Coordination Chemistry Reviews, 72 (1986) 197—294
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

2 MANGANESE

N. TURP

CONTENTS

Introduction 198
2.1 High Oxidation States 198
2.2 Manganese(IV) 199
2.2.1 Oxides 199
2.2.2 Halides and Halocompounds 200
2.2.3 Other Complexes 200
2.3 Manganese(III) 201
2.3.1 Oxides and Hydroxides 201
2.3.2 Phosphates 202
2.3.3 Fluorides and Oxocyanide Complexes 202
2.3.4 Compounds of Phosphorus and Arsenic 202
2.3.5 Other Complexes 203
2.4 Manganese(II) 206
2.4.1 Oxides 206
2.4.2 Sulfides 207
2.4.3 Halides, Pseudohalides and Oxohalides 208
2.4.3.1 Fluorides and Oxofluorides 208
2.4.3.2 Chlorides, Bromides and Iodides 210
2.4.3.3 Cyanides 213
2.4.4 Salts, Intercalates and Doped Crystals 213
2.4.4.1 Salts 213
2.4.4.2 Intercalates 216
2.4.4.3 Doped Crystals 216
2.4.5 Phosphine and Phosphine Oxide Complexes 218
2.4.6 Schiff Base Complexes 221
2.4.7 Complexes with *N* Donor Ligands 228
2.4.8 Complexes with *O* Donor Ligands 232
2.4.9 Complexes with Mixed *N*, *O* or *S* Donor Ligands 237
2.4 10 Complexes with *S* or *Se* Donor Ligands 244
2.4.11 Other Complexes 246
2.5 Manganese(I) 247
2.6 Carbonyl Complexes of Manganese 248
2.6.1 Carbonyl and Hydridocarbonyl Complexes 248
2.6.2 Halides 250
2.6.3 Compounds with *O* Donor Ligands 251
2.6.4 Compounds with *S* or *Se* Donor Ligands 252
2.6.5 Compounds with *N* Donor Ligands 256
2.6.6 Compounds with Other Group 15 Donor Ligands 260
2.6.7 Organometallic Complexes 266
2.6.8 Silyl and Germyl Complexes 268
2.6.9 Mixed Metal Complexes 271
2.7 Phthalocyanin and Porphyrin Complexes 275
2.8 Binary and Ternary Oxides 278
2.9 Mixed Oxidation State and Nitrosyl Complexes 280

0010-8545/86/$34.30

2.10 Binary Compounds of Group 15 Elements 281
2.11 Other Compounds 281
References 282

Introduction

This review deals mainly with the inorganic and coordination chemistry of manganese which was cited in Chemical Abstracts, Volumes 98 and 99. Most of the work, therefore, was published in 1983, while some papers from the end of 1982 have been included. The major journals (*i.e. J. Chem. Soc., Dalton Trans., J. Chem. Soc., Chem. Commun., Inorg. Chem.* and *J. Am. Chem. Soc.*) are reviewed for the full year of 1983. Organometallic chemistry is not formally included, but reference is made to some papers, possibly of general interest. Kinetic and mechanistic work is also excluded, as is purely magnetic, except where some direct relationship to coordination chemistry is involved.

2.1 HIGH OXIDATION STATES

The UV-VIS and IR spectra are reported for $[Mn_2O_7]$ in the solid state and in low temperature matrices. The IR spectra are consistent with a bridged structure, and suggest a wide Mn-O-Mn angle. The electronic spectra show vibrational progressions and are compared with other manganese(VII) oxo species [1]. A study of the spin-spin and spin-lattice relaxation rates in the quadrupolar manganese nucleus in $[MnO_4]^-$ has been undertaken, and shows that when these rates are a minimum with temperature, the lifetime of the excited vibrational state is less than the correlation time of the orientational motion [2]. The vibrational spectrum of $[MnO_3F]$ was presented and analysed, and all related constants calculated. These were compared to its chromium fluoro- and chloro- analogues [3]. Reduction of the oxides $K[MnO_4]$ and $[MnO_2]$ by hydroxylamine produces manganese(II) species. In alkaline media, the reduction of manganese(VII) and manganese(VI) is rapid, while that of manganese(IV) is slow [4].

2.2 MANGANESE(IV)

2.2.1 *Oxides*

The oxidation of manganese(II) salts by $K[ClO_3]$ and $Na[ClO_3]$ to MnO_2 has been reported. The products differ in crystalline form with the oxidant and the conditions used, and were characterised by X-ray powder diffraction, IR spectroscopy, and chemical and electrochemical reactivity [5]. Examination of possible structures has provided information into the enhanced electrochemical performance of MnO_2 in aqueous solution and in lithium cells [6], while reoxidation of crude MnO_2 yields chemical MnO_2 (CMD) [7]. The structural data of electrolytic and chemical MnO_2 has been reviewed [8]. By doping iron into MnO_2, the thermal characteristics of the compound have been changed, as shown by DTA, thermogravimetry and X-ray diffraction; the results were discussed in detail [9]. A statistical thermodynamics approach to the electrical potential of manganese(IV) oxohydroxides has been presented, including modifications for two types of current carrier, and solid solutions of varying composition [10,11]. So-called δ-MnO_2 was reinvestigated and found to be a mixture of two other forms in sodium hydroxide solution, while in potassium hydroxide solution only one form was observed. High temperature treatment of the compound in alkaline solution led to a range of oxides and hydroxides depending on reaction conditions [12]. The MnO_2/H_2SO_4 equilibrium has been studied by titration, complexometric titration, electron microscopy and electron diffraction techniques. The process of dissolution has been analysed and the results presented [13].

The new heteropolymolybdate $K_2H_8[MnMo_7O_{28}].4H_2O$ has been prepared and characterised by diffuse reflectance electronic spectroscopy, magnetic moments, DTA and TGA, and shown by X-ray powder diffraction to be isomorphous with the nickel(IV) compound [14].

2.2.2 *Halides and halocomplexes*

The fluoromanganate(IV) salt $K[MnF_5]$ has been synthesised from MnO_2 and $K[HF_2]$, and characterised by X-ray powder diffraction, DTA and TGA [15]. The electronic spectrum of $[MnF_6]^{2-}$ has been studied in detail and is interpreted in terms of its electronic configuration [16].

A series of dichlorobis(*N*-alkylsalicylidene-aminato)manganese(IV) complexes $[Mn\{N(R)X\text{-sal}\}_2Cl_2]$ were prepared by oxidation with HCl of a manganese(III) complex $[Mn\{N(R)X\text{-sal}\}_2Cl]$. The products were characterised by their physical properties, magnetic moments, UV-VIS and IR spectra, and electrochemistry [17].

2.2.3 *Other complexes*

Aerial oxidation of aqueous solutions of manganese(II) in the presence of 1,4,7-triazacyclononane and bromide ions produces a black compound $[(C_6H_{15}N_3)_4Mn_4O_6]Br_{3.5}(OH)_{0.5}.6H_2O$. The crystal structure has been determined, and the central unit of the molecule is shown in Fig. 1:

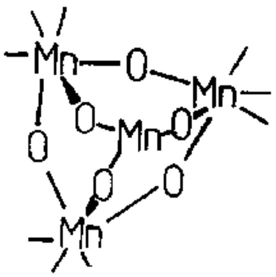


Fig. 1: Central $\{Mn_4O_6\}$ Unit

Redox titrimetric, UV–VIS and IR spectroscopic and magnetic moment data were also quoted [18]. 3,5–di*tert*butylcatechol ($dtbcH_2$) has been used to synthesise the complex $Na_2[Mn(dtbc)_3].6CH_3CN$, which was characterised by X-ray crystallography and $^1H/^{13}C$ NMR spectroscopy and shown to have almost perfect octahedral symmetry in the solid which is retained in solution. The reaction of the anion with the superoxide ion, $[O_2]^-$, has been studied by magnetic, spectroscopic and electrochemical techniques [19].

2.3 MANGANESE(III)

2.3.1 Oxides and Hydroxides

The mixed oxides $Ln_2Mn_{4/3}W_{2/3}O_7$ have rhombohedral pyrochlore structures, as shown by X-ray diffraction studies. The magnetic susceptibilities were also presented [20]. Solid phase studies have been carried out on Bi_2O_3–MO_3(M = Mo or W)–Mn_2O_3 systems in an attempt to synthesise $Bi_{36}Mn_2MO_{60}$. The products were solid solutions with the δ–Bi_2O_3 structure: the lattice parameters were quoted [21]. The mixed oxide system γ–Mn_2O_3–α–Fe_2O_3–α–Mn_2O_3 exhibits superparamagnetic behaviour, and the results were discussed [22].

The manganese(III) hydroxides, $M_3[Mn(OH)_6]_2$ (M = Ca or Sr) were prepared from basic $Mn(CH_3COO)_3/MCl_2$ solutions and thoroughly characterised by XPES and IR spectroscopy. Crystal structure analysis indicates that both have the cubic hydrogarnet structure, with parameters a = 12.437(5) Å (Ca) and a = 12.882(5) Å (Sr) [23,24]. The heteropolytungstate $[BeMn(OH_2)W_{11}O_{39}]^{7-}$ has been prepared as the potassium and ammonium salts, and has analogous properties to those of anions with other hetero–central atoms: B, P, Si, or Zn [25]. High temperature decomposition of lanthanum and manganese oxalates yields amorphous compounds up to 540 °C, but at 600 °C $LaMnO_3$ is produced. X-ray powder diffraction spectra were presented and discussed [26].

2.3.2 *Phosphates*

The crystal structure of twinned $MnH_3[PO_3]_2.2H_2O$ is reported. The unit cell is monoclinic, space group $P2_1/b$. The manganese(III) ions are in a distorted octahedral environment with two *trans*-H_2O molecules and bidentate, bridging $\{PO_3\}^{2-}$ ions [27]. $MnH[P_2O_7]$ also has a monoclinic unit cell, with space group $P2_1/n$. The manganese has an octahedral environment, the crystal consisting of $\{Mn_2O_{10}\}$ units: two $\{MnO_6\}$ units sharing one edge. A hydrogen bond projection was given [27].

2.3.3 *Fluoride and Oxocyanide Complexes*

Three polymorphs of $Cs_2Na[MnF_6]$ have been prepared and the structures solved by X-ray diffraction. At pressures >5 atm, a cubic α-phase is formed; by quenching from 700 °C, a γ-form can be trapped; while the normal β-phase is a variant of the γ-phase [29]. The salts $M[MnF_5].H_2O$ (M = Ba or Sr) were prepared, and studied by X-ray crystallography. The structure contains "*trans*-chains" of $\{MnF_6\}$ octahedra, and these one-dimensional chains show antiferromagnetic interactions which were studied by magnetic susceptibility and Mossbauer spectroscopy [30]. The vibrational, resonance Raman and electronic spectra of the polycrystalline $K_7[Mn_2O(CN)_{10}][CN]$ were recorded and assignments made [31].

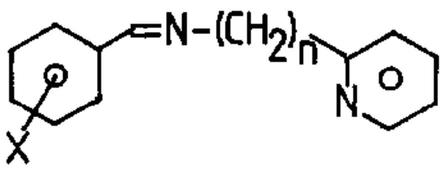
2.3.4 *Compounds of Phosphorus and Arsenic*

The crystallographic parameters of $[MnAs_{1-x}P_x]$ ($0 < x < 0.275$) were determined as functions of temperature over the range 100–600 K, and the temperature dependence of these parameters was related to the variation of magnetic properties with temperature [32].

2.3.5 Other Complexes

The manganese(III) complex $Na[Mn(dtbc)_3].4CH_3CN$ ($dtbcH_2$ = 3,5-ditertbutylcatechol) was synthesised in a manner analogous to that of the manganese(IV) complex, and its reaction with the superoxide ion $[O_2]^-$ investigated by CV [19]. When alcoholic solutions of $[Mn(acac)_3]$ or $[Mn(acac)_2(tfa)]$ are irradiated with UV radiation, the manganese(II) $[Mn(acac)_2]$ complex is produced. EPR spectra of the photolysed solutions at 77 K show the reduced $[Mn(acac)_2]$ species and the oxidation product [33]. $[Mn(acac)_3]$ has also been shown to react with protic and aprotic solvents in the presence of perchloric acid to form pentane-2,4-dione and a ligand-displaced complex [34].

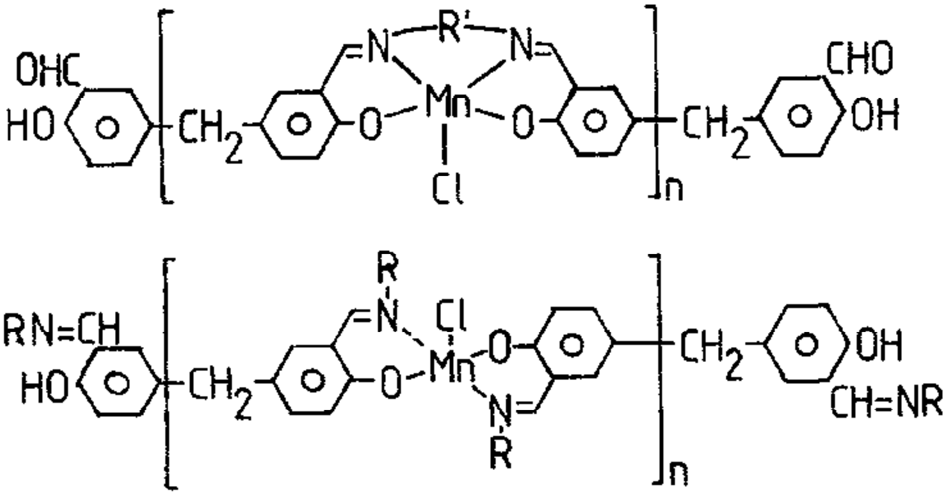
Complexes with the tridentate Schiff bases 5-Xsalamp; (1), and 5-Xsalaep; (2),



n = 1:salamp; (1); *n* = 2:salaep; (2)

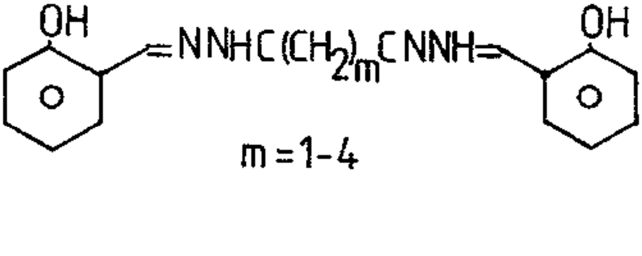
X=NO_2, MeO, H, Cl

$[Mn(5\text{-}Xsalamp)_2][NCS]$ and $[Mn(5\text{-}Xsalaep)_2][NCS]$ were prepared, and characterised by spectral, magnetic and conductance techniques. Chemical and electrochemical studies were also carried out [35]. The reactions of the chloromanganese(III) Schiff base complexes (3):

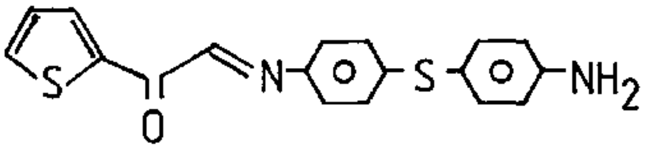


(3)

with superoxide ion $(O_2)^-$ in dmso solution were compared for the monomers (n = 1) and higher oligomers (n = 3–5). While the monomeric complexes were reduced to manganese(II) species, the polymers tended to form oxygenated complexes. Magnetic susceptibilities, UV-VIS spectra and polarograms were recorded and the data are presented [36]. The complexes $[Mn_2(H_2L)X_4].nH_2O$ and $[Mn_2LX_2].nH_2O$ (X = Cl, NO_3, O_2CMe or OH), where LH_4 is the ligand formed from the reaction between salicylaldehyde and various aliphatic dicarboxylic acid dihydrazides:



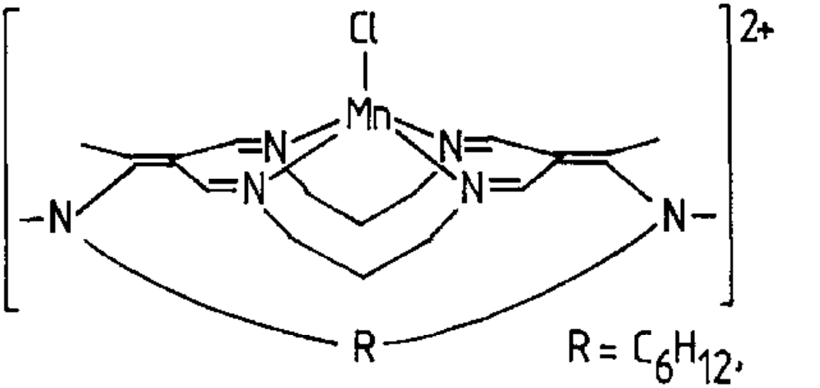
were prepared from solutions of low and high pH respectively, and were characterised by elemental analysis, magnetic susceptibility and IR, electronic and Mossbauer spectroscopy. The complexes have low magnetic moments (μ_{eff} = 3.3–4.6 μ_{β}), which was explained in terms of antiferromagnetic interactions. The ligand is hexadentate, and complexes are believed to be polymeric with phenoxide bridges [37]. The ligand L' (4), shown below;



(4)

formed in the reaction between bis(4-aminophenyl)sulfide and 2-acetylthiopheneglyoxal, has been used to synthesise the complex $[MnL'_2]Cl_3$ which was subsequently characterised by IR and electronic spectroscopy and magnetic moments; ligand field parameters were quoted. The complex is paramagnetic, octahedrally coordinated and high spin, with the ligand bonding through the thiophene *S*, carbonyl *O* and azomethine *N* atoms [38]. The five-coordinate complex [Mn(tetraeneN$_4$)Cl]; (5), has been synthesised and can be electrochemically reduced to the manganese(II) complex. This then reacts with oxygen gas to reform the manganese(III) species [38a].

A series of complexes of manganese(III) with dipicolinic acid (pyridine-2,6-dicarboxylic acid; pdcH$_2$) and one of the monobasic acids (HL"): picolinic acid (pyridine-2-carboxylic acid), nicotinic acid (pyridine-3-carboxylic acid), isonicotinic acid (pyridine-4-carboxylic acid), aminophenol, glycine or 2- and 4-aminobenzoic acids, formulated as



(5)

$[Mn(pdc)L'']\cdot xH_2O$, have been prepared, and characterised by elemental analyses, magnetic susceptibility and electrical conductivity measurements, and IR and electronic spectroscopy. A polymeric structure is suggested with the ligand L" being bidentate, while the authors propose dipicolinic acid to be a pentadentate bridging chelating ligand [39]. The spin-free five-coordinate complexes $[MnL_2Cl]$, (where HL is diethyldithiocarbamic acid, morpholinodithiocarbamic acid, piperidinodithiocarbamic acid, 8-hydroxyquinoline or pyridine-2-carboxylic acid) were prepared by reacting $[MnL_3]$ with HCl in dichloromethane solution. The monomeric compounds are non-electrolytes, and molar conductance, magnetic susceptibility, molecular weight and spectral data were quoted [40]. A study of the Jahn-Teller effect in $[\{(NH_2)_2CO\}_6Mn][ClO_4]_3$ is reported [41].

2.4 MANGANESE(II)

2.4.1 Oxides

Self-consistent Korringa-Kohn-Rostoker band calculations indicate that antiferromagnetic MnO is an insulator. The equilibrium lattice constant and total energy are calculated for this state [42]. The solid solution formed between MnO and CaO has been investigated over a wide range of compositions by magnetic susceptibility, EPR and diffuse reflectance spectroscopy techniques [43]. Melts of MnO in SiO_2 under helium were studied by X-ray diffraction, and radial distribution functions and interatomic distances are quoted. The melt contains {SiO_4} tetrahedra and {MnO_6} octahedra [44].

The polycrystalline compound $MnGa_2O_4$ is a spinel-like double oxide; the crystal structure was presented and discussed [45]. The ferrites $(Zn,Mn)Fe_2O_4$ have been synthesised directly from MnO, and some properties briefly noted [46]. Another preparation of the ferrites $MnFe_2O_4$ and $Mn_{0.5}Zn_{0.5}Fe_2O_4$ involves the hydrolysis of pentane-2,4-dionato complexes of manganese(II) with $Fe(OC_2H_5)_3$, with or without the presence of pentane-2,4-dionato zinc complexes [47]. The anisotropic thermal expansion coefficients of $MnSb_2O_4$ have been examined, and the anomalous expansion between 6 K and 115 K related to manganese(II) ion magnetic ordering [48].

2.4.2 Sulfides

Reactions of elemental manganese with anhydrous sodium carbonate and elemental sulfur at 870 K yields the thiomanganate(II), $Na_2[Mn_2S_3]$, as bright red crystals; X-ray diffraction shows that the unit cell is monoclinic, with the new space group *C2/c*. The crystal contains {MnS_4} tetrahedra sharing edges to form four-membered chains, which are cross-linked into sheets. Magnetic susceptibility measurements show that there are antiferromagnetic interactions between manganese atoms [49]. X-ray diffraction studies of $KLi[MnS_2]$ indicate that the unit cell is tetragonal, space group P. The compound is not isomorphous with the zinc or iron analogues [50].

High temperature reaction of manganese(II) sulfide with sodium and potassium polyphosphates in a nitrogen atmosphere produces hydrogen sulfide, elemental sulfur and sulfur dioxide, while the phosphate is reduced to phosphide and some manganese(II) is oxidised to manganese(III) [51].

A crystal of $[Zn_{0.25}Mn_{0.12}Fe_{0.13}S_{0.5}]$ found in Franckeite was analysed by electron microscopy and microanalysis. The crystal is polytypic, and the diffraction patterns were indexed in terms of an hexagonal unit cell [52]. The crystal structure of $La_6Mn_2Ga_2S_{14}$ has been determined, and also has an hexagonal unit cell, space group $P6_3$. The coordination of the manganese atom is in the form of a triangular antiprism, with the metal being almost central [53].

2.4.3 *Halides, Pseudohalides and Oxohalides*

2.4.3.1 *Fluorides and Oxofluorides*

The electron diffraction study of MnF_2 in the gas phase at 1400 K is reported. The molecule has a linear structure with an Mn-F distance of 1.813(5) Å and an F-F distance of 3.615(5) Å [54]. A detailed theoretical analysis of the first-order Raman spectra of MnF_2 single crystals measured at 4.2 – 563 K is presented, covering frequency shifts and the temperature dependence of line widths [55]. The crystal structure analysis of MnF_2 has been used for a reliability test of intensity variances as developed by Gonschorek [56]. The absorption, emission and excitation spectra of MnF_2 doped with Ni^{2+} ions have been recorded and are discussed [57]. Watson's SCF procedure has been used to calculate energy levels in MnF_2, and a close correlation is observed with the results of optical absorption spectroscopy [58], while the photoemission energy distributions have been obtained from the valence bands of MnF_2 and $KMnF_3$, and the results are interpreted on the matrix element model. The t_{2g}–e_g separations agree with the SCF-Xα calculations on $[MnF_6]^{4-}$ [59]. A method for regulated crystal growth of, especially, MnF_2 and $KMnF_3$ is reported [60].

The trifluoroaquamanganates(II), $A[MnF_3(H_2O)]$ (A = NH_4, Na or K), have been prepared by reacting $K[MnO_4]$ with hydrazine hydrate in the presence of $A[HF_2]$. The rubidium and caesium salts were also prepared. Characterisation was by elemental analysis, magnetic susceptibility, pyrolysis, IR spectroscopy and chemical determination of oxidation state [61]. From an X-ray diffraction study of $KMnF_3$ at 293 K, the unit cell was deduced to be cubic with space group *Pm3m*: dimensions are quoted. Furthermore, a study of the electron density distribution has shown that the Mn^{2+} ions are in the high spin $(t_{2g})^3(e_g)^2$ state [62]. The absorption and magnetic circular dichroism spectra of $RbMnF_3$ have been recorded and the Faraday effect studied in the range 9000 - 37000 cm^{-1}, at 90 - 570 K. The components of the Faraday effect were calculated and the spectra analysed [63]. The anomalous propagation of an acoustic pulse in $KMnF_3$ is reported, and an equation derived to describe the phenomenon [64]. The magnetic properties of $[NH_4]MnF_3$ have been thoroughly investigated and are discussed with respect to the solid state structure [65].

β-$Cs_2[MnF_4]$ was prepared from CsF and MnF_2 at 900 K under hydrogen gas, with rapid cooling to prevent formation of α-$Cs_2[MnF_4]$ [66]. X-ray and neutron diffraction studies of $Ba[MnF_4]$ have failed to confirm the observation of distortion with the wave vector reported by Scott. A detailed analysis of the measurements taken was presented [67].

The compounds $[NH_4]MnFeF_6$, $[NH_4]MnCrF_6$ and $RbMnFeF_6$ have been prepared and analysed by X-ray crystallography. The structure was solved for $[NH_4]MnFeF_6$, and shown to contain $(MnFeF_{10})$ bioctahedra connected by vertices. Magnetic and Mossbauer spectroscopic studies have also been carried out. A detailed discussion of the structure was presented [68]. The structure of $LiMnFeF_6$ has also been examined by X-ray and neutron diffraction, and shows a phase change from the α-form to the β-form at 560 $^{\circ}C$. The structure is of the $Na_2[SiF_6]$ type with a new form of cationic order, and was discussed in detail [69]. ^{57}Fe Mössbauer spectra were recorded for the modified pyrochlore $CsMnFeF_6$ between 1.5 K and room temperature. Although the Fe^{3+} ions are randomly situated in the crystal, there are two distinct sites, as recently reported. The compound is antiferromagnetic with a Néel temperature of 25 K [70]. Specific heat measurements on $CsMnFeF_6$ also show a magnetic specific heat at about 27 K [71].

The mixed fluorides $Mn_xM_{1-x}F_2$ (M = Zn or Co) were prepared for a range of compositions, and the magnetic susceptibilities studied over a wide range of temperatures to discover the variation of Néel temperature with composition [72]. For the mixed fluorides $Mn_xCd_{1-x}F_2$, photoelectron spectroscopy was used to study the distribution of the density of states in the valence band region and the results related to composition [73]. Furthermore, the valence and conduction band structures have been examined by UPS [74], and Auger spectroscopic analysis shows that the Cd^{2+}(4d) band is shifted to lower energy as the concentration of manganese ions increases [75].

Reaction of KF, MgF_2, MgO, SiO_2 and $Mn[C_2O_4]$ yielded mica crystals which were studied by X-ray diffraction and shown to be $K(Mg_{2.44}Mn_{0.24})(Si_{3.82}Mn_{0.18})O_{10}F_2$. Analysis of the structure shows that manganese has substituted partially for silicon in four-coordinate sites, and partially for magnesium in six-coordinate sites [76].

2.4.3.2 Chlorides, Bromides and Iodides

The low temperature perovskite-type structure of $[C_3H_7NH_3]_2[MnCl_4]$ has been studied by neutron diffraction and the observed phase modulation analysed [77], while an X-ray study of the phase transition in the same compound is reported [78]. The complex $[cystH]_2[MnCl_4]$ (cyst = cystamine) has also been prepared and characterised [79].

A neutron scattering study was performed on $[NH_3(CH_2)_3NH_3][MnCl_4]$ to examine the motions of the NH_3 groups over a temperature range of 40 – 300 K [80]. The low frequency Raman and inelastic neutron scattering spectra of $[CH_3NH_3]_2[MnCl_4]$ at low temperature were recorded and analysed, and a complete assignment proposed [81]. The low temperature structure of $[(CH_3)_4N]MnCl_3$ has been investigated by Raman spectroscopy and was discussed with reference to previous NMR spectroscopic and neutron diffraction work [82]. The EPR spectrum of $[(CH_3)_4N]MnCl_3$ was measured with far-IR lasers and pulsed magnetic fields. The observed behaviour was considered in terms of an antiferromagnetic resonance spectrum [83]. Luminescent parameters for $[C_5H_5NH]_2[MnX_4]$ (X = Cl, Br) which were not previously accessible have been determined from the force constants from vibrational spectra [84].

Although the cell dimensions previously determined for $MnBr_2.4H_2O$ are correct, an EXAFS study has shown that the bond-lengths are in error [85].

The low temperature EPR spectra in matrix isolation of $MnCl_2$, $MnBr_2$, MnI_2 and MnS, together with the manganese(I) halides, have been recorded and are presented along with zero-field splittings, ^{55}Mn hyperfine interactions and *g*-values. A correlation is shown between these values and the change in ionicity [85a]. The optical spectra of Mn^{2+} ions in both dipolar form and forming Suzuki-phase precipitates have been studied by photostimulated luminescence methods at room temperature and 77 K. An analysis of the spectra is presented in terms of the electronic configurations of the species [86]. A detailed study of the energy level schemes for MnF_2, $MnCl_2$, $MnCl_2.2H_2O$, $MnCl_2.4H_2O$ and $MnBr_2$ indicates that the participation of 3d electrons in Mn-X bonding in the crystals can be quantified by an effective occupation number. The values calculated, *i.e.* numbers of 3d electrons participating in bond formation, are: MnF_2 0.08; $MnCl_2$ 0.1; $MnBr_2$ 0.2 [87].

