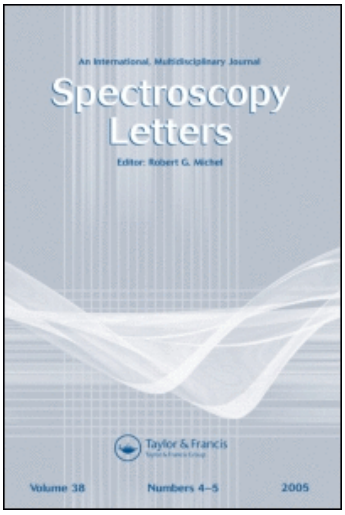

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ANGULAR OVERLAP TREATMENT OF cis-DIFLUOROBIS(ETHYLENEDIAMINE)CHROMIUM(III)-CHLORIDE IN AQUEOUS SOLUTION

Key Words: angular overlap model, electronic spectra, chromium(III) complexes, ethylenediamine, molecular structure, low symmetry.

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ABSTRACT

In this work a general method for analysis of the d-d transition energies is used to derive the angular overlap model (AOM) parameters of chromium(III) complexes with C_{2v} symmetry. It allows investigation of various complexes in solutions with low symmetries (*cis*-$[MX_2(LL)_2]$, LL = bidentate ligand) and different π-bonding abilities of ligands. Successful application of method to the interpretation of the spectrum of *cis*-$[CrF_2(en)_2]^+$ chromophore (en = ethylenediamine) in aqueous solution demonstrates the utility of this approach.

INTRODUCTION

The studies aimed at explaining molecular and electronic structure of the transition metal complexes in solutions are belong in a category of timely investigations still. Quantitative interpretations of the electronic spectra of the chelate chromium(III) complexes presented up to date have been limited to observed spin-allowed, or only few spin-forbidden bands and, moreover, to the solid state only.

Six-coordinate *cis*-$[MX_2(LL)_2]^{n+}$ as well as *trans*-$[MXY(LL)_2]^{n+}$ complexes[1,2] belong to C_{2v} point group, however symmetry of the energy states is quite different. The structural and spectroscopical properties of the *trans* isomers are well known, while those for *cis* are not yet. The spectra of the *trans*-$[CrXY(LL)_2]$ complexes, where LL is bidentate ligand, have been thoroughly studied previously[3,4,5]. These complexes have been characterized by effective C_{4v} (D_{4h}) symmetry with the fourfould axis X-Cr-Y. *cis*-$[MX_2L_4]$ complexes were treated as pseudo *trans*-$[M(L)_2(XL)_2]$ and an averaging ligand field strengths (for X and L ligators) were calculated within the framework crystal field theory[6] (CFM). Structural data reveal that the bidentate ligand as primary amine forms a bite angle different from 90°. In these all systems of chromium(III) and ethylenediamine a bite angle is about 83°. Because of that these spectra should be interpreted assuming the C_{2v} effective symmetry. So far, a few cases have been reported where authors take into account the ligand bite angle distortion. Vanquickenborne and Ceulemans discussed *cis*-$[CrCl(NCS)(en)_2]^+$, within the AOM framework, as orthorhombic system[7]. Hoggard reported the transition energy diagrams for low symmetry doublet states assuming for the chelate ligands bite angle[8]. Recently, Hoggard and Kirk[9] presented a detailed description of the both *cis*- and *trans*- isomers of $[Cr(NH_3)_2cyclam]^{3+}$. The

main aim of this work is calculation of the ligand field parameters for low-symmetry complex in aqueous solution (and room temperature) allowing all the transitions which are required in the ligand field theory (LF). The deconvolution (Gaussian analysis) of these "poor" spectra is only way of quantitative interpretation of this kind experiment. All absorption bands presented in this work arise from Gaussian analysis of the experimental spectrum.

EXPERIMENTAL

cis-$[CrF_2(en)_2]Cl \times 0.5H_2O$ complex was obtained according to paper[10] by using filtrate from synthesis of *trans*-isomer and recrystallization from the aqueous solution. *trans*-$[CrF_2(en)_2]Cl$ presented by us in work[1] was prepared by the method described in papers[11]. The results of elementary analysis agreed with the expected composition. Found: Cr, 20.5; C, 19.3; H, 7.5; N, 21.6; Cl, 14.4%. Calc.: Cr, 20.4; C, 18.9; H, 6.7; N, 22.0; Cl, 13.9%.

