Coordination Chemistry Reviews, 71 (1986) 37—112
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

2. COBALT

R.W. HAY

CONTENTS

INTRODUCTION

The present survey covers the bulk of the 1982 literature, and follows broadly the same format as the last article [1]. Reviews of interest include the following: coordinating properties of the amide bond (including a discussion of cobalt(II) and cobalt(III) complexes) [2], circular dichroism of transition metal complexes [3], NMR studies of chelate ring conformations [4], base hydrolysis of cobalt(III) complexes [5], the formation and stability of cobalt dioxygen complexes in aqueous solution [6], and a Russian text dealing with the chemistry and technology of cobalt [7].

0010-8545/86/$26.60

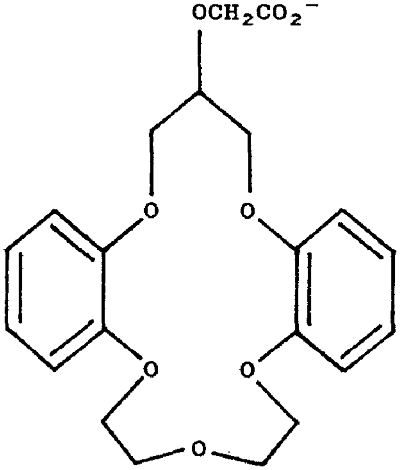
2.1 COBALT(III)

2.1.1 Complexes with oxygen donor ligands

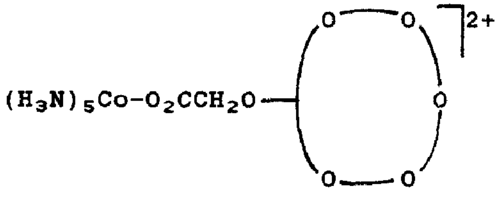
2.1.1.1 Complexes with simple ligands

The complex $[Co(acac)_3]$ has been partially resolved on a sodium-montmorillonite column, in which all the cation-exchange sites have been replaced by Δ-$[Ni(phen)_3]^{2+}$ [8]. A 2.5 cm column gave a 36% resolution of the Λ enantiomer for the first eluted fraction [9].

The reaction of $[Co(CN)_5]^{3-}$ with 2,6-di-*tert*-butyl-1,4-benzoquinone (dtbq) in dmf gives a cobalt(III) complex $[Co(CN)_5(dtbq)]^{3-}$, containing the $[dtpq]^-$ semiquinone radical, by a one-electron oxidative addition [10]. The methyl hydrogens of the β-diketonato complexes $[Co(N_4)(RCOCHCOMe)]^{2+}$ (N_4 = $(NH_3)_4$, $(en)_2$, $(tn)_2$ or $(bipy)_2$; R = CH_3 or CF_3) undergo base-catalysed deuteration in D_2O [11]. A mixed complex of sodium and cobalt(III) with *sym*-dibenzo-[16]-crown-5-oxyethanoate, (*1*), with the formulation $[(NH_3)_5Co(L)Na][ClO_4]_3.2H_2O$, (*2*), has been described [12]. The introduction of amine, thiol or carboxylic functions into crown ethers allows their ready attachment to the $[Co(NH_3)_5]^{3+}$ moiety.



(1; L)



(2)

The crystal structure of the complex $(+)_{589}$-$[Co(tren)(acac\text{-}R)][BF_4]_2.2H_2O$ (acac-R = 3-(1-napthyl)pentane-2,4-dionato) has been determined [13]. The naphthalene ring is almost perpendicular to the coordination plane of the acac ring. The crystal structure and absolute configuration of $(-)_{589}$-$[Co(tren)(acac\text{-}R)]Br_2$ (acac-R = 3-(2,4-dinitro-1-naphthyl)pentane-2,4-dionato) has been established [14]. In this case, the acac ring adopts a somewhat deformed boat conformation. Photodecomposition of $[Co(acac)_2(N_3)(NH_3)]$ gives $Co(acac)_2$ and azide radicals [15]. $[Ln(fod)_3]$

(Ln = La, Pr, Nd, Sm or Eu) induced ^{59}Co shifts (δ_{Co}) for a series of tris(β-diketonato)cobalt(III) complexes have been investigated [16].

Kinetic studies have dealt with the aquation of $[Co(mal)_2(en)]^-$ in perchloric acid to give $[Co(mal)(H_2O)_2(en)]^+$ and subsequently $[Co(H_2O)_4(en)]^{3+}$ [17], the reactions of $[Co(en)_2(acac)]^{2+}$ in basic solution where ring opening of the acac-ring occurs [18], and the thermal decomposition of cobaltic acid, CoO(OH), to give the microcrystalline spinel Co_3O_4 {*n.b.* cobalt(III) oxide hydroxide occurs in nature as the mineral heterogenite and is a rare example of a simple but stable cobalt(III) species} [19].

The kinetics of iodination of the malonato and pyruvato ligands in $[Co(NH_3)_5(O_2CCH_2CO_2)]^+$, $[Co(en)_2(mal)]^+$ and $[Co(NH_3)_5(O_2CCOCH_3)]^{2+}$ have been studied [20]. Free malonic acid or its anions are not known to undergo facile electrophilic substitution, but activation occurs on coordination to cobalt(III).

Near UV flash photolysis of *trans*-$[Co(tfacac)_3]$ (tfacacH = $CF_3COCH_2COCH_3$) in cyclohexane generates a long-lived ($t_{\frac{1}{2}} \sim 3$ s) transient assigned as a cobalt(II) complex containing a carbon-bonded ligand [21].

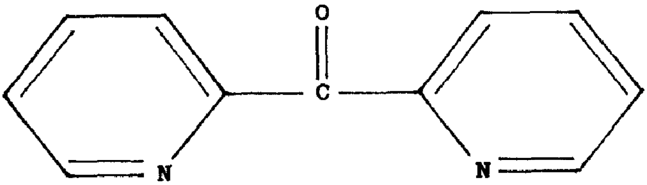
Initial resolutions of $[Co(acac)_2(gly)]$ and $[Co(acac)(gly)_2]$ on columns of Δ-*tris*(1,10-phenanthroline)nickel(II)-montmorillonite columns has been described [22]. The β,γ-bidentate and α,β,γ-tridentate complexes of cobalt(III) with ATP (adenosine 5'-triphosphate), which are useful kinetic and spectroscopic probes of enzymes catalysing phosphoryl-transfer reactions, have been found to decompose at elevated pH and temperature to give either free ATP or the products of ATP hydrolysis, ADP, and to a lesser extent, AMP [23]. The participation of polynuclear metal complexes in the cobalt(III) promoted hydrolysis of ATP has also been studied [24].

Other studies have been concerned with hydroxide ion addition to the mixed ligand complex (1,1,1,5,5,5-hexafluoropentane-2,4-dionato)bis(1,2-diaminoethane)cobalt(III) [25], the preparation and characterisation of zinc cobaltate ($ZnCo_2O_4$) [26], the synthesis and properties of tris{1-(4-substituted phenyl)-butane-1,3-dionato}cobalt(III) complexes [27] and studies of $[Co(acac)_2(NO_2)(amine)]$ complexes [28].

2.1.1.2 Complexes with peroxide and superoxide ligands

A series of new μ-peroxodicobalt(III) complexes have been prepared using the ligand di-2-pyridyl ketone {dpk = (*3*)} [29]. Thermogravimetric studies reveal the stoicheiometric loss of O_2 and H_2O below 100 °C.

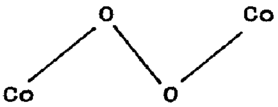
The rotating ring-disc electrode has been used to study the reduction of O_2 to H_2O_2 catalysed by *trans*-$[Co(cyclam)(OH_2)_2]^{3+}$ [30]. With an excess of cobalt, the μ-peroxo complex *trans*-$[\{Co(cyclam)(OH_2)\}_2O_2]^{4+}$ is formed at



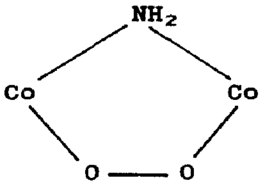
(3;dpk)

potentials where the initial cobalt(III) complex is reduced. At more negative potentials, the μ-peroxo complex is reduced to H_2O_2 and $[Co(cyclam)(OH_2)_2]^{2+}$, which re-enters the catalytic cycle. With an excess of O_2, the initial product of the reaction between the cobalt(II) complex and dioxygen is very rapidly reduced to a new complex, thought to be *trans*-$[Co(cyclam)(OH_2)(O_2H)]^{2+}$ containing end-bonded hydroperoxide.

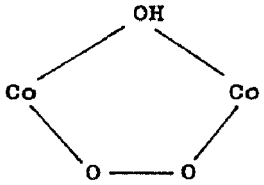
Reduction potentials (*versus* SHE) have been determined by cyclic voltammetry for eleven μ-superoxo/μ-peroxo-dicobalt(III) couples based on the structural types (*4*), (*5*) and (*6*) [31]. The $E°$ values are a function of the bridging and terminal ligands, and the degree of chelation. Protonation of μ-peroxo ligands at pH < 3 is indicated by changes in $E°$ values.



(4)



(5)



(6)

Three apparently different reactions of $[(en)_2(NH_3)Co^{III}(\mu\text{-}O_2{}^{2-})Co^{III}(NH_3)(en)_2]^{4+}$ have been studied in aqueous solution: (a) decomposition to cobalt(II) and O_2 (pH 1.1-10.2), (b) spontaneous conversion into $[(en)_2Co^{III}(\mu\text{-}OH,\ O_2{}^{2-})Co^{III}(en)_2]^{3+}$ (pH 8.4-9.9), and (c) reaction with NO_2^- to give *trans*-$[(en)_2(NO_2)Co^{III}(\mu\text{-}O_2{}^{2-})Co^{III}(NO_2)(en)_2]^{2+}$. The three reactions proceed at identical rates, being first order in the initial complex concentration, but independent of $[H^+]$, $[NO_2^-]$ and [edta]. The common rate-determining step is decomposition of the initial complex to Co(II) and O_2 [32].

Isomerisation of $[(dien)(R\text{-}pn)Co^{III}(\mu\text{-}O_2{}^{2-})Co^{III}(R\text{-}pn)(dien)]^{4+}$ also appears to involve a labile cobalt(II) species in equilibrium with the initial complex [33].

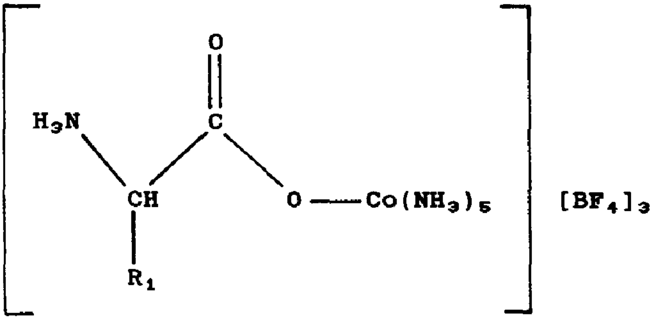
2.1.2 *Complexes with oxygen-nitrogen donor ligands*

The reaction of [Co(glygly)(NO$_2$)(en)] with acetaldehyde in aqueous solution at pH 11 gives four condensation products [34]. Reaction occurs with the glygly ligand to give threogly and *allo*-threogly; and with the NH$_2$ groups of glygly and en to give *N*-ethylideneglygly and *N*-ethylideneethylenediamine.

The preparations of three cobalt(III) complexes of tetraglycine have been described [35]. In one complex $[Co(NH_3)_2(H_{-3}GGGG)]^-$ (GGGG = tetraglycinate) the peptide is coordinated as a quadridentate ligand *via* the terminal NH$_2$ and three peptide nitrogens. In the other two complexes, $[Co(NH_3)_2(H_{-2}GGGG)]$ and $[Co(NH_3)_3(H_{-1}GGGH)]^{2+}$, the peptide is terdentate, coordinated in the former *via* the terminal NH$_2$ and two peptide nitrogens, and in the latter *via* the terminal NH$_2$, the adjacent peptide nitrogen and a peptide oxygen. The reactions of the complexes in acid have also been studied. Complexes of the [Co(tripeptidato)(NH$_3$)$_2$] and [NH$_4$][Co(tetrapeptidato)(NH$_3$)$_2$] types (tripeptidato and tetrapeptidato denote the tri- and tetra-anions of the coordinating peptides) have been prepared and characterised [36]. In the $[Co(tetrapeptidato)(NH_3)_2]^-$ complex, the peptide bonds as a quadridentate ligand *via* the terminal amino group and three deprotonated amide nitrogens. Rapid aquation of the coordinated NH$_3$ ligands occurs in aqueous solution.

The major metal-containing hydrolysis product of both orange and green cobalt(III) bleomycin has been shown to contain the pseudotetrapeptide A of bleomycin bound to the cation [37]. The hydrolysis product has a $[Co^{III}(N_5O)]$ chromophore with the primary amino group of the peptide and a water molecule occupying the axial sites.

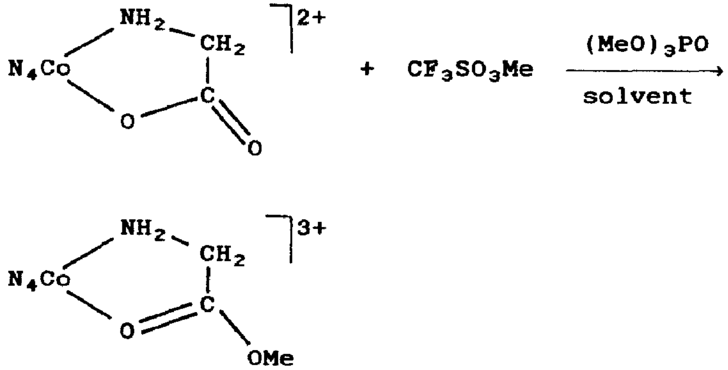
The use of cobalt(III) complexes in peptide synthesis has been studied. Pentaamminecobalt(III) is a useful *C*-terminal protecting group for sequential peptide synthesis [38]. The reaction of complexes of type (*7*) with BOC-amino



(7; [Co(AA$_1$)])

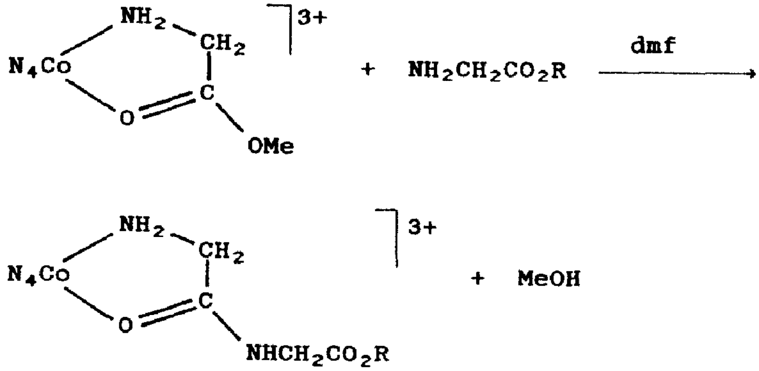
acid active esters or BOC-symmetric anhydrides gives [Co(AA_1)(AA_2)BOC]. The BOC group is removed with 95% CF_3CO_2H to give [Co(AA_1)(AA_2)], which is further used for sequential peptide synthesis. The $\{(NH_3)_5Co\}^{3+}$ moiety is selectively removed using Na[BH_4] or Na[HS].

The use of cobalt(III) as both an *N*-protecting and activating group has been developed [39]. Chelated amino-acids can be alkylated using CF_3SO_3Me to give the chelated esters (equation 1; N_4 = (en)$_2$ or trien). Rapid aminolysis



(1)

of the cobalt(III)-chelated esters in aprotic solvents can be used for peptide synthesis (equation 2). The technique has been applied to the synthesis of

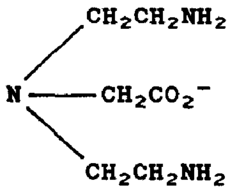


(2)

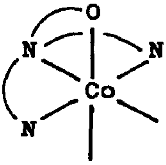
tetrapeptides and [leu^5] enkephalin [40].

The cobalt(III) complex of ethylenebis{(2-hydroxyphenyl)glycine} has been prepared as a potential model for the iron transport protein transferrin [41]. ^{15}N chemical shifts of cobalt(III) amino acid complexes have been determined at the natural abundance (0.4%) level [42]. Coordination to cobalt induces displacements of the amino acid ^{15}N resonance by 24-42 ppm to higher field compared with the protonated amino acid. These changes should be useful in determining binding sites to cobalt(III). The rate of the α-hydrogen exchange reaction of glycinato ligands in *mer*-[Co(gly)$_3$] has been found to differ for the three stereochemically different glycinato ligands [43]. The carboxyl oxygen ligand is more effective than the amino ligand in labilising the *trans* α-hydrogen.

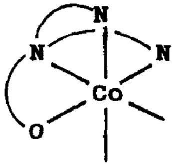
The tripod-like quadridentate *N*,*N*-bis(2-aminoethyl)glycinate (*8*) can give the *sym* (*9*) and *unsym* (*10*) configurations on cobalt(III). Complexes in which



(8)

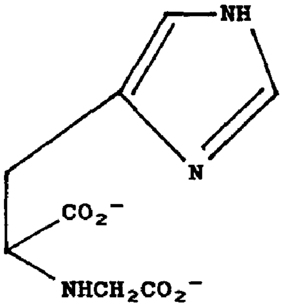


(9; *sym*)



(10; *unsym*)

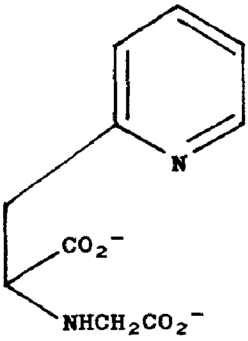
gly, L-ala and R-1,2-pn occupy the vacant sites have been studied [44]. The ligand *N*-(carboxymethyl)-L-histidinate {[*N*-Cm-L-his]$^{2-}$ = (*11*)} has been prepared



(11; [*N*-Cm-L-his]$^{2-}$)

by Na[BH$_4$] reduction of the Schiff base formed from L-his and glyoxylate [45]. Several mixed ligand complexes with cobalt(III) of the type [Co(*N*-Cm-L-his)(AA)] (AA$^-$ = an amino acid anion) have been prepared. Although four geometric isomers are possible the only one isolated was the *fac*-isomer with the carboxylate group of the *N*-carboxymethyl moiety *trans* to the imidazole group. A series of mixed ligand complexes of the type [Co(*N*-Cm-L-Pyala)(AA)] {*N*-Cm-L-Pyala = (*12*)} have also been prepared [46]. The *fac*-[CoN_3O_3] isomer in which the *N*-carboxymethyl group is coordinated *trans* to the pyridyl group is favoured.

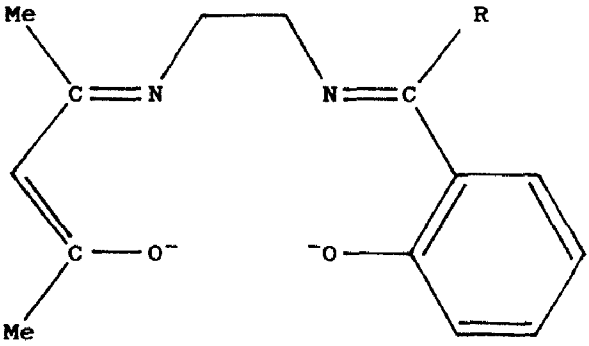
Solvent effects on the stereoselectivity between Λ and Δ-β$_2$-diastereoisomers of cobalt(III) complexes with the general formula [Co(Schiff base)(L-AA)] (Schiff base = [sal$_2$en]$^{2-}$, [α-Mesal$_2$en]$^{2-}$, *etc.*) have been investigated [47]. Generally, the Λ-β$_2$-isomer was more stable than the Δ-β$_2$-isomer in solution. Acid catalysed aquation of [Co(biguanide)$_2$(gly)]$^{2+}$



(12; [*N*-Cm-L-Pyala]$^{2-}$)

has been studied [48]. Up to ∿ 50 °C, the dissociation of only one biguanide occurs with formation of the α-diaqua product.

A number of unsymmetric tetradentate Schiff bases of the type (*13*) have

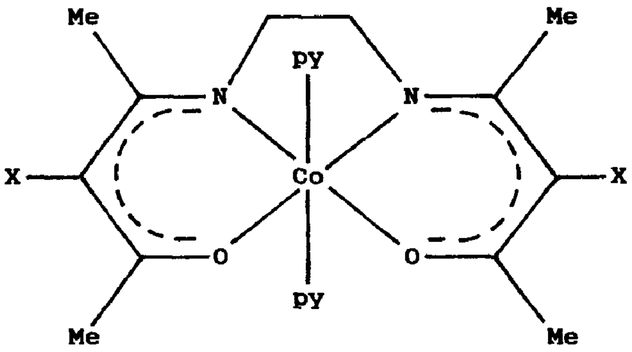


(13; R = H or Me)

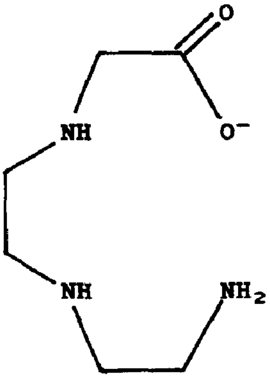
been prepared by a two-step condensation process, and cobalt(III) complexes characterised [49]. The use of unsymmetric or substituted ligands of this type allows the reduction potential of the cobalt centre to be gradually modified [50]. The effects of halogen substitution on the electron distribution within cobalt(III) complexes of the type (*14*) have been studied by ^{1}H and ^{13}C NMR and IR spectroscopy and half-wave potential measurements [51].

The crystal structure of $(-)_{435}$-Λ_{RS}-β_2(*mer*)-[Co(α-Me-sal$_2$en)(*N*-Bz-L-ala)]-.3H$_2$O with a non-planar Schiff base ligand has been determined [52]. *Cis*-complexes [Co(sal$_2$en)L] (L = 1-ℓ-menthyloxy-3-benzoylacetonate) have also been studied [53]. A ^{13}C NMR study of alkyl complexes of [Co(sal$_2$en)] and [Co(sal$_2$dien)], with the O_2N_2 and O_2N_3 donor sets respectively, has been published [54].

A large variety of cobalt(III) complexes of 8-amino-3,6-diazaoctanoate (*15*) have been characterised and their detailed stereochemistry studied [55,56].

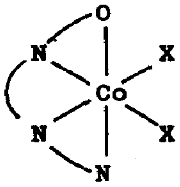


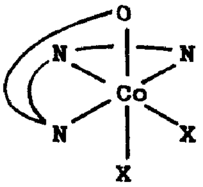
(14; X = H, Cl, Br or I)

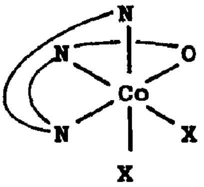


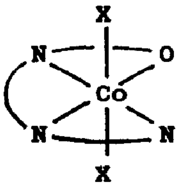
(15)

Four geometrical isomers α,β-*mer*(*N*), β-*fac* (*N*) and *trans* are possible (*16*)-(*19*).



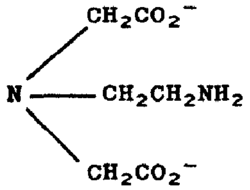




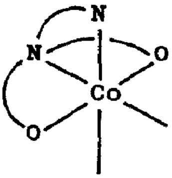


(16; α) (17; **β-mer**) (18; **β-fac**) (19; **trans**)

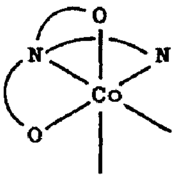
Cobalt(III) complexes of the tripod-like ligand *N*-(2-aminoethyl)iminodiacetate (*20*), with the auxiliary ligands gly, L-ala, en, Me_2en, R-1,2-pn, cyclohexanediamine or *meso*-2,3-butanediamine, have been prepared [57]. Complexes can be derived from the *sym*- and *unsym*-isomers, (*21*) and (*22*), respectively. Bis(iminodiacetates) of cobalt(III) have also been studied [58], and the ^{13}C NMR spectra of cobalt(III) complexes containing glycine or β-alanine in various linkage forms obtained [59].



(20)



(21; *sym*)



(22; *unsym*)

Crystal structures determined include the following: $(+)_{486}$-S-bis-{R-*N*-(2-amino(R)propyl)salicylaldiminato}cobalt(III) iodide trihydrate [60]; $(+)_{489}$-S-[{R-*N*-(2-aminopropyl)salicylaldiminato}-{R-*N*-[(2-amino-1-methyl)ethyl]salicylaldiminato}]cobalt(III) perchlorate, $[C_{22}H_{26}N_4O_2Co][ClO_4].0.75C_2H_5OH$ [61] and potassium bis(thiocyanato-*N*)(salicylaldiminato-*N*,*N'*,*O*,*O'*)cobaltate(III) monohydrate [62].

The stereochemistry and CD spectra of some cobalt(III) complexes with ethylenediamine-*N*,*N'*-diacetic acid and *N*,*N'*-dimethyl-ethylenediamine-*N*,*N'*-diacetic acid have been studied in a recent thesis [63]. Other theses have dealt with the kinetics of the chromium(III) reductions of glycinato- and related amino acidato-ethylenediamine and ammine complexes of cobalt(III) [64], and the synthesis, characterisation and optical resolution of bis(aminoacidato)bis(nicotinato)cobalt(III) complexes [65].

Acylcobalt(III) salen has been employed as a new reagent for the synthesis of unsymmetrical ketones [66]. The synthesis of the 8-hydroxyquinolinatocobalt(III) complex has been described, and its radiolysis studied [67]. Mixed ligand complexes of ethylenediamine-*N*,*N*,*N'*-triacetato-cobalt(III) with en and 1,3-pn have been prepared [68]. Other studies in this area include the synthesis of ethylenediamine-*N*,*N'*-di-S-α-isovalerate and isomers of its cobalt(III) complexes [69] and a molecular mechanical study of the relative stability of cobalt(III) complexes of 2,3-diaminobutane-*N*,*N*,*N'*,*N'*-tetraacetate [70].

Additional synthetic work has dealt with cobalt(III) complexes of amino acids and peptides [71], cobalt(III) (and cobalt(II)) complexes with heterocyclic and aliphatic amino acids [72], and the synthesis and properties of amino acid-imidazole complexes of cobalt with dioxygen [73]. The kinetics and mechanism of the acid-catalysed dissociation of tris(1-amidino-*O*-alkylurea)cobalt(III) complexes have also been studied [74].

The CD and EPR spectra of mononuclear and binuclear cobalt(III)-dioxygen adducts of bleomycin have been reported [75].

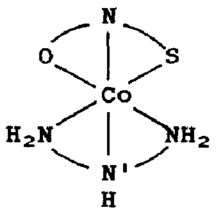
2.1.3 *Complexes with sulphur and selenium donor ligands*

A series of cobalt(III) complexes containing symmetrical disulphides bonded to cobalt *via* one sulphur atom, *e.g.* $[Co(en)_2\{S(SCH_2CO_2H)CH_2CO_2\}]^{2+}$, have been prepared by one-equivalent oxidation of the thiolato complexes, *e.g.* $[(en)_2Co(SCH_2COO)]^+$ [76]. Crystal structures have been determined, establishing that oxidation of a coordinated thiolato ligand to a coordinated disulphide causes a lengthening of the Co-S bond.

Non-coordinated sulphenic acids, RSOH, are elusive species known to play an important role in the reactions of organo-sulphur compounds. The chemistry of cobalt(III) complexes containing *S*-bonded sulphenato ligands, Co-S(O)-R, have now been discussed in detail [77]. Twelve new mixed sulphenato and sulphinato cobalt(III) complexes have been prepared by successive H_2O_2 oxidation of $[Co(SCH_2CH_2NH_2)_3]$, $[Co\{SCH_2CH(COOCH_3)NH_2\}_3]$ and related complexes [78]. The oxidation products $[Co(sulphenato\text{-}N,S)_n(sulphinato\text{-}N,S)_{3-n}]$ (n = 3, 2, 1 or 0) were resolved by column chromatography.

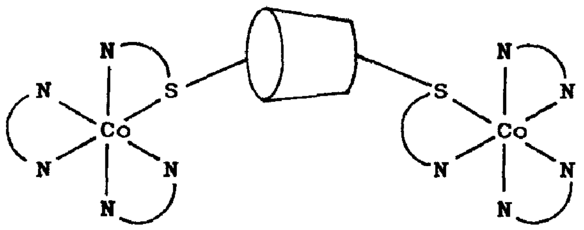
Methylation of the chelated sulphenate ion in bis(ethane-1,2-diamine)(cysteaminesulphenate-*S*)cobalt(III) occurs at sulphur with complete retention of chirality at the S centre [79]. The crystal structure of one of the racemic diastereoisomeric products Δ(R), Λ(S)-bis(ethane-1,2-diamine)(cysteaminesulphoxide-*O*)cobalt(III) triodide hydrate has been determined; the sulphoxide moiety forms a six-membered ring with the oxygen bonded to cobalt.

The complex $[Co(L\text{-pen})(dien)]Cl.H_2O$ (L-pen = L-penicillaminate) has been characterised and its crystal structure determined [80]. Three isomers are possible and the complex was shown to have the configuration (*23*) {*i.e. trans* (*N'*,*N*)} with the *N* donor of L-pen *trans* to the *sec*-NH of the dien ligand. Two complexes of *fac*(NH_3)-$[Co(NH_3)_3L]^+$ (L = (R)-2-(carboxymethylthio)propionate or (R)-2-(2-carboxyethylthio)propionate) have been prepared and separated into two isomers by column chromatography [81]. Complexes of the type $[Co(en)_2(NH_2CH_2CH_2SR)]^{3+}$ (R = long alkyl or bromoalkyl chains, $(CH_2)_nBr$ or



(23)

$(CH_2)_n(CH_3)$ have been partially resolved by stereoselective inclusion of the free side chain into α- or β-cyclodextrin (CDX). The α- and β-CDX preferentially include the Δ- and Λ-complexes, respectively [82]. Rotaxane derivatives of the type shown in (*24*) have been prepared by reacting



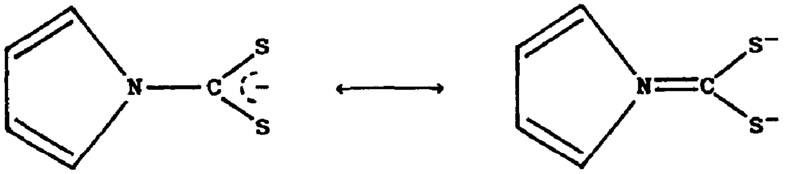
(24; [ΔΔ]-[α-CDX])

$[Co(en)_2(NH_2CH_2CH_2S)]^{2+}$ and α,ω-dibromoalkanes in the presence of a cyclodextrin [83]. As a result of the different end hole sizes of the cyclodextrin, four diastereoisomers arise (neglecting the R and S chiralities of the donor sulphur atoms), *viz.* [ΔΔ]-[α-CDX], [ΔΛ]-[α-CDX], [ΛΔ]-[α-CDX] and [ΛΛ]-[α-CDX].

