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# 3. COBALT

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## CONTENTS

## *INTRODUCTION*

This survey covers the literature for 1985, and is based on a data search of Volumes 102 and 103 of Chemical Abstracts, although *Journal of*

0010-8545/88/$45.85

*the American Chemical Society, Inorganic Chemistry,* and *Journal of the Chemical Society (Dalton Transactions, and Chemical Communications)* have been covered separately from January to the end of December 1985. The general format of this review is compatable with that of previous years.

The review does not cover multinuclear cobalt cluster compounds, cobaltaboranes nor cobaltacarboranes

I should like to thank Dr. Edwin C. Constable for suggesting that I write this review, thus providing me with a somewhat unorthodox introduction to cobalt coordination chemistry.

## *3.1 COBALT(IV)*

The complex $[Co(S_2CNRR')_3]ClO_4$ has been formed by the oxidation with Fe(III) of $[Co(S_2CNRR')_3]$; a cautionary note on the explosive nature of the complex is given [1]. Electrochemistry and spectral properties are reported.

A detailed mechanism is discussed for the oxidation of $H_2O$ by $Co^{2+}/[Ru(dipy)_3]^{3+}$; during the induction period, Co(III) is oxidised to Co(IV) [2].

## *3.2 COBALT(III)*

### *3.2.1 Complexes with halide ligands*

$CoBr_3$ catalyses the oxidation of toluene in acetic acid [3]. A complex involving $Co^{3+}-Br^-$ with $PhCH_2OH$ is proposed.

$[Co(CN)_6]^{3-}$ has been the subject of comparative neutron and X-ray diffraction studies [4]; bond distances of Co-C = 1.894(3)Å and C-N = 1.178(3)Å agree between the two methods.

The preparation of dinuclear Co(III)-M(II) (M = Ni, Pd, Pt) complexes with a bridging $CN^-$ ligand between the hetero-metals is pH dependent. Spectral and analytical characterisation of the complexes $[(H_3N)_4(OH_2)CoCNM(CN)_3]_2[M(CN)_4]$ and $[(en)_2(OH_2)CoCNM(CN)_3]_2[M(CN)_4]$ are described [5].

### 3.2.2 *Complexes with oxygen donor ligands*

#### 3.2.2.1 *Simple oxygen donor ligands*

The kinetics of the solvation of $[(H_3N)_5Co(H_2O)]^{3+}$ by $Me_2SO$ or $(CH_2)_4SO$ have been the subject of attention [6]. The reaction of $[(H_3N)_4Co(CN)(OH)]^+$ with $SO_2$ gives an O-bound $OSO_2$ moiety which exhibits linkage isomerism as a function of pH. Kinetics and mechanism of the formation of the complex and its hydrolysis are discussed [7]. The solvolysis of $[(H_3N)_5Co(OSO_2CF_3)]^{2+}$ occurs smoothly to give $[(H_3N)_5Co(S)]^{3+}$ (S = solvent molecule); the kinetics of the process have been studied and activation parameters determined [8].

An investigation of the kinetics at 25°C of the hydrolysis of $[Co(NH_3)_5(CrO_4)]^+$, replacing $CrO_4^{2-}$ by $H_2O$, over a range of pH's shows that the equilibrium constant for the process minimises at pH 6 [9].

Substitution of the $CO_3^{2-}$ ligand for $OH^-$ in $[Co(en)_2(CO_3)]^+$ is reported to involve intermediates with unidentate carbonate and ethylenediamine ligands [10].

The catalytic effect of $NO_3^-$ ion on the substitution reaction of Co(III) complexes has been investigated by looking at solvent exchange data for the system:

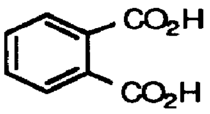
$$cis\text{-}[Co(en)_2(H_2{}^{17}O)_2]^{3+} + 2H_2O \rightarrow cis\text{-}[Co(en)_2(H_2O)_2]^{3+} + 2H_2{}^{17}O\ .$$

$^{17}O$ n.m.r. data, collected over a range of temperatures and in various solvents, compares the effects of having the $NO_3^-$ ion present [11].

The rôle of $H_3O_2^-$ as a bridging ligand has been investigated. The ligand bridges between two cobalt centres in the complex *trans*-$[Co(en)_2(H_3O_2)](ClO_4)_2$; there are infinite chains of ---Co-$H_3O_2$-Co--- units with an O·····O separation of 2.441(2)Å. On the other hand, the *cis*-complex is dimeric with two μ-$H_3O_2$ units per cation [231].

### 3.2.2.2 *Carboxylato, oxalato, acetylacetonato and related ligands.*

The coordination chemistry of carboxylato and β-diketonato ligands is discussed in this review in several sections, since it occurs in many cases in parallel with the chemistry of other donor ligand types. Those examples in which the latter ligands are predominant, or on which the descriptive chemistry centres, are collected here. A study of the structural influence of the carboxylato ligand, L, on the electrochemistry of Co(III) complexes of type $[Co(NH_3)_5L]^{2+}$ has been described [12]. The complexation of Co(III) with $CH_3COO^-$ ions in aqueous acetic acid at varying acid concentrations and pH has shown that the distribution of products $[Co(H_2O)_6]^{3+}$, $[Co(H_2O)_5(OAc)]^{2+}$, $[Co(H_2O)_4(OH)(OAc)]^+$, $[Co(H_2O)_4(OAc)_2]^+$, and $[Co(H_2O)_3(OH)(OAc)_2]$ is a function of pH [13]. The kinetics of the complexation of the dicarboxylato ligand (**1**) with *cis*-$[Co(H_2O)_2(NH_3)_4]^{3+}$ has been investigated [14]. (**1**) is also one member of a series of ligands studied for its reaction with $[Co(en)_3]^{3+}$; other ligands reported are salicylic acid, benzoic acid, and (**2**) and (**3**) [15].



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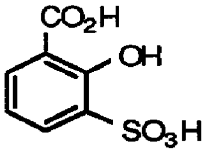

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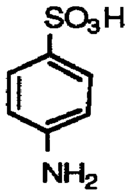


**(3)**

The reduction of Co(III) acetate complexes appears in three papers, each in a different context. In acetate buffer solutions, cobalt(III) acetate complexes associate to produce binuclear and trinuclear Co(II) acetate compounds [16], whilst irradiation of $[Co(en)(CH_3CO_2)_4]$ produces Co(II) [17]. A detailed mechanistic study of the oxidation of bromide ion by Co(III) acetate in acetic acid and in the presence of pyridine proposes that the reaction involves a cobalt(III) dimer and that bromide anion radicals are present as intermediates [18].

As usual, there is a significant literature devoted to oxalato ligand chemistry. The kinetics of the base hydrolysis of $[Co(ox)(1,2\text{-}pn)_2]^+$ and $[Co(ox)(1,3\text{-}pn)_2]^+$ have been discussed [19]. Related to this, is a study of the hydrolysis and O-exchange in $[Co(ox)(OH)(en)_2]^+$ in which acidic cyclisation of the *cis* isomer is found to be more facile than that of the *trans* isomer [20]. The mechanism of the reduction of $[CoL_2(en)]^-$ by Fe(II) depends on L; when L = ox, the rate is independent of $H^+$, but for L = $HO_2CCH_2CO_2H$, the rate depends on $H^+$ and an inner sphere mechanism is proposed which involves a protonated monodentate-malonate ligand [21].

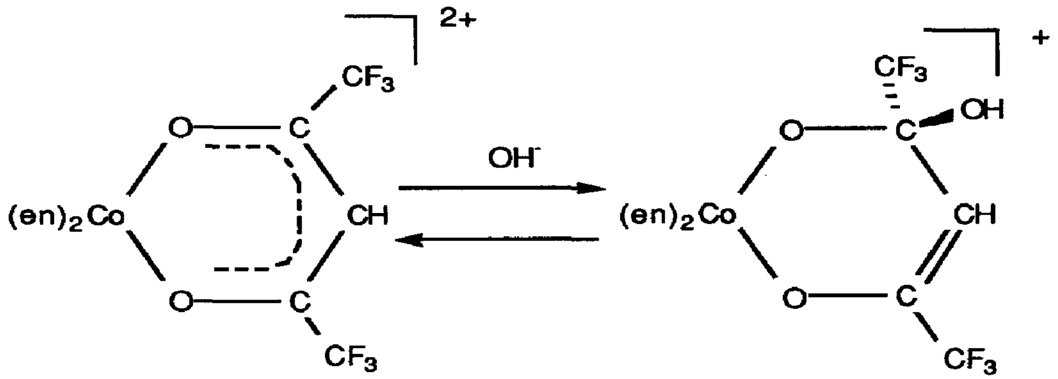
The reduction of $[Co(ox)_3]^{3-}$ to $[Co(ox)_3]^{4-}$ by ruthenium(II) species obeys the rate equation:

$$\rho = k_{obs}[Co(III)][Ru(II)]$$

The acid dependence of the reaction in the range $[H^+] = 0.01\text{-}0.1$ mol dm$^{-3}$ is discussed, and activation parameters are reported [22]. A related investigation looks at the intramolecular redox decompostion of $[Co(ox)_3]^{3-}$ to Co(II), free ligand and $CO_2$; the rate is accelerated when the acidified reaction mixture is irradiated in the presence of $[Ru(bipy)_3]^{2+}$ [23].

A crystallographic study of $K_3[Co(ox)_3]$ hydrates shows the spontaneous crystallisation of two sets of racemic crystals and an optically active complex. Conditions for resolution are discussed [24].

The electrochemistry of $[Co(acac)_3]$ is described [25], and an investigation [26] of the catalytic properties of the same complex indicates that $[Co(acac)_3]$ acts as an initiator rather than as a genuine catalyst during the photochemical oxidation of ethylbenzene and related compounds. A study [27] of a series of complexes of the hexafluoroacetylacetonato ligand with Co(III) illustrates an interesting reaction with base which is common to all the complexes; *e.g.*:



Complexes of the type [Co($p$-$BrC_6H_4COCHCOMe)_n(MeCOCHCOMe)_{3-n}$] have been prepared; separation of diastereomers for n = 2 and 3 has been achieved by using t.l.c. methods. For these complexes, an investigation of their electrochemistry has led to a correlation between electron transfer kinetics and the steroechemistry of a given isomer [266].

The $Co^{3+}$ ion is involved in a metal ion promoted hydration of a coordinated alkene [28]. The reaction concerns a methyl maleate or ethyl fumarate ligand, L, in either case bound in a monodentate fashion through the carboxylate ion *cis* to an $H_2O$ molecule in $[Co(en)_2(H_2O)L]^{2+}$. Abstraction of $H^+$ from the water molecule is followed by rapid intramolecular cyclisation.

### *3.2.2.3 Amino acids with oxygen donor*

The kinetics and mechanism of the base hydrolysis of the complex $[Co(NH_3)_5L]^{2+}$ (HL = $H_2N(CH_2)_nCO_2H$, n = 1,2) at various concentrations of hydroxide ion has been described; it is shown that $Co-O_L$ bond cleavage is more difficult in the case of n=2 [29].

The unusual unidentate coordination of an amino acid through the carboxylate group has been exemplified in the complex $[Co(NH_3)(HOOCCH(NH_2)CH(OH)CH_3)]^{3+}$; an X-ray structural determination gives Co-O = 1.91(1)Å. The new complex is of interest in terms of application to peptide synthesis [30].

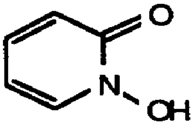
### *3.2.2.4 Miscellaneous*

A comparative study of the solubilisation by crown ethers of K[Co(edta)].$2H_2O$ has illustrated that the solubility of the complex increases along the series neat $CH_3CN$, 18-crown-6 in $CH_3CN$ to 15-crown-5 in $CH_3CN$. After comparisons with the solubilities in other ethers, it is suggested that the interaction of the [$K^+$-ether] complex with acetonitrile solvent is important [31].

Complexes with the sugars *D*-ribose, *L*-sorbose and *D*-glucosamine are formed by the reactions of *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ with the respective monosaccharide [32].

The octahedral complex $[CoL_3]$, HL = (**4**) has been synthesised and structurally characterised; there is an orientational disorder between *cis* and *trans*-isomers brought about by disordered carbon and nitrogen atoms [33].

The base hydrolyses of free and coordinated phosphates and pyrophosphate have been compared [34]. There is no detectable enhancement of the rate of hydrolysis in going from free to coordinated $P_2O_7{}^{4-}$; however for some substituted phosphates, a rate enhancement *is* observed upon coordination.



(**4**)

Chloride ion is displaced by $RC(O)NHO^-$ from *cis*-$[Co(en)_2Cl_2]^+$, but the product distribution depends on R (R = Me, Et, Ph) [35].

### 3.2.3 *Complexes with oxygen–nitrogen donor ligands*

#### 3.2.3.1 *Amino acids*

The displacement of carbonate from $[Co(CO_3)_3]^{3-}$ by L (L = glycine or alanine) gives two geometric isomers of $[Co(CO_3)L_2]^-$, the isomer formation being dependent upon L [36]. Related to these complexes is *trans(CN)*-$[Co(CN)_2(L\text{-alanine})_2]^-$, the spectral characteristics of which have been reported [37]. The photolysis of the complex $[CoL_2L'Cl]Cl_2$ (L = $H_2NCH_2CO_2H$ and L' = $H_2NCH_2CO_2CH_3$) has been investigated [38].

A series of complexes of *L*-alanine with the Co(III) ion has allowed a study of the effect which the overall charge on the complex has on the racemisation of the chelating ligand. The rate is found to be proportional to the charge, n, (n = −2,−1,0,+1,+2); the larger the positive charge, the faster the racemisation [39].

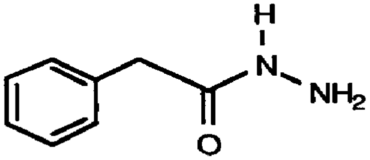
The $Co^{3+}$ ion promotes the base catalysed elimination reactions of *o*-acetyl- and *o*-sulphonyl-serine. The kinetics and mechanism of the reactions are discussed [40].

The preparation and complexation to Co(II) of the amino acidato ligand L (HL = (**5**) ) is reported. The ligand is tetradentate; isomer formation is discussed, as well as the steric effects which are introduced when R = Me [41].

(**5**)

#### 3.2.3.2 *Acid anhydrides*

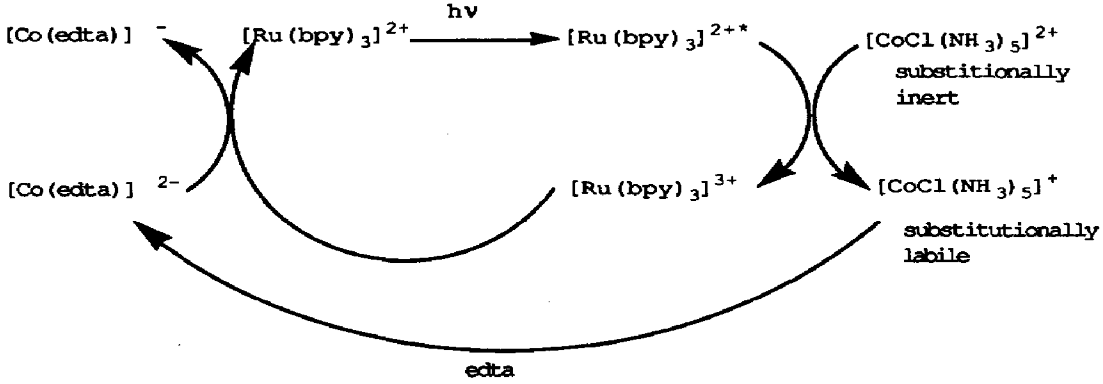
The complexes $[Co(HL)_3]X_2$ (X = Cl, $0.5SO_4$, or $NO_3$) and $[CoL_3]$ have been prepared from the reactions of $CoX_2$ and $[Co(NH_3)_5Cl]Cl_2$ with HL, respectively; (HL = (**6**) ). Spectral and magnetic moment data evidence that both HL and L behave as bidentate ligands, chelating through the carbonyl-oxygen and the amino-nitrogen atoms [42].



**(6)**

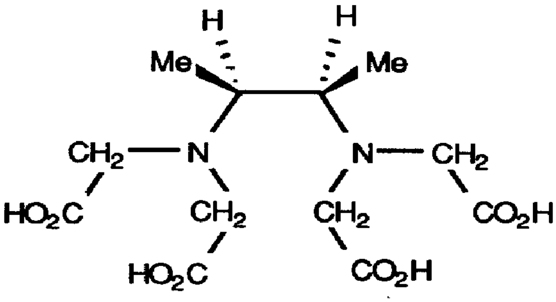
### *3.2.3.3 Aminopolycarboxylic acids and related ligands*

The mechanism of the light induced ligand substitution reaction of $[CoCl(NH_3)_5]^{2+}$ with edta in the presence of $[Ru(bipy)_3]^{2+}$ is presented as follows:



The scheme works well at pH 4.75 [43].

A crystallographic study of the complex $[CoL]^-$ ($H_4L$ = **(7)**) investigates sources of strain in edta complexes. Strain due to the fusion of 5-membered chelate rings is common to all edta complexes, but in the given example, there is additional repulsion between the axial methyl groups and methylene hydrogen atoms. The N-C$_{(CHMe)}$ bond lengthens to relieve the latter, and angular distortions are also noted; Co-N = 1.916(10), 1.913(10)Å, Co-O = 1.878-1.909Å [44]. The racemic ligand $H_4L$,



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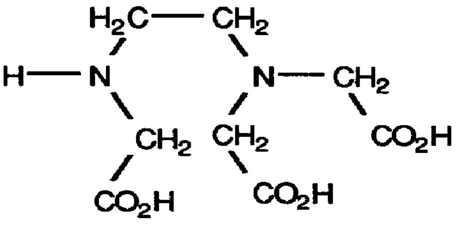

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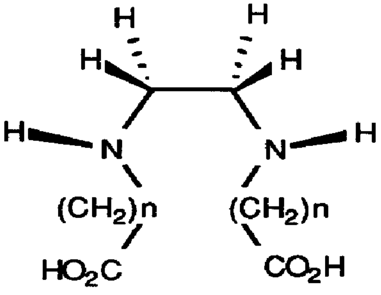
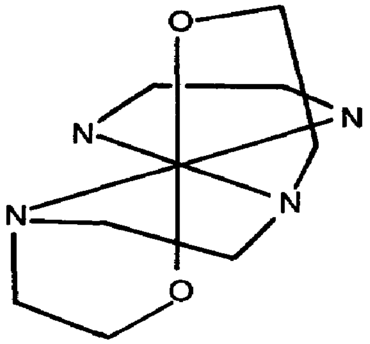


**(9)** n=2; **(10)** n=3; **(11)** n=1

(**7**), has also been studied in its reaction with $Co(OAc)_3.4H_2O$. The two independent enantiomeric pairs of product complexes have been isolated [45]. The pentadentate ligand, $H_3L$, (**8**), has been the subject of several papers. The preparation and characterisation of complexes $[CoL(NH_3)]$ and $[CoL(HL')]Cl$ are reported (L'=1,3-pn); it is proposed that each complex exhibits only one isomer [46].

The selective ligation of $H_2L$, (**9**), leads to the formation of only the Δ-*cis*-isomer of the complex $[CoLCl_2]^-$ [47]. Geometric preference for the tetradentate ligand is again observed in the complexes $[CoLCl_2]^-$, $[CoLCl(H_2O)]$, $[CoL(CO_3)]^-$ and $[CoL(H_2O)_2]^+$ ($H_2L$ = (**10**) ) [48]. For the related complex, $[CoL(CO_3)]^-$ (L = (**11**) ), an unprecedented inversion from the Λ-β-to Δ-α-form is observed; equilibration of diastereomers for the complex $[Co(en)_2(ox)]^+$ is also discussed [49]. Reasons for the conformation (**12**) of the prolinate ligand in $[Co(en)L]^+$, ($H_2L$ = (**13**) ) have been suggested [50].

A detailed study of the complex [CoL], where HL is $H_2N(CH_2)_2NHCO_2H$, has lead to the resolution of five chiral isomers and isolation of all six geometric isomers; spectroscopic and crystallographic data are reported [51].



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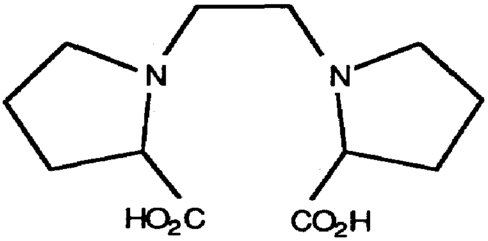


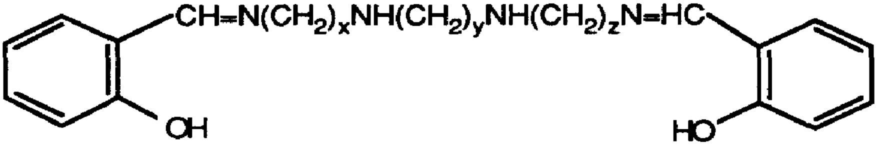
**(13)**

### *3.2.3.4 Imines*

The structure of the binuclear complex $[Co_2(OH)(L_4H_5)]^{2+}$ ($H_2L$ = dimethylglyoxime) has been determined; the two Co(III) ions are bridged by the hydroxyl ligand and by the N–O chelate of one L [52].

Several papers report complexes of $sal_2enH_2$ or related ligands with Co(III). The kinetic stability of the Co-R (R = alkyl) bond in the complex $[RCo(sal_2en)(py)]$ has been investigated [53]. In the octahedral complexes $[Co(sal_2en)X_2)]^{n+/-}$, the $sal_2en$ ligand occupies the equatorial plane when $X_2$ comprises two monodentate ligands (X = py, $CN^-$, $NH_3$, $N_3^-$, $H_2O$), but a change in conformation is enforced when $(X_2)$ = $CO_3^{2-}$; the catalytic activity of the complexes is described [54]. The preparation and characterisation by $^1H$ n.m.r. of $[Co(sal_2en)(NH_2R)_2)PF_6$ complexes (R = Et, Pr, $^i$Pr, Bu, amyl) is accompanied by a structural report for the complex when R = Bu [55].

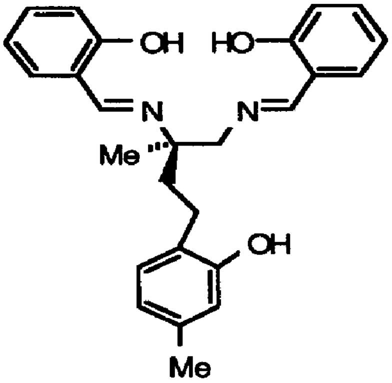
The introduction of nitrogen donors into the carbon chain in $sal_2enH_2$ gives a hexadentate ligand, $H_2L$ (**14**); $^1H$ and $^{13}C$ n.m.r. have been used to elucidate the ligand conformation in each of three related complexes [56].



(**14**)

Complex(I) x=2; y=3; z=2
Complex(II) x=3; y=2; z=3
Complex(III) x=3; y=3; z=3

A square pyramidal environment for the $Co^{3+}$ ion is exemplified in the complex [Co(sal-Hpen)] and in the product of the reaction of a Co(III)-($sal_2en$) complex with $PhO^-$ derivatives; (sal-Hpen = (**15**) ) [57].

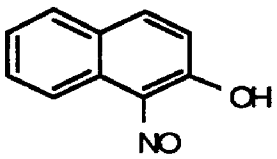


**(15)**

### *3.2.3.4 Miscellaneous*

Macrocylic ligands are covered largely in the section on nitrogen donors, but one study has focussed on the effects of substituting either an oxygen or a sulphur atom for a nitrogen atom in the macrocycles 1,4,7-triazacyclononane (tacn) to give 1-oxa-4,7-diazacyclononane (taon) and 1-thia-4,7-diazacyclononane (tasn) respectively. The cobalt(III) complexes [Co(tacn)(taon)]$Cl_3.4.5H_2O$, [Co(mtcn)(taon)]$Cl_3.4.5H_2O$, [Co(tacn)(tasn)]$Cl_3.3H_2O$, [Co(mtcn)(tasn)]$Cl_3.4.5H_2O$ and $[Co(tasn)_2]Cl_3.4.5H_2O$ (mtcn = 2-methyl-1,4,7-triazacyclononane) have been compared, and their electronic spectra show that the ligand field strengths of the O- and S-donors increase when they are incorporated into the macrocycles [58].

The preparation, spectral and magnetic characteristics, and stability in acidic media of the complex $[CoL_3]$, HL = **(16)**, have been described; ligation occurs through the phenoxy-oxygen and nitroso-nitrogen atoms [59]. Related to this complexation type is that shown by the ligand HL **(17)**, again in the homoleptic complex $[CoL_3]$; the nitroso-N and acetyl-O are the chelation sites [60].



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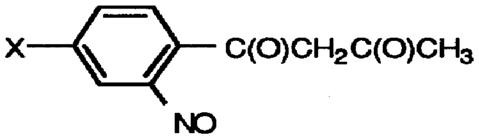

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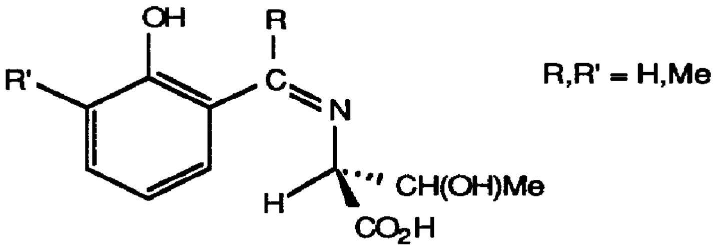
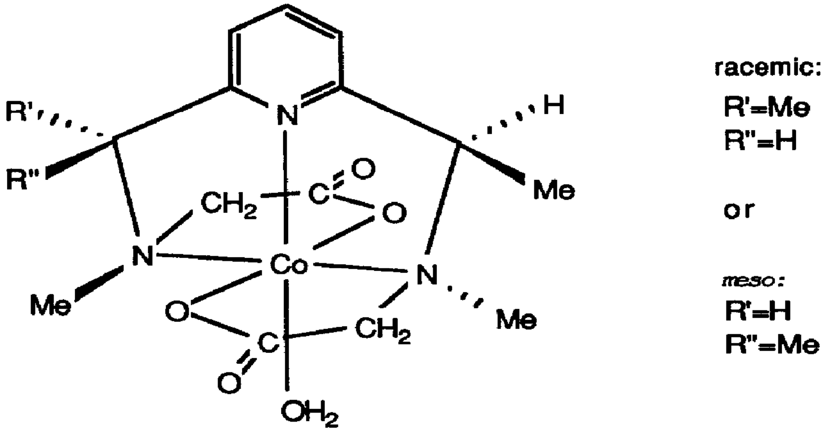


(18)

A kinetic investigation of C-C and C-H bond fission in the threonine fragment of the ligand, $H_2L$ **(18)**, complexed to Co(III) has shown that C(α)-H cleavage is 3-times *faster* than C(α)-C(β) cleavage when R=H and R'=H or Me, but 100-times *slower* when R=Me. Steric effects are proposed as the cause of this difference [61].



(19)

An interesting complex, **(19)**, of a pentadentate ligand has been structurally characterised. The two distinct crystalline forms depend on the identities of R' and R"; in one, the pyridine ring is twisted about the $C-N_{py}$ bond by 17.2(2)°, while in the other, the twist angle is 19.7(1)° [62].

### *3.2.4 Complexes with oxygen-sulphur donor ligands*

This section is warranted by a sole publication; a series of complexes incorporating the ligand $S_2O_3^{2-}$ has been prepared. Crystal structures of two of the complexes, $[Co(en)_2(S_2O_3)]ClO_4$ and *cis*-$[Co(en)_2(S_2O_3)(NO_2)]$, evidence bidentate (S-O) and monodentate (S) ligation respectively. The thiosulphate ligands in $[Co(en)_2(S_2O_3)(NO_2)]$ and a third complex, $[Co(en)_2(S_2O_3)_2]^-$, are readily oxidised by iodine leaving photoreactive Co(III) compounds [63].

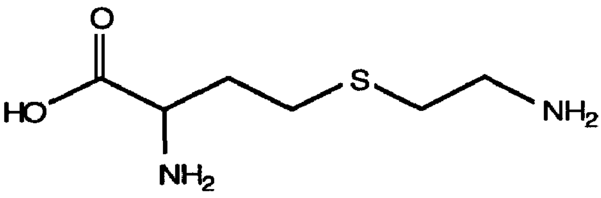
### *3.2.5 Complexes with oxygen-sulphur-nitrogen donor ligands*

A series of studies has involved ligands related to cysteine. Isomers of the complex ion $[CoL(gly)]^+$ (HL = **(20)** ) have been characterised by using electronic absorption, CD and $^{13}C$ n.m.r. spectroscopy. The ligand L chelates *via* the carboxyl-O, the two amino-N and the S-atoms [64]. Again, spectral characterisation is reported for the related species, $[CoL(en)]^+$, where $H_2L$ = **(21)**; the effects of chelate ring-size on the CD spectra are noted [65]. The sexidentate ligand, L, ($H_2L$ = **(22)** ) is shown by X-ray analysis (for n=2) to have an $N_2S_2O_2$-bonding mode to the $Co^{3+}$ ion [66].

### *3.2.6 Complexes with sulphur donor ligands*

#### *3.2.6.1 S-bound thiocyanate*

A kinetic study of the substitution of water by thiocyanate ion is found to proceed, in part, by a previously unrecognised complex involving S-bound thiocyanate. This complex then rearranges to the N-bound $NCS^-$



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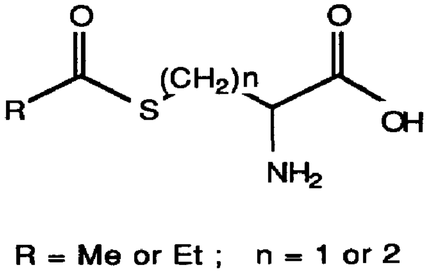

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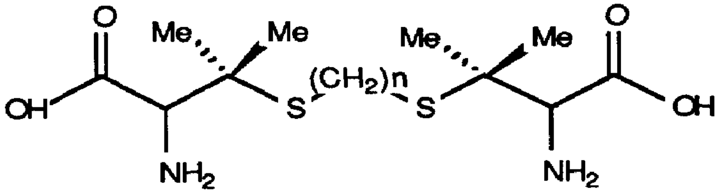


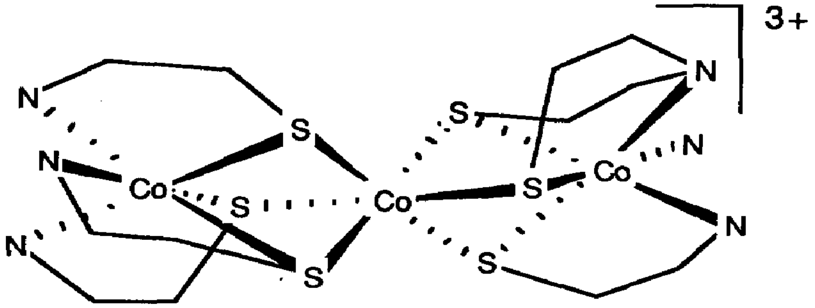
(22)

form, the rate constant for this process is known to be 8.2 x $10^{-7}$ $s^{-1}$. In the present work, the ratio of the rate constants for the formation of S- to N-bound ligand in the early stages of the reaction is found to be 0.36 [67].

