JOURNAL OF CHEMICAL RESEARCH 2010 NOVEMBER, 637–640 **RESEARCH PAPER** 637

A dissymmetric, singly phenoxido-bridged Cu^{II} dinuclear coordination compound: synthesis, characterisation, magnetic and computational study

Amitabha Datta[a]*, Nien-Tsu Chuang[a], Fu-Xing Liao[a], Ching-Han Hu[a], Wen-Yen Huang[a], Jui-Hsien Huang[a], Kuheli Das[b], Patrick Gamez[c] and José Sánchez Costa[d]

[a]*Department of Chemistry, National Changhua University of Education, Changhua 50058, Taiwan*

[b]*Department of Chemistry, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung, Taiwan*

[c]*Leiden University, Leiden Institute of Chemistry, PO Box 9502, 2300 RA Leiden, The Netherlands*

[d]*Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028, Barcelona, Spain*

A singly phenoxido-bridged dinuclear Cu^{II} complex, $[Cu_2(L)_2(SCN)_2(H_2O)]$, has been obtained from a Schiff-base ligand (2-[{[2-(dimethylamino)ethyl]imino}methyl]-6-methoxyphenol), generated by condensation of *o*-vanillin with *N,N*-dimethylethane-1,2-diamine. The Cu(II) complex has been fully characterised by analytical, spectroscopic, magnetic susceptibility and EPR measurements and DFT calculations, as well as single-crystal X-ray diffraction analysis. It consists of two geometrically distinct square-pyramidal and octahedral copper(II) centres, exhibiting N_2O_3 and N_4O_2 donor sets. In the dimeric unit, the copper atoms are connected by a μ_2-phenolato oxygen atom, belonging to one bridging Schiff-base ligand. Variable-temperature magnetic susceptibility measurements indicate strong antiferromagnetic exchange interactions between the Cu(II) centres, with a $2J$ value of –89(1) cm^{-1}.

Keywords: copper(II), phenoxido-bridge, spectroscopic study, antiferromagnetic coupling

Dinuclear transition-metal complexes and ligands capable of yielding them have been attracting increasing interest in the field of synthetic and biological chemistry, most likely as the result of their important role in many applications. Actually, dinuclear metal coordination compounds have been used successfully for the recognition and assembly of external species of different natures, such as inorganic or organic substrates.[1–9] If the two metal ions display unsaturated coordination environments, the dinuclear complex can be used as receptor for a secondary species. In this way, dinuclear complexes are able to mimic many biological sites, especially those where the two metals can cooperate to form an active centre as, for example, in dioxygen receptors, activators, and carriers.[10] The nature of the two metal ions, their coordination requirements, and the distance between them are the key elements in assembling host species, which are current targets of research investigations. Dinuclear hosts are often obtained by using different ligands with a high number of donor atoms, and usually, the transition-metal ions guide the ligand arrangement fixed by the coordination requirements of the ions.[11] The coordinating ability of compartmental ligands has been the subject of intensive research owing to the potentially interesting optical, magnetic and structural properties of their polynuclear complexes.[12,13] Furthermore, there is much interest in the development of new polydentate ligands that can organise supermolecules upon coordination to two or more metal ions.[14] Thus, recent emphasis has been placed on detailed studies of the properties of Cu(II) phenolate complexes because of their postulated involvement in a range of biological and catalytic processes. While mononuclear Cu(II)–phenolate complexes are common, Cu(II)–phenoxyl radical and Cu(I)–phenol(ate) complexes are quite rare. Multiple N-donor ligands based on mono and bis(pyridyl)alkylamine, and *N,N′*-alkyl-bis(salicylimine) (salen) frames have been most thoroughly investigated,[15–21] since they are well known to be of general utility in transition-metal chemistry and to be particularly useful for the isolation and characterisation of copper complexes. The Cu(II)-phenolate complexes so far reported exhibit coordination numbers ranging from 4 to 6, as typical observed in the coordination chemistry of Cu(II). In addition, the phenolate moieties in most of these compounds are usually incorporated as part of multidentate ligand systems;[22] complexes with simple, exogenous phenolate ligands are less common.[23–25] The series of four-coordinate complexes [Cu Tp^{iPr2} (OAr)] (Ar = C_6H_4-4-F, C_6H_3-2,6-Me_2 or C_6H_3-2,6-*t*Bu) recently reported is of particular interest since these compounds exhibit unusual thermal and air sensitivity, attributed to the contribution of Cu(I)-phenoxyl radical resonance forms to their ground-state structures.[26] A self-assembled Cu(II) polymeric complex having two *μ*-phenoxido bridges has been described earlier,[27] which was accessed through the preparation of a [4 + 4 + 4] trinuclear Cu(II) bis-helicate complex, involving $d_{x^2-y^2}$ orbitals, as expected for tetrahedrally-distorted square-planar Cu(II) chromophores.[28] Dinuclear, singly phenoxido-bridged copper(II) complexes from Schiff-base ligands are still very scarce in the literature.[29–30]

