X-ray powder diffraction data for bis (1-amidino-2-ethylisourea) copper(II) nitrate

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X-ray powder diffraction data, unit-cell parameters and space group for $C_8H_{20}CuN_{10}O_8$ are presented [$a = 5.262$ (2) Å, $b = 14.051$ (3) Å, $c = 12.183$ (3) Å, $\beta = 96.912$ (5)°, unit-cell volume $V = 894.3$ Å^3, $Z = 2$, space group $P2_1/n$]. All measured lines were indexed and are consistent with the $P2_1/n$ space group. No detectable impurities were observed. © *2013 International Centre for Diffraction Data*. [doi:10.1017/S0885715613000353]

Key words: X-ray powder diffraction, pyrotechnic, automobile safety systems

I. INTRODUCTION

Bis (1-amidino-2-ethylisourea) copper(II) nitrate belongs to complexes which may be suggested to be part of pyrotechnics compositions for inflating automobile safety systems, namely airbags and seatbelt pretensioners (Zigmund *et al.*, 2012) and (Jalový *et al.*, 2011). The main reason to use these complexes is to replace sodium azide and double-base propellants (based on nitrocellulose) in gas-generating mixtures. The use of sodium azide causes problems from many aspects: it is itself highly toxic, in neutral or acidic solutions it releases the very poisonous and volatile hydrazoic acid, it is a broad-spectrum biocide with an as yet unknown environmental fate and thus it has been criticized from many points of view (Betterton, 2003), (Hambrook and Fink, 2006) and (Chang and Lamm, 2003). Also, sodium azide, as a major part of safety pyrotechnics devices, causes problems during recycling of vehicles and the handling of highly toxic waste. As for double-base propellants, based on nitrocellulose, they are excellent propellants (Blomquist, 2002) and (Gottwald, 2009), but long-term stability and toxic gaseous products (containing nitrogen oxides and carbon monoxide) have limited its application in recent years.

The presented complex shown in Figure 1 is formed by ion pairs of doubly chelated copper metal center by two neutral ligands and two nitrate anions out of the primary coordination sphere of the metal atom.

We have inspected CSD database (Allen, 2002) for the compound summary formula and found the crystal structure data for this organic substance $C_8H_{20}CuN_{10}O_8$ (Meenongwa *et al.*, 2009). The compound is monoclinical [$a = 5.2547(6)$ Å, $b = 14.0087(15)$ Å, $c = 12.1511$ (13) Å, $\beta = 96.982$ (2)°, unit-cell volume $V = 887.83$ (17) Å^3, $Z = 2$, space group $P2_1/n$, and $T = 293$ K]. The calculated powder pattern of this compound is in very good agreement with the measured powder pattern presented in this article.

II. EXPERIMENTAL

A. Synthesis

The title compound was prepared by dissolving of bis (cyanoguanidine) copper(II) nitrate in ethanol and heating of the solution under reflux for two hours. The starting bis(cyanoguanidine) copper(II) nitrate was prepared by heating under reflux of stoichiometric amounts of cyanoguanidine and copper nitrate trihydrate for two hours in ethyl acetate (Jalový *et al.*, 2012).

B. Specimen preparation

The sample was prepared by careful grinding in an agate mortar and front-loaded into the specimen holder.

C. Diffraction data collection and reduction

The diffraction pattern for the title compound was collected at room temperature with an X'Pert PRO θ-θ powder diffractometer with parafocusing Bragg-Brentano geometry using Cu$K\alpha_1$ radiation ($\lambda = 1.5406$ Å, Ni filter, generator setting: 40 kV, 30 mA). An ultrafast X'Celerator detector was employed to collect XRD data over the angular range from 4 to 70°2θ with a step size of 0.017°2θ and a counting time of 81.28 s step^{-1}.