### *3.2.6.2 Thiolates, and thiocarboxylic acids*

The ability of a coordinated thiol to bridge two metals is beautifully exemplified in the formation (*via* the oxidation of $CoL_3$) of the trinuclear complex $[Co(CoL_3)_2]^{3+}$, L = $H_2NCH_2CH_2S^-$. A structural determination of the complex, **(23)**, gives average distances of $Co_{central}$-S = 2.626(11)Å, $Co_{terminal}$-S = 2.238(7)Å and $Co_{terminal}$-N = 1.996(8)Å. The

$Co_{central}\cdots Co_{terminal}$ separation is 2.857(1)Å [68].



(**23**)

An unusual square planar cobalt(III) complex, $[Co(S\text{-}2,4,6\text{-}{}^{i}PrC_3H_2)_4]^-$, has been prepared using the lithium salt of the ligand. Structural characterisation gives Co-S distances in the range 2.204-2.211(3)Å; the adoption of a square planar arrangement is put down to a high electron density on cobalt, and thus a high ligand field splitting, rather than any steric reasons [69].

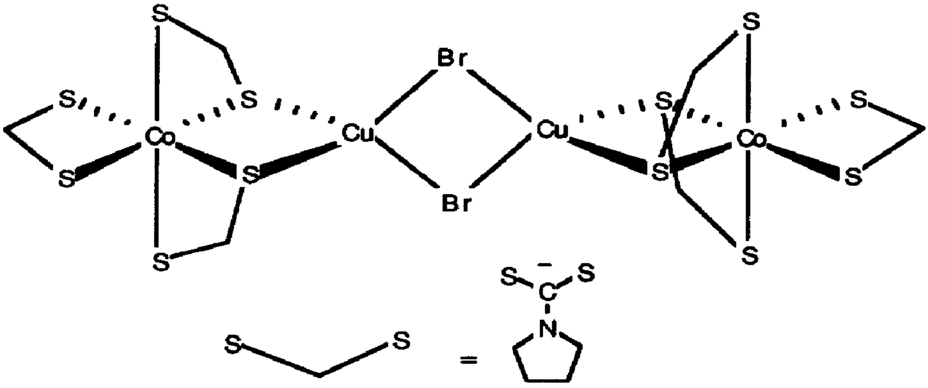
Several complexes with dithiocarboxylate (dtc) ligands have been reported, all of them dinuclear with respect to cobalt. The reactions :

$$[Co(R_2dtc)_3] + BF_3.OEt_3 \rightarrow [Co_2(R_2dtc)_5]^+BF_4^-$$

$$[Co(R_2dtc)_3] + NOXF_6 \rightarrow [Co_2(R_2dtc)_5]^+XF_6^- \quad (X = P \text{ or } Sb)$$

$$R = Et,\ {}^{i}Pr,\ C_6H_{11},\ \text{benzyl} \quad \text{or } R_2 = \text{morpholino}$$

give complexes which slowly decompose back to starting material [70]. The compound $[CoL_3]$, (L = pyrrolidinedithiocarboxylate ion) reacts with copper(I) bromide to give an interesting Cu-Cu bromide bridged complex (**24**) in which sulphur atoms bridge between copper(I) and cobalt(III) centres [71].



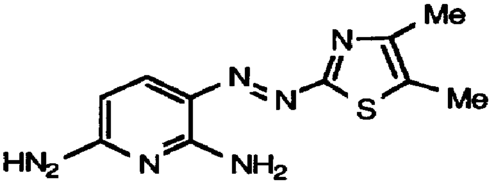
**(24)**

### 3.2.6.3 *Thioamides*

Stability constants for some mono- and di-acetoacetarylthioamides have been determined [72]. Some complexes of thiourea have been prepared and spectroscopically characterised; infra red data indicates S-bound thiourea [73].

### 3.2.6.4 *Miscellaneous*

The extraction of $Co^{3+}$ ions form aqueous solution by using the thiazole **(25)** has been described [74].



**(25)**

The reaction of $CoCl_3$ with $[Et_3NH][SPh]$ in acetonitrile in the presence of $[Et_4N]_2[MoS_4]$ produces >70% of the tetraethyl- ammonium salt of a tetrahedral Co(III) complex containing the thiomolybdate ion. Characterisation is *via* spectral, magnetic moment and electrochemical data [75].

### *3.2.7 Complexes with selenium donor ligands*

There is only one true example in this section, that of the Co(III) complex $[Co(1,2\text{-}C_6H_4(Se)_2)_2]^-$; e.s.r. studies on the compound are reported, and the structure of an analogous Ni(II) complex has been determined [76].

The thermal decomposition of the complexes $[Co(py)_4(NCX)_2]$ for X = O, S, Se has shown that initial decomposition is by loss of pyridine. For X = Se, the intermediate $[Co(NCSe)_2]$ is oxidised at high temperatures to $[Co_2(SeO_3)_3]$ and, finally , to $Co_3O_4$ [77].

### *3.2.8 Complexes with nitrogen donor ligands*

#### *3.2.8.1 Azides*

In this section are collected the few examples in which $N_3^-$ is the ligand of interest. The complex $[Co(N_3)_3(en)]_2$ has been used to prepare $[Co(N_3)_4(en)]^-$; a series of related mono-ethylenediamine complexes have also been reported [78]. In the base catalysed ammoniation of *trans*-$[CoXY(en)_2]ClO_4$ ($X = N_3^-$ or $NCS^-$; Y = Cl, Br), the halide is displaced; a conjugate base mechanism is proposed and activation parameters are calculated [79]. A discussion of the kinetics of the solvolysis of *cis*-$[Co(N_3)(en)_2Cl]^+$ in water/butanol mixtures has appeared [80].

#### *3.2.8.1 Ammonia*

Three crystallographic studies on Co(III)-$NH_3$ complexes are accompanied this year by a neutron diffraction investigation. The latter confirms the results of a low temperature X-ray study and shows that the cation in $[Co(NH_3)_5(H_2O)][Cr(CN)_6]$ is highly disordered, with the water ligand having a fractional occupancy in each of the six octahedral sites; while the normal N-H$_{av.}$ = 1.01(1)Å, one the hydrogen atoms of *one* of the $NH_3$ ligands is involved in an C≡N···H interaction with N···H = 1.933(5)Å [81]. The results of an X-ray determination of $[Co(NH_3)_6][Fe(O_2CCH_2CO_2)_3]$ list Co-N bond distances in the range 1.957(2)-1.970(2)Å [82]. In addition, the structures of $[Co(NH_3)_5(H_2O)][IO_3]_3$ and $[Co(NH_3)_6][Fe(C_2O_4)_3]$ have been reported [83,84].

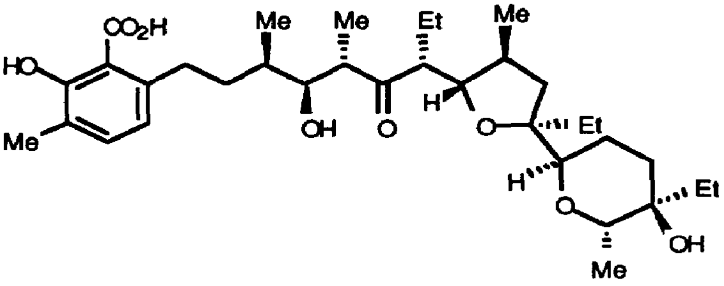
The structures and chemistry of some cobalt-cobalt bridged compounds containing $NH_3$ has been the focus of attention. The structure of the ion $[Co_2(NH_3)_8(\mu\text{-}NH_2)(\mu\text{-}CHO_2)]^{4+}$ shows an average distance of Co-N(NH$_3$) = 1.963(17)Å, and for the bridges, Co-N = 1.958(2)Å and Co-O = 1.912(2)Å [85]. Five novel complexes of formula $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)CoL_4]^{n+}$ with L = $H_2O$, $CN^-$, $NO_2^-$, $0.5[(^-O_2C)NH]$, or $N_3^-$ have been prepared from $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(CO_3)_2]$; UV-visible and infra red spectra are recorded [86]. A detailed kinetic study of the spontaneous cleavage of $[(NH_3)_5Co(\mu\text{-}OH)Co(NH_3)_5]$ in the presence of $NO_3^-/ClO_4^-$ or $NCS^-/ClO_4^-$ anions illustrates competition between stepwise and concerted substitution [87].

The kinetics of the aquation of cobalt(III) ammine complexes has been studied by several groups of workers [88,89,90,91].

The $^{15}N$ labelled complexes *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{3+}$, where X is a weakly coordinating ligand, have been prepared and used in a study of the stereochemistry of the base catalysed solvolysis of penta-ammine Co(III) complexes in aprotic solvents [92]. The same authors have looked at the kinetics of the ammoniation, acid dissociation and H-exchange processes in $[Co(NH_3)_5Cl]^{2+}$ and the *trans*- and *cis*-isomers of $[Co(NH_3)_4Cl_2]^+$; the acidity of the coordinated ammonia in these and related complexes is independent of (i) the formal charge on the complex and (ii) the nature and position of other ligands [93]. Base catalysed ammoniation reactions of $[Co(en)_2XY]^{n+}$ complexes have been studied [79,94].

A kinetic investigation of the oxidation of $[Co(NH_3)_5(NCS)]^{2+}$ by $S_2O_8^{2-}$ or $IO_4^-$ has been reported [95]; solvent effects are discussed.

The results of a study of the reaction between ammonia and *trans*-$[Co(N_3)(en)_2(dmso)][ClO_4]_2$ indicated that a 5-coordinate intermediate (which involves an N-donor π-bonding to the $Co^{3+}$) is formed [96].



**(26)**

The ionophore **(26)** interacts with the hexammine cobalt(III) cation without any disruption of the Co-N bonds; the second sphere coordination complex is characterised spectroscopically [97].

A series of novel bimetallic complexes involving Co, Rh, or Ir with Cr has been prepared by the reaction [98]:

$$[M(H_2O)(NH_3)_5][Cr(CN)_6] \quad + \quad [M(H_2O)(NH_3)_5][Cr(NO)(CN)_5]$$

$$\downarrow$$

$$[(NH_3)_5M(CN)Cr(CN)_5] \qquad M = Rh,\ Ir$$

$$+$$

$$[(NH_3)_5M(CN)Cr(NO)(CN)_4] \qquad M = Co,\ Rh,\ Ir$$

Two thermal decomposition studies of hexa-ammine complexes have been carried out. A mass spectral study investigates the decompositon of $[Co(NH_3)_6]Cl_3$ [99]. The decomposition of $[Co(NH_3)_6][HCO_2]_2.4HCO_2NH_4$ over a range of temperatures gives cobalt(II) and ammonium formates, ammonia and nitrogen [100].

An interpretation of spectral measurements of $[Co(NH_3)_6]^{3+}$ has been presented in the form of a detailed investigative experiment aimed at an undergraduate audience [101]. Raman polarisation measurements have been used to differentiate between the geometrical isomers of $[Co(NH_3)_2(en)(NO_2)]^+$ and of $[Co(NH_3)_2(en)(CN)_2]^+$ [102]. Finally, the complexation of $[Co(NH_3)_5Cl]^{2+}$ benzoquinone has been studied [103].

### *3.2.8.2 Amines*

The effects on reduction potentials of changing the reaction conditons during the electrochemical reduction of some complexes of type $[Co(RNH_2)_5(H_2O)]^{3+}$ (R = H, alkyl) has been described [104]. An investigation of the kinetics of the hydrolysis of the methylamine and butylamine complexes, $[Co(RNH_2)(en)_2X]^{2+}$, compares the effects of changing X from I to Br to Cl [105]. And in general terms, a critical examination of the requirement of the E2 process for the formation of a 5-coordinate intermediate during the base hydrolysis of substituted Co(III) amine complexes has been presented [106].

The coverage of diamine-Co(III) chemistry began in a previous section with the mixed azide-ethylene diamine complexes [78,80]. As usual, the number of complexes in the literature which involve diamine ligands is a large one. A survey of ethylenediamine (en) complexes will proceed to substituted derivatives thereof, to longer chain diamines, and then to polyamines.

An isothermal saturation method has been used to study the solubility in isopropanol of $[Co(en)_2Cl_2]ClO_4$ [107].

Electrochemical methods have been used to measure the stability constants for the formation of the outer sphere complexes $[Co(en)_3](SO_4)_2^-$ and $[Co(en)_3](SO_4)^+$ [108]. For the redox couple $[Co(en)_3]^{3+/2+}$, the change in redox potential as 3M $NaClO_4$ is replaced by 3M NaNCS solution has been recorded; a comparison of the behaviour of this, and related complexes, has been made [109].

The association between the complex cation *cis*-$[Co(en)_2(CN)_2]^+$ and hydrated silver(I) ions has been studied in detail; a shift from 2120 to 2180 $cm^{-1}$ for $\nu_{CN}$ was observed as a result of the cation-cation association [110].

Resolution of some Co(III)-diamine optical isomers has been achieved by using ion exchange chromatography with chiral eluants [111], and by the use of amino acids [112].

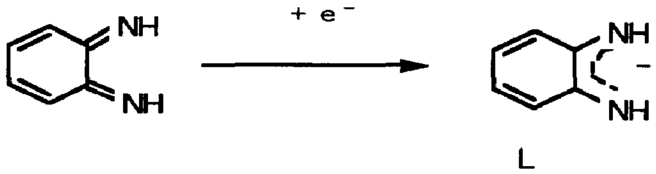
A range of kinetic studies has been published. Activation volumes for the *trans-cis*-isomerism of the cationic complex $[Co(en)_2Cl(H_2O)]^{2+}$ suggest a tetragonal-pyramidal transition state, with a water molecule outside the coordination sphere [113]. The kinetics of the solvolysis of *cis*-$[Co(en)_2(NCS)Cl]^+$ have been reported to depend significantly on the solvent structure [114]. Related to this, the effects of various solvents on the substitution of chloride for thiocyanate ion in *cis*- $[Co(en)_2Cl_2]^+$ has been presented [115]. A rhombic twist mechanism has been proposed for the racemisation of $[Co(en)_2Cl_2]^+$; thermal racemisation is reported to occur without any *cis-trans* interconversion [116]. A detailed discussion is presented concerning proton exchange rates for *trans*-$[Co(en)_2XY]^{n+}$ in liquid ammonia (X,Y = dmso, $NCS^-$, $N_3^-$, $Cl^-$, $Br^-$, $NH_3$, $NO_2^-$, $CN^-$, $SO_3^{2-}$ ) [117]. Finally, the *intra*dimer and *inter*dimer exchange coupling in $[Co(en)_3]_2[Cu_2Cl_8]Cl_2.2H_2O$ has been investigated by using magnetic and e.p.r. techniques [118].

The complex $[Co(en)_2Cl_2]Cl$ has been the subject of photolysis ($\lambda \geq$ 310 nm) and the spin trapping of the radicals so produced [119].

Variations on the ethylenediamine ligand are, as usual, prolific. Complexes of the substituted diamine, $H_2NCH_2CH_2NHPh$ (L), have been prepared; epimerisation of $[Co(acac)L_2]^{2+}$ occurs in water and alcohols to give an equilibrium mixture of isomers [120]. The same authors have also looked at the equilibrium distribution of isomers of $[Co(acac)_2L]^+$, (L = $H_2NCH_2CH_2NHPh$; $PhHNCH_2CH_2NHPh$; $H_2NCH_2CH_2NHMe$; $MeHNCH_2CH_2NHMe$; 1,2-$C_6H_4(NH_2)_2$) [121]. Stereoselectivity in reactions of Co(III) complexes containing *d*- and *l*-$H_2NCH(Ph)CH_2NH_2$ has been investigated [122]. Comparative studies of the complexes $[Co(en)(1,3\text{-pn})L]X_3$ (L=various bidentate diamines and X=halide) are reported [123], as well as of the complexes $[CoL_3]X_3$ (L=en; 1,3pn; 1,2-pn; bipy; phen) [124]. The aquation of the complexes *cis*-$[Co(L)_2(H_2O)(SeO_3)]^+$ (L=en; 1,2-pn; $Me_2$en; $Me_3$en) has been discussed [125]. The kinetics of the acid catalysed hydrolysis of *cis*- or *trans*-$[Co(OAc)_2(1,2\text{-pn})_2]^+$ obey the equation:

$$\rho = \alpha Q[H^+] + Q[H^+]$$

where $\alpha$ is the aquation rate constant for the protonated species and Q is the pre-equilibrium constant for protonation [126]. An X-ray structural determination of the complex $[CoL_2Cl]$ (L = (**27**) ) has shown a 5-coordinate Co(III) ion, with the metal atom displaced 0.15Å above the plane of the four nitrogen donor atoms [127].



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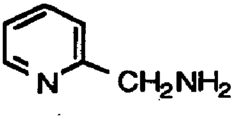

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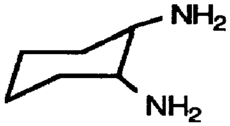
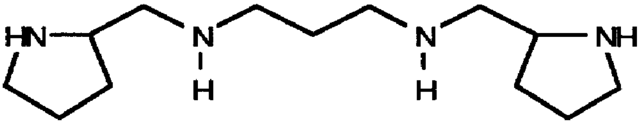


**(29)**

The preparations and spectroscopic properties of some Co(III) complexes of type $[Co(cyclen)L]^{3+}$ (L = en; 1,2-pn; 1,3-pn; $H_2NCH_2CH(Me)CH_2NH_2$; **(28)**; **(29)**; or HL = α-alanine) have been reported; ligands field parameters are at lower energies than those of the corresponding tetramine complexes, probably because of the small bite-size of the cyclen chelate [128]. Several other discussions have appeared concerning complexes of Co(III) with **(29)** or derivatives of this ligand [129, 130, 131, 132].

Triamine-ligands are exemplified as follows. Spectroscopic characterisation along with ligand field parameters for *cis*- and *trans*-$[CoL_2]Cl_3.nH_2O$ and $[CoL(NH_3)_3]Cl_3$ (L = $HN_2CH_2C(Me)NH_2CH_2NH_2$) is discussed [133]. The kinetics of the $Hg_2{}^{2+}$ assisted aquation of the complex ions $[Co(en)(dien)X]^{2+}$ (X = Cl,Br) and $[Co(en)(dpt)Cl]^{2+}$ have been studied [134]. The preparation and resolution of isomers of $[Co(dien)(aepn)]^{3+}$ (aepn = 1,5,8-triazaoctane) are described; there are five geometrical isomers possible, and two are completely resolved and their configurations assigned *via* spectroscopic methods [135]. A structural characterisation of $[CoClLL']^{+}$ (L = $H_2NCH_2CMe_2NH_2$; L' = $H_2NCH_2CMe_2N{=}CHCMe_2NH_2$) shows that the tridentate ligand lies in the equatorial plane of the octahedral array; the kinetics of chloride loss are also reported [136]. An accompanying paper reports complexes of the bidentate ligand L [137].

The ligand trien, and derivatives thereof, features in several publications. In a kinetic and mechanistic study of the CNS$^-$ anation of [Co(trien)(H$_2$O)$_2$]$^{3+}$, rate constants and activation parameters have been measured as a function of pH [138]. The synthesis and resolution of isomers of the related complex [Co(trien)(NH$_3$)$_2$]$^{3+}$ is also reported [139]. For the methyl-substituted trien, $H_2N(CH_2)_2NH(CH_2)_2CHMeNH(CH_2)_2NH_2$, two stereoisomers of [Co(ox)L]$^+$ are preferentially formed; strain energy minimization calculations are presented [140]. Related pieces of work report the stereochemistry and relative stabilities of isomers of *trans*-[CoLCl$_2$]$^+$, L = $H_2NCHRCHR'NH(CH_2)_2NHCHR'CHRNH_2$ (R=H, Me, Me$_2$CH,



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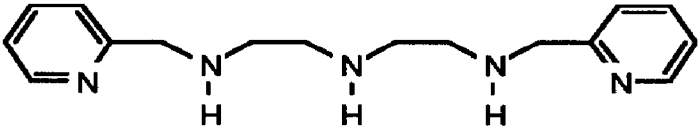
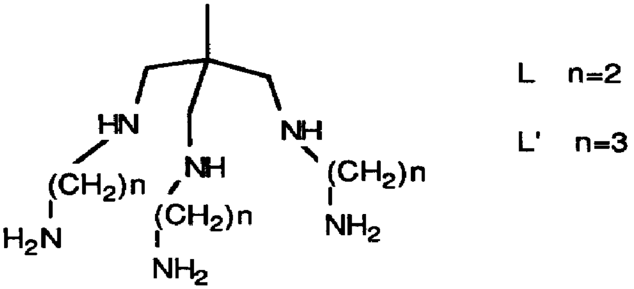


**(31)**

PhCH$_2$; R'=H, Me) [141] and L = **(30)** [142]. The ability of the tripodal tren ligand to prevent geometrical isomerism during substitution reactions of other coordinating ligands has been discussed for a series of [Co(tren)XY]$^{n+}$ complexes [143].

The oxidative rearrangement of the linear pentadentate ligand **(31)** has been observed when the ligand is coordinated to the Co(III) ion [144].

Complexes of the noncyclic polyamines **(32)** and **(33)** with Co$^{3+}$ ion have been described [145,146]; resolutions of diastereomers are reported for the former, and an X-ray analysis and thermal racemisation for the latter. In the complex [CoL](ClO$_4$)$_3$.H$_2$O where L = $\{(H_2N(CH_2)_2\}_2NCHMeCH_2CHMeN\{(CH_2)_2NH_2\}_2$, an equatorial preference for the methyl substituents is observed [147].



(**32**) L; (**33**) L'

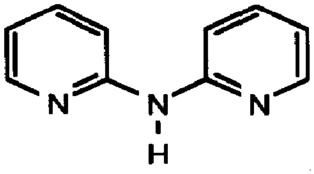
### *3.2.8.3 Heterocyclic ligands*

The simplest heterocyclic ligand is, obviously, pyridine. Several examples have already been mentioned [128, 131, 144]. The influence of solvent structure on the kinetics of the solvolysis of *trans*-$[Co(py)_4Cl_2]^+$ in $H_2O$ or dmso has been discussed [148]; the work includes a determination of some thermodynamic functions for the process. For the reduction of various Co(III) complexes by pyridyl radicals, the rate constants are consistent with Marcus theory [149]. Complexes of substituted pyridines are studied in a comparative sense in two papers [150, 151].

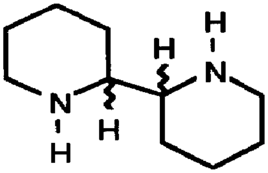
Pyridine-derived ligands, not surprisingly, make up a large contribution to this section on heterocyclic N-donors. The preparation of the mixed metal complex $[(NC)_5Co(pz)M(NH_3)_5]^{n+}$ (M = Ru(II), Ru(III) or Rh(III), and Co is either Co(II) or Co(III) ) is reported along with redox chemistry [152].

Some cobalt(III) complexes with the bipy and phen ligands and which are related to compounds mentioned in the previous section, have been prepared: $[CoL_3]X_3$ (X = Cl, Br, $NO_3$, I, $ClO_4$) [124]; $[Co(ox)_2L]^-$ [111]. An investigation of the kinetics of the aquation of *cis*-$[Co(bipy)_2Cl(CN)]^+$ and the corresponding phen complex have shown that a *trans*-labilising effect by either bipy or phen is not observed; a comparison with $[Co(en)_2Cl(CN)]^+$ is made [153]. The reduction of $[Co(bipy)_2(acac)]^{2+}$ by

Cr(II) was found to be too rapid to be monitored by the stopped flow method [154]. Carbon-carbon bond formation takes place when the metal ion in *cis*-$[Co(R)_2(bipy)_2]^+$ (R = Me; Et) is reduced in acetonitrile to Co(II) [155]. An interesting example of a hydrophobic interaction between anions and metal complexes is observed when $CH_3SO_3^-$ and $PhSO_3^-$ are present in the $Hg^{2+}$ assisted aquation of *cis*-$[CoL_2Cl(H_2O)]^{2+}$ (L = bipy or phen) [156]. The photocatalytic reduction of some Co(III) complexes by dimethyl-phen and tetramethyl-bipy complexes of Cu(I) have been investigated [157]. One Co(III) bound ligand (**34**) in the complex $[Co(HL)_3]^{3+}$ undergoes



(**34**)



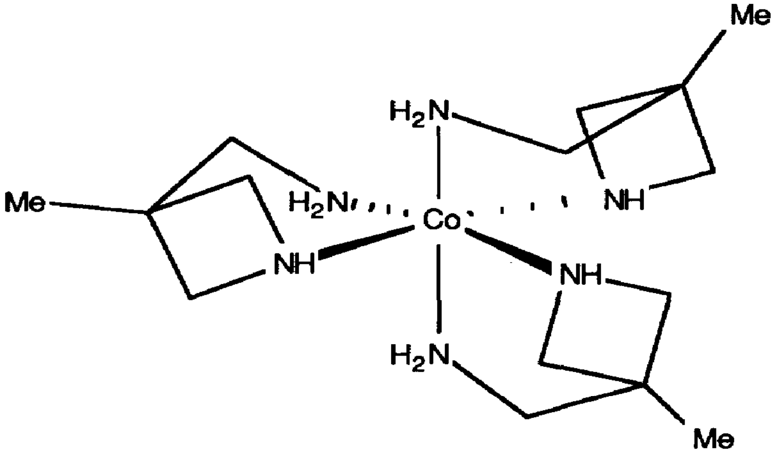
(**35**)

deprotonation and rearrangement. The 5-coordinate complex so- formed either decomposes or racemises rapidly; the kinetics have been followed by changes in optical activity [158].

The outer sphere electron transfer between $[Co(terpy)_2]^{2+}$ and $[Co(bipy)_3]^{3+}$ has been studied under pseudo-first order conditions; activation volumes have been determined [159].

The reaction of racemic 2,2'-bipiperidine, L = (**35**), with $[Co(NO_2)_6]^{3-}$ is reported to give a single *DL*-pair for the product *trans*-$[CoL_2(NO_2)_2]^+$ complex [160].

An unusual complex involving a derivative of azetidine has been prepared [161]. The structure of the product complex, (**36**), has been elucidated crystallographically; the complex is susceptible to base hydrolysis.



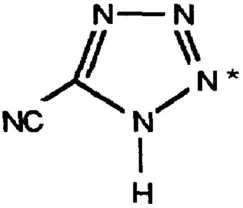
(36)

A large number of imidazole and related complexes were reported in 1985. Sixteen complexes of the type $[Co(acac)_2(N_3)(imidH)]$ (where imidH may be a substituted imidazole as well as imidazole itself) have been spectroscopically characterised; a facile *trans-cis* interconversion takes place in $CHCl_3$ solution and was observed while $^1H$ n.m.r. spectra were being recorded [162]. This is in contrast to the stable *trans*-$[Co(acac)_2(NO_2)(imidH)]$. The results of a detailed $^1H$ n.m.r. study of nine imidazole complexes list $T_1$ measurements and N.O.E. observations; the importance of this piece of work is in its potential application to the unambiguous assignments of proton resonances in metalloproteins [163]. A related piece of research looks at displacement of water from $[Co(en)_2(SO_3)(H_2O)]^+$ by a series of imidazole ligands; the reaction is monitored by $^1H$ n.m.r. and the products are found to vary with the pH of the reaction medium [164].

Complexes containing the mixed ligands imidH, morpholine, azide, and dimethylglyoxime have been prepared and characterised by spectroscopic and other physical methods [165].

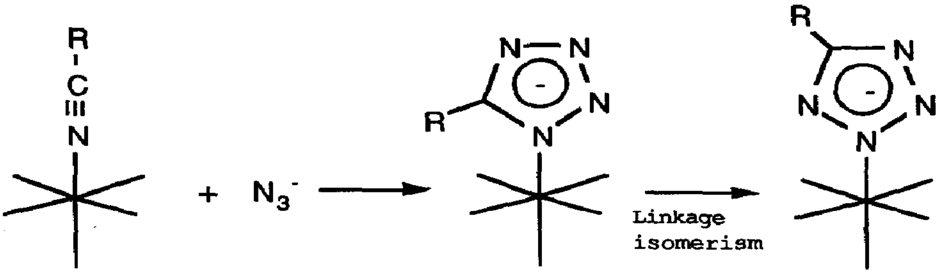
The base hydrolysis of *cis*-$[Co(en)_2ClL]^{2+}$, where L = *N*-methylimidazole, is second order and is found to have a rate constant which is similar to that when L = imidH; a comparative study of the complexes containing L = *N*-methylimidazole or benzimidazole, shows that hydrolysis is retarded in the latter case [166].

The complex $[Co(NH_3)_5L]^{3+}$, where L is the tetrazolato ligand (**37**), has been developed with explosive applications in mind [167].



(**37**) (* = coordination site)

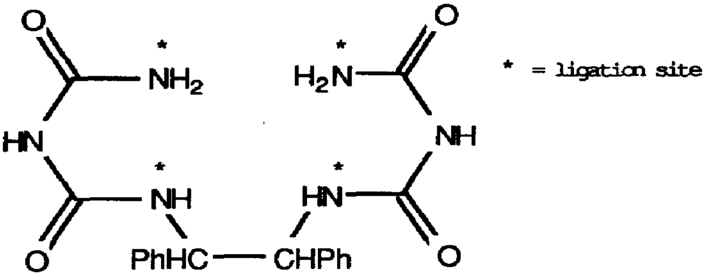
When azide ion reacts with $[Co(NH_3)_5(NCR)]^{3+}$, the heterocyclic ring complex which forms, undergoes the unusual linkage isomerism shown in the scheme:



The first step in the reaction is second order overall; two mechanisms are consistent with the observed data. Either there is a concerted 1,3-dipolar cycloaddition across the C≡N bond, or there is initial attack on the nitrile which then leads to cyclisation [168].

