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On Ammonium-bis(dithiocarbamato)-copper(I)-monohydrate and Mono(dithiocarbamato)-copper(I)

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Dedicated to Professor Wolfgang Bensch on the Occasion of His 60th Birthday

Keywords: Dithiocarbamates; Copper; Preparation; X-ray diffraction; Thermal decomposition

Abstract. The title compounds NH₄[Cu(S₂CNH₂)₂]·H₂O (A) and CuS₂CNH₂ (B) were prepared from aqueous alcoholic solutions by reaction of ammoniumdithiocarbamate with copper sulfate in presence of excess cyanide as reductive. (A) crystallizes in the orthorhombic space group C222₁ (No. 20) with a = 8.9518(6), b = 9.6414(6) and c = 10.6176(8) Å, Z = 4. (B) crystallizes in the orthorhombic space group P2₁2₁2₁ (No. 19) with a = 5.9533(4), b = 6.6276(4) and c = 9.4834(5) Å, Z = 4. In the crystal structure of (A) copper has a tetrahedral surrounding of four monodentate dithiocarbamate ligands. These

Introduction

Copper dithiocarbamates exist for all three oxidation states I-III. Most common are copper(II) complexes $Cu(S_2CNR_2)_2$ (R = organic moieties), which have been prepared and crystallographically investigated.^[1-5] Dithiocarbamates have also played a prominent role in the development of Cu^{III} chemistry.^[6,7] Copper(I)-dithiocarbamate can be prepared e.g. by disproportionation of copper(II) salts together with a co-generated copper(III) species,^[8] from the conproportionation reaction of activated copper powder with Cu^{II} salts^[9] or by chemical reduction of Cu^{II} species with NH₂OH·HCl in presence of alkalidithiocarbamate.^[10] Meanwhile several Cu^I-dithiocarbamates have been prepared and some crystal structures were established.^[11–15] However, it is noteworthy that no crystal structure determination or further advanced investigation of the most simple copper dithiocarbamate complex with R = H exists. This article reports on the preparation and crystal structures of NH₄[Cu(S₂CNH₂)₂]·H₂O and CuS₂CNH₂.

Experimental Section

Preparation

Chemical reduction of the royal blue-colored solution of $[Cu(NH_3)_4]^{2+}$ with NH_2OH ·HCl (and N_2H_4 ·H_2O, respectively) in presence of dithiocarbamates has disadvantages. It affords working under

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structural units form 2D nets stacked along [001]. Staggered chains consisting of H₂O and NH₄⁺ penetrate the crystal structure along [001] yielding additional coherence via hydrogen bonds. The crystal structure of (B) comprises a three-dimensional tetrahedral framework of CuS₄ units exclusively linked by vertices. The arrangement is reminiscent of a filled β -cristobalite structure with the dithiocarbamate ligands extending into the hollow spaces. Thermal decomposition precedes stepwise finally giving Cu₂S in each case.

inert gas atmosphere and recystallization of the raw product.^[10] This report is on the substituted synthesis of copper(I)- dithocarbamates using solutions of ammoniumdithiocarbamate in the presence of an excess of cyanide as reductive.

a) NH₄[Cu(S₂CNH₂)₂]·H₂O: In an Erlenmeyer flask a solution of freshly prepared white ammoniumdithiocarbamate (3.3 g, 30 mmol)^[16] in EtOH/H₂O (60 mL, 1:2) was mixed with a solution of KCN (2.6 g, 40 mmol) in H₂O (25 mL). While stirring at room temp. a solution of CuSO₄•5H₂O (2.5 g, 10 mmol) in water (25 mL) was slowly added (ca. 10 min). Spontaneously, a first precipitation started. Nevertheless, a largely complete precipitation of the bright yellow complex ammonium salt required several hours. A small sample (precipitate plus its mother liquor) was shortly warmed up until most of the precipitate had dissolved again. After cooling down at room temp. and leaving undisturbed for several days, bright yellow transparent single crystals suitable for X-ray investigations had formed (Figure 1, bottom). The residual microcrystalline product was collected via filtration after two days, washed with H₂O, an aqueous solution of two percent NH₄Cl, again with H₂O and subsequently with EtOH and dried in an air current at ambient temperature. When NH₄[Cu(S₂CNH₂)₂]·H₂O was stored at open air at room temp. it decayed slowly becoming more and more ocher yellow. The percent composition data (standard deviation in brackets) were determined by combustion analysis on a CHNS-Rapid-Element-Analyzer (Heraeus GmbH) using thiourea as standard: $NH_4[Cu(S_2CNH_2)_2] \cdot H_2O Mw = 283.93 \text{ g} \cdot \text{mol}^{-1}; C 8.49(7) \text{ (calcd.}$ 8.46); H 3.03(9) (calcd. 3.55); N 14.4(3) (calcd. 14.78); S 45.0(5) (calcd. 45.17)%.

