Spectrochemical Properties of Noncubical Transition Metal Complexes in Solutions. VIII. Angular Overlap Treatment of a Schiff Base Copper(II) Complex in Various Solvents

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The electronic absorption spectra of *trans*-[Cu(Brsap)₂], where [HBrsap = 5bromosalicylidine-o-aminopyridine (Schiff base)], were measured in various solvents at room temperature. The d-d transition energies were used to derive the angular overlap model (AOM) parameters in the C_{2h} symmetry. The experimental curves were resolved by Gaussian analysis. A comparison of the spectra and ligand field parameters in various solutions was made. The effect of the solvents upon the σ -, π -bonding, and bite angle of the bidentate asymmetric ligand is discussed.

KEY WORDS: Angular overlap model; Schiff base; copper(II) complexes; solutions; 5-bromosalicylidene-*o*-aminopyridine; electronic spectra; molecular structure.

1. INTRODUCTION

Schiff base compounds include various types, but in this work, we are concerned mainly with the neutral copper(II) complex of this ligand derived from 5-bromosalicylaldehyde and 2-aminopyridine. Generally, Schiff base complexes with transition metals have been studied for their interesting and important properties, ⁽¹⁾ *e.g.*, their ability to reversibly bind oxygen, catalytic activity in hydrogenation of olefins and transfer of an amino group, photochromic properties, and complexing ability toward some toxic metals. In particular, copper(II) complexes with quadridentate Schiff bases play an important role

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in biological systems. Metal complexes of bidentate Schiff bases, as presented in this work, have played an important role in the development of metallomesogens.⁽²⁾

In our previous paper⁽³⁾ we presented the interpretation of the electronic spectra of the trans- [Cu(sap)₂] complex in various solvents, i.e., ethanol (EtOH), N,N'-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), methanol (MeOH), acetonitrile (CH₃CN), 1,4-dioxane (C₄H₈O₂), carbon tetrachloride (CCl₄), benzene (C_6H_6), and chloroform (CHCl₃). The present studies are intended to show the interpretation of the electronic spectra of trans-[Cu(Brsap)₂] in different solvents. The X-ray data for the studied complex are not known to us. Structural studies have shown that the variation of the size and nature of the substituent of the salicylaldimine ligand could be responsible for changes in the coordination geometry around the metal atom. It has been reported⁽⁴⁾ that copper complexes with N-substituted salicylaldimine ligand can occur in a planar or a tetrahedral configuration. The X-ray data are known for the complexes with different salicylideneamine derivatives. Generally, the ligands have an approximately trans-planar configuration around the Cu²⁺ ion.^(5,6) Scheme 1 shows the molecular geometry of salicylideneamine complexes of copper(II); in our study X = Br, R = pyridine ring.

The bis-[2-pyridyl(5-bromosalicylideneiminato)]copper(II) complex was studied earlier.^(7,8) Castiňeiras *et al.*⁽⁷⁾ have synthesized this complex electrochemically and discussed electronic (reflectance) and i.r. spectra of the solid state in relation to the molecular structure. In that work,⁽⁸⁾ this complex was prepared by a general procedure and characterized on the basis of i.r. spectra, magnetic properties, and electronic spectra of a methanol-acetone solution.

2. EXPERIMENTAL

The *trans*-[Cu(Brsap)₂] complex was prepared using the usual method as described by Bailes and Calvin⁽⁹⁾ by reaction of bisacetate copper(II) with 5-bromosalicylidene-*o*-aminopyridine. The ligand was dissolved in deoxygenated methanol. A solution of bisacetate copper(II) in doubly distilled deoxygenated water was then added. The mixture was refluxed for about 1 hr. The



solid complex was filtered and washed with methanol. The product was a yellowish brown crystalline compound easily soluble in common solvents, like N,N-dimethylformamide (DMF), 1,4-dioxane (C₄H₈O₂), dimethyl sulfoxide (DMSO), and chloroform (CHCl₃).

The 5-bromosalicylidene-o-aminopyridine ligand was prepared in the following way.⁽¹⁰⁾ 5-Bromosalicylaldehyde and α -aminopyridine were combined in methanol and the orange solution refluxed for approximately 0.5 hr. The ligand was filtered and washed with methanol. It is an orange-red crystal-line compound easily soluble in the same solvents as the complex.

Both the compounds, complex and ligand (Schiff base), were analyzed for purity. Carbon, hydrogen, and nitrogen analyses were carried out by the Laboratory of Microanalysis and Automation of Analytical Methods (Polish Academy of Science, Łódź, Poland). The results of elementary analysis agreed with the expected composition. Analytical data of the complex are as follows: found—C, 45.59; H, 2.34; N, 8.35%; calc.—C, 45.48; H, 2.86; N, 8.84%. Those for the ligand are: found—C, 52.05; H, 3.79; N, 9.85%; calc.—C, 52.01; H, 3.27; N, 10.11%.