### *3.2.8.4 Amino acids and peptides*

The structure of a complex of the tetradentate ligand, L = (**38**), with the $Co^{3+}$ ion has been elucidated *via* low temperature (105K) X-ray crystallography. The complex, $[CoL][Bu_4N]$, is square planar, and the average Co-N bond length is quite short at 1.837(3)Å [169].



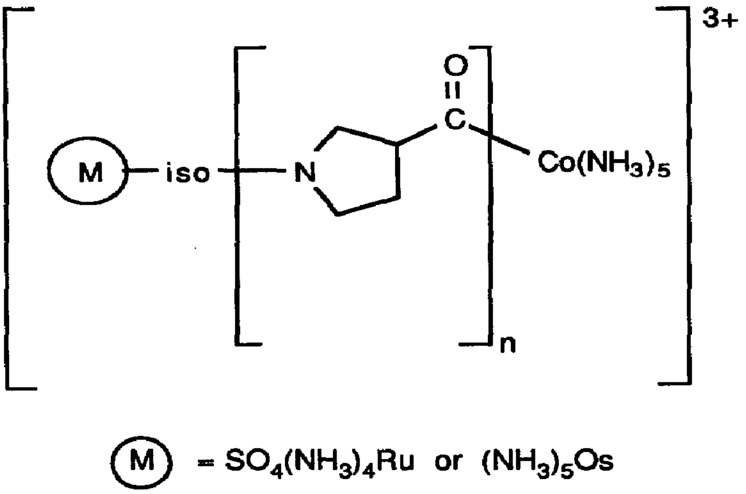
(**38**)

glygly = $H_2NCH_2C(O)NHCH_2CO_2H$; L = $H_2O$, $CN^-$, $NCS^-$; n = 0,1 ), and an X-ray crystallographic study for the complex ion where L = $NCS^-$ have been published [170].

The rate of intramolecular electron transfer across polyprolines of the type (**39**) has been studied as a function of the chain length, n, [171].

### *3.2.8.5 Oximes*

The reaction of $[Co(CNS)_2]$ with $dmgH_2$ and L' in ethanol in the presence of air, leads to the formation of the Co(III) complexes *trans*-$[Co(dmgH)_2L'(SCN)]$ where L' is an N-donor heterocyclic ligand, (imidazole, benzimidazole or morpholine). Characterisation of the products has been *via* spectroscopic methods [172]. Some closely related complexes have already been mentioned [165]. An accompanying piece of work by the same authors addresses the analogous selenocyanto complexes; coordination through the selenium atom for the SeCN ligand is proposed [173]. A related Co(III) complex is *trans*-$[Co(LH)_2(py)_2]^+$ in which $H_2L$ is an alkylated derivative of $dmgH_2$; $^1H$ and $^{13}C$ n.m.r. investigations

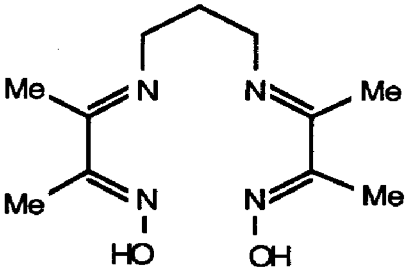


**(39)**

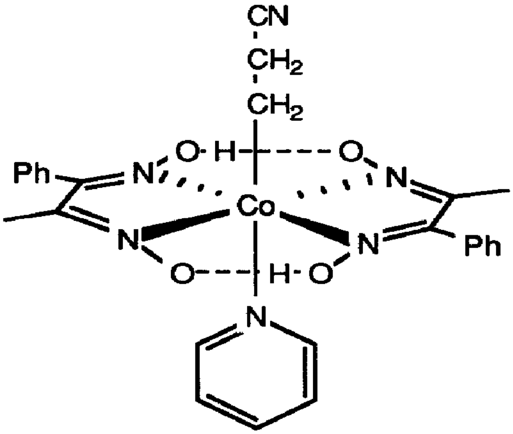
of the complexes show perturbation in $\delta^1H$(alkyl) which are attributed to ring current shielding by the axial pyridine ligands. $^{13}C$ n.m.r. relaxation times have also been determined [174]. The thermal decomposition of $[Co(dmgH)_2L_2]X$ and $[CoX(dmgH)_2L]$ (L = aniline or a derivative thereof; X = Cl, Br, I, SCN, $NO_3$, $ClO_4$) proceeds *via* a different pathway for each complex. The temperature at which $[Co(dmgH)_2L_2]X$ converts to $[CoX(dmgH)_2L]$ by the replacement of the axial ligand, L, by an outer sphere anion $X^-$, depends upon the basicity of L [175].

Complexes of the general formula [L'CoLR]X (HL = (**40**); L' = $H_2O$, py; X = $ClO_4$, $PF_6$; R = $^iPr$, neo-$C_5H_{11}$, $CH_2CO_2CH_3$, $CH_2CF_3$, $CH_2Br$, $CH_2SiMe_3$) have been prepared, and the structures of two of the complexes elucidated. The kinetics of complex dissociation by loss of the L' when L' is py, have also been discussed [176].

Complexes of Co(III) with (**41**), $Me_2C(NHOH)C(R){=}NOH$ (R = Ph; Me), are pentacoordinate. Their electrochemical behaviour has been studied [177]. The spectroscopic and magnetic properties of $[CoL_2]X$ (HL = $HON{=}C(Me)C(Me){=}N(CH_2)_2NHR$; R = Me, Et, Ph; X = Cl, Br, I, $NO_3$,



**(40)**



**(42)**

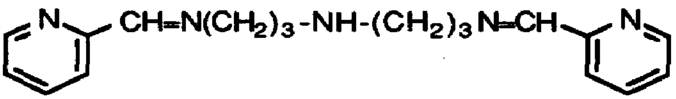
$ClO_4$) are consistent with diamagnetic, 6-coordinate complexes in which $L^-$ is terdentate [178].

The cobaloxime complex (**42**) has been studied crystallographically: axial Co–C = 2.005(5)Å and Co–N = 2.094(4)Å [179].

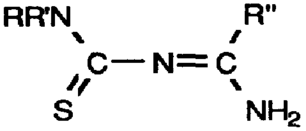
### *3.2.8.6 Imines and amidines*

A study of the synthesis of $[CoLCl](ClO_4)_2$ (L = (**43**) ) has been complemented by an investigation of the kinetics of complex hydrolysis.

Hydrolysis is very rapid *via* a conjugate base mechanism; the *cis*-orientation of the secondary amino group with respect to the leaving group ensures a single site for deprotonation [180].

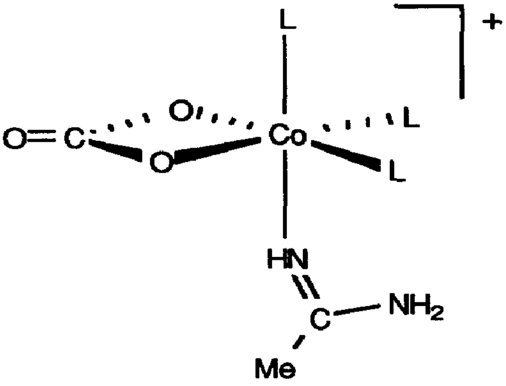


**(43)**



**(44)**

The amidine **(44)** (R',R = Et, Bu or $NR'_2$ = morpholino; R" = Ph) reacts with cobalt(III) ion to give the complex $[CoL_3]$; spectroscopic characterisation indicates ligation by the $NR_2$ group [181]. An X-ray structural



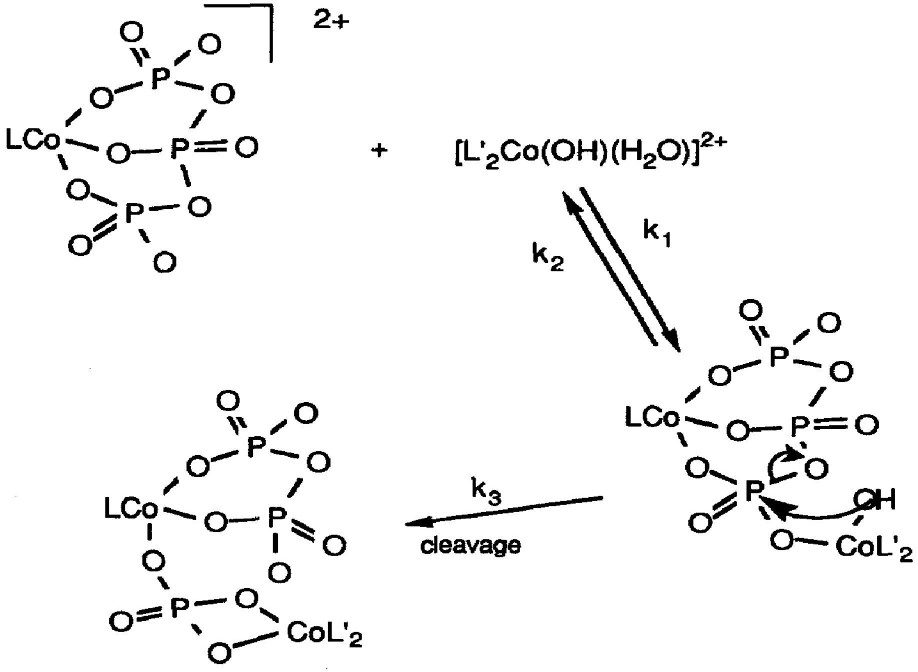
**(45)**

determination, carried out at 117K, of the complex (**45**) gives distances of Co-O = 1.918(6) and 1.933(5)Å, and Co-N bonds range from 1.913(6) to 1,942(6)Å [182].

### *3.2.8.6 Macrocyclic ligands*

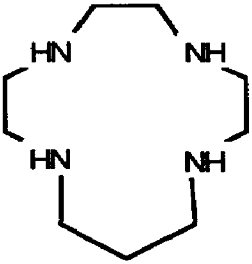
A series of complexes of type $[CoLL']^{3+}$, in which L = cyclen and L' is a diamine, has already been mentioned [128]. A closely related complex involving a tri- rather than a di-amine ligand has also been reported; $[CoLL']Cl_3.0.75H_2O$ (in which L = $H_2NCH_2C(Me)(NH_2)CH_2NH_2$ and L' = 1,4,7-triazacyclononane) has been spectroscopically characterised [133].

The cyclic ligand 1,4,7-triazacyclononane figures in a Co(III) complex which also contains a tripolyphosphate residue [183]. The complex undergoes an interesting reaction with $[L'_2Co(OH)(H_2O)]^{2+}$ ion; intramolecular hydrolysis of the polyphosphate leads to cleavage of a P-O-P bridge as shown schematically below:

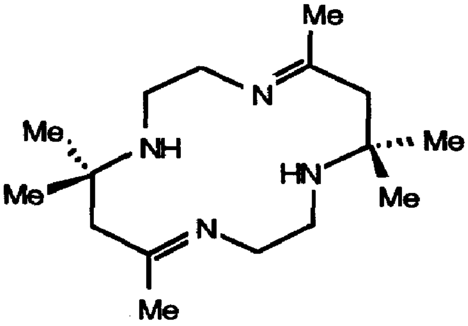


For the complex [Co(cyclen)$Cl_2$]$^+$, an examination of the exchange processes of amine-attached protons with deuterons from $D_2O$ in deuterated buffer solutions, has shown that the NH groups *trans* to the Cl atoms are specifially involved; no exchange involving mutually *trans*-NH groups occurs [184].

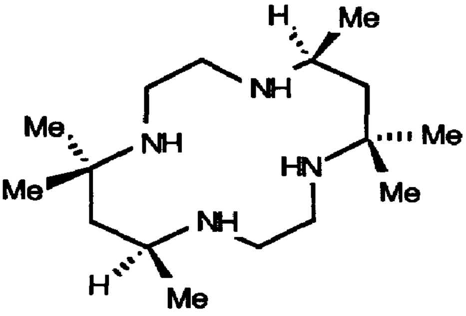
The effects of ring size on the stereochemistry of a complex involving a tetradentate macrocycle have been investigated; the complex [CoXYL]Z ( $H_4L$ = (**46**) ; X = Y = Z =Cl (green complex) ; X = Br, Y =Cl (green complex), Z =Br; X = Y =Cl, Z = $ClO_4$ (red complex) ; X = Y = Z =Br (olive-green complex) ) exhibits the ligands X and Y *trans* to one another, whereas the analogous complexes [CoXYL]Z in which L = cyclen give only the *cis*-isomers [185]. Expanding the carbon chain of the macrocycle gives ligands $H_2L$, (**47**), and $H_4L'$, (**48**). These coordinated tetradentate chelates have been characterised in the Co(III) complexes, [$CoLX_2$]$ClO_4$ and [CoL'$Cl_2$]$NO_3$, (X = NCS, NCO, $N_3$, Cl, $NO_2$, Br and CN). XPS has been used to probe the core electronic structure of these complexes; the binding



(**46**)



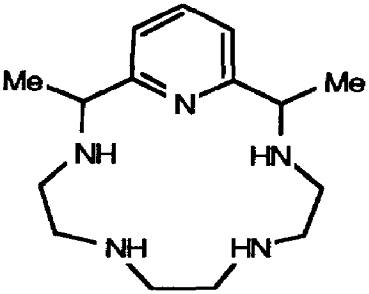
(**47**)



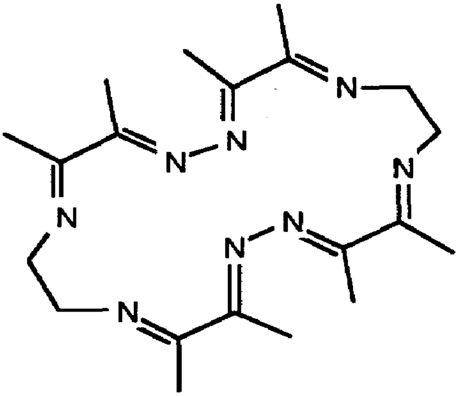
(**48**)

energies of the 1s electron of nitrogen and the $2p_{3/2}$ electron of the cobalt atom decrease as a function of $X^-$ ($CN^- \cong Br^- > NO_2^- \cong Cl^- \cong N_3^- > NCO^- > NCS^-$), and the positive charge on the metal atom is greater for the L than for the L' complexes [186].

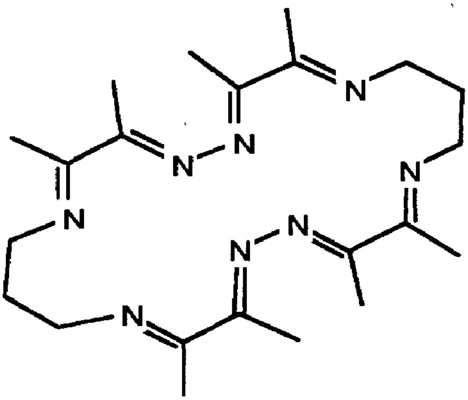
A crystallographic study of a complex with $Co^{3+}$ of the pentadentate ligand $H_4L$, **(49)**, has shown that the metal ion is six-coordinate in $[CoLCl][ClO_4]$, with distances of Co-N ranging from 1.812(16)Å to 2.001(12)Å, and Co-Cl = 2.173(5)Å; a discussion concerning the factors governing the conformation of the macrocyclic ligand is reinforced by force field calculations, and a general method for calculating the "hole-size" in a macrocyclic ligand is proposed [187]. The



**(49)**



**(50)**



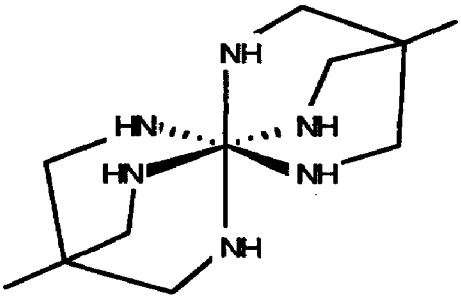
**(51)**

complexation reactions of two related macrocyclic ligands have been studied. The ligands are **(50)** and **(51)**, and examples of their complex behaviour are found in $[CoLX_4]$ (X = SCN, $NO_2$) and $[CoL(H_2O)_4](ClO_4)_4$; analyses and spectroscopic characteristion are given accompanied by a discussion of the redox chemistry of the complexes, and an appreciation of how the macrocycle-ring cavity size influences electrode potential [188].

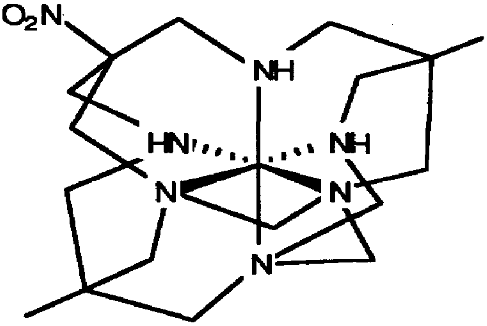
Complexes of Co(III) with the sepulchrate (sep) ligand, have been the subject of some attention. Ion pair formation with oxalate ion [189] and iodide ion [190] has been studied. A photochemical study of the $[Co(sep)]^{3+}/I^-$ ion pair in a deoxygenated solution shows that Co(II) and $I_3^-$ form, with a quantum yield of $3.4 \times 10^{-3}$. The same authors have reported, in general terms, the importance of ion pairing to the promotion of photosensitised reactions involving $[Co(sep)]^{3+}$ [191].

The stereospecific template synthesis of a macrotetracylcic hexacryptate has been reported. The starting material for the preparation is **(52)**, and an X-ray structural determination of the product complex has established its identity, **(53)**, as well as the ligand conformation [192]. A closely related template reaction is one in which the synthesis of a macrobicyclic hexamine Co(III) complex is formed, **(54)** [193]. Measurements of p$K_a$ values for several macrotricyclic hexamine complexes of type **(55)** have been made [194].

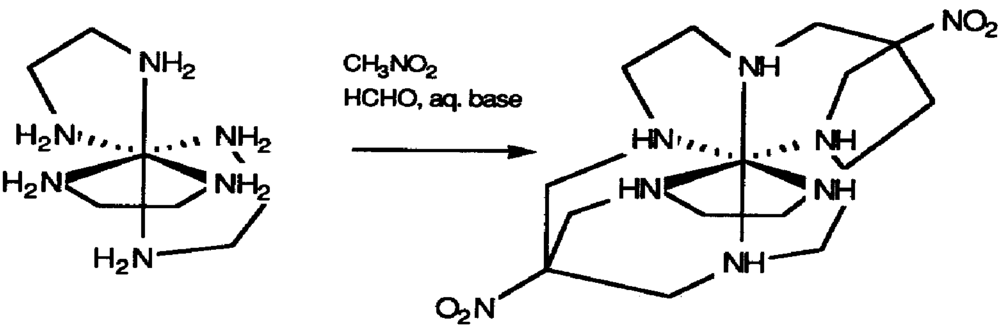
A survey of eighteen Co(III) complexes which function as electron transfer agents in the quenching of excited state $[Ru(bipy)_3]^{2+}$ complexes, has concluded that the complex $[CoL]^{3+}$ containing the macrocyclic ligand **(56)** is very effective. The applications of these complexes to the photoreduction of water is discussed [195].



**(52)**



**(53)**



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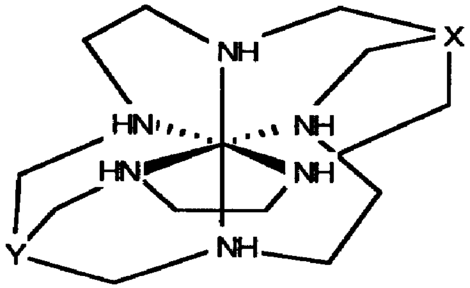
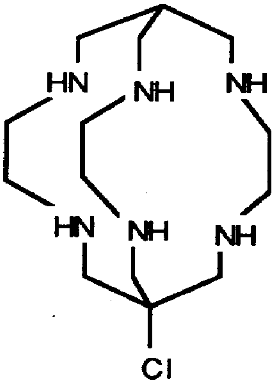


| X | Y |
|---|---|
| CNO$_2$ | CNO$_2$ |
| CMe | CMe |
| N | N |
| N | CMe |

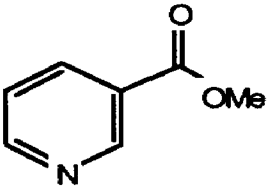
(55)



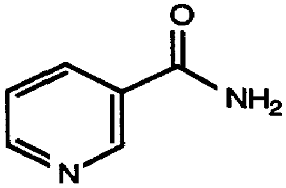
(56)

The cyclocondensation of diamino-β-isoindigo in the presence of [Co(OAc)$_2$] in ethyleneglycol leads to the formation of a Co(III) complex containing two metal centres bridged by peroxide group. The spectral characteristics of the complex are reported, along with its semiconducting properties [196].

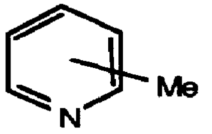
Porphyrin chemistry has been as widely studied as ever. For $H_2P$ = tetra(4-*N*-methylpyridyl)porphine, several complexes of formula $[CoP(H_2O)L]^+$, which exhibit axially coordinated derivatives, L, of pyridine, have been synthesised; stability constants vary in the order L = **(58)** > **(59)** > **(60)** > **(61)** [151].



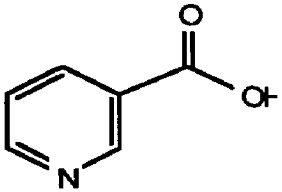
**(57)**



**(58)**



**(59)**

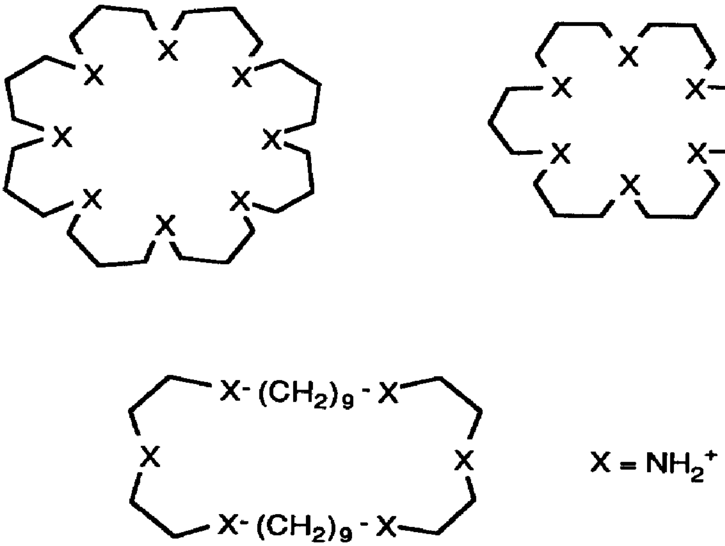


**(60)**

Reactions of $[Co(CN)_6]^{3-}$ with the cationic macrocyclic receptors, **(61)**, are reported to produce complexes, the photo- chemical behaviour of which has been compared; the effects of substituting $CN^-$ for $H_2O$ has also been the subject of study [197].

For the protoporphyrin-IX-dimethyl ester, P, complex of Co(III), [CoPCl], the reaction with methanol and subsequent proton loss to yield [CoP(MeO)(MeOH)] has been discussed; the kinetics of substitution reactions of the latter complex, (*i.e.* MeOH followed by $MeO^-$ being replaced by various ligands, L), illustrate a dissociative mechanism being prevalent [198].

Electron spin resonance results for the octahedral, radical complexes, [Co(TPP)$X_2$] (TPP = tetraphenyl porphyrin), have been reported. The effects of varying the axial ligands as well as the solvent medium are discussed; it is found that the axial ligands preferentially coordinate in the order $BF_4^-$ ~ $ClO_4^-$ ~ $PF_6^-$ ~ $NO_3^-$ < RCN < halide < EtOH < $CF_3COO^-$ ~ $AcO^-$ ~ $SCN^-$ ~ $CN^-$ [199].



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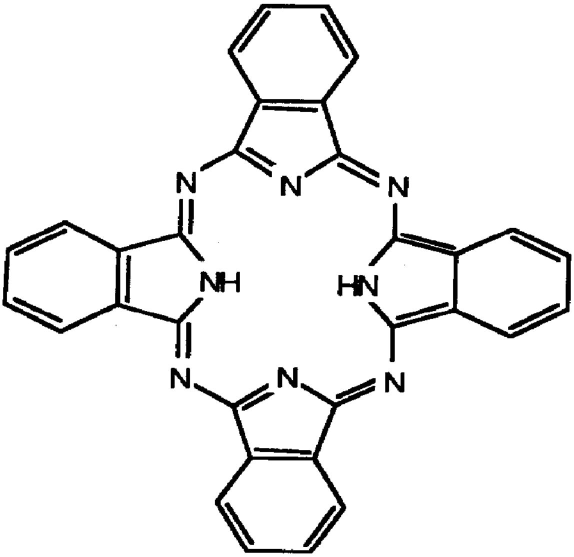


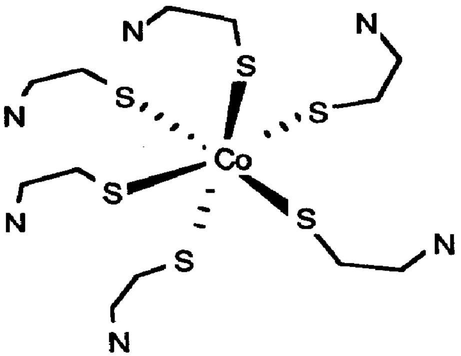
(62)

The complexes $[CoX_2(Pc)]^-$ and $[CoX_2(Pc)]^{2-}$ ( X = Cl, Br for Co(III) and OH, F, Cl, Br for Co(II); $H_2(Pc)$ = **(62)** ) have been the subject of a detailed spectroscopic investigation; UV-visible, infra-red, and Raman spectra have been recorded. The compound $[CoX_2(HPc)]$ (X = Cl, Br) has also been prepared [200]. The dissociation of axially coordinated water molecules from the Co(II) and Co(IIII) complexes involving the porphyrin, L, ( where $H_2L$ = 4- methylpyridylporphyrin ) illustrate that only a single dissociation occurs for the Co(II) complex [201]. An investigation of the photoreduction of complexes between Co(III) and TPP in 2-methyltetrahydrofuran has been reported [202]. Related to this is the reduction by $[Fe(H_2edta)]$ of porphyrin complexes of Co(III); the rate law obeyed was found to depend upon the charge type of the porphyrin [203].

### 3.2.9 *Complexes with nitrogen-sulphur or nitrogen-selenium donor ligands*

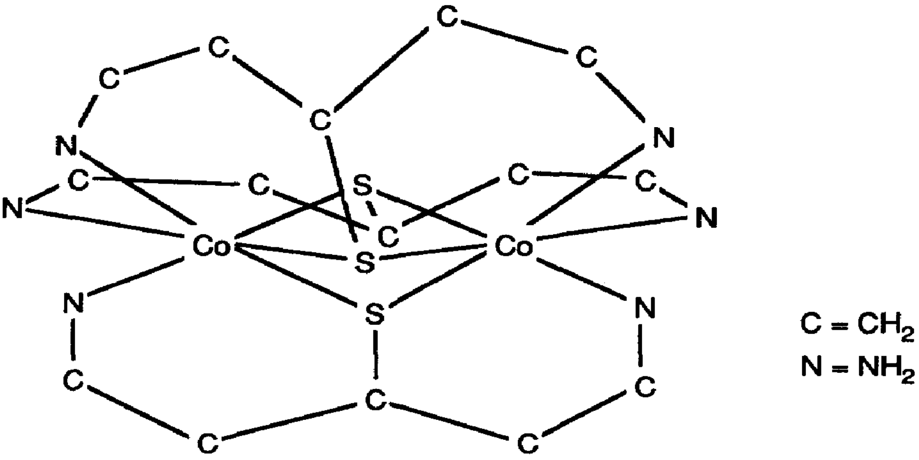
#### 3.2.9.1 *Aminothiols and related ligands*

The compound $[CoL_3]$, ( L = $HSCH_2CH_2NH_2$ ) reacts with $Co^{3+}$ ion to give an unusual trinuclear complex which is supported by Co-S-Co bridges; the presence of a dodecadentate "$[M(S-N)_6]$" ligand, **(63)**, is proposed [204]. The same complex has been independently prepared and its structure, **(23)**, determined [68].



**(63)**

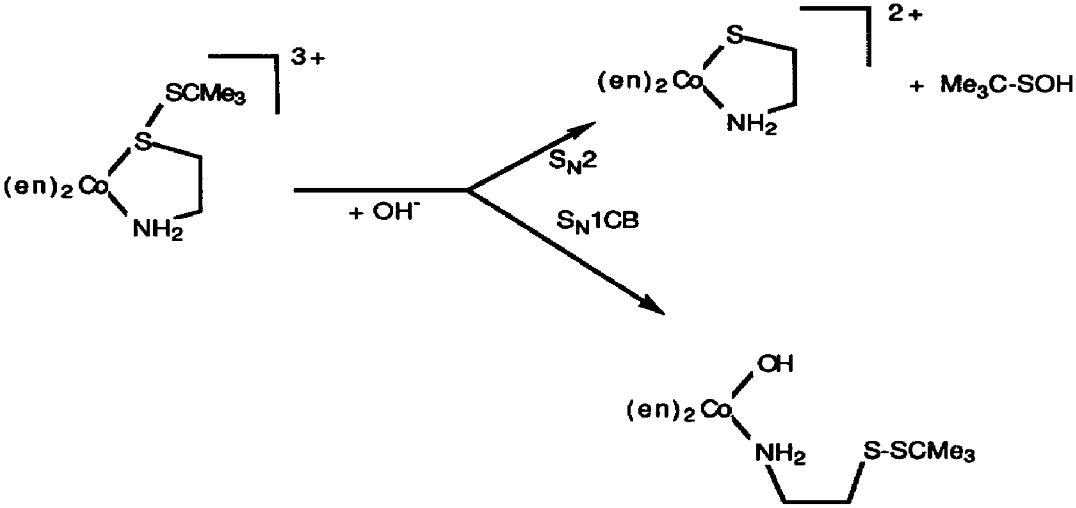
Closely related to this work is a report of the formation of the complex $[Co_3\{S(CH_2)_3NH_2\}_6]Cl_3$; the structure of this compound has beer determined and is described as consisting of three octahedra sharing opposite faces. The inter-cobalt distance is 2.974(1)Å [205]. Again, bridging thiolate units figure in the binuclear complex (**64**); here the bridged Co---Co separation is 2.955(2)Å, and Co-S and Co-N bonds lie in the ranges 2.229-2.257Å and 1.996-2.013Å respectively [206]. The Co-N bonds are considered to be lengthened by the *trans* influence of the ligating sulphur atoms.



