

# THE INTERELECTRONIC REPULSION PARAMETERS IN CUBIC HIGH SPIN VANADIUM(II) AND CHROMIUM(III) COMPLEXES OF *p*-DIETHYLAMINO ANIL OF PHENYL GLYOXAL

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## ABSTRACT

The calculations of ligand field parameters for the complexes of vanadium(II) and chromium (III) with *p*-diethylamino anil of phenyl glyoxal (DEAPG) have been made in such a way that the problem associated with Racah parameter may be avoided. It has been concluded that in the case of six coordinated  $d^3$  ion V(II) and Cr(III), the method which results from fitting the sum of second and third band should be preferred provided all the three spin-allowed  $d-d$  transitions are observed.

## INTRODUCTION

RECENTLY König<sup>7-10</sup> has discussed the phenomenon of nephelauxetism and shows its importance in evaluating the covalency factors. The calculations of ligand field parameters, viz., cubic ligand field splitting parameters ( $10 D_q$ ), Racah's interelectronic parameter ( $B$ ) and nephelauxetic effect  $\beta$  ( $\beta = B$  complex/ $B$  free ion) depend significantly on the method adopted for their calculations. In the present study the electronic ligand field spectra of some of the complexes having  $d^3$ -configuration of DEAPG are reported and calculations of various ligand field parameters have been made by various methods available in the literature. For the purpose of comparison spectral data on  $VCl_3$  and  $[Cr(H_2O)_6]^{+3}$  have been included from the work of Clark<sup>4</sup> and Plane<sup>11,13</sup>.

## EXPERIMENTAL

Chemicals of AnalaR grade are used throughout. The ligand (DEAPG) was prepared by condensing phenyl glyoxal hydrate with *p*-diethylamino aniline<sup>12</sup> in alcoholic medium in equimolar quantities. The purity of this was checked by analysis. The complexes of V(II) ion obtained by reducing vanadyl solution using excess of zinc amalgam (in an inert atmosphere) and Cr(III) ion with DEAPG have been isolated by mixing the solutions of the metal ions and ligand in the ratio 1 : 2 and 3 : 5 respectively<sup>14</sup>. The absorption spectra of the complexes were recorded in non-aqueous medium at room temperature using UNICAM SP-500 spectrophotometer.

## RESULTS AND DISCUSSION

In a cubic field, the configuration  $d^3$  will give two quartet terms  $^4F$  and  $^4P$ . Under the influence of the octahedral field,  $^4F$  will split into  $^4A_{2g}$  and  $^4T_{2g}$  states whereas  $^4P$  will give only one state, i.e.,  $^4T_{1g}$ ; there-

fore three spin allowed transitions from the ground state  $^4F$  to the excited state  $^4P$  are expected.

The calculated values of the transitions  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  may be obtained by the following equations:

$$\nu_1 = 10 D_q \quad (i)$$

$$\nu_{2,3} = 1/2 (15B + 30 D_q) \pm 1/2 [(15B - 10D_q)^2 + 15B \cdot 10D_q]^{1/2} \quad (ii)$$

and the value of the Racah parameter may then be calculated according to one of the following methods which differ by the bands on which fit is based:

$$B = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)/(15\nu_2 - 27\nu_1) \quad (a)$$

$$B = (2\nu_1^2 + \nu_3^2 - 3\nu_1\nu_3)/(15\nu_3 - 27\nu_1) \quad (b)$$

$$B = (\nu_2 + \nu_3 - 3\nu_1)/15 \quad (c)$$

$$B = 1/75 [3\nu_1 \pm \{25(\nu_3 - \nu_2)^2 - 16\nu_1^2\}^{1/2}] \quad (d)$$

out of all the above four methods applicable in the case of V(II) and Cr(III) complexes, the best fitting procedure is (c) in which there is a good agreement between observed and calculated values of the transitions but in case of the methods (a) and (b) there is a large percentage of deviation ( $\delta\nu\%$ ) (Table I). The method (d) is not applicable as the value of  $B$  was found to be negative which has no physical significance. In Table I the value of Racah parameter  $B$  for the complex (5) is  $496.6 \text{ cm}^{-1}$  as compared to the complex (6) ( $646.3 \text{ cm}^{-1}$ ), it may be due to covalence. The L.F.S.E. for the complex (6) ( $53.05 \text{ kcal/mole}$ ) is also greater than the complex (5) ( $51.42 \text{ kcal/mole}$ ). Similarly for the Cr(III) complexes, the complexes (1) and (2) have their values of  $B$  as  $685.3 \text{ cm}^{-1}$  and  $728.0 \text{ cm}^{-1}$ . The corresponding values of L.F.S.E. are  $60.00 \text{ kcal/mole}$  and  $61.23 \text{ kcal/mole}$ . The values of  $\beta$  of the complexes under study are between 0.5 and 1.0 clearly indicate the partial covalent character of the bond concerned.