Here we report the synthesis and X-ray structural characterisation of a singly phenoxido-bridged Cu(II) Schiff-base[31] complex, $[Cu_2(L)_2(SCN)_2(H_2O)]$ (**1**). This compound exhibits two monodentate thiocyanate ions on one copper centre. The analytical, spectroscopic and magnetic results are consistent with the crystal structure.

A representation of the molecular structure of complex **1** is depicted in Fig. 1 and the selected bond lengths and angles are

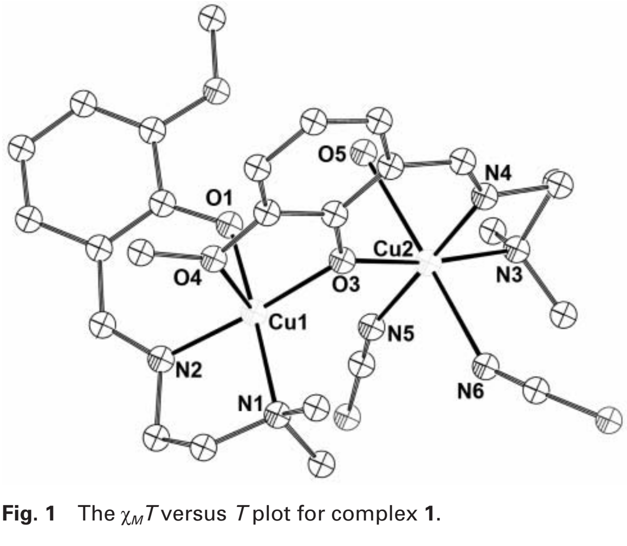


Fig. 1 The $\chi_M T$ versus *T* plot for complex **1**.

