halides,[4] there is no resonance enhancement to the a_1 bands of boron trichloride and boron tribromide and only very slight enhancement to that of boron triiodide. The average values for $\bar{\alpha}'_{BCl}$ and $\bar{\alpha}'_{BBr}$ are 1.89 and 2.57 Å^2, respectively, and the value for $\bar{\alpha}'_{BI}$ found by extrapolation of the plot of $\bar{\alpha}'_{BI}$ at each exciting frequency against the frequency function of Shorygin,[6] $[1 + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2]^2$, is 3.75 Å^2.

The experimental values of $\bar{\alpha}'_{BX}$ for each halide are compared in Table II with the values calculated on the basis of the Long and Plane equation.[3,5] The agreement is certainly as good and probably considerably better than might have been expected bearing in mind the uncertainties associated with some of the parameters in the Long and Plane equation (in particular that associated with defining the value for Z_{eff}). The experimental values are all somewhat higher than the calculated values, which suggests that $^1/_2n > 1$, *i.e.*, that the BX bond order is somewhat greater than one for boron trichloride, boron tribromide, and boron triiodide. Although not much weight can be put on this suggestion for the reasons given above, it is nevertheless in agreement with the results of nqr and other studies on these halides.[7] Thus the Long and Plane equation appears to be surprisingly good in its prediction of bond polarizability derivatives, not only for group IVb tetrahalides[4] but also for the boron trihalides.[1]

TABLE II

BOND POLARIZABILITY DERIVATIVES α'_{BX} (Å^2) FOR THE BORON TRIHALIDES

Halide	$100p$[a]	r_e,[b] Å	$\bar{\alpha}'_{BX}$ (calcd)[c]	$\bar{\alpha}'_{BX}$ (exptl)
BF_3	39.0	1.295	0.39	...
BCl_3	73.1	1.75	1.72	1.89
BBr_3	80.9	1.87	2.28	2.57
BI_3	90.8	2.10	3.53	3.75

[a] The fractional covalent character, p, is defined as $p = \exp(-^1/_4(\chi_M - \chi_X)^2)$. [b] Values taken from *Chem. Soc., Spec. Publ.*, **No. 11** (1958); **No. 18** (1965). The r value for boron triiodide is taken from M. A. Ring, J. D. H. Donnay, and W. S. Koski, *Inorg. Chem.*, **1,** 109 (1962). [c] Calculated according to the equation given in ref 3 and 5.

Acknowledgment.—P. D. M. thanks the Science Research Council for financial support.

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(7) J. A. S. Smith and D. A. Tong, *J. Chem. Soc. A*, 173 (1971), and references therein.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
GEORGETOWN UNIVERSITY, WASHINGTON, D. C. 20007

Origin of Some Charge-Transfer Spectra. Oxo Compounds of Vanadium, Molybdenum, Tungsten, and Niobium Including Heteropoly Anions and Heteropoly Blues

BY HYUNSOO SO AND MICHAEL T. POPE*[1]

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Since the original assignment of the lowest energy charge-transfer (LCT) bands to $^2B_2 \rightarrow {}^2E(II)$ ($e_\pi^b \rightarrow b_2^n$) for $VOSO_4 \cdot 5H_2O$ by Ballhausen and Gray[2] and for $CrOCl_5^{2-}$ and $MoOCl_5^{2-}$ by Gray and Hare,[3] there has been growing evidence that the LCT band originates in an electron transfer from an orbital on halogen to b_2^n (or b_2^* when it is treated as an antibonding orbital) on the metal ion for some oxyhalides.[4-7] We show here that some charge-transfer (CT) energies for oxo compounds of vanadium, molybdenum, tungsten, and niobium with zero or one d electron can be directly related to an optical electronegativity difference between the metal and ligand involved as found for the hexahalometalates, MX_6^{n-6}.[8,9] We have also applied these electronegativities to a discussion of the spectra of heteropoly blues.

Results and Discussion

Following Jørgensen,[8,9] the energy of the LCT band can be expressed as

$$E = x(X) - x(M) + q[\Delta x(M) + 4D/3] \qquad (1)$$

where x is the electronegativity of ligand X or metal M, q is the number (0 or 1) of d electrons, $\Delta x(M)$ is the difference in electronegativities between d^0 and d^1 states of the metal, and D is the spin-pairing energy parameter.

