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Ring Cleavage of Imidazole to Oxamide by Reaction with Dioxygen in the Presence of a Cu^I-Amine Complex. Structure of μ -Oxamidato-bis[(1,4,7-trimethyl-1,4,7-triazacyclononane)copper(II)] Triiodide Iodide

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Abstract

An oxamidato group in a *trans* conformation bridges two trimethyltriazacyclononane moieties. Each Cu atom is fivefold coordinated by four N and one O atoms. The N and O atoms of the oxamidato ligand are disordered over two sites giving two different *trans* conformations. The cations are packed along [100] with iodide and triiodide anions between them. The I₃⁻ ions are disordered and have asymmetric I—I bond lengths.

Comment

This work stems from our interest in the polynuclear complexes of copper(II) with multi-atom bridging ligands (Chaudhuri *et al.*, 1992; Chaudhuri & Oder, 1990). In this paper we present the isolation, although in very low yield, and characterization of an oxamidato-bridged binuclear copper(II) complex, which results from the oxidation of an imidazolate ring, presumably by dioxygen in the presence of a Cu^I-amine unit. Activation of oxygen by Cu^I complexes is of particular interest as a model for a number of copper proteins, such as haemocyanin, tyrosinase and ascorbate oxidase. Imidazole itself is reasonably resistant to oxidation (Katritzky & Rees, 1984), being attacked only by strong oxidizing agents such as MnO₄⁻ and various peracids. These reactions usually result in ring degradation, leading to ammonia or ammonia derivatives and aliphatic carbonyl compounds, while hydrogen peroxide has been reported to oxidize some imidazoles to oxamide.

The structure consists of dinuclear [(LCu)₂(oxam)]²⁺ cations (*L* = trimethyltriazacyclononane and oxam = oxamidato), and both I⁻ and I₃⁻ anions. The geometrical centre of the oxamide which bridges the two Cu_L moieties is situated on a crystallographic inversion centre. The Cu atoms reach distorted square-pyramidal configurations with three N and one O ligand atoms in the equatorial plane with bond distances of Cu—N(*L*) = 2.039 (9) and 2.039 (8) Å, and Cu—N,O(oxam) = 1.993 (7) and 1.998 (6) Å. A fourth N atom from the *L* ligand completes the coordination in the axial position with a distinctly longer Cu—N(1) bond length of 2.255 (10) Å. This geometry has been observed previously in other square-pyramidal *L* complexes of copper(II) (Chaudhuri *et al.*, 1991, 1992). The N₃O coordination plane around the copper and the plane of the oxamidato group form a dihedral angle of 8.6°. The distance between the two copper centres is 5.229 (2) Å which is in the range of other reported dicopper oxamidato structures: 5.189 (2) (Bencini, Di Vaira, Fabretti, Gatteschi & Zanchini, 1984), 5.192 (2) (Okawa, Matsumoto, Koikawa, Takeda & Kida, 1990) and 5.290 (1) Å (Lloret, Julve, Faus, Journaux, Philoche-Levisalles & Jeannin, 1989). In these structures, the copper has four, five and sixfold coordination.

During refinement the anisotropic displacement parameters of the oxamidato N and O atoms indicated positional disorder which was successfully treated by a split model with half occupation of positions X1 and X2 with both N and O atoms. This leads to two indistinguishable *trans* conformations of the oxamide. The disorder is also reflected by the equal Cu—X (*X* = N, O) bond lengths of 1.993 (7) and 1.998 (6) Å. In the structures of Bencini *et al.* (1984) and Lloret *et al.* (1989), with unambiguous N and O positions, the Cu—N bonds are clearly shorter [1.899 (6) and 1.924 (3) Å, respectively] than the Cu—O

bonds [1.988 (5) and 2.043 (2) Å]. A similar disorder problem concerning the oxamidato group seems to occur for the structure of the $[\text{Cu}_2(\text{bpy})_2(\text{oxam})]^{2+}$ cation (bpy = 2,2'-bipyridine) reported by Okawa *et al.* (1990), as may be deduced from the unusually large and small vibrational ellipsoids of the corresponding O and N atoms, and the equal Cu—N,O bonds.

The I_3^- anion has a common configuration with an angle of $174.6 (1)^\circ$ which is close to linear. In the crystal, these anions are packed with their axes along [010]. As the shortest non-bonding $\text{I} \cdots \text{I}$ contacts are 5.080 Å and as hydrogen-iodine interactions (> 3.2 Å) are of negligible influence, the I_3^- groups may be regarded as isolated anions. Nevertheless, the group is asymmetric with two I—I distances [2.895 (3) and 2.942 (3) Å] different from the value of 2.920 Å for a 'free' triiodide anion (Runsink, Swen-Walstra & Migchelsen, 1972). However, the large anisotropic displacement parameters indicate that the atomic positions of the triiodide suffer from disorder and so the derived bonding parameters are less meaningful. Probably at least two different orientations of the I_3^- near the special site positions have to be considered and this gives rise to superposition. Attempts to resolve this problem by a split model were not successful.

