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First Example of Equatorial−Equatorial Disposition of End-to-End Thiocyanate Bridges in a Polynuclear Copper(II) Complex and Its Relation to the Very Efficient Transmission of the Magnetic Interaction

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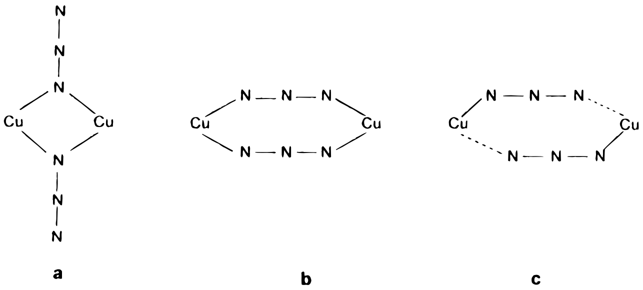
The preparation, X-ray structure, and spectroscopic and magnetic properties of $[Cu(NCS)(\mu\text{-}NCS)(Hmtpo)(H_2O)]_2$ (where Hmtpo= 4*H*,7*H*-5-methyl-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine) are described. This compound crystallizes in triclinic space group $P\bar{1}$, with unit cell dimensions $a = 8.408(2)$ Å, $b = 10.581(3)$ Å, $c = 7.927(2)$ Å, $\alpha = 89.45(2)°$, $\beta = 77.44(2)°$, $\gamma = 69.75(2)°$, and $Z = 1$ (binuclear unit). The structure was refined to final $R = 0.033$ for 2143 data with $I \geq 3.0\sigma(I)$. The structure is comprised of polymeric 1-D copper(II) complexes supported by two different kinds of thiocyanate bridges. The coordination geometry around each of the metal centers is a distorted octahedron ($N_3S + O + S^*$). The equatorial positions are occupied by a monodentate Hmtpo ligand, coordinated via N3, two bridging thiocyanate groups coordinated in a "symmetric" end-to-end fashion, and the N-donor atom of an asymmetric end-to-end thiocyanate bridge. Finally, a water molecule and a weakly bonded S-donor atom from the asymmetric end-to-end thiocyanate bridge, with a Cu···S separation of 2.959(1) Å, occupy the apical sites. The presence of two "symmetric" thiocyanate bridges with short Cu−SCN and Cu−NCS distances of 2.402(1) and 1.938(3) Å, respectively, results in a Cu−Cu separation of 5.499(1) Å. The magnetic susceptibility data measured in the 11−290 K temperature range shows a strong antiferromagnetic coupling between the copper ions through the "symmetric" thiocyanate bridges. Fitting the data to the Bleaney−Bowers equation gives the exchange parameter $2J = -148.2$ cm^{-1}, which is many times higher than those previously found in other copper(II) thiocyanate bridged complexes, and $g = 2.20$. The unprecedented equatorial−equatorial disposition of the thiocyanate bridging entities appears to be responsible for the magnetic behavior of this compound.

Introduction

The magneto-structural studies carried out on polynuclear divalent first-row transition metal complexes supported by N_3^-,[2] NCO^-,[3] NCS^-,[4] and $NCSe^-$ [5] pseudohalide bridges has received great attention in recent years, in view of their interesting properties. In this set, the azide group has received the major attention owing to its versatility as a ligand and the wide variety of magnetic properties of its compounds. The different coordination modes exhibited by the azide group toward copper(II) ions,[6] which lead to very different magnetic behavior, are shown in Chart 1. The end-on coordination mode (**a**) gives rise to ferromagnetic interactions[7,8] between the metal ions, whereas complexes with end-to-end bridges, such as shown in **b**, show strong antiferromagnetic interactions.[9] Finally, in complexes with asymmetric end-to-end azide bridges, with a short and a long Cu−N bond (type **c**), the interaction is either negligible[10] or weakly antiferromagnetic.[11] By contrast, the literature available for magneto-structural studies on copper(II) complexes containing bridging thiocyanate groups is scarce, this ligand behaving with less versatility and less efficiently as a transmitter of magnetic interactions than the azide. Thus, thiocyanate has been found to form mainly bridges analogous to **c**[12,13] with only a few cases of type **a**,[3,14] both resulting in a very weak magnetic coupling between the copper centers. The

Chart 1



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lack of copper(II) complexes containing bridges of “type **b**” should be related to the chemical nature of the thiocyanate group, since both extremes are equivalent in the azide group, whereas in the thiocyanate two very different donor groups (N and S) are present. So far, this fact appears to have hindered the isolation of the “symmetric” end-to-end bridges analogous to **b**.

