

evidence³³⁻³⁶ also suggests a sq py based structure in these complexes. It was suggested that the low barriers for the σ, σ -bonded diazabutadiene complexes may be related to the local C_{3v} symmetry of the $Fe(CO)_3$ group. The results for σ, σ -bonded tetraazabutadiene complexes, $FeL_3(N_4Me_2)$ ($L = CO, P(OMe)_3$), are also lower than has been found in corresponding diene complexes.^{2,12,13}

Steric properties of L do not appear to be chemically significant in $Fe(CO)_2L(N_4Me_2)$ complexes; however, kinetic studies²³ have shown that severe steric crowding may occur in the 6-coordinate transition state that leads to their formation from $Fe(CO)_3(N_4Me_2)$. Ground-state steric effects are evident in the $Fe(CO)L_2(N_4Me_2)$ compounds and may partially account for the reluctance of these species to undergo either thermal²³ (associative) or photochemical²⁴ (dissociative) replacement of CO . Fluxional properties of these metallacyclic tetraazabutadiene complexes have analogues in the diazabutadiene and diolefin complexes. Available data suggest that the barriers for equilibration of sq py isomers in the metallacyclic systems are less than in the corresponding diolefin complexes.

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Registry No. $Fe(CO)(PCy_3)_2(N_4Me_2)$, 79301-43-2; $Fe(CO)(PPh_3)_2(N_4Me_2)$, 76299-46-2; $Fe(CO)(PMe_3)_2(N_4Me_2)$, 76299-45-1; $Fe(CO)(P(OMe)_3)_2(N_4Me_2)$, 76299-44-0; $Fe(CO)_3(N_4Me_2)$, 38668-89-2; $Fe(CO)_2(P(OMe)_3)(N_4Me_2)$, 76299-41-7; $Fe(CO)_2(PMe_3)(N_4Me_2)$, 76299-42-8; $Fe(CO)_2(PPh_3)(N_4Me_2)$, 76299-43-9; $Fe(CO)_2(PCy_3)(N_4Me_2)$, 78328-98-0.

(33) Otsuka, S.; Yoshida, T.; Nakamura, A. *Inorg. Chem.* 1967, 6, 20-25.

(34) tom Dieck, H.; Orlopp, A. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 251-252; *Angew. Chem.* 1975, 87, 246-247.

(35) Fruhauf, H. W.; Grevels, F. W.; Landers, A. *J. Organomet. Chem.* 1979, 178, 349-360.

(36) Staal, L. H.; Polm, L. H.; Vrieze, K. *Inorg. Chim. Acta* 1980, 40, 165-170.

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Molecular Structure of a Mixed-Valence Isopolyvanadate

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It is well-known that vanadium in its high oxidation states has a profound tendency to form isopolyions of various types.

Several vanadium(V) polyoxoions have been structurally characterized.¹ Among them few appear as a discrete unit like the decavanadate ion which occurs in salts such as $K_2Zn_2V_{10}O_{28} \cdot 16H_2O$.² The $V_{10}O_{28}^{6-}$ unit consists of ten VO_6 octahedra linked together. Recently, $HV_4O_{12}^{3-}$ has been prepared, and an X-ray structural analysis³ shows that it has a cyclic arrangement of four tetrahedral VO_4 units formed by linking vertices.

One vanadium(IV) polyoxoion has been structurally characterized.⁴ In that compound, $Na_{12}V_{18}O_{48} \cdot 24H_2O$, the 18 vanadium(IV) atoms are in their usual geometry, i.e., the tetragonal pyramid, forming a rather symmetric sphere by sharing the edges of the VO_5 pyramids.

Mixed-valence vanadium(IV,V) compounds are scarce. One such compound, $K_2V_3O_8$, has been characterized.⁵ The structure of that compound consists of infinite layers formed by $V^{IV}O_4$ tetrahedra and $V^{IV}O_5$ tetragonal pyramids sharing vertices.

We report here the structure of the first mixed-valence isopolyvanadate ion $V_{10}O_{26}^{4-}$, which exists as a discrete entity.

