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Tetrakis(glycine)dimolybdenum Disulfate Tetrahydrate

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The interaction of the $Mo_2Cl_8^{4-}$ ion in hydrochloric acid with amino acids has been surveyed. In all cases, replacement of Cl^- by amino acids is evidenced by changes in color (from red to orange or yellow) and in spectra. With glycine, a yellow powder of approximate composition $Mo_2(gly)_4Cl_4 \cdot 2H_2O$ is precipitated. This can be converted to $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$, a yellow crystalline solid, whose crystal structure has been determined. The crystals belong to the tetragonal system, space group $I\bar{4}$, with $a = 11.290$ (2) Å, $c = 9.150$ (2) Å, and $Z = 2$. The structure was refined to convergence with $R_1 = 0.0220$ and $R_2 = 0.0285$ for the correct choice of enantiomorph. The $Mo_2(O_2CCH_2NH_3)_4^{4+}$ ions are linked by hydrogen bonds from the $-CH_2NH_3^+$ groups to sulfate ions and water molecules. All Mo_2^{4+} groups are parallel to the c axis; the Mo–Mo distance is 2.115 (1) Å. The Raman spectrum has a strong band at 393 cm^{-1}.

Introduction

It is now well established that the dimolybdenum(II) unit, Mo_2^{4+}, is very stable and a prolific former of complexes ranging from the simple aquo ion, through cationic (e.g., $Mo_2(en)_4^{4+}$), neutral (e.g., $Mo_2Cl_4(PR_3)_4$, $Mo_2(O_2CR)_4$), anionic (e.g., $Mo_2Cl_8^{4-}$, $Mo_2(SO_4)_4^{4-}$), and organometallic (e.g., $Mo_2(allyl)_4$, $Mo_2(CH_3)_8^{4-}$) ones, for a total of more than 50 well-characterized species.[1]

In view of the special affinity of Mo_2^{4+} for carboxylato ions, we thought it might be of interest to study its interaction with amino acids, first because amino acids constitute an important and convenient class of water-soluble carboxylic acids and second because of possible application of the Mo_2^{4+} unit in biochemistry as a stain or as a heavy scatterer for crystallographic phase determination.

In the course of this work we have discovered a compound which has an unusually beautiful and regular crystal structure that has allowed us, in collaboration with Professor D. S. Martin of Iowa State University, to investigate in detail the electronic spectrum of the $Mo_2(O_2CR)_4$ type of unit. The spectroscopic work will be reported elsewhere. Here we present some of the results of our chemical investigation of the interaction of amino acids with Mo_2^{4+}(aq), the preparation of $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$, and the crystallographic study of this compound.

Experimental Section

Preparation of $Mo_2(gly)_4Cl_4 \cdot xH_2O$. Fresh $K_4Mo_2Cl_8$[2] (1.0 g) was added to a solution of glycine (2.0 g) in 15 ml of HCl (0.8 M) under nitrogen. The powdery yellow product, which precipitated almost immediately, was filtered through a medium-porosity sintered-glass frit, washed with two 20-ml portions each of ethanol and ether, and air-dried. Typical yields were 0.90–1.05 g. A yellow powder was also produced when $K_4Mo_2Cl_8$ was added to glycine dissolved in water; the ir spectra of the two powders are identical. However, the product obtained from acidified solutions is cleaner in appearance. A similar yellow powder is also obtained with glycine in 6 M HCl. The compound is stable to air and moisture and is soluble in water and dilute aqueous acids. Analytical data are presented in Table I.

Ir spectrum (Nujol mull, 4000–650 cm^{-1}): 3390 (m, b), 3060 (s, vvb), 1600 (m, b), 1550 (s), 1450 (s), 1345 (s), 1310 (m), 1115 (m, b), 1045 (m, b), 1020 (m), 900 (s).

Uv–visible spectrum (solution, 1.0 g of glycine in 50 ml of 0.25 M HCl, 215–650 nm): 445 (ϵ 1 × 10^2 M^{-1} cm^{-1}), 297 (ϵ 8 × 10^3 M^{-1} cm^{-1}), 227 (ϵ 3 × 10^3 M^{-1} cm^{-1}).