b) CuS_2CNH_2 : A similar process as described above was applied to prepare CuS_2CNH_2 but at elevated temperature. After the first step, when all of the copper solution was added, the yellow suspension was boiled. The temperature increased with decreasing content of EtOH. At about 82 °C all of the initially formed yellow precipitate had dis-



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Figure 1. SEM images of the copper dithiocarbamate crystals prepared from aqueous alcohol solutions $(NH_4[Cu(S_2CNH_2)_2]\cdot H_2O$ bottom and CuS_2CNH_2 top).

solved again. The heating was continued while stirring and the initially yellow solution became light orange. In the temperature range of $T \approx$ 90–95 °C an ocher, crystalline precipitate appeared. After additional 15 min of heating, hot suspension was quickly sucked off, washed with hot EtOH/H₂O (1:2) and later with cold NH₄Cl solution and finally with EtOH and dried under vacuum. Honey-colored, transparent crystals of CuS₂CNH₂ had formed (Figure 1, top). Analysis: CuS₂CNH₂ Mw = 155.71 g·mol⁻¹; C 7.77(5) (calcd. 7.71); H 1.21(1) (calcd. 1.29); N 8.87(3) (calcd. 8.99); S 41.72(15) (calcd. 41.19)%.

Differential Thermal Analysis (DTA-TG-MS)

For thermal analysis a STA-409CD instrument from Netzsch, which was connected to a quadrupole mass spectrometer (Balzers) via Skimmer coupling was used. The DTA-TG investigations were carried out in a N₂ atmosphere (purity: 5.0 / at heating rates of 1, 4 and 8 K·min⁻¹). Analogue scan modes were applied for the MS measurements in a dynamic He atmosphere at heating rates of 8 K·min⁻¹. All measurements were performed at a flow rate of 75 mL·min⁻¹ in the temperature range T = 25-800 °C (crucible: sintered Al₂O₃). The residues and some intermediates were isolated for X-ray powder diffraction. Corrections for buoyancy and current effects were applied during data evaluation. The instrument is calibrated with standard reference samples from Netzsch.

X-ray Powder Diffraction (XRPD)

XRPD experiments were performed using a STOE Transmission Powder Diffraction System STADI P (Cu- $K_{\alpha 1}$ radiation; $\lambda = 1.54056$ Å) equipped with a MYTHEN 1K detector from DECTRIS. Single Crystal X-ray Investigation

Single crystal X-ray diffraction data were collected with a STOE Imaging Plate Diffraction System (IPDS-1) with graphite monochromatized Mo- K_{α} radiation ($\lambda = 0.7107$ Å) at 200(2) K. The raw data were corrected for Lorentz and polarization effects, and an absorption correction was applied using X-Red^[17] and X-Shape.^[18] The structures were solved by Direct Methods employing the SHELXTL program package^[19] and the refinement was performed against F^2 . The nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of the amino groups were allowed to ride on their parent atom with idealized geometry and were refined with fixed bond length (N–H = 0.86 Å). The isotropic displacement parameters were fixed $[U_{iso}(H) = 1.2 \ U_{eq}(N)]$. For the ammonium ions of NH₄[Cu(S₂CNH₂)₂]·H₂O, an ideal tetrahedral H-N-H angle was assumed where the corresponding H-H distances are 1.486 Å.^[20] Also fixed isotropic displacement parameters $[U_{iso}(H) = 1.5U_{eq}(N)]$ were used. In the early stages of the refinement of the structure model for NH₄[Cu(S₂CNH₂)₂]·H₂O, the calculation was carried out only with 8 NH4⁺ which is not consistent with the empirical formula. To satisfy the analytically confirmed composition in the final refinement, the position (8c) was occupied (50:50) by N(2) and O respectively, and the occupancy factors of the hydrogen atoms of NH_4^+ became *sof* = 0.75. More technical details of the data acquisition and some selected results of the refinement are summarized in Table 1. The final atomic coordinates as well as the equivalent isotropic displacement parameters are