The visible and ultraviolet spectrum of *cis*-$[CrF_2(en)_2]Cl$ in aqueous solution was recorded on a Specord M40 (Carl Zeiss Jena) spectrophotometer equipped with water-jacketted cell block, allowing to mainting absorption cells at 4°C to minimize aquation. The spectrum was recorded digitally ($40cm^{-1}$ step) over the range 13000-$43000cm^{-1}$ (l=1.0 cm, $c=2.5\times10^{-2}$ M) after 2 h from dissolving the sample and resolved into Gaussian components.

METHOD OF CALCULATION

The strong field wave functions of Perumareddi[1,6] were used to derive the ligand field energy matrices, without spin-orbit coupling. Neglect of spin-orbit perturbation in first row transition metal complexes can be

justified on the basis of experimental expedience, if not on purely theoretical grounds. Parametric values necessarily assumed for strong field square bipyramidal Ni(II), for example, clearly ilustrate that spin-orbit effects have essentially no influence of the energies of the perturbation levels[12] . The symmetries of the states belonging to each configuration have been deduced by standard group theory method. The d^3 strong field states under D_{2h} symmetry have been determined to possess the symmetries listed in work[1]. This collection of the wave functions is also suitable for C_{2v} point group. On the basis of these wave functions the energy matrices for chromium(III) systems (sym. D_{2h}, C_{2v}), without spin-orbit coupling, have been constructed and presented[1]. Six-coordinate *cis*-$[MX_2(LL)_2]$ as well as *trans*-$[MXY(LL)_2]$ complexes[2] belong to C_{2v} group, however symmetry of the energy states is different. The correlation between the symmetry of the wave functions in D_{2h} and $C_{2v}^{(y)}$ (twofould *y* axis) ligand fields is as follows: A_g, B_{1g}, B_{2g}, B_{3g} (D_{2h}) and A_1, B_2, A_2, B_1 ($C_{2v}^{(y)}$), repectively.

The matrix elements of the exited states[2] given as a functions of the orbital energies and the Racah parameters allow the calculations for complexes with all the geometries (within discussed point group) and different π-bonding properties of ligands. In conjunction of suitable orbital energies they can also be easily applied for other systems. Below we present calculations of d-orbital energies for six-coordinate complexes belong to C_{2v} symmetry. The d-orbital energies for these complexes have been obtained using the standard procedure of finding the orbital energies[13]. In this work we choose orientation of the *cis*-$[M(L2)_2(L1L1)_2]$ molecule where $L1^{(3)}$-$L1^{(4)}$-M-$L2^{(1)}$-$L2^{(2)}$ plane coincides with the cartesian *xy* plane, and *y* axis bisects the L2-M-L2 and $L1^{(3)}$-M-$L1^{(4)}$ angles (where superscripts refer to number of the ligator). Figure 1 illustrates the scheme of cis-

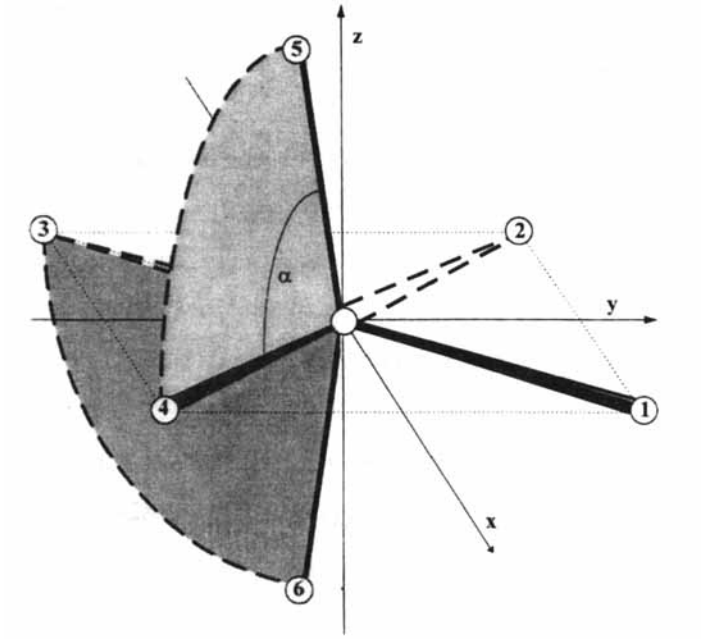

FIG. 1. Coordinate system and numbering the donor ligand atoms (ligators) of *cis*-$[M(L2)_2(L1L1)_2]$ complexes; $C_{2v}^{(y)}$ principal axis; α - bite angle.

