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The Crystal and Molecular Structure of Hexakis(thiourea)nickel(II) Bromide

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The crystal structure of hexakis(thiourea)nickel(II) bromide, $Ni[SC(NH_2)_2]_6Br_2$, has been determined by three-dimensional X-ray diffraction techniques from 1219 reflections measured at ambient temperature with an automatic diffractometer. The compound crystallizes in the monoclinic space group I2/c with $a = 16.703 \pm 0.005$ Å, $b = 8.979 \pm 0.002$ Å, $c = 16.909 \pm 0.002$ Å, $\beta = 92.8 \pm 0.1°$, $D_m = 1.80$ g/cm^3, and $D_c = 1.78$ g/cm^3 for four molecules per unit cell. The structure, including hydrogen atoms, was refined by least-squares methods to a conventional R of 0.053. The structure consists of $Ni[SC(NH_2)_2]_6^{2+}$ molecular ions and Br^- ions. The nickel atom is located on a center of symmetry and is coordinated to six sulfur atoms in a distorted octahedral (D_{3d}, trigonal antiprism, if the NH_2 groups are disregarded) local environment. The orientation of the thiourea groups relative to the nickel atom is such that each sulfur atom uses an sp^2 orbital to form the metal–sulfur bond. The three independent Ni–S distances are 2.503, 2.517, and 2.498 Å (all ±0.006 Å) and the Ni–Br distance is 6.190 ± 0.004 Å. The three independent S–C distances are 1.752, 1.737, and 1.697 (all ±0.013 Å), not significantly different from the 1.720 ± 0.009 Å found in free thiourea. The C–N distances are likewise not significantly different from the 1.340 (6) Å of free thiourea. The thiourea groups are all planar well within experimental error.

Introduction

In recent years considerable interest has been generated in the nature of the metal–sulfur bond in transition metal complexes. A part of this interest has been in the spectroscopic,[2–4] magnetic,[4–7] and structural[8–13] properties of transition metal–thiourea [hereafter, tu = thiourea = $SC(NH_2)_2$] complexes. This laboratory has been active in the determination of crystal structures of three general classifications of thiourea complexes: $M(tu)_2X$, where M = Cu(I), Ag(I) and X = Cl, NO_3; $M(tu)_4X_2$, where M = Mn(II), Fe(II), Co(II), Cd(II), Ni(II) and X = Cl, Br and where M = Pt(II), Pd(II) and X = Cl; $M(tu)_6X_2$, where M = Ni and X = Br, I, NO_3.

In the first grouping are the chain structures of $Ag(tu)_2Cl$[14,15] and $Cu(tu)_2Cl$[16] which show three-center electron-deficient bridge bonds as well as essentially trigonal-planar metal ions. Another structure that more or less fits into this grouping is the structure of $Cu_4(tu)_9(NO_3)_2$[17] which is a metal cluster compound also containing three-center electron-deficient bridge bonds. In the second grouping are the isomorphous *trans*-octahedral structures of Mn(II), Fe(II), Cd(II), and Co(II)[18] that may be contrasted to the square-pyramidal geometry of $Ni(tu)_4Cl_2$.[8] The Pd(II)[19] and Pt(II)[20] complexes of this grouping are essentially "square-planar" ionic structures. As a continuation of our study of the transition metal–thiourea complexes, we have determined the crystal and molecular structure of hexakis(thiourea)nickel(II) bromide, $Ni[SC(NH_2)_2]_6Br_2$, the first member of the $M(tu)_6X_2$ series to be studied by single-crystal X-ray diffraction techniques.

Experimental Section

Crystals of hexakis(thiourea)nickel(II) bromide, $Ni[SC(NH_2)_2]_6Br_2$, suitable for X-ray analysis were prepared by Dr. Chatterjee of this laboratory.[21] The single crystal chosen for data collection measured 0.62 mm (length) × 0.16 mm × 0.14 mm and was mounted about the needle axis. Preliminary Weissenberg and precession photographs (0*kl*, *h*0*l*, *hk*0, . . ., *hk*4) indicated a monoclinic system with systematic extinctions of *hkl* reflections for $h + k + l = 2n + 1$ and of *h*0*l* reflections for $l = 2n + 1$. These extinctions indicate the space group I2/c or Ic and solution of the structure confirmed I2/c (*vide infra*). Although this space group is an unconventional, body-centered choice of the space group C2/c,[22] it was retained because of the approximate orthogonality of the unit cell in I2/c.

The lattice constants were determined by least-squares refinement of the setting angles of 54 reflections that had been carefully centered on a Picker full-circle automatic diffractometer. The crystal was aligned on this apparatus by variations of well-known methods.[23] Using Mo Kα radiation (λ 0.71068 Å) the lattice constants at room temperature were found to be $a = 16.703 \pm 0.005$ Å, $b = 8.979 \pm 0.002$ Å, $c = 16.909 \pm$

