Coordination Chemistry Reviews, 37 (1981) 167—197
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

9. MANGANESE

R.I. CRISP and K.R. SEDDON

CONTENTS

The period of this review essentially coincides with the coverage of Vols. 90 and 91 of Chemical Abstracts. Thus, although a majority of the papers

0 010-8545/81/0000—0000/$07.75

covered were published in 1979, many from 1978 are also included. The review concentrates upon those aspects of the chemistry of manganese which would be conventionally considered as coordination chemistry. Thus, no attempt has been made to review work of an essentially organometallic nature. Areas of high activity this year include manganese complexes with macrocyclic ligands, the physical and spectroscopic properties of salts of trihalomanganate(II) and tetrahalomanganate(II), and the preparation of surfaces modified by the chemical attachment of manganese complexes. The study of manganese carbonyl complexes is, as ever, popular.

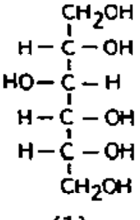
9.1 HIGH OXIDATION STATES

The pseudo-potential method for calculating molecular orbital energies has been applied with success to the $[MnO_4]^-$ anion [1]. The solution chemistry of both $Na[MnO_4]$ and $Na_2[MnO_4]$ has been studied [2], and an EPR study of manganate(VI) doped in K_2SO_4 has been undertaken [3]. The optical and vibronic spectra of $[MnO_4]^{2-}$ doped in CsBr have also been reported [4].

9.2 MANGANESE(IV)

Improved methods of preparation, unit-cell dimensions and magnetic susceptibility data have been reported for the ternary oxide system $AMnO_3$ (A = Gp.IIA cation). Magnetic data and unit-cell dimensions are also reported for the quaternary oxides $ATi_{1-x}Mn_xO_3$ and $AZr_{1-x}Mn_xO_3$ [5]. The compounds $Ca_2Mn_3O_8$ and $Cd_2Mn_3O_8$ have also been prepared and order antiferromagnetically near 60 K and 10 K, respectively [6]. Optical spectra of Mn^{4+} in octahedral coordination in MgO, $Y_3Al_5O_{12}$ and α-Al_2O_3 have been reported [7].

$[Me_4N]_2[Mn(sorbH_4)_3]$ {$sorbH_6$ = sorbitol (1)} was isolated from the reaction of $[Mn_2(H_2O)_2(sorbH_4)_4]^{4-}$ with O_2, and represents the first example of a high-spin tris(chelate) monomeric complex of Mn(IV). EPR and other spectroscopic data are consistent with the formulation and indicate axially-distorted octahedral symmetry [8].



$$\begin{array}{c}CH_2OH\\ |\\ H-C-OH\\ |\\ HO-C-H\\ |\\ H-C-OH\\ |\\ H-C-OH\\ |\\ CH_2OH\end{array}$$

(1)

A complex of haematoporphyrin with manganese(IV) [(Hm)Mn(IV)] has been shown to be a powerful oxidising agent, typically degrading $PhCH_2OR$ (R = H, Me, $CHMe_2$ or CH_2Ph), $PhCH_2NH_2$, $PhCH_2COCO_2H$ and $PhCH_2CH$-

$(NH_2)CO_2H$ to PhCHO. In the presence of NaOCl, [(Hm)Mn(IV)] was shown to exhibit pseudo-catalytic activity, the complex slowly being consumed [9].

Ab initio molecular orbital calculations performed on a series of metal(IV) hydrides, including that of manganese, have led to the prediction of bond-dissociation energies and M—H bond lengths [10].

9.3 MANGANESE(III)

9.3.1 *Halides*

Ligand field spectra of $[MnF_6]^{3-}$ octahedra in a variety of host lattices reveal splittings due to Jahn—Teller distortion. Magnetic studies at low temperatures show that both ferrodistortive order and antiferrodistortive order may be observed, depending on the host lattice [11]. X-ray crystal structures of $Cs_2MnF_5 \cdot H_2O$ [12] and $Rb_2MnF_5 \cdot H_2O$ [13] show chains of tetragonally elongated $\{MnF_6\}^{3-}$ octahedra, linked by sharing *trans*-vertices. The crystal structures of the complexes $A[MnF_4(OH_2)_x]$ (A = $[NMe_4]$, $x = 2$; A = Rb, $x = 1$) have been determined. The former complex contains tetragonally elongated *trans*-$[MnF_4(OH_2)_2]^-$ octahedra linked by hydrogen bonds to form layers, whereas the latter complex consists of alternating $[MnF_6]^{3-}$ and *trans*-$[MnF_4(OH_2)_2]^-$ octahedra [14]. $A[O_2CMe]$ (A = Na, K or $[NH_4]$) react with $[Mn(O_2CMe)_3]$ in $MeCO_2H$ and MeCOCl to give the complexes $A_2[MnCl_5]$ which were shown to be polymeric. Complexes $[BH_2][MnCl_5]$ (B = bipy or phen) and $A_2[MnCl_5]$ (A = pyH, quinH or Li) were also obtained and shown to be monomeric, containing the square pyramidal $[MnCl_5]^{2-}$ entity [15]. The luminescence spectra of the antiferromagnet $[RNH_3][MnCl_4]$ (R = CH_3 or C_2H_5) between 4.2 and 100 K have been compared with those of paramagnetic $[pyH][MnCl_4]$ [16], and found to be anomalous.

9.3.2 *Oxides*

The effect of H_3O^+ and Mn^{2+} on the disproportionation of Mn_2O_3 in acid solution has been investigated [17].

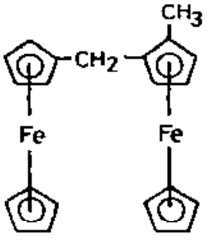
For $LaMnO_3$, the stoicheiometric phase exists only over a limited range of oxygen partial pressure and has an orthorhombically distorted perovskite structure [18]. A similar thermogravimetric study of $AMnO_3$ (A = Sm, Dy, Y, Er or Yb) indicates that the degree of non-stoicheiometry is dependent on the radius of the rare-earth ion [19]. The X-ray crystal structure of $Mn(OH)(SO_4) \cdot 2\,H_2O$ shows two types of Jahn—Teller distorted $\{MnO_6\}$ octahedra linked by sharing vertices to form chains [20].

9.3.3 *Complexes with oxygen donor ligands*

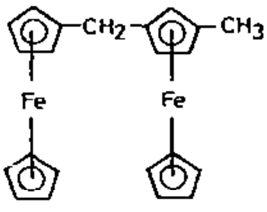
The molecular structure of γ-$[Mn(acac)_3]$ has been determined. Tetragonally distorted octahedral coordination is reported, with $\bar{r}$(Mn—O; short) =

0.1935 nm and $\bar{r}$(Mn—O; long) = 0.2111 nm [21]. The crystal structure of polymeric [Mn(acac)$_2$(NCS)] indicates that quasi-planar [Mn(acac)$_2$]$^+$ groups are linked by bridging NCS$^-$ ligands, each manganese atom thus being coordinated by four O, one S and one N atoms in a distorted octahedral configuration [22]. Kinetic studies indicate that the electron transfer step of the reduction of [Mn(acac)$_3$] by Fe(II) in ethanenitrile is preceded by formation of a bridged binuclear species, which was not isolated [23]. A similar intermediate, [(acac)$_2$Mn(acac)Fe(dmf)$_5$]$^{2+}$, is proposed for the electron transfer from [Fe(dmf)$_6$]$^{2+}$ to [Mn(acac)$_3$] in 1,2-propanediol-carbonate [24]. A kinetic study of the reaction in ethanenitrile indicates that the first step is the elimination of one molecule of dmf to form [Fe(dmf)$_5$]$^{3+}$ prior to dimer formation [25].

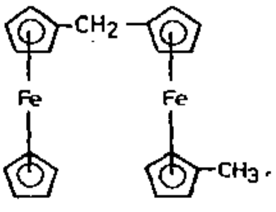
Manganese(III) complexes are finding increasing use as synthetic reagents in organic chemistry. Manganese(III) sulphate has been shown to be a useful oxidising agent for the production of quinones from their parent hydrocarbons [26], whilst a diphosphate complex of Mn(III) has been used to oxidise *N,N,N*′*,N*′-tetramethylbenzidine and Malachite green to give diphenoquinone-4,4′-bis(dimethylimine) [27]. Manganese(III) ethanoate in ethanoic acid oxidises methylferrocene to give three products (2), (3) and (4), evidence being presented for a mechanism involving the ferrocenylmethyl radical [28].



(2)



(3)



(4)

In the oxidation of citric acid (to HCO$_2$H and CO$_2$) by Mn$_2$(SO$_4$)$_3$, complexes of the type [Mn{R$_2$C(OH)CO$_2$H}]$^{2+}_{aq}$ and [Mn{R$_2$C(OH)CO$_2$H}]$^{3+}_{aq}$ are believed to be involved [29].

The negative ion mass spectrum of Mn(LL)$_3$ (LLH$_2$ = 2,2,6,6-tetramethyl-3,5-heptanedione) is reported [30], and its possible use for ultra-trace metal analysis is indicated.

9.3.4 Porphyrin complexes and related species

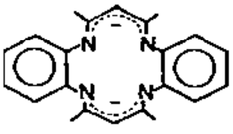
Electrochemical measurements on a series of manganese(III) porphyrin complexes show a good linear correlation with similar measurements upon the free porphyrins and the analogous iron(III) complexes [31]. Chloromanganese(III) tetracyanotetraphenylporphyrin has also been examined electrochemically, as part of a study to determine the effects of substituents on the electroreduction of porphyrins and metalloporphyrins [32]. The equilibrium

(1) (Por = tetraphenylporphyrin sulphonate or haematoporphyrin) has also

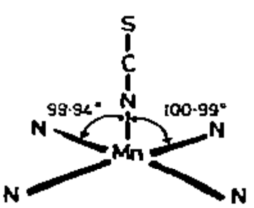
$$[(Por)Mn(OH_2)]^+ + H_2O \rightleftharpoons [(Por)Mn(OH)] + H_3O^+ \qquad (1)$$

been studied and the results interpreted in terms of the ligand-field model [33]. Reduction of [(Por)Mn(III)] {Por = tetrakis(2-*N*-methylpyridinyl)-porphinato or tetrakis(4-*N*-methylpyridinyl)porphinato} by Sn(II) gives the corresponding Mn(II) complex [34]. The unusually high stability of the tetraphenylporphyrin complex of manganese(III) in strongly deprotonating solvents has also been discussed [35].

The crystal structure of the high-spin complex [$Mn(C_{22}H_{22}N_4)(NCS)$] containing the ligand (5) has been determined. The manganese is in a 5-coordinate, square-pyramidal environment (6), being slightly raised (0.036 nm) out of the plane of the macrocycle [36].



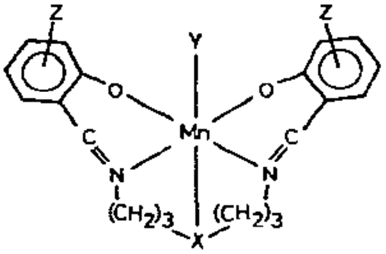
(5)



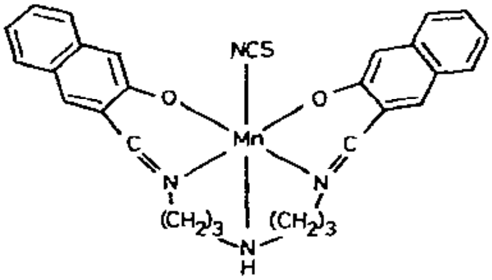
(6)

9.3.5 Schiff base complexes

Manganese(III) complexes {(7) and (8)} of pentadentate Schiff bases have been studied by cyclic voltammetry. The reduction potentials were observed to be lower for electron-withdrawing Z relative to electron donating Z, and there was also found to be a dependence upon the nature of X. A correlation between the electrochemical results and the reactivity of the complexes with O_2 and NO was also presented [37].



(7)



(8)

X = NH, NCH_3, NC_3H_7 or O

Y = I^-, Br^-, NO_2^- or NCS^-

Z = H, 5-NO_2, 3-NO_2, 5-CH_3, 3-CH_3O, 5-CH_3O or 5-Cl

9.3.6 *Complexes with nitrogen—oxygen donor ligands*

Diethanolamine (deaH$_2$) reacts with Mn(OH)$_3$ to give the complex anion [Mn(dea)$_2$]$^-$ [38]. An X-ray study of tris(pyridine-2-carboxylato)manganese(III) monohydrate indicates that coordination at manganese is *mer*-[MnN$_3$O$_3$] [39].

9.4 MANGANESE(II)

9.4.1 *Halides*

9.4.1.1 *Fluorides*

MnF$_2$ exhibits polymorphism at high pressures, the normal rutile structure being replaced by a denser distorted fluorite structure at pressures of ca. 35 kbar and a temperature of 200°C [40]. The magnetic properties of MnF$_2$ at 0 K have also been discussed [41]. The temperature dependence of the fluorescence spectra of nominally pure MnF$_2$ and that doped with Eu^{3+} or Er^{3+} has been studied [42], and the angular dependence of the photoemission energy distribution of MnF$_2$ single crystals reported [43]. The X-band EPR spectra of MnF$_2$ (and MnH$_2$) trapped in argon matrices at 4 K have been recorded and interpreted [44].

