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5. MANGANESE

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CONTENTS

INTRODUCTION

The period of this review covers papers published in 1980 and 1981 included in volumes 94 and 95 of Chemical Abstracts. Some papers from volume 93 are

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also included, where these were omitted from last year's review [1].

The format is essentially the same as last year. The photochemistry of manganese complexes has been adequately reviewed elsewhere [2]. Once again, work of an essentially organometallic nature has been excluded, together with reports of purely kinetic or mechanistic interest.

5.1 HIGH OXIDATION STATES

The differences in the structures of K_α X-ray absorption edges of solid $K[MnO_4]$ and aqueous $K[MnO_4]$ and $K_2[MnO_4]$ were determined using synchrotron radiation. Activation parameters for the $[MnO_4]^{2-}/[MnO_4]^-$ electron exchange reaction have been calculated [3], and detailed excitation profiles for the $[MnO_4]^-$ ion in the vicinity of the $^1T_2$ state ($\nu \sim 19000$ cm^{-1}) were measured for $K[MnO_4]/K[ClO_4]$ mixtures and $[Ph_4P][MnO_4]$ [4]. Kinetic bistability in the manganate(VII) oxidation of oxalate was observed [5], and a study of the oxidation of alkenes by $K[MnO_4]$ found some evidence for intermediate complexes [6,7]. The IR spectra of $[MnO_3F]$ and its ^{18}O isotopomers were recorded in an argon matrix [8]. The reduction of $[MnO_4]^-$ by dihydrogen showed a kinetic isotope effect [9], and the reduction of $K[MnO_4]$ by H^+ and Mn^{2+} has also been studied [10,11].

The properties of binuclear manganese complexes with mono-oxo, dioxo- and peroxo-bridges have been reviewed [12].

Using pulse radiolysis experiments, $[MnO_4]^{2-}$ was reduced to the metastable $[MnO_4]^{3-}$ ion, which protonates to give $[HMnO_4]^{2-}$ [13]. The dynamic Jahn-Teller effect in a ligand field excited state of $[MnO_4]^{3-}$, in a $Sr_5[PO_4]_3Cl$ matrix was observed [14].

5.2 MANGANESE(IV)

5.2.1 Halides and pseudohalides

A thermochemical study of $[MnF_6]^{2-}$ established its enthalpies of solution and hydrolysis, as well as an estimate of its ion hydration enthalpy [15]. The reaction between $[NH_4][MnF_3]$ and XeF_6 yielded $[NH_4][XeF_5][MnF_6]$ [16]. The salts $A[MnF_5]$ {A = Na, K or Rb} were prepared by a new route; the manganese(III) intermediate $K_2[MnF_5].H_2O$ showed a very low magnetic moment due to metal-metal exchange interactions through the fluoride ion [17]. The complex $[O_2][Mn_2F_9]$ was prepared for the first time by the reaction of MnO_2 or MnF_n {n = 2, 3 or 4} with F_2/O_2 mixtures at high temperatures and pressures. Ruby-red crystals were characterised by single crystal X-ray diffraction, IR and magnetic susceptibility measurements [18].

5.2.2 Oxides

The following mixed metal oxides have been reported: MnM_2O_4 {M = Mg, Co or Ni} [19], $Cu_{1.5}Mn_{1.5}O_4$ [20], $MCu_3Mn_4O_{12}$ {M = Ca or Cd} [21] and $M[Mn_2O_5]$ {M = Nd, Sm, Eu, Gd, Dy, Tb, Ho, Er, Yb, Lu or Y} [22]. Treatment of the spinel-type material $LiMn_2O_4$ with aqueous acid yielded a new crystalline form of MnO_2, designated λ-MnO_2; a mechanism for this conversion was proposed [23]. Sixteen synthetic MnO_2 samples of different crystalline modifications and purity have been prepared, and found to be mainly non-stoicheiometric [24]. Some physical properties of electrolytic MnO_2 and chemical MnO_2 have also been measured and compared [25]. The reaction order for the dissolution of MnO_2 and MnO in acids with respect to $[H^+]$ have been reported [26]. Simultaneous TGA, DTGA and DTA studies have been performed on MnO_2, Mn_3O_4 and Mn_2O_3 [27], and the interaction of propene with MnO_2, Mn_2O_3 and MnO has been studied by IR spectroscopy [28].

5.2.3 Other complexes

The catecholate complex $[Mn(dtbc)_3]^{2-}$ has been prepared in aprotic solvents and characterised by cyclic voltammetry, UV and EPR spectroscopy, as well as by magnetic susceptibility measurements [29].

A soluble manganese(IV) species has been observed in the manganate(VII) oxidation of 2,4(1H,3H)pyrimidinediones (uracil and 5-methyl-, 6-methyl-, 5-fluoro-, 5-chloro-, 5-bromo-, 5-iodo-, 5-ethanoyl- or 5-nitro-uracil); orders of reaction and thermodynamic constants were obtained, and the mechanism investigated [30].

Six complexes of the stoicheiometry MnL_2X_2 (L = acac, $[S_2CNEt_2]^-$ or morpholinedithiocarboxylate; X = Cl or Br) have been prepared and characterised [31].

5.3 MANGANESE(III)

5.3.1 Fluorides

The formation of manganese(III) fluoride complexes has been studied in ionic aqueous media of $Li[ClO_4]$ and $H[ClO_4]$. The equilibrium constants for the formation of the species $[MnF_n]^{3-n}$ {n = 1, 2 or 3} and the $[Mn(OH)F]^+$ were determined [32]. On reduction of $K[MnO_4]$ with acacH in the presence of an excess of alkali metal difluorides $A[HF_2]$ {A = $[NH_4]$, Na, K or Cs}, the complexes $A_2[MnF_5]$ {A = $[NH_4]$ or Na} or $A_2[MnF_5].H_2O$ {A = K or Cs} resulted in almost quantitative yield [33]. The complex $K_2[MnF_5]$ has been prepared [16] (see section 5.2.1).

The electric quadruple coupling constant at the ^{19}F site has been determined for MnF_3 [34].

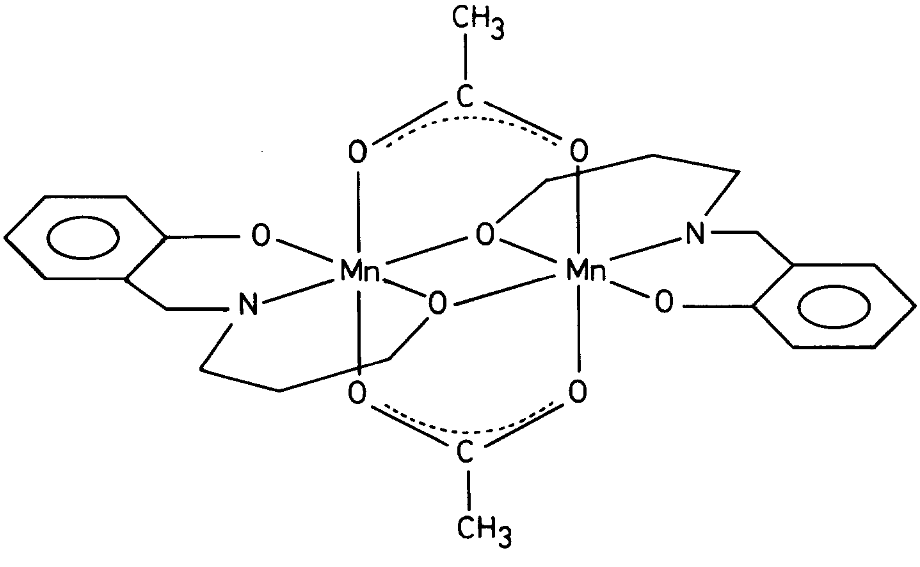
Thermolysis of $[Ph_2I]_3[Mn(CN)_6].nH_2O$ and $[Ph_2I]_3[Mn(CN)_5NO]$ have been studied by DTGA and TGA; PhI and PhNC were observed as decomposition products [35]. The electronic energy levels of $[Mn_2O(CN)_{10}]^{6-}$ were calculated using the self-consistent-charge and configuration MO method [36].

5.3.2 Oxides

The complexes $AMnO_3$ {A = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, Lu or Y} have been prepared by coprecipitation [37]. The phase diagram of the Mn_2O_3-Cr_2O_3 system in air between 1100 and 1620 K has been determined [38].

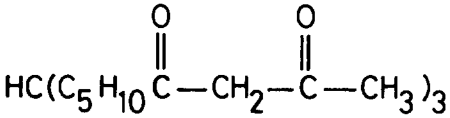
5.3.3 Complexes with Group VIB donor ligands

Crystals of [Mn(spa)(O_2CMe)] {H_2spa = 3-salicylideneamino-1-propanol} were studied by single crystal X-ray diffraction. The determined structure, *(1)* is



(1)

consistent with its observed magnetic properties [39]. The complexes [Mn(thac)$_3$] and [Mn(thtfac)$_3$] {thacH = 1-(2-thienyl)-1,3-butanedione, thtfacH = 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione} have been prepared and characterised [40]. The hexaketone 10-(nona-6,8-dionyl)-2,4,16,18-nonadecatetraone *(2)* was found to give



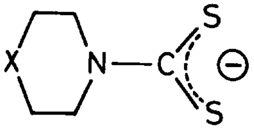
$$HC(C_5H_{10}C(=O)-CH_2-C(=O)-CH_3)_3$$

(2)

a very stable complex of manganese(III). The complex was found to be readily reduced to the manganese(II) derivative, which itself was found to be kinetically stable to ligand exchange [41]. The complexes $[Mn(dik)_2Cl]$ (dikH = acacH, benzacH or dbzmH) were prepared and found to be five-coordinate in CH_2Cl_2; adduct formation with various donor solvents was measured [42]. The chemical relaxation curves for the complex equilibria in solution for the complexes $[Mn(C_2O_4)_n(H_2O)_m]^{3-2n}$ $\{n = 2$ or $3;$ $m = 0, 2$ or $4\}$ have been reported [43], and the magnetic properties of the complex formed with 2,4-dihydroxybenzoic acid have been studied [44].

The oxidations of cyclohexanone and glycine by $[Mn(H_2O_6]^{3+}$ in perchloric acid and of tartaric acid, malic acid, cyclohexanol, allylic alcohols, halophenols and halonaphthols by $Mn_2(SO_4)_3$ have been studied [45-48]. Manganese(III) ethanoate was used as a radical source in the oxidation of allyl- and allenylcolbaloximes [49], but when used to oxidise flavones yielded mainly cleavage products [50].

Complexes of the type $[Mn(S_2CNR_2)_3]$ $\{S_2CNR_2$ = *(3)*$\}$ have been characterised



(3; X = CH_2, O, NMe or S)

and contain bidentate dithiocarbamate ligands [51,52]. The related complex $[Mn\{S_2CN(Et)(2\text{-}MeC_6H_4)\}_3]$ has also been prepared, characterised and DTGA and TGA studies have been performed [53].

The first evidence that manganese does bind to the sulphur group in metalloproteins has been observed for a manganese(III) complex containing acid phosphatase [54].

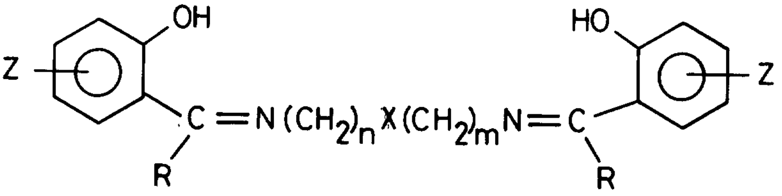
The stability constant for $[Mn(H_2O)_5Cl]^{2+}$ was calculated in $H[ClO_4]$ solution [55].

5.3.4 *Complexes with nitrogen-donor ligands*

Nearly all manganese(III) complexes are high-spin (^5E in O_h), the only known low-spin manganese(III) complex occurs with CN^- ligands $[Mn(CN)_6]^{3-}$, however for the ligand {tris[1-(2-azolyl)-2-azabuten-4-yl]amine} = trp the manganese(III) complex [Mn(trp)] uniquely shows a spin-crossover between 40 and 50 K ($^3E_g \rightleftharpoons {}^3T_{1g}$ in O_h symmetry). An X-ray crystal structure was obtained to give further information about the manganese environment [56].

5.3.5 *Schiff base complexes*

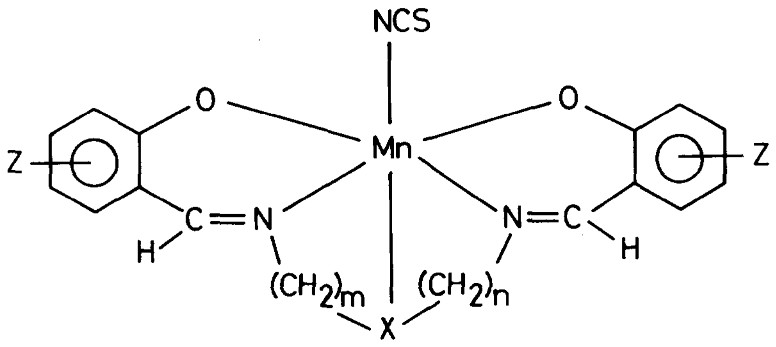
Manganese(III) complexes incorporating acyclic potentially pentadentate Schiff bases (*4*) were prepared from manganese(II) precursors. The complexes prepared were $[Mn(5\text{-}NO_2SALEPT)NCS].\frac{1}{2}H_2O$, $[Mn(3\text{-}NO_2SALEPT)NCS].\frac{1}{2}H_2O$, $[Mn(SALEPT)NCS].H_2O$, $[Mn(5\text{-}NO_2SALBPT)NCS]$, $[Mn(3\text{-}NO_2SALBPT)NCS].H_2O$, $[Mn(SALBPT)NCS].\frac{1}{2}H_2O$, $[Mn(5\text{-}CH_3OSALBPT)NCS].H_2O$, $[Mn(3\text{-}NO_2SALDAPE)NCS].2H_2O$ and $[Mn(SALDAPE)NCS]$ (*5*). These were characterised by magnetic susceptibility measurements, UV spectroscopy and conductivity measurements, and it was suggested that the manganese(III) is in a pseudooctahedral environment. Their reduction potentials as measured by cyclic voltammetry, were shown to depend on the aromatic ring substituent effect, and compared to the complexes formed by the potentially hexadentate ligands (*6*). The complexes prepared of these



(4;

R	*n*	*m*	*X*	*name*
H	*1*	*1*	-	*ZSALEN*
H	*2*	*2*	*N-H*	*ZSALDIEN*
H	*2*	*2*	*-S-*	*ZSALDAES*
H	*2*	*3*	*N-H*	*ZSALEPT*
H	*3*	*3*	*N-H*	*ZSALDPT*
H	*3*	*4*	*N-H*	*ZSALBPT*
H	*3*	*3*	*-O-*	*ZSALDAPE*
C_6H_5	*3*	*3*	*N-H*	*ZHBPDPT*

; Z = H, 3-NO_2*, 5-*NO_2 *or 5-MeO)*



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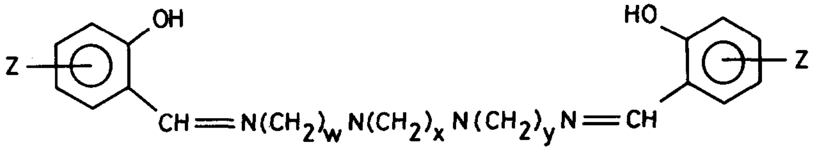
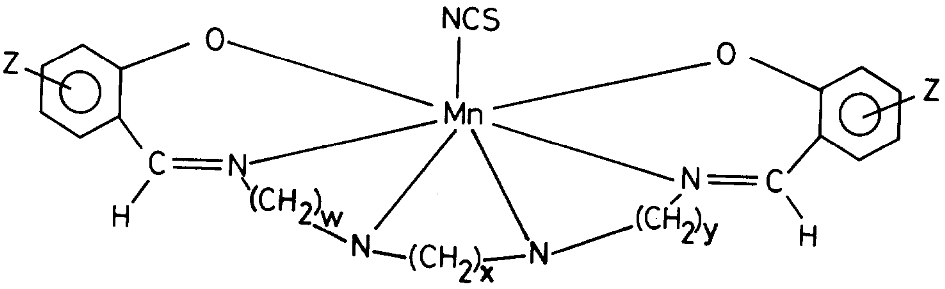


(6;	w	x	y	name	
	2	2	2	SAL-1,4,7,10	
	3	2	3	SAL-1,5,8,12	
	3	3	3	SAL-1,5,9,13	; Z = H or 5-NO_2)

ligands were [Mn(SAL-1,4,7,10)NCS], [Mn(SAL-1,5,8,12)NCS] and [Mn(SAL-1,5,9,13)NCS].½H_2O (*7*) [57]. For the complexes [Mn(ZSALDPT)NCS] {Z = H, 3-NO_2, 5-NO_2 or 5-CH_3O} it has been shown that the reduction potentials E_p correlate with the ^{13}C NMR chemical shifts of the ketonic carbon atom, as Z is varied [58]. In addition the manganese(III) complexes [Mn(SALDAES)NCS] and [Mn(5-NO_2SALDIEN)NCS] were prepared and their reaction with NO and O_2 in solution and in the solid state were studied [59]. Both the manganese(III) and manganese(II) complexes with donor sets of $\{O_2N_2P\}$ and $\{N_4P\}$ derived from substituted aldehydes and bis(3-amino-propyl)phenylphosphine (*8*) and (*9*) were synthesised [Mn(SALPhDAPP)NCS].H_2O, [Mn(5-CH_3OSALPhDAPP)NCS].½H_2O,



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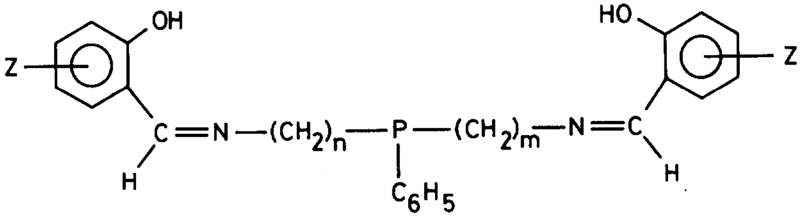
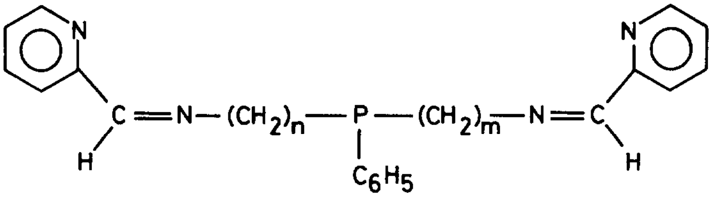


(8; ZSALPhDAPP; $n = m = 2$; $Z = H$, $5\text{-}NO_2$ or $5\text{-}MeO$)



(9; PYPhDAPP; $n = m = 2$)

$[Mn(5\text{-}NO_2SALPhDAPP)NCS].H_2O$ and $[Mn(PYPhDAPP)(NCS)_2].H_2O$. All complexes were high spin and pentacoordinate and their reactivity with NO and O_2 was discussed [60]. The Schiff base (H_2L) derived from N,N'-bis(3-aminopropyl)piperazine and salicylaldehyde, was found to give the complex $[MnL][ClO_4]$, on which the ligand is hexadentate [61]. The complexes $[Mn(L)]$ $\{H_3L = R\text{-}2\text{-}HOC_6H_3CH{=}NCH_2CH(OH)CH_2N{=}CHC_6H_3\text{-}2\text{-}OH\text{-}5\text{-}R;$ $R = H, Cl, Br, NO_2$ or $CH_3O\}$

were synthesised and shown to be dimeric with each manganese atom octahedrally coordinated [62].

5.3.6 Complexes with other nitrogen-oxygen donor ligands

The solid complexes $[Mn(L)(O_2CMe)]$ $\{H_2L$ = 2-HOC_6H_4CH=$NNHCO(CH_2)_nCONHN$=CHC_6H_4OH-2; n = 0, 1 or 2$\}$ were prepared and shown to be octahedral [63]. The complexes formed with 4-amino-3-(2-hydroxyphenyl)-1,2,4-triazoline-5-thione and 3-(2-hydroxyphenyl)-4-(2-hydroxybenzylideneamino)-1,2,4-triazoline-5-thione were prepared and characterised as six-coordinate pseudooctahedral complexes [64]. Other complexes prepared include $[Mn(tsc)_2(acac)]$, $[Mn(tsc)_2(py\text{-}2\text{-}COO)]$, $[Mn(tsc)_2(S_2CNEt_2)]$, $[Mn(acac)_2(py\text{-}2\text{-}COO)]$, $[Mn(acac)(py\text{-}2\text{-}COO)_2]$ $\{tsc = NH_2NHC(NH_2){=}S\}$ [65], $[Mn(3\text{-}O\text{-}quin)_3]$, $[Mn(3\text{-}O\text{-}quin)_2(OH)]$ and possibly $K[Mn(3\text{-}O\text{-}quin)_2(OH)_2]$ {3-HO-quin = 3-hydroxyquinoline} [66], and also the complexes of acrylamide and acrylic acid, which were studied spectrophotometrically [67].

5.4 MANGANESE(II)

5.4.1 Halides

5.4.1.1 Fluorides

The unit cell parameters and crystal structures of the rutile-type MnF_2 at high pressure were measured [68], and radiation defects in MnF_2 have been observed [69]. EPR spectroscopy has been used to estimate the Neél temperature for fine particles of MnF_2 [70] and the antiferromagnetic to paramagnetic transition in MnF_2 has been studied [71,72]. Moreover, the 180° antiferromagnetic domains in zero field conditions have been observed using neutron topography [73]. The magnetic properties of single crystals of $Mn_{1-x}Zn_xF_2$ have been investigated [74] and the stability constant of $[MnF]^+$ has been measured [75].

The cubic perovskite $K[MnF_3]$ was studied by high resolution elastic neutron diffraction [76] and absorption spectra from the inner 3p shell of the transition metal ion was measured using synchrotron radiation [77]. Magnetoacoustic solutions in $K[MnF_3]$ single crystals were observed in the NMR region [78]. The magnetic and structural phase transition in the vicinity of 186 K was measured for $K[MnF_3]$ and the temperature dependence of both the total and the elastic-inelastic neutron intensities observed [79,80,81]. The volumes of the structural domains (T = 186 K) were also determined by X-ray diffraction [82] and the transition from cubic to tetragonal phase was studied by ultrasonic techniques [83].

Using $[NH_3D]^+$ ion as an IR probe, it was shown that the perovskite $[NH_4][MnF_3]$ showed a low temperature transition from a cubic phase to one of lower symmetry [84]; by neutron diffraction studies this phase was shown to be tetragonal [85]. $[NH_4][MnF_3]$ was shown to react with XeF_6 (see section 5.2.1).