In this paper we present the crystal structure and spectroscopic and magnetic properties of $[Cu(NCS)(\mu\text{-}NCS)(Hmtpo)(H_2O)]_2$ (where Hmtpo = 4*H*,7*H*-5-methyl-7-oxo[1,2,4]triazolo[1,5-*a*]-pyrimidine) which represents the first example of a coordination mode “type **b**” for the thiocyanate group in a copper(II) complex, showing the unprecedented ability of this entity as an efficient transmitter of magnetic interactions.

Experimental Section

Reactants and Methods. 4*H*,7*H*-5-methyl-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine was purchased from Aldrich Chemical Co. and used as received. The other chemical reagents and solvents were supplied from commercial sources. All experiments were performed in an open atmosphere.

Preparation of $[Cu(NCS)(\mu\text{-}NCS)(Hmtpo)(H_2O)]_2$, 1. An ice-cooled solution containing $Cu(NO_3)_2{\cdot}5H_2O$ (0.833 g, 3 mmol) and Hmtpo (0.450 g, 3 mmol) in *ca.* 25 mL of water was added to an ice cooled solution of NH_4NCS (0.456 g, 6 mmol) in *ca.* 5 mL of water. The resulting turbid green solution was filtered and allowed to stand at 4 °C. After 24 h, black crystals of **1** were collected. They were filtered off, washed with ice cooled water, and air dried. In successive days decoloration of the mother liquor due to reduction of Cu(II) as well as crystallization of the free ligand were observed. Yield: 39%. Anal. Calcd (found) for $C_{16}H_{16}N_{12}O_4S_4Cu_2$: C, 27.7 (27.2); H, 2.3 (2.3); N, 24.2 (24.2); S, 18.5 (18.7); Cu, 18.5 (18.7). IR (cm^{-1}): 220 s, 320 s, 340 s, 530 s, 750 s, 775 w, 850 s, 1140 s, 1190 s, 1395 m, 1575 vs, 1625 vs, 1700 vs, 2115 vs, 2145 vs, 3000 s, br, 3500 s.

Instrumentation. Microanalysis of C, H, N, and S was performed on a Fisons-Instruments EA-1008 at the “Centro de Instrumentación Científica” of the University of Granada. Infrared spectra were recorded in the 4000−180 cm^{-1} range on a Perkin-Elmer 983G spectrophotometer, using KBr and polyethylene pellets. Copper and water contents were determined thermogravimetrically at a heating rate of 20 K min^{-1}, using an atmosphere of pure air (100 mL min^{-1}) on a Shimadzu TGA-50 thermobalance provided with infrared (Nicolet 550 FT-IR) and mass (Thermolab) equipment to analyze the evolved gases. DSC curves were obtained on a Shimadzu DSC-50 differential scanning calorimeter at a heating rate of 10 K min^{-1}, using an atmosphere of pure air (100 mL min^{-1}). The magnetic susceptibility was measured in the 11−290 K temperature range on a Manics DSM-8 equipment at the “Centro de Instrumentación Cientifica” of the University of Granada. The magnetic data were corrected for diamagnetism (Pascal) and temperature-independent paramagnetism, the values used being -420×10^{-6} and 120×10^{-6} emu per mol of binuclear unit, respectively.

X-ray Crystallography. Intensity data for a black crystal of $[Cu(NCS)(\mu\text{-}NCS)(Hmtpo)(H_2O)]_2$ (0.07 × 0.16 × 0.29 mm) were measured at 293 K on a Rigaku AFC6R diffractometer fitted with graphite-monochromatized Mo Kα radiation, $\lambda = 0.710\,73$ Å; the ω:2θ scan technique was employed to measure data such that θ_{max} was 27.5°. No significant decomposition of the crystal occurred during the data collection, and only absorption-corrected data[15] which satisfied the $I > 3.0\sigma(I)$ criterion were used in the subsequent analyses. Crystal data are summarized in Table 1.

