Redetermination of (diazoamino-benzene)copper(I) at 150 K

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Abstract

The crystal structure of the title compound, di-μ-diazoaminobenzenido-N^1:N^3-dicopper(I)(Cu—Cu), $[Cu_2(C_{12}H_{10}N_3)_2]$, has been redetermined at 150 K with diffractometer data. The molecule is a dimer in which the two Cu atoms are bridged by two DAB ligands (DAB is diazoaminobenzene). Each Cu atom is bonded to the other Cu atom [Cu—Cu 2.4405 (10) Å] and to one N atom of each DAB ligand in such a way that each metal center shows a distorted T-shaped environment. The results provide the same qualitative picture as the previous structure, but with the expected differences attributable to the use of low-temperature diffractometer data. The structure had previously been determined from room-temperature photographic data by Brown & Dunitz [*Cryst. Struct. Commun.* (1961), **14**, 480–485].

Comment

As part of our investigations of coordination complexes with polyfunctional ligands, we have analyzed the crystal structure of Cu_2DAB_2 (DAB is diazoaminobenzene) using modern diffractometer methods, so as to permit comparisons of accurate structural parameters for this compound with those of other dinuclear copper complexes possessing possible conjugated bridges. The structure had previously been determined from room-temperature photographic data by Brown & Dunitz (1961), and was exceptionally accurate considering the experimental and computational techniques available at that time.

Cu_2DAB_2
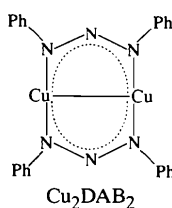
The compound crystallizes as a dimeric molecule with crystallographic inversion symmetry. The two Cu atoms are bridged by two DAB molecules in such a way that each Cu center is linked to the other Cu atom and to one N atom of each DAB ligand, giving a distorted T-shaped environment. The Cu—Cu bond distance [2.4405 (10) Å] is similar, within experimental error, to that reported previously [2.451 (8) Å; Brown & Dunitz, 1961] and is unusually short when compared with those reported for other dinuclear Cu^I derivatives. For instance, Cu—Cu distances are in the limited range 2.9–3.2 Å for symmetrical two-atom bridging (Hathaway, 1987), and the Cu—Cu bond distance in $[Cu(HBpz_3)]_2$, which forms a very compact Cu_2N_2 bridged complex, is 2.66 Å (Arcus *et al.*, 1974, 1976). Shorter Cu^I—Cu^I bond distances [2.348 (2) and 2.358 (2) Å] have been found in the trinuclear complex $[Cu(p\text{-tolyl-N},N,N,N,N\text{-}p\text{-tolyl})]_3$ (Beck & Strähle, 1985). The reasons for such short bonds remain unclear. The T-shaped coordination environment around each copper is not often observed since dinuclear complexes of Cu^I usually adopt trigonal-planar or tetrahedral arrangements (Hathaway, 1987).

The two Cu—N bond distances are equal within experimental error [1.896 (3) and 1.900 (3) Å] and are also equal to those reported previously [1.898 (18) and 1.939 (18) Å; Brown & Dunitz, 1961]. These distances are shorter than the mean value reported for the Cu—N distance in copper triazenido-bridging complexes [2.019 (44) Å; Orpen *et al.*, 1989]. On the other hand, the N—N bond distances [1.302 (3) and 1.298 (3) Å] are equal within experimental error, and are also equal to the mean value reported by Brown & Dunitz [1.30 (3) Å], although the previously reported individual values were quite different [1.274 (29) and 1.316 (29) Å]. In the same way, Brown & Dunitz reported quite different values for the C—N bond distances [1.48 (3) and 1.39 (3) Å] and they suggested that this difference might be relevant. However, in our determination, the two C—N bond distances are equal within experimental error [1.428 (4) and 1.422 (4) Å]. The C—C bond distances in the phenyl rings are unremarkable.

In spite of the quantitative differences found between the two determinations, analysis of our structural parameters supports the general points discussed in the previous report of this structure, and we do not repeat that discussion here.

