

Fig. 2. View of the crystal structure, viewed parallel to the *z* axis.

An inquiry of the Cambridge Structural Database (1989) for octahedrally coordinated Ni^{II} ions resulted in 104 compounds with Ni—O and/or Ni—N bonds. The average Ni—O and Ni—N distances are 2.084 and 2.110 Å, respectively. They are significantly longer than in the square-planar configuration.

The coordination of the ligands around the Ni atom is fairly planar, and the bonding angles of the ligands are between 87.6 and 95.1°. The Ni atom is 0.033 Å out of the plane of its ligands. The angles between the planar organic groups are smaller than 8°. The Ni atom deviates from these planes by less than 0.165 Å.

The piperidine ring has an almost ideal chair conformation: the perpendicular distances of the two

Table 3. Bond lengths (Å) in some nickel(II) complexes

	(I)	(II)	(III)	(IV)	
C01—C02	1.402 (6)	1.401 (7)	1.397 (5)	1.427 (6)	1.422 (8)
C01—C11	1.430 (5)	1.429 (4)	1.429 (4)	1.446 (6)	1.416 (8)
C02—O1	1.323 (5)	1.318 (5)	1.305 (4)	1.332 (5)	1.296 (5)
C11—N1	1.298 (5)	1.302 (5)	1.297 (4)	1.279 (6)	1.292 (5)
C12—C13					1.410 (6)
C12—N1					1.434 (7)
C13—O2					1.334 (6)
Ni1—N1	1.913 (4)	1.918 (4)	1.912 (3)	1.941 (3)	1.848 (4)
Ni1—N2					1.947 (4)
Ni1—O1	1.829 (2)	1.828 (2)	1.832 (2)	1.828 (3)	1.804 (4)
Ni1—O2					1.830 (4)

(I) Bis{*N*-[(1,3-dioxolan-2-yl)methyl]salicylaldiminato}nickel(II); (II) bis{*N*-[(1,3-dioxolan-2-yl)methyl]-2-hydroxy-1-naphthaldiminato}nickel(II); (III) bis{*N*-[(1,3-dioxolan-2-yl)methyl]-3-hydroxy-2-naphthaldiminato}nickel(II) (Fernandes-G., Rosales-Hoz, Rubio-Arroyo, Salcedo, Toscano & Vela, 1987); (IV) present work.

para positioned chair atoms from the plane of the other four atoms of the six-membered ring are between 0.608 and 0.650 Å. The ideal theoretical value is 0.726 Å.

References

- Cambridge Structural Database (1989). *Users Manual*. Cambridge Crystallographic Data Centre, Cambridge, England.
- FERNANDEZ-G., J. M., ROSALES-HOZ, M. J., RUBIO-ARROYO, M. F., SALCEDO, R., TOSCANO, R. A. & VELA, A. (1987). *Inorg. Chem.* **26**, 349–357.
- KOPFMANN, G. & HUBER, R. (1968). *Acta Cryst.* **A24**, 348–351.
- MAGGIO, F., PIZZINO, T. & ROMANO, V. (1974). *Inorg. Nucl. Chem. Lett.* **10**, 1005–1008.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- SHELDRIK, G. M. (1983). *SHELXTL Users Manual*. Revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1991). **C47**, 72–75

Structure of μ -Pyrazine-bis[(diethylenetriamine-*N,N',N''*)(diperchlorato-*O*)copper(II)]

BY DUANJUN XU, CHENGGANG CHEN, YUANZHI XU AND CHAORONG CHENG

Department of Chemistry, Zhejiang University, Hangzhou, People's Republic of China

AND JIE CHEN AND WEIZHONG TANG

Shanghai Institute of Biochemistry, Academia Sinica, People's Republic of China

(Received 22 March 1990; accepted 20 June 1990)

Abstract. [Cu₂(ClO₄)₄(C₄H₁₃N₃)₂(C₄H₄N₂)], *M_r* = 76.54 (5)^o, *V* = 690.0 (7) Å³, *F*(000) = 1648, *Z* = 1, 811.1, triclinic, *P* $\bar{1}$, *a* = 7.204 (4), *b* = 7.814 (5), *c* = 12.612 (5) Å, α = 87.90 (4), β = 89.08 (4), γ = 20.76 cm⁻¹, room temperature, *R* = 0.052 for 2489

observed reflections. The crystal structure consists of discrete binuclear molecules. The coordination geometry around the Cu^{II} atom is a tetragonally elongated octahedron. The chelate rings of the diethylenetriamine ligand adopt a $\delta\lambda$ conformation. The bridge ligand pyrazine ring cants relative to the equatorial coordination plane of the Cu^{II} atom with a dihedral angle of 58.8°, and this may provide a pathway for a magnetic superexchange interaction between the two Cu^{II} atoms.

