ELSEVIER

Coordination Chemistry Reviews
169 (1998) 237–361

COORDINATION CHEMISTRY REVIEWS

Cobalt 1995

Michael B. Davies *

Applied Sciences, Anglia Polytechnic University, East Road, Cambridge, CB1 1PT, UK

Contents

Introduction

This is the last of this series to appear in the present form. The benefit of general reviews of this type becomes obvious in the preliminary sorting of the references for

* E-mail: mdavis@bridge.anglia.ac.uk

PII S0010-8545(98)00008-3

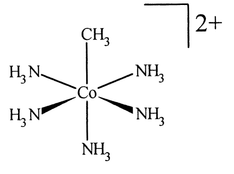
this review. The number of papers published on cobalt chemistry each year is reasonably consistent at around 5000; the number of papers per year in coordination chemistry may be around 500 or 600. As in previous years, the review does not contain information on cluster compounds, though this also remains a favourite area of research. Also, as usual, organometallic compounds are excluded. The literature was largely searched electronically. It is inevitable that in the above process a number of papers are left out of the review, and the author apologises in advance to those whose papers have not been included, for whatever reason. The structure of the review remains similar to that of previous papers in this series with the compounds being broadly classified according to the donor atoms occupying the majority of sites around the metal ion [1]. Various reviews have been published which are of interest to cobalt coordination chemists. There is the usual Annual Report of the Royal Society of Chemistry on inorganic mechanisms [2], which contains a wealth of information on the mechanisms of reactions many of which involve cobalt. Information on the kinetics of cation macrocycle interactions has been accumulated [3]. The uses of pressure in the investigation of the rates of inorganic reactions in solution have been reviewed [4,5].

1. Cobalt(III)

It is remarkable that the study of the reactions of cobalt(III) has held the interest of chemists throughout this century and continues to result in papers in very large numbers, but also, and more importantly, of high quality and immense variety.

1.1. Complexes with nitrogen donor ligands

As in previous years, the majority of the studies of cobalt(III) complexes have been on those involving ligands which are nitrogen donors and within this group there is a large number of complexes with ammine and amine ligands. A most interesting development in the chemistry of simple coordination compounds of Co(III) is that the complex $[Co(NH_3)_5(CH_3)]^{2+}$ (**1**) which is isoelectronic with the very well-known $[Co(NH_3)_6]^{3+}$ [6] and has now been prepared as the nitrate salt by the reaction of $Co(NO_3)_2.6H_2O$ with methylhydrazine in 25% aqueous ammonia at 20 °C in the presence of dioxygen. The crystals produced from this reaction were



(1)

orange and were stable for some months at 4 °C over silica gel. As well as elemental analysis, the complex was characterized using a variety of techniques, including ^{13}C and ^{59}Co NMR spectroscopy. The former gave a single broad signal at δ 3.2 ppm and the latter a very broad band at δ 7370 ppm. The UV–VIS spectrum measured in 5.0 M ammonia solution had bands at $\lambda_{max}=358$ nm (128) and 481 nm (50). As might be anticipated, the spectra of the two isoelectronic species $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5(CH_3)]^{2+}$ turn out to be very similar. The NMR spectra indicate clearly the presence of a Co–C σ-bond in the complex.

In a study of the effect of a condensed tetrabutylammonium film on the reduction of the hexaamminecobalt(III) ion at the water mercury interface, the reduction process was found to be inner sphere [7]. The conclusion drawn by the authors from this is that the mechanism of the this process must involve the opening of the film to allow the cation access to the mercury. However, an outer sphere mechanism is proposed when Br^- is the counter ion. The effect of varying the temperature on the conductivities of solutions containing $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ ions with SO_4^{2-} ions as counter ions shows that second as well as first ion association constants have to be taken into consideration [8] to explain the data satisfactorily. The overall influence of temperature is explained in terms of the effect of temperature variation on the bulk structure of water, with the effects of hydrogen bonding being particularly important.

A kinetic study of the reduction of $[Co(NH_3)_5(H_2O]^{3+}$ by L-ascorbic acid has been shown to involve the complex $[Co(NH_3)_5(OH)]^{2+}$ [9]. The rate law for the reaction was determined to be that shown in Eq. (1). The mechanism for the reaction for which this rate law is appropriate is shown in Eq. (2). The value of k_4 was determined to be 2.7×10^2 dm^{-3} mol^{-1}s^{-1} at 25 °C.

$$\frac{\mathrm{d}(complex)}{\mathrm{d}t}=\frac{\{(k_3[\mathrm{H}^+]+k_4K_{\mathrm{a1}})K_{-2}[A]_{\mathrm{T}}[complex]_{\mathrm{T}}\}}{\{([\mathrm{H}^+ +K_{-\mathrm{a1}})([\mathrm{H}^+]+K_{-2})\}}, \tag{1}$$

$$\mathrm{H_2A} \xrightleftharpoons{K_1} \mathrm{HA^-} + \mathrm{H^+HA^-} \xrightleftharpoons{K_2} \mathrm{A^{2-}} + \mathrm{H^+} \tag{2}$$

$$[(\mathrm{NH_3})_5\mathrm{Co(H_2O)}]^{3+} \xrightleftharpoons{K_3} [(\mathrm{NH_3})_5\mathrm{Co(OH)}]^{2+} + \mathrm{H^+}$$

$$[(\mathrm{NH_3})_5\mathrm{Co(H_2O)}]^{3+} + \mathrm{HA^-} \xrightarrow{k_1} \mathrm{Co(II)} + \mathrm{radical}$$

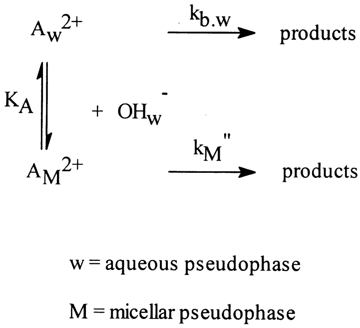
$$[(\mathrm{NH_3})_5\mathrm{Co(H_2O)}]^{3+} + \mathrm{HA^-} \xrightarrow{k_2} \mathrm{Co(II)} + \mathrm{radical}$$

$$[(\mathrm{NH_3})_5\mathrm{Co(OH)}]^{2+} + \mathrm{HA^-} \xrightarrow{k_3} \mathrm{Co(II)} + \mathrm{radical}$$

$$[(\mathrm{NH_3})_5\mathrm{Co(OH)}]^{2+} + \mathrm{A^{2-}} \xrightarrow{k_4} \mathrm{Co(II)} + \mathrm{radical}$$

$$\mathrm{Co(II)} + \mathrm{radical} \xrightarrow{\text{fast}} \text{product2 radicals} \xrightarrow{\text{fast}} \text{product.}$$

The base hydrolysis of the complex $[Co(NH_3)_5Cl]^{2+}$ has been studied in aqueous solution containing mixed micelles [10]. The micelles used in the mixture were sodium dodecyl sulphate (SDS) and non-ionic *n*-dodecylpenta(oxyethylene glycol) monoether over a range of molar fractions of SDS. The rate constants were found to decrease with increasing surfactant concentration and molar fraction of SDS. The mechanism of the processes involved may be summarized as in (**2**).



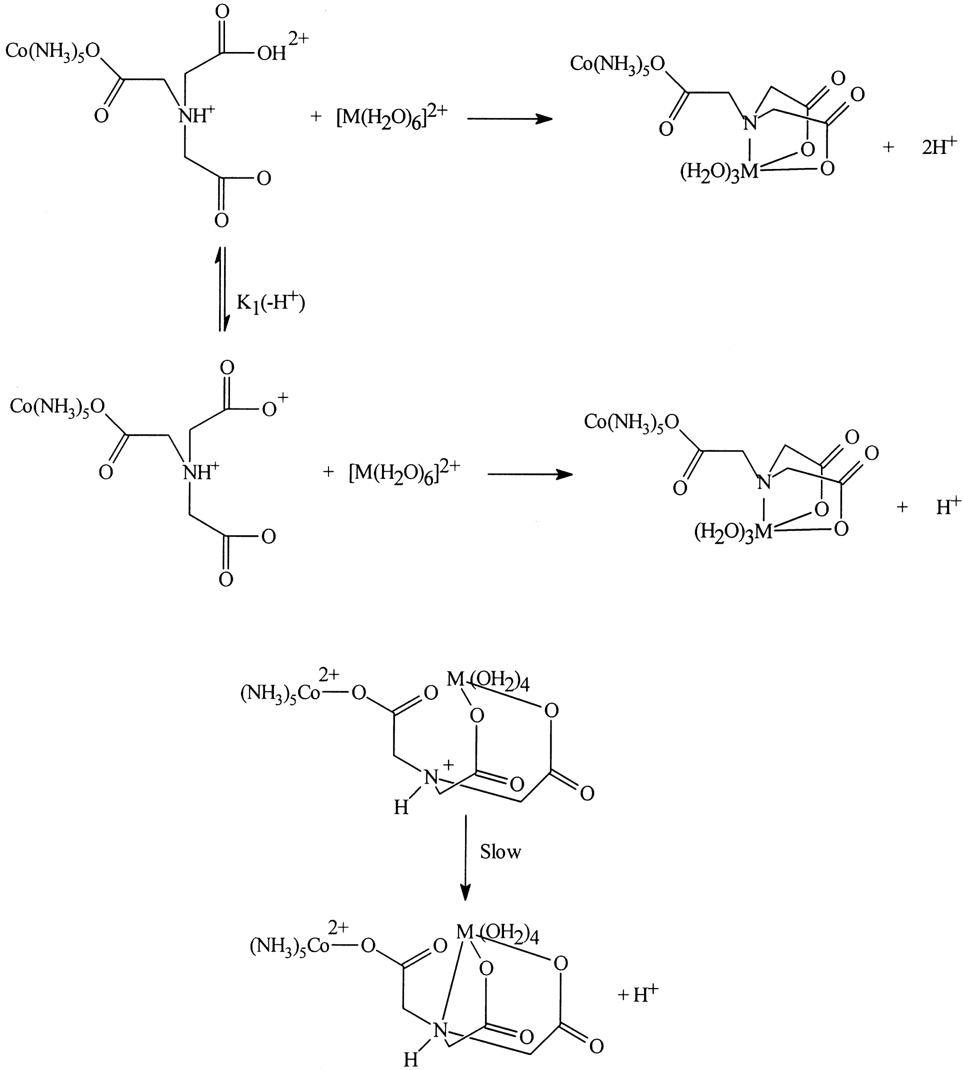
(2)

The binding fraction of the complex cation was found to diminish with decreasing SDS molar fraction. The effect ion pairing on the kinetics of the aquation [11,12] and of solvent effects on the photolysis [13] of $[Co(NH_3)_5Br]^{2+}$ have been studied, as have the effects of solvent on the base hydrolysis of $[Co(tetren)(O_2CC_6H_4OH\text{-}2)]^{2+}$ and $[Co(tetren)(O_2CC_6H_4OMe\text{-}2)]^{2+}$ [14,15]. The kinetics of reactions between a series of metal ions, Ni(II), Co(II), Fe(II), Al(III) and Fe(III) with complexes $[Co(H_2ida)(NH_3)_5]^{3+}$, $[Co(Hida)(NH_3)_4]^{2+}$, $[Co(H_2nta)(NH_3)_5]^{2+}$ $[Co(Hox)(NH_3)_5]^{2+}$, and $[Co\{O_2CC_6H_3(OH)\text{-}2,(NO_2\text{-}3)(NH_3)_5]^{2+}$ have been investigated [16–19]. Thus, the complex pentaammine(nitriloacetato)cobalt(III) has been found reversible to form complexes with the ions Ni(II), Co(II) and Cu(II) and also complexes with Al(III) and Fe(III) ions [19]. With bivalent metal ions the rate law for the process is given in Eq. (3) where k_f and k_d are the formation and dissociation rate constants, respectively. These, in turn, are given by the equations shown in Eq. (4). The proposed mechanism for the reaction is that shown in (**3**). For the trivalent metal ions, however, the processes involved are as shown in (**4**). The rate determining step in the reaction is believed to described by the reactions in (**5**).

$$k_{obs} = k_f[M^{2+}] + k_d, \tag{3}$$

$$\left.\begin{aligned} k_f &= \frac{\{k_1([H^+/K_1\}}{(1+[H+])/K_1} \\ k_d &= k_{-1}[H^+]^2 + k_{-2}[H^+] \end{aligned}\right\}. \tag{4}$$

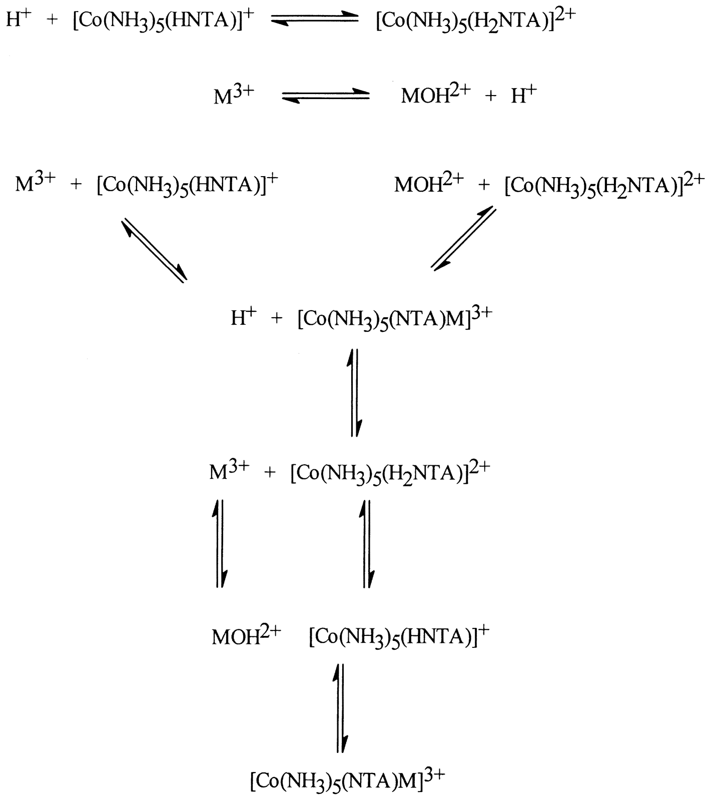
The solution kinetics of the reaction of iminodiacetato(pentaammine)cobalt(III)



(3)

and iminodiacetato(tetraammine)cobalt(III) with Co(II) ion were also investigated using stopped-flow spectrophotometry [16] at various pH values. It was possible to obtain the rate constants for both the formation and dissociation of the binuclear species and these are interpreted in terms of an I_d mechanism.

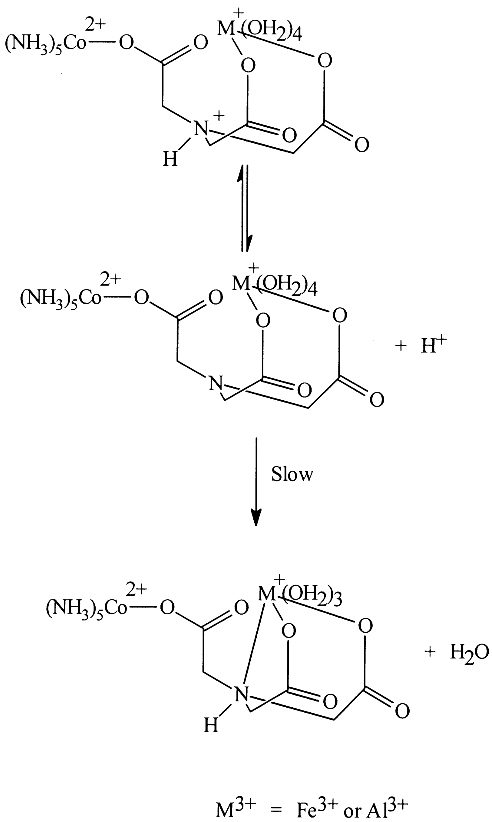
A photochemical study at pH 3.2 of solutions of the complexes $[Co(NH_3)_4(HC_2O_4)](ClO_4)_2$ and $[Co(NH_3)_4(C_2O_4)](ClO_4)$ has been carried out in mixtures of ethylene glycol and water with incident radiation of various wavelengths



(4)

[20]. The results show that there was a significant increase in quantum yield with increasing ethylene glycol concentration. The *p*-*p*- and *o*-*o*-dimers of *o*-phenylphenol and Co(II) have been found to be the main products of the photolysis of $[Co(NH_3)_5N_3]^{2+}$ in the presence of *o*-phenylphenol [21]. Flash photolysis shows that $N_3^{\cdot}$ and $OPP^{\cdot}$ radicals are present as intermediates in the process.

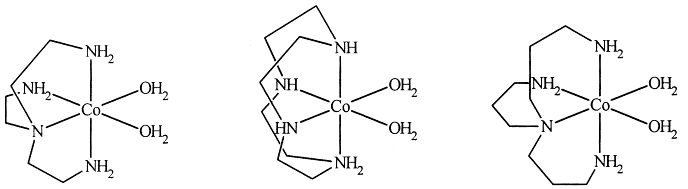
The factors affecting the chelation of carboxylates to *cis*-diaquacobalt(III) complexes have been the subject of investigation for many years. In a recent study, the equilibrium constants for the chelation of a number of carboxylates to cobalt(III) complexes containing a variety of tetraamine ligands (**6**) have been studied in different solvents [22]. As an example of the type of situation that arises, it was found that for each of the complexes in (**6**), NMR spectroscopic data show that the acetate forms chelates with Eqs. (1) and (2), but not with (**1**), where a monodentate complex is formed. The reactions were found to be greatly influenced by such features as the structure of the tetraamine ligand, its basicity and the nature of the solvent. In the case of the tetraamine ligands, a significant factor was found to be



(5)

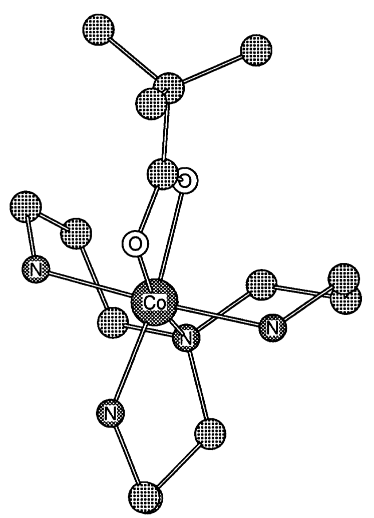
the value of the N–Co–N bond angle which lies opposite to the O–Co–O bond angle in the various complexes. In addition, there was found to be a relationship between the facility for chelation and the reactivity of the complexes in enhancing the hydrolysis of esters, amides, nitriles and phosphates. As part of this study, the X-ray crystal structure of the complex $[(trpn)Co(\eta^2\text{-}O_2CC(CH_3)_3](ClO_4)_2$ was also determined, the cation of which is shown in (**7**).

The rate of tritium exchange from the C-2 position of the imidazole in the complexes $[Co(NH_3)_5[2\text{-H-3}]\text{-imidazole}]^{3+}$ and $[Co(NH_3)_5\text{-1-methyl-}[2\text{-H-3}]\text{-imidazole}]^{3+}$ (**8**) as a function of pH has been determined and it is shown that the reactions of both species involve a rate-determining attack by OH^- [23]. The mechanisms proposed for the tritium exchange in these complexes are shown in (**9**). The rate law for the Me-substituted complex is found to be as given in Eq. (5) giving the expected linear dependence of rate on $[OH^-]$. The rate versus pH profile for the protonated complex is more complicated in that an S-shaped curve is found



1 **2** **3**

(6)



(7)

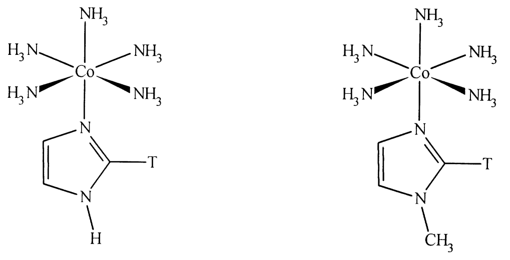
over the pH range 7.77–10.46. This is shown to agree with the rate law (Eq. (6)).

$$k_{obs} = k^{M+}[OH^-], \tag{5}$$

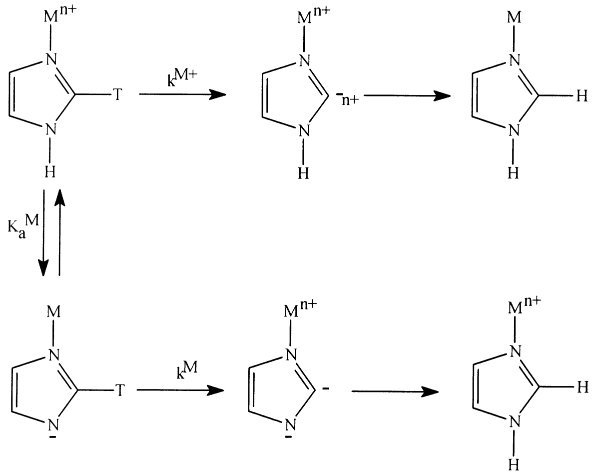
$$k_{obs} = \frac{(k^{M+}K_w + k^M K_a^M[OH^-])}{(K_a^M + [H^+])}. \tag{6}$$

The effect of complexes of the type $[H(Gyl)_nOCo(NH_3)_5]^{2+}(n=1–4)$ on acyl transfer reactions which are catalysed by α-chymotrypsin has been investigated [24].

The reduction of complexes of the form $[Co(N_5)(H_nPO_4)]^{n+}$, in which N_5 represents $(NH_3)_5$, $(NH_2Me)_5$ or 19-amino-10-methyl-1,4,8,1-2 tetraazocyclopentadecane by $[Fe(CN)_6]^{4-}$ is outer-sphere and the kinetics of the reaction have been studied as a function of temperature and pressure [25]. The mechanism for this type of



(8)



(9)

reaction is given in (**10**). The experimental data support this rate law and are shown consistency to fit Eq. (7). It was, thus, possible to differentiate between the formation of the encounter complex and the rate constant for the electron transfer process. Rather surprisingly, considering the fairly large variation in charge for these species, there was little change in the ion-pair formation constant. The electron transfer rate constant was found to increase with increasing size of the monodentate amines, other things being equal, but by the same token the introduction of the macrocyclic ligand resulted in a significant decrease in the electron transfer rate constant. The variation of the activation parameters is concluded to indicate important changes in hydrogen bond formation behaviour in the production of the transition state.

$$[Co\{N_5\}(H_nPO_4)]^{n+} + [Fe(CN)_6]^{4-} \underset{}{\overset{K_{os}}{\rightleftharpoons}} \{[Co\{N_5\}(H_nPO_4)]^{n+}.[Fe(CN)_6]^{4-}\}$$

$$\{[Co\{N_5\}(H_nPO_4)]^{n+}.[Fe(CN)_6]^{4-}\} \xrightarrow{k} \{[Co\{N_5\}(H_nPO_4)]^{(n-1)+}.[Fe(CN)_6]^{3-}\}$$

$$\{[Co\{N_5\}(H_nPO_4)]^{(n-1)+}.[Fe(CN)_6]^{3-}\} \xrightarrow{\text{fast}} \text{products}$$

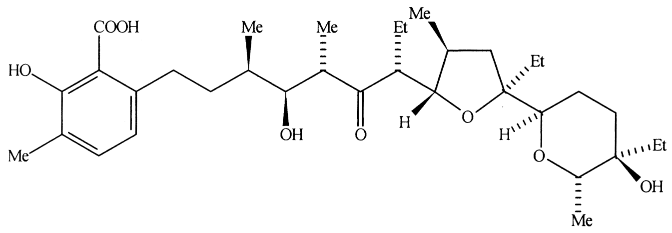
(10)

$$k_{obs} = \frac{kK_{os}[Fe(CN)_6^{4-}]}{\{1 + K_{os}[Fe(CN)_6^{4-}]\}}. \qquad (7)$$

Eighty-five new compounds involving a number of transition metals, of which $[CoL_x][Ln(dipic)_3] \cdot nH_2O$ (where dipic is pyridine-2,6-carboxylate and L is ammonia, urea or various amines), is one have been synthesized [26]. The X-ray crystal structure of $[Co(sar)][Eu(dipic)_3] \cdot 13H_2O$ has been determined and it has the monoclinic space group $P2_1/n$ and $a = 10.611$, $b = 26.500$, $c = 17.583$ Å and $Z = 4$. Mono(N-ethanediamine) and mono(N-benzylethanediamine) complexes of Co(III), in which the other four ligands were either NH_3 or CN^- have been prepared [27]. The NMR spectra of these complexes show that the Me and Ph groups are anti with respect to the central metal ion in the most favoured conformation. The crystal structure of $[Co(NH_3)_4(N\text{-benzylethanediamine})](NO_3)_3 \cdot 1.5H_2O$ showed that it belonged to space group $P2_1$ with $a = 8.639$, $b = 21.240$, $c = 10.897$ Å and $\beta = 94.11°$ with $Z = 2$.

The low-temperature EPR spectra measured at various temperatures below 77 K of $Co(en)_3CuCl_5 \cdot H_2O$ single crystal have been studied [28]. The structure of the crystal is such that it contains layers of the ion $[Cu_2Cl_8]^{4-}$ which are parallel to the *ab* crystal plane. These layers are separated by $[Co(en)_3]^{3+}$ ions which are, of course, diamagnetic. The results show that the Cu(II) ions in the crystal are antiferromagnetically coupled in the dimer giving singlet-triplet splitting with $2J_0 = -14.8$ cm^{-1}. Also superexchange coupling between dimers in the next layers was found to be given by $J_1 = 0.00712$ at about room temperature, becoming 0.00325 at about 100 K. Below this temperature there is no further change with variation of temperature. Carrier mediated transport of *cis* and *trans* diamminebis-(ethane-1,2-diamine)cobalt(III), $[Co(en)_2(NH_3)_2]^{3+}$, across a chloroform membrane by lasalocid A, a natural carboxylic acid ionophore (**11**), showed that the *trans* complex was more readily transported under the same conditions than was the *cis* species [29]. The ratio of *cis*:*trans* in the new phase was found to be 1:3 after about 24 h.

The photolysis of *cis*-(benzimidazole)(chloro)bis(ethylenediamine)cobalt(III) complexes in aqueous solution yields Co^{2+} and Cl^- as the primary products [30].

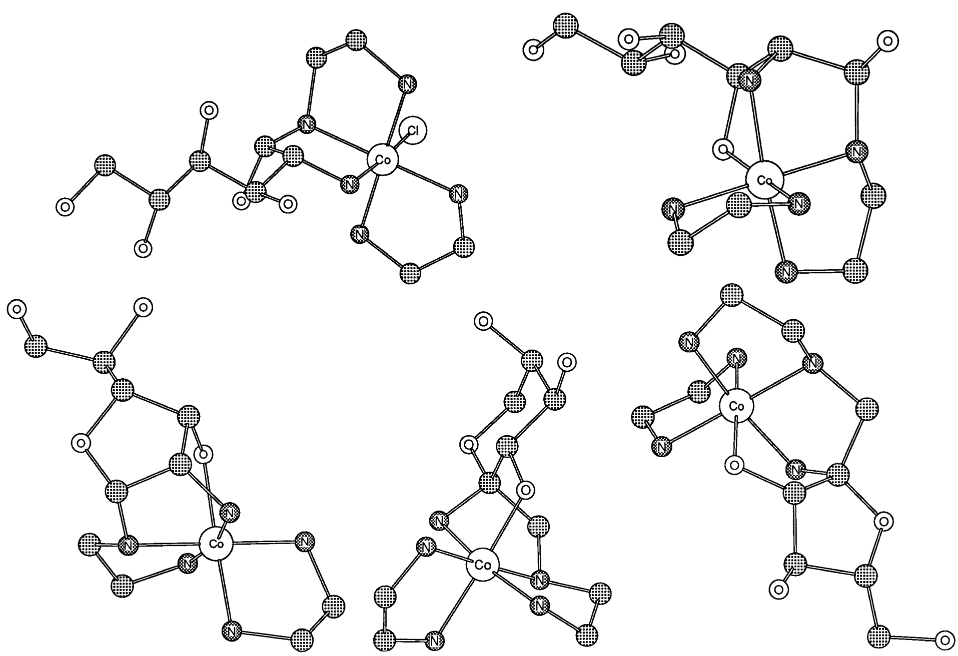


lasalocid A

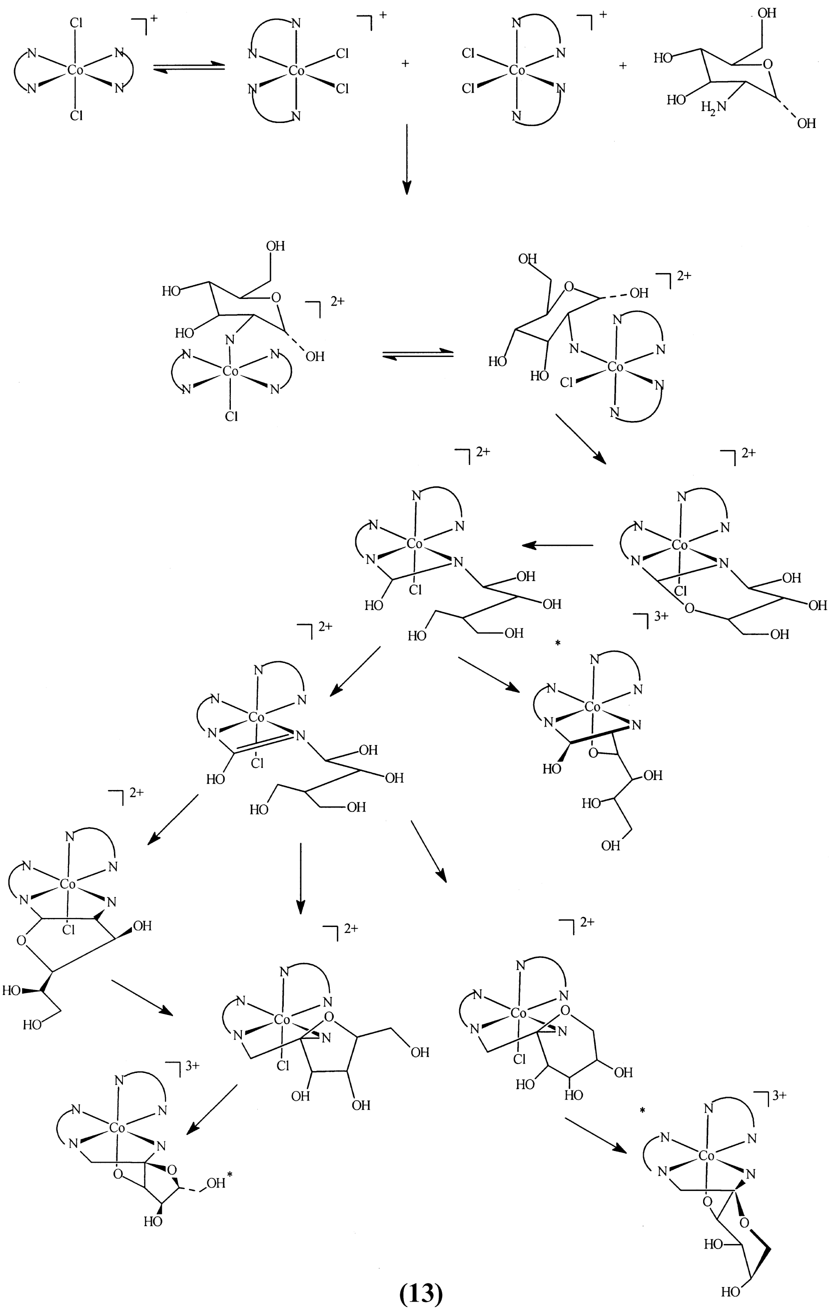
(11)

The data are interpreted to suggest that above pH 0.5 photoaquation and photoreduction are important factors. Below a pH of 0.5 the intervention of solvent-caged radical pairs is invoked.

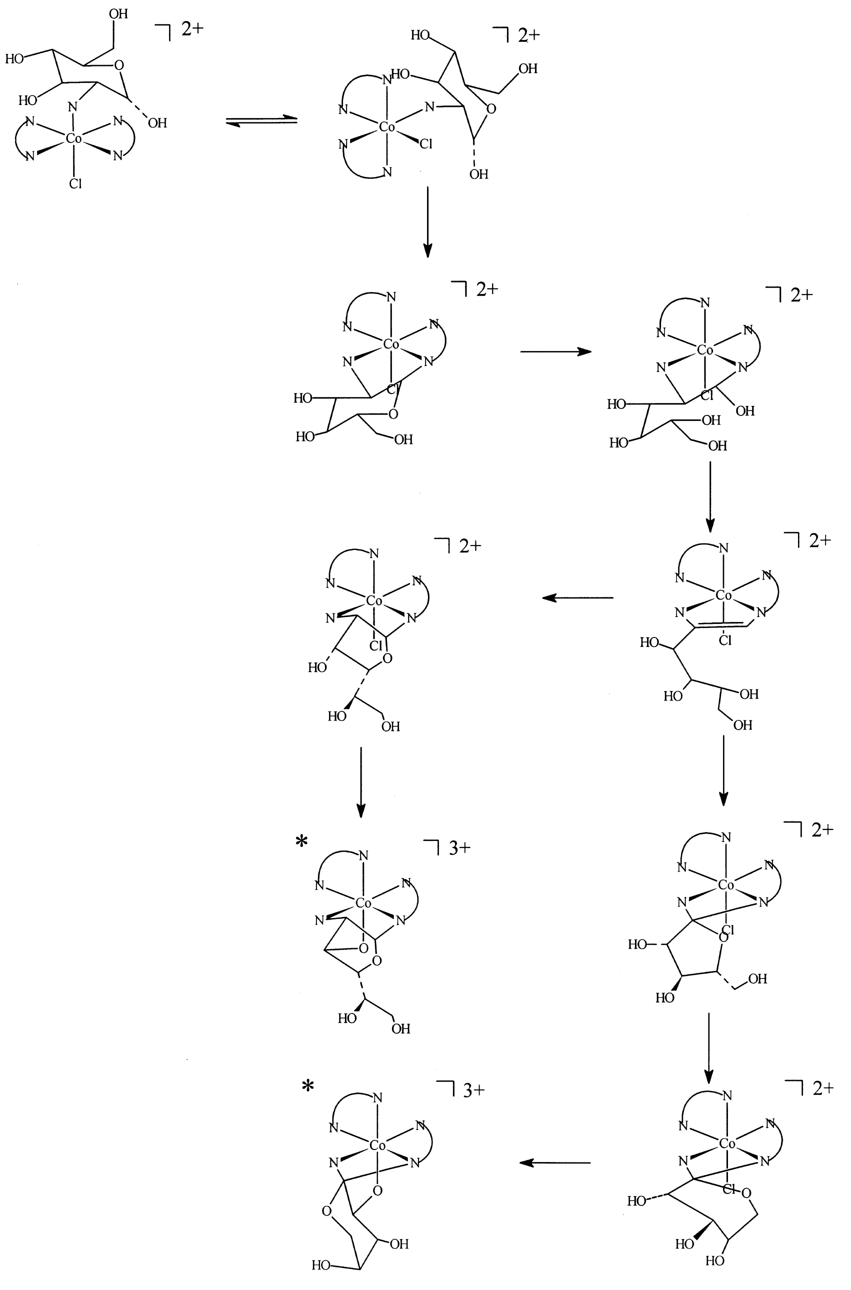
Both *cis* and *trans*-$[Co(en)_2Cl_2]^+$ react with 2-amino-2-deoxy-D-glucopyranose (D-glucosamine) to produce a complex mixture which contains glucosamine-substituted complexes [31]. The reactions are very complex, but the mixtures were separated using HPLC and it was found that there were complexes which contained a ligand



(12)



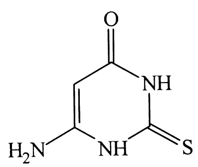
(13)



(14)

formed by reaction of en viz. an *N*-(2′-amino-substituted) glycosylamine and it is suggested that the reaction involves the Amadori rearrangement of the glucosamine. The crystal structures of eight of the species formed in the reaction were obtained and five of these are shown in (**12**). Perhaps the best way to summarize the very extensive chemistry described in this paper is via the possible reaction pathways described by the authors to give the major products of the reaction as in (**13**) and (**14**), where the asterisks indicate structures which the authors indicate have been structurally characterized. There is a similar thorough summary in the paper of the pathways which result in the formation of the minor products as well.

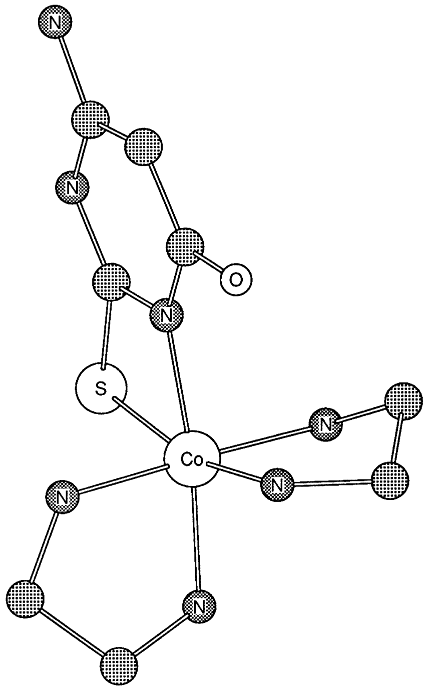
The reaction between *trans*-$[Co(en)_2Cl_2]Cl$ and H_2atuc (6-amino-2-thiouracil) (**15**) in the presence of OH^- and activated charcoal yielded the two complex cations $Co(en)_2(atuc)]^{2+}$ and the red $[Co(en)_2(HL)]^+$, where H_3L is 6-amino 5-5-amino-4-oxo(1H)-pyrimidin-2-yl]thio-2,3-dihydro-2-thioxo-(1H)-pyrimidin-4-one [32]. The X-ray crystal structures of these two species have been determined and are shown in (**16**) and (**17**). A mechanism for the formation of $[Co(en)_2(HL)]^+$ was proposed and this is shown in (**18**). The complex $[Co(en)_2(HL)]^+$ is of particular interest with the atuc having been dimerized. An unusual feature of the preparation of *trans*-$[CoCl(NH_2Me)(en)_2]^{2+}$ is that in its formation from *trans*-$[CoCl(NO_2)(en)_2]^+$ by reaction with $MeNH_2$, Cl^- is first replaced by $MeNH_2$ and then NO_2 replaced by Cl^- [33]. The X-ray crystal structure of *trans*-$[CoCl(NH_2Me)(en)_2]Cl_2$ shows that it is monoclinic, $P1_1/c$ with $a=11.515$, $b=7.421$, $c=17.257$ Å, $\beta=99.220°$, $V=1455.6$ Å^3 and $Z=4$. The complex *cis*-$[CoCl(NH_2Me)(en)_2]Cl_2$ is orthorhombic, Fdd2, with $a=26.64$, $b=27.26$, $c=7.570$ Å, $V=5497$ Å^3 and $Z=16$. The kinetics of the aquation of both the complexes were studied and the replacement of Cl^- was found to be faster in the case to the *trans* complex than for the *cis* species. The authors point out that this is in keeping with the longer Co–Cl bond in the *trans* complex as determined in the X-ray crystal structures.



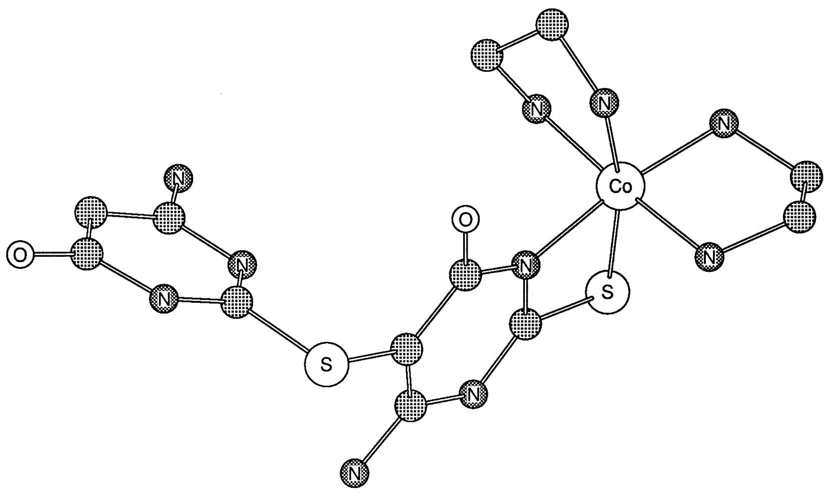
H_2atuc

(15)

A whole series of complexes has been prepared of the form $[(nta)Cr(\mu\text{-}OH)_2ML]Cl \cdot nH_2O$[M = Co(III) or Cr(III); L4 = $(NH_3)_4$, $(en)_2$, $(tn)_2$, {(R,R)chxn)$_2$, (trien), $(amp)_2$, $(bpy)_2$ or $(phen)_2$: nta = nitrilotriacetate. chxn = *trans*-cyclohexane-1,2-diamine, amp = 2-aminomethylpyridine and phen = 1,10-phenanthroline [34]. The X-ray crystal structures of a number of the species has been determined and that for $[(nta)Cr(\mu\text{-}OH)_2Co(tn)_2]Cl \cdot 1.5H_2O$ is shown in (**19**).

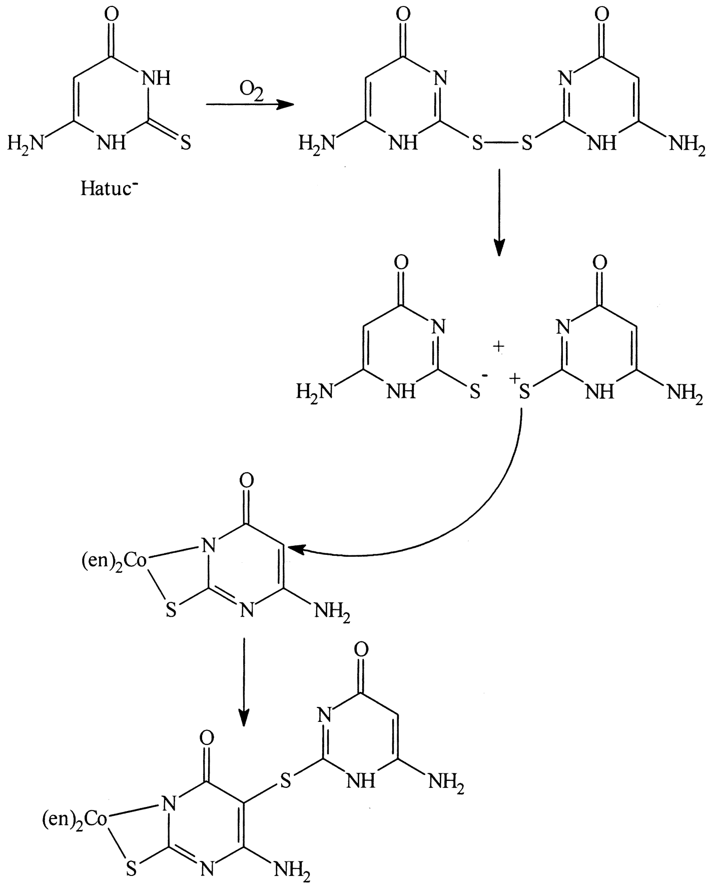


(16)



(17)

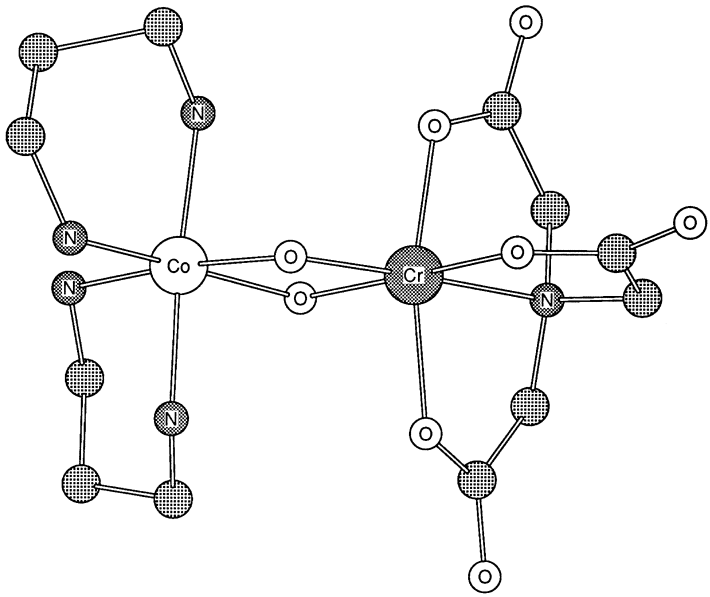
The photolysis of a series of complexes of the form $[LCo(NH_2,O_2^-)CoL]^{4+}$, where $L=4NH_3$, en$=2NH_3$, 2en and tren has been investigated [35]. The products were different for the various complexes. Thus, the tren complex yielded [(tren)Co(OH,



(18)

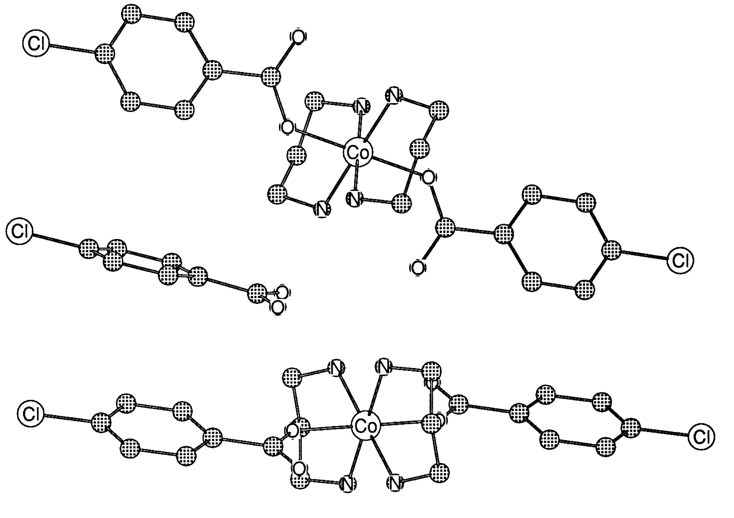
O_2^{2-})Co(tren)]$^{3+}$ and [Co(NH_3)(tren)(H_2O)]$^{3+}$, while the NH_3^- containing complexes produced a mononuclear species and Co(II). The nature of the products was often different in neutral and acidic solutions.

