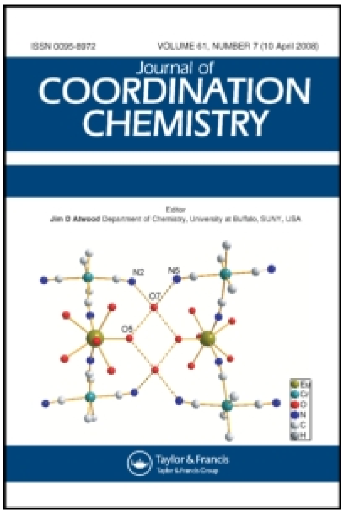

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CRYSTAL AND MOLECULAR STRUCTURE AND MAGNETIC PROPERTIES OF DI-μ-(4-METHYL-PYRIDINE-1-OXIDE)-BIS(DIBROMOCOPPER(II))

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The crystal structure of the oxygen-bridged dimer formed between copper(II) bromide and 4-methylpyridine-1-oxide has been determined and refined to a final *R* value of 0.027. The dinuclear units crystallize in the monoclinic space group $P2_1/c$ with dimensions: $a = 6.086(1)$, $b = 15.064(3)$, $c = 10.469(2)$ Å, $\beta = 106.14(1)°$. Each Cu(II) ion is five coordinate with two bridging oxygen atoms and two bromine atoms in the square base and a bromine atom from an adjacent molecule in the apical site (Cu-0 = 1.983(3), Cu-0' = 2.007(3), Cu-Br(1) = 2.337(1), Cu-Br(2) = 2.346(1), Cu-Br(2)'' = 3.272(1) Å). The temperature dependence of the magnetic susceptibilities shows strong antiferromagnetic coupling. The data fitting procedure to the Bleaney-Bowers-equation gives the parameters $g = 2.05(2)$, $2J = -927(20)\text{cm}^{-1}$, $N\alpha = 64(5)\ 10^{-6}$ c.g.s.u. Structural and magnetic properties are discussed in relation to those of the 1:1 complex formed between copper(II) bromide and pyridine-1-oxide.

INTRODUCTION

The magnetic properties of 1:1 aromatic *N*-oxide bridged copper(II) dimers have been extensively studied[1-7] but only three X-ray structural determinations have been reported. The structures of di-μ-(pyridine-1-oxide)-bis(dichlorocopper(II)),[8-9] di-μ-(4-phenyl-pyridine-1-oxide)-bis(dichlorocopper(II))[10] and di-μ-(pyridine-1-oxide)-bis(dibromocopper(II))[11] have been determined. The various pyridine ring substitutions lead to a very wide experimental range of the exchange interaction in the 1:1 pyridine-*N*-oxide dimers of copper(II) halides[2] but the lack of sufficient crystallographic data has limited an understanding of the empirical relationships.[3,12-14] To continue attempts to understand the factors contributing in sign and magnitude to the exchange interaction in these strongly coupled systems we have calculated the singlet-triplet energy gap using *ab initio* SCF calculations.[15] For these investigations it was necessary to have sufficient structural data to compare the calculated exchange integrals with the experimental ones. Some new complexes have been investigated and we here report the structure and the magnetic properties of the complex di-μ-(4-methyl-pyridine-1-oxide)-bis(dibromocopper(II)).

EXPERIMENTAL

Preparation

Di-μ-(4-methyl-pyridine-1-oxide)-bis(dibromocopper(II)) was prepared by mixing ethanol solutions of 4-methyl-pyridine-1-oxide and copper(II) bromide in a 1:1 molar

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ratio. The dark brown precipitate was filtered off and very slow evaporation of the resulting filtrate yielded dark brown crystals suitable for X-ray analysis. The elemental analysis gave C, 21.86; H, 2.00; N, 4.21%. Calcd. for $C_6H_7NOCuBr_2$: C, 21.68; H, 2.12; N, 4.21%.

X-ray Data Collection and Structure Determination

A needle-shaped crystal measuring approximately 0.54×0.16^2 mm was selected. Lattice constants at 293 K were obtained from a least-squares refinement of the 2θ values of 55 reflections collected on a STOE-SIEMENS AED2 diffractometer. The crystal data are: $C_{12}H_{14}Br_4Cu_2N_2O_2$; Mol. Wt. = 665.0, monoclinic; a = 6.086(1), b = 15.064(3), c = 10.469(2) Å, β = 106.14(1)°; $P2_1/c$, $Z = 4$, V = 922.0 Å^3; D_m (by flotation in $CCl_4/CHBr_3$) = 2.41(2), D_c = 2.396 M g m^{-3}; μ = 107.5 cm^{-1}, $\lambda(MoK_\alpha)$ = 0.71073 A, $F(000)$ = 628. A total of 1966 intensities scanned in the range $4.9° \leq 2\theta \leq 45°$ were measured. 1209 unique reflections were obtained (R_{int} = 0.029) giving 1058 with $F_o < 2\sigma(F_o)$ which were used in the analysis. The index range was: h 0/6, $k \pm 16$, $l \pm 11$. Three standard reflections (102, 141, 102) measured every hour showed constant intensity. Absorption corrections were made with transmission factors 0.30–0.43.