The differential paramagnetic susceptibility, χ, was measured as a function of the applied field for the antiferromagnets $MnCl_2.4H_2O$ and $MnBr_2.4H_2O$. Simple models were used to describe the systems [88]. The temperature-dependence of the ^{35}Cl NQR frequencies of the chloroanilinium cation in $[4\text{-}ClC_6H_4NH_3]_2[MnCl_4]$ was studied, and the results analysed in terms of a two-dimensional antiferromagnetic behaviour [89].

The equilibrium involving $MnCl_2$ and oxygen gas, with and without water, to regenerate chlorine gas was studied over a wide range of temperature, pressure and composition, and the products of the reaction were discussed in detail, being mainly higher oxides and hydroxides of manganese [90]. The $MnBr_2$-dmf-H_2O ternary system has been investigated by isothermal solubility measurements. The congruently soluble $MnBr_2.2dmf.2H_2O$ was found; solubility data were presented [91]. The solublity isotherm at 298 K was determined for the $MnCl_2$–dmso system, and the equilibrium solid phase was shown to contain $MnCl_2.4H_2O$ and $MnCl_2$.dmso.$2H_2O$ [92]. The diffusion of $MnCl_2$ in aqueous sodium chloride solution has been examined by an electrochemical technique, and it has been shown that the diffusion coefficient increases with sodium chloride concentration. The hydration number of $MnCl_2$ is 3.5 [93].

The phase diagram of $[CH_3NH_3]_2[Mn_{1-x}Cu_xCl_4]$ $(0.03 \leqslant x \leqslant 0.96)$ is presented and discussed. For $x = 0.03$, the crystal structure has been solved and presented [94]. The phase transitions in $[(CH_3)_4N]MnCl_3$ between 20 K and 300 K were followed by Raman spectroscopy. Spectral data and group theoretical analysis indicate that the space group is $P2_1/b$ [95]. The heat capacity of $[(CH_3)_4N]MnCl_3$ over the range 1.5 – 300 K was reported, and an anomalous entropy gain at 126 K noted and associated with the monoclinic to hexagonal transition [96].

The heterometallic compound $[NH_4]_4Fe_2MnCl_{12}$ was prepared, and characterised by elemental analysis, electronic spectroscopy and magnetic susceptibility. The data were interpreted in terms of octahedral iron atoms, and a linear arrangement of metal atoms with manganese at one end [97]. The temperature dependences of EPR spectra and magnetic susceptibility in zero magnetic field have been studied in a new spin-glass $Rb_2[Mn_{1-x}Cr_xCl_4]$ over a range of compositions [98].

The emission spectra of europium(III) doped into $KMnCl_3$ or $RbMnCl_3$ were recorded, together with the diffuse reflectance spectra of $RbMnCl_3.EuCl_3$, $KMnCl_3.EuCl_3$, $RbMnCl_3$ and $KMnCl_3$. The observed emission bands were assigned to europium(III) electronic transitions, and the absorption bands to manganese(II) d–d transitions; crystal field and Racah parameters were quoted [99].

The IR and Raman spectra of MnI_2 were recorded and used to interpret the $^6A_{1g} \rightarrow ^4E_g, ^4A_{1g}$ transition in terms of one phonon progressions [100]. The optical absorption and magnetic circular dichroism spectra of single crystals of MnI_2 were reported over the range 1.5 – 300 K. All electronic and magnetic circular dichroism parameters were calculated and a detailed assignment is given for the fine structure of the $^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ transitions [101].

2.4.3.3 Cyanides

The compound $[(CH_3)_4N]MnFe(CN)_6.8H_2O$ was examined by X-ray crystallography, and shown to contain low spin, octahedral iron(III), and high spin manganese(II) bonded to two NC^- ligands and four water molecules [102]. Detailed magnetic studies have been carried out and show the compound to be antiferromagnetic below 9.3 K [103]. The IR and Raman vibrational spectra of the $[Mn(CN)_6]^{4-}$ anion have been analysed and assigned completely, using calculations based on the valence force field method, and there is good agreement with experimental results [104].

2.4.4 Salts, Intercalates and Doped Crystals

2.4.4.1 Salts

Reaction of manganese(II) ethanoate with ammonium chromate(VI) can lead to isolation of $[NH_4]_2Mn[CrO_4]_2.2H_2O$; (6), and $[NH_4]_6Mn[CrO_4]_4.2H_2O$; (7), which have been identified from X-ray diffraction data. (7) irreversibly converts to (6), which can further convert to $[NH_4]_2Mn_2[CrO_4]_3$ and $[NH_4]Mn_2[CrO_4]_2OH.H_2O$ [105]. Manganese(II) hexafluoroniobate(IV), $Mn[NbF_6]$, has been studied spectroscopically and shown to have an ReO_3–type structure. The electronic spectrum has been assigned in terms of crystal field theory [106]. The salt $Mn[NbO_3]_2$ was prepared by exchange reactions in aqueous solutions, and characterised by DTA and X-ray diffraction. $Mn[NbO_3]_2$ is completely soluble in water in the presence of excess niobate(V), and manganese(II) is partially oxidised [107]. The Raman spectra of $Mn[TiF_6].6H_2O$ crystals were recorded and analysed, and mode frquencies assigned [108], and the phase transition at about 200 K has been studied by variable temperature IR spectroscopy and related to variations in the Mn–O stretching frequency [108a].

The vibrational spectra (Raman, IR and far IR) of $K_2Mn_2[SO_4]_3$ were recorded and have been comprehensively studied and assigned. The spectra were discussed with reference to similar salts [109]. The manganese(II) dioxouranium(VI) salt $Mn[UO_2]_2[SO_4][OH]_4.1.5H_2O$ was synthesised, and the crystal structure determined by X-ray powder diffraction. The space group is monoclinic, *B2/m*. A thermochemical study has also been conducted on the compound and compared with those on isostructural salts [110]. Crystallisation of manganese(II) and piperazine sulfate solutions produced three branches, identified as $MnSO_4.5H_2O$, piperazine sulfate and $MnSO_4.[C_4H_{12}N_2][SO_4].6H_2O$. The products were characterised by thermogravimetric analysis [111].

The crystal structure of $MnPt_3O_6$, as refined from neutron diffraction experiments, shows the unit cell to contain a framework of planar $\{PtO_4\}$ and octahedral $\{PtO_6\}$ groups with a distorted, eight-coordinate manganese site. Some cation disorder was also noted [112].

The crystal structure of $Mn[VO_3]_2.4H_2O$ was reported to be isostructural with $Cd[VO_3]_2.4H_2O$, by X-ray powder diffraction evidence, the unit cell having space group *Cc*, with the manganese octahedrally surrounded by two water molecules and four oxygen atoms from the anion [113].

An investigation has been carried out into the precipitation of manganese(II) from aqueous solutions of $Mn[ClO_4]_2$ and $Na_4[P_2O_7]$ over a range of pH values. $Mn_2[P_2O_7]$, $Na_2Mn[P_2O_7]$ and MnO were identified. Equilibrium constants and solubility data were quoted [114]. The thermal stability of $Mn[H_2PO_4]_2.2H_2O$ has been investigated with reference to structural changes, and the dehydration of the crystalline hydrate was also studied by X-ray powder diffraction. The variation between the results for manganese(II) and those for magnesium and cadmium was discussed [115]. The dehydration of $Mn[H_2PO_4]_2.2H_2O$ was also followed by IR spectroscopy, and the influence of bonding within the compound on the spectra discussed [116]. Thermogravimetric analysis of the cyclic hexaphosphate $Mn_3[P_6O_{18}].nH_2O$ showed decomposition to occur through pyrophosphates and phosphoric acids, to a cyclic tetraphosphate as final product [117]. Absorption and fluorescence spectra of manganese(II) in phosphate, fluorophoshate and fluoride glasses, together with EPR spectroscopic data, indicate the manganese ions to be in octahedral sites, while the ionic contribution of the chemical bond between the Mn^{2+} ions and the ligands increases with fluoride content [118]. The solid solution γ-$(Zn_{0.75}Mn_{0.25})_3[PO_4]_2$ has been studied by neutron powder diffraction and the structure shows that the zinc ions occupy five-coordinate sites while the manganese ions occupy six-coordinate sites [119].

The crystal structure of $Mn[ClO_4]_2 {,} 6H_2O$ has been reported, where the manganese is octahedrally coordinated to the six water molecules. IR and Raman spectra were recorded over the temperature range 100 - 360 K, and observed bands were assigned [120]. The thermal decomposition of the perchlorate hexahydrate salt has been studied by DTA and TGA, which showed that decomposition was to the oxide *via* the dihydrate [121].

The solid solution formed between $Mn[CO_3]$ and $Ca[CO_3]$ has been investigated over a wide range of compositions by magnetic susceptibility, EPR spectroscopy and diffuse reflectance spectroscopy [43].

^1H NMR spectroscopy studies on ethanoic acid exchange with manganese(II) indicates that solvent exchange occurs as a whole ethanoic acid molecule. Rate and energy constants have been calculated [122]. The magnetic moment of manganese(II) in ethanoic acid solution has also been determined (μ_{eff} = 5.8 μ_β) [123].

The isothermal and nonisothermal dehydration and decomposition of $Mn[C_2O_4].2H_2O$ in a dinitrogen atmosphere have been studied. Thermodynamic parameters for the system have been evaluated and analysed [124]. An immersion analysis of $Mn[C_2O_4].n[N_2H_4]$ (where $0 < n < 4$) has shown that, where n is integral, the salt is an individual compound, while, where n is fractional, the salt is a mixture of phases [125].

An investigation of the systems $Mn(HCOO)_2/Mg(HCOO)_2$ and

$Mn(HCOO)_2/Cd(HCOO)_2$ shows a continuous series of mixed crystals cocrystallising, as the compounds $M(HCOO)_2.2H_2O$ are isomorphous [126].

2.4.4.2 Intercalates

Intercalation compounds of the crystalline solid $MnPS_3$ have been studied: pyridine forms an intercalate with $MnPS_3$ in which the pyridine molecules are arranged between the $\{PS_3\}$ layers, perpendicular to the layers. The basal spacing is 12.4 Å [127]. The low frequency motions of $[Co(cp)_2]^+$ and $[Cr(C_6H_6)_2]^+$ intercalated in $Mn[PS_3]$ have been studied by inelastic neutron scattering, and compared with the IR and Raman spectra of the equivalent iodides $[Co(cp)_2]I$ and $[Cr(C_6H_6)_2]I$. Assignments of the various modes were made [128]. The IR and Raman spectra of $[Ru(bipy)_3]^{2+}$ and 2,2'-bipyridine intercalated in $MnPS_3$ were compared and related to the spectra of 4,4'-bipyridine and *N,N'*-dimethyl-4,4'-bipyridinium chloride, and *N,N'*-dimethyl-4,4'-bipyridinium cations in $CdPS_3$ [129].

2.4.4.3 Doped crystals

The X-band EPR spectra of manganese(II) doped into crystals of $Zn[SiF_6].6H_2O$ were measured and analysed to evaluate the spin Hamiltonian parameters [130]. Single crystals of $Mg[SiF_6].6H_2O$ doped with manganese(II) have been studied by X-band EPR spectroscopy at various temperatures and the results analysed [131], and have also been examined with reference to their solid state transitions, paramagnetic resonance spectra and structure [132]. The EPR spectra of manganese(II) ions doped into $[Mg(H_2O)_6][SnCl_6]$ single crystals at 77 K and 290 K were reported. The manganese(II) ions are shown to be in unique, axially symmetric environments: $[Mn(H_2O)_6]^{2+}$ [133].

The EPR spectra of manganese(II) ions doped into $K_2Zn[XO_4]_2.6H_2O$ (X = S or Se) were recorded, and the parameters determined were found to agree with those of Saraswat and Upreti [134].The absorption spectra of manganese(II) in $LiK[SO_4]$ was studied at room temperature and liquid nitrogen temperature. The structure of the bands was discussed and assigned, and the crystal field and Racah parameters calculated [135]. An analysis of the luminescence spectrum of a triglycine sulfate crystal doped with manganese(II) has given information on the spatial distribution of the ions in the crystal [136].

EPR and luminescence spectra of $Ca[ZnF_4]$ doped with about 1% manganese(II) showed the Mn^{2+} ions to occupy only zinc sites. The parameters determined are in the same range as those for $[MnF_6]^{4-}$. The luminescence spectra do not serve as criteria to distinguish between four- and eight-coordination [137]. The effect on the EPR spectrum of the trigonal distortion on manganese(II) ions doped into $Na_2[ZnCl_4].3H_2O$ was studied. The axial splitting parameter *D* showed a dependence on the distortion when the two were aligned [138]. Crystals of SrF_2 doped with manganese(II) have been studied by EPR spectroscopy, and as well as cubic symmetry, some Mn^{2+} ions show trigonal symmetry due to defects in the crystal. Parameters were evaluated and discussed [139]. The manganese(II)-doped solid solutions of trissarcosine/calcium chloride and trissarcosine/calcium bromide were studied by EPR spectroscopy. The bromide shows a non-linear relationship between the axial fine structure parameter *D* and the bromide ion concentration [140]. The EPR spectrum of manganese(II)-doped $[NH_4]I$ single crystals has been studied at room temperature and analysed, being analogous to the $[NH_4]Br/Mn^{2+}$ and $CsCl/Mn^{2+}$ systems [141]. The EPR spectra of manganese(II)-doped $CsCdCl_3$ at varying hydrostatic pressures were studied, and the effect on the axial splitting parameter noted [142].

The EPR powder spectrum of Mn^{2+} in ZnS doped with copper has been presented and discussed, together with a simple analytical method [143]. When $Cs_2Zn_3S_4$ doped with 4% manganese was studied by EPR spectroscopy, two non-equivalent Mn^{2+} centres were observed: fine and hyperfine structure parameters were given [144].

The EPR spectra of manganese(II) ions doped into tetragonal and monoclinic ZnP_2 have been recorded and analysed in terms of the symmetry of the crystals and ionic interactions therein [145]. When manganese(II) is doped into a TeO_2/PbO glass, EPR spectra show several environments for the manganese ion. At <5 mol. % MnO, the hyperfine sextet is clearly resolved, while for >5 mol. % MnO, antiferromagnetic behaviour is detected [146].

2.4.5 Phosphine and Phosphine Oxide Complexes

A series of compounds of formula $MnLX_2(Q)_n$ (where L is a general phosphine ligand; X is Cl, Br, I, CN, NO_2, NO_3, OH, SCN, SeCN, or OCN; Q is a solvent molecule) have been prepared and characterised. Their uses in the removal of dioxygen from nitrogen gas, in the production of oxygen gas, and in the absorption of dihydrogen, sulfur dioxide, alkenes and carbon monoxide were discussed [147]. The reversible coordination of O_2 to $MnX_2(PR_3)$ (X = Cl, Br, I or NCS) was discussed with reference to solution (for the halide complexes) and solid state (isothiocyanate complex) systems. Equilibrium constants and electronic and IR spectral data were also presented. Data on the uptake of dioxygen were presented and the reversibility of the reaction discussed [148]. The solution EPR spectra of the oxygenated manganese(II) species $[Mn(O_2)(PR_3)X_2]$ (X = Cl, Br or I; R = Bu or Pent) were recorded between 0 °C and −60 °C, and indicate that the species in thf solution are six-coordinate high-spin complexes with axial symmetry [149]. The previously published work of Green and coworkers on manganese(II) halide phosphine systems was discussed and their conclusions confirmed, while divergences from the method of McAuliffe were noted. Further properties of such systems were also reported [150]. A reply by Green to this latter paper was also published [151]. A detailed summary of work by McAuliffe and coworkers, with preparations, properties and spectral data, has been published [152]. Other workers in the field present IR spectral evidence which confirms the reversible reaction of $MnX_2(PR_3)$ with dioxygen, while suggesting that the chromophore is a manganese(III) superoxide [153], and EPR spectroscopic and spectrophotometric studies of $[Mn_2Cl_4(PR_3)_2]$ in toluene and thf have shown uptake of oxygen to be reversible at about 100 ^{o}C, forming a manganese(III) species [154]. Future developments are awaited with interest.

The reactions of manganese(II) dialkyls with tertiary phosphines or of manganese(II) dichloride with manganese(II) dialkyls in the presence of phosphines leads to dimers $[Mn_2R_4(PMe_3)_2]$ (R = CH_2SiMe_3, CH_2CMe_3 or CH_2Ph) and $[Mn_2(CH_2SiMe_3)_4(PR'_3)_2]$ (PR'_3 = PEt_3, $PPhMe_2$, PPh_2Me or $P\{cychl\}_3$). The crystal structures of three of the compounds have been determined by X-ray diffraction methods, and each contains two asymmetrically bridging alkyls, one terminal alkyl and one terminal phosphine per manganese. Typical interatomic distances are: r(Mn–Mn) 2.667–2.828 Å, r(Mn–P) 2.562–2.684 Å based on the unit shown in Fig. 2 [155]:

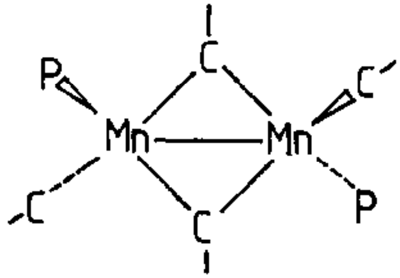
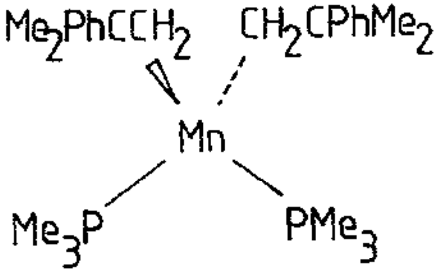
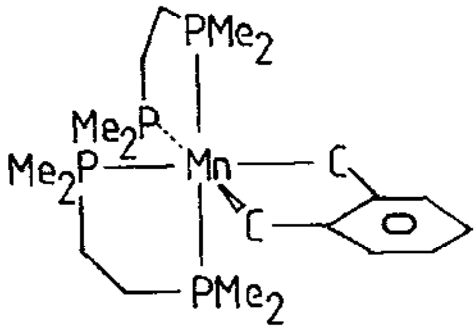


Fig. 2: Central unit of $[Mn_2R_4(PR'_3)_2]$

The preparation, and characterisation, using solution EPR spectroscopy techniques, of the monomeric four-coordinate complexes $[MnR_2(PR'_3)_2]$ (PR'_3 = PMe_3: R = CH_2CMe_2Ph; PR'_3 = dmpe: R = CH_2CMe_2Ph, CH_2CMe_3, CH_2SiMe_3 or CH_2Ph) and the six-coordinate complex $[Mn\{2\text{-}(CH_2)_2C_6H_4\}(dmpe)_2]$ have also been described. The X-ray crystal structures of $[Mn_2(CH_2CMe_2Ph)_2(PMe_3)_2]$ and

$[Mn\{2\text{-}(CH_2)_2C_6H_4\}(dmpe)_2]$ have been determined

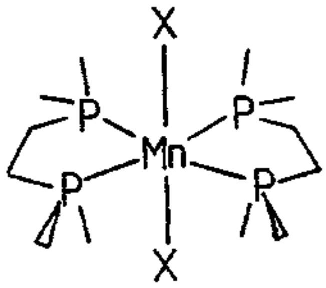




and the former shows considerable distortion from tetrahedral. In the six-coordinate complex, the low-spin manganese(II) ion has a smaller radius than the four-coordinate high-spin manganese(II) species, and this is reflected in the shorter Mn–C and Mn–P distances in the octahedral complex:

	r(Mn–C)/Å	r(Mn–P)/Å
$[Mn_2(CH_2CMe_2Ph)_2(PMe_3)_2]$	2.149(6)	2.633(4)
$[Mn_2\{2\text{-}(CH_2)_2C_6H_4\}(dmpe)_2]$	2.104–2.110	2.230–2.298

The X-band EPR spectra are discussed in terms of distorted tetrahedral high-spin and octahedral low-spin manganese(II) species [156]. The preparation of $[MnX_2(dmpe)_2]$ (X = Br, I or Me) has been reported, along with the crystal structures of $[MnBr_2(dmpe)_2]$; (8), and $[MnMe_2(dmpe)_2]$; (9).



(8); X = Br, (9); X = Me.

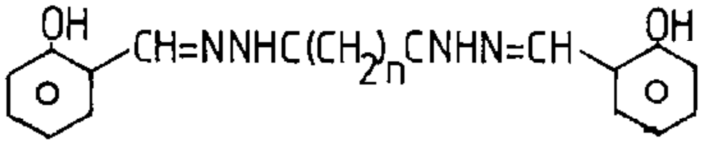
The complexes all have the *trans*-configuration the halide complexes being colourless, high-spin species (μ_{eff} = 5.9 μ_β), while the methyl complex is a red, low-spin species (μ_{eff} = 2.4 μ_β). The stronger ligand field of the methyl group is further confirmed by the Mn-P bond lengths, which are *ca.* 0.4 A shorter in the methyl complex than in the bromo complex. While reaction of $[MnBr_2(dmpe)_2]$ with $MgMe_2$ yields the dimethyl complex above, reaction with $MgEt_2$ or $Li[AlH_4]$ yields manganese(I) complexes, which will be considered later (Section 2.5) [157].

A detailed study of the mechano-, electro- and high pressure photoluminescence of $[Mn(Ph_3PO)_2Br_2]$ has been reported [158].

2.4.6 Schiff Base Complexes

The complex of manganese(II) chloride with α-hydroxy-β-naphthaldehydethiosemicarbazone, of formula [Mn(L)Cl] (where L is the ligand), has been prepared, and its magnetic and EPR spectroscopic properties examined. It has been assigned a square planar structure, with S = 3/2, $\mu_{eff.}$ = 3.86 μ_β [159]. $[Mn(qa)_2X_2]$ (where qa is quinoline-2-aldoxime, isoquinoline-3-aldoxime; X is Cl, Br, I, NCS, NCSe, O_2CMe or $1/2[SO_4]$) and

$[Mn(qa)_2(NO_3)][NO_3]$ have been prepared, and characterisation includes molar conductance, X-ray powder diffraction, VT magnetic susceptibility and spectroscopy. For X = Cl, Br or I, the structure is a dimeric, halo-bridged distorted octahedron, while the others are monomeric pseudooctahedra [160]. The complexes $[Mn(LH_2)]$ and $[Mn_2L(H_2O)_4]$ (where LH_4 is the ligand formed from the reaction between salicylaldehyde and various aliphatic dicarboxylic acid hydrazides):

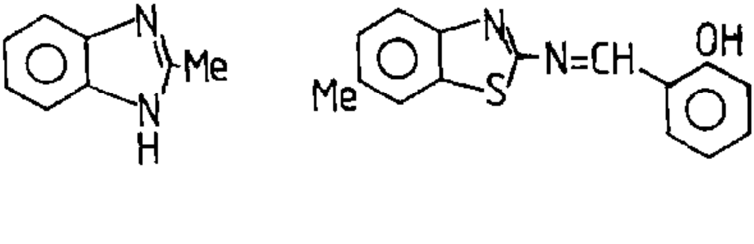


n = 1, 2 or 4

were prepared and characterised. The ligands are hexadentate and crystal field parameters have been calculated [161]. The manganese(II) complex with the Schiff base vanillin sulfanilate was prepared and characterised, and shown to be a low-spin octahedral complex [162]. The vanillin azine (vanaz) complexes, of general formula $[Mn(vanaz)X_2]$ (X = NO_3, Cl or NCS) and $[Mn(vanaz)_2][ClO_4]_2$, were prepared, and characterisation indicates that the ligand is bidentate through both nitrogen atoms [163]. Cinnamaldehyde azine (cinaz) is also bidentate, forming tetrahedral complexes $[Mn(cinaz)X_2]$, $[Mn(cinaz)_2]X_2$ (X = NO_3, Cl or NCS) and $[Mn(cinaz)_2][ClO_4]_2$ [164].

Manganese(II) complexes with the Schiff bases made from 2-(aminomethyl)pyridine or 2(2-aminoethyl)pyridine and substituted salicylaldehyde or substituted pyridine-2-carboxaldehyde have been prepared and characterised, and their properties compared [35]. $[Mn(mbim)_2(nmbts)_2]$;

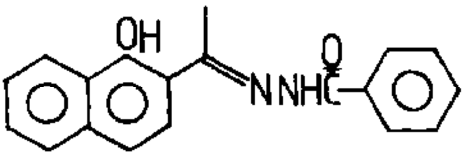
(10), (mbim = 2-methylbenzimidazole, nmbtsH = *N*-6-methylbenzothiazol-2-yl salicylaldimine) has been synthesised, and is a non-electrolyte, with octahedral coordination,



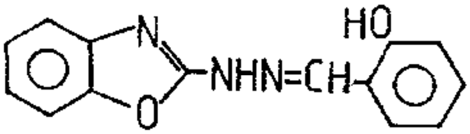
(10)

the ligand $nmbts^-$ binding through the phenolic *O* and exocyclic *N* atoms [165].

The hydrazone complexes $[Mn(bdnph)_2][ClO_4]_2$ (bdnph = benzil-2,4-dinitrophenylhydrazone) [166] and $[Mn(bdh)_2Cl_2]$ (bdh = biacetyldihydrazone) [167] have been synthesised and identified by standard characterisation techniques. Two methods of bonding have been noted for the ligand 2-aceto-1-naphthol-*N*-benzoylhydrazone (anbhzH):



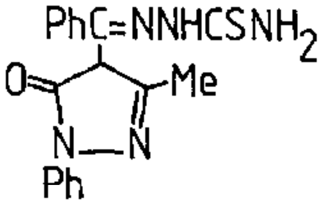
the deprotonated form is tridentate through phenolic *O*, carbonyl *O* and azomethine *N*, forming a complex [Mn(anbhz)Cl].nH$_2$O, while the protonated form is bidentate through carbonyl *O* and azomethine *N* in the complex [Mn(anbhzH)$_2$Cl$_2$] [168]. Other hydrazone complexes published include [Mn(hbs)Cl].2H$_2$O, where [hbs]$^-$ is the tridentate anion of the Schiff base prepared from salicylaldehyde and 2-hydrazinobenzoxazole; (11) [169]:



(11)

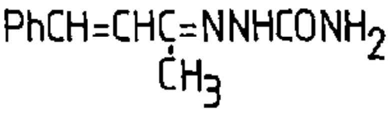
and [Mn(hppd)$_2$] and [Mn(hppd)(MeOH)$_3$][O$_2$CMe], where [hppd]$^-$ is the anion of 3-(2-hydroxyphenyl)-hydrazonopentane-2,4-dione: the anionic ligand is tridentate [170].

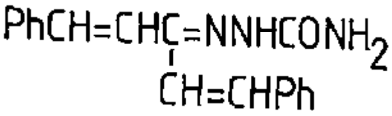
Semicarbazone complexes prepared include [Mn(bms)X$_2$] (X = Cl, [NO$_3$], [NCS] or [ClO$_4$]), where bms is benzilmonosemicarbazone [171], [Mn(btp)$_2$(H$_2$O)$_2$], where btpH is 4-benzoylthiosemicarbazone-3-methyl-1-phenyl-2-pyrazoline-5-one; (12) [172]:



(12)

and [Mn(bas)X_2] (X = [NCS], [NO_3] or Cl), [$Mn(bas)_2$]X_2 (X = Cl, [ClO_4] or [NO_3]) and [Mn(das)X_2] (X = Cl, [NCS], [NO_3] or [ClO_4]), where bas is benzalacetonesemicarbazone; (13), and das is dibenzalacetonesemicarbazone; (14) [173]:



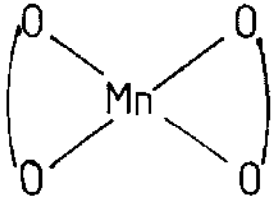


(13) (14)

The cationic ligand 1-acetyltrimethylammonium-3-thio-4-phenylsemicarbazide (atps) has been used to prepare the complex [Mn(atps)X_2]Cl.$n$$H_2O$, where X is Br, Cl, 1/2[SO_4], [O_2CMe] or [NO_3]. The mode of coordination is either through the carbonyl *O* or the thio *S*, and the azide *N* [174]. The complex of 1-salicyl-4-benzylamidothiosemicarbazone (sbtsH), [$Mn(sbts)_2$], was prepared and characterised by standard techniques. The complex is six-coordinate with the ligand binding through the thioketo *S*, imino *N* and phenolic *O* atoms [175].

