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V-51 and Mn-55 NMR Studies of Metal Carbonyls

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The metal chemical NMR shifts of metal carbonyls are reported and discussed in relation to the bonding nature characteristic of carbonyl compounds of the $M(CO)_6$- and $Mn(CO)_5X$-types, where M is V or Mn, and X is a halogen or SCN. Theoretically evaluated chemical shift data based upon Ramsey's expression agree well with those observed for the $M(CO)_6$-type carbonyls. Regarding $Mn(CO)_5X$, the variation of the shifts for halogens is elucidated theoretically and revealed to be dependent upon the π-bonding nature between the metal and the halogen atom.

The stability of organometallic complexes in low oxidation states has been interpreted in terms of the formation of the covalent bonding between the metal atom and ligands, such as carbon monoxide and tertiary phosphines. This covalent bonding may be divided into σ-bonding and π-bonding parts; the latter is frequently called "back bonding" or "back donation." The basicity of carbon monoxide is relatively weak[1] and the coordination through a σ-bond is not enough to stabilize the complexes. On the other hand, the formation of the π-bond between the unfilled antibonding π-orbital on the carbon atom and the metal d-orbitals (d_{xy}, d_{yz}, d_{xz}) increases the double-bond character thereby strengthening the bonding between CO and the metal. Simultaneously, the back donation results in the dilution of the negative charge of the central metal, reducing the repulsive energy among the electrons. Cotton and Kraihanzel[2] calculated the force constants of the CO vibrations in a model system of metal carbonyls where both the σ- and π-bonds were taken into consideration. This led Graham[3] to the idea of the σ- and π-parameters in the bonding of metal carbonyls.

^{59}Co and ^{55}Mn NMR of metal carbonyls have been reported by Calderazzo *et al.*,[4] Onaka *et al.*,[5] and Bancroft *et al.*,[6] and ^1H NMR signals have been obtained for hydrides of metal carbonyl complexes.[7] ^{13}C NMR chemical shifts suggest the existence of a strong covalent bond between carbon and metal atoms.[8]

In order to investigate the bonding nature of metal carbonyls from the viewpoint of the magnetic character, $[V(CO)_6]^-$ and $[Mn(CO)_6]^+$ were chosen as typical compounds for the present study; they are highly symmetric and isotropic geometrically, electronically, and furthermore, magnetically. The ^{55}Mn chemical shifts of $Mn(CO)_5X$ with C_{4v} symmetry, as referred to below, are dependent on halogen atoms,[4] reflecting the bonding characters of the metal carbonyl derivatives.

The ^{51}V and ^{55}Mn chemical shifts were calculated using suitable molecular orbitals and the general formula derived by Ramsey;[9,10] the latter has been successfully applied to the calculation of ^{19}F chemical shifts by Saika and Slichter.[11]

Experimental

Metal Carbonyl Compounds. $Mn_2(CO)_{10}$ and $Na[V(CO)_6]$ were obtained from Pressure Chemical Company and Strem Chemicals Inc., respectively. Other metal carbonyl compounds were prepared by methods described in the literature.[12-19]

NMR Measurements. ^{51}V and ^{55}Mn NMR spectra were recorded on a Varian VF-16 spectrometer at 10.55 or 7.35, and 11.20 MHz, respectively.

A tetrahydrofuran or acetone solution, or a neat liquid of the metal carbonyls was sealed in glass tubes 15 mm in diameter. NMR measurements were carried out at 20°C.

The NMR signals of ^{51}V and ^{55}Mn of $KMnO_4$ were obtained in dispersion modes in order to avoid saturation. All other signals were recorded in absorption modes.

For the manganese compounds, potassium permanganate was used as the standard compound for the shifts and for the vanadium compounds, vanadium oxotrichloride was employed.