The boundary between the intermediate and spin-flop phases of $Rb[MnF_3]$ has been determined [86]. The interactions between non-equilibrium phonons and nuclear spin waves in $Cs[MnF_3]$ have been studied [87,88].

Point groups of the commensurate phase both below T_0 and T_N for $Ba[MnF_4]$ have been determined [89], the phase was studied by Raman spectroscopy [90]. The dynamics of the commensurate-incommensurate phase transition at 247 K has been reported [91]. Weak Bragg reflections from the (100) plane observed in large samples of $Ba[MnF_4]$ at 273 K suggest that the $A2_{1am}$ space group; which was assigned after studying small samples of $Ba[MnF_4]$, to be incorrect for large samples [92].

The complexes $Mn[InF_5].nH_2O$ (n = 6, 5 or 0) were prepared from $InF_3.H_2O$ and $MnCO_3$ in dilute hydrofluoric acid; TGA studies were performed [93]. The polarised absorption spectra of single crystals of $Mn[SiF_6].6H_2O$ were recorded; there were marked differences between the spectra at 298 K and 80 K [94]. The entropy of transition associated with changes in H-bonding between the water molecules and the fluorine atoms was measured [95].

Several mixed metal fluorides have been prepared containing manganese(II). It was found $NaMnCrF_6$ that the magnetic sub-lattices ordered below 21 K [96]. Evidence of a spin-glass transition in the vitreous insulating fluorides $PbMnFeF_7$ and Pb_2MnFeF_9 have been observed [97], and in the former case the remanent magnetisation and anisotropic susceptibility were determined [98].

5.4.1.2 Chlorides

Using a simple model, a theoretical fit of the lattice dynamics of $MnCl_2$ was obtained [99]. For the system $HCl + MnCl_2 + H_2O$ at various temperatures it was shown that Harned's rule does not hold for $MnCl_2$ at most ionic strengths [100]. The diffusion coefficient and the activation energy of diffusion for aqueous solutions of $MnCl_2$ have been determined [101].

The reaction of $MnCl_2$ with papaverine hydrochloride has been reported [102], and the thermodynamics of the $MnCl_2/CoCl_2$ and $MnCl_2/AgCl$ systems have been studied [103,104]. The temperature dependence of the vapour pressure of the $MnCl_2/DyCl_3$ system has been determined [105], as have the antiferromagnetic resonances in $MnCl_2$ and the EPR line widths in aqueous polyethylene glycol over a range of temperatures (T = 77-453 K) [106,107]. Experiments were carried out on 4.3 mol dm^{-3} MCl_2 (M = Ni or Mn) D_2O solutions, to test the method of isomorphic substitution [108]. In addition a detailed study of the spin-flop-transition in $MnCl_2.4D_2O$ was carried out by neutron diffraction [109], and the Neél temperature of $Mn(Br_{1-x}Cl_x)_2.4H_2O$ was measured [110].

The complex $[Me_4N][MnCl_3]$ has been studied extensively because it is a *quasi*-one-dimensional antiferromagnet. Proton-spin lattice relaxation rates were compared with theoretical values [111], and measured over a wide range of temperatures (T = 20-300 K) [112]. In addition, its EPR width has been studied over a range of temperatures and orientations [113], and the breather contributions to the dynamical form factors of the sine-Gordon systems measured [114]. The electronic absorption spectra of single crystals of $[(CH_3)_3NH][MnCl_3].2H_2O$ was observed and the crystal field parameters evaluated [115]. The structures of $[CH_3NH_3][MnCl_3].2H_2O$ and $[(CH_3)_2NH_2][MnCl_3].2H_2O$ were determined by X-ray diffraction. Both salts were found to contain the *cis*-$[MnCl_4(H_2O)_2]$ unit [116,117]. Proton spin-lattice relaxation rates were measured for cadmium-doped $[Me_4N][MnCl_3]$ and EPR measurements were performed on copper-doped $[Me_4N][MnCl_3]$ [118,119].

The structure of $Na[MnCl_3]$ was determined by neutron diffraction [120] and an antiferromagnetic-paramagnetic transition was observed at low temperature (6.5 K) under high magnetic fields [121]. The ferroelastic domain structure of $Rb[MnCl_3]$ was reported [122], as was the rapid exciton migration in the crystals of the infinite chain salts $Cs[MnX_3].2H_2O$ {X = Cl or Br}, which indicated that $Cs[MnCl_3].2H_2O$ was not strictly one-dimensional [123]. A neutron diffraction study on cobalt-doped $Cs[MnCl_3].2D_2O$ was performed and T_N determined [124].

The magnetic resonances in $[CH_3NH_2]_2[MnCl_4]$ in the antiferromagnetic and spin-flop regions were reported [125]. The elastic mode in the layer material $[CH_3NH_3]_2[MnCl_4]$ was measured [126] and the zero field splitting parameter D of the $^6S_{5/2}$ ground state of Mn^{2+} ions in chloride ion environments was discussed [127]. The thermal decomposition of $[MeNH_3]_2[MnCl_4]$ has been observed [128].

The incommensurate-commensurate phase transition of $[Me_4N]_2[MnCl_4]$ has been studied by X-ray diffraction; the incommensurate phase was found to be monoclinic and ferroelastic [129]. The complex $[(NH_3CH_2CH_2)_2NH_2][MnCl_4]Cl$ was prepared and its crystal structure determined [130]. The average structure of $[C_3H_7NH_3]_2[MnCl_4]$ was determined and a superspace group was also assigned [131]. The thermal behaviour of long chain *N*-alkylammonium tetrachloromagonate salts has been investigated [132]; in particular data was obtained calorimetrically [133]. Bis(tryptaminium) and bis(diphenylbutylammonium) tetrachloromanganate(II) salts were prepared as examples of two-dimensional antiferromagnets, and their electronic spectra were recorded (T = 10-290 K) [134]. Raman and resonance Raman spectra of $[C_5H_7S_2]_2[MnCl_4]$ were measured. The visible band which gives rise to the intense colour of the complex was assigned as a anion → cation sulphur-metal charge-transfer transition [135].

Complex ion formation in the ionic melts $2MCl.MnCl_2$ {M = Li, Na, K, Rb or Cs} have been summarised [136]. The symmetries of the Raman active modes of the suzuki phase in the system $6NaCl{:}MnCl_2$ were calculated [137]. The polarised electronic absorption spectra of $Rb_2[MnCl_4]$ single crystals down to 77 K was recorded and the manganese(II) ion shown to be in an octahedral environment [138]. The temperature dependence of the linear birefringence of light has been studied [139].

Single crystals of the incongruent melting materials $K_3[Mn_2Cl_7]$, $K_4[MnCl_6]$ and $Cs[Mn_4Cl_9]$ were grown and characterised [140]. The use of trioctylmethylammonium chloride as a means of extracting Mn^{2+} ions from hydrochloric acid solution was investigated [141].

5.4.1.3 Bromides

Information about the pair distribution function and exchange dynamics of MnX_2 {X = Cl, Br or $[BF_4]$} were obtained [142]. He-I and He-II PES were observed for MnX_2 {X = F, Br and I} and interpreted in terms of both *ab initio* M.O. calculation and intensity differences between spectra recorded with He-I and He-II radiation [143].

The structure of $Li_2[MnBr_4]$ was found to be cubic at 673 K and tetragonal at 298 K [144]. Ligand field parameters were calculated for the $[MnBr_4]^{2-}$ ion and compared to experimental data [145], and the formation constants for a range of manganese(II) halide complexes of Cl, Br and I have been evaluated [146]. The trigonal distortions of the $[MnX_6]^{4-}$ {X = Br or Cl} octahedra in some MnX_2 layer compounds were evaluated [147].

5.4.1.4 Iodides

Neutron powder diffraction and magnetic susceptibility and magnetisation measurements on single crystals of $Cs[MnI_3]$ indicated three-dimensional ordering takes place at T = 11.1(3) K [148]. The ligand field parameters for the $[MnI_4]^{2-}$ ion were calculated, and compared to experimental data [145].

The hydration numbers of manganese(II) as a function of the anion concentration {I^-, Br^-, ClO_4^- or SO_4^{2-}} has been measured by NMR spectroscopy [149].

5.4.2 Oxides, sulphides, selenides and tellurides

5.4.2.1 Oxides

MnO was shown to have a face-centred cubic crystalline structure above $T_N \sim 110$ K. At T_N an antiferromagnetic ordering takes place and this was studied in terms of the magnetoelastic coupling [150]. In very pure crystals of MnO the temperature dependence (T = 4.2-300 K) of the principal magnetic susceptibilities $\chi_{\parallel}$ and $\chi_{\perp}$ was observed [151]. The anomaly in the elastic constant of MnO near 43 K has been assigned to the presence of the Mn_3O_4 phase [152]. The effect of non-stoicheiometry on the magnetic properties of MnO was studied and this also revealed the presence of the Mn_3O_4 phase [153]. A variety of non-stoicheiometric manganese monoxides, and the probable separation of the phase diagram into two principal areas, was observed [154]. The elasticity constant of single crystals of MnO was reported [155] and sulphurization of MnO to MnS was studied [156]. A non-equilibrium thermodynamic model for the precipitation and oxidation of naturally occurring manganese oxyhydroxides was proposed [157].

Several two-component phase systems have been studied; ^{11}B NMR was used to investigate the paramagnetic MnO/B_2O_3 system [158]. The study of the MnO/SiO_2 system at various temperatures (T = 1673, 1773 and 1873 K) indicated the stability of SiO_2 in MnO/SiO_2 melts was a function of oxygen pressure [159]. The antiferromagnetic solid solution of MnO/CoO was studied thermomagnetically and the Neél temperatures were determined [160]. The interaction of As_2O_5 with MnO was studied thermographically [161]. The system $GeO_2/MnO/Mn_2O_3$ was studied at 1173 K and was found to behave similarly to that of the $SiO_2/MnO/Mn_2O_3$ but quite differently from $GeO_2/FeO/Fe_2O_3$ system [162].

Several mixed metal oxides containing manganese(II) ions have been observed. Four complex oxides $Ca_2Mn_3O_8$, $CaMn_3O_6$, $CaMn_4O_8$ and $CaMn_7O_{12}$ were prepared using a low temperature route [163]. The preferential of α-TiO_2 needles in crystals of $Mn[TiO_3]$ was studied [164]. A convenient method of preparation of the spinel $MnFe_2O_4$ was discovered [165] and $(Mn,Zn)Fe_2O_4$ was also prepared [166]. The complex oxide La_2TiMnO_6 was prepared by a solid state reaction and analysed by X-ray crystallography [167]. The manganese(II) ions in the A- and Y-type erionite zeolites exist in a coordinatively unsaturated state under specific conditions and are surrounded by three oxygen atoms of the zeolite crystal lattice [168]. $[MnPbO_3].xH_2O$ was prepared, and the perovskite phase was found to be orthorhombic [169].

The oxide pnictides $Ba_2Mn_2Sb_2O$ and $Ba_2Mn_2Bi_2O$ have been reported and their structures determined [170].

The preparation of $Na_{10}[MnW_6O_{24}].28H_2O$ has been described [171] and an X-ray diffraction study of $[Mn(H_2O)SiMo_{11}O_{39}]^{n-}$ showed it to be similar to other heteropolytungstates and heteropolymolybdates [172]. The spherulitic products of manganese(II) ions and $[CrO_4]^{2-}$ ions have also been studied [173].

5.4.2.2 *Sulphides, selenides and tellurides*

The effect of antiferromagnetic ordering on the optical absorption edge in α-MnS was studied theoretically and experimentally [174]. The phase transition of β-MnS was found to be first order [175]. The free energy of formation of MnS was determined as -218.85±0.88 kJ mol^{-1} by electrochemical measurements [176]. The far-IR reflectance spectra of the pyrites type compounds MnS_2, $MnSe_2$ and $MnTe_2$ were determined [177], and the physical properties of α-Mn_xS sulphide magnetic semi-conductors were measured [178].

The solid solution in the systems $(Mn,Mg)Gd_2S_4$ and $(Mn,Mg)Yb_2S_4$ were found to have the cubic Th_3P_4 and cubic spinel structures respectively; all materials were paramagnetic above 77 K [179]. The vaporization reactions of $MnGa_2S_4(s)$ and $Mn_3Ga_2S_6(s)$ were established to be:

$$3/2MnGa_2S_4(s) = \tfrac{1}{2}Mn_3Ga_2S_6(s) + Ga_2S(s) + S_2(g)$$
$$Mn_3Ga_2S_6(s) = 3MnS(s) + Ga_2S(g) + S_2(g) \quad (T = 1150\text{-}1315\ K)$$

[180]. The α and β phases of $MnGa_2S_4$ have been prepared and characterised. Both were antiferromagnetic with T_N at 23.5 K and 11 K, respectively [181]. The magnetic structure of $MnCr_2S_4$ at high magnetic fields cannot be fully described by magnetisation or by neutron diffraction [182]. The mixed metal sulphide $(Mn,Fe)S_2$ was investigated by analytical electron microscopy and Mössbauer spectroscopy [183].

5.4.3 *Sulphates, selenates, carbonates, nitrates and phosphates*

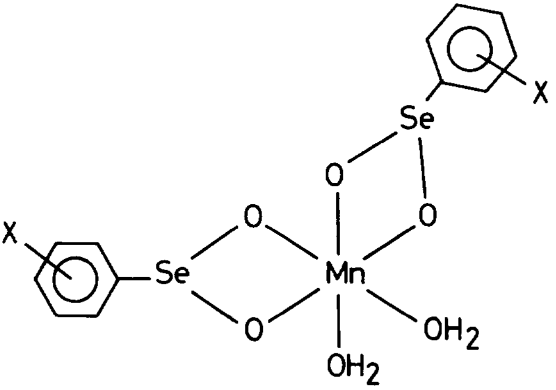
5.4.3.1 *Sulphates and selenates*

The exchange interactions in α-$MnSO_4$ was studied [184]. The effect on the line widths of the EPR spectra of $MnSO_4.nH_2O$ (n = 5, 4, 1 or 0) with decreasing water of crystallisation was studied [185] and the ^1H NMR spectra of the protons of the water of crystallisation in $MnSO_4.H_2O$ were also reported [186].

A mechanism for the oxidation of DL-proline by $MnSO_4$ has been proposed [187] and the rate equation for the auto-oxidation of SO_2 in aqueous $MnSO_4$ was determined [188]. The reduction mechanism of $MnSO_4$ to Mn on a Hg electrode was investigated by chronopotentiometry [189]. $MnSO_4$ was formed by the decomposition of $[Mn(N_2H_5)_2][SO_4]_2$ [190].

The shape and extended fine structure of the manganese K-absorption (EXAFS) discontinuity in the octahedral complexes $MnSO_4.H_2O$, $MnCl_2.4H_2O$, $MnC_2O_4.2H_2O$ and α-MnS were determined [191]. The angular and temperature dependences of the second moment of single crystals of $[NH_4]_2SO_4.MnSO_4$ were measured [192], and a new double salt $[NH_4]_2SO_4.2MnSO_4$ has been reported [193].

Complexes of the 3- and 4-substituted benzeneseleninic acids $XC_6H_4SeO_2H$ {X = H, 3-Cl, 4-Cl, 3-Br, 4-Br or 4-Me} have been reported and characterised; IR spectra suggest that the complex contains a bidentate seleninato-*O,O'* ligand, and possesses distorted octahedral geometry (*10*) [194]. In addition, the selenate(IV) complexes $Na_2[Mn(SeO_3)_2(H_2O)]$ and $K_2[Mn_2(Se_2O_5)_3(H_2O)_3]$ have been prepared and characterised [195].



(10; X = H, 4-Cl, 4-Br, 4-Me, 3-Cl or 3-Br)

5.4.3.2 Carbonates

Dense $MnCO_3$ was made by the decomposition of manganese(II) ammonium carbamate [196]. The stepwise stability constants, 11 and 3.7 were calculated for $[Mn(HCO_3)]^+$ and $[Mn(HCO_3)_2]$, respectively [197].

5.4.3.3 Nitrates

The mechanism and kinetics of the thermal decomposition of hydrated $Mn(NO_3)_2$ under air, N_2 and vacuum and anhydrous $Mn(NO_3)_2$ under air and vacuum have been investigated. Mechanisms and activation energies have been proposed [198-202]. A *N,N*-diethylacetamide/water solution of $Mn(NO_3)_2$ was investigated by EPR spectroscopy and three ionic species were detected: (i) Mn^{2+} with mixed dea, H_2O solvation, (ii) dea solvated ions (loose ion pairs), (iii) (tight ion pair) species. (ii) and (iii) are not well defined "chemical" species [203].

The solubility diagrams of the $Mn(NO_3)_2/Co(NO_3)_2/H_2O$ and $Mn(NO_3)_2/Ni(NO_3)_2/H_2O$ systems were determined [204], also the solid system $[Er(NO_3)_2 + Mn(NO_3)_2]/M[C_2O_4]$ {M = K or NH_4}/water was studied [205].

5.4.3.4 Phosphates

It was found that $[Mn(NH_4)][P_2O_7]$ decomposes, according to a redox reaction, to $Mn_2[P_2O_7]$ [206].

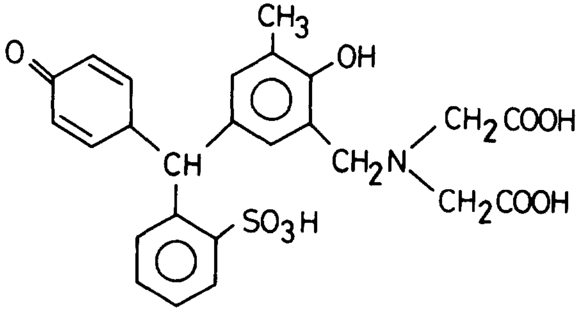
5.4.4 Carboxylates

The kinetic and thermodynamic characteristics of the dehydration of $Mn(O_2CMe)_2.4H_2O$ were determined [207]. The IR spectra of $Mn(O_2CMe)_2.nH_2O$ $(0 \leqslant n \leqslant 4)$ were recorded and vibrational bands due to H_2O assigned [208]. $(Mg_xMn_{1-x})(O_2CMe)_2.4H_2O$ was studied by X-ray diffraction, DTGA and IR spectroscopy; some Mn-doped species $(Mn_xCo_{1-x})(O_2CMe)_2.4H_2O$ and $(Mn_xNi_{1-x})(O_2CMe)_2.4H_2O$ were also investigated [209].

The complexes of the alkanedicarboxylic acids of formula $HO_2C(CH_2)_nCO_2H$ $\{1 \leqslant n \leqslant 7\}$ have been prepared [210]. The extraction of manganese(II) ions by long-chain alkylammonium carboxylates has been studied, and found to be a poor method [211]. The manganese(II) complex of 3,4-dihydroxybenzoic acid was studied by EPR in alkaline solution [212]. The complex $MnL.nH_2O$ $\{H_2L$ = acid; $n = 1$ or $4\}$ was prepared and its solubility measured [213].

The complex MnL_2 {HL = 3,5-dinitrosalicyclic acid} was prepared and screened for antifugal and antibacterial properties [214]. The complex $[Mn(salH)_2(H_2O)_2]$ has also been prepared, and preliminary X-ray data presented [215].

Potentiometric and spectrophotometric investigations of the potentially tetradentate ligand semi-xylenol orange *(11)* $\{H_4sxo\}$ have been reported, and the formation constant was measured [216]. The complex $Ca[Mn(edta)].nH_2O$ was characterised by IR and X-ray diffraction and the complexes $MnCo(edta).6H_2O$ and $MnNi(edta).6H_2O$ were also reported [217]. The ^1H NMR relaxation rates of water protons were measured in manganese(II)/edta solutions. Proton of water molecules hydrogen-bonded to coordinating carboxylate oxygen atoms contributed significantly

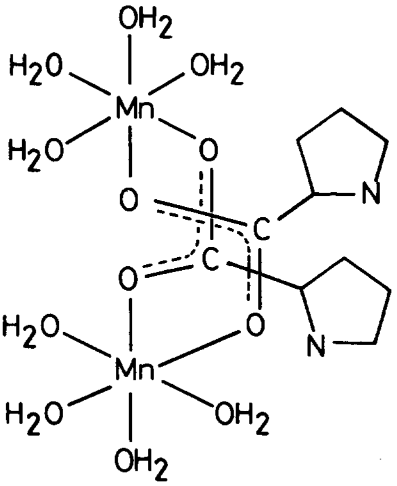


(11)

to overall relaxation rates. One water molecule was found to be directly bonded to the metal ion [218]. The solubility of manganese(II) ions in water after treating with fulvic acid was determined [219].

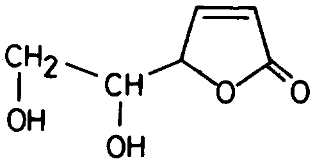
5.4.5 *Complexes with Group VIB donor ligands*

The high energy modification and crystal hydrates of Tutton's salt containing manganese(II) were prepared and their latent heats of solution measured [220]. The structure of (DL-proline)manganese(II) sulphate tetrahydrate $[(C_4H_9NCO_2)Mn(H_2O)_4][SO_4]$ was determined and found to be polymeric with the manganese atom exhibiting a distorted octahedral geometry (*12*) [221].



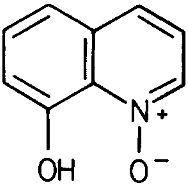
(*12*)

The effect of spin lattice relaxation times of the ^{13}C nuclei in ascorbic acid (*13*) when complexed with manganese(II) was measured, and the coordination sites determined [222].



(*13*)

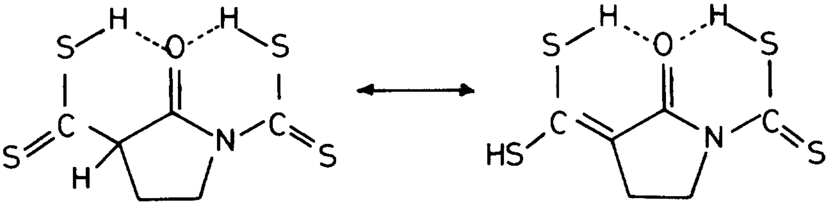
The complex $[Mn(nap)_3][SbCl_6]_2$ {nap = *N*-acetylpyrrolidinone}, in which nap is bidentate, was shown to contain Mn^{2+} in a regular octahedral environment [223]. The complex $[Mn(quin\text{-}8\text{-}OH\text{-}N\text{-}O)_4(H_2O)_2][ClO_4]_2.2H_2O$ {quin-8-OH-*N*-O = 8-hydroxyquinoline *N*-oxide} (*14*) was prepared and characterised as hexacoordinated, containing $\{MnO_6\}$ moieties (*i.e.* four-phenolic oxygen-bonded unidentate quin-8-OH-*N*-O ligands and two water ligands [224]. The complex of β-alanine, $[Mn_3(\beta\text{-}ala)_8][ClO_4]_6.2H_2O$, was prepared and characterised. The molecules of β-alanine link infinite, almost linear, chains of manganese atoms by *syn,syn* and *syn,anti* carboxyl bridges, one molecule of β-alanine being tridentate [225]. The normal vibrations of the manganese(II) complex of malonic acid diamide were reported [226].