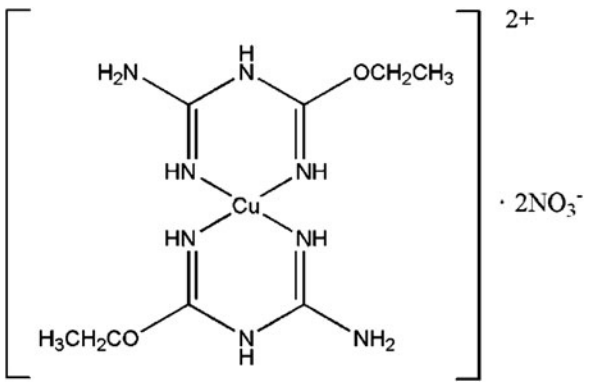


Figure 1. Structural formula $C_8H_{20}CuN_{10}O_8$-ethanol

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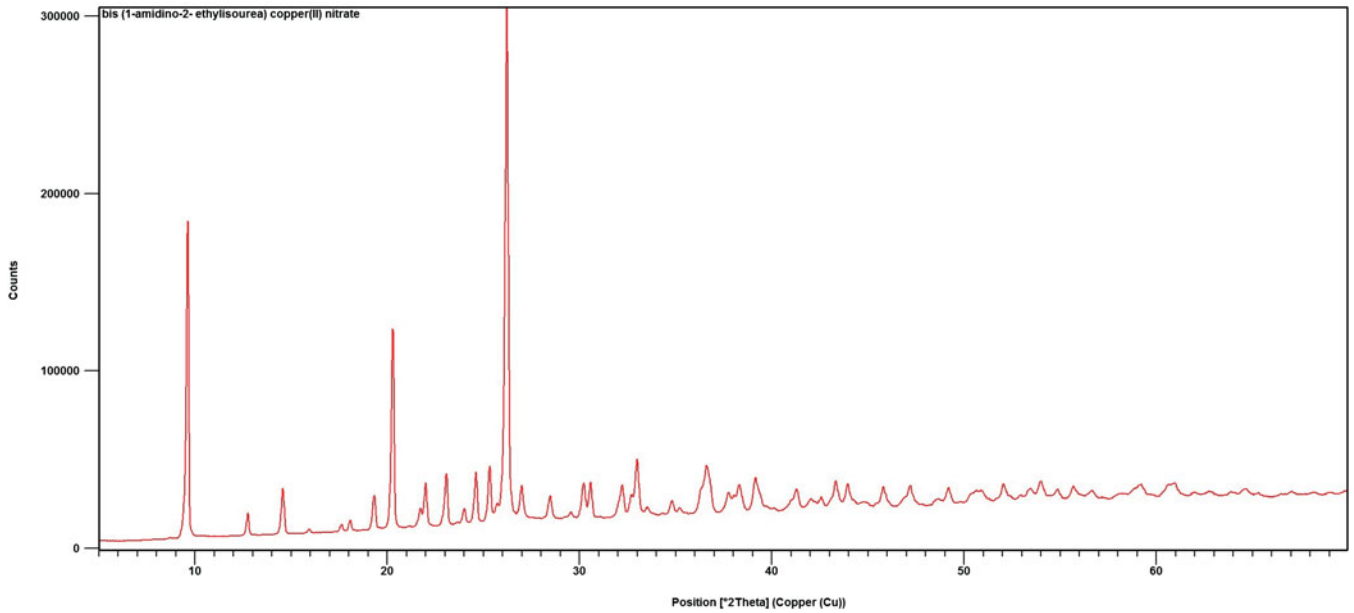


Figure 2. (Colour online) X-ray powder diffraction pattern of $C_8H_{20}CuN_{10}O_8$-ethanol

The software package HIGHSCORE PLUS V 3.0e (PANalytical, Almelo, Netherlands) was used to smooth the data, to fit the background, to eliminate the $K\alpha_2$ component, and the top of the smoothed peak method was used to determine the peak positions and intensities of the diffraction peaks (Table I).

