Short Communications

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The crystal structure of urea nitrate. By S. HARKEMA and D. FEIL, *Department of Chemical Technology, Technische Hogeschool Twente, Enschede, The Netherlands*

The structure of urea nitrate has been solved, by the use of three-dimensional X-ray data. Data were collected using Cu $K\alpha$ and Mo $K\alpha$ radiations. The structure consists of layers with urea and nitrate groups held together by hydrogen bonds. The positions of all hydrogen atoms were found. The final R values for Cu and Mo measurements are 4·8% and 6·2% respectively. The agreement between the two sets of data is good.

Introduction

The position of the extra proton in the (thio)urea cation has been the subject of many contradictory publications. There are two possibilities for the structure: one in which the proton is attached to the oxygen atom and another in which the proton is bonded to one of the nitrogen atoms in urea. Attempts to locate the extra proton have been carried out by means of infrared spectroscopy (Davies & Hopkins, 1957; Janssen, 1961) but no unanimous conclusion could be drawn. To clarify this situation we started the determination of the crystal structure of thiourea nitrate (Feil & Song Loong, 1968) and urea nitrate.

Experimental

Crystals of urea nitrate were prepared by cooling a saturated solution of urea nitrate in methanol. The transparent crystals were extremely soft and flexible and great care had to be taken in handling them. Data were collected on a Nonius automatic diffractometer at room temperature. Reflexions of two crystals were measured, one with nickel-filtered Cu $K\alpha$ radiation ($\theta \le 55°$) and the other with zirconium-filtered Mo $K\alpha$ radiation ($\theta \le 25°$). With Cu radiation 628 reflexions were measured of which 26 were below the threshold value for an observed reflexion. These numbers are 906 and 253 respectively for Mo radiation.

The space group of the crystal is $P2_1/c$ as found by earlier workers (Lonsdale, 1940). The cell dimensions and their standard deviations are: $a = 9·527 \pm 0·007$, $b = 8·203 \pm 0·005$ and $c = 7·523 \pm 0·006$ Å; $\beta = 124·37 \pm 0·05°$. With 4 molecules in the unit cell the calculated density is 1·68 g.cm^{-3}. The experimental value is 1·69 g.cm^{-3} (Lonsdale, 1940). Apart from the systematic absences due to the space group symmetry the reflexions $0kl$ with $k = 2n + 1$ are extremely weak.

Structure determination

A three-dimensional Patterson synthesis was calculated. All peaks in this synthesis occurred at $z/c = 0·0$ and $z/c = 0·5$ indicating that the compound has a layer structure with layers parallel to the xy plane. From the fact that the $0kl$ reflexions for $k = 2n + 1$ are very weak it can be concluded that the z/c coordinates of all atoms in the unit cell should be near to 0·25 or 0·75.

Inspection of sharpened Patterson maps suggested some trial structures, one of which gave rather good agreement with experiment using only low-order reflexions ($R = 20\%$). Calculations up to this point were done with the use of one atomic form factor (that of nitrogen) for all atoms. The difficulty arising now was to distinguish the urea and nitrate groups. Comparison with the structure of thiourea nitrate (Feil & Song Loong, 1968) suggested two possibilities, one of which gave a slightly better comparison with experi-

Table 1. *Final atomic parameters for urea nitrate*

The standard deviation in the last decimal is given in brackets. The deviation given is applicable to all heavy or hydrogen atoms in one column. The neutron diffraction results of Worsham & Busing (1968) are given for comparison.

