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Spectrochemical Properties of Noncubic Transition Metal Complexes in Solutions.

XVII. Angular Overlap Treatment of *cis*-Bis(2,2′-bipyridyl)malonatechromium(III) Iodide in Aqueous Solution*

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A mixed ligands chromium(III) complex with bidentate ligands: 2,2′-bipyridyl (bpy) and malonic acid deprotonated (mal$^-$, malonate ion), has been synthesized, investigated and characterized structurally and spectroscopically. Electronic spectra of this complex were recorded in an aqueous solution at room temperature. The 'poor' experimental contours were resolved into the component bands by Gaussian analysis. The spectra were interpreted using C_{2v} symmetry. The resolved spectra have been treated using an angular overlap model (AOM). The effect of σ- and π-bonding of the bidentate ligands upon the chromium(III) ion in aqueous solution was described and discussed.

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

Transition metal complexes in solutions require an explanation of the molecular and electronic structure. This work is a part of our research concern the solvent effect on the structure and stability of transition metal complexes. Interpretations of the electronic spectra of the chelate chromium(III) complexes, presented up to date, have been limited to the spin-allowed observed, or 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 [2,3], where authors took into account the bite angle distortion. Our previous papers [1,4–6] presented the interpretation of the electronic spectra of the chromium(III) complexes with nonlinear, bidentate ligands bond with π-interaction.

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 (AOM) parameters. The calculations were carried out within the framework of the angular overlap simple model developed by Schäffer [10] and Jørgensen [11].

EXPERIMENTAL

Chemical: *cis*-Bis(2,2′-bipyridyl)malonatechromium(III) iodide was prepared by the method described in papers [1,12], based on the *cis*-bis(2,2′-bipyridyl)dichlorochromium(III) chloride dihydrate [4,13] that was added to aqueous solution of potassium malonate 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(mal)(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(mal)(bpy)$_2$]I complex has the molar conductivity value 95.7 S mol^{-1} cm^2 at 25°C. It is very close to the range anticipated for 1:1 electrolytes, *i.e.*, 70–130 at 25°C [14,15]. We have checked the lack of the 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 interpreting 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 (1.36×10^{-3}M). The visible and ultraviolet spectra of [Cr(mal)(bpy)$_2$]I in aqueous solution were recorded on a SPECORD M40 spectrophotometer. The spectra were recorded digitally (20 nm step) over the range 11000–30000 cm^{-1} after dissolving the sample. The spectral data at selected 744 wave numbers, over the range 13600–28460 cm^{-1} (l = 1.0 cm, c = 1.36×10^{-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 calculations. 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]. The same geometry and bonding abilities (for the [M(L2L2)(L1L1)$_2$] type complexes) as for *cis*-[Cr(ox)(bpy)$_2$]$^+$ (ox = oxalate ion) [1] was assumed. 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)malonatechromium(III) iodide in aqueous solution. The electronic spectra of this complex were not studied earlier. 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. They are known for the chromium(III) complexes with 2,2′-bipyridyl and different monodentate ligands. Generally, the Cr atom is in a pseudo-octahedral environment, coordinated by two bidentate bipyridyls and one bidentate malonate ion. The *cis*-diaqua- (**1**) and *cis*-aquahydroxo-bis(2,2′-bipyridyl)chromium(III) complexes (**2**) have been studied early and their X-ray data confirmed *cis*- configuration [21–23]. The chelate bite angles of bipyridyls are about 79.3° for (**1**), and 78.5° for (**2**). It is likely that the bite angle, which is less than 80° in the similar compounds, should be kept in the complex studied. Coordinate system and geometrical model (C_{2v} symmetry point group), which has been presented in [4,9], was used in this study.

