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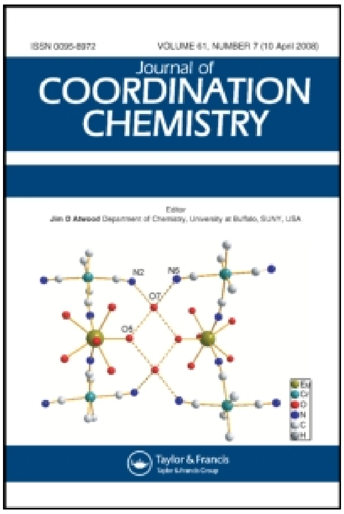

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Tridentate (NNO) Schiff-base copper(II) complex: synthesis, crystal structure, and magnetic study

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Tridentate (NNO) Schiff-base copper(II) complex: synthesis, crystal structure, and magnetic study

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A new azido adduct of a tridentate Schiff-base copper(II) complex has been synthesized and characterized structurally and magnetically. X-ray single crystal structure analysis reveals that the asymmetric unit of $[Cu_2(L)_2(\mu_{1,1}\text{-}N_3)_2][Cu(L)(N_3)]$ (**1**) [HL = 1-(N-ortho-hydroxyacetophenimine)-2,2-diethyl-aminoethane] has two independent moieties. One of these forms a dimer, containing end-on azido bridges, with its center of inversion related equivalents. The complex crystallizes in monoclinic space group P_21/c with $a = 10.112(2)$, $b = 31.938(4)$, $c = 9.718(2)$ Å and $\beta = 95.00(2)^\circ$. Variable temperature magnetic susceptibility data show antiferromagnetic interactions between copper(II) centers.

Keywords: Crystal structure; Tridentate Schiff-base ligand; Copper(II) azide complex; Antiferromagnetism

1. Introduction

Remarkable progress has been achieved recently in synthesizing inorganic–organic hybrid coordination polymers with novel architectures [1] and with different functionalities [2]. Various synthetic strategies [3–5] are applied to make such polymers of which self-assembly [3] is the most suitable. The use of metal ions, blocking ligands, and bridging units afford arrays of new architectures [6]. Pseudo halide anions are excellent for obtaining complexes of varied structural motifs [7, 8]; azido has been extensively used since it affords efficient super exchange pathways between paramagnetic centers such as Cu(II), Ni(II), Mn(II), Mn(III), Fe(III), etc. [9]. This capability of azide attracts a lot of attention to multi-dimensional metal-assembled azido complexes [9, 10]. Control over molecular dimensions and geometry of coordination complexes could lead to the control over their magnetic properties [9]. In fact,

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remarkable structural variations of azido complexes have resulted in diverse magnetic behaviors. Synthesis of non-serendipitous products is particularly interesting to get deeper insight into magneto-structural correlations. Different organic blockers are used to vary nuclearity through available coordination sites in combination with suitable metal ions and bridges. The chemistry of copper(II) azides is well-documented [11–14] through structural and magneto-structural characterization of a plethora of mono-, di-, and polynuclear complexes of different dimensionalities. The main focus is to synthesize magnetic materials [14] and to model natural copper proteins and their derivatives [15]. Schiff bases have [16, 17] been versatile organic blockers because of their preparative accessibilities, structural varieties, and varied denticities. Previously, we synthesized and characterized a series of copper azido complexes using different tridentate Schiff-base co-ligands [18]. As part of our continuing study on metal-azido complexes of tridentate Schiff bases based on substituted ethylenediamines, we report here the synthesis, characterization, X-ray crystallographic study, and magnetic properties of a copper azido complex of a tridentate Schiff base.

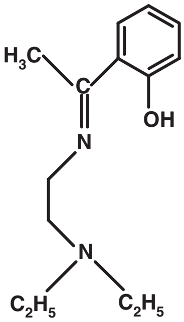
2. Experimental

2.1. *Materials and synthesis*

Copper(II) nitrate trihydrate (Aldrich) and sodium azide (Sigma) were purchased and used without purification. All other chemicals were of analytical grade and used as received.

Caution! Although our samples never exploded during handling, metal azido complexes are potentially explosive; only a small amount of material should be prepared and it should be handled with care.

