Chemistry of Heterocyclic Compounds, Vol. 33, No. 3, 1997

SYNTHESIS AND SPECTRA OF COPPER(II) CHLORIDE AND COPPER(II) BROMIDE COMPLEXES OF BISPIDINES. MOLECULAR AND CRYSTAL STRUCTURE OF COPPER CHLORIDE COMPLEXES OF 1,5-DIPHENYL-3,7-DI(2-CYANOETHYL)-9-BISPIDONE AND COPPER BROMIDE COMPLEXES OF 1,5-DIPHENYL-3,7-DIALLYL-9-BISPIDONE*

S. Z. Vatsadze, V. K. Bel'skii, S. E. Sosonyuk,
N. V. Zyk, and N. S. Zefirov

By reaction of copper(II) chloride and bromide with the 1,5-diphenyl-3,7-dialkyl-9-bispidone series, we have synthesized a number of new complex compounds. In the IR spectra of the complexes, the absorption band for the carbonyl group is shifted toward longer wavelengths compared with the original ligands. This shift can be a criterion indicating formation of complexes of the given composition and structure. We have determined the crystal structure of two new complexes. We show that for complexes with alkylmethyl substituents at the nitrogen atoms, significant distortion of the coordination environment of the metal compared with the methyl analog is typical; this distortion is connected with the interaction between the substituents and the halogen atoms. We hypothesize that this type of interaction affects the structure and spectral properties of the complexes in solution.

Ligand design is a key method in coordination chemistry for creation of selective complexing agents and obtaining complexes with specified properties. Well-known effects include the chelate effect and the effect of podands, crown ethers, and cryptands [2]. The closer the conformation of the free ligand is to its conformation in the complex, the more *spatially preorganized* is the ligand, and complexes with such ligands exhibit high stability [2]. As seen from these standpoints, 3,7-diazabicyclo[3.3.1]nonanes and their structural analogs have the following quite promising complexing properties: first of all, the presence of two donor atoms suggests a possible chelate effect; secondly, rigid fixation of the geometry for the direction of the unshared electron pairs of the nitrogen atoms and the distance between them in the double chair conformation suggests spatial preorganization for selective complexation [3].

X-ray diffraction data show that bispidines and their structural analogs in fact are bidentate ligands and form 1:1 complexes with chlorides of copper(II), nickel, and cobalt [1, 4-6]. However, no data are available in the literature on the synthesis and structure of the copper bromide complexes, and in the papers known to us on the chlorides there is practically no discussion of the relation between the structure and spectral properties of these compounds. So we synthesized a number of copper chloride and copper bromide complexes of bispidones and obtained structural and spectral data for these compounds.

The complex compounds Ia [5], Ib, IIa [8], IIb, IIIa [1], IIIb, IVa were synthesized from anhydrous $CuCl_2$ and $CuBr_2$ according to the scheme:

---

*Communication 3 in the series "Complexing properties of 3,7-diazabicyclo[3.3.1]nonanes." For Communication 2, see [1].

Chemistry Department, M. V. Lomonosov Moscow State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 356-366, March, 1997. Original article submitted November 25, 1996.

0009-3122/97/3303-0300$18.00

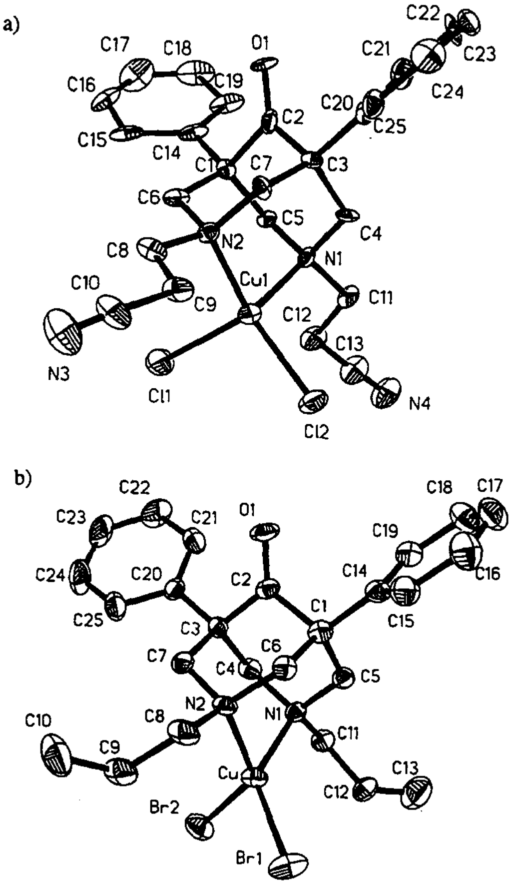
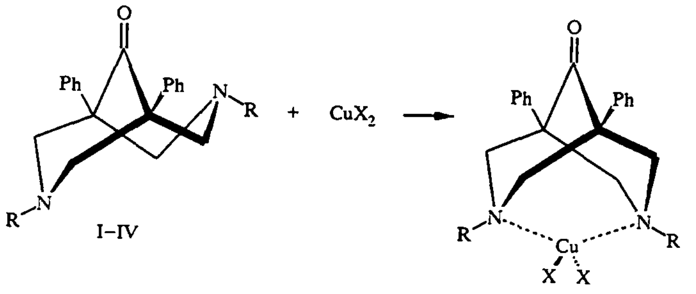


Fig. 1. Perspective view of one of the independent molecules of complex IVa (*a*) and a molecule of complex IIIb (*b*).