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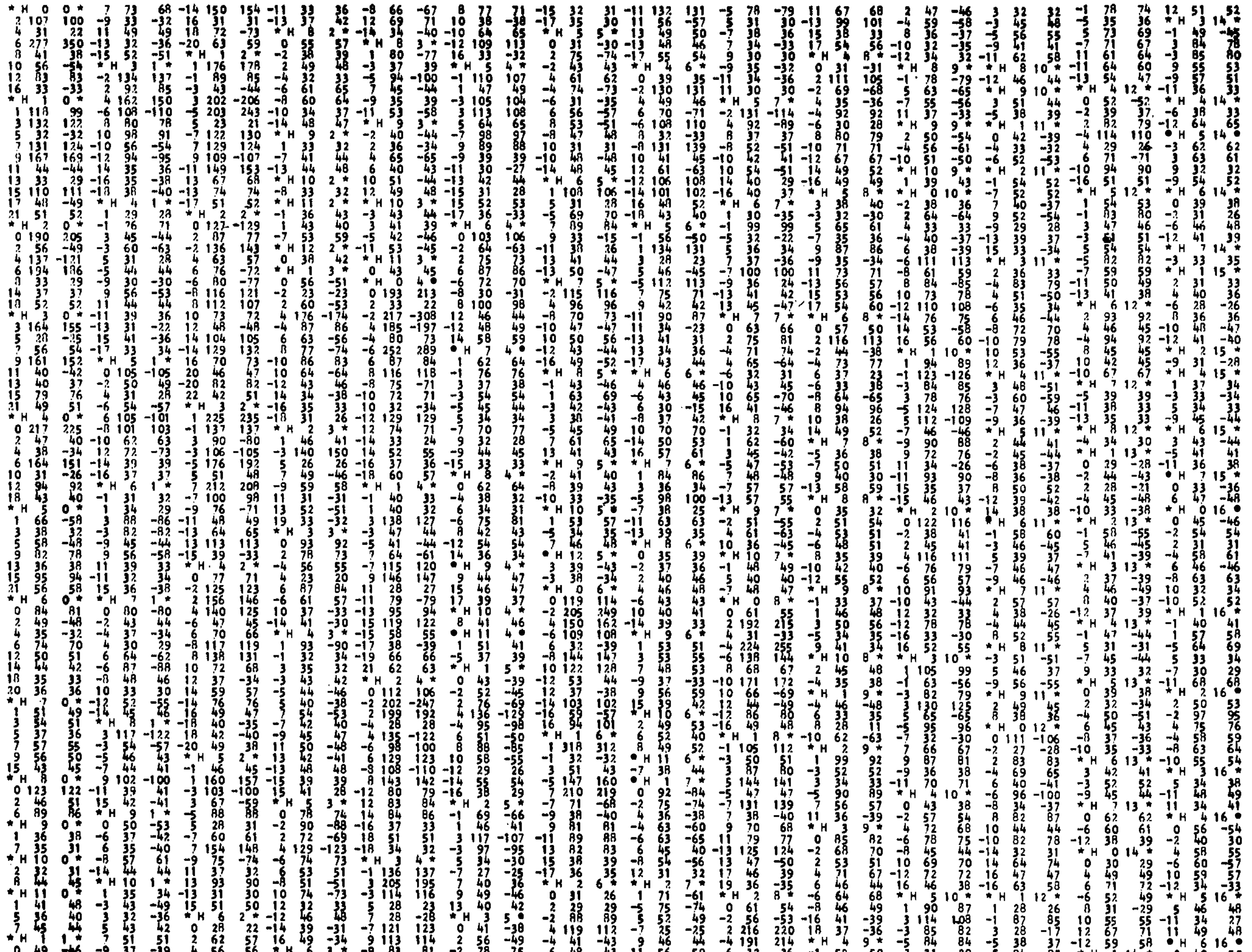
TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]



[a] The respective columns are h, then $(10)F_o$, followed by F_c. F_c(absolute) = $F_c/(20 \times \text{scale factor})$; scale factor = 0.1398 ± 0.0005.

0.002 Å, and $\beta = 92.8 \pm 0.1°$. The experimental density of 1.80 ± 0.02 g/cm^3, measured by flotation in a bromoform–benzene mixture, agrees well with the calculated density of 1.78 g/cm^3 based on four molecules per unit cell.

The intensities of 3900 independent *hkl* reflections were recorded by the θ–2θ scan technique using Zr-filtered Mo Kα radiation at room temperature. All independent reflections to $2\theta = 60°$ were measured. The peaks were scanned for 90 sec and backgrounds were estimated by stationary counting for 40 sec at $2\theta \pm 0.75°$ from the peak maximum. Integrated intensities were calculated assuming a linear variation in background from the function $I_{\text{net}} = I_{\text{scan}} - 1.125(B_1 + B_2)$, where B_1 and B_2 are the background counts. Reflections were considered to be absent if the integrated intensity was less than $3\sqrt{1.125(B_1 + B_2)}$. Of the 3900 measured reflections 1219 were considered nonzero by this criteria. A standard reflection was measured after every ten reflections to ensure stability of the operation. Total variation in the standard peak was less than 2σ $\{\sigma(I_{\text{net}}) = [I_{\text{net}} + 1.125(B_1 + B_2)]^{1/2}\}$ during the period of data collection, but the variation from one standard peak to the next was generally far less than σ, roughly 0.1σ–0.3σ. The takeoff angle, source to crystal, and crystal to counter values were 3.7°, 18 cm, and 23 cm, respectively, and the receiving aperture at the counter was 6 mm wide × 8 mm high. The half-width at half-peak-height for an average reflection was 0.21° at the 3.7° takeoff angle, indicating a reasonable mosaic width for the peaks. The 0.21° is not to be interpreted as an absolute value of the mosaic spread since this quantity depends upon instrumental factors as well; rather it is only indicative that the peaks are well within the scan width. The counting rate never exceeded 5000 counts/sec and no attenuators were used.

The linear absorption coefficient (μ) for this compound with Mo Kα radiation was calculated to be 46.7 cm^{-1}. With this low value of μ an upper limit to the effect of absorption in intensities would be approximately 15%. No corrections were made for absorption, but anomalous dispersion effects were included in the refinement. Lorentz–polarization corrections were made and intensities were reduced to structure factors.

