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Spectrochemical Properties of Noncubic Transition Metal Complexes in Solutions. XVI. Angular Overlap Treatments of *cis*-Bis(2,2′-bipyridyl)oxalatechromium(III) Iodide in Aqueous Solution[*]

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The electronic absorption spectrum of *cis*-[Cr(ox)(bpy)$_2$]I (bpy = 2,2′-bipyridyl; ox = oxalate ion) of aqueous (H_2O) solution, has been measured at room temperature and interpreted using the angular overlap model (AOM), and assuming C_{2v} as the effective symmetry. All the experimental transitions are derived from Gaussian analysis of the solution spectrum. The calculations of the ligand field parameters take into account all the transitions, which are required from the ligand field theory (except those energetically higher than the range of the measured spectrum). The coordination properties of the ligators and their bonding abilities have been discussed.

Key words: angular overlap model, electronic spectra, chromium(III) complexes, 2,2′-bipyridyl, oxalate, molecular structure, low symmetry, aqueous solution

This work is a part of our research concern the interpretation of the electronic spectra of Cr(III) complexes with nonlinear, bidentate ligands form bonds with π interaction [2–4]. Interpretations of the electronic spectra of the chelate chromium(III) complexes presented up to date have been limited mostly to the spin-allowed and only few spin-forbidden bands and, moreover, to the solid state only. Because structural data reveal that the bidentate ligand forms a bite angle different from 90°, these spectra should be interpreted assuming the C_{2v} symmetry. So far, a few cases have been reported, where authors take into account the bite angle distortion. Vanquickenborne and Ceulemans discussed *cis*-$[CrCl(NCS)(en)_2]^+$, within the AOM framework, as an orthorhombic system [5]. Hoggard and Kirk [6] presented a description of *cis*- and *trans*-isomers of $[Cr(NH_3)_2cyclam]^{3+}$.

The aim of this work is the calculation of the ligand-field parameters for the low-symmetry complex in aqueous solution at room temperature, allowing all the transitions that are required in the ligand field theory. The Gaussian analysis of these "poor" spectra is the only way of a quantitative interpretation of this kind of experiment. General method for the analysis of the d-d transition energies [7–9] (and refe-

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rences herein), observed in the ligand field spectra of the chromium(III) complexes with C_{2v} symmetry, is used to derive the angular overlap model parameters. The calculations were carried out within the framework of the angular overlap simple model developed by Schäffer [10] and Jørgensen [11].

EXPERIMENTAL

Chemicals: *cis*-Bis(2,2′-bipyridyl)oxalatechromium(III) iodide was prepared by method described in paper [12], based on *cis*-bis(2,2′-bipyridyl)dichlorochromium(III) chloride dihydrate [2,13] that was added to aqueous solution of potassium oxalate at the boiling point. The reaction mixture was cooled in ice, and orange iodide complex was filtered off, washed with 96% ethanol, and air-dried. Complex was analysed for purity by elemental analysis. Chromium content was established by spectrophotometric determination of chromium as chromate ion ($\varepsilon_{CrO_4^-} = 1.4\times10^3$ dm^3 mol^{-1} cm^{-1}, at$\lambda = 373$ nm). The results agreed with the expected composition.

