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4. COBALT

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INTRODUCTION

The present survey covers the bulk of the 1980 literature together with references to the 1979 literature received too late to be included in the previous review. A useful book "Cobalt in Biology and Biochemistry" [1] has appeared and should stimulate interest in the bioinorganic chemistry of this element. A 4th edition of Underwood's book "Trace Elements in Human and Animal Nutrition", which includes a section on cobalt, has also been published [2].

Other books or review articles of interest include, "Some New Developments in the Chemistry of Metallophthalocyanines" [3], "Stereochemistry of Optically Active Transition Metal Compounds" [4], several chapters of which concentrate on the synthesis and optical activity of various cobalt(III) complexes, and "Metal Ion Activation of Dioxygen" [5]. Volume 27 of "Progress in Inorganic Chemistry" includes a review of dithiolium salts and dithiodiketone complexes of the transition metals [6]. The catalytic activity of polymer-metal complexes, including a variety of polymer-cobalt(III) complexes, has been reviewed [7] and

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a very useful data compilation and discussion of ^{59}Co NMR spectroscopy has appeared [8]. A new book, "Coordination Chemistry of Macrocyclic Compounds" [9], provides a wealth of information for those with interests in this important area of coordination chemistry. A Russian text on "Substitution Reactions in Cobalt Coordination Compounds" has also been published [10]. A Japanese review deals with the synthesis of cobalt complexes [11] and a further review discusses trimethylphosphine complexes of nickel, cobalt and iron as model compounds for homogeneous catalysis [12]. Phosphorus donor complexes of cobalt(III) [13], the photochemistry of transition metal complexes [14], and cobalt(II) complexes capable of reversibly binding dioxygen [15] have also been reviewed.

4.1 COBALT(IV)

The chemistry of labile organocobalt(IV) complexes, $[RCoL]^+$ (where LH_2 = tetradentate or bis-bidentate equatorial ligand of the salen or $(dmgH)_2$ type) generated by one-electron oxidation of the corresponding organo-cobalt(III) complexes, has been investigated [16]. In most cases pyridine reacts rapidly with the complexes to displace the organic ligand R and possible mechanisms have been discussed.

4.2 COBALT(III)

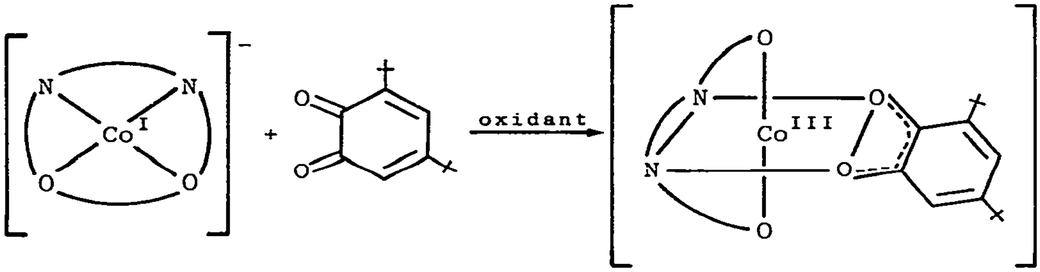
A great deal of chemistry has been published dealing with this classical, kinetically inert, metal centre. The work reported can be subdivided into three broad areas, (a) synthesis, (b) stereochemistry (including X-ray crystallography) and (c) kinetics, reactivity and mechanism. Other areas of growing interest are electrochemistry and ^{59}Co NMR spectroscopy [8]. The subdivision which follows is somewhat arbitrary since almost all cobalt(III) complexes are mixed ligand complexes of one type or another, and the use of a single type of ligand classification thus has its limitations. For example, it is convenient to think in terms of bis-1,2-diaminoethane complexes, ammines, *etc*, and this classification has therefore been adopted in the review, even though the chemistry described may relate to other ligands present in the complex.

4.2.1 Complexes with oxygen donor ligands

Partial resolution of $[Co(acac)_3]$ by salting-in chromatography on SP-Sephadex in the Δ-$[Ni(phen)_3]^{2+}$ form has been achieved. The Δ-isomer of $[Co(acac)_3]$ is enriched in an aqueous solution of Δ-$[Ni(phen)_3]^{2+}$, indicating that, in aqueous solution, a Δ-Δ ion pair is more stable than a Δ-Λ ion pair [17].

Tris(pentane-2,4-dionato[2-^{14}C])cobalt(III) undergoes ligand exchange in acacH at 85–190 °C without decomposition [18]. An intermediate involving a unidentate acac ion and an acacH molecule was concluded to be formed in the rate determining step. The spectroscopic and magnetic properties of the trivalent metal complexes $[M(dik)_3]$ {M(III) = Al,Cr,Mn,Fe or Co} of 1-(2-thienyl)-butane-1,3-dione and 4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dione have been examined [19].

Reaction (1) represents a new method for obtaining cobalt(III)-*o*-semiquinone



(1)

complexes [20].

The preparation and X-ray structure determination of $[\{(-)_{589}$-3-(6-methyl-2,4-dinitrophenyl)pentane-2,4-dionato}{tris(2-aminoethyl)amine}cobalt(III)] dibromide dihydrate have been described [21]. The six-membered acac ring adopts a flattened boat form, to which the aromatic ring is almost perpendicular.

The structure of $[Co_4{}^{III}I_3{}^{VII}O_{24}H_{12}]^{3-}$, a heteropoly periodate, has been determined [22] and used to indicate the existence of a sizeable and potentially important new category of heteropoly complexes, composed of $I^{VII}O_6$ octahedra sharing oxygen atoms with numerous lower charged transition metal atoms. Rare earth trioxocobaltates(III), $LnCoO_3$, with Ln = Pr,Nd,Tb,Dy or Yb, exhibit low-spin to high-spin transitions of the cobalt characterised by a maximum in the Δ_χ^{-1} against temperature plots, where Δ_χ is the cobalt contribution to the magnetic susceptibility [23].

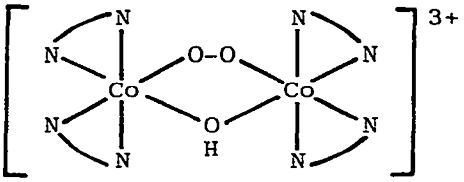
Tris(oxalato)cobalt(III) is known as a typical thermo- and photoreactive compound. Substitution of oxalate by α-diimines reduces the thermally induced redox decomposition. EHT calculations have been accomplished for diimine substituted cobalt(III) complexes with different aliphatic and aromatic diimine ligands [24], and should be helpful for planned syntheses of photocatalytically interesting systems. The structural, spectral, and magnetic properties of (3,5-di-*t*-butylcatecholato)(3,5-di-*t*-butylsemiquinone)(2,2'-bipyridine)cobalt(III), a complex containing mixed-valence organic ligands, have been studied [25]. The syntheses and characterisation of some sodium salts of the *trans*-$[Co(\beta\text{-diketone})_2(NO_2)_2]^-$ type have been described [26], and the spectroscopic and catalytic properties of di-μ-methoxo-μ-ethanoatocobalt(III) complexes have been reported [27].

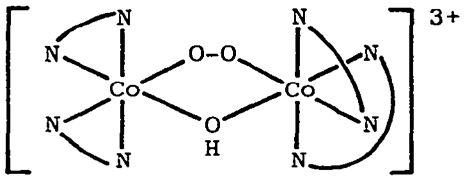
Mixed ligand complexes involving acac en and flexidentate isonitroso-β-diketones and isonitrosomonoketones of cobalt(III) have been studied [28], and ligand exchange between ^{14}C-acacH and $[M(acac)_3]$ (M = Co(III) or Cr(III)) in propan-1-ol investigated [29]. Optically active mixed ligand complexes of cobalt(III) (and cobalt(II)) with acac and aromatic amino-acids have been prepared and their ORD and CD spectra measured [30].

4.2.1.1 Peroxide and superoxide ligands

Catalytic rate constants have been reported for the disproportionation of $[O_2]^{\cdot -}$ by iron(III) and cobalt(III) derivatives of tetrakis(4-*N*-methyl-pyridyl)porphine [31]. These studies may have relevance to the function of the metalloproteins (superoxide dismutases) which catalyse the disproportionation of the superoxide radical anion $[O_2]^{\cdot -}$.

Oxygenation of aqueous solutions of bis(1,2-diaminoethane)cobalt(II) gives a mixture of diastereoisomeric complexes of the μ-peroxo-μ-hydroxo-bis{(1,2-diaminoethane)cobalt(III)} cation. A *meso*-diastereoisomer has been isolated and its structure confirmed by X-ray analysis [32]. In acidic solution the *meso*-diastereoisomer (1) decomposes four times faster than the *rac*-diastereoisomer (2), and in basic solution (1) isomerises to (2).



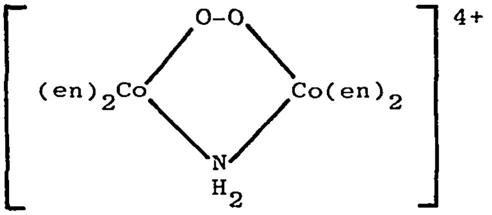


NN = 1,2-diaminoethane

(1)

(2)

The singly-bridged complex, $[(tren)(NH_3)Co(\mu\text{-}O_2)Co(NH_3)(tren)]^{4+}$, reacts with excess tren by replacement of NH_3 in a *cis*-position to the peroxo group to give $[(tren)Co(\mu\text{-}O_2)(\mu\text{-}tren)Co(tren)][ClO_4]_2.2H_2O$ [33], in which the additional tren forms a macrocyclic bridging ring. In acidic solution, the complex decomposes to Co(II) and O_2 and, in basic solution, the bridging tren is replaced by a hydroxo bridge. Cadmium(I) has been observed to reduce the μ-amido-μ-superoxo-bis{$(en)_2$cobalt(III)} cation by an inner-sphere electron transfer process [34]. The complex $[Co^{III}(pan)_2]^+$ (panH = 1-(2-pyridylaza)-2-naphthol) reacts with superoxide $[O_2]^{\cdot -}$ to give $[Co^{II}(pan)_2]$ in dmso solution [35]. A procedure for the standardisation of $[O_2]^{\cdot -}$ in dmso is also described in this paper. The reaction between $[O_2]^{\cdot-}$ and the superoxo complexes (3) and (4) has been studied



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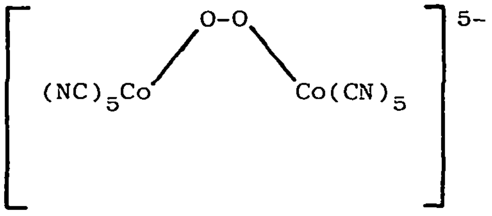


(4)

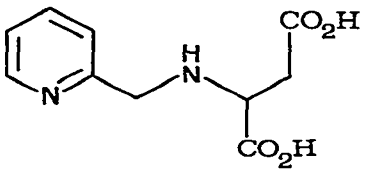
by pulse radiolysis [36]. Electronic spectral studies of the μ-peroxo complexes $[CoL(\mu\text{-}O_2)CoL]^{4+}$ and $[CoLCl]^{2+}$ (L = tetren, epyden, pydien, pydpt, imdien or imdpt), show that chelate ring size has a noticeable influence on the ligand field strength [37]. The frequencies of the oxygen → cobalt charge transfer bands are linearly related to the redox potentials of the complexes and to log K_{O_2}. Although the basicity of the ligand is the major factor in determining the magnitude of K_{O_2}, the ligand field may exert a sizeable perturbation. Electrochemical studies of a series of peroxo-bridged binuclear cobalt complexes [38] have established that the cobalt(III)/cobalt(II) potential shows a linear correlation with log K_{O_2} for the cobalt(II) complexes. Photosensitisation of superoxo-bridged dinuclear cobalt(III) cations by the excited state of tris-$[Ru(bipy)_3]^{2+}$ has been investigated [39].

The preparation of μ-peroxo-bis pentacyanocobaltate(III) has been described [40] and the selective formation of peroxy-*p*-quinolatocobalt(III) complexes has been observed in the oxygenation of 4-alkyl-2,6-di-*tert*-butyl phenols with cobalt(II)-Schiff base complexes [41]. The preparation and structure of $[(papd)Co(O_2)Co(papd)][S_2O_6][NO_3]_2.4H_2O$ (papd = pentaazapentadecane) has been described [42], as has the preparation of tetrakis(1,2-diaminopropane)-μ-peroxo-μ-amido- and μ-peroxo-μ-thiocyanatodicobalt(III) complexes [43]. Siebert [44] has also described some μ-hydroperoxo- and μ-peroxocarbonato complexes of cobalt(III) with cyanide ligands.

4.2.2 Complexes with oxygen-nitrogen donor ligands

The preparations of cobalt(III) complexes of a series of tripeptides have been reported [45], in which the peptides are coordinated as quadridentate chelates *via* the terminal NH_2, two peptide N^- and terminal CO_2^- groups. The ^1H and ^{13}C NMR spectra for the free peptides in the anionic, zwitterionic, and cationic forms, and for the cobalt(III) complexes, have been determined.

The new $Co^{III}N_3O_3$ complex, $[Co(plasp)(L\text{-}Phe)].3H_2O$, has been synthesised by oxidation of Co(II) to Co(III) in the presence of *N*-(2-pyridylmethyl)-L-aspartic acid (plaspH_2 = (5)) and L-phe [46]. X-ray analysis has established that, of the



(5)

four possible geometrical isomers, the only isomer isolated was a *fac*-isomer in which the β-CO_2^- and the pyridine groups of plasp are mutually *trans*. Mixed-ligand cobalt(III) complexes [Co(L-pyala)A] (where A = L-his, L- or D-asp, or imda; L-pyala = L-$H_2NCH(CH_2C_5H_4N)CO_2$) have been prepared and structures assigned to the isolated isomers on the basis of their visible and CD spectra [47].

The *cis*-dinitrobis(sarcosinato)cobaltate(III) ion, *cis*-$[Co(NO_2)_2(sar)_2]^-$, has been prepared and its stereochemistry studied [48]. The quadridentate ligand (2S,2'S)-1,2'-(ethane-1,2-diyl)bis(pyrrolidine-2-carboxylic acid) dihydrochloride (prenH_2.2HCl) has been derived from S-pro [49]. The cobalt(III) complexes $Na[Co(pren)(CO_3)].3H_2O$, $[Co(pren)(H_2O)_2][ClO_4].2H_2O$ and $[Co(pren)(H_2O)Cl]1.5H_2O$, appear to exist as the *cis*-α isomers on the basis of their ^{13}C NMR and visible spectra.

A number of cobalt(III) complexes of ethylnitrosolate, $[R\text{-}C(NO){=}NO]^-$, have been prepared [50] and the stereochemistry of Λ-*uns*-(2S,2Sp)-1,1'-trimethylenedipyrrolidine-2,2'-di-carboxylatocobalt(III) complexes with *N*-alkyl substituted amino or cyclic imino acids studied [51]. Cobalt(III) complexes of *N*,*N'*,*N''*-triethanoate type ligands, with H_2O or NO_2^- in the sixth coordination site, have been investigated by ^{13}C NMR spectroscopy [52]. Pressure effects on the base hydrolysis rates of α-, β-$[Co(edda)(NH_3)_2]^+$ and α-$[Co(edda)(NO_2)_2]^-$ give $\Delta V^{\ddagger}$ = 16.6, 22.3 and 11.9 cm^3 mol^{-1}, respectively [53]. The electrochemistry of a series of perfluoroalkyl (R_F) and alkyl (R_H) cobalt(III) complexes of the type $[CoR(sal_2en)]$ shows the reduction steps [54]:

$$[Co^{III}R(sal_2en)] \xrightarrow{e^-} [Co^{II}R(sal_2en)]^- \xrightarrow{e^-} [Co^{I}R(sal_2en)]^{2-}$$

The $[CoR_F(sal_2en)]$ species are more stable than the R_H complexes; $[CoR(sal_2en)]$ decomposes very rapidly to $[Co(sal_2en)]^-$.

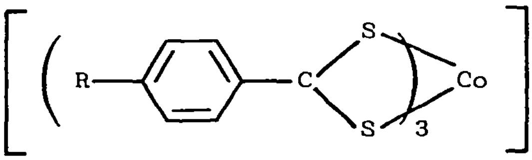
X-ray studies of twelve cobalt(III) complexes have shown that the Co-NO_2 bond is shorter by an average of 0.05 Å, when *trans* to carboxylato oxygen than when *trans* to a nitrogen ligand [55]. The use of cobalt-nitro complexes as oxygen transfer agents has been studied. Oxygen transfer from the nitro ligand to an organic substrate is accompanied by the formation of the corresponding metal nitrosyl and a novel model of catalytic olefin oxidation by dioxygen obtained. In the presence of nucleophiles, the cobalt-nitro complexes play a similar rôle to copper(II) in the classical Wacker process [56].