MnF$_2$ is hydrolysed by moist argon at high temperatures, reacts only at the surface with sulphur vapour, but does not react with NO or O$_2$ [45].

The exchange interaction of $\{Mn^{2+}\}^*$ in KMnF$_3$ has been studied [46], and an NMR investigation of CsMnF$_3$ has shown that two non-equivalent magnetic sublattices, with mutually opposite magnetic moments, were present at 77 K [47]. EPR studies upon K$_2$MnF$_4$ provide evidence for spin diffusion [48], and the magnetic structure of the double layer antiferromagnet K$_3$Mn$_2$F$_7$ has been investigated by neutron scattering [49]. Pb$_2$-[MnF$_6$] has been shown by EPR measurements to be antiferromagnetic with $T_N = 30$ K (the results were confirmed by ^{19}F NMR) [50].

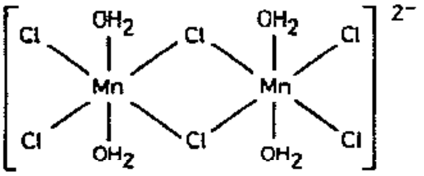
9.4.1.2 *Chlorides*

Magnetisation and antiferromagnetic resonance studies on a single crystal of MnCl$_2$ · 2 H$_2$O at liquid helium temperatures have been performed [51].

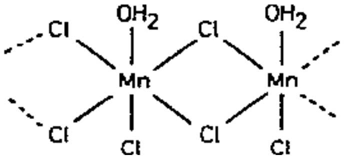
Single crystal X-ray structures of [NH$_4$][MnCl$_3$] at temperatures of 343, 295 and 128 K have been determined. The two high temperature determinations were identical, but there was observed to be a crystallographic transition below 258 K [52]. Observations on the Mössbauer spectra of ^{57}Fe doped samples suggest that there may be two phase transitions in this region [52]. Phase transitions in the chain complexes [(CH$_3$)$_4$N][MnCl$_3$] and [(CD$_3$)$_4$N][MnCl$_3$] have been studied by Raman spectroscopy [53], as has a phase transition in Rb[MnCl$_3$] under a small mechanical stress [54]. The latter transition was shown to be ferroelastic.

Two independent determinations of the structure of [(Me$_2$CH)NH$_3$]-

$[MnCl_3] \cdot 2\ H_2O$ have been reported [55,56]. The crystal contains discrete $[Mn_2Cl_6(H_2O)_4]^{2-}$ (9) anions $\{r(Mn \cdots Mn) = 0.3828$ nm$\}$. Similarly, crystal structures of the quasi-one-dimensional magnetic systems [pyH]$[MnCl_3]$ H_2O and [quinH]$[MnCl_3] \cdot H_2O$ indicate extended chains of bi-bridged $[MnCl_5(OH_2)]^{3-}$ octahedra (10) [57], and the magnetic properties of the quinolinium salt were discussed in terms of this structure.



(9)



(10)

The magnetic properties of alkali metal $[MnCl_3]^-$ salts have been studied [58—60]. Luminescence spectra [61] and the temperature dependence of antiferromagnetic resonance [62] for the quasi-one-dimensional Cs$[MnCl_3] \cdot$ 2 H_2O system have also been examined. NMR measurements have been used to determine the magnetic structure of the antiferromagnetically ordered phase of $[(CH_3)_2NH_2][MnCl_3]$ [63].

The systems $[N(CH_3)_4][MnCl_3]$ (TMMC) and $[N(CD_3)_4][MnCl_3]$, are the archetypal examples of one-dimensional antiferromagnets. Natsume et al. [64] have proposed a theoretical treatment of the EPR spectra of such systems, and the calculated results for TMMC agreed well with experimental measurements. Temperature dependent EPR measurements on TMMC have identified two paramagnetic species, one with one-dimensional character and another with three-dimensional character [65]. Neutron scattering has been used to study magnetic interactions in TMMC [66,67].

Lutz et al. [68] present far IR, Raman and X-ray data to indicate 1 : 1 ordering on the octahedral sites in $Li_2[MnCl_4]$ and to demonstrate a reversible phase change to a cubic defect structure at 460°C. IR studies of the compounds $[CH_3NH_3]_2[MnCl_4]$ and $[CH_3ND_3]_2[MnCl_4]$ indicate that, at high pressures and at 25°C, they undergo discontinuous phase changes [69]. An X-ray study of the series of compounds $[C_nH_{2n+1}NH_3]_2[MnCl_4]$ (n = 1—10) shows the propyl compound to exhibit unique structural properties [70]. The crystal structure of $[C_4H_9NH_3]_2[MnCl_4]$ has been reported, and compared with those of the ethyl and propyl homologues [71]. The vibrational spectra of $[enH_2][MnCl_4]$ and isostructural salts of other transition metals have been discussed in relation to the known structure of the nickel analogue [72].

A method has been developed for calculating the composition of the vapour phase over molten salt systems [73] and the calculations checked using the $MnCl_2$—KCl system. The Raman spectra of tetrahedral $[MnCl_4]^{2-}$ ions in molten $A_2[MnCl_4]$ (A = Li, Na, K, Rb or Cs) have been measured [74], and X-ray studies upon the melts (A = Li or K) confirm the presence of tetrahedral $[MnCl_4]^{2-}$ units [75].

The change in linear magnetic birefringence in $Rb_2[MnCl_4]$ with a pulsed magnetic field has been studied [76]. EPR studies upon $[enH_2][MnCl_4]$ provide evidence for spin diffusion [48]. The magnetic and optical properties of $[ND_3(CH_2)_2ND_3][MnCl_4]$ [77] show it to be a good example of an isotropic two-dimensional antiferromagnet. The results of a high-field magnetisation study of $[(CH_3)_3NH]_3[Mn_2X_7]$ (X = Cl or Br) at 4.2 K are consistent with the existence of two independent antiferromagnetic Mn^{2+} chain systems [78].

9.4.1.3 *Bromides*

$Rb_2[MnBr_4]$ is reported to contain $\{MnBr_6\}^{4-}$ octahedra sharing equatorial vertices to form layers, with the Rb^+ ions lying in the same planes as the axial Br^- ions [79]. The complex $[(CH_3)_2NH_2]_4[MnBr_6]$ has been prepared by reacting $[(CH_3)_2NH_2]Br$ and $MnBr_2$ in the correct molar ratio, and the temperature dependence of the luminescence spectra reported [80].

9.4.1.4 *Iodides*

The coordination symmetry of Mn^{2+} in the linear chain compound $CsMnI_3$ has been deduced from the ^{129}I Mössbauer spectrum. Magnetic transitions are observed and antiferromagnetic alignment of spins along the chain axis is suggested [81].

9.4.2 *Oxides*

An X-ray determination of the electron density distribution in MnO gave a nett charge of +1.4 for the manganese atom [82]. The EPR spectrum of MnO has been measured [83] and the effects of non-stoicheiometry discussed. The crystal structure of the hitherto unknown compound $BaMn_2O_3$ has been determined, and represents a new structure type for the compounds AB_2O_3 [84].

The crystal structures of a number of oxide pnictides $A_2Mn_3B_2O_2$ (A = Sr, Ba; B = As, Sb or Bi) have been determined. The manganese and B atoms form tetragonal pyramids, connected by common edges to form two-dimensional sheets. These sheets are separated by double layers of A atoms, in which Mn and O atoms form square planar $\{MnO_4\}$ units [85].

9.4.3 *Sulphates, nitrates, phosphates and perchlorates*

Exchange interactions in the compounds α-$MnSO_4$ and β-$MnSeO_4$ have been studied by neutron scattering, and it has been shown that interactions between fourth neighbours are important [86].

Liquid—liquid distribution studies of the Mn^{2+}/NO_3^- interactions for the formation of mononitrato-complexes indicate that only outer-sphere interaction occurs [87].

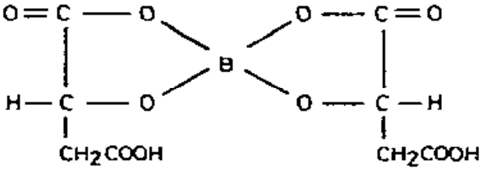
A convenient preparation of $Mn_2P_2O_7$ {a useful calibrant for magnetic susceptibility measurements} by the reaction of $Na_2P_2O_7$ with an $MnCl_2/KCl$ eutectic ($MnCl_2 \cdot 2.03$ KCl) has been reported [88]. Stability constants for complexes of Mn(II) with $[HP_2O_7]^{3-}$ or $[P_2O_7]^{4-}$ have been reported [89].

The complex $[MnL_5(OClO_3)][ClO_4]$ (L = 3-methylisoquinoline *N*-oxide) has been isolated [90].

9.4.4 Carboxylates

The thermal decomposition of $Mn(O_2CH)_2 \cdot 2\ H_2O$ has been studied [91] with subsequent calculation of the thermodynamic properties, and its electronic spectrum has been recorded and interpreted in terms of Mn^{2+} in a cubic crystalline field [92]. The magnetic structure of $Mn(O_2CCH_3)_2 \cdot 4\ H_2O$ has been studied by measurement of temperature-dependent optical spectra [93] and studies of this compound in a very high external magnetic field gives the first clear example of a full magnetisation process in a Heisenberg magnet [94]. Thermodynamic properties and solution equilibria of $Mn(O_2CCF_3)_2$ have been reported [95] and the strengths of the Mn—O bonds in $Mn(C_2O_4) \cdot 2\ H_2O$ have been measured [96]. An IR study of manganese(II) iodoethanoate has been reported [97].

The X-ray crystal structure of bis(4-aminobenzoate)tetraaquamanganese(II) shows the Mn atom to be at the centre of a distorted octahedron of O atoms (4 H_2O and 2 benzoate) [98]. The stability of the benzoate complexes with Mn(II) in aqueous $NaClO_4$ has also been investigated [99], and complexes with citric acid have also been reported [100]. The complex $Mn(bdm)_2 \cdot 4\ H_2O$ ($bdmH_2$ = borodimalic acid (**11**)) has been prepared and characterised [101].



(11)

The complex $H_2[Mn(cydta)(H_2O)_2] \cdot H_2O$ ($cydtaH_4$ = *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid) has been prepared [102].

The preparations of the ligand ethylenediaminetetraacetamide (edtam) and a number of its complexes including $Mn(edtam)Cl_2 \cdot 0.5\ H_2O$ have been reported; IR evidence shows the ligand to be hexadentate [103].

$Mn(O_2CCH_2CN)_2$ has been prepared and shown to be octahedral and polymeric, with the metal atom coordinated by carboxylate and *N*-bonded cyanide groups. This compound reacts with pyridine or 2,2′-bipyridine to form $[Mn(O_2CCH_2CN)_2(py)_2]$ or $[Mn(O_2CCH_2CN)_2(bipy)_2]$, respectively; the former contains bidentate, and the latter monodentate, carboxylate groups with neither compound involving coordination of the cyanide nitrogen atoms [104].

9.4.5 *Complexes with oxygen donor ligands*

Metallic manganese dissolves in a mixture of dimethylsulphoxide (dmso) and SO_2 to form a yellow complex $[Mn(dmso)_6][S_2O_7]$, in which dmso is coordinated via oxygen [105]. ^{31}P NMR spectra of $MnBr_2(OPPh_3)_2$ have been reported [106].

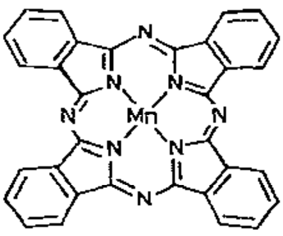
Complexes of the types MnA^+, MnA_2 and MnA_3^- (HA = 3-hydroxy-2-methyl-4-pyrone, 3-hydroxy-6-hydroxymethyl-4-pyrone) have been prepared and their thermodynamic stabilities determined [107].

A series of twenty-four air-sensitive alkoxides $Mn(OR)_2$ have been prepared by alcoholysis of $Mn\{N(SiMe_3)_2\}_2 \cdot$ thf, and spectroscopically characterised [108]. Complexes of manganese(II), (III) and (IV) with sorbitol (1) have been prepared and their electronic and redox properties investigated [109]. Their reactions with molecular oxygen and hydrogen peroxide are reported. Molecular oxygen oxidises the Mn(II) and Mn(III) complexes to the Mn(III) and Mn(IV) complexes, respectively, itself being reduced to the peroxide anion [109]. Cornwell and Harrison report that a biproduct of their previously reported synthesis of $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2\{Sn(bppd)\}]$ {bppd = bis(1,3-diphenyl-1,3-propanedione)} is the claret-red, air-sensitive complex $[Mn(bppd)_2(thf)_2]$. An X-ray crystal structure determination reveals that the coordination sphere is a near perfect octahedron, with the bppd ligands being bidentate and the thf ligands *trans*- and coplanar [110].

Complexes of manganese(II) with *N*,*N*-dimethyl- and *N*,*N*-diethylurea [111], methyl-, ethyl- and phenylsalicylates [112], neutral phosphonate alkyl esters [113], picolinic acid *N*-oxide [114], 2-hydroxy-4-methoxyacetophenoneoxime [115], 8-quinolinol *N*-oxide [116], 1,4-dihydroxyanthraquinone (quinizarin) [117] and benzoxazole-2-thione [118] have also been reported, as have the complexes $Mn[Al(OCHMe_2)_4]_2$ [119], $[Mn(thf)_6][SbCl_6]_2$ [120] and $[Mn\{MePh(MeO)PO\}_4(OH_2)][ClO_4]_2$ [121].