TABLE I

OPTICAL SPECTRAL DATA FOR SOME d^0 SYSTEMS

Compound	Band max, kK						Ref
$VOCl_4^-$	10.5	16.0	19.1	30.4	34.3	42.0	*a*
$VOCl_5^{2-}$		15.9	21.3	29.4			*b*
VOF_3	25.7	27.4	39.2				*c*
VOF_5^{2-}	30.1	38	40.8	46.3			*c*
$VW_5O_{19}^{3-}$	26.0	37.4					*d*
$V_2W_4O_{19}^{4-}$	25.3	40.0					*d*
$MoOCl_4$	14.4	20.8	37.2				*e*
$Mo_6O_{19}^{2-}$	30.8	39.1	45.0				*f*
$PMo_{12}O_{40}^{3-}$	32.3	47.2					*f*
$P_2Mo_{18}O_{62}^{6-}$	31	47					*g*
$MoO_2(acac)_2$	31.6	38.0	48.1				*h*
$WOBr_5^-$	21.6	26	36.3	43.1			*i*
$WOCl_5^-$	22.9	28.4	35.2	37.0	43.5		*i*
$PW_{12}O_{40}^{3-}$	38	50					*j*
$P_2W_{18}O_{62}^{6-}$	34	39					*j*
$NbOBr_5^{2-}$	21.7	25.3	28.0	33.9			*k*
$NbOCl_5^{2-}$	29.8	36.4	43.5				*k*
$Nb_6O_{19}^{8-}$	43						*l*

[a] D. Nicholls and D. N. Wilkinson, *J. Chem. Soc. A*, 1103 (1970). The band at 10.5 kK was observed only for the solid sample. [b] Reference 6. Solution spectrum. [c] Reference 7. [d] C. M. Flynn, Jr., and M. T. Pope, *Inorg. Chem.*, **10,** 2524 (1971). [e] M. L. Larson and F. W. Moore, *Inorg. Chem.*, **5,** 801 (1966). [f] M. T. Pope and J. J. Altenau, unpublished data. [g] E. Papaconstantinou and M. T. Pope, *Inorg. Chem.*, **9,** 667 (1970). [h] H. Gehrke, Jr., and J. Veal, *Inorg. Chim. Acta*, **3,** 623 (1969). acac = acetylacetonate ion. [i] G. W. A. Fowles and J. L. Frost, *J. Chem. Soc. A*, 1631 (1966). [j] G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, **9,** 662 (1970). [k] S. M. Horner, R. J. H. Clark, B. Crociani, D. B. Copley, W. W. Horner, F. N. Collier, and S. Y. Tyree, Jr., *Inorg. Chem.*, **7,** 1859 (1968). [l] C. M. Flynn, Jr., private communication.

By using the experimental data listed in Tables I and II, we have derived formula 2, which is valid to

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(1) To whom correspondence should be addressed.

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

TABLE II

OPTICAL SPECTRAL DATA FOR SOME d^1 SYSTEMS[a]

Compound	Band max, kK									Ref
$VOCl_4^{2-}$	11.8	13.9	*24.0*	32.4	37.8	41.6	45.5			*b*
$V(OR)Cl_5^{2-}$	13.5	14.5	*26.1*	41						*c*
$VOSO_4 \cdot 5H_2O$	13.1	16.0	*41.7*	50						*d*
VOF_5^{3-}	8.9	10.4	11.4	15.5	19.9	22.7	29.4	39.2	46	*e*
$MoOBr_4^-$	13.8	*20.6*	23.8	25.6						*f*
$MoOBr_5^{2-}$	12.4	13.1	13.8	*20.0*	21.5	24.4	28.0	36.2	44.4	*f*
$MoOCl_4^-$	13.8	22.5	*26.0*							*f*
$MoOCl_5^{2-}$	13.8	23.0	*26.7*	32.1	35.7	41.7				*g*
$Mo(OR)_2Cl_4^-$	11.9	21.8	*27.4*							*h*
$W(OR)_2Br_4^-$	11.9	14.6	*23.5*	26						*h*
$WOBr_4^-$	10	*24.7*								*f*
$WOBr_5^{2-}$	13.3	14.6	21.6	*26*	28.8	31.6	35.8	44.4		*f*
$W(OR)_2Cl_4^-$	10.6	13.7	21.1	25	*30.8*	34.6				*i*
$WOCl_5^{2-}$	13.0	15.4	25.2	*32.8*	37.2	44.4				*j*