The complex $[Co(en)_2(siea)]^{3+}$ (siea = 2-seleninatoethylamine), derived from the cobalt(III) complex of the selenium bonded 2-selenolatoethylamine (sea), can be siea-*N*,*Se* or siea-*N*,*O* bonded. X-ray work confirms bonding *via* the *N* and *O* atoms and the asymmetric selenium atom has an S-configuration [84]. Raman spectra of $[CoL_3]$ (HL = 2-mercaptoethylamine) and trinuclear complexes of the type $[M(CoL_3)_2]^{n+}$ {M = Co(III), Fe(III), Ru(III), Cd(II) or Ni(II); n = 2 or 3} have been obtained under resonance and off-resonance conditions [85]. Strong Raman bands near 343 and 261 cm^{-1} observed in the trinuclear complexes are assigned to the totally symmetric CoS_3 stretching and CoS_3 bending vibrations.

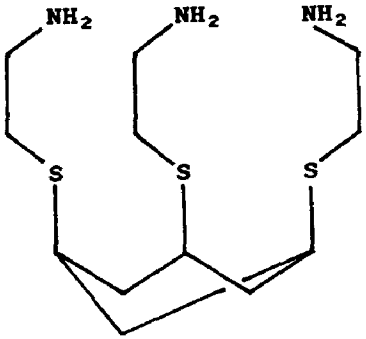
The first example of the coordination of the thionitro group in a cobalt(III) complex, dichlorothionitrobis(triphenylphosphito)cobalt(III), has been reported [86]. A band in the IR spectrum at 1540 cm^{-1} is assigned to ν(NO) and a band at 990 cm^{-1} to ν(NS).

The preparation and characterisation of $[CoL_3]$ {L = pyrrole-*N*-carbodithioato = (*25*)} has been described [87]. The average ligand bite angle is 76.3°, and the compound is isostructural with its iron(III) analogue. The synthesis of the potentially hexadentate ligand



(25)

2,2',2"-{(cyclohexane-1,3,5-triyl)trithio}tris(ethanamine) {atch = (*26*)} has been described [88]. The ligand forms a hexadentate cobalt(III) complex which has been resolved into its catoptric forms.



(26; atch)

New mixed-ligand cobalt(III) dithiocarbamato complexes of the general formula $[Co(Et_2NCS_2)_2L][BF_4]$ (L = dithiooxamide) have been characterised [89]. The dithiooxamide acts as a bidentate sulphor donor. A kinetic study of the reaction shown in equation 3 has also appeared [90].

$$[Co_2(Et_2NCS_2)_5][BF_4] + L \longrightarrow [Co(Et_2NCS_2)_2L][BF_4] + [Co(Et_2NCS_2)_3] \qquad (3)$$

Four optical isomers of cobalt(III) complexes with a coordinated selenium atom $[Co(en)_2L]^{n+}$ {L = 2-selenolatoethylamine, 2-selenenatoethylamine, 2-seleninatoethylamine or 2-(methylseleno)ethylamine} have been prepared and characterised on the basis of *d*-*d* and CD spectra [91]. The photochemistry of a series of sulphur- and selenium-containing cobalt(III) complexes of the type $[Co(en)_2L]^{n+}$ ($L = {}^{-}SCH_2CH_2NH_2$, ${}^{-}SeCH_2CH_2NH_2$, ${}^{-}SeCH_2CO_2{}^{-}$, *etc.*) has been studied in detail [92].

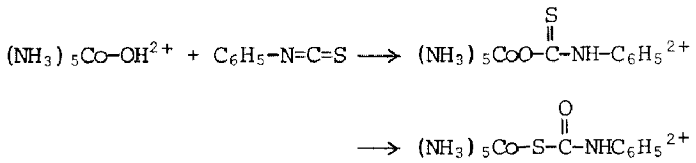
The optically active selenide complex *trans* (tertiary amine nitrogen, *Se*)-$[Co(CH_3SeCH_2CH_2NH_2)\{N(CH_2CH_2NH_2)_3\}]^{3+}$ has been obtained by SP-Sephadex column chromatography [93]. The complex loses *ca.* 50% of its optical activity in 1 h at 22 °C in 1*M* $Na[ClO_4]$.

The crystal structures of geometric isomers of trithiosemicarbazidecobalt(III) chloride have been determined [94].

2.1.4 *Complexes with nitrogen donor ligands*

2.1.4.1 *Ammine complexes*

The complex $[Co(NH_3)_5(SCONHPh)][ClO_4]_2$ has been prepared by the addition of $[Co(NH_3)_5(OH_2)][ClO_4]_2$ to phenyl isothiocyanate in dmf [95]. It is suggested that the *O*-bonded complex is initially formed and then isomerises rapidly to the stable *S*-bonded species (see equation 4). Traditionally the preparation of



$$(NH_3)_5Co{-}OH^{2+} + C_6H_5{-}N{=}C{=}S \longrightarrow (NH_3)_5CoO{-}\overset{\overset{S}{\|}}{C}{-}NH{-}C_6H_5{}^{2+}$$
$$\longrightarrow (NH_3)_5Co{-}S{-}\overset{\overset{O}{\|}}{C}{-}NHC_6H_5{}^{2+} \qquad (4)$$

pentaamminecobalt(III) complexes has required reaction times of several hours at elevated temperatures, preventing the use of thermally unstable ligands. However, the use of a good leaving group such as $[CF_3SO_3]^{-}$ allows milder conditions to be employed. A convenient preparation of $[Co(NH_3)_5(O_3SCF_3)]^{2+}$ has been described with applications to the synthesis of other pentaammine complexes [96].

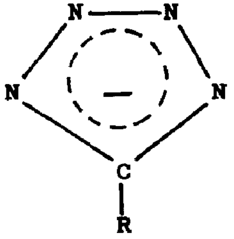
The $[(NH_3)_5Co(\mu\text{-}CO_3)Co(NH_3)]^{4+}$ ion has been prepared and characterised, and its acid catalysed decomposition studied over the pH range 1-7 [97]. The rate-determining reaction is $[Co(NH_3)_5CO_3H^{2+} \longrightarrow [Co(NH_3)_5(OH)]^{2+} + CO_2$. The complex $[Co(NH_3)_5(OH)]^{2+}$ reacts with SO_2 in aqueous solution to give the *O*-bonded sulphito complex $[Co(NH_3)_5(OSO_2)]^{+}$ which, on acidification, releases SO_2 and forms the corresponding aqua-complex [98]. These reactions are rapid, and similar to the corresponding CO_2 uptake and acid catalysed decarboxylation processes [99].

The pentaamminecobalt(III) complexes of $NH_2SO_2NH^{-}$, $4\text{-}CH_3C_6H_4SO_2NH^{-}$ and $4\text{-}NO_2C_6H_4SO_2NH^{-}$ have been prepared and their aquation kinetics studied in aqueous solution [100]. Aromatic sulphonamides are well known to be strong inhibitors of carbonic anhydrase, and there is general agreement that the sulphonamide is complexed as the anion to zinc(II).

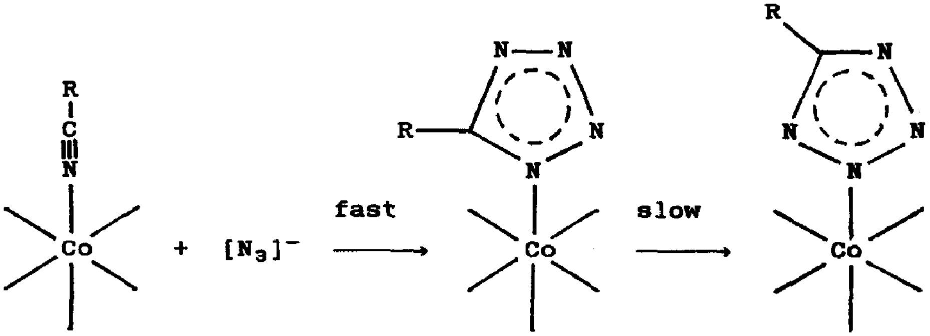
Transition metal hydroxo complexes $[M(NH_3)_5(OH)]^{2+}$ {M = Co(III), Rh(III) or Ir(III)} react rapidly with CO_2 to give the corresponding carbonato complexes [99]. The formation and decarboxylation kinetics of the complexes $[M(NH_3)_5(OCO_2)]^+$ have now been studied as a function of pressure up to 1000 bar [101].

Other synthetic studies have dealt with the preparation and characterisation of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion [102] and nicotinic acid derivatives of the pentaamminecobalt(III) ion [103].

Tetrazoles with substituents at ring position 5 (*27*) are conveniently prepared from organonitriles *via* nucleophilic attack of azide ion by a 1,3-dipolar cycloaddition [104]. Coordination of organonitriles to the $\{Co(NH_3)_5\}^{3+}$ moiety is known to enhance the susceptibility of the nitrile carbon to nucleophilic attack by hydroxide ion [105] and cyanide ion [106]. It has now been shown [107] that azide ion reacts with $[Co(NH_3)_5(N{\equiv}CR)]^{3+}$ to give tetraazoles, as shown in equation 5. The formation of 5-methyltetraazole from



(27)



(5)

sodium azide and ethanenitrile requires a reaction time of 25 h at 150 °C, compared with only 2 h at ambient temperature for coordinated acetonitrile.

The paramagnetic complexes $[Co(NH_3)_4(5\text{-NOsal})]X_2.nH_2O$ (5-NOsal = 5 nitrososalicylato) with μ_{eff} = 1.6-1.8 μ_B have been characterised [108]. The Raman and IR spectra of tetraamminecobalt(III) complexes have been measured to differentiate between *cis* and *trans* isomers [109]. Significant differences were observed in the $\nu(Co-NH_3)$ region, where the *trans* isomers have two bands at *ca.* 480 and *ca.* 450 cm^{-1} in the Raman spectra and one band at *ca.* 510 cm^{-1} in the IR spectra. The *cis*-isomers display more than three bands in both the Raman and IR spectra. Spontaneous resolution of $[Co(NH_3)_4(DL\text{-}val)]X_2$ (X = Cl or Br) at 5-55 °C and $[Co(NH_3)_4(DL\text{-}leu)][SO_4]$ at 30-55 °C in aqueous solution has been observed [110].

The ^1H and ^{13}C NMR spectra of the complex $[Co(NH_3)_5(imidH)]^{3+}$ have been studied [111]. The pK_a value of the coordinated imidazole determined from the pH dependence of the chemical shift is 10.0. The complexes *cis*-α-$[Co(trien)(imidH)_2]^{3+}$ and *cis*-β-$[Co(trien)(imidH)_2]^{3+}$ have pK_a values of 9.6 and 10.1 respectively.

A large number of kinetic studies on ammine complexes have been reported and these are briefly noted below. Neighbouring group participation in the base hydrolysis of aromatic nitriles coordinated to $\{Co(NH_3)_5\}^{3+}$ has been studied in detail [112]. For the 2-substituent-$CONH_2$, there is evidence for neighbouring group participation. The $[Co(NH_3)_5(OH)]^{2+}$ promoted hydrolysis of the activated esters 2,4-dinitrophenyl ethanoate and 4-nitrophenyl ethanoate has been the subject of a detailed kinetic investigation [113]. A correlation is reported which allows the prediction of reaction rates between $[Co(NH_3)_5(OH)]^{2+}$ and other activated charge-neutral carbonyl compounds.

The formation kinetics of the sulphur-bonded sulphito complexes $[Co(NH_3)_5(SO_3)]^+$ and *trans*-$[Co(NH_3)_4(SO_3)_2]^-$ have been studied at pH > 9 as a function of temperature, pressure, $[SO_3^{2-}]$ and pH [114]. Substitution and aquation reactions of these complexes were also considered. Electron transfer kinetics in the reduction of carboxylato-bridged [115] and pyridine-carboxylato-bridged [116] dicobalt(III) complexes with ammine ligands have been studied.

Homolytic cleavage of the chromium-carbon bond in the complex $[(H_2O)_5CrC(CH_3)_2OH]$ provides a ready source of the carbon-centred radical $\cdot C(CH_3)_2OH$. The reduction of several cobalt(III) complexes such as $[Co(NH_3)_6]^{3+}$ and $[Co(ND_3)_6]^{3+}$ by this radical has been studied kinetically [117]. The specific rates of reduction of $[Co(NH_3)_6]^{3+}$ by a series of nitrobenzoate and nitrogen heteroaromatic anion radicals have also been reported [118].

Other electron-transfer studies have dealt with the effects of pressure on the reduction of $[Co(NH_3)_5(N_3)]^{2+}$ by iron(II) in dmso [119], a reinvestigation of the chromium(II) reduction of $[Co(NH_3)_4(AA)]^{2+}$ (AA = glycinate, DL-alaninate or DL-phenylalaninate) [120], kinetics and mechanism of the reduction of $[Co(NH_3)_5X]^{2+}$ (X = F, Cl, Br or I) complexes by a variety of ruthenium(II) complexes [121], intramolecular electron transfer from pentacyanoferrate(II) to pentaamminecobalt(III) with linkage isomers of 3- and 4-cyanopyridine as bridging ligands [122], reductions of various substituted (pyridine)pentaamminecobalt(III) complexes by hexacyanoferrate(II) [123], reductions of $[Co(NH_3)_5(C_2O_4)]^+$ and $[Co(NH_3)_5(HC_2O_4)]^{2+}$ by ruthenium(II) ammines [124] and reduction kinetics of pentaamminecobalt(III) complexes containing 4,4'-bipyridine and related ligands at mercury, platinum and gold electrodes [125].

Solvent dependence, metal ion catalysis and base catalysis of the nitrito to nitro linkage isomerisation of $[(NH_3)_5Co(ONO)]^{2+}$ has been investigated in detail [126], using sixteen solvents. The results indicate intramolecular isomerisation in all solvents. Comments on the formation and acid-catalysed aquation reactions of carbonato-, *O*-bonded sulphito- and nitritopentaamminecobalt(III) ions have been published [127]. The kinetics and mechanism of the formation of $[Co(NH_3)_5(ONO)]^{2+}$ from $[Co(NH_3)_5(OH_2)]^{3+}$ and $[NO_2]^-$ in acidic aqueous solution has been studied [128]. The data favour a mechanism in which $[Co(NH_3)_5(OH)]^{2+}$ reacts with $[NO]^+$ (from N_2O_3) in the rate-determining step.

Activation volumes for the aquation of $[Co(NH_3)_5L]^{3+}$ complexes (L = methanol, ethanol, 2-propanol, formamide, dmf, urea or dmso) have been determined [129]. The average $\Delta V^{\ddagger}$ of *ca*. 2 $cm^3\ mol^{-1}$ is indicative of an I_d mechanism. Base hydrolysis of $[Co(NH_3)_5L]^{3+}$ complexes {L = urea, dmso or $(MeO)_3PO$} has also been studied [130]. The ions cleave by Co-O bond rupture and competition experiments also support an S_N1CB process. Nitrosation of the $[Co(NH_3)_5(N_3)]^{2+}$ ion in the presence of added anions (Cl^-, NO_3^- or ClO_4^-) has been investigated in detail [131]; ion association in ion-pair intermediates is of importance.

Other kinetic studies have dealt with the kinetics of the acid catalysed dissociation of $[Co(NH_3)_5(NH_2CH_2CO_2H)]^{3+}$ in $HClO_4$ solutions [132], the kinetics and mechanism of complex formation between (salicylato)pentaamminecobalt(III) and iron(III) [133] and an analogous study of $[Co(NH_3)_5(HC_2O_4)]^{2+}$ with iron(III) [134].

The presence of multivalent anions such as sulphate, oxalate and malonate ions accelerate the aluminium(III)-assisted aquation of $[CoF(NH_3)_5]^{2+}$ to give the anionopentaamminecobalt(III) ion, in addition to the aqua complex [135].

Additional studies have appeared on the use of the $\{Co(NH_3)_5\}^{3+}$ moiety as a *C*-protecting group in peptide synthesis. The optical purity of amino-acids and peptides bound to pentaamminecobalt(III) has been studied [136] and the separation of $(NH_3)_5Co$-bonded amino-acids and peptides by reverse phase HPLC investigated [137].

A number of crystal structures have been published, including $[Co(NH_3)_4(PO_4)]$ [138], μ-hyperoxobis{pentaamminecobalt(III)} hydrogensulphate bissulphate trihydrate [139], μ-peroxo-bis{pentaamminecobalt(III)} tetranitrate dihydrate [140] and $(-)_{589}$-*fac*-$[Co(NH_3)_3(gly)(NO_2)][ClO_4]$ [141].

A thesis dealing with the solid state photochemistry of $[Co(NH_3)_5(NO_2)]X_2$ complexes has been published [142] and the complex tetraammine(salicylideneiminato)cobalt(III) chloride hydrate characterised [143].

Additional kinetic studies have dealt with base hydrolysis of $[Co(NH_3)_5(OPO_3COCH_3)]^+$ (containing the acyl phosphate ligand), the metal hydroxide promoted hydrolysis of acetyl phenyl phosphate [144], the kinetics of reduction of $[Co(NH_3)_5(OH_2)]^{3+}$ by oxalic acid [145], the cerium(IV) oxidation of $[Co(NH_3)_5(OOCCO_2H)]^{2+}$ [146], activation volumes for the aquation of $[Co(NH_3)_5Br]^{2+}$ and its chromium(III) analogue [147], and the kinetics of anation of $[Co(NH_3)_5(OH_2)]^{3+}$ by $[NCS]^-$ in aqueous organic mixtures [148].

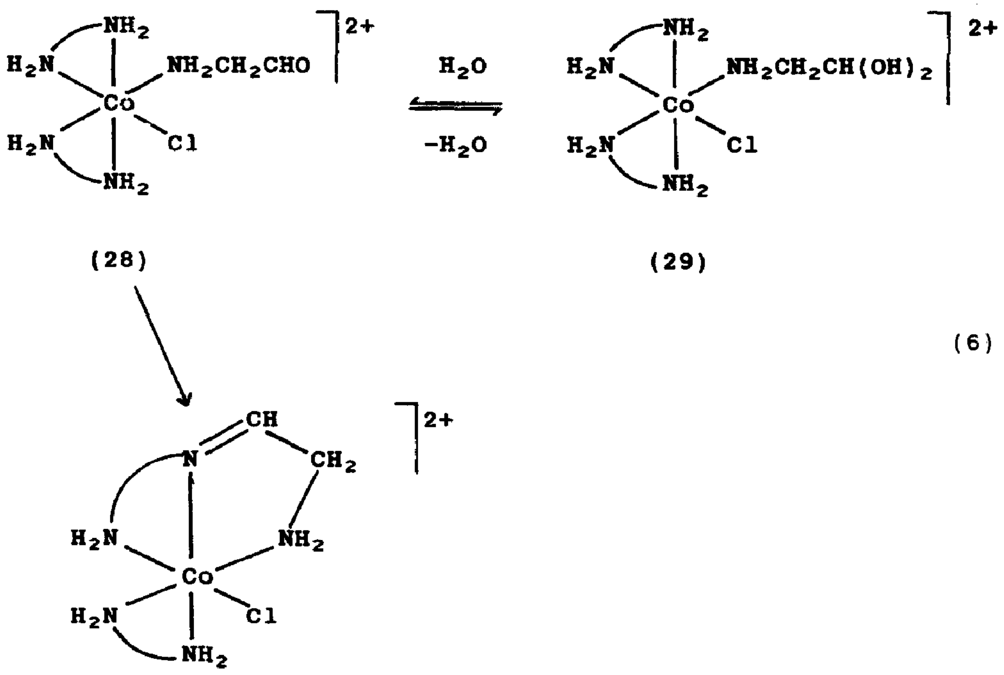
An undergraduate experiment involving cobalt(III) ammines has been described [149], and the kinetics and mechanism of the redox reaction of hexakis(hydroxylamine)cobalt(III) with cerium(IV) studied [150].

2.1.4.2 Diamine complexes

Comments on the synthesis and aquation of *cis*- and *trans*-$[Co(en)_2(NO_2)Cl]^+$ have been published [151]. The complex *cis*-$[Co(en)_2\{NH_2CH_2CH(OCH_3)_2\}Cl]^{2+}$ undergoes hydrolysis in dilute HCl solution to the aminoacetaldehyde complex (*28*), which is in equilibrium with its hydrate (*29*). In aqueous solution an intramolecular condensation occurs between the 1,2-diaminoethane ligand and the aldehyde group to give the imine derivative (*30*); crystallographic data confirm that condensation occurs at an amino group *cis* to Cl^-, so that the tridentate imine ligand adopts a *fac*-configuration [152].

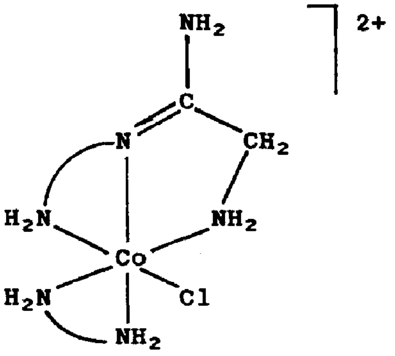
The condensation of the deprotonated amine function *trans* to halide in the aminoacetonitrile complex *cis*-$[Co(en)_2(NH_2CH_2CN)X]^{2+}$ (X = Cl or Br) results in the rapid formation of the tridentate amidine complex $[Co\{NH_2CH_2CH_2NC(NH_2)CH_2NH_2\}(en)X]^{2+}$ (*31*) with full retention of configuration at the metal centre [153]. The formation of the amidine complex and subsequent hydrolysis of the halide ligand has been studied kinetically. The results obtained support previous studies on this reaction [154].

Complete ligand replacement in $[Co(en)_3]^{2+}$ by the bis(2-hydroxyethyl)dithiocarbamate ion, htc^-, forming $[Co(htc)_3]$ is induced by visible light in aqueous solution [155]. Cobalt(III) complexes with an $\{N_6\}$ donor set such as $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_4(1,3\text{-pn})]^{3+}$ and $[Co(dien)_3]^{3+}$ also undergo similar photoreactions. Photochemistry of *cis*-$[Co(en)_2(NO_2)_2]^+$



(30)

(6)



(31)

(excitation of the ligand-to-metal charge transfer band) gives cobalt(II) and the nitrito-linkage isomer in aqueous solution [156].

The linkage isomerisation mechanism of *cis*-$[Co(en)_2(ONO)_2]^+$ consists of two reactions; a fast step to give *cis*-$[Co(en)_2(NO_2)(ONO)]^+$ followed by a slower step (k = 7.1×10^{-4} s^{-1} at 35 °C) to produce *cis*-$[Co(en)_2(NO_2)_2]^+$ [157]. In the *trans*-complex there is an initial slow isomerisation to give *trans*-$[Co(en)_2(NO_2)(ONO)]^+$ followed by a rapid reaction to give the *trans*-dinitro complex. Other kinetic studies have dealt with the rates and steric course of the aquation of *trans*-$[Co(en)_2Cl_2]^+$ and *trans*-$[Co(en)_2Br_2]^+$ in 0.1 *M* CF_3SO_3H [158], the pressure dependence of the inner sphere reduction of *cis*-$[Co(en)_2Cl_2]^+$ by iron(II) in dmso [159], and isomerisation and base hydrolysis of the *cis*- and *trans*-isomers of the dithiosulphatobis(1,2-diaminoethane)cobalt(III) ion in aqueous solution [160].

Heats of isomerisation for

$$cis\text{-}[Co(en)_2Cl_2]Cl(s) \longrightarrow trans\text{-}[Co(en)_2Cl_2]Cl(s)$$

$$cis\text{-}[Co(en)_2Br_2]Br(s) \longrightarrow trans\text{-}[Co(en)_2Br_2]Br(s)$$

are -11.4 kJ mol^{-1} and -6.4 kJ mol^{-1} respectively [161]. The free energy changes are estimated to be $\Delta G° = -8.0$ kJ mol^{-1} and -3.0 kJ mol^{-1} for the isomerisation of *cis*-$[Co(en)_2Cl_2]Cl$ and *cis*-$[Co(en)_2Br_2]Br$ respectively. The crystal structure of $(-)_{589}$-*cis*-$[Co(1,3\text{-}pn)(NCS)_2].\frac{1}{2}[Sb_2(+)\text{-}tart_2].2H_2O$ establishes the absolute configuration Λ, which agrees with that assigned from CD spectra [162].

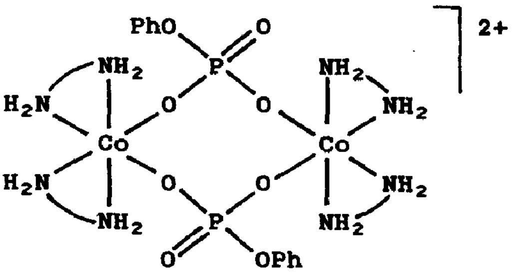
The thermodynamics of ion exchange of singly charged cobalt(III) complexes (*e.g.* $[Co(en)_2(NO_2)_2]^+$) with Na^+ on Dowex AG 50W-X2 have been studied in detail [163]. Cation exchangers with tartrate residues as chiral exchanging groups have been prepared from Toyopearl gel [164]. Short columns of these exchangers were successfully used for the complete resolution of $[Co(en)_3]^{3+}$, $[Co(1,3\text{-}pn)_3]^{3+}$ and *fac*-$[Co(\beta\text{-}ala)_3]$ by recycling chromatographic techniques. Sephadex and its derivatives are unsuitable for HPLC work, but Toyopearl HW-40(Fine), commercially available from the Toyo Soda Co., may be useful in this respect.

Spontaneous resolution of $[Co(en)_2(gly)][CH_3CO_2][ClO_4]$ at 5-50 °C, and for $[Co(en)_2(gly)][SO_4]$ at 39-50 °C in water has been observed [165], other studies in this area have been reported [166].

A series of papers have appeared dealing with the conformational analysis of chelate rings in cobalt(III)-diamine complexes, including 1,2-pn complexes [167], 2-methyl-pentane-2,4-diamine complexes [168] and a series of diamines [169]. The *tert*-butyl-substituted diamine (S)-3,3-dimethyl-1,2-butanediamine forms five-membered chelate rings with metals which are effectively limited to the δ-conformation in which the *tert*-butyl group is equatorial [170].

The mode of ion association between *cis*-$[Co(en)_2X_2]^+$ and halide ions in dmso (X = CN^-, NO_2^-, NCS^-, Cl^- or N_3^-) has been studied by ^1H NMR and CD spectroscopy [171]. Association of the anions with the amine hydrogens which are *trans* to the X substituent is indicated. A number of associated studies have appeared, including the solvent dependence of the CD spectra of *cis*-$[Co(en)_2X_2]^+$ complexes where stereoselective hydrogen bonding is of importance [172], and the determination of association constants for Λ-$[Co(en)_3]^{3+}$-$[S_2O_3]^{2-}$ and Δ-$[Co(\ell\text{-chxn})_3]^{3+}$-$[S_2O_3]^{2-}$ [ℓ-chxn = (1R,2R-1,2-cyclohexanediamine)] in water [173].

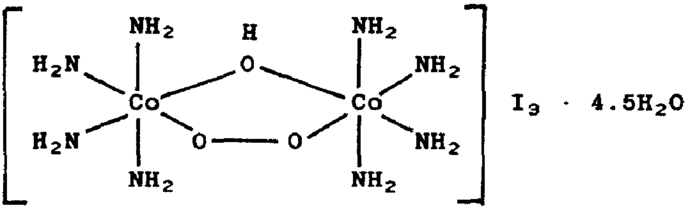
The crystal structure of lel,lel,lel-$[Co(\pm\text{-}2,3\text{-butanediamine})_3]Cl_3$ has been determined [174]. Three of the possible four diastereoisomers of $[Co(S\text{-phtn})_3]^{3+}$ (*fac*-Δ, *fac*-Λ and *mer*-Δ) have been characterised (S-phtn = (S)-1-phenyl-1,3-diaminopropane) [175]. The complex $[Co(S\text{-phtn})(NH_3)_4]^{3+}$ was also prepared. The reaction between *cis*-$[Co(en)_2Cl_2][ClO_4]$ and silver phenylphosphate in anhydrous dmso gives the dimeric cation $\{[Co(en)_2(\mu\text{-}O_3POC_6H_5)]_2\}^{2+}$ as the major product [176]. An X-ray analysis of the *meso*-diastereoisomer as the triflate salt monohydrate confirms the structure (*32*); the two cobalt atoms and the two bridging ligands define an eight-membered ring. Effects of *N*-methylation in complexes $[Co(diamine)(acac)_2]Br$ on ion pair formation in nitrobenzene have been studied by conductivity measurements [177].



(32)

Crystal structures of interest include the following, $\Delta\Lambda$-abc,def-(1,5-diamino-3-azapentane,*NNN*)(1,3-diaminopropane-2-ol,*NNO*)-cobalt(III) chloride tetrachlorozincate ($C_7H_{23}Cl_5CoN_5OZn$) [178], $[Co(en)_2(CO_3)]Cl$ [179], Δ-$(-)_{589}$-*cis*(NO_2)-*trans*-(NH_2)(D-alanine)dinitrotrimethylenediaminecobalt(III) ([Co(1,3-pn)(D-ala)$(NO_3)_3$]) [180] and the μ-hydroxo-μ-peroxo complex (*33*) [181].

