^{55}Mn NMR Characteristics of Carbonylmanganese Complexes with Hetero-substituted Dithioformato-, Thioformamido- and Thioformamide Ligands [1]

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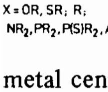
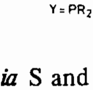
Complexes with the general formulae $[(CO)_4MnS_2CZ]$ *(Z = OR, SR,* NR_2*,* PR_2*,* $P(S)R_2$*,* $AsPh_2$*, Ph),* $[(CO)_4MnSC(NR')PR_2]$*,* $[(CO)_4MnSC(NR')P(S)R_2]$ *and* fac-$[(CO)_3BrMnSC(NHR')PR_2]$ *exhibit* ^{55}*Mn chemical shift ranges which allow classification with respect to the mode of coordination of the thio ligand and the ring size of the chelate structure. Shielding decreases, in the series chelate-4 ring (S,P-coordinated) > chelate-5 ring (S,S') > chelate-4 ring (S,S'). Within the group of* $[(CO)_4MnS_2CZ]$ *complexes, shielding decreases in the order* NR_2 *> OR > Ph >* $AsPh_2$ *>* $P(S)R_2$ *> SR. The trends are explained in terms of varying contributions of molecular parameters to the paramagnetic term of the shielding constant, and related to structure data. There is no apparent correlation between line widths of the* ^{55}*Mn resonance signals and molecular parameters.*

Introduction

Heterosubstituted dithioformato (i), thioformamido (ii) and thioformamide ligands (iii) may principally coordinate as bidentate chelate ligands to a


i

X = OR, SR; R;
NR₂, PR₂, P(S)R₂, AsR₂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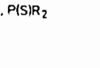
iii

Y = PR₂, P(O)R₂, P(S)R₂

metal center *via* S and S, S and N, or if X, Y = PR_2, $P(O)R_2$ or $P(S)R_2$, via P and S, P and N, S and S' or S and O, forming chelate-4 and chelate-5 ring structures. Most of these structures have been realized in various complexes synthesized by Kramolowsky et al. [2–4], Kunze *et al.* [5–9] and the group of Steggerda at the University of Nijmegen [10–15]. The mode of coordination in these complexes has largely been discussed in terms of IR and Raman as well as ^{1}H, ^{13}C [16] and ^{31}P NMR spectroscopy. Only recently, X-ray data on several tetra- and tricarbonylmanganese derivatives of i, ii and iii (Table I) have established 4-ring structures with S,P coordination in the case of ii and iii, and S,S coordination if the structural unit contains the $-CS_2$ or $=C(S)P(S)$ moiety.

We discuss here the chemical shift values $\delta(^{55}Mn)$ as a diagnostic tool to elucidate the coordination behaviour of i, ii and iii and related ligands towards carbonylmanganese complexes in solution. The discussion will be based upon the parameters influencing the paramagnetic deshielding contribution (which dominates variations of the overall shielding [20]), quantified by

$$\sigma'_{para} = -\text{const.}\ \overline{\Delta E}^{-1}\ \langle r^{-3}\rangle c^2$$

$\overline{\Delta E}$ is the mean electronic excitation energy between HOMOs and LUMOs, $\langle r^{-3}\rangle$ is the quantum-mechanical expectation value of r^{-3} (r = distance of the manganese-3*d* electrons from the nucleus), and c^2 is the square of the LCAO coefficient of the Mn-3*d* orbitals taking part in electronic transitions.