Preparation of $Mo_2(gly)_4(SO_4)_2 \cdot 4H_2O$. A nitrogen-purged solution of glycine (0.10 g) in 0.5 M H_2SO_4 (15 ml) was saturated with $Mo_2(gly)_4Cl_4 \cdot xH_2O$. The resulting solution was filtered through a fine-porosity glass frit, purged with nitrogen, and left overnight at 3° in a stoppered flask. The product, a mass of yellow, needlelike crystals, was filtered, washed with alcohol and ether, and air-dried. The crystals are stable for several weeks in air.

Ir spectrum (Nujol mull, 4000–650 cm^{-1}): 3580 (m, b), 3360 (m, b), 3160 (s, b), 1650 (m), 1600 (m), 1580 (m), 1550 (s, b), 1430 (s), 1350 (s), 1150 (m), 1080 (s, b), 920 (s).

Table I. Analytical Data for $Mo_2(O_2C_2NH_5)_4Cl_4 \cdot xH_2O$

	% C	% H	% Cl
Found	14.28	3.23	20.36
Calcd for $Mo_2(O_2C_2NH_5)_4Cl_4$	15.16	3.18	22.38
Calcd for $Mo_2(O_2C_2NH_5)_4Cl \cdot 2H_2O$	14.34	3.61	21.16
Calcd for $Mo_2(O_2C_2NH_5)_4Cl_4 \cdot 4H_2O$	13.60	4.00	20.08
Calcd for $Mo_2(O_2C_2NH_5)_3Cl_4$	12.89	2.70	25.37

Raman spectrum (6471-Å line of Kr laser, 30–500 cm^{-1}): 106 (m, b), 134 (m, b), 197 (s), 307 (m), 393 (vs), 434 (m, b).

Preparation of a Molybdenum(II)–Glycylglycine Complex. To 1.0 g of $K_4Mo_2Cl_8$ in 15 ml of 0.8 M HCl was added 2.0 g of glycylglycine. Over a period of several minutes the red solution turned yellow-orange, and a pale yellow powder precipitated. The product was filtered on a fine-porosity glass frit, washed with alcohol and ether, and air-dried; yield 0.95 g. The solid decomposes in laboratory air after a few days.

Ir spectrum (Nujol mull, 4000–650 cm^{-1}): 3350 (s, b), 3100 (s, vb), 1680 (s), 1550 (s), 1530 (m), 1450 (sh), 1420 (m), 1325 (s), 1265 (s), 1100 (m), 1080 (m), 1040 (m), 1010 (m), 900 (s), 770 (m).

Reactions of Other Amino Acids with $K_4Mo_2Cl_8$. Reactions of other amino acids were carried out similarly to the glycine reaction in the pH range 1–3 with 6–8 mol of amino acid/mol of $K_4Mo_2Cl_8$. The following reactants were examined: in HCl solution, L-aspartic acid, L- and DL-lysine, L-arginine, L-histidine, L-serine, L-isoleucine, L- and DL-alanine, L-cysteine; in HBF_4, DL-lysine; in H_2SO_4, L-lysine, L-arginine, L-aspartic acid, L-glutamic acid, L- and DL-alanine. In each case, yellow or yellow-orange solutions were obtained almost immediately after mixing. However, no precipitate formed, and cooling to 3° or adding small amounts of alcohol and cooling to −10° did not cause precipitation.

Spectra and Analyses. Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. Electronic spectra were measured on Cary 14 and Beckman Acta III spectrophotometers. Raman spectra were measured on a Cary 82 laser Raman spectrophotometer. Microanalyses were obtained from Chemalytics, Inc., Tempe, Ariz.

Crystallographic Data Collection. Crystals of $Mo_2(gly)_4(SO_4)_2 \cdot 4H_2O$ form as square-based needles elongated parallel to c. One such yellow needle, approximately 0.07 × 0.07 × 0.23 mm, was mounted on a glass fiber with the needle axis nearly coincident with the ϕ axis of the goniometer. Preliminary precession photographs and axial photographs on a Syntex $P\bar{1}$ autodiffractometer indicated that the crystal belonged to the tetragonal class, with Laue symmetry $4/m$. Systematic absences (hkl for $h + k + l \neq 2n$) indicated possible space groups $I4$, $I\bar{4}$, and $I4/m$; $I\bar{4}$ was ultimately chosen as correct. From ω scans of several intense reflections, a peak width of 0.15° at half-height was measured. Cell constants and an orientation matrix for the unit cell were obtained from least-squares refinement of the setting angles of 15 computer-centered reflections in the range 27° $< 2\theta <$ 35°. The cell constants are $a = 11.290$ (2) Å, $c = 9.150$ (2) Å, and $V = 1166.4$ (5) $Å^3$. For $Z = 2$, the calculated density is 2.154 g cm^{-3}; the experimental density (flotation in $CHBr_3$–CCl_4) is 2.15 ± 0.02 g cm^{-3}.