Other investigations have dealt with the preparation of the optically active *mer*-isomers of bis(methyliminodiethanoate)cobaltate(III) and (methyliminodi-thanoato ethanoato)cobaltate(III) and (methyliminodiethanoato)(dien)cobalt(III) [57], the photolysis of $[Co(edda)(en)]^+$ [58], the preparation of solid complexes of the new complexone, *rac*-ethylenediamine-*N*,*N'*-disuccinic acid with cobalt(III) [59], kinetic studies of the aquation of *cis*-α-$[CoCl(edda)(H_2O)]$ in mixed solvents [60], the pK_a value and volume change for neutralisation of $[Co(edda)(NH_2CH_2CH_2OH)]^+$ [61], kinetics and mechanism of the reduction of $[Co(edta)]^-$ by hydrazine and hydroxylamine in acid solution [62], and stereochemical studies of cobalt(III) complexes of edta and its related ligands [63].

The crystal structure of *trans*-amine-$[Co(his)_2][ClO_4]_2.2H_2O$ has been published [64]. A number of other studies concerned with amino-acid derivatives have appeared, including the structure and absolute configuration of *trans*-(O)-*N*,*N'*-ethylenebis(S-methyl-L-cysteinato)cobalt(III) [65], the deuteration of α-hydrogen atoms in cobalt(III) complexes of α-amino carboxylates [66], the photolysis of cobalt(III) complexes of ethylenediaminetetrapropanoate containing a six-membered chelate ring [67] and the preparation of methioninatobis(biguanide)cobalt(III) [68].

4.2.3 Complexes with sulphur donor ligands

The tridentate *NSO* Schiff base, 1-salicyl-4-benzyl-amidothiosemicarbazone (sbtsH), forms octahedral complexes of composition $[Co(sbts)_2]^+$ and the bidentate *NS* Schiff base, 1-phenyl-4-benzylamidothiosemicarbazone (pbts), forms $[Co(pbts)(H_2O)_2]^{3+}$ [69]. Cobalt(III) complexes $[Co(RHNCS_2)_3]$ (where R = Ph, $4\text{-}MeC_6H_4$, $4\text{-}OMeC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, $4\text{-}IC_6H_4$ or $2,4\text{-}Me_2C_6H_3$) have been prepared by reaction of the requisite ammonium dithiocarbamate salts with $[Co(H_2O)_6]^{2+}$ [70]. Cobalt(III) complexes of substituted dithiobenzoates (6;

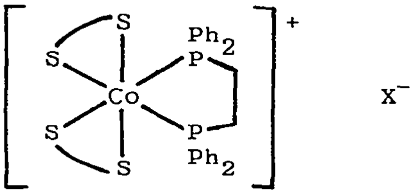


(6)

R = H, Me, OMe, Me_2N, or Et_2N) have been studied electrochemically; two reduction steps occur at a Pt electrode in CH_2Cl_2 solvent [71].

Cobalt(III) complexes of the new difluoro monothio-β-diketones, $RC(S)CH_2C(O)CHF_2$ (R = 2-thienyl, phenyl or 4-tolyl), have been prepared and their mass spectra and dipole moments measured [72]. Protonation of the coordinated thiolato sulphur atom of the complex $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$ has been observed in 4-8 *M* H[ClO$_4$]: the coordinated sulphur retains considerable Lewis basicity, and therefore nucleophilicity [73]. Protonation of the coordinated sulphur atom in $[Co(en)_2\{SCH_2CH(CO_2H)NH_2\}]^{2+}$ in 70% $HClO_4$ has been previously observed [74]. The kinetics of the reaction of H_2O_2 with the thiolato complexes, $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$, $[Co(en)_2(SCH_2CO_2)]^{+}$, $[Co(en)_2\{SC(CH_3)_2CO_2\}]^{+}$, or $[Co(en)_2\{SCH(CH_3)CO_2\}]^{+}$ in aqueous media have been studied; all of the cobalt(III) complexes undergo two-equivalent oxidation to isolable *S*-bonded sulphenic acid complexes [75]. The thermal racemisation in solution of some optically active tris(*N*-substituted carbamodithioato)cobalt(III) complexes has been investigated polarimetrically, for a variety of solvents (dmf,MeCN,CCl_4,C_6H_5Cl,$CHCl_3$,MeC_6H_5, or EtOH) and activation parameters for the metal-centred ($\Delta \rightleftharpoons \Lambda$) inversion obtained [76].

No mixed donor system of the type $[Co^{III}S_4E_2]$ appears to have been previously characterised. However, the bis(diethyldithiocarbamato)(1,2-bis(diphenylphosphino)ethane)cobalt(III) cation (7) has now been synthesised and characterised



(7; X = Cl or BPh_4)

as its chloride and tetraphenylborate salts [77]. The pressure-dependence of the racemisation of $[Co(pydtc)_3]$ (pydtc = pyrrolidinecarbodithioate) suggests a twist mechanism involving a low spin   high spin pre-equilibrium [78]. The tris-complex of cobalt(III) with *N*,*N'*-diethyldithiophosphate has been studied by UVPES [79]. Ligand exchange reactions of some diethyldithiocarbamato complexes of cobalt(III) in dioxane and dmf has been studied using isotope labelling techniques [80], and some new tris(dithioethanoato) complexes of cobalt(III) prepared [81]. The oxidative synthesis, optical resolution and characterisation of mixed sulphenato and sulphinato cobalt(III) complexes has been described [82], and the reactions and stereochemistry of thiolato- and sulphenatocobalt(III) complexes have been discussed in a recent thesis [83].

4.2.4 Complexes with nitrogen donor ligands

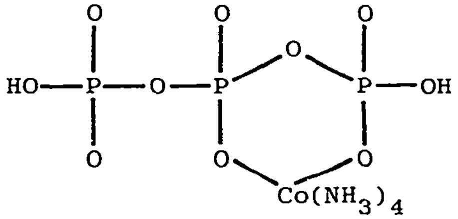
4.2.4.1 Ammines

The interesting mixed-metal complex $[\{Co(NH_3)_5(NCS)\}_2Hg][ClO_4]_6.H_2O$ has been prepared [84]: the Hg(II) ion plays an important rôle in the catalysed aquation of transition metal complexes of the type $[ML_5X]^{2+}$ (where M = Co,Rh,Cr or Ru; X = halide or *pseudo*-halide) and the reaction is generally accepted to involve the bridged intermediate $[L_5M\text{-}X\text{-}Hg]^{4+}$.

Dissolved sulphur dioxide reacts almost instantaneously with aqueous $[Co(NH_3)_5(OH)]^{2+}$ to give the oxygen-bonded sulphito complex $[Co(NH_3)_5(OSO_2)]^+$, which rapidly loses SO_2 when acidified. However, at higher pH values, a relatively slow intramolecular redox decomposition can be observed which produces $[Co(H_2O)_6]^{2+}$ and $[SO_4]^{2-}$ in a 2:1 ratio and kinetic studies of these reactions have been carried out [85]. The kinetics of anation of $[Co(NH_3)_5(OH_2)]^{3+}$ by succinic acid or succinate (mono- or dianion) have been studied in detail [86]. The pK_a values of $[Co(NH_3)_5\{NH_2(CH_2)_nNH_3\}]^{4+}$ (n = 2-8 or 10) have been determined at 25 °C and I = 0.1 *M* (NaCl) [87]. Intramolecular hydrogen-bonding leads to significant effects in the UV region of the spectrum.

The nitrito ions $[M(NH_3)_5(ONO)]^{2+}$ {M = Co(III), Rh(III) or Ir(III)} rearrange to their nitro isomers $[M(NH_3)_5(NO_2)]^{2+}$ in basic solution with $k_{obs} = k_s + k_{OH}[OH^-]$, [88]. For the cobalt complex, the pressure dependence of k_{OH} ($\Delta V^{\ddagger} = +27\ cm^3\ mol^{-1}$) suggests a conjugate base pre-equilibrium for the base-catalysed pathway. This paper also includes a discussion on *cis*- and *trans*-$[Co(en)_2(ONO)_2]^+$ and $[Co(en)_2(ONO)(NO_2)]^+$. The rate of linkage isomerisation of $[Co(NH_3)_5(ONO)]^{2+}$ to the nitro-isomer in poly(vinyl alcohol) has also been studied [89].

There is growing interest in the effect of cobalt(III) complexes on the rate of hydrolysis of phosphate esters and polyphosphates. The rate of hydrolysis of bidentate triphosphate in $[Co(NH_3)_4H_nP_3O_{10}]^{x+}$ (derived from (8)) proceeds at two-thirds the rate of the free ligand [90] and further studies of this reaction have appeared [91]. The interaction of four nucleotides with $[Co(NH_3)_5(OH_2)]^{3+}$ has been studied [92] and, in each case, there is no measurable perturbation of



(8)

the base or phosphate vibrations and only an outer sphere complex appears to be formed.

Studies of the photochemical reduction of some carboxylatopentamminecobalt(III) complexes, $[Co(NH_3)_5O_2CR]^{2+}$, by $\{[Ru(bipy)_3]^{2+}\}^*$ have provided evidence for cage recombination reactions [93]. Spectroscopic investigations of the $^1T_{1g}$, $^3T_{1g}$ and $^5T_{2g}$ excited states of $[Co(NH_3)_6]^{3+}$ have been published [94].

A considerable number of kinetic studies on ammine systems have been reported and a selection of these are briefly noted below. The solvent-exchange rate between $[Co(NH_3)_5(Me_2SO)]^{3+}$ and Me_2SO solvent, in the presence of 4-toluenesulphonic acid is 6.33×10^{-5} s^{-1} at 45.3 °C and $I = 1.0$ *M*, and the bromide anation of the complex has also been investigated [95]. Nitrate ion competition and rates of nitrosation of $[Co(NH_3)_5(N_3)]^{2+}$ have been determined over a range of nitrate ion concentrations at 25 °C and $I = 1.0$ *M*, in an attempt to obtain evidence for pentacoordinate intermediates [96]. The activation volume ($\Delta V^{\ddagger}$) for aquation of $[Co(NH_3)_5(urea)]^{3+}$ is $+1.3$ cm^3 mol^{-1} [97]. One conclusion of this latter study is that the activation volume alone may be a less useful mechanistic probe for aquation studies of charged leaving groups than for neutral leaving groups. A survey of the products of the reactions of (*O*-bonded aminopolycarboxylato)pentaamminecobalt(III) complexes, $[Co(NH_3)_5(H_nY)]^{(n+1)+}$ with $[Cr(H_2O)_6]^{3+}$ (Y = imda or edda) has been carried out [98] and kinetic and mechanistic data have been reported. In the case of reduction of $[Co(NH_3)_5Cl]^{2+}$ by iron(II) in dmf solution, values of K (the equilibrium constant for the formation of the bridged intermediate) and k (the rate constant for electron transfer) have been determined as a function of temperature [99]. These results have been interpreted in terms of a bridged intermediate, in which the iron is tetrahedrally coordinated. A detailed analysis of the kinetics of the oxidation of $[Cr(bipy)_3]^{2+}$ by $[Co(NH_3)_6]^{3+}$ in ethanoate buffers has been published [100]. Rate constants have been reported for the Hg(II) catalysed aquation of $[Co(NH_3)_5Cl]^{2+}$ or *trans*-$[Co(en)_2Cl_2]^+$ in binary aqueous solvent mixtures. The observed reactivities have been discussed and, where possible, analysed into initial- and transition state components from estimated single-ion Gibbs free energies of transfer [101]. Aquation of $[Co(NH_3)_5X]^{2+}$ (X = Cl or Br) in aqueous and ethanol-water solutions containing $[SO_4]^{2-}$ and dicarboxylates has been examined [102]. Solvolysis of *trans*-$[Co(py)_4Cl_2]^+$ in water and water-methanol has also been studied kinetically [103]. The photochemistry of complexes of the type $[Co(CN)_5L]^{n+}$ (where L = a pyridine or a pyrazine derivative) has also been studied in detail [104]. Photolysis of carboxylatopentamminecobalt(III) complexes has been reported to give alkylpentammine complexes [105].

A discussion on the purity of μ-carbonatobis{pentaamminecobalt(III)} sulphate tetrahydrate, as obtained by a new synthetic route, has appeared [106], and the crystal structure of μ-amido-hexaammine-di-μ-hydroxo-dicobalt(III) bromide has been established [107]. Formation of the carbamato ligand in aqueous solution on a cobalt(III) centre has been observed and the crystal structure of $[Co(O_2CNH_2)(NH_3)_5][NO_3]_2$ determined [108].

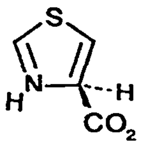
The residual paramagnetism of cobalt in nitroamminecobalt(III) complexes has been studied [109], and the visible and NMR spectra of azidoamminecobalt(III) complexes investigated [110]. A thesis dealing with studies of substitution reactions of $[Co(NH_3)_5(dmso)]^{3+}$ has been published [111] and the effects of ion-pairing on the solvolytic aquation of $[Co(NH_3)_5Cl]^{2+}$ in the presence of oxalate anion studied [112].

4.2.4.2 Diamines

The aromatic thiolato complex, $[Co(en)_2(SC_6H_4NH_2)]^{2+}$, has been synthesised by reduction of the disulphide $[2\text{-}C_6H_4(NH_2)S\text{-}]_2$ with a 1,2-diaminoethane-cobalt(II) mixture in H_2O-thf solution [113]. The complex undergoes the same oxidation, alkylation and adduct formation reactions as $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$. The thiooxalate complex, $[Co(en)_2\{SC(O)COO\}]_2[S_2O_6].2H_2O$ has been prepared, both by oxidation of $[Co(en)_2(SCH_2CO_2)]^+$ and by reaction of monothiooxalate with *trans*-$[Co(en)_2Cl_2]^+$. The crystal structure of this complex has also been determined; the sulphur-induced *trans* influence is smaller for the thiooxalate complex than for $[Co(en)_2(SCH_2CO_2)]^+$ (0.005(8) *vs*. 0.043(5) A) [114].

Oxidation of *cis*-$[Co(en)_2(S_2O_3)_2]^-$ with aqueous iodine gives free sulphate and *trans*-$[Co(en)_2(OH_2)(S_3O_3)]^+$ containing the very reactive ligand disulphane monosulphonate [115]. The ability of sulphinic acids, RSO_2H, to coordinate to main group and to transition metal ions is well established [116,117]. All reported cobalt(III) complexes containing sulphito, sulphinato or sulphenato ligands display only Co-S bonding, although the transient in the reaction of $[Co(NH_3)_5(OH)]$ with SO_2 is assigned as $[Co(NH_3)_5(OSO_2)]^{2+}$ [85]. Adamson and coworkers have now reported [118] the photochemical preparation of the *O*-sulphinato complex $[Co(en)_2(OS(O)CH_2CH_2NH_2)][ClO_4]_2$. The new complex *trans*-$[Co(en)_2(OH_2)(S_2O_3)]^+$ has been prepared by stoicheiometric oxidation of *trans*-$[Co(en)_2(S_2O_3)_2]^-$ with $[I_3]^-$ [119]; the *trans* effect of the *S*-bonded thiosulphate ligand has been studied by anation of the complex with $[SCN]^-$ or $[NO_2]^-$. The crystal structure of $Na[Co(en)_2(SO_3)_2].3H_2O$, which has *trans*-stereochemistry, has been determined [120]. The cobalt-sulphur bond length is 2.267 Å, the longest Co-S distance so far reported in a cobalt(III)-sulphite complex. The crystal structure of the monothiooxalate complex, $[Co(en)_2\{SC(O)COO\}]Cl.H_2O$, has also been reported [121]. This complex was obtained as the only tractable product from the reaction of an excess of ethanoic anhydride in dmso with $[Co(en)_2(SCH_2CO_2)]^+$. A similar preparation of this complex ion has been reported by Deutsch and coworkers [114].

