

# Crystal Structure and Magnetic Properties of Bis( $\mu$ -1-diethylamino-2-propanolato)-bis(isothiocyanato)dicopper(II)

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The crystal and molecular structure of  $[\text{Cu}\{\text{OCH}(\text{CH}_3)\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2\}\text{NCS}]_2$  was determined by single-crystal X-ray diffraction at 294 and 113 K. The compound crystallizes in the monoclinic space group  $P2_1/c$  (No. 14), with  $a = 8.007(2)$ ,  $b = 15.059(3)$ ,  $c = 9.555(2)$  Å,  $\beta = 103.67(3)^\circ$  and  $Z = 4$ . At 113 K the unit-cell dimensions were  $a = 7.993(2)$ ,  $b = 14.853(3)$ ,  $c = 9.457(2)$  Å and  $\beta = 103.58(3)^\circ$ . The structure was refined by full-matrix least-squares methods to  $R$ -factors of 0.034 at 294 K and 0.072 at 113 K. The magnetic susceptibility was measured over the temperature range 70–300 K. The calculated  $g$  was 1.85 and  $-2J = 78.5(1)$  cm<sup>-1</sup> from the Bleaney–Bowers equation. The compound consists of discrete dimers with weak interactions between adjacent dimers formed by linking isothiocyanate groups. On cooling, the distance between the copper(II) atom and the sulfur atom from the adjacent dimer's isothiocyanate group was observed to decrease. This, as well as, the strong deviation from planarity on the copper coordination sphere, could be the reasons for the observed subnormal magnetic susceptibility.

The temperature dependence of magnetic susceptibility has been interpreted by the Bleaney–Bowers equation<sup>1</sup> for most of the binuclear copper(II) complexes:

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

where  $\chi'_M$  and  $-2J$  are the molar magnetic susceptibility per copper atom and the energy separation of the ground singlet and the lowest triplet states, respectively, and the other symbols have their usual meanings. The  $J$ -value is assumed to be independent of the temperature. However, in some cases the Bleaney–Bowers formula is unable to explain the behavior of the susceptibility, even though a discrete binuclear structure has been observed by X-ray analysis. Some of the observed subnormal magnetic susceptibilities in dialkoxo-bridged copper complexes have been explained by the non-planarity of the  $\text{Cu}_2\text{O}_2$  core,<sup>2</sup> or the  $J$ -value has been assumed to vary with the temperature.<sup>3–5</sup> The origin of this kind of phenomenon is then attributed to the temperature dependence of the molecular structure.<sup>5</sup>

Here we report the magnetic properties of a dimeric copper(II) complex formed with 1-diethylamino-2-propanol and isothiocyanate ligands. The observed magnetic susceptibility could not be explained by the Bleaney–Bowers formula. Thus, the crystal and molecular structure determination of the compound was carried out at two different temperatures in order to find out whether the molecular structure is changing with temperature.

## Experimental

**Preparation.** The compound was prepared by addition of copper(II) acetate monohydrate (2.4 g; 12.0 mmol) to the methanolic (100 cm<sup>3</sup>) solution of 1-diethylamino-2-propanol (3.1 g; 23.6 mmol). Potassium thiocyanate (2.3 g; 23.7 mmol) dissolved in 100 cm<sup>3</sup> methanol was added to this mixture. The obtained solution was heated gently and filtered as hot. After several days at room temperature dark green, platelike crystals were formed. Their density, 1.49(1) g cm<sup>-3</sup>, was determined by flotation.

**Data collection at 294 K.** A summary of the crystal data, intensity collection and structure refinement is given in

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Table 1. The unit-cell parameters were determined on the basis of 14 well centered reflections measured on a Nicolet P3F diffractometer.

Intensity data were collected in the  $\omega$ -scan mode using graphite-monochromatized Mo  $K\alpha$  radiation. The intensities of three reference reflections, recorded after every 100 measurements, remained essentially constant throughout the data collection. In the  $\psi$ -scans of seven strong reflections maximum loss in the intensities due to absorption was 37.1% and the empirical absorption correction was applied.

*Data collection at 113 K.* A summary of the crystal data, intensity collection and structure refinement is given in Table 1. The unit-cell parameters were determined on the basis of 25 well centered reflections measured on a Rigaku AFC7S diffractometer.