	Α	В
Empirical formula	C ₂ H ₁₀ CuN ₃ OS ₄	CH ₂ CuNS ₂
Formula weight	283.91	155.70
Temperature /K	200(2)	200(2)
Wavelength /Å	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic
Space group	C222 ₁	$P2_{1}2_{1}2_{1}$
a /Å	8.9518(6)	5.9533(4)
b /Å	9.6414(6)	6.6276(4)
c /Å	10.6176(8)	9.4834(5)
Volume /Å ³	916.38(11)	374.18(4)
Z	4	4
ρ (calcd.) /g·cm ⁻³	2.058	2.764
μ /mm ⁻¹	3.243	6.709
F(000)	576	304
Crystal size /mm	0.09 imes 0.06 imes	0.09 imes 0.08 imes
	0.03	0.04
Color	yellow	honey-colored
θ range /°	3.11 to 27.97.	3.75 to 27.94
Reflections collected	7254	3660
Independent reflections	1102	891
R _{int}	0.1161	0.0363
Completeness /%	99.2	99.5
Absorption correction	numerical	numerical
Max. /min. transmission	0.6756 / 0.4451	0.4304 / 0.2925
Data / restraints / parameters	1102 / 10 / 64	891 / 0 / 47
GOOF (F^2)	1.088	1.058
$R_1 (F_{\rm o} > 4\sigma(F_{\rm o}))$	0.0297	0.0239
$wR_2 (F_o > 4\sigma(F_o))$	0.0757	0.0576
R_1 (all data)	0.0316	0.0253
wR_2 (all data)	0.0771	0.0582
Absolute structure parameter	0.013(19)	0.021(19)
Extinction coefficient	0.0034(7)	0.011(3)
δF /e·Å ⁻³	0.516 / -0.445	0.557 / -0.349

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listed in Table 2. Table 3 shows a list of the shortest interatomic distances and some selected bonding angles as well as the hydrogen bonding geometry for $NH_4[Cu(S_2CNH_2)_2]$ ·H₂O. The corresponding

Table 2. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10³) (standard deviations in parenthesis). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	X	У	Z	$U_{\rm eq}$
Cu	0	9903(1)	2500	25(1)
S ₍₁₎	1391(1)	11302(1)	3862(1)	27(1)
S ₍₂₎	1480(1)	8632(1)	1137(1)	25(1)
C	2306(2)	7283(3)	1928(3)	23(1)
N ₍₁₎	1954(2)	7012(3)	3098(2)	35(1)
N ₍₂₎ /O	4510(2)	9232(3)	3856(2)	43(1)

Calculated coordinates of hydrogen atoms ($\times 10^4$)

 U_{eq} х Ζ. v H₍₁₎ 1286 7525 3489 42 H₍₂₎ 2385 6318 3494 42 3488(11) 9120(40) 3870(30) H₍₃₎ 64 H₍₄₎ 4910(40) 8374(18) 3970(30) 64 64 4770(40) H₍₅₎ 9610(40) 3117(19) H₍₆₎ 4740(30) 9780(30) 4520(20) 64 CuS₂CNH₂ $U_{\rm eq}$ Z. x y Cu 9147(1) 2410(1) 8693(1) 20(1)5952(1) 4058(1) 9414(1) 18(1) $S_{(1)}$ 6775(1) 8542(1) 282(1)18(1)S(2) 4195(5) 4440(4) 7994(3) 17(1)C Ν 4982(5) 4179(5) 24(1)6711(3)

 $\begin{tabular}{|c|c|c|c|c|} \hline Calculated coordinates of hydrogen atoms (× 10⁴) \\ \hline \hline x y z U_{eq} \\ \hline $H_{(1)}$ 6389 3815 6586 28 \\ $H_{(2)}$ 4101 4370 5978 28 \\ \hline \end{tabular}$

data for CuS₂CNH₂ are listed in Table 4. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http:// www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD-426584 for NH₄[Cu(S₂CNH₂)₂]·H₂O and CSD-426583 for CuS₂CNH₂.