Further kinetic work has dealt with the kinetics of substitution of aqua ligands in *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ by picolinic acid in water-ethanol mixtures [182], the kinetics of thermal deamination of *cis*-$[Co(en)_2(aniline)Br]Br_2$ and



(33)

cis-[Co(en)$_2$(3-picoline)Cl]I$_2$ [183], kinetics of solvolysis of *trans*-[Co(en)$_2$Cl$_2$]$^+$ in water and (water + isopropanol) [184], the kinetics of aquation, base and mercury(II)-catalysed hydrolysis of [Co(1,2-pn)$_2$(amine)Cl]$^{2+}$ complexes [185] and the isomerisation of [Co(diamine)$_2$(NO$_2$)$_2$]$^+$ complexes [186].

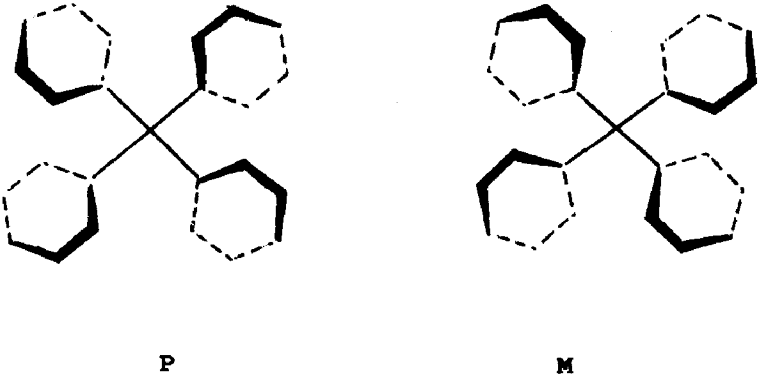
The preparation of *cis*-[Co(1,3-pn)$_2$(NO$_2$)$_2$]NO$_2$ using dmso as solvent has been described [187], as has the synthesis of mixed ligand cobalt(III) complexes with en and 3-amino-1-propanol [188]. New cobalt(III) complexes containing 1,3-pn and 1,2-pn ligands have also been described [189].

Additional studies have dealt with the photolysis of mixed ligand cobalt(III) complexes with α-amino acid, en and phen ligands [190], structures and thermodynamic properties of mixed 1,2-diaminoethane and 1,3-diaminopropane cobalt(III) complexes [191], and ^{1}H NMR studies of *cis*-bis(1,2-diaminoethane)cobalt(III) complexes in solution [192].

2.1.4.3 Pyridine, 2,2'-bipyridine 1,10-phenanthroline and 2,2'-bipiperidine complexes

Trans-[CoCl$_2$(py)$_4$]$^+$ has neither configurational chirality nor conformational chirality due to a chelate ring. However, steric interaction between the 2,6-hydrogens of adjacent pyridine molecules causes all four pyridine rings to be obliquely inclined with respect to the {CoN_4} plane (*34*). The chiroptical properties of the complex have now been studied in detail [193], and the $(-)^{\mathrm{CD}}_{630}$[CoCl$_2$(py)$_4$]$^+$ assigned the conformation P.

The crystal structures of *cis*-[Co(bipy)$_2$(CO$_3$)][NO$_3$].5H$_2$O and *cis*-[Co(phen)$_2$(CO$_3$)]Br.4H$_2$O have been determined by X-ray diffraction [194]. The kinetics of the complete decomposition of *cis*-[Co(py)$_2$(CO$_3$)$_2$]$^-$ in HClO$_4$ solution has been studied [195]. Decomposition occurs *via* two successive decarboxylation steps and a final reduction step which gives cobalt(II) as the

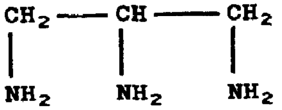


(34)

only cobalt-containing product. Other kinetic studies have dealt with mercury(II)-assisted aquation of *cis*-$[CoCl(en)_2(py-X)]^{2+}$ (py-X = 4-amino pyridine, 4-dimethylaminopyridine and 4-methylpyridine) complexes [196], activation volumes for the aquation of *cis*-$[Co(bipy)_2(NO_2)Cl]^+$, *cis*-$[Co(bipy)_2(NO_2)Br]^+$ and *cis*-$[Co(phen)(NO_2)Br]^+$ [197] and solvolysis of *trans*-$[CoCl_2(py)_4]^+$ in water-isopropanol mixtures [198]. The crystal structure of $(-)_{546}$-$[Co(NO_2)_2\{(-)_{589}$-2,2'-bpp$\}_2]$[d-bcs]$.4H_2O$ (2,2'-bpp = 2,2'-bipiperidine, d-bcs = d-3-bromocamphor-9-sulphonate) has been determined [199]. The absolute configurations around the asymmetric carbon atoms are both R for $(-)_{589}$-2,2'-bipiperidine, and the two five-membered chelate rings are λ.

2.1.4.4 *Triamine complexes*

A convenient synthesis of 1,2,3-triaminopropane, ptn (*35*), has been developed by the reduction of 1,2,3-triazidopropane [200]. The cobalt(III)

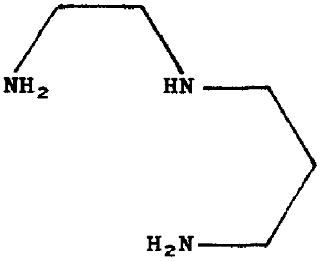


$$\begin{array}{ccccc} CH_2 & - & CH & - & CH_2 \\ | & & | & & | \\ NH_2 & & NH_2 & & NH_2 \end{array}$$

(35; ptn)

complex $[Co(ptn)_2]Cl_3$ has been characterised by ^{13}C NMR spectroscopy and X-ray analysis, and shown to have an s-*fac* configuration with a crystallographic centre of symmetry.

Two geometric isomers (red and violet) of [CoCl(diamine)(2,3-tri)]$[ZnCl_4]$ (diamine = en,1,2-pn or 1,3-pn; 2,3-tri = 1,6-diamino-3-azahexane (*36*)) have



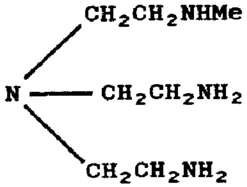
(36; 2,3-tri)

been prepared [201]. The unsymmetrical tridentate is meridionally coordinated, with the red and violet forms corresponding to the (R,S)-sec NH proton being adjacent to and remote from the chloro-ligand respectively. Redox decomposition of 1,2,6-[Co(dien)$(NO_2)_3$] in acidic solution has been the subject of a kinetic study [202].

The crystal structure of *mer*-[Co$(dpt)_2$]$[ClO_4]_3$ has been determined [203], and an energy minimisation analysis of the [Co$(dpt)_2]^{3+}$ {dpt = bis(3-aminopropyl)amine} system carried out. The preparation and characterisation of *mer*-[Co$(dpt)_2$]$[ClO_4]_3$ has been described [204]. The complex undergoes slow hydrolysis in neutral water, but hydrolysis is inhibited by acid. X-ray crystallography establishes that the isolated hydrolysis product is the racemic geometric isomer (C_2 symmetry) of [(dpt)Co$(OH)_3$Co(dpt)]$[ClO_4]_3$. The reaction of [Co(dpt)Cl_3] with dien in propan-2-ol gives *mer*-[Co$(dpt)_2]^{3+}$ and the three geometric isomers of [Co$(dien)_2]^{3+}$ almost quantitatively [205]. However, the reaction of [Co(dien)Cl_3] with dpt in propan-2-ol, catalysed by water, gives the three isomers of [Co(dien)(dpt)$]^{3+}$ as the main products in the approximate ratio μ-*fac*:*mer*:s-*fac* of 4:2:1. X-ray crystallography of *mer*-[Co(dien)(dpt)$]_2[S_2O_6]_3.H_2O$.EtOH confirms the assigned *mer* geometry.

2.1.4.5 Tetramine complexes

The ligand 2-(methylamino)-2,2"-diaminotriethylamine {Metren = (*37*)} has been prepared and a number of cobalt(III) complexes characterised [206]. The



(37)

detailed stereochemistry of the complexes are discussed and kinetic studies described.

^{13}C NMR spectra of a series of *trans*-$[Co(3,2,3\text{-tet})X_2]^{n+}$ (X = Br^-, Cl^-, N_3^-, NH_3, NO_2^- or OAc^-) complexes and *trans*-$[Co(2,3,2\text{-tet})X_2]^{n+}$ (X = Cl^-, glyH, OAc^-, NH_3 or NO_3^-) complexes have been studied [207]; the ^{13}C chemical shift is found to be linearly dependent on the ligand field strength (estimated from the electronic spectrum) of the axial ligands X. A further ^{13}C NMR study deals with cobalt(III) complexes of the tetraamine ligands 2,2,2-tet, 2,2,3-tet, 2,3,2-tet and 3,2,3-tet [208]. In such complexes three geometrical isomers are possible (*trans*, *cis*-α and *cis*-β) and these stereochemistries are readily assigned on the basis of ^{13}C NMR data.

The complex (citrato)(trien)cobalt(III) hydrate, $[Co(trien)(C_6H_5O_7)].5H_2O$ has been prepared as a possible model for complexation of citrate to a metal-containing enzyme [209]. X-ray work indicates that the citrate ion coordinates *via* the hydroxyl group and the central carboxylate group.

The sulphito complex $[Co(tren)(OH_2)(OSO_2)]^+$ is produced by the rapid reversible uptake of SO_2 by the hydroxo-aquo complex $[Co(tren)(OH_2)(OH)]^{2+}$ [210]. The sulphito species undergoes an internal redox process giving cobalt(II) and $[SO_4]^{2-}$ in the pH range 2.9-5.4.

Kinetic studies have dealt with the aquation and base hydrolysis of *cis*-α- and *cis*-β_2-$[Co(trien)(aniline)Cl]^{2+}$ [211], anation of *cis*-β-$[Co(trien)(OH_2)_2]^{3+}$ by oxalate [212], and the determination of activation volumes for the aquation of a range of tetra-amine complexes [213].

The Λ-β_2-$[Co(2,3,2\text{-tet})(AA)]^{n+}$ (2,3,2-tet = 1,9-diamino-3,7-diazonane; AA = aspartate, asparaginate and glutamate) complexes have been prepared and the hydroxide ion catalysed epimerisations of these complexes studied [214].

2.1.4.6 *Oximes, cobaloximes and vitamin B_{12}*

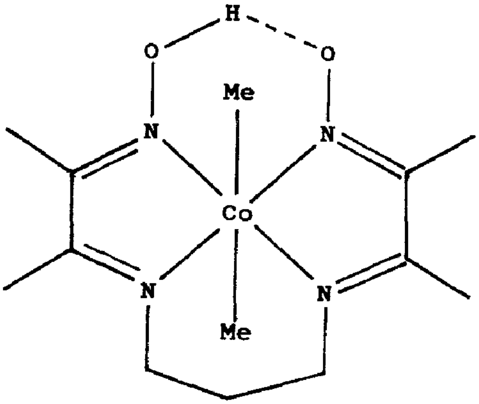
As always there is a considerable literature on cobaloxime chemistry. The reaction between several alkyl(pyridine)-cobaloximes $[RCo(dmg)_2(py)]$ and CF_3CO_2H in $CDCl_3$ has been studied by ^1H NMR spectroscopy [215]. Addition of CF_3CO_2H causes reversible protonation without loss of pyridine followed by a second protonation leading to pyridine loss. With an excess of CF_3CO_2H, the alkylcobaloximes lose their alkyl group as RH and give the red *cis*-bis(butane-2,3-dione dioxime)bis(trifluoroacetoxy)cobalt(II). Geometrical distortions have been investigated in the crystal structure of $[Co(CHMe_2)(dmg)_2\{CH_3C(CH_2O)_3P\}]$ containing a phosphite with a very small cone angle [216].

The compounds $[RCo(dmg)_2py]$ are cleaved by anhydrous HCl in chlorinated solvents to give RH (R = Me, Et, $CHMe_2$, neopentylcyclohexyl) probably by an

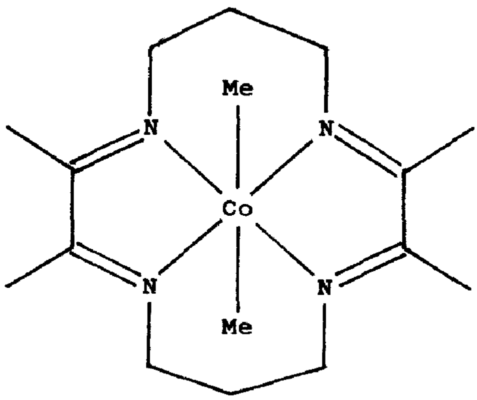
$S_{E}2$ process [217]. When R = benzyl, homolysis of the carbon-carbon bond predominates to give bibenzyl. Alkyl substitution and bridge formation by the cyano group in $[Co(dmg)_2]^+$ complexes have been studied [218]. Polymeric compounds $\{CN\text{-}Co(dmg)_2\text{-}CN\text{-}Co(dmg)_2\}_n$ were prepared with conducting properties. Crystals of $[\{(S)\text{-1-cyanoethyl}\}Co(dmg)_2py]$ undergo racemisation in the crystalline state on exposure to X-rays [219]. Linkage isomerism in $[(CN)Co(dmg)_2(OH_2)]$ has been studied; both the cyano and isocyano complexes were prepared and shown to be isostructural [220]. The reaction of cobalt(II) cobaloximes with organohaloarsines has been studied and the crystal structure of an arsine derivative of a cobalt(III) cobaloxime determined [221].

Further crystal structures determined this year include the following: $[Co(dmg)_2(CN)\{P(OMe)_3\}]$ [222], $[Co(dmg)_2(CH_2CMe_3)(OH_2)]$ and $[Co(dmg)_2(CH_2CMe_3)(PPh_3)]$ [223], $[Co(dmg)_2(CH_2CMe_3)(PMe_3)]$ [224], $[Co(dmg)_2(Me)(PMe_3)]$ and $[Co(dmg)_2(Me)\{P(C_6H_{11})_3\}]$ [225], and $[Co(dmg)_2(C_6H_5CH_2)(\text{morpholine-}N)].H_2O$ [226]. In view of the wealth of crystallographic data on cobaloxime complexes, the aim of further work in this area should be clearly defined, and its chemical significance carefully considered.

The pK_a values of (carboxymethyl)(ligand)cobaloximes and (1-carboxyethyl)(ligand)cobaloximes with sixteen different axial ligands have been determined in an effort to quantify the "β-effect" [227]. The *trans*-dimethyl cobalt(III) complexes (*38*) and (*39*) rapidly transfer methyl groups to zinc(II) and cadmium(II) in CH_3CN [228]. Methyl transfer to lead(II) and $[(Me_3C)_3Pb]^+$ in ethanenitrile is also rapid [229].



(38)



(39)

^{19}F NMR chemical shifts for 3- and 4-fluorophenyl(ligand)cobaloximes with twenty-one different axial ligands have been determined [230]. The results indicate pronounced π-electron donation from cobalt to the covalently-bound organic ligand, which varies markedly with the nature of the cobalt centre. Reaction of cobalt dimethylglyoxime dihydrate with amines gives a catalyst for the hydrogenation of $PhNO_2$. EPR studies of this system have now been published [231].

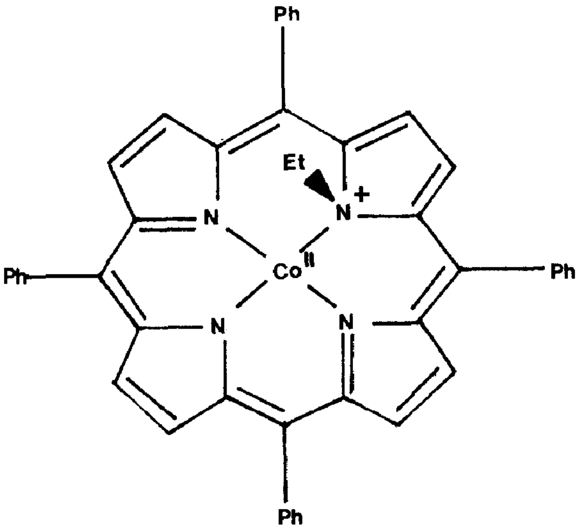
Electron transfer between the clathrochelate $Co(dmg)_3(BF)_2BF_4$ and ferrocene in ethanenitrile has been studied kinetically [232]. The complex $[Co(dmho)_3]$ (dmho is the monoanion of 5,5-dimethyl-cyclohexane-1,2,3-trione 2-oxime) has been characterised [233]; this complex spontaneously resolved on crystallisation to the *fac*-Λ isomer. Complexes of cobalt(III) with 2-nitroso-1-naphthol and 1-nitroso-2-naphthol (mono-oximes of 1,2-naphoquinone) have also been studied [234].

The syntheses of organocobalamines in which the cobalt atom carries substituents derived from esters of dimethylmalonic and methylmalonic acid have been described [235]. The compounds are of interest as models for possible intermediates in the coenzyme B_{12} dependent methylmalonyl-CoA mutase reaction. The reactions of these compounds leads to the suggestion of a carbanionic mechanism for the methylmalonyl-CoA mutase reaction. Electrochemical oxidation and reduction of methylcobalamin and coenzyme B_{12} has been studied using spectroelectrochemical techniques [236]. Protonation of the phosphodiester of the nucleotide loop of methylcobalamin is indicated by the pH dependence of the ^{31}P NMR spectrum [237].

Reactions of B_{12r} with aliphatic free radicals have been investigated by pulse radiolysis [238]. The reaction of methylcobalamin (CH_3-B_{12}) with $[AuX_4]^-$ (X = Cl or Br) under anaerobic conditions gives aquocobalamin with an oxidised corrin ring, CH_3X and metallic gold [239]. The reaction is interpreted in terms of one-electron oxidative demethylation of CH_3-B_{12}.

A kinetic approach to the determination of transition metal-alkyl bond dissociation energies has been developed and its application to organocobalt compounds related to B_{12} coenzymes discussed [240]. The one-electron electrochemical oxidation of $[EtCo^{III}(TPP)]$ (TPP = tetraphenylporphinato) causes intramolecular rearrangement of the ethyl group to a ring nitrogen to give $[N\text{-}EtCo^{II}(TPP)]^+$ (*40*) [241]. Reduction of $[N\text{-}EtCo^{II}(TPP)]^+$ with $Na[BF_4]$ regenerates $[EtCo^{III}(TPP)]$, but by an intermolecular arrangement.

Cobaloximes containing phosphorus-donor ligands have been reviewed [242] and a thesis deals with structural studies of the *trans*-effect in octahedral bis(dimethylglyoximato)cobalt(III) complexes [243]. Cobalt(III) complexes of dimethylglyoxime with 3-amino-1-propanol have been studied [244], and the kinetics of reduction of some *trans*-bis(dimethylglyoximato)cobalt(III) complexes by vanadium(II) investigated [245]. A further paper deals with the crystal structure and deprotonation of a cobalt(III) complex $[Co(HL)L][ClO_4]_2$, where



(40; [*N*-EtCo^{II}(TPP)]$^+$)

HL = 2-(3-aminopropyl)imino-3-butanone oxime [246].

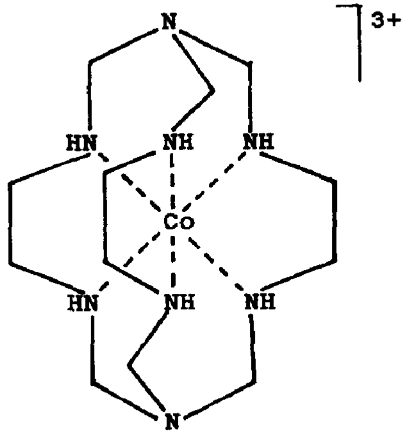
The reaction of ethene with hydroxyl radicals under reducing conditions produces radicals which are trapped by vitamin B_{12r} to give 2-hydroxyethylcobalamin [247]. The kinetics of the acid-catalysed decomposition of (2-hydroxy-, (2-ethoxy- or (2-phenoxyethyl)cobaloximes to form ethene and cobaloxime(III), provides evidence for the formation of a cationic intermediate (upon loss of the β-leaving group) [248]. The cationic intermediate is believed to be a cobaloxime(III)ethene π complex. The kinetics of decomposition of (α-phenylethyl)aquocobaloxime in aqueous acidic methanol suggest parallel homolytic ($\sim$ 72%) and β-elimination ($\sim$ 28%) pathways [249].

The mechanism of the cyanide-induced formation of methyl ethanoate from [(methoxycarbonyl)methyl]cobalamin has been studied in detail [250].

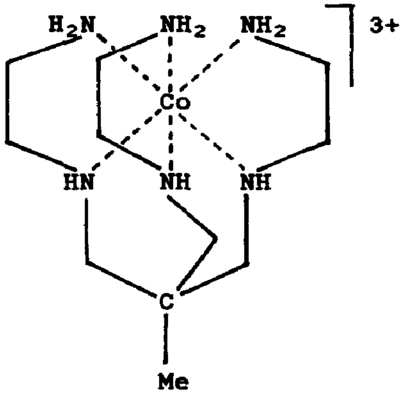
The crystal structure of bis[di(α-furyl)glyoximato]ditriphenylphosphinecobalt(III) nitrate confirms an octahedral stereochemistry with the phosphine donors in the axial sites [251]. Sterically unstable alkylcobalamins are discussed in a recent thesis [252].

2.1.4.7 Macrocycles

The synthesis of the cage complexes $[Co(sep)]^{2+/3+}$ (*41*) (sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) from $[Co(en)_3]^{3+}$ and analogous cages from $[Co(sen)]^{3+}$ (*42*) (sen = 5-methyl-5-(4-amino-2-azabutyl)-3,7-diazanonane-1,9-diamine) have now been described in detail and the crystal structure of $[Co(sep)][S_2O_6].H_2O$ determined [253]. The complexes are



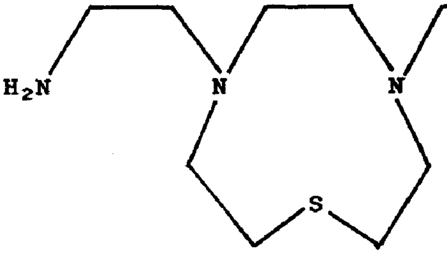
(41; $[Co(sep)]^{3+}$)



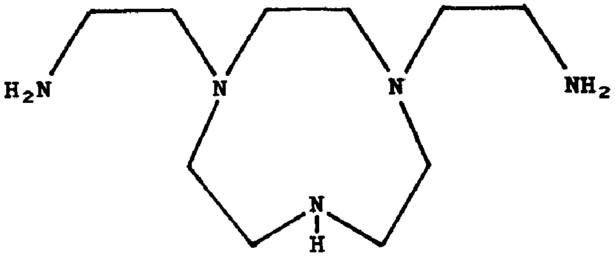
(42; $[Co(sen)]^{3+}$)

unusually stable, and display many novel features, thus the Co(II)-Co(III) electron self exchange rates are extremely fast (5.1 and 2.9 M^{-1} s^{-1} at 25 °C) and *ca.* 10^5 times greater than for $[Co(en)_3]^{3+/2+}$. The $[Co(sep)]^{2+}$ reduction of O_2 to H_2O_2 is also very rapid and appears to occur by an outer sphere pathway.

Synthetic routes to the resolved *unsym*-isomers of $[Co(dats)Cl][ClO_4]_2$ {dats = 4,7-bis(2-aminoethyl)-1-thia-4,7-diazacyclononane = (*43*)} and $[Co(datn)Cl][ClO_4]_2$ {datn = 1,4-bis(2-aminoethyl)-1,4,7-triazacyclononane = (*44*)} have been reported [254]. The new macrocyclic ligand

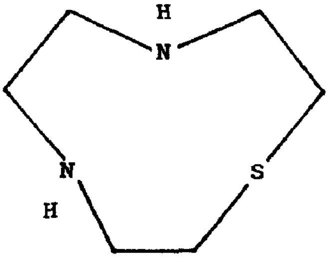


(43; dats)



(44; dath)

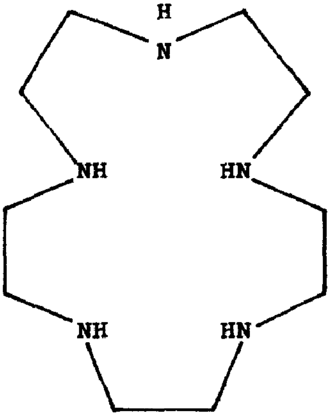
1-thia-4,7-diazacyclononane {tasn = (*45*)} was also synthesised and the *cis*-$[Co(tasn)_2][ClO_4]_3$ complex prepared. Base hydrolysis of each chloro-complex occurs in two consecutive steps, the initial reaction being chloride hydrolysis. The second reaction for the dats complex is base catalysed dissociation of the thioether to give *cis*-$[Co(dats)(OH)_2]^+$. The



(45; tasn)

datn complex undergoes base catalysed terminal ring opening to *cis*-[Co(datn)(OH)$_2$]$^+$.

The preparation of the pentadentate macrocycle [15]aneN$_5$, {1,4,7,10,13-penta-azacyclopentadecane = (*46*)} has been described in detail

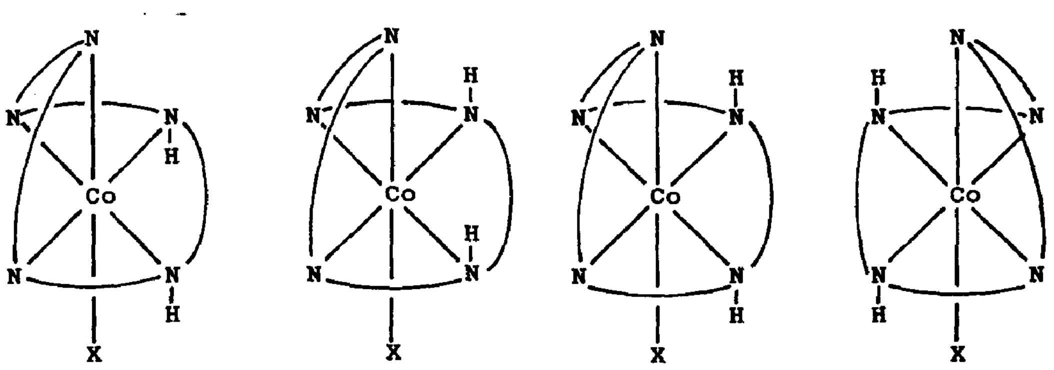


(46)

and the complex [Co([15]aneN$_5$)Cl][ClO$_4$]$_2$ characterised [255]. This complex can have three possible configurations as a result of the two chiral centres, Scheme 1.

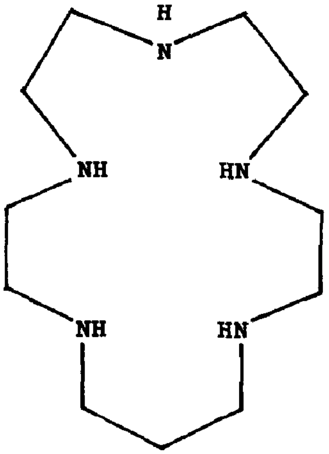
^{13}C NMR measurements establish that the cobalt(III) complex is a mixture of the possible stereoisomers. Base hydrolysis of [Co([15]aneN$_5$)Cl]$^{2+}$ is quite rapid with $k_{\text{OH}} = 2.45 \times 10^4$ M^{-1} s^{-1}, a result which can be rationalised in terms of the equatorial {N_4} donor set. The crystal structure of [Co([16]aneN$_5$)Cl][ClO$_4$]$_2$ {[16]aneN$_5$ = 1,5,8,11,14-pentaazacyclohexadecane = (*47*)} establishes that the six-membered chelate ring lies in the "backbone" of the molecule (*48*) [256]. The six-membered ring assumes a "chair" conformation while all five-membered rings are gauche. The two "flat" nitrogens have opposite chirality (*meso*).

The complexes [Co([15]aneN$_5$)dmf][ClO$_4$]$_3$ (*49*) and [Co([15]aneN$_5$)(OOCH)][ClO$_4$]$_2$ have been characterised [257]. Base hydrolysis of (*49*) is biphasic giving both the methanoato complex (hydrolysis of the *O*-coordinated amide) and the hydroxo-complex (*50*). The hydroxo-complex has

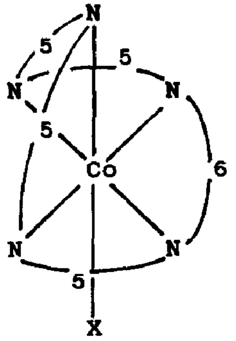


meso-syn *meso-anti* *racemate*

SCHEME 1: Possible configurations of $[Co([15]aneN_5)Cl]^{2+}$.



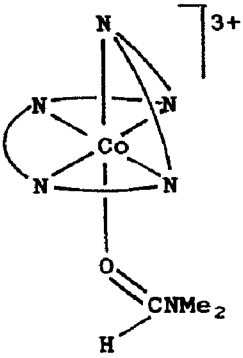
(47)



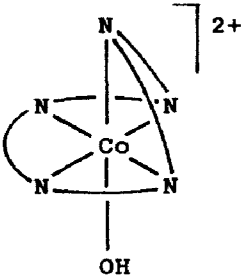
(48)

also been shown to be effective in promoting the hydrolysis of 4-nitrophenyl ethanoate [258].

Sargeson's group has continued its work on the encapsulation of metal ions using nitrogen-sulphur ligand atom cages. The synthetic strategies employed are summarised in the Scheme 2 [259]. These reactions should be applicable to many other systems.