Intensity data were collected in the  $2\theta/\omega$ -scan mode using graphite-monochromatized Mo  $K\alpha$  radiation. The intensities of three reference reflections, recorded after every 200 measurements, showed on average a  $-1.3\%$  loss in intensity, and the decay correction was applied. The

maximum loss in the intensities due to absorption was 35.7%, and an empirical absorption correction was applied.

*Structure determination.* The structure was solved using direct methods and refined by a full-matrix least-squares analysis. All the calculations were performed with SHELXTL PLUS PC Version.<sup>6</sup> Neutral atom scattering factors<sup>7</sup> including corrections for anomalous dispersion were used as they were given in the program. The figures were drawn using the same program package.

The hydrogen atoms bonded to carbon atoms were included at the calculated positions, and the final refinement with anisotropic thermal parameters for all non-hydrogen atoms gave  $R = 0.034$  at 294 K and  $R = 0.072$  at 113 K.

The atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table 2.

*Magnetic susceptibility measurement.* The purity of the material used in the measurement of magnetic susceptibility was checked by the powder diffraction X-ray pattern

Table 1. Summary of crystal data, intensity collection and structure refinement for [Cu{OCH(CH<sub>3</sub>)CH<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}NCS]<sub>2</sub> at 294 and 113 K.

T/K	294(1)	113(2)
Formula	Cu(C <sub>7</sub> H <sub>16</sub> NO)NCS	Cu(C <sub>7</sub> H <sub>16</sub> NO)NCS
Formula weight	251.8	251.8
Crystal size/mm	0.25 × 0.20 × 0.10	Same crystal
Color, habit	Dark green, plate	
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$
Unit-cell dimensions	$a = 8.007(2)$ Å $b = 15.059(3)$ Å $c = 9.555(2)$ Å $\beta = 103.67(3)^\circ$	$a = 7.993(2)$ Å $b = 14.853(3)$ Å $c = 9.457(2)$ Å $\beta = 103.58(3)^\circ$
Volume/Å <sup>3</sup>	1119.4(6)	1091.3(6)
Z	4	4
$d_{\text{calc}}/\text{g cm}^{-3}$	1.494	1.533
$d_{\text{obs}}/\text{g cm}^{-3}$ (flotation)	1.49(1)	
Absorption coefficient/mm <sup>-1</sup>	2.103	2.157
$F(000)/e$	524	524
Diffractometer used	Nicolet P3F	Rigaku AFC7S
Radiation	Mo $K\alpha$ ( $\lambda = 0.71069$ Å)	Mo $K\alpha$
Monochromator	Graphite crystal	Graphite crystal
$2\theta$ -Range/ $^\circ$	3.0–55.0	5.0–50.0
Scan type	$\omega$ -scan	$2\theta/\omega$ -scan
Scan rate/ $^\circ \text{ min}^{-1}$	2.0–30.0	8.0–32.0
Standard reflections	3 measured every 100 reflections	3 measured every 200 reflections
Variation in standard intensities (%)	$\pm 3$	$-1.3$ (Decay)
Index ranges	$0 \leq h \leq 10,$ $0 \leq k \leq 19,$ $-12 \leq l \leq 12$	$0 \leq h \leq 9,$ $0 \leq k \leq 17,$ $-11 \leq l \leq 10$
No. of reflections collected	2575	1735
No. of observed reflections ( $ F_o  > 4.0\sigma F_o $ )	1976	1310
Absorption correction	Empirical, $\psi$ -scan	$\psi$ -scan
No. of variables	118	118
$R = \Sigma( F_o  -  F_c )/\Sigma F_o $	0.034	0.072
$R_w = \Sigma[ ( F_o  -  F_c )^2 w ] / \Sigma F_o ^2 w^{1/2}$	0.035 <sup>a</sup>	0.094 <sup>b</sup>
Residual electron density/e Å <sup>-3</sup>	0.35	0.90

<sup>a</sup>  $w = 1/[\sigma^2(F_o) + 0.0002 F_o^2]$ . <sup>b</sup>  $w = 1/[\sigma^2(F_o) + 0.0056 F_o^2]$ .