The electronic spectra of a series of the chromium(III) complexes with 2,2′-bipyridyl have been presented previously [1,12,24]. 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 in aqueous solution of *cis*-$[Cr(mal)(bpy)_2]I$ (Figure 1) characterize one maximum and three shoulders at the same wave numbers, similar as spectra described in [1,12,24]. Other d-d bands should appear at energetically higher region, but they are fully overlapped by the most intensive charge-transfer 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 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]. AOM parameter values of the *cis*-$[Cr(mal)(bpy)_2]I$ complex in aqueous solution are collected in Table 2 together with the resolved and calculated transitions. B Racah parameter is larger than that for *cis*-$[CrCl_2(bpy)_2]Cl \cdot 2H_2O$

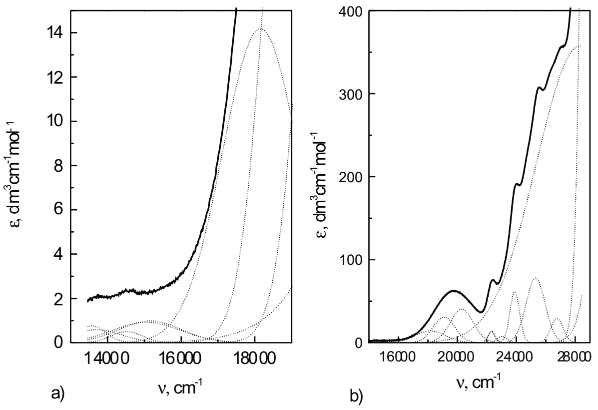

Figure 1. Electronic absorption spectrum and Gaussian line-shapes of *cis*-$[Cr(mal)(bpy)_2]I$ in aqueous solution at room temperature; (a) low-energy visible region (doublet-transitions region), (b) higher visible region (doublet-quartet transitions region).

[4], and it is comparable with this one for *cis*-$[Cr(ox)(bpy)_2]I$ [1]. Broomhead *et al.* [12] and Baker *et al.* [25] have calculated this parameter using Crystal Field Model (CFM). This one is not significantly different from ours for *cis*-$[Cr(mal)(bpy)_2]I$.

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

Band No.	ε (M^{-1} cm^{-1})	ν (cm^{-1})	$\delta_{1/2}$ (cm^{-1})	f_{osc}
1	0.7	13570	890	2.8×10^{-06}
2	0.6	13710	1570	4.2×10^{-06}
3	0.5	14520	2570	6.1×10^{-06}
4	0.9	15060	2380	1.0×10^{-05}
5	1.0	15160	2180	9.8×10^{-06}
6	14.2	18150	2430	1.6×10^{-04}
7	30.8	19090	1740	2.5×10^{-04}
8	40.2	20290	1850	3.4×10^{-04}
9	13.2	22300	540	3.3×10^{-05}
10	13.7	22340	550	3.5×10^{-05}
11	7.8	23030	780	2.8×10^{-05}
12	61.3	23890	770	2.2×10^{-04}
13	77.9	25310	1520	5.4×10^{-04}
14	29.1	26760	980	1.3×10^{-04}
15	357.6	28330	6970	1.1×10^{-02}
16	6622.7	29900	1630	5.0×10^{-02}
17	9799.7	33680	3840	1.7×10^{-01}
RMS%	0.6			

*range: 13600–28460 cm^{-1}, 744 measurement points; full (doublet-quartet) region.

The α chelate angle in solution is more obtuse (about 4°) than those given in 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°, similar as for $[Cr(ox)(bpy)_2]I$ in aqueous solution [1]. The AOM parameters of the nitrogen suggest that bipyridyl molecule is stronger σ- and π-donor than the malonate ion. In our previous papers [1,4] the spectrophotometric data on aqueous solution of *cis*-$[CrCl_2(bpy)_2]Cl\cdot 2H_2O$ and *cis*-$[Cr(ox)(bpy)_2]Cl\cdot 2H_2O$ (ox = oxalate) were analysed and ligand-field parameters were given. Presented in these papers survey by enhanced spectroscopy of solution has demonstrated that nitrogen donor has a significantly stronger σ- and π-bonding interaction than the remaining donor (chloride) in both complexes, so as and for the $[Cr(ox)(bpy)_2]I$ complex. However, σ-interactions for complex with 2,2′-bipyridyl are stronger than for complex with 1,10-phenanthroline [6]. Figure 2 shows comparison of electronic absorption spectra of: *cis*-$[CrCl_2(bpy)_2]Cl$ – 1, *cis*-$[Cr(ox)(bpy)_2]I$ – 2, and *cis*-$[Cr(mal)(bpy)_2]I$ – 3, in aqueous solution at room temperature. As can be seen, bathochromic effect of the lowest energetically band ($^4A_1$, $^4B_1$, and $^4A_2$ rhombic states), observed in the spectrum of *cis*-$[CrCl_2(bpy)_2]Cl$ is displayed only. Other band maxima (or shoulders) differ significantly in their intensities. Table 3 presents the bonding abilities of the bipyridyl nitrogen ligators in a variety of mixed-ligands (ternary) complexes in aqueous solutions. The α' chelate angle (O–Cr–O) has been fixed in all the calculations (α' = 90°) for comparison of those. The stronger orthorhombic distortion (N–Cr–N chelate angle) characterizes the complex with linear ligators (Cl^-), as well as π-bonding abilities, while the weaker characterizes the complexes with bidentate ligands.