Results and Discussion

a) Crystal Structures

1) $NH_4[Cu(S_2CNH_2)_2] \cdot H_2O$

In the crystal structure, the copper atoms are coordinated by four monodentate dithiocarbamate ligands in tetrahedral alignment (Figure 2). Tetrahedral and trigonal geometries are the norm for d¹ °Cu^{I.[21]} The four distances Cu–S (Cu–S(1) = $2 \times$ 2.3136(7), Cu–S(2) = $2 \times 2.3370(8)$ (Table 3a), Cu–S_{average} = 2.3255(8)) are consistent with average Cu-S distances from literature (e.g. 2.285(2) and 2.286(2) Å $\{[Cu(S_2CMe_2)]_2\}_n$ ^[14] 2.33 Å, $[Cu(Me_2NC(S)SC(S)Me_2)_2]_2^+$ SO₄^{2-[22]} and 2.322 Å in the tetrahedral surrounding of Cu^I in the crystal structure of covellite (CuS)^[23]). Every dithiocarbamate ligand connects two CuS₄ units forming a two-dimensional framework (Figure 3 and Figure 4), where every sulfur atom has only one next copper neighbor. The layers are stacked along [001] and the coherence among the layers is firstly given by weak to medium strong hydrogen bonds N-H···S (Table 3a). A staggered chain consisting of H₂O and NH₄+which is incorporated among the layers running along [001] (Figure 4 left) provides for additional hydrogen bonds ([N/O]-H···N and [N/O]-H···S) (Table 3). During the refinement of the crystal structure model, the O and N₍₂₎ atoms were assigned statistically to the same position (vide supra). Actually, no differentiation is possible, but significant differences among the hydrogen bonds are no-

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Table 3. Selected bond lengths /Å and angles /° and hydrogen bonding geometry for $NH_4[Cu(S_2CNH_2)_2]\cdot H_2O$ (standard deviations in parenthesis).

Cu–S ₍₁₎	2.3370(8)	S ₍₂₎ ⁽ⁱ⁾ -Cu-S ₍₂₎	116.04(4)	N ₍₁₎ -C-S ₍₂₎	120.8(2)	$H_{(4)}$ – $[N_{(2)}/O]$ – $H_{(5)}$	112(2)
$Cu - S_{(1)}^{(1)}$	2.3370(8)	$S_{(2)}^{(1)}$ -Cu- $S_{(1)}$	102.93(3)	$N_{(1)}-C-S_{(1)}^{(m)}$	121.1(2)	$H_{(3)}-[N_{(2)}/O]-H_{(6)}$	106.3(19)
$Cu - S_{(2)}^{(i)}$	2.3136(7)	$S_{(2)}$ -Cu- $S_{(1)}$	112.80(3)	$S_{(2)} - C - S_{(1)}^{(iii)}$	118.06(19)	$H_{(4)-[N_{(2)}/O]-H_{(6)}}$	110(2)
Cu–S ₍₂₎	2.3136(7)	$S_{(2)}^{(i)}$ -Cu- $S_{(1)}^{(i)}$	112.80(3)	$C-N_{(1)}-H_{(1)}$	120.0	$H_{(5)}-[N_{(2)}/O]-H_{(6)}$	112(2)
$S_{(1)} - C^{(ii)}$	1.720(3)	$S_{(2)}$ -Cu- $S_{(1)}^{(i)}$	102.93(3)	$C - N_{(1)} - H_{(2)}$	120.0		
S ₍₂₎ –C	1.716(3)	$S_{(1)}$ -Cu- $S_{(1)}^{(i)}$	109.51(4)	$H_{(1)} - N_{(1)} - H_{(2)}$	120.0		
$C - N_{(1)}$	1.308(4)	$C^{(ii)}$ – $S_{(1)}$ – Cu	112.14(11)	$H_{(3)}-[N_{(2)}/O]-H_{(4)}$	106.2(19)		
C-S ₍₁₎ ⁽ⁱⁱⁱ⁾	1.720(3)	C-S ₍₂₎ -Cu	110.01(11)	$H_{(3)}-[N_{(2)}/O]-H_{(5)}$	109(2)		
D–H···A	D–H	Н…А	D····A	< D-H•••A			
$\overline{N_{(1)}-H_{(1)}-S_{(2)}}^{(i)}$	0.88	2.726	3.543	154.96			
$N_{(1)}-H_{(1)}-S_{(1)}^{(iv)}$	0.88	3.032	3.648	128.76			
$N_{(1)} - H_{(2)} - S_{(2)}^{(v)}$	0.88	2.809	3.639	157.95			
$N_{(1)}-H_{(2)}-S_{(2)}^{(vi)}$	0.88	2.984	3.572	125.89			
$[N_{(2)}/O]-H_{(3)}-N_{(1)}$	0.92	2.586	3.234	127.87			
$[N_{(2)}/O]-H_{(3)}-S_{(1)}$	0.92	2.819	3.432	125.01			
$[N_{(2)}/O] - H_{(3)} - S_{(1)}^{(iv)}$	0.92	3.080	3.732	129.34			
$[N_{(2)}/O] - H_{(4)} - S_{(1)}^{(vii)}$	0.92	2.403	3.289	165.33			
$[N_{(2)}/O] - H_{(5)} [N_{(2)}/O]^{(viii)}$	0.90	2.221	3.010	146.76			
[N ₍₂₎ /O]-H ₍₆₎ [N ₍₂₎ /O] ^(iv)	0.90	1.983	2.846	159.24			
Symmetry transformations u $y+2, -z+1; (v) -x+1/2, y-1/2$	used to generate $2, -z+1/2;$ (vi	ate equivalent aton) $-x+1/2$, $-y+3/2$, x	ns: (i) $-x$, y , $-x$ z+1/2; (vii) $x+$	z+1/2; (ii) $-x+1/2, y+1/2, y-1/2, z;$ (viii) $-x$	1/2, -z+1/2; (i z+1, y, -z+1/2.	ii) - <i>x</i> +1/2, <i>y</i> -1/2, - <i>z</i> +	1/2; (iv) <i>x</i> , –

