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bath at 70 °C for 1 h, 2 h, and finally overnight. The cap was at no time removed, and the NMR tube was stored in a freezer until the spectrum was run. The final ^1H NMR spectrum was that of H_2Sal_2en. ^1H NMR ($CDCl_3$): δ 3.80 (s, 4 H), 6.5–7.7 (m, 8 H), 8.3 (s, 2 H), 13.19 (s, br, 2 H). ^{13}C NMR ($CDCl_3$): δ 59.66, 116.89, 118.60, 131.41, 132.32, 160.96, 166.41. IR (Nujol): 1630 (s), 1050 (s), 1030 (s), 990 (s), 980 (s), 950 (m), 870 (s), 780 (s), 779–750 (s), 660 cm^{-1} (s). The ^1H NMR spectrum matched that of a known sample of H_2Sal_2en made from salicylaldehyde and ethylenediamine. When the reaction tube was cooled in a dry-ice bath and the ^1H NMR spectrum was recorded within ca. 30 s, some additional peaks in the aliphatic region were observed. These peaks disappeared after ca. 1 min at room temperature and were not investigated further.

Reaction of 1,2,3,5,6,11b-Hexahydroimidazo[1,2-*d*][1,4]benzoxazepine with *N*-[2-(1-Aziridinyl)ethyl]salicylaldimine. A mixture of 0.107 g (0.566 mmol) of the benzoxazepine, 0.0487 g (0.566 mmol) of *N*-(2-aminoethyl)aziridine, 0.0700 g (0.573 mmol) of salicylaldehyde, and 0.0955 g (0.556 mmol) of 48% aqueous HBr and 8.0 mL of 1-BuOH were heated at reflux for 34 h. The original yellow solution began turning orange after ca. 0.5 h of heating. At the end of the reaction, the solution was orange and slightly basic to pH test paper. After cooling in ice afforded no crystals, a TLC (MeOH) showed one yellow component and one spot which did not move at all. The solvent was then evaporated to 2 mL and added dropwise to the top of a 1 × 12 in. silica gel column and eluted with dry Et_2O and then MeOH. Both solvents were completely evaporated, leaving a yellow semisolid. The ^1H NMR spectrum was identical with that of H_2Sal_2en except for an additional multiplet at δ 0.6–2.0.

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Kinetics of Reduction of $Co(NH_3)_4C_2O_4^+$ by Oxalato Complexes of Titanium(III)

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Oxalate ion is an efficient bridging ligand for electron transfer (ET) between transition-metal ions, but the detailed mechanism of the ET step depends on which metal ions are involved. The rate law for reaction of $Ru(NH_3)_4C_2O_4^+$ with Ti(III)[1] differs from the rate law for reaction of $Co(NH_3)_4C_2O_4^+$ with the same reductant.[2] The difference is such as to indicate that cross-bridge electronic interaction, through bridging oxalate ion, is more efficient in the Ru(III)–Ti(III) case than it is in the Co(III)–Ti(III) case.[1] Rate and equilibrium constants have been measured[3] for the formation of oxalato complexes of Ti^{3+}. We now report results of a study of the influence of oxalate ion as a nonbridging ligand on the rate of Co(III)–Ti(III) ET reactions which also involve oxalate as a bridging ligand.

Ti(III) solutions were prepared as described elsewhere.[1] $[Co(NH_3)_4C_2O_4]Cl$ was prepared by the method of Jørgensen.[4] Absorbances (*A*) were measured at 288 nm with use of a Gilford 2400 spectrophotometer and nitrogen-purged solutions of ionic strength 1.0 M (LiCl supporting electrolyte), at 25.0 ± 0.2 °C. For a determination of the effect of additional oxalate, LiCl, Ti(III), and oxalate solutions were mixed with sufficient HCl to give a final $[H^+]$ near 0.15 M and allowed to stand for sufficient time for complex-formation reactions to reach equilibrium. The redox reaction was then initiated by injecting oxidant solution (through platinum needles). Concentrations were chosen such that the injection caused only a small perturbation to the preestablished equilibria.