Introduction. In the last decade, a number of binuclear transition-metal complexes in which the metal ions are bridged by heterocyclic aromatic diamines, especially pyrazine or imidazolate, have been investigated as models of metalloenzymes (Matsumoto, Ooi, Nakao, Mori & Nakahara, 1981; Richardson & Hatfield, 1975). The main topic under investigation is the effectiveness of a bridge ligand in propagating a spin-spin exchange interaction between two transition-metal ions. Some investigations have shown the relationship between structure and magnetic superexchange interaction (Coronado, Drillon & Beltran, 1984). In this paper we report the structure of a binuclear copper(II) complex, bridged by pyrazine, which exhibits a spin-spin exchange interaction in its ESR spectrum.

Experimental. 4 mmol Cu(ClO₄)₂·6H₂O and 4 mmol diethylenetriamine (dien) were mixed in methanol, and, after filtration, 2 mmol pyrazine (pyz) was added to the solution. The mixture was refluxed for three hours. Dark blue crystals were grown by slow evaporation at room temperature.

A well shaped crystal of μ -pyz-[Cu(dien)(ClO₄)₂]₂ with dimensions 0.10 × 0.22 × 0.30 mm was used for data collection. Preliminary examination of the crystal and data collection were performed on an Enraf-Nonius CAD-4 diffractometer. Unit-cell parameters were determined by a least-squares fit of the 2 θ values of 25 reflections (20 ≤ 2 θ ≤ 30°). Intensity data were collected by ω -2 θ scans using graphite-monochromated Mo K α radiation, the scan rate was variable from 2.0 to 5.5° min⁻¹ and the scan width was $\Delta\omega = (0.80 + 0.35\tan\theta)^\circ$. A total of 2985 independent reflections were measured with 2 θ up to 54° and index range $h = -9$ to 0, $k = -10$ to 10, $l = -16$ to 16. 2489 observed reflections [$|F_o| \geq 3\sigma(F_o)$] were employed in the refinements. Three standard reflections were measured every hour, no intensity variation was observed. Lorentz and polarization corrections were applied, no absorption or extinction corrections.

Structure was solved by the Patterson method followed by Fourier syntheses. For refinement, the function $\sum w(|F_o| - |F_c|)^2$ was minimized by block-diagonal least squares with the program *HBL5-V*

(Ashida, 1979), and unit weights were used. In the final refinement stage, the H atoms were placed 1.0 Å from bonded non-H atoms and refined isotropically, while all non-H atoms were refined anisotropically. Final refinement reached convergence with $R = 0.052$ and $wR = 0.055$. A final difference map showed two highest peaks (1.0 e Å⁻³) within 1.0 Å of the Cu^{II}-atom position. $S = 1.52$ and $(\Delta/\sigma)_{\max} = 0.55$ for non-H atoms. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 71). All computations were performed on a Honeywell DPS8/49 computer at the Computation Center, Zhejiang Univ., People's Republic of China.

Discussion. The atomic coordinates and thermal parameters for non-H atoms are listed in Table 1,* and bond distances and angles are given in Table 2. The crystal structure consists of discrete binuclear molecules as shown in Fig. 1.

The molecule is located about a crystallographic inversion centre. The coordination geometry around the Cu^{II} atom is a tetragonally elongated octahedron with four N atoms in the xy plane of the Cu^{II} atom and two O atoms in the axial direction. The coordination bonding is not strong, the observed Cu-N mean distance being 1.999 Å. A tridentate dien ligand chelates meridionally to the Cu^{II} atom, and the two chelated rings adopt a $\delta\lambda$ conformation. It is noteworthy that the C(2)-N(2)-C(3) bond angle of 125.4 (6)° is much larger than those found in other complexes containing the dien ligand (Huang, 1989; Melanson & Rochon, 1978). The bridge ligand pyrazine links two Cu^{II} atoms by means of two terminal N atoms. The bond distances in the pyrazine ligand agree well with those observed in the pyrazine molecule (Wheatley, 1957). The C(5)-N(4)-C(6) (third atom at $1-x, -y, 1-z$) bond angle falls in the range reported previously (Wheatley, 1957; Belford, Fenton & Truter, 1974; Darriet, Haddad, Duesler & Hendrickson, 1979; Xu, Chen, Xu & Zhou, 1987; Santoro, Mighell & Reimann, 1970). Comparison of those angles and Cu-N(pyz) bond distances shows that the shorter the bond distance, the larger the bond angle. This is probably due to the involvement of the lone pair electrons on the N atom in bonding to the Cu^{II} atom. So stronger Cu-N(pyz) bonding is accompanied by weaker repulsion between the lone-pair electron of the N atom and the pyz ring electrons, which results in a