Data were collected at 24° using Mo $K\alpha$ radiation filtered by a graphite-crystal monochromator. The θ–2θ scan technique with a

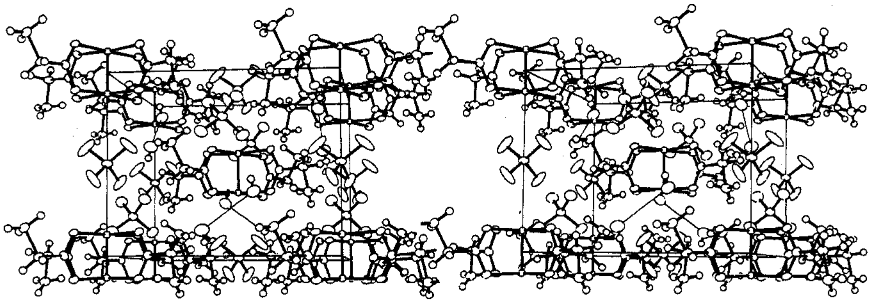

Figure 1. Stereoscopic view of the unit cell. The reader is urged not to be discouraged by the appearance of this figure when viewed monoptically. Under a magnifying stereoviewer it offers a very clear picture of the arrangement.

scan rate varying from 2 to 24°/min, depending on the intensity of the reflection, was used to collect 986 *hkl* reflections (804 with $F_o^2 > 3\sigma(F_o^2)$) in the range $0° < 2\theta \leq 60°$ and 196 $hk\bar{l}$ reflections in the range $0° < 2\theta \leq 35°$. The scan range was from 0.7° below the $K\alpha_1$ peak to 0.7° above the $K\alpha_2$ peak. The parameter *p*, used in data reductions,[3] was set equal to 0.05. No significant change in the intensities of four standard reflections, remeasured every 100 reflections, was observed. Additional details of data reductions have been given previously.[4]

No effects from secondary extinction were observed in the data set. The linear absorption coefficient is 13.3 cm^{-1} for Mo Kα radiation. No absorption correction was applied.

Solution and Refinement of the Structure.[3] The positions of the Mo atom, both S atoms, one O atom from a sulfate ion, and the C and O atoms of the glycine ligand were obtained from the three-dimensional Patterson function. Since the presence of a sulfate ion at (0, 0, $^1/_2$) is not consistent with an ordered structure in space groups $I4$ and $I4/m$, $I\bar{4}$ was tentatively chosen for refinement. The Patterson solution indicated that much of the electron density was reflected through the $z = 0$ plane, although this mirror is not a symmetry element of $I\bar{4}$. The position of S(1) was chosen as (0, $^1/_2$, $^1/_4$) to fix the enantiomorph in this noncentrosymmetric space group. Two cycles of isotropic refinement on positional and thermal parameters produced $R_1 = \sum \| F_o| - |F_c\| / \sum |F_o| = 0.123$ and $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2} = 0.165$. The remaining nonhydrogen atoms were located in a difference map, the more intense of the paired peaks being selected. Isotropic refinement produced $R_1 = 0.065$ and $R_2 = 0.092$. Although all atoms seemingly refined well, the bond distances within the sulfate ions were unreasonable. When the nitrogen atom was reflected through the pseudomirror, the residuals dropped to $R_1 = 0.046$ and $R_2 = 0.061$, and all distances appeared reasonable. Three cycles of anisotropic refinement gave $R_1 = 0.028$ and $R_2 = 0.040$. A difference map indicated positions for all glycine hydrogen atoms and one water hydrogen atom. Isotropic temperature factors for these atoms were fixed at 0.5 $Å^3$ greater than the converged isotropic temperature factor for the corresponding C, N, or O atom. Refinement was caused to converge to give final residuals of $R_1 = 0.0236$ and $R_2 = 0.0312$.

