Notes

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^{51}V Shielding in Vanadium(V) Complexes: A Reference Scale for Vanadium Binding Sites in Biomolecules

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The role of vanadium as a biometal is well established[1] and encompasses stimulating and regulatory[2] as well as inhibitory functions, e.g. toward Na,K-ATPase.[3] Vanadium has also been recognized as an essential element in photosynthesis,[4] as a storage for redox potentials in the "blood" of ascidians,[5] and as an integral part in amavadine, a hydroxamate complex of V occurring in *Amanita muscaria*.[6] Lately, vanadium has adopted the status of an catalytically active center in the nitrogenase system of a special strain of *Azotobacter chroococcum*[7] and in the vanadate(V)-dependent halide peroxidases of several marine brown algae such as *Ascophyllum nodosum*.[8,9] Further, the binding of V(IV) and V(V) to serum transferrin has been documented.[10,11]

More recently, the excellent NMR properties of the ^{51}V nucleus[12] have been exploited in the evaluation of the interaction between vanadate(V) and large biomolecules such as ribonuclease,[13] transferrin,[11] and peroxidase from *A. nodosum*,[14] the latter being the first ^{51}V NMR detection of an enzyme containing vanadate(V) as the prosthetic group.

In order to provide a basis for the interpretation of vanadium NMR data of biological material, we report here on a referencing scale for ^{51}V chemical shifts, $\delta(^{51}V)$, incorporating the presently available shift data on V^{5+} compounds (including recent work on the interaction between vanadate and biorelevant ligands[15]),

Chart I

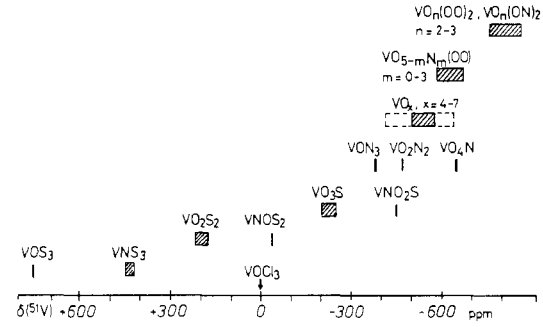

Table I. $\delta(^{51}V)$ Values of Neutral and Anionic Vanadium Complexes

compd[a]/solvent	coordn environment	$\delta(^{51}V)$[b]
Coordination Number 4		
VO(O-*n*-C_8H_{17})$_3$/*n*-octanol	O_4	−590
VO(O-*n*-C_5H_{11})$_3$/pentane (neat)	O_4	−543 (−549)
VOCl(O-*n*-C_5H_{11})$_2$/pentane	O_3Cl	−466
Coordination Number 6		
VO(O-*t*-Bu)(ac)$_2$/CH_2Cl_2–$CDCl_3$	O_6[g]	−584*[g]
VO(O-*t*-Bu)(prop)$_2$/CH_2Cl_2–$CDCl_3$	O_6[g]	−585*[g]
$[VO_2(ox)_2]^{3-}/D_2O$	O_6	−529
$[\{VO(O_2)_2\}_2(\mu\text{-}O)]^{4-}/D_2O$	O_6	−746*
VO(OR)(pbha)$_2$[c]/$CDCl_3$	O_6	−440
VOCl(pbha)$_2$/$CDCl_3$	O_5Cl	−280
VO(NR_2)(pbha)$_2$[d]/$CHCl_3$	O_5N	−430
$[VO(O_2)dipic]^-/D_2O$	O_5N	−595*
VO(OH)(oxin)$_2$/$CDCl_3$	O_4N_2	−483
VO(OR)(oxin)$_2$[e]/$CDCl_3$	O_4N_2	−466 to −478
VO(OR')(oxin)$_2$[f]/$CDCl_3$	O_4N_2	−492 to −497
VO(OH)(Me-oxin)$_2$/$CDCl_3$	O_4N_2	−450
VO(OEt)(Me-oxin)$_2$/$CDCl_3$	O_4N_2	−466
$[VO_2(edta)_2]^{3-}/D_2O$	O_4N_2	−519
VO(OH)(S_2CNEt_2)$_2$/$CDCl_3$	O_2S_4	−468*
VO(OEt)(S_2CNEt_2)$_2$/$CDCl_3$	O_2S_4	−551*
VO(OH)(S_2C(py)$_2$/$CDCl_3$	O_2S_4	−474*
VO(S_2CNEt_2)$_3$/$CDCl_3$	S_6	−506*
VO(S_2C(py)$_3$/$CDCl_3$	S_6	−469*
Coordination Number 7		
VO(ac)$_3$/CH_2Cl_2	O_7[g]	−589*[g]
$[VO(O_2)(ox)_2]^{3-}/D_2O$	O_7	−590*
$[VO(O_2)_2ox]^{3-}/D_2O$	O_7	−733*
$[VO(O_2)_2phen]^-/D_2O$	O_5N_2	−741*
$[VO(O_2)_2bpy]^-/D_2O$	O_5N_2	−746*
$[VO(O_2)_2ox]^{3-}/D_2O$	O_7	−729*
$[VO(O_2)_2phen]^-/D_2O$	O_5N_2	−733*

