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Abstract

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DIPOLE MOMENTS AND THE STRUCTURE OF INTRACOMPLEX COPPER COMPOUNDS WITH AROMATIC SCHIFF BASES

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Although intracomplex compounds (ICC) of Cu(II), obtained on the basis of Schiff bases from *o*-hydroxyaldehydes, have been studied in detail ($^{1-4}$), questions of their stereochemistry continue to remain debatable.

According to X-ray and electron-diffraction data, in the crystalline state ICC of Cu(II), as well as Ni(II), VO(II), have a planar trans structure, provided that this possibility is not excluded by the structure of the ligand (^{5,6}).

Table 1

R	T, °K	$\chi_g \cdot 10^6$	$\chi'_m \cdot 10^6$	μ_{eff}, μ_B
H	292	3.07	1633	1.96
4-CH_3	291	2.79	1602	1.94
3-CH_3	293	2.80	1606	1.95
2-CH_3	293	2.60	1509	1.89
2-Br	293	2.67	1557	1.92
2,4 $(CH_3)_2$	293	2.51	1560	1.92
2,4,6 $(CH_3)_3$	292	2.38	1583	1.93

At the same time, measurements ($^{7-9}$) of the molecular polarization of ICC Cu(II) of this type reveal a significant (up to 100% of P_{el}) difference $P_{2\infty} - P_{\text{el}}$, which can be reconciled with the assumption of a planar structure of the complex only by assigning it to the atomic polarization P_A.

Recently, however, the widespread ideas about anomalously high atomic polarization of ICC (^{10}) have been criticized (^{11,12}); therefore, we considered it appropriate to examine further the question of the configuration of the coordination unit of Cu(II) in solutions.

As the object of study we selected ICC of Cu(II) with aromatic Schiff bases of the type

R = H (I); 4-CH_3 (II); 3-CH_3 (III);
2-CH_3 (IV); 2-Br (V).
2,4-$(CH_3)_2$ (VI); 2,4,6-$(CH_3)_3$ (VII)

Compounds I—VII were synthesized by a method analogous to (^{1,3}) and, according to elemental-analysis data, had the composition $Cu(Lig)_2$.

Measurements of magnetic susceptibilities in the solid state (Table 1) were carried out by the Gouy method, as described earlier (^{13}). The correction for ligand diamagnetism was introduced on the basis of experimental data (^{14}). The magnetic moments μ_{eff} of compounds I—VII were also determined in benzene solutions. Although the low solubility (not more than 0.03 M) reduces the accuracy of the determinations, the mean value of μ_{eff} from several measurements agrees with the data given in Table 1.

The values of μ_{eff}, elevated in comparison with pure spin paramagnetism (1.73 μ_B), indicate a contribution from spin-orbit interaction. It is assumed (^{8}) that this interaction should be especially strong for the tetrahedral configuration. The μ_{eff} values obtained by us, however, can be correlated with both square and tetrahedral forms (^{3,15}) and do not provide sufficient grounds for choosing between them.

A much more refined criterion for the configuration of ICC Cu(II) proves to be the magnitude of the electric dipole moment. Table 2 pre—

···the results of determinations of the dipole moments μ of I—VII in various solvents at 25° are presented.

To take account of atomic polarization P_A, the value of the deformation polarization P_D was determined by us by measuring the dielectric polarization in the solid phase (^{12}). The values found, $P_A = P_D - P_{\text{el}}$, amount to only 7—14% of P_{el}, which contradicts the idea ($^{7-10}$) of an anomalously high P_A for intracomplex compounds of this type.* Also unsatisfactory is the assumption (^{7}) of the presence of a cis-trans equilibrium, which could explain the large value of $P_2 - P_{\text{el}}$ for compounds I—VI, since the planar cis form is sterically impossible.