The structure was solved by direct methods and Fourier maps using the SHELX-76 package.[16] Full-matrix least-squares refinement with isotropic thermal parameters converged to the R value of 0.37. Refinement with anisotropic thermal parameters and geometrical positioning of all hydrogen atoms (C–H distance = 1.08 Å) led to the final values of $R = 0.027$ and $R_W = 0.020$ ($W = 1/\sigma^2(F)$) for 104 variables. The atomic factors were taken from the "International Tables for X-ray Crystallography".[17] The final atomic coordinates for heavy atoms are given in Table I.

Magnetic measurements

The magnetic susceptibility of crushed selected crystals was measured by the Faraday method at approximately 6×10^6 G^2 cm^{-1} (G = 10^{-4}T) using Hg[Co(SCN)$_4$] as a susceptibility standard. Experimental susceptibility data were corrected for underlying diamagnetism. To convert into S.I. units χ should be multiplied by $4\pi \times 10^{-6}$. The exchange parameters were obtained using a modified simple routine.[18] The function minimized was $\Sigma\,(\chi_{esp} - \chi_{calc})/\chi_{exp}$.

TABLE I
Positional parameters with e.s.d.'s in parentheses.

Atom	x/a	y/b	z/c
Cu	0.2468(1)	0.4804(1)	0.4013(1)
Br(1)	0.1422(1)	0.3647(1)	0.2477(1)
Br(2)	-0.0849(1)	0.5675(1)	0.3338(1)
O	0.5404(5)	0.4250(2)	0.5002(3)
N	0.5887(6)	0.3379(3)	0.4884(3)
C(1)	0.7225(8)	0.3159(3)	0.4120(4)
C(2)	0.7685(9)	0.2274(3)	0.3951(4)
C(3)	0.6704(8)	0.1615(4)	0.4538(4)
C(4)	0.5296(9)	0.1891(3)	0.5313(4)
C(5)	0.4916(9)	0.2770(3)	0.5482(4)
C(6)	0.7129(10)	0.0663(3)	0.4343(5)

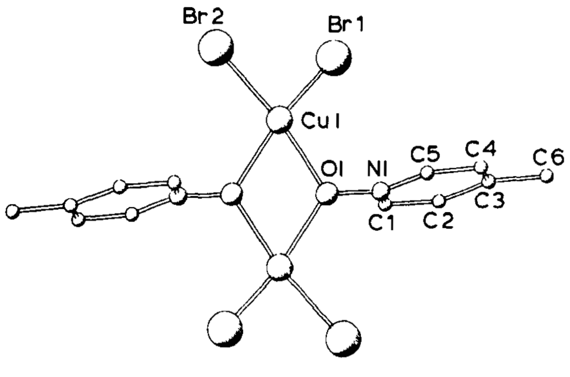

FIGURE 1 Perspective view of $[(C_6H_7NO)CuBr_2]_2$.

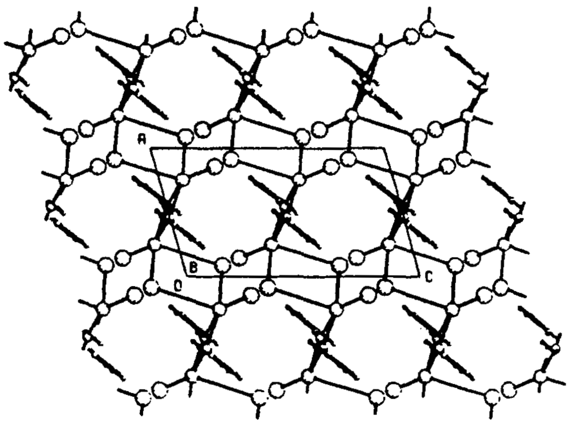

FIGURE 2 View of the unit cell along *b*.

The calculations were performed on the IBM 3081 K computer at the Technische Hochschule Darmstadt. The anisotropic thermal atomic parameters, H-atom parameters, lists of observed and calculated structure factors, experimental and calculated magnetic susceptibilities are available as supplementary material from the editor on request.

RESULTS AND DISCUSSION

X-ray Structure

A perspective view of the complex with atomic labeling is shown in Figure 1 and the packing of the molecules in Figure 2. Selected distances and angles are given in Table II.

