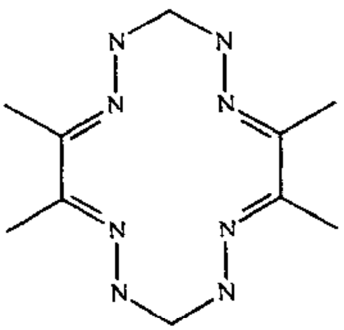
**(117)**

1,3-diaminopropane and *o*-phenylenediamine with methyl acetoacetate or ethyl acetoacetate have been prepared and characterized [230].



**(118)**

The structure of the molecular **g** tensor of the complex $[CoL(H_2O)Cl)]^+$ [L = (**119**)] has been determined using single crystal EPR spectroscopy and confirmed using powder laser EPR spectroscopy [231]. A comparison is made between the results from these experiments and those involving samples diluted with the Ni complex [Ni(L)Cl]Cl and this confirms that in these circumstances there is a significant phase-coupling effect in the ligand field of L.



**(119)**

The complex [Co(ddae)$(NO_3)_2$], where ddae = bis(2-(3,5-dimethyl-1-pyrazolyl)ethyl)ethylamine, is among one of six similar compounds of Co, Ni and Cu which have been prepared and structurally investigated [232]. The crystal structure shows that the organic ligand behaves in a didentate fashion and that the corresponding Co and Ni complexes are isomorphous.

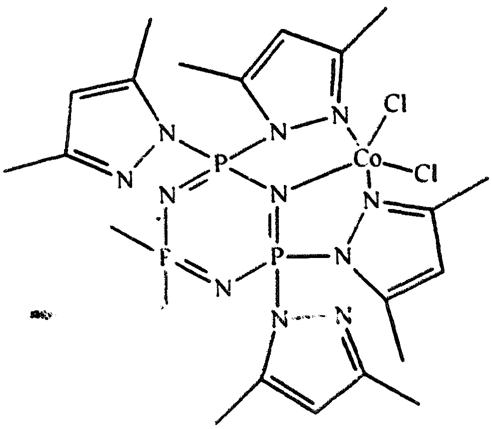
The crystal structure of the dinuclear complex [$Co_2$(BTBI)$Br_4$]·2DMF (BTBI = 1,2,4,5-tetrakis(benzimidazol-2-yl)benzene), which has been prepared among a number of other similar compounds of Co(II), shows that it is monoclinic with space group $P2_{1/n}$, $a = 10.021$, $b = 25.569$, $c = 11.518$ Å, $\beta = 111.78°$, $V = 2700.4$ $Å^3$ and $Z = 2$ [233]. Each Co is surrounded tetrahedrally to produce a centrosymmetric arrangement.

The reduction of two manganese(III) porphyrin complexes by $[Co(sep)]^{2+}$ has been studied from a mechanistic point of view [234]. In the case of the [Mn(TCPP)] complex ($H_2$TCPP = tetrakis(4-carboxyphenyl)porphin) an interesting feature is that the reaction is biphasic and the authors interpret this as being due to simultaneous attack at the edge of the porphyrin ring on the one hand and the axial waters on the other.

The great interest in the role of nitric oxide in living systems has resulted in the development of a number of analytical techniques which are capable of measuring very low concentrations of NO and related compounds *in situ*. A recent example has been the preparation of a fibre optic sensor for the analysis of nitrite ion [235]. This consists of deposition of Co(II) tetrakis(*o*-aminophenyl)porphyrin onto the surface of an In(Sn) oxide glass slide in contact with the end of a fibre optic. By measuring the absorbance change produced by the reaction of the $NO_2$ with the Co(II) porphyrin it was possible to detect down to $6 \times 10^{-9}$ M.

The synthesis of the most unusual Co(II) complex, [Co(L)$X_2$], where L is illustrated in the proposed structure (**120**), has been described [236].

The process of oxidation of Co(II)-*meso*-octaalkylporphyrinogen using $CuCl_2$ or benzoquinone in $Et_2O$ proceeds according to the series of reactions shown in (**121**)



**(120)**

[237]. The crystal structure of 5,5,10,10,15,15,20,20-octaethylporphyrinato cobalt(II) (**122**) has been determined.

Cobalt(II) complexes $[Co\{HB(C_2H_2N_3)_3\}_2]\cdot 6H_2O$, and $[Co\{H_2B(CHN_4)_2\}_2(H_2O)_2]\cdot H_2O$, where $HB(C_2H_2N_3)$ and $H_2B(CHN_4)_2$ are drawn in diagram (**123**) [238]. The X-ray crystal structure of the complex $[Co\{HB(C_2H_2N_3)_3\}_2]\cdot 6H_2O$, (**124**)$\cdot 6H_2O$ with the tridentate ligand shows an octahedral arrangement around the cobalt centre, while in the complex $[Co\{H_2B(CHN_4)_2\}_2(H_2O)_2]\cdot H_2O$, (**125**)$\cdot H_2O$ containing the didentate ligand there is a structure involving bridging ligands between the metal atoms producing a 2-dimensional polymeric arrangement.

### *3.2. Complexes with oxygen donor ligands*

The crystal structure of the complex hexaaquacobalt(II) bis(3,3′,3″-phosphinidynetripropanoato)dicobaltate(II,II) hexahydrate has been determined [239]. Although the structure of this complex is very similar to the corresponding Zn(II) compound, nevertheless the environment around the Zn is trigonal bipyramidal, while that around one of the cobalt ions is octahedral. This arises because of a small difference in the position of one of the oxygen atoms in the structures.

In solution in propylene carbonate, conductance measurements of complexes $Co(ClO_4)_2$, $CoCl_2$, and $CoBr_2$ show anomalous behaviour [240]. This is attributed to equilibria of the type:

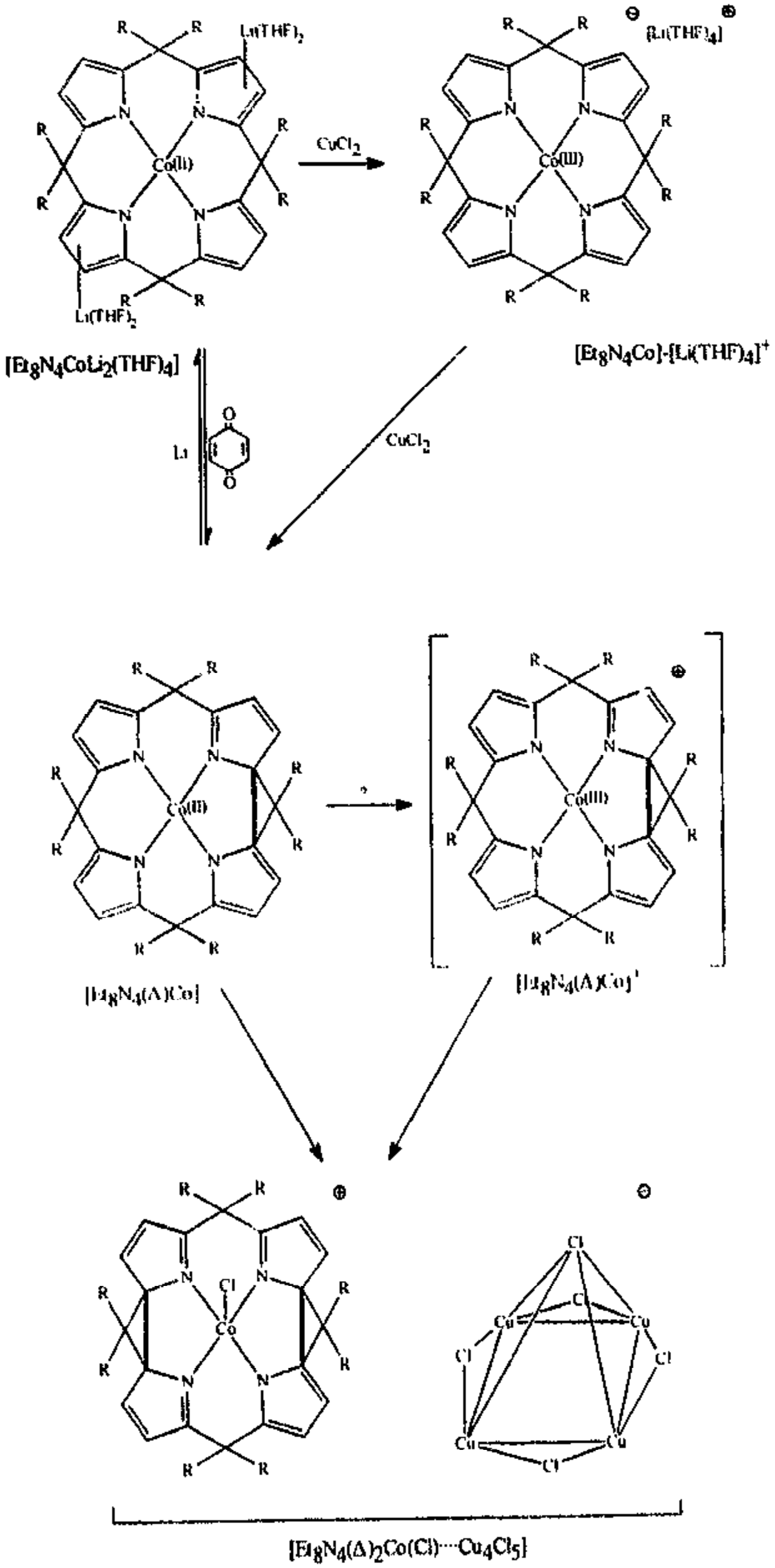
$$MX_2 \rightleftharpoons MX^+ + X^-$$

$$MX_2 + X^- \rightleftharpoons MX_3^-$$

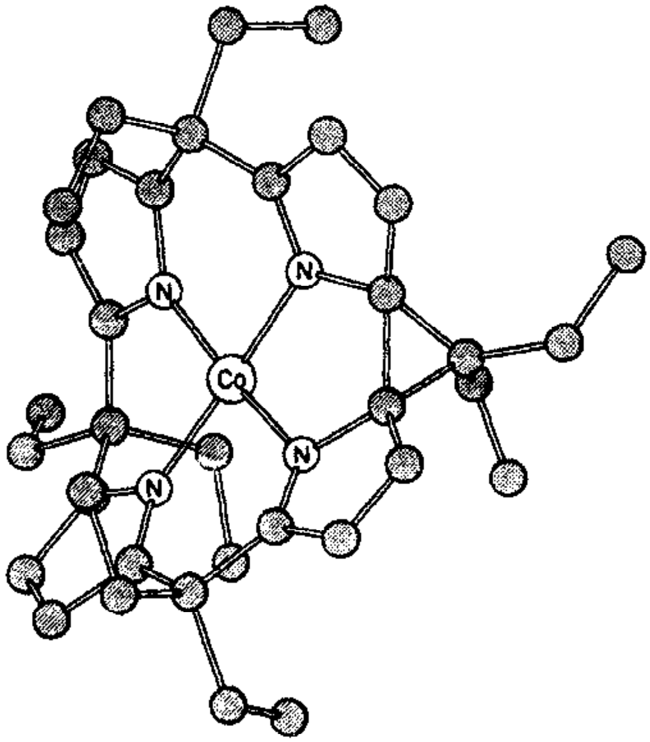
$$MX^+ \rightleftharpoons M^{2+} + X^-$$

$$MX^+ + MX_3^- \rightleftharpoons (MX_2)_2$$

There have been two studies of the reduction of cobalt(II) acetate in aqueous


Li(THF)2
Co(II)
Li(THF)2
[Et8N4CoLi2(THF)4]
CuCl2
[Li(THF)4]
Co(III)
[Et8N4Co]-[Li(THF)4]+
Li
CuCl2
Co(II)
?
Co(III)
[Et8N4(Δ)Co]
[Et8N4(Δ)Co]+
Cl
Co
Cu
Cl
[Et8N4(Δ)2Co(Cl)···Cu4Cl5]
R

**(121)**

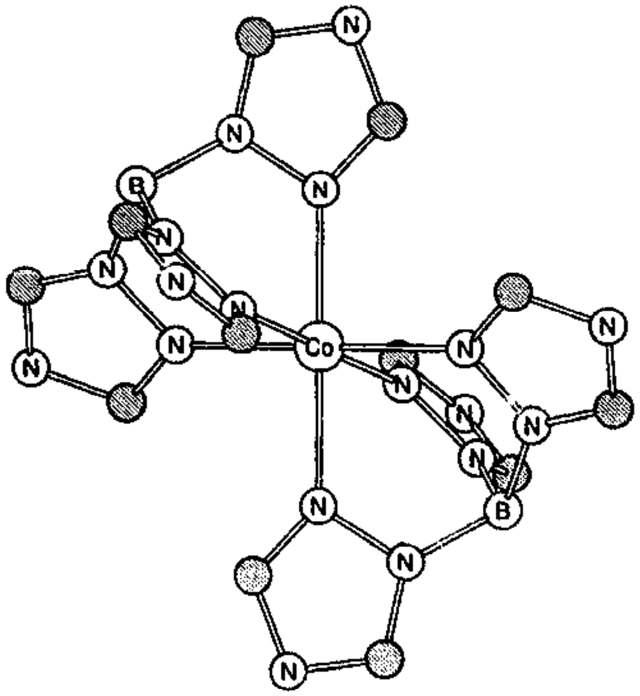


**(122)**

(123)

solution by hydrogen, one involving kinetics in the presence of Al powder [241] and the other electrochemically at an Al electrode [242]. The reaction involving Al powder was found to be first order in [Co(II)] and kinetically controlled. The electrochemical study gave results which correlated well with those from the kinetic investigation. Cobalt(II) complexes of lactic acid have been prepared by the use of electrochemical synthesis techniques [243].

The solvation structure of Co(II) ions dissolved in 1,1,3,3-tetramethylurea have been studied along with that of 7 other metal(II) ions [244]. The structures were examined using EXAFS and electronic absorption spectroscopy. In solutions of


N
N
N
B
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Co
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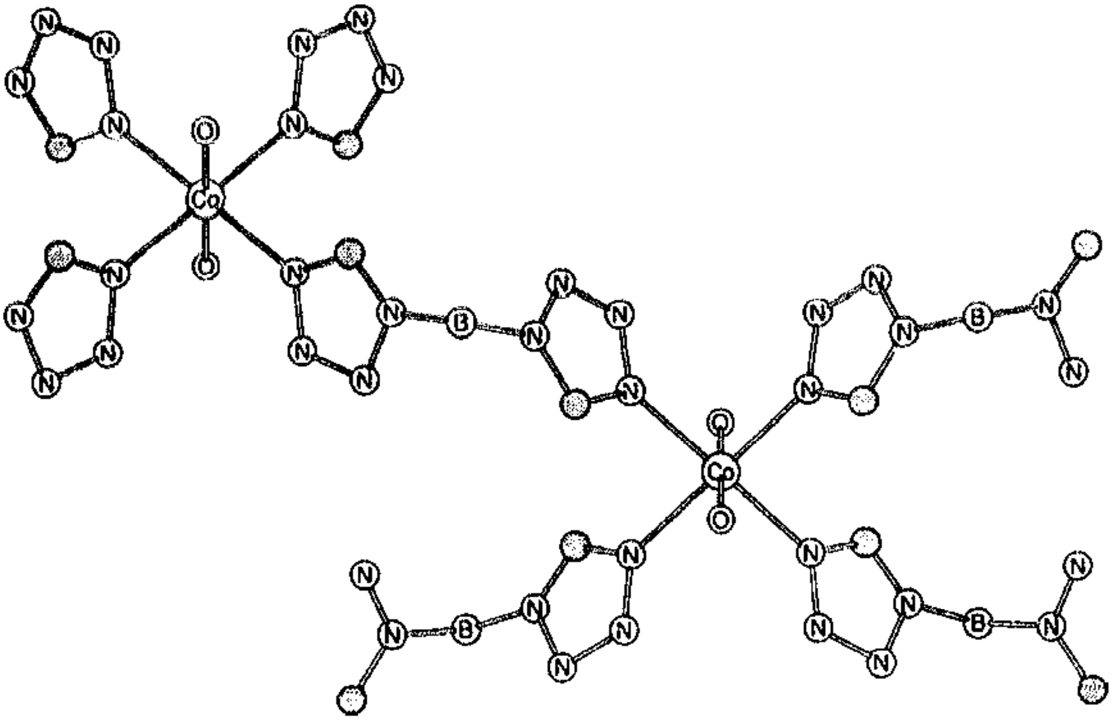
N
N

**(124)**


N
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N
N
N
N
B
N
N
O
Co
O
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N
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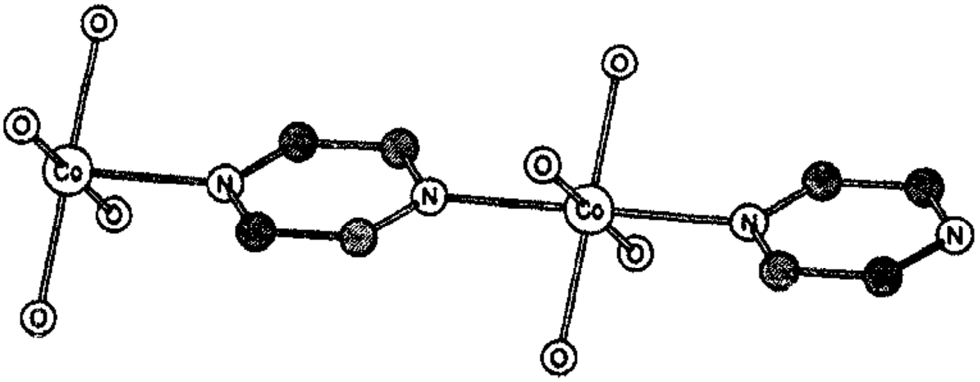
B
N
N

**(125)**

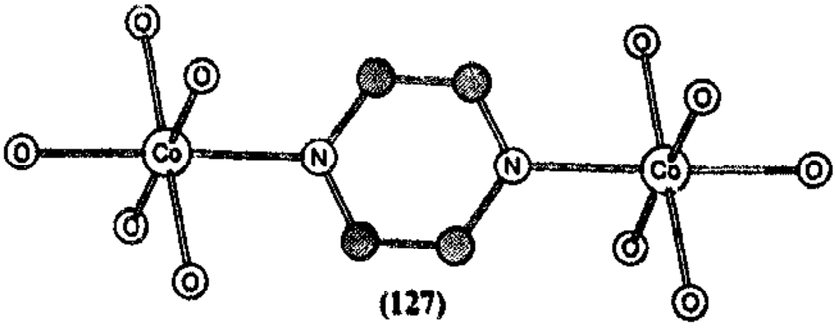
Co(II) there was found to be a distorted tetrahedral solvation structure, with a Co–O bond length of 2.00 Å.