[a] Abbreviations: ac = acetate(1−), prop = propionate(1−), pbha = *N*-phenylbenzohydroxamate(1−), oxin = 8-hydroxychinolate(1−), Me-oxin = 2-methyloxin, ox = oxalate(2−), dipic = dipicolinate(2−), phen = *o*-phenanthroline, bpy = 2,2'-bipyridyl. [b] Relative to $VOCl_3$; an asterisk denotes that shielding is influenced by chelate-3 or -4 ring structures present in the complex. [c] R = Et, CH_2CH_2OH, Ph, L-rhamnosyl. [d] NR_2 = pyrrolate(1−). [e] R = Me, Et, *n*-Pr, allyl, CH_2CH_2OH, $CH_2CH_2CH_2OH$, D-ribosyl, 2-deoxy-D-ribosyl. [f] R' = *i*-Pr, *sec*-Bu. [g] Assuming the η^2 mode of the carboxylate ligand. Both the η^1 and the η^2 coordination have been reported in complexes of the composition VO(OR)$_{3-n}$(carboxylate)$_n$: Preuss, F.; Towae, W.; Woitschach, J.; *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 817. Preuss, F.; Woitschach, J. *Z. Naturforsch, B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 163.

supplemented by new data for compounds from our own laboratory that model potential protein binding sites. A briefing on the

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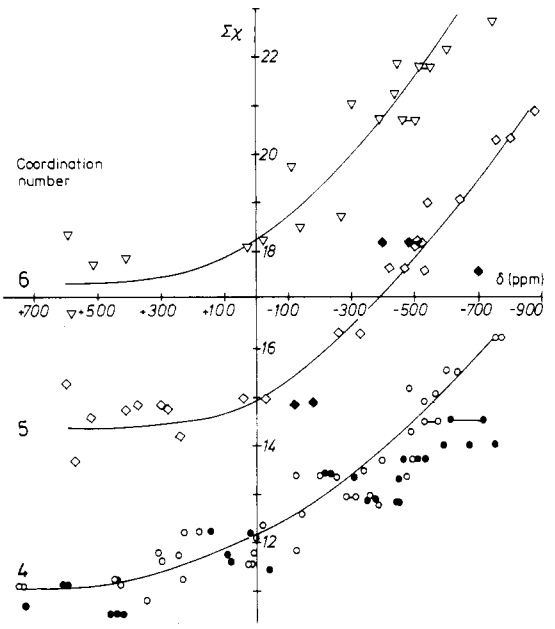

Figure 1. Relation between ^{51}V chemical shfits δ (relative to $\delta(VOCl_3)$ = 0 ppm) and the sum of the electronegativities of the ligands Z on vanadium, $\sum\chi$, for the coordination numbers 4 (○, ●), 5 (◇, ◆) and 6 (▽). Solid symbols represent compounds with bulky substituents (*i*-Pr, *t*-Bu). The scale extends to +1457 ($[(VS_3)_2\mu\text{-}S]^{4-}$ [19g]) and +1395 ppm ($[VS_4]^{3-}$ [19f,g]), $\sum\chi$ = 9.92. Complexes containing the peroxo, hydroxylamido, nitrato, or carbonato ligand are not included (cf. Table III). The χ scale by Zhang[23] has been employed. δ values were taken from the following sources: Z = S^{2-},[19f,g] SR^-,[19a,d] O^{2-},[18] OR^-,[15,17,19b,e,20a] NR_2^- and NR^{2-},[17,19a,d,h,i] $N_3S_2^{3-}$,[20c,f,g] Br^-,[20a,g] Cl^-,[17,19b,h,i,20a,c,f,h] F^-,[17,20b,d,e] and σ-C.[21]

background theory, which allows for a rationalization of the observed shielding trends, is also presented, based on an improved PE/SCF–Xα investigation of VOX_3 (X = Br, Cl, F),[16] several aspects of which have been noted previously.[17a]