Results and Discussion

$\delta(^{55}Mn)$ and half-widths $\Delta\nu_{1/2}$ are collected in Table II. The shift values span a range of 1000 ppm, flanked by $[(CO)_3py\overline{MnS_2CO}]^+$ on the high-frequency and $(CO)_4\overline{MnSC(NPh)P}Cy_2$ on the low-frequency side. As shown in Fig. 1, the manganese shielding in these tri- and tetracarbonyl complexes compares with that of $Mn(CO)_5Hal$ (where Hal is

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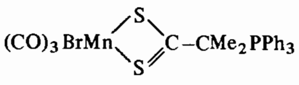
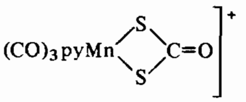
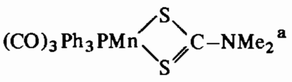
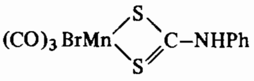
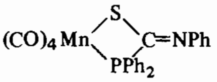
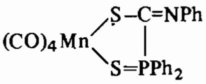
TABLE I. Structure Data for Selected Samples of the Title Compounds (Angles in deg, Bond Lengths (d) in pm).

Complex	Refs.	angles at Mn	d(MnS)	d(MnP)	d(SC)	d(PC)	d(CE)
	17	72.5(1)	235.1(1) 238.0(1)		169.1(5) 167.5(5)		152.2(6) d(CC)
	18	74.0(1)	238.1(1)		175.8(7)		122.4(10) d(CO)
	19	73.6(2) 73.1(2)	237.5(6) 238.0(6)		167.0(18) 170.2(18)		139.6(22) 132.4(21) d(CN)
	4, 9	72.5(1)	238.1(3)	231.5(3)	168.4(10)	185.1(9)	129.8(17) d(CN)
	4, 9	72.9(0)	239.8(1)	231.6(1)	176.0(5)	183.9(4)	129.0(5) d(CN)
	9	90.01(3)	239.0(1) 241.0(1)		173.3(3)	182.6(3)	126.6(4) d(CN)

[a]Two independent molecules.

TABLE II. Chemical Shifts (rel. MnO_4^-) and Half-widths.

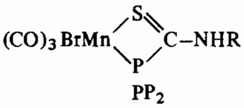
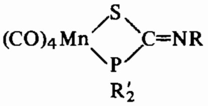
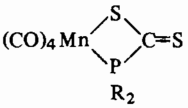
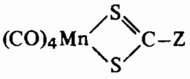
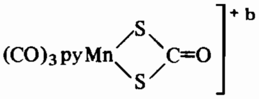
Complex	Type	$\delta(^{55}Mn)$ (ppm)	$\Delta\nu_{1/2}$ (kHz)
	**2**	R = Me −1570[a] Et −1570[a] Ph −1550[a]	2.0 1.8
	**2**	R′ = Ph, R = Me −1545 R′ = Ph, R = Ph −1530 R′ = Cy, R = Ph −1620	3.0 0.90 0.89
	**2**	R = Ph −1450 Cy −1480	0.95 0.83
	**1**	Z = NEt_2 −1035 NMe_2 −1030 OEt/OMe −970/−960 Ph −925 $AsPh_2$ −805 $P(S)Cy_2$ −790 SEt/SMe −780/−780	3.35 2.3 3.2/1.5 4.1 4.9 4.5 3.2/3.5
	**1**	−620	

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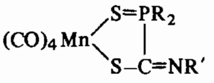
TABLE II. *(continued)*

Complex	Type	$\delta(^{55}Mn)$ (ppm)	$\Delta\nu_{1/2}$ (kHz)
	3	R′ = Me, R = Ph −980 R′ = Ph, R = Ph −1150 R′ = Ph, R = Cy −1100	5.9 0.61 0.33
$(CO)_4BrMnPHCy_2$		−1290	3.4
$(CO)_4BrMnPPh_2C(O)NHR$		R = Me −1130 Ph −1060	3.0 6.0

[a] A second signal (−470 to −500 ppm; $\Delta\nu_{1/2}$ *ca.* 5 kHz) is observed. [b] In THF/CH_3CN 1/1.

