J. inorg. nucl. Chem., 1969, Vol. 31, pp. 3203 to 3209. Pergamon Press. Printed in Great Britain

BAND SHIFT IN CHROMIUM (III) COMPLEXES WITH MIXED LIGANDS
A MOLECULAR ORBITAL APPROACH

S. BUNEL
Centro de Investigaciones Químicas
and
C. IBARRA and L. ADAN
Laboratorio de Química Inorgánica, Facultad de Química y Farmacia, Universidad de Chile, South America

Abstract—The shift of the first and second spin allowed bands due to the stepwise replacement of the nitrogen atoms in a complex of Cr(III) of the CrN_6 type by oxygen atoms of water or of carboxylic groups is analyzed in terms of perturbational molecule orbital theory. The set of parameters necessary to account for this effect has been obtained. Results agree fairly well with experimental data.

THE PROGRESSIVE substitution of the nitrogen atoms in a complex of the CrN_6 type by oxygen atoms belonging to ligands such as water, oxalate ion, aminoacid anion, etc, causes a marked shift of the spin allowed bands to the red region of the spectrum, as shown in Table 1.

Table 1

Compound	Environments	First band (m u)	Second band (m u)	References
$[Cr(en)_3]^{3+}$	6 N	458	351	[1]
$[Cr(en)_2(ox)]^+$	4 N, 2 O	495	369	[2]
trans-$[Cr(en)_2(H_2O)_2]^{3+}$	4 N, 3 O	508—443	361	[3, 5]
cis-$[Cr(en)_2(H_2O)_2]^{3+}$	4 N, 2 O	484	367	[3]
$[Cr(ala)_3]$	3 N, 3 O	507	382	This work
$[Cr(en)(ox)_2]^-$	2 N, 4 O	530	395	[4]
trans-$[Cr(ox)_2(H_2O)_2]^-$	6 O	542	407	This work
cis-$[Cr(ox)_2(H_2O)_2]^-$	6 O	562	411	This work
$[Cr(ox)_3]^{3-}$	6 O	572	419	[6]
$[Cr(H_2O)_6]^{3+}$	6 O	575	407	[7]

en = ethylenediamine; Ox = oxalate; ala = alaninate; gly = glycinate, amac = aminoacid anion.

The position of the absorption maxima depend, mainly, on the chromophore's composition, and, in a more restricted way, on its symmetry.

1. M. Linhard and M. Weigel, *Z. anorg. allg. Chem.* **49**, 266 (1951).
2. A. Mead, *Trans. Faraday Soc.* **30**, 1050 (1934).
3. F. Woldbye, *Acta chem. scand.* **12**, 1079 (1958).
4. H. L. Schläfer, O. Kling, L. Mähler and H. P. Opitz, *Z. phys. Chem.* **24**, 307 (1960).
5. W. A. Baker and M. G. Phillips, *Inorg. Chem.* **5**, 1042 (1966).
6. C. K. Jørgensen, *Acta chem. scand.* **8**, 1502 (1954).
7. C. K. Jørgensen, *Acta chem. scand.* **8**, 1495 (1954).

Only one of the compounds listed (*trans*-$[Cr(en)_2(H_2O)_2]^{3+}$) shows splitting of the first absorption band; in the remaining ones, changes in symmetry are accompanied by band broadening and shifting.

The present study is an attempt of calculation of these experimental data by means of molecular orbital perturbation theory, introducing some modifications to the equivalent treatments given by Yamatera[8], McClure[9], Schaffer[10] and Schaffer–Jørgensen[11].

According to these authors, each ligand exerts its effect on the *d* orbitals of the central ion through σ antibonding orbitals or a combination of σ and π antibonding orbitals.

The basic idea in the above treatment consists in perturbing the octahedral "parent complex'" by successive substitution of its ligands without altering its orthoaxial character[11]. In this way, *dxy*, *dxz*, *dyz* orbitals do not mix with dx^2-y^2 and dz^2 orbitals, which permits their direct utilization to obtain the energy changes introduced by bond formation.