An aqueous solution containing [Co(en)$_3$(OH)$_3$, aluminium oxyhydroxide and 85% H_3PO_4 was heated at 150 °C for 2 days to produce an orange, layered aluminium phosphate, [Co(en)$_3$Al$_3$P$_4$O$_{16}$ · 3H$_2$O], which on heating to 300 °C for 2 h, resulted in an amorphous blue powder after loss of en [36]. The X-ray crystal structure showed that the layered aluminium phosphate consisted of three distinct four- and six-membered rings in sheets between which lay [Co(en)$_3$]$^{3+}$ ions and H_2O molecules. An unusual feature of the structure is a chiral motif repeated along one direction in the aluminium phosphate layers, which the authors point out shows similarities to [3.3.3] propellane. In a related study, a chiral aluminium phosphate has also been



(19)

prepared using $[Co(tn)_3]^{3+}$(tn = 1,3-diaminopropane) as template [37]. The name given to the layered species produced is Gtex-2 and has the general formula $[Co(tn)_3.Al_3P_4O_{16} \cdot H_2O]$. This time, the reactants were in the form of a gel made up from Al_2O_3, orthophosphoric acid and water, to which was added NMe_4OH and



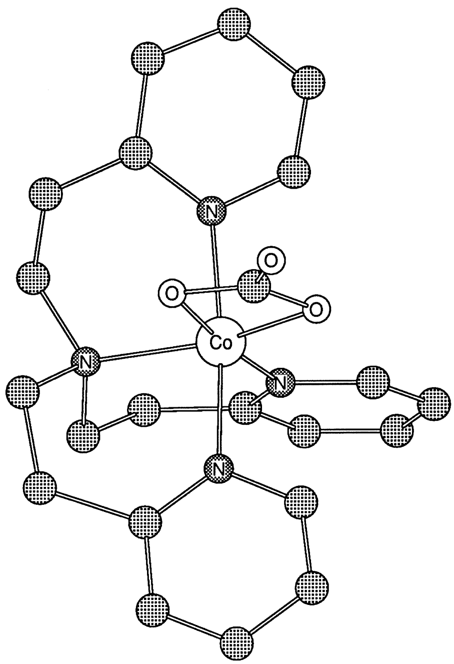
(20)

then $[Co(tn)_3]Cl_3$ followed by a period in an autoclave. The X-ray crystal structure showed sheets with the complex ions acting as "pillars" between them.

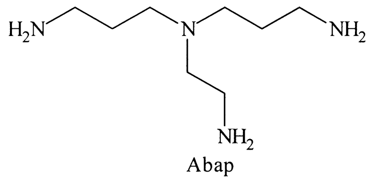
The determination of the X-ray crystal structure of the complex *trans*-di(4-chlorobenzoato-*O*)bis(1,3-diaminopropane-*N,N′*)cobalt(III) 4-chlorobenzoate (**20**) dihydrate affords an opportunity to study the disposition of the ligands in two crystallographically independent complex ions in the same unit cell [38]. The chelate rings produced by the 1,3-diaminopropane ligands are in the chair configuration in both of the units in the unit cell. The benzoate structures are present as axial ligands and are monodentate through oxygen with there being a significant difference in the relative tilting of the rings. In addition, there are differences between the two complex units arising from axial bond lengths and bite angles which are influenced largely by hydrogen bonding and the stacking arrangements of the benzoate anions.

In the course of a study of a number of complexes of the type $[Co(tn)_2(py)Cl]Y$ (tn = 1,3-diaminopropane; Y = $2ClO_4$ or $ZnCl_4$), the X-ray crystal structure of the complex $[Co(tn)_2(py)Cl][ZnCl_4] \cdot H_2O$ was determined [39]. This species was shown to have a *cis* arrangement around the Co centre with the Co–tn rings having chair conformations.

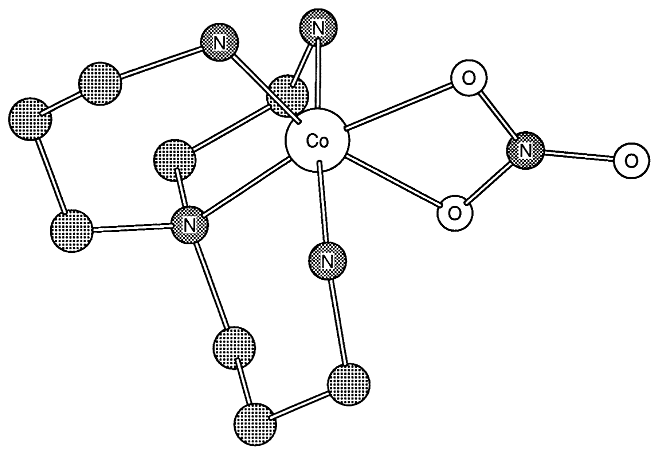
A chelated bicarbonato complex, $[Co(tepa)(O_2COH)](ClO_4)_2 \cdot 3H_2O$, (tepa = tris(2-(2pyridyl)ethyl)amine) has been prepared by protonation of $[Co(tepa)(O_2CO)](ClO_4)$ in acidic aqueous solution [40]. The X-ray crystal structure (**21**) showed that it was distorted from a regular tetrahedral arrangement around the Co centre by vitue of a small O–Co–O angle of 67.64° produced by the



(21)



(22)



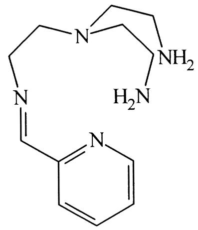
(23)

bicarbonato ligand. X-ray crystal structures have been obtained for the complexes *trans-(N,t-N)*-[Co(norleucinato)(tren)]I_2 and [Co(methioninato)(tren)]I_2 (tren = tris(2-aminoethyl)amine) [41]. An interesting feature that comes out of the X-ray crystal structures is the fact that in the crystal, D- and L-aminoacidate ligands co-exist in the unit cells with two each of D- and L-rich domains in each site. A new tripodal tetraamine ligand, abap, (**22**) and its Co(III) complex have been described [42]. In the complex synthesis, the mixture of $Co(ClO_4)_2 \cdot 6H_2O$ and $NaNO_2$ and ligand first gave a dimeric species and then $[(abap)(O_2NO)CO]^{2+}$, (**23**), structurally characterized as the perchlorate salt. After hydrolysis, this gave $[(abap)Co(H_2O)_2]^{3+}$.

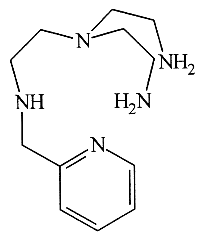
Three isomers of the cation $[Co(meen)_2(C_2O_4)]^+$, where meen is *N*-methylethylenediamine, have been crystallized using selected anions [43]. The X-ray crystal structures of $[Co(meen)_2(C_2O_4)][Pb_2Cl_5] \cdot 2H_2O$ and $[\{[Co(meen)_2(C_2O_4)]Bro\}_2]$ show that they are conformational isomers differing from each other only in the position of the axial Me groups.

Complexes of the form $[Co(L)X]^{n+}$ have been prepared in which X is H_2O or CI^- and L or HL are the ligands shown in (**24**) [44]. The X-ray crystal structures of $[CoL_4(H_2O)](ClO_4)_3 \cdot H_2O$ and $[Co(HL_3)(CI)](ClO_4)_2 \cdot H_2O$ [the cations are shown in (**25**)] were determined.

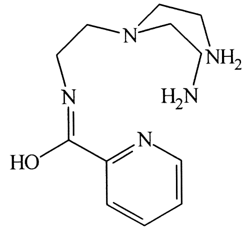
The X-ray crystal structure of the red-brown complex



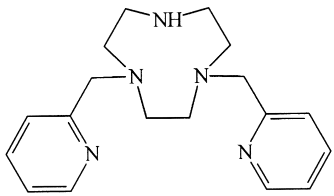
L1



L2

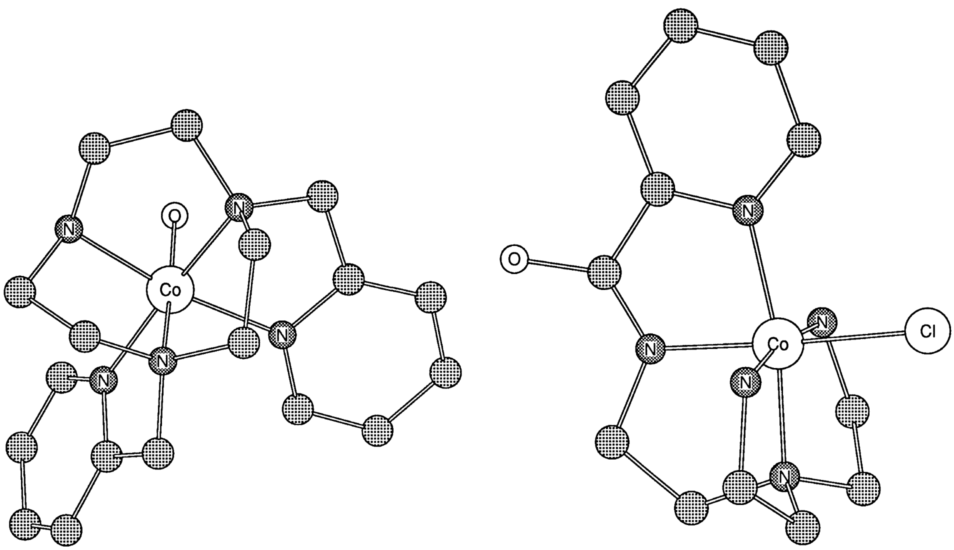


L3



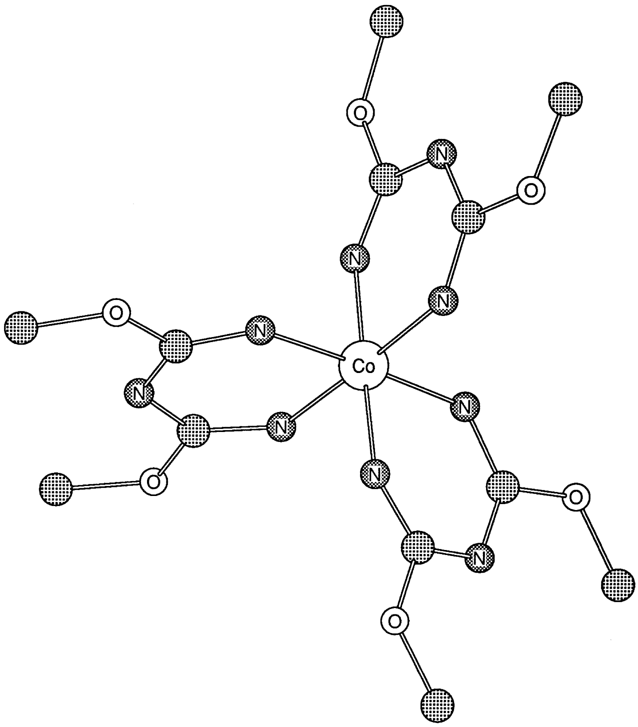
L4

(24)



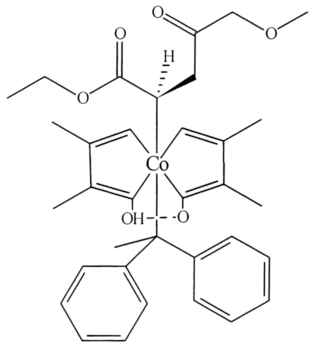
(25)

$[Co(HNCOMeNCOMeNH)_3]$, prepared from the reaction of a suspension of CoS with a solution of $[Cu(HNCOMeNCOMeNH)_2]$ in dimethyl sulphoxide in air, has been determined and is shown in (**26**) [45]. The electronic spectrum of the complex was interpreted in the light of the X-ray structure and molecular orbital calculations were carried out at the Mo-LCAO-SCF level.

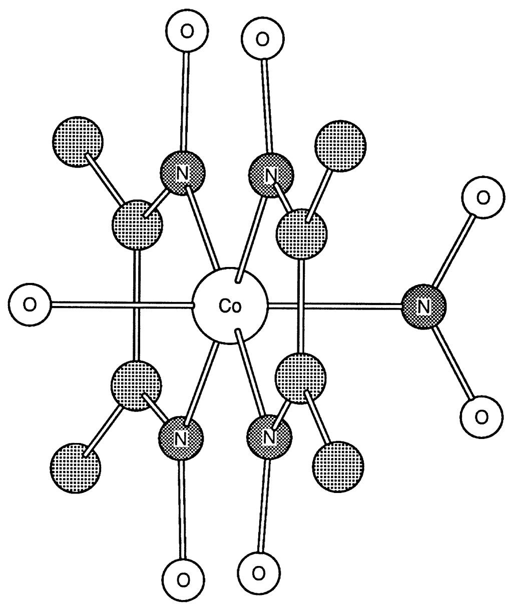


(26)

Although many dioxime complexes of Co are prepared with the express purpose of using them as vitamin B_{12} model compounds, many are not. For this reason, these complexes are included here rather than in Section 7. The kinetics of solvent exchange for a number of complexes of the form $[Co(II)L_2(solv)_x]$, where $L^- =$ Hdmg, H_2dpg, (BF_2)dmg and the solvents were MECN, MEOH and Me_2CO have been investigated [46]. The values were compared with those for $[Co(II)(solv)_6]^{2+}$ and found to be of about the same magnitude. The X-ray crystal structure of the complex [(*R*)-1,2-diethoxycarbonylethyl]bis(dimethylglyoximato)(methyldiphenylphosphine)cobalt(III) (**26**) has been determined [47], as has that of aquanitrobis(dimethylglyoximato)cobalt(III) butanone clathrate, part of the structure of which is shown in (**28**) [48]. The reason given for carrying out this study was to investigate the effect of visible radiation or X-rays on the racemization of the chiral 1,2-diethoxycarbonylethyl group. Neither X-rays nor visible radiation produced racemization in the crystal, but the latter did cause slow racemization in the powder.



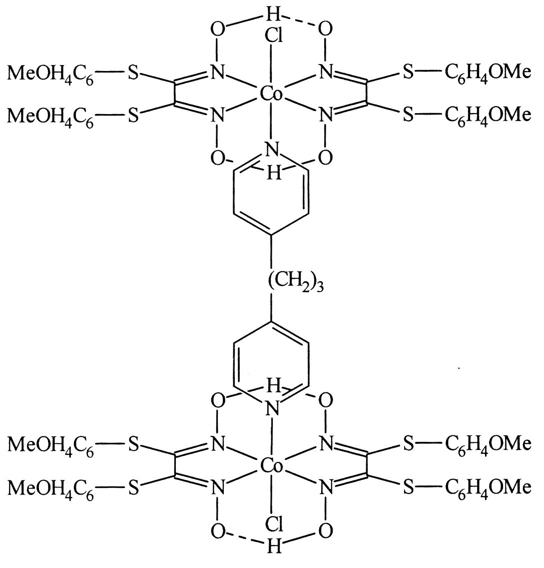
(27)



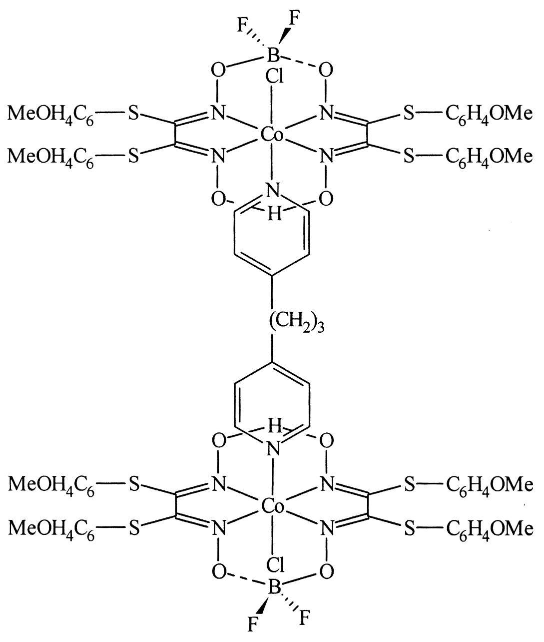
(28)

The synthesis and characterization of new Co(III) complexes, (**29**) and (**30**) with and without BF_2^+-bridged, bis(α-dioximato) ligands has been described [49].

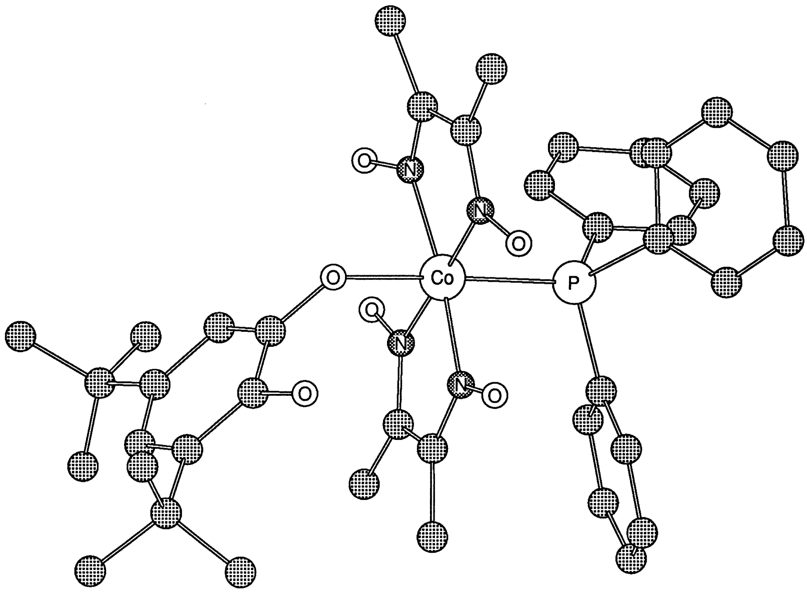
The X-ray crystal structure of the intercalated solvent structures formed by crystallizing the complex aquabis(dimethylglyoximato)nitrocobalt (III) from appropriate solvents shows that the space group, $P2_1$/m, of the complex remains unaltered, but there are changes in the values of c and β[50]. The X-ray crystal structure has also been determined of the complex [(*S*)-1,2-bis(allyloxycarbonyl)ethyl] bis(dimethylglyoximato)[(*R*)-1-phenylethylamine]cobalt(III) isopropanol solvate [51]. Dark blue crystals of $[Co(Hdmg)_2(Ph_3P)(3,5\text{-DTBCatH})]$ are formed



(29)

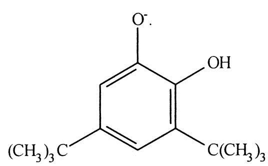


(30)



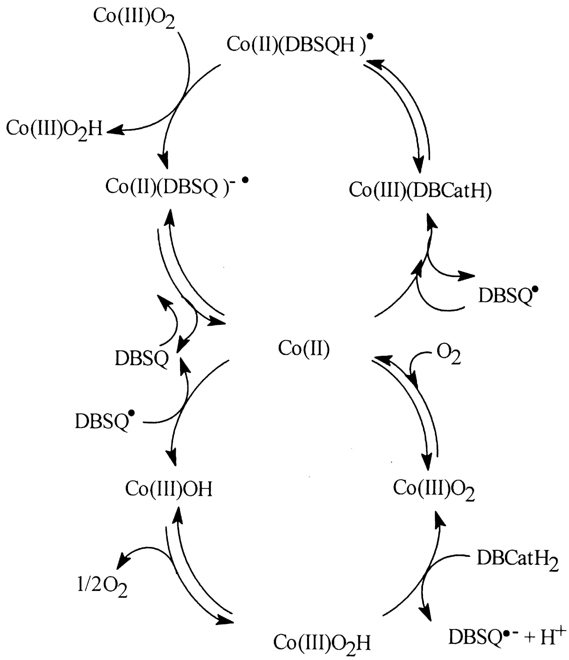
(31)

when $[Co(II)(Hdmg)_2(Ph_3P)_2]$ is reacted with 3,5-DBCatH$_2$ in the presence of O_2 in acetone solution, where 3,5-DTBCatH = 3,5-di-tert-butylcatechol have been shown using X-ray diffraction to have structure (**31**) [52]. The most significant feature of the structure is the presence in the complex of a monodentate [3,5-DTBCat]$^-$ ligand in one of the axial positions. The authors attribute this structure to the presence of the very bulky *tert*-butyl groups on the [3,5-DTBCat]$^-$ ring which force the choice of the oxygen in position-1 of the ligand for bonding to the cobalt. This ligand is lost when the complex is dissolved in benzene and heated to 47 °C under N_2 and is present in solution as the free anionic 3,5-di-*tert*-butylcatecholato radical (**32**) as detected using ESR. ESR spectroscopy at room temperature has been used to investigate the oxidation of 3,5-DTBCatH$_2$ by O_2 catalysed by $[Co(III)(Hdmg)_2(Ph_3P)(3,5\text{-DTBCatH})]$ and has shown that the reaction is consistent with the mechanism shown in (**33**); the author's labelling is used in this scheme



(32)

and an important feature is that the presence of (5), (6) and (7) is required to account for the fact that H_2O_2 is not a product of the reaction.

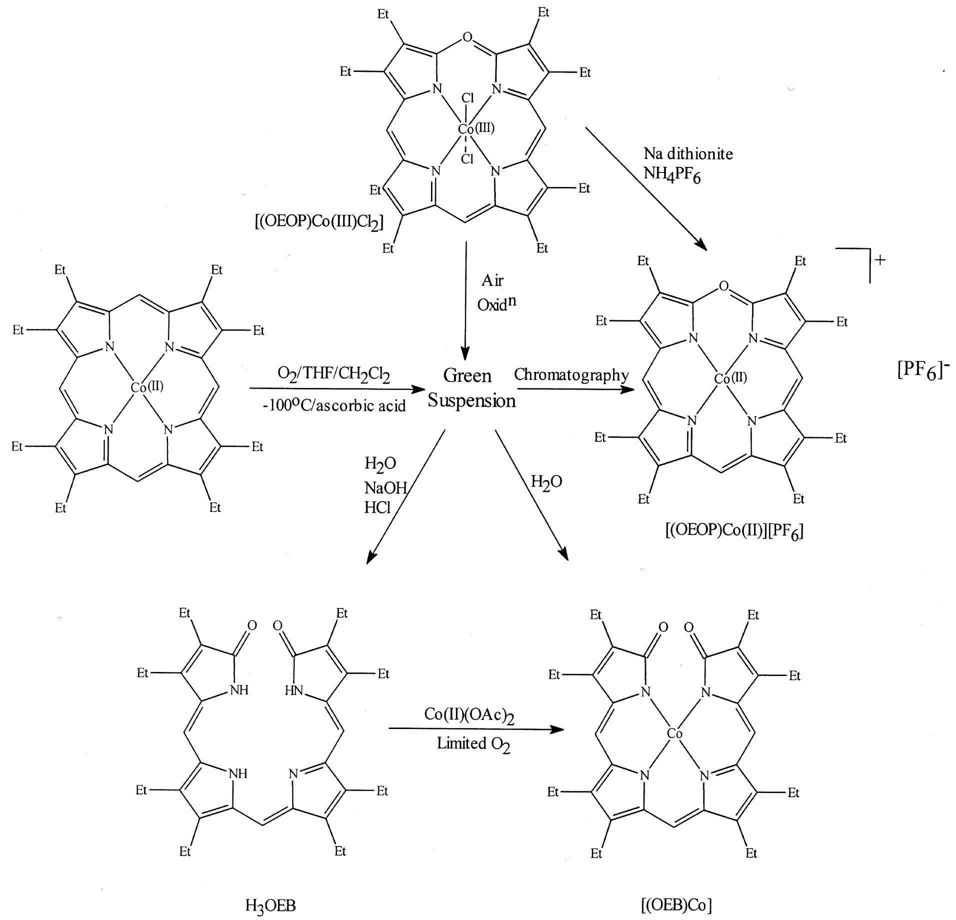


(33)

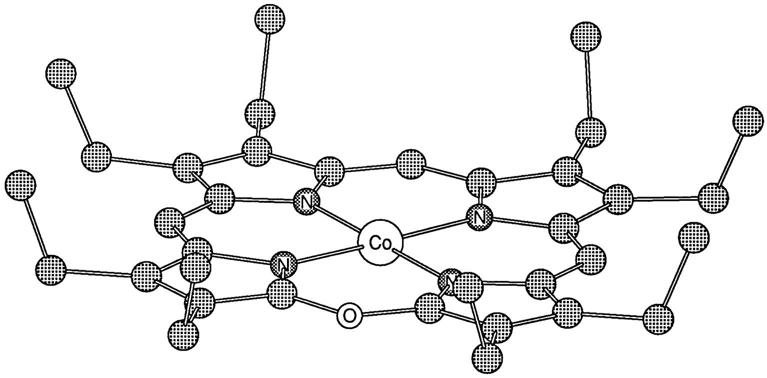
Trans-2-butenyl)bis(dimethylglyoximato)(pyridine)cobalt(III), when irradiated by a high flux xenon lamp shows significant changes in its crystal structure [53]. The effect is produced by the gradual change from *trans*-2-butenyl)bis(dimethylglyoximato)(pyiridine)cobalt(III) to the *cis* isomer. This change took about 2 h and produced a 0.25 Å increase in the a axis and a 0.39 Å change in length of the *b* axis of the orthorhombic unit cell. The photolysis of a series of complexes [LCo(chelate)B] in which L = azide, thiolate, and chelate = dimethylglyoxime, *N,N′*-*o*-phenylenebis(salicylidenimine) = salphen, *N,N′*-ethylene-bis(salicylidenimine) = salen and B = py, imidazole or triphenylphosphine, has been shown to produce homolytic cleavage of the Co–L bond resulting in the production of reactive cobalt(II) chelates of the type [Co(chelat)B] and ligand radicals L·. The effect on the efficiency of the photolysis was studied for the variation of a wide range of parameters, including the nature of the substrates, the wavelength of the irradiating light, its intensity and also the effect of changing the solvent. The use of $[Ru(bpy)_3]Cl_2$ as sensitizes in these systems was also studied [54]. The complexation of *N,N′*-bis(salicylidene)ethylenediiminatocobalt(III) anion by anilines in dimethyl formamide has been studied [55].

A non-linear relationship was found between the rate constant and the dielectric constant of solvent mixtures for the salvation of the complex cation *trans*-dichlorotetra(*tert*-butylpyridine)cobalt(III) [56,57]. Unlike many other systems, and particularly those involving relatively hydrophobic co-solvents, there was found to be very little effect of solvent composition on the enthalpies and entropies of activation.

Studies of the complexes of D-fructose and 1,10-phenanthroline with Co(III) using CD, ORD and ^1H NMR spectroscopies show that the Λ diastereoisomer occurs to the greatest extent [58]. Spectroscopic data are interpreted in the light of molecular mechanics calculations. The X-ray crystal structures of the cobalt(III) complexes $[(en)_2Co(AnErytH\text{-}2)]I$, Δ-$[(en)_2Co(Me\text{-}\alpha\text{-}D\text{-}ManP_3,4H\text{-}2)]ClO_4 \cdot NaClO_4 \cdot 2H_2O$, and Δ-$[(en)_2Co(Me\text{-}\beta\text{-}D\text{-}Galp_2,3H\text{-}2)]ClO_4 \cdot H_2O$, prepared in aqueous, alkaline solutions of *trans*-$[(en)_2COCl_2]Cl$, have been determined [59]. A Λ-configuration was also found by the same group in the



(34)

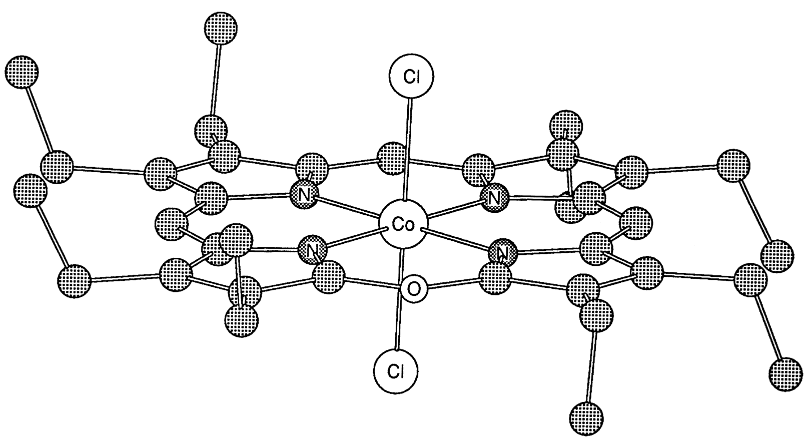


(35)

bis(1,10-phenanthroline)cobalt(III) complex formed with L-sorbose and it has been possible to assign ^{1}H NMR spectroscopic signals for the α-L-sorbopyranose complex [60].

The complex $[Co(phen)_3]^{3+}$ has been used to quench $[Ru(bpy)_3]^{2+}$ luminescence when both are incorporated between the layers in and on bentolite-H clay [61]. Careful control of the disposition of the ruthenium and cobalt complexes in the clay substrate allowed the quenching rates to be modulated.

When the complex (octaethylporphyrin)cobalt(II) is reacted with ascorbic acid in the presence of dioxygen in a partly frozen mixture of dichloromethane and tetrahydrofuran, which is then warmed up to room temperature a green suspension containing a mixture of complexes is produced [62]. From this, the purple complex $[(OEOP)Co(II)](PF_6)$ is prepared by chromatographic separation in the absence of dioxygen along with dark red $[(OEOP)Co(III)]Cl_2$ in which OEOP is the monoanion of octaethyloxaporphyrin. Washing the green suspension with water followed by chromatographic separation yielded the olive-green species [(OEB)Co], a complex



(36)

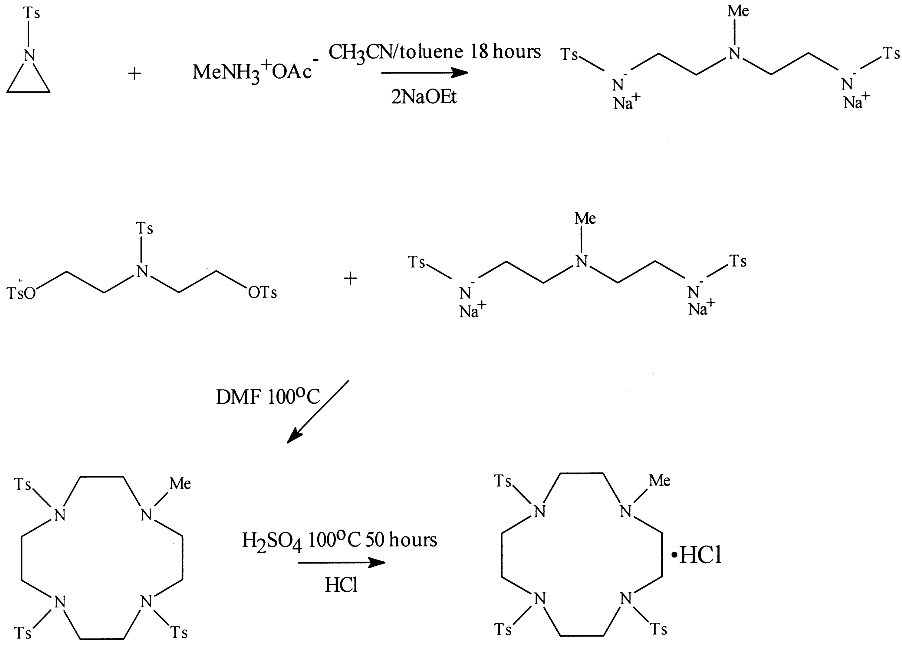
of the open-chain tetrapyrrole octaethylbilindione (H_3OEB). Treatment of the green suspension, first with water and then with an aqueous solution of NaOH followed by HCl, yielded the free ligand H_3OEB. These reactions are summarized in (**34**). The X-ray crystal structures of the species $[(OEOP)Co(II)][(PF)_6].CH_2Cl_2$ and $[(OEOPCo(III)]Cl_2.2CH_2Cl_2$ were determined and the structures of $[(OEOP)Co(II)][(PF_6)]$ and $[(OEOPCo(III)Cl_2]$ are shown in (**35**) and (**36**), respectively.

In the complex bis(2-methylbenzimidazole)tetraphenylporphyrinatocobalt(III) it has been found that the axial 2-methylbenzimidazole ligand is fixed relative to the non-planar porphyrin ring [63] and this is ascribed by the authors to extensive steric repulsion between this ligand and the *meso*-substituents.

A copolymer which was electroactive for Co(III)/Co(II) and Co(II)/Co(I) redox couples has been prepared by the electropolymerization of 5-amino-1,10-phenanthroline cobalt(III) complex with 1-vinylimidazole in cyanomethane solution [64]. The synthesis of vinyl cobalt(III)porphyrins has been achieved by reaction of 2-diazopropane and 1-diazo-1-phenylethane with *meso*-tetraphenylporphin cobalt(III) bromide (Co(III)TPPBr), producing vinyl Co(III)TPP derivatives [65]. These were then copolymerized with MMA to produce alkyl CO(III)TPP complexes which were covalently bound to macromolecules.

A neat synthesis of 1-methyl-1,4,7,10-tetraazacyclododecane (Mecyclen) involving fewer steps than previous methods from *p*-tosylaziridine, methylammonium acetate and tris(*p*-tosyl)diethanolamine has been described; see (**37**) [66]. This was then used to prepare the deep red complex $[Co(Mecyclen)Cl_2]Cl$ which was reacted with S-alanine or its Me-ester. The reaction mixture contained six isomers of $[Co(Mecyclen)(S\text{-}AlaO)]^{2+}$, of which five were isolated using cation exchange chromatography and fractional crystallization. The sixth was detected in solution and a possible structure inferred from spectroscopic studies. The structural differences in the complexes isolated were found to be extremely small and the UV–VIS spectra were as expected virtually identical to each other. However, it is shown in this paper how it is possible to use nuclear Overhauser effect (NOE) spectroscopy to determine the structures of the complexes which were isolated and then the structures of three of them in the forms of $([Co(Mecyclen)(S/R\text{-}AlaO)](ClO_4)_2 \cdot H_2O$, $[Co(Mecyclen)(S\text{-}AlaO)][ZnCl_4] \cdot 2H_2O$ and $[Co(Mecyclen)(SAlaO)](ClO_4)_2 \cdot H_2O$ isomers were confirmed using single crystal X-ray crystallography. The five isomers isolated and the method of structure determination are shown in (**38**). The structure of the sixth which was determined in solution but it was not isolated in the solid state is suggested to be possibly the *anti*(Me), *syn*(N), *syn*(N) isomer.

The absolute configuration of the complex *trans*-dichloro(1,5,8,12-tetraazadodecane)cobalt(III) nitrate has been determined [67] and the structure of (+)-*trans*-1,5,8,12-tetraazatetradecanedinitrocobalt(III) nitrate has also been determined [68]. Didentate O,N complexes are formed when Λ-α-$[Co(S,S\text{-}picchxnMe_2)Cl_2]^+$, where S,S-picchxn$Me_2$ is *N,N′*-dimethyl-*N,N′*-di(2-picolyl)-1S,2S-diaminocyclohexane, is reacted with proH (proline), alaH (alanine) or $AMMAH_2$ (2-amino-2-methylpropandioic acid) [69]. When a racemic mixture of proline is used as the reactant, it was found that there was a significant discrimination in

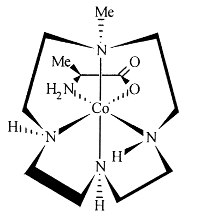


(37)

favour of *S*-proline, but in the case of the other two ligands there was no such discrimination. The X-ray crystal structure of the complex $[Co(S,S\text{-picchxnMe}_2)(S\text{-pro})](ClO_4)_2 \cdot H_2O$ showed that it belonged to space group $P2_12_12_1$, with $a=11.082$, $b=13.838$, $c=19.387$ Å and $Z=4$. The dichlorocobalt(III) complexes involving the ligands (2*S*,*SS*,9*S*)-trimethyltriethylenetetraamine (L′) and (2*S*,*SR*,9*S*)-trimethyltriethylenetetraamine (L″) have been prepared and shown to exhibit three isomers each. In the case of L′, these are Λ-*cis*-α, △-*cis*-β and *trans* isomers and L″ they are △-*cis*-α, △-*cis*-β and *trans* isomers. [70]. In methanol solution both of the *trans* complexes are converted into the *cis*-α-dichloro complex, while the *cis*-α-dichloro complexes are converted to the *trans*-diaqua species in water.

Variable temperature X-ray diffraction studies of crystals of *rac*-$[Co(en)_2\{NHC(S)COO\}](CF_3SO_3) \cdot H_2O$ showed a reversible phase transition at 155 K [71]. Thus, it was observed that at 110 K the space group was monoclinic, $P2_1/n$, $a=6.1509$, $b=14.872$, $c=17.421$ Å, $\beta=93.71°$, $V=1590.3$ Å^3 and $Z=4$, while at 295.5 K the space group was the same, but $a=12.558$, $b=14.978$, $c=18.139$ Å, $\beta=104.44°$, $V=3304$ Å^3 and $Z=8$. It is the differences in hydrogen bonding which largely account for changes in structure which occur at the phase change.

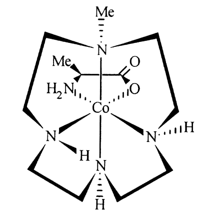
A number of cobalt(III) complexes of the ligand (*R,R*-Me(6)[14]aneN(4)= 7(*R*),14(*R*)-5,5,7,12,12,14-hexamethyl-1,4,8,1-1-tetraazacyclotetradecane, and three didentate ligands (glycinate, *S*-alaninate or oxalate) have been prepared [72]. In each case, the tetraamine ligand in the complex was arranged such as to have a



syn(Me), *syn*(N), *anti*(O)

NOE

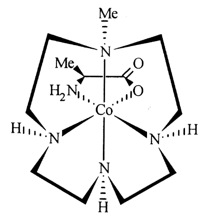
X-ray



syn(Me), *anti*(N), *syn*(O)

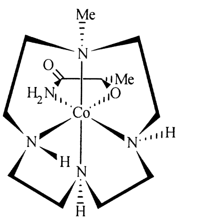
NOE

X-ray



syn(Me), *syn*(N), *syn*(O)

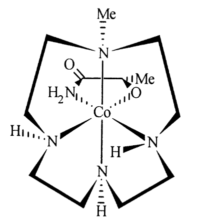
NOE



anti(Me), *syn*(N), *anti*(O)

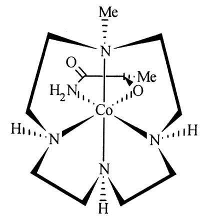
NOE

X-ray



anti(Me), *anti*(N), *syn*(O)

NOE



anti(Me),*syn*(N), *syn*(O)

NOE

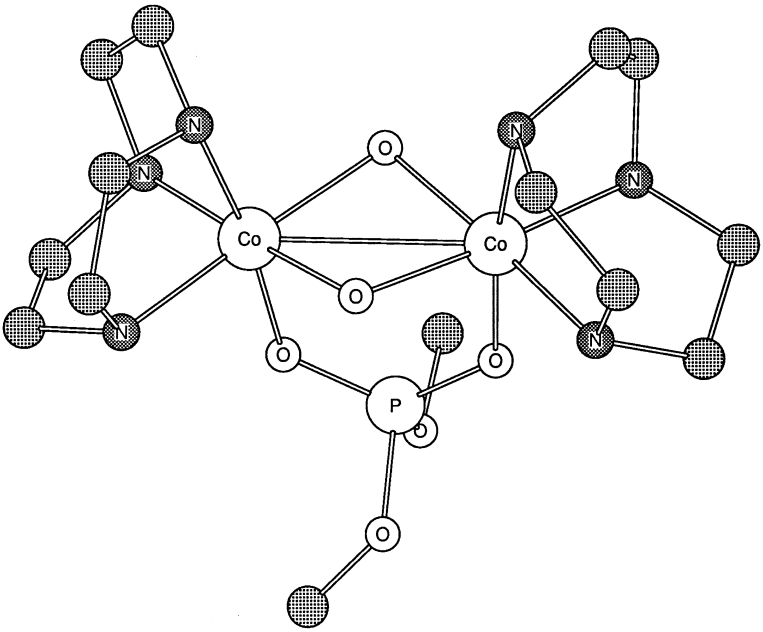
Possible sixth isomer

(38)

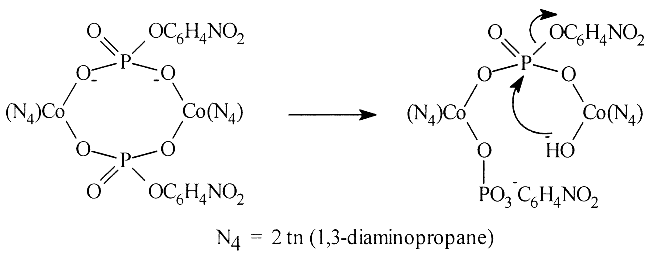
folded *cis*-type configuration. The electronic and ^{59}Co NMR spectra of the complexes show what the authors describe as an "unusual decrease in field strength" which is considered to arise from stereochemical modification of the 14-membered cyclic ligand. A study of the dissociation of alaninate from [Co(S-alaninato){R-Me61141aneN(4)}]$^{2+}$ shows that it is rapid and this is also attributed to the ligand field strength.

The structure of the complex $[Co_2([9]aneN_3)_2(OH)_2\{O_2P(OCH_3)\}(OC_6H_4NO_2)]^{3+}$ (**39**) has been established using X-ray diffraction [73]. The kinetics of hydrolysis of this complex have also been studied, and using $^{18}0$ labelling experiments, it is suggested that the process involves the dissociation of the bridging phosphate diester with the next step being an intramolecular attack on a hydroxy ligand, as shown in (**40**).

Cobalt(III) complexes of 1,4,8,11-tetraazacyclotetradecane-5,7-dione and 6-(2-(2-pyridyl)ethyl)-1,4,8,11-tetraazacyclotetradecane-5,7-dione have been prepared as being capable of selective recognition of nitrite and thiocyanate ions [74].



(39)



(40)

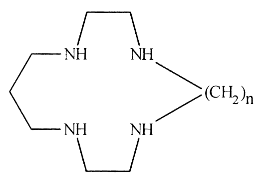
X-ray diffraction data and the application of other techniques show that in the solid state the complexes have an iminol tautomeric structure and that the amide oxygen, but not the nitrogen atoms are protonated. The iminol groups were found to be relatively strong acids in water.

The complex [Co{[15]aneN(4)}], where [15]aneN(4) = 1,4,8,12-tetra-azacyclopentadecane is found in aqueous solution to exist as three complexes in which the axial positions are occupied by aqua and/or hydroxo ligands [75]. There is some evidence that ligands such as Cl^- or NO_3^- also are able to occupy these positions.

Complexes of the type $[CoD_3(SnX_3)_2]^{2-}$ have been reduced to produce

$[CoD_3(SnX_3)_2]^{2-}$ in both of which D = a dioxime and X = a halogen and the redox properties have been investigated [76].

A range of new macrocyclic ligands viz. (1,4,8,11-tetraazacyclooctadecane ($232N_410$), -cyclononadecane ($232N_411$), -cycloicosane ($232N_412$), -cyclohenicosane ($232N_413$), and -cyclotricosane ($232N_415$)) (**41**) which have varying ring sizes have been prepared [77]. Cobalt(III) complexes of the form *trans*-$[CoCl_2(232N_4x)]^+$ have also been made with $x = 7$ to 13 and 15 and isomers separated. Two methods were used to produce the complexes using different sources of cobalt reacting with the appropriate $232N_4x$.HBr. The first was using $CoCl_2 \cdot 6H_2O$ and the second using an aqueous solution of $K_3[Co(CO_3)_3]$. Although the overall product in each case was similar, the isomers present differed and various isomers were isolated from each of the mixtures. There are six possible isomers arising from the four chiral N atoms (**42**). The first method gave the *RRRR(SSSS)* isomer for $232N_47$, and the *RRRS(SSSR)* isomer for $232N_4x$, where $x = 8$–15 and 15. The second method gave the *RSRR(SRSS)* isomer for $x = 8$–13 and 15. The variation in ligand field parameters with ring size were determined. The electrochemically determined redox potentials for the Co(III)/Co(II) couple showed that reduction becomes easier moving from $x = 6$–7–8, but then becomes more-or-less constant. The variations are interpreted in terms of the strain produced in the ring systems.

