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1. COBALT

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CONTENTS

INTRODUCTION

The present survey covers the bulk of the 1981 literature, together with references to the 1980 literature received too late to be included in the previous review. Books and review articles relevant to the area are summarised below. A two volume treatise providing a complete and comprehensive review of the major chemical, biochemical and medical aspects of vitamin B_{12} has been published [1]. A review dealing with "Recent Developments in the Studies of Molecular Oxygen Adducts of Cobalt(II) Compounds and Related Systems" has also appeared [2]. A recent edition of Inorganic Syntheses [3] includes an account of the preparation of cobalt(III) complexes of a variety of tetra-azamacrocyclic ligands. Activation volumes for the reactions of transition metal complexes in solution including cobalt(III) complexes have been reviewed [4] and mechanistic aspects of bioinorganic reactions in solution discussed [5]. The CD spectra of low-symmetry cobalt(III) complexes have also been reviewed [6] as has the charge-transfer photochemistry of cobalt(III) complexes [7]. Some additional reviews are also listed in the appropriate sections below.

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1.1 COBALT(III)

The subdivision which follows is somewhat arbitrary as almost all cobalt(III) complexes are mixed ligand complexes of one type another and the use of a single type of ligand classification thus has its limitations. Chemists working in the area tend to think in terms of ammines, bis-1,2-diaminoethane complexes, tetraamine complexes, etc., and this classification has been adopted in the review, even though the chemistry described may relate to other ligands present in the complex.

The work reported can be divided into three broad areas, (a) synthesis, (b) stereochemistry (including X-ray crystallography), and (c) kinetics, reactivity and mechanism. Kinetic work is not reported in great detail as this area is now covered in a new publication [8].

1.1.1 Complexes with oxygen donor ligands

1.1.1.1 Carbonates and β-diketonates

Five carbonato-complexes $[Co(CO_3)(ox)(tn)]^-$, *cis*-$[Co(CO_3)(ox)(py)_2]^-$, *cis-cis*-$[Co(CO_3)(NH_3)_2(py)_2]^+$, *cis*-$[Co(CO_3)(en)(py)_2]^+$ and *cis*-$[Co(CO_3)(NH_3)_2(bipy)]^+$ have been prepared and resolved [9]. Absolute configurations have been assigned on the basis of CD spectra.

Bis(pentane-2,4-dionato)cobalt(III) complexes containing a variety 2-aminoalkylphosphines or dppe have been prepared and resolved into optical isomers by SP-Sephadex column chromatography; ^{13}C NMR spectra of the complexes were also reported [10]. Titration calorimetry has been used to study the reaction of the lanthanide shift reagent $[Eu(fod)_3]$ with tris(β-diketonato)-cobalt(III) complexes of pentane-2,4-dione, benzoylacetone, and dibenzoylmethane in benzene [11]. The formal reduction potential of the couple $[Co(mal)_3]^{3-} + e^- = [Co(mal)_3]^{4-}$ is 0.741 V at $I = 1.0$ M (KCl). The value of $\log_{10}\beta_3$ for $[Co(mal)_3]^{3-}$ is calculated to be 23, and $\log_{10}\beta_3 = 29$ for $[Co(CO_3)_3]^{3-}$ [12].

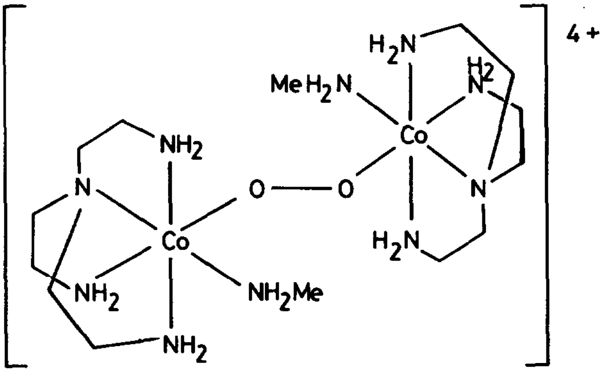
The photodecomposition of *cis*-$[Co(acac)(N_3)(NH_3)]^+$ occurs with the formation of $[Co(acac)_2]$ and azide radicals [13]. The crystal structure of *cis*-$[Co(3\text{-hydroxyimino-2,4-pentanedionato})_2(\text{pyridine})_2][ClO_4]$ has been determined [14]. Mechanisms for the electrochemical reduction of cobalt pentane-2,4-dionate complexes have been discussed [15], and the electrochemical generation and uses of cobalt(III) ethanoate have been described [16]. Other papers in this area have dealt with spectral studies on mixed ligand complexes of $Na[Co(acac)_2(NO_3)_2]$ with imidazole ligands [17], metal ion catalysis of the reduction of $[Co(C_2O_4)_2(OH_2)_2]^-$ by iodide ion in aqueous acid [18], and lanthanoid-induced ^{59}Co NMR shifts in $[Co(acac)_3]$ with $[Ln(fod)_3]$ and $[Ln(dpm)_3]$ [19].

The synthesis and characterisation of cobalt(III) complexes of the heterocyclic β-diketone, 1-phenyl-3-methyl-4-trifluoroethanoyl-5-pyrazolone, including proton NMR and IR studies, have been described [20]. Kinetic studies of the oxidation of methanoic acid by $[Co(H_2O)_6]^{3+}$ [21], and polyelectrolyte catalysis in the aquation of $[Co(C_2O_4)_3]^{3-}$ in binary mixtures of water with dmf or dmso [22], have been published.

The crystal structure of $[Co(acac)_3].2(selenourea)$, $C_{17}H_{29}CoN_4O_6Se_2$, has been reported [23], and cobalt(III) complexes of the ambidentate ligand isonitrosobenzoylacetone have been described [24]. The preparation, characterisation, and thermal stability of $[NH_4][Co(C_2O_4)_3].3H_2O$ have been discussed [25]. The reactions of sulphur and nitrogen donor ligands with $[Co(acac)_2(NO_2)_2]^-$, to give mixed ligand complexes, have been investigated [26].

1.1.1.2 Peroxide and superoxide ligands

The rate of exchange of ^{18}O in the complex (*1*), where trien is the tetradentate ligand, has been found to be the same as *both* the rate of decomposition by acids to cobalt(II) and O_2 and the rate of formation of $[(tren)Co(\mu\text{-}O_2,\mu\text{-}OH)Co(tren)]^3$ from (*1*) in neutral or basic solution [27]. The results indicate that a cobalt(II) complex is a common intermediate.

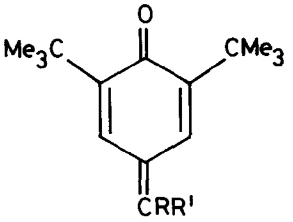


(1)

The crystal structure of $[(en)_2Co(NH_2)(O_2)Co(en)_2][NO_3]_3.15/8(AgNO_3).H_2O$ has been determined. The Ag atom is bound to each of the two peroxo-oxygen atoms, with an Ag-O bond length of 2.27(1) Å. The formation constant of Ag^+ and $[(en)_2Co(NH_2)(O_2)Co(en)_2]^{3+}$ in aqueous solution was found to be less than 0.5 [28].

Considerable success has been achieved in interpreting the charge transfer electronic spectra of superoxocobalt(III) complexes, but there is little information on the location of the $\pi\rightarrow\pi^*$ transition of terminally coordinated superoxide. A discussion on this topic has now appeared [29]. Resonance Raman studies on the potassium μ-peroxobis{pentacyanocobaltate(III)} ion, in $K_6[(CN)_5Co(O_2)Co(CN)_5].H_2O$, and the μ-superoxobis{pentacyanocobaltate(III)} ion, in $K_5[(CN)_5Co(O_2)Co(CN)_5].H_2O$, have appeared [30]. Additional resonance Raman investigations have been carried out with peroxocobalt(III) complexes of 1,2-diaminoethane and L-histidine [31], and peroxodicobalt(III)oxime complexes [32].

The superoxo-cobalt(III) complexes $[Co(salpr)(O_2)]$, $[NEt_4]_3[Co(CN)_5(O_2)]$ and $[(Ph_3P)_2N^+][Co(CN)_5(O_2)]$ react with methides of type (*2*) to give 2,6-di-*tert*-butyl-1,4-benzoquinone and the cyclohexadienonespirooxiranes (*3*) as



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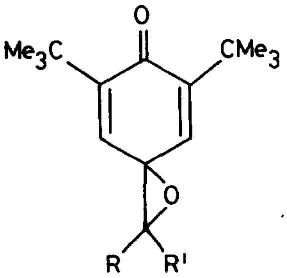


(*3*)

the major products, the latter resulting from the nucleophilic attack by the superoxo-species on the *exo* double bond of (*2*) [33].

1.1.2 Complexes with oxygen-nitrogen donor ligands

The deuteriation equilibrium

$$[Co(en)_2(glyO)]^{2+} + D^+ \rightleftharpoons [Co(en)_2(glyOD)]^{3+}$$

in strongly acidic solution has been investigated by ^1H NMR spectroscopy; similar pK_{BD^+} values (*ca.* -1.2) are observed in D_2SO_4 and DCl solutions [34]. The downfield ^{13}C NMR shifts of the α-carbons in *N*-alkylglycines chelated to cobalt(III) are larger than those in *C*-alkylglycines [35]. Several complexes of non-functionalised amino-acids, $[Co(en)_2(glyO)]^{2+}$ and $[Co(tren)(AA)]^{2+}$ (AA = glycinate, alaninate or leucinate), have been esterified, either by alkylation with dimethylsulphate or methyl toluene-4-sulphonate or by acid-catalysed esterification in methanol [36]. Complexes of the general types

$[Co(en)_2\{(S)\text{-}AB\}]^{2+}$ and $[Co(en)\{(S)\text{-}AB\}_2]^+$, where AB represents asparagine or glutamine, have been prepared and their electronic spectra, circular dichroism and ^1H NMR spectra determined [37].

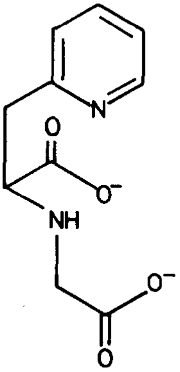
The complexes $[Co(CN)_2(gly)_2]^-$ and $[Co(CN)_2(\beta\text{-ala})]^-$, which have *cis*,*cis*,*cis* geometry with respect to the donor atoms *C*, *N* and *O*, have been prepared by a new method, and resolved into enantiomers [38]. The CD spectra of the resolved complexes have been determined [38]. The ^1H NMR spectra of carboxylate-bonded amino-acid complexes, $[Co(NH_3)_5\{OOCCH(R)NH_3\}]^{3+}$, have been studied [39]. In pentaammine(L-histidine)cobalt(III), the long range coupling between the imidazole C_4 hydrogen and only one of the β-hydrogens was observed, suggesting restricted rotation about the $C_\beta\text{-}C_\gamma$ bond.

The crystal structure and absolute configuration of one of the isomers of (+)K[Co(L-valinato)$_2$(CO$_3$)] has been determined and shown to be Λ(+)-*cis*(*N*)-*cis*(*O*)-K[Co(L-valinato)$_2\delta\delta$(CO$_3$)].2H$_2$O [40]. In the presence of air, the reaction of [Co(α-Mesal$_2$en)] with *L*-aaH {where α-Mesal$_2$en represents the dianion of *N*,*N'*-ethylenebis(α-methylsalicylideneamine) and *L*-aaH denotes *L*-proline, hydroxy-*L*-proline, or *allo*-hydroxy-*L*-proline} proceeds rapidly to give Λ-*cis*-β_2-[Co(α-Mesal$_2$en)(*L*-aa)] stereoselectively, followed by the slow isomerisation of the Λ-*cis*-β_2-isomer to the Δ-*cis*-β_2-isomer in a yield of *ca.* 100% under equilibrium conditions [41]. Further studies of this type of reaction, using *N*-benzyl-*L*-alanine, *N*-methyl-*L*-alanine or *N*-benzyl-*N*-methyl-*L*-alanine, have been reported [42] and the stereospecificity of the (1S,2S)-*N*,*N'*-1,2-cyclohexylenebis(salicylideneaminato)cobalt(III) complex towards *N*-benzyl-L-alanine observed.

Peptide complexes of the type $[Co(dipeptidato)_2]^-$ (where dipeptidato denotes the dianions of glycylglycine, glycyl-β-alanine, glycyl-L-alanine, glycyl-L-leucine, β-alanylglycine, β-alanyl-L-alanine, L-alanylglycine, L-alanyl-β-alanine, L-leucylglycine or L-prolylglycine) and the complex $[Co(gly\text{-}gly)(L\text{-}pro\text{-}gly)]^-$ have been prepared by oxidation of the cobalt(II) complexes with lead dioxide [43]. These complexes have been separated into two diastereoisomers or enantiomers by column chromatography and the absolute configurations of the optical isomers determined on the basis of their CD spectra.

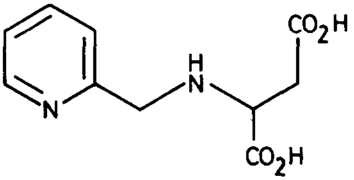
Chromatographic techniques, using SP-Sephadex ion exchangers, have been applied successfully over the last decade to resolve optical isomers and to separate geometrical isomers of metal complexes. The preparation of Sephadex derivatives derived from L-alanine, L-valine, L-aspartic acid and L-threonine has been described [44]. Their application to the resolution of some cobalt(III) complexes (e.g. *mer*-[Co(gly)$_3$]) has been studied; partial resolution was achieved.

The synthesis and spectral characterisation of *fac*- and *mer*-[*N*-carboxymethyl)-*L*-β-(2-pyridyl)-α-alaninato](D-threoninato)cobalt(III), *i.e.* [Co(*N*-Cm-L-Pyala)(D-Thr)] (where (*4*) = *N*-Cm-L-Pyala) and the molecular



(4; *N*-Cm-L-Pyala)

structure of the *mer*-isomer have been reported [45]. A series of mixed-ligand cobalt(III) complexes of the type [Co(plasp)(AA)] (where plasp = *N*-(2-pyridylmethyl)-L-aspartate (*5*) and AA^- is a bidentate amino-acidate ligand)

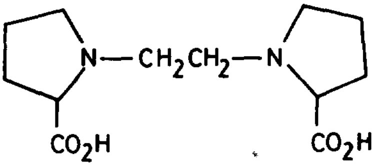


(5;plasp)

have been prepared. For glycinate, α-aminoisobutyrate, L-alaninate, L-threoninate, L-prolinate, D- and L-asparaginate, D- and L-phenylalaninate and D-, L- and DL-valinate, only the *fac*-$\{Co^{III}N_3O_3\}$ isomer, in which the β-CO_2^- group of $[plasp]^{2-}$ is coordinated *trans* to the pyridyl group of $plasp^{2-}$, was isolated [46].

A series of ternary cobalt(III) complexes of $[edda]^{2-}$ and bidentate azo ligands have been prepared and characterised as models for cobalt(III) azo protein derivatives [47]. Asymmetric induction on the decarboxylation of α-amino-α-alkylmalonic acids chelated to chiral cobalt(III) complexes of 2,3,2-tet and trien has been studied [48]. The ^1H NMR spectrum (400 MHz) of cobalt(III)bleomycin (a glyco-peptide antibiotic) has been studied in detail [49]. Crystal structures of cobalt(III) *N,O* complexes reported this year include:

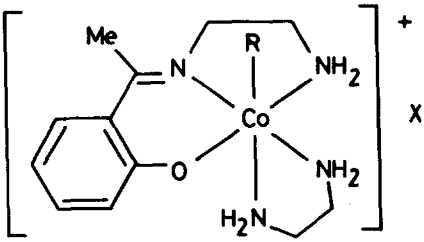
$(+)_{546}$-*cis*-α-sodium carbonato[(2S,2'S)-1,1'-ethylenedi-2-pyrrolidinecarboxylato-(2-)]cobaltate(III) trihydrate, *i.e.* $Na[Co(pren)(CO_3)].3H_2O$ {where H_2pren = (*6*)}



(6)

[50], lithium[(R,S)-*N*,*N*'-ethylenediaminedisuccinato]cobaltate(III) trihydrate, *i.e.* $Li[Co(C_{10}H_{12}N_2O_8)].3H_2O$ [51], and tris(picolinato)cobalt(III) monohydrate [52].

Cobalt(III) complexes containing tripodlike quadridentate ligands, such as tris(2-aminoethyl)amine or nitrilotriacetate, and a chiral bidentate (L-amino carboxylate or (R)-propylenediamine) have been prepared and separated into their respective geometrical isomers [53]. The oxygenation of 2,6-di-*t*-butylphenols with five-coordinate cobalt(II) Schiff-base complexes in aprotic solvents, such as CH_2Cl_2, thf, or dmf, results in regioselective formation of peroxyquinolatocobalt(III) complexes [54]. Representatives of a novel class of σ-organocobalt(III) complexes, (*7*), which contain both a tridentate and a bidentate ligand have been characterised and X-ray data obtained [55].



(7; R = Me, Et or Bu;
X = Br or $[ClO_4]$)

The kinetics of the reduction cobalt(III)-edta complexes with chromium(II) have been studied by stopped-flow techniques [56]. Electrode kinetics of the redox couples of cobalt(III)/cobalt(II) complexes with ethylenediamine-*N*-acetate (edma), iminodiacetate or diethylenetriamine have been investigated [57]. The potentials corresponding to the redox processes $[Co^{II}L]^0 \rightleftharpoons [Co^{III}L]^+$, for cobalt complexes with tetradentate Schiff bases (sal_2en or $acac_2en$) and

$[Co^{III}L(R)]^{0} \rightleftharpoons [Co^{IV}L(R)]^{+}$ for their organometallic derivatives have been determined in different donor solvents [58].

A new synthesis of (R)- and (S)-2-deuterioamino acids, including (R)- and (S)-2-deuterio-glycine has been described using stereochemically inert cobalt(III) complexes [59]. A recent thesis has dealt with stereoselective coordination of optically active amino-acids and their derivatives to cobalt(III) [60]. Photochemical decarboxylation of $[Co(phen)_2(gly)]^{2+}$ has been studied [61], as has the reduction of cobalt(III)-bovine carbonic anhydrase with L-ascorbic acid [62]. A further investigation has dealt with the kinetics and mechanism of hydrazine oxidation by the $[Co_2(L\text{-}his)_4O_2]$ complex [63].

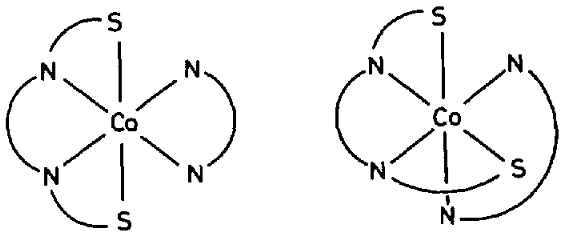
The synthesis and photolysis of dicyano(ethylenediamine-*N*,*N*'-diacetato)-cobaltate(III) and dicyanobis(glycinato)cobaltate(III) complexes has been described [64]. The complexes hydroxyaquaglycinatobiguanidecobalt(III) and *cis*-β-dichloroglycinatobiguanidecobalt(III) have also been characterised [65]. Related synthetic work has dealt with the preparation and reactions of *uns-fac* isomers of the bis(*N*-alkyliminodiacetato)cobaltate(III) ions [66]; the preparation and characterisation of cobalt(III) complexes of glycine methyl ester [67], and a variety of amine derivatives of $[Co(salen)]^{+}$ [68]. Other studies have dealt with the stereochemistry of cobalt(III) complexes with *N*-substituted ethylenediamine-*N*,*N*'-diacetic acids and 1(*R*),2(*R*)-1,2-cyclohexanediamine [69].

