The Chalcogen Dependence of ^{51}V and ^{55}Mn Shielding in the Complexes [V(CO)$_5$L]$^-$, [V(NO)(CO)$_4$L] and [Mn(NO)$_3$L]

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Shielding of the metal nuclei in transition metal complexes, quantified by the shift parameter δ(M), is sensitive to the electronegativity or related quantities (such as the polarizability or bond ionicity) of the ligand functions attached to the metal. This phenomenon has been investigated for the halogen dependence of metal shielding, where a so-called normal trend (increase of metal shielding in the series F < Cl < Br < I) has been noted for systems with partially filled metal(d) orbitals, while an inverse trend is observed for d^0 systems [1, 2]. Corresponding dependencies have also been reported sporadically for group IVa, Va and VIa ligands and across the periods [2]. Well-documented examples for an inverse chalcogen dependence of δ(M) include the complexes $Tl_3[VE_4]$ and $Cu_3[VE_4]$ [3], $[NbEX_4]^-$ [4], $[MoE_4]^{2-}$ [5] and $[MoE_2(ONR_2)_2]$ [6], where E is a chalcogeno ligand. Normal trends have been observed for [CpV(NO)$_2$L] (d^4, L = ether and thioether [7]), [Co(LL)$_3$] (d^6, LL = acac$^-$, $S_2CNMe_2^-$, $Se_2CNMe_2^-$) [8], and [Mo(NO)$_2$(LL)$_2$] (d^4, LL = acac$^-$, $S_2CNMe_2^-$) [9], but also for the Zn(d^{10}) complexes $[ZnL_4]^{2-}$ (L = SPh, SePh) [10].

In the present work the chalcogen dependence of ^{51}V shielding in [V(CO)$_5$L]$^-$ and [V(NO)(CO)$_4$L], and of ^{55}Mn shielding in [Mn(NO)$_3$L] is investigated systematically for L = THF, SMePh, SePh$_2$ and TePh$_2$, and related to the metal shieldings in the parent carbonyls and complexes containing the ligands CNCy, NCMe, pyridine (py) and NEt$_3$. The data are collected in Table I and presented graphically in Fig. 1.

The complexes [Et$_4$N] [V(CO)$_5$L] were obtained by UV irradiation (high pressure mercury lamp) of [Et$_4$N] [V(CO)$_6$] at low temperatures in the respective solvent (L = THF, MeCN, py) or in THF/MeCN

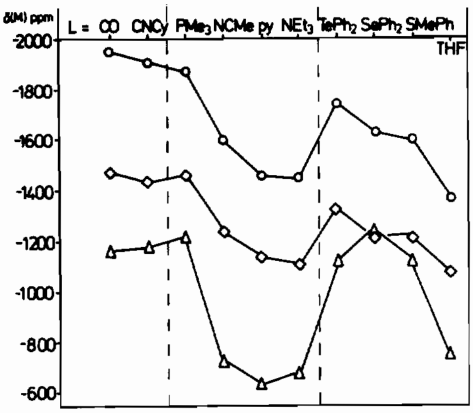

Fig. 1. δ(M) values of the complexes [V(CO)$_5$L]$^-$ (○), [V(NO)(CO)$_4$L] (◇) and [Mn(NO)$_3$L] (△), relative to neat VOCl$_3$ (M = ^{51}V) and aqueous, satur. K[MnO$_4$] (M = $^{55}_{55}$Mn).

TABLE I. Metal Chemical Shifts.^{a}

L	δ(^{51}V)^b [V(CO)$_5$L]$^-$		Phase	[V(NO)(CO)$_4$L]		Phase	δ(^{55}Mn)^{b,c} [Mn(NO)$_3$L]	χ$_L$^{d}
CO		−1952^e	THF	(−1489[245])	−1475^f	CH$_2$Cl$_2$	−1171^g	2.53
CNCy		−1901^e	MeCN		−1441	CH$_2$Cl$_2$	−1175	2.53
PMe$_3$		−1875	THF	−1460^f		THF	−1240	2.13
NCMe	(−1615[255])	−1601	MeCN	(−1261[241])	−1247	NCMe	−730	3.06
py		−1467^e	pyridine	(−1160[239])	−1145	CH$_2$Cl$_2$	−640	3.06
NEt$_3$	(−1482[202])	−1456	THF	(−1139[233])	−1122	CH$_2$Cl$_2$	−680	3.03
TePh$_2$		−1753	THF		−1329	CH$_2$Cl$_2$	−1130	1.94
SePh$_2$	(−1658[207])	−1635	THF	(−1241[241])	−1227	CH$_2$Cl$_2$	−1250	2.29
SMePh	(−1628[207])	−1605^e	THF	(−1241[241])	−1227	CH$_2$Cl$_2$	−1130	2.48
THF	(−1390[207])	−1367^e	THF	(−1099[241])	−1085	THF	−750	3.64

^{a}δ(^{51}V) relative to VOCl$_3$ (neat), δ(^{55}Mn) relative to satur., aqueous K[MnO$_4$]. The spectra were scanned on a Bruker SWL 3-100 Wideline Spectrometer at 16.0 MHz. $B_0(VOCl_3)$ = 14.2973, $B_0([MnO_4]^-)$ = 15.1681 T. Absolute error of δ(M) *ca.* ±10 ppm. ^{b}Data in parentheses were obtained for temperature-labile species at the indicated temperatures (in square brackets); others are room temp. data or data extrapolated to room temp. with a gradient of 0.25 ppm/deg. ^{c}In pentane except of L = McCN (in acetonitrile). ^{d}Ref. [11]. ^{e}Ref. [12]. ^{f}Ref. [13]. ^{g}Ref. [14].