(**64**)

In the presence of chiral additives, the kinetic resolution of $\Delta\Lambda$-$[Co(SCH_2CH_2NH_2)(en)_2](ClO_4)_2$ has been achieved; resolution of the $\Delta\Lambda$-forms of three related complexes containing $C_2O_4{}^{2-}$ or $NO_2{}^{-}$ chelates in place of the aminothiolate are also reported [207].

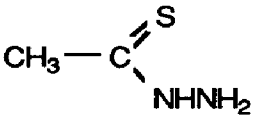
The kinetics of the base hydrolysis of the complex $[(en)_2Co\{S(SCR_3)CH_2CH_2NH_2\}]^{3+}$ ( R = Me; Et; $CHMe_2$; $CMe_3$ ) illustrate competitive S-S and Co-S cleavage:



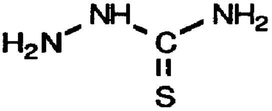
When R = $CMe_3$, the steric bulk of the substituent allows an $S_N1CB$ mechanism to compete with the $S_N2$ pathway which prodominates for the smaller R groups. The relative rates of hydrolysis are 1.7 x $10^6$ for Me, 5.6 x $10^5$ for Et, 2 x $10^4$ for $CHMe_2$, and 9 for $CMe_3$ [208]. A study of the complexation of $[Co(en)_3]^{3+}$ by thioether and selenoether ligands to give $[(en)_2Co(RXCH_2CH_2NH_2)]^{3+}$ (X = S; Se), has shown that the nature of the reaction depends on the X-bound substituent, R; most reactions follow a simple Co-X bond cleavage, but if R possesses an acidic methylene group, a mixture of products is obtained [209].

### *3.2.9.2 Thioamides and related ligands*

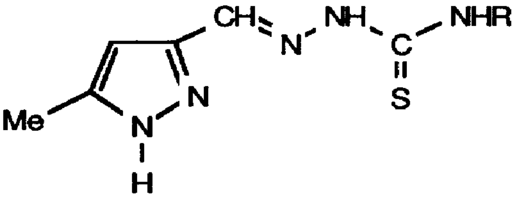
The reaction of Co(III) acetate with HL, **(65)**, followed by HX (X = CL; Br; $NO_3$; $0.5SO_4$) leads to the formation of a complex, $[Co(HL)_3]X_3$; the bidentate nature of HL has been established by crystallographically [210]. The thiosemicarbazide, HL, **(66)**, is reported to react with $Co^{3+}$ ions in a weakly alkaline solution to give $[Co_3L]$; on the grounds of infra red data, the authors propose the existence of an imido-thiol tautomeric equilibrium [211].



**(65)**

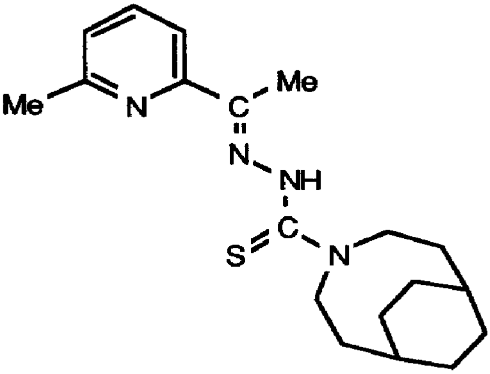


**(66)**

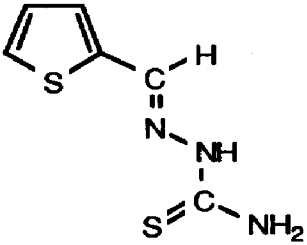


**(67)**

Two new pyrazole-based ligands, ( HL = **(67)**, with R = H or Ph), have been synthesised, and the chemistry of their coordination to Co(III) has been reported; the results of spectroscopic characterisation suggest that chelation is *via* the pyrazolyl ring nitrogen atom, and the azomethine nitrogen and sulphur atoms [212,213]. The complex $[CoL_2]ClO_4$, where HL is the thiosemicarbazone **(68)**, has been prepared and characterised; the sites of coordination are proposed as being S, imino-N, and pyridyl-N [214]. Spectroscopic characteristion of some complexes of Co(III) involving the thiosemicarbazone **(69)** suggests that the ligand is bidentate, chelating only *via* the thione and imino groups [215].



**(68)**



**(69)**

### *3.2.9.3 Aminoselenols and related ligands*

Several complexes involving N-Se chelates have been reported this year. The oxidation of $[Co(tren)Cl_2]$ with $(HN_2CH_2CH_2Se- SeCH_2CH_2NH_2)$

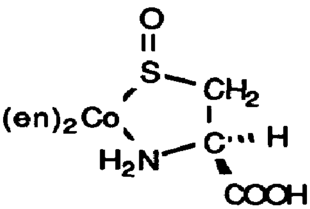
leads to the formation of *p*- and *t*-isomers (in a ratio 3 : 1) of the complex ion, $[Co(SeCH_2CH_2NH_2)(tren)]^{2+}$; a structural determination of Rh(III) analogue of the *p*-isomer has been carried out [216]. In a related paper, the same authors report the formation and racemisation of $[Co(RSeCH_2CH_2NH_2)(tren)]^{3+}$ (R = Me; Et; $PhCH_2$); $^{13}C$ NMR studies have been used to compare the inversion rates of the *p*- and *t*-isomers [217]. (The nomenclature *p*- and *t*- refers to "*cis*-tertiary N-Se" and "*trans*-tertiary N-Se" respectively). A determination of $\Delta H_{activation}$ for inversion at selenium in $[Co(MeSeCH_2CH_2NH_2)(acac)_2]^+$ has produced a value of 113 kJ $mol^{-1}$ which represents the highest reported value for such a process; the application of HPLC to separate the diastereomers is of distinct interest [218].

The complexes $[Co(en)_2(RSeCH_2CH_2NH_2)]$ (R = $CH_2Ph$; $CH_2CH_3$; $CH_3$) have been prepared and spectroscopically characterised; for R = Et, a structural determination shows a regular octahedral array of donor atoms about the cobalt atom ( $\angle$'s = $90\pm6^\circ$ ), and a Co-Se distance of 2.386(3)Å [219].

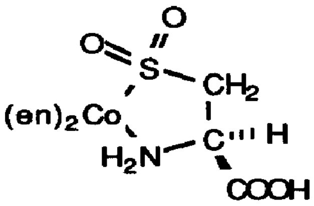
### *3.2.9.4 Miscellaneous*

It has been proposed that the complex $[Co(dmgH)_2(SeCN)L]$ (L = various imidazoles) exhibits a *trans*-geometry, with the SeCN ligand coordinating through the selenium atom [173].

A kinetic study of the reaction of the complexes **(70)** and **(71)** with Cr(II) illustrates rapid reduction; activation parameters have been determined [220].



**(70)**

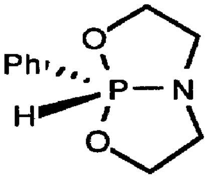


**(71)**

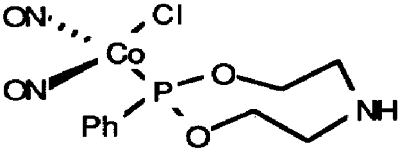
### *3.2.10 Complexes with phosphorus donor ligands*

The preparation of $[CoL_2Cl_2]Cl$ (L = 1,2-$C_6F_4(PMe_2)_2$) appears as part of a series of syntheses of Co(III), Ni(II), Ni(III), Pd(II), Pd(IV) and Fe(III) complexes of the ligand L; a comparison of the electrochemical properties of some of these complexes with the corresponding 1,2-$C_6H_4(PMe_2)_2$ compounds illustrates the electron withdrawing effects of the fluorine substituent [221].

The room temperature reaction of $[Co(NO)_2Cl]_2$ with the ligand (**72**) leads to the formation of the complex (**73**); assignment of $\nu_{NH}$ at 1822 and 1755 $cm^{-1}$ in the product illustrates that hydrogen transfer has accompanied complex formation. An X-ray structural determination for (**73**) confirms a tetrahedral coordination sphere with the ligand in an open conformation; Co----$N_{NH}$ = 3.682Å and P----$N_{NH}$ = 2.978Å. The ability of the complex to carry $CO_2$ is also discussed [222].



(**72**)



(**73**)

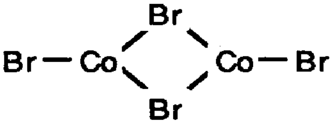
Cobalt(III) complexes of the quadridentate ligand, PNNP, $R_2P(CH_2)_2NH(CH_2)_2NH(CH_2)_2PR_2$ (R = Me or Ph) have been prepared and their structures deduced from spectroscopic data; the compounds $[Co(PNNP)X_2]$, where X is $Cl^-$ or $CNS^-$, exhibit three geometric isomers, but for chelating $X_2$ (*viz.* acac or $CO_3^{2-}$), the complex is restricted to one structure [492].

## *3.3 COBALT(II)*

### *3.3.1 Complexes with halide ligands*

A few simple halide complexes of Co(II) have been described this year. The optical absorption spectrum of $[Me_3NH][CoCl_3].2H_2O$ has been assigned; it illustrates the presence of the $[CoCl_4(H_2O)_2]$ moiety [223]. The extraction of $Co^{2+}$ ion from HCl solutions by either $R_3N$ or $R_3R'NCl$ (R = octyl; R' = Me) has been studied; of the complexes $(R_3NH)_2CoCl_4$ and $(R_3R'N)_2CoCl_4$ so-formed, the latter exhibits a more ionic Co-Cl bond [224].

An electron diffraction study of cobalt(II) bromide ($r_g$(Co-Br) = 2.241(5)Å ) has lead to the detection of a small precentage of the dimer, (**74**), in which $r_g(\text{Co-Br})_{\text{terminal}}$= 2.241(5)Å and $r_g(\text{Co-Br})_{\text{bridge}}$= 2.429(14)Å [225].



(**74**)

An electrochemical investigation of the $[Co(CN)_5]^{3-}$/ $[Co(CN)_5]^{4-}$ couple has shown it to be a completely reversible reaction in $Me_2SO$, with $E^o$ = −1.272 V at 25±1°C [226].

### *3.3.2 Complexes with oxygen donor ligands*

### *3.3.2.1 Simple oxygen donor ligands*

A crystallographic structural determination of $[Co(H_2O)_6][(C_6H_6O_7)_2B]_2$ has shown that the Co(II) ion is in a distorted octahedral environment [227].

Cobalt(II) perchlorate has been the subject of EXAFS, infra red and Raman spectroscopic studies [228]. Vibrational and electronic spectra of the same compound indicate respectively that the perchlorate ion is tridentate, and that the $Co^{2+}$ ion is octahedrally coordinated; preparation of anhydrous $[Co(ClO_4)_2]$ and related complexes is described [229].

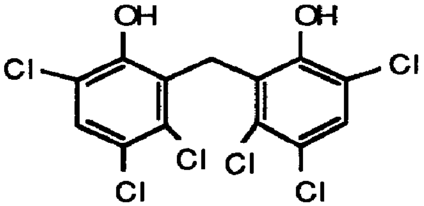
The complex $[KL]_2[Co(SCN)_4]$, where L is 18-crown-6, has been prepared and its structure determined; the coordinating ability of L with the Co(II) ion exceeds that of $SCN^-$ [230].

### *3.3.2.2 Alcohols and phenols*

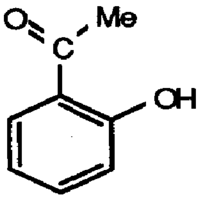
Determinations of the equilibrium constants for the solvolysis of $[Co(H_2O)_6]^{2+}$ by MeCN, 1-PrOH, 2-PrOH and $(CH_2OH)_2$ indicate that the relative donor capacities of the solvents are MeCN > 2-PrOH > 1-PrOH > $(CH_2OH)_2$ [232].

Proton n.m.r. shifts and spin-lattice relaxation times have been used to probe the preferred orientation of the pyridine ligand bound in the outer sphere of the complex $[Co(CD_3OD)_6]^{2+}$, **(75)** [233]. Pulsed n.m.r. studies, carried out in methanol, have been used to examine the coordination mode of triethyleneglycol with $Co^{2+}$ ion [234]. $^1H$ n.m.r. has also been utilised to study the complexation of polyethylene glycols with $[Co(ClO_4)_2]$; stable adducts containing the core $[Co(II)O_4]$, where O = glycolic OH, are formed [235].

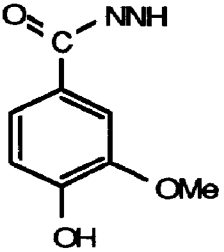
Several complexes containing ligands which are derived from phenol have been reported. Hexachlorophene, HL, **(76)**, reacts with $Co^{2+}$ to form the 1:1 and 1:2 complexes; stability constants have been measured [236]. The mixed ligand complex $[CoL_2L'_2]$, where L = **(77)** and L' = quinoline, has been synthesised and spectroscopically characterised [237]. The formation constant for the complexation of a vanillin-derived ligand, **(78)**, with $Co^{2+}$ ion has been determined [238].



**(76)**



**(77)**



**(78)**

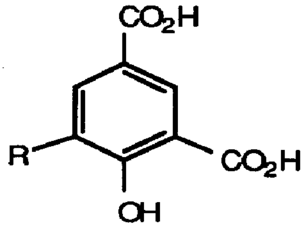
### *3.3.2.3 Carboxylato, oxalato, acetylacetonato and related ligands*

The thermal decomposition of hydrated cobalt(II) oxalate has been studied [239].

Formation of Co(III) by the reaction of ozone with cobalt(II) acetate has been discussed [240]. The mixed acetate complexes, [Co(OAc)($O_2CR$)] (R = $C_{15}H_{31}$, $C_{17}H_{35}$, $C_{21}H_{43}$) have been prepared and characterised by spectral and magnetic methods; trimeric and tetrameric structures with bridging $RCO_2^-$ ligands are postulated [241]. Another mixed ligand complex which has been characterised is [$Co_2(Me_3CCO_2)_4(4\text{-}MeC_5H_4N)_2$]. An X-ray structural determination of the compound has shown that each cobalt atom is coordinated to an γ-picoline ligand, and to one oxygen atom of each carboxylate group; the latter act as bridges between the two Co centres [242].

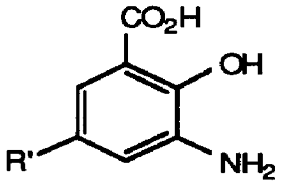
Stability constants for the complex formed between Co(II) and mandelic acid ($C_6H_5CH(OH)CO_2H$) have been measured over the temperature range 283 to 303K; thermodynamic parameters were determined by using pH-potentiometric methods [243]. $\Delta H_f^o$ for the complex formed between $Co^{2+}$ and L, ( $H_2L = HN(CH_2CO_2H)_2$ ), has been reported [244].

The relative chelating abilities to $Co^{2+}$ of some isophthalic acid derived ligands have been discussed; the parent acids in question are shown in **(79)** to **(81)** [245].



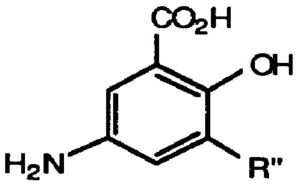
R = Me; $^i$Pr; Bu

**(79)**



R' = 3° alkyl

**(80)**

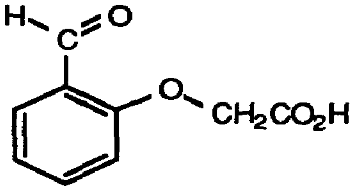


R'' = H; $^i$Pr

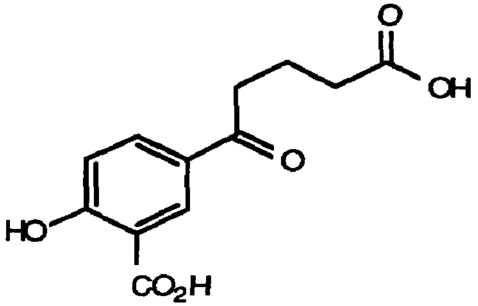
**(81)**

The characterisation of new complexes of salicylic acid, and the chemistry of these and of previously known complexes, have, of course, been reported numerously. During the thermal decomposition of the complex $[CoL_2].3H_2O$, (HL = salicylic acid), intermediate compounds have been identified [246]. In a related piece of work, pyrolysis of $[CoL_2]$ is reported to give CoL and $Co_3O_4$; these products have been characterised by infra red spectroscopy and by X-ray structural analysis, and are in contrast to the products (*viz.* NiL and NiO) of the analagous nickel(II) reaction [247]. Thermal decomposition studies have also been carried out for several complexes of formula $[CoL_2].2H_2O$ in which HL is a derivative of salicylic acid: 4-aminosalicylic acid [248], 5-amino salicylic acid [249], and 5-sulphonatosalicylic acid [250].

Complexes of hydroxysalicylic acid have been prepared as humic models. $[CoL_2(H_2O)_4]$ (HL = 5-hydroxysalicylic acid) has been spectroscopically and analytically characterised; an X-ray structural determination of the analogous Zn(II) complex shows that both carboxylate ligands are axially coordinated [251]. The related complex with HL = 4-hydroxysalicylic acid has also been spectroscopically characterised, and is reported to exhibit axially bound $L^-$ ligands [252]. Related to this work is a report of the structural determination of the octahedral complex $[CoL_2(H_2O)_4]$, HL = **(82)**; the structure of HL has also been elucidated. Again, the carboxylate ligands are monodentate, and are axially coordinated [253]. The preparation and characterisation of the complex $[Co(H_2L)_2(H_2O)_2]$ ($H_3L$ = **(83)** ) has also been described [254].



(82)

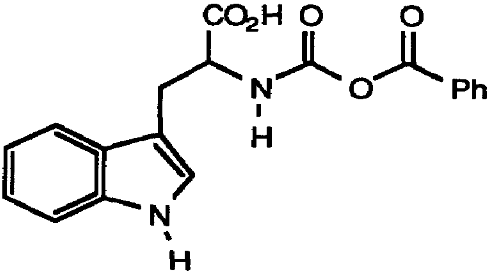


(83)

Thermal decomposition of hydrated cobalt(II) tartrate has been reported to proceed *via* the initial loss of water at 401K [255]. Mixed ascorbate and tartrate complexes of $Co^{2+}$ have been described [256]. Electrophoresis experiments which lead to the formation of the complex ion $[CoL]^-$ and related Ni(II), Zn(II) and Cu(II) complexes, ( $H_3L$ = $HO_2CCH_2C(OH)(CO_2H)CH_2CO_2H$ ), have been carried out [257].

The reaction of $Co^{2+}$ ions with HL, **(84)**, in an alkaline medium, is reported to lead to the complex $[CoL_2]$, which, with excess ligand and alkali, forms $[Co(OH)_2]$ *via* an intermediate ion, $[CoL_2(OH)_2]^{2-}$ [258].

The complexation of *N*-tosylamino acids, HL, with Co(II) ions has been studied; for HL = **(85)**, a structural determination of $[CoL_2(H_2O)_4]$ illustrates slight tetragonal distortion in the octahedral coordination sphere, with $L^-$ coordinating through the carboxylate group only ( $Co{-}O_L$ = 2.100(4)Å, and $Co{-}O_{water}$= 2.077(5) and 2.082(4)Å ) [259].



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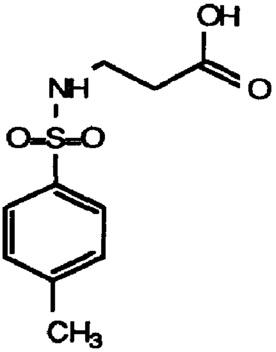

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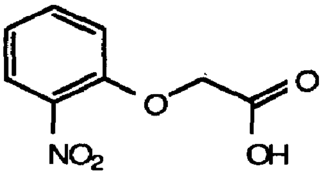
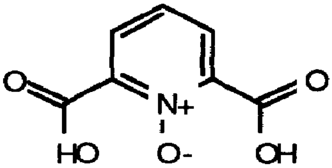


**(86)**

The reaction of cobalt(II) acetate with $[NH_4][L]$, (HL = **(86)** ), in 1:2 molar amounts, forms the complex $[CoL_2(H_2O)_2]$; this is yet another example of a bis-carboxylate species in which the two $L^-$ ligands coordinate in a monodentate fashion and are *trans* to one another in the complex. The paper also includes a structural investigation of the free acid [260].

An unusual trimeric array of metal ions has been observed in the complex $[Co_3Cl(CF_3CO_2)_3(SO_4)(CH_3OCH_2CH_2OCH_3)_3]$. An X-ray determination of the latter reveals that the sulphate moiety behaves rather like a tripod ligand; there is a distorted octahedral arrangement of donor atoms around each cobalt centre, and Co----Co = 3.786(1)Å [261].

The preparation and spectroscopic characterisation of the complex $[CoL(H_2O)_2]$ has been described in which $H_2L$ = **(87)**; the measured magnetic moment of the complex is 4.75 BM, and an octahedral environment is inferred from electronic spectra. However, a structural determination for the related manganese(II) complex shows significant distortion, and this compound is, in fact, polymeric [262].



**(87)**

Complexes of the carboxylic acid derived ligand, $C_6H_5C(O)SSC(O)CC_6H_5$, have been prepared and characterised; a 7-membered chelate ring is proposed [263].

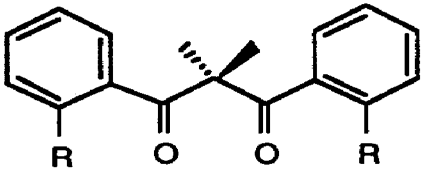
Reports of complexes involving the acac or related ligands coordinated to Co(II) are various. The catalytic properties of $[Co(acac)_2]$ are illustrated by its use in the isomerisation of $CH_3OC(O)H$ in the presence of MeI [264]. For the β-diketonate, $(CH_3)_3CC(O)CH_2C(O)C(CH_3)_3$, complexation with Co(II) has been investigated thermochemically; $\Delta H^o{}_f[CoL_2]$ is determined to be $-1227.1 \pm 7.6$ kJ $mol^{-1}$ [265]. Complexation of isonitroso- acetylacetone or benzoylacetone with $Co^{2+}$ ion is reported to give compounds of formula $[CoL_n]^{(2-n)+}$ (n = 1-3) [267]. The versatility of the ligand $L^-$, ( HL =(**88**) ), to bind either in a mono- or bidentate fashion has been illustrated by some equilibrium studies, in dmso, of the complex $[CoL_2]$; the scheme shown below summarises the mechanism by which $[CoL_2]$ is converted to $[CoL_3]^-$:

$$[Co(bi\text{-}L)_2] \rightleftharpoons [Co(bi\text{-}L)(mono\text{-}L)] \rightleftharpoons [Co(bi\text{-}L)]^+ [L^-]$$

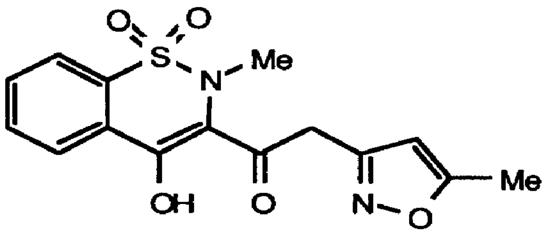
$$[Co(bi\text{-}L)_2] + [L]^- \rightleftharpoons [Co(bi\text{-}L)_3]^-$$

bi-L = bidentate; mono-L = monodentate ligand

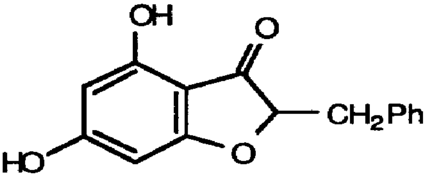
The same paper also describes the electrochemical reduction of the $[CoL_2]$ complex [268].



(**88**) R = H; (**89**) R = OH



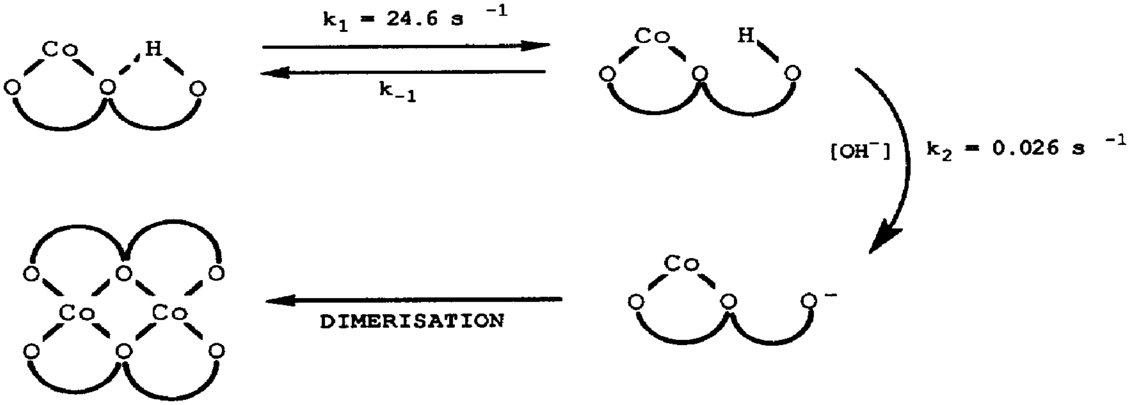
(**90**)



**(91)**

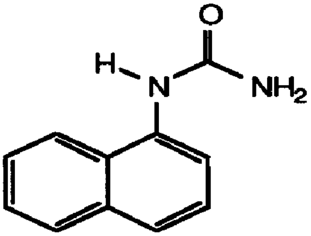
Some new β-diketonate coordination chemistry involves $H_3L$, **(89)**; the formation of and further complexation of $[Co(H_2L)_2].S.S'$ (S and S' = solvent molecules) has been described [269]. In a report of the preparation and spectral characterisation of the complex $[CoL_2].4H_2O$, for which HL = **(90)**, it is proposed that coordination is *via* the enolate and carbonyl O-atoms [270]. Again, only spectroscopic methods have been used to characterise the newly prepared β-diketonate complex, $[CoL_2].2H_2O$, (HL = **(91)** ); the carbonyl and *o*-phenolate O-atoms are proposed to be the sites of ligation [271].

A series of two papers [272,273] has discussed the complexation of Co(II) ions with triones. Formation constants for complexes involving the ligands heptane-2,4,6-trione, 1-phenyl-1,3,5-trione, 1,5-diphenylpentane-1,3,5-trione, and 2,2'-dihydroxybenzophenone have been measured [272]. For the reaction of $Co^{2+}$ with heptane-2,4,6-trione in methanol:water at room temperature, the formation of both 1:1 and 2:2 complexes is observed; conversion from monomer to dimer proceeds by a 2-step mechanism which is outlined in the scheme below [273]:



### *3.3.2.4 Amides with oxygen donor*

Several Co(II) complexes with amide ligands have been the subject of investigations this year. With HC(O)NHMe as the ligand, L, the reaction of cobalt(II) chloride with L leads to the formation of the complex ions $[CoCl_4]^{2-}$, $[CoCl_3L]^-$, $[CoClL_5]^+$ and $[CoL_6]^{2+}$; characterisation by UV-visible absorption spectra has been described [274]. The preparation and spectral characterisation of the complex $[CoL_2Cl_2(H_2O)_2].2H_2O$, in which L = $MeC(O)NMe_2$, has also been reported [275]. Related to this is a discussion of the solvating effects of dmf with $Co^{2+}$ ions has been presented [276]. When the amido ligand, L, (**92**) complexes with Co(II) ions, one of two complexes is reported to form depending on whether the counter ion is chloride or nitrate(V); the stability constants relating to the formation of these complexes have been determined [277].

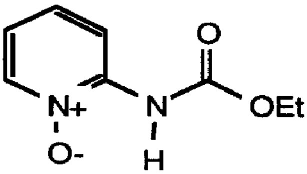


(**92**)

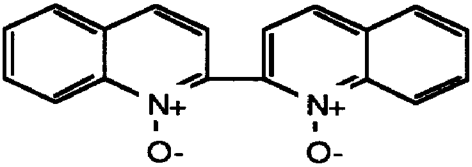
### *3.3.2.5 N-Oxide ligands*

The complexation of one *N*-oxide ligand, (**87**), is summarised above. Several other related species have appeared in the 1985 literature. The simplest ligand, L, in this category is pyridine *N*-oxide; the complexes $[CoL_6][MX_4]$, (M = Co or Zn; X = Cl or Br) have been prepared and their magnetic properties investigated [278]. Nineteen mixed ligand complexes of general formula $[CoL_2L']$ or $[CoL_2L''_2]$ in which HL is a halocarboxylic acid, L" is dimethylurea, tetramethylurea, hmpa or thf, and L' is pyridine *N*-oxide, picoline *N*-oxide, or 2,2'-bipyridine *N,N'*-dioxide have been made and characterised [279].

The ligand **(93)** chelates to Co(II) ion through two oxygen donor atoms; complexes $[CoL_2X_2]$ (X = Cl, Br, NCS) and $[CoL_3X_2]$ (X = I, $ClO_4$, $NO_3$) have been prepared and their physical properties investigated [280]. Finally, the *N,N'*-dioxide, $biquO_2$ = **(94)**, chelates to $Co^{2+}$ to give an octahedrally sited metal ion in the complexes $[Co(biquO_2)_3]X_2$, (X = $ClO_4$, $CF_3SO_3$, $NO_3$) [281].