(*14*)

The stability constants of the complexes formed with L-adrenaline and noradrenaline systems were determined pH-metrically over a pH range of 5 to 11, and it was shown that in the presence of an excess of ligand only *ortho*-phenolic hydroxy groups participate in coordination [227]. The stability and stoicheiometry of adrenaline (A) complexes were determined from 1:6 to 1:1 ratio of Mn:A and the titration curves were explained by assuming that complexes of the type MnAH, MnA, MnA_2H_2, MnA_2H and MnA_2 were present [228].

The binuclear complex $[Mn(pdt)_2]$ {H_2pdt = 2-pyrrolidone-1,3-bis(carbodithioic acid)} was prepared; the ligand H_2pdt exists in two tautomeric forms (*15*); magnetic susceptibility measurements indicate the presence of some metal-metal spin-coupling [229]. The 1:1 complex formed with manganese(II) and



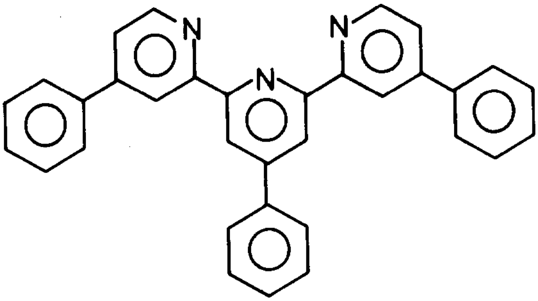
(*15*)

ethylenediamino(dithiocarbamate) was studied by IR spectroscopy and X-ray crystallography. Only the sulphur atoms were coordinated giving rise to a polymeric structure [230].

Complexes of manganese(II) with *cis,cis*-1,3,5-trihydroxycyclohexane [231], 2,3-dihydroxynaphthalene [232], 3,5-dichloro-2-hydroxyacetophenone [233], 1,1,1,5,5,5-hexafluoro-2,4-pentadione [234], mono(hydroxyethyl)phthalate [235], dibenzoylmethanate [236] and 5-hydroxy-2-methyl-1,4-naphthoquinone [237] have also been reported. The complexes of manganese(II) with dichlorophosphates have also been reported [239].

5.4.6 Complexes with nitrogen donor ligands

The tendency for manganese(II) to form complexes with pyrazole and substituted pyrazoles was investigated using polarographic methods and the coordination numbers and stability constants of the complexes formed were determined [238]. The voltammetric behaviour of the complexes [Mn(terosite)$_2$] {terosite = 2,6-bis(4-phenyl-2-pyridyl)-4-phenylpyridine (*16*)} have been studied in ethanenitrile using DC and AC polarography and cyclic voltammetry. The complex undergoes two one-electron reductions to the +1 and 0 oxidation states respectively, and a poorly defined one-electron oxidation to the +3 oxidation state [240]. The manganese(II) azide system was studied potentiometrically using a glass electrode, and the stability constants were calculated [241].

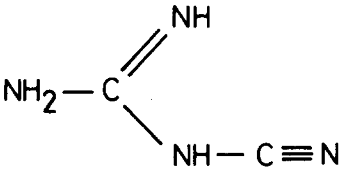


(16)

The structure of the complex *cis*-[Mn(bipy)$_2$(SCN)$_2$] was determined by X-ray diffraction. The observed distortion from octahedral symmetry being due to the bite angle of approximately 75.5° of the two bipyridine ligands [242]. The absolute configuration and axial rotational strengths of [Mn(en)$_3$][NO$_3$]$_2$ were determined using single crystal doping techniques [243].

Heat capacity measurements of $[Mn(trz)_2(NCS)_2]$ {trz = 1,2,4-triazole} were taken in the range 1-90 K; a λ-anomaly was found at T_c = 3.292 K. Recent X-ray data show the space group of this compound to be *Pcbn*, not *Aba*2 as previously reported [244].

The complexes $[MnL_2Cl_2]$ and $[MnL_2X_4]$ {X = Br, NCS or NO_3} and $[MnL_4][ClO_4]_2$ {L = (*17*)} have been prepared and characterised [245]. The complex $[MnL'_2Cl_2]$ {L' = (*18*)} was formed from the 2:1 addition of (*18*) to $MnCl_2$ [246].



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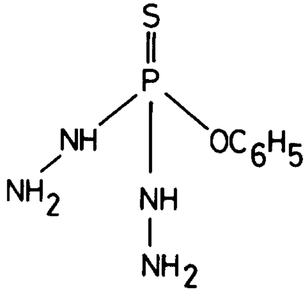
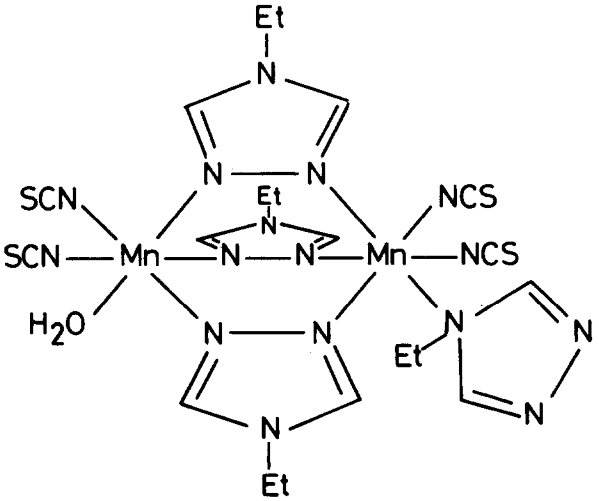


(*18*)

The complex of empirical formula $[Mn(Ettrz)_2(NCS)_2(H_2O)_{3/2}]$ {Ettrz = 4-ethyl-1,2,4-triazole} has been identified and characterised as a dimer containing both η^2-bridging and η^1-non-bridging triazole ligands. The structure deduced from IR spectroscopy, and magnetic susceptibility, DTA and DTGA measurements is shown in (*19*) [247].



(*19*)

[Mn(ap$_2$ac)$_2$X$_2$] {ap$_2$ac = RN=CMeCH$_2$MeC=NR, R = 2-pyridyl} have been reported and were found to have a distorted octahedral geometry, coordinating through the azomethine atoms, not through the pyridine group [248].

Other complexes with nitrogen-donor ligands that have been studied include [MnL] and [Mn(HL)$_2$] {H$_2$L = 1,4-quinone and dioxime} [249], [MnL] {H$_2$L = H$_2$NC(O)N=NC(O)NH$_2$} [250] [MnL$_4$Cl$_2$] {L = acrylamide} [251] and [MnL$_6$]X$_2$ {L = *tert*-butylurea; X = [ClO$_4$] or [NO$_3$]} [252]. Complex formation between manganese(II) and triethylenetetramine [253], hmpa [254], 1,4-diaminobenzene [255], aminopyridines [256], 4-methylpyridine [257], 1,2,3-benzotriazole [258], pyridine [259], hydrazodicarbonimide [260] and 4-butyl-4H-1,2,4-triazole [261], have been studied, as have the mixed ligand complexes formed between manganese(II) and bipy as the primary ligand, with several purine derivatives as secondary ligands {adenine, hypoxanthine, xanthine, guanosine and xanthosine} [262].

5.4.7 Schiff base complexes

The following Schiff base complexes involving the pentadentate ligands (*4*) (Section 5.3.5) have been prepared and characterised; [Mn(SALDIEN)], [Mn(5-NO$_2$SALDIEN)(H$_2$O)], [Mn(SALDAES)(H$_2$O)], [Mn(3-NO$_2$SALDAPE)(H$_2$O)], [Mn(SALEPT)], [Mn(5-NO$_2$SALEPT)], [Mn(5-NO$_2$SALBPT)], [Mn(NAPDPT)] and [Mn(HBPDPT)].½H$_2$O. Reactions with NO and O$_2$ in solution and solid state were studied, and subtle differences in reactivity noted [59]. The complex [Mn(dss)(H$_2$O)] {H$_2$dss = 2,3-dinitrilo-*cis*-2-butene-2,3-diiminomethyl)di-2-phenol} was prepared by a template reaction of a solution of MnX$_2$ (X = Cl, Br or I), diaminomaleonitrile and salicylaldehyde in a ratio of 1:1:2 [263].

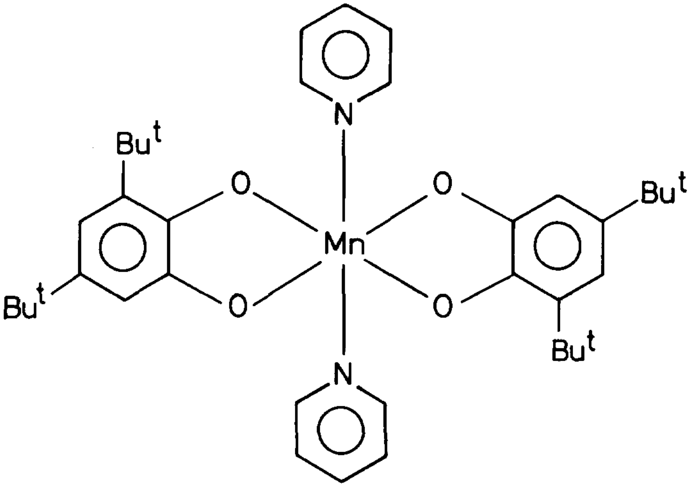
The manganese(II) complexes of the Schiff bases made from sulphaphurazole, sulphamethoxypyridazine or sulphaphenazole with 2-hydroxy-5-methylacetophenone or 2-hydroxy-5-chloro-acetophenone have been reported [264], as have the complexes MnL$_2$.2H$_2$O {L = furfurylidene benzoyl hydrazine or 5-nitrofurfurylidene benzoyl hydrazine} [265] and the polychelate prepared from the Schiff base formed from 5,5'-methylene-bis-salicylaldehyde and aniline [266].

The tetrahedral complexes [MnQ].H$_2$O {Q = L or L'; H$_2$L = Methyl-β-(2-hydroxy-1-naphthylmethylene)dithiocarbazate and H$_2$L' = Methyl-β-[1-(5-bromo-2-hydroxyphenyl)ethylidene]dithiocarbazate} have been prepared [267].

5.4.8 Complexes with mixed-donor ligands

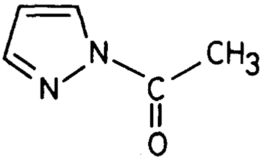
Irradiation of [Mn$_2$(CO)$_{10}$] and 3,5-di-*tert*-butyl-1,2-benzoquinone in toluene gave the complex [Mn$_4${O$_2$C$_6$H$_2$(CMe$_3$)$_2$}$_8$], while in pyridine the complex

$[Mn\{O_2C_6H_2(CMe_3)_2\}(py)_2].2py$ was obtained. The former complex is a centrosymmetric tetramer with the bond lengths suggesting a manganese(II) semiquinone formulation. The latter complex exists as a monomer (*20*) [268].



(*20*)

The crystal structure of $[MnL_2(H_2O)_2]_n$ {HL = 4-amino-3,5,6-trichloropicolinic acid} was determined [269]. The complex $[Mn(acpzl)_3][BF_4]_2$ {acpzl = *N*-acetyl pyrazole (*21*)} has been characterised by IR and NMR measurements and the ligand found to be bonded in its enol form (*22*) [270]. The complex $[Mn(H_2L)(H_2O)_2]Cl_2$



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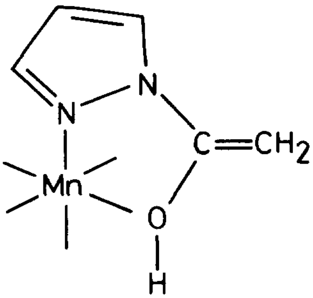
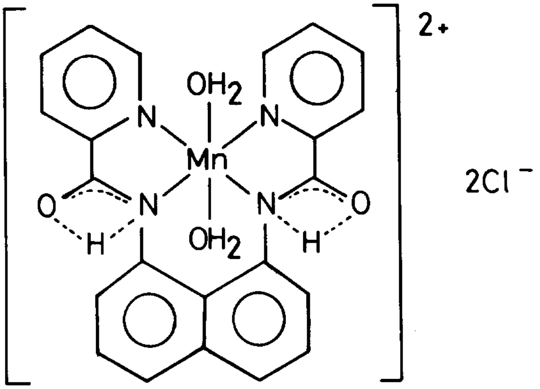


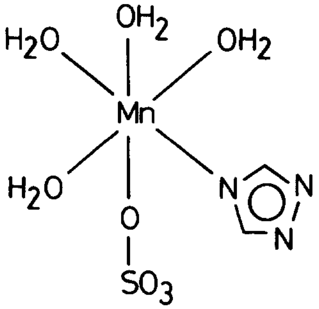
(*22*)

{H_2L = *N*,*N*'-(dipicolyl)-1,8-diaminonaphthalene} was prepared, the ligand was thought to be tetradentate, giving rise to a distorted octahedral geometry around the manganese atom; a structure, (*23*), was proposed [271].



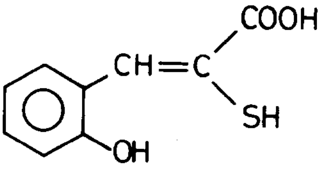
(23)

The complexes $[MnL_3](picrate)_2$, $[MnL_2(H_2O)_2](picrate)_2$ {L = bipy or phen} and $[MnL'_4(H_2O)_2](picrate)_2$ {L' = py, 4-Mepy, quinoline or 2,6-Me_2py} have been prepared [272]. The structure of the complex $[Mn(trz)(H_2O)_4(SO_4)]$ {trz = 1,2,4-triazole} was determined by single crystal X-ray diffraction (*24*). An



(24)

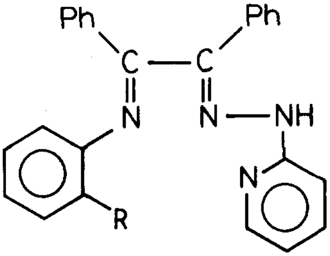
oxygen atom of the sulphate ion is coordinated [273]. The complex $[Mn(HL)_2]$ {H_2L = 3-(2-hydroxyphenyl)-2-mercaptopropenoic acid (*25*)} was prepared and was



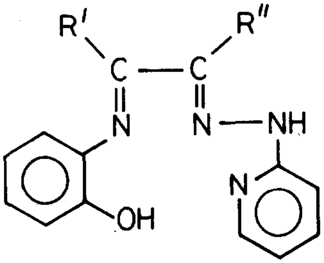
(25)

extracted readily into organic solvents [274]. The complexes [$MnL_2(H_2O)_2$] {HL = 2-(2-hydroxybenzylidone)amino-5-phenyl-1,3,4-oxadiazole} and [MnL_2X_2] {L = cytosine, X = Cl or Br}, [MnL_4]X_2.$2H_2O$ {L = cytosine, X = [ClO_4] or [NO_3]} have also been reported [275,276].

From the new ligands, (*26*) and (*27*), several new manganese(II) complexes

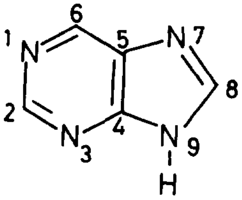


(*26; R = OH, NH$_2$, CO$_2$H, CHO, SH, SMe or AsMe$_2$*)



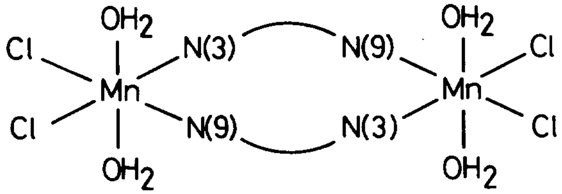
{*27; R′ = R″ = Ph,*
R′ = R″ = H,
R′ = R″ = Me,
R′ = Me, R″ = H,
R′ R″ = (CH$_2$)$_4$}

have been synthesised. Ligands (*27*), yielded on drying, dimeric complexes [$Mn_2L_2(H_2O)_4$] {H_2L = (*27*)}. Ligands (*26*) gave the complexes [$Mn(H_2L)(H_2O)$][ClO_4]$_2$ {H_2L = (*26*), except when R = OH since (*26*) ≡ (*27*); R′=R″=Ph}. In addition the complexes of empirical formula [MnL] were obtained from manganese(0) compounds with ligands (*26*). Magnetic moment measurements indicated that these complexes were probably dimeric, similar to the dimeric species above, but the bonding in these dimers appeared to be weaker. In all these complexes the ligands, (*26*) and (*27*), act as stable planar ligands [277]. The purine (*28*; purH) forms a complex [$Mn(purH)Cl_2(H_2O)_2$], the structure being



(*28; purH*)

postulated as either dimeric (*29*) or polymeric (*30*). (*28*) was favoured on the basis of magnetic moment measurements [278].



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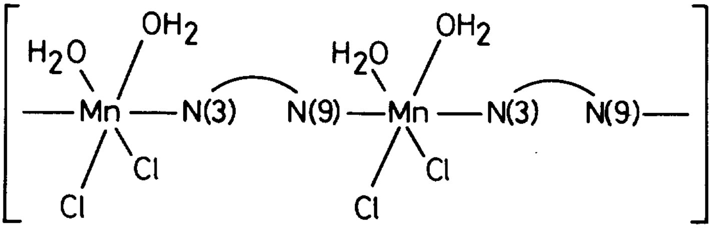

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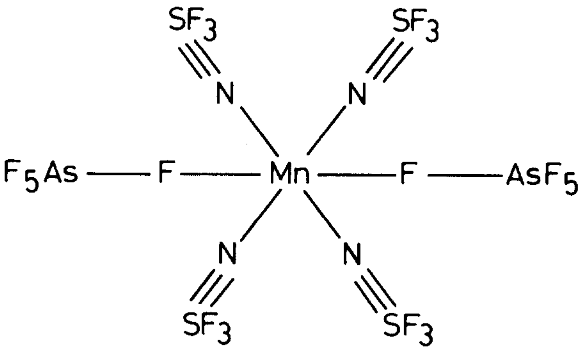
The complex [Mn(tpdtidp)$_2$] {tpdtidp = tetraphenyldithioimidophosphate} was prepared and the chelate rings were shown, by X-ray crystallography, to have nearly an S_4 axis of symmetry; thus it was possible to perform normal coordinate analyses on a 1:1 metal-ligand model possessing C_2 symmetry [279]. The magnetic susceptibility of [Mn(S$_2$CNEt$_2$)$_2$] was determined from 2-300 K, for a range of magnetic fields; the results were correlated with an intrachain antiferromagnetic exchange $J/K = -7.5$ [280].

The complex [Mn(N≡SF$_3$)$_4$(AsF$_6$)$_2$] contains an octahedral manganese atom with coordinated [AsF$_6$]$^-$ groups. The NS triple bond is one of the shortest observed between first and second row elements (*31*) [281].

Other complexes of manganese(II) reported this year include $A_2MnL_2.nH_2O$ and $BaMnL_2.5H_2O$ {H_2L = iminodiethanoic acid; A = Na, n = 7.5; A = Li, n = 4; A = K, n = 2} [282]. Complexes with the following ligands have been reported: tetracycline [283], DL-4,4'-dithiobis(2-aminobutyric acid) [284], 2-phenylamino-5-carboxymethylthio-1,3,4-thiadiazole [285], phenylhydrazine derivatives of pyridine carboxylic acids [286], isonicotinic acid [287], 8-hydroxyquinoline and halogen-substituted ethanoic acids [288], acacH and nicotinic acid [289], 4-benzoyloxime-3-methyl-1-phenyl-2-pyrazolin-5-one [290,291], 2-[4-amino-3-1-(1,2,4-triazolylazo)]naphthol-4-sulphonate [292], bipy, 4,4'-bipy and their dioxides [293], 2-aminoethanol [294], *N*-(5-phenyl-1,3,4-thiadiazol-2-yl)



(31)

benzamide and acetamide [295], 4-oximino-3-methyl-1-phenyl-2-pyrazolin-5-one, 4-oximino-3-methyl-2-pyrazolin-5-one, 4-oximino-3-phenyl-2-pyrazolin-5-one [296], 1-(2-pyridylazo)-2-naphthol [297], *N*-carbamoylpyrazole [298], phenoxyethanoic acid [299], pyridine-2-aldoxime, 6-methylpyridine-2-aldoxime [300], 4-amino-*N*-(5-ethyl-1,3,4-thiadiazol-2-yl)benzenesulphonamide [301], 2-aminonicotinic acid [302], *syn*-phenyl-2-pyridylketoxime, *syn*-methyl-2-pyridylketoxime [303], sulphathiazole [304], 2-hydroxy-1-naphthaldoxime [305], 2-hydroxynaphthalene-1-azo-2'-pyridine-*N*-oxide [307], α-benzoylmethylbenzylideniminobenzenesulphonic acid, 2-(α-benzoylmethylbenzylideniminо)ethanesulphonic acid [306], 4,4'-bis(3-formyl-4-hydroxyphenylazo(diphenylsulphone [307], methionine, glycine [308,309], hydrazodithioamide [310], 1,2-dimercaptoethane, β-dimercaptoethylamine, cysteine, 3,4-dimercaptotoluene, β-mercaptoethylalcohol, mercaptoethanoic acid [311], 3-bromo-2-hydroxy-5-methyl acetophenone, oxime and hydrazone [312], 2,6-diacetylpyridine salicyloylpicolinoyl hydrazones [313], 4-[(2-hydroxyphenyl)hydrazonol]-*N*-(benzylsulphonyl)-3-methyl-2-pyrazolin-5-one [314], *S*-trityl-L-cysteine [315], 2-hydrazinobenzimidazole [316], 1,3-di-4-piperidylpropane [317], salicylaldoxime, O-vanillin oxime [318], antipyrine, 4-aminoantipyrine pyramidone [319], cycloserine [320], alizarine, lumomagneson [321], cystine [322], 2-hydroxy-1-naphthaldoxime [323], 6-amino-2,4-hexadienoic acid [324], glycine [325], dithiooxamide [326], and ternary complexes of the ligands 2-methyl-8-quinolinol, 4-methyl-8-quinolinol and various heterocylic bases [327], bipy, tropolone and β-isopropyltropolone [328], 1,10-phenanthroline, 2,2'-bipyridine and 2-phenyl acetohydroxamic acid [329], 1-amino-2-naphthol-4-sulphonic acid and 2,2'-bipyridine, 1,10-phenanthroline, pyridine, 4-methylpyrroline and quinoline [330], glycine, alanine, β-alanine, phenylalanine and 2-phenylacetohydroxamic acid [331], folic acid, 7,8-dihydrofolic acid and glycine, alanine, serine, hystidine, phenylalanine [332], *N*-phenyl-*N*'-benzothiazol-2-yl thiocarbamide and 2-methylbenzimidazole [333], adenosine-5'-triphosphoric acid and 2,2'-bipyridyl [334], antipyrine, 4-aminoantipyrine and picramic acid [335].

