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Synthesis and Characterization of Four Vanadium(II) Compounds, Including Vanadium(II) Sulfate Hexahydrate and Vanadium(II) Saccharinates

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Three new vanadium(II) saccharinate compounds have been prepared and their structures studied by X-ray crystallography along with the structure of vanadium(II) sulfate hexahydrate. Because of the high stability toward air and its solubility in some organic solvents, the saccharinate $[V(C_7H_4NO_3S)_2(H_2O)_4]\cdot 2H_2O$ (**2**) is a potentially useful starting material in the preparation of other vanadium(II) compounds. In it, and in $VSO_4\cdot 6H_2O$ (**1**), extensive hydrogen bonding surrounding the metal atom plays an important role in the stabilization of these compounds in the crystalline state. In **2** the saccharinate ligand is N-bonded to the vanadium atom, but substitution of the water molecules by pyridine gives a product in which saccharinate is ligated through the oxygen atom of the carbonyl group. This configuration is found both in $[V(C_7H_4NO_3S)_2(py)_4]\cdot 2py$ (**3**) and in $[V(C_7H_4NO_3S)_2(py)_4]\cdot 2THF$ (**4**). Compound **1** crystallizes in space group $C2/c$ with $a = 10.081$ (3) Å, $b = 7.286$ (2) Å, $c = 24.445$ (7) Å, $\beta = 98.78$ (2)°, $V = 1774.4$ (8) Å^3, and $Z = 8$. Compound **2** is isomorphous with other divalent first-row transition-metal analogues. It crystallizes in space group $P2_1/c$, with cell constants $a = 7.936$ (2) Å, $b = 16.149$ (5) Å, $c = 7.731$ (2) Å, $\beta = 99.84$ (2)°, $V = 976.2$ (8) Å^3, and $Z = 2$. Compounds **3** and **4** are isomorphous but a detailed X-ray structural study was not completed for **4**. They crystallize in space group *Pbna* with $Z = 4$. The unit cell parameters for **3** are $a = 15.430$ (6) Å, $b = 18.323$ (4) Å, $c = 15.966$ (5) Å, and $V = 4514$ (2) Å^3, and for **4**, they are $a = 15.289$ (5) Å, $b = 17.644$ (4) Å, $c = 16.249$ (3) Å, and $V = 4383$ (3) Å^3.

Introduction

The chemistry of vanadium(II) has not been studied as widely as that of the M(II) species of the other first-row elements.[2a]

In general, the lack of extensive studies is due to the high instability toward air of most of the V(II) compounds[2b] and the consequent difficulty of maintaining the low oxidation state under certain reaction conditions.[3] Perhaps equally important is the difficulty in the preparation of suitable starting materials, particularly those that could be used in nonaqueous solvents.[4]

In an effort to understand better the variables involved in this system we have prepared and structurally characterized two new vanadium(II) saccharinate compounds; we also have determined the structure of the known but structurally uncharacterized vanadium(II) sulfate hexahydrate.

Another factor which led us to pursue this investigation was the need for accurate data to complete the correlation of structural changes in divalent first-row transition-metal saccharinates with respect to their d^n configurations. We have presented data on this correlation in saccharinates of the type $[M(C_7H_4NO_3S)_2(H_2O)_4]\cdot 2H_2O$ in a previous paper,[5] but at the time we had not succeeded in obtaining a crystalline vanadium(II) saccharinate, and the corresponding data were extrapolated. We now report the structure in order to complete the set of experimental data. The experimental V–L bond lengths as well as the unit cell volume are very close to the predicted values.

A surprising result found in the study of that series of metal saccharinates was the high degree of air stability of the compounds for M = V, Cr, and Fe. This is perhaps due to the presence of an extensive hydrogen-bonding network surrounding the metal atom. To provide more evidence to support this explanation, we are also reporting the structure of the vanadium(II) sulfate hexahydrate; we compare it to another very stable hydrogen-bonded compound—viz., vanadium(II)ammonium sulfate hexahydrate. The structure of the latter was reported by Montgomery and co-workers.[6]

In this paper we will deal mainly with the X-ray structural parameters. Optimization of the synthetic procedures mentioned here is currently under way and will be reported elsewhere.[7]

Experimental Section

All reactions were done under a nitrogen or argon atmosphere by using standard Schlenk type techniques. Water was refluxed under nitrogen prior to distillation. The rest of the solvents were dried and deoxygenated thoroughly prior to use.

Preparations. $VSO_4\cdot 6H_2O$ (1). A modification of the procedure reported by Kranz[8] was used. A solution of V(IV) was prepared by mixing 10.5 g (52.8 mmol) of $VOSO_4\cdot 2H_2O$, 3 mL of concentrated H_2SO_4, and enough water to make 100 mL of solution. This was transferred to a flask equipped with a bent arm containing a fritted disk at the level of the base. This second chamber was filled to the same level as the V(IV) solution with 2 M H_2SO_4. The reactants were electrolized for 6 h with a mercury electrode and a platinum electrode, while the current was ca. 0.85 A. Cooling with running tap water was required. The resulting violet solution was transferred to another flask and was concentrated in vacuum to ca. 20–25% of the original volume. Then, 70 mL of ethanol was added very carefully, giving a system of two liquid phases, which was cooled to −5 °C. Slowly the ethanol diffused into the aqueous layer, and very large crystals formed. After a few days, they were filtered and washed with two 15-mL portions of ethanol. The blue-purple crystals were quickly dried under vacuum, yielding 11.7 g (85%). In the crystalline form, the compound is stable in air for some hours.

$[V(C_7H_4NO_3S)_2(H_2O)_4]\cdot 2H_2O$ (2). A solution of 0.67 g (2.4 mmol) of **1** was prepared in 3 mL of H_2O at 0 °C. Separately, a solution of 1.2 g (5.0 mmol) of sodium saccharinate dihydrate was made by using 10 mL of water and 7 mL of ethanol. This solution was cooled and added to the vanadium sulfate. Upon addition, there was an immediate color change from violet to red. After 2 weeks at −13 °C a crop of brick red crystals, which had formed, was filtered and washed with three 10-mL portions of cooled (~0 °C) water. After drying, 1.0 g (73%) of fairly air-stable crystals were obtained.

