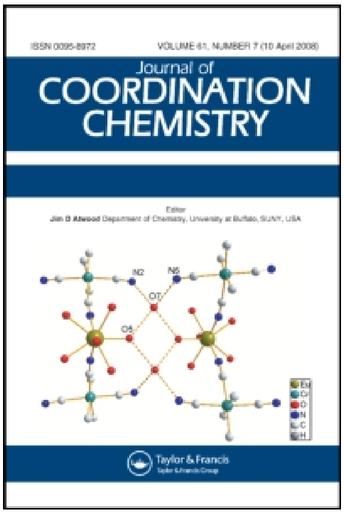

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and crystal structure of a novel binuclear copper(II) complex

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To cite this Article Sao, Yun , Chen, Ya-Guang , Zhu, Dong-Sheng and Liu, Qun(2006) 'Synthesis, characterization and crystal structure of a novel binuclear copper(II) complex', Journal of Coordination Chemistry, 59: 5, 537 — 544
To link to this Article: DOI: 10.1080/00958970500252172
URL: http://dx.doi.org/10.1080/00958970500252172

Journal of Coordination Chemistry
Vol. 59, No. 5, 20 March 2006, 537–544

Synthesis, characterization and crystal structure of a novel binuclear copper(II) complex

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(*Received in final form 25 May 2005*)

The binuclear copper(II) complex $[Cu_2(dyma)_2(phen)_2]\cdot 4H_2O\cdot 2DMF$ (Na_2dyma = sodium 2-[1,3]-dithiolan-2-ylidene-malonate, phen = 1,10-phenanthroline) has been synthesized and characterized by analysis, IR and electronic spectroscopy, and variable temperature magnetic susceptibility measurements. A single-crystal X-ray diffraction analysis shows that each copper atom exhibits distorted square-pyramidal coordination geometry, bonded to two oxygen atoms of dyma, two nitrogen atoms of phen and an oxygen atom from a neighbouring molecule, thus forming a binuclear complex. The binuclear units form columns along the *b* axis via π–π interactions between phen ligands. Hydrogen bonds between 1D columns lead to a 2D network. IR and electronic spectra are consistent with the structure. In the temperature range 230–290 K, the complex exhibits weak antiferromagnetic behaviour and, below 230 K, ferromagnetic behaviour.

Keywords: Copper(II); 2-[1,3]-dithiolan-2-ylidene-malonate; 1,10-phenanthroline; Binuclear complex; π–π interaction; Hydrogen bonding; X-ray structure

1. Introduction

The design and synthesis of polymetallic coordination compounds has been of considerable interest to inorganic and bioinorganic chemists [1–3]. One important area of this research concerns binuclear complexes, especially the binuclear Cu(II) complexes [4, 5], because of their use as molecular-based ferromagnets [6, 7] and catalysts, and their particular molecular structure [8, 9]. There are several types of binuclear Cu(II) complexes; one-, two- and four-carboxylate-bridged [10–15] and non-carboxylate-bridged examples [4] are well-known. In these complexes, Cu–Cu distances range from 2.435 Å [15] to 2.633 Å [12], depending on terminal ligands, and short distances result in magnetic interactions. Varied structures and coordination geometries are a feature of these systems and include 1D double-helical chains [4],

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500252172

2D open-frame networks [15], 3D open frameworks [16–20] and 3D nano-sized channel frameworks [4]. New ligands may, of course, result in novel structure types and, with this in mind, we have explored a carboxylate ligand containing sulfur atoms, 2-(1,3)-dithiolan-2-ylidene-malonic acid (dyma). Herein, we report the synthesis, spectroscopic and magnetic properties, and the crystal and molecular structures of a binuclear Cu(II) complex of this ligand and 1,10-phenanthroline (phen).

2. Experimental

2.1. *Materials and physical measurements*

Reagent grade chemicals were obtained from commercial sources and used without further purification. Elemental analyses were carried out on a Perkin-Elmer PE 2400 CHN instrument and a Leeman inductively coupled plasma spectrometer (ICP) for Cu. IR spectra were recorded on an Alpha Centauri FTIR spectrophotometer (400–4000 cm^{-1} range, KBr disks) and electronic spectra on a Varian Cary 500 spectrophotometer. Variable temperature magnetic susceptibility measurements were performed using an MPMS-XL5 magnetometer at 1.0 T and 2–300 K.