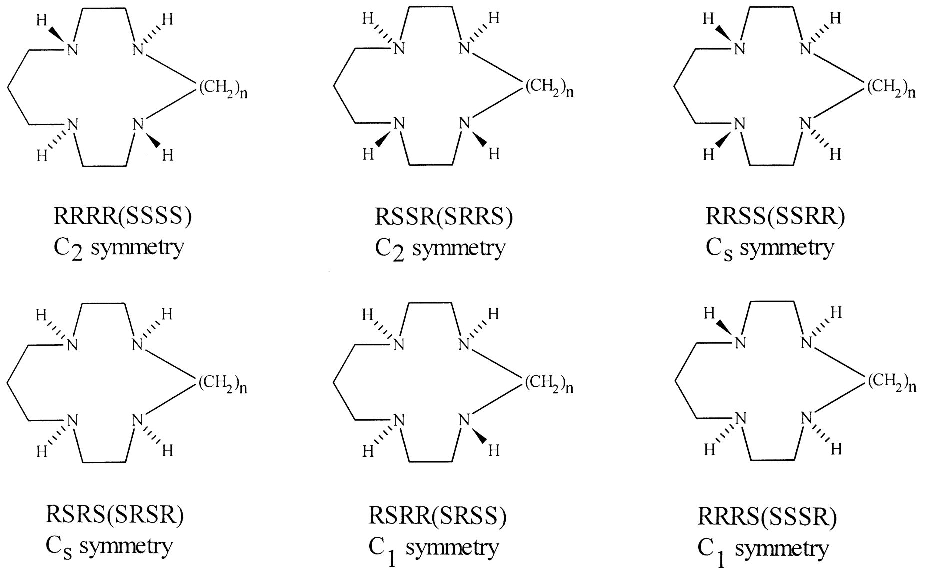


$232N_4x$

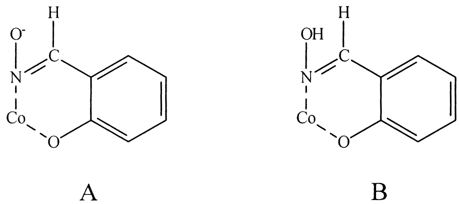
(41)

When *cis*-α-$[CoCl_2(trien)]Cl$ and Ag_2O are reacted with salicylaldoxime [78] a mixture of complexes of the type $[Co(A)(trien)]Cl \cdot nH_2O$ and $[Co(B)(trien)]Cl_2$, in which A and B are salicylaldoxime ligands with and without a proton, respectively, as shown in (**43**). The configurations of the complexes prepared and separated using ion exchange chromatography were *cis*-β_1-(*RR,SS*)-, *cis*-β_1-(*RS,SR*)-, *cis*-β_2-(*RR,SS*)-, and *cis*-β_2-(*RS,SR*)-$[Co(A)(trien)]Cl \cdot nH_2O$ and also *cis*-β_1-(*RR,SS*)-, *cis*-β_1-(*RS,SR*)-, and *cis*-β_2-(*RR,SS*)-$[Co(B)(trien)]Cl_2$. The X-ray crystal structure of *cis*-β_1-(*RS,SR*)$[Co(A)(trien)]Cl \cdot (CH_3COCH_3) \cdot 2H_2O$ was determined and it was found that it was orthorhombic, $Pb2_1a$ with $a = 14.091$, $b = 22.385$, $c = 7.011$ Å, $V = 2211.5$ Å^3 and $Z = 4$.

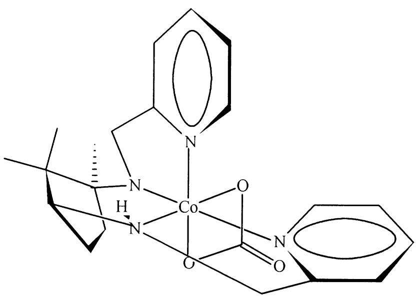
The preparations of the two new chiral amines, *N,N′*-di(2-picolyl)-1*R*, 3*S*-diamino-1,2,2-trimethylcyclopentane (*R,S*-pictmcp) and 3*S*-di(2-picolyl)-amino-*N*-(2-picolyl)hexahydroazepine (*S*-ahazterpy), together with their Co(III) complexes have been described (**44**) [79]. The (*R,S*-pictmcp) complex has potentially 20 isomers,


RRRR(SSSS)
C_2 symmetry
RSSR(SRRS)
C_2 symmetry
RRSS(SSRR)
C_s symmetry
RSRS(SRSR)
C_s symmetry
RSRR(SRSS)
C_1 symmetry
RRRS(SSSR)
C_1 symmetry

(42)

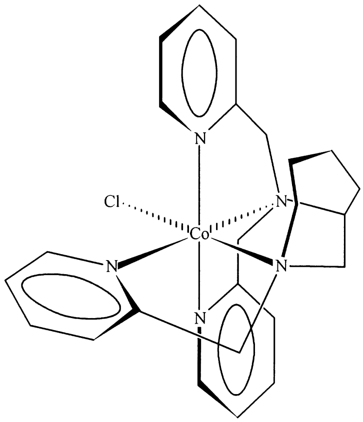

A
B

(43)



(44)

but the preparation as described in the paper resulted in only one isomer. The absolute configuration of the Co(III) complex △-β-[Co(*R,S*-Pictmcp)CO_3]$ClO_4 \cdot 2H_2O$ was established by using a combination of infrared, visible CD, and ^1H and ^{13}C NMR spectroscopies. The complex *trans-equatorial*-[Co(S-ahazterpy)Cl]$(ClO_4)]_2$ was prepared in a rather small yield which prevented any conclusions about the extent of stereoselectivity in the preparation (**45**).



(45)

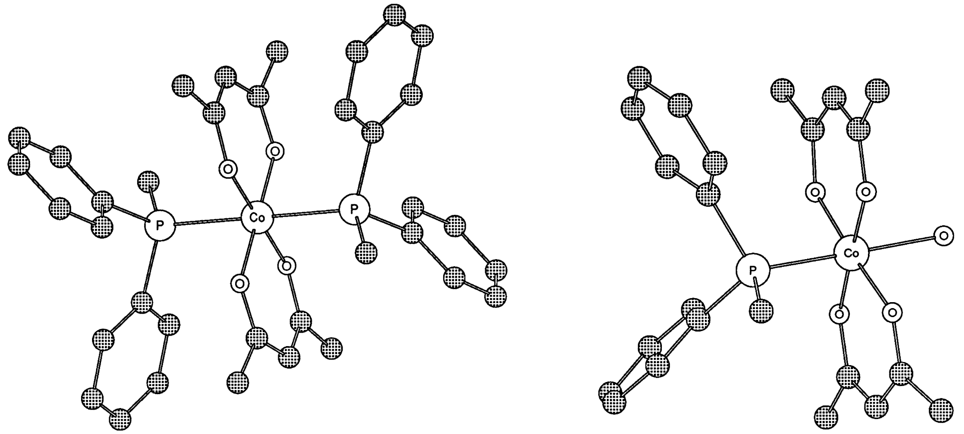
1.2. Compounds with oxygen donor ligands

There have not been many complexes in this category this year. Chemistry taking place in moleten salt media do not appear very often in these reviews. One such is a report of the electrochemical reactions of Co and CoO in moleten eutectic mixtures of Li_2CO_3–K_2CO_3 and K_2CO_3–Na_2CO_3 which were saturated with a mixture of 0.9 O_2/0.1 CO at 1000 K [80]. In the Li_2CO_3–K_2CO_3 mixture Co is oxidized and this is believed to occur through the intermediacy of an unstable species, but not in K_2CO_3–Na_2CO_3 mixture. In the case of CoO in M_2CO_3–K_2CO_3, however, $MCoO_2$ is the product.

The X-ray crystal structures of three related complexes, *trans*-[Co(acac)$_2$(PMePh$_2$)$_2$]PF_6 (i), *trans*-[Co(acac)$_2$(H_2O)(PMePh$_2$)]ClO_4 (ii), and *trans(P,P)*-[Co(acac)(CN)$_2$(PMePh$_2$)$_2$] (iii) have been determined [81]. The structures of (i) and (iii) are shown in (**46**).

The monoclinic polymorph of the complex tris(1,3-diphenylpropane-1,3-dionato)cobalt(III) crystallizes in the space group $P2_2/c$ and with $a=$ 17.257, $b=$ 9.951, $c=20.786$ Å, $\beta=92.73°$, $V=3565$ Å^3 and $Z=4$ [82]. The structure determination showed that the environment around the cobalt consisted of a distorted octahedral arrangement with different Co–O bond lengths.

A series of complexes of the form [Co(III)(4,4′-X(py)$_2$)(DBSQ)(DBCat)]$_n$, where



(46)

X = S, Se or Te have been prepared by the reaction of $Co_2(CO)_8$ with the corresponding 4,4′-chalcogenobispyridine [83] where DBSQ = 3,6-di-*tert*-butylsemiquinone and DBCat = 3,6-di-*tert*-butylcatechol. When the temperature is increased, these complexes undergo a Cat→Co electron transfer. The effect of this essentially is to produce the species $[Co(III)(4,4'\text{-}X(py)_2)(DBSQ)_2]_n$. This effect varies according to the chalcogen substituent. In another study, the equilibria involved in the conversion of [Co(III)(bpy)(3,5-DBSQ)(3,5-DBCat)] to $[Co(II)(bpy)(3,5\text{-}DBSQ)_2]$ (**47**), have been examined in both in the solid state and in solution in toluene [84].

$$[Co(III)(N\text{-}N)(DBSQ)(DBCat)] \rightleftharpoons [Co(N\text{-}N)(DBSQ)_2]$$

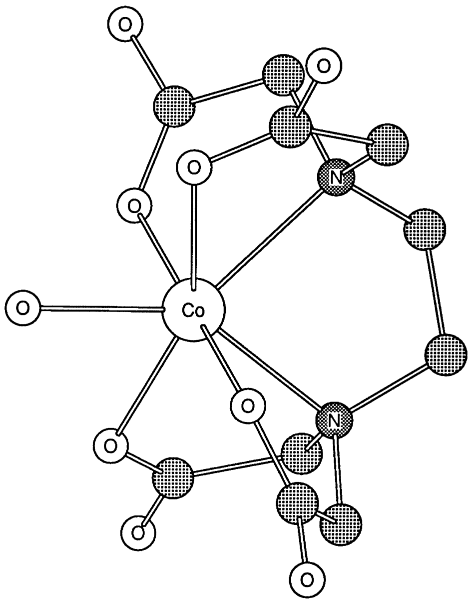
(47)

In toluene solution the values of ΔG and ΔS were obtained from magnetic and optical band measurements and by magnetic measurements in the solid state. Thermodynamic data from the solutions show values of ΔH and ΔS of 33.9 kJ mol^{-1} and 124 J K^{-1} mol^{-1}, respectively, and a similar value for ΔH in the solid state, though the transition temperature is about 50 K higher. The high value for ΔS is attributed largely to the increase in low-frequency vibrational activity due to the presence of weaker Co(III)-ligand bonds.

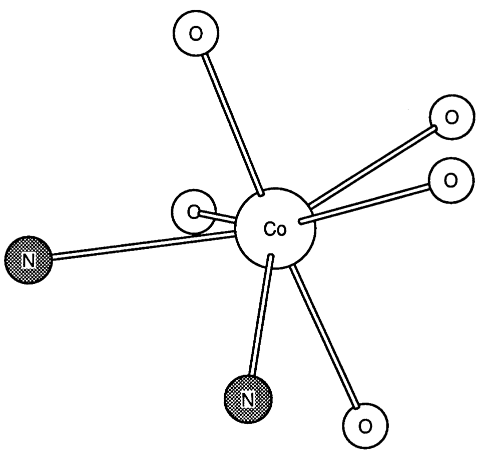
A series of new binuclear complexes of Co(III) with crown ethers have been prepared [85]. Complexes of cyclodextrins have become a fertile area of research. Cobalt complexes of catenated cyclodextrins have been studied [86]. A range of catenanes has been synthesized in aqueous solution from the partially methylated cyclodextrin, heptakis(2,6-di-O-methyl-β-cyclodextrin) and a range of compounds which contain a hydrophobic central core in the form of a 4,4′-disubstituted biphenyl unit such as bitolyl which has two hydrophilic polyether side chains terminated by primary amine functions.

1.3. Compounds with nitrogen–oxygen donor ligands

The archetypal complexes belonging in this section are those of H_4edta; the X-ray crystal structure of the complex aqua(ethylenediaminetriacetatoacetic acid)cobalt(III) dihydrate [Co(H_2O)(edtaH)].2H_2O, has been determined [87]. The arrangement around the Co, (**48**) and (**49**), may roughly be described as a pentagonal bipyramid.



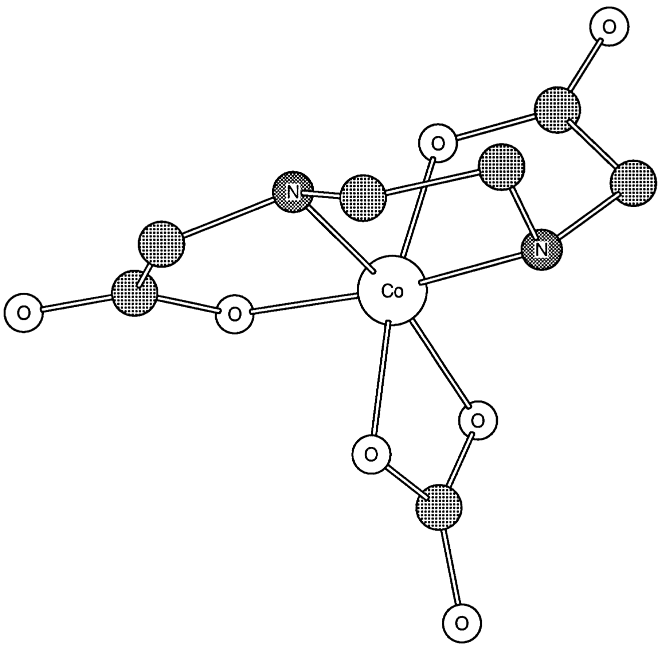
(48)



(49)

Photolysis of the complex α-[Co(Me$_2$eddp)(en)]$^+$ where Me$_2$eddp is $\{CH_2N(CH_3)(CH_2)_2COO^-\}_2$, yields the complex α-[Co(Me$_2$eedmp-C,N,N′,O)(en)]$^+$ where Me$_2$eedmp = (CH_2CH_2N)-C-$(CH_3)(CH_2)_2N(CH_3)$-$(CH_2)_2COO^-$ and the X-ray crystal structure of the latter has been determined [88].

The photolysis products of the Λ-α, Λ-β_1, and Λ-β_2 optical isomers of [Co(eddp)(en)]$^+$ were studied using CD and ^{13}C NMR spectroscopy The Λ-β_1 species gave Δ-α-[Co(eedmp-C,N,N′,O)(en)]$^+$, where eedmp is (CH_2CH_2NH)-C-$(CH_2)_2NH(CH_2)_2COO^-$ and the Λ-β_2 complex gave $(-)(543)_{CD}$-β-[Co(edmp-C,N, N′,O)(en)]$^+$ as the major product and Λ-α-[Co(eedmp-C,N,N′,O)(en)]$^+$ as a minor product. The X-ray crystal structure of the complex guanidinium β-*cis*-(carbonato-*O,O′*)(*N,N′*-ethylenediaminediacetato-*N,N′,O,O″*)cobalt(III) (**50**) has also been determined [89].

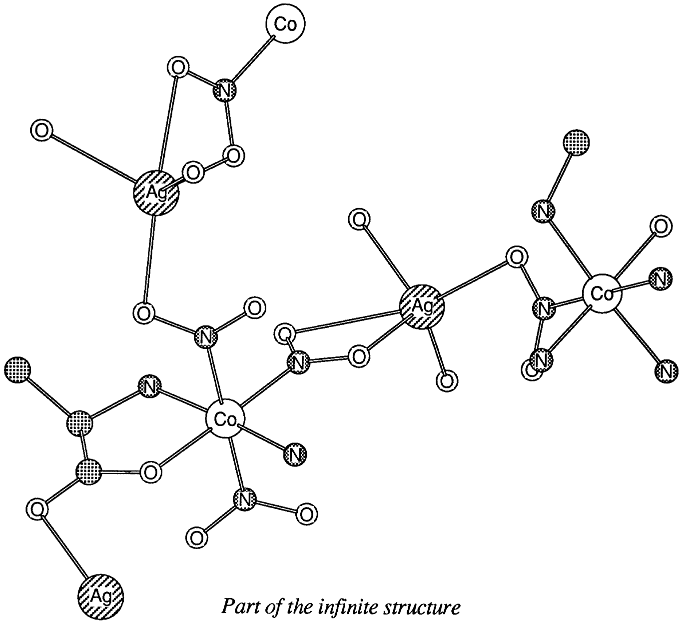


(50)

The red complex $[K(H_2O)_4(Me_2CO)_2](H_5O_2)[Co(azp)_2]_2$, where H$_2$azp is 2,2′-dihydroxoazobenzene, has been prepared by the reaction of cobalt(II) acetate in strongly basic solution with H$_2$azp [90]. The X-ray crystal structure of the [Co(azp)$_2$]$_2$ ion shows that the arrangement around the Co(III) is *trans*-CoO_4N_2. The compound 5,6:13,14-dibenzo-9,10-benzo(15-crown-5)-2,3-bis(hydroxy-imino)-7,12-dioxo-1,4,8,11-tetraazacyclotetradecane (H$_2$L) has been prepared and mononuclear complexes with Co(III) isolated [91]. A trinuclear complex including palladium and involving BF$_2$ bridges has also been made.

A range of complexes of the form *fac*-tris(L)cobalt(III) in which HL = D-alanine, D-valine, D-leucine, L- and D-prolines as well as L- and D-serines have been prepared and the temperature dependence of their solubilities in water investigated to obtain various thermodynamic parameters such as $\Delta G°(s)$ $\Delta H°(s)$ and $\Delta S°(s)$ [92]. Hydrophobicity was identified as a factor in determining the values of $\Delta H°(s)$ and $\Delta S°(s)$.

The structure of silver(I) *mer*-(NO_2) *trans*-(NH_2, NH_3)[(S)-alaninato]amminetrinitrocobaltate(III) monohydrate (**51**) has been confirmed by an X-ray structure determination to involve a five-membered chelate arrangement around the Co [93].

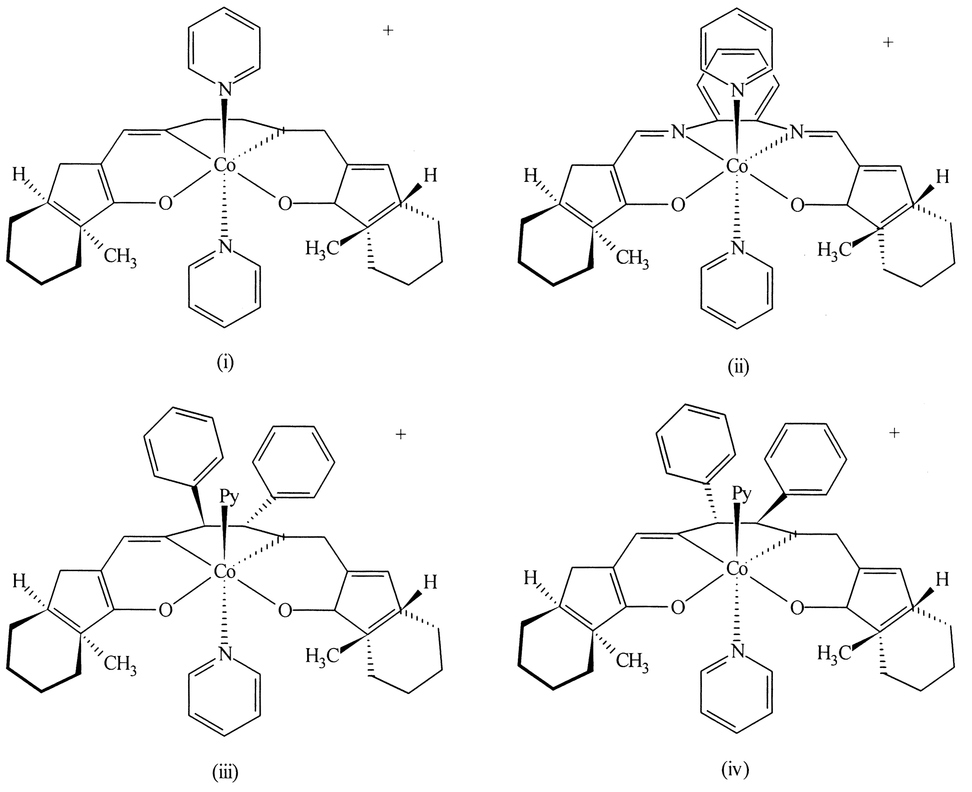


(51)

A series of Schiff-base complexes of the form $[Co(L)(L')_2]Cl$, where L = acacen, salen, salpn, hapen or saloph and L′ = aziridine or methylamine, have been prepared and characterized using ^1H and ^{13}C NMR spectroscopy [94]. Dark purple crystals of the Co(III) complex (i) in (**52**) were formed by heating $CoCl_2$ with the ligand in air [95]. Other complexes in the same series were also produced. The photolysis of cobalt(III) aminopolycarboxylates has been investigated [96].

1.4. Complexes with sulfur donor ligands

The anion $[Co(NO_2)_6]^{3-}$ reacts with K_2CS_3 to produce $[Co(CS_3)_3]^{3-}$ ions [97], which are then precipitated out as the tetraphenylphosphonium salt. The compound was characterized by a variety of spectroscopic techniques including ^{59}Co NMR spectroscopy. A series of complexes of Co(III) and Co(II) have been prepared

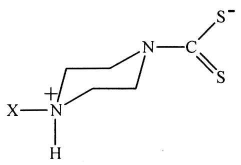


(52)

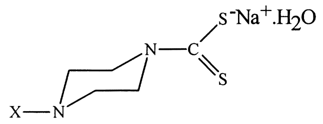
using the carbodithioate ligands shown in (**53**) [98]. In every case it is deduced that the complexes are bonded to the Co via the sulfur and in the Co(III) complexes that they are octahedral. In the case of three of the Co(II) complexes the μ_{eff} values lie in a region between that expected for square planar and that expected for tetrahedral geometry around the Co. In addition, the temperature variation of μ_{eff} shows a decrease with decreasing temperature, behaviour which may indicate a square-planar–tetrahedral equilibrium.

1.5. Complexes with sulfur–oxygen donor ligands

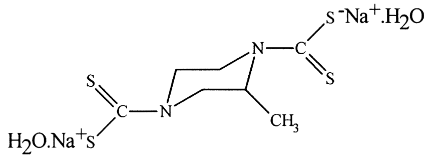
The X-ray crystal structures of the two closely related species *fac*-$[Co(C_5H_4NOS)_3] \cdot H_2O \cdot 1/2CH_3OH$ and *fac*-$[Co(C_5H_4NOS)_3]$-$1/3CH_3OH$ have been determined; the cobalt complex is shown in (**54**) [99], where C_5H_4NOS is 2-mercaptopyridine-*N*-oxide. Each of the complexes contains an O_3S_3 arrangement around the cobalt centre in the $[Co(C_5H_4NOS)_3]$ part of the structure.



Carbodithionic acid

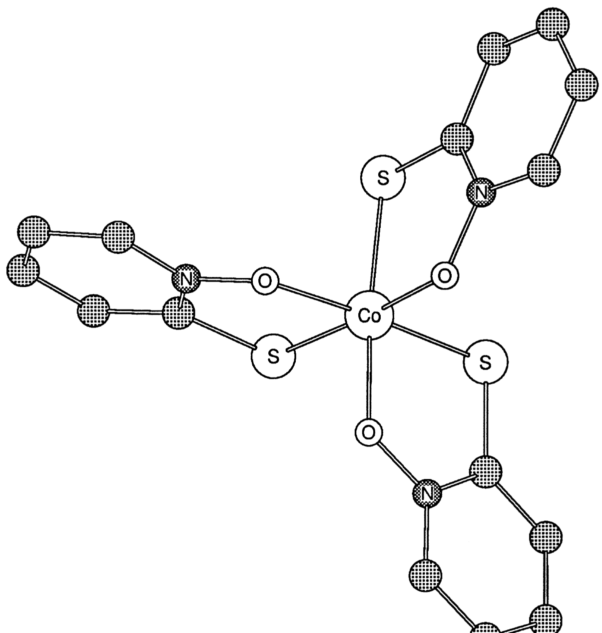


sodium dithiocarbodithionate hydrate



Disodium 2-methylpiperazine-1,4-dicarbodithionate dihydrate

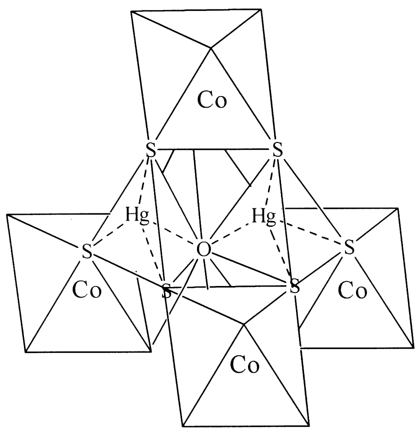
(53)



(54)

1.6. Complexes with sulfur–nitrogen donor ligands

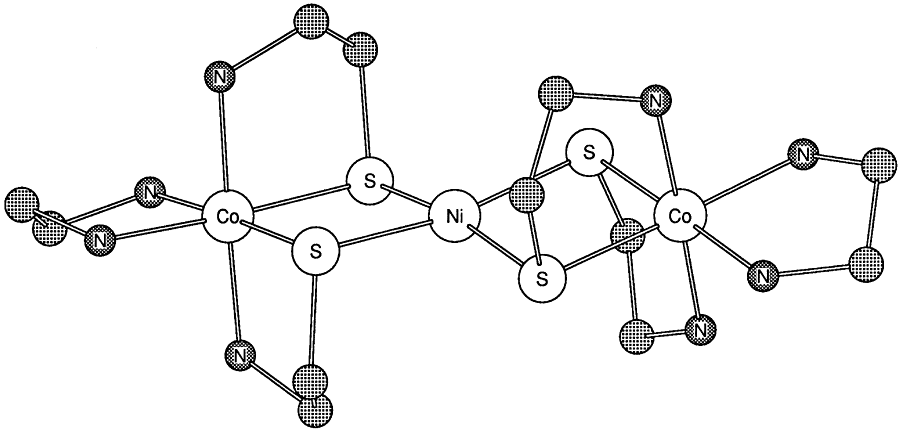
A series of papers has been published in which the preparation of new multinuclear Co(III) complexes of the ligand 2-aminoethanethiolate (aet) ($NH_2CH_2CH_2S^-$) are described [100–102]. In the first of these, black crystals of complexes which are shown to be of the form $[\{Co(III)(aet)_3\}_4(4Hg(II)_4O)]^{6+}$ are produced by reaction of *fac*(S)$[Co(aet)_3]$ with HgO in water. This octanuclear complex is produced as only two isomers viz. ΔΔΔΔ and ΛΛΛΛ which have been resolved using $K_2[Sb_2$(d-tartrato)$_2]$ and characterized. A proposed structure is shown in (**55**). The crystal structure of the trinuclear complex (**56**) has been determined. A tetranuclear Co(III) complex was produced by reaction of $[(NH_3)_5\ CoCl]^{2+}$ with $[Ni(aet)_2]$ in water, during which the green colour of the Ni complex changed over several hours to a black solution from which black crystals of the nitrate were obtained. The complex is of the form $[\{Co_2(aet)_2]\}\{Co(aet)_3\}_2]^{4+}$. The X-ray crystal structure of this species showed that it had the four Co atoms bridged by a double sulfur bridge and two triple sulfur bridges. The result is that the Co atoms have what is described as a kind of boat structure. The crystal contained both ΔSSΔ and ΛRRΛ isomers, so that it is racemic. Two isomers are shown in (**57**). The compound was in fact successfully resolved by using $[Sb_2$(R,R-tartrato)$_2]^{2-}$ and the reaction solution was found chromatographically to have two isomers present. One was ΔSSΔ/ΛRRΛ and the other ΔRRΔ/ΛSSΛ.



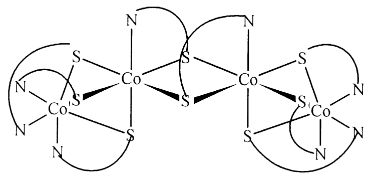
(55)

When a solution of $[CoL(NO_2)_2][BF_4]$, in which L is 3,6-dithiaoctane-1,8-diamine, is left for several weeks at 21 °C, two compounds were found to have crystallized and these were manually separated. The X-ray crystal structure determination showed that one of these crystallized in space group $Pca2_1$, with $a=12.811$, $b=12.213$, $c=18.906$ Å and $Z=8$, while the other crystallized in space group $P2_1/n$ with $a=8.054$, $b=13.833$, $c=12.564$ Å and $\beta=105.26°$ with $Z=4$. L behaved as a tetradentate ligand via the two *trans*- axial N atoms and the two *cis*- S atoms. The structure of both species consisted of $\Lambda(\delta\lambda\lambda)$ and $\Delta(\lambda\lambda\delta)$ pairs.

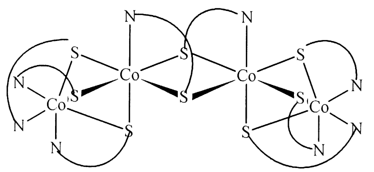
Significant photocurrents have been produced by the electro-oxidation of an acetonitrile solution of the complex tris(dimethyldithiocarbamato-*S*,*S*′)cobalt(III)



(56)



ΔSSΔ



ΔRRΔ

(57)

$[Co(S_2CNMe_2)_3]$, using platinum electrodes and radiation of between 300 and 600 nm [103]. In the absence of light, the rate determining step involves the dimerization of this cation followed by a redox reaction resulting in the production of $[Co_2(S_2CNMe_2)_5]^+$ and the oxidation of the ligand. Radiation at 480 nm produces the maximum photocurrent and results in a parallel photochemical route. A mechanism is proposed in which it is suggested that the process begins by a one-electron oxidation of the complex to produce $[Co(S_2CNMe_2)_3]^+$ (**58**). The kinetics of the decomposition of this species have been measured. For reaction 3, the kinetic parameters determined were; $D_x = 1.7 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ and $k_3 = 0.08\,\mathrm{s^{-1}}$, where $X = [Co(S_2CNMe_2)_2]$. The X-ray crystal structure of the complex tris(S-Methyl N-phenyl-dithiocarbamato-*S,N*)cobalt(III) has been determined [104].

$$[Co(S_2CNMe_2)_3] - e \longrightarrow [Co(S_2CNMe_2)_3]^+ \qquad (1)$$

$$2[Co(S_2CNMe_2)_3]^+ \longrightarrow [Co_2(S_2CNMe_2)_6]^{2+} \qquad (2)$$

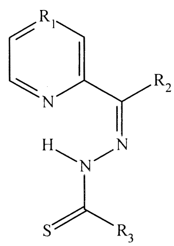
$$\downarrow$$

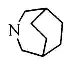
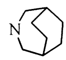
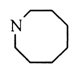
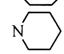
$$[Co_2(S_2CNMe_2)_6]^{2+} + \text{oxidized ligand}$$

$$[Co(S_2CNMe_2)_3]^+ + h\nu \longrightarrow [Co(S_2CNMe_2)_2] + \text{oxidized ligand} \qquad (3)$$

$$[Co(S_2CNMe_2)_2] - e \longrightarrow \text{products} \qquad (4)$$

(58)



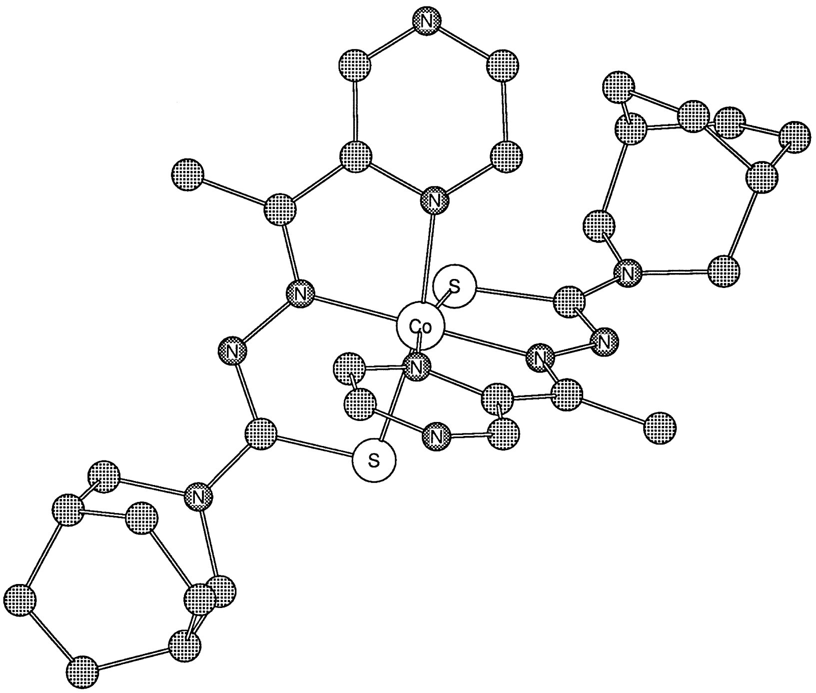
Thiosemicarbazone	R_1	R_2	R_3
HOzbcn	N	Me	
HLbcn	CH	Me	
HLhexim	CH	Me	
HLpip	CH	Me	
HLDO	CH	Me	N
Hbcn	CH	H	N
Hhexim	CH	H	N
Hpip	CH	H	N

(59)

A range of reddish-brown Co(III) complexes of the 2-acetylpyridine 3-pyrrolidinyl-, 3-piperidinyl-, 3-hexamethyleneiminyl- and 3-azabicyclo-

[3.2.2]nonylthiosemicarbazone, $[Co(LPO)_2]BF_4$, $[Co(Lpip)_2]BF_4$, $[Co(Lhexim)_2]BF_4$ and $[Co(Lbcn)_2]BF_4$, respectively; 2-formylpyridine 3-piperidinyl-, 3-hexamethyleneiminyl- and 3-azabicyclo[3.2.2]nonylthiosemicarbazone, $[Co(PiP)_2]BF_4$, $[Co(hexim)_2]BF_4$ and $[Co(bcn)_2]BF_4$, respectively; and acetylpyrazine 3-azabicyclo[3.2.2]nonylthiosemicarbazone, $[Co(Pzbcn)_2]BF_4$, have been prepared (**59**) [105].

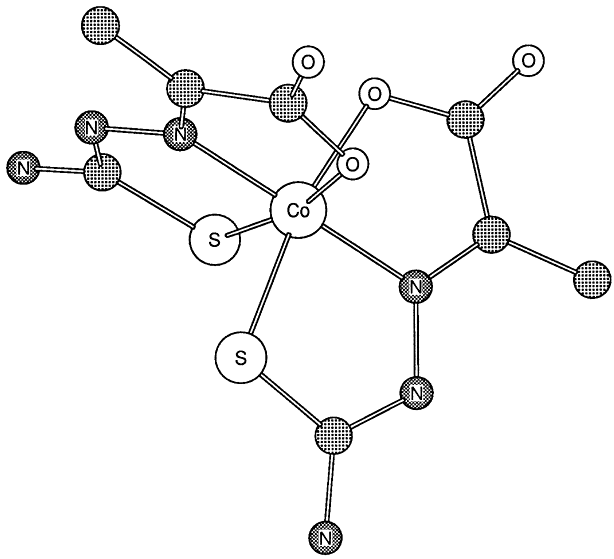
The X-ray crystal structure of $[Co(Pzbcn)_2]BF_4$ (**60**) shows that the ligand is tridentate and the arrangement around Co is octahedral. In this particular case, the crystals only contain one isomer of this molecule which is chiral. The ligands are in the *mer* configuration and are bonded to the Co by the pyrazinyl N, the azomethine N and the thiolate S atoms.



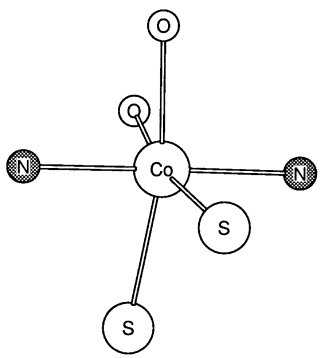
(60)

1.7. Complexes with sulfur–nitrogen–oxygen donor ligands

The X-ray crystal structures of the Co(III) complexes $[Co(HL)_2]Cl.EtOH$ and [Co(Hpt)(pt)], (**61**), in which H_2L and H_2pt are pyridoxal and pyruvic acid thiosemicarbazones, respectively, have been determined [106] and the IR and CD spectra also obtained. The arrangement around the Co in both of these species is such that the ligands are found in a *mer* configuration with the S and O atoms *cis* to each other and the N atoms *trans* to each other giving a pseudo-octahedral environment for the Co, (**62**). The pyridoxal-derived complex is chiral and both ligands are protonated. In the pyridoxal-derived complex, on the other hand, the two ligands attached to the cobalt centre differ in that one of them is monoprotonated. The pyridoxal complex is chiral and the authors point out that this constitutes an example of the resolution of optical isomers by preferential crystallization.



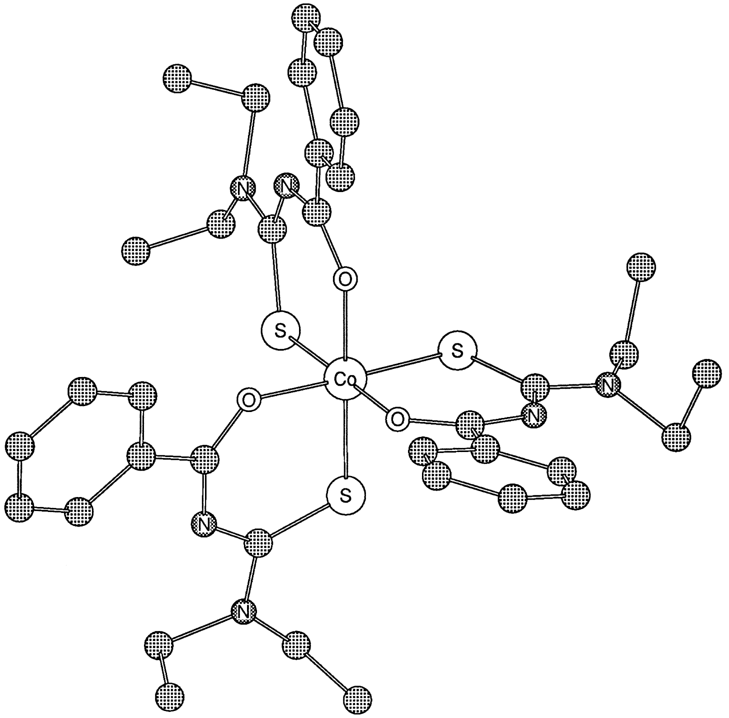
(61)



(62)

Benzothiazolines are the products of the reactions of acetylacetone and salicylaldehyde with 2-aminobenzenethiol [107]. These were reacted with various Co salts and produced Schiff-base chelates and complexes containing N_2S_2 and S,S-bonding to Co(II) and Co(II) were obtained.

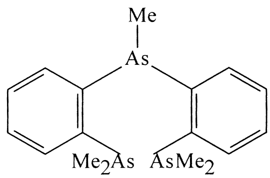
The crystal structure of the complex tris(*N*,*N*-diethyl-*N*′-benzoylthioureato)cobalt(III) (**63**) has been determined [108]. A cobalt(III) complex of the ligand dibenzo[e,kl-2,3-bis(hydroxyimino)-1,4-dithia-7,10-diaza-2,3,8,9-tetrahydrocyclododecine has been prepared with the Co:ligand ratio being 1:2 [109]. In addition, mono- and trinuclear macrocyclic species were prepared with BF_2^+ forming bridges.



(63)

1.8. Complexes with phosphorus donor ligands

The complexes $[Co(mtaS)_2](ClO_4)_3$, $[Co(mtas)_2](ClO_4)_2$, $[Co(mtas)_2](BPh_4)_2$, where mtas is bis[2-(dimethylarsino)phenyl]methylarsine (**64**), provide water-soluble and insoluble species and their voltammetry has been carried out in a variety of conditions, including in solution and by attaching the microcrystalline form to graphite electrodes [110]. In acetonitrile solution, cyclic voltammetry of the complex $[Co(mtas)_2](BF_4)_3$ with 0.1 M Bu_4NClO_4 as supporting electrolyte, shows that there are three reversible one-electron steps taking place, as shown in (**65**). This contrasts with the situation in CH_2Cl_2 solution where only the first two of these reactions are observed. The spectroelectrochemistry of $[Co(mtas)_2](BF_4)_3$ in acetonitrile showed the spectral changes corresponding to these reactions. Spectra were also measured of $[Co(mtas)_2](BF_4)_3$ and $[Co(mtas)_2](BPh_4)_3$ in solution and in the solid phase. The authors draw attention to the fact that the experiments show that when there is a change of oxidation state from Co(III) to Co(II) the electronic changes involving the first coordination sphere are the same whether they are in the solid or in solution. The work on solid state voltammetry highlighted the importance of the negative counterion in the electrometric behaviour of the cation. The voltammetric response could vary from zero to significant values, depending on the nature of the anion in the crystal. In the case of the anion BPh_4^-, the nature of its influence on the voltammetric response arises from it hydrophobic properties.



bis(2-(dimethylarsino)phenyl)methylarsine

(64)

$$[Co(mtas)_2]^{3+} + e^- \rightleftharpoons [Co(mtas)_2]^{2+}$$

$$[Co(mtas)_2]^{2+} + e^- \rightleftharpoons [Co(mtas)_2]^{+}$$

$$[Co(mtas)_2]^{+} + e^- \rightleftharpoons [Co(mtas)_2]^{0}$$

(65)

1.9. Complexes with halide and pseudohalide donor ligands

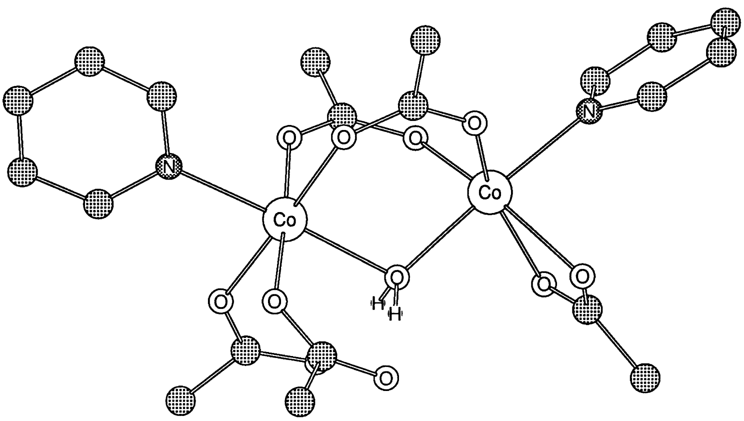
The kinetics of the light-induced replacement of azide in the complex anion $[Co(CN)_5(N_3)]^{3-}$ by SCN^- in aqueous solution have been found to be affected by the nature of the counterion: Li^+, Na^+, K^+ and NH_4^+ [111]. The ratio of aquation:anation was found to be inversely related to the hydrated radius of the cation. The crystal structure of the complex *trans*-bis(isothiocyanato)-bis(ethylenediamine)cobalt(III) thiocyanate has been determined [112].

2. Cobalt(II)

2.1. Complexes with nitrogen donor ligands

Solvent exchange reactions which take place between Co^{2+} ions and ethylenediamine have been carried out with ethylenediamine as the solvent [113]. The methods chosen to study the system were ^{14}N, ^{13}C and ^{1}H NMR spectroscopic line-broadening. This allowed the determination of the solvent exchange rate constant, k_{ex}, which at 298 K $=5.4\times10^3$ s^{-1}, as well as $\Delta H^{\ddagger}=56.5$ kJ mol^{-1}, $\Delta S^{\ddagger}=16$ J K^{-1} mol^{-1} and $\Delta V^{\ddagger}=0.9$ cm^3. The values of k_{ex} are compared with those available for corresponding solvents which are potentially monodentate ligands and these are generally larger than for ethylenediamine. The $\Delta H^{\ddagger}$ values for the metal ions studied alongside Co^{2+} (Mn^{2+}, Fe^{2+}) show that there changes are much more pronounced for the didentate species than for monodentate. The $\Delta V^{\ddagger}$ values, which are a useful guide to the mechanism of reactions, show that there is not a change from an I_d mechanism to an I_a mechanism in moving along from Ni^{2+} to Mn^{2+}. The authors attribute the differences in the behaviour of potentially didentate ligand solvents with those which are potentially monodentate to the chelate effect and in terms of what they term the "kinetic chelate strain effect".

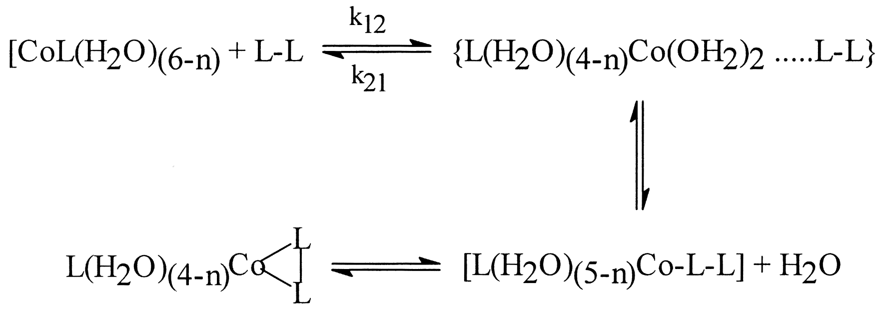
The structures of a number of glyoximato complexes of Co(II) have been inferred from NMR and IR spectroscopies and magnetic measurements [114,115]. The X-ray crystal structure of [py(η^1-AcO)$_2$Co(μ-H_2O)(μ-O,O-AcO)$_2$Co(η^2-AcO)$_2$py] (**66**) has been determined [116]. The structure turns out to be asymmetric with one water molecule and two acetates as bridges between the two Co atoms.



(66)

The kinetics of the formation and dissociation of the 1:1 complex which is produced by reaction between Co^{2+} ions and 2,2′-bipyridine have been investigated using fast reaction techniques [117]. In addition, the ternary complexes between 2,2′-bipyridine and Co^{2+} complexes of a range of ligands viz. polytriphosphate, nitrilotriacetate, -ethylenediamine-N,N-diacetate, ethylenediamine-N,N'-diacetate, triethylenetetramine and 2,2′,2″-triaminotriethylamine. These data allowed comparisons to be made with similar reactions with other metal ions, particularly Ni^{2+}. The data were interpreted in terms of (**67**). When a steady-state approximation is applied to this description of the system, then it is possible to express k_f in terms of the rate constants in Eq. (8).

$$k_f=K_{os}k_{23}k_{34}/(k_{32}+k_{34}) \quad \text{(in which } K_{os}=k_{12}/k_{21}\text{)}. \tag{8}$$



(67)

The values of k_f may also be statistically adjusted to give k_f^s so that they reflect the different numbers of replaceable water molecules in the molecules and therefore aid comparisons between different species. Log(k_f^s) has a linear relationship and the electron withdrawing ability of the ligand in an equation which includes terms which express "accelerating" effects, a_1, describing the effect of each N atom and a_2, effect of pyramidally bound ligand and "retarding" effects, r_1, a steric term and r_2 an electrostatic term (Eq. (9)).