Two groups have published results of a crystal structure determination of $Co(HSeO_3)_2 \cdot 2H_2O$ [245,246] and mercifully they are in agreement, with the structure having a slightly distorted octahedral arrangement around the Co and the layers being held together via hydrogen bonding involving the water molecules and $HSeO_3^-$ ion. These latter ions appear in the basal plane. Both groups also investigated the thermal decomposition of the species and conclude that it occurs through a number of steps with CoO as the final product.

The complexes tetraaqua-*m*-pyrazinocobalt(II) sulfate dihydrate, $[(\mathbf{126})][SO_4] \cdot 2H_2O$, and *m*-pyrazinobis[pentaaquacobalt(II)] disulfate dihydrate, $[(\mathbf{127})][SO_4]_2 \cdot 2H_2O$, consist respectively of a polymeric structure involving alternating linear chains with molecules joined by pyrazine and a dinuclear complex containing bridging pyrazine [247].



(126)

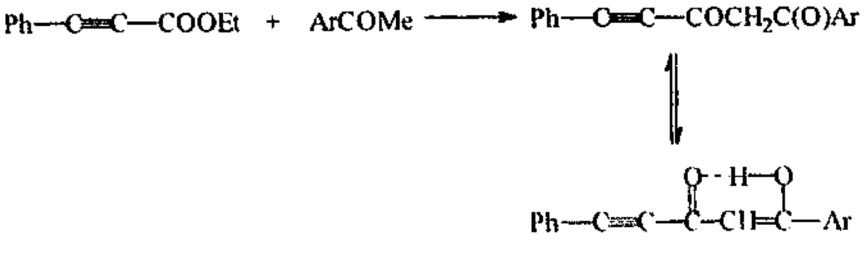


(127)

An X-ray crystal structure shows that the Co(II) in *trans*-tetraaquabis(*p*-nitrohippurato)cobalt(II) dihydrate is at the centre of an essentially octahedral environment which consists of the two monodentate *p*-nitrohippurato groups in axial positions with the water molecules in equatorial positions [248].

Blue/violet crystals are produced when $CoBr_2$ is reacted with NaOAr in THF when air and moisture are rigorously excluded [249,250] where OAr = *o*-nitro, *o*-chloro, *o*-bromo, *m*-chloro, *p*-bromo, 2,4-dichloro, 2,6-dichloro, 2,4-dimethyl-phenoxide. The complexes were of the form $Na_2[Co(OAr)_4]$ and believed to have the OAr tetrahedrally arranged around the cobalt.

A regular octahedral arrangement is to be found around the Co in the complex $[Co(MeLH)_4(NO_3)_2]$, where MeLH = 2-hydroxy-6-methylpyridine [251] with the hydrogen atoms on MeLH being involved in hydrogen bonding. An interesting feature of this Co(II) compound is that it was prepared in this work as were the complexes of a number of other metals by ligand transfer of the hydrated nitrate from $[Cu_6Na(MeL)_{12}][NO_3]$. The species 5-(α-furyl)-1-phenylpent-1-yne-3,5-dione and 5-(a-pyridyl)-1-phenylpent-1-yne-3,5-dione are produced by the reaction shown in (**128**) [252]. These react with Co(II) acetate to produce brown complexes $[CoL_2(H_2O)_2]$ in which the Co is believed to be in a square planar environment.



Ar = α-furyl or α-pyridyl

**(128)**

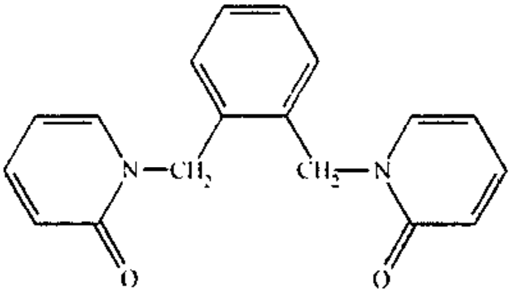
A tetrahedrally coordinated cobalt ion is found in an open framework structure in $CoPO_4 \cdot 0.5C_2H_{10}N_2$ [253]. The deep blue cobalt phosphate forms crystals belonging to space group *I*2/b (non-standard setting) with $a = 14.719$, $b = 14.734$, $c = 17.891$ Å and $\gamma = 90.02°$ and it involves alternating $CoO_4$ and $PO_4$. This structure is unusual in that it is the first framework structure in which there is only Co, P and O with the Co in a tetrahedral environment. The phosphate $M_{14}Co(P_3O_9)_2 \cdot xH_2O$, in which M = Na, K, Rb, Cs, $NH_4$, contains Co in octahedral sites [254]. This environment was used to study the EPR and absorption spectra of $Co^{2+}$ ions which are fairly isolated from their nearest neighbours. It is concluded that the $Co^{2+}$ ion is very sensitive to its immediate surroundings in such structures.

The dodecatungstatocobaltate(II) ion is frequently used to examine the behaviour of Co(II) in a tetrahedral environment. The kinetics of the reaction of $[CoW_{12}O_{40}]^{6-}$ with $MnO_4^-$ have been examined to see if such a reaction would be an exception to the usual redox reactions of $[MnO_4]^-$ by being outer sphere in nature rather than inner sphere [255]. The rate equation for the process was found to be:

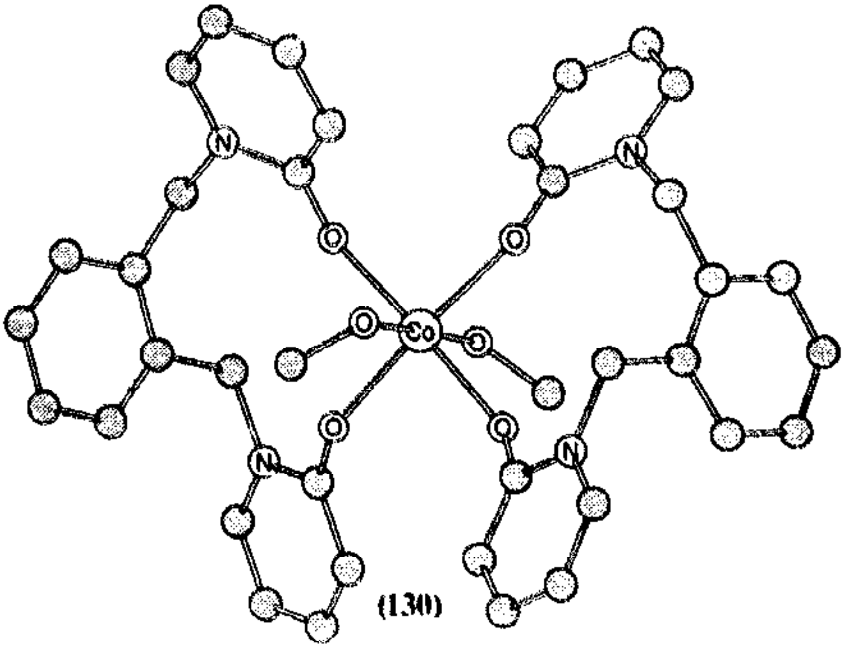
$$\text{Rate} = 5K_a k[H^+][MnO_4^-][CoW_{12}O_{40}^{6-}]$$

with $K_a = 2.99 \times 10^{-3}$ mol$^{-1}$ dm$^3$ and $k = 2.00 \times 10^3$ dm$^6$ mol$^{-2}$ s$^{-1}$. Application of Marcus calculations to the system strongly supported the notion of an outer sphere mechanism.

The Co(II) complex $[Co(o\text{-xbp})_2(MeOH)_2]I_2 \cdot 2MeOH$ is one of the complexes of *o*-xbp (**129**) which have been prepared with five metal ions [256]. The X-ray crystal structure of the Co(II) complex shows that in the cation (**130**) the two methanol molecules in the inner coordination sphere are to be found in the axial positions and are hydrogen bonded to the solvate methanol molecules. The ligand *o*-xbp occupies the equatorial positions in a didentate fashion. 1:1-Complexes have been observed in aqueous solution between Co(II) and 25-hydroxycholecalciferol or 1α25-dihydroxycholecalciferol (**131**) [257]. These two ligands are believed to be the active forms of vitamin $D_3$ (cholecalciferol) and the authors claim that these are the first examples of spectrophotometric detection of complexes of these ligands.

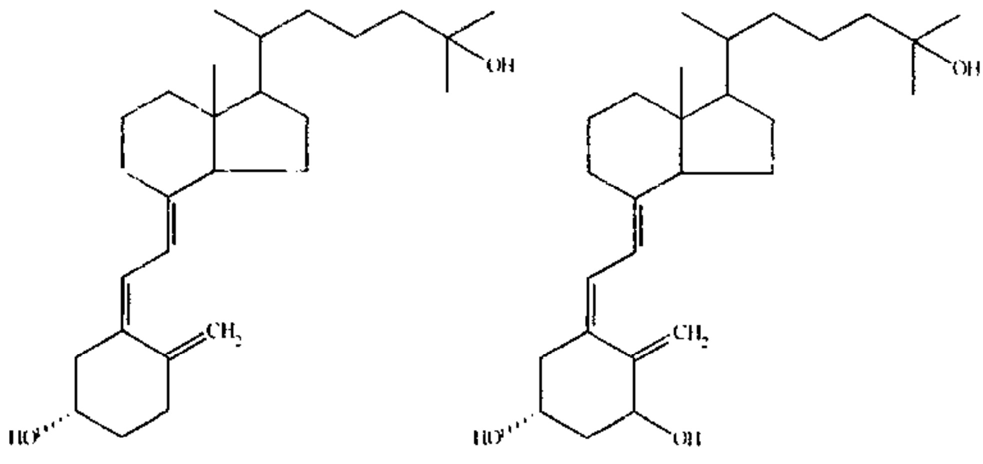


**(129)**



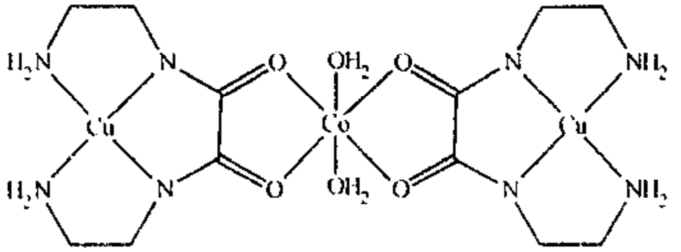
**(130)**

Complexes formed by the coordination of the ligand attached to one metal to another metal are always of interest. Such a species is $[Cu_2(oxae)_2(H_2O)_2Co](ClO_4)_2$, in which oxae = *N*,*N*′-bis(2-aminoethyl)oximido



25-hydroxycholecalciferol 1α,25-hydroxycholecalciferol

**(131)**



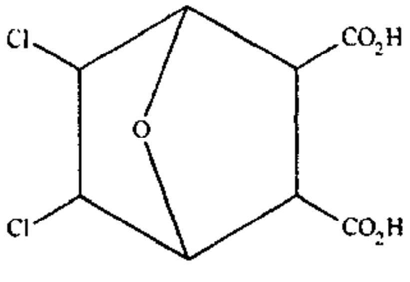
**(132)**

anion which is formed as dark red crystals by reaction of Cu(oxae) with $Co(ClO_4)_2$ in ethanol [258]. The proposed structure is shown in (**132**). The magnetic properties of the complex show that there is antiferromagnetic spin-exchange between the neighbouring metal ions.

$[CoL_3(H_2O)_3]$ in which L = 5,5-dihalogeno-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid (**133**) has been shown by its X-ray crystal structure to have Co(II) in an octahedral environment with the dicarboxylate behaving as a tridentate ligand [259], the other positions being occupied by three water molecules.

Potentiometric methods have been used in the measurement of equilibrium constants for the reactions of Co(II) ions with D-glucoheptanoic, D-gluconic, D-galactonic, D-ribonic, D-glucuronic and D-galacturonic acids at 20°C [260].

Equilibrium data have been obtained for the formation of a number of ternary complexes of Co(II) involving adenosine-5′-mono-, di- and tri-phosphates in mixtures containing malic, maleic, succinic, tartaric, citric, and oxalic acids [261]. The complexes formed had stoichiometries of 1:1:1 and the stabilities were in the order AMP < ATP and succinic > maleic > tartaric > malic > citric > oxalic acids.



**(133)**

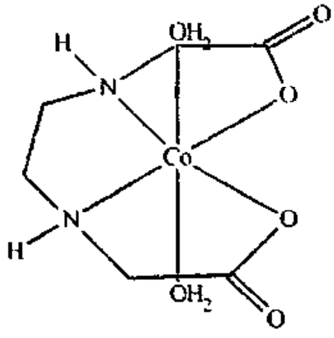
### 3.3. *Complexes with nitrogen–oxygen donor ligands*

Many coordination compounds of cobalt(II) which may otherwise have appeared in this section are included in Section 4 since they commonly are involved in reactions with molecular dioxygen.

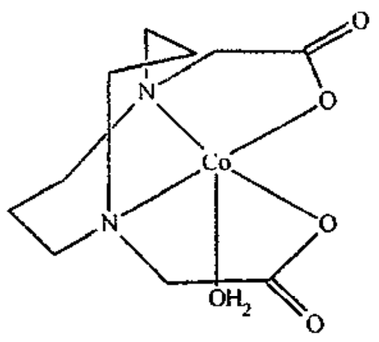
Perhaps the most common complexes of metal ions involving nitrogen and oxygen as donor atoms are those of edta$^{4-}$ and related complexes commonly found in many analytical applications. The complex $[Co(edta)]^{2-}$ has been found to be readily oxidized by $H_2O_2$ in the presence of activated carbon to $[Co(edta)]^-$ at pH 4.7 [262]. The mechanism for the process has been found to involve a chain reaction in which the AC/AC$^+$ (AC = activated carbon) cycle is the governing factor because of an electron transfer process from the AC to $H_2O_2$ giving the radical $OH^{\cdot}$ which can then oxidize $[Co(edta)]^{2-}$. Measurement of the kinetics of the reaction and the similar $S_2O_8^{2-}$ oxidation lead the authors to conclude that the AC in this process behaves rather like Fe(II) in the Fenton reagent. A study of the kinetics of the anation reaction of $SCN^-$, bpy and phen with $[Co(nta)]^-$ (nta = nitrilotriacetate) has allowed the mechanism of the reaction to be elucidated [263].

EPR spectra of a series of complexes which contain water molecules and nitrogen-oxygen donors have been studied [264]. A major purpose for this investigation was to see if electron spin echo modulation, ESEEM, would be a useful technique in the investigation of biological species containing high spin metal ions to detect water, histidine or imidazole residues attached to the metal. The molecules studied are shown in **(134)** using this technique and it was found that it is indeed possible to detect water using studies in $D_2O$ and $H_2O$ and also coordinated imidazole. The authors conclude that ESEEM has significant potential for the investigation of species having high spin Co(II).