TABLE 1. CHEMICAL SHIFTS AND LINE WIDTHS OF METAL CARBONYLS

Compound	Solvent	Shift(ppm)	Width(Oe)
$[V(CO)_6]^-$	THF	2010 ± 5	0.1
$[Mn(CO_6)]^+$	acetone	935 ± 5	4.28
$HMn(CO)_5$	neat	2560 ± 10	2.45 ± 0.05
	THF	2630[a]	2.39[a]
	THF	2578[b]	2.28[b]
$Mn(CO)_5Cl$	THF	1003 ± 10	0.30 ± 0.01
	THF	1005[a]	0.182[a]
$Mn(CO)_5Br$	THF	1200 ± 10	0.66
	THF	1160[a]	0.378[a]
$Mn(CO)_5I$	THF	1520 ± 10	0.84 ± 0.02
	THF	1485[a]	0.557[a]
$Mn(CO)_5SCN$	THF	1130 ± 10	3.51

a) Values from Ref. 4. b) Values from Ref. 7.

Chemical Shift Data. The observed ^{51}V and ^{55}Mn chemical shift data are summarized in Table 1, together with those reported in the literature. All compounds examined give signals higher than that of the reference compound.

Calculation of the Chemical Shifts

The symmetries of the $M(CO)_6$- and $Mn(CO)_5X$-type compounds allow their electronic structures to be analyzed with the aid of the molecular orbital theory. The results can be compared with photoelectron and ultraviolet spectra.

The molecular orbitals of $[V(CO)_6]^-$ and $[Mn(CO)_6]^+$, and $Mn(CO)_5X$ reported by Beach and Gray[20] and Fenske and DeKock[21] were applied here to estimate the

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chemical shifts in these compounds.

According to Ramsey,[10] the chemical shift is expressed by the following formula,

$$\sigma = e^2/mc^2\langle 0|\sum_k(x_k^2+y_k^2)/r_k^3|0\rangle$$
$$-2\sum_n(1/(E_n-E_0))\{\langle 0|\sum_k m_{zk}^0|n\rangle\langle n|\sum_{k'} m_{zk'}^0/r_{k'}^3|0\rangle$$
$$+\langle 0|\sum_k m_{zk}^0/r_k^3|n\rangle\langle n|\sum_{k'} m_{zk'}^0|0\rangle\}, \tag{1}$$

where

$$m_{zk}^0 = -e\hbar/2mci(x_k\partial/\partial y_k - y_k\partial/\partial x_k) \tag{2}$$

and $|0>$ and $|n>$ denote the ground state and the n th excited state wave functions of the molecule, respectively, with E_0 and E_n being the energies of the corresponding states. The other symbols have their usual meanings.

In order to simplify the system, we assumed that only the d-electrons of the central atoms contribute to the paramagnetic term; the core electrons are assumed not to contribute to the matrix elements $<0|m_{zk}^0|n>$ and $<0|m_{zk}^0/r_k^3|n>$. Contribution from 4p-electrons and the variation of the orbital exponents caused by the bond formation are neglected here.

M(CO)$_6$-type Carbonyls. Applying Eq. 1 to the M(CO)$_6$-type carbonyls, we obtain the following reduced equation for the chemical shift,

$$\sigma = \sigma_P + \sigma_D \tag{3}$$

$$\sigma_P = -8e^2\hbar^2/m^2c^2\langle 1/r^3\rangle_{3d}\sum_{i,j}C_i^2C_j^2/\Delta E(i,j) \tag{4}$$

$$\sigma_D = e^2/3mc^2\{\langle 1/r\rangle_{3d}P_{3d} + \langle 1/r\rangle_{4s}P_{4s}$$
$$+\langle 1/r\rangle_{4p}P_{4p} + \sum_k^{\text{core}}\langle 1/r\rangle_k\}, \tag{5}$$

where C_i is the coefficient of the i th atomic d-orbital in the molecular orbital of t_{2g} or e_g symmetry and $<1/r>_k$ and $<1/r^3>_k$ are the average values of $1/r$ and $1/r^3$ for the k th orbital, respectively. Here, we assume that the $<r^n>_k$ values are those of free atoms. P_i is the electron population of the corresponding orbital defined by Mulliken.[22] $\Delta E(i, j)$ is the transition energy between the i th and j th levels.

