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Spectrochemical Properties of Noncubic Transition Metal Complexes in Solutions. XIII. Angular Overlap Treatment of Diaquabis(salicylideneaminothiazole)cobalt(II)

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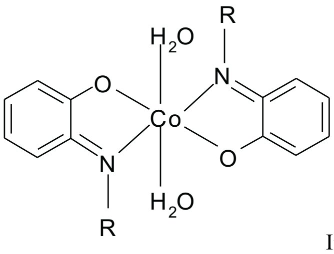
Mixed ligand cobalt(II) complex with monodentate (water) and bidentate (Schiff base: salicylidene-2-aminothiazole) ligands has been characterized by elemental analyses, molar conductivities, ultraviolet (UV) and visible (VIS) spectroscopy. The electronic spectra of solids as well as solutions exhibit pseudo-octahedral coordination geometry for the cobalt centre. The molar conductivities indicate their non-electrolytic properties in solvents studied. Combined multi-technique experiments have been used to postulate the C_{2h} geometry for the species in solutions and to determine the coordination properties of ligators and their bonding abilities (ligand-field parameters).

Key words: cobalt(II) complexes, Schiff base, salicylidene-2-aminothiazole, solutions, electronic spectra, angular overlap model

This paper is a continuation of our studies on interpretation of the electronic spectra of the cobalt(II) complexes with Schiff bases derived from salicylaldehyde and aromatic amines in various solvents [1,2]. This study deals with interpretation of the electronic absorption spectra of diaquabis(salicylidene-2-aminothiazole)cobalt(II) ($[Co(sat)_2(H_2O)_2]$) in DMF and DMSO solutions in NIR-VIS region (d-d transitions) and calculation of the ligand-field parameters (AOM) allowing all the transitions, which are required in a ligand-field theory. The d-d spectra presented are complicated further by overlapping of more intense spectral bands from UV region. Because of this, the interpretation of the ultraviolet spectra was necessary and helpful to make a clear and unequivocal quantitative interpretation of the visible spectra, *i.e*., ligand-field (d-d) region only.



In our study R = thiazole ring

Scheme 1. Cobalt(II) complex with salicylideneamine derivatives.

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EXPERIMENTAL

Measurements: The molar conductances were measured using a microcomputer pH/conductivity meter CPC-551 (Elmetron, Poland) and platinum dip electrode CD-2. The ultraviolet (UV) spectra were recorded on a SPECORD M40 (Zeiss Jena) spectrophotometer digitally (20 cm^{-1} step) after dissolving the sample for concentration $c \sim 1.0\times10^{-2}$ M. The near infrared (NIR) and visible (VIS) spectra (both solutions and solid state) were carried out digitally (1 nm step) on a Cary 5E (Varian) spectrophotometer. The conductivities were measured for the concentration $c \sim 1.0\times10^{-2}$ M at room temperature. The NIR-VIS and UV spectra were resolved into the Gaussian components. These spectra were used for calculations of ligand-field (AOM) parameters (in NIR-VIS region).

Chemicals: The $[Co(sat)_2(H_2O)_2]$ complex was prepared by reaction of bisacetate cobalt(II) tetra hydrate with 2-aminothiazole and salicylaldehyde in deoxygenated methanol [3]. The solid complex was precipitated as red crystals. The solubility of the complex was examined in ten common solvents. It was insoluble in: water, ethylene glycol (EG), formamide (FM), chloroform ($CHCl_3$), dioxane (Dx), methanol (MeOH), ethanol (EtOH), and acetonitrile (ACN) but easy soluble in: dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). The complex was analysed for purity by elemental analysis. Cobalt analyses were performed by EDTA titration using murexide as an indicator. The results agreed with the expected composition.

