Correspondence

Charge-Transfer Spectra of Ruthenium(III)- and Osmium(III)-Halogenoammine Complexes

Sir:

In a recent paper, Allen and Stevens[1] reported the synthesis and the electronic spectra of $[Os(NH_3)_5X]X_2$, *cis*-$[Os(NH_3)_4X_2]X$, and *trans*-$[Os(NH_3)_4X_2]X$, with X = Cl, Br, I. These spectra can be compared with those of the corresponding Ru(III) complexes.[1,2] Apart from the ligand field bands, both series of compounds are seen to exhibit a simple regularity in the occurrence of the charge-transfer bands. The pentaammines, as well as the trans tetraammines, are characterized in all cases by *one* intense absorption band; the cis tetraammines are characterized by two intense absorptions. The band positions are given in Table I.

The charge-transfer excitations are interpreted[1] as transitions from a π orbital on the halogen ligands to a metal d orbital. This assignment appears quite reasonable when the corresponding bands are compared in complexes with different halogen ligands; their energy differences agree fairly well with what one expects from the optical electronegativities of Cl, Br, and I.[3,4] It is the purpose of this note to show how the experimental facts of Table I can be understood qualitatively on the basis of some very simple assumptions.

In the first place, it is useful to compare the results on the Ru(III) and Os(III) compounds with the work of Zwickel and Creutz[5] on Ru(II) complexes. The latter authors discuss the charge transfer spectra of the complexes $[Ru(NH_3)_5L]^{2+}$, *cis*-$[Ru(NH_3)_4L_2]^{2+}$, and *trans*-$[Ru(NH_3)_4L_2]^{2+}$, where L is a nitrogen heterocycle (pyridine, pyrazine, isonicotinamide, methyl isonicotinate). Here too, *one* band is observed in the spectra of the pentaammines and the trans tetraammines, while *two* bands are observed for the cis compounds.

In this case, the bands are assigned[5] as "inverted" metal-to-ligand charge-transfer transitions. In analogy with Jorgensen's iridium-pyridine bands,[6] the electron is considered to be transferred from a metal d orbital to a vacant ligand orbital. Zwickel and Creutz rationalized their spectral data in terms of a very simple semiempirical molecular orbital scheme.

For energetic reasons, the NH_3 orbitals are not taken into account; the electron transfer is supposed to take place from a metal d orbital to a vacant π^* orbital on L. By symmetry and overlap arguments, they exclude all but one metal 4d orbital and all but one π^* orbital for each L ligand as being of spectroscopic importance. This reduces the problem to a two-orbital case in the pentaammines and a three-orbital problem in the cis and trans tetraammines. The energy of the four spectral bands which are found in one series of compounds (one given L) can be expressed as a function of only two parameters. The thus predicted relations between the different band positions are borne out quite nicely by experiment.[7]

As far as charge transfer is concerned, the halogenoammines studied by Allen and Stevens[1] represent a very similar series of compounds. For energetic reasons, the metal and the one or two halogen ligands can be thought of as forming a submolecule, within which the relevant transitions take place. The main difference is that the charge transfer is now from the ligand-to-metal type. In principle, it seems reasonable to test the applicability of the simplified theory discussed above, in an attempt to explain the data of Table I.

Accordingly, in Table II, the relevant symmetry-adapted π orbitals were written down and characterized by the appropriate irreducible representation. The halogen ligands are situated on the *z* axes in the pentaammines and the trans tetraammines; in the cis tetraammine compounds ligand 1 is situated on the $-y$ axis, and ligand 2 on the $+x$ axis. The coordinate systems on the ligands are parallel to the central coordinate system. Figure 1 shows the corresponding energy level diagram. For a d^5 system, it is rather easy to see that the only relevant orbitals in C_{4v} and D_{4h} are the ones shown in Table II. For the cis compounds, however, it may not be so obvious why only three MO's were taken into account in Table II. Indeed, from Figure 1, it is obvious that the π interaction between the a_2 metal orbital $(d_{xz} + d_{yz})$ and the $(p_{z1} - p_{z2})$ ligand orbital is certainly not negligible; the same is true for the b_2-π interaction between $(d_{xz} - d_{yz})$ and $(p_{z1} + p_{z2})$. As a first approximation, however, the a_2^* and b_2^* orbitals are seen to be degenerate, and they are lower in energy than the a_1^* orbital. In the strong-field d^5 systems under consideration, this a_1^* orbital is singly occupied. The point is that the electron transfer from the ligand a_2 and b_2 orbitals to a_1^* need not be considered, because the $a_1^* \leftarrow a_2$ transition is symmetry forbidden, while the $a_1^* \leftarrow b_2$ transition has a negligible probability. Indeed, several authors have shown[8-10] that the main contribution to the transition moment comes from the diagonal elements on the ligand atoms. It can easily be verified that the $a_1^* \leftarrow b_2$ transition moment does not contain such elements, as opposed to the $a_1^* \leftarrow a_1$ transition.

