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# The Crystal and Molecular Structure of Tris(ethylenediamine)nickel(II) Sulfate, Ni(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>SO<sub>4</sub>

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Tris(ethylenediamine)nickel(II) sulfate, Ni(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>SO<sub>4</sub>, crystallizes in the trigonal space group  $P\overline{3}1c$  with unit cell dimensions a = b = 8.946 (5) Å and c = 9.634 (5) Å. The unit cell contains two formula units. Intensities of 350 reflections were measured on a GE XRD-5 diffractometer; 294 of these reflections were observed. The structure was solved using Patterson and Fourier methods and positions of all atoms including hydrogens were refined by full-matrix least squares to a conventional *R* factor of 4.2%. The sulfate groups are located at positions of point symmetry 32 and are sixfold disordered in an unusual way. Hydrogen bonding between the amine hydrogens of the ethylenediamine and the sulfate group is extensive and has the unusual feature that in one case all three of the "axial" hydrogens are involved in bonding to an adjacent sulfate group.

# Introduction

A detailed X-ray investigation of the structure of tris(ethylenediamine)nickel(II) sulfate (Ni(en)<sub>3</sub>SO<sub>4</sub>) has been carried out in this laboratory. This structure was originally undertaken because it presented some interesting crystallographic features. The refined structure, however, is somewhat different from similar structures previously reported,<sup>1-6</sup> and two features are of particular interest to inorganic chemists. The sulfate ions are disordered in a previously unknown way, and the apparent hydrogen bonding departs significantly from some of the rules for such bonding recently proposed for  $\partial \partial \partial$  isomers of M(en)<sub>3</sub> species by Raymond, Corfield, and Ibers.<sup>7</sup>

### **Experimental Section**

Data were collected on General Electric XRD-5 diffractometer equipped with a scintillation counter as a detector, using a  $\theta$ -2 $\theta$  scan technique. Scans of 100 sec were taken across each peak; background was counted for 50 sec on each side of the peak. The scan rate was 2.0°/min and the takeoff angle was 4°.

Cell parameters were determined by least-squares refinement of 18 selected  $2\theta$  values. Results were a = b = 8.946 (5) Å and c = 9.634 (5) Å.<sup>8</sup> Laue symmetry was 3m and the space group was determined to be either  $P\overline{3}1c$  or P31c from the systematic extinction of reflections *hkl* with *l* odd. Successful refinement in  $P\overline{3}1c$  indicates that the centric space group is the correct one. The calculated density was  $1.664 \text{ g/cm}^3$  for Z = 2; the measured density determined by flotation in a mixture of bromoform and carbon tetrachloride was  $1.669 \text{ g/cm}^3$ .

The crystal used for the collection of intensity data was approximately cylindrical, 0.2 mm in diameter and 1.0 mm in length. The radiation used was Cu K $\alpha$  ( $\lambda$  1.5418 Å), and the linear absorption coefficient for the crystal was calculated to be 36.46 cm<sup>-1</sup>. Of a total of approximately 560 unique reflections

available in the copper sphere, 350 (out to a limit of  $\theta = 60^{\circ}$ ) were scanned; 294 of these were observed. Lorentz and polarization corrections were applied in the usual way, and absorption corrections were calculated. Corrections for anomalous scattering were made for the sulfur and nickel atoms only. All data were collected at 25°.

Determination of the structure and least-squares refinement proceeded normally except that the disorder of the sulfate group presented some difficulty.<sup>9</sup> Scattering factors for all atoms except hydrogen were taken from Cromer and Waber;<sup>30</sup> hydrogen scattering factors were those of Stewart, Davidson, and Simpson.<sup>11</sup> Least-squares refinement of all atoms except hydrogens using a block-diagonal approximation converged at  $R_1 = 0.089^{12}$ with all reflections equally weighted. A difference Fourier map at this stage showed a number of peaks corresponding to possible hydrogen positions but also showed many shallow holes not so easily assignable.

Instead of trying to determine hydrogen positions from this rather noisy Fourier map, the hydrogen positions determined by Cullen and Lingafelter<sup>13</sup> for the isomorphic compound tris-(ethylenediamine)copper(II) sulfate were used successfully as trial positions in a final full-matrix refinement of the structure. All reflections were weighted as described by Stout and Jensen.<sup>14</sup> Positions and isotropic temperature factors were refined for the hydrogen atoms and the disordered oxygen atoms; for all other atoms positions and anisotropic temperature factors were refined. This refinement converged at  $R_1 = 0.042$  and  $R_2 = 0.043$ . A difference Fourier map at this point showed no peaks higher than  $0.3 e^{-/\text{Å}^3}$  above background.