Complexes of cobalt(III) with α-furil dioxime(LH) of the general type $[CoXL_2Y]$ (X = Cl, Br, or NCS; Y = NH_3, py, or thiourea) and of the type $[CoL_2Y_2]X$ (Y = thiourea, or PPh_3; X = Cl, Br, or NO_3) have been characterised [70].

1.1.3 Complexes containing sulphur donor ligands

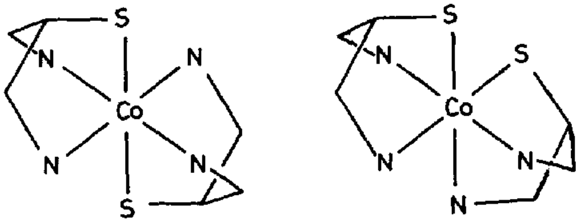
Cobalt(III) complexes containing the multidentate ligands 3,6-dimethyl-3,6-diazaoctane-1,8-dithiol $\{HSCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2SH = H_2eddt\}$ and 1,3-diamino-2-propanethiol $\{NH_2CH_2CH(SH)CH_2NH_2 = Hdqt\}$ have been characterised [71]. The geometrical isomers of $[Co(eddt)(en)]^{+}$ and $[Co(dqt)_2]^{+}$ have been separated by column chromatography and their geometrical configurations (*8*) and (*9*) assigned on the basis of ^{13}C NMR and UV spectra. The sulphur → nitrogen charge transfer band of the *trans*(*S*)-isomer appears at a lower energy than that of the *cis*-isomer.

Some sulfenic acids which are *S*-coordinated to cobalt(III) are more stable than their corresponding free acids, and the crystal structure and absolute configuration of one such example, the d-tartaric acid salt, $d\text{-}C_4H_6O_6.(+)^{CD}_{500}\text{-}[Co\{S(O)CH_2CH_2NH_3\}_3].H_2O$, has now been obtained [72]. Dipole



trans(S) *cis(S)*

(8; two geometrical isomers of $[Co(eddt)(en)]^+$)

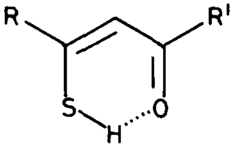


trans(S) *cis(S)*

(9; two geometrical isomers of $[Co(dqt)_2]^+$)

moments have been determined for cobalt(III) complexes of the fluorinated monothio-β-diketones $RC(SH){=}CHCOCF_3$ (R = 5'-methyl-2'-thienyl, 5'-chloro-2'-thienyl, 4'-isopropylphenyl, 4'-*tert*-butylphenyl or 3'-fluoro-4'-methoxyphenyl) [73]. The ^{13}C and ^{19}F NMR spectra of perfluoroethylmonothio-β-diketonate complexes, of the type $M[RC(S)CHC(O)C_2F_5]_n$ {M = Co(III), Ni(II) or Pd(II)} have been determined [74]. These ^{13}C NMR data support a *fac*-octahedral geometry for the cobalt complex (n = 3). ^{13}C and ^{19}F NMR spectra have also been recorded for the cobalt(III) complexes of 1,1-difluoro-4-mercapto-4-(2'-thienyl)but-3-en-2-one, 1,1,1-trifluoro-4-mercapto-4-(2'-thienyl)but-3-en-2-one, and 1,1,1-trifluoro-4-mercapto-4-(2'-naphthyl)but-3-en-2-one, with the structures shown in (*10*) [75]; the data support a *fac* geometry for the various complexes.

The synthesis of cobalt(III) complexes containing cysteine and penicillamine, as analogues for the active metal sites of cysteine and cysteamine dioxygenases has been described in a recent thesis [76]. The work also discussed the oxidation of the complexes. Geometrical isomerism in cobalt(III) complexes



(10; R = 2'-thienyl; R' = CHF_2;
R = 2'-thienyl; R' = CF_3;
R = 2'-naphthyl; R' = CF_3)

with multidentate thiolato ligands has also been discussed [77]. Other studies have dealt with cobalt(III) complexes with potassium *N*-butylxanthate [78] and cobalt(III) complexes with triazolinethiones [79]. The crystal structures of trithiosemicarbazidecobalt(III) chlorides have been determined [80].

1.1.4 Complexes with nitrogen donor ligands

1.1.4.1 Ammines

Facile synthetic routes to cobalt(III) amine complexes of the labile unidentate trifluoromethanesulphonate anion, $[CF_3SO_3]^-$, *e.g.* $[Co(NH_3)_5(OSO_2CF_3)]^{2+}$, *cis*-$[Co(en)_2(OSO_2CF_3)_2]^+$ and *fac*-$[Co(dien)(OSO_2CF_3)_3]$ have been developed [81]. These complexes can be used to prepare a large variety of derivatives, for example in the pentaamminecobalt(III) system, the syntheses of $[Co(NH_3)_5L]^{n+}$ (L = OH_2, NH_3, CH_3OH, CH_3CH_2OH, CH_3CN, $OP(OCH_3)_3$, dmf, dmso, urea, $NCNH_2$, $[CH_3CO_2]^-$, or $[Cl_2CHCO_2]^-$) in high yield are reported.

The syntheses of $[(NH_3)_5Co(OSO_2R)][ClO_4]_2$ (R = CH_3, CF_3, or $4\text{-}NO_2C_6H_4$) have been described, and the kinetics of acid and base hydrolysis studied [82]. The extreme lability of the complex is seen in the aquation (k_{H_2O}) and base hydrolysis (k_{OH}) rate data. Thus, for R = CF_3, $k_{H_2O} = 2.7 \times 10^{-2}$ s^{-1} and $k_{OH} = 10^6$ $M^{-1}s^{-1}$ at 25 °C and I = 1.0 *M*.

Fluorosulphonic acid is the strongest simple acid known [83]. The labile complex $[Co(NH_3)_5(O_3SF)][ClO_4]_2$ has been synthesised [84] and its rate of aquation studied ($k_{H_2O} = 2.2 \times 10^{-2}$ s^{-1} in 0.01 *M* $HClO_4$ at 25 °C). The complex solvolyses with Co–O cleavage to give $[Co(NH_3)_5(solvent)]^{3+}$ and, concurrently, with S-F cleavage to give $[Co(NH_3)_5F]^{2+}$ and SO_3 rather than $[Co(NH_3)_5(OSO_3)]^+$ and F^-. Five new complexes, $[(NH_3)_5Co(dicarboxylate)Co(NH_3)_5]X_4$, (dicarboxylate = oxalate, succinate, pimelate, fumarate or maleate; X = $[ClO_4]$ or Cl) have been prepared and characterised by their chromatographic behavior and electronic and NMR spectra [85].

In a recent paper [86], it was concluded that an intense absorption in the UV region observed for $[Co(NH_3)_5(NH_2CH_2CH_2NH_2)]^{3+}$ was a charge-transfer band, due to intramolecular hydrogen bonding between the free amino group and an NH proton on the cobalt(III) centre. A number of other pentaamminecobalt(III) complexes containing a variety of substituted 1,2-diaminoethanes have now been prepared and their pK_a values determined [87]. The spectral characteristics are discussed in terms of the hydrogen bonding mentioned above.

The dinuclear μ-carbonato complex $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co(NH_3)_3][SO_4].5H_2O$ has been prepared and its structure determined by X-ray crystallography [88]. The carbonate ligand causes some perturbation in the octahedral environment about the cobalt(III) ions. The two complexes $[Co(NH_3)_4L]Cl_2.H_2O$ and $[Co(NH_3)_2(L)_2]Cl.H_2O$, where L is the anion of 8-hydroxyquinoline, have been prepared and characterised [89]. The deep green paramagnetic tetraammine-5-tetraammine-5-nitrosalicylato-cobalt complex, originally considered as a cobalt(IV) compound, has been investigated by X-ray photoelectron and other spectroscopic techniques [90]. The EPR, NMR, IR and photoelectron spectral data suggest that the electron deficiency is not centred on cobalt but is delocalised over the cobalt atom and the organic ligand.

The complex $[Co(NH_3)_6][HgCl_5]$ has been prepared and its crystal structure determined. The average Co-N bond distance is 1.960(6) Å [91]. The ^{35}Cl NQR spectrum was also reported in this paper. The interaction of pyridine-2-carboxylato-pentaamminecobalt(III) and pyridine-3-carboxylatopentaammine-cobalt with Co(II), Ni(II), Cu(II), and Zn(II)

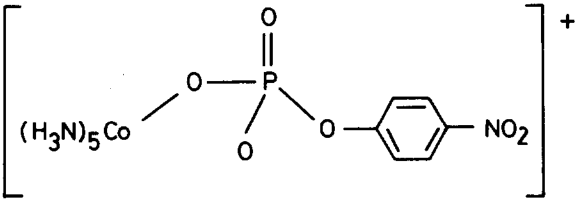
$$i.e.\quad [(NH_3)_5CoL]^{2+} + M^{2+} \overset{K}{\rightleftharpoons} [(NH_3)_5CoLM)]^{4+}$$

has been studied and the formation constants K determined at 30 °C and $I = 0.3\ M$ [92]. Thermal studies on the compounds $[Co(NH_3)_5(H_2O)][M(CN)_6]$ {where M = Co(III), Fe(III) or Cr(III)} have been carried out; only in the case of M = Co(III), was dehydration separated from the loss of HCN [93].

The ^1H and ^{13}C NMR spectra of $[Co(NH_3)_5(imidH)]^{3+}$ and the ^1H NMR spectra of *cis*-α-$[Co(tren)(imidH)_2]^{3+}$ and *cis*-β-$[Co(tren)(imidH)_2]^{3+}$ have been studied [94]. The pK_a values, determined from the dependence of the chemical shift on pH, are 10.0, 9.6 and 10.1, respectively, for the ionisation equilibrium (1).

$$[L_5Co(imidH)]^{3+} \rightleftharpoons [L_5Co(imid)]^{2+} + H^+ \qquad (1)$$

A number of interesting papers have appeared dealing with the reactions of various ligands coordinated to the $\{Co(NH_3)_5\}^+$ moiety. The (4-nitrophenylphosphato)pentaamminecobalt(III) ion (*11*) undergoes base hydrolysis to generate 4-nitrophenolate ion, 4-nitrophenylphosphate ion and



(11)

hydroxo(phosphoramido)tetraamminecobalt(III) [95]. The ester hydrolysis is accelerated at least 10^8 fold, relative to uncoordinated 4-nitrophenylphosphate.

Base hydrolysis of coordinated acetyl phosphate in $[(NH_3)_5Co(OPO_3COCH_3)]^+$ (k_{OH} = 0.53 $M^{-1}s^{-1}$, 25 °C and I = 1.0 *M*) has been shown to proceed with exclusive carbon-oxygen bond fission [96]. The hydrolysis of acetylphosphate monoanion was also shown to be significantly catalysed by the kinetically inert hydroxocomplex $[(NH_3)_5Co(OH)]^{2+}$ (k_{OH} = 2.9 x 10^{-2} $M^{-1}s^{-1}$, 25 °C), which operates via a nucleophilic pathway involving attack at carbonyl carbon. The $[Co(NH_3)_5(NH_2CH_2COCH_3)]^{3+}$ ion undergoes an intramolecular base-catalysed cyclisation reaction to produce a coordinated carbinolamine, which undergoes a slower base-catalysed dehydration to give a chelated imine [97]. The synthesis, characterisation, and kinetics of formation of various reaction products have been described. The base hydrolysis of coordinated acrylonitrile in $[(NH_3)_5Co(N{\equiv}CCH{=}CH_2)]^{3+}$ to the acrylamide complex in carbonate buffer follows the rate law $k_{obs} = k_{OH}[OH^-] + k_c[CO_3^{2-}]$ [98]. Hydrolysis by $[CO_3]^{2-}$ has been shown by ^{18}O studies to involve direct nucleophilic attack at the nitrile group by $[CO_3]^{2-}$, with subsequent elimination of CO_2.

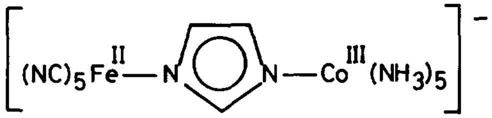
The reaction of $[Co(NH_3)_4(OH_2)_2]^{3+}$ with oxalate has been found to occur in a single stage [99]. The kinetics of this process were interpreted in terms of an ion pairing mechanism, with an ion-pairing equilibrium constant of 0.52 for $H_2C_2O_4$ and 5.3 from $[HC_2O_4]^-$. The effect of nitrate ion on the kinetics has also been studied [100] and the anation of $[Co(NH_3)_4(OH_2)_2]^{3+}$ by oxalate has been investigated in the pH range 3.0-4.0 [101]. The kinetics of the anation of $[Co(NH_3)_5(OH_2)]^{3+}$ by $H_2PO_4^-/H_3PO_4$ have been studied over a temperature range [102]. The results indicate a rate law of the type $k_{obs} = k[H_2PO_4^-]$ with no (or only a small) contribution from H_3PO_4.

Solvent-interchange reaction rates have been determined for $[Co(NH_3)_5(NCCH_3)][ClO_4]_3$ in MeCN/H_2O and in MeCN/dmso solvent mixtures [103]. A kinetic study of the aluminium(III)-assisted aquation of $[Co(NH_3)_5F]^{2+}$ has been carried out, the rate equation is of the form $k_{obs} = k_{Al}[Al^{3+}]$, with k_{Al} = 1.6 x 10^{-3} $M^{-1}s^{-1}$ at 25 °C and I = 2.0 *M* [104]. The acceleration of the mercury(II) induced aquation of $[Co(NH_3)_5X]^{2+}$ (X = Cl or Br) by the mucopolysaccharides chondroitin sulphate A and C has been investigated, as a function of the concentrations of the polyion and mercury(II), of pH and of the ionic strength [105]. Activation volumes have been determined for the acid-independent and acid-dependent aquation pathways of $[Co(NH_3)_5(SO_4)]^+$ [106], and for the aquation of alcoholpentaamminecobalt(III) ions, $[Co(NH_3)_5(OHR)]^{3+}$ {where R = H, CH_3, CH_3CH_2 or $CH(CH_3)_2$} [107].

The ^2H-^1H exchange rates on the fully *N*-deuteriated derivatives of $[Co(NH_3)_6][ClO_4]_3$, $[Co(NH_3)_5Cl][ClO_4]_2$, $[Co(NH_3)_5F][ClO_4]_2$, and *trans*-$[Co(RS\text{-}2,3,2\text{-}tet)Cl_2][ClO_4]$ have been determined using liquid ammonia as solvent [108].

Irradiation of $[(NC)_5Co(\mu\text{-}CN)Co(NH_3)_5]$, in the wave-length range 254-365 nm, leads to photoaquation of the pentacyanocobaltate(III) centre giving $[Co(CN)_5(OH_2)]^{2-}$ and $[Co(NH_3)_5(CN)]^{2+}$ as products, with large quantum yields (0.2-0.3 mol einstein^{-1}) [109]. Oxidation of $[Co(NH_3)_5(N_3)]^{2+}$ with hydroxyl radicals ($k = 1.1 \times 10^9\ M^{-1}s^{-1}$) gives a surprisingly stable coordinated radical, presumed to be $[Co(NH_3)_5(NNNOH\cdot)]^{2+}$, which decays by a first-order intramolecular redox process ($k = 60 \pm 10\ s^{-1}$ at 25 °C) to give Co(II), N_2 and N_2O as products [110]. The reduction of several cobalt(III) ammine complexes by various hydroxyalkyl radicals produces cobalt(II) [111]. The thermal behaviour of a number of pentaamminenitrosylcobalt(III) complexes has been studied [112]; in the simple nitrosyl $[Co(NH_3)_5(NO)]Cl_2$, the NO^- group reduces the cobalt(III) ion and dissociates as NO.

The reaction of (imidazolato)pentaamminecobalt(III) with $[Fe^{II}(CN)_5(OH_2)]^{3-}$ proceeds in two stages, with the first stage leading to the imidazolate-bridged precursor complex (*12*) and the second stage involving intramolecular electron transfer from Fe(II) to Co(III) in (*12*) [113]. The alteration of intramolecular electron-transfer rates by bridging groups in complexes of the type $[(O_2NPh\text{-}X\text{-}CO_2)Co^{III}(NH_3)_5][ClO_4]_2$ {X = CH_2(2, 3 or 4), CH=CH(2, 3 or 4), $CH_2CH_2CH_2$(4), $CONHCH_2$(4) or $CONHCH_2CONHCH_2$(4)} has also been investigated [114].



(12)

The kinetics of the outer-sphere reductions of a series of binuclear μ-(carboxylato)-di-μ-hydroxo-bis(triammine)cobalt(III) cations (carboxylate =

methanoate, ethanoate, or mono-, di- or trifluoroethanoate) by various reductants, $[Cr(OH_2)_6]^{2+}$, $[V(OH_2)_6]^{2+}$, $[Ru(NH_3)_6]^{2+}$, $[Ti(dipic)_2]^-$ and $[Fe(dipic)_2]^{2-}$, (dipic = pyridine-2,6-dicarboxylate) have been determined at 25 °C [115]. An increasing oxidising ability of the Co(III) centres with increasing electron-withdrawing capability of the substituents is noted. Bromide ion has been shown to be a poor bridging ligand for Co(III)-Ti(III) electron transfers, whilst hydroxide ion and especially fluoride ion are efficient bridging ligands [116]. Thus $[Co(NH_3)_5Br]^{2+}$ reacts with $[Ti(H_2O)_5(OH)]^{2+}$ with $k = 0.18\ M^{-1}s^{-1}$ while $[Co(NH_3)_5F]^{2+}$ reacts with $[Ti(H_2O)_6]^{3+}$ with $k = 1 \times 10^3\ M^{-1}s^{-1}$ at 25 °C. Electron transfer reactions between the μ-peroxo-complexes $[(H_3N)_5Co(\mu\text{-}O_2)Co(NH_3)_5]^{4+}$, $[(H_3N)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4]^{3+}$ or $[(L)_2Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(L)_2]^{3+}$ (L = en, bipy, or phen) and $[Ru(bipy)_3]^{3+}$, to give the corresponding superoxo-complex and $[Ru(bipy)_3]^{2+}$ have been studied using flash-photolysis techniques [117].

The synthesis of $[(pmdt)Cu(imid)Co(NH_3)_5][ClO_4]_4$ has been reported and its crystal structure determined [118]. The Co-*N*(imidazolate) bond distance is 1.933(5) Å. The pK_a values for the mononuclear components $[(NH_3)_5Co(imidH)]^{3+}$ and $[(pmdt)Cu(OH_2)]^{2+}$, generated from the bridged complex in solution, are in good agreement with those previously reported.

The kinetics of the chromium(II) reduction of complexes of the type $[Co(NH_3)_5(NCCH_2R)]^{3+}$ (R = H, CH_2CN, CO_2CH_3, $CONH_2$, or CO_2H) have been studied in detail [119]. The kinetics of reduction of $[Co(NH_3)_4(C_2O_4)]^+$ by oxalato-complexes of titanium(III) have also been investigated [120].

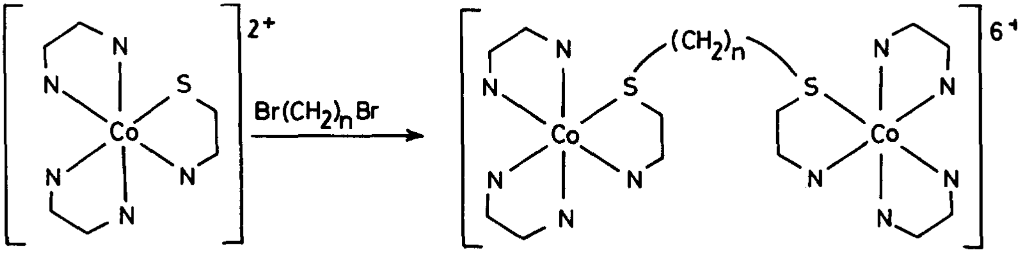
The complex 2-(5-cyanotetrazolato)pentaamminecobalt(III) perchlorate is a useful inorganic explosive [121]. Double ligand-exchange reactions between $[Co(NH_3)_5F]^{2+}$ and dicarboxylato complexes of aluminium(III) have been studied [122]. The preparation and optical resolution of a novel triammineglycinatonitrocobalt(III) complex has been described [123], as has the synthesis and characterisation of (monomethylcarbonato)pentaaminecobalt(III) perchlorate [124].