The *N,O* mode of bonding of thiazolidine-4-carboxylate (9) and the crystal



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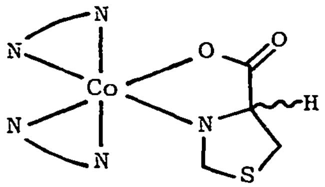
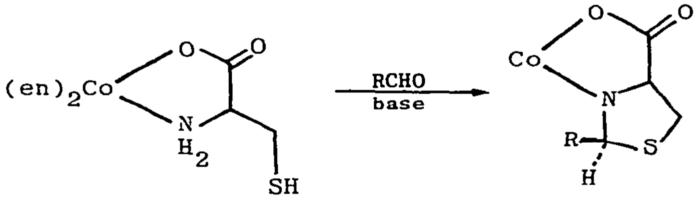


(10)

structure of its cobalt(III) complex (10) have been determined by X-ray crystallography [122]. Ring closure reactions of the type (11) → (12) can be used to



(11) (12)

synthesise chiral thiazolidines, which are intermediates for the synthesis of penicillins.

The crystal structure of *trans*-[Co(en)$_2$(NH$_3$)(SO$_3$)][ClO$_4$] has been determined [123], although the Co–S bond is "normal" at 2.227(2) Å, the Co–N bond is remarkably long, due presumably to a structural *trans*-influence. The crystal structure of [Co(en)(LL)$_2$][Co(CN)$_6$].2H$_2$O {LL = 2-(aminomethyl)pyridine} has been published [124]. A variety of stereochemical studies have been published dealing with 1,2-diaminoethane complexes. These include, the measurement of the CD spectra of *trans*-[Co(LL)$_2$Cl$_2$]$^+$, *trans*-[Co(LL)$_2$Br$_2$]$^+$, [Co(LL)(NH$_3$)$_4$]$^{3+}$, and [Co(LL)(CN)$_4$]$^-$ (where LL = 1-phenyl-1,2-diaminoethane) [125], the induced CD spectra of *racemic-cis*-bis(1,2-diaminoethane)cobalt(III) complexes in aqueous (R,R)-tartrate and (R,R)-tartratoantimonate(III) solutions and their optical resolution by ion exchange chromatography [126], the crystal structure of (−)$_{589}$-[Co(en)$_2$(ox)][H-*d*-tart].2H$_2$O [127] and NMR studies of the stereoselective association between [Co(en)$_2$(acac)]$^{2+}$ and malonate [128]. CD spectra have been determined for diastereoisomers of tris(*trans*-1,2-diaminocyclopentane)cobalt(III), [Co(cptn)$_3$]. The (lel$_3$), (lel$_2$ob) and (lelob$_2$) isomers [129a] of [Co(*rac*-cptn)$_3$]$^{3+}$ were obtained by reaction of *trans*-[Co(py)$_4$Cl$_2$]$^+$ with *rac*-cptn [129b]. Two papers have appeared dealing with CD spectra and stereochemistry of tetranuclear cobalt(III) complexes of the hexol type, including the $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ ion [130] and similar complexes involving *meso*-2,3-diaminobutane, (R)-1,2-pn and (R,R)-1,2-diaminocyclohexane [131]. Stereochemical studies on diastereo-2,3-diaminobutane isomers of the tris(2,3-diaminobutane)cobalt(III) cation have also appeared [132].

The results of a variety of investigations have been published dealing with the glycinato ligand in en-cobalt(III) complexes. These include ^1H and ^{13}C NMR chemical shifts in complexes of the type $[Co(en)_x(ox)_y(gly)_2]^{n+}$ [133], the kinetics of deuteration of α-hydrogen atoms in a variety of cobalt(III) complexes containing α-amino carboxylates [134], oxygen exchange and glycinato ring opening in $[Co(en)_2(gly)]$ [135] and the crystal structures of two diastereoisomeric salts, (+)-*trans*(*O*)-$[Co(gly)_2en][H$-*d*-tart$].3H_2O$ and (−)-*trans*(*O*)-$[Co(gly)_2en][H$-*d*-tart$].H_2O$ [136].

The crystal structure and kinetic investigations of the Hg(II) promoted aquation of $(-)_{589}$-Δ(S)-*cis*-$[Co(en)_2\{NH_2CH_2CH(OH)CH_3\}Cl][ZnCl_4]$, where 1-amino-propane-2-ol is *N*-bonded have been reported [137]. Base hydrolysis of $[Co(en)_2(ox)]^+$ has been shown to occur in two stages, the first being dechelation and the second loss of oxalate [138]. The preparation, acid-catalysed aquation and base hydrolysis of *trans*-$[Co(en)_2Cl(OCO_2)]^+$, containing monodentate carbonate [139], and studies of the rate of decarboxylation of *cis*-$[Co(py)_2(CO_3)_2]$ [140] have been described. There has been an interesting investigation of the kinetics of complexing of *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ with $[WO_4]^{2-}$ in the pH range 8.0-9.0 [141]. Base hydrolysis of $(+)_{589}$-*cis*-$[Co(en)_2X(gly)]^+$ has been studied in detail and ion pairing effects considered [142]. The preparation of $(+)_{589}$-$[Co(en)_2(NH_3)(Me_2SO)][ClO_4]_2[NO_3]$ and $(+)_{589}$-$[Co(en)_2(NH_3)(tmp)][ClO_4]_3$ has been described, in conjunction with kinetic and stereochemical studies of base hydrolysis [143]. The kinetics of anation of *cis*-$[Co(en)_2(NH_3)(OH_2)]^{3+}$ by oxalate [144] and the kinetics of substitution of a chloride ligand in *trans*-$[Co(en)_2Cl_2]^+$ by organic bases (piperidine, Et_2NH_2, cyclohexylamine, butylamine or benzylamine) in methanol and dmf have been reported [145]. Other kinetic investigations include a polarographic study of the kinetics of the aquation of $[CoX(NH_3)_5]^{2+}$ and *trans*-$[CoX_2L_4]^+$ complexes $\{X = Cl$ or Br; $L_4 = (NH_3)_4$, $(en)_2$, $(1,3\text{-pn})_2$ or $(1,2\text{-diaminocyclohexane})_2\}$ [146], a determination of $\Delta V^{\ddagger}$ for the isomerisation of *trans*-$[Co(en)_2(O_2CMe)(OH_2)]^{2+}$ in aqueous acid, where $\Delta V^{\ddagger} = +6.5$ cm^3 mol^{-1} in 0.05 *M* $H[ClO_4]$ consistent with a dissociative aqua ligand release in an I_d mechanism [147], and the kinetics of aquation and base hydrolysis of *cis*-$[Co(en)_2(imidH)(O_2CC_6H_4\text{-}2\text{-}OH]^{2+}$ [148]. The labilising effect of coordinated imidazolate anion is 10^3 times that of imidazole in base hydrolysis.

Complex formation between $[CoL_4(OH_2)_2]^{3+}$ complexes ($L_4 = (en)_2$, $(1,3\text{-pn})_2$ or trien) and pyrophosphate and its influence on the hydrolysis of pyrophosphate to orthophosphate have been studied by ^{31}P NMR spectroscopy over the pH range

0-12 [149]. The reactive species, with regard to hydrolysis, appears to be a 3:1 L Co^{III}-pyrophosphate complex. Rate enhancements of ~10^5 for pyrophosphate hydrolysis were observed in some of these reactions (see also Section 4.2.4.1). A spectroscopic study of the bis(1,2-diaminoethane)diphosphatocobaltate(III) anion has been published [150], where diphosphate acts as a bidentate ligand.

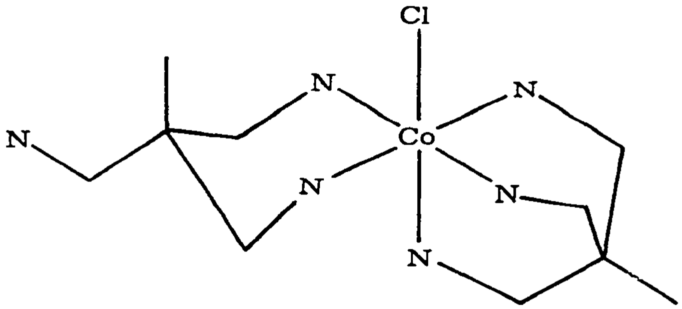
The kinetics of oxidation of *cis*-$[Co(en)_2(NCS)(NO_2)]^+$ by peroxodisulphate have been studied [151]. The preparation of a series of *trans*-$[Co(en)_2Cl(O_2CR)]^+$ (R = H, Et or CMe_3) complexes have been described and the kinetics of their base hydrolysis studied [152]. These workers have also described the preparation of isomeric pairs of $[Co(en)_2Cl(\text{amino acid})]^{n+}$ complexes containing the *trans*-carboxylato bonded and the *cis*-amino bonded amino acids [153]. The kinetics of anation of *cis*-$[Co(en)_2(NH_3)(OH_2)]^{3+}$ by salicylate has been studied [154] and the kinetics of the iron(II) reduction of *cis*-$[Co(en)_2Cl_2]^+$ in dmso investigated over a temperature range [155]. The crystal structures of $[Co(en)_3]I_3.H_2O$ [156] and $[(+)Co(en)_3][(-)Cr(en)_3][SCN]_6$ [157] have been determined, and structural relationships for tris(1,2-diaminoethane)-metal(III) complexes considered [158]. A thesis describing the kinetics and mechanism of the formation and decomposition of *cis* and *trans*-$[Co(en)_2(NH_3)(OCOO)]^+$ complexes has been published [159].

4.2.4.3 2,2'-Bipyridine and 1,10-phenanthroline complexes

The preparation and characterisation of some new cobalt(III) complexes of bipy and phen have been described [160] and the crystal structure of $[Co(phen)_2(CO_3)]Cl.3H_2O$ has been determined [161]. Mixed complexes of cobalt(III) with glycine and bipy or phen have been prepared [162]. A study of the outer-sphere complexes of $[Co(bipy)_3]^{3+}$ with $[SO_4]^{2-}$ has been published [163], and the absolute configuration of $(-)_{589}$-$[Co(bipy)_3]^{3+}$ determined [164]. The preparation, thermochemistry and photochemical behaviour of $[Co(bipy)_2(ox)]^+$ has been studied [165] and the crystal structure of $[Co(phen)_2(CO_3)]Br.4H_2O$ determined [166]. Nucleophilic addition of α-hydroxyalkyl radicals to polypyridine complexes of cobalt(III) in aqueous solution has been studied [167].

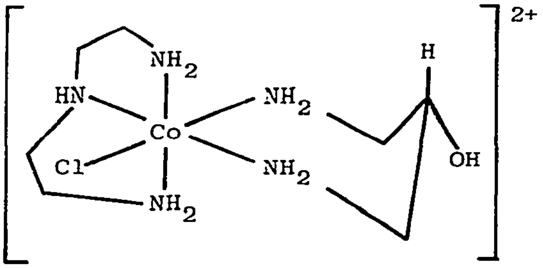
4.2.4.4 Triamines

The preparation of the interesting complexes, $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})X]^{n+}$ {X = Cl^-, Br^-, OH^-, H_2O, $[SO_4]^{2-}$ or SCN^-; tame = 1,1,1-tris(aminomethyl)ethane} have been described [168] and the crystal structure of $[Co(\eta^2\text{-Htame})(\eta^3\text{-tame})Cl]Cl_3.2H_2O$, (13), determined. Base hydrolysis of the chloro-complex gives the hydroxo complex in a clean reaction, without any formation of a hexamine species. A variety of other complexes with pendant amino functions are known, including $[CoCl(\eta^2\text{-en})_2(\eta^1\text{-Hen})]Cl_3.H_2O$ [169,170] and $[CoCl(\eta^2\text{-en})_2(\eta^1\text{-Hpn})]Cl_3$ [171]. The 1,2-diaminoethane complex also undergoes base hydrolysis without any formation of a hexamine species [170]. Base hydrolysis of optically active



(13)

mer-chloro(dien)(1,3-diaminopropan-2-ol-*N*,*N'*)cobalt(III) (14) occurs with full



(14)

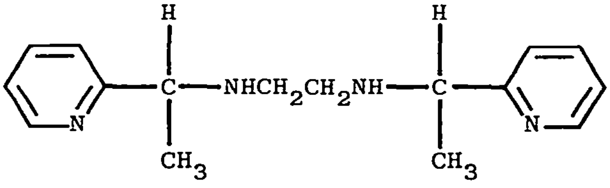
racemisation and with retention of the *mer*-configuration of the dien ligand. The optically active hydroxo complex, prepared independently with retention of configuration, racemises ~10^4 times more slowly. This unique result can be rationalised in terms of classical π-stabilisation in the conjugate base [172].

A variety of *unsym-fac-cis*-$[CoCl(dien)L_2]^{2+}$ (L = NH_3, $MeNH_2$, $EtNH_2$, $PrNH_2$, $BuNH_2$, pentylamine, hexylamine, benzylamine, py, 4-propylpyridine, 3-ethyl-4-methyl-pyridine or 3,5-dimethylpyridine) complexes have been prepared and the kinetics of aquation, mercury(II) assisted aquation and base hydrolysis studied [173].

The crystal structure of $(+)_{589}$-*mer*-$[Co(dien)_2]Br_3.1.6H_2O$ has been determined [174] and the synthesis of cyclohexanetriaminecobalt(III) complexes described [175].

4.2.4.5 Tetramines

Solid *cis*-α-[Co(trien)Cl$_2$]Cl, on heating to 160 °C, is slowly converted to the β-isomer and this rearrangement has been interpreted as evidence for a trigonal twist mechanism [176]. The optically active ligands (2S,7S)-2,7-di(2-pyridyl)-3,6-diazaoctane (15) and (2R,8R)-2,8-di(2-pyridyl)-3,7-diazanonane (16)



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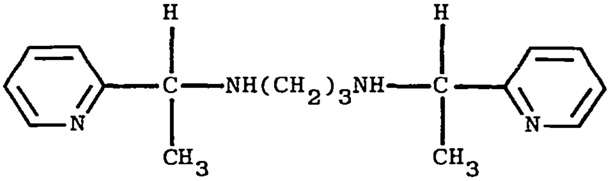
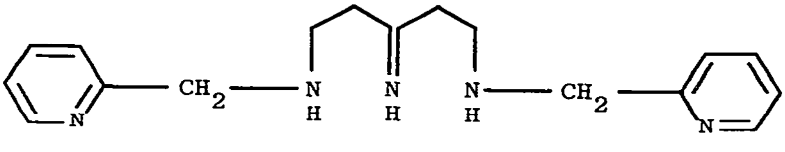


(16)

have been prepared [177]. The [CoLCl$_2$] complexes of these ligands have been synthesised; (15) gives one *cis*-α and two *cis*-β isomers, while (16) gives only one *cis*-β-isomer.

The preparation and structural assignments of *N*-methyl-(S)- and -(R)-alaninato-cobalt(III) complexes with chiral derivatives of 2,3,2-tet and trien have been described [178] and epimerisation of the complexes at pH 10 studied. The crystal structure of [Co(picditn)Cl][CoCl$_4$].0.5H$_2$O (picditn = 1,11-bis(2-pyridyl)-2,6,10-triazundecane) (17) has been determined [179]. The pentadentate ligand



(17)

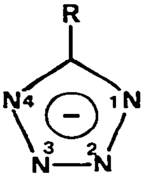
has the α,β configuration, with the chloride ligand *trans* to an angular secondary nitrogen and the chiral NH groups at N(2) and N(10) are R and S, respectively. Also the crystal structure of (+)$_{589}$-β$_2$-[Co(R-ala)-(S,S-pyht)][ClO$_4$]$_2$.2H$_2$O (pyht =

1,7-bis{2(S)-pyrrolidyl}-2,6-diazaheptane) has been determined [180]. Utsuno and coworkers [181] have isolated the entire set of the three possible isomers of *trans*-$[Co(trien)(NH_3)_2]^{3+}$. When solutions of *cis*-α and *cis*-β-$[Co(trien)(CO_3)]^+$ and *cis*-α and *cis*-β-$[Co(trien)(NO_2)_2]^+$ are heated in 3 *M* *d*-tartaric acid for two hours, intense CD spectra develop in the visible region [182]. The hydroxide ion catalysed epimerisation of chelated amino-acidates in complexes Λ-β_2-$[Co(N_4)(S\text{- or }R\text{-ala})]^{2+}$ (N_4 = tetramine ligand) is an example of a "first-order asymmetric transformation" of α-amino acids promoted by chiral cobalt(III) complexes [183]. A series of new cobalt(III) complexes $[Co(trien)(LL)]X_n$ (LL = tropolone, acetoacetanilide, ethylacetoacetate, biguanide, 2-guanidinobenzimidazole, pn, picolylamine, bipy, 3-aminopyridine, picolinic acid or quinaldinic acid; X = Cl or Br) have been prepared and characterised [184].