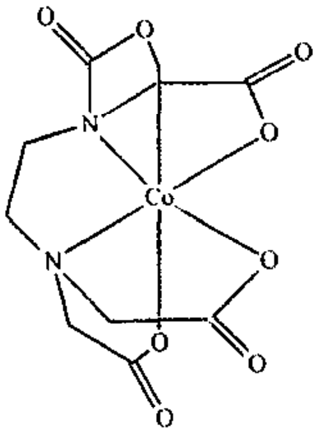
The kinetics of the very rapid reactions between *N,N'*-dimethyl(*p*-pyridin-2-ylazo)aniline and the Co(II) complexes of *N*-methyliminodiacetate, ethylenediamine-*N,N'*-diacetate, diethylenetriamine and triethylenetetramine have been investigated using temperature jump techniques [265]. The equilibrium constants have also been obtained and it is shown that such factors as the number of bound nitrogen atoms affect the rate and this is similar to the situation found for other related systems. There has also been a study, again using temperature jump techniques, of



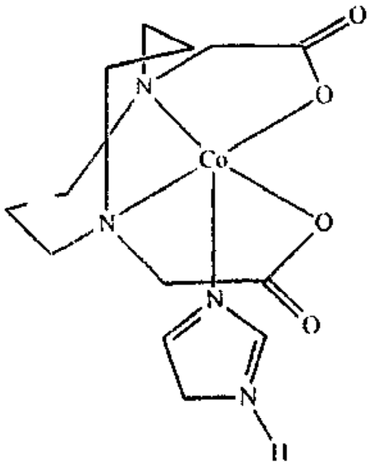
[Co(EDDA)(H$_2$O)$_2$]



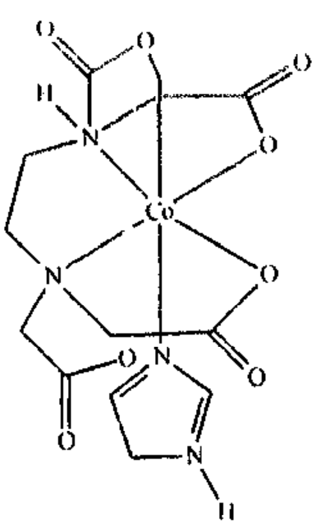
[Co(dacoda)H$_2$O)]



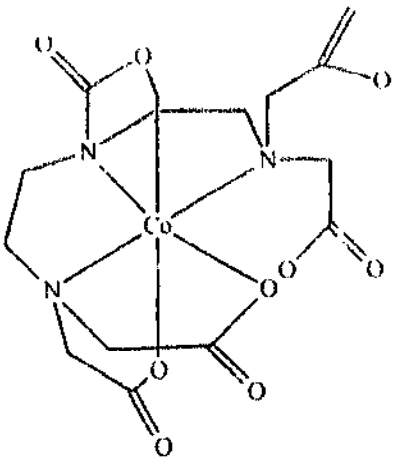
[Co(EDTA)]



[Co(dacoda)Im]



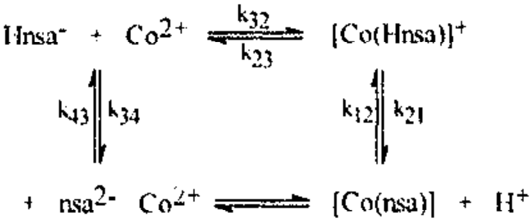
[Co(EDTA)Im)]



[Co(DTPA)]

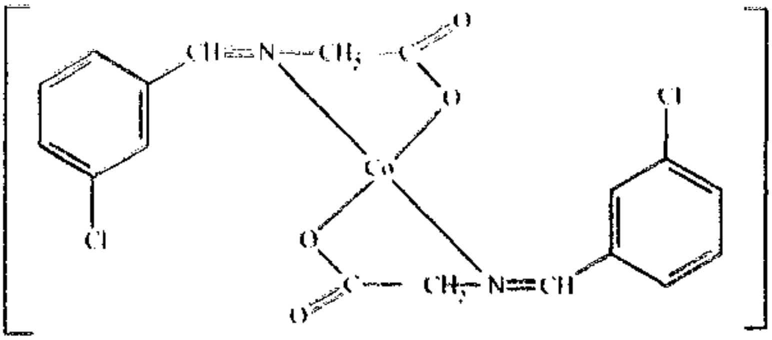
(134)

the 1:1 reactions between 5-nitrososalicylate(2−) ($nsa^{2-}$) and $Co(aq)^{2+}$ and also for ternary complexes which involve a variety of other ligands e.g. nitrilodiacetate, ethylenediamine-*N,N'*-diacetate, ethylenediamine-*N,N*-diacetate and triethylenetetraamine and Co(II) complexes with polytriphosphate, iminodiacetate and diethylenetriamine [266]. The pH dependence of the rate constants was determined and a typical series of equilibria involved is shown for Co(II) in (**135**). The rate constant, $k_f$, for the $Co^{2+}$ reaction is given by log $k_f = 6.81$ and $\Delta H_f^{\ddagger} = 42$ kJ mol$^{-1}$. Where the other complexes are concerned, the positive charge on the metal certainly had a significant effect on the rate as did the number of bound nitrogen atoms.



**(135)**

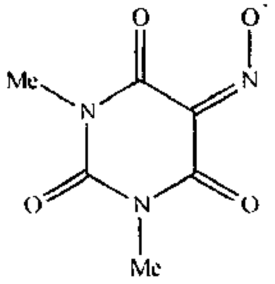
Formation constants have also been determined for Co(II) histidine complexes [267] and also for 1:1 complexes [Co(L)], where L = picolinic acid *N*-oxide and several of its derivatives and also 1:1:1 ternary complexes involving, in addition a number of *N,O*-donors, *N,N*-donors and *O,O*-donors [268]. The Co(II) complex of the Schiff base made by reaction of 3-chlorobenzaldehyde and glycine has been prepared and has the suggested structure shown in (**136**) [269]. It has been tested for fungicidal activity and has been found to inhibit *Gypseum floccosum Canis* and *Rubrum*.



**(136)**

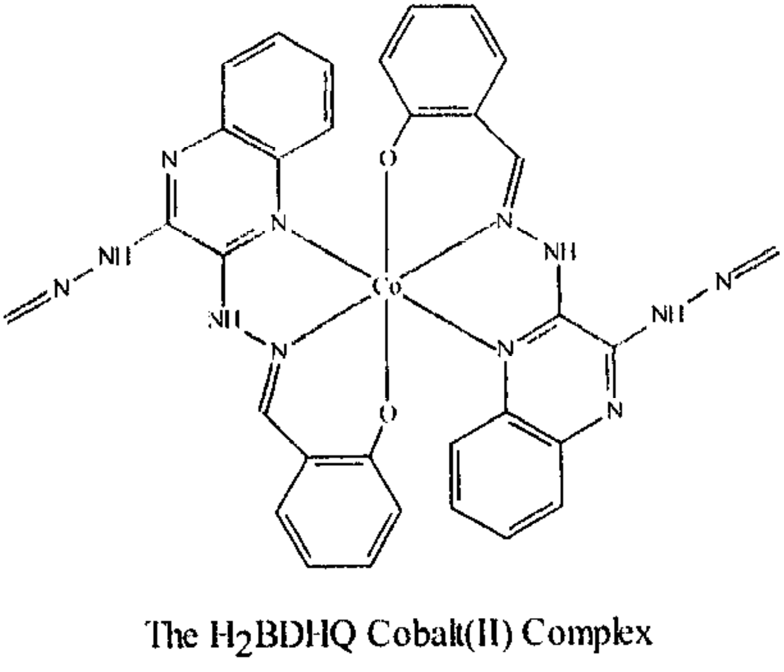
In a search for the unusual situation of a Co(II) complex which exhibits spin crossover, Faus and coworkers sought to synthesize $[Co(dmvi)(phen)_2]^-$ (dmvi = dimethylviolurato (**137**)) because it lies between the low spin $[Co(dmvi)_2(phen)]$ and the high spin $[Co(phen)_3]^{2+}$ in the expectation that it would show spin crossover

[270]. The X-ray crystal structure of the complex $[Co(dmvi)(phen)_2]ClO_4 \cdot 3H_2O$ was determined at 294 K and 92 K and two different structures were observed, but each with a distorted octahedral $N_5O$ arrangement around the Co. At 294 K, the structure strongly indicates that it is a mixture of the high and low spin forms. At 92 K rather poorer X-ray data were available but it is clear that the Co-donor atom distances are significantly shorter at 92 K, a result which is keeping with there being a spin crossover. This conclusion is confirmed by variable temperature magnetic and EPR spectroscopic measurements.



1,3-dimethylviolurate

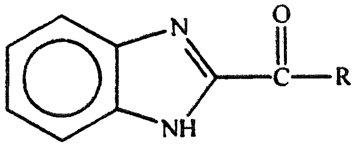
**(137)**



The $H_2$BDHQ Cobalt(II) Complex

**(138)**

The structure suggested for the complex [CoL], in which L = bis(*N*-salicylidene)-2,3-dihydrazino-1,4-quinoxaline, is shown in (**138**) [271]. An octahedral structure is also assigned to the complex [Co(OPCAA] where OPCA = 3-oxo-2-phenylhydrazonobutane-1-carbamidoxime [272]. The ligand (**139**) forms the Co(II) complex $[Co(L)_2]X_2$, X = Cl, Br, $NO_3$, $ClO_4$ [273].



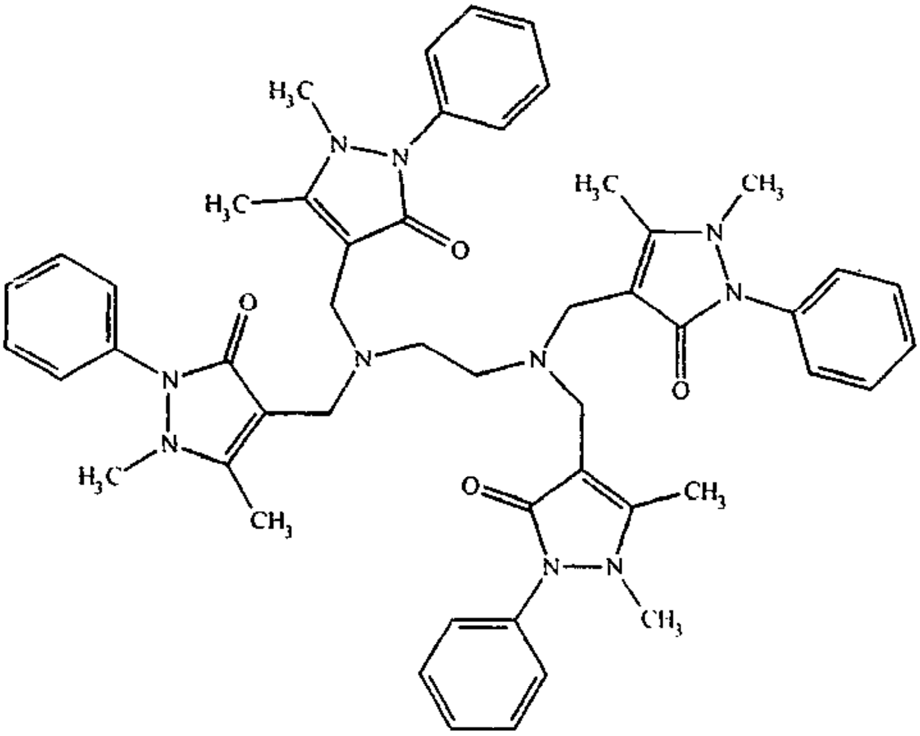
R = Me, Acbim

R = Ph, Bzbim

(**139**)

The crystal structure of 1,10-phenanthrolinebis(2-[2-pyrrole)methylimino] phenolato)cobalt(II) has been determined [274]. The synthesis of the complex $[Co_2(TAMEN)Cl]^{4-}$, in which TAMEN = (**140**) has been reported and the properties show that the ligand TAMEN bridges the two cobalt atoms via coordination utilizing the carbonyl oxygens and the 1,2-diaminoethane nitrogen [275]. A series of pale pink Co(II) complexes of the ligands shown in (**141**) have been prepared and characterized along with a range Ni(II) and Cu(II) complexes [276]. The data indicate that the complexes have an octahedral arrangement. Their stability constants for ligands $L^1$, $L^2$ and $L^3$ are 7.1, 7.3 and 8.5, respectively.

A study of the formation of dimetallic complexes prompted by the possibility of producing analogues of metalloproteins and the study of the physical chemistry arising from interactions between adjacent metals in such compounds has resulted in some fascinating chemistry and general methods for the preparation of dinuclear complexes in which one metal exhibits octahedral 6-coordination and the other square planar 4-coordination [277]. The processes for the preparation of the complexes are worth considering here. The first step involves the reaction of Co(II) acetate with the ligand to form the macrocyclic mononuclear complex shown (**142**). This species is then reacted with a diamine (e.g. en, tren, *S*-1,2-propylenediamine) which were incorporated into both the 6 and 4 coordinated sites in the presence of acetic acid to give a mononuclear species with an 'empty' cavity, i.e. a cavity occupied by two protons as shown in scheme (**143**). This was then reacted with typically a metal chloride such as $ZnCl_2$ to produce the dimetallic product (**144**). The X-ray crystal structure of the complex $[Co(enenim)ZnCl](PF_6)_2 \cdot EtOH$ (enen indicated an en link in each of the coordination sites) is described and the cation is shown in diagram (**145**). The presence of *S*-1,2-propylenediamine as the so-called closed site link, i.e. on the six coordinate structure, results in only one chiral topology *viz* *Δ*. Measurement of the Co(III)/Co(II) redox couples using cyclic voltammetry in acetonitrile resulted in quasi-reversible waves for the complexes containing Co(II) and Zn in the 4-coordinate structure. The number of atoms in the closed site ring



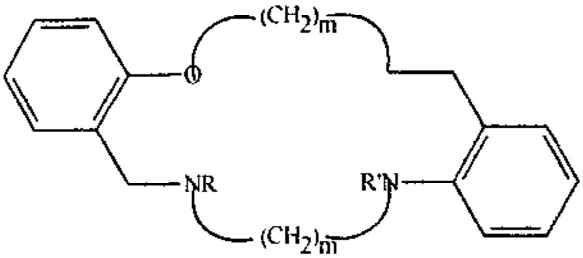
TAMEN

**(140)**

significantly affected the value of the potentials such that the Co(III) state was found to be destabilized in 6-membered ring structures.

Hbitp and Hsitp are ligands which are produced by the reaction of 5-acetyl-2,2′-pyridylthiophene with benzoyl- and salicylhydrazine respectively (**146**) [278]. These ligands react with $Co(Ac)_2$ to produce complexes of the form $[Co(bitp)_2L_2]$ and $[Co(sitp)L_2]$, where L = solvent molecule. The X-ray crystal structure of the $[Co(bitp)_2(DMSO)_2]$ complex (**147**) shows a distorted octahedral environment and that the ligands assume a *Z*-configuration around the hydrazone C = N bond while being didentate through –(O)C–N–N = hydrazide.

When a methanolic solution of D-mannose or L-rhamnose together with tren are heated at 60°C for 1 hr and then refluxed with $CoX_2 \cdot 6H_2O$ (X = Cl/Br), purification of the mixture produced red crystals of $[Co(aldose3\text{-}tren]X_2 \cdot nH_2O$ and a similar compound was produced when the sulfate was used, *viz* $[Co(aldose3\text{-}tren][SO_4] \cdot nH_2O$ [279]. When these were examined however, it was found that the sign of the Cotton effect for the Cl/Br-containing complexes was the opposite to that for the sulfate containing complex. The X-ray crystal structure of the complex $[Co(L\text{-}Rha)3\text{-}tren)][SO_4] \cdot 3H_2O \cdot CH_3OH$ showed a 7-coordination



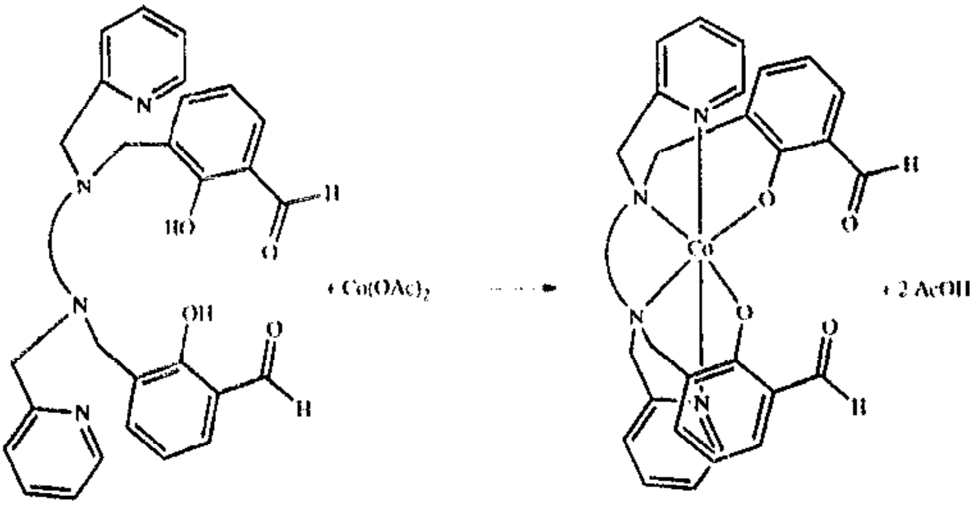
$L^1$: m =2, n = 3, R = R' = $CH_2C_5H_4N$

$L^2$: m = 3, n = 3, R = R' = $CH_2C_5H_4N$

$L^3$: m = 4, n = 3, R = R' = $CH_2C_5H_4N$

$L^4$: m =2, n = 3. R =H, R' = $CH_2C_5H_4N$

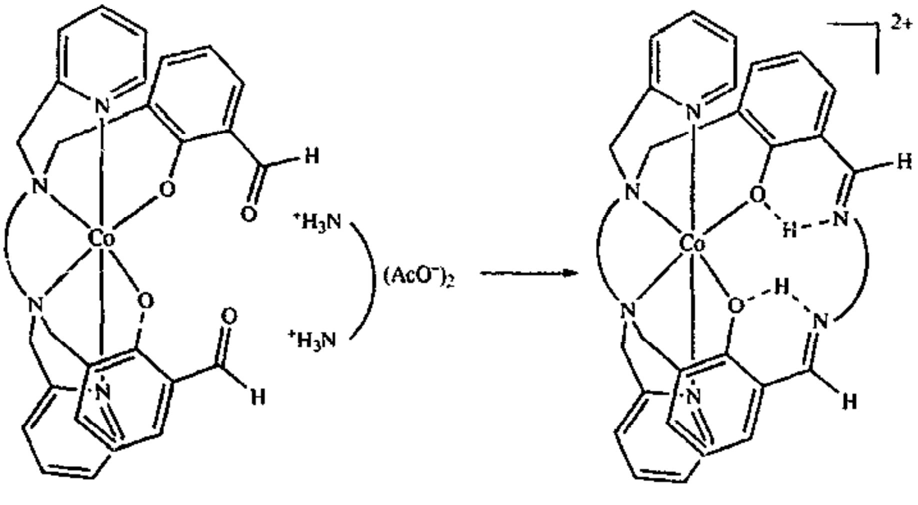
**(141)**



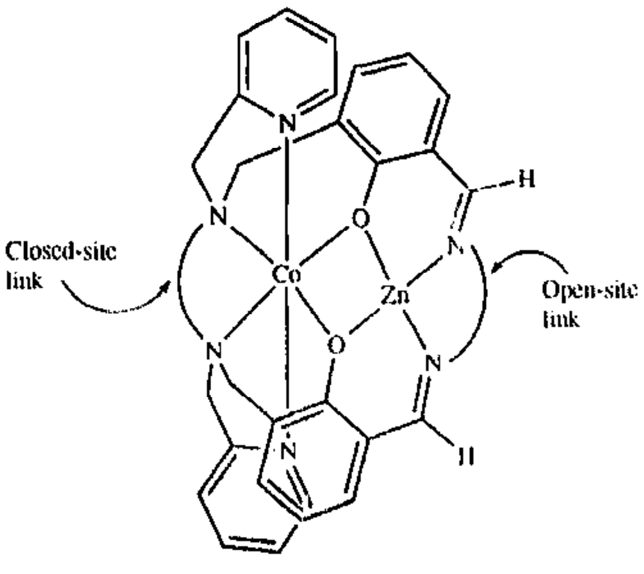
**(142)**

arrangement of (L-Rha)3-tren around the Co in the cation (**148**) giving a mono-capped octahedron where the absolute configuration with respect to the helical axis is Δ. The arrangement seems to be encouraged by the presence of the $[SO_4]^{2-}$ anion which caps the other facial site. It is suggested that in the case of the Cl/Br-containing complexes the structure is "closed up" (**149**) without the hydrogen bonding capability of $[SO_4]^{2-}$. The authors describe this process rather elegantly as being "just like flowers open and close".

