1884 reflections
88 parameters
Only H-atom U's refined
$w = 1.1433/\sigma^2(F)$

Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) with e.s.d.'s (Schomaker & Marsh, 1983) in parentheses*

$$B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33}).$$

	x	y	z	B_{eq}
Pt	0.15462 (2)	0.25	0.65042 (3)	1.426 (5)
Ir	0.10152 (2)	0.25	0.14085 (3)	1.078 (4)
Cl1	0.15298 (9)	−0.0330 (2)	0.6463 (3)	3.35 (4)
Cl2	0.0243 (1)	0.25	0.5671 (3)	1.99 (3)
Cl3	0.2844 (1)	0.25	0.7451 (3)	2.79 (5)
Cl4	−0.0105 (1)	0.25	−0.0140 (3)	2.13 (3)
N1	0.1964 (5)	0.25	0.2829 (9)	2.67 (2)
N2	0.1562 (3)	0.0671 (7)	0.0173 (6)	2.05 (8)
N3	0.0464 (3)	0.0665 (7)	0.2601 (6)	2.18 (9)

Table 2. *Geometric parameters (Å, °)*

Pt—Cl1	2.296 (2)	Ir—N1	2.067 (8)
Pt—Cl2	2.298 (2)	Ir—N2	2.094 (6)
Pt—Cl3	2.328 (3)	Ir—N3	2.080 (6)
Ir—Cl4	2.364 (2)		
N2—Ir—Cl4	89.6 (2)	N1—Ir—N3	88.9 (2)
N3—Ir—Cl4	89.5 (2)	Cl1—Pt—Cl2	89.03 (4)
N2—Ir—N3	89.2 (2)	Cl1—Pt—Cl3	91.00 (4)
N1—Ir—Cl4	177.7 (2)	Cl2—Pt—Cl3	177.45 (9)
N1—Ir—N2	92.0 (2)		

Program used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program used to refine structure: *SHELX*76 (Sheldrick, 1976). Program used for complete geometry: *PARST* (Nardelli, 1983). Chemical analysis: Ir/Pt = 1 (quantitative electron microprobe). H atoms refined isotropically (common B_{iso}) with constrained geometry [*DFIX* parameter in *SHELX*76: $d(\text{N—H}) = 1.01$ Å]. Considering $\Delta\rho_{min}$ and $\Delta\rho_{max}$, no attempt was undertaken to refine the positional parameters of each H atom.

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Structure of (Nitrato-O)(nitrato-O,O')-tris(pyridazine-N)copper(II)

Tom Otieno, Steven J. Rettig, Robert C. Thompson* and James Trotter

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1

Abstract

The coordination polyhedron about the copper(II) atom in $Cu(pdz)_3(NO_3)_2$, where pdz is pyridazine, is a distorted octahedron consisting of three N atoms from the pyridazine ligands, one O atom from the monodentate nitrate group and two O atoms from the unsymmetrically bidentate nitrate group.

Comment

Studies on pyridine complexes of divalent metal nitrates having the general formula $M(py)_3(NO_3)_2$, where M is Co, Ni, Cu, Zn or Cd, have been reported by several workers (Choca, Ferraro & Nakamoto, 1972; Cameron, Taylor & Nuttall, 1971; Ouellette & Haendler, 1969; Biagetti & Haendler, 1966; Frank & Rogers, 1966; Rosenthal & Drago, 1965). With the exception of the zinc complex (Cameron, Taylor & Nuttall, 1971), however, their molecular geometries have not been determined unequivocally. Indeed, some workers have even expressed doubt as to the actual existence of $Cu(py)_3(NO_3)_2$ (Biagetti, Bottjer & Haendler, 1966). The lack of definitive structural assignment for these compounds arises from the ability of the nitrate group to function as an ionic species (Procter & Stephens, 1969), a monodentate ligand (Cameron, Taylor & Nuttall, 1972; Scavnicar & Matkovic, 1969), a chelating ligand (Santoro, Mighell & Reimann, 1970; Thompson, Lee & Gabe, 1988) or a bridging ligand (Thompson, Lee & Gabe, 1988; Wallwork & Addison, 1965). In the latter case, more than one bridging mode is possible. Furthermore,