III. RESULTS AND DISCUSSION

The experimental powder diffraction pattern is depicted in Figure 2. Automatic indexing of results obtained using DICVOL04 (Boultif and Louër, 2004) show that title compound $C_8H_{20}CuN_{10}O_8$ is monoclinical with space group $P2_1/n$ and

TABLE I. Indexed X-ray powder diffraction data for $C_8H_{20}CuN_{10}O_8$. Only the peaks with I_{rel} of 1 or greater are presented [$a = 5.262$ (2) Å, $b = 14.051$ (3) Å, $c = 12.183$ (3) Å, $\beta = 96.912$ (5)°, unit-cell volume $V = 894.3$ Å^3, $Z = 2$, space group $P2_1/n$]. All lines were indexed and are consistent with the $P2_1/n$ space group. The d-values were calculated using Cu$K\alpha_1$ radiation ($\lambda = 1.5406$ Å).

$2\theta_{obs}$ (deg)	d_{obs} (Å)	I_{obs}	h	k	l	$2\theta_{cal}$ (deg)	d_{calc} (Å)	$\Delta 2\theta$
9.615	9.191	61	0	1	−1	9.641	9.167	−0.025
12.747	6.939	4	0	2	0	12.590	7.025	0.086
14.561	6.079	9	0	2	−1	14.569	6.075	−0.004
17.620	5.030	2	1	0	−1	17.651	5.021	−0.009
18.070	4.905	2	1	1	0	18.103	4.896	−0.009
19.318	4.591	7	1	0	1	19.287	4.598	0.007
20.282	4.375	39	1	1	1	20.304	4.370	−0.005
21.719	4.089	4	1	2	−1	21.740	4.085	−0.004
21.992	4.039	9	1	1	−2	22.014	4.035	−0.004
23.071	3.852	10	1	2	1	23.098	3.848	−0.004
24.000	3.705	3	0	3	2	24.013	3.703	−0.002
24.610	3.615	10	1	2	−2	24.624	3.612	−0.002
25.320	3.515	11	0	4	0	25.335	3.513	−0.002
25.713	3.462	4	1	3	0	25.523	3.487	0.025
26.213	3.397	100	1	0	−3	26.225	3.395	−0.002
26.986	3.301	7	1	1	−3	26.994	3.300	−0.001
28.466	3.133	5	1	3	−2	28.477	3.132	−0.001
29.537	3.022	2	1	0	3	29.549	3.021	−0.001
30.207	2.956	7	0	1	−4	30.210	2.956	0.000
30.567	2.922	7	1	3	2	30.580	2.921	−0.001
32.018	2.793	7	1	4	1	32.037	2.791	−0.002
32.212	2.777	7	0	2	4	32.204	2.777	0.001
32.701	2.736	5	0	5	−1	32.689	2.737	0.001
32.987	2.713	11	1	1	−4	32.988	2.713	0.000
34.799	2.576	3	2	1	−1	34.818	2.575	−0.001
35.186	2.549	2	0	5	−2	35.187	2.548	0.000
36.322	2.471	5	2	1	−2	36.325	2.471	0.000
36.602	2.453	9	2	1	1	36.594	2.454	0.001

