other. This might be taken as an indication that the equilibrium constant for binuclear complex formation ($K_0 = k_3/k_4$) should be relatively insensitive to the change of the Ti(III) species. On this basis the ratio $k/k'/k''$ of $1/250/10^4$ seem too large to be ascribed to assembly of the binuclear complex and must be taken to apply to subsequent steps, deprotonation and/or electron transfer. One likely source of this effect is modification of the degree of cross-bridge electronic interaction, caused by nonbridging oxalate ion.

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Registry No. $Co(NH_3)_4C_2O_4^+$, 21560-02-1; Ti^{3+}, 22541-75-9; $C_2O_4^{2-}$, 338-70-5.

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Crystal and Molecular Structure of the Thiovanadyl Complex (*N,N'*-Ethylenebis(acetylacetonylideniminato))-thiovanadium, V=S(acen)

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The first preparation of complexes of the thiovanadyl ion, $V{=}S^{2+}$, was recently reported.[2] These species are of considerable interest, being the only known examples of this ion. Spectral data were consistent with their formulation as monomers with a multiple V-S bond analogous to the ubiquitous vanadyl ion, $V{=}O^{2+}$, but additional confirmation by X-ray crystallography was sought.

The crystal structure of the title compound has been independently determined at UCLA and the University of Arizona. The crystal studied at UCLA was provided by the original investigators,[2] while that used at Arizona was synthesized according to the published method.[2] The independent investigations are in excellent agreement and confirm the monomeric nature of the complex, as well as the multiple V-S bond.

Experimental Section

Dark red crystals of V=S(acen) were prepared from V=O(acen) and B_2S_3 as previously described[2] and recrystallized from methylene chloride-hexane. The crystallographic data for the two independent determinations are given in Table I. The instrumentation used, procedures for data reduction, computer programs used, and sources of scattering factors are described in previous publications.[3,4] No crystal decomposition was observed during data collection.

The position of the vanadium atom was determined from a Patterson function, and the remaining atoms were located by sequential difference electron density maps and least-squares refinements. Table II gives the final atomic coordinates, and Table III (supplementary material) gives the final thermal parameters for the structure determination carried out at the University of Arizona using Mo Kα radiation. These parameters resulted from full-matrix least-squares refinement using the 1785 reflections with $F_o^2 \geq 3\sigma(F_o^2)$. Refinement was based upon F, and $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 4F_o^2/[\sigma^2F_o^2 + (pF_o^2)^2]$ and $p = 0.03$. All atoms were included in the refinement, all nonhydrogen atoms were treated anisotropically, and the vanadium and sulfur atoms were corrected for anomalous dispersion. Hydrogen atoms were given fixed isotropic temperature factors. The final parameters for the structure determination at UCLA using Cu Kα agree within experimental error and are available as supplementary material.

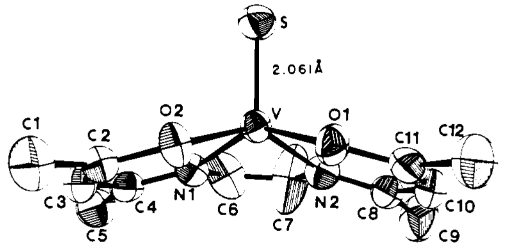

Figure 1. Molecular structure of V=S(acen): see Table IV for bond distances and angles; see the text and Figure 2 for discussion of the disorder of atoms C6 and C7. Thermal ellipsoids are drawn to enclose 50% of the probability distribution.

Results and Discussion

The coordination geometry of the title compound is shown in Figure 1; bond distances and angles are presented in Table IV. It can be seen from Figure 1 that the complex has the gross geometry of a rectangular pyramid with the sulfur atom at the apex and the coordinated atoms of the tetradentate acen ligand comprising the basal plane. The closest intermolecular contact, HO12-HO52, is at a distance of 2.49 Å; there is no evidence of intermolecular association.