2.1. Measurements

Solutions of trans-[Cu(Brsap)2], were prepared by dissolving a weighed amount of the complex in DMF, C₄H₈O₂, DMSO, and CHCl₃. The composition of the complex species in various solutions has been confirmed by conductance measurements. The molar conductance was measured using the conductivity meter OK-120/1 and electrode OK-902 (Radelkis). The trans-[Cu(Brsap)₂] complex has the molar conductivity values 9.7, 0.9, 6.9, 0.1 S mol^{-1} -cm², for DMF, C₄H₈O₂, DMSO, and CHCl₃, respectively. The low conductance values of trans-[Cu(Brsap)₂] in all solutions show that they are nonelectrolytes and indicate that the coordinated ligands are not removed by the solvent. Typical values for 1:1 type electrolytes are in the ranges 50-70 and 65-90 S-mol⁻¹- cm² for DMSO and DMF, respectively.⁽¹¹⁾ The measurement conditions for the conductivity were the same as for the electronic absorption spectra (*i.e.* $\sim 6.0 \times 10^{-4}$ M). The visible and ultraviolet spectra were recorded on a SPECORD M40 spectrophotometer. Measured spectra of solutions were recorded digitally (20 cm⁻¹ steps) over the range 11000–48000 cm⁻¹. The spectral data at selected 350 wavenumber intervals over the range 11000-19000 cm⁻¹ were employed for analysis and resolved into Gaussian components.

2.2. Method of Calculations

All the band maxima reported here are derived from Gaussian analysis of the experimental curves. Our calculations take into account all the transitions that are given by ligand field theory. The details of the method have been reported by Kurzak⁽¹²⁾ (and refs. herein). The absorption spectrum of the studied complex was fitted to Gaussian components using a CFP program. Ligand field parameters were calculated using the LFP program⁽¹³⁾ based on two minimization techniques: the Powell method (nongradient) and the Davidon–Fletcher–Powell method (gradient estimation). The computer programs were written in FORTRAN77. The AOM calculations were carried out within the framework of the angular overlap model developed by Schäffer⁽¹⁴⁾ and Jørgensen.⁽¹⁵⁾ The *d*-orbital energies for this complex have been obtained using the standard procedure of finding the orbital energies⁽¹⁶⁾ and presented in an earlier work.⁽³⁾ The matrix elements of the excited states given by Kurzak and Kuźniarska-Biernacka⁽³⁾ for the orthorhombic d^9 system (C_{2h} symmetry) were used for these calculations. Coordinate system and numbering of the ligators used for AOM calculations are the same as in the previous paper.⁽³⁾ All the calculations were carried out using an IBM PC.

3. RESULTS AND DISCUSSION

Our study is focused on an interpretation of the electronic spectra of *trans*-bis{*N*-[2-pyridyl (5-bromosalicylideneiminato)]}copper(II) in various solvents. It takes into account a low symmetry of the complex and, in particular, a bite angle distortion. The X-ray data for this complex are not known. Castineiras et al.⁽⁷⁾ have synthesized and characterized thirteen copper(II) complexes of Schiff bases derived from substituted salicylaldehydes and 2aminopyridine derivatives. The crystal and molecular structure of two copper(II) complexes have been determined. In both complexes: (1) bis- $\{N$ -[2-(3-methylpyridyl)]-5-methoxysalicylideneiminato copper(II), and (2) bis- $\{N-[2-(6-methylpyridyl)]$ salicylideneiminato $\}$ copper(II), the Cu atoms adopt trans square-planar coordination geometries and the pyridyl nitrogen atoms are not coordinated. Authors suggest that the remaining complexes (including those in our work) must also be square-planar. The Cu-N distances are 1.992(2) Å in complex (1) and 2.002(5) Å in (2) and Cu-O distances are 1.874(2) Å in complex (1) and 1.873(4) Å in (2). As seen, in both compounds the Cu-N bond lengths are slightly longer than Cu-O bonds. The bond angles N-Cu-O (bite angle α) are 91.42(7) in complex (1) and 90.2(2) in complex (2). The N--Cu-N (O-Cu-O) groups are linear in both compounds $[180,1(4)^{\circ}]$. Thus, the assumed geometrical model (C_{2h} group) is adequate for the X-ray structure and our calculations of the AOM parameters, especially for the solution spectra.