[a] The lowest charge-transfer bands are italic. The assignment does not always agree with that given in the reference. R = CH_3. [b] References 5 and 6. [c] R. D. Bereman and C. H. Brubaker, Jr., *Inorg. Chem.*, **8**, 2480 (1969). [d] Reference 1. [e] Reference 6. [f] B. J. Brisdon, D. A. Edwards, D. J. Machin, K. S. Murry, and R. A. Walton, *J. Chem. Soc. A*, 1825 (1967). [g] Reference 2. [h] D. P. Rillema and C. H. Brubaker, Jr., *Inorg. Chem.*, **8**, 1645 (1969). [i] D. P. Rillema, W. J. Reagan, and C. H. Brubaker, Jr., *ibid.*, **8**, 587 (1969). [j] E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Chem. Soc. A*, 4649 (1963).

TABLE III

CALCULATED AND EXPERIMENTAL LOWEST CHARGE-TRANSFER BANDS[a]

		d^0			d^1		
M	X	Calcd	Exptl	Compd	Calcd	Exptl	Compd
V	Cl	10	9.6–10.5	$VOCl_4^-$	25	23.0–24.5	$VOCl_4^{2-}$
						25.9–26.3	$V(OR)Cl_5^{2-}$
V	O	26	26.0	$VW_5O_{19}^{3-}$	41	41.7	$VOSO_4 \cdot 5H_2O$
Mo	Br	7			19	20.6	$MoOBr_4^-$
						20.0	$MoOBr_5^{2-}$
Mo	Cl	15	14.4	$MoOCl_4$	27	26.0–26.7	$MoOCl_4^-$
						28.0	$MoOCl_5^{2-}$
						27.4	$Mo(OR)_2Cl_4^-$
Mo	O	31	30.8	$Mo_6O_{19}^{2-}$	43		
			32.3	$PMo_{12}O_{40}^{3-}$			
			31–32	$MoO_2(acac)_2$			
W	Br	14			24	23.5	$W(OR)_2Br_4^-$
						24.7	$WOBr_4^-$
						25.6	$WOBr_5^{2-}$
W	Cl	22	22.9	$WOCl_5^-$	32	30.8	$W(OR)_2Cl_4^-$
			22.4	WCl_6[b]			
W	O	38	38	$PW_{12}O_{40}^{3-}$	48		
Nb	Br	21	21.7	$NbOBr_5^{2-}$			
			18.9[c]	$NbBr_6^-$			
Nb	Cl	29	29.8	$NbOCl_5^{2-}$			
			29.4[c]	$NbCl_6^-$			
Nb	O	45	43	$Nb_6O_{19}^{8-}$			

[a] See Tables I and II for references. R = alkyl group. [b] Reference 8. [c] Reference *k* of Table I.

within 2 kk. (All quantities are in units of kK.) The

$$E = \left\{\begin{matrix} \mathrm{Br} & 82 \\ \mathrm{Cl} & 90 \\ \mathrm{O} & 106 \end{matrix}\right\} - \left\{\begin{matrix} \mathrm{V} & 80 - 15q \\ \mathrm{Mo} & 75 - 12q \\ \mathrm{W} & 68 - 10q \\ \mathrm{Nb} & 60 \end{matrix}\right\} \qquad (2)$$

value of x(Cl) has been chosen so that it corresponds to that found for MCl_6^{n-} when divided by 30 kK.[8]

In order to calculate the LCT energy for a certain oxo compound, we choose the ligand with the smallest electronegativity Calculated and experimental values are listed in Table III. The good agreement between calculated and experimental data and similar LCT energies for some oxyhalides, alkoxyhalides, and halides show clearly that bromine or chlorine is responsible for the LCT band. For an oxyfluoride, however, the LCT transition must come from the oxygen atom, since the electronegativity of oxygen is smaller than that of fluorine by about 12 kK (see Table IV). While the LCT band for VOF_2, 25.7 kK,[7] agrees with the calculated value, 26 kK, VOF_5^{2-} shows the LCT band at a considerably higher energy, 30.1 kK.[7] Another notable exception is the reported LCT energy for $WOBr_5^-$, 21.6 kK, which is much larger than the predicted value, 14 kK. These differences may be due to a failure of observing weak LCT bands.