TABLE II

FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS AND ESTIMATED STANDARD DEVIATIONS[a]

ANISOTROPIC TEMPERATURE FACTORS OF THE FORM $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}kh + 2\beta_{13}hl + 2\beta_{23}kl)]$

Atom	x	y	z	Atom	x	y	z
Ni	0.5000(–)	0.5000(–)	0.5000(–)	N(6)	0.2313(7)	0.6644(6)	0.5409(9)
Br	0.3309(1)	0.0256(1)	0.2833(1)	H(1)	0.417(11)	1.013(22)	0.660(11)
S(1)	0.5231(2)	0.7670(3)	0.5370(2)	H(2)	0.473(9)	1.050(17)	0.576(9)
S(2)	0.4769(2)	0.6048(4)	0.3625(2)	H(3)	0.406(9)	0.783(17)	0.708(9)
S(3)	0.3568(2)	0.4898(4)	0.5351(2)	H(4)	0.450(10)	0.628(20)	0.662(10)
C(1)	0.4682(7)	0.8296(13)	0.6116(7)	H(5)	0.377(10)	0.747(20)	0.251(10)
C(2)	0.3877(9)	0.5487(14)	0.3133(8)	H(6)	0.298(12)	0.609(21)	0.233(12)
C(3)	0.3008(8)	0.6499(13)	0.5103(7)	H(7)	0.385(10)	0.341(19)	0.361(10)
N(1)	0.4528(8)	0.9770(14)	0.6173(9)	H(8)	0.320(12)	0.381(20)	0.295(11)
N(2)	0.4392(8)	0.7411(13)	0.6650(7)	H(9)	0.290(11)	0.841(20)	0.447(11)
N(3)	0.3508(9)	0.6421(13)	0.2621(8)	H(10)	0.381(11)	0.738(19)	0.436(10)
N(4)	0.3579(8)	0.4139(13)	0.3226(8)	H(11)	0.212(9)	0.587(18)	0.578(10)
N(5)	0.3260(8)	0.7505(14)	0.4603(8)	H(12)	0.198(11)	0.756(21)	0.527(11)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.0013(1)	0.0038(3)	0.0018(1)	0.0000(1)	0.0001(1)	0.0001(1)
Br	0.0025(1)	0.0078(2)	0.0030(1)	−0.0010(1)	0.0002(1)	0.0000(1)
S(1)	0.0020(1)	0.0052(4)	0.0017(1)	0.0000(2)	0.0003(1)	−0.0003(2)
S(2)	0.0018(1)	0.0075(4)	0.0019(1)	−0.0003(2)	0.0000(1)	0.0004(2)
S(3)	0.0013(1)	0.0056(4)	0.0029(1)	0.0000(2)	0.0001(1)	0.0003(2)
C(1)	0.0020(5)	0.0065(15)	0.0011(5)	0.0000(7)	−0.0004(4)	−0.0001(7)
C(2)	0.0027(5)	0.0065(17)	0.0017(5)	−0.0004(7)	0.0001(4)	−0.0011(7)
C(3)	0.0023(5)	0.0064(16)	0.0015(5)	0.0008(7)	0.0000(4)	−0.0003(7)
N(1)	0.0040(6)	0.0079(17)	0.0049(7)	0.0019(8)	0.0021(5)	0.0000(9)
N(2)	0.0049(6)	0.0062(15)	0.0018(5)	0.0015(7)	0.0010(4)	0.0001(7)
N(3)	0.0033(6)	0.0077(15)	0.0037(6)	−0.0015(8)	−0.0011(5)	0.0019(8)
N(4)	0.0030(5)	0.0069(14)	0.0033(6)	−0.0008(7)	−0.0012(4)	0.0001(7)
N(5)	0.0030(5)	0.0107(18)	0.0031(6)	0.0026(8)	0.0003(4)	0.0021(8)
N(6)	0.0028(5)	0.0145(21)	0.0052(7)	0.0042(9)	0.0018(5)	0.0046(10)

Atom	B(isotropic)	Atom	B(isotropic)	Atom	B(isotropic)	Atom	B(isotropic)
H(1)	7(9)	H(4)	6(9)	H(7)	5(8)	H(10)	5(8)
H(2)	4(7)	H(5)	6(9)	H(8)	6(9)	H(11)	5(8)
H(3)	5(8)	H(6)	7(10)	H(9)	6(9)	H(12)	7(9)

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits; (–) indicates a fixed parameter.

Determination of the Structure

A three-dimensional Patterson function[24] indicated that the space group was I2/c with the nickel atoms on centers of symmetry at 0, 0, 0; $^1/_2$, $^1/_2$, $^1/_2$; $^1/_2$, $^1/_2$, 0; 0, 0, $^1/_2$, while the bromine atoms were in the general positions (0, 0, 0; $^1/_2$, $^1/_2$, $^1/_2$) $\pm(x, y, z$ and $-x, y, {}^1/_2 - z)$. Trial coordinates for the bromine atom were obtained from the Patterson map and three cycles of least-squares refinement[25] of these bromine atom positions with the nickel atom held constant at 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$ resulted in an unweighted discrepancy factor, R,[26] of 0.384. The phases from this structure factor calculation were used to calculate a three-dimensional electron density function.[24] All nonhydrogen atoms were readily located and five cycles of a full-matrix least-squares refinement using isotropic temperature factors resulted in $R = 0.080$ and weighted R[26] = 0.100. Conversion to anisotropic temperature factors and three cycles of least-squares refinement of all parameters reduced R to 0.062 and weighted R (wR) to 0.085. A three-dimensional difference Fourier map was calculated[24] and the 12 hydrogen atoms were clearly resolved. Using anisotropic temperature factors for nonhydrogen atoms and isotropic temperature factors for hydrogen atoms, a full-matrix least-squares refinement of all parameters resulted in final R, wR, and standard error values of an observation of unit weight[26] of 0.053, 0.068, and 0.48, respectively.

The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ with unit weights for all reflections. Usually with counter data weights are assigned based upon counting statistics,[27,28] and our use of constant weights may appear somewhat unusual. We have found in several cases that the final results, *i.e.*, bond lengths and even rms amplitudes of atomic motions, are well within statistical error and are iden-

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[24] Patterson and electron density syntheses were calculated using "ERFR-3, a Three-Dimensional Fourier Summation Program Adapted for the IBM 7040 from ERFR-2 of Sly, Shoemaker, Van den Hende," by Dr. R. Harris, Roswell Park Memorial Institute, Buffalo, N. Y.

[25] Structure factor calculations and least-squares refinements were performed with a local version of "ORFLS, a Fortran Crystallographic Least-Squares Program," by W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, 1962, Report ORNL-TM-305.

