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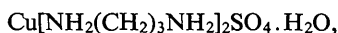
The Crystal Structure of the Sulfate and Selenate Monohydrates of Bis-(1,3-propanediamine)copper(II)*

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The crystal structures of bis-(1,3-propanediamine)copper(II) sulfate monohydrate,



and the corresponding isomorphous selenate have been refined by the full-matrix least-squares method using three-dimensional Mo $K\alpha$ intensity data to reliability indices below 0.07. The lattice constants are: $a_0 = 11.747$, $b_0 = 15.841$, and $c_0 = 7.164$ and $a_0 = 11.998$, $b_0 = 15.702$ and $c_0 = 7.352$ Å for the sulfate and selenate respectively; $Z = 4$ in space group $Pnam$. The copper ion is surrounded by four nitrogen atoms (~ 2.0 Å) in a planar arrangement and by two more distant oxygen atoms (at unequal Cu–O distances of 2.57 and 3.34 Å for the sulfate and 2.52 and 3.52 Å for the selenate) forming a weak chain-like arrangement.

Introduction

The low temperature magnetic and thermal properties of several nitrogen coordinated copper compounds have been interpreted as those of substances containing a magnetic linear chain structure (Griffiths, 1964; Lowndes, 1968; Bonner, 1968); the first such material studied was $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ (hereafter CTASUL). Nasanen, Luukkonen & Virtamo (1967) (hereafter NLV) reported the lattice constants for bis(1,3-propanediamine)copper(II) sulfate monohydrate, $\text{Cu}[\text{NH}_2(\text{CH}_2)_3\text{NH}_2]_2\text{SO}_4 \cdot \text{H}_2\text{O}$, (hereafter CUPSUL); from their values, it appeared that there might be a close structural resemblance between CTASUL and CUPSUL. Preliminary structural results and specific heat measurements indicated a good fit to the expression $J = ar^{-n}$, where J is the exchange constant, r the interionic Cu–Cu separation and n an exponent with the value 10.9, could be obtained for several of these

materials, including CUPSUL, which contain linear chains (Lowndes, Finegold, Rogers & Morosin, 1969). We report here our structure results on CUPSUL and the corresponding isomorphous selenate compound (CUPSEL).

Experimental

Crystals of CUPSUL and CUPSEL were prepared by the method of NLV. The complexes are prepared by dropwise addition of a saturated methanol solution of copper sulfate (or selenate) to a methanol solution of the amine. The resulting blue precipitates of the corresponding anhydrous complexes were converted to the very soluble, purple monohydrates by addition of water.

The quality of the crystals used for data collection was checked optically and by X-ray photographic techniques to insure the absence of twinning. The space group, $Pna2_1$ or $Pnam$ was determined on the basis of extinctions observed on these photographs (for $0kl$, $k+l=2n+1$ absent, for $h0l$, $h=2n+1$ absent and for $00l$, $l=2n+1$ absent).

A piezoelectric effect was detected for both CUPSUL and CUPSEL using a circuit similar to that of Robin-

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son (1959); (also see Dewsberry & Williams, 1966). On this basis, the structures of these materials were initially considered to be noncentrosymmetric belonging to space group $Pna2_1$. After the crystal structures were determined, the dielectric behavior as a function of temperature and pressure was investigated in order to establish whether these materials might be ferroelectric. Unfortunately, the polar axis in these crystals coincides with the growth (needle) axis. In addition, the resistance ($\sim 10^7$ ohm.cm⁻²) of these materials proved unfavorable for the detection of the typical hysteresis loops which ferroelectric materials exhibit. By measuring the dielectric constant as a function of temperature on polycrystalline slabs, a Curie point can usually be established. We found an increasing dielectric constant and loss factor with temperatures near 50°C which was accompanied by decomposition (dehydration) of our materials. This behavior prevented the observation of the dielectric anomaly usually obtained at the Curie point. We then attempted to use high hydrostatic pressure (to 15 kbar) to suppress dehydration of the sample as well as to possibly shift the Curie temperature to a lower value. However, decomposition still occurred. A similar pressure behavior has been observed in GASH with decomposition occurring even at pressures as high as 20 kbar (Samara, 1969). Thus, we have been unable to unambiguously determine whether these materials are ferroelectric.

