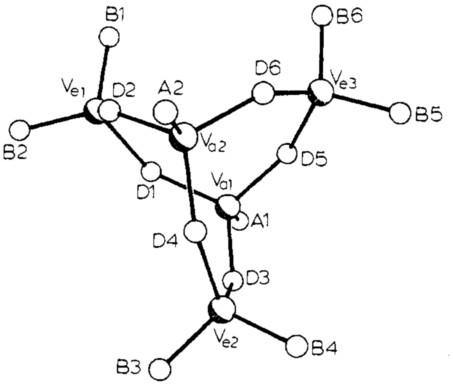

Figure 1. Perspective plot of the $V_5O_{14}^{3-}$ anion as observed in crystalline $[V_5O_{14}][(n\text{-}C_4H_9)_4N]_3$. Vanadium atoms are represented by shaded spheres and oxygen atoms by open spheres. Oxygen atoms are labeled with a capital letter (A, B, or D) and a number.

solution volume to 15–20 mL by boiling off solvent over a 15–20-min period. Crystalline $V_5O_{14}[(n\text{-}C_4H_9)_4N]_3$[9] (1.1 g) is obtained in 80% yield by adding 30–40 mL of diethyl ether to the reaction solution at ambient temperature with stirring and crystallizing the resulting white precipitate by dissolving it into 15 mL of acetone followed by 2–3 mL of ethyl acetate and cooling to −7 °C for 12 h. The compound is slightly moisture-sensitive and should not be exposed to atmospheric moisture for extended time periods.

X-ray structural analysis[10] of crystalline $(V_5O_{14})[(n\text{-}C_4H_9)_4N]_3$, obtained as described above, revealed the presence of discrete $(n\text{-}C_4H_9)_4N^+$ cations[11] and $V_5O_{14}^{3-}$ anions which each contain five tetrahedral vanadium(V) centers in a nearly trigonal-bipyramidal arrangement (Figure 1). The two "axial" vanadiums (V_{a1} and V_{a2}) each have a single terminally bonded (O_A) oxygen, while the three "equatorial" vanadiums (V_{e1}, V_{e2}, and V_{e3}) each have two (O_B). Although the $V_5O_{14}^{3-}$ anion possesses no rigorous crystallographic symmetry in the solid state, it approximates rather closely its maximum possible symmetry of D_{3h}. The three "equatorial" V_e atoms and their six terminal O_B oxygens are coplanar to within 0.07 Å; each of the three $(O_AV_a)_2V_e(O_D)_2$ groupings are coplanar to within 0.21 Å, and their least-squares mean planes make dihedral angles of 115.2–125.9° with each other and dihedral angles of 89.8–90.0° with the "equatorial" $[V_e(O_B)_2]_3$ mean plane. D_{3h}-averaged bond lengths and angles of interest include the following: V_a–O_A, 1.580 (7, 3, 3, 2) Å;[12] V_e–O_B, 1.601 (8, 14, 28, 6) Å; V_a–O_D, 1.723 (7, 11, 25, 6) Å; V_e–O_D, 1.818 (7, 11, 26, 6) Å; and V_a–O_D–V_e, 143.3 (4, 62, 105, 6)°. The 30 O–V–O angles range from 107.6 (4)° to 112.7 (3)°. This anion provides the first example of a transition-metal polyoxoanion cage structure based on corner-sharing of tetrahedral coordination polyhedra, a type of cage structure frequently observed for main group polyoxoanions.

The $V_5O_{14}^{3-}$ salt reported here has good solubility in polar organic solvents such as acetonitrile, acetone, 1,2-dichloroethane, and dichloromethane. Preliminary experiments indicate that $(V_5O_{14})[(n\text{-}C_4H_9)_4N]_3$, like $(Mo_2O_7)[(n\text{-}C_4H_9)_4N]_2$ and $(\alpha\text{-}Mo_8O_{26})[(n\text{-}C_4H_9)_4N]_4$, is reactive toward a wide variety of inorganic, organometallic, and organic reagents. We are currently investigating the products of these reactions.

Acknowledgment. We acknowledge the National Science Foundation for support of this work. Chris Frank provided invaluable technical assistance.

Supplementary Material Available: Crystal structure analysis report, Table I (atomic coordinates for non-hydrogen atoms), Table II (anisotropic thermal parameters for non-hydrogen atoms), Table III (atomic coordinates for methylene hydrogen atoms in the cations), Table IV (bond lengths and angles for the anion), Table V (bond length and angles for the cations), Figure 2a–c (perspective ORTEP plots of nitrogen, carbon, and methylene hydrogen atoms in the three cations), and Figure 3 (perspective ORTEP plot of the anion) (23 pages); table of observed and calculated structure factors for $(V_5O_{14})[(n\text{-}C_4H_9)_4N]_3$ (14 pages). Ordering information is given on any current masthead page.