I–IV

Ia,b–IIIa,b, IVa

I R = Me, II R = Et, III R = allyl, IV R = CH_2CH_2CN; I–IVa X = Cl, b X = Br

The need to use anhydrous halides was established in synthesis of complex IVa from copper chloride and 3,7-di(2-cyanoethyl)bispidone IV. We could not obtain compounds with satisfactory elemental analysis when using the conventional procedure ($CuCl_2 \cdot 2H_2O$, boiling in ethanol [4]). After repeated attempts, we established that synthesis of compound IVa should be done as follows: Carefully (without stirring) add a solution of an equimolar amount of anhydrous $CuCl_2$ in absolute alcohol to a solution of the ligand in absolute chloroform at room temperature. Let the two-phase system obtained stand for a week in a refrigerator. The crystals growing at the phase interface are the desired product, and do not require further purification. The structure of complex IVa was confirmed by an x-ray diffraction study (Figs. 1a, 2a).

Using this synthesis as an example, we can say that the possibility of the occurrence of a complexation reaction even at low temperatures is due to the specific characteristics of bispidines as ligands. In fact, we have established that the complexes

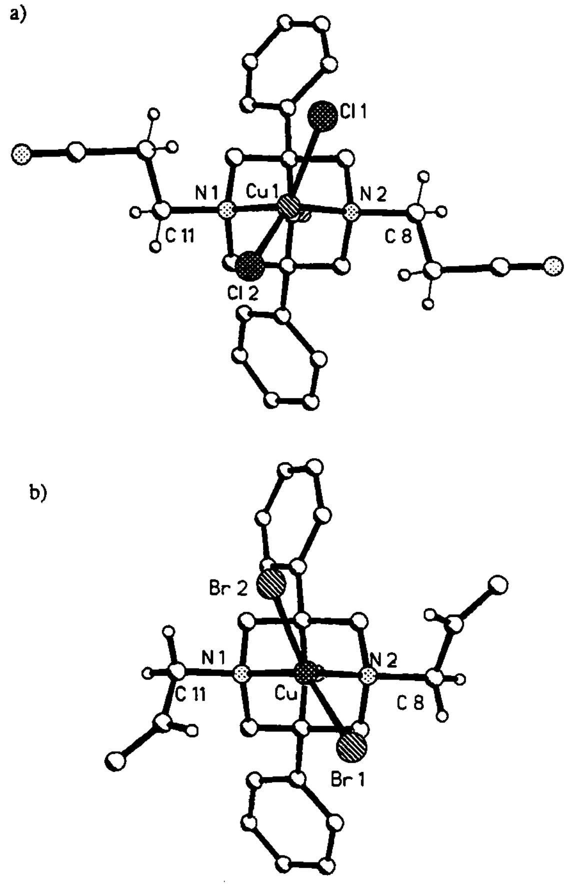


Fig. 2. Projection onto the plane of the methylene groups of the framework of one of the independent molecules of complex IVa (*a*) and a molecule of complex IIIb (*b*).

can also be synthesized under heterophase conditions. When obtaining compounds IIa,b and IIIb, we used chloroform as the solvent for the ligand; the inorganic copper salts are insoluble in chloroform. The process of formation of a chloroform-soluble complex begins even without heating, as was noted from the rapid green coloration of the solution in the case of copper(II) chloride and the rapid brownish-red coloration in the case of copper(II) bromide. The copper bromide complexes are isolated as solvates with chloroform; the structure of one of them (IIIb) was proven by x-ray diffraction (Figs. 1b, 2b).

As was noted in an investigation of compound IIIa [1], in the IR spectrum of the complex the absorption band of the carbonyl group is observed at higher frequencies than for the original ligand, which is also the case for the rest of the complexes we studied in this work. This effect is also apparent in solution, as was shown for the example of complex Ib. An increase in vibrational frequency can occur as a result of geometric changes (for example, a decrease in the angle at the CO group) and/or as a result of electronic factors. From x-ray data for ligand IV [8] and its complex IVa and also complexes IIIa [1] and IIIb and literature data for compound III [9], the $C_1-C_9-C_5$ angle at the carbonyl group decreases on going from the chair–boat conformation of free bispidone to the chair–chair conformation in the complex. However, it is difficult to clearly identify the reason for the observed shifts in the IR spectra, since the appearance of a heavy, charged ion in the structure should affect the dipole moment of the molecule and the nature of the bond vibrations. Nevertheless, the observed shifts are systematic for the complexes and can be used as criteria for complex formation.

We must note the fact that the IR spectra of complexes with like ligands are practically the same over the entire investigated range (4000-700 cm^{-1}). This observation can be widely used in the IR spectroscopic analysis of new bispidone complexes.

In the electronic spectra (220-700 nm, $CHCl_3$) in solutions of all the investigated complexes, we observe absorption bands at 356, 300, and 256 nm for the chlorides and 425, 325, and 240 nm for the bromides, which we have assigned to charge transfer bands in analogy with complexes of isomeric sparteines [10]. The bathochromic shift of the charge transfer band for the bromides is connected with the lower ionization potential of bromine compared with chlorine [11].

TABLE 1. X-Ray Diffraction Conditions for Compounds IIIb and IVa

Parameter	Complex IIIb	Complex IVa
Empirical formula	$C_{26}H_{28}N_2O_2Br_2Cl_3Cu$	$C_{25}H_{28}N_4OCl_2Cu$
Space group	R-3	P 2_1
Z	18	4
a, Å	23,568(3)	10,858(3)
b, Å	23,568(3)	21,844(6)
c, Å	30,382(6)	11,447(3)
α, °	90	90
β, °	90	116,32(3)
γ, °	120	90
Cell volume Å^3	14615(4)	2433,6(2,6)
Density (calc.), g/cm^3	1,493	1,460
Diffractometer	Syntex P-1	Nicolet P3
Scanning	$\theta/2\theta$	$\theta/2\theta$
Absorption coefficient	3,40 mm^{-1}	1,15 mm^{-1}
Radiation	MoKα	MoKα
Number of reflections	2809	2372
Deciphering of structure	Direct method	Direct method
Refinement of structure	Least-squares, F^2	Least-squares, F^2
R	0,065	0,063
Rw	0,171	0,066