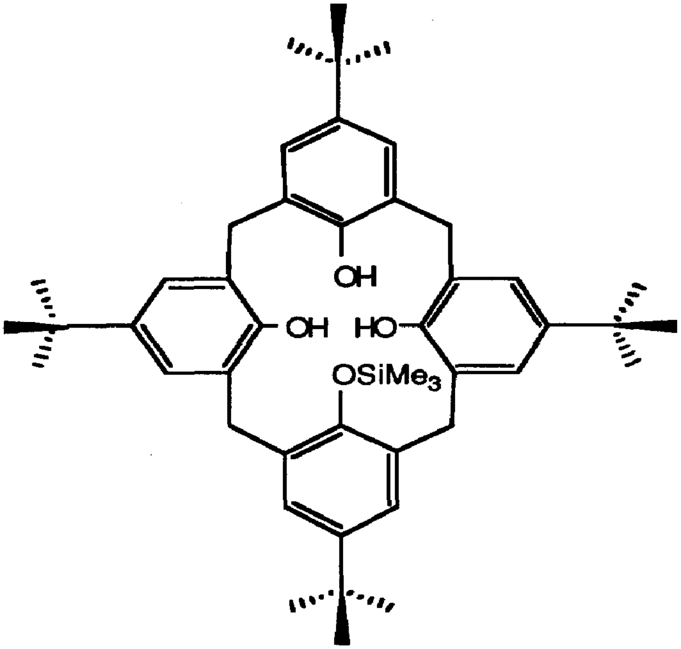
**(93)**



**(94)**

### *3.3.2.6 Macrocyclic ligands*

A variety of complexes of Co(II) with crown ethers has been investigated. One study has compared the coordinating ability of 18-crown-6 with that of the $SCN^-$ ligand [230]. When cobalt(II) perchlorate reacts with 15-crown-5, (L), the hydrophobic nature of the ether ligand is reported to be the driving force for the formation of an inner sphere complex, $[CoL_2][ClO_4]_2$; spectroscopic data suggests that the cationic complex $[CoL(ClO_4)]^+$ is also formed [282]. $^2H$ NMR studies involving 12-crown-4 have illustrated that in $CD_3NO_2$/MeOH solutions, there is fast exchange between the free ether and coordinated ligand in the complex ion, $[Co(12\text{-crown-}4)_2(MeOH)_n]^{2+}$; the kinetics of the process are presented [283]. The extraction of $Co^{2+}$ ions from aqueous $ClO_4^-$ solution by a range of crown ethers has been explored; extraction constants are reported, and formation constants for the cobalt(II) crown ether complexes have been determined. The trend in these measured parameters is related to the basicity of, rather than the "hole-size" of, the crown ether [284].



**(95)**

The first example of a transition metal complex involving the macrocyclic ligand, $H_3L$, **(95)**, has been exemplified by $[Co_3L_2.thf].5PhMe$; although the yield is very low, (5%), it is reproducible. An X-ray structural determination has shown that two of the Co(II) centres are 6-coordinate, and one is 5-coordinate; in addition, of the five toluene molecules of crystallisation, two are involved in host-guest interactions [285].

### *3.3.2.7 Miscellaneous*

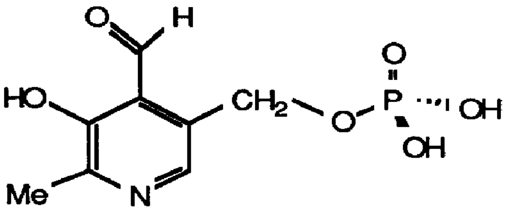
Reports of some miscellaneous ligands which are oxygen donors, and which coordinate to Co(II) ions, are summarised below. Firstly, there have been several studies concerning phosphorus containing ligands. The structure of the complex $[Co(O_2PF_2)_2].2MeCN$ has been elucidated; a polymeric material, the complex exhibits $\mu$-$O_2PF_2$ units around an octahedral Co(II) centre [286]. Related to this work is the preparation of $[Co(O_2PF_2)_2].HPO_2F_2$; again, this compound is polymeric, and contains bridging $O_2PF_3$ groups [287]. The reaction of $H_2L$, **(96)**, with $[Co(OAc)_2]$ in dmso produces the complex $[CoL].nH_2O$. Infra red spectral data indicate that the complex is polymeric, and that, for one ligand, coordination is *via* the aldehydic CO moiety and the phenolic O atom, while for second ligand attaches *via* the $P(OH)_2$ groups [288].

Compounds with sulphonamide ligands include the previously discussed complex of ligand **(85)**, [259]. In addition to this, for HL = $C_6H_5SO_3NH_2$, the preparation and characterisation of the complex $[CoL_2]$ has been described; stability constants have been measured [289].

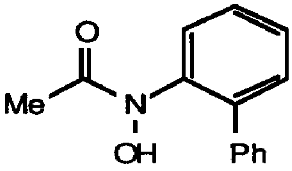
The thermodynamics of the formation of a complex between Co(II) ions and the ligand $L^-$, ( HL = **(97)** ), has been reported [290].

When the pyrrolidinone ligand, **(98)**, complexes with cobalt(II), two distinct compounds are reported to form; both the tetrahedral $[CoL_4][ClO_4]_2$ and the octahedral complex $[CoL_6][ClO_4]_2$ have been characterised, and their magnetic moments measured [291].

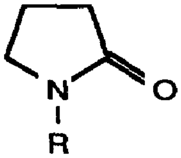
Finally, polymeric complexes of Co(II) have been proposed as the products of the reaction of $Co^{2+}$ ions with the ligand L, **(99)**; the complexes $[CoL(MeOH)(NCS)_2]$ and $[CoL_2(NCS)_2].MeOH$ have been characterised by various physical methods [292].



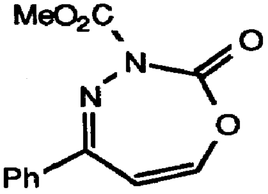
**(96)**



**(97)**

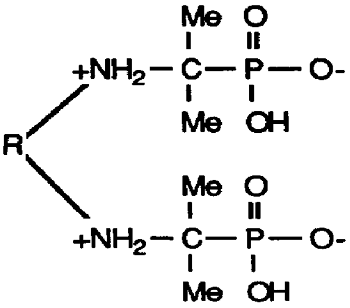


**(98)**



**(99)**

Polymeric complexes of Co(II) with the ligand L, **(100)** (R = -($CH_2$)- or *o*-phenylene), have been reported; each ligand is terdentate, and spectral and magnetic properties of the complexs $Co_2L.2H_2O$ indicate an octahedral environment for the metal ion [293]. Phosphates have also been used in the preferential extraction of Co(II) ions from a Ni(II)/Co(II) [294].

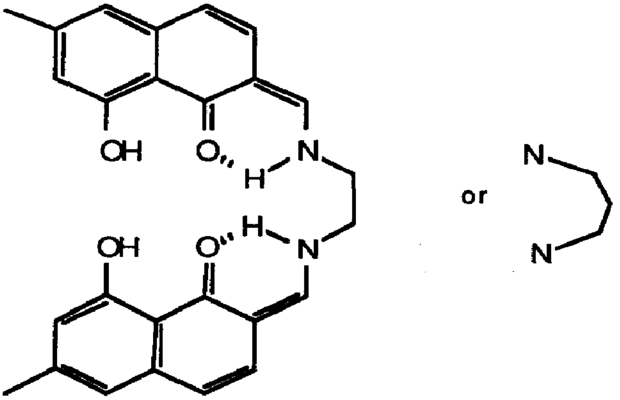


**(100)**

### 3.3.3 *Complexes with oxygen-nitrogen donor ligands*

#### 3.3.3.1 *Amines, amides and amino acids*

The amine $H_4L$, **(101)**, is reported to react with $[Co(acac)_3]^-$ to give the complex $[Co(H_2L)]$ which is stable up to 300°C; infra red data indicates that coordination of the ligand is *via* an $N_2O_2$ mode, around a square planar metal ion [295]. The mixed ligand complex $[Co(glygly)(NO_2)(en')].H_2O$, in which en' is a derivative of en, and glygly is $H_2NCH_2C(O)NHCH_2CO_2H$, has been prepared and structurally characterised; the glygly ligand is terdentate and resides in the equatorial plane of an octahedral coordination sphere [296].



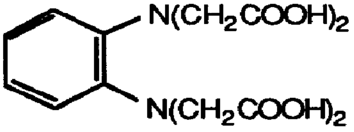
**(101)**

A series of related complexes of general formula $[CoL_2].nH_2O$ (HL = $C_6H_4R(NHCH_2CO_2H)$; R = H, *o*-Me, *m*-Me, *p*-Me, *p*-Cl, *m*-$NO_2$, *p*-$NO_2$) has been prepared and spectroscopically characterised [297]. For the ligand *L*-histidine, a proton n.m.r. study of its complexation with $Co^{2+}$ ions has illustrated a stepwise mechanism; the sites of chelation are the $CO_2^-$, $\alpha$-$NH_2$, and N'-residues [298].

The stability constants of a series of related Co(II)-amino acid complexes have been measured and compared [299]. Continuing the physical chemistry, there has been a report of the thermal properties of several Co(II) glycinates and iminoacetates [300].

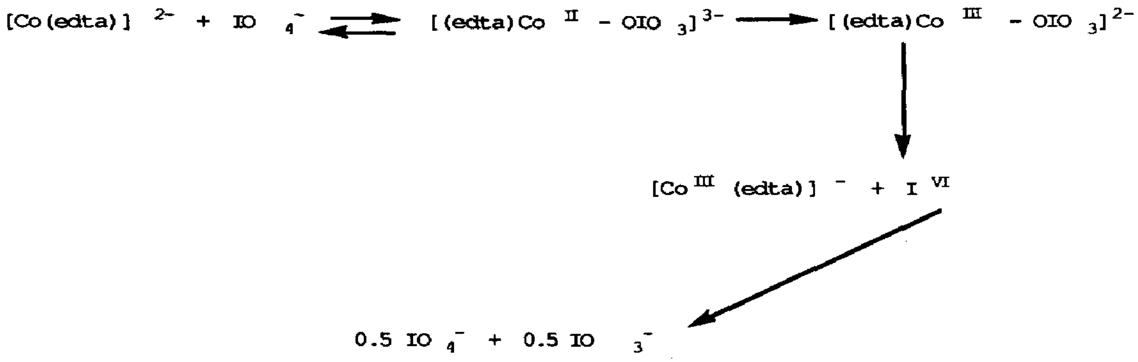
### *3.3.3.2 Aminopolycarboxylic acids and related ligands*

Only a few complexes involving Co(II) and amino- polycarboxylic acid ligands have been reported. The first example is really a simple monocarboxylate ligand, but its relationship to edta means that inclusion in this section is reasonable. The deprotonated form of the acid $H_2NCH_2CH_2NHCH_2CO_2H$, HL, complexes with Co(II) ions to give $[CoL(H_2O)]$ or $[CoL_2]$; $L^-$ is terdentate, and in the former complex, a tetrahedral metal is suggested, while in the latter, an octahedral environment is implied. Formation constants are also reported [301]. The formation constant of the edta-related complex [CoL], $H_4L$ = **(102)**, has also been determined [302].

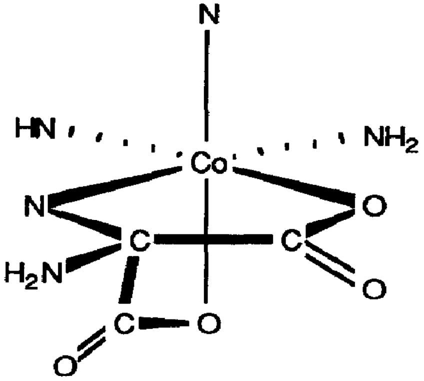


**(102)**

A study of the kinetics of the oxidation of $[Co(edta)]^{2-}$ by $IO_4^-$ in ethanol/water mixtures leads to the proposal of an inner sphere mechanism as outlined below [303]:



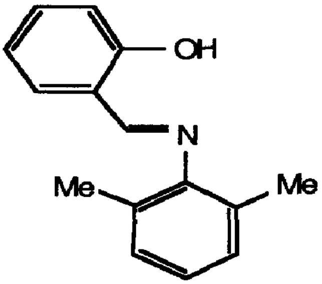
Finally, the structure of an unusual complex, **(103)**, has been elucidated by X-ray analysis; the ligand was prepared *in situ* by the reaction of $H_2NCH(CO_2^-)_2$ with the coordinated tetramine, L, $H_2N(CH_2)_nNH(CH_2)_nNH(CH_2)_nNH_2$ in the complex $[CoLCl_2]$ [304].



**(103)**

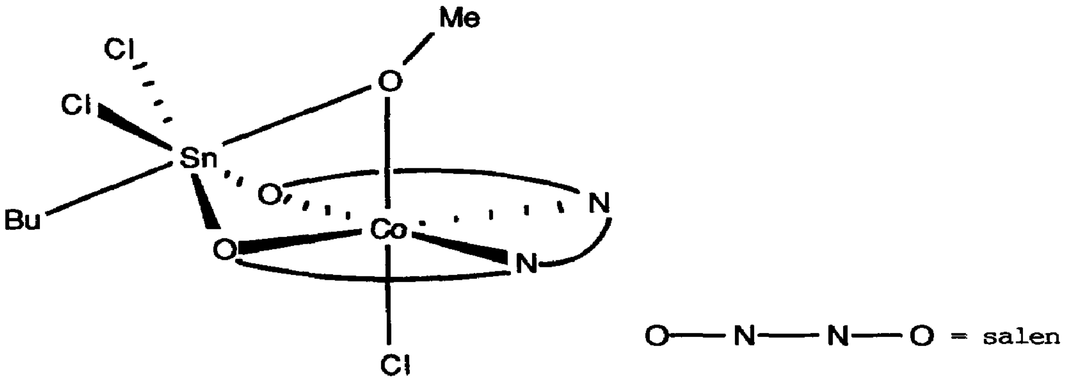
### 3.3.3.3 *Imines*

An X-ray structural determination of the complex $[CoL_2]$, HL = **(104)**, shows a tetrahedrally sited metal ion with the imine coordinating through N and O atoms. The measured bond lengths of Co-N = 2.035(8) and 2.003(8)Å, and Co-O = 1.879(7) and 1.873(8)Å, in this complex illustrate a greater than normal difference between Co-N and Co-O distances; the authors attribute this discrepency to the bulky nature of the *N*-substituent [305].



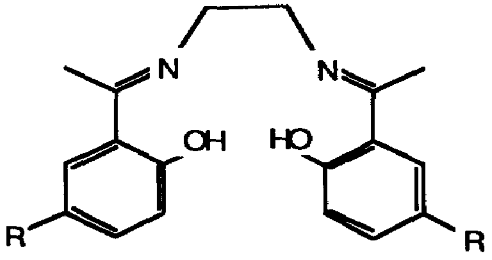
**(104)**

As in the case of Co(III), reports involving complexes of Co(II) with the ligand sal$_2$en$^{2-}$ are numerous. A spectrophotometric study of the equilibrium system formed between [Co(sal$_2$en)] and [Co(sal$_2$phen)] on adding NaBPh$_4$ has illustrated the formation of chelate adducts with cation and anion pairs; analogous Ni(II) chemistry has also been described [306]. An interesting complex, [Co(sal$_2$en){$^n$Bu(OMe)SnCl$_2$}Cl], **(105)**, has been isolated and structurally characterised; the Co(II) is oxidatively activated in the presence of $^n$BuSnCl$_3$ [307].



**(105)**

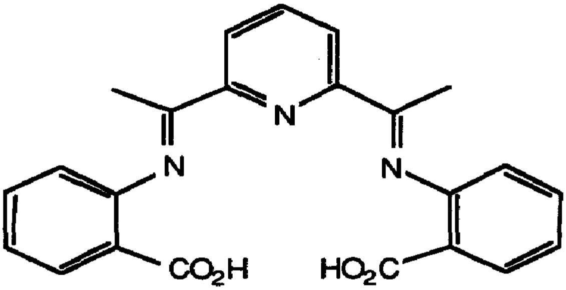
The application of Marcus theory to the one electron oxidation and reduction of [Co(sal$_2$en)] in a variety of organic solvents has been discussed [308]. Another study has looked at the reduction of organic halides with [Co(sal$_2$en)] in thf/hmpt solution at room temperature [309].



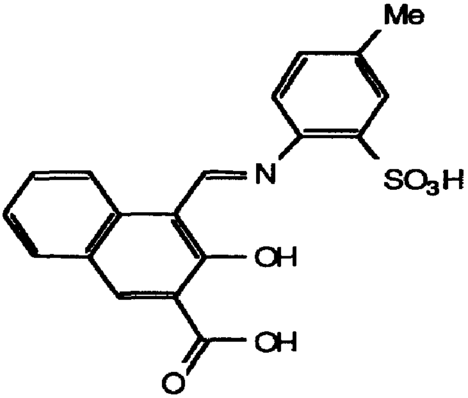
**(106)** R =Me;Cl **(107)** R = COOH

Cobalt(II) complexes with the substituted $sal_2enH_2$ and $sal_2enH_4$ ligands, (**106**) and (**107**) respectively, have been prepared and spectroscopically characterised [310,311]. An investigation of the magnetic properties of $[Co(H_2L)(H_2O)_2]$, $H_4L$ = (**107**), has illustrated a high to low spin transition in the solid state [311].

The complexation of the ligand, $H_2L$, (**108**), with Co(II) and with Mn(II) has been described; the manganese complex has been structurally characterised, and is found to exhibit an unusual 7-coordinate metal ion at the centre of a pentagonal bipyramid array of donor atoms. The products are recognised as having potential for template reactions [312].



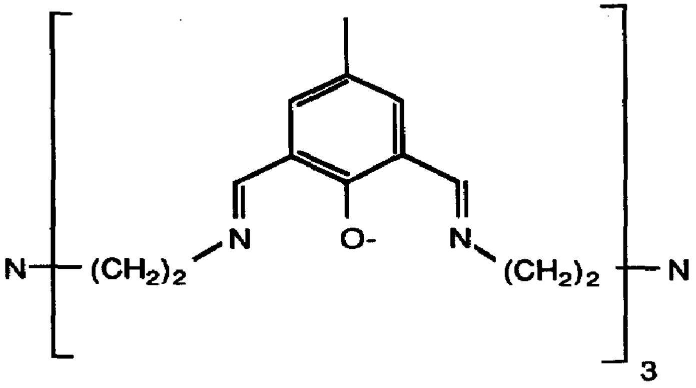
(**108**)



(**109**)

Several related Schiff base complexes of types $[CoL_n(H_2O)_2]$ (n = 1,2) and $[CoL(H_2O)X_2]$ have been prepared and characterised by spectroscopic techniques [313-316]. For the high spin complexes, $[CoL(H_2O)_2]$, in which $H_2L$ = RC(O)CH=N-*p*-$C_6H_4CO_2H$ (R = 2-thienyl), ligand field parameters have been determined [316]. Further ligand field effects have been described for some square planar complexes of Co(II) [317]. For the Schiff base complex $[CoL_2]$, HL = 1-OH-2-N=CHC(O)R-$C_6H_4$, R = β-naphthyl, a stability constant determination accompanies a report of the preparation and characterisation [318]. Coordination to $Co^{2+}$ stablises the enol- iminium zwitter ionic form of the Schiff base, $H_3L$, **(109)** [319].

The dinuclear complexes $[Co_2L]BF_4$ and $[CoLFe]BF_4$, $L^{3-}$ = **(110)**, have been made and the latter, structurally characterised; important distances involving cobalt are Co-O = 2.20(1), 2.15(1) and 2.17(1)Å, and Co-N = 2.15(1), 2.19(1) and 2.09(1)Å [320].

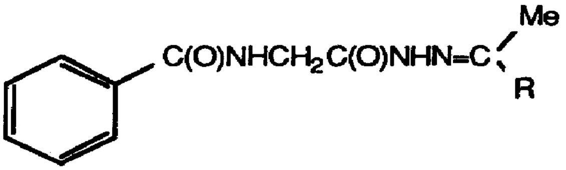


**(110)**

The inner sphere oxidation of $[Co(edta)]^{2-}$ by imine and oxime complexes of Cu(II) shows rapid electron transfer, but long lived intermediates which convert only slowly to products; a first order dependence on each reactant is observed [321].

### *3.3.3.4 Hydrazides and hydrazones*

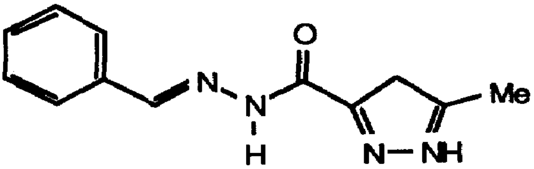
The complex *cis*-$[CoL_2(NCS)_2]$, where L = $H_2NNHC(O)NHNH_2$, has been prepared and structurally characterised; ligand field parameters have been determined [322]. For $H_2L$ being *N*-benzoylglycine hydrazide, a series of complexes have been isolated from the reaction of $H_2L$ with $Co^{2+}$ ions; $[Co(H_2L)_2Cl_2]$, $[Co(H_2L)_2].nH_2O$ (n = 1 or 2), and $[CoL].3H_2O$ have been characterised by magnetic and spectroscopic measurements, and are high spin, octahedral complexes. The denticity of the ligand changes from two in $H_2L$ and $HL^-$, to three in $L^{2-}$ [323]. Two related papers report the formation of complexes $[Co(H_2L)_nCl_2]$ and $[CoL].3H_2O$ in which $H_2L$, **(111)**, has either R = Me [324] or *o*-$(HO)C_6H_5$ [325]; as with *N*-benzoylglycine hydrazide, the denticity of **(111)** differs from that of its conjugate base. The same authors have reported coordination of the ligand *p*-$HO$-$C_6H_4CH_2CH(NH_2)C(O)NHN{=}C(Me)C_6H_4$-$OH$-*o* to Co(II), and again complexes of the type $[Co(H_2L)_2Cl_2]$ and $[CoL].nH_2O$ are formed [326].



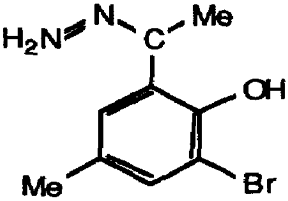
R = o-$C_6H_4OH$; Me

**(111)**

The complexes $[CoL_2X_2]$, (L = **(112)**; X = Cl, Br, I, $NO_3$, $BF_4$, $ClO_4$, SCN; n = 0,2,4,) have been reported; characterisation by physicochemical methods suggest that the compounds are octahedral, except for the halo-derivatives which are either octahedral or tetrahedral [327].

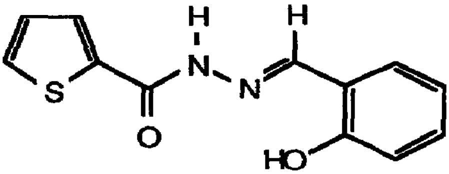


**(112)**

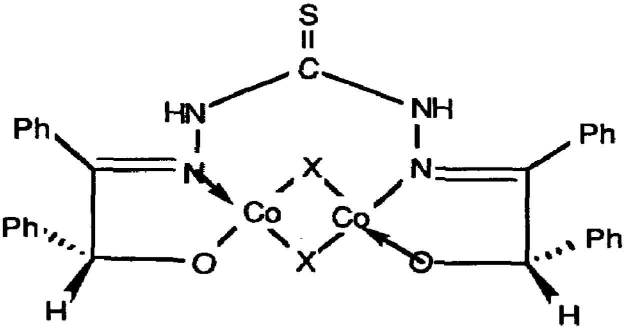


**(113)**

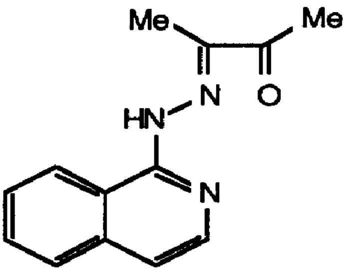
The syntheses of both HL, **(113)**, and the complex $[CoL_2]$ have been described; characterisation by spectroscopic methods and magnetic measurements suggest that the ligand coordinates *via* the phenoxy group and the imino nitrogen atom [328]. The product of complexation of the ligand $H_2L$, **(114)**, with $CoCl_2$ depends upon the mode of preparation; the compounds $[CoL(H_2O)_2]$, $[Co(HL)Cl]$, and $[CoL_2]$ are all orange, and the first two are reported to be octahedral [329].



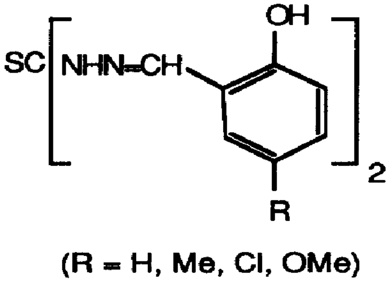
**(114)**



**(115)**



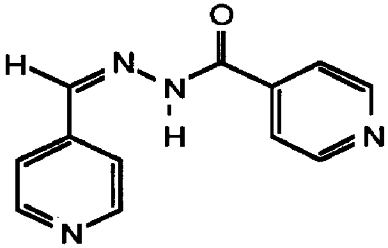
**(116)**



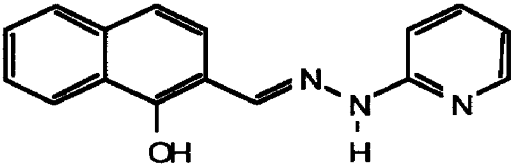
**(117)**

The preparation and spectral characterisation of the complex **(115)** have been described; a measured magnetic moment of 1.9BM is indicative of octahedral coordination and hence, the presence of coordinated water molecues in the axial sites is implied [330]. For the complex $[CoL_2]Cl_2$ in which L = **(116)**, an octahedral coordination sphere is implied from spectroscopic and magnetic moment data [331].

The bactericidal activity of the complex [CoL] ($H_2L$ = **(117)** ) has been investigated; within the complex, the phenoxy-O and imino-N donor atoms are reported to form a square planar array [332]. Antibacterial activity is also reported for the complexes $[Co(HL)SO_4].2H_2O$, $[Co(HL)(NCS)_2]$ and $[CoL_2].2H_2O$ in which HL is the isonicotinic acid-derived ligand **(118)** [333].



**(118)**

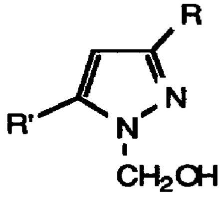


**(119)**

Finally, the preparation of, and reaction with Co(II) of, the ligand HL, **(119)**, have been described; again, only spectroscopic and magnetic moment data are available for the new complex $[CoL_2]Cl$ [334].

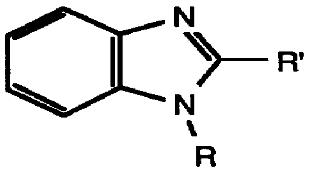
### *3.3.3.5 Heterocyclic ligands*

There have been several reports of Co(II) complexes with 8-hydroxyquinoline, HL, or derivatives thereof. The effects of different electron releasing or withdrawing substituents in the 4-position of 8-hydroxyquinoline have been investigated for the complex $CoL_2$ [335]. For HL = 4-methyl-8-hydroxyquinoline, reaction of the complex $[CoL_2]$ with NO in $CH_2Cl_2$ or dmf at room temperature, leads to the formation of $[CoL_2(NO)]$; $[CoL_2]$ and $[CoL_2(NO)]$ both react with NO in a solution of 10% pyridine in dmf at 283-288K to produce $[CoL_2(NO)(py)]$, or at higher temperatures to give $[CoL_2(NO_2)(py)]$. Further reaction of $[CoL_2(NO)(py)]$ with NO gives $[CoL_2(NO_3)(py)].py.H_2O$. In each case, infra red spectroscopy was used to monitor the coordination of the NO based ligand [336]. The complexation of 7-dicyclohexylaminomethyl-8-hydroxyquinoline with Co(II) ions has been described; stability constants for the new complex, and other related first row transition metal complexes, have been determined [337]. An interesting dimeric structure has been proposed from spectroscopic data and X-ray diffraction powder patterns for the complexes $[CoL_2].nH_2O$ (n=0,1) where HL = 8-hydroxyquinoline or its 2-methyl derivative; it is suggested that two cobalt atoms are bridged by the phenoxy-O atoms of two ligands, while each ligand chelates separately to one metal ion [338].



R ≠ R' = Me
R ≠ R' = $CO_2H$

**(120)**



R = H
R' = CH(OH)(Ph)

**(121)**

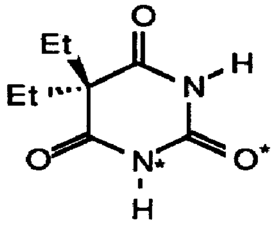
R = n=Pr
R = 2-$C_6H_5$-OH

**(122)**

The mixed ligand complexes $[CoL_2L'_2].nH_2O$ and $[CoL_2L''].nH_2O$ (HL = (**120**); L' = $H_2O$, $NH_3$, py, Me-py; L" = phen, py; n = 0,2) have been prepared and spectroscopically and magnetically characterised; all structures are proposed as being pseudo- octahedral, with $L^-$ coordinating as a bidentate ligand through the carboxylate O- and the tertiary N-atoms [339]. The complexes $[CoL_2].nH_2O$ and $[CoL_2L'_2].nL_2$ in which HL = (**121**) or related ligand; L' = py, β-picoline; n = 0, 0.5, or 1, have been reported; characterisation is *via* spectroscopic and magnetic moment observations, and it is concluded that the complexes may be tetrahedral or octahedral depending upon the nature of the ligands [340]. Related to this work, is a discussion of the complexes $[Co(HL)_{1.5}X_2]$, $[Co(HL)_2Y_2]$, and $[Co(HL_2)L]ClO_4$ ($H_2L$ = (**122**); X = Cl, Br; Y = I, $NO_3$, SCN); an X-ray diffraction study of the Ni(II) analogue of $[Co(HL_2)L]ClO_4$ evidences a strongly hydrogen-bonded dimeric structure in which each Ni(II) is octahedrally sited, and the ligands function as N-O chelates [341].

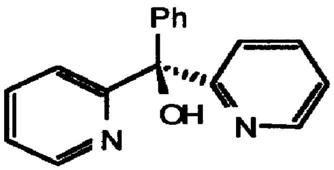
The reaction of 1-(hydroxymethyl)-3,5-dimethylpyrazole (HL) with Co(II) halides, X, (in ethanol, followed by treatment with ethanolic KOH, produces a novel tetrameric cluster, $\{CoX(L)(EtOH)\}_4$; the analogous nickel(II) cluster has been crystallographically characterised, and exhibits a cubic $Ni_4O_4$ core with "edge bridging" chelates [342].

The cyclic ligand, $L^-$, (HL = (**123**) ), coordinates to Co(II) ions to produce the compound $[CoL_2].2H_2O$; preparation and spectroscopic characterisation have been reported [343]. The pyridine derived ligand HL, (**124**), and its conjugate base both have the same ligation properties; coordination is proposed to be *via* an N-N-O tridentate mode in the complex cation $[CoL(HL)]^+$ [344].