Table I. Kinetics of Reduction of $Co(NH_3)_4(C_2O_4)^+$ by Ti^{3+} at 25.0 °C in 1 M LiCl

$10^3 \times [H^+]$, M	$10^3 \times$ [Co(III)], M	$10^3 \times$ [Ti(III)], M	10^3k_1, s^{-1}	k_2,[a] $M^{-1}\,s^{-1}$		10^2k,[b] s^{-1}
10.2	0.257	2.68	11.8	4.4		4.5
29.7	0.286	4.02	5.9	1.48		4.4
49.8	0.286	3.35	2.88	0.86		4.3
74.3	0.286	4.02	2.37	0.59		4.4
100.2	0.286	3.35	1.41	0.42		4.2
100.2	0.286	4.69	2.02	0.43		4.3
99.8	0.465	4.69	2.06	0.44		4.4
123.7	0.469	5.36	1.88	0.35		4.3
152.7	0.286	5.36	1.47	0.28		4.2
177.7	0.269	5.36	1.29	0.24		4.3
211.4	0.469	5.36	1.07	0.20		4.2
					av	4.3 ± 0.1

[a] $k_2 = k_1/[Ti(III)]$. [b] $k = k_2[H^+]$.

Experiments carried out under second-order conditions demonstrated that 1.0 mol of Co(III) was reduced for each mole of Ti(III) reacted, both in the presence of added oxalate and in its absence. Normally, kinetic runs were carried out with Ti(III) in large excess over Co(III). Plots of log ($A - A_0$) were linear for at least 85% reaction. Rate constants (k_1) were calculated with use of data taken over 2 half-times. Rate constants for replicate runs generally agreed within 5%.

Equilibria that need to be considered to discuss the influence of added oxalate on the rate of the reaction of interest are given by eq 1–4. The symbols (H), (HL), (M), (ML), and so on

$$H_2C_2O_4 \rightleftharpoons HC_2O_4^- + H^+ \qquad K_1 = \frac{(H)(HL)}{(H_2L)} \tag{1}$$

$$HC_2O_4^- \rightleftharpoons C_2O_4^{2-} + H^+ \qquad K_2 = \frac{(H)(L)}{(HL)} \tag{2}$$

$$Ti^{3+} + C_2O_4^{2-} \rightleftharpoons TiC_2O_4^+ \qquad K_3 = \frac{(ML)}{(M)(L)} \tag{3}$$

$$TiC_2O_4^+ + C_2O_4^{2-} \rightleftharpoons Ti(C_2O_4)_2^- \qquad K_4 = \frac{(ML_2)}{(ML)(L)} \tag{4}$$

refer to the activities of the corresponding chemical species H^+, $HC_2O_4^-$, Ti^{3+}, $TiC_2O_4^+$, etc. Values of K_1 and K_2 have been determined[5] to be 0.09 and 4×10^{-4} M under conditions of our experiments. Chaudhuri and Diebler[3] have measured K_3 and K_4 (in 1 M NaCl) as 3×10^6 and 1×10^6 M^{-1}, but at 10 °C rather than 25 °C.

In the absence of added oxalate, the reaction of interest is

$$Co(NH_3)_4C_2O_4^+ + Ti^{3+} \rightarrow \text{products} \tag{5}$$

In agreement with the prior report,[2] we find (Table I) that

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Table II. Influence of Added Oxalate on the Rate of Reaction of $Co(NH_3)_4C_2O_4^+$ with Ti(III) at 25 °C and $\mu = 1.0$ M (LiCl)[a]

