

The Crystal Structure, Thermal Behaviour and IR Spectrum of Copper Tetraammine Dithionate

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$\text{Cu}(\text{NH}_3)_4\text{S}_2\text{O}_6$ crystals were obtained from ammoniacal copper acetate solution which had been saturated with sulfur dioxide. The compound was characterized by chemical and thermal analyses and IR spectra and the crystal structure was determined from three-dimensional X-ray diffraction data. The dithionate crystallizes in the monoclinic space group $P2_1/c$ (No. 14). The cell parameters are $a = 7.148(2)$, $b = 10.604(3)$, $c = 11.675(3)$ Å, $\beta = 145.12(1)^\circ$, $Z = 2$. The structure was refined to a final R -value of 5.2 %.

The structure consists of chains formed by Cu-octahedra and dithionate groups. The Cu-atom is six-coordinated by four nitrogen atoms and two oxygen atoms at average distances of 2.05 and 2.62 Å, respectively.

The existence of copper dithionate and copper tetraammine dithionate has been known a long time. In 1926 De Baat prepared copper dithionate from $\text{BaS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.¹ The dithionate ion for $\text{BaS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ was prepared from sulfite solution, which had been oxidized with MnO_2 . This remains one of the standard methods of producing dithionates. A few years later Garreau² prepared $\text{Cu}(\text{NH}_3)_4\text{S}_2\text{O}_6$ from a solution containing $(\text{NH}_4)_2\text{SO}_3$, NH_4OH and $\text{NH}_3\text{Cu}(\text{OH})_2$, showing that in alkaline solution sulfite ion can be oxidized to dithionate ion by air alone.

Although the crystal structures of several simple dithionates^{3–6} and those of some complex ones⁷ have been solved, the structures of copper dithionates have remained unknown. Only the IR and molecular spectrum of these compounds have been measured by Duval and Lecomte.^{8,9}

EXPERIMENTAL

Crystal preparation and analyses. Crystals suitable for X-ray analysis were obtained by dissolving 2 g of copper acetate in 50 ml of distilled water and adding 30 ml of ammonia (25 %). This deep blue solution was saturated with sulfur dioxide by bubbling it through the solution for 1 h. On evaporation of the solution at room temperature dark violet $\text{Cu}(\text{NH}_3)_4\text{S}_2\text{O}_6$ needles were formed. All reactions were carried out in air so that the oxidation could take place.

Elemental analyses were carried out by Novo Microanalytical Laboratory, Novo Industri A/S, DK-2880 Bagsvaerd, Denmark, supervised by Rolf E. Amsler. Found: 21.59 % Cu, 22.29 % S and 19.21 % N. Calc. for $\text{Cu}(\text{NH}_3)_4\text{S}_2\text{O}_6$: 21.77 % Cu, 22.01 % S and 19.20 % N.

The thermal decomposition was investigated in a Mettler thermoanalyzer TA-1 by simultaneous recording of the TG, DTG and DTA curves. The investigations were made both in air and in nitrogen. The flow rate of the gases was 100 cm³/min and the heating rates were 6 °C min⁻¹ and 1 °C min⁻¹. The sample holder was a platinum crucible (diam. 7 mm, depth 19 mm). In DTA measurements alumina was used as reference material.

IR spectrum were measured on a Perkin-Elmer 521 instrument using the KBr pellet technique.

Structure determination. The X-ray intensities were recorded with a Syntex $P2_1$ (Fortran version) automatic four-circle diffractometer employing graphite monochromatized $\text{MoK}\alpha$ -radiation. The unit cell parameters were calculated by least-squares refinement of 24 reflections. The intensities of 1845 independent reflections up to 2θ of 70° were measured and the 1429 reflections with $I > 4\sigma(I)$ were considered significant. The $\theta/2\theta$ scan technique was used and the scan speed was 0.8–3.5°/min. The intensity, I , of each reflection was calculated by subtracting the total background count, BG,