Crystal structures have been published for the novel phosphate complexes $[Co(NH_3)_3(H_2P_3O_{10})]$, containing the α, β, γ-tridentate ligand [125], and the α, γ-bidentate tetraamine(dihydrogentriphosphato)cobalt(III) monohydrate [126]. The molecular structure of $[Co(NH_3)_4\{(\pm)\text{-pentane-2,4-diamine}\}]$ dithionate has also been discussed [127]. The structures of pentaamminepyrophosphatocobalt(III) monohydrate, containing monodentate pyrophosphate and tetraamminepyrophosphatocobalt(III) dihydrate, $[Co(NH_3)_4(HP_2O_7)].2H_2O$, containing bidentate pyrophosphate, have also been determined [128].

Kinetic studies have dealt with the aquation of $[Co(NH_3)_5(dmso)]^{3+}$ in aqueous cetyltrimethylammonium bromide solutions [129], the oxidation and reduction of $[Co(NH_3)_6]^{3+}$ in alkaline media [130] and the linkage isomerisation of $[Co(NH_3)_5(ONO)]^{2+}$ in polyvinylalcohol [131]. Other kinetic investigations have included studies on *cis-trans* isomers of $[Co(NH_3)_4Cl_2]Cl$ [132], NMR and magnetic susceptibility studies of nitroamminecobalt(III) complexes [133], the interaction of $[Co(NH_3)_6]Cl_3$ with nitric oxide [134], and a reinvestigation of the structure of μ-hyperoxobis(pentaamminecobalt)tris(hydrogensulphate)monosulphate at room temperature and 17 K [135].

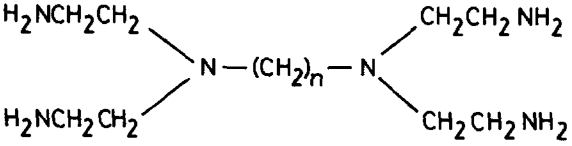
1.1.4.2 Diamines

The reaction of (2-aminoethanethiolato)bis(1,2-diaminoethane)cobalt(III) (*13*) with α,ω-dibromoalkanes $Br(CH_2)_nBr$ (n = 1-8 or 10) gives a series of novel monobridged dinuclear cobalt(III) complexes (*14*) [136]. Three isomers are possible (*meso*, ΛΛ and ΔΔ). In the case of n = 2, two geometrical isomers *meso* and *rac* were isolated and identified.

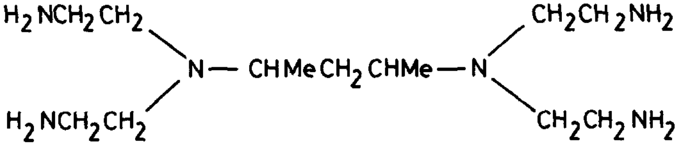


(13) (14 ; meso)

Complexes of the type $[Co(en)(pn)(AA)]^{n+}$ (where AA is a bidentate ligand, but not pn or en) have hitherto been unknown. However, the preparation of complexes of this type have now been described [137]. Cobalt(III) complexes of a number of new sexidentate ligands based on diamine systems, (*15*) and (*16*), have been prepared [138]. All of the complexes were resolved, except the RR-tptn complex which formed the Δ-isomer exclusively. The monocyano-complexes of ten and ttn, in which the ligands are quinquidentate, were also prepared. Absorption and *d-d* spectra of these complexes and the known $[Co(ten)]^{3+}$ complex have been compared. Cobalt(III) complexes of the *trans*(*O*)-$[Co(en)_2(OCOR)_2]^{n+}$ type (OCOR denotes an amino acid or aliphatic carboxylic acid) have been prepared [139]. A linear correlation was observed between the ^1E_g component of the first *d-d* band and the ^{13}C chemical shifts of the carboxyl- and α-carbons. The ^1H NMR spectra (amine region) of the *cis*-$[Co(en)_2X_2]^{n+}$ complexes (X_2 = $(CN)_2$, $(NO_2)_2$, acac, mal, or ox) have been determined using d_6-dmso and D_2O as solvent [140].



(15; *n* = 2, ten; *n* = 3, ttn; *n* = 4, ttmd)



(16; R,R- and R,S-tptn)

One of the NH hydrogens undergoes large, counterion-dependent shifts in d_6-dmso and is assigned to the *trans* hydrogen which is approximately parallel to the C_2 axis. In the nitro compound, this hydrogen is the first to be deuterated in D_2O.

The aminosulphonic acid complexes *cis*-$[Co(en)_2\{NH_2(CH_2)_nSO_3\}Cl]Cl$ (*n* = 1 or 2) have been prepared and their hydrolysis in basic solution investigated [141]. The complex ion $[Co(metn)_3]^{3+}$ (metn = 2-methyl-1,3-diaminopropane) has been synthesised and the *fac* and *mer* isomers separated by column chromatography and identified by ^{13}C and ^{1}H NMR spectroscopy [142]. The preparation of *N*-arylmethylglycinatobis(1,2-diaminoethane)cobalt(III) complexes has been described [143], for aryl = phenyl, 2-methyl-phenyl or naphthyl. The diastereotopic glycinate methylene protons in the 2-methylphenyl and naphthyl derivatives proceeds non-stereoselectively in borax buffer (pD 9.7), in contrast to the observations for the phenyl derivative.

The Pfeiffer effect [144] refers to a shift in a chiral equilibrium between the two enantiomers of a labile metal complex in solution upon the addition of an optically active compound, (often called a chiral environment substance). The Pfeiffer effect of $[Cr(C_2O_4)_3]^{3-}$ has been examined, using the optically stable metal complexes of the type *cis*-$[Co(diamine)_2(X)(Y)]^{n+}$ (diamine = en or tn; X,Y = anionic monodentate ligands) [145]. It was found that the chiral equilibrium of $[Cr(C_2O_4)_3]^{3-}$ is always displaced in favour of its Δ enantiomer in the presence of Λ enantiomers of those complexes added as an environmental substance.

Stereoselective ion pair formation between $[Co(en)_3]^{3+}$ and $[Co(C_2O_4)_2(gly)]^{2-}$ has been investigated [146]. The Δ-$[Co(C_2O_4)_2(gly)]^{2-}$ ion, like *L*-tartrate ion and $[Sb_2(\mathit{L}\text{-tart})_2]^{2-}$, unambiguously discriminates Λ- from Δ-$[Co(en)_3]^{3+}$ in solution. Solubility isotherms of systems containing optically active $[Co(en)_3]^{3+}$ have been studied in detail [147]. The crystal structure and absolute configuration $[\Delta(\delta\delta\delta)\text{-}Co(en)_3][(+)_{589}\text{-}(R,R)\text{-}tart]Cl\cdot 5H_2O$ has been determined [148], in an effort to document the mechanism(s) of chiral resolution by simple resolving agents, such as tartrate and its derivatives. A variety of other crystal structures dealing with diamine derivatives have been determined. These include: *cis*-$[Co(en)_2(imidazole)Cl]Cl_2$ [149], $[(+)Co(en)_3][(-)Cr(en)_3][SCN]_6$ [150], *cis*-$[Co(en)_2(NCS)_2]Cl\cdot H_2O$ containing the isocyanate ligand [151], and $[Co\{(\pm)\text{-}ptn\}(NH_3)_4][S_2O_6]_{1.5}\cdot 2H_2O$ (where ptn = 3,4-diaminopentane) [152]. In this latter complex, the six-membered diamine chelate ring has a skew-boat conformation in which the two methyl groups are in equatorial orientations. A strain energy minimisation calculation reveals an energy difference of 8.3 kJ mol^{-1} between the preferred skew-boat conformation and the chair conformation.

During attempts to prepare *trans*-$[Co(en)_2Cl_2]Cl$ from $CoCl_2.6H_2O$, 1,2-diaminoethane and H_2O_2 by the method of Krishnamurthy [153], the complex *trans*-$[Co(en)_2Cl_2]_2[CoCl_4]$ was isolated [154]. The compound is paramagnetic, $\mu_{eff} = 3.71\ \mu_B$ {somewhat less than expected for tetrahedral cobalt(II)}, and the crystal structure has been determined.

The complex Δ-*cis*(*O*,*O*),*trans*(*O*,*O*)-$[(en)_2Co(tart^{3-})Co(tart^{1-})(en)_2]Na[ClO_4]_3.5H_2O$ has been prepared by the reaction of L-tartaric acid with $[Co(en)_2(CO_3)]Br$ [155]. *X*-ray analysis has confirmed that the complex contains a dimeric cation, in which two cobalt atoms are bridged *via* a tridentate tartrate anion. The configuration about one cobalt is Δ-*cis* and about the other *trans*(*O*,*O*).

The complexes $[Co(en)_2(quin\text{-}8\text{-}O)]Cl_2.2H_2O$ and $[Co(en)(quin\text{-}8\text{-}O)_2]Cl.2H_2O$ (quin-8-O = the monoanion of 8-hydroxyquinoline) have been isolated and characterised [156]. Three geometrical isomers of the latter complex are possible and its ^1H NMR spectrum indicates that the oxygen atoms of the two oxine ligands lie *cis* to each other.

New cobalt(III) complexes of the type *trans*-$[CoCl_2(L)_2]^+$, $[Co(NH_3)_4L]^{3+}$, *cis*-$[Co(NH_3)_2(L)_2]^{3+}$, and $[Co(en)_2L]^{3+}$ (where L denotes a seven-membered chelate diamine ligand, (R)-2-methyl-1,4-diaminobutane or *meso*- and (R or S)-2,5-diaminohexane) have been prepared [157]. The dichloro complexes decompose slowly in the solid state, and rapidly in methanol. The ammine and 1,2-diaminoethane complexes are stable in acidic water, but decompose gradually at neutral pH.

The preparation and characterisation of $[Co(en)_2(S_2O_3)]^+$, containing chelated *O*,*S*-thiosulphate, have been described [158]. Early reports of the preparation of this complex appear to have been in error [159]. The isomers of $[Co(NH_3)_2(1,3\text{-}pn)_2]^{3+}$ have been separated by recycling chromatography and their chiroptical properties studied [160]. The magnitude of the CD intensity of a bisdiamine complex is roughly one-third of that of the corresponding trisdiamine complex. The preparation and resolution of $[Co(en)_n\{NH_2CH_2CH_2P(CH_3)_2\}_{3-n}]^{3+}$ and its related complexes have been described, and the absolute configuration of $(+)_{589}$-*fac*-$[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]^{3+}$ determined by X-ray crystallographic analysis [161]. Isomers of tris[(R)-1-phenyl-1,2-diaminoethane]cobalt(III) and tris[(S)-3,3-dimethyl-1,2-diaminobutane]cobalt(III) have been studied in detail [162].

Formation of $[Co(en)_2(glyO)]^{2+}$, from monodentate *trans*-$[Co(en)_2(H_2O/OH)(glyO/H)]^{3+/2+/+}$, species has been studied kinetically [163]. ^{18}O-tracer studies have shown that cyclisation of *cis*-$[Co(en)_2(OH_2)(glyOH)]^{3+}$ and *cis*-$[Co(en)_2(OH_2)(glyO)]^{2+}$ to give $[Co(en)_2(glyO)]^{2+}$, containing chelated glycinate, occur intramolecularly without displacement of the coordinated water molecule [164]. Detailed kinetic studies of these reactions, which can be considered as intramolecular lactonisation at a metal centre, have been described. The complex *trans*-$[Co(en)_2(dmso)Cl][ClO_4]_2$ has been prepared and its rate of isomerisation to the *cis*-isomer measured using dmso as solvent [165]. The solvent exchange rate has also been determined by ^1H NMR spectroscopy. The *trans*-$[Co(en)_2(dmso)Cl]^{2+}$ ion aquates rapidly at 25 °C in 0.1 M $HClO_4$, with $k_{aq} = 8.7\ 10^{-4}\ s^{-1}$ [166].

Mixed-metal binuclear complexes are formed between $[Co(en)_2(OH)_2]^+$ and divalent metal ions with log β_2 = 5.9 (Mn), 7.5 (Co), 8.8 (Ni), 13.1 (Cu) and 7.9 (Zn) at 25 °C and $I = 3.0\ M$ ($Na[ClO_4]$) [167]. The kinetics of base hydrolysis of *cis*-$[Co(en)_2(bzmH)Cl]^{2+}$ (bzmH = benzimidazole) has been studied, the pK_a of the coordinated benzimidazole is 8.9 at 25 °C [168]. Kinetic studies of the aquation and base hydrolysis of *cis*-$[Co(en)_2(btzH)Cl]^{2+}$ and *cis*-$[Co(en)_2(btzMe)Cl]^{2+}$ (btzH = benzotriazole; btzMe = *N*-methylbenzotriazole) have also been reported [169]. Second order rate constants, k_{Hg}, for the Hg(II) assisted aquation of ΔΛ-*cis*-$[Co(en)_2(imidazole)Cl]^{2+}$ have been measured over the range of ionic strength 0.1-3.0 M at 25 °C [170]. Pressure and medium effects on the kinetics of anation of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ by oxalic acid in acidic solution have been studied [171]. The aquation of *cis*-$[Co(en)_2(NH_3)Br]^{2+}$ in mixtures of water and organic solvents (EtOH, $CHMe_2OH$, CMe_3OH or MeCn) has been studied in detail [172]. The base hydrolysis of *cis*-$[Co(en)_2(etaH)X]$ (X = Cl or Br; etaH = 2-aminoethanol) results in the formation of $[Co(en)_2(eta)]^{2+}$ (*ca*. 35%) and $[Co(en)_2(etaH)(OH)]^{2+}$ (*ca*. 65%), the product ratio being independent of pH [173].

The complexes $[Co(bamp)(dapo)X]^{2+}$ (bamp = 2,6-bis(aminomethyl)pyridine; dapo = 1,3-diamino-2-propanol; X = Cl, Br, or N_3) have been prepared to test whether, in base hydrolysis, a trigonal bipyramid or a square pyramid is the preferred intermediate, following loss of the leaving group [174]. The complexes were resolved using dibenzoyltartaric acid (optical purity > 97%). Base hydrolysis (X = Cl, $k_{OH} = 2.9 \times 10^3\ M^{-1}s^{-1}$; X = Br, $k_{OH} = 1.6 \times 10^4\ M^{-1}s^{-1}$ at 25 °C and I = 1.0 *M*) occurs with full retention of configuration on cobalt. In the classical S_N1 CB mechanism, the accelerated loss of the leaving group from the deprotonated reactant is interpreted in terms of π-orbital overlap of the type 2p(deprotonated nitrogen) → $3d_{x^2-y^2}$(Co(III)). The present results suggest that π-stabilisation is not significant in the intermediate after loss of the leaving group, possibly due to the inability of pyridine π-orbitals to give significant bonding.

The photochemical formation of $[Cl(en)_2Co\text{-}N{\equiv}C\text{-}Fe(CN)_5]^{2-}$, from $[Co(en)_3]^{3+}$ and $[Fe(CN)_6]^{4-}$, has been exploited [175]. The reaction of the benzohydroxamate anion, $[PhCONHO]^-$, with Λ-*cis*-$[Co(en)_2Cl_2]^+$ gives $(+)_{589}$-$[Co(en)_2(PhCONHO)]^{2+}$ in aqueous solution but $(-)_{589}$-$[Co(en)_2(PhCONHO)]^{2+}$ in aqueous pastes [176]. The solubility of Δ- and *rac*-$[Co(en)_2(ox)]_2[C_2O_4]$ have been determined in water at 5-60 °C. The oxalate is not spontaneously resolvable and forms the racemic compound Λ-$[Co(en)_2(ox)]$.Δ-$[Co(en)_2(ox)][C_2O_4].nH_2O$ [177]. Solubility isotherms of systems containing the optically active $[Co(en)_3]^{3+}$ ion have been determined [178].

Stereoselectivity has been observed in the outer-sphere redox reaction between Δ,Δ-$[(en)_2Co^{III}(\mu\text{-}NH_2,O_2^-)Co^{III}(en)_2]^{4+}$ and $[Mo_2^VO_4(R,S\text{-}pdta)]^{2-}$ ($pdtaH_4$ = propylenediaminetetraacetic acid) [179]. The occurrence of stereoselectivity in outer-sphere redox reactions has been discussed previously but definitive experimental data has been lacking.

Polarographic studies of ligand dissociation from dibromocobalt(III) complexes of the type *trans*-$[Co(N)_4Br_2]^+$ ($(N)_4$ = $(en)_2$, $(pn)_2$, $(tn)_2$, or $(NH_3)_4$) have been published [180]. Related kinetic studies of interest include: the kinetics and mechanism of substitution of chloride ion in *cis*-$[Co(en)_2Cl_2]Cl$ by 4-hydroxybenzoic acid [181], the mechanism of substitution of amines into halocobalt(III)-1,2-diaminoethane complexes [182]; deuterium solvent isotope effects in the pressure and temperature dependent isomerisation reactions of aquabis(1,2-diaminoethane)cobalt(III) complexes [183]; the kinetics and mechanism of substitution of chloride ion in *trans*-$[Co(en)_2Cl_2]Cl$ by 4-hydroxybenzoic acid [184]; Hammett relationships in the reactions of *cis*-$[Co(en)_2Cl(OH_2)]^{2+}$ with substituted benzoic acids [185], and the effect of temperature and dielectric constants on these relationships [186]; the kinetics of solvolysis of *cis*-$[Co(en)_2Cl(N_3)]^+$ in water and water-isopropanol [187]; activation parameters for the aquation of *trans*-$[Co(1,3\text{-}pn)_2Cl_2]^+$ [188]; and isotopic exchange of $^{36}Cl^-$ in *cis*-$[Co(en)_2Cl(CN)]^+$ in methanol and ethyleneglycol solvents [189].

Crystal structures of cobalt(III) diamine complexes reported this year include the following: *cis*-$[Co(en)_2(CO_3)]I.2H_2O$ [190]; *cis*-$[Co(en)_2(NCS)_2]Cl.H_2O$ [191]; and *cis*-*mer*-bis{*N*-(2,2-diacetylvinyl)-1,2-phenylenediamine}cobalt(III) iodide hydrate [192]. Crystallographic data on polymorphs of *rac*-$[Co(en)_3]F_3$ have been published [193], as has a preliminary study on the conformational analysis of ion pairs containing $[Co(en)_3]^{3+}$ [194].

Synthetic studies of these complexes have dealt with the synthesis and properties of isomers of $[Co(en)_2(NH_2CH_2CH_2OH)_2]^{3+}$ [195]; cobalt(III) complexes with 1,2-diaminoethane and 3-amino-1-propanol [196]; stereoselective effects in aminoacidato(1,2-diaminoethane)oxalatocobalt(III) complexes [197]; mixed ligand complexes of cobalt(III) containing diaminopropane and bidentate *N,N* and *O,O* donors [198]; synthesis and configuration of a $[Co(1,3\text{-pn})_2(NO_2)_2]^+$ complex [199]; and the preparation and IR spectra of *s*-hydroxymethylthiosulphates of *trans*-$[Co(en)_2Cl_2]^+$ and *trans*-$[Co(dmg)_2(amine)_2]^+$ complexes [200].