The acid catalysed decarboxylation of Δ-$(+)_{436}$-β_1-[{(2S,9S)-2,9-diamino-4,7-diazadecane}{S-aminomethylmalonate}cobalt(III)]$[ClO_4].H_2O$ and Λ-$(-)_{436}$-β_2-[Co(trien)(R-aminomethylmalonate)]$[ClO_4]$ each lead to unequal amounts of R- and S-alanine products [185]. The excess of S-ala over R-ala is effected by steric considerations. The acid catalysed decarboxylation of *cis*-α- and *cis*-β-$[CoL(CO_3)]^+$ (L = 3,6-dimethyl-1,8-diamino-3,6-diazaoctane) follows a rate expression $k_{obs} = k_0 + k_1[H^+]$ [186]. Activation parameters and solvent deuterium isotope effects are consistent with an A-1 type of mechanism with a rapid pre-equilibrium protonation of the substrate and formation of a five-coordinate intermediate. The rates of hydrolysis of eleven dipeptides by *cis*-β-$[Co(trien)(OH)(OH_2)]^{2+}$ have been studied by amino-acid release [187]. The complexes $[Co(eee)(OH)(OH_2)]^{3+}$ (eee = 1,8-diamino-3,6-dithiaoctane) and the (aqua)(hydroxo){1,6-bis(2-pyridyl)-2,5-diazahexane}cobalt(III) cation did not hydrolyse glygly at 65 °C and pH 8 to any significant extent. The effect of the inert tetradentate ligand on the ability of hydroxoaquacomplexes of cobalt(III) to hydrolyse peptides requires detailed examination. The kinetics of the base hydrolysis of some *t*-$[Co(tren)(NH_3)X]^{n+}$ ions (n = 2, X = NO_3, $MeSO_3$, Cl or N_3; n = 1, X = Me_2SO) have been studied [188] (*n.b.* the stereochemical designation for the $[Co(tren)(NH_3)X]^{n+}$ ions arises from the position of X relative to the tren ligand; either *trans* to a primary nitrogen donor (*p*) or *trans* to the tertiary nitrogen (*t*); IUPAC nomenclature designates the two positions as *b* and *f* respectively) and the results interpreted in terms of important contributions from pre-formed ion pairs. A conformational study of an isomer of $[Co(trien)Cl(py)][ClO_4]Cl$ has been carried out [189]. The preparations of *cis*-α-$[Co(trien)Cl(imidazole)]^{2+}$ and *cis*-β-$[Co(trien)Cl(imidazole)]^{2+}$ have been described and the kinetics of aquation, Hg(II)-catalysed aquation and base hydrolysis have been studied; deprotonation of imidazole occurs in basic solution [190].

4.2.4.6 Oximes, Cobaloximes and Vitamin B_{12}

A number of studies have appeared concerning complexes containing the *trans*-bis(dimethylglyoximato)cobalt(III) unit and a recent paper has discussed the linkage isomeric ratios for thiocyanate (Co-*S*CN/Co-*N*CS) as a function of *trans* influence and solvent polarity [191]. A series of complexes of the type $[Co(dmg)_2(Bu_3P)$-(5R-tetrazolate)] (where R = CF_3, CH_3, C_6H_5, $C_6H_5CH_2$, $(CH_3)_2N$, 4-FC_6H_4, or 3-FC_6H_4) have been prepared and characterised and the ambidentate 5R-tetrazolate anion (18) is coordinated to cobalt *via* N(2), showing that regiospecific coordination is sterically induced [192]. The syntheses of several new mono- or dinuclear cobaloxime selenocyanate or thiocyanate complexes, containing phosphines, arsines or stibines, has been described [193]. Pyridinium ylide complexes of methylcobaloxime have been prepared by treatment of an ylide with $[MeCo(dmg)_2(SMe_2)]$ and the crystal structure of one such complex, $[MeCo(dmg)_2(C_5H_5NCHCOPh)].C_6H_6$, has been determined [194]. The crystal structure of *trans*-$[Co(dmg)_2(NH_3)_2]Br$, in which the Co-NH_3 bond length is 1.960(2) Å, shows no evidence of a *cis*-influence when compared with the structure of $[Co(NH_3)_6]Cl_3$ [195]. Other related crystal structures include *trans*-$[Co(dmg)_2Cl(Bu_3P)]$ [196], *trans*-$[Co(dmg)_2Cl$(dimethylphosphate)] [196] and the *N*-iminopyridine complex *trans*-$[CH_3Co(dmg)_2(HNNC_5H_5)]$ [197].



(18)

The base catalysed decomposition of $[EtCo(dmg)_2(OH_2)]$ at 50 °C gives a mixture of ethane and ethene, and no photolabile organocobalt complex is formed [198]. An ^{1}H NMR study of alkyl transfer reactions between cobalt and tin centres, in the system $[MeCo(dmg)_2(SMe_2)]$-$MeSnCl_3$, has been published [199]. Bis-dimethyglyoximato)cobalt(II) reacts with dihydrogen at room temperature, its reactivity being enchanced by added pyridine; it has now been observed [200] that $[Co(dmg)_2(OH)(py)]$ is autocatalytically reduced by dihydrogen in the presence of added cobaloxime(II). The ^{31}P NMR spectra of a large number of cobaloximes $[Co(dmg)_2(L)X]$ (where L is a phosphorus donor ligand) have been determined [201]. Polarographic studies of the neutral cobaloxime complexes $[Co(dmg)_2(L)X]$ (where L = py, NH_3, or aniline; X = I, Br, Cl, N_3, SCN or NO_2), in aqueous solution identified two waves corresponding to the redox processes Co(III) → Co(II) and Co(II) → Co(I). In all cases the first wave was found to be irreversible [202].

The rate of isotopic $[NO_2]^-$ exchange of *trans*-dinitrobis(2-amino-2-methyl-3-butanoneoximato)cobalt(III) with free $[NO_2]^-$ in aqueous solution, is first order in the complex and independent of $[NO_2]^-$ concentration over a range of pH [203]. Iron(III) undergoes a reversible association with $[MeCo(dmg)_2(OH_2)]$ or $[Co(dmg)_2(OH_2)_2]^+$, in each case it replaces the hydrogen-bonded proton in one O-H---O group of the parent cobaloxime [204]. The kinetics of the iron(II) reduction of *trans*-$[Co(dmg)_2(N_3)(py)]$ and *trans*-$[Co(dmg)_2(N_3)(NH_3)]$ show an inverse dependence on $[H^+]$, suggesting an inner-sphere mechanism involving protonated and deprotonated complexes [205].

The interaction of *cis*-$[Pt(NH_3)_2(OH_2)_2]^{2+}$ with adenosylcobalamin and alkylcobalamins has been studied by ^{13}C NMR spectroscopy. With these cobalamins, *cis*-$[Pt(NH_3)_2(OH_2)_2]^{2+}$ forms adducts in which N(3) of the 5,6-dimethylbenzimidazole moiety is coordinated to platinum(II), rather than to cobalt(III) of the corrin [206].

Vitamin B_{12r} reacts with certain organic halides (RX) according to the stoicheiometry [207]:

$$2B_{12r} + RX + H_2O \text{ (or MeOH)} \rightarrow B_{12a} + R\text{-}B_{12} + X^-$$

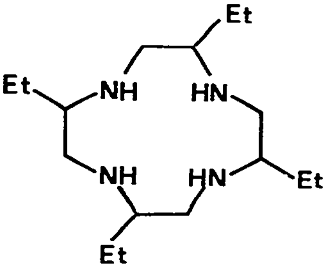
$$\text{(where } B_{12a} = [(H_2O)B_{12}]^+ \text{ or } [(MeOH)B_{12}]^+\text{)}$$

Two papers have appeared dealing with the electrochemistry of vitamin B_{12} [208, 209]. The cobalt complexes of 1,19-dimethyl-AD-didehydrocorrin (BDHC) and its tetradehydrospanalogue (TDHC), both having additional double bonds at peripheral positions and an additional angular methyl group compared with the parent correnoid, have been investigated from the viewpoint of B_{12} chemistry [210]. Evidence has been presented for a radical-like process in a model reaction for methylmolonyl-CoA mutase, a B_{12} dependent molecular rearrangement [211]. Model studies of diol dehydratase, an adenosylcobalamin-dependent rearrangement, have appeared [212] and cobalamin ligation and interaction with sodium dodecyl sulphate and bovine serum albumin have been studied by ^{31}P and ^{13}C NMR spectroscopy [213].

The deprotonation constants of some *trans*-acidopyridinebis(dmg)cobalt(III) complexes have been determined [214]. Bridged complexes involving $[\{MeCo(sal_2en)\}\{(NC)(Me)Co(dmg)_2\}]$ have been prepared and characterised as $[AsPh_4]$ and $[NEt_4]$ salts [215]. Monodimethylglyoximinato-bis(1,10-phenanthroline)cobalt(III) thiocyanate dihydrate has been prepared and its crystal structure determined [216]. The preparation of some mixed dimethylglyoxime complexes containing the sulphito ligand have also been described [217] and the X-ray structure of *trans*-$[Co(dmg)_2(vinyl)(py)]$ has been determined [218].

4.2.4.7 Macrocycles

Isomers of the bis(1,4,7-triazacyclodecane)cobalt(III) ion have been prepared and characterised by ^{13}C NMR spectroscopy [219]. This paper also discussed the occurrence of higher cyclic and non-cyclic amines in the Richman-Atkins synthesis of macrocyclic amines [220]. A cobalt(III) complex of (2R,5R,8R,11R)-tetraethyl-1,4,7,10-tetra-azacyclododecane (19; tecyclen) has been prepared [221] from the optically active ligand, and characterised as [CoBr(H_2O)(tecyclen)]Br_2, which presumably has a *cis*-configuration. A convenient preparation of the macrocyclic diamide (20; LH_2) has been described [222], the cobalt(III) complex



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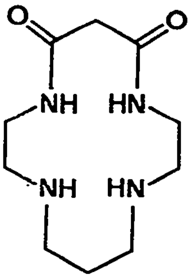

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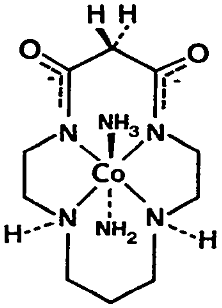

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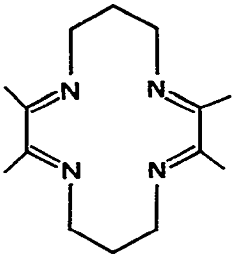

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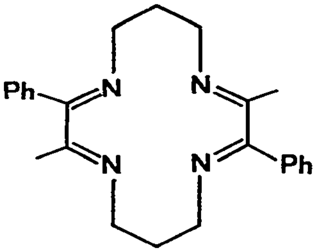
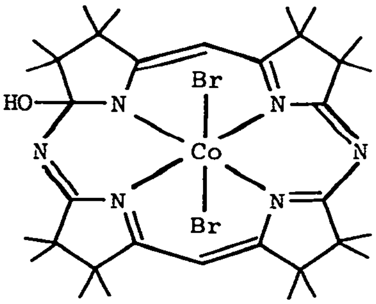


(23)

trans-[$CoL(NH_3)_2$]Cl has been characterised, and ^1H NMR spectroscopic measurements have established the N-*meso* stereochemistry (21) at the chiral nitrogen centres. Complexes of the macrocyclic ligand (22; tim) were originally prepared [223] *via* a template synthesis, in which 1,3-pn.HCl and biacetyl were allowed to react together, followed by addition of the metal(II) ethanoate. Cobalt(III) complexes of tim have been prepared by the corresponding procedure [224,225]. Eggleston and Jackels [226] have studied the macrocyclic complexes derived from 1,3-pn, 1-phenylpropane-1,2-dione and a metal(II) ethanoate (M = Fe, Co, or Ni). This synthesis is regiospecific, giving only complexes of *trans*-MePhtim (23) and X-ray data for [$Co(MePhtim)Cl_2$][PF_6] are also consistent with a centrosymmetric *trans*-isomer.

The synthesis of *trans*-[$CoBr_2(L)$] (24) (where L = 1-hydroxy-2,2,3,7,7,8,8,12,12,13,13,17,17,18,18-hexadecamethyl-10,20-diaza-octahydroporphine) has been described. The dicyano complex, *trans*-[$Co(CN)_2L$], has also been prepared and the annulene complex (25) obtained by elimination of the hydroxyl group of (24) [227]. The reduction of metal(III) corrole complexes {M = Co(III) or Fe(III)} to the metal(II) species (26) can be carried out with hydroxide ion



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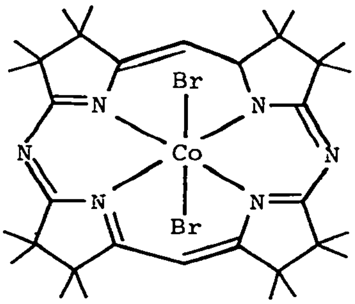

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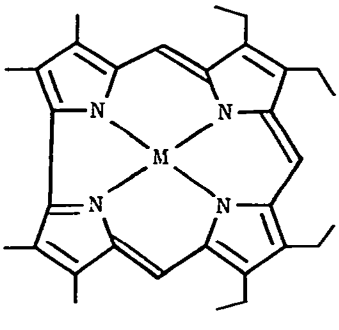

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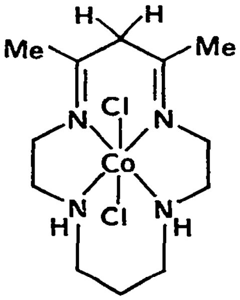
and an olefin [228]. The base-induced reduction of aqueous $[Co(Me_2[14]1,11\text{-diene}N_4)Cl_2]^+$ (27), in the absence of air, gives the cobalt(II)



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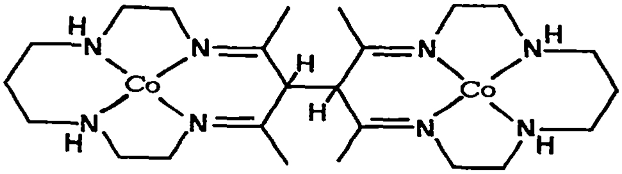
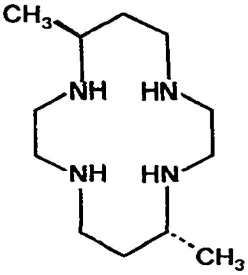


(28)

complex of the dimer (28) which may be oxidised by air to the corresponding cobalt(III) complex [229].

A variety of kinetic studies have been accomplished with macrocyclic cobalt(III) complexes. The acid catalysed decarboxylation of *cis*-$[Co(cyclen)(CO_3)]^+$ has been studied in detail [230]. This reaction is subject to a deuterium solvent isotope effect $k_{D_2O}/k_{H_2O} = 2.1$, consistent with a mechanism involving rapid pre-equilibrium protonation of the complex, followed by a slow rate-determining ring opening of the carbonato ring. Evidence has been presented [231] in support of a concerted E2 mechanism for the base hydrolysis of *cis*-$[CoCl_2(cyclen)]^+$, in which cleavage of the N-H and Co-Cl bonds occurs synchronously to give a five-coordinate intermediate without the intervention of a six-coordinate conjugate base. The possible occurrence of the E2 mechanism for a variety of other diacido-cobalt(III) complexes of tetra-aza macrocycles has been considered [232]. The activation volumes for aquation of $[CoL(N_3)X]$ (L = C-*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (29); X = Cl or Br) have been determined



(29)

[233]; $\Delta V^{\ddagger} = +8.3\ cm^3\ mol^{-1}$ (X = Cl) and $\Delta V^{\ddagger} = +5.3\ cm^3\ mol^{-1}$ (X = Br). The observed positive $\Delta V^{\ddagger}$ values are consistent with a dissociative mechanism and differ markedly from reported negative $\Delta V^{\ddagger}$ values for aquation of $[Co(NH_3)_5X]^{2+}$ ions.

A series of dimeric metalloporphyrin molecules have been prepared, in which the two porphyrin rings are constrained to lie parallel to one another by two amide bridges of varying length which link the rings together. Such porphyrins have been applied to the surface of graphite electrodes and tested for catalytic activity towards the electro-reduction of dioxygen to water. Only the dicobalt complex gave a catalysed reduction to water, other metal porphyrins gave mainly H_2O_2 [234].