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and selected least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53317 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters of non-H atoms with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)*
Cu	0.19417 (9)	0.09081 (8)	0.29207 (5)	2.33
Cl(1)	-0.2033 (2)	0.3657 (2)	0.4231 (1)	2.9
Cl(2)	0.4864 (2)	-0.2471 (2)	0.1225 (1)	3.3
O(1)	-0.0472 (6)	0.2133 (6)	0.4381 (4)	4.3
O(2)	-0.2826 (6)	0.4152 (6)	0.5237 (4)	4.1
O(3)	-0.3381 (7)	0.3168 (8)	0.3562 (4)	5.1
O(4)	-0.1358 (9)	0.5034 (7)	0.3725 (4)	6.7
O(5)	0.6798 (7)	-0.3162 (8)	0.0993 (5)	5.5
O(6)	0.3799 (11)	-0.2345 (10)	0.0307 (5)	8.3
O(7)	0.4643 (7)	-0.0771 (6)	0.1690 (5)	5.3
O(8)	0.4250 (8)	-0.3569 (7)	0.2016 (5)	6.3
N(1)	0.2804 (9)	0.2995 (8)	0.2331 (6)	6.3
N(2)	0.0013 (8)	0.1528 (7)	0.1776 (4)	4.5
N(3)	0.0871 (6)	-0.1222 (6)	0.3173 (4)	2.9
N(4)	0.3771 (6)	0.0365 (5)	0.4145 (3)	2.1
C(1)	0.1565 (10)	0.3878 (8)	0.1483 (5)	4.1
C(2)	0.0530 (11)	0.2676 (11)	0.1006 (6)	6.0
C(3)	-0.0748 (10)	0.0036 (9)	0.1563 (6)	4.6
C(4)	-0.0799 (10)	-0.1080 (9)	0.2501 (5)	4.5
C(5)	0.3729 (7)	0.1514 (7)	0.4894 (4)	2.4
C(6)	0.4928 (7)	0.1173 (7)	0.5753 (4)	2.3

* As defined by Hamilton (1959).

larger C(5)—N(4)—C(6) bond angle. In the axial direction of the Cu^{II} atom, two perchlorate groups exist with Cu—O distances of 2.566 and 2.604 Å, which are much longer than the distance of 2.37 Å in Cu(py₂z)₂(ClO₄)₂ (Darriet, Haddad, Duesler & Hendrickson, 1979). But the fact that the bond distances Cl(1)—O(1) [1.444 (5) Å] and Cl(2)—O(7) [1.446 (6) Å] are significantly longer than the other Cl—O bond distances suggests that O(1) and O(7) are actually coordinated to the Cu^{II} atoms.

The least-squares analysis indicates that the pyrazine ring in the present complex is essentially planar, and canted relative to the *xy* plane of the Cu^{II} atom with a dihedral angle of 58.8°. Such a tilt seems to be the result of short contacts between the pyz ring and the neighbouring coordinated atoms as verified by the O(1)···C(5) distance of 3.028 (7) Å. The ESR spectrum of a powdered sample of the present crystal (Chen, 1989) implies an exchange interaction between the unpaired electrons of two Cu^{II} atoms. Because the nearest distance between the Cu^{II} atoms is 6.99 Å in the crystal, the exchange interaction should be a superexchange propagated through the bridge ligand. According to the superexchange mechanism proposed by Richardson & Hatfield (1975), inclination of the bridge ligand to the *xy* coordination plane of the Cu^{II} atom might provide a π propagating pathway for exchange interaction between the two unpaired electrons of the Cu^{II} atoms.