Infrared, ^1H and ^{13}C NMR spectra have been obtained for *cis*-$[Co(en)_2(imidazole)Cl]Cl_2$ [201] and ^{59}Co NMR spectra reported for $[Co(en)_2(amine)Cl]^{2+}$ complexes [202]. The application of Raman spectroscopy to differentiate between the *cis*- and *trans*-isomers of $[Co(en)_2(L)_2]^{n+}$ type complexes has been described [203].

Outer sphere complexes of $[Co(phen)_2(en)]^{3+}$ with halide, $[NCS]^-$ and $[ClO_4]^-$ in aqueous solution have been studied [204], as have outer sphere complexes of diacidobis(1,2-diaminoethane)cobalt(III) [205]. The crystal structure of *trans*-dichlorobis{(+)-(S,S)-*trans*-1,2-diaminocyclopentane}cobalt(III) chloride hydrochloride dihydrate, *trans*-$[CoCl_2\{(+)\text{-cptn}\}_2]Cl.HCl.2H_2O$ has been determined [206]. The synthesis and characterisation of mixed ligand complexes of diamines and monohydroxamic acids with cobalt(III) has also been studied [207].

1.1.4.3 2,2'-Bipyridine and 1,10-phenanthroline complexes

Twenty-eight cobalt(III) complexes of the types $[Co(L)_3]^{3+}$ and $[Co(L)_2XX]^{n+}$ (where L = bipy or phen and XX = 2CN, $2NO_2$, en, $2NH_3$, gly, $2H_2O$, C_2O_4, CO_3, 2SCN, $2N_3$, $2O_2CMe$, 2Cl or 2Br) have been prepared and their ^{13}C NMR spectra have been recorded [208].

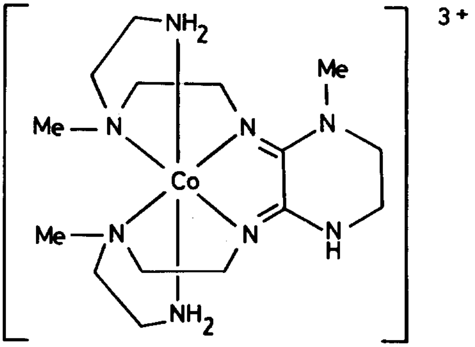
The kinetics of racemisation of $(+)_{589}$-$[Co(bipy)_2(paox)][NO_3]$ (paox is the dianion of 2-ketopropanoic acid oxime) has been studied at pH 7, between 70 and 98 °C [209]. The kinetics of reactions of $[Co(phen)_3]^{3+}$, $[Co(bipy)_3]^{3+}$, and $[Co(en)(phen)_2]^{3+}$ with ascorbic acid have been studied [210]. The effect of solvent composition (for aqueous mixtures of methanol, ethanol, propan-1-ol and propan-2-ol), on the rate constants and activation parameters for the outer-sphere electron transfer between $[Co(phen)_3]^{3+}$ and ferrocene, has been investigated [211]. The dependence of the kinetic parameters on the solvent composition cannot be rationalised in terms of the macroscopic parameters of the solvents. Limiting kinetics are observed for the $[Co\{4,7-(SO_3C_6H_4)_2phen\}_3]^{3-}$ oxidation of $HIPIP_{red}$ to $HIPIP_{ox}$, consistent with association prior to electron transfer [212] (HIPIP = high potential iron-sulphur protein).

Rate constants, activation parameters and equilibrium constants have been reported for the outer sphere electron transfer between $[Co(terpy)_2]^{2+}$ and $[Co(bipy)_3]^{3+}$, as measured for reactions in five protic and ten aprotic solvents [213]. Comparisons of experimental activation parameters for the $[Co(terpy)_2]^{2+}$-$[Co(bipy)_3]^{3+}$ redox reaction with those obtained from the Marcus Theory have been made [214]. The crystal structure and absolute configuration of $(-)_{589}$-$[Co(bipy)_3][Fe(CN)_6].8H_2O$ has been determined [215].

Intermediates obtained in the photolysis of cobalt(III) complexes with aminopolycarboxylic acids and bipy or phen have been studied [216], and the thermodynamics of the formation of outer sphere complexes of $[Co(phen)_3]^{3+}$ with $[SO_4]^{2-}$ have been investigated [217].

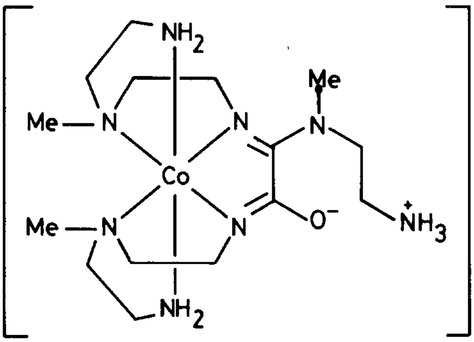
1.1.4.4 Triamines

The homogeneous intramolecular isomerisation reactions of all the isomers of $[Co(dien)_2][ClO_4]_3$ and $[Co(dien)(medien)][ClO_4]_3$ (medien = 4-methyl-1,4,7-triazaheptane) have been studied at 90 °C and various pressures [218]. The same equilibrium isomer distribution was obtained, regardless of the starting isomer or of the pressure conditions. These results have been interpreted on the basis of a common mechanism for all isomerisations involving Co-N bond rupture, followed by rearrangement of the resultant five-coordinate intermediate. Aqueous solutions of *sym-fac*-$[Co(medien)_2]^{3+}$ in the presence of charcoal and oxygen give *unsym-fac*-$[Co(aman)][ClO_4]_3.H_2O$ (*17*) (aman = 2,3-bis-2-aminoethyl-(methyl)aminoethylimino-1-methylpiperazine) [219]. The structure of the product



(17; ***unsym,fac***-**$[Co(aman)]^{3+}$)**

has been confirmed by *X*-ray crystallographic studies. The complex is inert in acid but hydrolyses in base in two clean sequential stages through the amidine imide complex (*18*) to the diimide complex (*19*) [220].



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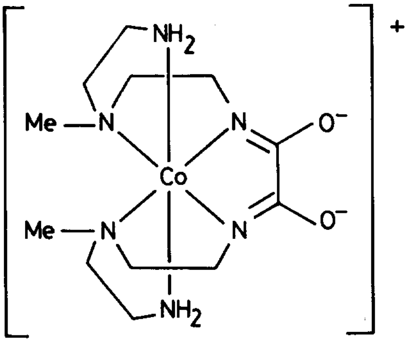

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The crystal structure of (–)-*mer*-{*N*-2-aminoethyl-(1,3-diaminopropane)}-(1,4,7-triazaheptane)cobalt(III) iodide monohydrate has been published [221]. There are seven potential geometric isomers of $[CoCl(Metmd)(dien)][ZnCl_4]$ (Metmd = *N*-methyltrimethylenediamine) six of which have been isolated. The crystal structure of one of these isomers Λ-(s)-*a,cb,edf*-$[CoCl(Metmd)(dien)][ZnCl_4]$ has been published [222]. Also, the crystal structure of (dien)(*L*-penicillaminato)cobalt(III) chloride has been described [223]. Mixed ligand complexes of cobalt with dien and leucine have been studied [224] and the crystal structure of *s*-*fac*-$[Co(dien)(NH_3)(NO_2)_2]Cl$ determined [225]. *X*-ray crystallography has established the structure of *mer*-$[Co(dien)(NO_2)_3]$ [226]. In this latter complex, the cobalt ion has a slightly distorted octahedral geometry and the Co-NO_2 bonds range from 1.916(3) to 1.997(3) Å.

1.1.4.5 *Tetraamines*

The kinetics of solvolysis of $[Co(tren)Cl_2]Cl.0.5H_2O$ has been studied in dmso, dmf and nmf [227]; these reactions occur by a dissociative mechanism. A number of complexes $[CoCl(solvent)(tren)][ClO_4]_2$ (solvent = dmso, dmf or *N*-methylmethanamide) have been isolated and characterised. The chloride anation of $[CoCl(tren)(dmso)]^{2+}$ was suggested to occur by an $(S_N1)_{IP}$ mechanism. The anation of $[Co(tren)(OH)_2]^+$ by carbonate ion has been investigated in the pH range 10.5-13 over a range of temperature [228] and the results discussed with reference to earlier studies on CO_2 uptake, the base catalysed ring opening of $[Co(tren)CO_3]^+$, and base hydrolysis of $[Co(tren)(OH)(OCO_2)]$.

Evidence has been presented [229] that the mercury(II) and NO^+ induced aquations of t-$[Co(tren)(NH_3)Cl]^{2+}$ and t-$[Co(tren)(NH_3)(N_3)]^{2+\dagger}$ follow different paths and do not involve a common intermediate of the type $[Co(tren)(NH_3)]^{3+}$. The k_{Hg} rate constants for the mercury(II) catalysed aquations of p-$[Co(tren)(NH_3)Cl]^{2+\dagger}$ and t-$[Co(tren)(NH_3)Cl]^{2+\dagger}$ are 5.6 $M^{-1}s^{-1}$ and 9.7 $M^{-1}s^{-1}$ at 25 °C.

The crystal structure of $[Co(tren)(py)Cl][ZnCl_4]0.5H_2O$ has been determined [230]. The pyridine ligand is bound *via* its nitrogen atom *trans* to the tertiary nitrogen of the tren ligand. The rate of the rapid uptake of SO_2 by $[Co(tren)(OH_2)_2]^{3+}$ has been studied by stopped-flow techniques [231] and comparisons made with similar previous studies involving CO_2, SO_2, $[SO_3]^{2-}$, $[HSeO_3]^-$, $[HMoO_4]^-$ and $[HWO_4]^-$.

The synthesis *unsym-cis*-$[Co(3,2,3\text{-tet})(CN)_2]Cl$, by the addition of hot aqueous solutions of NaCN to an aqueous solution of *trans*-$[Co(3,2,3\text{-tet})Cl_2]Cl$, has been described [232]. The stereochemistry of this complex has been established by ^1H and ^{13}C NMR and vibrational spectroscopy. Some *trans*-(RR,SS)-$[CoCl(3,2,3\text{-tet})(amine)][ZnCl_4]$ complexes (amine = NH_3, $MeNH_2$, or imidazole) have been prepared and characterised [233]; base hydrolysis and mercury(II) catalysed aquation rates have been studied. The preparation and characterisation of isomers of the (4R,6R)-4,6-dimethyl-3,7-diaza-1,9-diaminononane (5R,7R-Me_2-2,3,2-tet) and of the (6R,8R)-6,8-dimethyl-2,5,9,12-tetraazatridecane-(1,5R,7R,11-Me_4-2,3,2-tet) complexes, of the type *trans*-$[CoCl_2(tetraamine)]^+$, have been described [234].

Several dipeptide complexes of the type $[Co(tren)(NH_2CHRCONHCHR'CO_2CH_3)][4\text{-}CH_3C_6H_4SO_3]$ have been obtained by coupling the chelated ester complex $[Co(tren)(NH_2CHRCO_2CH_3)]^{3+}$ with a free amino-acid ester [235]. The half life of proton exchange in the complex $[Co(en)_2(NH_2CH_2CO_2CH_3)]^{3+}$ is *ca*. 20 s.

The preparation of *cis*-β_2-$[CoCl(trien)(benzimidazole)]^{2+}$ (*20*) has been described and the kinetics of aquation, Hg(II) catalysed aquation, and base hydrolysis studied [236]. Oxalato(ammine)(trien)cobalt(III) and salicylato(ammine)(trien)cobalt(III) perchlorates have been synthesised and tentatively assigned a *cis*-α configuration [237]. The complexes are formulated *cis*-α-$[Co(trien)(NH_3)(C_2O_4H)][ClO_4]_2$ and *cis*-α-$[Co(trien)(NH_3)(O_2CC_6H_4)(OH)][ClO_4]_2$ and the base hydrolysis kinetics of these complexes were also discussed.

The paramagnetic β_1- and β_2-isomers of 5-nitrosalicylato(trien)cobalt(III) have been characterised [238]. The electron hole is considered to be delocalised

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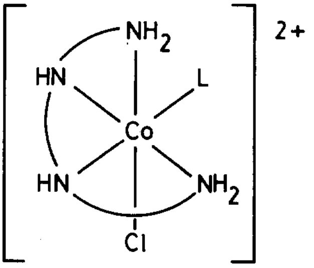
† The letters *t* and *p* denote the isomers with the tertiary and primary amine centre, respectively, *trans* to the electronegative group X.



(20; L = benzimidazole)

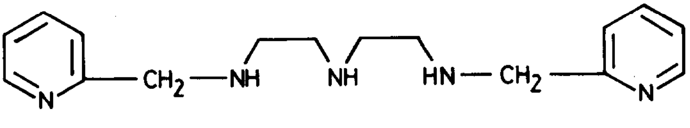
over the chelage ring containing the cobalt atom and the 5-nitrosalicylate ligand.

A dimethyliminium species, formed from dmf and $POCl_3$, adds at the methylene carbon of the bidentate glycinato complex *p*-[Co(tren)(gly)][ClO_4]$_2$ to give the *p*-[Co(tren){3-(dimethylamino)-2-aminoacrylylchloride}]$^{3+}$ ion [239]. The crystal structure of the [$ZnCl_4$]$^{2-}$ salt of this cation has been established by *X*-ray diffraction studies.

Interligand steric effects in tetraaminecobalt(III) amino acid complexes have been studied by CD techniques [240], and a thesis dealing with some cobalt(III) complexes of tren has been published [241]. Another thesis has dealt with crystallographic studies of cobalt(III) complexes of tren [242]. Cobalt(III) complexes with asymmetric tetraamine ligands have been prepared and characterised [243]. The isolation of all five geometrical and conformational isomers of [Co(trien)(NCS)$_2$]$^+$ has been described [244] and the β_1- and β_2-(8-quinolinolato)(1,4,7,10-tetraazadecane)cobalt(III) ions have been isolated and characterised [245]. The rates of acid hydrolysis of some diacido cobalt(III) tetraamine complexes, containing asymmetric tetraamine ligands, have also been studied [246].

1.1.4.6 Pentaamines

The preparation of the $\alpha\beta$-S-[Co(tetren)($O_2CC_6H_4OH$)][ClO_4]$_2$ has been described and the kinetics of base hydrolysis studied [247]. The crystal structure of an isomer of [Co(picdien)Cl][$ZnCl_4$] {picdien = (*21*)} has been



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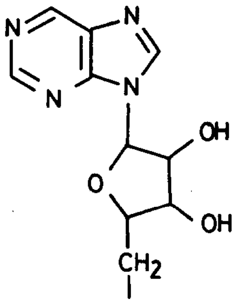
determined [248]. In this latter complex, the pentadentate picdien ligand is present in the α,β-configuration, with the Cl ligand *trans* to an "angular" secondary nitrogen. This complex is extremely sensitive to base hydrolysis.

Recent investigations have shown that *O*-bonded sulphito complexes are formed on the stopped-flow time scale, by reaction of acidic aqueous sulphite with aquapentaamminecobalt(III) complexes [249]. The kinetics of SO_2 uptake by αβ-*S*-$[Co(tetren)(OH)]^{2+}$ has been studied [250]; the product is the *O*-bonded sulphito complex. The acid-catalysed decomposition of the *O*-bonded complex, and its intramolecular isomerisation to the *S*-bonded complex, have been studied kinetically; also, the base hydrolysis of the *S*-bonded complex has been investigated.

1.1.4.7 Oximes, Cobaloximes, and Vitamin B_{12}

The coenzyme of the cobalt correnoids, which are present in the isomerase and ribonucleotide reductase enzymes, possess the ligand 5'-deoxy-5'-adenosyl (*22*), attached to cobalt *via* the primary carbon atom. Experimental evidence shows that the Co-C bond undergoes reversible and probably homolytic fission during the enzymic reaction. It has been suggested that the Co-C bond of the coenzyme might be labilised by a steric mismatch between the binding of the adenosine by the cobalt atom and the protein. The effects of steric distortion of the cobalt-carbon bond on the pK values and spectra of organocobalamins have now been studied [251]. The equilibria between the "base on" and unprotonated "base off" forms of a series of organocobalamins has also been investigated and values of ΔH and ΔS determined [252]. Neopentylcobalamin in neutral solution at 25 °C is stable under N_2 but is decomposed by O_2 and by imidazole to give cob(III)alamin, and by hydrogen-atom donors, such as thiols and isopropanol,



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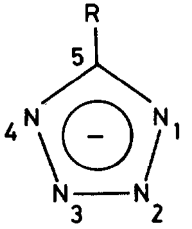
to give cob(II)alamin and neopentane. It has been suggested that neopentylcobalamin provides a model for the labilisation of the Co-C bond in the vitamin B_{12} coenzymes and possible mechanisms for the isomerase reactions have been discussed [253].

The crystal structures of the complexes *trans*-[Co(dmg)$_2$(neopentyl)(py)] and *trans*-[Co(dmg)$_2${$(Me_3Si)_3C$}(py)] have been reported [254]. Of particular note, the Co-$\hat{\text{C}}$-Y angle (Y = C or Si) is 130.3° in the carbon derivative and 127.7° in the (trimethylsilyl)methyl compound, the latter value being similar to that of 125° observed in the coenzyme. It appears that steric effects are important in destabilising the Co-C bond in such compounds, but an additional factor controlling Co-C bond lability is a distortion of the Co-$\hat{\text{C}}$-C bond angle from the normal tetrahedral angle. The longest Co-C bond in a vitamin B_{12} model is reported to be found in *trans*-[Co(dmg)$_2$($CHMe_2$)(Ph_3P)], where Co-C is 2.22(2) Å [255], even longer than the bond length of 2.085 Å found for *trans*-[Co(dmg)$_2$($CHMe_2$)(py)] [256].

Direct observation of Co-C bond cleavage in *trans*-[Co(dmg)$_2${(R)-1-cyanoethyl}{(S)-(-)-α-methylbenzylamine}] has been reported during exposure to *X*-rays [257]. The reaction is so slow that three-dimensional intensity data can be obtained at the initial, intermediate, and final stages of the reaction. EPR spectra of the crystal indicate that the Co-C bond is cleaved homolytically by *X*-radiation.

The preparation of *trans*-[Co(dmg)$_2$(nitromethyl)(py)] has been described and its crystal structure determined [258]. Preparations and structural characterisation of the complexes [Co(dmg)$_2$(L)(X)] {where L = 3- or 9-alkylated adenine; X = alkyl or P(O)(OCH_3)$_2$} have been reported [259]. Details of the preparation of further alkylcobalt complexes as models for coenzyme B_{12} have been published [260].

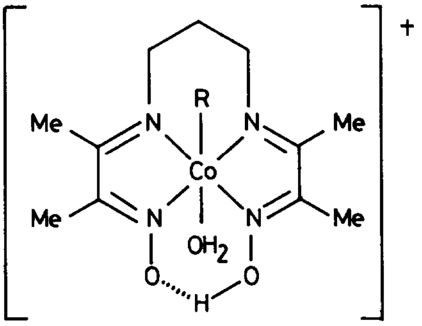
A series of complexes of the type [Co(dmg)$_2$(Bu_3P)(5-R-tetrazolate)] {where R = CF_3, CH_3, C_6H_5, $C_6H_5CH_2$, $(CH_3)_2N$, 4-FC_5H_5, or 3-FC_6H_4; 5-R-tetrazolate = (*23*)}



(23)

have been treated with a variety of alkylating agents. Comparison of NMR spectra with those of known compounds established that, in each case, regiospecific alkylation of the coordinated tetrazolate produced exclusively 1,5-disubstituted tetrazoles [261]. The pK_a values for the carboxyl group ionisation in fifteen complexes of the type $[Co(dmg)_2(2\text{-carboxyethyl})L]$ (where L = *S*-methyl sulphides, primary amines, substituted pyridines, or thiolate anions) have been determined [262]. The observed pK_a values only vary from 4.71 to 5.11, although the proton basicity of the axial ligands varies by about 16 orders of magnitude.