The oxime complexes [$Mn(pao)_2Cl_2$] (pao = pyridine-2-aldoxime) [176] and

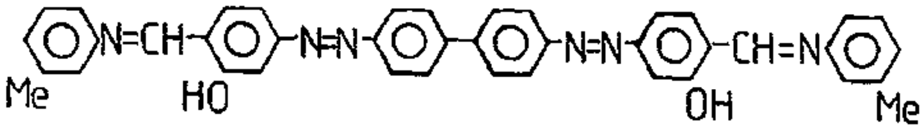
$[Mn(dab)_2Cl_2]$ (dab = diacetylmonoximebenzoylhydrazone) [177] have been prepared and characterised by standard techniques. The bisacetylmonoximesalicylhydrazone anion, $[bmsh]^-$, has been used to prepare $[Mn(bmsh)_2]$ [178], 2-bromo-4-methyl-6-acetylmonoxime-phenol (bmapH) forms a manganese(II) complex $[Mn(bmap)_2]$ [179], and the anion of α-benzilmonoxime, $[bmo]^-$, forms a complex $[Mn(bmo)_2]$; (**15**), which is reported by the authors to have square planar geometry [180].



bmoH = PhCOC(Ph)=NOH

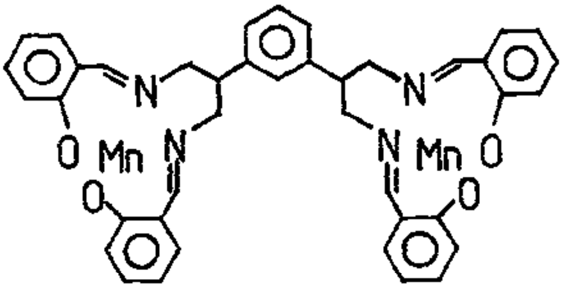
(**15**)

Of the polymeric Schiff base complexes which have ben synthesised, one is based on the tetradentate terephthalaldehyde bissemicarbazone ligand, with general formula $[MnL.2H_2O]_n$ [181], while other ligands prepared from terephthalaldehyde and the hydrazides of benzoic acid or pyridine-3-carboxylic acid have also been used [182]. The Schiff base derived from 3-toluidine and 4,4'-(4,4'-biphenylenebisazo)di(salicylaldehyde); (**16**),



(16)

forms a dark, insoluble polychelate of manganese(II) [183], and reaction of manganese(II) ethanoate with salicylaldehyde and 3-xylylenebis{2-(1,3-diamino)propane} results in the formation of the dimeric complex (17), which was fully characterised [184].



(17)

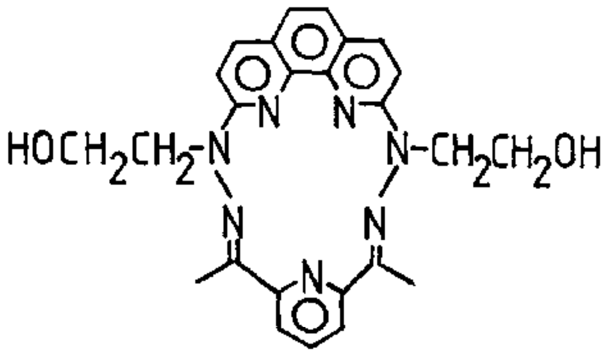
Spectrophotometric evidence is presented to show that a 1:2 complex is formed between manganese(II) and methyl(benzothiazolyl)azoketoxime [185]. An electrochemical study of the complex of manganese(II) with the Schiff base formed from 2,6-diacetylpyridine and diethylenetriamine indicates that, at the cathode, the ligand is reduced in preference to the metal, while oxidation has allowed the isolation of the analogous manganese(III) complex [186]. Stability constants in aqueous media are reported for the chelate [$Mn(tb)_2$] (Htb = 2-(thiophene-2-aldimino)benzoic acid) together with other thermodynamic and characterisation data [187]. Stability constants are also recorded for the manganese(II) complexes of 2-carboxyphenylhydrazoacetoacetanilide, 2-carboxyphenylhydrazo-4-chloroacetoacetanilide or acetoacetamide [188,189].

2.4.7 Complexes of Nitrogen Donor Ligands

The complex [$Mn([9]aneN_3)_2]Cl_2$ (where [9]aneN_3 is 1,4,7-triazacyclononane) was prepared by adding the macrocyclic ligand to a solution of manganese(II) chloride in dmso. The electrochemistry was investigated by cyclic voltammetry, and electronic spectra and magnetic data were also presented [190]. The macrocyclic ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ($Me_6[14]aneN_4$) reacts with manganese(III) ethanoate in methanolic hydrochloric acid to form the complex [$Mn(Me_6[14]aneN_4)Cl_2].2H_2O$. Characterisation was by IR and ^1H NMR spectroscopy and elemental analysis [191].

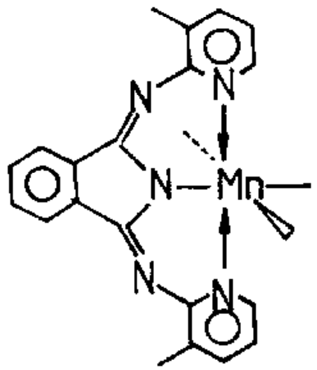
The EPR and photoacoustic spectra of the complexes of manganese(II) thiocyanate and sulfate with the ligand hexamethylene tetramine have been recorded in the solid state and in solution. Magnetic moments, photoacoustic and EPR spectral parameters were presented in detail. The metal ions have axial symmetry, and are six-coordinate [192]. The stability constant for the 1:1 complex of manganese(II) with hexamethylene tetramine at 25°C in a solution of ionic strength 0.5 has been evaluated [193].

The preparation and crystal structure of a manganese(II) macrocycle adduct [MnLCl][BF_4] are reported, where L is the macrocycle (18):



(18)

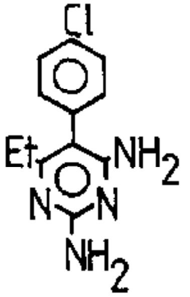
The manganese(II) acts as a template for cyclising 2,9-di(*N*-2'-hydroxyethylhydrazine)-1,10-phenanthroline with 2,6-diacetylpyridine [194]. The novel complex $K_2[Mn(basen)_2]$ (basen = bis(2-aminobenzenesulfonyl)ethylenediamine) has been prepared, and characterised by standard spectroscopic and physical techniques. The discussion of the structure and bonding proposes a distorted octahedral environment with a possible polymeric configuration [195]. The crystal structure of the manganese(II) adduct of bis(3-methyl-2-pyridylimino)isoindoline (Hbpi), $[Mn(bpI)_2]$; (19), is reported. The ligands are anionic, tridentate and meridional in configuration, forming a distorted octahedron around the central manganese [196].

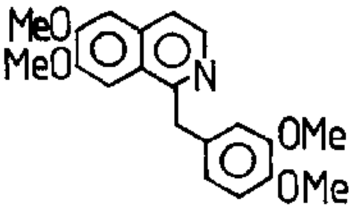


(19)

The complex $[Mn(bipy)(NCS)_2]$ has been prepared by the thermolysis of $[Mn(bipy)_2(NCS)_2]$, and has been shown by various spectroscopic techniques to contain a polymeric structure of zigzag chains. Variable temperature magnetic susceptibility measurements have also been made [197]. The cyanide complexes $Na_2[MnL(CN)_4].nH_2O$, where L is bipy or 1,10-phen, were prepared from the metal, ligand and sodium cyanide in solution, and characterised by IR spectroscopy and magnetic moment data [198].

The formation of $[Mn(py)_6]^{2+}$ in the presence of methanamide and dmf were investigated polarographically: formation constants were quoted [199]. The complex of manganese(II) chloride with perimethamine (2,4-diamino-5-(4-chlorophenyl)-6-ethyl-1,3-diazine: pma), $[MnCl_2(H_2O)_3(pma)]$ was prepared, and characterised by elemental analysis, conductivity and IR spectroscopy. The stability constant was determined and the authors suggest coordination through the hetero-*N*(1) atom [200].





perimethamine papaverine

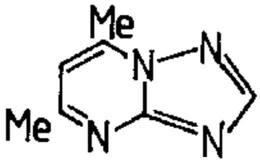
The adduct $MnCl_2.2pap.HCl$ (pap = papaverine) has been prepared and characterised by standard techniques. The papaverine ligand is coordinated through the hetero-*N* atom [200a].

The crystal structure of *trans*-$[Mn(NCS)_2(pyrazole)_4]$ has been reported showing *trans*-isothiocyanate groups and four pyrazole ligands in an equatorial plane, the molecule being centrosymmetric. Variable temperature magnetic studies, IR and diffuse reflectance electronic spectroscopy and TGA have been carried out and the results were interpreted [201].

The crystal structure of $[Mn(imidH)_6]Cl_2.4H_2O$ has been reported, and shown to contain manganese in an octahedral environment, coordinated to all six imidazole molecules [202]. The crystal structure of $[Mn(imidH)_4(H_2O)_2]Cl_2$ also shows octahedral coordination of the manganese, but the $Mn-OH_2$ bonds are longer than in the hexaaqua complex, and two Mn-imidH bonds are shorter than in the hexaimidazole complex (the remaining two Mn-imidH bonds being comparable) [203]. The polymeric complex $Mn(triaz)_3Cl_2$ (triaz = 4-butyl-4H-1,2,4-triazole) was prepared and characterised. The ligand is bidentate through *N*1 and *N*2, and the complex is six-coordinate and paramagnetic [204].

The complex $[Mn(NCS)_2(dmtp)_2(H_2O)_2]$ (dmtp = 5,7-dimethyl-

[1,2,4]triazolo[1,5-a]pyrimidine; (**20**),} has been prepared:



(**20**)

IR and electronic spectra were discussed. The ligand is monodentate through *N*3 [205]. The complexes $[Mn(mnb)_2Cl_2]$ and $[Mn(mnb)_2Br_2]$ (where mnb is 2-methyl-5-nitrobenzimidazole) have been synthesised, and characterised by standard methods, and a polymeric, halide-bridged structure proposed [206]. The complexes $[Mn(mab)_2X_2]$ and $[Mn(mab)_4X_2]$ (where mab is 6-methyl-2-aminobenzothiazole; X is I, NCS or O_2CMe) were prepared and characterised [207]. Reaction of 2-thiobarbituric acid (Htb) with manganese(II) chloride yields a complex formulated as Mn(tb)Cl, characterised by spectroscopic and magnetic techniques. The authors state the structure to be octahedral, with the ligand being *N*-coordinated, bridging manganese atoms [208].

2.4.9 *Complexes with Oxygen Donor Ligands*

Ab initio calculations on $[Mn(H_2O)_6]^{2+}$ have been made and the Mn–O distance agrees closely with the experimentally determined value. Coordination energies, optimised geometries and electron density changes were discussed [209]. The complex of manganese(II) with the tetrabasic 1-hydroxyethylidenediphosphonic acid (H_4hedp) was prepared and formulated as

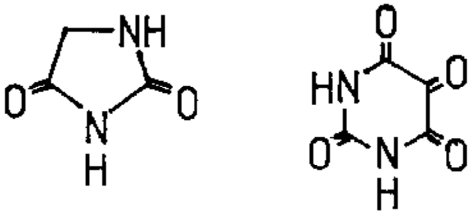
$[Mn_2(hedp)(H_2O)_6]$ [210]. The crystal structure of the crown ether complex $[Mn_2Cl_2(18\text{-crown-}6)(H_2O)_8]Cl_2$ has been described, consisting of $\{Mn_2Cl_2(H_2O)_8\}$ units bonded to the crown ether *via* the hydrated water [211].

The ligand biuret, $H_2NC(O)NHC(O)NH_2$ was used to synthesise $[Mn(biuret)_2X_2].nH_2O$ (X = Cl, NO_3 or O_2CMe) and $[Mn(biuret)_2(SO_4)(H_2O)]$. The ligand is bidentate through the carbonyl oxygen atoms, and the manganese(II) has distorted octahedral symmetry [212]. Complex adducts were prepared of the form $[MnL_2.2Q]$ where HL is one of the following bidentate ligands: pentane-2,4-dione, 1,1,1-trifluoropentane-2,4-dione, 1,1,1,5,5,5-hexafluoropentane-2,4-dione, 1,1,2,2,3,3,4,4-octafluorooctane-5,7-dione or heptafluoro-2,2-dimethyloctane-3,5-dione and Q is one of the molecules pyridine, dmf, dmso, tributylphosphate or butanone: thermal stabilities were compared [213]. A mass spectrometric study of $[Mn(tca)_2]$ (Htca = 1,1,1-trichloropentane-2,4-dione) has shown that although standard mass spectrometric reactions occur, a very facile chlorine rearrangement is of greater importance: a summary and fragmentation scheme was presented [214].

The manganese(II) complexes $[Mn(bap)_2(H_2O)_2]$ and $[Mn(aap)_2(H_2O)_2]$ (Hbap = 2-(benzoylaceto)phenol; Haap = 2-(acetoacetyl)phenol) were prepared, and characterised as monomeric complexes by standard techniques. Although other metal complexes of these potentially tridentate ligands can be converted to binuclear species, the authors suggest this is not the case for manganese(II) [215].

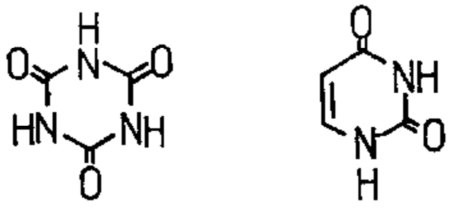
The reaction of anhydrous manganese(II) chloride in methanol with lithium 2,2'-diphenylenedioxide (Li_2dpd) yielded the corresponding complex $[Mn(dpd).2CH_3OH]$ ($\mu_{eff.}$ = 5.52 μ_β) which will react with bases such as pyridine and 2,2'-bipyridine to form octahedral complexes. Pyrocatechol (LH_2) reacts with manganese(II) chloride in the presence of an excess of triethylamine to form $[MnL(NEt_3)_4]$ ($\mu_{eff.}$ = 5.59 μ_β) [216]. 1,8-dihydroxyanthroquinone (Hdaq) has been shown to form a mononuclear chelate of formula $[Mn(daq)_2(H_2O)_2]$. Spectroscopic and magnetic data were presented and discussed with reference to the bonding in the complex [217].

The complexes $[Mn(hyd)_2Cl_2].4H_2O$, $[Mn(hyd)_2(NCS)_2].EtOH$, $[Mn(hyd)_2SO_4].2H_2O$ and $[Mn(hyd)_2(O_2CMe)_2].2H_2O$ (hyd = hydantoin) have been prepared. The ligand is bridging and bidentate through the carbonyl oxygen atoms [218]. The complexes of alloxan, $[Mn(alloxan)_2X_2].nH_2O$ (X = Cl, NO_3, O_2CMe or $1/2[SO_4]$) and $[Mn(alloxan)_2(NCS)_2.1.5EtOH$, were prepared, and characterised by IR spectroscopy. The ligand is reported to coordinate through "several" carbonyl oxygen atoms [219].



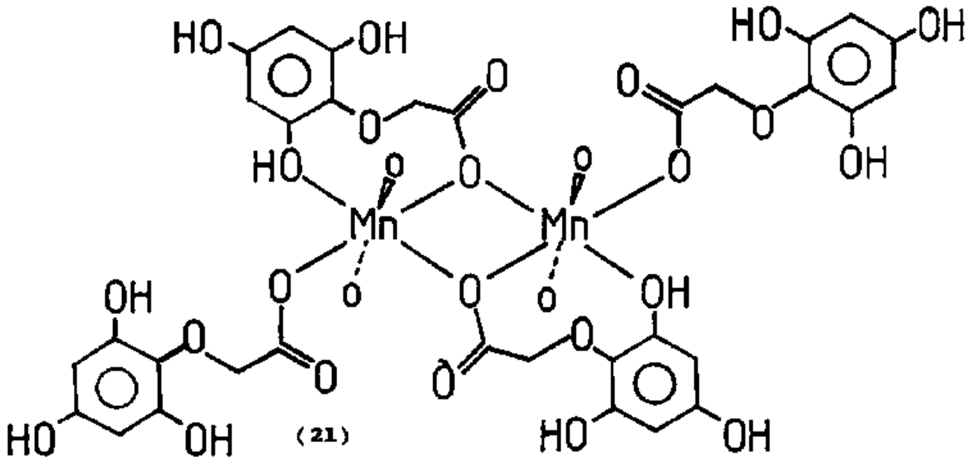
hydantoin alloxan

Manganese(II) cyanuric acid complexes $[MnL_2Cl_2].0.5H_2O$, $[MnL_2SO_4].H_2O$, $[MnL_2(NCS)_2].EtOH$ and $[MnL_2(O_2CMe)_2].3H_2O$ have been synthesised, and characterised by analytical, spectroscopic and thermogravimetric techniques. The cyanuric acid is *O*-bonded [220,221,222]. The isolation and characterisation of $[Mn(uracil)_4(H_2O)_2]Cl_2$ and $[Mn(uracil)_2Cl_2]$ were reported, together with analytical, IR spectroscopic and TGA data [223].



cyanuric acid uracil

The IR spectrum of manganese(II) monochloroethanoate was recorded and compared to that of its nickel analogue [224]. The third polymorph of the manganese(II)/(2,4,5-T) series (2,4,5-T = 2,4,5-trichlorophenoxyethanoic acid) has been prepared and the structure shown by X-ray crystallography to be $[\{(2,4,5\text{-T})Mn(H_2O)_2\}_2\text{-}\mu\text{-}(2,4,5\text{-T})_2]$; (21) [225].



(21)

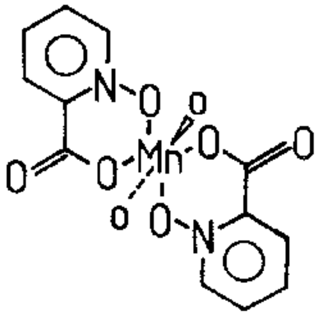
The manganese(II) copper tartrate complex $Mn_3\{Cu_4C_{12}H_{17}O_{18}\}_2.18H_2O$ has been prepared and a thermal decomposition scheme proposed [226]. The Mossbauer spectrum of iron(III) manganese(II) oxo iodoethanoate $[Fe_2MnO(CH_2ICOO)_6(H_2O)_6]$ was recorded to analyse the structure of the complex [227].

$[N(CH_3)_4]_2[Mn(O_2CCF_3)_4]$ was prepared and, on the basis of magnetic, IR and diffuse reflectance spectroscopic data, the structure is believed to consist of tetrahedral manganese(II) with unidentate trifluoroethanoate ligands [228]. Formation constants are reported for the levulinate complexes of manganese(II) at 25 $^{\circ}C$ in 0.1 *M* chloride solution [229].

Synthesis of the salicylate complex $[Mn(sal)_2(H_2O)_2]$ was reported, together with some IR spectroscopic and conductivity data. The EPR spectra and magnetic moment of the complex were discussed: the complex is high spin ($\mu_{eff.}$ = 5.90 μ_{β}) [230]. The basic salicylate complex [Mn(OH)(sal)].1/2H_2O was prepared from aqueous solution at pH 6-9, and characterised by IR spectroscopy and TGA [231].

The citric acid complexes $[Mn(H_2O)_6][Mn(C_6H_5O_7)H_2O]_2.2H_2O$ and $[Mn(C_6H_6O_7)H_2O]$ were studied by IR spectroscopy, which suggested that the alcohol group is involved in chelate formation. The latter complex is believed to be tetrahedral, with one uncoordinated acid group. In the former complex, the carboxylate groups are either monodentate or bridging [232]. Complexation of thiodiethanoic acid, thiodipropanoic acid and diglyconic acid with manganese(II) was followed potentiometrically at various temperatures and ionic concentrations: formation constants and other thermodynamic parameters were determined [233].

The crystal structure of manganese(II) pyridine-2-carboxylate-*N*-oxide $[Mn(C_6H_4NO_3)_2(H_2O)_2]$; (22), was reported: the H_2O molecules are axially coordinated [234].



(22)

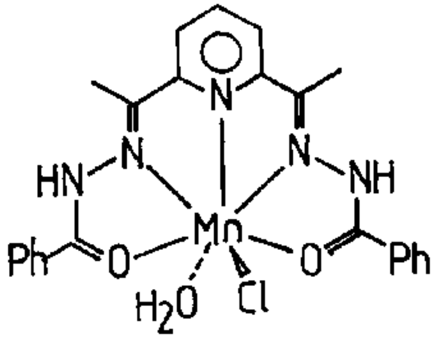
The fusion diagram for the $[MnCl_2(urea)]$/urea system was studied and the heat of fusion calculated [235].

2.4.9 Complexes with Mixed N, O and S Ligands

The formation constants for the reaction of manganese(II) with the 2-(arylhydrazino)propanoic acids (aryl = phenyl, 4-tolyl or 4-nitrophenyl) were determined at various ionic strengths and temperatures, and in a range of solvents using potentiometric techniques: parameters were quoted and discussed [236]. The adduct of manganese(II) oxalate and triethanolamine (tea), $[Mn(tea)_2(C_2O_4)]$, was prepared, characterised by IR spectroscopy and its thermal decomposition followed by TGA and DSC: thermodynamic parameters were discussed [237]. Hydrazinium hydrazinecarboxylate reacts with manganese(II) in aqueous solution to form a complex $[Mn(N_2H_3COO)_2(H_2O)_2]$. IR spectroscopy, DTA and TGA were used to characterise the product [238].

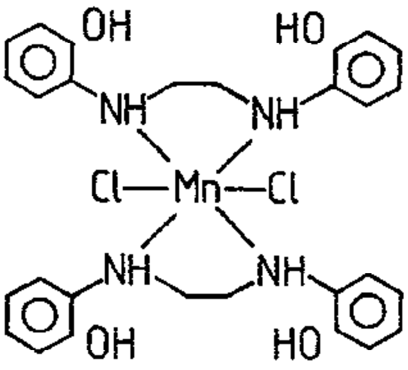
The ligands 2-(pyrrolylmethyleneamino)benzenesulfonic acid (H_2pbs) and 2-(pyrrolylmethyleneamino)ethanesulfonic acid (H_2pes) have been prepared and, when reacted with manganese(II), yield $[Mn(pbs)(H_2O)_3]$ and $[Mn(pes)(H_2O)_3]$ respectively. Electrical conductivity, magnetic and spectroscopic measurements were recorded [239]. The complexes $[Mn(pyrr)_2Cl_2]$ (pyrr = pyrrolidine) and $[Mn(\epsilon\text{-capr})_3Cl_2]$ (ϵ-capr = ϵ-caprolactam) have been prepared, and characterised by IR spectroscopy [240]. Reaction of manganese(II) with pyrazine-2-amide and pyrazine-2,3-diamide yields a complex with the protonated ligands bound through the heterocyclic *N* and amide *O* atoms [241].

The preparation and crystal structure were reported for $[Mn(dapb)(H_2O)Cl]Cl$; (23), (where dapb is 2,6-diacetylpyridinebis(benzoylhydrazone)) [242].



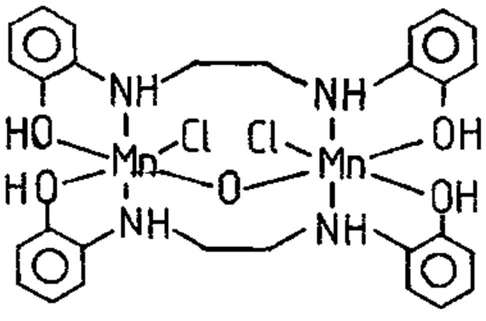
(23)

Reaction of manganese(II) chloride with *N,N'*-**bis**(2-hydroxybenzyl)-1,2-diaminoethane in ethanol yields a six-coordinate adduct; (**24a**), formulated from IR spectra as:



(**24a**)

With the anhydrous salt, a dimeric oxo-bridged structure; (**24b**), is formed:



(**24b**)

IR spectral data were presented and discussed [243].

The complexation of manganese(II) with 2-substituted thiazolidine-4-carboxylic acids (where the substituent is propyl, phenyl or 2-furyl) was followed by potentiometric titration at different temperatures and ionic strengths. The thermodynamic quantities ΔG, ΔH and ΔS were determined [244]. Work has been published on the complexation of *N*-hydroxymaleamic acid with manganese(II) [245]. The 2-aminobenzoate (2-ambenz) complexes [Mn(2-ambenz)(HO-8-quin)].nH_2O [246], [Mn(acac)(2-ambenz)$(py)_2$] and [Mn(acac)(2-ambenz)$(H_2O)_2$] [247] were prepared, and characterised by standard techniques. The polymeric complex MnL, where L is 5,5'-(4-phenylenebisazo)diquinolin-8-ol, has been prepared and characterised: each manganese ion has octahedral symmetry [248]. The manganese(II) complexes of Terizidone (trz; Terizidone is the Schiff base derived from terephthalaldehyde and cycloserine), formulated as $[Mn(trz)_6]X_2$ and $[Mn(trz)_4X_2]$ (X = Cl, Br or I), have been prepared from the hydrated halides, and characterised by standard methods; electronic spectral parameters have been evaluated [249]. The complexes of *N,N'*-dibenzoyl-2,6-diaminopyridine (dbap) with manganese(II): $[Mn(dbap)X_2]$ (X = Cl, Br, NO_2 or NCS) have been prepared and characterised. They are five-coordinate trigonal bipyramidal complexes, with axial X ligands and a tridentate organic ligand [250].

The stability constants of 4-hydroxy, 4-methoxy and 4-ethoxy-picolinic acid *N*-oxide complexes of manganese(II) were determined by pH titration: 1:1 and 1:2 chelates were observed [251]. The chloromanganese(II) complexes of some pyridine-carboxylic acid derivatives were prepared, having a general formula $[MnCl_2L_2]$: the acids and their derivatives include nicotinic acid, nicotinic amide, *N*-methylnicotinic amide, isonicotinic acid and nicotinic acid *N*-oxide. The complexes have been studied by various analytical and spectroscopic techniques, and stereochemistries were suggested for the complexes [252,253]. The 2-, 3- and 4-benzoylpyridine (bzp) complexes

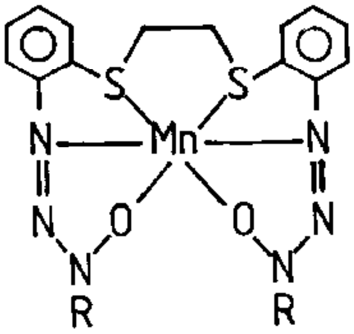
$[Mn(bzp)_2(NCS)_2]$ have also been prepared. Coordination of 2-benzoylpyridine is through the *O* and *N* atoms, while the 3- and 4-benzoylpyridines coordinate only through the *N* atom: the thiocyanate ligand is *N*-bonded. Spectral parameters are discussed [252,253,254]. The stability constants for manganese(II) with pyridine-2,5-dicarboxylic acid were determined, and the thermodynamic parameters ΔS, ΔH and ΔG quoted [255]. The isonicotinic acid hydrazide (inh) complex $[Mn(inh)_2Cl_2]$ was prepared and characterised: the complex is six-coordinate [256]. Manganese(II) complexes of formylhydrazide have been synthesised and formulated as $[MnL_2Cl_2]$ and $[MnL_2(SO_4)]$: analytical, magnetic and spectral data were quoted [257].

In the extraction of manganese(II) from perchlorate solutions with antipyrylmethane, a number of metal complexes of the ligand were isolated [258]. An isothiocyanatomanganese(II) complex of bis(methylaminoantipyryl)ethane was prepared and characterised by standard methods [259]. The ligand *N,N'*-bis(antipyrylmethyl)piperazine (apmp) has been used to synthesise the complexes $[Mn_2(apmp)Cl_4]$ and $K_2[Mn(apmp)Cl_4]$. In the dimeric compound $[Mn_2(apmp)Cl_4]$, the ligand, which bonds through the oxygen atoms, bridges the two metal centres [260]. The formation constants for the 1:1 and 1:2 adducts of manganese(II) with the monoanion of *N*-(2,3-dimethyl-1-phenyl- 5-oxo-3-pyrazoline-4-yl)-N'-benzoylthiourea have been determined [261]. Manganese(II) complexes with 4-(4-substituted phenylazo)-3-amino-2-pyrazolin-5-one have been prepared in which the ligand bonds through the carbonyl-*O* and arylazo-*N* atoms [262].

The reactions of manganese(II) with 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline and 2,4-dinitrobenzeneazopyrocatechol have been followed by EPR and IR spectroscopy. The stability constants of the complexes have also been evaluated, and possible structures for these complexes proposed [263].

