Synthesis and Crystal Structure of Bis[1,3-bis(2-methoxyphenyl)triazene]-copper(I) Iodide

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The crystal structure of $[\text{Cu}_2\text{I}_2\text{L}_2]$, $\text{L} = 1,3\text{-bis}(2\text{-methoxyphenyl})\text{triazene}$ was determined by X-ray diffraction. The complex crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 9.0976(8)$, $b = 12.4229(12)$, $c = 14.4204(11)\text{\AA}$, $\beta = 106.582(3)^\circ$, $V = 1562.0(2)\text{\AA}^3$, $Z = 2$. The structure was solved by the full-matrix least-squares on F^2 and had a refined R value of 0.0245 for 3486 reflections ($I > 2\sigma(I)$). The Cu_2I_2 moiety is coordinated by two molecules of the ligand *via* azide nitrogen and oxygen from a methoxy group in a trigonal pyramidal geometry.

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Triazenes are well-known and important substances, especially for the synthesis of supramolecular compounds of transition metals, like $\text{Hg}(\text{II})$.¹ We reported on the synthetic procedures and the structural features of 1,3-bis(2-methoxyphenyl)triazene² (L) and its complex with $\text{Ag}(\text{I})$ and $\text{Hg}(\text{II})$ elsewhere.^{1,3}

Copper(I) halides can form halocuprate(I) complexes in which the halide ions can bridge two or more $\text{Cu}(\text{I})$ ions, besides acting as the terminal ligand.^{4,5} In this work, the coordination property of the title complex was demonstrated by reacting Cu_2I_2 with L . A CH_3CN solution of L (0.257 g, 1 mmol) was added to a solution of Cu_2I_2 (0.190 g, 1 mmol) in CH_3CN , and after stirring for 20 min, a reddish-brown precipitate was observed. The reaction mixture was filtered, and then the precipitate was dissolved in CH_3CN and stored in a refrigerator. After 2 weeks, reddish-brown crystals were formed; M. P. , $133 - 135^\circ\text{C}$. The crystal structure of the complex $[\text{Cu}_2\text{I}_2\text{L}_2]$ was determined by direct methods, and refined on F^2 by full-matrix least-squares using the program SHELXTL-97.⁶ An X-ray diffraction study of the compound showed that it crystallized in a monoclinic system with the $P2_1/c$ space group. The crystallographic data for crystals of the title complex are summarized in Table 1.

The chemical structure and atomic numbering of the crystal structure are shown in Figs. 1 and 2, respectively. As shown in

Fig. 1 Chemical structure of $[\text{Cu}_2\text{I}_2\text{L}_2]$.

Fig. 2, the $\text{Cu}(\text{I})$ is tetra-coordinated in a trigonal pyramidal geometry with the trigonal plane formed by two bridged iodine atoms and a ligand nitrogen atom ($\text{N}(3)$). The bond distances of $\text{Cu}(1)\text{-I}(1)$ ($2.5716(4)\text{\AA}$), $\text{Cu}(1)\text{-N}(3)$ ($2.000(19)\text{\AA}$) and $\text{Cu}(1)\text{-O}(2)$ ($2.3298(17)\text{\AA}$) are comparable with the corresponding values reported in a number of other structurally related copper ion complexes.^{5,6} Selected bond distances and bond angles for the complex are listed in Table 3.

Both iodine atoms act as a μ -bridging mode to link two adjacent $\text{Cu}(\text{I})$ atoms to form a four-membered Cu_2I_2 ring with a $\text{Cu}\cdots\text{Cu}$ separation of $2.5996(6)\text{\AA}$ and a Cu-I-Cu bridging angle of $60.672(12)^\circ$. Each of two L ligands acts as a bridge with its one nitrogen and one oxygen atoms chelating to a Cu center of a

Table 1 Crystal data and structure refinement details for $[\text{Cu}_2\text{I}_2\text{L}_2]$

Formula:	$\text{C}_{28}\text{H}_{30}\text{Cu}_2\text{I}_2\text{N}_6\text{O}_4$
Formula weight:	895.46
Crystal system:	monoclinic
Space group:	$P2_1/c$
Z :	2
a :	$9.0976(8)\text{\AA}$
b :	$12.4229(12)\text{\AA}$
c :	$14.4204(11)\text{\AA}$
β :	$106.582(5)^\circ$
V :	$1562.0(2)\text{\AA}^3$
T :	100 K
D_x :	1.904 Mg m^{-3}
No. of reflection:	3486
$2\theta_{\text{max}}$:	58 with $\text{Mo } K_\alpha$
R :	0.0245, R_w = 0.0514
$(\Delta/\sigma)_{\text{max}}$:	0.001
$(\Delta\rho)_{\text{max}}$:	$0.712\text{ e \AA}^{-3}$
$(\Delta\rho)_{\text{min}}$:	$-0.903\text{ e \AA}^{-3}$
Measurement:	Bruker APEX2 CCD area detector
Program system:	APEX II, version 2.0-1; Bruker SAINT
Structure determination:	SHELXS-97 (Sheldrick, 1997)
Refinement:	full-matrix least-squares on F^2