Table 1. Crystal Data for $[Cu(NCS)(\mu\text{-}NCS)(Hmtpo)(H_2O)]_2$

formula[a]	$C_{16}H_{16}Cu_2N_{12}O_4S_4$	fw[a]	695.8
a, Å	8.408(2)	space group	$P\bar{1}$
b, Å	10.581(3)	*T*, °C	19
c, Å	7.927(2)	λ(Mo Ka), Å	0.710 73
α, deg	89.45(2)	ρ_{calcd}, g cm^{-3}	1.793
β, deg	77.44(2)	μ, cm^{-1}	20.25
γ, deg	69.75(2)	$R(F_o)$[b]	0.033
V, Å^3	644.2(3)	$R_w(F_o)$[c]	0.036
Z[a]	1		

[a] Considering the binuclear unit as the “molecule”. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \sum(||F_o| - |F_c||w^{1/2})/\sum(|F_o|w^{1/2})$, where $w^{-1} = \sigma^2(F_o)$.

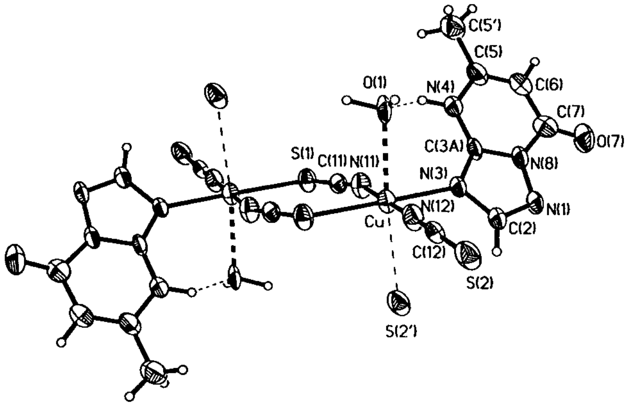

Figure 1. Ortep view of **1** with the atom-numbering scheme. Thermal ellipsoids are plotted at the 50% probability level.

The structure was solved by direct methods and refined by a full-matrix least-squares procedure based on *F*.[16] The non-H atoms were refined with anisotropic thermal parameters, the C−H atoms were included at their calculated positions and fixed, and the O−H and N−H atoms were located from a difference map but their positions were not refined. At convergence (σ weights, $1/\sigma^2(F)$), $R = 0.033$ and $R_w = 0.036$; final refinement details are collected in Table 1. Scattering factors for all atoms were those incorporated in teXsan program.[16]

Results and Discussion

Structure of $[Cu(NCS)(\mu\text{-}NCS)(Hmtpo)(H_2O)]_2$, 1. A view of the molecular structure of **1**, together with its numbering scheme, is depicted in Figure 1, and selected interatomic parameters are collected in Table 2. The structure of the complex is made up of binuclear $[Cu(NCS)(\mu\text{-}NCS)(Hmtpo)(H_2O)]_2$ units, weakly linked among them to form polymeric chains. The copper atoms are located in a distorted octaedral $[N_3S + O + S^*]$ environment. The equatorial positions are occupied by a monodentate Hmtpo ligand, coordinated via N3, two bridging thiocyanate groups coordinated in a “symmetric” end-to-end fashion (one via N and the other via S), and a N-donor atom of an asymmetric end-to-end thiocyanate bridge. The axial positions are occupied by a weakly bonded S-donor atom of the latter thiocyanate group, such that the Cu···S(2)′ separation is 2.959 (1) Å (symmetry operation: $-x, 1 - y, -z$) and a weakly bonded water molecule (Cu−O(1) 2.491(2) Å). The two different thiocyanate groups present in the compound give rise to a polymeric chain aligned along the crystallographic *c*-axis (see Figure 2), in which the “symmetric” bridges (with short Cu−N and Cu−S distances; see Table 2) alternate with the weakly S-bonded thiocyanate bridges. Thus, the “symmetric” bridges give rise to a Cu···Cu separation of 5.499(1) Å

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Table 2. Selected Bond Distances (Including H-Bonded Distances) and Angles for [Cu(NCS)(μ-NCS)(Hmtpo)(H_2O)]$_2$[a]