TABLE 2. CALCULATED VALUES FOR $\langle 1/r\rangle$, $\langle 1/r^3\rangle$, AND $\langle r^2\rangle$ IN ATOMIC UNITS

	Vanadium complexes	Manganese complexes
$\langle 1/r\rangle_{1s}$	22.395	24.385
$\langle 1/r\rangle_{2s}$	5.018	5.540
$\langle 1/r\rangle_{3s}$	1.507	1.680
$\langle 1/r\rangle_{4s}$	0.322	0.347
$\langle 1/r\rangle_{2p}$	4.625	5.075
$\langle 1/r\rangle_{3p}$	1.237	1.392
$\langle 1/r\rangle_{4p}$	0.191	0.200
$\langle 1/r\rangle_{3d}$	0.849	1.020
$\langle 1/r^3\rangle_{3d}$	2.0755	3.2484
$\langle r^2\rangle_{1s}$	0.0060	0.0050
$\langle r^2\rangle_{2s}$	0.1132	0.0937
$\langle r^2\rangle_{3s}$	1.0441	0.8508
$\langle r^2\rangle_{4s}$	14.7720	12.5757
$\langle r^2\rangle_{2p}$	0.0877	0.0728
$\langle r^2\rangle_{3p}$	1.1978	0.9489
$\langle r^2\rangle_{4p}$	39.0585	36.1045
$\langle r^2\rangle_{3d}$	3.9738	2.7711

On estimating the $<r^n>_k$ values, the Richardson wave functions[23] for the radical parts of the metal orbitals were adopted as in the treatments of the calculations of the molecular orbitals.[20,21] The calculated values of $<1/r>_k$ and $<1/r^3>_k$ are listed in Table 2 together with the values of $<r^2>_k$ which are used in the Appendix.

For the closure approximation in this system, one should consider that t_{2g} is the highest occupied orbital and e_g is the lowest vacant one, and that only the $<t_{2g}|m|e_g>$ and $<t_{2g}|m/r^3|e_g>$ components have non-zero values. Thus, the transition energy is between the $^1A_{1g}$ and $^1T_{1g}$ states. Though the electron transition between the t_{2g} and e_g levels is forbidden and is masked in the intensive charge-transfer bands, the values of ΔE_{av} were adopted from the results obtained by Beach and Gray,[20] employing Gaussian analysis of the electronic spectra. These values are 25500 cm^{-1} for [V(CO)$_6$]$^-$ and 41050 cm^{-1} for [Mn(CO)$_6$]$^+$.

TABLE 3. ESTIMATED CHEMICAL SHIFT VALUES FOR [Mn(CO)$_6$]$^+$ AND [V(CO)$_6$]$^-$

Compound	Calculated value (ppm)				Experimental value (ppm) *vs.* KMnO$_4$ or K$_3$VO$_4$
	σ_D	σ_P	$\sigma=\sigma_D+\sigma_P$	Chemical shift	
[Mn(CO$_6$)]$^+$	1915	−6102	−4187	928	935±5
KMnO$_4$	1900	−7015	−5115		
[V(CO)$_6$]$^-$	1718	−5993	−4275	612	1480±5
K$_3$VO$_4$	1708	−6595	−4887		

The results are summarized in Table 3. The chemical shifts for the reference compounds are estimated in the Appendix.** The calculated values of σ_D are in good agreement with those obtained by Dickinson[24] in the Hartree-Fock approximation. Here, the following values are used: $P_{3d}=6.37$, $P_{4s}=0.00$, $P_{4p}=0.14$ for manganese and $P_{3d}=4.36$, $P_{4s}=0.06$, $P_{4p}=0.19$ for vanadium.[20]

In order to further improve the approximation, one should consider other non-zero matrix elements between the more highly-excited states and the ground state. The transition energies are assumed to be the difference between the orbital energies of the corresponding molecular orbitals, which are partly quoted in Table 4.

