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# The $^{13}$C Isotope Effect in the $^{51}$V NMR Spectra of $[V(^{12}CO)_{6-n}(^{13}CO)_n]^-$

KLAUS IHMELS, DIETER REHDER* and VOLKER PANK

*Institut für Anorganische Chemie, Martin Luther King Platz 6, D 2-Hamburg 13, F.R.G.*

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The origin and extent of the ligand-induced isotope effect upon metal shielding in transition metal complexes have been of some practical and theoretical interest (for data compilation and discussion see [1]). There is only one report for the $^{51}$V nucleus in $[V(^{16}O)_{4-n}(^{17}O)_n]^{3-}$, where a slight asymmetry of the $^{51}$ resonance of $[V(^{16}O)_4]^{3-}$, caused by $[V(^{16}O)_3(^{17}O)]^{3-}$ was noted [2]. Here we report on the $^{13}$C isotope shift of the $^{51}$V NMR signals in $[V(^{12}CO)_{6-n}(^{13}CO)_n]^-$. In Fig. 1, the $^{51}$V NMR spectra of $^{13}$CO enriched (12% and 42%, respectively) hexacarbonylvanadate samples are shown along with the characteristic IR and $^{13}$C NMR spectra. For data, see Table I.

For preparation, red-violet $[Et_4N][V(CO)_5THF]$ was generated by UV irradiation (Duran filter, 195 K, argon atmosphere) [3] of a THF solution containing 100 mg $[Et_4N][V(^{12}CO)_6]$ (0.29 mmol) in 15 ml. Removal of the photochemically released $^{12}$CO and subsequent treatment with $^{13}$CO, followed by 20 min shaking at room temperature, yielded yellow $[Et_4N]$-$[V(^{12}CO)_{6-n}(^{13}CO)_n]$ 12% enriched in $^{13}$CO (**I**). Two further cycles of this procedure yielded a complex mixture containing 42% $^{13}$CO (**II**).

The IR spectra in the CO stretching region exhibit a pattern consistent with the loss of $O_h$ symmetry on substituting $^{12}$CO partially by $^{13}$CO. However, a differentiation of the ten species which might be present cannot be carried out. The assignments of the five absorptions (Fig. 1 and Table I) follow those of Bor and Jung for $^{13}$CO enriched $[Mo(CO)_6]$ [4]. The $^{13}$C NMR spectra show only one single eight-line system in the temperature range 300 to 235 K, indicating equivalence of all of the $^{13}$CO (and possibly excluding the isomers *mer*-$[V(^{12}CO)_3(^{13}CO)_3]^-$ and *cis*-$[V(^{12}CO)_2(^{13}CO)_4]^-$). The pattern, which is produced by coupling to the spin 7/2 nucleus $^{51}$V, is reminiscent of that of the $^{31}$P resonance of $[V(PF_3)_6]^-$ [1, 5], and also of the $^{13}$C resonance of $[V(\eta^5\text{-}C_5H_5)(CO)_4]$ [6]. The signal position