The choice of enantiomorph was now reconsidered. Parallel refinements using the Friedel data $hk\pm l$ with $\Delta f'' > 0$ and $\Delta f'' < 0$ were inconclusive, as most of the intense reflections have effectively centric phases. Refinement of the mirror image of the original structure with the 984 *hkl* data produced $R_1 = 0.0229$ and $R_2 = 0.0297$. The result suggests at the 99+% confidence level[5] that the original choice of enantiomorph was wrong. The positional parameters of the two enantiomorphs are (except for the coordinate transformation) virtually identical. We report positional and thermal parameters for the second enantiomorph.

The one hydrogen atom not previously found was located in a difference map. Its peak height was 0.70 e $Å^{-3}$, whereas previous hydrogen peaks were in the range 0.87–1.18 e $Å^{-3}$. The atom was added, and refinement was continued to convergence at $R_1 = 0.0220$ and $R_2 = 0.0285$. The error in an observation of unit weight is 0.84.

The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight w is $4F_o^2/\sigma^2(F_o^2)$. Scattering factors of Cromer and Waber[6] were used, with H scattering factors from Stewart, Davidson, and Simpson.[7] Anomalous dispersion for Mo and S was included in F_c,[8] with values from Cromer and Liberman.[9]

No unusual trends were observed in an analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of reflection number, $\lambda^{-1} \sin\theta$, $|F_o|$, or various classes of Miller indices. A final difference map showed a number of ghost peaks around the Mo atom; peak heights were comparable to those for the hydrogen atoms.

Table III. Final Positional Parameters[a,b]

Atom	x	y	z
Mo	0	0	0.11555 (4)
S(1)	0	$^1/_2$	$-^1/_4$
S(2)	0	0	$^1/_2$
O(1)	0.1609 (3)	0.0984 (3)	0.1181 (8)
O(2)	0.1615 (3)	0.0955 (4)	−0.1255 (7)
O(3)	0.0783 (5)	0.4275 (4)	−0.1572 (5)
O(4)	0.1014 (5)	0.0327 (4)	0.4076 (6)
O(5)	0.1188 (5)	0.3918 (5)	0.1441 (6)
N	0.3438 (4)	0.2504 (4)	0.1359 (5)
C(1)	0.2051 (3)	0.1257 (3)	−0.0017 (10)
C(2)	0.3171 (3)	0.1984 (4)	−0.0096 (9)
H(1C)	0.392 (7)	0.159 (7)	−0.031 (9)
H(2C)	0.329 (9)	0.264 (7)	−0.078 (10)
H(1N)	0.347 (8)	0.184 (8)	0.202 (10)
H(2N)	0.403 (9)	0.297 (8)	0.126 (11)
H(3N)	0.285 (8)	0.290 (8)	0.137 (11)
H(1O)	0.102 (9)	0.399 (9)	0.062 (12)
H(2O)	0.067 (11)	0.366 (12)	0.165 (15)

[a] The numbers in parentheses indicate the estimated standard deviation in the least significant digit. [b] Fractional tetragonal coordinates.

Table VI. Bond Lengths (Å)

Mo–Mo	2.115 (1)	C(2)–H(2C)	0.97 (9)
Mo–O(1)	2.120 (4)	N–H(1N)	0.96 (10)
Mo–O(2)	2.130 (4)	N–H(2N)	0.85 (10)
O(1)–C(1)	1.243 (10)	N–H(3N)	0.80 (9)
O(2)–C(1)	1.281 (10)	S(1)–O(3)	1.474 (5)
C(1)–C(2)	1.510 (5)	S(2)–O(4)	1.470 (4)
C(2)–N	1.486 (8)	O(5)–H(1O)	0.68 (13)
C(2)–H(1C)	0.97 (8)	O(5)–H(2O)	0.78 (11)

Table VII. Bond Angles (deg)

