

Correspondence

Ligand Field Theory and the Energy of the So-Called "Third Band" in Chromium(III) and Vanadium(II) Complexes

Sir:

According to a widespread opinion which is exemplified by several recent reviews of chromium(III) spectra¹⁻³ the three-parameter ($10Dq$, B , C) ligand field theory is supposed to be unable to reproduce adequately the energy of the so-called "third band" (i.e., the ${}^4A_{2g} \rightarrow b^4T_{1g}$ transition) in octahedrally coordinated d^3 complexes and solids. To investigate the soundness of this statement, we tested and applied methods which may be used to obtain a numerical fit to the relevant experimental data.

The electronic configuration d^3 is very favorable in this respect. Thus if only the spin-allowed d-d bands are considered, problems associated with the treatment of the Racah parameter C may be avoided.⁴⁻⁷ In addition, it is convenient to limit the study to those complex ions where *all three* spin-allowed bands are observed. In this way a convenient check on the accuracy of the method is provided by a calculation of the extra band energy.

lowing one of four methods which differ by the bands on which the fit is based: (a) fitting the second band

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

(b) fitting the third band

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

(c) fitting the sum of the second and third bands

$$B = (\nu_2 + \nu_3 - 3\nu_1)/15 \quad (4)$$

(d) fitting the difference between the second and third bands

$$B = 1/75 [3\nu_1 \pm [25(\nu_3 - \nu_2)^2 - 16\nu_1^2]^{1/2}] \quad (5)$$

Equations 2-5 were applied to the spectra of relevant chromium(III) and vanadium(II) complexes and the extra band energy was calculated from eq 1. Results of the analysis of three selected compounds are compiled in Table I.

Experimental transition energies are listed, for each compound, in line 1. Subsequent lines contain the calculated transition energies, their deviation from the corresponding experimental value, $\delta\nu = \nu_{\text{calcd}} - \nu_{\text{exptl}}$ (in reciprocal centimeters and in per cent), and the values of the parameters B_{35} and $\beta_{35} = B_{35}^{\text{complex}}/B_{35}^{\text{free ion}}$.

TABLE I
OBSERVED AND CALCULATED TRANSITION ENERGIES (IN cm^{-1}) OF OCTAHEDRAL VANADIUM(II) AND CHROMIUM(III) ($B_{V^{2+}^{\text{free}}} = 766 \text{ cm}^{-1}$, $B_{Cr^{3+}^{\text{free}}} = 918 \text{ cm}^{-1}$)

Compd	Method	ν_1	ν_2	ν_3	$\delta\nu$		B_{35} , cm^{-1}	β_{35}
		${}^4A_{2g} \rightarrow {}^4T_{2g}$	${}^4A_{2g} \rightarrow a^4T_{1g}$	${}^4A_{2g} \rightarrow b^4T_{1g}$	cm^{-1}	%		
$V(\text{H}_2\text{O})_6^{2+}$	Exptl	12,300	18,500	27,900				
	a	$10Dq$	Fitted	28,790	+890	3.09	692.7	0.90
	b	$10Dq$	17,938	Fitted	-562	3.13	595.8	0.78
	c	$10Dq$	18,167	28,233	∓ 333	1.50	633.3	0.83
$\text{Cr}(\text{urea})_6^{3+}$	Exptl	16,100	22,600	34,400				
	a	$10Dq$	Fitted	35,481	+1081	3.04	652.0	0.71
	b	$10Dq$	21,328	Fitted	-1272	5.96	495.2	0.54
	c	$10Dq$	22,042	34,958	∓ 558	2.06	580.0	0.63
$V\text{Cl}_2 (22^\circ\text{K})$	Exptl	9300	14,220	22,244				
	a	$10Dq$	Fitted	22,231	-7	0.03	570.1	0.74
	b	$10Dq$	14,226	Fitted	+6	0.04	571.3	0.75
	c	$10Dq$	14,224	22,240	± 4	0.02	570.9	0.75
d	$10Dq$		14,231	22,255	+11	0.06	572.3	0.75

Specifically, three spin-allowed transitions from the ${}^4A_{2g}$ ground state to the excited states ${}^4T_{2g}$, a^4T_{1g} , and b^4T_{1g} are expected within the octahedral d^3 configuration. The energy of the lowest transition is always determined as $\nu_1({}^4A_{2g} \rightarrow {}^4T_{2g}) = 10Dq$. The energies of the two higher transitions follow according to

$$\nu_{2,3} = 1/2(15B + 30Dq) \mp 1/2[(15B - 10Dq)^2 + (12B)(10Dq)]^{1/2} \quad (1)$$

The Racah parameter B may then be determined fol-

(1) L. S. Forster, *Transition Metal Chem.*, **5**, 1 (1969).