2.2. *Syntheses*

2.2.1. Ligand. Sodium 2-[1,3]-dithiolan-2-ylidene-malonate (Na_2dyma) was prepared as follows. Diethylmalonate (10.0 mmol, 1.52 cm^3) was added to a DMF (20 cm^3) solution of anhydrous potassium carbonate (20.0 mmol, 2.76 g) with stirring. The mixture was stirred for 30 mins at room temperature and then carbon disulphide (11.0 mmol, 0.66 cm^3) was added with stirring and cooling in an ice bath. After 30 mins, the ice bath was removed and 1,2-dibromoethane (11.0 mmol, 0.95 cm^3) added to the mixture. The mixture was stirred for about 14 h (monitored by TLC) and then poured into ice water. The resulting precipitate was filtered off, washed thoroughly with water and dried at room temperature to give 2-[1,3]-dithiolan-2-ylidene-diethyl malonate as a light yellow powder (yield: 97.0%). Aqueous 1M NaOH (40 cm^3) was cooled in ice and added dropwise to an ethanolic solution of the isolated compound (10.0 mmol, 2.62 g) at room temperature. The mixture was then refluxed for 8 h (monitored by TLC) and filtered while hot. The filtrate was cooled in ice water and adjusted to pH 1 using aqueous 4 M HCl. The resulting precipitate was filtered off, washed with water and dried *in vacuo* to afford pale yellow 2-[1,3]-dithiolan-2-ylidene-malonic acid (yield: 92.0%).

2.2.2. $[Cu_2(dyma)_2(phen)_2 \cdot 4H_2O \cdot 2DMF$. An aqueous solution (10 cm^3) of $CuCl_2 \cdot 2H_2O$ (341 mg, 2 mmol) was slowly added to an aqueous solution (10 cm^3) of Na_2dyma (500 mg, 2 mmol) and stirred for 10 h at ambient temperature. The green crystalline solid formed in the reaction was collected by filtration, washed with water and ethanol, and dried in air. The green solid and *o*-phen (396 mg, 2 mmol) was added to DMF (10 cm^3) and stirred at 55?–60?°C for 2 h. After cooling to room temperature, it was placed in a test tube and covered with the same volume of ethyl-acetate. The mixture was allowed to stand for 24 h, yielding the green single crystals of the product. Elemental analyses were consistent with the stated stoichiometry.

Table 1. Crystal data and details of structure refinement parameters for the complex.

Formula	$C_{21}CuH_{23}N_3O_7S_2$
M	557.08
Temperature/K	293(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	14.7108(11)
b/Å	8.9926(8)
c/Å	18.286(2)
$\beta/^\circ$	106.286(6)
V/Å^3	2321.9(4)
Z	4
D_{calc}/g cm^{-3}	1.594
Absorption coefficient/(mm^{-1})	1.169
$F(000)$	1148
Reflections collected	4078
Independent reflections	2069 [$R_{int} = 0.1077$]
Completeness to $\theta = 25.01$(%)	99.6
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.867
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0504$, $wR_2 = 0.1001$
R indices (all data)	$R_1 = 0.1203$, $wR_2 = 0.1216$

IR: 3469m, 1586s, 1529s, 1429m, 1377s, 1294w, 1223w, 1145w, 1107w, 875w, 852w, 823w, 784m, 723m, 559w, 468w cm^{-1}. Electronic absorption maxima (aqueous solution): 274, 297, 615 nm.

2.3. *X-ray crystallography*

Diffraction data for the complex using a crystal of dimensions 0.26 mm × 0.29 mm × 0.38 mm were collected at 293(2) K on a Bruker SMART-CCD diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å) in the θ range 2.09–25.01°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques (SHELXL 97) [21] on F^2. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were generated geometrically. Parameters concerning data collection and refinement are given in table 1. Atomic coordinates and thermal parameters for non-hydrogen atoms are given in table 2.

3. Results and discussion

3.1. *Spectroscopic characterization*

IR spectra of **1** show a strong, broad band at 3610–3280 cm^{-1}, assignable to ν(OH) of lattice water molecules, in agreement with participation in hydrogen bonds. Characteristic bands of the carboxyl groups at 1586 and 1529 cm^{-1} for ν_{as} and at 1377 and 1342 cm^{-1} for ν_s were observed. $\Delta(\nu_{as} - \nu_s)$ values are 209 and 187 cm^{-1}, indicating the monodentate coordination mode. The two groups of stretching vibrations implies the presence of two different carboxyl groups, as confirmed by the single-crystal analysis. The electronic spectrum exhibits three electronic transitions

Table 2. Atomic coordinates and thermal parameters of non-hydrogen atoms.