Mo–Mo–O(1)	90.6 (2)	N–C(2)–H(1C)	100 (5)
Mo–Mo–O(2)	92.5 (2)	N–C(2)–H(2C)	105 (6)
O(1)–Mo–O(1)	178.7 (4)	H(1C)–C(2)–H(2C)	99 (8)
O(2)–Mo–O(2)	175.1 (4)	C(2)–N–H(1N)	105 (5)
O(1)–Mo–O(2)	90.8 (2)	C(2)–N–H(2N)	107 (7)
O(2)–Mo–O(1)	89.1 (2)	C(2)–N–H(3N)	93 (7)
Mo–O(1)–C(1)	117.5 (5)	H(1N)–N–H(2N)	121 (8)
Mo–O(2)–C(1)	115.3 (4)	H(1N)–N–H(3N)	117 (8)
O(1)–C(1)–O(2)	124.0 (3)	H(2N)–N–H(3N)	107 (7)
O(1)–C(1)–C(2)	120.8 (6)	O(3)–S(1)–O(3)	109.7 (4)
O(2)–C(1)–C(2)	115.1 (6)	O(3)–S(1)–O(3)	109.4 (2)
C(1)–C(2)–N	110.0 (5)	O(4)–S(2)–O(4)	109.3 (3)
C(1)–C(2)–H(1C)	119 (5)	O(4)–S(2)–O(4)	109.8 (3)
C(1)–C(2)–H(2C)	121 (6)	H(1O)–O–H(2O)	96 (13)

The observed and calculated structure factors in the form of $10|F_o|$ and $10|F_c|$ are listed in Table II.[10] The final positional parameters are listed in Table III; thermal parameters are given in Table IV.[10] Table V gives rms amplitudes of thermal vibration.[10] Table VI gives bond lengths and Table VII lists bond angles in the structure. A stereoscopic view of the entire unit cell is presented in Figure 1. A

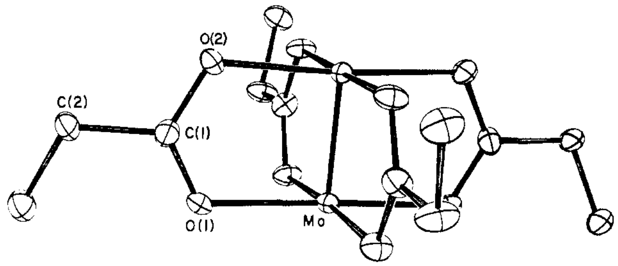

Figure 2. The $\mathrm{Mo_2(O_2CCH_2NH_3)_4^{4+}}$ units, with hydrogen atoms omitted for clarity. This view shows very clearly the $\bar{4}(S_4)$ symmetry of the unit as it resides in the crystal.

Table VIII. Raman Frequencies and Bond Lengths in Some Dimolybdenum Species[a]

	$\nu_{\text{Mo-Mo}}$ cm^{-1}	Bond length, Å
$\mathrm{Mo_2(diphenylbenzamidinato)_4}$	410[e]	2.090 (1)[e]
$\mathrm{Mo_2(O_2CH)_4}$	410[b]	2.093[b]
$\mathrm{Mo_2(O_2CCH_3)_4}$	406	2.093 (1)[c]
$\mathrm{Mo_2(O_2CCF_3)_4}$	397	2.090 (4)
$\mathrm{Mo_2(glycine)_4^{4+}}$	393[d]	2.115 (1)[d]
$\mathrm{Mo_2(SO_4)_4^{4-}}$	370	2.110 (1)
$\mathrm{Mo_2(O_2CCF_3)_4 \cdot 2py}$	367	2.129 (2)
$\mathrm{Mo_2Cl_8^{4-}}$	348 (av)	2.141 ± 0.006 (av)

[a] For most references see ref 1; structures published since that time are referenced in the following footnotes. [b] F. A. Cotton and T. R. Webb, unpublished work. [c] F. A. Cotton, Z. C. Mester, and T. R. Webb, *Acta Crystallogr., Sect. B*, 29, 2768 (1974). [d] This work. [e] F. A. Cotton, T. Inglis, M. Kilner, and T. R. Webb, *Inorg. Chem.*, 14, 2023 (1975).

view of the complex ion $\mathrm{Mo_2(O_2CCH_2NH_3)_4^{4+}}$ is shown in Figure 2.