This work was supported by the National Natural Science Foundation of China. The authors are

Table 2. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

Cu—O(1)	2.566 (5)	C(3)—C(4)	1.450 (10)
Cu—N(2)	1.987 (6)	Cl(1)—O(2)	1.413 (5)
N(1)—C(1)	1.452 (10)	Cl(2)—O(5)	1.402 (7)
N(3)—C(4)	1.463 (9)	Cl(2)—O(8)	1.424 (6)
C(1)—C(2)	1.477 (11)	Cu—N(1)	1.991 (7)
Cl(1)—O(1)	1.444 (5)	Cu—N(4)	2.014 (4)
Cl(1)—O(4)	1.409 (7)	N(2)—C(3)	1.434 (10)
Cl(2)—O(7)	1.446 (6)	N(4)—C(6) ⁱ	1.345 (7)
Cu—O(7)	2.604 (6)	C(5)—C(6)	1.375 (8)
Cu—N(3)	2.005 (5)	Cl(1)—O(3)	1.422 (6)
N(2)—C(2)	1.402 (10)	Cl(2)—O(6)	1.387 (8)
N(4)—C(5)	1.322 (7)		
O(1)—Cu—O(7)	169.8 (2)	O(1)—Cu—N(1)	104.6 (2)
O(1)—Cu—N(2)	93.4 (2)	O(1)—Cu—N(3)	82.2 (2)
O(1)—Cu—N(4)	83.0 (2)	O(7)—Cu—N(1)	82.5 (2)
O(7)—Cu—N(2)	94.7 (2)	O(7)—Cu—N(3)	92.4 (2)
O(7)—Cu—N(4)	89.0 (2)	N(1)—Cu—N(2)	83.5 (3)
N(1)—Cu—N(3)	166.8 (3)	N(1)—Cu—N(4)	96.9 (2)
N(2)—Cu—N(3)	84.8 (2)	N(2)—Cu—N(4)	176.3 (2)
N(3)—Cu—N(4)	95.2 (2)	Cu—N(1)—C(1)	111.2 (5)
Cu—N(2)—C(2)	111.5 (5)	Cu—N(2)—C(3)	110.0 (5)
C(2)—N(2)—C(3)	125.4 (6)	Cu—N(3)—C(4)	109.5 (4)
Cu—N(4)—C(5)	121.0 (4)	Cu—N(4)—C(6) ⁱ	122.1 (4)
C(5)—N(4)—C(6) ⁱ	116.9 (5)	N(1)—C(1)—C(2)	111.3 (6)
N(2)—C(2)—C(1)	111.3 (7)	N(2)—C(3)—C(4)	112.3 (6)
N(3)—C(4)—C(3)	112.3 (6)	N(4)—C(5)—C(6)	122.6 (5)
C(5)—C(6)—N(4) ⁱ	120.5 (5)	O(1)—Cl(1)—O(2)	108.1 (3)
O(1)—Cl(1)—O(3)	107.3 (3)	O(1)—Cl(1)—O(4)	109.6 (3)
O(2)—Cl(1)—O(3)	111.7 (3)	O(2)—Cl(1)—O(4)	111.0 (3)
O(3)—Cl(1)—O(4)	109.0 (4)	O(5)—Cl(2)—O(6)	109.7 (4)
O(5)—Cl(2)—O(7)	109.3 (4)	O(5)—Cl(2)—O(8)	109.1 (4)
O(6)—Cl(2)—O(7)	111.2 (4)	O(6)—Cl(2)—O(8)	111.4 (4)
O(7)—Cl(2)—O(8)	105.9 (4)		

Symmetry code: (i) 1 - *x*, -*y*, 1 - *z*.

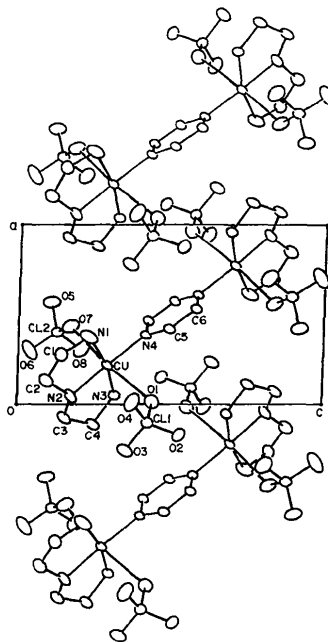


Fig. 1. Crystal structure viewed along the *b** axis with the atomic numbering system; H atoms are omitted for clarity.

deeply grateful to Professor N. Kasai and his co-workers in Osaka University for providing the computer program library.

