

## The Crystal and Molecular Structure of Tris(ethylenediamine)nickel(II) Sulfate, $\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3\text{SO}_4$

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Tris(ethylenediamine)nickel(II) sulfate,  $\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3\text{SO}_4$ , crystallizes in the trigonal space group  $P\bar{3}1c$  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 ( $\text{Ni}(\text{en})_3\text{SO}_4$ ) 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  $\theta\theta\theta$  isomers of  $\text{M}(\text{en})_3$  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  $\bar{3}m$  and the space group was determined to be either  $P\bar{3}1c$  or  $P31c$  from the systematic extinction of reflections  $hkl$  with  $l$  odd. Successful refinement in  $P\bar{3}1c$  indicates that the centric space group is the correct one. The calculated density was 1.664 g/cm<sup>3</sup> for  $Z = 2$ ; the measured density determined by flotation in a mixture of bromoform and carbon tetrachloride was 1.669 g/cm<sup>3</sup>.

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>10</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  $R_1 = 0.089$ <sup>12</sup> 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 isomorphous 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<sup>-</sup>/Å<sup>3</sup> 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

(9) 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 full-matrix least-squares refinement was carried out on the Montana State University Sigma 7 computer using a modified version of Busing and Levy's *uculs-r*.

(10) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

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(12)  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ; the parameter minimized was  $R_2 = \sum w ||F_o| - |F_c||^2 / \sum w F_o^2$ .

(13) D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, **9**, 1858 (1970).

(14) 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.

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



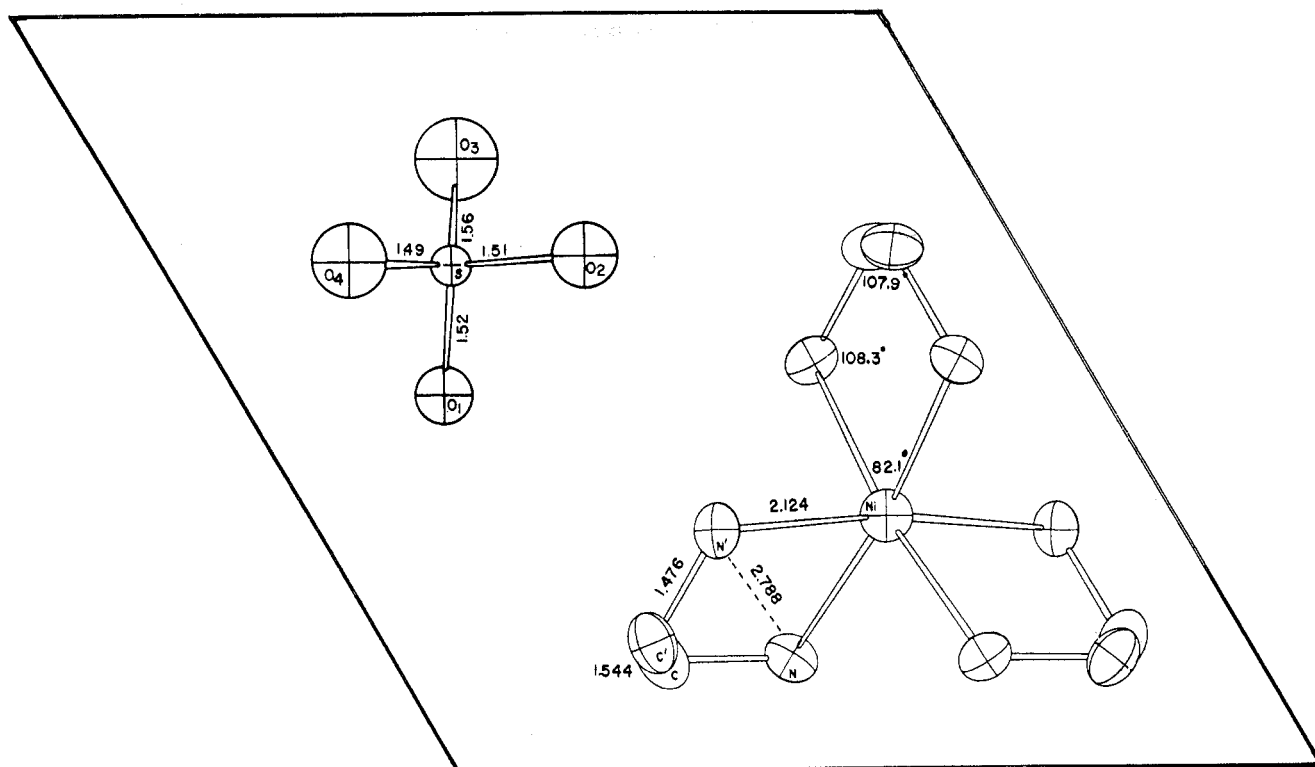


Figure 1.—[001] projection showing one asymmetric unit of the structure of  $\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3\text{SO}_4$ .

