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Crystallographic and Magnetic Study of Tetraisothiocyanato-cuprate(I)-bis{μ-{2-[(3-aminopropyl)amino]ethanolato}-N,N',μ-O}dicopper(II) Polymer Thiocyanate*

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The title compound, $[Cu_2(C_5H_{13}N_2O)_2]_2$-$[Cu(NCS)_4](NCS)$, crystallizes in the tetragonal space group $P/4n$ with the unit cell dimensions $a=b=14.295(10)$, $c=10.359(6)$ Å and $Z=2$. The crystal structure has been determined by direct and Fourier methods from 1336 independent reflections collected with an automatic four-circle diffractometer and refined by block-diagonal least-squares methods to an R value of 0.056.

The structure consists of $[Cu_2(C_5H_{13}N_2O)_2]^{2+}$ dimers, where Cu···Cu distance is 2.973 Å. The copper(II) ion has square-pyramidal (4+1)-coordination with two nitrogen atoms and two oxygen atoms in the basal plane with normal coordination bond distances and a sulfur atom in the apical position with Cu–S distance of 2.732 Å. The nitrogen atom of the thiocyanate ion with the Cu–N distance of 1.999 Å is coordinated to the copper(I) ion, forming a nearly tetrahedral $[Cu(NCS)_4]^{3-}$ anion. Each $[Cu(NCS)_4]^{3-}$ anion lies between four dimers, giving rise to a two-dimensional net-like structure. The thiocyanate ion operating as a counter ion is disordered.

The temperature dependence of the magnetic susceptibility (range 93.2–303.2 K) shows an intramolecular antiferromagnetic coupling with a singlet-triplet separation of 141 cm^{-1}.

Recently a number of papers dealing with the correlation between the structural details and magnetic behaviour of alkoxy-bridged polynuclear copper(II) complexes have been published.[1–4] The structures of the complexes have been found to be dimeric, trimeric, tetrameric or polymeric. Nishida and Kida[5] have classified the complexes into four groups according to their magnetic properties. The complexes whose magnetic behaviour can be interpreted in terms of the Bleaney-Bowers equation (*type-A*) are assumed to be dimeric. The complexes that obey the Curie-Weiss law with positive Weiss constants (*type-B*) are assumed to be tetrameric. The complexes whose magnetic moments are subnormal at room temperature, but whose data cannot be interpreted in terms of the Bleaney-Bowers equation, are classified as *type-C*. The *type-C* complexes, all of which are assumed to be polymeric with dimeric units, are classified into two subgroups: those that obey the Curie-Weiss law (*type-C(a)*) and those that do not (*type-C(b)*).

The present work continues the study of {2-[(3-aminopropyl)amino]-ethanolato}copper(II)-1:1-complexes being undertaken in our Department, and was performed to investigate further the correlation between structural and magnetic properties of polynuclear copper(II) complexes.

EXPERIMENTAL

Preparation and analysis of the compound. A solution of 0.020 mol KSCN in 25 cm^3 of water was mixed with 0.010 mol $Cu(NO_3)_2.3H_2O$ in 25 cm^3 of water. The black precipitate was separated, 25 cm^3 of methanol was added to the precipitate and the suspension was added to a stirred solution of 0.020 mol amine in 25 cm^3 of methanol. The dark green crude product that appeared was recrystallized from a boiling n-propane–water

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mixture (15:1). After several days dark green crystals were formed.

Analysis for $[Cu_2(C_5H_{13}N_2O)_2]_2[Cu(NCS)_4]$-(NCS) (calculated values in parentheses): C 27.73 (27.89), H 4.99 (4.87), N 16.72 (16.91) %.