2.1.1. Synthesis of $[Cu_2(L)_2\mu_{1,1}\text{-}N_3)_2][Cu(L)(N_3)]$ (1). To prepare **1**, a methanolic solution (40 mL) of N,N-diethyl-ethylenediamine (1 mmol, 0.106 g) was mixed with *ortho*-hydroxy-acetophenone (1 mmol, 0.136 g) under stirring to prepare the Schiff base *in situ* (scheme 1). The mixture immediately turns pale yellow. Stirring was continued for another 30 min. Then $Cu(NO_3)_2 \cdot 3H_2O$ (1 mmol, 0.241 g) dissolved in methanol



HL

Scheme 1. Schiff base ligand HL.

(20 mL) was added and stirred for about 10 min. Finally, 5 mL aqueous solution of NaN_3 (2 mmol, 0.130 g) was added dropwise to the resulting mixture with continuous stirring and filtered. Green filtrate, thus obtained, was kept in air. Dark crystals formed within a few days from the solution were collected by filtration and dried in a desiccator. A suitable crystal was selected for X-ray crystallographic analysis (yield *ca* 70%). Anal. Calcd for $C_{14}H_{21}CuN_5O$ (%): C, 49.6; H, 6.2; N, 20.7. Found: C, 49.9; H, 7.0; N, 21.3.

2.2. *Physical measurements*

Elemental analyses for carbon, hydrogen, and nitrogen were obtained with a Perkin-Elmer 240C elemental analyzer. Infrared spectra (4000–200 cm^{-1}) were recorded on a Nicolet Magna IR 760 Series II FT-IR spectrophotometer. UV-visible electronic spectral measurements were carried out in methanol solvent using a Perkin-Elmer LAMBDA EZ-301 spectrophotometer. Electron Paramagnetic Resonance (EPR) spectra were measured on a Varian E-112 EPR spectrometer at room temperature using DPPH ($g = 2.0036$) as calibrant. The magnetic susceptibility of the complex was measured with a Quantum Design MPMS-XL SQUID susceptometer under a 1T magnetic field. Diamagnetic corrections were estimated from Pascal constants.

2.3. *X-ray structure determination*

X-ray diffraction data of the complex were collected on a Bruker Nonius MACH3 diffractometer using Mo-Kα radiation. The data were corrected for Lorentz, polarization, and absorption effects using psi-scan (ψ scans) technique. The structure was solved by direct methods using SHELXL [19] and refined by full-matrix least-squares based on $|F_{obs}|^2$ using SHELXL [19]. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms, generated using idealized geometry, were made to "ride" on their parent atoms and used in the structure factor calculations. Neutral atom scattering factors were taken from Cromer and Weber [20] and anomalous dispersion effects were included in F_{calc} [21]. The crystallographic data are summarized in table 1. The final positional and thermal parameters are available as supplementary material.

3. Results and discussion

3.1. *Crystal structure*

The ORTEP [22] diagram of the complex showing the atom-labeling scheme is given in figure 1. The crystal structure of **1** consists of two independent molecules, labeled A and B, in the crystallographic asymmetric unit. One forms a dimer (B) with its center of inversion related equivalent. The copper(II) ion in dimer and monomer units exists in the centrosymmetric and non-centrosymmetric environment in the crystallographic asymmetric unit of **1**. The presence of different molecules in the crystallographic asymmetric unit had been reported previously [23].

Table 1. Crystal data and structure refinement for $[Cu_2(L)_2\mu_{1,1}\text{-}N_3)_2][Cu(L)(N_3)]$ (**1**).

Empirical formula	$C_{14}H_{21}CuN_5O$
Formula weight ($g\,mol^{-1}$)	338.9
Crystal system	Monoclinic
Space group	P_21/c
Unit cell dimensions (Å, °)	
a	10.112(2)
b	31.938(4)
c	9.718(2)
β	95.00(2)
Volume ($Å^3$), Z	3126.6(10), 8
Independent reflection	$[R(\text{int}) = 0.054]$
Absorption coefficient (cm^{-1})	1.40
Temperature (K)	293(2)
Calculated density($g\,cm^{-3}$)	1.440
$\theta_{\max}$ (°)	25.68
Crystal size (mm^3)	$0.05 \times 0.11 \times 0.17$
$F(000)$	1416
Absorption correction	Empirical (ψ scans)
Final R indices $R_1{}^a$ $[I > 2\sigma(I)]$	0.068
$wR_2{}^b$ (all reflections)	0.209
Refinement method	Full-matrix least-squares on F^2
No. of reflections used	6135
Unique reflections	5850
Number of refined parameters	379
Goodness-of-fit, s ("observed" reflections)	1.043

$^aR_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.
$^bwR_2 = [\Sigma w(|F_o| - |F_c|)^2]/\Sigma[w(F_o^2)]]^{1/2}$.