On examination of the ir spectrum of various complexes of DEAPG with V(II) and Cr(III), indicate that the point of attachment are keto  $\nu(C=O)$

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TABLE I  
 Electronic Spectra and relevant ligand field parameters

Complex	Methods of calculation	Observed and calculated transition energies				B cm <sup>-1</sup>	$\beta_{35}$	$\delta\nu$ cm <sup>-1</sup>	$\delta\nu$ (%)	L.F.S.E. kcal/mole
		$^4A_2(F) \rightarrow ^2E_g \rightarrow ^4T_2$	$(F) \rightarrow ^4T_1$	$(F) \rightarrow ^4T_1(P)$						
(1)	Expt.	13500	17500	24750	38030	..	..	..	..	..
	(a)		10D <sub>q</sub>	fitted	38759	733.9	0.79	+ 729	1.91	60.00
	(b)		10D <sub>q</sub>	23993	fitted	635.0	0.69	- 757	3.05	
	(c)		10D <sub>q</sub>	24389	38391	685.3	0.74	± 361	0.94	
(2)	Expt.	13200	17860	25110	38390	..	..	..	..	..
	(a)		10D <sub>q</sub>	fitted	39400	728.6	0.79	+1010	2.63	61.23
	(b)		10D <sub>q</sub>	23971	fitted	585.4	0.63	-1139	4.53	
	(c)		10D <sub>q</sub>	26058	37442	728.0	0.79	± 948	2.46	
(3)	Expt.	..	17400	24600	38000	..	..	..	..	..
	(a)		10D <sub>q</sub>	fitted	38510	728.0	0.79	+ 510	1.39	
	(b)		10D <sub>q</sub>	24000	fitted	657.0	0.71	- 600	2.50	
	(c)		10D <sub>q</sub>	24530	38070	693.0	0.75	± 70	0.23	
(4)	Expt.		9000	14000	21500	..	..	..	..	..
	(a)		10D <sub>q</sub>	fitted	22090	606.0	0.79	+ 590	2.67	30.85
	(b)		10D <sub>q</sub>	13754	fitted	550.3	0.71	- 246	1.78	
	(c)		10D <sub>q</sub>	13831	21669	566.6	0.73	± 169	1.00	
	(d)		10D <sub>q</sub>	13500	21000	500.0	0.63	- 500	3.04	
(5)	Expt.	..	15000	21850	30600	..	..	..	..	..
	(a)		10D <sub>q</sub>	fitted	33990	722.6	0.94	+3390	11.07	51.42
	(b)		10D <sub>q</sub>	17000	fitted	173.3	0.22	-4850	22.19	
	(c)		10D <sub>q</sub>	20175	32275	496.6	0.64	±1675	5.47	
(6)	Expt.	..	15475	22320	33800	..	..	..	..	..
	(a)		10D <sub>q</sub>	fitted	34777	711.5	0.92	+ 977	2.89	53.05
	(b)		10D <sub>q</sub>	21430	fitted	585.6	0.76	- 890	3.98	
	(c)		10D <sub>q</sub>	21867	34250	646.3	0.84	± 453	1.34	

\* (1) [Cr<sub>3</sub>(C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O)<sub>5</sub>Cl<sub>4</sub>]Cl<sub>5</sub>(2) [Cr<sub>3</sub>(C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O)<sub>5</sub>(CN)<sub>4</sub>]Cl<sub>5</sub>(3) [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>+3</sup>(4) VCl<sub>2</sub>(5) [V(C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>](6) [V(C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub>.

and azo methine v (-CH=N-) groups, since the frequencies of these groups shift to more negative side on complexation. Many workers<sup>1,2,6</sup> reported several cyano complexes in which they found the frequencies of cyano group in bridging and terminal positions. In the present complexes of Cr(III)-DEAPG a frequency of cyano group is observed at 2125 cm<sup>-1</sup> indicating the bridging position. In addition to the -C≡N frequency, the complexes also show (M-C≡N) and (M-C) vibrations<sup>3-5</sup>.

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