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STRUCTURE OF 3,7-DIAZABICYCLO-[3.3.1]NONANE COMPLEXES AS THE BASIS OF CREATING NEW METALLOCYCLIC SUPRAMOLECULAR ENSEMBLES*

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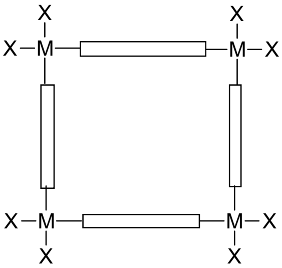
The molecular and crystal structure of the complex of cupric bromide with 1,5-diphenyl-3,7-dimethyl-3,7-diazabicyclo[3.3.1]nonan-9-ones was studied. The geometry of the complexes of bispydines with cupric halides was shown to depend on the substituent at the nitrogen atom.

Keywords: 3,7-diazabicyclo[3.3.1]nonanes, copper complexes, supramolecular ensembles.

There has been considerable interest recently in the construction of supramolecular metallocyclic polygons and polyhedrons [2, 3].



The feasibility of the self-assembly of discrete metallocyclic structures is a function of the coordination polyhedron of the metal complexing agent and geometry of the orientation of the donor electron pairs of the ligand(s). Infinite polymeric complexes are predominantly formed using free metal ions and linear and/or "angular" ligands [4]. The preparation of discrete structures requires that some of the coordination vacancies of the metal be occupied by additional strongly bound ligands. For example, a square tetramer is formed using the complex of palladium(II) in reaction with 1,3-bis(diphenylphosphino)propane with 4,4'-dipyridine [2].

We have investigated the use of chelating bidentate ligands derived from 3,7-diazabicyclo[3.3.1]nonane (bispydine) as new reagents for obtaining supramolecular metallocycles.

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* Part 4 of the series Complexing Capacity of 3,7-Diazabicyclo[3.3.1]nonanes. Part 3, see Ref. [1]. Dedicated to Prof. N. S. Zefirov on his sixty-fifth birthday.

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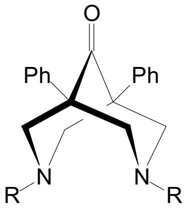
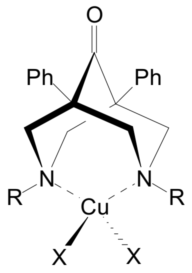
The major coordination features of bispydines permitting such use are [1, 5, 6]: 1) fixation of the double chair conformation upon complexation leads to stable 2-metal-1,3-diazaadamantane structure with a rigidly set distance between the nitrogen atoms and virtually constant nitrogen–metal–nitrogen bond angle and 2) in the case of formation of 1:1 complexes, coordination vacancies remain at the metal atom, which may be utilized for chelate bonds with a linear linking ligand.

Important questions concern the orientation of these coordination bonds and the factors controlling the geometry of the complexes. For ideal tetrahedral coordination, in which the angle between the linear ligands is 109°, we would expect the formation of pentamer structures. For square planar coordination, as in the case of palladium and platinum [3], the probability of obtaining square tetramers is high. Realization of a whole spectrum of angles between the linking ligands and, thus, the creation of metal complexes with different structures are possible when the coordination polyhedron of the metal is distorted.

As shown in [1, 5, 6], ligands **1a-c** form 1:1 complexes with cupric chloride and bromide. Increasing bulk of the substituent at the nitrogen atom in the chloride complexes leads to a significant distortion of the tetrahedral coordination of the cupric ion, specifically, compression of the angle between the N–Cu–N and Cl–Cu–Cl planes and decrease in the Cl–Cu–Cl bond angle [1]. The structural data obtained for chloride **2b** and bromide **3b** with ligand **1b** indicate very similar geometries of these complexes, suggesting that the structure of the complex is independent on the halide for bispydine ligands.