* =coordination site

**(123)**

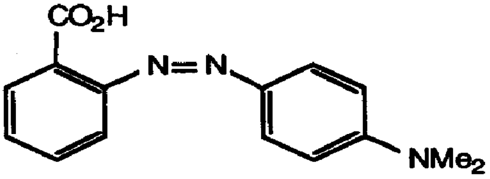


**(124)**

### *3.3.3.6 Miscellaneous ligands*

The first example of coordination *via* the O atom of an N=S=O group in a deprotonated *N*-sulphinylphenylhydrazine ligand has been reported; the complex [Co(PhNNSO$_2$)(py)$_2$] has been structurally characterised, and possesses an octahedral coordination sphere with *trans*-py ligands, and N-O chelating PhNNSO$_2$ groups which are *trans* with respect to one another [345].

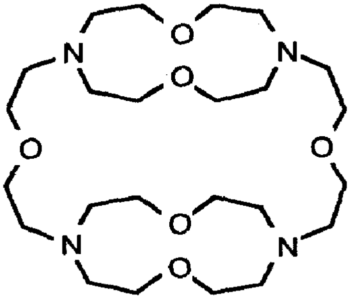
The complex [CoL$_2$] in which HL = **(125)** has been synthesised; it is paramagnetic and a tetrahedral geometry is proposed [346]. Stability constants have been determined for a series of complexes of Co(II) containing substituted azocresol ligands [347].



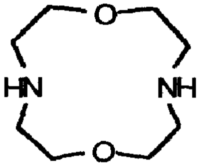
**(125)**

The identification of isobacteriochlorins in sulphite reductases is justification for a detailed investigation of their coordination chemistry; the oxidation of Co(II) nitrosyl complexes of porphyrins, chlorins and isobacteriochlorins yields stable, recyclable, Co(II) nitrosyl π-cation radicals [348].

Nitrogen-oxygen macrocyclic chemistry is represented this year by a report of the complexes [CoL] in which L = **(126)** or **(127)**; the macrotricycle **(126)** envelopes the metal ion, forming a "cylindrical" cage. A comparison of stabilities of the two complexes is presented [349].



**(126)**

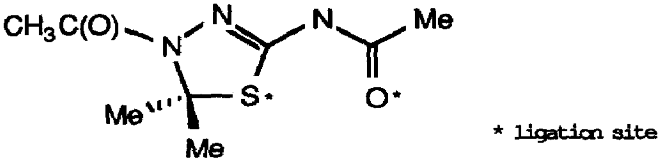


**(127)**

### 3.3.4 *Complexes with oxygen-sulphur donor ligands*

Complexes with O-S chelates to cobalt(II) are sparse. For $H_2L$ = $(CF_3)_2C(OH)CH_2SCH_2C(OH)(CF_3)_2$, the complexes [CoL(tmed)], [CoL(py)$_2$], and [CoL(bipy)$_2$] have been synthesised. [CoL(py)$_2$] has been structurally characterised as trigonal bipyramidal complex; one py is axially bound, and the other lies in the equatorial plane, while the $L^{2-}$ ligand is tridentate, with the S-atom axially sited. Pertinent bond parameters are: Co-O = 1.911(4); Co-S = 2.553(2); Co-$N_{axial}$ = 2.102(5); Co-$N_{equat.}$ = 2.087(4)Å [350].

The complex ion, $[CoL_2(H_2O)_2]^{2+}$, has biological significance and the fungal toxicity of both this and the free ligand, **(128)**, have been studied [351].



**(128)**

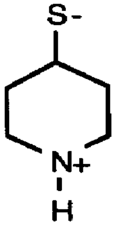
### 3.3.5 *Complexes with sulphur donor ligands*

#### 3.3.5.1 *Thiolates and thiocarboxylic acids*

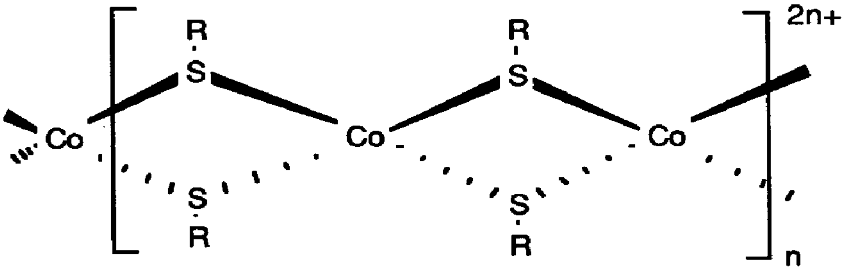
The synthesis and structural characterisation of the complex ion $[CoL_2]^{2-}$, in which $H_2L = HS(CH_2)_2SH$, have been described; the ion is tetrahedral with an average Co-S distance of 2.284(6)Å. The oxidised product, $[CoL_2]^-$, has also been fully characterised, and is a planar, spin triplet Co(III) species; the average Co-S bond length is 2.167(5)Å [352].

The known thiolato complex $[Co_4(SPh)_{10}]^{2-}$, has been found to react with $SH^-$ ion, in acetone, to produce the near cubic cluster ion $[Co_8S_6(SPh)_8]^{4-}$; reduction of this species in acetonitrile gives $[Co_8S_6(SPh)_8]^{5-}$, again possessing a cubic core. The significance of these new materials in relation to synthetic pentlandite is discussed [353].

The ability of 2-thiolatoquinoline to extract Co(II) ions from solution has been studied as a function of pH, and of $Co^{2+}$ ion and ligand concentration; formation constants for the complexes so formed are reported [354]. The zwitter-ionic ligand, **(129)**, ligates *via* the S-atom to Co(II) ions to form the green complexes $[CoLX_2].0.5H_2O$ (X = Cl, Br) and $CoL_3X_3$ (X = $NO_3$, $ClO_4$) which are prone to decomposition in polar solvents.



**(129)**



**(130)**

Both complexes are polymeric; the former complex contains tetrahedrally sited CO atoms, and structure **(130)** is proposed on the basis of spectroscopic data; $CoL_3X_3$, on the other hand, exhibits octahedral cobalt(II) [355].

A potentiometric investigation of the complexation of Co(II) ions with $CH_3CH(SH)CO_2H$ or $HSCH_2CO_2H$ in aqueous medium, indicates the formation of 1:1 and 1:2 (M:L) complexes; stability constants have been obtained [356]. A closely related article by the same authors has also appeared [357]. Related to this is the complexation of $HSCH_2CH(NH_2)CO_2H$ with cobalt(II) ions; under oxygen free conditions, 1:1 and 2:3 complexes are formed [358]. Thermodynamic parameters and a stability constant have been determined for the complex formed between $Co^{2+}$ and $CH_2(C(O)SH)_2$ [359].

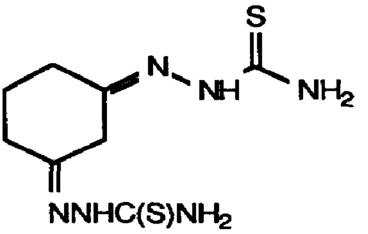
### *3.3.5.2 Thioamides*

The preparation of the complexes $[CoL_2X_2]$ and $[CoL_3Y_2]$ ( L = $Me_2NC(S)-SS-C(S)NMe_2$; X = Cl, Br, $NO_3$, NCS; Y = I, $ClO_4$), and their characterisation by spectroscopic methods and by magnetic moment and conductivity measurements, have been reported [360]. Two closely linked papers deal with the complexation of $BzNHNHC(S)NHNH_2$ with cobalt(II) ions; preparation and specroscopic characterisation of $[Co_2(H_2O)_2]$ [361] is accompanied by the determination of thermodynamic parameters [362].

The conjugate base of the thioamide $H_2L$, (**131**), ligates to Co(II) ions to produce the paramagnetic complex, $[Co(HL)]Cl.2H_2O$; in acidic solution, infra red spectroscopic data indicate that $HL^-$ is tetradentate. The thermal decomposition of the complex is also discussed [363].

### *3.3.5.3 Miscellaneous*

The synthesis and spectroscopic characterisation of the high spin complexes $[Co(HL)_2X_2]$ and $[CoL_2]$ where HL is a thiosemicarbazone, ( with various $X^-$ ), has been described [364]. A distorted tetrahedral structure is proposed on the basis of infra red and Raman spectral data for the complex, $CoL_2Cl_2$, (L = (**132**) [365].



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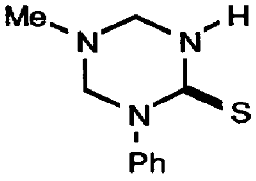
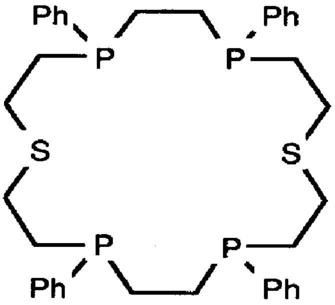


(132)

Finally, an unusual trimethylarsine sulphide complex of cobalt(II), $[Co(Me_3AsS)_4][ClO_4]_2$ has been prepared; depending upon the choice of solvent, ethanol or acetone, one of two conformational isomers (one green and the other blue ), is isolated. X-ray diffraction studies show that the $[Co(Me_3AsS)_4]^{2+}$ cations are stacked in a columnar arrangement, with S-Co-S angles and S-Co-S-As torsion angles differing for the two isomers [366].

### *3.3.6 Complexes with sulphur-phosphorus donor ligands*

Two papers have appeared concerning the chelation of the sulphur-phosphorus containing macrocycle, (**133**), to Co(II) ions [367,368]. The complications of optical isomerism are well addressed, and the chiral conformation of the ε-diastereoisomer of the complex $[Co(\varepsilon\text{-}L)][BF_4]_2$ has been confirmed by an X-ray diffraction study. The ε-diastereoisomer exhibits a distorted octahedral array of donor atoms about the central metal ion with Co-S = 2.62(2), 2.56(2)Å and Co-P = 2.35(2), 2.24(2), 2.31(1), 2.21(1)Å; the shorter Co-P bonds are the axial ones. The γ-diastereoisomer of the same complex has also been structurally elucidated; the macrocycle (**133**) is oriented with the four P-donors in a plane, while the S-atoms of the ligand are not coordinated [368].



**(133)**

Although they are perhaps better thought of as clusters rather than as coordination complexes, the compounds $[(triphos)M(E_2S)M'(triphos)]Y_2$ (E = P, As; M = M' = Co, or M = Co, M' = Rh, Y = $BF_4$; M = M' = Rh, Y = $BPh_4$ ) are included here because of their novelty. X-ray analysis shows the $E_2S$ unit to be $\eta^3$ coordinated to each metal atom [369].

### 3.3.7 *Complexes with nitrogen donor ligands*

### 3.3.7.1 *Thiocyanate complexes*

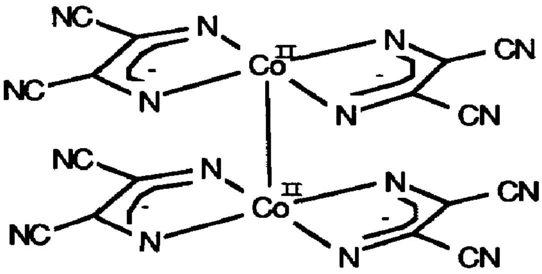
A spectrophotometric study of the equilibrium (in methanol) between tetrahedral and octahedral forms of the complex $[Co(H_2O)_{6-n}(NCS)_2]^{2-n}$ (n = 1-3) has been described; thermodynamic parameters for successive complexation steps were also determined [370]. In a related piece of work, complexation of Co(II) ions with thiocyanate ion is reported to lead to the formation of $[Co(SCN)_n]^{2-n}$ where n = 1,2,4 but not 3; log $\beta$ values wer determined [371]. A neutron diffraction study of the complex $K_2[Co(NCS)_4].H_2O.CH_3NO_2$, carried out at 120K, evidences chains of tetrahedral $[Co(NCS)_4]^{2-}$ units which are interconnected by OH---S hydrogen bonds; pertinent distances are Co-N = 1.964(2), H---S = 3.377(2)Å [372]. The alkaline hydrolysis of $[Co(NCS)_2]$ has been the subject of study; the reaction leads first to $[Co(NCS)_2].[Co(OH)_2]$, and then to cobalt(II) hydroxide [373].

The structure of the mixed metal complex [CoHg(SCN)$_4$(H$_2$O)$_2$].MeC(O)NMe$_2$ has been elucidated; the cobalt(II) ion is octahedrally coordinated, with the thiocyanate ligands in the equatorial plane. The same ligands bridge between Co and Hg centres, thus forming 2-dimensional networks parallel to the (001) plane [374].

### *3.3.7.2 Amines*

The dinuclear complex [Co(NPh$_2$)$_2$]$_2$ has been prepared by the reaction of LiNPh$_2$ with CoCl$_2$ in hexane/thf solution at low temperature. Structural characterisation of the complex shows each cobalt(II) centre to be 3-coordinate with two terminal and one bridging NR$_2$ group; the Co-Co separation in the complex is 2.566(3)Å [376].

The reaction of Co(OAc)$_2$ with (NC)(H$_2$N)C=C(NH$_2$)(CN) in dmf in the presence of O$_2$ leads to the formation of the dinuclear cobalt(II) complex (**134**), which, on treatment with a suitable reducing agent, produces a cobalt(I) monomer. In the cobalt(II) dimer, the Co-Co distance is short (2.633(3)Å); each cobalt atom lies 0.19Å below the plane of the four nitrogen atoms and displaced towards the other metal atom. In the cobalt(I) complex, the average Co-N distance is 1.831(2)Å [377].



(**134**)

A number of cobalt(II) octahedral complexes of type [CoL$_{2-n}$(amine)$_2$] (n = 0,1) have been prepared by the reaction of

$[CoL_2].3H_2O$ (HL = o-$H_2N$-$C_6H_4CO_2H$) with different amines; the base strength of the amines influences the mode of coordination of L [378]. Reaction of the ligand $H_2N(CH_2)_4CH(NH_2)CO_2H.HCl$ with Co(II) ions forms complexes which have been characterised by conductivity and magnetic measurements; stability constants have also been determined [379].

Kinetic studies involving the trigonal bipyramidal complex ion, $[Co(hmtren)L]^{2+}$ ( hmtren = $(Me_2NCH_2CH_2)_3N$; L = HC(O)$NEt_2$ ) have been reported; rate and activation parameters for exchange of L have been determined, and it was found that the lability of $[Co(hmtren)L]^{2+}$ is substantially less than that of the octahedral $[CoL_6]^{2+}$ ion [380]. An $I_a$ mechanism is supported for substitution by $NCS^-$, $N_3^-$ or $Br^-$ of dmf in $[Co(hmtren)(dmf)]^{2+}$ [381]. Related work involves use of the optically active tripodal ligand, L', $(Me_2NCH_2CHMe)N(Me_2NCH_2CH_2)_2$; the preparation and structural elucidation of the trigonal bipyramidal complex $[CoL'(NCS)]^+$ is reported [382].

Coordination to cobalt(II) of the chelating diamine $RR'N(CH_2)_nNRR'$ ( R = Me; R' = pyryl; n = 3,4 ) has been investigated, and the complex $[CoL(SCN)_2].nH_2O$ has been characterised [383].

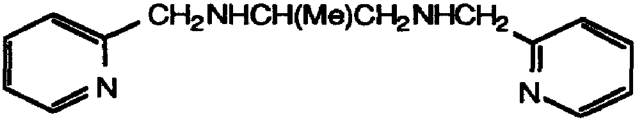
A derivative of ligand (**29**), cyclo-$C_6H_{10}(NH(CH_2CO_2H)_2)_2$ ($H_4L$), forms complexes with Co(II) ions; at pH 2.5 to 5.5, a solution containing $Co^{2+}$ ions and $H_4L$ was subjected to radiolysis and the cobalt was oxidised to Co(III). Under these conditions, the Co(II)- and Co(III)-complexes with $H_4L$ decomposed by a radical reaction [384]. The complexation of cobalt(II) with the ligand $CH_3(CH_2)_5N(CH_2CO_2H)_2$ ($H_2L$) has been reported [385]. The related tertiary amine, ($ntaH_3$), forms the complex $[Co_2\{Co(nta)_2\}].nH_2O$ which has been isolated by ion exchange and characterised spectroscopically and by X-ray analysis [386].

### 3.3.7.3 *Heterocyclic ligands*

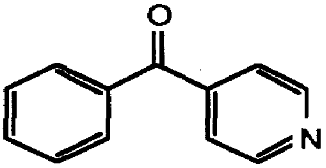
As one would anticipate, there are numerous reports of cobalt(II) complexes involving ligands derived from pyridine. The complexes [CoXLL'], $[CoXLL'_2(H_2O)]$, $[CoXLL'_3]$ and $[CoXL(H_2O)_3]$ ( HL = acetoacetanilide; L' = py, γ-picoline, quinoline; X = Br, Cl, $NO_3$, $ClO_4$) have been prepared and characterised spectroscopically and magnetically [387]. A variety of mixed pyridine-based ligand complexes of Co(II) have been synthesised and relevant ligand field parameters determined; all complexes are proposed as being octahedral, except for those which contain morpholine as one of the ligands. The latter complexes are tetrahedral. [388].

*N,N*-disubstituted 2-(aminomethyl)pyridines have been found to complex with cobalt(II) ions to give the blue, dinuclear complex ions, $[Co_2L_4(OH)]^{3+}$, in which the Co(II) centres are held together by a hydroxide bridge, and two amino-N bridges; kinetic and spectral data on these complexes is presented [389]. Complexes of nicotinamide, have been reported; in $[Co(nic)_2(H_2O)_4][OAc]_2.2H_2O$, each nic ligand is coordinated *via* the heterocyclic N-atom [390], and in $[Co\{C(CN)_3\}_2(nic)_2]$, nic shows the same mode of coordination, but the complex is polymeric, with the $\{C(CN)_3\}$ moiety acting as a tridentate bridge [391].

Within a single crystalline sample of the complex $\beta_1$-[Co(±picpn)(*S*-ala)]$ClO_4$, (picpn = **(135)** ), four diastereomers have been identified; pertinent bond lengths (averages) are Co-O = 1.89(1), $Co-N_{py}$ = 1.93(1), and $Co-N_{amine}$ = 1.94(3)Å [392]. Two related compounds, $[CoL_4(NCS)_2]$ and $[CoL_2(H_2O)_2(NCS)_2]$ (L = **(136)**), have been structurally elucidated; both complexes are octahedral, with like ligands *trans* to one another; in the former, $Co-N_{NCS}$ = 2.058(7), $Co-N_{py}$ = 2.215(6) and 2.217(6)Å, while in the latter complex, $Co-N_{NCS}$ = 2.080(5), and $Co-N_{py}$ = 2.195(4)Å [393].



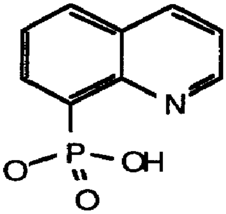
**(135)**



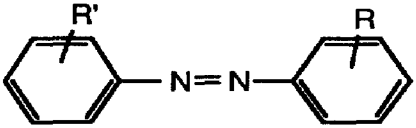
**(136)**

The thermal behaviour of the complexes $[CoL_2]$, in which L = $R(CH_2)_nNHSO_2Ph$ (n = 0,1,2) or $RSO_2NHPh$ and R = 2-py, has been investigated; the mechanism of decomposition is ligand dependent, and is either by direct loss of L, or by elimination accompanied by hydrolytic cleavage of L [394]. $^{14}N$ n.m.r. spectroscopy has been used to monitor py ligand exchange in bis(py)bis($\beta$-diketonato)cobalt(II) complexes;

activation parameters have been determined [395]. Stability constants and thermodynamic parameters have been reported for complexes of ligand **(137)** with $Co^{2+}$ ions [396].



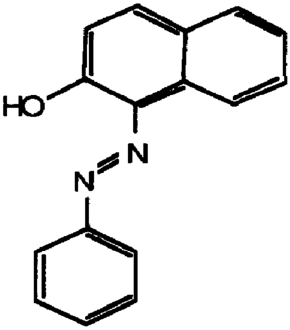
**(137)**



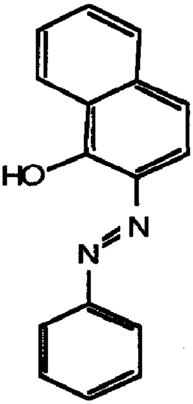
R = 2-hydroxy-5-methyl; 2,4-dihydroxy
R' = H; 2'-carboxyazobenzene

**(138)**

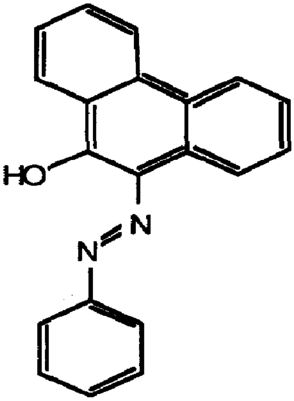
Ligation of the azo-compounds **(138)** to Co(II) has been described [397]. The related py based ligands, **(139)**-**(141)**, give red 1:2 ( Co(II):L ) complexes, which are oxidised to green Co(III) compounds by Cu(II) in dmso; the ligand dependence of the electrode potential for this redox couple has been assessed [398].



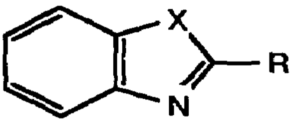
**(139)**



**(140)**



**(141)**



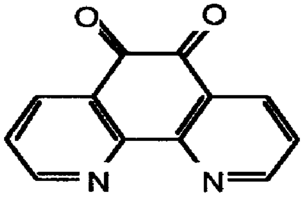
mqbo: X=O; R=4-methyl-2-quinolyl
mq'bo: X=O; R=4-methyl-8-quinolyl
mpbi: X=NH; R=4-methyl-2-pyridyl
mpbt: X=S; R=4-methyl-2-pyridyl
mpbo: X=O; R=4-methyl-2-pyridyl

**(142)**

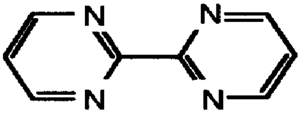
Cobalt(II) complexes of the type $[CoL_2Cl_2].2H_2O$ have been described for L = **(142)**; the compounds are pseudo-tetrahedral, except in the case of L = mpbo where an octahedral coordination is evidenced [399].

Complexes of bipy and phen are well exemplified as usual. The preparations of the $[CoL(SCN)_4]^{2-}$ anion (L = bipy, phen) [400] and of the mixed ligand complex [CoL$_2$L'] (L = bipy; L' = phen) [401] have been described. The electrochemistry of $[Co(bipy)_3][ClO_4]_2$ and $[Co(bipy)_2Cl_2].nH_2O$ has been investigated as a function of pH [402]. The reaction of the related compound $[Co(bipy)_3]Cl_2$ with $SnCl_2$ in HCl leads to $[Co(bipy)_3]SnCl_3$, the spectroscopic, conductance, and magnetic properties of which have been reported [403]. A discussion of trends in the stabilities of cobalt(II) complexes with aryl substituted phen ligands [404] compliments a separate paper, which describes the extraction of Co(II) into 1,2-dichloroethane using phenyl substituted phen [405]. The complexation of aqueous $Co^{2+}$ ions with bipy and phen has been studied as a function of ligand concentration, and in terms of competition with other metal ions; an $I_d$ mechanism is proposed for Co(II) but this mechanism is found not to appertain to all the metal ions studied [406].

The complexes $[CoL_2L'](ClO_4)_2$, *trans-(O)*-$[CoL'_2L]ClO_4$, and *trans-(N)*-$[CoL'_2L]ClO_4$, ( L = phen; L' = picolinic acid) have been isolated and spectroscopically characterised; some photochemistry of the new compounds is also reported [407]. The ligand **(143)** reacts with cobalt(II) chloride to give the complex ion $[CoL_3]^{3+}$, isolated as the $PF_6^-$ salt; some electrochemistry of the complex has been investigated [408].



**(143)**



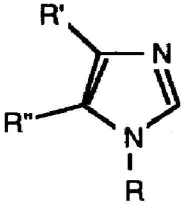
**(144)**

The oxidative, reductive and energy transfer pathways which are involved in the quenching of (polypyridine)ruthenium(II) complexes by Co(II) ions have been described; the oxidative route leads to a new $H_2O$ photoreduction sequence or reactions [409]. In related work, use of Co(II) tetramacrocyclic complexes as electron transfer agents in the sequence:

$$[Ru(bipy)_3]^{2+} + [Co^{II}(macrocycle)] + \text{electron donor} \longrightarrow \text{products}$$

in which the ruthenium complex is the photosensitiser, has been examined [410].

The tetradentate heterocycle, bpym, **(144)**, is able to act as a bridging ligand between two Co(II) centres; the dinuclear complex $[L_2Co(bpym)CoL_2]$ ( HL = $F_3CC(O)CH_2C(O)CF_3$ ) has been structurally characterised, and bpym chelates to *each* metal atom, the Co---Co separation being 5.750(4)Å [411]. The compound $[Co(bpym)_3](ClO_4)_2$ has been prepared and its electronic spectral properties examined; the complex is paramagnetic, and is a potential precursor for polymeric compounds [412].



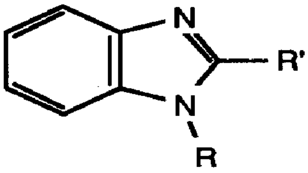
| **(145)** | **(146)** | **(147)** | **(148)** |
|---|---|---|---|
| R=Bu | R=$O_2SPh$ | R=H | R=H |
| R'=H | R'=$CH_2CH(NH_2)CO_2H$ | R'=$CH_2S(CH_2)_2NHC(NCN)NHMe$ | R'=$CH_2CH_2NH_2$ |
| R"=H | R"=H | R"=Me | R"=H |

Extraction of cobalt(II) ions from solutions containing sulphate and nitrate ions, by using the ligand **(145)**, has been described [413]. For L = **(146)**, coordination to Co(II) ion gives 1:1 and 1:2 complexes [414]. Related species of type $[CoL_2]X_2.nH_2O$ where L = **(147)**, have also been prepared, and characterised by physical methods [415]. The solubility of dinitrogen in aqueous media, in the presence of $[CoL_2]^{2+}$ for HL = **(148)** or hisH, has been described in terms of the equilibrium:

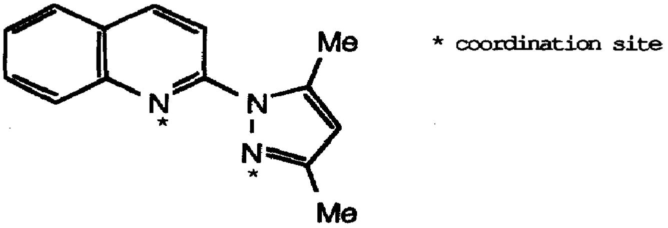
$$[CoL_2]^{2+} + N_2 \Leftrightarrow [CoL_2(N_2)]^{2+}$$

Equilibrium constants for the systems with the different ligands have been determined at 298K; $K_{equ.}$**(148)** > $K_{equ.}$(hisH) [416]. The preparation of complexes of type $[CoL_2X_2]$, where L is 1-methyl-3,4-diphenylpyrazole, have been reported; spectroscopic, conductance, and magnetic moment data suggest that when X = halide, the complexes are tetrahedral, but when X = nitrate, octahedral coordination occurs [417].

Formation constants for cobalt(II) mixed ligand complexes containing $H_2NCH_2CO_2H$ and **(149)** have been determined, and compared with values for analogous complexes with other metal ions [418]. A related piece of work gives formation constants for similar complexes in which the ligands are shown in **(150)** [419]. A report of the preparation and characterisation of complexes $[CoL_2Cl_2]$ (L = **(151)** ), also includes a discussion of their thermally induced polymerisation; the polymer structure and heat of polymerisation depends upon the substituents, R' [420].



| | | |
|---|---|---|
| R=H<br>R'=H | R=H<br>R=2-HO-$C_6H_4$<br>2-HO-5-Br-$C_6H_3$<br>2-HO-3-MeO-$C_6H_3$<br>CH(OH)Me | R=vinyl<br>R'=H; Me;Et;Pr;<br>Bu; $C_5H_{11}$; o-tolyl;<br>p-tolyl |
| **(149)** | **(150)** | **(151)** |

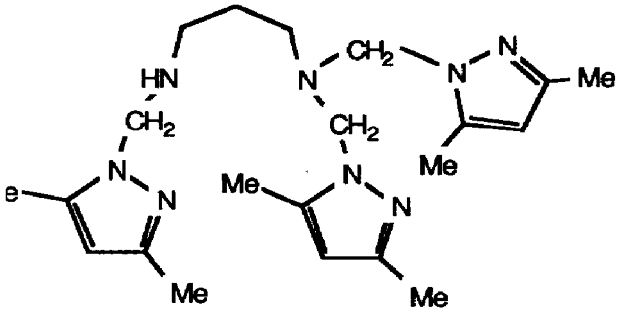


**(152)**

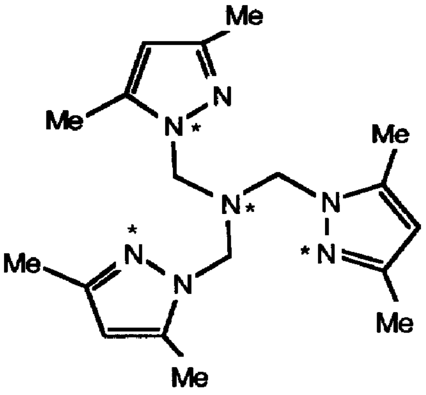
The complexes $[CoLCl_2].nH_2O$, containing the ligand, L, **(152)**, are blue and purple respectively; spectroscopic characterisation, supported by structural data, evidences 5-coordinate cobalt(II) with the heterocycle chelating between axial and equatorial sites [421].

An extended pyrazole array is found in ligand, ap3d, **(153)**. The complex $[Co(ap3d)(H_2O)][ClO_4]_2.H_2O$ has been prepared and fully characterised; the ligand is pentadentate, with Co-N distances lying in the range 2.100 to 2.255Å [422]. Complexes involving the related tripodal ligand, **(154)**, have been reported, and one, $[Co_2(ap3d)_2F][BF_4]_3.(EtOH)_x(H_2O)_y$, is especially interesting because the cobalt centres are held together in pairs by H-bonded solvent molecules; the Co atoms are separated by 6.254(2)Å [423]. The same authors have also prepared and studied the complexation of the bispyrazolyl ligand, bdmpab, **(155)** which has the ability to be either bi- or tridentate. A structural elucidation of $[Co(bdmpab)Cl_2]$ shows a distorted tetrahedral complex with a bidentate bdmpab ligand; two Co-N distances are 2.038(2) and 2.044(2)Å respectively, while the third, at 3.854(2)Å, is regarded as a non-bonding contact [424].