$[V(C_7H_4NO_3S)_2(py)_4]\cdot 2py$ (3). In a distillation apparatus 75 mL of pyridine was added to 1.0 g (1.9 mmol) of **2**. The deep red solution was warmed, and about 57 mL of the solvent was removed by distillation at pressure slightly above ambient (regulated by a mercury bubbler). The solution was allowed to return to room temperature, and then a layer of 40 mL of hexane was added. After 2 days at −20 °C, the resulting black crystals were filtered and washed with two 10-mL portions of hexane. The yield was 1.6 g (94%).

X-ray quality crystals were grown by using the following modification of the above procedure: 0.32 g of **2** was dissolved in pyridine, and then 10 mL of the solvent was distilled at slightly above ambient pressure. The solution was left undisturbed for several days at −20 °C. Crystals of compound **3** are stable in air for a few hours.

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(1) (a) Texas A&M University. (b) University of Costa Rica.

(2) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th Ed.; Wiley: New York, 1980, pp 717–718. (b) See for example some of the problems reported by Lippard and co-workers in: Silverman, L. D.; Corfield, P. W. R.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 3106.

(3) Cotton, F. A.; et al., manuscript in preparation.

(4) Cotton, F. A.; Murillo, C. A. *Ing. Cienc. Quim.* **1985**, *9*, 1.

(5) Cotton, F. A.; Lewis, G. E.; Murillo, C. A.; Schwotzer, W.; Valle, G. *Inorg. Chem.* **1984**, *23*, 4038.

(6) Montgomery, H.; Chastain, R. V.; Natt, J. J.; Witkowska, A. M.; Lingafelter, E. C. *Acta Crystallogr.* **1967**, *22*, 775.

(7) A manuscript is currently in preparation to be submitted to *Inorg. Synth.*

(8) Kranz, M. *Inorg. Synth.* **1963**, *7*, 94.

(9) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

0020-1669/86/1325-3423$01.50/0

Table I. Crystal Data for $VSO_4 \cdot 6H_2O$ (**1**), $V(sacch)_2(H_2O)_4 \cdot 2H_2O$ (**2**), and $V(sacch)_2(py)_4 \cdot 2py$ (**3**)

	1	**2**	**3**
formula	$VSO_{10}H_{12}$	$VC_{14}H_{20}O_{12}N_2S_2$	$VS_2O_6N_8C_{44}H_{38}$
fw	255.09	523.4	889.90
space group	*C*2/*c*	*P*2$_1$/*c*	*Pbna*
syst absences	*hkl*: $h + k \neq 2n$ h0l: $l \neq 2n$	0k0: $k \neq 2n$ h0l: $l \neq 2n$	0kl: $k \neq 2n$ h0l: $h + l \neq 2n$ hk0: $h \neq 2n$
a, Å	10.081 (3)	7.936 (2)	15.430 (6)
b, Å	7.286 (2)	16.149 (5)	18.323 (4)
c, Å	24.445 (7)	7.731 (2)	15.966 (5)
β, deg	98.78 (2)	99.84 (2)	90
V, Å^3	1774.4 (8)	976.2 (8)	4514 (2)
Z	8	2	4
d_{calcd}, g/cm^3	1.910	1.78	1.309
cryst size, mm	0.68 × 0.57 × 0.56	0.2 × 0.15 × 0.1	0.5 × 0.4 × 0.3
μ(Mo Kα), cm^{-1}	14.39	7.63	3.80
data colln instrum	Nicolet P3/F equivalent	Syntex P$\bar{1}$	Syntex P$\bar{1}$
radiation (monochromated in incident beam)^d	Mo Kα	Mo Kα	Mo Kα
orientation reflcns: no.; range (2θ), deg	15; 20–36	15; 12–24	15; 10–24
temp, °C	23 ± 1	5 ± 2	10 ± 2
scan method	ω–2θ	ω–2θ	ω–2θ
data colln range (2θ), deg	4.0–75.0	4.0–50.0	4.0–45.0
no. of unique data; total with $F_o^2 > 3\sigma(F_o^2)$	3486; 2028	...; 893	1871; 1484
no. of params refined	159	142	246
trans factors: max, min	calcd 0.45, 0.22 obsd 1.00, 0.96	calcd 0.9, 0.8	calcd 0.9, 0.8 obsd 1.00, 0.93
R^a	0.039	0.056	0.063
$R_w{}^b$	0.063	0.072	0.083
quality-of-fit indicator^c	1.445	1.58	1.609
largest shift/esd, final cycle	0.38	0.05	0.04
largest peak, e/Å^3	0.66	0.06	0.35

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$. $^d \lambda_{\bar{\alpha}} = 0.71073$ Å.

[$V(C_7H_4NO_3S)_2(py)_4$]·2THF (4). In a typical experiment, 0.20 g (0.22 mmol) of **3** was dissolved in 13 mL of refluxing THF. The solution was quickly filtered while still hot. Nothing remained on the filter frit. The filtered solution was allowed to return to room temperature over a period of several hours. Crystals that tended to stick to the walls of the flask were formed. They were filtered and dried. The yield was 0.11 g (56%) of dark red crystals.

X-ray Structure Determination. Crystals of compound **1**, $VSO_4 \cdot 6H_2O$, were in the first instance ground into spheres and mounted with thin coverings of epoxy. Each crystal which was handled in this way gave a strong diffraction pattern, which rapidly deteriorated to the extent that after a day no diffraction could be measured. The crystal from which data were finally gathered was not ground and showed no appreciable decomposition. Two monitor reflections, which were measured after each 98 data scans, changed in intensity by an average of less than 1% during 37 h of X-ray exposure. Those crystals that decomposed appeared to have undergone a physical rather than a chemical change, since the color of the bulk samples remained the same.

In the case of compound **3**, $V(sacch)_2(py)_4 \cdot 2py$, the intensities of three check reflections decreased by an average of 47% through 66 h of X-ray exposure time. Part of this decrease was caused by diminution of the power of the X-ray source, associated with an electrical event within the X-ray generation chain, but part was a genuine crystal effect. The intensity data were scaled according to the intensities of the check reflections, which were remeasured after every 97 data scans.