[26] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; weighted $R = [\Sigma w[|F_o| - |F_o|]^2]^{1/2}/[\Sigma w F_o^2]^{1/2}$; standard error $= [\Sigma w(F_o - F_c)^2/(NO - NV]^{1/2}$, where $NO = 1219$, $NV = 124$.

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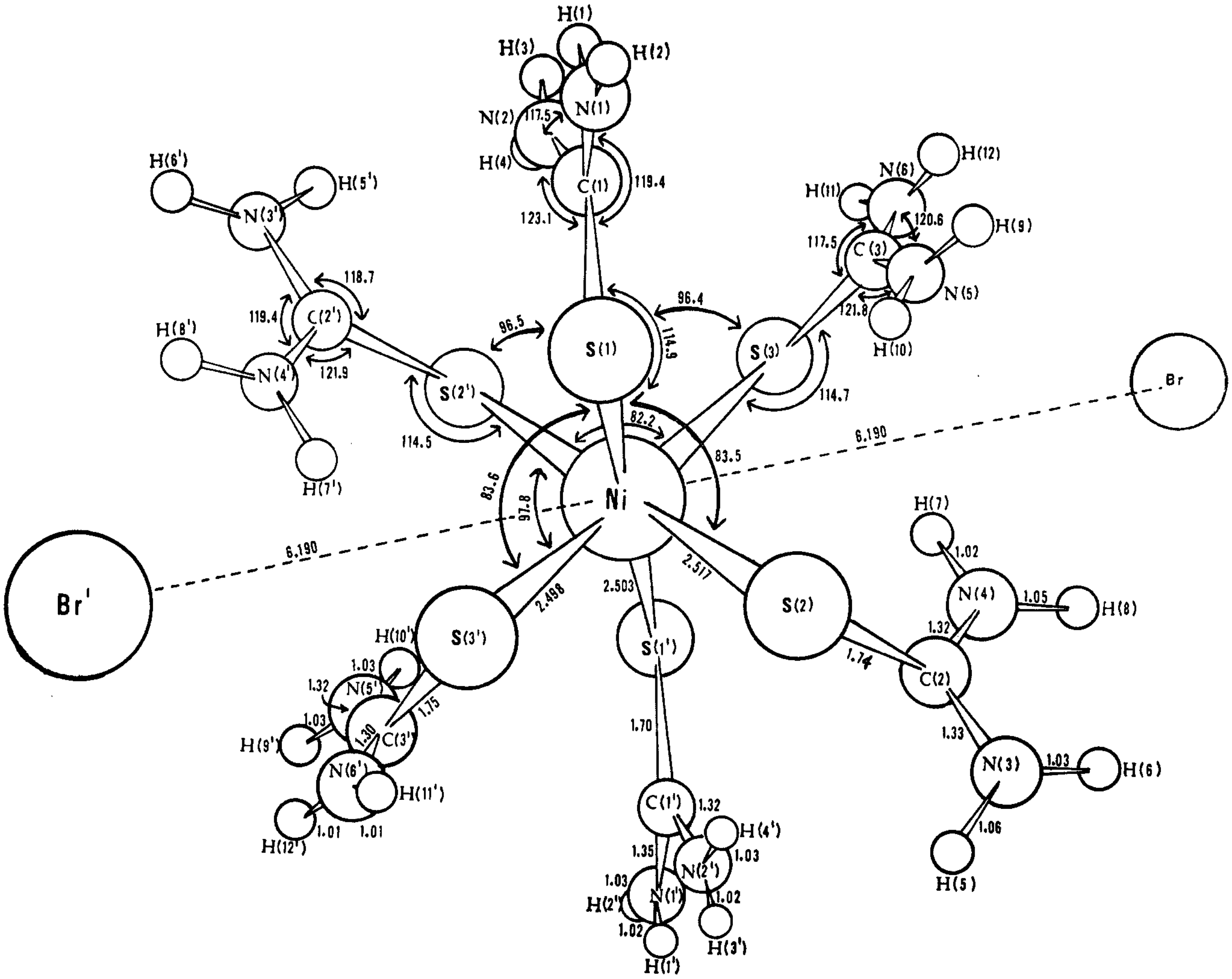

Figure 1.—A perspective view of the molecular configuration of $Ni(tu)_6Br_2$. The nickel atom lies on a center of symmetry and only independent distances and angles are indicated.

tical for constant weights based upon counting statistics.[18,19,29,30] It is clear from the nature of the form factor curve for hydrogen that most of the data concerning hydrogen atom parameters must be in the low-order reflections. These very same reflections are generally weighted very low in most weighting schemes. This approach to hydrogen atom positional parameters by Fourier techniques has been used, implicitly, by other workers.[31,32] Unfortunately, some of these same reflections are also the most strongly affected by extinction and other systematic errors. Based upon our previous experience with unit weights, we decided to adopt unit weights for the benefit of hydrogen atom refinement. The refinement of hydrogen atom positional and temperature factors proceeded smoothly with only the additional constraint of a damping factor of 0.5–0.25 on the shifts. It is possible that the use of unit weights may have weighted the low-order reflections too high, and these are reflected in the "long" (*vide infra*) N–H distances which are not statistically meaningful in the light of the large standard deviations. We were pleasantly surprised that the hydrogen atoms could be located and refined in the presence of nickel and bromine atoms.