Within this scheme the energy of the σ and π orbitals in a complex with mixed ligands, can be approximated to a sum of contributions in which the central ion is involved, expressed by means of empirical parameters.

In the present work the equations representing the energies of the different states originated by symmetry variations in each of the complexes studied have been derived considering only these atoms directly bonded to the central metallic ion, assuming that the complexes keep their orthoaxial character.

In the case of the oxygen atoms belonging to the carboxylic group of the oxalate ion or aminoacidate ion, the π bonding has been restricted to those *p* orbitals perpendicularly oriented to the ligand's ring[12].

In the nitrogen atoms belonging to ethylenediamine and aminoacid anions a conventional arrangement considering only the σ system has been used. The presence of a single free electron pair for coordination in the nitrogen atom enables us to assume that the contribution to the π bond is null.

The energies of the fundamental and excited states for the different chromophoric symmetries were obtained by building up the octahedral determinantal wave functions and perturbing each orbital by bonding.

The interelectronic repulsion energy, on which the components of the second absorption band depend, has been included in the calculations in terms of B, the Racah parameter. In spite of the changes in microsymmetry, the repulsion has been considered to be equivalent to that existing in a complex having octahedral molecular geometry.

In order to calculate the location of the different band components in the complexes under study, it has been necessary to have five empirical parameters available besides that representing the interelectronic repulsion. Three of them correspond to σ interaction between chromium and aminic nitrogen, chromium

8. H. Yamatera, *Bull. chem. Soc. Japan* **31**, 95 (1958).
9. D. S. McClure, *Advances in the Chemistry of Coordination Compounds* (Edited by S. Kirshner), p. 498. MacMillan, New York (1961).
10. C. E. Schäfer, *Theoret. chim. Acta* **4**, 166 (1966).
11. C. E. Schäfer and C. K. Jørgensen, *Mat. Fys. Medd. Dan Vid Selzk* **34**, 13 (1965).
12. A. D. Liehr, *J. phys. Chem.* **68**, 665 (1964).

and carboxylic oxygen and chromium and water oxygen, designated as σ_N, σ_O and σ_A respectively; the other two express the contribution of carboxylic oxygen and water oxygen to the bond and they have been designated as π_O and π_A respectively. It should be borne in mind that in McClure's notation $\sigma_B = \sigma_A + \delta\sigma$ and $\pi_B = \pi_A + \delta\pi$.

The orbital energies of an octahedral complex including σ and π interactions are:

$$dz^2 = \tfrac{8}{3}\sigma_z + \tfrac{2}{3}\sigma_x + \tfrac{2}{3}\sigma_y$$

$$dx^2 - y^2 = 2\sigma_x + 2\sigma_y$$

$$dxy = 2\pi_x + 2\pi_y$$

$$dxz = 2\pi_x + 2\pi_z$$

$$dyz = 2\pi_y + 2\pi_z$$

where x, y and z represent the coordinate axes.

σ_N is obtained directly from the equations and the "parent complex" spectrum, $[Cr(en)_3]^{3+}$, where $4\sigma_N$ is made equal to the energy of the first spin allowed absorption band of $[Cr(en)_3]^{3+}$.

The parameters σ_o and π_o can be derived approximately from the equations and spectra of the complexes $[Cr(ox)_3]^{3-}$ and $[Cr(ox)(NH_4)_4]^{+}$[13] taking $4\sigma_o - 2\pi_o$ equal to the energy of the first spin allowed band of the complex $[Cr(ox)_3]^{3-}$.

In the case of the water molecule, the corresponding parameters can be obtained by combination of the equations and spectra of $[Cr(H_2O)_6]^{3+}$ and $[Cr(NH_3)_5H_2O]^{3+}$[14] following a similar procedure to that outlined previously.

The parameters thus obtained and used in this work are: $\sigma_N = 5{\cdot}46$; $\sigma_o = 4{\cdot}61$; $\sigma_A = 4{\cdot}90$; $\pi_o = 0{\cdot}47$ and $\pi_A = 0{\cdot}55$ kK.