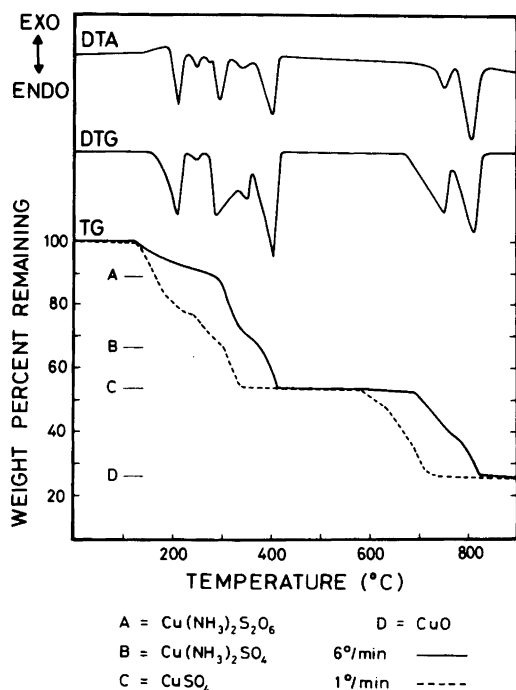


Fig. 1. Thermal decomposition of $\text{Cu}(\text{NH}_3)_4\text{S}_2\text{O}_6$ in air. Sample weight 53 mg.

from the total scan count, SC. The standard deviation, $\sigma(I)$ was obtained from $\sigma(I) = (\text{SC} + \text{BG})^{1/2}$. The values obtained were then multiplied with the scan rate to compensate for the different scan speeds. The net intensities were corrected for Lorentz and polarization effects. Empirical absorption correction were made on the basis of the ϕ -scan data with 9 different 2θ values. The largest measured relative reduction in intensity was from 1.000 to 0.557. The systematic absences in the original intensity data indicated the space group $P2_1/c$ (No. 14). The dimensions of the crystal were ap-

Table 1. Infrared absorption frequencies and their assignments in the region $4000 - 400 \text{ cm}^{-1}$.

Observed frequency	Assignments
3310 s	$\nu_4(\text{NH}_3)$
3220 s	$\nu_1(\text{NH}_3)$
2330 vw	$\nu_7 + \nu_1(\text{S}_2\text{O}_6)$
2200 vw	$\nu_{10} + \nu_5(\text{S}_2\text{O}_6)$
2085 vw	$\nu_1 + \nu_5(\text{S}_2\text{O}_6)$
1620 m	$\nu_5(\text{NH}_3)$
1600 m	$\nu_1 + \nu_8(\text{S}_2\text{O}_6)$
1390 m	$\nu_1 + 290(\text{S}_2\text{O}_6)^a$
1245 vs	$\nu_7(\text{S}_2\text{O}_6), \nu_2(\text{NH}_3)$
1210 s	$\nu_{10}(\text{S}_2\text{O}_6)$
1090 m	$\nu_1(\text{S}_2\text{O}_6)$
995 s	$\nu_5(\text{S}_2\text{O}_6)$
780 m	$\nu_{11} + 204(\text{S}_2\text{O}_6)^a$
700 s	$\nu_6(\text{NH}_3)$
565 vs	$\nu_{11}(\text{S}_2\text{O}_6)$
510 s	$\nu_8(\text{S}_2\text{O}_6)$
420 vw	$\nu_3(\text{NH}_3)$

^a The low frequencies of the $\text{S}_2\text{O}_6^{2-}$ groups are according to Palmer.¹⁵

proximately $1.0 \times 0.5 \times 0.2 \text{ mm}$.

The positions of Cu and S atoms were obtained by direct methods, using the 244 *E*-values larger than 1.4. Solving, refinement and plotting were carried out with the X-RAY SYSTEM 1976.¹⁰ The scattering factors were those of Cromer and Mann for neutral atoms.¹¹ After refinement of the positions of Cu and S atoms the value of *R* was 0.288. The positional parameters of all the oxygens were obtained from the difference Fourier map. The structure was then refined with isotropic temperature factors to an *R*-value of 0.077 and, after block-diagonal refinement with anisotropic temperature factors, to an *R*-value of 0.052. No weighting scheme was used, all intensities had a unit weight. The $|F_o|$ and $|F_c|$ listing is available from the authors upon request.

Table 2. Atomic coordinates and anisotropic temperature coefficients with their estimated standard deviations. The temperature coefficients are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$, and have been multiplied by 10^4 .