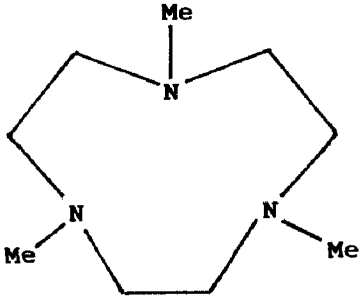


(49)

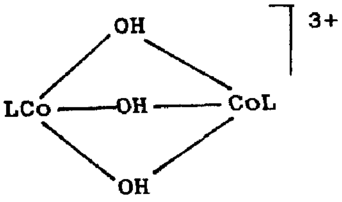


(50)

The synthesis of the cyclic amine 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3[9]aneN_3) (*51*) has been reported [260], and triply OH-bridged binuclear cations [(Me_3[9]aneN_3M(OH)$_3$M(Me_3[9]aneN_3)]$^{3+}$ (*52*) prepared with cobalt(III),



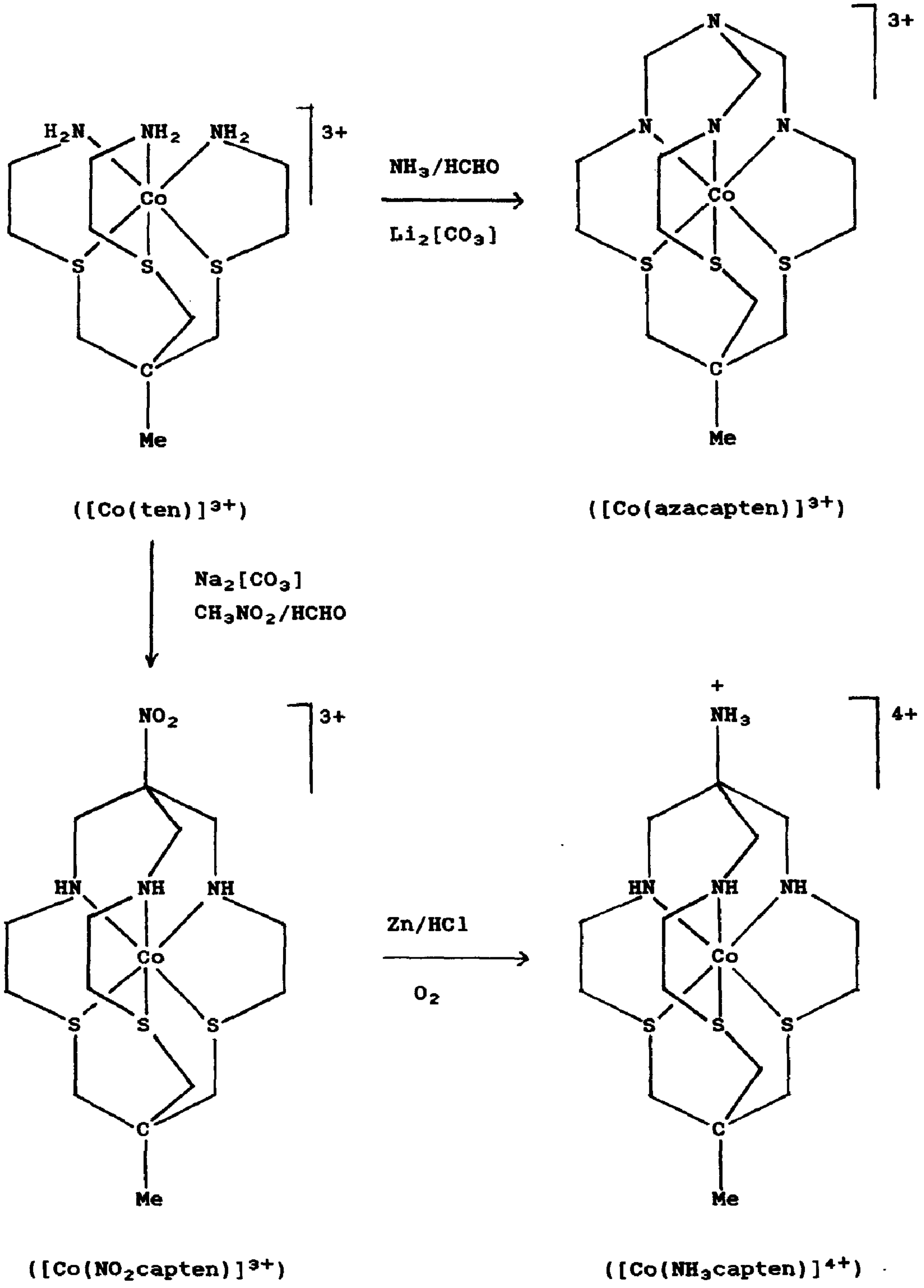
(51; L)



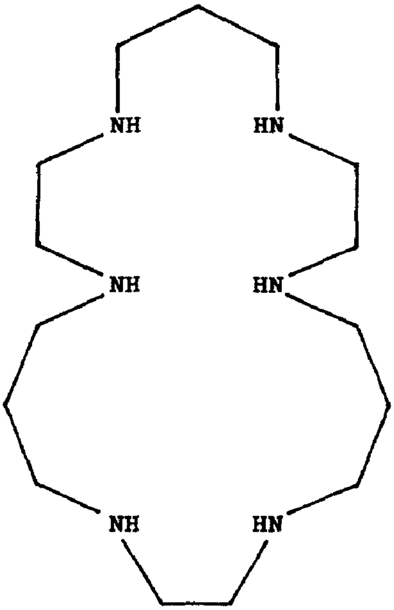
(52)

chromium(III) and rhodium(III). In contrast to their analogues containing the non-methylated ligand 1,4,7-triazacyclononane, the binuclear cations are stable in 2 *M* perchloric acid, and acid-catalysed OH-bridge cleavage is not detected.

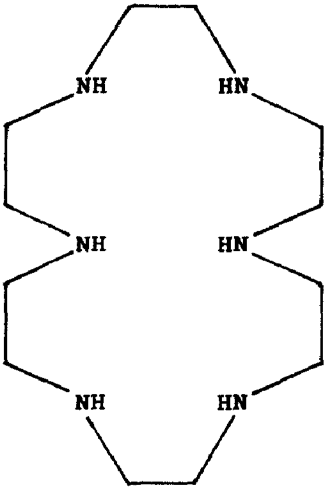
The preparation of the symmetrical hexaaza macrocycles [21]aneN_6 (*53*), [18]aneN_6 (*54*) and 1,4,7,10,13,16-tri(R,R)cyclohexano[b,h,n]hexaazacyclooctadecane tc[18]aneN_6 (*55*) and their cobalt(III) complexes has been studied [261]. Cobalt(III) complexes of [18]aneN_6 have previously been characterised [262]. The complex [Co([21]aneN_6)]$^{3+}$ was optically resolved and evidence for two geometrical isomers obtained. Column chromatography of the optically active [Co(tc[18]aneN_6)]$^{3+}$ gave five geometric isomers and some evidence for the existence of a sixth isomer was obtained. The two chiral isomers of [Co([18]aneN_6)] were resolved.



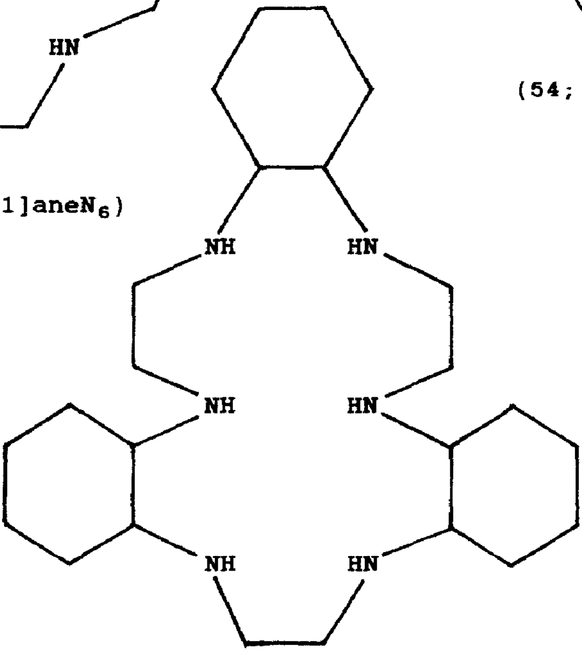
SCHEME 2: Capping strategies for the encapsulation of metal ions.



(53; [21]aneN$_6$)



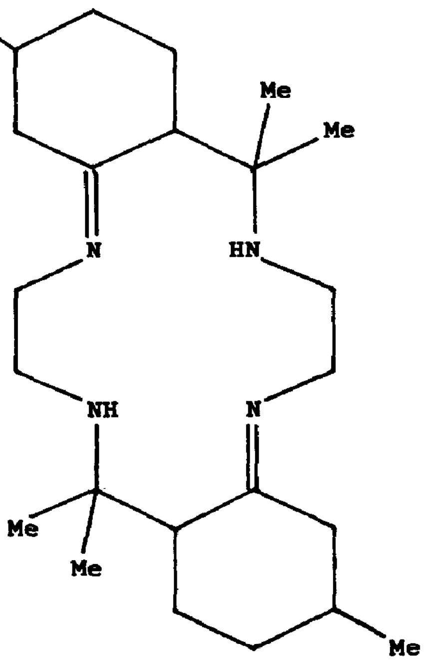
(54; [18]aneN$_6$)



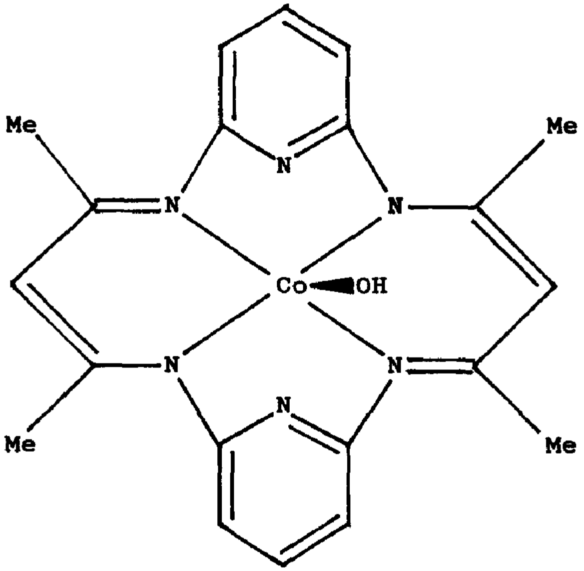
(55; tc[18]aneN$_6$; the cyclohexanediamine residues have the RR configuration)

The synthesis of the new macrocyclic ligand {(*56*) = L} derived from (+)-pulegone has been described and a variety of *trans*-[CoLX$_2$][ClO$_4$] {X$_2$ = Cl$_2$, (NO$_2$)$_2$ or Cl(NO$_2$)} prepared [263]. The synthesis provides a useful route to a chiral macrocycle.

The tetradentate *N*$_6$ macrocyclic ligand obtained by template reactions of 2,6-diaminopyridine and pentane-2,4-dione gives complexes of the type (*57*) with cobalt(III), which are suggested to be five coordinate [264].



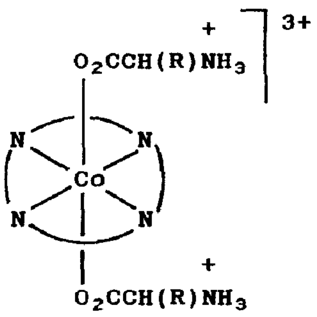
(56)



(57)

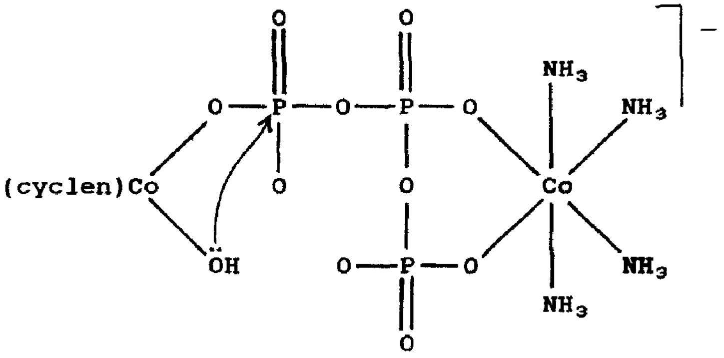
The complexes *cis*-[Co(cyclam)(en)]$^{3+}$ and *cis*-[Co([13]aneN$_4$)(en)]$^{3+}$ have been resolved by elution from SP-Sephadex C-25 with sodium tartratoantimonate(III) [265]. *Trans*-bis(imidazole) and *trans*-bis(amino acid) derivatives of the type (*58*) have been prepared with the macrocyclic diene ligand Me$_2$[14]dieneN$_4$ [266]. It has been concluded that the prosthetic groups of the cobalt(III)-containing proteins from *Desulphovibrio gigas* and *D. desulphuricans* are cobalt(III) isobacteriochlorins [267].

A number of interesting kinetic studies have appeared. The reduction of several macrocyclic N_4 cobalt(III) complexes by L-ascorbic acid (H_2A) has been studied at 25 °C ($I = 0.1$ *M* $LiClO_4$) over the pH range 1.64-3.47 [268]. Unsaturation in the macrocycle facilitates electron transfer. The [Co(cyclen)(OH)$_2$]$^+$ promoted hydrolysis of $\beta\gamma$-[Co(NH$_3$)$_4$H$_2$P$_3$O$_{10}$] is believed



(58)

to proceed *via* the intermediate (*59*) [269,270].

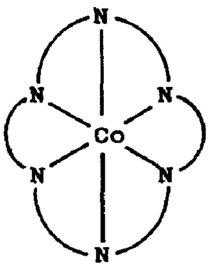


(59)

Rates of the $[Co(OH_2)_6]^{3+}$ oxidations of $[Co(N_4)(OH_2)_2]^{2+}$ (N_4 = a tetraaza macrocycle) and $[Co(sepulchrate)]^{2+}$ have been determined [271] and electronic requirements of inner-sphere electron-transfer pathways in macrocyclic complexes discussed [272].

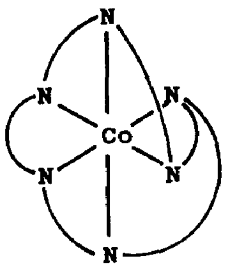
Other studies have dealt with the photolysis of $[Co(Me_4[14]tetraeneN_4)(OH_2)_2]^{3+}$ [273], ^1H NMR spectroscopic and electrochemical investigations of the (*meso*-5,10,15,20-tetraarylporphine)cobalt(III) complexes [274], CNDO/2 calculations on cobalt(III)-porphyrins [275], evidence for a dissociative mechanism obtained from values of $\Delta V^{\ddagger}$ for substitution of diaqua[*meso*-tetrakis(*N*-methyl-4-pyridyl)porphinato]cobalt(III) with thiocyanate [276] and the direct measurement of electron self-exchange rates in cobalt porphyrins by outer-sphere [277] and inner sphere [278] pathways.

Both *sym* (*meso*) (*60*) and *unsym* (*racemic*) (*61*) isomers of $[Co([18]aneN_6)]^{3+}$



(meso)

(60; *sym*)



(racemic)

(61; *unsym*)

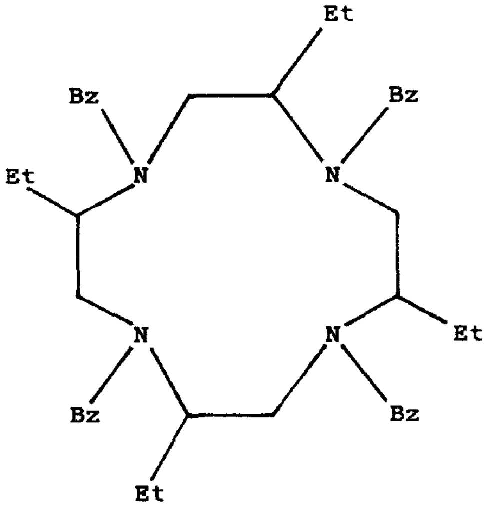
{[18]aneN_6 = 1,4,7,10,13,16-hexaazacyclooctadecane = (*54*)} have been characterised [262]. The *meso*-isomer is a minor component (< 1%). The crystal structure of the *meso*-isomer has now been determined [279]. The Co-N distance is 1.9966(8) Å and the N-Co-N angle in the chelate ring is 83.62°. The molecular dimensions are in good agreement with those obtained from conformational analysis.

The complexes $[Co([9]aneN_3)(L\text{-}val)(NH_3)]^{2+}$, ([9]ane$N_3$ = 1,4,7-triazacyclononane), $[Co(Me[9]aneN_3)(gly)(NH_3)]^{2+}$ {Me[9]aneN_3 = (2R)-2-methyl-1,4,7-triazacyclononane} have been prepared and separated into diastereoisomers by column chromatography [280]. Six other complexes $[CoL(\beta\text{-}ala)([9]aneN_3)]^{n+}$ (L = CN^-, NO_2^- or NH_3) and $[CoL(gly)([10]aneN_3)]^{n+}$ (L = NO_2^-, NCS^- or H_2O; [10]aneN_3 = 1,5,9-triazacyclododecane) have also been prepared and resolved into enantiomers.

The kinetics of anation of *trans*-$[Co(OH)(N_4)(H_2O)]^{2+}$ (N_4 = [14]aneN_4, *meso*-Me_6[14]aneN_4 (tet *a*), *rac*-Me_6[14]aneN_4 (tet *b*), Me_6[14]4,11-dieneN_4 or Me_4[14]tetraeneN_4) by ethanoate ions has been studied at 25 °C and $I = 0.1$ *M* over the pH range 3.62-5.17 [281]. The reaction is considered to proceed *via* a dissociative mechanism.

X-ray structural studies on complexes of the chiral cyclen ligand (2R,5R,8R,11R)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane (*62*) have been published including [CuLCl]Cl and [CoLCl]Cl [282]. The crystal structure of diaqua(tetraphenylporphinato)cobalt(III) perchlorate has also been published [283]. An unusually short cobalt-bromine bond has been observed by EXAFS studies in bromo-($\alpha,\beta,\gamma,\delta$)-porphinatocobalt(III) [284] and a thesis deals with resonance Raman investigations of some cobalt (and copper) macrocyclic complexes (and transition metal-containing proteins) [285].

The synthesis of *trans*-dimethylcobalt(III) complexes of tetradentate macrocyclic ligands and their reactions with metallic electrophiles such as



(62)

zinc(II) and cadmium(II) is described in a thesis [286]. Some of this work has now been published and is referred to in Section 2.1.4.6 (ref. 228).

2.1.4.8 Azide complexes

Hexaazidocobaltates(III), $[Co(N_3)_6]^{3-}$ have been studied and their spectral parameters and hazards considered [287]. Several electron-poor dipolarophiles (alkynes, alkenes and nitriles) react with azido cobalt chelate complexes of the type $[LCo(chelate)(N_3)]$ under mild conditions [288]. Coordinated five-membered-ring heterocycles are the initial products of these 1,3-dipolar cycloadditions, thus non-terminal alkynes give triazoles, alkenes give triazolines and nitriles give tetrazoles.

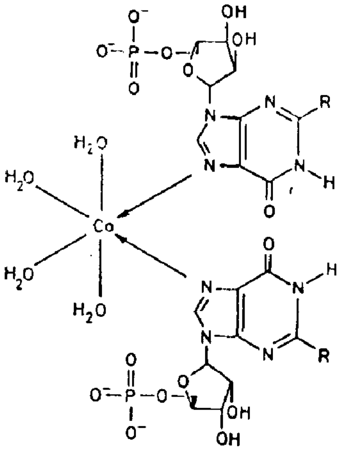
2.1.4.9 Complexes with miscellaneous nitrogen ligands

X-ray structural studies on the ternary complexes $[Co(en)_2(OH_2)_2][Co(5'\text{-IMP})_2(OH_2)_4]Cl_2.4H_2O$ (*63*) and $[Co(en)_2(OH_2)_2][Co(5'\text{-GMP})_2(OH_2)_4]Cl_2.4H_2O$ (*64*) (5'-IMP = inosine 5'-monophosphate; 5'-GMP = guanosine 5'-monophosphate) show that they are isomorphous and that cobalt binds to two symmetry-related nucleotide moieties in the *cis*-position through the N(7) donor of the base [289]. This mode of bonding has not previously been observed in a 1:1 metal-nucleotide complex.

Cobalt(III)-nitro complexes are effective as oxygen transfer agents and their use in the epoxidation of olefins has been studied [290].

2.1.5 Complexes with phosphorus donor ligands

Cobalt(III) phosphine complexes $[Co(CN)_{4-2n}(acac)_nL_2]^{(n-1)+}$



(63; R = H)
(64; R = NH_2)

{L = $P(CH_3)_x(C_6H_5)_{3-x}$} and several related complexes have been characterised [291]. For $[Co(acac)_2L_2]^+$, the ligands $P(CH_3)_3$ and $P(CH_3)(C_6H_5)_2$ give the *cis*- and *trans*-isomers respectively. New complexes of the [Co(O-O)(edpp)$_2$] and [Co(O-O)(en)(dppe)] (O-O = $acac^-$, mal^{2-}, ox^{2-} or $CO_3{}^{2-}$; edpp = (2-aminoethyl)diphenylphosphine; dppe = 1,2-bis(diphenylphosphino)ethane) type have been prepared [292].

2.1.6 *Cyanide complexes*

The crystal structure of $K_3[Co(CN)_5(N_3)].2H_2O$ has been determined [293]. Cyanide bridged complexes $[(en)_2(H_2O)M\text{-}NC\text{-}M'(CN)_5]$ {M,M' = Co(III) and/or Cr(III)} have been characterised and their reactions studied [294]. Linkage isomerism in cyanoaquabis(dimethylglyoximato)cobalt(III) has also been investigated [295]. Hydrogen bonding involving the $[Co(CN)_6]^{3-}$ anion has been studied by infrared techniques [296] and ^{59}Co NMR spectroscopy [297].

The crystal structure of the *trans*-complex $Na_5[Co(CN)_4(SO_3)_2].13H_2O$ containing the sulphito ligand has been determined [298] and the preparation of potassium pentacyanodithionatocobaltate(III) described [299]. The complexes $[Co(CN)_5(dmf)]^{2-}$ and $[Co(CN)_5(dmso)]^{2-}$ have been characterised [300] and the preparation and characterisation of a mixed-valence cyano-bridged cobalt(III)-ruthenium(II) complex described [301].

Kinetic investigations have dealt with the photoaquation of $[Co(CN)_6]^{3-}$ [302], a reinvestigation of the kinetics of the $[Co(CN)_5OH_2]^{2-}$-$N_3{}^-$ reaction [303] and the kinetics of the reduction of cyano-cobalt(III) porphyrins by dithionite [304].

2.2 COBALT(II)

2.2.1 Complexes with halide ligands

The crystal structure of Cs_3CoBr_5 has been determined at 4.2 K by single crystal neutron diffraction [305]. The Co-Br bond length is 239.8(2) pm and the Br-Co-Br angles of the distorted tetrahedral environment are 107.58(9) and 110.43(9)°. The absorption and CD spectra of the tetrahedral halide complexes $[Co\{(-)\text{-}\alpha\text{-isosparteine}\}X_2]$ have been examined in detail [306]. Absorption spectra indicate that cobalt(II) is tetrahedrally coordinated as $[CoCl_4]^{2-}$ in molten $AlCl_3$-(*N*-Bupy)Cl^- (0.8 to 1 mole ratio), but at a 2:1 molar ratio octahedrally coordinated species, possibly $[Co(Al_2Cl_7)_m]^{2-m}$ with $m = 2$, are formed [307].

Equilibria of cobalt(II) perchlorate with LiCl in 0.1 *M* $LiClO_4$-propanone have been studied, and stepwise formation constants obtained for the four chloro-complexes [308]. The crystal structure of benzotriazolium tetrachlorocobaltate(II) has been determined [309].

2.2.2 Complexes with oxygen donor ligands

2.2.2.1 Complexes with general oxygen-donor ligands

The X-ray structure of the $\{CoO_8\}$ unit in cobalt garnet, a new synthetic silicate of the composition $Co_3Al_2Si_3O_{12}$, reveals a deformed cube with its central cobalt(II) more regularly 8-coordinate than in the previously studied $[Co(NO_3)_4]^{2-}$ [310].

A VIOLENT EXPLOSION DURING THE PREPARATION OF COBALT(II) PERCHLORATE HAS BEEN REPORTED [311]; this was attributed to the hexa-aquo cobalt(II) perchlorate undergoing partial loss of water of hydration to form an unstable lower hydrate. The cobalt(II)-perchlorate-water system in propanone has been investigated [312]. NMR measurements indicate that water coordination dominates even in the presence of large concentrations of propanone.

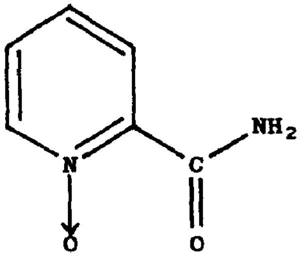
The cobalt(II)-carboxylates, $[Co(O_2CR)_2]$ ($R = C_{11}H_{23}$ and $C_{17}H_{33}$), have been characterised and their nonisothermal decomposition,

$$(RCO_2)_2Co \longrightarrow R_2CO + CoCO_3$$

$$CoCO_3 \longrightarrow CoO + CO_2$$

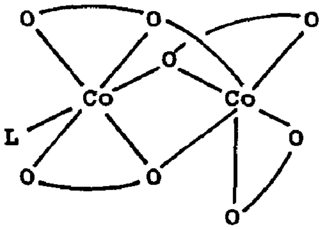
studied by TGA [313].

Complexes of 2-pyridinecarboxamide *N*-oxide {(*65*) = pco} with cobalt(II)



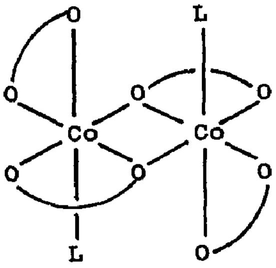
(65)

have been prepared [314]. Infrared evidence indicates that the ligand is an *O*,*O* donor *via* the *N*-oxide and carboxamide groups. The binuclear complex $[Co_2(py)(acac)_4]$ has been characterised, and its crystal structure determined [315]. Three oxygen atoms from chelating pentane-3,4-dionato ligands form monoatomic bridges between the two metal atoms, so that the metal atom coordination polyhedra share a triangular face (*66*). The magnetic properties



(66)

of the binuclear complexes $[Co_2L_2(acac)_4]$ {*e.g.* (*67*); L = cyclohexylamine}



(67)

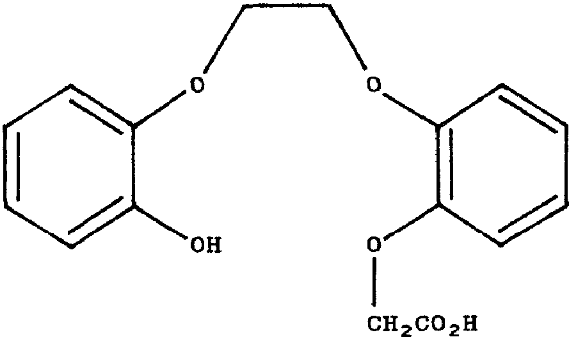
have also been determined [316]. The cobalt compounds have magnetic moments similar to those of monomeric octahedral complexes.

A variety of equilibrium studies have also appeared, including a calorimetric investigation of the interaction of furan-2-carboxylate with cobalt(II) [317], and investigations of ternary complexes of cobalt(II) involving imidazole or ammonia with uridine 5'-triphosphate or adenosine 5'-triphosphate [318]. A series of ternary complexes between adenosine 5'-triphosphoric acid (ATP), bipy and cobalt(II) (including other metals) have been characterised in the solid state [319]. These complexes can be formulated $[M(II)\text{-}H_2ATP\text{-}bipy]_2.4H_2O$ (Mbipy ATP), and have been investigated by a variety of techniques. IR spectra indicate that ATP coordinates *via* the oxygen of the phosphate groups. These complexes are particularly stable towards hydrolysis and may provide models for ATP transport. (Divalent metal ions usually catalyse the dephosphorylation of nucleoside di- and triphosphates, whereas ternary complexes often display remarkable stability towards hydrolysis). Complexation between ATP and cobalt(II) has also been studied by a Hungarian group [320]. Different complexation modes between cobalt(II) and 5'-AMP has been demonstrated by direct NMR observation of the low-temperature complex [321].

Bis-complexes of cobalt(II) with the anions of 2,2'-dihydroxy-diphenyl oxide and sulphide have been studied and the crystal structure of sodium bis{diphenylsulphide-2,2'-diolato(2-)}cobaltate(II)-propanone-water determined [322]. The synthesis of cobalt(II) methoxyphenolates has also been described, and the crystal structure of tetrakis{μ-3-methoxo(2,4,6-trichlorophenolato)-(methanol)cobalt(II)} obtained [323].

Other investigations have dealt with cobalt(II) complexes of ascorbic acid [324], solvent exchange at cobalt(II) in mixtures of weak and strong donors (MeOH, dmf, hmpa) using NMR techniques [325], and spectrophotometric studies on 2-hydroxyphenylazoacetylacetone and its cobalt(II) complex [326].

Reaction of the potassium salt of 1-(2-carboxymethoxyphenoxy)-2-(2-hydroxyphenoxy)ethane {HL = (*68*)} with cobalt(II) chloride gives $[Co(L_2K)_2]$

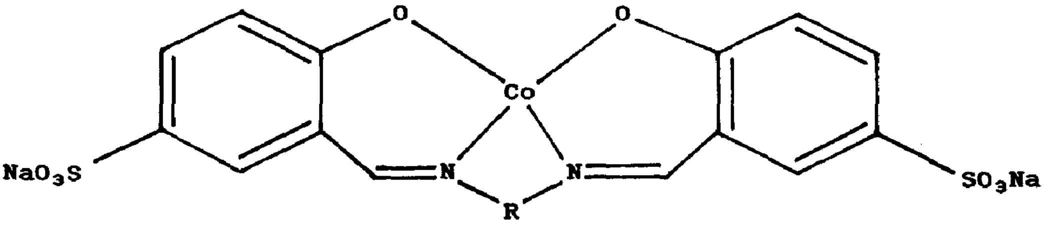


(68)

[327]. Crystallography establishes that cobalt(II) is tetrahedrally coordinated by four carboxyl oxygens, one from each of four open chain polyether hydroxyacid anion ligands, L^-.

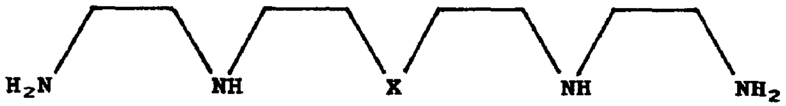
2.2.2.2 Dioxygen complexes

The formation and stability of cobalt dioxygen complexes in aqueous solution has been reviewed [6]. The apomyoglobin complexes of cobalt(II) protoporphyrin IX and cobalt(II) 3,10,17,24-tetrasulphonated phthalocyanine have been prepared and the EPR spectra of their adducts with dioxygen recorded and evaluated [328]. The protein provides appropriate conditions for the oxygenation of cobalt(II) tetrasulphonated phthalocyanine at room temperature. The cobalt(II) complexes of a series of *N,N'*-substituted bis(salicylaldiminesulphonic)acids, (*69*), have been prepared as water soluble salts [329]. The cobalt(II) complexes react readily with dioxygen at room temperature to give mixtures of the superoxo-type [CoL(O_2)(OH_2)] and peroxo-type [{CoL(OH_2)}$_2$(O_2)] complexes. Formation of the superoxo complexes is reversible at room temperature.