TABLE 2. Bond Lengths in the Molecule of Compound IIIb

Bond	d, Å	Bond	d, Å
Cu—N$_{(1)}$	1,999(9)	C$_{(9)}$—C$_{(10)}$	1,29(2)
Cu—N$_{(2)}$	2,027(8)	C$_{(11)}$—C$_{(12)}$	1,47(2)
Cu—Br$_{(1)}$	2,335(2)	C$_{(12)}$—C$_{(13)}$	1,26(2)
Cu—Br$_{(2)}$	2,345(2)	C$_{(14)}$—C$_{(15)}$	1,36(2)
O$_{(1)}$—C$_{(2)}$	1,18(1)	C$_{(14)}$—C$_{(19)}$	1,39(2)
N$_{(1)}$—C$_{(11)}$	1,51(1)	C$_{(15)}$—C$_{(16)}$	1,39(2)
N$_{(1)}$—C$_{(5)}$	1,48(1)	C$_{(16)}$—C$_{(17)}$	1,35(2)
N$_{(1)}$—C$_{(4)}$	1,50(1)	C$_{(17)}$—C$_{(18)}$	1,35(2)
N$_{(2)}$—C$_{(6)}$	1,50(2)	C$_{(18)}$—C$_{(19)}$	1,37(2)
N$_{(2)}$—C$_{(7)}$	1,49(1)	C$_{(20)}$—C$_{(25)}$	1,37(2)
N$_{(2)}$—C$_{(8)}$	1,52(1)	C$_{(20)}$—C$_{(21)}$	1,38(2)
C$_{(1)}$—C$_{(5)}$	1,53(2)	C$_{(21)}$—C$_{(22)}$	1,39(2)
C$_{(1)}$—C$_{(14)}$	1,52(2)	C$_{(22)}$—C$_{(23)}$	1,35(2)
C$_{(1)}$—C$_{(6)}$	1,55(2)	C$_{(23)}$—C$_{(24)}$	1,33(2)
C$_{(1)}$—C$_{(2)}$	1,55(2)	C$_{(24)}$—C$_{(25)}$	1,38(2)
C$_{(2)}$—C$_{(3)}$	1,53(2)	C$_{(26)}$—Cl$_{(1)}$	1,70(2)
C$_{(3)}$—C$_{(20)}$	1,52(2)	C$_{(26)}$—Cl$_{(3)}$	1,72(2)
C$_{(3)}$—C$_{(7)}$	1,53(2)	C$_{(26)}$—Cl$_{(2)}$	1,71(2)
C$_{(3)}$—C$_{(4)}$	1,55(2)	C$_{(27)}$—Cl$_{(4)}$	1,68(1)
C$_{(8)}$—C$_{(9)}$	1,49(2)		

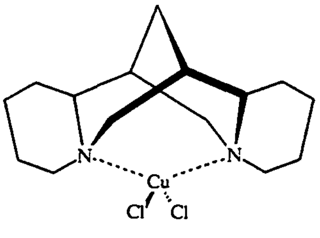
The x-ray diffraction conditions are given in Table 1. The bond lengths and bond angles for compounds IIIb and IVa are presented in Tables 2-5. The crystal structure of IIIb contains two types of solvated chloroform molecules: one of them is found is a special position on a three-fold axis, the other is located in a general position within a void of the structure between molecules of the complex. In the structure of IVa, there are two crystallographically independent molecules of the complex.

In Figs. 1a and 1b, we present a general view of one of the crystallographically independent molecules of complex IVa and a molecule of complex IIIb. In Fig. 2a and 2b, we present projections of the indicated molecules onto the plane of the methylene groups of the framework.

TABLE 3. Bond Angles in the Molecule of Compound IIIb

Angle	ω, degrees	Angle	ω, degrees
N(1)—Cu—N(2)	88,9(4)	C(7)—C(3)—C(4)	112,8(9)
N(1)—Cu—Br(1)	136,5(3)	N(1)—C(4)—C(3)	113,7(9)
N(2)—Cu—Br(1)	101,7(3)	N(1)—C(5)—C(1)	115,9(9)
N(1)—Cu—Br(2)	100,2(3)	N(2)—C(6)—C(1)	112,4(9)
N(2)—Cu—Br(2)	129,6(3)	N(2)—C(7)—C(3)	114,6(9)
Br(1)—Cu—Br(2)	104,44(8)	C(9)—C(8)—N(2)	114(1)
C(11)—N(1)—C(5)	110,0(9)	C(10)—C(9)—C(8)	125(1)
C(11)—N(1)—C(4)	106,0(8)	N(1)—C(11)—C(12)	113(1)
C(5)—N(1)—C(4)	109,6(8)	C(13)—C(12)—C(11)	126(2)
C(11)—N(1)—Cu	110,9(7)	C(15)—C(14)—C(19)	117(1)
C(5)—N(1)—Cu	110,0(6)	C(15)—C(14)—C(1)	125(1)
C(4)—N(1)—Cu	110,3(7)	C(19)—C(14)—C(1)	118(1)
C(6)—N(2)—C(7)	112,1(8)	C(14)—C(15)—C(16)	121(1)
C(6)—N(2)—C(8)	106,1(9)	C(17)—C(16)—C(15)	120(1)
C(7)—N(2)—C(8)	108,3(9)	C(18)—C(17)—C(16)	121(1)
C(6)—N(2)—Cu	111,9(7)	C(19)—C(18)—C(17)	120(1)
C(7)—N(2)—Cu	106,7(7)	C(18)—C(19)—C(14)	121(1)
C(8)—N(2)—Cu	111,8(7)	C(25)—C(20)—C(21)	117(1)
C(5)—C(1)—C(14)	109,2(9)	C(25)—C(20)—C(3)	121(1)
C(5)—C(1)—C(6)	111,5(9)	C(21)—C(20)—C(3)	122(1)
C(14)—C(1)—C(6)	111,0(9)	C(20)—C(21)—C(22)	120(1)
C(5)—C(1)—C(2)	111,1(9)	C(23)—C(22)—C(21)	121(2)
C(14)—C(1)—C(2)	111,1(9)	C(22)—C(23)—C(24)	120(1)
C(6)—C(1)—C(2)	102,8(9)	C(23)—C(24)—C(25)	120(1)
O(1)—C(2)—C(3)	125(1)	C(24)—C(25)—C(20)	122(1)
O(1)—C(2)—C(1)	123(1)	Cl(1)—C(26)—Cl(3)	111(1)
C(3)—C(2)—C(1)	117,9(9)	Cl(1)—C(26)—Cl(2)	114(1)
C(20)—C(3)—C(2)	114,3(9)	Cl(3)—C(26)—Cl(2)	112(1)
C(20)—C(3)—C(7)	111,6(9)	Cl(4)—C(27)—Cl(4)#1	116(1)
C(2)—C(3)—C(7)	103,7(9)	Cl(4)—C(27)—Cl(4)#2	115(1)
C(20)—C(3)—C(4)	105,5(9)	Cl(4)#1—C(27)—Cl(4)#2	115(1)
C(2)—C(3)—C(4)	109,1(9)		

