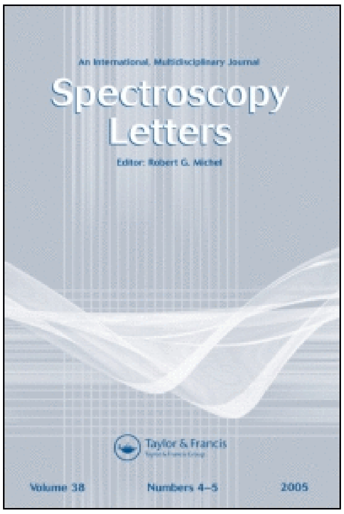

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The Spectrochemical Properties of Noncubic Transition Metal Complexes in Solutions. VII. Angular Overlap Treatment of the *trans-bis*(Salicylidene-o-aminopyridine)copper(II) Complex in Various Solvents.

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THE SPECTROCHEMICAL PROPERTIES OF NONCUBIC TRANSITION METAL COMPLEXES IN SOLUTIONS. VII. ANGULAR OVERLAP TREATMENT OF THE trans-BIS(SALICYLIDENE-o-AMINOPYRIDINE)COPPER(II) COMPLEX IN VARIOUS SOLVENTS.

Key Words: angular overlap model, Schiff base, copper(II) complexes, salicylidene-o-aminopyridine, electronic spectra, molecular structure.

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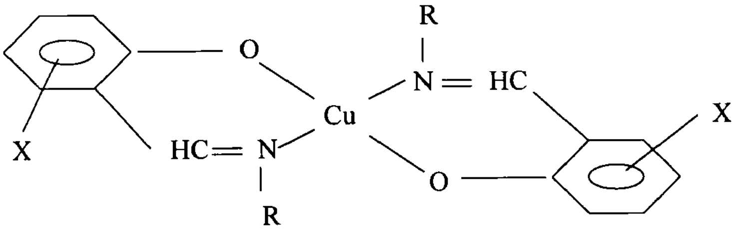
ABSTRACT

The electronic absorption spectra of *trans*-[Cu(sap)$_2$], where (Hsap = salicylidene-o-aminopyridine (Schiff base)), were measured in various solvents at room temperature. The d-d transition energies is used to derive the angular overlap model (AOM) parameters in C_{2h} symmetry. The experimental curves were resolved by Gaussian analysis. A comparison of the spectra, ligand field parameters and stereochemistries in various solutions was made. The effect of the solvents upon the σ-, π-bonding, and bite angle of the bidentate ligand is discussed.

INTRODUCTION

Metal complexes derived from Schiff bases were know for over one hundred years. These complexes, containing different central metal atoms such as Cu, Ni, Co and Pd, have been studied in great detail for their enzymatic reactions and steric effect. Schiff bases are those compounds containing the azomethine group (-RC=N-). The compounds include various types, but in this work, we are concerned mainly with neutral copper(II) complexes of Schiff base derived from salicylaldehyde and 2-aminopyridine. Those compounds especially with copper(II) ions play an important role in biological systems (i.e. synthetic oxygen carriers). The x-ray data for studied complex are not known by us. Those are known for the complexes with different salicylideneamine derivatives. Generally, the ligands have an approximately *trans*-planar configuration around Cu^{2+} ion[1,2]. The molecular geometry of salicylideneamine complexes of copper(II) shows scheme 1; in our study X=H, R=pyridine ring.



Scheme 1

The bis-[2-pyridyl(salicylideneiminato)]copper(II) complex has been studied early[3,4] . Castiñeiras *et al.*[3] have synthesized this complex electrochemically and discussed electronic (reflectance) and i.r. spectra of solid state in relation to the molecular structure. In the work[4] complex has been prepared by general procedure and characterized on the basis of i.r. spectra, magnetic properties, and electronic spectra of methanol/acetone solution.

EXPERIMENTAL

The *trans*-[Cu(sap)$_2$] complex was prepared according to paper[5] by reaction of bisacetate copper(II) with salicylaldehyde in deoxygenated methanol. The green solution was refluxed for about 0.5 hour. Then a solution of 2-aminopyridine in methanol was added. The mixture was refluxed until it changed its color to brown. The solid complex was filtered and washed with methanol. It is a brown crystalline compound easily soluble in common solvents like ethanol (EtOH), N,N-dimethylformamide (DMF), dimethyl sulphoxide (DMSO), methanol (MeOH), acetonitrile (CH_3CN), 1,4-dioxane ($C_4H_8O_2$), carbon tetrachloride (CCl_4), benzene (C_6H_6), and chloroform ($CHCl_3$).

