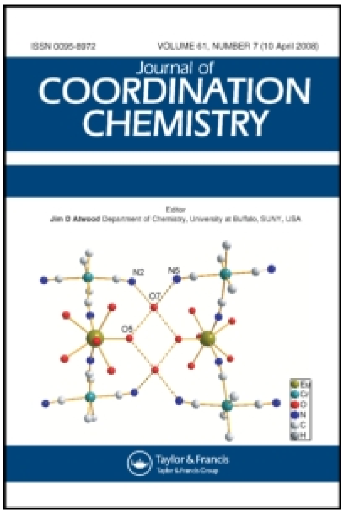

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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF A THIOCYANATE BRIDGED ONE-DIMENSIONAL CHAIN COPPER(II) COMPLEX: $\{[(232\text{-tet})Cu(NCS)](ClO_4)\}_n$

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A thiocyanate bridged one-dimensional chain copper(II) complex, $\{[(232\text{-tet})Cu(NCS)](ClO_4)\}_n$, where 232-tet = *N,N′-bis*(2-aminoethyl)-1,3-propanediamine, has been synthesised and its crystal structure determined at room temperature. This complex crystallises in the orthorhombic system, space group $Pca2_1$, with $a = 23.565(3)$, $b = 9.011(2)$, $c = 14.290(3)$ Å and $Z = 4$. Least-squares refinement of the structure leads to conventional R_1 and wR_2 factors of 0.052 and 0.142. The asymmetric unit consists of two $[(232\text{-tet})Cu(NCS)]^+$ units and two perchlorate anions. The two symmetric independent $[(232\text{-tet})Cu(NCS)]^+$ units form two different chains in the crystal lattice. The intrachain copper(II)–copper(II) separations are 7.282(5) [Cu(1)–Cu(1)^a, a: $1.5 - x, y, 0.5 + z$] and 7.334(5) Å [Cu(2)–Cu(2)^b, b: $1 - x, 1 - y, 0.5 + z$], respectively. The interchain copper(II)–copper(II) separation is 6.870(5) Å [Cu(1)–Cu(2)^b, b: $1 - x, 1 - y, 0.5 + z$]. The coordination environments of the two Cu(II) atoms are similar. Each Cu(II) atom is $(4 + 1 + 1')$ coordinated in a distorted, elongated, tetragonal octahedron with four N atoms of the 232-tet ligand in the equatorial positions and one N atom of the thiocyanate and one S atom of the other thiocyanate in the axial positions. The ESR spectrum appeared to show axial symmetry with $g_\perp = 2.05$ and $g_\parallel = 2.16$. Variable temperature magnetic susceptibility shows that there is a weak antiferromagnetic interactions in intrachains.

Keywords: Crystal structure; magnetic property; copper; thiocyanate; *N, N′-bis*(2-aminoethyl)-1,3-propanediamine; X-ray structure

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INTRODUCTION

The problem of exchange interaction between transition metal ions through extended molecular bridges, both in synthetic polynuclear compounds and in functionalised examples, has given rise to much interest among inorganic chemists over the past few years.[1] Pseudohalide ions have been shown to be good bridging ligands for obtaining magnetic molecular compounds of high nuclearity.[2–4] The thiocyanate anion can be coordinated with transition metal ions in terminal *N*-bonded, terminal *S*-bonded, end-to-end and end-to-on bridged modes. The most common modes are Cu–NCS and Cu–NCS–Cu coordination modes in copper complexes.[5] Herein we report the synthesis, crystal structure and magnetic properties of a new chain copper(II) complex bridged by the thiocyanate anion.

EXPERIMENTAL

Physical Measurements

Elemental analysis for carbon, hydrogen, nitrogen was performed with a Perkin-Elmer model 240C instrument. The IR spectrum was recorded with a Nicolet 170 SX FT-IR spectrometer using KBr discs. Magnetic measurements on powder sample were carried out in the 75–300 K temperature range by means of a Faraday-type magnetometer. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$ (en = ethylenediamine). Diamagnetic corrections were estimated from Pascal's constants as -182×10^{-6} emu mol^{-1} (1 emu = SI × $10^6/4\pi$).[6] X-band ESR spectra were recorded at room temperature with a Bruker ER 200 spectrometer.