The least-squares plane through the pyridine ring and C(6) atoms ($-0.594x - 0.027y - 0.804z + 5.371 = 0$) gives the largest deviation for the C(2) atom, 0.012(2) Å. The dihedral angle between this mean plane and the copper oxygen bridging plane is 73.8° while that in the corresponding bromine complex is 82.0°.[15] The N–O bond makes an angle of 5.1° with the copper-oxygen plane.

TABLE II
Selected distances (Å) and angles (°) with e.s.d.'s in parentheses

Cu–Br(1)	2.337(1)	N–C(1)	1.332(5)
Cu–Br(2)	2.346(1)	C(1)–C(2)	1.384(6)
Cu–O	1.983(3)	C(2)–C(3)	1.387(6)
Cu–O′[a]	2.007(3)	C(3)–C(4)	1.396(6)
Cu–Cu′	3.252(1)	C(4)–C(5)	1.364(6)
Cu–Br(2)″	3.272(1)	C(5)–N	1.338(5)
O–O′	2.311(6)	C(6)–C(3)	1.482(6)
O–N	1.358(4)		
Br(1)–Cu–Br(2)	99.4(1)	O–N–C(1)	118.6(4)
O–Cu–O′	70.8(2)	O–N–C(5)	119.1(4)
Cu–O–Cu′	109.2(2)	N–C(1)–C(2)	119.8(5)
O–Cu–Br(1)	94.5(1)	C(1)–C(2)–C(3)	120.3(4)
O–Cu–Br(2)	165.4(1)	C(2)–C(3)–C(4)	117.0(5)
O–Cu–Br(2)″	84.5(1)	C(3)–C(4)–C(5)	121.2(5)
Br(1)–Cu–Br(2)″	109.2(1)	C(4)–C(5)–N	119.5(4)
Br(2)–Cu–Br(2)″	86.7(1)	C(5)–N–C(1)	122.2(4)
Cu–O–N	123.1(2)	C(6)–C(3)–C(2)	121.2(4)
Cu′–O–N	127.4(4)		

[a] Primed atoms are related to the symmetry positions 1−*x*, 1−*y*, 1−*z*, doubled primed atoms to the symmetry positions −*x*, 1−*y*, 1−*z*.

The oxygen-bridged dimer contains a center of symmetry which requires the two Cu and the two O atoms to lie in a plane. Additionally to the square basal coordination (Br(1), Br(2), O,O′) of copper, a Br(2)″ atom from an adjacent dimeric unit occupies an axial site at a distance of 3.272(1)Å. This leads to infinite chains along the *a* axis (Figure 2). This distance is longer than the Cu–Br″ distance of 3.145(1)A observed in di-μ-(pyridine-1-oxide)-bis(dibromocopper(II)).[15]

Other geometric parameters are directly compared in Table III with those of the 1:1 complex formed between copper(II) bromide and pyridine-*N*-oxide. As mentioned in a theoretical work on this class of compounds,[15] it was necessary to refine the structure of $[(C_5H_5NO)CuBr_2]_2$ for reasons of convergence in the calculations. A comparison of the structural parameters obtained from this refined structure and from the determination

TABLE III
Comparison of selected distances (A) and angles (°) in the $[(C_5H_5NO)CuBr_2]_2$ and $[(C_6H_7NO)CuBr_2]_2$ complexes.

	$[(C_5H_5NO)CuBr_2])_2$[a]	$[(C_5H_5NO)CuBr_2]_2$[b]	$[(C_6H_7NO)CuBr_2]_2$[c]
Cu–O	1.965(9)	2.000(5)	1.983(3)
Cu–O′[d]	1.994(6)	1.994(5)	2.007(3)
Cu–Cu′	3.244(2)	3.264(1)	3.252(1)
Cu–Br(1)	2.333(2)	2.335(1)	2.337(1)
Cu–Br(2)	2.332(2)	2.342(1)	2.346(1)
Cu–Br(2)″[e]	3.130(3)	3.145(1)	3.272(1)
O–Cu–O′	69.9(3)	70.4(2)	70.8(2)
Cu–O–Cu′	110.1(4)	109.6(1)	109.2(2)
dihedral angle between pyridine ring and Cu_2O_2 unit	83.0	82.0	73.8
deviation out of plane			
Br_1/Cu_2O_2 unit	0.18	0.17	−0.87
Br_2/Cu_2O_2 unit	0.16	0.18	+0.38

[a] Reference 11; [b] Refined structure, reference 15; [c] This work; [d] Primed atoms are related by a center of symmetry; [e] Bromine atom of an adjacent molecule.