---

* Correspondent. E-mail: amitd_ju@yahoo.co.in

shown in Table 2. The dinuclear complex consists of two geometrically distinct copper(II) centres with a N_2O_3 donor set for Cu1 and a N_4O_2 donor set for Cu2. In the dinuclear unit, the copper atoms are held together by one distinct μ-phenolato-oxygen atom belonging to one of the two Schiff-base ligands. In the present system, the Cu1···Cu2 distance is 3.282(2) Å. The Cu1–O3–Cu2 angle is 111.83(7)°, with Cu1–O3 and Cu2–O3 distances of 1.9971(15) and 2.0204(15) Å, respectively. This Cu–O–Cu angle value is comparable with those of previously reported complexes,[30] but is larger than for doubly phenoxido-bridged systems, whose values are within the range 95.7–107.5°.[32–35] In **1**, one of the Schiff-bases acts as a tetradentate ligand while the other behaves as a tridentate ligand with a non-coordinated –OMe group. The coordination geometry around the Cu1 centre can be best described as a distorted (NNOO + O) square-based pyramid. The four atoms constituting the basal plane are the phenolic oxygen atom (O1), the imine (N2) and amino-nitrogen (N1) atoms from a Schiff-base ligand and another phenolato-oxygen atom (O3) that bridges the two copper atoms. The axial site is occupied by the oxygen atom O4 belonging to a coordinated methoxy group from the second Schiff-base ligand. In the basal plane, the bond distances, Cu1–O1, Cu1–N1, Cu1–O3 and Cu1–N2 of respectively 1.9358(16), 2.098(2), 1.9971(15) and 1.9438(19) Å, are well comparable to bond lengths found in the literature.[32,34] The axial bond length (Cu1–O4, 2.3418(17) Å) is slightly longer than the basal ones. The deviation from the ideal square-pyramidal geometry is illustrated by the *cis* angles, ranging from 84.03(8)–95.28(7)°, as well as by the angles involving the *trans* positions, in the range 170.80(7)–173.34(8)°. The coordination geometry around Cu2 is best described as an octahedron (NNNO + N + O), whose basal plane is formed by the bridging phenolato oxygen atom (O3), the imine (N4) and amino (N3) nitrogen atoms from a Schiff-base ligand and one nitrogen atom (N5) of a terminal thiocyanato-anion. The axial positions are occupied by the nitrogen atom N6 from a second coordinated terminal thiocyanate and by a water molecule (oxygen atom O5). The basal and axial bond lengths, [Cu2–O3, Cu2–N5, Cu2–N4 and Cu2–N3; 2.0204(15), 1.960(2), 1.940(2) and 2.113(2) Å, respectively, and Cu2–N6, Cu2–O5, 2.464(3) and 2.466(3) Å, respectively] are comparable with distances observed for related phenoxido-bridged compounds previously described,[32,34,35] and with those of the Cu1 centre. The distortion of the octahedral geometry around the Cu2 centre, is shown by the deviations of both the basal *cis*- and *trans*-angles [84.61(9)–94.06(9)° and 172.34(8)–177.87(9)°, respectively] from the ideal values of 90 ° and 180 °, respectively.

The IR spectrum of complex **1** is consistent with the structural data presented here. The absorption bands at 3538 and 1629 cm^{-1} are attributable to O–H stretching and bending vibration modes of water ligands (Cu2). The strong absorption band at 2082 cm^{-1} characterises the presence of NCS ions, terminally coordinated to a metal centre.[36] The band at 2943 cm^{-1} is due to the imine stretching frequency. The bands observed at 1268 and 1282 cm^{-1} correspond to phenolic C=O stretching vibrations.[37]

The ligand-field spectrum of **1** exhibits two strong absorption bands at 232 and 281 nm, which are due to ligand charge-transfer transitions. The UV absorption bands observed at 376 nm can be assigned to ligand-to-metal charge-transfer transitions. The spectrum also shows a low-intensity absorption band at 647 nm, originating from d–d transitions.[9,37,38]

The $\chi_M T$ versus T plot for the dinuclear copper complex **1** under a constant magnetic field of 0.1 T is shown in Fig. 2. At room temperature, the $\chi_M T$ product amounts to 0.76 cm^3·K·mol^{-1} in agreement with the value for two non-coupled copper(II) ions. The $X_M T$ value decreases with the temperature to reach a value close to zero below 25 K, suggesting an antiferromagnetic $S = 0$ ground state. The magnetic susceptibility data were fitted to the Bleaney-Bowers equation[39] for two interacting copper(II) ions, using the isotropic Heisenberg exchange Hamiltonian $H = 2JS_1S_2$. The least-squares fitting of the data leads to:

$2J = -89(1)$ cm^{-1}, $g = 2.14(1)$,
TIP = 60×10^{-6} cm^3·mol^{-1} per Cu^{II} ion, $p = 1.18(1)\%$ and
$R = 5\cdot10^{-6}$ ($R = \sum_i (\chi_{calcd} - \chi_{obs})^2 / \sum_i (\chi_{obs})^2$).