Atom	X/a	y/b	z/c	U^*
Cu1	0.01103(5)	0.34023(8)	0.04484(4)	0.0346(2)
S1	−0.17702(10)	0.66659(19)	0.23679(9)	0.0465(4)
S2	−0.29502(10)	0.71383(19)	0.08044(9)	0.0492(5)
N1	0.1235(3)	0.2086(5)	0.0848(3)	0.0334(11)
O3	−0.0967(2)	0.4594(4)	−0.0022(2)	0.0340(9)
N2	−0.0004(3)	0.2235(5)	−0.0509(3)	0.0317(11)
C13	−0.1952(3)	0.6257(6)	0.1402(3)	0.0326(14)
C18	−0.1605(4)	0.5067(6)	0.0295(3)	0.0347(14)
O2	−0.0362(3)	0.4942(5)	0.2371(2)	0.0590(13)
C17	−0.0498(4)	0.4728(6)	0.1684(4)	0.0375(14)
O4	−0.2426(3)	0.5328(5)	−0.0102(2)	0.0571(13)
C16	−0.1364(3)	0.5350(6)	0.1130(3)	0.0303(13)
C5	0.1344(4)	0.1076(6)	0.0328(3)	0.0330(14)
O1	0.0115(2)	0.3973(4)	0.1436(2)	0.0447(11)
C6	0.0670(4)	0.1145(6)	−0.0415(3)	0.0313(14)
C9	−0.0646(4)	0.1352(7)	−0.1784(3)	0.0488(17)
C11	0.2088(4)	−0.1031(7)	−0.0121(4)	0.0531(19)
C7	0.0729(4)	0.0135(6)	−0.0984(3)	0.0397(15)
C10	−0.0648(4)	0.2316(7)	−0.1178(4)	0.0418(15)
C1	0.1838(4)	0.2041(7)	0.1542(3)	0.0433(16)
C3	0.2686(4)	−0.0022(7)	0.1215(4)	0.0507(17)
C4	0.2056(4)	−0.0017(6)	0.0481(3)	0.0374(15)
C8	0.0031(4)	0.0271(7)	−0.1688(4)	0.0498(17)
C2	0.2580(4)	0.0998(7)	0.1745(4)	0.0477(17)
C12	0.1454(4)	−0.0975(6)	−0.0806(4)	0.0494(17)
O1W	0.0472(3)	0.2399(5)	0.3173(3)	0.0617(13)
O2W	−0.2832(3)	0.4369(6)	−0.1642(3)	0.0795(15)
N3	0.4807(4)	−0.2906(6)	−0.0749(3)	0.0506(14)
O5	0.4410(3)	−0.2097(6)	0.0290(3)	0.0789(16)
C15	−0.3131(4)	0.8419(7)	0.1504(4)	0.0574(18)
C21	0.5313(5)	−0.1610(9)	−0.0853(5)	0.106(3)
C19	0.4419(5)	−0.3045(9)	−0.0193(5)	0.075(2)
C14	−0.2880(4)	0.7653(7)	0.2255(4)	0.062(2)
C20	0.4842(6)	−0.4171(9)	−0.1250(5)	0.119(3)

$^*U$ is defined as third of the sum of U_{ij}.

at 274, 297, 615 nm, attributed to of $\pi \rightarrow \pi^*$, $\pi \rightarrow d(x^2-y^2)$, $d(z^2)$ and $d(xz)$, $d(yz) \rightarrow d(x^2-y^2)$, respectively. The broad band at 615 nm is consistent with a five-coordinate copper(II) chromophore [22].

3.2. *Crystal structure*

The molecular structure of the complex is shown in figure 1. The aymmetric unit consists of a DMF molecule, two water molecules and a copper(II) complex containing the two ligands. The central copper atom bonds to two oxygen atoms of dyma and two nitrogen atoms of phen. O(1)–Cu(1)–O(3) and N(1)–Cu(1)–N(2) angles are 93.38(15) and 82.37(18)°, and O–Cu(1)–N angles range from 91.76(17) to 174.85(17)°. The N–Cu–N angle is considerably smaller than the O–Cu–O angle. Cu(1)–O(1) and Cu(1)–O(3) bonds are 1.876(4) and 1.906(3) Å, and Cu(1)–N(1) and Cu(1)–N(2) bonds are 1.999(4) and 2.007(4) Å. The dihedral angle between the two chelating rings formed by dyma and phen is 21.7°. The mean deviation of the copper atom from the distorted square plane is 0.126 Å. The copper atom Cu(1) has a fifth coordinating oxygen atom from an adjacent molecule, to form a binuclear complex