The X-ray crystal structure of the Co(II) complex of the Schiff base which

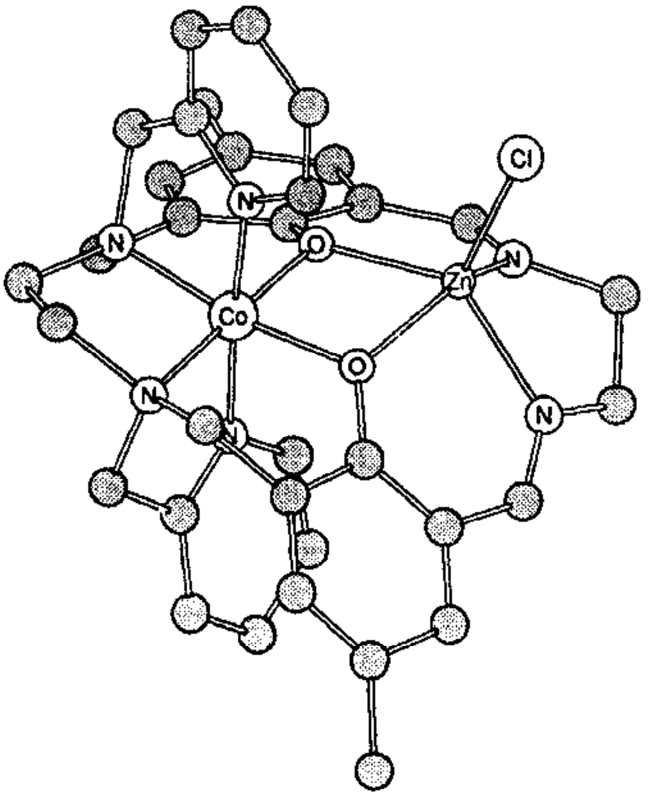


(143)

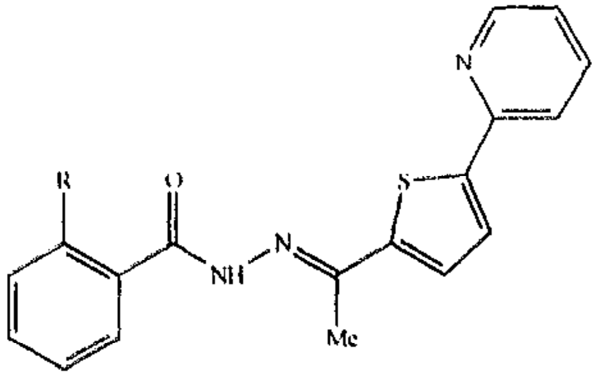


(144)

is produced by reaction of 2-hydroxybenzophenone and *rac*-1,2-diphenylethylenediamine shows that the ligand is tetradentate with the phenyl groups in the N–N part in axial positions [280]. It is to the steric effect of these axial phenyl groups that the significant increase in the redox potential for the Co(II)/Co(II) couple for the complex compared with the [Co(II)(salen)] is attributed. The spectroscopic properties of the complex [Co(saloph)] have been examined (in DMF and $CH_2Cl_2$) rather than those of the corresponding salen complex in order to avoid possible structural complexity which may be associated with the latter complexes [281]. The species produced in DMF were found to be



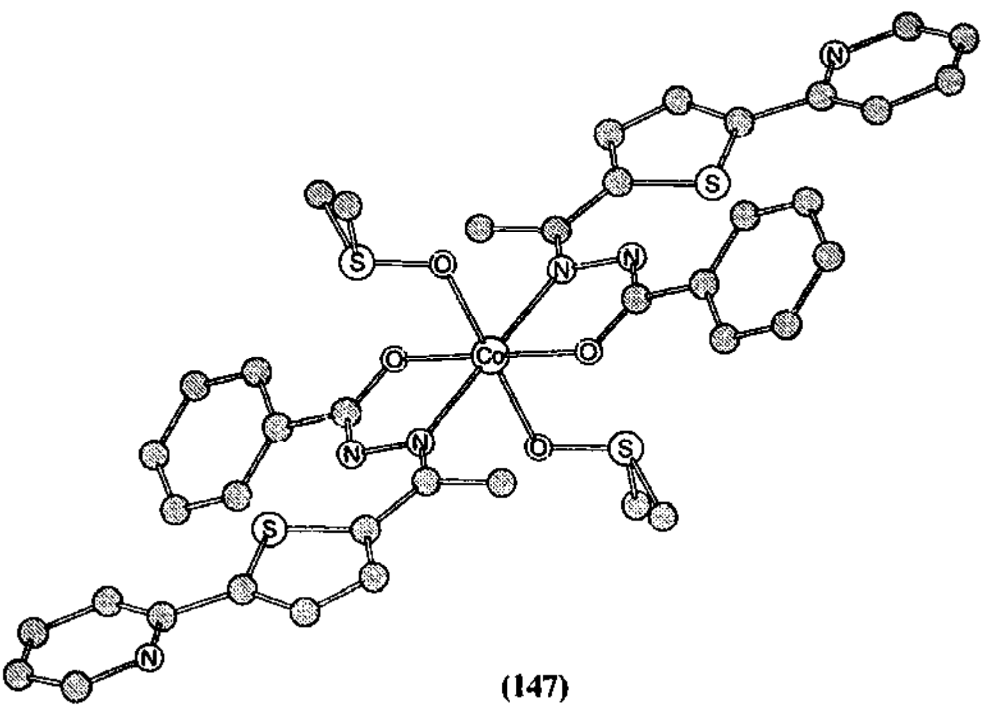
**(145)**



R = H: Hbitp
R = OH: Hsitp

**(146)**

[Co(saloph)(DMF)], [Co(saloph)(DMF)$_2$] and [Co(saloph)(DMF)]$_2$. As well as the UV–VIS and the $^1$H NMR spectra for each of these, the values of $\Delta H^\circ$ and $\Delta S^\circ$ were determined for the formation of each complex; the values are, respectively, −3.7, −1.7; −3.6, −145; −39, −110 kJ mol$^{-1}$.



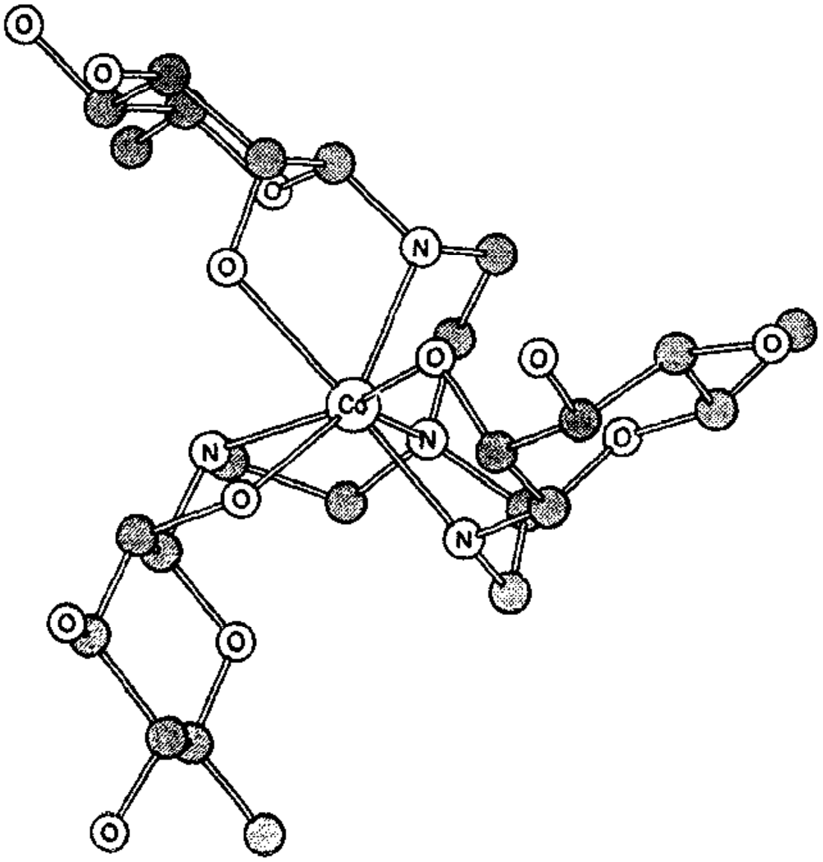
**(147)**

Coordination compounds of 1,2-diphenyl-2-(benzoylhydrazino)ethanol and 1,2-diphenyl-2-(*p*-nitrobenzoylhydrazino)ethanol react with Co(II) salts to form complexes $[Co(H_2L)_2]X_2$ and $[M_2L_2]$, X = Cl or $NO_3$ [282]. The dinuclear complexes are believed to have oxygen bridges and in each case the ligand is tridentate *via* the carbonyl oxygen, the azomethine nitrogen and the alcohol oxygen.

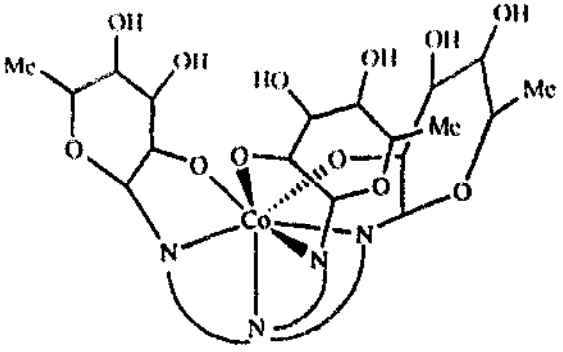
### *3.4. Complexes with sulfur donor ligands*

The species $[perylene][Co(mnt)_2]$, in which perylene is the hydrocarbon shown in **(150)** and $Co(mnt)_2$ has the structure **(151)**, is metallic at room temperature and undergoes metal-to-semiconductor (277 K) and semiconductor-semiconductor (190-170 K) transitions [283]. Extended Hückel tight binding band structure calculations have been applied to this system which show that the conductivity comes from the perylene chains and that the charge transfer from the perylene to the $Co(mnt)_2$ should be rather less than 1.

The kinetics of the reductions of $[Fe(H_2O)_6]^{3+}$ by $[Co([9]aneS_3)_2]$ and also by $[Co(sepulchrate)_2]$ have been studied and the data interpreted using the Marcus theory [284]. Using the usual nomenclature for the Marcus theory, the value for the rate constant of the cross reaction $k_{12}$ was $4.5 \times 10^3$ kg mol$^{-1}$, while the value calculated from the Marcus relationship was $4.4 \times 10^4$ kg mol$^{-1}$; the tenfold discrepancy is considered to be typical for this type of reaction. The activation volumes $\Delta V^{\ddagger}_{2}$ determined from high pressure studies were $-15.9$ cm$^{-1}$ mol$^{-1}$ in 0.1 mol kg$^{-1}$ $CF_3SO_3^-$ and $-13.7$ cm$^3$ mol$^{-1}$ in $ClO_4^-$ and this value agrees well with that calculated using the Marcus relationship. However the value of

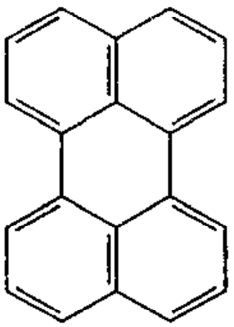


**(148)**

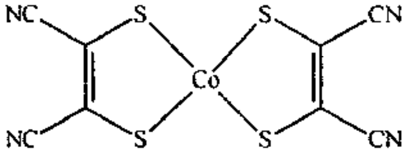


**(149)**

$6.4 \times 10^4$ kg mol$^{-1}$ for $k_{12}$ for the reduction by [Co(sepulchrate)$_2$] is rather lower than the calculated value of $8.4 \times 10^6$ kg mol$^{-1}$ and a measured $\Delta V^{\ddagger}_{12}$ value of $-5.0$ cm$^3$ mol$^{-1}$ is significantly higher than the calculated value of $-9.5$ cm$^{-1}$ mol$^{-1}$. The authors suggest that the results show that the volume cross relation serves as a useful mechanistic criterion.

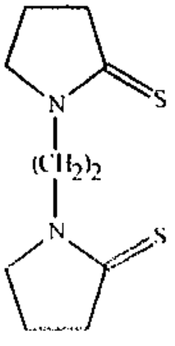


(150)



(151)

The ligand *N′,N′*-ethylenebis(pyrrolidin-2-thione) (ebpt) (**152**) reacts with $CoBr_2 \cdot 6H_2O$ to form the blue complex $[Co(ebpt)Br_2]_2$ (**153**) [285]. The X-ray crystal structure of the complex shows that each of the cobalt atoms is tetrahedrally coordinated to the bridging ebpt ligands and the Br atoms giving a centrosymmetric 18 membered ring.



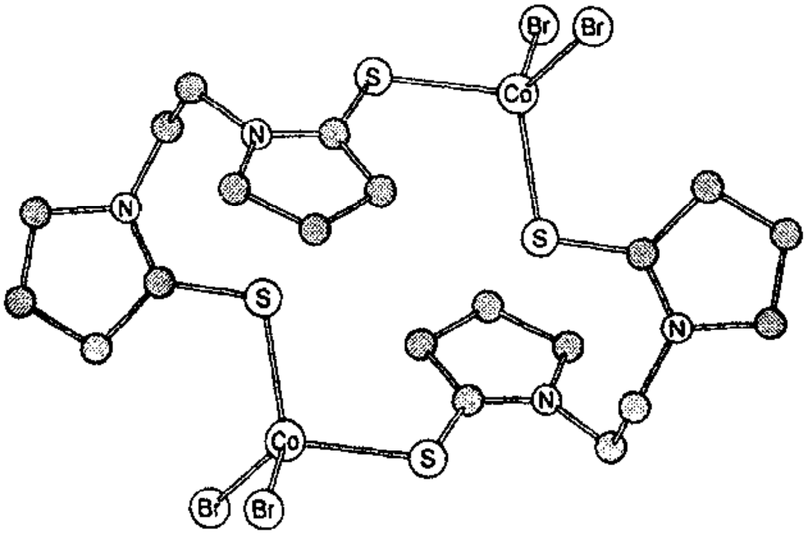
(152)

### 3.5. *Complexes with sulfur–oxygen donor ligands*

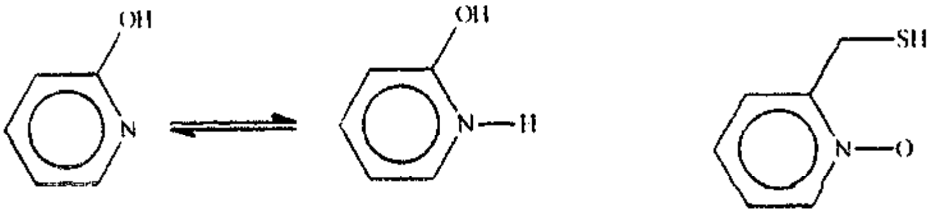
The complexes $[Co(PMTO)_2] \cdot 2H_2O$ and $[Co(Opy)_2]$ in which HPMTO and HOpy are shown in (**154**) have been prepared using electrochemical techniques [286].

### 3.6. *Complexes with sulfur–nitrogen donor ligands*

The syntheses of new $S_2N_2$ ligands, *S,S′*-diethyl(1,3-diaminopropane)-dithiocarbamate (**155**) and *S,S′*-cyclohexylspiro(1,3-diaminopropane)dithiocarbamate (**156**) and their complexes with Co(II) have been described [287]. It is suggested that the complexes are square planar, but that treatment with bis-(trimethylsilyl)amine produces the octahedral complexes (**157**).