All three sets of data were reduced and processed by routine procedures.[10a] For **1** and **3**, empirical absorption corrections were applied by the ψ-scan method.[10b]

Relevant crystallographic parameters for all three structures are given in Table I.

Table II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $V(SO_4) \cdot 6H_2O$ (**1**)^a

atom	*x*	*y*	*z*	*B*, Å^2
V(1)	0.000	0.000	0.000	1.863 (8)
V(2)	0.000	−0.05565 (6)	0.250	1.618 (8)
S	0.86941 (6)	0.44786 (7)	0.12405 (2)	1.959 (9)
O(1)	0.7765 (2)	0.5960 (3)	0.13478 (8)	2.61 (3)
O(2)	0.9835 (2)	0.4412 (3)	0.1685 (1)	3.66 (4)
O(3)	0.9148 (2)	0.4873 (3)	0.07038 (8)	3.12 (4)
O(4)	0.7991 (2)	0.2694 (2)	0.11923 (9)	2.84 (3)
O(5)	0.0931 (2)	0.2249 (3)	0.04661 (8)	2.87 (3)
O(6)	0.0335 (2)	−0.1764 (3)	0.06988 (9)	3.86 (4)
O(7)	−0.1934 (2)	0.0535 (3)	0.02207 (9)	3.60 (4)
O(8)	−0.1188 (2)	0.1508 (2)	0.28256 (7)	2.33 (3)
O(9)	−0.1160 (2)	−0.2591 (2)	0.28283 (8)	2.76 (3)
O(10)	−0.1470 (2)	−0.0528 (2)	0.17786 (8)	2.85 (3)
H(1)	0.038 (3)	0.305 (4)	0.063 (1)	1.8 (5)*
H(2)	0.141 (4)	0.196 (5)	0.069 (2)	3.8 (8)*
H(3)	0.113 (4)	−0.193 (6)	0.091 (2)	5 (1)*
H(4)	0.005 (3)	−0.275 (5)	0.067 (1)	3.3 (7)*
H(5)	−0.202 (4)	0.113 (5)	0.050 (2)	4.1 (8)*
H(6)	−0.248 (7)	0.025 (7)	0.001 (3)	9 (1)*
H(7)	−0.070 (4)	0.233 (6)	0.295 (2)	5 (1)*
H(8)	−0.167 (4)	0.117 (6)	0.308 (2)	4.4 (9)*
H(9)	−0.196 (4)	−0.285 (7)	0.272 (2)	6 (1)*
H(10)	−0.081 (4)	−0.344 (6)	0.298 (2)	5 (1)*
H(11)	−0.155 (5)	−0.125 (8)	0.163 (2)	7 (1)*
H(12)	−0.155 (4)	0.036 (6)	0.157 (2)	4.8 (9)*

^{a}Starred values denote isotropically refined atoms. *B* values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Atomic positions for structures **1** and **2** were taken from previously reported studies on isomorphous structures containing transition elements other than vanadium.[5,11] Structure **3** was solved by direct methods. All three structures were refined by full-matrix least-squares analysis, with data-to-parameter ratios of 12.7, 6.3, and 6.0 for **1**–**3**, respectively. For **1**, the refinement was completed with data up to 60° in 2θ—this left a high data-to-parameter ratio. All hydrogen atoms in structure **1** were located in difference maps and refined freely with isotropic displacement parameters. In **3** a solvent pyridine molecule was found. The identities of the carbon and nitrogen atoms were not proved; we assigned the nitrogen atom so as to give an even distribution of displacement parameters for the atoms of this group.

The residuals from the final, convergent refinements of **1**–**3** are given in Table I. Tables II–IV list the atomic positional parameters and

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(10) (a) Computing was done by a PDP-11/60 (RSX-11M V4.1) with programs from the package SDP/P with SDP/V simulation and by a VAX-11/780 (VMS V4.2) with the package VAXSDP. (b) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *24*, 351.

(11) Zalkin, A.; Ruben, H.; Templeton, D. H. *Acta Crystallogr.* **1962**, *15*, 1219. See also references cited therein for other analogues.

Table III. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $V(C_7H_4NO_3S)_2(H_2O)_4 \cdot 2H_2O$ (**2**)[a]

atom	*x*	*y*	*z*	*B*, Å^2
V	0.000	0.000	0.000	1.40 (3)
S(1)	0.3490 (2)	-0.0592 (1)	0.2800 (3)	1.44 (3)
O(1W)	-0.0969 (7)	-0.0991 (3)	-0.1732 (7)	2.1 (1)
O(1)	0.4618 (7)	-0.0116 (3)	0.1923 (8)	2.1 (1)
O(2)	0.2910 (7)	-0.0203 (3)	0.4275 (7)	2.2 (1)
O(2W)	-0.1750 (7)	-0.0370 (4)	0.1737 (8)	2.6 (1)
O(3)	0.0650 (7)	-0.2169 (3)	0.0449 (7)	2.1 (1)
O(3W)	-0.0043 (7)	-0.1124 (3)	0.4910 (7)	2.4 (1)
N(1)	0.1844 (7)	-0.0914 (4)	0.1400 (9)	1.6 (1)
C(1)	0.587 (1)	-0.1745 (5)	0.455 (1)	1.8 (2)
C(2)	0.626 (1)	-0.2600 (5)	0.479 (1)	2.1 (2)
C(3)	0.517 (1)	-0.3202 (5)	0.395 (1)	2.2 (2)
C(4)	0.365 (1)	-0.2993 (5)	0.282 (1)	2.2 (2)
C(5)	0.3269 (9)	-0.2150 (5)	0.256 (1)	1.6 (2)
C(6)	0.4348 (9)	-0.1572 (5)	0.339 (1)	1.4 (1)
C(7)	0.1791 (9)	-0.1761 (5)	0.137 (1)	1.6 (1)