The tetraethylammonium salt of this ion was synthesized by one of us several years ago.^{6,7} It was obtained by the hydrolytic dissociation of vanadyl acetylacetonate in methylene chloride or chloroform. The formula $((C_2H_5)_4N)_4(V_{10}O_{28}H_4)$ was proposed for the compound, and it was found that of the ten vanadium atoms, eight were quinquivalent and two were quadrivalent. The results reported here require a revision of the above formula to $((C_2H_5)_4N)_4(V_{10}O_{26}) \cdot H_2O$.

Experimental Section

Preparation. Details of preparation of this compound have been described in an earlier study.^{6,7} A 3-5-g sample of the compound was dissolved in 100 mL of CH_3CN . The solution was filtered and partially evaporated in a Petri dish at 60 °C. The resulting needlelike, deep violet crystals were collected and washed with dichloromethane.

X-ray Crystallography. A crystal of dimensions $0.1 \times 0.1 \times 0.15$ mm was attached to the end of a glass fiber and mounted on a PW 1100 Philips four-circle computer-controlled diffractometer. $Mo K\alpha$ ($\lambda = 0.71069 \text{ \AA}$) radiation with a graphite-crystal monochromator in the incident beam was used. Preliminary examination showed that the crystal belonged to the monoclinic system, space group $P2_1/n$. The unit cell dimensions $a = 19.182(3) \text{ \AA}$, $b = 22.042(5) \text{ \AA}$, $c = 13.856(2) \text{ \AA}$, $\beta = 91.10(4)^\circ$, and $V = 5857(3) \text{ \AA}^3$ were obtained by a least-squares fit of 25 reflections in the range $12^\circ < \theta < 16^\circ$. With $Z = 4$ and a molecular weight of 1464, the calculated density is 1.66 g cm^{-3} .

Data were measured by using a ω - 2θ motion. The scan width, $\Delta\omega$, for each reflection was 1° with scan time of 20 s. Background measurements were made at both limits of each scan.

A total of 7309 reflections in the range $3^\circ < 2\theta < 45^\circ$ were collected, 3839 of which having $I > 3\sigma(I)$ were used to solve and refine the structure. During data collection, three intensity standards were measured after every hour. No decay was observed. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient is 15.11 cm^{-1} , no absorption correction was applied.

The vanadium atoms were located by using the results of MULTAN⁸ direct-method analysis, and all nonhydrogen atoms were located in a series of difference Fourier maps. The structure was refined⁹ in space group $P2_1/n$ to convergence by using anisotropic thermal parameters for all vanadium and oxygen atoms in the $V_{10}O_{26}^{4-}$ ion and isotropic ones for the rest of the atoms. The discrepancy index, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, had a final value of 0.092. The final difference map showed no peaks of structural significance. A list of observed and calculated structure factors is available as supplementary material.

Results and Discussion

The positional parameters of all atoms are listed in Table I. Figure 1 shows the structure of the $V_{10}O_{26}^{4-}$ ion and the atomic numbering scheme used in the tables. The important interatomic distances and angles are listed in Table II. The asymmetric unit contains an entire $V_{10}O_{26}^{4-}$ ion; hence, there is no crystallographic symmetry imposed on this ion. However, the complex nearly possesses S_8 symmetry. The $(C_2H_5)_4N^+$ ions are of no particular interest and require no discussion. One $(C_2H_5)_4N^+$ ion was subjected to twofold disorder, but

(5) Galy, J.; Carpy, A. *Acta Crystallogr., Sect. B*, 1975, B31, 1794.

(6) Heitner-Wirguin, C.; Selbin, J. *J. Inorg. Nucl. Chem.* 1968, 30, 3181.

(7) Heitner-Wirguin, C.; Selbin, J. *Isr. J. Chem.* 1969, 7, 27.

(8) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN-78, a System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", Universities of York, England, and Louvain, Belgium.

(9) All crystallographic computing was done on a CYBER 74 computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package. Two separate blocks were used in the refinement: anisotropic for the $V_{10}O_{26}^{4-}$ atoms and isotropic for the Et_4N^+ and water atoms.

(1) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed, Wiley-Interscience, New York, 1980; p 711.

(2) Evans, H. T., Jr. *Inorg. Chem.* 1966, 5, 967.

