Coordination Chemistry Reviews, 35 (1981) 85—112
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

3. COBALT

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CONTENTS

INTRODUCTION

The annual survey of cobalt, rhodium and iridium chemistry covering the year 1976 has been published (366 references) [1]. Synthetic oxygen carriers related to biological systems have been reviewed in detail with a section dealing with cobalt—dioxygen carriers [2]. A review dealing with isomerism in complexes of bidentate ligands with enantiotopic donor atoms has been published [3], which deals with a large number of cobalt(III) complexes. A brief review of the history of studies of the mechanism of ligand substitution reactions of cobalt(III) has appeared [4], as has a review dealing with the stereochemistry of chelate-ring-containing cobalt(III) complexes [5].

The correlation of volumes and entropies of activation for racemisation and isomerisation reactions of octahedral metal complexes has been studied [6], and Table 1 lists the available data for cobalt(III) complexes. For a variety of cobalt(III), chromium(III), iron(II) and nickel(II) complexes, the data can be represented by the expression

$$\Delta S^{\ddagger} = 13.7\ (\pm 5.8) + (5.4(\pm 0.5)) \times \Delta V^{\ddagger}$$

It is contended that appreciable deviation from this correlation is indicative of a twist mechanism for racemisation or isomerisation.

TABLE 1

Activation volumes and entropies for racemisation and geometrical isomerisation of cobalt(III) complexes [6]

Complex	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}
trans-$[Co(en)_2(SeO_3H)(OH_2)]^{2+}$	+53 (±4)	+7.5 (±0.2)
trans-$[Co(en)_2(OH_2)_2]^{3+}$	+103 (±5)	+14.3 (±0.2)
trans-$[Co(en)_2(OH_2)_2]^{3+}$	+64 (±4)	+12.6 (±0.8)
trans-$[Co(en)_2(acet)(OH_2)]^{2+}$	+61 (±9)	+7.9 (±0.3)
trans-$[Co(en)_2(acet)(OH_2)]^{2+}$	+47 (±8)	+5.6 (±0.6)
trans-$[Co(en)_2(SeO_3)(OH_2)]^{+}$	+36 (±10)	+7.3 (±0.3)
trans-$[Co(en)_2(OH)(OH_2)]^{2+}$	+100 (±20)	+14.5 (±1.1)
β-[Co(edda)(tn)]$^{+}$	+124 (±10)	+19.9 (±0.4)
β-[Co(edda)(en)]$^{+}$	+174 (±15)	+25.2 (±0.5)

The use of activation volume measurements in the elucidation of reaction mechanisms in octahedral coordination complexes has recently been reviewed by Lawrance and Stranks [7]. The review covers racemisation reactions, isomerisation, aquation, base hydrolysis and redox reactions.

Yoshikawa and Yamasaki [8] have published a useful review dealing with the chromatographic resolution of cobalt(III) complexes on Sephadex ion exchangers. Some of the practical problems involved are particularly emphasised and discussed.

Other reviews of interest are "Kinetics and mechanism of substitution reactions of cobalt(III) *trans*-dioximines in non-aqueous media" [9] and the "Splitting of *d*-orbitals in square planar complexes of copper(II), nickel(II) and cobalt(II)" [10].

3.1 COBALT(IV)

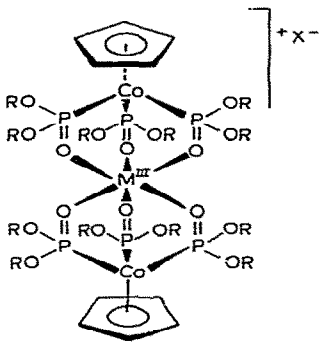
Organobis(dioximato)cobalt(III) complexes can be oxidised either chemically (Br_2, PbO_2 or cerium(IV) nitrate) or electrochemically to generate radical cations $[RCo(DH)_2L]^{+}$. The EPR results support the formulation of these radical cations as organocobalt(IV) complexes [11].

3.2 COBALT(III)

As always, a great deal of chemistry is published dealing with this classical, kinetically inert, oxidation state. The work reported can be subdivided into three broad areas, (a) synthesis, (b) stereochemistry (including X-ray crystallography) and (c) kinetics, reactivity and mechanism. There is also a developing interest in electrochemistry, and such areas as ^{59}Co NMR. As many cobalt(III) complexes are synthesised for kinetic and stereochemical studies, it is appropriate that some attention is devoted to these areas. However, it

should be stressed that these studies do not constitute a central area of the review.

An interesting report [12] deals with the observation of a high spin—low spin equilibrium in a six-coordinate cobalt(III) complex. Among octahedral-d^6 complexes, those of Fe^{II} with 1,10-phenanthroline, and 2,2′-bipyridine have been known as crossover systems for several years [13]. In the isoelectronic Co^{III} d^6-series, all complexes known until now are diamagnetic, the only exception being the high spin $[CoF_6]^{3-}$ ion [14]. The green cobalt(III) complexes (1) and (2) at 300K ($CHCl_3$ solution) have $\mu_{eff} = 2.6\ \mu_B$. On heating, the solid state magnetic moment of (1) increases steadily with $\mu_{eff} = 4.1\ \mu_B$ at 393K.



(1) M = Co^{III}, X = PF_6
(2) M = Co^{III}, X = ClO_4

There has been growing use of ^{59}Co NMR in studies of cobalt(III) complexes including hexakis(phosphite)cobalt(III) complexes [15], cobalt(III) complexes containing aminocarboxylato ligands [16], and solvent effects on the structure of $[Co(en)_3]^{3+}$ [17]. The technique has also provided useful information about the structure and dynamics of cobalt(III) metal environments. The ^{59}Co NMR chemical shifts are known to be very large, so that even subtle differences in the second coordination sphere of complexes may be detected. Although the cobalt(III) NMR spectrum is readily detected, a major difficulty arises if the symmetry at the cobalt nucleus is low, because the lines become prohibitively broad through very efficient relaxation by the nuclear electric quadrupole interaction. On the other hand, symmetrical cobalt complexes are readily investigated in solution by standard techniques. Rose and Bryant [18] have published a useful paper dealing with ^{59}Co and ^{14}N longitudinal and transverse relaxation times in the symmetrical complexes $[Co(CN)_6]^{3-}$, $[Co(en)_3]^{3+}$ and $[Co(NH_3)_6]^{3+}$. The mechanism of the ^{59}Co spin relaxation and the crystal structure of tris(tropolonato)cobalt(III) has also been reported [19].

The bis(acetylacetonato)(nitro)(1,9-dimethyladeninium)cobalt(III) cation has been prepared and its crystal structure determined [20]. This is the first example of the coordination chemistry of 1,9-disubstituted adenine deriva-

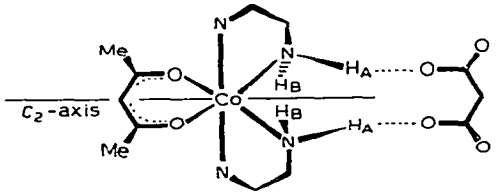
tives. The 1,9-dimethyl-adeninium cation is bound to the metal via N(7) and one of the amino protons forms a bifurcated hydrogen-bond system with two of the equatorially bound oxygen atoms of the acac ligands.

3.2.1 Complexes with oxygen or oxygen—nitrogen donor ligands

The enantioselective reduction of tris(pentane-2,4-dionato)cobalt(III) with a series of chiral supporting electrolytes in CH_3CN at a mercury cathode has been studied [21].

$$\begin{matrix} \text{D - (+) - [Co(acac)}_3\text{]} \xrightarrow{k_D} \\ \text{L - (—) - [Co(acac)}_3\text{]} \xrightarrow{k_L} \end{matrix} \xrightarrow[\text{chiral electrolyte}]{e^-} \text{Co(acac)}_2 + \text{acac}^-$$

The stereoselective association between pentane-2,4-dionato-bis(1,2-diaminoethane)cobalt(III) and malonate ion has been investigated by studying the rate of amine hydrogen exchange [22]. Malonate ion associates with the complex from the side opposite to acac and hydrogen bonds only to *trans* hydrogens in the direction approximately parallel to the two-fold axis of the complex (3). Stereoselective ion pairing of this type is important in the development of chromatographic separation techniques for metal complexes.



(3)

Stereoselective deuteration of the methylene hydrogens in some bis(malonato)cobalt(III) complexes, $[Co(mal)_2L]^{n-}$ (L = 1,2-diaminoethane, *N*-methyl-1,2-diaminoethane, glycinate and sarcosinate) has been investigated [23]. The proton first deuterated is probably the one which is closer to the chelate L.