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Fable 4. Selected bond lengths	Å and angles /°	and hydrogen bonding geometry	for CuS ₂ CNH ₂	(standard deviations in	parenthesis).
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Table 4. Science bond rengins // and angles / and hydrogen bonding geometry for eus_civity (standard deviations in parentices).								
Cu–S ₍₁₎	2.2973(9)	$S_{(1)}$ -Cu- $S_{(1)}^{(i)}$	110.77(2)	Cu-S ₍₁₎ -Cu ⁽ⁱⁱⁱ⁾	114.62(3)	C-N-H ₍₂₎	120.0	
$Cu - S_{(1)}^{(i)}$	2.3074(8)	$S_{(1)}$ -Cu- $S_{(2)}$	113.09(3)	$C^{(iV)}$ – $S_{(2)}$ – Cu	103.95(11)	$H_{(1)} - N - H_{(2)}$	120.0	
Cu-S ₍₂₎	2.3300(8)	$S_{(1)}^{(i)} - Cu - S_{(2)}$	115.09(3)	$C^{(iV)} - S_{(2)} - Cu^{(v)}$	107.92(10)	., .,		
$Cu-S_{(2)}^{(ii)}$	2.3900(9)	$S_{(1)}$ -Cu- $S_{(2)}^{(ii)}$	98.82(3)	$Cu-S_{(2)}-Cu^{(v)}$	122.56(3)			
S ₍₁₎ –C	1.723(3)	$S_{(1)}^{(i)}$ -Cu- $S_{(2)}^{(ii)}$	102.25(3)	$N-C-S_{(1)}$	119.2(3)			
$S_{(2)}-C^{(iV)}$	1.737(3)	$S_{(2)}$ -Cu- $S_{(2)}^{(ii)}$	115.21(2)	$N-C-S_{(2)}^{(vi)}$	119.5(3)			
C–N	1.315(4)	$C-S_{(1)}-Cu$	109.86(11)	$S_{(1)} - C - S_{(2)}^{(vi)}$	121.21(18)			
$C - S_{(2)}^{(vi)}$	1.737(3)	$C-S_{(1)}-Cu^{(iii)}$	112.77(11)	C-N-H ₍₁₎	120.0			
D–H•••A	D–H	Н…А	D…A	< D–H•••A				
N-H1-S ₍₂₎	0.880	2.675	3.342	133.43				
$N-H1-S_{(1)}^{(vii)}$	0.880	2.956	3.460	118.22				
$N-H2-S_{(2)}^{(viii)}$	0.880	2.642	3.434	150.28				
Symmetry transfe	rmations used t	o ganarata aquivalant a	tome: (i) $x \perp 1/2$	$x + 1/2 = \pi + 2 \cdot (ii) = x + 2$	$1/2 = -2/2 \cdot 6$	$(1) \times 1/2 \to 1/2$	712.	