Chiral cobalt(III) complexes of hexa-aza macrocycles have been described in a recent thesis [235]. The crystal structure of $(-)_{589}$-[Co(NH$_3$)(gly)(1,4,7-triazacyclononane)]I$_2$0.84H$_2$O has been determined [236]. The preparation of perchlorate salts of cobalt(III) porphyrins have been described and their reactions with vinyl ethers investigated [237].

4.2.5 *Complexes with Group VB donor ligands*

The preparation and properties of *mer*-trimethyltris(dimethylphenylphosphine)cobalt(III) have been described [238]. This complex is conveniently synthesised by the reaction of $[CoMe_2(acac)(Me_2PhP)_2]$ with a slight excess of MeLi in Et_2O. The complex $[CoPh_2(acac)(PEt_3)_2]$ has also been prepared [239].

The reaction of CH_3SH or H_2S with the binuclear dihydroxo-bridged complex [(triphos)Co(μ-OH)$_2$Co(triphos)] and, in some cases, a suitable redox agent gives the dinuclear sulphur-bridged complexes $[(triphos)Co(\mu\text{-}SCH_3)_2Co(triphos)]^{2+}$ and $[(triphos)Co(\mu\text{-}S)_2Co(triphos)]^{0,1+,2+}$. The structures of these compounds have been determined by X-ray analysis [240]. Substitution, alkyl transfer and thermal-decomposition reactions of $[(\eta^5\text{-}cp)Co(PPh_3)(CH_3)_2]$ have been studied in detail [241]. An X-ray photoelectron spectral study of cobalt nitrosyl complexes of diars identified a linear relationship between ν_{NO} and the N 1s binding energy [242].

The preparation and resolution of the *fac*-tris(2-aminoethyldimethylphosphine)cobalt(III) complex has been described and the absolute configuration of the $(+)_{589}$-isomer determined by X-ray analysis [243].

4.2.6 *Bioinorganic aspects*

A comparative kinetic study of the electron-transfer reactivities of the oxidants $[Co(phen)_3]^{3+}$ and $[Co(ox)_3]^{3-}$ with a series of metalloproteins (Cu^{I}-stellacyanin, horse heart ferrocytochrome *c*, Cu^{I}-plastocyanin, ferrocytochrome *c*-551, Cu^I-azurin and reduced HPIP) has been made [244]. The reactivity ratio $k[Co(phen)_3]^{3+}/k[Co(ox)_3]^{3-}$ provides a quantitative measure of the accessibility of the metalloprotein active centre to outer sphere contact with redox reagents. An isokinetic relationship has been observed in the oxidation of Cu^I-stellacyanin by a variety of cobalt(III) complexes [245]. While $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ show marked variations, the room temperature rate constants (3.6-34.5 M^{-1} s^{-1}) are relatively constant, as expected from Marcus theory for outer sphere electron transfer.

Selective intermolecular transfer of the nitrosyl group from cobalt nitrosyls to haemoglobin or myoglobin has been studied [246]. The interactions of the complex ions $[Co(NH_3)_5(OH_2)]^{3+}$, *trans*-$[Co(en)_2Cl_2]^+$ and $[Co(tren)(OH_2)_2]^{3+}$ with the potential ligands adenine, cytosine, adenosine, cytidine and 2-deoxyadenosine have been investigated spectroscopically [247] and some evidence for complex formation was obtained.

Cobalt(III) has been used recently to probe the active sites of enzymes. Thus cobalt(III)-bovine carbonic anhydrase B and cobalt(III)-bovine pancreatic carboxypeptidase A have been prepared and shown to be diamagnetic, suggesting that the cobalt(III) ion is octahedrally coordinated. The visible spectra of cobalt(III) carbonic anhydrase and its $[N_3]^-$ and $[NCO]^-$ substituted derivatives have been determined [248]. The energy of the lowest energy - band can be predicted using Jørgensen's rule of average environment and so can be of value in identifying the ligands bound to cobalt(III) in the active site of some enzymes.

4.2.7 Miscellaneous topics

^{59}Co has received considerable attention from the early days of NMR spectroscopy and is now a useful method of investigating diamagnetic cobalt(III) complexes. ^{59}Co is 100% abundant and is among the top six nuclear species for ease of detection. The nucleus has a nuclear spin I = 7/2 and a quadrupole moment of 0.4 x 10^{-28} cm^2. A quadrupole moment of this intermediate magnitude makes ^{59}Co linewidths sensitive to electric field gradients at cobalt and hence to the symmetry about the cobalt atom. Departures from strict octahedral symmetry cause line broadening which can also be useful for detecting subtle variations in structure. Cobalt-59 NMR spectroscopy has been the subject of an excellent review [8]. Juranic and coworkers [249] have investigated the ^{59}Co chemical shift in the NMR spectra of 30 cobalt(III) complexes and the results have been discussed in terms of ligand field theory. A linear relationship between ^{59}Co resonant frequencies and the longest wavelength *d-d* transition in octahedral cobalt(III) is expected and nephelauxetic effects in the interpretation of ^{59}Co resonant frequencies in cobalt(III) complexes have been studied [250].

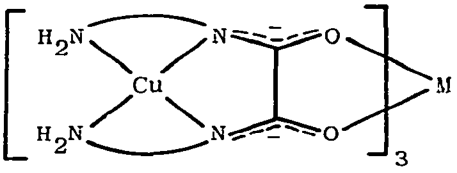
The cobalt(III) complexes $[(\eta^5\text{-}C_5H_5)Co(L)(ArN_3Ar)]^+$ (where L = PEt_3, PPh_3, $P(OMe)_3$, or $P(OPh)_3$ and ArN_3Ar = a diaryl triazenido anion) can be reduced electrochemically to the corresponding neutral cobalt(II) species [251] and the syntheses and properties of the above cobalt(III) complexes have also been described [252].

4.3 COBALT(II)

4.3.1 Complexes with oxygen or sulphur donor ligands

4.3.1.1 Oxygen ligands

Interesting hetero-metal tetranuclear complexes of type (30) have been prepared



(30)

for M = Co(II) or Ni(II) [253]. A strong antiferromagnetic spin-exchange interaction is operative between the copper(II) and the cobalt(II) or nickel(II) centres. Cobalt(II) propanoate or butanoate react with L (L = pyridine *N*-oxide, 3-methylpyridine *N*-oxide or quinoline *N*-oxide) in methanol, to give the corresponding solid $[Co(O_2CR)_2L]_2$ complexes which exhibit low magnetic moments at room temperature [254]. A large number of complexes of pyridine ligands with different cobalt(II) aryl carboxylates have been prepared and shown to have the *trans*-$[Co(O_2CC_6H_4R)_2L_2]$ structure [255]. Kinetic studies of the reaction of cobalt(II) with malonate, malate, or glycolate by the pressure shock technique have been reported [256], as have temperature-jump studies of the reaction of cobalt(II) with salicylic acid [257]. Bis(bromomalonato)cobaltate(II) has been prepared by bromination (Br_2 or N-bromosuccinimide) of the corresponding malonato complex suspended in an organic solvent [258]. Bromination occurs at room temperature without metal-malonate bond cleavage.

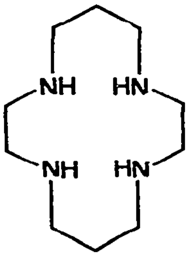
The crystal structure of diaquabis(phenoxyethanoato)manganese(II) has been determined [259], and the complex was found to be isomorphous and isostructural with the cobalt(II) derivative. The synthesis and properties of $[Co\{OCH(CMe_3)_2\}_2]$ have been described [260] and the methyl methylphenylphosphinate, MePh(MeO)PO, complex $[CoL_4(OClO_3)][ClO_4]$ has been characterised [261]. The cobalt(II) complex of 2'-hydroxy-3'-bromo-4-methoxy-5'-methylchalkone oxime has been synthesised, and its magnetic susceptibility shown to follow the Curie-Weiss law, with the observed temperature dependence taken as indicative of an octahedral stereochemistry [262]. Cobalt(II) complexes $CoL_2.nB$ (where L = 2-hydroxy-5-X-crotonophenone; X = H, CH_3, or Cl; B = H_2O or pyridine; n = 0,1, or 2) have been reported [263]. Heterocyclic base adducts of cobalt(II) chelates of acetoacetanilide [264] and isotropic ^1H NMR shifts of adducts of bis(β- to-ketoesterato)cobalt(II) complexes have been investigated [265]. The crystal structures of hexa(*N*-methylurea)cobalt(II) sulphate and thiosulphate [266] and of mercury(II) tetrakis(thiocyanato)bis(dimethylformamide)cobaltate(II) [267] have been published. The thermodynamics of the synergic extraction of cobalt(II) by thenoyltrifluoropropanone and tertiary amine ligands [268] and formation constants for the cobalt(II)-2-hydroxy-1-naphthaldehyde system in dioxane-water [269] have been reported. Tetrahedral and octahedral cobalt(II) occurs in hexaaquacobalt tetrachlorocobaltate-18-crown-6-propanone [270].

A large number of studies have appeared dealing with cobalt(II) complexes of β-diketones including: adducts of uni- and bidentate imidazoles and morpholines with $Co(acac)_2$ [271]; reactions of a variety of chelating ligands with $Co(acac)_2$ [272]; an NMR study of outer-sphere coordination of $CHCl_3$ and CH_2Cl_2 by $[Co(acac)_2(py)_2]$ [273]; thiourea and picoline derivatives of $Co(acac)_2$ [274]; a thermochemical study of adducts of $Co(acac)_2$ with Lewis bases [275]; cobalt(II) complexes of arylhydrazopentane-2,4-dione [276]; configurations of bis 1-(4-substituted phenyl)-1,3-butanedionato cobalt(II) complexes [277]; studies of the cobalt(II) complex of 4,6-dihydroxycoumaran-3-one [278]. Investigations of carboxylato complexes of cobalt(II) include: the determination of the crystal structure of bis(4-aminobenzoato)tetraaquacobalt(II) [279]; adducts of cobalt(II) haloethanoates with pyridine, quinoline, or isoquinoline [280]; mixed ligand complexes of bis(ethylmalonato)cobalt(II) with picoline or quinoline [281]; adducts of cobalt(II)-chloroethanoates with quinoline *N*-oxide [282]; mixed dmso-ethanoic acid solvates of cobalt(II)-ethanoate [283]. Other studies have dealt with hydrates and tertiary amine complexes of cobalt(II) trifluoromethanesulphonates [284] and investigations of octahedral$\rightleftharpoons$tetrahedral equilibria in aqueous solutions of cobalt(II) at high temperatures [285]. Complexes of D-glucose with cobalt(II) in aqueous solution have been studied by NMR techniques [286]. The crystal structure of $[Co(H_2O)_6][SnF_3]_2$ has been determined [287].

4.3.1.2 Dioxygen complexes

There has been considerable interest in the interaction of dioxygen with various cobalt(II) complexes. Oxygenation is usually viewed as a reversible internal redox reaction, in which cobalt(II) is formally oxidised to cobalt(III) and the O_2 formally reduced to peroxide, $[O_2]^{2-}$, (in 2:1 complexes) or superoxide, $[O_2]^{\dot{-}}$, ion (in 1:1 complexes). The μ-peroxo-complexes are generally more stable and preferred, unless inhibited sterically or if low temperatures or non-aqueous solvents are employed. A second (μ-hydroxo-) bridge is rapidly formed in aqueous solution whenever a site *cis* to the dioxygen bridge is readily available.

The reactions of dioxygen with some cobalt(II) complexes of macrocyclic tetra-amine ligands have been studied: all these ligands were saturated, 12-, 13- or 14-membered ring systems and the ring size was found to strongly influence the stability of the oxygenated products. The 12- and 13-membered rings stabilised the $[(CoL)_2(O_2)(OH)]^{3+}$ complex, whilst the 14-membered rings (cyclam (31) and isocyclam) formed $[(CoL)_2(O_2)]^{4+}$. As compared with linear tetramine systems, the macrocycles increase the $[CoL]^{2+}$ stability, lower the O_2 affinity of the complexes, and decrease (by *ca.* 10^2) the overall rate of O_2 uptake [288]. Cobalt(II) complexes of the two 16-membered macrocycles, (32) and (33), are oxygenated at pH~5 to form the corresponding μ-peroxo-bridged complex $[(CoL)_2O_2]^{4+}$. Comparisons with cyclam, (31), suggest that the fifth *N* or *O* donor atom appreciably promotes the rates and equilibrium of O_2 uptake. This effect is particularly marked with the *N* donor. The reaction of $[Co(cyclam)(OH_2)_2]^{2+}$ or $[Co([15]aneN_4)(OH_2)_2]^{2+}$ with O_2 gives the corresponding μ-peroxo complex $[\{(H_2O)Co([n]aneN_4)\}_2O_2]$ (n = 14 or 15). This reaction occurs in two stages and the initial stage involves the generation of a very reactive 1:1 adduct. The $[14]aneN_4$ {*i.e.* cyclam, (31)} complex is low spin whereas the $[15]aneN_4$ complex high spin, but these different spin states do not appear to have a marked effect on the reactivity [290].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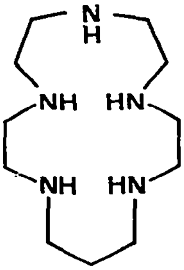
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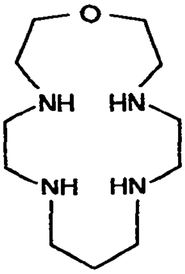
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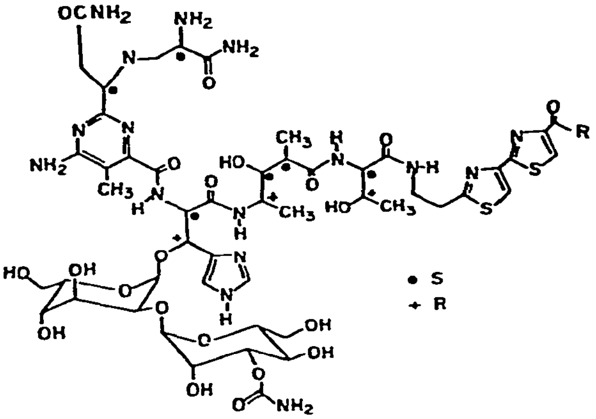
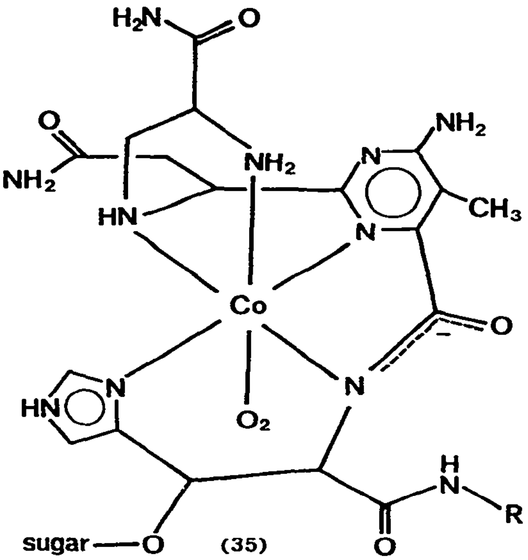
Bleomycin is an antitumour antibiotic which is currently employed clinically for the treatment of various lymphomas and carcinomas. Bleomycin is a glycopeptide and forms stable complexes with many divalent {Cu(II), Zn(II), Co(II), and Hg(II)} and trivalent {Ga(III) and In(III)} ions. The structure of the antibiotic is shown in (34). Anaerobically, Co(II) forms a stable complex with



(34)

bleomycin, but addition of O_2 leads to formation of a dioxygen adduct which is unstable and decomposes to give a Co(III)-bleomycin complex [291]. Spectral data suggest that cobalt-bleomycin has similar binding sites to that of copper(II)-bleomycin, that is the N(1) of the imidazole group, the N(1) of the 4-aminopyrimidine group, the amino group of the α-aminocarboxyamide, and the O atom of the sugar carbamoyl group. Sugiura [292], on the basis of EPR studies has suggested that Co(II)-bleomycin is a low spin square pyramidal cobalt(II) complex, with the $(d_{xz})^2(d_{yz})^2(d_{xy})^2(d_{z^2})^2$, configuration. These results also suggest a new type of ligand environment for the monomeric bleomycin-cobalt(II)-dioxygen adduct (35) and the depyruvamide - bleomycin complexes with an axial base (B) (36).