5.5 CARBONYL COMPLEXES

5.5.1 Carbonyls and hydridocarbonyls

The photochemical reactions of $[Mn_2(CO)_{10}]$ with pyridine and 4-alkyl- and 3-halo-substituted pyridines, as neat solvents have been studied. The rate of conversion of $[Mn_2(CO)_{10}]$ to products was found to be increased slightly for 4-alkyl-substituted pyridines and decreased markedly for 3-chloro or 3-bromopyridines. The mechanism probably involves homolytic fission of the Mn-Mn bond to give the radical $[Mn(CO)_5]^\bullet$, which is then rapidly attacked by pyridine to give the radical $[Mn(CO)_3(py)_2]^\bullet$. Isolable species include $[Mn_2(CO)_9(py)]$, $[Mn(CO)_3(py)_3][Mn(CO)_5]$ and $[Mn(py)_6][Mn(CO)_5]_2$. The relative amount of ionic product was found to be slightly higher for alkyl-pyridines and markedly lower for the halogen-substituted compounds; supporting the proposed mechanism [336]. Hexane solutions of $[Mn_2(CO)_{10}]$ were subjected to flash photolysis under an atmosphere of CO, and the recombination of radicals was observed to obey a simple bimolecular rate law in non-degassed solvents, but far more complex kinetics were observed in thoroughly degassed solvents [337]. The radical $[Mn(CO)_5]^\bullet$ was generated by the UV photolysis of $[Mn_2(CO)_{10}]$ in a solid CO matrix, ^{13}CO enrichment and IR spectroscopy indicate the radical to have a square pyramidal C_{4v} geometry [338].

The crystal structure of $[Mn_2(CO)_{10}]$ was redetermined [339], and the Mn-Mn bond length was found to be 0.29038(6) nm, as compared to 0.2923(3) nm previously reported [340]. A solid state phase transition was discovered (*ca.* 8 Kbar) for $[Mn_2(CO)_{10}]$ consistent with a change in molecular geometry from staggered (D_{4d}) to eclipsed (D_{4h}) [341].

In the presence of Bu_3PO, exchange of CO in $[Mn_2(CO)_{10}]$ was achieved at 348 K, and was used for ^{13}CO incorporation [342].

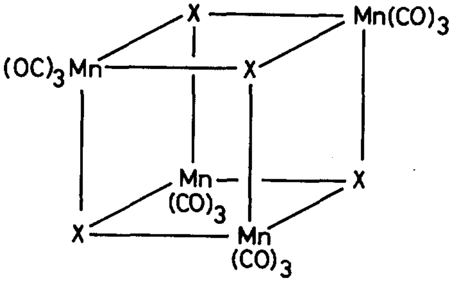
The electronic and physical properties of $[Mn_2(CO)_{10}]$ have been calculated by LCAO-Hartree-Fock-Slater method with a double-zeta STO basis [343]; it should be noted that the Mn-Mn bond length used in these calculations was old value [340], not the recently redetermined value [339]. Multiphoton dissociation of $[Mn_2(CO)_{10}]$, followed by multiphoton ionization of the fragments, was achieved using a tunable pulsed-dye laser [344]. ^{17}O NMR spectra of manganese carbonyls were recorded, and the linewidths achieved found to be narrower than for ^{13}C NMR spectroscopy, in some derivatives [345].

$[Mn_2(CO)_{10}]$ was used to obtain manganese(II) complexes of the ligand (*26*) (Section 5.4.8) [277].

$[HMn(CO)_5]$ was subjected to electron impact; the $[MnH]^+$ ion was formed, and its base strength assessed using ion-cyclotron resonance [346].

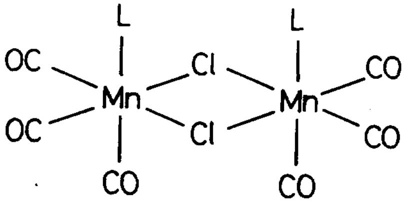
5.5.2 Halides

Reaction of $[Mn(CO)_5X]$ {X = Cl or Br} with TlF of AgF in CH_2Cl_2 gave the cluster $[Mn_4(CO)_{12}F_x(CO)_{4-x}]$ {for TlF, x = 1 or 2; AgF, x = 2 or 3}. The structures which are isomorphous are shown in (*32*). The OH groups result from the reactants containing small amounts of water, and as would be expected, rigorously drying the reactants results in an increase in x [347].



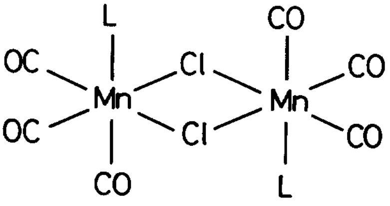
(32; X = F or OH)

The complex of empirical formula $\{MnCl(CO)_3(thf)\}$ was shown to be dimeric by X-ray diffraction, with a C_{2h} structure (*33*) *not* a C_{2v} structure (*34*) [348].



(33; C_{2h}; L = thf)

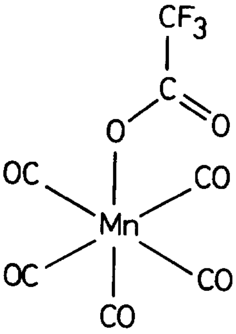
The ion $[Mn(CO)_5Cl]^-$ was observed by EPR spectroscopy in $[Cr(CO)_6]$ [349].



(34; C_{2v}; L = thf)

5.5.3 *Complexes with oxygen donor ligands*

The complexes $[Mn(CO)_5(O_2CCF_3)]$ and $[Mn(CO)_3(py)_2(O_2CCF_3)]$ were prepared and characterised by X-ray diffraction, *(35)* and *(36)*, and the effect that the



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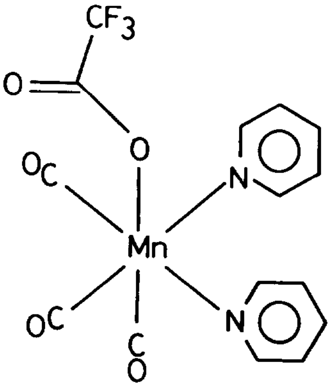
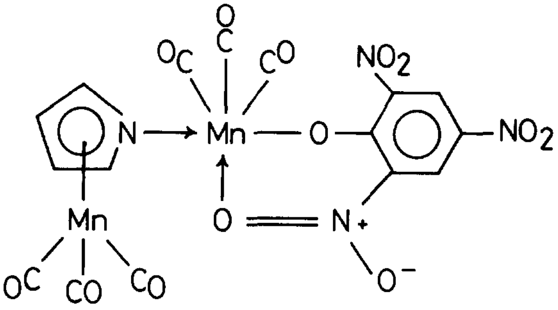


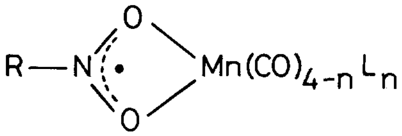
(36)

effective charge on the metal atom has in determining the bond lengths of the carboxyl group was discussed [350]. (π-pyrolyl)tricarbonylmanganese(I) was treated with picric acid to give a binuclear complex (*37*); the picrate ion acts as a 3e-ligand [351].



(*37*)

A new class of transition metal complex containing radicals, (*38*), has been made from the reaction of $[Mn(CO)_5]^{\bullet}$ radicals with aliphatic nitro compounds in the presence of PBu_3 [352].



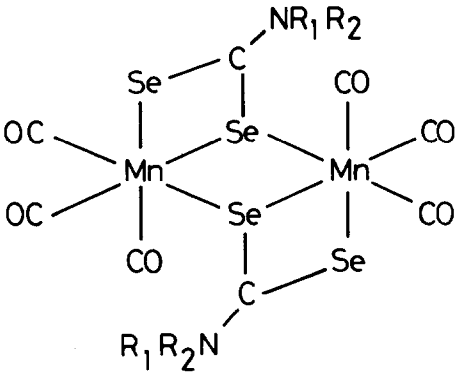
(*38*; *R* = CMe_3, $CHMe_2$, *Ph*, 3,5-$Cl_2C_6H_3$, *2-thienyl or 3-thienyl*; *L* = PBu_3)

5.5.4 *Complexes with sulphur and selenium-donor ligands*

The complexes *cis*-$[Mn(CO)_4\{XC(Y)PPh_2\}]$ {X,Y = NR, O or S} and *cis*-$[Mn(CO)_3(Z)\{HXC(Y)PPh_2\}]$ {X,Y = NR, O or S; Z = Cl or Br} have been prepared, and in the case of the ambidentate thioformamide ligand, shown to be coordinated *via* sulphur and phosphorous atoms [353]. The complexes $[Mn(CO)_4(S_2CNHR)]$ and $[Mn(CO)_3(CNMe)(S_2CNHR)]$ {R = Me or other unspecified groups} have been prepared from RNCS and $[Mn(CO)_4(CONHMe)(NH_2Me)]$ [354,355].

Irradiation of $[Mn_2(CO)_{10}]$ in CH_2Cl_2 in the presence of an excess of L-L {L-L = $R_1R_2NC(Se)SeC(Se)NR_1R_2$ or $R_1R_2NC(Se)Se_3C(Se)NR_1R_2$; R_1= R_2= C_2H_5; NR_1R_2= morpholyl; R_1= CH_3, R_2= C_6H_5} produced $[Mn(CO)_4\{Se_2CNR_1R_2\}]$ almost quantitatively.

Refluxing this product in thf produced the complex $[Mn(CO)_3L]_2$ in variable yield. This complex was assigned a dimeric structure (*39*) [356,357]. The photochemical

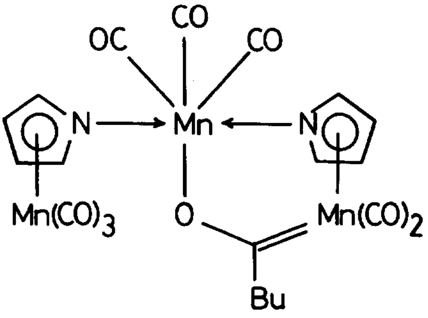


(39; $R_1 = R_2 = C_2H_5$,
R_1R_2N = morpholyl,
R_1 = Me, R_1 = Ph)

reaction to yield those products has been extensively studied, and an S_N1 type reaction proposed, involving Mn-Mn bond fission [358].

5.5.5 *Complexes with nitrogen donor ligands*

The treatment of [(π-pyrolyl)Mn(CO)$_3$] with BuLi gave the complex shown as (*40*), which was characterised by X-ray diffraction [359]. The complexes



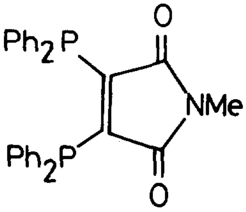
(40)

$[Mn(CO)_3(NH_2NHCS_2CH_3)_2]Br^-$ and $[Mn(CO)_3(NH_2NHCS_2CH_3)Br]$ were formed by the action of *S*-methyldithiocarbazate on $[Mn(CO)_5Br]$. The former complex was characterised by single crystal X-ray diffraction [360].

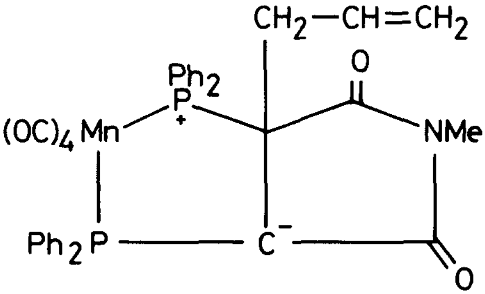
5.5.6 Complexes with phosphorus, arsenic, antimony and bismuth donor ligands

The neutral complexes *fac*-$[O_3ClOMn(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ ($1{\leq}n{\leq}4$) were prepared, and by the facile displacement of $[ClO_4]^-$ a variety of related adducts *fac*-$[Mn(CO)_3\{Ph_2P(CH_2)_nPPh_2\}L][ClO_4]$ {L = phosphines, phosphites, pyridine, MeCN, C_4H_4S, CO or Me_2CO} were synthesised [361]. The complexes *cis,cis*-$[MnBr(CO)_2(L{-}L)L]$ were prepared and oxidised by either NO_2 or $[NO][PF_6]$ to give the unstable cationic species *trans*-$[MnBr(CO)_2(L{-}L)L]^+$. Bromide substitution has also been observed by *N*- or *P*- donor ligands [362]. The IR and ^{55}Mn NMR spectra of the complexes $[Mn(CO)_6]Cl.HCl$, $[Mn(CO)_5(O_2CEt)]$, $[Mn(CO)_5(PR_3)][PF_6]$ and $[Mn_2(CO)_8(PR_3)_2]$ {PR_3 = $PPh(OPh)_2$, PPr_3, $PHPh_2$, $PPh(NEt_2)_2$ or $P(4{-}C_6H_4F)_3$} have been reported, and the above ligands arranged in order of ligand strength. The structure of $[Mn_2(CO)_8(PHPh_2)_2]$ was suggested to be $[(OC)_5Mn{-}Mn(CO)_3(PHPh_2)_2]$, in contrast to the symmetrical structure of the other dimeric complexes $[PR_3(OC)_4Mn{-}Mn(CO)_4PR_3]$ [363].

Reaction of (*41*) with $[(\sigma{-}C_3H_5)Mn(CO)_5]$ gave the complex (*42*) which shows some unusual bonding properties [364].

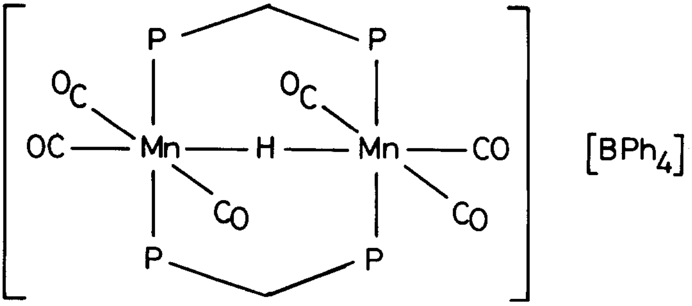


(*41*)



(*42*)

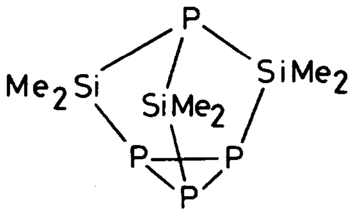
The complex $[Mn_2(CO)_4(\mu{-}CO)(\mu{-}dppm)_2]$ has been shown to react with acids, in the presence of CO to give (*43*). The complex was characterised by IR, ^{31}P and ^1H NMR spectroscopy, and in addition a preliminary single crystal X-ray



(43; P P = dppm)

diffraction data has been collected. The Mn-Mn separation was shown to have extended from 0.293 nm to 0.32 nm on protonation showing that the bridging distance of the dppm ligand is sufficient to accommodate such a change. In thf (*43*) reacts with $Li[BHEt_3]$ at 0°C to generate $[Mn_2(CO)_4(\mu\text{-}CO)(\mu\text{-dppm})_2]$, and it has been postulated that this reaction occurs *via* nucleophilic attack at CO, to give $[Mn_2H(CHO)(CO)_5(\mu\text{-dppm})_2]$ as an intermediate [365].

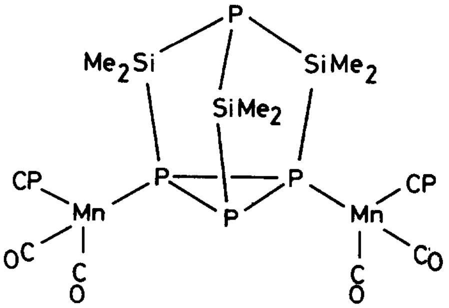
Treatment of $[Mn(cp)(CO)_2(thf)]$ with equimolar quantities of $P_4(SiMe_2)_3$ (*44*)



(44)

gave $[Mn(cp)(CO)_2L]$ $\{L = P_4(SiMe_2)_3\}$, L being monodentate, while in a 2:1 molar ratio the complex $[Mn_2(cp)_2(CO)_4L]$ (*45*) was isolated in which L was bidentate [366].

When the sodium derivative of 2-(diphenylphosphino)ethanethiol was reacted with $[Mn(CO)_5Br]$ a binuclear complex was isolated with the probable structure shown as (*46*) [367]. Other complexes prepared this year include $[Mn(CO)_4\{S(X)CPR_2\}]$ $\{X = S$ or NPh; $R = Ph$ or cycl$\}$, *fac*-$[MnBr(CO)_3\{R_2PC(S)NPhH\}]$ $\{R = Ph$ or cycl$\}$, $[Mn(CO)_4\{S(NPh)CPPh_2\}]$, *cis*-$[MnBr(CO)_4\{P(cycl)_2H\}]$ [368], (*47*) [369]. $[(cp)Mn(CO)\{1,2\text{-}C_6H_4(EPh_2)(E'Ph_2)\}]$ $\{E = P, E' = As; E = E' = P; E = E' = As\}$ $[(cp)Mn(CO)_2\{1,2\text{-}C_6H_4(PPh_2)(BiPh_2)\}]$ and $[(cp)Mn(CO)L]$ $\{L = Ph_2PCH{=}CHPPh_2\}$ [370].



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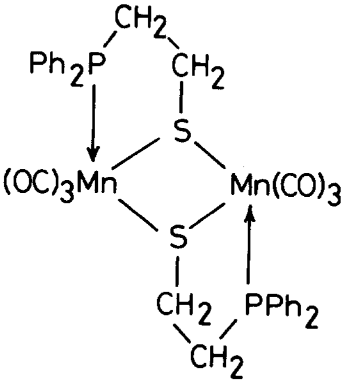

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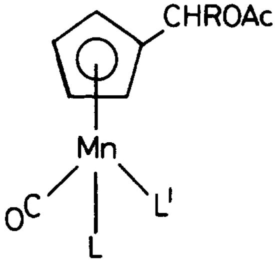
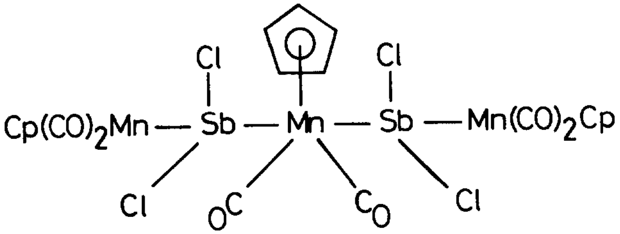


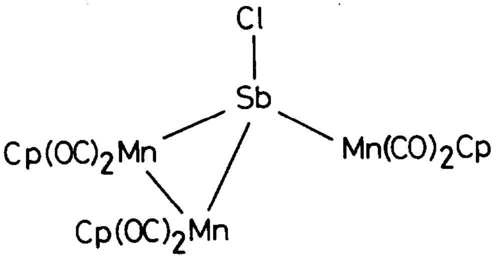
{47; R = Ph, Me or H;
LL' = $(CO)_2$, $(CO)(PEt_3)$,
$(CO)(PPh_3)$ or dppe}

The complexes $[(OC)_4Mn(EMe_2)]$ {E = P or As} have been studied using electrochemical techniques [371]. The cation radical of $[Mn_2(\mu\text{-}AsPh_2)(CO)_8]$ was observed by EPR in a glass formed from a freon mixture [372]. In a usual reaction, dimethylarsinous acid was stabilised and isolated as a complex of manganese [$Mn(CO)_4Cl\{As(CH_3)_2OH\}$] [373].

The reaction of [(cp)$Mn(CO)_2$(thf)] with $SbCl_3$ gave two different products, depending on the conditions, (*48*) and (*49*). Both of these structures were



(*48*)



(*49*)

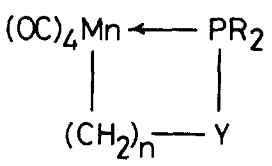
confirmed by X-ray crystallography [374]. By an analogous reaction with $BiCl_3$, a complex of composition {(cp)$Mn(CO)_2\}_2BiCl$ was prepared. X-ray diffraction showed the complex to contain the unsymmetrical Bi_2Cl_2 bridging moiety, the formula of the complex being [$(cp)_4Mn_4(CO)_8Bi_2Cl_2$] [375].

5.5.7 *Organometallic complexes*

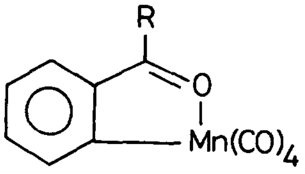
Many cyclic complexes involving carbon-oxygen and carbon-phosphorus coordination of manganese have been reported this year, including (*50*) [376-378], (*51*) [379] and (*52*) [380].

For [$MeMn(CO)_5$] the stereochemistry of insertion of CO into the Me-Mn bond was studied using ^{13}C NMR spectroscopy [381], and the degree of acceleration that proton acids have on methyl migration was measured [382].

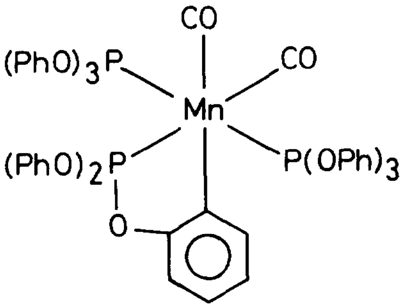
The photochemistry of [(cp)$Mn(CO)_3$] and [(Mecp)$Mn(CO)_3$] in glasses at 77 K yielded [(cp)$Mn(CO)_2$], [(cp)Mn(CO)], [(Mecp)$Mn(CO)_2$] and [(Mecp)Mn(CO)] while in the presence of ethers or alcohols yielded [(cp)Mn(CO)$(thf)_2$], [(cp)$Mn(CO)_2$(thf)],



(*50; Y* = *O*, *n* = *1,2,3 or 4*, *R* = *Ph*;
Y = *S*, *n* = *3*, *R* = *Me*;
Y = CH_2, *n* = *3*, *R* = *Ph*;
Y = *CHMe*, *n* = *3*, *R* = *Ph*)



(*51*; *R* = *Ph or 2-*C_6H_4Ph)



(*52*)

[(cp)Mn(CO)$_2$(mthf)] {mthf = 2-methyltetrahydrofuran}, [(Mecp)Mn(CO)$_2$(mthf)], [(cp)Mn(CO)$_2$(ROH)] and [(Mecp)Mn(CO)$_2$(ROH)] {R = Me or Et} [383]. The crystal structure of [(cp)Mn(CO)$_3$] was reinvestigated and evidence for deviation from planarity of the cyclopentadiene was obtained [384].

An excellent review of the coordination chemistry of the [(cp)Mn(CO)$_2$] fragment has been published [385].