(3) Fuchs, J.; Mahjour, S.; Pickardt, J. *Angew. Chem., Int. Ed. Engl.* 1976, 15, 374.

(4) Johnson, G. K.; Schlemper, E. O. *J. Am. Chem. Soc.* 1978, 100, 3645.

Table I. Positional Parameters and Standard Deviations^a for [(C₂H₅)₄N]₄V₁₀O₂₆·H₂O

atom	x	y	z	atom	x	y	z
V(1)	0.5282 (2)	0.2732 (2)	0.5846 (3)	C(13)	0.881 (1)	0.438 (1)	-0.074 (2)
V(2)	0.5944 (2)	0.3293 (2)	0.8090 (3)	C(14)	0.959 (1)	0.434 (1)	-0.071 (2)
V(3)	0.5756 (2)	0.1267 (2)	0.6784 (3)	C(15)	0.869 (1)	0.385 (1)	0.088 (2)
V(4)	0.5915 (2)	0.2098 (2)	0.3651 (3)	C(16)	0.856 (1)	0.445 (1)	0.144 (2)
V(5)	0.6102 (2)	0.4067 (2)	0.4898 (3)	C(17)	0.861 (1)	0.325 (1)	-0.054 (2)
V(6)	0.7583 (2)	0.2507 (2)	0.5822 (3)	C(18)	0.844 (2)	0.317 (1)	-0.162 (2)
V(7)	0.7095 (2)	0.3970 (2)	0.6731 (3)	N(2)	0.816 (1)	0.1053 (9)	0.197 (2)
V(8)	0.6835 (2)	0.2030 (2)	0.8066 (3)	C(21)	0.754 (1)	0.148 (1)	0.188 (2)
V(9)	0.6798 (2)	0.1152 (2)	0.4913 (3)	C(22)	0.771 (2)	0.208 (1)	0.138 (2)
V(10)	0.7075 (2)	0.7075 (2)	0.3573 (3)	C(23)	0.789 (1)	0.049 (1)	0.249 (2)
O(1)	0.5439 (9)	0.1959 (8)	0.644 (1)	C(24)	0.844 (2)	-0.000 (1)	0.271 (2)
O(2)	0.6303 (7)	0.1376 (6)	0.786 (1)	C(25)	0.844 (2)	0.090 (1)	0.098 (2)
O(3)	0.7300 (9)	0.3311 (7)	0.624 (1)	C(26)	0.788 (2)	0.063 (2)	0.031 (3)
O(4)	0.6618 (8)	0.4407 (7)	0.587 (1)	C(27)	0.877 (1)	0.133 (1)	0.250 (2)
O(5)	0.5237 (8)	0.2006 (8)	0.300 (1)	C(28)	0.860 (2)	0.152 (1)	0.358 (2)
O(6)	0.6466 (9)	0.2614 (7)	0.303 (1)	N(3)	0.9183 (9)	0.0839 (8)	0.695 (1)
O(7)	0.7494 (9)	0.2818 (7)	0.451 (1)	C(31)	0.961 (1)	0.133 (1)	0.641 (2)
O(8)	0.7308 (8)	0.0606 (7)	0.469 (1)	C(32)	1.037 (2)	0.125 (2)	0.660 (2)
O(9)	0.5578 (8)	0.4583 (7)	0.446 (1)	C(33)	0.931 (1)	0.022 (1)	0.654 (2)
O(10)	0.7644 (8)	0.3313 (8)	0.278 (1)	C(34)	0.908 (2)	0.011 (2)	0.551 (2)
O(11)	0.4466 (8)	0.2772 (8)	0.566 (1)	C(35)	0.840 (1)	0.102 (1)	0.676 (2)
O(12)	0.6316 (8)	0.1369 (6)	0.382 (1)	C(36)	0.788 (1)	0.057 (1)	0.721 (2)
O(13)	0.6651 (9)	0.3816 (7)	0.394 (1)	C(37)	0.936 (1)	0.080 (1)	0.802 (2)
O(14)	0.572 (1)	0.2378 (8)	0.472 (1)	C(38)	0.924 (2)	0.143 (1)	0.856 (2)
O(15)	0.563 (1)	0.3495 (6)	0.534 (1)	N(4)	0.965 (1)	0.3661 (9)	0.508 (2)
O(16)	0.6215 (7)	0.0927 (7)	0.582 (1)	C(41)	0.987 (2)	0.357 (2)	0.410 (3)
O(17)	0.7804 (8)	0.4319 (7)	0.703 (1)	C(42)	0.924 (3)	0.314 (3)	0.451 (4)
O(18)	0.7461 (8)	0.1856 (8)	0.878 (1)	C(43)	0.947 (2)	0.298 (2)	0.357 (2)
O(19)	0.6570 (8)	0.3862 (6)	0.776 (1)	C(44)	0.889 (2)	0.375 (2)	0.526 (3)
O(20)	0.5130 (8)	0.0840 (7)	0.707 (1)	C(45)	0.948 (5)	0.426 (4)	0.447 (6)
O(21)	0.5479 (8)	0.3087 (7)	0.712 (1)	C(46)	0.857 (2)	0.427 (2)	0.454 (3)
O(22)	0.6356 (8)	0.2649 (6)	0.860 (1)	C(47)	1.010 (3)	0.422 (3)	0.540 (5)
O(23)	0.8385 (8)	0.2446 (7)	0.604 (1)	C(48)	0.927 (4)	0.374 (3)	0.595 (5)
O(24)	0.5450 (8)	0.3569 (7)	0.889 (1)	C(49)	0.992 (3)	0.427 (2)	0.656 (4)
O(25)	0.7270 (9)	0.1746 (7)	0.530 (1)	C(50)	0.986 (2)	0.309 (2)	0.575 (4)
O(26)	0.7172 (9)	0.2247 (8)	0.700 (1)	C(51)	1.048 (5)	0.356 (5)	0.501 (7)
N(1)	0.8464 (9)	0.3881 (8)	-0.017 (1)	C(52)	1.068 (2)	0.296 (2)	0.570 (3)
C(11)	0.765 (1)	0.402 (1)	-0.028 (2)	OW	0.643 (2)	0.028 (1)	0.896 (2)
C(12)	0.718 (2)	0.358 (1)	0.022 (2)				