[a] *B* values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table IV. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $[V(C_7H_4NO_3S)_2(py)_4] \cdot 2py$ (**3**)[a]

atom	*x*	*y*	*z*	*B*, Å^2
V1)	0.2878 (1)	0.250	0.500	3.60 (4)
S(1)	0.4255 (2)	0.1275 (1)	0.2270 (1)	4.94 (5)
O(1)	0.2773 (4)	0.2061 (3)	0.3809 (3)	4.5 (1)
O(2)	0.4844 (4)	0.1750 (4)	0.1853 (4)	7.1 (2)
O(3)	0.4519 (4)	0.0530 (4)	0.2326 (4)	7.7 (2)
N(1)	0.1856 (4)	0.1732 (4)	0.5380 (4)	4.0 (1)
N(2)	0.3855 (4)	0.1726 (4)	0.5407 (4)	4.3 (2)
N(3)	0.3989 (4)	0.1589 (4)	0.3177 (4)	4.2 (2)
N(4)	0.7305 (7)	0.4059 (6)	0.3716 (7)	9.7 (3)*
C(1)	0.3160 (5)	0.1773 (4)	0.3207 (5)	3.6 (2)
C(2)	0.2672 (5)	0.1629 (4)	0.2401 (5)	3.7 (2)
C(3)	0.3217 (5)	0.1337 (5)	0.1803 (5)	4.2 (2)
C(4)	0.2935 (6)	0.1160 (6)	0.1000 (6)	6.1 (2)
C(5)	0.2049 (6)	0.1287 (6)	0.0821 (6)	6.2 (2)
C(6)	0.1488 (6)	0.1559 (5)	0.1441 (6)	5.4 (2)
C(7)	0.1803 (5)	0.1743 (5)	0.2238 (6)	4.8 (2)
C(8)	0.1854 (6)	0.1436 (5)	0.6158 (5)	4.8 (2)
C(9)	0.1260 (7)	0.0928 (5)	0.6389 (6)	6.4 (3)
C(10)	0.0626 (7)	0.0704 (6)	0.5813 (7)	7.3 (3)
C(11)	0.0617 (6)	0.1021 (5)	0.5013 (7)	6.5 (2)
C(12)	0.1251 (5)	0.1528 (5)	0.4819 (6)	4.9 (2)
C(13)	0.3737 (6)	0.1013 (5)	0.5280 (6)	5.9 (2)
C(14)	0.4325 (7)	0.0472 (6)	0.5595 (7)	7.2 (3)
C(15)	0.5081 (7)	0.0721 (6)	0.6017 (7)	7.2 (3)
C(16)	0.5192 (7)	0.1466 (5)	0.6132 (7)	6.7 (3)
C(17)	0.4565 (5)	0.1956 (5)	0.5831 (6)	5.1 (2)
C(18)	0.7567 (9)	0.4733 (8)	0.3408 (8)	9.5 (3)*
C(19)	0.8341 (9)	0.4778 (7)	0.2977 (8)	9.7 (4)*
C(20)	0.8826 (9)	0.4190 (8)	0.2884 (8)	10.0 (4)*
C(21)	0.8595 (9)	0.3532 (7)	0.3234 (8)	9.5 (3)*
C(22)	0.7799 (9)	0.3504 (7)	0.3641 (8)	9.3 (3)*

[a] Starred values denote isotropically refined atoms. *B* values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

equivalent isotropic displacement parameters for the three structures. Important bond distances and angles are given in Table V.

Results and Discussion

Compound 1. The structure of $VSO_4 \cdot 6H_2O$ (**1**) is depicted in Figure 1. The general features of this structure are similar to those of the cobalt[11] and magnesium[12] analogues and need not be discussed again in detail here. There are two independent and essentially octahedral $V(H_2O)_6^{2+}$ ions. In one case the vanadium atom is located on a crystallographic inversion center at (0, 0, 0), while in the other case it is on a 2-fold axis at (0, *y*, $^1/_4$). The sulfate ions serve as bridges between the vanadium-containing ions through hydrogen bonding.

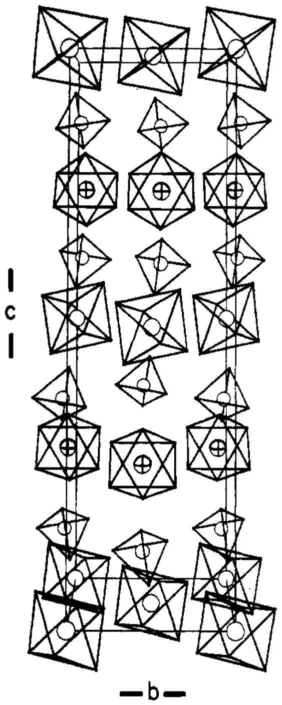

Figure 1. Projection on the (100) plane of the extended structure of $VSO_4 \cdot 6H_2O$ (**1**), showing sulfate tetrahedra and vanadium coordination octahedra. Vanadium atoms that reside on crystallographic inversion centers are shown as open circles. Crosses are inscribed in vanadium atoms lying on 2-fold axes. In this drawing the *b* axis is horizontal, the *c* axis is vertical, and the *a* axis is out of the plane of the paper.

Figure 1 is a perspective drawing of the extended structure—projected on (100)—showing the relative dispositions of the SO_4^{2-} and $V(H_2O)_6^{2+}$ polyhedra. Three of the oxygen atoms of the sulfate ion each act as an acceptor in three hydrogen bonds while the fourth oxygen atom accepts two of them. A twelfth hydrogen bond is formed by an intermolecular interaction between two water molecules. The latter is described as O(9)–H(9)···O(8). The distance of 2.979 (2) Å between O(9) and O(8) is the longest of the oxygen-to-oxygen distances where there is hydrogen bonding. The rest range from 2.697 (2) to 2.939 (3) Å. A wide range of these values seems to be typical of this type of structure. All individual values are listed in Table VI.

As expected, the vanadium(II) to oxygen bond distances, in the $V(H_2O)_6^{2+}$ ion, are larger than those found in the $V(H_2O)_6^{3+}$ ion. When the mean distances are compared, the 2.131 [11] Å V–O distance found in **1** is similar to the one found in $(NH_4)_2V(SO_4)_2 \cdot 6H_2O$ (2.15 [2] Å), but in $[V(H_2O)_6][H_5O_2](CF_3SO_3)_4$ this mean distance is only 1.995 [8] Å.[13] Thus, the radius of V^{2+} is approximately 0.14 Å larger than that of V^{3+}, a figure that may be useful in discussing electron-transfer rates involving the V^{2+}/V^{3+} couple.