The salicylidene-o-aminopyridine ligand was prepared in the following way[6]: salicylaldehyde and 2-aminopyridine were combined in methanol, and the yellow solution was refluxed for approximately 0.5 hour. The ligand was filtered and washed with methanol. It is a yellow crystalline compound easily soluble in the same solvents as the complex.

Both the compounds: complex and ligand (Schiff base) were analyzed for purity. Copper analyses were performed by EDTA titration using pirocatechol violet as the indicator. Carbon, hydrogen and nitrogen analyses carried out by the Laboratory of Microanalysis and Automation of Analitycal Methods (P.A.S., Łódź, Poland). The results of elementary analysis agreed with the expected composition. Analitycal data of the complex are as follows: found: Cu, 13.9; C, 62.95; H, 3.99; N, 12.35%; calc.: Cu, 13.88; C, 62.94; H, 3.99; N, 12.23%. Those one for the ligand are: found: C, 71.97; H, 5.14; N, 14.39%; calc.: C, 72.71; H, 5.08; N, 14.13%.

The solutions of *trans*-[Cu(sap)$_2$], were prepared by dissolving a weighed amount of the complex in: EtOH, DMF, DMSO, MeOH, CH_3CN, $C_4H_8O_2$, CCl_4, C_6H_6, and $CHCl_3$. The composition of the complex species in various solutions has been confirmed by conductance measurements. The molar conductances were measured using the conductivity meter OK-120/1 and electrode OK-902 (Radelkis). The *trans*-[Cu(sap)$_2$] complex has the molar conductivity values 0.2, 11.0, 4.0, 5.0, 0.0, 0.2, 0.0, 0.0 and 0.0 $\Omega^{-1}mol^{-1}cm^2$, for EtOH, DMF, DMSO, MeOH, CH_3CN, $C_4H_8O_2$, CCl_4, C_6H_6, $CHCl_3$, respectively. The low conductance values of *trans*-[Cu(sap)$_2$], in all solutions show that they are non-electrolytes. The measurement conditions for the conductivity are the same as for the electronic absorption spectra (i.e. $\sim 1.0\times10^{-3}$M). The visible and ultraviolet spectra were recorded on a Beckman DU68 spectrophotometer. Measured spectra were recorded digitally (0.5 nm step) over the range 900-200 nm after dissolving the sample. The spectral data at selected 350 wavenumbers over the range 11000-19000 cm^{-1} were employed for analysis and resolved into Gaussian components.

METHOD OF CALCULATIONS

The d-orbital energies for this complex have been obtained using the standard procedure of finding the orbital energies[7]. In this work we choose orientation of the *trans*-[M(L1L2)$_2$] molecule where L1$^{(1)}$-L2$^{(2)}$-M-L1$^{(3)}$-L2$^{(4)}$ plane is coplanar with the cartesian *xy* plane, and *y* axis bisects the L1$^{(1)}$-M-L2$^{(2)}$ and L1$^{(3)}$-M-L2$^{(4)}$ angles (where superscripts refer to number of the ligator). The scheme of *trans*-[M(L1L2)$_2$] molecule and coordinate system is the same as in papers[8]. Assuming that M (metal ion) and LL ligands form the plane, total equations for matrix elements are derived and presented in previous papers[8a]. The ligators have angular coordinates as follows:

ligator	L1$^{(1)}$	L2$^{(2)}$	L1$^{(3)}$	L2$^{(4)}$
θ	90	90	90	90
ϕ	90-(α/2)	90+(α/2)	270-(α/2)	270+(α/2)

where α is the L1-M-L2 bite angle and numbers 1, 2 refer to different ligators of the bidentate ligands, respectively.

The salicylidene-o-aminopyridine is coordinated to copper(II) through both oxygen (L1, from hydroxyl group) and nitrogen (L2, from amines group) ligators. This bidentate ligand, when coordinated to metal ion, forms a bite angle which is different from 90°. The oxygen and nitrogen donors of this Schiff base derived from salicylaldehyde and aminopyridine are assumed to have different π-interactions with the metal ion. Thus, oxygen atom has $\pi_\perp$ and $\pi_\parallel$ interactions, while nitrogen donor atom, which can be considered to be sp^2 hybridized, has perpendicular interaction to the ligand plane ($\pi_\perp$) only. In the case when only in-plane ligand field disturbances are taken into account (four-coordinate) and assuming hole formalism, the full matrix elements from[8a] are transformed for the studied salicylidene-o-aminopyridine system with d^9 ion as follows:

$$E[a_g(1), xy] = -1.5(e_\sigma(O)+e_\sigma(N))\sin^2\alpha - 2(e_{\pi\perp}(O)+e_{\pi\perp}(N))\cos^2\alpha \tag{1a}$$

