

- Picard, J.-P., Baud, G., Besse, J.-P., Chevalier, R. & Gasperin, M. (1984). *J. Less-Common Met.* **96**, 171–176.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
- Slimane, Z. A. A., Silvestre, J.-P., Freundlich, W. & Rimsky, A. (1982). *Acta Cryst.* **B38**, 1070–1074.
- Stout, G. H. & Jensen, H. (1968). *X-ray Structure Determination*. New York: Macmillan.
- Todorov, T. & Macíček, J. (1995). *Acta Cryst.* **C51**, 1034–1038.
- Verhoef, L. H. W. & Boeyens, J. C. A. (1968). *Acta Cryst.* **B24**, 1262–1266.
- Walker, N. G. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

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Tetrakis(*N,N'*-diphenylbenzamidinato)-dicopper(II) Dichloromethane Solvate

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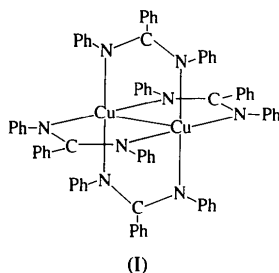
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Abstract

The title compound, $[\text{Cu}_2(\text{C}_{19}\text{H}_{15}\text{N}_2)_4] \cdot 2\text{CH}_2\text{Cl}_2$, forms a cage structure with fourfold symmetry. The cage comprises two Cu atoms lying on the axis and four bridging ligand units related by the fourfold rotation. The ligand units also have approximate twofold axial symmetry. The Cu1—Cu2 separation of 2.460 (2) Å is consistent with a single-bond distance. The metal–ligand distances, Cu1—N1 of 2.020 (5) and Cu2—N2 of 2.027 (4) Å, are effectively equal. A cavity within the structure is occupied by disordered molecules of dichloromethane solvent.

Comment

As part of a study of amidino complexes of Cu^{I} and Cu^{II} , the title compound, (I), was prepared from anhydrous copper(II) chloride and lithio(*N,N'*-diphenylbenzamidino) in monoglyme solution (Kilner &



Pietrzykowski, 1983), and recrystallized from dichloromethane.

In the structure, the two non-equivalent Cu atoms lie on the same fourfold axis of the space group and are bridged by four ligand molecules forming a binuclear cage (Figs. 1 and 2). The ligand has approximate twofold symmetry about an axis in the C1—C8...C11 direction, which relates the two halves of the molecule. The point-group symmetry of the molecule is thus approximately 422 (D_4), the fourfold symmetry, of course, being exact. The two Cu atoms are sufficiently close [2.460 (2) Å] to be regarded as single bonded and the two Cu—N distances [2.020 (5) and 2.027 (4) Å] are very similar. In the ligand, the distances C1—N1 and C1—N2 of 1.327 (8) and 1.335 (8) Å, respectively, are virtually identical, indicating that delocalization has occurred, which is in contrast to the significantly different mean values of 1.360 (8) and 1.302 (7) Å found for C—N and C=N, respectively, in the free uncoordinated ligand dimer (Alcock, Barker & Kilner, 1988). These workers considered there to be a marked interaction between the C—N(amine) part of the skeleton and its associated phenyl ring, with a tendency towards planarity. This effect is absent in the present structure where the dihedral angles between the N1—C1—N2 plane and the planes of the phenyl groups at C2 and C14 are nearly equal at 63.7 (5) and 65.2 (5)°, respectively. This feature is evidenced also by the pseudosymmetry of the ligand moiety. The increased C1—C8 length of 1.524 (6) Å, compared with the mean value 1.485 Å in the free ligand, is evidence of the loss of conjugation with the phenyl group in that structure in favour of delocalization

