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The unexpected fixation of CO_2 employing a $Cu^IBr(bpy)_2$ complex

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The attempt to crystallize $Cu^IBr(bpy)_2$, where bpy is bipyridine, from an acetonitrile solution in a glove-box led unexpectedly to a dimeric carbonato-bridged Cu^{II} precipitate, *viz.* μ-carbonato-bis[bis(bipyridine)copper(II)] dibromide diacetonitrile monohydrate, $[Cu_2(C_{10}H_8N_2)_4(CO_3)]Br_2\cdot 2CH_3CN\cdot H_2O$. The μ_2-carbonato ligand is probably the result of an oxidation of traces of CO_2 by Cu^I. The resulting structure contains two square-pyramidally coordinated Cu^{II} atoms bridged by a CO_3^{2-} unit.

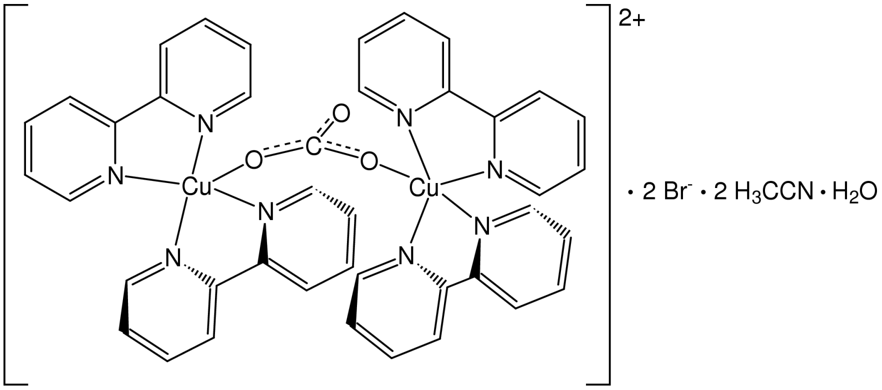
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.012 Å
R factor = 0.047
wR factor = 0.110
Data-to-parameter ratio = 8.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The fixation of atmospheric CO_2 by copper complexes is a widely known phenomenon (Van Albada *et al.*, 2000; Sertucha *et al.*, 1999; Escuer *et al.*, 1997; Kitajima *et al.*, 1993). However, it is still not easy to predict whether fixation will occur or not. The crystals studied in this report were obtained from a reaction in an argon-filled glove-box where CO_2 should not usually be present. Currently, we do not know the source of the CO_2. Either there were small impurities in the argon atmosphere or the chemicals, such as the acetonitrile, were carriers of CO_2 impurities. A possible explanation for the reaction is an oxidation of traces of CO_2 by Cu^I resulting in CO_3^{2-} ions. In addition, H_2O was also found in the structure; therefore, probably traces of $Cu(OH)_2$ were also present in the acetonitrile solution. This has been described already in the literature as promoting CO_2 fixation (Kruger *et al.*, 1995; Kitajima *et al.*, 1991; Menif *et al.*, 1991).



(I)

In the title complex, (I), each copper has a square-pyramidal environment with a basal plane formed by three N atoms of the two chelating bipyridine ligands and the O atom of the bridging carbonato group (Fig. 1). The axial position is

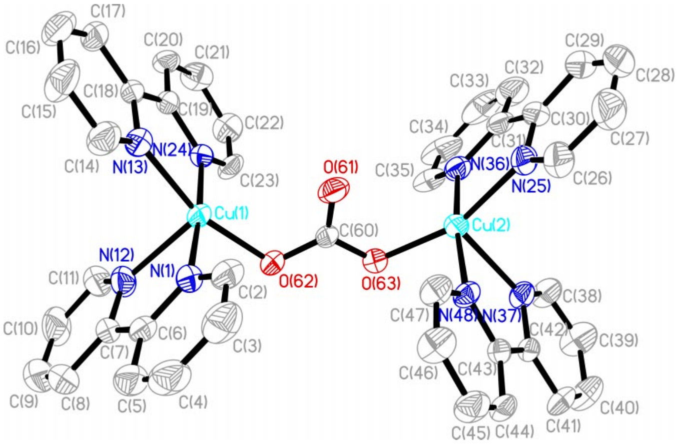


Figure 1
The structure of (I) showing displacement ellipsoids at the 50% probability level. For clarity, H atoms have been omitted. The asymmetric unit also contains (not shown) two molecules of acetonitrile, one molecule of water and two bromide counter-ions.