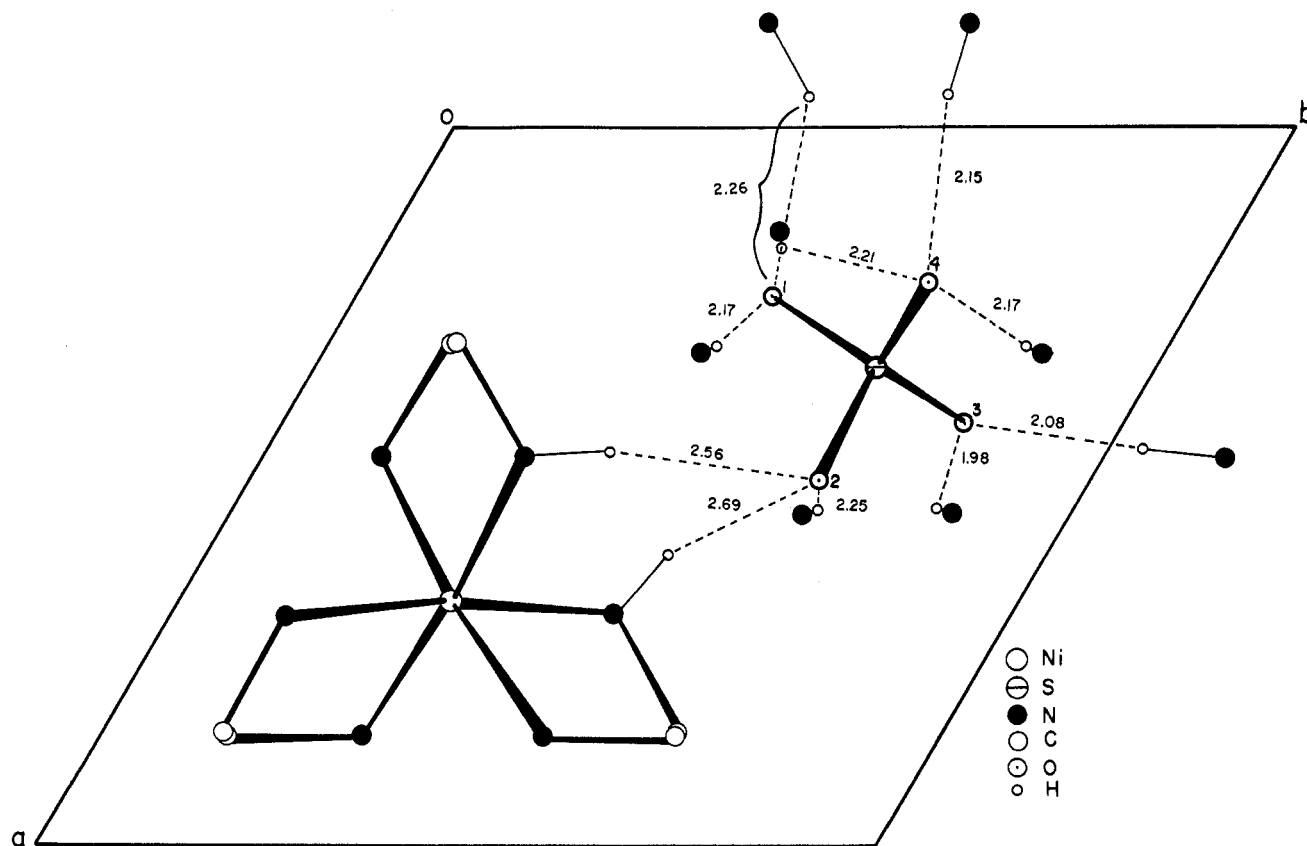


Figure 2.—Hydrogen-bonding scheme shown in the [001] projection of the structure of  $\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3\text{SO}_4$ .

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  $\theta\theta\theta$  in the  $\text{Ni}(\text{en})_3^{2+}$  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  $\theta\theta\theta$  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 hydrogen-bonded 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  $\theta\theta\theta$  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

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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 molybdenum 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  $4^\circ 4'$  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,<sup>1-3</sup> 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 relation-

ship 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  $\bar{a}$ . Preliminary Weissenberg photographs taken about  $\bar{a}$  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  $P2_1/c$  ( $C_{2h}^5$ ).

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  $\bar{a}$ ,  $\bar{b}$ , and  $\bar{c}$ , 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  $\bar{b}$  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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