more than one type of the above mentioned nitrate groups may exist in the same compound (Thompson, Lee & Gabe, 1988). Thus, the central metal atom in mononuclear transition-metal complexes of the type $M(py)_3(NO_3)_2$ may, in principle, have coordination numbers ranging from three, in which both the nitrate groups are ionic, to seven, in which both are bidentate chelating. A seven-coordinate structure has in fact been observed in $Zn(py)_3(NO_3)_2$ by single-crystal X-ray diffraction (Cameron, Taylor & Nuttall, 1971). A similar structure has been proposed for $Cu(py)_3(NO_3)_2$ and $Co(py)_3(NO_3)_2$ on the basis of their being isomorphous with the zinc compound (Choca, Ferraro & Nakamoto, 1972). However, spectroscopic and magnetic properties of $Co(py)_3(NO_3)_2$ and $Ni(py)_3(NO_3)_2$ have been interpreted by other workers as suggesting a six-coordinate structure comprising both monodentate and bidentate nitrate groups (Biagetti & Haendler, 1966; Rosenthal & Drago, 1965). Unequivocal structures for this type of complex can be determined only by single-crystal X-ray diffraction. We report here the crystal structure of the analogous pyridazine (1,2-diazine) complex, $Cu(pdz)_3(NO_3)_2$.

The structure of $Cu(pdz)_3(NO_3)_2$ with atomic labelling is depicted in Fig. 1. The Cu atom is coordinated by three monodentate pyridazine ligands, one monodentate nitrate group (which is disordered) and one asymmetrically chelating nitrate group, resulting in a distorted octahedral stereochemistry. The geometry about the Cu atom may be described as a $(1 + 4 + 1)$ type, the square plane being defined by the three donor N atoms of the pyridazine ligands and O(4) of the bidentate nitrate group. The Cu—O bond length involving the second O atom of the bidentate nitrate group is 2.624 (3) Å. Although this bond length is considerably longer than the other two Cu—O bond lengths in this compound, it is less than the sum of the van der Waals radii of Cu and O atoms, which is 2.90 Å (Huheey, 1978), indicating that there is significant copper–oxygen interaction. The distortion of the copper(II) chromophore in $Cu(pdz)_3(NO_3)_2$ is also reflected in the significant deviations of the L—Cu—L bond angles (L represents the donor atoms of the pyridazine and nitrate groups) from ideal values. The cis and trans L—Cu—L bond angles lie in the ranges 53–110° and 149–178°, respectively.

The free nitrate ion has a symmetrical planar structure with all O—N—O angles equal to 120° and N—O bond lengths equal to 1.245 (2) Å (Cherin, Hamilton & Post, 1967). In previous studies on a number of copper(II) and nickel(II) complexes containing monodentate nitrate groups (Addison, Logan, Wallwork & Garner, 1971) it was found that the N—O bond involving the coordinated O atom is
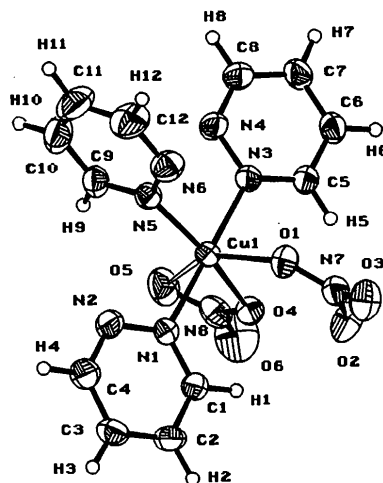

Fig. 1. Structure of $Cu(pdz)_3(NO_3)_2$ with the atom-labelling scheme.

longer (1.26–1.32 Å), and those involving the other two O atoms are shorter (1.21–1.24 Å), than the N—O bonds of the free nitrate ion. It was observed also that the O—N—O bond angle opposite the coordinated O atom is generally greater, and the other two less, than 120°. Similar variations were observed in the N—O bond lengths and O—N—O bond angles of unsymmetrical bidentate nitrate groups. The dimensions of the chelating nitrate group in $Cu(pdz)_3(NO_3)_2$ show the expected trends and are comparable to those listed by Addison, Logan, Wallwork & Garner (1971) for this type of nitrate group. For the monodentate nitrate group in $Cu(pdz)_3(NO_3)_2$, however, all the three N—O bond lengths are equal, within experimental error, to the free ion value. In addition, only one of the O—N—O bond angles involving this nitrate group is greater than 120°; the other two are equal to this value within experimental error. These unexpected dimensions may be attributed to the fact that the monodentate nitrate group in $Cu(pdz)_3(NO_3)_2$ is disordered.