The decomposition of cobalt-dioxygen complexes of three dipeptides has been studied and selective oxidation of the *N*-terminal amino acid residue occurs in



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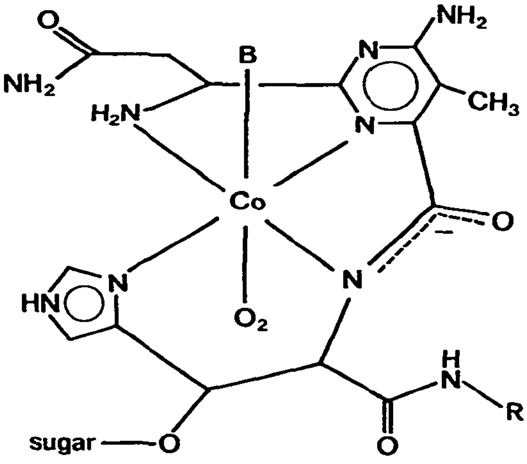
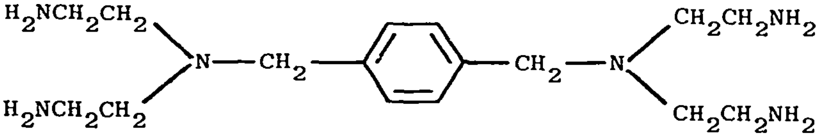


(36)

the presence of O_2 [293]. Ligands with two multidentate moieties separated by a rigid bridging group, such as 1,3- or 1,4-dimethylenebenzene, are of considerable interest for the formation of binuclear complexes capable of the biscoordination of suitable bridging ligands. Therefore, the reaction of (37) with



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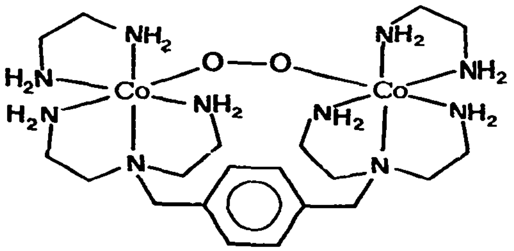
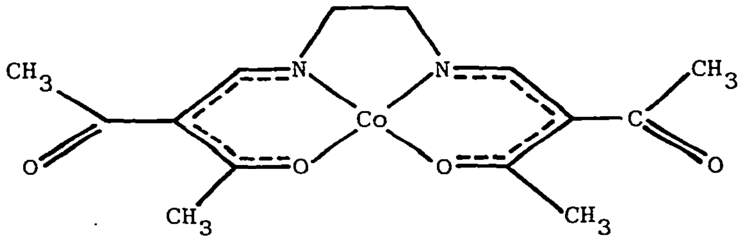


(38)

cobalt(II) and 1,2-diaminoethane in the presence of O_2 gives the interesting peroxobridged complex (38) [294]. Martell and coworkers [295] have found that the primary factors governing the stability of the cobalt(II)-dioxygen bond are those that increase σ-donation by the ligands to the cobalt, with π-bonding effects having little or no influence. There is a good linear relationship between log K_{O_2} and ΣpK of the ligand donor groups. The crystal structures of *N,N'*-ethylenebis(3-*t*-butylsalicylideniminato)cobalt(II) and its monomeric dioxygen adduct with pyridine as the axial base have been determined [296].

Resonance Raman spectra have been measured for the dimeric oxygen adduct $[\{BCo(sal_2en)\}_2O_2]$ (where B = py, pyNO, or dmf): the O_2 and CoO stretching vibrations of these compounds are in the ranges 910-888 and 542-535 cm^{-1}, respectively [297]. Thermodynamic measurements for the binding of O_2 to native myoglobins and their cobalt analogues have been discussed [298] and resonance Raman work has dealt with the dioxygen adducts of the cobalt(II) complex of the Schiff base (39) [299]. Molecular-orbital studies of dioxygen activation by cobalt(II) complexes [300] and of the coordination of dioxygen in monomeric cobalt(II) complexes [301] have been published.



(39)

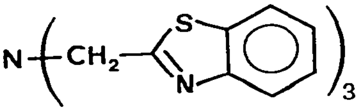
Interest continues in Schiff base complexes of the sal_2en type with cobalt(II) as oxygen carriers. The preparation of 3-fluoro-2-hydroxybenzaldehyde and its condensation product with 1,2-diaminoethane, to give a substituted sal_2en ligand which was then complexed with cobalt(II), have been described [302]. Other studies have dealt with the effect of remote substituents on dioxygen carriers of the $Co(acac_2en)$ type [303], the equilibrium and kinetic parameters for oxygenation of $Co(sal_2en)$ [304], and a study of the degradation of a cobalt(II)-fluorosal$_2$en complex during oxygenation and deoxygenation cycles [305]. Oxygenation of $[Co(phen)_2]^{2+}$ [306] and $[Co(phen)(gly)]^{+}$ [307] have been reported. Also, studies of the reversible addition of dioxygen to mixed ligand complexes of cobalt(II) with nucleotides and histidine [308], and an EPR study of the association of O_2 with tetraphenylporphyrincobalt(II) [309] have been published.

A recently published thesis has discussed some cobalt-dioxygen complexes

[310] and the cobalt(II) complex of *N*,*N*'-bis(2-thioformyl-2-phenylvinyl)trimethylenediamine has been found to act as an O_2 carrier [311]. The interesting work on cobalt(II) complexes of "dry cave" macrocycles, which act as extremely efficient O_2 carriers, is discussed in Section 4.3.3.2.

4.3.1.3 Sulphur-containing ligands

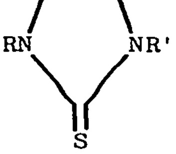
Cobalt(II) and nickel(II) form complexes $[ML_2X_2]$ (X = Cl,Br, or I; L = 2-methylthioethanol), $[M_2L'_2X_2]$ (L' = 2-methylthioethanethiol), and $[ML''X_2]$ (L'' = di-(2-methylthioethyl)disulphide), and their probable structures have been proposed on the basis of spectral and magnetic data [312]. The tetradentate "tripod" ligand tris(2-benzothiazolylmethyl)amine (**40**; ntbt) has been found to



(**40**; ntbt)

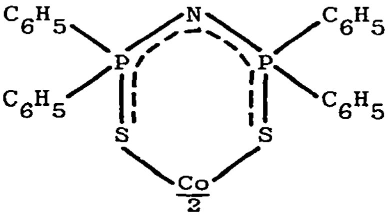
form trigonal bipyramidal cations $[Co(ntbt)X]^+$ (X = Cl or Br) in the complexes $[Co(ntbt)X][BPh_4].2CH_3CN.xH_2O$, $[Co(ntbt)X][CoX_3(CH_3CN)].CH_3CN$, and $[Co(ntbt)Br]_2[CoBr_4].2MeNO_2.1.5$ EtOH whereas *pseudo*-octahedral structures exist in the solid state in all of the other systems investigated [313]. The crystal structure of dichlorobis(2,2'-thiodiethanol)cobalt(II) has been determined. The cobalt is six-coordinate with the two chlorine atoms occupying the *trans*-apical positions, and each thiodiethanol molecule is bonded to the cobalt through a sulphur $\{\bar{r}(Co\text{-}S) = 2.508$ Å$\}$ and an oxygen atom $\{\bar{r}(Co\text{-}O) = 2.066$ Å$\}$ [314].

The influence of cobalt(II) chloride on the proton chemical shifts of imidazolidine-2-thione (**41**) and its *N*-mono- and *N*,*N*'-dialkyl-substituted



(**41**)

derivatives have been studied in CD_3OD and $CDCl_3$ mixtures and changes of the chemical shifts (and in the IR spectra) are indicative of *S*-coordination to the metal [315]. IR and Raman spectra of bis(imidotetraphenyldithiodiphosphino-*N*,*N*')cobalt(II) (42) have been obtained [316]. Treatment of CoX_2 (X = Cl,Br,I, or $[BF_4]$) with (41; R = R' = Me or Et) gives the complexes $[CoL_2X_2]$ (X = Cl,Br or I) and $[CoL_4][BF_4]_2$ [317]. Their NMR and IR spectra show all of them to be *S*-bonded to the metal atom. Electronic spectral and magnetic measurements are consistent with a tetrahedral stereochemistry about cobalt [315]. The cobalt(II) complex of 2-amino-5(2-hydroxyphenyl)-1,3,4-thiadiazole (43; R = OH) has been prepared and shown to be six-coordinate [318]. Mixed pyridine complexes of (43; R = H) with cobalt(II) sulphate have also been characterised [319], as have a number of cobalt(II) complexes of 2,4-dimercapto-s-triazolo-[4,3-b]-1,3,4-thiadiazole [320] (one tautomer of this latter ligand is shown in (44)). ^1H NMR spectroscopic studies of cobalt(II) complexes of benzothiazole and substituted benzothiazoles indicate large isotropic shifts [321], and all the complexes are labile and partially dissociated in ethanenitrile solution.



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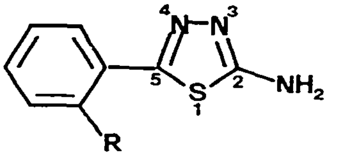

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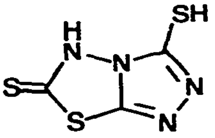

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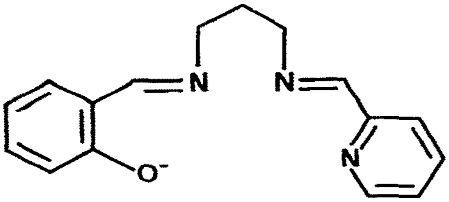
Complexes of cobalt(II) with substituted 2-amino and 2-acetylamino thiazoles, with the stoicheiometry CoL_2Cl_2, have been characterised [322]. Complexes of 4,6-dimethylpyrimidine-2-thione with cobalt(II), with the stoicheiometry CoL_2X_2 (X = Cl or Br), each exist in isomeric forms: blue, containing tetrahedral

$[CoL_2]$ units involving *N/S* chelation; and green in which the metal is in a distorted octahedral environment [323]. Isomerism of this type was not found for the cobalt(II) halide complexes of 4,6-dimethylpyrimidine-2-one or 1-methylpyrimidine-2-one. The crystal structure of $CoL_{2.5}Cl_2$ (L = methyl 2-methyldithiocarbazate) has been determined [324]. The compound consists of octahedral $[CoL_2Cl_2]$ units, in which the two L molecules act as chelating ligands, and free disordered L molecules.

A range of metal thiosulphate complexes of the type $[ML_n(S_2O_3)]^{x+}$ (M = Ni(II), Co(II) or Co(III); L = a nitrogen donor ligand) have been prepared [325]. Bis{(propythio)ethano}cobalt(II) hexamer has been found by X-ray analysis to have a structure in which the six cobalt(II) atoms form a ring in a boat conformation which is bridged by the ligands [326]. Sulphur base ligation to cobalt(II) porphyrins has been investigated [327], and the cobalt(II)-thiomalate complex studied in solution [328]. Thermogravimetric investigations of the decomposition of cobalt(II) and other metal(II) dithiocarbamates has been studied [329]. The crystal structure of dichlorobis(pyridinium-2-thiolate)cobalt(II) has been published [330]. Other investigations involving sulphur containing ligands and cobalt(II) include: the synthesis and characterisation of polymeric complexes of terephthaldehyde bis(4-phenylthiosemicarbazone [331]; the preparation of complexes with β-aminovinylthiones [332]; mixed ligand thiocyanato complexes [333]; complexes with thiophene-2-carboxylic acid hydrazide [334]; and thiosemicarbazide complexes [335].

4.3.2 Complexes with oxygen-nitrogen donor ligands

Cobalt(II) complexes of tetramethylethylenediaminetetraacetate [336] and ethylenediaminetetraacetamide [337] have been prepared and characterised. Other cobalt(II) complexes prepared involve the ligands 2-carbethoxypyridine(ethyl picolinate) [338], and 2- or 4-pyridinecarboxylic acid *N*-oxide [339]. Unsymmetrical ligands, derived from salicylaldehyde and 1,3-diaminopropane with either pyridine-2-carbaldehyde (45) or pyrrole-2-carbaldehyde (46), have been used to prepare



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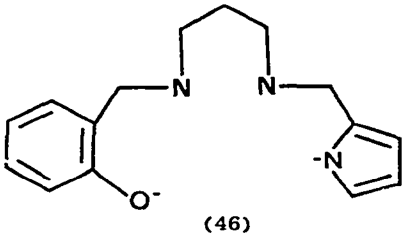


(46)

cobalt(II) complexes [340]. Dicobalt(II) complexes of three binucleating Schiff base ligands have been prepared, and shown to be readily oxidised to their dicobalt(III) analogue [341]. Cobalt(II) complexes of some heterocyclic Schiff bases, derived from hydroxy aromatic aldehydes (salicylaldehyde, 4-hydroxobenzaldehyde, or vanillin) and 2-aminopyridine, have also been characterised [342].

Cobalt(II)-manganese(II)-cobalt(II) trinuclear complexes have been synthesised by the reaction of *N,N'*-disalicylidenealkanediaminatocobalt(II) and a manganese(II) halide in a 2:1 mole ratio. Antiferromagnetic spin exchange interaction operates between the low spin cobalt(II) and the high spin manganese(II) ions [343]. Cobalt(II) (and cobalt(III)) complexes of Schiff bases derived from hydrazine-*S*-methyldithiocarboxylate and thiosemicarbazide have been studied [344], as have cobalt(II) complexes of the potentially dianionic tridentate Schiff bases, *N*-(*O*-hydroxyphenyl)-5,6-benzosalicylideneimine and its isomer *N*-(*O*-hydroxy-5,6-benzophenyl)-salicylaldimine [345]. EPR studies of axial ligation to cobalt(II) complexes of some oxo-, thio- or seleno-Schiff bases have been published [346].

The interactions between the 8-quinolinol group of the chelating ion-exchange resin Spheron oxine 1000 and cobalt(II) (and a variety of other divalent metal ions) have been studied by EPR and electronic spectroscopy [347].

Metal induced enolisation of *N*-acetylpyrazole in the presence of divalent cations, including cobalt(II), has been observed [348] and the enolic complexes isolated. Cobalt(II) complexes of *anti*-2-furan carboxaldoxime have been prepared [349]. NMR studies of the configuration and ligand rearrangement in complexes of cobalt(II) with diethylenetriaminepentaethanoic and triethylenetetraminehexaethanoic acid have appeared [350], and cobalt(II) complexes of methylene bis(1,1-dicyano-2,2'-dimethylethyl)acrylate have been studied [351].

The results of kinetic investigations of the forward and reverse reactions of $[Ru(NH_3)_5L]^{3+} + [Co(edta)]^{2-} \rightleftharpoons [Ru(NH_3)_5L]^{2+} + [Co(edta)]^{-}$ (L = py or 4,4'-bipy) [352], and the reaction of H_2O_2 with *N*(2-hydroxyethyl)ethylenediaminetriacetatocobaltate(II) [353] have been published.

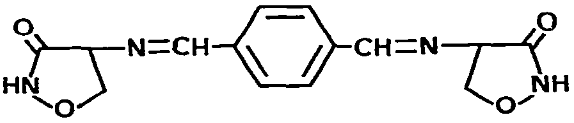
Diethanolamine complexes of cobalt(II) and other divalent metal ions have been characterised [354] and the crystal structure of triethanolamine cobalt(II) bromide has been determined [355]. The results of a number of investigations connected with *N*-ethanoic acid type ligands have been published, including, the crystal structure of disodium bis(iminodiethanoato)cobaltate(II) heptahydrate [356] and the preparation of cobalt(II) complexes of hexamethylenediaminetetraethanoate [357], tetramethylpyrrolidin-1-oxyl-3-amino-*N*,*N*-diethanoic acid [358], *N*-(carbamoylmethyl)iminodiethanoic acid and *N*-(2-carbamoylethyl)iminodiethanoic acid [359], and DL-*N*(2,3-dihydroxypropyl)-N-carboxymethylaminoethanoic acid [360]. Cobalt(II) complexes of amides reported this year, include those of dicyanadiamide [361], malonamide [362], benzamide [363], the monoamides of maleic and phthalic acids [364] and hydrazodicarbonamide [365]. Cobalt(II) complexes of glutaric and adipic dihydrazides have been prepared [366], as have those of isonicotinic acid hydrazide [367].

