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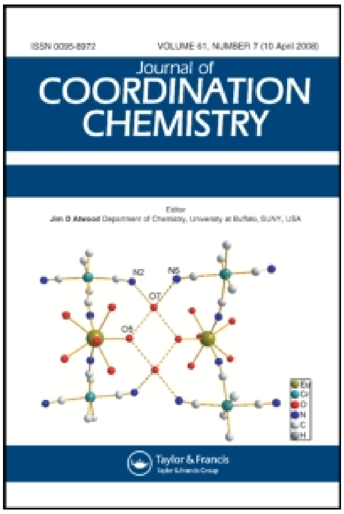

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TRANSITION METAL COMPLEXES WITH HYDRAZIDES AND HYDRAZONES. PART 8[1]. X-RAY CRYSTAL STRUCTURE OF A *CATENA*-POLYBROMO (ACETONE-1-NAPHTHOYLHYDRAZONE) COPPER(II)-COPPER(I) COMPLEX

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NOTE

TRANSITION METAL COMPLEXES WITH HYDRAZIDES AND HYDRAZONES. PART 8[1]. X-RAY CRYSTAL STRUCTURE OF A *CATENA*-POLYBROMO (ACETONE-1-NAPHTHOYLHYDRAZONE) COPPER(II)–COPPER(I) COMPLEX

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The title compound [$Cu_3Br_4C_{28}H_{28}N_4O_2$] is a type of polymeric three-centre octahedral-trigonal planar coordination complex. The copper(II) atom located at a centre of symmetry is six-coordinate with two bidentate (N3, O1) ligands of acetone-1-naphthoylhydrazone forming the equatorial plane and two bromine ions in axial positions (Cu1-Br1 = 2.946(1)Å). The ligands are in *trans* positions. The Cu(I) atoms are in trigonal planar coordination by two bridging Br^- ions (Cu2-Br2 = 2.412(1)Å, Cu2-Br2* = 2.407(2)Å) which connect two Cu(I) atoms and a third bromine ion shared with the octahedral Cu(II) ion (Cu2-Br1 = 2.304(1)Å). The arrangement forms an infinite chain along the *b* axis.

KEYWORDS: acetone-1-naphthoylhydrazone, bromide, copper, polymer, X-ray structure

INTRODUCTION

Within the framework of a systematic study of transition metal complexes with hydrazides and hydrazones[1–9] we present here the structure of a newly synthesized

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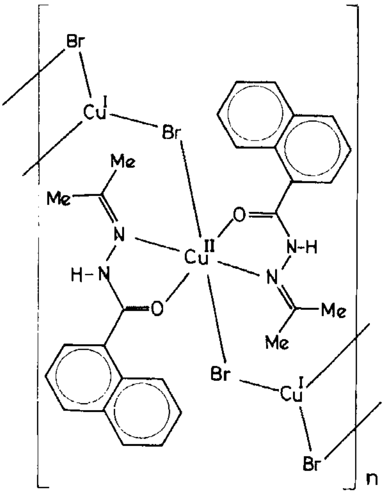
polymeric copper(II)-copper(I) complex with acetone-1-naphthoylhydrazone (Scheme 1).



Scheme 1

EXPERIMENTAL

Dark green, single crystals of the complex were obtained by slow evaporation of an EtOH/Me_2CO (6:4 v/v) solution of $CuBr_2$ and acetone-1-naphthoylhydrazone at mol ratio 1:1. A single crystal of dimensions 0.24 × 0.20 × 0.12 mm was mounted on an Enraf-Nonius turbo CAD-4 diffractometer equipped with a graphite monochromator. Intensities were recorded with MoK_α radiation (λ = 0.71070Å) using the ω-2θ scan technique in the range $2.40 < \theta < 32.0°$. Three standard reflections were monitored every hour; no decay correction was applied. Cell constants were determined by least-squares refinement of diffractometer angles for 25 automatically centred reflections collected in the range $15.96 < \theta < 16.89°$.

Data were corrected for Lorentz and polarization effects. Computations were carried out for data collection, cell refinement and data reduction, with the MolEN package.[10] The structure was solved by direct methods with SHELXS86,[11] and the program used to refine the structure was SHELX76.[12] Positions of hydrogen atoms were generated from assumed geometry, checked in a $\Delta\rho$ map and refined isotropically. For methyl hydrogens and the nitrogen H2 atom a common isotropic displacement parameter was calculated (U = 0.081(9)Å^2). A residual maximum ($\Delta\rho_{max}$ = 1.81 eÅ^{-3}) appears in the vicinity of Br1 and probably corresponds to the position of a free electron pair. Atomic scattering factors for Cu^{2+}, Cu^+ and Br^- were taken from International Tables for X-ray Crystallography (1974), Vol. IV, Table 2.2B.[13] Software used to prepare the material for publication was CSU[14] and, for molecular graphics, PLUTO.[15] All calculations were carried out on a PC/AT computer.

Crystal data and refinement parameters are given in Table I. Fractional atomic coordinates and their equivalent isotropic displacement parameter, are given in

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Table I Summary of crystal data, intensity collection and structure refinement for the complex.