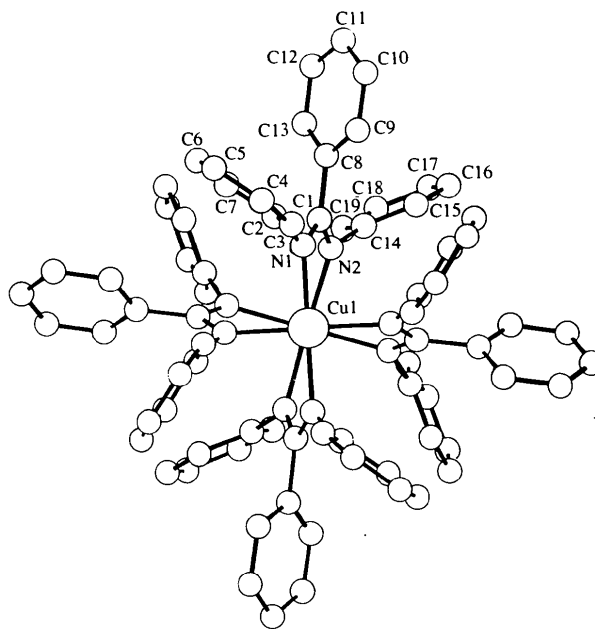


Fig. 1. The title molecule viewed along the fourfold axis, with independent atoms labelled. Atom Cu2 is overlapped exactly by Cu1.

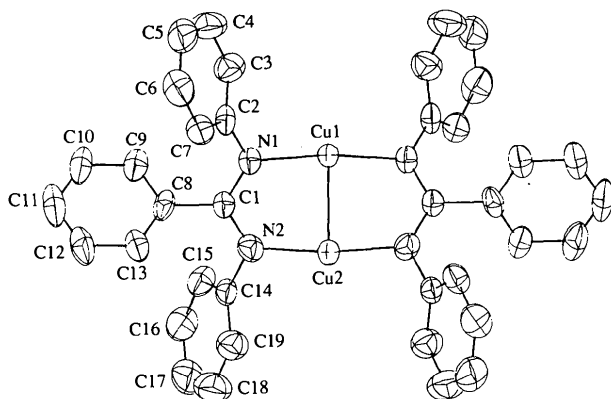


Fig. 2. The Cu atoms and two symmetry-equivalent ligands shown with 50% probability ellipsoids.

around Cu1—N1—C1—N2—Cu2 in the present structure.

The title structure is analogous to that of tetrakis(*N,N'*-diphenylbenzamidinato)dimolybdenum(II) (Cotton, Inglis, Kilner & Webb, 1975), which has an Mo—Mo distance of 2.090 (1) Å. The two structures, although similar, are not isomorphous, the molybdenum structure having only twofold molecular symmetry about an axis perpendicular to the Mo—Mo direction, *i.e.* one of the pseudosymmetry axes in the present Cu compound.

In the structure of tetrakis(μ -*N,N'*-diphenylbenzamidinato-*N,N'*)dipalladium(II) ethanol solvate (Yao, He, Korp & Bear, 1988), the molecule, although essentially D_4 and similar to the present molecule, has no exact crystallographic symmetry elements; the Pd—Pd distance is 2.576 Å. The solvent is lost in the early stages of X-ray irradiation. More recent determinations by He, Yao, Naris, Lee, Korp & Bear (1992) of three similar structures (one cobalt and two rhodium compounds) show analogous molecules. The cobalt(II) compound forms monoclinic crystals in which the molecule has crystallographic twofold symmetry along the metal—metal axis, with a Co—Co distance of 2.302 Å. There is no included solvent in this structure. A rhodium compound isomorphous with the present Cu^{II} compound but with ethanol of solvation around the fourfold alternating axis is reported to have an Rh—Rh distance of 2.389 Å, and a rhodium structure with a carbonyl added axially to one Rh atom has an increased Rh—Rh distance of 2.435 Å and crystallizes as the octahydrate. It is apparent that the presence of included solvent plays a key role in determining the crystal structure adopted by these compounds and in doing so affects the precise symmetry adopted by the molecule.

Experimental

The crystals were supplied by Kilner (Kilner & Pietrzykowski, 1983) and found to be suitable for analysis without further recrystallization.