Activation parameters for the axial water substitution reactions of the complexes $[RCo(dmg)_2(OH_2)]$ ($R = CH_3$) and $[RCo\{(DO)(DOH)pn\}(OH_2)]^+$ ($R = CH_3$, or C_2H_5) (*24*) have been reported [263]. Comparison of the activation parameters, with those for the corresponding aquacobalamin, suggests that the lability of the biological complex is mainly due to entropy effects. An electrochemical comparison of both alkyl and nonalkyl cobaloxime, and $Co\{C_2(DO)(DOH)pn\}$ B_{12} model complexes, with five coenzyme B_{12} complexes has been made [264]. The results have established that the $Co\{C_2(DO)(DOH)pn\}$ model is a closer electrochemical mimic of B_{12} than is the cobaloxime model. A neglected feature of the cobaloxime model is the formal -2 charge on its bis(dimethylglyoximato)tetradentate ligand. The corrin in coenzyme B_{12} and the $Co\{C_2(DO)(DOH)pn\}$ B_{12} model have equatorial ligands with formal -1 charges. Thermodynamic parameters for the bonding of a sixth ligand to a number of five coordinate alkylcobalt(III) complexes have been measured [265]. Substantial differences in the enthalpies of axial bond formation are caused by changes in both the *trans* and *cis* ligands.



(24; $[RCo\{(DO)(DOH)pn\}(OH_2)]^+$)

The reaction between methylcobalamin and metal compounds plays a major role in biological transmethylation and may also be involved in the geochemical cycling of metals [266]. Methyl compounds of mercury, arsenic, selenium and tin occur in nature. It has been found that the rate of methyl exchange between methylcobalamin and metal substrates is very dependent on the nature of the ligands on the metal. The effect of halide ions on such reactions has now been studied in detail [267].

The kinetics of axial ligation by ammonia of a series of *trans*-organoaquacobalt(III) complexes, having a near macrocyclic equatorial chelate ring, have been measured for aqueous solutions as a function of the hydroxide ion concentration [268]. In the case of [RCo{(DO)(DOH)pn}] complexes, evidence for the conjugate base mechanism, involving deprotonation of the equatorial system, was obtained not only for base hydrolysis but also in the substitution of the axial water ligand.

Sterically hindered secondary alkylcobalamins, carrying hydrogen in the β-position, decompose spontaneously in neutral aqueous media by a β-elimination process [269]. The cleavage of the Co-C bond in these compounds is believed to be caused by "upward" distortions of the corrin ligand, in response to the attachment of the axial base, 5,6-dimethylbenzimidazole, as well as by thermal motions of the corrin ring system.

The proton transfer reactions of $[Co^{III}(dmg)_2X_2]^{n+}$ ions with OH^- have been studied in dioxane-water media by temperature jump techniques [270]. The kinetics of the iron(II) reduction of *trans*-$[Co(dmg)_2(py)X]$ complexes (X = Cl, Br, or I) have been investigated [271]. These latter reactions show an inverse dependence on $[H^+]$, suggesting an inner sphere mechanism involving protonated and unprotonated species of the complex. The iron(II) and vanadium(II) reductions of *trans*-$[Co(dmg)_2(N_3)_2]$ and *trans*-$[Co(dmg)_2(NCS)_2]$ have also been studied [272].

Retention of stereospecific ^{31}P chemical shift and coupling phenomena in heterocyclic diphosphine ligands on complexation with $[Co(dmg)_2(CH_3)]$ has been observed [273].

A number of tris chelates derived from dihydrogenviolurate (the monoanion of 1H,3H,5H-pyrimidine-2,4,5,6-tetraone-5-oxime) or 1,3-dimethylviolurate (the monoanion of 1,3-di-methylpyrimidine-2,4,5,6-tetraone-5-oxime have been synthesised [274]. The complexes $[ML_3]^{n-}$, with Co(III) (n = 0), Fe(II) or Ru(II) (n = 1), have the same *fac* stereochemistry. The effect of axial ligands on the kinetics of the base catalysed cleavage of ethylcobaloxime has been studied [275].

Papers describing the synthesis of dimethylglyoximatocobalt(III) complexes with 4-picoline *N*-oxide and 4-cyanopyridine ligands [276], *trans*-acido-bis(diphenylglyoximato)(diphenylguanidine)cobalt(III) complexes [277], *trans*-bis(dimethylglyoximato)di(amine)cobalt(III) complexes (amine = anisidine, pyridine, or urea) [278], cobalt(III) complexes with methylisopropylglyoxime [279], and oligomeric cobalt(III) complexes with dodecane-2,3,10,11-tetraone-3,10-dioxime [280] have been published.

An X-ray structural analysis of 2-methyladeninyl-cyano-cobamide, a native B_{12} analog, has been published [281]. Other related crystal structures reported this year include those of *trans*-diamminebis(dimethylglyoximato)-cobalt(III) nitrate and thiocyanate [282], and potassium *trans*-iodonitrobis(dimethylglyoximato)cobaltate(III) [283].

A thesis describing details of ligand exchange reactions of cobaloxime complexes has been published [284]. Other kinetic investigations described this year have dealt with: the replacement of the nitro-group in $[Co(dmg)_2(NO_2)(amine)]$ complexes by protonic (MeOH) and dipolar aprotic (dmf) solvents [285]; the hydrolysis of *trans*-thiosulphato-containing dioxime complexes of cobalt(III) [286]; and the aquation kinetics of $[Co(dmg)_2(NO_2)(X)]^-$ (X = halide) complexes [287].

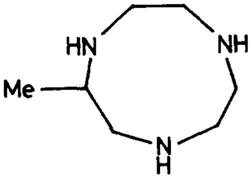
^1H NMR spectra of cobalt(III) complexes of dimethylglyoxime and diphenylguanidine have been published [288]. A complete interpretation of the ^{13}C NMR spectrum of dicyanocobyrinic acid heptamethyl ester and a partial assignment of its ^1H NMR spectrum has been made [289]. Also, coordination compounds of cobalt(III) with dioxime and sulphanilamide ligands have been reviewed [290].

The crystal structure of *trans*-$[Co(dmg)_2Br(PPh_3)]$ has been determined [291]. Remarkably stable cobaloximes of composition $[(R)_2C{=}C{=}CCHCo(dmg)_2(py)]$ have been characterised [292] and ^1H and ^{59}Co NMR spectra of cobaloxime complexes have been investigated [293].

1.1.4.8 Macrocycles

The [(R)-2-methyl-1,4,7-triazacyclononane][1,1,1-tris(aminomethyl)ethane]-cobalt(III) ion and some mono-[(R)-2-methyl-1,4,7-triazacyclononane]cobalt(III) complexes have been prepared and characterised and CD spectra determined [294]. The 2-methyl-1,4,7-triazacyclononane ligand is shown in (*25*).

A new (triazacyclononane)(tribenzo[*b*, *f* ,*j*][1,5,9]triazacyclododecane)cobalt(III) complex has been prepared and resolved, and the CD spectra have been reported [295]. The nitrogen-containing macrocycle tribenzo[*b*,*i*,*p*]1,4,8,11,15,18-hexaazacycloheneicosane (*26*) has been synthesised by a series of reactions involving the alkylation of doubly deprotonated aromatic amine complexes of cobalt(III) [296]. The free macrocycle was recovered from its cobalt(III) complex and characterised.



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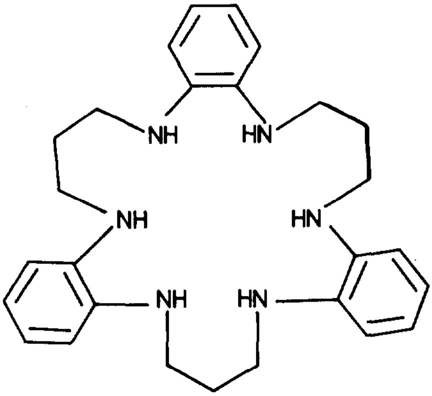

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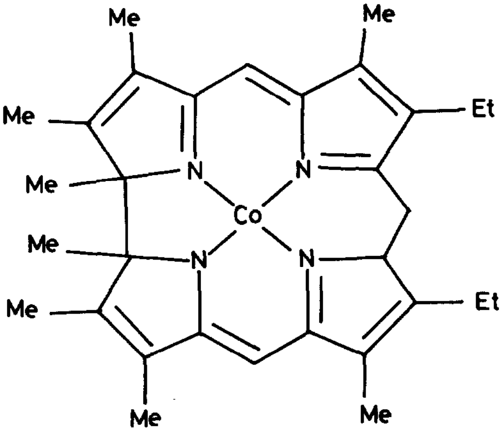
The stereochemistry of the (1,4,7,11,14,17-hexaazacycloeicosane)cobalt(III) ion has been studied [297]. For this complex, three geometric isomers are possible, two of which can have NH diastereoisomeric forms, giving a total of six geometrically distinct species. ^{13}C NMR spectroscopic studies indicate that the isolated complex is one diastereoisomer only, with C_2 symmetry, and its structure has been assigned as the Λ-*mer*, *cis*-RR/Δ-*mer*, *cis*-SS racemate.

Preparation of 1,4,7-triazacyclodecane.3HBr (tacd.3HBr), by the Richman-Atkins synthesis for cyclic polyamines, has given the *trans* and *cis*-isomers of $[Co(tacd)_2]^{3+}$, in the equilibrium ratio 96:4 [298]. Two other complexes were also obtained in these studies, and these have been characterised (^{13}C, ^{1}H NMR and *d-d* spectra) as single isomers *mer,cis*-$[Co(hace)]^{3+}$ and *cis*-$[Co(dtah)]^{3+}$ (hace = 1,4,7,11,14,17-hexaazacycloeicosane; dtah = 1,16-diamino-3,7,10,13-tetraazahexadecane). These hexamine ligands are coproducts with tacd in the Richman-Atkins synthesis.

The crystal structure of $[Co(N\text{-}rac\text{-}Me_6[14]diene\ N_4)(OH_2)(CH_3)][ClO_4]_2$ has been reported [299]. The cobalt(III) complex of tetradehydrocorrin (*27*), with



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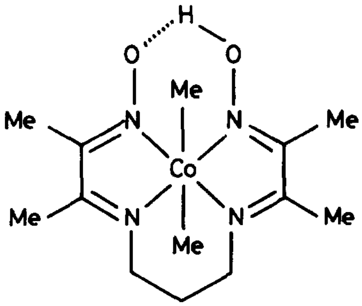
pK_a's of 6.15 and 11.50 for the successive ionisation of axial aqua ligands, undergoes auto-reduction to the cobalt(II) complex in aqueous carbonate solutions [300]. Kinetic analysis has indicated that the reaction sequence is, one-electron transfer from the axial hydroxo ligand to the metal, subsequent homolytic cleavage of the Co-OH bond and, finally, scavenging of the resulting hydroxyl radical by $[CO_3]^{2-}$.

The thermally stable dimethylcobalt(III) macrocycles, *trans*-$Me_2Co(dpnH)$ (*28*) and *trans*-$[Me_2Co(tim)][ClO_4]$ (*29*), are strongly labilised upon chemical and



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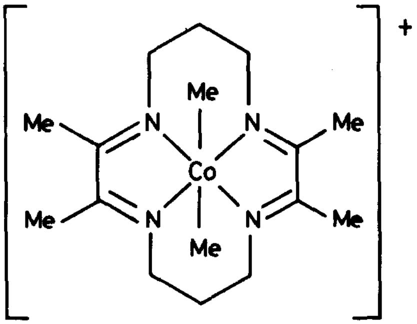

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electrochemical oxidation, leading to the selective scission of only one methyl ligand [301]. The formation of highly labile dimethylcobalt(IV) cations, as reactive intermediates in these reactions, is evident from the irreversibility of the cyclic voltammetric wave, even at -78 °C.

Structure-reactivity relations, and reorganisational barriers for outer-sphere electron-transfer reactions of low-spin cobalt(III)-cobalt(II) couples of structurally homologous macrocyclic complexes of the type *trans*-$[Co(N_4)(OH_2)_2]^{3+,2+}$, have been studied [302]. The $[\{(H_2O)Co([14]aneN_4)\}_2O_2]^{4+}$ μ-peroxo complex decomposes slowly in acidic aqueous solution [303]; the process has been proposed to involve rate-limiting homolytic dissociation of the μ-peroxo complex, with the reactive intermediate species being $[Co([14]aneN_4)(OH_2)_2]^{2+}$ and $[Co([14]aneN_4)(OH_2)(O_2)]^{2+}$. The effect of anions (*e.g.* Cl^-) on the decomposition was also considered.

The two geometrical isomers of *N-rac-trans*-$[CoCl(Me_6[14]diene)(NO_2)]^+$ have been isolated, in which the chloride ligand lies *syn* or *anti* to the two chiral N-H groups [304]. The *syn*-isomer aquates slowly, whilst the *anti*-isomer aquates rapidly. These results have been rationalised in terms of the macrocycle folding towards or against the leaving group in the transition state of the reaction. On this basis, it is possible to rationalise the aquation rates of a variety of macrocyclic complexes of cobalt(III).

The photodealkylation of dimethylcobalt(III) macrocycles has been studied [305] and the crystal structure of the complex *cis*-(SSSR)-{bromo(dibromoaqua(2-))-(2R,5R,8R,11R)(2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane)}cobalt(III) has been determined [306].

The rates of substitution of cobalt(II) into $[ZnL]^{2+}$ complexes, where L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, in nitrate media, has been studied spectrophotometrically. Absorption changes were recorded at 28,700 cm^{-1}, corresponding to the absorption maximum of the binuclear complex $[LCo(O_2)CoL]^{4+}$, formed by interaction of $[CoL]^{2+}$ with dissolved O_2 [307].

1.1.4.9 Porphyrins

The first accurate direct measurements of electron exchange rates of cobalt(III)-cobalt(II) tetraphenylporphyrins indicate rate constants of 9.69 $M^{-1}s^{-1}$ {outer-sphere for bis(pyridine)complexes} and 2.71 x 10^4 $M^{-1}s^{-1}$ (chloride bridged inner-sphere) in $CDCl_3$ [308]. A kinetic and equilibrium study of the reaction of pyridine with {*meso*-tetrakis(4-sulphonatophenyl)porphyrinato}diaquacobaltate(III), $[Co(TPPS)(H_2O)_2]^{3-}$, between pH2 and 13 at I = 1.0 M ($Na[ClO_4]$), has been published [309]. A further kinetic study has dealt with the reaction of *meso*-tetrakis(4-*N*-methylpyridyl)porphinediaquacobalt(III), $[Co(N_4)(H_2O)_2]^{5+}$ with $[Co(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$, $[Mo(CN)_8]^{3-}$, and $[W(CN)_8]^{3-}$ [310]: the formation constants for $[Co(N_4)(H_2O)(anion)]^{2+}$ are 446, 1320, 3100 and 1380 M^{-1}, respectively.

The EPR spectra of the paramagnetic species generated electrochemically from α, β, γ, δ-tetraphenylporphinatocobalt(II), $[Co^{II}(TPP)]$, have been observed at low temperature in chlorinated or non-chlorinated solvents [311]. From the EPR parameters obtained, three different paramagnetic species $[Co^{III}(TPP)]^{2+}(X^-)_2$, $[Co^{III}(TPP)]^{2+}(Y^-)_2$, and $[Co^{III}(TPP)]^{2+}(X^-)(Y^-)$ have been identified.

Photoreduction of $[Co^{III}(TPPS)]^{3-}$ by methanol and 2-propanol in deaerated solutions has been observed. The resulting cobalt(II)-porphyrin can be reoxidised by O_2 or air, thus providing a catalytic system for the oxidation of alcohols [312]. The synthesis of α-styrylcobalt(III) porphyrins has also been described [313].

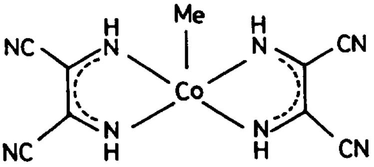
1.1.4.10 Other Nitrogen Ligands

A variety of tris(pyridine)cobalt(III) complexes have been prepared and their spectroscopic properties studied [314]. The synthesis of tri-μ-hydroxo-bis{tris(pyridine)cobalt(III)} perchlorate has also been described [315]. Other synthetic work has dealt with the preparation of octahedral *N,N'*-bis(2-bipyridylmethyl)-1,2(R)-diaminopropane complexes of cobalt(III) [316] and complexes of cobalt(III) with 2-hydrazinobenzimidazole [317].

NMR spectra and C-2 hydrogen exchange for cobalt(III) complexes of imidazoles [318] and the polarography of a cobalt(III) complex of poly(4-vinylpyridine) [319] have been discussed.

Crystal structures of interest reported this year include: $(-)_{589}$-*cis*-β-(2R,8R)-2,8-di(2-pyridyl)-3,7-diazanonane(oxalato)cobalt(III) perchlorate [320]; $(-)_{589}$-tris(biguanide)cobalt(III) chloride D-tartrate pentahydrate [321], and $(+)_{589}$-*ab*-oxalato-*cd*,*ef*-bis{(-)-1(S)-(2-pyridyl)ethylamine}·cobalt(III) perchlorate [322].

The diamagnetic cobalt(II) complexes $[\{Co(C_4H_2N_4)_2L\}_2]$ (L = H_2O or dmso), dimers of bis(diethyliminosuccinonitrile)cobalt(II) have been synthesised and converted to the planar cobalt(I) complex $[Co(C_4H_2N_4)_2]^-$ and the square-pyramidal cobalt(III) complexes, $[Co(Me)(C_4H_2N_4)_2]$ (*30*) and $[Co(CN)(C_4H_2N_4)_2]$; the structure of the latter compound has been determined by *X*-ray analysis [323].



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Intramolecular electron transfer in ruthenium(II)-cobalt(III) binuclear complexes, containing pyrazine, 4,4'-bipyridine and selected pyridinecarboxylate anions as bridging ligands, has been studied [324].

1.1.5 *Complexes with phosphorus donor ligands*

The complexes $[Co(NO_2)(acac)_2L]$ have been prepared for L = PBu_3, PBu_2Ph, PMe_2Ph or $PMePh_2$. Moreover, $[Co(NO_2)_2(acac)(PMe_2Ph)_2]$ has been obtained by the reaction of phosphines with $Na[Co(NO_2)(acac)_2]$ [325]. A *cis*(NO_2,P) configuration has been assigned to $[Co(NO_2)(acac)_2L]$ and a *trans*(P,P) configuration to $[Co(NO_2)_2(acac)(PMe_2Ph)_2]$.

The temperature dependent $^5T_2 \rightleftharpoons {}^1A_1$ spin equilibrium in the six-coordinate $[CoL_2][PF_6]$ complex ($L = \{C_5H_5Co[P(O)(OC_2H_5)_2]_3\}^-$) has been studied in solution by ^{31}P NMR spectroscopy [326]. The preparation of a novel complex of the $[Co^{III}P_6]^{3+}$ type, tris{1,2-bis(dimethylphosphino)ethane}cobalt(III) perchlorate, has been described [327].

1.1.6 *Cyanide complexes*

A variety of papers dealing with cobalt(III) cyanocomplexes have appeared. The substitution of $[Co(CN)_5(OH)]^{3-}$ by $[N_3]^-$ in aqueous solution has been shown to occur *via* $[Co(CN)_5(OH_2)]^{2-}$ in equilibrium with the hydroxo-complex [328]. The photo-aquation of $[Co(CN)_6]^{3-}$ has been studied as a function of pressure up to 1500 bar and evidence for an I_d type of photo-aquation presented [329]. A new discussion of the structural and physical changes which occur in dehydration of $Co_3[Co(CN)_6]_2.12H_2O$ has been published [330]. *Ab initio* calculations have been carried out on the electronic structure of $[Co(CN)_6]^{3-}$ [331], and the charge transfer photochemistry of $[Co(CN)_5(OH)]^{3-}$ has been investigated [332]. The electronic absorption spectra of pentacyano complexes of cobalt(III) have been studied [333], and the preparations of new μ-oxalatobis{pentacyanocobaltate(III)} salts have been described [334].

