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Spectroscopic Study of the $Tc_2Cl_8^{3-}$ Ion

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Abstract: The visible spectrum of the $Tc_2Cl_8^{3-}$ ion in aqueous hydrochloric acid has been recorded. A band between 6000 and 8000 cm^{-1} has been recorded also at 5 K using a pressed CsI pellet. The latter band shows vibrational structure, with an origin at 5900 cm^{-1}, and its intensity is insensitive to temperature. A scattered wave Xα-SCF calculation previously reported for the ground state of the $Tc_2Cl_8^{3-}$ ion has been extended to afford predictions of the electronic spectrum. The band originating at 5900 cm^{-1} is assigned as the $\delta \rightarrow \delta^*$ band, for which the calculated energy is 6050 cm^{-1}. Assignments of other transitions are suggested and discussed. All observed bands can be convincingly assigned with good numerical agreement. For the first time the position of a $\delta \rightarrow \delta^*$ transition is accurately predicted; the reason for this is discussed. The generally satisfactory agreement between the observed and calculated spectra validates the description of bonding.

The $Tc_2Cl_8^{3-}$ ion was prepared[3] prior to the recognition[4] of the existence of quadruple bonds, and its similarity to the $Re_2Cl_8^{2-}$ ion immediately led to crystallographic investigation[5,6] of its structure. The structure, by its analogy to that of $Re_2Cl_8^{2-}$ [6] (as well as that of $Mo_2Cl_8^{4-}$ [7]), leads naturally to its formulation as a species with eight electrons forming a Tc–Tc quadruple bond plus one more electron occupying a nonbonding or weakly antibonding orbital. A study of its EPR spectrum[8] suggested that this "excess" electron occupies the δ^* orbital, thus, in effect, reducing the Tc–Tc bond order to 3.5. This $\sigma^2\pi^4\delta^2\delta^*$ configuration has been suggested by a CNDO calculation,[9] by a Fenske–Hall calculation,[10] and, more significantly, is supported by a SCF-Xα-SW calculation.[11]

In order to make a stringent test of the bonding description produced by the SCF-Xα-SW calculation, the results have been used as the basis for predicting the electronic spectrum of $Tc_2Cl_8^{3-}$ and the spectrum has been measured experimentally. In this report the calculated and measured spectra are reported and compared.

Experimental Section

Spectroscopic Measurements. Salts of the $Tc_2Cl_8^{3-}$ ion were prepared according to literature procedures.[3,5,6] Solutions were prepared in thoroughly deoxygenated aqueous HCl to avoid contamination by $TcCl_6^{2-}$. The spectrum of that species, which is the only observed[5] oxidation product of $Tc_2Cl_8^{3-}$, was recorded by us, found to be in good agreement with that in the literature,[12] and we were thus able to be

Table I. Calculated Energies for all Electronic Transitions in the Visible, Near IR, and Near UV Spectrum of $Tc_2Cl_8{}^{3-}$