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cu	0	0	0	271(5)	232(4)	289(5)	8(4)	240(4)	5(4)
S1	.8638(4)	.0322(1)	.3591(2)	240(6)	280(6)	270(6)	24(5)	209(6)	36(5)
O1	.4161(11)	.5986(5)	.2331(7)	255(21)	381(25)	345(24)	-93(18)	220(21)	-60(19)
O2	.7798(13)	.9161(5)	.2547(7)	442(30)	492(31)	344(26)	35(24)	314(25)	-67(22)
O3	.0899(13)	.1151(5)	.4107(8)	374(27)	571(34)	448(30)	-23(24)	338(27)	136(25)
N1	.8427(15)	.3912(6)	.2877(9)	388(31)	367(29)	338(28)	-25(23)	313(27)	-55(22)
N2	.0830(15)	.6493(5)	.4339(9)	496(36)	284(26)	469(35)	-12(24)	424(32)	26(23)

RESULTS AND DISCUSSION

Thermal analysis. With the heating rate of 6°/min there is first an endothermic reaction in the temperature range 160–230 °C (Fig. 1). The observed weight loss corresponds to two ammonia molecules. In the following stage dithionate decomposes to sulfate and sulfur dioxide is released. Then the two other ammonia molecules are released. At 410 °C there remains only anhydrous copper sulfate, which decomposes as expected in two stages to copper oxide in the temperature range of 690–820 °C. The decomposition was found to proceed similarly in nitrogen atmosphere.

When the heating rate is 1°/min the four ammonia molecules and sulfur dioxide are released in succession so that clear plateaus between the different decomposition stages are not found. As expected, the reactions take place in a temperature range which is 50–80 °C lower than with the higher heating rate.

The results of the thermal analyses correspond well with those obtained by Liptay for zinc tetraammine dithionate.¹²

Infrared analysis. The IR spectrum of copper tetraammine dithionate showed the normal frequencies of the symmetries C_{3v} for NH_3 and D_{3d} for $S_2O_6^{2-}$ (Table 1).^{13–15} Outside the investigated range were the following: S–S stretching at 290 cm^{-1} , SO_3 rocking at 205 cm^{-1} and SO_3-SO_3 torsion at 155 cm^{-1} .¹⁵

Structure analysis. The positional and thermal parameters for nonhydrogen atoms are given in Table 2 and crystal data in Table 3. The Cu atom is

Table 3. Crystal data for $Cu(NH_3)_4S_2O_6$.

Formula	$Cu(NH_3)_4S_2O_6$
Formula weight	291.79
Lattice constants (Å)	$a = 7.148(2)$ $b = 10.604(3)$ $c = 11.675(3)$
(°)	$\beta = 145.12(1)$
Cell volume (Å ³)	$V = 506.1(2)$
Molecules per unit cell	$Z = 2$
Space group	$P2_1/c$ (No. 14)
Density (g cm^{-3})	$D_x = 1.915$
Linear absorption coefficient (cm^{-1})	$\mu(MoK\alpha) = 26.7$

Table 4. Distances (Å) and angles (°) around the Cu atom.

Cu–O1	2.624(5) (*2)	N1–Cu–N2	91.2(4)
Cu–N1	2.041(10) (*2)	O1–Cu–N1	91.6(3)
Cu–N2	2.050(10) (*2)	O1–Cu–N2	94.9(3)

Table 5. Distances (Å) and angles (°) in the dithionate group.

S–O1	1.457(8)	O1–S–O2	114.4(4)
S–O2	1.470(7)	O1–S–O3	113.4(4)
S–O3	1.467(9)	O2–S–O3	113.9(6)
S–S	2.138(4)	S–S–O1	104.9(4)
		S–S–O2	104.2(3)
		S–S–O3	104.7(3)

Table 6. Interatomic S–O and S–S distances in some dithionates.