$$E[a_g(2), x^2-y^2] = -1.5(e_\sigma(O)+e_\sigma(N))\cos^2\alpha - 2(e_{\pi\perp}(O)+e_{\pi\perp}(N))\sin^2\alpha \tag{1b}$$

$$E[a_g(3), z^2] = -0.5(e_\sigma(O) + e_\sigma(N)) \tag{1c}$$

$$E[b_g(1), yz] = -(1+\cos\alpha)e_{\pi\parallel}(O) \tag{1d}$$

$$E[b_g(1), xz] = -(1-\cos\alpha)e_{\pi\parallel}(O) \tag{1e}$$

$$\langle a_g(1)|V_{C_{2h}}|a_g(2)\rangle = [-1.5(e_\sigma(O)+e_\sigma(N)) - 2(e_{\pi\perp}(O)-e_{\pi\perp}(N))] \sin\alpha\cos\alpha \tag{1f}$$

$$\langle a_g(1)|V_{C_{2h}}|a_g(3)\rangle = -(\sqrt{3}/2)(e_\sigma(N) - e_\sigma(O)) \sin\alpha \tag{1g}$$

$$\langle a_g(2)|V_{C_{2h}}|a_g(3)\rangle = -(\sqrt{3}/2)(e_\sigma(O) - e_\sigma(N)) \cos\alpha \tag{1h}$$

$$\langle b_g(1)|V_{C_{2h}}|b_g(2)\rangle = - e_{\pi\parallel}(O) \sin\alpha \tag{1i}$$

All the band maxima reported here are derived from Gaussian analysis of the experimental curve. Our calculations take into account all the transitions which are given by ligand field theory. The details of the method are presented in work[9] (and refs. herein). Absorption spectrum of the studied complex was fitted with Gaussian components using CFP program. Ligand field parameters were calculated using the LFP program[10] (former DAFP) based actually on two minimization techniques: the Powell method (non-gradient) and the Davidon-Fletcher-Powell method (gradient estimation). The computer programs are written in FORTRAN77. All the calculations were carried out on an IBM PC.

RESULTS AND DISCUSSION

Our study is centered on an interpretation of the electronic spectra of *trans*-bis{N-[2-pyridyl(salicylideneiminato)]}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. Castiñeiras *et al.*[3] have synthesized and characterized thirteen copper(II) complexes of

Schiff bases derived from substituted salicylaldehydes and 2-aminopyridine 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), (**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 studied by us in this 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 slight shorter then Cu-O bonds. The bond angles N-Cu-O (bite angle α) are 91.42(7) in **1** and 90.20(2) in **2**. The N-Cu-N (O-Cu-O) groups are linear in both the compounds (180.1(4)°). Thus, the assumed geometrical model (C_{2h} group) is adequate for x-ray structure and our calculations of the AOM parameters, especially for the solution spectra.

The spectrum of bis(salicylidene-o-aminopyridine)copper(II) complex in methanol/acetone solution has been presented[4] in literature. Authors have reported that spectrum shows only one broad medium intensity band at 12500-16666 cm^{-1}. The solid state electronic spectrum of this complex[3] shows two d-d bands at 13160 and 16670(shoulder) cm^{-1}, and one *ca* 21000 cm^{-1}, assigned by authors to a charge-transfer transition. The electronic absorption spectra of *trans*-[Cu(sap)$_2$] in various solutions shows Figure 1. All the spectra exhibit only one very broad band with maximum at 14000-16000cm^{-1} (ε~150-250, $cm^{-1}\cdot M^{-1}$) which correspond 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