	Transition		Calculated energy,[a] $cm^{-1} \times 10^3$						
			Allowed			Forbidden			
	Orbitals	Excited state	(a)	(b)	(c)	(a)	(b)	(c)	Description[b,c]
1	$2b_{2g}\downarrow \rightarrow 2b_{1u}\downarrow$	$^2B_{2g}$	6.1	6.0	5.8				$\delta \rightarrow \delta^*$
2	$2b_{1u}\uparrow \rightarrow 5e_g\uparrow$	^2E_g		15.8	16.1				$\delta^* \rightarrow \pi^*$
3	$5e_u\downarrow \rightarrow 2b_{1u}\downarrow$	^2E_u				16.3	15.3	14.7	$\pi \rightarrow \delta^*$
4	$2b_{1u}\uparrow \rightarrow 4b_{1g}\uparrow$	$^2B_{1g}$					17.7	17.6	$\delta^* \rightarrow d_{x^2-y^2}$
5	$1a_{1u}\downarrow \rightarrow 2b_{1u}\downarrow$	$^2A_{1u}$					18.5	17.4	LMCT
6	$3b_{2u}\downarrow \rightarrow 2b_{1u}\downarrow$	$^2B_{2u}$					19.4	18.4	LMCT
7	$2b_{1u}\uparrow \rightarrow 4a_{2u}\uparrow$	$^2A_{2u}$					20.2	20.3	$\delta^* \rightarrow \sigma^*$
8	$1a_{2g}\downarrow \rightarrow 2b_{1u}\downarrow$	$^2A_{2g}$					20.1	19.0	LMCT
9	$2b_{2g}\downarrow \rightarrow 5e_g\downarrow$	^2E_u					21.9	21.9	$\delta \rightarrow \pi^*$
10	$2b_{1u}\uparrow \rightarrow 4b_{2u}\uparrow$	$^2B_{2u}$					23.1	21.5	$\delta^* \rightarrow$ M-Cl*
11	$2b_{2g}\downarrow \rightarrow 4b_{1g}\downarrow$	$^2B_{2u}$				23.2	23.2	23.4	$\delta \rightarrow d_{x^2-y^2}$
12	$2b_{2g}\downarrow \rightarrow 4a_{2u}\downarrow$	$^2A_{1g}$					26.0	26.1	$\delta \rightarrow \sigma^*$
13	$2b_{2g}\downarrow \rightarrow 4b_{2u}\downarrow$	$^2B_{1g}$					27.1	27.3	$\delta \rightarrow$ M-Cl*
14	$4e_g\downarrow \rightarrow 2b_{1u}\downarrow$	^2E_g	28.3	21.2	20.2				LMCT
15	$3e_g\downarrow \rightarrow 2b_{1u}\downarrow$	^2E_g	29.1	22.3	21.2				LMCT
16	$5e_u\downarrow \rightarrow 5e_g\downarrow$	$^2A_{1g}$, $^2A_{2g}$, $^2B_{1g}$					31.2	30.7	$\pi \rightarrow \pi^*$
17	$5e_u\downarrow \rightarrow 5e_g\downarrow$	$^2B_{2g}$		31.2	30.7				$\pi \rightarrow \pi^*$
18	$5e_u\downarrow \rightarrow 4b_{1g}\downarrow$	^2E_g	32.5	32.4	32.3				$\pi \rightarrow d_{x^2-y^2}$
19	$1a_{1u}\downarrow \rightarrow 5e_g\downarrow$	^2E_g		34.5	33.6				LMCT
20	$5e_u\downarrow \rightarrow 4a_{2u}\downarrow$	^2E_u					35.2	34.9	$\pi \rightarrow \sigma^*$
21	$3b_{2u}\downarrow \rightarrow 5e_g\downarrow$	^2E_g		35.3	34.5				LMCT
22	$1a_{1u}\downarrow \rightarrow 4b_{1g}\downarrow$	$^2A_{1g}$					35.7	35.1	LMCT
23	$5e_u\downarrow \rightarrow 4b_{2u}\downarrow$	^2E_u					36.3	36.2	$\pi \rightarrow d_{x^2-y^2}$
24	$3b_{2u}\downarrow \rightarrow 4b_{1g}\downarrow$	$^2B_{2g}$		36.5	36.0				LMCT
25	$1a_{1u}\downarrow \rightarrow 4a_{2u}\downarrow$	$^2B_{2u}$					38.5	37.7	LMCT
26	$3b_{2u}\downarrow \rightarrow 4a_{2u}\downarrow$	$^2A_{1u}$					39.4	38.6	LMCT
27	$1a_{1u}\downarrow \rightarrow 4b_{2u}\downarrow$	$^2A_{2u}$					39.6	39.0	LMCT/LL
28	$3b_{2u}\downarrow \rightarrow 4b_{2u}\downarrow$	$^2B_{1u}$					40.5	39.9	LMCT/LL

[a] Columns (a) give results by the transition state method; columns (b) give orbital differences using spin-unrestricted calculations; columns (c) give orbital differences using spin-restricted calculations. [b] LMCT means ligand to metal charge transfer. [c] LL means between orbitals both of mainly ligand character.

certain that no significant feature of the $Tc_2Cl_8{}^{3-}$ spectrum shown in Figure 1 is attributable to $TcCl_6{}^{2-}$.

The solid-state spectrum was obtained by grinding the $K_3Te_2Cl_8 \cdot 2H_2O$ together with CsI and pressing the mixture to form a pellet. The low-temperature spectrum was obtained using a sample mounted in an Andonian Associates liquid helium cryostat and the spectrum recorded with pumping on liquid helium. The temperature was recorded with a germanium resistance thermometer against the sample mount.

Calculations. All transitions that could occur below 40×10^3 cm^{-1} were examined. They are listed in Table I, where each one is described by the orbitals involved, the symbol for the upper state, a brief characterization of the transition (e.g., $\delta \rightarrow \delta^*$, $\delta^* \rightarrow \pi^*$, etc.) and several calculated energy values. The latter are listed in separate sections for orbitally allowed and orbitally forbidden transitions (using electric dipole selection rules).

The energies were calculated in three ways. For six of the transitions, of various types, the transition state approximation, which allows for relaxation effects, was employed. For these six as well as all of the other transitions the transition energies were also estimated simply as the orbital energy differences using the results of both the spin-unrestricted and the spin-restricted calculations.[11] These three methods, denoted (a), (b), and (c), respectively, in Table I give results which follow a simple pattern with respect to the degree of agreement among them.