$[M(L2)_2(L1L1)_2]$ molecule and coordinate system. Assuming that M (metal ion), $L1^{(3)}$ and $L1^{(4)}$, and two L2 ligators form the plane, whereas $L1^{(5)}$ and $L1^{(6)}$ ligators get out of *z* axes, the following equations for matrix elements are derived and presented below (1a)-(1f). The ligators have angular coordinates as follows:

ligator	$L2^{(1)}$	$L2^{(2)}$	$L1^{(3)}$	$L1^{(4)}$	$L1^{(5)}$	$L1^{(6)}$
θ	90	90	90	90	90-α	90+α
ϕ	45	90+45	180+45	270+45	270	270

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

$$E[b_2(xy)] = 1.5e_\sigma(2) + 1.5e_\sigma(1) + (2\cos^2\alpha)e_{\pi\perp}(1) + + (2\sin^2\alpha)e_{\delta\perp}(1) + 0.5[e_{\delta\parallel}(2) + e_{\delta\parallel}(1)] \quad (1a)$$

$$E[b_1(yz)] = (1.5\sin^2\alpha)e_\sigma(1) + e_{\pi\parallel}(2) + (1+2\cos^2 2\alpha)e_{\pi\parallel}(1) + + e_{\delta\perp}(2) + e_{\delta\perp}(1) + (0.5\sin^2 2\alpha)e_{\delta\parallel}(1) \quad (1b)$$

$$E[a_2(xy)] = (2\sin^2\alpha)e_{\pi\perp}(1) + e_{\pi\parallel}(2) + e_{\pi\parallel}(1) + e_{\delta\perp}(2) + + (1+2\cos^2\alpha)e_{\delta\perp}(1) \quad (1c)$$

$$\langle z^2|V|z^2\rangle = 0.5e_\sigma(2) + [0.5 + 0.125(1-3\cos 2\alpha)^2]e_\sigma(1) + + (1.5\sin^2 2\alpha)\, e_{\pi\parallel}(1) + 0.375(1+\cos 2\alpha)^2 e_{\delta\parallel}(1) + 1.5[e_{\delta\parallel}(2) + e_{\delta\parallel}(1)] \quad (1d)$$

$$\langle x^2-y^2|V|x^2-y^2\rangle = [0.375(1+\cos 2\alpha)^2]e_\sigma(1) + 2\, e_{\pi\perp}(2) + 2e_{\pi\perp}(1) + + (0.5\sin^2 2\alpha)e_{\pi\parallel}(1) + 0.125(3-\cos 2\alpha)^2 e_{\delta\parallel}(1) \quad (1e)$$

$$\langle z^2|V|\, x^2-y^2\rangle = - (\sqrt{3}/8)(1+\cos 2\alpha)(1-3\cos 2\alpha)e_\sigma(1) + + ((\sqrt{3}/2)\sin^2 2\alpha)e_{\pi\parallel}(1) - - (\sqrt{3}/8)(1+\cos 2\alpha)(3-\cos 2\alpha)e_{\delta\parallel}(1) \quad (1f)$$

Ignoring δ-contributions to the M-L bond, setting isotropy of π-bonding effect about M-L2 bond ($e_{\pi\perp}(L2) = e_{\pi\parallel}(L2)$) and non π-bonding abilities of L1 ($e_{\pi\perp}(L1) = e_{\pi\parallel}(L1) = 0$) the orbital energy matrices for *cis*-$[CrF_2(en)_2]^+$ are obtained.

All the band maxima reported here are derived from Gaussian analysis of the experimental curve. Table 1 sumarizes 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%). Our calculations take into account all the transitions which are given by ligand field theory,

TABLE 1

Parameters of the component bands resulting from Gaussian analysis of the electronic absorption spectrum* of cis-$[CrF_2(en)_2]Cl$, symmetry C_{2v}.