An interesting chemical comparison, related to stability toward air in the solid state of V^{2+} and Fe^{2+}, can be made among the isostructural pairs $MSO_4 \cdot 6H_2O$[14] and $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$.[6] Even though V(II) and Fe(II) are normally prone to oxidation in the presence of air, these compounds seem to do it less readily than most of the non-hydrogen-bonded compounds containing these metal atoms. Futhermore, since those in the second pair contain the ammonium ion, which is also capable of forming hydrogen bonds, its stability is greatly enhanced.

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(12) Zalkin, A.; Ruben, H.; Templeton, D. H. *Acta Crystallogr.* **1964**, *17*, 235.

(13) Cotton, F. A.; Fair, C. K.; Lewis, G. E.; Mott, G. N.; Ross, F. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 5319.

(14) Tudo, J.; Laplace, G. *C. R. Seances Acad. Sci., Serie-C*, **1972**, *274*, 1388.

Table V. Important Bond Distances (Å) and Bond Angles (deg) and Their Estimated Standard Deviations[a] for $VSO_4 \cdot 6H_2O$ (**1**), $[V(C_7H_4NO_3S)_2(H_2O)_4] \cdot 2H_2O$ (**2**), and $[V(C_7H_4NO_3S)_2(py)_4] \cdot 2py$ (**3**)

1 (molecule I)		**1** (molecule II)		**2**		**3**	
				Distances			
V(1)-O(5)	2.131 (2)	V(2)-O(8)	2.150 (2)	V-N(1)	2.225 (5)	V-N(1)	2.199 (6)
-O(6)	2.123 (2)	-O(9)	2.120 (2)	-O(1W)	2.143 (4)	-N(2)	2.169 (6)
-O(7)	2.136 (2)	-O(10)	2.124 (2)	-O(2W)	2.174 (5)	-O(1)	2.071 (4)
				Angles			
O(5)-V(1)-O(6)	91.85 (8)	O(8)-V(2)-O(9)	88.77 (7)	N(1)-V-O(1W)	86.8 (2)	N(1)-V-N(2)	89.8 (2)
-O(7)	93.97 (7)	-O(10)	86.73 (7)	-O(2W)	87.4 (2)	-O(1)	87.0 (2)
O(6)-V(1)-O(7)	86.93 (9)	O(9)-V(2)-O(10)	88.04 (8)	O(1W)-V-O(2W)	89.0 (2)	N(2)-V-O(1)	94.3 (2)
O(5)-V(1)-O(6′)	88.15 (8)	O(8)-V(2)-O(9′)	179.47 (7)	N(1)-V-O(1W′)	93.2 (2)	N(1)-V-N(2′)	178.0 (2)
-O(7′)	86.03 (7)	-O(10′)	92.48 (7)	-O(2W′)	92.6 (2)	N(1′)-V-O(1)	86.5 (2)
O(6)-V(1)-O(7′)	93.07 (9)	O(9)-V(2)-O(10′)	92.74 (8)	O(1W′)-V-O(2W)	91.0 (2)	N(2′)-V-O(1)	91.9 (2)
		O(8)-V(2)-O(8′)	91.20 (9)			N(1)-V-N(1′)	88.4 (3)
		O(9)-V(2)-O(9′)	91.3 (1)			N(2)-V-N(2′)	92.0 (3)
		O(10)-V(2)-O(10′)	178.9 (1)			O(1)-V-O(1′)	171.0 (3)

[a] Estimated standard deviations of individual distances and angles are given in parentheses for the least significant digits.

Table VI. Hydrogen Bonds[a] for $VSO_4 \cdot 6H_2O$ (Hydrogen Atom Located Nearer to the Atom Referred to as "Donor")

donor	H	acceptor	acceptor coord	donor to acceptor dist, Å	angle at H, deg
O(5)	H(2)	O(1)	$-{}^1/_2 + x, -{}^1/_2 + y, z$	2.780 (2)	176 (4)
O(5)	H(1)	O(3)	$-1 + x, y, z$	2.746 (3)	160 (2)
O(6)	H(4)	O(3)	$-1 + x, -1 + y, z$	2.728 (3)	169 (3)
O(6)	H(3)	O(4)	$-{}^1/_2 + x, -{}^1/_2 + y, z$	2.792 (3)	166 (4)
O(7)	H(6)	O(3)	${}^1/_2 - x, {}^1/_2 - y, -z$	2.939 (3)	166 (6)
O(7)	H(5)	O(4)	$-1 + x, y, z$	2.860 (3)	173 (3)
O(8)	H(8)	O(1)	${}^1/_2 - x, -{}^1/_2 + y, {}^1/_2 - z$	2.784 (2)	169 (4)
O(8)	H(7)	O(2)	$1 - x, y, {}^1/_2 - z$	2.697 (2)	168 (4)
O(9)	H(10)	O(2)	$1 - x, -1 + y, {}^1/_2 - z$	2.736 (2)	175 (4)
O(9)	H(9)	O(8)	$-{}^1/_2 - x, -{}^1/_2 + y, {}^1/_2 - z$	2.971 (3)	161 (4)
O(10)	H(11)	O(1)	$-1 + x, -1 + y, z$	2.829 (3)	159 (7)
O(10)	H(12)	O(4)	$-1 + x, y, z$	2.761 (2)	167 (4)

[a] Estimated standard deviations are given in parentheses for the least significant digits.

Table VII. Hydrogen Bonds[a] for $[V(C_7H_4NO_3S)_2(H_2O)_4] \cdot 2H_2O$

donor	acceptor	acceptor coord	donor to acceptor dist, Å
O(1W)	O(3)	x, y, z	2.716 (6)
O(1W)	O(3W)	$x, y, -1 + z$	2.824 (6)
O(2W)	O(3W)	x, y, z	2.864 (7)
O(2W)	O(1)	$-1 + x, y, z$	2.939 (6)
O(3W)	O(3)	$x, -{}^1/_2 - y, {}^1/_2 + z$	2.827 (6)
O(3W)	O(2)	x, y, z	2.888 (6)

[a] Estimated standard deviations are given in parentheses for the least significant digits.