The following lattice constants were obtained by least-squares fit of high 2θ values taken with Cu $K\alpha$

($\lambda_{K\alpha 1} = 1.54050$ Å) radiation using a 115 mm diameter Weissenberg camera employing Straumanis loading: for CUPSUL $a_0 = 11.747$ (4) $b_0 = 15.841$ (3) $c_0 = 7.164$ (2) Å and for CUPSEL $a_0 = 11.998$ (3) $b_0 = 15.702$ (2) $c_0 = 7.352$ (2) Å. With four molecules per cell, the observed and calculated densities for CUPSUL are 1.59 (NLV) and 1.61 g.cm⁻³, respectively; those for CUPSEL are 1.81 and 1.78 g.cm⁻³, respectively. Three-dimensional Mo $K\alpha$ intensity data were measured with a scintillation counter employing pulse height discrimination and the $\theta-2\theta$ scan technique. A Datex automatic-control module was used for setting the angles on the Picker diffractometer and on the E & A full-circle Eulerian orienter. For CUPSUL, intensity data were measured for 3717 unique reflections; of these 2113 were found to be less than three times the standard deviation of the measurement, σ , hence, were assigned a value equal to 3σ and were considered unobserved in subsequent calculations. In the case of CUPSEL, 2163 reflections were measured, of which 938 were considered unobserved by the same criteria just mentioned.

No absorption corrections were included for the crystal specimens mounted along the longest direction; their dimensions were $0.29 \times 0.29 \times 0.41$ mm with $\mu_{\text{Mo } K\alpha}$ 17.7 cm⁻¹ and $0.12 \times 0.16 \times 0.58$ mm with $\mu_{\text{Mo } K\alpha}$ 45.4 cm⁻¹ for the CUPSUL and CUPSEL crystals, respectively. The effect of ignoring absorption is very small since the transmission coefficients (0.654 to 0.670 and 0.590 to 0.618 for CUPSUL and CUPSEL respectively) vary by less than 5%. Lorentz and pola-

Table 1. Final atomic coordinates and thermal factors for CUPSUL

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Cu	0.13162 (6)	0.24402 (4)	$\frac{1}{4}$	2.29 (3)	2.02 (3)	1.50 (3)	0.03 (2)	—	—
S	0.37734 (11)	0.26597 (9)	$\frac{1}{4}$	1.68 (2)	3.83 (4)	1.26 (2)	0.27 (3)	—	—
O(1)	0.2733 (4)	0.2149 (4)	$\frac{1}{4}$	2.2 (2)	4.9 (4)	2.4 (3)	-1.6 (3)	—	—
O(2)	0.4781 (5)	0.2141 (5)	$\frac{1}{4}$	2.7 (2)	7.3 (5)	2.2 (2)	1.6 (3)	—	—
O(3)	0.3777 (3)	0.3196 (2)	0.5806 (4)	3.1 (3)	4.6 (3)	1.8 (2)	-0.3 (2)	-0.1 (1)	0.6 (2)
O(4)	0.3497 (9)	0.2307 (5)	$\frac{1}{4}$	10.3 (6)	6.4 (4)	2.3 (2)	0.1 (2)	—	—
N(1)	0.1331 (3)	0.3319 (2)	0.0446 (5)	2.6 (3)	2.4 (2)	1.6 (3)	0.0 (2)	-0.1 (2)	0.2 (2)
N(2)	0.1201 (4)	0.1577 (2)	0.0430 (5)	3.0 (3)	2.6 (2)	1.9 (3)	0.1 (2)	0.0 (2)	-0.4 (2)
C(1)	0.0928 (6)	0.4198 (3)	0.0745 (8)	5.5 (4)	2.1 (2)	3.1 (3)	0.3 (2)	-0.7 (2)	0.1 (2)
C(2)	0.1515 (7)	0.0692 (4)	0.0755 (9)	6.9 (4)	3.2 (2)	3.3 (2)	1.3 (2)	0.4 (2)	-0.7 (3)
C(3)	0.1381 (10)	0.4586 (5)	$\frac{1}{4}$	6.5 (5)	2.8 (2)	3.1 (3)	0.1 (6)	—	—
C(4)	0.1009 (12)	0.0344 (5)	$\frac{1}{4}$	9.3 (7)	1.8 (2)	4.1 (4)	-0.6 (9)	—	—