The parameters of the coordination environment of the metal for complexes IIIb and IVa and also for previously studied compounds Ia, IIIa and the copper chloride complex of β-isosparteine Va [6] are presented in Table 6.



Va

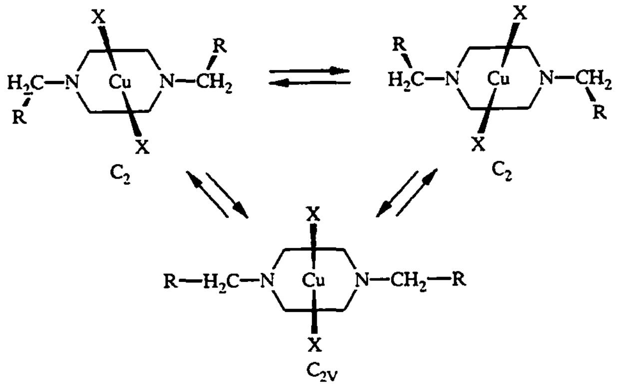
Note the decrease in the halogen−metal−halogen angle with an increase in the distortion of the structure (from complex Va through Ia to IIIa, IIIb, and IVa), which according to our hypothesis in [1] is connected with interaction of the halide ions with substituents at the nitrogen atom. The increase in the angle for the metal−N−carbon atom of the exocyclic substituent ($Cu-N-C_{exocyclic}$) is explained analogously. We also note that there are no fundamental differences between the geometric characteristics of dibromo and dichloro complexes IIIa and IIIb (except for the metal−halogen bond lengths). Consequently, the deviation of the symmetry of the complexes with alkylmethyl groups at the nitrogen from the ideal C_{2v} symmetry is dictated by the nature of the ligands themselves. The need for compact packing in the crystal "freezes in" one of the hindered conformers connected with rotation about the endocyclic N−C bonds. The steric requirements of bulky substi-