Physical measurements. The crystal used for data collection was plate-like approximate dimensions $0.35 \times 0.35 \times 0.10$ mm. Both the crystal and intensity data were collected on an automatic Syntex $P2_1$ four circle diffractometer using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å). The cell dimensions were obtained by least-squares refinement of setting angles for 15 reflections. Preliminary Weissenberg photographs taken with a Nonius Weissenberg goniometer revealed systematic absences $hk0$ for $h+k=2n+1$, and indicated the centrosymmetric tetragonal space group $P4/n$ (No. 85).

The intensity data were collected by ω-scan technique at room temperature (scan range 1.0°, scan speed 2.0–29.3° min^{-1}, and $3.0° \leq 2\theta \leq 53.0°$). Of the 2372 reflections recorded, 1336 independent reflections had $I \geq 3\sigma(I)$ and were regarded as observed. The intensity of a standard reflection recorded after every 59 reflections varied about ±1.5 % during the data collection. Data were corrected for Lorentz and polarization effects and also for absorption from ϕ-scan data.

The magnetic data of the compound were measured over the temperature range 93.2–303.2 K by Gouy method, using a Newport variable temperature Gouy balance. Copper(II) sulfate pentahydrate was used for calibration.[3] Diamagnetic corrections were applied with Pascal's constants for the atoms of the amine and the calculated correction values the copper(I) ion and thiocyanate ion.[6]

The infrared spectra were recorded in KBr pellets on a Perkin-Elmer 577 grating infrared spectrophotometer.

CRYSTAL DATA

$[Cu_2(C_5H_{13}N_2O)_2]_2[Cu(NCS)_4]$ (NCS),
$FW = 1076.80$
Crystal system: tetragonal
Space group: P_4/n (No. 85) (Origin at $\bar{1}$)
$a = b = 14.295(10)$, $c = 10.359(6)$ Å
$V = 2117(2)$ Å^3, $Z = 2$, $F(000) = 1090$,
μ(Mo$K\alpha$) = 28.5 cm^{-1}
$D_m = 1.71(1)$ (by flotation), $D_x = 1.69$ g cm^{-3}

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by direct methods and Fourier syntheses. The positions of two independent copper atoms and one sulfur atom were located from an F_o statistical map based upon 100 reflections having $|E_o| \geq 1.70$. The other non-hydrogen atoms were located from successive Fourier maps and the hydrogen atoms from a difference map.

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters[a] ($\times 10^3$) for non-hydrogen atoms. Estimated standard deviations are given in parentheses.

Atom	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	2500(−)	7500(−)	0(−)	40(1)	40(−)	50(−)	0(−)	0(−)	0(−)
Cu2	−452(1)	259(1)	1242(1)	47(1)	36(1)	27(1)	5(1)	2(1)	−5(1)
S1	593(2)	−768(2)	2936(2)	58(2)	67(2)	37(1)	23(1)	4(1)	7(1)
S2	2500(−)	2500(−)	7311(12)	143(5)	143(−)	212(12)	0(−)	0(−)	0(−)
O1	607(3)	615(4)	172(5)	43(3)	38(3)	31(4)	−5(3)	−1(3)	−4(3)
N1	−1590(5)	−60(5)	2245(7)	56(5)	54(5)	45(5)	7(4)	4(4)	−13(4)
N2	−345(4)	1544(4)	2011(6)	45(4)	37(4)	31(4)	10(3)	1(4)	−5(4)
N3	1706(5)	−1667(5)	1097(8)	36(4)	48(5)	68(6)	9(4)	3(4)	−7(5)
N4	2500(−)	2500(−)	5049(33)	355(30)	355(−)	107(28)	0(−)	0(−)	0(−)
C1	−1637(6)	254(6)	3618(9)	45(5)	75(7)	34(6)	4(5)	2(5)	−12(6)
C2	−1491(7)	1294(7)	3750(9)	58(6)	104(8)	26(5)	26(6)	1(6)	−18(6)
C3	−539(6)	1637(6)	3405(8)	63(6)	45(6)	33(5)	8(5)	1(5)	−20(5)
C4	579(6)	1902(6)	1605(9)	58(6)	37(5)	48(6)	6(4)	0(5)	−20(5)
C5	772(6)	1590(6)	254(9)	53(6)	37(5)	45(6)	−4(4)	−3(5)	−1(5)
C6	1247(6)	−1270(5)	1855(8)	40(5)	26(5)	53(6)	−3(4)	−11(5)	12(5)
C7	2500(−)	2500(−)	5939(33)	738(82)	738(−)	15(20)	0(−)	0(−)	0(−)

[a] The anisotropic thermal parameters are of the form $\exp\{-2\pi^2[(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]\}$.