In Chart I, the $\delta(^{51}V)$ shift ranges for vanadium complexes with ligand functions related to biomolecules (O, N, S) are summarized; they were taken from ref 14, 15, 17a, 18, and 19 and from Tables I and II. Figure 1 is a collation of data with the inclusion of halide and carbon functionalities and the thiazeno ligand $N_3S_2^{3-}$, and correlated with the electronegativities χ of the substituents on V. In Table III, some connections between $\delta(^{51}V)$ values and chelate ring sizes are summarized.

We note the following trends: (i) In unstrained systems (open structures formed with monodentate ligands; chelate-5 rings), shielding increases with increasing χ (decreasing polarizability) of the ligands Z on vanadium; there is no unambiguous differenciation between O and N (Table I). (ii) Strained structures (bulky substituents and, even more so, three- and four-membered rings) give rise to substantially higher shielding values than unstrained ones in the same coordination environment. Bidentate functionalities, such as the peroxo, the hydroxylamido or the carboxylato group, can therefore be considered as ligands of high

Table II. $\delta(^{51}V)$ Values for Vanadate–Dipeptide Complexes[a]

dipeptide[b]	pH	$c(V)/c(peptide)$[c]	$\delta(^{51}V)$ of main resonance[d]
glu-glu	7.5	1/2	−507
glu-gly	7.4	1/40	−500
Z-glu-tyr	7.5	1/22	−544
Z-glu-tyr[e]	7.9	1/30	−546
gly-tyr	7.8	1/10	−509
gly-tyr[e]	7.8	1/10	−497
gly-ser[f]	7.5	1/30	−493 and −506
gly-ser[e]	7.5–7.8	1/1–1/60	−493 to −502
gly-asp	7.3	1/60	−508
gly-glu	7.3	1/60	−503
gly-gly	7.1	1/60	−504

[a] The overall valandium concentration is $c(V)$ = 10–20 mmol/L; measuring frequency ν_0 = 23.66 MHz (except for *f*). [b] Abbreviations: glu = glutamic acid, asp = aspartic acid, tyr = tyrosine, gly = glycine, ser = serine, Z = *N*-carbobenzoxy. [c] Concentration ratio vanadium/peptide. [d] The relatively broad (half-width ca. 250–500 Hz) resonance (carrying, in some cases, an unresolved low-field shoulder) is tentatively assigned to a vanadate–peptide complex with the nitrogen of the peptide linkage participating in coordination. Additional signals corresponding to oligovanadates[18] (cf. Figure 2) and a minor resonance arround −547 ppm indicating vanadate–peptide and/or vanadate–Tris interaction via CO_2^- (η^1) or RO^- are observed. [e] In Tris buffer. [f] The resonance at low field (−493 ppm), which becomes resolved at ν_0 = 94.7 MHz and carries about 10% of the integral intensity, is assigned to coordination via the peptide N plus the alcoholic function.