^a Estimated standard deviations in the least significant digits are shown in parentheses.

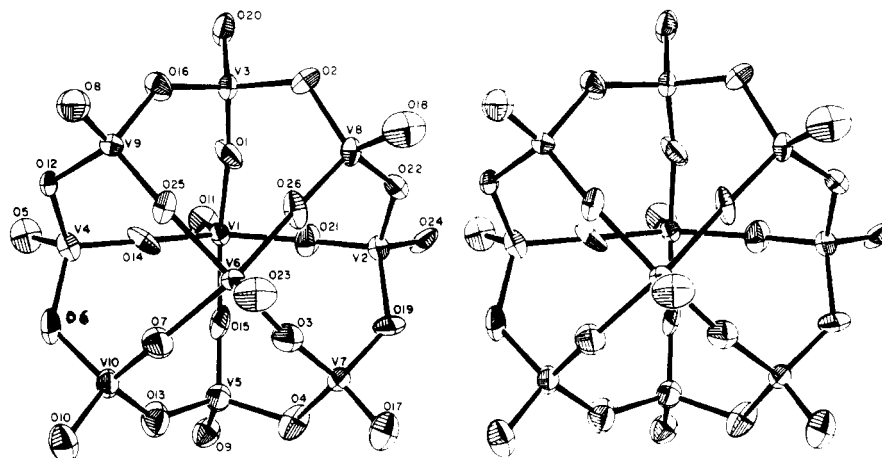


Figure 1. Stereoscopic view of V₁₀O₂₆⁴⁻.

otherwise all atoms in these ions refined normally. Their bond distances and angles are listed in a table included in the supplementary material.

The single water molecule (OW) in this lattice was found to be hydrogen bonded to the oxygen atom O(2) and to the oxygen atom O(17) from a neighboring polyion.