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in the presence of a large excess of L (NEt_3, PMe_3, CNCy), or by addition of L to a solution of $[Et_4N][V(CO)_5THF]$ generated at 195 K [12]. Except for the compounds formed with py, CNCy, PMe_3 and $TePh_2$, the complexes are not stable at room temperature (*cf.* Table I). The complexes $[V(NO)(CO)_4L]$ were prepared by ligand exchange reactions between $[V(NO)(CO)_5]$ (obtained from $[Et_4N][V(CO)_6]$ and $NO[BF_4]$ in CH_2Cl_2 [15]) and L. They form red-orange (L = py, NEt_3, CNCy, NCMe) to brown-violet complexes (SMePh, $SePh_2$, $TePh_2$) and, with the exception of L = PMe_3, CNCy and $TePh_2$, they decompose above *ca.* 250 K. For the preparation of $[Mn(NO)_3L]$, $[Mn(NO)_3\text{-}THF]$ was synthesized by UV irradiation of a THF solution containing equimolar amounts of $[Mn_2\text{-}(CO)_{10}]$ and $[Co(NO)_2Cl]_2$ [16]. After the evaporation of THF and $[Co(NO)(CO)_3]$, $[Mn(NO)_3THF]$ was dissolved in pentane, and the THF was replaced by addition of a three-fold molar excess of L. $SePh_2$ and SMePh do not react quantitatively. The green to brown solutions are stable at room temperature. Characterization of the complexes was – in addition to the metal NMR shifts – carried out by IR. The IR patterns typical of the three series of compounds are documented for L = $TePh_2$: $[V(CO)_5L]^-$, ν(CO) = 1958(w-m), 1820(s), 1790(sh); $[V(NO)(CO)_4L]$, ν(CO) = 1953(s), 1945(sh), ν(NO) = 1628; $[Mn\text{-}(NO)_3L]$, ν(NO) = 1784(s), 1688(vs) cm^{-1}.

Within the series of chalcogen complexes there is the expected normal trend, *i.e.* an increase of metal shielding on going down group VIa, with an inconsistency however for $[Mn(NO)_3SePh_2]$, reminiscent of corresponding observations for the ligands $SnPh_3^-$ and $SbPh_3$ in carbonyl vanadium complexes [17, 18]. The normal trend reflects a decrease of the paramagnetic contribution:

$$\sigma^{para} \propto \overline{\Delta E^{-1}}\langle r^{-3}\rangle \overline{C^2}$$

to the local terms of the overall shielding $\sigma = \sigma^{dia} + \sigma^{para}$ (where σ^{dia} is practically constant). Nonlocal (diamagnetic) contributions may add to the observed trends, although they are usually considered negligibly small, a view which has recently been supported by MO calculations [19, 20].

$\langle r^{-3}\rangle$ (r is the distance of the metal (3d) electrons from the metal nucleus) is inversely related to the ligand nephelauxetic effect, which increases with increasing size and polarizability (decreasing electronegativity) of L. The metal (3d) LCAO coefficient C correlates with the ionicity (covalency) of the M–L bond and hence becomes smaller on going down from oxygen to tellurium ligands. The influences imparted by $\langle r^{-3}\rangle$ and C^2 point in the same direction and (except perhaps in the case of $[Mn(NO)_3SePh_2]$) apparently override counteracting influences arising from the mean HOMO–LUMO splitting ΔE. The latter, which quantifies the strength of the ligand field (in our compounds with low-valent metal centers this is mainly the π strength of the ligands), becomes the predominant factor if L is an excellent to good π acceptor (CO, CNCy, PMe_3). Nitrogen ligands (NCMe, NEt_3 and py) do not effectively delocalize π electrons from the metal (they are 'weak' ligands), nor do they give rise to a sizable nephelauxetic expansion of the metal(3d) cloud. They are, in this respect, comparable to the oxygen ligands and induce low metal shieldings.

The normal trends observed in the vanadium complexes of chalcogen ligands, and also for the pairs of PMe_3/N-ligands, SMePh/PMe_3 and N-ligands/THF, is in contrast to the inverse trend noted earlier for closed shell (d^0) systems, where the main factor responsible for the decrease of metal shielding with decreasing ligand electronegativity appears to be enhanced bond participation of originally empty M(d) orbitals by effective $\pi(L) \rightarrow M$ donation [21].

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