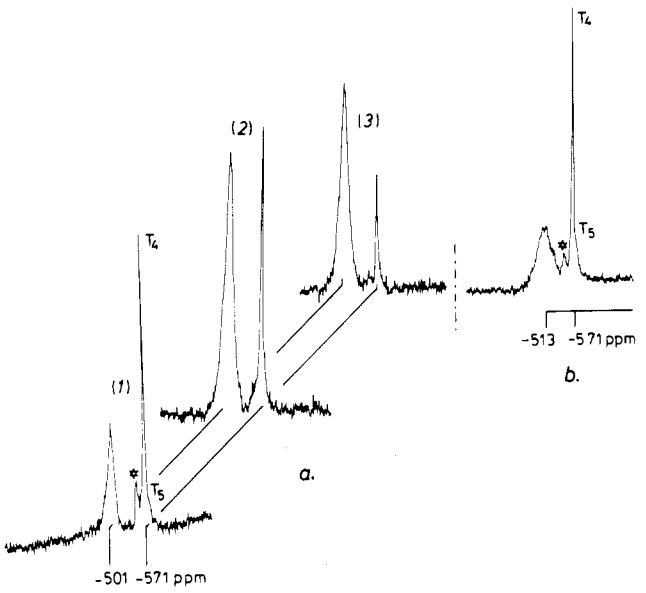

Figure 2. 23.66-MHz ^{51}V NMR spectra of vanadate (v)/dipeptide (p) mixtures in Tris buffer–D_2O (pH 7.6). The broad signals at low field (high frequency) correspond with v–p interaction, possibly including the peptide linkage (cf. Table II). Key: (a) v/gly-ser, (1) $c(v)$ = 10 mmol/L and $c(v)/c(p)$ = 0.1, (2) $c(v)$ = 32 mmol/L and $c(v)/c(p)$ = 0.05, and (3) $c(v)$ = 25 mmol/L and $c(v)/c(p)$ = 0.04; (b) v-glu-glu, $c(v)$ = 15 mmol/L and $c(v)/c(p)$ = 0.04. The sharp signals at high field represent $[V_4O_{12}]^{4-}$ (T_4), $[V_5O_{15}]^{3-}$ (T_5),[18a,b] and a v–Tris complex (☆).

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(17) (a) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1985**, *24*, 3058 and references cited therein. (b) The exact shift for VOF_3 is not known since VOF_3 is insoluble in nonpolar solvents and soluble in polar solvents with a change in its coordination sphere only. Several shift values reported in the literature for VOF_3 have therefore to be reasigned (e.g. −622 ppm for VOF_3 in $CHCl_3$,[17a] which actually is the shift for $VOF(OEt)_2$ formed as VOF_3 reacts with the ethanol contained in $CHCl_3$ as a stabilizing additive; VOF_3 in MeCN (δ = −793[20e]) is $[VOF_4]^-$). In THF, we observe a quartet at −757 ppm ($J(VF)$ = 77 (5) Hz) in accord with the VOF_3 moiety present in an apparently more complex compound.[17a] Note added in proof: In Cl_3CMe, where VOF_3 is sparingly soluble, an unstructured signal appears at −767 ppm (Rehder, D.; Priebsch, W., unpublished results).

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Table III. $\delta(^{51}V)$ Values for Compounds Containing OO and ON Chelate-Ring Structures[a]

CN	no substantial strains open structures, 5-ring(s)		strains caused by chelate-ring(s): one 3-ring/4-ring		strains caused by chelate-ring(s): two or three 3-rings/4-rings	
4	520–580[b]	O_4				
5	500–520	$O_3(\overline{O\,O})$	630	$O_3(OO)$		
	530	$O_2(\overline{O\,N\,O})$				
6	540	$O_4(\overline{O\,O})$	595	$O(\overline{O\,N\,O})(OO)$	584–770	$O_2(OO)_2$, $O_2(\overline{O\,O})_2$[c]
	440–530	$O_2(\overline{O\,O})_2$			690–710	$O_2(ON)_2$
	460–520	$O_2(\overline{O\,N})_2$				
7			595	$O(\overline{O\,O})_2(OO)$	793	$O(\overline{O\,O})_3$[c]
			595	$O_2(\overline{O\,N\,O})(OO)$	695–750	$O_3(\overline{O\,O})(OO)$, $O(\overline{O\,O})_2(OO)$[c]
			600–670	$O_2(\overline{O\,N\,O})(NO)$	730	$O(\overline{O\,O})_2(OO)_2$
			580	$O(\overline{O\,N})(\overline{N\,N})(OO)$	750	$O_3(OO)_2$
					695	$O(\overline{O\,O})(OO)_2$
					745	$O(\overline{N\,N})(OO)_2$
					830	$O(\overline{N\,N})(ON)_2$
					880	$O(\overline{O\,N})(ON)_2$
					830	$O(OO)_3$