(69; R = $(CH_2)_2$, $(CH_2)_3$, CH_2CHMe or 2-C_6H_4)

The synthesis of six ether and thioether pentadentate ligands, of which (*70*) is an example, have been described [330]. The cobalt(II)-thioether derivatives form more stable dioxygen adducts than their oxygen analogues, but less stable complexes than the cobalt(II) derivatives of the analogous amino nitrogen ligands. The oxygenation of cobaloxime(II) has been shown by stopped-flow measurements to consist of three distinct stages; (a) formation



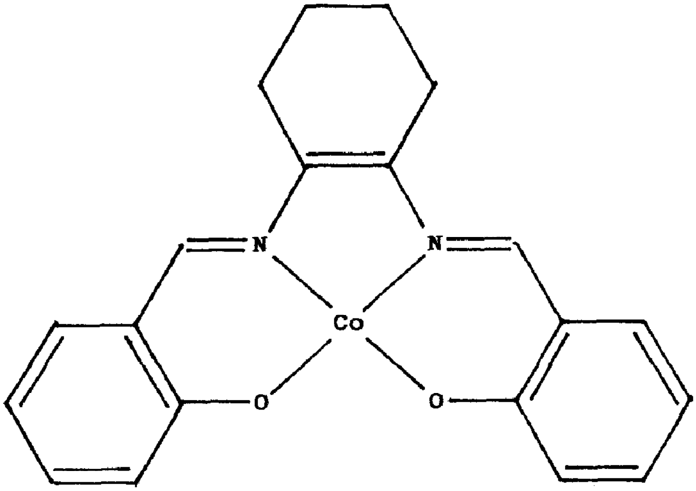
(70; X = O or S)

of μ-peroxo-dicobaloxime(III) in a rapid process followed by (b) its slower disproportionation to μ-superoxo-dicobaloxime(III) and stable cobaloxime(III) and (c) solvolytic decomposition of the μ-peroxo complex to cobaloxime(III) [331].

The previously reported [332] correlation between the sum of the ligand p*K*'s and the equilibrium constants (K_{O_2}) for oxygenation of cobalt(II) complexes has now been shown [333] to result from a combination of entropy and enthalpy terms. Both enthalpies and entropies of oxygenation of complexes having six-membered chelate rings are shown to be less negative (by 50-59 kJ mol^{-1} and 105-125 J K^{-1} mol^{-1}, respectively) than the values for analogous complexes having only five-membered chelate rings.

The IR spectrum of base-free [Co(acacen)(O_2)] has $\nu(O_2)$ at 1146 cm^{-1}, a much lower value than that of [Co(TPP)(O_2)] (1278 cm^{-1}) [334]. This low frequency shift suggests that the negative charge on O_2 increases markedly on going from [Co(TPP)(O_2)] to [Co(acacen)(O_2)]. Both axial (base) and in-plane ligand effects on $\nu(O_2)$ were also noted and discussed.

Cobalt(II) complexes of salicylaldazine, 5,5'-dichlorosalicylaldazine, 3,3'-dimethoxysalicylaldazine and salicylaldehyde hydrazone have been prepared and characterised [335]. The high-spin cobalt(II) complexes form reversible adducts with O_2 in $CHCl_3$ solution containing various bases at room temperature and the EPR spectra have been recorded and discussed. EPR spectra have also been reported for the monomeric oxygen adduct of cobalt(II) salcen (*71*) [336].



(71; Co^{II}salcen)

The oxidation of various substituted phenols by cobalt(II) bis{3-(salicylideneamino)propyl}methylamine has been studied [337]. Coordination of dioxygen to the cobalt(II) complex enhances the ability of dioxygen to abstract hydrogen atoms and to react with phenoxy radicals. The oxidation of ascorbic acid by dioxygen catalysed by cobalt(II) tetrasulphophthalocyanine (CoTSP) has been investigated and two reactive intermediates [O_2.CoTSP.ascorbic acid] and [O_2.CoTSP] detected with absorption bands at 570 nm and 634 nm, respectively [338]. Superoxide, $O_2^{\cdot -}$, may be generated in a cobalt(II)-tetraphenylporphyrin-thiolate-O_2 system [339].

IR spectra of (octaethylporphinato)cobalt(II) and its dioxygen adduct in argon matrices have been studied [340], as have the resonance Raman and IR spectra of O_2 adducts of *N,N'*-ethylenebis(2,2-diacetylethylideneaminato)-cobalt(II) [341].

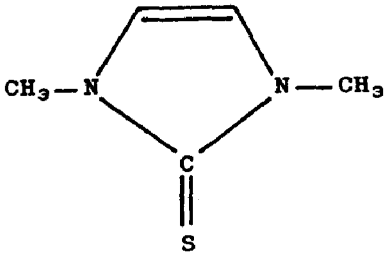
The syntheses of some new ligands containing imidazole donors has been described [342] and the reversible oxygenation of the cobalt(II) complexes studied. A thesis dealing with structural effects on the chemistry of a series of synthetic cobalt(II) oxygen carriers has been published [343]. Photochemical generation of superoxide ions from aqueous solutions of the superoxo complex $[(NC)_5CoO_2Co(CN)_5]^{5-}$ has been described [344].

The synthesis and properties of a binuclear cobalt(II) oxygen adduct with 2,6-bis{bis(2-pyridylmethyl)aminomethyl}-4-methylphenol has been discussed [345]. A thesis deals with the interaction of dioxygen with the axial sites of cobalt(II) complexes of macrocyclic complexes [346], and a useful review dealing (in part) with the interaction of O_2 with macrocyclic cobalt(II) complexes has appeared [347].

Binding of dioxygen to cobalt(II) complexes of polyamino-polyamides derived from 1,5-diamino-3-azapentane and adipic acid has been investigated [348], and a molecular orbital study of dioxygen activation by cyano-complexes of cobalt(II) published [349]. Light induced formation of a reversible dioxygen complex of a cobalt(II) tetraphenylporphyrin at a micellar interface has been studied [350] and mass-spectrometric determinations of the activation energy of thermal deoxygenation of complexes of cobalt with molecular oxygen described [351].

2.2.3 Complexes with sulphur-containing ligands

Complexes of dimethylimidazoline-2-thione {(*72*) = L} have been prepared

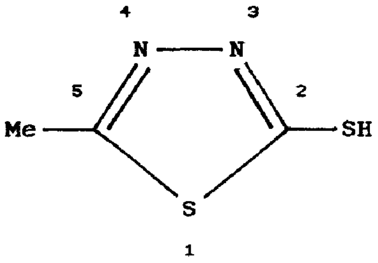


(72)

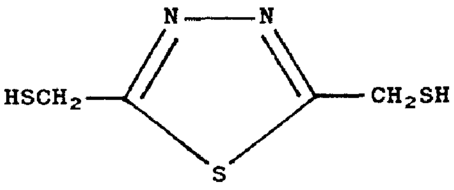
with cobalt(II) having the stoicheiometries ML_4X_2 (X = ClO_4 or NO_3) and ML_2X_2 (X = SCN or NO_3) [352]. Ligand field parameters were derived and the ligand placed in the spectrochemical and nephelauxetic series of heterocyclic thione-*S* donors.

A variety of cobalt(II) complexes with 3-, 4- and 5-methylisothiazoles, L, have been characterised [353]: $[CoL_2X_2]$, $[CoL_4X_2]$ (X = Cl or Br) and $[CoL_6][ClO_4]_2$. The perchlorates are 1:2 electrolytes, while the other complexes are non-electrolytes.

2-Mercapto-5-methyl-1,3,4-thiadiazole (*73*) and 2,5-bis(methylmercapto)-1,3,4-thiadiazole (*74*) complexes of cobalt(II) have been prepared and characterised [354]. The complexes $CoX_2.2L$ (L = mttz, X = Cl, Br or I; L = bmttz, X = Br or I) and $CoCl_2$.bmttz are pseudotetrahedral.



(73; mttz)

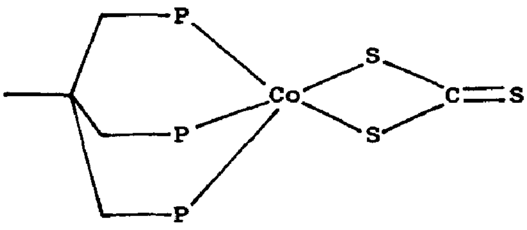


(74; bmttz)

Although the chemistry of iron-sulphide-thiolate clusters $[Fe_nS_n(SR)_4]^{2-,3-}$ (n = 2 or 4; R = alkyl or aryl) has been developed in considerable detail, attempts to prepare analogous cluster species with other transition metal ions have not met with great success. The $[Co_8S_6(SC_6H_5)_8]^{4-}$ system containing an octanuclear $\{Co_8S_6\}$ rhombic dodecahedron related to that of cobalt pentlandite has now been prepared by Holm and coworkers [355]. ^1H NMR studies of the series $[M_4(SPh)_{10}]^{2-}$ {M = Fe(II), Co(II), Zn(II) or Cd(II)} have revealed rapid pyramidal inversion of μ-SPh ligands [356]. The systems $[M_4(SPh)_{10}]^{2-}/[M_4'(SPh)_{10}]^{2-}$ {M/M' = Fe/Co, Co/Zn or Co/Cd} undergo rapid metal exchange leading to mixed-metal species.

The trithiocarbonate complex $[Co(tppme)(S_2CS)]$ (*75*) {tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane} is highly activated towards electrophilic reagents [357]. The uncoordinated sulphur is sufficiently nucleophilic to displace the halide ion from alkyl halides, or weakly bound ligands from other organometallic derivatives, to give sulphur alkylated cations or CS_3-bridged binuclear complexes respectively. The crystal structure of the complex $[Co(tppme)(S_2CSCH_3)][BPh_4]$.1.5 thf has been determined.

The bis(maleonitriledithiolato)cobalt redox series has been studied [358]



(75)

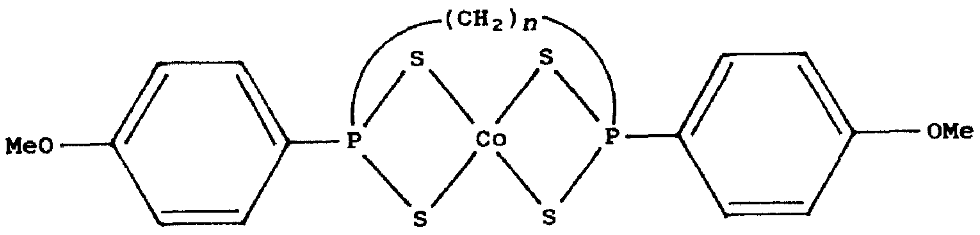
and the syntheses, structure and properties of several bis(*O*,*O'*-dialkyl dithiophosphato)cobalt(II) adducts with amines and phosphines described [359]. Cobalt(II) complexes of thiourea are catalysts for the formation of Schiff bases, and the mechanism of the reaction has been studied [360]. Formation constants have been determined for complexes of cobalt(II) with sulphadiazene [361].

The syntheses of the 1,1-dithiolate cobalt(II) complexes [(triphos)Co{$S_2C(H)PEt_3$}][BPh_4], [(triphos)Co(S_2CO)] and [(triphos)Co(S_2CS)] {triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane} by the reaction of the complex [(triphos)Co(S_2CPEt_3)][BPh_4]$_2$ with nucleophiles has been described [362]. The X-ray structure of [(triphos)Co(S_2CO)] establishes that the cobalt is five-coordinate *via* the three phosphorus atoms of the triphos ligand and by the two sulphur atoms of the dithiocarbonate group in a distorted square-pyramidal stereochemistry. Depending upon the reaction conditions three different complexes, [(triphos)Co(S_2CPEt_3)][BPh_4]$_2$, [(triphos)Co{$S_2C(H)PEt_3$}][BPh_4]$_2$ and [(triphos)Co(μ-CS_2)Co(triphos)][BF_4]$_2$, can be obtained by the reaction of the $Et_3P.CS_2$ adduct with cobalt(II) in the presence of triphos [363].

Crystal structures of interest include bis(1,3-benzothiazole)dichlorocobalt(II) [364], the cobalt(II) complex of (2-mercapto-5-ethyl-3-thenylidene)cyclohexylamine [365] and tetrakis(thiourea)cobalt(II) sulphate methanolate, [Co{$SC(NH_2)_2$}$_4$][SO_4].CH_3OH [366].

Other investigations have included magnetic and spectral studies of mixed ligand complexes of bis(thioformohydroxamato)cobalt(II) with bipy and phen [367], cobalt(II) complexes with benzenecarbothioamides [368] and studies of the reflectance spectra and magnetic properties of cobalt(II) complexes of some thiosemicarbazones [369]. Formation constants have been obtained for binary and ternary complexes of L-cysteine and D-penicillamine with cobalt(II) [370].

Alkali metal or ammonium salts of difunctional dithiophosphonic acids react with cobalt(II) to give complexes of type (*76*), some of which are soluble in organic solvents [371]. The complexes contain tetrahedral {Co*S*$_4$} chromophores. Cobalt(II) reacts with 1,1,1-tris(diphenylphosphinomethyl)ethane

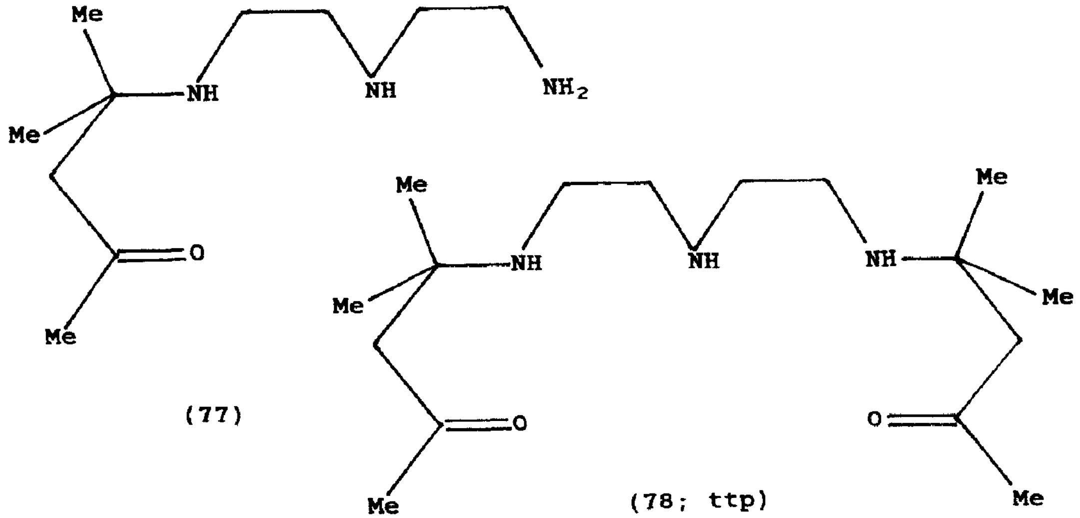


(76; *n* = 4-10)

(L) and HSR (R = Me or H) to give $[LCo(\mu\text{-}SR)_2CoL]^{2+}$ and $[LCo(\mu\text{-}S)_2CoL]^{n+}$ (n = 0, 1 or 2) [372]. Solvent extraction of cobalt(II) using 4-(2-thiazolylazo)resorcinol has been studied [373].

2.2.4 *Complexes with oxygen-nitrogen donor ligands*

The diperchlorate salts of the mono(β-aminoketone) (*77*), (10-amino-4,4-dimethyl-5,8-diazadecan-2-one), and the bis(β-aminoketone) (*78*),



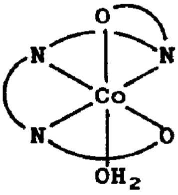
(77)

(78; ttp)

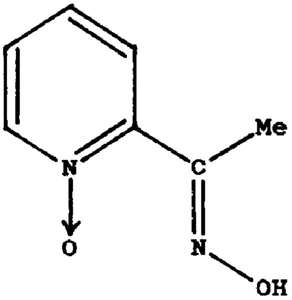
(4,4,12,12-tetramethyl-5,8,11-triazapentadecane-2,14-dione = ttp), have been prepared by reaction of $[dienH_2][ClO_4]_2$ with propanone [374]. The salt $[ttpH_2][ClO_4]_2$ has been used to prepare the six-coordinate $[Co(ttp)(H_2O)][ClO_4]_2.1.5H_2O$; X-ray data establish that this complex has the stereochemistry (*79*).

Complexes of cobalt(II) with 2-acetyl pyridine *N*-oxide oxime {(*80*) = pxo} have been characterised [375]. The ligand behaves as an *O*,*N*-donor *via* the *N*-oxide oxygen and the oxime nitrogen atom. The complex $Co(pxo)Cl_2.CH_3OH$ is antiferromagnetic and thought to be *N*-oxide-bridged.

The complex bis[*N*-(2,6-diisopropylphenyl)salicylideneaminato]cobalt(II) and analogous complexes with substituents at the 5-position of the salicyl

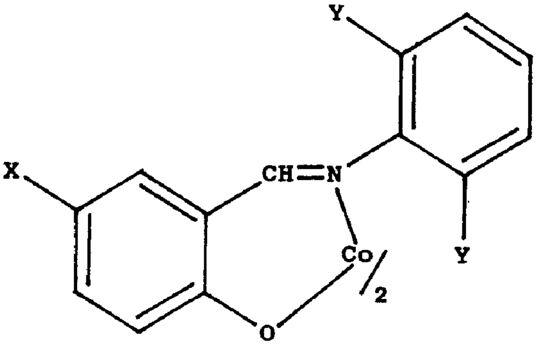


(79)



(80; pxo)

ring, (*81*), have been prepared [376]. In non-donor solvents the complexes are tetracoordinate. In pyridine solvent, five-coordinate species are formed and monopyridine adducts have been isolated.



(81)

Schiff bases of salicylaldehyde and 2-hydroxybenzaldehyde with bulky amines (*t*-butylamine or 2,5-diamino-2,5-dimethylhexane) have been prepared and cobalt(II) complexes characterised [377]; *pseudo*-tetrahedral stereochemistry is observed. Other synthetic studies have dealt with cobalt(II) complexes of *N*,*N*'-bis(aceto-glucose)-1,2-diaminoethane [378], salicylaldimine ligands prepared from the amino sugar 2-amino-2-deoxy-D-glucopyranose and their cobalt(II) complexes [379] and cobalt(II) complexes of formyl hydrazide [380].

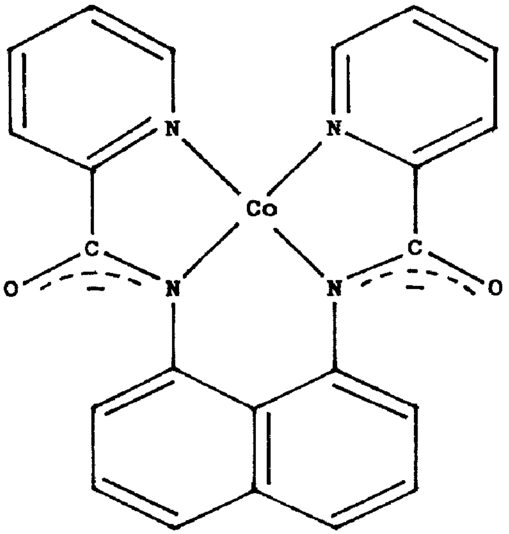
Cobalt(II)-substituted squid hemocyanin has been prepared by dialyzing the apohemocyanin against pH 8.0 tris-HCl buffer containing 5 m*M* cobalt(II) [381]. The spectral characteristics (visible, CD and MCD) of the metallo-protein were also studied. A ^{1}H NMR study of cobalt(II)-substituted carboxypeptidase A provides evidence for two water ligands on five-coordinate cobalt [382].

The structures of 4-coordinate bis(ethanoato)bis(imidazole)cobalt(II) and -zinc(II) and the bis(propanoato) analogues have been determined as models for cobalt(II)-substituted zinc metalloenzymes [383]. The metal-ligand bond distances are virtually identical for cobalt(II) and zinc(II), and distortions from pure tetrahedral stereochemistry appear to be independent of the metal. The same research group have also determined the crystal structures of four bis(alkanecarboxylato)bis(2-alkylimidazole)cobalt(II) complexes and one zinc(II) analogue [384]. Some of the complexes are six-coordinate with bidentate carboxylato ligands, but become four-coordinate on dissolution in ethanol.

The oxidation of $[Co^{II}(edta)]^{2-}$ with $[MnO_4]^-$ has been studied spectrophotometrically [385]. The first step in the oxidation is the rapid formation of $[Co^{III}(edta)(OH_2)]^-$, followed by ring closure to $[Co^{III}(edta)]^-$. The kinetics of the oxidation of cobalt(II) complexes of hedta {*N*-(2-hydroxyethylethylenediaminetetraacetate} and ethylenediaminediacetate by periodate have also been studied [386]. A further kinetic study in this area deals with the oxidation of $[Co^{II}(cdta)]^{2-}$ ($cdta^{4-}$ = *trans*-1,2-diaminocyclohexanetetraacetate) by periodate [387].

Metal exchange reactions between cobalt(II) and lead(II) complexes of nitrilotriacetic acid and copper(II) have been investigated kinetically [388]. The extraction of cobalt(II) with mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one and trioctylamine has been studied [389]. Ternary complex formation between cobalt(II)-bovine carbonic anhydrase and various bidentate ligands such as 2-pyridine carboxylate has been investigated in detail [390].

Deprotonated and non-deprotonated cobalt(II) complexes of the bisamide tetradentate ligand *N,N'*-(dipicolyl)-1,8-napthalenediamine (*82*) have been studied [391] and three different modes of coordination by the ligand observed.



(82)

Studies involving peptide and protein ligands include: cobalt(II)-substituted horseshoe crab hemocyanins [392], spectral studies of cobalt(II)-(and nickel(II)-)metallothionein [393], cobalt(II) binding to D-lactate dehydrogenase [394], stability constants for the interaction of cobalt(II) with reduced glutathione, oxidised glutathione and glycylmethionine [395], metal thiolate clusters in cobalt(II)-metallothionein [396], and the use of X-ray absorption edge spectroscopy to study cobalt(II) binding sites of copper(II)- and zinc(II)-containing proteins [397].

Crystal structures determined include *trans*-tetraaquabis(nicotinamide)cobalt(II) dichloride dihydrate [398], $Ca[Co^{II}(edta)(OH_2)]$ [399] and di-μ-chloro-bis[{bis(methoxyethoxy)ethane}-cobalt(II)] hexachloroantimonate(V) (a complex of "triglyme") [400].

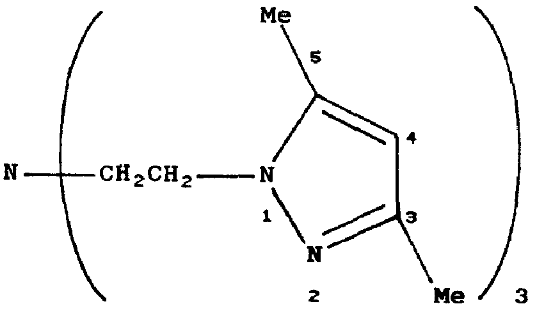
Kinetic studies have included a kinetic investigation of the exchange reaction between cerium(IV)-edta and cobalt(II) [401], the kinetics and mechanism of the peroxodisulphate oxidation of bis(iminodiacetato)cobaltate(II) in aqueous acid [402], and the silver ion-catalysed oxidation of the 1:1 cobalt(II) nitrilotriacetate complex by peroxydisulphate [403].

Other studies have dealt with cobalt(II) complexes of substituted 4-arylazopyrazol-5-ones [404], cobalt(II) chelates of bis(*N*-salicylidene)dicarboxylic acid dihydrazides [405], the use of a cobalt(II) complex as a NMR shift reagent in an undergraduate experiment [406], and cobalt(II) complexes of the following ligands: *N*,*N'*-1,2-phenylenediimine-bis(5-nitrosalicylaldehyde) [407], 5(3)-methylpyrazole-3(5)-carboxamide [408], esters of hydrazine carboxylic acids [409], tridentate Schiff bases derived from salicylaldehyde, substituted salicylaldehydes and 2-hydroxybenzylamine [410] and pyridoxine [411].

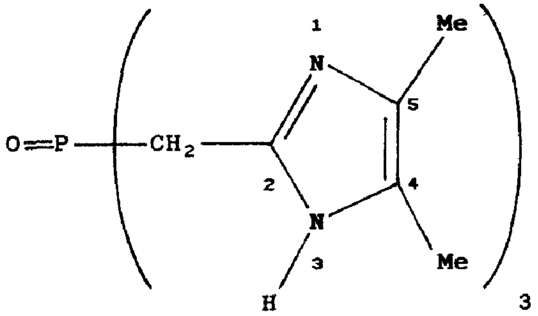
2.2.5 Complexes with nitrogen donor ligands

2.2.5.1 Simple and chelating ligands

The use of polydentate ligands containing pyrazole rings has become fashionable in recent years. The recently synthesised ligand tris(3,5-dimethyl-1-pyrazolyethyl)amine, (*83*, L), is tripod-like containing one apical amine nitrogen and three fairly flexible arms. The cobalt(II) complex $[CoL][BPh_4]_2$ has been characterised, and the ligand synthesis described [412]. Further studies [413] indicate that the cobalt(II) complex has a distorted tetrahedral geometry with the electronic spectra showing *d*-*d* transitions at unusually high energies. The ligand tris[(4,5-dimethyl-2-imidazolyl)methyl]phosphine oxide (*84*) when bound to



(83)

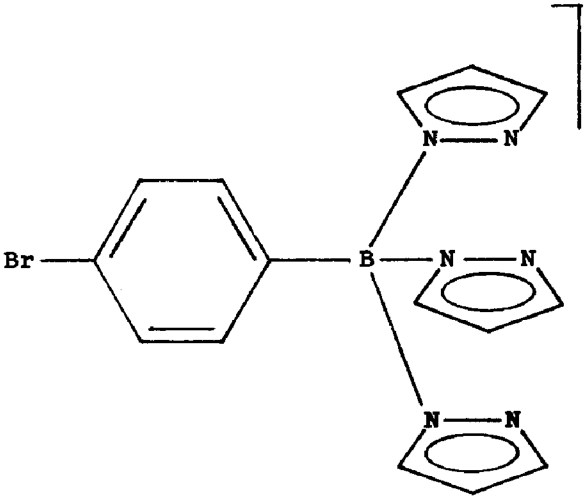


(84)

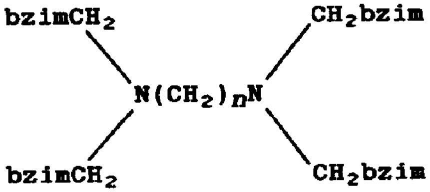
zinc(II) or cobalt(II) displays some properties in common with carbonic anhydrase [414]. Thus, the visible spectrum of the cobalt(II) complex is anion dependent, and in the presence of anions the spectrophotometric pK_a shifts to higher values.

The cobalt(II) complex of (4-bromophenyl)tris(1-pyrazolyl)borate, *(85)*, has been prepared. Conversion of [{4-BrC$_6$H$_4$B(pz)$_3$}$_2$Co$^{\mathrm{II}}$] to the corresponding 4-lithium compound provides a versatile lithium derivative which can be covalently bound to substrates as a paramagnetic shift reagent [415].

A range of *N*,*N*,*N'*,*N'*-tetrakis{2-benz[d]imidazoylmethyl}alkanediamines of the type *(86)* have been prepared, where the alkanediamine is en, 1,2-pn 2-hydroxy-1,3-propanediamine or 1,4-butanediamine [416]. Cobalt(II) gives tetrahedral complexes with these ligands. The natural conformation of the ligand *cis*,*cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexane, (py$_3$)tach, is one in which the nitrogen atoms occupy the vertices of a trigonal prism (if the substituents of the cyclohexane ring occupy axial sites). The cation [Zn{(py)$_3$tach}][ClO$_4$]$_2$ has a slightly tapered trigonal prismatic structure



(85)



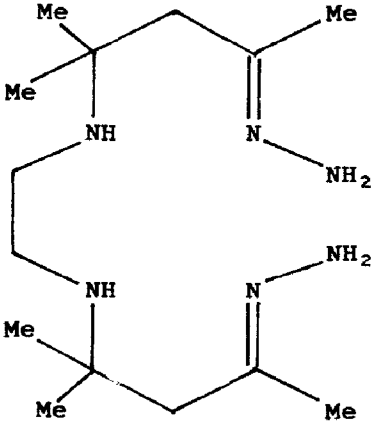
(86)

(in fact the first complex with "innocent" ligands where this type of stereochemistry has been observed). The cobalt(II) complex has now been shown to have approximate trigonal-prismatic stereochemistry in the solid state [417].

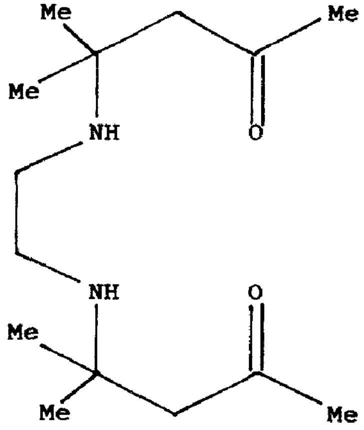
A new class of linear-chain compounds containing the $[SiF_6]^{2-}$ ion as a bridging ligand has been described [418]. The cobalt(II) complex, $Co(viz)_4SiF_6$ (viz = *N*-vinylimidazole), has tetragonal coordination geometry, with four equatorially coordinated *N*-vinylimidazole ligands and two fluorine atoms belonging to different $[SiF_6]^{2-}$ anions. The $[SiF_6]^{2-}$ groups connect the $[Co(viz)_4]^{2+}$ ions by forming strictly linear chains with a sequence -F-Co-F-Si-.

The crystal structure of $[Co(NCS)_2(4\text{-vinylpyridine})_4]$ establishes a *trans*-octahedral stereochemistry with four vinylpyridine ligands arranged in a propellor-shape and two isothiocyanato ligands [419].

