Polish J. Chem., **76**, 503–509 (2002)

Angular Overlap Treatment of *cis*-Dichlorobis(1,10-phenanthroline)chromium(III) Chloride Dihydrate in Aqueous Solution

by K. Kurzak[*] and K. Biernacki

Department of Chemistry, University of Podlasie, ul. 3-go Maja 54, PL-08110 Siedlce, Poland

(Received April 20th, 2001; revised manuscript December 27th, 2001)

Low-symmetry mixed-ligands *cis*-$[CrCl_2(phen)_2]Cl$ complex (phen = 1,10-phenanthroline) has been characterized spectroscopically. Electronic spectrum of aqueous solution of this complex has been measured at room temperature and interpreted using the angular overlap model (AOM), and assuming C_{2v} symmetry. All the experimental transition energies 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 in the ligand-field theory (except those energetically higher than the range of the measured spectrum).

Key words: angular overlap model, electronic spectra, chromium(III) complexes, 1,10-phenanthroline, molecular structure, low symmetry

The studies of the transition metal complexes in solutions, aimed at explaining molecular and electronic structure, are timely 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.

Six-coordinate *cis*-$[MX_2(LL)_2]^{n+}$ as well as *trans*-$[MXY(LL)_2]^{n+}$ complexes belong to C_{2v} point group, however, symmetry of the energy states is quite different. The structural and spectroscopic properties of the *trans* isomers are well known, but not for *cis* isomers. The interpretation of the electronic spectra of the first-row transition metal complexes, including spin-orbit perturbation, is still controversial. In general, the experimental solution spectra at room temperature are not sufficiently resolved to consideration of this effect. Previously the spectra of *cis*-dichlorobis(1,10-phenanthroline)chromium(III)chloride dihydrate in solid state [1] (diffuse reflectance spectra), and DMF and H_2O solutions [2] have been presented. A general method for the analysis of the d-d transition energies [3,4,5] (and references herein), observed in the ligand-field spectra of 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 [6–8].

---

[*] Author to whom correspondence should be addressed.

EXPERIMENTAL

Synthesis: *cis*-Dichlorobis(1,10-phenanthroline)chromium(III) chloride dihydrate was prepared by the method [9]. Anhydrous chromic chloride and 1,10-phenanthroline in ethanol were mixed and heated to boiling after addition of a trace of zinc dust as catalyst. A vigorous reaction took place, the chromic chloride dissolving to a deep brown solution. The mixture was kept in the air for ten minutes and then cooled. Brown-green crystals were separated and filtered off and dissolved in a small quantity of hot water. This solution was filtered and recrystallized. The chloride complex was precipitated as brown-green crystals, which were air-dried. This one was analyzed for purity. The results of elementary analysis agreed with the expected composition.

Measurements: The solution of *cis*-$[CrCl_2(phen)_2]Cl\cdot 2H_2O$ was prepared by dissolving a weighed amount of the complex in distilled water. The composition of the complex species in this solution has been confirmed by conductance measurements. The molar conductance was measured using the conductivity meter OK-120/1 and platinum dip electrode OK-902 (Radelkis). The *cis*-$[CrCl_2(phen)_2]Cl\cdot 2H_2O$ complex has the molar conductivity value 91 S mol^{-1} cm^2 at 25°C. The molar conductance for this one reported in [1] equals 70–100 S mol^{-1} cm^2 at 20°C (different polymorphic solid materials dissolved in water). Our value is very close to the range anticipated for 1:1 electrolytes, *i.e.* 70–130 S mol^{-1} cm^2 for aqueous solution [10] (values in the range 160–210 S mol^{-1} cm^2 are predicted for 1:2 electrolytes). It follows, that complex studied has 1:1 electrolytic properties in aqueous solution. Furthermore, the kinetics presented earlier [1] and suggested a slow aquation rate (half-life of *ca.* 3 h). Lack of the equilibrium in solution has been checked by us by time-dependent spectral measurements. No spectral changes were observed upon time elapsed up to 90 minutes. 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 upon time elapsed up to 4 h. However, the interpreting spectrum was recorded as rapidly as possible, *i.e.*, 5 minutes after dissolution of the sample. The measurement conditions for the conductivity were the same as for the electronic absorption spectra ($\sim 2.225\times 10^{-3}$ M). The visible and ultraviolet spectra of *cis*-$[CrCl_2(phen)_2]Cl\cdot 2H_2O$ in aqueous solution were recorded on a spectrophotometer SPECORD M-40 (Zeiss Jena). The spectra were recorded digitally (40 cm^{-1} step) over the range 11000–28000 cm^{-1} after dissolving the sample. The spectral data at selected ~420 wavenumbers, over the ranges: 12920–16080 cm^{-1} ($l = 5.0$ cm, $c = 2.225\times 10^{-3}$ M) and 13480–27200 cm^{-1} ($l = 1.0$ cm, $c = 2.225\times 10^{-3}$ M), were employed for analysis and resolved into Gaussian components.