Continued

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TABLE I. Continued

$2\theta_{obs}$ (deg)	d_{obs} (Å)	I_{obs}	h	k	l	$2\theta_{cal}$ (deg)	d_{calc} (Å)	$\Delta 2\theta$
36.792	2.441	6	1	4	−3	36.785	2.441	0.000
37.747	2.381	4	1	3	−4	37.749	2.381	0.000
38.025	2.365	3	2	2	−2	38.035	2.364	−0.001
38.299	2.348	6	2	2	1	38.293	2.349	0.000
39.145	2.299	7	2	0	2	39.148	2.299	0.000
39.389	2.286	4	2	3	−1	39.387	2.286	0.000
41.014	2.199	2	1	3	4	41.016	2.199	0.000
41.275	2.186	4	2	2	2	41.282	2.185	0.000
42.020	2.149	2	0	3	−5	42.005	2.149	0.001
42.559	2.123	2	1	6	−1	42.564	2.122	0.000
43.044	2.100	5	2	4	−1	43.046	2.100	0.000
43.321	2.087	5	1	6	1	43.324	2.087	0.000
43.943	2.059	5	0	5	4	43.952	2.058	0.000
44.934	2.016	1	0	0	6	44.932	2.016	0.000
45.790	1.980	4	0	7	−1	45.785	1.980	0.000
46.855	1.937	2	0	2	−6	46.850	1.938	0.000
47.191	1.924	4	2	4	2	47.208	1.924	−0.001
48.603	1.872	1	2	5	−2	48.593	1.872	0.000
49.187	1.851	4	1	6	3	49.191	1.851	0.000
50.345	1.811	2	1	7	−2	50.315	1.812	0.001
50.612	1.802	3	1	4	5	50.586	1.803	0.001
50.870	1.794	3	1	1	6	50.852	1.794	0.001
52.044	1.756	4	0	8	0	52.026	1.756	0.001
52.920	1.729	2	3	1	0	52.944	1.728	−0.001
53.432	1.713	3	1	4	−6	53.458	1.713	−0.001
53.987	1.697	4	2	0	−6	53.967	1.698	0.001
54.843	1.673	3	0	7	−4	54.854	1.672	0.000
55.686	1.649	3	2	6	−3	55.683	1.649	0.000
56.629	1.624	2	1	7	−4	56.615	1.624	0.000
58.116	1.586	1	1	0	7	58.173	1585	−0.001
58.839	1.568	6	2	7	−2	58.859	1.568	0.000
59.178	1.560	3	1	8	−3	59.179	1.560	0.000
60.615	1.526	3	3	4	1	60.610	1.527	0.000
60.933	1.519	3	2	1	−7	60.934	1.519	0.000
61.968	1.496	1	1	9	0	61.990	1.496	0.000
62.740	1.480	1	3	5	0	62.720	1.480	0.000
63.853	1.457	1	3	3	3	63.844	1.457	0.000
64.492	1.444	2	1	4	7	64.458	1.444	0.001
64.637	1.441	2	1	9	2	64.651	1.441	0.000
9.213	9.5912	100	1	1	−1	9.219	9.5846	0.006
13.489	6.5591	9	2	0	−2	13.484	6.5613	−0.005
14.296	6.1906	5	1	2	−1	14.303	6.1874	0.008
14.898	5.9417	2	2	1	−2	14.893	5.9437	−0.005
16.698	5.3051	1	2	0	1	16.703	5.3035	0.005
18.504	4.7911	7	2	2	−2	18.499	4.7923	−0.005
20.138	4.4059	17	1	3	−1	20.138	4.4060	0.000
20.351	4.3602	16	0	1	−3	20.353	4.3597	0.002
20.977	4.2316	1	2	2	1	20.980	4.2309	0.004
23.156	3.8380	6	0	2	3	23.149	3.8392	−0.007
23.534	3.7772	35	4	0	−1	23.524	3.7789	−0.010
24.411	3.6435	3	3	0	−4	24.381	3.6478	−0.029
24.519	3.6276	3	1	1	−4	24.525	3.6268	0.005
25.365	3.5086	4	0	4	0	25.368	3.5082	0.003
26.936	3.3074	3	1	2	−4	26.912	3.3103	−0.024
27.133	3.2839	2	3	3	0	27.126	3.2846	−0.006
27.938	3.1910	4	1	4	−2	27.938	3.1910	0.000
29.600	3.0155	13	5	1	−2	29.572	3.0183	−0.028
30.524	2.9263	4	2	4	1	30.528	2.9260	0.004
31.802	2.8116	1	2	2	−5	31.774	2.8140	−0.028
32.605	2.7441	2	1	5	−1	32.601	2.7445	−0.004
34.867	2.5711	3	4	4	−1	34.868	2.5710	0.002
36.217	2.4783	2	1	5	2	36.203	2.4792	−0.014
39.130	2.3003	1	5	4	−3	39.117	2.3010	−0.013
39.298	2.2908	1	5	3	−5	39.333	2.2888	0.035
40.957	2.2017	1	1	3	5	40.973	2.2009	0.016
43.412	2.0828	2	0	6	−3	43.395	2.0835	−0.017