Crystal data

[Cu₂(C₁₉H₁₅N₂)₄].2CH₂Cl₂
M_r = 1382.33
 Tetragonal
*P*4/*n*
a = 17.601 (11) Å
c = 12.235 (8) Å
V = 3790.3 Å³
Z = 2
D_x = 1.211 Mg m⁻³

Mo K α radiation

λ = 0.7107 Å
 Cell parameters from 15 reflections
 θ = 5–25°
 μ = 0.75 mm⁻¹
T = 288 K
 Flat tetragonal prism with {001} and {110}
 0.6 × 0.6 × 0.2 mm
 Purple

Data collection

Stoe Stadi-2 two-circle diffractometer
 Variable ω scans
 Absorption correction: by integration from crystal shape (SHELX76; Sheldrick, 1976)
T_{min} = 0.689, *T_{max}* = 0.864
 5082 measured reflections
 2975 independent reflections

1873 observed reflections

[*I* > 3 σ (*I*)]

R_{int} = 0.03

θ_{max} = 30°

h = -13 → 13

k = 0 → 20

l = 0 → 14

One standard reflection per layer monitored every

20 reflections

intensity decay: 5%

Refinement

Refinement on *F*
R = 0.056
wR = 0.056
S = 1.427
 1873 reflections
 192 parameters
 H atoms riding with common *U_{iso}*
 Unit weights applied

(Δ/σ)_{max} = 0.007

$\Delta\rho_{max}$ = 0.48 e Å⁻³

$\Delta\rho_{min}$ = -0.27 e Å⁻³

Atomic scattering factors from SHELX76 (Sheldrick, 1976) for C, H, N and Cl, and Cromer & Mann (1968) for Cu

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

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cu1	1/4	1/4	0.04687 (13)	0.0357 (5)
Cu2	1/4	1/4	-0.15418 (12)	0.0331 (5)
N1	0.2543 (3)	0.3645 (3)	0.0365 (4)	0.047 (5)
N2	0.2913 (2)	0.3573 (3)	-0.1441 (4)	0.038 (4)
C1	0.2798 (3)	0.3980 (3)	-0.0535 (5)	0.038 (5)
C13	0.2711 (2)	0.5291 (2)	-0.1376 (3)	0.055 (6)
C8	0.2976 (2)	0.4827 (2)	-0.0535 (3)	0.046 (5)
C9	0.3425 (2)	0.5134 (2)	0.0294 (3)	0.054 (6)
C10	0.3609 (2)	0.5905 (2)	0.0283 (3)	0.071 (8)
C11	0.3343 (2)	0.6369 (2)	-0.0559 (3)	0.080 (9)
C12	0.2894 (2)	0.6062 (2)	-0.1388 (3)	0.070 (8)
C2	0.2188 (2)	0.4073 (2)	0.1244 (3)	0.042 (6)
C7	0.1583 (2)	0.4561 (2)	0.1024 (3)	0.053 (6)
C6	0.1206 (2)	0.4924 (2)	0.1881 (3)	0.071 (8)
C5	0.1435 (2)	0.4799 (2)	0.2957 (3)	0.084 (10)
C4	0.2041 (2)	0.4311 (2)	0.3177 (3)	0.086 (10)
C3	0.2417 (2)	0.3948 (2)	0.2320 (3)	0.066 (8)
C14	0.3393 (2)	0.3834 (2)	-0.2316 (3)	0.045 (6)
C15	0.4140 (2)	0.4055 (2)	-0.2111 (3)	0.055 (6)
C16	0.4611 (2)	0.4271 (2)	-0.2974 (3)	0.076 (9)
C17	0.4334 (2)	0.4267 (2)	-0.4042 (3)	0.084 (10)
C18	0.3587 (2)	0.4046 (2)	-0.4247 (3)	0.086 (10)

C19	0.3116 (2)	0.3830 (2)	-0.3385 (3)	0.065 (8)
C11†	0.357 (2)	0.670 (3)	0.433 (4)	0.59 (12)
C12†	0.301 (2)	0.623 (2)	0.375 (4)	0.49 (8)
C20	0.396 (2)	0.772 (4)	0.485 (4)	0.26 (8)

† Occupancy factor = 0.5.