The reaction of *anti*-dichloroglyoxime with *N,N'*-diphenylmethylenediamine gives the ligand $H_2L$, **(156)**; complexation of $H_2L$ with cobalt(II) ions is reported to give the square pyramidal complex $[Co(HL)_2(H_2O)]$ [425].

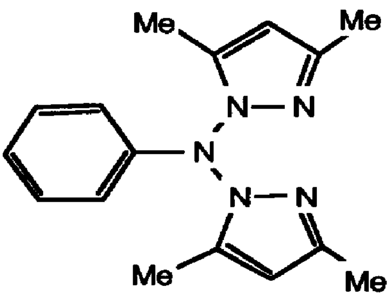


(153)

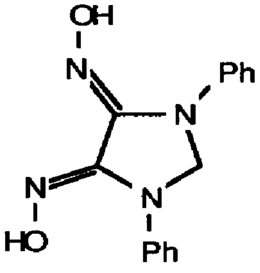


* coordination site

(154)

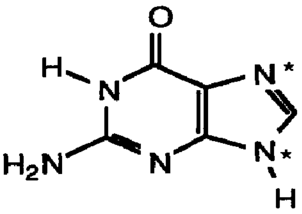


(155)



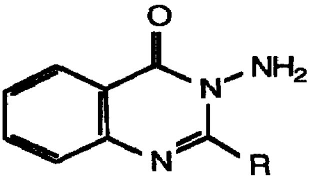
(156)

Cobalt(II) chloride reacts with HL, **(157)**, to give a tetrahedral 1:1 adduct; the product is reported to be a linear polymer with a $-(\text{CoLH})_n-$ backbone, and two terminal Cl ligands per metal atom [426]. Complexes of the related quinazoline ligand, **(158)**, have also been studied; e.s.r. measurements on the Co(II) complex are discussed in terms of geometry and electronic configuration [427].



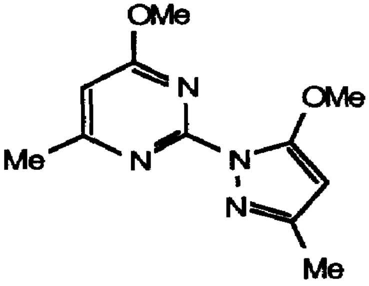
*coordination site

**(157)**

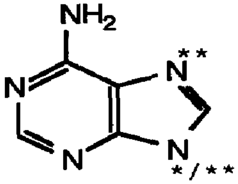


R=Me; Ph

**(158)**

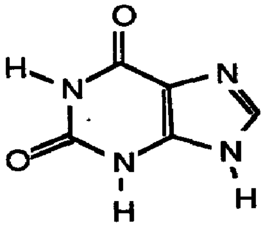


**(159)**

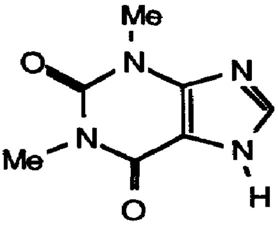


*ligation for terminal unidentate
**ligation for bridging bidentate

**(160)**



**(161)**

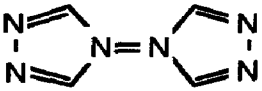


**(162)**

The complexes $[CoL_3][ClO_4]_2$, $[CoL(SO_4)].xH_2O$ and $[CoLCl_2]$ containing the heterocyclic ligand, L, **(159)** have been prepared and studied spectroscopically; octahedral cobalt(II) is evidenced in the first two complexes, and tetrahedral cobalt in the latter [428]. Reaction of $CoCl_2$ with the purine derivative, HL, **(160)**, leads to the formation of the complex $[Co(L)(HL)Cl].H_2O$; spectroscopic characterisation suggests a 5-coordinate metal atom, and a linear polymeric complex with HL molecules acting as bridges between adjacent metal centres [429]. Related to this is the characterisation of the complex ion $[Co(L)(HL)_2]^+$ in which HL is **(161)**; infra red spectral data indicate that the ligand is coordinated *via* ring N-atoms and not through the C=O moieties [430]. The final complex with a member of this same series of ligands is $[CoL_2].3H_2O$ in which HL is **(162)**; the synthesis of the ligand has also been reported [431].

There are several papers which discuss the preparation of complexes with thiazole ligands. The complex $[CoL_2]$, where L is 4-salicylideneamino-1,2,4-triazole, phosphoresces, and has fluorescence bands at 25,500 and 19,000 $cm^{-1}$; some photochemistry of this complex has been investigated [432]. A structural study of the compound $[Co_3L_8(NCS)_4][NCS]_2.9H_2O$ illustrates a bridging rôle for the ligand 4-butyl-1,2,4-triazole; adjacent pairs of octahedrally coordinated Co(II) centres are linked by three 1,2-bidentate thiazole ligands [433]. The same authors have reported the preparation and structure of another trimeric system, $[Co_3(HL)_6(NCS)_4F_2].2H_2O$ in which the ligand, HL, is 3,5-diethyl-1,2,4-thiazole; here, the nonbonded Co---Co separation is 3.3726(3)Å and the $Co\text{-}N_{thiazole}$ distances lie in the range 2.09 to 2.21Å

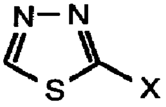
[434]. A related piece of work introduces a new class of 2-dimensional thiazole; the ligand btr, **(163)**, forms the complex $[Co(NCS)_2(btr)_2].H_2C$ which has been structurally characterised. The complex consists of layers of 6 coordinate cobalt(II) atoms, with an *intra*-layer Co---Co separation of 9.207(2)Å and an *inter*-layer separation of 8.584(1)Å [435].



**(163)**

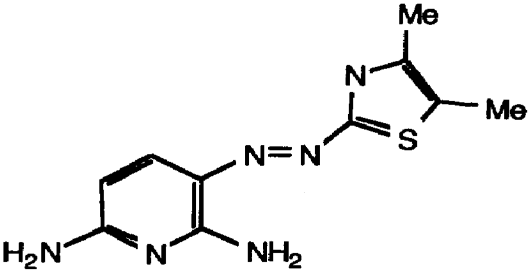
Reaction of Co(II) ions with tetrazole forms a polymeric complex $[CoL_{1.5}Cl_2].0.5H_2O$ containing octahedrally sited metal centres; characterisation is by spectroscopic and magnetic moment measurements [436].

Complexes containing the nitrogen-sulphur heterocycles shown in **(164)** and **(165)** have been prepared and spectroscopically characterised. Complexes of **(164)** are either pseudo-tetrahedral with a $CoN_2X_2$ core, or pseudo-octahedral with a $CoN_4X_2$ or $CoN_3O_3$ core; CNDO/2 calculations have been carried out on the free ligands and indicate that coordination *via* nitrogen in favourable [437]. For the ligand, L, **(165)**, the complex $[CoL_2][ClO_4]_3$ has been spectroscopically investigated; it is a low spin, diamagnetic octahedral complex, in which L is tridentate, bonding through the azo-N, the thiazolyl-N, and the amino-N atoms [438].



X = Cl; Br

**(164)**



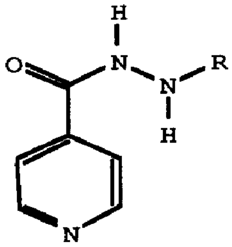
**(165)**

### *3.3.7.4 Amides, amino acids, and peptides*

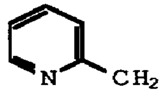
In this section, investigations of the ligation of the title species, as well as of thioamides, are considered; hydrazide and hydrazone derivatives are also included.

The reaction of aqueous Co(II) ions with $H_2NC(O)NHNH_2.HCl$ gives either neutral or cationic complexes, the infra red spectra of which have been reported [439]. The preparation of, spectral characterisation of, and determination of stability constants for complexes of type $[L_2Co(CNS)_2(NCSAg)_2]$ in which the ligand L is $(H_2N)_2C{=}X$, (X=O or S), $H_2C{=}CHCH_2NHC(O)NH_2$, $CH_3C(O)NH_2$, $C_6H_5C(O)NH_2$, $XC_6H_5C(O)NHCH_3$ (X = H, Br, $C(O)CH_3$), or imidazoline-2-thione), have been described; bridged structures are proposed on the basis of spectroscopic data [440].

The complexes $[CoLX_2]$ and $[CoL_2]$, where L is the ligand **(166)** and X = Cl, Br, or NCS, have been described; their spectroscopic properties suggest that the cobalt atom is tetrahedrally coordinated in $[CoLX_2]$, but is high spin octahedral in $[CoL_2]$, with L exhibiting a bidentate mode in the former complex and a tridentate mode in the latter complex [441]. The related nicotinic acid derivatives, HL and $H_2L'$, **(167)**, form the complexes $[CoCl_2(HL)_{1.5}].1.5EtOH$ and $[CoCl_2(H_2L')_2].nEtOH$ respectively; characterisation by infra red, $^1H$ nmr, diffuse reflectance, and e.s.r. spectroscopy has been described. The ligands and their complexes are of interest with respect to their tuberculostatic activity [442].



**(166)** R =



**(167)** R = H; $CH_3C(O)$

The reaction of $[Co(acac)_2]$ with pyridine carboxylic acid hydrazides, L, in methanol is reported to lead to $[Co(acac)_2L]$; spectral data for the latter complexes are consistent with their possessing octahedral structures [443]. The compounds $[CoL_2]$ and $[CoL_2L'_2]$, where L is $CH_3C(O)C(NNH_2)CH_3$ and L' is $C_6H_5NHNH_2$, have been prepared from $[Co(acac)_2]$ [444].

The ability of some cobalt(II)-copolymer complexes to decompose $H_2O_2$ have been assessed; the copolymers are produced from $HO_2CCH_2C(CO_2H)=CH_2$ and $H_2N(CH_2CH_2NH)_nH$, (n=1-4) [445].

Finally, an amide ligand, $H_4L$, which is related to (**38**), reacts with cobalt(II) ions in dmso to give $[CoL]^{2-}.4Me_2SO$; characterisation by spectroscopic methods and by X-ray powder patterns is reported to be consistent with a square planar environment for the cobalt atom [446].

### *3.3.7.5 Oximes*

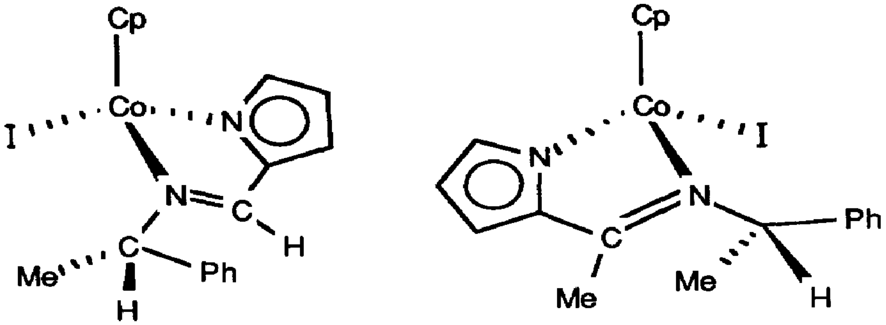
The oxime $dmgH_2$ provides one of the ligands in the complex $[Co(dmgH)_2(HL)(H_2L)]$ in which $H_2L$ is $H_2NC(S)NHN(CH_2CO_2H)_2$; the metal atom has a distorted octahedral coordination sphere comprising 4 N atoms from the two $dmgH^-$ ligands and two S atoms, one from each of the $HL^-$ and $H_2L$ units [447]. The structure of the complex $[Co(CH_3CO_2)L_2]$ (L = $CH_3C(CH_3)(NH_2)C(NOH)CH_2CH_3$ ) has been determined, and shows that the ligand L is bidentate *via* the amine- and oxime-N atoms [448].

A model system which is designed to measure directly the rate of intramolecular electron transfer between osmium(III) and cobalt(II) metal centres incorporates a dioxime ligand bridging the two metal ions has been described; the ligand is $HONC_6H_{10}NOH$ [449].

### *3.3.7.6 Imines and related ligands*

The complexes [CpCoIL] shown in (**168**) involve the bidentate ligand L, derived from 2-acetyl pyrrole; the stereochemistry of the complexes, as determined by X-ray analysis, is intimately dependent upon the substituent R, which in this case is either H or Me [450].

The preparation and spectroscopic characterisation of the complexes $[CoLX_2]$ (X = Cl, Br, I; L = $H_2NN=C(CH_3)C(CH_3)=NNH_2$) have been desribed; polymeric structures are proposed for these species with each Co(II) atom coordinated to two *trans*-$X^-$ ions, two imino-N atoms from the *same* L, and two amino-N atoms from *different* L ligands [451].



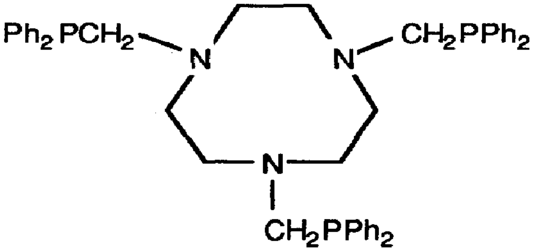
**(168)**

Cobalt(II) complexes of the hydrazone $H_2NN{=}C(Ph)C(Ph){=}NNH_2$, (L), have been prepared, and it has been observed that the reaction conditions necessary reflect the decreased basicity of the methine N atoms which results from the presence of the phenyl substituents in the ligand; the complexes $[CoX_2L_2]$ (X = Cl, Br, I, NCS, $NO_3$) are high spin octahedral, and solubility data implies that they are probably polymeric [452]. The mixed metal complexes $[CoHg(SCN)_4L]$ where L is the chelate $PhC(O)NHNH_2$ or $H_2NNHC(O)(CH_2)_nC(O)NHNH_2$ (n = 0,1) have been prepared in dilute ethanolic solution, and characterised by spectroscopic and magnetic measurements; interest in the complexes is in terms of their biological activity [453].

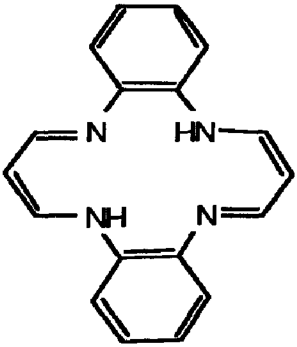
The compound $4\text{-}RC_6H_4N{=}CHCH{=}C(C_6H_4R'\text{-}4)NHC_6H_4R\text{-}4$ (where R=H, Me, MeO, EtO, Br, with R'= H, or R = H, Br, with R'= Br) has been synthesised, and its complexation with cobalt(II) ions studied; the ligand is bidentate (N-N' coordination) and forms a 1:2 high spin, tetrahedral complex [454]. The ligation to Co(II) of several Schiff bases, formed from the reaction of acetylacetone and aromatic diamines, has been the subject of investigation; square pyramidal complexes of formula $[Co_2Cl_2L_2]Cl_2$ are reported [455].

### 3.3.7.7 *Macrocyclic ligands*

The formation of the complex ion $[\{Co(NCS)]_n\}L]^{n+}$ (L = (**169**) ) has been studied; the ligand is able to adapt its bonding mode from tetra- to hexa-dentate, and the metal coordination alters accordingly [456]. The reaction of cobalt(II) nitrate with the ligand $H_4L$, **(48)**, in the presence of excess $SCN^-$ ion, leads to the formation of the complex $[Co(SCN)_4H_2L]$ which has been spectroscopically characterised [457].



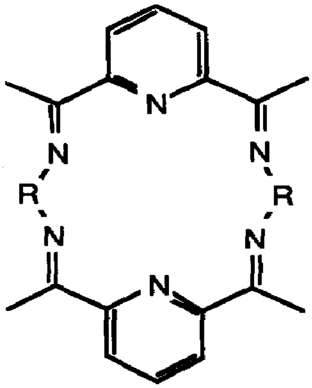
**(169)**



**(170)**

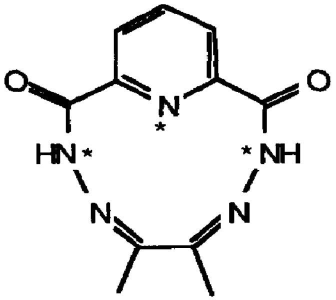
It has been reported that a template cyclocondensation reaction proceeds when 2,6-diacetylpyridine reacts with hydrazine in the presence of $[Co(SCN)_2]$; the product is characterised by physico-chemical methods as $[CoL(SCN)_2].5H_2O$, where L is the product of the cocondensation [458]. Similarly, the complex *trans*-$[CoL(H_2O)_2][NO_3]_2$, which exhibits an anomolous magnetic moment of 3.13BM, has been prepared [459]. For the same ligand, the complex $[CoL(H_2O)_2][ClO_4]$ has been independently described [460].

The coordination of pyridine bases to the complex [CoL], where $H_2L$ is **(170)**, has been studied; equilibrium constants for ten such complex-base equilibria have been measured, and steric effects operating between the ligand, $L^{2-}$, and the 2- or 6-substitutents of the pyridine base are found to result in weaker coordination for these hindered pyridine bases. An interesting correlation between $\lg K_a$ and the $^{13}C$ nmr chemical shift for the 4-position pyridine ring carbon is also presented in this work [461].



R = $(CH_2)_3NH(CH_2)_3$ for L'
R = $(CH_2)_3NMe(CH_2)_3$ for L"

**(171)**



* coordination site

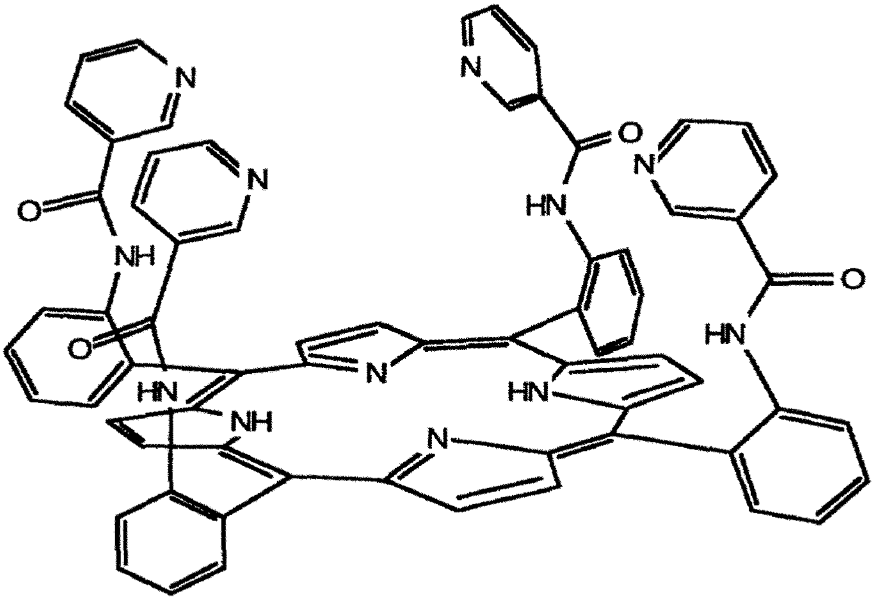
**(172)**

The ligand shown in **(171)** is particularly flexible, and is able to accommodate either 1 or 2 metal atoms; preparation of the complexes $[CoL"]^{2+}$, $[Co_2L'(MeCN)_2]^{4+}$ (5-coordinate from magnetic moment data), $[Co_2L'(NCS)_4]$ (proposed as octahedral), and $[Co_2L"(NCS)]^{3+}$ (dimeric with -NCS- bridges linking one Co(II) centre within one macrocycle to the next) was achieved *via* a template synthetic methodology [462].

Related to the ligand shown earlier in **(49)**, is the compounds **(172)**. The former acts as a novel tridentate ligand, (coordinating *via* the pyridine-N and amido-N atoms), and gives a brown complex with Co(II) ions which, on the basis of physico-chemical data, is proposed as being $[CoL(H_2O)_2]$; the geometry is proposed as trigonal bipyramidal [463].

An emphasis is placed on kinetics for any study involving complexes between Co(II) and the sepulchrate ligand. Firstly, the kinetics of electron transfer between $[Fe(H_2O)_6]^{3+}$ and $[Co(sep)]^{2+}$ has been presented [464]. Secondly, Marcus theory has been applied to an investigation of a series of [Co(II)(sep)]/Co(III) outer sphere redox couples [465].

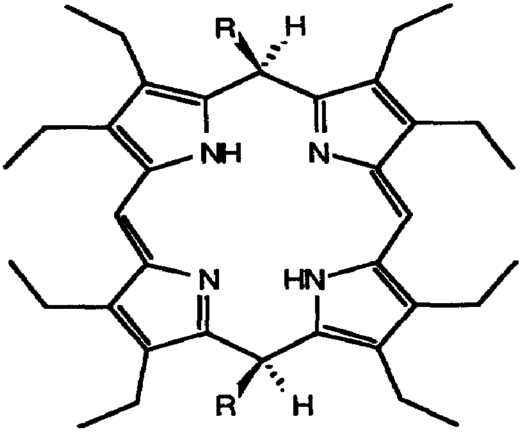
As one would anticipate, a variety of chemistry involving cobalt(II)-porphyrin complexes has been described. In a series of two papers, the rôle of electrode-bound cobalt(II) porphyrins in catalysing the formation of hydrogen from water has been investigated [466]. The electrochemical behaviour of binary, cofacial dicobalt, (initially both cobalt(II) ), porphyrins in benzonitrile has been studied [467]. Some interesting chemistry involving the porphyrin ligand (nic)$_4$H$_2$TPP, **(173)**, describes how this ligand is able to bind two metal ions in close proximity to one another; one ion is coordinated to the nicotinamide residue, while the second is sited normally within the TPP ring. For the mixed metal complex [RuCl$_n${(nic)$_4$TPP}Co], the presence of the ruthenium ion, and its oxidation state, influences the electrochemistry and spectral properties of the Co(II) ion [468].



**(173)**

The kinetics of Co(II)-tetrazaporphin complex formation has been the subject of study; a bimolecular mechanism is proposed and activation parameters are determined [469]. Continuing the theme of kinetics investigations, the coordination of TPP with cobalt(II) acetate in various solvent media has been described [470].

A detailed $^1$H n.m.r. spectroscopic study of the complexes [Co{OEPR$_2$}], ( H$_2${OEPR$_2$} = (**174**) ) has been presented; each complex is low spin square planar, and each is isolated as the stereoisomer in which the groups R are syn-axial [471]. Variable temperature $^1$H n.m.r. spectra of square planar tetraarylporphyrin complexes of cobalt(II) are reported to provide evidence for a low lying spin $^4A_2$ state, approximately 400 cm$^{-1}$ above the ground $^2A_1$ state [472]. Other proton n.m.r. studies have looked at *N*-methyl substituted TPP complexes of cobalt(II) ion [473].

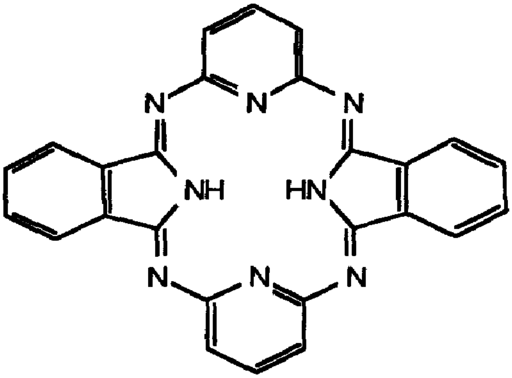


R = Me, Et, $^i$Pr, $^t$Bu

(**174**)

The final category of macrocyclic ligands to be considered here is that of phthalocyanine, PcH$_2$, derived compounds. The oxidation of [Co(Pc)] leads to a beautiful, metal-stacked compound, structurally elucidated, and having the potential for "metal-spine" conductivity [474]. Linking of two Co(Pc) residues occurs *via* a substitiuent bridge in the binuclear systems [Co$_2$L] where L is Pc-(OCH$_2$C(CH$_3$)(R)CH$_2$O)-Pc; the product complexes are known as "clamshell metallophthalocyanines", and are extremely soluble in organic solvents [475,476]. The dimerisation of cobalt(II) tetrasulphonated phthalocyanine is reported to occur in water and aqueous alcoholic solutions; physical constants for this process have been determined, and a finite and positive $\Delta C_p{}^{o}$ of 0.1 kcal mol$^{-1}$ K$^{-1}$ was found at 298-300K. This latter observation mitigates against hydrophobic bonding as being a major driving force for the dimerisation process, and it is concluded that a significant contribution to the entropy arises from the release of water molecules upon dimerisation [477].

The oxidation of 2-mercaptoethanol is catalysed by polymer bound [Co(Pc)]; the reaction rate has been examined as a function of the polymer structure [478]. The same authors have investigated the autooxidation of thiols using the complex [Co(Pc)$(NaSO_3)_4$] attached to polyvinylamine as the catalyst [479].



**(175)**

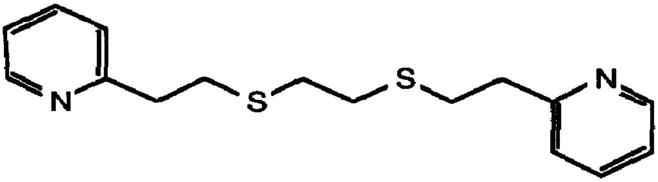
Ligand **(175)**, related to $H_2Pc$ by the replacement of two isoindoline units by pyridine rings, coordinates to the Co(II) ion to give a complex in which the 4-N atoms are strongly inequivalent; the loss of symmetry (i.e. that present in [Co(Pc)]) causes significant perturbation to the e.p.r. spectrum. Some extended Hückel results provide information on the ground state orbital structure [480].

### *3.3.8 Complexes with nitrogen-sulphur donor ligands*

#### *3.3.8.1 Aminothiols and thioethers*

In alkaline solution, a stable complex is formed between Co(II) ions and the enolic form the thiosemicarbazones, HL, RR'C=N-N=C(SH)$NH_2$. Complexes [$CoL_2$] for R = Me and R' = $^n$Pr, or R = R' = Et have been spectroscopically characterised and are found to be octahedral; it is proposed that each metal centre coordinates to two N-S chelating ligands, and inter-[$CoL_2$] Co---S interactions complete the octahedral coordination sphere [481].

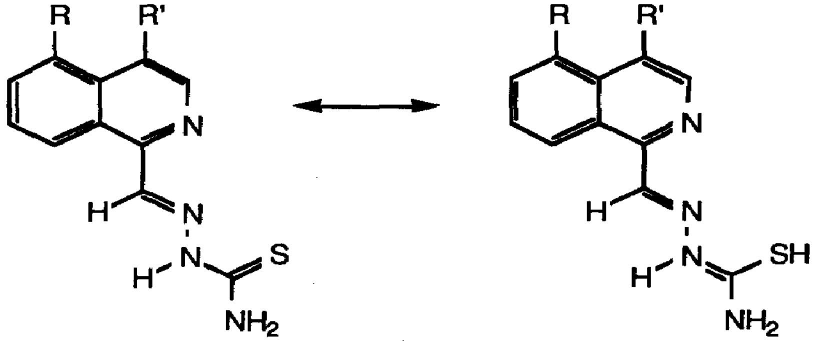
The ligand bpto, **(176)**, is tetradentate; its complex with Co(II), *viz.* [Co(bpto)$(H_2O)_2$] has been structurally characterised. The water molecules are *cis* to one another, and pertinent bond distances are Co-S = 2.467(1), 2.487(1)Å and Co-N = 2.146(3), 2.149(3)Å [482].



**(176)**

#### *3.3.8.2 Thioamides and related ligands*

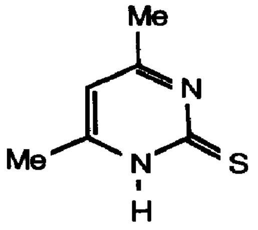
The preparation and physico-chemical characterisation of the complex [$CoL_2(H_2O)_2$]$Cl_2$ where L = 4-MeO-$C_6H_4$CH=NNHC(S)$NH_2$ has been reported. The anti-fugal activity of this compound has been tested and compared with that of related complexes containing different metal ions; toxicity depends upon the radius of the metal ion [483]. The effects on the anti-fungal activity of introducing a hydroxyl substituent onto the benzene ring of the same ligand, L, have also been explored [484]. Further interest in the fungicidal properties of Co(II)-thioamide complexes has been shown in an investigation of the complex $[CoL_2(H_2O)_2]$, where HL is the ligand $4\text{-Me-}C_6H_4NHC(S)NHBz$ [485]. Biological applications continue with the antitumor activity of the complexes $[CoL_2].2H_2O$ (HL = **(177)** ) and $[Co(HL')Cl_2]$ (HL' = **(178)** ) [486, 487]. Both complexes are water insoluble, and spectroscopic data imply a 6-coordinate structure for the former, red-brown complex, with L chelating through the azomethine-N and -S and through the isoquinoline-N atoms [486]; the latter, brown complex appears to be trigonal bipyramidal [487].



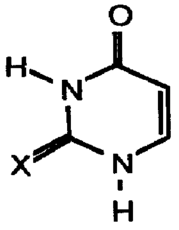
**(177)** R=R'=H; **(178)** R=$NH_2$, R'=Me

Stability constant data has been presented for the complex $[CoLCl_2]$ in which L = RHNPR'NR'C(S)NHR' (R = *o*-tolyl; R' = Ph or *o*-tolyl); infra red spectral results imply that L coordinates through the phosphazene-N and thiocarbonyl-S atoms [488].

Anhydrous cobalt(II) chloride or bromide reacts with HL, **(179)**, in dry acetone to give the blue complex $[Co(HL)_2X_2]$ which, it is proposed, contains tetrahedral $Co(HL_2)^{2+}$ units with N-S chelates. On standing, the compound first gains $H_2O$, and then is subject to oxidation to Co(III) but this latter process is dependent upon the counter ion; two complexes have been isolated, the pink compound $[Co(HL)_2X_2].2H_2O$, and the green *fac*-octahedral complex $[CoL_3]$ [489]. The mixed ligand complexes $[Co(gly)L_{NS}].H_2O$ and $[Co(gly)_2(L_N)_2].2H_2O$ (where $L_N$ is the ligand **(180)**, X = O, exhibiting a monodentate N-coordination mode, and $L_{SN}$ is **(180)**, X = S, and a chelating S-N mode); spectroscopic and magnetic moment data imply that the former complex is square planar, and that the latter complex is octahedral [490]. The grey-violet, tetrahedrally coordinated complex $[Co(mp)(OAc)(H_2O)]$ ( mp = **(181)**) has been prepared and characterised; interest in this species lies in its ability to act against the leukenine L-615 tumor system [491].