Scattering factors for Ni^{2+}, Br^-, and neutral S, C, and N were from Cromer and Waber[33] and for hydrogen from Stewart, *et al.*[34] The effects of anomalous dispersion were included in the structure factor calculations by addition to F_c;[35] the values for $\Delta f'$ and $\Delta f''$ for Ni, Br, and S were those given by Cromer.[36] The final tabulation of observed and calculated structure factors is listed in Table I. Unobserved data were not used in the structure refinement and are not included in the table. Final atomic positional and thermal parameters are listed in Table II. Interatomic distances and angles, root-mean-square components of

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TABLE III[a,c]

Interatomic Distances (Å)

Bonded distances		Nonbonded distances			
Ni–S(1)	2.503(6)[b]	S(1)–S(2)	3.341(5)	C(2)–C(3)	3.82(2)
Ni–S(2)	2.517(6)	S(1)–S(3)	3.727(4)	C(2)–N(2)	3.49(2)
Ni–S(3)	2.498(6)	S(2)–S(3)	3.780(6)	C(2)–N(5)	3.29(2)
S(1)–C(1)	1.697(13)	S(1)–S(2′)	3.746(5)	C(2)–N(2′)	3.89(2)
S(2)–C(2)	1.737(13)	S(1)–S(3′)	3.334(5)	C(1)–N(5)	3.46(2)
S(3)–C(3)	1.752(12)	S(2)–S(3′)	3.295(5)	C(1)–N(4′)	3.75(2)
C(1)–N(1)	1.35(2)	Ni–C(1)	3.57(1)	C(3)–N(4)	3.98(2)
C(1)–N(2)	1.32(2)	Ni–C(2)	3.60(1)	N(1)–N(2)	2.28(2)
C(2)–N(3)	1.33(2)	Ni–C(3)	3.60(1)	N(3)–N(4)	2.29(2)
C(2)–N(4)	1.32(2)	Ni–N(2)	3.72(1)	N(5)–N(6)	2.28(2)
C(3)–N(5)	1.32(2)	Ni–N(4)	3.79(1)	N(1)–N(5)	3.87(2)
C(3)–N(6)	1.31(2)	Ni–N(5)	3.70(1)	N(2)–N(5)	3.85(2)
N(1)–H(1)	1.02(20)	Br–N(4)	3.57(1)	N(3)–N(5)	3.54(2)
N(1)–H(2)	1.03(16)	Br–C(1′)	3.92(1)	N(4)–N(5)	3.87(2)
N(2)–H(3)	1.02(17)	Br–N(1′)	3.89(1)	N(2)–N(4′)	3.66(2)
N(2)–H(4)	1.03(17)	S(1)–C(3)	3.86(1)		
N(3)–H(5)	1.06(19)	S(2)–C(3)	3.99(1)	S(2)–C(2)$^{\mathrm{I}}$	3.87(1)
N(3)–H(6)	1.03(21)	S(3)–C(1)	3.76(1)	S(2)–N(3)$^{\mathrm{I}}$	3.68(2)
N(4)–H(7)	1.02(18)	S(3)–C(2)	3.85(1)	S(3)–N(5)$^{\mathrm{II}}$	3.74(1)
N(4)–H(8)	1.05(19)	S(1)–N(1)	2.64(1)	Br–N(6)$^{\mathrm{II}}$	3.44(1)
N(5)–H(9)	1.03(18)	S(1)–N(2)	2.66(1)	S(3)–N(6)$^{\mathrm{II}}$	3.48(1)
N(5)–H(10)	1.03(18)	S(2)–N(3)	2.65(1)	N(4)–N(6)$^{\mathrm{II}}$	3.60(2)
N(6)–H(11)	1.01(17)	S(2)–N(4)	2.68(1)	N(6)–N(5)$^{\mathrm{II}}$	3.84(2)
N(6)–H(12)	1.01(20)	S(3)–N(5)	2.70(1)	Br–C(2)$^{\mathrm{III}}$	3.97(1)
		S(3)–N(6)	2.62(1)	Br–N(3)$^{\mathrm{III}}$	3.44(1)
Br–H distances		S(1)–N(5)	3.47(1)	Br–N(4)$^{\mathrm{III}}$	3.58(1)
Br–H(11)$^{\mathrm{II}}$	2.54(17)	S(1)–N(4′)	3.42(1)	Br–N(1)$^{\mathrm{IV}}$	3.56(1)
Br–H(6)$^{\mathrm{III}}$	2.48(21)	S(2)–N(5)	3.36(1)	Br–N(2)$^{\mathrm{IV}}$	3.47(1)
Br–H(8)$^{\mathrm{III}}$	2.66(20)	S(2)–N(2′)	3.45(1)	C(2)–N(2)$^{\mathrm{IV}}$	3.75(2)
Br–H(1)$^{\mathrm{IV}}$	2.62(20)	S(3)–N(2)	3.38(1)	N(4)–N(2)$^{\mathrm{IV}}$	3.36(2)
Br–H(3)$^{\mathrm{IV}}$	2.51(17)	S(3)–N(4)	3.66(1)	Br–N(3)$^{\mathrm{V}}$	3.48(1)
Br–H(12)$^{\mathrm{II}}$	3.87(20)	C(1)–C(3)	3.57(2)	Br–N(5)$^{\mathrm{V}}$	3.88(1)
Br–H(5)$^{\mathrm{V}}$	2.68(19)				
Br–H(6)$^{\mathrm{V}}$	3.86(20)				
Br–H(9)$^{\mathrm{V}}$	3.34(19)				
Br–H(10)$^{\mathrm{V}}$	3.72(17)				

Interatomic Angles (deg)