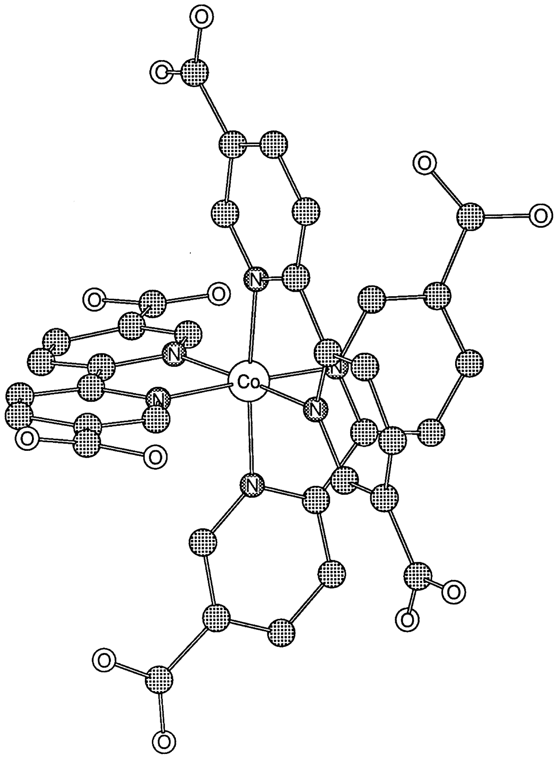
$$\log_{10} k_f^s = \log_{10} k_f^o + pa_1 + a_2 + r_1 + r_2, \tag{9}$$

where p is simply the number of N atoms. In comparison to the Co(II) and Ni(II) systems, it is a_2 which accounts for significant differences between the two. The solvent structure around Co^{2+} ions in 4- and 3-methylpyridine solutions, studied using EXAFS shows a six-coordinate octahedral arrangement [118]. This contrasts with the tetrahedral four-coordinate arrangements found in similar solutions of Zn^{2+} ions.

A range of Co(II) complexes of the ligand 2,4′-bipyridine corresponding to the formulae: $[CoL_2Cl_2(OH_2)_2]$, $[CoL_2Br_2(OH_2)_2]L \cdot 4H_2O$, $[CoL_2(OH_2)_4]L_2(NO_3)_2$ and $[COL_4(OH_2)_2](ClO_4)_2 \cdot 2H_2O$ have been prepared and characterized [119]. The X-ray crystal structure of the complex tris(2,2′-bipyridyl-5,5-dicarboxylate-NM)-cobalt(III) (**68**) sesquihydrate has been determined [120].

The pyridine complex $[Co(C_5H_5N)_4](Cl)(PF_6)$ has been isolated from a reaction mixture containing an aqueous mixture of cobalt(II) acetate, pyridine, acetic acid, ozone and ammonium hexafluorophosphate [121]. The X-ray crystal structure shows that the cation has a planar arrangement of the py molecules around the Co.

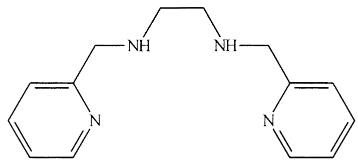
The preparation of the first simple binuclear μ-oxalato complexes of Co(II) has been described [122]. The complexes were $[(N_4)Co(C_2O_4)Co(N_4)](ClO_4)_2$, where N_4 is *N,N′*-bis(2-pyridylmethyl)-1,2-ethanediamine, bispicen, *N,N′*-bis(2-pyridylmethyl)-1,3-propanediamine, bispinctn, and *N,N′*-bis(2-pyridylmethyl)-*N,N′*-dimethyl-1,2-ethanediamine, bispicMe_2en. These were prepared by reaction of the hydrochloride of the ligand with $CoCl_2 \cdot 6H_2O$ as yellow–pink crystals. The X-ray crystal structure of the complex $[(bispicen)Co(C_2O_4)Co(bispicen)](ClO_4)_2 \cdot H_2O$, in



(68)

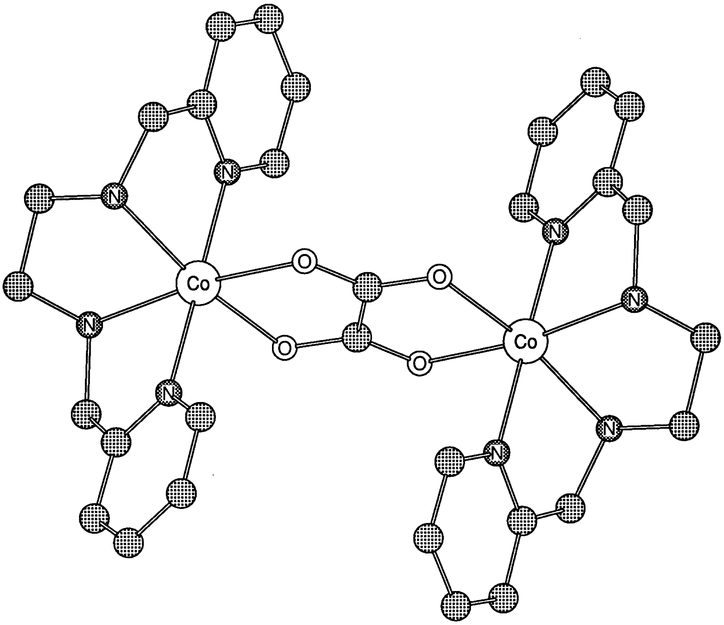
which bisicen is **(69)**, shows that it crystallizes in the triclinic space group $P\bar{1}$ with one complex cation formula unit in a cell with $a=8.832$ Å,$b=9.297$ Å, $c=13.045$ Å, $\alpha=108.01°$, $\beta=98.48°$, and $\gamma=93.31°$. The structure **(70)** consists of a six-coordinate arrangement around the Co with the two cobalt atoms bridged by two planar oxalate groups. The Co complex was studied as one of a series of first row transition metal complexes of these ligands and in addition to structural information, magnetic measurements were carried out and the room temperature values of the effective magnetic moments for the complexes were in the range 6.7–7.2 μ_B, rather larger than in "normal" Co(II) complexes. There was a range of J values for the ions Mn(II), Fe(II), Co(II), Ni(II) and Cu(II), giving J values of about 2, 6, 10, 33, and 2 cm^{-1}, respectively, a variation which the authors attribute to magnetic interaction between the $d(x^2-y^2)$ orbitals of the metal ions in the complex.

The reduction of CO_2 remains an area of active study and the planar structure and hydrophobic nature of 2,2′:6′,2″:6 ″,2‴-quaterpyridine (qtpy) and the electrochemical advantages that might give have prompted a study of complex $[Co(qtpy)(OH_2)_2][ClO_4]_2$ which has been prepared by the reaction of $Co(ClO_4)_2 \cdot 6H_2O$ with qtpy in acetonitrile [123]. Cyclic voltammetric studies of $[Co(qtpy)(OH_2)_2]^{2+}$ in acetonitrile show that for the couple



Bispicen

(69)



(70)

$[Co(qtpy)(OH_2)_2]^{2+/+}$ $E_{1/2}=0.67$ V versus SCE with a further couple at -0.96 V, which is assigned to a Co^+/Co^0 couple and the suggested processes involved are in Eq. (10). The complex could be electrodeposited onto an electrode surface and this electrode as a multilayer by controlled potential electrolysis of a solution of the complex at -1.65 V, when a complex concentration of $\geq 0.2\times10^{-3}$ mol dm^{-3} was used. This modified electrode has been shown to be active in the reduction of CO_2 to Co at -1.7 V with a current efficiency of 80% with a turnover of catalyst of about 20 cycles. It is clear from other experiments performed that it is the Co complexes on the surface of the electrode which produce the catalytic effect. These experiments were carried out in acetonitrile, but other experiments showed that the catalytic activity towards CO_2 reduction also operates in aqueous solution.

$$\text{Couple 1 } [Co(qtpy)(H_2O)_2]^{2+} + e^- \rightleftarrows [Co(qtpy)(H_2O)_2]^+ \tag{10}$$

$$[Co(qtpy)(H_2O)_2]^+ \overset{slow}{\rightleftarrows} [Co(qtpy)]^+ + H_2O$$

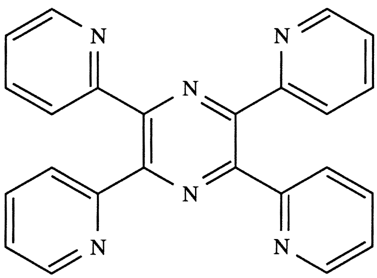
$$\text{Couple 2 } [Co(qtpy)]^+ + e^- \rightleftarrows [Co(qtpy)].$$

The complexes $[Co(TA)X_2]$ and $[Co(TA)_2X_2]$, where TA = 1,2,4-triazole and X = Cl or Br have been prepared and characterized [124]. They are shown to exhibit antiferromagnetic behaviour.

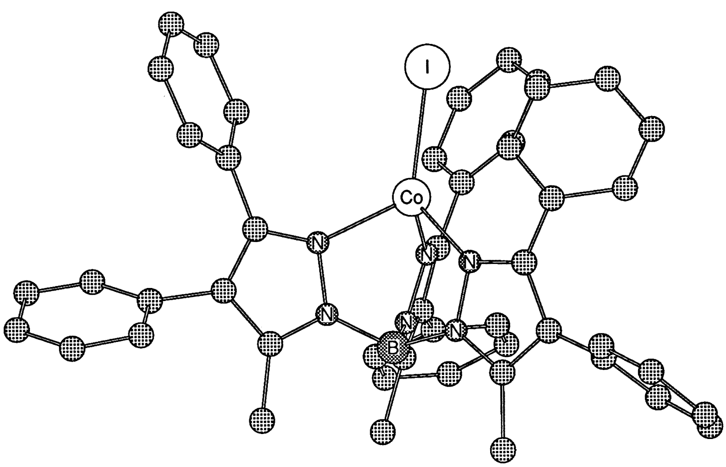
Catalysts for the electroreduction of dioxygen in fuel cells may be produced by adsorbing tetracarboxylato cobalt(II) phthalocyanine on carbon black followed by heating to a temperature between 100 and 1100 °C [125]. Although the highest catalytic activity is found when the adsorbed species was heated to between 500 and 700 °C, the resulting electrodes are not very stable. In fact, the most stable electrodes were produced at temperatures at the higher end of the range studied, where significant decomposition of the complex has occurred and where cobalt is present to some extent as the metal and/or oxides and that this may afford some protection to the electrode. Both cobalt(II) phthalocyaninetetracarboxylic acid ($[CoPc(COOH)_4]$) and cobalt(II) phthalocyanineoctacarboxylic acid ($[CoPc(COOH)_8]$) catalyse the autoxidation of 2-mercaptoethanol [126]. The catalytic reaction is promoted by 2,4-ionene. Key features in the process are the dimerization of the $[CoPc(COOH)_4]$ and the loss of the μ-peroxo complex which is not catalytically active in this process when 2,4-ionene is present produces an increase in rate of the oxidation by a factor of about 40.

For the complex cations bis(terpyridine)cobalt(II), (i), and bis(2,6-*N*-$NHCH_3$–pyridinedicarboxaldimine)cobalt(II), (ii), the absence of any excess ultrasonic absorption in water (and methanol in the case of the former) is taken to show that there is a spin-equilibrium time of <2 ms [127]. Using measurement of magnetic moments of solutions of these two complexes over a range of temperatures the following thermodynamic parameters were determined. For (i) in methanol, $\Delta H^\circ = 8.715$ kJ mol^{-1} and $\Delta S^\circ = 26.46$ J K^{-1} mol^{-1}, and in water $\Delta H^\circ = 16.4$ kJ mol^{-1} and $\Delta S^\circ = 54.84$ J K^{-1} mol^{-1}. For (ii) in methanol, $\Delta H^\circ = 11.45$ kJ mol^{-1} and $\Delta S^\circ = 30.48$ J K^{-1} mol^{-1}, and in water $\Delta H^\circ = 17.18$ kJ mol^{-1} and $\Delta S^\circ = 45.35$ J K^{-1} mol^{-1}. The complex bis(2,6-*N*-$NHCH_3$-pyridinedicarboxaldimine)cobalt(II) in methanol and water and for bis(2,6-*tert*-butylpyridinedicarboxaldimine)cobalt(II) in methanol there was a significant excess sound absorption, which the authors suggest may be due to a dechelation process occurring.

When the ligand 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) (**71**) is reacted with $CoCl_2$/NaCl a mixture of polynuclear complexes were produced [128]. When the mixture is recrystallized from acetonitrile a linear polymer was produced in which the Co was found to be present in three different chemical environments. The complex was shown to be $[\{(\mu\text{-Cl})_2(MeCN)Co(tppz)Co(CoCl_4)\}_n]$. The X-ray crystal structure has been determined.

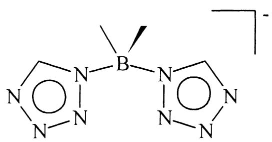


(71)



(72)

A so-called "half-sandwich" structure for a Co complex involving hydridotris(pyrazoyl)borate ligand has been prepared [129]. The ligands used were hydridotris(3,4-diphenyl-5-methylpyrazoyl)borate and hydrido(3,4-diphenyl-5-methylpyrazoyl(3-methyl-4,5-diphenylpyrazoyl)borate. The X-ray crystal structure of the complex $Co[BH(3,4\text{-}Ph_2\text{-}5\text{-}Mepz)_3]$ (**72**) has been determined. In related work, the complex $[Tp^{ant}]CoCNS$ has been prepared, in which Tp^{ant} is tris[3-(*p*-anthyl)pyrazal-1-yl]hydroborate [130]. The reactant used was $Tl[Tp^{ant}l$ and the crystals used for the X-ray structure determination were found to contain about 6% of this species which had cocrystallized with the complex. It is surmised that the cocrystallization occurred because the disordered site can be contained within a pocket in the tris(pyrazoyl)hydroborato ligand. A range of complexes of the form $[M(NH_3)_2\{\mu\text{-}H_2B(CHN_4)_2\}_2]_n$ including that of Co(II) have been prepared [131]. The result is a series of two-dimensional polymers utilizing the ligand (**73**). In this structure the metal is octahedrally coordinated to the two *trans* NH_3 ligands and four $H_2B(CHN_4)_2^-$ ligands.



(73)

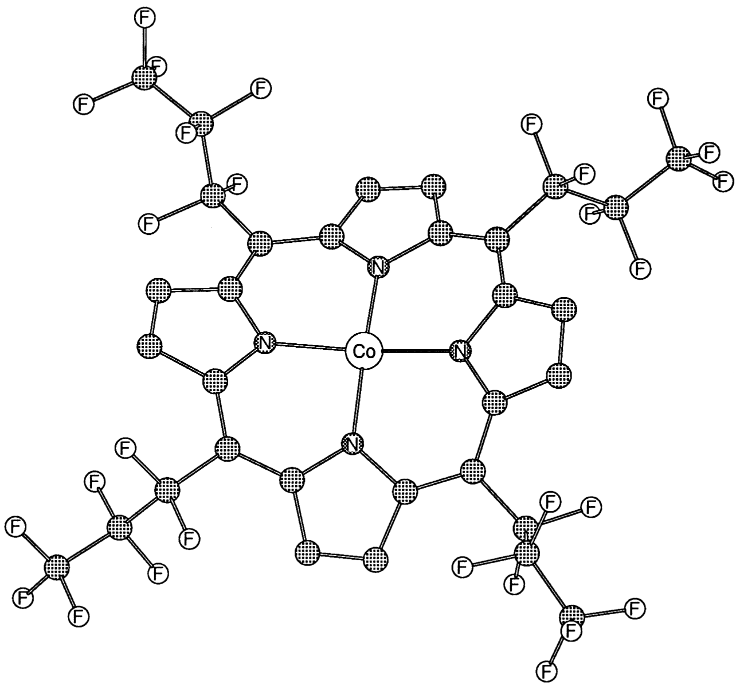
It is reported that polymeric cobalt(H) phthalocyanine is a much better catalyst for the oxidation of the sulphide ion than is the monomer [132]. Reversible disproportionation of the form has been observed in alkaline solution (Eq. (11)).

$$2Co^{2+} \rightleftharpoons Co^{+} + Co^{3+} \tag{11}$$

Cyanogen (in excess) reacts in an autoclave at room temperature in chloroform with complexes (phthalocyaninato)- and (2,3-naphthalocyaninato)cobalt(II) complexes $(t\text{-Bu})_4$PcCo, 2,3,9,10,16,17,23,24-$(C_7H_{15})_8$PcCo, 1,4,8,11,15,18,22,25-$(C_7H_{15})_8$PcCo, and $(t\text{-Bu})_4$-2,3-NcCo [133]. The knack in carrying out these reactions is that since the porphyrin reactants were insoluble in chloroform, they were peripherally substituted with *tert* butyl group or similar, which made them soluble and hence able to react with the cyanogen. The products are largely cyano-bridged oligomers $[(mac)Co(CN)]_n$, where mac = Pc or 2,3-Nc. The complex $[(t\text{-Bu})_4\text{-2,3NcCo(CN)}]_n$ has an extremely high conductivity of 8×10^{-2} S cm^{-1}.

The kinetics of NO loss from nitrosylcobalt(II)tetraphenylporphyrinate have been studied on the femtosecond timescale and above [134]. When measurements were made on the femtosecond timescale, two exponential processes having rate constants of 4.7×10^{11} and 9.0×10^{10} s^{-1}. The second of these was attributed to the vibrational cooling of the freed porphyrin, while the first was attributed to the conversion of one of the states localized on the porphyrin π system to a metal centred electronic state. This leads to the conclusion that loss of NO from this species results from an extremely rapid process indeed. In order to probe the effects on the electronic structures of porphyrins of distortions of the ring the X-ray crystal structure of the complex [5,10,15,20-tetrakis(heptafluoropropyl)porphinato]cobalt(II) (**74**) has been determined [135]. The information from this structure, the electronic spectra of the complex and that of the free ligand, it has been possible to show that non-polar conformations do not greatly influence the electronic properties of these electron deficient, non-planar ligands. When corrolato or porphyrinato species are produced by the reaction of 2-α-hydroxyalkyl)pyrroles with Co^{2+} the type of tetrapyrrole produced depends very much upon the extent of steric hindrance produced by the substituents on the starting material [136]. When the pyrroles shown in (**75**) were reacted with trifluoroacetic acid, sodium acetate, cobalt(II) acetate and triphenyl phosphine, 3-ethyl-4-methyl-2-(α-hydroxybenzyl)pyrrole-5-carboxylic acid (a) produced [(triphenylphosphine)(5,10,15-triphenyl-2,7,12,17-tetramethyl-3,8,13,18-

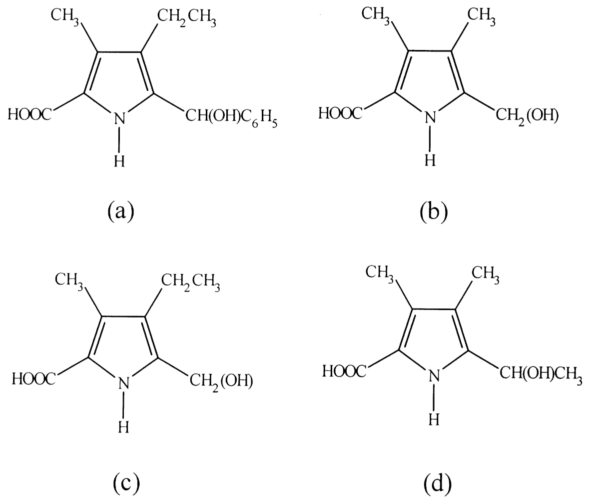
tetraethylcorrolato)cobalt(III), [Co(TMTETPC)(PPh_3)] (**76**) which has alternate Me and Et groups in the β-pyrrolic positions, (b) produced octamethylporphyrin, (c) gave etioporphyrin and (d) did not show any sign of cyclization.



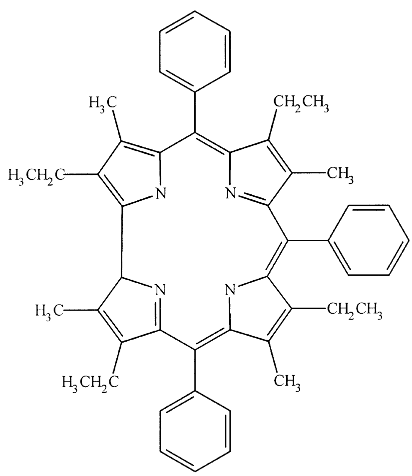
(74)

Compounds of the type [Cr(III)$_2$M(II)O($MeCO_2$)$_6$(py)$_3$].py show an unexpected increase by a factor of about 2.3 in M(III)–M(III) spin–spin exchange interaction as measured from the magnetic properties rather than the expected decrease [137]. In order to ascertain whether the cause of this effect lay in the consequences of polarization of the μ_3-oxygen atom and the effect of this, in turn, on the structure of the M_3O triangle in the structure of the compounds, an attempt was made to determine the structure of [Cr(III)$_2$M(II)O($MeCO_2$)$_6$(py)$_3$].py with particular reference to this part of the overall structure. X-ray crystal structure determination is found to be hampered by the effects of long range disorder in the crystals. EXAFS was, therefore, used to study the Cr(III)Co(II) compound utilizing both the Cr and the Co K-edge, since it does not suffer from the long-range disorder problem. Although the structural data showed that there were small distortions in the appropriate geometry in the structure, these were insufficient to explain on their own the observed magnetic effects.

Reductive electrochemical polymerization of a dinuclear cobalt complex with pyrrole substituents has been used in the production of metallopolymer films [138]. Unusually, the mechanism of the polymerization appears to involve the cleavage of



(75)



[(triphenylphosphine)(5,10,15-triphenyl-2,7,12,17-tetramethyl-3,8,13,18-teraethyl corrolato)cobalt(III)

[Co(TMTETPC)PPh3]

(76)

the pyrrole rings of the complex. The polymer has some useful properties, in that it is an electrical conductor when reduced and is also electrochromic.

A readily used, sensitive and specific method of determining ascorbic acid is badly needed. A possible method is the solid state membrane electrode based on the complex [(4,4′,4″,4‴-tetra-*tert*-butylphthalocyanine)cobalt(II) [139]. The electrode is usable over a concentration range of 2×10^{-6} to 1×10^{-3} mol dm^{-3}. The kinetics of the reaction between pyridine and [Co(Pc)] in dmso solution at 25 °C have been investigated [140]. The reaction was found to be biphasic, with, (under suitable conditions), two consecutive pseudo first order reactions. The final product is [Co(Pc)(py)$_2$]. The equilibrium constants for each of the steps were found to be $K_1 = 160$ dm^3 mol^{-1} and $K_2 = 15$ dm^3 mol^{-1} for the formation of [CoPc(py)(dmso)] and [CoPc(py)$_2$], respectively. The fact that cobalt phthalocyanine is an important feature of the Li/$SOCl_2$ battery has led Bernstein and Lever to investigate the reaction of tetraneopentoxyphthalocyanine, Co($TnPc^{2-}$) and $SOCl_2$ [141]. The reaction between cobalt(II) tetraneopentoxyphthalocyanine and thionyl chloride was carried out in 1,2-dichlorobenzene with the strict exclusion of water, HCl and SO_2. When the two were mixed, there followed a reaction which was complete in less than 1 s, and which resulted in loss of Co($TnPc^{2-}$) in a two-electron redox process where the oxidation products consist of a mixture of Cl_2Co(III)($TnPc^{1-}$) and ($SOCl_2$)Co(II)($TnPc^{2-}$) (Eq. (12)). The term “SO” is used by the authors to mean some initial reduction product of $SOCl_2$. The reaction was followed using stopped flow kinetic measurements. Only $k_1 + k_2$ could be determined and a value of 18140 M^{-1} s^{-1} was obtained. This very fast reaction was followed by a very much slower reaction, taking many minutes to complete. Possible reaction pathways are then those in Eq. (13) and by losing $SOCl_2$ followed by the k_1 pathway shown in Eq. (12). These give rise to the rate expression (Eq. (14)). The value of k_4 derived from this is 1.51 M^{-1} s^{-1}. Estimates were made for the other rate constants. The presence of HCl added to the reaction mixture causes a 100-fold decrease in rate due to the formation of the species Co(II)($TnPc^{2-}$).HCl which prevents the formation of the $SOCl_2$ adduct.

$$\mathrm{Co(II)TnPc(2-)} + \mathrm{SOCl_2} \xrightarrow{k_1} \mathrm{Cl_2Co(III)TnPc(1-)} + \text{“SO”} \tag{12}$$

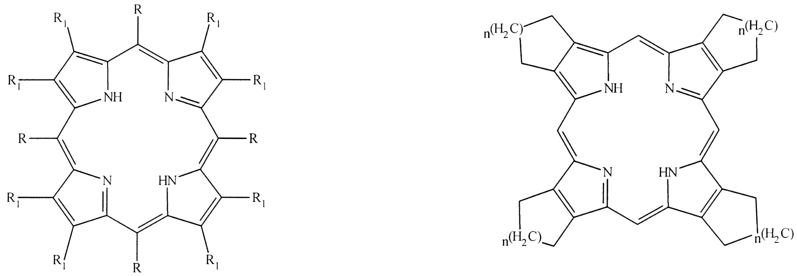
$$\mathrm{Co(II)TnPc(2-)} + \mathrm{SOCl_2} \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} \mathrm{(SOCl_2)Co(II)TnPc(2-)},$$

$$\mathrm{(SOCl_2)Co(II)TnPc(2-)} \xrightarrow{k_3} \mathrm{Cl_2Co(III)TnPc(1-)} + \text{“SO”} \tag{13}$$

$$\mathrm{(SOCl_2)Co(II)TnPc(2-)} + \mathrm{SOCl_2} \xrightarrow{k_4} \mathrm{Cl_2Co(III)TnPc(1-)} + \text{“SO”} + \mathrm{SOCl_2},$$

$$k_{obs} = k_1 k_{-2}/(k_1 + k_2) + k_3 + k_4[\mathrm{SOCl_2}]. \tag{14}$$

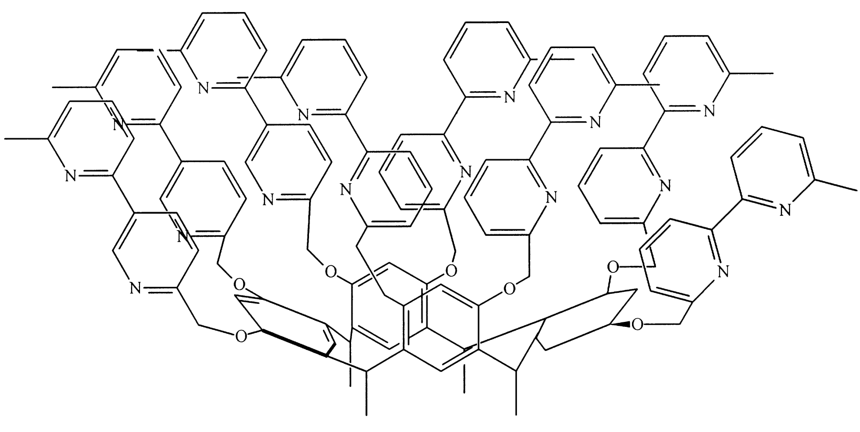
The X-ray crystal structure of many porphyrins show that they have a non-planar structure in which there is a cavity, the presence of which influences the chemical and physical properties of the molecule [142]. By using a combination of ^{1}H NMR spectroscopy and molecular mechanics calculations, it has proved possible to show that the conformations of seven dodeca-substituted porphyrins (**77**) are similar in solution and in the crystal and that the molecular cavities seen in the crystal structure are still present in solution. This conclusion has considerable importance in terms of the behaviour of porphyrins in solution. Variable temperature NMR studies in this work showed that the cavity structure in solution was, however, fluxional because of the effect of macrocyclic inversion in some of the porphyrins studied. It was also shown that, like the planar porphyrins, these non-planar molecules are able to form π-complexes with molecules such as 1,3,5-trinitrobenzene.



In the porphyrins studied: $R = C_6H_5$ $R_1 = CH_3$
$R = C_6H_5$ $R_1 = CH_2CH_3$
$R = C_6H_5$ $R_1 = CH2CH_2CH_3$

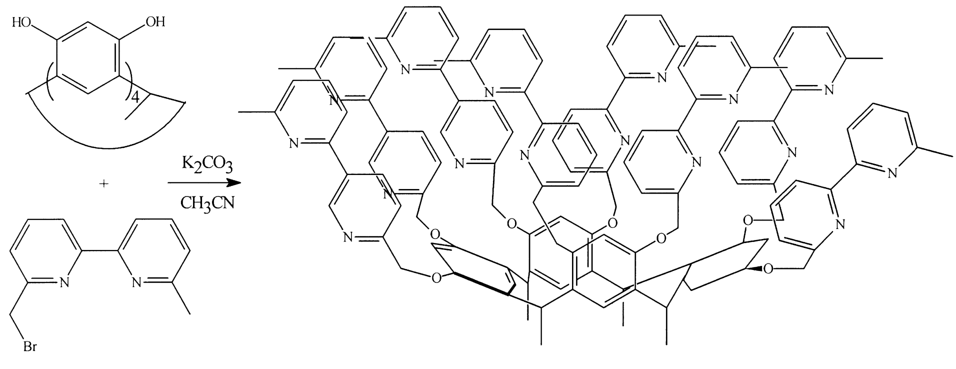
In the porphyrins studied: n = 1 $R = C_6H_2$(3,4,5-OMe)
n = 2 $R = C_6H_5$
n = 3 $R = C_6H_5$

(77)

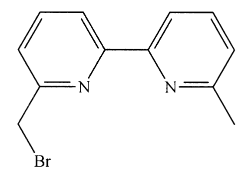


(78)

A new "octopode" cobalt(II) complex has been prepared [143]. The new ligand, calix[4]resorcinarene-bipyridyl podand, (**78**) has been prepared by the alkylation of 2,8,14,20-tetra(methyl)calix[4]resorcinarene (**79**) with 6-bromomethyl-6′-methyl-2,2′-bipyridine (**80**). The turquoise blue Co(II) complex was prepared by the reaction of this compound with $CoCl_2$ in a mixture of MeOH and CH_2Cl_2 under



(79)

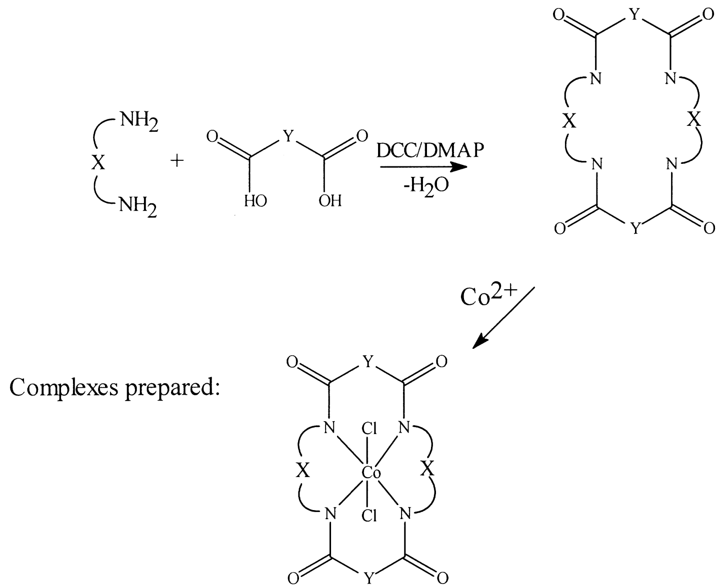


(80)

an N_2 atmosphere and was found to contain eight $CoCl_2$ groups for each molecular formula.

Some new 16- and 18-membered tetraazamacrocycles have been prepared and their corresponding Co(II) complexes characterized [144]. The ligands were made by the condensation of phthalic acid with primary diamines followed by reduction with $LiAlH_4$ which resulted in the corresponding tetraazamacrocycles. The complexes produced were of the form [Co(L)Cl_2]. The same group have also prepared a range of 14- to 22-membered tetraoxomacrocyclic tetraamines, producing Co(II) complexes of the same stoichiometry as the above [145]. The ligands (**81**) were prepared by the reaction of some aliphatic diamines of the type $H_2N(CH_2)_nNH_2$ (where $n=2$ or 3) with dicarboxylic acids in the presence of (dicyclohexylcarbodiimide) and [4-(dimethylamino)pyridine]. In all, four reddish-brown cobalt(II) complexes of the ligands L^1, L^2, L^3 and L^4 [defined in (**81**)] were prepared. Both the ESR and electronic spectral data are consistent with a low-spin octahedral environment for the Co(II).

A range of red–green dichroic crystals of the complexes based on the variations to the ligand papyH, pyridine-2-carbaldehyde pyridin-2′-ylhydrazone (**82**), which are of the form [Co(papy)$_2$] and also [Hpapy][$CoCl_4$], have been prepared by electrochemical oxidation of cobalt in an acetone solution of the ligand [146]. The ligands were produced by the alteration of the substituents R^1 and R^2, both in terms of their nature and the position of R^2 on the pyridine ring. The advantage of



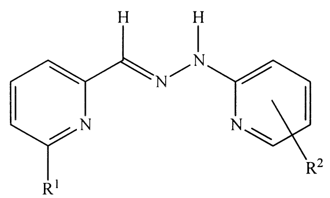
L^1 $X = (CH_2)_2$ $Y = (CH_2)_3$

L^2 $X = (CH_2)_3$ $Y = (CH_2)_3$

L^3 $X = (CH_2)_2$ $Y = (CH_2)_4$

L^4 $X = (CH_2)_3$ $Y = (CH_2)_4$

(81)



(82)

the electrochemical synthesis in this case is that conventional chemical synthesis is susceptible to oxidation, whereas the method described in this work readily produces very good crystalline products in high yields. Measurements of magnetic moments were carried out over a range of temperatures and these showed that some of the complexes obeyed the Curie–Weiss law, while others showed anomalous behaviour. Furthermore, some of the complexes behaved as expected for low-spin species, i.e. very small variations with temperature, while others were clearly showed high-spin behaviour. At least in part, high-spin behaviour is attributed to steric crowding in those complexes where it is observed. The same author has used a similar technique to produce a series of cobalt(II) imidazolate and pyrazolate complexes with yields in the range 50–100% [147]. The violet (or orange in the case of Co(III) species), high-melting powders which were produced were found to be air-stable and insoluble in most solvents, though slightly soluble in dmso. The complexes were of the type $[Co(II)(Iz)_2]$ (where Iz = imidazolate); $[Co(II)(Melz)_2]$ (where Melz = 4-methylimidazolate); $[Co(II)(Pr(i)Iz)_2]$ (where Pr(i)Iz = 2-isopropylimidazolate); $[Co(III)(pyIz)_n]$ (where pyIz = 2-(2′-pyridyl)imidazolate); $[Co(III)(Pz)_n]$ (where Pz = pyrazolate); $[Co(III)(ClPz)_n]$ and $[Co(III)(IPZ)_n]$ (where ClPz = 4-chloropyrazolate; IPz = 4-iodopyrazolate); $[Co(II)(Me_2Pz)_n]$ (whereMe_2Pz = 3,5-dimethylpyrazolate) and $[Co(II)(BrMe_2Pz)_n]$ ($BrMe_2Pz$ = 3,5-dimethyl-4-bromopyrazolate). From the IR spectra, the absence of N–H stretching bands was taken to imply the absence of protonated diazoles, in keeping with some sort of polymeric structure. Plots of μ_{eff} against temperature from magnetic measurements showed that these complexes obeyed the Ising equation of interacting S = 3/2 spin. The magnetic measurements also support the polymeric structure. The reaction of glycine with *o*-hydroxybenzaldehyde yields a new tridentate Schiff base [149]. A series of mixed-ligand complexes which were found to have the general formulae $[Co(SB)(L)_3]$,in which SB = Schiff base and L = quinoline, isoquinoline, 2-picoline, 4-picoline and pyridine.

A range of di-(5-substituted-salicylidene)(ethylenediamine) cobalt(II) complexes are found to be metallomesogens [150]. Their properties have been investigated by a number of techniques, including optical, X-ray, DSC and magnetic susceptibility methods. Some of the complexes react with dioxygen and whether they are active or inactive and the process involved was investigated using X-ray diffraction.

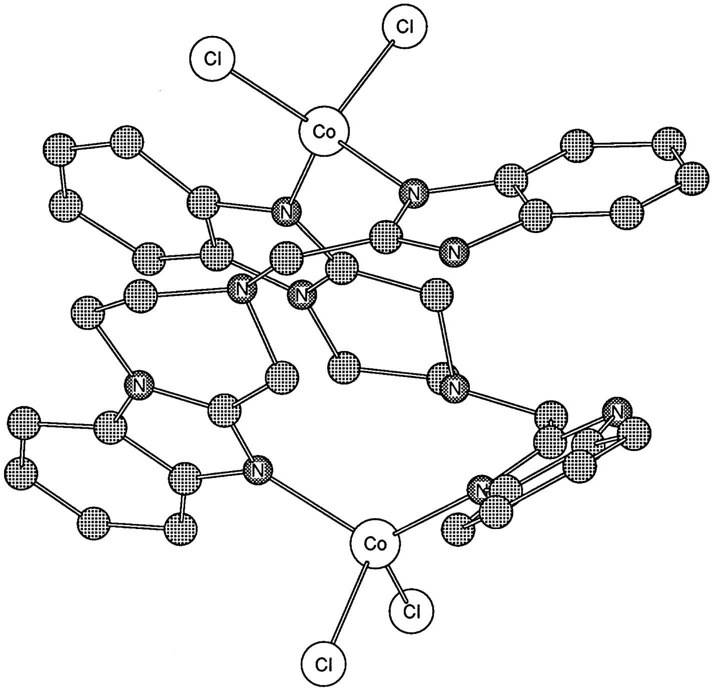
A series of complexes of six metal ions, among them Co(II) of the macrocyclic ligands *N,N′,N″,N‴*-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane (THEC-12) and *N,N′,N″,N‴*-tetrakis(2-hydroxyethyl)- 1,4,8,12-tetraazacyclopentadecane (THEC-15) have been investigated kinetically [151].The formation constants for each species were measured and showed that the presence of a hydroxyethyl group in the complex appeared to have a significant destabilizing effect. The kinetics of the loss of the ligands from the complexes (decomplexation) were measured and for the $[M(THEC\text{-}12)]^{2+}$ complexes the rate law was that given in Eq. (15).

$$k_{obs} = k_o + k_H[H^+]. \tag{15}$$

In Eq. (15), at 298.2 K, $k_o = 3.06 \times 10^{-5}\ s^{-1}$ and $k_H = 61.4\ dm^3\ mol^{-1}\ s^{-1}$ when M = Co. The corresponding reaction for $[M(THEC\text{-}15)]^{2+}$ complexes where M = Co or Ni, was very slow, having a half-life of more than a day.

The 1:1 complex between Co(II) and 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane has been prepared and investigated using ^1H NMR spectroscopy [152]. Analysis of the paramagnetic NMR spectrum has allowed the authors to assign all the paramagnetically shifted signals to methylene and methyl protons. The effect of temperature variation on the NMR spectrum has furnished information about the dynamic properties of the complex in solution. A structure is proposed in which the four donor nitrogen atoms are occupying the equatorial positions of an octahedral distribution around the Co. The presence of the Me groups on the ligand appears to prevent its having any reaction with dioxygen.

A dinuclear complex, $[Co_2Cl_4L_2]\cdot C_2H_5OH$ is the product of the reaction of Co(II) with the species [4′-(2″-methylene-benzimidazole-yl)-1′,4′-dinitrogencyclo-hexane](1,2)-benzimidazole dissolved in ethanol [153]. The X-ray crystal structure (**83**) shows that there is a tetrahedral arrangement around the Co atoms with the environment consisting of two N atoms and two Cl atoms and benzimidazole bridges.



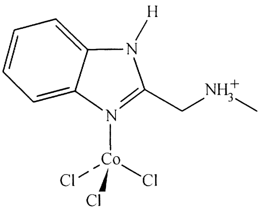
(83)

The Co(II) complex of 5-cyano-1, 6-dihydro-4-methyl-l-*p*-tolyl-6-oxopyridazine-3-carboxylic acid hydrazide is one of a series of such complexes of first row transition metals which has been prepared [154]. This complex has the form $[CoL_2]\cdot nH_2O$ and the ligand is tridentate. Reaction of bis(Δ_2-2-imidazolinyl) with cyanogen-di-*N*-oxide yields the potential ligand bis(Δ_2-2-imidazolinyl)-5,5′-dioxime [155]. This reacts with Co(II) to produce $[CoL_2]$ and reaction of this with Cu(II) produces a trinuclear complex of the form $[(HL)_2Co(II)Cu(II)_2Cl_4]$.

As part of a search for models of coordination of metal ions to active sites of proteins and other biologically active molecules, the X-ray crystal structure of the species trichloro[(1H-benzimidazol-2-ylmethyl)(ethyl)ammonium-*N*-3]cobalt(II)

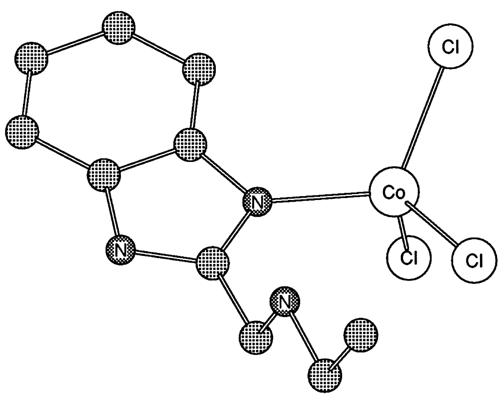
(**84**) and (**85**) has been determined [156]. The complex has the ligand bonded to the Co in a monodentate fashion through N and the other three positions occupied by Cl atoms. This results in a distorted tetrahedral arrangement around the Co.

The X-ray crystal structure of the complex [Co(L-N_4Me_2)Cl_2] formed by reaction

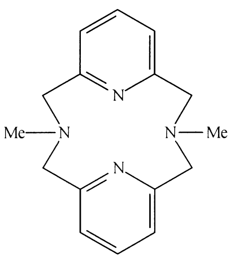


Trichloro[1H-benzimidazole-2-ylethyl)(ethyl)ammonium-N-3]cobalt(II)

(84)



(85)



L-N_4Me_2

(86)

of *N*,*N*′-dimethyl-2,11-diaza[3,3](2,6)pyridinophane (**86**) (L-N_4Me_2) with Co(II) has also been determined [157]. The structure shows that the complex contains a *cis*-octahedral coordination geometry at the metal site which the authors attribute to the fact that the 12-membered ring of the ligand has only a small cavity. The two axial sites are occupied by the amine N atoms of the ligand, while the pyridine N atoms are to be found in the equatorial positions, with the other two places being taken by the two Cl ligands. The X-ray crystal structure of the ligand was also determined and it was found to have a characteristic "folded" structure in a chair–chair conformation with equatorial Me groups.

The reaction of 2-aminopyrimidine and $CoSO_4 \cdot 7H_2O$ in aqueous solution leads to the production of pale red crystals of bis[triaqua(2-aminopyrimidine)-μ-sulphato-*O,O*′-cobalt(II)] dihydrate, $[Co(2\text{-}AP)(H_2O)_3SO_4]_2 \cdot 2H_2O$ [158]. The crystal structure of this moiety was determined by X-ray diffraction. This shows that the complex is dimeric and the two Co(II) units are bridged by two sulphato groups. The thermal analysis of the complex as studied using thermogravimetry showed that the final product was Co_3O_4, which was produced by four distinct steps, as shown in (**87**).

$$[Co(C_4H_5N_3)(H_2O)_3SO_4].H_2O$$

$$\downarrow -3H_2O \qquad 60 - 200^{o}C$$

$$[Co(C_4H_5N_3)(H_2O)_3SO_4]$$

$$\downarrow -H_2O\ -HCN \qquad 200 - 380^{o}C$$

$$[Co(C_3H_4N_2)SO_4]$$

$$\downarrow -C_2H_2\ -H_2NCN \qquad 380 - 665^{o}C$$

$$[Co(SO_4)_2]$$

$$\downarrow -SO_3 \qquad 665 - 985^{o}C$$

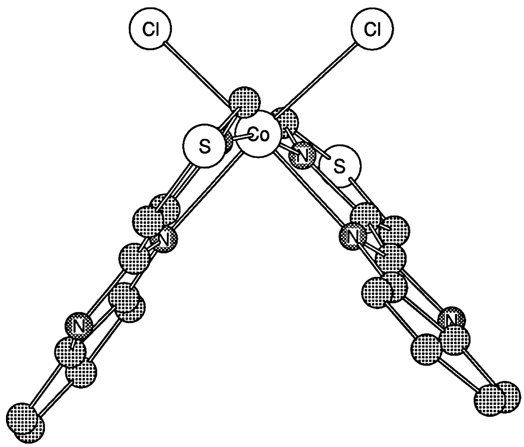
$$Co_2O_4$$

Thermal Decomposition of $[Co(2\text{-}AP)(H_2O)_3SO_4]_2.2H_2O$

(87)

Reaction of *anti*-dichloroglyoxime with *sym*-bis(p-aminophenyl)oxamidine and *sym*-bis-4-(4′-aminobiphenyl)oxamidine yields two new polymeric bis(oxamidine)diaminoglyoximes [159]. They form complexes with Co(II) and these have been isolated and characterized. Complexes of the type $[Co(vn2bz)(H_2O)_2Cl_2]_2Cl_2$, where vn2bz = bis(vanillin)benzidine have also been isolated and characterized by a variety of techniques [160]. Coordination to the Co is through the azomethine N atoms of the ligand, giving what is believed to be a tetrahedral coordination environment around Co.