The reactions of manganese(II) salts with 2,2'-bipyridine, 4,4'-bipyridine, 2,2'-bipyridine-*N*-oxide and 4,4'-bipyridine-*N*-oxide yield complexes which have been thoroughly studied by EPR and optical absorption spectroscopy. The electronic state of the metal was examined, and magnetic moment data, electronic and photoacoustic spectra were presented and interpreted [264]. The stability constants of manganese(II) complexes with 1,10-phenanthroline and Tiron (disodium 1,2-dihydroxybenzene-3,5-disulfonate) in dioxane/water systems were determined by titrimetric techniques. pH stability was also studied [265].

The complexes [$Mn(stm)_2L_2$] (where Hstm is selenoylthienoylmethane and L is water, pyridine or 3- or 4-picoline) were prepared and characterised by IR spectroscopy and thermal analysis [266]. Another study of manganese/selenoylthienoylmethane compounds has also been published [266a]. The pyridine adduct of manganese(II) ascorbate has been prepared, and possible structures suggested on the basis of elemental analysis, IR and diffuse reflectance spectroscopy and magnetic properties [267]. Reaction of manganese(II) ethanoate with the ligand [$(2\text{-}RN(O){:}NNHC_6H_4SCH_2)_2$] (R = CH_3 or C_2H_5) yielded the complex [$Mn\{(2\text{-}RN(O){:}NNHC_6H_4SCH_2)_2\}$]; (25):



(25)

which was characterised by standard techniques and assigned a six-coordinate structure [268]. Adducts of 2-furanthiocarboxyhydrazide (Hftc) and its anion were prepared. $[Mn(Hftc)_2Cl_2]$ is six-coordinate, while $[Mn(ftc)_2]$ is a four-coordinate square planar compound. The ligand is bidentate through terminal-*N* and thiocarboxy-*S* atoms [269].

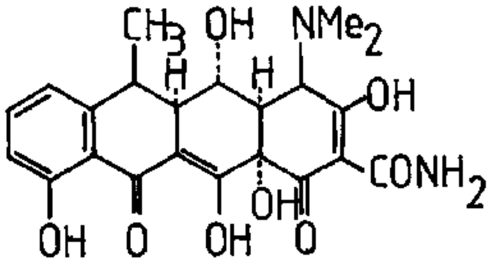
A series of mixed metal complexes of ethylenediamine tetraacetate have been prepared and formulated as $MnM(edta).6H_2O$ (M = Co, Ni, Cu or Zn). Characterisation by IR spectroscopy and X-ray diffraction showed the compounds to be isomorphous with $[Zn_2(edta)(H_2O)_4].2H_2O$, while the IR spectra indicate both bridging and terminal carboxylate groups [270]. A detailed study of the compounds was also presented, and differences discussed with reference to the ionic radii of the various metals [271]. The solid phase derived from manganese(II) ethylenediaminetetraacetate, manganese(II) perchlorate and water was identified by Schreinemaker's residue method, IR spectroscopy, X-ray diffraction, thermal analysis and magnetic measurements, and shown to have the composition $Mn_5(edta)_2(ClO_4)_2.20H_2O$ [272]. At pH 7–8, the complex $Mn_2(cdta).nH_2O$ can be prepared from aqueous solutions of manganese(II) carbonate and cyclohexanediaminetetraacetic acid ($cdtaH_4$) [273]. Stability constants were determined for manganese(II) and ethylenediphosphinetetraacetic acid by potentiometry and electronic spectroscopy [274].

Manganese(II) chlorosulfate was prepared from manganese(II) ethanoate and chlorosulfuric acid. It complexes with nitrogen-donor ligands to form $[MnL_4(O_3SCl)_2]$ (L = CH_3CN, py or py-*N*-oxide) and $[MnQ_2(O_3SCl)_2]$ (Q = bipy or acridine). The complexes are all six-coordinate, with the chlorosulfate ligand being mono- or bidentate [275]. Manganese(II) chloride reacts with 2-mercaptophenol in 1:1 molar ratio in methanol to yield methanolic adducts of manganese(II) 1,2-phenyleneoxidesulfide [276].

Reaction of an aqueous solution of manganese(II) with saccharin ($C_7H_5NO_3S$) gave an adduct $[Mn(C_7H_4NO_3S)_2(H_2O)_4].2H_2O$ which was characterised by standard methods. The manganese is six-coordinate with the saccharinate ligand *N*-bonded [277].

The complex of manganese(II) with sulfadiazine salicylaldimine was prepared and studied, and stability constant and ΔG values quoted [278]. Stability constants were determined by potentiometric titration in aqueous propanone over the pH range 3.5–5 for manganese(II) with sulfapyridazine, sulfadimesine, sulfadimethoxine, norsulfazole, sulfamonomethoxine, bucarban, butamid and albucid [279], and over the pH range 8–9 for manganese(II) with sulfadimesine, sulfadimethoxine, norsulfazole and sulfapyridazine [280]. Benzothiazolesulfonamide morpholide (btsm) has been used in the preparation of the complexes $[Mn(btsm)_2X_2]$ (X = NO_3, O_2CMe, Cl or picrate). The ligand is bidentate through the thiazole-*S* and sulfonamide-*N* atoms, and the complex is octahedral [281]. The analogous complexes have been prepared with cyclohexylbenzothiazolesulfonamide [282].

The complexation of L-DOPA (L-3,4-dihydroxyphenylalanine) with manganese(II) has been studied in detail by titrimetric and spectroscopic techniques: ΔH, ΔS and pK values were quoted and discussed [283], and the bonding deduced to involve an equilibrium between aminoacid-(*N,O*) and catechol-(*O,O*) groups [284]. Stability constants for the manganese(II)/DL-α-alanine/doxycycline hydrate system in aqueous solution were determined and discussed [285].



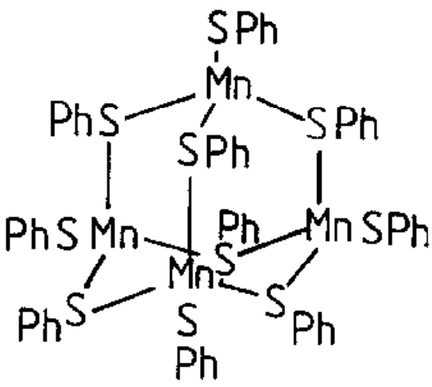
doxycycline

The aminoacid complex $[Mn(L\text{-lysine})_2].4H_2O$ has been prepared and characterised [286], and the interaction of manganese(II) with various bi- and tridentate aminoacids has been studied in aqueous media [287]. Complex formation between manganese(II) and a series of dipeptides has been followed by potentiometric titration, and EPR and NMR spectroscopy have been used to investigate the structures of the species detected [288].

Complexes of manganese(II) with L-tyrosine and various adenosine phosphates have been prepared, and stability constants evaluated [289]. Variations in formation constants of manganese(II) adenosinetriphosphate complexes with various aminoacids were studied and discussed [290].

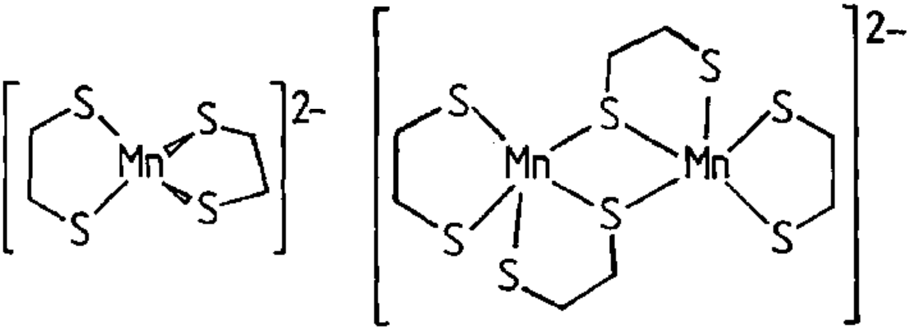
2.4.10 Complexes with S or Se Donor Ligands

A synthetic method has been reported for the preparation of $[PPh_4]_2]Mn(SPh)_4]$ and some properties were discussed [291]. The reaction of manganese(II) chloride tetrahydrate with sodium thiophenate in ethanol yields the complex $Na_2[Mn(SPh)_4]$, while the compound $Na_2[Mn_4(SPh)_{10}]$ has been isolated from the methanolic solution. The $[Mn_4(SPh)_{10}]^{2-}$ ion; **(26)**, has an adamantane-type structure, as shown by X-ray diffraction:



(26)

With sodium ethane-1,2-dithiolate (Na_2edt) in methanolic ethanenitrile, the compound $Na_2[Mn(edt)_2]$; **(27a)**, is produced, which is very sensitive to oxygen gas, and readily oxidises in ethanenitrile solution to the manganese(III) dimer $Na_2[Mn_2(edt)_4]$; **(27b)**. The crystal structures of these two manganese compounds have been determined:



(27a) (27b)

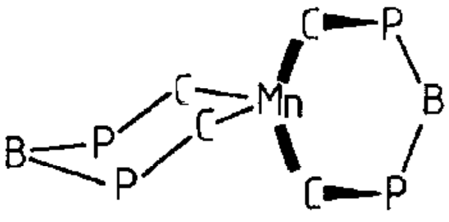
Electrochemical, magnetic and spectral properties were reported [292].

The phenylthiourea (ptu) adducts $[Mn(ptu)_2(O_2CMe)_2]$, $[Mn(ptu)_2(NO_3)_2(EtOH)]$, $[Mn(ptu)_2(SO_4)(H_2O)]$, $[Mn(ptu)_2Cl_2(H_2O)]$ and $[Mn(ptu)_2(NCS)_2(EtOH)_2]$ were prepared, and characterised by IR spectroscopy [293]. Complexes of 2,4-dithiobiuret ($NH_2C(S)NHC(S)NH_2$: dtb) were prepared, and formulated as $[Mn(dtb)_2SO_4]$ and $[Mn(dtb)_2X(EtOH)]X$ (where X = NCS or O_2CMe). The complexes are six-coordinate, and the ligand is bidentate [294]. Compounds of manganese(II) with selenoylacetone have been prepared and are discussed [295].

The complex $[Mn(tmd)_2]$ (tmdH = tetramethylenedithiocarbamic acid) has been prepared, and characterised by elemental analysis, magnetic measurements, TGA, IR and electronic spectroscopy. The molecule has pseudotetrahedral symmetry [296]. The mixed metal dithiocarbamate complexes $[MnM(S_2CNR_2)_4]$ were prepared for M = Zn, Cd or Hg andR = methylcyclohexyl-, ethylcyclohexyl- and isopropylcyclohexyl: characterisation was by standard techniques. The manganese has square planar coordination, while the other metal has tetrahedral coordination [297]. Reaction of manganese(II) chloride with 4-aminophenazonedithiocarbamic acid (apdtcH) yields the complex [Mn(apdtc)$_2$], which has been fully characterised. The ligand is reported to be bidentate through both sulfur atoms [289].

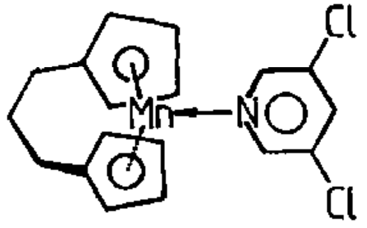
2.4.11 Other Complexes

The sulfur dioxide adduct [Mn(SO$_2$)$_2$][AsF$_6$]$_2$, prepared by oxidation of manganese with [AsF$_5$] in the presence of SO$_2$, has been characterised by spectroscopic techniques [299]. The complex of manganese(II) with hydrotris(1-indazoyl)borate (L), [MnLCl], was prepared and characterised by standard physical and spectroscopic techniques [300]. The ligand bis(dimethylmethylenephosphoranyl)dihydroborate(1-) has been synthesised and reacted with anhydrous MnBr$_2$, and the yellow complex formed has been shown by various methods to be of the form [MnL$_2$]; (28): X-ray crystallographic analysis has shown the molecule to contain {Mn-C-P-B-P-C} rings in a chair configuration, the whole complex having pseudotetrahedral geometry [301].



(28)

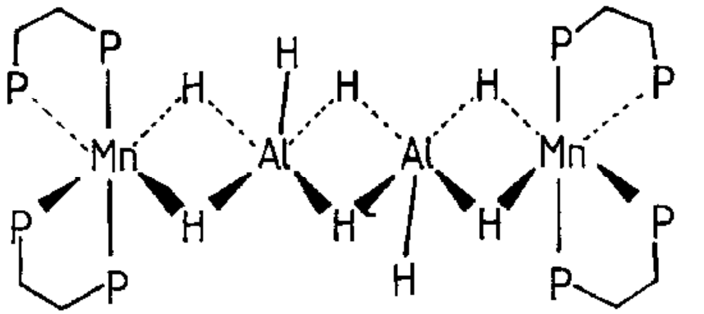
The synthesis of a [C_5H_5-$(CH_2)_3$-C_5H_5]$^{2-}$ metallocenophane of manganese(II) has been reported, as a 3,5-dichloropyridine adduct; (29). The crystal structure and nature of this high-spin, "electron-imbalanced" complex were discussed [302].



(29)

2.5 MANGANESE(I)

Localised molecular orbitals were presented for [$(NH_3)_5MnL$] (where L = H, CH_3, F, Cl) systems, and their derivation was discussed in depth [303]. The low temperature matrix isolation EPR spectra of MnCl, MnBr and MnI have been recorded and discussed [84]. The preparation of the complex [{$Mn(AlH_4)(dmpe)_2$}$_2$]; (30), was also reported, and the crystal structure presented and discussed.



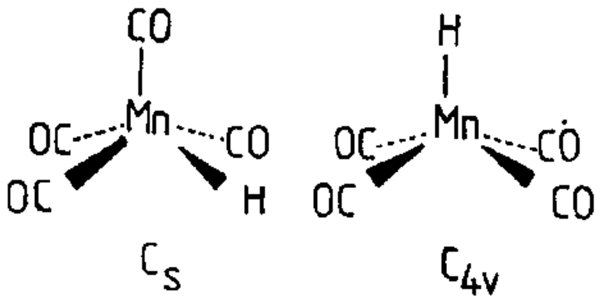
(30)

$[MnH(C_2H_4)(dmpe)_2]$ has also been prepared [157].

2.6 CARBONYL COMPLEXES OF MANGANESE

2.6.1 Carbonyl and Hydridocarbonyl Complexes

The electronic structures of $[Mn(CO)_5H]$ and $[Mn(CO)_5(CH_3)]$ have been studied through a Green's function approach [304]. The Raman spectra of $[Mn_2(CO)_{10}]$ and mixed manganese/rhenium carbonyls have been recorded in the range 10 - 170 cm^{-1}, 123 - 296 K, and thoroughly analysed [305]. A Raman spectroscopic study of $[MnRe(CO)_{10}]$ at high pressures shows that there are two first order phase transitions, at 7 kbar and 13 kbar, interpreted as due to a change of molecular conformation from staggered to eclipsed, and back to staggered: an assignment of the spectra was suggested [306]. The IR spectra of $[Mn_2(CO)_{10}]$ in the gas phase and 74 solvents were measured, and trends in solvent shifts discussed at length [307]. The EPR spectrum of $[Mn(CO)_5]$, generated by photolysis of the hydride, has been remeasured and reassigned [308]. The photochemistry of matrix-isolated $[HMn(CO)_5]$ has been investigated, and spectral analysis indicates that two isomers of [$HMn(CO)_4$] are formed [309].



The laser photolysis of [$Mn_2(CO)_{10}$] has been studied and shows that either Mn–Mn cleavage occurs to form [$Mn(CO)_5$]$^{\cdot}$ radicals or Mn–CO cleavage occurs to form [$Mn_2(CO)_9$] [310]. The low temperature photodissociation of [$Mn_2(CO)_{10}$] in an alkane matrix was followed by IR spectroscopy, and it was deduced that, at low temperatures, loss of CO to form [$Mn_2(CO)_9$] occurs in preference to Mn–Mn bond cleavage which is seen in solution at 298 K [311].

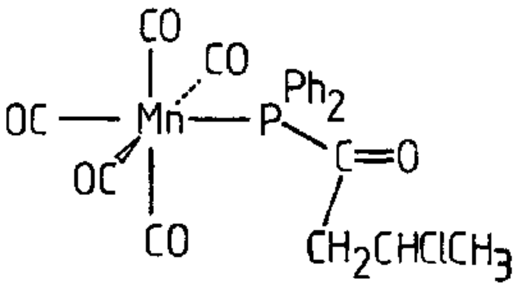
γ-irradiated single crystals of [$Mn_2(CO)_{10}$] exhibit EPR spectra at 85 K characteristic of a [$Mn_2(CO)_9$]$^-$ species with one CO bridge [312]. EPR spectral studies have shown that the electron is localised in a Mn–Mn σ^* orbital [313].

The mechanism of ligand substitution in [$Mn_2(CO)_{10}$] has been investigated by isotopic substitution [314]. The kinetics of the scrambling reaction between [$Mn_2(CO)_{10}$] and [$Re_2(CO)_{10}$] to give [$MnRe(CO)_{10}$] have been investigated and suggest that the reaction occurs via [$Mn_2Re_2(CO)_{20}$] or [$Mn_2Re_2(CO)_{16}$] clusters [315]. The vibronic activation of CO in [$Mn_2(CO)_{10}$] was studied to examine the change in electron density distribution as functions of the CO coordinates [316].

Reduction of [$Mn_2(CO)_{10}$] or [$MnRe(CO)_{10}$] with Li[Et_3BH] produces the anionic formyl complexes [$MnM(CO)_9(CHO)$]$^-$ (M = Mn or Re). Their reactivity and chemistry were examined in detail [317]. The reactions of [$Mn(CO)_5H$] with Lewis acids have been investigated, using VT multinuclear NMR techniques. Subsequently identified was: [$(CO)_5Mn{-}H{-}BCl_3$], while Al_2Br_6 only produces [$Mn(CO)_5Br$], [$Mn(CO)_5$][$AlBr_4$] and [$Mn_2(CO)_{10}$]. The phosphine complex [$Mn(CO)_4H(PPh_3)$] undergoes hydride cleavage with both Lewis acids to form the chloro and bromo derivatives [318]. Reaction of Na[$Mn(CO_5$] with MCl_3 (M = Ga or In) results in the formation of Na[$Cl_{4-n}M\{Mn(CO)_5\}_n$] (n = 1, 2 or 3). When $In(OOCCH_2CH_2CH_3)_3$ is allowed to react with Na[$Mn(CO)_4L$] (L = CO or PPh_3), the species [$(CH_3CH_2CH_2COO)_nInMn(CO)_4L$] is formed: IR data for the carbonyl groups was presented [319]. The binuclear complex [(OEP)$InMn(CO)_5$] (OEP = octaethylporphyrin) has been synthesised by addition of [$Mn(CO)_5$]$^-$ to [ClIn(OEP)], and characterised spectroscopically [319a].

2.6.2 Halides

The UV photoelectron spectra of the manganese(I) carbonyl halides [$Mn(CO)_5X$] (where X = Cl, Br or I) have been studied and analysed in terms of the σ-donor and π-acceptor properties of the X-ligand [320]. The photoinduced homolytic fission of [$Mn_2(CO)_{10}$] in CCl_4 in the presence of 2,3-butadione as photosensitiser yields [$Mn(CO)_5Cl$] [321]. Reaction of [$Mn(CO)_5Br$] with the ligands $Ph_2PC(O)R$ (where R = CH_2CH_2Cl or $CH_2CHClCH_3$) yields stable monomeric complexes [$(OC)_4BrMn(PPh_2C(O)R)$], where the phosphine ligand is monodentate. The crystal structure of [$(OC)_4BrMn(PPh_2\{C(O)CH_2CHClCH_3\})$], (**31**), has been determined and the molecule has the stereochemistry:

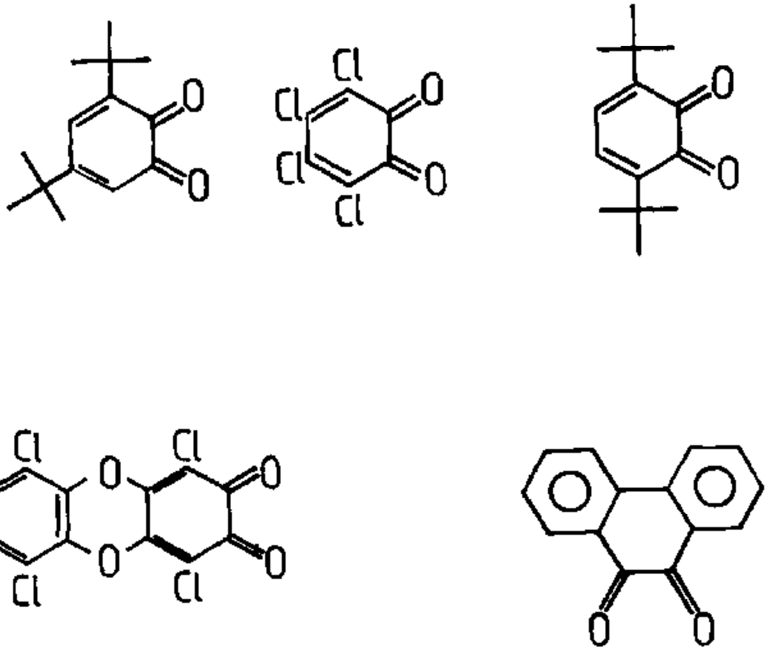


(**31**)

^{31}P NMR and IR spectral data were presented [322]. The phosphino- or thiophosphorylformamide ligands $Ph_2PC(O)NRSiMe_3$ (R = Ph or Me), $Ph_2PC(O)NHR$ (R = Ph, Me or CMe_3) or $Ph_2P(S)C(O)NHR$ (R = Ph or Me), have been used to prepare complexes of $[Mn(CO)_4X]$. Simple 1:1 adducts are formed with all three ligands, while the third also forms a bridged dimeric species with loss of PhNCO. Characterisation involved IR and ^{1}H NMR spectroscopy [323].

2.6.3 Compounds with O Donor Ligands

The EPR spectra have been recorded for the products of the reactions between $[Mn_2(CO)_{10}]$ and the semiquinone ligands Q; (32):



(32)

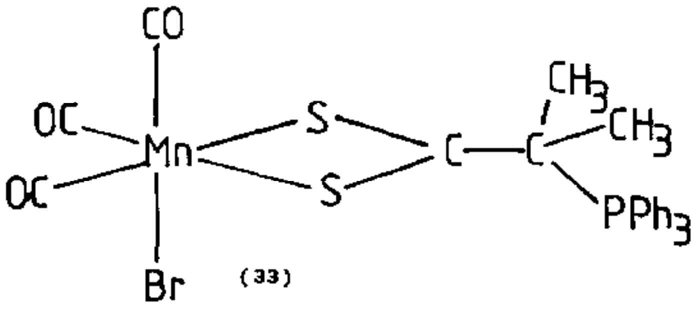
A series of adducts of $[Mn(CO)_4Q']$ (where Q' is the radical anion from 3,5-di*tert*butylsemiquinone) with a variety of *O*, *N*, *S* and *P* donor ligands have been prepared and analysed [324]. Reaction of 3,6-di*tert*butylsemiquinone (dbsq) with $[Mn(CO)_5]$ produces $[dbsq]^-[Mn(CO)_5]^+$, which loses CO to form $[(dbsq)Mn(CO)_4]$, and up to two further CO molecules can be replaced by triethylphosphite ligands. Tributylamine or propanone will replace only one CO molecule: electronic spectra were recorded [325]. The EPR spectra of these complexes have also been recorded [326]. The preparation and characterisation of the binuclear complex $[Mn_2(asq)_4L_2]$ and the tetranuclear complex $[Mn_4(asq)_4(CO)_8]$ (asq = acetylsemiquinone, L = CO, CH_3CN or dme) were reported, and the solution magnetic behaviour and internal redox properties discussed [327].

The nitrosobenzene adduct $[(cp)(CO)_2Mn(PhNO)]$ was synthesised by UV photolysis of $[(cp)Mn(CO)_3]$ in thf followed by treatment with nitrosobenzene. The complex was fully characterised and the ligand noted as a two-electron donor [328].

2.6.4 *Compounds with S, Se or Te Donor Ligands*

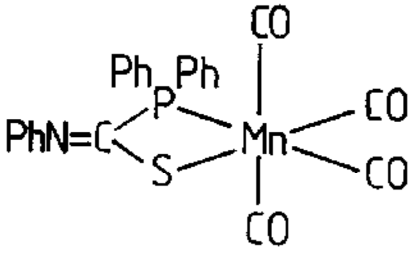
$[Mn(CO)_5Br]$ adds to $[(cp)(CO)_2Fe(CS_2)]^-$, losing CO and Br^- to form a bridged, heterodinuclear compound, $[(cp)(CO)_2Fe(CS_2)Mn(CO)_4]$, where the CS_2 group bonds: (FeC(S)SMn) to form a four-membered ring. The product was characterised by IR and ^1H NMR spectroscopy [329].

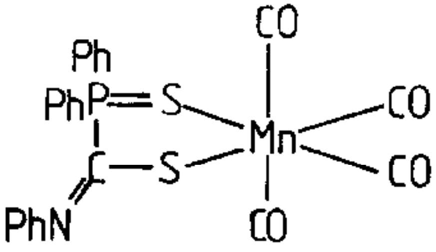
The ligand triphenylstannanedithiocarboxylate (L) has been prepared, and used to form the manganese(I) complexes $[Mn(CO)_4L]$ and *fac*-$[Mn(CO)_3(PPh_3)L]$, which have been fully characterised by spectroscopic techniques [330]. The reaction of $[Mn(CO)_4(NH_2R)(CONHR)]$ with the isothiocyanate R'NCS (R = CH_3 or C_6H_{11}; R' = CH_3, C_6H_{11}, C_6H_5 or $C_6H_5CH_2$) produces the disubstituted thiourea, the dithiocarbamato complex $[Mn(CO)_4(RHNCS_2)]$ and the isocyanide derivative *fac*-$[Mn(CO)_3(CNR)(RHNCS_2)]$. The products have been fully characterised by IR and ^1H NMR spectroscopy [331]. The compound $[Mn(CO)_3BrL]$; (33), (where L is 2-methyl-2-(triphenylphosphonio)dithiopropanoate) has been prepared and its crystal structure determined at room temperature and at -110 ^oC. At room temperature, the crystal decomposes with loss of triphenylphosphine [332].



(33)

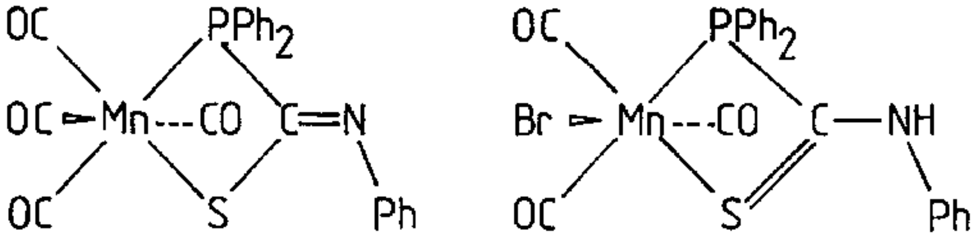
The tri- and tetracarbonyl complexes $[Mn(CO)_4(SC\{NR\}PR_2)]$, $[Mn(CO)_4(SC\{NR\}P\{S\}R_2)]$, $[Mn(CO)_3(SC\{NR\}P\{S\}R_2)]_2$, $[Mn(CO)_3X(SC\{NHR\}PPh_2)]$ (X = Cl, Br or I) and $[Mn(CO)_3I(CH_3SC\{NR\}PPh_2]$ have been prepared and identified by NMR spectroscopy [333]. The ^{55}Mn NMR spectra of the series of complexes $[(CO)_4Mn(S_2CZ)]$ (where Z = OR, SR, NR_2, PR_2, $P(S)R_2$, $AsPh_2$ or Ph), $[(CO)_4Mn(SC\{NR'\}PR_2)]$, $[(CO)_4Mn(SC\{NR'\}P\{S\}R_2)]$ and *fac*-$[(CO)_3BrMn(SC\{NHR'\}PR_2)]$ have been recorded, and show a relationship between the ^{55}Mn chemical shift and the nature of the coordinated thio ligand [334]. Crystal structures were reported for $[(CO)_4Mn(SC\{NPh\}PPh_2)]$; (34), and for $[(CO)_4Mn(SC\{NPh\}P(S)Ph_2)]$; (35) [335].