Bond Distances (Å)			
Cu−O(1)	2.491(2)	Cu−N(11)	1.938(3)
Cu−S(1)^{i}	2.402(1)	Cu−N(12)	1.923(3)
Cu−N(3)	2.074(2)	Cu−S(2)^{ii}	2.959(1)
S(1)−C(11)	1.643(3)	S(2)−C(12)	1.630(3)
C(11)−N(11)	1.150(4)	C(12)−N(12)	1.152(4)
N(4)···O(1)	2.737(4)	O(1)···N(1)^{iii}	2.904(3)
O(1)···O(7)^{iv}	2.872(4)		
Angles (deg)			
S(1)^{i}−Cu−O(1)	94.33 (6)	O(1)−Cu−N(11)	85.0 (1)
S(1)^{i}−Cu−N(3)	176.93(8)	O(1)−Cu−N(12)	94.0(1)
S(1)^{i}−Cu−N(11)	92.43(8)	N(3)−Cu−N(11)	90.1(1)
S(1)^{i}−Cu−N(12)	86.67(9)	N(3)−Cu−N(12)	90.7(1)
O(1)−Cu−N(3)	84.22(9)	N(11)−Cu−N(12)	178.6(1)
S(2)^{ii}−Cu−N(3)	88.5(1)	S(2)^{ii}−Cu−N(11)	89.3(1)
S(2)^{ii}−Cu−N(12)	91.8(1)	S(2)^{ii}−Cu−S(1)^{i}	93.2(1)
S(2)^{ii}−Cu−O(1)	170.7(1)	Cu−S(1)^{i}−C(11)^{i}	102.6(1)
Cu−N(11)−C(11)	163.1(3)	Cu−N(12)−C(12)	170.7(3)

[a] Equivalent atoms: (i) $1 - x, 1 - y, 1 - z$; (ii) $-x, 1 - y, -z$; (iii) $x, y, 1 + z$; (iv) $1 - x, -y, -z$.

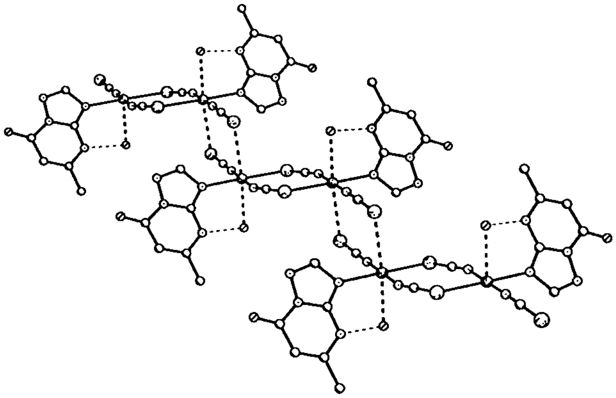

Figure 2. View down the *a*-axis of the polymeric 1-D chains of {[Cu(NCS)(μ-NCS)(Hmtpo)(H_2O)]$_2$}$_n$ along the *c*-axis. (The *c*-axis runs from top left to bottom right.)

compared to 5.669(1) Å which arises from the asymmetric bridging mode of the second thiocyanate group. The most interesting feature of this structure is that this complex represents the first reported case in which both the S-donor and N-donor groups of the bridging thiocyanate moieties occupy equatorial positions of the copper(II) coordination polyhedron. The most usual geometry is N-equatorial and S-axial.[17] The equatorial position of the S-donor atom is responsible for the short Cu−SCN bond distance, namely 2.402(1) Å, the shortest yet reported. A similar distance was found for β-[Cu(NCS)(μ-NCS)(dmtp)$_2$]$_2$ (where dmtp = 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine), namely 2.413(1) Å,[13a] but only the S-donor atom (not the N-atom) of the bridging entity is equatorial in this case. The Cu−NCS distances are in good agreement with those found in the literature.[17] The Cu−N(Hmtpo) separation of 2.074(2) Å is within the range of values reported for other copper(II) complexes with similar ligands,[18,19] including the anionic form of Hmtpo.[20] Also, it should be noted that the core formed by the equatorial Cu(II) coordination planes and the two "symmetric" bridging thiocyanate groups define a plane within ±0.044 Å with maximum deviation of 0.098 Å for atom N11. The geometry of Hmtpo itself, which is planar within ±0.027 Å, does not differ significantly from that of the uncoordinated ligand,[21] with a significant double-bond character for the N(1)−C(2), N(3)−C(3a), C(5)−C(6), and C(7)−O(7) bonds.