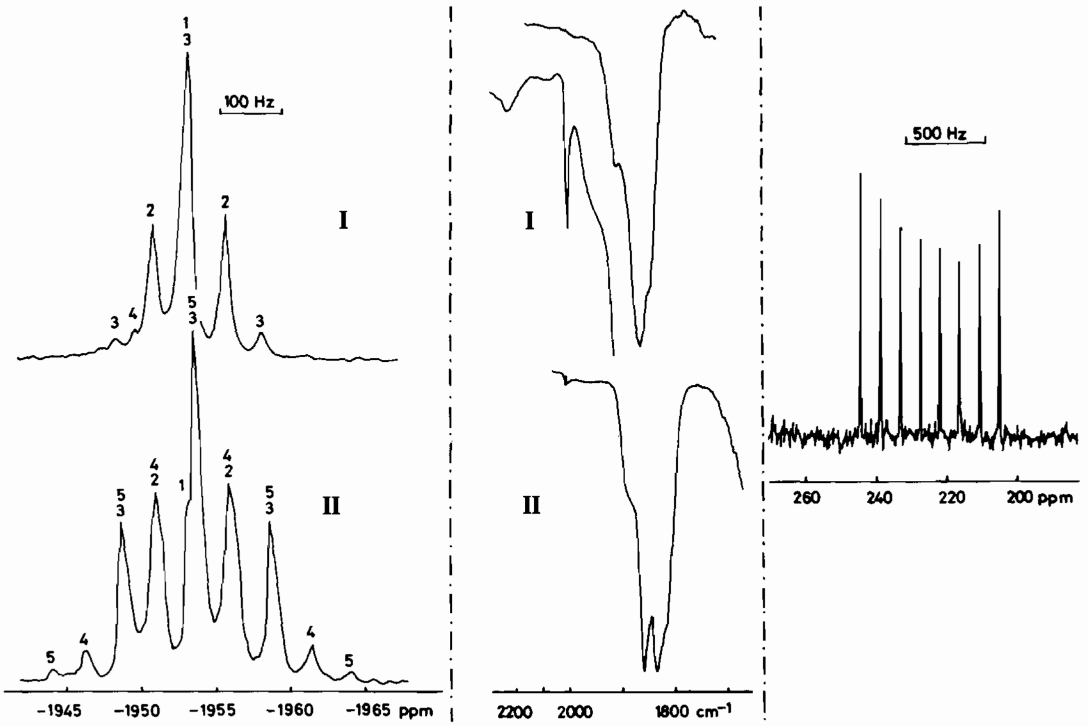

Fig. 1. $^{51}$V NMR (23.66 MHz, relative to $VOCl_3$, external lock acetone-$d_6$, pulse width 8 $\mu$s, acquisition time 0.16 s, 300(1) K, 1000 scans) of 0.02 M solutions of $[Et_4N][V(^{12}CO)_{6-n}(^{13}CO)_n]$ containing 12% (I) and 42% $^{13}$CO (II), and the corresponding IR (0.1 mm KBr cuvettes) and $^{13}$C NMR (300 K) spectra. For the numbering of the signals see Table I.

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*Author to whom correspondence should be addressed.

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TABLE I. $^{51}$V NMR[a] and IR Data.

| $\delta(^{51}V)$ (ppm) | $\Delta\delta(V)^{b}$ (ppm) | $\nu(CO)$ ($cm^{-1}$) | No. and Assignment |
|---|---|---|---|
| −1953.7 | 0 | | 1 $[V(^{12}CO)_6]^-$ |
| | −0.39(1) | | 2 $[V(^{12}CO)_5{}^{13}CO]^-$ |
| | −0.52(2) | | 3 $[V(^{12}CO)_4(^{13}CO)_2]^-$ |
| | −0.78(5) | | 4 $[V(^{12}CO)_3(^{13}CO)_3]^-$ |
| | −1.08(10) | | 5 $[V(^{12}CO)_2(^{13}CO)_4]^-$ |
| | | 2008 | 2 |
| | | 1889 | (1), 2, *trans*-3, 4 |
| | | 1856 | 1, 2, *cis*/*trans*-3, 5 |
| | | 1832 | 2, *cis*-3, 4, 5 |
| | | 1820(sh) | *trans*-3, 4, 5 |

[a] All $^{1}J(^{13}C-^{51}V)$ are 116 Hz. [b] $\delta[V(^{12}CO)_{6-n}(^{13}CO)_n]^- - \delta[V(^{12}CO)_6]^-$.

(centered at 225.3 ppm) and $^{1}J(^{13}C-^{51}V)$ (116 Hz) agree with the corresponding parameters reported by Bodner and Todd for $[Na(diglyme)_2][V(CO)_6]$ [7] with $^{13}CO$ in natural abundance.

The $^{51}$V NMR of **I** is the superposition of a singlet (1) a doublet (2) and a triplet (3) in the intensity ratio 1/2/3 = 1/1/0.3. **II** contains, in addition, a quartet (4) and a quintet (5), and the intensity ratio is 2/3/4/5 = 0.6/1.8/1/1. The different species are clearly discernable. The decrease in symmetry does not affect the signal positions; a similar observation holds for the complexes $[V(CO)_{6-n}(PF_3)_n]^-$ [6] and has been accounted for in terms of the very similar $\pi$-acceptor properties of the CO and $PF_3$ ligands.

The slight but clearly distinct low-frequency (high-field) shift of the $^{51}$V resonances as the contents of $^{13}CO$ increase is an isotope effect in the 'correct' direction, although much less pronounced than *e.g.* for the $^{59}$Co resonances in the isoelectronic $[Co(^{12}CN)_{6-n}(^{13}CN)_n]^{3-}$ [8] (this may be a consequence of the greater intrinsic shielding sensitivity of the $^{59}$Co nucleus [1]). In analogy to the hexacyanocobaltates, the low-frequency shift of the $^{51}$V resonance may be interpreted in terms of decreasing energy of vibronic levels, which leads to an increase of the HOMO-LUMO separation and thus to diminished paramagnetic de-shielding contributions (*i.e.* increase of the overall shielding). This effect is expected to impose a linear increase of metal shielding with increasing ligand isotope substitution, as observed with the series of $[Co(^{12}CN)_{6-n}(^{13}CN)_n]^{3-}$ complexes [8]. However, in our case $^{51}$V-shielding does not increase smoothly as the number of $^{13}CO$ ligands increases (*cf.* Table I). An alternative interpretation is a consideration on the basic of differing polarizabilities of $^{12}CO$ and $^{13}CO$. The polarizability concept has been employed successfully to explain the so-called normal trend (*i.e.* increase) of metal shielding in low-valent transition metal compounds as the polarizability of the ligand functions attached to the metal center increases [1, 9]. In the frame-work of this concept, the softer $^{13}CO$ should induce—relative to $^{12}CO$—a more pronounced covalency of the V–CO bond and an expansion of the V(3d) cloud, and thus a decrease of the de-shielding term and increase of overall shielding in a complex, not necessarily linear manner.

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