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 components. Some authors consider the bands, which can really be distinguished conclusively from the 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 complex studied was fitted with Gaussian components using CFP program [11,12]. Ligand-field parameters were calculated using the LFP program [13] (former DAFP [14,15]) 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 in [4], were used for calculations. For these the total one-electron matrix elements given in [3] were adopted. Coordinate system and numbering of the ligators used for AOM calculations are the same as in [3]. In order to apply them to interpretation of the complex studied, *i.e.* six-coordinate $[M(L2)_2(L1L1)_2]$ type complex (which allows isotropy of nitrogen ligators), the following simplification has been applied. Ignoring δ-contribution to the M–L bonding, setting isotropy of π-bonding effect about M–L2 bond ($e_{\pi\perp}(L2) = e_{\pi\|}(L2) = e_{\pi}(L2)$) and anisotropy of π-bonding effect about M–L1 bond ($e_{\pi\|}(L1) = 0$) the orbital energy matrices for *cis*-$[CrCl_2(phen)_2]^+$ are obtained. Since the nitrogen donor (non-linear donor with sp^2 hybridization in the ligand) has $\pi_\perp$ interaction only and chlorides are linear ligators, the above assumptions were accepted.

RESULTS AND DISCUSSION

In the interpretation of the electronic absorption spectrum of *cis*-dichlorobis(1,10-phenanthroline)chromium(III) chloride dihydrate in aqueous solution, we take into account a low symmetry of the complex in particular bite angle distortion. The X-ray structural data for this complex are not known for analogous bis-complexes of chromium(III) with 1,10-phenanthroline and monodentate ligands only. It is likely that surrounding the chromium in mononuclear *cis*-complex is very close to that in *cis* hydroxo-bridged dimeric complexes [16–18]. In those the hydroxo bridges force the *cis* configuration. Thus, the C_{2v} molecular symmetry point group is adequate for the geometry around each chromium(III) center. It seems reasonable to assume this molecular symmetry for theoretical analysis of monomeric species. Coordinate system and geometrical model (C_{2v} symmetry point group), which are adequate for X-ray structure of the bipyridyl analogous complex, has been presented in [3,19] and used in this study.

The reflectance spectra of a series of *cis*- and *trans*-$[MCl_2(LL)_2]^+$ cations (where M(III) = Co(III) or Cr(III), LL = bpy or phen) have been presented previously [2,20]. Those for *cis* isomers are characterized by two maxima at *ca.* 16500 and 19000 cm^{-1}, while for *trans* isomers at *ca.* 16500 and 25000 cm^{-1}. One maximum at 18000 and two shoulders at 23640 and 25400 cm^{-1} characterize the spectrum of $[CrCl_2(LL)_2]^+$ in aqueous solution (Figure 1). Other d-d bands should appear at energetically higher region, but they are fully overlapped by the most intensive charge-transfer bands. Figure 2