Table 2. Final atomic coordinates and thermal factors for CUPSEL

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Cu	0.13222 (9)	0.24496 (7)	$\frac{1}{4}$	2.45 (3)	2.27 (3)	1.61 (3)	0.01 (2)	—	—
Se	0.37701 (6)	0.25948 (6)	$\frac{1}{4}$	1.58 (2)	3.43 (4)	1.21 (2)	0.05 (2)	—	—
O(1)	0.2643 (6)	0.2016 (5)	$\frac{1}{4}$	3.3 (2)	4.8 (4)	2.9 (3)	-1.0 (3)	—	—
O(2)	0.4870 (6)	0.1995 (6)	$\frac{1}{4}$	2.6 (2)	7.4 (5)	3.1 (3)	1.5 (3)	—	—
O(3)	0.3770 (4)	0.3202 (3)	0.5689 (6)	3.3 (2)	4.1 (2)	2.2 (1)	-0.0 (2)	-0.3 (1)	0.5 (2)
O(4)	0.3411 (9)	0.2277 (7)	$\frac{1}{4}$	8.7 (5)	6.4 (5)	3.3 (3)	1.6 (5)	—	—
N(1)	0.1368 (4)	0.3333 (3)	0.0503 (7)	2.6 (2)	2.6 (2)	2.1 (2)	-0.0 (2)	0.2 (2)	0.5 (1)
N(2)	0.1171 (4)	0.1573 (3)	0.0492 (7)	3.1 (2)	2.7 (2)	1.8 (2)	0.1 (2)	0.7 (2)	-0.3 (2)
C(1)	0.0960 (7)	0.4124 (4)	0.0793 (11)	5.9 (4)	2.4 (2)	3.7 (3)	0.9 (2)	-1.0 (2)	0.8 (3)
C(2)	0.1485 (8)	0.0664 (4)	0.0784 (11)	7.4 (6)	2.7 (2)	3.5 (3)	0.3 (2)	0.1 (2)	-0.9 (3)
C(3)	0.1418 (11)	0.4613 (6)	$\frac{1}{4}$	6.5 (5)	2.6 (2)	3.7 (3)	-0.2 (2)	—	—
C(4)	0.0946 (15)	0.0329 (7)	$\frac{1}{4}$	10.6 (9)	2.2 (2)	4.3 (3)	-2.2 (2)	—	—

zation factors were applied and structure factors calculated using Cu2+, Se, S, C, N, O and H scattering factors from Table 3.3.1A (p. 202) and dispersion corrections for copper and selenium from Table 3.3.2C (p. 215) of International Tables for X-ray Crystallography (1962). Positional parameters were obtained from a Patterson synthesis and subsequent Fourier synthesis. Atomic positional and thermal parameters were refined by full-matrix least-squares refinement; Σw(Fo - Fc)2, was minimized with weights either as-

signed from counting statistics or, for unobserved reflections with |Fo| > |Fc|, set equal to zero. The reliability indices, where R = Σ|Fo| - |Fc| / Σ|Fo|, for the refinement in space group Pna21 were 0.069 and 0.068 for CUPSEL and CUPSEL, respectively. However, the parameters agreed (to within three times the estimated standard deviations, e.s.d.) with those required by space group Pnam. Hence, the structures were refined in the centrosymmetric space group, Pnam. The final R values for observed reflections using space

Table 4. Observed and calculated structure factors for CUPSEL

Table with 20 columns representing different reflections (e.g., K 10FO 10FC, K 10FU 10LC, etc.) and rows of numerical data values.

group $Pnam$ were 0.070 and 0.060 for CUPSUL and CUPSEL, respectively. The refinements in $Pnam$ exhibited smaller e.s.d.'s for the atoms which are situated off the mirror planes at $\frac{1}{4}$ and $\frac{3}{4}$ along the c axis than did the refinements in $Pna2_1$. The evidence for the noncentrosymmetric space group is the detected piezoelectric response for both materials; however, no structural evidence could be found. For example, a comparison of hkl and $hk\bar{l}$ reflections showed no differences to support the lack of the center of symmetry; however, domain twinning would yield similar results. There does not appear to be any slight rearrangement of oxygen atoms so as to make the hydrogen bonding polar and not obey the symmetry mirror perpendicular to c . Hence, in our subsequent discussion, we consider the compounds to be centrosymmetric. The final atomic positional and thermal parameters for the $Pnam$ refinement are given in Tables 1 and 2. The temperature factors are of the form