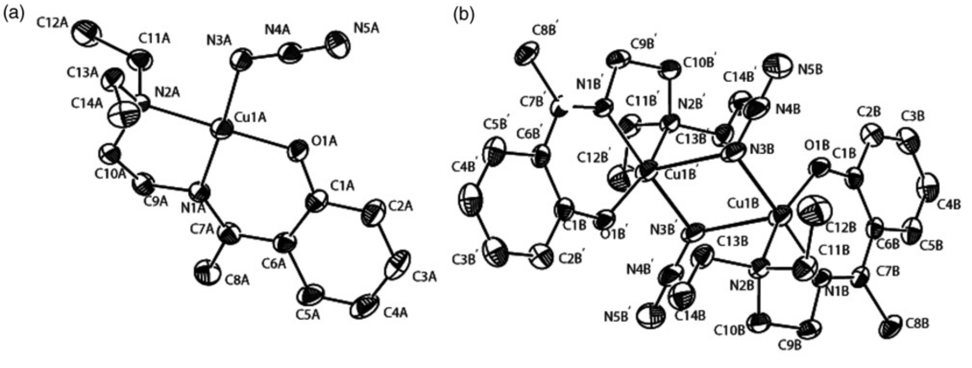


Figure 1. ORTEP view of **1**. The thermal ellipsoids are drawn at the 30% probability level. Hydrogens have been omitted for clarity.

In molecule B, the copper(II) ion assumes a distorted square pyramidal geometry in which the basal plane is composed of two nitrogens and one phenoxo oxygen of the tridentate Schiff base and another nitrogen of the coordinated azide. The fifth coordination site of the square pyramid is occupied by the nitrogen atom, N3B′, of another azide group related by a center of inversion (symmetry: $-x+2$, $-y+1$, $-z+1$), forming a Cu–N–Cu bridge [Cu–Cu distance = 3.605(1) Å]. The Cu–N(azido)–Cu angle is 99.40(17)°. The bridging Cu_2–N_2 network is constrained by the symmetry

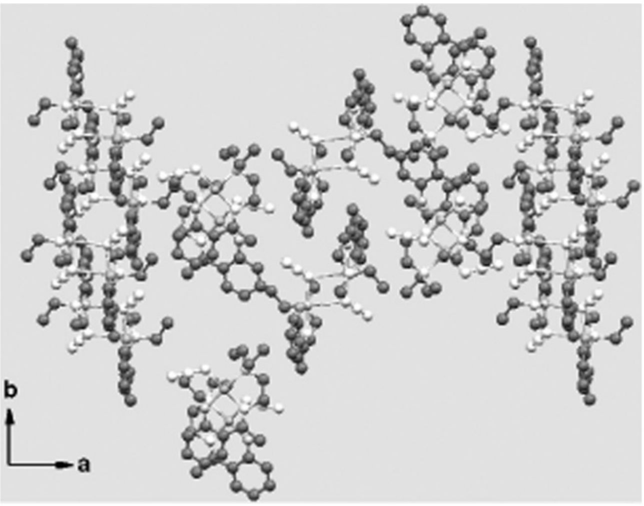


Figure 2. A view of the packing diagram of **1**.