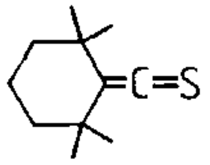
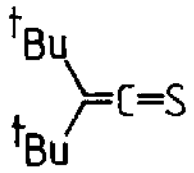
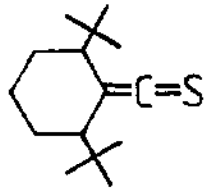
(34) (35)

The crystal structures of $[Mn(CO)_4L]$ and *fac*-$[Mn(CO)_3Br(HL)]$; (36), (where HL is the ligand *P,P,N*-triphenylphosphinothioformamide) have been determined. Coordination is via *P* and *S*, forming a four-membered ring. The structures were discussed in detail [336].



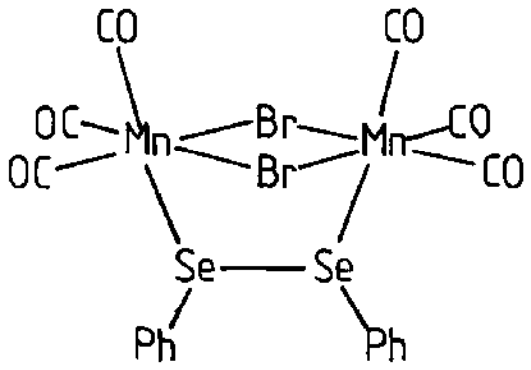
(36)

The reaction of $[(cp)(CO)_3Mn]$ with the alkylthioketenes:

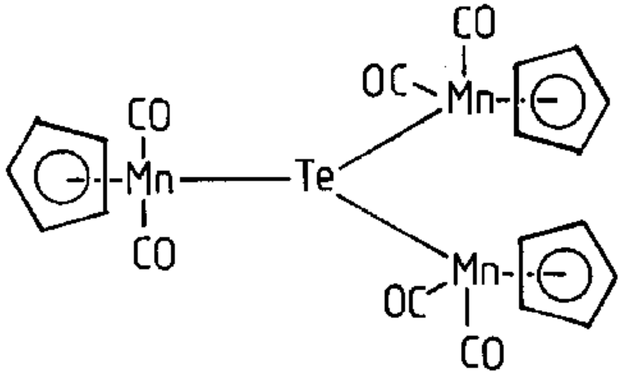
yields simple 1:1 adducts: [Mn(CO)(cp)L]. The complexes were all characterised by spectroscopic techniques, and the crystal structure of one adduct was reported and discussed [337].

The reaction of methylthiirane with manganese(I) hydride pentacarbonyl inserts sulfur into the Mn-H bond to form $[\{Mn(SH)(CO)_4\}_2]$, which has bridging SH groups [338]. The preparations were reported of the dimers $[Mn_2X_2(CO)_6(E_2Ph_2)]$ (X = Br or I; E = S, Se or Te), and the crystal structure of the bromo-seleno complex, (37), described [339].



(37)

The preparation and crystal structure of a novel tellurium complex; (38), were reported, involving three $\{Mn(CO)_2(cp)\}$ groups bonded to one tellurium atom. The $\{Mn_3Te\}$ unit is almost planar, but does not have equally spaced $\{Mn(CO)_2(cp)\}$ groups:

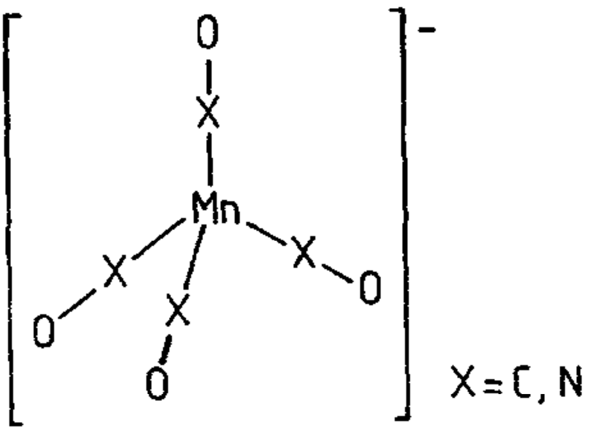


(38)

The compound $[Te_2(Mn(CO)_2(cp))_3]$ was also reported [340].

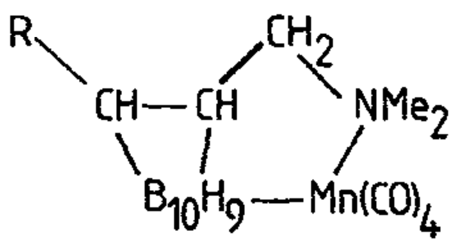
2.6.5 *Compounds with N Donor Ligands*

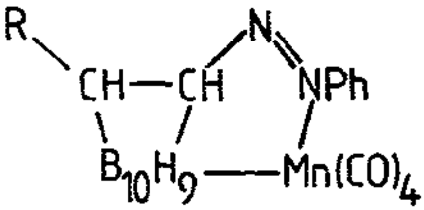
The complex $[Mn(CO)_3(NO)]^{2-}$ has been synthesised by reduction of $[Mn(CO)_4(NO)]$ or $[Mn(CO)_3(NO)(PPh_3)]$, and characterised by IR spectroscopy [341]. A new reagent $[PPN][NO_2]$ (where PPN^+ was $[Ph_3P{=}N{=}PPh_3]^+$) was reported to nitrosylate metal carbonyls such as $[Mn(CO)_6]^+$, $[Mn(CO)_5(MeCN)]$, $[Mn(CO)_4(NO)]$ and $[Mn_2(CO)_{10}]$ to generate CO_2 and incorporate $[NO]^-$ into the molecule. The crystal structure of $[Mn(CO)_2(NO)_2]^-$; (39), was reported [342]:



(39)

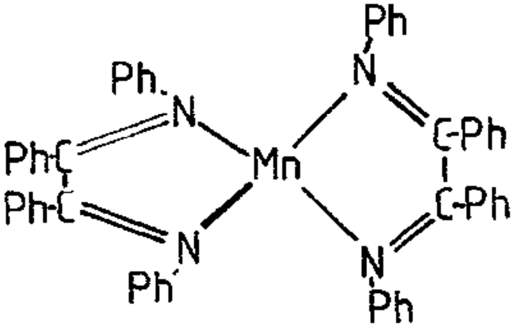
Oxidation of a 3-toluidine complex $[Mn(cp)(CO)_2(3\text{-}NH_2\text{-}C_6H_4CH_3)]$ yields a stable complex of an aminyl radical. This was characterised by spectroscopic measurements [343]. Novel amine and imine complexes, (40) and (41), involving a Mn-B σ-bond were reported from the reactions of $[(CH_3)Mn(CO)_5]$ with the two carboranes $B_{10}H_{10}CHRCHN(CH_3)_2$ and $B_{10}H_{10}CHRCHN{=}NPh$ [344].





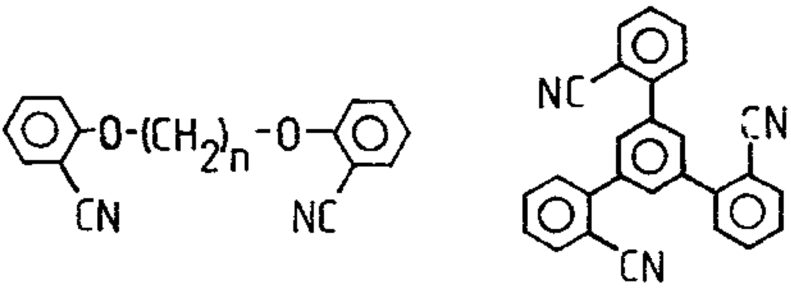
(40) (41)

The 1,2,3,4-tetraphenyl-1,4-diazabutadiene (benzilbisanil; bba) complex $[Mn(bba)_2]$; (**42**), has been prepared and characterised by spectroscopic and magnetic measurements (μ_{eff} = 3.93 μ_{β}): it was reported to be pseudooctahedral [345].



(**42**)

$[Mn(CO)_5Br]$ reacts with DiCN-*n* or Tri-CN:

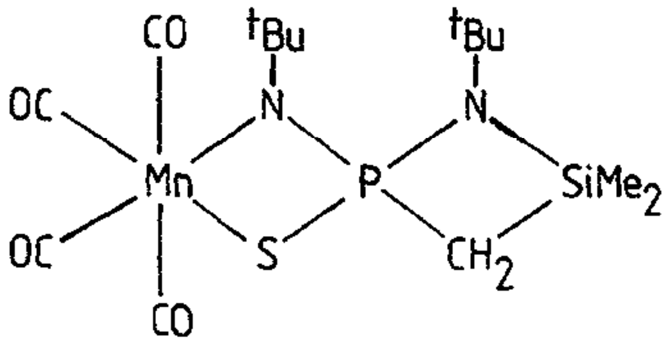


DiCN-*n* (*n* = 2, 3 or 4) TriCN

to form $[Mn(CO)_3(DiCN\text{-}n)Br]$, $[Mn(CO)_3(TriCN)Br]$ or $[Mn(CO)_3(TriCN)][PF_6]$ [346].

The thionylimide complex $[Mn(CO)_5(HNSO)][AsF_6]$ has been prepared, and the nature of the ligand HNSO briefly discussed, but no definitive conclusions were drawn: *N*-coordination was suggested [347]. Reaction of $[(CH_3)Mn(CO)_5]$ with $CF_3SO_2N{=}S{=}NSO_2CF_3$ yields a simple adduct $[(CH_3)Mn(CO)_4(CF_3SO_2N{=}S{=}NSO_2CF_3)]$. The mode of bonding is unknown, but coordination through one *N* atom is suggested [348].

The σ^3,λ^5-phosphazene $(Me_3Si)_2NP{=}(NSiMe_3)_2$ displaces CO from $[Mn(CO)_5Br]$ to yield the simple adduct $[Br(CO)_4MnN(SiMe_3){=}P({-}NSiMe_3)N(SiMe_3)_2]$; (43). However, the analogous thio compound $[(Me_3Si)(Me_3C)NP(S){=}NCMe_3]$ displaces CO and Br^- to form the spiro compound (44). The reactions have been studied by ^{31}P and ^{13}C NMR spectroscopy and an X-ray crystal structure of (44) is presented [349].



(44)

Reaction of $[\{Mn(CO)_4(\mu\text{-}Br)\}_2]$ with diimidazolate or dibenzimidazolate (NN in general) results in the formation of the bridged dimers $[Mn(CO)_4(\mu\text{-}NN)]_2$. Subsequent reactions with phosphines or phosphites yield $[Mn(CO)_{4-n}L_n(\mu\text{-}NN)]_2$ (L = phosphine or phosphite). Structures were assigned on the basis of IR srectroscopic data [350].

The crystal structures of the *cis*-dicarbonyl-(1,10-phenanthroline)-

cis-bis(trimethylphosphite)manganese(I) perchlorate [351] and *cis*-dicarbonyl-(1,10-phenanthroline)-*trans*-bis(trimethylphosphite) manganese(I) perchlorate [352] have been determined: both show manganese ions with pseudooctahedral coordination. In the latter complex, there are two crystalline forms, one of which shows one trimethylphosphite ligand to be statistically disordered.

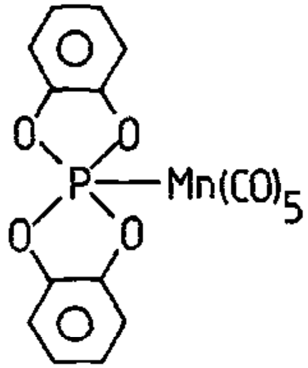
2.6.6 *Compounds with Other Group 15 Donor Ligands*

The complexes $[Mn(CO)_{6-n}L_n]^+$ and $[(cp)Mn(CO)_2L]$ have been prepared for a wide range of phosphines, and variations in the ^{55}Mn chemical shift measured and considered in relation to ligand field splitting, Nephelauxetic effect and the nature of the Mn–L bond [353]. The manganese(O) radicals $[Mn(CO)_3L_2]^{\cdot}$ were prepared for a number of trialkylphosphines and phosphites, and studied by EPR spectroscopy. The effect of the phosphine ligand L is related to the electron exchange process [354]. The steric effects of phosphine ligands on the photochemistry of $[Mn_2(CO)_{10}]$ have been studied, and shown to influence the photolysis products [355].

For a range of phosphines PR_3 (R = CHMeEt, Bu, $CHMe_2$ or $OCHMe_2$), reaction of the radical $[Mn(CO)_3(PR_3)_2]^{\cdot}$ with CCl_4 yields $[Mn(CO)_3(PR_3)_2Cl]$, while reaction with Bu_3SnH gives mainly $[Mn(CO)_3(PR_3)H]$. Characterisation of the starting radical and the products was by EPR, IR and UV-VIS spectroscopy [356]. Irradiation of $[Mn_2(CO)_8L_2]$ (L = PBu_3 or $P(OEt)_3$) with near UV radiation in the presence of HCl yields the products $[Mn(CO)_4LCl]$ and $[HMn(CO)_4L]$. The mechanism has been studied and an oxidative addition to metal carbonyl radicals proposed [357].

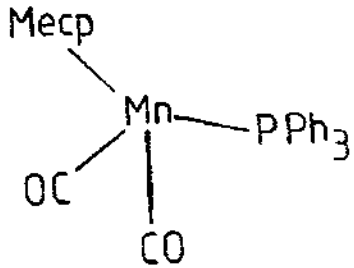
$[Mn(CO)_5(CH_2Cl)]$ reacts with triphenylphosphine to form the adduct $[Mn(CO)_3(PPh_3)Cl]$, while $[Mn(CO)_5(CH_2OMe)]$ with triphenylphosphine in ethanenitrile forms *cis*-$[Mn(CO)_4(PPh_3)(C(O)CH_2OMe)]$. In methanol, no CO is incorporated, and the product is *cis*-$[Mn(CO)_4(PPh_3)(CH_2OMe)]$ [358].

A novel synthesis of a transition metal-substituted phosphorane is reported. Reaction of 2-chloro-spirobi(1,3,2,benzodioxaphosphole) with Na[Mn(CO)$_5$] yields the product (45), which was characterised by standard spectrometric techniques [359].



(45)

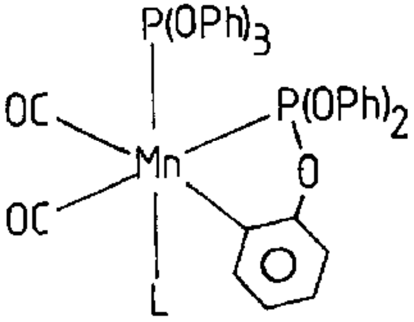
The crystal structure of [(Mecp)Mn(CO)$_2$(PPh$_3$)]; (46), has been reported and discussed [360].



(46)

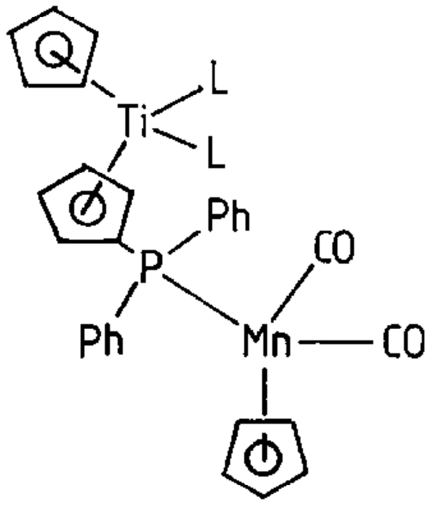
A series of cationic manganese(I) carbonyl phosphine complexes [Mn(CO)$_2$(L$_2$)$_2$]$^+$ and *mer*-[Mn(CO)$_3$(dppm)$_2$]$^+$ (L$_2$ = dppm or dppe) have been prepared, [Mn(CO)$_2$(dppm)$_2$]$^+$ in both *cis* and *trans* forms. In *mer*-$[Mn(CO)_3(dppm)_2]^+$, one ligand is monodentate, as shown by ^{31}P NMR spectroscopy [361]. The triphosphines L^1: $Ph_2PPCH_2CH_2P(cych)CH_2CH_2PPh_2$ and L^2: $(cych)_2PCH_2CH_2P(cych)CH_2CH_2P(cych)_2$ (cych = cyclohexyl) react photochemically with $[(cp)Mn(CO)_3]$ to form monoligate complexes $[(cp)Mn(CO)_nL^1]$ (n = 0 or 1) and $[(cp)MnL^2]$, and bridged dimers $[(cp)Mn(CO)(\mu\text{-}L^2)Mn(cp)(CO)_2]$. $[(cp)Mn(CO)L^1]$ also coordinates with $[(cp)Mn(CO)_2(thf)]$ to form a bridged dimer $[(cp)Mn(CO)(\mu\text{-}L^1)Mn(CO)(thf)]$, and with other carbonyl-thf complexes of the metals V, Cr, Mo, W or Co [362].

UV photolysis of $[Me_3SnMn(CO)_3(P(OPh)_3)_2]$ in benzene results in homolytic cleavage of the Sn-Mn bond and H-abstraction from a phenyl ring to leave two ortho-metallated compounds; (**47**) and (**48**):



(**47**) (**48**) L = CO or $P(OPh)_3$

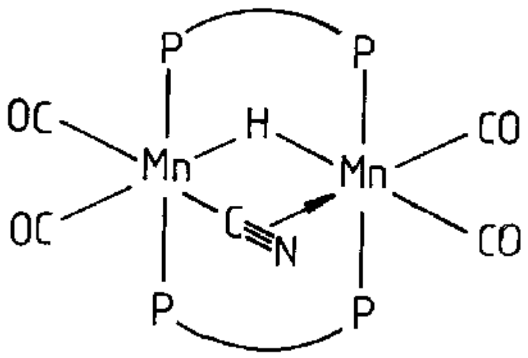
The crystal structures were determined for both ortho-metallated products [363]. Reaction of $[(cp)Mn(CO)_2(thf)]$ with $[TiL_2(cp)(\eta^5\text{-}cp\text{-}PPh_2)]$ (L = CO or Cl) produces the bimetallic complex; (**49**):



(49)

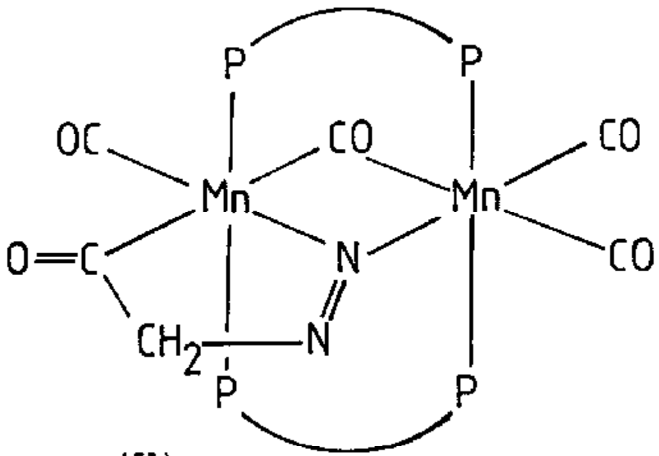
On exposure to air, this is oxidised to the phosphine complex $[(cp)Mn(CO)_2(PPh_2cp)]$. An X-ray crystal structure of the manganese/titanium complex was presented [364]. A series of manganese(I) complexes has been prepared from $[Mn_2(CO)_{10}]$ and $PHPh_2$, producing $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$, followed by reaction with various cyanides, isocyanides, phosphines and phosphites, yielding complexes with formulae: $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_7L]$,
$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6L_2]$ and
$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4((EtO)_2POP(OEt)_2)_2]$.
Reaction of $[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8]$ with alkynes gave the asymmetric alkenyl complexes $[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}\sigma{:}\eta^2\text{-}CR{=}CHR')(CO)_7]$. The crystal structures of
$[Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_6(CNCMe_3)_2]$ and
$[Mn_2(\mu\text{-}PPh_2)(\mu\text{-}\sigma{:}\eta^2\text{-}CH{=}CH_2)(CO)_7]$ were reported [365].

The reaction between $[Mn_2(CO)_{10}]$ and the diphosphine ligands $Et_2PCH_2PPh_2$ (depm) and $(C_6H_{11})_2PCH_2PPh_2$ (dcpm) were studied, and the products from boiling hexane were identified as $[Mn_2(CO)_6(depm)_2]$ and $[Mn_2(CO)_5(dcpm)_2]$. IR spectral evidence is presented to show that the *trans* isomer is most likely for the former, while the latter may be *trans*, but no definitive argument was provided [366]. Reaction of $[Mn_2(CO)_5(dppm)_2]$ with $H[BF_4]$ in ethanenitrile yields a manganese(II) hydride-bridged adduct; (**50**), with cyanide incorporated as a σ-bonded ligand to one Mn, and as a η^2-bonded ligand to the other [367].



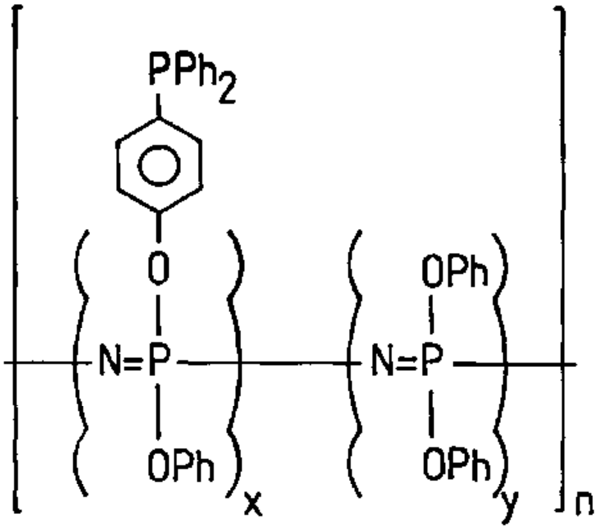
(**50**)

When diazomethane is allowed to react with $[Mn_2(CO)_5(dppm)_2]$, a 1:1 adduct is formed which has been shown by X-ray crystallography to be $[Mn_2(CO)_4(\mu\text{-dppm})_2(C(O)CH_2N_2)]$; (51) [368].



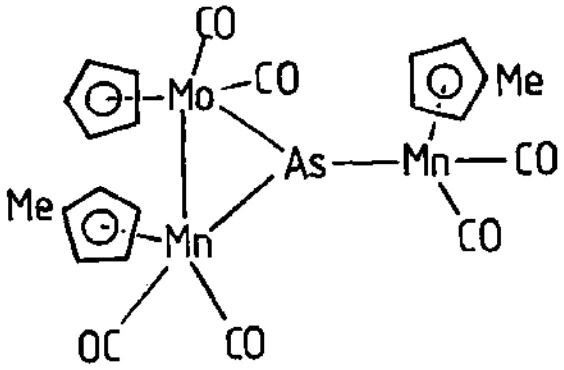
(**51**)

Reaction of an excess of $[(cp)Mn(CO)_3]$ (as the thf adduct [(cp)Mn(CO)$_2$(thf)]) with the cyclic phosphazene ligands [$N_3P_3(OPh)_5(p\text{-}OC_6H_4PPh_2)$]:L^1, [$N_3P_3(4\text{-}OC_6H_4PPh_2)_6$]:L^2 or the polymeric ligand L^3:



yields simple adducts where all the phosphine valencies have been saturated. The cyclic hexaphosphine L^2 can also act as a monodentate or bidentate ligand [369].

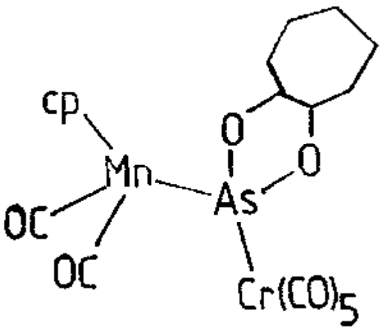
Reaction of [ClAs(Mn(CO)$_2$(Mecp))$_2$] with [(cp)Mn(CO)$_3$] yields the asymmetric complex (52):

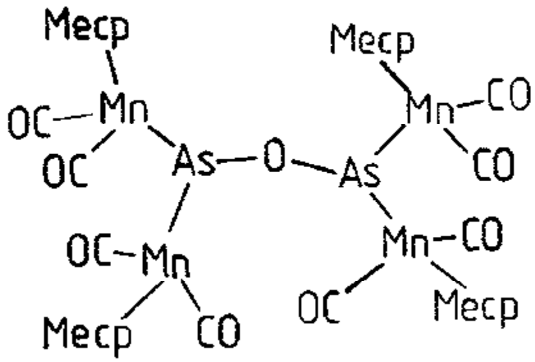


(52)

which has been fully characterised by spectroscopic and X-ray crystallographic techniques [370]. The complexes [RAs(Mn(CO)$_2$(cp))$_2$] (R = Ph, $CH_2CH(CH_3)_2$ or

CH_2CH_3) have been prepared from the chloroarsenic analogue with $[AlR_3]$, and fully characterised. Complexes also prepared include $[ClAs(Mn(CO)_2(cp))(Cr(CO)_5)]$, the tropolone adducts $[(C_7H_5O_2)As(Mn(CO)_3(cp))(Cr(CO)_5)]$ and $[(C_7H_5O_2)As(Mn(CO)_2(Mecp))_2]$, and the oxygen-bridged dimers $[(As\{Mn(CO)_2(cp)\}\{Cr(CO)_5\})_2O]$ and $[(As\{Mn(CO)_2(Mecp)\}_2)_2O]$. Crystal structures of the chromium-manganese tropolone complex, (53), and of the dimanganese oxo-bridged dimer, (54), were presented [371].





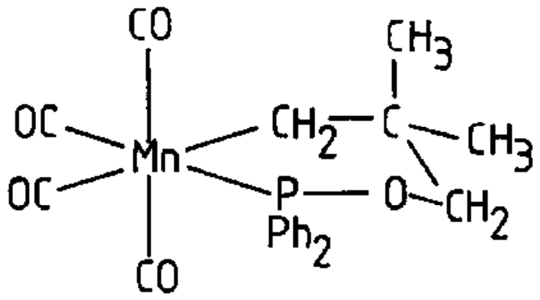
(53) (54)

An EPR spectral study of $[Mn_2(CO)_8(\mu\text{-}AsPh_2)_2]^{+\cdot}$ has shown the $\{Mn_2As_2\}$ rhomboid to be planar. Further, the electronic structure of the radical cation has been partially elucidated [372]. The compound $[(CO)_4FeMn(CO)_4AsMe_2]$ was studied and shown to react with CO at 45 °C to form a linear complex $[(CO)_4FeAs(Me_2)Mn(CO)_5]$ with no Mn–Fe bond [373].

2.6 7 Organometallic Compounds

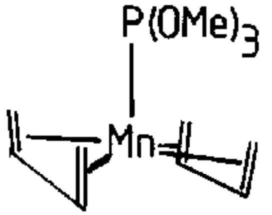
$[Mn(CO)_5]^-$ reacts with perfluoronorbornadiene to substitute a fluoride ion, giving $[(C_7F_7)Mn(CO)_5]$, and this reacts with $[Pt(PPh_3)_4]$ to form the complex $[(PPh_3)_2Pt(\eta^2\text{-}C_7F_7)Mn(CO)_5]$ [374]. Reaction of $[Mn(CO)_5Br]$ with

$Ag[CH(SO_2F)_2]$ yields $[(CO)_5Mn(CH(SO_2F)_2)]$ [375]. $[Mn(dinc)_3][PF_6]$ (where dinc = 1,2-bis(4-*tert*-butyl-2-isocyanophenoxy)ethane) has been prepared by treating $[Mn(CO)_5Cl]$ with dinc in the presence of $[PF_6]^-$. This has been further oxidised to $[Mn(dinc)_3][PF_6]_2$, which is stable in the solid state but decomposes in solution to the manganese(I) species [376]. Reaction of $[Mn(CO)_4(PMe_2O)]^{2-}$ with $[(CF_3SO_2OCH_2)_2C(CH_3)_2]$ affords the manganocyclohexane derivative $[(CO)_4MnPMe_2OCH_2CMe_2CH_2]$. The analogous complex $[(CO)_4MnPPh_2OCH_2CMe_2CH_2]$; (55), whose crystal structure is presented, takes up SO_2 to form the sulfinato complex $[(CO)_4MnPPh_2OCH_2CMe_2CH_2SO_2]$ [377].



(55)

Manganese(II) chloride reacts with $Mg[C_4H_6].2thf$ in the presence of Lewis bases and butadiene to form $[(\eta^4-C_4H_6)_2MnL]$ (where L = PMe_3, PEt_3, $P(OMe)_3$ or CO). Butadiene derivative complexes were prepared by metal vapour synthesis. The crystal structure of $[(\eta^4-C_4H_6)_2Mn(P(OMe)_3)]$; (56), shows the manganese to have square pyramidal coordination [378].