Compound 2. The structure of $[V(C_7H_4NO_3S)_2(H_2O)_4] \cdot 2H_2O$ (**2**) is shown in Figure 2, which defines the labeling scheme. It is qualitatively the same as the structures of the other transition-metal saccharinates.[5] The coordination of the metal atom is octahedral with a centrosymmetric arrangement of two saccharinate nitrogen atoms and four water molecules. As before, two more water molecules are found in the lattice. By participating in hydrogen bonding, they serve as bridges between molecules. Even though we did not make any attempts to locate the hydrogen atoms in this case, they have previously been clearly defined for its analogues. As shown in Table VII, the close oxygen-to-oxygen distances seem to indicate that the pattern is the same in this compound as the one found in the structures of the other $[M(C_7H_4NO_3S)_2(H_2O)_4] \cdot 2H_2O$ compounds, where every hydrogen atom is utilized in hydrogen bonding.[5] The inter- and intramolecular hydrogen bonds provide complete protection to the metal atom. This is presumably the cause of the high stability toward air that this compound exhibits in the crystalline state. This explanation is also consistent with the high stability shown by the compound $(NH_4)_2V(SO_4)_2 \cdot 6H_2O$, as described above, and the notable stability toward air of $VSO_4 \cdot 6H_2O$.

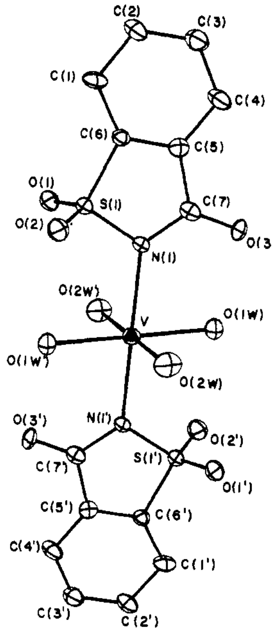

Figure 2. ORTEP view of the molecular geometry of $V(C_7H_4NO_3S)_2(H_2O)_4$ (**2**) at the 50% probability level. Primed atoms are related to unprimed atoms by an inversion center.

Another interesting aspect of the structure of **2** was that the metal-to-ligand bond lengths and the unit cell volume are very close to the values obtained by extrapolation from the data for the remaining first-row complexes. An updated graph of the variations in the structure as a function of change in d configuration is shown in Figure 3, which clearly shows the deviations from the monotonic trend for the high-spin d^4 and d^9 configurations. The values for hypothetical non-Jahn-Teller geometries can now be extrapolated with confidence. This result also shows that our original procedure of extrapolating the position of the

Table VIII. Comparison of the M–L Bond Distances (Å) in Hexacoordinated Vanadium(II) Compounds with Bonds to Oxygen- and/or Nitrogen-Containing Ligands[a–c]

	i	ii_x	ii_y	iii	iv	v	vi	vii	viii
V–O	2.16(1)	2.136 (2)	2.150 (2)	2.143 (4)	2.071 (4)		2.174 (4)		2.079[d]
V–O	2.16 (1)	2.123 (2)	2.120 (2)	2.174 (5)					2.163 (8)
V–O	2.12 (1)	2.131 (2)	2.124 (2)						2.177 (10)
mean V–O	2.15 [2]	2.130 [7]	2.131 [16]	2.158 [22]					2.140 [53]
V–N				2.225 (5)	2.199 (6)	2.189 (2)	2.045 (3)	2.048 (4)	
V–N					2.169 (6)		2.046 (4)	2.053 (4)	
mean V–N					2.184 [21]		2.046 [1]	2.050 [4]	
ref	6	this work	this work	this work	this work	17	18	18	16

[a] Key: i = $(NH_4)_2V(SO_4)_2\cdot 6H_2O$; ii = $VSO_4\cdot 6H_2O$ (two independent molecules in the same crystal); iii = $V(Sac)_2\cdot 6H_2O$; iv = $V(Sac)_2\cdot 6py$; v = $VCl_2\cdot 4py$; vi = [V(oep)(THF)$_2$]; vii = [V(oep)(PPhMe$_2$)$_2$]; viii = $[V(THF)_4][V(CO)_6]_2$. [b] In all cases shown, the coordination is of the type *trans*-ML_2X_4. [c] Numbers in parentheses are the estimated standard deviations in the least significant digits. The numbers in square brackets are deviations from the mean and were calculated according to the formula $[\sum(d - \bar{d})^2/n(n-1)]^{1/2}$. [d] The standard deviation for V–O (CO) was not reported.

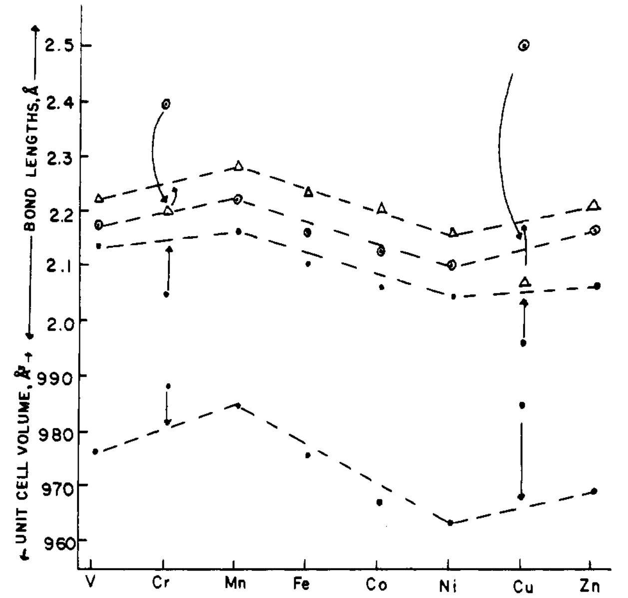

Figure 3. Variations in the structure of $[M(C_7H_4NO_3S)_2(H_2O)_4]\cdot 2H_2O$ as the metal atom changes: upper part, individual metal–ligand bond lengths (Δ, M—N; ○ and ●, M—O); lower part, unit cell volumes.