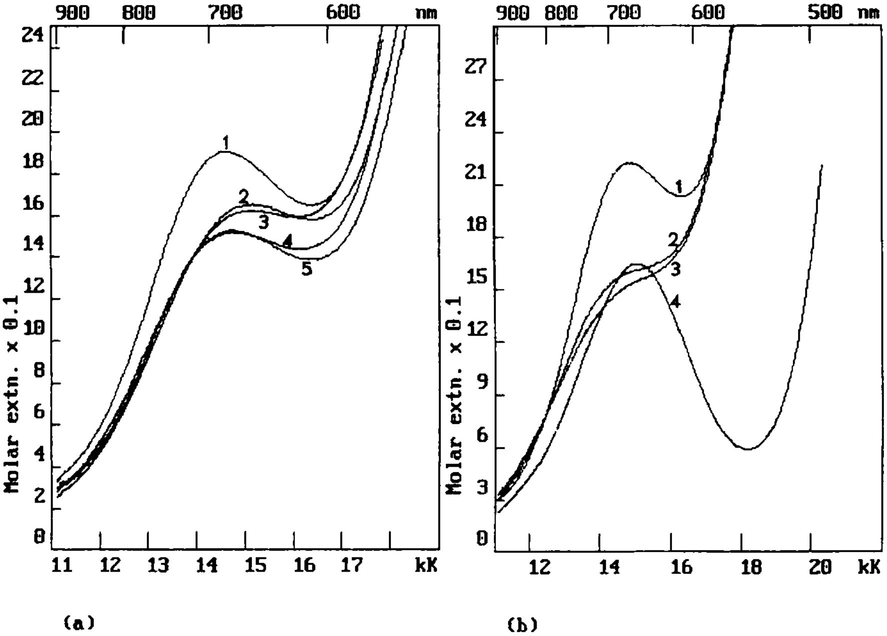
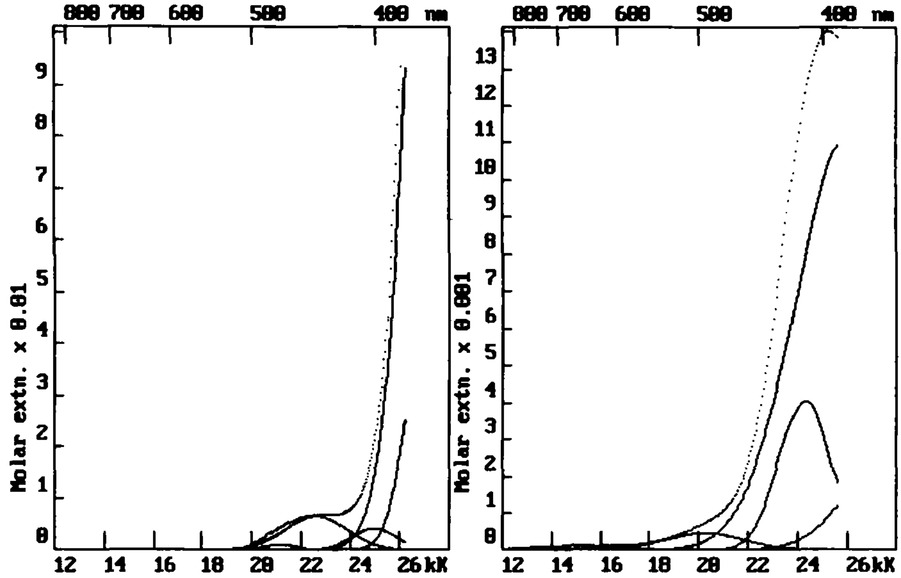


FIG. 1. Electronic absorption spectra of the *trans*-[Cu(sap)$_2$] complex at room temperature in various solvents; polar (a): 1 - CH_3CN, 2 - EtOH, 3 - MeOH, 4 - DMF, and 5 - DMSO; non-polar (b): 1 - $CHCl_3$, 2 - C_6H_6, 3 - CCl_4, and 4 - $C_4H_8O_2$; (computer print).

symmetry. The d-d spectra may also be complicated further by overlapping more intense charge-transfer (complex) or intramolecular (ligand) spectral bands. This effect is especially observed in C_6H_6 and CCl_4 solutions. Gaussian analysis of the spectra of complex and ligand in the near UV region confirmed that those are charge-transfer transitions. Figure 2 shows the comparison of the methanol solution spectra of the ligand (Fig. 2a) and complex (Fig. 2b) in the near UV region, together with their Gaussian analysis. As seen, the lowest intramolecular bands (21000 cm^{-1}, ε=10, and 22500 cm^{-1}, ε=65) are not overlap on the d-d transitions in the visible



(a) (b)

FIG. 2. Comparison of electronic absorption spectra in MeOH solution in visible and near ultraviolet region of the Hsap ligand (a) and *trans*-[Cu(sap)$_2$] complex (b); (computer print).

region, contrary to the significant more intensity charge-transfer transition (20000 cm^{-1}, ε=450) (see 5th bands in Table 1). As mentioned, the most overlapping is observed in C_6H_6 and CCl_4 solutions. Figure 3 shows, as example, visible region spectra of the *trans*-[Cu(sap)$_2$] complex in methanol solution, together with Gaussian components. Figures 4 and 5 show the experimental spectra in d-d region in all the other studied solvents along with Gaussian analysis. Tables 1 and 2 summarize 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%), for polar and non-polar solvents, respectively. The bands assignment on the energy

TABLE 1

Parameters of the component bands resulting from Gaussian analysis of the electronic spectra of $[Cu(sap)_2]$ in polar solutions, symmetry C_{2h} .