Method of calculations: A convenient approach has been presented for the tetragonally distorted Cr(III) complexes [4]. Here the matrix elements of the excited states presented in [4], given as a function of the orbital energies and Racah parameters, were used for cobalt(II) complexes, assuming hole-formalism. The total one-electron orbital energy equations given in [5] were reduced and applied for complex with C_{2h} symmetry [6,7]. The strong field wave functions [8,9] were adopted to derive the ligand field energy matrices, without spin-orbit coupling, for orthorhombic symmetry. The d^3 strong field states under D_{2h} symmetry have been determined to possess the symmetries listed in [9]. This wave functions collection is also suitable for C_{2v} and C_{2h} point groups. The correlation between the symmetry of wave functions in D_{2h} and $C_{2v}^{(z)}$ and C_{2h} ligand fields is as follows:

D_{2h}	:	A_g	B_{3g}	B_{2g}	B_{1g}
$C_{2v}^{(z)}$	:	A_1	B_2	B_1	A_2
C_{2h}	:	A_g	A_g	B_g	B_g

On the bases of the wave functions, the energy matrix for d^3 (d^7) systems [9] (symmetries D_{2h}, C_{2v} and C_{2h}) without spin-orbit coupling have been used. All the band maxima reported in this work are determined from Gaussian analysis of the experimental spectral contours. Absorption spectra were fitted with Gaussian components using CFP computer program [10] (and refs. herein), based on the Slavič [11] algorithm, which for the last few years has been successfully applied by us to the resolution of d-d (ligand-field) spectra. The ligand-field parameters (AOM) were calculated using the LFP computer program [12]. The AOM calculations were carried out within the framework of the angular overlap simple model developed in [13,14] and in [15]. The assignment of bands is based on fitting the resolved band maxima (from Gaussian analysis) with the calculated transition energies (eigenvectors) using the d^3 rhombic (C_{2h} symmetry) energy levels with full configuration interactions and without spin-orbit coupling. In this work the ligand-field (d-d) spectrum of $[Co(sat)_2(H_2O)_2]$ has been assigned by application of ligand-field (AOM) and C_{2h} symmetry. Then, for the complex studied a full set of ten AOM parameters ($e_\sigma(H_2O)$, $e_\sigma(N)$, $e_\sigma(O)$, $e_\pi(H_2O)$, $e_{\pi\perp}(N)$, $e_{\pi\perp}(O)$, $e_{\pi||}(O)$, B, C, and α) was fitted to seventeen bands, which result from Gaussian analysis.

RESULTS AND DISCUSSION

The electronic spectra [16–19] as well as magnetic moments [20,21] of cobalt(II) complexes depend upon the geometry of the complexes. The differences in the band positions and magnetic moments may be regarded as diagnostic of stereochemistry of the cobalt(II) complexes. In fact, those are rather straightforward ways, to determine the geometry of a cobalt(II) complex. Typical electronic spectrum for Co(II) with bidentate Schiff base complex [22] in pyridine (pseudo-octahedral) shows maxima at about 10000, 26000, 33100 cm^{-1} and a shoulder at 17000 cm^{-1}. Tetrahedral complexes [16–19] show maxima at about 7700, 11200, 25000, and 34100 cm^{-1}, and shoulders at 17000 and 28000 cm^{-1}. The magnetic moments [19–21] for the tetrahedral cobalt(II) complexes are in the range 4.2–4.7, whereas for octahedral: 1.7–2.0 or 4.4–5.5 μ_B. The solutions of $[Co(sat)_2(H_2O)_2]$ were prepared by dissolving a weigh amount of the complex in: DMF, and DMSO. Electronic absorption spectra of complex studied in solutions show maxima at *ca.* 8700, 25000, and 30000 cm^{-1}. Moreover, the solid-state spectrum of this complex is characterized by maxima at *ca.* 8800, 22800, 30000 and shoulder at 40000 cm^{-1}. Similar band positions (solid-state and solution) as well as low band intensities (*i.e.*, $\varepsilon < 10\ cm^{-1}M^{-1}$) in the d-d region, suggest the pseudo-octahedral geometry of complex studied in solution.

Ultraviolet spectra: The spectrum of $[Co(sat)_2(H_2O)_2]$ in methanol/acetone solution has been presented in [23]. The authors have reported that spectrum shows maxima at 9500–10500 and 20000–22000 cm^{-1}. Fig. 1 shows the electronic absorption spectra of $[Co(sat)_2(H_2O)_2]$ in DMF and DMSO solvents in NIR-VIS (a) and UV region (b). The spectra in UV region (Fig. 1b) exhibit two maxima at about 25000 and 30000 cm^{-1}. The former maximum for DMF solution is observed as a shoulder.