Symmetry transformations used to generate equivalent atoms: (i) x+1/2, -y+1/2, -z+2; (ii) -x+2, y+1/2, -z+3/2; (iii) x-1/2, -y+1/2, -z+2/2; (iv) -x+1, y-1/2, -z+3/2; (v) -x+2, y-1/2, -z+3/2; (v) -x+3/2; (vii) -x+3/2; (viii) x-1/2, -y+1/2, -z+1.

ticeable, though. An alternative (enlarged) view of the staggered chain is given in the ultimate left part of Figure 4 were an *arbitrarily* alternating arrangement of H_2O and NH_4^+ is illustrated. An appropriate reallocation of the hydrogen atoms demonstrates a plausible alignment of the hydrogen bonds (O– H···N and N–H···O = 1.983 Å, respectively and N–H···O = 2.221 Å).



Figure 2. Tetrahedral surrounding of copper in $NH_4[Cu(S_2CNH_2)_2]$ · H_2O . For symmetry transformations and distances see Table 3. Hydrogen atoms are drawn as circles of arbitrary radii. The displacement ellipsoids of the heavy atoms are drawn at the 80% probability.

2) CuS_2CNH_2

In the crystal structure, the copper atoms have also tetrahedral coordination spheres with four monodentate dithiocarbamate ligands. This copper surrounding is more irregular as in the crystal structure of the ammonium salt described above because of four different Cu–S distances (Table 4), but the average distance Cu–S = 2.3312(9) Å is similar. Furthermore, each sulfur atom has *two* next copper neighbors. Therefore, each sulfur atom is a common vertex of two "tetrahedra". The three-dimensional arrangement (via common vertices) with six-membered rings (Figure 5) is *reminiscent* of a filled β -cristobalite structure^[24] where the fourth vertex of each tetrahe-



Figure 3. Partial view of the three-dimensional crystal structure of $NH_4[Cu(S_2CNH_2)_2]\cdot H_2O$ (viewing direction along [001], for better clarity only one Cu-dithocarbamate layer is depicted).



Figure 4. Partial view of the three-dimensional crystal structure of $NH_4[Cu(S_2CNH_2)_2]\cdot H_2O$ (viewing direction along [010]). In the left part, the alternating alignment of $N_{(2)}$ and O has been *arbitrarily idealized* for the interpretation of the different hydrogen bonds (O–H···N and N–H···O = 1.983 Å, respectively and N–H···O = 2.221 Å).

dron is alternately pointing either upwards or downwards out of the plane of projection. The irregular Cu–S distances reflect the strongly distorted six-membered rings with tilted tetrahe-

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dra. The basal planes of the tetrahedra are not parallel and the apical vertices (marked as globes in Figure 5) do not point to the same opposite directions. The dithiocarbamate ligands extend into the hollow spaces of the three-dimensional tetrahedral framework providing medium strong and weak hydrogen bonds (N–H···S, Table 4).



Figure 5. CuS_4 tetrahedra in the crystal structure of CuS_2CNH_2 showing the *3D* linkage by common vertices (see text).

b) Thermal Decomposition Reactions

Thermal decomposition of aliphatic metal dithiocarbamates is supposed to take place via thiocyanate intermediates.^[25] Before entering upon further considerations, it must be noted that in each case the mass steps in the TG curves are not very well separated (Figure 6 and Figure 7). Nevertheless, some of the events, observable while heating up, will be assigned *tentatively* to plausible mass losses with the aid of stoichiometric calculations and XRPDs of the recovered intermediates and residues.

$NH_4[Cu(S_2CNH_2)_2] \cdot H_2O$

The thermal decomposition of NH₄[Cu(S₂CNH₂)₂]·H₂O is a complex endothermic process. On heating the thermal decomposition starts *early* in the range of $T \approx 33-95$ °C depending on the heating rate. The process proceeds in several steps overlapping in the temperature range from RT to $T \approx 350$ °C (Figure 6) and ending up at $T \approx 800$ °C ($\Delta_{m(exp)} = 69.9\%$). The theoretical mass loss for the formation of Cu₂S is $\Delta_{m(theo)} = 71.96\%$. During the analogue scans (MS measurements) the following *characteristic* gaseous decomposition products were detected: NH₃ m/z = 17, H₂O m/z = 18, HCN m/z = 27, H₂S m/z = 34, H₂CNS⁻ m/z = 60, S₂ m/z = 64 and CS₂ = 76. On heating, a particular sharp endothermic peak on the DTA curve is observed at Tp = 170.9 °C which coincides with an inflection point on the TG curve. The experimental mass loss of $\Delta m = 51.2\%$ is in perfect accordance with a calculated loss of



Figure 6. Thermogram (DTA, TG, DTG curves) for $NH_4[Cu(S_2CNH_2)_2]\cdot H_2O$ (heating rate: 1 K·min⁻¹).