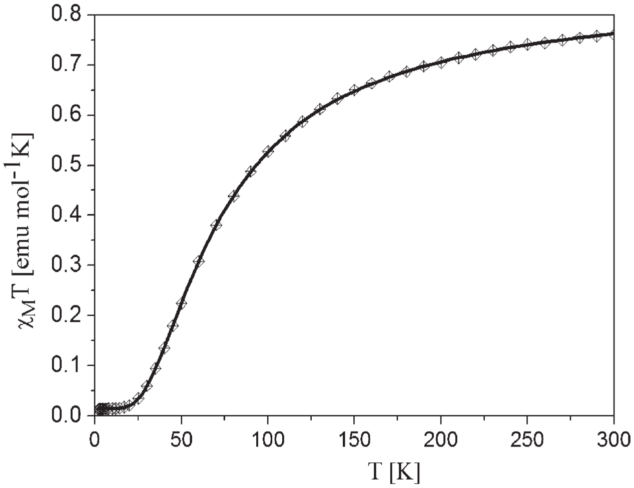


Fig. 2 X-band EPR spectrum of a polycrystalline sample of **1**, recorded at room temperature.

In Fig. 2, the solid line represents the theoretical curve obtained using the above parameters. Dinuclear copper(II) species bridged by a single oxygen-donor group are quite scarce.[40–42] For instance, only one example of a dicopper unit bridged by a single hydroxide-ligand has been reported so far together with its magnetic properties.[43] As mentioned above, the coordination environment around Cu1 is square pyramidal, while Cu2 exhibits a distorted octahedral geometry. In both cases, the unpaired electron occupies mainly the $d_{x^2-y^2}$ orbitals. Besides, the bridging phenoxido-oxygen atom occupies an equatorial position for both copper atoms with a large Cu1–O–Cu2 angle of 111.8°. This structural arrangement allows a strong overlap between the two $d_{x^2-y^2}$ orbitals belonging to the copper centres and the oxygen p orbital.[31] Such orbital overlaps are responsible for the antiferromagnetic behaviour observed for **1**. On the other hand, as pointed out by Choudhury and co-workers for a similar system,[31] the strength of the antiferromagnetic coupling is probably attenuated by the perpendicularity of the two $d_{x^2-y^2}$ magnetic orbitals, as reflected by the dihedral angle of 83.73 ° between the adjacent basal planes.

The experimental powder EPR spectrum (X-band, recorded at room temperature) is composed of allowed ($\Delta M_S = \pm1$) transitions centred at $g = 2.043$ and of a weak intensity, nominally forbidden, half-field ($\Delta M_S = \pm2$) peak observable at $g = 4.774$ (Fig. 3). This second feature characterises the presence of a dinuclear $S_T = 1$ species, in accordance with the solid-state structure of **1** (see Fig. 1).

The complex **1** has been investigated by theoretical calculations. For this purpose, the three-parameter hybrid of exact exchange and Becke's exchange energy functional has been used,[44] plus Lee, Yang, and Parr's gradient-corrected correlation energy functional[45] (B3LYP). The 6–31G(d) basis set was applied in all computations. The Gaussian03 suite of programs was used in our study.[46] For the copper coordination complex **1**, we found that the triplet state is significantly lower in energy than their singlet and quintet counterparts. In general, the