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\times 10^3 \text{ \AA}^2$ ) for  $[\text{Cu}\{\text{OCH}(\text{CH}_3)\text{-CH}_2\text{N}(\text{C}_2\text{H}_5)_2\}\text{NCS}]_2$  at 294 K.

Atom	x	y	z	$U^a$
Cu	1764(1)	5212(1)	829(1)	39(1)
O	-393(2)	5784(1)	122(2)	41(1)
N(1)	4004(3)	4672(2)	1361(3)	47(1)
N(2)	2072(3)	6131(2)	2457(2)	44(1)
S	7426(1)	4162(1)	1867(1)	54(1)
C(1)	5421(3)	4466(2)	1588(3)	36(1)
C(2)	-800(3)	6495(2)	939(3)	44(1)
C(3)	-1817(4)	7209(2)	-5(4)	66(1)
C(4)	884(4)	6857(2)	1821(3)	50(1)
C(5)	3842(4)	6487(3)	3046(3)	61(1)
C(6)	4666(4)	6890(3)	1936(4)	71(1)
C(7)	1439(4)	5715(2)	3663(3)	63(1)
C(8)	2212(5)	4847(3)	4171(4)	83(2)

<sup>a</sup>Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$ -tensor.

achieved from a Philips MPD 1880 powder diffractometer using Cu  $K\alpha$  radiation and by comparing the obtained result to the predicted powder pattern for this compound. This simulated pattern was obtained from the SHELXTL PLUS program package. No impurities could be observed in the XRD pattern.

Magnetic susceptibility measurements were carried out in the temperature range 70–300 K in a He atmosphere using a Faraday-type magnetometer (Oxford Instruments Ltd.).  $\text{Hg}[\text{Co}(\text{NCS})_4]$  was used as a standard for calibration.<sup>8</sup> The susceptibility measurements were made at 0.8 T. All data were corrected for diamagnetism.<sup>9</sup> The result was evaluated using a PC program for least-squares minimization. Fitting the Bleaney–Bowers equation<sup>1</sup> to the magnetic susceptibility data gave  $g = 1.85$ ,  $-2J = 78.5(1) \text{ cm}^{-1}$  (mean square error = 0.8%).

The temperature dependence of the experimental magnetic susceptibility is plotted in Fig. 1.

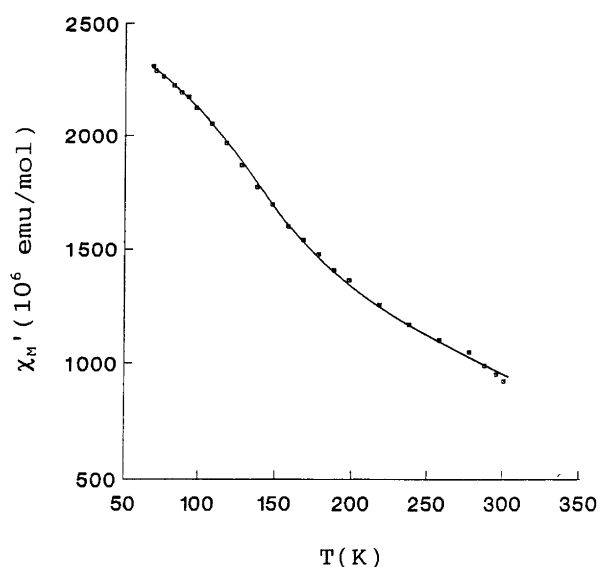


Fig. 1. The observed magnetic susceptibility plotted as a function of the temperature.