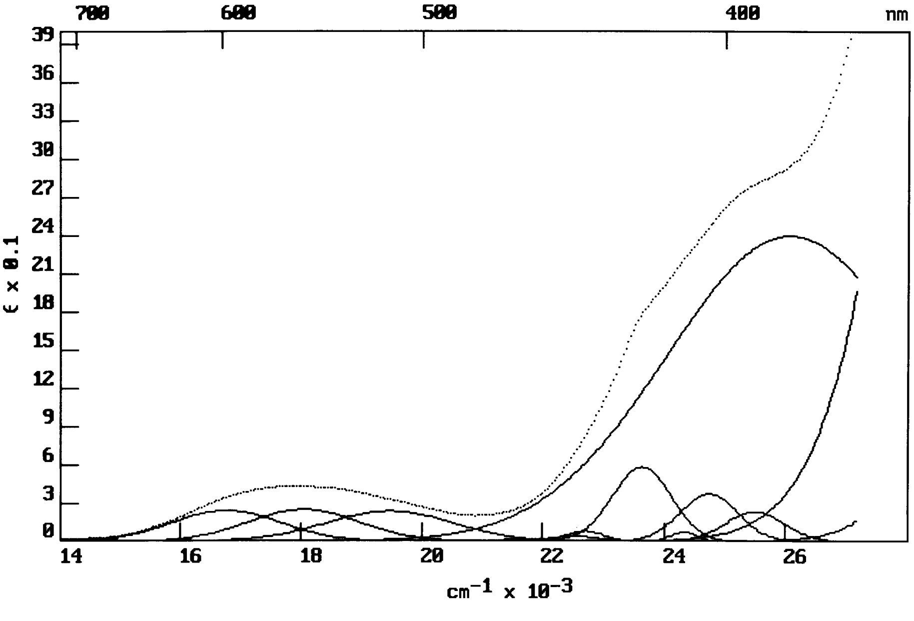


Figure 1. Electronic absorption spectrum and Gaussian line-shapes of the *cis*-$[CrCl_2(phen)_2]Cl{\cdot}2H_2O$ in aqueous solution at room temperature; full visible region (*computer printout*).

shows the electronic absorption spectra of *cis*-[CrCl$_2$(phen)$_2$]Cl·2H$_2$O in aqueous solution, together with Gaussian components in energetically lower doublet (a) and higher doublet-quartet region (b), respectively. On the basis of the band positions in the spectra and X-ray data for analogous complexes, we assumed the *cis* coordination of the ligands.

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 the energetically lower doublet region and doublet-quartet region, respectively. The AOM parameters of *cis*-[CrCl$_2$(phen)$_2$]Cl·2H$_2$O in aqueous solution together with the resolved and calculated transitions are collected in Table 3. The band 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 [4]. Parent terms of free ion, octahedral, and tetragonal ligand fields are shown in square brackets in the third column (Table 3). The ligand chelate angle for the complex studied in aqueous solution is more obtuse than given in the literature for dimeric (hydroxo bridged) phenanthrolino chromium(III) complexes [16,17] in the solid state, *i.e.* in the range 78.7–79.9°. The bite angle value in aqueous solution is greater about 4°. The chelate angle changes, associated with bonding abilities of ligands and geometry of complex (see Figure 3), can be explained by AOM calculations. Three possible results were obtained for the complex studied under consideration: taking the chelate angle as fitting parameter; neglecting (equal 90°) for the "pure" tetragonal