TABLE 4. Bond Lengths in the Molecule of Compound IVa

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
$Cu_{(1)}$—$Cl_{(1)}$	2,241(5)	$C_{(14)}$—$C_{(15)}$	1,44(2)	$C_{(1a)}$—$C_{(2a)}$	1,52(2)
$Cu_{(1)}$—$Cl_{(2)}$	2,225(5)	$C_{(14)}$—$C_{(19)}$	1,37(2)	$C_{(1a)}$—$C_{(5a)}$	1,56(2)
$Cu_{(1)}$—$N_{(1)}$	1,99(1)	$C_{(15)}$—$C_{(16)}$	1,44(3)	$C_{(1a)}$—$C_{(6a)}$	1,53(2)
$Cu_{(1)}$—$N_{(2)}$	2,00(1)	$C_{(16)}$—$C_{(17)}$	1,23(4)	$C_{(1a)}$—$C_{(14a)}$	1,49(2)
$O_{(1)}$—$C_{(2)}$	1,18(2)	$C_{(17)}$—$C_{(18)}$	1,35(4)	$C_{(2a)}$—$C_{(3a)}$	1,54(2)
$N_{(1)}$—$C_{(4)}$	1,46(2)	$C_{(18)}$—$C_{(19)}$	1,42(3)	$C_{(3a)}$—$C_{(4a)}$	1,52(3)
$N_{(1)}$—$C_{(5)}$	1,49(2)	$C_{(20)}$—$C_{(21)}$	1,43(2)	$C_{(3a)}$—$C_{(7a)}$	1,50(2)
$N_{(1)}$—$C_{(11)}$	1,53(2)	$C_{(20)}$—$C_{(25)}$	1,37(3)	$C_{(3a)}$—$C_{(20a)}$	1,53(2)
$N_{(2)}$—$C_{(6)}$	1,46(2)	$C_{(21)}$—$C_{(22)}$	1,38(3)	$C_{(8a)}$—$C_{(9a)}$	1,48(2)
$N_{(2)}$—$C_{(7)}$	1,51(2)	$C_{(22)}$—$C_{(23)}$	1,41(3)	$C_{(9a)}$—$C_{(10a)}$	1,47(3)
$N_{(2)}$—$C_{(8)}$	1,51(2)	$C_{(23)}$—$C_{(24)}$	1,35(3)	$C_{(11a)}$—$C_{(12a)}$	1,53(3)
$N_{(3)}$—$C_{(10)}$	1,13(3)	$C_{(24)}$—$C_{(25)}$	1,41(3)	$C_{(12a)}$—$C_{(13a)}$	1,50(3)
$N_{(4)}$—$C_{(13)}$	1,14(3)	$Cu_{(1a)}$—$Cl_{(1a)}$	2,231(6)	$C_{(14a)}$—$C_{(15a)}$	1,39(3)
$C_{(1)}$—$C_{(2)}$	1,57(3)	$Cu_{(1a)}$—$Cl_{(2a)}$	2,205(6)	$C_{(14a)}$—$C_{(19a)}$	1,36(3)
$C_{(1)}$—$C_{(5)}$	1,54(2)	$Cu_{(1a)}$—$N_{(1a)}$	2,01(1)	$C_{(15a)}$—$C_{(16a)}$	1,43(3)
$C_{(1)}$—$C_{(6)}$	1,57(2)	$Cu_{(1a)}$—$N_{(2a)}$	1,98(1)	$C_{(16a)}$—$C_{(17a)}$	1,36(3)
$C_{(1)}$—$C_{(14)}$	1,55(2)	$O_{(1a)}$—$C_{(2a)}$	1,19(2)	$C_{(17a)}$—$C_{(18a)}$	1,41(4)
$C_{(2)}$—$C_{(3)}$	1,52(2)	$N_{(1a)}$—$C_{(4a)}$	1,48(2)	$C_{(18a)}$—$C_{(19a)}$	1,39(3)
$C_{(3)}$—$C_{(4)}$	1,58(2)	N(1a)—$C_{(5a)}$	1,50(2)	$C_{(20a)}$—$C_{(21a)}$	1,40(3)
$C_{(3)}$—$C_{(7)}$	1,49(2)	$N_{(1a)}$—$C_{(11a)}$	1,49(3)	$C_{(20a)}$—$C_{(25a)}$	1,39(2)
$C_{(3)}$—$C_{(20)}$	1,55(2)	$N_{(2a)}$—$C_{(6a)}$	1,54(2)	$C_{(21a)}$—$C_{(22a)}$	1,37(3)
$C_{(8)}$—$C_{(9)}$	1,51(3)	$N_{(2a)}$—$C_{(7a)}$	1,50(2)	$C_{(22a)}$—$C_{(23a)}$	1,39(3)
$C_{(9)}$—$C_{(10)}$	1,46(3)	$N_{(2a)}$—$C_{(8a)}$	1,47(2)	$C_{(23a)}$—$C_{(24a)}$	1,34(4)
$C_{(11)}$—$C_{(12)}$	1,56(3)	$N_{(3a)}$—$C_{(10a)}$	1,15(3)	$C_{(24a)}$—$C_{(25a)}$	1,42(3)
$C_{(12)}$—$C_{(13)}$	1,50(3)	$N_{(4a)}$—$C_{(13a)}$	1,13(4)		

tuents at the C_8 and C_{11} atoms cause distortion of the structure with local C_{2v} symmetry and substantial deviation of the angle between the N−Cu−N and X−Cu−X planes from 90° (also see Figs. 2a and 2b).

Obviously the restrictions on the rotation about the indicated bonds disappear when the complexes go into solution, which should lead to the occurrence of several energy states of different symmetry, for example:



In the case when R = H (complexes Ia and Ib), in solution essentially there should be only symmetry states close to C_{2v}. For R = alkyl (the rest of the structures), the existence of states of lower symmetry can in principle be observed by optical spectroscopy methods, since electronic transitions may appear which are forbidden within the C_{2v} symmetry group. We are planning to perform the appropriate experiments in the future.

Thus in studying the properties of known and new bispidine complexes, in this work we have obtained the following data. In the IR spectra of the complexes, the absorption band of the carbonyl group is shifted toward longer wavelengths, which