to be exactly planar. Due to the formation of basal-apical $\mu_{2-1,1}$–N_3 bridging, the bridging Cu–N bond lengths are significantly different ($\Delta d = 0.569$ Å). The Cu–N3B′ bond is a little longer but this is not unusual as quite a few end-on azido bridged copper(II) complexes possess Cu–N(azide) bond lengths of 2.5 Å [18a, 24]. The trigonality index τ $(=\phi_1 - \phi_2)/60$, where ϕ_1, ϕ_2 are the two largest L–M–L angles of the coordination sphere, calculated for the five-coordinate copper [25] is 0.275 confirming the square-pyramidal character of the copper site ($\tau = 0$ infers a perfect square-pyramid, and a $\tau = 1$, a perfect trigonal bipyramid). The four basal donor atoms – O(1B), N(1B), N(2B), and N(3B) – in molecule B deviate from the least-squares mean plane through them by 0.164(4), −0.133(3), 0.177(4), and −0.322(5) Å, respectively. The Cu(1B) atom is slightly out of this plane towards the axially coordinated azide nitrogen, N(3B′). The distances from the basal plane of Cu(1B) is −0.168(6) Å. The six-membered chelate ring Cu(1B)–N(1B)–C(7B)–C(6B)–C(1B)–O(1B) has an approximate half boat or envelope conformation with puckering parameters $q_2 = 0.778(4)$, $q_3 = -0.009(6)$, $Q = 0.078(4)$, $\varphi_2 = -125.89(3)^\circ$, and $\theta = 96.74(3)^\circ$ [26], while the five-membered ring Cu(1B)–N(2B)–C(10B)–C(9B)–N(1B) is in the twist conformation with puckering parameters $q_2 = 0.466(4)^\circ$, $\varphi_2 = 133.46(5)^\circ$.

In molecule A, the copper has a distorted square planar arrangement. Out of its four coordination sites, three positions are occupied by the tridentate Schiff base through two nitrogens (amino and imino) and the deprotonated phenoxo. The fourth coordination site is occupied by nitrogen of an azido. The Cu–N bond lengths are Cu(1A)–N(1A) = 1.950(3), Cu(1A)–N(2A) = 2.060(3), Cu(1A)–N(3A) = 1.959(5) Å while the Cu(1A)–O(1A) bond length is 1.880(3) Å. Figure 2 shows the packing diagram of **1**. Selected bond lengths and angles are listed in table 2.

3.2. *IR and electronic spectra*

IR absorption of **1** at 1598 cm^{-1} confirms the presence of azomethine [27]. The bands at 2055 and 2031 cm^{-1} are assigned to the asymmetric vibration of coordinated azide

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Molecule A			
Bond lengths (Å)			
Cu(1A)–O(1A)	1.880(3)	Cu(1A)–N(2A)	2.060(3)
Cu(1A)–N(1A)	1.950(3)	Cu(1A)–N(3A)	1.959(5)
Bond angles (°)			
O(1A)–Cu(1A)–N(1A)	92.67(15)	N(1A)–Cu(1A)–N(3A)	176.37(16)
O(1A)–Cu(1A)–N(2A)	177.44(15)	N(3A)–N(4A)–N(5A)	176.90(47)
O(1A)–Cu(1A)–N(3A)	90.38(15)	Cu(1A)–N(3A)–N(4A)	118.47(32)
N(1A)–Cu(1A)–N(2A)	86.74(15)	N(2A)–Cu(1A)–N(3A)	90.13(16)
Molecule B			
Bond lengths (Å)			
Cu(1B)–O(1B)	1.882(3)	Cu(1B)–N(3B)	2.012(4)
Cu(1B)–N(1B)	1.979(4)	Cu(1B)–N(3B′)	2.681(5)
Cu(1B)–N(2B)	2.067(4)	Cu(1B)–Cu(1B′)	3.605(1)
Bond angles (°)			
O(1B)–Cu(1B)–N(1B)	92.11(14)	O(1B)–Cu(1B)–N(2B)	160.13(14)
N(3B)–Cu(1B)–N(3B)′	80.60(17)	O(1B)–Cu(1B)–N(3B)	88.17(15)
Cu(1B)–N(3B)– Cu(1B′)	99.40(17)	N(3B)–N(4B)–N(5B)	178.45(7)
N(2B)–Cu(1B)–N(3B′)	97.87(14)	N(1B)–Cu(1B)–N(2B)	85.34(14)
N(1B)–Cu(1B)–N(3B)	176.63(16)	N(2B)–Cu(1B)–N(3B)	95.52(15)
O(1B)–Cu(1B)–N(3B)′	102.00(14)		

Symmetry code: $-x+2$, $-y+1$, $-z+1$.

[ν_{as} N_3^-] and the band at 640 cm^{-1} is attributed to the bending of azide. Similar characteristic bands for azides have been observed in a number of mononuclear and polynuclear azido bridged complexes in previous studies [9, 13, 18a]. Electronic spectrum in methanolic solution shows two strong absorption bands in the region 268 and 296 nm which are clearly charge transfer in origin [28a]. The UV absorption band at 385 nm for **1** can be attributed to the ligand to Cu(II) charge transfer transition (LMCT) [28b, c]. The low-intensity absorption band associated with d–d transition at 606 nm may be assigned to a Cu(II) d–d transition [28b–e].