Discussion

Description of the Structure. The component of main interest in this structure is the cation $\mathrm{Mo_2(O_2CCH_2NH_3)_4^{4+}}$. This is the usual tetracarboxylato-bridged dimetal unit, quite similar to those found in other $\mathrm{Mo_2(O_2CR)_4}$ compounds. There is one small difference, however, and that is the slightly, but significantly, longer Mo–Mo distance. In the acetate, trifluoroacetate, and formate (see Table VIII) the Mo–Mo distance is 2.092 ± 0.002 Å, while here it is 2.115 Å. We see no simple reason for this increase of ca. 0.02 Å but note also that it is accompanied by a decrease in the frequency of the Raman band that corresponds, approximately, to Mo–Mo stretching. In general, as Table VIII shows, there is a fair, though not precise, inverse correlation of $\nu_{\text{Mo-Mo}}$ and $d_{\text{Mo-Mo}}$.

The $\mathrm{Mo_2(O_2CCH_2NH_3)_4^{4+}}$ ions are made up of the $\mathrm{Mo_2^{4+}}$ core and four zwitterionic glycine molecules, $\mathrm{H_3NCH_2CO_2}$. These units are then linked together by hydrogen bonds between the $\mathrm{RNH_3^+}$ groups and (1) sulfate ions at 0, $^1/_2$, $-^1/_4$, which are most extensively hydrogen bonded, (2) sulfate ions at 0, 0, $^1/_2$, which are less extensively hydrogen bonded, and (3) the water molecules.

The $\mathrm{Mo_2^{4+}}$ groups are all crystallographically equivalent and lie collinear with the crystallographic *c* axis. Moreover, while the symmetry about each $\mathrm{Mo_2^{4+}}$ unit approximates closely to D_{4h}, the true crystallographic symmetry, as evidenced in an obvious way by the orientations of the $\mathrm{-CH_2NH_3}$ groups seen in Figure 2, is lower, namely, $S_4(\bar{4})$. These two features, the parallel alignment of equivalent $\mathrm{Mo_2^{4+}}$ groups and the D_{4h} symmetry slightly degraded to S_4, form the basis for informative spectroscopic studies to be reported later.

A noteworthy feature of the crystal packing has to do with the nearest neighbors of the $\mathrm{Mo_2^{4+}}$ ions along the molecular axis (equivalent here to the crystallographic *c* axis). In each of the previously determined $\mathrm{Mo_2(O_2CR)_4}$ structures, as well as in the $\mathrm{Mo_2(SO_4)_4^{4-}}$ case, there has been a donor atom lying about 2.6 Å from each molybdenum atom, approximately on the extension of the Mo–Mo axis. In the present case there is no such atom; instead, two oxygen atoms from the sulfate group at 0, 0, $^1/_2$ each lie 2.93 Å from each molybdenum atom. A view of this unusual relationship is shown in Figure 3.

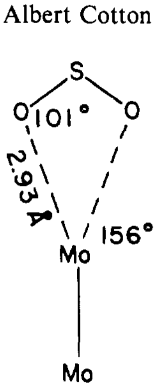

Figure 3. Relationship of the sulfate ions to the molybdenum atoms, showing the weak, bifurcate mode of interaction.

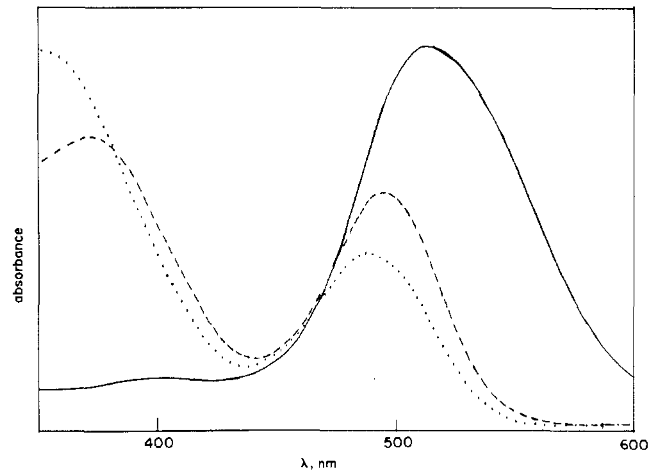

Figure 4. Spectra of 3 m*M* $\mathrm{K_4Mo_2Cl_8}$ in 2 *M* HCl as a function of added glycine: solid line, no glycine; dashed line, 15 m*M* total glycine; dotted line, 45 m*M* total glycine.