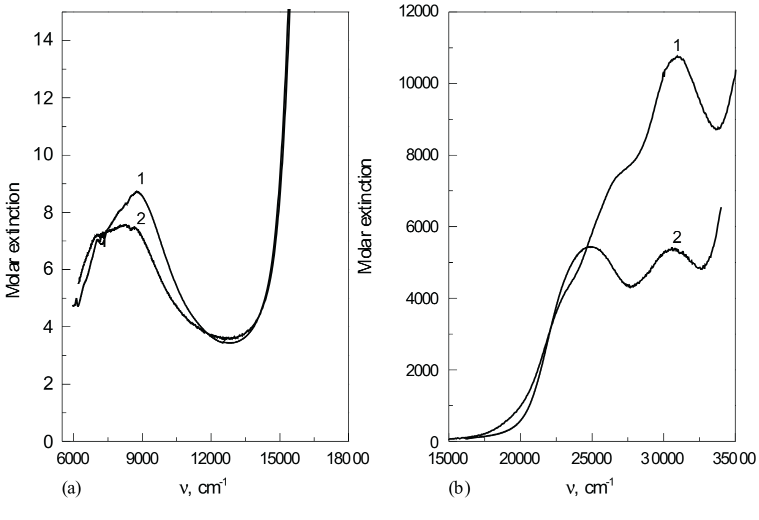

Figure 1. Electronic spectra of $[Co(sat)_2(H_2O)_2]$ at room temperature in solvents: 1 – DMF, 2 – DMSO in NIR-VIS region (a) and in UV region (b).

The latter characterizes the highest intensity in DMF solution, whereas the intensities of observed bands at *ca.* 25000 cm^{-1} are close together. These spectra were resolved into the component bands. The bands for Gaussian analysis of spectra in discussed region have been assumed from the analysis of the Hsat ligand spectra [24] and additional CT bands predicted for the complex. Usually, the observed absorption bands at *ca.* 25000 and 35000 cm^{-1} are attributed to the charge transfer transitions [25,26]. Based on [1,2] and [26,27] we have assigned the band at about 25000 cm^{-1} to MLCT *i.e.*, Co→O, and at higher energy to MLCT (Co→N) transitions.

Visible spectra and ligand-field analysis: No crystallographic data of [Co(sat)$_2$(H$_2$O)$_2$] are available. The X-ray data for distorted tetrahedral cobalt(II) complexes with Schiff bases are known [28–32]. Usually, Co(II) complexes of this type characterize longer Co–N distances than Co–O distances. Thus, we can expect weaker interactions between cobalt(II) and nitrogen-donor than oxygen in solutions too. Fig. 1a presents the electronic spectra of [Co(sat)$_2$(H$_2$O)$_2$] in DMF and DMSO solutions in NIR-VIS region. These spectra exhibit one maximum at 8800 cm^{-1} (7.5–9.0 cm^{-1}M^{-1}). We have confirmed predominance of an electrically neutral species in solutions by conductance measurements. The conductance values of both the [Co(sat)$_2$(H$_2$O)$_2$] solutions are 2.5, and 0.0 S mol^{-1}cm^2 for DMF, and DMSO, respectively. Electronic spectra have been used to postulate the pseudo-octahedral geometry for the species in solutions (q.v. Scheme 1). Thus, the assumed geometrical model (C$_{2h}$) is adequate for our calculations of the ligand-field parameters for the solution systems. Fig. 2 shows the experimental spectra in the NIR-VIS region in solvents studied along with Gaussian analysis. Table 1 summarizes the results of Gaussian analysis, *i.e.*, parameters of the component bands, their oscillator strength