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[9] IR (Nujol, 450–1000 cm^{-1}) 474 (w), 530 (w), 737 (m), 814 (vs), 886 (s), 941 (s), 967 (s); ^{51}V NMR (0.02 M, 25 °C, acetone) δ −539 (3V), −613 (2V) relative to external $VOCl_3$. Anal. Calcd for $C_{48}H_{108}N_3V_5O_{14}$: C, 47.80; H, 9.03; N, 3.48; V, 21.12. Found: C, 47.69; H, 8.93; N, 3.50; V, 20.96.

[10] Single crystals of $[V_5O_{14}][(n\text{-}C_4H_9)_4N]_3$ are at 20 ± 1 °C, orthorhombic, space group $Pbca$-D_{2h}^{15} (no. 61) with $a = 32.708$ (5) Å, $b = 16.956$ (3) Å, $c = 24.344$ (5) Å, and $Z = 8$ [$d_{calcd} = 1.187$ g cm^{-3}; μ_a(Mo K$\bar{\alpha}$) = 0.76 mm^{-1}]. A total of 9299 independent data having 2θ(Mo K$\bar{\alpha}$) < 45.8° were collected on a Nicolet P$\bar{1}$ autodiffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation and full 0.90° wide ω scans. The structure was solved using (SHELXTL) "direct methods" techniques, and the resulting structural parameters have been refined by using counter-weighted cascade block-diagonal least-squares techniques to R_1 (unweighted, based on F) = 0.059 and R_2 (weighted, based on F) = 0.067 for 3182 independent reflections having 2θ(Mo K$\bar{\alpha}$) < 45.8° and $I > 3\sigma(I)$. These refinement cycles employed anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic thermal parameters for all included hydrogen atoms. All methylene hydrogens of the cations (except for those on C_{g3} of cation 1) were included in the structural model at fixed idealized positions (assuming sp^3-hybridization and a C–H bond length of 0.96 Å), but hydrogens of terminal methyl groups were not included. The terminal methyl carbon C_{d3} of cation 1 is statistically disordered between two sites in the lattice.

[11] See paragraph at end of paper regarding Supplementary Material.

[12] The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the averaged value.

Ground Electronic States of the ScCO and NbCO Molecules

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An earlier paper considered the variation in bonding among the first-row transition-metal monocarbonyl molecules,[1,2] and here this is extended by electron spin resonance (ESR) studies of ScCO, NbCO, and attempts to observe FeCO. The ground state of ScCO is found to be $^4\Sigma$ with a low-lying $^4\Pi$ excited state, confirming the recent theoretical calculations of Jeung and Koutecký[3] and Barnes and Bauschlicher.[4] NbCO has a $^6\Sigma$ ground state, as did VCO,[5] but no experimental confirmation of the predicted $^3\Sigma$ or $^5\Sigma$ ground state of FeCO has been obtained.[6]

Figures 1 and 2 show the X-band ESR spectra of ScCO in solid argon at 4 K exhibiting eight hyperfine (hf) lines (^{45}Sc, $I = 7/2$) and NbCO with 10 hf lines (^{93}Nb, $I = 9/2$), respectively. The introduction of up to 0.2% ^{13}CO in the argon led to no observable splitting in the ScCO lines indicating that the hfs is within the line width, i.e., <1.5 G. Only the weaker series of lines in Figure 2 were split by ^{13}CO (~6.6 G), as shown in the inset, and are therefore identified with NbCO. Prior to ^{13}CO addition the stronger series of lines in Figure 2 exhibit hf structure and are

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(1) Bach, S. B. H.; Taylor, C. A.; Van Zee, R. J.; Vala, M. T.; Weltner, W. Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7104–5.

(2) A more thorough review of the first-row MCO molecules has recently been given by Weltner (Weltner, W., Jr.; Van Zee, R. J. Chapter in *Computational Chemistry: The Challenge of d- and f-Electrons*; ACS Symposium Series, to be published 1989).

(3) Jeung, G. H.; Koutecký, J. *J. Chem. Phys. Lett.* **1986**, *129*, 569–576.

(4) Barnes, L. A.; Bauschlicher, C. W., Jr. *J. Chem. Phys.*, to be published.

(5) Van Zee, R. J.; Bach, S. B. H.; Weltner, W., Jr. *J. Phys. Chem.* **1986**, *90*, 583–88.