Chemical Aspects. It is perhaps not surprising that glycine reacts with the $\mathrm{Mo_2Cl_8^{4-}}$ ion, but the ease with which that reaction occurs is notable and suggests that the $\mathrm{Mo_2(O_2CCR)_4}$ type of unit is a particularly stable one. Although most of our syntheses were carried out in glycine–HCl buffers with pH ~3, the same product is obtained from glycine solutions at pH 6 or from solutions containing ca. 4 *M* excess HCl. While the formation of a solid phase may provide some driving force for the reaction, ligand replacement also occurs readily under conditions where a solid phase does not form. Figure 4 shows the spectra of 3 m*M* $\mathrm{K_4Mo_2Cl_8}$ in 2 *M* HCl containing 0, 15, and 45 m*M* total glycine. The most prominent feature in the spectrum[11] of the (partially aquated) $\mathrm{Mo_2Cl_8^{4-}}$ ion in 2 *M* HCl is the maximum of ~520 nm, ε ~750 M^{-1} cm^{-1}. The addition of small amounts of glycine causes the maximum to shift to shorter wavelength and to decrease in intensity, while the absorbance in the near-uv region increases; the spectral changes are accompanied by a color change from red to orange. The spectra of the glycine-containing solutions do not correspond to the tetrakis(glycine) complex ($\lambda_{\max}$ 446 nm, ε ~100 M^{-1} cm^{-1}) or to mixtures of the octachloro and tetrakis(glycine) complexes but to intermediate mixed complexes such as $\mathrm{Mo_2Cl_6(gly)^{2-}}$. The fact that 45 m*M* glycine competes effectively for coordination sites on the binuclear core with chloride ion in 2 *M* HCl, as in reaction 1, suggests that the

$$\mathrm{Mo_2Cl_8^{4-} + HO_2CCH_2NH_3^+ \rightleftharpoons Mo_2Cl_6(O_2CCH_2NH_3)^{2-} + 2Cl^- + H^+} \qquad (1)$$

carboxyl group has a powerful affinity for the $\mathrm{Mo_2^{4+}}$ core. Qualitatively similar results have been observed in the reaction between the $Mo_2(SO_4)_4{}^{4-}$ ion and glycine in 2 *M* H_2SO_4. This result suggests that the driving force for reaction 1 is not due solely to the chelating nature of the carboxyl group but that electronic factors may also be involved.

The substance first precipitated from the solutions of glycine and $Mo_2Cl_8{}^{4-}$ in hydrochloric acid has a composition approximating to $Mo_2(O_2CCH_2NH_3)_4Cl_4\cdot xH_2O$ where x is approximately 2. However, the analyses, for several different preparations, never agreed precisely with any such formula and, in addition, the tetrachloride could never be obtained in crystalline (i.e., macrocrystalline as opposed to powder) form. It was for these reasons the conversion of the chloride to the sulfate was undertaken.

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Registry No. $Mo_2(gly)_4(SO_4)_2\cdot 4H_2O$, 57214-97-8; $Mo_2(gly)_4Cl_4$, 57214-98-9; $Mo_2(O_2CH)_4$, 51329-49-8; $K_4Mo_2Cl_8$, 25448-39-9; glycylglycine, 556-50-3; Mo, 7439-98-7.

Supplementary Material Available: A listing of structure factor amplitudes (Table II), thermal parameters (Table IV), and root-mean-square amplitudes of vibration (Table V) (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) F. A. Cotton, *Rev. Chem. Soc.*, **4**, 27 (1975).
(2) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **9**, 351 (1970).
(3) Calculations were performed on an IBM 360 computer using the following programs: DATARED by Frenz for data reduction, FOURIER by Robinson and Dellaca, based on Zalkin's FORDAP, for Fourier calculations; NUCLS, a full-matrix least-squares program by Ibers and Doedens, based on Busing and Levy's ORFLS; a modified version of SADIAN by Baur for calculating distances and angles; PERFACT by Frenz for analyzing structure factors and weighting schemes; ORFFE, a function and error program by Busing, Martin, and Levy as modified by Brown, Johnson, and Thiessen; ORTEP by Johnson for illustrations; and LIST by Snyder for listing the data.
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Preparation, Properties, and Crystal and Molecular Structure of Diaquosulfato(*N,N,N',N'*-tetramethylethylenediamine)copper(II) Hydrate