The spectrum of the bis-(5-bromosalicylidene-*o*-aminopyridine)copper-(II) complex in methanol-acetone solution has been presented.⁽⁸⁾ Those authors have reported that the spectrum shows only one broad medium

intensity band at 12500-16666 cm⁻¹. The solid state electronic spectrum of this complex⁽⁷⁾ shows two d-d bands at 13300 and 18800 (sh) cm⁻¹, and one ca. 22600 cm⁻¹, attributed by authors to a charge-transfer transition. The electronic absorption spectra of trans-[Cu(Brsap)₂], in various solutions (see Fig. 1) exhibit only one very broad band with maximum at 14000-16000 (150-250) cm⁻¹ (ϵ , cm⁻¹-M⁻¹), which corresponds to strongly overlapped low-symmetry components of the parent octahedral transition. In general, the solution spectra of copper(II) complexes at room temperature do not provide sufficient resolution to require consideration of the lower symmetry. The dd spectra may also be complicated further by overlapping of more intense charge-transfer (complex) or intramolecular (ligand) spectral bands. This effect is especially visible in the C₄H₈O₂ solution. Gaussian analysis of the spectra of the complex and ligand in the near-UV region confirmed that those are charge-transfer transitions. Figures 2 and 3 show the experimental spectra in the d-d region in all the studied solvents along with Gaussian analysis, i.e., polar and nonpolar, respectively. Table I summarizes the results of the Gaussian analysis, i.e., parameters of the component bands, their oscillator strength values, and the relative root mean square error (RMS%). The bands assignment to the energy transitions is based on fitting the resolved band maxima (Gaussian analysis) with the calculated transition energies using one-electron state energies.^(3,12) The values of AOM parameters of trans-[Cu(Brsap)₂] in various solutions, as well as the resolved and calculated transition energies, are summarized in Table II. The best fit with the experi-



Fig. 1. Electronic absorption spectra of the *trans*-[Cu(Brsap)₂] complex in various solvents at room temperature: (1) CHCl₃; (2) C₄H₈O₂; (3) DMF; and (4) DMSO (*computer print*).



Fig. 2. Electronic absorption spectra and Gaussian line-shapes of the *trans*-[Cu(Brsap)₂] in polar solvents: DMSO (a) and DMF (b) (*computer print*).



Fig. 3. Electronic absorption spectra and Gaussian line-shapes of the trans-[Cu(Brsap)₂] in nonpolar solvents: C₄H₈O₂ (a) and CHCl₃ (b) (*computer print*).

	ε	ν ₀	δ _{1/2}	
No.	$(dm^{3}-mol^{-1}-cm^{-1})$	(cm ⁻¹)	(cm ⁻¹)	10³ f
	Chlorofor	rm: RMS% = 0.22		
1	33.523	12499.8	5412.8	0.8342
2	65.198	14065.3	2567.4	0.7696
3	131.146	15137.4	3904.3	2.354
4	77.606	17142.4	5207.0	1.858
5	1170.782	20817.3	4265.6	22.96
	1,4-Dioxa	ne: $RMS\% = 0.07$		
1	27.097	11916.1	3951.5	0.4923
2	45.067	13442,1	2361.5	0.4893
3	108.170	15215.2	3088.5	1.536
4	34.250	17054.5	2237.0	0.3523
5	634.154	21279.4	5200.9	15.16
	DMF:	RMS% = 0.29		
1	26.076	11769.6	3911.1	0.4689
2	50.807	13579.1	2664.5	0.6224
3	118.886	15026.5	3402.3	1.860
4	72.685	17388.1	3354.1	1.121
5	709.631	20772.4	4015.6	13.10
6	9575.294	24299.8	3647.5	160.6
	DMSO	: RMS% = 0.27		
1	36.032	11598.5	4466.1	0.7398
2	50.343	13644.0	2574.8	0.5959
3	106.559	15128.1	3245.9	1.590
4	29.792	16805.5	2540.2	0.3479
5	712.479	21774.0	5218.7	17.09
6	5426.903	24971.2	3931.2	98.09

Table I. Parameters of the Component Bands Resulting from Gaussian Analysis of the Electronic Spectra of trans-[Cu(Brsap)₂] in Various Solutions, Symmetry C_{2b}

mental data has been obtained for these results. We have made assignment of the d-d bands of the studied complex and concluded that the energy order of the d-orbitals is as follow: $d_{xy} << d_{z^2} < d_{x^2-y^2} < d_{yz} < d_{xz}$. The strongest rhombic splitting (bite angle effect) is observed for the DMSO solution $- \{d_{z2}[^2A_g(3)] \text{ and } d_{x^2-y^2}[^2A_g(3)]\}$ orbitals. The splitting of the parent cubic levels by the additional ligand field (in plane) for all the solvents is shown in Fig. 4. The order of the d_{yz} and d_{xz} orbitals is $d_{yz} < d_{xz}$ for $\alpha < 90^{\circ}$ and $d_{yz} > d_{xz}$ for $\alpha > 90^{\circ}$. The splitting energies Δ_1 (see Fig. 4) is due to the deviation of the bite angle from 90°. The lowest value of the bite angle ($\alpha = 85.9^{\circ}$) is for the DMSO solution and highest, i.e., $\alpha = 88.9^{\circ}$ for CHCl₃ solution. Opening the chelate ring so as to obtain 90° is in the order: DMSO $\sim DMF < C_4H_8O_2 < CHCl_3$.