The preparation of the new ligand 4,9-dimethyl-5,8-diazadodeca-2,11-dione dihydrazone {amhy = (*87*)} as the dihydroperchlorate salt $[amhyH_2][ClO_4]_2$, and an improved synthesis of the dione precurser, amket (*88*), has been described [420]. The cobalt(II) complex $[Co(amhy)(NO_2)][ClO_4].1\frac{1}{2}\ H_2O$ has been characterised.



(87; amhy)



(88; amket)

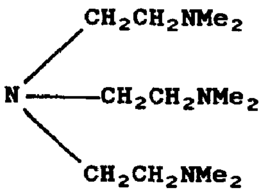
Octahedral high-spin $^4T_1$ and low-spin ^2E states of the d^7 configuration in the complexes $[Co(terpy)_2]X_2.nH_2O$ (X = Cl, Br, I, NO_3 or ClO_4) have been studied [421]. The crystal structure of the high-spin d^7 $[Co(terpy)_2][ClO_4]_2.0.5\ H_2O$ ($\mu_{eff} = 4\ \mu_B$ in the temperature range 4.2-300 K, indicating ≃ 70% of quartet ground states) has been determined [422].

Alkylmercurythiocyanates, RHgSCN, react with $Co(NCS)_2$ to give compounds $(SCN)_2Co(NCSHgR)_2$ (R = C_3H_7 or $CHMe_2$), which are tetrahedral [423]. Pyridine and nicotinamide form adducts of the type $L_2(SCN)_2Co(NCSHgR)_2$. A variety of diisothiocyanodihalocobaltates(II), $[Co(NCS)_2X_2]^{2-}$ (X = Cl, Br or I) have been characterised with the counter cations $[Et_4N]^+$, $[Ph_4As]^+$ or $[Ph_4P]^+$ [424]; the complexes have μ_{eff} values of *ca.* 4.6 μ_B.

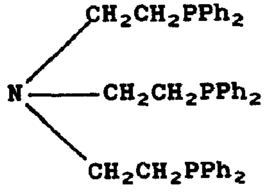
Magnetic susceptibility measurements have been carried out on $Co(2\text{-}MeIm)_2.2H_2O$ (2-MeIm = 2-methylimidazolato) [425]. The room temperature magnetic moment, 3.70 μ_B, is well below the spin only value for high-spin ($S = 3/2$) octahedral cobalt(II) ($\mu_{eff} = 5.10\ \mu_B$) and well above that for low spin octahedral complexes ($S = 1/2$, $\mu_{eff} = 1.86\ \mu_B$). There is a thermally accessible spin state equilibrium from room temperature to 40 K. The EPR spectra of the five-coordinate complexes $[CoX(Me_6tren)]Y$ {Me_6tren = (*89*); X = Cl, Br or I; Y = Cl, Br, I or BPh_4} and $[CoX(np_3)]Y$ {np_3 = (*90*); X = Cl, Br or I; Y = PF_6 or BPh_4} have been recorded [426]. EPR spectra of diaquacobaloxime and dimorpholine cobaloxime in different solvents indicate a strong solvent dependence in the case of aqua-derivative [427].

A spectrophotometric study of the reaction

$$[Co(dmg)_2] + salenH_2 \longrightarrow [Co(salen)] + 2dmgH$$



(89; Me$_6$tren)



(90; np$_3$)

has been reported [428]. At 22 °C (methanol solvent), rate = $k[Co(dmg)_2]$ with $k = 3.8 \times 10^{-4}\ s^{-1}$. Comments on the disproportionation of cobaloxime(II) in basic media have appeared [429]. Reaction (7) was originally discovered

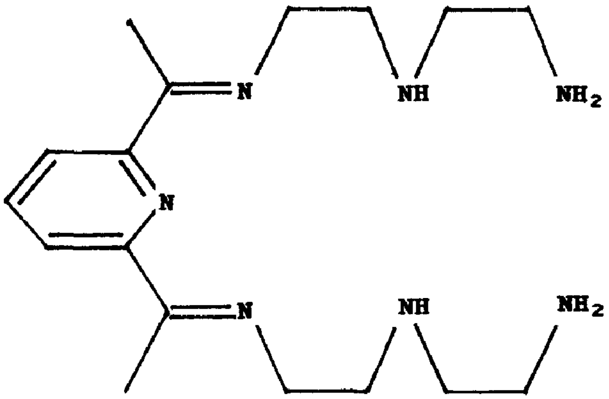
$$2Co^{II}(dmg)_2 + OH^- \longrightarrow Co^{I}(dmg)_2^- + Co^{III}(dmg)_2OH \qquad (7)$$

in 1966 [430] but requires 1 *M* NaOH for the disproportionation to be observed. In addition, cobalt(II) ethanoate rather than the perchlorate salt should be used for the synthesis of diaquacobaloxime(II).

Equilibria of the type shown in equation (8) have been studied using

$$\underset{\text{(tetrahedral)}}{[CoBr_2(R\text{-}py)_2]} + 2R\text{-}py \overset{K}{\rightleftharpoons} \underset{\text{(octahedral)}}{[CoBr_2(R\text{-}py)_4]} \qquad (8)$$

dibromoethane as solvent [431]. Log *K* values are 0.67, 0.11 and 0.53 for 4Me-py, 3Me-py and py, respectively. Electrochemical studies on the pentagonal bipyramidal complex of cobalt(II) with the heptadentate Schiff base ligand (*91*)



(91)

using CH_3CN and dmso solvents indicates stable cobalt(III) and cobalt(I) species [432].

There are little kinetic data on substitution reactions of tetrahedral complexes; the reactions (9) ($\overset{\frown}{N\;\;N}$ = bipy, 4,4'-Me_2bipy or phen; hmpa =

$$[Co(\overset{\frown}{N\;\;N})(hempa)_2]^{2+} + [Cu(hmpa)_4]^{2+} \longrightarrow$$

$$[Co(hmpa)_4]^{2+} + [Cu(\overset{\frown}{N\;\;N})(hmpa)_2]^{2+} \qquad (9)$$

hexamethylphosphoric triamide) have now been studied [433]. Complex formation between cobalt(II) and the linear tetraamines 2,2,2-tet, 2,3,2-tet and 2,4,2-tet has been investigated and enthalpy changes determined [434]. Formation constants of ternary cobalt(II) complexes containing the vitamin B_6 derivative pyridoxamine and 1,2-diaminoethane have also been measured [435].

Cobalt(II) complexes of pyridine-containing copolymers have been observed to catalyse the cross aldol condensations of aldehydes and ketones under neutral conditions in dmf or dmso to give α,β-unsaturated ketones without any biproducts [436].

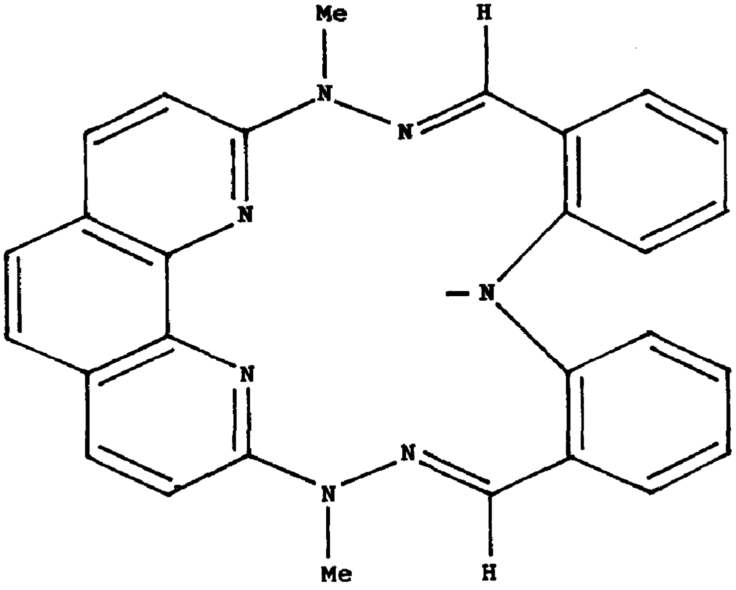
A variety of crystal structures have been published including di-μ-ethanoato-(*O*,*O'*)-μ-aqua-bis{ethanoato(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)cobalt(II)} and μ-aqua-di-μ-chloroethanoato-(*O*,*O'*)-bis{chloroethanoato-(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)cobalt(II)} [437], $Na_2[Co(NCS)_4].8H_2O$ [438], an adduct of thiourea with chloroaquabis(1,10-phenanthroline)cobalt(II) chloride [439] and the nitromethane solvate $[Me_4N]_2[Co(NCS)_4].CH_3NO_2$ [440]. Tetrahedral and octahedral cobalt(II) are observed in the structure of tris(pyridine)(salicylaldehyde S-methylisothiosemicarbazonato)cobalt(II) trichloro(pyridine)cobaltate(II) [441].

Other studies have dealt with complexes of cobalt(II) with substituted benzimidazoles [442], 5(3)-methylpyrazole-3(5)-carbohydrazide [443] and 2- and 4-(1H-pyrazol-1-yl)pyrimidine derivatives [444].

The synthesis and equilibration of octahedral and tetrahedral complexes of cobalt(II) with bis(2-pyridyl)amine has been studied [445] and the solid-state behaviour of heteroligand cobalt(II) thiocyanate complexes investigated [446]. A monobipyridine complex of cobalt(II) nitrate has been studied [447] and cobalt(II) complexes of *syn*-phenyl-2-pyridylketoxime and *syn*-methyl-2-pyridylketoxime characterised [448]. The kinetics of complexing of cobalt(II) with dimethylgloxime in aqueous solution has also been studied [449].

2.2.5.2 Nitrogen macrocycles

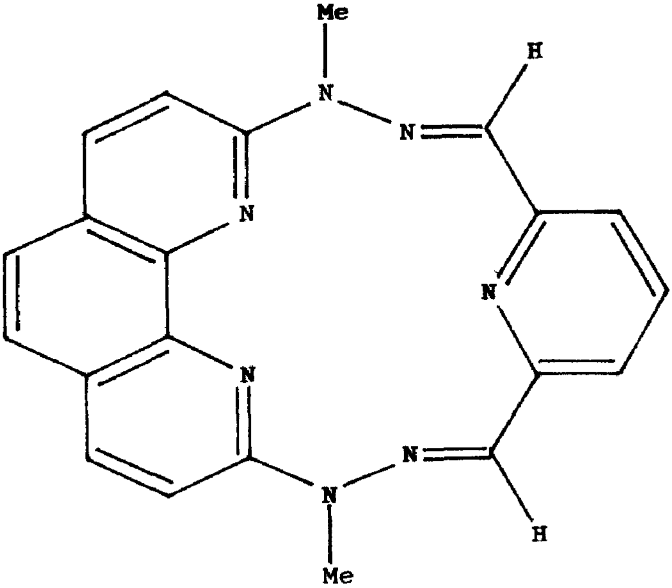
Reaction of 2,2'-iminobisbenzaldehyde with 2,9-di(1-methylhydrazine)-1,10-phenanthroline in the presence of cobalt(II) and pyridine gives the high-spin complex $[CoL(py)_2]^+$ isolated as the $[Ph_4B]^-$ salt {L = (*92*)} [450]. X-ray data confirms a seven-coordinate distorted pentagonal-bipyramidal geometry for the metal ion which is bound equatorially by five nitrogens from the macrocycle and by two axial pyridines. Condensation of 2,9-di(1-methylhydrazino)-1,10-phenanthroline with 2,6-pyridinedicarbaldehyde in the presence of cobalt(II) gives the seven-coordinate complex $[CoL(H_2O)_2]^{2+}$, isolated as the $[SiF_6]^{2-}$ salt {L = (*93*)}. The five nitrogens of the macrocycle and the two axial water molecules give a pentagonal bipyramidal stereochemistry on cobalt(II), confirmed by X-ray analysis [451].



(92)

The synthesis and reactivity of bis(porphyrinato)cobalt(II) complexes linked by a flexible polyatomic chain has been described [452]. "Face-to-face" porphyrin interactions in some of these compounds is indicated by blue- and red-shifted Soret and visible bands respectively.

The interaction of solvents and unidentate ligands (N_3^-, SCN^-, OCN^- and OH^-) with the cobalt(II) {and nickel(II) and copper(II)} complexes of *N*-tetramethylcyclam {tmc = (*94*)} has been studied [453]. The $[Co(tmc)]^{2+}$ complex is pentacoordinate in all the solvents investigated. The $CoOH_2 \rightleftharpoons CoOH + H^+$ interconversion in the two square-pyramidal high-spin cobalt(II) complexes, (*95*) and (*96*), has been investigated by water ^1H NMR T_1^{-1} measurements [454].

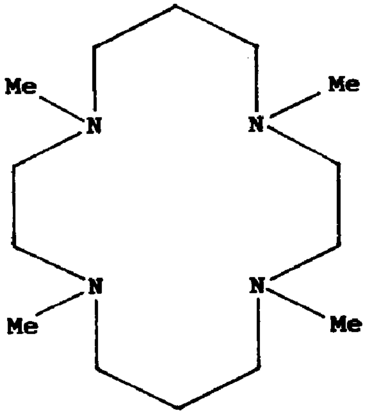


(93)

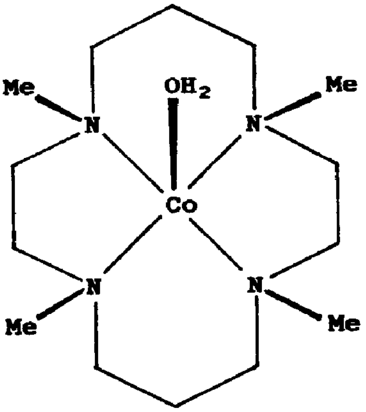
Formation constants for cobalt(II), nickel(II) and copper(II) complexes of the $\{N_2O_2\}$ macrocycles (*97*) have been obtained using 65% ethanol as solvent [455]. For cobalt(II), log*K* = 5.68 (14-membered) and log*K* = 5.23 (16-membered).

Coordination and reduction of NO on cobalt tetraphenylporphyrin anchored to imidazole on SiO_2 has been investigated [456]. Absorbed NO gives a ν(NO) band at *ca.* 1650 cm^{-1}, indicating significant activation of the NO group by back donation to the π^* orbital of the ligand. The coordinated NO is readily reduced by dihydrogen. Axial ligation constants for the reaction of {5,10,15,20-tetrakis(4-methoxyphenyl)porphinato}cobalt(II) with pyridine, piperidine and *N*-methylimidazole in a variety of solvents are nearly constant at room temperature [457]. A positive activation volume (8.0 cm^3 mol^{-1}) for cobalt(II) incorporation into *N*-methyltetraphenylporphine in dmf, obtained by a high-pressure stopped-flow technique, is consistent with a dissociative interchange mechanism [458]. ^{13}C NMR spectra for paramagnetic square-planar, low-spin cobalt(II) tetraphenylporphyrin derivatives confirm the results of an earlier ^1H NMR study which attributed downfield phenyl isotropic shifts to a dipolar mechanism [459]. The reaction of pyridine and associated ligands with cobalt(II) protoporphyrin IX dimethyl ester in alcohols has been studied kinetically [460].

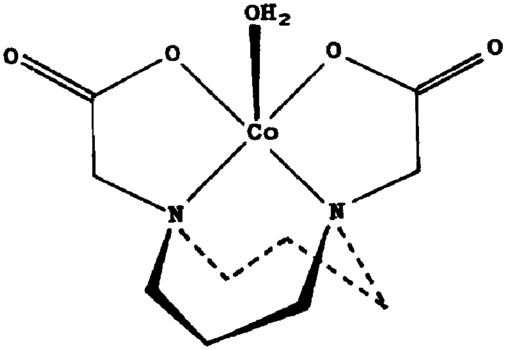
Macrocyclic Schiff base ligands derived from 1,3-diaminobenzene and 1-phenylbutane-1,3-dione, and their complexes with cobalt(II) and other metal ions {nickel(II) and copper(II)}, have been described [461]. Macropolycyclic ligands containing two binding subunits are able to form dinuclear cryptates



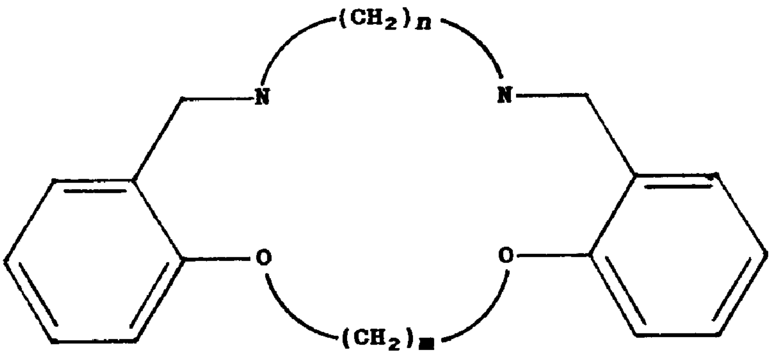
(94)



(95)

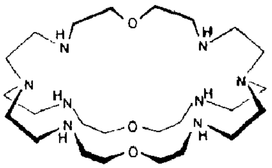


(96)



(97; n = 2 or 3, m = 2 or 3)

by inclusion of two metal cations into the molecular cavity [462]. Binding of cobalt(II) to the bis-tren ligand (*98*) has been studied by potentiometric



(98)

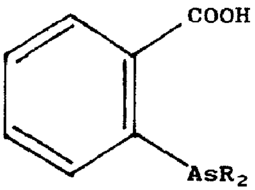
techniques [463], binding of the second cation is weaker than that of the first. The dinuclear cobalt(II) complex was found to combine reversibly with O_2 forming a doubly bridged species containing both hydroxo and peroxo bridges within the cryptate structure.

The synthesis of Baldwin's "capped porphyrins" by the pyrrole-tetraaldehyde condensation route and cobalt(II) {also zinc(II) and iron(II)} complexes of the ligand have now been described in detail [464]. A thesis deals with the guest-host properties of some novel cobalt(II) {and nickel(II)} vaulted macrocyclic host compounds [465].

Other studies have dealt with the synthesis and characterisation of phthalocyaninatocobalt(II) adducts with pyrazine, substituted pyrazines and bipy [466], cobalt(II) complexes of fluoroborato-bridged 14- and 16-membered macrocyclic ligands [467], and the kinetics of complexing of tetraphenylporphine with cobalt(II) ethanoate in mixed organic solvents [468].

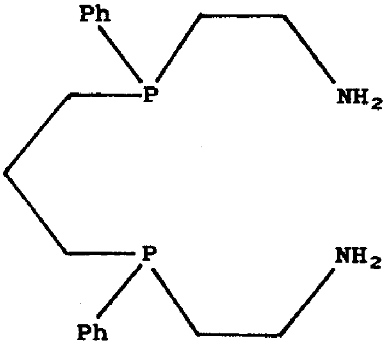
2.2.6 Complexes with Group VB donor ligands

Reactions of the oxygen-arsenic ligands (*99*) with $Co(O_2CMe)_2.4H_2O$ gives



(99; R = Et, cych or C_6H_4-4-Me)

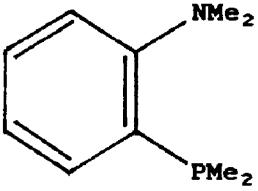
$[Co(2\text{-}R_2AsC_6H_4CO_2)_2]$ with tetrahedral stereochemistry [469]. The five-coordinate complex $[CoCl(3,3,3\text{-}N_2P_2)][BF_4].0.8H_2O$ {3,3,3-N_2P_2 is the linear tetradentate diphosphine diamine (*100*)} has been characterised [470].



(100)

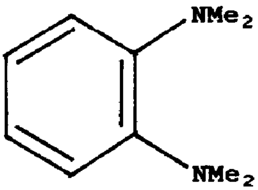
X-ray data indicates a square-pyramidal stereochemistry with the chlorine in the axial site with a *meso* stereochemistry on the chiral phosphorus centres.

Some new 2,6-bis(diphenylphosphinomethyl)pyridine (pnp) complexes of cobalt(II) have been prepared [471]. The penta-coordinated high-spin $Co(pnp)(NO_3)_2$ and the hexa-coordinated low-spin $[Co(pnp)_2][ClO_4]_2$ are described. The ligand 2-dimethylaminophenyldimethylphosphine {(*101*) = L}

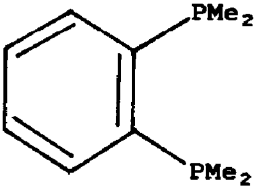


(101)

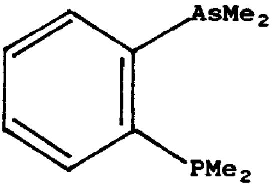
forms pseudotetrahedral $[CoLX_2]$ (X = Cl, Br, I or NCS), low-spin five-coordinate $[CoL_2X][ClO_4]$ (X = Cl, Br or I) and planar $[CoL_2][ClO_4]_2$. The complex $[CoL(NO_3)_2]$ appears to be octahedral [472]. The structurally similar diamine (*102*) gives pseudotetrahedral and octahedral complexes. The ligands (*103*) and (*104*) form only 2:1, L:Co complexes of the types $[CoL_2X][ClO_4]$ and CoL_2X_2, which are low-spin and five-coordinate.



(102)



(103)

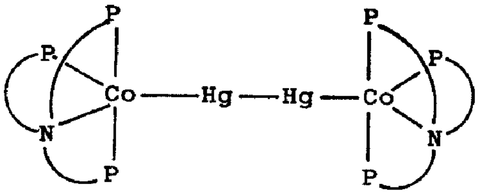


(104)

The ligand 1,8-naphthalenebis(dimethylarsine) (nas) gives the complexes $[Co(nas)_3][CoX_4]$ (X = Cl or Br), $[Co(nas)_3][ClO_4]_2$, $[Co(nas)_2I]I$ and $[Co(nas)_2I][ClO_4]$ [473]. From the temperature dependence of the magnetic susceptibility of $[CoL(NCS)_2]$ (L = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH{=}CHPPh_2$), thermal oxidation of the phosphine ligands is preceded by a structural transition from distorted square-planar to tetrahedral [474].

Reaction of 2-{2-(diphenylphosphino)ethyl}pyridine (L) with CoX_2 in MeCOOH gives CoL_2X_2, where L is bidentate [475]. The crystal structure of {1,1,1-tris(diphenylphosphinomethyl)ethane}(4-toluenesulphinato)cobalt(II) perchlorate, $[(triphos)CoL][ClO_4]$ (L = 4-toluenesulphonate), establishes a distorted square-pyramidal geometry with the sulphonate group acting as a bidentate ligand *via* the two oxygen atoms [476].

The reaction of $[LCoCl][BPh_4]$ {L = $N(CH_2CH_2PPh_2)_3$} with sodium amalgam (50 °C, thf, 40 min) gives the novel complex (*105*), whose structure was confirmed by X-ray crystallography [477]. The dimeric $Hg_2{}^{2+}$ ion forms a linear bridge between the two cobalt atoms.



(105)

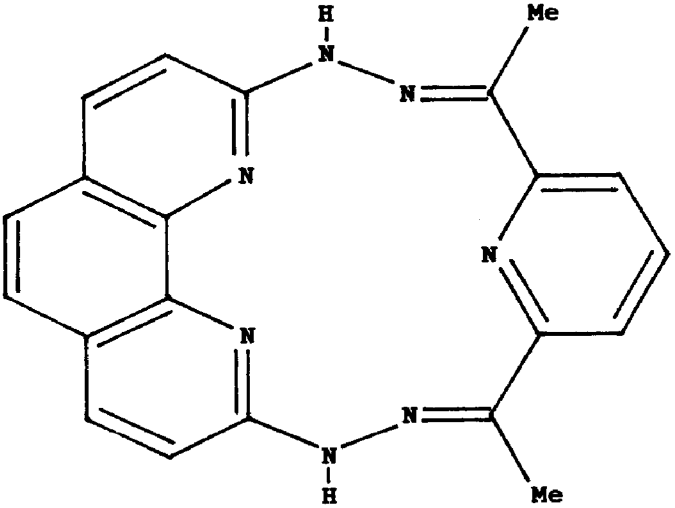
2.3 COBALT(I) AND COBALT(0)

2.3.1 Cobalt(I)

The reactions of 2-(allyloxy)ethyl halides with cobaloxime(I) gives (tetrahydro-3-furanyl)methylcobaloximes *via* an electron transfer from cobaloxime(I) to the halides to give radical anions [478]. Configurational effects in the reaction of cobalt(I) Schiff base complexes with alkyl bromides has been studied kinetically [479]. The electrochemical behaviour of $[Co\{P(OEt)_3\}_2(NO)_2][BPh_4]$ has been studied in ethanenitrile [480]. The complex undergoes two subsequent reduction processes and a single oxidation process. The electrochemistry of bis(2,2'-bipyridine)cobalt(I) and bis(6,6'-dimethyl-2,2'-bipyridine)cobalt(I) in acetonitrile solvent has also been studied [481]. Hydrodimerisation of methyl vinyl ketone is catalysed by cobalt(I)-bipyridine complexes [482].

Carbon dioxide fixation by cobalt(I) complexes [Co(R-salen)M] (R-salen =

substituted salen ligand; M = Li, Na, K or Cs) has been studied [483]. X-ray analysis of [Co(Pr-salen)K(CO_2)(thf)] shows that carbon dioxide is anchored to the cobalt by a Co–C σ bond, while the oxygens interact with the alkali cation in a polymeric structure. The cobalt(I) complex of the macrocyclic ligand (*106*), [Co^I(L){P(OCH_3)$_3$}][BF_4], has been prepared by electrochemical reduction



(106; L)

of [CoL(H_2O)$_2$][BF_4]$_2$ in ethanenitrile in the presence of P(OCH_3)$_3$ [484]. X-ray data establish that the cobalt ion is displaced out of the plane of the five donor nitrogen atoms by 0.36 Å towards the phosphorus ligand.

The reaction of [Co^IBr(PMe_3)$_3$] with ethene in various solvents has been studied [485]. In toluene, propanone and methanol, ethene adds reversibly to the paramagnetic tetrahedral d^8 cobalt(I) complex to give the diamagnetic [CoBr(C_2H_4)(PMe_3)$_3$] species with C_2H_4 and Br in equatorial positions. The crystal structure of [Co(MeCN)(C_2H_4)(PMe_3)$_3$][BPh_4].MeCN establishes a distorted trigonal bipyramid in which MeCN and PMe_3 are axial.

Reduction of [Co(terpy)Cl_2] with Na[BH_4] gives [Co(terpy)(BH_4)] [486]. The cobalt has a distorted tetragonal pyramidal stereochemistry in which the apex and one equatorial site are occupied by bridging hydrides of the bis-chelate [BH_4]$^-$ ligand.

2.3.2 Cobalt(0)

The reaction between cobalt(II) and [CN]$^-$ ions in aqueous solution, under specified conditions, gives a new cobalt(0) cyanogen complex [487]. The ligand CH_3N[P(OCH_3)$_2$] reacts readily with [Co_2(CO)$_8$] to give [{CH_3N[P(OCH_3)$_2$]$_2$}$_2Co_2$(CO)$_4$] with a cobalt-cobalt bond at 2.698 Å [488]. The two cobalt atoms are five-coordinate with identical donor sets, but one is trigonal bipyramidal and the other square pyramidal. The dimer

$[Co_2(CO)_6(Ph_2PCH_2PPh_2)]$ reacts with H_2 to give $[(\mu\text{-}H)(\mu\text{-}PPh_2)Co_2(CO)_4(Ph_2PCH_2PPh_2)]$ [489]. The paramagnetic complexes $[CoL\{P(OR)_3\}_3]$ (L = ethylfumarate and maleic anhydride) have been prepared as potential catalysts [490].

REFERENCES

1 R.W. Hay, *Coord. Chem. Rev.*, 54 (1984) 1.
2 H. Sigel and R.B. Martin, *Chem. Rev.*, 82 (1982) 385.
3 R.D. Peacock and B. Stewart, *Coord. Chem. Rev.*, 46 (1982) 129.
4 C.J. Hawkins and J.A. Palmer, *Coord. Chem. Rev.*, 44 (1982) 1.
5 P. Moore, *Inorg. React. Mech.*, 7 (1981) 200 **(see also refs. 491 and 492)**.
6 A.E. Martell, *Acc. Chem. Res.*, 15 (1982) 155.
7 K.A. Bol'shakov, "Chemistry and Technology of Cobalt", *Chem. Abstr.*, 97, 119589.
8 A. Yamagishi, *Inorg. Chem.*, 21 (1982) 3393.
9 A. Yamagishi, R. Ohnishi and M. Soma, *Chem. Letters*, (1982) 85.
10 A. Vlcek, J. Klima and A.A. Vlcek, *Inorg. Chim. Acta*, 58 (1982) 75.
11 U. Sakaguchi, H. Okazaki and H. Yoneda, *Inorg. Chim. Acta*, 64 (1982) L175.
12 C-W. Young, R.A. Bartsch and R.A. Holwerda, *Inorg. Chim. Acta*, 65 (1982) L79.
13 Y. Nakano and S. Sato, *Inorg. Chem.*, 21 (1982) 1315.
14 Y. Nakano and S. Sato, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1683.
15 J.L. Reed, *Inorg. Chem.*, 21 (1982) 2829.
16 M. Hirayama, Y. Kawamata, Y. Fujii and Y. Nakano, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1798.
17 S. Das, S. Bhattacharya, R.N. Banerjee and D. Banerjea, *Transition Met. Chem.*, 7 (1982) 249.
18 L.S. Bark, M.B. Davies and S.R. Dawson, *Polyhedron*, 1 (1982) 203.
19 P. O'Brien and U. Patel, *J. Chem. Soc. (Dalton)*, (1982) 1407.
20 A.C. Dash, N. Mullick and R.K. Nanda, *Transition Met. Chem.*, 7 (1982) 204.
21 G. Ferraudi, P.A. Grutsch and C. Kutal, *Inorg. Chim. Acta*, 59 (1982) 249.
22 A. Yamagishi and R. Ohnishi, *Inorg. Chem.*, 21 (1982) 4233.
23 S.H. McClaugherty and C.M. Gresham, *Inorg. Chem.*, 21 (1982) 4133.
24 M. Hediger and R.M. Milburn, *J. Inorg. Biochem.*, 16 (1982) 165.
25 Y. Fukuda, M. Ishigi and T. Ito, *Chem. Lett.*, 12 (1981) 1699.
26 P.A. Reyes, U. Angne and R.E. Arriagada, *Bol. Soc. Chil. Quim.*, 27 (1982) 94. *Chem. Abstr.*, 97, 65358.
27 H. Imai, T. Shiraiwa and T. Tai, *Nippon Kagaku Kaishi*, 3 (1982) 408. *Chem. Abstr.*, 96, 227957.
28 M. El-Absy, S. Abdel, G. Marcu and J. Zsako, *Rev. Roum. Chim.*, 26 (1981) 1245. *Chem. Abstr.*, 96, 14572.
29 J.D. Orteggo and M. Seymour, *Polyhedron*, 1 (1982) 21.
30 T. Geiger and F.C. Anson, *J. Am. Chem. Soc.*, 103 (1981) 7489.
31 D.T. Richens and A.G. Sykes, *J. Chem. Soc. (Dalton)*, (1982) 1621.
32 Y. Sasaki, K.Z. Suzuki, A. Matsumoto and K. Saito, *Inorg. Chem.*, 21 (1982) 1825.
33 Y. Sasaki, M. Tachibana and K. Saito, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3651.
34 L.R. Solujic and M.B. Celap, *Inorg. Chim. Acta*, 67 (1982) 103.
35 C.J. Hawkins and M.T. Kelso, *Inorg. Chem.*, 21 (1982) 3681.
36 H. Kawaguchi, M. Ishii, T. Ama and T. Yasui, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3750.
37 J.C. Dabrowiak and M. Tsukayama, *J. Am. Chem. Soc.*, 103 (1981) 7543.
38 S.S. Isied, A. Vasilan and J.M. Lyon, *J. Am. Chem. Soc.*, 104 (1982) 3910.
39 C.R. Clark, R.F. Tasker, D.A. Buckingham, D.R. Knighton, D.R.K. Harding and W.S. Hancock, *J. Am. Chem. Soc.*, 103 (1981) 7023.