Thus, the paramagnetic part of Eq. 1 becomes

$$\sigma_P = -e^2\hbar^2/m^2c^2\langle 1/r^3\rangle_{3d}\{8C_{3e_g}^2C_{2t_{2g}}^2/\Delta E(3e_g, 2t_{2g})$$
$$+4C_{3t_{2g}}^2C_{2t_{2g}}^2/\Delta E(3t_{2g}, 2t_{2g})$$
$$+8C_{3t_{2g}}^2C_{2e_g}^2/\Delta E(3t_{2g}, 2e_g)\}, \tag{6}$$

where C_i is the coefficient of the d-orbital of the molecular orbitals, i denotes the symmetry of the corresponding orbital, and $\Delta E(i, j)$ is the difference in energy between the i and j levels.

The values obtained are given in Table 5, and the non-zero terms are listed with transition energies and calculated σ_P values. The values of σ_P are not very far

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** The signal for vanadium oxotrichloride appears at a value 533 ppm below that for potassium vanadate.[25]

TABLE 4. MOLECULAR ORBITAL COEFFICIENTS FOR $M(CO)_6$[a)]

Molecular orbital		Metal orbital			CO orbital			
		3d	4s	4p	σ_1	σ_2	π	π^*
$[Mn(CO)_6]^+$	$2e_g$	−0.45595			0.01381	−0.76603		
	$2t_{2g}$	−0.89269					0.40850	−0.23794
	$3e_g$	1.0173			0.59145	−0.75222		
	$4t_{1u}$			−0.45919	−0.25475	0.23124	0.17384	−0.81047
	$2t_{2u}$						—	—
	$3t_{2g}$	0.50218					−0.03841	−1.0138
$[V(CO)_6]^-$	$2e_g$	0.19191			0.15206	−0.91938		
	$2t_{2g}$	−0.75519					0.39318	−0.44528
	$3e_g$	1.1750			0.55442	−0.62517		
	$4t_{1u}$			−0.46568	−0.22002	0.20197	0.17636	−0.80884
	$2t_{2u}$						−0.06406	−1.0006
	$2t_{1g}$						−0.17892	−1.0040
	$3t_{2g}$	0.76817					−0.17376	−0.97471

a) The values were taken in part from the results of Beach and Gray.[20)]

TABLE 5. CHEMICAL SHIFT VALUES, σ_P, FOR $M(CO)_6$

Mixing	$[Mn(CO)_6]^+$		$[V(CO)_6]^-$	
	$\Delta E(i,j)$ (eV)	$-\sigma_P$ (ppm)	$\Delta E(i,j)$ (eV)	$-\sigma_P$ (ppm)
$3e_g$ $2t_{2g}$	8.601	5784	5.442	5577
$3t_{2g}$ $2t_{2g}$	10.984	552	9.614	675
$3t_{2g}$ $2e_g$	17.982	186	18.571	45
Total		6522		6297

from those obtained in the closure approximation.

$Mn(CO)_5X$-type Carbonyls. The chemical shifts of $Mn(CO)_5X$-type carbonyls are evaluated in a similar way. The molecular orbitals adopted here are described partly in Tables 6-1 to 6-3 based in the work of Fenske and DeKock,[21)] who have comfirmed the orbital energies of the highest occupied MOs by photoelectron spectroscopy.

The paramagnetic terms in Eq. 1 are summarized as follows,

TABLE 6-1. AO COEFFICIENTS FOR MO OF $Mn(CO)_5Cl$[a)]

MO	$3d_{z^2}$	$3d_{x^2-y^2}$	$3d_{xy}$	$3d_{xz}$
11e				0.0190
$6b_1$		0.0000		
10e				0.0036
$11a_1$	−0.3272			
9e				−0.5496
$5b_1$		−0.7634		
$3b_2$			0.5997	
$10a_1$	−0.7054			
8e				0.3379
7e				0.7333
$2b_2$			0.7679	
$9a_1$	0.2648			
6e				−0.0111
$8a_1$	0.3886			
$4b_1$		0.4730		

a) The values were taken in part from the molecular orbitals of Fenske and DeKock.[21)]