Other investigations of the chemistry of cobalt(II) include; the preparation of complexes of 3-pyridinealdehyde [368], studies of the thermodynamics of the interaction of cobalt(II) with *N*-phenyl-2-furohydroxamic acid and its analogues [369], the isolation of complexes of 5-methylpyrazole-3-carboxylic acid [370] and 3(2'-furoyl)-2-cyanoethyl crotonate [371], thermodynamic measurements of the interaction of cobalt(II) with 2-(*N*-α-furfuralideneimino)benzene sulphonic acid [372], and an NMR study of the complexing of cobalt(II) with substituted 2-naphthoquinonediazide [373].

Schiff base complexes of cobalt(II) always attract considerable attention and developments in this area include: the investigation of complex formation with Schiff bases derived from sulphamethoxypyridazine [374]; complexes of 5-phenylazosalicylideneaniline [375]; the isolation of complexes with *N*,*N*'-hexamethylene bis(2,5-dihydroxyacetophenone-propiophenone- or benzophenone) [376]; binuclear cobalt(II) complexes with *N*-(3-carbosalicylidene)amines [377]; EPR studies of axial ligation of low-spin cobalt(II)-Schiff base complexes [378]; preparation of complexes with the Schiff base derived from 2-hydroxy-5-methylacetophenone and 4-toluidine [379]; the interaction of cobalt(II) Schiff base complexes with aromatic nitro compounds [380]; determination of the formation constant for the interaction of cobalt(II) with salicylidene-2-iminopyridine [381]; investigation of the complex with the heterocyclic Schiff base hydroxybenzylidene-2-amino-4-phenylthiazole [382]; studies of the reaction of cobalt(II) with semicarbazones of salicylaldehyde, cinnamaldehyde and diphenyl ketone [383]; the formation of adducts of oxygen-, sulphur-, selenium-, tellurium-, nitrogen- or phosphorus-bases with a planar low-spin cobalt(II) complex of phenylenebissalicylideneiminate [384].

4.3.2.1 Amino-acid, peptide and protein ligands

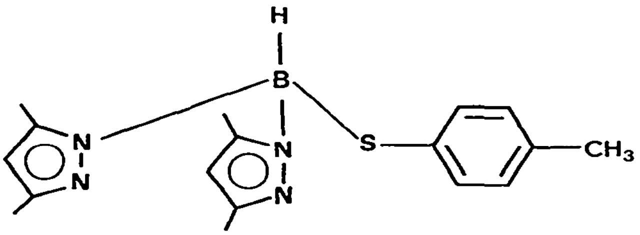
Potentiometric studies of complex formation between cobalt(II) and di- and tetrapeptides containing tyrosine and glycine residues have been published [385] and selective oxidation of the *N*-terminal amino acid residue of cobalt(II)-dipeptides in the presence of O_2 has been noted [293]. The cobalt(III) complex of the cycloserine derivative, N_4,N'_4-tereftal-bis(cycloserine) ("Terizidone") (47) has been prepared and characterised [386] as have a variety of cobalt(II) complexes of *N*-acetyl-DL-leucine [387]. Binding of cobalt(II) to glycyl-L-tyrosine has been studied by potentiometric techniques and amide proton ionisation at high pH was observed [388]. Serum albumin is known to bind several divalent metal ions at the amino terminus of the protein and two peptide analogues of the amino terminus of human albumin, L-asp-L-ala-L-his-*N*-methyl amide and gly-gly-L-his-*N*-methyl amide, have been prepared and their interaction with cobalt(II) (and zinc(II)) studied potentiometrically. Although cobalt(II) is a valuable tool for the study of zinc(II) interaction with apoenzymes, it is considerably less useful as a zinc(II) model with small peptide molecules [389].



(47)

^1H NMR spectra of cobalt(II) complexes with potentially tridentate amino acids (L-ser, L-thr, L-4-hydroxy-pro, DL-arg, L-citrulline, DL-lys, L-β-asparagine, and DL-orn) have been determined in an attempt to define the metal binding sites [390]. Parameters affecting the stability of nitrosyl cobalt complexes, obtained by reacting NO with cobalt(II)-amino acids, have been investigated [391] and the influence of amino-acid side chains on the effectiveness of NO binding has also been studied [392]. Ternary complex formation between cobalt(II)-pyridoxamine and some amino-acids has been investigated potentiometrically [393], and the kinetics of CO binding to cobalt hybrid haemoglobins have been studied [394].

In an attempt to model the site characteristics of a metalloprotein the synthesis and characterisation of $M^{II}(N_2S)(SR)$ complexes (M = Co or Cu) have been studied, as synthetic approximations of the active site in poplar plastocyanin. The (N_2S) ligand involved was hydrobis(3,5-dimethyl-1-pyrazolyl)-(*S*-4-toluenethiolato)borate (48) [395]. The complex cation $[Co\{tris(3,5\text{-}dimethyl\text{-}1\text{-}pyrazolylmethyl)amine\}H_2O]^{2+}$, containing the tripod ligand (49) has been prepared as a model for metalloenzymes containing bipositive zinc(II)



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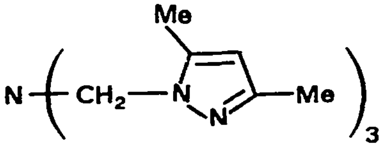


(49)

chromophores with a water molecule in the coordination sphere [396].

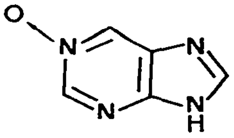
The electronic spectrum of cobalt(II) bovine and human carbonic anhydrase B has been recorded as a function of pH and the results discussed in terms of the acid-base equilibria of the cobalt(II) enzyme [397]. The interaction of cobalt(II) bovine carbonic anhydrase B and the hydrate of trichloroacetaldehyde has been investigated as a function of pH by Fourier transform NMR spectroscopy [398]. Spectroscopic studies on cobalt(II) metallothionein provide evidence for *pseudo*-tetrahedral metal coordination [399], and evidence for the binding of cobalt at the copper(II) binding site of copper-free superoxide dismutase has been obtained [400]. The coordination geometry about the metal in the ternary complex of cobalt(II) bovine carbonic anhydrase and 2-pyridinecarboxylate has been discussed [401] and the interaction of bovine cobalt(II) carbonic anhydrase with pyridine-2,6-dicarboxylate, and other chelating ligands, have been studied [402]. The binding of cobalt(II) and other metal ions to plasma proteins has been investigated [403].

The nature of the interactions of cobalt(II) with a number of amino acids in aqueous solution have been investigated. These include Co(II)-imidazole complexation [404], the formation of Co(II)-histidine-phenylacetohydroxamic acid ternary complexes [405], Co(II)-*N*-benzenesulphonyl-L-cysteine interactions [406], the formation of Co(II)-L-lysine complexes, studied by NMR spectroscopy [407], Co(II)-sarcosine dithiocarbamate interactions [408], interactions of Co(II) with oxidised glutathione [409], and the formation of Co(II)-histidine complexes [410]. A thesis dealing in part with Co(aminoacidate)$_2$ complexes, has been published [11], and potentiometric and spectrophotometric investigations of the interaction of cobalt(II), or other divalent metal ions, with L-β-phenylalanine carried out [412]. Mixed ligand complexes of cobalt(II) with histidine and heterocyclic bases have also been prepared [413].

4.3.3 Complexes with Group VB donor ligands

4.3.3.1 Nitrogen ligands

Adenine *N*(1)-oxide (50) complexes of cobalt(II), nickel(II), and copper(II)



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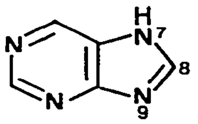
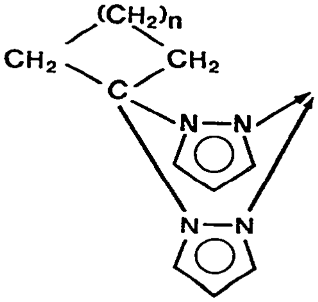


(51)

have been prepared [414]. The cobalt(II) complex CoL$_2$(ClO$_4$)$_2$.2MeOH has, from IR data, been ascribed one ionic and one monodentate [ClO$_4$]$^-$ group. A series of M(purH)$_2$[ClO$_4$]$_2$.3H$_2$O (M = Mn,Fe,Co,Ni,Cu, or Zn) complexes with the neutral purine (51; purH), presumably protonated at N(7), have been synthesised by the reaction of the ligand and a metal salt in ethanol/triethyl orthoformate solution [415]. The syntheses of 1,1-dipyrazoylcycloalkane (52) complexes of

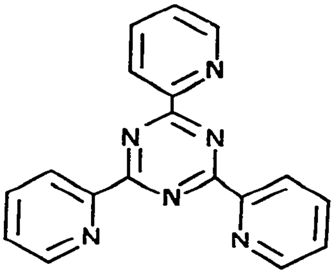


(52; *n* = 1,2 or 3)

cobalt(II) have been described [416], and [Et$_3$P]$^+$ – and nitro-substituted pyridine and 2,2'-bipyridine complexes of cobalt(II) have been prepared and their pK values and redox potentials determined [417].

The complex [(η^5-C$_5$H$_5$)Co(PPh$_3$)(RN$_3$R)], containing a triazenido ligand, has a spin state of ½ [418]. The new tripod ligand, tris(3,5-dimethyl-1-pyrazolylmethyl)amine (49), has been prepared and the cobalt(II) complexes [CoLX][BPh_4] (X = Cl,Br,I, or NCS) and CoL(NO_3)$_2$ have been characterised. These cobalt complexes appear to have a coordination geometry intermediate between trigonal-bipyramidal and tetrahedral [419]. A cobalt(II) complex of 4-methylpyrazole has been shown to contain the bidentate pyrazolate ion [420] and a variety of 3- or 4-picolylamine complexes of cobalt(II) have been prepared and their physical properties studied [421].

The complex $[Co(tpt)_2]^{2+}$ (tpt = 2,4,6-tri-(2-pyridyl)-1,3,5-triazine (53) is



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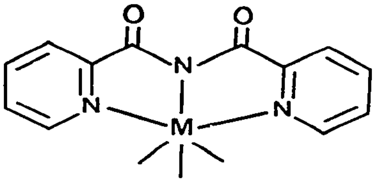


(54)

reported to react with hydroxide ion in aqueous solution to form a "pseudo-base" species, prior to dissociation of a ligand molecule, and the kinetics of "pseudo-base" formation have been monitored [422]. The complex $[Co(tpt)(OH)_3]^-$ is also reported to be attacked by $[OH]^-$ to form a "pseudo-base" species, prior to hydrolysis to the carboximate complex (54) [423]. A determination of the crystal structure of [Co(terpy)(NCO)] has established that cobalt(II) is five coordinate in this complex, [424]. The electrochemical behaviour of a variety of cobalt(II) complexes of phenyl substituted terpyridines has been investigated in some detail [425] and ferromagnetic interactions in a cobalt(II) complex of 1-(2-pyridylazo)-2-phenanthrol have been studied [426]. A variety of EPR investigations have been carried out on cobalt(II) complexes, including $[Co(EtNHCH_2CH_2NHEt)_2X_2]$ (X = Cl,Br,NCS, or NO_3) and $[Co(MeNHCH_2CH_2NHMe)_2(NO_3)_2]$ [427], dichloro-tetrakis(pyridine)- and dichlorotetrakis(pyrazole)cobalt(II) [428], and a series of low spin cobalt(II) complexes with imine ligands [429].

Cobalt(II) salts catalyse the autoxidation of 1,2-diaminobenzene in slightly basic solution. Deeply coloured metal complexes are formed during this reaction, suggesting the formation of intermediate radical or semiquinonediimide species. One of these complexes, bis(1,2-benzoquinonediimide)(1,2-benzosemiquinonediimido)cobalt(II), has been isolated and its crystal structure determined [430].

The crystal structure of [Co(*N*-methylimidazole)$_2$(tcf)$_2$] (tcf = 2,4,6-trichlorophenolate) has been determined and the complex contains five-coordinate high spin cobalt(II) [431]. The kinetics of redox reactions between $[Co(CN)_5]^{3-}$ and dicyano(porphyrinato)iron(III) complexes [432] or 1,4-napthoquinone [433] have been studied. Other investigations include: the reaction of cobalt fluoride with hydrazine [434]; the determination of the activation volume for solvent exchange with $[Co(CH_3CN)_6]^{2+}$ ($\Delta V^{\ddagger}$ = +6.7 cm^3 mol^{-1}) [435]; the effect of chloroform on the relative stabilities of [CoCl$_2$(py)$_2$] and [CoCl$_2$(py)$_4$] complexes in solution [436]; a potentiometric study of Co(II)-azide complexes [437]; the characterisation of new pentacoordinate mononitrosyl cobalt complexes [438].

A number of potentiometric investigations have been published dealing with complex formation between cobalt(II) and aliphatic or aromatic diamines in solution; the ligands include *N*-methyl-1,3-diaminopropane [439], 1,3-diaminopropane [440] and 1,2-diaminobenzene [441]. Some 1,2-diaminoethane and diaminobenzene derivative of cobalt(II) cyanates and azides have been characterised [442] and the induced optical rotation in cobalt(II) complexes of 1,1,1-tris(aminomethyl)ethane and *cis*,*cis*-1,3,5-triaminocyclohexane have been studied [443]. The syntheses of some interesting tridentate ligands containing pyridine and imidazole have been described [444] and their zinc(II) and cobalt(II) complexes have been studied as models of the metal centre of carbonic anhydrase [511].

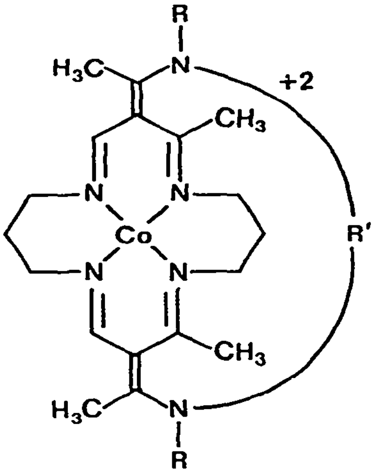
A variety of cobalt(II) complexes involving pyridine or substituted pyridines as ligands have been studied. These include the identification of cobalt(II) complexes involving alkylpyridines [445], the formation of polynuclear complexes between cobalt(II) and 2-aminomethylpyridine [446], linkage isomerism in [Co(py)$_4$(NCS)$_2$], [Co(4Mepy)$_2$(SCN)$_2$] and [Co(4Mepy)$_4$(SCN)$_2$] [447], the determination of the crystal structures of *trans*-[Co(py)$_4$(NCS)$_2$] [448], *trans*-[Co(py)$_4$(NCS)$_2$].2CHI$_3$ [449] and aquachlorobis{*N*-(2-pyridylmethylene)aniline}-cobalt(II) nitrate monohydrate [450].

Three papers have appeared dealing with complexes between 1,2,4-triazole and cobalt(III); 3-amino-1,2,4-triazole and 4-amino-1,2,4-triazole have been used as ligands [451], and the crystal structures of a triazole bridged cobalt(II) complex [452] and of a bis(*iso*thiocyanato)-bis-μ-(1,2,4-triazole-N_2,N_4)-cobalt(II) complex have been determined [453]. Anionic trihalomonoquinoline or *iso*quinoline cobalt(II) complexes have been prepared [454] and complexes of cobalt(II) with piperazine have been studied [455]. The crystal structure of bis(3,5-dimethyl-1-phenylpyrazole)bis(*iso*thiocyanato)cobalt(II) has been determined [456], the cobalt(II) complex of 3,4,5-trimethyl-1-nitroguanylpyrazole has been synthesised [457], and an NMR study of the solution structure of cobalt(II) complexes of alkylpyrazoles has been published [458]. Other reports include the thermal behaviour of [Co(ox)(bipy)$_2$] [459], the magnetic and spectral properties of cobalt(II) complexes of a substituted 4-arylazo-2-pyrazoline-5-one [460], and the synthesis of the cobalt(III) complex of *syn*-thiophene-2-aldoxime [461].

4.3.3.2 Nitrogen macrocycles

A considerable volume of work has been published this year on cobalt(II) complexes of nitrogen macrocycles and the interaction of O_2 with some of these complexes is considered in Section 4.3.1.2.