^1H and ^{13}C NMR studies on malonic and ethyl malonic acids show that the α-protons exchange with deuterium in both acidic and basic D_2O. In basic solution the $[Co(en)_2mal]^+$ ion undergoes a fast ring opening with hydroxide ion and the α-protons exchange with deuterium from the solvent [24]. Stereochemical studies of cobalt(III) complexes of sexadentate aminopolyacids using ^{13}C NMR has been reported [25], as have CD investigations of cobalt(III) complexes which contain phenyl-substituted ethylenediamine-*N*,*N'*-diacetate analogues [26].

The X-ray crystal structure of an interesting cobalt(III)—cobalt(II) complex derived from bis(2-hydroxyethyl)-amine, $[Co_4\{NH(C_2H_4OH)_2\}_2\{NH(C_2H_4O)_2\}_4][ClO_4]_2$ has been published [27]. The complex contains the

ligand in both its protonated and deprotonated forms. The kinetics of the isomerisation of some tris(*O,N*-chelate) complexes of cobalt(III) have been studied [28], as has charge transfer in cobalt(III) complexes of a variety of β-diketones [29]. The reduction of (1,2-diaminoethanetetracetato)cobaltate-(III) and related complexes by titanium(III) has been investigated [30]. A ^{1}H NMR study of cobalt(III) complexes containing 5-membered amino-alcohol chelate rings has been published [31], and the synthesis of some new cobalt(III) complexes with the quadridentate ligands *N,N'*-trimethylenebis(salicylideneimine) and *N,N'*-tetramethylenebis(salicylideneimine) described [32]. Redox mediation by bound pyridinedicarboxylato groups in cobalt(III) complexes has been studied in a recent thesis [33] and the aquation kinetics of *cis*-diaquabis(biguanide)cobalt(III) investigated [34]. The stereospecific coordination of (SS)-1,2-diaminoethane-*N,N'*-succinic acid in cobalt(III) complexes has been studied in detail [35] and the same group have investigated ring strain in the cobalt(III) complex of 1,2-diaminoethane-*N',N',N'',N''*-tetraacetic acid [36]. Cobalt(III) complexes of 1,2-diiminoethanebis(pentane-2,4-dione) have been prepared [37]. Cobalt(III) complexes of 4-(2-pyridylazo)resorcinol and 1-(2-pyridylazo)-2-naphthol and their thiazolyl analogues have been studied in aqueous and aqueous-dioxane media by rapid scan techniques [38].

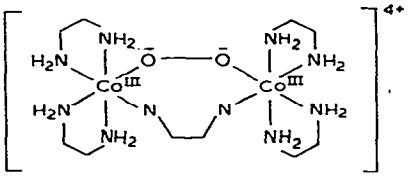
The reaction of the lanthanide shift reagent (Eu(fod)$_3$ with a series of tris-(β-diketonato)cobalt(III) complexes in $CDCl_3$ leads to 1 : 1 adduct formation in each case [39]. Two of the adducts have been isolated and characterised; adduct formation occurs along a C_3 axis of the cobalt complex so that three β-diketone oxygen atoms (around one face of the octahedron) bridge to the shift reagent. Reversal of the stereoselectivity in deuteration of the malonate methylenes in some bis-(malonato)cobalt(III) complexes, as a function of the pH of the solution, has been reported [40].

The syntheses of complexes of the type $[Co(amOH)(N)_2(O)_2]$ have been described [41], where amOH is 2-amino-ethanol or (S)-2-amino-1-propanol and $(N)_2(O)_2$ represents (glycinate)$_2$, (β-alaninate)$_2$, (ox)(en) or (ox)$(NH_3)_2$ and CD and visible spectra of these complexes discussed. The products of the reactions of $[Co(H_n edta)(NH_3)_5]^{(n-1)+}$, $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$, $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$ or $[Co(edta)]^-$ with $[Cr(H_2O)_6]^{2+}$ in acid solutions have been separated using SP-Sephadex column chromatography and identified [42]. A spectrophotometric study of complex formation between cobalt(III) and *trans*-1,2-cyclohexanenitrolotetraacetic acid (CyDTA) has shown that, in addition to the usual 1 : 1 complex, a 1 : 2 complex is formed at higher metal : ligand ratios [43].

3.2.1.1 μ-Peroxo complexes

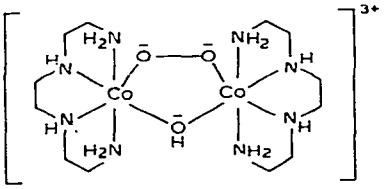
In biological systems, iron(II) (e.g. hemoglobin and myoglobin) or copper-(I) (hemocyanin) complexes serve as reversible oxygen carriers for the transport and storage of oxygen. Cobalt(II) forms many simple complexes which react reversibly with oxygen to give 1 : 1 and 2 : 1 metal complex to oxygen

adducts which have been widely studied as models for biological systems. Potentiometric, ultraviolet—visible and NMR studies [44] of the oxygenation of aqueous solutions of 5 : 2 and 3 : 1 molar ratios of 1,2-diaminoethane : cobalt(II) indicate that the equilibrium product is tetrakis (1,2-diaminoethane)-μ-(1,2-diaminoethane)-μ-peroxo-dicobalt(III) (4). Studies also indicate that the oxygenation of 2 : 2 : 1 or 2 : 1 : 3 solutions of cobalt(II) :



(4)

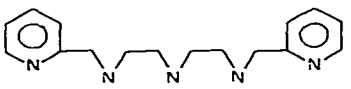
trien : en results in the formation of $[Co_2(trien)_2(en)O_2]^{4+}$ (5), or of (4) and (5), respectively. An important equilibrium involved in the formation of (5) is



$$+ [enH_2]^{2+} \rightleftharpoons [Co_2(trien)_2(en)O_2]^{4+} + [H_3O]^+$$

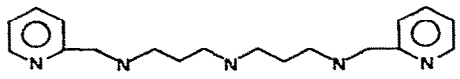
Raman spectroscopy has been used to study a range of binuclear μ-peroxo- and μ-superoxo-cobalt(III) complexes of macrocyclic ligands such as Me_6-[14]diene and Me_2[14]diene [45]. Monobridged μ-peroxo complexes exhibit a strong resonance Raman band at 800 ± 10 cm^{-1} (solid state or solution) and monobridged μ-superoxo-complexes show a band at 1120 ± 10 cm^{-1} in solution.

The structure of μ-peroxo-bis(1,9-bis(2-pyridyl)-2,5,8-triazanonane)-cobalt(III) tetraiodide, $[\{Co(pydien)\}_2O_2]I_4$, where pydien is the ligand (6) has been determined by single crystal X-ray diffraction [46]. The O—O distance of 1.489 Å and the Co—O—O angle of 112.5° are characteristic of peroxide bound to cobalt(III). The two pyridyl groups and the peroxo group are *cis* to each other, with the central aliphatic nitrogen donor *trans* to a pyridyl ring.



(6)

The crystal structure of the reversible oxygen carrier μ-peroxo-bis{[1,11-bis(2-pyridyl)-2,6,10-triazaundecane]cobalt(III)} tetraiodide trihydrate, $[\{Co(pydpt)\}_2O_2]I_4 \cdot 3\ H_2O$, where pydpt possesses the structure (7), has also been described [47]. The pyridyl nitrogens are *cis* to one another and



(7)

to the dioxygen bridge in the distorted octahedral geometry around the cobalt atoms, so that an imine nitrogen is *trans* to the dioxygen bridge. The O—O distance of 1.456 Å is consistent with the formulation of the dioxygen group as a peroxide ion.

3.2.1.2 Amino-acid and peptide ligands

The synthesis and X-ray crystal structure of Λ-*NS*-[Co(en)$_2$(S)-S-methyl-(R)cysteinato][NCS]$_2$ has been described [48]. Sulphur bonding of the sulphide occurs, and the chiral S-methyl centre is stereospecifically orientated; rearrangement of the *N,S*-bonded isomer to the *N,O*-bonded isomer does not occur under acidic conditions. The synthesis, structure and stereochemistry of some cysteine- and penicillaminecobalt(III) complexes have been reported [49]. The complexes prepared are Λ- and Δ-*N,S*-[Co(en)$_2${(R)-cysteinato}]$^{n+}$ and [Co(en)$_2${(S)-penicillaminato}]$^{n+}$. The less stable Λ-cysteine isomer can be prepared in ⩾95% yield by a second-order asymmetric synthesis. A series of complexes or geometrical isomers, [Co(β-ala or gly)(en)$_2$]$^{2+}$, [Co(β-ala or gly)$_2$(en)]$^+$, [Co(β-ala or gly)(ox)$_2$]$^{2-}$ and [Co(β-ala or gly)$_2$(ox)]$^-$ have been synthesised and their ^{13}C NMR spectra measured [50].