TABLE 6-2. AO COEFFICIENTS FOR MO OF $Mn(CO)_5Br$

MO	$3d_{z^2}$	$3d_{x^2-y^2}$	$3d_{xy}$	$3d_{xz}$
11e				0.0197
$6b_1$		0.0000		
10e				0.0033
$11a_1$	−0.3098			
9e				−0.5497
$5b_1$		−0.7648		
$3b_2$			0.6013	
$10a_1$	−0.6974			
8e				0.2470
7e				0.7686
$2b_2$			0.7669	
$9a_1$	0.3048			
6e				−0.0113
$8a_1$	0.3887			
$4b_1$		0.4719		

TABLE 6-3. AO COEFFICIENTS FOR MO OF $Mn(CO)_5I$

MO	$3d_{z^2}$	$3d_{x^2-y^2}$	$3d_{xy}$	$3d_{xz}$
11e				0.0202
$6b_1$		0.0000		
10e				0.0029
$11a_1$	−0.2987			
9e				−0.5520
$5b_1$		−0.7665		
$3b_2$			0.6035	
$10a_1$	−0.6865			
8e				0.1897
7e				0.7831
$2b_2$			0.7654	
$9a_1$	0.3401			
6e				−0.0112
$8a_1$	0.1065			
$4b_1$		0.4704		

$$\begin{aligned}\sigma_P = {} & -e^2\hbar^2/3m^2c^2\langle 1/r^3\rangle_{3d}\{8\sum_{i,j}^{b_1,b_2} C_i^2C_j^2/\Delta E(i,j) \\ & + 4\sum_{i,j}^{e,b_1} C_i^2C_j^2/\Delta E(i,j) + 12\sum_{i,j}^{e,a_1} C_i^2C_j^2/\Delta E(i,j) \\ & + 4\sum_{i,j}^{e,e} C_i^2C_j^2/\Delta E(i,j) + 4\sum_{i,j}^{e,b_2} C_i^2C_j^2/\Delta E(i,j)\}, \qquad (7)\end{aligned}$$

where $\sum_{i,j}^{k,l}$ means the summation of matrix elements between the orbitals of k and l symmetries, and $\Delta E(i,j)$ is the transition energy between the i and j levels. All possible excited states for a single electron transition from the ground state are considered. The values of σ_P resulting from the above calculation are listed in Table 7, together with the values of σ_D which are calculated from Eq. 5 for 3d-orbital populations of $P_{3d}(Cl)=5.687$, of $P_{3d}(Br)=5.723$, of $P_{3d}(I)=5.747$, those of the other P_is being unity.[21]

Table 7. Estimated chemical shift values for Mn(CO)$_5$X

Compound	Calculated value (ppm)		Observed (ppm)
	σ_D	σ_P	σ_P
Mn(CO)$_5$Cl	1897	−2722	−6009
Mn(CO)$_5$Br	1898	−2696	−5813
Mn(CO)$_5$I	1899	−2615	−5494

Though the calculated values for σ_P are almost one half of those obtained experimentally, the order of the chemical shifts for the halogen atom series is in agreement with that observed.

Discussion

The calculated values of the shifts of hexacarbonylmetal compounds based upon the molecular orbitals of Beach and Gray[20] agree well with the experimental results. This leads us to conclude that the paramagnetic term contributes dominantly to the shifts, and that the chemical shift directly reflects the nature of the chemical bond. This is more clearly revealed in the case of pentacarbonylmanganese halides and thiocyanate.

Though the calculated chemical shifts of pentacalbonylmanganese halides do not quite agree with the experimental values, it is clear that the dominant change of the shifts is due to the paramagnetic terms, while the diamagnetic terms vary only slightly. In the approximation described above, in which only the matrix elements involving the d-orbitals are taken into account, the calculated values of the paramagnetic terms are about one half of those observed. The paramagnetic terms under consideration involve only with the squares of the coefficients of the metal d-orbitals, so that the calculated values should be somewhat smaller than those obtained experimentally. In order to improve the agreement between the theoretical and experimental results, the cross terms between the d-orbitals of the metal and the orbitals of the ligand should be considered.***

The chemical shifts are linearly correlated with the electronegativity of the halogen and pseudohalogen; the shifts decrease with increasing electronegativity. In plotting the shifts versus the Schwarzenbach bond strength,[25] an appropriately linear relationship is obtained.