The complex [(Mecp)Mn(CO)$_3$] was used to protect Ph_2SiH_2 [386]. The gas

$$[(\mathrm{Mecp})\mathrm{Mn(CO)_3}] + \mathrm{Ph_2SiH_2} \longrightarrow [(\mathrm{Mecp})\mathrm{MnH(CO)_2(SiHPh_2)}]$$

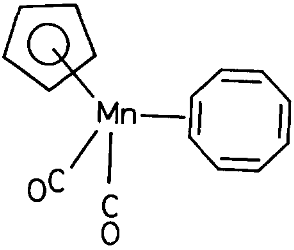
$$[(\mathrm{Mecp})\mathrm{MnH(CO)_2(SiHPh_2)}] + \mathrm{X_2} \longrightarrow [(\mathrm{Mecp})\mathrm{MnH(CO)_2(SiXPh_2)}] + \mathrm{HX}$$

$$[(\mathrm{Mecp})\mathrm{MnH(CO)_2(SiXPh_2)}] + \mathrm{CO} \longrightarrow [(\mathrm{Mecp})\mathrm{Mn(CO)_3}] + \mathrm{Ph_2SiHX}$$

$$\mathrm{X = F,\ Cl,\ Br\ or\ I}$$

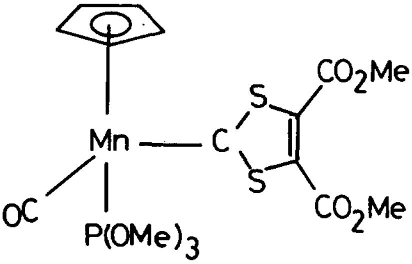
phase He-I and He-II PES spectra of [{$(CH_3)_nC_5H_{5-n}$}Mn(CO)$_2$L] {L = CO, *n* = 0, 1 or 5; L = C_2H_4, C_3H_6, *n* = 1 or 5} have been measured [387,388], as has the He-I PES spectrum of [(μ-CH_2){($CH_3C_5H_4$)Mn(CO)$_2$}$_2$] [389]; the ionisation energies from the studies were compared with each other.

The complex $[\mathrm{Mn(CO)_2(\eta^2\text{-}C_8H_8)(\eta^5\text{-}C_5H_5)}]$ has been prepared and its structure determined, (*53*). This complex is unusual in having a η^2-C_8H_8 ligand, and analogous complexes were obtained from cycloheptatriene and cycloocta-1,3,6-triene [390].



(*53*)

Some $[(\eta^3\text{-allyl})(cp)\mathrm{Mn(CO)_2}]^+$ salts have been prepared [391], and other organometallic complexes studied include the cyclohexadiene manganese tricarbonyl anion (which was prepared by two different routes) [392], $[\mathrm{RCOCH_2Mn(CO)_5}]$ {R = Me, Ph or MeO} [393], $\mathrm{Li[(OC)_4Mn(Bz)(CHO)]}$ [394], $[\mathrm{Mn(\eta^2\text{-}CS_2)(CO)L(C_5H_4R)}]$ {R = H, L = $\mathrm{P(OMe)_3}$ or $\mathrm{PMe_3}$, R = Me, L = $\mathrm{PMe_2Ph}$}, the latter complexes react with one equivalent of dimethyl acetylenedicarboxylate to yield $[\mathrm{Mn\{CS_2C_2(CO_2Me)_2\}(CO)L(C_5H_4R)}]$ (*54*) [395]. $[(\mathrm{RC_5H_4})\mathrm{Mn(CO)_5}]$ {R = $(\mathrm{CH_2})_n\mathrm{P(O)(OEt)_2}$;

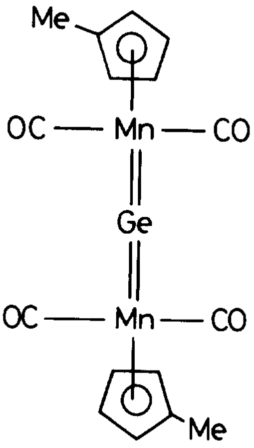


(*54; R = H*)

n = 3, 5 or 7} has been prepared [396]. In addition the reaction between $\mathrm{Na[Mn(CO)_5]}$ and $\mathrm{(ClCH_2)Me_2SiC{\equiv}CCH_2Cl}$ has been investigated [397], and the complex $[\mathrm{Mn(C_5H_5BCH_3)(CO)_3}]$ containing a 1-methylborinato moiety, has been obtained and acetylated [398].

5.5.8 Silyl and germyl complexes

The complex $[Mn(CO)_5\{Si(CH_3)_3\}]$ was treated with a range of organic carbonyls, in order to develop new metal-carbon bond forming reactions; many organic products were obtained and characterised [399]. The complexes $Li[\{RPhMeGe\}Mn(Mecp)(CO)_2]$, $[\{RPhMeGe\}Mn(Mecp)(CO)_2Me]$ and $[\{Ph_3E\}Mn(Mecp)(CO)_2R']$ {R' = Me or Ph, E = Si or Ge} were prepared, the first two containing optically active groups [400]. When $[(Mecp)Mn(CO)_3]$ was reacted with $K[GeH_3]$, $K[(Mecp)Mn(CO)_2(GeH_3)]$ was obtained, which was readily converted to the crystalline salt $[Et_4N][(Mecp)Mn(CO)_2(GeH_3)]$ on addition of $[Et_4N]Cl$. With $GeCl_4$, $[(Mecp)Mn(CO)_2(GeCl_3)_2]$ was obtained; in both compounds, shortening of the Mn-Ge bond was observed [401]. Treatment of $K[(Mecp)Mn(CO)_2(GeH_3)]$ with ethanoic acid yielded $[\{(Mecp)Mn(CO)_2\}_2Ge]$ (*55*) containing a linear Mn=Ge=Mn system, which represents the first example of a Mn-Ge double bond. A related complex $[\{(Mecp)Mn(CO)_2\}_3Ge]$, (*56*), was also synthesised, which also contained a Ge=Mn(CO)$_2$(Mecp) moiety [402].



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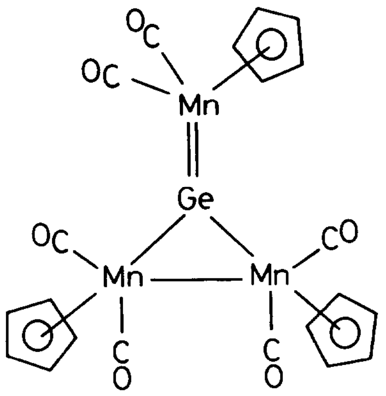
5.5.9 Mixed metal carbonyls

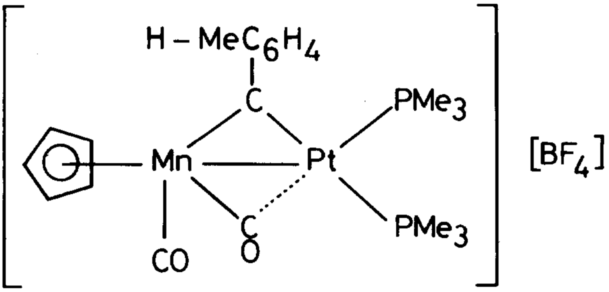
The best thermodynamic parameters for the formation, and phase transition and dissociation of $[MnRe(CO)_{10}]$ and $[Mn_2(CO)_{10}]$ have been proposed [403]. The heteronuclear carbonyl $[MnTc(CO)_{10}]$ was synthesised by treating $[Tc(CO)_5Br]$ with $[Mn(CO)_5]^-$ in thf [404]. For the carbonyl $[MnCo(CO)_9]$, the C=O stretching region



(56)

has been completely assigned. The results point to the polarisation of the metal-metal bond in the sense [(OC)$_5$Mn$^{\delta+}$-Co$^{\delta-}$(CO)$_4$] [405]. The mixed metal complex [MnCo(CO)$_6$(dab)] {dab = 1,4-diazabutadiene} has been prepared, and the dab ligand was observed to be a 6e$^-$-donor [406]. The low temperature resonance Raman spectra of [Re(CO)$_3$(NC$_5$H$_4$CH=NC$_6$H$_4$Me-4){Mn(CO)$_5$}] has been reported [407].

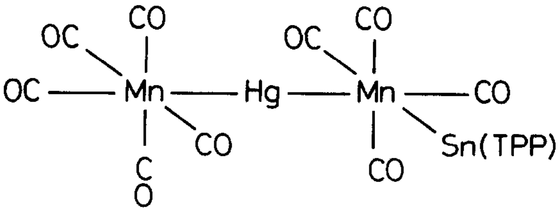
The Mn-Pt bonded complexes [(cp)(OC)$_2\overline{\text{Mn}\{\mu\text{-C(PR}_3)\text{C}_6\text{H}_4\text{Me-4}\}\text{Pt}}$(PR$_3$)$_2$][BF$_4$] and [(cp)(OC)$\overline{\text{Mn}\{\mu\text{-C(PR}_3)\text{C}_6\text{H}_4\text{Me-4}\}(\mu\text{-CO})\text{Pt}}$(SC$_6H_4$Me-4)(PR$_3$)] {PR$_3$ = PMe$_3$ or PMe$_2$Ph] were prepared. In both cases (PR$_3$ = PMe$_3$) crystal structures were obtained [408]. The complex [MnPt(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_2$(cp)][BF$_4$] has also been reported, in which one CO is semi-bridging, (57), [409]. The related complex



(57)

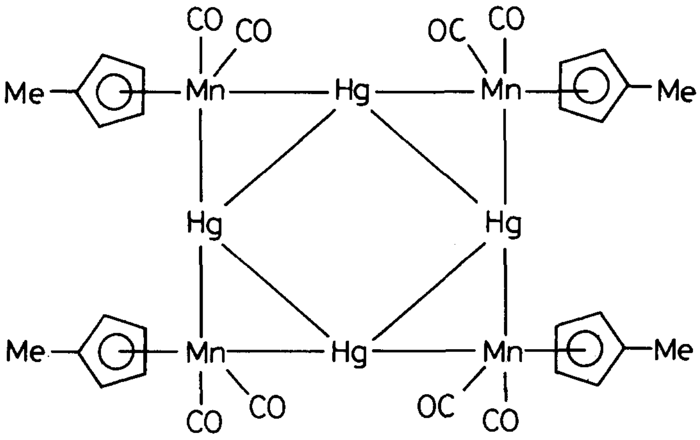
[MnPt(μ-CS)(CO)$_2$(PR$_3$)(cp)] {PR = PMe$_2$Ph or PMePh$_2$} has also been reported [410].

The complex [(TTP)Sn{Mn(CO)$_4$}Hg{Mn(CO)$_5$}].0.5CH$_2$Cl$_2$ has been characterised by X-ray diffraction, and was found to contain the novel Sn-Mn-Hg-Mn unit, in which the Mn-Hg-Mn part is nearly linear, (*58*), [411]. The reaction of



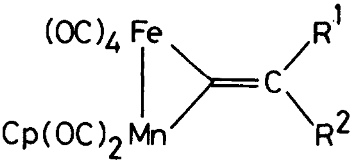
(*58*)

K[(Mecp)Mn(CO)$_2$(GeH$_3$)] with Hg$_2$Cl$_2$ also gave a very interesting product (*59*), with a unique structure [412].

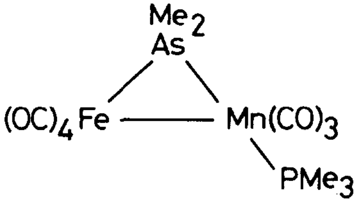


(*59*)

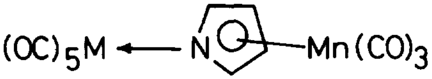
The complex [(PPh$_3$)$_2$N][(C$_6$F$_5$)$_3$Au-Mn(CO)$_5$] has been prepared [413], as have the complexes (*60*) [414], (*61*) [415] and (*62*) [416]. Other complexes that have



(*60*; $R^1 = H$, $R^2 = CO_2Me$;
$R^1 = CO_2Me$, $R^2 = H$;
$R^1 = R^2 = Ph$)

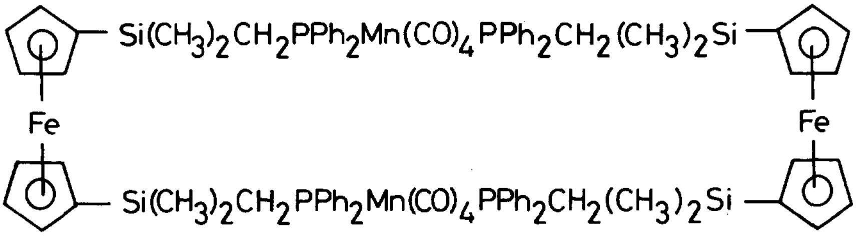


(*61*)



(62; M = Cr, Mo or W)

been reported are [$\{Ph_2MeSn\}Mn(CO)_5$], [$\{Me(PMe_2CCH_2)PhSn\}Mn(CO)_5$] [417], [$(cp)Ti(Mo_5O_{18})Mn(CO)_3]^{2-}$ [418] and *(63)* which is probably oligermeric [419].



(63)

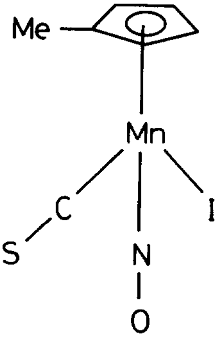
Finally, the kinetics of the system [Me_4Pb]/[$(Me_3Pb)Mn(CO)_5$]/[$(Me_2Pb)\{Mn(CO)_5\}_2$] have been studied [420].

5.6 NITROSYL COMPLEXES

Projected Xα-SW and configuration interaction calculations were used to discuss the bonding and PES of [$Mn(CO)_4(NO)$] [421]. Using the interesting reagent [$(PPh_3)_2N$][NO_2], the complexes [$Mn(CO)_4(NO)$] and [$(PPh_3)_2N$][$Mn(CO)_2(NO)_2$] were prepared in high yield [422]. The reactions of [$Mn(CO)(NO)_3$] with L (L = $P(CMe_3)_3$, $PH(CMe_3)_2$, $P(SiMe_3)_3$, $P(GeMe_3)_3$, $P(SnMe_3)_3$, $P(CMe_3)(SiMe_3)_2$, $P(CMe_3)(GeMe_3)_2$ or $P(CMe_3)(SnMe_3)_2$) all resulted in the elimination of CO. The resulting complexes [$Mn(L)(NO)_3$] were studied by ^{31}P and ^{55}Mn NMR spectroscopy [423].

The chiral nitrosyl complexes [$(C_5H_4R)Mn(NO)(L)I$] {R = H or Me, L = PPh_3, $P(OPh)_3$ or $P(C_6H_{11})_3$} were prepared along with the dimeric species [$(C_5H_4R)_2Mn_2(NO)_3X$] {R = H or Me, X = Cl, Br, I, CN, SCN or various organic anions} [424]. The structure of the complex [$(Mecp)Mn(CS)(NO)I$] has been determined by X-ray diffraction *(64)* [425].

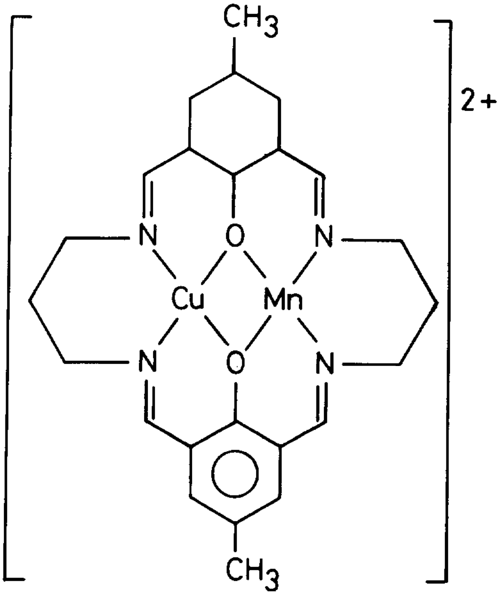
Other complexes that have been reported include the mixed-metal nitrosyl $Ag[(cp)Mn(CN)(NO)(PPh_3)]_2$ [426], [$(cp)Mn(CO)(NO)L$][BF_4], [$(C_9H_7)Mn(CO)(NO)L$][BF_4] {L = CO or PPh_3} [427], and [$LMn(CO)_2(NO)$][BF_4] {L = η^5-indenyl} [428].



(64)

5.7 HETERONUCLEAR COMPLEXES

The binucleating macrocyclic ligands {L^{2-}}, derived from two equivalents of 2,6-diformyl-4-methylphenol and two equivalents of 1,3-diaminopropane, results in two identical {N_2O_2} coordination sites from which the heteronuclear complex [$Mn^{II}Cu^{II}L$]$^{2+}$ was prepared (*65*) [429].



(65)

The crystal structure and magnetic properties of the Ni(II)/Mn(II); Cu(II)/Mn(II)-dithiooxalato systems were obtained. These complexes were found to be isostructural with infinite-chain molecules ····$A(S_2C_2O_2)[Mn(H_2O)_3](O_2C_2S_2)$····· {A = Ni or Cu}. The magnetic behaviour of the Cu(II)/Mn(II) system is unusual, the manganese(II) and copper(II) ions appear to be antiferromagnetically coupled [430].

A heteronuclear complex of 1-methylthymine, containing both the *cis*-$\{Pt(NH_3)_2\}^{2+}$ unit and Mn^{2+} has been prepared and characterised by X-ray diffraction, and shown to be $[Mn\{Pt(NH_3)_2(C_6H_7N_2O_2)_2\}_2Cl_2].10H_2O$ [431]. In the complex $[Cu\{(prp)_2en\}Mn(hfacac)_2]$ {where $(prp)_2en$ is the Schiff base derived from 2-hydroxypropiophenone and ethylenediamine}, the EPR and zero field splitting of the exchange coupled Cu(II)/Mn(II) pairs, were measured [432].

In addition the mixed-metal complexes $Mn[Ni(CN)_4]$ and $[\{(cp)_2(CO)Nb\}_2(\mu\text{-}H)][Mn(CO)_5]$ have also been reported [433,434].

5.8 MIXED OXIDATION STATE COMPLEXES

The unusual dodecanuclear crystalline complex containing manganese(II) and manganese(IV) $[Mn_{12}(CH_3COO)_6(H_2O)_4O_{12}].2CH_3COOH.4H_2O$ has been prepared, and has been studied by X-ray diffraction. In this complex the manganese atoms are linked by triply bridging oxo-oxygen atoms and by carboxylate bridges [435]. The crystal structure of $\{CaMn_3\}Mn_4O_{12}$ was obtained using neutron diffraction; it contained both manganese(IV) and manganese(III), the latter being present in two different types of Jahn-Teller distorted polyhedra [436]. The related complexes $\{LnCu_3\}Mn_4O_{12}$ {Ln = La-Lu or Y} were also studied and found to be ferrimagnetic [437].

Mn_2FeO_4 was studied by Mössbauer spectroscopy, and a cation distribution for this spinel was proposed [438]. The structural and magnetic properties of the $Pr_{1-x}Mn_{1+x}O_3$ perovskites have also been studied [439].

5.9 PHTHALOCYANINE AND PORPHYRIN COMPLEXES

$[Mn^{III}(TPP)Cl]$ {$TPPH_2$ = *meso*-tetraphenylporphyrin} was found to catalyse the specific oxidation of ketones by dioxygen, in the presence of $[Bu_4N][BH_4]$ [440]. The hyperfine proton interactions have been analysed to give information about the spin populations on the hemaglobin derivatives of $[Mn^{II}(TPP)X]/[Mn^{III}(TPP)X]$ {X = H_2O or Cl} with metmyoglobin or fluoromyoglobin as the six ligand [441].

Water soluble manganese(III) porphyrins were reduced by dithionite in aqueous solution, and a mechanism was proposed. In addition, water soluble manganese(II) porphyrins were found to be oxidised by dioxygen *via* an axial inner-sphere mechanism. It was found that quinones also oxidised manganese(II) porphyrins, far more rapidly than dioxygen [442]. No ground state reactions were observed between manganese(III) porphyrins and benzo-1,4-quinone, naphtho-1,4-quinone or anthra-9,10-quinone, but irradiation with visible light lead to reduction of the quinones to hydroquinones. In the case of benzo-1,4-quinone, manganese(IV) porphyrins and semiquinone were produced initially, which then reacted to give manganese(III) porphyrin and hydroquinone [443]. The luminescence properties of $[Mn^{II}(TPP)]$ were measured, and these showed that there was little interaction between the metal and the porphyrin π-system [444]. In $[Mn^{III}(TPP)]$ the luminescence was found to originate from the second tripmultiplet state [445]. The preparation of manganese(II) porphyrin in an aqueous environment (the water soluble porphyrin used was prepared by the addition of four ethylene diamine molecules to protoporphyrin IX [446]) and the exchange reaction with zinc has been reported [447].

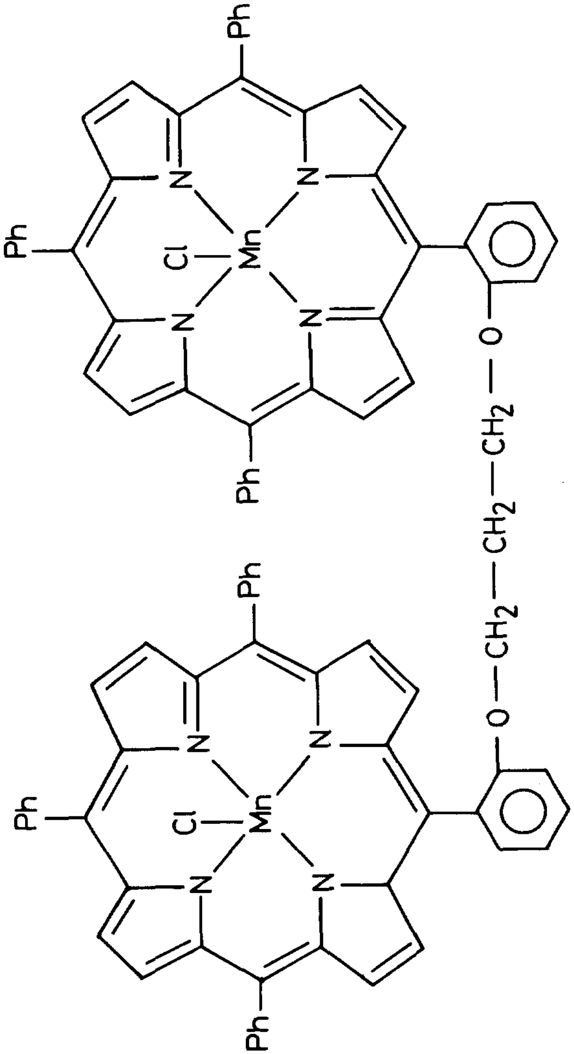
The average magnetisation between 2 and 20 K and 10-50 KOe of $[Mn^{III}(TPP)Cl]$ and $[Mn^{III}(TPP)Cl(py)]$ has been studied and analysed [448]. [Mn(TPP)Cl] and (*66*) were reduced by $[Fe_4S_4(SPr)_4]^{2-}$ and were observed by EPR [449].