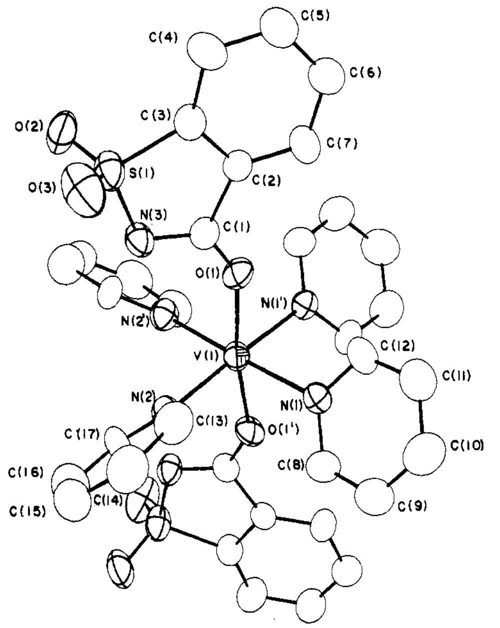

Figure 4. ORTEP view of the molecular structure of $V(C_7H_4NO_3S)_2(py)_4$ (3). Ellipsoids are at the 40% probability level.

vanadium data points by using the same slope for the line vanadium-to-manganese as for the line nickel-to-zinc was adequate and might be valuable in other cases in which parameters for one of the compounds are not available.

Compound 3. The structure of $[V(C_7H_4NO_3S)_2(py)_4]\cdot 2py$ (3) is shown in Figure 4, which also indicates the labeling scheme. The arrangement of atoms around the vanadium center is octahedral, with deviations from regularity. A crystallographic 2-fold axis bisects the angle subtended by two of the pyridine nitrogen atoms at the vanadium center. There is a square set of four pyridine nitrogen atoms and two trans oxygen atoms from the carbonyl groups of saccharinate ligands surrounding the vanadium atom. Two more pyridine molecules are found in the lattice, but no close contacts are found between them and the vanadium-containing molecule. A very similar arrangement is also found in **4**.[15]

The major difference between this structure and that of **2** is the ligation of saccharinate through oxygen in this case, rather than through nitrogen as in the case of **2** and all other saccharinate complexes whose structures have previously been determined. Thus, we observe that, in going from **2** to **3**, none of the bonds to the vanadium atom remains intact.

Presumably, the appearance of the interaction through the carbonyl oxygen atom of the saccharinate anion is due to steric effects, although other factors cannot be ruled out. Crowding around the metal center would be very high if the manner of coordination of the saccharinate ligand did not change.

Interestingly, the bond distances in the saccharinate anion show no significant variations in the N-bonded and the O-bonded compounds, including the C–O bond length, which is 1.241 (7) Å for the first case and 1.248 (7) Å for the second case.

A somewhat similar carbonyl interaction is known for the compound $[V(THF)_4][V(CO)_6]_2$[16] in which two trans V–C–O–V bridges exist and no effect on the infrared stretching frequency of the carbonyl group is found. Also, no particular lengthening of the C–O bond was observed in that case. The average terminal C–O bond length was 1.157 [19] Å, while the bridging C–O distance was 1.157 (12) Å.

Other vanadium(II) complexes containing four nitrogen atoms in the equatorial plane have been described previously. One of them, $VCl_2(py)_4$,[17] has a similar configuration around the metal center. Two others, [V(oep)(THF)$_2$] and [V(oep)(PPhMe$_2$)$_2$],[18]

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(15) The structure of **4** is similar to that of **3**, except that the pyridine molecules from the lattice have been substituted by THF. Because the crystal suffered severe decomposition (>45%) and because the data set had a low data to parameter ratio (3.9:1), we did not attempt a complete refinement of the structure. However, the chemical composition was clear from the preliminary study. It crystallizes in space group *Pbna* with unit cell parameters a = 15.289 (5) Å, b = 17.644 (4) Å, c = 16.249 (4) Å, V = 4383 (3) Å^3, and Z = 4. Data were gathered on an Enraf-Nonius CAD-4F diffractometer with Mo Kα radiation. The structure was refined (867 observations with $F_o^2 \geq 2\sigma(F_o^2)$; 242 parameters) to residuals of R = 0.093, R_w = 0.107, and quality of fit = 1.523. With an atom-naming scheme the same as that for compound **3**, the important distances for **4** are as follows: V(1)–O(1), 2.08 (1) Å; V(1)–N(1), 2.20 (2) Å; V(1)–N(2), 2.20 (2) Å. Crystal data and atomic coordinates for **4** are available as supplementary material.

(16) Schneider, M.; Weiss, E. *J. Organomet. Chem.* **1976**, *121*, 365.

(17) Braver, D. J.; Krüger, C. *Cryst. Struct. Commun.* **1973**, *3*, 421.

get their four nitrogen atoms from the macrocycle octaethylporphyrinate.

For comparative purposes the M-L bond distances of some hexacoordinated vanadium(II) compounds with bonds to oxygen- and/or nitrogen-containing ligands are provided in Table VIII. In general, the mean V-O distance is fairly constant, but significant deviations of the individual bond lengths appear in **2** and in $[V(THF)_4][V(CO)_6]_2$. In the latter case the vanadium-to-oxygen distance of the bridging carbonyl group is very short. This is also the case in **3**, where the corresponding bond distance is 2.071 (4) Å. However, the shortening of the bond is accompanied by a lengthening of the V-N bonds (2.184 [21] Å) as compared to the case where the nitrogen atoms are provided by a porphyrin ring as in $[V(oep)(THF)_2]$ and $[V(oep)(PPhMe_2)_2]$, in which the mean V-N bond distances are only 2.046 [1] and 2.050 [4] Å, respectively. In the case of the porphyrin ligand, it is possible that electrons in the plane formed by the VN_4 species can be delocalized, allowing π interaction between the electrons from the metal and those of the ring, thus making the V-N bonds shorter and the other V-L bonds longer, as is the case in $[V(oep)(THF)_2]$.

When the ligand is pyridine, the same extended delocalization is not possible. Perhaps this allows a clear contact with the axial ligands as in the case of the carbonyl oxygen atom of the saccharinate ligand. In this case, it is tempting to use the same argument and assume some electron delocalization over the saccharinate ring, which is planar, or π bonding to the chlorine atom in the case of $VCl_2(py)_4$. However, if that is the case, it does not manifest itself in a lengthening of the C-O bond.