Four kinds of [Co(N)$_2$(O)$_3$(S)] type mixed, (L- or D-aspartato)(L-methionato) and (L- or D-aspartato)(S-methyl-L-cysteinato)cobalt(III), complexes have been prepared [51], and chromatographically separated into their three geometrical isomers *trans(N)*, *trans(S,O)* and *trans(S,N)*, respectively. The isomers were identified by their electronic and ^{1}H NMR spectra. The preparation and characterisation of *unsym-cis*-trimethylenediamine-*N,N'*-diacetato cobalt(III) complexes with several L-amino-acids (L-ala, L-val, L-pro, L-aspH and L-gluH) have also been described [52]. The developing use of column chromatography using Dowex 1-X8 and Sephadex C-25 for the separation of isomers in this type of work is noted.

The six isomers of the [Co(L- or D-asp)(L-his)] complex have been prepared [53] and their thermal isomerisation studied in the absence of a catalyst; absolute values of the rate constants at 80° C have been determined. The absence of tridentate coordination of S-glutamic acid in [Co(dien)(S-glutamato)]$^+$ has been established [54]. If glutamic acid coordinates in [Co(dien)(S-glu)]$^+$ as a tridentate ligand, forming 5- and 7-membered chelate rings, the dien ligand must be facial. However, dien favours a *mer*-topology on cobalt and S-glutamic acid behaves as a bidentate ligand with a "free" -(CH$_2$)$_2$COO$^-$ group, the sixth site being occupied by a water molecule.

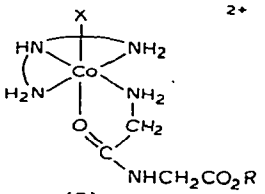
The preparation and separation of the *mer*-isomers of complexes of the type [Co(dipeptidato)$_2$]$^-$, where the dipeptides are glygly, L-phe-L-phe and mixed peptides of these two amino acids, have been described. The mixtures

of the two diastereoisomers (where applicable) have been separated. Detailed comparison of the ^1H NMR spectrum of the pairs of diastereoisomers enabled the absolute configuration of $[Co(L\text{-}phe\text{-}glyO)_2]^-$ and $[Co(gly\text{-}L\text{-}pheO)_2]^-$ to be determined. The protons of the C-terminal residue undergo exchange in basic solution, and Knoevenagel reactions were carried out with $[Co(glyglyO)_2]^-$ [55].

The crystal structure of *fac*(N)-Δ-tris(L-asparaginato)cobalt(III) trihydrate has been published [56], and the complete resolution of the *mer*-isomer of tris(β-alaninato)cobalt(III) achieved using CM-Sephadex cation exchanger and Sb_2-*d*-tartrate^{2-} as eluant [57]. A versatile, high resolution thin-layer chromatographic system for the analytical and preparative separation of cobalt complexes of amino-acids has been developed [58]. Some cobalt(III) complexes of α-amino acids (including glutamic acid) have been prepared [59], and the photoinduced ring contraction of glycine coordinated to cobalt(III) studied [60].

The kinetics of oxidation of (cysteinato-*N*,*S*)bis(1,2-diaminoethane)-cobalt(III) and related thiolato complexes to sulfenato-cobalt(III) complexes has been studied [61] and the synthesis and structure of the complexes $[Co(en)_2(CH_3SCH_2CH_2NH_2)][Fe(CN)_6]$ and $[Co(en)_2(C_6H_5CH_2SCH_2COO)][SCN]_2$ reported [62]. The kinetics of the chromium(II) reduction of chelated amino-acido-bis(1,2-diaminoethane)cobalt(III) complexes has also been studied [63]. Buckingham and co-workers have continued their investigations of the intramolecular hydrolysis of glycinamide and glycine dipeptides coordinated to cobalt(III) [64]. The mercury(II) catalysed removal of Br^- from *cis*-$[Co(en)_2Br(glyNHR)]^{2+}$ results in the immediate formation of $[Co(en)_2(glyNHR)]^{3+}$, containing the chelated amide or dipeptide residue and there is no intermediate formation of the aqua-complex.

Hay and Piplani [65] have reported rate constants at 298.2 K for the base hydrolysis of glycine peptides coordinated to cobalt(III). These constants fall in the range 0.67—0.88 $dm^3\ mol^{-1}\ s^{-1}$, ca. 2×10^4 times as large as for the free ligands. The complexes are of the type shown in (8)



(8)

3.2.2 Complexes with sulphur donor ligands

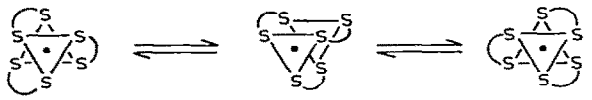
The tris dithioacetato complex of cobalt(III) has been prepared [66] and its properties compared with the corresponding dithiobenzoates, dithiocarbamates and xanthates. The reduction at the mercury electrode of a series of cobalt(III) dithiocarbamates in dmso has been investigated using a number

of electrochemical techniques [67]. The complexes undergo reduction in two successive diffusion controlled steps: the first a one-electron quasi-reversible; the second a two-electron irreversible step. The ease of reduction is a function of the alkyl substituent

$$[Co(Me_2dtc)_3] < [Co(Et_2dtc)_3] < [Co(Bu_2dtc)_3] < [Co(\{CHMe(Et)\}_2dtc)_3]$$

The preparation and characterisation of the flexible, linear pentadentate ligand 7-methyl-4,10-dithia-1,7,13-triazatridecane(L) and several mono-acidocobalt(III) complexes of the type $[Co(L)X]^{n+}$ (X = Cl^-, Br^-, N_3^-, SCN^- or H_2O) have been described [68]. The flexible carbon chain between the donor atom sequence nitrogen—sulphur—nitrogen—sulphur—nitrogen gives the possibility of four distinct geometric isomers designated $\alpha\alpha$, $\alpha\beta$, $\beta\beta$ and *β-trans*. The preferred pyramidal nature of sulphur and the methyl group positional requirements on the central nitrogen donor result in the selective formation of the $\alpha\alpha$-geometry.

Cobalt(III) complexes of thiosemicarbazide have been studied [69]. The preparation and assignment of absolute configuration to optically active tris-(dithiocarbamato)cobalt(III) complexes have been described [70]. The use of di(trifluoroethyl)dithiocarbamates of cobalt(III) for gas chromatographic elemental analysis has been investigated [71] and the syntheses of some cobalt(III) complexes of *o*-phenyl dithiocarbamates have been described [72]. Studies of the pressure dependence of the rates of racemisation of tris-(pyrrolidyldithiocarbamato)cobalt(III) in non-aqueous solvents provide evidence for a twist mechanism (9) incorporating a low spin ⇌ high spin pre-equilibrium in the transition state [73]



(9)

3.2.3 Complexes with nitrogen donor ligands

3.2.3.1 Ammines

The complex ion $[Co(NH_3)_5dmso]^{3+}$ is a useful synthetic intermediate [74]. The complex *cis*-$[Co(NH_3)_4(dmso)_2]^{3+}$ has now been prepared and characterised as its $[ClO_4]^-$ and Cl^- salts [75]. The shift in ν(S—O) from free dmso (1060 cm^{-1}) to 935—940 cm^{-1} in the complexes confirms that the ligand is bonded to cobalt(III) via oxygen. The bis(dmso) complex has been used to prepare *cis*-$[Co(NH_3)_4(pyridine)_2][ClO_4]_3$ and *cis*-$[Co(NH_3)_4(4\text{-methylpyridine})_2][ClO_4]_3$ and thus may provide a useful synthetic intermediate for the preparation of *cis*-$[Co(NH_3)_4L_2]^{n+}$ complexes.

The synthesis and characterisation of chloritopentaamminecobalt(III) nitrate has also been described [76]. In acidic solution, the complex

decomposes by an internal oxidation—reduction process with the formation of chlorine dioxide and cobalt(II). The crystal structure of hexaaminecobalt-(III) chloride chromate trihydrate has been determined [77]. A considerable number of kinetic studies have appeared dealing with ammines (particularly pentaammines) and these are briefly noted: specific rates of reduction of pentamminecobalt(III) derivatives of nitriles [78]; reduction of cobalt(III)-ammine complexes by dithionite [79]; reduction of acetato-complexes of pentaamminecobalt(III) [80]; and intramolecular electron transfer from pentacyanoferrate(II) to pentaamminecobalt(III) mediated by 4,4'-bipyridines [81]. Reynolds and co-workers have continued their detailed kinetic and mechanistic studies of various pentaamminecobalt(III) systems [82—85]. Intramolecular electron transfer in the reaction of hydroxyl radicals with (pyridine)-pentaamminecobalt(III) ion has also been studied [86], and the hydrolysis of 1-acetylimidazole in the presence of $[Co(NH_3)_5(OH)]^{2+}$ investigated as a potential model for carbonic anhydrase [87].