(6) Bursten, B. D.; Freier, D. G.; Fenske, R. F. *Inorg. Chem.* **1980**, *19*, 1810–11. Barbier, C.; Del Re, G. *Folia Chim. Theor. Lat.* **1984**, *12*, 27–44. Guenzburger, D.; Saitovitch, E. M. B.; De Paoli, M. A.; Manela, H. *J. Chem. Phys.* **1984**, *80*, 735–744. Daoudi, A.; Suard, M.; Barbier, C. *C. R. Acad. Sci. Paris, Ser. II* **1985**, *301*, 911–914. Bauschlicher, C. W., Jr.; Bagus, P. S.; Nelin, C. J.; Ross, B. O. *J. Chem. Phys.* **1986**, *85*, 354–364. Sawaryn, A.; Aldridge, L. P.; Blaes, R.; Marathe, V. R.; Trautwein, A. X. *Hyperfine Interact.* **1987**, *36*, 39–58. Daoudi, A.; Suard, M.; Barbier, C. *J. Chim. Phys.* **1987**, *84*, 795–798.

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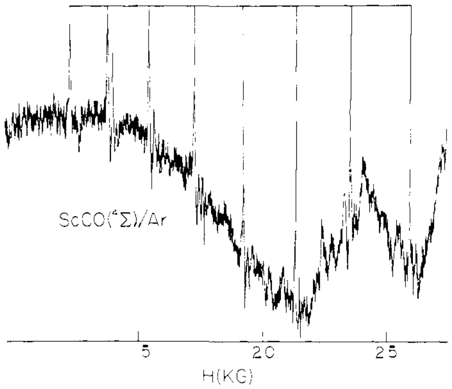

Figure 1. ESR spectrum of the ScCO molecule in an argon matrix at 4 K showing the eight ^{45}Sc (I = 7/2) hyperfine lines on a varying background (ν = 9.5792 GHz).

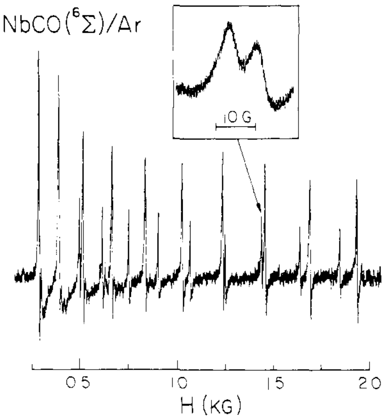

Figure 2. ESR spectrum of the NbCO molecule in an argon matrix at 4 K. The two series of ten lines are due to hyperfine interaction with the ^{93}Nb (I = 9/2) nucleus. Each line of the weak series is split by 6.6 G by introduction of ^{13}CO, as shown in the inset, and is therefore identified with NbCO. The stronger series is due to an unidentified molecule (see text): (ν = 9.5773 GHz).

unchanged by introduction of ^{13}CO in the matrix. They are possibly due to a niobium carbene molecule formed from background hydrocarbon and require further investigation. The procedures for forming the matrices and measuring these spectra were the same as used previously.[7] The magnetic parameters, obtained in the usual way,[5,8] are listed in Table I. At least one higher field fine structure transition could also appear in each of these spectra but only if the zero-field-splitting (zfs) parameter $|D|$ is not too large.[8] Our inability to detect it in each case probably indicates that $|D| \geqslant 1$ cm^{-1}.

The unpaired spin configuration[3,4] in ScCO is nominally $s\sigma^1 d\pi^2$, but the $s\sigma$ orbital is hybridized with $d\sigma$ and $p\sigma$, and the π electrons are partially $p\pi$ of the metal and $2\pi^*$ of CO. (The negligible ^{13}C hfs indicates very little spin density in the $s\sigma$ orbital on CO.) From ^{45}Sc atomic data[9] $A_{\text{iso}} = 2823 \times {}^1/_3 = 941$ MHz, and comparison with the value in Table I yields 58% s character at the metal, as given there. The observed A_{dip} (^{45}Sc) = +58 ± 11 MHz suggests that this value may be too high since a large contribution of $4p\sigma$ and perhaps $d\sigma$ character, which contribute positively to the anisotropic hf, would appear to be required. For example, the configuration $(s\sigma^{0.58} + p\sigma^{0.42})d\pi^2$ yields a value of $A_{\text{dip}} \cong +36$ MHz, and placing spin in the $2\pi^*$ orbital would lower this value further. These approximate deductions are not in agreement with theoretical calculations[4] which predict a considerably higher % s character.