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Registry No. **1** (CC entry), 22364-10-9; **1** (salt entry), 22257-76-7; **2**, 103563-29-7; **3**, 103563-31-1; **4**, 103563-32-2; $VOSO_4$, 27774-13-6.

Supplementary Material Available: Tables of anisotropic thermal parameters and all bond distances and angles for **1-4** and crystal data and positional parameters for **4** (17 pages); tables of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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(18) Oumous, H.; Lecomte, C.; Protas, J.; Poncet, J. L.; Barbe, J. M.; Guilard, R. *J. Chem. Soc., Dalton Trans.* **1984**, 2677.

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$In_{11}Mo_{40}O_{62}$: A Molybdate with Units of Four and Five Condensed Mo_6 Octahedra and Linear In_5^{7+} and In_6^{8+} Ions

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Received August 28, 1985

$In_{11}Mo_{40}O_{62}$ is prepared from a stoichiometric mixture of In, Mo, and MoO_2 at 1100 °C. The crystal structure ($Pmc2_1$, a = 2887.8 (5) pm, b = 951.3 (1) pm, c = 988.3 (1) pm, Z = 2, R = 0.038 for 3017 reflections with $F > 2\sigma(F)$) of the metallic looking compound exhibits several novel features. Chains of four and five Mo_6 octahedra condensed via opposite edges occur that are surrounded by O atoms above all free octahedra edges (Mo-Mo distances between 264 and 312 pm). The channels between these cluster units are filled with chains of five and six In atoms with metal-metal-bonded In_5^{7+} and In_6^{8+} ions (In-In distances between 262 and 268 pm). The structure is discussed in terms of bond length-bond strength calculations.

Introduction

A large number of metal-rich compounds of d metals and p elements, e.g. halogens, chalcogens, etc., have structures that contain isolated or condensed clusters.[1] Oxides that exhibit these structural features are rather scarce. Triangular clusters of molybdenum atoms occur in the compounds $A_2Mo_3O_8$ (A = divalent elements like Mg, Mn, Zn, etc.)[2-4] and $LiZn_2Mo_3O_8$ or $ScZnMo_3O_8$.[5] Tetranuclear clusters were found in $Ba_{1.14}Mo_8O_{16}$[6] and $K_2Mo_8O_{16}$.[7] These tetranuclear clusters are condensed to form ribbons in $Na_{0.9}Mo_2O_4$.[8,9] The only oxides containing isolated octahedral M_6 units are $Mg_3Nb_6O_{11}$[10] and $Mn_3Nb_6O_{11}$.[11] The extreme of a 3-dimensional framework of condensed M_6 units was found in NbO[12,13] and TiO.[1,14] A fascinating group of structures was worked out by McCarley et al.[8] Compounds with the composition AMo_4O_6 (A = Na,[15] K,[16] Rb,[9] Sr,[9] Ba[6,9] Eu,[9] Pb,[6,9] In, Sn[8,9] as well as $Sc_{0.75}Zn_{1.25}Mo_4O_7$ and $Ti_{0.5}Zn_{1.5}Mo_4O_7$[17] contain infinite chains of trans-edge-sharing Mo_6 octahedra, the oxygen environment corresponding to the M_6X_{12} type cluster. The variation of the Mo/O ratio is due to different ways of interconnection of such chains via oxygen bridges. Combinations of different structural elements were found in $Ca_{5.45}Mo_{18}O_{32}$.[8] This compound contains chains of condensed M_6 and M_4 units together with chains of single atoms. By means of Extended Hückel calculations the chemical bonding in reduced molybdates containing such chains of octahedra has been discussed in detail.[18]

Our interests in ternary molybdenum oxides were focused in two directions. On one side the close structural relationship of $NaMo_4O_6$ with metal-rich lanthanide halides[1,19] prompted the question as to whether the extent of condensation can be increased, leading to twin chains or ultimately layers of condensed octahedra.

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(1) Simon, A. *Angew. Chem.* **1981**, *93*, 23; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1.

(2) McCarroll, W. H.; Katz, L.; Ward, J. *J. Am. Chem. Soc.* **1957**, *79*, 5410.

(3) McCarroll, W. H. *Inorg. Chem.* **1977**, *16*, 3351.

(4) Ansell, G. B.; Katz, L. *Acta Crystallogr.* **1966**, *21*, 482.

(5) Torardi, C. C.; McCarley, R. E. *Inorg. Chem.* **1985**, *24*, 476.

(6) Torardi, C. C.; McCarley, R. E. *J. Solid State Chem.* **1981**, *37*, 393.

(7) Torardi, C. C.; Calabrese, J. C. *Inorg. Chem.* **1984**, *23*, 3281.

(8) McCarley, R. E., Lii, K.-H.; Edwards, P. A.; Brough, L. F. *J. Solid State Chem.* **1985**, *57*, 17.

(9) Mattausch, Hj.; Simon, A., unpublished results.

(10) Marinder, B. O. *Chem. Scr.* **1977**, *11*, 97.

(11) Abbattista, F.; Rolando, P. *Ann. Chim.* (*Rome*) **1971**, *61*, 196.

(12) Anderson, G.; Magneli, A. *Acta Chem. Scand.* **1957**, *11*, 1065.

(13) Schäfer, H.; von Schnering, H. G. *Angew. Chem.* **1964**, *76*, 833.

(14) Watanabe, D.; Castles, J. R.; Jostous, A.; Matin, A. S. *Acta Crystallogr.* **1967**, *23*, 307.

(15) Torardi, C. C.; McCarley, R. E. *J. Am. Chem. Soc.* **1979**, *101*, 3963.

(16) Bauer, K.; Rau, F.; Abriel, W.; Range, K.-J. 2. Vortragstagung Fachgruppe Festkörperchemie in der GDCh, Stuttgart, FRG, 1980.

(17) McCarley, R. E. *Philos. Trans. R. Soc. London, A* **1982**, *308*, 141.

(18) Hughbanks, T.; Hoffmann, R. *J. Am. Chem. Soc.* **1983**, *105*, 3528.

(19) Simon, A. *J. Solid State Chem.* **1985**, *57*, 2.