The structural parameter of primary interest is the V-S bond length, which was found to be 2.061 (1)Å. The multiple nature of this bond is evident when its length is compared with the average V-S distance of 2.14 Å found in $(NH_4)_3VS_4$,[5] ($1^1/_3$ bond order) and that in $V{=}O(S_2CNEt_2)_2$, 2.387 (2)Å[6] (bond order 1). It is informative to compare these changes in bond distance with those observed in isoelectronic Mo(V) complexes. A bond length decrease of ca. 0.36 Å is seen on going from Mo—S to Mo=S.[7] The V—S distance in $V{=}O(S_2CNEt_2)_2$ is 0.33 Å longer than the V=S distance we measured for V=S(acen). A similar trend occurs for vanadium-oxygen bond lengths: the unique, multiply bound oxygen atom in vanadyl complexes is generally found to be about 1.6 Å from the metal atom, while a typical V-O single bond is ca. 2 Å in length.[8] This close agreement is encouragingly consistent with our model of V=S(acen) being the thio analogue of V=O(acen).

The vanadyl (V=O) analogue of the title compound has previously been examined crystallographically.[9] The compounds crystallize in different space groups, but both molecules have the shape of rectangular pyramids. As expected, there is a major difference in the metal to apex ligand bond distances, with V=O being 1.585 (7) Å. The other bond distances and angles are in remarkable agreement and reflect little influence of the apical ligand on bonding in the basal plane. The difference between the V=O and V=S distances in this pair of compounds of 0.47 Å. The difference in the appropriate

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(1) (a) University of Arizona. (b) University of California. (c) Occidental Research Corp.

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Table I. Crystallographic Data for VS(acen)

	Arizona[a]	UCLA[b]
mol formula	$C_{12}H_{18}N_2O_2SV$	$C_{12}H_{18}N_2O_2SV$
mol wt	305.30	305.30
space group	$P2_1/n$	$P2_1/n$
cell dimens (25 °C)		
a, Å	7.286 (1)	7.285 (3)
b, Å	24.247 (6)	24.295 (9)
c, Å	8.184 (2)	8.170 (4)
β, deg	101.24 (2)	101.319 (1)
V, Å^3	1418.0 (6)	1418.0 (1)
Z	4	4
d_{obsd}, g cm^{-3}	1.43 (1)	
d_{calcd}, g cm^{-3}	1.43	1.43
cryst dimens, mm	0.5 × 0.4 × 0.2	0.3 × 0.15 × 0.125
radiation, Å	λ (Mo Kα) 0.710 69	λ (Cu Kα) 1.5418
monochromator	graphite crystal	graphite crystal
data collection method	$\theta-2\theta$	$\theta-2\theta$
scan speed, deg min^{-1}	variable, 2–29	6
scan range, deg	Kα_1 − 1.0 to Kα_2 + 1.0	Kα_1 − 1.0 to Kα_2 + 1.0
total bkgd time/scan time	0.5	1.0
d_{min}, Å	0.84	1.01
total unique data	2513	
obsd data, $I > 3\sigma(I)$	1785	1570
abs coeff (μ), cm^{-1}	8.77	74.81
range of abs cor	1.0–1.376[c]	2.08–3.23[d]
no. of variables	217	160
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.040	0.050
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w(F_o)^2]^{1/2}$	0.045	0.066
goodness of fit	1.77	2.28

[a] See ref 3 for details and procedures. [b] See ref 4 for details and procedures. [c] Empirical absorption correction; see ref 3. [d] Analytical absorption correction; see ref 4.

Table II. Atomic Fractional Coordinates

atom	x	y	z
V	0.42425 (8)	0.122935 (25)	0.18244 (8)
S	0.26682 (15)	0.06282 (4)	0.04215 (13)
O1	0.3349 (3)	0.19586 (10)	0.0999 (3)
O2	0.3109 (4)	0.14374 (11)	0.3714 (3)
N1	0.6217 (4)	0.08096 (12)	0.3460 (4)
N2	0.6492 (4)	0.13503 (13)	0.0764 (4)
C1	0.2064 (9)	0.14250 (24)	0.6253 (7)
C2	0.3430 (6)	0.12289 (17)	0.5232 (5)
C3	0.4851 (6)	0.08855 (18)	0.5858 (5)
C4	0.6231 (5)	0.06923 (15)	0.5037 (5)
C5	0.7742 (8)	0.03361 (23)	0.6017 (7)
C6	0.7704 (8)	0.06134 (24)	0.2631 (7)
C7	0.7894 (12)	0.0918 (4)	0.1248 (15)
C8	0.6798 (6)	0.17483 (18)	−0.0247 (5)
C9	0.8551 (8)	0.1754 (3)	−0.0956 (8)
C10	0.5527 (7)	0.21779 (20)	−0.0696 (5)
C11	0.3922 (6)	0.22654 (16)	−0.0117 (5)
C12	0.2672 (9)	0.27422 (21)	−0.0700 (7)