S(1)–Ni–S(2)	83.5(2)	C(1)–N(1)–H(1)	119(11)
S(1)–Ni–S(3)	96.4(2)	C(1)–N(1)–H(2)	120(8)
S(2)–Ni–S(3)	97.8(2)	C(1)–N(2)–H(3)	120(9)
S(1)–Ni–S(2′)	96.5(2)	C(1)–N(2)–H(4)	120(10)
S(1)–Ni–S(3′)	83.6(2)	C(2)–N(3)–H(5)	119(9)
S(2)–Ni–S(3′)	82.2(2)	C(2)–N(3)–H(6)	119(11)
		C(2)–N(4)–H(7)	120(10)
Ni–S(1)–C(1)	114.9(8)	C(2)–N(4)–H(8)	122(10)
Ni–S(2)–C(2)	114.5(10)	C(3)–N(5)–H(9)	118(11)
Ni–S(3)–C(3)	114.7(10)	C(3)–N(5)–H(10)	120(10)
		C(3)–N(6)–H(11)	120(9)
S(1)–C(1)–N(1)	119.4(1.1)	C(3)–N(6)–H(12)	118(12)
S(1)–C(1)–N(2)	123.1(1.0)		
S(2)–C(2)–N(3)	118.7(1.0)	H(1)–N(1)–H(2)	120(13)
S(2)–C(2)–N(4)	121.9(1.1)	H(3)–N(2)–H(4)	120(14)
S(3)–C(3)–N(5)	121.8(1.0)	H(5)–N(3)–H(6)	122(14)
S(3)–C(3)–N(6)	117.5(1.1)	H(7)–N(4)–H(8)	118(14)
		H(9)–N(5)–H(10)	122(14)
N(1)–C(1)–N(2)	117.5(1.2)	H(11)–N(6)–H(12)	121(14)
N(3)–C(2)–N(4)	119.4(1.3)		
N(5)–C(3)–N(6)	120.6(1.3)		

Dihedral Angles (deg) between Normals to Planes

[Ni–S(1)–C(1)] [S(1)–C(1)–N(1)]	24.0(1.0)	[S(1)–Ni–S(3)] [Ni–S(1)–C(1)]	30.6(0.8)
[Ni–S(1)–C(1)] [S(1)–C(1)–N(2)]	24.1(1.3)	[S(1)–Ni–S(2)] [Ni–S(1)–C(1)]	52.6(1.0)
[Ni–S(2)–C(2)] [S(2)–C(2)–N(3)]	31.8(1.0)	[S(2)–Ni–S(3)] [Ni–S(2)–C(2)]	32.7(1.0)
[Ni–S(2)–C(2)] [S(2)–C(2)–N(4)]	35.2(1.3)	[S(2)–Ni–S(1)] [Ni–S(2)–C(2)]	51.5(0.9)
[Ni–S(3)–C(3)] [S(3)–C(3)–N(5)]	15.9(1.3)	[S(3)–Ni–S(1)] [Ni–S(3)–C(3)]	39.2(0.8)
[Ni–S(3)–C(3)] [S(3)–C(3)–N(6)]	13.5(1.1)	[S(3)–Ni–S(2)] [Ni–S(3)–C(3)]	45.1(1.0)

TABLE III (*Continued*)

Best Least-Squares Planes[d,e]

Thiourea group	Values for eq		Dev from best plane, Å			
1	*A*	−0.8089	S(1)	0.0000(23)	H(1)	0.054(126)
	B	−0.1179	C(1)	0.0004(80)	H(2)	0.013(103)
	C	−0.5760	N(1)	−0.0006(84)	H(3)	−0.002(103)
	D	−12.7478	N(2)	−0.0001(77)	H(4)	−0.007(115)
2	*A*	+0.5640	S(2)	0.0003(23)	H(5)	0.054(118)
	B	−0.3538	C(2)	−0.0192(85)	H(6)	−0.011(139)
	C	−0.7461	N(3)	0.0061(88)	H(7)	−0.018(117)
	D	−2.165	N(4)	0.0066(81)	H(8)	−0.048(132)
3	*A*	−0.4056	S(3)	0.0003(24)	H(9)	0.010(129)
	B	−0.4921	C(3)	−0.0138(82)	H(10)	−0.014(120)
	C	−0.7703	N(5)	0.0051(82)	H(11)	−0.008(115)
	D	−11.3662	N(6)	0.0060(93)	H(12)	−0.009(131)

Root-Mean-Square Components of Thermal Displacements along the Principal Axes (Å)

Atom	Axis 1	Axis 2	Axis 3
Ni	0.125(5)	0.140(4)	0.162(4)
Br	0.162(2)	0.204(2)	0.212(2)
S(1)	0.141(6)	0.155(5)	0.178(5)
S(2)	0.157(5)	0.161(6)	0.187(5)
S(3)	0.138(5)	0.152(5)	0.209(5)
C(1)	0.117(28)	0.164(20)	0.182(20)
C(2)	0.131(26)	0.181(21)	0.200(20)
C(3)	0.144(24)	0.154(23)	0.195(19)
N(1)	0.146(22)	0.212(19)	0.304(18)
N(2)	0.144(21)	0.157(22)	0.275(17)
N(3)	0.155(20)	0.178(20)	0.283(19)
N(4)	0.151(22)	0.175(19)	0.260(17)
N(5)	0.141(22)	0.206(19)	0.265(18)
N(6)	0.127(25)	0.192(20)	0.348(20)

[a] A primed atom refers to an atom related by the crystallographic center of symmetry of the molecule. Superscripts refer to the transformations: (I) $1 - x, y, {}^1/_2 - z$; (II) ${}^1/_2 - x, -{}^1/_2 + y, 1 - z$; (III) ${}^1/_2 - x, {}^1/_2 - y, {}^1/_2 - z$; (IV) $x, 1 - y, -{}^1/_2 + z$; (V) $x, y - 1, z$. [b] ORFFE calculates ±0.003, but these values have been doubled to give a more realistic assessment of error since the Ni positional parameters have no variance associated with them in I2/c. [c] Excluding hydrogen atoms. [d] Equation of the form $Ax + By + Cz - D = 0$, where x, y, z refer to an internal orthogonal-coordinate system: J. S. Rollett, "Computing Methods in Crystallography," Pergamon Press Inc., New York, N. Y., 1965, p 22. Esd's of atomic coordinates provided weights for the respective atoms. [e] Internal orthogonal axes for monoclinic system with b unique: $x_0 = a(x/a) + c(z/c) \cos \beta$; $y_0 = b(y/b)$; $z_0 = (cz/c)$.

thermal displacement, dihedral angles between normals to planes, and their errors were computed[37] with the parameters and variance–covariance matrix from the last cycle of least-squares refinement and are listed in Table III. Best least-squares planes for the thiourea groups are also listed in Table III.[38]