If halogen atoms withdraw electrons from the central metals, the diamagnetic shielding would decrease and the nuclei would be less shielded. However, the fact that the total 3d-orbital populations are essentially constant, as shown by the Fenske molecular orbitals, indicates that a variation in σ_D terms is unlikely. Thus, the order of the shifts for the various halogens can be elucidated using the paramagnetic term. Thus, the next problem is to determine which part should dominantly contribute to the paramagnetic term.

Table 8. Chemical shift values, σ_P, in parts of Mn(CO)$_5$X

Mixing		Mn(CO)$_5$Cl		Mn(CO)$_5$Br		Mn(CO)$_5$I	
		$\Delta E(i,j)$ (eV)	$-\sigma_P$ (ppm)	$\Delta E(i,j)$ (eV)	$-\sigma_P$ (ppm)	$\Delta E(i,j)$ (eV)	$-\sigma_P$ (ppm)
2b$_2$	5b$_1$	12.325	560.7	12.274	563.6	12.229	566.0
4b$_1$	3b$_2$	25.680	63.0	25.595	63.3	25.217	63.5
2b$_2$	9e	13.443	133.2	13.294	134.4	13.129	136.7
7e	3b$_2$	11.835	164.3	11.641	184.5	11.514	195.0
8e	3b$_2$	8.975	46.0	8.057	27.5	7.536	17.5
9a$_1$	9e	13.599	47.0	12.671	66.8	11.806	90.0
8a$_1$	9e	26.066	52.8	25.952	53.1	25.618	4.1
7e	11a$_1$	17.455	99.5	17.211	99.4	16.968	97.3
8e	11a$_1$	14.595	25.3	13.629	13.0	12.990	7.5
7e	10a$_1$	10.414	775.0	10.475	827.4	10.465	833.0
8e	10a$_1$	7.554	226.9	6.891	129.9	6.487	78.9
7e	5b$_1$	11.929	264.1	11.766	295.3	11.681	310.1
8e	5b$_1$	9.090	73.8	8.182	43.9	7.703	27.6
4b$_1$	9e	26.893	25.3	26.741	25.3	26.584	25.5
7e	9e	13.048	125.2	12.786	140.4	12.581	149.3
8e	9e	8.586	40.4	9.202	20.1	8.603	12.8

As shown in Table 8, which gives the parts of the paramagnetic terms, the variations of the paramagnetic shifts are caused mostly by terms involving mixing between the 8e and 10a$_1$ levels. The summation of the other parts leads to almost the same values for three halogen derivatives. For the values of $\Delta E(i, j)$, no significant variations are found. On the other hand, the variation of the coefficients of the d-orbitals in the 8e orbitals plays an important role in the evaluation of matrix elements such as $\langle 8e|\boldsymbol{m}|10a_1\rangle$.

While the a$_1$ symmetric orbitals form the σ-bonds, the e symmetric orbitals form π-bonds between the metal and halogen atoms. Consequently we conclude that the π-bonding between metal and halogen atoms is a dominant cause of the chemical shifts, and the σ-bonding does not vary the values very much. This suggests that the Graham σ-parameter makes almost no contribution to the chemical shifts but that π-parameter must be closely related to these values.

It should be pointed out that the variation of the chemical shifts depends upon the π-bond which has been neglected so far in discussing the nature of halogen-metal bonds. If the ligands have the ability to form π-type bonds with the metal, this effect appears to be larger than that of the halogen ligands.

