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Polyhedron 26 (2007) 1740–1744

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Two new pseudohalide bridged di- and poly-nuclear copper(II) complexes: Synthesis, crystal structures and magnetic studies

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Received 21 November 2006; accepted 8 December 2006
Available online 16 December 2006

Abstract

Two new pseudohalide bridged di- and poly-nuclear copper(II) complexes $[Cu_2(L)_2(\mu_{1,1}\text{-}N_3)_2]$ (**1**), $[Cu(L)(\mu_{1,3}\text{-}NCS)]_n$ (**2**), [$\mathbf{LH} = C_6H_5C(O)NHN{=}C(CH_3)C_5H_4N$] have been synthesised and characterised by elemental analysis, IR and UV–Vis spectral studies. Structures of both the complexes have been established by X-ray crystallography. A tridentate hydrazone ligand (**LH**) obtained by the condensation of benzhydrazide and 2-acetylpyridine is used for the preparation of complexes **1** and **2**. Variable temperature magnetic susceptibility measurement studies indicate there is a weak ferromagnetic interaction between the two copper(II) ions in **1** ($J = +0.75\ \text{cm}^{-1}$), while weak antiferromagnetic interaction is observed with J values $-0.23\ \text{cm}^{-1}$ for **2**.

Keywords: Copper(II) complexes; Tridentate hydrazone ligand; Crystal structures; Magnetic studies

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1. Introduction

Multinuclear metal complexes have demonstrated many important properties in systems such as catalysis [1], clathration [2] and molecular sieving [3]. In addition, they are very useful for developing new functional molecule-based materials [4]. The design and synthesis of polynuclear coordination complexes, aimed at understanding the structural and chemical factors that govern the exchange coupling between paramagnetic centres, are of continuing interest in biology, chemistry and physics [5]. Pseudohalide bridged polynuclear and dinuclear complexes continue to be the subject of much interest, and intensive investigations have taken place as a result of their diverse structures and potential applications as magnetic materials. Among the pseudohalides, the azido group has received much attention due to its versatility as a ligand and to the wide variety of magnetic properties of its compounds. Less literature is available for magneto-structural studies on copper(II) complexes containing bridging thiocyanate groups as this ligand is less efficient as a transmitter of magnetic interactions than azide.

To examine the versatility of the pseudohalides, several pseudohalide bridged di- and poly-nuclear transition metal complexes have already been reported by our group using various Schiff bases, amines etc. as co-ligands [6–8]. In continuation of this work, here we have synthesised one dinuclear and a polynuclear copper(II) complexes $[Cu_2(L)_2(\mu_{1,1}\text{-}N_3)_2]$ (**1**), $[Cu(L)(\mu_{1,3}\text{-}NCS)]_n$ (**2**), using azide, thiocyanate as bridging ligands with the ions of a hydrazone ($\mathbf{LH} = C_6H_5C(O)NHN{=}C(CH_3)C_5H_4N$) as coligand. The hydrazone ligand is the condensation product of benzhydrazide and 2-acetylpyridine. The present paper describes the syntheses, X-ray crystal structures, variable temperature magnetic (VTM) susceptibility studies and spectroscopic results of two new Cu(II) complexes **1** and **2**.

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doi:10.1016/j.poly.2006.12.015

2. Experimental

2.1. Materials and measurements

Benzhydrazide, 2-acetylpyridine, copper(II) perchlorate hexahydrate (Fluka), sodium thiocyanate and sodium azide (Aldrich) were used as received. The solvents used were of reagent grade.

Elemental analyses were carried out using a Perkin–Elmer 2400 II elemental analyser. The infrared spectra were recorded on a Perkin–Elmer RX 1 FT-IR spectrophotometer with a KBr disc. The electronic spectra were recorded, in acetonitrile, on a Perkin–Elmer Lambda 40 (UV–Vis) spectrophotometer. Magnetic susceptibility measurements for the complexes **1** and **2** were carried out with a Quantum Design MPMS-5S SQUID magnetometer under an applied magnetic field of 5000 Oe. The temperature dependence of the molar magnetic susceptibility, χ_M, for the complexes **1** and **2** was measured on polycrystalline samples in the temperature range 2–300 K. Diamagnetic corrections were estimated from Pascal tables and magnetic data were corrected for diamagnetic contributions of the sample holder.