The circular dichroism and stereochemistry of the tetranuclear cobalt(III) complex dodecaammine-hexa-μ-hydroxotetracobalt(III), $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ has been discussed [88]. The absolute configuration of the $(+)_{589}$ isomer is assigned a Δ on the basis of the negative sign of the E_a component for the CoO_6 chromophore. Volumes of activation for the mercury induced aquation of halopentamminecobalt(III) complexes have been determined [89]. The kinetics of outer-sphere electron-transfer reactions between $[Co(NH_3)_5(dmso)]^{3+}$ and a series of $[Fe(CN)_5L]^{3-}$ complexes (L = imidazole, ammonia, pyridine, pyrazine, isonicotinamide or pyrazine-2-carboxamide) have been studied [90]. The formation constants of the precursor $[Co(NH_3)_5(dmso)]^{3+} \cdot [Fe(CN)_5L]^{3-}$ complexes are nearly constant (400—550 $dm^3\ mol^{-1}$), while the electron transfer rates show a systematic increase from the pyrazinamide complex to imidazole.

3.2.3.2 Diamines

The *cis*-chloro(2,2-diallcoxyethylamine)bis(1,2-diaminoethane)cobalt(III) ion has been prepared and its solvolytic aquation studied [91]. Early reports of the preparation of the thiosulfate complexes $[Co(en)_2S_2O_3Cl]$ and $[Co(en)_2S_2O_3]Br$ appear to be in error; the appropriate formulation of $[Co(en)_2S_2O_3Cl]$ or $([Co(pn)_2S_2O_3Cl])$ is as the monocationic—monoanionic salt *trans*-$[Co(en)_2Cl_2]^+$ *trans*-$[Co(en)_2(S_2O_3)_2]^-$, and similarly for the pn analogue [92]. No evidence was obtained for the production of the salt $[Co(en)_2S_2O_3]Br$ as reported by Duff [93]. The complexes *trans*-$[Co(en)_2Cl(RCH_2CO_2)]ClO_4$ (R = H, Cl, Br, I, CH, NH_2 or $\overset{+}{N}H_3$) have been prepared and characterised [94] and the kinetics of aquation, base and Hg(II)-assisted hydrolysis studied.

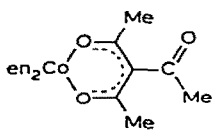
Five chiral cobalt(III) complexes of the orthotelluratobis(diamine)cobalt-(III) type have been synthesised [95]. The complexes belong to one of the three following types: mononuclear $[Co(TeO_6H_4)(diamine)_2]^+$ (diamine = en and R-(—)-1,2-pn); dinuclear $[Co(diamine)_2TeO_{10}H_4Co(diamine)_2]^{2+}$

(diamine = en and RR-1-*trans*-1,2-cyclohexanediamine); and tetranuclear $[\{Co(diamine)_2\}_2(Te_2O_{10})\{Co(diamine)_2\}_2]^{4+}$. Geometric isomers of cobalt(III) complexes containing 2-aminomethylpyridine and 1,2-diaminoethane or 2,2′-bipyridine have been prepared [96]. 2-Aminomethylpyridine is structurally intermediate between en and bipy. As the ligand (L) lacks a two-fold axis, geometrical isomers are expected for the complexes $[Co(L)_3]^{3+}$ and $[Co(X)_2L_2]$, where X = NO_2^-, Cl^-, H_2O or NH_3.

The crystal structure of *racemic cis*-dinitrobis(1,3-diaminopropane)cobalt(III) chloride monohydrate has been determined [97], and the CD spectra of cobalt(III) complexes of the type *trans*-$[CoX_2(1,3\text{-diamine})_2]^{n+}$ (X = Cl^-, CN^- or NH_3; 1,3-diamine = (S,S)-1,3-diphenyl-1,3-diaminopropane, (RR)-2,4-diaminopentane, (S)-1,3-diaminobutane or (S)-1-phenyl-1,3-diaminopropane) obtained [98]. The crystal structure of disodium *cis*-bis(1,2-diaminoethane)disulphitocobaltate(III) perchlorate trihydrate has been determined [99] as has that of [*N*,*N*-bis(2-aminoethyl)1,2-diaminoethane-*N*,*N*′,-*N*″,*N*‴](1,2-diaminoethane)cobalt(III) trichloride dihydrate [100]. Conformational analysis of tris(2-methyl-1,2-diaminopropane)- and (2,3-diaminobutane)bis(1,2-diaminoethane)cobalt(III) complexes has been reported [101]. A further paper deals with tris(diamine)cobalt(III) complexes [102].

The reaction of thiolatobis(1,2-diaminoethane)cobalt(III) complexes with hydrogen peroxide has been studied [103]. A variety of cobalt(III) complexes containing trimethylenediamine and some bidentate *NN*, *NO* and *OO* donor ligands have been prepared [104] and the conformational analysis of tris(1,2-diaminoethane)- and tris(2,3-diaminobutane)cobalt(III) complexes studied [105]. A proton NMR and conformational study of cobalt(III)-(R)-1-phenyl-1,2-diaminoethane has appeared [106].

The crystal structure of $(-)_{589}$-*cis*-dinitrobis((2S)-2-amino-4-azapentane)-cobalt(III) chloride has been determined [107]. The complex cation has the absolute configuration Λ, and the conformations of the chelate rings are both δ, the two *N*-methyl and the two *C*-methyl groups lie in equatorial positions with respect to the chelate rings. The nitrito—nitro isomerisation in the solid state has been investigated by X-ray structure determinations of the perchlorate and iodide salts of *trans*-$[Co(en)_2(NCS)(ONO)]^+$ and the corresponding nitro complexes [108]. The structures of the two isomers indicate that the isomerisation is intramolecular and that the reaction takes place in a plane by rotation of the NO_2 group, possibly via a seven-coordinate transition state. The photochemical nitro → nitrito reaction also appears to occur by rotation of the NO_2^- group: The kinetics of the chromium(II) reduction of $[Co(en)_2(3\text{-acetyl-ptdn})]^{2+}$ (**10**) and $[Co(en)_2(2\text{-acetyl-btdn})]^{2+}$ (**11**) have been studied [109]. Product studies indicate attack at the uncoordinated



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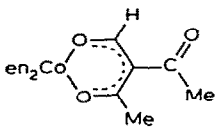

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acetyl function in both complexes.

A number of stereochemical papers have appeared. Sakakibara et al. [110] have suggested an empirical rule for the elution order of $[CoN_6]^{3+}$-type complexes in chromatography on SP-Sephadex columns. The relative elution rates have been correlated with the number and the kind of the octahedral faces of the complex on which ion association with a phosphate ion occurs. A further chromatographic paper deals with observations of the inversion of elution order in ion-exchange chromatography for *cis*- and *trans*-isomers of $[Co(en)_2X_2]^+$ (X = N_3, NO_2 or NCS) by the addition of dioxane to aqueous solutions of $[NH_4]Cl$ or $[NH_4]_2SO_4$ used as eluant [111]. Solubility isotherms and their application to the resolution of $[Co(en)_2ox]^+$ via the 3-bromocamphor-9-sulphonate have been investigated [112].

A series of complexes of the type *trans*-$[Co(en)_2X(^-O_2CCH(R)\overset{+}{N}H_3)][ClO_4]_2$ (X = Cl or Br) containing the monodentate carboxylato-bonded amino-acids, glycine (R=H), DL-α-alanine (R=Me) and DL-aminobutyric acid (R=Et) have been prepared and characterised [113]. All the complexes behave as monobasic acids and the pK values for the $-\overset{+}{N}H_3 \rightleftharpoons -NH_2 + H^+$ ionisation have been obtained. Base hydrolysis and mercury(II) catalysed aquation kinetics were also discussed. A variety of kinetic investigations have been reported dealing with bis(1,2-diaminoethane)cobalt(III) complexes. An interesting paper [114] deals with the observation of mercury(II) assisted base hydrolysis of complexes of the type *cis*-$[Co(en)_2(RNH_2)Cl]^+$ (R = C_6H_5, 4-$CH_3C_6H_4$ or 3-$CH_3C_6H_4$). Although mercury(II) assisted aquation is well documented, this appears to be the first example of mercury(II) promotion in base hydrolysis.