It should be emphasized that the values of the paramagnetic term increase in the order H<I<Br<Cl<CO; especially we note here that hydrogen has the

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*** The theoretical treatmant will be reported elsewhere.

least tendency to form π-bond and carbon monoxide has the greatest. The π-bonding which seems to stabilize the low oxidation states in the metalcarbonyl can be estimated from the NMR chemical shifts. The π-bond formation in other halogen compounds can be predicted from these shifts.

For pentacarbonylmolybdenum halides reported by Takano,[26] a similar relation between the chemical shifts and the halogen atoms has been found, although the differences between the chemical shifts are less than those in the case of manganese compounds: 1584 ppm for $Mo(CO)_5Cl$, 1596 ppm for $Mo(CO)_5Br$, and 1709 ppm for $Mo(CO)_5I$ against potassium molybdate.

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Appendix

Evaluation of the Chemical Shifts of $KMnO_4$ and K_3VO_4. The molecular orbitals of the $[MnO_4]^-$ ion have been calculated by several authors, but the computation of the energies is not yet adequate to explain the electronic structure accurately. The bonding between oxygen and manganese is covalent, and the electrons which contribute to the paramagnetism come from ligand oxygen; the d-electron population of the central manganese atom is 6.15 according to the molecular orbitals of Brown.[27]

Since the results of the calculation of the paramagnetism are not satisfactory, the shifts are estimated empirically as follows.

The magnetic susceptibility of $KMnO_4$, $\chi_g = 0.175 \times 10^{-6}$ cm³/g,[28] is divided into two parts, paramagnetic and diamagnetic terms, which in units of moles, is

$$\chi_M(KMnO_4) = \chi_M^D(KMnO_4) + \chi_M^P(KMnO_4) \qquad (1)$$

and

$$\chi_M^D(KMnO_4) = \chi_M^D(Mn) + \chi_M^D(K^+) + \chi_M^D(4O^{2-}) \qquad (2)$$

$$\chi_M^D(Mn) = -\boldsymbol{N}(e^2/6mc^2)\sum_i \langle r^2 \rangle_i, \qquad (3)$$

where

$$\sum_i \langle r^2 \rangle_i = \sum_i^{\text{core}} \langle r^2 \rangle_i + P_{4s}\langle r^2 \rangle_{4s} + P_{4p}\langle r^2 \rangle_{4p} + P_{3d}\langle r^2 \rangle_{3d}, \qquad (4)$$

$\boldsymbol{N}$ is the Avogadro number, and P_i is the electron population of the i th orbital; $P_{4s} = 0.24$, $P_{4p} = 0.16$, $P_{3d} = 6.15$.[27]

$\chi_M^D(4O^{2-})$ is estimated to be the difference of the sums of the empirical values for O^{2-} and O ($\chi_M^D(O^{2-}) = -13.7 \times 10^{-6}$ and $\chi_M^D(O) = -5.3 \times 10^{-6}$ cm³/mol[28]):

$$\chi_M^D(4O^{2-}) = (8 - P_{3d} - P_{4s} - P_{4p}) \times (\chi_M^D(O^{2-}) - \chi_M^D(O)) + 4 \times \chi_M^D(O). \qquad (5)$$

$\chi_M^D(Mn) = -26.82 \times 10^{-6}$ and $\chi_M^D(K^+) = -14.9 \times 10^{-6}$ cm³/mol.[28] From Eq. 2, $\chi_M^D(KMnO_4) = -68.6 \times 10^{-6}$ cm³/mol.

Since $\chi_M(KMnO_4) = \chi_g \times$ (molecular weight) $= 27.7 \times 10^{-6}$ cm³/mol, Eq. 1 gives $\chi_M^P(KMnO_4) = 96.36 \times 10^{-6}$ cm³/mol.

The paramagnetic shift has the following relation to $\chi_M^P(KMnO_4)$:

$$\sigma_P = 2/\boldsymbol{N} \times \langle 1/r^3 \rangle_{3d} \chi_M^P(KMnO_4) \qquad (6)$$

neglecting the contribution from 4p-electrons. $\sigma_P(KMnO_4)$ is calculated to be 7015 ppm.