Table 2. Fractional atomic coordinates ($\times 10^3$) for hydrogen atoms. Estimated standard deviations are given in parentheses.

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
H1	−176(4)	−63(4)	224(7)	H8	3(4)	132(4)	397(6)
H2	−190(4)	24(4)	189(6)	H9	−78(4)	182(4)	154(6)
H3	−228(4)	12(4)	394(6)	H10	44(4)	271(4)	173(6)
H4	−121(4)	−2(4)	402(6)	H11	119(4)	168(4)	216(6)
H5	−165(4)	143(4)	460(6)	H12	150(4)	179(4)	6(7)
H6	−198(4)	176(4)	337(6)	H13	40(4)	206(4)	−43(6)
H7	−39(4)	210(4)	367(6)				

The refinement yielded abnormally short bond lengths for the non-coordinated thiocyanate ion. However, neither the rigid group refinement with fixed normal bond lengths nor attempts to locate the group around the 4-axis gave any better result.

In the calculation of F_c, atomic acattering factors from Ref. 7 were used for all non-hydrogen atoms and from Ref. 8 for hydrogen atoms. Anomalous dispersion coefficients for copper and sulfur atoms were included in the calculations.[9]

Atomic coordinates were refined by block-diagonal least-squares technique to an R value of 0.056 (R_w=0.055) with the weighting scheme $w=4F_o^2/\sigma^2(F_o^2)$ used in minimizing the function $\Sigma w(|F_o|-|F_c|)^2$ ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)$). Anisotropic thermal parameters were used for all non-hydrogen atoms and a fixed isotropic value of 0.03 Å^2 for the hydrogen atoms. The computations were performed on a UNIVAC 1108 computer with the X-Ray 76 program system.[10] The figures were drawn with the PLUTO 78 program.

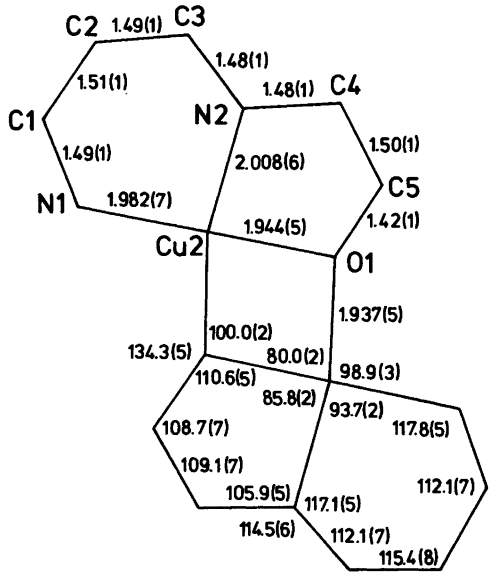

Fig. 1. View of the dimeric cation with bond lengths and angles. Estimated standard deviations are in parentheses.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The fractional atomic coordinates and thermal parameters for non-hydrogen atoms are given in Table 1 and the fractional atomic coordinates for hydrogen atoms in Table 2. A list of observed and calculated structure factors can be obtained from the author.