The influence of ligands *trans* to the leaving group on the rates and steric courses of the hydrolysis of *trans*-chloro(formato)-, *trans*-chloro(propionato)- and *trans*-chloro(pivalato)bis(1,2-diaminoethane)cobalt(III) complexes has been studied and the preparation of these complexes described [115]. The isomerisation of *trans*-$[Co(en)_2(O_2CMe)(OH_2)]^{2+}$ in aqueous acid is retarded by increased pressure with $\Delta V^{\neq} = +7.9 \pm 0.3$ cm^3 mol^{-1} [116]. The data is most consistent with isomerisation proceeding via dissociative aqua ligand release. The rate and stereochemical course of the ammoniation of *cis*- and *trans*-$[Co(en)_2Cl_2][ClO_4]$ to $[Co(en)_2(NH_3)_2][ClO_4]_3$ has been studied in the temperature range −40 to −55°C; *trans*-$[Co(en)_2Cl_2]^+$ and *cis*-$[Co(en)_2(NH_3)Cl]^+$ react with full retention of configuration [117]. A model inferred from features of the ammoniation of cobalt(III) haloamines has been extended to base hydrolysis in aqueous solution [118]; this model connects the reactivity of the conjugate base to a large volume increase on passing to the transition state in a limiting dissociative mode. The reactions of the cobalt(III)-polyamine complexes $[Co(en)_3]^{3+}$, $[Co(dien)_2]^{3+}$, $[CoCl_2(en)_2]^+$ and $[CoCl_2(trien)]^+$ with $^{\cdot}OH$ radicals has been studied by conductometric pulse radiolysis in weakly acid solutions [119]. All the complexes react with $^{\cdot}OH$, with $k = (3.0 \pm 0.2) \times 10^8\ M^{-1}\ s^{-1}$. The hydroxyl radical abstracts $H^{\cdot}$ from a CH_2 of the ligand: the radical—ligand thus formed

reduces the Co(III) to Co(II), itself being oxidized to a protonated imine which is more slowly eliminated from the complex.

3.2.3.3 Triamines

The reaction of *mer*-[$CoCl_3$(dien)] with >2.5 molar equivalents of several monoamines A (A = methylamine, ethylamine, propylamine, butylamine, 2-aminobutane, pentylamine, hexylamine, benzylamine, cyclohexylamine or pyridine) in aqueous or aqueous-methanol solution gives various amounts of *rac-unsym-fac*-X-*a,bcf,de*-[$CoCl(dien)A_2]^{2+}$, *mer-cis-a,bcd,ef*-[$CoCl(dien)A_2]^{2+}$ and *trans-af,bcd,e*-[$CoCl_2(dien)A]^+$ complexes [120]. The isomeric purity and composition of the complexes was established using ^{13}C NMR and IR spectroscopy and the *unsym-fac-cis*-geometry confirmed by resolution of the complexes where A = pentylamine or pyridine. A ^{13}C NMR study of some ammine complexes of diethylenetriaminecobalt(III) has been published [121], and configurations established in this basis. Searle et al. have studied the homogeneous and charcoal catalysed isomerisations of (diethylenetriamine)(methyldiethylenetriamine)cobalt(III) and bis(dien)cobalt(III) cations, [122].

An efficient synthesis of 4-methyldiethylenetriamine (Medien) has been described and a variety of cobalt (III) complexes prepared [123]. Pure s-*fac*-[Co(dien)(Medien)][ClO_4]$_3$ can be isolated by chromatography on SP-Sephadex cation exchange resin.

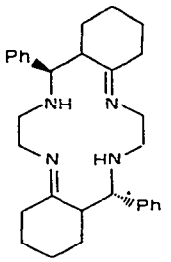
3.2.3.4 Tetramines

The ligand field photolysis of *cis*-β-[$Co(2,3,2\text{-tet})ClX]^{n+}$ (2,3,2-tet = 1,4,-8,11-tetra-aza-undecane; X = Cl or H_2O) has been studied in acidic aqueous solution [124]; photolysis of *cis*-β-[$Co(2,3,2\text{-tet})Cl_2]^+$ and *cis*-β-[$Co(2,3,2\text{-tet})Cl(H_2O)]^{2+}$ gives *trans*-[$Co(2,3,2\text{-tet})Cl(H_2O)]^{2+}$ as the only photoproduct. A variety of cobalt(III) complexes of the unsymmetrical flexible tetraamine ligand 3,6-diaza-1,9-nonanediamine (2,2,3-tet) have been prepared [125]. The preparation of the β_1 and β_2 isomers of [Co(trien)(salicylate)]$^{2+}$ has been reported [126]. The IR spectra of the β_1 and β_2 isomers have four strong bands in the 990—1100 cm^{-1} consistent with the β-configuration of the tetramine. The β_1 and β_2 configurations were distinguished by ^1H NMR spectroscopy in D_2SO_4.

3.2.3.5 Macrocycles

The preparations of several cobalt(III) complexes of the new macrocyclic ligand C-*meso*-7,14-diphenyl-5,6-butano-12,13-butano-1,4,8,11-tetra-aza-cyclotetradeca-4,11-diene (L = 12) have been described [127]. These complexes, *trans*-[$CoLX_2$] (X = Cl, Br, NO_2 or N_3) have the C-*meso*-N-*meso* arrangement of the chiral centres (13) which places the bulky phenyl groups in equatorial sites.

Halide mediated electron transfer involving low spin cobalt(III)-cobalt(II) couples has been studied for some macrocyclic complexes [128]. The



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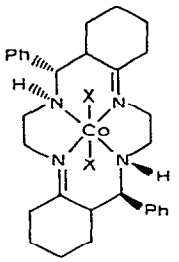

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preparation and ligand substitution kinetics of *trans*-dihalogeno- and *trans*-halogenoisothiocyanatocobalt(III) complexes of 2,12-dimethyl- and 2,7,12-trimethyl-3,7,11,17-tetra-azabicyclo(11,3,1)-heptadeca-1(17),2,11,13,15-pentaene have been reported [129] and the preparation and base hydrolysis of cobalt(III) complexes of some quadridentate macrocyclic amines investigated [130]. The cycloaddition reaction of acetylene with cobalt(III) complexes of 7,16-dihydro-6,8,15,17-tetramethyldibenzo[b,i][1,4,8,11]tetra-azacyclotetradecinate gives a novel dianionic pentadentate macrocycle with four equatorial nitrogen donor atoms and a vinylide carbon σ donor occupying one axial site [131]; the crystal structure of the complex $[Co(C_{24}H_{24}N)(C_5H_5N)][PF_6] \cdot CH_3CN$ has been described [131].

The acid-catalysed decarboxylations of *cis*-$[Co(cyclen)CO_3]^+$ [132] and *cis*-$[Co(Me_2[14]diene)CO_3]^+$ [133] have been shown to be consistent with a mechanism involving rapid pre-equilibrium protonation of the carbonato ligand, followed by slow rate-determining ring opening of the carbonato ring. The reactions display solvent deuterium isotope effects k_{D_2O}/k_{H_2O} of 2.1—2.6 which excludes rate-determining proton transfer.

3.2.3.6 Oximes, cobaloximes and vitamin B_{12}

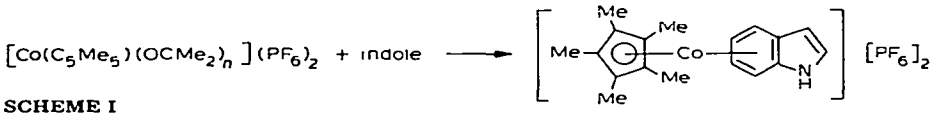
Homolytic cleavage of the Co—C bond is generally accepted as a key step in the mechanism of action of many enzymes which require a B_{12} coenzyme. The X-ray structure of *trans*-bis(dimethylglyoximato)(isopropyl)(pyridine)-cobalt(III) indicates an unusually long cobalt—carbon bond of 2.085 Å [134]. There appears to be a linear relationship between the number of substituents on the alkyl carbon bonded to cobalt for $pyCo(DH_2)R$ complexes and this may have implications regarding the conformational trigger mechanism of cobalt—carbon bond cleavage in coenzyme B_{12}. A novel heterolytic cleavage of the carbon—cobalt bond has been observed for 1,19-dimethyl-AD-bisdehydrocorrinato)cobalt complexes in aqueous media [135]. A number of papers dealing with the synthesis of cobalt(III)-α-dioxime complexes have appeared [136—138] and the synthesis of cobalt(III)clathrochelates derived from dioximes has been described in detail [139].