TABLE 5. Bond Angles (°) for Compound IVa

Angle	ω, degrees	Angle	ω, degrees
1	2	3	4
Cl$_{(1)}$—Cu$_{(1)}$—Cl$_{(2)}$	101,9(2)	Cl(1)—Cu$_{(1)}$—N$_{(1)}$	126,5(5)
Cl$_{(2)}$—Cu$_{(1)}$—N$_{(1)}$	104,6(3)	Cl$_{(1)}$—Cu$_{(1)}$—N$_{(2)}$	99,7(4)
Cl$_{(2)}$—Cu$_{(1)}$—N$_{(2)}$	138,9(4)	N$_{(1)}$—Cu$_{(1)}$—N$_{(2)}$	89,6(5)
Cu$_{(1)}$—N$_{(1)}$—C$_{(4)}$	113(1)	Cu$_{(1)}$—N$_{(1)}$—C$_{(5)}$	108,5(7)
C$_{(4)}$—N$_{(1)}$—C$_{(5)}$	110(1)	Cu$_{(1)}$—N$_{(1)}$—C$_{(11)}$	111(1)
C$_{(4)}$—N$_{(1)}$—C$_{(11)}$	105(1)	C$_{(5)}$—N$_{(1)}$—C$_{(11)}$	109(1)
Cu$_{(1)}$—N$_{(2)}$—C$_{(6)}$	107(1)	Cu$_{(1)}$—N$_{(2)}$—C$_{(7)}$	111(1)
C$_{(6)}$—N$_{(2)}$—C$_{(7)}$	111(1)	Cu$_{(1)}$—N$_{(2)}$—C$_{(8)}$	112(1)
C$_{(6)}$—N$_{(2)}$—C$_{(8)}$	106(1)	C$_{(7)}$—N$_{(2)}$—C$_{(8)}$	109(1)
C$_{(2)}$—C$_{(1)}$—C$_{(5)}$	110(1)	C$_{(2)}$—C$_{(1)}$—C$_{(6)}$	106(1)
C$_{(5)}$—C$_{(1)}$—C$_{(6)}$	113(1)	C$_{(2)}$—C$_{(1)}$—C$_{(14)}$	109(1)
C$_{(5)}$—C$_{(1)}$—C$_{(14)}$	107(2)	C$_{(6)}$—C$_{(1)}$—C$_{(14)}$	112(1)
O$_{(1)}$—C$_{(2)}$—C$_{(1)}$	123(1)	O$_{(1)}$—C$_{(2)}$—C$_{(3)}$	127(2)
C$_{(1)}$—C$_{(2)}$—C$_{(3)}$	109(1)	C$_{(2)}$—C$_{(3)}$—C$_{(4)}$	110(1)
C$_{(2)}$—C$_{(3)}$—C$_{(7)}$	104(1)	C$_{(4)}$—C$_{(3)}$—C$_{(7)}$	113(1)
C$_{(2)}$—C$_{(3)}$—C$_{(20)}$	110(1)	C$_{(4)}$—C$_{(3)}$—C$_{(20)}$	107(1)
C$_{(7)}$—C$_{(3)}$—C$_{(20)}$	113(2)	N$_{(1)}$—C$_{(4)}$—C$_{(3)}$	114(1)
N$_{(1)}$—C$_{(5)}$—C$_{(1)}$	113(1)	N$_{(2)}$—C$_{(6)}$—C$_{(1)}$	112(1)
N$_{(2)}$—C$_{(7)}$—C$_{(3)}$	116(2)	N$_{(2)}$—C$_{(8)}$—C$_{(9)}$	114(1)
C$_{(8)}$—C$_{(9)}$—C$_{(10)}$	111(1)	N$_{(3)}$—C$_{(10)}$—C$_{(9)}$	178(2)
N$_{(1)}$—C$_{(11)}$—C$_{(12)}$	112(1)	C$_{(11)}$—C$_{(12)}$—C$_{(13)}$	109(1)
N$_{(4)}$—C$_{(13)}$—C$_{(12)}$	179(3)	C$_{(1)}$—C$_{(14)}$—C$_{(15)}$	120(1)
C$_{(1)}$—C$_{(14)}$—C$_{(19)}$	120(1)	C$_{(15)}$—C$_{(14)}$—C$_{(19)}$	120(2)
C$_{(14)}$—C$_{(15)}$—C$_{(16)}$	114(1)	C$_{(15)}$—C$_{(16)}$—C$_{(17)}$	126(2)
C$_{(16)}$—C$_{(17)}$—C$_{(18)}$	120(3)	C$_{(17)}$—C$_{(18)}$—C$_{(19)}$	122(2)
C$_{(14)}$—C$_{(19)}$—C$_{(18)}$	118(2)	C$_{(3)}$—C$_{(20)}$—C$_{(21)}$	118(2)
C$_{(3)}$—C$_{(20)}$—C$_{(25)}$	121(1)	C$_{(21)}$—C$_{(20)}$—C$_{(25)}$	121(2)
C$_{(20)}$—C$_{(21)}$—C$_{(22)}$	119(2)	C$_{(21)}$—C$_{(22)}$—C$_{(23)}$	119(2)
C$_{(22)}$—C$_{(23)}$—C$_{(24)}$	121(2)	C$_{(23)}$—C$_{(24)}$—C$_{(25)}$	122(2)
C$_{(20)}$—C$_{(25)}$—C$_{(24)}$	118(2)	Cl$_{(1a)}$—Cu$_{(1a)}$—Cl$_{(2a)}$	100,9(2)
Cl$_{(1a)}$—Cu$_{(1a)}$—N$_{(1a)}$	99,7(4)	Cl$_{(2a)}$—Cu$_{(1a)}$—N$_{(1a)}$	137,1(3)
Cl$_{(1a)}$—Cu$_{(1a)}$—N$_{(2a)}$	134,5(3)	Cl$_{(2a)}$—Cu$_{(1a)}$—N$_{(2a)}$	101,0(4)
N$_{(1a)}$—Cu$_{(1a)}$—N$_{(2a)}$	90,5(5)	Cu$_{(1a)}$—N$_{(1a)}$—C$_{(4a)}$	111(1)
Cu$_{(1a)}$—N$_{(1a)}$—C$_{(5a)}$	104,5(7)	C$_{(4a)}$—N$_{(1a)}$—C$_{(5a)}$	113(1)
Cu$_{(1a)}$—N$_{(1a)}$—C$_{(11a)}$	110(1)	C$_{(4a)}$—N$_{(1a)}$—C$_{(11a)}$	110(1)
C$_{(5a)}$—N$_{(1a)}$—C$_{(11a)}$	110(1)	Cu$_{(1a)}$—N$_{(2a)}$—C$_{(6a)}$	106(1)
Cu$_{(1a)}$—N$_{(2a)}$—C$_{(7a)}$	114,5(8)	C$_{(6a)}$—N$_{(2a)}$—C$_{(7a)}$	107(1)
Cu$_{(1a)}$—N$_{(2a)}$—C$_{(8a)}$	112,6(9)	C$_{(6a)}$—N$_{(2a)}$—C$_{(8a)}$	107(1)
C$_{(7a)}$—N$_{(2a)}$—C$_{(8a)}$	109(1)	C$_{(2a)}$—C$_{(1a)}$—C$_{(5a)}$	101(1)
C$_{(2a)}$—C$_{(1a)}$—C$_{(6a)}$	113(2)	C$_{(5a)}$—C$_{(1a)}$—C$_{(6a)}$	110(1)
C$_{(2a)}$—C$_{(1a)}$—C$_{(14a)}$	113(1)	C$_{(5a)}$—C$_{(1a)}$—C$_{(14a)}$	113(2)
C$_{(6a)}$—C$_{(1a)}$—C$_{(14a)}$	108(1)	O$_{(1a)}$—C$_{(2a)}$—C$_{(1a)}$	124(2)
O$_{(1a)}$—C$_{(2a)}$—C$_{(3a)}$	124(1)	C$_{(1a)}$—C$_{(2a)}$—C$_{(3a)}$	112(1)
C$_{(2a)}$—C$_{(3a)}$—C$_{(4a)}$	102(2)	C$_{(2a)}$—C$_{(3a)}$—C$_{(7a)}$	112(1)
C$_{(4a)}$—C$_{(3a)}$—C$_{(7a)}$	113(1)	C$_{(2a)}$—C$_{(3a)}$—C$_{(20a)}$	112(1)
C$_{(4a)}$—C$_{(3a)}$—C$_{(20a)}$	111(1)	C$_{(7a)}$—C$_{(3a)}$—C$_{(20a)}$	108(1)
N$_{(1a)}$—C$_{(4a)}$—C$_{(3a)}$	115(1)	N(1a)—C$_{(5a)}$—C$_{(1a)}$	115(1)
N$_{(2a)}$—C$_{(6a)}$—C$_{(1a)}$	115(1)	N$_{(2a)}$—C$_{(7a)}$—C$_{(3a)}$	115(1)
N$_{(2a)}$—C$_{(8a)}$—C$_{(9a)}$	115(2)	C$_{(8a)}$—C$_{(9a)}$—C$_{(10a)}$	112(2)
N$_{(3a)}$—C$_{(10a)}$—C$_{(9a)}$	176(2)	N$_{(1a)}$—C$_{(11a)}$—C$_{(12a)}$	111(2)
C$_{(11a)}$—C$_{(12a)}$—C$_{(13a)}$	112(2)	N$_{(4a)}$—C$_{(13a)}$—C$_{(12a)}$	177(3)