No	ε [dm^3 $mole^{-1}$ cm^{-1}]	ν_0 [cm^{-1}]	$\delta_{1/2}$ [cm^{-1}]	f_{osc}
EtOH: RMS% = 0.15				
1	20.803	11502.2	2722.6	2.604×10^{-04}
2	42.153	13260.3	2432.8	4.726×10^{-04}
3	100.848	14602.7	2705.6	1.254×10^{-03}
4	60.008	16418.6	3182.8	1.262×10^{-03}
5	1019.019	21718.9	5001.2	2.343×10^{-02}
DMF: RMS% = 0.29				
1	27.257	11818.2	3259.8	4.085×10^{-04}
2	47.138	13584.4	2488.2	5.392×10^{-04}
3	114.518	15037.1	3215.6	1.693×10^{-03}
4	68.380	17530.8	3337.8	1.049×10^{-03}
5	500.067	20529.7	3919.6	9.012×10^{-03}
DMSO: RMS% = 0.35				
1	28.462	11823.9	3150.2	4.117×10^{-04}
2	51.332	13705.0	2376.4	5.608×10^{-04}
3	110.416	15112.7	3269.0	1.659×10^{-03}
4	37.237	17191.3	3517.2	6.021×10^{-04}
5	659.666	21303.5	4705.4	1.427×10^{-02}
MeOH: RMS% = 0.19				
1	30.420	11896.8	3321.2	4.645×10^{-04}
2	70.106	13869.1	2614.6	8.427×10^{-04}
3	122.065	15478.6	2988.8	1.677×10^{-03}
4	57.384	17448.6	2598.4	6.855×10^{-04}
5	444.624	20351.1	3735.2	7.635×10^{-03}
6	11193.363	25894.1	4987.0	2.566×10^{-01}
CH_3CN: RMS% = 0.20				
1	36.093	11929.3	3215.4	5.335×10^{-04}
2	94.112	13778.6	2385.8	1.032×10^{-03}
3	123.543	15265.1	2837.6	1.612×10^{-03}
4	60.008	17654.1	3600.4	9.933×10^{-04}
5	785.304	21217.5	4619.6	1.668×10^{-02}

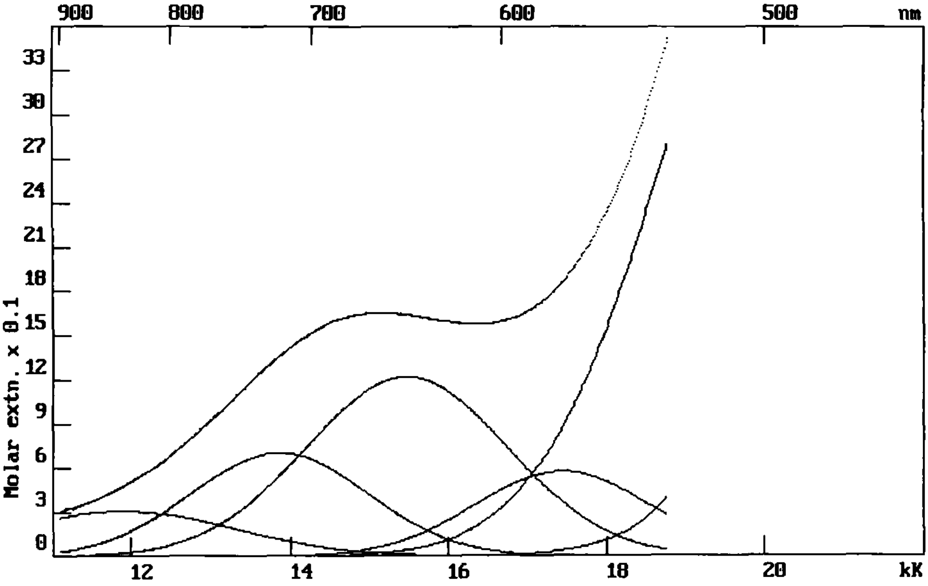


FIG. 3. Absorption electronic spectrum and Gaussian line-shapes of *trans*-[Cu(sap)$_2$] complex in MeOH solution; (computer print).

transitions is based on fitting the resolved band maxima (Gaussian analysis) with the calculated transition energies using one-electron state energies (Eqns. 1a-i). The values of AOM parameters of *trans*-[Cu(sap)$_2$] in various solutions together with resolved and calculated transition energies are collected in Table 3. The best fit with the experimental data was 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 DMF solution (d_{z^2} ($^2A_g(3)$), 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 Figure 6. The order of the d_{yz}