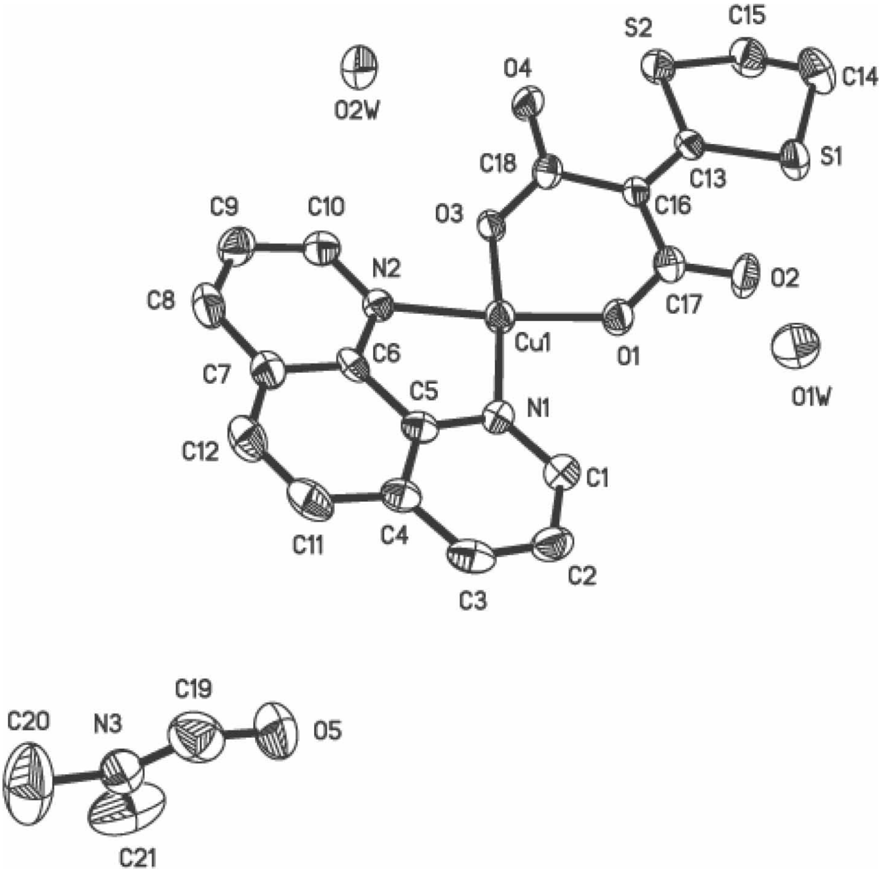

Figure 1. Perspective drawing of the asymmetric unit showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

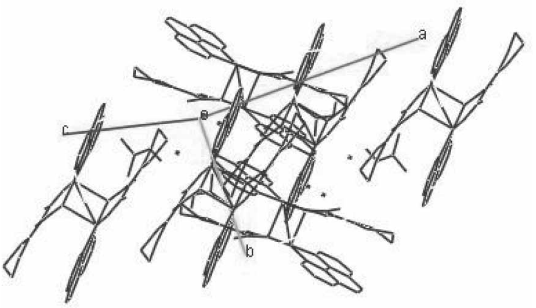

Figure 2. Packing of the binuclear units of the complex.

(see figure 2) with Cu–μ–O 2.448 Å and Cu–Cu of 3.279 Å. These are much longer than that in paddle-wheel complexes [10–14, 16] and even longer than in some binuclear complexes [5, 23]. Each Cu(II) ion thus adopts a distorted square pyramidal geometry. The formation of the Cu–μ–O bond leads to differences in coordination modes of the two carboxyl groups in the dicarboxylate ligand dyma (η^1 and $\eta^1 - \mu$).