(2) C. K. Jørgensen, "Oxidation Numbers and Oxidation States," Springer-Verlag, Berlin, 1969.

(3) D. Reinen, *Struct. Bonding (Berlin)*, **6**, 30 (1969).

(4) In the semiempirical form of ligand field theory, the approximation $C = 4B$ is often introduced. This assumption has been severely criticized.^{5,6} In addition, it is usually assumed that, in the complex, the parameter values of B and C have decreased by equal amounts due to the nephelauxetic effect. However, there is recent evidence that, particularly in chromium(III) complexes, C is not reduced to the same extent as B .^{6,7}

(5) A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

(6) H. Witzke, *Theor. Chim. Acta*, **20**, 171 (1971).

(7) J. Ferguson, *Progr. Inorg. Chem.*, **12**, 159 (1970).

$B^{\text{free ion}}$. Each line applies to a different method marked with reference to the above listing.

The results on the $V(\text{H}_2\text{O})_6^{2+}$ and $\text{Cr}(\text{urea})_6^{3+}$ ions are typical of room-temperature solution spectra.^{8,9} The values of B_{35} and β_{35} depend noticeably on the method adopted to their calculation. The deviation $\delta\nu$ of the calculated transition energy is of the order of a few per cent and is always largest if method (b) is applied and smallest if method (c) is used. Evidently, if ν_2 is employed in the fit, $\delta\nu_3$ (in per cent) is smaller than $\delta\nu_2$ which results if ν_3 is used. Finally, in method (c), $|\delta\nu_2| = |\delta\nu_3|$. Therefore, within the approximation of the three-parameter ligand field theory, the energies of both the "second" and "third" bands (i.e., ν_2 and ν_3) are reproduced equally well. In addition, there does simply not exist a misfit of ν_3 which could be redistributed on ν_2 and ν_3 if method (c) is applied. If this were true, one would expect a value of $\delta\nu$ intermediate between

(8) C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).

(9) C. K. Jørgensen, *Struct. Bonding (Berlin)*, **1**, 3 (1966).

$\delta\nu(a)$ and $\delta\nu(b)$. However, $\delta\nu(c)$ is always smaller than both $\delta\nu(a)$ and $\delta\nu(b)$.

A significantly different result is obtained if the single-crystal spectrum of VCl_2 at 22°K is studied.¹⁰ In this case, the values of B_{35} and β_{35} are practically independent of the calculation method.¹¹ The deviation $\delta\nu$ is smaller by a factor of about 10^{-2} than in room-temperature solution spectra, although the order of the various $\delta\nu$ values is preserved. Similarly accurate results have been obtained apparently¹² with a number of V^{2+} -doped single crystals at 4.2°K. It is evident that the simple three-parameter ligand field theory may reproduce accurate experimental values of transition energies quite well.

The reason for the strikingly different results of room-temperature solution spectra *vs.* low-temperature single-crystal spectra seems to be obvious. In ligand field theory, transition energies are calculated always at a constant $10Dq$ (*cf.* "vertical" transitions in a Tanabe-Sugano diagram). Since $10Dq = (5/3)Ze^2\langle r^4 \rangle / R^5$, this corresponds to a fixed metal-ligand distance, R . In addition, the states involved in spin-allowed d-d transitions originate always in different configurations $t_{2g}^m e_g^n$ and, consequently, the potential minima of the excited state and ground state do not coincide. The calculated transition energy corresponds, therefore, to the energy of a transition from the zero-point vibrational level of the electronic ground state to an excited vibrational level of the excited state (*cf.* "vertical" transition according to the Franck-Condon principle). This statement is by no means trivial since a problem in ligand field theory is essentially one of a perturbed atom. Neither do interatomic distances appear explicitly in the calculations nor are vibrational interactions considered. Thus any comparison between theoretical and experimental energies should use the Franck-Condon maxima of the absorption bands determined, in principle, at 0°K (*cf.* footnote 11). These energies may be approximated by the centers of gravity of individual bands in spectra measured at cryogenic temperatures. With increasing temperature, however, higher vibrational levels of the ground state become populated and the corresponding band is progressively shifted to lower energy.¹³ Consequently, at room temperature, *e.g.*, significant differences between calculated and observed band energies should be expected.