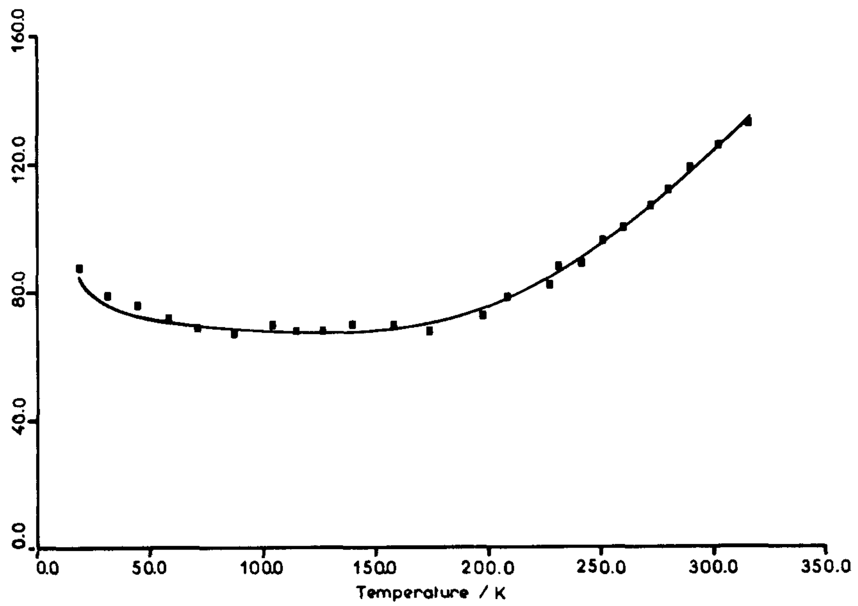

FIGURE 3 Temperature dependence of the magnetic susceptibility of $[(C_6H_7NO)CuBr_2)_2$. The solid line represents the fit to equation (*1*) with the parameters given in the text.

of Whinnery and Watson[11] is also made in Table III. The most significant difference is observed in the Cu–O bond length. The two 1:1 complexes formed between copper(II) bromide and pyridine-*N*-oxide and 4-methylpyridine-*N*-oxide, respectively, present quite similar geometries about the copper atoms. The main difference concerns the deviation of the bromine atoms out of the Cu_2O_2 plane. Br(1) lies 0.87 Å below the Cu_2O_2 plane, while the other one, Br(2), lies 0.38 Å above. In the corresponding bromine derivative[15], both bromine atoms lie 0.17 and 0.18 Å respectively above this plane.

Magnetic Properties

The temperature dependence of the magnetic susceptibility of the dimer is shown in Figure 3. Measurements were carried out in the temperature range 19.4–315.6 K. The temperature dependence of the magnetic susceptibility is characteristic of strongly spin-coupled copper(II) dimers with a very small amount of paramagnetic impurities. Fitting the experimental susceptibilities to the Bleaney-Bowers equation (*1*)

$$\chi_{\mathrm{dim.}}/2 = (1-x)\,\frac{N_A \cdot g^2 \cdot \beta^2}{kT}\left[\frac{1}{3+\exp(-2J/kT)}\right] + \frac{x \cdot N_A \cdot g^2 \cdot \beta^2}{4kT} + N\alpha \qquad (1)$$

(corrected for the presence of paramagnetic impurities and the temperature independent paramagnetism, $N\alpha$), we obtained the calculated exchange parameters resulting from the isotropic Heisenberg-Dirac-van Vleck model: $g = 2.05(2)$, $x = 0.0012(4)$, $N\alpha = 64(5)\ 10^{-6}$ c.g.s.u. and $2J = -927(20)\,\mathrm{cm}^{-1}$. The uncertainties given in parentheses for g, x and 2J are taken from correlation effects within the non-linear optimization; for $N\alpha$ the error in χ_{diam} is assumed. Figure 3 shows good agreement between the experimental and calculated values. This new structurally investigated dimer presents strong exchange coupling as usually observed in the series of the 1:1 pyridine-*N*-oxide bridged copper(II) dimers. This coupling is comparable to that of the 1:1 complexes formed between copper(II) bromide and pyridine-*N*-oxide[3] ($2J = -935$ cm^{-1}) or copper(II) bromide and 3-methylpyridine-N-oxide[3] ($2J = -990$ cm^{-1}). The quite similar geometric factors of the two bromine derivatives, $[(C_5H_5NO)CuBr_2]_2$ and $[(C_6H_7NO)CuBr_2]_2$ explain the comparable exchange interactions.

We studied recently with theoretical treatments the geometric parameter effects on the exchange interaction in this class of compounds and pointed out the significant importance of slight geometric variations on the calculated splitting energy. To carry on these investigations, it would be necessary to dispose of structural data for aromatic-*N*-oxide dimers which present an exchange coupling very different to that usually experimentally observed in this class of compounds (about -1000 cm^{-1}). These structural data are required to extend the relationships between structural factor effects and experimentally observed couplings and calculated singlet-triplet energy gaps.

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