### **Results and Discussion**

The final atomic parameters are given in Table I. Table II gives a selection of distances and angles. Table III gives the observed and calculated structure factors from the final least-squares cycle. Figure 1

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<sup>(5)</sup> L. N. Swink and M. Atoji, Acta Crystallogr., 13, 639 (1960).

<sup>(6)</sup> N. di M. Cola, G. Guiseppetti, and F. Mazzi, Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Natur., 96, 1 (1961-62).

<sup>(7)</sup> K. N. Raymond, P. W. Corfield, and J. A. Ibers, Inorg. Chem., 7, 842 (1968).

<sup>(8)</sup> Throughout this paper estimated standard deviations (esd) of the last digit of a number will be given in parentheses immediately after the number.

<sup>(9)</sup> Most programs used were from the Montana State University Library for Crystallographic Computing for the IBM 1620, written by C. T. Li, G. W. Svetich, C. N. Caughlan, R. D. Witters, K. D. Watenpaugh, and D. D. Swank. Some intermediate refinements were carried out at the University of Washington using programs available there. The final fullmatrix least-squares refinement was carried out on the Montana State University Sigma 7 computer using a modified version of Busing and Levy's UCLLS-R.

<sup>(10)</sup> D. T. Cromer and J. T. Waber, Acta Crystallogr., 18, 104 (1965).

<sup>(11)</sup> R. F. Stewart, E. R. Davidson, and W. T. Simpson, J. Chem. Phys., 42, 3175 (1965).

<sup>(12)</sup>  $R_1 = \Sigma ||F_0| - |F_0||/\Sigma |F_0|$ ; the parameter minimized was  $R_2 = \Sigma w ||F_0| - |F_0||^2 / \Sigma w F_0^2$ .

<sup>(13)</sup> D. L. Cullen and E. C. Lingafelter, Inorg. Chem., 9, 1858 (1970).

<sup>(14)</sup> G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, p 457. An instrument stability of 0.02 was used.

				,	Table I				
			FINAL POSIT	ional and The	REMAL PARAMET	ERS FOR Ni(e	n <sub>3</sub> )SO <sub>4</sub>		
Atom	X	Y	Ζ	B or $\beta_{11}^{a}$	<b>\$</b> 22	<b>\$</b> 88	$\beta_{12}$	$\beta_{13}$	<b>B23</b>
Ni	2/3	1/8	1/4	$0.0068 (4)^{b}$	0,0068 (4)	0.0019(2)	0.0034(4)	0	0
s	1/3	2/8	1/4	0.0081(5)	0.0081(5)	0,0035 (4)	0.0041(5)	0	0
Ν	0.4598 (6)	0.1459 (7)	0.1281 (5)	0.0119 (10)	0,0110 (10)	0.0046(5)	0.0054(8)	-0.0004(6)	-0.0018 (6)
С	0.3001 (7)	0.1437 (8)	0.1701 (5)	0.0085 (10)	0.0147 (13)	0.0075 (7)	0.0048 (10)	-0.0019(7)	-0.0007 (8)
O(1)	0.227(5)	0.503 (5)	0.166 (4)	2.9 (6)			. ,		
O(2)	0.502 (4)	0,696 (7)	0.310 (3)	3.2 (5)					
O(3)	0.446 (9)	0.820 (5)	0,150 (5)	6,2 (9)					
O(4)	0.219(4)	0.651(8)	0,358 (3)	3.9 (6)					
H(1)	0.190 (7)	0.043 (7)	0,110 (5)	4,6 (14)					
H(2)	0.300 (6)	0.251(6)	0.111(5)	2,7(12)			*		
H(3)	0,455 (7)	0.055 (6)	0.117 (6)	3.1 (16)					
H(4)	0.471(8)	0.171(8)	0.042 (6)	5.6 (17)					

<sup>a</sup> The form of the anisotropic ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . <sup>b</sup> Figures in parentheses are standard deviations computed from the inverse matrix; no deviations are given for symmetry-determined parameters.

Table	II

SELECTED DISTANCES (Å) AND ANGLES (DEG)

I.	Bond Distances—Cation			Distances between H-Bonded Atoms			
	Ni–N 2.124 (6)Å			Α.	Axial H Be	onds	
	N-C 1.476 (9)						
	C-C 1.544 (9)				N-O(1)	2.92(4)	
					N-O(2)	3.16(4)	
II.	Bond Distances—Ani	on			$N'-O(2)^a$	3.30 (5)	
					N-O(3)	2.86(5)	
	S-O(1) 1.52 (4)				N-O(4)	2.90 (5)	
	S-O(2) 1.51 (5)						
	S-O(3) 1.56 (5)			в.	Equatorial	H Bonds	
	S-O(4) 1.49 (4)						
					N-O(1)	3.02(4)	
III.	N-Ni-N Bond Angles	5			N-O(2)	3.09(3)	
					N-O(3)	2.78(5)	
	Within chelate ring	82.1 (2)			N-O(4)	2.96 (4)	
	About threefold axis	92.4(2)			$N'-O(4)^{a}$	2.92(4)	
	Across twofold axis	93.7 (2)					

<sup>a</sup> In these cases two symmetry-related nitrogen positions form H bonds to the same sulfate oxygen.