Two copper(II) ions and two tridentately coordinated 2-[(3-aminopropyl)amino]ethanolato (L^-) ions form a dimeric complex $[Cu_2L_2]^{2+}$ of C_i symmetry (Fig. 1). The interatomic distance between the copper(II) ions is 2.973(1) Å, being identical with the values in $[Cu_2L_2I]I.2H_2O$[4] and in agreement with those reported for other alkoxo-bridged dimers.[1-3]

The coordination around the copper(II) ion is distorted square-pyramidal. Two nitrogen atoms and two oxygen atoms lie in the basal plane with interatomic distances of Cu2−N1 1.982, Cu2−N2 2.008, Cu2−O1 1.944, Cu2−O1′ 1.937 Å, and a sulfur atom in the apical position with Cu2−S1 distance of 2.732(3) Å. The Cu−S distance is longer than the typical basal coordination bond length 2.26−2.34 Å reported in several papers.[11-15] It is, however, in agreement with the approx. 20 % axial bond distance elongation in the (4+1) copper(II) coordination sphere reported by Hathaway.[16]

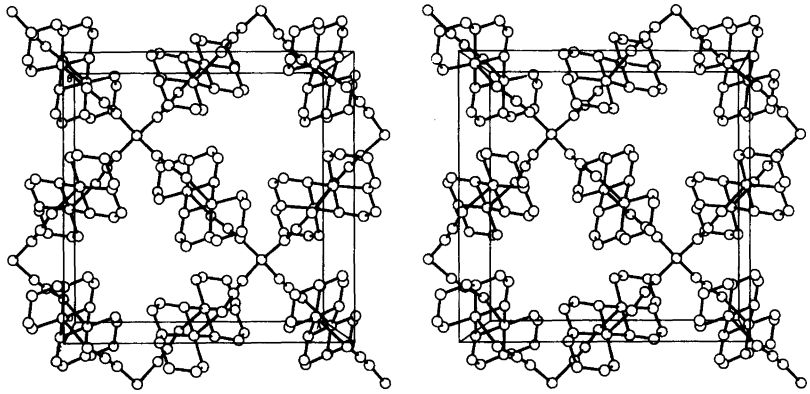

Fig. 2. Stereo view of the packing. The disordered thiocyanate ion is omitted for clarity.

The coordination has somewhat tetrahedral distortion; the equatorial atoms deviate ±0.18 Å from the basal plane, and the dihedral angle between the planes CuN_2 and CuO_2 is 22.7°. The distortion is less in this case than in $[Cu_2L_2I]I.2H_2O$, where the respective dihedral angles are 28.7° and 29.4°. The Cu(II) ion is located 0.22 Å toward the sulfur atom from the basal plane in the present complex.

The six-membered ring of the ligand amine is in chair conformation. The Cu2 and C2 atoms lie 0.78 and −0.69 Å, respectively, from least-squares plane [N1,N2,C1,C3]. In the five-membered chelate ring the C4 and C5 atoms deviate 0.35 and −0.29 Å, respectively, from the plane [Cu2,N2,O1], and the dihedral angle between the planes [N2,C4,C5] and [C4,C5,O1] is 49.8°. The bridging oxygen atom deviates 0.37 Å from the plane [Cu2,Cu2',C5]. The bond lengths and the bond angles are normal to the amine, and the hydrogen atoms are at distances of 0.72–1.18 Å from the parent atoms.

The copper(I) ion lies on a $\bar{4}$-axis and the nitrogen atom of the thiocyanate ion is coordinated to it with Cu1–N3 distance of 1.999(7) Å. According to the symmetry a nearly tetrahedral $[Cu(NCS)_4]^{3-}$ ion is formed. The $[Cu(NCS)_4]^{3-}$ ion is semi-coordinated to four dimers, forming a two-dimensional net-like polymeric structure (Fig. 2). The bond lengths in the NCS^- ion are N3–C6 1.170(11), C6–S1 1.625(9) Å and the bond angle N3–C6–S1 177.2(7)°.