The size of this effect depends predominantly on the character of the solvent.⁽¹⁷⁾ The DN (Gutmann's donor number⁽¹⁷⁾) and AN (acceptor number)

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	Solution				
Assignment	DMSO	DMF	C ₄ H ₈ O ₂	CHCl ₃	
$\frac{1}{^{2}A_{g}(3), d_{z^{2}}}$	11598	11770	11916	12500	
${}^{2}A_{g}(2), d_{x^{2}-y^{2}}$	13644	13579	13442	14065	
${}^{2}B_{g}(1), d_{yz}$	15128	15026	15215	15137	
$^{2}B_{g}(2), d_{xz}$	16805	17388	17054	17142	
$e_{q}(\mathbf{O})$	6794	6866	6870	7227	
$e_{\rm rr}({\rm N})$	4137	4531	4199	3660	
$e_{\pi\perp}(0)$	1131	1237	1168	936	
$e_{\pi \parallel}(0)$	838	1181	919	1002	
$e_{\pi \perp}(N)$	523	773	664	608	
α	85.9	86.0	88.0	88.9	

Table II. Assignments, Transition Energies, and AOM Parameters for trans-[Cu(Brsap)₂] Complex in Various Solutions",b

^{*a*} Ground term: ${}^{2}A_{g}(1)$, d_{xy} . ^{*b*} Units, cm⁻¹.



Fig. 4. Spectral transitions (energy diagram) of the *trans*- $[Cu(Brsap)_2]$ complex (in relation to d_{xy} orbital) for various solutions.

are the determining factors in those changes, but also solvent polarity, e.g., dielectric constant (ϵ) is an important element. The complex species in solutions can be divided into two groups. The first group is the case where the bite angle values are close to 86°, for higher DN values⁽¹⁸⁾ of solvents, i.e., DMF (26.6) and DMSO (29.8). The second type is the case where the bite angle is opened to 90° (i.e., >88°), for lower DN values⁽¹⁸⁾ of solvent, i.e., CHCl₃ (-0.5) and dioxane (14.8). Similarly, opposite dependence of the bite angle values on dielectric constant of solvents is observed. For the solvents of high ϵ values ($\epsilon > 20$) the bite angle is about 86°, while for the low ϵ values ($\epsilon < 5$) the angle is higher (88–89°).

4. CONCLUSION

The oxygen atom (from the hydroxyl group; *sp* hybridized) has different π interactions than nitrogen (from the amine group; *sp*² hybridized). Oxygen donor atoms have different π interactions, i.e., π_{\perp} and π_{\parallel} to the salicylic ring, while nitrogen donor atoms have only π_{\perp} interactions. Therefore, comparison of the π -bonding abilities of both the ligators in various solutions is not simple. The oxygen π_{\perp} interaction is the strongest in the DMF solution, and decreases in the following order: DMF > DMSO > C₄H₈O₂ \geq CHCl₃.

It can be seen that the π interactions of the oxygen donor in DMF and $C_4H_8O_2$ are similar: in DMSO the π_{\perp} interaction is stronger than π_{\parallel} and in CHCl₃ the π_{\parallel} interaction is stronger than the π_{\perp} interactions. The $\pi_{\perp}(O)$ parameters for *trans*-[Cu(Brsap)₂] are higher than those for *trans*-[Cu(sap)₂]⁽³⁾ complex in all solutions, except 1,4-dioxane where it is slightly lower. The values for both complexes are similar in DMF and $C_4H_8O_2$ solutions.

The nitrogen π_{\perp} interactions are slightly different in all solutions. The lowest value is for DMSO and the highest is for DMF. Generally, they are slightly weaker than those for the bis-(salicylidene-*o*-aminopyridine)copper(II) complex.⁽³⁾

The oxygen σ interactions $[e_{\sigma}(O)$ parameter] depend on the solvent, and their values decrease in agreement with decreasing DN values of solvents: CHCl₃ > C₄H₈O₂ \geq DMSO \geq DMF. These values are quite similar to those for bis-(salicylidene-*o*-aminopyridine)copper(II) complex.⁽³⁾

This dependence was not observed for the nitrogen σ interactions, which change as follows:

$$DMF > C_4H_8O_2 \ge DMSO >> CHCl_3$$
.

As seen, the $e_{\sigma}(N)$ parameters for the *trans*-{(CuBrsap)₂} complex are similar to those for the earlier studied compound⁽³⁾ in DMSO and DMF (polar), and C₄H₈O₂ (nonpolar). Moreover, these are lower in all the solutions for former complex.

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