$$\exp\left(-\frac{1}{4}\sum_i^3\sum_j^3B_{ij}h_ih_ja_i^*a_j^*\right).$$

The correctness of the structure was verified by final Fourier and difference syntheses. Hydrogen positions could not unambiguously be assigned from the difference synthesis and hence were not included in our determinations. The observed and calculated structure factors are given in Tables 3 and 4. These Tables do not list the reflections which were considered unobserved. The calculated structure factor exceeded the assigned observed value for 8% and 10% of the 'unobserved' reflections for CUPSUL and CUPSEL,

respectively. Fig. 1 shows the structural arrangement found in these materials.

Discussion

The gross structure for these two propanediamine monohydrates has a close resemblance to that of the corresponding ammonia derivative, CTASUL (Mazzi, 1955; Morosin, 1969). In these materials nearly square planar coordinated copper(II) ions are linked by the oxygen atoms of water molecules to form a weak chain zigzagging along the c axis. The difference in the location of the symmetry related chains in CTASUL compared with CUPSUL and CUPSEL probably is due to the more bulky carbon structure for the propanediamine compounds. An additional similarity for these materials is the copper environment. This consists of four nitrogen atoms at about 2.0 Å in a near-square planar arrangement and of two more distant oxygen atoms. These oxygen atoms are not equidistant from the copper atoms (Table 5; for CTASUL, 2.34 and 3.48 Å). The inclusion of the more bulky SeO_4^{2-} ion increases the longer Cu-O separation with only a small change in the shorter Cu-O separation; however, the proposed hydrogen bond separations along the weak chains are almost identical in the two salts.

A significant difference between CTASUL and either CUPSUL or CUPSEL is the location of the copper atom; in CTASUL the copper lies approximately 0.2 Å above the plane defined by the nitrogen atoms while in the latter compounds the copper lies on this plane. It appears that an oxygen-copper separation

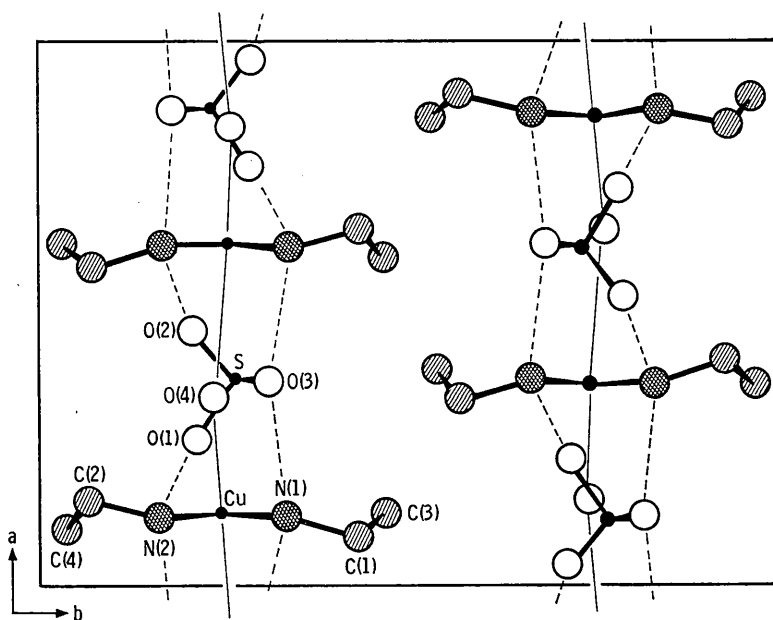


Fig. 1. A representation of the crystal structure of $Cu[NH_2(CH_2)_3NH_2]_2SO_4 \cdot H_2O$ viewed along the c axis. In this structure the copper atom of the weak-Cu-O(4)-Cu-chain on the left-hand side lies on the mirror at $z = \frac{1}{4}$ while the sulfate ions on this same side are situated on the mirror at $z = \frac{3}{4}$. In the isomorphous selenate compound, the larger selenate ion results in an increase only in the longer Cu-O(4) separation; the hydrogen bonding separations (shown by dashed lines) are nearly identical in the two compounds.