All the pyridazine rings in $Cu(pdz)_3(NO_3)_2$ are planar within experimental error and their bonding parameters are comparable to published data (Cotton & Hanson, 1976).

Experimental

Crystal data

[Cu(NO₃)₂(C₄H₄N₂)₃]
M_r = 427.82
Monoclinic
$P2_1/n$
a = 8.390 (1) Å
b = 15.585 (1) Å
c = 13.058 (1) Å
β = 92.22 (1)°

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 75.0– 106.4°
μ = 2.237 mm^{-1}
T = 294 K
Prism

$V = 1706.2 \ (3) \ \text{Å}^3$

$Z = 4$

$D_x = 1.665 \ \text{Mg m}^{-3}$

0.40 × 0.40 × 0.35 mm

Blue

Data collection

Rigaku AFC-6S diffractometer

ω-2θ scans

Absorption correction:
empirical, ψ scans
$T_{min} = 0.81$, $T_{max} = 1.00$

4045 measured reflections

3640 independent reflections

2772 observed reflections
$[I > 3\sigma(I)]$

$R_{int} = 0.022$

$\theta_{max} = 155°$

$h = 0 \rightarrow 10$

$k = 0 \rightarrow 19$

$l = -16 \rightarrow 16$

3 standard reflections
monitored every 200
reflections
intensity variation: 21%
linear decay

Refinement

Refinement on F

$R = 0.036$

$wR = 0.038$

$S = 2.83$

2772 reflections

271 parameters

$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = 0.10$

$\Delta\rho_{max} = 0.29 \ \text{e Å}^{-3}$

$\Delta\rho_{min} = -0.42 \ \text{e Å}^{-3}$

Extinction correction:
secondary

Extinction coefficient:
$1.49 \ (15) \times 10^{-5}$

Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu(1)	0.33519 (4)	0.20556 (2)	0.54427 (3)	3.85 (2)
O(1)	0.2189 (2)	0.15704 (13)	0.3966 (2)	5.0 (1)
O(2)*	0.2241 (13)	0.0243 (7)	0.4291 (8)	6.9 (5)
O(2A)*	0.1314 (1)	0.0327 (7)	0.4328 (9)	6.9 (5)
O(2B)*	0.300 (2)	0.0257 (12)	0.378 (2)	7.0 (4)
O(3)*	0.156 (2)	0.0668 (13)	0.2788 (12)	6.6 (6)
O(3A)*	0.108 (3)	0.069 (2)	0.288 (2)	6.8 (8)
O(3B)*	0.279 (4)	0.039 (2)	0.305 (3)	6.5 (6)
O(4)	0.3683 (2)	0.08943 (12)	0.6080 (2)	4.6 (1)
O(5)	0.4692 (3)	0.1726 (2)	0.7249 (2)	6.9 (1)
O(6)	0.4368 (4)	0.0383 (2)	0.7553 (2)	11.0 (2)
N(1)	0.5493 (2)	0.19728 (14)	0.4785 (2)	3.9 (1)
N(2)	0.6313 (3)	0.2696 (2)	0.4640 (2)	5.4 (1)
N(3)	0.1228 (3)	0.21322 (14)	0.6149 (2)	4.1 (1)
N(4)	0.0826 (3)	0.2904 (2)	0.6514 (2)	5.1 (1)
N(5)	0.3251 (3)	0.3315 (2)	0.5226 (2)	4.1 (1)
N(6)	0.2375 (4)	0.3611 (2)	0.4440 (2)	6.1 (1)
N(7)	0.1866 (3)	0.0826 (2)	0.3685 (2)	4.6 (1)
N(8)	0.4280 (3)	0.0999 (2)	0.6992 (2)	5.7 (1)
C(1)	0.6034 (3)	0.1238 (2)	0.4454 (2)	4.6 (1)
C(2)	0.7449 (4)	0.1164 (2)	0.3945 (3)	5.4 (2)
C(3)	0.8292 (4)	0.1887 (2)	0.3786 (3)	5.2 (2)
C(4)	0.7662 (4)	0.2633 (2)	0.4152 (3)	5.9 (2)
C(5)	0.0283 (3)	0.1468 (2)	0.6253 (2)	4.6 (1)
C(6)	−0.1155 (4)	0.1530 (2)	0.6740 (3)	5.4 (2)
C(7)	−0.1580 (4)	0.2299 (2)	0.7113 (3)	5.5 (2)
C(8)	−0.0533 (4)	0.2970 (2)	0.6976 (3)	5.5 (2)
C(9)	0.3869 (4)	0.3819 (2)	0.5940 (2)	4.9 (1)
C(10)	0.3615 (5)	0.4682 (3)	0.5898 (4)	7.5 (2)
C(11)	0.2746 (6)	0.5014 (2)	0.5109 (4)	8.6 (3)
C(12)	0.2152 (5)	0.4466 (3)	0.4379 (3)	7.9 (2)