Band No	ε ($dm^3\ mol^{-1}\ cm^{-1}$)	υ (cm^{-1})	$\delta_{1/2}/2$ (cm^{-1})	f_{osc}
1	1.063	12865.7	1476.4	1.443×10^{-5}
2	0.275	14951.2	518.6	1.313×10^{-6}
3	0.264	15138.6	720.9	1.751×10^{-6}
4	0.148	15460.7	902.7	1.231×10^{-6}
5	0.165	15847.0	419.7	6.373×10^{-7}
6	0.217	16239.8	622.5	1.244×10^{-6}
7	4.792	19102.8	1641.8	7.235×10^{-5}
8	5.747	19298.2	1755.5	9.277×10^{-5}
9	5.786	19747.7	1909.0	1.016×10^{-4}
10	0.597	22185.5	1154.7	6.337×10^{-6}
11	0.379	22212.4	1141.7	3.978×10^{-6}
12	0.401	22594.9	1125.2	4.148×10^{-6}
13	3.948	25035.7	2881.9	1.046×10^{-4}
14	5.446	27075.5	2446.1	1.225×10^{-4}
15	10.457	27803.2	2915.7	2.803×10^{-4}
16	3.110	30948.3	1569.6	4.489×10^{-5}
17	3.679	33413.7	3207.0	1.085×10^{-4}
18	4.855	32641.4	2556.5	1.141×10^{-4}
19	4.098	32458.0	2221.1	8.369×10^{-5}
20	2.448	33175.4	2871.6	6.463×10^{-5}
21	1.905	34638.1	2352.9	4.121×10^{-5}
22	1.002	34771.1	2320.9	2.139×10^{-5}
23	3.045	35342.4	2145.3	6.006×10^{-5}
24	3.345	35893.1	1684.9	5.183×10^{-5}
25	11.499	36693.8	2814.2	2.976×10^{-4}
26	5.007	37166.4	1876.5	8.639×10^{-5}
27	3.528	39042.5	2385.6	7.739×10^{-5}
28	12.853	40709.7	2954.2	3.491×10^{-4}
29	12.689	41156.0	3262.1	3.806×10^{-4}
30	12.706	42230.3	3349.4	3.913×10^{-4}
31	631.285	51110.0	4564.4	2.649×10^{-2}
RMS%	0.550			

/* whole range: 13880 - 42000 cm^{-1}, 704 measurement points

even those strong overlapped in UV region. The details of the method are presented in work[1] (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[14] (former DAFP[15]) based actually on two minimization techniques: the Powell method (non-gradient) and the Davidon-Fletcher-Powell method (gradient estimation). Full energy matrices for the d^3 configuration (D_{2h} and C_{2v} symmetry) given in paper[1] were used for calculations. 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 absorption spectrum of *cis*-difluorobis(ethylenediamine)chromium(III) chloride in aqueous solution. It takes into account a low symmetry of the complexes in particular ligand bite angle distortion. The x-ray structural data are known[16,17] for the *cis* isomer. The Cr atom is an octahedral environment coordinated by two bidentate ethylenediamines and two F atoms in a *cis* positon. Cr - F and Cr - N bonds are 1.883(3), and from 2.072(4) to 2.093(4) A. The bond angles are: N1-Cr-N2 92.7(2) and F-Cr-F 93.5(1) (in *xy* plane). This suggests that N1-Cr-F (N2-Cr-F) group is near linearity. As can be see from the molecular structures, the bite angle N-Cr-N of $[CrF_2(en)_2]^+$ chromofores is about 83°, with the slight torsion angle of ethylenediame's planes about diagonal, which causes the lowering symmetry of the complex to C_{2v} (allowing the different bond lengths Cr-N and Cr-F in *trans* positions). The (NN)-Cr-(FF) quadrilateral is slightly and unsifigantly deformed from planarity with the angles less then 3°. Thus the

assumed geometrical model (Fig. 1) is adequate for x-ray structure and our calculations of AOM parameters, especially for the solution spectra .

The electronic absorption spectrum of *cis*-$[CrF_2(en)_2]Cl$ in aqueous solution exhibits two bands with maxima at 19400(17.5) and 27400(19.0) cm^{-1} (cm^{-1} M^{-1}) which correspond to strongly overlapped low-symmetry components of the first and second parent octahedral transitions, and two shoulders at 15000 and 36000 cm^{-1}. The bands assignment of the energy transitions is based on fitting the resolved band maxima with the calculated transition energies using d^3 matrix elements given in work[1] in conjunction with one-electron state energies given in Eqns. (1a)-(1f). The values of AOM parameters of *cis*-$[CrF_2(en)_2]Cl$ in aqueous solution together with the resolved and calculated transition energies are collected in Table 2. The standard deviations of the parameters have been given in parentheses. The ligand chelate angle in *trans*-isomer[1] and *cis*-isomer in solution is practically the same (see Table 3) and close to that for the solid state. The value of $e_\sigma(N)$ characterizing the ethylenediamine nitrogen is close to those given in the literature for chromium(III) complexes[13c] in the solid state. The π-bonding effect of the fluoride ions in *cis*- isomer is slightly greater than in *trans*- isomer, while the σ-bonding effect is practically the same. The AOM parameters of the nitrogen suggest that ethylenediamine molecule is weaker σ-donor than the fluoride ion.