$10^3 \times [C_2O_4^{2-}]_t$, M	$10^3 \times [H^+]_t$, M	$10^3 \times [H^+]_f$, M	$10^4 \times [Ti^{3+}]$, M	$10^4 \times [TiC_2O_4^+]$, M	$10^4 \times [Ti(C_2O_4)_2^-]$, M	$10^{-2}k_1$, s^{-1}	$10^6 \times [C_2O_4^{2-}]_f$, M	χ,[b] $M^{-1}\ s^{-1}$	$10^{-2}k''$, $M^{-1}\ s^{-1}$
2.5	153	152	8.9	17.5	0.3	4.8	0.65	11.1	*d*
5.0	157	153	3.1	22.1	1.6	6.1	2.38	11.2	3.1
7.5	162	154	1.7	22.2	3.0	7.5	4.5	13.9	3.7
10.0	166	155	1.1	22.1	4.3	10.1	6.7	19.5	5.3
20.0	182	155	0.38	18.0	8.4	12.8	15.6	29.4	4.4
30.0	198	155	15.3	11.3	14.1	24.8	24.8	38.3	4.0
40.0	215	156	0.13	13.3	13.4	15.7	33.7	49.6	4.0
50.0	232	157	0.09	11.7	15.0	15.7	42.5	63.5	4.3
									av 4.1 ± 0.5

[a] Concentrations of H^+, Ti^{3+}, $TiC_2O_4^-$, and $Ti(C_2O)_4^{2-}$ are calculated from initial total concentrations (subscript t) with use of an iterative computer program and the values $K_1 = 0.09$ M, $K_2 = 4 \times 10^{-4}$ M, $K_3 = 3 \times 10^6\ M^{-1}\ s^{-1}$, and $K_4 = 3 \times 10^4\ M^{-1}$ (eq 1-4). [b] χ is defined by eq 11 and computed from the values of concentrations given in the table. [c] k'' is obtained as $(\chi - 9.0)/([C_2O_4^{2-}]_f)K_4$. [d] Not used in the computation of the average value of k''.

this reaction follows rate law 6 with $k = (4.3 \pm 0.1) \times 10^{-2}$ s^{-1}.

$$k_1 = k_2[\mathrm{Ti(III)}] = k[\mathrm{Ti(III)}][\mathrm{H}^+]^{-1} \qquad (6)$$

Additional reactions that would be expected to occur in the presence of added oxalate are

$$\mathrm{Co(III)} + \mathrm{Ti(C_2O_4)^+} \rightarrow \text{products} \qquad (7)$$

$$\mathrm{Co(III)} + \mathrm{Ti(C_2O_4)_2^-} \rightarrow \text{products} \qquad (8)$$

If the acid dependence of these reactions is the same as that of reaction 5, rate law 9 would be expected. With use of the same conventions as before, eq 9 can be rewritten as eq 10 and 11.

$$k_1[\mathrm{H}^+] = k_2[\mathrm{Ti(III)}][\mathrm{H}^+] = k[\mathrm{Ti}^{3+}] + k'[\mathrm{TiC_2O_4}^+] + k''[\mathrm{Ti(C_2O_4)_2}^-] \qquad (9)$$

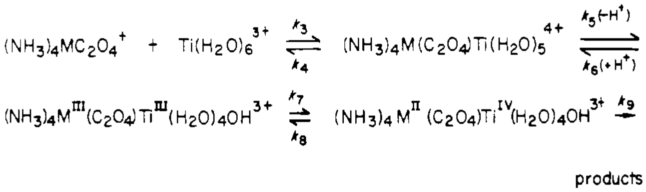
$$k_1(\mathrm{H}) = (k + k'K_3(\mathrm{L}) + k''K_3K_4(\mathrm{L})^2)(\mathrm{M}) \qquad (10)$$

$$\frac{(k_1(\mathrm{H})/(\mathrm{M})) - k}{K_3(\mathrm{L})} = \chi = k' + k''K_4(\mathrm{L}) \qquad (11)$$