1a, 1b, 1c



2a–c, 3a–c

1a R = Me; **1b** R = Et; **1c** R = allyl;
2a-c X = Cl; **3a-c** X = Br

The crystal structure of **3a** (Fig. 1) was studied to find evidence for this hypothesis. Complex **3a** was found isostructural to the complex of 3,7-dimethyl-1,5-diphenyl-3,7-diazabicyclo[3.3.1]nonan-9-one with cupric chloride (**2a**) [5]. The bond lengths (except for the copper–halogen bonds) and bond angles in **2a** coincide with those for complex **3a** within experimental error. The bond lengths and angles for compound **3a** are given in Tables 1 and 2. The complex molecule in the crystal has approximately C_2 symmetry and the coordination polyhedron of the central cupric ion is a distorted tetrahedron (the ligand–Cu–ligand bonds are in the range from 88.4 to 118.7°). The small value for the N–Cu–N angle (88.4°) is probably related to the steric requirements of the bicyclic ligand. The bispydine fragment in **3a** has double chair conformation, in contrast to the geometry found for free ligand **1a**, which exists in chair–boat conformation [7].

In searching for structure of complexes of cupric ions with coordination number 4 such as $CuBr_2L_2$ (where L is a ligand coordinated at the metal atom by means of a nitrogen atom) using the Cambridge Structural Data Bank (CSDB) [8], we found 22 structures, nine of which have the cupric ion in square planar coordination with *trans* arrangement of the bromide ions, three have the cupric ion in square planar coordination with *cis* arrangement of the bromide ions, and ten have very distorted tetrahedral coordination (the largest ligand–Cu–ligand angle is in the range from 133.8 to 173.2°). Thus, compound **3a** is the first example of a tetrahedral complex of cupric bromide with nitrogen-containing ligands. The Cu–$Br_{(2)}$ bond (2.311(1) Å) is the shortest such bond for this type of complex (2.337-2.494 Å according to the CSDB). We should note the large difference in the Cu–Br bond lengths (0.085(1) Å), which cannot be attributed to steric factors since no short intra- or intermolecular contacts were found in the structure of **3a**.

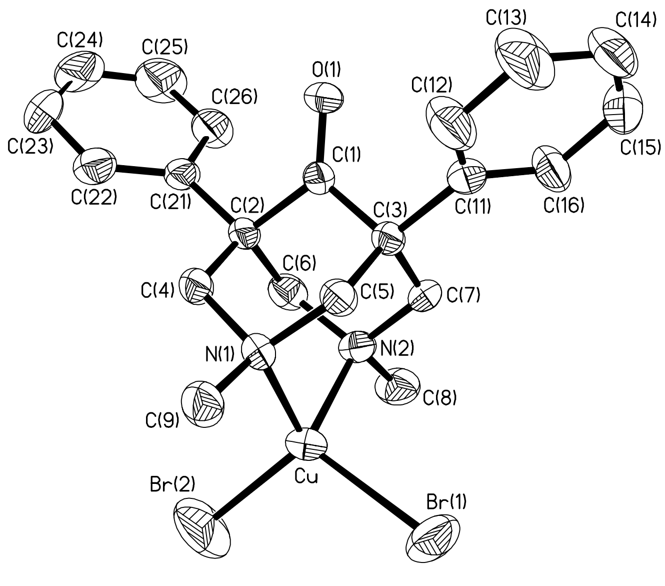


Fig. 1. Molecular structure of complex **3a**.

Crystallographic Data, Experimental Details, and Refinement of the Structure of Compound **3a**

Empirical formula	$C_{21}H_{24}Br_2Cu_1N_2O_1$
Molecular mass	543.78
Crystal size, mm	0.3 × 0.2 × 0.2
Color, habitus	Red-brown parallelepipeds
Symmetry	Monoclinic
Space group	$P2_1/n$
a, Å	7.940(2)
b, Å	20.803(4)
c, Å	13.127(3)
β, deg.	99.08(3)
V, Å^3	2141.1(8)
Z	4
Calculated density, g/cm^3	1.687
F(000)	1084
μ(MoKα), mm^{-1}	4.765
Scan type/width, deg.	ω / 1.0 + 0.35tan(θ)
Scanning region over θ, deg.	2.51 - 25.00
Reflection index ranges	$-10 \leq h \leq 10$
	$-22 \leq k \leq 29$
	$-12 \leq l \leq 18$
Reflections measured	5424
Independent reflections	3358 (R_{int} = 0.0653)
Reflections with $I > 2\sigma(I)$	2062
Refinement perameters	247
R-factors for $I > 2\sigma(I)$	R_1 = 0.0602, wR_2= 0.1471
over all reflections	R_1 = 0.1211, wR_2= 0.1710
Weighting sheme, w^{-1}	$\sigma^2(F_o^2) + (0.1029 - P)^2$, where $P = (F_o^2 + 2F_c^2)/3$
Fit according to F^2	1.027
Extinction coefficient	0.0025(7)
Residual electron density, min/max, e/Å^3	-0.775 / 1.405 (near Br atom)