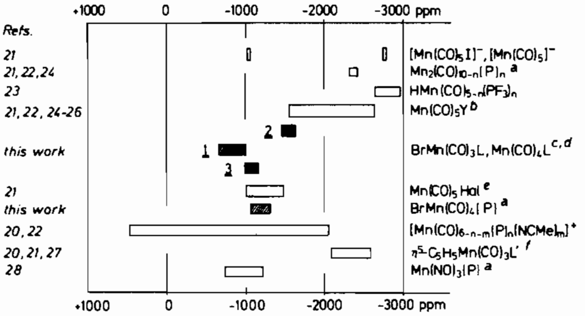
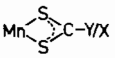


Fig. 1. Presentation of chemical shifts $\delta(^{55}Mn)$ relative to $KMnO_4/H_2O$ (δ = 0). Shaded areas: this work. [a]{P} = Phosphine ligand. [b]Y = R, O=CR, CO_2Et, $E^{IV}R_3$. [c]L = thioamido, thioformamide or dithioformato ligand; for further specification *cf.* Table II. [d]The extreme high-frequency position is occupied by $[(CO)_3pyMnS_2CO]^+$ (py = pyridine). [e]Hal = Cl, Br, I. [f]L′ = {P}, CO.

a halogen), but is considerably less than in the pentacarbonylmanganese complexes of the general formula $Mn(CO)_5R$, where R = alkyl, acyl, CO_2Et or a group IVa triorganyl. This may be considered to be in accord with general observations in transition metal carbonyls, where substitution of CO by a less powerful π-acceptor usually results in successive deshielding of the metal nucleus (mainly *via* a decrease of ΔE). In fact, the complexes $BrMn(CO)_4$-$PPh_2C(O)NHR$ show the expected high-frequency shift relative to that of the parent compound $BrMn(CO)_5$ (δ = −1160 ppm [21]). The comparatively short MN–P bonds in $Br(CO)_3MnSC(NHPh)PPh_2$ and $(CO)_4MnSC(NPh)PPh_2$ (Table I), indicating substantial π-interaction between manganese and phosphorus, also agree with this view. However, as has been demonstrated in several instances [21–26], the ^{55}Mn shielding in carbonyl manganese complexes with Mn in the formal oxidation state +I is also subject to variations in the σ-donor power of the ligand system. Comparison of the shielding data for tetra- and tricarbonyl complexes clearly shows that in our case a simple $\pi/\Delta E$ relation does not hold. Further, since we are dealing with chelating ligands, the chelate-ring effect [29, 30] has to be taken into account.

Following the coordination behaviour of the thio ligands, the complexes listed in Table II may be allocated to three groups: chelate 4-rings, coordinating *via* two S functions (**1**), chelate-4 rings coordinating *via* S and P (**2**), and chelate-5 rings with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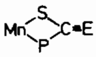
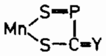

2 E = S, NR′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S,S′ coordination (**3**). S,S and P,S coordination have been established by X-ray structural analysis (Table I). P, S coordination in group 2 may also be derived from the broad ^{31}P resonances ($\Delta\nu_{1/2}$ = 60 to 100 Hz), while the ^{31}P coordination shift $\Delta\delta(^{31}P)$ [29] is not always an unambiguous criterion for S, P or S,S coordination.

Generally, the shielding decreases in the order **2** > **3** > **1** (there is a small range of overlap between **1** and **3**), *i.e.* shielding is larger in S,S coordinated 5-rings than in 4-ring structures, and P, S coordination produces a larger ^{55}Mn shielding than S,S, coordination. This effect may well be accounted for in terms of influences dominated by ΔE (*vide supra*). The larger ΔE observed in S,P coordinated phosphinothioamides has been verified for Ni^{2+} complexes [31]. The term $\langle r^{-3}\rangle c^2$, which represents nephelauxetic effects ($\langle r^{-3}\rangle$) and the covalency of the manganese–ligand bond (c^2), should be approximately the same for the two neighbours in the third period, S and P.

A high-frequency shift of the metal resonance on introduction of a sulfur ligand into the coordination sphere has also been reported for S-coordinated ligands in derivatives of $[V(CO)_6]^-$ [32], η^5-$C_5H_5V(NO)_2CO$ [33] and $\{\eta^5$-$C_5H_5Mo(CO)_3\}$ [34], and is quite commonly observed in Mo(VI) [35] and Nb(V) complexes [36].