Figure 1 shows two vanadium atoms in a tetragonal pyramid geometry [V(1) and V(6)] with V–O distances similar to those in other quadrivalent vanadium complexes. The two *tetragonal pyramids* are positioned above and below a crown of eight vertices shared *tetrahedra* containing VO₄ units. These tetrahedral VO₄ units have V–O distances similar to other

quivalent vanadium complexes, and the O–V–O angles are very near to 109° as shown in Table II. The pertinent average V–V distances in V₁₀O₂₆⁴⁻ are as follows: V^V–V^V, ca. 3.25 Å; V^V–V^{IV}, ca. 3.59 Å; V^{IV}–V^{IV}, ca. 4.44 Å. The distance between the two quadrivalent vanadium atoms is similar to that found in many dimeric V(IV) compounds with a coupling between the two d electrons.¹⁰ This mixed-valence ion has indeed also a “mixed” structure. The crownlike structure of vanadium(V) tetrahedra (as in HV₄O₁₂³⁻) attains a spherelike

(10) McIlwain, M. E.; Tapscott, R. E.; Coleman, W. F. *J. Magn. Reson.* 1977, 26, 35.

Table II. Bond Distances (Å) and Bond Angles (Deg) for $V_{10}O_{26}^{4-}$

V(1)-O(1)	1.91 (2)	V(6)-O(3)	1.95 (2)
V(1)-O(11)	1.58 (1)	V(6)-O(7)	1.94 (1)
V(1)-O(14)	1.95 (2)	V(6)-O(23)	1.59 (1)
V(1)-O(15)	1.95 (1)	V(6)-O(25)	1.92 (1)
V(1)-O(21)	1.96 (2)	V(6)-O(26)	1.91 (1)
V(2)-O(19)	1.80 (1)	V(7)-O(3)	1.65 (2)
V(2)-O(21)	1.66 (2)	V(7)-O(4)	1.77 (2)
V(2)-O(22)	1.77 (1)	V(7)-O(17)	1.61 (2)
V(2)-O(24)	1.59 (2)	V(7)-O(19)	1.78 (2)
V(3)-O(1)	1.71 (2)	V(8)-O(2)	1.78 (1)
V(3)-O(2)	1.82 (1)	V(8)-O(18)	1.59 (2)
V(3)-O(16)	1.78 (1)	V(8)-O(22)	1.81 (1)
V(3)-O(20)	1.58 (2)	V(8)-O(26)	1.69 (2)
V(4)-O(5)	1.58 (2)	V(9)-O(8)	1.59 (2)
V(4)-O(6)	1.79 (2)	V(9)-O(12)	1.82 (1)
V(4)-O(12)	1.79 (1)	V(9)-O(16)	1.77 (1)
V(4)-O(14)	1.66 (2)	V(9)-O(25)	1.67 (2)
V(5)-O(4)	1.82 (2)	V(10)-O(6)	1.81 (2)
V(5)-O(9)	1.63 (2)	V(10)-O(7)	1.68 (2)
V(5)-O(13)	1.80 (2)	V(10)-O(10)	1.61 (2)
V(5)-O(15)	1.67 (2)	V(10)-O(13)	1.76 (2)
O(1)-V(1)-O(11)	105.4 (8)	O(3)-V(6)-O(7)	86.2 (6)
O(1)-V(1)-O(14)	85.3 (7)	O(3)-V(6)-O(23)	107.4 (8)
O(1)-V(1)-O(15)	150.6 (8)	O(3)-V(6)-O(25)	145.3 (7)
O(1)-V(1)-O(21)	86.8 (7)	O(3)-V(6)-O(26)	84.1 (7)
O(11)-V(1)-O(14)	109.6 (8)	O(7)-V(6)-O(23)	106.1 (8)