Table I. Derived Magnetic Parameters for ^{45}Sc^{13}CO($^4\Sigma$) and ^{93}Nb^{13}CO($^6\Sigma$) in Solid Argon at 4 K

	^{45}Sc^{13}CO	^{93}Nb^{13}CO
$g_\parallel$	2.0023^a	2.0023^a
$g_\perp$	1.772 (4)	1.980 (2)
$\lvert D\rvert$ (cm^{-1})	$\geqslant$1.0	$\geqslant$1.0
$\lvert A_\parallel\rvert^b$ (MHz)	658 (30)	420 (30)
$\lvert A_\perp\rvert^b$ (MHz)	483 (2)	442 (1)
$A_{\text{iso}}{}^{b,c}$ (MHz)	541 (11)	434 (13)
$A_{\text{dip}}{}^{b,c}$ (MHz)	58 (11)	−7 (12)
$\lvert\psi(0)\rvert^{2\,b}$ (au)	0.497 (10)	0.40 (1)
$\langle(3\cos^2\theta - 1)/r^3\rangle^b$ (au)	0.89 (7)	0.11 (19)
% s character on metal	58	33
$\lvert A_\perp(^{13}\text{C})\rvert$ (MHz)	<4	16 (2)

^{a}Assumed. ^{b}At metal nucleus. ^{c}Assuming $A_\perp$ and $A_\parallel$ are positive in sign.

The large negative value of $\Delta g_\perp = g_\perp - g_e = -0.23$ found for ScCO indicates that a low-lying $^4\Pi(s\sigma^1 d\pi^1 d\delta^1)$ state is coupled to the $X^4\Sigma$. This is in general accord with the ab initio calculations which place such a state at ~3000 cm^{-1}.[3,4] From $\Delta g_\perp$, assuming an average spin-orbit coupling constant of 60 cm^{-1} [10] and a simple $d\pi \rightarrow d\delta$ excitation, we find $\Delta E \cong 500$ cm^{-1}!

NbCO appears to be like VCO in all respects except that the value of $|D| \geqslant 1$, and this is presumably related to the higher spin-orbit coupling constant of Nb relative to V (480 vs 150 cm^{-1}). The % s character on the metals are quite close, 33 vs ~27%; A_{dip} values are −7(12) vs ~ −10(8) MHz, and the ^{13}C splittings are both about 6 G. The analyses of the ESR results are then much the same and imply that the electronic structures of $^6\Sigma$ VCO and NbCO are surprisingly similar.

Since several theoretical calculations have indicated that the lowest states of the FeCO molecule are $^3\Sigma$ and $^5\Sigma$, the nonobservance of an ESR spectrum is attributed here to a zfs parameter $|D| \geqslant 2$ cm^{-1}. This is reasonable in comparison with ScCO and VCO since $|D|$ varies roughly as the square of the spin-orbit coupling constant.

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE-8814297).

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[7] Van Zee, R. J.; Baumann, C. A.; Weltner, W., Jr. *J. Chem. Phys.* **1985**, *82*, 3912–20. Van Zee, R. J.; Ferrante, R. F.; Zeringue, K. J.; Weltner, W., Jr. *J. Chem. Phys.* **1988**, *88*, 3465–74.

[8] Weltner, W., Jr. *Magnetic Atoms and Molecules*; Van Nostrand Reinhold: New York, 1983.

[9] Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577–582.

[10] Dunn, T. M. *Trans. Faraday Soc.* **1961**, *57*, 1441–1444.

Shape-Selective Targeting of DNA by (Phenanthrenequinone diimine)rhodium(III) Photocleaving Agents

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There has been considerable interest in the design of molecules which recognize and react at DNA sites in a sequence-defined fashion.[1,2] We report here the design of a family of new, highly efficient, photocleaving molecules which appear to recognize ostensibly B-form DNA sites on the basis of considerations of shape. Phenanthrenequinone diimine (phi) complexes[3] of rho-

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[1] Dervan, P. B. *Nucleic Acids Mol. Biol.* **1988**, *2*, 49. Moser, H. E.; Dervan, P. *Science* **1987**, *238*, 645. Chen, C.-H. B.; Sigman, D. S. *Science* **1987**, *217*, 1197. Hecht, S. M. *Acc. Chem. Res.* **1986**, *19*, 383.

[2] Barton, J. K. *Science* **1986**, *233*, 727. Fleisher, M. B.; Mei, H.-Y.; Barton, J. K. *Nucleic Acids Mol. Biol.* **1988**, *2*, 65. Mei, H.-Y.; Barton, J. K. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 1339. Kirshenbaum, M. R.; Tribolet, R.; Barton, J. K. *Nucleic Acids Res.* **1988**, *16*, 7943.

[3] The syntheses and characterizations of [Rh(phen)$_2$phi]Cl$_3$ and [Rh(phi)$_2$bpy]Cl$_3$ are available as Supplementary Material. Full details will be provided in a subsequent publication.

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