These values are in good agreement with the "highly speculative" ones proposed by Jørgensen[15] for Yamatera's parameters.

In the case of water the value of π_A is about 11 per cent that of σ_A, which is consistent with suggested values for this parameters[16]. The low value of π_A and the still lower value of π_o, corresponding to the oxalate ion, gives support, in a certain way, to Adamson's hypothesis[17] concerning the lack of linear correlation between the spin allowed and spin forbidden bands of $[Cr(ox)_3]^{3-}$ as compared to the other Cr(III) complexes.

In order to keep the number of variables at a minimum, a value of 0·580 kK[5] was used in all cases for the interelectronic repulsion parameter, B, which in the literature is given different values for the same compound[18], [19].

13. E. Kyuno, M. Kamada and N. Tanaka, *Bull. chem. Soc. Japan* **40**, 1848 (1967).
14. M. R. Edelson and R. A. Plane, *J. phys. Chem.* **63**, 327 (1959).
15. C. K. Jørgensen, *Advances in Chemical Physics* (Edited by Prigogine) p. 33. Interscience, New York (1963).
16. C. K. Jørgensen, *J. Phys.* **26**, 825 (1965).
17. A. W. Adamson, *J. inorg. nucl. Chem.* **28**, 1955 (1966).
18. K. Krishnamurty, W. S. Schaap and J. R. Perumareddi, *Inorg. Chem.* **6**, 1338 (1967).
19. C. K. Jørgensen, *Progress in Inorganic Chemistry* (Edited by A. Cotton), p. 73, Vol. IV. Interscience, New York (1962).

Table 2 contains the expression of the orbital energy in terms of the σ and π parameters and the interelectronic repulsions for the different states of some complexes under study. In the cases of *cis-trans* isomerism the energy difference between the components of the first band of the *trans* isomer is twice that of the *cis* isomer. Thus a given band of a *trans* isomer can be expected to be splitted or notoriously broader than the band of the corresponding *cis* isomer.

Table 2

Compound and microsymmetry		State	Orbital energy and repulsion*
$[Cr(en)_2(ox)]^+$	C_{2v}	$^4T_2$ $^4A_1$	$2\sigma_N+2\sigma_o$
		$^4A_2, {}^4B_2$	$3\sigma_N+\sigma_o-\pi_o$
		$^4T_1$ $^4B_1$	$\frac{10}{3}\sigma_N+\frac{8}{3}\sigma_o+12B$
		$^4A_2, {}^4B_2$	$\frac{7}{3}\sigma_N+\frac{5}{3}\sigma_o-\pi_o+12B$
trans-$[Cr(en)_2(H_2O)_2]^{3+}$	D_{4h}	$^4T_2$ $^4B_2$	$4\sigma_N$
		^4E	$2\sigma_N+2\sigma_A-2\pi_A$
		$^4T_1$ $^4A_2$	$\frac{4}{3}\sigma_N+\frac{8}{3}\sigma_A+12B$
		^4E	$\frac{10}{3}\sigma_N+\frac{8}{3}\sigma_A-2\pi_A+12B$
cis-$[Cr(en)_2(H_2O)_2]^{3+}$	C_{2v}	$^4T_2$ $^4A_1$	$2\sigma_N+2\sigma_A-2\pi_A$
		$^4A_2, {}^4B_2$	$3\sigma_N+\sigma_A-\pi_A$
		$^4T_1$ $^4B_1$	$\frac{10}{3}\sigma_N+\frac{8}{3}\sigma_A-2\pi_A+12B$
		$^4A_2, {}^4B_2$	$\frac{7}{3}\sigma_N+\frac{5}{3}\sigma_A-\pi_A+12B$
fac-$[Cr(amac)_3]$	C_{3v}	$^4T_2$ $^4A_1, {}^4E$	$2\sigma_N+2\sigma_o-\pi_o$
		$^4T_1$ $^4A_2, {}^4E$	$2\sigma_N+2\sigma_o-\pi_o+12B$