2.2. Synthesis of ligand and metal complexes

2.2.1. $[C_6H_5C(O)NHN{=}C(CH_3)C_5H_4N]$ (*LH*)

The ligand **LH** was prepared by the condensation of benzhydrazide (1.36 g, 10 mmol) with 2-acetylpyridine (1.12 ml, 10 mmol) in methanol (50 ml) according to the procedure reported elsewhere [9]. The resulting light yellow liquid was used without further purification.

Caution! Perchlorate salts are potentially explosive and should be used in small quantity and with much care.

2.2.2. $[Cu_2(L)_2(\mu_{1,1}\text{-}N_3)_2]$ (*1*)

To a methanolic solution (20 ml) of copper perchlorate hexahydrate (0.370 g, 1 mmol), the solution of the hydrazone ligand (**LH**) (1 mmol) was added, followed by the addition, with constant stirring, of a solution of sodium azide (0.065 g, 1 mmol) in minimum volume of water–methanol mixture. The final solution was kept at refrigerator temperature yielding dark green, hexagonal crystals suitable for X-ray diffraction after 6 days. Crystals were isolated by filtration and were air-dried. Yield – 61%. *Anal.* Calc. for $C_{14}H_{12}N_6OCu$: C, 48.86; H, 3.52; N, 24.42. Found: C, 48.61; H, 3.32; N, 24.09%.

2.2.3. $[Cu(L)(\mu_{1,3}\text{-}NCS)]_n$ (*2*)

The complex **2** was synthesised in a similar manner as described for **1**, except that sodium thiocyanate was used instead of sodium azide. Dark green, hexagonal crystals suitable for X-ray diffraction were obtained after 7 days. Crystals were collected by filtration and were air-dried. Yield – 53%. *Anal.* Calc. for $C_{15}H_{12}N_4OSCu$: C, 50.01; H, 3.36; N, 15.56. Found: C, 49.00; H, 3.32; N, 14.94%.

2.3. X-ray crystallography

The determination of the unit cell and the data collection for dark green coloured crystals of **1** and **2** was performed on a Bruker-Nonius X8 Apex2 Diffractometer. All data were collected with Mo Kα radiation ($\lambda = 0.71073$ Å). The structures of all the complexes were determined by direct method procedures in SHELXS [10a], and refined by full-matrix least-squares methods in SHELXL [10b]. Carbon-bonded hydrogen atoms were included in idealised positions and set to ride on the parent atoms. The crystallographic data and the refinement results are listed in Table 1.

3. Results and discussion

3.1. Description of the crystal structures

3.1.1. $[Cu(L)_2(\mu_{1,1}\text{-}N_3)_2]$ (*1*)

An ORTEP diagram of **1** with atom numbering scheme is given in Fig. 1. Bond dimensions about the copper atom in **1**, together with those **2**, are in Table 2; dimensions in the main chains of the **L** ligand and in the bridging ligands in both the complexes **1** and **2** are collated in Table 3. The structural study reveals that **1** is a semi-bridging centrosymmetric dimer. The azide ion bridges in an asymmetric (basal-apical) fashion so the bridging Cu–N bond lengths are significantly different ($\Delta d = 0.566$ Å). The copper centres are five-coordinate, bonded to three coordinating

Table 1
Crystallographic and refinement data for complexes **1** and **2**

Complex	1	2
Chemical formula	$C_{28}H_{24}N_{12}O_2Cu_2$	$C_{15}H_{12}N_4OSCu$
Formula weight	687.68	359.89
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	Cc
Z	1	4
a (Å)	7.877(13)	11.424(3)
b (Å)	10.465(7)	11.281(3)
c (Å)	10.616(7)	11.173(3)
α (°)	115.71(2)	90
β (°)	97.73(3)	93.466(4)
γ (°)	103.04(3)	90
V (Å^3)	740.9(14)	1437.3(6)
Temperature (K)	100(2)	100(2)
Density (Mg/m^3)	1.541	1.663
Absorption coefficient (mm^{-1})	1.484	1.671
$F(000)$	350	732
Crystal size (mm)	$0.22 \times 0.12 \times 0.08$	$0.38 \times 0.36 \times 0.04$
θ Range for data collection (°)	2.28–25.36	4.05–37.24
Reflections collected	6690	4456
Independent reflections (R_{int})	1961(0.117)	3387(0.0327)
Number of 'observed' reflections	726	2551
Goodness-of-fit, S	0.788	1.053
R indices (all data)	$R_1 = 0.196$, $wR_2 = 0.187$	$R_1 = 0.0597$, $wR_2 = 0.103$
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0719$, $wR_2 = 0.158$	$R_1 = 0.0424$, $wR_2 = 0.0968$
Largest difference in peak and hole (e Å^{-3})	0.88 and −0.98	0.83 and −1.54