For potassium vanadate, the values were calculated similarly using the following data: $P_{4s} = 0.0148$, $P_{4p} = 0.3519$, $P_{3d} = 3.7167$,[30] and $\chi_g = -0.08 \times 10^{-6}$ cm³/g.[31]

Thus, we obtain $\chi_M^P(K_3VO_4) = 95.9$ cm³/mol and evaluate the shift for potassium vanadate to be $\sigma_p(K_3VO_4) = 6595$ ppm.

The shift of the diamagnetic term is found to be

$$\sigma_D = e^2/3mc^2 \sum_i \langle 1/r \rangle_i,$$

where

$$\sum_i \langle 1/r \rangle_i = \sum_i^{\text{core}} \langle 1/r \rangle_i + P_{4s}\langle 1/r \rangle_{4s} + P_{4p}\langle 1/r \rangle_{4p} + P_{3d}\langle 1/r \rangle_{3d}. \qquad (8)$$

The values in Table 2 are used for $<1/r>_i$s and the values of P_is as above, and we obtain $\sigma_D(KMnO_4) = 1900$ ppm and $\sigma_D(K_3VO_4) = 1708$ ppm.

References

1) For example, L.E. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand Field Theory," 2nd ed, Muthuen, London (1966), Chap. 9.

2) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **81**, 4432 (1962).

3) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

4) P. Carderazzo, E, A. C. Lucken, and D. F. Williams, *J. Chem. Soc.*, **1967**, 154.

5) S. Onaka, T.Miyamoto, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **44**, 1851 (1971).

6) G. M. Bancroft, H. C. Clark, R. G. Kidd, A. T. Rake, and H. G. Spinny, *Inog. Chem.*, **12**, 728 (1973).

7) R. M. Stevens, C. W. Kern, and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 279 (1962).

8) For example, E. W. Randall, *Chem. Brit.*, **1971**, 371.

9) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

10) N. F. Ramsey, *Phys. Rev.*, **86**, 243 (1952).

11) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

12) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, **1959**, 1501.

13) R. B. King, "Organometallic Syntheses," Vol. 1, Transition-metal compounds, Academic Press (1965), p. 174.

14) R. B. King, "Organometallic Syntheses," Vol. 1, Transition-metal compounds, Academic Prsss (1965), p. 149.

15) W. F. Edgell and W. M. Reseny,Jr., *J. Am. Chem. Soc.*, **88**, 5451 (1966).

16) W. Schropp, Jr., *Chem. Ber.*, **94**, 305 (1961).

17) T. Kruck and M. Noack, *Chem. Ber.*, **97**, 1703 (1964).

18) C. G. Barraclough and J. Lewis, *J. Chem. Soc.*, **1960**, 4842.

19) A. Wojicicki and M. F. Farona, *Inorg. Chem.*, **3**, 151 (1963).

20) N. A. Beach and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5713 (1968).

21) R. F. Fenske and R, L. DeKock, *Inorg. Chem.*, **9**, 1053 (1970).

22) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

23) J. W. Richardson, W. C. Nieuwpoort, R. R. Powel, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

24) W. C. Dickinson, *Phys. Rev.*, **80**, 563 (1950).

25) H. E. Walchli and H. W. Morgan, *Phys. Rev.*, **87**, 541 (1952).

26) T. Takano, Dissertation submitted for the degree, Doctor of Philosophy in Chemistry, to The University of Tokyo, 1972.

27) R. D. Brown, B. H. James, M. F. O'Dwyer, and K. R. Roby, *Chem. Phys. Lett.*, **1**, 459 (1967).

28) A. Pacault, J. Hoarau, A. Marchand, "Advances in Chemical Physics," Vol. 3, Interscience (1961), p. 209.

29) V. C. G. Trew, *Trans. Faraday Soc.*, **37**, 476 (1941).

30) R. Kebabcioglu and A Müller, *Chem. Phys. Lett.*, **8**, 59 (1971).

31) G. Wehrmeyer, *Diss. Münster*, **1957**, 91.