1.1.7 *Miscellaneous Topics*

The use of preparative high-pressure liquid chromatography to separate cobalt(III) complexes has been discussed [335], as has the resolution of some cobalt(III) complexes by adsorption on a colloidal clay [336].

The potential of ^{59}Co NMR spectroscopy with a chemical shift range of over 14000 p.p.m., is beginning to be realised. Thus the ^{59}Co chemical shift of $[Co(CN)_6]^{3-}$ provides a sensitive method for studying electron acceptance and hydrogen bond donation by protic solvents and there is a linear relationship between the chemical shift and the Gutmann acceptor number of the solvent employed [337,338]. A ^{59}Co NMR study of the magnetic shielding of the cobalt nucleus in a variety of cobalt(III) complexes has also been published [339].

Lewis acids dramatically enhance the oxidative power of cobalt nitro complexes [340]. Thus, in the presence of $BF_3{\cdot}Et_2O$ or $Li[PF_6]$, cobalt nitro complexes oxidise primary alcohols to aldehydes, and secondary alcohols to ketones. However, no reaction is observed in the absence of Lewis acids. A process (i) $M\text{-}NO_2 + S \rightarrow SO + M\text{-}NO$, (ii) $2M\text{-}NO + O_2 \rightarrow 2M\text{-}NO_2$, for the catalytic oxidation of organic substrates (S) by dioxygen is possible. Oxidation of certain cobalt nitrosyl complexes by O_2 to cobalt nitro complexes has been reported previously [341]. The reaction of $[Co(NO_2)_6]^{3-}$ with L-histidine has been studied [342].

1.2 COBALT(II)

1.2.1 Halide Complexes

Mixed pentahalocobaltates(II) [343] and the thermodynamics of formation of cobalt(II)-fluoride complexes in aqueous solution have been studied [344]. Mixed halocobaltates(II) of the type A[CoLXX'] (A = NEt_4, NPr_4, PPh_4, $AsPh_4$; L = Ph_3P; X,X' = Cl, Br, or I) containing two different kinds of halogen atoms have been isolated and characterised [345]. Inner-sphere coordination of chloroform in the tetrahedral high-spin complexes $[CoX_2(PPh_3)_2]$ (X = Cl, Br, or I) and $[NR_4][CoI_3(PPh_3)]$ has been detected by ^{1}H and ^{13}C NMR spectroscopy [346]. Sorbtion of cobalt(II) halide species on an ion exchange membrane has been studied by spectral measurements in the UV visible and far IR regions [347]. A microcalorimetric and spectrophotometric investigation of the cobalt(II)-bromide system in ethanol has been published [348]. Temperature-jump studies on the ligand substitution reactions

$$[CoCl_4]^{2-} + [SCN]^- \longrightarrow [CoCl_3(SCN)]^{2-} + Cl^-$$

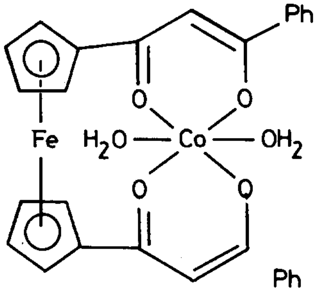
$$[CoCl_3(SCN)]^{2-} + [SCN]^- \longrightarrow [CoCl_2(SCN)_2]^{2-} + Cl^-$$

in reversed micellar systems have been published [349].

1.2.2 Complexes with oxygen or sulphur donor ligands

1.2.2.1 Oxygen ligands

1,1'-Dibenzoylacetylferrocene complexes of cobalt(II) have been prepared and characterised [350]. Two configurations (*31*) and (*32*) are possible for



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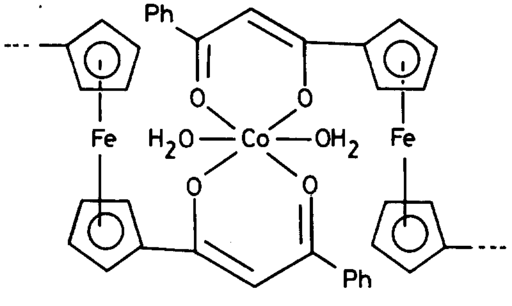

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such complexes and their structures have been discussed on the basis of UV/vis and Mossbäuer spectra and magnetic measurements.

The reaction of $Co(acac)_2.2H_2O$ with Ph_3AsO in ethanol gives mainly $Co(acac)_2.2Ph_3AsO$, with a small amount of $[\{Co(acac)_2\}_2Ph_3AsO]$. The latter complex is binuclear with three Co-O-Co bridges [351]; one bridging oxygen arises from the arsine oxide ligand, and the other two come from the pentanedionato ligands. Several new complexes of cobalt(II) aryl carboxylates, $Co(O_2CC_6H_4R)_2$ (R = 2-Me, 2- or 3-Cl; 2- or 3-NO_2; or 3-MeO), have been prepared by heating an ethanolic solution of the cobalt(II) aryl carboxylate under reflux with quinoline or isoquinoline [352]. Magnetic and spectral studies suggest that the quinoline derivatives may have the copper(II) ethanoate monohydrate type dimeric carboxylate bridged structures, formulated as $[Co_2(O_2CC_6H_4R)_4(L)_2]$, in which cobalt(II) is square pyramidal. The isoquinoline derivatives are monomeric bis(amine) complexes, with a *trans* configuration involving bidentate carboxylate ligands.

The complex $Co_2(L)(py)_4$ (where L is the dianion 1,1,1-trifluoro-2,4,6-heptanetrionate) has been characterised and shown to exhibit antiferromagnetic exchange [353]. The question of the occurrence of cobalt(II)-ether bonds has been discussed in two letters [354,355]. An etherate of $CoBr_2$ has been known for many years [356] and the solids $[CoCl_2(diox)]$, $[CoBr_2(diox)]$, and $[CoBr_2(diox)_2]$ (diox = 1,4-dioxan) have been shown, on the basis of magnetic data, to contain octahedral cobalt(II) with dioxan oxygen as a ligand [357].

The single-crystal EPR spectra of the base adducts of cobalt(II) pentane-2,4-dionate with 6-methylquinoline, pyridine, or water have been recorded [358]. A further EPR study has dealt with pentakis(picoline *N*-oxide)cobalt(II) perchlorate, which is high spin with a trigonal-bipyramidal structure [359].

Crystals of $Co(H_2O)_6(NO_3)_2.5hmta.4H_2O$ have been the subject of a recent X-ray study [360]. The low temperature (2-70 K) magnetic properties of polycrystalline bis(2,2,6,6-tetramethylheptane-3,5-dionato)cobalt(II) have been studied [361].

Dimethylsulphoxide complexes of cobalt(II) and various other transition metal ions have been characterised as their perchlorate salts [362]. The complexes are liable to incorporate additional dmso and perchloric acid beyond the composition $M(dmso)_6(ClO_4)_n$; dmso is comparable to urea in its spectrochemical and nephelauxetic strength. Variable temperature and pressure ^{17}O NMR studies on the water exchange on $[Co(H_2O)_6][ClO_4]_2$ in water give the following parameters: $k_{298} = 3.18 \times 10^6\ s^{-1}$, $\Delta H^{\ddagger} = 46.9$ kJ mol^{-1}. $\Delta S^{\ddagger} = +37$ JK^{-1} mol^{-1}, and $\Delta V^{\ddagger} = +6.1$ cm^3 mol^{-1} [363]. There is a gradual mechanistic changeover from I_a to I_d for water exchange from manganese(II) to nickel(II). The formation constant for the 1:1 complex between cobalt(II) and ethanoate ions, $[Co(O_2CMe)]^+$, has been determined over the temperature range 25-75 °C, both by spectrophotometry and by potentiometric titration [364]; at $I = 1.0$ M, a near zero enthalpy of formation was observed. A comparative study of solvent extraction of cobalt(II) with benzoyl- and thiobenzoyltrifluoroacetones has been made [365].

Solution studies of related cobalt(II) complexes reported this year have included the determination of formation constants with cobalt(II) with the following ligands; 2,2'-bipyridine-1-hydroxy-2-naphthoic acid and 2-hydroxy-1-naphthoic acid [366]; 3,5-dichloro-2-hydroxyacetophenone [367], glutarate [368]; 2-hydroxy-3-isopropyl-6-methylbenzaldehyde [369]; diglycollic acid [370]; phloroacetophenone [371]; cyanoethanoate [372]; 5-hydroxy-2-methyl-1,4-naphthoquinone [373] and 2-oxopropanoate [374]. Synthetic studies have dealt with the preparation of cobalt(II) arylates and their mixed complexes with diethylamine [375]; the preparation and characterisation of cobalt chloride phosphate $[Co_2(PO_4)Cl]$ [376]; the synthesis and physical properties of alcoholatocobalt(II) chlorides [377]; mixed ligand complexes of cobalt(II) trifluoro- and hexafluoropentane-2,4-dionates with *N*-donor heterocycles [378]; cobalt(II) complexes of *cis*,*cis*-1,3,5-trihydroxycyclohexane [379], and cobalt(II) complexes of 2-furancarboxaldehyde [380].

Seven-coordinate cobalt(II) has been observed in dinitratocobalt(II)-[12]-crown-4 and diaquacobalt(II)dinitrate-[15]-crown-5 [381]. Also, the structure of dinitratobis(phosphoric acid)tris(dimethylamide)cobalt(II) has been determined [382].

A thesis has dealt with complexes of cobalt(II) chloride with tertiary phosphorus esters [383] and a further thesis has dealt with the single crystal electronic absorption spectrum of potassium 12-tungstocobaltate(II) [384].

NMR investigations have included a study of the complexing of cobalt(II) by several organic acids [385], an NMR relaxation study of molecular motion and microstructure of the hydration shell of cobalt(II) [386], and a ^1H NMR investigation of the composition of the first coordination sphere of cobalt(II) in mixed solvents [387].

The reactions of cobalt(II) complexes of dibenzoylmethane with nitrogen heterocycles have been studied [388] and the use of dibenzoylmethanate as a reagent for the solvent extraction of cobalt(II) has been investigated [389].

The antimicrobial activity of cobalt(II) complexes of 3,5-dinitrosalicylic acid has been studied [390] and kinetic studies on the formation of cobalt(II) carboxylates by the shock wave method have been reported [391].

The complexes $[Co(O_2CR)_3][SbCl_6]_2$ have been prepared (with methanoic, ethanoic, propanoic and chloroethanoic acids) by reacting aliphatic acids with $[Co(MeNO_2)_6][SbCl_6]_2$ [392].

1.2.2.2 Dioxygen complexes

Molecular oxygen adducts of cobalt(II) complexes have been reviewed [393]. The resonance Raman spectrum of $[\{Co(salen)\}_2(O_2)]$ has been determined in the crystalline state [394]. The O_2 stretching and symmetric and antisymmetric CoO stretching vibrations occur at 1011, 533 and *ca.* 370 cm^{-1}, respectively. Vibrational studies of (tetraphenylporphyrinato)cobalt(II) and its adducts with O_2, CO and NO in gas matrices have also been reported [395].

The thermal stability of dioxygen adducts $Co(bzac_2en)(B)(O_2)$ {where B is a series of pyridine or alkylamine derivatives and $bzac_2en$ = *N,N'*-ethylenebis(benzoylacetoneiminato)dianion} have been investigated [396]. The complex $[Co(en)_3]^{2+}$ can be synthesised in the supercages of faujasite-type zeolites by adsorption of gaseous 1,2-diaminoethane [397]. Upon heating, $[Co(en)_3]^{2+}$ decomposes to $\{Co(en)_2\}^{2+}$ and $\{Co(en)\}^{2+}$. The mono and tris complexes are not capable of binding O_2, whereas the bis complex forms the 1:1 superoxo-complex $[Co(en)_2(O_2)]^{2+}$ and the 2:1 monobridged peroxo-complex $[\{Co(en)_2\}_2(O_2)]^{4+}$ with O_2.

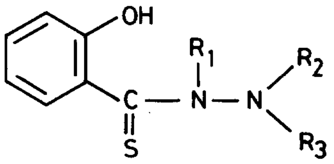
Steric conformational effects on the reversible oxygenation reaction in pyridine solutions of cobalt(II) complexes with Schiff bases derived from salicylaldehyde and 1,2-disubstituted 1,2-diaminoethanes have been studied [398]. The "annelides" represent a new type of surfactant containing a polar head able to bind selectively to a metal ion and a hydrophobic tail to impart amphiphilic character to the ligand and allow the formation of ordered aggregates [399]. The interaction of O_2 with the cobalt(II) complexes of such systems has now been studied [400]. The direct determination of the rate constant from the reaction of dioxygen with a cobalt(II) amine complex has been reported [401]. Reaction of O_2 with some mixed ligand complexes of cobalt(II) containing diethylenetriamine as one ligand has been studied [402]. The fixation of O_2 by some cobalt(II) complexes of Schiff bases in the solid state [403] and the oxygenation kinetics of cobalt(II) complexes containing tripodal polyamine ligands [404] have also been investigated.

A thesis dealing with cobalt(II) and iron(II) complexes of capped porphyrins which act as models for biological oxygen carriers has appeared [405], and resonance Raman investigations of the dioxygen carrier [Co(sal$_2$en)] and its μ-peroxo-complexes [{(L)(sal$_2$en)Co}$_2$(O$_2$)] (where L = dmso, py, dmf, pyO or NO) reported [406]. A further review of synthetic oxygen carriers has appeared [407] and a thesis dealing with the effects of σ-basicity, donor type and chelate ring size on the thermodynamics of dioxygen binding to cobalt(II) complexes has been published [408].

1.2.2.3 Sulphur-containing ligands

Cobalt(II) and nickel(II) complexes of the sulphur containing ligands 1-methoxy-2-methylthioethane and 2-methoxyethane thiol have been characterised [409]. The complex [Co{Ag(SCN-SeCN)}$_2$] has been prepared and the products obtained with a variety of Lewis bases (thf, dioxan, aniline, dmso or dmf) studied [410]. Coordination polymers of cobalt(II) {and nickel(II), copper(II) and palladium(II)} with 2,6-dimercapto-4-amino-1,3,5-triazine have been studied and spectral and magnetic data reported [411]. The synthesis and structural characterisation of the paramagnetic octahedral cobalt-sulphur cluster [Co$_6$(μ-S)$_8$(PEt$_3$)$_6$][PBh$_4$] has been described [412]. Each cobalt atom is located at the vertices of an octahedron with the sulphur ligands triply bridging all the octahedral faces.

Cobalt(II) {and cobalt(III)} complexes of thiosalicylohydrazide (*33*; R$_1$=R$_2$=R$_3$=H) and a variety of its derivatives have been prepared and characterised [413], as have cobalt(II) complexes of the ligand 1,4-diphenylthiosemicarbazide [414], which can exist as thioketo (*34*) and thioenol (*35*) tautomers.



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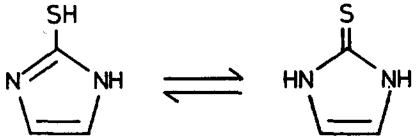
The complex Co(NO)$_2$(S$_3$N) can be obtained by treating the primary product of the reaction of [Co$_2$(CO)$_8$] and S$_4$N$_4$ with gaseous nitrogen oxide [415]. An X-ray crystallographic study indicates that the cobalt atom is in a

(34) (35)

pseudo-tetrahedral environment and is part of an almost planar $\{CoS_3N\}$ metallocycle. Complexes of imidazoline-(1,3H)-2-thione {which can exist as the tautomers (*36*) and (*37*)} with cobalt(II) have been prepared [416].



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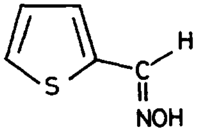
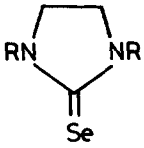
The properties and crystal structure of diaquabis(methylthioethanoato)cobalt(II), $[Co(C_3H_5SO_2)_2(H_2O)_2]$, and the anhydride obtained on heating to 140-150 °C have been investigated [417]; each methylthioethanoate ligand is bidentate *via* a sulphur atom and a carbonyl oxygen atom. The infrared and visible spectra of the anhydride resemble that of the bis(propylthioethanoato)cobalt(II) hexamer.

Cobalt(II) complexes of *syn*-thiophene-2-aldoxime (*38*) [418] and



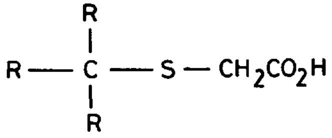
(38)

N-(5-phenyl-1,3,4-thiadiazol-2-yl)dithiocarbamic acid [419] have been characterised). The latter complex has been tested for fungicidal activity, but activity was only observed with the manganese(III), iron(III) and copper(II) complexes. The complexes CoL_2X_2 (X = Cl, Br, or I) have been prepared by reacting cobalt(II) halides with *N*-methyl-*N*'-ethyl-, *N*,*N*'-dimethyl- or *N*,*N*'-diethyl-imidazolidine-2-selone (*39*) [420]. The ligands (*39*) with $Co(BF_4)_2$ gave the $CoL_4(BF_4)_2$ complexes only with the disubstituted ligands.



(39)

Crystal structures have been reported for the dithiophosphato complexes $[NR_4][M(S_2PPh_2)_3]$ (M = Zn or Co; R = Et or Me) [421]. Electrochemical and spectroscopic studies of the cobalt(II) complexes of the sulphonephthalein derivative, xylenon orange, have been published [422]. Spectral and magnetic studies on cobalt(II) complexes of 2,5-dimercapto-1,3,4-thiadiazole and 5-mercapto-3-phenyl-1,3,4-thiadiazoline-2-thione have been reported [423]. The cobalt(II) complexes are tetrahedral. An additional investigation has dealt with the extraction of cobalt(II) from aqueous solution using *S*-terdodecylthioglycolic (*40*) acid [424].



$$R_3C{-}S{-}CH_2CO_2H$$

(40; R = $C_{11}H_{25}$)

Crystal structures of cobalt(II) complexes with *S*-donor ligands reported this year include those of bis(2-aminothiazole)dichlorocobalt(II) [425] and ethanoatobis(propanone *S*-methylsemicarbazone)cobalt(II) iodide [426].

Further investigations involving sulphur containing ligands include the following: complexes of cobalt(II) with 3-methyl- and 3-ethyl derivatives of 4-amino-5-mercapto-1,2,4-triazole [427]; cobalt(II) complexes of methylenebisthioethanoic acid and their interaction with pyridine [428]; cobalt(II) complexes of the pseudohalide 1,2,3,4-thiatriazol-5-thiolate [429]; cobalt(II) complexes of dithioxamide [430,431]; spectral and magnetic studies on cobalt(II) complexes of 2,5-dimercapto-1,3,4-thiadiazole and 5-mercapto-3-phenyl-1,3,4-thiadiazoline-2-thione [432]; complexes of cobalt(II) chloride with macrocyclic thioureas [433]; cobalt(II) complexes of *N*-phenyl-*N'*-benzothiazol-2-yl thiocarbamide [434] and substituted aminobenzothiazoles [435]; base adducts of *N*,*N'*-di(thiocarbamyl)hydrazinatocobalt(II

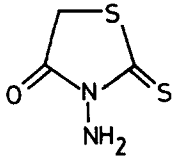
[436] and cobalt(II) complexes of hydrazodithioamide ($H_2NCSNHNHCSNH_2$) [437].