# TABLE III Observed and Calculated Structure Factors

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K 4   Im. <th>In , 7 6111128 4 7 8 6 3 7 4 0 6 1 3392 6 44 3 9 1 5 20 1 7 8 9 8 7 1 1 1 1 2 8 6 5 8 4 8 6 5 8 7 8 6 7 8 7 8 5 7 8 7 8 5 7 8 7 8 5 7 8 7 8 5 7 8 7 8</th> <th>h</th> <th>1 2 7 9 7 1<th>. 127-140140 1157544378744233874521858574166116412768878899101162512 115516422249069475929443387595944297574966649216611641276889899101162512 1155164222490159941372894123387595952741665116412768892899101162512 11571749661243890412338759594419117754489114254899101162512 115717496612438904123387591161279 11571749661243890412338754116511641243899101162512 11571749661243890412338754116511641243899101162512 1157174966124389041162512 11571749661243890412338754116511641243899101162512 115717497661243891041162512 115717497661244489116412438875411651164124389101162512 11571749766124489116412438875411651164124389101162512 115717497661244891164124389101162512 11571749766124489116412438875411651164124389101162512 11571749766124489116412438875411651164124389101162512 11571749766124489101162512 11571749766124489101162512 11571749766124489101162512 11571749766124489101162512 11571749766124489101162512 11571749766124489101162512 115717497661244889101162512 115717497661244889101162512 115717497661244889101162512 115717497661244889101162512 115717497661244889101162512 115717497661244889101162512 115717497661244889101162512 115717497661244889101162512 115717497661244889101162512 115717497661244889101162512 115717488889101162512 115717488889101162512 1157174888889101162512 1157174888889101162512 1157174888889101162512 1157174888889101162512 1157174888889101162512 1157174888889101162512 1157174888889101162512 1157174888889101162512 115718888889101162512 1157188888891001162512 1157188888891000000000000000000000000000000</th><th><math display="block"> \begin{array}{c} h &amp; 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shows a projection of the structure down the c axis without showing sulfate disorder. Only one group is shown on each threefold axis, but the cations and anions are stacked alternately along each threefold axis.

The sulfur atom lies on position c in  $P\overline{3}1c$  (space group no. 163) and hence has point symmetry 32. One of the twofold axes of the tetrahedral sulfate group is approximately collinear with the crystallographic threefold axis. Since the asymmetric unit contains one complete sulfate group, the symmetry of the sulfate position generates a total of 24 disordered oxygen positions, each with an occupancy factor of 1/6. Refinement of oxygen atoms in this case is thus not very different from refining hydrogen atom positions, since each disordered oxygen contributes  $1 \frac{1}{3}$  electrons to the total scattering. These disordered oxygen posiarranged in two rings of 12 each encircling the threefold axis above and below the sulfur atom.

The possibility that the sulfate ion is randomly disordered about the threefold axis so that the rings are simply toroids of electron density has been considered. However, refinement of the four unique positions for oxygen gives convergence with the sulfate ion tilted at an angle of  $5.5^{\circ}$  to the threefold axis of the crystal. If the sulfate group were randomly disordered, one would expect the twofold axis of the tetrahedron to coincide with the crystallographic threefold axis. One would TRIS(ETHYLENEDIAMINE)NICKEL(II) SULFATE



Figure 1.---[001] projection showing one asymmetric unit of the structure of Ni(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>SO<sub>4</sub>.



Figure 2.—Hydrogen-bonding scheme shown in the [001] projection of the structure of Ni(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>SO<sub>4</sub>.

also expect larger than normal temperature factors for the oxygens when discrete positions are refined as has been done in this case, and the temperature factors for oxygen are normal in this structure. The possibility that the threefold axis of the sulfate tetrahedron coincided with the crystallographic threefold axis was also considered. This orientation would require that one oxygen atom lie on the threefold axis, and at any reasonable distance from the sulfur atom it would be much too close to the axial hydrogens of the adjacent complex cation. Oxygen-hydrogen distances of about 1 Å would be required to achieve this orientation.