Preparation

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

N,N′-bis(2-amioethyl)-1,3-propanediamine, 232-tet, was prepared according to the procedure of Hamilton and Alexander.[7] To an aqueous solution (10 cm^3) of copper perchlorate hexahydrate (741 mg, 2 mmol) was added an aqueous solution of 232-tet (320 mg, 2 mmol) with stirring. An aqueous solution of sodium thiocyanate (162 mg, 2 mmol) was then poured dropwise into the above mixure solution. After several days at room temperature well-shaped, blue, single crystals were obtained by slow evaporation; yield:

615 mg, 82%. Found: C 25.07, H 5.35, N 18.05%; calculated for $Cu_2C_{16}H_{40}Cl_2N_{10}O_8S_2$: C 25.20, H 5.29, N 18.37%.

X-ray Crystallography

Diffraction data were collected at 293 K with an Enraf-Nonius CAD-4 four-circle diffractometer[8] using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Crystal data and details of the data collection are given in Table I. Unit cell parameters and orientation matrix were determined from angular setting 25 carefully centred reflections. Intensities of three standard reflections measured every 97 reflections showed no significant variations. Intensity data were collected by the $\omega/2\theta$ scans technique and were corrected for absorption by empirical *via* ψ scans. Some 2782 reflections were considered as independent and used in the structure analysis. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL version 5.0.[9] Non-H atom coordinates were

TABLE I Crystal data and data collection details for $\{[(232\text{-tet})Cu(NCS)](ClO_4)\}_n$

Empirical formula	$C_{16}H_{40}Cl_2Cu_2N_{10}O_8S_2$
Formula weight	762.68
Crystal system	Orthorhombic
Space group	$Pca2_1$
a (Å)	23.565(5)
b (Å)	9.011(2)
c (Å)	14.290(3)
V (Å^3)	3034.4(11)
Z	4
F(000)	1576
D_{calc} (Mg/m^3)	1.669
Crystal size (mm)	0.21 × 0.24 × 0.46
θ range (°)	1.73 ~ 25.00
μ(MoK$_\alpha$) (cm^{-1})	17.72
Data collection instrument	Enraf-Nonius CAD-4
Radiation Type, Wavelength λ (Å)	MoK$_\alpha$, 0.71073
Temperature (K)	293(2)
Data collection's method	$\omega/2\theta$ scan
Range of h, k, l	0 ~ 27, 0 ~ 10, 0 ~ 16
Reflections collected	2782
Independent reflections	2782 [$R(int)$ = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2782/1/361
Goodness-of-fit on F^2	1.042
R_1, wR_2 [$I > 2\sigma(I)$]	0.052, 0.142
R_1, wR_2 (all data)	0.061, 0.147
Absolute structure parameter	0.00
Extinction coefficient	0.0039(2)
$\Delta\rho_{max}$ (e.Å^{-3})	0.799
$\Delta\rho_{min}$ (e.Å^{-3})	−0.488

obtained by Fourier syntheses. After all the coordinates and isotropic and anisotropic thermal parameters of non-H atoms were refined, all hydrogen atoms were placed in calculated positions (C–H, 0.96; N–H, 0.90 and O–H, 0.85), assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. Finally, the coordinates, the anisotropic thermal parameters of non-H atoms, and isotropic thermal parameters of H atoms were refined by least-squares methods to final conventional $R_1 = 0.052$ and $wR_2 = 0.142$. All calculations were performed by an IBM compatible 486/DX^2 personal computer using the SHELXTL/PC program package. Analytical expressions for neutral-atom scattering factors employed and anomalous dispersion corrections were incorporated.[10]