TABLE 1. Bond Lengths (*d*) in Compound **3a**

Bond	*d*, Å	Bond	*d*, Å
Cu–$N_{(2)}$	1.975(6)	$C_{(3)}$–$C_{(7)}$	1.514(9)
Cu–$N_{(1)}$	1.992(5)	$C_{(3)}$–$C_{(5)}$	1.539(9)
Cu–$Br_{(2)}$	2.311(1)	$C_{(3)}$–$C_{(11)}$	1.563(9)
Cu–$Br_{(1)}$	2.395(1)	$C_{(11)}$–$C_{(12)}$	1.35(1)
$O_{(1)}$–$C_{(1)}$	1.199(8)	$C_{(11)}$–$C_{(16)}$	1.38(1)
$N_{(1)}$–$C_{(9)}$	1.479(9)	$C_{(12)}$–$C_{(13)}$	1.38(1)
$N_{(1)}$–$C_{(4)}$	1.486(8)	$C_{(13)}$–$C_{(14)}$	1.36(1)
$N_{(1)}$–$C_{(5)}$	1.494(8)	$C_{(14)}$–$C_{(15)}$	1.32(1)
$N_{(2)}$–$C_{(8)}$	1.475(9)	$C_{(15)}$–$C_{(16)}$	1.40(1)
$N_{(2)}$–$C_{(6)}$	1.477(9)	$C_{(21)}$–$C_{(22)}$	1.38(1)
$N_{(2)}$–$C_{(7)}$	1.488(8)	$C_{(21)}$–$C_{(26)}$	1.39(1)
$C_{(1)}$–$C_{(3)}$	1.516(9)	$C_{(22)}$–$C_{(23)}$	1.41(1)
$C_{(1)}$–$C_{(2)}$	1.548(9)	$C_{(23)}$–$C_{(24)}$	1.35(1)
$C_{(2)}$–$C_{(21)}$	1.530(9)	$C_{(24)}$–$C_{(25)}$	1.37(1)
$C_{(2)}$–$C_{(6)}$	1.53(1)	$C_{(25)}$–$C_{(26)}$	1.39(1)
$C_{(2)}$–$C_{(4)}$	1.53(1)		

Thus, the geometry of the coordination of the metal in complexes of bispydines **1** with cupric halides is a function of the nature of substituent R. If R = Me, the complex has slightly distorted tetrahedral structure and the ligand–Cu–ligand angle is 110-110.9°. Extension of the alkyl radical at the nitrogen atom in bispydines leads to greater distortion of the complex geometry and the ligand–Cu–ligand angle is 104.1-104.4°.