The ring conformation is  $\partial \partial \partial$  in the Ni(en)<sub>3</sub><sup>2+</sup> ion and both  $\Lambda$  and  $\Delta$  enantiomers must be present in the centric cell. The hydrogen bonding is extensive and differs in one respect from that previously proposed for the  $\partial \partial \partial$  conformation.<sup>7</sup> For any one of the disordered sulfate orientations five of the six axial as well as five of the six equatorial amine hydrogens are at hydrogenbonded distances from sulfate oxygens. A drawing of the unit cell with just one sulfate orientation and all the associated hydrogen bonds is shown in Figure 2. Raymond, Corfield, and Ibers<sup>7</sup> have suggested that no more than one of the axial hydrogens at either end of the cation can form a hydrogen bond in the  $\partial \partial \partial$  conformation. This is certainly true when the two H-bond acceptors are constrained by van der Waals forces to be no closer than 3 Å or so, but in this case the two acceptors are sulfate oxygens and are only 2.5 Å apart. By orienting the sulfate group as it occurs in this structure it is possible to form H bonds to three axial hydrogens in one neighboring cation and two axial hydrogens in the other. The disorder of the sulfate group will vary the orientation of the H-bond pattern, but the basic pattern will be the same for any of the disordered positions of the anion.

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# Crystal and Molecular Structure of Diacetylferrocene

### By GUS J. PALENIK

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Diacetylferrocene crystallizes as orange needles in the monoclinic space group  $P2_1/c$  with  $a = 5.898 \pm 0.002$  Å,  $b = 13.036 \pm 0.005$  Å,  $c = 14.962 \pm 0.006$  Å, and  $\beta = 90.68 \pm 0.04^\circ$ . There are four molecules per unit cell;  $d_c = 1.559 \pm 0.002$  g/cm<sup>3</sup> and  $d_m = 1.54 \pm 0.01$  g/cm<sup>3</sup>. The structure was refined by full-matrix least-squares methods with anisotropic thermal parameters to a final R of 6.7% for the 2570 observed reflections measured using an automatic diffractometer with molyb-denum radiation. The cyclopentadienide rings are planar and parallel with an average C-C distance 1.426  $\pm 0.014$  Å. The acetyl groups are in the 1,3' configuration with an average rotation of 4° 4' of the rings from the eclipsed configuration.

### Introduction

The dependence of the configuration of ferrocene derivatives on the nature of substituents on the cyclopentadienide (Cp) rings is obscure. Although the relationship between the angle of rotation of the Cp rings about their centers and intermolecular forces has been discussed, 1-3 no definitive conclusions were reached. In fact, although only van der Waals interactions exist between molecules in ferrocenedicarboxylic acid, the Cp rings are almost completely eclipsed.<sup>4</sup> However, the eclipsed configuration may be rationalized in terms of the dimerlike molecules formed by hydrogen bonding between carboxylic acid groups from two molecules. Therefore, an investigation of diacetylferrocene was undertaken since hydrogen bonding between molecules is not possible for this compound. The results provide information regarding the preferred configuration of substituted ferrocenes and the relationship between the rotation of the Cp rings and intermolecular forces.

## **Experimental Section**

Diacetylferrocene was purchased from Alfa Inorganics. The crystals are orange needles elongated along  $\tilde{a}$ . Preliminary Weissenberg photographs taken about  $\tilde{a}$  revealed that the crystals were monoclinic. The systematic absences of h0l for l = 2n + 1 and 0k0 for k = 2n + 1 indicated that the space group was  $P2_1/c$  ( $C_{2h}$ <sup>6</sup>).

One well-developed needle was cleaved with a razor blade to give a crystal (0.176  $\times$  0.110  $\times$  0.065 mm parallel to  $\tilde{a}$ ,  $\tilde{b}$ , and  $\tilde{c}$ , respectively) which was mounted on a glass fiber. The fiber and crystal were dipped into liquid nitrogen and then mounted on a General Electric single-crystal orienter. The  $\tilde{b}$  axis was parallel to the  $\phi$  axis of the orienter. The unit cell dimensions were determined using a narrow beam of molybdenum radiation ( $\lambda(\alpha_1)$  0.70926 and  $\lambda(\alpha_2)$  0.71354 Å). The average of these measurements were  $a = 5.898 \pm 0.002$  Å,  $b = 13.036 \pm 0.005$  Å,  $c = 14.962 \pm 0.006$  Å, and  $\beta = 90.68 \pm 0.04^\circ$ . The density calculated for four molecules per unit cell is  $1.559 \pm 0.002$  g/cm<sup>3</sup>; the density determined by flotation is  $1.54 \pm 0.01$  g/cm<sup>3</sup>.

The intensity measurements were made with a scintillation counter using a wide beam of molybdenum radiation (takeoff angle of  $3.7^{\circ}$ ). A linear amplifier-pulse height selector combination together with a zirconium filter at the counter window

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