## Results and discussion

*Description of the structure.* The structure of  $[\text{Cu}\{\text{OCH}(\text{CH}_3)\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2\}\text{NCS}]_2$  consists of discrete dimeric bis( $\mu$ -1-diethylamino-2-propanolato)bis(isothiocyanato)dicopper(II) units as shown in Fig. 2. The bridging oxygen atoms and the copper atoms form a centrosymmetric planar  $\text{Cu}_2\text{O}_2$  core. The N(2) atom of the chelate ring deviates by 1.04 Å from the  $\text{Cu}_2\text{O}_2$  plane, whereas the N(1) atom of the isothiocyanate group deviates by only 0.20 Å. The  $\text{Cu}\cdots\text{Cu}^i$  distance of 2.964(1) Å agrees well with the distances found in other dimeric alkoxo-bridged Cu(II) complexes;<sup>†</sup> also the  $\text{Cu}-\text{O}-\text{Cu}^i$  and  $\text{O}-\text{Cu}-\text{O}^i$  angles of 100.4(1) and 79.6(1)°, respectively, are very similar to those found in the other dimers (Table 3).<sup>10,11</sup> The  $\text{Cu}-\text{O}$ ,  $\text{Cu}-\text{O}^i$ ,  $\text{Cu}-\text{N}(1)$  and  $\text{Cu}-\text{N}(2)$  distances of 1.914(2), 1.951(2), 1.924(2) and 2.052(2) Å, respectively, are typical for copper atom coordination bonds. In the coordination sphere of Cu there is a strong tetrahedral distortion. The dihedral angle between the  $\text{Cu}-\text{O}-\text{O}^i$  and  $\text{Cu}-\text{N}(1)-\text{N}(2)$  planes is 30.5(1)°.

In the closely related structure of (2-diethylaminoethanolato)copper(II) thiocyanate<sup>12</sup> the thiocyanate groups formed bridges between dimers, the  $\text{Cu}-\text{S}$  distance being 2.851(4) Å, and the angles of  $\text{Cu}-\text{S}-\text{C}$  and  $\text{Cu}-\text{N}-\text{C}$  to the NCS group being 99.1(4) and 167.0(10)°, respectively. In the title compound the  $\text{Cu}-\text{S}^{\text{ii}}$  distance is 2.955(1) Å and the corresponding angles are 100.3(1) and 169.4(3)°.

The bond distances and angles of the 1-diethylamino-2-propanolato ligand are as expected. The five-membered aminopropanolato chelate ring has the *gauche* form. In the ring C(2) and C(4) lie 0.02(1) Å above and 0.54(1) Å below the plane defined by  $\text{O}-\text{Cu}-\text{N}(2)$ . The degree of puckering of the ligand can be seen from the dihedral angle between the planes  $\text{N}(2)-\text{C}(4)-\text{C}(2)$  and  $\text{O}-\text{C}(4)-\text{C}(2)$ , which is 43.2(1)°.

<sup>†</sup> Symmetry codes: <sup>i</sup>  $-x, 1-y, -z$ ; <sup>ii</sup>  $1-x, 1-y, -z$ .

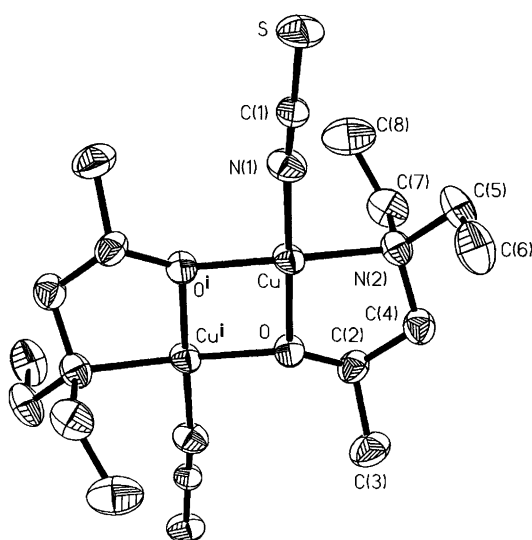


Fig. 2. Schematic drawing of the dimeric unit also showing the atomic labeling. Symmetry code: <sup>i</sup>  $-x, 1-y, -z$ .