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

Experimental		Assignments		Calculated	
Observed	Resolved			α optimized	
–	13570	$^2A_1(1)$	$[G,A_{1g}(A_{1g})]$	13770	
–	13710	$^2A_2(1)$	$[G,T_{1g}(E_g)]$	13820	
14500	14520	$^2B_2(1)$	$[H,T_{2g}(B_{2g})]$	14500	
–	15060	$^2B_1(1)$	$[G,T_{1g}(E_g)]$	14830	
–	15160	$^2B_2(2)$	$[H,T_{1g}(1)(A_{2g})]$	14890	
–	18150	$^4A_1$	$[F,A_{2g}(B_{1g})]$	18110	
20000	19090	$^4B_1(1)$	$[P,T_{1g}(E_g)]$	19040	
-	20290	$^4A_2(1)$	$[P,T_{1g}(E_g)]$	20290	
22500	22300	$^2B_1(2)$	$[F,T_{1g}(E_g)]$	22100	
–	22340	$^2A_1(2)$	$[F,A_{2g}(B_{1g})]$	22590	
–	23030	$^2A_2(2)$	$[F,T_{1g}(E_g)]$	23130	
24000	23890	$^4B_2(2)$	$[F,T_{1g}(A_{2g})]$	23840	
25500	25310	$^4A_2(2)$	$[F,T_{1g}(E_g)]$	25520	
–	26760	$^4B_1(2)$	$[F,T_{1g}(E_g)]$	26660	
			r.m.s.	160	
			$e_\sigma(N)$	7940	(50)
			$e_\sigma(O)$	7520	(50)
			$e_{\pi\perp}(N)$	1600	(50)
			$e_{\pi\perp}(O)$	960	(80)
			$e_{\pi\parallel}(O)$	1170	(80)
			B	560	(10)
			C	3390	(40)
			C/B	6.0	
			α	82.7	(0.3)

[a] α' chelate angle (O–Cr–O) has been fixed (α' = 90°).

Table 3. Comparison of the AOM parameters for the $[Cr(X)(bpy)_2]^+$ complexes in aqueous solution.

X	Cl_2	ox	mal
Parameter	[4]	[1]	this work
$e_\sigma(N)$	8060 (80)	7920 (70)	7940 (50)
$e_{\pi\perp}(N)$	2020 (70)	1590 (50)	1600 (50)
α	79.8 (0.1)	82.7 (0.4)	82.7 (0.3)

α' angle (Cl–Cr–Cl/O–Cr–O) has been fixed in all the calculations (α' = 90°).

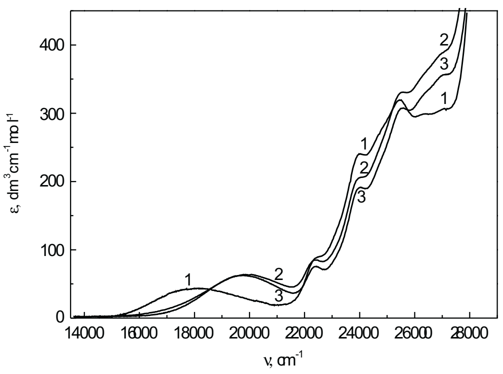

Figure 2. Comparison of electronic absorption spectra of: *cis*-[$CrCl_2(bpy)_2$]Cl – 1, from [1]; *cis*-[Cr(ox)$(bpy)_2$]I – 2, from [4]; and *cis*-[Cr(mal)$(bpy)_2$]I – 3 (this work), in aqueous solution at room temperature.

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