Vanadium-51 NMR Characteristics of New Pentacarbonylvanadates(–I)

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There is increasing interest in metal NMR data of transition metal coordination compounds as an analytical tool and aid for structure determination. The nucleus ^{51}V is approaching the state of a routine nucleus in diamagnetic low-valent and high-valent complexes [1–7]. This is due to its favourable nuclear properties ($I = 7/2$, $Q = -0.05 \cdot 10^{-28}$ m^2, respectively relative to $^1H = 0.24$ at constant magnetic field). The low nuclear electric quadrupole moment Q is exceptional among the quadrupolar transition metal nuclei, allowing the observation of sufficiently narrow signals even in compounds of rather low point symmetry.

Pentacarbonylvanadates(–I) with group Va ligands (chiefly trivalent phosphorus) have extensively been studied in our laboratory by ^{51}V NMR (see, *e.g.*, refs. 1 and 7 for a survey), and have proven a rich source for methodological and theoretical studies of electronic and steric factors influencing ^{51}V NMR parameters such as the shielding of the ^{51}V nucleus. Because of preparative difficulties, introduction of other than P, As and Sb ligands has only been undertaken sporadically. Two routes to new pentacarbonylvanadates have recently been reported, starting from $[V(CO)_5NH_3]^-$ [8] and $[V(CO)_5DMSO]^-$ [5], respectively, $[V(CO)_5NH_3]^-$, which can be prepared by UV irradiation of $[V(CO)_6]^-$ in liquid ammonia [9] or — more conveniently — from Ellis' super-reduced vanadium species $V(CO)_5^{3-}$ [10], and $[V(CO)_5DMSO]^-$ both contain a labile ligand which may be replaced by other donor/acceptor functions. Alternatively, $[V(CO)_5THF]^-$ (formerly characterized by its IR pattern in MeTHF glass at 90 K [11]) and $[V(CO)_5NCMe]^-$ (previously characterized by its electronic absorption spectrum [12], and by IR and elemental analysis [8]), which we have now obtained by UV irradiation of $[Et_4N][V(CO)_6]$ in the respective solvents at low temperatures, may be employed to extend the range of suitable starting materials for ligand exchange reactions (Table I).

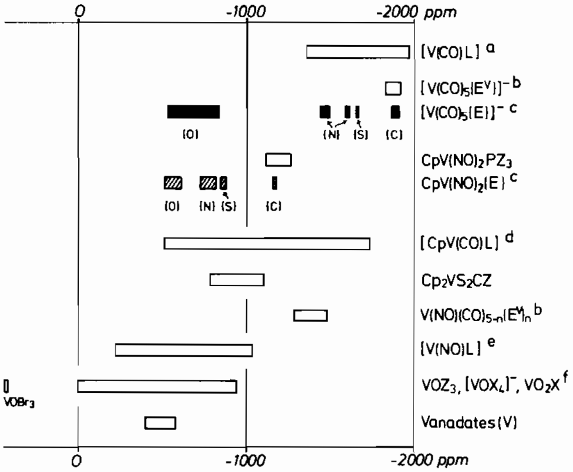

Fig. 1. ^{51}V chemical shifts relative to $VOCl_3$; data adapted from ref. 1. Full areas: this work; shaded areas: ref. 3. [a] $[V(CO)_6]^-$, $HV(CO)_6$, $(\eta^3\text{-Allyl})V(CO)_5$ and derivatives. [b] $\{E^V\} = PR_3$ (excluding PF_3, $P(t\text{-}Bu)_3$ and other extremes. [c] $\{E\}$ is a ligand bonding as specified. For $[V(CO)_5\{E\}]^-$: $\{O\} = O_2NPh$, OC(Ph)Py, THF; $\{N\}$ = pyridines (high-frequency) and nitriles; $\{S\}$ = DMSO; $\{C\} = CN^-$, isonitirles. [d] $CpV(CO)_4$, $[CpV(H)(CO)_3]^-$, $Cp_2V_2(CO)_5$ and derivatives. [e] Mono-, di- and trinitrosylvanadium complexes (ref. 2; and M. Herberhold and H. Trampisch, private communication). [f] $Z = X$, OR, NR_2; X = halogen and other.