[a] Abbreviations: $\overline{O\,O}$ = dicarboxylate, glycolate; $\overline{O\,N}$ = pic, oxin, edta; $\overline{O\,N\,O}$ = dipic; $\overline{N\,N}$ = bpy, *o*-phen; $\overline{O\,O}$ = acetate, carbonate, nitrate; OO = peroxo; ON = R_2NO^-. Data were taken from Table I and ref 14 (carbonate, acetate), 15a,b (oxalate, lactate, glycolate), 18c (oxalate), 19c (peroxo), 20e (nitrate), 22 (picolinate, hydroxylamido). All shift values (relative to $VOCl_3$) are negative. [b] "Inner" range only. [c] Assuming bonding of the ligand $\overline{O\,O}$ in the η^2 mode (cf. footnote *g* in Table I).

effective electronegativities. (iii) Variations of the coordination number, CN, have a minor effect only in that the overall increase of χ is counterbalanced (sometimes even overbalanced) by the increase of CN. Nonetheless, the effect of CN may be important for the assignment of signals arising from the interaction of vanadate (CN = 4) with alcohols,[15,19c] carboxylates,[15a] and dipeptides (Table II). A downfield (high-frequency) shift relative to $[V_4O_{12}]^{4-}$ (the main species present in ca. 0.04 M vanadate solutions in the pH range 6.5–8.5; $\delta = -575$[18a,b]) of up to 80 ppm is observed ongoing to CN = 5 and 6. A representative spectrum illustrating this situation is shown in Figure 2.

Alterations of the overall shielding $\sigma'(\text{total}) = \sigma'(\text{para}) + \sigma'(\text{dia})$ are almost exclusively brought about by the paramagnetic deshielding term, which correlates with the mean HOMO–LUMO gap $\overline{\Delta E}$, the vanadium LCAO coefficients $C(3d)$ and $C(4p)$ of MOs taking part in electronic transitions, and the delocalization of 3d and 4p electrons, r, in the following manner:

$$\sigma'(\text{para}) = \text{const} \times \Delta E^{-1}[(r^{-3}C^2)_{4p} + (r^{-3}C^2)_{3d}] \qquad (1)$$

with the main contribution coming from transitions between orbitals with large V(3d) population.[12,17] As shown in Figure 3 for VOX_3 (X = Br, $\delta = +432$;[20a] X = Cl, $\delta = 0$; X = F, δ ca. -700[17b]), contributing HOMOs are $\sigma(VX)$, $\pi(VX)$ and $\pi(V{=}O)$ bonding orbitals in the case of $VOBr_3$ and $VOCl_3$, and $\pi(V{=}O)$ only for VOF_3. LUMOs are substantially nonbonding V(3d) orbitals,

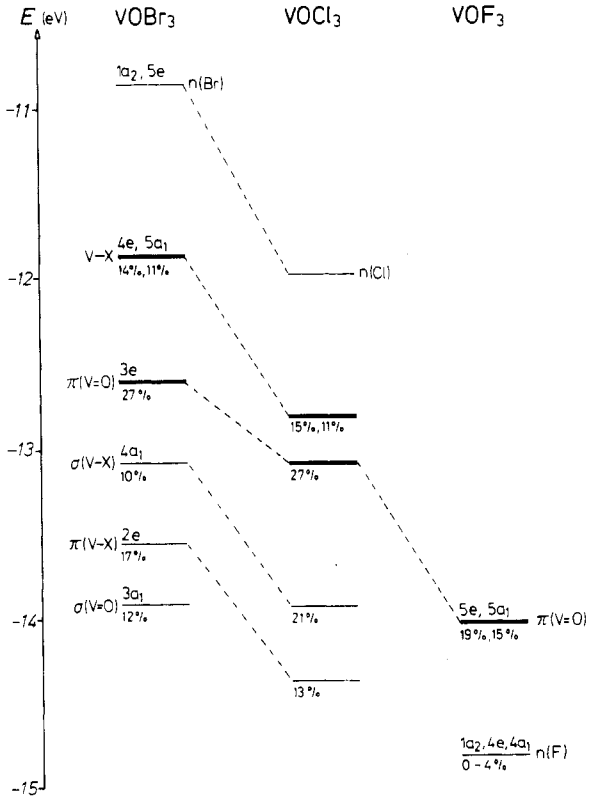

Figure 3. Correlation diagrams for selected occupied MO levels of VOX_3 (X = Br, Cl, F), with data adapted from PE measurements and SCF-Xα MO calculations carried out by Elbel and co-workers.[16] The V(3d) percentage is indicated underneath the bars. Levels that have been emphasized by solid bars are the main contributors to electronic excitations (cf. eq 1) into suitable LUMOs, i.e. unoccupied V 3d orbitals, the energy levels (VOIEs) of which are between -10.5 and -8.5 eV.[24]

located around -10 eV.[24] With increasing $\chi(X)$, ΔE increases, inducing an increase of $\sigma'(\text{total})$ (decrease of $\sigma'(\text{para})$), the