The rate of electron transfer between the $[Co(I)]^-$ and $[Co(III)]^+$ derivatives of vitamin B_{12} (B_{12s} and B_{12a}) has been studied using pulse radiolysis [140]. A number of other kinetic investigations have appeared; reactions of

cyanide with cobalamins [141], cleavage and rearrangement reactions of (β-hydroxyalkyl)cobaloximes in acid solution [142], and the mechanism of base-catalysed methane formation from methyl(aquo)cobaloxime [143].

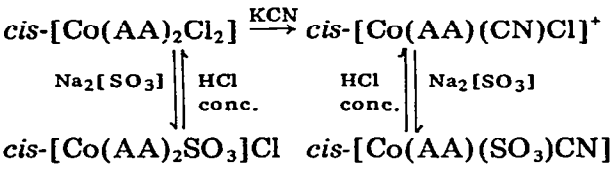
3.2.4 Other complexes

The synthesis of pentamethylcyclopentadienyl cobalt(III) complexes by the reaction of $[\{Co(C_5Me_5)I_2\}_n]$ with the appropriate Lewis base (PMe_2Ph, $P(OPh)_3$ or $CNCMe_3$) has been described, and the preparation and properties of $[Co(C_5Me_5)(solvent)_n]X_2$ (solvent = NCMe, n = 3, X = PF_6; solvent = $OCMe_2$, n = 3, X = PF_6 or BF_4) discussed [144]. Cyclopentadienyl- or pentamethylcyclopentadienyl(arene)cobalt(III) complexes (arene = indole, benzene, mesitylene, hexamethylbenzene, 1,4-dihydroxy- or 1-hydroxy-4-methoxytetramethylbenzene) have been prepared by reactions of the type shown in Scheme I [145].



SCHEME I

The reaction of *cis*-$[Co(AA)_2Cl_2]Cl$ (AA = 2,2′-bipyridine or 1,10-phenanthroline) with sodium sulphite gives *cis*-$[Co(AA)_2SO_3]Cl$, with bidentate sulphite coordinated via the oxygen atoms [146]. (The only possible isomer for octahedral complexes of cobalt(III) with two bipy or phen ligands is the *cis*-isomer.) The complex $[Co(AA)(SO_3)CN]$, containing monodentate sulphite, was obtained as shown in Scheme II.



SCHEME II

A direct determination of the absolute configuration of $(-)_D$-tris(2,2′-bipyridine)cobalt(III) has established that it has the Δ configuration [147], and the absolute configuration of $(+)_{546}$-β-(oxalato)((2S,4S,9S,11S)-4,9-dimethyl-5,8-diazadodecane-2,11-diamine)cobalt(III) bromide trihydrate is Λ [148]. The Pfeiffer effect with cinchoninium ion as a chiral environment has been studied with $[Co(phen)_3]^{3+}$ [149]. The aquation of the bromopentacyanocobaltate(III) ion has been studied in the presence of several hard acids (H^+, Na^+ or Mg^{2+}) or halomercury(II) complexes [150]; the hard acids had small effects, while the mercury(II) halides significantly accelerated the aquation.

3.3 COBALT(II)

3.3.1 Complexes with oxygen or sulphur donor ligands

The compounds $[Co(H_2O)_6][CF_3SO_3]_2 \cdot H_2O$ and $Co(CF_3SO_3)_2$ have been prepared and characterised [151]. $Co(acac)_2$ reacts with the hydroperoxide ion (generated electrochemically) to give $[(acac)_2Co{-}O_2{-}Co(acac)_2]^{2-}$ [152]. Several new cobalt(II) complexes with 4-substituted phenylmethyl sulphoxides have been prepared [153]; all are six-coordinate and exhibit metal—oxygen bonding as indicated by IR spectroscopy. Direct conversion of cobalt(II), fixed on an ion—exchange resin, to its bis(trifluoroacetylacetonate) {which is useful for gas chromatography} has been described [154]. The complex $[Co\{O_2C_6H_2(CMe_3)_2\}_2]$ has been prepared by treating $[Co_2(CO)_8]$ with 3,5-di-*tert*-butyl-1,2-benzoquinone in benzene solution [155]; the dark green complex has been shown by X-ray crystallography to be tetrameric, $[Co_4\{O_2C_6H_2(CMe_3)_2\}_8]$, in which cobalt(II) is octahedrally coordinated.

The kinetics of aquation of $[Co(acac)_3]^-$ have been studied as a function of pH [156]; the reactions leading to the loss of each of the three ligands are well separated. The results are consistent with a mechanism in which the bidentate bound ligand is in equilibrium with a monodentate form; the latter is lost by an acid-catalysed process, with an acid-independent contribution. The oxidation of acetamide, formamide, *N*-methylformamide, and *N,N*-dimethylformamide by cobalt(III) in perchloric acid media at 20°C has been studied [157], and a free radical mechanism proposed.

3.3.1.1 Dioxygen complexes

There has been considerable interest in the interaction of dioxygen with cobalt(II) complexes. Oxygenation of cobalt(II) complexes of tetradentate ligands such as 1,4,7,10-tetraazadecane (2,2,2-tet) in aqueous solution gives μ-peroxo-μ-hydroxo-dicobalt(III) complexes [158]. Eight different stereoisomers are possible, however, the introduction of methyl groups in the 4 and 7 positions of 2,2,2-tet destabilises the isomers with a β-configuration. The crystal structure of a perchlorate salt obtained by oxygenation of 4,7-dimethyl-1,4,7,10-tetraazadecanecobalt(II) in basic solution has been determined [158]. The preparation and crystal structure of the dioxygen adduct of aqua-*N,N'*-(1,1,2,2-tetramethylethylene)bis(3-methoxysalicylideniminato)-cobalt(II) has been described [159]. The dioxygen molecule is disordered between two positions with an average Co—O distance of 1.88 Å and an average O—O distance of 1.25 Å.

Equilibrium data have been reported [160] for the complexation of dioxygen by the cobalt(II) complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Me_6[14]diene) in the presence of various *trans* axial donors (pyridine, imidazole, ammonia, cyanide or coordinated water). A switch in

preferred stoicheiometry from 2 : 1 to 1 : 1 occurs from the saturated to unsaturated systems. Equilibrium data for oxygenation of a number of cobalt(II) complexes of pentadentate ligands which form 5-membered chelate rings indicate [161] that the logarithms of the formation constants of the dioxygen adduct do not correlate with the stability constants of the cobalt(II)—ligand complexes, but correlate linearly with the ΣpK's of the ligand donor groups coordinated to cobalt. The solution O—O stretching frequency of a monomeric dioxygen cobalt complex has been determined by resonance Raman spectroscopy (pyridine - dmf solvent) [162]. EPR measurements have been made on dioxygen adducts $[Co^{II}L] \cdot O_2$ of certain quadridentate Schiff base ligands (L) in frozen solutions containing pyridine or 2,6-dimethylpyridine [163].

Dioxygen complexes of tetraethylenepentaminecobalt(II) have been studied [164] and the electrocatalytic formation of superoxides in the presence of cobalt complexes investigated [165]. The stabilities of cobalt(II) complexes of imidazolyl containing pentadentate polyamines and their dioxygen complexes have been reported [166]. Oxygenation of cobalt(II) carboranylporphyrinates have been studied in the solid state, non-aqueous and aqueous solutions [167]. Such properties as solubility and degree of oxygenation can be altered by suitable modification of the carboranyl cages while keeping the immediate environment of the porphyrinate core approximately constant. Catalytic oxidations of phosphines to phosphine oxides and isonitriles to isocyanates have been shown to occur using metal peroxo complexes. A recent paper discusses oxygen transfer from ligands using cobalt nitro complexes as oxygenation catalysts [168]. These reactions can be represented by the equation

$$[Co(saloph)(py)NO_2] + Ph_3P \rightarrow [Co(saloph)(NO)] + Ph_3PO + py$$

where saloph = *N,N'*-bissalicylidene-*o*-phenylenediamine. Dioxygen(pyridine)-*N,N*-ethylenebis(acetylacetoniminato)cobalt(II) reacts with acids in organic solvents containing excess pyridine, to give 0.5 mol of molecular oxygen, 0.5 mol H_2O_2 and 1 mol of dipyridine-*N,N'*-ethylenebis(acetylacetoniminato)cobalt(III) as an ion pair with the anion of the acid [169].