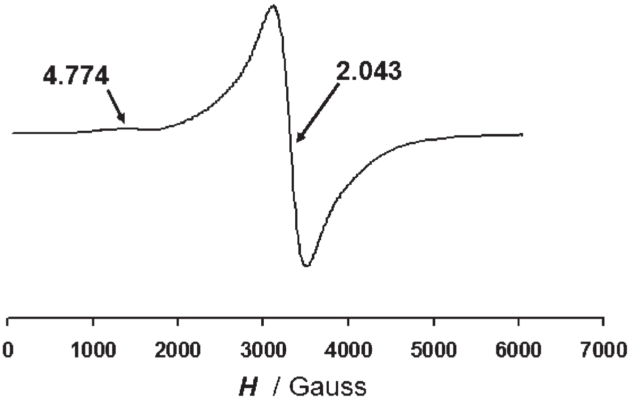
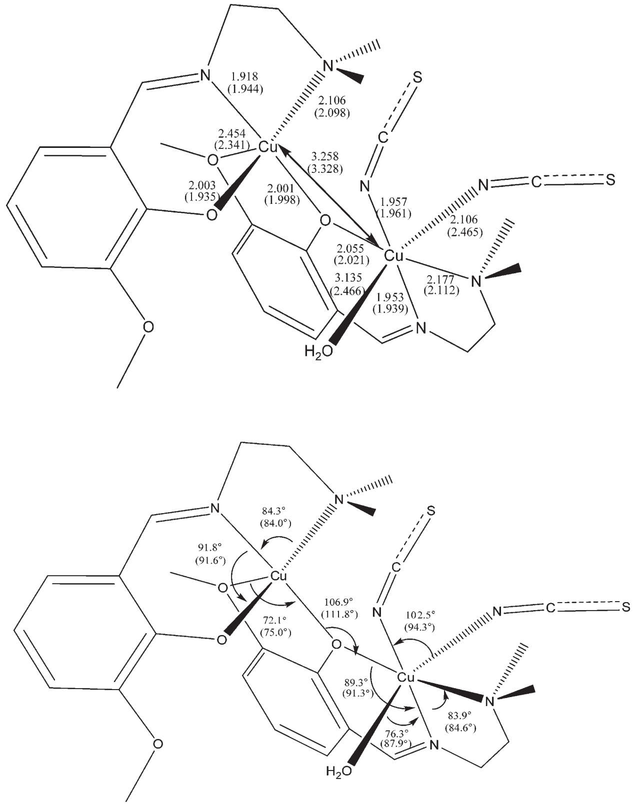


Fig. 3 Representation of the molecular structure of compound **1**. The atoms are drawn with 40% probability ellipsoids and the hydrogen atoms have been omitted for clarity.

theoretically predicted geometrical parameters are in good agreement with those resolved by X-ray diffraction studies. The geometries predicted by DFT (first entry) and those resolved from the X-ray data (second entry) of complex **1** are presented and compared in Fig. 4.



1	
Charge & mult.	Rel. energy (kcal mol^{-1})
0 1	35.69
0 3	0.0
0 5	50.48

Rel. energy is ΔH_{298}

Fig. 4 DFT predicted geometries (first entry) and those resolved from X-ray (second entry).

In summary, a dinuclear copper(II) complex exhibiting distinct metal coordination geometries has been prepared and fully characterised. The dissymmetric compound has been obtained from a Schiff-base ligand (namely 2-[{[2-(dimethylamino)ethyl]imino}methyl]-6-methoxyphenol; HL) that contains four potential donor atoms. This ligand is compartmented by the phenol group, since in its deprotonated form, it has a strong tendency to bridge two metal ions. For this reason, the two metal ions are forced by the dinucleating ligand to remain close to each other, and the phenolato-group appears to play an important role in determining the molecular geometry of the dinuclear species.

Experimental

Synthesis of **1**: To a methanolic solution (20 mL) of copper acetate monohydrate (0.199 g, 1 mmol), the Schiff base (2-[-{[2-(dimethylamino)ethyl]imino}methyl]-6-methoxyphenol; HL) (1 mmol) was added, followed by a solution of sodium thiocyanate (0.081 g, 1 mmol) in a minimum volume of water, with constant stirring for 10 min. The mixture was kept at room temperature. After a few days, deep green, rectangular single crystals of **1**, suitable for X-ray diffraction studies, were formed. The crystals were collected and dried in air. Yield: 62%. Anal. Calcd for $C_{26}H_{36}Cu_2N_6O_5S_2$: C, 44.37; H, 5.16; N, 11.94. Found: C, 44.48; H, 5.29; N, 11.86%.