The orbital energy differences from the spin-unrestricted and the spin-restricted orbitals always agree closely, seldom differing by more than 1.0×10^3 cm^{-1}. Moreover, these simple estimates of the transition energies agree very well with those calculated by the transition state method for all transitions *except charge transfer (CT) transitions*, where (see, for example, numbers 14 and 15) the orbital energy differences are too low by about 7×10^3 cm^{-1}. Evidently, orbital relaxation plays a more important part in the charge transfer transitions.

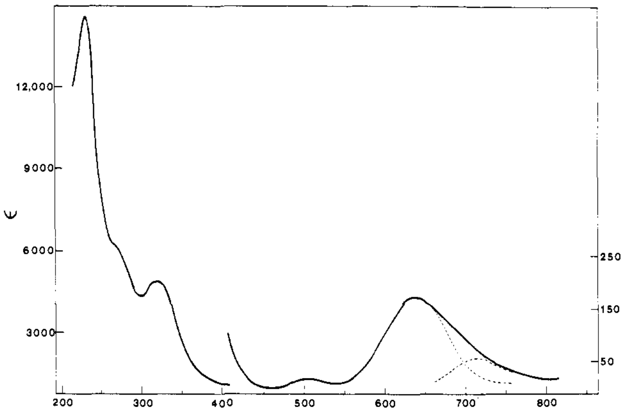

Figure 1. The absorption spectrum of the $Tc_2Cl_8{}^{3-}$ ion in solution.

This is certainly reasonable, since the shifting of charge from one atomic center to another should cause far greater relaxation effects than occur for transitions in which the centroids of electron density for the orbitals involved are more nearly coincident. It is, of course, this same physical effect that explains why the strengths of the allowed transitions of the latter type (e.g., numbers 1 and 2) are relatively small, as indicated quantitatively in Table II.

The transition state procedure was not routinely used for all transitions in order to save computing costs, but the comparisons just discussed suggest that routine use of the transition state procedure is not really necessary. For non-charge-transfer transitions the orbital energy differences may be taken as reliable predictions of the transition energies, while for CT transitions, the predicted energy should

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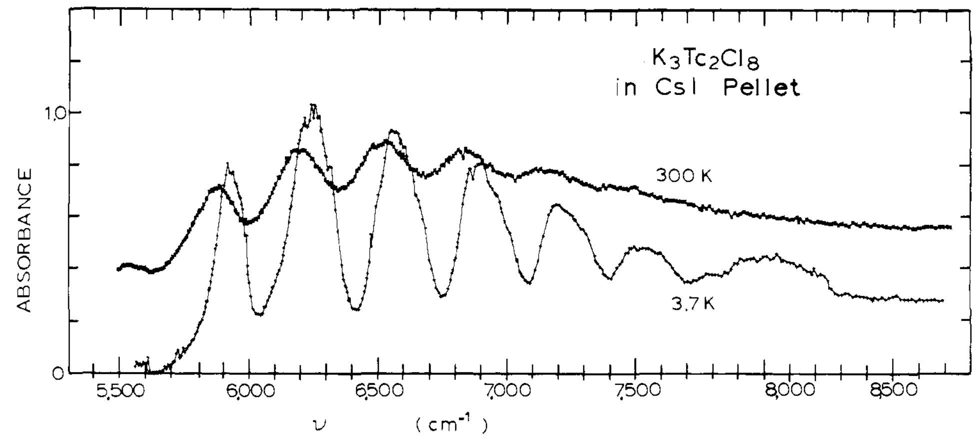

Figure 2. The near infrared band of the $Tc_2Cl_8^{3-}$ ion recorded at room temperature and at ca. 5 K.

Table II. Observed Spectrum and Possible Assignments

Obsd band			Possible assignment(s)		
ν_{max}[a]	ϵ_{max}	$f(\times 10^3)$	Calcd energy[a]	No.[b]	Type
5.9[c]	630	5.4	6.0	**1**	$\delta \rightarrow \delta^*$
13.6	35		16.3	3	$\pi \rightarrow \delta^*$
15.7	172	2.0	15.8	**2**	$\delta^* \rightarrow \pi^*$
20.0	10		17.7	4	$\delta^* \rightarrow d_{x^2-y^2}$
			20.2	7	$\delta^* \rightarrow \sigma^*$
			21.3	9	$\delta \rightarrow \pi^*$
			23	11	$\delta \rightarrow d_{x^2-y^2}$
31.4	3900		28.3	**14**	LMCT
			29.1	**15**	LMCT
			31.2	**17**	$\pi \rightarrow \pi^*$
			32.5	**18**	$\pi \rightarrow d_{x^2-y^2}$
37.2	5600		~42[d]	**19**	LMCT
43.5	14000		~41[d]	**21**	LMCT
			~44[d]	**24**	LMCT

[a] Energies in cm^{-1} × 10^3; ϵ in L mol^{-1} cm^{-1}; f is the oscillator strength (dimensionless). [b] Bold numbers indicate electric dipole allowed transitions. [c] Energy of first vibrational component. [d] Estimated; see text.

be given reasonably reliably by adding 7 × 10^3 cm^{-1} to the orbital energy difference. This is how the predicted values listed for transitions 19, 21, and 24 in Table 11 were obtained.