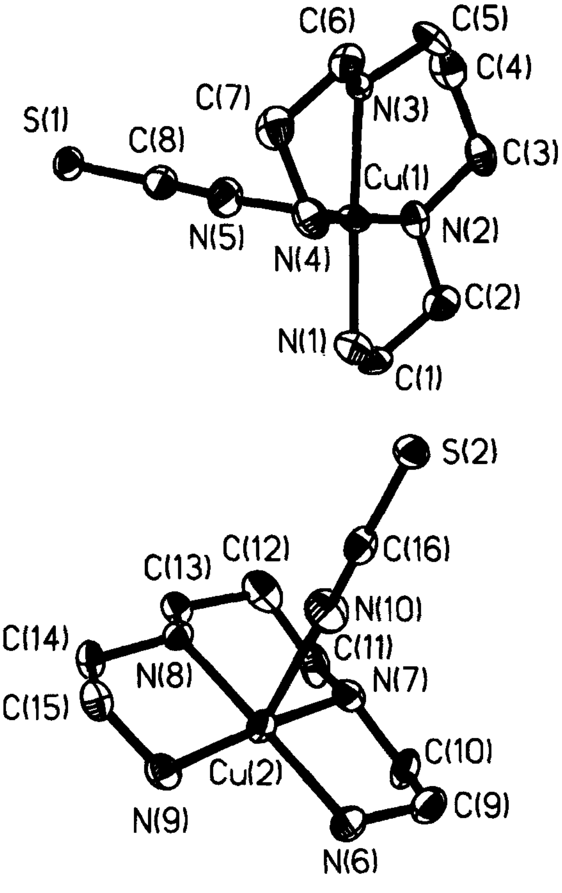

FIGURE 1 Structure of the $\{[(232\text{-tet})Cu(NCS)](ClO_4)\}_n$ cation with the atom labelling scheme. H atoms have been omitted for clarity.

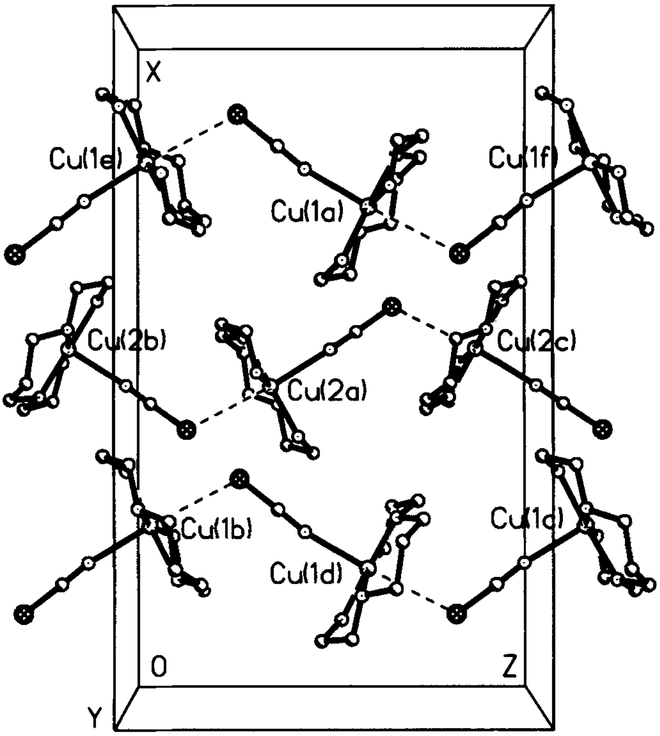

FIGURE 2 Stereoview of the packing of $\{[(232\text{-tet})Cu(NCS)](ClO_4)\}_n$. The view is down the *b* axis.

The cation structure and molecular packing are illustrated in Figures 1 and 2. Fractional atomic coordinates for all non-H atoms are listed in Table II and selected bond lengths and angles in Table III. Full lists of crystallographic data are available from the authors upon request.

RESULTS AND DISCUSSION

Infrared Spectra

The perchlorate salt shows strong bands near 1091 cm^{-1} (antisymmetric stretch) and sharp bands at 622 cm^{-1} (antisymmetric bend), indicative of uncoordinated perchlorate anions. The thiocyanate group can function as a unidentate ligand in two ways depending on whether the nitrogen or the sulphur atom is bonded to the metal. It also functions as a bridging ligand, M–NCS–M. The band at 2066 cm^{-1} falls in the region expected for terminal