Busch and coworkers have synthesised macrocyclic cobalt(II) complexes of type (55) [462]. The bridge group R' provides a "dry cave" near the metal atom,



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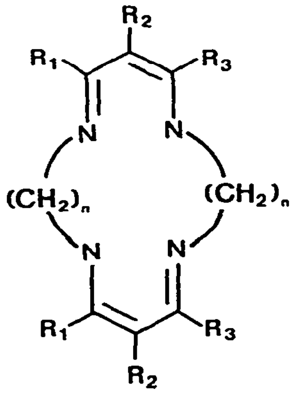
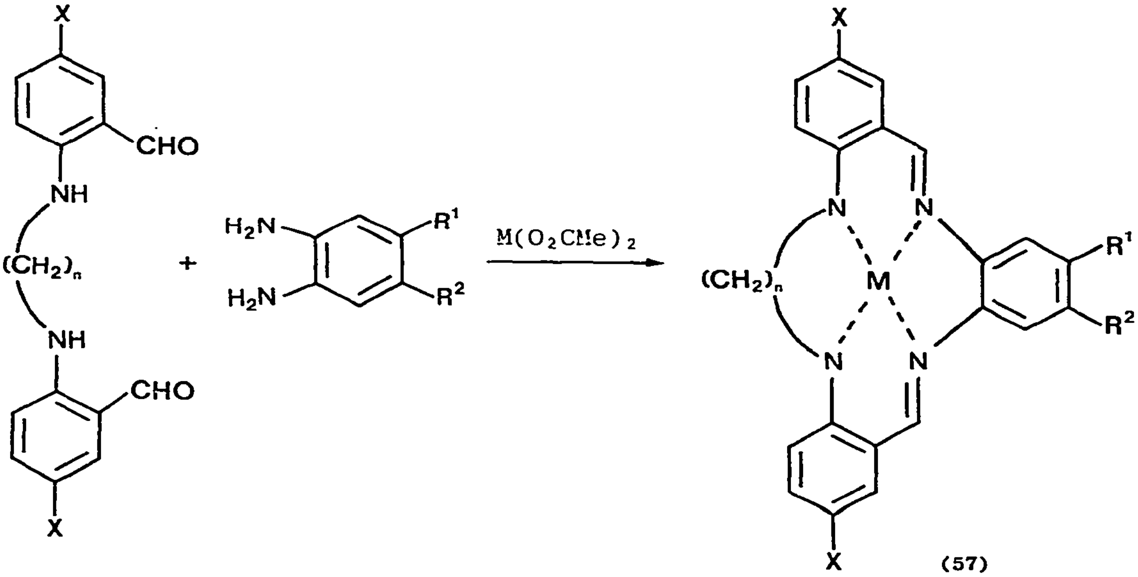


(56)

which is intended to shelter small ligands from interaction with other cobalt centres or with solvent. X-ray data have established that the cobalt(II) is four-coordinate and square planar. The cobalt(II) complex can be oxidised in the presence of small ligands X^- (*e.g.* NCS^-, N_3^-, or NCO^-) to give the corresponding $[Co^{III}LX_2]^+$ complexes. For (56; R = Me, R' = $(CH_2)_6$), reversible UV-VIS spectral changes were observed for oxygenation of aqueous solutions containing *N*-methylimidazole [463]. The data indicate a simple equilibrium between the five-coordinate cobalt(II) complex and the 1:1 dioxygen adduct. The P_{50} value is 0.63±0.04 Torr at 20 °C, indicating that it is the most thermodynamically stable 1:1 cobalt-O_2 adduct yet reported. The appropriate P_{50} values for cobalt myoglobin and iron myoglobin are 33 Torr and 0.5 Torr, respectively, at 20 °C.

EPR and electronic spectral studies of cobalt(II) complexes with Jager's N_4-macrocyclic ligands (56) have been described. The introduction of electron withdrawing groups (R = $COCH_3$ or $CO_2C_2H_5$) decreases the π-electron delocalisation [464]. The preparations of a wide range of cobalt(II), nickel(II), or copper(II) complexes of macrocyclic ligands derived from diamino dialdehydes and various substituted 1,2-diaminoarenes have been described [465]. The resulting macrocyclic complexes (57) contain an extensive chromophore of the Wurster type,

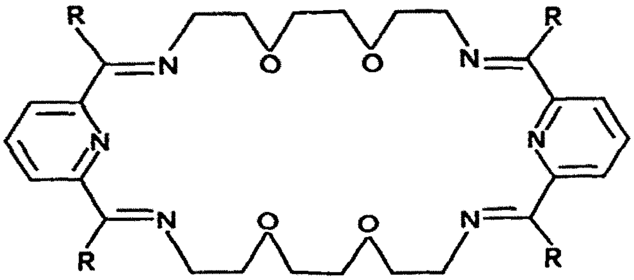


(57)

which is the reduced form of a possible two-step redox system. The structure of the β-polymorphic form of phthalocyaninatocobalt(II) has been determined by single-crystal neutron diffraction methods [466]. The reactions of cobalt(II) sulphophthalocyanine dimers with a variety of free radicals have been studied by optical pulse-radiolysis methods [467].

Complexes of the type $M(N_2O_2)X_2$ (where M = Co,Zn, or Cd; N_2O_2 = macrocycle;

X = Cl,Br,I or NCS) have been synthesised from a range of 14- to 17-membered macrocycles incorporating N_2O_2-donor sets [468]. These cobalt(II) complexes exhibit either tetrahedral or octahedral geometries. The crystal structure of $[CoL][ClO_4]_2.H_2O$ (where L is the 30-membered macrocyclic ligand (58) with an N_6O_4 donor set) has established that the metal has a distorted octahedral environment comprised of the six nitrogen donors, the four oxygen atoms being uncoordinated [469]. The low spin cobalt(II) complex exhibits Jahn-Teller distortion as a result of the $(t_{2g})^6(e_g)^1$ configuration. Complexes of the macrocyclic triamine, 2,4,4,9-tetramethyl-1,5,9-triazacyclododeca-1-ene (59), with cobalt(II), nickel(II), or copper(II) have been prepared by reaction of propanone with complexes of these ions with 4-methyl-4-azaheptane-1,7-diamine [470].



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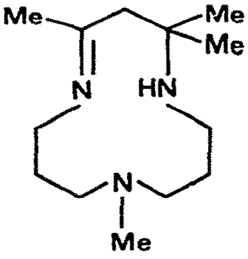
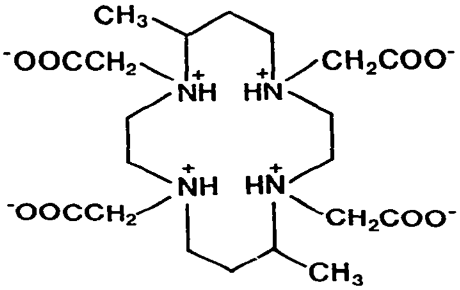


(59)

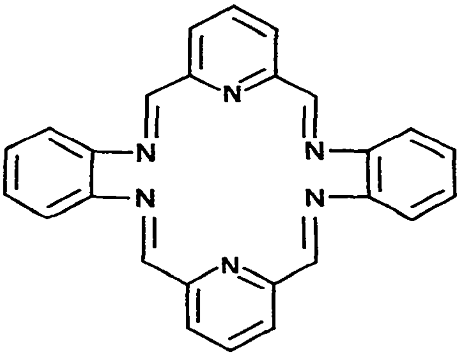
The complexone-like macrocycle (60; LH_4) forms a series of metal complexes with cobalt(II), nickel(II), copper(II) and zinc(II) of the types $[MLH_2]$, $[ML]^{2-}$, and $[M_2L]$ [471]. Rate and equilibrium measurements for the methyl bridged electron



(60)

transfer reactions of several $[Co(N_4)(OH_2)CH_3]^{2+}/[Co(N_4)(OH_2)_2]^{2+}$ (N_4 = a tetra-aza macrocyclic ligand) couples, the $[Co(dmgH)_2(OH_2)CH_3]/[Co(dmgH)_2]$ couple, and for the methylcobalamin/cob(II)alamin couple have been reported [472].

An interesting example of a metal induced ring contraction in a macrocyclic ligand has been published [473]. Ring contraction of the macrocycle (61) to the macrocycle (62) appears to be a consequence of a mis-match in metal ion size and cavity size of a non-flexible macrocyclic ligand. The X-ray crystal structure of the cobalt(II) complex of (62), $[CoL(OH_2)(MeOH)]^{2+}$, has established that cobalt(II) has a pentagonal bipyramidal environment, with five nitrogens in the equatorial plane and the water and methanol ligands in axial sites. Cobalt(II) complexes of the macrocycles $Me_4[14]1,3,8,10\text{-tetraeneN}_4$ (tim) and $Me_2[14]1,3\text{-dieneN}_4$ (dim) have been prepared. These complexes are formally five-coordinate in the solid state but exhibit a tendency towards six-coordination in the presence of potential axial ligands. This paper [474] provides a useful



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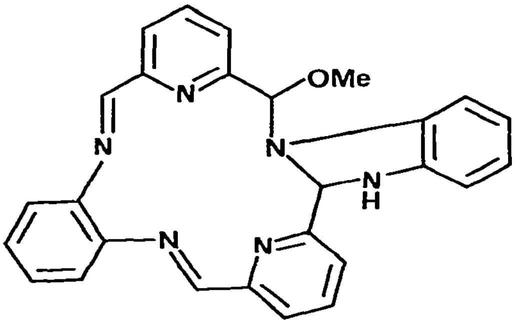
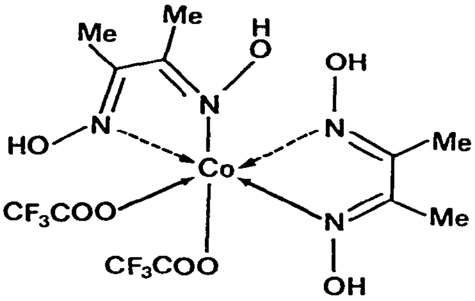


(62)

discussion of the stereochemistry of cobalt(II) complexes of macrocycles.

The only known cobaloxime of Co(II) which contains neither coordinated amine nor phosphine is [Co(dmgH)$_2$(H$_2$O)$_2$]. The new cobaloximes [Co(dmgH)(dmgH$_2$)(OAc)] and [Co(dmgH)(dmgH$_2$)]$_2$[CO$_3$] have been described and their use as hydrogenation catalysts has been discussed [475]. The reaction of dihydrogen with [Co(dmgH)$_2$] or its 1:1 pyridine adduct gives 3-aminobutan-2-one oxime, *via* hydrogenation of the coordinated [Hdmg]$^-$ group, [476]. Treatment of several alkyl(pyridine)-cobaloximes with an excess of trifluoroethanoic acid in chloroform gives the crystalline *cis*-cobaloxime(III) complex (63) [477]. In an atmosphere of air or



(63)

dioxygen, [Co(dmgH)$_2$(Ph$_3$P)$_2$] and [Co(dmgH)$_2$(py)] catalyse the oxidation of 1,4-dihydroxybenzene (to 1,2-benzoquinone), triphenylphosphine (to Ph$_3$P=O), and hydrazobenzene (to azobenzene) [478]. The reactions are quantitative at 20–25 °C.

EPR spectra of square planar cobalt(II) complexes of a variety of N_4-macrocyclic ligands [479] and cobalt(II) tetraphenylporphyrin have been reported [480]. The reversible oxygenation of complexes of cobalt(II) with macrocyclic tetraaza ligands has been studied [481] and the synthesis of the cobalt(II) complex of 1,10,11,20-tetrahydro-1,2,5,8,9,12-hexaazacyclotetradecine derivative has been described [482]. Other studies of cobalt(II) porphyrin complexes include: the reactivity of the pyrrolic nitrogen atoms of cobalt(II) porphyrin with diazoalkanes [483]; the kinetics of incorporation of cobalt(II) into tetraphenylporphine in dmf solution [484]; a spectrophotometric study of complex formation between hydroperoxide and cobalt(II)-tetraphenylporphyrin [485]. The synthesis of polystyrene-bound cobalt(II)-4,4',4'',4'''-tetracarboxyphthalocyanine has been described and its catalase-like activity has been assessed [486]. The cobalt(II) complex of dioxadiazacyclopentadecadiene [487] and the synthesis of a cobalt(II) complex of a tridentate macrocyclic ligand derived from picolinic hydrazide and pentane-2,4-dione [488] have been described.

4.3.3.3 *Phosphorus and arsenic donor ligands*

The crystal structures of bis(tribenzylphosphine oxide) dichlorocobalt(II) [489] and diaquabis(aminomethylphosphonate)cobaltate(II) monohydrate [490] have been determined. Evidence for cobalt(II) catalysis, and for the formation of an intermediate dioxygen adduct in the autooxidation of cobalt(II) chloride complexes of ethyl phosphinite, phosphonite and phosphite esters have been obtained [491]. Ion association between tribromo(triphenylphosphine)cobaltate(II) and substituted pyridinium cations in nitrobenzene has been investigated by ^{1}H NMR spectroscopy [492].

A number of cobalt(II) complexes of the substituted tritertiary arsine, 2-chloroethylbis(3-dimethylarsinopropyl)arsine (trias), have been prepared [493]. Both $[Co(trias)Br]_2[CoBr_4]$ and $[Co(trias)Br][ClO_4]$ appear to contain pseudo-tetrahedral cations, but $[Co(trias)_2][ClO_4]_2$ has been assigned a pentacoordinate structure containing a tridentate and a bidentate ligand.

Complexes of cobalt(II) cyanide with phosphine monoxides have been described [494]. The reaction of halotetrakis(phosphite)cobalt(II) with nitric oxide give new pentacoordinate mononitrosyl cobalt complexes [495]. The molecular structure of bromocarbonyl{1,1,1-tris(diphenylphosphinomethyl)ethane}cobalt(II) as the $[PPh_4]^+$ salt has been discussed [496].

4.3.4 *Miscellaneous topics*

Hexakis(thionitrosylfluoride)cobalt(II), $[Co(NSF)_6][AsF_6]_2$ has been the subject of a recent X-ray analysis [497]. Direct reduction and ligand substitution reactions in $[Co(ArNC)_5]^{2+}$ complexes have been studied [498] and the stability constants of cobalt(II)-azide complexes in aqueous solution have been determined [499].

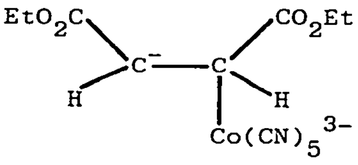
4.4 COBALT(I) AND COBALT(0)

4.4.1 *Cobalt(I)*

Kinetic studies of the reactions of acrylonitrile, methyl mercaptide and cyanide ion with the phosphine-cobalt(I) complex of bis(difluoroboryl)dimethylglyoximato cobaltate(I), $[Co(dmgBF_2)_2(PBu_3)]^-$ have been carried out [500]. The reaction occurs in a stepwise fashion, with dissociation of phosphine preceding entry of the other ligand. The reaction of electrogenerated $[Co^I(sal_2en)]$ with Me_3CBr or Me_3CCl gives $[Co^{II}(sal_2en)]$ and organic products [501]. All the available evidence is consistent with the formation of an unstable organometallic intermediate, which decomposes into $[Co(sal_2en)]$, 2-methylpropene and dihydrogen, the two latter products arising from the butyl radical.

The preparation of tris(phenylisocyanide)bis(triphenylarsine)cobalt(I) perchlorate has been described [502] and this compound may be used to prepare a number of disubstituted pentakis(phenylisocyanide)cobalt(I) complexes [503]. Triphenylphosphine and tris(4-chlorophenyl)phosphine replace arylisocyanide, in $[Co(CNR)_5]X$ ($X = [ClO_4]$ or $[BF_4]$) at 25 °C to give $[Co(CNR)_3(PR'_3)_2]X$ and/or $[Co(CNR)_4(PR'_3)]X$, depending upon the nature of the isocyanide, the phosphine and the reaction conditions [504]. The redox behaviour of mixed-ligand five coordinate cobalt(I) complexes of isocyanides and phosphines has been studied [505].

^{13}C and ^{1}H NMR spectroscopic evidence has been obtained for the formation of olefin π-complexes of $[Co(CN)_4]^{3-}$ with the ligands diethyl maleate, diethyl fumarate, disodium maleate, and disodium fumarate [506]. Diethyl maleate is isomerised to diethyl fumarate probably *via* a σ-complex (64) of a carbanion.



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The preparation of the stereochemically non-rigid complex, tetrakis(isocyanide)-(tetracyanoethene)cobalt(I) has been described [507], and the solution structure of some pentakis(arylisocyanide)cobalt(I) complexes investigated by NMR and IR spectroscopy [508]. The synthesis and X-ray analysis of a porphyrin-type cobalt(I) complex has also been studied [509].

4.4.2 Cobalt(0)

EPR studies of the tetrahedrally coordinated cobalt(0) complex bis(benzil-bis-*N*-phenylimine)cobalt(0) have been published [510].

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