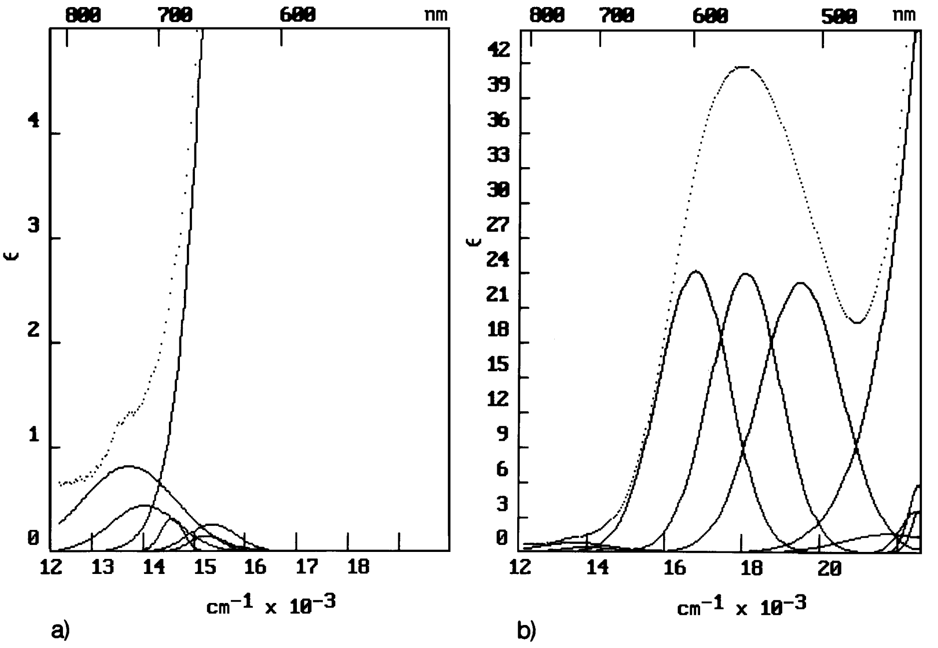


Figure 2. Electronic absorption spectrum and Gaussian line-shapes of the *cis*-[CrCl$_2$(phen)$_2$]Cl·2H$_2$O in aqueous solution at room temperature: a) energetic lowest doublet region, b) doublet-quartet region (computer printout).

geometry and assuming this one as fixed for the solid state (equal 79°). In the 4th, 5th and 6th columns of Table 3 these results are collected, respectively. By comparing the results of the fourth and fifth columns of Table 3, it can be seen that the main effect of the 4° extend of bite angle is a weaker bonding ability (σ and π) of the phenanthroline and a stronger for chloride. Totally, this situation, *i.e.* influence of the chelate ring on shortening phenanthroline and lengthening chloride bonds, is presented in Figure 3. The π-bonding parameters suggest that both the ligands are π donors toward the chromium(III) ion. The AOM parameters of the nitrogen suggest, that the phenanthroline molecule is a significantly stronger σ- and π-donor than the chloride ion. Previously [19] the spectrophotometric data of an aqueous solution of *cis*-$[CrCl_2(bpy)_2]Cl\cdot 2H_2O$ were analyzed. Presented in this work survey by enhanced spectroscopy of solution has demonstrated that phenanthroline molecule is a slightly weaker σ- and π-donor than the bipyridyl molecule in these complexes, whilst bonding abilities of the chloride ions are comparable in both. X-ray data both for analogous complexes, $[CrCl_2(phen)_2]^+$ and $[CrCl_2(bpy)_2]^+$, suggest that phenanthroline and bipyridyl bite angle are similar, *ca.* 78.5°–79.3° and 78.7°–79.9° respectively. This angle for bipyridyl compound is similar in the solid state and in the solution, but for phenanthroline compound it is larger in solution than in the solid state.

Table 1. Parameters of the component bands resulting from Gaussian analysis of the electronic spectrum* of *cis*-$[CrCl_2(phen)_2]Cl\cdot 2H_2O$; for the energetically lower doublets region, symmetry C_{2v}.