Figure 7. Thermogram (DTA, TG, DTG curves) for CuS_2CNH_2 (heating rate: 1 K·min⁻¹).

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 $\Delta m_{(theo)} = 51.16\%$ for the release of NH₃, CS₂, H₂O and H₂S (ratio: 2:1:1:0.5). Technically this corresponds to the decay of one mol NH₄S₂CNH₂ and the total loss of all water of crystallization. However, the additional emergence of H₂S is an evidence for at least partial formation of CuSCN. The XRPD of an intermediate taken from the temperature range T≈ 180 to 200 °C shows the lines of β -CuSCN.^[26] The next distinct mass loss occurs at $T \approx 425$ °C ($\Delta m = 15.6\%$). An emission of HCN and S (ratio: 2:1) corresponds to a theoretical loss of $\Delta m_{\text{(theo)}} = 15.5\%$. Both steps add up to $\Delta m = 66.8\%$. The calculated $\Delta m = 66.4\%$ applies to the formation of CuS. (This applies also for a decomposition via NH₃,CS₂, H₂O and H₂CNS⁻; ratio: 2:1:1:1). The trends of the TG curves of both dithiocarbamates in the temperature region above $T > 400 \text{ }^{\circ}\text{C}$ are very similar (Figure 6 and Figure 7). That is why this region was not further investigated assuming that the final formation of Cu₂S (vide infra) would most likely proceed similarly in both cases.

CuS_2CNH_2

The thermal decomposition of CuS₂CNH₂ is also a complex endothermic process. It starts at $T \approx 170$ °C and is completed at $T \approx 800$ °C (Figure 7). The overall experimental mass loss is $\Delta m = 48.7\%$ which corresponds perfectly to a calculated loss of $\Delta m = 48.9\%$ for the formation of Cu₂S. During the first the large step, at least two strongly overlapping decompositions occur. At best, one can assume that at $T \approx 434$ °C (onset of an endothermic effect Figure 7) a first partial decomposition might be completed before the start of the next reaction. The associated experimental loss $\Delta m = 43.8\%$ corresponds to a technically calculated mass loss of $\Delta m = 43.7\%$, of HCN, H₂S and S (ratio: 2:1:1.5). The same theoretical Δm corresponds to a loss of two thiooxime anions (H₂CNS⁻ m/z = 60, vide supra) and 1/2 S. The XRPD from an intermediate at $T \approx 400$ °C reflections of covellite basically the comprises $(CuS)^{[23]}$ and $Cu_9S_5^{[27]}$ (Figure 8). The XRPD from the end product is very rich in lines. Nevertheless, the characteristic



Figure 8. X-ray powder diagram of an intermediate taken at $T \approx 400$ °C from the decomposition of CuS₂CNH₂ (arrows indicate the lines of covellite, circles indicate the lines of Cu₉S₅).

lines of $Cu_2S^{[28]}$ and $Cu_{1.81}S^{[29]}$ which partly coincide are definitely observable.

Conclusions

It was shown that the preparation of Cu^I-dithiocarbamates applying cyanide as reductive is a convenient method. The new compounds $NH_4[Cu(S_2CNH_2)_2] \cdot H_2O$ (A) and CuS_2CNH_2 (B) were obtained. (A) is the first example comprising of the anion $[Cu(S_2CNH_2)_2]^-$ which is known as $[Cu(S_2CNR_2)_2]^-$ (R =organic moiety) from electrochemical investigations of transition metal dithiocarbamates.^[30] Obviously, this anion has never been isolated before.^[31] In both crystal structures of (A) and (B) copper has a tetrahedral surrounding of its next sulfur neighbors (from monodentate dithiocarbamate ligands) which is a characteristic feature for Cu^I. Both new compounds decompose at elevated temperatures in the course of complex endothermic processes finally giving Cu₂S.

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