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The compound diaquosulfato(*N,N,N',N'*-tetramethylethylenediamine)copper(II) hydrate, $[Cu(tmen)SO_4(OH_2)_2]\cdot H_2O$, has been prepared and its structure determined crystallographically. This substance crystallizes in space group *Pbca* with eight molecules per unit cell of dimensions $a = 12.543$ (1), $b = 15.782$ (1), and $c = 13.862$ (1) Å. The observed and calculated densities are 1.59 (2) and 1.597 g/cm^3, respectively. From a total of 2189 independent reflections measured with Ni-filtered copper x radiation, 1869 statistically significant reflections ($|F_o| > 3\sigma(F_o)$) were used to determine the structure and resulted in final values of $R = 0.067$ and $R_w = 0.061$ (154 parameters were least-squares refined). Hydrogen atoms were located but not refined. The molecular structure consists of monomeric $[Cu(tmen)SO_4(OH_2)_2]$ units in which the coordination polyhedron about copper is a tetragonal pyramid. The Cu–OH_2 apical bond length of 2.205 (5) Å is 10% longer than the four remaining bonds to water, 1.974 (5) Å, monodentate sulfate oxygen, 1.986 (5) Å, and chelated diamine nitrogens, 2.024 (5) and 2.025 (5) Å. Copper is situated 0.25 Å above the basal plane, and chelate ring conformation is gauche. All water molecules participate in an extensive hydrogen-bonding network to noncoordinated sulfate oxygens with an average O–O separation of 2.68 Å. The room-temperature magnetic moment is 1.87 BM.

Introduction

Reported complexes of copper(II) and the highly substituted ligand *N,N,N',N'*-tetramethylethylenediamine (tmen) may be grouped in two classes depending on formula type: (A) $Cu(tmen)X_2$, $X^- = Cl^-$,[2] Br^-,[3] SCN^-, picrate;[4] (B) $Cu(tmen)(OH)X$, $X^- = ClO_4{}^-$,[3] $NO_3{}^-$,[4] Cl^-,[5] Br^-.[6] Many of these are known or assumed to be dimeric-bridged structures with room-temperature magnetic moments less than that expected for the spin-only case. For example, $[Cu(tmen)OH]_2(ClO_4)_2$ has a four-coordinate hydroxy-bridged structure with noncoordinated perchlorate anions ($\mu_{eff} = 1.20$ BM),[7] and $[Cu(tmen)Cl_2]_2$ has a five-coordinate chloride-bridged structure.[2] The fact that only monovalent anions are present in the above complexes prompted us to attempt preparations incorporating divalent sulfate anion. We were particularly interested in comparing the sulfate and perchlorate copper(II) complexes of tmen because both anions are of similar size, geometry, and coordinating ability. The preparation and isolation of the reaction product between copper sulfate and tmen and its molecular structure and properties are reported here.

Experimental Section

Preparation of Complex. A 5.8-ml (0.04-mol) amount of ligand in 20 ml of methanol was mixed with 20 ml of an aqueous solution containing 4.98 g (0.02 mol) of copper sulfate. Repeated partial evaporation at the boiling temperature and subsequent addition of methanol to maintain volume decreased the aqueous content of the reaction mixture. Further slow evaporation at room temperature afforded a light blue powder which contained many larger hard and irregularly shaped crystal fragments. The solid was separated by filtration, washed with ether, and air-dried (yield 5.8 g, 88% based on copper). Elemental analyses, ir and electronic spectra, and room-temperature magnetic susceptibility measurements were made on finely ground samples of the isolated bulk solid using methods previously described.[8] The spectral and magnetic information is included in the Discussion. Anal. Calcd for $CuC_6H_{22}N_2O_7S$: Cu, 19.26; C, 21.85; H, 6.72. Found: Cu, 19.3; C, 21.6; H, 6.65.

Unit Cell and Space Group. A crystal fragment, trimmed to an effective size of 0.3 × 0.2 × 0.2 mm, was temporarily mounted on a glass fiber with a thin film of grease and orientated by precession techniques. After location of a reciprocal lattice plane with twofold symmetry, the crystal was remounted with epoxy glue along one of the major reciprocal axes. Further precession (complete set of zero and first levels) and Weissenberg photos (levels 0–7) indicated the