9.4.6 *Phthalocyanine and porphyrin complexes*

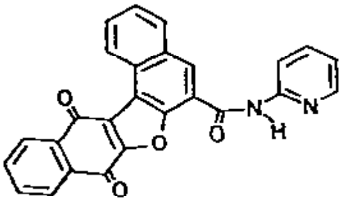
An X-ray determination of the phthalocyaninato-complex [Mn(pc)] shows it to have the structure (12) [122]. Evidence has been presented to support



(12)

the earlier proposition by Uchida et al. [123] that the intermediate in the reaction of [Mn(pc)] with dioxygen in pyridine solution is $[(O_2)Mn(pc)]$

[124]. The formation constant of a 1 : 1 charge-transfer complex between manganese phthalocyanine and (13) has been determined by absorption and luminescence spectroscopy [125].



(13)

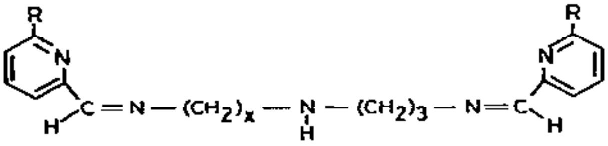
The rate of oxidation of tetra(4-sulphonatophenyl)porphinatomanganese(II) in aqueous solution by dioxygen has been reported. The products are the Mn(III) porphyrin complex and hydrogen peroxide [126]. Tetra(4-*t*-butylbenzo)porphinatomanganese(II) has also been prepared and characterised [127].

The crystal structures of the 5-coordinate complex nitrosyl(tetratolylporphinato)manganese(II), and the 6-coordinate complex nitrosyl(4-methylpiperidine)(tetraphenylporphinato)manganese(II) have been determined. Both complexes contain an essentially linear Mn—N—O unit [128].

The complexes [Mn(TPP)(L)] (TPPH$_2$ = *meso*-tetraphenylporphyrin; L = py, 1-methylimidazole, Me$_2$CHCH$_2$NH$_2$, 3,4-dimethylpyridine, 4-cyanopyridine, *N,N'*-ethylenebis(benzoylacetiminato)cobalt(II) or tributylphosphine) react with dioxygen at −78°C to give the complex Mn(TPP)(O$_2$) [129]. EPR studies of a series of dioxygen adducts of manganese(II) porphyrins [Mn(Por)(O$_2$)] (Por = 4-substituted tetraphenylporphyrin or octaethylporphyrin) indicate that, unlike the Co, Fe and Cr analogues which are octahedral, they exhibit five coordination. NMR data support their formulation as $Mn^{IV}—O_2^{2-}$ with a symmetric, edge-on oxygen molecule [130].

9.4.7 Complexes with nitrogen donor ligands

Complexes of manganese(II) with the potentially five-coordinate Schiff bases (14) have been shown to be six-coordinate, the sixth site being occupied by solvent, halide or NCS$^-$ ion [131]. The lack of reactivity with O$_2$ and NO was also discussed.



(14)

x = 2, 3, or 4, R = H; x = 3, R = CH$_3$

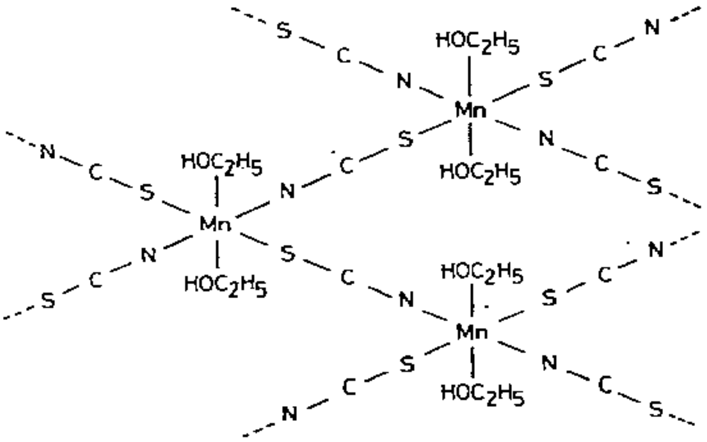
Horvath et al. [132] report that carefully prepared anhydrous MnCl$_2$ reacts with lithium hexamethyldisilylamide, $Li[N(SiMe_3)_2]$ in thf to give $[Mn\{N(SiMe_3)_2\}_2(thf)]$ in good yield. With excess of L (L = thf, py or $NCCMe_3$) the tetrahedral complexes $[Mn\{N(SiMe_3)_2\}_2L_2]$ were obtained. Reaction of $MnCl_2$ with the stoicheiometric amount of $Li[N(SiMe_3)_2]$ in thf led to the formation of $[ClMn\{N(SiMe_3)_2\}(thf)]$ which was used in situ for a variety of syntheses, including that of the novel complex $[Mn\{N(SiMe_3)_2\}(benzene)_2]$. $[ClMn\{N(SiMe_3)_2\}(thf)]$ may also be prepared by the reaction of $[MnCl_2(thf)_2]$ with $[Mn\{N(SiMe_3)_2\}_2(thf)_2]$ [132].

Manganese complexes with picolinoyl hydrazide [133], *N,N'*-bis(2'-pyridinecarboxamide)-1,2-benzene [134] or 1-propylimidazole [135] have been reported, together with several salts of $[Mn(NCMe)_6]^{2+}$ [136,137].

9.4.8 Other complexes of manganese(II)

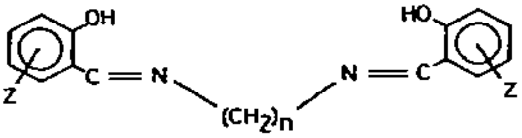
Complexes, $Mn(TCNQ)_2 \cdot n\ H_2O$ (n = 0, 1 or 2.5), of manganese(II) with the radical anion 7,7,8,8-tetracyanoquinodimethane ($TCNQ^-$) have been reported, and it was found that the Mn—Mn exchange interaction changes from antiferromagnetic to ferromagnetic at 20 K [138].

The crystal structure of dichlorobis(picoline hydrazide)manganese(II) indicates that the metal atom is octahedrally coordinated by 2 Cl, 2 N and 2 O atoms, the Cl atoms being *cis* [139]. The thermal decompositions of complexes $MnL_2 \cdot 2\ Q$ ($HL = RCOCH_2COR'$ where $R = CF_3$, $CF(CF_3)_2$ or C_3F_7 and R' = Me, CF_3 or CMe_3; Q = py or dmf) have been studied [140]. $MnCl_2$ reacts with $[NH_4]CN$ in coordinating solvents (L), e.g. Me_2SO, dmf or dma, to give complexes $Mn(CN)_2L$ [141]. The crystal structure of the two-dimensional Heisenberg magnet $[Mn(NCS)_2(C_2H_5OH)_2]$ is reported [142], it having the layer structure (15). The magnetic properties of the complexes $MnC_2O_4 \cdot 2\ H_2O$, $MnC_2O_4 \cdot N_2H_4$ and $MnC_2O_4 \cdot 2\ N_2H_4$ have also been studied and interpreted [143].



(15)

Numerous manganese(II) complexes of (16) have been isolated [144] and their reactions with dioxygen investigated.



(16)

Polarographic studies of the complexes between Mn(II)/ethylene glycol/ammonia [145] and Mn(II)/triethanolamine/hydroxylamine [146] in solution, together with electronic spectra have been reported. Complexes with the following ligands have also been reported: 3,3′-benzidine dicarboxylic acid [147], diacetylhydrazine [148], quinoxaline 1,4-dioxide [149], dihydro-bis-(1-indazolyl)borate [150], 8-hydroxyquinoline [151,152], isopropoxyphenylsuccinimide [153], a butanedioic ester [154], sulphafurazole salicylaldimine [155], orotic acid [156], chlorodimorpholinophosphine oxide [157], 2,4-dihydroxyvalerophenone oxime [158,159], 2-carbethoxypyridine [160], 3-(1-hydroxyphenyl)-5-phenyloxazole [161], *N*,*N*-diethylnicotinamide [162], nicotinamide [163], 2-benzoylpyridine [164], cysteic acid [165], acrylamide [166], α-aminobutanoic acid [167], 3-(*N*-2-furfuralideneimino)propanoic acid [168], diphenylthiovioluric acid [169], ethylenediamine-*N*,*N*′-diacetic acid [170], dimethylurea [171], 2,2-diphenylacetohydroxamic acid [172], 2-hydroxy-5-methylbenzophenoneanil [173], 2-hydroxy-5-methylacetophenoneanil [174], 1-(2-lepidylazo)-2-acenaphthylenol, 1-(2-quinolylazo)-2-acenaphthylenol [175], sulphadimethoxine [176], succinyl diacetone hydrazone [177], 1,4-di(4-methylanilino)anthraquinone, 1-amino-2-bromo-4(2-sulpho-4-methylanilino)anthraquinone [178], tolylbenzohydroxamic acids [179,180], formylchromone acylhydrazones [181,182], oxalyl dihydrazine [183], acetophenone acylhydrazones [184], 1-vinylimidazole [185] and nicotinic acid [186].

9.5 MANGANESE(I)

The crystal structure of hexakis(ethylisocyanide)manganese(I) tri-iodide, $[Mn(CNC_2H_5)_6][I_3]$ has been shown to exhibit approximately octahedral coordination [187].

9.6 CARBONYL COMPLEXES

9.6.1 Carbonyls and hydridocarbonyls

The obvious fact that, for Mn—Mn bonds, there is no correlation between bond-length and bond-order has been explicitly stated [188].

The Raman spectra of crystalline $[Mn_2(CO)_{10}]$, $[Re_2(CO)_{10}]$, mixed Re/Mn crystals and ^{13}C doped samples have been reported [189]. An EPR study of the reaction between manganese metal (in thf) and $[Mn_2(CO)_{10}]$ has indicated that the solutions contain both Mn^{2+} and $[Mn(CO)_5]^-$ [190]. $A[R_3BH]$ {A = Li or K; R = Et or Me_2CHCH_2} react with $[Mn_2(CO)_{10}]$ to give near quantitative yields of $A[Mn(CO)_5]$, which may be used to prepare mixed-metal and other complexes [191].

Three new in situ preparations of anhydrous $[HMn(CO)_5]$ have been reported [192].

$Li[Mn(CO)_5] + CF_3SO_3H \rightarrow [HMn(CO)_5] + Li[CF_3SO_3]$

$[(Ph_3P)_2N][Mn(CO)_5] + CF_3SO_3H \rightarrow [HMn(CO)_5] + [(Ph_3P)_2N][CF_3SO_3]$

$[(Me_3Si)Mn(CO)_5] + MeOH \rightarrow [HMn(CO)_5] + Me_3SiOMe$

$H^{13}C(O)OC(O)CH_3$ reacts with $Na[Mn(CO)_5]$ at 0°C to give $[HMn(CO)_4(^{13}CO)]$ via a formyl intermediate $[(CO)_5Mn\text{-}^{13}CHO]$ [193].

The XPES spectra of $[Mn_2(CO)_{10}]$ and $[HMn(CO)_5]$ have been measured [194]. Photolytic decomposition of $[H_3Mn_3(CO)_{12}]$ in 2,2,4-trimethylpentane solution has been reported to lead to the formation of $[Mn_2(CO)_{10}]$ and $[HMn(CO)_5]$ in approximately equal amounts. An insoluble brown precipitate is also formed, but this is not observed if the reaction is performed under an atmosphere of carbon monoxide [195]. The photochemistry of $[HMn(CO)_5]$ in inert and CO matrices has been reported. In CO the principal product shows a spectrum consistent with C_{4v} $[Mn(CO)_5]$ and a new species with $\nu(CO)$ bands at 1989 and 1976 cm^{-1} was also observed, along with HCO [196].

9.6.2 *Halides*

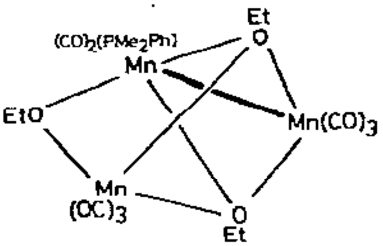
Methods for preparing $[Mn(CO)_5Cl]$ in 86% yield [197], $[Mn(CO)_5Br]$ in 90% yield [198] and $[Mn(CO)_5I]$ in 80% [199] and 50% [200] yields have been reported. An IR and Raman spectroscopic study of $[Mn(CO)_5Br]$ has been described [201], and the systems $[Mn_xRe_{1-x}(CO)_5X]$ ($0 \leqslant x \leqslant 1$; X = Cl or Br) and $[Mn(^{12}CO)_{5-y}(^{13}CO)_yX]$ ($0 < y < 5$) have also been studied by the same techniques [202]. The reactions between $[Mn(CO)_5X]$ and $[Et_4N]X$ (X = Cl or Br) in boiling trichloromethane yield the binuclear complexes $[Et_4N][Mn_2(CO)_6(\mu\text{-}X)_3]$ [203].

Kinetic studies of the reactions of $[Mn(CO)_5X]$ (X = Cl, Br or I) with cyanide ion to give $[Mn(CO)_4(CN)_2]^-$ have indicated that for chloride, the intermediate is $[Mn(CO)_5(CN)]$, whereas for bromide or iodide the intermediate is $[Mn(CO)_4(CN)X]^-$ (X = Br or I) [204].