Measurements: The solution of *cis*-$[Cr(ox)(bpy)_2]I$ was prepared by dissolving a weighed amount of the complex in redistilled water. The composition of the complex species in this solution has been confirmed by conductance measurements. The molar conductance was measured using a microcomputer pH/conductivity meter CPC-551 (Elmetron, Poland) and platinum dip electrode CD-2. The *cis*-$[Cr(ox)(bpy)_2]I$ complex solution has the molar conductivity value 85.1 S mol^{-1} cm^2 at 25°C. This one is very close to the range anticipated for 1:1 electrolytes, *i.e.*, 70–130 S mol^{-1} cm^2 for aqueous solution [14,15]. It follows, that studied complex has 1:1 electrolytic properties in aqueous solution. We have checked the lack of equilibrium in solution by time-dependent spectral measurements. No spectral changes were observed upon time elapsed up to 2 hrs. These observations indicate either that a coordinate change does not take place or that the accompanying absorbance changes are too small to be observed. Moreover, no conductivity changes were observed up to 4 hrs. However, the interpreted spectrum was recorded as rapidly as possible, *i.e.* 5 minutes after dissolution of the sample. The conditions for the conductivity measurements were the same, as for the electronic absorption spectra (1.19×10^{-3} M). The visible and ultraviolet spectra of *cis*-$[Cr(ox)(bpy)_2]I$ in aqueous solution were recorded on a SPECORD M40 spectrophotometer. The spectra were recorded digitally (20 cm^{-1} step) over the range 11000–30000 cm^{-1} after dissolving sample. The spectral data at selected 738 wave numbers, over the range 13620–28360 cm^{-1} ($l = 1.0$ cm, $c = 1.19\times10^{-3}$ M) were employed for analysis and resolved into Gaussian components.

Method of calculations: All the band maxima reported here are derived from Gaussian analysis of the experimental contour. Most important problem in Gaussian analysis is setting the number of component bands. Some authors consider the bands, which can really be distinguished conclusively from experimental curve, *i.e.* band maxima and shoulders. Our calculations take into account all the transitions, which are given by ligand field theory, even those strong overlapped.

Absorption spectrum of the studied complex was fitted with Gaussian components, using CFP program [16,17]. Ligand field parameters were calculated, using the LFP program [18] (former DAFP [19,20]) based on two minimization techniques: the Davidon-Fletcher-Powell method (gradient estimation) and Powell method (non-gradient). Full energy matrices for the orthorhombic six-coordinate d^3 system (C_{2v} symmetry) given by Kurzak and Kołkowicz [7] were used. For these calculations the total one-electron matrix elements given in [9] were adopted. Coordinate system and numbering of the ligators, used for AOM calculations, are the same as in [9]. In order to apply them to interpretation of the complex studied, *i.e.* six-coordinate $[M(L2L2)(L1L1)_2]$ type complex (which allows isotropy of nitrogen and oxygen ligators), the simplification has been made as follows: ignoring δ-contribution to the M-L bonding, setting isotropy of π-bonding effect about M-L2 bond ($e_{\pi\perp}(L2) \neq e_{\pi\|}(L2)$) and about M-L1 bond ($e_{\pi\|}(L1) = 0$) the orbital energy matrices for *cis*-$[Cr(ox)(bpy)_2]^+$ are obtained. Since, the nitrogen donor (ligator with sp^2 hybridization in ligand) has $\pi_\perp$ interaction only, and oxygen donor (ligator with sp^3 hybridization in ligand) has $\pi_\perp$ and $\pi_\|$ interaction, the above assumptions can be accepted. All the calculations were carried out on an IBM PC.

RESULTS AND DISCUSSION

Our study is centred on interpretation of the electronic absorption spectrum of *cis*-bis(2,2′-bipyridyl)oxalatechromium(III) iodide in aqueous solution. It takes into account a low symmetry of the complex, in particular the bite angle distortion. The X-ray structural data for this complex are not available. Those are known for the chromium(III) complexes with 2,2′-bipyridyl and different monodentate ligands. Generally, the Cr atom has a pseudo-octahedral environment, coordinated by two bidentate bipyridyls and one bidentate oxalate ion. The *cis*-diaquabis(2,2′-bipyridyl) chromium(III) nitrate (**1**) and *cis*-aquahydroxo-bis(2,2′-bipyridyl)chromium(III) iodide monohydrate complexes (**2**) have been studied early and their X-ray data are known [21–23]. The nitrogen donors of bidentate ligands we are noted by N1, N2 and N′1, N′2 for the different ligand molecules, respectively, *i.e.*, the numbers refer to different ligators and prim refer to other ligand. The X-ray data suggested that there are two nitrogen donors (N1,N′1) and two oxygen donors derived from water molecules for (**1**) or from water and hydroxyl group for (**2**) and chromium(III) ion (N1N′1–Cr–OO) in plane. These groups are not strictly planar in both complexes, a planarity is less in complex (**2**) than (**1**). N2 and N′2 donors occupy axial positions. The chelate bite angles (N1–Cr–N2 and N′1–Cr–N′2) are about 79.3° for (**1**), and 78.5° for (**2**). It is likely that the bite angle, which is less than 80° in similar compound, should be kept in the complex studied. Coordinate system and geometrical model (C_{2v} symmetry point group), which are adequate for X-ray structure, has been presented in [2,9] and used in this study.