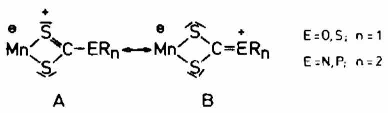
The high-frequency shift in chelate-4 rings relative to chelate-5 rings reflects variations in $\langle r^{-3}\rangle c^2$ rather than in ΔE. These variations come about by enhanced ring strains on going from the 5-membered to the 4-membered ring system, resulting in non-optimal bond angles (and bond lengths) at the manganese centre (Table I). These non-ideal overlap conditions affect a more pronounced manganese participation to the 3*d*-type MOs taking part in electronic transitions; hence an increase of c^2 and of $\langle r^{-3}\rangle$, *i.e.* an overall increase of the paramagnetic deshielding term and decrease of the overall shielding (decrease of $|\delta|$). This chelate-ring effect has also been described for chelate-ring structures involving, among others, the nuclei ^{51}V [30] and ^{195}Pt [37].

It is of further interest to compare influences induced by a substituent X/Y in the type **1** complexes. Here, ^{55}Mn shielding decreases in the series

$$NR_2 > OR > Ph > AsPh_2 > P(S)R_2 > SR,$$

partly paralleling similar observations for $\delta(^{51}V)$ in $(\eta^5\text{-}C_5H_5)_2VS_2CY$ ($OR > NR_2 \approx AsPh_2 > PPh_2 > P(O)Bz_2 > P(S)Ph_2$ [38]) and for $\delta(^{59}Co)$ in $[Co(S_2CY)_3]^{3+}$ ($OR > SR > NR_2$ [39]). In the case of ^{59}Co shielding , this trend is related to the ΔE values and this is also true for $\delta(^{51}V)$, if Y = $P(O)R_2$ and $P(S)R_2$, for which rather small ΔE values have been observed.

For the pairs OR/SR and NR_2/PR_2, there is a high-frequency shift on going from the 2nd to the 3rd period. This effect, originating from influences imposed by atoms in the second coordination sphere of manganese, is somewhat surprising and should account for a substantial participation of the group X/Y in the overall electronic arrangement within the metalla cycle. It may be traced back to increased participation of the resonance structure B, if X/Y = OR and NR_2, giving rise to an increased σ-interaction between the metal and the donating ligand function (*i.e.* an increase of ΔE and a decrease of $\langle r^{-3}\rangle$ and c^2).



The complexes $Br(CO)_3MnSC(NHR)PPh_2$ exhibit, in addition to the comparatively narrow signal ($\Delta\nu_{1/2} \leqslant 2$ kHz) at −1570 ppm typical of S,P coordination (**2**) with facial arrangement of the three CO ligands, a broad signal (*ca.* 5 kHz) at around −500 ppm. This resonance may be due either to an N, P or N, S coordinated isomer and/or to an isomer with meridional arrangement of the CO ligands (for which the point charge model predicts a large electric field gradient at the ^{55}Mn nucleus and hence a broad line). Alternatively, dimerization to SS bridged species may occur. Further investigations into this problem are in progress.

Experimental

The complexes were prepared as described in refs. 3, 5, 6, 8 and 18. NMR spectra were obtained on a Bruker WH 90 (at 22.31 MHz) and a Bruker SWL 3-100 wide-line spectrometer (16.0 MHz; central field 1.5185 T) with the specifications given in refs. 20 and 22. Approximately 0.1 *M* THF solutions in 7.5 (WH 90) and 15 mm (SWL 3-100) diameter vials were employed. Measuring temperature was 300 ± 2 K, external standard saturated aqueous $KMnO_4$. The spectra were digitilized and fitted to a Gaussian function. The absolute errors of δ are ±5 to ± 20 ppm, depending on the line width (0.8 to 6 kHz), the error of $\Delta\nu_{1/2}$ ±0.1 to ±0.3 kHz.

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