9.6.3 *Complexes with oxygen ligands*

EPR studies of the photolytic reactions of $[Mn_2(CO)_{10}]$ in the presence of air or dioxygen at low temperatures have yielded EPR parameters for the complexes $[Mn(CO)_4L(O_2)]$ (L = CO, PPh_3, PBu_3 or $P(OEt)_3$). Isotropic coupling constants for the two atoms in the dioxygen moiety have been determined by ^{17}O labelling [205].

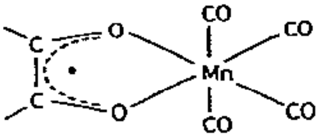
$[Mn(CO)_5Br]$ reacts with $SnMe_3(OR)$ (R = Me, Et, Pr, Me_2CH, Bu, C_6H_{11}, $CH_2CH{=}CH_2$ or CH_2Ph) to form complexes $[\{Mn(OR)(CO)_3\}_3]$ and also (when R = CH_2Ph) $[\{Mn(OCH_2Ph)(CO)_3\}_4]$. Reaction of $[\{Mn(OEt)(CO)_3\}_3]$ with Me_2PhP leads to the formation of $[Mn_3(OEt)_3(CO)_8(PMe_2Ph)]$ (17)



(17)

which was shown by X-ray crystallography to contain an Mn_3 unit. Reaction of $[\{Mn(OEt)(CO)_3\}_3]$ with phenol leads to the formation of $[Mn_3(OEt)_2(OPh)(CO)_9]$, whereas reaction with thiophenol gives the well known tetrameric complex $[\{Mn(SPh)(CO)_3\}_4]$ [206].

The photolytic reactions between $[Mn_2(CO)_{10}]$ and some 1,2-dicarbonyl compounds gave octahedrally coordinated radical adducts (18), the EPR

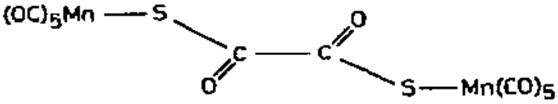


(18)

spectra of which were reported [207]. Pentane-2,4-dionato complexes of manganese carbonyls and their derivatives have also been studied [208,209]. Some complexes of propanone and thf are discussed in Section 9.6.6.

9.6.4 Complexes with sulphur and selenium ligands

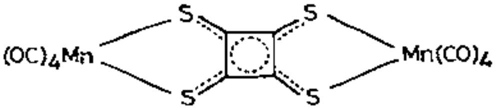
The preparation and molecular structure of μ-1,2-dithiooxalato(*S*,*S'*)-bis-(pentacarbonylmanganese(I)) (19) have been reported [210], and a related



(19)

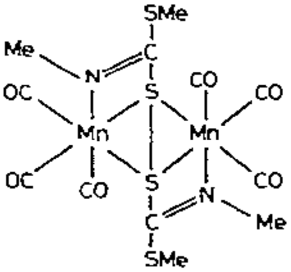
red manganese bis-chelate complex (20) of tetrathiosquarate ($C_4S_4^{2-}$) has also been prepared [211].

$Na[Mn(CO)_5]$ reacts with RNCS (R = Me or Ph) to give the dithiocarbamato-complexes $[Mn(CO)_4\{S_2CN(H)R\}]$ and $[Mn(CO)_3(CNR)\{S_2CN(H)R\}]$;



(20)

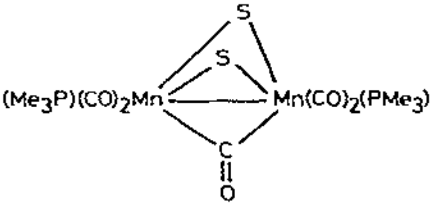
addition of RNCS to the former also leads to formation of the latter. Treatment of Na[Mn(CO)$_5$] with MeNCS followed by MeI, gives predominantly [Mn$_2$(CO)$_6${μ-SC(SMe)(NMe)}$_2$] (21), which has been crystallographically characterised {r(MnMn) = 0.323 nm} [212].



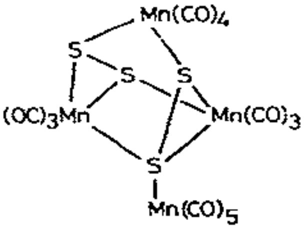
(21)

Treatment of [N(PPh$_3$)$_2$][Mn(CO)$_5$] with CS$_2$ in thf leads to the formation of [N(PPh$_3$)$_2$][Mn(CO)$_4$(S$_2$CS)], methylation of which with MeI, SFO$_2$(OMe) or GeBrMe$_3$, gives [Mn(CO)$_4$(S$_2$CSMe)], whereas phenylation with [PhN$_2$]-[BF$_4$] gives only low yields of [Mn(CO)$_4$(S$_2$CSPh)]. Treatment of Na[Mn-(CO)$_5$] with CS$_2$, followed by MeI, gives only low yields of trithiocarbonato-complexes, together with very small amounts of the dimeric species [(OC)$_4$-Mn(μ-S$_2$CS)Mn(CO)$_5$]. On addition of free sulphur to [N(PPh$_3$)$_2$][Mn(CO)$_5$], an immediate colour change from yellow to red occurs, due to formation of [N(PPh$_3$)$_2$][MnS$_n$(CO)$_5$] (n = 1—8). With CS$_2$, this generates the species [N(PPh$_3$)$_2$][Mn(CO)$_4$(S$_2$CS)], whilst MeI gives [N(PPh$_3$)$_2$][MnI$_2$(CO)$_4$] [213].

The chemical oxidation of [(Me$_3$P)$_2$(CO)$_3$Mn(SX)], [(Me$_3$P)$_2$(CO)$_5$Mn$_2$-(SX)$_2$] (22) and [(CO)$_8$Mn$_2$(SX)$_2$] (23) (X = H or SnMe$_3$) has been studied



(24)



(25)

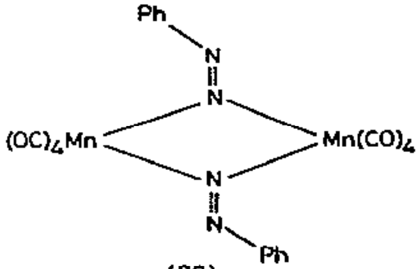
[214]. No identifiable products were obtained when X = H, but when X = SnMe$_3$, oxidation of (22) gave (24) and oxidation of (23) gave (25), whose structure was confirmed crystallographically.

The selenium bridged dimers [(CO)$_4$Mn(SeX)]$_2$ (X = H or SnMe$_3$) have been reacted with Me_3P to give the dimers $[(Me_3P)(CO)_3Mn(SeX)]_2$ and/or the monomers $[(Me_3P)_2(CO)_3Mn(SeX)]$ [215].

9.6.5 Complexes with nitrogen ligands

The tricarbonylmanganese complex of the tridentate tris-chelating ligand methyltris(3,5-dimethylpyrazol-1-yl)gallate, $[MeGa(N_2C_5H_7)_3]^-$, has been prepared and characterised and the ligand shown to coordinate via the free pyrazolyl nitrogen atoms [216]. The tricarbonylmanganese complexes of the tridentate tris-chelating ligand $[Me_2Ga(OCH_2CH_2NH_2)(N_2C_3H_3)]^-$ (and its methyl substituted derivatives) have been prepared and characterised [217].

The weak acid $HNSOF_2$ also coordinates through nitrogen in the complex $[Mn(CO)_5(HNSOF_2)]$ [218]. $[Mn(CO)_5Br]$ reacts with $PhN{=}NSiMe_3$ to give bis(μ-phenyldiazenido)octacarbonyldimanganese (26), which reacts with triphenylphosphine to give two mononuclear five-coordinate complexes $[Mn(CO)_3(N_2Ph)(PPh_3)]$ and $[Mn(CO)_2(N_2Ph)(PPh_3)_2]$ [219]. $[Mn(CO)_5\{M'(CO)_3(RN{=}CHCH{=}NR)\}]$ (M' = Mn or Re; R = Me_2CH, 4-Me-C_6H_4 or 4-MeO-C_6H_4) [220] and *fac*-$[Mn(CO)_3X(RN{=}CHCH{=}NR)]$ (X = Cl, Br or I; R = CMe_3, Me_2CH, Ph, 4-Me-C_6H_4, 4-MeO-C_6H_4 or 4-Cl-C_6H_4) have been reported; $[Mn(CO)_3Cl(Me_3CN{=}CHCH{=}NCMe_3)]$ reacts with $Ag[BF_4]$ under CO to yield $[Mn(CO)_4(Me_3CN{=}CHCH{=}NCMe_3)][BF_4]$ [221].



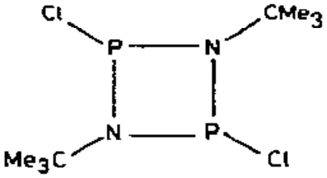
(26)

EPR measurements have been used to establish that, when a solution of $[Mn_2(CO)_{10}]$ in thf is irradiated in the presence of 4-methylpyridine, a paramagnetic species is produced. A similar but more stable species is produced on irradiating in the presence of polyvinylpyridine. The species involved are believed to be $[Mn(CO)_4L]^-$-(L = 4-methylpyridine or polyvinylpyridine) [222].

9.6.6 Complexes with phosphorus and arsenic ligands

Treatment of $[Mn(CO)_5Br]$ with $Ag[ClO_4]$ in CH_2Cl_2, followed by addition of ligand L, leads to the formation of the complexes $[Mn(CO)_5L][ClO_4]$ (L = PEt_3, PBu_3, $PEtPh_2$, $PMePh_2$, PEt_2Ph, PPh_3, $AsPh_3$, $SbPh_3$, $PPh_2(OEt)$, $P(OMe)_3$, $P(OEt)_3$, o-$C_6H_4(NH_2)_2$, 4-methylpyridine, Me_2CO or thf). Solutions of $[Mn(CO)_5L][ClO_4]$ (L = Me_2CO or thf) in their respective solvent L are trans-formed to the complexes *fac*-$[Mn(CO)_3L_3][ClO_4]$. *fac*-$[Mn(CO)_3(Me_2CO)_3]$-$[ClO_4]$ reacts with L′ (L′ = PEt_3, PBu_3, PEt_2Ph, $PMePh_2$, $PEtPh_2$, $PPh_2(OEt)$ or 4-methylpyridine) to give *fac*-$[Mn(CO)_3L'_3][ClO_4]$ and these complexes are readily isomerised to the *mer*- forms. With L′ (L′ = $PPh(OEt)_2$, $PPh(OMe)_2$ or $P(OMe)_3$), *cis*-$[Mn(CO)_2L'_4][ClO_4]$ are formed, which may be isomerised to their *trans* forms [223]. Cationic aquatetracarbonylmanganese(I) complexes *cis*-$[Mn(CO)_4(OH_2)(L)][BF_4]$ {L = PPh_3, PEt_3, PMe_2Ph, $PMePh_2$ or PPh-$(OMe)_2$} have been reported, and the PPh_3 derivative has been used to prepare $[Mn(CO)_4L'(PPh_3)]^+$ (L′ = py, $CNCMe_3$, $CH_2{=}CHCN$, SMe_2, H_2S, PPh_3 or CO) salts [224].

$[Mn_2(CO)_{10}]$ reacts with 2,4-dichloro-1,3-di-*t*-butyldiazaphosphetidine (27) to give a complex which has been tentatively formulated as [Mn(CO)-$\{Cl_2P_2N_2(CMe_3)_2\}_2$] on the basis of ^1H NMR and IR evidence [225].



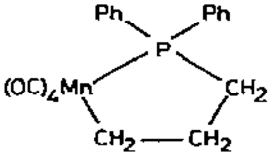
(27)

The σ-bonded phosphole, arsole and stibole complexes $[(Ph_4C_4E)Mn(CO)_5]$ (28) (E = P, As or Sb) have been prepared by reaction of Ph_4C_4ECl with Na-$[Mn(CO)_5]$. Controlled decomposition of (28) (E = P or As) led to the formation of the bridged dimers $[\{Mn(CO)_4(\mu\text{-}EC_4Ph_4)\}_2]$ (29), from which one or two carbonyl groups may be replaced by other π-acceptor ligands such as PPh_3 [226]. On heating (28) (E = P or As) they lose carbon monoxide to give the complexes $[Mn(CO)_3(\eta^5\text{-}EC_4Ph_4)]$ (30), which may also be formed by loss of CO from the dimers (29), by the action of $Ph_4C_4E\text{-}EC_4Ph_4$ (E = P or As) upon $[Mn_2(CO)_{10}]$, or by the action of $Ph_4C_4AsSiMe_3$ upon $[Mn(CO)_5Cl]$. One carbonyl group may be displaced from (30) (E = As) by reaction with π-acceptor ligands such as PPh_3, $PhC{\equiv}CPh$ or NO^+ [227].