O(11)-V(1)-O(15)	84.1 (7)	O(7)-V(6)-O(25)	86.4 (6)
O(11)-V(1)-O(21)	107.3 (7)	O(7)-V(6)-O(26)	150.6 (7)
O(14)-V(1)-O(15)	84.1 (7)	O(23)-V(6)-O(25)	107.3 (8)
O(14)-V(1)-O(21)	143.1 (7)	O(23)-V(6)-O(26)	103.3 (8)
O(15)-V(1)-O(21)	85.4 (7)	O(25)-V(6)-O(26)	85.9 (7)
O(19)-V(2)-O(21)	109.5 (7)	O(3)-V(7)-O(4)	108.9 (7)
O(19)-V(2)-O(22)	111.4 (7)	O(3)-V(7)-O(17)	108.7 (8)
O(19)-V(2)-O(24)	108.6 (7)	O(3)-V(7)-O(19)	110.8 (7)
O(21)-V(2)-O(22)	109.6 (7)	O(4)-V(7)-O(17)	109.8 (8)
O(21)-V(2)-O(24)	110.4 (8)	O(4)-V(7)-O(19)	108.6 (7)
O(22)-V(2)-O(24)	107.3 (7)	O(17)-V(7)-O(19)	110.1 (8)
O(1)-V(3)-O(2)	108.0 (7)	O(2)-V(8)-O(18)	109.2 (7)
O(1)-V(3)-O(16)	110.1 (7)	O(2)-V(8)-O(22)	112.4 (6)
O(1)-V(3)-O(20)	109.6 (8)	O(2)-V(8)-O(26)	108.4 (7)
O(2)-V(3)-O(16)	112.6 (6)	O(18)-V(8)-O(22)	108.0 (8)
O(2)-V(3)-O(20)	107.6 (7)	O(18)-V(8)-O(26)	108.4 (9)
O(16)-V(3)-O(20)	109.0 (7)	O(22)-V(8)-O(26)	110.4 (7)
O(5)-V(4)-O(6)	107.1 (8)	O(8)-V(9)-O(12)	109.9 (7)
O(5)-V(4)-O(12)	107.8 (8)	O(8)-V(9)-O(16)	109.1 (8)
O(5)-V(4)-O(14)	111.2 (9)	O(8)-V(9)-O(25)	109.0 (8)
O(6)-V(4)-O(12)	112.2 (7)	O(12)-V(9)-O(16)	110.2 (7)
O(6)-V(4)-O(14)	109.9 (8)	O(12)-V(9)-O(25)	109.0 (7)
O(12)-V(4)-O(14)	108.6 (8)	O(16)-V(9)-O(25)	109.6 (7)
O(4)-V(5)-O(9)	108.2 (7)	O(6)-V(10)-O(7)	110.0 (7)
O(4)-V(5)-O(13)	110.9 (8)	O(6)-V(10)-O(10)	107.7 (8)
O(4)-V(5)-O(15)	109.4 (8)	O(6)-V(10)-O(13)	111.3 (8)
O(9)-V(5)-O(13)	107.6 (8)	O(7)-V(10)-O(10)	108.0 (8)
O(9)-V(5)-O(15)	109.3 (8)	O(7)-V(10)-O(13)	110.7 (8)
O(13)-V(5)-O(15)	111.3 (8)	O(10)-V(10)-O(13)	109.0 (8)
V(3)-O(1)-V(1)	165 (1)	V(5)-O(15)-V(1)	167 (1)
V(8)-O(2)-V(3)	123.7 (8)	V(9)-O(16)-V(3)	138.1 (9)
V(7)-O(3)-V(6)	173 (1)	V(7)-O(19)-V(2)	133.5 (9)
V(7)-O(4)-V(5)	122.7 (8)	V(2)-O(21)-V(1)	158 (1)
V(10)-O(6)-V(4)	126.3 (8)	V(8)-O(22)-V(2)	131.9 (8)
V(10)-O(7)-V(6)	155 (1)	V(9)-O(25)-V(6)	165 (1)
V(9)-O(12)-V(4)	123.6 (8)	V(8)-O(26)-V(6)	178 (1)
V(10)-O(13)-V(5)	138 (1)		
V(4)-O(14)-V(1)	167 (1)		

structure (as in $V_{18}O_{48}^{12-2}$) by the addition of the two V(IV) tetragonal pyramids.

Registry No. $[(C_2H_5)_4N]_4V_{10}O_{26} \cdot H_2O$, 79482-74-9.