There is a significant intramolecular hydrogen bond formed between N(4)−H and the coordinated O atom of the water molecule such that N(4)···O(1) is 2.737(4) Å (angles C(5)−N(4)···O(1) and C(3A)−N(4)···O(1) are 96.6(3) and 139.2(3)°), which may contribute to the stabilization of molecular conformation.

Spectroscopic and Thermal Studies. The thermal behavior has been deduced from their TG and DSC curves. Thus, it can be observed that the dehydration process starts at 100 °C, the corresponding endothermic effect being centered at 117 °C, with a value of 103 kJ/mol of binuclear unit for the associated dehydration enthalpy. Once dehydrated, the compound starts its pyrolytic decomposition, which finishes around 750 °C, leaving CuO as residue.

The IR spectrum of **1** presents only small changes when compared to free Hmtpo, the only appreciable change above 600 cm^{-1} being two very strong absorption bands centered at 2144 and 2110 cm^{-1}, assigned to ν(CN) of the symmetrically and asymmetrically bridged thiocyanate groups, respectively.[22] Finally, in the far-infrared spectrum a double band (340, 320 cm^{-1}) and a sharp absorption centered at 220 cm^{-1} have been assigned to ν(Cu−NCS) and ν(Cu−SCN), respectively.

The electronic spectrum (diffuse reflectance), which has a major absorption with a low-energy shoulder (13 900, 9000 cm^{-1} due to d−d transitions), is not conclusive of the stereochemistry of copper.[23] The ligand-to-metal charge-transfer transitions appear as a broad band in the 34 000−17 000 cm^{-1} range that appear to be characteristic of polynuclear bridged transition metal complexes, since they are not present in the spectra of the corresponding mononuclear compounds and are also observed to occur at lower energy when a high antiferromagnetic coupling is present.[24]

Complex **1** is EPR silent at room temperature. This fact may be due to the large antiferromagnetic interaction between the metal ions which could be responsible for a broadening in the signal (proportional to (Δg)*JT*).[25]

Magnetism. The χ_M vs T curve is displayed in Figure 3. The curve exhibits a smooth maximum centered around 130 K followed by a decrease at lower temperatures indicating that a strong antiferromagnetism between the metal centers takes place. The increase at very low temperature can be related to the occurrence of uncoupled species. The solid curve in Figure 3 is the best fit of the data to the Bleaney−Bowers equation for exchange coupled dimers:

$$\chi_M = \frac{2Ng^2\mu^2}{kT(3 + \exp(-2J/kT))}(1 - \rho) + \frac{Ng^2\mu^2}{2kT}\rho$$

which results from a consideration of the eigenvalues of $H = -2JS_1S_2$, the Heisenberg exchange Hamiltonian. In this expression χ_M represents the susceptibility per mole of binuclear unit corrected for diamagnetism and temperature independent para-

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Table 3. Magnetic and Structural Parameters for Thiocyanate-Bridged Copper(II) Complexes

compd	Cu−N, Å	Cu−S, Å	Cu−N−C, deg	Cu−S−C, deg	geom	J, cm^{-1}	ref
$[Cu(NCS)_2(bpym)]_n$	$2.009(6)_{eq}$	$3.174(2)_{ax}$	165.0(6)	83.1(2)	OC	−0.6	3
α-$[Cu(NCS)_2(dmtp)_2]_2$	$1.953(8)_{ba}$	$2.886(4)_{ax}$	167.7(8)	95.2(4)	SP	≈0	13a
β-$[Cu(NCS)_2(dmtp)_2]_2$	$2.205(2)_{ax}$	$2.413(1)_{eq}$	142.8(2)	99.2(2)	SP	≈+1	13a
$[Cu(NCS)(Et_3dien)]_2(ClO_4)_2$	$1.978(2)_{eq}$	$2.7575(9)_{ax}$	169.0(2)	99.82(7)	OC	+7.7	13b
$[Cu(NCS)(Me_5dien)]_2(ClO_4)_2$	$1.943(7)_{eq}$	$2.678(3)_{ax}$	164.4(9)	99.8(4)	SP	+1.6	13b
$[Cu(NCS)(ept)]_2(ClO_4)_2$	$1.946(4)_{eq}$	$2.978(2)_{ax}$	171.4(4)	90.6(2)	OC	+1.3	13b
1	$1.939(3)_{eq}$	$2.402(1)_{eq}$	163.0(3)	102.6(3)	OC	−74	*b*

[a] bpym = 2,2′-bipyrimidine, Et$_3$dien = 1,4,7-triethyldiethylenetriamine, Me$_5$dien = 1,1,4,7,7-pentamethyldiethylenetriamine, ept = *N*-(2-aminoethyl)-1,3-propanediamine. [b] This work.

magnetism. $2J$ is the singlet−triplet energy gap. The last term in the expression is a correction for the presence of uncoupled species impurity, ρ being the proportion of such impurity.