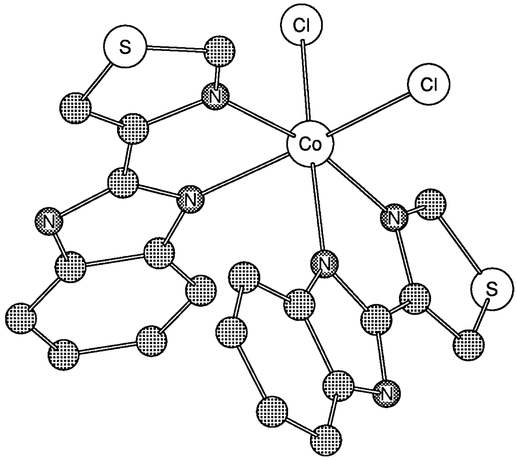
The complex dichloro(2-(4-thiazolyl)-1H-benzimidazole)cobalt(II) monohydrate $[CoCl_2(C_{10}H_7N_3S)_2 \cdot H_2O]$ has been prepared and characterized [161]. The X-ray crystal structure (**88**) and (**89**) shows that the Co is surrounded octahedrally by two didentate 2-(4-thiazolyl)-1H-benzimidazole ligands and the other two positions are occupied by the Cl atoms. The bonding of the ligand is through the thiazolyl and benzimidazole ring N atoms which are in a *cis* configuration.



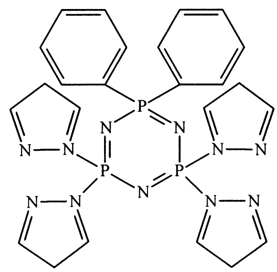
(88)

A distorted trigonal bipyramidal structure around the Co has been found for the dark blue complex $(N_3P_3Ph_2Pz_4)CoCl_2.0.5CH_2Cl_2$ [162], where $N_3P_3Ph_2Pz_4$ is 2,2-diphenyl-4,4,6,6-tetrakis(l-pyrazolyl) cyclotriphosphazene (**90**). The X-ray crystal structure of $(N_3P_3Ph_2Pz_4)CoCl_2$, (**91**), shows that the bonding of the ligand is through the pyridine N atoms at two of the equatorial positions, while one of the axial positions and the remaining equatorial are occupied by the two Cl atoms. The remaining axial position is occupied by a cyclophosphazene ring nitrogen. The pyrazoyl rings were found to be planar and the cyclotriphosphazine ring non-planar.

Eight compounds with general formulae $[CoX_2L]$, $[CoXL_2]X$, $[CoX_2L_2]$, $[CoL_3]X_2$, where $X^- = Bro^-$, Cl^-, NCS^-, ClO_{4-} where L = O-methyl-pyridine-2-carboximidate, have been obtained [163]. The structures of these complexes were tentatively assigned using various physical techniques as have a pseudo-tetrahedral, octahedral or tetragonally distorted arrangement of the donor groups around the Co.



(89)

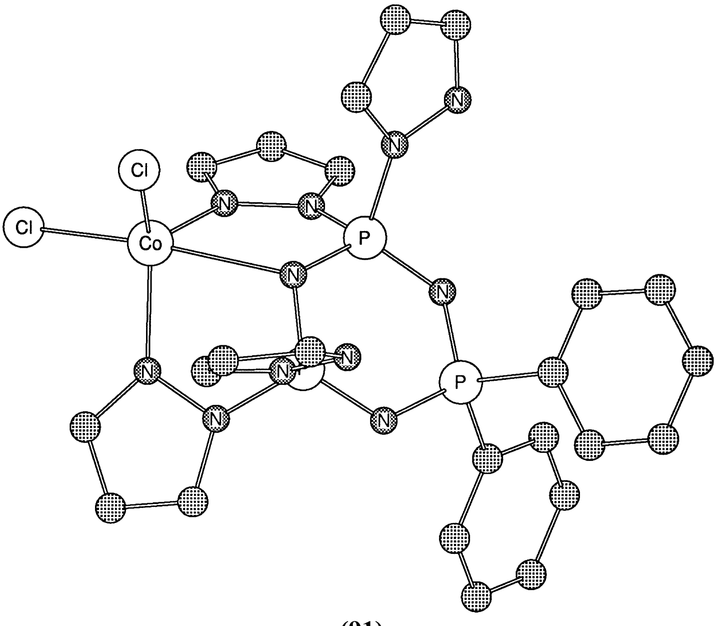


$N_3P_3Ph_2Pz_4$

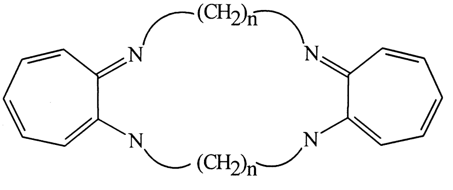
(90)

The ligands shown in (**92**) are collectively referred to as tropocoronands. The new ligand N,N-bis(pyrazol-1-ylmethyl)benzylamine (**93**) has been synthesized and from it the complex $[Co(L)X_2]$, where X is Cl^-, Br^- or NCS^- have been prepared [164]. The X-ray crystal structures of the Cl^- and NCS^- complexes show that the geometry around the Co(II) lies between trigonal bipyramidal and distorted tetrahedral. These have been used to produce a series of Co(II) complexes [165]. X-ray crystal structures have been obtained for $[Co(TC_{n,m}]$, where $n,m = 3,3$; 4,4; 4,5; 5,5; and 6,6. The structure of the binuclear complex $[Co_2(\mu\text{-OAc}(\mu\text{-OH})(Tc_{7,7})$ has also been determined and found to have a bridging acetato and hydroxo group lying on each side of the ligand plane as shown in (**94**). The X-ray crystal structure of the Co(II) red complex $[\{CoCl(NPEt_3)\}_4]$ has a heterocubane structure, illustrated diagrammatically in (**95**) [166].

A number of new M(II) complexes, including that of Co(II) have been prepared by the reaction of formaldehyde with 4-hydroxy-L-proline while it is coordinated to



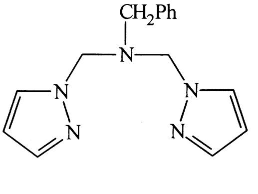
(91)



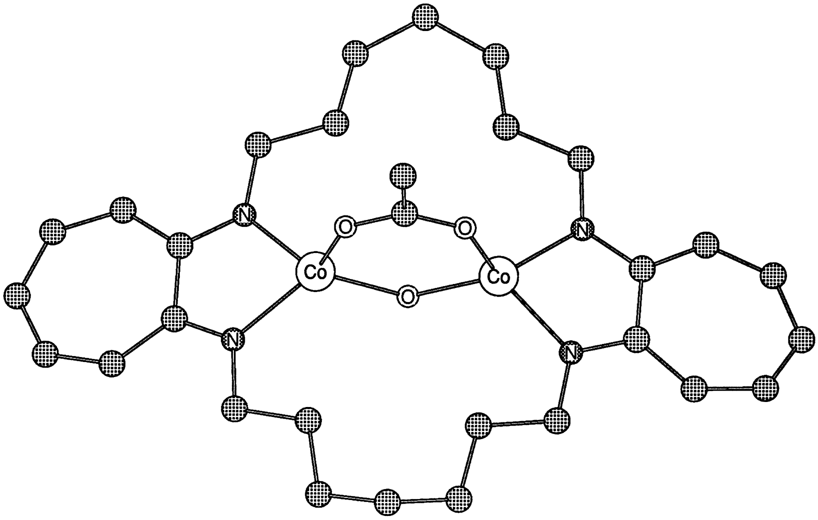
$H_2TC_{n,m}$

n,m = 3,3; 3,4; 4,4; 5;5 6,6; 7,7

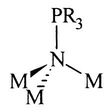
(92)



(93)



(94)

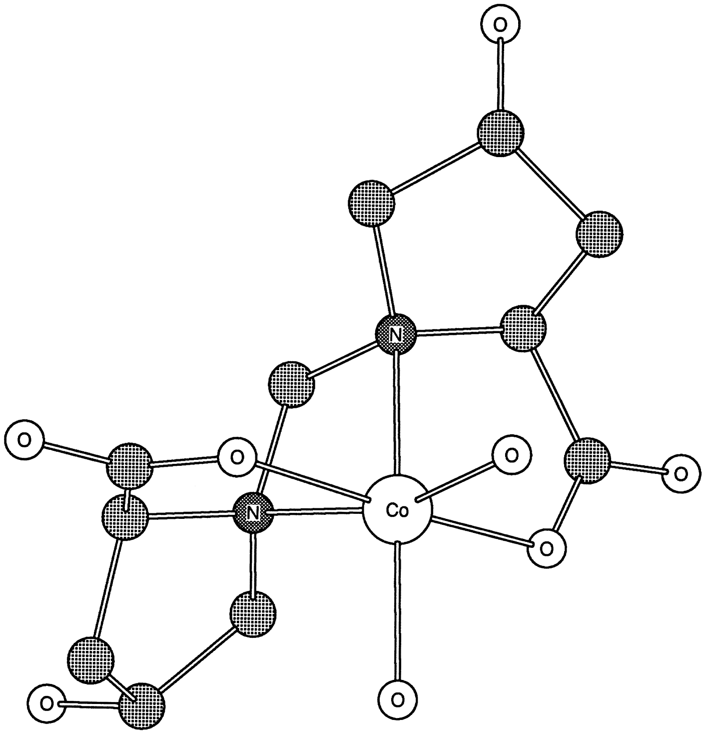


(95)

the metal [167]. This results in an *N,N'*-methylenedi(4-hydroxy-L-proline) complex, Co[My(OH-Pro)$_2$] (**96**). In this complex the amino N atoms are joined by the methylene bridge.

2.2. Complexes with oxygen donor ligands

The most deceptively simple oxygen donor coordination compounds of Co(II) are of course the aqua and hydroxo compounds which often form the starting point for the synthesis of other coordination compounds. A new form of cobalt(II) hydroxide has been produced electrochemically from solutions of $Co(NO_3)_2$ which also contain species such as glucose, fructose, lactose, glycerol or citric acid [168]. In strongly acid solution Co(II) ions catalyse the decomposition of H_2O_2 and peroxomonosulphate ion ($HOOSO_3^-$) and the kinetics of this process have been investigated [169]. The overall stoichiometry of the reaction is represented in Eq. (16) with a rate law (Eq. (17)) derived from the kinetic investigation. There is clearly a link between the two peroxo species in mechanistic terms, since the behaviour in the mixture is significantly different from that seen when only one of the peroxo compounds is present, so the k^H in the above equation is some six times larger when H_2O_2 is not present. The mechanism proposed is shown in Eq. (18) and it indicates the intermediacy of Co(III) which is trapped by H_2O_2 forming the peroxo radical.



(96)

$$HOOSO_3 + HOOH \rightarrow O_2 + H_2O + HSO_4^-, \tag{16}$$

$$-d\frac{[HOOSO_3^-]}{dt} = k_H\left\{\frac{[Co^{2+}][HOOSO_3^-]}{[H^+]}\right\}, \tag{17}$$

$$Co^{2+} + H_2O \rightleftarrows CoOH + H^+ \tag{18}$$

$$CoOH + HOOSO_3^- \rightarrow CoO^+ + H_2O + SO_4^{\cdot -}$$

$$CoO^+ + 2H^+ \rightarrow CO(III) + H_2O$$

$$Co^{2+} + SO_4^{\cdot -} \rightarrow Co(III) + SO_4^{2-}$$

$$Co(III) + HOOSO_3^- \rightarrow Co^{2+} + H^+ + {}^{\cdot}OOSO_3^-$$

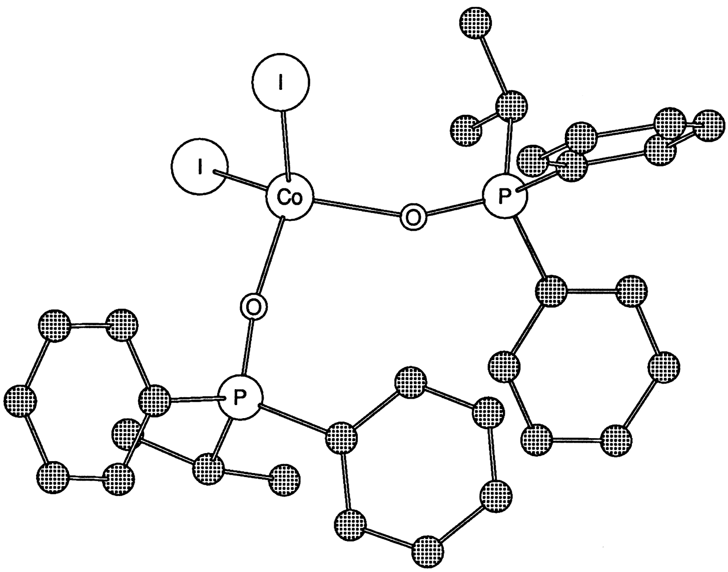
$$Co(III) + HOOH \rightarrow Co^{2+} + H^+ + HOO^{\cdot}$$

$$SO_4^{\cdot -} + HOOH \rightarrow SO_4^{2-} + H^+ + HOO^{\cdot}$$

$${}^{\cdot}OOSO_3^- + HOOH \rightarrow HOOSO_3^- + HOO^{\cdot}$$

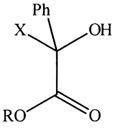
$$2HOO^{\cdot} \rightarrow HOOH + O_2.$$

The chemistry of the solution of cobalt metal in acetic acid has been studied together with the influence of dissolved oxidants on the process [170]. Crystals of the complex dirubidium *trans*-tetraaquabis(carbonato)cobaltate(II), $Rb_2[Co(CO_3)_2(H_2O)_4)]$ have been prepared and the crystal structure determined [171]. Oxidation and cleavage of the ion *cyclo*-hexaphosphate(III) in an aqueous solution containing ethanol and ammonia yield the compound $Co_2P_2O_6 \cdot 12H_2O$ [172]. The structure was found to consist of chains of $[P_2O_6]^-$ ions which are connected to each other by the Co^{2+} ions and together with the water molecules this results in pairs of octahedra which share edges formed by the $[P_2O_6]^-$ oxygen atoms. The compound diiodobis(isopropyldiphenylphosphine oxide-*O*)cobalt(II), $[CoI_2\{(C_6H_5)_2(C_3H_7)OP\}_2]$, (**97**), has been found from an X-ray crystal structure determination to contain Co which is surrounded in a distorted tetrahedral manner by the two I atoms and the $(C_6H_5)_2(C_3H_7)OP$ groups [173].



(97)

Perhaps the most common type of complexes studied using thermoanalytical techniques are oxalates. The compound $Co(NH_3NH_3)(C_2O_4)_2 \cdot 2H_2O$, has been prepared by the reaction of $CoSO_4$ with hydrazinium oxalate [174] and its thermal decomposition studied. Cobalt(II) complexes of benzilic and mandelic esters (**98**) have also been made and characterized using a range of techniques [175]. It is proposed that the structures involve a distorted octahedral arrangement around the cobalt centre. 3,4-Dichlorobenzoates of a number of first row transition metal ions, including Co(II) have been prepared [176]. Thermal decomposition studies show that the anhydrous complex is produced in two stages by the loss of water from $Co(C_7H_3O_2Cl_2)_2 \cdot nH_2O$. The same group has also determined the crystal structure of hexaaquacobalt(H)bis(2,6-dichlorobenzoate) [177]. The crystals belong to the monoclinic space group $P2_1/c$ with $a=5.378$, $b=6.144$, $c=30.562$ Å, and $\beta=92.18°$. Essentially, the complex consists of $[Co(H_2O)_6]^{2+}$ cations linked to the 2,6-dichlorobenzoate anions by hydrogen bonds.

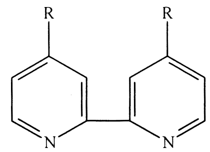


For benzilic ester, X = Ph and R = Me
For mandelic ester, X = H and R = Et

(98)

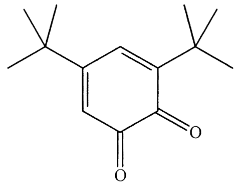
A study has been carried out on the dynamics of the high-spin [Co(II)(3,5-dtbsq)$_2$] to low-spin [Co(III)(3,5-dtbsq)(3,5-dtbcat)1 interconversion produced by photoinduction using picosecond time-resolved optical experiments [178]. The complexes involved in these experiments were [Co(dpbpy)(3,5-dtbsq)(3,5-dtbcat)1 and [Co(dmbpy)(3,5dtbsq)(3,5-dtbcat)] where dpbpy is 4,4′-diphenyl-2,2′-bipyridine and dmbpy is 4,4′-dimethyl-2,2′-bipyridine; 3,5-dtbsq and 3,5-dtbcat are, respectively, the semiquinone and catecholate forms of 3,5-di-tert-butyl-1,2-benzoquinone (**99**). It is clear from the variation of the UV–VIS spectrum over the temperature range 298–348 K that there is a decreasing amount of the Co(III) species and increasing amount of the Co(II) complex as the temperature is increased. When a 70 ps pulse at the LMCT wavelength of the Co(III) complex from a laser is incident on the solution there is a rapid increase in absorbance at 720 nm and an equally rapid decrease in absorbance at 600 nm, the time constant, τ, was found to be 1.15 ns for each of these wavelengths. This is interpreted as the photolytic formation of high spin [Co(II)(NN(sq)$_2$], which decays back to equilibrium. These processes are highly solvent dependent, with transient lifetimes varying between 1.1 ns for toluene to 10 ns in dichloromethane. For the complex containing dmbpy, the lifetime of the excited state was found to be about 8 ns in toluene.

A method for the analysis of cobalt by spectrophotometric methods by extraction using trifluoroacetylacetone and pyridine has been developed [179]. The coloured complex produced allows spectrophotometric measurement at 315 nm. A similar method of analysis has been developed in which the extraction of cobalt utilizes penta-2,4-dione and 4-phenylbuta-2,4-dione as complexing agent [180]. The technique has the advantage that it can be used to extract Co from a number of other metal ions.



R = Ph = 4,4'-diphenyl-2,2'-bipyridine

R = Me = 4,4'-dimethyl-2,2'-bipyridine



3,5-di-tert-butyl-1,2-benzoquinone

(99)

Finding ways of removing SO_2 from industrial waste such as flue gases could be crucially important in reducing atmospheric pollution and it is possible that coordination compounds of transition metal would have a role in any processes which are developed for this purpose. McAuliffe and coworkers have had a long-standing interest in the reactions of SO_2 with transition metal complexes and have studied the reactions of SO_2 with pseudotetrahedral Co(II) complexes of the type $[Co(OEPh_3)_2X_2]$ in which, E = P or As and X = Cl, Br, I or NCS and $[Co(OPMe_3)_2I_2]$, the method used being to react the Co(II) salt with Ph_3EO [181]. Under anaerobic conditions, many of these deep blue complexes react in the solid state with gaseous SO_2 and $[Co(OEMe_3)_2I_2]$, where E = P or As forms 1:1 complexes containing SO_2 with some change in the appearance of the solids. Some similar reactions occur when the process is carried out anaerobically in toluene solution. In the presence of air, $[Co(OEPh_3)_2I_2]$ undergoes a series of reactions, which are illustrated in (**100**), that ultimately result in the oxidation of SO_2 to SO_4^{2-} and producing $CoSO_4 \cdot H_2O$.

The reaction of $[Co(OPMe_3)_3]_2]$ in air with SO_2 in toluene solution results in the precipitation of pale pink crystals, which were suitable for X-ray diffraction and which turned out to contain both five- and six-coordinated $[Co(OPMe_3)_3(OH_2)_2]I_2$ and $[Co(OPMe_3)_3(OH_2)_3]I_2$ respectively. The crystal structures of these complexes which had crystallized together were determined (**101**). They were found to consist of octahedral *mer*-$[Co(OPMe_3)_3(OH_2)_3]^{2+}$ and trigonal bipyramidal $[Co(OPMe_3)_3(OH_2)_2]^{2+}$. The authors draw attention to the fact that it is remarkable that the structure of *mer*-$[Co(OPMe_3)_3(OH_2)_3]^{2+}$ features an almost linear Co–O–P bond instead of the normal bent arrangement. It is proposed that the SO_2 in the

$$[Co(OPPh_3)_3I_2] + 2SO_2 \xrightarrow{\text{toluene/air}} (Ph_3PO)(Ph_3POH)(HSO_4) + I_2 + \text{brown solid} \xrightarrow{CH_2Cl_2/\text{air}} CoSO_4.H_2O$$

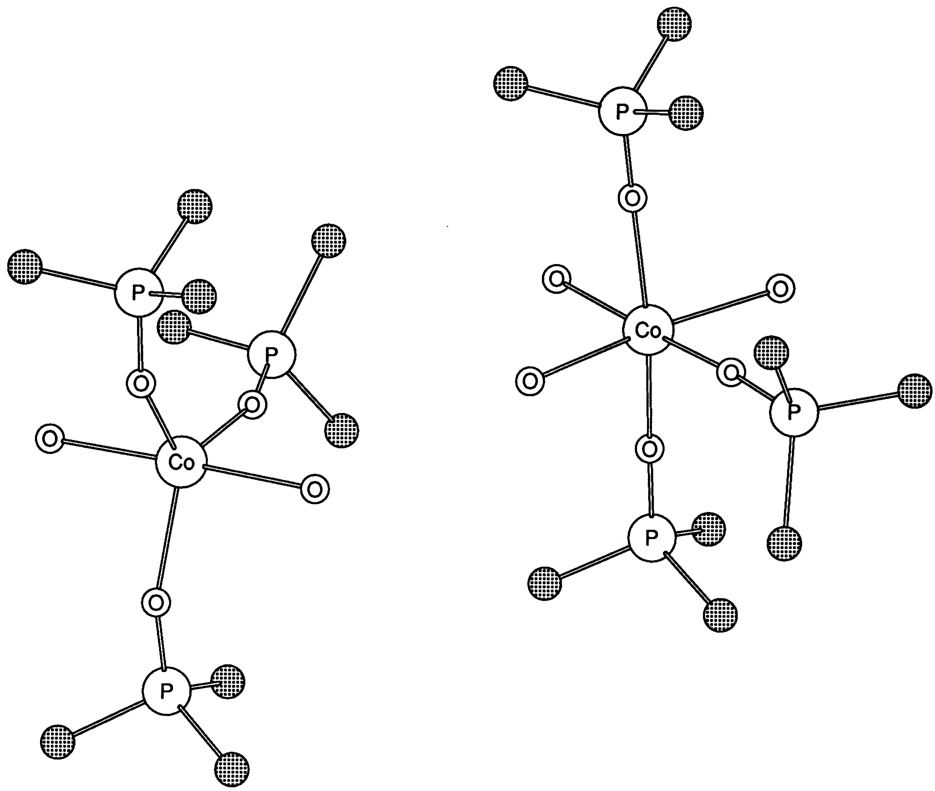
(100)

resulting complex is bonded, not directly to the metal ion, but to the ligand in some way.

The compounds $[Co(H_2L)_3](ClO_4)_2 \cdot 2H_2O$ and $[Co(H_2O)_6]L$, where L= piperazine-1,4-diylbis(methylene)bis(phosphinic) acid (**102**) have been prepared [182]. The X-ray crystal structure of $[Co(H_2L)_3](ClO_4)_2 \cdot 2H_2O$ shows that it consists of a network of Co atoms, around which, arranged in an approximately octahedral fashion are six oxygen atoms from the phosphinate groups and in which the ligand H_2L performs the role of bridging between metal atoms. The ligand is monodentate, being coordinated to the Co via the phosphinate groups; the structure of the cation $[Co(H_2L)_3]^{2+}$ is shown in (**103**). The complex $[Co(H_2O)_6]L$ has a structure in which a network of Co(II) species are bridged by the ligand and the whole is held together by hydrogen bonds.

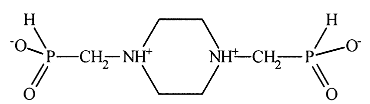
For many years, the so-called nitroso-R complexes formed with cobalt by disodium 1-nitroso-2-naphthol-3-6-disulphonate (nitroso-R salt) have been used as a qualitative and sometimes qualitative reagents for the detection of cobalt. It has now been found that the Co complex forms a compound with tetradecyldimethylbenzylammonium iodide on a naphthalene ($TDBA^+I^-$-naphthalene) packed column [183]. This adduct is insoluble in water and the metal ion complex can be dissolved out of the column using a dimethylformamide/chloroform mixture and the Co determined spectrophotometrically at 425 nm. Nitroso-R salt also features in a method of analysis of Co using hexaacetatocalix(6)arene in toluene as the extraction agent [184]. The cobalt(II) was extracted at pH 7.4 with 10×10^{-4} M solution of hexaacetocalix(6)arene which was then stopped with 2 M nitric acid, and the Co determined spectrophotometrically at 500 nm as the nitroso-R-salt complex.

Reaction of cobalt(II) nitrate with H_2XDK (xylenediaminebis-(Kemp's triacid imide)) (**104**) and neocuproine (neo), 2,9-dimethyl- 1,10-phenanthroline (**105**) yielded the blue crystals of the complex [Co(XDK)(neo)l The X-ray crystal structure of $[Co(XDK)(neo)] \cdot 3CH_3OH$ ($1.3CH_3OH$) has been determined [185]. The arrangement around the Co was found unusually to be a distorted trigonal bipyramid to which three O atoms from the XDK and two N atoms from the neocuprine contributed. When alkali metal salts were added to a solution of this complex there



Cations only are shown

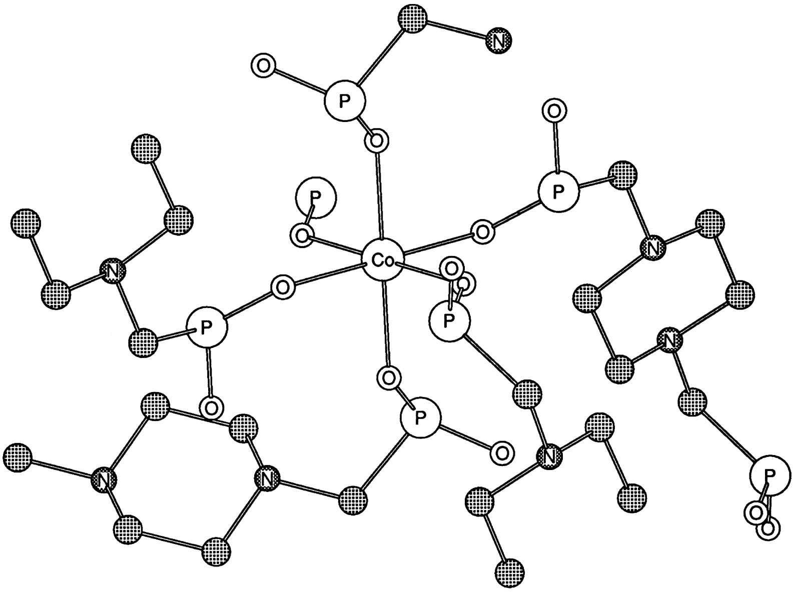
(101)



Piperazine-1,4-diylbis(methylene)phosphonic acid

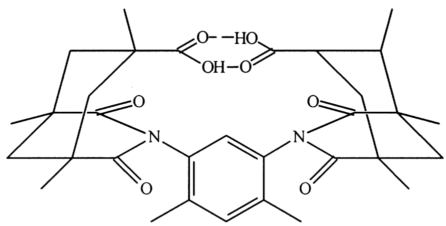
(102)

were significant changes to the UV–VIS spectrum which signalled the coordination of the cobalt complex with the alkali metals. Typical complexes formed in this way were: $[KCo(XDK)(neo)(PF_6)]$ and $[Rb_2Co_2(XDK)_2(neo)_2(H_2O)(BPh_4)_2]$. The X-ray crystal structures of $[KCo(XDK)(neo)(PF_6)]\cdot 2CH_3CN$ (2.2CH_3CN) and also of $[Rb_2Co_2(XDK)_2(neo)_2(H_2O)(BPh_4)_2]\cdot 2CHCl_3$ (3.2$CHCl_3$) have been determined. In the potassium compound, the K^+ ion is to be found in a seven-coordinate environment of O atoms from the XDK and F atoms from the PF_6^-. To allow this



(103)

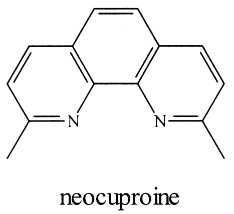
to happen, the geometry around the Co has to change and now becomes trigonal pyramidal (**106**).



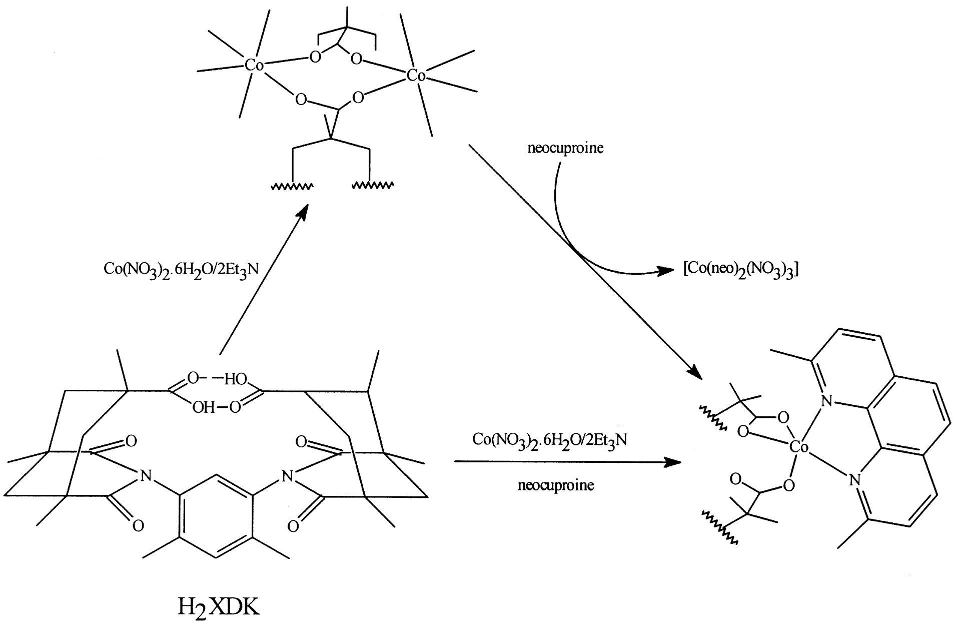
(104)

The synthesis of complexes $[Co(HXCA)_2] \cdot nH_2O$ where HXCA = 2-hydroxy-ω-4-X-cinnamoylacetophenone (**107**), X = H, Cl, Me or OMe and $n = 0$ or 2 has been described [186]. It is deduced from spectroscopic data that coordination to the Co occurs through the carbonyl and enolic oxygen atoms and that the structure involves a polymeric arrangement based on an octahedral arrangement around the Co, though it is believed that the diaqua and dipyridine species are monomeric.

The homoleptic complex, $Co(AAEMA)_2$ is obtained when $Co(NO_3)_2$ is reacted in alkaline solution with 2-(acetoacetoxy)ethylmethacrylate (HAAEMA) (**109**)



(105)

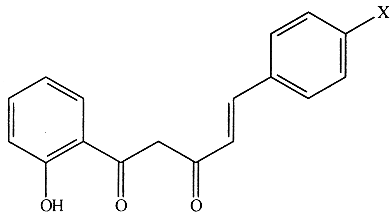


(106)

[187]. The heteroleptic [Co(AAEMA)(AcO)] complex is formed when $Co(AcO)_2$ and HAAEMA are the starting materials. From the infrared spectra it is deduced that the structure of this species contains a CoO_6 environment in which there is an oligomeric arrangement with acetate bridging the Co atoms. It is very air sensitive, being readily converted into the green Co(III) complex. It also reacts with water to give the blue [Co(OH)(OAc)]. $[Co(AAEMA)_2]$ is also proposed to have an oligomeric structure, but this time with β-ketoester bridging.

The complex hexapyridine-*N*-oxide cobalt(II) perchlorate, $Co(C_5H_5NO)_6(ClO_4)_2$ has been studied using high-resolution single crystal X-ray diffraction collected at 78 K; the cation is shown in structure (**109**) [188].

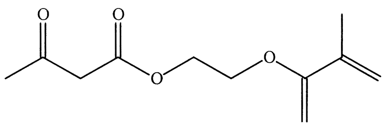
Reaction of the imidazoline nitroxide free radical 4-(2-oxoethen-



2-hydroxy-ω-4-X-cinnamoylacetophenone

X = H, Cl, Me, OMe

(107)



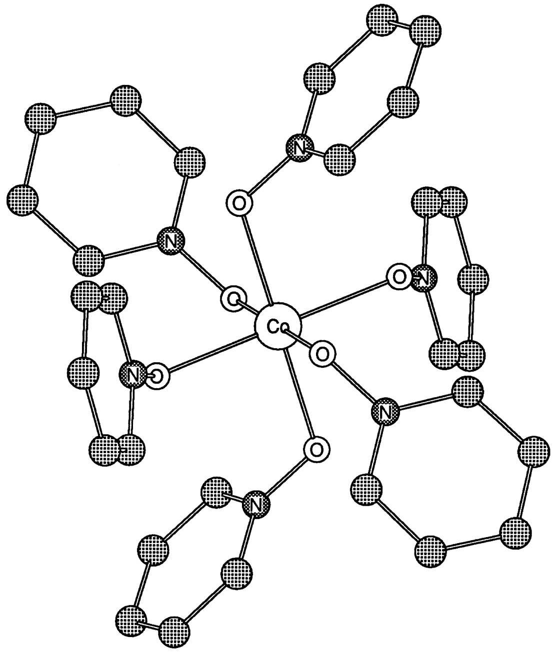
2-(acetoacetoxy)ethylmethacrylate, HAAEMA

(108)

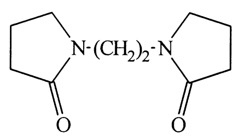
1-yl)-2,2,5,5-tetramethyl-3-in-imidazolyl-1-oxy Co(II) acetate produces the centrosymmetric pentacoordinated binuclear species, $[Co_2(L_4)]$ [189]. The X-ray crystal structure of this complex showed that it belonged to space group $P2_1/c$, with $a = 12.169$, $b = 11.300$, $c = 15.944$ Å, $\beta = 101.16°$ and $Z = 2$. The structure around the Co is described as being between a square pyramidal and a trigonal bipyramidal arrangement.

A whole range of complexes of the ligand *N,N'*-ethylenebis(pyrrolidin-2-one), ebpyrr (**110**) have been prepared and among them are the blue $[Co(ebpyrr)(NO_3)_2(MeCN)_n]$ (**111**) and the magenta $[Co(ebpyrr)Cl_2]_n$ (**112**), for which X-ray crystal structures have been obtained [190]. For (**111**), limited data were obtained because of its rapid decomposition; however, it was shown to have an octahedral arrangement around the Co and contains one monodentate and one didentate NO_3, as well as the CH_3CN molecule and one O atom from each of the two ebpyrr molecules.

A cobalt(II) containing heteropolyanion involving paradodecatungstate has been prepared. The pink complex $K_6[(Co(H_2O)_4)_2(H_2W_{12}O_{42})]] \cdot 14H_2O$ has been found to consist of the heteropolyanion $([(Co(H_2O)_4)_2(H_2W_{12}O_{42})]_n^{6n-}$ [191]. The X-ray crystal structure of this complex has been determined; the complex consists of a novel chain-like structure containing four groups containing three edge-sharing WO_6 octahedra. The crystal structures of $\alpha_1ET_8[CoW_{12}O_{40}] \cdot 5.5H_2O$ and



(109)

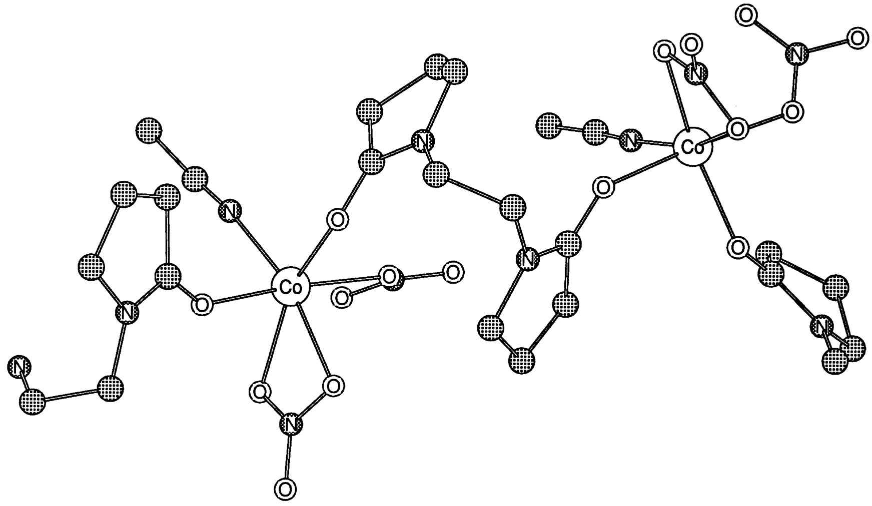


(110)

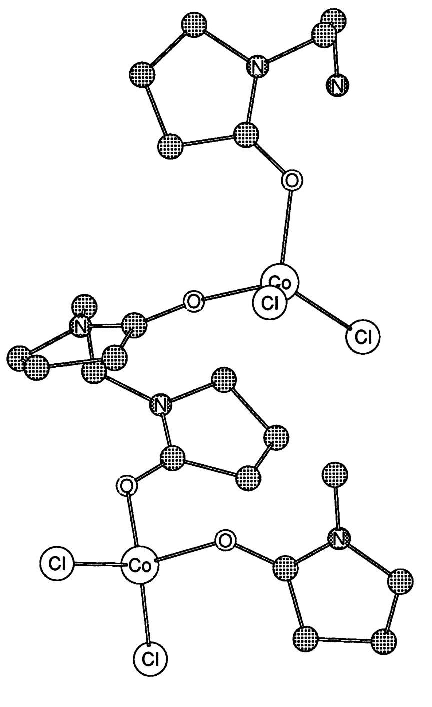
$\alpha_2ET_8[CoW_{12}O_{40}]\cdot 0.5CH_3CN\ 3H_2O$, in which ET is bis(ethylenedithio)tetrafulvalene (**113**), have been determined [192]. Infrared and Raman data were obtained, giving information about the degree of ionicity. Bulk electronic properties were also determined. It was then possible to link these with dynamic properties, (ESR spectroscopy), giving electronic exchange information about the organic species and between the organic and inorganic moieties.

2.3. Complexes with nitrogen–oxygen donor ligands

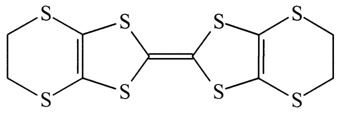
The nature of the solvent structure around metal ions is a notoriously difficult area of study. The solvent structure around Co^{2+} dissolved in *N,N*-dimethylformamide has been investigated using X-ray diffraction [193]. The cobalt in the form of the perchlorate had in its first coordination sphere a total of six dmf molecules. The disposition of these was such that the distances of the O, C_1 and N atoms from the


N
N
N
Co
O
O
O
O
O
O
N
O
N
N
N
N
Co
O
O
O
O
O
O
N
O
O
N

(111)


N
N
O
Co
Cl
Cl
O
N
N
O
Cl
Co
O
N
Cl

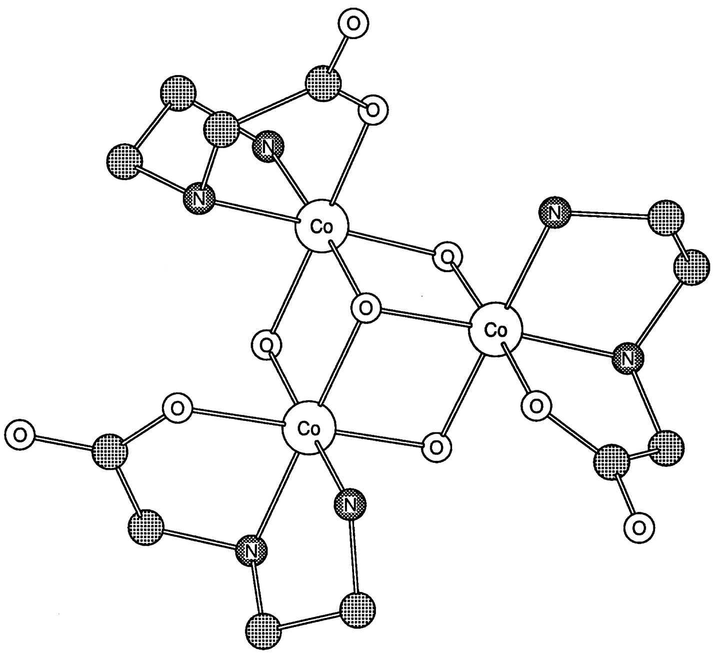
(112)



Bis(ethylenedithio)tetrafulvalene

(113)

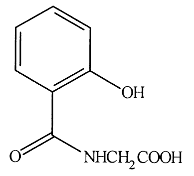
Co^{2+} were, respectively: 2.13, 2.99 and 4.23 Å and the Co–O–C_1 bond angle 123°. Three isomers of the trinuclear complex $[Co_3(L)_3(\mu_2\text{-OH})_3(\mu_3\text{-O})]Cl$, in which L= ethylenediamine-*N*-acetate have been prepared [194]. The structure of one of these isomers (**114**) was determined by X-ray diffraction and the partial cubane core of this complex can readily be seen.



(114)

Turning now to more tangible complexes of Co(II) containing *N*-donor ligands, the malonamato (HL−) complex *trans*-$[Co(HL)_2(H_2O)_2]$ is one of a series of such species of transition metal complexes which have been prepared [195]. The X-ray structures of the Cu(II) and Zn(II) complexes have been determined and this information and the application of spectroscopic techniques to the Co(II) complex suggest that it also contains didentate malonamate coordinated through the amide and a carboxylate oxygen. The thermodynamic parameters of glycine complexes of Co(II) as a function of temperature and ionic strength have been determined [196].

The data have allowed these workers to develop a computer model which is able to simulate speciation in this system in a variety of solution environments. Salicylglycine (**115**) is a metabolite of aspirin and the complex [Co(HL)$_2$] has been prepared and characterized [197]. Infrared spectroscopic and other data suggest that the ligands are monodentate with the Co in an octahedral environment and is bonded through the carboxylato group. The other positions are occupied by solvent molecules (H_2O or CH_3OH).



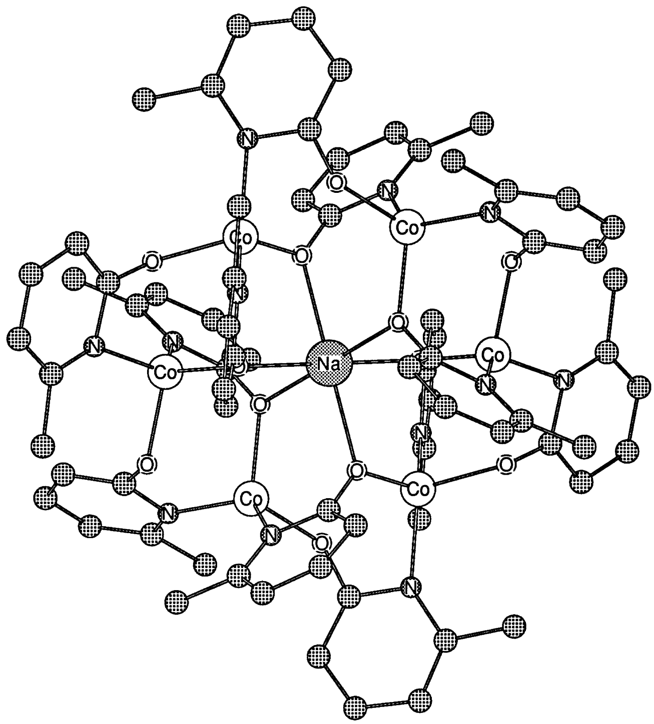
(115)

^{19}F NMR spectroscopy has been used to study complexes of the type $(Et_4N)_2$[Co(Z-Cys-Pro-Leu-Cys-Gly-X)$_2$] in which Z = benzyloxycarbonyl and X = NHC$_6$H$_4$-*p*-F, NHC$_6$H$_4$-*m*-F and NHCH$_2$CH$_2$C$_6$-*p*-F [198]. The NMR spectra show that it is likely that an important feature of the structures of these complexes is the presence of NH–S hydrogen bonds as well as interactions between the S atom and aromatic groups.

The success of edta as a titrating agent for a wide variety of metal ion in many different matrices lies in its ability to complex metal ions which are already bonded to other ligands. Edta, nitrilotriacetic acid (NTA), 1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetic acid (CyDTA), and ethylenebis(oxyethylenenitrilo)tetraacetic acid (egta) all act in this way by removing Co (and Ni) from complexes of the form bis(heptane-2,4,6-trionato)Co(II) and the kinetics of such reactions over a range of pH values have been investigated using stopped flow kinetic methods [199]. The reactivities of the complexing agents in these systems varied markedly. Thus, in the case of NTA, there was a non-linear dependence on ligand concentration. Mechanisms involving an essentially associative model are proposed.

A range of ligands has been prepared by reaction of isonitrosoacetylacetone (Hiso) with *o*-aminophenol (H$_2$isoaph), *p*-aminophenol (H$_2$isopph) or aniline (Hisoanil) [200]. When these were reacted with Co(II) salts, the complexes [(Hisoaph)$_2$Co], [(Hisopph)$_2$Co]·H_2O and [(isoanil)$_2$Co] resulted.

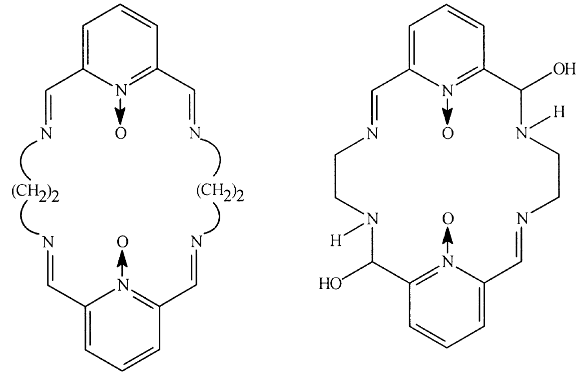
A hexanuclear Co(II) complex results from the reaction of cobalt(II) acetate with the sodium salt of 2-hydroxy-6-methylpyridine [201]. This complex is most interesting because it belongs to a group of complexes in which the ligands already bonded to a transition metal ion also bond to an alkali metal. The complex, [Na{Co(mhP)$_2$}$_6$](O$_2$CCH$_3$)·$_2$CH$_2$Cl$_2$ (**116**) has been found from an X-ray structure determination to have Co atoms in a four-coordinate environment in which adjacent Co atoms are bridged by hydroxy-methylpyridine ligands such that the Co atoms lie in a planar hexagonal ring. They are bonded to two N atoms and two O atoms from four 2-hydroxy-6-methylpyridine molecules in each case. The sodium ions are found at the centre of the whole structure in an octahedral environment provided by oxygen atoms from 2-hydroxy-6-methylpyridine molecules.