TABLE 2. Bond Angles (ω) in Compound **3a**

Angle	ω, deg.	Angle	ω, deg.
$N_{(2)}$–Cu–$N_{(1)}$	88.4(2)	$C_{(7)}$–$C_{(3)}$–$C_{(1)}$	106.3(5)
$N_{(2)}$–Cu–$Br_{(2)}$	118.7(2)	$C_{(7)}$–$C_{(3)}$–$C_{(5)}$	112.4(5)
$N_{(1)}$–Cu–$Br_{(2)}$	115.5(2)	$C_{(1)}$–$C_{(3)}$–$C_{(5)}$	108.1(5)
$N_{(2)}$–Cu–$Br_{(1)}$	105.8(2)	$C_{(7)}$–$C_{(3)}$–$C_{(11)}$	111.9(5)
$N_{(1)}$–Cu–$Br_{(1)}$	116.9(2)	$C_{(1)}$–$C_{(3)}$–$C_{(11)}$	109.1(5)
$Br_{(2)}$–Cu–$Br_{(1)}$	110.07(6)	$C_{(5)}$–$C_{(3)}$–$C_{(11)}$	108.9(5)
$C_{(9)}$–$N_{(1)}$–$C_{(4)}$	108.4(5)	$N_{(1)}$–$C_{(4)}$–$C_{(2)}$	113.3(5)
$C_{(9)}$–$N_{(1)}$–$C_{(5)}$	109.8(6)	$N_{(1)}$–$C_{(5)}$–$C_{(3)}$	113.2(5)
$C_{(4)}$–$N_{(1)}$–$C_{(5)}$	109.1(5)	$N_{(2)}$–$C_{(6)}$–$C_{(2)}$	113.9(5)
$C_{(9)}$–$N_{(1)}$–Cu	106.8(4)	$N_{(2)}$–$C_{(7)}$–$C_{(3)}$	113.9(5)
$C_{(4)}$–$N_{(1)}$–Cu	112.5(4)	$C_{(12)}$–$C_{(11)}$–$C_{(16)}$	118.6(7)
$C_{(5)}$–$N_{(1)}$–Cu	110.2(4)	$C_{(12)}$–$C_{(11)}$–$C_{(3)}$	120.1(7)
$C_{(8)}$–$N_{(2)}$–$C_{(6)}$	109.4(6)	$C_{(16)}$–$C_{(11)}$–$C_{(3)}$	121.2(7)
$C_{(8)}$–$N_{(2)}$–$C_{(7)}$	108.9(5)	$C_{(11)}$–$C_{(12)}$–$C_{(13)}$	120.9(8)
$C_{(6)}$–$N_{(2)}$–$C_{(7)}$	111.5(5)	$C_{(14)}$–$C_{(13)}$–$C_{(12)}$	120.7(9)
$C_{(8)}$–$N_{(2)}$–Cu	106.7(4)	$C_{(15)}$–$C_{(14)}$–$C_{(13)}$	119.0(8)
$C_{(6)}$–$N_{(2)}$–Cu	108.7(4)	$C_{(14)}$–$C_{(15)}$–$C_{(16)}$	121.6(8)
$C_{(7)}$–$N_{(2)}$–Cu	111.4(4)	$C_{(11)}$–$C_{(16)}$–$C_{(15)}$	119.1(8)
$O_{(1)}$–$C_{(1)}$–$C_{(3)}$	124.9(6)	$C_{(22)}$–$C_{(21)}$–$C_{(26)}$	118.0(7)
$O_{(1)}$–$C_{(1)}$–$C_{(2)}$	123.9(6)	$C_{(22)}$–$C_{(21)}$–$C_{(2)}$	122.4(7)
$C_{(3)}$–$C_{(1)}$–$C_{(2)}$	111.1(5)	$C_{(26)}$–$C_{(21)}$–$C_{(2)}$	119.6(7)
$C_{(21)}$–$C_{(2)}$–$C_{(6)}$	109.4(6)	$C_{(21)}$–$C_{(22)}$–$C_{(23)}$	120.4(8)
$C_{(21)}$–$C_{(2)}$–$C_{(4)}$	111.3(6)	$C_{(24)}$–$C_{(23)}$–$C_{(22)}$	119.9(8)
$C_{(6)}$–$C_{(2)}$–$C_{(4)}$	112.6(5)	$C_{(23)}$–$C_{(24)}$–$C_{(25)}$	120.9(8)
$C_{(21)}$–$C_{(2)}$–$C_{(1)}$	110.3(5)	$C_{(24)}$–$C_{(25)}$–$C_{(26)}$	119.4(9)
$C_{(6)}$–$C_{(2)}$–$C_{(1)}$	107.2(5)	$C_{(21)}$–$C_{(26)}$–$C_{(25)}$	121.3(8)
$C_{(4)}$–$C_{(2)}$–$C_{(1)}$	105.9(6)		

EXPERIMENTAL

Complex **3a** was synthesized according to a method described in our previous work [1]. The crystals for X-ray diffraction structural analysis were grown in chloroform. The diffraction study of **3a** was carried out on an Enraf–Nonius CAD4 automatic diffractometer at room temperature using MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) with a graphite monochromator. The structure was solved by the direct method using the SHELX-86 program [9]. All the non-hydrogen atoms were refined anisotropically by the full-matrix method of least squares relative to F^2 (SHELXL-93 [10]). The hydrogen atoms were placed at the calculated positions and refined according to the rider scheme.

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