Cobalt(II) complexes of *N*-benzoyl-*N'*-(4-phenylthiazol-2-yl)thiocarbamide have been investigated as potential fungicides [438] and the synthesis and properties of cobalt(II) complexes with α,β-unsaturated thioaldehydes and 1-alkylthiacyclobutenium salts have been reported in a recent thesis [439]. The structure of the cobalt(II) complex of ethylenediaminebis(dithiocarbamate), which is an active fungicide, has been investigated [440].

Solution studies of mixed ligand complexes of cobalt(II) with bidentate mercapto acid amides have been published [441] and mixed ligand complexes of cobalt(II) with 6-mercaptopurine and thioguanine investigated [442]. Cobalt(II) complexes of biacetyl thiosemicarbazone and biacetyl 4-phenylthiosemicarbazone have been characterised [443]. Cobalt(II) complexes of thio-Schiff bases derived from methyl dithiocarbazate and the carbonyl compounds, 2-hydroxy-1-naphthaldehyde and 2-hydroxy-5-bromoacetophenone have also been characterised [444].

Spectral, magnetic and thermal studies have been published for cobalt(II) complexes of 4-*S*-benzyl-1-(4-chlorophenyl)-5-phenyl-2,4-isodithiobiuret [445]. Cobalt(II) complexes of the following ligands have also been studied: 2-phenylamino-5-carboxymethylthio-1,3,4-thiadiazole [446]; 1,4- 1,5- and 1,6-bisthiosemicarbazones [447]; and dithiophosphate and dithiophosphinate [448].

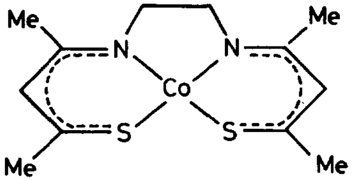
Cobalt(II) complexes of *N*-amino-rhodamine (*41*), of the type CoL_2X_2, have been prepared [449]. The ligand is bonded *via* the amine nitrogen atom and the thiocarbonyl sulphur atom, and the complexes have a distorted octahedral stereochemistry. Redox properties of cobalt(II) complexes with the extended π-system *N*,*N'*-ethylenebis(monothioacetylacetoniminate) (*42*) have been studied in MeCN by cyclic voltammetry and controlled potential coulometry [450]. The electrochemical synthesis of (*42*) has also been described [451].



(41)

1.2.3 Complexes with oxygen-nitrogen donor ligands

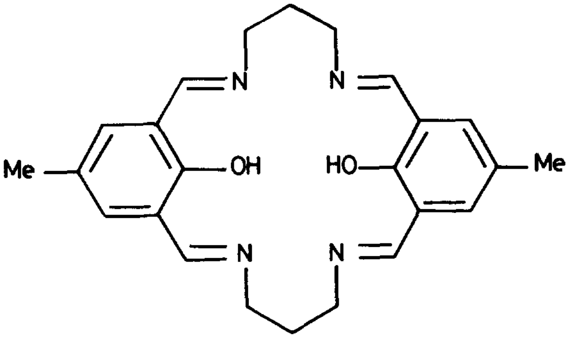
Over thirty-five transition metal complexes of cobalt(II) {and nickel(II)



(42)

and copper(II)} with pentadentate Schiff base ligands derived from various β-diketones (Hacac, Htfacac, Hbenzac and 4-XHbenzac) and triamines (dipropylenetriamine and its *N*-methyl and *N*-phenyl derivatives) have been isolated and characterised [452]. The cobalt(II) complexes are all high spin five coordinate species with average μ_{eff} values of 4.3 μ_B, which bind dixoygen reversibly in solution.

The properties and structure of the five-coordinate cobalt(II) complex of *N*,*N*'-bis[(5-chloro-2-hydroxyphenyl)phenylmethylene]-4-oxaheptane-1,7-diamine have been described [453]. The metal environment is distorted trigonal bipyramidal, with the two Co-N bonds axial and the three Co-O bonds equatorial. Complexes of the binucleating ligand (*43* = LH_2) can be formed from the condensation

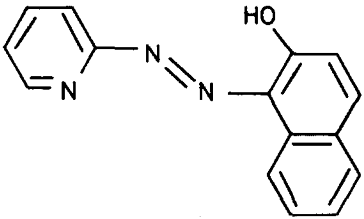


(43; LH_2)

of two moles of 2,6-diformyl-4-methylphenol with two moles of 1,3-diaminopropane, in the presence of divalent transition metal ions [454]. Variable temperature (4.2-286 K) magnetic susceptibility data for the binuclear high-spin six-coordinate $[LCo_2(py)_4][BF_4]_2$ complex have now been reported [455].

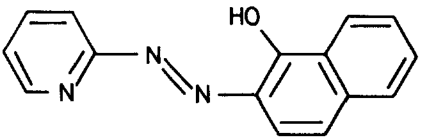
Pyrazine, when coordinated to transition metals, is an excellent bridging ligand, allowing electron coupling between the metal centres *via* orbital overlap with the ligand π*-orbitals. The synthesis and the structural and magnetic characterisation of three cobalt(II) complexes of 2-pyrazinecarboxylic acid and 2,3-pyrazinedicarboxylic acid have now been described [456]. In each case the cobalt is in a distorted octahedral environment, coordinated to two nitrogen atoms and two carboxylate oxygen atoms from different ligands and two water molecules.

Cobalt(II) complexes of 1-(2-pyridylazo)-2-naphthol (β-pan) (*44*), 2-(2-pyridylazo)-1-naphthol (α-pan) (*45*) and 10-(2-pyridylazo)-9-phenanthrol (paphen) (*46*) have been isolated and characterised [457]. The cobalt(II) complexes are oxidised to the cobalt(III) complexes in dmso in the presence of copper(II).



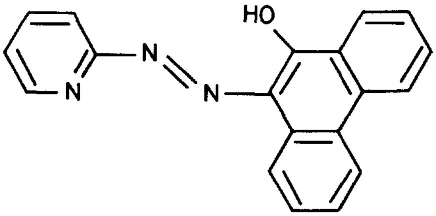
β -PAN

(44)



α-PAN

(45)



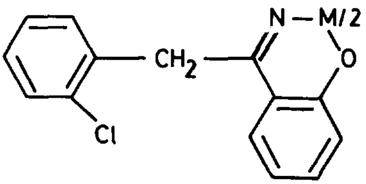
PAPhen

(46)

2-Methylaminopyridine *N*-oxide complexes have been prepared with CoX_2 (X = ClO_4, BF_4, NO_3, or Cl) [458] and this ligand appears to function rarely as a bidentate donor. A variety of cobalt(II) complexes of 2- or 4-pyridinecarboxyaldehyde have also been characterised [459].

Ligands such as 8-quinolinolate, dithiocarbamate, and ethylbenzoylcyanoethanoate are versatile uninegative bidentate chelating ligands possessing anti-fungal and/or antibacterial properties. The biological activity of these ligands is enhanced by chelation with metal ions. Heterochelates containing two such different ligands often give rise to more powerful antifungal/antibacterial action. The syntheses of the mixed ligand (8-quinolinolato)(propane-2,4-dionato) complexes of cobalt(II), and a variety of other first transition series metal ions, have recently been described [460].

Cobalt(II) and zinc(II) induced amide deprotonation in bis{(*N*-2-ethanamido)iminodiethanoato} complexes has recently been observed [461]. This is the first example of amide deprotonation induced by zinc(II). Previously copper(II), nickel(II) and cobalt(II) were believed to be the only first-row transition metal ions capable of inducing amide deprotonation. Pseudotetrahedral cobalt(II) {and nickel(II) and copper(II)} complexes of *N*'-(2-chlorophenyl)-2-(2',4'-dihydroxyphenyl)-2-benzylazomethine of the type shown in (*47*) have been prepared and their fungicidal and herbicidal activity accessed [462].



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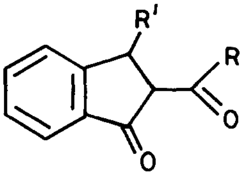
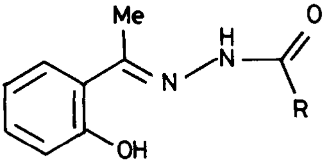


(48)

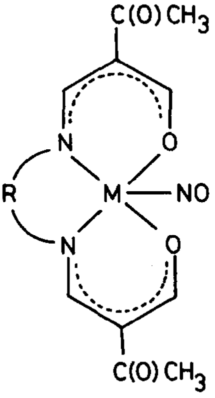
Reaction of cobalt(II) salts with 1-[(substituted-phenyl)azo]-2]naphthol and 1-[(substituted phenylimino)methyl]-2]naphthol ligands in ethanol gives [CoL_2], *cis*-[$Co(HL)_2X_2$], and *fac*-[CoL_3] [463]. Tautomerism in the complexes were also studied. Schiff base ligands derived from the β-diketone (*48*) have been prepared and cobalt(II) complexes characterised [464].

The crystal and molecular structure of [$LCo_2\{S_2P(OEt)_2\}_2$] (where LH_2 is the binucleating ligand (*43*) formed by condensation of the moles of 1,3-diaminopropane with two moles of 2-hydroxy-5-methylisophthalaldehyde) has been determined by X-ray diffraction [465]. Each cobalt atom is in an octahedral environment, with an {N_2O_2} equatorial plane, and two sulphur atoms of bridging dithiophosphate ligands in the axial positions. Cobalt(II) and copper(II) complexes of some α-(2-hydroxyphenyl)ethylidene acyl and aroyl hydrazones of the type shown in (*49*) have been characterised [466].



(49; R = Me, Ph or 2-HO-C_6H_4)

Cobalt(II) complexes with Jäger-type ligands can reversibly bind dioxygen at room temperature. A variety of nitrosyl cobalt and nitrosyl iron complexes of the general type shown in (*50*) have been prepared and their vibrational and EPR spectra examined, in terms of the electron-withdrawing effect of the ethanoyl group [467].



(50; R = $(CH_2)_2$, $(CH_2)_3$ or 2-C_6H_4)

Acid dissociation constants of epimeric threonines (thr, *allo*-thr) and isoleucines (ileu, *allo*-ileu) and the formation constants of their complexes with cobalt(II) and copper(II) have been determined [468]. The natural epimers form more stable complexes than the *allo* forms. The mass spectra and fragmentation patterns of a number of cobalt(II) and nickel(II) complexes of 2-hydroxy-1-naphthaldoxime, 2-hydroxy-1-naphthylideneaniline, and 2-hydroxy-1-naphthylidene-1,2-diaminoethane have been studied [469].

The EPR spectra of cobalt(II)- and copper(II)-doped bis{*N*,*N*-bis(2-diethylamino)ethyl}{(2-hydroxyethyl)amino-*O*}dinickel(II) diperchlorate, $[Ni_2(bdhe)_2][ClO_4]_2$, have shown the presence of nickel(II)-cobalt(II) and nickel(II)-copper(II) pairs [470]. Weak magnetic exchange interactions between paramagnetic metal ions and coordinated ortho-semiquinones in

[M(9,10-phenanthrenesemiquinone)$_2$(pyridine)$_2$] and tetranuclear [M$_4$(ortho-semiquinone)$_8$] complexes {where M = nickel(II) or cobalt(II)} have been studied [471].

Formation constants have been obtained for cobalt(II) complexes of ethylenediamine-*N*-acetate (edma), diethylenetriamine (dien), and iminodiethanoato (imda) at 25 °C and I = 1.0 M (Na[ClO$_4$]) [472]. The structures of a variety of cobalt(II) complexes of diaminetetraacetic acids have been studied by ^{1}H NMR spectroscopy [473]. The kinetics of oxidation of ethylenediaminetetraacetato and *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetato complexes of cobalt(II), by H_2O_2 in acidic solution, have been studied in detail over the temperature range 30-60 °C [474]. Formation constants for cobalt(II) complexes with the ligands 4-oximino-3-methyl-1-phenyl-2-pyrazolin-5-one, 4-oximino-3-methyl-2-pyrazolin-5-one have been determined at 20 and 30 °C in 50% (*v*/*v* aqueous-ethanol) [475]. Formation constants have also been reported for cobalt(II) complexes of inosine and 7-methylinosine [476], for oxonic acid [477], and for a number of cryptands [478]. Solvent extraction and oxidation of cobalt(II) complexes of 8-hydroxyquinoline and 7-(1-vinyldecyl)-8-hydroxyquinoline have also been studied [479].

Other studies have dealt with cobalt(II) complexes of phenyl urea [480] and *N*-*tert*-butylurea [481]; five coordinate cobalt(II) complexes with acetamidopyridine and diacetamidopyridine [482]; cobalt(II) complexes of salicylaldehyde semicarbazone [483], the biologically active 5-pyrazolone [484], and pyridine-4-aldehyde [485]; cobalt(II) complexes of acylhydrazones of acetoacetate [486] and of azodicarbonamide [487].

Crystal structures have been determined for diaqua{2,6-diacetylpyridinebis-(salicyloylhydrazone)}cobalt(II) nitrate hydrate [488]; a complex of cobalt(II) thiocyanate with propanoic acid hydrazide [489], and cobalt(II) isothiocyanate complexes with carboxylic acid hydrazides [490].

Formation constants for cobalt(II) complexes with the following ligands have been determined: the 1:1 complex with murexide in methanol-water solvent [491]; 3-bromo-2-hydroxy-5-methylacetophenone, including its oxime and hydrazone [492]; bromobenzoic acid hydrazides [493]; sodium 2-{4-amino-3-(1,2,4-triazoylazo)}-naphthol-4-sulphonate [494]; 3-(α-benzoylmethylbenzylideneamino)propanoate [495]; 4-{(2-hydroxyphenyl)hydrazono}-*N*-benzylsulphonyl)-3-methyl-2-pyrazolin-5-one [496]; 2-hydroxy-5-methyl-4-substituted-azobenzenes [497]; 2-amino-nicotinic acid [498]; 4-{*N*-(2-hydroxyphenyl)}toluene sulphonamide [499]; 2-(*N*-α-pyrrolideneimino)ethane sulphonate [500]; diaminoacetyl urea [501]; *N*-(5-methyl-salicylidene)benzylamine [502]; 2-hydroxy-1-naphthalidine-4-acetylaminoaniline [503]; diethyl 2-carboxyphenylhydrazonomalonate [504], and 2,2',4'-trihydroxy-5-chloro(1-azo-1')-benzene-3-sulphonic acid [505].

Investigations involving Schiff base ligands include the following: preparation and structural studies of *N*,*N*'-ethylenebis(benzoylacetonimato)cobalt(II) [506]; complexes of cobalt(II) with *N*,*N*'-ethylenebis(2-hydroxy-5-methylpropiophenoneimine) [507]; a single crystal EPR and cobalt ENDOR study of [Co(acac$_2$en)] [508]; cobalt(II) complexes of *N*,*N*'-bis(benzamido)acetylacetoneimine [509]; cobalt(II) complexes of Schiff bases derived from aminophenols and aromatic hydroxyaldehydes [510]; cobalt(II) complexes of Schiff bases derived from salicylaldehyde and the amino-acids valine, methionine and α-aminobutyric acid [511]; cobalt(II) complexes of the Schiff base derived from isatin and 2-aminophenol [512], [513]; pyridine and picoline derivatives of [Co(sal$_2$en)] [514]; cobalt(II) complexes of *N*,*N*-2-phenylenediiminebis(2-aminobenzaldehyde) [515]; cobalt(II) complexes of polymeric quadridentate Schiff based on salicylaldehyde [516] and cobalt(II) complexes of bis(azomethines) of 4-nitrophenyl-malondialdehydes [517].

The kinetics of the persulphate oxidation of *N*-(2-hydroxyethyl)ethylenediaminetriacetatocobaltate(II) [518] and diaqua(nitrilotriethanoato)cobaltate(II) [519] has been studied and mechanisms proposed. The reaction of NO with bis(8-quinolinolato)nitrosylcobalt has also been investigated [520].

A number of cobalt(II) complexes have been synthesised as potential fungicides. The ligand systems used were nitrosopyrazolimone [521]; furfurylidene- and 5-nitrofurylidenebenzoylhydrazides [522] and 2-pyrazolin-5-one derivatives [523].

Cobalt(II) complexes of the following ligands have also been characterised: 2,3-dioxobutyranilide 2-oxime hydrazone and β-resorcylaldazine [524]; (3,7-dimethyl-2-benzofuryl)glycine and (3-methyl-2-benzofuryl)alanine [525]; picolideneamino-2-naphthol [526]; 4-benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-one [527]; 4,4'-diaminodiphenyl oxide [528] α-benzoylmethylbenzylidenimino)benzenesulphonic acid and 2-(α-benzoylmethylbenzylidenimino)ethanesulphonic acid [529]; 2-quinoxalinecarboxamide [530] and nicotinic acid [531,532].

Polynuclear metal complexes of cobalt(II) with bis(3-hydroxyimino-2-butylidene)-3-phenylenediamine have been characterised [533], and the structural and magnetic properties of dichlorobis(urea)cobalt(II) dihydrate have been investigated [534].

Mixed ligand complexes of cobalt(II) with 1-nitroguanyl-5-methylpyrazole-3-carboxylic acid and heterocyclic amines have been studied [535] and nitrogen base adducts of some methyl substituted *N*-phenylbenzohydroxamates of cobalt(II) have been prepared [536].

An electronic absorption spectral study of the interaction of maleamide with copper(II) and cobalt(II) has been published [537] and the electronic spectra and magnetic susceptibilities of tetrahedral complexes of cobalt(II) with

1-methyl-2-carbethoxy-1-glyoxalanyl-(2)-(bromophenyl)hydrazones have been studied [538].

1.2.3.1 Amino acid, peptide and protein ligands

The successful preparation of cobalt(II) substituted hemocyanin has been reported [539]. A thesis dealing with synthesis, spectral studies and structure of model systems for cobalt(II) substituted zinc metalloproteases has been published [540]. A ^{13}C NMR and an EPR study of the structure of different forms of the cobalt-bleomycin A_2 complex has been carried out [541], and the interaction of cobalt(II) with fibrinogen investigated [542]. The ternary complex between cobalt(II) bovine carbonic anhydrase and various bidentate ligands (including pyridine-2-carboxylate, quinoline-2-carboxylate and pyridyl-2-ethanoate) has also been studied [543].

Formation constants have been determined for cobalt(II) complexes of the following ligands: *cyclo*(L-histidyl-L-histidyl) [544]; *N*-benzoylglycyl-L-leucine [545]; D-cycloserine [546]; S-ethyl-L-cysteine [547]; *N*-benzoyl-glycylglycine [548], and S-carboxymethyl- and S-carboxyethyl-L-cysteine [549].

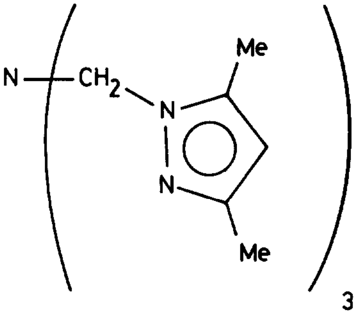
Cobalt(II) complexes of S-trityl-L-cysteine have been prepared [550], and cobalt(II) complexes of cystine studied [551]. Cobalt(II) complexes with DL-methionine and DL-leucine have been investigated by ^{1}H NMR spectroscopy [552].

The kinetics of formation of the monocomplex of *O*-phospho-DL-serine with cobalt(II) has been studied [553]. The stereospecific co-micelle promoted hydrolysis of *N*-acyl-phenylalanine 4-nitrophenyl esters, in the presence and absence of cobalt(II), has been investigated as a potential enzyme model system [554]. Other investigations have dealt with mixed ligand complexes of cobalt(II) with gly, ala, β-ala or phe, as a primary ligand, and 2-phenylacetohydroxamic acid or these amino-acids as secondary ligands [555], and cobalt(II) complexes of aspartic and glutamic acid hydrazides [556].