(116)

In an attempt to prepare complexes of the ligand **1** shown in (**117**), the nickel complex was found to have a structure containing the ligand **2** [202]. The binuclear Co(II) complex, $Co_2L(NO_3)_4.2CH_3OH \cdot nH_2O$, which is formed by reaction of pyridine-1-oxide-2,6-dialdehyde and 1,2-diaminoethane with Co(II) nitrate is assumed on the basis of infrared and magnetic data to be a complex of **2** as well.

Co(II) complexes of the following range of ligands have been prepared and characterized: 5,5-dimethylcyclohexane-1,2,3-trione-2-(p-nitrophenylhydrazone), 5,5-dimethyl-cyclohexane-1,2,3-trione-2-(p-chlorophenylhydrazone), 5,5-dimethyl-cyclohexane-1,2,3-trione-2-(o-chlorophenylhydrazone), 5,5-dimethylcyclohexane-1,2,3-trione-2-(o-methylphenylhydrazone) and 5,5-dimethylcyclohexane-1,2,3-trione-2-(m-methylphenylhydrazone) [203]. Complexes of the type $ML_2.nB$, where HL = 3-(2-hydroxy-1-naphthyl)-5-(4-X-phenyl)-2-isoxazoline, X = H, Cl or OMe, $n = 0$ or 2 and B = H_2O or py, have been prepared and characterized [204]. Evidence from IR, electronic and EPR spectroscopies and other techniques suggest that these complexes are formed through bonding to the tertiary nitrogen of the isoxazoline ring and the phenolic oxygen. Ethylenediamine-*N,N,N′,N′*-tetraacetanilide (edtan)



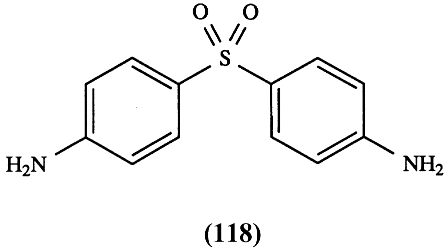
1 **2**

(117)

has been found to form the pink complex $[Co(edtan)(H_2O)[ClO_4]_2 \cdot H_2O \cdot 0.5C_2H_5OH$ with Co(II) by reaction of a suspension of the ligand with a Co^{2+} salt in ethanol [205]. The X-ray crystal structure of this complex shows an environment around the Co which is seven-coordinate, with the edtan ligand behaving in a hexadentate manner and the other position being occupied by a water molecule. The arrangement results in coordination through the N atoms of the en and the four O atoms of the amide groups. The stability constant and associated thermodynamic quantities were determined to be $\log K_s = 4.18$, $\Delta G^\circ = -23.85$ kJ mol^{-1}, $\Delta H^\circ = -22.16$ kJ mol^{-1} and $\Delta S^\circ = 5.7$ J K^{-1} mol^{-1}.

Reaction of 4,4′-diaminodiphenyl sulfone (**118**) with salicyladehyde or 2-hydroxy-1-naphthaldehyde results in Schiff bases which react with Co(II) to produce binuclear complexes containing an ON–X–NO donor set [206]. The same group has prepared Co(II) complexes with the ONNO donor azo dye, 4,4′-bis(ethylcyanoacetate-2′-azo)diphenyl [207]. Trinuclear complexes, such as $CoNiCoL_2(H_2O)_n\, mH_2O$, are produced by the reaction of 1,8-di(2′-hydroxyphenyl)-4,5-diphenyl-2,3,6,7-tetrazaoctan-1,3,5,7-tetraene with Co(II) [208].

A blue–green complex is formed with Co(II) by 2-(8-quinolylazo)-5-*N*,*N*′-dimeth-

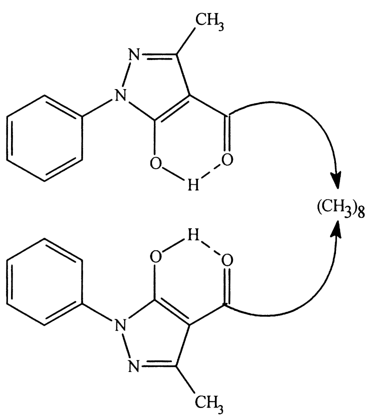


(118)

ylaminobenzoic acid, which is a good chromogenic reagent for the analysis of Co [209]. It turns out to be very highly selective.

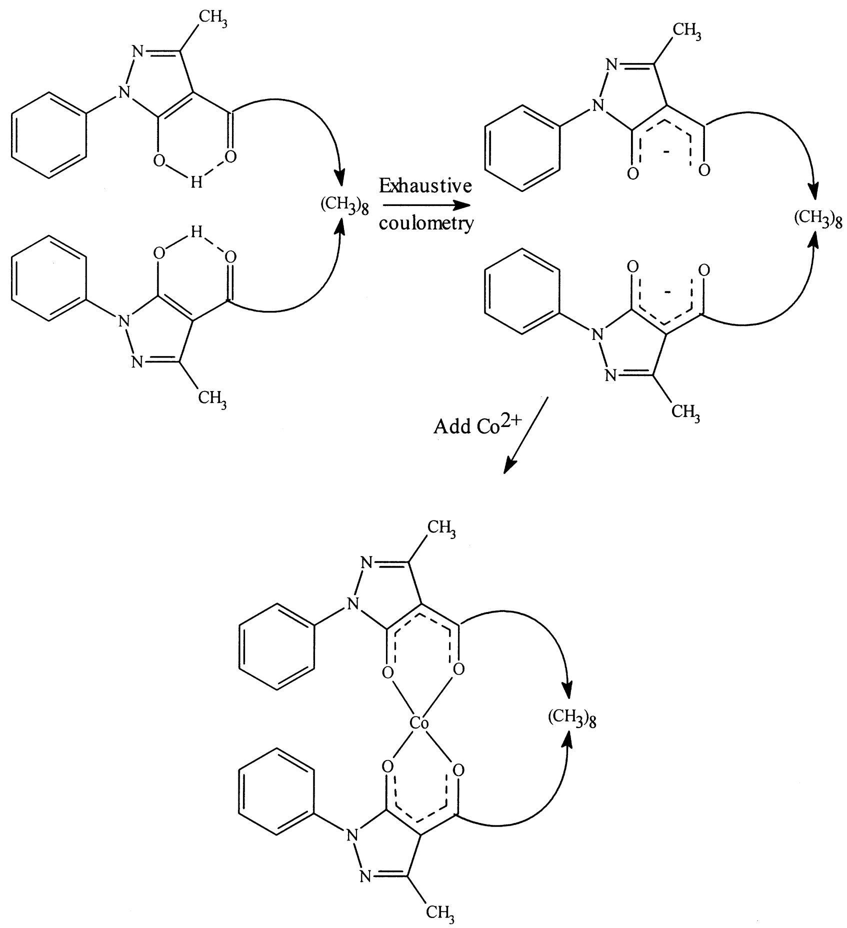
When cobalt(II) acetate is reacted with $H_2[H_4]L^1$ ($H_2[H_4]L^1$ = *N,N′*-bis(2-hydtoxy-3-tert-butyl-5-methylbenzyl) 2,3-dimethylbutane) or $H_2[H_4]$-L^2 ($H_2[H_4]L^2$ = *N,N′*-bis(2-hydroxy-3-tert-butyl-5-chlorobenzyl)-2,3-diamino-2, 3-dimethylbutane) in the presence of dioxygen, instead of the expected tetrahydrogenated complexes, red crystals of the compounds CoL^1 and CoL^2 were produced (H_2L^1 = *N,N′*-bis(3-tert-butyl-5-methylsalicylidene)-2,3-diamino-2,3-dimethylbutane and H_2L^2 = *N,N′*-bis(3-tert-butyl-5-chlorosalicylidene) (**119**) [210]. In the absence of dioxygen, however, the complexes [Co[H_4L^1] and [Co[H_4L^2] are produced and bubbling air into a solution of either one of these produces CoL^1 or CoL^2 as appropriate. They have been investigated using EPR, magnetic susceptibility and quantum chemical methods. For the cobalt complexes: CoL^1 and CoL^2 the EPR spectra in frozen toluene were poorly resolved because the complexes aggregated in the frozen solvent but were much improved by using the complex with py in the axial position and this then gave well-resolved hyperfine structures, which in the presence of dioxygen suggested that there was addition of dioxygen to the Co, where the pyridine adducts showed rhombic symmetry and nicely resolved hyperfine structures. The authors used the INDO/2 method which gave results for the O_2 addition compound in keeping with MO models.

The stable anion produced by the electrochemical reduction of 1, 10-bis(1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl)-1,10-decanedione (**119**) may be reacted with divalent transition metal ions, including Co(II) to produce the pale brown [Co(II)L_3] complex [211]. The process involved in the electrochemical preparation is shown in (**120**). Unlike the Cu(II) and Ni(II) complexes which required a stoichiometric amount of the metal ion to be used in the final step, the Co(II) complex needed 1.5 equivalent of the Co(II) salt. Although there was no ESR signal found at room temperature, when the complex was cooled to 4.2 K in chloroform, a large signal



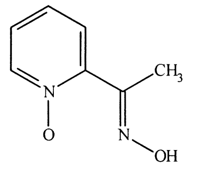
(119)

was recorded, which was strongly reminiscent of a high-spin Co(II) complex. It is suggested that the breadth of the signal and other features point to a distorted octahedral environment around the Co.Co(II) complexes of furfurylidene-nicotinamide Schiff base [212] and with the Schiff base formed by condensation of *p*-chloroaniline and 2-furfuraldehyde [213] have been prepared and characterized.



(120)

The arrangement around Co in the dimeric complex $[Co(pxo)(CH_3OH)Cl_2]_2$ pxo is 2-acetylpyridine 1-oxide oxime (**121**) has been found from its X-ray crystal structure to be six-coordinate NO_3Cl_2 [214]. This environment arises from one of the pxo groups coordinating to the Co by N,O donation and the second bridging through its *N*-oxide. The complex $[Co(pxo)Cl_2]$ was also prepared and it is inferred that there is an octahedral arrangement around Co but involving Cl bridging between dimer molecules which themselves involve bridging *N*-oxide.



2-acetylpyridine 1-oxide oxime

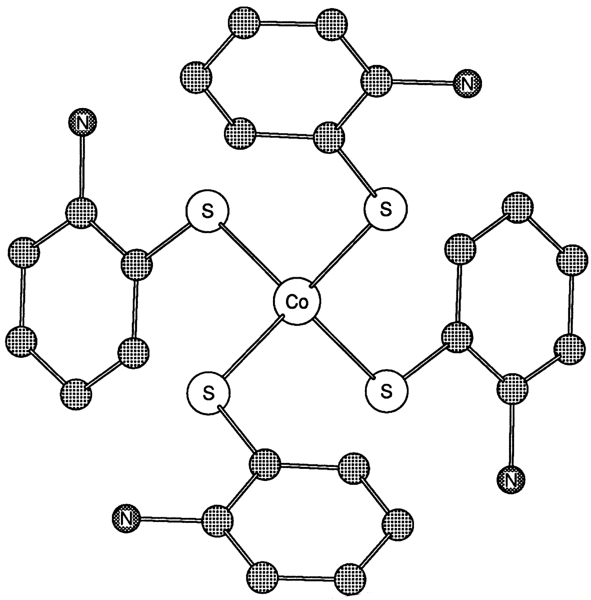
(121)

2.4. Complexes with sulfur donor ligands

There are still not many references to Co(II) complexes in which sulfur is the only donor atom. Thus, in the 1991 contribution in this series [215] there were listed only four references in this section and this year there are still only six references given. By passing dihydrogen over a melt consisting of a mixture of carbonate, sulfur and cobalt, a number of compounds were prepared viz. $K_9Co_2S_7$, $Rb_9Co_2S_7$ and $Cs_9Co_2S_7$ [216]. The X-ray crystal structure of the potassium compound showed that the basis for the structure was trigonal planar $[CoS_3]$ which contained both Co(II) and Co(III). Examination of the other compounds with X-ray powder diffraction indicated that they had the same basic structure. These complexes are compared with the analogous Fe compounds and the magnetic behaviour were compared. The crystal structure was also obtained for $Co[(SPMe_2)_2N]_2$, containing the tetramethyldithioimidodiphosphinato ligand bonded through two sulfur donors [217]. It was found that the electronic spectra and the magnetic behaviour were consistent with a tetrahedral arrangement around the Co. The complex was found to consist of discrete molecules of the complex and that environment around the Co was CoS_4 arranged in a distorted tetrahedral manner. A similar distribution of S atoms around the Co was found in the complex $(Me_4N)_2[Co(SPh)_4]$ [218]. This was examined both by single crystal EPR and X-ray diffraction. The structure was derived from the X-ray data; the CO–S–PH units in this structure are virtually planar.

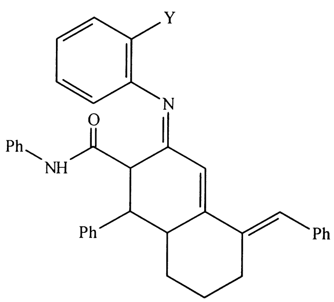
The green Co(II) complex $[(C_2H_5)_4N]_2[Co(SC_6H_4NH_2)_4]$ has been synthesized by reaction of sodium 2-aminobenzenethiolate with $(C_2H_5)_4NCl$ and $CoCl_2$ in methanol [219]. The X-ray crystal structure, (**122**), shows that the arrangement of the S atoms around the Co is such as to produce approximately S_4 symmetry. Studies in solution in CH_3CN show that the changes in the UV–VIS absorption spectrum are consistent with a tetrahedral-pseudo-octahedral equilibrium (Eq. (19)) of the species $[Co(SC_6H_4NH_2)_4]^{2-}$ and $[Co(SC_6H_4NH_2)_3]^-$ and this is borne out by the ^1H NMR spectroscopic data.

$$[Co(SC_6H_4NH_2^{-2})_4]^{2-} \rightleftharpoons [Co(SC_6H_4NH_2^{-2})_3]^- + [SC_6H_4NH_2^{-2}] \qquad (19)$$



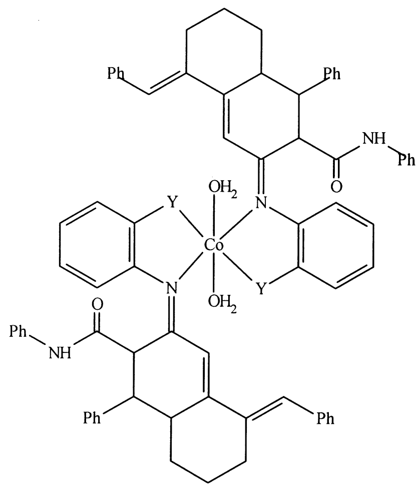
(122)

Tridentate Schiff-base Co(II) complexes have been produced by reacting 1,2,3,5,6,7,8,8a-octahydro-3-oxo-N-1-diphenyl-5-(phenylmethylene)-2-naphthalene-carboxamide with *o*-aminophenol, *o*-aminothiophenol or *o*-aminobenzoic acid (**123**) and Co(II) [220]. These complexes were found to be of the form $[Co(NX)_2] \cdot nH_2O$ where X = phenolic oxygen, thiophenolic sulphur or carboxylic oxygen and $n = 0$ or 2. It is proposed that in the Co complex, the ligand behaves as a monobasic didentate ligand (**124**).



Y = OH, SH or COOH

(123)



Y = O, S or COO

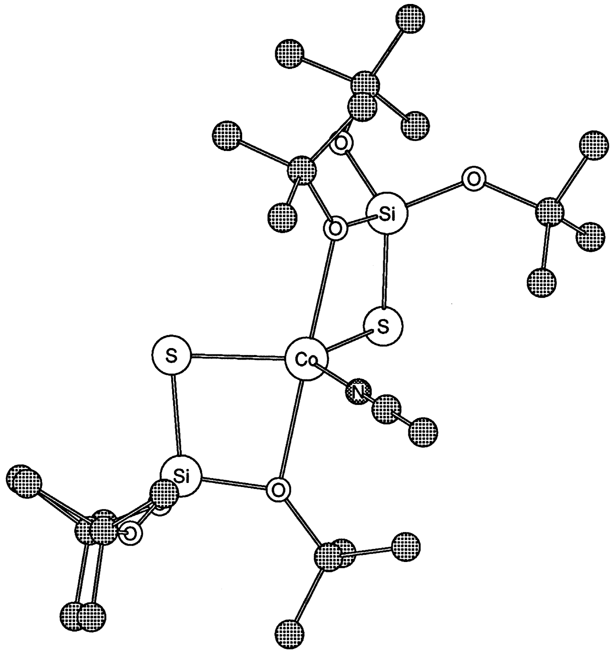
(124)

2.5. Complexes with sulfur–oxygen donor ligands

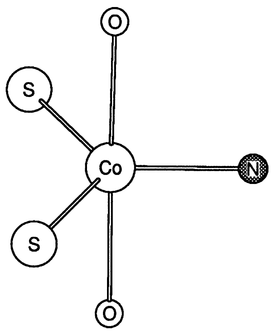
Again, this year, coordination compounds formed by Co(II) with ligands having sulfur-oxygen donor ligands are comparatively rare. Deep blue crystals of bis(tri-*tert*-butoxysilanethialato)(acetonitrile)cobalt(II)[$(t\text{-}C_4H_9O)_3SiS]Co_2(NCCH_3)$ (**125**) have been prepared by reacting anhydrous $CoCl_2$ with tri-*tert*-butoxysilanethiol and triethylamine in solution in acetonitrile [221]. The X-ray crystal structure shows a distorted trigonal bipyramidal arrangement (**126**) around the Co. One position is occupied by the acetonitrile, which is bonded to the Co through N. The ligand occupies the other positions bonding via two O atoms and two S atoms.

The kinetics of stereospecific deuteration rates of 2,2′-thiodiacetate (tda) in s-*fac*- and u-*fac*-$[Co(dien)(tda)]^+$ have been investigated using NMR spectroscopy [222]. The rates were determined at 70.2 °C in D_2O over a range of pD values between 4.4 and 6.4. The rate constants were proportional to $[OD^-]$. It was possible to measure separately the rates of the outer and inner protons of both s-*fac*- and u-*fac*-$[Co(dien)(tda)]^+$. The ratio of the pseudo first order rate constants, $k^{s'}_{out}/k^{s'}_{in}$ for the s-*fac* complex was determined to be about 7. For the corresponding u-*fac* complex, the ratio $k^{u'}_{out}/k^{u'}_{in}$ was about 1.3.

The crystalline, brown mixed polymeric cobalt compound $[Co_3(SCH_2CH_2S)_3(PEt_3)_3]_2[Co_2Cl_4(\mu\text{-}O_2SEt_2)_2]$ has been prepared and its X-ray crystal structure determined. Structures (**127**) and (**128**) show the cation and anion, and structure (**129**) illustrates more clearly details of the core of one cation [223]. The structure is unusual in that in fact it contains two very similar trimeric cationic species which each contain a triangle of Co atoms and a dimeric anion in which the



(125)

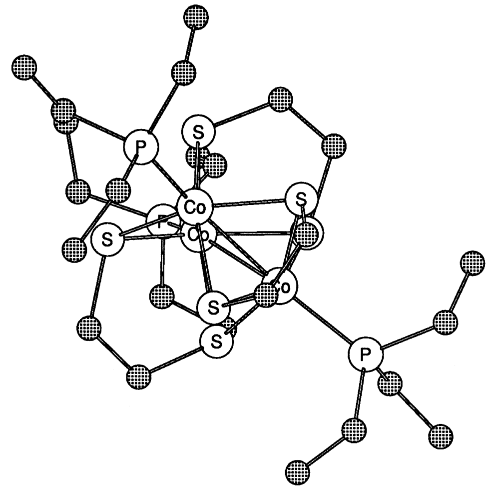


(126)

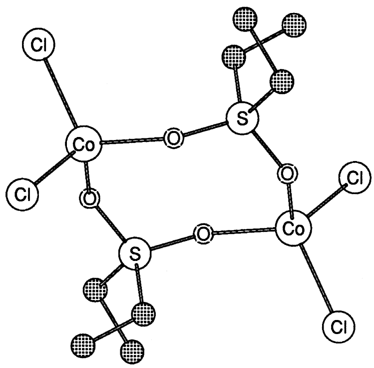
two Co atoms are bridged via the oxygen atoms of the diethylsulfone ligand. The arrangement of the donor atoms around the S may broadly be described as a distorted tetrahedron.

2.6. Complexes with sulfur–nitrogen donor ligands

A series of complexes of ligands which are based on Schiff bases of 4-benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-thione and various diamines have been prepared [224] and the structure of the Co(II) complex is shown in (**130**).



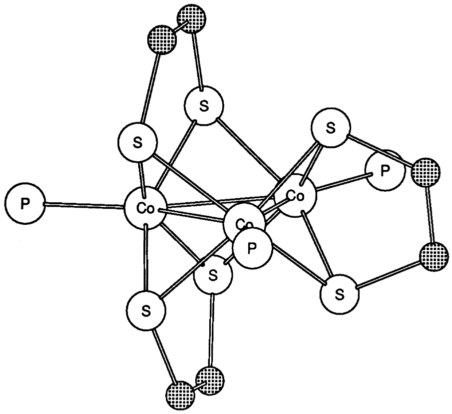
(127)



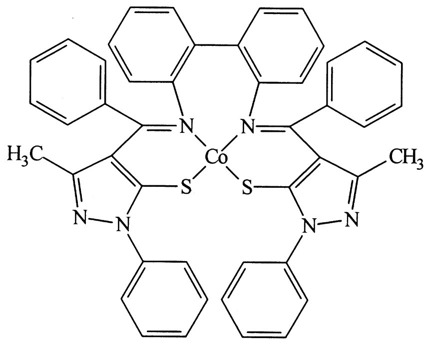
(128)

The sulfur-containing macrocycles 1,4,7,11,14,17-hexathiacycloeicosane (L1), 1,4,7-trithiecan-9-ol (L2), 1,11-dioxa-4,8,14,18-tetrathiacycloeicosane (L3), 1-oxa-4,8-dithiacyclodecane (L4) (**131**) have been made and the following Co(II) complexes of these ligands have been prepared: $[Co(L1)][ClO_4]_2$, $[Co(L2)_2][ClO_4]_2$ and $[Co(L3)][ClO_4]_2$ [225]. The X-ray crystal structure of $[Co(L3)][ClO_4]_2$ has been determined. This structure shows no Jahn–Teller distortion; the magnetic moment of 4.37 BM, the electrochemistry and the absence of an ESR signal at 77 K all indicate that the L3 complex is high-spin. The L1 complex appears to be low spin and the L2 has a magnetic moment appropriate for neither a low- or high-spin species.

The complex anion $[Co(mnt)_2]^{2-}$, in which mnt^{2-} is *cis*-1,2-dicyano-1,2-ethenedithiolate (**132**) forms ion pair charge transfer complexes of the type $\{A^{2+}[Co(mnt)_2]^{2-}\}$ and where A^{2+} is a bipyridinium derivative [226]. These



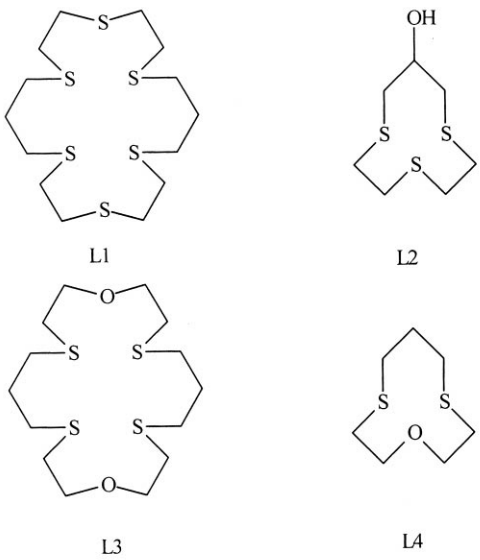
(129)



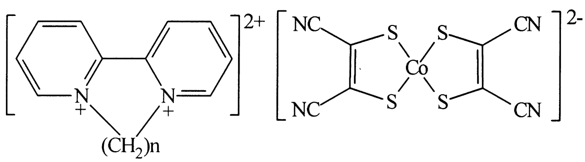
(130)

species are detected by way of a charge transfer band between 590 and 950 nm. The X-ray crystal structure has been determined for one such complex, viz. $\{BQ^{2+}\ [Co(mnt)_2]^{2+}\}$, where BQ^{2+} is 6,7,8,9-tetrahydrodipyrido[1,2-a:2,1-cl[1,4]diazocinium. This shows that the structure contains an arrangement which has a strongly twisted acceptor and a planar donor which do not form into mixed stacks and the authors point out that this is different from systems in which there is a less twisted arrangement. The electrical conductivities of compressed discs of these compounds were measured and found to be in the range 10^{-15} to $10^{-7}\ \Omega^{-1}\ cm^{-1}$ without there being a simple relationship between the conductivity and the driving force for the electron transfer process between the two components of the ion pair, might have been expected.

A tetrahedral arrangement around the cobalt(II) has been suggested in the com-



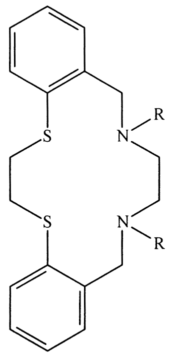
(131)



(132)

plexes $CoL_2X_2 \cdot nH_2O$, where L = N-acylurea or N-acylthiourea, X = Cl and $n = 6$ [227], from magnetic and spectral measurements. The compound 8,11-bis(2-pyridylmethyl)5,6,7,8,9,10,16,17-octahydrodibenzo[e,m][1,4]dithia[8,11]-diazacyclotetradecine (**133**) forms an air-stable complex with brown prismatic crystals, $[CoL]^{2+}$, when reacted with $Co(ClO_4)_2 \cdot 6H_2O$ in solution in ethanol [228].

The analytical possibilities of 2-acetylpyridine-4-phenyl-3-thiosemicarbazone (APPT) as complexing reagent for cobalt have been explored [229]. The technique lends itself to the analysis of Co and other first row transition metal ions in pharmaceutical preparations. The solution of the complex when formed is injected onto an HPLC reversed-phase C-18 column and eluted isocratically using a solution of sodium acetate and tetrabutyl ammonium bromide. The solvent extraction step involved in many complexometric/spectrophotometric determinations of transition metals has been eliminated by the use of diethyldithiocarbamate (DDTC) in the presence of aqueous sodium and ammonium dodecylsulfate to provide an anionic



8,11-bis(2-pyridylmethyl)5,6,7,8,9,10,16,17-octahydro-dibenzo[e,m][1,4]dithia[8,11]diazacyclotetradecine

(133)

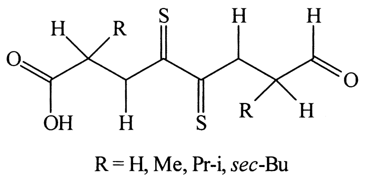
micellar medium [230]. The technique has been successfully used in the analysis of cobalt(II). Complexes of isopropylmethylketone or isobutylmethylketone semicarbazones and thiosemicarbazones with Co(II) have been prepared and characterized [231]. These compounds were of the form $[Co(L)_2]X_2$ or $[Co(L)_2]SO_4$, where $X^- = Cl^-$, Br^-, NCS^- or CH_3COO^-.

The equilibria involved in the formation of Co(II) mixed ligand complexes involving the ligands ampicillin (α-d-(−)aminobenzylpenicillin, ampH(±) and nucleic acid bases, such as; adenine, guanine, thymine, uracil, and cytosine [232]. Stability constants were measured at the biological temperature of 37 °C for the complexes involving each of the bases and the order of these was guanine > adenine > uracil > thymine > cytosine. The stability constants have also been determined the Co(II) complex (and other transition metal ion complexes) of 2-methyl-indole-3-carboxaldehyde 4-phenyl-3-thiosemicarbazone at various temperatures in 60% (v/v) aqueous dmf, allowing various thermodynamic parameters to be determined [233].

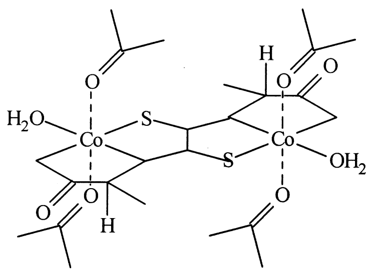
The condensation of 2-aminothiazole and its derivatives with *vic*-hydroxyaldehydes has been shown to produce Schiff bases which react with Co(II) salts form complexes of the type $[CoL_2]$ [234]. These complexes show the possibility of coordination with the Co through N and S.

2.7. Complexes with sulfur–nitrogen–oxygen donor ligands

Cobalt(II) complexes of a number of N,S,O donor ligands have been studied [235]. The ligands were *N,N′*-bis(1-carboxy-methyl)dithioxamide (GLYDTO), *N,N′*-bis(1-carboxyethyl)dithioxamide (ALADTO), *N,N′*-bis(1-carboxy-2-methylpropyl) dithioxamide (VALDTO) and *N,N′*-bis(1 -carboxy-3-methylbutyl)dithioxamide (LEUDTO) (**134**), in parenthesis are the authors' abbreviations. The complexes produced were $[Co_2(L\text{-}4H)(H_2O)_2]$, when L = GLYDTO, ALADTO, VALDTO or LEUDTO and $[Co_2(L\text{-}4H)(H_2O)_6]$, when L = ALADTO or VALDTO. In all cases, the magnetic and spectroscopic data pointed to each of the complexes having a distorted octahedral arrangement around the Co and the bonding was through the oxygen of the carboxylate, the nitrogen of the deprotonated thioamide and the sulfur atom of the thiocarbonyl group (**135**).

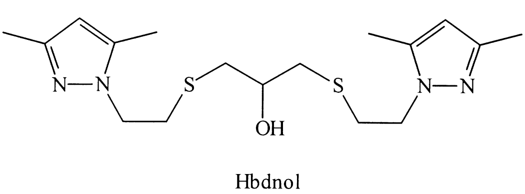


(134)

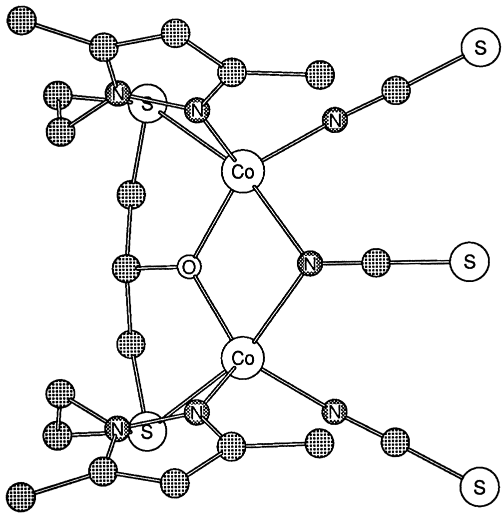


(135)

The dinuclear compound $[Co_2(bdnol)(NCS)_3]$, where bdnol is the pentadentate ligand 1,9-bis(3,5-dimethyl-l-pyrazoyl)-3,7-dithia-5-nonanol (**136**) has been found to have a roughly trigonal bipyramidal arrangement around the Co as is shown in structure (**137**) [236]. It has also been found that the thio ether sulfur and the bridging anion, which are to be found in the apical position, leaving the trigonal plane to be formed by the pyrazoyl N.



(136)



(137)

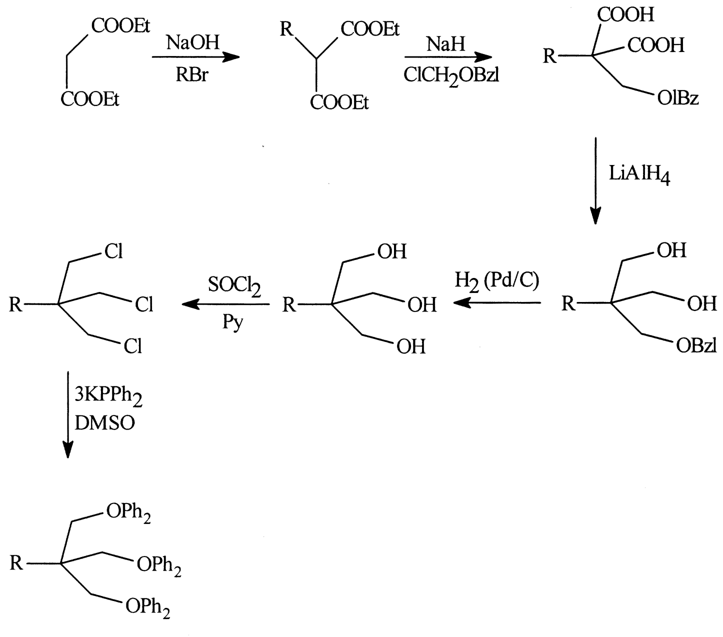
2.8. Complexes with phosphorus donor ligands

Cobalt and nickel have been separated by the use of phenylphosphonic acid mono-4-*tert*-octylphenyl ester using liquid surfactant membranes [237]. The kinetics of the extraction of these metals as a function of the surfactant were studied together with the extraction equilibrium.

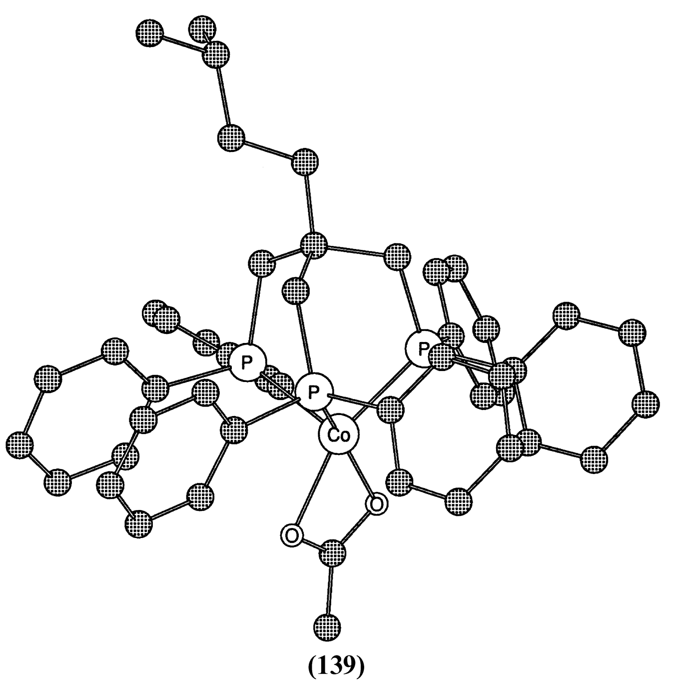
When the cation$[(pp_3)Co(solvent)]^{2+}$, where pp_3 = tris(2-diphenylphosphinoethyl)phosphine, is generated in situ in the presence of pyridine or 4,4′-bipyridine it has been found to produce the new complexes $[(pp_3)Co(py)]Y_2$ and $[[(pp_3)M]_2(\mu\text{-bpy})]Y_4$, where $Y = BF_4$ or ClO_4 [238]. The structure is believed to involve the metal in low-spin five-coordination. The tripod ligand $(CH_3)_2CH(CH_2)_2C(CH_2PPh_2)_3$ has been prepared from diethylmalonate (**138**) [239]. The X-ray crystal structure of the complex, $[(CH_3)_2CH(CH_2)_2C(CH_2PPh_2)_3Co\{O(O)CCH_3\}](BPh_4)$ has been determined and the cation is shown in (**139**), with the core more easily seen in (**140**).

The reaction of the compound $(CH_3C(CH_2P(Ph)_2)_3)$ (triphos) with $Co(III)(aq)(BF_4)_2$ followed by reaction with aminoacids leads to the complexes $([triphosCoNH_2CH(R)COO]^+$, where R = H; Gly, R = Me; L-Ala, D-Ala, R = iso-propyl; L-Val, R = N-propyl; L-Pro, R = phenyl; D-phenylglycine, R = benzyl; L-Phe [240]. When the ligand $PhCH_2C(CH_2P(Ph)_2)_3$ was treated in the same way with L-alanine the product was $[PhCH_2C(CH_2P(Ph)_2)_3Co(\text{L-ala})]^+$. The X-ray crystal structures of these complexes demonstrated the five-coordinate arrangement around the Co(II).

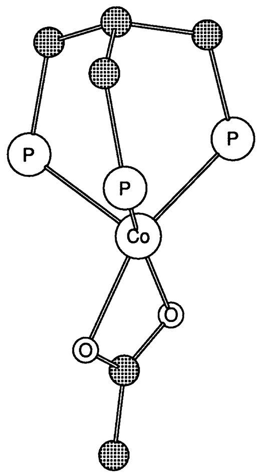
Dark violet crystals of the complex $[Co\{(Ph_2CH_2)_3CMe\}(o\text{-}S_2C_6H_4][PF_6]_n$ [here, $n = 1$ for the Co(III) complex and $n = 0$ for the Co(II) complex] have been prepared [241]. The X-ray crystal structure was determined for the Co(II) complex and


COOEt
COOEt
NaOH
RBr
R
COOEt
COOEt
NaH
ClCH2OBzl
COOH
COOH
R
OlBz
LiAlH4
OH
OH
R
OBzl
H2 (Pd/C)
OH
R
OH
OH
SOCl2
Py
Cl
R
Cl
Cl
3KPPh2
DMSO
OPh2
R
OPh2
OPh2

(138)

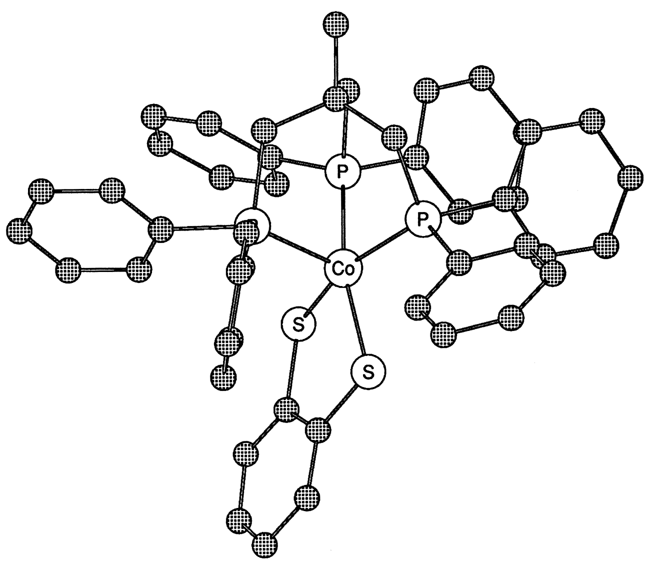

P
P
P
Co
O
O

(139)



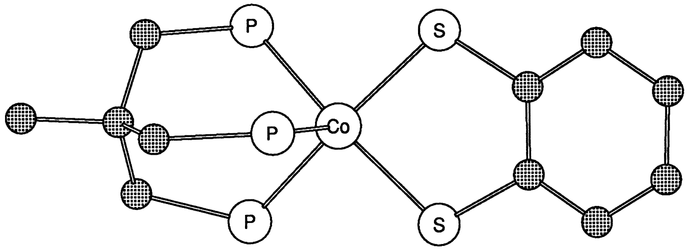
(140)

electrochemistry carried out on the Co complexes. The structure is shown in (**141**), with diagram (**142**) illustrating more clearly the environment around the cobalt centre.



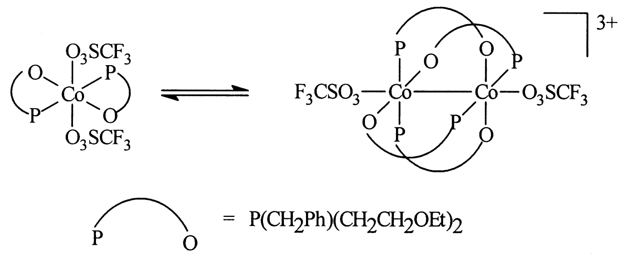
(141)

Reaction of benzylbis(2-ethoxyethyl)phosphine (L) with $CoCl_2$ and $AgCF_3SO_3$ leads to the formation of $[CoCl_2L_2]$ and $CoL_2(O_3SCF_3)_2]$ [242]. In the former it was found that the ligand was monodentate through P and in the latter didentate



(142)

through P and O. Studies of the NMR spectra led the authors to suggest that reactions such as that in (**143**) take place.



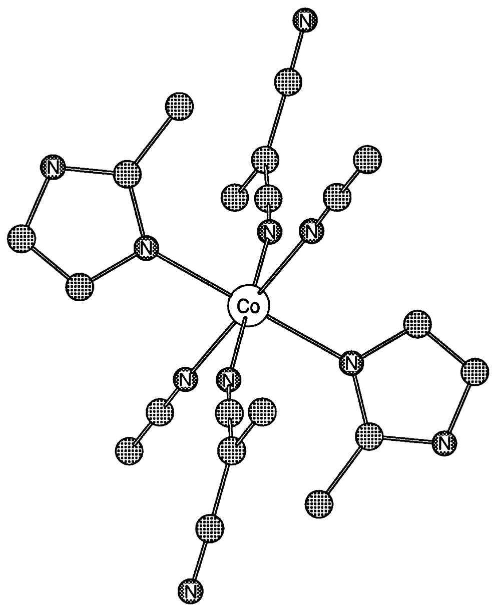
(143)

2.9. Complexes with halide and pseudohalide donor ligands

The electronic structure of the ion, $[CoCl_4]^{2-}$ has been examined by a variety of physical techniques such as visible spectroscopy, X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS) [243]. This ion has also been studied by Feist and coworkers [244]. They obtained the X-ray crystal structure of 1,4-dimethylpiperazinium tetrachlorocobaltate(II), $(dmpipzH_2)[CoCl_4]$, which was found to crystallize in the monoclinic space group $P2_1/m$ with $a=6.133$, $b=14.306$, $c=6.902$ Å $\beta=90.54°$ and $Z=2$. C–H$\cdot\cdot\cdot$Cl bonding is invoked in order to explain discrepancies in some of the non-bonding distances. The X-ray crystal structure of hexakis(tetrahydrofuran)cobalt tetrahydrofurantriiodocobalt tetrahydrofuran solvate has been determined [245].

Formation constants, enthalpies and entropies of the isothiocyanato complexes $[Co(NCS)_n]^{(2-n)+}$ (and the corresponding Mn(II) and Zn(II) complexes) have been determined in N,N-dimethylacetamide (DMA) [246]. The formation of the complexes is enhanced in DMA relative to dmf. There is evidence that the structure around the Co(II) changes from octahedral to tetrahedral occurred earlier in the reaction sequence in DMA than in dmf, possibly attributable to the more sterically hindered DMA molecules. When pentakis(arylisocyanide)cobalt(II) perchlorate, $[Co(CNC_6H_4Me\text{-}o)_5(ClO_4)_2]$ is reacted with triphenylarsine, $AsPh_3$ and triphenylstibine, $SbPh_3$ in CH_2Cl_2, the product is found to be $[Co(CNC_6H_4Me\text{-}o)_4(ClO_4)_2]$ [247]. The formation of such compounds via this type of route appears to be affected by steric hindrance since the complex $[Co(CNPh)_5](ClO_4)_2 \cdot H_2O$ does not undergo an analogous reaction and ease of reaction involving related substituents increases with increasing steric hindrance.

Cobalt(II) salts have been found to react with $N(CN)_2^-$ or $C(CN)_3^-$ and imidazole or its Me derivatives, 2-meiz and 4-meiz to produce a large number of complexes, among which were α and β isomeric pairs of $[Co\{C(CN)_3\}_2(2\text{-meiz})_2]$ and $[Co\{C(CN)_3\}_2(4\text{-meiz})_2]$ [248]. The X-ray crystal structure of $\alpha[Co\{C(CN)_3\}_2(2\text{-meiz})_2]$, (**144**), showed that the C(CN) anions formed chains by bridging with Co atoms. The geometry around the Co was almost octahedral and coordination was through two N atoms of the 2-meiz and four N atoms from the $C(CN)_3^-$.



(144)

There has been a study of the effects of the nature of cations on the thermochromic behaviour of cobalt(II) hexacyanoferrate(III,II) films [249], which is olive-brown in the presence of hydrated K^+ or Cs^+ ions. However, when the larger hydrated cations, Na^+ and Li^+, are used, the colour changes to green. In the absence of counter-ions the colour is deep green.

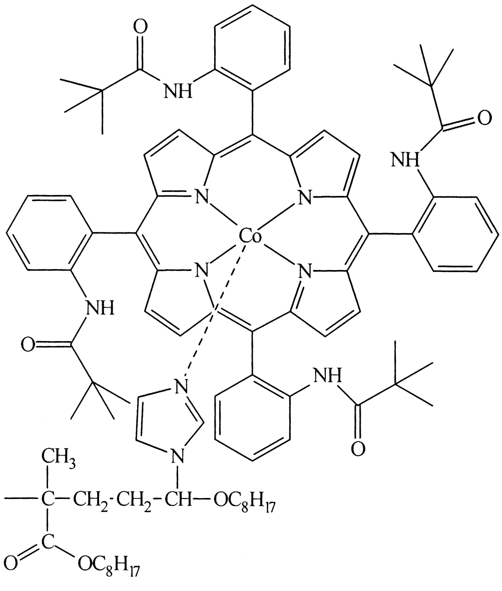
3. Reactions of cobalt complexes involving dioxygen

As in previous years, there continues to be great interest in the uptake of dioxygen by cobalt complexes, frequently as models for biological systems and with a wide variety of different structures and ligands.