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $\{[(232\text{-tet})\mathrm{Cu(NCS)}](\mathrm{ClO_4})\}_n$; $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

	x/a	*y/b*	*z/c*	*U(eq)*
Cu(1)	7201(1)	692(1)	5795(1)	35(1)
Cu(2)	4717(1)	5543(1)	3526(1)	37(1)
S(1)	8444(1)	962(1)	2847(1)	47(1)
S(2)	5912(1)	4189(1)	6484(1)	45(1)
N(1)	6460(1)	1318(2)	5204(2)	55(1)
N(2)	6912(1)	−1394(2)	5623(1)	42(1)
N(3)	7931(1)	80(2)	6451(1)	30(1)
N(4)	7416(1)	2759(2)	6226(2)	48(1)
N(5)	7717(1)	562(4)	4370(2)	73(1)
N(6)	3993(1)	6127(2)	4201(2)	50(1)
N(7)	4441(1)	3438(2)	3674(2)	44(1)
N(8)	5438(1)	5023(2)	2855(1)	35(1)
N(9)	4926(1)	7661(2)	3224(2)	47(1)
N(10)	5266(1)	5201(3)	4972(2)	70(1)
C(1)	6223(1)	−23(3)	4744(2)	46(1)
C(2)	6317(1)	−1304(3)	5408(2)	54(1)
C(3)	7055(1)	−2517(3)	6368(2)	53(1)
C(4)	7688(1)	−2618(3)	6512(2)	58(1)
C(5)	7948(1)	−1298(3)	7023(2)	51(1)
C(6)	8129(1)	1382(3)	6988(2)	46(1)
C(7)	8011(1)	2744(3)	6406(2)	56(1)
C(8)	8021(1)	716(3)	3748(2)	48(1)
C(9)	3731(1)	4770(3)	4564(2)	57(1)
C(10)	3829(1)	3568(3)	3892(2)	59(1)
C(11)	4590(1)	2416(3)	2918(2)	57(1)
C(12)	5221(1)	2333(3)	2776(2)	63(1)
C(13)	5471(1)	3684(2)	2267(2)	40(1)
C(14)	5631(1)	6343(3)	2346(2)	44(1)
C(15)	5519(1)	7677(3)	2966(2)	46(1)
C(16)	5533(1)	4771(3)	5593(2)	42(1)
Cl(1)	9552(1)	− 152(1)	5483(1)	52(1)
Cl(2)	7065(1)	5028(1)	3822(1)	47(1)
O(1)	9760(1)	− 315(3)	4556(2)	100(1)
O(2)	9294(1)	1273(3)	5573(2)	111(1)
O(3)	9993(1)	− 418(3)	6150(2)	91(1)
O(4)	9120(1)	− 1246(3)	5646(2)	107(1)
O(5)	7274(1)	4991(3)	4750(2)	76(1)
O(6)	7520(1)	4756(3)	3211(2)	86(1)
O(7)	6630(1)	3917(3)	3717(2)	82(1)
O(8)	6796(1)	6398(3)	3656(2)	95(1)

S-bonded and that at $2018\,\mathrm{cm}^{-1}$ in the region expected for terminal *N*- bonded.[11] Thus, the thiocyanate group is coordinated to Cu(II) atom in both ways.

Description of the Structure

The complex crystallises in the orthorhombic system, space group $Pca2_1$, $Z = 4$. The asymmetric unit consists of two $[(232\text{-tet})\mathrm{Cu(NCS)}]^+$ units and

TABLE III Selected bond lengths and angles for $\{[(232\text{-tet})Cu(NCS)](ClO_4)\}_n$ (Å, °)

Cu(1)-N(1)	2.020(2)	Cu(2)-N(6)	2.031(2)
Cu(1)-N(2)	2.014(2)	Cu(2)-N(7)	2.017(2)
Cu(1)-N(3)	2.035(2)	Cu(2)-N(8)	2.017(2)
Cu(1)-N(4)	2.026(2)	Cu(2)-N(9)	2.018(2)
Cu(1)-N(5)	2.374(3)	Cu(2)-N(10)	2.456(3)
Cu(1)-S(1)[a]	3.313(3)	Cu(2)-S(2)[b]	3.283(3)
N(2)-Cu(1)-N(1)	85.2(1)	N(2)-Cu(1)-N(4)	168.3(1)
N(1)-Cu(1)-N(4)	94.9(1)	N(2)-Cu(1)-N(3)	95.1(1)
N(1)-Cu(1)-N(3)	177.3(1)	N(4)-Cu(1)-N(3)	84.2(1)
N(2)-Cu(1)-N(5)	91.3(1)	N(1)-Cu(1)-N(5)	95.6(1)
N(4)-Cu(1)-N(5)	100.3(1)	N(3)-Cu(1)-N(5)	87.1(1)
N(8)-Cu(2)-N(7)	96.0(1)	N(8)-Cu(2)-N(9)	85.0(1)
N(7)-Cu(2)-N(9)	172.3(1)	N(8)-Cu(2)-N(6)	178.5(1)
N(7)-Cu(2)-N(6)	85.5(1)	N(9)-Cu(2)-N(6)	93.6(1)
N(8)-Cu(2)-N(10)	85.8(1)	N(7)-Cu(2)-N(10)	87.9(1)
N(9)-Cu(2)-N(10)	99.8(1)	N(6)-Cu(2)-N(10)	94.4(1)