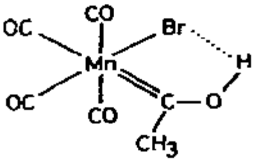
$[MnBr(CO)_4\{P(OH)R_2\}]$ (R = CH_3 or C_6H_5) reacts with sodium amalgam in ether to form the binuclear salt $Na_2[(OC)_4Mn\{P(O)R_2\}]_2$, which, with excess sodium, gives the mononuclear salt $Na_2[Mn(CO)_4\{P(O)R_2\}]$; these react with dimethyl sulphate to give $[CH_3Mn(CO)_4\{P(OCH_3)R_2\}]$ [228]. Treatment of $[HMn(CO)_5]$ with $P(CF_3)_2(OCH_2CH_2Cl)$, (L), gives $[HMn(CO)_4L]$ which reacts with CCl_4 to give a mixture of $[MnCl(CO)_4L]$ and $[Mn_2Cl_2(CO)_8]$. Treatment of $[MnX(CO)_4L]$ (X = H or Cl) with NMe_3 (X = H) or Na/Hg (X = Cl) gives $[Mn(CO)_4(\eta\text{-}C_2H_4)\{P(CF_3)_2O\}]$ by a novel rearrangement reaction [229]. $[Mn(CO)_3\{(R_2PCH_2)_3CCH_3\}][ClO_4]$ (31a) (R = C_6H_5) reacts with $NaBH_4$ on UV irradiation to give $[HMn(CO)_2\{(R_2PCH_2)_3CCH_3\}]$. However, the tetraphenylborate salt (31b) gives only decomposition products. Reaction of (31a) or (31b) with NaOH in propanone/water gives $[HMn(CO)_3\{(R_2PCH_2)_2\text{-}C(CH_3)CH_2PR_2\}]$ where the ligand is now only bidentate [230]. The reaction of $[Mn_2(CO)_{10}]$ with 2,3-bis(diphenylphosphine)maleic anhydride (PP) leads to formation of the paramagnetic complex $[(PP)Mn(CO)_4]$, and EPR studies indicate that the unpaired electron is localised on the phosphine ligand [231].

9.6.7 Organometallic complexes

The mechanism of the "carbonyl insertion reaction" in $[CH_3Mn(CO)_5]$ has been discussed on the basis of a molecular orbital study; a five-coordinate intermediate has been postulated [232]. Reaction of $[Mn(CO)_5Br]$ with $Ph_2P(CH_2)_3MgCl$ in thf leads to formation of the five-membered metallocycle (32), the structure of which is confirmed by X-ray crystallography. The six-membered homologue has been prepared by an analogous reaction [233]. It is reported that $ClCH_2COCl$ reacts with $Na[Mn(CO)_5]$ to produce $[(CO)_5MnCOCH_2Cl]$, thermal decomposition of which gives $[Mn(CO)_5Cl]$ and $[Mn(CO)_4Cl]_2$. However, photochemical decomposition gives only $[Mn(CO)_5Cl]$ [234]. A new route to the carbene (33) has been developed and involves treatment of $[MnBr(CO)_5]$ with MeLi at −78°C to give *cis*-$[Mn(CO)_4Br\{C(O)Me\}]^-$, which is then protonated [235].



(32)

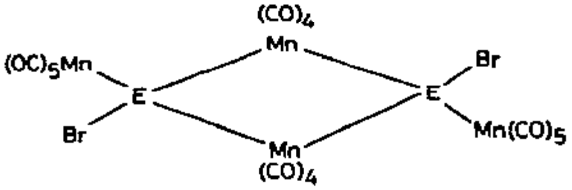


(33)

Reaction of $[Mn(CO)_{5-n}(CNC_6H_5)_nBr]$ (n = 2, 3 or 4) with CO or CNC_6H_5 and the presence of a halide acceptor is reported to yield the compounds $[Mn(CO)_{6-m}(CNC_6H_5)_m][PF_6]$ (m = 2–6). Replacement of Br^- by CO or CNC_6H_5 is stereospecific, allowing synthesis of *fac*- and *mer*-isomers (n = 3) and *cis*- and *trans*-isomers (n = 4) [236].

9.6.8 Germyl and stannyl complexes

Methods for the preparation of the germanium—manganese cluster compounds $[Mn_2(CO)_8\{\mu\text{-}GeXMn(CO)_5\}_2]$ (X = Br or I) have been reported [237] and the structures of $[Mn_2(CO)_8\{\mu\text{-}E(Cl)Mn(CO)_5\}_2]$ (E = Ge or Sn) (34) have been shown to contain a planar Mn_2E_2 rhombus with Mn—Mn bond distances of 0.2923 or 0.3091 nm, respectively [238,239]. The reaction of



(34)

Me_3SnBr with $[Mn(CO)_3(PPh_3)_2]^-$ is unusual in that methyl (rather than bromide) elimination occurs yielding the complex $[\{BrMe_2Sn\}Mn(CO)_3(PPh_3)_2]$, which has been studied crystallographically [240]. The molecular structure of $[BrSn\{Mn(CO)_5\}_3]$ has also been determined and possesses a distorted tetrahedral configuration with three different Mn—Sn bond distances [239]. The thermal decomposition of $[Ph_3SnMn(CO)_5]$ has been studied [241].

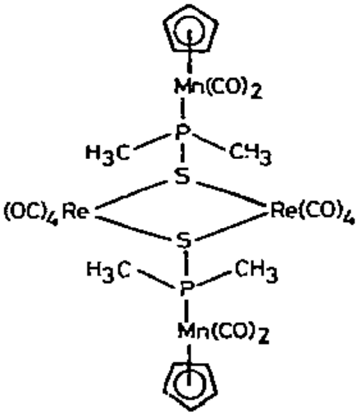
$[(PPh_3)_2N][Mn(CO)_5]$ has been proposed as a convenient starting material for the synthesis of alkyl, germyl and stannyl derivatives of $[Mn(CO)_5]^+$ [242] and indeed $[Mn(CO)_5]^-$ is reported to replace $[Co(CO)_4]^-$ from $[Co(CO)_4(Ge_2H_5)]$ to give $[Mn(CO)_5(Ge_2H_5)]$ [243].

9.6.9 Complexes with group IIIB ligands

A convenient high yield preparation of the complex $[(CO)_4Mn(B_3H_8)]$, has been reported [244]. The crystal structure of $[Fe_2(CO)_8][InMn(CO)_5]_2$ has also been reported [245].

9.6.10 Mixed-metal carbonyls

The reactions of $[MnRe(CO)_{10}]$ with $As_2(CF_3)_4$ and of $[MnCo(CO)_9]$ with $E_2(CF_3)_n$ (E = P or As, $n = 4$; E = S or Se, $n = 2$), $(CF_3)_2E'I$ (E′ = P or As), $(CF_3)_2AsH$, $(CF_3)_2AsE''CF_3$ (E″ = S or Se), $(CF_3)_2PSeCF_3$, Me_2AsI or $(CF_3)_2$-



(35)

$PPMe_2$ are reported to yield, in addition to the known mono- and binuclear species, the heteronuclear complexes $[MnRe(CO)_8\{As(CF_3)_2\}_2]$ or $[MnCo(CO)_7\{E(CF_3)_2\}_2]$, respectively [246]. $[MnTc(CO)_{10}]$ has been prepared by reaction of $[Tc(CO)_5Br]$ with $[Mn(CO)_5]^-$ [247].

The reaction of $Na[(\eta^5\text{-}C_5H_5)Mn(CO)_2P(CH_3)_2S]$ with $[Re(CO)_5Cl]$ gives the complex (35) [248]. The reaction of $Na[Mn(CO)_5]$ with $(C_2H_5)_2AlCl \cdot thf$, in thf with excess of Na/Hg, is reported to give $[\{(CO)_5Mn\}_2Hg] \cdot thf$ [249], which irreversibly loses thf at room temperature.

Reaction of *cis*-$[Pt(C_6H_{11}NC)_2Cl_2]$ or *trans*-$[Pt(Me_3CNC)_2Cl_2]$ with $Na[Mn(CO)_5]$ in thf led to the formation of the complexes $[(CO)_5Mn\text{-}PtL_2\text{-}Mn(CO)_5]$ ($L = C_6H_{11}NC$ or Me_3CNC) [250].

9.7 NITROSYL COMPLEXES

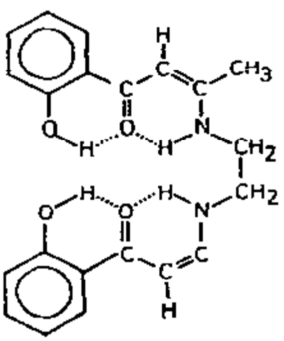
The crystal structures of the monoclinic [251] and triclinic [252] forms of chlorodinitrosylbis(dimethylphenylphosphonite)manganese and also of dinitrosyltris(dimethylphenylphosphonite)manganese tetrafluoroborate have been reported. Each structure is based on trigonal bipyramidal coordination, with two axial phosphonite ligands [253]. The preparation, properties and thermal decomposition of the complex $[Ph_3PH]H_2[Mn(CN)_5NO] \cdot H_2O$ are reported [254].

9.8 MIXED OXIDATION STATE COMPLEXES

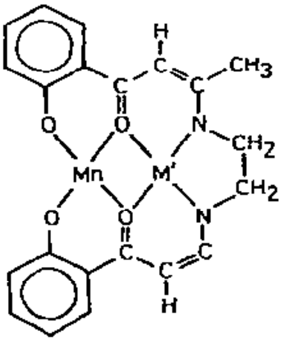
EPR and magnetic susceptibility studies on the di-μ-oxo-bridged complexes $[(LL)_2MnO_2Mn(LL)_2]^{3+}$ (LL = 2,2′-bipyridine or 1,10-phenanthroline) show that, at room temperature, the complexes possess non-equivalent manganese ions that are strongly antiferromagnetically coupled [255].

9.9 HETERONUCLEAR COMPLEXES

The Schiff base (36; H_4aapen) has been used to prepare the heterobinuclear complexes, [MnM′(aapen)] (M′ = Ni or Cu) (37). The manganese ion is coor-

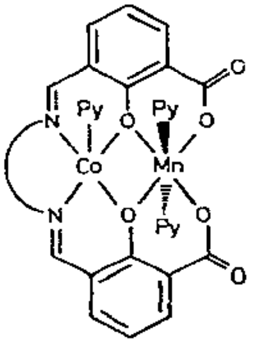


(36)



(37)

dinated by four O atoms and the M′ ion by two O and two N atoms [256]. Complexes [CoMn(fsaen)(py)$_3$] and [CoMn(fsapn)(py)$_3$] (H_4fsaen = *N,N′*-bis(3-carboxysalicylidene)ethylenediamine, H_4fsapn = *N,N′*-bis(3-carboxysalicylidene)propylenediamine) have been prepared [257]. Electronic spectra are consistent with the structures (38) and variable-temperature magnetic measurements show no exchange interaction between low-spin five-coordinate Co(II) and high-spin six-coordinate Mn(II).



(38)

The crystal structure and low-temperature magnetic properties of the biphenyl clathrate complex [$Mn(NH_3)_2Ni(CN)_4 \cdot 2\ C_{12}H_{10}$] have been reported [258,259].

9.10 MODIFIED SURFACES

The field of modified surfaces is one of growing interest, and this is reflected both by the appearance of a recent review [260] and also by the significant number of reports which have appeared this year involving manganese complexes.

Tetra(aminophenyl)porphyrin has been bonded via the amino function to oxidised glassy carbon surfaces, and the immobilized porphyrin was then metallised with Mn(II) and studied by cyclic voltammetry [261,262]. A study of the comparative rates of metallation by Mn^{2+} and other divalent metal ions of surfactant porphyrins both in solution and bound as monolayer films to surfaces has also been made [263]. Manganese(III) phthalocyanine and porphyrin complexes have previously been observed to disproportionate upon irradiation with visible light to give a powerfully reducing Mn(II) complex and powerfully oxidising Mn(IV) complex. The surface-active porphyrin complex *meso*-tetrakis-(4-*N*-stearylpyridinium)porphyrin manganese(III) tetraiodide monohydroxide was used to modify a platinum electrode, which was then successfully used to generate electricity in a wet solar cell [264,265]. Photoelectrochemical evolution of dioxygen from water has been achieved using a liquid crystal membrane incorporating manganese chlorophyll, attached to a platinum electrode [266].

9.11 COMPLEXES OF BIOCHEMICAL SIGNIFICANCE

This section is brief; for a more detailed review of this literature please refer to The Chemical Society Specialist Periodical Reports upon Inorganic Biochemistry (Ed. H.A.O. Hill).

A review of the importance of manganese in biological systems has been published [267], and work on manganese dioxygen carriers included in a more general review of synthetic oxygen carriers related to biological systems [268].

Formation constants for the complex MnA (H_2A = *S*-carboxymethyl-L-cysteine) and related complexes of other metals are reported [269]. Interactions between Mn^{2+} ions and the dinucleotides NAD and NADP have been studied by circular dichroism [270], EPR [271] and NMR [272]. NMR measurements have also been used to examine the formation of ternary complexes of 5'-ATP and numerous amino acids with Mn^{2+} [273].

Complexes of manganese(II) with salicyloylhydrazine or benzoylhydrazine (HL) and histidine (HZ) have been reported, of types MnLZ, $[Mn(HL)(HZ)Cl_2] \cdot n\ Q$ (Q = EtOH, Me_2CO, H_2O or NH_3), [MnCl(HL)Z] and $[Mn(HL)_2(HZ)]Cl_2$ [274,275]. Manganese(II) complexes with glycine [276,277], glutamine [278], histidine [278,279], valine [280,281], β-alanine [280, 282], 9-methyladenine [283], γ-globulin and human serum albumin [284], and various penicillins [285] have also been prepared.