When either of the species [$CH_3Co(DH)_2py$], or [$C_2H_5Co(DH)_2py$], where DH is dimethylglyoxime are subject to flash photolysis in the presence of dioxygen, a series of reactions with the latter occur [250]. The first step involves the formation of the mononuclear superoxo Co(III) complex. Further steps are the formation of the μ-superoxo Co(III) complex from this species by reaction with the alkyl cobalamine, by reaction with the photo-produced cobalamine (II) and by direct conversion.

Measurement of the kinetics of the reaction show that the fastest process is the reaction with the photo-produced cobalamin.

By bonding modifications of [*meso*-α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphyrinato]cobalt (**145**) to polymer membranes it has been possible to change the permeability of the membranes to dioxygen [251]. The variation of the permeability was found to be related to the size of the cavity in the porphyrin. The larger the cavity the better the permeability. There exists a relationship between the dioxygen binding on the porphyrin and the diffusion constant of dioxygen.



(145)

It is now possible to compare the effectiveness of homogeneous catalysis of dioxygen reduction by [5,10,15,20-tetrakis((pentaammineruthenino(II))-4-pyridyl)porphyrinato]cobalt(II) and graphite electrode surfaces because the complex has now been prepared in solution [252]. On the graphite surface the complex catalyses a four-electron reduction of the O_2, whereas in solution, only a two-electron process was observed. The kinetics of both processes have been studied and the reactions proposed in interpreting the kinetic data are shown in (**146**). It is shown that the intramolecular electron transfer in solution from the Ru centres to O_2 is slow. Catalysis of the electrochemical reduction of O_2 has been demonstrated by a cobalt porphyrins which contain three $Ru(NH_3)_5^{2+}$ groups coordinated to pendant cyanophenyl ligands on the porphyrin ring (**147**) which have been prepared [253]. The 3-cyanophenyl complex was adsorbed onto graphite electrodes and placed in contact with a solution of $[Ru(NH_3)_5H_2O]^{2+}$ to produce the Ru species shown in (**147**). This electrode was then used to catalyse the reduction of O_2 to H_2O_2. On the other hand, the corresponding 4-cyanophenyl compound is shown to catalyse the reduction of O_2 to all the way to H_2O. It is concluded that an important feature of the ability of these species to carry out a two or a four-electron reduction lies in the back-bonding interactions between the Ru(II) and the porphyrin ring.

$$\mathrm{CoP} + O_2 \rightleftharpoons \mathrm{CoPO_2}$$

$$\mathrm{CoPO_2} + \mathrm{Ru(II)} \longrightarrow \mathrm{CoPO_2^-} + \mathrm{Ru(III)}$$

$$\mathrm{CoPO_2^-} + \mathrm{Ru(II)} \xrightarrow[2H^+]{\text{fast}} \mathrm{CoP} + H_2O_2 + \mathrm{Ru(III)}$$

Where CoP is $[\mathrm{CoP(pyH)_4}]^{4+}$. At the same time, the uncatalyzed reduction occurs:

$$\mathrm{Ru(II)} + O_2 \longrightarrow \mathrm{Ru(III)} + O_2^-$$

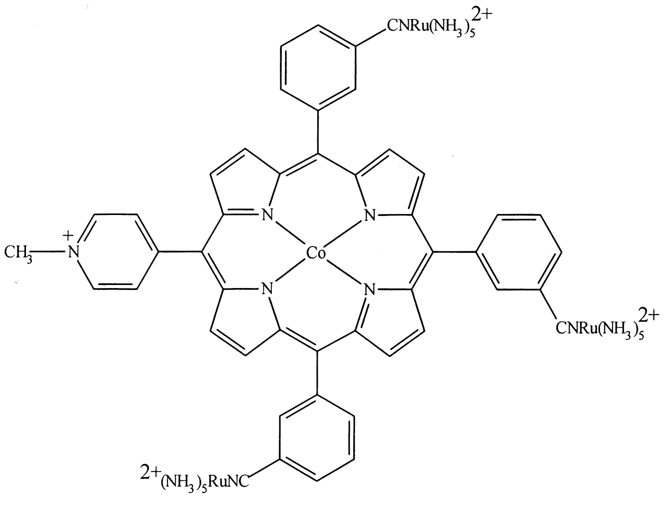
$$\mathrm{Ru(II)} + O_2^- \xrightarrow[2H^+]{\text{fast}} \mathrm{Ru(III)} + H_2O_2$$

$$[\mathrm{O_2CoP(pyRu(II)(NH_3)_5)_4}]^{8-} \longrightarrow [\mathrm{O_2^-CoP(pyRu(II)(NH_3)_5)_3pyRu(III)(NH_3)_5}]^{8+}$$

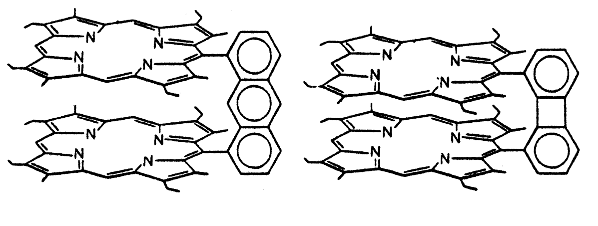
$$[\mathrm{O_2^-CoP(pyRu(II)(NH_3)_5)_3pyRu(III)(NH_3)_5}]^{8+} \xrightarrow[H^+]{\text{fast}} [\mathrm{CoP(pyRu(II)(NH_3)_5)_3pyRu(III)(NH_3)_5}]^{9+} + H_2O_2$$

(146)

A new group of heterodinuclear cofacial biphenylene- or anthracene-bridged bisporphyrins of the form (DP)CoM(X), has been prepared, where DP^{4-} is the anion of 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]biphenylene (DPB^{4-}), or 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]anthracene (DPA^{4-}) (**148**), and in which X is O, OAc, Cl, acac, or OH which are coordinated to one of the metal centres Ti, Ga, In, Lu, or Sc [254]. The structure is such that each of the porphyrin rings lie face-to-face and are joined by a rigid aromatic spacer. Each porphyrin ring contains a metal and may contain the

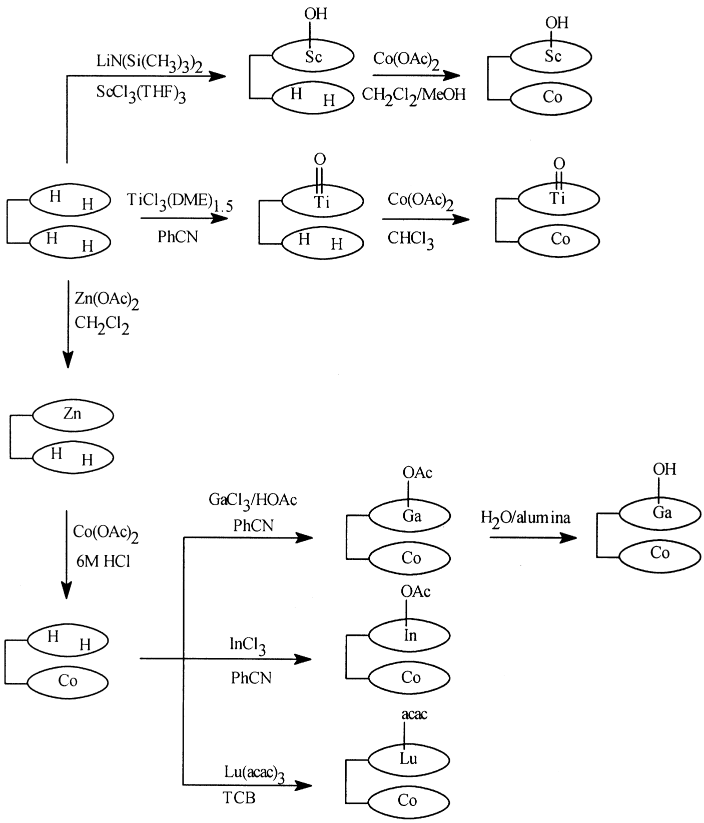


(147)



(148)

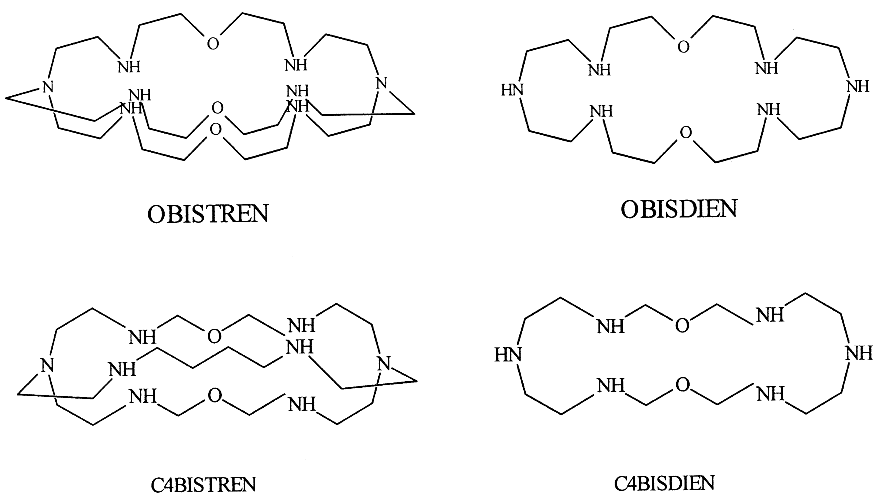
same metal or there may be a different metal in one ring from the other. When there is a Co(II) ion in one ring, the metal in the other ring was carefully chosen have a high Lewis acidity. The method of preparation of some of these compounds is of particular interest and the scheme in (**149**) shows how this is achieved. The ESR spectra of the complexes which contained dioxygen were different from those of the starting materials and indicated that the species were superoxido. However, the DPB species did not show any evidence of dioxygen in the cavity between the porphyrin moieties. The electrochemical study of complexes (DP)CoLu(X) and (DP)CoSc(X) in particular showed that good catalytic behaviour did not necessarily require two Co centres for four-electron reduction of O_2, since such activity remains when the second Co is swapped by a cation which is a strong Lewis acid. It is worth noting that this appears to be the time that it has been demonstrated that a heterodimetallic complex of the type described in this work in acid solution is capable of performing a four-electron reduction of dioxygen. The authors also draw attention to the fact that it appears that the two-electron and four-electron pathways operate together in that H_2O_2 is to be found in the reaction mixture when dioxygen is reduced at



(149)

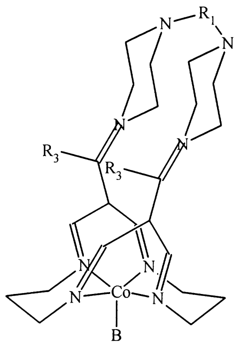
different reaction times for each of the catalysing complexes. The formation of both mononuclear superoxo and a μ-peroxo complex complicated previous studies of the involvement of dioxygen in redox reactions of (cyclam)Co(II) complexes [255]. In order to avoid this complication a more sterically crowded ligand, C-meso-5,7,7,12,14,14-hexamethyl- 1,4,8,11-tetraazacyclotetradecane (hmc), has been used [256]. The catalytic cycle for the reduction of dioxygen involving the Co complex of (hmc) has as an intermediate the metastable species (hmc) $CoOO^{2+}$. This complex is a strong oxidizing agent which is rapidly reduced to the species (hmc)$CoOOH^{2+}$ at the potential where (hmc)Co^{3+} is reduced to (hmc)Co^{2+}, i.e. at 0.38 V versus NHE. This latter species (hmc)$CoOOH^{2+}$ is involved in the electro-reduction of O_2 to H_2O_2 when, at 0.07 V, it is reduced in an irreversible reaction to H_2O_2 and (hmc)Co^{2+}.

The macrobicyclic ligand 1,4,9,12,19,20,25,30-octaazabicyclo(10.10.10)-dotriacontane, C4BISTREN has been synthesized and the synthetic methods for the compounds 7,9,30-trioxa-1,4,10,13,16,22,-27,33-octaazabicyclo(11.11.11)pentatriacontane, OBISTREN and 1,13-dioxa-4,7,10,16,19,22-hexaazacyclotetracosane, OBISDIIEN have been described and those for the ligands [7,9,30-trioxa-1,4,10,13,16,22,-27,33-octaazabicyclo(11.11.11)pentatriacontane, OBISTREN and 1,13-dioxa-4,7,10,16,19,22-hexaazacyclotetracosane, OBISDIEN] have been improved (**150**) [257]. The Co(II) complexes of all these ligands take up dioxygen. Rates of uptake of dioxygen were measured. of the two complexes C4BISTREN, and C4BISDIEN, the former was found to absorb dioxygen more slowly than the latter. A similar situation obtained for OBISTREN and OBISDIEN. The most stable dioxygen species formed from amongst those studied were those of the binuclear Co(II) complexes of the ligands OBISTREN and OBISDIEN. The authors suggest that a crucial role in the formation of stable dioxygen complexes by OBISTREN and OBISDIEN is the presence of flexible ether bridging groups.



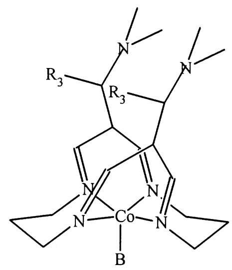
(150)

Cyclidene Co(II) complexes having an organic superstructure (**151**) have been studied as part of the catalytic cycle for the oxidation of various phenols using dioxygen [258]. The effect of the variation of the superstructure is to change the cavity available in the complex. When the catalyst is $[Co(MeVD)]^{2+}$, where MeVD is the complex (i) in the scheme with R_1=durene and R_3=Me, then the products of the oxidation for each of the phenols are as shown in (**152**). As far as the phenols are concerned, the electron-releasing properties and positions of the ring substituents are cited as a factor in affecting their reactivity. Among the factors affecting the nature and composition of the products are the structures and dioxygen binding behaviour. A mechanism is proposed for the oxygenation of *tert*-butylphenol by the cobalt cyclidene dioxygen complexes is shown in (**153**). The kinetics of the oxidation reactions have been investigated and used alongside molecular modelling techniques to re-examine the mechanism of the reaction and it is suggested that there is electron transfer for the formation of the intermediate phenoxy radical. A crucial factor in the control of catalytic activity was found to be the stability of the complexes.



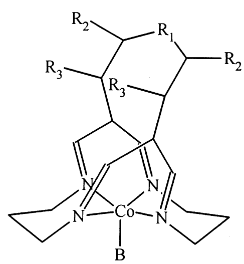
Vaulted cyclidene complex

(i)



Unbridged cyclidene

(ii)

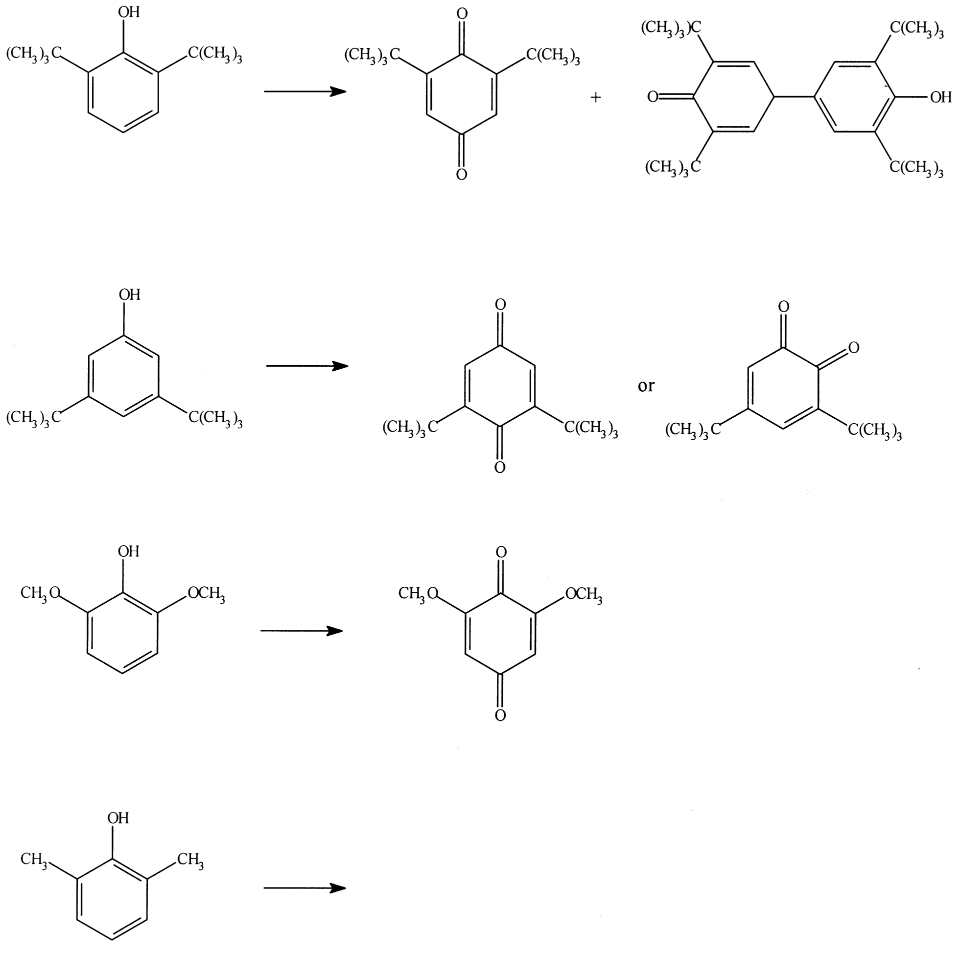


Lacunar cyclidene comple

(iii)

(151)

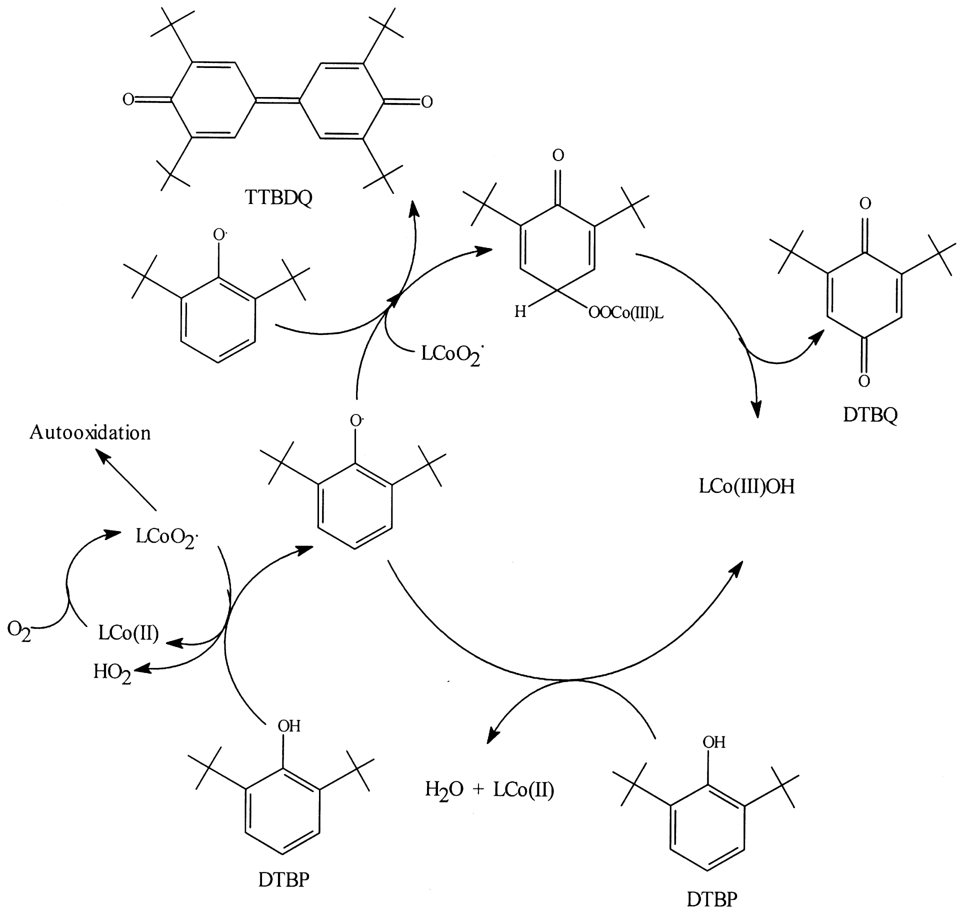
The nature of the Schiff-base complex used as the catalyst for the oxidation of *p*-substituted phenolics to the corresponding benzoquinone by dioxygen is a key factor in determining the nature of the products of the reaction [259]. The catalysts investigated were either five- or four-coordinate. In the case of the former, such as (pyridine)bis(salicylidene)ethylenediamine)cobalt(II) [(py)Co(salen)] and [bis[(salicylideneamino)ethyl]amine]cobalt(II) [Co(N-Me salpr)] (**154**), when the starting material is syringyl alcohol (3,5-dimethoxy-4-hydroxybenzyl alcohol), the product is 2,6-dimethoxybenzoquinone (**155**). The mechanism proposed for these reactions is shown in (**156**). The latter on the other hand produced, 2,6-dimethoxybenzoquinone from syringaldehyde (3,5-dimethoxy-4-hydroxybenzaldehyde), a reaction which does not occur at all with the five-



(152)

coordinated catalyst. These five-coordinate catalysts have also been used to convert *p*-substituted phenols to quinones.

Carbon electrodes modified by the addition of the Schiff-base Co(II) complex, Co(II),3,3′, 4,4′-tetra(salicylidene imino)-1,1′-biphenyl tetrahydrate (**157**) have been used in electrochemical dioxygen reduction processes in aqueous solution [260]. The modified carbon electrodes were either of the carbon-paste type or glassy carbon. Dioxygen reduction at these $[Co(II)_2(DSP)]\cdot 4H_2O$-modified carbon electrodes was found to be almost reversible in alkaline solution and the apparent number of electrons transferred to be about one. An exchange rate constant was determined to be about 0.04 cm s^{-1}. The rate determining step for the catalysis was the first electron transfer and an important feature of the process was found to be the



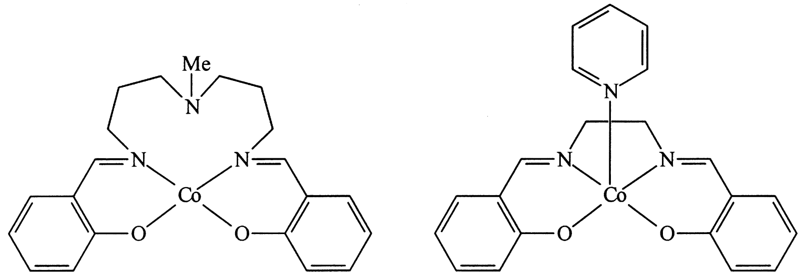
(153)

reversible uptake of dioxygen to form the adduct [Co(III)$_2$(disalophen)$\cdot$2O$_2$]$^-$. The suggested mechanism for the reduction of dioxygen is shown in Eq. (20).

$$Co(II)_2-DSP+2O_2 \rightleftarrows Co(III)_2-DSP+2O_2^{-\cdot} \quad \text{Fast} \tag{20}$$

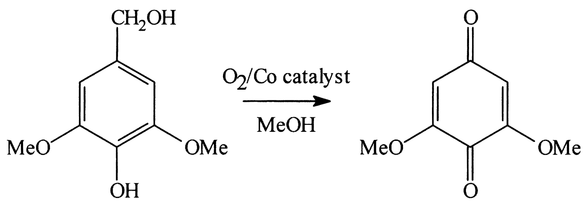
$$Co(III)_2-DSP+2O_2^{-\cdot}+2e \rightarrow Co(II)_2-DSP+2O_2^{-\cdot} \quad \text{Rate determining}$$

A novel binuclear cobalt dioxygen complex has been investigated in connection with dioxygen activation [261]. The ligand involved in these complexes was hydrotris(3-tert-butyl-5-methylpyrazoyl)borate, Tp″ (**158**). When a solution of [Tp″Co(O$_2$)] in CD$_2$Cl$_2$ is cooled down to around 220 K it was found that a dark-green paramagnetic species was produced, which turned out to be the dimer



[Co(N-Mesalpr)] [(py)Co(salen)]

(154)



(155)

[{Tp″Co(O$_2$)}$_2$], which is produced by Eq. (21)

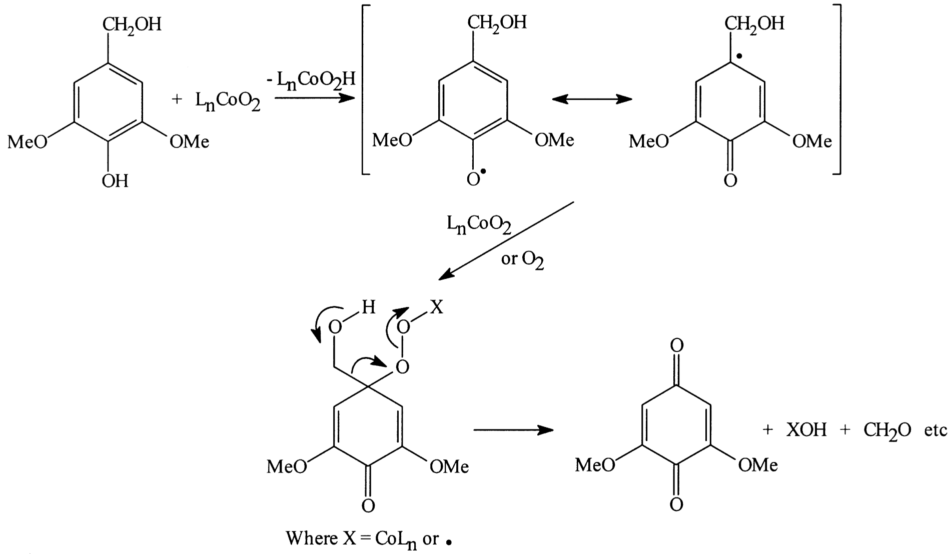
$$2[\text{Tp}'\text{Co(O)}_2] \rightleftharpoons [\{\text{Tp}'\text{Co(O)}_2\}_2]. \qquad (21)$$

Crystallization of a similar green solution from acetonitrile yielded [(Tp″Co(O$_2$)}$_2$.2CH$_3$CN] and the X-ray crystal structure of this complex was determined. In this the Co is bonded to three nitrogens of the Tp″ ligand and there are two dioxygen bridges between the Co atoms, producing a six-membered chair arrangement There is a roughly square pyramidal environment around each Co atom. From the variation of the equilibrium constant for the reaction shown in Eq. (21), values of $\Delta H = -60.1$ kJ mol^{-1} and $\Delta S = 251$ J K^{-1} mol^{-1} were obtained.

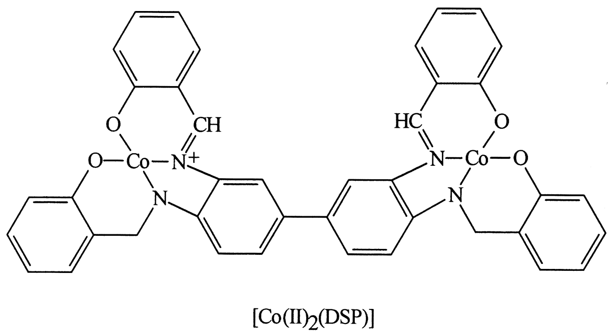
Reaction of the ligand *N,N*′-bis-2-(2-pyridyl) ethyl)-2,6-pyridinedicarboxamide (**159**), a podand with Co(OAC)$_2$ results in a very efficient catalyst for the reaction of phenols with molecular oxygen to produce *o*- or *p*-quinones [262].

4. Cobalt(I) complexes

There has been a review of the synthesis of chiral pyridines by Co(I)-catalysed cocyclotrimerization of acetylene with chiral cano compounds [263].



(156)



(157)

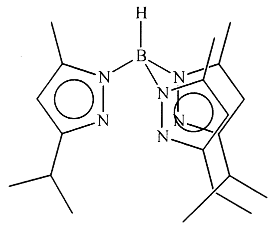
$$TP+TEA+h\nu \rightarrow TP^{\cdot -}+TEA^{\cdot +} \tag{22}$$

$$TP^{\cdot -}+Co(II)L^{2+} \rightarrow TP+Co(I)L^{+}$$

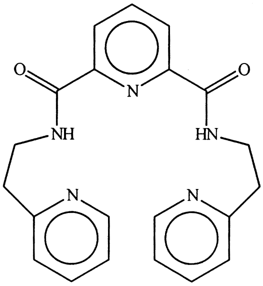
$$Co(I)L^{+}+CO_2 \rightleftarrows Co(I)L(CO_2)^{+}$$

$$Co(I)L(CO_2)^{+}+S \rightleftarrows [S-Co(III)L-(CO_2^{2-})]^{+}$$

Various cobalt macrocycles act as mediators to electron transfer processes in the photoreduction of CO_2 when *p*-terphenyl is a photosensitizer and a tertiary amine

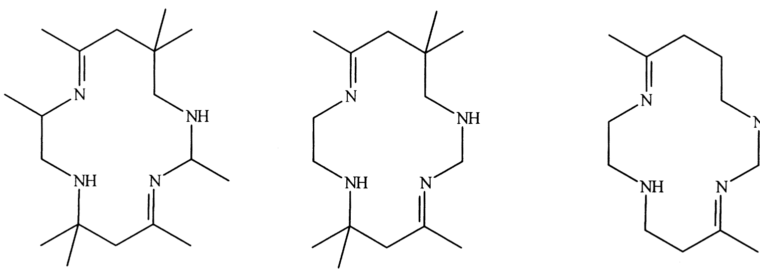


(158)



N,N'-bis-2-(2-pyridyl) ethyl)-2,6-pyridinedicarboxamide

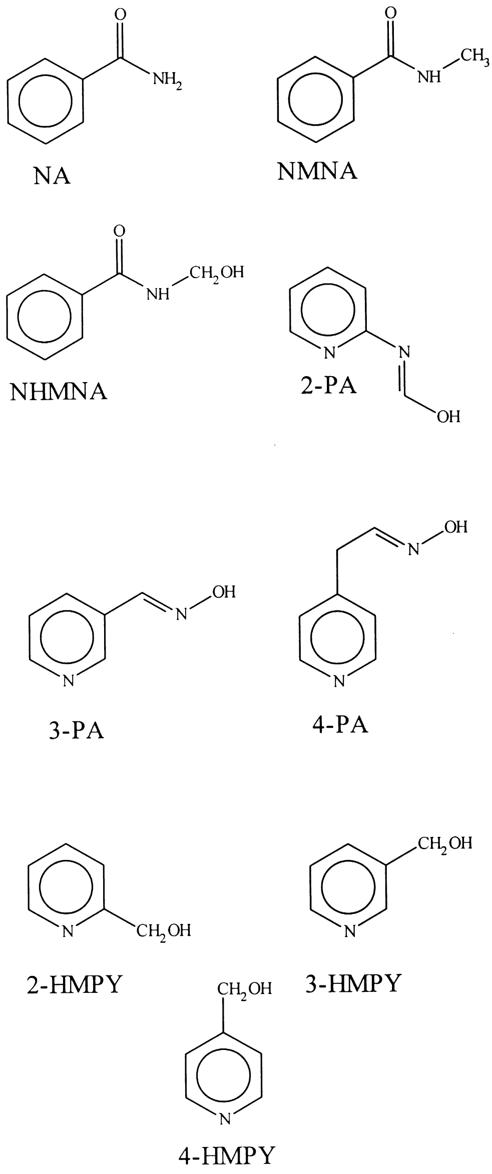
(159)



OMD HMD DMD

(160)

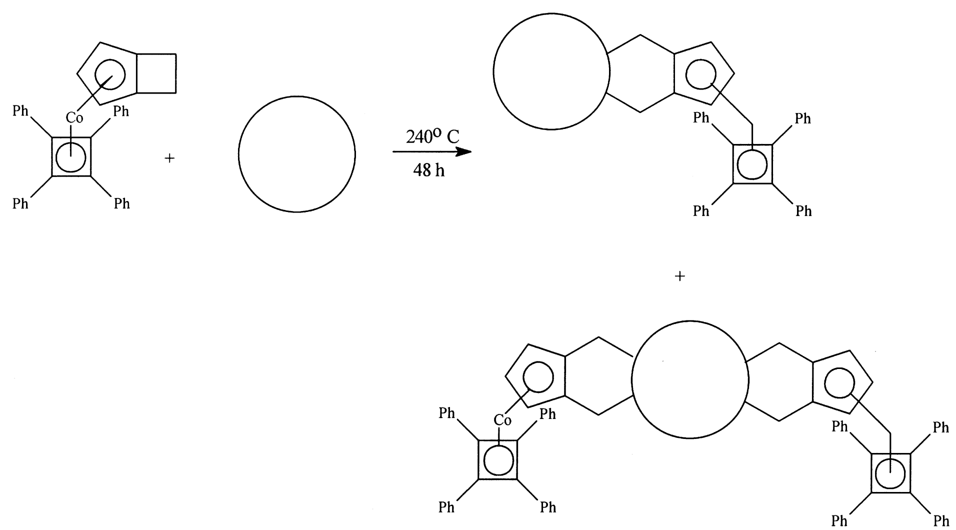
behaves as a sacrificial electron donor in an acetonitrile/methanol mixture [264]. Photolysis (both flash and continuous) has been used in the study of the kinetics of the above reactions and mechanism has been deduced (Eq. (22)), TP = *p*-terphenyl, TEA = triethylamine, L = OMD, HMD or DMD (**160**). From the flash photolysis, the spectra obtained show, in the catalytic system, the formation of first the *p*-terphenyl radical anion, then the complex $[Co(I)L]^+$, followed by the $[Co(I)L(CO_2)]^+$ complex, and the $[S\text{-}Co(III)L(CO_2^{2-})]^+$ complex, in these, L is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (HMD) and



(161)

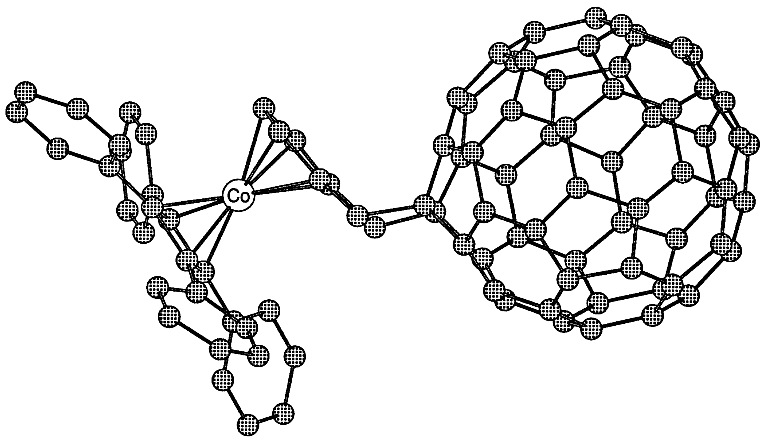
S = solvent. The rate of the electron-transfer in the reaction of *p*-terphenyl radical anion with $[Co(II)L]^{2+}$ is probably diffusion controlled. The formation of the complex between CO_2 to $[Co(I)L]^{+}$ has a rate constant of $1.7 \times 10^{8}\ M^{-1}\ s^{-1}$ and an equilibrium constant $1.1 \times 10^{4}\ M^{-1}$. The system was also studied when L is a different ligand and also the complexes $Co(II)DMD^{2+}$ or $Co(II)OMD^{2+}$. The complex was prepared from the corresponding $[Co(III)DMDBr_2]ClO_4$ by irradiation at 313 nm, when it was converted to the Co(II) species. One effect of these two species was to decrease the lifetime of $TP^{\cdot -}$. A difference between these two was that the life time of $Co(I)DNM^{+}$ was 16 μs against 5.8 h for $Co(I)OMD^{+}$ in the absence of CO_2. The rate constant for binding CO_2 by $Co(I)DMD^{+}$ was 3.7×10^{8}, while that for $Co(I)OMD^{+}$ was $1.1 \times 10^{6}\ M^{-1}\ s^{-1}$. A series of mixed-ligand cyanonitrosyl complexes of cobalt(I) has been prepared by the reaction of $K_2[Co(NO)(CN)_4(H_2O)] \cdot H_2O$ with a number of heterocyclic bases viz. nicotinamide, *N*-methylnicotinamide, *N*-hydroxymethylnicotinamide, pyridine-2-aldoxime, pyridine-3-aldoxime, pyridine-4-aldoxime, 2-hydroxymethylpyridine, 3-hydroxymethyl-pyridine and 4-hydroxymethylpyridine, Eq. (23) and (**161**) [265]. The complexes formed have the formula: $K_2[Co(NO)(CN)_4(L)] \cdot H_2O$. It is proposed that the environment around the Co(I) is a tetragonally distorted octahedron with the heterocyclic bases behaving as neutral monodentate ligands bonded to the Co(I) by the ring nitrogen.

$$K_2[Co(NO)(CN)_4(H_2O)].H_2O + L \rightarrow K_2[Co(NO)(CN)_4(L)].H_2O \qquad (23)$$



(162)

Reaction of C_{60} with (η_5-bicyclo[3.2.0]hepta-1,3-dienyl)(η_4-tetraphenylcyclobutadiene)cobalt(I) in o-dichlorobenzene resulted in black crystalline 1:1 adduct and the 1:2 adduct (**162**). [266]. The X-ray crystal structure is shown in (**163**), which, as one might expect, has a number of novel features. The redox behaviour of the complex was investigated. The cyclic voltammogram shows three reduction waves corresponding to C_{60}^{-}, C_{60}^{2-}, and C_{60}^{3-}.



(163)

The well-known complex $[Co(bpy)_3]^{2+}$ has been investigated electrochemically and it has been found that the cathodic wave in the process $[Co(bpy)_3]^{2+}/[Co(bpy)_3]^{+}$ shows catalytic character in the presence of hydrogen ions [267]. The rate constant of the equivalent chemical reaction was found to be $2.2\times10^4\ M^{-1}\ s^{-1}$.

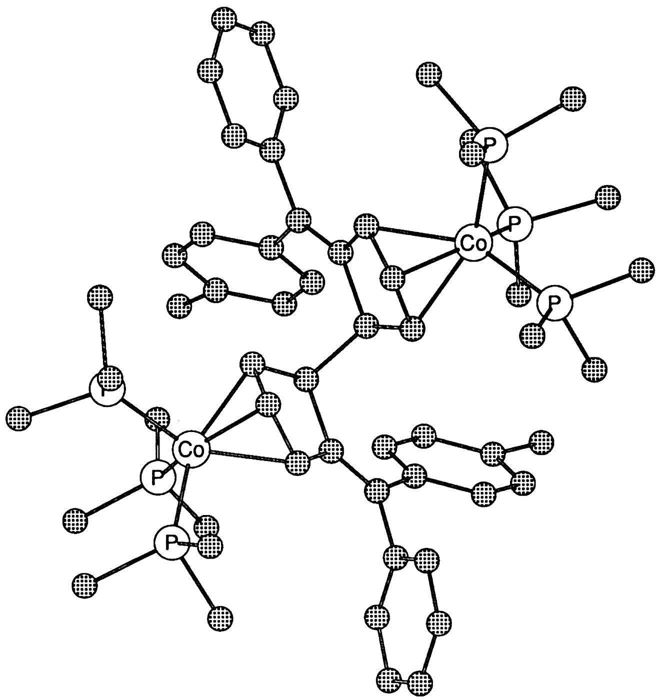
The complex $[Co(CNR)_4(ClO_4)_2]$, in which $R=2,6-(Me_2CH)_3C_6H_3$ has been found to react with py, 3-Mepy and 4-Mepy (L) [268]. The result is the formation of complexes of the form $[Co(CNR)_4L_2]$ $(ClO_4)_2$. Using a variety of physical techniques, these complexes were shown to have tetragonal structures. When the above reaction involving pyridine was carried out over an extended time, the product was the Co(I) complex $[Co(CNR)_5]ClO_4$.

Oxidation polymerization of the cobalt complex of 2,6-diacetylpyridine mono(ethylenediamine) in MeCN using Pt electrodes resulted in a stable film which produced peaks due to the Co(II)/Co(I) redox couple [269].

The X-ray crystal structure of the complex {1,2,3-η:1′,2′,3′-η-4,4′-bis[(4-methylphenyl)phenylmethylidene]-5,5′-dihydro fulvalene}-hexakis(trimethylphosphine)dicobalt(1) (**164**) has been determined [270].

5. Cobalt(IV) complexes

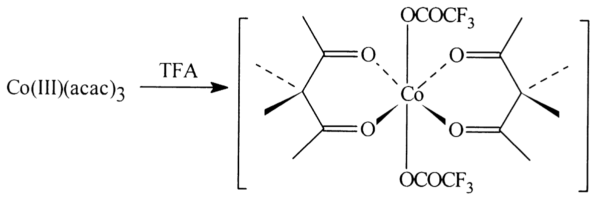
Cobalt(IV) is a very rare oxidation state for cobalt and it is unusual to find any papers in any given year that even mention it. A Co(IV) species has been proposed



(164)

as an intermediate in reactions of tris(acetylacetonato)cobalt(III) in solution in trifluoroacetic acid (TFA) [271]. During the course of these reactions a range of free radical complexes were detected and characterized. At room temperature in an inert atmosphere there is a reaction in the presence of TFA which is that shown in (**165**) in which the green colour of the starting material changes to a red–brown colour. The description of the radicals involved in the process can be as β-ketoenolyl cobalt(III) complexes or alternatively as cationic cobalt(IV) β-ketoenolates depending on the structure of the β-ketoenolate ligand. The process which gives rise to the formation of cationic cobalt(III) complexes is facilitated by the ready protonation of the tris(acetylacetonato)cobalt(III) complex.

A series of complexes of the type (5,10,15-tri-X-phenyl-2,3,7,8,12,13,17,18-octamethylcorrolato)cobalt(III) triphenylphosphine, (OMTXPC) Co(PPh(3)), where X was p-OCH_3, p-CH_3, p-Cl, m-Cl, m-F, o-Cl, o-F, or H, have been prepared and characterized media using electrochemical, spectroelectrochemical, and EPR techniques [272]. The redox potentials were determined and were found to be strongly influenced by the substituents on the phenyl rings in the complex. There were four one-electron changes and the first one was for the formation of Co(IV). An interesting feature of these complexes is that the o-Cl complex is found to exist in solution, for example in toluene, as different

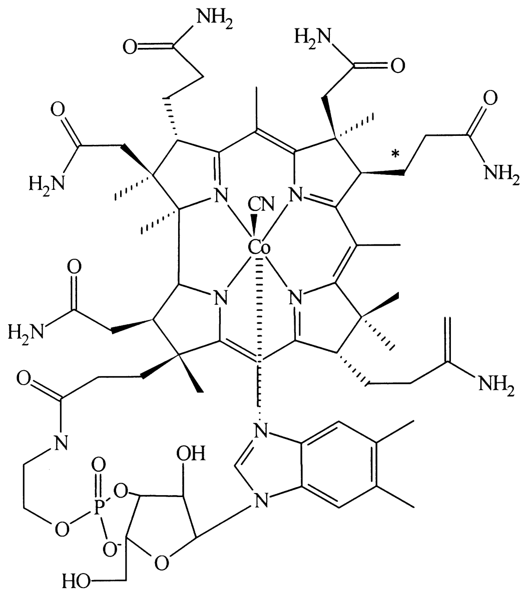


(165)

atropisomers. It was possible to determine activation parameters for the interconversion using proton NMR spectroscopy. Values of between 20 and 193 M^{-1} were obtained for the formation constants between the five-coordinate corroles and py in solution in benzene and the electron donating ability of the substituent on the phenyl rings was an important factor in determining the magnitude of these.