Crystal data	
Chemical formula	1/2 $[Cu_3Br_4C_{28}H_{28}N_4O_2]$
Formula weight	481.40
Crystal system	triclinic
Space group	$P\bar{1}$
Cell constants	a = 7.510(1)Å
	b = 9.700(1)Å
	c = 11.570(1)Å
	α = 99.38(1)°
	β = 106.20(1)°
	γ = 91.49(1)°
	V = 796.4(2)$Å^3$
Z	2
F(000)	492
D_x	2.007 Mgm^{-3}
Radiation	MoK_α (λ = 0.71073 Å)
μ	6.994 mm^{-1}
Measurement temperature	294K
Data collection	
Min. and Max. transmission values	T_{min} = 0.82, T_{max} = 0.98
No. of reflections measured	5788
No. of independent reflections	5505
No. of observed reflections	2954
Criterions for observed reflections	$F > 3\sigma(F)$
R_{int}	0.019
Max. value of θ	31.99°
Range of h,k,l	h = $-11 \rightarrow 11$
	k = $0 \rightarrow 14$
	l = $-17 \rightarrow 16$
Refinement	
Final R	0.051
R_w	0.041
Weight scheme	$1/\sigma^2(F)$

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Table II. Selected bonding parameters are listed in Table III. A perspective view of the molecule with atom numbering for non-hydrogen atoms is shown in Figure 1.

RESULTS AND DISCUSSION

Structure of $[Cu_3Br_4C_{28}H_{28}N_4O_2]$

As depicted in Figure 1, the Cu(II) cation fixed deliberately at the unit cell origin is surrounded by two bidentate 1-naphthoylhydrazone ligands forming an elongated coordination octahedron (Table III) together with two, also centre-of-symmetry related Br^- ions. The Cu1-Br1 distance is 2.946(1)Å and is similar to those observed by Willett and coworkers[16,17] while the two symmetry-independent bonds, Cu1-O1 = 1.923(4) and Cu1-N3 = 2.080(4)Å are shorter but common for equatorial ligand positions.[18,19,20] Both Br^- ions are coordinated subsequently to Cu(I) cations with a much shorter Cu2-Br2 distance of 2.304(1)Å. The Cu1-Br1-Cu2 angle is 93.2(1)°. Each Cu(I) cation is on a plane (Δ = 0.0026Å) formed by three Br^- anions in a triangular array. Two of these are the centre of symmetry

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Table II Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) with e.s.d.'s in parentheses for the non-hydrogen atoms; $U_{eq} = 1/3\ \Sigma_i \Sigma_j U_{ij} a^*_i a^*_j a_i a_j$.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Cu1*	0.0000(0)	0.0000(0)	0.0000(0)	0.0402(2)
Cu2	-0.1118(1)	0.3758(1)	-0.0421(1)	0.0606(2)
Br1	-0.2992(1)	0.1701(1)	-0.1104(1)	0.0538(2)
Br2	-0.0679(1)	0.5232(1)	0.1544(1)	0.0604(2)
O1	0.0403(5)	-0.0366(4)	-0.1588(3)	0.0430(9)
N2	0.2594(6)	0.1393(5)	-0.0831(4)	0.0378(11)
N3	0.2170(5)	0.1510(4)	0.0290(3)	0.0326(10)
C1	0.1629(7)	0.0410(5)	-0.1744(4)	0.0344(12)
C2	0.3103(7)	0.2470(5)	0.1161(5)	0.0351(12)
C3	0.4446(9)	0.3538(7)	0.0999(6)	0.0487(15)
C4	0.2875(9)	0.2538(7)	0.2406(5)	0.0484(16)
C5	0.2068(6)	0.0289(6)	-0.2929(4)	0.0364(13)
C6	0.2364(8)	0.1504(7)	-0.3331(5)	0.0431(15)
C7	0.2673(8)	0.1464(7)	-0.4481(6)	0.0541(17)
C8	0.2708(8)	0.0205(7)	-0.5187(5)	0.0500(18)
C9	0.2418(7)	-0.1064(6)	-0.4812(5)	0.0422(15)
C10	0.2465(9)	-0.2381(8)	-0.5544(5)	0.0590(20)
C11	0.2176(10)	-0.3573(8)	-0.5179(6)	0.0610(18)
C12	0.1867(9)	-0.3569(7)	-0.4041(6)	0.0527(16)
C13	0.1813(8)	-0.2343(6)	-0.3296(5)	0.0428(14)
C14	0.2078(6)	-0.1040(6)	-0.3651(4)	0.0349(13)

* Occupancy = 0.50.

Table III Selected bond lengths (Å) and angles (°) with e.s.d.'s in parentheses.