(56)

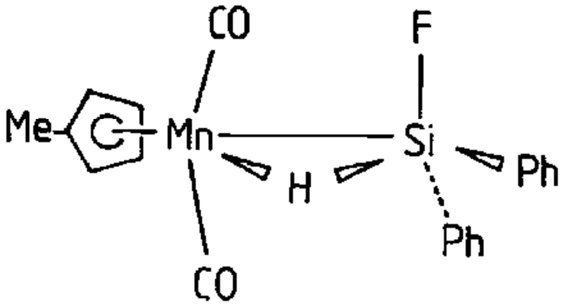
The crystal structure of $[(CO)_4Mn(C_5H_4COCH_2)W(CO)_3(cp)]$ has been presented, showing a bridging 1-ferrocenyl-1-oxoethyl group, η^5-bonded to manganese and σ-bonded to tungsten [379]. IR matrix isolation studies of $[Mn(CO)_4(COCH_3)]$ indicate the ethanoyl ligand to be σ-bonded [380].

The X-ray fluorescence and XPS spectra of $[(cp)Mn(CO)_3]$, $[(cp)Mn(CO)_2(PPh_3)]$, $[(cp)Mn(CO)(dppe)]$, $[(cp)Mn(NO)(CO)_2][PF_6]$, $[(cp)Mn(CO)(NO)(PPh_3)][PF_6]$ and $[(cp)Mn(NO)(dppe)][PF_6]$ were recorded and the results analysed in terms of the Mn–cp interaction [381,382]. The donor properties of the manganese(I) adducts $[(cp)Mn(CO)_3]$ and $[(cp)Mn(CO)_n(PR_3)_{3-n}]$ (n = 1 or 2) have been investigated with reference to the Lewis acids Al_2Br_6 and $GaCl_3$. Coordination of the Lewis acid is to the metal centre [383].

A molecular orbital study of the complexes $[\{(cp)Mn(CO)_2\}_2L]$ (where L = Ge, N_2 or PPh) has provided an explanation of the bonding in these complexes in accordance with observed spectroscopic data [384].

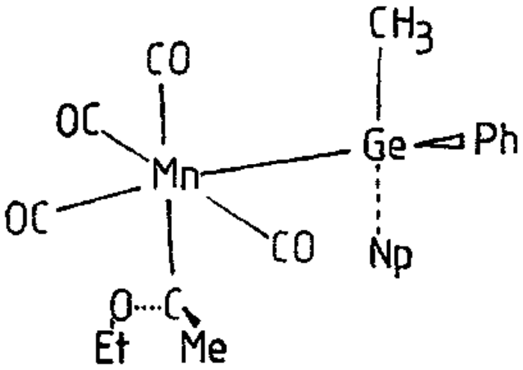
2.6.8 *Silyl and Germyl complexes*

A neutron diffraction study of $[(Mecp)(CO)_2MnH(SiFPh_2)]$, (57), has located the hydride 1.569(4) Å from the manganese atom (a typical Mn-H distance) and 1.802(3) Å from the silicon atom. Although the Si-H distance is longer than typical Si-H bonds (*ca.* 1.48Å), it is much shorter than the sum of the Van der Waal radii and the geometry around the silicon tends towards five-coordinate. The authors, therefore, tend to favour a three-centred two-electron Mn-H-Si bond [385].



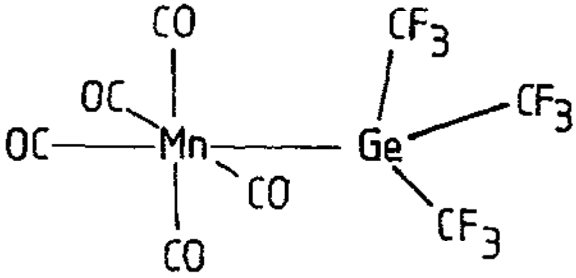
(57)

A series of manganese(I) carbonyl complexes with optically active silyl or germyl groups was synthesised and the stereochemistry of the cleavage of the Mn-Si or Mn-Ge bond examined. It was observed that the manganese complexes show poor retention of configuration [385a]. The optically active germyl ligand S-(-)-(MePh-1-NpGe) (1-Np = 1-naphthyl) can replace a CO ligand in $[MeMn(CO)_5]$ resulting in CO insertion in the Mn-Me bond. The anion thus formed $[R_3GeMn(CO)_3(COMe)]^-$, can be isolated or reacted with $[Et_3O][BF_4]$ to yield the carbene complex $[R_3GeMn(CO)_4(C(OEt)Me)]$; (58). The crystal structure of the carbene complex was reported [386].



(58)

Photolysis of $(CF_3)_3GeH$ in the presence of $[Mn_2(CO)_{10}]$, or reaction of $Na[Mn(CO)_5]$ with $[(CF_3)_3GeX]$ (X = Cl or I) produced $[(CF_3)_3GeMn(CO)_5]$; (59), in high yield. This complex has subsequently been analysed by ^{55}Mn, ^{19}F NMR and vibrational spectroscopy, and single crystal X-ray diffraction:



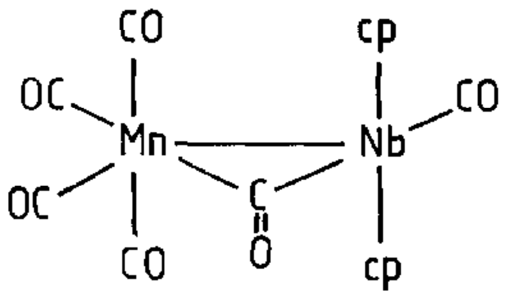
(59)

The carbonyl force constants and Graham constants were evaluated [387]. The presence of a strong π-acceptor such as $[GeBr_3]^-$ in the carbonyl complex

$[Br_3GeMn(CO)_5]$ results in the formation, on reaction with 1-leucine, methyl ester, of the complex *trans*-$[Br_3GeMn(CO)_4L]$ (where L = 1-leucine, methyl ester) [388]. Thermogravimetric analysis of $[Mn(CO)_5(GeXPh_2)]$ (X = F or Cl) shows that, in the presence of oxygen, CO is lost first, followed by Ph and then X, the fluoro compounds being more stable than the chloro compounds [389].

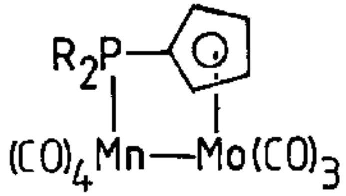
2.6.9 *Mixed Metal Complexes*

$[Ph_4As][(CO)_5MnV(CO)_4(NO)]$ has been synthesised from $[Ph_4As][Mn(CO)_5]$ and $[V(CO)_4(NO)]$, and characterised by IR spectroscopy [390]. The preparation and crystal structure of $[(cp)_2(CO)Nb(\mu\text{-}CO)Mn(CO)_4]$, (60), were reported [391].



(60)

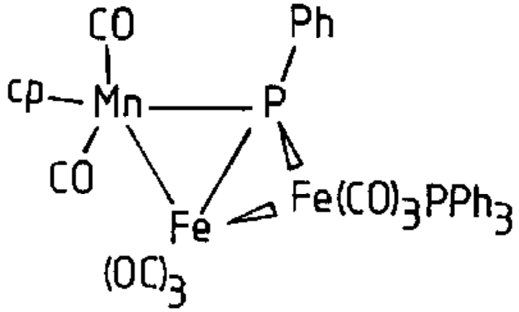
The phosphorus in $[(CO)_3Mo(\eta^5\text{-}C_5H_4PR_2)]$ (R = Ph or 4-tolyl) acts as a ligand when reacted with $[\{Mn(CO)_4Br\}_2]$ to form the structure (61):



(61)

The crystal structure for R = Ph has been solved, and indicates the presence of a Mn–Mo bond (3.054 Å). ^{1}H, ^{13}C and ^{31}P NMR spectral data were also quoted [392].

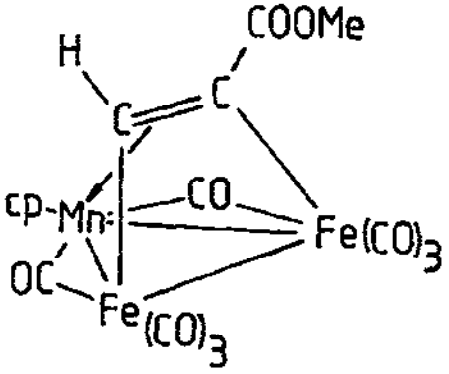
The crystal structure of $[(cp)(CO)_2MnFe_2(CO)_6(PPh_3)(\mu^3\text{-}PPh)]$; **(62)**, has been determined and shows the molecule to contain a $\{MnFe_2P\}$ pseudoetrahedron [393].



(62)

The room temperature ^{57}Fe Mössbauer spectra were reported for the clusters $[(cp)(CO)_2MnFe_2(CO)_6L(\mu^3\text{-PPh})]$ (L = CO, $P(OMe)_3$, PPh_3, $AsPh_3$ or $SbPh_3$) and show that the structures are in agreement with the lattice constants of low-spin Mn/Fe clusters [394].

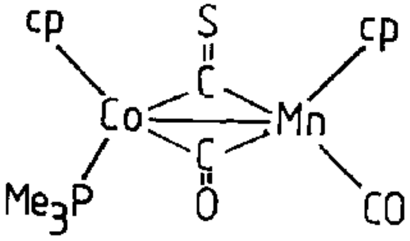
Reaction of $[(cp)Mn(CO)_2(\eta^2\text{-HC}{\equiv}\text{CCOOCH}_3)]$ with $[Fe_2(CO)_9]$ yields three products, one of which is a cluster: (1-η^5-cyclopentadienyl)-(1,2;1,3-μ-dicarbonyl)(1-η^2:2,3-σ-methylacrylate)(2,2,2,3,3,3-hexacarbonyl)-*triangulo*-1-manganese-2,3-diiron; (63), whose crystal structure was presented.

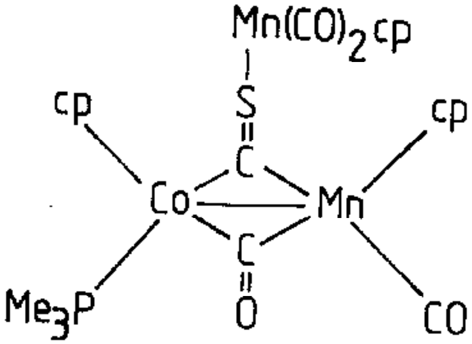


(63)

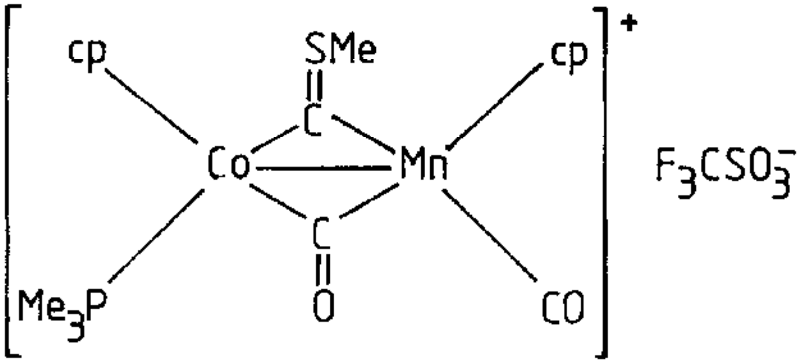
*[(cp)Mn(CO)$_2$(μ-C=CHCOOMe)*Fe(CO)$_4$] is also formed in the reaction [395].

Reaction of $[(cp)Co(PMe_3)(CS)]$ with $[(cp)Mn(CO)_2(thf)]$ yields (64) in a 1:1 reaction, and (65) in a 1:2 reaction. Methylation of (65) with $CH_3O_3SCF_3$ yields (66). Characterisation was by IR and ^{1}H NMR spectroscopy [396].





(64) (65)

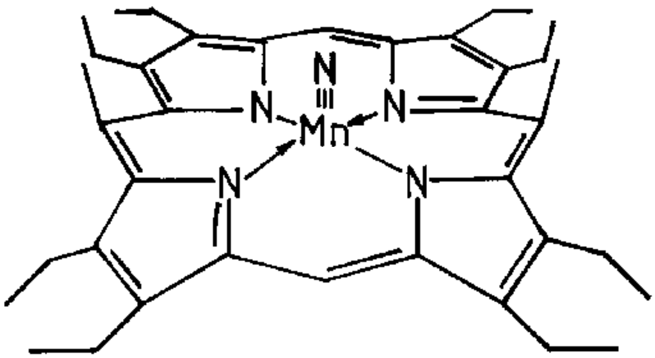


(66)

The crystal structure of $[\{(PPh_3)(CO)_4Mn\}_3SnBr]$ has been reported and discussed. The manganese is six-coordinate with planar $\{Mn(CO)_4\}$ groups, and the tin is four-coordinate [397].

2.7 PHTHALOCYANIN AND PORPHYRIN COMPLEXES

The first complexes of the type [MnN(OEP)] and [MnN(TTP)] (OEP^{2-} = octaethylporphinate; TTP^{2-} = meso-tetra(4-tolyl)porphinate) have been prepared by $[OCl]^-$ oxidation of [Mn(OMe)(porph)] in the presence of ammonia. The red complexes are diamagnetic and have been characterised by standard spectroscopic techniques: some chemical behaviour was also reported [398]. (2,3,7,8,12,13,17,18-octaethylporphinatonitrido)manganese(V), [MnN(OEP)], can be reduced by the methylating reducing agent sodium anthracenide and methyl iodide to 5,15-dimethyl-2,3,7,8,12,13,17,18-octaethyl-5H,15H-porphinatonitrido manganese(V); (**67**), which indicates that the Mn≡N bond is very resistant to reduction. The dimethyl complex has been fully characterised, and the crystal structure described. The Mn≡N bond, at 1.512 Å, is the shortest recorded example of such a bond [399].



(67)

Tetraphenylporphinatomanganese(IV), [Mn^{IV}(TPP)], was generated *in situ* in tetrachloroethane at 77 K by a one-electron oxidation of [Mn^{III}(TPP)Cl], and EPR and optical absorption spectra were recorded. Oxidation occurs at the metal centre, and the spin state of [Mn^{IV}(TPP)] was assigned as 3/2 [400]. The manganese(IV) porphyrins [Mn(TPP)X_2] (where X = N_3 or NCO) have been synthesised, but are unstable at room temperature in solution, decomposing to [Mn(TPP)X]. Magnetic and spectroscopic properties were noted, and the crystal structure of the toluene solvate [Mn(TPP)$(NCO)_2$].0.5$CH_3C_6H_5$; (68), reported [401].

Some novel manganese(IV) porphyrin complexes, [XMn(TPP)(OIPh)]$_2$O (where X = Cl or Br) and [{PhI(O_2CMe)O}$_2$Mn(TPP)], have been synthesised and characterised, and their reactions as potential oxidants of hydrocarbons (as well as other substrates) were investigated [402,403,404].

The manganese(III) porphyrin [Mn(TPP)CN]; (69), has been prepared, and characterised by X-ray crystallography. Some IR spectral and magnetic data were presented [405].

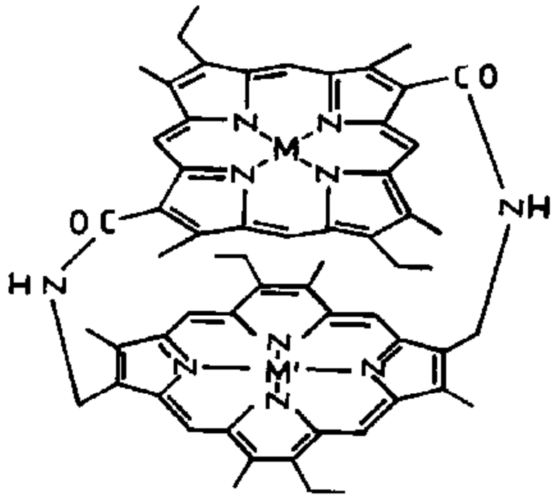
The compound [Mn(TPP)$(MeOH)_2$][ClO_4].MeOH; (70), has been prepared, and its crystal structure presented. The metal is bonded within the plane of the porphyrin, and the coordinated methanol molecules are in axial positions. The structure and electronic configuration were discussed with reference to similar systems [406].

The redox and photoreductive properties of manganese(III) tetra(4-methylpyridyl)porphyrin in water have been examined. Reduction can be effected by dithionite in the absence of dioxygen, while oxidation can be through persulfate, hypochlorite or chloropentamminocobalt(III) [407]

The electrochemistry of the bridged phthalocyanin complex [(PcMn)$_2$O] has been studied in detail, and a four-electron ECE reduction mechanism proposed [408]. The tetra(4-*N*,*N*',*N*"-trimethylanilinium)porphyrin Mn(II)/Mn(III) couple has been investigated electrochemically in aqueous media over the entire pH range, and the electronic spectral properties reported [409].

A matrix isolation IR spectral study of [MnPc] and [Mn(OEP)] indicates that both molecules bind dioxygen gas in a side-on manner [410]. A single crystal magnetic study has been performed on ferromagnetic [MnPc] at 1.2 - 25 K, and the results discussed in terms of the crystal structure [411]. The kinetics of the reaction of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin with manganese(II) in the presence of cadmium(II) were studied spectroscopically [412]. It is reported that, on exposure to ^{60}Co γ-rays at 77 K, manganese(III) porphyrins are reduced to manganese(II) porphyrins. Characterisation of the products was by EPR spectroscopy [413].

Two face-to-face bimetallic complexes [MM'(FTF4)], (71), have been synthesised with the diporphyrin, cryptically known as FTF4, one complex having M = M' = Mn, the other having M = Co, M' = Mn: spectral data were presented [414].



(71)

Reaction of manganese(II) ethanoate with the porphyrins tetraphenylporphyrin (TPP), tetra-4-methoxyphenylporphyrin (TMPP), hematoporphyrin IX (HPIX) or coproporphyrin (CP) at high pressure and shear deformation yields the complexes [Mn(TPP)], [Mn(TMPP)], [Mn(HPIX)] or [Mn(CP)], respectively [415]. The temperature dependencies of the magnetic susceptibilities of a number of manganese porphyrins were determined, and the factors influencing the magnetic behaviour were discussed [416].

Other work on porphyrins includes the isolation, characterisation and reactivity of high-valent oxomanganoporphyrins [417]; the electrochemical and spectroscopic study of 3,5-di-*tert*-butylcatecholato and 3,5-di-*tert*-butyl-2-benzosemiquinonato complexes of manganese(III) and manganese(IV) porphyrins [418]; and factors affecting the electron transfer and ligand addition reactions of manganese tetraphenylporphyrins [419].

2.8 BINARY AND TERNARY OXIDES

When $MnCl_2$, $MnSO_4$, Mn_2O_3, $MnCO_3$, Mn_3O_4, MnO_2 or $K[MnO_4]$ are added to a $Li_2CO_3/Na_2CO_3/K_2CO_3$ eutectic under argon or carbon dioxide, the final products are salts, mainly of manganese(IV) oxoanions, including $[MnO_2]^-$, $[MnO_3]^{2-}$, $[MnO_3]^-$ and $[Mn_2O_5]^{2-}$ [420]. High temperature X-ray analysis of the spinels $Mg_xMn_{3-x}O_4$ has given information on the distribution of cations in tetrahedral and octahedral sublattices. The distribution is independent of temperature between 700 °C and 1000 °C [421]. Using the EPR signal of Mn_3O_4 impurities in MnO, it has been possible to show that the Mn_3O_4 is primarily concentrated on the surface of the MnO [422]. Oxidation of manganese(II) ions with O_2 gas at 298 K yields a synthetic cryptomelane $K_2Mn_8O_{16}$. A detailed study of the interrelation of the manganese ores nsutite, hausmannite, manganite, pyrolysite and cryptomelane has been presented [423]. Reaction of Mn_3O_4 with butyllithium at room temperature yielded the mixed oxides $Li_xMn_3O_4$ ($0 < x < 2$): electrochemical and X-ray diffraction data were presented [424].

Photoelectron spectroscopy was used to study the reactions of manganese with dioxygen and water at different pressures and temperatures, to yield MnO, Mn_2O_3, Mn_3O_4 and $Mn(OH)_2$ [425]. A thermogravimetric method was used to examine the equilibria:

$$3Mn_2O_3 = 2Mn_3O_4 + 1/2O_2$$

$$2MnO_2 = Mn_2O_3 + 1/2O_2$$

at 790 - 990 °C and 466 - 495 °C respectively, at partial pressures of dioxygen less than one atmosphere [426].

$BiMn_2O_5$ was shown to have ferroelectric properties with antiferromagnetic ordering by studying the temperature dependence of the pyroelectricity, dielectric constant, dielectric loss, conductivity and magnetic susceptibility of the compound [427]. The lattice constants for $(La_{0.8}Ca_{0.2})MnO_3$ have been determined by X-ray powder diffraction, and the results are presented [428]. The synthesis and characterisation of the layered manganates $Ca_{1+x}Mn_xO_{1+3x}$ was reported [429]. A Mössbauer spectroscopic study of the octahedral sites in $Co_xFe_yMn_{3-x-y}O_4$ and $Ni_xFe_yMn_{3-x-y}O_4$ has shown that the iron(III) ions are incorporated into two sites of octahedral symmetry [430].

2.9 MIXED OXIDATION STATE AND NITROSYL COMPLEXES

Polarographic reduction of $[Mn_2L_4O_2]^{3+}$ (where L = 2,2'-bipyridine or 1,10-phenanthroline) shows three well defined diffusion controlled waves corresponding to 1, 2 and 3-electron transfers for both diimine ligands [431]. Detailed calculations on $[Mn(H_2O)_5(O_2)]^{n+}$ (n = 0–3) were carried out by CNDO-UHF and MO-LCAO-SCF techniques, and the complexes have been classified according to the degree of oxygen activation [432].

A large number of complexes of the general formula $[Cl(NH_3)_4Mn(N_2)M(NH_3)_4Cl]_n^{m+}$ (where M is Cr or V) have been studied theoretically to examine the electronic factors involved in (μ-N_2) activation, using CNDO-UHF and MO-LCAO-SCF techniques [433]. For $[Mn(CN)_5(NO)]^{n-}$ (n = 2 or 3), calculations with the scaled-INDO method have been used to give data on the electron density on the NO ligands, the bond order and bond lengths of the N–O, C–N, Mn–C and Mn–N bonds, and the NO and CN stretching frequencies [434].

The compound $[Me_4N][Mn_2(CN)_6].8H_2O$ was examined by X-ray crystallography and shown to contain low spin octahedral manganese(III) ions *C*-coordinated, and high spin octahedral manganese(II) ions bonded to two NC groups and four H_2O groups [102]. The magnetic properties were discussed [103].

Reaction of manganese(II) chloride with tetramethylammonium 1,2-dicyanocyclopentadienide ([Me_4N][dccp] in water, and recrystallisation of the product from ethanenitrile affords a complex which analyses as $[Me_4N]_2[Mn_2(dccp)_3(MeCN)_2H_2O]$; the product may be polymeric [435]. The trimeric species $[(Mecp)_3Mn_3(\mu\text{-}NO)_3(\mu^3\text{-}NO)]$ has been synthesised and the reduction reactions of the NO ligands investigated. The crystal structures of the protonated species $[(Mecp)_3Mn_3(NO)_3(\mu^3\text{-}NOH)][BF_4]$ and

$[(Mecp)_3Mn_3(NO)_3(\mu^3\text{-}NOH)][PF_6]$ were reported. Other spectral data were also presented [436]. The crystal structure has been reported of the trimer $[Mn_3(3\text{-}MeC_5H_6)_4]$, which has two $(MnL_2)^-$ groups (HL = 3-methyl-1,4-pentadiene) bridged by one manganese(II) centre. Its electronic structure has also been studied [437].

2.10 BINARY COMPOUNDS OF THE GROUP 15 ELEMENTS

The heat capacity of the manganese nitride Mn_4N was determined over a temperature range 5 - 500 K: no anomaly was observed, and various thermodynamic functions were quoted [438]. The structural properties of the phosphide and arsenide $Ni_{16}Mn_6P_7$ and $Ni_{16}Mn_6As_7$ have been investigated by X-ray powder diffraction. The structures, which are isomorphous with the silicide $Ni_{16}Mn_6Si_7$, were briefly discussed [439].

2.11 OTHER COMPOUNDS

The laser photoelectron spectra of $[MnH]^-$ and $[MnD]^-$ have been reported, with a qualitative description of the electronic structure of low- and high-spin metal hydrides. An interpretation of the spectra was given [440]. The titanium manganese hydride $Ti_{1.2}Mn_{1.8}H_3$ was studied by high resolution quasi-elastic neutron scattering to follow the hydride diffusion in the Laves phase hydride. A detailed analysis of the results was presented [441]. The hydrides of $ZrMn_2Fe_{0.8}$ were examined by Mossbauer and ^1H NMR spectroscopy, and show an increased hydrogen uptake over $ZrMn_2$ [442].

The intercalate $Mn_{0.25}TaS_2$ shows X-ray photoemissions which are related to charge transfer from the manganese to the host band structure [443].

A review has been published covering manganese clusters [444].