*Wave functions used to calculate the orbital energies and repulsion

$^4T_2$: $|xz\,yz\,x^2-y^2|$,
$-\frac{1}{2}|xy\,yz\,x^2-y^2|+\sqrt{\frac{3}{2}}|xy\,yz\,z^2|$,
$-\frac{1}{2}|xy\,xz\,x^2-y^2|-\sqrt{\frac{3}{2}}|xy\,xz\,z^2|$

$^4T_1$: $|xz\,yz\,z^2|$,
$-\frac{1}{2}|xy\,yz\,z^2|-\sqrt{\frac{3}{2}}|xy\,yz\,x^2-y^2|$,
$-\frac{1}{2}|xy\,xz\,z^2|+\sqrt{\frac{3}{2}}|xy\,xz\,x^2-y^2|$

The values obtained with the above parameters appear in the third column of Table 3 where it is clear that the bathochromic effect accompanying the increase in oxygen atoms bonded to Cr(III) is correspondently reproduced in the calculated values for both the first and the second absorption band.

In general, agreement between the experimental and calculated spectra is good, considering that in the absence of splitting, the maximum of an absorption curve will be an intermediate value of the components.

Only two of the complexes listed present *cis*-trans isomerism: they are $[Cr(en)_2(H_2O)_2]^{3+}$ and $[Cr(ox)_2(H_2O)_2]^-$. In the former, there is a clear difference in the spectra of each geometrical isomer. The *trans* compound shows splitting of the first band in its components $^4B_2$ and ^4E with an experimental separation of 2·79 kK, while the *cis* isomer does not present splitting. Calculations give a value of 2·22 kK for the difference between the $^4B_2$ and ^4E states of the *trans* isomer, while the calculated separation between the $^4A_1$ and $^4A_2$ ($^4B_2$) states of the *cis* isomer is 1·11 kK. It is necessary to bear in mind at this point that the

Table 3

Complex	Observed maxima (kK)	Calculated components of first and second band (kK)		
$[Cr(en)_2(ox)]^+$	20, 2	20, 14	$^4A_1$	
		20, 52	$^4A_2$	$^4B_2$
	27, 1	26, 91	$^4A_2$	$^4B_2$
		28, 23	$^4B_1$	
	19, 68	19, 62	^4E	
trans-$[Cr(en)_2(H_2O)_2]^{3+}$	22, 57	21, 84	$^4B_2$	
	27, 70	27, 31	$^4A_2$	
		27, 33	^4E	
cis-$[Cr(en)_2(H_2O)_2]^{3+}$	20, 66	19, 62	$^4A_1$	
		20, 73	$^4A_2$	$^4B_2$
	27, 25	27, 32	$^4A_2$	$^4B_2$
		27, 33	$^4B_1$	
		*19, 67	$^4A_1$	^4E
		26, 63	$^4A_2$	^4E
$[Cr(ala)_3]$	19, 72	†18, 35	$^4A_2$	
	26, 18	19, 67	$^4B_1$	
		20, 99	$^4B_2$	
		26, 25	$^4B_2$	
		26, 63	$^4A_1$	
		27, 01	$^4A_2$	
$[Cr(en)(ox)_2]^-$	18, 87	18, 82	$^4A_2$	$^4B_2$
		19, 20	$^4A_1$	
	25, 32	25, 03	$^4B_1$	
		26, 35	$^4A_2$	$^4B_2$
trans-$[Cr(ox)_2(H_2O)_2]^-$	18, 45	16, 98	^4E	
		18, 44	$^4B_2$	
	24, 57	23, 56	^4E	
		26, 18	$^4A_2$	
cis-$[Cr(ox)_2(H_2O)_2]^-$	17, 79	16, 98	$^4A_1$	
		17, 71	$^4A_2$	$^4B_2$
	24, 33	23, 56	$^4B_1$	
		24, 87	$^4A_2$	$^4B_2$

*Calculated for facial model.
†Calculated for meridional model.

spectra of aqueous solution of Cr(III) complexes with mixed ligands show marked splitting of a band components when the energy difference between them is greater than 2·2 kK [5].