Results and Discussion

The structure consists of $Ni[SC(NH_2)_2]_6^{2+}$ molecular ions well separated from the Br^- ions as can be seen in the molecular diagram in Figure 1 as well as in the arrangement of molecules in the unit cell shown in Figure 2. Each nickel atom is coordinated to six sulfur atoms of a thiourea group with Ni–S–C angles (114°) that are not significantly different from one another (Table III). Hence, each sulfur contributes an sp^2 nonbonding orbital and an electron pair to form the Ni–S bonds. Although the difference between the smallest and largest Ni–S distances (2.498, 2.503, and 2.517 Å, all ±0.006 Å) seems to be statistically significant, there does not seem to be any chemical or physical reason for this difference. We do not believe this to be a real difference, and our estimate of error may be somewhat optimistic owing to the neglect of systematic errors such as absorption, extinction, etc. They are, nevertheless, significantly larger than the 2.43 Å expected from the sum of their covalent radii[39] and longer than the 2.46-Å Ni–S distance found in *trans*-$Ni(tu)_4Cl_2$.[8]

A pronounced distortion from the octahedral configuration around the nickel atom is observed. It can be seen from the S–Ni–S angles (Table III and Figure 1) that three of the sulfur atoms [S(1), S(2), S(3′)] are displaced toward each other by more than 6° from the idealized 90°. Owing to the center of symmetry, the same is true for the other three sulfur atoms [S(1′), S(2′), S(3)] so that the distortion is approaching a

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[37] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, 1964.

[38] Local program for best least-squares plane for the IBM 1620 due to W. A. Spofford, III.

[39] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 246–249.

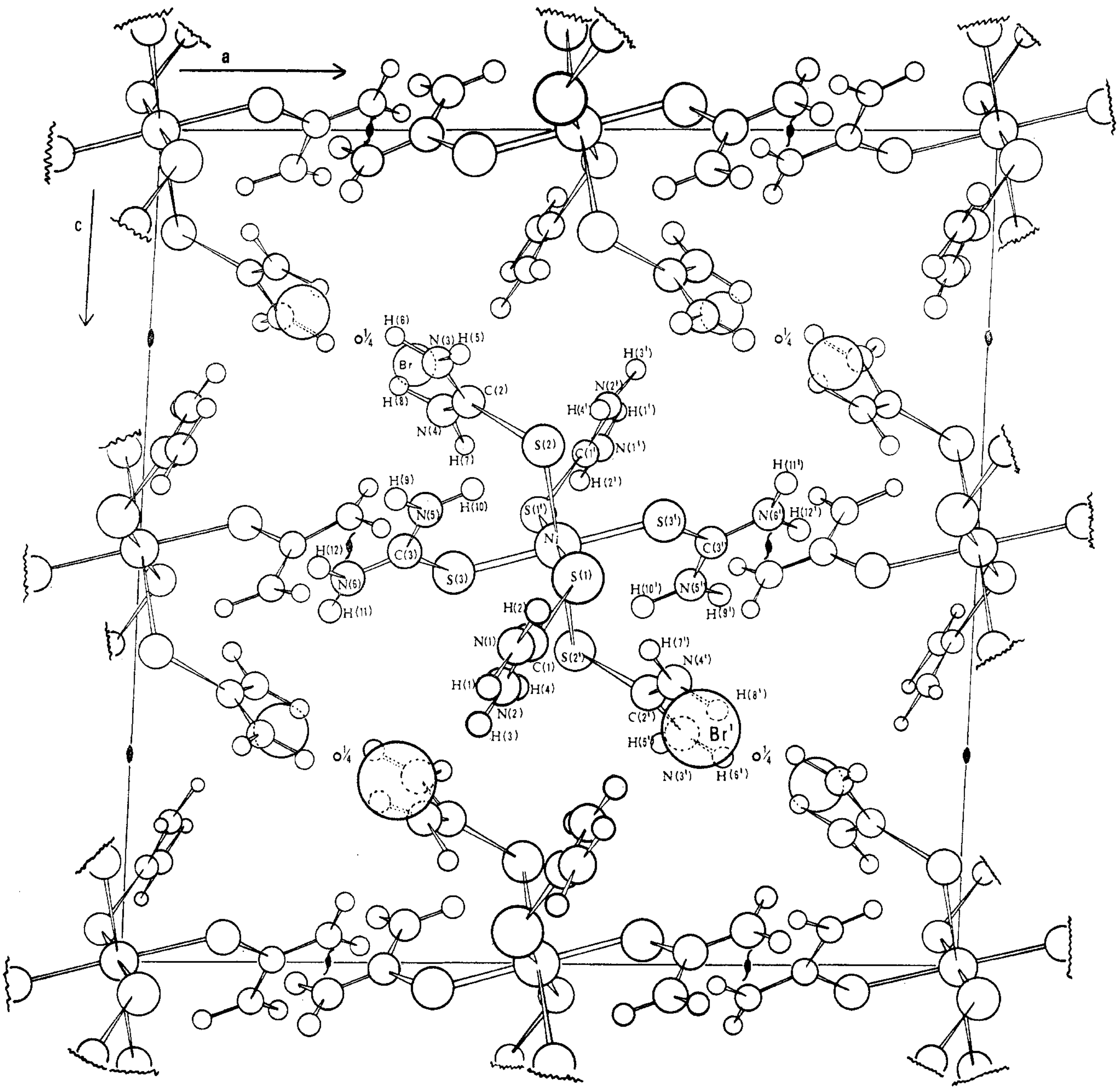

Figure 2.—A projection of the unit cell onto (010).