The reported cation, synthesized by a different route, and its magnetic properties have been described earlier (Chaudhuri & Oder, 1990).

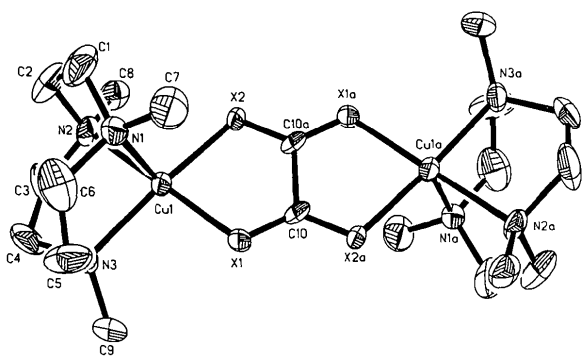


Fig. 1. Molecular structure of the cation.

Experimental

Crystal data

$[\text{Cu}_2(\text{C}_2\text{H}_2\text{N}_2\text{O}_2) \cdot (\text{C}_9\text{H}_{21}\text{N}_3)_2][\text{I}_3][\text{I}]$

$M_r = 1063.3$

Orthorhombic

Pbcm

$a = 7.851 (2) \text{ \AA}$

$b = 15.851 (3) \text{ \AA}$

$c = 26.854 (3) \text{ \AA}$

$V = 3341.9 (11) \text{ \AA}^3$

$Z = 4$

$D_x = 2.117 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 33 reflections

$\theta = 6-17^\circ$

$\mu = 4.96 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Plate

$0.19 \times 0.15 \times 0.09 \text{ mm}$

Brown

Data collection

Siemens *R3m/V* diffractometer

ω - 2θ scans

Absorption correction:

empirical via ψ -scans

$T_{\min} = 0.77$, $T_{\max} = 1.00$

5381 measured reflections

3942 independent reflections

2198 observed reflections

$[F > 4\sigma(F)]$

Refinement

Refinement on F

Final $R = 0.060$

$wR = 0.045$

$S = 1.622$

2198 reflections

169 parameters

H-atom parameters not refined, fixed at idealized positions

$R_{\text{int}} = 0.030$

$\theta_{\text{max}} = 27.5^\circ$

$h = -7 \rightarrow 10$

$k = 0 \rightarrow 20$

$l = 0 \rightarrow 34$

3 standard reflections

monitored every 400

reflections

intensity variation: none

Calculated weights

$w = 1/[\sigma^2(F) + 0.0001F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 1.3 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -1.8 \text{ e \AA}^{-3}$

Atomic scattering factors

from *SHELXTL-Plus*

(Sheldrick, 1990)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
I1	0.4499 (1)	0.2500	0.0000	0.052 (1)
I2	0.3005 (3)	1.1042 (2)	0.2500	0.161 (2)
I3	0.1206 (2)	0.7473 (2)	0.2500	0.106 (2)
I4	0.1927 (2)	0.9264 (1)	0.2500	0.063 (1)
Cu1	0.3197 (2)	0.4265 (1)	0.0694 (1)	0.026 (1)
N1	0.2266 (11)	0.5327 (6)	0.1182 (4)	0.031 (7)
N2	0.0779 (10)	0.3820 (6)	0.0783 (3)	0.029 (6)
N3	0.3718 (11)	0.3696 (6)	0.1358 (3)	0.031 (6)
X1 †	0.5584 (8)	0.4661 (4)	0.0586 (3)	0.027 (5)
X2 †	0.2837 (7)	0.4792 (4)	0.0029 (3)	0.024 (4)
C1	0.0391 (17)	0.5285 (9)	0.1087 (6)	0.062 (12)
C2	-0.0291 (14)	0.4431 (9)	0.1049 (5)	0.049 (10)
C3	0.1046 (16)	0.3043 (9)	0.1084 (5)	0.061 (10)
C4	0.2253 (15)	0.3162 (9)	0.1494 (6)	0.066 (11)
C5	0.3949 (15)	0.4406 (10)	0.1718 (5)	0.059 (10)
C6	0.2712 (18)	0.5066 (9)	0.1695 (5)	0.064 (11)
C7	0.2942 (15)	0.6152 (7)	0.1057 (5)	0.052 (10)
C8	-0.0052 (13)	0.3592 (7)	0.0305 (4)	0.038 (8)
C9	0.5288 (14)	0.3174 (8)	0.1352 (4)	0.047 (9)
C10	0.5798 (12)	0.4961 (7)	0.0162 (4)	0.022 (7)

† X1 and X2 are the positions of disordered oxamide N and O atoms.