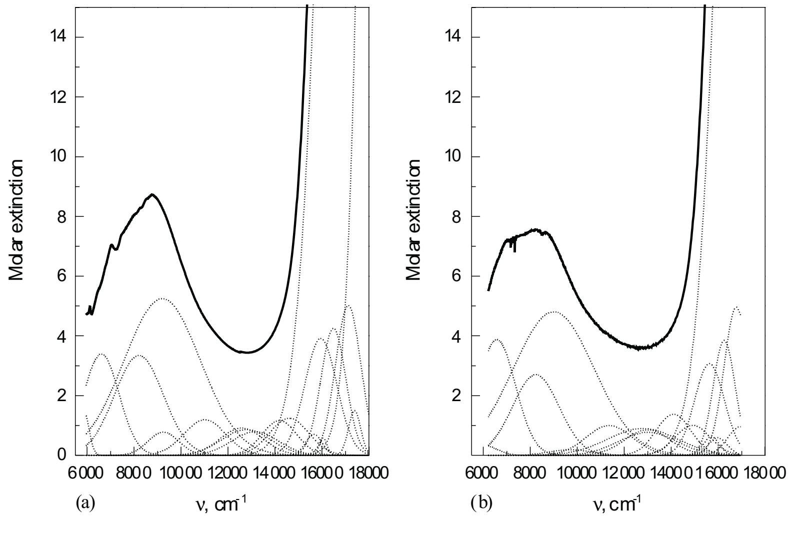

Figure 2. Electronic spectra and the Gaussian line-shapes of [Co(sat)$_2$(H$_2$O)$_2$] at room temperature in NIR-VIS region in solvents: DMF (a), DMSO (b).

Table 1. Parameters of the component bands resulting from the Gaussian analysis of the electronic spectra of $[Co(sat)_2(H_2O)_2]$ in DMF and DMSO solutions and visible region; C_{2h} symmetry.

Band No	ε ($M^{-1}cm^{-1}$)	ν_0 (cm^{-1})	$\delta_{1/2}$ (cm^{-1})	f_{osc}
DMF: RMS% = 0.97				
1	1.4	5879.1	495.4	3.3×10^{-06}
2	3.4	6608.9	1774.0	2.8×10^{-05}
3	3.3	8209.0	2449.4	3.8×10^{-05}
4	5.2	9201.8	3823.8	9.2×10^{-05}
5	0.8	9251.6	1534.4	5.5×10^{-06}
6	1.2	11011.7	2068.4	1.1×10^{-05}
7	0.9	12577.0	2163.4	9.1×10^{-06}
8	0.9	12773.6	2454.8	9.7×10^{-06}
9	0.8	13150.0	2340.6	8.5×10^{-06}
10	1.2	14187.3	1733.4	9.3×10^{-06}
11	1.2	14604.4	1951.2	1.1×10^{-05}
12	0.7	15653.1	821.6	2.7×10^{-06}
13	3.9	15951.3	1606.2	2.9×10^{-05}
14	0.6	16051.5	376.8	1.0×10^{-06}
15	4.3	16488.6	1247.2	2.4×10^{-05}
16	5.0	17117.7	1273.0	2.9×10^{-05}
17	1.5	17387.9	611.2	4.2×10^{-06}
18	130.3	18601.3	3372.4	2.0×10^{-03}
19	355.9	20093.1	2502.2	4.1×10^{-03}
DMSO: RMS% = 0.55				
1	0.3	5993.4	1345.2	2.1×10^{-06}
2	3.9	6574.2	1877.0	3.3×10^{-05}
3	2.7	8236.8	2331.6	2.9×10^{-05}
4	4.8	9000.7	4045.0	8.9×10^{-05}
5	0.2	9706.5	2086.0	1.8×10^{-06}
6	1.0	11361.4	2290.0	1.0×10^{-05}
7	0.9	12780.9	3483.0	1.4×10^{-05}
8	0.9	12983.8	2267.0	8.9×10^{-06}
9	0.8	12995.4	2894.2	1.0×10^{-05}
10	1.4	14098.5	1738.0	1.1×10^{-05}
11	1.0	14908.8	1762.6	8.1×10^{-06}
12	3.1	15630.4	1487.0	2.1×10^{-05}
13	0.6	15711.2	793.2	2.3×10^{-06}
14	0.6	15980.5	955.0	2.6×10^{-06}
15	3.8	16256.0	1100.6	1.9×10^{-05}
16	5.0	16775.0	1224.0	2.8×10^{-05}
17	1.0	16953.7	1298.8	5.7×10^{-06}
18	120.4	18598.5	3273.6	1.8×10^{-03}

values, and the relative root mean square error (RMS%). Transition energies, their assignments, values of the angular overlap (AOM) parameters, and root mean squares error (r.m.s.) are collected in Table 2. The Hsat ligand has two different donor atoms; the oxygen atom (from hydroxyl group; sp hybridized in ligand) has different π interactions than nitrogen (from amine group; sp^2 hybridized in ligand).