9.12 REVERSIBLE OXYGENATION OF MANGANESE(II) PHOSPHINE COMPLEXES

Following two secondary accounts [286,287], a primary report [288] that the novel complexes $MnLX_2$ (X = various anions, L = various tertiary phosphines but not PPh_3) resemble haemoglobin and myoglobin in their behaviour as dioxygen carriers has been published. More than two hundred complexes of this general formulation are claimed and are believed to be at least dimeric (possibly tetrameric), containing both terminal and bridging X ($\mu_{eff} \sim 6\mu_B$: no observable EPR signals). They are pale in colour, and described as reacting with dioxygen (either in the solid state or in many non-hydroxylic solvents) to form deeply coloured red, blue, purple or green complexes, of formulation $MnLX_2(O_2)$. The absorption of dioxygen is reported to be stoicheiometric and completely reversible, as a function of the partial pressure of O_2 present over the complex. These dioxygen adducts are described as having $\mu_{eff} \sim 6.9$ μ_B (explained in terms of the complexes containing 50 : 50 mixtures of coordinated singlet and triplet O_2) and $\nu(O—O) = 1402$–$1430\ cm^{-1}$. The complex $[Mn(PBu_3)Br_2(O_2)]$ in thf shows two bands in its visible spectrum at 569 nm ($\epsilon \sim 270\ l\ mol^{-1}\ cm^{-1}$) and 414 nm ($\epsilon \sim 200\ l\ mol^{-1}\ cm^{-1}$) [288]. If substantiated, this could be the most important chemical discovery of recent years.

In an independent investigation of this system [289], tetrahydrofuran solutions of manganese(II) halides with a variety of tertiary phosphines are found also to undergo reversible colour changes when dioxygen is added to or removed from the solutions. An identical electronic spectrum to that reported above for [$Mn(PBu_3)Br_2(O_2)$] was obtained by passing O_2 into a solution of $MnBr_2$ in thf containing PBu_3, except that the extinction coefficient of the 569 nm band was >9000 l mol^{-1} cm^{-1}. Moreover, the same spectrum was generated by oxidation of this solution (with the addition of Li[ClO_4] as support electrolyte) at a platinum electrode *in the absence of dioxygen.* The deeply coloured compounds formed have been tentatively described as manganese(III) phosphine complexes {or possibly mixed-valence Mn(III/II) species} and are thermally unstable at room temperature. Solutions, quasi-stable in the presence of excess O_2, decolourise when that excess is removed, giving rise to the appearance of reversible uptake of dioxygen.

REFERENCES

1 A. Serafini, J.C. Barthelat and Ph. Durand, Mol. Phys., 36 (1978) 1341.
2 K.A. Chapichadze and R.I. Agladze, Magnanumis Elektrokimia, Elektrokhimiya Margantsa (Tbilisi), (1978) 96.
3 R.Yu. Abdulsabirov, Yu.S. Greznev and V.G. Stepanov, Paramagn. Rezon., 12 (1976) 95.
4 S. Radhakrishna and K. Hariharan, Phys. Status Solidi B, 92 (1979) 293.
5 M. Arjomand and D.J. Machin, J. Less-Common Met., 61 (1978) 133.
6 T.R. White, W.S. Glaunsinger, H.S. Horowitz and J.M. Longo, J. Appl. Phys., 50 (1979) 1926.
7 D.T. Sviridov, R.K. Sviridova, N.I. Kulik and V.B. Glasko, Zh. Prikl. Spektrosk., 30 (1979) 481.
8 D.T. Richens and D.T. Sawyer, J. Am. Chem. Soc., 101 (1979) 3681.
9 I. Tabushi and N. Koga, Tetrahedron Lett., (1978) 5017.
10 D.M. Hood, R.M. Pitzer and H.F. Schaefer, J. Chem. Phys., 71 (1979) 705.
11 P. Köhler, W. Massa, D. Reinen, B. Hofmann and R. Hoppe, Z. Anorg. Allg. Chem., 446 (1978) 131.
12 V. Kaučič and P. Bukovec, Acta Crystallogr., Sect. B, 34 (1978) 3337.
13 P. Bukovec and V. Kaučič, Acta Crystallogr., Sect. B, 34 (1978) 3339.
14 V. Kaučič and P. Bukovec, J. Chem. Soc., Dalton Trans., (1979) 1512.
15 S. Sarkar, B. Sharma, R.C. Maurya, S.C. Chaurasia and S.K. Srivastava, Acta Cienc. Indica, 4 (1978) 21.
16 F. Lignou, Ber. Bunsenges. Phys. Chem., 83 (1979) 276.
17 I.G. Gorichev, L.V. Malov and F.G. Ashkharua, Kinet. Katal., 20 (1979) 67.
18 T. Nakamura, G. Petzow and L.J. Gauckler, Mat. Res. Bull., 14 (1979) 649.
19 K. Kamata, T. Nakajima and T. Nakamura, Mat. Res. Bull., 14 (1979) 1007.
20 K. Mereiter, Acta Crystallogr., Sect. B, 35 (1979) 579.
21 B.R. Stults, R.S. Marianelli and V.W. Day, Inorg. Chem., 18 (1979) 1853.
22 B.R. Stults, R.O. Day, R.S. Marianelli and V.W. Day, Inorg. Chem., 18 (1979) 1847.
23 R. Schmid and V.N. Sapunov, Int. J. Chem. Kinet., 11 (1979) 741.
24 R. Schmid, Ber. Bunsenges. Phys. Chem., 83 (1979) 522.
25 R. Schmid and V.N. Sapunov, Int. J. Chem. Kinet., 11 (1979) 1.
26 M. Periasamy and M.V. Bhatt, Tetrahedron Lett., (1978) 4561.
27 J. Barek, A. Berka and L. Nováková, Collect. Czech. Chem. Commun., 43 (1978) 1597.
28 T. Izumi, Y. Satou, Y. Yoshida and A. Kasahara, Bull. Chem. Soc. Jpn., 52 (1979) 1551.
29 J. Barek, A. Berka and A. Pokorná, Collect. Czech. Chem. Commun., 44 (1979) 1134.

30 J.L. Garnett, I.K. Gregor and M. Guilhaus, Org. Mass Spectrom., 13 (1978) 591.
31 R.F.X. Williams and P. Hambright, Bioinorg. Chem., 9 (1978) 537.
32 A. Giraudeau, H.J. Callot, J. Jordan, I. Ezhar and M. Gross, J. Am. Chem. Soc., 101 (1979) 3857.
33 G. McLendon and M. Bailey, Inorg. Chem., 18 (1979) 2120.
34 P. Hambright and R.F.X. Williams, Porphyrin Chem. Adv. (Pap. Porphyrin Symp.) 1977 (Pub. 1979) 284.
35 T.N. Lomova and B.D. Berezin, Zh. Neorg. Khim., 24 (1979) 1574.
36 M.C. Weiss and V.L. Goedken, Inorg. Chem., 18 (1979) 274.
37 W.M. Coleman, R.R. Goehring, L.T. Taylor, J.G. Mason and R.K. Boggess, J. Am. Chem. Soc., 101 (1979) 2311.
38 P. Gnanasundaram and H. Kothandaraman, Curr. Sci., 47 (1978) 897.
39 B.N. Figgis, G.L. Raston, R.P. Sharma and A.H. White, Aust. J. Chem., 31 (1978) 2545.
40 T. Yagi, J.C. Jamieson and P.B. Moore, J. Geophys. Res., B 84 (1979) 1113.
41 J. Barak, V. Jaccarino and S.M. Rezende, J. Magn. Magn. Mater., 9 (1978) 323.
42 B.A. Wilson, W.M. Yen, J. Hegarty and G.F. Imbusch, Phys. Rev. B: Condens. Matter, 19 (1979) 4238.
43 P.M.A. Sherwood, F.R. McFeely, S.P. Kowalczyk and D.A. Shirley, J. Chem. Soc., Faraday Trans. II, 75 (1979) 201.
44 R.J. van Zee, C.M. Brown and W. Weltner, Jr., Chem. Phys. Lett., 64 (1979) 325.
45 E.G. Ippolitov, T.A. Tripol'skaya and B.M. Zhigarnovskii, Zh. Neorg. Khim., 24 (1979) 539.
46 A.S. Moskvin and A.S. Luk'yanov, Fiz. Tverd. Tela (Leningrad), 21 (1979) 1826.
47 V.S. Kasperovich and V.V. Moskalev, Fiz. Tverd. Tela (Leningrad), 20 (1978) 3715.
48 T.T.P. Cheung, K.T. McGregor and Z.G. Soos, Chem. Phys. Lett., 61 (1979) 457.
49 C.M.J. van Uijen, E. Frikkee and H.W. de Wijn, Phys. Rev. B: Condens. Matter, 19 (1979) 509.
50 R. Dorshow, R.D. Hogg and V. Jaccarino, Phys. Lett. A, 73 (1979) 250.
51 M. Motokawa, J. Phys. Soc. Jpn., 45 (1978) 1528.
52 J.D. Tornero, F.H. Cano, J. Fayos and M. Martínez-Ripoll, Ferroelectrics, 19 (1978) 123.
53 Y. Mlik, A. Daoud and M. Couzi, Phys. Status Solidi A, 52 (1979) 175.
54 K.S. Aleksandrov, A.T. Anistratov, S.V. Mel'nikova, V.I. Zinenko, L.A. Shabanova and A.D. Shefer, Fiz. Tverd. Tela (Leningrad), 21 (1979) 1119.
55 K. Dörhöfer and W. Depmeier, Z. Anorg. Allg. Chem., 448 (1979) 131.
56 R.D. Willett, Acta Crystallogr., Sect. B, 35 (1979) 178.
57 R. Caputo and R.D. Willett, J. Chem. Phys., 69 (1978) 4976.
58 N.V. Fedoseeva, I.P. Spevakova and B.V. Beznosikov, Rezonansn. Magnit. Svoistva Magnitodielektrikov, (1978) 206.
59 M.A. Popov, I.P. Spevakova and N.V. Fedoseeva, Rezonansn. Magnit. Svoistva Magnitodielektrikov, (1978) 221.
60 N.V. Fedoseeva, T.A. Velikanova and A.G. Zvegintsev, Phys. Status Solidi A, 51 (1979) K93.
61 R.Yu. Bron, V.V. Eremenko and E.V. Matyushkin, Fiz. Nizk. Temp. (Kiev), 5 (1979) 659.
62 A.G. Anders, A.I. Petutin, Yu.V. Pereverzev and A.I. Zvyagin, Fiz. Nizk. Temp. (Kiev), 5 (1979) 636.
63 J.A.H.M. Buys, G.J.M. van Workum and W.J.M. de Jonge, J. Chem. Phys., 70 (1979) 1811.
64 Y. Natsume, F. Sasagawa, M. Toyoda and I. Yamada, J. Phys. Soc. Jpn., 46 (1979) 1949.
65 D. Bourdel, F. Ruiz, G. Ablart, J. Pescia, S. Clement and J.P. Renard, Solid State Commun., 29 (1979) 727.

66 I.U. Heilmann, R.J. Birgeneau, Y. Endoh, G. Reiter, G. Shirane and S.L. Holt, Solid State Commun., 31 (1979) 607.

67 J.P. Boucher, L.P. Regnault, J. Rossat-Mignod, J. Villain and J.P. Renard, Solid State Commun., 31 (1979) 311.

68 H.D. Lutz, W. Schmidt and H. Haeuseler, Z. Anorg. Allg. Chem., 453 (1979) 121.

69 S.D. Hamann, High Temp. — High Pressures, 10 (1978) 497.

70 W. Depmeier, J. Solid State Chem., 29 (1979) 15.

71 W. Depmeier and G. Chapuis, Acta Crystallogr., Sect. B, 35 (1979) 1081.

72 S. Skaarup and R.W. Berg, J. Solid State Chem., 26 (1978) 59.

73 B.P. Burylev, T.B. Pochinok and V.L. Mironov, Zh. Fiz. Khim., 53 (1979) 1429.

74 K. Tanemoto and T. Nakamura, Jpn. J. Appl. Phys., 17 (1978) 2161.

75 Y. Takagi, T. Nakamura, T. Sata, H. Ohno and K. Furukawa, J. Chem. Soc., Faraday Trans. I, 75 (1979) 1161.

76 E.A. Popov and B.V. Beznosikov, Fiz. Tverd. Tela (Leningrad), 20 (1978) 3448.

77 H. von Känel, Physica B&C, 96 (1979) 167.

78 J.J. Smit, M. Mostafa and L.J. de Jongh, J. Phys. Colloq. (Orsay, Fr.), (1978) 725.

79 J. Goodyear, E.M. Ali and H.H. Sutherland, Acta Crystallogr., Sect. B, 35 (1979) 456.

80 M. Larignon, D. Magnant and H. Payen de la Garanderie, C.R. Acad. Sci., Ser. B, 288 (1979) 119.

81 J.P. Sanchez, J.M. Friedt and G. Jehanno, J. Phys. Colloq. (Orsay, Fr.), (1979) 398.

82 S. Sasaki, K. Fujino and Y. Takeuchi, Proc. Jpn. Acad., Ser. B, 55 (1979) 43.

83 V.G. Anufriev, Latv. PSR Zinat. Akad. Vestis, Fiz. Teh. Zinat. Ser., (1979) 119.

84 K. Sander and Hk. Müller-Buschbaum, Z. Anorg. Allg. Chem., 451 (1979) 35.

85 E. Brechtel, G. Cordier and H. Schäfer, Z. Naturforsch., Teil B, 34 (1979) 777.

86 W. Wegener, J. Vanderhaeghen, D. Scheerlinck, S. Hautecler, E. Legrand and G. Will, Phys. Status Solidi B, 93 (1979) 597.