The electronic spectra of a series of the chromium(III) complexes with 2,2′-bipyridyl have been presented previously [12,24]. One maximum at about 18000–20000 cm^{-1} and three shoulders at 22500, 24000 and 25500 cm^{-1} characterize the electronic spectra of these complexes. The electronic spectrum of *cis*-$[Cr(ox)(bpy)_2]I$ in aqueous solution (Figure 1) is characterized by one maximum and three shoulders at

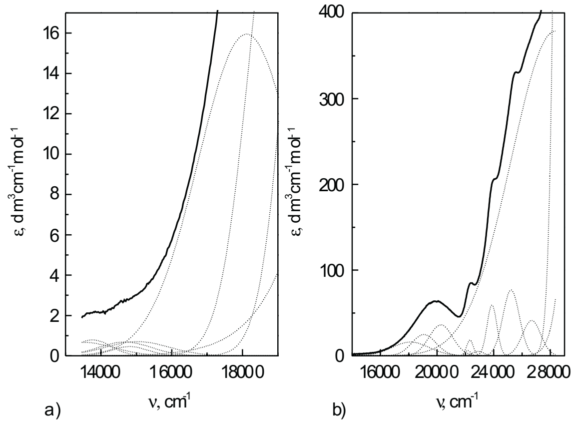


Figure 1. Electronic absorption spectrum and Gaussian line-shapes of *cis*-$[Cr(ox)(bpy)_2]I$ in aqueous solution at room temperature; (a) low-energy visible region (doublet-transitions region), (b) higher visible region (doublet-quartet transitions region).

same wave numbers, similar as spectra described in [12,24]. Other d-d bands should appear at an energetically higher region, but they are fully overlapped by the more intensive charge-transfer and intramolecular bands.

Table 1 summarizes the results of the Gaussian analysis (Figure 1), *i.e.*, parameters of the component bands, their oscillator strength values and the relative root mean square error (RMS%) for the energetically lower doublet region and higher doublet-quartet region, respectively. The band assignment of the energy transitions is based on fitting the resolved band maxima to the calculated transition energies, using d^3 matrix elements given in [7]. The values of AOM parameters, of *cis*-$[Cr(ox)(bpy)_2]I$ in aqueous solution together with the resolved and calculated transitions, are collected in Table 2. Parent terms of a free ion, octahedral, and tetragonal ligand fields are shown in square brackets in the third column. The best fit with the experimental data was obtained for the second resolution (II, 5th column). Table 2 contains comparison of this one with additional two resolutions (I and III, 4th and 6th columns). The calculated B Racah parameter value for this complex is larger than that given in [2] for the *cis*-$[CrCl_2(bpy)_2]Cl\cdot 2H_2O$ complex. Broomhead *et al.* [12] and Baker *et al.* [25] have calculated this parameter using Crystal Field Model (CFM) for the chromium(III) complex with 2,2′-bipyridyl. The calculated B Racah parameter value, for *cis*-$[Cr(ox)(bpy)_2]I$, is very close to those given by Broomhead *et al.* [12] and Baker *et al.* [25]. The α chelate bipyridyl angle in solution is more obtuse than that given in the literature for the chromium(III) complexes with 2,2′-bipyridyl [21,23,26,27] in the solid state, *i.e.* in the range 78.7–79.9°. The bite angle value in aqueous solution is greater for about 4°. The chelate angle changes, associated with bonding abilities of ligands and geometry of complex (see Figure 2), can be explained by AOM calculations. Three possible results were obtained for the complex studied: taking the chelate angle as fitting parameter (full calculations), neglecting (equal 90°) for the ’pure’ tetragonal geometry, and assuming this one as fixed for the solid state (equal 79°). In the 4th, 5th, and 6th columns of Table 2 these results are collected, respectively. By comparing the results of the fourth and sixth columns, one can see that the main effect of extended bite angle are weaker bonding abilities (σ and π) of the bipyridyl and stronger of oxalate. Totally, this situation, *i.e.*, influence of the chelate ring on shortening bipyridyl and lengthening oxalate bonds, is presented in Figure 2. The AOM parameters of the nitrogen suggest that bipyridyl molecule is stronger σ- and π-donor than the oxalate ion. In our previous works [2,4] the spectrophotometric data on aqueous solution of *cis*-$[CrCl_2(bpy)_2]Cl\cdot 2H_2O$ and *cis*-$[CrCl_2(phen)_2]Cl\cdot 2H_2O$ (phen = 1,10-phenanthroline) were analysed and ligand-field parameters were given. Presented in those works survey by enhanced spectroscopy of solution has demonstrated that nitrogen donor has significantly stronger σ- and π-bonding interactions than the remaining donor in both complexes, like the *cis*-$[Cr(ox)(bpy)_2]I$ complex. However, σ-interactions in the complex with 2,2′-bipyridyl are stronger than in complex with 1,10-phenanthroline.