The geometrical isomers of the $[Cr(ox)_2(H_2O)_2]^-$ ion behave unlike the complexes $[Cr(en)_2(H_2O)_2]^{3+}$, since its absorption bands do not show any kind of separation in their components. Calculations indicate that the state ^4E and $^4B_2$ of the *trans* isomer have a separation of 1·46 kK and the state $^4A_1$ and $^4A_2$ ($^4B_2$) of the *cis* isomer differ by 0·73 kK (Fig. 1).

It must be pointed out that the position of the first spin allowed band of the *cis* compound is clearly shifted to the red as compared to the first band of the *trans*

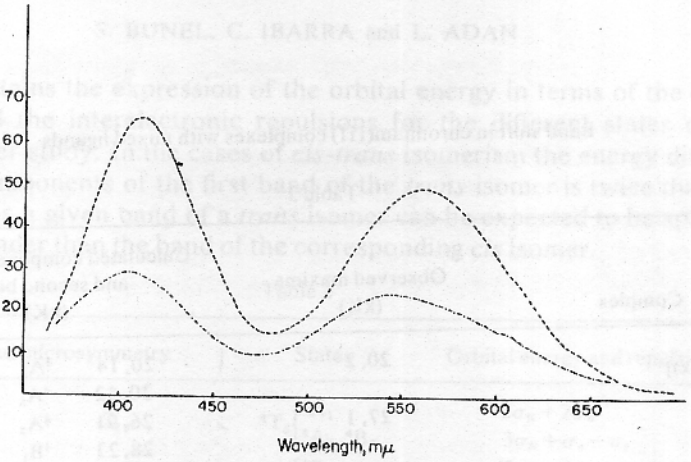

Fig. 1. Absorption spectra of:
– – – – *cis* $[Cr(ox)_2(H_2O)_2]^-$; ·—·—· *trans* $[Cr(ox)_2(H_2O)_2]^-$.

compound. The experimental difference is 0·66 kK. Since calculations give the same value of energy for one of the components in both the *cis* and the *trans* isomers, the shifting must be ascribed to the different values of the $^4A_2$ ($^4B_2$) compounds for the *cis* and $^4B_2$ component for the *trans* compound.

The compounds $[Cr(en)(ox)_2]^-$ and $[Cr(en)_2(ox)]^+$ experimentally do not show partition of their bands. This is consistent with the low value of the energy differences between the band components of the compounds.

The compound $[Cr(ala)_3]$ may exist in two isomeric forms belonging to the microsymmetries C_{3v} (facial) and C_{2v} (meridional) [20], respectively. Theoretically the former should present only two spin allowed absorption bands since both the components ^4E and $^4A_1$ of the first band and ^4E and $^4A_2$ of the second one do not differ one another, as shown in Table 3.

The isomer of chromophoric symmetry C_{2v}, on the other hand, presents each of its bands formed by three components of different energy. From the values obtained it can be expected the C_{2v} isomer to present the band of lower energy of an asymmetric shape or else to be slightly splitted in its components.

Unlike the two types of complexes, red and violet, formed by Co(III) with aminoacid anions of general formula $[Co(amac)_3]$, in the case of Cr(III), we have been able to obtain only red compounds obeying the formula $[Cr(ala)_3]$ and $[Cr(gly)_3]$.

The experimental maxima are 19,700 and 26,200 cm^{-1}, they present neither shoulder nor asymmetry and seem to correspond clearly to two gaussian curves [21], whereby we can assume that the compound formed is the C_{3v} isomer (Fig. 2), as proposed by Banerjea and Chaudhuri [22].

20. E. Larsen and S. F. Mason, *J. chem. Soc.* 313 (1966).
21. C. K. Jøgensen, *Absorption Spectra and Chemical Bonding in Complexes*, p. 85. Pergamon Press, Oxford (1962).
22. D. Banerjea and S. Dutta Chaudhuri, *J. inorg nucl. Chem.* 30, 871 (1968).