Table 2. Selected geometric parameters (Å, °)

Cu1—Cu2	2.460 (2)	N1—C1	1.327 (8)
Cu1—N1	2.020 (5)	C1—C8	1.524 (6)
Cu2—N2	2.027 (4)	C1—N2	1.335 (8)
C2—N1	1.453 (6)	N2—C14	1.439 (6)
N1—Cu1—Cu2	86.43 (10)	C2—N1—C1	121.9 (4)
Cu1—Cu2—N2	86.54 (9)	N1—C1—C8	120.3 (5)
Cu2—N2—C1	119.7 (4)	C8—C1—N2	119.6 (5)
N2—C1—N1	120.1 (5)	C14—N2—C1	122.4 (4)
C1—N1—Cu1	120.5 (4)	C14—N2—Cu2	117.6 (3)
C2—N1—Cu1	117.0 (3)		

Weissenberg photographs taken using Cu $K\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$) indicated Laue symmetry $4/m$. Difficulty was experienced in measuring the crystal density by flotation; wide variations in the density of different crystals and density values changing with the time of immersion caused problems. The explanation was undoubtedly that solvent of crystallization, revealed later in the investigation to be present, was undergoing replacement in the immersion liquid. Intensity measurements were made with a two-circle diffractometer employing equi-inclination Weissenberg geometry. The angle θ' is the projection of θ onto the equatorial plane. The crystal was set to rotate about the a axis. A separate standard was required for each layer measured, but because of the equivalence of the a and b axes in the tetragonal system, refinement of interlayer scale factors was unnecessary. Refinement was carried out with phenyl groups constrained as rigid hexagons having individual U_{ij} parameters for the C atoms and H atoms at calculated sites with a common U_{iso} . A difference map showed a broad region of electron density around the fourfold alternating axis which was interpreted as disordered CH₂Cl₂.

Data collection: Stoe Stadi-2 software. Data reduction: *DATR* (Small, 1977). Program(s) used to solve structure: *SHELX76* (Sheldrick, 1976). Program(s) used to refine structure: *SHELX76*. Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1005). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Alcock, N. W., Barker, J. & Kilner, M. (1988). *Acta Cryst.* C44, 712–715.
- Cotton, F. A., Inglis, T., Kilner, M. & Webb, T. R. (1975). *Inorg. Chem.* 14, 2023–2026.
- Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A24, 321–324.
- He, L.-P., Yao, C.-L., Naris, M., Lee, J. C., Korp, J. D. & Bear, J. L. (1992). *Inorg. Chem.* 31, 620–625.
- Kilner, M. & Pietrzykowski, A. (1983). *Polyhedron*, 2, 1379–1388.
- Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.

- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Small, R. W. H. (1977). *DATR. Program for Reducing Raw Stadi-2 Data to Intensities*. Univ. of Lancaster, England.
- Yao, C.-L., He, L.-P., Korp, J. D. & Bear, J. L. (1988). *Inorg. Chem.* 27, 4389–4395.

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Bis[(2-hydroxyethyl)dimethylammonium] Tetrakis(μ -benzoato-*O*:*O'*)bis[(benzoato-*O*)cuprate(II)]

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Abstract

Copper(II) benzoate reacts with 2-dimethylaminoethanol in ethanol forming a green copper(II) complex, (C₄H₁₂NO)₂[Cu₂(C₇H₅O₂)₆]. The two Cu atoms, with a Cu...Cu distance of 2.670 (2) Å in the centrosymmetric molecule, are held together by the four carboxylate groups. Each Cu atom is bound in a square-pyramidal configuration to five carboxylate O atoms. The (2-hydroxyethyl)dimethylammonium cation is hydrogen bonded to the uncoordinated O atom of the unidentate carboxylate group.

Comment

Monomeric, tetrameric, hexameric and nonameric complexes have been obtained from reactions between 2-dimethylaminoethanol and Cu^{II} carboxylates (Turpeinen, Hämäläinen & Ahlgrén, 1980, 1985; Turpeinen, Hämäläinen & Reedijk, 1987, 1988). Blue and green crystals precipitate simultaneously during the slow evaporation of an ethanol solution containing equimolar amounts of copper(II) benzoate and 2-dimethylaminoethanol. The structure of the blue complex is monomeric, the Cu atom being six-coordinate with two 2-dimethylaminoethanol and one benzoate group acting as bidentate ligands (Turpeinen, Hämäläinen & Ahlgrén, 1985). The structure of the green compound, (I), is a variant of the classical dimeric copper(II) acetate monohydrate compound (van Niekerk & Schoening, 1953).

The structure of (I) is composed of centrosymmetric [Cu₂(C₇H₅O₂)₆]²⁻ anions and (2-hydroxyethyl)dimethylammonium cations joined together by