Crystal Structure of Di- μ -bromo-bis{[bis(2-nitrocinnamaldehyde)-2,2'-diiminobiphenyl-*N,N'*]}copper(I)}

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The title complex, [Cu(μ -Br)(nca₂dab)]₂ [nca₂dab is *N,N'*-bis(2-nitrocinnamaldehyde)-2,2'-diiminobiphenyl], has a dimeric structure, where two copper(I) ions are doubly bridged by bromo substituents. The coordination geometry around the Cu atom is a distorted tetrahedron formed by two N atoms from a bidentate nca₂dab ligand and two bromo substituents. The distance between the two Cu atoms is 2.6650(8) Å. The nca₂dab ligand adopts a *Z,Z* configuration.

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In our ongoing studies on the synthesis, structural and spectroscopic characterization of copper(I) halogeno complexes,^{1,2} we report here on the crystal structure of the title complex (Fig. 1). *N,N'*-bis(2-nitrocinnamaldehyde)-2,2'-diiminobiphenyl (0.14 g, 1.2 mmol) was reacted with CuBr (0.17 g, 1.2 mmol) in 5 ml of acetonitrile. Slow evaporation of the solvent gave dark-red crystals. The data collection and refinement parameters are listed in Table 1. The positions of the hydrogen atoms were obtained from a difference Fourier map. The atomic coordinates of non-hydrogen atoms are listed in Table 2 and selected interatomic parameters are collected in Table 3. A view of the complex, including the atom-numbering scheme, is illustrated in Fig. 2. The coordination environment around the metal ion in this complex is pseudotetrahedral with a large angular distortion arising from the low intraligand N(6)-Cu(1)-N(5), N(1)-Cu(2)-N(2) chelate angles (99.83(14)°, 97.80(14)°). Of the other five angles around the Cu-atom, the Br-Cu-Br and N-Cu-Br, angles lie within $\pm 5^\circ$ of those of a regular tetrahedron; however, the N(1)-Cu(2)-Br(2) and N(6)-Cu(1)-Br(1) angles (119.75(10), 118.28(10)°), have opened up due to steric effects from the bulky diimine ligands. This angle is comparable to the angle observed in similar

Fig. 1 Chemical structure.

Table 1 Crystal data and structure refinement for **1**

Empirical formula: C ₆₀ H ₄₄ Br ₂ Cu ₂ N ₈ O ₈
Formula weight = 1291.93
Crystal structure: triclinic
Space group: <i>P</i> $\bar{1}$
<i>Z</i> = 2
<i>a</i> = 13.6106(17) Å
<i>b</i> = 13.8277(17) Å
<i>c</i> = 15.650(2) Å
α = 89.045(3)°
β = 88.164(3)°
γ = 67.400(3)°
<i>V</i> = 2717.8(6) Å ³
Calculated density = 1.579 Mg/m ³
Absorption coefficient/mm ⁻¹ = 2.318
Temperature = 120(2) K
<i>F</i> (0 0 0) = 1304
Crystal size = 0.15 × 0.1 × 0.05 mm ³
No. of reflection used = 25813
No. of parameters = 721
λ (Mo- <i>K</i> α) = 0.71073 Å
$\theta_{\max}$ = 27.00°
<i>R</i> 1 = 0.0544 [<i>I</i> ≥ 2σ(<i>I</i>)]
<i>wR</i> 2 = 0.1256
Goodness-of-fit on <i>F</i> ² = 1.033
(Δσ) _{max} = 0.001
(Δρ) _{max} = 1.362 e Å ⁻³
(Δρ) _{min} = -1.168 e Å ⁻³
Measurement: Bruker SMART 1000 CCD
Program system: SADABS
Structure determination: SHELXTL
Refinement: full-matrix least-squares on <i>F</i> ²

CCDC 295167 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data_request/cif.