3.3. *EPR spectroscopy*

The powder EPR spectrum of **1** is given in figure 3. The principal g values have been calculated by usual methods [29]. The $g_{\|}$ and $g_{\perp}$ values of the complex are 2.18 and 2.08, respectively, in a typical axial spectrum in which copper(II) possesses either a square planar or a five-coordinate geometry. The X-ray crystal structure shows that the complex indeed possesses both square planar and square-pyramidal ligand environment in two different asymmetric units. The g_{av} calculated using $g_{\|}$ and $g_{\perp}$ is found to be 2.11.

3.4. *Magnetic properties*

Temperature dependence of the magnetic susceptibility of **1** has been measured in the temperature range 300–2 K (figure 4). Upon cooling χ_M remains almost constant to 50 K and then rapidly increases with temperature. The χ_M at room temperature, 1.25×10^{-3} cm^3 mol^{-1}, is comparable with spin-only value of 1.25×10^3 cm^3 mol^{-1}, which is expected for isolated copper(II) ions ($S = ½$) assuming $g = 2.00$. The fitting

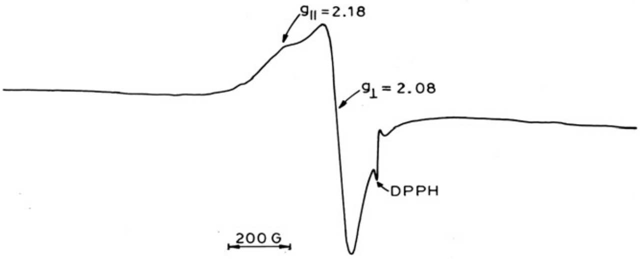


Figure 3. EPR spectrum of **1**.

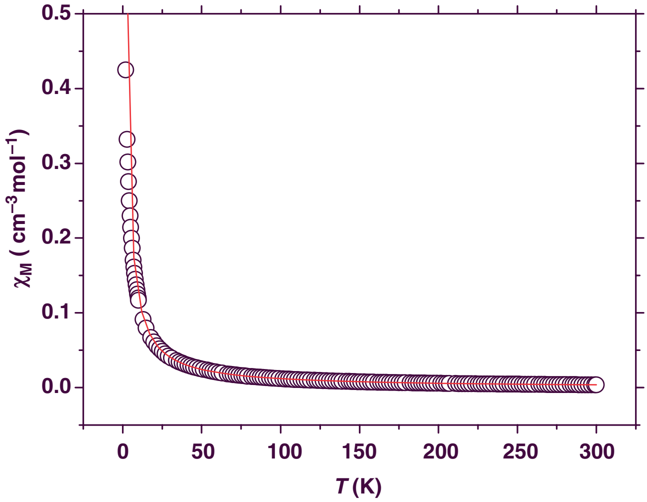


Figure 4. $\chi_M T$ *vs.* T (○) plot for **1**. Solid lines represent the best fit of the data with the model described in the text.

of $1/\chi_M$ *versus* T plot with the Curie–Weiss equation affords $C = 0.37$ emu mol^{-1} K and $\theta = -22.23$ K for **1** (Supplementary Material). The negative Weiss constant indicates predominant anti-ferromagnetic interaction between copper(II) ions and azido bridges in the dimer moiety of **1**. The μ_{eff} *versus* temperature plot of **1** confirms the predominant anti-ferromagnetic interaction between the metal centers (Supplementary Material). To estimate the magnitude of the anti-ferromagnetic coupling, the magnetic susceptibility data (300–2K) were fitted to the modified Bleaney–Bowers equation [14a] for two interacting copper(II) ions ($S = ½$) with the Hamiltonian in the form $H = -J\hat{S}_1 \cdot \hat{S}_2$. The susceptibility equation for such a dimer–monomer mixed system can be written as follows giving 50% of weightage for dimer and 50% of weightage for monomer:

$$\chi = Ng^2\beta^2/kT \times [3 + \exp(-J/kT)]^{-1} + Ng^2\beta^2/4kT \qquad (1)$$

where N, g, β, and k parameters in the equation bear their usual meaning.