References

1 W. Levason, J.S. Ogden and J.W. Turff, *J. Chem. Soc., Dalton Trans.*, (1983) 2699
2 V.P. Tarasov, V.I. Privalov and Yu.A. Buslaev, *Dokl. Akad. Nauk. SSSR*, 269(3) (1983) 640 (Russ.)
3 S. Mohan, K.G. Ravikumar and S. Gunasekaran, *Ind. J. Pure Appl. Phys.*, 20 (1982) 660
4 A.P. Chudnov and N.N. Churilova, *Deposited Doc.*, (1981) SPSTL 643 KHP-D81 (Russ.)
5 J.B. Fernandes, B. Desai and V.N. Kamat Dalal, *Electrochim. Acta*, 28(3) (1983) 309
6 H. Voinov, *Electrochim. Acta*, 27(7) (1982) 833
7 I. Tanabe, N.Miyamoto and R. Nagata, *Mang. Dioxide Symp., (Proc.) 2nd. (1980)*, (1981) 59
8 R. Giovanoli, *Mang. Dioxide Symp., (Proc.) 2nd. (1980)*, (1981) 113
9 B.P. Varma, *Mang. Dioxide Symp., (Proc.) 2nd. (1980)*, (1981) 256
10 W.C. Maskell, J.E.A. Shaw and F.L. Tye, *Electrochim. Acta*, 28(2) (1983) 225
11 W.C. Maskell, J.E.A. Shaw and F.L. Tye, *Electrochim. Acta*, 28(2) (1983) 231
12 N. Yamamoto and M. Horibe, *Ferrites, Proc. I.C.F. 3rd. (1980)*, (1982) 443
13 P. Ruetschi and R. Giovanoli, *Mang. Dioxide Symp., (Proc.) 2nd. (1980)*, (1981) 552
14 A. Roy and M. Chaudhury, *Bull. Chem. Soc. Jpn.*, 56(9) (1983) 2827
15 A.I. Prisyazhnyuk and A.A. Opalovskii, *Deposited Doc.*, (1982) SPSTL 507 KHP-D82 (Russ.)
16 R. Acevedo and C.D. Flint, *Mol. Phys.*, 49 (1983) 1065
17 T. Matsushita and T. Shono, *Polyhedron*, 2(7) (1983) 613
18 K. Wieghardt, U. Bossek and W. Gebert, *Angew. Chem. (Int. Ed.)*, 22 (1983) 328
19 Der. Hang Chin, D.T. Sawyer, W.P. Schaefer and C.J. Simmons, *Inorg. Chem.*, 22 (1983) 752
20 G.V. Bazuev, O.V. Makarov and G.P. Shveikin, *Russ. J. Inorg. Chem.*, 28(8) (1983) 1088
21 Yu.F. Kargin, N.I. Nelyapina and V.M. Skorikov, *Zh. Neorg. Khim.*, 28(2) (1983) 303 (Russ.)
22 B. Banerjee and S. Lahiry, *Phys. Status Solidi A*, 76(2) (1983) 683
23 N.A. Nevskaya, B.N. Ivanov-Emin and B.E. Zaitsev, *Deposited Doc.*, (1982) VINITI 3814-Pt.2-82 111-13
24 B.N. Ivanov-Emin, N.A. Nevskaya, B.E. Zaitsev and T.M. Ivanova, *Russ. J. Inorg. Chem.*, 27(12) (1982) 1755
25 T.J.R. Weakly, *J. Chem. Soc. Pak.*, 4(4) (1982) 251
26 J.M.D. Tascon and T.L. Gonzalez, *Z. Phys. Chem. (Wiesbaden)*, 130(2) (1982) 219
27 I. Cisarova, C. Novak, V. Petricek, B. Kratochvil and J. Loub, *Acta Cryst.*, B38 (1982) 1687
28 A. Durif and M.T. Averbuch-Pouchot, *Acta Cryst.*, B38 (1982) 2883 (Fr.)
29 W. Massa, *Z. Anorg. Allgem. Chem.*, 491 (1982) 208 (Ger.)
30 W. Massa and J. Pebler, *Stud. Inorg. Chem.*, 3 Solid State Chem., (1983) 577
31 A.H. Jubert, J.A. Espindola and E.L. Varetti, *J. Raman Spectrosc.*, 14 (1983) 259
32 T. Suzuki and H. Ido, *J. Phys. Soc. Jpn.*, 51(10) (1982) 3149

33 A.I. Kryukov, Z.A. Tkachenko and V.K. Bukhtiyarov, *Teor. Eksp. Khim.*, 19(2) (1983) 197 (Russ.)
34 A.K. Bhattacharjee and M.K. Mahanti, *Ind. J. Chem., Sect. A*, 21A(10) (1982) 1009
35 F.C. Frederick, W.M. Coleman and L.T. Taylor, *Inorg. Chem.*, 22 (1983) 792
36 T. Matsushita, M. Nishino and T. Shono, *Bull. Chem. Soc. Jpn.*, 55 (1982) 2663
37 R. Chandra, S.K. Sahni and R.N. Kapoor, *Acta Chim. Hung.*, 112(4) (1983) 385
38 H.S. Verma, A. Pal, R.C. Saxena and J.L. Vats, *J. Ind. Chem. Soc.*, 59(10) (1982) 1184
38a N. Herran and D.H. Busch, *Inorg. Chem.*, 22 (1983) 3470
39 S.K. Sengupta, S.K. Sahni and R.N. Kapoor, *Synth. React. Inorg. Met.-Org. Chem.*, 13(2) (1983) 117
40 B.K. Kanungo, B. Pradhan and D.V.R. Rao, *Ind. J. Chem., Sect. A*, 21A(6) (1982) 625
41 H. Aghaborzorg, *Diss. Abstr. Int. B*, 43(6) (1982) 1838
42 J. Yamashita and S. Asano, *J. Phys. Soc. Jpn.*, 52(10) (1983) 3514
43 B. Fubini and F.S. Stone, *J. Chem. Soc., Faraday Trans. I*,79 (1983) 1215
44 V.E. Sokol'skii, V.P. Kazimirov and V.I. Galinich, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 19(4) (1983) 629 (Russ.)
45 P. Garcia Casado and I. Rasines, *Z. Krystallog.*, 160(1–2) (1982) 33
46 C.E. Deshpande and P.P. Bakare, *Bull. Mater. Sci.*, 5(1) (1983) 1
47 Y. Suwa, S. Hirano and K. Hozawa, *Ferrites, Proc. I.C.F., 3rd. (1980)*, (1982) 23
48 J.R. Gavarri, G. Calvarin and B. Chardon, *J. Solid State Chem.*, 47(2) (1983) 132 (Fr.)
49 K. Klepp, P. Boettcher and W. Bronger, *J. Solid State Chem.*, 47(3) (1983) 301
50 D.M. Nicholas, M.S. Waite and T.M. Ho, *J. Appl. Crystallog.*, 16(1) (1983) 141
51 E.V. Novikova, Z.A. Shevrina and V.P. Kochergin, *Zh. Neorg. Khim.*, 28(4) (1983) 995 (Russ.)
52 Z.C. Kang, *J. Microsc. Spectrosc. Electron.*, 8(1) (1983) 19
53 N. Rodier, M. Guittard and J. Flahaut, *C. R. Seances Acad. Sci., Ser. 2*, 296(1) (1983) 65 (Fr.)
54 G.V. Girichev, N.Yu. Subbotina and N.I. Giricheva, *Zh. Strukt. Khim.*, 24(2) (1983) 158 (Russ.)
55 T. Sato and T. Okazaki, *Sci. Rep. Hirosaki Univ.*, 29(1) (1982) 23
56 L.M. Alte da Veiga, L.R. Andrade and W. Gonschorek, *Z. Krystallog.*, 160(3–4) (1982) 171
57 L.N. Feuerhelm and W.A. Sibley, *J. Phys., C*, 16(4) (1983) 799
58 M.G. Zhao, G.R. Bai and H.C. Jin, *J. Phyc., C*, 15(29) (1982) 5959
59 K. Broomfield and P.M.A. Sherwood, *J. Chem. Soc., Faraday Trans. II*, 79(6) (1983) 785
60 A.G. Oliveira and J.Y. Gesland, *Rev. Bras. Fis., Pt.2*, 12(4) (1982) 826
61 M.N. Bhattacharjee and M.K. Chaudhuri, *Ind. J. Chem., Sect. A*, 21A(10) (1982) 977
62 N. Kijima, K. Tanaka and F. Marumo, *Acta Cryst., Sect. B, Struct. Sci.*, B39(5) (1983) 557
63 A.V. Malakovskii, T.P. Morozova and V.I. Yuzvak, *Phys. Status Solidi B*, 119(1) (1983) 411
64 Kh.G. Boddanova and R.A. Bagautdinov, *Pis'ma Zh. Eksp. Teor. Fiz.*, 37(10) (1983) 483 (Russ.)
65 J. Bartolome, R. Burriel, F. Palacio and D. Gonzalez, *Physica B+C (Amsterdam)*, 115(2) (1983) 190
66 A.A. Majmudar, Y.W. Gokhale and G.S. Rao, *Ind. J. Chem., Sect. A*, 22A(2)

(1983) 145
67 D.E. Cox, S.M. Shapiro, R.J. Nelmes and T.W. Ryan, *Phys. Rev. B, Condens. Mater.*, 28(3) (1983) 1640
68 M. Leblanc, G.Ferey, Y. Calage and R. de Pape, *J. Solid State Chem.*, 47(1) (1983) 24
69 G. Courbion, C. Jacoboni and R. de Pape, *J. Solid State Chem.*, 45(1) (1982) 127
70 P.J. Picone, N. Saegusa and R.G. Srivastava, *Solid State Commun.*, 44(2) (1982) 279
71 C. Pappa, J. Hammann and C. Jacoboni, *J. Magn. Magn. Mater.*, 31–34(3) (1983) 1391
72 E. Bakshi and T.J. Hicks, *J. Phys., C*, 15(31) (1982) 6449
73 B.A. Orlowski, T. Czeppe, J. Stoch and J. Haber, *Proc. Conf. Phys.*, 4 "Phys. Semicond. Comp." (1982) 318
74 B.A. Orlowski and W. Chab, *Solid State Commun.*, 44(6) (1982) 819
75 T. Warminski, M. Maier and B.A. Orlowski, *Phys. Status Solidi B*, 115(1) (1983) K7
76 H. Toraya, F. Marumo and M. Hirao, *Mineral. J.*, 11(5) (1983) 240
77 W. Depmeier and S.A. Mason, *Solid State Commun.*, 44(5) (1982) 719
78 W. Depmeier, *Solid State Commun.*, 45(12) (1983) 1089
79 N.T. Alimkhodzhaeva, *Deposited Doc.*, (1981) VINITI 4150 (Russ.)
80 C. Sourisseau, G. Lucazeau and A.J. Dianoux, *J. Phys., (Les Ulis, Fr.)*, 44(8) (1983) 967
81 R. Mokhlisse, M. Couzi and J.C. Lassegues, *J. Phys., C*, 16(8) (1983) 1353
82 Y. Mlik and M. Couzi, *J. Phys., C*, 15(34) (1982) 6891
83 P. de Groot, P. Janssen, F. Herlach and G. de Vos, *J. Magn. Magn. Mater.*,31-34(2) (1983) 637
84 R. Robert, *Spectrochim. Acta, A*, 39A(1) (1983) 29 (Fr.)
85 C.A. Baumann, R.J. Van Zee and W. Weltner Jr., *J. Phys. Chem.*, 86 (1982) 5084
85a E.D. Crozier, N. Alberding and B.R. Sundheim, *Acta Cryst.,Sect. C, Cryst. Struct. Commun.*, C39(6) (1983) 808
86 F. Rodriguez, M. Moreno, F. Jaque and F.J. Lopez, *J. Chem. Phys.*, 78 (1983) 73
87 N.A. Kulagin and D.T. Sviridov, *Phys. Status Solidi B*, 112(1) (1982) K61
88 S.S. Vianna and C.C. Becerra, *Phys. Rev. B, Condens. Mater.*, 28(5) (1983) 2816
89 J. Ishikawa, T. Asaji and D. Nakamura, *J. Magn. Reson.*, 51(1) (1983) 95
90 V.Yu. Mindin, R.I. Agladze and L.G. Kapanadze, *Zh. Prikl. Khim. (Leningrad)*, 56(2) (1983) 391 (Russ.)
91 T.P. Kim and B.I. Imanakunov, *Russ. J. Inorg. Chem.*, 28(7) (1983) 1079
92 B.B. Abdybakirova and B.I. Imanakunov, *Izv. Akad. Nauk Kirg. SSSR* 1 (1983) 47 (Russ.)
93 Yu.A. Afanas'ev, L.T. Azhipa and T.V. Shumkina, *Deposited Doc.*, (1982) SPSTL 511 KHP-D82 (Russ.)
94 G. Chapuis, G. Brunisholz, C. Javet and R. Roulet, *Inorg. Chem.*, 22 (1983) 455
95 Y. Mlik and M. Couzi, *Raman Spectrosc., Proc. Int. Conf., 8th.*, (1982) 435
96 A.G. Dunn, M. Jewess, L.A.K. Staveley and R.D. Worswick, *J. Chem. Thermodyn.*, 15(4) (1983) 351
97 G. Munteanu, C.I. Lepadatu and L. Patron, *Rev. Roum. Chim.*, 27(6) (1982) 727
98 M. Tanimoto and K. Katsumata, *J. Magn. Magn. Mater.*, 31-34(3) (1983) 1389
99 M. Pawlowska and W. Wojciechowski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*,

30 (1983) 63
100 L. Paltrinieri, L. Piseri and I. Pollini, *Raman Spectrosc., Proc. Int. Conf., 8th.* (1982) 479
101 H.J.W.M. Hoekstra, P.R. Boudewijn and H. Groenier, *Physica B+C (Amsterdam)*, 121(1-2) (1983) 62
102 D. Babel and W. Kurtz, *Stud. Inorg. Chem.*, 3 Solid State Chem., (1983) 593
103 W. Kurtz and D. Babel, *Solid State Commun.*, 48(3) (1983) 277
104 O. Zakharieva-Pencheva and V.A. Dementiev, *THEOCHEM.*, 7(3-4) (1982) 241
105 G. Ozolins and A. Krumina, *Latv. Psr Zinat Akad. Vestis, Kim. Ser.*, 5 (1982) 535 (Russ.)
106 J. Chassaing, C. Monteil and D. Bizot, *J. Solid State Chem.*, 43(3) (1982) 327
107 B. Tanirbergenov and R.V. Maksakova, *Ukr. Khim. Zh. (Russ. Ed.)*, 48(12) (1982) 1241
108 P. Choudury, B. Ghosh and G.S. Raghuvanshi, *J. Raman Spectrosc.*,14(2) (1983) 99
108a P. Choudury, B. Ghosh, O.P. Lamba and H.D. Bist, *J. Phys., C*, 16(9) (1983) 1609
109 S. Kreske and V. Devarajan, *J. Phys., C*, 15(36) (1982) 7333
110 L.M. Kovba, N.V. Tabachenko and V.N. Serezhkin, *Doklady Chemistry*, 266(5) (1983) 373
111 R. Rapkomova, N.V. Saleeva and M.K. Kydynov, *Deposited Doc.*, (1981) VINITI 3626-81 (Russ.)
112 K.B. Schwartz, J.B. Parise and C.T. Prewitt, *Acta Cryst., Sect. B, Struct. Sci.*, B39 (1983) 217
113 L. Ulicka, L. Smrcok and C. Goczeova, *Proc. Conf. Coord. Chem., 9th.*, (1983) 425
114 H. Bilinski, *Polyhedron*, 2 (1983) 353
115 E.D. Dzyuba, V.V. Pechkovskii, G.I. Salonets, V.I. Kovalishina, N.A. Ivkovich and A.V. Chubarov, *Russ. J. Inorg. Chem.*, 27 (1982) 1095
116 V.V. Pechkovskii, E.D. Dzyuba, R.Ya. Mel'nikov, G.I. Salonets, V.I. Kovalishina and I.E. Malashonok, *Russ. J. Inorg, Chem.*, 28 (1982) 1237
117 E.V. Lazarevski, L.V. Kubasova, N.N. Chudinova and I.V. Tananaev, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 18 (1982) 1544 (Russ.)
118 H. Liu and F. Gan, *Guangxue Xuebao*, 2 (1982) 541 (Ch.)
119 A.G. Nord and T. Stefanidis, *Polyhedron*, 1 (1982) 349
120 M.B. Patel, S. Patel, D.P. Khandelwal and H.D. Bist, *Chem. Phys. Letts.*, 101 (1983) 93
121 C.N. Ani, K.C. Patil and V.R.P. Verneker, *Natl. Acad. Sci. Letts. (India)*, 5 (1982) 59
122 A. Hioki, S. Funahashi and M. Tanaka, *Inorg. Chem.*, 22 (1983) 749
123 I'.I. Chuev, *Zh. Fiz. Khim.*, 57 (1983) 1021 (Russ.)
124 D. Dollimore and N.M. Guindy, *Thermochim. Acta*, 58 (1982) 191
125 V.N. Loginov, V.A. Sharov and E.A. Nikonenko, *Russ. J. Inorg. Chem.*, 27 (1982) 1251
126 Kh. Balarev, D. Stoilova and V. Vasileva, *Dokl. Bolg. Akad. Nauk*, 35 (1982) 933
127 S. Yamanaka and M. Hattori, *Nippon Kagaku Kaishi*, 2 (1983) 315
128 C. Sourisseau, Y. Mathey and C. Poinsignon, *Chem. Phys.*, 71 (1982) 257
129 O. Poizat, J. Belloc, C. Sourisseau and R. Clement, *Raman Spectrosc., Proc. Int. Conf., 8th.*, (1982) 639
130 S.K. Misra and M. Jalochowski, *Physica B+C (Amsterdam)*, 119 (1983) 295
131 S.K. Misra and M. Kahrizi, *Solid State Commun.*, 45 (1983) 967
132 A.M. Ziatdinov, V.Ya. Shevchenko, R.M. Gumerov and R.L. Davidovich, *Sovrem. Metody YAMR i EPR v. Khimii Tverd. Tela. Mater.3 Vses. Koord. Soveshch. Uchenykh i Spets In-tov AN. SSSR, Noginsk, 1-3 Iyunya 1982*

Chernogolovka, (1982) 210 (Russ.)
133 R. Hrabanski, *Phys. Status Solidi A*, 77 (1983) K143
134 V.K. Jain and S.K. Yadav, *Phys. Status Solidi B*, 114 (1982) K131
135 S.V.J. Lakshman and A.S. Jacob, *Spectrosc. Letts.*, 16 (1983) 379
136 J. Mroz and S. Gebala, *Opt. Appl.*, 12 (1982) 403
137 M. Heming, G. Lehmann, K. Recker and F. Wallrafen, *Phys. Status Solidi B*, 117 (1983) 271
138 S.N. Lukin, O.P. Teslya and G.A. Tsintsadze, *Fiz. Tverd. Tela (Leningrad)*, 25 (1983) 1075 (Russ.)
139 R. Alcala, P.J. Alonso and R. Cases, *J. Phys., C*, 16 (1983) 4693
140 J. Kuechler, B. Malige, R. Meister and R. Triebeneck, *Cryst. Res. Technol.*, 18 (1983) 1325
141 P. Chand and G.C. Upreti, *J. Chem. Phys.*, 78 (1983) 5930
142 E.A. Petrakovskaya, V.V. Velichko and I.M. Krygin, *Fiz. Tverd. Tela (Leningrad)*, 25 (1983) 862 (Russ.)
143 A. Jankowka-Frydel, *Acta Phys. Pol. A*, A63 (1983) 373
144 M. Heming and G. Lehmann, *Z. Naturforsch., A: Phys. Phys. Chem. Kosmophys.*, 38A (1983) 149
145 B. Frick and D. Siebert, *Ber. Bunsen-Ges. Phys. Chem.*, 87 (1983) 558
146 M. Peteanu, I. Ardelean and A. Nicula, *Rev. Roum. Phys.*, 28 (1983) 47
147 W.E. Hill and C.A. McAuliffe, *PCT Int. Appl.*, WO 81 03494
148 C.A. McAuliffe, H.F. Al-Khateeb, D.S. Barratt, J.C. Briggs, A. Challita, A. Hosseiny, M.G. Little, A.G. Mackie and K. Minten, *J. Chem. Soc., Dalton Trans.*, (1983) 2147
149 C.A. McAuliffe, M.G. Little and J.B. Raynor, *J. Chem. Soc., Chem. Commun.*, (1982) 68
150 C.A. McAuliffe, *J. Organomet. Chem.*, 228 (1982) 255
151 M.L.H. Green, *J. Organomet. Chem.*, 228 (1982) 263
152 C.A. McAuliffe and K. Minten, *Symp. Pap.- Inst. Chem. Eng. North West Branch* (1981) (6. What's New Absorpt. Chem. React.?) 2.1-2.19
153 H.D. Burkett, V.F. Newberry, W.E. Hill and S.D. Worley, *J. Amer. Chem. Soc.*, 105 (1983) 4097
154 K.B. Yatsimirskii, Yu.I. Bratushko and N.I. Ermokhina, *Teor. Eksp. Khim.*, 18 (1982) 367 (Russ.)
155 C.G. Howard, G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1983) 2025
156 C.G. Howard, G.S. Girolami, G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1983) 2631
157 G.S. Girolami, G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, *J. Amer. Chem. Soc.*, 105 (1983) 6752
158 B.P. Chandra and B.R. Kaza, *J. Lumin.*, 27 (1982) 101
159 Y.K. Bhoon, *Polyhedron*, 2 (1983) 365
160 M. Mohan and M. Kumar, *Synth. React. Inorg. Met-Org. Chem.*, 13 (1983) 331
161 R. Chandra and R.N. Kapoor, *Acta Chim. Hung.*, 112 (1983) 11
162 P.B. Chakrawarti and P. Khanna, *J. Ind. Chem. Soc.*, 59 (1982) 828
163 R.C. Mishra, B.K. Mohapatra and D. Panda, *J. Inst. Chem. (India)*, 55 (1983) 7
164 R.C. Mishra, B.K. Mohapatra and D. Panda, *J. Inst. Chem. (India)*, 55 (1983) 19
165 M.R. Chaurasia, P. Shukla and N.K. Singh, *Def. Sci. J.*, 32 (1982) 333
166 R.C. Mishra, B.K. Mohapatra and D. Panda, *J. Ind. Chem. Soc.*, 60 (1983) 11
167 A.E. Sanchez Pelaez and M.J. Gonzalez Garmendia, *Polyhedron*, 1 (1982) 831
168 M.A. Khattab, G. El-Enany and F.M. Ebeid, *Egypt J. Chem.*, 25 (1983) 31

169 V. Atre, G. Reddy and L.N. Venkat Sharada, *Ind. J. Chem., Sect. A*, 21A (1982) 934
170 R. Jain, D.D. Agarwal and A.K. Jain, *Acta Chim. Acad. Sci. Hung.*, 111 (1982) 27
171 R.C. Mishra, B.K. Mohapatra and D. Panda, *J. Ind. Chem. Soc.*, 59 (1982) 836
172 A.K. Rana and J.R. Shah, *Ind. J. Chem., Sect. A*, 21A (1982) 929
173 R.C. Mishra, B.K. Mohapatra and D. Panda, *J. Ind. Chem. Soc.*, 60 (1983) 80
174 A.A. El-Asmy and M.M. Mostafa, *J. Coord. Chem.*, 12 (1983) 291
175 M.C. Jain, R.K. Sharma and P.C. Jain, *Proc. Natl. Acad. Sci., India Sect. A*, 51 (1981) 25
176 G.S. Sanyal, A.B. Modak and A.K. Mudi, *Ind. J. Chem., Sect. A*, 22A (1983) 307
177 M.A. Khattab and A.M. Hilmy, *Proc. Pak. Acad. Sci.*, 19 (1982) 69
178 M.M. Mostafa, M.A. Khattab and K.M. Ibrahim, *Polyhedron*, 2 (1983) 583
179 M.K. Lal and R. Sita, *An. Quim., Ser.B*, 79 (1983) 56
180 P.P. Bhargava, R. Bembi and M. Tyagi, *J. Ind. Chem. Soc.*, 60 (1983) 214
181 B. Singh, P.L. Maurya and B.V. Agarwala, *J. Ind. Chem. Soc.*, 59 (1982) 1130
182 P.L. Maurya, C.P. Dube and B.V. Agarwala, *J. Ind. Chem. Soc.*, 59 (1982) 1400
183 U.G. Deshpande and J.R. Shah, *J. Macromol. Sci., Chem.*, A20 (1983) 355
184 B.C. Whitmore and R. Eisenberg, *Inorg. Chem.*, 22 (1983) 1
185 L.F. Dubinina and V.N. Podchainova, *Koord. Khim.*, 9 (1983) 460
186 A. Cinquantini, R. Seeber and R. Cini, *Trans. Met. Chem., (Weinheim, Ger.)*, 7 (1982) 271
187 R.S. Shekhawat, K.G. Sharma and R.K. Mehta, *Z. Phys. Chem., (Leipzig)*, 263 (1982) 974
188 A.A. Taha and G.A. El-Enany, *J. Chin. Chem. Soc., (Taipei)*, 29 (1982) 249
189 G.A. El-Enany, A.M. Zahara and A.A. Taha, *Egypt J. Chem.*, 25 (1983) 567
190 K. Wieghardt, W. Schmidt, W. Herrmann and H-J. Kuppers, *Inorg. Chem.*, 22 (1983) 2953
191 Z. Yang and M. Wang, *Huaxue Tongbao*, 1 (1983) 17
192 R. Singh, I.S. Ahuja and C.L. Yadava, *J. Mol. Struct.*, 96 (1982) 181
193 U.I. Isaeva and B.I. Imanakunov, *Izv. Akad. Nauk Kirg. SSR*, 4 (1982) 46 (Russ.)
194 C.W.G. Ansell, J. Lewis, P.R. Raithby and T.D. O'Donohue, *J. Chem. Soc., Dalton Trans.*, (1983) 177
195 S.P. Perlepes, Th.F. Zatiropoulos, A.G. Galinos and J.M. Tsangaris, *Z. Naturforsch.*, 38B (1983) 350
196 P.J. Domaille, R.L. Harlow, S.D. Ittel and W.G. Peet, *Inorg. Chem.*, 22 (1983) 3944
197 B.W. Dockum, G.A. Eismann, E.H. Witten and W.M. Reiff, *Inorg. Chem.*, 22 (1983) 150
198 R.C. Srivastava, W.U. Malik and P.P. Bhargava, *Acta Cienc. Indica, (Ser. Chem.)*, 8 (1982) 104
199 S.C. Khurana and I.J. Nigam, *Ind. J. Chem., Sect. A*, 21A (1982) 849
200 K.K. Pendnekar, S. Siddiqui and S.S. Gupta, *Vijnana Parishad Anusandhan Patrika*, 25 (1982) 243 (Hindi)
200a A.L. Kats, A.D. Khamraev and S.I. Ibatov, *Dokl. Akad. Nauk Uzb. SSR*, 6 (1982) 35
201 P. Lamme, I. Mutikainen and E. Lindell, *Inorg. Chim. Acta*, 71 (1983) 217
202 T.P.J. Garrett, J.M. Guss and H.C. Freeman, *Acta Cryst., Sect. C: Cryst. Struct. Comm.*, C39 (1983) 1027

203 T.P.J. Garrett and J.M. Guss, *Acta Cryst., Sect. C: Cryst. Struct. Comm.*, C39 (1983) 1031
204 S. Randhawa, B.S. Pannu and S.L. Chopra, *J. Ind. Chem. Soc.*, 60 (1983) 112
205 J. Dillen, A.T.H. Lenstra and J.G. Haasnoot, *Polyhedron*, 2 (1983) 195
206 V. Callaghan, D.M.L. Goodgame and R.P. Tooze, *Inorg. Chim. Acta*, 78 (1983) L1
207 M.R. Chaurasia, P. Shukla and N.K. Singh, *Def. Sci. J.*, 32 (1982) 75
208 K.S. Siddiqui, P. Khan, S. Khan and S.A.A. Zaidi, *Synth. React. Inorg. Met.-Org. Chem.*, 12 (1982) 681
209 M. Sano and H. Yamatera, *Stud. Phys. Theor. Chem.*,27 Ions Mols. Solns., (1983) 109
210 D.M. Puri and N. Patta, *Ind. J. Chem., Sect. A*, 21A (1982) 624
211 X. Jin, Z. Pan, Y. Tang and D. Huang, *Kexue Tonbao*, 27 (1982) 1044 (Ch.)
212 Yu.Ya. Kharitonov and L.N. Ambroladze, *Koord. Khim.*, 8 (1982) 1569
213 E.A. Mazurenko, S.V. Volkov and Zh. N. Bublik, *Probl. Khim. Primen. β(Beta)-diketonatov Met.*, (Mater. Vses. Semin.) (1978), (1982) 57 (Russ.)
214 M.L. Morris and R.D. Koob, *Org. Mass Spectrom.*, 17 (1982) 503
215 U. Casellato, S. Tamburini, P.A. Vigato, A. de Stefani, M. Vidal and D.E. Fenton, *Inorg. Chim. Acta*, 69 (1983) 45
216 K. von Andra and F. Fleischer, *Z. Anorg. Allgem. Chem.*, 485 (1982) 210
217 C.A. Tsipis, E.G. Bakalbassis, V.P. Papageorgiou and M.N. Bakola-Christianopoulou, *Can. J. Chem.*, 60 (1982) 2477
218 Yu.Ya. Kharitonov and L.N. Ambroladze, *Koord. Khim.*, 9 (1983) 278 (Russ.)
219 Yu.Ya. Kharitonov and L.N. Ambroladze, *Koord. Khim.*, 9 (1983) 424 (Russ.)
220 Yu.Ya. Kharitonov and L.N. Ambroladze, *Koord. Khim.*, 8 (1982) 1431 (Russ.)
221 Yu.Ya. Kharitonov and L.N. Ambroladze, *Zh. Neorg. Khim.*, 28 (1983) 1206 (Russ.)
222 Yu.Ya. Kharitonov and L.N. Ambroladze, *Russ. J. Inorg. Chem.*, 28 (1983) 980
223 A.R. Sarkar and P. Ghosh, *Inorg. Chim. Acta*, 78 (1983) L39
224 A.R. Clemente and M.L.M. Sarrion, *Rev. Chim. Miner.*, 19 (1982) 274
225 C.H.L. Kennard, G. Smith, E.J. O'Reilly and W. Chiangjin, *Inorg. Chim. Acta*, 69 (1983) 53
226 Yu.I. Sal'nikov, R.I. Valiullina and K.P. Pribylov, *Russ. J. Inorg. Chem.*, 28 (1983) 906
227 Kh.M. Yukabov, K.I. Turte and T.A. Zhemchuzhnikova, *Dokl. Akad. Nauk Tadzh. SSR*, 25 (1982) 734 (Russ.)
228 M. Puri and R.D. Verma, *Ind. J. Chem., Sect. A*, 22A (1983) 418
229 P.W. Linder, R.G. Torrington and U.A. Seemann, *Talanta*, 30 (1983) 295
230 E.S. Alambar, J.A. Carlisle and G.O. Carlisle, *Inorg. Chim. Acta*, 78 (1983) L65
231 Yu.Ya. Kharitonov and Z. Tuiebakhova, *Koord. Khim.*, 8 (1982) 1571 (Russ.)
232 T. Fujita, *Chem. Pharm. Bull.*, 30 (1982) 3461
233 S.N. Dubey, R.K. Beweja and D.M. Puri, *Ind. J. Chem., Sect. A*, 22A (1983) 450
234 P. Knuutila, *Acta Chem. Scand.*, 36A (1982) 767
235 K. Rysmendeev and Ya.D. Fridman, *Izv. Akad. Nauk Kirg. SSR*, 3 (1983) 40 (Russ.)
236 R.N.K. Vishwanatham, K. Ram and M.G.R. Reddy, *Ind. J. Chem., Sect. A*, 22A (1983) 270
237 C.S.R. Murthy and G.N. Rao, *Thermochim. Acta*, 68 (1983) 75
238 K.C. Patil, R. Soundararajan and E.P. Goldberg, *Synth. React. Inorg.*