TABLE 5 (continued)

Angle	ω, degrees	Angle	ω, degrees
1	2	3	4
$C_{(1a)}$—$C_{(14a)}$—$C_{(15a)}$	124(2)	$C_{(1a)}$—$C_{(14a)}$—$C_{(19a)}$	119(2)
$C_{(15a)}$—$C_{(14a)}$—$C_{(19a)}$	117(2)	$C_{(14a)}$—$C_{(15a)}$—$C_{(16a)}$	120(2)
$C_{(15a)}$—$C_{(16a)}$—$C_{(17a)}$	121(2)	$C_{(16a)}$—$C_{(17a)}$—$C_{(18a)}$	119(2)
$C_{(17a)}$—$C_{(18a)}$—$C_{(19a)}$	118(2)	$C_{(14a)}$—$C_{(19a)}$—$C_{(18a)}$	125(2)
$C_{(3a)}$—$C_{(20a)}$—$C_{(21a)}$	119(1)	$C_{(3a)}$—$C_{(20a)}$—$C_{(25a)}$	123(2)
$C_{(21a)}$—$C_{(20a)}$—$C_{(25a)}$	119(2)	$C_{(20a)}$—$C_{(21a)}$—$C_{(22a)}$	122(2)
$C_{(21a)}$—$C_{(22a)}$—$C_{(23a)}$	119(2)	$C_{(22a)}$—$C_{(23a)}$—$C_{(24a)}$	120(2)
$C_{(23a)}$—$C_{(24a)}$—$C_{(25a)}$	121(2)	$C_{(20a)}$—$C_{(25a)}$—$C_{(24a)}$	119(2)

can be a criterion for the formation of complexes of the given composition and structure. We have found that the copper chloride and copper bromide complexes have similar structural characteristics. We have confirmed data on the effect of the degree of branching of the substituent at the nitrogen atom on the geometry of the coordination environment of the metal. We discuss the hypothesis that the indicated interactions also appear in solutions of the complexes.

EXPERIMENTAL

The x-ray diffraction conditions are given in Table 1. The bond lengths and bond angles are given in Tables 2-5. Data on atomic coordinates and thermal parameters for complexes IIIb and IV can be obtained from the authors.

The IR spectra (in Vaseline oil) were recorded on UR-20 and IKS-29 spectrophotometers. The electronic absorption spectra were recorded on a Varian DMS 100. The solvents used were purified and dehydrated according to standard procedures.

Copper Bromide Complex of Compound I (Ib). A solution of 1.25 g (3.9 millimoles) of compound I in 30 ml ethanol was heated to boiling, and a heated solution of 0.87 g (3.9 millimoles) anhydrous copper(II) bromide in 30 ml ethanol was added to it. This was boiled with reflux for 1 h. The solution was allowed to stand in a refrigerator overnight. The precipitated crystals were filtered off, washed with ethanol, and recrystallized from ethanol. Obtained: 1.83 g (86%) orange crystals of the complex. T_{mp} 167°C with decomposition (from ethanol). IR spectrum: 1748 (C=O); 1510 and 1455 cm^{-1} (C=C ar). Found, %: C 46.14; H 4.42; N 4.73. $C_{21}H_{24}N_2OCuBr_2$. Calculated, %: C 46.36; H 4.45; N 5.10.