Table 2. Assignments, transition energies, and AOM parameters of [Co(sat)$_2$(H$_2$O)$_2$] in DMF and DMSO solutions (in cm^{-1}); C$_{2h}$ symmetry and ground term: ^{4}B$_g$[F,T$_{2g}$(E$_g$)].

Assignments	DMF		DMSO	
	resolved	calculated	resolved	calculated
$^2A_g[G,A_{1g}(A_{1g})]$	5880	6240	5990	6330
$^4A_g[F,A_{2g}(B_{1g})]$	6610	6670	6570	6550
$^4B_g[P,T_{1g}(E_g)]$	8210	8590	8240	8410
$^4B_g[F,T_{1g}(E_g)]$	9200	9020	9000	8740
$^2A_g[D(2),T_{2g}(B_{2g})]$	9250	9330	9710	9620
$^2B_g[G,T_{1g}(E_g)]$	11010	10770	11360	10850
$^2B_g[H,T_{2g}(E_g)]$	12580	12410	12780	12620
$^2B_g[H,T_{2g}(E_g)]$	12770	12420	12980	12630
$^2B_g[H,T_{1g}(2)(E_g)]$	13150	12630	13000	12740
$^2A_g[P,T_{1g}(A_{2g})]$	14190	13910	14100	13840
$^2B_g[H,T_{1g}(2)(E_g)]$	14600	15330	14910	15420
$^2A_g[G,E_g(B_{1g})]$	15650	15670	15710	15660
$^4A_g[F,T_{2g}(B_{2g})]$	15950	16040	15630	15800
$^2B_g[G,T_{1g}(E_g)]$	16050	16410	16260	16160
$^4B_g[P,T_{1g}(E_g)]$	16490	16420	15980	16410
$^4B_g[F,T_{1g}(E_g)]$	17120	16920	16780	16540
$^2A_g[F,T_{1g}(A_{2g})]$	17390	17390	16950	17360
r.m.s.		300		300
$e_\sigma(H_2O)$		4060 (360)		4220 (390)
$e_\sigma(N)$		3770 (330)		3200 (240)
$e_\sigma(O)$		5580 (220)		5280 (290)
$e_\pi(H_2O)$		2120 (280)		1780 (270)
$e_{\pi\perp}(N)$		1320 (350)		1190 (340)
$e_{\pi\perp}(O)$		1540 (350)		1440 (340)
$e_{\pi\|\|}(O)$		1760 (190)		1720 (250)
B		600 (20)		600 (20)
C		2960 (60)		3030 (60)
α		89.5 (0.5)		89.5 (0.5)

Oxygen donor atoms exhibit different π interactions, *i.e.* $\pi_\perp$ and $\pi_{||}$ to the salicylic ring, while nitrogen donor atoms present only $\pi_\perp$ interactions. Thus, a comparison of the π-bonding abilities of both ligands in various solutions is not simple. Comparing the σ interaction of donor atoms derived from Schiff base, we can see that it is stronger for oxygen than for nitrogen. The [Co(sat)$_2$(H$_2$O)$_2$] complex in DMSO characterizes the weaker σ- and π-bonding of Schiff base than in DMF solution. The bonding abilities of water ligand in transitions metal complexes have been presented previously [33–35]. The AOM parameters obtained are significantly different. In chromium(III) complexes [33,35] they are in regions $e_\sigma(H_2O)$ = 7500–9300 and $e_\pi(H_2O)$ = 1400–300 cm^{-1}. For cobalt(II) complexes, $e_\sigma(H_2O)$ has been found [34] in the range 2900–3400 cm^{-1}, with $e_\pi(H_2O)$ small and never exceeding 480 cm^{-1}. In our study these are $e_\sigma(H_2O)$ = 4100, 4200 and $e_\pi(H_2O)$ = 2100, 1800 cm^{-1} for DMF and DMSO respectively. Thus, the water interactions with cobalt(II) are weak.

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