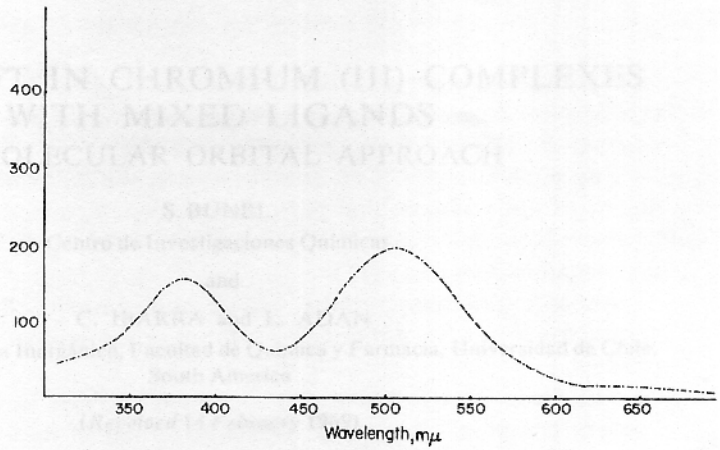

Fig. 2. Absorption spectra of $[Cr(ala)_3]$.

EXPERIMENTAL

Preparation of red $[Cr(ala)_3]$. It was prepared by a procedure analogous to that given by G. Brauer [23] for the tris-glycinate of Cr(III). It was necessary to separate the insoluble "basic" compound by repeated filtrations. The last portions of this compound, which were mixed with the red complex, were suspended in plenty of ice-cooled water. The red crystals were thus collected in the bottom of the beaker. The yield is low. The compound thus obtained is slightly soluble in water and the solution changes slowly from red to violet. *Anal.* Calc. for $C_9H_{18}N_3O_6Cr$: C, 34·18; H, 5·74; N, 13·29; Cr, 16·44. Found: C, 34·61; H, 5·77; N, 12·72; Cr, 15·92.

Preparation of *trans*-$[Cr(ox)_2(H_2O)_2]K$ and *cis*-$[Cr(ox)_2(H_2O)_2]K$. They were prepared by Werner's methods [24] and also by the techniques used by Hamm and Perkins [25] for potassium dimalonate diaquo chromates(III), the results being identical in both cases. Analysis of the *trans* isomer: Calc. for $C_4H_8O_{12}CrK$: $Cr(C_2O_4)_2(H_2O)_2K.2H_2O$: C, 14·17; H, 2·37; Cr, 15·33. Found: C, 13·60; H, 2·80; Cr, 15·30. Analysis of the cis isomer. Calc. for $C_4H_4O_{10}CrK$, $Cr(C_2O_4)_2(H_2O)_2K$: C, 15·85; H, 1·33; Cr, 17·15. Found: C, 16·30; H, 1·60; Cr, 16·94.

The analysis of chromium was carried out in our Laboratory by oxidation of the Cr(III) ion into chromate with sodium peroxide in alkaline medium. To the dichromate ion obtained by acidifying the solution, an excess solid potassium iodide was added. The free iodine was titrated with sodium thiosulfate.

The analysis of C, H and N was made in the Organic Microanalysis Laboratory in our School.

The reagents used were all analytical grade. Alanine was DL-Alanine from Matheson Coleman and Bell.

Spectra. The absorption curves were obtained in a Unicam SP 800 and a Beckmann DU-2 spectrophotometer from aqueous solutions of the complexes in a 10 mm path cell, except the spectrum of *tris* alaninate of Cr(III) which was made in 10% aqueous solution of potassium chloride in a 100 mm path cell.

Acknowledgement—The authors gratefully acknowledge Professor Klixbull C. Jørgensen for valuable criticism and help.

23. G. Brauer, *Química Inorgánica Preparativa* (Edited by Reverté), p. 827 (1958).
24. A. Werner, *Justus Liebigs Annln Chem.* **406**, 261 (1914).
25. R. Hamm and R. Perkins, *J. Am. chem. Soc.* 77, 2083 (1955).