Met.-Org. Chem., 13 (1983) 29
239 C.P. Gupta, K.G. Sharma, R.P. Mathur and R.K. Mehta, *Acta Chim. Acad. Sci. Hung.*, 111 (1982) 19
240 S.S. Kukalenko, Yu.T. Struchkov and S.I. Shestakova, *Koord. Khim.*, 9 (1983) 312
241 G.S. Sanyal, A.B. Modak and A.K. Mudi, *Ind. J. Chem., Sect. A*, 21A (1982) 1044
242 C. Lorenzini, C. Pelizzi, G. Pelizzi and G. Predieri, *J. Chem. Soc., Dalton Trans.*, (1983) 721
243 K.K. D'yachenko, V.E. Ivanov, K.N. Lyubomirova and N.A. Ostapkevich, *J. Gen. Chem. of USSR*, 52 (1982) 2353
244 P. Ramesh, B.V. Kumar and M.G.R. Reddy, *J. Ind. Chem. Soc.*, 60 (1983) 231
245 V.A. Ivanov and V.A. Syrbu, *I. Khim. Tekhnol, Kishinev*, (1983) 30
246 R.C. Aggarwal, R.A. Rai and T.R. Rao, *Ind. J. Chem., Sect. A*, 22A (1983) 255
247 R.C. Aggarwal, R. Bala and R.L. Prasad, *Ind. J. Chem., Sect. A*, 22A (1983) 568
248 V. Banerjee and A.K. Dey, *J. Ind. Chem. Soc.*, 59 (1982) 991
249 C. Preti, L. Tassi, G. Tosi, P. Zannini and A.F. Zanoli, *J. Coord. Chem.*, 12 (1983) 177
250 S.K. Sangal, S.K. Sahni and V.B. Rana, *Acta Chim. Acad. Sci. Hung.*, 110 (1982) 19
251 M.S. Reddy and M.G.R. Reddy, *Ind. J. Chem., Sect. A*, 21A (1982) 8534
252 I.S. Ahuja, *Ind. J. Chem., Sect. A*, 22A (1983) 262
253 R. Singh, I.S. Ahuja and C.L. Yadava, *J. Mol. Struct.*, 98 (1983) 183
254 R. Singh, I.S. Ahuja and C.L. Yadava, *J. Mol. Struct.*, 98 (1983) 175
255 V. Pal, M.P. Sawhney and K.N. Sharma, *Ind. J. Chem., Sect. A*, 22A (1983) 177
256 H.S. Gowda and R. Janardhan, *Proc. Ind. Acad. Sci., (Ser.) Chem. Sci.*, 91 (1982) 339
257 P.K. Biswas, M.K. Dasgupta, S. Mitra and N.R. Chaudhuri, *J. Coord. Chem.*, 11 (1982) 225
258 B.I. Petrov, T.B. Moskvitinova and G. Rudzitis, *Latv. Psr Zinat. Akad. Vestis, Kim. Ser.*, 1 (1983) 78 (Russ.)
259 I. Havlik, T. Simonescu and I. Havlik, *Rev. Roum. Chim.*, 28 (1983) 375
260 O. Costisor, A. Maurer and S. Policec, *Bull. Stiint. Teh. Inst. Politeh. "Traian Vuia" Timisoara, Ser. Chim.*, 26 (1981) 87
261 M.M. Shoukry, A.K. Ghoneim and E.M. Shoukry, *Synth. React. Inorg. Met.-Org. Chem.*, 12 (1982) 815
262 M.R. Mahmoud, F.A. Adam and K. Yousef, *Bull. Soc. Chim. Belg.*, 92 (1983) 13
263 S.A. Zeinalova, I.K. Guseinov, I.N. Marov, N.Kh. Rustamov and N.B. Kalinichenko, *Russ. J. Inorg. Chem.*, 27 (1982) 1752
264 R. Singh, I.S. Ahuja and C.L. Yadava, *Polyhedron*, 1 (1982) 327
265 M. Otto, F. Ehrentreich and G. Werner, *Z. Chem.*, 22 (1982) 392 (Ger.)
266 A.I. Byrke, Yu.Ya. Kharitonov and V.N. Shafranskii, *Koord. Khim.*, 9 (1983) 51 (Russ.)
266a V.T. Balan, A.I. Byrke and K.G. Kaptar, *I. Khim. Tekhnol., Kishinev*, (1983) 11 (Russ.)
267 J.S. Siddiqui and S.C. Srivastava, *Ind. J. Chem., Sect. A*, 22A (1983) 353
268 M. Mukkanti, Y.K. Bhoon, K.B. Pandeya and R.P. Singh, *J. Ind. Chem. Soc.*, 59 (1982) 830
269 N.K. Singh, S. Agrawal and R.G. Aggarwal, *Ind. J. Chem., Sect. A*, 21A (1982) 973
270 E. Escriva, D. Beltran and J. Beltran, *An. Quim., Ser. B*, 77 (1981)

330
271 X. Solans, M. Font-Altaban, J. Oliva and J. Herrera, *Acta Cryst., Sect. C: Cryst. Struct. Commun.*, C39 (1983) 435
272 L.I. Myachina, V.A. Logvinenko and S.A. Grankina, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 6 (1982) 112 (Russ.)
273 L.I. Myachina, V.A. Logvinenko and S.A. Grankina, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 2 (1983) 75 (Russ.)
274 J. Podlahova and J. Podlaha, *Collect. Czech. Chem. Commun.*, 47 (1982) 1078
275 Z.A. Siddiqi, M. Shakir, M. Aslam and T.A. Khan, *Synth. React. Inorg. Met.-Org. Chem.*, 13 (1983) 397
276 K. Andrae and K.D. Schmidt, *Z. Anorg. Allgem. Chem.*, 498 (1983) 199 (Ger.)
277 S.Z. Haider and K.M.A. Malik, *J. Bangladesh Acad. Sci.*, 6 (1982) 119
278 R.R. Gupta, K. Usha and R. Kaushal, *Vijnana Parishad Anusandhan Patrika*, 25 (1982) 269 (Hindi)
279 M.G. Tskitishvili, I.I. Mikadze, N.B. Zhorzholiani and M.B. Chrelashvili, *Koord. Khim.*, 9 (1983) 369 (Russ.)
280 M.G. Tskitishvili, I.I. Mikadze, N.B. Zhorzholiani and M.B. Chrelashvili, *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.*, 8 (1982) 270 (Russ.)
281 S.K. Srivastava, A. Gupta and A. Verman, *Chim. Acta Turc.*, 11 (1983) 99
282 S.K. Srivastava, A. Verman and A. Gupta, *J. Ind. Chem. Soc.*, 59 (1982) 925
283 T. Kiss and A. Gergely, *Inorg. Chim. Acta*, 78 (1983) 247
284 T. Kiss and A. Gergely, *Magy. Kem. Foly.*, 89 (1983) 78 (Hung.)
285 G. Dai and B. Yan, *Sichuan Yixueyuan Xuebao*, 14 (1983) 31 (Ch.)
286 U. Sharma and N. Chandra, *Thermochim. Acta*, 59 (1982) 115
287 R.K. Boggess, J.R. Absher, S. Morelen, L.T. Taylor and J.W. Hughes, *Inorg. Chem.*, 11 (1983) 1273
288 W.S. Kittl and B.M. Rode, *Inorg. Chim. Acta*, 63 (1982) 47
289 P.A. Manorik and N.K. Davidenko, *Russ. J. Inorg. Chem.*, 28 (1983) 1299
290 H. Sigel, B.E. Fisher and E. Farkas, *Inorg. Chem.*, 22 (1983) 925
291 D. Coucouvanis, C.N. Murphy, E. Simhon, P. Stremple and M. Draganjac, *Inorg. Synth.*, 21 (1982) 23
292 T. Costa, J.R. Dorfman, K.S. Hagen and R.H. Holm, *Inorg. Chem.*, 22 (1983) 4091
293 Yu.Ya. Kharitonov and L.N. Ambroladze, *Koord. Khim.*, 8 (1982) 1287 (Russ.)
294 Yu.Ya. Kharitonov and L.N. Ambroladze, *Koord. Khim.*, 8 (1982) 1705 (Russ.)
295 A.I. Byrke, M.S. Fedoseev and K.G. Kaptar, *I. Khim. Tekhnol., Kishinev*, (1983) 16 (Russ.)
296 K.S. Siddiqi, M.A.A. Shah and S.A.A. Zaidi, *Bull. Soc. Chim. Fr.*, 1-2(Pt1) (1983) 49
297 K.N. Johri, N.K. Kaushik and R.K. Bajaj, *Acta Chim. Hung.*, 113 (1983) 325
298 H.B. Singh, S. Maheshwari, S. Srivastava and V. Rani, *Synth. React. Inorg. Met.-Org. Chem.*, 12 (1982) 659
299 R. Hoppenheit, W. Isenberg and R. Mews, *Z. Naturforsch.*, 37B (1982) 1116
300 K.S. Siddiqi, M.A. Neyazi and Z.A. Siddiqi, *Ind. J. Chem., Sect. A*, 21A (1982) 932
301 G. Muller, D. Neugebauer, W. Geike, F.H. Kohler, J. Pebler and H. Schmidbauer, *Organometallics*, 2 (1983) 257
302 J.T. Weed, M.F. Rettig and R.M. Wing, *J. Amer. Chem. Soc.*, 105 (1983) 6510
303 D.S. Marynick and C.M. Kirkpatrick, *J. Phys. Chem.*, 87 (1983) 3273
304 M.C. Bohm, *Inorg. Chem.*, 22 (1983) 83
305 V.E. Volkov, I.Yu. Danilov and L.L. Zhidkov, *Russ. J. Inorg. Chem.*, 28 (1983) 777

306 D.M. Adams and I.O.C. Ekejiuba, *J. Phys. Chem.*, 78 (1983) 5408
307 D.J. Parker, *Spectrochim. Acta*, 39A (1983) 463
308 M.C.R. Symons and R.L. Sweany, *Organometallics*, 1 (1982) 834
309 S.P. Church, M. Poliakoff, J.A. Timney and J.J. Turner, *Inorg. Chem.*, 22 (1983) 3259
310 H. Yesaka, T. Kobayashi, K. Yasufuku and S. Nagakura, *J. Amer. Chem. Soc.*, 105 (1983) 6249
311 A.F. Hepp and M.S. Wrighton, *J. Amer. Chem. Soc.*, 105 (1983) 5934
312 T. Lionel, J.R. Morton and K.F. Preston, *Inorg. Chem.*, 22 (1983) 145
313 M.C.R. Symons, J. Wyatt, B.M. Peake, J. Simpson and B.H. Robinson, *J. Chem. Soc., Dalton Trans.*, (1982) 2037
314 N.J. Coville, A.M. Stolzenberg and E.L. Muetterties, *J. Amer. Chem. Soc.*, 105 (1983) 2499
315 A. Marcomini and A. Poe, *J. Amer. Chem. Soc.*, 105 (1983) 6952
316 A.P. Svitin, S.S. Budnikov and I.B. Bersuker, *Teor. Eksp. Khim.*, 18 (1982) 694 (Russ.)
317 W. Tam, M. Marsi and J.A. Gladysz, *Inorg. Chem.*, 22 (1983) 1413
318 T.G. Richmond, F. Basolo and D.F. Shriver, *Organometallics*, 1 (1982) 1624
319 H.J. Haupt, F. Neumann and B. Schwab, *Z. Anorg. Allgem. Chem.*, 485 (1982) 234 (Ger.)
319a P. Cocolios, C. Moise and R. Guilard, *J. Organomet. Chem.*, 228 (1982) C43 (Fr.)
320 W.L. Jolly, *J. Phys. Chem.*, 87 (1983) 26
321 A. Fox, A. Poe and R. Ruminski, *J. Amer. Chem. Soc.*, 104 (1982) 7327
322 E. Lindner, M. Steinwand and S. Hoehne, *Chem. Ber.*, 115(7) (1982) 2478 (Ger.)
323 U. Kunze and A. Antoniadis, *Z. Naturforsch. B*, 37B (1982) 560 (Ger.)
324 G.A. Abakumov, V.K. Cherkasov, K.G. Shalnova, I.A. Teplova and G.A. Razuvaev, *J. Organomet. Chem.*, 236 (1982) 333
325 S.P. Solodovnikov, K. Sarbasov, B.L. Tumanskii, N.N. Bubnov, A.I. Prokof'ev and M.I. Kabachnik, *Dokl. Chem.*, 265(4) (1982) 251
326 K. Sarbasov, B.L. Tumanskii, S.P. Solodovnikov, N.N. Bubnov, A.I. Prokof'ev and M.I. Kabachnik, *Bull. Acad. Sci. USSR*, 31 (1982) 490
327 P. Mathur and G.C. Dismukes, *J. Amer. Chem. Soc.*, 105 (1983) 7093
328 V.N. Setkina, S.P. Dolgova, D.V. Zagorevskii, V.F. Sizoi and D.N. Kursanov, *Bull. Acad. Sci. USSR*, 31 (1982) 1239
329 L. Busetto, A. Palazzi and M. Monari, *J. Chem. Soc., Dalton Trans.*, (1982) 1631
330 U. Kunze and T. Hattich, *Chem. Ber.*, 115 (1982) 3663 (Ger.)
331 L. Busetto and A. Palazzi, *Inorg. Chim. Acta Letts.*, 64 (1982) L39
332 W. Winter, R. Merkel and U. Kunze, *Z. Naturforsch. B*, 38B (1983) 747 (Ger.)
333 A. Antoniadis, U. Kunze and M. Moll, *J. Organomet. Chem.*, 235 (1982) 177
334 D. Rehder, R. Kramolowsky, K.G. Steinhauser, U. Kunze and A. Antoniadis, *Inorg. Chim. Acta*, 78 (1983) 243
335 A. Antoniadis, W. Hiller, U. Kunze, H. Schaal and J. Strahle, *Z. Naturforsch. B*, 37B (1982) 1289 (Ger.)
336 B. Just, W. Klein, J. Kopf, K.G. Steinhauser and R. Kramolowsky, *J. Organomet. Chem.*, 229 (1982) 49 (Ger.)
337 D. Wormsbacher, F. Edelmann and U. Behrens, *Chem. Ber.*, 115 (1982) 1332 (Ger.)
338 W. Danzer, W.P. Fehlhammer, A.T. Liu, G. Thiel and W. Beck, *Chem. Ber.*, 115 (1982) 1682 (Ger.)
339 J.L. Atwood, I. Bernal, F. Calderazzo, L.G. Canada, R. Poli, R.D. Rogers, C.A. Veracini and D. Vitali, *Inorg. Chem.*, 22 (1983) 1797
340 M. Herberhold, D. Reiner and D. Neugebauer, *Angew. Chem., Int. Ed.*, 22 (1983) 59

341 Yu-Han Chen and J.E. Ellis, *J. Amer. Chem. Soc.*, 105 (1983) 1689
342 R.E. Stevens and W.L. Gladfelter, *Inorg. Chem.*, 22 (1983) 2034
343 D. Sellmann, J. Muller and P. Hofmann, *Angew. Chem., Int. Ed.*, 21 (1982) 691
344 V.N. Kalinin, A.V. Usatov, I.A. Popello and L.I. Zakharkin, *Bull. Acad. Sci. USSR, Chem. Sect.*,31 (1982) 1281
345 D. Walther, G. Kreisel and R. Kirmse, *Z. Anorg. Allgem. Chem.*, 487 (1982) 149 (Ger.)
346 D.T. Plummer, G.A. Kraus and R.J. Angelici, *Inorg. Chem.*, 22 (1983) 3492
347 G. Hartmann, R. Hoppenheit and R. Mews, *Inorg. Chim. Acta*, 76 (1983) L201
348 H.W. Roesky and L. Schonfelder, *Chem. Ber.*, 115 (1982) 1460 (Ger.)
349 O.J. Scherer, J. Kerth, B.K. Balbach and M.L. Ziegler, *Angew. Chem., Int. Ed.*, 21 (1982) 136
350 R. Uson and J. Gimeno, *J. Organomet. Chem.*, 220 (1981) 173
351 M. Ulibarri and J. Payos, *Acta Cryst., B*, 38B (1982) 952
352 J. Payos and M. Ulibarri, *Acta Cryst., B*, 38B (1982) 3086
353 D. Rehder, H-C. Bechthold, A. Kececi, H. Schmidt and M. Siewing, *Z. Naturforsch. B*, 37B (1982) 631 (Ger.)
354 C.P. Cheng, A.H. Cheng and P.J. Shyong, *Proc. Natl. Sci. Counc. Repub. China, Part B*, 6(3) (1982) 298
355 C. Busetto, A.M. Mattucci, E.M. Cernia and R. Bertani, *J. Organomet. Chem.*, 246 (1983) 183
356 S.B. McCullen and T.L. Brown, *J. Amer. Chem. Soc.*, 104 (1982) 7496
357 B.H. Byers and T.P. Curran, *Organometallics*, 2(3) (1983) 459
358 S. Pelling, C. Botha and J.R. Moss, *J. Chem. Soc., Dalton Trans.*, (1983) 1495
359 M. Lattman, B.N. Anand, D.R. Garrett and M.A. Whitener, *Inorg. Chim. Acta*, 76 (1983) L139
360 M.J. Zaworotko, R. Shakir, J.L. Atwood, V. Sriyunyongwat, S.D. Reynolds and T.A. Albright, *Acta Cryst., B*, 28B (1982) 1572
361 G.A. Carriedo, V. Riera and J. Santamaria, *J. Organomet. Chem.*, 234 (1982) 175
362 A. Kececi, D. Rehder, W. Roose and R. Talay, *Chem. Ber.*, 115 (1982) 3257 (Ger.)
363 S. Onaka, Y. Kondo, N. Furuichi, K. Toriumi and T. Ito, *Bull. Chem. Soc. Jpn.*, 56 (1983) 87
364 M.D. Rausch, B.H. Edwards, R.D. Rogers and J.L. Atwood, *J. Amer. Chem. Soc.*, 105 (1983) 3882
365 J.A. Iggo, M.J. Mays, P.R. Raithby and K. Hendrick, *J. Chem. Soc., Dalton Trans.*, (1983) 205
366 T.E. Wolff and L.P. Klemann, *Organometallics*, 1 (1982) 1667
367 B.C. Aspinall, A.J. Deeming and S. Donovan-Mtunzi, *J. Chem. Soc., Dalton Trans.*, (1983) 2669
368 G. Ferguson, W.J. Laws, M. Parvez and R.J. Puddephatt, *Organometallics*, 2 (1983) 276
369 H.R. Allcock, K.D. Lavin, N.M. Tollefson and T.L. Evans, *Organometallics*, 2 (1983) 267
370 G. Huttner, B. Sigwarth, J. van Seyerl and L. Zsolnai, *Chem. Ber.*, 115 (1982) 2035 (Ger.)
371 B. Sigworth, L. Zsolnai, O. Scheidsteger and G. Huttner, *J. Organomet. Chem.*, 235 (1982) 43
372 T. Kawamura, S. Enoki, S. Hayashida and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3417
373 C.P. Casey and R.M. Bullock, *J. Mol. Catal.*, 14 (1982) 283
374 B.L. Booth, S. Casey and R.N. Haszeldine, *J. Organomet. Chem.*,226 (1982) 289
375 I.I. Gerus, Yu.L. Yagupol'skii and N.D. Volkov, *Zh. Org. Khim.*, 18 (1982)

1186 (Russ.)
376 D.T. Plummer and R.J. Angelici, *Inorg. Chem.*, 22 (1983) 4063
377 E. Lindner, G. von Au, H.J. Eberle and S. Hoehne, *Chem. Ber.*, 115 (1982) 513 (Ger.)
378 R.L. Harlow, P.J. Krusic, R.J. McKinney and S.S. Wreford, *Organometallics*, 1 (1982) 1506
379 W.B. Rybakov, A.I. Tursina, L.A. Aslanov, S.A. Yeremin, H. Schrauber and L. Kutschabsky, *Z. Anorg. Allgem. Chem.*, 487 (1982) 217 (Ger.)
380 R.B. Hitam, R. Narayanaswamy and A.J. Rest, *J. Chem. Soc., Dalton Trans.*, (1983) 615
381 A.T. Shuvaev, A.G. Kochur, Yu.A. Teterin and A.S. Baev, *Dokl. Akad. Nauk SSSR*, 266 (1982) 924 (Russ.)
382 A.G. Kochur, A.T. Shuvaev, M.A. Tyzykhov, A.G. Ginzburg, Yu.A. Teterin and A.S. Baev, *Deposited Doc.*, (1981) VINITI 4220 (Russ.)
383 E.N. Gur'yanov, A.G. Ginzburg, E.S. Isaeva, V.N. Setkina and D.N. Kursanov, *Dokl. Chem.*, 262 (1982) 58
384 N.M. Kostic and R.F. Fenske, *J. Organomet. Chem.*, 233 (1982) 337
385 U. Schubert, K. Ackermann and B. Worle, *J. Amer. Chem. Soc.*, 104 (1982) 7378
385a G.Cerveau, E. Colomer and R.J.P. Corriu, *J. Organomet. Chem.*, 236 (1982) 33
386 F. Carre, G. Cerveau, E. Colomer and R.J.P. Corriu, *J. Organomet. Chem.*, 229 (1982) 257
387 D.J. Brauer and R. Eujen, *Organometallics*, 2 (1983) 263
388 A.A. Ioganson, Yu.G. Kovalev and T.V. Aksenova, *Bull. Acad. Sci. USSR, Chem. Sect.*, 32 (1983) 1316
389 A.M. Seyam and G.M.A. Eddein, *Dirasat, [Ser]: Nat. Sci. (Univ. Jordan)*, 7 (1980) 41
390 K.L. Fjare and J.E. Ellis, *J. Amer. Chem. Soc.*, 105 (1983) 2303
391 Yu.V. Skripkin, A.A. Pasynskii, V.T. Kalinnikov, M.A. Porai-koshits, L.Kh. Minacheva, A.S. Antsyshkina and V.N. Ostrikova, *J. Organomet. Chem.*, 231 (1982) 205
392 C.P. Casey, R.M. Bullock, W.C. Fultz and A.L. Rheingold, *Organometallics*, 1 (1982) 1591
393 J. Schneider, L. Zsolnai and G. Huttner, *Cryst. Struct. Commun.*, 11 (1982) 943
394 B. Schafer-Stahl, J. Schneider and G. Huttner, *Z. Naturforsch. B*, 37B (1982) 610 (Ger.)
395 N.E. Kolobova, L.L. Ivanov, O.S. Zhvanko, A.S. Batsanov and Yu.T. Struchkov, *J. Organomet. Chem.*, 231 (1982) 37
396 O. Kolb and H. Werner, *Angew. Chem., Int. Ed.*, 21 (1982) 202
397 H. Preut and H.J. Haupt, *Acta Cryst. B.*, 38B (1982) 1290
398 J.W. Buchler, C. Dreher and K.L. Lay, *Z. Naturforsch.*, 37B (1982) 1155 (Ger.)
399 J.W. Buchler, C. Dreher, K.L. Lay, Y.J.A. Lee and W.R. Scheidt, *Inorg. Chem.*, 22 (1983) 888
400 S. Konishi, M. Hoshino and M. Imamura, *J. Phys. Chem.*, 86 (1982) 4537
401 M.J. Camenzind, F.J. Hollander and C.L. Hill, *Inorg. Chem.*, 22 (1983) 3776
402 J.A. Smegal and C.L. Hill, *J. Amer. Chem. Soc.*, 105 (1983) 2920
403 J.A. Smegal, B.C. Schardt and C.L. Hill, *J. Amer. Chem. Soc.*, 105 (1983) 3510
404 J.A. Smegal and C.L. Hill, *J. Amer. Chem. Soc.*, 105 (1983) 3515
405 W.R. Scheidt, Y.J. Lee, W. Luangdilok, K.J. Haller, K. Anzai and K. Hatano, *Inorg. Chem.*, 22 (1983) 1516
406 K. Hatano, K. Anzai and Y. Iitaka, *Bull. Chem. Soc. Jpn.*, 56 (1983) 422
407 K. Takahashi, T. Komura and H. Imanaga, *Kanazawa Daigaku Kogakubu Kiyo*,

16 (1983) 103 (Jpn.)
408 P.C. Minor and A.B.P. Lever, *Inorg. Chem.*, 22 (1983) 826
409 A. Bettelheim, D. Ozer and R. Parash, *J. Chem. Soc., Faraday Trans. I*, 79 (1983) 1555
410 T. Watanabe, T. Ama and K. Nakamoto, *Inorg. Chem.*, 22 (1983) 2470
411 S. Mitra, A.K. Gregson, W.E. Hatfield and R.R. Weller, *Inorg. Chem.*, 22 (1983) 1729
412 M. Tabata and M. Tanaka, *J. Chem. Soc., Dalton Trans.*, (1983) 1955
413 R. Rao, M.C.R. Symons and A. Harriman, *J. Chem. Soc., Faraday Trans. I*, 78 (1982) 3393
414 J.P. Collman, C.S. Bencosme, R.R. Darand Jr., R.P. Kreh and F.C. Anson, *J. Amer. Chem. Soc.*, 105 (1983) 2699
415 V.A. Zhorin, G.A. Nikiforov and A.L. Khristyuk, *Dokl. Akad. Nauk SSSR*, 271 (1983) 650 (Russ.)
416 V.V. Zelentsov, A.K. Stroesku and T.A. Koroleva, *Koord. Khim.*, 9 (1983) 168 (Russ.)
417 J.W. Kruper Jr., *Diss. Abst. Int. B*, 44 (1983) 497
418 S.E. Jones, *Diss. Abst. Int. B*, 43 (1982) 1835
419 S.L. Kelly, *Diss. Abst. Int. B*, 43 (1982) 3583
420 I. Salarzadeh and S.A. Tariq, *Aust. J. Chem.*, 36 (1983) 25
421 V.P. Barkhatov, V.F. Balakirev Yu.V. Golikov and E.G. Kostitsin, *Phys. Status Solidi A*, 76 (1983) 57
422 M.S. Seehra and G. Srinivasan, *J. Appl. Phys.*, 53 (1982) 8345
423 R. Hypolito and R. Giovanoli, *An. Acad. Bras. Cienc.*, 54 (1982) 713 (Port.)
424 M.M. Thackeray, W.I.F. David and P.G. Bruce, *Stud. Inorg. Chem.*, 3 Solid State Chem., (1983) 801
425 M. Borges-Soares, F. Menes and R. Fontaine, *J. Microsc. Spectrosc. Electron.*, 8 (1983) 93 (Fr.)
426 Q. Chen and X. Chen, *Zhongnan Kuangye Xueyuan Xuebao*, 3 (1982) 1 (Ch.)
427 I.D. Zhitomirskii, N.E. Skorokhodov and A.A. Bush, *Fiz. Tverd. Tela (Leningrad)*, 25 (1983) 953 (Russ.)
428 J. Tanaka, K. Takahashi, Y. Yajima and M. Tsukioka, *Chem. Letts.*, (1982) 1847
429 M.L. Norton, *Diss. Abst. Int. B*, 43 (1983) 2917
430 V.K. Singh and S. Lokanathan, *Pramana*, 20 (1983) 1
431 S.S. Sen, B. Banerjee and D. Sen, *Ind. J. Chem., Sect. A*, 21A (1982) 1140
432 R. Boca, *J. Mol. Catal.*, 18 (1983) 41
433 R. Boca and P. Pelikan, *J. Mol. Catal.*, 14 (1982) 121
434 E. Wasielewska and A. Colebiewski, *Pol. J. Chem.*, 55 (1981) 1099
435 D. Nalewajek, F. Wudl, M.L. Kaplan, R.D. Bereman, J. Dorfman and J. Bordner, *Inorg. Chem.*, 22 (1983) 4112
436 P. Legzdins, C.R. Nurse and S.J. Rettig, *J. Amer. Chem. Soc.*, 105 (1983) 3727
437 M.C. Bohm, R.D. Ernst, R. Gleiter and D.R. Wilson, *Inorg. Chem.*, 22 (1983) 3815
438 J. Garcia, J. Bartolome and D. Gonzalez, *J. Chem. Thermodyn.*, 15 (1983) 465
439 P. Chaudouet, R. Madar, R. Fruchart and B. Lambert, *Mater. Res. Bull.*, 18 (1983) 713 (Fr.)
440 A.E. Stevens, C.S. Fiegerle and W.C. Lineberger, *J. Chem. Phys.*, 78 (1983) 5420
441 R. Hempelmann, D. Richter and A. Heidermann, *J. Less Common Met.*, 88 (1982) 343
442 D. Rambabu, R. Nagarajan and S.K. Malik, *J. Magn. Magn. Mater.*, 31 (1983) 759
443 J.J. Barry and H.P. Hughes, *J. Phys., C*, 15 (1982) 497
444 J.A. Iggo, M.J. Mays and P.L. Taylor, *Philos. Trans. R. Soc. London, Ser. A*, 308(1501) (1982) 27