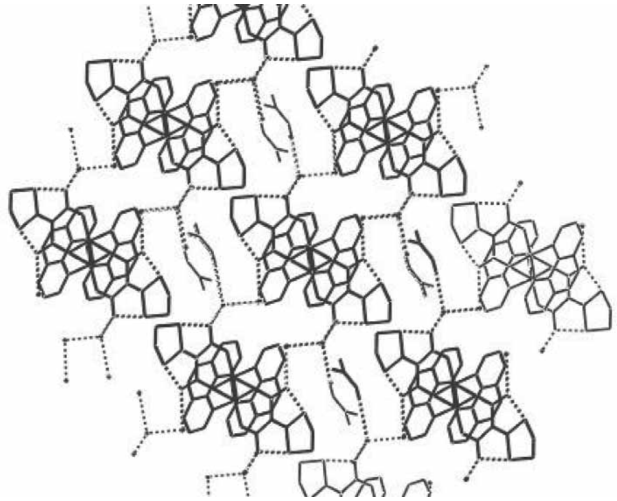

Figure 3. The 2D-structure of sheets of the complex in the crystal extending in the [$\bar{1}$01] plane.

In the lattice, the binuclear complexes stack one-dimensionally in such a manner that the phen planes of neighboring binuclear complexes lie parallel to each other. Short distances, C6–C5′(C6′–C5) 3.613 Å, C7–N1′(C7′–N1) 3.578 Å, C4–N2′(C4′–N2) 3.630 Å, are found between them and these are shorter than 3.8 Å, the accepted maximum value for a π–π interaction [24]. It is these π–π interactions that are responsible for the 1D column. In the column, the long molecular axis of the binuclear complex is inclined at 45° to the b axis and, between neighbouring columns in the [$\bar{1}$01] plane, the planes of the binuclear complexes are perpendicular to each other (figure 2).

Each binuclear complex contains four uncoordinated carboxylic oxygen atoms that form hydrogen bonds with water molecules (O2–Ow1 2.806 Å, O4–Ow2 2.844 Å), and between water molecules there exists a further hydrogen bond (Ow1–Ow2 2.897 Å). As a result of these, a two-dimension layer is created, extending in the [$\bar{1}$01] plane (figure 3). DMF molecules are also hydrogen-bonded to water molecules (O5(DMF)–Ow1 2.804 Å) and unusually short distances (S1–O2 2.586 Å, S2–O4 2.590 Å) exist between S atoms of bithiolan groups and oxygen atoms of carboxyl groups in the same ligand. Only van der Waals forces involving bithiolan and the two methyl groups of DMF hold the layers together.

3.3. *Magnetic susceptibilities*

A plot of variable temperature molar magnetic susceptibilities versus temperature is shown in figure 4. On cooling from room temperature (290 K), the susceptibility decreases slowly to 230 K, and then increases. At 7 K it reaches a maximum value, indicating weak antiferromagnetic behaviour of the complex in the range of 290–230 K and weak ferromagnetic behaviour below 230 K. It is reported [23] that the superexcharge interaction (J) between paramagnetic nuclei depends on the electron donating nature of the R substituent of the carboxylate bridging ligands, the σ-donor ability of the axial ligand and the Cu–Cu distance. The magnitude of the ferromagnetic

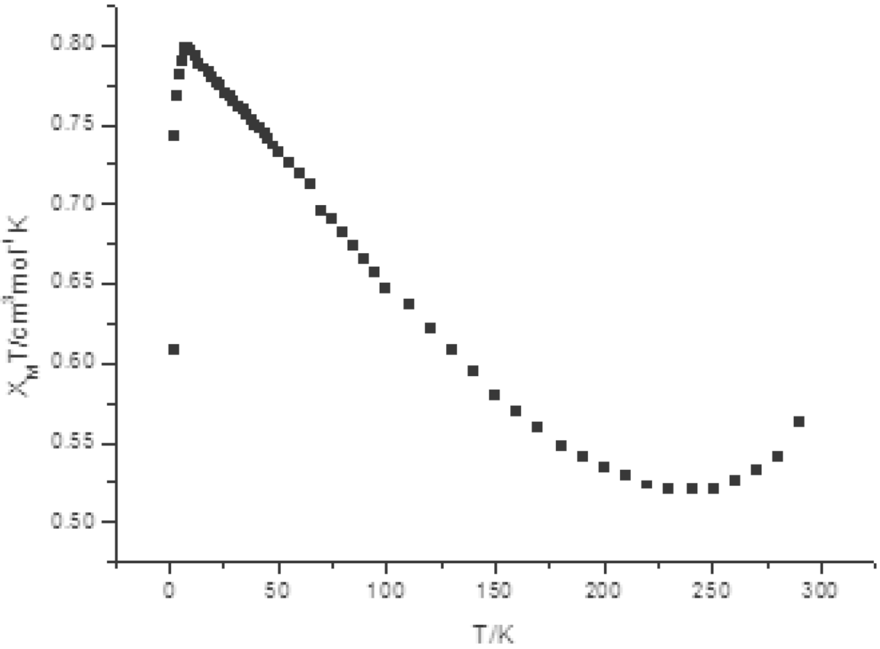

Figure 4. $X_M T$ *vs.* T plot for the complex in the temperature range 4–300 K.