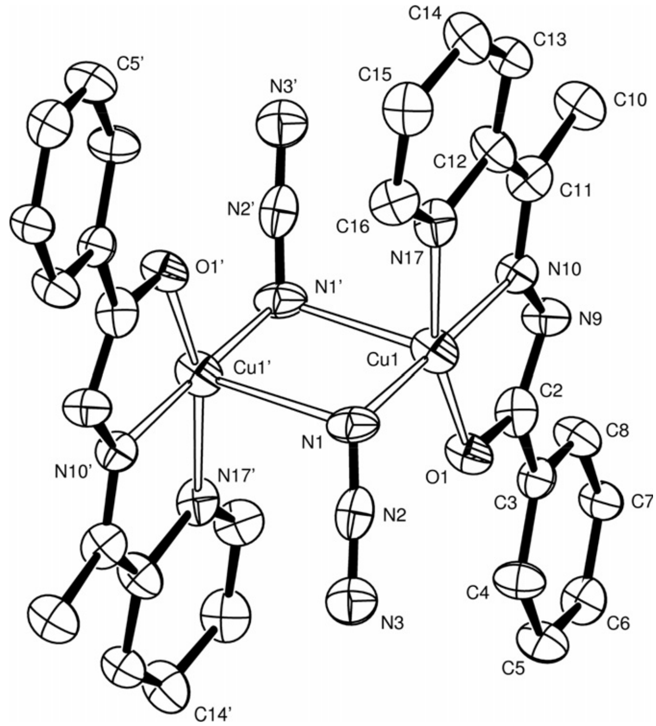

Fig. 1. View of the dimeric unit of **1**, with atom labels. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 3
Selected bond dimensions (Å and °) in the main chains of the **L** ligand and in the bridging ligands in complexes **1** and **2**

Complex **1**		Complex **2**	
C(29)–O(4)	1.326(11)	O(1)–C(2)	1.295(5)
N(4)–C(29)	1.353(12)	C(2)–N(9)	1.335(5)
N(1)–N(4)	1.424(11)	N(9)–N(10)	1.379(5)
N(1)–C(22)	1.319(13)	N(10)–C(11)	1.303(5)
C(22)–C(6)	1.502(14)	C(11)–C(12)	1.466(6)
N(2)–C(6)	1.421(11)	C(12)–N(17)	1.358(5)
C(29)–O(4)–Cu(1)	108.9(6)	C(2)–O(1)–Cu(1)	110.9(2)
O(4)–C(29)–N(4)	126.8(10)	O(1)–C(2)–N(9)	124.5(4)
C(29)–N(4)–N(1)	105.3(8)	C(2)–N(9)–N(10)	107.1(3)
C(22)–N(1)–N(4)	122.0(8)	C(11)–N(10)–N(9)	123.0(4)
N(1)–C(22)–C(6)	112.5(9)	N(10)–C(11)–C(12)	113.3(4)
N(2)–C(6)–C(22)	113.3(10)	N(17)–C(12)–C(11)	114.2(3)
C(6)–N(2)–Cu(1)	112.4(7)	C(12)–N(17)–Cu(1)	113.0(3)
Complex **1**, azide ligand		Complex **2**, thiocyanate ligand	
N(21)–N(22)	1.209(11)	S(2)–C(1)	1.648(4)
N(23)–N(22)	1.208(12)	C(1)–N(1′)	1.150(6)
N(22)–N(21)–Cu(1)	123.4(8)	C(1)–S(2)–Cu(1)	97.01(13)
N(22)–N(21)–Cu(1′)	109.2(8)	N(1′)–C(1)–S(2)	179.7(4)
Cu(1)–N(21)–Cu(1′)	89.9(4)	C(1″)–N(1)–Cu(1)	160.0(4)
N(23)–N(22)–N(21)	176.3(11)		

E.s.ds are in parentheses.

atoms [N_2O] from the ligand **L** and nitrogen atoms from two bridging azide anions. Both azides bridge in an *end-on* fashion and this leads to a relatively small Cu–Cu (3.205 Å) separation.