References

- ASHIDA, T. (1979). *HBL5-V. The Universal Crystallographic Computing System—Osaka*. The Computation Center, Osaka Univ., Japan.
- BELFORD, R. C. E., FENTON, D. E. & TRUTER, M. R. (1974). *J. Chem. Soc. Dalton Trans.* pp. 17–24.
- CHEN, C. (1989). Master Degree Thesis, Zhejiang Univ., People's Republic of China.
- CORONADO, E., DRILLON, M. & BELTRAN, D. (1984). *Inorg. Chim. Acta*, **82**, 13–17.
- DARRIET, J., HADDAD, M. S., DUESLER, E. N. & HENDRICKSON, D. N. (1979). *Inorg. Chem.* **18**, 2679–2682.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- HUANG, L. (1989). Master Degree Thesis, Zhejiang Univ., People's Republic of China.
- MATSUMOTO, K., OOI, S., NAKAO, Y., MORI, W. & NAKAHARA, A. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2045–2048.
- MELANSON, R. & ROCHON, F. D. (1978). *Acta Cryst.* **B34**, 3594–3598.
- RICHARDSON, H. W. & HATFIELD, W. E. (1975). *J. Am. Chem. Soc.* **98**, 835–839.
- SANTORO, A., MIGHELLI, A. D. & REIMANN, W. (1970). *Acta Cryst.* **B26**, 979–984.
- WHEATLEY, P. J. (1957). *Acta Cryst.* **10**, 182–187.
- XU, D., CHEN, C., XU, Y. & ZHOU, K. (1987). *J. Struct. Chem.* **6**(1), 39–42.

Acta Cryst. (1991). **C47**, 75–78

Structure of Copper(II) Terephthalate Trihydrate

BY SÉNIDA CUETO

Technisch-Chemisches Laboratorium, ETH-Z, CH-8092 Zürich, Switzerland

VOLKER GRAMLICH AND WALTER PETER

Institut für Kristallographie, ETH-Z, CH-8092 Zürich, Switzerland

FRANZ S. RYS

*Technisch-Chemisches Laboratorium, ETH-Z, CH-8092 Zürich, Switzerland and
ERCOFTAC, EPF-L, CH-1015 Lausanne, Switzerland*

AND PAUL RYS

Technisch-Chemisches Laboratorium, ETH-Z, CH-8092 Zürich, Switzerland

(Received 5 January 1990; accepted 31 May 1990)

Abstract. $\text{Cu}[\text{C}_6\text{H}_4(\text{COO})_2]\cdot 3\text{H}_2\text{O}$, $M_r = 281.71$, orthorhombic, $Pbcn$, $a = 6.869$ (3), $b = 22.985$ (11), $c = 6.298$ (3) Å, $V = 994.4$ (14) Å³, $Z = 4$, $D_x = 1.88$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.22$ mm⁻¹, $F(000) = 572$, room temperature, $R = 0.036$ for 812 unique reflections having $|F| > 4\sigma(|F|)$. The Cu atoms are coordinated by two carboxylate O atoms and four water-molecule O atoms in a significantly distorted octahedral arrangement. There are three different coordination Cu—O distances: two of 1.925 (2) Å with the two carboxylate O atoms, two of 1.981 (2) Å and the largest two of 2.479 (2) Å. The octahedra share common edges with octahedra of two neighbouring Cu atoms to form zigzag chains in the c direction. The chains are linked by hydrogen bonds and in addition the resulting layers are held together *via* hydrogen bridges building a three-dimensional network.

Introduction. In the search for new metal–aromatic compounds with a tetra- or hexacoordinated copper(II) atom, copper(II) terephthalate trihydrate (CuTT) was synthesized by polycondensation and obtained in single-crystalline form. The X-ray structure analysis revealed a regularly crystallized structure characterized by zigzag-like polymer chains described below. As expected, the compound is highly insulating in the range between room and liquid-nitrogen temperature, thus showing neither intrinsic conduction nor significant charge-carrier concentration. Previous reports on structures of copper carboxylates are known where Cu atoms are joined *via* four carboxylate groups forming dimers, like copper acetate tetrahydrate with a Cu—Cu distance of less than 3 Å (van Niekerk & Shoening, 1953), or copper arylcarboxylates forming polymer networks with Cu—Cu distances larger than 3 Å, like copper ben-