Therefore, the number of molecular orbitals can be effectively restricted to those listed in Table II. If the following notation is adapted

$$(np, \mathcal{H}np) = \alpha_X \qquad n = 3, 4, 5$$

$$(n'\mathrm{d}, \mathcal{H}n'\mathrm{d}) = \alpha_M \qquad n' = 4, 5$$

$$(np, \mathcal{H}n'\mathrm{d}) = \beta$$

$$\alpha_M - \alpha_X = \delta$$

the energy expressions of Table II are readily obtained.

The transitions $e^* \leftarrow e$ in C_{4v}, $a_1^* \leftarrow a_1$ and b_1 in C_{2v}, and $e_g^* \leftarrow e_u$ in D_{4h} are electric dipole allowed; the other transition possible for the trans compounds $(e_g^* \leftarrow e_g)$ is parity forbidden. The four spectral bands observed within one given series are assigned to these four transitions. It is predicted that the band in the trans complex should have the same energy as the lowest band of the cis complex. Moreover, it should be possible to calculate its position from the position of the other two bands. In Table III the experimental and the calculated values of the different transition energies

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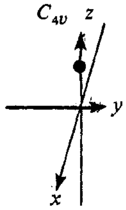
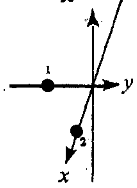
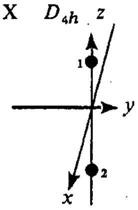
Table I. Charge-Transfer Spectra of $M(NH_3)_5X^{2+}$ and *cis*- and *trans*-$M(NH_3)_4X_2^+$ (M = Ru, Os; X = Cl, Br, I)[a]

		Band maxima		
Metal	Ligand (X)	Pentaammine	Cis tetraammine	Trans tetraammine
Ru(III) ($4d^5$)	Chloride	30.48 (1.93)	32.25 (1.38), 28.40 (1.64)	30.2 (4.75)
	Bromide	25.12 (1.92)	27.02 (1.37), 22.62 (1.67)	25.0 (4.95)
	Iodide	18.50 (2.05)		
Os(III) ($5d^5$)	Chloride	37.45 (2.01)	39.22 (2.03), 35.20 (1.68)	36.9 (4.81)
	Bromide	31.85 (1.87)	33.56 (1.60), 29.07 (1.62)	31.5 (4.69)
	Iodide	24.57 (1.97)	26.46 (1.68), 21.28 (2.07)	23.9 (4.92)

[a] The positions of the band maxima are given in kK. Molar extinction coefficients are added in parentheses (except for a common factor of 10^3).

Table II. Approximate Molecular Orbitals and Energy Expressions for $M(NH_3)_5X^{2+}$ and *cis*- and *trans*-$M(NH_3)_4X_2^+$ (M = Ru, Os; X = Cl, Br, I)[a]

Complex	Coordinate system	MO	Irred repres	Energy	Transition energy
$[M(NH_3)_5X]X_2$	C_{4v} 	$c_1d_{xz} + c_2p_x$ $c_2d_{xz} - c_1p_x$	e e*	$(1/2)[\alpha_X + \alpha_M - (\delta^2 + 4\beta^2)^{1/2}]$ $(1/2)[\alpha_X + \alpha_M + (\delta^2 + 4\beta^2)^{1/2}]$	$(\delta^2 + 4\beta^2)^{1/2}$
cis-$[M(NH_3)_4X_2]X$	C_{2v} 	$c'_1d_{xy} + c'_2(1/2)^{1/2}(p_{y_2} - p_{x_1})$ $(1/2)^{1/2}(p_{y_2} + p_{x_1})$ $c'_2d_{xy} - c'_1(1/2)^{1/2}(p_{y_2} - p_{x_1})$	a_1 b_1 a_1*	$(1/2)[\alpha_X + \alpha_M - (\delta^2 + 8\beta^2)^{1/2}]$ α_X $(1/2)[\alpha_X + \alpha_M + (\delta^2 + 8\beta^2)^{1/2}]$	$(1/2)[\delta + (\delta^2 + 8\beta^2)^{1/2}]$ $(\delta^2 + 8\beta^2)^{1/2}$
trans-$[M(NH_3)_4X_2]X$	D_{4h} 	$c'_1d_{xz} + c'_2(1/2)^{1/2}(p_{x_1} - p_{x_2})$ $(1/2)^{1/2}(p_{x_1} + p_{x_2})$ $c'_2d_{xz} - c'_1(1/2)^{1/2}(p_{x_1} - p_{x_2})$	e_g e_u e_g*	$(1/2)[\alpha_X + \alpha_M - (\delta^2 + 8\beta^2)^{1/2}]$ α_X $(1/2)[\alpha_X + \alpha_M + (\delta^2 + 8\beta^2)^{1/2}]$	$(1/2)[\delta + (\delta^2 + 8\beta^2)^{1/2}]$