The di-$\mu_{1,1}$-azido bridging nitrogen atom is in a planar Cu_2N_2 ring about a crystallographic inversion centre. The azide ions are nearly linear with N–N–N angle of 176.3(11)°. The geometry of the Cu(II) centres is close to square pyramidal with $\tau = 0.268$, [$\tau = |\beta - \alpha|/60^\circ$, where β and α are the two largest angles around the central atom; $\tau = 0$ and 1 for the perfect square pyramidal and trigonal bipyramidal geometries, respectively] [11]. The square base is formed by pyridyl and imine nitrogen atoms, a benzoyl oxygen atom and the closer of bridging azido nitrogen atoms. The nitrogen atom from the semi-bridging azide group with the longer Cu–N distance is at the apex. The distortion in the geometry is evident from the variation of the basal angles (Table 2) from equivalent *cis* and *trans* values.

Table 2
Molecular dimensions (bond lengths in Å and angles in °) about the copper atoms in complexes **1** and **2**

Complex **1**		Complex **2**	
Bond lengths			
Cu1–O4	1.988(7)	Cu1–O1	1.965(3)
N1–Cu1	1.947(8)	Cu1–N10	1.928(3)
Cu1–N2	2.028(9)	Cu1–N17	2.012(3)
Cu1–N21	1.968(9)	Cu1–N1	1.965(4)
Cu1–N21A	2.534(10)	Cu1–S2	2.7110(11)
Bond angles			
N1–Cu1–O4	80.5(3)	N10–Cu1–O1	79.41(13)
O4–Cu1–N2	161.1(3)	O1–Cu1–N17	158.96(13)
N21–Cu1–O4	102.1(3)	O1–Cu1–N1	96.89(14)
O4–Cu1–N21A	92.8(3)	O1–Cu1–S2	102.22(8)
N1–Cu1–N2	81.1(4)	N10–Cu1–N17	80.32(14)
N1–Cu1–N21	177.2(4)	N10–Cu1–N1	159.77(14)
N1–Cu1–N21A	90.9(4)	N10–Cu1–S2	101.29(10)
N21–Cu1–N2	96.2(4)	N1–Cu1–N17	100.17(15)
N2–Cu1–N21A	91.5(4)	N17–Cu1–S2	87.26(9)
N21–Cu1–N21A	90.1(4)	N1–Cu1–S2	98.93(11)

3.1.2. [$Cu(L)(\mu_{1,3}\text{-}NCS)]_n$ (2)

An ORTEP representation of **2** with the atom numbering scheme is shown in Fig. 2 and relevant bond dimensions are included in Tables 2 and 3. The structure is made up of infinite chains, in which Cu(II) centres are connected by single *end-to-end* thiocyanate bridges. The copper(II) pentacoordination sphere comprises the N_2O donor atoms from the tridentate deprotonated hydrazone ligand **L**, and a nitrogen and a sulfur atom from two molecules of bridging thiocyanate ligands. The geometry around the copper centre can be described as square pyramidal with $\tau = 0.0135$. The basal plane is formed by the N_2O donor atoms of **L** and the nitrogen atom of a thiocyanate ligand. The sulfur atom from the other thiocyanate ligand is at the apex. The apical Cu–S bond distance is significantly longer [2.7110(1) Å] than the basal bond distances [1.924(4)–2.020(5) Å], even when taking into account the larger covalent radius of sulfur . The bond dimensions around the Cu(II) ion are comparable to those in similar systems [7]. The thiocyanate ligand is almost linear at C1. The intrachain copper–copper separation is

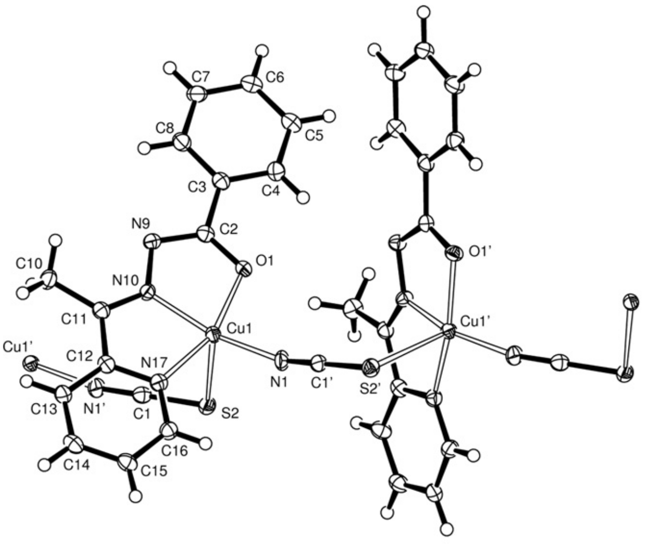

Fig. 2. View of two units in a chain of **2**, with atom labels. Displacement ellipsoids are shown at 50% probability level.