ration, less than ~ 2.43 Å, results in an interaction sufficient to displace the copper atom from the nitrogen atom plane. Thus, in $\text{Cu}(\text{NO}_3)_2 \cdot \text{CH}_3\text{NO}_2$ (with Cu–O separation of 2.31 Å; Duffin & Wallwork, 1966), $\text{Cu}(\text{C}_9\text{H}_7\text{NO}_3) \cdot 5\text{H}_2\text{O}$ (2.35 Å; Ueki, Ashida, Sasada & Kakudo, 1969), $[\text{Cu}(\text{C}_3\text{H}_{10}\text{N}_2)_2]_2(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (2.355 and 2.322 Å; Hussain & Hope, 1969), $\text{Cu}(\text{C}_{12}\text{H}_{18}\text{ON})_2 \cdot \text{H}_2\text{O}$ (2.3 Å; Hall, Morgan & Waters, 1966), and CTASUL, the copper atom lies off the plane; in $\text{Cu}(\text{NH}_3)_4\text{SeO}_4$ (2.45 Å; Morosin, 1969), $\text{Cu}(\text{en})_2(\text{ClO}_4)_2$ (2.60 Å; Pajunen, 1967), $\text{Cu}(\text{en})_2(\text{NO}_3)_2$ (2.59 Å; Komiyama & Lingafelter, 1964), $\text{Cu}(\text{C}_3\text{H}_{10}\text{N}_2)_2(\text{NO}_3)_2$ (2.55 Å; Pajunen, 1969), $\text{Cu}(\text{C}_8\text{H}_5\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ (2.68 Å; Cingi, Guastini, Musatti & Nardelli, 1969), $\text{Cu}(\text{C}_5\text{H}_5\text{NO}_4)(\text{ClO}_4)_2$ (3.38 Å; Lee, Brown & Melson, 1969), CUPSUL (2.57 Å), and CUPSEL (2.52 Å), it cannot be considered significantly displaced from this plane.

The two propanediamine rings are in a *trans* arrangement about the copper atom and their configuration is similar to that found in the corresponding nitrates of nickel (Pajunen, 1968) and copper (Pajunen, 1969). The N–Cu–N angle in these rings exceed 90° and may be contrasted to that found in ethylenediamine compounds in which the angle usually is smaller than 90° . The shortest non-bonding interpropanediamine ring contact separations involve C(1) and O(2). These separations are 3.42 and 3.34 Å for C(1)–O(2) and 3.52 and 3.57 Å for C(1)–C(1') in CUPSUL and CUPSEL, respectively.

The sulfur–oxygen and selenium–oxygen separations found in the SO_4^{2-} and SeO_4^{2-} ions are in good agree-

ment with values found in other sulfate and selenate compounds (Larson, 1965; Morosin, 1969). Although a 'riding motion' correction (Busing & Levy, 1964) does not significantly change these values, it does reduce the spread in the values shown in Table 5.

The hydrogen bond interactions involving the water molecule are identical to those observed in CTASUL and those involving the nitrogen atoms are all within the span observed in CTASUL. There is no hydrogen bonding along the *b* direction as is found in CTASUL; hence the crystals are mechanically weak in that direction.

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Table 5. *Interatomic separations and angles in CUPSUL and CUPSEL*

Values for CUPSUL are given first.

(a) Those which involve the copper environment:

Cu–N(1)	2.03 (1) Å	2.02 (1) Å	N(1)–Cu–N(2)	86.1 (8)°	86.6 (8)°
Cu–N(2)	2.02	2.03	N(1)–Cu–N(1')	93.2	93.2
Cu–O(4)	2.57	2.52	N(2)–Cu–N(2')	94.3	93.5
Cu–O(4')	3.34	3.52	O(4)–Cu–N(1)	85.7	86.8
			O(4)–Cu–N(2)	90.9	89.7
			O(4)–Cu–O(4')	177.8	179.2

(b) Those which involve the XO_4 ion:

X–O(1)	1.47 (1) Å	1.63 (1) Å	O(1)–X–O(2)	111.8 (8)°	110.5 (8)°
X–O(2)	1.44	1.62	O(1)–X–O(3)	108.6	108.9
X–O(3)	1.48	1.64	O(2)–X–O(3)	109.0	109.8
			O(3)–X–O(3')	110.0	108.8