CCDC 665837 contains the supplementary crystallographic data for this paper copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk.

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Fig. 2 ORTEP drawing of the molecule structure $[\text{Cu}_2\text{I}_2\text{L}_2]$ (50% probability level).

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Cu}_2\text{I}_2\text{L}_2]$, $\text{L} = 1,3\text{-bis}(2\text{-methoxybenzene})\text{triazene}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	$U(\text{eq})$
I(1)	4678(1)	3632(1)	914(1)	20(1)
Cu(1)	6453(1)	5026(1)	463(1)	15(1)
N(1)	8479(2)	3171(2)	87(2)	13(1)
N(2)	9384(2)	3870(2)	672(2)	13(1)
N(3)	8692(2)	4677(2)	899(2)	13(1)
O(1)	6687(2)	1612(2)	-838(2)	22(1)
O(2)	7481(2)	6163(1)	1773(1)	17(1)
C(1)	9165(3)	2309(2)	-275(2)	14(1)
C(2)	8209(3)	1494(2)	-777(2)	16(1)
C(3)	8833(3)	652(2)	-1177(2)	20(1)
C(4)	10408(3)	613(2)	-1050(2)	20(1)
C(5)	11355(3)	1414(2)	-535(2)	18(1)
C(6)	10740(3)	2271(2)	-152(2)	15(1)
C(7)	9714(3)	5391(2)	1548(2)	12(1)
C(8)	9062(3)	6191(2)	1997(2)	13(1)
C(9)	9979(3)	6930(2)	2615(2)	17(1)
C(10)	11552(3)	6892(2)	2793(2)	19(1)
C(11)	12227(3)	6098(2)	2362(2)	18(1)
C(12)	11311(3)	5354(2)	1746(2)	15(1)
C(13)	5720(3)	706(2)	-1174(2)	25(1)
C(14)	6747(3)	6965(2)	2206(2)	23(1)

Cu_2I_2 ring into a two-dimensional layer of the complex (Fig. 3). The N(1) and N(2) atoms of the ligand molecules are not involved in coordination to the Cu(I) center. The directions of the aromatic rings indicate the presence of a strong edge to face π - π stacking interactions between the aromatic ring (C1-C6) and H(4A) with a distance of 2.583 $\text{\AA}$ ($x, 1/2-y, -1/2+z$) and mild face-to-face π - π stacking interactions between the aromatic rings (C1-C6) and (C7-C12) with a distance of 3.651 $\text{\AA}$ ($2-x, 1-y, -z$). These interactions extend the one-dimensional supermolecular chain further into a two-dimensional network (Fig. 3).

Table 3 Selected bond lengths ($\text{\AA}$) and bond angles ($^\circ$)

Atoms	Distances
I(1)-Cu(1A)	2.5716(4)
I(1)-Cu(1)	2.5750(4)
Cu(1)-N(3)	2.0003(19)
Cu(1)-O(2)	2.3298(17)
Cu(1)-I(1A)	2.5716(4)
Cu(1)-Cu(1A)	2.5996(6)
Angles	
Cu(1A)-I(1)-Cu(1)	60.677(13)
N(3)-Cu(1)-O(2)	74.86(7)
N(3)-Cu(1)-I(A1)	122.03(6)
O(2)-Cu(1)-I(A1)	102.27(5)
N(3)-Cu(1)-I(1)	115.49(6)
O(2)-Cu(1)-I(1)	109.79(5)
I(A1)-Cu(1)-I(1)	119.323(13)
N(3)-Cu(1)-Cu(A1)	161.99(6)
O(2)-Cu(1)-Cu(A1)	123.07(4)
I(A1)-Cu(1)-Cu(A1)	59.727(13)
I(1)-Cu(1)-Cu(A1)	59.596(13)

Fig. 3 Perspective view of the two-dimensional structure of the complex $[\text{Cu}_2\text{I}_2\text{L}_2]$.

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