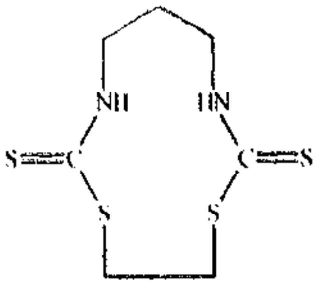
**(153)**



HOpy

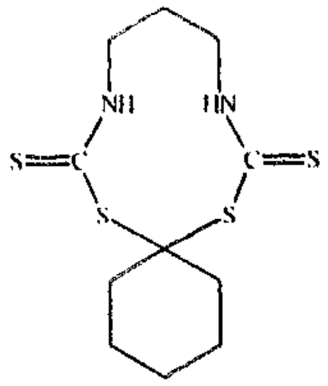
**(154)**

HPMTO



L

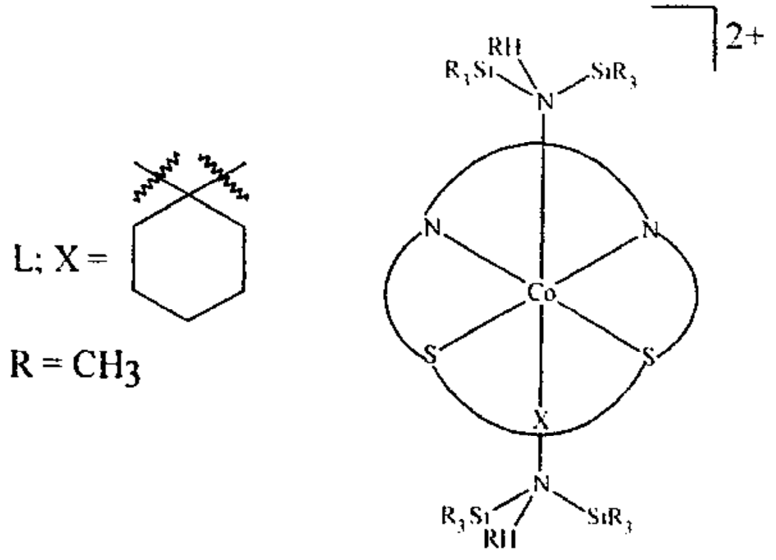
**(155)**



L'

**(156)**

The X-ray crystal structure of [CoL(mim)] (**158**), where L = *N,N'*-bis(5-mercapto-3-methyl-1-phenylpyrazole-4-ylene)-*o*-phenylenediamine and mim = *N*-methylimidazole, shows that it is five-coordinate so that around the Co(II) centre there is a



**(157)**

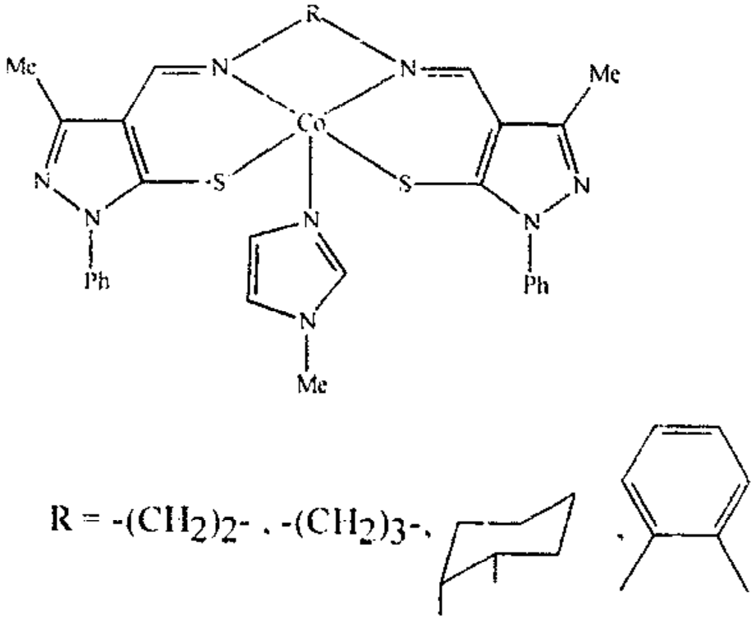
distorted trigonal pyramidal arrangement in which the N and S from the metallocycle occupy the axial positions and the another N and S and the imidazole N are in the equatorial positions as is shown in structure (**159**) [288]. The X-ray structure was investigated at different temperatures, 103 K and 293 K, and the data indicate that there are conformational changes involving variation in the metal-ligand bond lengths which are in keeping with a spin transition occurring. The variable temperature magnetic measurements over the range 77 to 320 K show that there is a minimax in the $\chi^{-1}$ *vs* $T$ curves behaviour due to $S = 1/2 \rightleftharpoons 3/2$ spin equilibrium.

The Co(II) complexes of 2-thiouracil and its arylazo derivatives (**160**) have been prepared and characterized [289]. The ligand L (**161**) forms complexes with the formulae $[CoL_2X_2]$, where X = Cl or Br [290]. Spectroscopy, and conductivity and magnetic measurements which were used to characterize the complexes suggest that they are pseudotetrahedral.

In complexes of the form $[CoCl_2(taz)]$, $[Co(taz)_2(H_2O)]$, $[CoX_2(taz)_2]$ (where taz is (**162**), and, typically, X = Br, I, SCN or $NO_3$) and $[Co(taz)_2(H_2O)_2]X_2$ ($X = ClO_4$, $BF_4$ or $NO_3$) the triazine molecule was found to behaving either as a monodentate *N*-donor or as a didentate *N*,*S*-donor [291]. The Schiff base (**163**) forms a range of complexes with transition metal ions such as $[Co(NNS)_2]Cl$ [292]. It is suggested that this complex exhibits octahedral geometry around the cobalt centre.

### 3.7. *Complexes with sulfur-nitrogen-oxygen donor ligands*

The preparation of the complex $[Co(itba)_2]$, in which Hitba is (**164**), has been described and the X-ray crystal structure of $[Co(itba)_2]$ (**165**) has been determined [293]. An octahedral arrangement around the Co(II) is observed.



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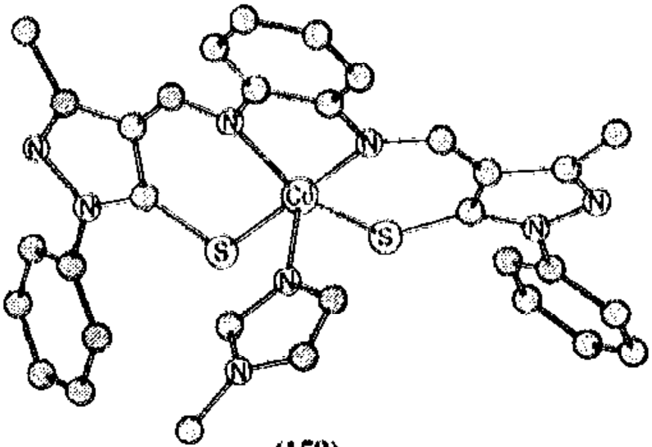

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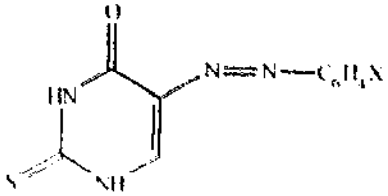
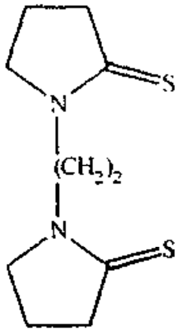


X = H, 4-COOH, 3-Cl, 3-$NO_2$, 3-Me, 2-Br, 2-OMe, 2-Me, 2,5-$Cl_2$, 2,4-$(NO_2)_2$

**(160)**



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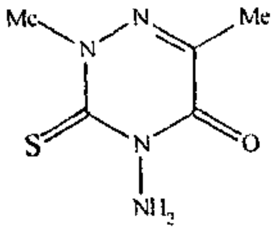
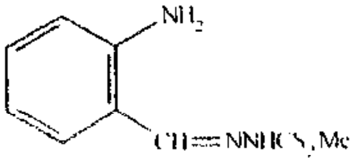


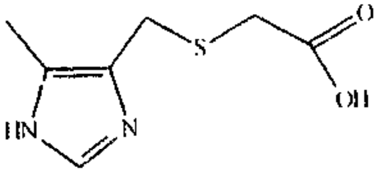
Taz

**(162)**



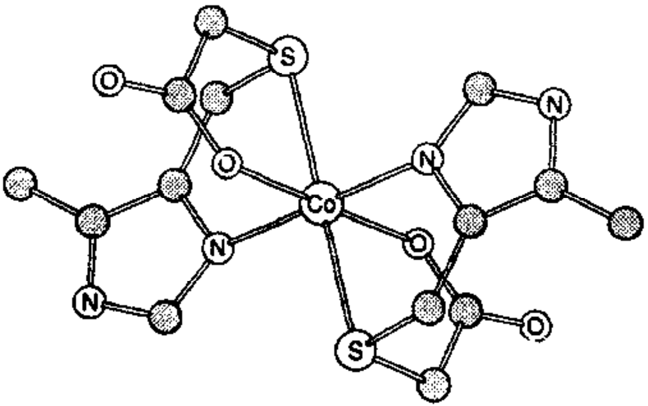
HNNS

**(163)**



Hitba

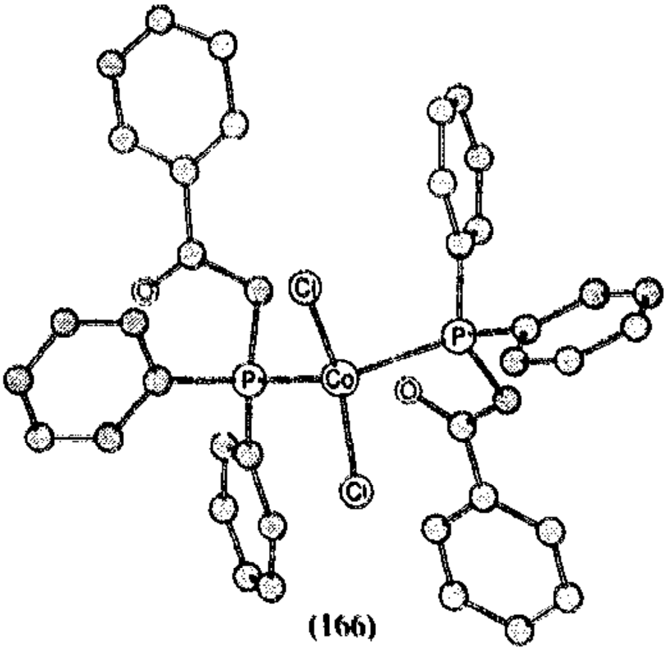
**(164)**



**(165)**

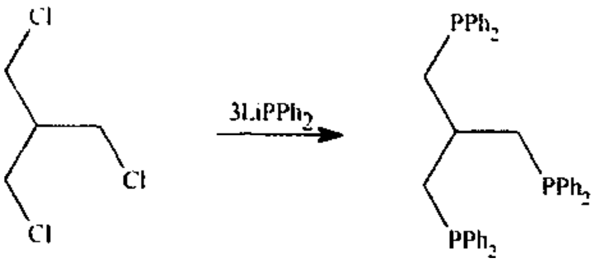
### 3.8. *Complexes with phosphorus donor ligands*

A range of Co(II) ketophosphine complexes of the type $[CoX_2\{Ph_2PCH_2C(O)Ph\}_2]$, in which X = Cl, Br and I, have been prepared and the chemistry in solution compared with that of the corresponding complex $[CoX_2(PPh_3)_2]$ [294]. These complexes show tetrahedral–octahedral equilibria in solution in methanol and a feature of these equilibria is that it is the solvent molecules which are involved in the process rather than the carbonyls. The crystal structures of several complexes have been determined including that of $[CoCl_2\{Ph_2PCH_2C(O)Ph\}_2]$ **(166)**.

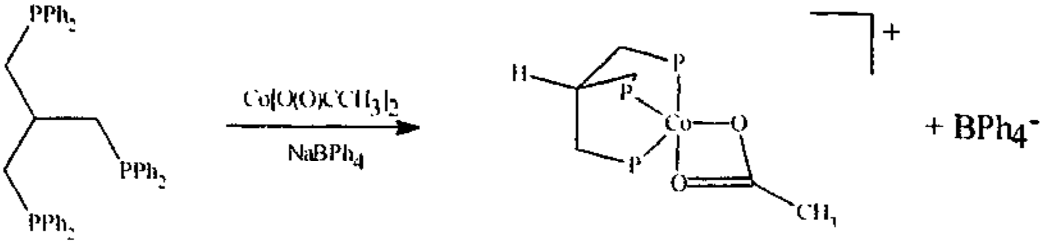


**(166)**

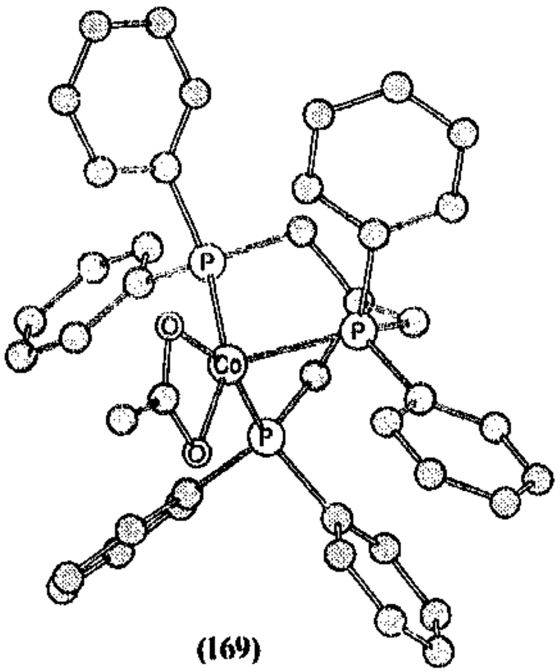
The ligand 1,1,1-tris[(diphenylphosphanyl)methyl]methane has been prepared by the reaction shown in **(167)** [295]. The ligand forms a Co(II) complex by the reaction shown in **(168)** and the X-ray crystal structure of the cobalt(II) complex confirms that for the cation shown in **(169)**.



**(167)**



**(168)**



**(169)**

### *3.9. Complexes with halide and pseudohalide donor ligands*

Data from a spectrophotometric and conductivity study of $CoCl_2$ and $CoBr_2$ in solution in acetone show that they are present as the electrically neutral pseudotetrahedral complexes $[CoX_2(acetone)_2]$ [296] and the stability constants have been obtained. Similar experiments with $Co(SCN)_2$ in aqueous DMSO showed the presence of $[Co(SCN)]^+$ and again association constants were obtained [297].

When anaerobic solutions of pentacyanocobaltate(II) in aqueous ethanol were irradiated by a high pressure Hg lamp it was found that hydrogen and acetaldehyde were produced in a 1:1 ratio [298]. Similar behaviour resulted when pentacyanocobaltate(II) was replaced by Co(II)–mixed complexes to which $CN^-$ and en had been added, although in the presence of en the yield of acetaldehyde was lowered.

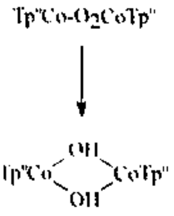
### 3.10. *Complexes with arsenic donor ligands*

Tetrakis(alkylisocyanide)bis(triarylarsine)cobalt(II) complexes have been prepared by the reaction of pentakis(alkylisocyanide)cobalt(II) in ethanol with triarylarsines [299]. Magnetic and solid state spectrophotometric measurements suggest that the structures of these complexes are tetragonal *trans*-$[Co(CNR)_4(AsR_3)_2]X_2$. In a related study [300], the complex $[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$ has been prepared and it is suggested that this too has a tetragonal arrangement around the Co(II) with the arsenic-containing ligand being monodentate.

## 4. Reactions of cobalt complexes involving dioxygen

As is usually the case, this area of cobalt chemistry has attracted much interest. The topic has been reviewed in various aspects on a number of occasions. There has been a survey of the chemistry of synthetic heme dioxygen complexes which contains a number of examples involving cobalt [301]. The photochemical reactions of metalloporphyrins which contain dioxygen have been reviewed and the reactivity of various porphyrin complexes compared with Co(II) tetraphenylporphyrin [302]. The properties of transition metal dioxygen complexes have been reviewed from the point of view of using them industrially in the future as an alternative method to cryogenics for separating dioxygen from the other gases in the atmosphere in a more efficient and cost-effective manner [303]. The effect of pH and the nature of the ligand on the uptake of dioxygen by a number of Co(II) complexes has been investigated for a wide variety of dipeptide complexes [304]. The dipeptides studied were glycylglycine, alanylglycine, leucylglycine, tyrosylglycine, phenylalanineglycine, glycylalanine, glycylleucine, glycyltyrosine and glycylphenylalanine. The method of comparison was to measure the rate of uptake of dioxygen by a solution of $Co(ClO_4)_2$ in the presence of an excess of the appropriate dipeptide. Below pH 6.5, dioxygen adducts were not formed and this is believed to be a function of the deprotonation of the dipeptide amine groups. The rate of uptake of dioxygen was also related to the occurrence of steric hindrance by side chains in the dipeptides, with the rate increasing when there is substitution on the *N*-terminal amino acid and decreasing when there is substitution on the terminal C atom. Histidine and monoiodohistidine complexes of Co(II) have been found to bind dioxygen, whereas diiodohistine complexes do not [305]. The formation of dioxygen complexes with Co(II) asparagine compounds is found to be enhanced at pH higher than 13 as a result of the formation of a tridentate complex between the asparagine and the Co(II) [306]. This in contrast to the behaviour of other similar amino acids.

Reaction of the complex Tp″Co($O_2$) with 0.5 equiv of Tp″Co–$N_2$–CoTp″ yields the species Tp″Co–$O_2$–CoTp″, where Tp″=hydridotris(3-isopropyl-5-methylpyrazoyl)borate [307]. The kinetics of the decomposition of this complex (**170**) in $CD_2Cl_2$, followed by $^1H$ NMR spectroscopic studies showed that the reaction was first order and $k=2.27\times10^{-3}\,s^{-1}$ at 281 K with $\Delta H^{\ddagger}=16.4\ \mathrm{kcal\ mol^{-1}}$ and $\Delta S^{\ddagger}=-12$ eu. It was further shown that there was a very significant isotope effect with $k_H/k_D=22$. It is concluded that C–H bond breaking is the rate determining step in the reaction with the probability of tunnelling being a factor in the H transfer. The scheme proposed by the authors for the activation of the dioxygen molecule is shown in scheme (**171**).