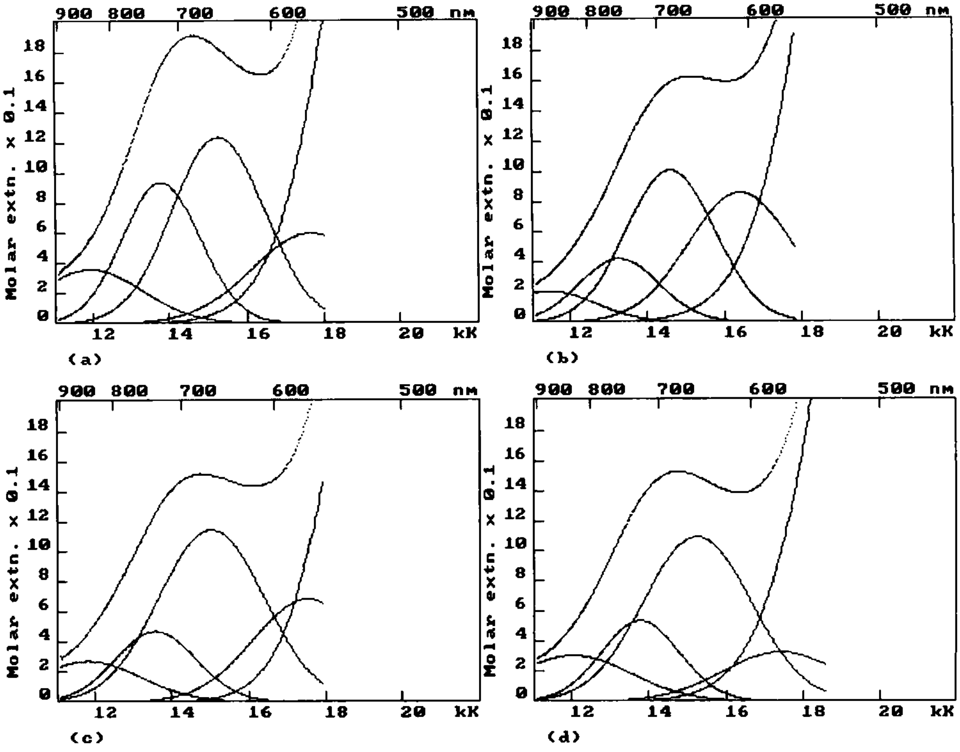


FIG. 4. Absorption electronic spectra and Gaussian line-shapes of *trans*-[Cu(sap)$_2$] complex in polar solvents: CH_3CN (a), EtOH (b), DMF (c), DMSO (d); (computer print).

and d_{xz} orbitals is $d_{yz} < d_{xz}$ for $\alpha < 90°$, and $d_{yz} > d_{xz}$ for $\alpha < 90°$. The splitting energies Δ_1 (see FIG. 6) is due to the deviation of the bite angle from 90°. The lowest values of the bite angle ($\alpha = 86.0°$) is for DMF solution, and highest i.e. $\alpha = 88.4°$ for C_6H_6 and CCl_4 solutions. Opening the chelate ring so as obtain 90° is in order:

$DMF \sim CH_3CN \sim EtOH \sim C_4H_8O_2 \sim DMSO = MeOH < CHCl_3 \sim C_6H_6 = CCl_4$