Table IV. Selected Bond Distances (Å) and Angles (Deg)[a]

V–S	2.061 (1)		
V–O1	1.959 (3)	V–O2	1.956 (3)
V–N1	2.037 (3)	V–N2	2.019 (3)
O1–C11	1.308 (5)	O2–C2	1.319 (5)
N1–C4	1.319 (5)	N2–C8	1.318 (5)
N1–C6	1.465 (6)	N2–C7	1.465 (6)
C1–C2	1.496 (7)	C11–C12	1.492 (6)
C2–C3	1.349 (6)	C10–C11	1.361 (6)
C3–C4	1.394 (6)	C8–C10	1.395 (6)
C4–C5	1.503 (6)	C8–C9	1.502 (7)
C6–C7	1.380 (9)		
S–V–O1	109.5 (1)	S–V–O2	110.4 (1)
S–V–N1	105.0 (1)	S–V–N2	105.9 (1)
O1–V–N1	145.4 (1)	O2–V–N2	143.6 (1)
O1–V–N2	87.9 (1)	O2–V–N1	87.8 (1)
O1–V–O2	82.9 (1)	N1–V–N2	80.0 (1)
V–O1–C11	128.7 (3)	V–O2–C2	128.4 (3)
V–N1–C4	128.4 (3)	V–N2–C8	128.8 (3)
V–N1–C6	110.4 (3)	V–N2–C7	111.2 (3)
C4–N1–C6	121.1 (4)	C7–N2–C8	120.0 (4)

[a] C–H distances are in the range 0.64 (7)–1.09 (5) Å. The average C–H distance is 0.89 (9) Å.

covalent radii of O and S is about 0.3 Å.[10] Thus, the V=S distance in thiovanadyl is ~0.17 Å greater than would be predicted from the covalent radii of O and S. The relatively longer V=S distance is also consistent with the low V=S stretching frequency in the infrared spectrum.[2] The observed V=S distance is also in agreement with the prediction from molecular orbital calculations that the V=S bond should be substantially weaker than the V=O bond.[11] Similar behavior is found for the related d^1 species of molybdyl (Mo=O^{3+}) and thiomolybdyl (Mo=S^{3+}) although identical square-pyramidal complexes are not available for comparison.[7]

The thermal parameters of C6 and C7 (Figure 1) and the abnormally short C6–C7 distance (1.380 Å) suggest static or dynamic torsional disorder of these atoms of the ethylenediamine portion of the ligand. The final model refined at UCLA assumed a 1:1 mixture of two conformers with two sets of C6 and C7 coordinates. This disorder converged to give C6A–C7A = 1.588 (17) and C6B–C7B = 1.431 (17) Å. A difference electron density map based upon a structure factor calculation from which C6 and C7 were omitted is shown in Figure 2 along with the final positions of the atoms in the two models examined.

The disorder in the V=S(acen) crystals raises the question of such an occurrence in the oxo analogue. Although the thermal parameters of the relevant carbon atoms in V=O(acen) are not greatly different from those of the other atoms, they do have the first and fourth largest values. Furthermore, the C–C distance in the V–N–C–C–N ring of this compound, reported[9] as 1.421 (21) Å, is well below that expected for a C–C single bond. The corresponding C–C bond distances in

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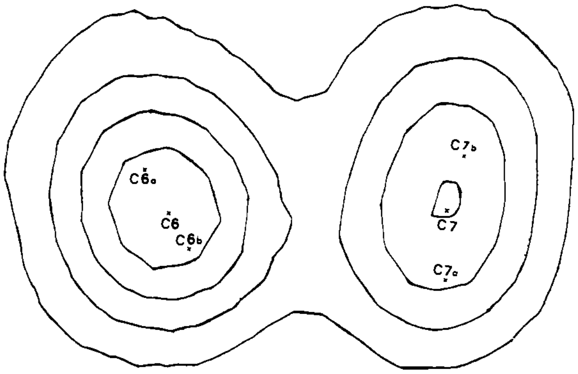

Figure 2. Difference electron density map of C6, C7 region of V=S(acen). This map is based upon a structure factor calculation from which C6 and C7 were omitted. Other atoms were given the final refined parameters of Tables II and III. Electron density contours start at 0.55 Å^{-3} and are in intervals of 0.55 Å^{-3}. The final coordinates for the ordered and disordered refinement models (see text) are indicated.