Details concerning crystal data, data collection characteristics and structure refinement are summarised in Table 1. The crystal was mounted in a capillary, transferred to a goniostat and held at 298(2) K under a dinitrogen stream. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo-K$_{\alpha}$ radiation and applying the $\omega : 2\theta$ scan technique within a θ range of 1.95–26.01°. No significant crystal decay was found. Data were corrected for absorption empirically by means of ψ scans. A total of 16660 reflections were collected from which 5933 independent [R(int) = 0.0200] reflections were measured. The stability of the crystals was checked by measuring standard reflections at fixed intervals during the data collection. However, no significant loss of intensity was noted. Data were processed using the CRYSALIS-CCD and –RED[47] programs. The structure was solved by direct methods using the SHELXTL PLUS[48] system and refined by a full-matrix least-squares methods based on F^2 using SHELXL93[49] using all 16660 data to final wR_2 (on F^2, all data) = 0.0930 and R_1 (on F, with [I>2σ(I)]) = 0.0321. The functions minimised were $\Sigma w[|Fo|^2 - [|Fc|^2]^2$, where $w = [\sigma^2(I) + (0.0849P)^2 + 0.3606P]^{-1}$ for **1** with $P = (|Fo|^2 + 2|Fc|^2)/3$. The hydrogen atom positions were calculated and they were constrained to idealised geometries and treated as riding where the H atom displacement

Table 1 Crystallographic data for **1**

Empirical formula	$C_{26}H_{36}Cu_2N_6O_5S_2$
Formula weight	703.81
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P2(1)/c*
Unit cell dimensions	*a* = 16.2989(9) Å α = 90° *b* = 13.8799(7) Å β = 102.8730(10)° *c* = 13.7369(7) Å γ = 90°
Volume	3029.6(3) Å^3
Z	4
Density (calculated)	1.543 Mg m^{-3}
Absorption coefficient	1.588 mm^{-1}
F(000)	1456
Crystal size	0.32 × 0.30 × 0.25 mm^3
Theta range for data collection	1.95–26.01 °
Reflections collected	16660
Independent reflections	5933 [R(int) = 0.0200]
Data / restraints / parameters	5933 / 0 / 376
Goodness-of-fit on F^2	1.049
Final R indices [I>2σ(I)]	R^1 = 0.0321, wR^2 = 0.0894
R indices (all data)	R^1 = 0.0370, wR^2 = 0.0930
Largest diff. Peak and hole	0.735 and –0.742 e Å^{-3}

Table 2 Selected bond lengths and bond angles for **1** (Å, °)

Cu(1)–O(1)	1.9358(16)	Cu(1)–N(2)	1.9438(19)	Cu(1)–O(3)	1.9971(15)
Cu(1)–N(1)	2.098(2)	Cu(1)–O(4)	2.3418(17)	Cu(2)–N(4)	1.940(2)
Cu(2)–N(5)	1.960(2)	Cu(2)–O(3)	2.0204(15)	Cu(2)–N(3)	2.113(2)
Cu(2)–N(6)	2.464(3)	Cu(1)–O(3)–Cu(2)	111.83(7)		
N(2)–Cu(1)–N(1)	84.03(8)	O(1)–Cu(1)–O(3)	89.84(7)		
O(3)–Cu(1)–ON(1)	95.28(7)	N(2)–Cu(1)–O(1)	91.59(8)		
N(4)–Cu(2)–N(3)	84.61(9)	O(3)–Cu(2)–N(4)	91.33(8)		
N(5)–Cu(2)–O(3)	89.80(8)	N(5)–Cu(2)–N(3)	94.06(9)		
O(3)–Cu(2)–N(3)	172.34(8)	N(4)–Cu(2)–N(5)	177.87(9)		

parameter was calculated from the equivalent isotropic displacement parameter of the bound atom.

Crystallographic data for structural analysis has been deposited to the Cambridge Crystallographic Data Center, bearing 720076. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44-1223-336-033; e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

The authors gratefully acknowledge financial support from the National Science Council of Taiwan. JHH would also like to thank the National Changhua University of Education for the purchase of the CAD-4 diffractometer system.