The empirical values (eq 2) of the quantity ($\Delta x(M) + 4D/3$) are 10–15 kK for oxo compounds of tungsten, molybdenum, and vanadium, whereas the value for WCl_6^- is only 4 kK.[10] If the latter figure implies that the transferred electron pairs up with the d electron for the oxo compounds but not for WCl_6^-, then $2D = 10 - 4 = 6$ kK and $4D/3 \approx 3.5$ kK for the tungsten compounds. By using the approximation[9] $4D/3 \approx 7B$, this quantity is approximately 6 kK for vanadium compounds. Δx(M) is estimated to be 4–9 kK based on the optical electronegativities given by Jørgensen.[11] Thus the empirical values for the third term in eq 1 are seen to be reasonable.

On dividing the electronegativities given in eq 2 by 30 kK, we place them on the scale of optical elec-

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(10) R. A. Walton, P. C. Crouch, and B. J. Brisdon, *Spectrochim. Acta, Part A*, **24**, 601 (1968). The LCT energies are 22.4 kK for WCl_6 and 26.6 kK for WCl_6^-.

(11) C. K. Jørgensen, "International Review of Halogen Chemistry," V. Gutmann, Ed., Springer-Verlag, New York, N. Y., 1966.

tronegativities (x_{opt}) as defined by Jørgensen.[9] The resultant values are listed and compared with the corresponding values for halo complexes in Table IV.

TABLE IV

OPTICAL ELECTRONEGATIVITIES

	Oxo compds	Halides[a]		Oxo compds	Halides[a]
F		3.9	V(V)	2.7	
O	3.5	3.5 (H_2O)[b]	Mo(VI)	2.5	
Cl	3.0[c]	3.0[c]	W(VI)	2.3	2.2[d]
Br	2.8	2.7	Nb(V)	2.0	2.0[d]

[a] Reference 9. [b] This value was estimated from the lowest charge-transfer band of $Ru(H_2O)_6^{3+}$. [c] x(Cl) was chosen as the reference. See the text. [d] The lowest charge-transfer bands given in Table III were used. Smaller literature values are based on the Laporte-allowed transitions occurring at higher energies.

The derived x_{opt}'s follow the trend generally accepted. We also note that on going from $3d^0$ to $4d^0$ and from $4d^0$ to $5d^0$ in the same oxidation states the x_{opt}'s decrease by 0.7 and 0.2, respectively. A similar shift between 4d and 5d was noted for the halo complexes.[8] On going from Nb(V) to Mo(VI), the x_{opt} increases by 0.5. The x_{opt} of Nb(V) is larger than that of Zr(IV) by 0.2.[10]

Now the question is, "Which molecular orbitals are involved in this charge transfer?" Kon and Sharpless[4,5] assigned this to $b_1^b \rightarrow b_2^*$, but, as a recent molecular orbital calculation for $VOCl_4^{2-}$ shows, about 20 kK below the b_2^* orbital there is a group of close-lying nonbonding and bonding orbitals which are of mainly ligand character. The e_π^b and b_1^b orbitals lie more than 30 kK below this group of orbitals.[6] Thus it is more likely that the LCT band comes from the former group of orbitals for chlorides and bromides.

Another point is that the transition energy for the second lowest charge transfer is always about 6 kK higher than that of the LCT band for metal oxychlorides with no d electron (see Table I). Since this energy is much smaller than the lowest d–d transition energy for the corresponding d^1 system, the second LCT band must be attributed to another orbital on chlorine, probably the b_2^b orbital which is about 6 kK below the nonbonding orbitals b_1^n and a_2^n.[6] Thus the assignment of the CT bands for $MoOCl_5^{2-}$ based on a single bonding orbital[3] is doubtful.