40 D.R. Knighton, D.R.K. Harding, M.J. Friar, W.S. Hancock, G.D. Reynolds, C.R. Clark, R.F. Tasker and D.A. Buckingham, *J. Am. Chem. Soc.*, 103 (1981) 7025.

41 M.G. Patch, K.P. Simolo and C.J. Carrano, *Inorg. Chem.*, 21 (1982) 2972.

42 N. Juranic, R.L. Lichter, M.B. Celap, M.J. Malinar and P.N. Radivojsa, *Inorg. Chim. Acta*, 62 (1982) 131.

43 A. Miyanaga, U. Sakaguchi, Y. Morimoto, Y. Kushi and H. Yoneda, *Inorg. Chem.*, 21 (1982) 1387.

44 K. Akamatsu, T. Komorita and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 55 (1982) 140.

45 L.A. Meiske and R.J. Angelici, *Inorg. Chem.*, 21 (1982) 738.

46 L.A. Meiske and R.J. Angelici, *Inorg. Chem.*, 21 (1982) 731.

47 Y. Fuji, Y. Kuwana, S. Takahashi, K. Shimizu and K. Hiroi, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2598.

48 B. Chakravarty, S. Modak, P.K. Das and A.K. Sil, *J. Inorg. Nucl. Chem.*, 43 (1981) 3253.

49 J.P. Costes, G. Cros, M-H. Darbieu and J.P. Laurent, *Inorg. Chim. Acta*, 60 (1982) 111.

50 J.P. Costes, G. Cros, M-H. Darbieu and J.P. Laurent, *Transition Met. Chem.*, 7 (1982) 219.

51 M.H. Darbieu, G. Cros, D. de Montauzon and J.P. Laurent, *Transition Met. Chem.*, 7 (1982) 149.

52 Y. Kushi, T. Tada, Y. Fuji and H. Yoneda, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1834.

53 M. Nakamura, H. Okawa, T. Inazu and S. Kida, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2400.

54 W.M. Coleman and L.T. Taylor, *J. Inorg. Nucl. Chem.*, 43 (1981) 3217.

55 K. Watanabe, *Bull. Chem. Soc. Jpn.*, 55 (1982) 427.

56 K. Watanabe, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2866.

57 K. Akamatsu, T. Komorita and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2390.

58 I. Lukes and I. Smidova, *Inorg. Chim. Acta*, 58 (1982) 95.

59 T. Ama, H. Kawaguchi and T. Yasui, *Kochi Diagaku Rigakubu Kiyo*, *Kagaku* 3 (1982) 1. *Chem. Abstr.*, 97, 137471.

60 M.S. Bilton, *Cryst. Struct. Commun.*, 11 (1982) 101.

61 M.S. Bilton, *Cryst. Struct. Commun.*, 11 (1982) 109.

62 R. Faggiani, C.J.L. Lock and D.R. Eaton, *Cryst. Struct. Commun.*, 10 (1981) 1191.

63 G.C. Mbah, *Diss. Abstr.*, B41 (1980) 2174.

64 R.D. Williams, *Diss. Abstr.*, B42 (1981) 1451.

65 T.J. Wierenga, *Diss. Abstr.*, B42 (1982) 2843.

66 I. Tabushi, K. Seto and Y. Kobuke, *Tetrahedron* 37 (1981) 863.

67 S.A.C. Mestnik and C.P.G. da Silva, Publ. IPEN 1981, IPEN-Publ-39, *Chem. Abstr.*, 97, 48598.

68 M.K. Doh, B.G. Kim and T.S. Cho, *Yongnam Taehakky Nonmunjip*, *Chayon Kwahak Pyon*, 14 (1981) 43. *Chem. Abstr.*, 96, 78908.

69 M. Strasak, F. Bachraty and J. Majer, *Collect. Czech. Chem. Commun.*, 47 (1982) 210.

70 F. Pavelcik and J. Majer, *Collect. Czech. Chem. Commun.*, 47 (1982) 465.

71 A.B. Zegel'man, T.Yu Yusupov and N. Karimov, *Dokl. Akad. Nauk Tadzh. SSR*, 24 (1981) 238. *Chem. Abstr.*, 95, 231080.

72 M.A. Azizov, S.S. Faizieva and A.A. Shabilalov, *Koord. Khim.*, 7 (1981) 1227. *Chem. Abstr.*, 95, 231070.

73 Yu I. Bratushko and N.G. Mel'nikova, *Zh. Neorg. Khim.*, 26 (1981) 3007. *Chem. Abstr.*, 96, 27707.

74 B. Chakravarty and S. Modak, *Indian J. Chem.*, 21A (1982) 480.

75 A. Garnier-Suillerot and J-P. Albertini, *Biochem. Biophys. Res. Commun.*, 102 (1981) 499.

76 J.D. Lydon, R.C. Elder and E. Deutsch, *Inorg. Chem.*, 21 (1982) 3186.

77 J.D. Lydon and E. Deutsch, *Inorg. Chem.*, 21 (1982) 3180.

78 M. Kita, K. Yamanari and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2873.

79 G.J. Gainsford, W.G. Jackson and A.M. Sargeson, *J. Am. Chem. Soc.*, 104 (1982) 137.

80 K. Okamoto, K. Wakayama, H. Einaga, M. Ohmasa and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3473.

81 M. Suzuki, K. Okamoto, H. Einaga and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3929.

82 K. Yamanari and Y. Shimura, *Chemistry Letters*, (1982) 1957.

83 K. Yamanari and Y. Shimura, *Chemistry Letters*, (1982) 1959.

84 K. Okamoto, T. Konno, M. Nomoto, H. Einaga and J. Hidaka, *Chemistry Letters*, (1982) 1941.

85 D.P. Strommen, K. Bajdor, R.S. Czernuszewicz, E.L. Blinn and K. Nakamoto, *Inorg. Chim. Acta*, 63 (1982) 151.

86 R.D. Tiwari, K.K. Pandey and U.C. Agarwala, *Inorg. Chem.*, 21 (1982) 845.

87 T.C. Woon, M.F. Mackay and M.J. O'Connor, *Inorg. Chim. Acta*, 58 (1982) 5.

88 L.R. Gahan and A.M. Sargeson, *Aust. J. Chem.*, 34 (1981) 2499.

89 P. Deplano and E.F. Trogu, *Inorg. Chim. Acta*, 61 (1982) 261.

90 P. Deplano and E.F. Trogu, *Inorg. Chim. Acta*, 61 (1982) 265.

91 T. Konno, K. Okamoto and J. Hidaka, *Chemistry Letters*, (1982) 535.

92 V.H. Houlding, H. Mäcke and A.W. Adamson, *Inorg. Chem.*, 20 (1981) 4279.

93 K. Nakajima, M. Kojima and J. Fujita, *Chemistry Letters*, (1982) 925.

94 M.E. Rusanovskii, I.D. Samus and N.M. Samus, *Dokl. Akad. Nauk SSSR*, 260 (1981) 98. *Chem. Abstr.*, 95, 213383.

95 R.J. Balahura, G. Ferguson, L. Ecott and P.Y. Siew, *J. Chem. Soc. (Dalton)*, (1982) 747.

96 W.C. Kupferschmidt and R.B. Jordan, *Inorg. Chem.*, 21 (1982) 2089.

97 K. Koshy and T.P. Dasgupta, *Inorg. Chim. Acta*, 61 (1982) 207.

98 R. van Eldik, J. von Jouanne and H. Kelm, *Inorg. Chem.*, 21 (1982) 2818.

99 See for example R. van Eldik, D.A. Palmer, H. Kelm and G.M. Harris, *Inorg. Chem.*, 19 (1980) 3679.

100 J.L. Laird and R.B. Jordan, *Inorg. Chem.*, 21 (1982) 855.

101 U. Spitzer, R. van Eldik and H. Kelm, *Inorg. Chem.*, 21 (1981) 2821.

102 R.A. Holwerda and J.D. Clemmer, *Inorg. Chem.*, 21 (1982) 2103.

103 T.J. Wierenga and J.I. Legg, *Inorg. Chem.*, 21 (1982) 2881.

104 W.G. Finnegan, R.A. Henry and R. Lofquist, *J. Am. Chem. Soc.*, 80 (1958) 3908.

105 See for example R.J. Balahura, P. Cock and W.L. Purcell, *J. Am. Chem. Soc.*, 96 (1974) 2739.

106 See for example D.G. Butler, I.I. Creaser, S.F. Dyke and A.M. Sargeson, *Acta Chem. Scand. Ser. A*, 32 (1978) 789.

107 W.R. Ellis Jr. and W.L. Purcell, *Inorg. Chem.*, 21 (1982) 834.

108 Y. Yamamoto, H. Kudo, M. Mori and H. Konno, *Bull. Chem. Soc. Jpn.*, 55 (1982) 136.

109 K. Kanamori and K. Kawai, *Bull. Chem. Soc. Jpn.*, 55 (1982) **764**.

110 K. Yamanari, S. Naito and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 54 (1981) 3780.

111 N.S. Rowan, C.B. Storm and R. Rowan, *J. Inorg. Biochem.*, 14 (1981) 59.

112 R.J. Balahura and W.L. Purcell, *Inorg. Chem.*, 20 (1981) 4159.

113 D.A. Buckingham and C.R. Clark, *Aust. J. Chem.*, 35 (1982) 431.

114 U. Spitzer and R. van Eldik, *Inorg. Chem.*, 21 (1982) 4008.

115 V.S. Srinivasan, A.N. Singh, K. Wieghardt, N. Rajasekar and E.S. Gould, *Inorg. Chem.*, 21 (1982) 2531.

116 V.S. Srinivasan, N. Rajesekar, A.N. Singh, C.A. Radlowski, J.C-K Heh and E.S. Gould, *Inorg. Chem.*, 21 (1982) 2824.

117 J.H. Espenson, M. Shimura and A. Bakac, *Inorg. Chem.*, 21 (1982) 2537.

118 H. Cohen, M. Nutkovich, D. Meyerstein and K. Wieghardt, *J. Chem. Soc. (Dalton)*, (1982) 943.

119 R. van Eldik, *Inorg. Chem.*, 21 (1982) 2501.

120 R.D. Williams, D.E. Pennington and W.B. Smith, *Inorg. Chim. Acta*, 58 (1982) 45.

121 G. Daramola, J.F. Ojo, O. Olubuyide and F. Oriaifo, *J. Chem. Soc. (Dalton)*, (1982) 2137.

122 A.P. Szecsy and A. Haim, *J. Am. Chem. Soc.*, 104 (1982) 3063.

123 A.J. Miralles, A.P. Szecsy and A. Haim, *Inorg. Chem.*, 21 (1982) 697.

124 J.F. Ojo, A.O. Ojudun and O.A. Olubuyide, *J. Chem. Soc. (Dalton)*, (1982) 659.

125 V. Srinivasan, S.W. Barr and M.J. Weaver, *Inorg. Chem.*, 21 (1982) 3154.

126 W.G. Jackson, G.A. Lawrance, P.A. Lay and A.M. Sargeson, *Aust. J. Chem.*, 35 (1982) 1561.

127 R. van Eldik and G.M. Harris, *Inorg. Chim. Acta*, 65 (1982) L125.

128 H. Ghazi-Bajat, R. van Eldik and H. Kelm, *Inorg. Chim. Acta*, 60 (1982) 81.

129 G.A. Lawrance, *Inorg. Chem.*, 21 (1982) 3687.

130 N.E. Dixon, W.G. Jackson, W. Marty and A.M. Sargeson, *Inorg. Chem.*, 21 (1982) 688.

131 D.A. Buckingham, C.R. Clark and W.S. Webley, *Inorg. Chem.*, 21 (1982) 3353.

132 A. Dhur, S. Das, R.N. Banerjee and D. Banerjea, *Transition Met. Chem.*, 7 (1982) 125.

133 A.C. Dash and G.M. Harris, *Inorg. Chem.*, 21 (1982) 2336.

134 A.C. Dash and G.M. Harris, *Inorg. Chem.*, 21 (1982) 1265.

135 M. Iida, M. Ando and H. Yamatera, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1441.

136 S.S. Isied, J. Lyon and A. Vassilian, *Int. J. Pept. Protein Res.*, 19 (1982) 354. *Chem. Abstr.*, 97, 110374.

137 S.S. Isied, J. Lyon and A. Vassilian, *J. Liq. Chromatogr.*, 5 (1982) 537.

138 X. Solans, J. Rius and C. Miravitlles, *Z. Kristallogr.*, 157 (1981) 207. *Chem. Abstr.*, 96, 77956.

139 W.P. Schaefer, S.E. Ealick and D. Finley, *Acta Crystallogr.*, B38 (1982) 2232.

140 U. Thewalt, *Z. Anorg. Allg. Chem.*, 485 (1982) 122. *Chem. Abstr.*, 96, 208776.

141 S. Ohba, Y. Saito and S. Fujinami, *Acta Crystallogr.*, B38 (1982) 1305.

142 E.J. Rose, *Diss. Abstr.*, B41 (1981) 3461.

143 Y. Yamamoto and E. Toyota, *Chem. Pharm. Bull.*, 30 (1982) 2262. *Chem. Abstr.*, 97, 137636.

144 D.A. Buckingham and C.R. Clark, *Aust. J. Chem.*, 34 (1981) 1769.

145 N.M. **Guindy**, S.A. Selim and E.N. Rizhalla, *Egypt J. Chem.*, 23 (1981) 389.

146 R.K. Nanda and N.K. Mohanty, *Indian J. Chem.*, 21A (1982) 522.

147 N. Ise, T. Okubo and Y. Yamamura, *J. Phys. Chem.*, 86 (1982) 1694.

148 V. Holba and M. Talapka, *Chem. Zvesti*, 35 (1981) 447. *Chem. Abstr.*, 95, 176502.

149 A.M. Greenaway and R.J. Lancashire, *J. Chem. Educ.*, 59 (1982) 419.

150 A. Olexova and L. Treindl, *Chem. Zvesti.*, 35 (1981) 605. *Chem. Abstr.*, 96, 41622.

151 W. Rindermann and R. van Eldik, *Inorg. Chim. Acta*, 64 (1982) L203.

152 P.D. Ford, K.B. Nolan and D.C. Povey, *Inorg. Chim. Acta*, 61 (1982) 189.

153 D.A. Buckingham, C.R. Clark, B.M. Foxman, G.J. Gainsford, A.M. Sargeson, M. Wein and A. Zanella, *Inorg. Chem.*, 21 (1982) 1986.

154 R.W. Hay and K.B. Nolan, *J. Chem. Soc. (Dalton)*, (1974) 914.

155 M. Nakashima and S. Kida, *Bull. Chem. Soc. Jpn.*, 55 (1982) 809.

156 P. Natarajan and A. Radhakrishnan, *J. Chem. Soc. (Dalton)*, (1982) 2403.

157 W. Rindermann, R. van Eldik and H. Kelm, *Inorg. Chim. Acta*, 61 (1982) 173.

158 W.G. Jackson and C.M. Begbie, *Inorg. Chim. Acta*, 61 (1982) 167.

159 R. van Eldik and H. Kelm, *Inorg. Chim. Acta*, 60 (1982) 177.

160 B. Chakravarty and P.K. Das, *Transition Met. Chem.*, 7 (1982) 340.

161 R. Tsuchiya, A. Uehara and Y. Muramatsu, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3770.

162 K. Matsumoto, S. Ooi, H. Kawaguchi, M. Nakano and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1840.

163 K. Kurotaki and S. Kawamura, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1947.

164 M. Fujita, Y. Yoshikawa and H. Yamatera, *Chemistry Letters*, (1982) 437.

165 S. Kaki, K. Yamanari and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 55 (1982) 769.

166 A. Fuyuhiro, K. Yamanari and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 55 (1982) 775.
167 T.W. Hambley, C.J. Hawkins, J. Martin, J.A. Palmer and M.R. Snow, *Aust. J. Chem.*, 34 (1981) 2505.
168 T.W. Hambley, C.J. Hawkins, J.A. Palmer and M.R. Snow, *Aust. J. Chem.*, 34 (1981) 2525.
169 C.J. Hawkins, R.H. Holm, J.A. Palmer and D.D. Traficante, *Aust. J. Chem.*, 35 (1982) 1815.
170 C.J. Hawkins and J. Martin, *Inorg. Chem.*, 21 (1982) 1074.
171 H. Nakazawa, U. Sakaguchi and H. Yoneda, *J. Am. Chem. Soc.*, 104 (1982) 3885.
172 U. Sakaguchi, H. Nakazawa, K. Sakai and H. Yoneda, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1862.
173 K. Yoneda, K. Miyoshi and H. Matsukawa, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1969.
174 E.N. Duesler and M. Gargallo, *Acta Crystallogr.*, B38 (1982) 1300.
175 M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1454.
176 D.R. Jones, L.F. Lindoy, A.M. Sargeson and M.R. Snow, *Inorg. Chem.*, 21 (1982) 4155.
177 K. Ito, E. Ewamoto and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3190.
178 G.J. Gainsford, D.A. House, W. Marty and P. Comba, *Cryst. Struct. Commun.*, 11 (1982) 215.
179 P.C. Healy, C.H.L. Kennard and G. Smith, *Cryst. Struct. Commun.*, 10 (1981) 883.
180 M.J. Malinar, R. Herak and M.B. Celap, *Glas. Hem. Drus, Beograd.*, 46 (1981) 303. *Chem. Abstr.*, 96, 62083.
181 F. Bigoli, M. Lanfranchi and E. Leporati, *Cryst. Struct. Commun.*, 10 (1981) 1445.
182 K. Dutta and G.S. De, *Indian J. Chem.*, 21A (1982) 477.
183 J. Zsako, C. Varhelyi and S. Magyarosi, *Stud. Univ. Babes-Bolyai, (Ser.) Chem.*, 26 (1981) 52. *Chem. Abstr.*, 96, 223976.
184 G.S. Groves and C.F. Wells, *J. Chem. Soc., Faraday Trans.*, 78 (1982) 619.
185 A.C. Dash and M.S. Dash, *Indian J. Chem.*, 21A (1982) 224.
186 R.O. Torovic and M.B. Celap, *Glas. Hem. Drus. Beograd.*, 47 (1982) 55. *Chem. Abstr.*, 96, 187918.
187 M. Muto and C. Nakao, *Acta Chem. Scand.*, A36 (1982) 89.
188 I. Jitaru, M. Dinculescu and C. Ruva, *Rev. Chim. (Bucharest)*, 32 (1981) 639. *Chem. Abstr.*, 96, 62079.
189 A. Syamal and P.K. Mandal, *Rev. Roum. Chim.*, 26 (1981) 1431. *Chem. Abstr.*, 97, 48577.
190 A.L. Poznjak and V.I. Pawlowski, *Z. Anorg. Allg. Chem.*, 485 (1982) 225. *Chem. Abstr.*, 97, 82564.
191 S.R. Niketic and K. Rasmussen, *Acta Chem. Scand.*, A35 (1981) 623.
192 Y. Morimoto, *J. Sci. Hiroshima Univ., Ser. A; Phys. Chem.*, 45 (1981) 173. *Chem. Abstr.*, 96, 45103.
193 S. Utsuno, *J. Am. Chem. Soc.*, 104 (1982) 5846.
194 E.C. Niederhoffer, A.E. Martell, P. Rudolf and A. Clearfield, *Inorg. Chem.*, 21 (1982) 3734.
195 J.F. Glenister, K.E. Hyde and G. Davies, *Inorg. Chem.*, 21 (1982) 2331.
196 D.A. House and W. Marty, *Inorg. Chim. Acta*, 65 (1982) L47.
197 Y. Kitamura, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3625.
198 C.N. Elgy and C.F. Wells, *J. Chem. Soc. (Dalton)*, (1982) 1617.
199 M. Sato, Y. Sato, S. Yano, S. Yoshikawa, K. Toriumi, H. Itoh and T. Itoh, *Inorg. Chem.*, 21 (1982) 2360.
200 K. Henrick, M. McPartlin, S. Munjoma, P.G. Owston, R. Peters, S.A. Sangoklya and P.A. Tasker, *J. Chem. Soc. (Dalton)*, (1982) 225.
201 D.A. House, A.R. Gainsford and J.W. Blunt, *Inorg. Chim. Acta*, 57 (1982) 141.
202 A.K. Banerjee, A. Misra, A.K. Basak and D. Banerjea, *Transition Met. Chem.*, 7 (1982) 239.

203 T.W. Hambley and G.H. Searle, *Aust. J. Chem.*, 35 (1982) 1285.

204 G.H. Searle and T.W. Hambley, *Aust. J. Chem.*, 35 (1982) 1297.

205 G.H. Searle and T.W. Hambley, *Aust. J. Chem.*, 35 (1982) 2399.

206 D.A. Buckingham, J.D. Edwards and G. McLaughlin, *Inorg. Chem.*, 21 (1982) 2770.

207 G.R. Brukaker and D.W. Johnson, *Inorg. Chem.*, 21 (1982) 2223.

208 G.R. Brukaker and D.W. Johnson, *Inorg. Chim. Acta*, 62 (1982) 141.

209 R. Job, P.J. Kelleher, W.C. Stallings, C.T. Monti and J.P. Glusker, *Inorg. Chem.*, 21 (1982) 3760.

210 A.A. El-Awady and G.M. Harris, *Inorg. Chem.*, 20 (1981) 4251.

211 N.K. Mohanty and R.K. Nanda, *Transition Met. Chem.*, 7 (1982) 202.

212 A.C. Dash, R.K. Nanda and N. Ray, *J. Coord. Chem.*, 11 (1982) 213.

213 G. Daftner, D.A. Palmer and H. Kelm, *Inorg. Chim. Acta*, 61 (1982) 57.

214 M. Yamaguchi, Y. Masui, M. **Saburi** and S. Yoshikawa, *Inorg. Chem.*, 21 (1982) 4138.

215 N.W. Alcock, M.P. Atkins, B.T. Golding and P.J. Sellars, *J. Chem. Soc. (Dalton)*, (1982) 337.

216 N. Bresciani-Pahor, G. Nardin, L.L. Randaccio and E. Zangrando, *Inorg. Chim. Acta*, 65 (1982) L143.

217 S.B. Ferguson and M.C. Baird, *Inorg. Chim. Acta*, 63 (1982) 41.

218 S. Alvarez and C. Lopez, *Inorg. Chim. Acta*, 63 (1982) 57.

219 Y. Ohashi, K. Yanagi, T. Kurihara, Y. Sasada and Y. Ohgo, *J. Am. Chem. Soc.*, 104 (1982) 6353.

220 S. Alvarez and C. Lopez, *Inorg. Chim. Acta*, 64 (1982) L99.

221 L.M. Mihichuk, M.J. Mombourquette, F.W.B. Einstein and A.C. Willis, *Inorg. Chim. Acta*, 63 (1982) 189.

222 N. Bresciani-Pahor, M. Calligaris, L. Randaccio and P.J. Toscano, *J. Chem. Soc. (Dalton)*, (1982) 1009.

223 N. Bresciani-Pahor, L. Randaccio, P.J. Toscano and L.G. Marzilli, *J. Chem. Soc. (Dalton)*, (1982) 567.

224 N. Bresciani-Pahor, M. Calligaris, G. Nardin and L. Randaccio, *J. Chem. Soc. (Dalton)*, (1982) 2549.

225 N. Bresciani-Pahor, L. Randaccio, P.G. Toscano, A.C. Sandercock and L.G. Marzilli, *J. Chem. Soc. (Dalton)*, (1982) 129.

226 M. Van Hooste, A.T.H. Lenstra, M. Kwiecinski and S. Tyrlik, *Transition Met. Chem.*, 7 (1982) 50.

227 K.L. Brown and E. Zohonyi-Budo, *J. Am. Chem. Soc.*, 104 (1982) 4117.

228 J.H. Dimmit and J.H. Weber, *Inorg. Chem.*, 21 (1982) 700.

229 J.H. Dimmit and J.H. Weber, *Inorg. Chem.*, 21 (1982) 1554.

230 K.L. Brown and L-Y. Lu, *Inorg. Chem.*, 20 (1981) 4178.

231 S. Tyrlik, M. Kwiecinski, A. Rockbauer and M. Gyor, *J. Coord. Chem.*, 11 (1982) 205.

232 D. Borchardt, K. Pool and S. Wherland, *Inorg. Chem.*, 21 (1982) 93.

233 F. Abraham, C. Bremard, B. Mouchel, G. Nowogrocki and S. Sueur, *Inorg. Chem.*, 21 (1982) 3225.

234 J. Charalambous, G. Soobramanien, A. Betts and J. Bailey, *Inorg. Chim. Acta*, 60 (1982) 151.

235 J.H. Grate, J.W. Grate and G.N. Schrauzer, *J. Am. Chem. Soc.*, 104 (1982) 1588.

236 K.A. Rubinson, E. Itabashi and H.B. Mark, *Inorg. Chem.*, 21 (1982) 3571.

237 K.L. Brown and J.M. Hakimi, *Inorg. Chim. Acta*, 67 (1982) L29.

238 W.A. Mulac and D. Meyerstein, *J. Am. Chem. Soc.*, 104 (1982) 4124.

239 Y-T. Fanchiang, *Inorg. Chem.*, 21 (1982) 2344.

240 T-T. Tsou, M. Loots and J. Halpern, *J. Am. Chem. Soc.*, 104 (1982) 623.

241 D. Dolphin, D.J. Halko and E. Johnson, *Inorg. Chem.*, 20 (1981) 4348.

242 L.G. Marzilli and P.J. Toscano, *Adv. Chem. Ser.*, 196 (1982) 85-99.

243 R.R. Whittle, *Diss. Abstr.*, B42 (1981) 1884.

244 M. Brezeanu, I. Jitaru and M. Dinculescu, *Rev. Roum. Chim.*, 26 (1981) 1097. *Chem. Abstr.*, 96, 62131.

245 P.N. Balasubramanian and V.R. Vijayaraghaven, *Indian J. Chem.*, 20A (1981) 892. *Chem. Abstr.*, 96, 58543.

246 J. Korvenranta, H. Saarinen and T. Raikas, *Finn. Chem. Lett.*, 3-4 (1981) 29. *Chem. Abstr.*, 95, 179116.

247 G.N. Schrauzer, J.W. Grate, A. Maihub and H.B. Xu, *Z. Naturforsch B. Anorg. Chem. Org. Chem.*, 36B (1981) 1338.

248 K.L. Brown and S. Ramamurthy, *Organometallics*, 1 (1982) 413.

249 H.B. Gjerde and J.H. Espenson, *Organometallics*, 1 (1982) 435.

250 W.W. Reinstra, R.H. Abeles and W.P. Jencks, *J. Am. Chem. Soc.*, 104 (1982) 1016.

251 M.M. Botoshanski, Yu.A. Simonov and O.A. Bologa, *Zh. Strukt. Khim.*, 22 (1981) 132. *Chem. Abstr.*, 96, 77876.

252 J.H. Grate, *Diss. Abstr.*, B42 (1981) 623.

253 I.I. Creaser, R.J. Geue, J.MacB. Harrowfield, A.J. Herlt, A.M. Sargeson, M.R. Snow and J. Springborg, *J. Am. Chem. Soc.*, 104 (1982) 6016.

254 L.R. Gahan, G.A. Lawrance and A.M. Sargeson, *Aust. J. Chem.*, 35 (1982) 1119.

255 R.W. Hay, R. Bembi, W.T. Moodie and P.R. Norman, *J. Chem. Soc. (Dalton)*, (1982) 2131.

256 G. Bombieri, E. Forsellini, A. Del Pra, C.J. Cooksey, M. Humanes and M.L. Tobe, *Inorg. Chim. Acta*, 61 (1982) 43.

257 R.W. Hay and R. Bembi, *Inorg. Chim. Acta*, 64 (1982) L199.

258 R.W. Hay and R. Bembi, *Inorg. Chim. Acta*, 64 (1982) L179.

259 L.R. Gahan, T.W. Hambley, A.M. Sargeson and M.R. Snow, *Inorg. Chem.*, 21 (1982) 2699.

260 K. Wieghardt, P. Chaudhuri, B. Nuber and J. Weiss, *Inorg. Chem.*, 21 (1982) 3086.

261 D.J. Royer, G.J. Grant, D.G. van Derveer and M.J. Castillo, *Inorg. Chem.*, 21 (1982) 1902.

262 (a) Y. Yoshikawa, *Chem. Lett.*, (1978) 109.
(b) R.W. Hay, B. Jeragh, S.F. Lincoln and G.H. Searle, *Inorg. Nucl. Chem. Lett.*, 14 (1978) 435.