5.806 Å which is comparable to previously reported singly thiocyanate bridged copper complexes [12].

The crystal packing of the complex indicates that adjacent chains have pairwise π–π interactions, by overlap of phenyl with pyridine rings, with four adjacent chains (Fig. 3), thus connecting the chains in a three-dimensional network.

3.2. Infrared spectra

The infrared spectra of the complexes **1** and **2** display absorption bands at *ca.* 1563 cm^{-1} which can be assigned to the C=N stretching frequency of the coordinated ligand **L** [13]. In the spectra of complexes **1** and **2**, strong, well-resolved sharp bands at 2086 and 2028 cm^{-1} are assigned to $\nu_{\text{N=N}}$ of the azide (N_3) group and $\nu_{\text{C=N}}$ of the NCS group respectively. The ligand coordination to the metal centre is substantiated by two bands appearing for each complex, at 422, 312 (**1**) and 424, 315 (**2**) cm^{-1} attributable to $\nu_{\text{Cu–N}}$ and $\nu_{\text{Cu–O}}$ respectively.

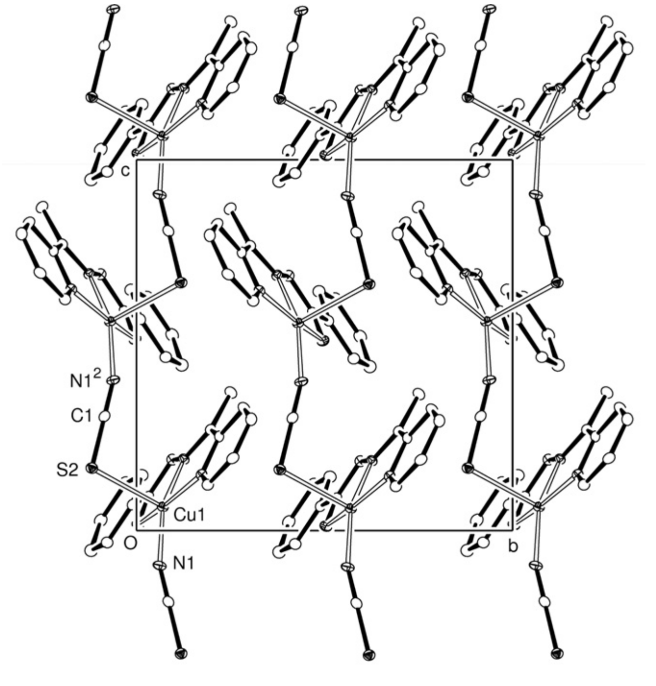

Fig. 3. Crystal packing showing the parallel chains of **2**, and the alignment of overlapping phenyl and pyridine rings.

3.3. Electronic spectra

The electronic spectral data for the complexes in acetonitrile are in good agreement with their geometries. The UV absorption bands exhibit a charge transfer transition (CT) in the range 350–420 nm for Cu(II) complexes and may be assigned to the ligand-to-metal charge transfer transition for each of the compounds **1** and **2**. The spectra of complexes **1** and **2** each display a broad band at 623 and 635 nm respectively, consistent with the expected five-coordinate geometry.

3.4. Magnetic studies

The temperature dependence of $\chi_M T$ for **1** is depicted in Fig. 4. The curve of $\chi_M T = f(T)$ is almost constant above 60 K with a value near 0.825 $\text{cm}^3\,\text{K}\,\text{mol}^{-1}$, in good agreement with the expected value for two Cu(II) ions. Below 60 K, $\chi_M T$ slightly increases as T decreases to reach 0.875 $\text{cm}^3\,\text{K}\,\text{mol}^{-1}$ at 4 K. According to the dimeric structure of the complex, the $\chi_M T$ curve has been fitted using a classical Bleaney and Bowers law, using the phenomenological Hamiltonian $\mathbf{H} = -J\mathbf{S}_A \cdot \mathbf{S}_B$. The resulting law has the following form:

$$\chi_M T = \frac{2Ng^2\beta^2}{k[3 + \exp(-J/kT)]}$$

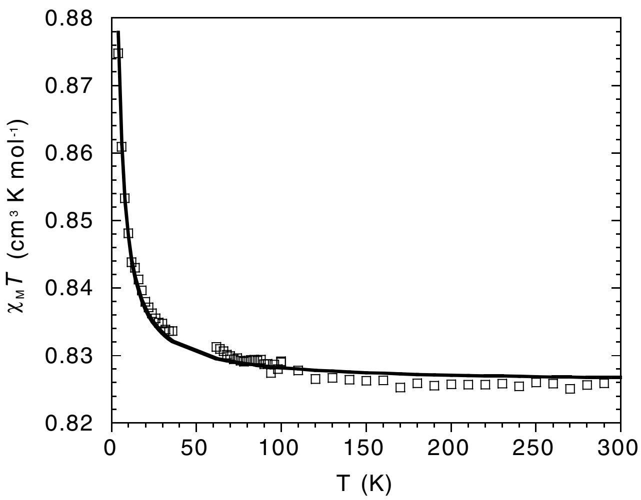

Fig. 4. Experimental (□) and calculated (—) temperature dependence of $\chi_M T$ for **1**.

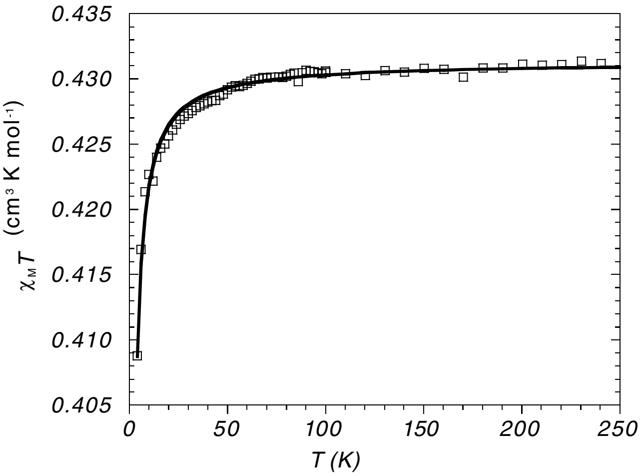

Fig. 5. Experimental (□) and calculated (—) temperature dependence of $\chi_M T$ for **2**.

The best fit was obtained with a Lande factor, *g* of 2.1, isotropic interaction parameter $J = +0.75\ \mathrm{cm}^{-1}$. The two copper atoms of the dinuclear unit are linked by two azido bridging ligands in an *end-on* fashion. The copper atoms have a square pyramidal geometry and the bridging nitrogen atom of each azido ligand is in a basal position of one copper and the apical position of the second copper.

The temperature dependence of $\chi_M T$ for **2** is shown in Fig. 5. Due to the chain structure of the complexes, the model of equally spaced copper(II) ions has been used. The spin Hamiltonian in zero-field is $H = -J\sum_{i=1}^{n-1} S_{A_i} \cdot S_{A_{i+1}}$ where the summation runs over the *n* sites of the chain. When *n* tends to infinity, there is no analytical method to determine the magnetic susceptibility. However, the results can be fitted using the numerical expression for $J < 0$ [14]

$$\chi_M T = \frac{Ng^2\beta^2}{k}\,\frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3}$$

with $x = -J/kT$.

For **2**, the best fit was obtained with a Lande factor, *g* of 2.14 and isotropic interaction parameter $J = -0.23\ \mathrm{cm}^{-1}$. The sulfur atom of the thiocyanate bridge occupies the apical position of the copper cation.

The weak coupling for both the complexes may be explained as follows: the magnetic orbital describing the unpaired electron on a copper(II) ion in square pyramid is of the $d_{x^2-y^2}$ type (the *x* and *y* axes being defined by the short basal bonds). The overlap between the magnetic orbitals of two neighbouring coppers is thus very small, and the isotropic interaction parameter (roughly proportional to the square of this overlap) is expected to be small.

4. Conclusion

A double *end-on* azido bridged dinuclear copper(II) hydrazone complex, and a 1D chain copper(II) polymer of the same hydrazone ligand (**L**) with single *end-to-end* thiocyanate bridges have been isolated. Electronic spectra of the complexes support their geometries as established from X-ray analysis. Magnetic studies indicate a weak ferromagnetic interaction operates between the two metal centres in the doubly azido bridged complex **1**, whereas complex **2** exhibits weak antiferromagnetic interactions.

5. Supplementary material

CCDC 615282 and 615283 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgement

We acknowledge the financial assistance to S. Sen from the CSIR (New Delhi, India).

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