Copper Bromide Complex of Compound II (IIb). 0.64 g (2.87 millimoles) anhydrous copper(II) bromide was added to a solution of 1.0 g (2.87 millimoles) compound II in 40 ml chloroform. This was boiled for 4 h. The solution was evaporated down to half volume and allowed to stand in a refrigerator. The precipitated crystals were filtered off, washed with chloroform, and recrystallized from chloroform. Obtained: 1.53 g (85%) brown crystals. T_{mp} 135°C with decomposition (from chloroform). IR spectrum: 1750 (C=O), 1510 and 1455 cm^{-1} (C=C ar). Found, %: C 44.88; H 4.76; N 4.42. $C_{23}H_{28}N_2OBr_2 \cdot 0.5CHCl_3$. Calculated, %: C 44.69; H 4.55; N 4.44.

Copper Bromide Complex of Compound III (IIIb). 0.051 g (0.24 millimoles) anhydrous copper(II) bromide was added to a solution of 0.085 g (0.24 millimoles) compound III in 10 ml chloroform. This was boiled for 1 h, cooled down to 25°C, and allowed to stand overnight in a refrigerator. The precipitated crystals of the complex were filtered off and washed with chloroform. Obtained: 0.135 g (83%) brown crystals of the complex. T_{mp} 117°C with decomposition (from chloroform). IR spectrum: 1740 (C=O); 1510 and 1450 cm^{-1} (C=C ar). Found, %: C 43.08; H 4.02; N 3.50. $C_{25}H_{28}N_2OCuBr_2 \cdot 1.3CHCl_3$. Calculated, %: C 43.50; H 4.04; N 3.90.

Copper Chloride Complex of Compound IV (IVa). A solution of 0.1 g (0.7 millimoles) anhydrous copper(II) chloride in absolute ethanol was added dropwise to a solution of 0.3 g (0.7 millimoles) compound IV in 10 ml absolute chloroform and allowed to stand in a refrigerator. The precipitated green crystals were filtered off and washed with chloroform. Obtained: 0.3 g (75%) compound IVa. T_{mp} 173-174°C. IR spectrum: 2265 and 2250 (CN), 1725 cm^{-1} (CO). Found, %: C 55.80; H 4.86; N 10.59. $C_{25}H_{26}N_4OCuCl_2$. Calculated, %: C 56.23; H 4.85; N 10.14.

TABLE 6. Most Important Bond Lengths (Å), Distances (Å), and Angles (°) in Halide Complexes of Bispidines $CuLX_2$ from X-Ray Diffraction Data

Complex (independent molecules A and B)	Cu—N	Cu—X	N—N'	N—Cu—N'	X—Cu—X'	Between planes N−Cu−N and X−Cu−X	$Cu-N-C_{exocyclic}$	Lit.
Va, X = Cl	1,994(4)	2,255(4)	2,84	90,6	116,0	87,3	103,7	[6]
Ia, X = Cl	2,00	2,262	2,71	86,3	110,9	82,0	106,3(7)	[5]
	1,96	2,182					103,9(7)	
IIIa (A)	2,022(4)	2,221(2)	2,81	88,3(2)	104,1(1)	62,7	110,0(3)	[1]
	2,010(4)	2,228(2)					110,8(3)	
(B)	2,021(4)	2,242(2)	2,80	88,1(2)	104,2(1)	62,6	110,1(3)	
X = Cl	2,003(4)	2,212(2)					109,3(3)	
IIIb, X = Br	1,999	2,335	2,82	88,9	104,4	63,8	111,8(7)	This work
	2,027	2,346					110,9(7)	This work
IVa, (A)	1,99(1)	2,241(5)	2,81	89,6(5)	101,9(2)	65,5	112,0(10)	
	2,00(1)	2,225(5)					111,0(10)	
(B)	2,01(1)	2,231(6)	2,84	90,5(5)	100,9(2)	60,7	112,6(9)	This work
X = Cl	1,98(1)	2,205(6)					109,5(10)	This work

This work was done with the financial support of the Russian Foundation for Basic Research (grant 94-03-09592) and the International Science Foundation (grant MTD 000).

REFERENCES

1. S. Z. Vatsadze, S. E. Sosonyuk, N. V. Zyk, K. A. Potekhin, O. I. Levina, Yu. T. Struchkov, and N. S. Zefirov, Khim. Geterotsikl. Soedin., No. 6, 770 (1996).
2. R. D. Hancock and A. E. Martell, Chem. Rev., **89**, 1875 (1989).
3. G. D. Hosken and R. D. Hancock, J. Chem. Soc., Chem. Commun., No. 11, 1363 (1994).
4. V. A. Palyulin, Dissertation in competition for the academic degree of Candidate of Chemical Sciences, Moscow State University, Moscow (1985).
5. O. I. Levina, K. A. Potekhin, E. N. Kurkutova, Yu. T. Struchkov, O. N. Zefirova, V. A. Palyulin, and N. S. Zefirov, Dokl. Akad. Nauk, **289**, 876 (1986).
6. L. S. Childers, K. Folting, L. L. Merrit, Jr., and W. E. Streib, Acta Crystallogr., Sect. B, **31**, 924 (1975).
7. S. Z. Vatsadze, N. V. Zyk, R. D. Rakhimov, K. P. Butin, and N. S. Zefirov, Izv. Akad. Nauk, Ser. Khim., 456 (1995).
8. S. Z. Vatsadze, S. E. Sosonyuk, N. V. Zyk, K. A. Potekhin, O. I. Levina, Yu. T. Struchkov, and N. S. Zefirov, Dokl. Akad. Nauk, **341**, 201 (1995).
9. M. Zh. Buranbaev, Yu. P. Gladii, T. T. Omarov, A. Sh. Gubasheva, V. A. Palyulin, and N. S. Zefirov, Zh. Strukt. Khim., **31**, 189 (1990).
10. E. Boschmann, L. M. Weinstock, and M. Carmac, Inorg. Chem., **13**, 1297 (1973).
11. V. A. Rabinovich (ed.), Properties of Inorganic Compounds [in Russian], Khimiya, Moscow (1983), p. 392.