**Description of the magnetic behavior.** In the title compound the  $\mu_{\text{eff}} = 1.50(1)$  B.M. at 295 K and decreases slightly

with the temperature, and at 70 K it is 1.14(1) B.M. The parameters obtained from the Bleaney–Bowers fitting were found to be unreasonably low. The correlation between  $-2J$  and the Cu–O–Cu<sup>i</sup> angle for dialkoxobridged dimers has been presented earlier.<sup>13</sup> In the title complex the angle Cu–O–Cu<sup>i</sup> is 100.4(1)°, and then  $-2J$  should be ca. 270 cm<sup>-1</sup>. The reason for the low  $g$ -value in the title compound can be explained by the strong tetrahedral distortion around the copper atom, i.e. the dihedral angle between the planes Cu–N(1)–N(2) and Cu–O–O<sup>i</sup> is 30.5(1)°. This distortion can affect the superexchange pathway between copper atoms, and as a result of this only a weak intradimer coupling is observed, and  $-2J$  is smaller than expected. In the structure of (2-diethylaminoethanolato)copper(II) thiocyanate a stronger antiferromagnetic coupling was observed.<sup>12,14</sup> In that compound the dihedral angle between the planes of Cu–N(1)–N(2) and Cu–O–O<sup>i</sup> was 25.7(2)°, and the calculated  $g$ - and  $-2J$ -values were 1.93 and 279.0(1) cm<sup>-1</sup>, respectively. In the dimethyl and diethyl derivatives of (1-*N,N*-dialkylamino-3-propanolato)isothiocyanatocopper(II) complexes the Cu–S distances were 2.893(1) and 2.887(1) Å, respectively.<sup>11</sup> Both of these complexes showed very

Table 3. Selected interatomic distances (in Å) and angles<sup>a</sup> (in °) with standard deviations in parenthesis for [Cu{OCH(CH<sub>3</sub>)CH<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}NCS]<sub>2</sub> at 294 K and 113 K.

294 K		294 K	
Cu–O	1.914(2)	O–Cu–O <sup>i</sup>	79.6(1)
Cu–O <sup>i</sup>	1.951(2)	O–Cu–N(1)	174.1(1)
Cu–N(1)	1.924(2)	O–Cu–N(2)	84.3(1)
Cu–N(2)	2.052(2)	O–Cu–S <sup>ii</sup>	85.1(1)
Cu···Cu <sup>i</sup>	2.964(1)	N(1)–Cu–O <sup>i</sup>	100.7(1)
Cu···S <sup>ii</sup>	2.955(1)	N(1)–Cu–N(2)	98.5(1)
O–C(2)	1.408(4)	Cu–O–C(2)	117.2(1)
N(2)–C(4)	1.482(4)	Cu–O–Cu <sup>i</sup>	100.4(1)
N(2)–C(5)	1.495(4)	C(2)–O–Cu <sup>i</sup>	131.6(2)
N(2)–C(7)	1.501(4)	Cu–N(1)–C(1)	169.4(3)
C(2)–C(3)	1.512(4)	Cu–N(2)–C(4)	103.7(2)
C(2)–C(4)	1.513(4)	Cu–N(2)–C(5)	117.4(2)
C(5)–C(6)	1.503(5)	Cu–N(2)–C(7)	107.4(2)
C(7)–C(8)	1.479(6)	O–N(2)–C(7)	104.1(2)
N(1)–C(1)	1.147(3)	C(4)–N(2)–C(7)	108.7(2)
C(1)–S	1.629(3)	C(4)–N(2)–C(5)	110.4(2)
		C(7)–N(2)–C(5)	108.8(2)
		O–C(2)–C(4)	106.9(2)
		O–C(2)–C(3)	111.9(3)
		N(2)–C(5)–C(6)	114.4(2)
		C(1)–S–Cu <sup>ii</sup>	100.3(1)
		N(1)–C(1)–S	178.4(1)
113 K		113 K	
Cu–O	1.914(6)	O–Cu–O <sup>i</sup>	80.1(3)
Cu–O <sup>i</sup>	1.961(6)	O–Cu–N(1)	174.7(3)
Cu–N(1)	1.923(7)	O–Cu–N(2)	84.5(3)
Cu–N(2)	2.058(8)	N(1)–Cu–O <sup>i</sup>	99.7(3)
Cu···Cu <sup>i</sup>	2.966(2)	N(1)–Cu–N(2)	98.4(3)
Cu···S <sup>ii</sup>	2.890(3)	Cu–O–Cu <sup>i</sup>	99.3(3)
N(1)–C(1)	1.172(11)	Cu–N(1)–C(1)	167.9(8)
C(1)–S	1.630(9)	C(1)–S–Cu <sup>ii</sup>	99.9(3)
		N(1)–C(1)–S	177.5(7)

<sup>a</sup>Symmetry codes: <sup>i</sup>  $-x, 1-y, -z$ ; <sup>ii</sup>  $1-x, 1-y, -z$ .