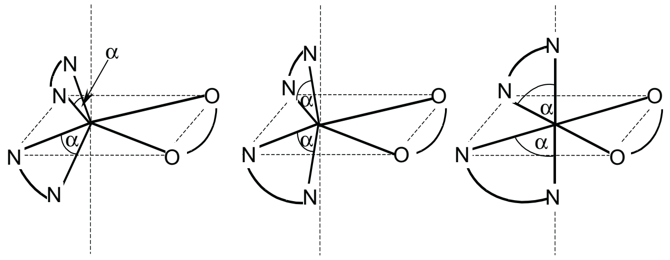
Table 1. Parameters of the component bands resulting from Gaussian analysis of the electronic spectrum* of *cis*-[Cr(ox)(bpy)$_2$]I (C_{2v} symmetry).

Band No.	ε (M^{-1} cm^{-1})	ν (cm^{-1})	$\delta_{1/2}$ (cm^{-1})	f_{osc}
1	0.6	13510	3230	8.4×10^{-06}
2	0.4	13770	2400	4.3×10^{-06}
3	0.6	14680	2960	7.9×10^{-06}
4	0.3	14820	990	1.2×10^{-06}
5	0.4	15030	2320	4.3×10^{-06}
6	15.9	18110	3120	2.3×10^{-04}
7	24.8	19060	2010	2.3×10^{-04}
8	36.1	20270	1950	3.2×10^{-04}
9	6.2	22170	450	1.3×10^{-05}
10	18.4	22320	550	4.7×10^{-05}
11	5.2	22890	910	2.2×10^{-05}
12	59.1	23870	810	2.2×10^{-04}
13	76.7	25230	1370	4.8×10^{-04}
14	41.2	26670	1520	2.9×10^{-04}
15	378.8	28350	7330	1.3×10^{-02}
16	6941.4	29850	1680	5.4×10^{-02}
17	15959.2	33830	3890	2.9×10^{-01}
RMS%	0.4			

*range: 13620–28360 cm^{-1}, 738 measurement points; full (doublet-quartet) region.