Received 29 July 2010; accepted 26 September 2010
Paper 100272 doi: 10.3184/030823410X12886325735063

References

1 C.J. Pedersen, *J. Am. Chem. Soc*., 1967, **89**, 7017.
2 J.M. Lehn, *Pure Appl. Chem*., 1977, **49**, 857.
3 D.J. Cram, J.M. Cram, *Science*, 1984, **183**, 4127.
4 J.M. Lehn, *Angew. Chem., Int. Ed. Engl*., 1988, **27**, 89.
5 P. Guerriero, S. Tamburini and P.A. Vigato, *Coord. Chem. Rev*., 1995, **110**, 17.
6 C. Bazzicalupi, A. Bencini, V. Fusi, C. Giorgi, P. Paoletti and B. Valtancoli, *Inorg. Chem*., 1998, **37**, 941.
7 Q. Lu, J.J. Reibespiens, A.E. Martell, R.I. Carroll and A. Clearfield, *Inorg. Chem*., 1996, **35**, 7246.
8 T. Koike, M. Inoue, E. Kimura and M. Shiro, *J. Am. Chem. Soc*., 1996, **118**, 3091.
9 C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, E. Garcia-España, C. Giorgi, J.M. Llinares, J.A. Ramirez and B. Valtancoli, *Inorg. Chem*., 1999, **38**, 620.
10 J.-M. Lehn, *Supramolecular chemistry. concepts and perspectives*, VCH: Weinheim, Germany, 1995.
11 C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, E. Garcia-Espana, C. Giorgi, J.M. Llinares, J.A. Ramirez and B. Valtancoli, *Inorg. Chem*., 1999, **38**, 620.
12 K.D. Karlin, J. Zubieta, *Copper coordination chemistry and biochemistry. biochemical and inorganic perspectives,* Adenine, Guilderland, NY, 1983.
13 P.A. Vigato, S. Tamburini and D.E. Fenton, *Coord. Chem. Rev*., 1990, **106**, 25.
14 E.C. Constable, *Comprehensive supramolecular chemistry*, ed. J.L. Arwood, J.E.D. Davies, D.D. McNicol, F. Vögtle, J.P. Sauvage and M.W. Hosseini, Pergamon, Oxford, 1996, p. 213.
15 P. Chaudhuri, C. Stockheim, K. Wieghardt, W. Deck, R. Gregorzik, H. Vahrenkamp, B. Nuber and J. Weiss, *Inorg. Chem*., 1992, **31**, 1451.
16 S. Uhlenbrock and B. Krebs, *Angew. Chem., Int. Ed. Engl*., 1992, **31**, 1647.
17 N.N. Murthy and K.D. Karlin, *J. Chem. Soc., Chem.Commun*., 1993, 1236.
18 X.-M. Chen, Y.-X. Tong and T.C.W. Mak, *Inorg. Chem*., 1994, **33**, 4586.
19 C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, P. Paoletti, and B. Valtancoli, *J. Chem. Soc., Chem. Commun*., 1994, 881.
20 C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, L. Mazzanti, P. Paoletti and B. Valtancoli, *Inorg. Chem*., 1995, **34**, 3003.
21 C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, P. Paoletti, G. Piccardi and B. Valtancoli, *Inorg. Chem*., 1995, **34**, 5622.
22 B.A. Jazdzewski and W.B. Tolman, *Coord. Chem. Rev*., 2000, **200**, 633.
23 W.-L. Kwik, *J. Coord. Chem*., 1988, 19, 279.
24 M. Whittaker, Y. Chuang and J. Whittaker, *J. Am. Chem. Soc*., 1993, **115**, 10029.