Band No.	ε (M^{-1} cm^{-1})	ν (cm^{-1})	$\delta_{1/2}$ (cm^{-1})	f_{osc}
1	0.8	13720	2150	8.0×10^{-6}
2	0.4	14030	1570	3.2×10^{-6}
3	0.3	14570	520	7.6×10^{-7}
4	0.2	15240	760	5.3×10^{-7}
5	0.3	15360	1110	1.3×10^{-6}
6	24.2	16750	2130	2.4×10^{-4}
RMS%	3.3			

*range: 12920–15760 cm^{-1}, 72-measurement points.

Table 2. Parameters of the component bands resulting from Gaussian analysis of the electronic spectrum* of *cis*-$[CrCl_2(phen)_2]Cl\cdot 2H_2O$; doublet-quartet region, symmetry C_{2v}.

Band No.	ε (M^{-1} cm^{-1})	ν (cm^{-1})	$\delta_{1/2}$ (cm^{-1})	f_{osc}
1	1.4	13570	3440	2.3×10^{-5}
2	23.9	16770	2110	2.3×10^{-4}
3	24.7	18050	2150	2.4×10^{-4}
4	23.4	19480	2480	2.7×10^{-4}
5	1.1	21810	4490	2.4×10^{-5}

Table 2 (continuation)

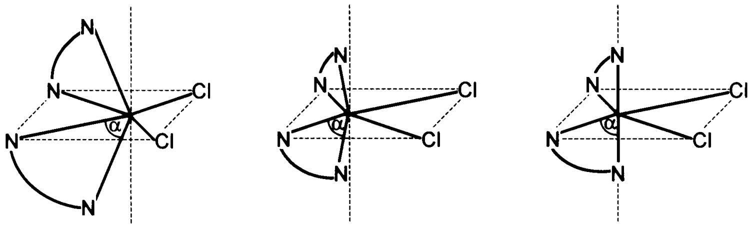
6	3.9	22510	940	1.7×10^{-5}
7	7.8	22700	730	2.6×10^{-5}
8	58.0	23630	1140	3.0×10^{-4}
9	7.2	24340	500	1.6×10^{-5}
10	37.1	24750	1130	1.9×10^{-4}
11	23.2	25510	1140	1.2×10^{-4}
12	239.9	26070	4790	5.3×10^{-3}
13	2573.2	31220	4210	5.0×10^{-2}
14	10927.4	33610	4200	2.1×10^{-1}
RMS%	0.6			

*range: 13480–27200 cm^{-1}, 344-measurement points.

Table 3. Transition energies, assignments and AOM parameters of an aqueous solution spectrum of *cis*-[CrCl$_2$(phen)$_2$]Cl, (in cm^{-1}); C$_{2v}$ symmetry, $^4B_2$ (F,$T_{2g}(B_{2g})$) ground term.

Experimental		Assignments	Calculated					
Ob-served	Resolved		α = 79(a)		α optimize		α = 90	
	13720	$^2A_1(1)$ [G,$A_{1g}(A_{1g})$]	13810		13840		13850	
	14030	$^2A_2(1)$ [G,$T_{1g}(E_g)$]	13970		14030		14060	
14500	14570	$^2B_2(1)$ [H,$T_{2g}(B_{2g})$]	14520		14530		14540	
	15240	$^2B_1(1)$ [G,$T_{1g}(E_g)$]	15020		15000		14970	
	15360	$^2B_2(2)$ [H,$T_{1g}(1)(A_{2g})$]	15040		15000		15000	
	16770	$^4A_1$ [F,$A_{2g}(B_{1g})$]	16840		16830		16830	
18000	18050	$^4B_1(1)$ [P,$T_{1g}(E_g)$]	18070		18130		18170	
	19480	$^4A_2(1)$ [P,$T_{1g}(E_g)$]	19220		19190		19180	
	21810	$^2B_1(2)$ [F,$T_{1g}(E_g)$]	22030		21950		21900	
	22520	$^2A_1(2)$ [F,$A_{2g}(B_{1g})$]	22580		22550		22540	
23640	22700	$^2A_2(2)$ [F,$T_{1g}(E_g)$]	22840		22910		22970	
	23630	$^4B_2(2)$ [F,$T_{1g}(A_{2g})$]	23720		23740		23740	
	24750	$^4A_2(2)$ [F,$T_{1g}(E_g)$]	24740		24640		24560	
25400	25510	$^4B_1(2)$ [F,$T_{1g}(E_g)$]	25530		25610		25670	
		r.m.s.	150	–	170	–	180	–
		e_σ(N)	8390	(90)	7540	(100)	6960	(90)
		e_σ(Cl)	6080	(130)	6370	(160)	6550	(160)
		$e_{\pi\perp}$(N)	2280	(90)	1620	(80)	1180	(90)
		$e_{\pi\|\|}$(N)(b)	0	–	0	–	0	–
		e_π(Cl)	240	(140)	430	(150)	530	(170)
		B	610	(10)	610	(20)	610	(20)
		C	3300	(0)	3290	(40)	3290	(0)
		C/B	5.3	–	5.3	–	5.4	–
		α	79.0	(.0)	82.7	(.2)	90	(.0)