Of course, all three spin-allowed d-d bands may be observed only in those complexes of vanadium(II) and chromium(III) which involve weak-field ligands. With most medium- and strong-field ligands, the third band is masked by intense ligand or charge-transfer absorption. It is possible that, with these ligands, larger deviations would be encountered than in the examples discussed here.¹⁴

(10) S. S. Kim, S. A. Reed, and J. W. Stout, *Inorg. Chem.*, **9**, 1584 (1970).

(11) The values of the parameters $10Dq$ and B_{35} calculated here are different from those reported by Kim, *et al.*¹⁰ In their original paper, these authors employed the estimated energy of the $0'' \rightarrow 0'$ transition in the calculation. It will be shown below that this procedure is not appropriate.

(12) W. E. Smith, *J. Chem. Soc. A*, 2677 (1969).

(13) J. Lee and A. B. P. Lever, *J. Mol. Spectrosc.*, **26**, 189 (1968).

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Relative Covalencies from Nuclear Magnetic Resonance Contact Shifts in Isostructural Transition Metal Complexes

Sir:

The capability for detailed mapping of the delocalized spin density over a paramagnetic complex, using nmr contact shifts,¹ allows one, in principle, to arrive at some data which can be related to the metal-ligand covalency if the metal-ligand overlap is known.² The lack of these latter overlap data has placed the emphasis more on evaluating trends in covalency^{1,3-6} in a series of isostructural complexes than on characterizing the covalency in individual cases.² Thus proton nmr studies of isostructural complexes, where either the metal ion was varied³⁻⁵ or the oxidation state of a given metal was altered,⁷ have been used to gauge the relative extents of mixing of the metal and various ligand orbitals. There exist in the literature, however, certain ambiguities as to both the exact form of some of the equations used to obtain the spin density and the nature of the proper index (contact shift, hyperfine coupling constant, spin density, or other variable) from which information on the relative metal-ligand covalency may be derived.

The Hamiltonian for the chemically interesting Fermi contact interaction^{8,9} for a complex possessing m spins is

$$\mathcal{H} = A \tilde{S}^m \cdot \tilde{I} \quad (1)$$

where A is the proton-electron hyperfine coupling constant, \tilde{S}^m is the total electron spin, and \tilde{I} is the nuclear spin operator. For cases of "spin-only" magnetic moments, the proton nmr contact shift is given by the conventional equation^{9,10}

$$\frac{\Delta H}{H} = - \frac{Ag\beta S(S+1)}{(\gamma/2\pi)(3kT)} \quad (2)$$

where $S = S^m$. This coupling constant, A , is further related to the effective spin density, ρ , in the one-electron molecular orbital approximation conventionally used to describe the bonding in metal complexes, by the generalized relationship^{11,12}

$$\rho = \frac{2SA}{Q} \quad (3)$$

For aromatic π -spin density, ρ is the spin density in the carbon $2p_z$ orbital,¹¹ while for σ -spin density,¹² ρ is the proton spin density. The Q 's for π - and σ -spin density are -63 and $+1420$ MHz, respectively. However, dif-

(1) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

(2) J. Owen and J. H. M. Thornley, *Rep. Progr. Phys.*, **29**, 675 (1966).

(3) B. B. Wayland and R. S. Drago, *J. Amer. Chem. Soc.*, **87**, 2372 (1965).

(4) Z. Luz and R. G. Shulman, *J. Chem. Phys.*, **43**, 3750 (1965).

(5) G. N. La Mar, W. D. Horrocks, Jr., and L. C. Allen, *ibid.*, **41**, 2126 (1964).

(6) D. R. Eaton, *J. Amer. Chem. Soc.*, **87**, 3097 (1965); D. R. Eaton and K. L. Chua, *Can. J. Chem.*, **49**, 56 (1971).

(7) G. N. La Mar and E. O. Sherman, to be submitted for publication.

(8) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(9) R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).

(10) We will assume here, for the sake of simplicity, that we have "spin-only" magnetic moments, such that eq 2 is applicable. For more complicated systems, the appropriate equation in ref 9 must be used. As we will emphasize here only the relationships among A , ρ , and the covalency, our assumptions are not too restrictive.

(11) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

(12) F. Keffer, T. Oguchi, W. O'Sullivan, and J. Yamashita, *Phys. Rev.*, **116**, 1553 (1959).