interaction might be expected to be small because there is no bidentate carboxylate bridging ligand and the Cu–μ–O (2.448 Å) and Cu–Cu (3.279 Å) distances are longer than normal. The effective magnetic moment at room temperature calculated from the magnetic susceptibility $[2.828(X_M T)^{1/2} = 1.57\mu_B]$ is consistent with the antiferromagnetic nature of the complex in the range 230–290 K.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 239835. Copies of this information may be obtained free of charge 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).

Acknowledgements

This project was supported by the National Natural Science Foundation of China.

References

[1] O. Kahn. *Struct. Bonding (Berlin)*, **68**, 89 (1987).
[2] Z.J. Zhong, X.Z. You, Q.C. Yang. *Polyhedron*, **13**, 1951 (1994).
[3] Z.J. Zhong, X.Z. You, T.C.W. Mak. *Polyhedron*, **13**, 2157 (1994).

[4] J.Y. Lu. *Coord. Chem. Rev.*, **246**, 327 (2003).
[5] J. Pons, A. Chadghan, A. Alvarez-Larena, J.F. Piniella, J. Ros. *Inorg. Chem. Commun.*, **4**, 610 (2001).
[6] F. Lloret, Y. Journaux, M. Julve. *Inorg. Chem.*, **29**, 3967 (1990).
[7] K. Nakatani, J..Carriat, Y. Journaux, O. Kahn, F. Lloret, J.P. Reard, Y. Pei, J. Sletten, M.J. Verduguer. *J. Am. Chem. Soc.*, **111**, 5739 (1989).
[8] R. Costa, C. Lopez, E. Molins, E. Espinosa. *Inorg. Chem.*, **37**, 5686 (1998).
[9] C. Lopez, R. Costa, F. Illas, E. Molins, E. Espinosa. *Inorg. Chem.*, **39**, 4560 (2000).
[10] P.D. Meester, S.R.Fletcher, A.C. Skapski. *J. Chem. Soc., Dalton Trans.*, 2575 (1973).
[11] F. Hanic, D. Stempelova, K. Hanicova. *Acta Cryst.*, **17**, 633 (1964).
[12] M. Bukowska-Strzyzewska, A. Tosik. *Acta Cryst.*, **B38**, 2904 (1982).
[13] G. Davey, F.S. Stethens. *J. Chem. Soc.* (*A*), **92**, 2803 (1970).
[14] M.M. Borel, A. Leclaire. *Acta Cryst.*, **B32**, 1275 (1976).
[15] J.Y. Lu, K.R. Runnels. *Inorg. Chem. Commun.*, **4**, 678 (2001).
[16] R. Cao, Q. Shi, D. Sun, M. Hong, W. Bi, Y. Zhao. *Inorg. Chem.*, **41**, 6161 (2002).
[17] X.-F. Chen, P. Cheng, X. Liu, B. Zhao, D.-Z. Liao, S.-P. Yan, Z.-H. Jiang. *Inorg. Chem.*, **40**, 2652 (2001).
[18] X.-H. Bu, W. Chen, S.-L. Lu, R.-H. Zhang, D.-Z. Liao, W.-M. Bu, M. Shionoya, F. Brisse, J. Ribas. *Angew. Chem. Int. Ed.*, **40**, 3201 (2001).
[19] X.-M. Zhang, X.-M. Chen. *Eur. J. Inorg. Chem.*, 413 (2003).
[20] S.S.S. Cui, S.M.F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams. *Science*, **283**, 1148 (1999).
[21] G.M. Sheldrick. *SHELX97. Program for Crystal Structure Solution and Refinement*, University of Göttingen, Germany (1997).
[22] W. Fitzgerald, J. Foley, D. McSweeney, N. Ray, D. Sheahan, S. Tyagi, B. Hathaway, P. O'Brien. *J. Chem. Soc., Dalton Trans.*, 1117 (1982).
[23] Y.-P. Tian, X.-J. Zhang, J.-Y. Wang, H.-K. Fun, M.-H. Jiang, Z.-Q. Xu, A. Usman, S. Chantrapromma, L.K. Thompson. *New J. Chem.*, **26**, 1468 (2002).
[24] C. Janiak. *J. Chem. Soc., Dalton Trans.*, 885 (2000).