[a] $1.5 - x, y, 0.5 + z$;
[b] $1 - x, 1 - y, -0.5 + z$.

two perchlorate anions. There are no obvious bonding interactions between independent $[(232\text{-tet})Cu(NCS)]^+$ units. The two symmetric independent $[(232\text{-tet})Cu(NCS)]^+$ units form two different chains in the crystal lattice. The intrachain copper(II)–copper(II) separations are 7.282(5) [Cu(1)–Cu(1)^{a}, a: $1.5 - x, y, 0.5 + z$] and 7.334(5) Å [Cu(2)–CU(2)^{b}, b: $1 - x$, $1 - y, 0.5 + z$], respectively. The interchain copper(II)–copper(II) separation is 6.870(5) Å [Cu(1)–Cu(2)^{b}, b: $1 - x, 1 - y, 0.5 + z$]. The coordination environments of the two Cu(II) atoms are similar. Each Cu(II) atom is $(4 + 1 + 1')$ coordinated in a distorted, elongated, tetragonal octahedron with four N atoms of the 232-tet ligand in the equatorial positions and one N atom of the thiocyanate and one S atom of the other thiocyanate in the axial positions. Cu(1), N(1), N(2), N(3) and N(4) are coplanar, with N(5) and S(1)^{a} (a: $1.5 - x, y, 0.5 + z$) of thiocyanate groups lying 2.459 and 3.185 Å out of this plane; Cu(2), N(6), N(7), N(8) and N(9) are coplanar, with N(10) and S(2)^{c} (c: $1 - x, 1 - y, -0.5 + z$) of thiocyanate groups lying 2.489 and 3.217 Å out of this plane. These planes' dihedral angle is 57.6°. The $Cu{-}N_{(NCS)}$ apical bond lengths [2.374(3), 2.456(3) Å] are longer than the mean $Cu{-}N_{(232\text{-tet})}$ bond lengths [2.024(3), 2.018(3) Å], comparable with the values of 2.384(13) Å found in the structure of $[Cu(tim)(NCS)](PF_6)$,[12] shorter than the values of 2.517(7) and 2.720(10) Å found in the structures of $[Cu(Me_2en)_2(NCS)_2]$ and $[Cu(en)_2(NCS)](BF_4)$,[13,14] longer than the values of 2.296(2) and 2.237(14) Å found in the structures of [Cu(decane)(NCS)] · H_2O and $[Cu(Meen)_2(NCS)](NCS)$.[15,16] The Cu–S apical bond lengths [3.313(3), 3.283(3) Å] are much longer than a normal Cu–S single bond (2.39 Å), comparable with the values of 3.286(9), 3.270(5) and 3.158(4) Å found in the structures of $[Cu_2(NH_3)_3(NCS)_3]$, $[Cu(3\text{-Mepy})_{0.25}(NCS)_2]$ and $[Cu(4\text{-Mepy})_2(NCS)_2]$.[17–19]

Magnetic Properties

The X-band ESR spectrum was measured for a polycrystalline powder at room temperature and is shown in Figure 3. Spectra of polycrystalline copper(II) complexes, exhibiting two types of g values, $g_{\|}$ and $g_{\perp}$, have been used[20–23] to distinguish unambiguously between $d_{x^2-y^2}$ and d_{z^2} ground states for which $g_{\|} > g_{\perp}$ and $g_{\perp} > g_{\|} \approx 2.00$, respectively. The copper(II) complex studied here shows a pronounced peak ($g_{\perp} = 2.05$) and a broad shallow peak ($g_{\|} = 2.16$) typical of a d^9 complex possessing axial symmetry and with the unpaired electron present in the $d_{x^2-y^2}$ orbital. In axial symmetry the g values are related by the expression $G = (g_{\|} - 2)/(g_{\perp} - 2)$, which measures the exchange interaction between copper centres in the polycrystalline solid. If $G > 4$, the exchange interaction is negligible; $G < 4$ indicates considerable