Data on the new complexes, including those reported lately for $[V(CO)_5CN]^{2-}$, $[V(CO)_5py]^-$, $[V(CO)_5DMSO]^-$ [5], and group Va ligands of normal steric and electronic behaviour (*i.e.* medium cone angle and medium π/σ-interacting capability), are compiled in Table I and are presented graphically in the context of other ^{51}V NMR data in Fig. 1.

From the position of the resonance signal for $[V(CO)_54\text{-}NCpy]^-$ it is clear that 4-cyanopyridine bonds *via* the pyridine-N (and not *via* the nitrile group), while, in $[V(CO)_5O_2NPh]^-$ and $[V(CO)_5OC(Ph)py]^-$, the ligand is coordinated through oxygen. The O-coordination is also revealed by the shift of ν(NO) (free ligand: 1652, complex: 1590 cm^{-1}).

The most salient feature is the large shift range exhibited by the pentacarbonylvanadates, flanked by –534 ppm for $[V(CO)_5O_2NPh]^-$ on the high-frequency and –1961 for $[V(CO)_5PF_3]^-$ [7] on the low-frequency side. This wide shift range for structurally equivalent (V(–I) complexes, which overlaps with the shift range observed for V(V), demonstrates that concepts relating nuclear shielding to oxidation numbers of the nucleus under consideration are misleading. An intrinsic feature of this commonly applied concept is the participation of variable local diamagnetic contributions to the overall shielding. The diamagnetic term, dominated by the core electrons, is, however, practically constant for a given nucleus: in other words the actual charge at the nucleus is equilibrated by the ligand system to a value close to zero in V(–I) *and* V(V) compounds.

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TABLE I. ^{51}V NMR Spectral Data (Relative to $VOCl_3$) and CO Stretching Frequencies.

$[V(CO)_5L]^-$ L =	Coord. *via*	$\delta(^{51}V)$ (ppm)	Temperature (K)	$\delta(300)^a$	Solvent	$\nu(CO)$ (cm^{-1})	Mode of prepn.^{b}
O_2NPh^c	O	−534	300	−534	acetone	2005 1880	I
2-C(Ph)(O)py	O	−781	300	−781	acetone	1950 1855	I
$THF^{d,e}$	O	−872	200	−837	THF		IV
4-$NCpy^f$	py-N	−1440	300	−1440	acetone	1950 1810	I
$py^{f,g,h}$	py-N	−1473	275	−1464	pyridine	1960 1800 1760	I
		−1486	235				
2-NH_2py^f	py-N	−1493	304	−1494	acetone	1955 1800 1750	I
$NCMe^{i,j}$	nitrile-N	−1606	275	−1597	NCMe		IV
		−1620	235				
$NCPh^f$	nitrile-N	−1606	300	−1606	NCPh/THF	1955 1815 1765	I, III
$DMSO^{f,g}$	S	−1657	305	−1659	DMSO/THF	1977 1827	IV
$BiEt_3{}^k$	Bi	−1740	300	−1740	THF		IV
$AsPh_2CH_2R^l$	As	−1824	300	−1824	THF		IV
PPh_2Me^l	P	−1839	300	−1839	THF		IV
$SbPh_3{}^l$	Sb	−1881	300	−1881	THF		IV
$CN^{-\,g,m}$	C	−1864	300	−1864	NCMe	1950 1790 1745	II
$CNCy^{g,n,o}$	C	−1900	303	−1901	NCMe	1953 1823	I, II
CO	C	−1952	298	−1951	THF		

[a] $\delta(300) = \delta$ corrected for 300 K, assuming an average temperature gradient of 0.35 ppm/degree. [b] I: $[V(CO)_5DMSO]^- + L$, II: $[V(CO)_5NCMe]^- + L$, III: $[V(CO)_5THF]^- + L$, IV: $[V(CO)_6]^- + L + h\nu$; L is usually added in large excess. [c] Decomposes if pressure is released. [d] Decomposes above 230 K; dppe reacts to $[V(CO)_5dppe]^-$ in 100% yield. [e] See also ref. 11. [f] Decomposes in solution at room temperature. [g] Isolated in substance. [h] See also refs. 5 and 12. [i] Decomposes above 265 K; $[Et_4N]CN$ reacts to $[Et_4N]_2[V(CO)_5CN]$ in almost 100% yield. [j] See also refs. 8 and 12. [k] Ref. 13. [l] Ref. 6. [m] See also refs. 5, 8 and 9. [n] Standing for several hours at room temperature yields $[V(CO)_4L_2]^-$ ($\delta = -1837$ ppm) and $[V(CO)_5CN]^{2-}$. [o] $\nu(CN) = 2080$ cm^{-1}, *cf.* also ref. 8.