Fitting of the magnetic susceptibility data up to 2 K with equation (1) yielded the parameter values $J = -146(5)\,\text{cm}^{-1}$, $g = 2.3(1)$, with an agreement factor $R = 1.9 \times 10^{-8}$.

For the $\mu_{1,1}$–N_3 bridging mode, ferromagnetic ordering is established when the Cu–N–Cu angle is small, which has been attributed to a spin polarization effect [30a]. However, J_{ferro} is expected to decrease with increasing Cu–N–Cu angle, and the coupling constant for the EO azido bridge enters into the anti-ferromagnetic regime when this angle crosses the critical value of $\sim 108^\circ$ [30b]. Recent theoretical studies of this type of complexes, based on the density functional calculations (DFT), show that the nature of coupling between two copper ions with double end-on azido bridge depends on two parameters, (i) the $M–N_{(azido)}–M$ angle and (ii) the $M–N_{(azido)}$ bond distance [31a]. The interaction is ferromagnetic if the $M–N_{(azido)}–M$ angle falls in the 96–104° range, otherwise it is anti-ferromagnetic. The cut-off distance ($M–N_{(azido)}$) is 2.05 Å for ferromagnetic while antiferromagnetic behavior is observed for ($M–N_{azido}$) distance of 2.1–2.8 Å. Triki *et al.* [31b], however, reported that these conditions cannot be applied for dimeric complexes having considerable asymmetry in $M–N_{azido}$ distances, and they have shown that an opposite interaction is expected to that of the symmetric analogues. In a more recent study, Chastanet *et al.* [32] performed *ab initio* calculations to clarify the observed ferromagnetic coupling for an end-on azido bridged copper(II) complex $[Cu(L^1)(N_3)]_n$ [where $HL^1 = $ 1,1,1-trifluoro-7-(dimethylamino)-4-methyl-5-aza-3-hepten-2-onato] having a tridentate Schiff-base co-ligand like **1**. The strong ferromagnetic interaction in $[Cu(L^1)(N_3)]_n$ may be due to asymmetric coordination modes despite having high Cu–N–Cu angles (131.0–145.1°). For **1**, the low $Cu–N_{(azido)}–Cu$ angle (99.4°) warrants a ferromagnetic interaction between the copper(II) centers. However, asymmetry in $Cu–N_{azido}$ bond distances [Cu(1B)–N(3B′) or Cu(1B)′–N(3B) = 2.681(5) Å] and [Cu(1B)–N(3B) = 2.012(4) Å] with great influence on the sign and level of interaction probably cause an antiferromagnetic coupling to occur in **1**.

Supplementary material

Supplementary data are available from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk/http://www.ccdc.cam.ac.uk) upon request, quoting deposition number CCDC 706752.

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References

[1] M.J. Zaworotko. *Chem. Commun.*, 1 (2001).
[2] P. Gamez, P. de Hoog, O. Roubeau, M. Lutz, W.L. Driessen, A.L. Spek, J. Reedijk. *Chem. Commun.*, 1488 (2002).
[3] (a) G.F. Swiegers, T.J. Malefetse. *Chem. Rev.*, **100**, 3483 (2000); (b) B.J. Holliday, C.A. Mirkin. *Angew Chem., Int. Ed.*, **40**, 2022 (2001).

[4] (a) O. Kahn. *Adv. Inorg. Chem.*, **43**, 179 (1995); (b) H. Furatachi, H. Okawa, D.E. Fenton. *Coord. Chem. Rev.*, **51**, 174 (1998).

[5] (a) S.L. Castro, Z. Sun, C.M. Grant, J.C. Bollinger, D.N. Hendrickson, G. Christou. *J. Am. Chem. Soc.*, **120**, 2365 (1998); (b) A. Escuer, S.B. Kumar, F. Maunter, R. Vicente. *Inorg. Chim. Acta*, **269**, 313 (1998); (c) P. Day. *J. Chem. Soc., Dalton Trans.*, 701 (1997).

[6] S.T. Hyde, B. Ninham, S. Anderson, Z. Blum, T.K. Landh Larsson, S. Liddin. *The Language of Shape*, Elsevier, Amsterdam (1997).

[7] (a) A.M. Golub, H. Kohler, V.V. Skopenko. *Chemistry of Pseudohalides*, Elsevier, Amsterdam (1986); (b) C. Blanchet-Boiteux, J.M. Mouesca. *J. Am. Chem. Soc.*, **861**, 122 (2000).