[a] solid state. [b] value assumed.



a) α << 90° **b)** α < 90° **c)** α = 90°

Figure 3. Effect of opening the chelate angle (α) on bonding abilities of phenanthroline and chloride as ligands in the $[Cr(Cl)_2(phen)_2]^+$ complex and its geometry: a) α = 79° for solid state; b) α ~ 83° optimized for aqueous solution; c) α = 90° for "pure" tetragonal geometry.

REFERENCES

1. Gibson J.G. and McKenzie E.D., *J. Chem. Soc.*, **(A)**, 2637 (1969).
2. Hancock M.P., Josephsen J. and Schäffer C.E., *Acta Chem. Scand.*, **A30**, 79 (1976).
3. Kurzak K. and Kołkowicz A., *Spectrosc. Lett.*, **30**, 805 (1997).
4. Kurzak K. and Kołkowicz A., *Polish J. Chem.*, **68**, 1501 (1994).
5. Kurzak K. and Kołkowicz A., *Polish J. Chem.*, **68**, 1519 (1994).
6. Schäffer C.E., *Structure & Bonding*, **5**, 68 (1968).
7. Schäffer C.E., *Structure & Bonding*, **14**, 69 (1973).
8. Jørgensen C.K., *Modern Aspects of Ligand Field Theory*, North-Holland Publishing Co., Amsterdam, 1970.
9. Burstall F.H. and Nyholm R.S., *J. Chem. Soc.*, 3570 (1952).
10. Geary W.J., *Coord. Chem. Rev.*, **7**, 81 (1971).
11. Kurzak K., *Spectrochim. Acta*, **A47**, 1041 (1991).
12. Bartecki A., Sołtowski J. and Kurzak K., *Comp. Enhanced Spect.*, **1**, 31 (1983).
13. Kurzak K., *Comput. Chem.*, **43**, 519 (1999).
14. Kurzak K., Kołkowicz A. and Bartecki A., *Polyhedron*, **10**, 1795 (1991).
15. Kurzak K., Kołkowicz A. and Bartecki A., *Trans. Met. Chem.*, **17**, 155 (1992).
16. *Cambridge Structural Database*. Version 5.16, Cambridge Crystallographic Data Center, Cambridge: England, 1998.
17. Scaringe R.P., Singh P., Eckberg R.P., Hatfield W.E. and Hodgson D.J., *Inorg. Chem.*, **14**, 1127 (1975).
18. Veal J.T., Hatfield W.E. and Hodgson D.J., *Acta Cryst.*, **B29**, 12 (1973).
19. Kurzak K. and Biernacki K., *Polish J. Chem.*, **72**, 660 (1998).
20. Ryu C.K. and Endicott J.F., *Inorg. Chem.*, **27**, 2203 (1988).