6. Reactions involving vitamin B_{12}

A modified method has been developed for the preparation of cyano-8-epicobalamin (CN-8-epiCbl) (**166**), which results in a much higher yield [273]. The difference between this species and vitamin B_{12} itself, being only a different positioning of the starred propionamide side chain in relation to the corrin ring (**167**). The new method has allowed the preparation of sufficient quantities of this complex to produce a crystal for an X-ray crystal structure. The structure is similar to that of cyanocobalamin; however, there are some small but significant differences. Thus, for example, the fold angle for the CN-8-epiCbl along the Co· · ·C10 axis is 23.8° which is rather larger than that for CNCbl which is 17.7°. A complete ^{1}H and ^{13}C and ^{15}N assignment of the NMR spectra has also been carried out and this also highlights the divergence between the two species and are greatly affected by the differences in the conformation of the corrin ring. Brown and coworkers have also prepared and characterized neopentylcobinamide and neopentyl-13-epicobinamide [274]. An effect of the equilibrium between the base-on and base-off species of these complexes is that both the ^{1}H and the ^{13}C NMR spectra are extremely broad. On the other hand, this work has shown that the two complexes neopentyl cobinamide ($NpCbi^{+}$) and neopentyl-13-epicobinamide ($Np\text{-}13\text{-}epiCbi^{+}$), produce NMR spectra which are very sharp and well resolved. From the NMR spectra, it is deduced that in $NpCbi^{+}$, the fold angle which the authors define as the angle between the "northern" and "southern" planes of the corrin ring, is less than that in $AdoCbi^{+}$ and that in $NpCbi^{+}$ the fold angle is larger than that in $Np\text{-}13\text{-}epiCbi^{+}$. Spectrophotometric kinetic studies have been carried out on the thermoleysis of NpCbl analogues viz. c-monocarboxylate, and the c-N-

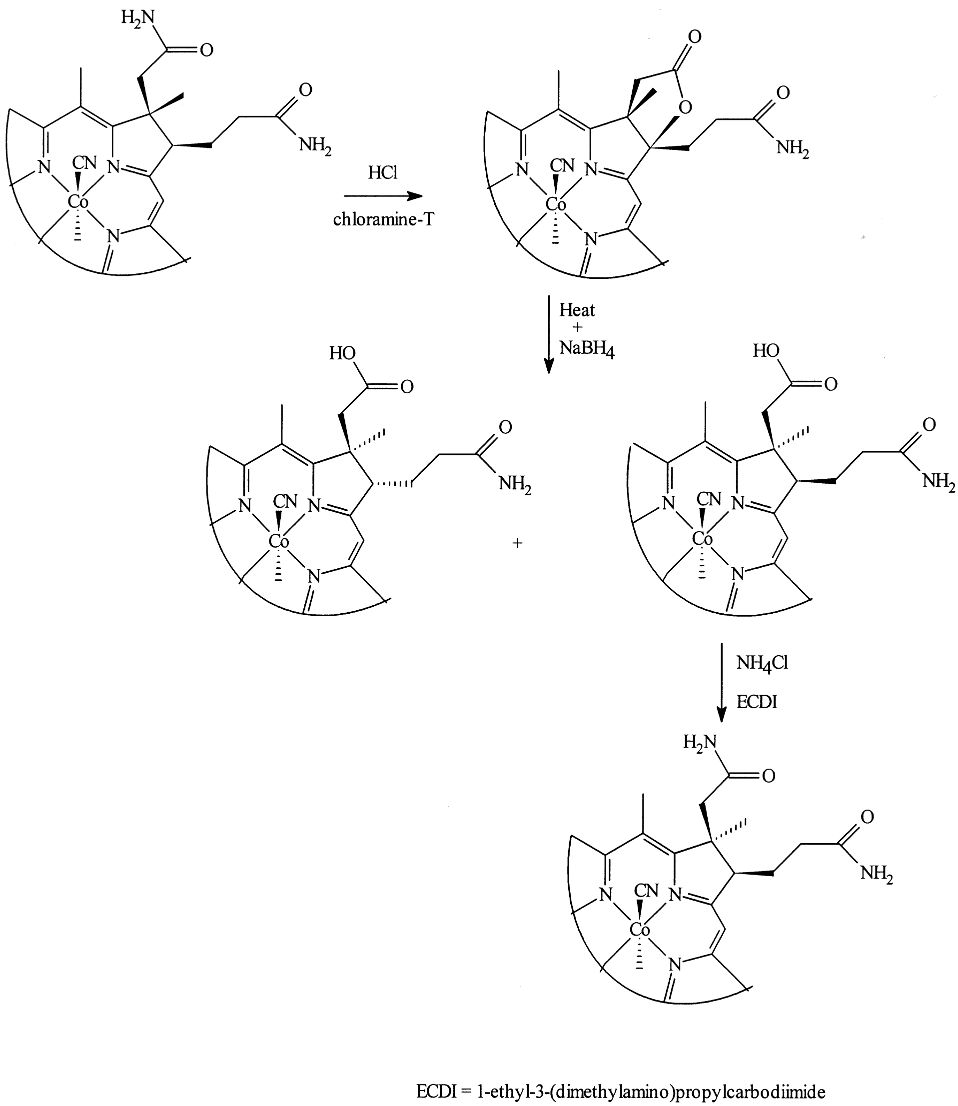


(166)

methyl, c-N,N-dimethyl, and c-N-isopropyl derivatives in neutral aerobic aqueous solution [275]. After making the appropriate corrections, the enthalpy of activation was determined to be essentially constant (118.7 ± 4.6 kJ mol^{-1}), while the entropy of activation was found to increase with increasing size of the c-COX group from 68.5 to 104 J K^{-1} mol^{-1}. It is concluded that this is caused by increased restriction of c side chain rotation in the ground state which is then partly relieved on the formation of the transition state for the homolysis of the Co–C bond. It is proposed that these results may be used to provide insight into the mechanism for enzyme catalysis of thermolysis of 5′-deoxyadenosylcobalamin (coenzyme B_{12}) where it may be that the enzyme restricts the ground-state rotational freedom of the acetamide side chains.

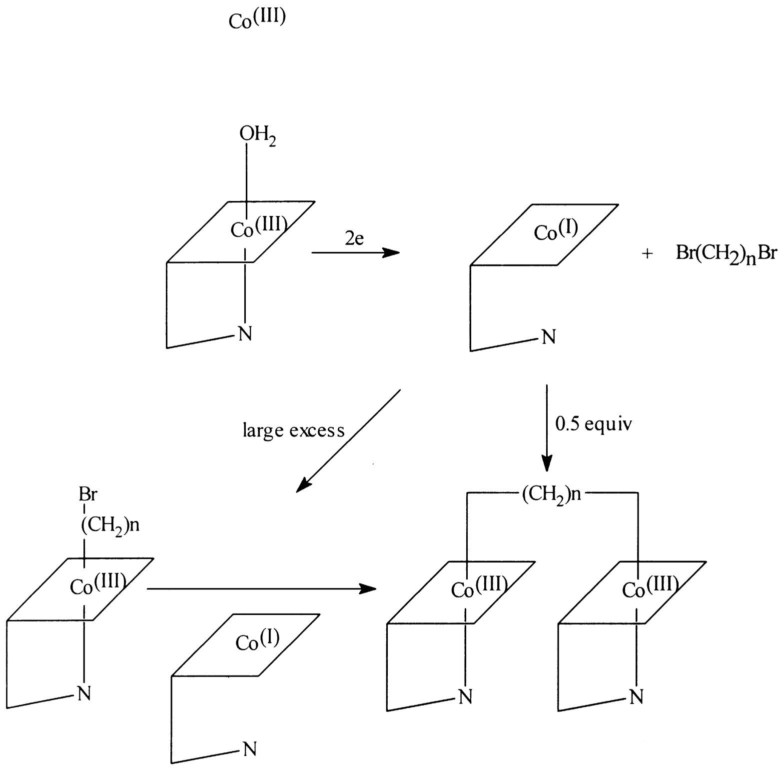
There has been a study of oligomethylene-bridged vitamin B_{12} dimers [276]. These have been prepared by, for example, reacting electrochemically generated Co(I)balmamin with 0.5 equivalent of 1,4-dibromobutane in methanol, to produce red crystals of the dimer. The use of a large excess of the 1,4-dibromobutane resulted in the formation of the monomer, which was also isolated. The formation of these various species is diagrammatically illustrated in (**168**). The structure of the dimer deduced from spectroscopic observations was confirmed using an X-ray crystal structure determination.

Care has to be taken to ensure that the salt used to maintain ionic strength in



(167)

kinetics measurements does not interfere with the reaction being studied. This is illustrated in the paper on the reaction between HN_3 and N_3^- and aquacobalamin [277]. The reaction and related reactions had previously been studied by Marques and coworkers using KCl to maintain the ionic strength [278]. If we represent aquacobalamin as Co–(H_2O), then the reactions studied were those in delineated in Eq. (24). When the kinetics of these reactions were measured with $NaClO_4$ rather than KCl to maintain ionic strength it was found that k_1 at 678 dm^3 mol^{-1} s^{-1} was



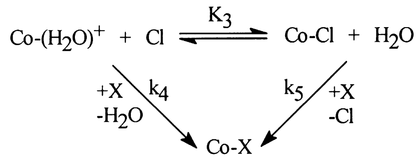
(168)

higher than that measured in KCl where the measured rate constant was 525 $dm^3\ mol^{-1}\ s^{-1}$, and similarly k_2 is much higher in $NaClO_4$ than in KCl solution. The reason suggested for these differences is the intervention of the anation of the aquacobalamin by Cl^- ions. The processes involved in this are those shown in (**169**) together with the rate equation which corresponds to this mechanism. The effects of variation of various parameters on the rate constants, particularly the effects of pressure, allowing activation volumes to be determined, were studied. A significant finding was that a reverse acid catalysed aquation reaction was an important feature in determining the rate profile of these reactions.

$$Co-(H_2O)^+ + N_3^- \xrightarrow{k_1} Co-N_3 + H_2O \ ....(1) \qquad (24)$$

$$Co-(H_2O)^+ + HN_3 \underset{k_{-2}}{\overset{K_2}{\rightleftarrows}} Co-HN_3^+ + H_2O \ ....(2)$$

Vitamin B_{12} is such an important molecule that it is crucial to have accurate data about its structure. The most accurate X-ray structure of aquacobalamin to date



$$k_{obs} = \left(\frac{k_4 + k_5K_3[Cl^-]}{(1 + K_3[Cl^-])}\right)[X]$$

Where X is the appropriate nucleophile

(169)

has been published [279]. This allows the observation that steric interaction from the very short Co–dimethylimidazole bond results in a fairly large "butterfly" deformation in the corrin ring. The structure was also investigated in solution using EXAFS and was found to be virtually identical to that in the crystal, with NMR spectroscopic studies confirming that the axial position is occupied by a water molecule. There are, however, differences in the hydrogen bonding of the C-acetamide chain indicated by NOE studies.

Acknowledgements

The author expresses his thanks for the patience and forbearance of his wife, Jackie Davies and brother Colin Davies, during the preparation of the manuscript, to Catherine Housecroft for producing reference data and Steve Marshall for flexibility in other deadlines.

References

[1] M.B. Davies, Coord. Chem. Rev. (1997) in press.
[2] N. Winterton, R. Soc. Chem. A. Rep. 92 (1996) 481.
[3] R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruening, Chem. Rev. 95 (1995) 2529.
[4] C.D. Hubbard, R. van Eldik, Instrum. Sci. Technol. 23 (1995) 1.
[5] T.W. Swaddle, Can. J. Phys. 73 (1995) 258.
[6] P. Kofod, Inorg. Chem. 34 (1995) 2768.
[7] T. Wandlowski, R. Delevie, J. Electroanal. Chem. 380 (1995) 201.
[8] H. Yokoyama, H. Kon, T. Hiramoto, K. Shinozaki, Bull. Chem. Soc. Jpn 67 (1994) 3179.
[9] D.A. Dixon, N.P. Sadler, T.P. Dasgupta, Transition Metal Chem. 20 (1995) 295.
[10] G. Calvaruso, F.P. Cavasino, C. Sbiziolo, M.L.T. Liveri, J. Chem. Soc. Faraday Trans. 91 (1995) 1075.
[11] A.A. Zaghoul, Indian J. Chem. Sect. A 34 (1995) 248.

[12] A.A. Zaghoul, Sh.A. El-Shazly, M.M. Khalil, M.F. Amira, Indian J. Chem. Sect. A 34 (1995) 52.
[13] S. Saha, D. Mukerji, S.K. Sarkar, J. Indian Chem. Soc. 72 (1995) 701.
[14] A.C. Dash, G.C. Pradhan, R. Acharya, Int. J. Chem. Kinet. 27 (1995) 1033.
[15] A.N. Acharya, A.C. Dash, J. Chem. Soc. Faraday Trans. 91 (1995) 1715.
[16] N. Das, R. Das, Transition Metal Chem. 20 (1995) 463.
[17] P. Mohanty, A.C. Dash, Transition Metal Chem. 20 (1995) 153.
[18] A.C. Dash, P. Mohanty, A.N. Acharya, Transition Metal Chem. 20 (1995) 406.
[19] R. Das, N. Das, A.C. Dash, J. Chem. Soc. Dalton Trans. (1995) 3627.
[20] S. Saha, D. Mukherji, S.K. Sarkar, J. Indian Chem. Soc. 71 (1994) 597.
[21] M. Sarakha, A. Rossi, M. Bolte, J. Photochem. Photobiol. A 85 (1995) 231.
[22] J.A. Connolly, J.H. Kim, M. Banaszczyk, M. Drouin, J. Chin, Inorg. Chem. 34 (1995) 1094.
[23] E. Buncel, F. Yang, R.Y. Moir, I. Onyido, Can. J. Chem. 73 (1995) 772.
[24] M.F. Andreasen, S. Bagger, A.M. Sorensen, K. Wagner, J. Inorg. Biochem. 57 (1995) 271.
[25] M. Martinez, M.A. Pitarque, J. Chem. Soc. Dalton Trans. (1995) 4107.
[26] P.A. Brayshaw, J.-C.G. Bunzli, P. Froidevaux, J.M. Harrowfield, Y. Kim, A.N. Sobolev, Inorg. Chem. 34 (1995) 2068.
[27] H. Kurosaki, S. Koga, M. Goto, Bull. Chem. Soc. Jpn 68 (1995) 843.
[28] W. Hilczer, J. Goslar, J. Trittgoc, S.K. Hoffmann, Inorg. Chem. 34 (1995) 1852.
[29] P.S.K. Chia, A.J. Leong, L.F. Lindoy, G.W. Walker, Aust. J. Chem. 48 (1995) 879.
[30] A.C. Dash, S.K. Sarkar, D. Mukerji, S. Aditya, Indian J. Chem. A 34 (1995) 393.
[31] J.M. Harrowfield, M. Mocerino, B.W. Skelton, W.Y. Wei, A.H. White, J. Chem. Soc. Dalton Trans. (1995) 783.
[32] K. Yamanari, M. Kida, M. Yamamoto, T. Fujihara, A. Fuyuhiro, J. Chem. Soc. Dalton Trans. (1995) 2627.
[33] T. Mizuta, K. Kusakari, M. Hashimoto, K. Miyosh, Bull. Chem. Soc. Jpn 68 (1995) 2263.
[34] T. Fujihara, A. Fuyuhiro, S. Kaizaki, J. Chem. Soc. Dalton Trans. (1995) 1813.
[35] N. Shinohara, H. Shibukawa, K. Shinozaki, M. Yoshikai, Bull. Chem. Soc. Jpn 68 (1995) 178.
[36] K. Morgan, G. Gainsford, N. Milestone, J. Chem. Soc. Chem. Comm. (1995) 425.
[37] D.A. Bruce, A.P. Wilkinson, M.G. White, J.A. Bertrand, J. Chem. Soc. Chem. Comm. (1995) 2059.
[38] M.R. Sundberg, R. Uggla, ? Kivekas, Inorg. Chim. Acta 232 (1995) 1.
[39] S.K. Chawla, J.H. Aupers, D.C. Povey, Polyhedron 15 (1996) 683.
[40] K.E. Baxter, L.R. Hanton, J. Simpson, B.R. Vincent, A.G. Blackman, Inorg. Chem. 34 (1995) 2795.
[41] K. Yamanari, A. Fuyuhiro, Bull. Chem. Soc. Jpn 68 (1995) 2543.
[42] R.L. Fanshawe, A.G. Blackman, Inorg. Chem. 34 (1995) 421.
[43] J. Cai, J. Myrczek, I. Bemal, J. Chem. Soc. Dalton Trans. (1995) 611.
[44] G.A. McLachlan, S.J. Brudenell, G.D. Fallon, R.L. Martin, L. Spiccia, E.R.T. Tiekink, J. Chem. Soc. Dalton Trans. (1995) 439.
[45] R. Boca, M. Hvastijova, J. Kozisek, J. Chem. Soc. Dalton Trans. (1995) 1921.
[46] K. Wang, R.B. Jordan, Inorg. Chem. 34 (1995) 5672.
[47] T. Yarnada, A. Sekine, H. Uekusa, Y. Ohashi, Acta Crystallogr. Sect. C 51 (1995) 828.
[48] U. Englert, A. Fischer, A. Gammersbach, Struct. Chem. 6 (1995) 115.
[49] Y. Gok, S. Karabocek, H. Kantekin, Transition Metal Chem. 20 (1995) 234.
[50] U. Englert, A. Fischer, A. Gammersbach, Struct. Chem. 6 (1995) 115.
[51] Y. Sakai, H. Sato, Y. Ohashi, Y. Arai, Y. Ohgo, Analyt. Sci. 11 (1995) 873.
[52] L.I. Simandi, T. Barna, G. Argay, T.L. Simandi, Inorg. Chem. 34 (1995) 6337.
[53] T. Yamada, H. Uekusa, Y. Ohashi, Chem. Lett. (1995) 187.
[54] H. Hennig, K. Ritter, J. Prakt. Chem. Chem. Z. 337 (1995) 125.
[55] B. Speiser, H. Stahl, Angew. Chem. Int. Ed. Engl. 34 (1995) 1086.
[56] K.H. Halawani, C.F. Wells, J. Chem. Kinetics 27 (1995) 17.
[57] K.H. Halawani, C.F. Wells, Int. J. Chem. Kinetics 27 (1995) 89.
[58] E. Moraga, S. Bunel, C. Ibarra, A. Blasko, C.A. Bunton, Carbohydrate Res. 268 (1995) 1.
[59] J. Burger, P. Klufers, Chem. Ber. 128 (1995) 75.
[60] A. Blasko, C.A. Bunton, E. Moraga, S. Bunel, C. Ibarra, Carbohydrate Res. 278 (1995) 315.

[61] A. Awaluddin, R.N. Deguzman, C.V. Kumar, S.L. Suib, S.L. Burkett, M.E. Davis, J. Phys. Chem. 99 (1995) 9886.
[62] A.L. Balch, M. Mazzanti, T.N. St-Claire, M.M. Olmstead, Inorg. Chem. 34 (1995) 2194.
[63] M. Nakamura, A. Ikezaki, Chem. Lett. (1995) 733.
[64] K. Mesfar, B. Carre, J. Devynck, F. Bedioui, Electrochim. Acta 40 (1995) 253.
[65] O. Anac, O. Sezer, A. Daut, Angew. Makromolekulare Chem. 226 (1995) 213.
[66] D.A. Buckingham, C.R. Clark, A.J. Rogers, J. Simpson, Inorg. Chem. 34 (1995) 3646.
[67] I. Bernal, J. Cetrullo, J. Cai, S.S. Massoud, Struct. Chem. 6 (1995) 99.
[68] I. Bernal, J. Cetrullo, J. Cai, S.S. Massoud, Struct. Chem. 6 (1995) 99.
[69] R.R. Fenton, F.S. Stephens, R.S. Vagg, P.A. Williams, Inorg. Chim. Acta 236 (1995) 109.
[70] S.K. Yun, M.J. Jun, Polyhedron 14 (1995) 3525.
[71] L. Grondahl, A. Hammershoi, S. Larsen, Acta Chem. Scand. 49 (1995) 792.
[72] M. Yashiro, M. Komiyama, K. Kuroda, S. Miura, S. Yoshikawa, S. Yano, Bull. Chem. Soc. Jpn 67 (1994) 3276.
[73] D. Wahnon, A.-M. Lebuis, J. Chin, Angew. Chem. Int. Ed. Engl. 34 (1995) 2412.
[74] A. Jyo, Y. Terazono, H. Egawa, Anal. Sci. 11 (1995) 51.
[75] H.L. Li, B.Y. Zhang, L. Ma, L.L. Wu, J.Q. Chambers, Transition Metal Chem. 20 (1995) 552.
[76] V.V. Strelets, S.V. Kukharenko, Y.Z. Voloshin, Polish J. Chem. 69 (1995) 1520.
[77] M. Tsuchimoto, Y. Ito, J. Fujita, Bull. Chem. Soc. Jpn 68 (1995) 866.
[78] E. Toyota, K. Umakoshi, Y. Yamamoto, Bull. Chem. Soc. Jpn 68 (1995) 858.
[79] R.D. Gillard, P.D. Newman, R.S. Vagg, P.A. Williams, Inorg. Chim. Acta 233 (1995) 79.
[80] P. Tomczyk, H. Sato, K. Yamada, T. Nishina, I. Uchida, J. Electroanal. Chem. 391 (1995) 133.
[81] K. Kashiwabara, M. Kita, H. Masuda, S. Kurachi, S. Ohba, Bull. Chem. Soc. Jpn 68 (1995) 883.
[82] B. Kaitner, E. Mestrovic, Z. Kristallogr. 210 (1995) 952.
[83] D.H. Jo, J.H. Jeong, H.J. Yeo, Y.S. Sohn, O.S. Jung, Bull. Korean Chem. Soc. 16 (1995) 504.
[84] C.G. Pierpont, O.S. Jung, Inorg. Chem. 34 (1995) 4281.
[85] Y. Gok, Z. Anorg. Allg. Chem. 621 (1995) 1243.
[86] D. Armspach, P.R. Ashton, R. Ballardini, V. Balzani, A. Godi, C.P. Moore, L. Prodi, N. Spencer, J.F. Stoddart, M.S. Tolley, T.J. Wear, D.J. Williams, Angew. Chem. Int. Ed. Engl. 34 (1995) 33.
[87] J.D. Zubkowski, D.L. Perry, E.J. Valente, S. Lott, Inorg. Chem. 34 (1995) 6409.
[88] T. Ama, K.I. Okamoto, T. Yasui, Bull. Chem. Soc. Jpn 68 (1995) 874.
[89] T.J. Egan, D.A. Baldwin, L. Denner, D.C. Levendis, H.M. Marques, Acta Crystallogr. Sect. C 51 (1995) 1994.
[90] S. Dutta, Indian J. Chem. Sect. A 34 (1995) 303.
[91] Y. Gok, H. Kantekin, H. Alp, M. Ozdemir, Z. Anorg. Allg. Chem. 621 (1995) 1242.
[92] Y. Yoshimura, Bull. Chem. Soc. Jpn 68 (1995) 2311.
[93] B. Prelesnik, K. Andjelkovic, M. Malinar, N. Juranic, Acta Crystallogr. Sect. C 51 (1995) 1767.
[94] D.C. Ware, D.S. Mackie, P.J. Brothers, W.A. Denny, Polyhedron 14 (1995) 1641.
[95] G. Crisci, T. Hahm, G.W. Weaver, E. Winterfeldt, Chem. Ber. 128 (1995) 449.
[96] A.L. Poznyak, L.V. Stopolyanskaya, Z. Neorg. Khim. 40 (1995) 1122.
[97] A. Muller, E. Krickemeyer, F. Elkatri, D. Rehder, A. Stammler, H. Bogge, F. Hellweg, Z. Anorg. Allg. Chem. 621 (1995) 1160.
[98] B.S. Manhas, B.C. Verma, S.B. Kalia, Polyhedron 14 (1995) 3549.
[99] Y.J. Xu, B.S. Kang, X.T. Chen, L.R. Huang, Acta Crystallogr. Sect. C 51 (1995) 370.
[100] Y. Kageyama, T. Konno, K. Okamoto, J. Hidaka, Inorg. Chim. Acta 239 (1995) 19.
[101] T. Konno, K. Okamoto, Chem. Lett. (1995) 675.
[102] T. Konno, J. Hidaka, K.-I. Okamoto, Bull. Chem. Soc. Jpn 68 (1995) 1353.
[103] R.G. Compton, J.C. Eklund, A. Hallik, S. Kumbhat, L. Nei, A.M. Bond, R. Colton, Y.A. Mah, J. Chem. Soc. Dalton Trans. 12 (1995) 1917.
[104] K. Schulbert, R. Mattes, Z. Anorg. Allg. Chem. 621 (72) (1995
[105] C. Maichle, A. Castineiras, R. Carballo, H. Gebremedhin, M.A. Lockwood, C.E. Ooms, T.J. Romack, D.X. West, Transition Metal Chem. 20 (1995) 228.
[106] M.B. Ferrari, G.G. Fava, G. Pelosi, M.C. Rodriguez-Arguelles, P. Tarasconi, J. Chem. Soc. Dalton Trans. (1995) 3035.

[107] K. Day, D. Bandyopadhyay, K. Chakraborty, A.K. Mallick, K. Mondal, Synth. React. Inorg. Metal-org. Chem. 25 (1995) 1429.
[108] W. Bensch, M. Schuster, Z. Kristallogr. 210 (1995) 68.
[109] Y. Gok, S. Karabocek, Z. Anorg. Allg. Chem. 621 (4) (1995) 654.
[110] A.J. Downard, A.M. Bond, L.R. Hanton, G.A. Heath, Inorg. Chem. 34 (1995) 6387.
[111] A.D. Kirk, D.M. Kneeland, Inorg. Chem. 34 (1995) 1536.
[112] Y. Liu, F.R. Fronczek, S.F. Watkins, G.W. Shaffer, R.L. Musselman, Acta Crystallogr. Sect. C 51 (1995) 1992.
[113] S. Aizawa, K. Matsuda, T. Tajima, M. Maeda, T. Sugata, S. Funahashi, Inorg. Chem. 34 (1995) 2042.
[114] M.A. Deveci, G. Irez, Synth. React. Inorg. Metal-org. Chem. 25 (1995) 1295.
[115] H.C. Sevindir, Synth. React. Inorg. Metal-org. Chem. 25 (1995) 1365.
[116] D. Coucouvanis, R.A. Reynolds, W.R. Dunham, J. Am. Chem. Soc. 117 (1995) 7570.
[117] D.N. Hague, A.R. White, J. Chem. Soc. Dalton Trans. (1995) 449.
[118] M. Kurihara, K. Ozutsumi, T. Kawashima, J. Solution Chem. 24 (1995) 719.
[119] D. Czakissulikowska, J. Radwanskadoczekalska, B. Kuznik, A. Malinowska, Transition Metal Chem. 20 (1995) 203.
[120] P.G. Desmartin, A.F. Williams, G. Bernardinelli, New J. Chem. 19 (1995) 1109.
[121] J.K. Beattie, T.W. Hambley, J.A. Klepetko, A.F. Masters, P. Turner, Polyhedron 15 (1996) 473.
[122] J. Glerup, P.A. Goodson, D.J. Hodgson, K. Michelsen, Inorg. Chem. 34 (1995) 6255.
[123] K.N. Lam, K.Y. Wong, S.M. Yang, C.M. Che, J. Chem. Soc. Dalton Trans. (1995) 1103.
[124] S. Zaydoun, M.S. Idrissi, A. Zrineh, B. Agricole, C. Garrigoulagranage, Polyhedron 14 (1995) 1477.
[125] G. Lalande, R. Cote, G. Tamizhmani, D. Guay, J.P. Dodelet, L. Dignardbailey, L.T. Weng, P. Bertrand, Electrochim. Acta 40 (1995) 2635.
[126] E.T.W.M. Schipper, J.P.A. Heuts, R.P.M. Pinckaers, P. Piet, A.L. German, J. Polymer Sci. Part A 33 (1995) 1841.
[127] J.K. Beattie, R.A. Binstead, M.T. Kelso, P. Delfavero, T.G. Dewey, D.H. Turner, Inorg. Chim. Acta 235 (1995) 245.
[128] E.C. Constable, A.J. Edwards, D. Phillips, P.R. Raithby, Supramolecular Chem. 5 (1995) 93.
[129] A.A. Zaghoul, Sh.A. El-Shazly, M.M. Khalil, M.F. Amira, Indian J. Chem. Sect. A 34 (1995) 52.
[130] R. Han, G. Parkin, S. Trofimenko, Polyhedron 14 (1995) 387.
[131] C. Janiak, T.G. Scharmann, K.-W. Brzezinka, P. Reich, Chem. Ber. 128 (1995) 323.
[132] A. Andreev, V. Ivanova, L. Prahov, I.D. Schopov, J. Molec. Catalysis A (1995) 197.
[133] M. Hanack, R. Polley, S. Knecht, U. Schlick, Inorg. Chem. 34 (1995) 3621.
[134] E.A. Morlino, L.A. Walker II, R.J. Sension, M.A.J. Rodgers, J. Am. Chem. Soc. 117 (1995) 4429.
[135] S.G. DiMagno, A.K. Wertsching, C.R. Ross, J. Am. Chem. Soc. 117 (1995) 8279.
[136] S. Licoccia, E. Tassoni, R. Paolesse, T. Boschi, Inorg. Chim. Acta 235 (1995) 15.
[137] A.B. Edwards, J.M. Charnock, C.D. Garner, A.B. Blake, J. Chem. Soc. Dalton Trans. (1995) 2515.
[138] X.M. Ren, S.K. Mandal, P.G. Pickup, J. Electroanalyt. Chem. 389 (1995) 115.
[139] J.Z. Li, G.L. Shen, R.Q. Yu, Analyst 120 (1995) 2259.
[140] T. Nyokong, Polyhedron 14 (1995) 2325.
[141] P.A. Bernstein, A.B.P. Lever, Inorg. Chem. 34 (1995) 933.
[142] C.J. Medforth, J.D. Hobbs, M.R. Rodriguez, R.J. Abraham, K.M. Smith, J.A. Shelnutt, Inorg. Chem. 34 (1995) 1333.
[143] S. Pellet-Rostaing, J.B.R. De-Vains, R. Lamartine, Tetrahedron Lett. 36 (1995) 5745.
[144] M. Shakir, S.P. Varkey, Indian J. Chem. Sect. A 34 (1995) 355.
[145] M. Shakir, S.P. Varkey, Polyhedron 14 (1995) 1117.
[146] A.M. Vecchio-Sadus, Transition Metal Chem. 20 (1995) 38.
[147] A.M. Vecchio-Sadus, Transition Metal Chem. 20 (1995) 46.
[149] M.S. Islam, M. Begum, H.N. Roy, Synth. React. Inorg. Metal-org. Chem. 25 (1995) 293.
[150] R. Paschke, S. Diele, I. Letko, A. Wiegeleben, G. Pelzl, K. Griesar, M. Athanassopoulou, W. Haase, Liquid Crystals 18 (1995) 451.
[151] M.L. Turonek, P.A. Duckworth, G.S. Laurence, S.F. Lincoln, K.P. Wainwright, Inorg. Chim. Acta 230 (1995) 51.

[152] I. Bertini, L. Messori, G. Golub, H. Cohen, D. Meyerstein, Inorg. Chim. Acta 235 (1995) 5.
[153] L.Q. Yang, S.P. Yan, G.L. Wang, H.G. Wang, R.J. Wang, X.K. Yao, Polyhedron 14 (1995) 2037.
[154] M.M. Shoukry, A.K.A. Hadi, W.M. Hosny, S.M. Shouheib, Indian J. Chem. Sect. A 34 (1995) 716.
[155] B. Mercimek, G. Irez, Synth. React. Inorg. Metal-org. Chem. 25 (1995) 1391.
[156] J.A. Cooley, P. Kamaras, M. Rapta, G.B. Jameson, Acta Crystallogr. Sect. C 51 (1995) 1811.
[157] H.J. Krüger, Chem. Ber. 128 (1995) 531.
[158] P.O. Lumme, H. Knuuttila, Polyhedron 14 (1995) 1553.
[159] B. Mercimek, G. Irez, J. Macromolec. Sci. A 32 (1995) 147.
[160] -. Arvind, M. Sayeed, K. Iftikhar, N. Ahmad, Indian J. Chem. Sect. A 34 (1995) 79.
[161] B. Umadevi, P.T. Muthiah, X.G. Shui, D.S. Eggleston, Inorg. Chim. Acta 234 (1995) 149.
[162] K.R.J. Thomas, V. Chandrasekhar, S.R. Scott, A.W. Cordes, Polyhedron 14 (1995) 1607.
[163] M. Jamnicky, P. Segla, M. Koman, Polyhedron 14 (1995) 1837.
[164] S.-C. Sheu, M.-J. Tien, M.-C. Cheng, T.-I. Ho, S.-M. Peng, Y.-C. Lin, J. Chem. Soc. Dalton Trans. (1995) 3503.
[165] B.S. Jaynes, L.H. Doerrer, S. Liu, S.J. Lippard, Inorg. Chem. 34 (1995) 5735.
[166] H.-J. Mai, R. Meyer zu Kocker, S. Wocadlo, W. Massa, K. Dehnicke, Angew. Chem. Int. Ed. Engl. 34 (1995) 1235.
[167] S.-B. Teo, S.-G. Teoh, C.-H. Ng, H.-K. Fun, J.-P. Declercq, Polyhedron 14 (1995) 1447.
[168] J. Ismail, M.F. Ahmed, P.V. Kamath, G.N. Subbanna, S. Uma, J. Gopalakrishnan, J. Solid State Chem. 114 (1995) 550.
[169] J. Kim, J.O. Edwards, Inorg. Chim. Acta 235 (1995) 9.
[170] A.E. Kapustin, E.E. Milko, E.V. Kapustina, S.B. Milko, Russian J. Appl. Chem. 67 (1995) 1225.
[171] Y.Q. Zheng, A. Adam, Z. Kristallogr. 210 (1995) 447.
[172] S. Hagen, M. Jansen, Z. Anorg. Allg. Chem. 621 (1995) 149.
[173] S.K. Bauer, C.J. Willis, N.C. Payne, Acta Crystallogr. Sect. C 51 (1995) 586.
[174] V. Jordanovska, R. Trojko, Thermochim. Acta 258 (1995) 205.
[175] Y.M. Issa, W.F. Elhawary, H.A. Abdelsalam, Transition Metal Chem. 20 (1995) 423.
[176] W. Brzyska, W. Wolodkiewicz, Polish J. Chem. 69 (1995) 1109.
[177] W. Wolodkicwicz, W. Brzyska, Z. Rzaczynska, T. Glowiak, Polish J. Chem. 69 (1995) 1392.
[178] D.M. Adams, B.L. Li, J.D. Simon, D.N. Hendrickson, Angew. Chem. Int. Ed. Engl. 34 (1995) 1481.
[179] V.P. Pillai, V.M. Shinde, Indian J. Chem. Sect. A 34 (1995) 407.
[180] T.S. Lobana, P.V.K. Bhatia, Proc. Indian Acad. Sci. 107 (1995) 35.
[181] S.M. Godfrey, D.G. Kelly, C.A. McAuliffe, R.G. Pritchard, J. Chem. Soc. Dalton Trans. (1995) 1095.
[182] I. Lukes, I. Cisarova, P. Vojtisek, K. Bazakas, Polyhedron 14 (1995) 3163.
[183] B.K. Puri, S. Balani, Talanta 42 (1995) 337.
[184] A. Gupta, S.M. Khopkar, Talanta 42 (1995) 1493.
[185] S.P. Watton, M.I. Davis, L.E. Pence, J. Rebek, S.J. Lippard, Inorg. Chim. Acta 235 (1995) 195.
[186] P. Athappan, G. Rajagopal, Transition Metal Chem. 20 (1995) 356.
[187] P. Mastrorilli, C.F. Nobile, G. Marchese, Inorg. Chim. Acta 233 (1995) 65.
[188] J.S. Wood, Inorg. Chim. Acta 229 (1995) 407.
[189] J. Laugier, V. Ovcharenko, P. Rey, Inorg. Chim. Acta 236 (1995) 49.
[190] G.A. Doyle, D.M.L. Goodgame, S.P.W. Hill, S. Menzer, A. Sinden, D.J. Williams, Inorg. Chem. 34 (1995) 2850.
[191] C. Gimenez-Saiz, J.R. Galan-Mascaros, S. Triki, E. Coronado, L. Ouahab, Inorg. Chem. 34 (1995) 524.
[192] C.J. Gomez-Garcia, C. Gimenez-Saiz, S. Triki, E. Coronado, P. Le Magueres, L. Ouahab, L. Ducasse, C. Sourisseau, P. Delhaes, Inorg. Chem. 34 (1995) 4139.
[193] H. Yokoyama, S. Suzuki, M. Goto, K. Shinozaki, Y. Abe, S. Ishiguro, Z. Naturforsch. Teil A 50 (1995) 301.
[194] T. Ama, J. Miyazaki, K. Hamada, K. Okamoto, T. Yonemura, H. Kawaguchi, T. Yasui, Chem. Lett. (1995) 267.
[195] C. Vansant, H.O. Desseyn, V. Tangoulis, C.P. Raptopoulou, A. Terzis, S.P. Perlepes, Polyhedron 14 (1995) 2115.

[196] A. Casale, A. Derobertis, C. Destefano, A. Gianguzza, G. Patane, C. Rigano, S. Sammartano, Thermochim. Acta 255 (1995) 109.
[197] K.B. Nolan, A.A. Soudi, Inorg. Chim. Acta 230 (1995) 209.
[198] W.Y. Sun, T. Ueno, N. Ueyama, A. Nakamura, Magnetic Resonance Chem. 33 (1995) 174.
[199] M.J. Hynes, M.T. Doody, Int. J. Chem. Kinet. 27 (1995) 419.
[200] M.M. Aly, S.M. Imam, Monatsh. Chem. 126 (1995) 173.
[201] S. McConnell, M. Motevalli, P. Thornton, Polyhedron 14 (1995) 459.
[202] A.B. Blake, E. Sinn, A. Yavari, B. Moubaraki, K.S. Murray, Inorg. Chim. Acta 229 (1995) 281.
[203] F.A. Elsaied, E.S.H. Elashry, Transition Metal Chem. 20 (1995) 309.
[204] P.R. Athappan, P. Shanthi, C. Natarajan, Indian J. Chem. Sect. A 34 (1995) 648.
[205] A.F.D. de Namor, J.D.C. Garcia, J.I. Bullock, Pure Appl. Chem. 67 (1995) 1053.
[206] B.B. Mahapatra, M.K. Raval, A.K. Behera, A.K. Das, J. Indian Chem. Soc. 72 (1995) 161.
[207] B.B. Mahapatra, D.D. Mahapatro, R.R. Mishra, S.K. Kar, J. Indian Chem. Soc. 72 (1995) 347.
[208] A.K. Panda, H. Mohanty, D.C. Dash, Indian J. Chem. Sect. A 34 (1995) 911.
[209] H.X. Shen, Y.P. Tang, X.L. Xiao, S.F. Zhang, R.X. Liu, Analyst 120 (1995) 1599.
[210] M. Valko, R. Klement, P. Pelikan, R. Boca, L. Dlhan, A. Bottcher, H. Elias, L. Muller, J. Phys. Chem. 99 (1995) 137.
[211] A. Louati, A. Kuncaka, M. Gross, C. Haubtmann, M. Bernard, J.J. Andre, J.P. Brunette, J. Organometal. Chem. 486 (1995) 95.
[212] V. Srivastava, S.K. Srivastava, A.P. Mishra, J. Indian Chem. Soc. 72 (1995) 47.
[213] V. Srivastava, S.K. Srivastava, A.P. Mishra, Synth. React. Inorg. Metal-org. Chem. 25 (1995) 21.
[214] G.C. Chiumia, D.J. Phillips, A.D. Rae, Inorg. Chim. Acta 238 (1995) 197.
[215] M.B. Davies, Coord. Chem. Rev. 134 (1994) 195.
[216] W. Bronger, W. Koelman, D. Schmitz, Z. Anorg. Allg. Chem. 621 (1995) 405.
[217] C. Silvestru, R. Rosler, I. Haiduc, C. Ceaolivares, G. Espinosaperez, Inorg. Chem. 34 (1995) 3352.
[218] K. Fukui, H. Masuda, H. Ohyanishiguchi, H. Kamada, Inorg. Chim. Acta 238 (1995) 73.
[219] J. Huang, J.C. Dewan, M.A. Walters, Inorg. Chim. Acta 228 (1995) 199.
[220] P. Athappan, S. Sevagapandian, G. Rajagopal, Transition Metal Chem. 20 (1995) 472.
[221] B. Becker, K. Radacki, A. Konitz, W. Wojnowskf, Z. Anorg. Allg. Chem. 621 (1995) 904.
[222] T. Yonemura, S. Kawai, T. Ama, H. Kawaguchi, T. Yasui, Chem. Lett. (1995) 59.
[223] F.L. Jiang, X.L. Xie, M.C. Hong, B.S. Kang, R. Cao, D.X. Wu, H.Q. Liu, J. Chem. Soc. Dalton Trans. (1995) 1447.
[224] L. Hennig, R. Kirmse, O. Hammerich, S. Larsen, H. Frydendahl, H. Toftlund, J. Becher, Inorg. Chim. Acta 234 (1995) 67.
[225] C.R. Lucas, S.A. Liu, J.N. Bridson, Can. J. Chem. 73 (1995) 1023.
[226] G. Schmauch, F. Knoch, H. Kisch, Chem. Ber. 128 (1995) 303.
[227] J.A. Obaleye, C.L. Ojiekwe, O. Famurewa, Indian J. Chem. Sect. A 34 (1995) 310.
[228] N. Ehlers, R. Mattes, Inorg. Chim. Acta 236 (1995) 203.
[229] M.Y. Khuhawar, Z.P. Memon, S.N. Lanjwani, Chromatographia 41 (1995) 236.
[230] M.P.S. Andres, M.L. Marina, S. Vera, Analyst 120 (1995) 255.
[231] S. Chandra, L. Gupta, V.P. Tyagi, Synth. React. Inorg. Metal-org. Chem. 25 (1995) 537.
[232] G. Mukherjee, T. Ghosh, J. Inorg. Biochem. 59 (1995) 827.
[233] T. Atalay, E. Ozkan, Thermochim. Acta 254 (1995) 371.
[234] C.K. Bhaskare, P.P. Hankare, J. Indian Chem. Soc. 72 (1995) 585.
[235] A. Castineiras, M.C.F. Vidal, Transition Metal Chem. 20 (1995) 477.
[236] R. Bouwman, P. Evans, R.A.G. de Graaf, H. Kooijman, R. Poinsot, P. Rabu, J. Reedijk, A.L. Spek, Inorg. Chem. 34 (1995) 6302.
[237] T. Kakoi, M. Goto, K. Sugimoto, K. Ohto, F. Nakashio, Separation Sci. Technol. 30 (1995) 637.
[238] M. Divaira, P. Stoppioni, J.A. McCleverty, Gazz. Chim. Ital. 125 (1995) 277.
[239] B.C. Janssen, V. Sernau, G. Huttner, A. Asam, O. Walter, M. Buchner, L. Zsolnai, Chem. Ber. 128 (1995) 63.
[240] V. Semau, G. Huttner, M. Fritz, B. Janssen, M. Buchner, C. Emmerich, O. Walter, L. Zsolnai, D. Gunauer, T. Seitz, Z. Naturforsch. Teil B 50 (1995) 1638.

[241] C.A. Ghilardi, F. Laschi, S. Midollini, A. Orlandini, G. Scapacci, P. Zanello, J. Chem. Soc. Dalton Trans. (1995) 531.
[242] S.J. Chadwell, S.J. Coles, P.G. Edwards, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1995) 3551.
[243] M. Scrocco, A.M. Paoletti, J. Electron Spectrosc. Relat. Phenomena 74 (1995) 231.
[244] M. Feist, S. Trojanov, E. Kemnitz, Z. Anorg. Allg. Chem. 621 (1995) 1775.
[245] J.J. Schneider, R. Goddard, C. Kruger, Z. Naturforsch. Teil B 50 (1995) 448.
[246] M. Koide, S. Ishiguro, Z. Naturforsch. Teil A 50 (1995) 11.
[247] C.A.L. Becker, Synth. React. Inorg. Metal-org. Chem. 25 (1995) 1455.
[248] M. Hvastijova, J. Kozisek, J. Kohout, L. Jager, H. Fuess, Transition Metal Chem. 20 (1995) 276.
[249] J. Kulesza, M.A. Malik, S. Zamponi, M. Berrettoni, R. Marassi, J. Electroanalyt. Chem. 397 (1995) 287.
[250] S. Selvaraj, P. Natarajan, Indian J. Chem. Sect. A 34 (1995) 253.
[251] T. Suzuki, Y. Soejima, H. Nishide, E. Tsuchida, Bull. Chem. Soc. Jpn 68 (1995) 1036.
[252] C.N. Shi, F.C. Anson, Inorg. Chem. 34 (1995) 4554.
[253] B. Steiger, F.C. Anson, Inorg. Chem. 34 (1995) 3355.
[254] R. Guilard, S. Brandes, C. Tardieux, A. Tabard, M. Lher, C. Miry, P. Gouerec, Y. Knop, J.P. Collman, J. Am. Chem. Soc. 117 (1995) 11721.
[255] T. Geiger, F.C. Anson, J. Am. Chem. Soc. 103 (1981) 7489.
[256] C. Kang, F.C. Anson, Inorg. Chem. 34 (1995) 2771.
[257] D. Chen, R.J. Motekaitis, I. Murase, A.E. Martell, Tetrahedron 51 (1995) 77.
[258] Y.P. Deng, D.H. Busch, Inorg. Chem. 34 (1995) 6380.
[259] J.J. Bozell, B.R. Hames, D.R. Dimmel, J. Org. Chem. 60 (1995) 2398.
[260] Y.K. Choi, K.H. Chjo, S.M. Park, N. Doddapaneni, J. Electrochem. Soc. 142 (1995) 4107.
[261] O.M. Reinaud, G.P.A. Yap, A.L. Rheingold, K.H. Theopold, Angew. Chem. Int. Ed. Engl. 34 (1995) 2051.
[262] T. Moriuchi, T. Hirao, T. Ishikawa, Y. Ohshiro, I. Ikeda, J. Molec. Catalysis A 95 (1995) L1.
[263] G. Chelucci, Tetrahedron: Asymm. 6 (1995) 811.
[264] T. Ogata, S. Yanagida, B.S. Brunschwig, E. Fujita, J. Am. Chem. Soc. 117 (1995).
[265] R.C. Maurya, D.D. Mishra, S. Mukherjee, J. Dubey, Polyhedron 14 (1995) 1351.
[266] M. Iyoda, F. Sultana, S. Sasaki, H. Butenschon, Tetrahedron Lett. 36 (1995) 579.
[267] D.A. Fungaro, R. Tokoro, Analyt. Lett. 28 (1995) 493.
[268] C.A.L. Becker, M.A.S. Biswas, Synth. React. Inorg. Metal-org. Chem. 25 (1995) 269.
[269] M.A. Azzem, F.A. Elsaied, M.A. Aboutabl, Z.F. Mohamed, J. Electrochem. Soc. 142 (1995) 2517.
[270] H.-F. Mein, E. Auer, T. Jung, C. Rohr, Organometallics 14 (1995) 2725.
[271] M. Bruni, P. Diversi, G. Ingrosso, A. Lucherini, C. Pinzino, A. Raffaelli, J. Chem. Soc. Dalton Trans. (1995) 1035.
[272] V.A. Adamian, F. Dsouza, S. Licoccia, M.L. Divona, E. Tassoni, R. Paolesse, T. Boschi, K.M. Kadish, Inorg. Chem. 34 (1995) 532.
[273] K.L. Brown, X. Zou, G.Z. Wu, J.D. Zubkowski, E.J. Valente, Polyhedron 14 (1995) 1621.
[274] K.L. Brown, D.R. Evans, Polyhedron 14 (1995) 2961.
[275] K.L. Brown, S.F. Cheng, H.M. Marques, Inorg. Chem. 34 (1995) 3038.
[276] B. Krautler, T. Derer, P.L. Liu, W. Muhlecker, M. Puchberger, C. Kratky, Angew. Chem. Int. Ed. Engl. 34 (1995) 84.
[277] F.F. Prinsloo, E.L.J. Breet, R. van Eldik, J. Chem. Soc. Dalton Trans. (1995) 685.
[278] H.M. Marques, J. Chem. Soc. Dalton Trans. (1991) 1437.
[279] C. Kratky, G. Farber, K. Gruber, K. Wilson, Z. Dauter, H.-F. Nolting, R. Konrat, B. Krautler, J. Am. Chem. Soc. 117 (1995) 4654.