Table 2

R	P_{el}, cm^3	P_D, cm^3	Dioxane $P_{2\infty}$, cm^3	Dioxane μ, D	Benzene $P_{2\infty}$, cm^3	Benzene μ, D	Anisole P_{op}, [23] cm^3	Anisole μ, D
H	136.2	150.8	264 (7)	2.29	309.7	2.70	259.7	3.56
4-CH_3	150.1	160.4	336.5	2.93	392.9	3.37	376.0	4.28
3-CH_3	147.3	161.6	313.4	2.72	374.1	3.22	349.2	4.13

structural diagram of a copper intracomplex compound with axes x and y, phenyl rings, substituents R, and Cu coordinated by O and N groups

Figure 1: structural diagram of a copper intracomplex compound with axes x and y, phenyl rings, substituents R, and Cu coordinated by O and N groups

R	P_{el}, cm^3	P_D, cm^3	Dioxane $P_{2\infty}$, cm^3	Dioxane μ, D	Benzene $P_{2\infty}$, cm^3	Benzene μ, D	Anisole P_{op}, [23] cm^3	Anisole μ, D
2-CH_3	146.2	164.3	197.2	1.27	225.8	1.73	96.4	2.17
2-Br	153.8	175.4	214.4	1.28	241.2	1.79	–	–
2,4-$(CH_3)_2$	156.1	176.1	233.1	1.67	258.5	2.01	142.3	2.64
2,4,6-$(CH_3)_3$	162.9	186.8	191.4	0.47	195.3	0.64	42.9	1.45

Cryoscopic measurements carried out in benzene and dioxane show that, in the investigated concentration range (up to 0.03 M), compounds I—VII are present as monomers and, consequently, the dimeric form proposed (^{16}) for analogous Ni(II) compounds is excluded; moreover, the dimers should not possess an electric dipole moment. Coordination of one solvent molecule is just as unlikely, since the dipole moment is minimal in the most basic solvent—dioxane.

Sacconi and coauthors (^{8,9}), who investigated intracomplex Cu(II) compounds with N-alkylsalicylaldimines, proposed a flattened square-pyramidal configuration with the copper atom at the apex (d^2sp^2-hybridization). Such a configuration explains the presence of a dipole moment in solution, but it cannot explain the regular decrease in dipole moment established in the present work when bulky substituents are introduced into positions 2 and 6. Since the dipole moments of the ligands used are approximately equal (^{17}), the decrease in the moments of the complexes can mean only centrosymmetrization of their molecules. Let us consider the stereochemical possibilities for intracomplex compounds I—VII.

It is known that ligand molecules are nonplanar: conjugation of the nitrogen n-electrons with the π-electrons leads to displacement of the amine aromatic ring from the common plane by an angle $\theta \approx 60^\circ$ (^{18}). Although upon complex formation this conjugation is largely removed, the amine ring is nevertheless deflected from the plane of the coordination unit already as a result of steric hindrance. In the crystalline state, compounds I—VII have a structure consistent with X-ray data (^{19}).

* Although the configuration of the complex in the solid state apparently differs from that in solution, this cannot significantly affect the value of P_A.

The transition from a planar configuration to a square pyramid corresponds to rotation of one half of the molecule relative to the y axis passing through the central atom.

It is not difficult to see that the introduction of *o*-substituents does not create additional spatial hindrance for the pyramidal configuration, which, consequently, does not explain why the dipole moment of compound VII falls almost to zero.

On the contrary, the assumption that the studied intracomplex compounds of Cu(II) can exist in solution in the form of a tetrahedral configuration (rotation about the X axis) explains well the character of the changes in μ on passing from I to VII. In the tetrahedron there should be significant repulsion between the *o*-substituents, which will lead either to distortion of the tetrahedron toward a planar square or, if there is an equilibrium square ⇄ tetrahedron, to its shift to the left.

When R in positions 2 and 6 is equal to H (compounds I—III), the repulsion is small and the dipole moment is considerable; upon introduction of one *o*-substituent (compounds IV—VI) the repulsion increases, and the moment decreases. If, however, both *o*-positions are substituted (compound VII), the steric obstacles to the tetrahedron are so great that the planar-square configuration completely predominates.

Of the two hypotheses expressed, the concept of an equilibrium existing in solution seems the more probable, since an explicit dependence of the configuration, for which the magnitude of μ serves as an indicator, on the solvent is observed (Table 2).

Concepts of the square ⇄ tetrahedron equilibrium have already been developed for intracomplex compounds of Ni(II) ([20,21]). From the point of view of such conformational equilibrium, for analogous I—VII complexes of Ni(II) one would have expected a decrease in paramagnetism in the same series in which the dipole moment of the Cu(II) complexes decreases. Such a dependence is indeed observed ([22]), although the authors of the cited work tend toward another explanation.

Thus, on the basis of the study of the dipole moments of intracomplex compounds of Cu(II) in various solvents, one may conclude that in solution there exists an equilibrium of the configurations tetrahedron ⇄ planar square.

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Note: Figure translations are in progress. See original paper for figures.