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Table 2 Fractional coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) of non-hydrogen atoms

	x	y	z	U(eq)
Br(1)	7338(1)	2010(1)	1189(1)	21(1)
Br(2)	7074(1)	2380(1)	3821(1)	23(1)
Cu(1)	6360(1)	3073(1)	2414(1)	18(1)
Cu(2)	8115(1)	1355(1)	2609(1)	19(1)
O(1)	12137(3)	3048(4)	4083(3)	56(1)
O(2)	12496(4)	4425(5)	4070(4)	85(2)
O(3)	6277(3)	-2725(3)	1169(2)	38(1)
O(4)	4825(3)	-2730(3)	1748(3)	55(1)
O(5)	2442(3)	621(3)	3605(3)	51(1)
O(6)	2952(4)	-821(4)	2895(3)	66(1)
N(1)	9697(3)	1092(3)	2469(2)	17(1)
N(2)	8282(3)	-162(3)	2863(2)	18(1)
N(3)	11877(4)	4007(4)	3998(3)	49(1)
N(4)	5343(4)	-2290(3)	1396(3)	31(1)
N(5)	4819(3)	3271(3)	2237(2)	16(1)
N(6)	6195(3)	4605(3)	2456(2)	18(1)
N(7)	3115(4)	-218(4)	3372(3)	34(1)
C(1)	10261(3)	173(3)	1970(3)	18(1)
C(2)	10562(4)	275(4)	1129(3)	25(1)
C(3)	11088(4)	-606(4)	637(3)	27(1)
C(4)	11327(4)	-1584(4)	986(3)	30(1)
C(5)	11023(4)	-1701(4)	1823(3)	26(1)
C(6)	10467(3)	-820(3)	2327(3)	21(1)
C(7)	10146(4)	-941(3)	3231(3)	19(1)
C(8)	9076(3)	-620(3)	3484(3)	17(1)
C(9)	8785(4)	-708(4)	4326(3)	24(1)
C(10)	9563(4)	-1155(4)	4930(3)	27(1)
C(11)	10625(4)	-1510(4)	4687(3)	28(1)
C(12)	10923(4)	-1413(3)	3841(3)	25(1)
C(13)	10207(4)	1683(3)	2607(3)	20(1)
C(14)	9758(4)	2647(3)	3070(3)	21(1)
C(15)	10357(4)	3204(4)	3198(3)	27(1)
C(16)	10024(4)	4235(4)	3601(3)	27(1)
C(17)	8958(5)	4893(4)	3640(3)	37(1)
C(18)	8620(5)	5918(4)	3915(4)	48(2)
C(19)	9340(6)	6322(4)	4144(4)	51(2)
C(20)	10422(6)	5692(4)	4144(3)	44(2)
C(21)	10739(5)	4668(4)	3887(3)	38(1)
C(22)	7766(3)	-699(3)	2615(3)	20(1)
C(23)	6903(3)	-307(3)	2022(3)	21(1)
C(24)	6306(4)	-851(3)	1872(3)	23(1)
C(25)	5343(4)	-502(4)	1370(3)	22(1)
C(26)	4828(4)	541(4)	1115(3)	26(1)
C(27)	3859(4)	889(4)	720(3)	29(1)
C(28)	3349(4)	212(4)	582(3)	36(1)
C(29)	3827(4)	-831(4)	828(3)	33(1)
C(30)	4812(4)	-1160(4)	1195(3)	25(1)
C(31)	4352(3)	4060(3)	1599(3)	17(1)
C(32)	4194(3)	3798(3)	781(3)	19(1)
C(33)	3787(4)	4553(4)	164(3)	24(1)
C(34)	3481(4)	5608(3)	368(3)	23(1)
C(35)	3638(3)	5878(3)	1187(3)	21(1)
C(36)	4091(3)	5118(3)	1817(3)	17(1)
C(37)	4273(4)	5426(3)	2690(3)	19(1)
C(38)	5293(4)	5204(3)	2981(3)	19(1)
C(39)	5450(4)	5499(3)	3793(3)	24(1)
C(40)	4584(4)	6024(3)	4339(3)	27(1)
C(41)	3568(4)	6271(3)	4043(3)	28(1)
C(42)	3394(4)	5989(3)	3222(3)	25(1)
C(43)	4313(3)	2704(3)	2476(3)	20(1)
C(44)	4776(4)	1814(3)	3041(3)	20(1)
C(45)	4288(4)	1147(4)	3182(3)	24(1)
C(46)	4708(4)	156(3)	3658(3)	20(1)
C(47)	5712(4)	-201(4)	4027(3)	26(1)
C(48)	6126(4)	-1161(4)	4448(3)	32(1)
C(49)	5566(4)	-1808(4)	4486(3)	35(1)
C(50)	4591(4)	-1496(4)	4112(4)	36(1)
C(51)	4176(4)	-523(4)	3725(3)	26(1)
C(52)	6868(4)	5014(3)	2232(3)	22(1)
C(53)	7828(4)	4436(4)	1745(3)	22(1)
C(54)	8554(4)	4831(4)	1522(3)	31(1)
C(55)	9544(4)	4252(5)	1020(3)	37(1)
C(56)	9542(5)	3488(4)	433(4)	45(2)
C(57)	10423(5)	2916(5)	-81(4)	54(2)
C(58)	11347(5)	3077(6)	-17(4)	54(2)
C(59)	11423(4)	3757(6)	560(4)	59(2)
C(60)	10507(5)	4364(5)	1072(3)	51(2)
N(8)	10442(13)	5281(11)	1602(11)	48(5)
O(7)	11192(14)	5411(16)	1939(12)	83(5)
O(8)	9717(13)	6082(11)	1874(11)	50(5)
N(8')	10753(5)	4963(5)	1706(4)	47(2)
O(8')	10047(6)	5801(5)	1847(5)	44(2)
O(7')	11633(5)	4660(5)	2004(4)	54(2)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