occupied by the remaining N atom of the bipyridine ligand. The same structural motif was also obtained by the recrystallization of a hexanuclear (μ_2-carbonato)copper(II) bipyridine complex (Kruger *et al.*, 1995). However, in this related compound, the counter-ion is PF_6^- and the structure crystallized in space group $P\overline{1}$. Additionally, the latter structure shows disorder over two sites of the bridging carbonate ligand, which seems to be a reasonably common phenomenon in bridged carbonate structures but was not observed in the current structure (Einstein & Willis, 1981; Palmer & van Eldik, 1983). Cu—O distances [Cu1—O62 1.944 (4) Å, Cu2—O63 1.928 (4) Å] are similar to those in other (μ_2-carbonato)-copper complexes (Kruger *et al.*, 1995). The Cu1···Cu2 separation is 5.339 Å, with the non-coordinated carbonate O atom sitting almost centrally between the two Cu atoms (Cu1—O61 2.808 Å and Cu2—O61 2.779 Å). The μ_2-carbonato ligand shows an internal asymmetry with three different C—O bond lengths [C60—O61 1.245 (8) Å, C60—O62 1.293 (8) Å and C60—O63 1.311 (8) Å]. These bond lengths also reveal the different bonding modes of the carbonato O atoms; two atoms are coordinated to the copper centers, which reduces the electron density on these atoms and leads to a lower C—O bond order with a longer bond, while the third O atom shows obviously no, or only a small, interaction with the copper centers resulting in a shorter C—O bond distance. Bipyridyl–bipyridyl π-stacking interactions in the crystal lattice may be a reason for the crystallization of this compound (Fig. 2).

Experimental

0.57 g (4.0 mmol) CuBr and 1.25 g (8.0 mmol) bipyridine were placed in a 50 ml round-bottomed flask in a glove-box containing an argon atmosphere. 10 ml of acetonitrile were slowly added with stirring. The mixture was heated for a short time until all of the solid completely dissolved. The maroon solution was cooled to room temperature and was allowed to stand for one week. The solvent was evaporated and green crystals were isolated.

Crystal data

$[Cu_2(C_{10}H_8N_2)_4(CO_3)]Br_2$·-
2CH_3CN·H_2O
M_r = 1071.77
Monoclinic, $P2_1/c$
a = 11.0977 (2) Å
b = 23.7744 (2) Å
c = 17.1024 (1) Å
β = 94.347 (1)°
V = 4499.34 (9) Å^3
Z = 4

D_x = 1.579 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5127 reflections
θ = 2.3–24.3°
μ = 2.78 mm^{-1}
T = 293 (2) K
Irregular, green
0.16 × 0.14 × 0.14 mm

Data collection

Siemens SMART diffractometer with CCD area detector
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.665, T_{max} = 0.697
10 354 measured reflections
4681 independent reflections

4013 reflections with $I > 2\sigma(I)$
R_{int} = 0.149
θ_{max} = 20.8°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 17$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.110
S = 1.17
4681 reflections
569 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0245P)^2 + 20.6621P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.02 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00015 (6)

Table 1
Selected geometric parameters (Å, °).

Cu1—O62	1.944 (4)	Cu2—O63	1.928 (4)
Cu1—N24	2.011 (5)	Cu2—N36	2.005 (5)
Cu1—N13	2.035 (5)	Cu2—N25	2.036 (6)
Cu1—N1	2.036 (6)	Cu2—N48	2.037 (5)
Cu1—N12	2.191 (6)	Cu2—N37	2.229 (5)
O62—Cu1—N24	92.2 (2)	N36—Cu2—N25	80.6 (2)
O62—Cu1—N13	163.4 (2)	O63—Cu2—N48	90.73 (19)
N24—Cu1—N13	80.5 (2)	N36—Cu2—N48	172.3 (2)
O62—Cu1—N1	92.2 (2)	N25—Cu2—N48	97.7 (2)
N24—Cu1—N1	175.5 (2)	O63—Cu2—N37	101.39 (19)
N13—Cu1—N1	95.3 (2)	N36—Cu2—N37	94.8 (2)
O62—Cu1—N12	98.1 (2)	N25—Cu2—N37	98.7 (2)
N24—Cu1—N12	100.9 (2)	N48—Cu2—N37	78.0 (2)
N13—Cu1—N12	98.0 (2)	O61—C60—O62	122.8 (6)
N1—Cu1—N12	78.1 (2)	O61—C60—O63	122.2 (6)
O63—Cu2—N36	93.4 (2)	O62—C60—O63	115.1 (6)
O63—Cu2—N25	159.4 (2)		

The data set was limited to a resolution of 1.0 Å, since only very weak diffraction was observed at higher angles. H atoms were located by difference Fourier maps and refined with a riding model, with the exception of the H atoms of the water solvate, which were not included.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL*97.

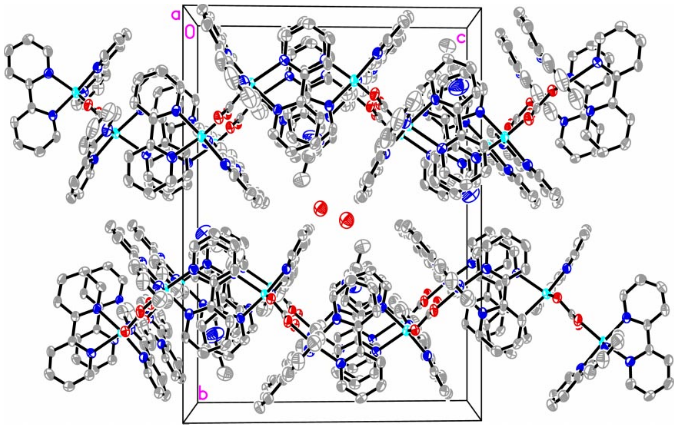


Figure 2
Projection of the structure of (I) along [100], showing displacement ellipsoids at the 50% probability level. For clarity, H atoms have been omitted.

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