[a] Overlap integrals were set equal to zero. X is designated by a small solid circle. Only one member of each degenerate orbital set is written down. The antibonding orbitals are labeled by an asterisk.

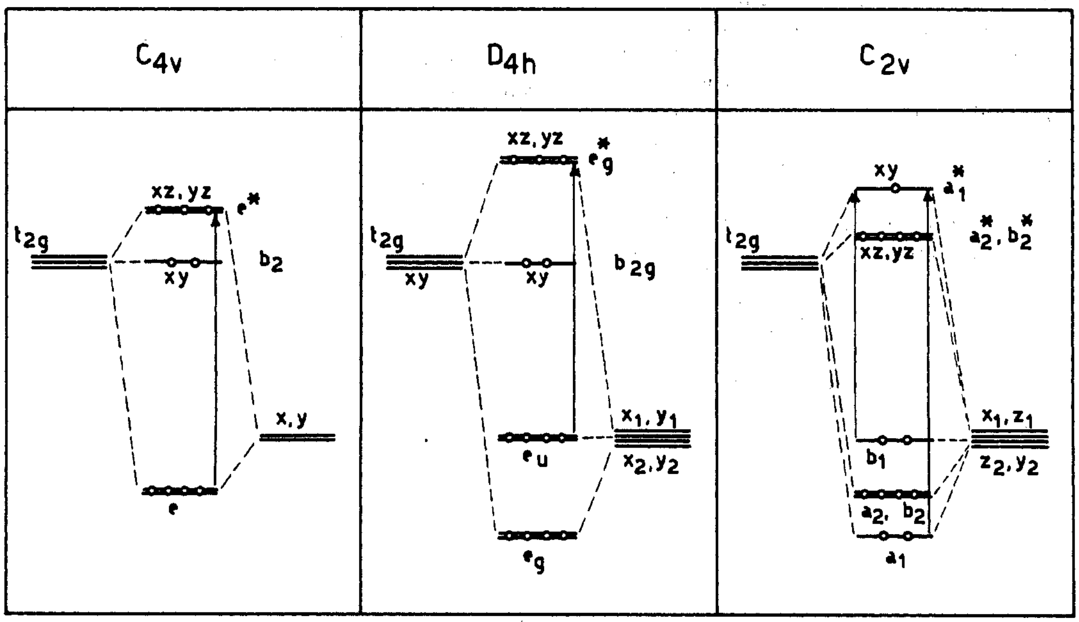


Figure 1. Approximate energy level scheme for the orbitals resulting from π interactions between the metal and the X ligands. The transitions to or from σ orbitals are too high in energy to be of importance in the present context. The shorthand notation x_1, y_2, xz, . . . stands for p_{x_1}, p_{y_2}, d_{xz}, etc.

Table III. Comparison between Calculated and Experimental Charge-Transfer Transition Energies (kK)[a]

					Exptl energy	
Metal	Ligand	δ	β	Calcd energy	*Cis* (1st band)	Trans
Ru(III)	Cl	28.6	5.3	30.42	28.40	30.2
	Br	23.1	5.0	25.04	22.62	25.0
Os(III)	Cl	35.6	5.8	37.41	35.20	36.9
	Br	30.0	5.3	31.80	29.07	31.5
	I	22.5	4.9	24.49	21.28	23.9

[a] Using the expressions of Table II, the δ and β values are obtained from the experimental data on the C_{4v} complexes and on the second band of the C_{2v} complexes.

are compared. The agreement is quite satisfactory for the trans tetraammines. The lowest band of the cis compounds is systematically overestimated by 2-3 kK; the deviation tends to increase with increasing atomic number of the halogen ligand. The reason for this small discrepancy is probably to be found in the energetic position of the b_1 nonbonding orbital. While it is a pure ligand orbital, its energy was put equal to α_X in Table II; this implies that ligand-ligand interactions are neglected. Certainly the interaction between two halogen ligands is more important in the cis than in the trans compounds, where they can be ignored.[4] From the overlap between p_{x1} and p_{y2}, we can get an idea of the order of magnitude of $(p_{x1}, \mathcal{H}p_{y2})$ and hence of the ligand-ligand interactions. Using standard sources for SCF orbitals,[11] the relevant matrix elements were determined for Cl^-, Br^-, and N. The latter atom was included in order to evaluate the relative magnitude of this effect for the heterocycle compounds of Zwickel and Creutz,[5] who apparently obtained satisfactory results without considering ligand-ligand interactions.