The J, g, and ρ were taken as adjustable parameters in a least-square fitting procedure that led to the values $2J = -148.2$ cm^{-1}, $g = 2.20$, and $\rho = 0.033$. The agreement factor R defined as $\Sigma(\chi_{M_{cal}} - \chi_{M_{obs}})^2/\Sigma(\chi_{M_{obs}})^2$ is then equal to 1.87×10^{-4}. The calculated curve fits the experimental points satisfactorily as shown in Figure 3.

Alternatively, we have tried to fit the data to the modified Bleaney−Bowers expression, taking into account the interbinuclear-unit interactions J' between z neighbors, by means of a zJ' term, in a molecular field approach (where zJ' is an additional adjustable parameter), but the least-squares fitting did not converge. The low expected value for a possible interbinuclear-unit interaction appears to be hidden by the much stronger intrabinuclear unit interaction, transmitted by the "symmetric" thiocyanate bridges. Thus, the partial delocalization of the spin density in the equatorial plane (unpaired electron in the $d_{x^2-y^2}$ orbital) should make the transmission through the weakly axial bonded S(2) atom very inefficient.

The information available in the literature about the magnetic properties of complexes of the type bis(μ-NCS) is scarce. In Table 3, the magnetic and structural parameters for such compounds are summarized. It can be concluded from an examination of these data that the magnetic interaction is negligible in all cases with the exception of the present work. The most significant difference between the present compound and of those previously studied is the fact that both the N and S donor groups of the two "symmetric" bridges occupy equatorial positions in the coordination polyhedra about the metal centers. The Cu−S and Cu−N distances in our compound are both close to the Bragg−Slater radii[26] sum ($r_S + r_{Cu} = 2.35$, $r_N + r_{Cu} = 2.00$ Å), so it can be assumed that both bonds are similarly strong, indicating that this compound is analogous to the "type **b**" azide-bridged complexes. As a consequence of the thiocyanate bridging mode, it appears that an important overlap of the orbitals of the bridging entities with the magnetic orbitals of the metal atoms takes place, in a similar way as the azide group,[6] leading to the observed magnetic interaction which is many times higher than those previously found in other thiocyanate bridged complexes.

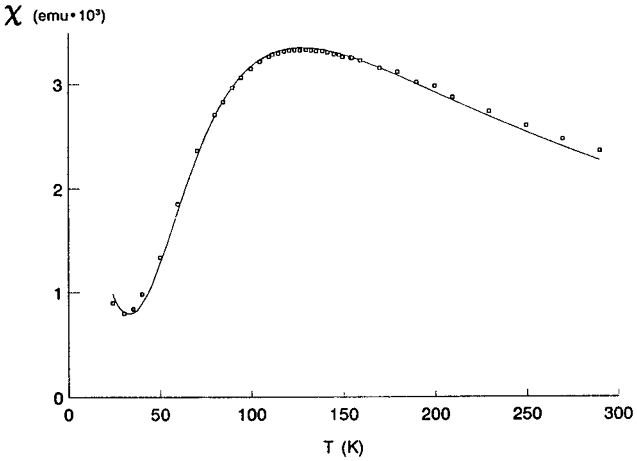

Figure 3. Thermal variation of the molar susceptibility (per binuclear unit): experimental points and theoretical (solid line) best fit.

It is clear that more structural and magnetic data for "type **b**" thiocyanate-bridged copper(II) complexes would be necessary to extract statistically significant correlations. Nevertheless, molecular engineering is very difficult due to the ambidentate nature of the ligand, the copper(II) atom's border line position in the Pearson's classification, and the redox characteristics of both.

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Supporting Information Available: A file, in CIF format, containing the crystallographic data and details of the structure refinement, atom coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations of **1** is available. Access information is given on any current masthead page.

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