87 D.F.C. Morris, J.D. MacCarthy and R.J. Newton, Electrochim. Acta, 23 (1978) 1383.

88 B. Durand and J.M. Paris, Inorg. Synth., 19 (1979) 121.

89 M.R. Melardi, G. Ferroni and J. Galea, Rev. Chim. Miner., 16 (1979) 19.

90 A.N. Speca, L.S. Gelfand, F.J. Iaconianni, L.L. Pytlewski, C.M. Mikulski and N.M. Karayannis, Inorg. Chim. Acta, 33 (1979) 195.

91 Y. Masuda and S. Shishido, Thermochim. Acta, 28 (1979) 377.

92 J.L. Rao, Solid State Commun., 28 (1978) 243.

93 T.E. Wood, G. Kokoska and P. Day, Inorg. Chem., 18 (1979) 2936.

94 M. Matsuura, Y. Okuda, M. Morotomi, H. Mollymoto and M. Date, J. Phys. Soc. Jpn., 46 (1979) 1031.

95 Z. Libuś and H. Tialowska, J. Phys. Chem., 83 (1979) 2594.

96 V.A. Sharov, T.M. Zhdanovskikh and E.A. Nikonenko, Zh. Neorg. Khim., 24 (1979) 1489.

97 J.A. Adejumobi, J.A. Faniran and K.S. Patel, Spectrochim. Acta, Part A, 34 (1978) 625.

98 I.R. Amiraslanov, Kh.S. Mamedov, E.M. Movsumov, F.N. Musaev and G.N. Nadzhafov, Zh. Strukt. Khim., 19 (1978) 1120.

99 J. Tummavuori and H. Pihlaja, Finn. Chem. Lett., 2 (1979) 35.

100 V.V. Grigor'eva and O.Ya. Dubik, Visnik Kiiv. Un-tu. Khimiya, 19 (1978) 33.

101 G.S. Sergeeva and E. Svarcs, Latv. PSR Zinat. Akad. Vestis, Kim. Ser., 2 (1979) 157.

102 E.C. Guzman and F.G. Garcia, An. Quim., 74 (1978) 1049.

103 R.W. Hay, K.B. Nolan and M.H. Shuaib, Transition Met. Chem. (Weinheim, Ger.), 4 (1979) 142.

104 M. Cartwright, D.A. Edwards and J.M. Potts, Inorg. Chim. Acta, 34 (1979) 211.

105 W.D. Harrison, J.B. Gill and D.C. Goodall, J. Chem. Soc., Dalton Trans., (1979) 847.

106 I. Bertini, C. Luchinat and A. Scozzafava, Inorg. Nucl. Chem. Lett., 15 (1979) 89.

107 G. Gérard and R.P. Hugel, J. Chem. Res. (S), (1978) 404.

108 B. Horvath, R. Möseler and E.G. Horvath, Z. Anorg. Allg. Chem., 449 (1979) 41.

109 D.T. Richens, C.G. Smith and D.T. Sawyer, Inorg. Chem., 18 (1979) 706.
110 A.B. Cornwell and P.G. Harrison, Acta Crystallogr., Sect. B, 35 (1979) 1694.
111 A. Kircheiss and J. Siodlaczek, Z. Chem., 19 (1979) 227.
112 A. Gupta and B.S. Pannu, Thermochim. Acta, 31 (1979) 101.
113 N.M. Karayannis, G.M. Mikulski, L.S. Gelfand and L.L. Pytlewski, J. Inorg. Nucl. Chem., 40 (1978) 1513.
114 F.J. Iaconianni, L.S. Gelfand, L.L. Pytlewski, C.M. Mikulski, A.N. Speca and N.M. Karayannis, Inorg. Chim. Acta, 36 (1979) 97.
115 V.S. Babu, D.U. Raju and R.R. Naidu, Indian J. Chem., Sect. A, 18 (1979) 87.
116 K.D. Ghuge, P. Umapathy and D.N. Sen, J. Indian Chem. Soc., 55 (1978) 864.
117 P.H. Merrell, Inorg. Chim. Acta, 32 (1979) 99.
118 C. Preti and G. Tosi, J. Coord. Chem., 8 (1978) 15.
119 J.V. Singh, N.C. Nain and R.C. Mehrotra, Synth. React. Inorg. Met.-Org. Chem., 9 (1979) 79.
120 W.L. Driessen and M. den Heijer, Inorg. Chim. Acta, 33 (1979) 261.
121 C.M. Mikulski, J. Unruh, J.L. Pytlewski and N.M. Karayannis, Transition Met. Chem. (Weinheim, Ger.), 4 (1979) 98.
122 R. Mason, G.A. Williams and P.E Fielding, J. Chem. Soc., Dalton Trans., (1979) 676.
123 K. Uchida, S. Naito, M. Soma, T. Onishi and K. Tamaru, J. Chem. Soc., Chem. Commun., (1978) 217.
124 A.B.P. Lever, J.P. Wilshire and S.K. Quan, J. Am. Chem. Soc., 101 (1979) 3668.
125 R.O. Loutfy and J.H. Sharp, J. Phys. Chem., 82 (1978) 2787.
126 E.B. Fleischer and R.V. Ferra, J. Inorg. Biochem., 10 (1979) 91.
127 V.N. Kopranenkov, E.A. Tarkhanova and E.A. Luk'yanets, Zh. Org. Khim., 15 (1979) 642.
128 W.R. Scheidt, K. Hatano, G.A. Rupprecht and P.L. Piciulo, Inorg. Chem., 18 (1979) 292.
129 F. Basolo, R.D. Jones and D.A. Summerville, Acta Chem. Scand., Ser. A, 32 (1978) 771.
130 B.M. Hoffmann, T. Szymanski, T.G. Brown and F. Basolo, J. Am. Chem. Soc., 100 (1978) 7253.
131 W.M. Coleman and L.T. Taylor, J. Inorg. Nucl. Chem., 41 (1979) 95.
132 B. Horvath, R. Möseler and E.G. Horvath, Z. Anorg. Allg. Chem., 450 (1979) 165.
133 R.C. Aggarwal and T.R. Rao, J. Inorg. Nucl. Chem., 40 (1978) 1177.
134 R.L. Chapman and R.S. Vagg, Inorg. Chim. Acta, 33 (1979) 227.
135 G.R. Chaudhury and K.C. Dash, J. Indian Chem. Soc., 56 (1979) 87.
136 J. Masaguer, C. Rodriguez and M.C. Pena, Acta Cient. Compostelana, 15 (1978) 3.
137 J.R. Masaguer, C. Rodriguez and M. Lopez, An. Quim., 74 (1978) 1041.
138 R.C. Thompson, V.K. Gujral, H.J. Wagner and C.F. Schwerdtfeger, Phys. Status Solidi A, 53 (1979) 181.
139 G.V. Tsintsadze, T.I. Tsivtsivadze and Z.O. Dzhavkhishvili, Koord. Khim., 5 (1979) 909.
140 E.A. Mazurenko, Zh.N. Bublik and S.V. Volkov, Ukr. Khim. Zh. (Russ. edn.), 45 (1979) 591.
141 O.I. Kuntyi, K.N. Mikhalevich and D.I. Semenishin, Koord. Khim., 5 (1979) 685.
142 J.N. McElearney, L.L. Balagot, J.A. Muir and R.D. Spence, Phys. Rev. B: Condens. Matter, 19 (1979) 306.
143 V.A. Sharov, T.M. Zhdanovskikh, V.A. Perelyaev, E.A. Nikonenko, E.I. Krylov and I.A. Polyakova, Koord. Khim., 5 (1979) 213.
144 S.J.E. Titus, W.M. Barr and L.T. Taylor, Inorg. Chim. Acta, 32 (1979) 103.
145 Yu.A. Mal'tsev, Zh. Fiz. Khim., 53 (1979) 1779.
146 E. Saviuc, Bul. Inst. Politeh. Iasi, Sect. 2, 24 (1978) 23.
147 M.N. Patel and J.B. Patel, Angew. Makromol. Chem., 80 (1979) 171.

148 Yu.Ya. Kharitonov, R.I. Machkhoshvili and L.V. Goeva, Koord. Khim., 5 (1979) 1150.
149 D.E. Chasan, L.L. Pytlewski, C. Owens and N.M. Karayannis, Chem. Chron., 8 (1979) 53.
150 S.A.A. Zaidi and M.A. Neyazi, Transition Met. Chem. (Weinheim, Ger.), 4 (1979) 164.
151 L.E. Pogosyan and S.N. Avakyan, Mater. Resp. Sovestich. Neorg. Khim., 5th, 1976 (Pub. 1977) 124.
152 T. Takeuchi, Y. Kosugi and K. Itoh, Fresenius' Z. Anal. Chem., 294 (1979) 275.
153 L.E. Pogosyan and S.N. Avakyan, Mater. Resp. Sovestich. Neorg. Khim. 4th, 1975 (Pub. 1976) 40.
154 L.E. Pogosyan and S.N. Avakyan, Mater. Resp. Sovestich. Neorg. Khim. 4th, 1975 (Pub. 1976) 36.
155 K. Lal, Acta Chim. Acad. Sci. Hung., 99 (1979) 281.
156 J. Masłowska and A. Dorabialski, Pol. J. Chem., 53 (1979) 917.
157 P.O. Dunstan and C. Maieru, An. Acad. Bras. Cienc., 50 (1978) 479.
158 J. Singh, K. Lal and S.P. Gupta, S. Afr. J. Sci., 75 (1979) 62.
159 J. Singh, K. Lal and S.P. Gupta, Acta Cienc. Indica, [Ser.] Chem., 5 (1979) 20.
160 R.W. Hay and C.R. Clark, Transition Met. Chem. (Weinheim, Ger.), 4 (1979) 28.
161 D.V. Rao, A.K. Murthy and P. Lingaiah, Indian J. Chem., Sect. A, 16 (1978) 722.
162 A.Yu. Tsivadze, Yu.Ya. Kharitonov, A.N. Smirnov, G.V. Tsintsadze and L.V. Gverdtsiteli, Zh. Neorg. Khim., 24 (1979) 1269.
163 O.F. Khodzhaev, T.A. Azizov and N.A. Parpiev, Zh. Neorg. Khim., 23 (1978) 2942.
164 M. Plytzanopoulos, G. Pneumatikakis, N. Hadjiliadis, D. Katakis and V. Papadopoulos, Chem. Chron., 8 (1979) 102.
165 N.K. Dzyuba and G.D. Zegzhda, Zh. Neorg. Khim., 24 (1979) 978.
166 M.I. Kalaeva, N.V. Zaruba, N.N. Gusak, S.A. Mirko and B.A. Mamaeva, Zh. Neorg. Khim., 24 (1979) 553.
167 T. Toktorbaev, Z.B. Bakasova and I.G. Druzhinin, Izv. Akad. Nauk. Kirg. SSR, 5 (1978) 105.
168 D.C. Sehgal, C.P. Gupta and R.K. Mehta, Indian J. Chem., Sect. A, 16 (1978) 910.
169 P. Mathur, D.P. Goel and R.P. Singh, Indian J. Chem., Sect. A, 16 (1978) 890.
170 R.J. Gualtieri, W.A.E. McBryde and H.K.J. Powell, Can. J. Chem., 57 (1979) 113.
171 R. Manaeva, Z. Kochkorova, K. Rysmendeev and S. Baichalova, Kompleksn. Pererab. Prir. Nedefitsitnogo Syr'ya Kirg. Probl. Ekol., (1978) 25.
172 V.V.S. Reddy, B. Sethuram and T.N. Rao, Indian J. Chem., Sect. A, 17 (1979) 199.
173 Y.Z. Pathak and G.B. Joshi, Chem. Era, 14 (1978) 419.
174 Y.Z. Pathak and G.B. Joshi, J. Indian Chem. Soc., 56 (1979) 419.
175 I. Singh, B.S. Garg and R.P. Singh, Indian J. Chem., Sect. A, 17 (1979) 104.
176 P.V. Gogorishvili and M.G. Tskitishvili, Issled. Obl. Khim. Kompleksn. Protykh Soedin. Nek. Perekhodnykh Redk. Met., 3 (1978) 5.
177 R.C. Aggarwal and B. Singh, J. Inorg. Nucl. Chem., 40 (1978) 1174.
178 K.A. Idriss, M.M. Seleim and M.M. Khalil, Monatsh. Chem., 109 (1978) 1383.
179 Y.K. Agrawal, Transition Met. Chem. (Weinheim, Ger.), 4 (1979) 109.
180 Y.K. Agrawal and A. Mudaliar, Transition Met. Chem. (Weinheim, Ger.), 4 (1979) 252.
181 M.A. Khattab, F.I.M. Taha and M. Khalifa, Pak. J. Sci. Ind. Res., 20 (1977) 172.
182 M.A. Khattab and M.I. Khalifa, Pak. J. Sci. Ind. Res., 20 (1977) 165.
183 R.C. Aggarwal and B. Singh, Z. Anorg. Allg. Chem., 445 (1978) 227.
184 Y.M. Temerk and M.M. Ghoneim, Bull. Fac. Sci., Assiut Univ., 3 (1978) 189.
185 V.K. Voronov, T.E. Moskovskaya, V.I. Glukhikh, A.I. Rezvukhin, E.S. Domnina and G.G. Skvortsova, Koord. Khim., 5 (1979) 218.
186 J.R. Allan, N.D. Baird and A.L. Kassyk, J. Therm. Anal., 16 (1979) 79.