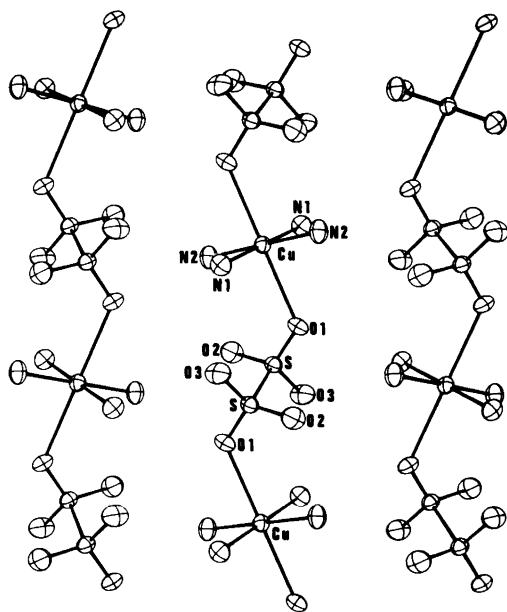
Compound	S–S distances (Å)	S–O distances (Å)	Ref.
$Li_2S_2O_6 \cdot 2H_2O$	2.14	1.447–1.457	4
$Na_2S_2O_6 \cdot 2H_2O$	2.15	1.450–1.463	4
$Na_2S_2O_6 \cdot 2H_2O$	2.141	1.450–1.457	25
$K_2S_2O_6$	2.14–2.15	1.42–1.43	16
$MgS_2O_6 \cdot 6H_2O$	2.123	1.447–1.449	17
$BaS_2O_6 \cdot 2H_2O$	2.15	1.46	5
$NiS_2O_6 \cdot 6H_2O$	2.123	1.446–1.454	17
$ZnS_2O_6 \cdot 6H_2O$	2.127	1.448–1.453	17
$NaK_2ClS_2O_6$	2.08	1.44–1.50	7
$NaK_5Cl_2(S_2O_6)_2$	2.08	1.47–1.49	7
$[(NH_3)_3Co(OH)_3Co(NH_3)_3]_2(S_2O_6)_3$	2.119–2.138	1.441–1.455	19
$(NH_4)_3ClS_2O_6$	2.13–2.16	1.41–1.53	18
$[(Cr(en)_2(OH))_2][S_2O_6]_2$	2.127	1.435–1.460	20
$Cu(NH_3)_4S_2O_6$	2.138	1.457–1.470	This work

Table 7. Interatomic distances between Cu—O and Cu—N atoms in some copper tetraammine compounds.

Compound	Cu—O (Å)	Cu—N (Å)	Ref.
Cu(NH ₃) ₄ SO ₄ ·H ₂ O	2.339(9)	2.031(6)–2.032(6)	21
Cu(NH ₃) ₄ SeO ₄	2.607(7), 2.451(8)	1.992(1)–2.017(9)	21
Cu(NH ₃) ₄ (NO ₃) ₂	2.517(5)–2.706(7)	2.008(5)–2.029(5)	22
Cu(NH ₃) ₄ S ₂ O ₆	2.624(5)	2.041(10)–2.050(10)	Present work

Table 8. Distances (Å) around nitrogen atoms (less than 3.3 Å).

N1—N2	2.863(14)
—N2	2.922(8)
—O3	3.097(8)
—O1	3.279(6)
—O2	3.128(14)
—O3	3.078(8)
N2—O2	2.952(10)
—O1	3.189(14)
—O2	3.105(8)
—O3	3.113(14)

Fig. 2. Perspective drawing showing the chain structure of Cu(NH₃)₄S₂O₆. The x-axis is vertical and the y-axis horizontal.

six-coordinated, of type 4+2; the four nitrogen atoms of the ammine group lie about 2.0 Å from Cu, forming a square planar arrangement around it, while the two oxygen atoms of the dithionate group are situated at a distance of about 2.6 Å (Table 4). The O1 atoms are above and below this plane. The Cu atoms are situated at the centres of symmetry. All distances are quite normal compared with other Cu compounds of the same type (Table 7).

The dithionate group consists of two SO₃ polyhedra connected together centrosymmetrically by an S—S bond of 2.138 Å. The S—O distance is slightly shorter than in sulfites (about 1.5 Å),²³ probably due to the second sulfur atom (Table 5). The distance between the sulfur atoms is longer than usual (about 2.06)²⁴ but this is observed in all dithionates (Table 6).

The structure consists of chains formed by dithionate and copper atoms (Fig. 2). These Cu—O1—S—S—O1—Cu chains are perpendicular to the yz-plane and are joined together by hydrogen bonds to ammine groups. Hydrogen atoms could not be located but the possible hydrogen bond distances listed in Table 8 are in good agreement with the distances given for Cu(NH₃)₄SO₄·H₂O and Cu(NH₃)₄SeO₄²¹ and Cu(NH₃)₄(NO₃)₂.²²

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