The porphyrin/Mn(III)/$Na[BH_4]/O_2$ oxidation model system was found to behave similarly to the enzyme system P-450/NADH/O_2 {cytochrome P-450 was used as a typical example of enzymic oxygen-activation} [450]. P-450 type dioxygen activation was achieved using H_2/colloidal Pt, as an effective electron donor rather than $Na[BH_4]$ [451].

$[Mn^{III}(TPP)]$ was shown to catalyse the oxidation of simple alkyl-substituted indoles, *via* first the ternary complex, then an indolenyl hydroperoxide which decomposes to give the final product [452]. The binding of imidazoles to manganese(III) protoporphyrins in water has also been studied [453].

The β-polymorphic form of $[Mn^{II}(pc)]$ was studied by single crystal neutron diffraction at 5.8 K, and systematic differences in bond lengths (compared to those seen in previous determinations of the structure at T = 116 K and 295 K) were revealed [454]. In addition the polarised neutron diffraction data at 4.2 K has been collected and interpreted to give a spin-density distribution in the $[Mn^{II}(pc)]$ crystal [455].

The electrochemical behaviour of $[Mn^{II}(pc)]$ dissolved in pyridine, dmso and dma has been reported, in the presence of X^- {X = Cl, Br or $[ClO_4]$}. Electron-transfer couples, representing net oxidations of the manganese, and of the phthalocyanine ring, and two net reductions of the phthalocyanine ring were observed by cyclic voltammetry, and showed close to ideal behaviour [456,457]. [Mn(pc)] was found not to react with O_2 in rigorously purified pyridine, but does react in dma to yield a dioxygen adduct, and the reaction was found to be reversible. An oxo-bridged $[Mn^{III}(pc)\text{-}O\text{-}Mn^{III}(pc)]$ species was observed, and



(66)

a solid containing a bound superoxide [Mn^{III}(pc)(O_2)] was isolated [458].

Artificial haemoglobins were prepared with manganese(III) tetrasulphonated phthalocyanine [Mn^{III}(tspc)] in place of heme. Spectrophotometric titration data indicates the ratio of reagents in this process to be 1:1. The artificial haemoglobin complex formed does not react reversibly with dioxygen, and cannot act as a physiological oxygen carrier [459]. In the solid state the dioxygen adduct of [Mn^{II}(tspc)] has been shown to be best formulated as [Mn^{III}(tspc)(O_2^-)], while in solution the EPR spectrum as a function of pH indicates that there is an intramolecular electron transfer between [Mn^{II}(tspc)O_2] and [Mn^{III}(tspc)(O_2^-)] [460].

The dimeric highly reactive μ-oxo-[azidotetraphenylporphyrinatomanganese(IV)] complex has been prepared and characterised by X-ray diffraction. The manganese atoms are coupled antiferromagnetically. It reacts quantitatively with Ph_3P to give Ph_3PO, and to give a variety of products in low yields with alkanes, alkenes and chlorocarbons [461].

The average oxidation state of manganese in photosynthetic membranes was measured by X-ray edge studies, and shown to be between +2 and +3 [462,463].

5.10 HYDRIDES, CARBIDES, NITRIDES AND PHOSPHIDES

The nature of binding in MnH was studied using a modified Phillips-Kleiman pseudopotential method [464], and the upper limit of the dissociation energy of MnH was estimated [465].

The systems A_6Mn_{23} {A = Gd, Ho and Er} were converted into the hydrides with the composition $A_6M_{23}H_x$ {$x \approx 22$}, and the magnetic properties of these systems were studied [466]. The hydrides of $YMn_{2-x}Fe_x$ and related materials were prepared [467], as were the hydrides $ErMnH_x$ {x = 4.6-4.0}. These hydrides were studied by X-ray diffraction [468]. The magnetic behaviour of Ti/Mn intermetallics and their hydrides were investigated by susceptibility measurement (T = 5-360 K) [469].

The enthalpy of formation of $Mn_{23}C_6$ was calculated by measuring standard enthalpies of combustion of $Mn_{23}C_6$ to Mn_3O_4. The value obtained was 12,746.0±15.6 kJ mol^{-1} [470].

A double helix magnetic structure for MnP was proposed [471]. The thermal expansion coefficient of MnP was measured and found to be anisotropic [472]. The valence bond PES of MnP crystals was measured using synchrotron radiation [473].

Crystals of 2-MnP_4 were examined by X-ray diffraction, and showed to contain a 2-layer stacking variant of the previously reported 8-MnP_4 and 6-MnP_4 [474]. A new phase of MnP_4 was examined by X-ray diffraction and shown to be triclinic (Mn-Mn = 3.21 Å compared to 2.94 Å in the monoclinic form) [475].

The phosphorescence and phosphorescence excitation spectra of octahedrally coordinated manganese in $MnPS_3$ was measured at 77 and 4 K [476]. $MnPS_3$ has also been shown to take up various cations from aqueous solution, where the electric charge was balanced by the loss of manganese cations from the layers. This reaction is limited, but has been extended to complex cations $[Cr(en)_3]^{2+}$ and $[Ru(bipy)_3]^{2+}$ [477].

The complex phosphide $YbMnCuP_2$ has been reported, and shown to be isotypic with the $CaAl_2Si_2$ type structure [478].

It was found that [MnN] was extensively decomposed in organic solvent-bromine mixtures, Mn going into solution [479]. The thermal conductivities of VN/MnN and CrN/MnN solid solution were measured at 100-1000 K [480]. The specific heat capacity of the cubic metallic perovskites Mn_3ZnN and Mn_3GaN were reported between 6-350 K. First order anomalies were detected [481].

REFERENCES

1 R.I. Crisp, *Coord. Chem. Rev.*, 45 (1982) 237.
2 A. Harriman, *Coord. Chem. Rev.*, 28 (1979) 147.
3 T.K. Sham and B.S. Brunschwig, *J. Am. Chem. Soc.*, 103 (1981) 1590.
4 R.J.H. Clark and B. Stewart, *J. Am. Chem. Soc.*, 103 (1980) 6593.
5 J.S. Reckley and K. Showalter, *J. Am. Chem. Soc.*, 103 (1981) 7012.
6 S. Wolfe, C.F. Ingold and R.U. Lemieux, *J. Am. Chem. Soc.*, 103 (1981) 938.
7 S. Wolfe and C.F. Ingold, *J. Am. Chem. Soc.*, 103 (1981) 940.
8 E.L. Varetti, R.R. Filgueira and A. Mueller, *Spectrochim. Acta*, 37A (1981) 369.
9 E.S. Rudakov, A.P. Yaroshanko and V.V. Zamashchikov, *React. Kinet. Catal. Lett.*, 17 (1981) 7.
10 V.I. Suprunovich, E.I. Zherebtsova, R.M. Sharonina, *UKr. Khim. Zh.*, 46 (1980) 1145.
11 R.I. Agladze and T.G. Lezhava, *Soobshch. Akad. Nauk. Gruz. SSR*, 101 (1981) 69.
12 T. Sakurai and A. Nakahara, *Kagaku (Kyoto)*, 35 (1980) 229.
13 L.J. Kuschenbaum and D. Meyerstein, *Inorg. Chim. Acta*, 53 (1981) L99.
14 P. Day, R. Borromei and L. Oleari, *Chem. Phys. Lett.*, 77 (1981) 214.
15 M.J. Blandamer, J. Burgess, S.J. Hamshere, R.D. Peacock, J.H. Rogers and H.D.B. Jenkins, *J. Chem. Soc. Dalton Trans.*, (1981) 726.
16 B. Zemva and J. Slivnik, *J. Fluorine Chem.*, 17 (1981) 375.
17 M.K. Chaudhuri, J.C. Das and H.S. Dasgulpta, *J. Inorg. Nucl. Chem.*, 43 (1981) 85.
18 B.G. Muller, *J. Fluorine Chem.*, 17 (1981) 409.
19 V.F. Balakirev, V.P. Barkhatov, A.P. Bobov, Yu.V. Golikov, A.G. Zalazinskii and G. Chufarov, *Teorg. Prakt. Metall. Margantsa*, (1977, published 1980) 5.
20 J. Jarrige and J. Mexmain, *Bull. Soc. Chim. Fr.*, 9-10 Pt.1 (1980) 363.
21 Y. Ozaki, *Kenky Hokoku-Asahi Garasu Kogyo Gijutsu Shoreikai*, 36 (1980) 101.
22 S.A. Nedil'ko, V.V. Pavlishchuk and N.P. Zyryanova, *UKr. Khim. Zh.*, 46 (1980) 1137.
23 J.C. Hunter, *J. Solid St. Chem.*, 39 (1981) 142.
24 K.M. Parida, S.B. Kanungo and B.R. Sant, *Electrochim. Acta*, 26 (1981) 435.
25 R. Nagata, *Ariake Kogyo Koto Senmon Gakko Kiyo*, 17 (1981) 105.
26 I.G. Gorichev, L.V. Malov and S.K. Vainman, *Kinet. Katal.*, 21 (1980) 1416.
27 R.D. Agrawal, *Trans. Jpn. Inst. Met.*, 22 (1981) 253.

28 K.P. Zhdanova, A.N. Panikarovskaya, N.V. Alekseeva and V.G. Lapovich, *Optich Metody v adsorbtsii i Katalize Irkutska*, (1980) 133.

29 S.E. Jones, D-H. Chin and D.T. Sawyer, *Inorg. Chem.*, 20 (1981) 4257.

30 F. Freeman, C.O. Fuselier, C.R. Armstead, C.E. Dalton, P.A. Davidson, E.M. Karchesfski, D.E. Krochman, M.N. Johnson and N.K. Jones, *J. Am. Chem. Soc.*, 103 (1981) 1154.

31 B. Pradhan and D.V.R. Rao, *J. Indian Chem. Soc.*, 58 (1981) 733.

32 L. Ciavatta, R. De Capua and R. Palombari, *J. Inorg. Nucl. Chem.*, 43 (1981) 1305.

33 M.N. Bhattacharjee, M.K. Chaudhuri, H.S. Dasgupta and D.T. Khathing, *J. Chem. Soc. Dalton Trans.*, (1981) 2587.

34 H. Barfuss, G. Boehnlein, H. Hohenstein, W. Kreische, H. Niedrig and A. Reimer, *Nucl. Phys. Methods Mater. Res.*, *Proc. Div. Conf.*, *7th*, (1980) 404.

35 K. Gyoryova and B. Mohai, *Acta Chim. Acad. Sci. Hung.*, 107 (1981) 77.

36 I. Szterenberg, K. Natkaniec and B. Jezowska-Trzebiatowska, *Proc. Conf. Coord. Chem.*, *8th*, (1980) 405.

37 S.A. Nedil'ko, V.V. Pavlishchuk and M.N. Ermakova, *UKr. Khim. Zh. (Russ Ed.)*, 46 (1980) 1044.

38 E. Pollert, M. Nevriva and J. Novak, *Mat. Res. Bull.*, 15 (1980) 1453.

39 M. Mikuriya, N. Torikara, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 54 (1981) 1063.

40 K.S. Patel and A.A. Adimado, *J. Inorg. Nucl. Chem.*, 42 (1980) 1241.

41 J.E. Hallgren and G.M. Lucas, *Tetrahedron Lett.*, 21 (1980) 3951.

42 Y. Ito and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 54 (1981) 150.

43 T. Oncescu and E. Jurconi, *Rev. Chim. (Bucharest)*, 31 (1980) 702.

44 T.I. Zaitseva, *Khim i Biokhim. Okislenie Sistem Soderzhashch. D-elementy, Chelyabinsk*, (1979) 24.

45 R.R. Nagori, M. Mehta and R.N. Mehrotra, *J. Chem. Soc. Dalton Trans.*, (1981) 581.

46 R. Varadarajan and M. Joseph, *Indian J. Chem.*, 19A (1980) 977.

47 F. Ahmad, V.S. Baswani and S. Kumar, *J. Indian Chem. Soc.*, 58 (1981) 162.

48 M.B. Gopinathan and M. Vivekananda Bhatt, *Indian J. Chem.*, 20B (1981) 71.

49 F. Gaudemer and A. Gaudemer, *Tetrahedron Lett.*, 21 (1980) 1445.

50 M. Hamado and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, 53 (1980) 2630.

51 C. Preti, G. Tossi and P. Zannini, *J. Mol. Structure*, 65 (1980) 283.

52 C. Preti, G. Tossi and P. Zannini, *Congr. Naz. Chim. Inorg.*, *[Atti]*, *13th*, (1980) 94.

53 S. Kumar, N.K. Kausik and I.P. Mittal, *Therm. Anal.*, *[Proc. Int. Conf. Therm. Anal.] 6th*, 2 (1980) 137.

54 Y. Sugiura, H. Kawabe, H. Tanaka, S. Fujimoto and A. Ohara, *J. Am. Chem. Soc.*, 103 (1981) 963.

55 P.L. Tikhonova, V.P. Goncharik and T.S. Ivashchenko, *Zh. Neorg. Khim.*, 25 (1980) 2720.

56 P.G. Sim and E. Sinn, *J. Am. Chem. Soc.*, 103 (1981) 241.

57 W.M. Coleman, R.K. Boggess, J.W. Hughes and L.T. Taylor, *Inorg. Chem.*, 20 (1981) 1253.

58 W.M. Coleman, *Inorg. Chim. Acta*, 53 (1981) L191.

59 W.M. Coleman, R.K. Boggess, J.W. Hughes and L.T. Taylor, *Inorg. Chem.*, 20 (1981) 700.

60 W.M. Coleman, *Inorg. Chim. Acta*, 49 (1981) 205.

61 H. Kuma and S. Yamada, *Bull. Chem. Soc. Jpn.*, 53 (1980) 3218.

62 V.V. Zelentov, I.K. Somova, R.Sh. Kurtanidze and T.B. Nikoloeva, *Koord. Khim.*, 6 (1980) 1576.

63 K.K. Narang and U.S. Yadav, *Curr. Sci.*, 49 (1980) 852.

64 S.K. Sengupta, S.K. Sahni and R.N. Kapoor, *Indian J. Chem.*, 19A (1980) 703.

65 B. Pradhan and D.V.R. Rao, *Indian J. Chem.*, 20A (1981) 751.

66 I.E. Kalinchenko, E.Ya. Matveeva and A.T. Pilipenko, *Zh. Neorg. Khim.*, 26 (1981) 115.

67 G.P. Perina, V.G. Shibalovich, V.M. Bondarenko and A.F. Nikolaev, *Probl. Sol'vatsii i Kompleksoobraz.*, *Ivanovo*, (1979) 70.

68 R.M. Hazen and L.W. Finger, *J. Phys. Chem. Solids*, 42 (1981) 143.

69 L.N. Fuerhelm, *Diss. Abstr. Int. B.*, 42 (1981) 269.

70 T. Fujita, K. Shibuya and T. Ichihashi, *Surf. Sci.*, 106 (1981) 422.

71 S. Das, S. Patz and P. Heller, *J. Appl. Phys.*, 52 (1981) 1938.

72 P. Nordblad, L. Lungren, E. Figueroa and O. Beckman, *J. Magn. Magn. Mater.*, 23 (1981) 333.

73 J. Baruchel, M. Schlenker and B. Barbara, *J. Magn. Magn. Mater.*, 15-18 (1980) 1510.

74 A. Bazhan and S.V. Petrov, *Zh. Eksp. Teor. Fiz.*, 80 (1981) 669.

75 L.A. Kul'vinova, V.V. Blokhin, Yu.A. Makashev and V.E. Mironov, *Koord. Khim.*, 7 (1981) 201.

76 J. Hutton and R.J. Nelmes, *J. Phys. C.*, 14 (1981) 1713.

77 S. Shin, S. Suga, H. Kanzaki, S. Shibuya and T. Yamaguchi, *Solid State Commun.*, 38 (1981) 1281.

78 Kh.G. Bogdanova, V.A. Golenishchev-Kutuzov, A.A. Monakhov, A.V. Kuz'ko, V.P. Lukomskii and Yu.V. Chovnyuk, *Pis'ma Zh. Eksp. Teorg. Fiz.*, 32 (1980) 476.

79 Yu.A. Izyvmov, F.A. Kassan-Ogly and V.E. Naish, *Fiz. Met. Metalloved.*, 51 (1981) 500.

80 E.P. Bashkin, *Fiz. Tverd. Tela.*, 23 (1981) 294.

81 K. Hanisch, *J. Phys. C. Solid St. Phys.*, 13 (1980) 4393.

82 H. Tietze, M. Muller and H. Jex, *Phys. Status Solidi, A*, 66 (1981) 239.

83 R.M. Holt and K. Fossheim, *Phys. Rev. B*, 24 (1981) 2681.

84 O. Knop, I.A. Oxton, W.J. Westerhaus and M. Falk, *J. Chem. Soc.*, *Faraday Trans. II*, 77 (1981) 309.

85 R.B. Helmholdt, G.A. Weigess and J. Bartolome, *J. Phys. C. Solid St. Phys.*, 13 (1980) 5081.

86 Y. Shapira, *J. Appl. Phys.*, 52 (1981) 1926.

87 Yu.M. Bun'kov, V.S. Lutovinov and A.A. Monakhov, *Zh. Eksp. Teorg, Fiz.*, 80 (1981) 1449.

88 Yu.M. Bun'kov and T.V. Maksimchuk, *Zh. Eksp. Teorg. Fiz.*, 79 (1980) 1408.

89 V. Dvorak and J. Fousek, *Phys. Status Solidi A*, 61 (1980) 99.

90 A.F. Murray and D.J. Lockwood, *C.R. - Conf. Int. Spectrosc. Raman, 7th*, (1980) 58.

91 D.J. Lockwood, A.F. Murray and N.L. Rowell, *J. Phys. C*, 14 (1981) 753.

92 R. Almairac, M. Regis, J. Nouet and C. Filippini, *J. Phys. Lett.*, 42 (1981) 385.

93 A.K. Sengupta and K. Sen, *Indian Chem. Soc.*, 58 (1981) 76.

94 S.K. Datta and D. De, *Indian J. Cryog.*, 4 (1979) 39.

95 D. Weir, K.E. Halstead and L.A.K. Staveley, *Farad. Discuss. Chem. Soc.*, 69 (1980) 202.

96 M. Bacmann, P. Wolfers and G. Courbion, *Mat. Res. Bull.*, 15 (1980) 1479.

97 J.P. Renard, J.P. Miranday and F. Varret, *Solid State Commun.*, 35 (1980) 41.

98 E. Velu, J.P. Renard and J.P. Miranday, *J. Phys. Lett.*, 42 (1981) 237.

99 C. Escribe, J. Bouillot and K.R.A. Ziebeck, *J. Phys. C. Solid St. Phys.*, 13 (1980) 4053.

100 R.N. Roy, J.J. Gibbons, J.K. Trower and G.A. Lee, *J. Soln. Chem.*, 9 (1980) 535.

101 Y. El-Tawil, *Chem. Petro-Chem. J.*, 12 (1981) 3.

102 I.D. Buric, A.D. Aleksic, K.R. Velasevic and B.J. Draskovic, *Glas. Hem. Drus. Beograd.*, 46 (1981) 99.

103 T.B. Pochinok and B.P. Burylev, *Fiz. Khimiya Ion. Rasplavov i Tverd. Elektrolitov*, *Kiev*, (1980) 92.

104 G.N. Papatheodorou and O.J. Kleppa, *J. Chem. Therm.*, 12 (1980) 807.

105 B.P. Burylev, *Kompleksn. Ispol'z. Miner. Syr'ya*, 5 (1981) 28.

106 M.O. Kostryukova and A.V. Ionov, *Vestn. Mosk. Univ., Ser. 3, Fiz. Astron.*, 22 (1981) 47.

107 G.P. Vishnerskaya, F.M. Gumerov and A.F. Grigoreva, *Zh. Strukt. Khim.*, 21 (1980) 114.

108 G.W. Neilson, J.R. Newsome and M. Sandstrom, *J. Chem. Soc., Faraday Trans. II*, 77 (1981) 1245.

109 R.A. Butera, L.M. Carliss, J.M. Hastings, R. Thomas and D. Mukamel, *Phys. Rev. B.*, 24 (1981) 1244.

110 C.H. Westpal and C.C. Becerra, *J. Phys. C. Solid St. Phys.*, 13 (1980) L527.

111 J.M. Viana and A.S.T. Pires, *Phys. Status Solidi B*, 106 (1981) Kl.

112 D. Bourdel, G. Ablart, J. Pescia, S. Clement and J.P. Renard, *Phys. Rev. B*, 23 (1981) 1339.

113 G. Ablart, D. Bourdel, J. Pescia, S. Clement and J.P. Renard, *J. Phys. Lett.*, 42 (1981) 219.

114 J. Timonen and K. Bullough, *Phys. Lett. A*, 82A (1981) 183.

115 B. Ghosh, P.K. Majumdar and R.K. Mukherjee, *Solid St. Commun.*, 37 (1981) 577.

116 R.E. Capito and R.D. Willett, *Acta Cryst.*, B37 (1981) 1616.

117 R.E. Capito and R.D. Willett, *Acta Cryst.*, B37 (1981) 1618.

118 S. Clement, Tron Van Hiep and J.P. Renard, *Solid St. Commun.*, 37 (1981) 967.

119 C. Lauer and H. Benner, *Phys. Rev. B.*, 24 (1981) 329.

120 N.V. Fedoseeva, I.P. Spevakova, S.P. Petrov and Yu.A. Dorofeev, *Fiz. Tverd. Tela*, 22 (1980) 2569.

121 A.F. Klimachev, I.N. Kurkin and Yu.K. Chirkin, *Fiz. Tverd, Tela*, 23 (1981) 513.

122 A.I. Belyaeia, M.M. Kotlyarskii, Yu.N. Stel'makhov and O.V. Miloslavskaya, *Fiz. Tverd, Tela*, 23 (1981) 1234.

123 G.L. McPherson and S.C. Willard, *Chem. Phys. Lett.*, 78 (1981) 135.

124 Y. Ajiro, K. Adachi and M. Meketa, *Solid St. Commun.*, 37 (1981) 449.

125 K. Strobel, J. Frank, K. Rosshirt and R. Geick, *Int. J. Infrared Millimeter Waves*, 1 (1980) 295.

126 T. Goto, B. Liithi, R. Geick and K. Strobel, *Phys. Rev. B*, 22 (1980) 3452.

127 A. Edgar, E. Siegel and W. Urbani, *J. Phys. C. Solid St. Phys.*, 13 (1980) 6649.

128 M.R. Alvarez, M.J. Tello and E.H. Bocanegro, *Thermochim. Acta*, 43 (1981) 115.

129 H. Mashiyama and S. Tanisaki, *J. Phys. Soc. Jpn.*, 50 (1981) 1413.

130 G.L. Breneman and R.D. Willett, *Acta Cryst.*, B37 (1981) 1293.

131 W. Depmeier, *Acta Crys.*, B37 (1981) 330.

132 V. Busico, *Congr. Naz, Chim. Inorg., [Atti], 13th* (1980) 253.

133 C. Paraggio, V. Salerno, V. Busico and M. Vacatello, *Thermochim. Acta*, 42 (1980) 185.

134 V. Haber, *Proc. Conf. Coord. Chem., 8th*, (1980) 111.

135 R. Callaghan and O. Siiman, *Inorg. Chem.*, 20 (1981) 1723.

136 T. Nakamura, *Kobutsugaku Zasshi*, 14 (1980) 51.

137 J.M. Calleja, A. Ruiz, F. Flores, V.R. Velasco and E. Lilley, *J. Phys. Chem. Solids*, 41 (1980) 1367.

138 B. Ghosh and R.K. Mukherjee, *Phys. Status Solidi*, 106 (1981) 699.

139 E.A. Popov and M.M. Kotlyarskii, *Fiz. Tverd, Tela*, 22 (1980) 3019.

140 A. Horowitz, D. Grazit and J. Makovsky, *J. Cryst. Growth*, 51 (1981) 489.

141 T. Sato, T. Shimomura, T. Nakamura and T. Fujimatsu, *Int. Solvent Extr. Conf., [Proc.], 3*, (1980) Paper 80-183, 10 pp.