As seen in a comparison of bond distances and angles, the molecule approximates to *mmm* symmetry, with the corresponding distances in the two halves of the molecule, related by the N2···N2A axis, being essentially identical. This, together with the fact that we do not observe any anomalies in the anisotropic displacement parameters, indicates that there is a symmetrical distribution of the electron density in the molecule. The N—N bond distances are intermediate between the mean values reported for a single [1.401 (8) Å]

and double bond [1.255 (16) Å] (Allen *et al.*, 1987), which means that these bonds possess partial double-bond character. In addition, the C—N bond distances are similar to the mean value reported for a C—N=N bond [1.431 (20) Å]. Finally, the angle N1—Cu1—N2 is 172.81 (10)° and the average bond-angle value around the N1 and N3 atoms is 120°.

All these data indicate an sp^2 hybridization for each N atom, which forms σ(C—N) and σ(N—N) bonds. The single electron at each N atom participates in a delocalized π orbital. This is responsible for the partial double-bond character of the N—N bonds (theoretical bond order 1.5) and can also be implicated in the nature of the C—N and Cu—N bonds. The remaining electron in each anionic ligand can be delocalized through the complete bridging system, contributing to the shortness of the Cu—N bond.
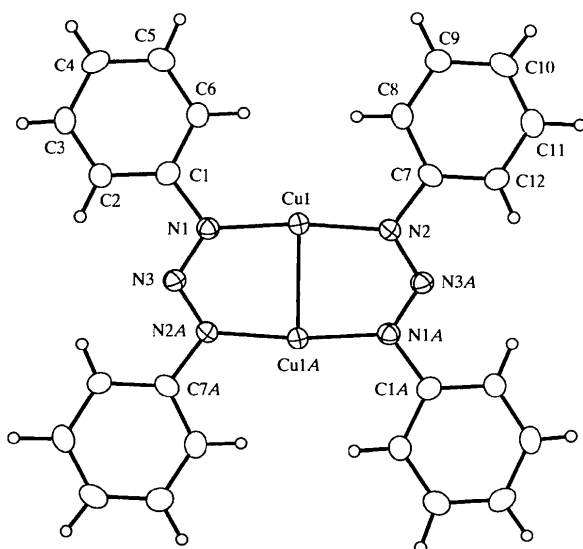

Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids for non-H atoms. H atoms are shown as spheres of arbitrary radii.

Experimental

The preparation of the title compound was performed under a nitrogen atmosphere. To a solution of DAB (0.603 g, 3.06 mmol) in degassed acetonitrile (20 ml) was added [Cu(NCMe)$_4$]ClO$_4$ (1.000 g, 3.06 mmol). The mixture became brown and after a few minutes stirring at room temperature, NEt$_3$ (0.61 g, 6.0 mmol) was added dropwise. During the addition, the title compound precipitated as an orange solid which was filtered, washed with NCMe (5 ml) and dried *in vacuo*. Crystals of X-ray quality were obtained by slow evaporation of a solution of the compound in CH$_2$Cl$_2$/*n*-hexane (1:1). The yield was 85%.

Crystal data

[Cu$_2$(C$_{12}$H$_{10}$N$_3$)$_2$]
$M_r = 519.54$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$C2/c$
$a = 26.174\,(7)$ Å
$b = 5.5429\,(7)$ Å
$c = 15.727\,(4)$ Å
$\beta = 116.60\,(2)°$
$V = 2040.2\,(8)$ Å^3
$Z = 4$
$D_x = 1.691$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 10.2-15.9°$
$\mu = 2.111$ mm^{-1}
$T = 150\,(1)$ K
Needle
$0.51 \times 0.14 \times 0.06$ mm
Orange

Data collection

Nonius CAD-4 diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.772$, $T_{max} = 0.881$
3587 measured reflections
1798 independent reflections