25 B. Ji, Z. Zhou, K. Ding and Y. Li, *Polyhedron*, 1998, **17**, 4327.
26 K. Fujisawa, Y. Iwata, N. Kitajima, H. Higashimura, M. Kubota, Y. Miyashita, Y. Yamada, K. Okamoto and Y. Moro-oka, *Chem. Lett*., 1999, 739.
27 J. Sanmartín, M.R. Bermejo, A.M. García-Deibe, O. Piro and E.E. Castellano, *Chem. Commun*., 1999, 1953.
28 J. Sanmartin, M.R. Bermejo, A.M. Garcia-Deibe, O.R. Nascimento, L. Lezama and T. Rojo, *J. Chem. Soc., Dalton Trans*., 2002, 1030.
29 N.N. Murthy, M.M. Tahir and K.D. Karlin, *J. Am. Chem. Soc*., 1993, **115**, 10404.
30 K. Bertoncello, G.D. Fallon, J.H. Hodgkin and K.S. Murray, *Inorg. Chem*., 1988, **27**, 4750.
31 C.R. Choudhury, S.K. Dey, R. Karmakar, C.D. Wu, C.Z. Lu, M.S. El Fallah and S. Mitra, *New J. Chem*., 2003, **27**, 1360.
32 R. Gupta, S. Mukherjee and R. Mukherjee, *J. Chem. Soc., Dalton Trans*., 1999, 4025.
33 S. Torelli, C. Belle, I. Gautier-Luneau, J.L. Pierre, E. Saint-Aman, J.M. Latour and L. Le Pape, D. Luneau, *Inorg. Chem*., 2000, **39**, 3526.
34 S.K. Dutta, U. Flörke, S. Mohanta and K. Nag, *Inorg. Chem*., 1998, **37**, 5029.
35 L.K. Thompson, S.K. Mandal, S.S. Tandon, J.N. Bridson and M.K. Park, *Inorg. Chem*., 1996, **35**, 3117.
36 K. Nakamoto, *Infrared and Raman spectra of inorganic and coordination compounds*, Wiley & Sons Interscience Publ., New York, 4th edn, 1986.
37 C.T. Yang, B. Moubaraki, K.S. Murray, J.D. Ranford and J.J. Vittal, *Inorg. Chem*., 2001, **40**, 5934.
38 B.A. Jazdzewski, P.L. Holland, M. Pink, V.G. Young jr., D.J.E. Spencer and W.B. Tolman, *Inorg. Chem*., 2001, **40**, 6097.
39 O. Kahn, *Molecular magnetism*. VCH: New York, 1993.
40 C.J. Harding, V. Mckee, J. Nelson and Q. Lu, *J. Chem. Soc., Chem. Commun*., 1993, **23**, 1768.
41 Y. Nishida, H. Shimo, H. Maehara and S. Kida, *J. Chem. Soc., Dalton Trans*., 1985, **9**, 1945.
42 Y. Nishida, M. Takeuchi, K. Takahashi and S. Kida, *Chem. Lett*., 1985, **5**, 631.
43 I.A. Koval, K. van der Schilden, A.M. Schuitema, P. Gamez, C. Belle, J.L. Pierre, M. Luken, B. Krebs, O. Roubeau and J. Reedijk, *Inorg. Chem*., 2005, **44**, 4372.
44 A.D. Becke, *J. Chem. Phys*., 1993, **98**, 5648.
45 C. Lee, W. Yang and R.G. Parr, *Phys. Rev*., 1988, **B37**, 785.
46 M.J. Frisch, G.W. Trucks, H.B. Schlegel, *et al*., Revision B.05 ed.; Gaussian, Inc.: Pittsburgh PA, 2003.
47 Programs CRYSALIS-CCD and -RED, Oxford Diffraction Ltd., Abingdon, UK 2005.
48 G.M. Sheldrick, SHELX97 – Programs for Crystal Structure Analysis: Structure Determination (SHELXS), University of Göttingen, Germany, 1997.
49 G.M. Sheldrick, SHELX97 – Programs for Crystal Structure Analysis: Refinement (SHELXL), University of Göttingen, Germany, 1997.