(c) Those which involve the amine group:

N(1)–N(1')	2.94 (2) Å	2.94 (2) Å	Cu–N(1)–C(1)	122.5 (1.2)°	121.8 (1.2)°
N(2)–N(2')	2.97	2.95	Cu–N(2)–C(2)	120.9	121.5
N(1)–C(1)	1.49	1.48	N(1)–C(1)–C(3)	113.1	112.8
N(2)–C(2)	1.47	1.49	N(2)–C(2)–C(4)	112.7	110.2
C(1)–C(3)	1.50	1.51	C(3)–C(1)–C(3')	114.2	112.8
C(2)–C(4)	1.49	1.51	C(4)–C(2)–C(4')	114.1	113.1

(d) Those which involve hydrogen bonds:

N(1)–O(3)	3.02 (2) Å	3.02 (2) Å	O(3)–N(1)–O(2)	111.6 (1.2)°	111.1 (1.2)°
N(1)–O(2)	2.89	2.89	O(1)–N(2)–O(3)	109.7	109.4
N(2)–O(1)	2.91	2.91			
N(2)–O(3)	3.00	3.03			
O(4)–O(3)	2.78	2.79	O(3)–O(4)–O(3')	117.2	114.3

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The Crystal and Molecular Structure of 2-Methylpseudourea Hydrochloride, $[(\text{NH}_2)_2\text{COCH}_3]^+\text{Cl}^-$

BY J. C. B. WHITE* AND S. A. MASON

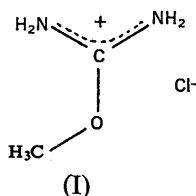
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The crystal structure of 2-methylpseudourea hydrochloride, $[(\text{NH}_2)_2\text{COCH}_3]^+\text{Cl}^-$, has been determined by the heavy-atom method and refined by the least-squares procedure to a final R value of 0.107. The space group is $P2_12_12_1$ and the cell dimensions are $a=9.43$, $b=11.16$, $c=5.00$ Å. A total of 681 unique intensities were obtained from visually estimated photographic data collected about two axes. Corrected bond lengths of 1.32 Å for C–O and 1.32, 1.35 Å (all ± 0.01 Å) for C–N were deduced. The cations are approximately planar and are linked *via* the chloride ions to form a three-dimensional hydrogen-bonded network, with N–H...Cl distances of 3.17, 3.22, 3.24 and 3.40 Å.

Introduction

The structure of 2-methylpseudourea hydrochloride (I)



has been determined as part of an investigation of amide and amide-like cations. The position of the mobile hydrogen atom in these cations was vigorously disputed in the chemical literature for over a decade; almost all the physico-chemical techniques that could be applied to the problem were used, and conflicting conclusions were drawn from much of the resulting information (see the review by Jones & Katritzky, 1961). Finally low-temperature nuclear magnetic resonance studies provided conclusive evidence for protonation at the oxygen atom rather than at the nitrogen atom (Gillespie & Birchall, 1963), and thus established the struc-

tures in principle but not in detail. To provide more precise information on the structures of these cations, a series of structures of amide and related cations is being determined. The crystal structures of urea nitrate and 2-hydroxypyridinium chloride have also been solved.

Experimental

The method of Brown & Hoerger (1954) was used to obtain methylisourea picrate which was then suspended in benzene, and the mixture shaken with concentrated hydrochloric acid. The aqueous phase was then evaporated, and the resulting solid 2-methylpseudourea hydrochloride was recrystallized from an ethanol/acetone mixture. Analysis showed C=21.53, H=6.33, N=25.01, Cl=32.9%. Calculated values for $\text{C}_2\text{H}_7\text{N}_2\text{OCl}$ are C=21.72, H=6.38, N=25.35, Cl=32.12%.

The crystals obtained were needles belonging to the orthorhombic system, and elongated along the c axis. Systematic absences on Weissenberg photographs were $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd, indicating uniquely the space-group $P2_12_12_1$. The axial lengths, determined from Pt-calibrated Weissenberg photographs, are $a=9.43$ (0.02), $b=11.16$ (0.02), $c=5.00$ (0.03) Å. The error estimates given are probably

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