Cu1 - Br1	2.946(1)	O1 - Cu1 - Br1	85.7(1)
Cu1 - N3	2.080(4)	N3 - Cu1 - Br1	96.1(1)
Cu1 - O1	1.923(4)	O1 - Cu1 - N3	81.0(2)
Cu1 - N2	2.807(5)	O1 - Cu1 - N3*	99.0(2)
Cu1 - C1	2.709(6)	O1 - Cu1 - Br1*	94.3(1)
Cu1 - Cu2	3.839(1)	N3 - Cu1 - Br1*	83.9(1)
Cu2 - Cu2**	2.773(1)	Cu1 - Br1 - Cu2	93.2(1)
Cu2 - Br2**	2.407(2)	Br2 - Cu2 - Br1	124.6(1)
Cu2 - Br1	2.304(1)	Br2 - Cu2 - Br2**	109.8(1)
Cu2 - Br2	2.412(1)	Br1 - Cu2 - Br2**	125.6(1)
O1 C1	1.244(7)	C6 C7	1.408(10)
N3 N2	1.407(6)	C7 C8	1.359(9)
N3 C2	1.281(5)	C8 C9	1.401(9)
N2 C1	1.326(6)	C9 C10	1.420(9)
C1 C5	1.485(7)	C9 C14	1.432(8)
C2 C3	1.497(9)	C10 C11	1.327(11)
C2 C4	1.489(9)	C11 C12	1.399(11)
C5 C6	1.370(9)	C12 C13	1.359(9)
C5 C14	1.419(7)	C13 C14	1.417(9)

* Symmetry related atoms at $-x$, $-y$, $-z$.
** At $-x$, $1-y$, $-z$.

(0,1/2,0) related Br2 and Br2* ions separated almost equally (2.412(1) and 2.407(2)Å) from Cu(I). They and the centre of symmetry-related Cu2 and Cu2* cations close a quadrilateral with Br2-Cu2-Br2* = 109.8(1)°. The Cu2-Cu2* distance is 2.773(1)Å. This motif is then continued by a second Cu2* – Br2* bond (Figure 1), and also on, forming a zig-zag chain along the *b* axis.

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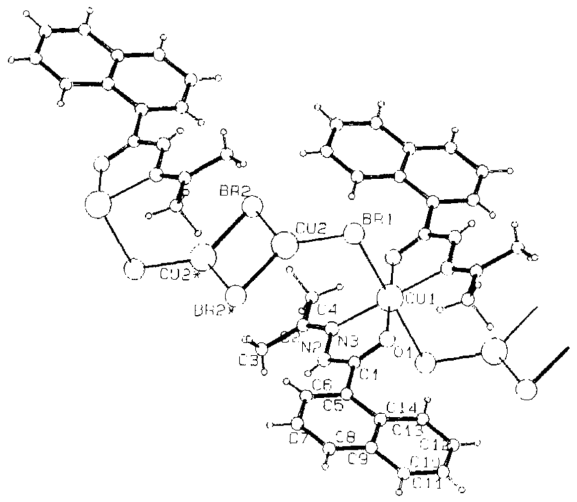

Figure 1 Perspective view of the molecule showing atomic numbering. The H atoms are shown but not labelled.

The geometry of the acetone-1-naphthoylhydrazone ligand is regular. The short N3-C2 distance (1.281(5)Å) indicates a localized double bond, while N2-N3 and N2-C1 bond lengths of 1.407(6) and 1.326(6)Å support the location of the H2 atom in a difference Fourier map followed by its refinement in isotropic mode (N2-H2 = 0.70(7)Å). Partial delocalization of π-electrons is indicated by the O1-C1 and C1-N2 distances of 1.244(7) and 1.326(6)Å, respectively.

Within molecules related by the centre of symmetry, there occurs a network of intramolecular and intermolecular hydrogen bonds of the type C13 – H13. . .O1 (2.957(7)Å, 123.4(4)°) and C4 – H4C. . .O1* (3.029(7)Å, 149.9(58)°; * $-x$, $-y$, $-z$), respectively. The infinite chains along *b* (Figure 2) are connected by weak van der

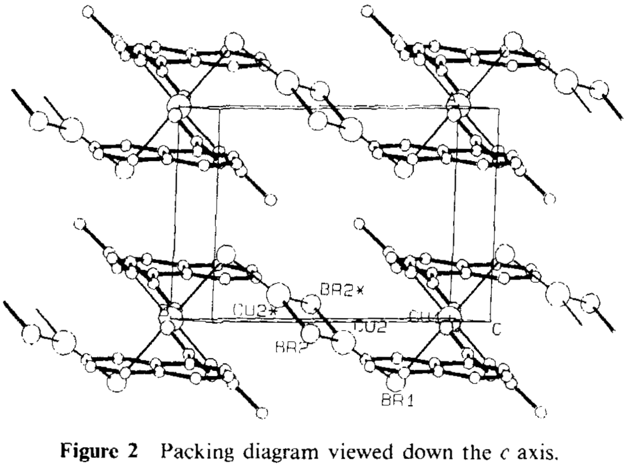

Figure 2 Packing diagram viewed down the *c* axis.

Waals contacts (Br1...N2* = 3.427(5)Å, Br1....H2* = 2.829(72)Å; * $-1+x,y,z$) and form layers parallel to the *ab* plane.

SUPPLEMENTARY MATERIAL

Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms, positional and temperature parameters for hydrogen atoms, bond lengths and angles and mean planes are available from Agneš Kapor upon request.

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