		x/a			y/b			z/c	
	Cu	Mo	W–B	Cu	Mo	W–B	Cu	Mo	W–B
C	0·1974 (3)	0·1977 (2)	0·1976 (2)	0·5894 (3)	0·5892 (2)	0·5889 (1)	0·2541 (4)	0·2556 (4)	0·2548 (3)
N(1)	0·3119	0·3114	0·3113	0·0827	0·0829	0·0833	0·2543	0·2545	0·2541
N(2)	0·3333	0·3338	0·3345	0·6237	0·6238	0·6233	0·2611	0·2609	0·2612
N(3)	0·1009	0·1012	0·1013	0·7042	0·7038	0·7040	0·2537	0·2535	0·2542
O(1)	0·3522	0·3518	0·3525	0·2273	0·2275	0·2273	0·2499	0·2492	0·2500
O(2)	0·1870	0·1871	0·1883	0·0542	0·0543	0·0540	0·2597	0·2601	0·2608
O(3)	0·3970	0·3968	0·3964	0·9708	0·9705	0·9708	0·2512	0·2514	0·2513
O(4)	0·1493	0·1494	0·1501	0·4397	0·4387	0·4395	0·2481	0·2483	0·2489
H(1)	0·387 (3)	0·396 (3)	0·4077 (4)	0·545 (4)	0·547 (3)	0·5376 (3)	0·253 (4)	0·257 (5)	0·2565 (6)
H(2)	0·381	0·377	0·3668	0·739	0·738	0·7416	0·268	0·282	0·2654
H(3)	0·133	0·139	0·1299	0·832	0·828	0·8234	0·253	0·250	0·2563
H(4)	0·013	0·006	−0·0024	0·683	0·682	0·6724	0·252	0·246	0·2483
H(5)	0·220	0·231	0·2286	0·349	0·357	0·3561	0·254	0·256	0·2515

mental results. Ultimately the position of the hydrogen atoms confirmed the correctness of the structure chosen.

The Cu data were refined first. The refinement was done by a modification of the *ORFLS* program (Busing, Martin & Levy, 1962). The weight for each reflexion was taken to be $w=1/\sigma^2$, where σ is the standard deviation of the structure factor. The σ was taken $\sigma=2S+0.01|F_o|$, where S is the standard deviation due to counting statistics and F_o is the observed structure factor. The function minimized was $w(|F_o|-1/s|F_c|)^2$ where F_c is the calculated structure factor and s is a scaling factor.

Refinement of the positions and isotropic temperature factors of the heavy atoms resulted in an R value of 15·4%. A difference-Fourier synthesis made at this stage clearly revealed the hydrogen atoms. A few cycles of refinement were then done with the temperature factors of the heavy atoms in anisotropic form. The R index dropped to 7·7%.

Inclusion of the hydrogen atoms and some cycles of refinement, in which positions and anisotropic temperature factors for the heavy atoms together with positions and isotropic temperature factors of the hydrogen atoms were refined, gave a final R value of 4·8%. In the last stages of refinement 9 strong reflexions were omitted.

The Mo data were then refined, starting with the parameters obtained from the refinement of the Cu data. After a few cycles of refinement the R index was 6·2%.

At this stage of the investigation, the publication of a paper (Worsham & Busing, 1969), giving the results of a structure determination of urea nitrate by means of neutron diffraction was announced. It is interesting to compare the results of these two independent determinations of the same structure. For convenience of comparison we transformed the y coordinates of the atoms in Worsham & Busing's paper, so that their unit cell agreed with ours.

The final positional parameters are given in Table 1. The labelling of the atoms is in accordance with the labelling in the paper of Worsham & Busing. Table 2 gives the final vibration parameters. The most important bond lengths and angles are listed in Tables 3 and 4 respectively.

Table 3. *Bond distances* (Å)

	Cu	Mo	W–B
N(1)–O(2)	1·235 (3)	1·231 (3)	1·227 (1)
N(1)–O(3)	1·234	1·238	1·236
N(1)–O(1)	1·253	1·255	1·250
C —O(4)	1·302	1·307	1·298
C —N(3)	1·315	1·309	1·315
C —N(2)	1·297	1·306	1·312
O(4)–H(5)	0·99 (4)	1·00 (4)	1·006 (3)
N(3)–H(4)	0·85	0·89	1·000
N(3)–H(3)	1·10	1·09	1·014
N(2)–H(1)	0·85	0·87	1·005
N(2)–H(2)	1·04	1·00	1·013
N(3)–O(2′)	2·955 (4)	2·957 (4)	2·969 (2)
N(3)–O(2″)	2·980	2·983	2·981
N(2)–O(3)	2·921	2·916	2·920
N(2)–O(3′)	2·907	2·906	2·904
O(1)–O(4)	2·597	2·589	2·596

Discussion of the results

The structure of urea nitrate consists of layers of planar groups, parallel to the xy plane. The basic unit in this structure consists of a uronium and nitrate ion bonded by two N–H---O hydrogen bonds. These basic units are concatenated to a chain by short O–H---O bonds. Bonding between two chains is effected by two N–H---O bonds. This study shows clearly that the 'extra' proton is attached to the oxygen atom of the urea molecule.