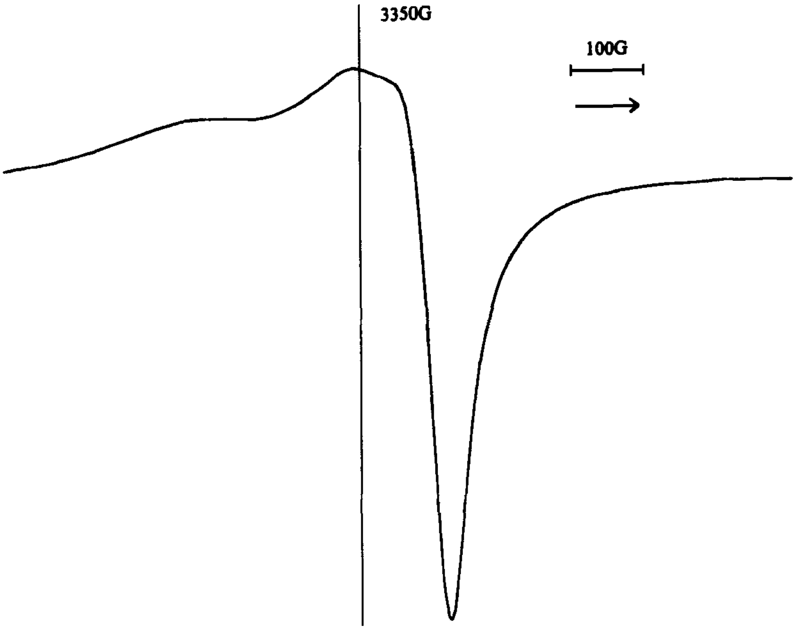

FIGURE 3 Solid powder ESR spectrum of $\{[(232\text{-tet})Cu(NCS)](ClO_4)\}_n$ at room temperature.

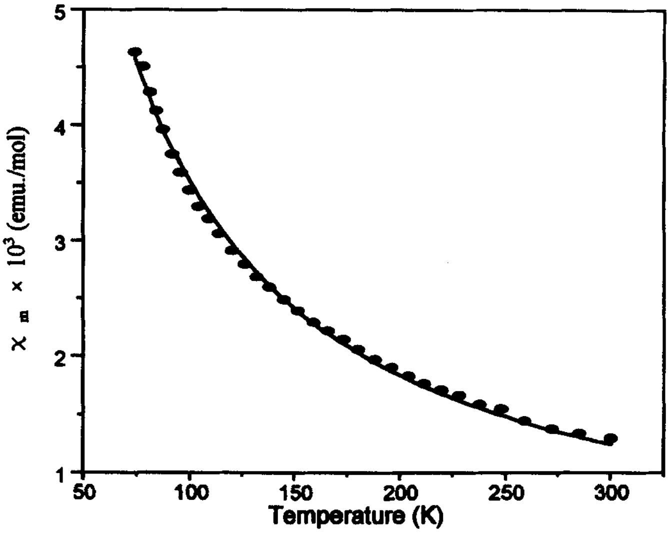

FIGURE 4 Molar magnetic susceptibility *vs* temperature curve for $\{[(232\text{-tet})Cu(NCS)](ClO_4)\}_n$. Experimental points are represented by circles, whereas the solid line is obtained by least-squares fitting of all experimental points.

exchange interaction. In this complex, $G = 3.2$ indicates there is a weak interaction.

The temperature dependence of the molar magnetic susceptibility, χ_m of $\{[(232\text{-tet})Cu(NCS)](ClO_4)\}_n$ is shown in Figure 4. Magnetic susceptibility data between 75 and 300 K obeyed the Curie–Weiss law $\chi_m = C/(T - \theta)$, with $C = 0.384 \pm 0.004$ emu K mol^{-1} and $\theta = -9 \pm 1$ K, respectively. The decrease of the effective magnetic moment from 1.77 μB per Cu(II) at 300 K to 1.67 μB per Cu(II) at 75 K and the negative Weiss constant may also indicate the presence of a weak antiferromagnetic interaction.

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