A free SCN^- ion lies on the 4-axis having abnormally short bond lengths of C7–N4 0.92 and S2–C7 1.42 Å. Despite the bond length shortening found in some thiocyanate ions lying on the rotation axis,[17] the indicated location along the axis cannot in this case be considered correct. More probably the free SCN^- ion is disordered around the 4-axis. The disordered structure is also supported by the thermal parameters of the atoms. The sulfur atom of the thiocyanate ion is surrounded by four hydrogen atoms with the interatomic S···H distance of 2.79(13) Å.

In Fig. 3 is shown the temperature dependence of the paramagnetic susceptibility in the range 93.2–303.2 K. The susceptibility data were interpreted in terms of the Bleaney-Bowers equation[18]

$$\chi'_M = \frac{Ng^2\beta^2}{3kT}\cdot\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}+N\alpha \qquad (1)$$

where $-2J$ is equal to the energy separation between the lowest singlet and triplet levels and the other symbols have their usual meanings. A fixed

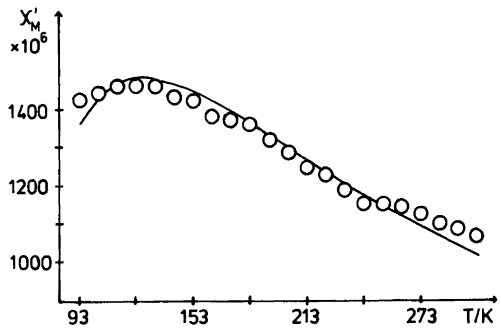

Fig. 3. Experimental temperature dependence of molar paramagnetic susceptibility for the complex. The solid curve represents susceptibilities calculated from eqn. (1), with $g=1.96$, $-2J=141$ cm^{-1} and $N\alpha=60\times10^{-6}$ (cgs units).

Table 3. Magnetic and structural properties of $[Cu_2L_2]^{2+}$ cation.

Compound	$-2J/cm^{-1}$	Cu−O−Cu/°	dist.[O...Cu_2C]/Å
This work	141	100.0	0.37
$[Cu_2L_2I]I.2H_2O$	65	98.1	0.48

value of 60×10^{-6} (cgs units) was used for $N\alpha$, and the values 1.96(2) for g and 141(2) cm^{-1} for $-2J$ were obtained in least-squares refinement. The $-2J$ value indicates that an antiferromagnetic interaction is operative in the crystal. A small interdimer exchange through the $[Cu(NCS)_4]^{3-}$ ion pathway is also possible. This interaction is in all probability very small compared with the intradimer interaction and no attempt was made to include it in the calculation.

The structural details and magnetic behaviour of the present complex are compared in Table 3 with the corresponding data for $[Cu_2L_2I]I.2H_2O$. It can be seen that the antiferromagnetic coupling (greater $-2J$) correlates with the increase of the bridging Cu−O−Cu angle and with the increase of the planarity of the bonds attached to the bridging oxygen atom. The former correlation has been reported by Hatfield,[19] and the latter by Kida, Nishida and Sakamoto.[20]

The magnetic moment, μ_{eff}, calculated the equation $\mu_{eff} = 2.828(\chi_M' T)^{\frac{1}{2}}$, has the slightly subnormal value of 1.60(1) B.M. at 293.2K. According to the μ_{eff} value and the χ-data interpretation in the terms of the Bleaney-Bowers equation, the complex can assumed to be *type-A* in the classification of Nishida and Kida.[5]

In the infrared spectrum of the present compound there is a strong peak at 2080 cm^{-1} indicating a CN-stretching frequency. The absorption energy is higher than that of 2040 cm^{-1} found in the monomeric copper(II) complex, $Cu(HL)_2(SCN)_2$, where the thiocyanate ion is not coordinated to Cu(II) ion.[21] The absorption peaks of ν_{CS} 775 cm^{-1} and ν_{NCS} 470 cm^{-1} are weak. The values are in agreement with those for double-coordinated SCN^- ions reported by Norbury.[22]

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