* Occupancy factors: O(2) 0.41, O(2A) 0.41, O(2B) 0.18, O(3) 0.53, O(3A) 0.37, O(3B) 0.10.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Polyhedron around the Cu atom

Cu(1)—O(1)	2.258 (2)	Cu(1)—N(1)	2.025 (2)
Cu(1)—O(4)	2.007 (2)	Cu(1)—N(3)	2.042 (2)
Cu(1)—O(5)	2.624 (3)	Cu(1)—N(5)	1.984 (2)
O(1)—Cu(1)—O(5)	149.10 (9)	O(4)—Cu(1)—N(1)	90.42 (8)
O(4)—Cu(1)—N(5)	162.83 (9)	O(4)—Cu(1)—N(3)	88.55 (8)
N(1)—Cu(1)—N(3)	178.2 (1)	O(5)—Cu(1)—N(1)	90.70 (8)
O(1)—Cu(1)—O(4)	95.78 (8)	O(5)—Cu(1)—N(3)	87.52 (8)
O(1)—Cu(1)—N(1)	88.71 (8)	O(5)—Cu(1)—N(5)	109.6 (1)
O(1)—Cu(1)—N(3)	92.84 (8)	N(1)—Cu(1)—N(5)	92.08 (9)
O(1)—Cu(1)—N(5)	101.25 (9)	N(3)—Cu(1)—N(5)	88.48 (9)
O(4)—Cu(1)—O(5)	53.33 (8)		

Bidentate NO₃		Monodentate NO₃	
O(4)*—N(8)	1.283 (3)	O(1)*—N(7)	1.243 (3)
O(5)*—N(8)	1.228 (4)	O(2)—N(7)	1.24 (1)
O(6)—N(8)	1.208 (4)	O(3)—N(7)	1.22 (2)
O(4)—N(8)—O(5)	117.8 (3)	O(1)—N(7)—O(2)	116.8 (5)
O(4)—N(8)—O(6)	118.4 (3)	O(1)—N(7)—O(3)	121 (1)
O(5)—N(8)—O(6)	123.8 (3)	O(2)—N(7)—O(3)	120 (1)

Pyridazine			
N(1)—N(2)	1.338 (3)	C(1)—C(2)	1.388 (4)
N(1)—C(1)	1.311 (3)	C(2)—C(3)	1.351 (4)
N(2)—C(4)	1.324 (4)	C(3)—C(4)	1.370 (4)
N(1)—C(1)—C(2)	123.0 (3)	N(2)—C(4)—C(3)	125.4 (3)
C(1)—C(2)—C(3)	117.8 (3)	N(2)—N(1)—C(1)	120.1 (2)
C(2)—C(3)—C(4)	116.3 (3)	N(1)—N(2)—C(4)	117.4 (2)

* Coordinated to copper.