[8] (a) D. Bose, S.H. Rahaman, G. Mostafa, R.D.B. Walsh, M.J. Zaworotko, B.K. Ghosh. *Polyhedron*, **23**, 545 (2004); (b) S. Iijima, Z. Honda, S. Koner, F. Mizutani. *J. Magn. Magn. Mater.*, **223**, 16 (2001); (c) S. Koner, S. Iijima, F. Mizutani, K. Harata, M. Watanabe, A. Nagasawa, M. Sato. *Polyhedron*, **18**, 2201 (1999).

[9] J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortés, L. Lezama, T. Rojo. *Coord. Chem. Rev.*, **193–195**, 1027 (1999) and references therein.

[10] (a) J. Ribas, M. Monfort, X. Solans, M. Drillon. *Inorg. Chem.*, **33**, 742 (1994); (b) Z.E. Serna, L. Lezama, M.K. Urtiaga, M.I. Arriortua, M.G.B. Barandika, R. Cortés, T. Rojo. *Angew. Chem., Int. Ed.*, **39**, 344 (2000); (c) M.A. Halcrow, J.S. Sun, J.C. Huffman, G. Christou. *Inorg. Chem.*, **35**, 4167 (1995); (d) G.S. Papaefstathiou, S.P. Perlepes, A. Escuer, R. Vicente, M. Font-Barida, X. Solans. *Angew. Chem., Int. Ed.*, **40**, 884 (2001).

[11] (a) H.Y. Shen, W.M. Bu, E.Q. Gao, D.Z. Liao, Z.H. Jiang, S.P. Yan, G.L. Wang. *Inorg. Chem.*, **39**, 396 (2000); (b) T.K. Maji, P.S. Mukherjee, G. Mostafa, T. Mallah, J. Cano-Boquera, N.R. Chaudhuri. *Chem. Commun.*, 1012 (2001).

[12] (a) A. Escuer, M. Font-Bardia, E. Penalba, X. Solans, R. Vicente. *Inorg. Chim. Acta*, **298**, 195 (2000); (b) A. Escuer, M.A.H. Goher, F.A. Mautner, R. Vicente. *Inorg. Chem.*, **39**, 2107 (2000).

[13] (a) S. Saha, S. Koner, JP. Tuchagues, A.K. Boudalis, KI. Okamoto, S. Banerjee, D. Mal. *Inorg. Chem.*, **44**, 6379 (2005) and references therein; (b) J. Luo, X.G. Zhou, S. Geo, L.H. Weng, Z.H. Shao, C.M. Zhang, Y.R. Li, J. Zhang, R.F. Cai. *Polyhedron*, **23**, 1243 (2004).

[14] (a) O. Kahn. *Molecular Magnetism*, VCH, New York (1993); (b) P. Day, A.E. Underhill. *Metal-organic and Organic Molecular Magnets*, RSC, London (2000); (c) J.S. Miller, M. Drillon. *Magnetism: Molecules to Materials IV*, Wiley-VCH, Weinheim (2003).

[15] (a) K.D. Karlin, J. Zubieta. *Copper Coordination Chemistry: Bio-chemical and Inorganic Perspectives*, Adenine, New York (1983); (b) S.J. Lippard, J.M. Berg. *Bioinorganic Chemistry*, University Science Books, Mill Valley, CA (1994); (c) W. Kaim, B. Schwederski. *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*, Wiley, Chichester (1994); (d) D.E. Fenton. *Chem. Soc. Rev.*, **28**, 159 (1999).

[16] (a) A.D. Garnovskii, A.L. Nivorozkin, V.L. Minkin. *Coord. Chem. Rev.*, **126**, 1 (1993); (b) V. Alexander. *Chem. Rev.*, **95**, 273 (1995); (c) M.K. Saha, D.K. Dey, B. Samanta, A.J. Edwards, W. Clegg, S. Mitra. *J. Chem. Soc., Dalton Trans.*, 488 (2003); (d) R. Paschke, S. Liebsch, C. Tschierske, M.A. Oakley, E. Sinn. *Inorg. Chem.*, **42**, 8230 (2003).

[17] (a) C.M. Liu, R.G. Xiong, X.Z. You, Y.J. Liu, K.K. Cheung. *Polyhedron*, **15**, 4565 (1996); (b) C.M. Liu, R.G. Xiong, X.Z. You, H.K. Sivakumar. *Polyhedron*, **16**, 119 (1997).