Zero-time concentrations of each of the species of interest were computed with use of an iterative computer program. Literature[5] values of K_1 and K_2 (0.09 and $4 \times 10^{-4}\ M^{-1}$) and systematically varied values for K_3 and K_4 were used. When the values of K_3 and K_4 measured in NaCl media at 10 °C (6×10^6 and $1 \times 10^6\ M^{-1}$) were used, a curve was obtained when the left-hand side of eq 11 was plotted against free oxalate ion concentration. A linear plot, as required by eq 11, was, however, obtained when $K_3 = 3 \times 10^6\ M^{-1}$ and $K_4 = 3 \times 10^4\ M^{-1}$ were used (see Table II). The ratio K_3/K_4 determined here is similar to that found at 25 °C for the Fe(III) system[6] but somewhat different from that found for Ti(III) at 10 °C. It is not clear whether this difference is a significant result of change of temperature and medium or an artifact of differing experimental technique. The intercept and slope of the straight line obtained with use of the stated values of K_3 and K_4 yielded the values $k' = 1 \times 10\ M^{-1}$ and $k'' = 4 \times 10^2\ M^{-1}\ s^{-1}$.

The rate law (eq 6) found for the reaction of $Co(NH_3)_4C_2O_4^+$ with Ti(III) differs from that for reduction[1] of $Ru(NH_3)_4C_2O_4^+$ by the same reductant. In the latter case the rate is independent of acid, until very high $[H^+]$, where protonation of the oxidant occurs. The value of 0.43 s^{-1} found for k (eq 6) is large when compared with the high-acid first-order rate constants for reduction by Ti(III) of Co(III) oxidants of similar reduction potential, but without effective lead-in groups.[7] The latter reactions involve outer-sphere reduction by $TiOH^{2+}$. The reaction of present interest follows the same phenomenological rate law, but the large value of the rate constant suggests that another mechanistic feature is involved.[7] The mechanism shown in Scheme I is more consistent with all the available data on reaction 5.

Scheme I



When M = Co, the overall redox reaction is slow with respect to substitution on Ti(III),[3] so that the formation of the binuclear complex attains equilibrium. The observed base catalysis results from competition between the two reaction channels described by $k_6[H^+]$ and k_7. For the case M = Ru, the absence of such catalysis may be taken as an indication that ET within the binuclear complex is rapid, so that proton-assisted decomposition of that complex cannot compete effectively. Rates of substitution reactions of Ti(III) have been reported to be dependent on the charge of the entering group.[3] The observed value of k is consistent with the substitution reaction (k_3) being rate determining. The process (k_6) which directly competes with ET (k_7) is a protonation. In the case of Co(III) that protonation is rapid enough to compete successfully, but such is not the case for the reaction of the Ru(III) oxidant. Cross-bridge ET from Ti(III) is more rapid when Ru(III) is oxidant than when Co(III) is oxidant. (This is presumably connected with efficient cross-bridge interaction of t_{2g} donor and acceptor orbitals in the Ru(III)-Ti(III) case.) Similar conclusions can be reached from comparisons of kinetics of Ti(III) reduction of the salicylato complexes of Co(III) and Ru(III).[7]

The present experiments were not designed to explore the acid dependences of the influence of nonbridging oxalate. In the derivation of eq 11 it was assumed that all three paths were base catalyzed, but the range of free acid concentrations employed is so small that other assumptions would have been consistent with the data. The values $k = 0.04\ M^{-1}\ s^{-1}$, $k' = 10\ M^{-1}\ s^{-1}$, and $k'' = 400\ M^{-1}\ s^{-1}$ may be taken to indicate the relative reactivity of Ti^{3+}, $TiC_2O_4^+$, and $Ti(C_2O_4)_2^-$, at $[H^+] = 0.15$ M.

The measurements made at 10 °C, and the present data, indicate that K_3 and K_4 are not greatly different from each

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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.

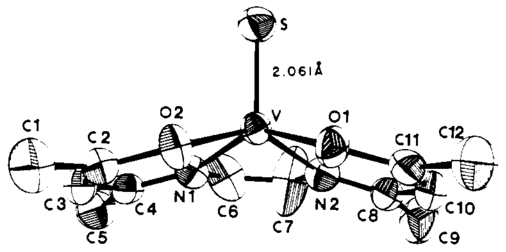

Figure 1. Molecular structure of V=S(acen): see Table IV for bond distances and angles; see the text and Figure 2 for discussion of the disorder of atoms C6 and C7. Thermal ellipsoids are drawn to enclose 50% of the probability distribution.

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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