**(170)**

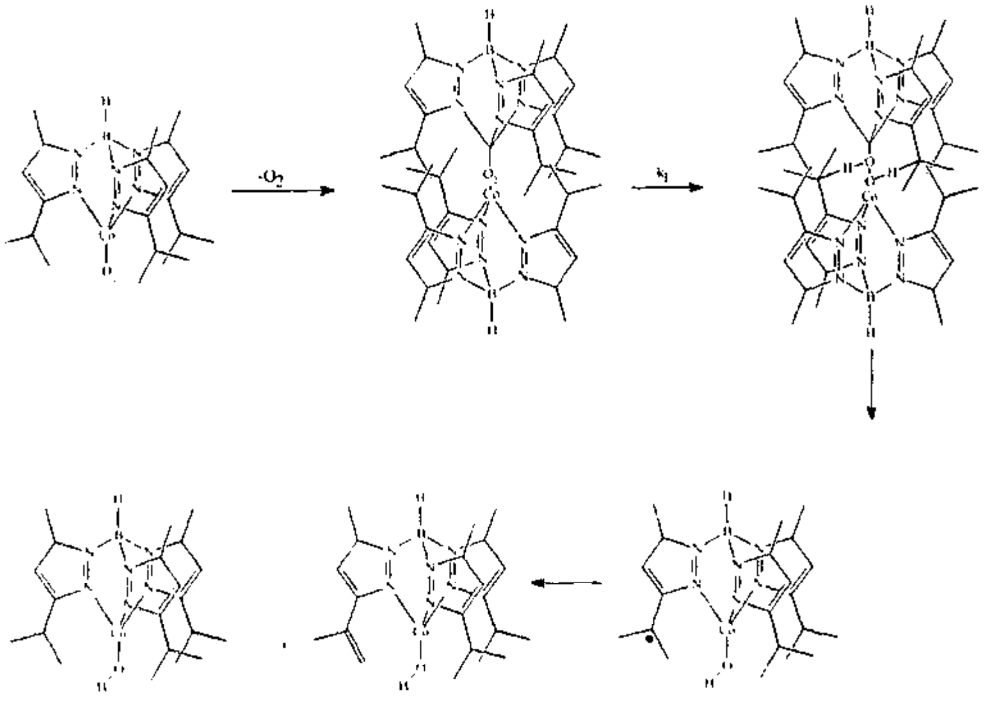
A number of complexes of the form [Co(terpy)(L)X] in which L=2,2′-bipyridine or 1,10-phenanthroline or one of a number of substituted 1,10-phenanthrolines, X is a weakly binding species such as triflate, have been prepared and characterized [308]. These reversibly bind dioxygen and this process has been studied by a variety of techniques. A typical example is the complex $[Co(terpy)(bpy)]^{2+}$. When an attempt is made to prepare this complex in acetonitrile under an inert atmosphere it is found that the product does not reversibly take up dioxygen. When, however the same preparation is carried out in air and the resulting solid is dissolved in acetonitrile, it reversibly took up $O_2$. During experiments to elucidate the nature of these reactions the authors prepared the peroxo species:

$$2Co(terpy)Br_2+4NH_4PF_6+2bpy\rightarrow[Co(terpy)(bpy)_2O_2](PF_6)_4+NH_4Br$$

The X-ray structure determination on this complex confirms that it is the peroxo complex. When solutions of this compound were saturated with $N_2$, the complex $[Co(terpy)(bpy)](PF_6)_2$ was formed quantitatively:

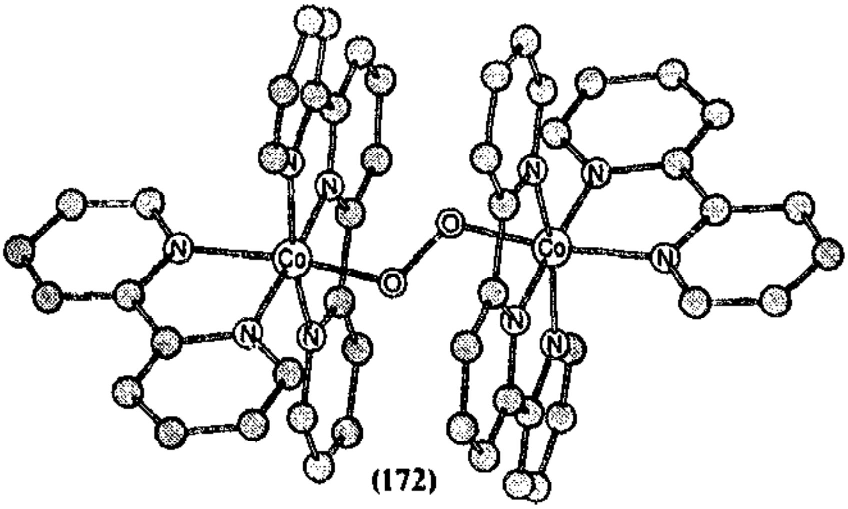
$$\underset{\text{orange}}{2[Co(terpy)(bpy)]^{2+}}+O_2\rightleftharpoons\underset{\text{deep brown}}{[Co(terpy)(bpy)_2O_2]^{4+}}$$

The presence of a band at 824 cm$^{-1}$ in the Raman spectrum confirms the presence of the peroxo moiety and at 25°C log $K_{O2}$ for the formation of $[\{Co(terpy)(bpy)\}_2O_2]^{4+}$ in acetonitrile is 4.4 $M^{-1}\,atm^{-1}$. Various coordinated solvents were investigated to examine their effect on dioxygen binding. Thus, in



**(171)**

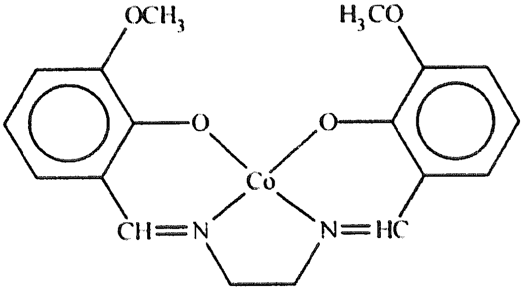
nitrobenzene the binding was extremely tight. By judicious choice of added weak ligands such as triflate, reversible binding could readily be achieved. The X-ray structure of solvated [{Co(terpy)(bpy)}$_2$O$_2$](PF$_6$)$_4$, [(**172**)](PF$_6$)$_4$, has been determined.



**(172)**

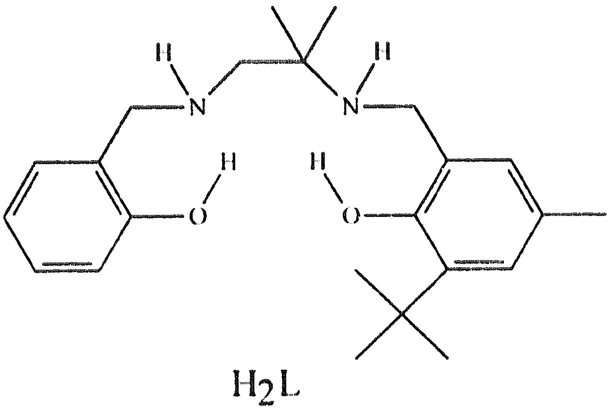
The complex [Co(nbsal)$_2$], where nbsal = *N*-*n*-butylsalicylideneiminate, reacts readily with both nitric oxide and dioxygen [309]. However, the complex [Co(tbsal)$_2$], where tbsal = *N*-*tert*-butylsalicylideneiminate shows no reactivity to either NO or O$_2$. The crystal structures of both these complexes have been determined and both are found to have a distorted tetrahedral arrangement around the Co. However, there is much greater distortion of the tetrahedral arrangement when there are *tert*-butyl groups present.

The response to dioxygen by CdSe coated with [Co(3-MeO-salen)] (**173**) raises the possibility of using this system as a sensor [310]. It has been found that band gap photoluminescence excited by light of wavelength 633 nm of etched single crystal of n-CdSe is significantly enhanced in MeCl solution in anaerobic conditions by the presence of [Co(3-MeO-salen)]. This effect depends on the concentration of the complex. Using the Langmuir isotherm model, an equilibrium constant between $10^4$ and $10^5$ was obtained. The photoluminescence is quenched by the presence of dioxygen in a way which depended on the dioxygen pressure.



**(173)**

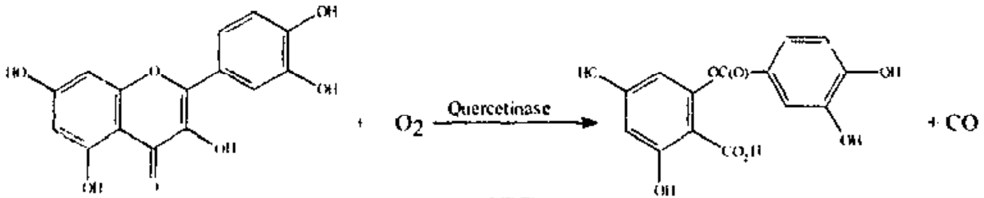
The complex [Co(II)L], where $H_2L$ is (**174**) has been prepared and characterized and it X-ray structure determined [311]. The crystal structure shows that it is monoclinic $C2/c$ and $a = 25.389$, $b = 18.139$, $c = 10.179$ Å, $\beta = 112.227°$ and $Z = 8$. The complex has a square planar $N_2O_2$ arrangement around the Co. In the presence of dioxygen the species [Co[$H_4$]L] and [Co[$H_2$]L] in acetone are easily oxidized to [CoL].



**(174)**

The dioxygenase, quercetinase, produced by *Aspergillus flavus*, catalyses reaction (**175**) [312] which results in the production of depsides and CO. This behaviour can to some extent be mimicked using [Co(salen)] in DMF as shown in scheme (**176**). This work involves a study of the mechanism of the reactions involving [Co(salen)] using cyclic voltammetry. The proposed mechanism is shown in scheme (**177**).

A study of the effectiveness of Co(II) Schiff base chelates incorporated into



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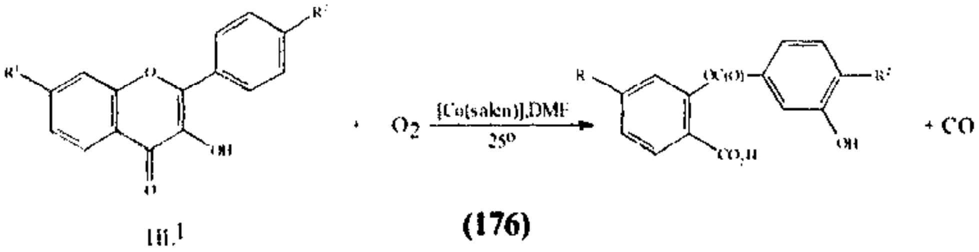

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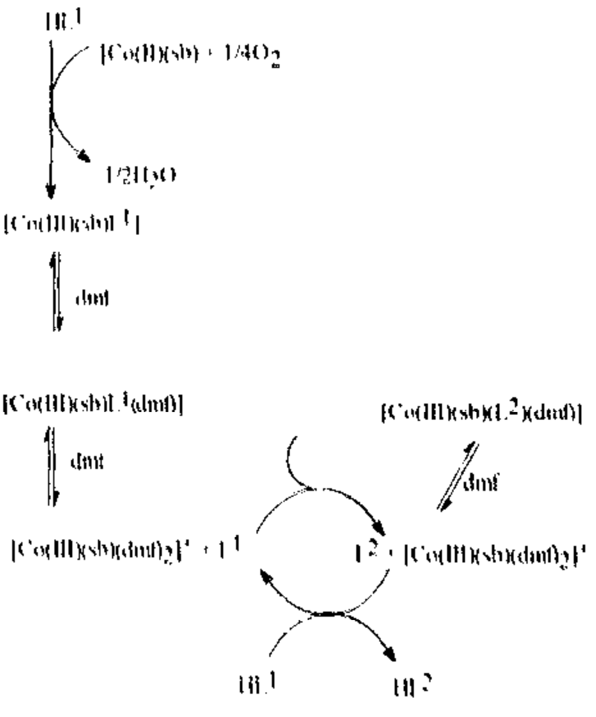


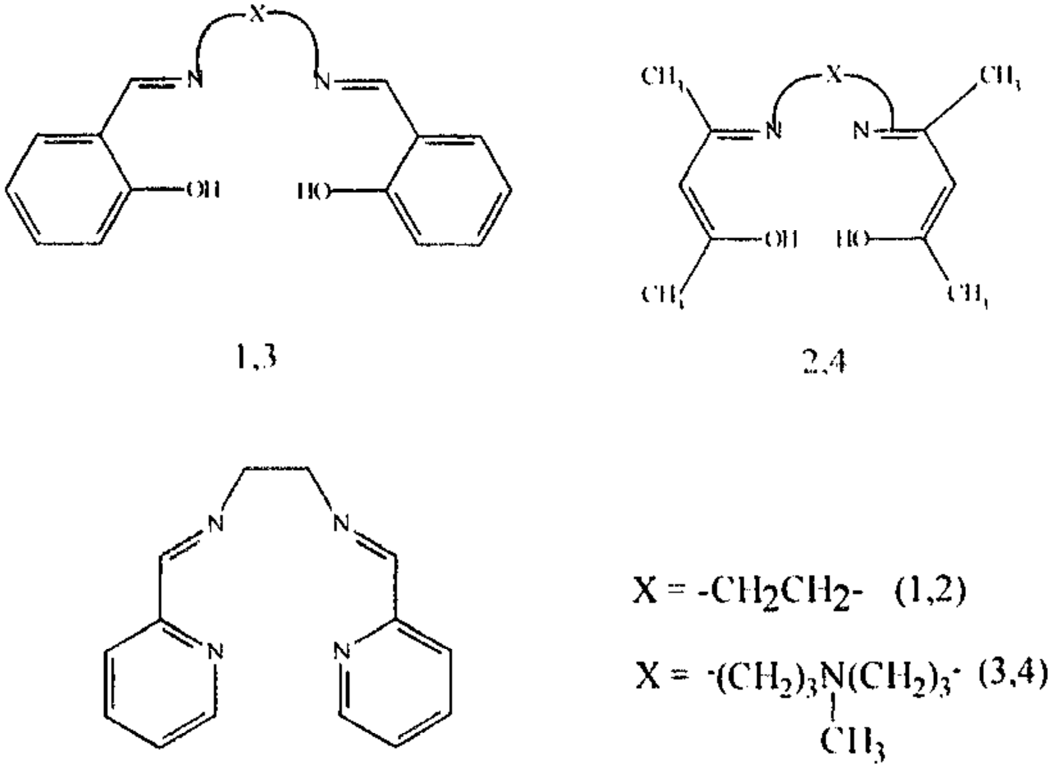
HL$^1$ = flavonol substrate

HL$^2$ = depside product

sb = Schiff base dianion

**(177)**

faujasite-type zeolites has focussed on the ligands shown in (**178**) [313]. The tetradentate ligands, acacen and salen in zeolite Y were rather poor in producing active oxygen binding Co(II). The pentadentate ligands, smpt = bis(salicylaldehyde)methylnitrilodipropylenediimine and amdpt = bis(acetylacetone)methylnitrilodipropylenediimine, on the other hand greatly improved the amount of Co(II) which was active in oxygen binding. Another Co(II)-zeolite interaction which has been examined this year for dioxygen affinity is the tetramethylporphyrinatocobalt complex with zeolite Y [314]. The dioxygen affinity has been studied as a function of partial pressure and temperature. The dioxygenation reaction is reversible and the kinetics show the process to be pseudo first order with $k = 2.7 \times 10^{-5}\ s^{-1}$ at 25°C. The kinetics of dioxygen binding reactions have been examined as a function of the structure of the porphyrins in a polymer membrane [315]. The new porphyrins were derivatives of *meso*-α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphinatocobalt. Very significant differences in rate for dioxygen binding were obtained for the different structures (**179a**) and (**179b**). There was a linear correlation between the logarithms of the dioxygen dissociation constant and the diffusion constant for the dioxygen via the porphyrin complexes in the membranes.