The large variations in δ then arise from the local paramagnetic term and hence reflect contributions induced by the valence electrons. Non-local contributions may account for small variations within the 10 to 30 ppm interval, but cannot be responsible for the large differences observed between, *e.g.*, N and O bonded ligands. The shift ranges are clearly distinct for the various coordinating functions, and the ordering $CO > CNR \approx SbR_3 > PR_3 > AsR_3 > BiR_3 >$ DMSO (S-coordinated) $> NCR > py > \{O\}$ reflects decreasing π and increasing σ interaction (increasing electronegativity of the ligand function). A virtually identical ordering has been established for $CpV(NO)_2L$ ($CO > PR_3 \approx CNR > SR_2 > NCR > NR_3 > \{O\}$ [3]) and $Mo(CO)_5L$ ($CO > SbR_3 > AsR_3 > PR_3 \approx CNR > NCR > py$ [14, 15]), and seems also to apply to $[Mn(CO)_5L]^+$ ($PR_3 > NCMe$ [7]). This 'normal dependence' of the metal shielding from the electronegativity (*i.e.* $\{N\} < \{P\} < \{Sb\}$; $\{O\} < \{S\}$) is commonly observed in *low*-valent transition metal complexes, contrasting the 'inverse dependence' in d^0 systems such as VOX_3 [1], $[NbE^{VI}X_4]^-$ [16] and $[MoE^{VI}{}_4]^{2-}$ [17] (E^{VI} = O, S, Se, Te; X = F, Cl, Br). While the inverse dependence may be understood in terms of increasing participation of metal-*d* orbitals to electronic transitions, the normal dependence rather reflects the expected trends arising from an increase of the nephelauxetic effect and the covalency upon going down the main groups.

References

1 D. Rehder, *Bull. Magn. Reson.*, *4*, (1982).
2 D. Rehder and K. Wieghardt, *Z. Naturforsch.*, *36b*, 1251 (1981).
3 M. Herberhold and H. Trampisch, *Z. Naturforsch.*, *37b*, 614 (1982).
4 F. Preuss and L. Ogger, *Z. Naturforsch.*, *37b*, 957 (1982).
5 K. Ihmels and D. Rehder, *J. Organometal. Chem.*, *232*, 151 (1982).
6 R. Borowski, D. Rehder and K. von Deuten, *J. Organometal. Chem.*, *220*, 45 (1981).
7 D. Rehder, H.-Ch. Bechthold, A. Keçeci, H. Schmidt and M. Siewing, *Z. Naturforsch.*, *37b*, 631 (1982).
8 J. E. Ellis and K. L. Fjare, *Organometallics*, *1*, 898 (1982).
9 D. Rehder, *J. Organometal. Chem.*, *37*, 303 (1972).
10 J. E. Ellis and K. L. Fjare, *J. Amer. Chem. Soc.*, *103*, 6100 (1981).
11 P. S. Braterman and A. Fullarton, *J. Organometal. Chem.*, *31*, C27 (1971).
12 M. S. Wrighton, D. I. Handel and D. L. Morse, *Inorg. Chem.*, *15*, 434 (1976).
13 R. Talay and D. Rehder, *Chem. Ber.*, *111*, 1978 (1978).
14 S. Dysart, I. Georgii and B. E. Mann, *J. Organometal. Chem.*, *213*, C10 (1981).
15 E. C. Alyea, R. E. Lenkinski, A. Somogyvari, *Polyhedron*, *1*, 130 (1982).
16 V. P. Tarasov, S. M. Sinitsyna, V. D. Kopanev, V. G. Khlebodarov and Yu. A. Buslaev, *Koord. Khim.*, *6*, 1568 (1980).
17 S. F. Gheller, P. A. Gazzana, A. F. Masters, R. T. C. Brownlee, M. J. O'Connor and A. G. Wedd, *Inorg. Chim. Acta*, *54*, L131 (1981).