D_{3d} (trigonal antiprism, neglecting the NH_2 groups) configuration. This seems like a sufficiently large distortion that it undoubtedly persists in solution and accounts for the broadening of the visible absorption bands of the complex in acetone solution.[21]

As expected, the S–C distances are significantly shorter than a "normal" single bond (1.81 Å), but they are not significantly different from the 1.720 ± 0.009 Å found for the free thiourea molecule by X-ray diffraction[40] or the 1.746 ± 0.009 Å found by neutron diffraction.[41] The S_1–C_1 distance of 1.697 Å seems significantly shorter than the other two S–C distances, but we see no physical reason for this shortening. The C–N distances are also not significantly different from the 1.340 (6) Å observed by Truter[40] nor from one another. The N–H distances are surprisingly long for X-ray values, which are generally shorter than those found by neutron diffraction. Truter[40] found N–H distances of 0.96 ± 0.06 Å, whereas Elcombe and Taylor[41] found N–H distances of 1.012 ± 0.011 Å. Our values are 1.01–1.06 Å, all ±~0.2 Å, and with such a large standard error no interpretations should be made. For this reason, we have not corrected these for thermal motions.

The thiourea groups remain planar as can be seen from the S–C–N angles and the least-squares planes in Table III. The rms displacements of Table III are all reasonable and it appears that the NiS_6 entity moves as a unit but the rest of the molecule is more con-

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(40) M. R. Truter, *Acta Cryst.*, **22**, 556 (1967).

(41) M. M. Elcombe and J. C. Taylor, *ibid.*, **A24**, 410 (1968).

strained by hydrogen bonding and packing requirements; however, this may be in part a reflection of absorption errors.

The dihedral angles that completely specify the orientation of the thiourea groups relative to the planes defined by Ni and S atoms are given in Table III. Three factors contribute to these orientations: (a) hydrogen bonding to the bromide ion, (b) steric requirements that restrict the thiourea groups, and (c) electrostatic interactions between electrons in the S–C pπ molecular orbitals and the metal d_{xz}, d_{yz}, d_{xy} orbitals, all of which are filled. Obviously all three factors contribute to the specific orientation of a thiourea group and studies are currently underway in this laboratory to determine which factor(s) predominate(s). Preliminary photographic data indicate that $Ni(tu)_6Br_2$ and $Ni(tu)_6I_2$ are isomorphous and a comparison of the specific orientations of thiourea groups in this series to the orientation of thiourea groups in $Pt(tu)_4Cl_2$,[20] $Pd(tu)_4Cl_2$,[19] and the isomorphous series $Mn(tu)_4Cl_2$, $Fe(tu)_4Cl_2$, $Cd(tu)_4Cl_2$, and $Co(tu)_4Cl_2$[18,42] is being made.

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(42) J. E. O'Connor and E. L. Amma, to be submitted for publication.

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The Crystallography and Structure of α-Zirconium Bis(monohydrogen orthophosphate) Monohydrate[1]

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The crystal structure of α-zirconium bis(monohydrogen orthophosphate) monohydrate, $Zr(HPO_4)_2 \cdot H_2O$, has been determined from integrated precession data (568 nonzero reflections). The crystals are monoclinic, space group $P2_1/c$, with cell dimensions $a = 9.076 \pm 0.003$ Å, $b = 5.298 \pm 0.006$ Å, $c = 16.22 \pm 0.02$ Å, and $\beta = 111.5 \pm 0.1°$. The calculated density with $Z = 4$ is 2.76 g/cm^3 compared to an observed density of 2.72 ± 0.04 g/cm^3. The structure was refined to an R factor of 8.4% by least-squares methods. The structure is a layered one, each layer consisting of planes of zirconium atoms bridged through phosphate groups which alternate above and below the metal atom planes. Each phosphate group bonds to three different zirconium atoms producing octahedral coordination about the zirconium atoms. The Zr–O bond distances range from 2.04 to 2.11 Å. The fourth phosphate oxygen bears the hydrogen and points toward an adjacent layer. The layers are arranged relative to each other in such a way as to form zeolitic-type cavities. A water molecule resides in the center of each cavity and is hydrogen bonded to phosphate groups. The relation between structure and ion-exchange properties of the crystals is discussed in this and a forthcoming paper.

Introduction

Preparations commonly called zirconium phosphate are of interest because they function as ion exchangers. These phosphates have been prepared in both amorphous and crystalline forms. When solutions containing phosphate ion and Zr(IV) salts are mixed, amorphous gels of variable composition result.[2] These gels are transformed into microcrystals by refluxing them in various phosphate-containing solutions. If the refluxing medium is phosphoric acid, the resultant crystals are the normal or α phase.[3] However, refluxing in a mixture of phosphoric acid and sodium dihydrogen phosphate produces the β and γ phases.[4]

The α phase (α-ZrP) has been shown to be zirconium bis(monohydrogen orthophosphate) monohydrate, $Zr(HPO_4)_2 \cdot H_2O$, on the basis of its composition, dehydration, and ion-exchange behavior.[3] Crystals large enough for a single-crystal X-ray diffraction study were prepared from the microcrystals as described below. An attempt to solve the structure by two-dimensional methods was only partially successful.[5]

Severe overlap of several oxygen atom peaks in the Fourier projections prevented a complete solution of the structure. A three-dimensional study has now been carried out, the details of which are reported here.

Experimental Section

Preparation.—Single crystals were prepared by heating a mixture of gel and 12 M phosphoric acid in a sealed quartz tube for several weeks at 170–180°. Very thin hexagonal or triangular platelets were obtained.

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(1) Portions of this paper were taken from the Ph.D. thesis of G. D. Smith presented to the Chemistry Department, Ohio University, June 1968. This work was supported by the National Science Foundation under Grant No. GP-6433.

(2) C. B. Amphlett, "Inorganic Ion-Exchangers," Elsevier Publishing Co., Amsterdam, 1964, pp 84–136.

(3) A. Clearfield and J. A. Stynes, *J. Inorg. Nucl. Chem.*, **26**, 117 (1964).

(4) A. Clearfield, R. H. Blessing, and J. A. Stynes, *ibid.*, **30**, 2249 (1968).

(5) A. Clearfield and G. D. Smith, *J. Colloid Interface Sci.*, **28**, 325 (1968).