1.2.4 Complexes with VB donor ligands

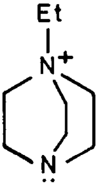
1.2.4.1 Nitrogen ligands

The complexes $[CoL(H_2O)][ClO_4]_2$ and $[CoL(N_3)][ClO_4]$ {where L = tris(3,5-dimethyl-1-pyrazolyl)methyl amine, (*51*)} have been prepared and characterised [557]. The aqua complex has two acidic groups in the pH range 5.5-9.5, which have been attributed to the bound water (pK_a = 9) and the apical nitrogen (pK_a = 7.4). The $\{CoN_4(OH_2)\}$ chromophore in this complex is a useful spectroscopic model for the cobalt(II) derivative of carbonic anhydrase. X-ray spectroscopic work indicates a distorted trigonal pyramidal structure for the complex [558]. Structural and ligand field parameters have been obtained for



(51)

the complexes $[Co^{II}(L_N^+)X_3]$ {X = Cl, or Br; L_N^+ = *N*-ethyl-1,4-diazabicyclo[2.2.2]octonium = (*52*)} [559]. The crystal structure

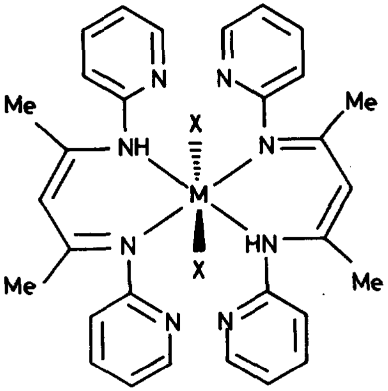


(52)

and properties of bis(2-methoxypyridine)cobalt(II) chloride have been described [560] and the cobalt shown to be tetrahedrally coordinated. The reaction of 2-aminopyridine with pentane-2,4-dione in the presence of cobalt(II), or a variety of other divalent transition metal ions, gives complexes of the type $[ML_2X_2]$ which have the structure (*53*) [561]. A new improved synthesis of the ligand 6,6'-dimethyl-2,2'-bipyridine (6,6'-Me_2bipy) has been published, and the preparations of complexes of the type M(6,6'-Me_2bipy)Cl_2 {M = Co(II), Pd(II), Pt(II), Cu(II) or Zn(II)} have been described [562].

Electrochemical and metathetical preparations of cyanotrihydroborato (BH_3CN^-) complexes of cobalt have been described [563], for example $[Co(BH_3CN)_2(CH_3CN)_2(py)_2]$, $[Co(BH_3CN)_2(py)_4]$ and $[Co(BH_3CN)_2(H_2O)_2(py)_2]$. The structure of *cis*-$[Co(bipy)_2(NCS)_2]$ has been determined by X-ray crystallography [564]. A variety of cobalt(II) complexes of 4,4'-bipyridine *N*,*N*'-dioxide (L) have been characterised, including $CoLCl_2$, $ClLBr_2$, $CoL(NO_3)_2$, and $CoL(NCS)_2$ [565].

Disproportionation and reduction of (tetradehydrocorrinato)cobalt complexes in basic aqueous solutions have been investigated [566]. This paper presents



(53)

evidence for the first example of disproportionation of a cobalt(II) complex of an N_4-macrocycle, in conjunction with further reduction of the resulting cobalt(III) complex. Electrocatalytic reduction of carbon dioxide using cobalt(II) {and nickel(II)} complexes of tetraazamacrocycles as catalysts has been reported [567]. The half cell reaction for the two electron reduction of CO_2 to CO is shown in equation (2):

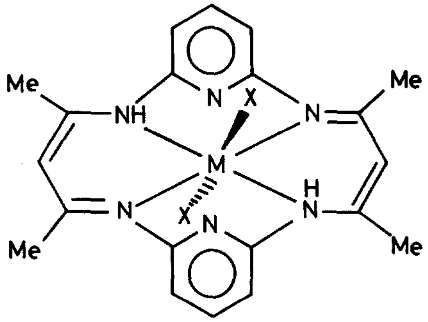
$$CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O \qquad (2)$$

Direct electroreductions have required potentials more negative than *ca.* -2v *vs* SCE The paper describes indirect electrochemical reduction of CO_2, which involves the initial reduction of the metal complexes and their subsequent reaction with CO_2.

The visible-light-induced formation of dihydrogen from water has been a subject of much current interest [568]. Irradiation of solutions containing $[Ru(bipy)_3]^{2+}$, ascorbate, cobalt(II), and bipy (or substituted bipy) or phen derivatives produces H_2 with a quantum yield of up to 0.13 mol einstein^{-1} [569].

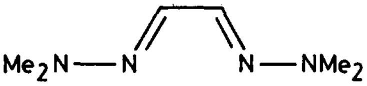
Cobalt(II) {and nickel(II) and copper(II)} salts react with 2,6-diaminopyridine and pentane-2,4-dione to give complexes containing the 16-membered N_6 tetradentate macrocyclic ligand (*54*). Complexes formulated as MLX_2 (where X = Cl, Br, NO_3 or NCS) have been characterised and assigned a distorted octahedral stereochemistry [570].

A detailed EPR study of low-spin cobalt(II) porphyrins, with the formula $[CoL(base)(O_2)]$, has shown that the spin-Hamiltonian parameters are not sensitive to changes in L (*meso*-substituted porphyrin) or the axial nitrogenous base [571]. The EPR spectrum of dichloro(tetrakispyrazole)cobalt(II), $[Co(pzlH)_4Cl_2]$, doped into a paramagnetic nickel(II) analogue, has been studied [572].



(54)

Complexes derived from glyoxal bis(dimethylhydrazone) (*55* = L) have been



(55)

prepared and characterised with cobalt(II) and a variety of other divalent ions [573]. New adducts of phthalocyaninatocobalt(II) with piperidine, 1-methylimidazole, 3,4-di-methylpyridine, 3,5-dimethylpyridine, and a variety of other substituted pyridines, have been synthesised [574]. Strong σ-donor bases form bis adducts, while weak σ-donor bases give mono adducts. All of the bis adducts are low spin species. Polarised neutron diffraction data for β-phalocyaninatocobalt(II) has been obtained [575].

The electronic and vibrational spectra of the cobalt(II) complexes of methyl-substituted pyridines have been studied in detail [576], as has the isotopic exchange of α- and β-cobalt phthalocyanine with carrier free $^{57}CoCl_2$ [577]. High pressure ^{13}C FT NMR spectroscopy has been used to study ethanenitrile exchange with $[Co(CH_3CN)_6][ClO_4]_2$ [578]. The solvent exchange rate is 2.56 x 10^5 s^{-1} at 25 °C, with $\Delta H^{\ddagger} = 48.8$ kJ mol^{-1}, $\Delta S^{\ddagger} = +22$ JK^{-1} mol^{-1} and $\Delta V^{\ddagger} = +7.7$ cm^3 mol^{-1}.

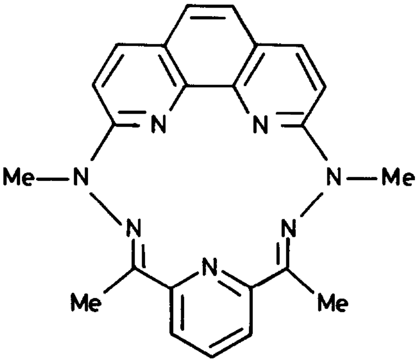
The kinetics of reactions of *meso*-tetra(4-pyridyl)porphine with cobalt(II) ethanoate and cobalt(II) nitrate in acetic acid solvent have been studied [579]. Formation constants for "sitting atop" complexes have been determined kinetically and possible mechanisms for metal ion incorporation considered. The kinetics of the disproportionation of the monoterpyridinecobalt(II) complex,

$$2[Co(trpy)(H_2O)_3]^{2+} \rightarrow [Co(trpy)_2]^{2+} + [Co(H_2O)_6]^{2+}$$

has been investigated as a function of added acid and metal ions at 25 °C [580].

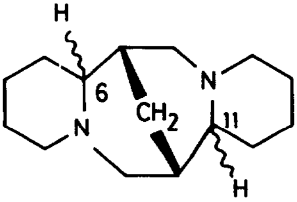
Formation constants for cobalt(II) complexes of bipy and 2,2':6',2"-terpyridine in the solvent hexamethylphosphoric triamide have been reported [581]. The formation of mixed ligand complexes of cobalt(II) with chloride and substituted pyridines in 1,2-dichloroethane has also been studied [582]. Enthalpy and entropy values have been determined by direct calorimetry for the association of cobalt(II) with pyrazole in aqueous solution [583].

Other studies have dealt with single crystal polarised electronic spectra and paramagnetic susceptibilities for the complex $[CoL(H_2O)_2][BF_4]_2$ {where L is the macrocycle (*56*)} and all the nitrogens act as donors [584], and the absorption



(56)

and CD spectra of tetrahedral dichloro(-)-spartein cobalt(II) [585] {where (-)spartein is the 6R, 11S epimer of (*57*)}.



(57)

Other investigations have dealt with the following: cobalt(II) complexes of the *s*-triazine melamine [586]; magnetic and spectral studies of 2-substituted benzimidazole complexes of cobalt(II) [587]; cobalt(II) complexes of 2-, 3- and 4-nitrobenzoyl hydrazides [588]; the structure of aniline complexes of cobalt(II) [589], and cobalt(II) complexes of 4,4'-diaminodiphenylmethane [590].

A thermodynamic investigation of ethanenitrile and propanenitrile interactions with $CoBr_2$ has been published [591] and the interaction of imidazole (and its derivatives) and pyrazole derivatives with $CoCl_2$ in *n*-butanol investigated [592]. Five coordinate complexes of cobalt(II) with dien derivatives have been reported [593], and the luminescence of cobalt(II) complexes of benzimidazole studied [594]. Binuclear complexes of a number of transition metal(II) thiocyanates with 4-ethyl-1,2,4-triazole have been characterised [595], and ternary complexes of cobalt(II) with bipy and adenosine 5'-triphosphoric acid have been prepared [596].

Activation volumes have been obtained for the ligand substitution reactions of cobalt(II) with pyridine-2-azo-4-dimethylaniline in various solvents [597]. A thesis dealing with ^1H NMR isotropic shifts of cobalt(II) methyl-substituted pyridine complexes has appeared [598], and some of this work has now been published [599]. ^{13}C NMR spectroscopic investigations of cobalt(II) complexes with alkylpyrazoles have been carried out [600] and the complexing of cobalt(II) nitrate with imidazole derivatives, primary aliphatic amines and piperidine in dmf investigated [601].

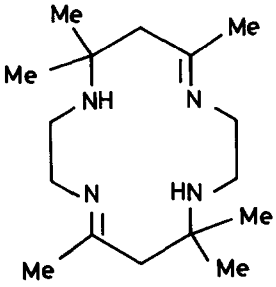
The crystal structures of dichloro(R(+)*N*,*N*,*N'*,*N'*-tetramethyl-1,2-diaminopropane)cobalt(III) [602] and of a dithiophosphate-bridged binuclear complex of a polyaza-macrocyclic ligand [603] have been published. Isophthalic dihydrazide complexes of cobalt(II) have been characterised [604] as have complexes of cobalt(II) with ditetrazolylpolyethylenimines [605] and picoline [606].

^1H NMR spectroscopy has been used to investigate mixed complexes of cobalt(II) in water-pyridine and water-ethanenitrile solution [607] and dilatometric techniques have been employed to study ion-pairing constants and volume changes involved in ion pairing of $[Co(en)_3]^{2+}$, with Br^-, I^-, NO_3^-, $[ClO_4]^{1-}$, $[SO_4]^{2-}$, citrate or oxalate [608]. Spectroscopic evidence for the out-of-plane displacement of cobalt in phthalocyaninatocobalt(II) and in its adducts with bases such as py, butylamine, methylimidazole, and imidazole, has been obtained [609].

Mixed cobalt(II)-bipy-purine complexes have been studied in solution [610], and EPR investigations of some adducts of cobalt(II) with chlorophyll-*a* have been published in a recent thesis [611]. Thermodynamic studies on the formation of cobalt(II)adenine nucleotide complexes have appeared [612] and the thermal decomposition of $[Co(py)_2(SCN)_2]$ has been studied [613].

The IR spectra of imidazole complexes of cobalt(II) nitrate and perchlorate have been studied in detail [614], and the electronic spectra of octahedral complexes of cobalt(II) with 2-(2-pyridyl)imidazole and 2-(2-pyridyl)benzimidazole have been investigated [615]. Axial coordination of pyridine to {dibenzo[b,i](1,4,8,11)tetraazacyclotetradecinato}cobalt(II) has been studied and the catalytic potential of the complex assessed [616]. Phenylenediamine derivatives of cobalt(II) pentane-2,4-dionate have been investigated [617] and the interaction of $CHCl_3$ with cobalt(II) complexes of pyrazole studied by ^1H NMR spectroscopy [618].

The masking of cobalt(II) and copper(II) with *trans*-[14]dienN_4 (*58*) has been described [619]. Procedures are given for the complexometric determination of magnesium(II) and europium(II) with edta, in the presence of an excess of copper(II) and cobalt(II), after masking with the macrocycle. A very simple preparation of the macrocycle (*58*) has been described previously [620].



(58)

Cobalt(II) complexes with dioximes, substituted by BF_2- or BEt_2- groups for the bridging hydrogens, have been prepared [621]. The BF_2-substituted cobalt(II) complexes are stable in air at room temperature both in the solid state and in dmf solution; a result attributed to the electron withdrawing effect of the BF_2- group. Asymmetric hydrogenation, catalysed by bis(dimethylglyoximato)cobalt(II)-chiral cocatalyst systems, has been studied in detail [622,623]. Cobaloxime(II)-catalysed oxidation of isocyanides to isocyanates and nitrosobenzene has also been investigated [624].

The acid dissociation constants of 1,2-cycloheptanedione dioxime, and 1,2-cyclooctanedione dioxime, and the formation constants with cobalt(II) have been determined in 75% dioxane-25% water (v/v) [625]. The kinetics of the reaction of cobaloxime(II) with hydroxide ions have been studied [626]. Other studies involving oxime ligands have included: cobalt(II) complexes of 2-hydroxy-1-naphthaldoxime [627]; the synthesis and characterisation of polymeric complexes of cobalt(II) with chloro-substituted 2-hydroxyacetophenone oximes [628]; cobalt(II) complexes with *para*-quinone dioxime [629]; synthesis and characterisation of cobalt(II) complexes with 2-furancarbaldehyde oxime [630]; spectral and magnetic studies of cobalt(II) complexes with 2-hydroxy-1-naphthaloxime [631]; the stability of cobalt(II) complexes of 1,2-cycloheptanedione dioxime and 1,2-cyclooctanedione dioxime in aqueous solution [632] and cobalt(II) complexes of 2'-hydroxy-3'-bromo-4-methoxy-5'-methylchalcone oxime [633].

1.2.4.2 Phosphorus ligands

The crystal structure of the pentacoordinate $[CoCl_2(PMe_3)_3]$ has been determined [634]; this paper also describes the preparation of the four- and five-coordinate complexes $[Co(PMe_3)_2X_2]$, $[Co(PMe_3)_3X_2]$, and $[Co(PMe_3)_4X]^+$ (X = halide). EPR and X-ray data are in agreement, indicating a distorted *cis*-equatorial trigonal bipyramidal structure for the five-coordinate complexes, the halide atom always being in an equatorial position.

High-spin tetrahedral $[CoLX_2]$ complexes (X = Cl, Br, I, or NCS; L = $PhHP(CH_2)_nNRR')$, containing an aminoalkylphosphine, have been characterised [635]; tetrahedral $[CoL_2X_2]$ complexes were also obtained depending on the donor ability of the nitrogen in L.

Cobalt(II) complexes with 1,1-bis(diphenylphosphinomethyl)-1-(diphenylphosphinoethyl)ethane (atriphos) and 1,1,1-tris(diethylphosphinomethyl)ethane (etriphos) have been prepared and the crystal structure of the trinuclear $[Co_3(atriphos)_2Cl_6]$ complex determined [636]. This latter structure consists of a non-linear trinuclear system of four-coordinate cobalt atoms, each linked to two chlorine atoms and to two phosphorus atoms in a slightly distorted tetrahedral arrangement. Cyclo-triphosphorus complexes of the type $[LCo\{\mu-(\eta^3-P_3)\}FeL][PF_6]_2.CH_2Cl_2$ $\{L = MeC(CH_2PPh_2)_3\}$ have been characterised and their crystal structure determined [637].

A general route for the preparation of $[Co(NO)(diphos)_2]X_2$ complexes (where diphos is a chelating diphosphine) has been developed [638]. Variable temperature NMR studies have established the fluxional nature of the five-coordinate cations; low temperature spectra are consistent with a linearly coordinated nitrosyl in the equatorial position. The synthesis and characterisation of some new five-coordinate mononitrosyl cobalt complexes $[CoL_4(NO)][BPh_4]_2$ (L = $P(OMe)_3$, $P(OEt)_3$, or $PPh(OEt)_2$) have been described [639]. The reactivity of these compounds with π-acceptor ligands, such as NO, CO phosphite or isocyanide, has been discussed and a new method of obtaining the cations $[CoXL_3(NO)]^+$ given.

EPR spectra have been recorded for frozen solutions of six different low-spin cobalt(II) complexes, with different phosphines or phosphites coordinated in the axial positions of [Co(mosalen)], [Co(salphen)] and $[Co(sacsac)_2]$ (mosalen =

N,*N*'-ethylene bis[(2-methoxy)salicylideneiminate], salphen = 2-phenylenebis(salicylideneiminate) and sacsac = pentane-2,4-dithione) [640]. The preparation and electronic structural investigations of some low-spin cobalt(II) complexes of the ligand *cis*-1,2-bis(diphenylphosphino)ethane have been reported [641]. The tripod ligand tris(2-dicyclohexylphosphinoethyl)amine (cynp$_3$) forms cobalt(II) complexes of the general formula [CoX(cynp$_3$)]Y (X = Cl, Br, I, or NCS; Y = BPh$_4$ and X = Y, Cl, Br, I, or NCS) [642]. The cobalt complexes [CoX(cynp$_3$)][BPh$_4$] are high-spin, five-coordinate, with a distorted trigonal bipyramidal geometry, both in the solid state and solution.

Complexes of pentaphenyldimethylenetriphosphine trioxide with cobalt(II) halides have been characterised [643]. Pentacoordinate [Co(S,S)(P,P)(NO)] type complexes have been prepared {where (H$_2$S,S) = NC(SH)C=C(SH)(CN) and (P,P = dppe or 2PPh$_3$)} [644].

1.2.4.3 Arsenic ligands

Complexes of cobalt(II) with *ortho*-phenylenebis(diphenylarsine) (pdpa) and *ortho*-phenylenebis(di-4-tolylarsine) (pdta) have been prepared [645]. The stoicheiometry of these complexes is markedly dependent on the reaction temperature employed in the synthesis; at 0 °C [M(pdpa)$_2$X$_2$] complexes are formed but, at higher temperatures, [M(pdpa)X$_2$] complexes are produced.

1.3 COBALT(I)

The crystal structure of *trans*-hydrido-carbonyltris(triphenylphosphine)cobalt(I) has been determined [646]. Distances and angles appear normal and resemble those of the isoelectronic complexes [RhH(CO)(PPh$_3$)$_3$] and [CoH(N$_2$)(PPh$_3$)$_3$]. The Co-H bond length is 1.50(5) Å. Aldol condensations, catalysed by [(Ph$_3$P)$_3$Co(CH$_3$)] have been studied [647]. The chemistry and crystal structure of tris(trimethylphosphite)(η^3-cyclooctenyl)cobalt(I) has also been investigated [648]; this compound is a catalyst precursor for arene hydrogenation. The complexes [CoX(PPh$_3$)$_3$] (X = halide) catalyses the hydrodimerisation of methyl acrylate to dimethyl adipate in methanol [649].

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