Table 2. Geometric parameters (\AA , $^\circ$)

I2—I4	2.942 (3)	Cu1—X1	1.998 (6)
I3—I4	2.895 (3)	Cu1—X2	1.993 (7)
Cu1—N1	2.255 (10)	X1—C10	1.245 (13)
Cu1—N2	2.039 (8)	X2—C10a	1.250 (12)
Cu1—N3	2.039 (9)	C10—C10a	1.531 (14)
I2—I4—I3	174.6 (1)	N2—Cu1—X2	96.8 (3)
N1—Cu1—N2	83.6 (4)	N3—Cu1—X2	176.2 (3)
N1—Cu1—N3	83.5 (4)	X1—Cu1—X2	82.6 (3)
N2—Cu1—N3	86.1 (4)	Cu1—X1—C10	112.3 (6)
N1—Cu1—X1	98.9 (3)	Cu1—X2—C10a	112.2 (6)
N2—Cu1—X1	177.5 (3)	X1—C10—X2a	127.6 (9)
N3—Cu1—X1	94.5 (3)	X1—C10—C10a	116.1 (11)
N1—Cu1—X2	99.3 (3)	X2a—C10—C10a	116.3 (12)

A suspension of CuI and imidazole (1:1) in methanol was refluxed under argon for 15 min. 1 equivalent of 1,4,7-trimethyl-1,4,7-triazacyclononane was then added under argon to the nearly clear solution and heating continued for another 30 min.

The solution was then exposed to air and the resulting brown precipitate filtered off. On leaving the green mother liquor at ambient temperature for 3 d brown crystals (*ca* 5%) were obtained. Structure solution, refinement and other calculations: *SHELXTL-Plus* (Sheldrick, 1990). Other programs used: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71190 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1044]

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2-[2,2-Bis(diphenylphosphanyl)ethyl-sulfanyl]phenylamine (NSPP), a New Hetero-Bifunctional Ligand and its PdCl₂ Complex †

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Abstract

The new ligand NSPP consists of a bis(diphenylphosphanyl)ethane part with coordination ability by the

† {2-[2,2-Bis(diphenylphosphino)ethylthio]phenylamine-*P,P*}dichloropalladium(II) dichloromethane solvate.

two P donor atoms, and of a second part, the 2-aminobenzenethio unit, which offers the two donor atoms N and S for coordination with metal atoms. Both P atoms are attached to the same C atom of the central ethane skeleton. The other C atom is linked to the S atom of the thio group. PdCl₂ is coordinated *via* the two P donors to give the complex [Pd(NSPP)Cl₂].

Comment

The syntheses of hetero-bifunctional ligands for the coordination of different metals led to the new ligand NSPP with four donor atoms. The ligand was prepared by reaction of 2-aminobenzenethiol and 1,1-bis(diphenylphosphanyl)ethane. Further reaction of the isolated ligand with [M(bn)₂Cl₂] (*M* = Pd, Pt; bn = benzonitrile) gave the monometal complexes [M(NSPP)Cl₂]. The detailed synthetic work has been reported elsewhere (Haupt, Kleineberg & Flörke, 1992).

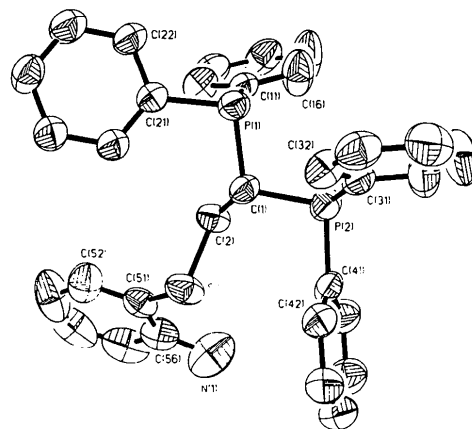


Fig. 1. Molecular structure of the ligand NSPP.

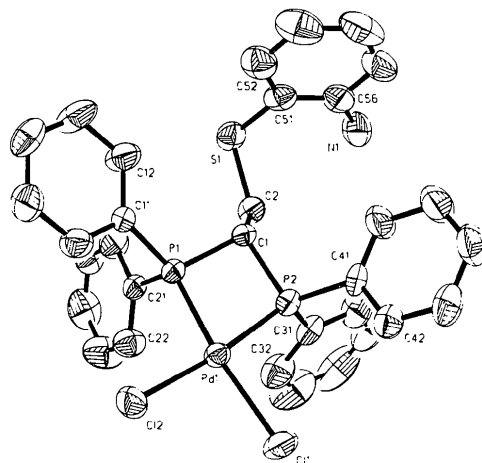


Fig. 2. Molecular structure of the complex [Pd(NSPP)Cl₂].