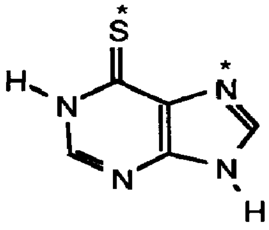


**(179)**



X = O or S

**(180)**

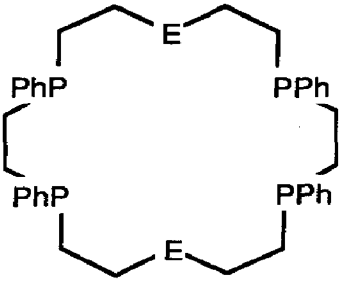


* ligation site

**(181)**

### 3.3.9 *Complexes with nitrogen-phosphorus donor ligands*

Only one piece of work is available to represent this section. The macrocyclic ligand, **(182)**, chelates to the cobalt(II) ion in a hexadentate fashion. A structural study of the $Ph_4B^-$ salt of the complex dication evidences *trans*-N atoms, with rather long Co-N bonds (2.629(12)Å); Co-P distances are 2.284(7) and 2.245(7)Å. The complex shows a large red shift, and this reflects a weak ligand field which may be attributed to the elongation of the octahedral ligand sphere along the N-Co-N axis; this distortion is also reflected in a magnetic moment of 2.26BM which is more in keeping with a square planar than with an octahedral Co(II) complex [493].



E = NPr; O; S

**(182)**

### 3.3.10 *Complexes with phosphorus donor ligands*

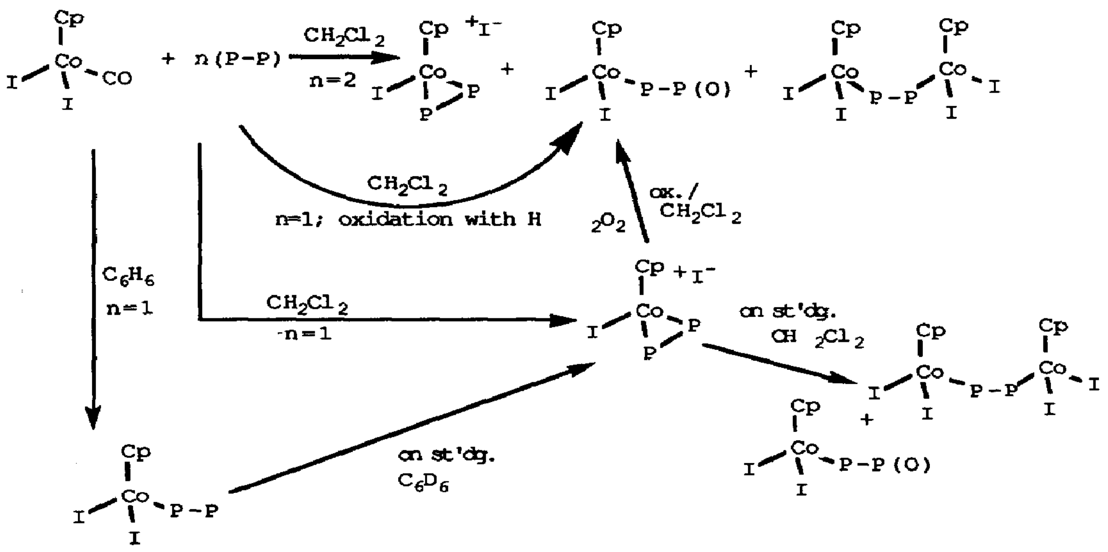
The chelation to cobalt(II) ions of several ligands of the type $Ph_2P(CH_2)_nPPh_2$ has been reported. A reinvestigation of the kinetics of the reaction:

$$\begin{tikzcd}
{[CpCo(dppe)X]^+ + P(OR)_3} \arrow[r, "k_1"] & {[CpCo(dppe)\{P(OR)_3\}]^{2+} + X^-} \arrow[d, "k_2"] \\
 & {[CpCo(dppe)\{P(O)(OR)_2\}]^+ + RX}
\end{tikzcd}$$

R = Me; Et

X = Cl; Br; I

has illustrated that the rate of reaction is influenced by the nucleophilicity of $X^-$ to a greater extent than had previously been thought; activation parameters for the reaction are given [494]. The following scheme:



summarises a detailed study of the self-reactivity of the complex ions [CpCo(P—P)I]$^+$, where P—P is $Ph_2P(CH_2)_nPPh_2$ (n = 1-4). The work provides an interesting survey of the factors which influence the modes of bonding of these bis-phosphine ligands; bridging and "dangling" ligands are observed, and conditions under which oxidation of a phosphine to a phosphoryl terminus occurs are reported. The relative stabilties of the complexes is discussed [495].

The reaction of cobalt(II) ions with borohydride in the presence of $Ph_2P(CH_2)_nPPh_2$ (n =2-6) or *cis*- or *trans*-$Ph_2PCH{=}CHPPh_2$, (L), leads to the complex [$CoHL_2$]. In the case of n = 4 and 5, an unusual dinuclear Co(I) complex, $[Co(BH_4)L]_2$ was isolated and structurally characterised; the two metal centres are held 2.869(1)Å apart by two bridging bis-phosphine ligands, and two bridging borohydride units [496]. The ability of phosphino ligands to produce dinuclear complexes is also exemplified by the formation of some cobalt(II) complexes involving the ligand eHTP, $(Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2$. Two equivalents of $CoCl_2$ react with eHTP to give [$Co_2Cl_4$(eHTP)], and an EXAFS study on the material suggests an open structure with no direct Co-Co bond. On standing, this complex loses $Cl^-$ to give a dication; the complex $[Co_2(CO)_4(eHTP)][CoCl_4]$ was also described, and X-ray analysis supported an open structure [497].

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

In this section, cobalt(II) and cobalt(III) complexes which incorporate coordinated dioxygen, peroxides, superoxides, or related ligands, are covered. Since the ligand types (i.e. other than $O_2$) in these complexes are so varied, no subsections have been allotted. However, the general sequence is from simple N- and O- donor ligand, to Schiffs bases, porphyrins and, finally, phthalocyanines. A review, with 220 references, which surveys the formation, stability, and properties of bridging-peroxo and bridging-superoxo complexes of cobalt has been presented [498].

Flash photolysis of the complex *cis*-$[Co(1,3\text{-}pn)_2(NO_2)_2]^+$ in the presence of dioxygen, produces a dinuclear cobalt(III) complex with a bridging superoxo moiety [499].

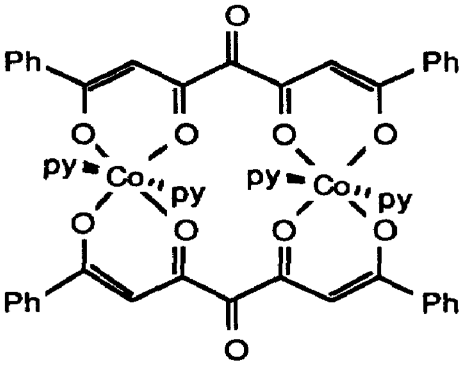
The results of a mechanistic study of the acid catalysed decomposition of $[(en)_2Co^{III}(\mu\text{-}O_2)(\mu\text{-}OH)Co^{III}(en)_2]$ suggest that reaction proceeds *via* attack by $H^+$ at the bridging hydroxyl group [500]. In an accompanying paper, the same authors explore the photoinitiated decomposition of $[(en)_2Co^{III}(\mu\text{-}O_2)(\mu\text{-}OH)Co^{III}(en)_2]$ to $[(Co^{II}(en)_2(H_2O)_2]^{2+}$ and $O_2$, and the thermally driven back reaction; continuous irradiation leads to an irreversible decompostion to $[(Co^{III}(en)_2(H_2O)_2]^{3+}$ [501].

The reaction of the complex ion $[Co(bipy)(H_2O)_4]^{2+}$ with $CH_3CH(NH_2)C(O)NHCH_2CO_2H$, $(H_2L)$, in the presence of $O_2$, gives $[\{Co(bipy)L\}_2(O_2)]$; spectroscopic and pH potentiometric studies on the product have been described [502]. The mechanism of oxygenation of a related complex has also been investigated [503]. Using a series of amino acids, $H_2L$, the oxygenation of complexes of type $[Co(bipy)(HL)(H_2O)_2]^+$ has been investigated; the authors find that increasing the chain length, and decreasing the degree of chain branching of the secondary amino acid lowers the stability of the product complex $[\{Co(bipy)L\}_2(O_2)]$ [504]. In the same series of papers, the formation of $[\{Co(bipy)L'\}_2(OH)(O_2)]^+$ and $[\{Co(bipy)L'(H_2O)\}_2(OH)]^+$ (L' = alanine, norvaline, norleucine or α-aminobutyric acid), have been described; equilibrium constants are reported [505].

The sequence of events which occurs when dioxygen is bubbled through a solution containing $[Co(ClO_4)_2].6H_2O$ and $H_2NC(S)NHNH_2$, has been explored mechanistically. Initially, free ligand oxidation is observed, and following this, Co(II) binds $O_2$; oxidation of Co(II) to Co(III) occurs only in aqueous medium [506]. For HL = $L$-$HSCH_2CH(NH_2)CO_2H$, reaction with aqueous cobalt(II) ions in the presence of $O_2$ leads to the formation of the complex $[L_2Co^{III}(O_2)Co^{III}L_2]$; the stability constant for this compound has bee determined [507].

Cobalt(II) and cobalt(III) complexes with edta take up dioxygen in solution at pH 9; the transient species so formed have been investigated [508].

The reaction of the β-polyketonate ligand $H_3dbaa$ (1,7-diphenyl-1,3,5,7-heptanetetraone) with cobalt(II) ions in py, and the product complex's subsequent oxidation with $O_2$, exemplifies some unusual chemistry. The initial complex is characterised as $[Co_2(Hdbaa)_2(py)_4]$; on dissolution in py in air, a product, (**183**), which exhibits a diagnostic, sharp carbonyl infra red absorption at 1695 $cm^{-1}$, is formed, and its structural elucidation shows that the 4-carbon of each β-polyketonate ligand has been oxidised [509].

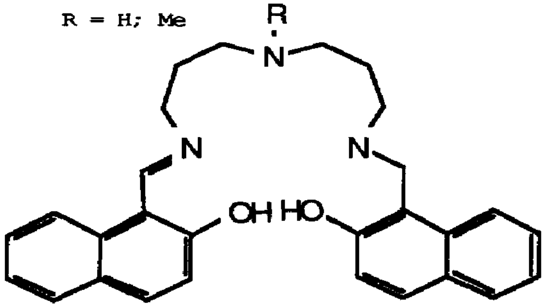


(**183**)

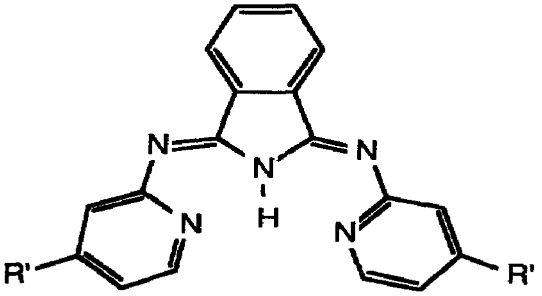
The oxidation of 2,6-di-$^t$butylphenol by $O_2$ is catalysed by several amine complexes of Co(II); a kinetic and mechanistic account of the reaction has been presented [510].

A comparative study of Co(III) and Rh(III) complexes as dioxygen carriers has been described [511], and comparisons between cobalt and ruthenium complexes have also been made [512]. In the latter piece of work, the kinetics of the exchange of free and coordinated RCOOH ( where R represents various alkyl and aryl substituents) in the complexes $[(AcO)_6Co_3(O_2)(HOAc)_3]$ were reported, and it was found that the rate of exchange depended on the structure of the carboxylic acid [512].

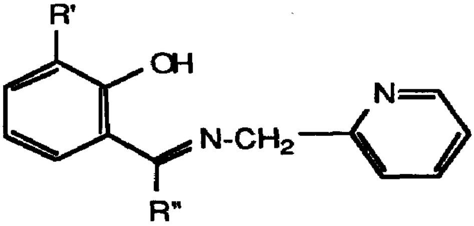
An unusual trinuclear complex, $[(py)_3Co_3(O)(OAc)_5(OH)]^+$, containing a $\mu_3$-O atom has been prepared and structurally characterised; the complex is the first example of an isolated oxo-centred Co(III) cluster, and may have significance as a catalytic precursor for aromatic hydrocarbon auto-oxidation. A related complex, $[(py)_3Co_3(O)(OAc)_6]^+$, was also prepared [513].



**(184)**



**(186)**



R' = R" = H

R' = H; R" = Et

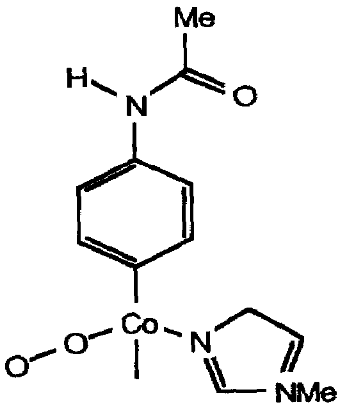
R' = OMe; R" = H

**(185)**

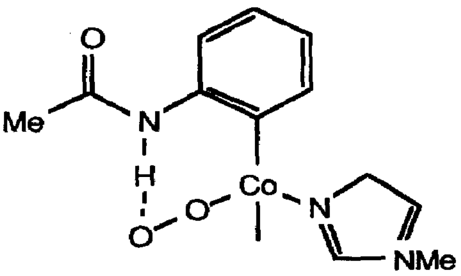
A variety of Schiff base complexes form $O_2$ adducts. The pentadentate ligand **(184)**, forms a complex with cobalt(II) which takes up dioxygen; the oxygenated complex has been studied by e.p.r. and it has been observed that the stability of the complex is strongly solvent dependent [514]. The ability of the complex formed from the reaction of cobalt(II) ions with the ligand $2-HO-C_6H_4NHC(CH_3)=CHC(O)CC_6H_5$ to absorb $O_2$ is greatly influenced by the presence of N-donors; in particular, it has been noted that amines inhibit dioxygen binding [515]. Dioxygen adducts of [Co(sal-H-pen)] and of the related complex formed with the *O*-methyl derivative of sal-H-pen, **(15)**, have been the subject of a resonance Raman spectroscopic study [516]. Complexes of type $[CoL_2]$, prepared from the Schiff bases HL, **(185)**, have been spectroscopically and magnetically characterised; they are high spin, octahedral, and a *mer*-geometry is proposed for each complex. Their reaction with $O_2$ has been described [517]. The complexation with Co(II) of ligands related to **(185)** has been described in an independent paper; the relative abilities of these complexes to take up $O_2$ have been discussed [518]. A study which covers a range of cobalt(II)-Schiff base complexes and their dioxygen adducts, assesses how the electronic and steric factors of the ligands influence the catalystic activity of the $Co-O_2$ species; the catalytic behaviour appears to follow trends in the basicity of the bound oxygen molecule [519]. Other Schiff base complexes have been investigated with respect to their ability to bind $O_2$ [520].

The synthesis, reactivity, and catalytic properties of some cobalt(III) alkylperoxy complexes have been described; one complex, $[LCo(O_2R)(R'CO_2)]$ where L = **(186)**, has been structurally elucidated and exhibits the three N-donor atoms of L defining one face of the octahedral donor set [521].

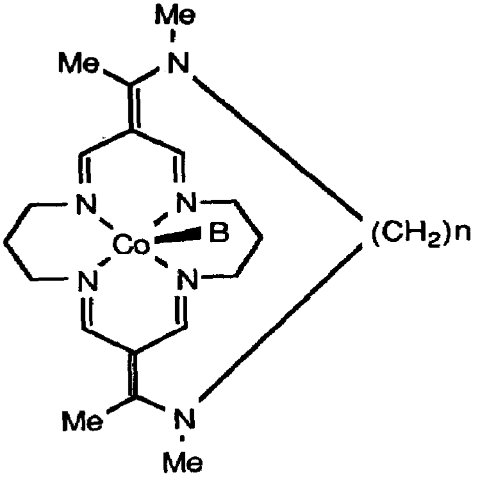
The position of the -NHCOMe substituent in the $Co-O_2$ model compounds represented schematically by structures **(187)** and **(188)** has been shown to have a significant effect upon the freedom of the bound $O_2$ molecule. In **(188)**, hydrogen-bonding between the -NHCOMe group and the bound dioxygen is sterically allowed, and as a result, no motional averaging of the e.p.r. spectrum is observed; however, in **(187)**, spectral data evidence rotation of the $O_2$ unit about the Co-O bond, a phenomenon which is possible when hydrogen bonding is sterically prohibited [522].



**(187)**



**(188)**



B = axial base

n = 3–8

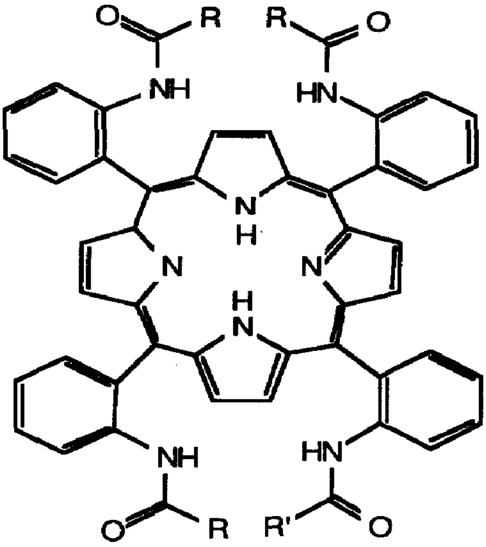
**(189)**

The formation of oxygen adducts with complexes of the type shown by **(189)** have been prepared and studied by $^{13}C$ n.m.r. spectroscopy; the latter technique has been developed as a method of quantifying the steric contraint of the polymethylene bridge [523].

The preparation and structure of the alkylperoxycobaloxime, $[(Hdmg)_2Co\{O-O-C(Me)CH=CHCO_2Et\}]$ has been described; the synthesis involves dioxygen insertion into a Co–C bond. Pertinent bond lengths in the product cobaloxime are Co-O = 1.923(4)Å, O-O = 1.415(7)Å, and $Co-N_{oxime}$= 1.896(3)Å [524].

It has been noted that the adsorption of cobalt porphyrins on electrode surfaces causes significant perturbation of their electrode potentials, and influences their ability to catalyse the reduction of $O_2$ to $H_2O_2$ [525].

When dissolved in oxygen saturated 2-methyl-thf, [Co(TPP)] forms an $O_2$-adduct; the photoinduced dissociation of the $O_2$ molecule is facile [526]. In dmso, the tetra-*p*-tolylporphyrin complex of Co(II), [Co(TPTP)], shows a red shift in the visible spectrum as it reacts with the $O_2^-$ ion to form $[Co(TPTP)(O_2)]^-$; this complex releases $HO_2^-$ to give $[Co(TPTP)]^+$, which, is able to oxidise $O_2^-$ to $O_2$, thereby completing a catalytic cycle to [Co(TPTP)] [527]. When the complex $[Co^{III}(TMPyP)]$ (TMPyP = tetra-*p*-methylpyridylporphyrin ) undergoes a one electron reduction in solution, the product Co(II) complex is able to catalyse the reduction of $O_2$ to $H_2O_2$ [528]. The same cobalt(II) complex has independently been shown to catalyse the reduction of $O_2$ by $[Ru(NH_3)_6]^{2+}$ [529]. In aqueous solution, $[Co(TMPyP)(H_2O)_2]I_4.4H_2O$ has been prepared and spectroscopically characterised; the oxygen carrying capability of the complex have been discussed [530]. The complex ion $[Co(TMPyP)(H_2O)_2]^{4+}$ has also been used in the electrochemical reduction of $O_2$; a mechanism for the process is proposed [531]. The porphyrin ligand, $H_2L$, **(190)**, forms a 1:1 complex with cobalt(II) ion; this species reacts with dioxygen, and its affinity for the diatomic molecule is enhanced by the presence of the protic substituent which is able to participate in intra-molecular hydrogen-bonding to $O_2$ [532]. Five- and six-coordinate complexes of Co(II) with thiolate substituted porphyrins have been characterised; the oxygen binding ability of these species are discussed [533].



R = $CH_2{}^tBu$

R'= $CH_2OH$;
$(CH_2)_nC(O)NH_2$
n=1,2;
2-HO-$C_6H_5$

(190)

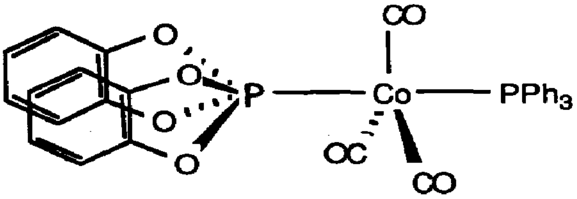
Resonance Raman spectroscopic studies have been described for some dioxygen adducts of porphyrin cobalt(II) complexes [534]. The effects of thiolato and some nitrogen-based ligands, L, on $v_{O-O}$ in complexes of type [Co(TPP)L($O_2$)] have also been examined [535].

For $H_2L$ being phthalocyanine, the complex [CoL] interacts with the nitrogen atom of a pyridine, which is itself bound to a surface of modified inorganic silica fibres; dioxygen reversibly coordinates to the now anchored cobalt centre, and e.s.r. and electronic reflectance spectra have been used to investigate the bonding modes at the surface [536]. The quantitative electrochemical reduction of $O_2$ to $H_2O_2$ is catalysed by the complex [Co(TCPc)], where TCPc is 4,4',4'',4'''-tetracarboxyphthalocyanine; mechanistic details are discussed for this reaction [537].

## *3.5 COBALT(I)*

The complex [Co{N($CH_2CH_2PPh_2$)$_3$Br] has been prepared and structurally characterised; the tripod-like ligand is interesting, because by 'breathing' out, it is able to take the N-atom out of the coordination sphere. In this case, the complex is tetrahedral, and Co---N is 3.34(1)Å, i.e. non-bonding. A qualitative MO discussion reveals that it is symmetry forbidden to bring in the N-atom to form a trigonal bipyramidal complex [538].

The metallophosphorane, **(191)**, is prepared from the reaction of $(C_6H_5O_2)_2PCl$ with $[Co(CO)_3(PPh_3]^-$ in thf at -78°C; spectroscopic and structural characterisations of the complex have been presented, and the $Co-P_{phosphorane}$ distance as longer than the $Co-P_{phosphine}$ bond length [539].



**(191)**

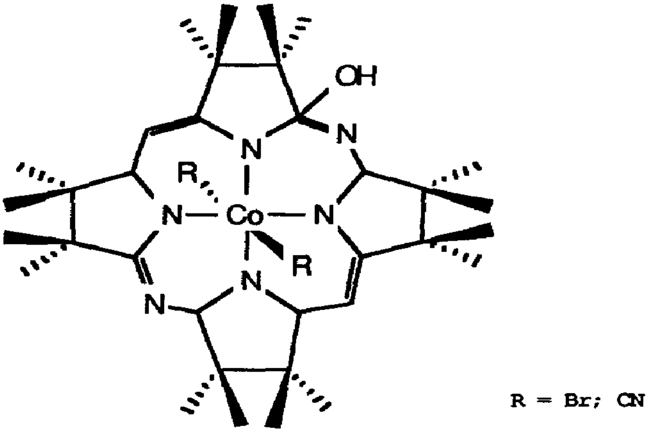
A study, using pulse radiolysis, of some cobalt(I) polypyridine complexes has provided information about the kinetics and thermodynamics of their substitution reactions in aqueous solution; the ligands reported are bipy based [540]. The same authors have discussed more generally the photogeneration of, and the reactivity of, Co(I) complexes [541], and have described in detail, the reduction of $CO_2$ by $[Co^I(bipy)_3]$ [542].

A series of two papers has described reduction reactions involving vitamin $B_{12r}$ and vitamin $B_{12s}$; the first, looks at the reduction of the Co(III) complexes $[Co(NH_3)_5X]^{n+}$ where X = Cl, Br, I, NCS, pyrazine, or $N_3$ [543], and the second piece of work deals with the reductions of the oxyhalogens $BrO_3^-$, $IO_3^-$ and $ClO_2^-$,[544].

The kinetics of the dealkylation by $[PtCl_6]^-$ in acid medium of methylcobalamin, $(Me-B_{12})$, have been investigated; the reaction is first order in $Me-B_{12}$, and there is a hyperbolic dependence of the rate on $[PtCl_6]^-$. The mechanistic implications of these results are discussed [545]. An accompanying paper described a monomer-dimer equilibrium for:

$$2\ Me-B_{12} \rightleftharpoons (Me-B_{12})_2$$

Whether or not the solution is buffered, is found to have no effect on the equilibrium constant for the above process [546]. An X-ray investigation of methylcobalamin has shown that the structure is similar to that of cyanocobalamin; the fold angle of the corrin ring is 15.8°, and important bond lengths are Co-$C_{methyl}$ = 1.99(2), Co-$N_{bzm}$ = 2.19(2), Co-$N_{equ.}$ = 1.88(2), 1.97(2), 1.93(2) and 1.89(2)Å [547]. The 5-coordinate organo-cobalt complex, [Co(saloph)R], in which $H_2$saloph = disalicylidene-o-phenylenediamine, has been used as a model for vitamin $B_{12}$; a structural study has been used to probe reasons for the thermal stability of such species [548].



**(192)**

During the electrochemical or chemical reduction of the complex (**192**), intramolecular transfer of electrons between metal and macrocycle has been evidenced; the product cobalt(I) complex has been spectroscopically and structurally characterised, and the metal atom is found to be approximately coplanar with the four N-atoms [549].

### 3.6 *COBALT(0)*

The compounds included in this section have been chosen with the coordination chemist in mind. Since neither organometallic compounds nor cluster species are reported in this review, it necessarily follows that the vast majority of cobalt(0) compounds have been omitted.

The first example of a fully characterised, paramagnetic cobalt(0) dimeric complex has appeared in this year's literature. The compound, $[(CoL)_2(\mu\text{-}N_2)]$, where L is $MeC\{CH_2PPh_2\}_3$, has an $N_2$ moiety bonded between two CoL fragments, each L being $\mu_3$ with respect to the metal; Co-N = 1.76(1), Co-P = 2.160(6)-2.168(6), N-N = 1.18(2)Å [550].

The reaction of hydrated $CoCl_2$ with $Ph_2PH$, NaOMe and CO in methanol yields the complex $[(Ph_2HP)(CO)_2Co(\mu\text{-}PPh_2)_2Co(CO)_2(PHPh_2)]$ which, on heating, loses 2 moles of CO; X-ray analysis of the former complex shows a puckered square $Co_2P_2$ unit (internal dihedral angle = 153.3°) [551]. Finally, e.s.r. data has been presented for the radical anion $[Co_2(CO)_2(\mu\text{-}L)_3]^-$ where L is the bidentate ligand, $F_2PN(Me)PF_2$ [552].

### 3.7 *THEORETICAL INVESTIGATIONS*

Papers discussing cobalt coordination chemistry from a theoretical standpoint are gathered briefly into this section.

Molecular mechanics force field modelling of the complexes $[Co(NH_3)_6]^{2+}$ and $[Co(dien)_2]^{2+/3+}$ includes in its discussion a comparison of the relative energies of the possible conformers of $[Co(dien)_2]^{2+/3+}$ and their dependence on the metal's oxidation state [553].

CNDO/2 calculations have been performed on the ligand (**164**) [437], on the complexes $[Co(TPP)X_2]$ to investigate the relative effects of a wide variety of axial ligands, X [199], and on tetraza-macrocyclic complexes such as $[Co\{14\text{-hexaen-}N_4\}]$ [554].

MNDO calculations have been used to construct energy profiles for ring closure reactions which involve vitamin $B_{12}$ as a cofactor [555]. PNDO calculations have been applied to the octahedral complexes $[Co(NH_3)_5L]^{n+}$ and $[Co(CN)_5L]^{n+}$ (L = $H_2O$, $NH_3$, $CN^-$, $OH^-$, $NO_2^-$, $Cl^-$) and the results related to electronic spectra [556].

The PRDDO method of calculation has been used on the model complexes $[Co(NH_3)_4(CO)_2]^{3+}$ and $[Co(NH_3)_2(CO)_4]^{3+}$ in order to show that, for cobalt(III), back bonding does not stablise the *cis*-isomers of these complexes in the same way as it does when the metal is Cr(0) or Mn(I); *cis-trans*-isomerism is also discussed [557]. PRDDO calculations have also been applied to a model coenzyme $B_{12}$ system; the effects on Co-C overlap population of angular distortion and steric crowding within the molecule have been examined with a view to understanding those factors which result in initialisation of homolytic bond activation in relevant enzymic processes [558].

Finally, extended Hückel MO calculations performed on complexes of glyoxime ligands have compared Co(II) complexes with those of Fe(II), Ni(II), and Cu(II) [559].

### *3.8 $^{59}$Co NMR STUDIES*

$^{59}$Co n.m.r. spectroscopy features in several works. A correlation between $^{59}$Co n.m.r. shifts and ligand field parameters for octahedral Co(III) complexes has been discussed [560].

Ligand substitution reactions of the cobalt(III) complexes, *cis*-$[CoL_2Cl_2]Cl$, (where L = bipy or phen, and using incoming ligands $NO_2^-$, $SO_3^{2-}$, $NCS^-$ and thiourea) have been investigated, using $^{59}$Co n.m.r. spectroscopy to establish the mode of ligand coordination [561]. $^{59}$Co n.m.r. spectroscopy has been applied to the complexes $[Co_2(RR'dtc)_5]$, described earlier in this review [70]. The same authors have discussed in detail the $^{59}$Co n.m.r. spectra of 37 dithiocarbamate containing cobalt(III) derivatives; the shift range is from δ 5990 for $[Co\{^nBu^tBu(dtc)\}_3]$ to δ 7200 for $[Co\{pyrr(dtc)\}_3]$, and peak widths vary significantly as a function of the symmetry about the Co atom, ($W_{1/2}$ is from 400 to 2800 Hz) [562].

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