In many iso- and heteropoly anions the metal ion is surrounded octahedrally by six oxygen atoms, one of which is an oxo-type oxygen.[12] The original motivation for the present study was to identify the oxygen responsible for the LCT bands of these compounds. Although the LCT bands have usually been assigned to $e_\pi^b \rightarrow b_2^n$ for oxo compounds on the basis of the molecular orbital treatment, x_{opt} of H_2O is so similar to that of oxygen in eq 2 that the bands may equally well be attributed to the "equatorial" oxygens. When the spectra of $PW_{12}O_{40}^{3-}$ and $P_2W_{18}O_{62}^{6-}$ are compared, the appearance of another band in the spectrum of the latter suggests that the equatorial oxygens are involved in the low-energy charge transfers. However, no such splitting is observed for $P_2Mo_{18}O_{62}^{6-}$, and the origins of the LCT bands of poly anions are still not clear.

The spectra of the reduced "heteropoly blue" complexes show intervalence charge-transfer transitions, *e.g.*, Mo(V) → Mo(VI). We may use the metal x_{opt}'s derived above to predict the position of the LCT bands in such compounds; see eq 3 and Table V.

$$E = 9 + \overset{\text{donor}}{\left\{\begin{matrix} \text{V} & 80 \\ \text{Mo} & 75 \\ \text{W} & 68 \end{matrix}\right\}} - \overset{\text{acceptor}}{\left\{\begin{matrix} \text{V} & 80 \\ \text{Mo} & 75 \\ \text{W} & 68 \end{matrix}\right\}} \qquad (3)$$

TABLE V

CALCULATED AND EXPERIMENTAL LOWEST INTERVALENCE CHARGE-TRANSFER BANDS IN HETEROPOLY BLUES

Donor	Acceptor	Calcd	Obsd	Compd	Ref
V	V	9	9	$MnV^{IV}V_{12}O_{38}^{8-}$	*a*
V	Mo	14	14	$PV^{IV}Mo_{11}O_{40}^{5-}$	*b*
V	W	21	20	$PV^{IV}W_{11}O_{40}^{5-}$	*b*
Mo	Mo	9	9	$H_2P_2Mo_2^{V}Mo_{16}O_{62}^{6-}$	*c*
Mo	W	16	16	$PMo^{V}W_{11}O_{40}^{4-}$	*d*
W	W	9	8.0	$PW^{V}W_{11}O_{40}^{4-}$	*e*
			8.6	$SiW^{V}W_{11}O_{40}^{5-}$	*e*
			8.5	$FeW^{V}W_{11}O_{40}^{6-}$	*e*
			11	$P_2W^{V}W_{17}O_{62}^{7-}$	*e*

[a] C. M. Flynn, Jr., and M. T. Pope, *J. Amer. Chem. Soc.*, **92,** 85 (1970). [b] M. T. Pope, D. P. Smith, J. J. Altenau, and J. Bender, *Proc. Int. Conf. Coord. Chem., 13th,* **1,** 127 (1970). [c] E. Papaconstantinou and M. T. Pope, *Inorg. Chem.*, **9,** 667 (1970). [d] J. J. Altenau, M.S. Thesis, Georgetown University, Washington, D. C., 1970. [e] G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, **9,** 662 (1970).

The constant, 9 kK, is attributed to a many-phonon jump with a large electron–phonon coupling constant following Hush.[13]

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF DETROIT, DETROIT, MICHIGAN 48221

The Hydrolysis of *trans*-Dichloro- and *trans*-Chlorohydroxobis(propylenediamine)chromium(III) Cations in Basic Solution

BY ROSITA R. BARONA AND JOHN A. MCLEAN, JR.*

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An appreciable amount of kinetic and mechanistic data is available for the base hydrolysis of *cis*- and *trans*-dihalo- or -halopseudohalobis(diamine)cobalt(III) cations.[1] On the other hand, very little attention has been focused on the chromium(III) analogs. Some time ago Basolo, *et al.*,[2] reported a brief investigation of the base hydrolysis of *cis*- and *trans*-dichlorobis(ethylenediamine)chromium(III) cations. More recently we have reported a more complete study of the *trans*-dibromo analog.[3] Tobe, *et al.*,[4] have studied *cis*- and *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) cations. The present study was undertaken

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