1465 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 24.97°$
$h = -30 \rightarrow 30$
$k = 0 \rightarrow 6$
$l = -18 \rightarrow 18$
3 standard reflections frequency: 30 min intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.081$
$S = 1.056$
1798 reflections
145 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 2.1865P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.570$ e Å^{-3}
$\Delta\rho_{min} = -0.243$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—Cu1^i	2.4405 (10)	N1—C1	1.422 (4)
Cu1—N1	1.900 (3)	N2—N3^i	1.302 (3)
Cu1—N2	1.896 (3)	N2—C7	1.428 (4)
N1—N3	1.298 (3)	N2—N3^i	1.302 (3)
N2—Cu1—N1	172.81 (10)	C1—N1—Cu1	122.2 (2)
N2—Cu1—Cu1^i	86.57 (8)	N3^i—N2—C7	112.0 (2)
N1—Cu1—Cu1^i	86.51 (8)	N3^i—N2—Cu1	125.1 (2)
N3—N1—C1	112.6 (2)	C7—N2—Cu1	122.8 (2)
N3—N1—Cu1	125.10 (19)	N1—N3—N2^i	116.6 (2)

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

The structure was solved by direct methods. The H atoms were located in a difference Fourier map and refined as riding atoms. The displacement parameters of the H atoms were refined as independent variables.

Data collection: *CAD-4/PC* (Nonius, 1996). Cell refinement: *CAD-4/PC*. Data reduction: *XCAD4B* (Harms, 1995). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *SHELXTL* (Siemens, 1996). Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1296). Services for accessing these data are described at the back of the journal.

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Trichloro[methylenebis(diphenylphosphine oxide-*O*)]antimony(III)

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Abstract

The asymmetric unit of the title complex, $[SbCl_3-\{[(C_6H_5)_2PO]_2CH_2\}]$, comprises two independent molecules, in both of which the Sb atoms are in flattened square-pyramidal environments, with the basal planes

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each defined by two O and two Cl atoms, and the apical atom being Cl in each molecule. The geometry can alternatively be described as distorted octahedral as a result of coordination by a sixth (Cl) atom at a longer distance.

Comment

It is known that $SbCl_3$ forms an addition complex with triphenylphosphine oxide, *i.e.* $SbCl_3 \cdot 2(C_6H_5)_3PO$ (Milicev & Hadzi, 1977; Golic & Milicev, 1978). In our study of the reaction of bis(diphenylphosphino)methane with $SbCl_5$ in acetonitrile, an analogous product, (I), was obtained and its structure is reported herein.

(I)
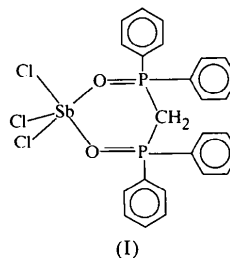
The asymmetric unit consists of two independent molecules which are not related by pseudosymmetry. In both molecules, the Sb atom is coordinated to the methylenebis(diphenylphosphine oxide) ligand through the O atoms. The Sb centres occupy a square-pyramidal geometry, with both oxide O atoms and two Cl atoms (Cl1 and Cl2) occupying the equatorial positions, and the third Cl atom (Cl3) in the axial position. The angles at antimony cluster around 90 or 180°, so that the square pyramid is flattened to an octahedron with one coordination site unoccupied. However, a sixth coordination is observed for both Sb atoms, at longer distances, with Sb1 coordinated to Cl2A^i at a distance of 3.6858 (14) Å and Sb2 coordinated to Cl2B^{ii} at a distance of 3.5450 (13) Å [symmetry codes: (i) $2 - x$, $-y$, $2 - z$; (ii) $2 - x$, $1 - y$, $1 - z$]. These distances are appreciably less than the sum of the relevant van der Waals radii of 4.01 Å. If this bonding is considered to be significant then the coordination around the Sb atoms may alternatively be described as distorted octahedral with the equatorial positions occupied by Cl1, Cl2, O1 and O2 in both molecules; the axial positions around Sb1 are occupied by Cl3 and Cl2A^i, and atoms Cl3 and Cl2B^{ii} occupy the axial positions of Sb2. This arrangement results in an edge-sharing octahedral environment involving the Sb1 atoms at (x, y, z) and $(2 - x, -y, 2 - z)$, and the Sb2 atoms at (x, y, z) and $(2 - x, 1 - y, 1 - z)$.

The Sb—Cl bond lengths range from 2.3881 (9) to 2.5360 (10) Å; the shortest Sb—Cl distance is observed for the non-bridging Cl atom, as was also observed in related structures (Porter & Jacobson, 1970; Yamin *et*