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well-documented "inverse electronegativity dependence of metal shielding" in low-valent (d^0) complexes.[12b,17a,25] Further, the ionicity of the V–X bond increases with increasing $\chi(X)$, and concomitantly, $C(3d)$ should decrease. While this is observed on going from $VOCl_3$ to VOF_3 (cf. Figure 3) and may well contribute to the high shielding for the latter, the V 3d character of the HOMOs is virtually the same for $VOCl_3$ and $VOBr_3$, a fact that may reflect the similar π-donating capacities of the chloro and bromo ligands.

Interpolation between $VOCl_3$ and VOF_3 places the trigonal-pyramidal $VO(O)_3$ (ca. −570 ppm) in a similar position as VOF_3, i.e. with the $\pi(V{=}O)$ level as the main HOMO taking part in relevant transitions. The situation does not change to a great extent, if we consider CN = 5 (e.g. $[VO(OH)_2$glycolate$]^-$, −522 ppm[15b]) and 6 (e.g. $[VO(OH)_3$oxalate$]^{2-}$, −536 ppm[15a,18c]). This has been exemplified for $[VO(H_2O)_5]^{2+}$, where the $\pi(V{=}O)$ MO is again energetically closer to the nonbonding V(3d) level than any of the MOs arising from the interaction of V^{4+} with the aqua ligands.[26]

The "inverse chelate effect" of metal shielding in low-valent complexes is less straightforwardly rationalized. We may assume, however, that strains in 4-ring structures (η^2-carboxylato and -carbonato complexes) and 3-ring structures (e.g. peroxo complexes) give rise to overlap perturbations and thus to diminished oxygen π donation into V(3d) and V(4p) orbitals and hence a net depletion of electron population resulting in decreased C^2 in (1). Alternatively, delocalization of bonding electron density over the three- or four-membered ring can give rise to an increase of r, which in turn diminishes σ'(para).

In conclusion, we have shown that *high* ^{51}V shielding is generally induced by ligands Z with large electronegativity values χ (Z = O, F), the gap between $\pi(V{=}O)$ orbitals of sizable V(3d) character and chiefly nonbonding V(3d) orbitals being the major factor responsible for the shielding variations at the ^{51}V nucleus. While variations of the coordination number between 4 and 6 (and 7) do not influence shielding significantly, additional shielding can be expected if bidentate ligands forming chelate-3 and -4 rings are constituents of the coordination sphere. A similar but less pronounced effect is also observed with very bulky Z. *Low* shielding values go along with highly polarizable ligands (Z = Br, S), for which electronic excitations from bonding orbitals associated with the V–Z bond become increasingly important as χ decreases. Ligands coordinating via nitrogen (Z = N) generally induce shielding values close to those of oxygen ligands.

The main bonding site of vanadate with dipeptides at pH 7.5 seems to involve the N function of the peptide linkage. The $\delta(^{51}V)$ value for the vanadate–peptide species is −501 ± 8 ppm relative to $VOCl_3$.

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Metal Atom Synthesis of Metallaborane Clusters. 9.[1] Synthesis and Structural Characterization of *iso*-8-(η-C_5H_5)$CoB_{17}H_{21}$

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We have previously demonstrated that metal vapor reactions can be used to generate a wide variety of metallaborane and -carborane clusters.[1-8] Although most of our studies have involved reactions with the smaller, more reactive boranes and carboranes, we have also achieved the synthesis of, for example, (η^6-arene)-metallaboranes derived from higher cage systems, such as $B_{10}H_{14}$,[6] SB_9H_{11}, and $SB_{10}H_{12}$.[9] We have recently begun to explore the synthesis of metal complexes based on larger fused and linked-cage boranes and carboranes, and we report here the isolation and structural characterization of a unique cobaltaborane complex, *iso*-8-(η-C_5H_5)$CoB_{17}H_{21}$, obtained from the reaction of cobalt vapor with cyclopentadiene and *n*-$B_{18}H_{22}$.