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unit-cell parameters: $a = 5.262$ (2) Å, $b = 14.051$ (3) Å, $c = 12.183$ (3) Å, $\beta = 96.912$ (5)°, unit-cell volume $V = 894.3$ Å^3, and $Z = 2$. The figures of merits are $F_{20} = 20.1(0.012381)$ (Smith and Snyder, 1979) and $M_{20} = 13.0$ (de Wolff, 1968). All measured lines were indexed and are consistent with the $P2_1/n$ space group.

Unit cell parameters from single crystal data at 293 K (Meenongwa *et al.*, 2009) display a slight shortening with respect to unit cell parameters derived from powder data at the same temperature at 293 K (this article).

SUPPLEMENTARY MATERIALS AND METHODS

Supplementary material accompanies this paper on the journals website (http://journals.cambridge.org/pdj).

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Allen, F. H. (**2002**). "The Cambridge structural database: a quarter of a million crystal structures and rising," Acta Cryst. **B58**, 380–388.

Betterton, E. A. (**2003**). "Environmental fate of sodium azide derived from automobile airbags," Crit. Rev. Environ. Sci. Technol. **33**, 423–458.

Blomquist, H. (**2002**). US 2002084010.

Boultif, A. and Louër, D. (**2004**). "Powder pattern indexing with the dichotomy method," J. Appl. Crystallogr. **37**, 724–731.

Chang, S. and Lamm, S. H. (**2003**). "Human health effects of sodium azide exposure: a literature review and analysis," Int. J. Toxicol. **22**, 175–186.

de Wolff, P. M. (**1968**). "A simplified criterion for the reliability of a powder pattern," J. Appl. Crystallogr. **1**, 108–113.

Gottwald, W. (**2009**). CA 2652645.

Hambrook, D. W. and Fink, J. N. (**2006**). "Airbag asthma: a case report and review of the literature," Ann. Allergy Asthma Immunol. **96**, 369–372.

Jalový, Z., Matyáš, R., Zigmund, J., and Lorenc, S. (**2011**). Use of Amidinoisourea Complex Compounds as Fuel for Pyrotechnic Compositions, and the Pyrotechnic Composition for Passive Safety Systems. Czech Utility Model CZ 22614.

Jalový, Z., Padělková, Z., Jirásko, R., Matyáš, R., Holčapek, M., Němec, O., Novotná, M., and Mišková, L. (**2012**). "Syntheses, crystal structures and properties of copper(II) complexes of 1-amidinoisourea and biguanide nitrates," Polyhedron **44**, 88–100.

Meenongwa, A., Chaveeracha, U., and Pakawatchaib, Ch. (**2009**). "Bis(1-carbamimidoyl-2-ethyl-isourea)-copper(II) dinitrate," Acta Crystallogr. **E65**, m1389–m1390.

Smith, G. S. and Snyder, R. L. (**1979**). "F_N: a criterion for rating powder diffraction patterns and evaluating the reliability of powder indexing," J. Appl. Crystallogr. **12**, 60–65.

Zigmund, J., Matyáš, R., Jalový, Z., and Šelešovský, J. (**2012**). Pyrotechnical composition for safety systems of passive protection, particularly for use in airbag or safety belt pretensioner. CZ 303225.

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