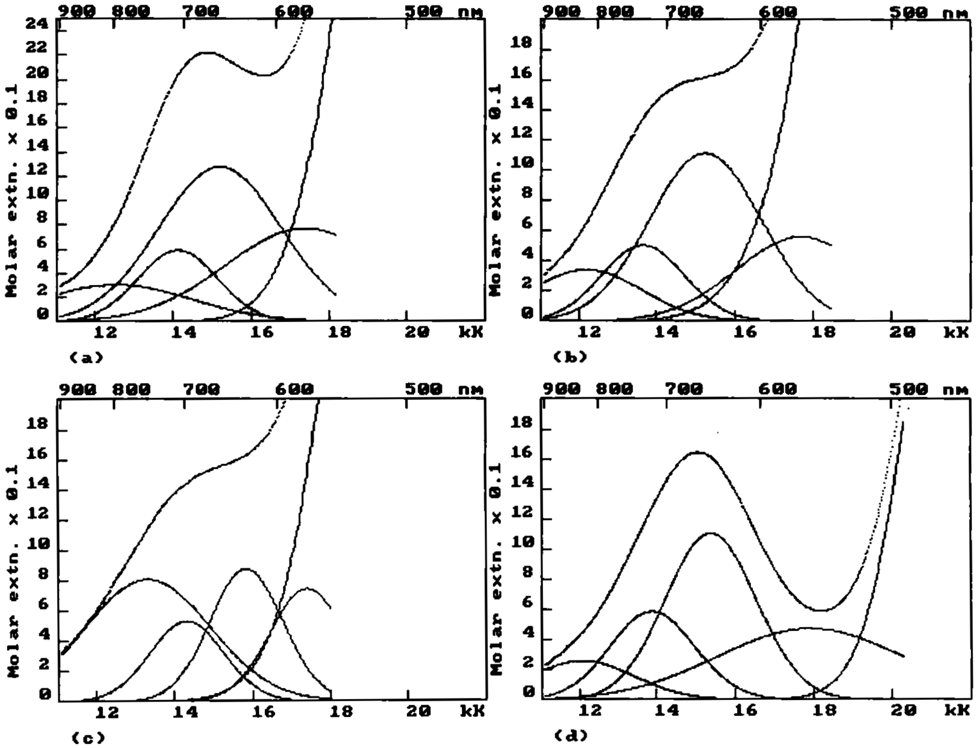


FIG. 5. Absorption electronic spectra and Gaussian line-shapes of *trans*-[Cu(sap)$_2$] complex in non-polar solvents: $CHCl_3$ (a), C_6H_6 (b), CCl_4 (c), $C_4H_8O_2$ (d); (computer print).

The size of this effect depends predominantly on the character of the solvent[11]. The DN (Gutmann's donor number[11]) and AN (acceptor number) are the determining factors in those changes, but also solvent polarity , e.g. dielectric constant (ε) is important element. The complexes 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[12] of solvents i.e. EtOH (20.0),

TABLE 2

Parameters of the component bands resulting from Gaussian analysis of the electronic spectra of [Cu(sap)$_2$] in non-polar solutions, symmetry C_{2h} .

No	ε [dm^3 mole^{-1} cm^{-1}]	ν_0 [cm^{-1}]	$\delta_{1/2}$ [cm^{-1}]	f_{osc}
$C_4H_8O_2$: RMS% =0.23				
1	26.046	12065.7	3144.8	3.766×10^{-04}
2	58.787	13883.0	2573.2	6.955×10^{-04}
3	110.627	15376.2	2721.8	1.384×10^{-03}
4	47.444	17919.4	5566.4	1.214×10^{-03}
5	486.269	22160.9	3176.46	7.101×10^{-03}
CCl_4: RMS% = 0.10				
1	34.835	12174.4	3511.8	5.624×10^{-04}
2	44.228	13602.5	2680.8	5.451×10^{-04}
3	194.395	15313.4	3488.0	1.754×10^{-03}
4	54.768	17496.1	3632.8	9.147×10^{-04}
5	730.546	20524.6	4148.2	1.393×10^{-02}
C_6H_6: RMS% = 0.12				
1	34.125	12190.3	3376.0	5.296×10^{-04}
2	50.433	13645.1	2516.8	5.836×10^{-04}
3	111.029	15236.4	3368.8	1.720×10^{-03}
4	56.110	17689.3	3909.8	1.009×10^{-03}
5	895.733	21075.5	4673.6	1.925×10^{-02}
$CHCl_3$: RMS% = 0.15				
1	30.451	12523.6	4596.6	6.435×10^{-04}
2	59.067	14117.8	2401.2	6.521×10^{-04}
3	127.649	15202.9	3722.4	2.184×10^{-03}
4	77.095	17388.4	4802.6	1.702×10^{-03}
5	692.193	20305.9	3672.4	1.169×10^{-02}

TABLE 3

Assignments, transition energies, and AOM parameters for *trans*-[Cu(sap)$_2$] complex in various solutions (in cm^{-1}); ground term:$^2A_g(1)$, d_{xy}.

Assignment	EtOH	DMF	DMSO	MeOH	CH_3CN	$C_4H_8O_2$	CCl_4	C_6H_6	$CHCl_3$
$^2A_g(3)$, d_{z^2}	11502	11818	11824	11897	11929	12065	12174	12190	12524
$^2A_g(2)$, $d_{x^2-y^2}$	13260	13584	13705	13869	13779	13883	13602	13645	14118
$^2B_g(1)$, d_{yz}	14603	15037	15113	15479	15265	15376	15313	15236	15203
$^2B_g(2)$, d_{xz}	16419	17531	17191	17449	17654	17919	17496	17689	17388
$e_\sigma(O)$	6737	6886	6878	6891	6925	6969	6982	6943	7265
$e_\sigma(N)$	3865	4622	4331	4535	4665	4818	4406	4631	3840
$e_{\pi\perp}(O)$	712	1197	944	1052	1063	1165	1063	1080	755
$e_{\pi\parallel}(O)$	908	1247	1039	985	1194	1270	1091	1226	1092
$e_{\pi\perp}(N)$	931	891	868	809	974	950	903	962	901
α	86.2	86.0	86.4	86.4	86.1	86.3	88.4	88.4	87.9