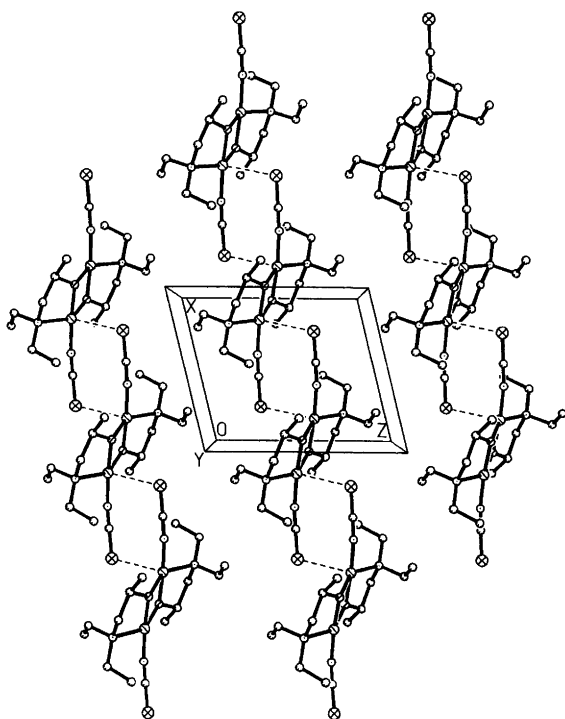


Fig. 3. A view of the molecular arrangement showing the weakly linked alternating chains of  $[\text{Cu}\{\text{OCH}(\text{CH}_3)\text{-CH}_2\text{N}(\text{C}_2\text{H}_5)_2\}\text{NCS}]_2$  dimers at 113 K.

strong antiferromagnetic spin couplings, and in the diethyl derivative the dihedral angle around the copper(II) atom was only  $18.8(1)^\circ$ .

The calculated  $-2J$ -values for the title compound at 294 and 113 K were  $220.0$  and  $104.3 \text{ cm}^{-1}$ , respectively, from the Bleaney–Bowers equation by fixing  $g$  and  $N\alpha$  at  $2.0$  and  $60 \times 10^{-6} \text{ cgs emu}$ . Based on these calculations, it was assumed that there could be some temperature dependence in the  $J$ -value. The change in the molecular structure with the temperature was studied at low temperature by single-crystal X-ray diffraction. In dialkoxo-bridged  $[\text{Cu}\{(\text{C}_3\text{H}_7)_2\text{NC}_2\text{H}_5\text{OSC}_2\text{H}_5\}\text{Cl}]_2$  the substantial change on cooling was observed in the deviation of the carbon atom, linked to the bridging oxygen atom, from the Cu–O–Cu plane.<sup>5</sup> The increase in the deviation of the C atom from the Cu–O–Cu plane was adequate to explain the decrease in  $-2J$ . In the title compound the change of the deviation for the C(2) atom from the Cu–O–Cu plane is minimal when the temperature is lowered. On cooling, the structure of the compound was very simi-

lar as at room temperature. The most considerable change was in the Cu–S<sup>ii</sup> distance, which decreased significantly as the temperature decreased, i.e. from  $2.995(1)$  to  $2.890(3) \text{ \AA}$ , while the N(1)–C(1) bond length increased slightly. This can lead to a weak exchange interaction between the dimers via the thiocyanate group and again to a lower  $-2J$ -value than expected.

The weakly linked alternating chains formed by alkoxy and NCS bridges running parallel to the  $a$ -axis can be seen in Fig. 3.

## Conclusions

Interesting magnetic properties were observed in bis( $\mu$ -1-diethylamino-2-propanolato)bis(isothiocyanato)dicopper(II). The magnetic susceptibility could be treated only approximately. The reasons why the antiferromagnetic coupling in the studied compound is much lower than expected could be the strong distortion in the coordination sphere of copper and in the linking isothiocyanate group, where the interatomic distances are changing, when the temperature decreases.

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