CONCLUSIONS

Though, low-symmetry chromium(III) complexes with bipyridyl have been widely and extensively investigated, their AOM parameters are not known. Moreover, from X-ray data we can use the chelate angle value (L–M–L) only to compare it with this one obtained from AOM optimization. The aim of our research was to explain the bonding abilities of bipyridyl in the chromium(III) complex. As known, they depend on state (solid and solution), solvent properties, coordination sphere (mixed-ligands



a) α << 90° b) α < 90° c) α = 90°

Figure 2. Effect of opening the chelate angle (α) on bonding abilities of bipyridyl and oxygen ligators in the *cis*-[Cr(ox)(bpy)$_2$]$^+$ complex and its geometry: a) $\alpha = 79°$ for solid state; b) $\alpha = 82.7°$ optimized for aqueous solution; c) $\alpha = 90°$ for 'pure' tetragonal geometry.

system), and symmetry. Based on the results of our simulation, we can state that in aqueous solution both σ and π interactions between nitrogen donor and central ion are weaker, and for oxygen donor are stronger in comparison to the solid state (Table 2). These strengths change of both donors interaction is a result that the bite angle α in aqueous solution is more obtuse in comparison to the solid state. However, this effect does not have any influence on Racah's parameter values (*c.f.* Table 2). Thus, geometrical changes (*i.e.*, chelate angle and Cr–N and Cr–O bonds) are observed, when the complex is dissolved. As can bee seen from this discussion, there exists a ligand-field theoretical evidence for weak bonding abilities of the bipyridyl, as an effect of opening chelate angle in the 5-membered ring in an aqueous solution.

Table 2. Transition energies, assignments and AOM parameters[a] of the aqueous solution spectrum of *cis*-[Cr(ox)(bpy)$_2$]I, (in cm^{-1}); C_{2v} symmetry, $^4B_2[F,T_{2g}(B_{2g})]$ ground term.

Experimental		Assignments	Calculated					
Observed	Resolved		I α = 79[b]		II α optimized		III α= 90	
–	13510	$^2A_1(1)$ $[G,A_{1g}(A_{1g})]$	13680		13740		13780	
–	13770	$^2A_2(1)$ $[G,T_{1g}(E_g)]$	13770		13790		13810	
14500	14680	$^2B_2(1)$ $[H,T_{2g}(B_{2g})]$	14430		14440		14450	
–	14820	$^2B_1(1)$ $[G,T_{1g}(E_g)]$	14810		14770		14750	
–	15030	$^2B_2(2)$ $[H,T_{1g}(1)(A_{2g})]$	14840		14840		14830	
–	18110	$^4A_1$ $[F,A_{2g}(B_{1g})]$	18110		18090		18090	
20000	19060	$^4B_1(1)$ $[P,T_{1g}(E_g)]$	19000		19050		19080	
–	20270	$^4A_2(1)$ $[P,T_{1g}(E_g)]$	20300		20260		20240	
22500	22170	$^2B_1(2)$ $[F,T_{1g}(E_g)]$	22100		22030		21980	
–	22320	$^2A_1(2)$ $[F,A_{2g}(B_{1g})]$	22530		22500		22480	
–	22890	$^2A_2(2)$ $[F,T_{1g}(E_g)]$	22960		23030		23070	
24000	23870	$^4B_2(2)$ $[F,T_{1g}(A_{2g})]$	23780		23800		23810	
25500	25230	$^4A_2(2)$ $[F,T_{1g}(E_g)]$	25530		25440		25380	
–	26670	$^4B_1(2)$ $[F,T_{1g}(E_g)]$	26480		26550		26600	
		r.m.s.	150	–	140	–	150	–
		$e_\sigma(N)$	8840	(130)	7920	(70)	7290	(80)
		$e_\sigma(O)$	7180	(90)	7460	(90)	7630	(100)
		$e_{\pi\perp}(N)$	2270	(60)	1590	(40)	1130	(70)
		$e_{\pi\perp}(O)$	770	(110)	930	(30)	1020	(90)
		$e_{\pi\|}(O)$	990	(180)	1120	(70)	1200	(160)
		B	550	(10)	560	(10)	560	(10)
		C	3390	(0)	3380	(30)	3380	(0)
		C/B	6.1	–	6.0	–	6.0	–
		α (°)	79.0	–	82.7	(0.4)	90.0	–

[a] α' chelate angle (O–Cr–O) has been fixed in all the calculations ($\alpha' = 90°$); [b] solid state.

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