In the case of N-N interactions, the results indicate that the overlap integral is practically zero; the b_1 energy level is virtually unaffected by the ligand-ligand interaction. For the Cl-Cl and Br-Br interactions, the b_1 level is found to be destabilized to the amount of about 2-4 kK, a value also proposed by Jorgensen for other complexes.[12,13] Moreover, the destabilization is larger for the bromide than for the chloride complexes. Qualitatively all these results are in complete agreement with the experimental data. The fact that both pentaammine and trans tetraammine complexes exhibit a band at nearly the same energy (Table I) can easily be understood from the previous considerations. In the pentaammines, the transition energy is given by $(\delta^2 + 4\beta^2)^{1/2}$ and in the trans tetraammines by $(1/2)[\delta + (\delta^2 + 8\beta^2)^{1/2}]$. If, as suggested by Table III, $\beta \ll \delta$, both energies converge to the same value, given by $\delta + 2\beta^2/\delta$.

From Table I, it follows that the band in the trans tetraammines is systematically more intense than any of the other three. We adopt again the assumption[8-10] that the main contribution to the transition moment integrals comes from the diagonal elements on the ligand atoms. Then the expressions of Table II can be used to calculate the relevant oscillator strengths. Qualitatively, one finds the correct order of the intensities: trans tetraammine > pentaammine > both cis tetraammine bands. Using first-order perturbation theory, one predicts theoretically the relative magnitude of the four oscillator strengths as 4:2:1:1, while the experimental intensity ratios are roughly 5:2:1.7:1.6

Summarizing, the following points should be retained.

(1) The simplified molecular orbital theory, developed by Zwickel and Creutz in order to account for metal-to-ligand charge-transfer transitions, is also capable of application in the study of the more common ligand-to-metal transitions. It allows for a rather gratifying prediction of both band positions and band intensities.

(2) The δ values of Table III are not as such transition energies but are obtained from a combination of several CT-band positions. They provide information on the energy differences between the one-electron basis orbitals—*i.e.*, the halogen *n*p and the metal *n*′d orbitals. The difference between the relevant chlorine and bromine one-electron energies has apparently about the same value in the Ru(III) and in the Os(III) complexes (5.5 and 5.6, respectively). This suggests that to a given basis orbital a very nearly constant energy can be associated, irrespective of the compound under consideration.

(3) Within the framework of first-order perturbation theory, the ratio β/δ can be taken as a rough measure for the covalency of the metal-halogen bond. From Table III, it follows that the Ru-X bonds are slightly more covalent than the Os-X bonds; of course, the covalency also increases from Cl to Br to I.

(4) The one-electron description of charge-transfer transitions is the basis for the concept of optical electronegativity. This concept has already been proven to be very successful in predicting the position of the lowest CT band. The present approach clearly illustrates the adequacy of the one-electron picture in going beyond the description of only the *lowest* CT band. In some cases, it also correctly predicts the number and relative position of *different* CT bands, both of the regular and of the inverted type.

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Registry No. $[Ru(NH_3)_5Cl]^{2+}$, 21560-19-0; $[Ru(NH_3)_5Br]^{2+}$, 21388-15-8; $[Ru(NH_3)_5I]^{2+}$, 25483-95-8; $[Os(NH_3)_5Cl]^{2+}$, 43031-57-8; $[Os(NH_3)_5Br]^{2+}$, 43031-58-9; $[Os(NH_3)_5I]^{2+}$, 43031-59-0; *cis*-$[Ru(NH_3)_4Cl_2]^+$, 25604-36-8; *cis*-$[Ru(NH_3)_4Br_2]^+$, 42281-09-4; *cis*-$[Os(NH_3)_4Cl_2]^+$, 43111-97-3; *cis*-$[Os(NH_3)_4Br_2]^+$, 43065-21-0; *cis*-$[Os(NH_3)_4I_2]^+$, 43111-98-4; *trans*-$[Ru(NH_3)_4Cl_2]^+$, 29871-95-2; *trans*-$[Ru(NH_3)_4Br_2]^+$, 43111-99-5; *trans*-$[Os(NH_3)_4Cl_2]^+$, 43112-00-1; *trans*-$[Os(NH_3)_4Br_2]^+$, 43112-01-2; *trans*-$[Os(NH_3)_4I_2]^+$, 43112-02-3.

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