CONCLUSION

Interpretations of the chelate chromium(III) complexes presented up to date have been limited to the observed spin-allowed and only few spin-forbidden bands (at the lowest energies). Those include the bands which can be really distinguished conclusively from the experimental

TABLE 2

Transition energies, assignments and AOM parameters of cis-$[CrF_2(en)_2]Cl$ in aqueous solution (in cm^{-1}); C_{2v} symmetry.

Observed	Resolved	Assignment	Calculated		
			I (all bands)	II (11 bands)	III (7 bands)
	14951	$^2A_1(1)$	14543	14651	14928
15000	15139	$^2B_2(1)$	14674	14790	15164
	15461	$^2B_1(1)$	14917	15752	15504
	15847	$^2A_2(1)$	15104	15863	15801
	16240	$^2B_2(2)$	15255	15956	-
	19103	$^4A_1(1)$	18555	19094	19101
19400	19298	$^4A_2(1)$	18928	19341	19283
	19748	$^4B_1(1)$	19321	19655	19768
	22185	$^2A_1(2)$	22194	22270	-
	22212	$^2A_2(2)$	22332	22408	-
	22595	$^2B_1(2)$	22747	22776	-
	25036	$^4B_2(1)$	24826	(28368)[a]	(26748)
27400	27075	$^4B_1(2)$	26539	(29360)	(29109)
	27803	$^4A_2(2)$	27161	(29971)	(29972)
	30948	$^2A_1(3)$	31040	-	-
	32458	$^2A_1(4)$	32996	-	-
	32641	$^2B_2(3)$	33142	-	-
	33175	$^2A_2(3)$	33200	-	-
	33414	$^2B_1(3)$	33832	-	-
	34638	$^2A_2(4)$	34273	-	-
	34771	$^2B_1(4)$	34558	-	-
	35342	$^2B_2(4)$	34920	-	-
36000	35893	$^2A_1(5)$	36228	-	-
	37166	$^2B_2(5)$	37707	-	-
	39042	$^2A_2(5)$	39676	-	-
	39042	$^2B_1(5)$	39780	-	-
	40710	$^4B_1(3)$	40775	(45249)	(43964)
	41156	$^4A_2(3)$	41200	(45507)	(44345)
	42230	$^4B_2(2)$	42132	(45917)	(45324)
		e_σ (N)	7134(38)	7111(44)	7337(41)
		e_σ (F)	7603(81)	7539(16)	8635(80)
		e_π (F)	1776(26)	1440(56)	2428(82)
		B	709(14)	1110(14)	986(27)
		C	3125(30)	2349(19)	2703(62)
		C/B	4.41	2.12	2.74
		α	82.85(2)	83.40(4)	82.38(12)
		r.m.s.	457	206	29

[a] in parenthesis only calculated values of the transition energies, i.e. not fitting;

TABLE 3

Comparison of the ligand fields parameters (AOM) for *cis*- and *trans*-isomers of the difluorobis(ethylenediamine)chromium(III) chloride.

Parameter	*cis*-isomer this work	*trans*-isomer from[1]
$e_\sigma(N)$	7134	7100
$e_\sigma(F)$	7603	7711
$e_\pi(F)$	1776	1550
B	709	575
C	3125	3563
C/B	4.4	6.2
α	82.9	83.1

spectrum. This approach is very unsafe. Contrary to this one, our calculations take into account all the transitions which are given by ligand field theory. Table 1 contains comparison of the full calculations (**I**) and two additional resolutions: **II** (limiting fitted transitions number to eleven, 5th column) and **III** (seven transitions, 6th column). As seen, all the "statistical good" resolutions are quite different. Which one on these resolutions is corret? It should be note that resolution **III** shows the significant difference. This one allows the least information from the experiment. Both last-mentioned resolutions (**II** and **III**) do not "physical" satisfy at least due to values of the Racah parameters. These exemplary calculations have confirmed our prediction: limited spectral data make quantitative interpretation incorrect.

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