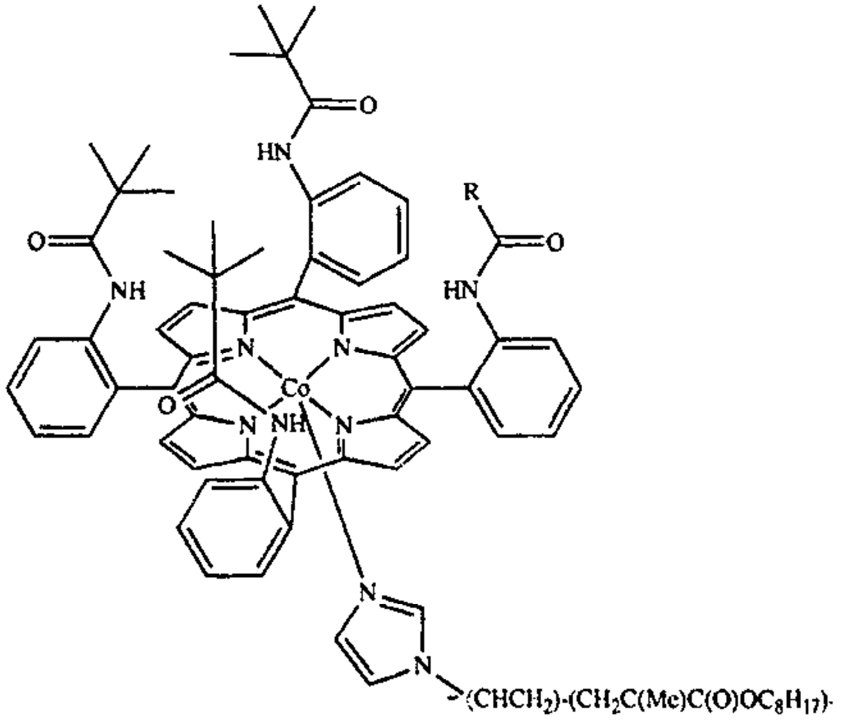


X = $-CH_2CH_2-$ (1,2)

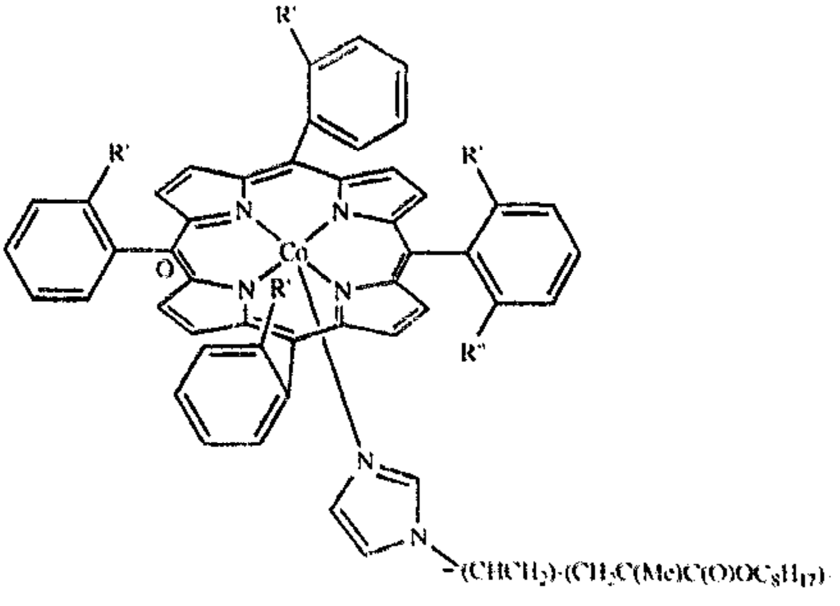
X = $-(CH_2)_3\underset{\displaystyle CH_3}{\underset{|}{N}}(CH_2)_3-$ (3,4)

(**178**)

A series of porphyrin complexes of Co(II) which had on the periphery of their structure either cyanophenyl groups or $N$-$CH_3$py structures have been prepared [316]. These porphyrins were mixed with a dilute alcoholic solution of Nafion and


O
HN
R
O
O
NH
HN
N
N
Co
O
N
NH
N
N
N
(CHCH$_2$)-(CH$_2$C(Me)C(O)OC$_8$H$_{17}$)-

**(179a)**


R'
R'
R'
N
N
Co
O
N
R'
N
R"
N
N
(CHCH$_2$)-(CH$_2$C(Me)C(O)OC$_8$H$_{17}$)-

**(179b)**

the mixture applied to the surface of a graphite electrode and then reacted *in situ* with $[Ru(NH_3)_5(H_2O)]^{2+}$. This resulted in electrodes which had coatings containing 0, 1, 2 or 3 Ru atoms per porphyrin molecule (**180**). These systems were then examined for activity in reducing $O_2$ to $H_2O$ via a 4-electron reduction. It was found that the species containing the 3 Ru atoms was the only one which exhibited significant 4-electron reduction. The 2 Ru species showed some tendency for 4-electron reduction, while the one-Ru atom complex only exhibited a 2-electron reduction of $O_2$ to $H_2O_2$.

New peroxo complexes of Co(II) have been synthesized [317]. The ligand used was 1,4-bis[bis2-pyridylmethyl)amino]-3-propanol, Htpdb (**181**). The parent complexes were of the form $[Co_2(tpdb)(RCOO)](ClO_4)\cdot nH_2O$, $R=CH_3$ or $C_6H_5$. These reacted with dioxygen in acetonitrile to produce the dioxygen complexes $[Co_2(tpdb)(RCOO)(O_2)]^{2+}$ (**182**) (R = Me). The X-ray crystal structure of the species $[Co_2(tpdb)(CH_3COO)(O_2)](PF_6)_2\cdot CH_3CN\cdot 0.5H_2O$ was determined, but there was a disorder in the backbone of the tpbd$^-$ ligand and the carbon atoms have been omitted from diagram (**182**). The bridging mode between the two Co atoms involves acetate, alkoxy and dioxygen. Single dioxygen bridging is a feature of reactions involving the complex $[(papd)Co(II)(H_2O]^{2+}$, in which papd = 1,5,8,11,15-pentaazapentadecane [318]. The overall reaction with dioxygen is:

$$2[(papd)Co(H_2O)]^{2+} \rightleftharpoons [(papd)Co-O_2-Co(papd)]^{4+}$$

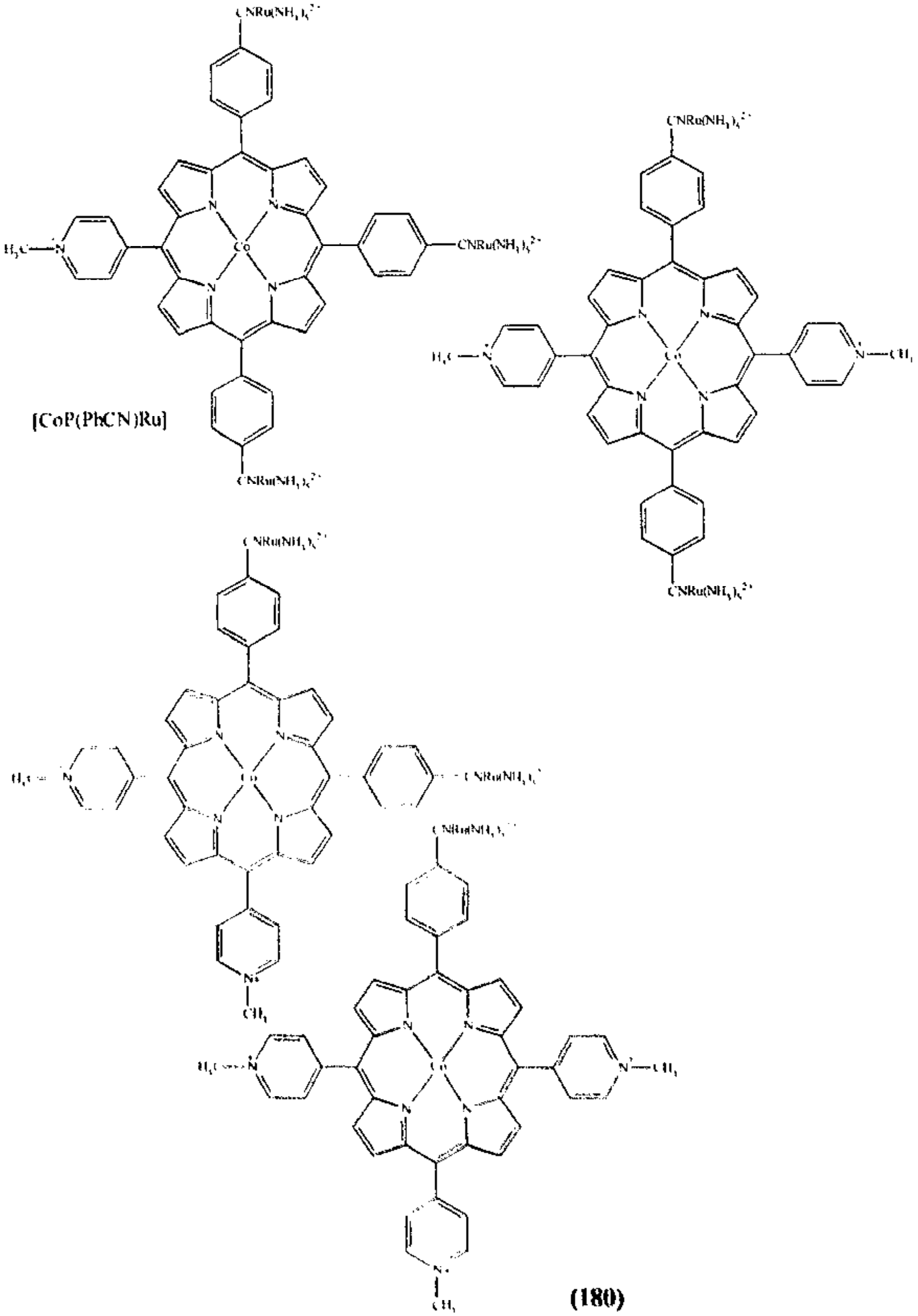
Early in the study, the authors found that when the dioxygen uptake by $[(papd)Co(II)(H_2O]^{2+}$ monitored by an oxygen sensitive electrode with $[O_2]>[complex]$ that there was a rapid decrease in $O_2$ producing a short-lived minimum and that this was followed by a release of oxygen. Under these conditions there was also observed a build-up of the superoxo complex and a clear separation of the steps in the process:

i) the formation of a mononuclear intermediate, $[(papd)CoO_2]^{2+}$, and

ii) the formation of the product dinuclear complex $[(papd)Co-O_2-Co(papd)]^{4+}$.

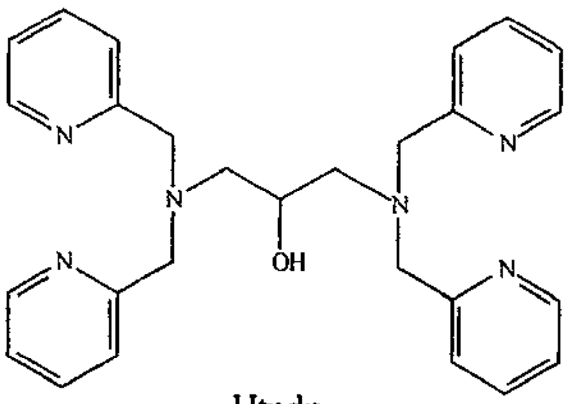
The kinetics of each of these steps were investigated and the respective rate constants at 25°C were $k_1 = 1.4\times10^7\ M^{-1}\,s^{-1}$ and $k_2 = 1.2\times10^7\ M^{-1}\,s^{-1}$. During these processes the first consists of the replacement of water in $[(papd)Co(II)(H_2O]^{2+}$ followed by electron transfer to produce superoxide ion and the second replacement of water in $[(papd)Co(II)(H_2O]^{2+}$ by $[(papd)CoO_2]^{2+}$ followed by electron transfer to produce the peroxide ion. In both cases the electron transfer process was fast and the water exchange the rate determining step.

It is reported that the Co(II) complexes of Obistren and Obisdien behave as very good dioxygen carriers because the ligands remain intact and the dioxygen in the complex may be removed or added readily according to conditions such as temperature and pressure [319]. Detailed studies have been made of the equilibria involving Obisdien (Bd = Free base), $Co^{2+}$ and phosphite (Ps) and also similar equilibria involving Bd, $Co^{2+}$ and phosphate [320]. In the former series of equilibria, there



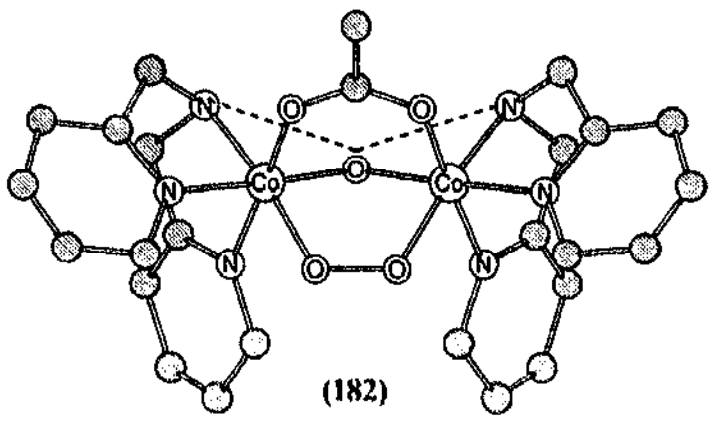
[CoP(PhCN)Ru]

**(180)**



Htpdp

**(181)**



**(182)**

were two reactions involving the formation of $Co_2$ dinuclear complexes:

$$\mathrm{Bd} + \mathrm{Ps}^{2-} + 2\mathrm{Co}^{2+} + \mathrm{H}^{+} \rightleftharpoons [\mathrm{BdCo_2PsH}]^{3+} \quad \log\beta = 23.00$$

$$\mathrm{Bd} + \mathrm{Ps}^{2-} + 2\mathrm{Co}^{2+} \rightleftharpoons [\mathrm{BdCo_2Ps}]^{2+} \quad \log\beta = 15.39$$

and only one in the case of phosphate:

$$\mathrm{Bd} + \mathrm{Ps}^{3-} + 2\mathrm{Co}^{2+} + \mathrm{H}^{+} \rightleftharpoons [\mathrm{BdCo_2PsH}]^{2+} \quad \log\beta = 27.00(?)$$

The complex $Co_2$–Obisdien–phosphite–dioxygen reacts at temperatures above 60°C such that the phosphite is oxidized to phosphate and the dioxygen in the complex is reduced to water. The kinetics of this internal redox reaction were studied and a typical pseudo first order rate constant was at pH 9 and Bd/$HPO_3^{2-}$ 1:1 $5.3 \times 10^{-9}\ s^{-1}$. By substituting $^{18}O_2$ for $^{16}O_2$ in the $Co_2$–Obisdien–phosphite–dioxygen system and examining the isotope distribution in the product, it was shown that the O which was in the phosphate derived from the oxidation of phosphite came from the original molecular dioxygen which produced the dioxygen adduct.

There is a delicate balance between the redox behaviour of the metal ion, the nature of the ligand and the structure of any given ligand on the uptake and retention of dioxygen. The effects of a series of lacunar cobalt(II) cyclidene ligands which are structurally altered in a systematic way on the affinity of complexes has been investigated [321,322]. The structures of the lacunar Co(II) cyclidenes are shown in (**183**) and the modifications carried out were by changing $R^1$, $R^2$, $R^3$. A key feature of the structural effect examined was the presence and variation of the polyethylene bridging ligand $R^1$. A total of 20 cyclidene complexes were prepared and it was found that there is a systematic decrease in the binding of dioxygen as the length of the chain in the bridge is decreased from the octamethylene complex to the tetramethylene species, (e.g. for $[\mathrm{MeMeC4[16]cyclidene(MeIm)}]^{2+}$ $K_{O_2}=0.005$ at $-40°\mathrm{C}$ and $[\mathrm{MeMeC8[16]cyclidene(MeIm)}]^{2+}$ $K_{O_2}=0.45$ at $25°\mathrm{C}$) becoming zero for the trimethylene-and-below complexes. The X-ray crystal structure of one of the $O_2$ adducts was determined and the position of the end-on bonded $O_2$ in relation to the cyclidene ligand can be clearly seen in (**184**). It is pointed out by the authors that the factor associated with the structure that most affects the dioxygen uptake is the cavity width controlled by the length of the polymethylene chain. In the case of the variation of the other substituents on the cyclidine ligand, i.e. $R^1$ and $R^2$, any changes in dioxygen affinity are attributed to the electron donating properties of the groups. The X-ray structure of the Co(III) complex $[\mathrm{Co\{MeMeC8[16]cyclidene\}(SCN)_2}](\mathrm{PF_6})$ was also determined in order to examine the conformational changes which occur due to the presence of a small molecule in the cyclidine cavity.

The rate constants for the uptake and release of dioxygen by the Co(II) complexes of cyclam ($L^1$) and hexamethylcyclam ($L^2$) have been measured as a function of pressure [323]. The method used was laser flash photolysis by using the reaction:

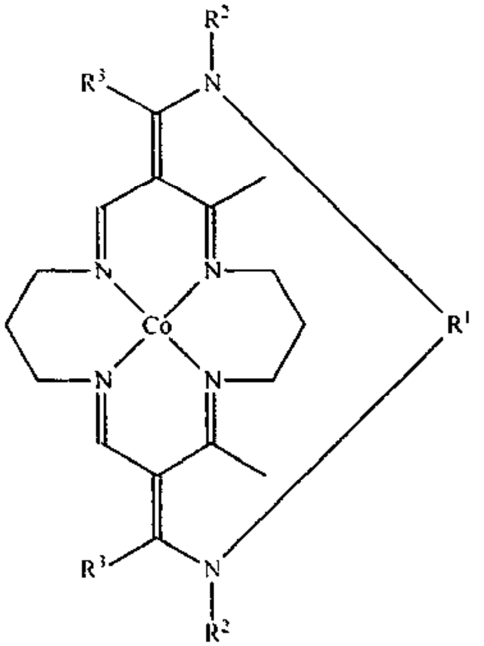
$$[(\mathrm{H_2O})\mathrm{LCoOO}]^{2+} \rightleftharpoons [\mathrm{LCo(H_2O)_2}]^{2+} + \mathrm{O_2}$$

The flash produces the right hand side products which then re-form the starting material, and this reaction may be kinetically followed. The rate law for the process involving $[\mathrm{L^2Co(H_2O)_2}]^{2+}$ is:

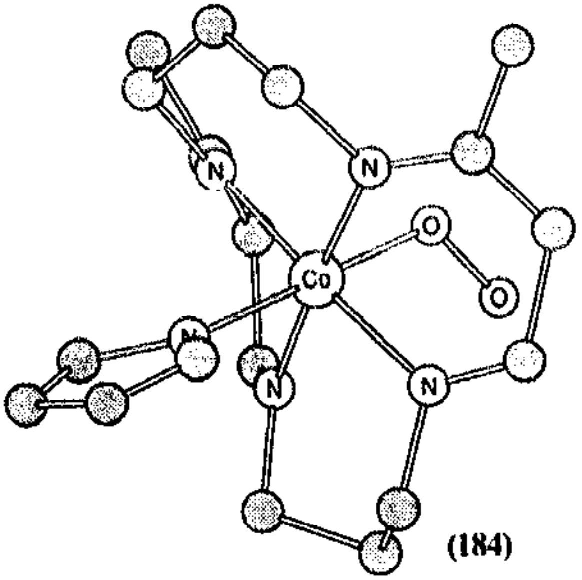
$$k_e = k_1[\mathrm{O_2}]_e + [\mathrm{L^2Co^{2+}}]e + k_{-1}$$

The pressure dependence was determined for $k_1$ and $k_{-1}$. For the $L^1$ complex the equilibrium lies towards the dioxygen species and a more straightforward approach is therefore possible. The pressure dependence of the equilibrium constants for the $L^2$ ligand is also studied. It is proposed that the reaction of the $L^2$ complex has an interchange mechanism.