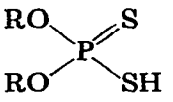
3.3.1.2 Sulphur-containing ligands

The salts $[(\mu\text{-}SPh_6)_6(CoSPh)_4]^{2-}$, $[(\mu\text{-}Sph)_6(CoSPh)_2(CoCl)_2]^{2-}$ and $[Co(SPh)_4]^{2-}$ have been synthesised (with $[Me_4N]^+$ and other cations) and the crystal structure of $[Me_4N]_2[(\mu\text{-}SPh)_6(CoSPh)_4]$ determined [170].

Cobalt(II) and cobalt(III) complexes of methyl esters of dithiocarbazic acid $NH_2NHCSSMe$ (HL) and of 2-methyldithiocarbazic acid $NH_2N(Me)CSSMe$ (MeL) have been prepared and characterised. HL can act as a ligand when neutral or deprotonated (L^-); MeL can be deprotonated at the terminal N only after coordination. The crystal structure of $[Co(HL)L_2]Cl \cdot H_2O$ has been determined [171]. Cobalt(II) complexes of pyridine-2-aldehyde semicarbazone and thiosemicarbazone have been studied [172]. The

synthesis of $Co(Cu(SCN)_2)_2$ has been reported and its reactions with Lewis bases (B) to give polymeric bridged complexes of the type $(B_2)Co(Cu(SCN)_2)_2$ studied [173].

The cobalt(II) complexes of 2,5-dimethyl-1,3,4-thiadiazole (L), $Co(L)_2X_2$ (X = Cl, Br, I or NO_3) have been prepared and investigated [174]. The complexes have magnetic moments in the range 4.4—4.6 μ_B and are assigned a pseudo-tetrahedral stereochemistry. The transition metal complexes of *O,O'*-dialkyl esters of dithiophosphoric acid (14) are of interest, the ligands being



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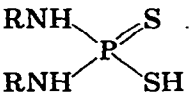

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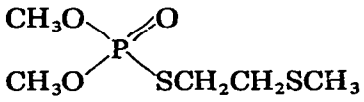
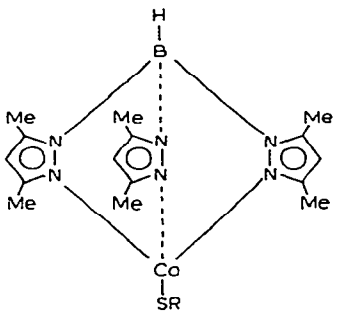


(16)

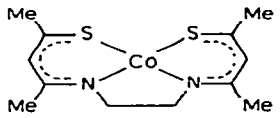
readily prepared by the reaction of alcohols with P_4S_{10}. Similar reactions of P_4S_{10} with primary and secondary amines give, among other products, dithiophosphoric acid amides (15). Some cobalt(II) and cobalt(III) complexes of some aryl esters and amides of dithiophosphoric acid have been isolated and characterised [175]. A further study has dealt with cobalt(II) halide complexes of *O,O*-dimethyl-2-(2-methylthioethyl)phosphoro-thiol (16) [176]. Cobalt(II) halides react with 3,6-disubstituted-2,7-dihydro-1,4,5-thiadiazepine derivatives (L) to give highly hygroscopic complexes $[CoX_2L]_2 \cdot n\ H_2O$. The cobalt complexes are tetrahedral, with a dimeric structure in which bridging only occurs via the thiadiazapine ring [177].

Complexes of the stoichiometry $Co^{II}N_3(SR)$ have been prepared by the reaction of CoCl(SR) (SR = *O*-ethylcysteinate) with potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate, $K[HB(3,5\text{-}Me_2pz)_3]$, or by the reaction of $[CoBr\{HB(3,5\text{-}Me_2pz)_3\}]$ with NaSR (SR = 4-nitrobenzenethiolate or pentafluorophenylthiolate) [178]. These complexes are regarded as synthetic approximations to the proposed active site in the cobalt(II)-substituted blue copper proteins. The complex pentafluorophenylthiolato(hydrotris(3,5-dimethyl-1-pyrazolyl)borato)cobalt(II) has also been characterised by X-ray diffraction (17).



(17)

Cobalt(II) complexes of 2,2′-*o*-phenylenebisbenzothiazole (a potential *N* or *S* donor ligand) have been reported. The complexes $[Co(L)X_2]$ (X = Cl, Br, I or NCS) have four coordinate pseudotetrahedral stereochemistries. A six-coordinate complex $[Co(L)(NO_3)_2]$ has also been characterised. Hydrogen-bonded chloroform solvate molecules appear to be present in $[Co(L)X_2]$ (where X = Cl, Br or NCS) [179].



(18)

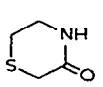
Schiff base complexes of the type (18) can form monomeric dioxygen adducts in the presence of Lewis bases. EPR measurements have shown that such complexes form 5-coordinate adducts with Lewis bases and CO which have rhombic symmetry with a $(d_{x^2-y^2}, d_{xz}, d_{yz})^6(d_{z^2})^1$ configuration [180].

3.3.2 Complexes with oxygen—nitrogen donor ligands

Magnetic and spectral properties of the pentagonal bipyramidal complexes chloroaqua- and diaqua-2,6-diacetylpyridine bis(semicarbazone) cobalt(II) have been reported [181], and the synthesis and characterisation of the pentagonal bipyramidal complex aqua(nitrato)[2,6-diacetylpyridinebis-(benzoic acid hydrazone)]cobalt(II) nitrate described [182]. Cobalt(II) and (III) complexes of the cyclic hydroxamic acid, 1-hydroxy-2-pyridone have been prepared [183], as have complexes of ethyl 5(3)-methylpyrazole-3(5)-carboxylate with cobalt(II) halides [184]. Coordination by hydroxy and ethereal oxygens to cobalt(II), in a variety of ligands such as $NH_2(CH_2)_2$-$NH(CH_2)_2OH$ and $CH_3OCH_2CH_2N(CH_2CO_2)_2$ has been suggested as a result of ^1H NMR investigations [185]. The reaction of the zwitterionic oxine ligand with cobalt(II) complexes of pyridine-2,6-dicarboxylate has been studied [186], and the cyanoacetates of cobalt(II) and its pyridine and 2,2′-bipyridine complexes discussed [187]. An interesting paper has appeared dealing with the interaction of the iminodiacetate group of the chelating ion-exchange resin Chelex 100 with cobalt(II), nickel(II) and copper(II) [188]; Chelex 100 acts as a tridentate ligand to these metal ions. Synthetic procedures for attaching multidentate ligands to organic polymers are likely to be of increasing economic importance. Chelating Schiff base ligands attached to macroreticular polystyrene which bind cobalt(II) (among other metals) have been described by Drago and Gaul [189].

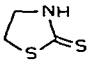
A number of metal complexes of acetophenone benzoic hydrazide and acetophenone salicylic hydrazide (including cobalt(II) derivatives) have been characterised [190]. Self-adduct formation in the extraction of cobalt-(II) complexes of substituted 8-quinolinols has been investigated [191]. Mixed complexes of cobalt(II) with tetrahydro-1,4-thiazin-3-one (tht; 19),

thiazolidine-2-thione (ttz; 20) and benzoxazole-2(3H)-thione (bot; 21) and aliphatic dicarboxylic acids such as oxalic, succinic and malonic have been prepared [192]. All physical measurements agree with a polymeric linear-chain structure for the complexes in which the oxalate, malonate



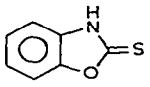
tht

(19)



ttz

(20)



bot

(21)

or succinate dianion acts as a tetradentate bridging ligand linking two metal ions.

If a small amount of a cobalt(II) salt containing radioactive cobalt is added to a solid cobalt(III) complex and then heated, some of the radioactive cobalt becomes incorporated in the complex [193], according to

$$^{57}Co^{II} + [Co(bipy)_3][ClO_4]_3 \rightarrow [^{57}Co(bipy)_3][ClO_4]_3 + Co^{II}$$

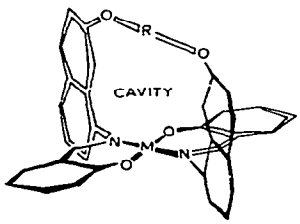
This "transfer annealing" has been studied by emission Mössbauer spectroscopy and has been shown to be a solid state isotopic process. Transfer annealing reactions also occur in mixed metal systems

e.g. $^{57}Co^{II} + [Fe(oxin)_3] \rightarrow Fe^{II} + [^{57}Co(oxin)_3]$

and it has been suggested that solid state isotopic exchange may provide a simple method of preparing labelled compounds. A noteworthy feature of these reactions is that they are generally stereoretentive.