[18] (a) S. Koner, S. Saha, T. Mallah, K.–I. Okamoto. *Inorg. Chem.*, **43**, 840 (2004); (b) M. Zbiri, S. Saha, C. Adhikary, S. Chaudhuri, C. Daul, S. Koner. *Inorg. Chim. Acta.*, **359**, 1193 (2006); (c) C. Adhikary, D. Mal, K.-I. Okamoto, S. Chaudhuri, S. Koner. *Polyhedron*, **25**, 2191 (2006); (d) C. Adhikary, D. Mal, S. Chaudhuri, S. Koner. *J. Coord. Chem.*, **59**, 699 (2006); (e) C. Adhikary, D. Mal, R. Sen, A. Bhattacharjee, P. Gütlich, S. Chaudhuri, S. Koner. *Polyhedron*, **26**, 1658 (2007).

[19] G.M. Sheldrick. *SHELX97, Program for the Refinement of Crystal Structure*, University of Göttingen, Göttingen, Germany (1997).

[20] D.T. Cromer, J.T. Weber. *International Tables for X-ray Crystallography*, Vol. iv, The Kynoch Press, Birmingham, UK (1994), Table 2.21.

[21] J.A. Ibers, W.C. Hamilton. *Acta Crystallogr.*, **17**, 781 (1964).

[22] I.J. Farrugia. *J. Appl. Crystallogr.*, **30**, 565 (1997).

[23] C. Adhikary, R. Bera, B. Dutta, S. Jana, G. Bocelli, A. Cantoni, S. Chaudhuri, S. Koner. *Polyhedro*, **27**, 1556 (2008).

[24] M.S. Ray, A. Ghosh, R. Bhattacharya, G. Mukhopadhyay, M.G.B. Drew, J. Ribas. *Dalton Trans.*, 252 (2004).

[25] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verchoor. *J. Chem. Soc., Dalton Trans.*, 1349 (1984).

[26] D. Cremer, J. Pople. *J. Am. Chem. Soc.*, **97**, 1354 (1975).

[27] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edn, Wiley, New York (1997), Part A and B.

[28] (a) A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd Edn, Elsevier, New York (1984); (b) P. Dapporto, M. Formica, V. Fusi, L. Giothi, M. Micheloni, P. Paoli, R. Pontellini, P. Rossi. *Inorg. Chem.*, **40**, 6186 (2001); (c) T. Gajda, A. Jancsó, S. Mikkola, H. Lönnberg, H. Sirges. *J. Chem.*

Soc., Dalton Trans., 1757 (2002); (d) B.A. Jazdzewski, P.L. Holland, M. Pink, V.G. Young, D.J.E. Spencer, W.B. Tolman. *Inorg. Chem.*, **40**, 6097 (2001); (e) J. Sanmartin, M.R. Bermejo, A. Garcia-Deibe, M.O.R. Nascimento, L. Lezama, T. Rojo. *J. Chem. Soc., Dalton Trans.*, 1030 (2002).

[29] (a) W.T.M. Andriessen. *Inorg. Chem.*, **14**, 792 (1975); (b) B.R. McGarvey, in R.L. Carlin (Ed.), *Transition Metal Chemistry*; Marcel Dekker, New York, 89 (1966).

[30] (a) M.A. Aebersold, M. Gillon, O. Plantevin, L. Pardi, O. Kahn, P. Bergerat, I.V. Seggern, F. Tuczek, L. Öhrström, A. Grand, E. Leliévre-Berne. *J. Am. Chem. Soc.*, **120**, 5238 (1998); (b) S.S. Tandon, L.K. Thompson, M.E. Manuel, J.N. Bridson. *Inorg. Chem.*, **33**, 5555 (1994).

[31] (a) E. Ruiz, J. Cano, S. Alvarez, P. Alemany. *J. Am. Chem. Soc.*, **120**, 11122 (1998); (b) S. Triki, C.J. Gómez-García, E. Ruiz, J. Sala-Pala. *Inorg. Chem.*, **44**, 5501 (2005).

[32] G. Chastanet, B. Le Guennic, C. Aronica, G. Pilet, D. Luneau, M.L. Bonnet, V. Robert. *Inorg. Chim. Acta*, **361**, 3847 (2008).