Experimental Section

Materials and Procedure. Cobalt metal (99.9% 50 mesh) was obtained from Alfa Ventron Corp. Cyclopentadiene was freshly distilled from dicyclopentadiene (Aldrich). The *n*-$B_{18}H_{22}$ was synthesized by using a modified version of Gaines' method,[10] in which the oxidation of *nido*-$B_9H_{12}^-$ was accomplished by ferrocenium ion.[11] Flash column chromatography was performed with silica gel (230–400 mesh, EM Science). The Chromatotron (7924T) was purchased from Harrison Research, Palo Alto, CA. The preparative 2-mm rotor for the Chromatotron was prepared by using silica gel PF-254 with $CaSO_4 \cdot {}^1/_2H_2O$ from EM Science and was oven dried for a day prior to use.

The ^{11}B NMR spectra at 160.5 MHz were obtained on a Bruker AM-500 Fourier transform spectrometer. All boron-11 shifts are referenced to $BF_3 \cdot O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual C_6H_6 from the lock solvent (99.5% C_6D_6) and are referenced to Me_4Si (0.00 ppm). High- and low-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. The infrared spectrum was obtained on a Perkin-Elmer 1310 spectrophotometer.

The metal vapor reactor used for this work was based on a design by Klabunde[12] and is described elsewhere.[2] Cobalt vapor was generated by electrical heating (~7.2 V, 60 A).

Reaction of Cobalt Vapor with Cyclopentadiene and *n*-$B_{18}H_{22}$. In a typical reaction, approximately 0.6 g of cobalt powder was placed in the evaporation crucible and 0.8 g of *n*-$B_{18}H_{22}$ (3.6 mmol) in the bottom of the metal atom reactor. The reactor was then evacuated and cobalt vapor and 20 mL of cyclopentadiene were condensed on the walls of the reactor that was maintained at −196 °C. After metal vaporization was complete, the reactor was allowed to warm to −78 °C and stirred for 30 min. The resulting dark slurry was then warmed to room temperature and stirred for an additional 90 min. Excess ligands were removed in vacuo, and the reactor was flushed with nitrogen gas. The dark residue was extracted with methylene chloride and filtered through a coarse frit. The filtrate was placed on a flash column and eluted with benzene. The first band was identified as *n*-$B_{18}H_{22}$ (0.2 g, 0.9 mmol). A second red band was collected, concentrated, and further separated by using the Chromatron with a 80:20 hexane/benzene mixture. This separation gave 20.1 mg of *iso*-8-(η-C_5H_5)$CoB_{17}H_{21}$ (0.06 mmol, 2.2%): R_f 0.23 in hexane/benzene (80:20); red; mp 163–164 °C; mass measurement calcd for $^{12}C_5{}^{59}Co^{11}B_{17}{}^1H_{26}$ 332.2949, found 332.2921; ^{11}B NMR (ppm, C_6D_6, 160.5 MHz) 27.0 (d, J_{BH} ~ 125 Hz), 18.7 (d, J_{BH} = 130), 17.2 (d, J_{BH} = 130), 14.9 (d, J_{BH} = 145), 12.3 (d, J_{BH} = 145), 8.9 (d, J_{BH} ~ 160), 7.8 (s), 2.9 (d, J_{BH} = 160), 1.8 (d, J_{BH} = 130), −0.5 (d, J_{BH} ~ 160), −1.0 (s), −4.9 (d, J_{BH} = 130), −19.8 (d, J_{BH} = 145), −20.1 (d, J_{BH} = 145), −27.3 (d, J_{BH} = 160), −28.7 (d, J_{BH} = 160), −37.1 (d, J_{BH} = 145); ^1H NMR(δ, C_6D_6, 250 MHz) 4.5 (s, 5, C_5H_5); ^1H NMR (δ, C_6D_6, 200 MHz, ^{11}B spin decoupled) −0.1 (s, br), −0.5 (s, br), −0.7 (s, br), −2.9 (s, br), −3.7 (s, br), −17.2 (s, br); IR (KBr pellet, cm^{-1}), 2960 (w), 2550 (s), 1425 (s, br), 1260 (m), 1190 (w), 1090 (m, br), 1020 (m), 840 (w), 800 (s), 650 (w).

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