Cu(acen),[12] Cu(acen)·$^1/_2$H$_2$O,[13] and Cu(acen)·H$_2$O[14] are 1.55, 1.43, and 1.55 Å, respectively. These data suggest the likelihood of disorder both in V=O(acen) and in the copper hemihydrate.

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Registry No. V=S(acen), 74354-70-4.

Supplementary Material Available: Listings of final thermal parameters (Table III), atomic parameters for hydrogen atoms (Table V), observed and calculated structure factors for the data collected at the University of Arizona with Mo Kα radiation (Table VI), final atomic parameters, bond distances and angles, and observed and calculated structure factors (Tables VII-IX) for the data collected at UCLA with Cu Kα radiation (20 pages). Ordering information is given on any current masthead page.

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Effect of Halide Ions on the Rates of Reaction of Methylcobalamin with Heavy-Metal Species

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The reaction between methylcobalamin (I) and metal compounds plays a major role in biological transmethylation and may also be involved in the geochemical cycling of metals.[1,2] The kinetics and mechanism of this reaction have been reported in detail for Hg(II) salts,[3-5] tetrachloropalladate(II),[6] and chloroplatinum(IV) compounds.[7-11] More qualitative studies for various metal-I reactions have also appeared.[12-14] Methyl compounds of mercury, arsenic, selenium, and tin occur in nature.[15,16] As more and more details of such reactions have been reported, it has become increasingly apparent that the rate of methyl exchange between I and metal substrates depends very much on the nature of ligands on the metal. This paper will report some observed effects of halides.

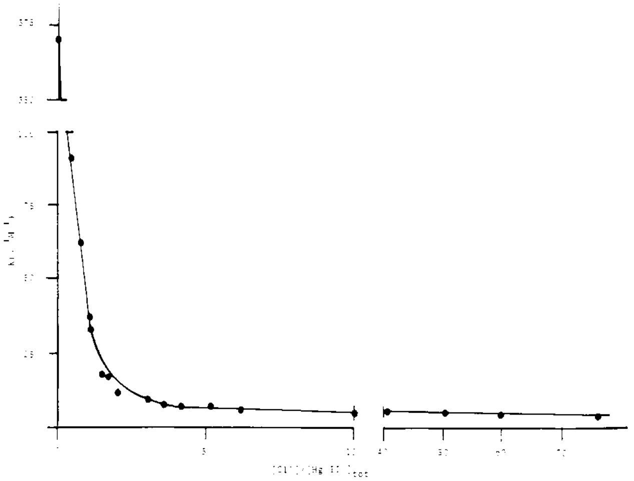

Figure 1. Effect of chloride ion on the Hg(OAc)$_2$–CH$_3$B$_{12}$ rate constant.

Experimental Section

Inorganic salts were purchased from various commercial sources and usually recrystallized before using. Methylcobalamin was purchased from Sigma Chemical Co. and stored in darkness at -10 °C. Solutions of reactants were prepared immediately before use. Reactions were carried out in spectroscopic cells or in sealed glass vessels protected from light. Reactions were studied until at least 75% of the methylcobalamin had reacted. The standard reaction medium was 0.10 M acetic acid–0.10 M sodium acetate buffer solution.

Spectroscopic investigations were performed, by methods described elsewhere,[14] on a Cary 14 recording visible–ultraviolet spectrophotometer. Certain gas-phase infrared spectra were obtained with the use of a 10-cm NaCl gas cell and a Perkin-Elmer Model 337 recording infrared spectrophotometer. Vapor-phase chromatographs were determined on a Hewlett-Packard Dual Column Model 5730 Chromatograph, using a 2-m glass column with DEGS packing. Helium served as the carrier gas, and the column temperature was 30–40 °C. Identities of methyl halides were confirmed by comparison of retention times with known samples. No other gaseous products were observed.

Results

Representative Metal Compounds. When the Tl(OAc)$_4^-$–I

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