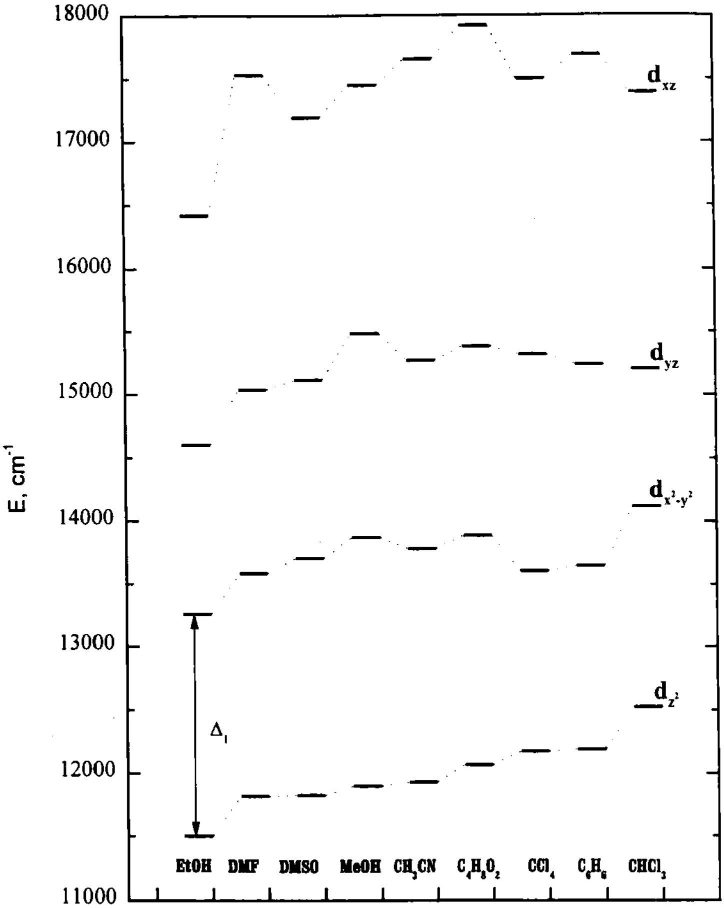


FIG. 6. Spectral transitions (energy diagram) of the *trans*-[Cu(sap)$_2$] complex (in relation to d_{xy} orbital) for various solutions.

DMF (26.6), DMSO (29.8), MeOH (19.1), CH_3CN (14.4), and $C_4H_8O_2$ (14.8). The second type is the case where the bite angle is opened to 90° (i.e. >88°), for lower DN values[12] of solvents i.e. CCl_4 (0.0), C_6H_6 (0.1), and $CHCl_3$ (-0.5). Similarly, contrary dependence of the bite angle values on dielectric constant of solvents is observed. For the solvents of high ε values ($\varepsilon > 20$) the bite angle is about 86°, while for the low ε values ($\varepsilon < 5$) this one is largest (~88°), except 1,4-dioxane solution where the angle is 86.3°.

CONCLUSION

The oxygen atom (from hydroxyl group; sp hybridized) has different π interactions then nitrogen (from amine group; sp^2 hybridized). Oxygen donor atoms have different π interactions i.e. $\pi_\perp$ and $\pi_\parallel$ to the salicylic ring, while nitrogen donor atoms have only $\pi_\perp$ interactions. Since, comparison of the π-bonding abilities of both the ligators in various solutions is not simply. The oxygen $\pi_\perp$ interaction is the weakest in ethanol solution and the strongest in DMF solution, and increases in following order:

$EtOH=CHCl_3<DMSO<MeOH=CH_3CN=CCl_4=C_6H_6<C_4H_8O_2<DMF$

Moreover, in CCl_4, DMF, MeOH and DMSO both π interactions are similar; in $CHCl_3$, C_6H_6, CH_3CN, and $C_4H_8O_2$ $\pi_\perp$ interactions are stronger then $\pi_\parallel$ interactions; only in EtOH $\pi_\perp$ is weaker then $\pi_\parallel$ interaction. The nitrogen $\pi_\perp$ interactions are similar in all the solutions.

The oxygen σ interactions (e_σ(O) parameter) depends on solution, and it values are decreased in agreement with decreasing DN values of solvents:

$CHCl_3>>CCl_4\sim C_6H_6\sim CH_3CN>C_4H_8O_2\sim MeOH\sim DMSO\sim DMF>>EtOH$

This dependence was not observed for the nitrogen σ interactions which are changed as follows:

$CHCl_3\sim EtOH>DMSO>CCl_4>MeOH>C_6H_6\sim DMF\sim CH_3CN>>C_4H_8O_2$

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