142 L. Helm and H.G. Hertz, *Ber. Bunsenges. Phys. Chem.*, 85 (1981) 158.

143 A.W. Potts, D. Law and E.P.F. Lee, *J. Chem. Soc., Farad. II*, 77 (1981) 797.

144 H.D. Lutz, W. Schmidt and H. Haeuseler, *Naturwissenschaften*, 68 (1981) 328.

145 R. Lissillour, M.A. Makhyoun and A.A. Hasanein, *J. Chim. Phys. Chim. Biol.*, 78 (1981) 335.

146 H. Ito, *Tokushima Daigaku Kyoyobu Kiyo, Shizen Kagaku*, 14 (1981) 61.

147 M. Heming and G. Lehmann, *Chem. Phys. Lett.*, 80 (1981) 235.

148 H.W. Zandbergen, *J. Solid St. Chem.*, 35 (1980) 367.

149 M. Holz, N.W. Lutz, F. Blumenthal and H.G. Hertz, *J. Soln. Chem.*, 9 (1980) 381.

150 R. Bidaux, R. Conte and J.A. Nasser, *J. Physique*, 41 (1980) 1317.
151 M.S. Jagadeesh and M.S. Seehra, *Phys. Rev. B*, 23 (1981) 1185.
152 M.S. Jagadeesh and M.S. Seehra, *Solid St. Commun.*, 37 (1981) 369.
153 M.S. Jagadeesh, P. Silinsky and M.S. Seehra, *J. Appl. Phys.*, 52 (1981) 2315.
154 C. Carel, *Bull. Soc. Sci. Bretagne*, 51 (1976, Publ. 1980) 105.
155 Y. Sumino, M. Kumazawa and O. Nishizawa, *J. Phys. Earth*, 28 (1980) 475.
156 D.A. Caillet, *Diss. Abstr. Int. B*, 41 (1981) 3112.
157 J.D. Hem, *Adv. Chem. Ser.*, 189 (1980) 45.
158 M.J. Park and P.J. Bray, *J. Korean Phys. Soc.*, 14 (1981) 67.
159 B.K.D.P. Rao and D.R. Gaskell, *Metall. Trans. B*, 12B (1981) 311.
160 J. Kleinclauss, R. Mainard, H. Fousse, N. Ciret, D. Bour and A.J. Poiton, *J. Phys. C*, 14 (1981) 1163.
161 M.Zh. Makhmetov and L.G. Gorokhova, *Tr. Khim. - Metallurg. In-ta. AN Kaz SSr*, 29 (1980) 52.
162 E. Takayama, *J. Solid St. Chem.*, 39 (1981) 135.
163 J.M. Longo, H.S. Horowitz and L.R. Clavenna, *Adv. Chem. Ser.*, 186 (1980) 139.
164 H. Takei, *J. Mater. Sci.*, 16 (1981) 1310.
165 R.T. Richardson, *J. Mater. Sci.*, 15 (1980) 2569.
166 M. Schaefer and H.J. Zacharias, *Hemsdorfer Tech. Mitt.*, 19 (1979) 1735.
167 K.V. Ramanujachary and C.S. Swamy, *Indian J. Chem.*, 20A (1981) 96.
168 N.N. Tikhomirova and I.V. Nikolaeva, *Proc. Int. Conf. Zeolites, 5th*, (1980) 230.
169 G. Nishiyama and H. Hayashi, *Nagoya Kogyo Gijutsu Shikensho Hokoku*, 30 (1981) 75.
170 E. Brechtel, G. Cordier and H. Schafer, *Z. Naturforsch.*, 36B (1981) 27.
171 H.C. Mishra, S.K. Roy and A.N. Ojha, *J. Indian Chem. Soc.*, 57 (1980) 929.
172 M. Faist, *(USSR) Deposited Doc.*, VINITI 3782 (1979) 31.
173 W. Halliop and J. Matysik, *Ann. Univ. Mariae Curie-Sklodowska Sect. AA*, 31-32 (1976-77, Publ. 1980) 197.
174 H. Terasawa, T. Kambara, K.I. Gondaira, T. Teranishi and K. Sato, *J. Phys. C. Solid St. Phys.*, 13 (1980) 515.
175 J.M. Hastings, L.M. Carliss, W. Kunnmann and D. Mukamel, *Phys. Rev. B.*, 24 (1981) 1388.
176 S.C. Schaefer, *Rep. Invest. - U.S., Bur. Mines*, RI 8486 (1980) 20 pp.
177 H.D. Lutz, G. Kliche and H. Haeuseler, *Z. Naturforsch.*, 36A (1981) 184.
178 G.V. Loseva, L.I. Ryabinkina and A.V. Baranov, *Magnit. i. Rezonansn. Svoistva Magnit. Materialov, Krasnoyarsk*, (1980) 131.
179 L. Ben-dor and I. Shilo, *J. Solid St. Chem.*, 35 (1980) 103.
180 A.S. Gates and J.G. Edwards, *J. Phys. Chem.*, 84 (1980) 3263.
181 R. Rimet, R. Buder, C. Schlenker, R. Roques and J.V. Zanchetta, *Solid St. Commun.*, 37 (1981) 693.
182 R. Plumier, *J. Phys. Chem. Solids*, 41 (1980) 871.
183 A.K. Cheetham, A.J. Cole and G.J. Long, *Inorg. Chem.*, 20 (1981) 2747.
184 W. Wegener, S. Hautecler and G. Will, *Phys. Status Solidi B*, 105 (1981) 491.
185 S. Kozuchova, S. Nagyova and M. Rakos, *Czech. J. Phys.*, 30B (1980) 1289.
186 J. Murin, D. Olcak, J. Oravcova, M. Rakos and K. Jelsovska, *Czech. J. Phys.*, 31B (1981) 313.
187 I. Ahmad, O. Odyek, C.M. Ashraf and A.D. Olal, *Bull. Soc. Chim. Belg.*, 90 (1981) 241.
188 W. Pasiuk-Bronikowska and T. Bronikowski, *Chem. Eng. Sci.*, 36 (1981) 215.
189 E. Barchese, H.C. Chagas and S. Wolynec, *An. Acad. Bras. Cienc.*, 52 (1981) 679.
190 B. Banarjee, P.K. Biswas and N.R. Chaudhuri, *Thermochim. Acta*, 47 (1981) 15.
191 M.Y. Apte and C. Mande, *J. Phys. Chem. Solids*, 42 (1981) 605.
192 J. Kapturczak and Z. Pajak, *Phys. Status Solidi B*, 104 (1981) 479.
193 V.E. Bomshtein, L.A. Leont'eva and L.D. Iskhakova, *Tr. Vnii Khim. Reaktivov i Osobo Chist. Khim. Veshchestv*, 41 (1979) 32.
194 C. Preti and G. Tosi, *Aust. J. Chem.*, 33 (1980) 1203.
195 S.P. Malela and B.L. Khandelwal, *Neorg. Khim.*, 25 (1980) 3019.

196 I. Tanabe, R. Nagata, T. Watanabe and N. Miyamoto, *Renkikagakuoyobi Kogyo Butsuri Kagaku*, 49 (1981) 192.

197 A.Ya. Sychev, U. Pfannmuller and V.G. Isak, *Zh. Fiz. Khim.*, 55 (1981) 365 (Russ.).

198 T.J.W. De Bruijn, W.A. De Jong and P.J. Van den Berg, *Therm. Anal. [Proc. Int. Conf. Therm. Anal.] 6th*, 1 (1980) 393.

199 T.J.W. De Bruijn, G.M.J. De Ruiter, W.A. De Jong and P.J. Van den Berg, *Thermochim. Acta*, 45 (1981) 279.

200 T.J.W. De Bruijn, A.N. Ipekoglu, W.A. De Jong and P.J. Van den Berg, *Thermochim. Acta*, 45 (1981) 293.

201 T.J.W. De Bruijn, A.N. Ipekoglu, W.A. De Jong and P.J. Van den Berg, *Thermochim. Acta*, 45 (1981) 305.

202 T.J.W. De Bruijn, W.A. De Jong and P.J. Van den Berg, *Thermochim. Acta*, 45 (1981) 265.

203 V. Kleinmann and M. Stockhausen, *Z. Naturforsch.*, 36A (1981) 751.

204 Kh. Balarov and D. Barkov, *God. Vissh. Khim. - Teknol. Inst. Burgas, Bulg.*, 13 (1978) 79.

205 E.G. Davitashvili and M.E. Modebadze, *Izv. Akad. Nauk. Gruz. SSR, Ser. Khim.*, 7 (1981) 7.

206 V. Trushinska, A. Dindune and V. Konstants, *Term. Anal. Tezisy Dokl. Vses. Soveshch.*, 1 (1979) 174.

207 Z.N. Prozorovskaya, I.V. Arkhandel-skii and L.N. Komissarova, *Term. Anal. Tezisy Dokl. Vses. Soveshch.*, 1 (1979) 209.

208 P. Baraldi and G. Fabbri, *Spectrochim. Acta*, 37A (1981) 89.

209 V. Iranzo, M.L. Martinez-Sarrion and J.I. Oliva, *Circ. Farm.*, 38 (1980) 173.

210 W. Brzyska and J. Kurcaba, *Biul. Lubel. Tow. Nauk. [Wydz.]: Mat.-Fiz.-Chem.*, 22 (1980) 53.

211 T. Sato, M. Yamamoto and H. Watanabe, *Int. Solvent Extr. Conf. [Proc.], 3*, (1980) Paper 80-178, 10 pp.

212 S. Paraskewas and L. Lapatsanis, *Chem.-Ztg.*, 105 (1981) 151.

213 W. Brzyska, *Ann. Univ. Mariae Curie-Sklodowska, Sect. AA, Phys. Chem.*, 31-32 (1976-77, Publ. 1980) 233 (Pol.).

214 B.D. Heda, S.G. Kaskedikav and P.V. Khadikar, *Indian J. Hosp. Pharm.*, 17 (1980) 39.

215 H.C. Mishra and R.R. Jha, *J. Indian Chem. Soc.*, 57 (1980) 769.

216 S. Murakami, *J. Inorg. Nucl. Chem.*, 43 (1981) 335.

217 V.A. Logvinenko, L.I. Myachina and T.V. Ipatova, *Izv. Sib. Otd. Akad. Nauk SSR, Ser. Khim. Nauk.*, 5 (1980) 41.

218 J. Oakes and E.G. Smith, *J. Chem. Soc., Faraday Trans. II*, 77 (1981) 299.

219 M. Schnitzer and H. Kerndorff, *Water, Air, Soil Pollut.*, 15 (1981) 97.

220 M. Badri, K.A. Crouse and W. Ibrahim, *Pertanika*, 3 (1980) 148.

221 Z. Ciunik and T. Glowiak, *Acta Cryst.*, B37 (1981) 693.

222 L. Nordenskiold, J. Kowalewski and N. Benetis, *Inorg. Chim. Acta*, 56 (1981) L21.

223 W.L. Driessen and P.L.A. Everstijn, *J. Coord. Chem.*, 10 (1980) 155.

224 F.J. Ianconianni, L.L. Pytlewskii, C.M. Mikulski and N.M. Karayannis, *Inorg. Chim. Acta*, 53 (1981) L21.

225 Z. Ciunik and T. Glowiak, *Acta Cryst.*, B36 (1980) 2029.

226 A.N. Smirnov, A.Yu. Tsivadze, Yu.Ya. Kharitonov and E.G. Tselebrovskaya, *Koord. Khim.*, 6 (1980) 1688.

227 A. Gergely, T. Kiss, G. Deak and I. Sovago, *Inorg. Chim. Acta*, 56 (1981) 35.

228 A. Gergely, T. Kiss, G. Deak and I. Sovago, *Magy. Kem. Foly.*, 87 (1981) 219.

229 P.A. Vigato, U. Casellato, B. Acone, M. Vidali and D.E. Fenton, *Inorg. Nucl. Chem. Lett.*, 16 (1980) 489.

230 M. Genchev and K. Davarski, *God. Vissh, Khim. - Tekhnol. Inst. Burgas*, 13 (1978) 39.

231 W. Marty, *Synth. React. Inorg. Met-Org. Chem.*, 11 (1981) 411.

232 H.L. Kalra and B.S. Khokhar, *Acta Cienc. Indica, [Ser.] Chem.*, 6 (1980) 6.

233 K. Lal and S.P. Gupta, *Bangladesh J. Sci. Ind. Res.*, 14 (1979) 316.
234 M.L. Morris and R.D. Koob, *Inorg. Chem.*, 20 (1981) 2737.
235 B. Durairaj and K. Venkataroo, *Thermochim. Acta*, 43 (1981) 125.
236 V.A. Alekseevskii, *Fiz-Khim. Issled, Sintetich. i Prirod Soedin., Samarkand*, (1980) 61.
237 B.V. Rao, D. Reddy and M.L.N. Reddy, *Indian J. Chem.*, 20A (1981) 209.
238 D.R. Crow and D. Fonseca, *J. Inorg. Nucl. Chem.*, 42 (1980) 1595.
239 W. Fichtner and A. Weiss, *J. Mol. Structure*, 66 (1980) 289.
240 M.C. Hughes, D.J. Macero and J.M. Rao, *Inorg. Chim. Acta*, 49 (1981) 241.
241 O.E.S. Godinho and L.M. Aleixo, *J. Coord. Chem.*, 10 (1980) 207.
242 M.V. Veidis, B. Dockum, F.F. Charron Jr., W.M. Reiff and T.F. Brennan, *Inorg. Chim. Acta*, 53 (1981) L197.
243 I. Bernal and R.A. Palmer, *Inorg. Chem.*, 20 (1981) 295.
244 D.W. Englelfreit, W.L. Groeneveld and G.M. Nap, *Z. Naturforsch.*, 35A (1980) 1387.
245 B.K. Sahu and B.K. Mohapatra, *J. Indian Chem. Soc.*, 57 (1980) 936.
246 V. Englelhardt, B. Friedrich and I. Kirner, *Z. Naturforsch.*, 36B (1981) 791.
247 G. Vos, J.G. Haasnoot and W.L. Groeneveld, *Z. Naturforsch.*, 36B (1981) 802.
248 V.B. Rana, D.P. Singh and M.P. Teotia, *Transition Met. Chem. (Weinheim, Ger.)*, 6 (1981) 189.
249 N.M. Titov, I.I. Kalinichenko, A.I. Purtov and E.A.N. Komenko, *Zh. Neorg. Khim.*, 26 (1981) 2153.
250 D.G. Batyr, B.M. Baloyan, E.V. Popa and Yu.Ya. Kharitonov, *Koord. Khim.* 7 (1981) 648.
251 M.S. Barvinok and L.V. Mashkov, *Zh. Neorg. Khim.*, 25 (1980) 2846.
252 A. Kircheiss, U. Pretsch and U. Borth, *Z. Chem.*, 20 (1980) 349.
253 Y. Bizri, M. Cromer-Marin and J.P. Scharff, *C.R. Seances Acad. Sci., Ser. 2*, 292 (1981) 447.
254 Y. Abe and G. Wada, *Bull. Chem. Soc. Jpn.*, 53 (1980) 3547.
255 F.J. Andres-Ordox, J.M. Merino and A. De Diego, *An. Quim., Ser. A*, 76 (1980) 235.
256 P.S. Relan, *Haryana Agric. Univ. J. Res.*, 10 (1980) 403.
257 A. Guarino, E. Possagno and R. Bassanelli, *J. Chem. Soc., Faraday Trans. I*, 76 (1980) 2003.
258 V.I. Simonenko, I.V. Pyatnitskii and G.K. Nizkaya, *UKr. Khim. Zh.*, 46 (1980) 1099.
259 W. Libus, B. Janaszewski, R. Pastewski and H. Twardowska, *J. Solution Chem.*, 9 (1980) 737.
260 D.G. Batyr, B.M. Baloyan, E.V. Popa and Yu.Ya. Kharitonov, *Koord. Khim.*, 7 (1981) 598.
261 S. Randhawa, B.S. Pannu and S.L. Chopra, *J. Indian Chem. Soc.*, 58 (1981) 437.
262 R. Ghose and A.K. Dey, *Rev. Chim. Miner.*, 17 (1980) 492.
263 M. Takahashi and T. Iwamoto, *J. Inorg. Nucl. Chem.*, 43 (1981) 253.
264 K. Lal and R.K. Shukla, *J. Indian Chem. Soc.*, 52 (1981) 115.
265 D.S. Rao and M.C. Ganorkar, *J. Indian Chem. Soc.*, 58 (1981) 217.
266 A.M. Karampurwala, R.P. Patel and J.R. Shah, *Angew, Makromol. Chem.*, 89 (1980) 57.
267 S.K. Sengupta, S.K. Sahni and R.N. Kapoor, *Acta Chim. Acad. Sci. Hung.*, 104 (1980) 89.
268 M.W. Lynch, D.N. Hendrickson, B.J. Fitzgerald and C.G. Pierpoint, *J. Am. Chem. Soc.*, 103 (1981) 3961.
269 G. Smith, E.J. O'Reilly and C.H.L. Kennard, *Aust. J. Chem.*, 34 (1981) 891.
270 W.L. Driessen and P.L.A. Everstijn, *Inorg. Chim. Acta*, 41 (1980) 179.
271 Th.F. Zafiropoulas, S.P. Perlepes, P.V. Ioannou, J.M. Tsangaris and A.G. Galinos, *Z. Naturforsch.*, 36B (1981) 87.
272 B.D. Pandey and D.C. Rupainwar, *Transition Met. Chem. (Weinheim, Ger.)*, 6 (1981) 249.
273 S. Garter and D.W. Engelfriet, *Acta Cryst.*, B37 (1981) 1214.
274 A. Izquierdo, M. Gine and R. Compano, *J. Inorg. Nucl. Chem.*, 43 (1981) 617.
275 R.S. Srivastara, *J. Inorg. Nucl. Chem.*, 42 (1980) 1526.

276 M. Goodgame and K.W. Johns, *Inorg. Chim. Acta*, 46 (1980) 23.

277 B. Chiswell, *Inorg. Chim. Acta*, 41 (1980) 165.

278 A.N. Speca, C.M. Mikulski, F.J. Iaconianni, L.L. Pytlewski and N.M. Karayannis, *Inorg. Chim. Acta*, 46 (1980) 235.

279 O. Siiman, *Inorg. Chem.*, 20 (1981) 2285.

280 G.A. Eisman and W.M. Reiff, *Inorg. Chem.*, 20 (1981) 3481.

281 B. Buss, W. Clegg, G. Hartmann, P.G. Jones, R. Mews, M. Noltmeyer and G.M. Sheldrick, *J. Chem. Soc. Dalton Trans.*, (1981) 61.

282 I. Lukes, I. Smidova and M. Ebert, *Z. Chem.*, 21 (1981) 190.

283 J.Y. Lee and G.W. Everett Jr., *J. Am. Chem. Soc.*, 103 (1981) 5221.

284 F. Bigoli, E. Leporati and M.A. Pellinghelli, *J. Chem. Soc. Dalton Trans.*, (1981) 1531.

285 R.S. Srivastava, L.D.S. Yadav, R.K. Khare and A.K. Srivastava, *Indian J. Chem.*, 20A (1981) 516.

286 V.V. Zelentsov, I.K. Somova, R.Sh. Kutanidze, V.V. Korotkova and G.V. Tsintsadze, *Koord. Khim.*, 7 (1981) 1072.

287 J.R. Allan, G.M. Baillie and N.D. Baird, *J. Coord. Chem.*, 10 (1980) 171.

288 M.M. Aly and A.M. Shalaby, *Monatsh. Chem.*, 111 (1980) 935.

289 R. Singh and R.S.S. Rao, *J. Mol. Structure*, 71 (1981) 23.

290 A.K. Rana and J.R. Shah, *Indian J. Chem.*, 20A (1981) 142; 20A (1981) 615.

291 S.K. Garg, S. Mukharjee, B.S. Garg and R.P. Singh, *Indian J. Chem.*, 20A (1981) 535.

292 I.S. Ahiya, R. Singh and C.L. Yadava, *J. Mol. Structure*, 74 (1981) 143.

293 R.D. Hancock, *Inorg. Chim. Acta*, 49 (1981) 145.

294 R.S. Srivastava, *Inorg. Chim. Acta*, 55 (1981) L71.

295 N.R. Shah and J.R. Shah, *J. Inorg. Nucl. Chem.*, 43 (1981) 1583.

296 K. Nakagana, T. Ogata, K. Haraguchi and S. Ito, *Bunseki Kagaku*, 30 (1981) 149.

297 J. Terheijden, W.L. Driessen and W.L. Groeneveld, *Transition Met. Chem. (Weinheim, Ger.)*, 5 (1980) 346.

298 W. Jaehnig, *Z. Chem.*, 20 (1980) 421.

299 M.M. Mohan, W.U. Malik, R. Dutt, *Monatsh. Chem.*, 111 (1980) 1273.

300 E.N. Zedelashvili, A.E. Shvelashvili and D.A. Gogorishvili, *Zh. Neorg. Khim.*, 25 (1980) 3309.

301 R.S. Sandhu and R.K. Kalia, *Ann. Chim.*, 70 (1980) 625.

302 M. Mohan and B.D. Paramhans, *Indian J. Chem.*, 19A (1980) 759.

303 M. Kunari and L. Narain, *Trans. SAEST*, 15 (1980) 265.

304 A. Ramesh, R.S. Naidu and R.R. Raghava, *Indian J. Chem.*, 19A (1980) 1133.

305 N. Koprivanac, J. Jonanovic-Kolar and D. Renko, *Croat. Chem. Acta*, 54 (1981) 149.

306 K.G. Sharma, R.P. Mathur and R.K. Mehta, *J. Indian Chem. Soc.*, 58 (1981) 225.

307 M.S. Patil, N.R. Shah, A.K. Rana, A.M. Karampurwala and J.R. Shah, *J. Macromol. Sci. Chem.*, A16 (1981) 737.

308 M.Ya. Abdybaliev and M.K. Kydynov, *Deposited Doc.*, VINITI 2511 (1980).

309 M.Ya. Nifad'eva and M.K. Kydynov, *Izv. Akad. Nauk. Kirg. SSR*, 4 (1980) 48.

310 D.G. Batyr, B.M. Baloyan, E.V. Popa and Yu.Ya. Kharinotov, *Koord. Khim.*, 7 (1981) 737.

311 M. Kareko, N. Ishihara and A. Yamada, *Macromol. Chem. Phys.*, 182 (1981) 89.

312 K. Lal and S.R. Malhotra, *S. Afr. J. Sci.*, 77 (1981) 237.

313 C. Pelizzi, G. Pelizzi and G. Predieri, *Congr. Naz. Chim. Inorg., [Atti], 12th*, (1979) 370.

314 R. Jain, D.D. Agarwal and A.K. Jain, *Thermochim. Acta*, 46 (1981) 61.

315 S. Paraskewas, L. Lapatsanis and C. Mantzos, *Chem.-Ztg.*, 105 (1981) 227.

316 G.V. Reddy, D.S. Rao and M.C. Ganorkar, *Natl. Acad. Sci. Lett.*, 4 (1981) 13.

317 C.E. Carraher Jr., V.R. Foster, H.M. Molloy, M.L. Taylor, T.O. Tiernan and T.A. Schroeder, *J. Macromol. Sci. Chem.*, A16 (1981) 231.