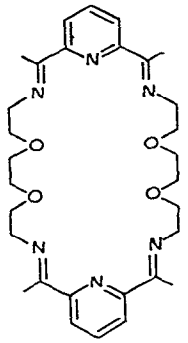
3.3.2.1 Schiff bases

Martin and co-workers [194] have described the synthesis of several sterically hindered N_2O_2 and N_4 ligands in which a quadridentate Schiff base is "capped" by condensation of salicylaldehyde or pyrrole-2-carbaldehyde with a series of bis(8-aminonaphthyl)alkyl diethers (22). A number of repre-



(22)

sentative complexes including cobalt(II) complexes have been prepared. The ^1H NMR spectrum of the neutral monomeric nickel(II) complex is consistent with the proposed *trans*-planar capped structure. The preparation of the 30-membered potentially decadentate macrocyclic Schiff base ligand (23) has been reported [195] and complexes with cobalt(II) and cobalt(III) characterised, in which only the six nitrogen atoms act as donors.



(23)

A recurrent theme in bioinorganic chemistry has been the quantitative evaluation of the effect of a variation in equatorial ligand structure on the redox potential of macrocyclic cobalt and copper complexes and on Schiff base complexes used as models for biological macrocycles. A series of 19 cobalt and copper complexes derived from Schiff bases have been studied by thin layer spectroelectrochemical techniques [196]; the Co^{II}/Co^{III} and Co^{I}/Co^{II} couples exhibit Nernstian reversibility and the copper(I) complexes are stabilised by ligand unsaturation as are the cobalt(I) analogues. A number of studies of the magnetic properties of cobalt(II) complexes of Schiff base ligands have appeared [197,198].

There has been considerable interest in the interaction of dioxygen with cobalt(II) complexes of Schiff bases and this area is summarised in Section 3.3.1.1.

3.3.2.2 Amino-acid and peptide ligands

Cobalt(II) complexes of amino-acids and their interaction with dioxygen have been discussed [199], and cobalt(II) complexes of *N*-acetyl-DL-leucine described [200]. Cobalt(II) complexes of bis(*N*-acetyl-DL-valinate) and their amine adducts have been studied [201]. The solution equilibria of di- and tetrapeptides containing tyrosine and glycine residues have been investigated in the presence and absence of cobalt(II) (and nickel(II) and copper(II)) ions [202].

3.3.3 Complexes with Group VB donor ligands

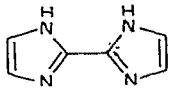
3.3.3.1 Nitrogen ligands

Bis- and tris-complexes of 2-hydrazino-4,6-dimethyl pyrimidine (L) of the type $CoL_2X_2 \cdot n\ H_2O$ and $CoL_3X_2 \cdot n\ H_2O$ (X = Cl, Br, I, NO_3, ClO_4, BF_4 or SCN; n = 0, 1 or 2) have been reported [203]. The reaction of cobalt(II) porphyrin with iodine in apolar solvents has been studied [204], the resulting complex has an I_2 bridge between the two cobalt(II) centres. The kinetics and mechanism of oxidation of cobalt(II) macrocycles by I_2, Br_2 or H_2O_2 has been studied [205]. Bromine and iodine in acidic aqueous solution give the

corresponding monohalocobalt(III) complex. EPR studies on frozen solutions of cobalt(II) dibenzo[b,i][1,4,8,11]tetraazacyclotetradecahexaenate have been published [206]. A comment on the use of $HgCo(NCS)_4$ as a susceptibility standard has appeared [207]. Pseudo-halo and halo complexes of cobalt(II)-3-iodopyridine have been prepared [208].

Homogeneous catalysis of the photoreduction of water by visible light using transition metal complexes has been a topic of considerable interest in recent years. Macrocyclic cobalt(I) complexes such as $[Co^{I}(Me_6[14]dieneN_4)]^{+}$ have been shown by pulse-radiolysis studies to react rapidly with H_3O^{+}; the related cobalt(I) macrocycle $[Co^{I}(Me_4[14]tetraeneN_4)]^{+}$ reacts with H_2O and other protic solvents with the evolution of H_2. From electrochemical data (CH_3CN solvent), the $[Ru(bipy)_3]^{+}$ ion is thermodynamically capable of reducing $[Co^{II}(Me_6[14]dieneN_4)(H_2O)_2]^{2+}$ to the corresponding Co^{I} complex. A system consisting of $[Ru(bipy)_3]^{2+}$, $[Co^{II}(Me_6[14]dieneN_4)]$ and either ascorbate or Eu(II) is therefore a potential system for the catalysed photoreduction of water using visible light. Such a system does indeed evolve dihydrogen on irradiation at 450 nm with a quantum yield of 0.05 [209].

Complexes of 2,2′-biimidazole (24) with cobalt(II) (and nickel(II), copper(II) and iron(III)) have been described [210].



(24)

The ligand produces a relatively weak ligand field; all complexes are high spin and markedly less stable than the corresponding complexes of 2,2′-bipyridine or 2-(2-pyridyl)imidazole. Deprotonated complexes $M(L{-}H)_2$ derived from the monoanion of biimidazole have also been described. The molecular and crystal structure of tetrakis(4-methylpyridine)cobalt(II) hexafluorophosphate has been determined [211]; the structure of the cation is a distorted tetrahedron of 4-methylpyridine ligands around cobalt (crystal symmetry S_4).

3.3.3.2 Phosphorus—nitrogen, phosphorus or arsenic donor ligands

A high spin—low spin crossover in cobalt(II) complexes of tris(2-diphenylphosphinoethyl)amine, caused by the application of high pressure, has been studied [212]. Iminophosphoranes ($R_3P{=}NR'$) are species isoelectronic with phosphine oxides ($R_3P{=}O$) and phosphorus ylids ($R_3P{=}CR'_2$); cobalt(II) chloride and bromide complexes of seven arylimino-triphenylphosphoranes have been prepared [213] and their spectral and magnetic properties studied.

The kinetics of the substitution reactions of five coordinate $[Co(Ph_2P(CH_2)_2PPh_2)_2Cl]Cl$ with 2,2′-bipyridine, 1,10-phenanthroline or 2,9-dimethyl-1,10-phenanthroline have been investigated [214]. Magnetic susceptibilities of single crystals of $[CoL_2X_2]$ (L = triphenylphosphine; X = Cl or Br) have been determined [215]. Chlorodimorpholinophosphine oxide complexes of cobalt(II) chloride, nitrate and perchlorate have been described [216].

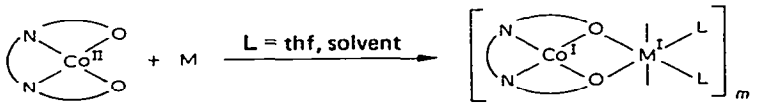
The reaction of white phosphorus or yellow arsenic with cobalt (and nickel) tetrafluoroborate in the presence of 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2Ph_2)_3$ ("triphos"), gives a series of metal complexes each containing the nivel cyclic P_3 or As_3 group. These compounds have the general formula $[M_2(D_3)(triphos)_2]Y_n$ (M = Co or Ni; D = P or As; Y = BF_4 or BPh_4; n = 1 or 2). X-ray structure determinations have shown that the compounds are of a double-sandwich structure, with two molecules of triphos as external slices. The internal layer in each complex is formed by an unprecedented *cyclo*-P_3 or *cyclo*-As_3 unit acting as a 3π system which connects the two metal atoms [217].

Nitratotetrakis(methyldiphenylarsine oxide) cobalt(II) nitrate has been described as a square—pyramidal complex with the cobalt ion in a C_4 site symmetry [218].

3.4 LOW OXIDATION STATES (Co^{I}, Co^{0}, Co^{-I})

The electrochemical synthesis of tetrakis(triphenylphosphite)cobalt(0) and its reduction to cobalt(—I) has been described [219]. Reaction of $B_9H_{11}C \cdot N(CH_3)_3$ with NaH and subsequent treatment with NaC_5H_5 and $CoCl_2$ gives $[(C_5H_5Co)B_9H_9C \cdot N(CH_3)_3]$ [220].

Reduction of (*N*,*N*'-ethylenebis(salicylideniminato)cobalt(II), [Co(salen)], with lithium and sodium metals in tetrahydrofuran (thf) gives the bimetallic systems [{Co(salen)}Na(thf)] and [{Co(salen)}Li$(thf)_{1.5}$] which are active in carbon dioxide fixation [221]. Structures of the complexes have been solved by single crystal X-ray diffraction; the cobalt(—1)-alkali cation—Schiff base complexes can be represented as shown in (25).



(25)

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