A range of Schiff bases made from 2-hydroxy-3-methoxy-5-methylbenzaldehyde and en, 1,2-propylenediamine, 2,3-dimethyl-2,3-butylenediamine, 1,3-propylene-



**(183)**



**(184)**

diamine or 1,2-phenylenediamine and having 4-methylpyridine in the axial position have been prepared and their dioxygen affinities measured in diglyme solution [324].

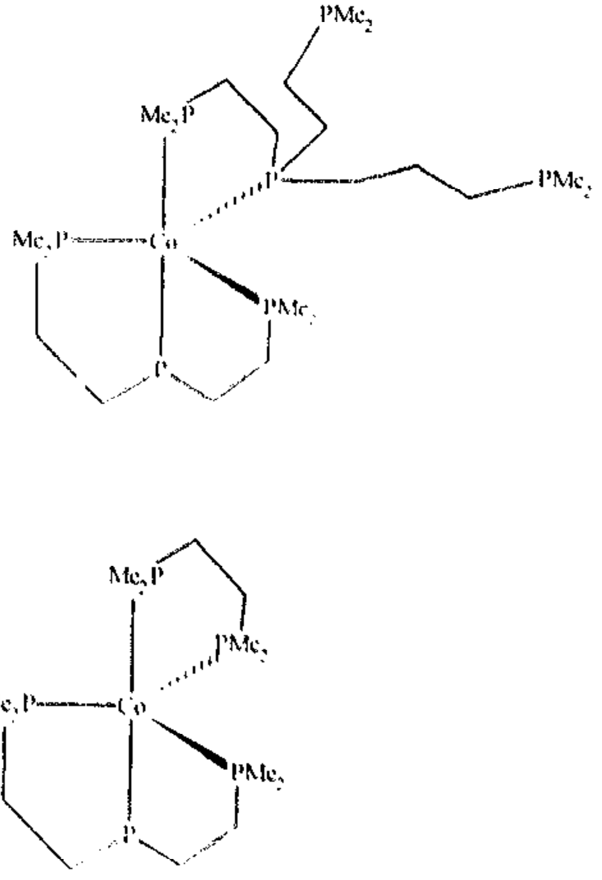
The use of Co–PMA complexes as models for the corresponding bleomycin complexes has been discussed in 2.1.1. Mascharak and coworkers have also examined the reaction of [Co(II)(PMA)] with $O_2$and found that the product is

$[Co(III)(PMA)(O_2^-)]^+$ [324a]. In solution, the superoxide species decomposes to produce $[Co(III)(PMA)(H_2O)]^{2+}$.

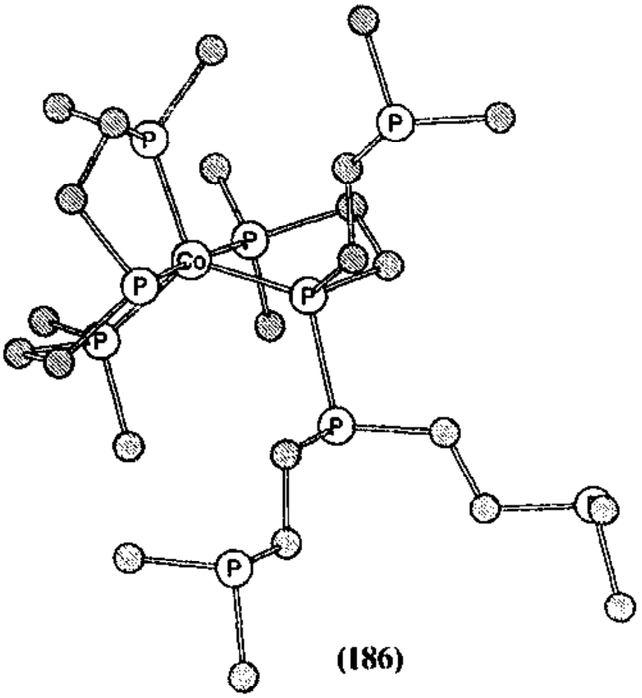
## 5. Cobalt(I) complexes

There has been a review of competitive redox reactions in which there is a cobalt(I) intermediate [325].

In a study of Co(I) phosphines, the complexes shown in (**185**) have been prepared and characterized [326]. The X-ray crystal structure of one, (**186**), has been determined and NMR spectroscopic studies carried out on the solution. The structures in the solid and in solution are similar, though variable temperature NMR spectra in the latter show that it is fluxional. The environment around the Co is roughly trigonal bipyramidal. The structure of the second complex was examined using $^{31}P-\{^1H\}$ NMR spectroscopy, and the geometry around the Co was similar to that of the first complex.

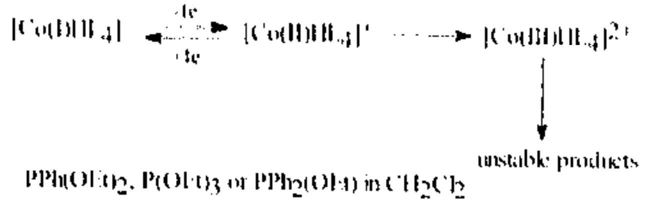


(**185**)



**(186)**

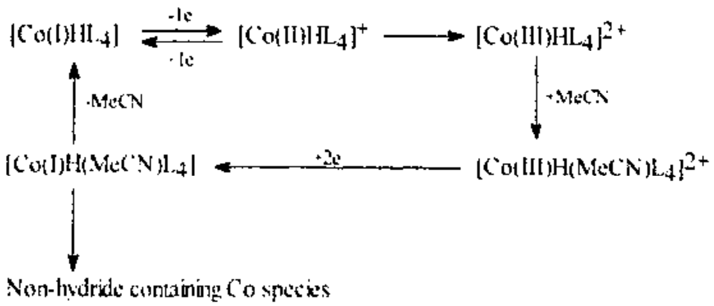
The mechanisms of the oxidation of a range of Co(I) hydride complexes of the form [$CoHL_4$], in which L = $P(OEt)_3$, $PPh(OEt)_2$ or $PPh_2(OEt)$ have been studied using electrochemical methods in $CH_2Cl_2$ and MeCN [327]. There were significant differences in the redox behaviour in the two solvents. Thus in $CH_2Cl_2$ there was a clear stepwise progression from Co(I) to Co(II) to Co(III) as shown in scheme **(187)** and the behaviour was the same for all the complexes studied. In MeCN solution, however the processes are complicated by the formation of MeCN-containing complexes and was not the same for all the complexes as is illustrated in schemes **(188)** and **(189)**.



**(187)**

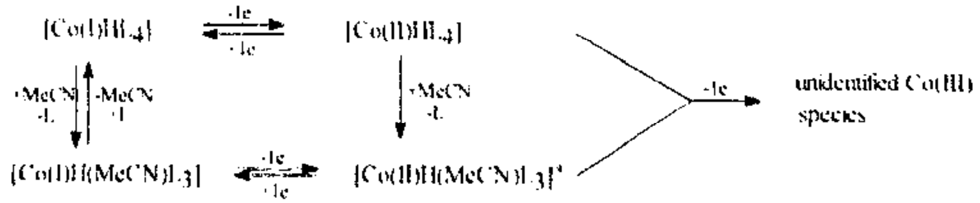
The Raman spectrum of tris(triphenylphosphine)cobalt(I) has been reported for the first time [328]. By comparison with other complexes it has been possible to assign the phosphine ligand vibrations and those of the Co Cl and Co P bonds.

The Co(I) state is produced electrochemically in an irreversible process from the complex [CoLCl]Cl, where L = dibenzo[C,K][1,6,9,14]tetraone [329]. The question of the nature of the bonding of the hydrogen in the complex [$(PP3)Co(H_2)]^+$, where



L = PPh(OEt)$_2$, P(OEt)$_3$ in MeCN

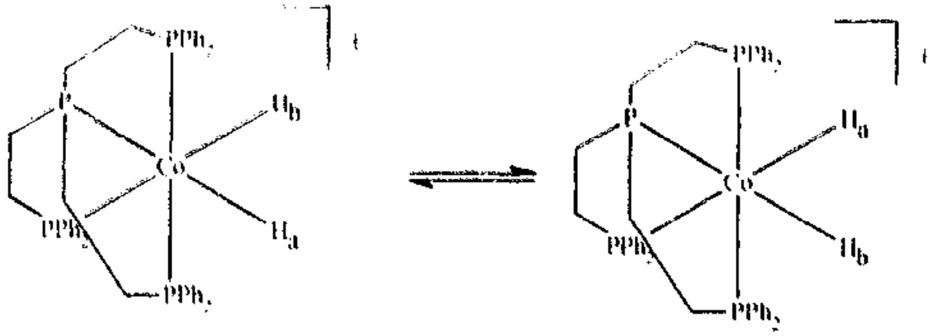
**(188)**



L = PPh(OEt)$_2$ in MeCN

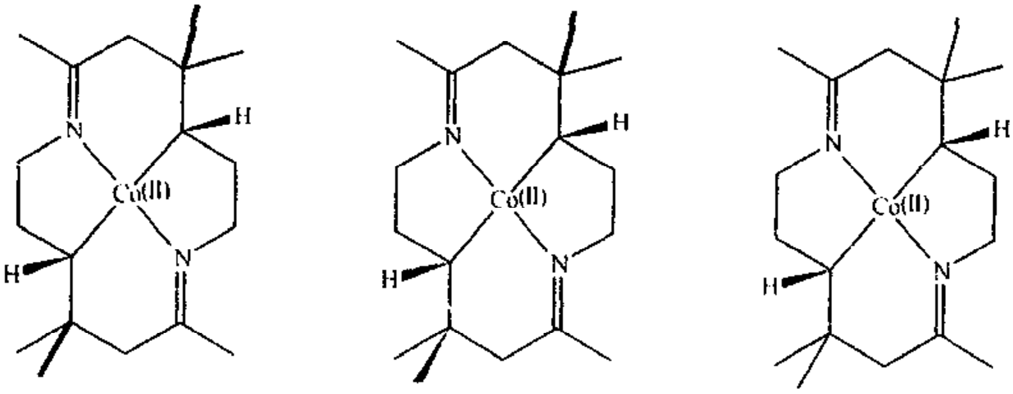
**(189)**

PP3 = P(CH$_2$CH$_2$PPh$_2$)$_3$, has been revisited [330]. It is concluded from $^1$H and $^1$H{$^{31}$P} NMR spectra that the complex is in fact (**190**) and involves the equilibrium shown.



**(190)**

We are accustomed to isotope exchange involving the $^1$H in complex ions and $^2$H in water, but isotope exchange of this type is very much more unusual in solvents such as acetonitrile. Fujita and Creutz have found that there is a relatively fast proton exchange involving the N–H groups of a Co(I) macrocycle, CoL$^+$, where L represents the species shown in structures (**191**), and CD$_3$CN with a half life of about 20 min [331]. The infrared spectra of [CoL] prepared from *N*-*rac*-Co(II)$L^{2+}$ show clear changes arising from H/D exchange involving N–H, giving a rate constant of $5 \times 10^{-4}$ $s^{-1}$ at 23°C. This is twice as fast as the exchange of the C–H protons of the macrocycle. Both the *meso* and the octamethyl complexes also show proton exchange, but the latter is about a factor of 20 slower than the former.

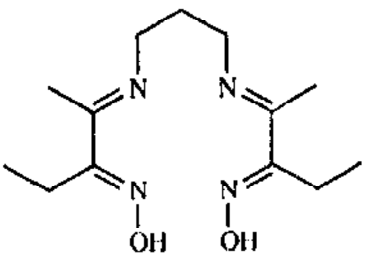


N-*rac*-Co(II)$L^{2+}$ N-*meso*-Co(II)$L^{2+}$ Co(II)$L^{2+}$

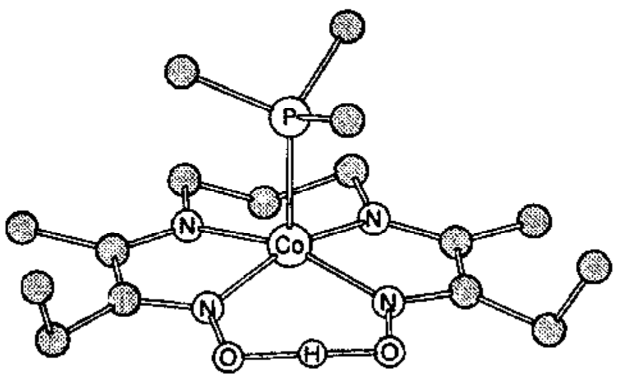
**(191)**

An insoluble tetrapyridinoporphyrazinocobalt(I) film has been laid down on a highly oriented pyrolytic graphite electrode by electroreduction of *N,N′,N″,N‴*-tetramethyltetra-3,4-pyridinoporphyrazinocobalt(II) in phosphate buffer [332]. When this electrode was then coated with Nafion it could be used as a sensor for $S^{2-}$ and 2-mercaptoethanol.

Complex formation between cobalt(I), $PPh_3$ and ligand (**192**) with cobalt(I) gives a complex (**193**) for which the X-ray crystal structure shows that the arrangement around the Co is square pyramidal [333].



**(192)**



(193)

## 6. Cobalt(IV) complexes

It is rare to find many studies of coordination compounds involving Co(IV) and in 1994 there appears to have been only one such investigation published [334]. The Co(IV) complex $[Co(S_2C_2R_2)_2L]$ (R=CN, L=$Et_3$; R=$CF_3$ or Ph, L=$PPh_3$ or $P(OPh)_3$; R=$C_6H_4Me$, L=$PPh_3$ or $PEt_3$; R=$C_6H_4OMe$, L=$PPh_3$) has been studied using isotropic and frozen solution ESR spectra in solution in $CH_2Cl_2$–$ClCH_2CH_2Cl$. The spectra confirm that the Co is low spin $d^5$ and formally Co(IV). The crystal structures of $[Co(S_2C_2(CF_3)_2)_2(P(OPh)_3]$ and $[Co(S_2C_2(CF_3)_2)_2(PPh)_3]$ were also determined. The geometry around the Co was found to be approximately square pyramidal.

## 7. Reactions involving vitamin $B_{12}$ and model compounds

Many of the reactions of vitamin $B_{12}$ are essentially organometallic in nature, involving Co–C bonds and are therefore strictly outside the scope of this review. This section therefore deals only with reactions of vitamin $B_{12}$ and appropriate related compounds which are confined to cobalamin complexes which do not have Co–C bonds nor involve reactions in which such bonds are formed, the only exception being Co–CN bonds.

In a study of three cobalamin complexes with ligands containing sulfur *viz.* glutathione, sulfite and cysteine, it has been shown using X-ray absorption spectroscopy that the bonding to the Co is via sulfur [335]. The X-ray spectra suggest that there is electron donation from S to Co reducing the charge on the Co to less than 3+.

Equilibrium data for replacement of water in aquacyanocobinamide have been determined for two different groups of compounds; imidazole, 1,2,4-triazole and several other azoles [336] and $NH_3$, 4 primary alkylamines, $NH_2NH_2$, $NH_2OH$ and four 4-substituted pyridines [337]. In all cases the systems obeyed the linear free energy relationship:

$$\log K = a.pK + b$$

For the azole systems, a = 0.42 and b = 1.3. For the amines, a = 0.58 and b = −2.6, while for the azines a = 0.47 and b = 0.18. $NH_2NH_2$ and $NH_2OH$ lie above the amine curve and 1,2-diazine pyridazine lies above the azine curve. The higher values are attributed by the authors to the α effect.

The X-ray crystal structure of Co-cyano-(5′-6′-dimethylbenzimidazolyl)cobamide (vitamin $B_{12}$) has been redetermined at 92 K (original work carried out by Hodgkin and coworkers [338]) and that of Co-cyanoimidazolylcobamide has been determined at 88 K [339]. The lower temperatures were used in order to minimize radiation damage. The interest that the authors had in these structures lay in the need to find out the extent to which the bulk of the nucleotide coordination contributes to the so-called upward folding of the corrin ring system. The crystals of the Co-cyanoimidazolylcobamide showed that it was orthorhombic $P2_12_12_1$ having $Z$ = 4 and $a$ = 15.335, $b$ = 21.974, $c$ = 25.501 Å and $V$ = 8705 Å$^3$. When the X-ray structure data for this species were compared with the $B_{12}$ data it was found that the bulk of the benzimidazole group in the latter complex contributed to the upward folding of the corrin ring system. Data are also presented in this paper of the application of 2D-HSQC-ROESY (heteronuclear single quantum coherence - rotating frame Overhauser spectroscopy) experiments to the compounds in solution.

The equilibrium constants for the base-on/base-of reactions for a series of alkyl cobalaminins, but including cyanocobalamin have been measured [340]. It is becoming increasingly likely that substitution of water in aquacobalamin occurs via a dissociative interchange ($I_d$) mechanism. Two papers have investigated this situation in 1994. Marques and coworkers [341] have examined the kinetics of the replacement of water in aquacobalamin by a number of anionic ligands ($I^-$, $S_2O_3^{2-}$, $NO_2^-$, $SCN^-$, $N_3$) and have found that plots of $k_{obs}$ *vs* ligand concentration over a wide range of concentrations exhibit small but significant departures from linearity showing that there is evidence for saturation behaviour and this is interpreted as evidence for the $I_d$ mechanism. Similarly, van Eldik and coworkers have studied the kinetics of the reaction between aquacobalamin and a number of substituted pyridine ligands [342]. They, too, have observed curvature in plots of $k_{obs}$ vs concentration of entering ligand, though this time the curvature was very much more pronounced. Again this is interpreted as indicating an $I_d$ mechanism but involving an unexpectedly strong precursor complex. This is confirmed by the observed values of $V^‡$ of between +4 and +7 cm$^3$ mol$^{-1}$. In terms of the formation of the precursor complexes by this particular set of ligands the strength of the interaction is ascribed to the possibility that it is produced by the interaction of the system of the py ligands with, for example, the corrin ring system.

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