318 I. Rani, K.B. Pandeya and R.P. Singh, *J. Indian Chem. Soc.*, 58 (1981) 73.

319 B. Lenarcik, M. Wisniewski and M. Gabryszewki, *Pol. J. Chem.*, 54 (1980) 1869.

320 C. Preti and G. Tosi, *Congr. Naz. Chim. Inorg., [Atti], 12th,* (1979) 96.

321 A.Ya. Sychev, U. Pfannmueller and V.G. Isak, *Zh. Fiz. Khim.*, 55 (1981) 794.

322 M. Marc and A. Ungureanu, *Rev. Roum. Chim.*, 26 (1981) 587.

323 R.S. Naidu, A. Ramesh and R.R. Naidu, *Proc. - Indian Acad. Sci., [Ser.] Chem. Sci.*, 89 (1980) 417.

324 B. Tieke and G. Wegner, *Angew. Chem.*, 93 (1981) 693.

325 L.P. Balkunova, B.K. Dzhashakueva and M.K. Kydynov, *Deposited Doc.*, VINITI 2512 (1980).

326 B.B. Mahapatra, A. Panda, N.C. Mishra and S.K. Pujani, *Indian Chem. Soc.*, 58 (1981) 75.

327 A.T. Rane, *J. Inorg. Nucl. Chem.*, 42 (1980) 1520.

328 R.K. Kadian, J.L. Sharma, S.B. Garg and R.P. Singh, *Indian J. Chem.*, 19A (1980) 819.

329 D. Reddy, B. Sethuram and T.N. Rao, *Indian J. Chem.*, 20A (1981) 533.

330 B.D. Pandey and D.C. Rupainwar, *Indian J. Chem.*, 20A (1981) 197.

331 D. Reddy, B. Sethuram and T.N. Rao, *Indian J. Chem.*, 20A (1981) 150.

332 V.F. Nazarov, Ya.D. Fridman and M.G. Levina, *Koord. Khim.*, 7 (1981) 53.

333 M.R. Chaurasia, S.K. Saxena and S.D. Khattri, *Indian J. Chem.*, 20A (1981) 741.

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

335 K. Lal, S.R. Malhotra, M. Mittal, S.K. Srivastava and S.P. Gupta, *Acta Cience. Indica, [Ser.] Chem.*, 6 (1980) 203.

336 S.B. McCullen and T.L. Brown, *Inorg. Chem.*, 20 (1981) 3528.

337 R.W. Wegman, R.J. Olsen, D.R. Gard, L.R. Faulkner and T.L. Brown, *J. Am. Chem. Soc.*, 103 (1981) 6089.

338 S.P. Church, M. Poliakoff, J.A. Timney and J.J. Turner, *J. Am. Chem. Soc.*, 103 (1981) 7515.

339 M.R. Churchill, K.N. Amohand and H.J. Hasserman, *Inorg. Chem.*, 20 (1981) 1609.

340 L.F. Dahl and R.E. Rundle, *Acta Cryst.*, 16 (1963) 419.

341 D.M. Adams, P.D. Hatton, A.C. Shaw and T-K. Tan, *J. Chem. Soc., Chem. Commun.*, (1981) 226.

342 D.J. Darensbourg, M.Y. Darensbourg and N. Walker, *Inorg. Chem.*, 20 (1981) 1918.

343 W. Heijser, E.J. Baerends and P. Ros, *Faraday Symp. R. Soc. Chem.*, 14 (1980) 211.

344 L.J. Rothberg, D.P. Gerrity and V. Vaida, *J. Chem. Phys.*, 74 (1981) 2218.

345 S. Aime, L. Milone, D. Osella, G.E. Hawkes and E.W. Randall, *Congr. Naz. Chim. Inorg., [Atti], 12th,* (1979) 232.

346 A.E. Stevens and J.L. Beauchamp, *Chem. Phys. Lett.*, 78 (1981) 291.

347 E. Horn, M.R. Snow and P.C. Zelany, *Aust. J. Chem.*, 33 (1980) 1659.

348 M.C. Van Derveer and J.M. Burlitch, *J. Organomet. Chem.*, 197 (1980) 357.

349 T. Lionel, J.R. Morton and K.F. Preston, *Chem. Phys. Lett.*, 81 (1981) 17.

350 F.A. Cotton, D.J. Darensbourg and B.W.S. Kolthammer, *Inorg. Chem.*, 20 (1981) 1287.

351 V.G. Andrianov, Yu.T. Struchkov, N.I. Pyshnograeva, V.N. Setkina and D.N. Kursanov, *J. Organomet. Chem.*, 206 (1981) 177.

352 A. Alberti and C.M. Camaggi, *J. Organomet. Chem.*, 194 (1980) 343.

353 U. Kunze, A. Antoniadis and M. Moll, *J. Organomet. Chem.*, 215 (1981) 187.

354 L. Bussetto and A. Palazzi, *Congr. Naz. Chim. Inorg., 12th,* (1979) 60.

355 L. Bussetto and A. Palazzi, *Congr. Naz. Chim. Inorg., 13th,* (1980) 122.

356 P. Deplano and E.F. Emanuele, *Congr. Naz. Chim. Inorg., 13th,* (1980) 199.

357 P. Deplano and E.F. Trogu, *J. Inorg. Nucl. Chem.*, 43 (1981) 711.

358 P. Deplano and E.F. Trogu, *J. Inorg. Nucl. Chem.*, 43 (1981) 1213.

359 N.I. Pyshnograeva, V.N. Setkina, V.G. Andrianov, Yu.T. Struchkov and D.N. Kursanov, *J. Organomet. Chem.*, 206 (1981) 169.

360 H. Weber and R. Mattes, *Chem. Ber.*, 113 (1980) 2833.

361 G.A. Carriedo and V. Riera, *J. Organomet. Chem.*, 205 (1981) 371.

362 F. Bombin, G.A. Carnedo, J.A. Miguel and V. Riera, *J. Chem. Soc., Dalton Trans.*, (1981) 2049.

363 A. Kececi and D. Rehder, *Z. Naturforsch.*, 36B (1981) 20.

364 D. Fenske, K. Brandt and P. Stock, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 36B (1981) 768.

365 H.C. Aspinall and A.J. Deeming, *J. Chem. Soc., Chem. Commun.*, (1981) 724.

366 G. Fritz and R. Uhlmann, *Z. Anorg. Allg. Chem.*, 465 (1980) 59.

367 M. Savignac, P. Cadiot and F. Matthey, *Inorg. Chim. Acta*, 45 (1980) L43.

368 K.G. Steinhauser, W. Klein and R. Kramolowsky, *J. Organomet. Chem.*, 209 (1981) 355.

369 A.G. Ginzburg, Sh.G. Kasumov, V.N. Setkina and D.N. Kursanov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 4 (1981) 884.

370 R. Talay and D. Rehder, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 36 (1981) 451.

371 T. Madach and H. Vahrenkamp, *Chem. Ber.*, 114 (1981) 513.

372 S. Hayashida, T. Kawamura and T. Yonezawa, *Chem. Lett.*, (1981) 985.

373 E. Lindner and J.-P. Gumz, *Chem. Ber.*, 113 (1980) 3262.

374 J. von Seyerl, L. Wohlfahrt and G. Huttner, *Chem. Ber.*, 113 (1980) 2868.

375 J. von Seyerl and G. Huttner, *J. Organomet. Chem.*, 193 (1980) 207.

376 E. Lindner, H-J. Eberle and S. Hoehne, *Chem. Ber.*, 114 (1981) 413.

377 E. Lindner, G. von Au and H-J. Eberle, *J. Organomet. Chem.*, 204 (1981) 93.

378 E. Lindner, G. Funk and S. Hoehne, *J. Organomet. Chem.*, 214 (1981) C7.

379 H.J. Haupt, F. Neumann, B. Schwab and G. Voigt, *Z. Anorg. Allg. Chem.*, 471 (1980) 175.

380 S. Onaka, Y. Kondo, N. Furuichi and K. Toriumi, *Chem. Lett.*, (1980) 1343.

381 T.C. Flood, J.E. Jensen and J.A. Statler, *J. Am. Chem. Soc.*, 103 (1981) 4410.

382 S.B. Butts, T.G. Richmond and D.F. Shriver, *Inorg. Chem.*, 20 (1981) 278.

383 J.D. Black, M.J. Boylan and P.S. Braterman, *J. Chem. Soc., Dalton Trans.*, (1981) 673.

384 P.J. Fitzpatrick, Y. le Page, J. Sedman and I.S. Butler, *Inorg. Chem.*, 20 (1981) 2852.

385 K.G. Caulton, *Coord. Chem. Rev.*, 38 (1981) 1.

386 U. Schubert, B. Woerle and P. Jandik, *Angew. Chem.*, 93 (1981) 683.

387 D.C. Calabro, J.L. Hubbard, C.H. Blevin II, A.C. Campbell and D.L. Lichtenberger, *J. Am. Chem. Soc.*, 103 (1981) 6839.

388 D. Calabro and D.L. Lichtenberger, *J. Am. Chem. Soc.*, 103 (1981) 6847.

389 D.C. Calabro, D.L. Lichtenberger and W.A. Hermann, *J. Am. Cbem. Soc.*, 103 (1981) 6853.

390 I.B. Benson, S.A.R. Knox, R.F.D. Stansfield and P. Woodward, *J. Chem. Soc., Dalton Trans.*, (1981) 51.

391 A.M. Rosan, *J. Chem. Soc., Chem. Commun.*, (1981) 311.

392 W. Lamanna and M. Brookhart, *J. Am. Chem. Soc.*, 103 (1981) 989.

393 J. Engelbrecht, T. Geiser and E. Weiss, *J. Organomet. Chem.*, 204 (1981) 79.

394 J.C. Selover, M. Marsi, D.W. Parker and J.A. Gladysz, *J. Organomet. Chem.*, 206 (1981) 317.

395 J.Y. Marouille, C. Lelay, A. Benoit, D. Grandjean, D. Touchard, H. Le Bozec and P. Dixneuf, *J. Organomet. Chem.*, 191 (1980) 133.

396 L.M. Korneva, M.I. Rybinskaya, G. Sonnek, K. Haage, H. Reinheckel and V.S. Kaganovich, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 9 (1980) 2159.

397 Sh.O. Guseinov, S.F. Karaev and Sh.V. Garaeva, *Azerb. Khim. Zh.*, 5 (1979) 98.

398 G.E. Herberich, B. Hessner and T.T. Kho, *J. Organomet. Chem.*, 197 (1980) 1.

399 D.L. Johnson and J.A. Gladysz, *Inorg. Chem.*, 20 (1981) 2508.

400 E. Colomer, R.J.P. Corriu and A. Vioux, *Angew. Chem.*, 93 (1981) 488.

401 W. Gaede and E. Weiss, *Chem. Ber.*, 114 (1981) 2399.

402 W. Gade and E. Weiss, *J. Organomet. Chem.*, 213 (1981) 451.

403 A.K. Baev, *Zh. Fiz. Khim.*, 54 (1980) 2169.

404 G.D. Michels and H.J. Svec, *Inorg. Chem.*, 20 (1981) 3445.

405 G. Sbrignadello, *Inorg. Chim. Acta*, 48 (1981) 237.

406 L.H. Staal, J. Keijsper, G. van Koten, K. Vrieze, J.A. Cras and W.P. Bosman, *Inorg. Chem.*, 20 (1980) 555.

407 R.W. Balk, D.J. Stufkens and A. Oskam, *J. Chem. Soc., Dalton Trans.*, (1981) 1124.

408 J.C. Jeffery, R. Navarro, H. Razay and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1981) 2471.

409 J.A.K. Howard, J.C. Jeffrey, M. Laguna, R. Navarro and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1981) 751.

410 J.C. Jeffrey, H. Razay and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1981) 243.

411 S. Onaka, Y. Kando, K. Toriumi and T. Ito, *Chem. Lett.*, (1980) 1605.

412 W. Gaede and E. Weiss, *Angew. Chem.*, 93 (1981) 796.

413 R. Uson, A. Laguna, M. Laguna, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1981) 366.

414 N.E. Kolobova, L.L. Ivanov and O.S. Zhvanto, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 6 (1981) 1435.

415 M. Boerner and H. Vahrenkamp, *Chem. Ber.*, 114 (1981) 1382.

416 N.I. Pyshnograeva, V.N. Setkina and D.N. Kursanov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 6 (1981) 654.

417 M. Gielen and V. Eynde, *Transition Met. Chem., (Weinheim, Ger.)*, 6 (1981) 128.

418 V.W. Day, M.F. Fredrich, M.R. Thompson, W.G. Klemperer, R-S. Liu and W. Shum, *J. Am. Chem. Soc.*, 103 (1981) 3597.

419 N.E. Schore, L.S. Benner and B.E. La Belle, *Inorg. Chem.*, 20 (1981) 3200.

420 W. Kodel, F. Huber and H-J. Haupt, *Inorg. Chim. Acta*, 49 (1981) 209.

421 B.E. Bursten, J.R. Jensen, D.J. Gordon, P.M. Treichel and R.F. Fenske, *J. Am. Chem. Soc.*, 103 (1981) 5226.

422 R.E. Stevens, T.J. Yanta and W.L. Gladfelter, *J. Am. Chem. Soc.*, 103 (1981) 4981.

423 H. Schumann and M. Heissner, *Z. Naturforsch.*, 35B (1980) 863.

424 B.W. Hames, B.W.S. Kolthammer and P. Ledzdins, *Inorg. Chem.*, 20 (1981) 651.

425 J.A. Potenza, R. Johnson, S. Rudich and A. Efraty, *Acta Cryst.*, B36 (1980) 1933.

426 N.G. Connelly, A.R. Lucy and A.M.R. Galas, *J. Chem. Soc., Chem. Commun.*, (1981) 43.

427 N.E. Kolobova, I.A. Lobanova, V.I. Zdanovich and P.V. Petrovskii, *Izd. Akad. Nauk. SSSR, Ser. Khim.*, (1981) 935.

428 N.E. Kolobova, I.A. Lobanova and V.I. Zdanovich, *Izv. Akad. Nauk, SSSR, Ser. Khim.*, 7 (1980) 1651.

429 R.R. Gagne, C.L. Spiro, T.J. Smith, C.A. Hamann, W.R. Thies and A.K. Shiemke, *J. Am. Chem. Soc.*, 103 (1981) 4073.

430 A. Gleizes and M. Verdaguer, *J. Am. Chem. Soc.*, 103 (1981) 7373.

431 B. Lippert and U. Schubert, *Inorg. Chim. Acta*, 56 (1981) 15.

432 L. Bonci, A. Bencini and D. Gatteschi, *Inorg. Chem.*, 20 (1981) 2734.

433 J.H. Mendez, J.M. Calatayud and M.C. Querol, *Afinidad*, 37 (1980) 111.

434 S. Baral, J.A. Labinger, W.R. Scheidt and F.J. Timmers, *J. Organomet. Chem.*, 215 (1981) C53.

435 T. Lis, *Acta Cryst.*, B36 (1980) 2042.

436 B. Bochu, J.L. Buevoz, J. Chenavas, A. Collomb, J.C. Joubert and M. Marezio, *Solid St. Commun.*, 36 (1980) 133.

437 B. Bochu, J.C. Joubert, A. Collomb, B. Ferrand and D. Samaras, *J. Magn. Magn. Mater.*, 15-18 (1980) 1319.

438 S. Bharali, M.P. Gupta, A.P.B. Sinha and S.K. Date, *Indian J. Pure Appl. Phys.*, 18 (1980) 747.

439 E. Pollert and Z. Jirak, *J. Solid St. Chem.*, 35 (1980) 262.

440 M. Perree-Fauvet and A. Gaudemer, *J. Chem. Soc., Chem. Commun.*, (1981) 874.

441 S.K. Mun, M.K. Mallick, S. Mishra, J.C. Chang and T.P. Das, *J. Am. Chem. Soc.*, 103 (1981) 5024.

442 I.A. Duncan, A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. II*, 76 (1980) 1415.

443 A. Harriman and G. Porter, *J. Chem. Soc., Faraday Trans. II*, 76 (1980) 1429.

444 A. Harriman, *J. Chem. Soc., Faraday Trans. I*, 76 (1980) 1978.

445 A. Harriman, *J. Chem. Soc., Faraday Trans. I*, 77 (1981) 369.

446 R.R. Das and B.S. Prabhananda, *J. Inorg. Nucl. Chem.*, 41 (1979) 1615.

447 R.R. Das and K.N. Rao, *Inorg. Chim. Acta*, 42 (1980) 227.

448 D.V. Behere, V.R. Marathe and S. Mitra, *Chem. Phys. Lett.*, 81 (1981) 57.

449 P. Krausz, P. Maillard, S. Gaspard and C. Gianotti, *C.R. Seances Acad. Sci., Ser. C*, 291 (1980) 129.

450 I. Tabushi and N. Koga, *Adv. Chem. Ser.*, 191 (1980) 291.

451 I. Tabushi and A. Yazaki, *J. Am. Chem. Soc.*, 103 (1981) 7371.

452 M.N. Dufour, A.L. Crumbliss, G. Johnston and A. Gaudemer, *J. Mol. Catal.*, 7 (1980) 277.

453 S. Neya, I. Morishima and T. Yonezawa, *Biochemistry*, 20 (1980) 2610.

454 B.N. Figgis, R. Mason and G.A. Williams, *Acta Cryst.*, B36 (1980) 2963.

455 B.N. Figgis, G.A. Williams, J.B. Forsyth and R. Mason, *J. Chem. Soc., Dalton Trans.*, (1981) 1837.

456 A.B.P. Lever, P.C. Minor and J.P. Wilshire, *Inorg. Chem.*, 20 (1981) 2550.

457 A.B.P. Lever and P.C. Minor, *Gov. Rep. Announce. Index (U.S.)*, 81 (1981) 1125.

458 A.B.P. Lever, J.P. Wilshire and S.K. Quan, *Inorg. Chem.*, 20 (1981) 761.

459 H. Przywarska-Boniecka and H. Swirska, *J. Inorg. Biochem.*, 13 (1980) 283.

460 N.T. Moxon, P.E. Fielding and A.K. Gregson, *J. Chem. Soc., Chem. Commun.*, (1981) 98.

461 B.C. Schardt, F.J. Hollander and C.L. Hill, *J. Chem. Soc., Chem. Commun.*, (1981) 765.

462 J.A. Kirby, D.B. Goodin, T. Wydrzynski, A.S. Robertson and M.P. Klein, *J. Am. Chem. Soc.*, 103 (1981) 5537.

463 J.A. Kirby, D.B. Goodin, T. Wydrzynski, A.S. Robertson and M.P. Klein, *J. Am. Chem. Soc.*, 103 (1981) 5529.

464 G. Das, *J. Chem. Phys.*, 74 (1981) 5766.

465 A. Kant and K.A. Moon, *High Temp. Sci.*, 14 (1981) 23.

466 F. Pourarian, E.B. Boltich, W.E. Wallace, R.S. Craig and S.K. Malik, *J. Magn. Magn. Mater.*, 21 (1980) 128.

467 H. Oesterreicher and H. Bittner, *J. Magn. Magn. Mater.*, 15-18 (1980) 1264.

468 P.J. Viccaro, G.K. Shenoy, D. Niarchos and B.D. Dunlop, *J. Less-Common Met.*, 73 (1980) 265.

469 R. Hempelmann and G. Hilscher, *J. Less-Common Met.*, 74 (1980) 103.

470 W.M. Dawson and F.R. Sale, *Metall. Trans. A.*, 11A (1980) 1849.

471 O.V. Kovalev, *Deposited Doc.*, VINITI 3081 (1979).

472 Y. Matsumura, *Kyoyobu Kenkyu Nenpo (Iwate Ika Daigaku)*, 14 (1979) 5.

473 A. Kakizaki, H. Sugawara, I. Nagakura and T. Ishii, *J. Phys. Soc. Jpn.*, 49 (1980) 2183.

474 W. Jeitschko, R. Riihl, U. Krieger and C. Heiden, *Mat. Res. Bull.*, 15 (1980) 1755.

475 B.I. Nolang and L-E. Tergenius, *Acta Chem. Scand.*, A34 (1980) 311.

476 J. Boerio-Goates, E. Lifshitz and A.H. Francis, *Inorg. Chem.*, 20 (1981) 3019.

477 R. Clement, *J. Am. Chem. Soc.*, 103 (1981) 6998.

478 A. Mewis, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 35B (1980) 939.

479 I.S. Busheina and J.B. Headridge, *Analyst (London)*, 106 (1981) 221.

480 M.I. Aivazov, T.I. Bryushkova and V.S. Mkrtchyan, *Teplofiz. Vys. Temp.*, 19 (1981) 309.

481 J. Garcia, R. Navarro, J. Bartolome, R. Burriel, D. Gonzalez and D. Fruchart, *J. Magn. Magn. Mater.*, 15-18 (1980) 1155.