The uncoordinated O atoms of the monodentate nitrate group were severely disordered; each was refined as threefold disordered. The population parameters could not be refined along with the thermal parameters but were adjusted as the refinement progressed to give approximately equal thermal parameters. All non-H atoms except the low-occupancy O atoms O(2B) and O(3B) were refined with anisotropic thermal parameters. H atoms were fixed in calculated positions with C—H = 0.98 Å and $B(H) = 1.2 \times B$(bonded atom). Blue crystals of $Cu(NO_3)_2(pdz)_3$ were obtained by keeping an ethanolic solution containing $Cu(NO_3)_2.3H_2O$ and pyridazine in approximate 1:2.7 mol ratio in a freezer (268 K) for a few days. The crystals were dried in a desiccator over drierite. Analysis: calculated for $C_{12}H_{12}Cu_8O_6$ C 33.69, H 2.83, N 26.19; found C 33.89, H 2.93, N 26.16.

Computer programs used include *TEXSAN* (Molecular Structure Corporation, 1985).

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Structure of a Binuclear Copper(II) Complex with both μ-Alkoxo and μ-Formato Bridges, [Cu2(C17H15N2O3)(HCOO)]

Takashi Kawata and Shigeru Ohba*

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223, Japan

Yuzo Nishida

Department of Chemistry, Faculty of Science, Yamagata University, Kojirakawa 1-4-12, Yamagata 990, Japan

Tadashi Tokii

Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan

Abstract

The crystal structure of a binuclear copper(II) complex, μ-formato-1κO:2$\kappa O'$-μ-2,2'-[1,3-(2-hydroxypropanediyl-1:2$\kappa^2 O$)bis(nitrilomethylidyne)]di-

phenolato(3 −)-1$\kappa^2 N,O$:2$\kappa^2 N',O'$-dicopper(II), [Cu2-(L-sal)(HCOO)], H3(L-sal) = N,N'-bis(salicylidene)-1,3-diamino-2-propanol, was determined by X-ray diffraction. The title compound is ferromagnetic as a result of the roof-shaped structure of the Cu2O(OCO) core ($-2J = -94$ cm^{-1}). The Cu···Cu distance is 3.260 (1) Å and the Cu—O—Cu bond angle is 115.2 (2)°.

Comment

The structures and magnetism of binuclear Cu^{II} complexes with both μ-alkoxo and μ-carboxylato bridges have been studied to reveal the orbital counter–complementary effect (Nishida & Kida, 1986; Kawata *et al.,* 1992). These Cu^{II} complexes are usually antiferromagnetic with the Cu—O—Cu angle greater than 130°. However, the antiferromagnetic interaction is depressed by the so-called roof-shaped distortion, which is measured by the dihedral angle between the two Cu coordination planes, τ (Charlot *et al.,* 1979; Charlot, Kahn, Jeannin & Jeannin, 1980). The $-2J$ value of the title complex is -94 cm^{-1} with $\tau = 51.4$ (2)°. The roof-shaped distortion is determined by the conformation of the five-membered chelate rings sharing an alkoxo group. When the combination of the enantiomeric conformation of the rings is $\delta\lambda$, the binuclear complex takes a flat form with a small τ angle (δ stands for a right-handed helical relation between the C—C bond axis and the line which connects the alkoxo O and secondary amine N atoms, λ for a left-handed helix). In Fig. 1 the combination is $\lambda\lambda$. It seems that the roof-shaped distortion is the result of the crystal packing force. Planar and roof-shaped structures of [Cu2(L-ac)(CH3COO)] (the ligand H3L-ac is a 1:2 Schiff base derived from 1,3-diaminopropan-2-ol and acetylacetone) are observed in hydrated (Nishida & Kida, 1986) and anhydrous crystals (Fallon, Murray, Mazurek & O'Connor, 1985), respectively, and the magnetic and structural features have been compared (Mazurek *et al.,* 1985). Crystal structure analysis of [Cu2(L-ac)(HCOO)] was also attempted in this study, but failed owing to the poor quality of
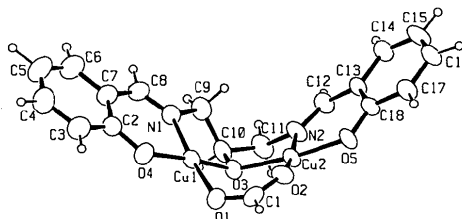

Fig. 1. *ORTEP*II drawing (Johnson, 1976) with the thermal ellipsoids scaled at the 50% probability level. The H atoms are represented by circles of radius 0.08 Å.