Supplementary Material Available: Tables of bond distances and angles in the tetraethylammonium ions (Table III), structure factors, and thermal parameters (47 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Tetrakis(trifluoroacetato)bis(dimethyl- d_6 sulfoxide)dirhodium(II): A Structural Deuterium Isotope Effect in an Oxygen-Bonded Sulfoxide Adduct

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Although the preference of platinum group metal ions to bind dimethyl sulfoxide (Me_2SO) through the sulfur atom was recognized¹ over 20 years ago, more recent studies have found that this affinity may be offset by steric²⁻⁴ or electronic^{5,6} factors imparted to the metal ion through the coordinated ligand atoms. Thus, steric effects favor oxygen-bonded Me_2SO ligands in the crowded four-coordinate $[M-(Ph_2PCH_2CH_2PPh_2)(Me_2SO)Cl]^+$ complexes⁴ ($M = Pd^{II}$, Pt^{II}), electronic effects govern oxygen coordination of Me_2SO in $Rh_2(O_2CCF_3)_4(Me_2SO)_2$,⁶ while both steric and electronic factors play a role in the mixed oxygen- and sulfur-bonded complexes of $Pd(Me_2SO)_4^{2+}$,³ $Rh(Me_2SO)_3Cl_3$,⁷ and $Ru(Me_2SO)_4Cl_2$.⁸

During our previous work⁶ involving the correlation of S-O bond lengths with $\nu(S-O)$ frequencies in Me_2SO adducts of $Rh_2(O_2CR)_4$ compounds, the perdeuterated compound $Rh_2(O_2CCF_3)_4(Me_2SO-d_6)_2$ was prepared in order to aid in the assignment of the infrared spectrum of the Me_2SO adduct. Earlier studies^{9,10} have noted that the advantage derived from recording the infrared spectra of both Me_2SO and Me_2SO-d_6 compounds stems from the near degeneracy of the S-O stretching and methyl rocking vibrations in the normal Me_2SO complex while in the Me_2SO-d_6 analogue these vibrations are well separated. Since the preparation of $Rh_2(O_2CCF_3)_4(Me_2SO-d_6)_2$ afforded a crystalline product, several of the crystals were examined on an X-ray diffractometer. Unexpectedly, all of the crystals examined possessed a triclinic cell which was not the same as that for the corresponding $Rh_2(O_2CCF_3)_4(Me_2SO)_2$ complex.⁶

In this paper we describe the structure of the Me_2SO-d_6 adduct of $Rh_2(O_2CCF_3)_4$, which has been refined with the inclusion of all deuterium atoms. This structure is compared to that of the undeuterated adduct⁶ which has been further refined with the inclusion of all hydrogen atoms. The two structures represent, to our knowledge, the first example of a crystal packing modification in a transition-metal complex effected solely by the substitution of deuterium for hydrogen.

Experimental Section

Rhodium(II) trifluoroacetate was prepared by the procedure given by Kitchens and Bear¹¹ and converted to the anhydrous form by heating at 150 °C for 30 min. Glistening dark blue irregularly shaped crystals of $Rh_2(O_2CCF_3)_4(Me_2SO-d_6)_2$ were obtained directly upon evaporation of a 1:1 mixture of benzene-chloroform containing $Rh_2(O_2CCF_3)_4$ and excess practical grade Bio-Rad Me_2SO-d_6 .

- (1) Cotton, F. A.; Francis, R. *J. Am. Chem. Soc.* **1960**, *82*, 2986.
- (2) Wayland, B. B.; Schramm, R. F. *Inorg. Chem.* **1969**, *8*, 971.
- (3) Price, J. H.; Williamson, A. N.; Schramm, R. F.; Wayland, B. B. *Inorg. Chem.* **1972**, *11*, 1280.
- (4) Davies, J. A.; Hartley, F. R.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* **1979**, 1705.
- (5) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 323.
- (6) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 2347.
- (7) Sokol, V. I.; Porai-Koshits, M. A. *Sov. J. Coord. Chem.* **1975**, *1*, 476.
- (8) Mercer, A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2480.
- (9) Cotton, F. A.; Francis, R.; Horrocks, W. D., Jr. *J. Phys. Chem.* **1960**, *64*, 1534.
- (10) Horrocks, W. D., Jr.; Cotton, F. A. *Spectrochim. Acta* **1961**, *17*, 134.
- (11) Kitchens, J.; Bear, J. L. *Thermochim. Acta* **1970**, *1*, 537.