Table 2. *Vibration parameters*

The temperature factor for the heavy atoms was

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots)\right].$$

The temperature factor for the hydrogen atoms was

$$\exp\left[-(B\sin^2\theta/\lambda^2)\right].$$

	U_{11} Cu	Mo	W–B	U_{22} Cu	Mo	W–B	U_{33} Cu	Mo	W–B
C	0·0388 (13)	0·0348 (11)	0·0291 (5)	0·0327 (12)	0·0215 (9)	0·0181 (4)	0·0392 (18)	0·0379 (15)	0·0409 (9)
N(1)	0·0363	0·0360	0·0313	0·0252	0·0218	0·0174	0·0465	0·0509	0·0468
N(2)	0·0356	0·0360	0·0363	0·0361	0·0283	0·0238	0·0623	0·0623	0·0597
N(3)	0·0391	0·0379	0·0366	0·0320	0·0225	0·0211	0·0703	0·0697	0·0629
O(1)	0·0626	0·0604	0·0501	0·0293	0·0164	0·0188	0·0931	0·0949	0·0857
O(2)	0·0492	0·0499	0·0488	0·0392	0·0310	0·0259	0·1035	0·1035	0·1077
O(3)	0·0467	0·0457	0·0404	0·0276	0·0215	0·0211	0·0767	0·0759	0·0714
O(4)	0·0448	0·0445	0·0398	0·0269	0·0191	0·0181	0·0712	0·0752	0·0670
H(1)	4·6 (7)	4·3 (7)							
H(2)	7·3	8·2							
H(3)	6·7	7·8							
H(4)	2·0	3·4							
H(5)	5·1	5·5							

	U_{12} Cu	Mo	W–B	U_{13} Cu	Mo	W–B	U_{23} Cu	Mo	W–B
C	0·0023 (10)	0·0033 (8)	−0·0013 (4)	0·0210 (13)	0·0208 (11)	0·0227 (7)	0·0000 (12)	−0·0015 (10)	−0·0018 (4)
N(1)	−0·0023	−0·0033	−0·0003	0·0250	0·0284	0·0262	−0·0018	0·0018	−0·0008
N(2)	−0·0013	0·0000	−0·0013	0·0339	0·0360	0·0344	−0·0021	−0·0005	0·0000
N(3)	0·0013	0·0000	0·0010	0·0381	0·0376	0·0338	−0·0033	−0·0026	−0·0036
O(1)	−0·0023	−0·0039	−0·0023	0·0551	0·0559	0·0502	−0·0018	−0·0005	−0·0018
O(2)	0·0023	−0·0020	0·0007	0·0554	0·0576	0·0574	0·0031	0·0003	0·0010
O(3)	0·0046	0·0039	0·0013	0·0410	0·0418	0·0401	−0·0003	−0·0010	−0·0005
O(4)	−0·0033	−0·0039	−0·0029	0·0363	0·0391	0·0356	−0·0021	−0·0026	−0·0023

Table 4. *Bond angles* (°)

	Cu	Mo	W–B
O(2)–N(1)–O(1)	119·6 (3)	119·9 (3)	120·4 (1)
O(2)–N(1)–O(3)	121·1	120·9	120·5
O(1)–N(1)–O(3)	119·3	119·2	119·0
O(4)–C —–N(3)	116·3	116·7	116·6
O(4)–C —–N(2)	122·0	121·7	121·7
N(3)–C —–N(2)	121·7	121·5	121·7
C —–O(4)–H(5)	119 (4)	113 (4)	113·6 (2)
C —–N(3)–H(4)	123	122	119·1
C —–N(3)–H(3)	119	115	120·8
C —–N(2)–H(1)	117	121	123·1
C —–N(2)–H(2)	127	122	119·1
H(1)–N(2)–H(2)	116 (6)	117 (6)	117·8
H(4)–N(3)–H(3)	118	122	120·1