structures.^{1,3} The average Cu-N bond distance (2.045 Å) is similar to those found in other Cu(I) pseudotetrahedral complexes.⁴

In spite of a sterical hindrance in this complex, the ligand adopts a Z,Z configuration. The mean value for the torsion angles of N=C-C=C is about 174.7°, indicating that this moiety is roughly planar. The Ph plane of the cinnamaldehyde moieties and the chain connecting the ring to the coordinated N-atom are roughly coplanar. The angle between the plane of the Ph ring and the

Table 3 Selected interatomic distances (Å) and angles between the interatomic vectors (°) for **1** with the standard uncertainties in parentheses

Br(1)-Cu(1)	2.4569(7)	Cu(1)-N(5)	2.037(3)
Br(1)-Cu(2)	2.4961(7)	Cu(1)-N(6)	2.045(4)
Br(2)-Cu(1)	2.4618(7)	Cu(2)-N(1)	2.047(3)
Br(2)-Cu(2)	2.4467(7)	Cu(2)-N(2)	2.053(3)
N(6)-Cu(1)-N(5)	99.83(14)	Br(1)-Cu(1)-N(5)	104.11(10)
N(1)-Cu(2)-N(2)	97.80(14)	Br(1)-Cu(2)-N(2)	113.44(10)
Br(1)-Cu(1)-Br(2)	114.94(3)	Cu(1)-Br(1)-Cu(2)	65.10(2)
Br(1)-Cu(2)-Br(2)	114.06(3)	Cu(1)-Br(2)-Cu(2)	65.77(2)

Fig. 2 ORTEP diagram of $[\text{Cu}(\mu\text{-Br})(\text{nca2dab})]_2$ showing 50% probability ellipsoids. One of the disordered part N(8)O(7)O(8) is shown.

plane spanned by N=C-C=C is 15.7°. This degree of coplanarity, which allows increased π -conjugation in the ligand, is consistent with the observed C-C bond distances in the coordinated ligands (e.g. C(44)-C(45), 1.341(6) Å < C(43)-C(44), 1.448(6) Å < typical single C-C bond, 1.507(5) Å.^{2,5} The nitro groups are exo relative to the Cu atom, and the plane of the nitro groups are roughly coplanar with the phenyl plane. However, one of the NO₂ groups (O(8)N(8)O(7)) is disordered, and the only one component of the disordered N(8)O(7)O(8) group is shown in Fig. 2.

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