187 M.-S. Ericsson, S. Jagner and E. Ljungstrom, Acta Chem. Scand., Ser. A, 33 (1979) 371.

188 I. Bernal, M. Creswick and W.A. Herrmann, Z. Naturforsch., Teil B, 34 (1979) 1345.

189 M. Arif, A.M. Cartner, D.N. Kariuki and S.F.A. Kettle, J. Chem. Phys., 70 (1979) 1031.

190 B.K. Nicholson, J. Organomet. Chem., 169 (1979) 185.

191 J.A. Gladysz, G.M. Williams, W. Tam, D.L. Johnson, D.W. Parker and J.C. Selover, Inorg. Chem., 18 (1979) 553.

192 J.A. Gladysz, W. Tam, G.M. Williams, D.L. Johnson and D.W. Parker, Inorg. Chem., 18 (1979) 1163.

193 R.A. Fiato, J.L. Vidal and R.L. Pruett, J. Organomet. Chem., 172 (1979) C4.

194 H.-W. Chen, W.L. Jolly, J. Kopf and T.H. Lee, J. Am. Chem. Soc., 101 (1979) 2607.

195 R.A. Epstein, T.R. Gaffney, G.L. Geoffroy, W.L. Gladfelter and R.S. Henderson, J. Am. Chem. Soc., 101 (1979) 3847.

196 J.A. Timney and J.J. Turner, Proc. IUPAC Symp. Photochem., 7th, (1978) 326.

197 K.J. Reimer and A. Shaver, Inorg. Synth., 19 (1979) 158.

198 M.H. Quick and R.J. Angelici, Inorg. Synth., 19 (1979) 160.

199 M.H. Quick and R.J. Angelici, Inorg. Synth., 19 (1979) 161, 163.

200 K.J. Reimer and A. Shaver, Inorg. Synth., 19 (1979) 162.

201 M. Vermeulen, G. Michel and J. Nasielski, Spectrochim. Acta, Part A, 35 (1979) 147.

202 D. Kariuki and S.F.A. Kettle, Spectrochim. Acta, Part A, 34 (1978) 563.

203 B.J. Brisdon, D.A. Edwards and J.W. White, J. Organomet. Chem., 161 (1978) 233.

204 M.J. Blandamer, J. Burgess and A.J. Duffield, J. Organomet. Chem., 175 (1979) 293.

205 W.E. Lindsell and P.N. Preston, J. Chem. Soc., Dalton Trans., (1979) 1105.

206 E.W. Abel, G. Farrow and I.D.H. Towle, J. Chem. Soc., Dalton Trans., (1979) 71.

207 A. Alberti and C.M. Camaggi, J. Organomet. Chem., 161 (1978) C63.

208 A.A. Ioganson, Stroenie, Svoistva Primenenie β-diketonatov Metallov, M., (1978) 150.

209 A.A. Ioganson, Str., Svoistva Primen. β[Beta]-Diketonatov Met., [Mater. Vses. Semin.], 3rd, 1977 (Pub. 1978) 150.

210 H. Weber and R. Mattes, Chem. Ber., 112 (1979) 95.

211 F. Götzfried, W. Beck, A. Lerf and A. Sebald, Angew. Chem., 91 (1979) 499.

212 S.R. Finnimore, R. Goddard, S.D. Killops, S.A.R. Knox and P. Woodward, J. Chem. Soc., Dalton Trans., (1978) 1247.

213 I.B. Benson, J. Hunt, S.A.R. Knox and V. Oliphant, J. Chem. Soc., Dalton Trans., (1978) 1240.

214 V. Küllmer, E. Röttinger and H. Vahrenkamp, Z. Naturforsch., Teil B, 34 (1979) 224.

215 V. Küllmer, E. Röttinger and H. Vahrenkamp, Z. Naturforsch., Teil B, 34 (1979) 217.

216 K.R. Breakall, S.J. Rettig, A. Storr and J. Trotter, Can. J. Chem., 57 (1979) 139.

217 K.S. Chong and A. Storr, Can. J. Chem., 57 (1979) 167.

218 R. Mews and H.C. Braeuer, Z. Anorg. Allg. Chem., 447 (1978) 126.

219 E.W. Abel and C.A. Burton, J. Organomet. Chem., 170 (1979) 229.

220 L.H. Staal, G. Van Koten and K. Vrieze, J. Organomet. Chem., 175 (1979) 73.

221 L.H. Staal, A. Oskam and K. Vrieze, J. Organomet. Chem., 170 (1979) 235.

222 C. Busetto, A.M. Mattucci, E. Cernia, G. Guizzi and U. Belluco, Inorg. Chim. Acta, 34 (1979) 155.

223 R. Usón, V. Riera, J. Gimeno, M. Laguna and M.P. Gamasa, J. Chem. Soc., Dalton Trans., (1979) 996.

224 P.J. Harris, S.A.R. Knox, R.J. McKinney and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1978) 1009.

225 L.S. Jenkins and G.R. Willey, J. Chem. Soc., Dalton Trans., (1979) 777.

226 E.W. Abel and C. Towers, J. Chem. Soc., Dalton Trans., (1979) 814.

227 E.W. Abel, N. Clark and C. Towers, J. Chem. Soc., Dalton Trans., (1979) 1552.
228 E. Lindner, G. von Au and H.-J. Eberle, Z. Naturforsch., Teil B, 33 (1978) 1296.
229 W. Clegg and S. Morton, J. Chem. Soc., Dalton Trans., (1978) 1452.
230 J. Ellermann and H.A. Lindner, Z. Naturforsch., Teil B, 34 (1979) 799.
231 D. Fenske, Chem. Ber., 112 (1979) 363.
232 H. Berke and R. Hoffmann, J. Am. Chem. Soc., 100 (1978) 7224.
233 E. Lindner, G. Funk and S. Hoehne, Angew. Chem., 91 (1979) 569.
234 M. Dilgassa and M.D. Curtis, J. Organomet. Chem., 172 (1979) 177.
235 K.P. Darst and C.M. Lukehart, J. Organomet. Chem., 171 (1979) 65.
236 P.M. Treichel, D.W. Firsich and G.P. Essenmacher, Inorg. Chem., 18 (1979) 2405.
237 W. Ködel, H.-J. Haupte and F. Huber, Z. Anorg. Allg. Chem., 448 (1979) 126.
238 H. Preut and H.-J. Haupt, Acta Crystallogr., Sect. B, 35 (1979) 729.
239 H.-J. Haupt, H. Preut and W. Wolfes, Z. Anorg. Allg. Chem., 446 (1978) 105.
240 S. Onaka, Chem. Lett., (1978) 1163.
241 B.I. Kozyrkin, K.S. Gasanov, T.Kh. Kurbanov, N.E. Kolobova, S.A. Klinichikova and V.N. Khandozhko, Zh. Obshch. Khim., 48 (1978) 2408.
242 D.N. Duffy and B.K. Nicholson, J. Organomet. Chem., 164 (1979) 227.
243 F.S. Wong and K.M. Mackay, J. Chem. Soc., Dalton Trans., (1978) 1752.
244 S.J. Hildebrandt and D.F. Gaines, Inorg. Synth., 19 (1979) 227.
245 H. Preut and H.-J. Haupt, Acta Crystallogr., Sect. B, 35 (1979) 2191.
246 G. Beysel, J. Grobe and W. Mohr, J. Organomet. Chem., 170 (1979) 319.
247 G.D. Michels, Report 1979 IS-T-837 (Chem. Abstr., 91 (1979) 163933).
248 E. Lindner, S. Hoehne and K-W. Rodatz, Z. Naturforsch., Teil B, 34 (1979) 520.
249 G.P. Kinstle and E.P. Schram, Inorg. Chim. Acta, 32 (1979) L61.
250 J. P. Barbier and P. Braunstein, J. Chem. Res. (S), (1978) 412.
251 M. Laing, R.H. Reimann and E. Singleton, Inorg. Chem., 18 (1979) 324.
252 M. Laing, R.H. Reimann and E. Singleton, Inorg. Chem., 18 (1979) 1648.
253 M. Laing, R.H. Reimann and E. Singleton, Inorg. Chem., 18 (1979) 2666.
254 S. Papp and S. Buza, Monatsh. Chem., 110 (1979) 377.
255 S.R. Cooper, G.C. Dismukes, M.P. Klein and M. Calvin, J. Am. Chem. Soc., 100 (1978) 7248.
256 M. Vidali, G. Rizzardi, P.A. Vigato, U. Castellato, S. Kida and H. Ikawa, Inorg. Chim. Acta, 34 (1979) 19.
257 N. Torihara, H. Okawa and S. Kida, Chem. Lett., (1979) 683.
258 S. Simizu, J. Phys. Soc. Jpn., 47 (1979) 444.
259 N. Yamanaka, Asahikawa Kogyo Koto Semmon Gakko Kenkyu Hobun, 13 (1976) 29.
260 K.D. Snell and A.G. Keenan, Chem. Soc. Rev., 8 (1979) 259.
261 R.D. Rocklin and R.W. Murray, Report 1979, AD-A066632 (Chem. Abstr., 91 (1979) 165501).
262 R.D. Rocklin and R.W. Murray, J. Electroanal. Chem., 100 (1979) 271.
263 R.H. Schmehl, G.L. Shaw and D.G. Whitten, Chem. Phys. Lett., 58 (1978) 549.
264 Y. Umezawa and T. Yamamura, J. Electrochem. Soc., 126 (1979) 705.
265 Y. Umezawa and T. Yamamura, J. Chem. Soc., Chem. Commun., (1978) 1106.
266 M. Aizawa, M. Hirano and S. Suzuki, Electrochim. Acta, 24 (1979) 89.
267 G.D. Lawrence and D.T. Sawyer, Coord. Chem. Rev., 27 (1978) 173.
268 R.D. Jones, D.A. Summerville and F. Basolo, Chem. Rev., 79 (1979) 139.
269 M. Cromer-Morin, J.P. Scharff, M. Claude and M.R. Pâris, Anal. Chim. Acta, 104 (1979) 299.
270 C. Zentz, G. Chottard and J. Bolard, J. Inorg. Nucl. Chem., 40 (1978) 2019.
271 M.K. Green and G. Kotowycz, Can. J. Biochem., 57 (1979) 995.
272 M.K. Green and G. Kotowycz, Can. J. Chem., 57 (1979) 2434.
273 R. Basosi, E. Gaggelli and G. Valensin, J. Inorg. Biochem., 10 (1979) 101.

274 M.V. Karkarashvili and I.A. Beshkenadze, Issled. Obl. Khim. Kompleksn. Prostykh Soedin. Nek. Perekhodnykh Redk. Met., 3 (1978) 32.
275 M.V. Karkarashvili and I.A. Beshkenadze, Issled. Obl. Khim. Kompleksn. Prostykh Soedin. Nek. Perekhodnykh Redk. Met., 3 (1978) 44.
276 U.K. Moldobaeva, K.R. Rysmendeev and S.M. Moldobaev, Kompleksn. Pererab. Prir. Nedefitsitnogo Syr'ya Kirg. Probl. Ekol., (1978) 32.
277 L.P. Berezina, A.I. Pozigun, A.V. Misyura and V.G. Samoilenko, Zh. Obshch. Khim., 49 (1979) 1595.
278 Kh.Kh. Khakimov, N.T. Alimkhodzhaeva, O.F. Khodzhaev and Kh.Kh. Khodzhaeva, Koord. Khim., 5 (1979) 21.
279 P.V. Gogorishvili, T.N. Sakvarelidze, M.V. Karkarashvili, A.K. Stroesku and V.V. Zelentsov, Soobshch. Akad. Nauk Gruz. SSR., 93 (1979) 341.
280 Zh. Moldosheva, S.M. Moldobaev and Sh.T. Talipov, Neorgan. Organ. Sintez, (1977) 57.
281 Zh. Moldosheva, S.M. Moldobaev and Sh.T. Talipov, Neorgan. Organ. Sintez, (1977) 60.
282 Zh. Moldosheva, S.M. Moldobaev and Sh.T. Talipov, Neorgan. Organ. Sintez, (1977) 53.
283 N.B. Behrens, D.M.L. Goodgame and Z. Warnke, Inorg. Chim. Acta, 31 (1978) 257.
284 A.P. Bondareva and I.V. Kolosov, Koord. Khim., 5 (1979) 870.
285 S.N. Avakyan, L.E. Pogosyan, A.S. Avakyan and M.Kh. Minasyants, Mater. Resp. Soveshch. Neorg. Khim., 4th 1975 (Pub. 1976) 64.
286 The Times, 20th November 1978, p. 1.
287 Chemical and Engineering News, 4th December 1978, p. 24.
288 C.A. McAuliffe, H. Al-Khateeb, M.H. Jones, W. Levason, K. Minten and F.P. McCullough, J. Chem. Soc., Chem. Commun., (1979) 736.
289 R.M. Brown, R.E. Bull, M.L.H. Green, J.J. Martin-Polo and D.M.P. Mingos, personal communication, 1979.