The bond lengths found in urea nitrate are significantly different from the distances found in the urea molecule (Worsham, Levy & Peterson, 1957). The C–O and C–N distances in urea are 1·243(6) and 1·351(7) Å respectively. It is seen that the C–O distance is lengthened and the C–N distance is shortened when the O atom becomes protonated. Another interesting feature is the large difference in the two O–C–N bond angles in the uronium ion. These effects have also been found in thiourea nitrate (Feil & Song Loong, 1968).

The nitrate group has two short and one long N–O distance. The longer one concerns the oxygen atom involved in the strongest hydrogen bond. In thiourea nitrate two long and one short N–O distance have been found. The oxygen atoms in the long bonds are involved in H-bonding, the short distance oxygen atom is not. The effect of appreciable hydrogen bonding seems to be to stretch the N–O distances.

Inspection of the Tables reveals that differences in the final position parameters of the two sets of measurements (Cu and Mo) are not significant. Comparing our results with those of Worsham & Busing shows that in general the difference in the position parameters is not significant. Differences in vibration parameters, however, are considerable. We believe the neutron results to be more reliable as it is well known that the thermal parameters in an X-ray refinement act as a dustbin for all sorts of errors: no correction for absorption, the use of the wrong atom-factors, neglect of bonding electrons *etc*. The importance of these bonding electrons was shown by the final difference-Fourier synthesis where maxima between atoms showed up clearly. In order to study this effect more carefully, we have started a structure determination at low temperatures.

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X-ray powder data, infrared spectra and crystal structures of some bis(selenourea)metal(II) thiocyanates.

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M[XC(NH$_2$)$_2$] (NCS)$_2$ with M = Co, Ni, Cd and X = S, Se, form an isostructural series. The structure is polymeric and consists of chains of coordination octahedra linked together by sulphur (or selenium) bridges; the NCS groups are terminal and *trans*-coordinated to metal through the nitrogen atoms.

As a general rule, substitution of selenium for sulphur in a family of compounds gives isostructural crystals*. This is seldom observed, however, in passing from oxygen to

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* One case in which this rule is not observed concerns bis(thiourea)CoCl$_2$ and bis(selenourea)CoCl$_2$ prepared by Piovesana & Furlani (1968); the first compound is monoclinic (Co[SC(NH$_2$)$_2$]$_2$Cl$_2$: $a = 8·13(2)$, $b = 11·78(1)$, $c = 10·79(1)$ Å, $\beta = 103·5°(0·1°)$, $Z = 4$, space group: Cc; the crystals are piezoelectric) the second triclinic (Co[SeC(NH$_2$)$_2$]$_2$Cl$_2$: $a = 6·08(1)$, $b = 7·22(3)$, $c = 13·86(2)$ Å, $\alpha = 100·7°(0·3°)$, $\beta = 90·2°(0·1°)$, $\gamma = 108·4°(0·1°)$, $Z = 2$); their structures are being studied in our laboratory at present.

sulphur compounds and this behaviour is accounted for by the difference of size, S and Se being smaller than O and S, and by the possibility that selenium and sulphur have to expand their valence shell, using d orbitals in bonding. According to this rule isostructurality is observed for the series of compounds of general formula M[XC(NH$_2$)$_2$]$_2$(NCS)$_2$ with M = Co,Ni,Cd and X = S,Se. Crystal data from a least-squares procedure applied to powder diffractometer spectra (Cu $K\alpha$) are shown in Table 1 in which the interpretation of the spectra is also given.

The structure of these compounds, already determined for bis(thiourea)nickel(II) thiocyanate (Nardelli, Braibanti