263 R.W. Hay, R. Bembi, K. Hideg and O. Hankovszky, *Inorg. Chim. Acta*, 64 (1982) L133.

264 V.B. Rana, P. Singh, D.P. Singh and M.P. Teotia, *Transition Met. Chem.*, 7 (1982) 174.

265 M. Nonoyama and O. Hirai, *Inorg. Chim. Acta*, 54 (1981) L283.

266 R.W. Hay and R. Bembi, *Inorg. Chim. Acta*, 65 (1982) L207.

267 A.R. Battersby and Z-C. Sheng, *J. Chem. Soc., Chem. Commun.*, (1982) 1393.

268 K. Tsukahara, T. Izumitani and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, 55 (1982) 130.

269 P.R. Norman and R.D. Cornelius, *J. Am. Chem. Soc.*, 104 (1982) 2356.

270 R.D. Cornelius and P.R. Norman, *Inorg. Chim. Acta*, 65 (1982) L193.

271 J.F. Endicott, B. Durham and K. Kumar, *Inorg. Chem.*, 21 (1982) 2437.

272 F.P. Rotzinger, K. Kumar and J.F. Endicott, *Inorg. Chem.*, 21 (1982) 4111.

273 T.G. Hoon and C.Y. Mok, *Inorg. Chim. Acta*, 62 (1982) 231.

274 J. Huet, A. Gaudemer, C. Boucly-Goester and P. Boucly, *Inorg. Chem.*, 21 (1982) 3413.

275 K. Nishimoto and E. Kai, *Inorg. Chim. Acta*, 58 (1981) 107.

276 S. Funahashi, M. Inamo, K. Ishihara and M. Tanaka, *Inorg. Chem.*, 21 (1982) 447.

277 R.D. Chapman and E.B. Fleischer, *J. Am. Chem. Soc.*, 104 (1982) 1575.

278 R.D. Chapman and E.B. Fleischer, *J. Am. Chem. Soc.*, 104 (1982) 1582.

279 Y. Yoshikawa, K. Toriumi, T. Ito and H. Yamatera, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1422.

280 S. Fujinami, Y. Matsunami and M. Shibata, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2101.

281 K. Tsukahara, H. Oshita, Y. Emoto and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2107.

282 T. Sakurai, K. Kobayashi and A. Hasegawa, *Acta Crystallogr.*, B38 (1982) 107.

283 H. Masuda, T. Taga and K. Osaki, *Bull. Chem. Soc. Jpn.*, 55 (1982) 4.

284 A. Michalowicz, J. Huet and A. Gaudemer, *Nouv. J. Chim.*, 6 (1982) 79. *Chem. Abstr.*, 97, 63589.

285 N.S. Ferris, *Diss. Abstr.*, B42 (1981) 2825.

286 J.H. Dimmit, *Diss. Abstr.*, B42 (1981) 1009.

287 H. Siebert and R. Macht, *Z. Anorg. Allg. Chem.*, 489 (1982) 77. *Chem. Abstr.*, 97, 119551.

288 T. Kemmerich, J.H. Nelson, N.E. Takach, H. Boehme, B. Jablonski and W. Beck, *Inorg. Chem.*, 21 (1982) 1226.

289 M.D. Poojary and H. Manohar, *J. Chem. Soc., Chem. Commun.*, (1982) 533.

290 S.E. Diamond, F. Mares, A. Szalkiewicz, D.A. Muccigrosso and J.P. Solar, *J. Am. Chem. Soc.*, 104 (1982) 4266.

291 K. Kashiwara, K. Katoh, T. Ohishi, J. Fujita and M. Shibata, *Bull. Chem. Soc. Jpn.*, 55 (1982) 149.

292 M. Atoh, I. Konoshita, K. Kashiwabara and J. Fujita, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3179.

293 E.E. Castellano, O.E. Piro and G. Punte, *Acta Crystallogr.*, B38 (1982) 2239.

294 J. Ribas, J. Casabo, M. Monfort and M.L. Alvarez, *An. Quim.*, B77 (1981) 26. *Chem. Abstr.*, 97, 32603.

295 S. Alvarez and C. Lopez, *Inorg. Chim. Acta*, 64 (1982) L99.

296 D.R. Eaton and A.C. Sandercock, *J. Phys. Chem.*, 86 (1982) 1371.

297 D.R. Eaton and C.V. Rogerson, *J. Phys. Chem.*, 86 (1982) 1365.

298 M. Asplund, S. Jagner and E. Ljungstroem, *Acta Crystallogr.*, B38 (1982) 1275.

299 M. Calvet, *Afinidad*, 38 (1981) 131. *Chem. Abstr.*, 96, 114844.

300 D.I. Kuntyi, D.I. Semenishin and V.Y. Zhukovskii, *Koord. Khim.*, 7 (1981) 1489. *Chem. Abstr.*, 96, 45251.

301 S. Bagger and P. Stoltze, *Acta Chem. Scand.*, A35 (1981) 509.

302 K. Angermann, R. Schmidt, R. van Eldik, H. Kelm and F. Wasgestian, *Inorg. Chem.*, 21 (1982) 1175.

303 A. Haim, *Inorg. Chem.*, 21 (1982) 2887.

304 A. Adeyemo, A. Valiotti and P. Hambright, *Inorg. Chim. Acta Letters*, 64 (1982) L251.

305 B.N. Figgis and P.A. Reynolds, *Aust. J. Chem.*, 34 (1981) 2495.

306 A.F. Drake, S.J. Hirst, R. Kuroda and S.F. Mason, *Inorg. Chem.*, 21 (1982) 533.

307 C.L. Hussey and T.M. Laher, *Inorg. Chem.*, 20 (1981) 4201.

308 K. Sawada, T. Onoda and T. Suzuki, *J. Inorg. Nucl. Chem.*, 43 (1981) 3263.

309 I. Soetofte and K. Nielsen, *Acta Chem. Scand.*, A35 (1981) 739.

310 K. Sone and H. Ohashi, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3806.

311 R.E. Cook and P.J. Robinson, *J. Chem. Research (S)*, (1982) 267.

312 R. Bedetti, U. Biader Ceipidor, V. Carunchio and A. Messina, *Inorg. Chim. Acta*, 62 (1982) 253.

313 R.P. Varma and P.K. Jain, *Transition Met. Chem.*, 7 (1982) 129.

314 A.E. Landers and D.J. Phillips, *Inorg. Chim. Acta*, 59 (1982) 125.

315 M.B. Hursthouse, M.A. Laffey, P.T. Moore, D.B. New, P.R. Raithby and P. Thornton, *J. Chem. Soc. (Dalton)*, (1982) 307.

316 M.A. Laffey and P. Thornton, *J. Chem. Soc. (Dalton)*, (1982) 313.

317 R. Aruga, *Transition Met. Chem.*, 7 (1982) 318.

318 N. Saha and H. Sigel, *J. Am. Chem. Soc.*, 104 (1982) 4100.

319 R. Cini and P. Orioli, *J. Inorg. Biochem.*, 14 (1981) 95.

320 L. Kiss and J. Csaszar, *Acta Chim. Acad. Sci. Hung.*, 109 (1982) 57. *Chem. Abstr.*, 96, 227967.

321 J.L. Leroy and M. Gueron, *Biochimie*, 64 (1982) 297. *Chem. Abstr.*, 96, 212694.

322 H. Mueller, A. Holzmann and W. Hinrichs, *Z. Naturforsch. B, Anorg. Chem. Org. Chem.*, 37B (1982) 341. *Chem. Abstr.*, 96, 227951.

323 Yu.A. Simonov, G.S. Matuzenko and M.M. Botoshanskii, *Zh. Neorg. Khim.*, 27 (1982) 407. *Chem. Abstr.*, 96, 173319.

324 J. Maslowska and A. Owczarek, *Pol. J. Chem.*, 55 (1981) 271. *Chem. Abstr.*, 95, 193180.

325 F.L. Dickert and S.W. Hellmann, *Ber. Bunsenges. Phys. Chem.*, 86 (1982) 153.

326 A.M. El-Atrash, F.M. Elzawawi and R.H. Ramadan, *Egypt. J. Chem.*, 23 (1981) 113. *Chem. Abstr.*, 96, 169651.

327 D.L. Hughes and J.N. Wingfield, *J. Chem. Soc. (Dalton)*, (1982) 1239.

328 I.M. Ruzic, T.D. Smith and J.R. Pilbrow, *J. Chem. Soc. (Dalton)*, (1982) 373.

329 K.J. Berry, F. Moya, K.S. Murray, A.M.B. van den Bergen and B.O. West, *J. Chem. Soc. (Dalton)*, (1982) 109.

330 S.A. Bedell, J.H. Timmons, A.E. Martell and I. Murase, *Inorg. Chem.*, 21 (1982) 874.

331 L.I. Simandi, C.R. Savage, Z.A. Schelly and S. Németh, *Inorg. Chem.*, 21 (1982) 2765.

332 W.R. Harris, J.H. Timmons and A.E. Martell, *J. Coord. Chem.*, 8 (1979) 251.

333 J.H. Timmons, A.E. Martell, W.R. Harris and I. Murase, *Inorg. Chem.*, 21 (1982) 1525.

334 M.W. Urban, Y. Nonaka and K. Nakamoto, *Inorg. Chem.*, 21 (1982) 1046.

335 T.D. Smith, I.M. Ruzic, S. Tirant and J.R. Pilbrow, *J. Chem. Soc. (Dalton)*, (1982) 363.

336 K. Sakata and I. Murase, *Inorg. Chim. Acta*, 64 (1982) L239.

337 A. Zombeck, R.S. Drago, B.B. Corden and J.H. Gaul, *J. Am. Chem. Soc.*, 103 (1981) 7580.

338 D.M. Wagnerova, J. Blanck and J. Veprek-Siska, *Coll. Czech. Chem. Commun.*, 47 (1982) 755.

339 H. Sakurai and K. Ishizu, *J. Am. Chem. Soc.*, 104 (1982) 4960.

340 M.W. Urban, K. Nakamoto and J. Kincaid, *Inorg. Chim. Acta*, 61 (1982) 77.

341 K. Nakamoto, Y. Nonaka, T. Ishiguro, M.W. Urban, M. Suzuki, M. Kozuka, Y. Nishida and S. Kida, *J. Am. Chem. Soc.*, 104 (1982) 3386.

342 S. Takano, Y. Yano and W. Tagaki, *Chemistry Letters*, (1981) 1177.

343 P.J. Jackson, *Diss. Abstr. Int. B*, 42 (1981) 1880. *Chem. Abstr.*, 95, 226083.

344 M. Hoshino, M. Nakajima and M. Takakubo, *J. Phys. Chem.*, 86 (1982) 221.

345 M. Suzuki, H. Kanatomi and I. Murase, *Chemistry Letters*, 12 (1981) 1745.

346 D.W. Smith, *Diss. Abstr.*, B42 (1982) 3260.

347 E. Kimura, *Yakugaku Zasshi.*, 102 (1982) 701.

348 S. Petri and K. Bodek, *Acta Pol. Pharm.*, 38 (1981) 453. *Chem. Abstr.*, 96, 154351.

349 R. Boca, *J. Mol. Catal.*, 14 (1982) 313.

350 D.A. Lerner, F.R. Ricchiero and C. Giannotti, *J. Photochem.*, 18 (1982) 193.

351 V.A. Pokrovskii and Yu.I. Bratushko, *Teor. Eksp. Khim.*, 18 (1982) 235. *Chem. Abstr.*, 97, 45069.

352 E.S. Raper and I.S. Rowell, *J. Inorg. Nucl. Chem.*, 43 (1981) 3137.

353 A.I.P. Sinha and J.L. Jain, *J. Inorg. Nucl. Chem.*, 43 (1981) 3384.

354 A.C. Fabretti, G.C. Franchini and G. Peyronel, *Transition Met. Chem.*, 7 (1982) 105.

355 G. Christou, K.S. Hagen and R.H. Holm, *J. Am. Chem. Soc.*, 104 (1982) 1744.

356 K.S. Hagen, D.W. Stephan and R.H. Holm, *Inorg. Chem.*, 21 (1982) 3928.

357 C. Bianchini, C. Mealli, A. Meli and G. Scapacci, *J. Chem. Soc. (Dalton)*, (1982) 799.

358 A. Vlcek and A.A. Vlcek, *Inorg. Chim. Acta*, 64 (1982) L273.

359 M. Shimoi, A. Ouchi, T. Uehiro, Y. Yoshino, S. Sato and Y. Saito, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2371.

360 D.R. Eaton, A. Majid and J.P.K. Tong, *Inorg. Chim. Acta*, 61 (1982) 25.

361 M. Kumari and L. Narain, *J. Coord. Chem.*, 12 (1982) 49.

362 C. Bianchini, A. Meli and A. Orlandini, *Inorg. Chem.*, 21 (1982) 4166.

363 C. Bianchini, A. Meli and A. Orlandini, *Inorg. Chem.*, 21 (1982) 4161.

364 R.E. Oughtred, E.S. Raper and I.W. Nowell, *Acta Crystallogr.*, B38 (1982) 2044.

365 L.M. Shkol'nikova, V.E. Zavodnik and A.L. Il'inskii, *Khim. Geterotsikl. Soedin*, (1981) 1484. *Chem. Abstr.*, 96, 61135.

366 R. Kamara, J.P. Declercq and G. Germain, *Bull. Soc. Chim. Belg.*, 91 (1982) 171. *Chem. Abstr.*, 97, 15025.

367 B.K. Sharma, S.P. Mathur, V. Iyer and U.C. Nag, *J. Macromol. Sci. Chem.*, A18 (1982) 421. *Chem. Abstr.*, 97, 137623.

368 A. Castineiras and J.R. Masaguer, *An. Quim. Ser. B*, 78 (1982) 42. *Chem. Abstr.*, 97, 103210.

369 N.V. Gerbeleu, K.I. Turte and I.T. Kashkaval, *Zh. Neorg. Khim.*, 26 (1981) 2143. *Chem. Abstr.*, 95, 180017.

370 B. Harman, K. Nagy and I. Sovago, *Magy. Kem. Foly.*, 88 (1982) 36. *Chem. Abstr.*, 96, 111098.

371 K. Diemert, P. Haas and W. Kuchen, *Z. Anorg. Allg. Chem.*, 480 (1981) 65. *Chem. Abstr.*, 96, 52395.

372 L. Sacconi, *A.C.S. Symp. Ser.*, 171 (1981) 487.

373 L. Marić, Z. Siroki, Z. Stefanac and M.J. Herak, *J. Inorg. Nucl. Chem.*, 43 (1981) 3357.

374 K.R. Morgan, G.J. Gainsford and N.F. Curtis, *Aust. J. Chem.*, 35 (1982) 1105.

375 A.E. Landers and D.J. Phillips, *Inorg. Chim. Acta*, 59 (1982) 41.

376 S. Yamada and K. Yamanouchi, *Bull. Chem. Soc. Jpn.*, 55 (1982) 453.

377 H.R. Engeseth, D.R. McMillin and E.L. Ulrich, *Inorg. Chim. Acta*, 67 (1982) 145.

378 S.M. Paraskewas, A.A. Danopoulos and Ch. Mantzos, *Inorg. Chim. Acta*, 64 (1982) L151.

379 M.J. Adam and L.D. Hall, *Can. J. Chem.*, 60 (1982) 2229.

380 P.K. Biswas, M.K. Dasgupta, S. Mitra and N.R. Chaudhuri, *J. Coord. Chem.*, 11 (1982) 225.

381 S. Suzuki, J. Kino, M. Kimura, W. Mori and A. Nakahara, *Inorg. Chim. Acta*, 66 (1982) 41.

382 I. Bertini, G. Canti and L. Luchinat, *J. Am. Chem. Soc.*, 104 (1982) 4943.

383 W.D. Horrocks, J.N. Ishley and R.R. Whittle, *Inorg. Chem.*, 21 (1982) 3265.

384 W.D. Horrocks, J.N. Ishley and R.R. Whittle, *Inorg. Chem.*, 21 (1982) 3270.

385 K. Doi, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1431.

386 A.A. Abdel-Khalek and Y. Sulfab, *J. Inorg. Nucl. Chem.*, 43 (1981) 3257.

387 A.A. Abdel-Khalek and Y. Sulfab, *Transition Met. Chem.*, 7 (1982) 297.

388 E. Mentasti, *J. Chem. Soc. (Dalton)*, (1982) 721.

389 J.P. Brunette, M. Lakkis, G. Goetz-Grandmont and M.J.F. Leroy, *Polyhedron*, 1 (1982) 461.

390 J. Hirose and Y. Kidani, *J. Inorg. Biochem.*, 14 (1981) 313.

391 A.G. Galinos and S.P. Perlepes, *Monatsh. Chem.*, 112 (1981) 1113. *Chem. Abstr.*, 95, 231107.

392 S. Suzuki, J. Kino and A. Nakahara, *Bull. Chem. Soc. Jpn.*, 55 (1982) 212.

393 M. Vasak, J.H.R. Kaegi and B. Holmquist, *Biochemistry*, 20 (1981) 6659.

394 F.F. Morpeth and V. Massey, *Biochemistry*, 21 (1982) 1318.

395 L. Abello, A. Ensuque and R. Touiti, *J. Chim. Phys. Phys.-Chim. Biol.*, 78 (1981) 615. *Chem. Abstr.*, 96, 25280.

396 M. Vasak and J.H.R. Kaegi, *Proc. Natl. Acad. Sci. USA*, 78 (1981) 6709.

397 A. Desideri, F. Comin, L. Morpurgo and D. Cocco, *Biochim. Biophys. Acta*, 670 (1981) 312.

398 A. Vegas, A. Perez-Salazar and F. Silio, *Acta Crystallogr.*, B37 (1981) 1916.

399 Ya.M. Nesterova and M.A. Porai-Koshits, *Koord. Khim.*, 8 (1982) 994. *Chem. Abstr.*, 97, 102119.

400 A.J. Kinneging, W.J. Vermin and S. Gorter, *Acta Crystallogr.*, B38 (1982) 1824.

401 E. Brucher and G. Laurenczy, *Magy. Kem. Foly.*, 88 (1982) 271. *Chem. Abstr.*, 97, 99086.

402 P. Banerjee and M.P. Pujari, *Indian J. Chem.*, 21A (1982) 1123.

403 R.K. Nandwana and S.K. Solanki, *Indian J. Chem.*, 21A (1982) 519.

404 H.S. Verma, R.C. Saxena and K.C. Mathur, *J. Indian Chem. Soc.*, 58 (1981) 1193.

405 A. El-Toukhy, A.F.M. Hefny and L. Sayed, *Monatsh. Chem.*, 113 (1982) 171. *Chem. Abstr.*, 96, 173322.

406 H.M. Goff, J. Hines and J. Griesel, *J. Chem. Educ.*, 59 (1982) 422.

407 R. Pastorek, F. Brezina and A. Sterbova, *Acta Univ. Polacki. Olomuc., Fac. Rerum Nat.*, 73 (1982) 17. *Chem. Abstr.*, 97, 103213.

408 N. Saha and K.M. Datta, *J. Indian Chem. Soc.*, 59 (1982) 728.

409 R. Mueller, R. Koch and M. Just, *Z. Chem.*, 22 (1982) 268. *Chem. Abstr.*, 97, 155306.

410 A. Syamal and B.K. Gupta, *J. Indian Chem. Soc.*, 59 (1982) 697.

411 A.A. Shabilalov and A.N. Yunuskhodzhaev, *Koord. Khim.*, 8 (1982) 1106.

412 F. Mani and C. Mealli, *Inorg. Chim.*, 63 (1982) 97.

413 L. Banci, C. Benelli, D. Gatteschi and F. Mani, *Inorg. Chem.*, 21 (1982) 1133.

414 R.S. Brown, D. Salmon, N.J. Curtis and S. Kusuma, *J. Am. Chem. Soc.*, 104 (1982) 3188.

415 D.L. White and J.W. Faller, *J. Am. Chem. Soc.*, 104 (1982) 1548.

416 T. Sakurai, H. Kaji and A. Nakahara, *Inorg. Chim. Acta*, 67 (1982) 1.

417 R.A.D. Wentworth, P.S. Dahl, C.J. Huffman, W.O. Gillum, W.E. Streib and J.C. Huffman, *Inorg. Chem.*, 21 (1982) 3060.

418 R.A.J. Driessen, F.B. Hulsbergen, W.J. Vermin and J. Reedijk, *Inorg. Chem.* 21 (1982) 3594.

419 B.M. Foxman and H. Mazurek, *Inorg. Chim. Acta*, 59 (1982) 231.

420 N.F. Curtis, *Inorg. Chim. Acta*, 59 (1982) 171.

421 S. Kremer, W. Henke and D. Reinen, *Inorg. Chem.*, 21 (1982) 3013.

422 W. Henke and S. Kremer, *Inorg. Chim. Acta*, 65 (1982) L115.

423 P.P. Singh and V.P. Singh, *Can. J. Chem.*, 60 (1982) 2351.

424 N.K. Jha, R.S. Prasad and A. Kumari, *J. Inorg. Nucl. Chem.*, 43 (1981) 3404.

425 Y.K. Bhoon, *Transition Met. Chem.*, 7 (1982) 93.

426 C. Benelli and G. Gatteschi, *Inorg. Chem.*, 21 (1982) 1788.

427 A. Rockenbauer, M. Gyor, M. Kwiecinski and S. Tyrlik, *Inorg. Chim. Acta*, 58 (1982) 237.

428 K. Mita, K. Hotta and S. Watanabe, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2669.

429 G.N. Schrauzer, *Inorg. Chim. Acta Letters*, 64 (1982) L279.

430 G.N. Schrauzer and R.J. Windgassen, *Chem. Ber.*, 99 (1966) 602.

431 K. Sawada, K. Miura and T. Suzuki, *Bull. Chem. Soc. Jpn.*, 55 (1982) 780.

432 A. Cinquantini, R. Seeber and R. Cini, *Transition Met. Chem.*, 7 (1982) 271.

433 Y. Abe and G. Wada, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3789.

434 G. Anderegg and P. Blauenstein, *Helv. Chim. Acta*, 65 (1982) 913.

435 H.M. Marafie, M.S. El-Ezaby, B.A. Abd-El-Nabey and N. Kittaneh, *Transition Met. Chem.*, 7 (1982) 227.

436 K. Watanabe and A. Imazawa, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3208.

437 U. Turpeinen, M. Ahlgren and R. Hamalainen, *Acta Crystallogr.*, B38 (1982) 1580.

438 K. Mereiter and A. Preisinger, *Acta Crystallogr.*, B38 (1982) 1084.

439 A.Ya. Kon, I.F. Burshtein and N.N. Proskina, *Koord. Khim.*, 8 (1982) 225. *Chem. Abstr.*, 96, 172424.

440 D.W. Hoffman and J.S. Wood, *Cryst. Struct. Commun.*, 11 (1982) 685.

441 V. Divjakovic, V.M. Leovac, B. Ribar and G. Argay, *Acta Crystallogr.*, B38 (1982) 1738.

442 N. Shashikala, E.G. Leelamani and G.K.N. Reddy, *Indian J. Chem.*, 21A (1982) 743.

443 N. Saha and K.M. Datta, *Indian J. Chem.*, 21A (1982) 180.

444 A.V. Ivashenko, A.I. Vasil'ev and O.N. Garicheva, *Koord. Khim.*, 7 (1981) 1236. *Chem. Abstr.*, 95, 196532.

445 S.P. Suh and Y.H. Oh, *Bull. Korean Chem. Soc.*, 3 (1982) 5. *Chem. Abstr.*, 96, 227989.

446 R. Mueller, U. Fickel and W. Pidde, *Z. Chem.*, 21 (1981) 300. *Chem. Abstr.*, 95, 180021.

447 D.M. Palade, V.S. Lin'kova and G.V. Chudaeva, *Zh. Neorg. Khim.*, 27 (1982) 1868. *Chem. Abstr.*, 97, 119516.

448 M. Mohan and B.D. Paramhaus, *Acta Chim. Acad. Sci. Hung.*, 108 (1981) 219. *Chem. Abstr.*, 96, 173313.

449 I.N. Terskaya, A.Yu. Surkov and L.P. Raizman, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 25 (1982) 136. *Chem. Abstr.*, 96, 169483.

450 C.W.G. Ansell, J. Lewis and P.R. Raithby, *J. Chem. Soc. (Dalton)*, (1982) 2557.

451 C.W.G. Ansell, J. Lewis, P.R. Raithby and J.N. Ramsden, *J. Chem. Soc. (Dalton)*, (1982) 2127.

452 M. Okamoto, N. Oishi, Y. Nishida and S. Kida, *Inorg. Chim. Acta*, 64 (1982) L217.

453 M. Micheloni, P. Paoletti, S. Burki and T.A. Kaden, *Helv. Chim. Acta*, 65 (1982) 587.

454 I. Bertini, G. Canti, C. Luchinat and L. Messori, *Inorg. Chem.*, 21 (1982) 3426.

455 B. Wang and C-S. Chung, *J. Chem. Soc. (Dalton)*, (1982) 2565.

456 K. Tsuji, M. Imaizumi, A. Oyoshi, I. Mochida, H. Fujitsu and K. Takeshita, *Inorg. Chem.*, 21 (1982) 721.

457 D.P. Rillema, C.M. Wicker, R.D. Morgan, L.F. Barringer and L.A. Scism, *J. Am. Chem. Soc.*, 104 (1982) 1276.

458 S. Funahashi, Y. Yamaguchi, K. Ishihara and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, (1982) 976.

459 A. Shirazi and H.M. Goff, *Inorg. Chem.*, 21 (1982) 3420.

460 Z. Dokuzovic, X. Ahmeti, D. Pavlovic, I. Murati and S. Asperger, *Inorg. Chem.*, 21 (1982) 1576.

461 J. Eilmes, D. Pelan and E. Sledziewska, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, 28 (1980) 371. *Chem. Abstr.*, 96, 114887.

462 See for example, J.M. Lehn, *Pure Appl. Chem.*, 52 (1980) 2441.

463 R.J. Motekaitis, A.E. Martell, J-M. Lehn and E. Watanabe, *Inorg. Chem.*, 21 (1982) 4253.

464 J. Almog, J.E. Baldwin and M.J. Crossley, *Tetrahedron*, 37 (1981) 3589.

465 K.J. Takeuchi, *Diss. Abstr.*, B42 (1981) 1883.

466 J. Metz and M. Hanack, *Nouv. J. Chim.*, 5 (1981) 541. *Chem. Abstr.*, 96, 209770.

467 J. Chakrabarty and B. Sahoo, *Indian J. Chem.*, 21A (1982) 48.

468 B.D. Berezin, O.A. Golubchikov and L.V. Klopova, *Zh. Fiz. Khim.*, 56 (1982) 1639. *Chem. Abstr.*, 97, 116091.

469 S.S. Parmar and H. Kaur, *Transition Met. Chem.*, 7 (1982) 167.

470 L.G. Scanlon, Y-Y. Tsao, K. Toman, S.C. Cummings and D.W. Meek, *Inorg. Chem.*, 21 (1982) 2707.

471 P. Giannoccaro, G. Vasapollo, C.F. Nobile and A. Sacco, *Inorg. Chim. Acta*, 61 (1982) 69.

472 A.L. Hale, W. Levason and H.E. Tuttlebee, *Inorg. Chim. Acta*, 60 (1982) 73.

473 L. Sindellari, B. Zarli, S. Sitran and E. Celon, *Inorg. Chim. Acta*, 64 (1982) L79.

474 Yu.N. Kukushkin, G.B. Avetikyan, E.D. Ageeva, V.E. Aleshin and A.N. Karpov, *Koord. Khim.*, 7 (1981) 1384.

475 Yu.N. Kukushkin, E.D. Ageeva, V.E. Aleshin, G.B. Avetikyan and G.N. Sedova, *Koord. Khim.*, 7 (1981) 1499. *Chem. Abstr.*, 96, 45252.

476 C.A. Ghilardi, S. Midollini and S. Moneti, *J. Organomet. Chem.*, 217 (1981) 391.

477 C.A. Ghilardi, S. Midollini and S. Moneti, *J. Chem. Soc., Chem. Commun.*, (1981) 865.

478 M. Okabe and M. Tada, *Bull. Chem. Soc. Jpn.*, 55 (1982) 1498.

479 A. Puxeddu and G. Costa, *J. Chem. Soc. (Dalton)*, (1982) 1285.

480 R. Seeber, G. Albertin and G-A. Mazzocchin, *J. Chem. Soc. (Dalton)*, (1982) 2561.

481 B.C. Willett and F.C. Anson, *J. Electrochem. Soc.*, 129 (1982) 1260.

482 H. Kanai, *J. Mol. Catal.*, 12 (1981) 231.

483 S. Gambarotta, F. Arena, C. Floriani and P.F. Zanazzi, *J. Am. Chem. Soc.*, 104 (1982) 5082.

484 C.W.G. Ansell, J. Lewis, M.C. Liptrot, P.R. Raithby and M. Schröder, *J. Chem. Soc. (Dalton)*, (1982) 1593.

485 B. Capelle, A.L. Beauchamp, M. Dartiguenave, Y. Dartiguenave and H.F. Klein, *J. Am. Chem. Soc.*, 104 (1982) 3891.

486 E.J. Corey, N.J. Cooper, W.M. Canning, W.N. Lipscomb and T.F. Koetzle, *Inorg. Chem.*, 21 (1982) 192.

487 S.K. Tobia and E.N. Rizkalla, *Inorg. Chim. Acta*, 61 (1982) 225.

488 G.M. Brown, J.E. Finholt, R.B. King and J.W. Bibber, *Inorg. Chem.*, 21 (1982) 2139.

489 B.E. Hanson, P.E. Fanwick and J.S. Mancini, *Inorg. Chem.*, 21 (1982) 3811.

490 G. Agnès, J.C.J. Bart, C. Santini and K.A. Woode, *J. Am. Chem. Soc.*, 104 (1982) 5254.

491 R.W. Hay, in "Mechanisms of Inorganic and Organometallic Reactions", ed. M.V. Twigg, Plenum Press, New York, 2 (1984) 153.

492 M.L. Tobe, in "Advances in Inorganic and Bioinorganic Mechanisms", ed. A.G. Sykes, Academic Press, London, 2 (1983) 1.