Discussion

General. It is immediately obvious by comparing Figures 1 and 2 with Table I that the observed and calculated spectra are very similar. In the low energy region allowed bands are predicted at ca. 6 and 16 × 10^3 cm^{-1} and these are observed. No strong bands are then predicted until we approach the ultraviolet, and none are observed until, beginning at 31.4 × 10^3 cm^{-1} a succession of increasingly intense absorptions progresses into the UV. All of this absorption in the 31.4-43.5 × 10^3 cm^{-1} region can readily be assigned to calculated allowed transitions. We shall now discuss explicitly the assignment of each observed maximum.

The Near IR Band. Figure 2 shows the band in the near IR both at room temperature and at ca. 5 K. Vibrational structure, evident even at room temperature, is very well resolved at 5 K. The integrated intensities at the two temperatures were measured by the cut-and-weigh procedure and found to be equal within the estimated error (±10%). Since the calculation clearly indicates that the lowest-energy band in the spectrum should be caused by the $\delta \rightarrow \delta^*$ ($^2B_{2g} \leftarrow {}^2B_{1u}$) transition, and furthermore the predicted energy is *very* close to that of the observed near IR band, it seems clear that this band can be assigned to the $\delta \rightarrow \delta^*$ transition. Since this is an orbitally allowed transition the observed temperature independence of the intensity is consistent with the assignment. Moreover, the observation of a vibrational progression in one or more totally symmetric vibrations, especially the one corresponding mainly to metal-metal stretching, is also expected both from general theory[13] and by comparison with experimental data on the $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$ systems.[14-18]

In the case of $Re_2Cl_8^{2-}$ the vibrational structure[14] appears to consist of two overlapping progressions, one in ν_2, $2\nu_2$, $3\nu_2$, etc., and the other ν_3, $\nu_3 + \nu_2$, $\nu_3 + 2\nu_2$, etc., where $\nu_2 \approx 248$ cm^{-1} and corresponds to Re-Re stretching in the excited electronic state (ground-state value:[19] 274 cm^{-1}) and $\nu_3 \approx 115$ cm^{-1} corresponds to the totally symmetric Re-Re-Cl bending mode (ground-state value:[19] 115 cm^{-1}). There is, however, one irregularity in these spacings that has no obvious explanation. It is known[6] that the unit cell contains two equivalent $Re_2Cl_8^{2-}$ ions, well separated from each other by the bulky cations, $N(C_4H_9)_4^+$, so that Davydov effects are unlikely. In $Mo_2Cl_8^{4-}$, which has been examined[17] in the form of both hydrated and anhydrous potassium salts, there is only one resolved progression, with spacings averaging 335 cm^{-1}. This may be compared with the ground-state frequency of ν_{Mo-Mo},[20] which is about 348 cm^{-1}. Again, there are certain irregularities in the spacings (the first few being 30-40 cm^{-1} too high) that have not been explained. Thus, in both $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$ the vibrational structure is not explainable solely in terms of a progression in ν_{M-M}, though this is the most evident feature.

For $Tc_2Cl_8^{3-}$ the vibrational pattern is also somewhat more complex than just a simple progression in one frequency. Each component appears to be a doublet or triplet of close, unresolved components. The average of the approximate spacings is 320 ± 5 cm^{-1}, which is certainly a reasonable frequency for ν_{Tc-Tc} in the excited state (the ground-state value is not known). The unit cell[5,6] of $K_3Tc_2Cl_8 \cdot 2H_2O$ contains three equivalent $Tc_2Cl_8^{3-}$ ions related by a threefold screw axis and packed rather closely together. Thus, the incipient multiple character of each vibrational component might be the result of Davydov splitting. Also, it has been noted in a recent careful study[6] that the crystal structure allows for three water molecules (i.e., for a formula of $K_3Tc_2Cl_8 \cdot 3H_2O$) and that the commonly observed analytical composition, $K_3Tc_2Cl_8 \cdot 2H_2O$, results from partial occupancy of one site. Thus, nonequivalence of the $Tc_2Cl_8^{3-}$ ions might also cause splitting of the peaks in the vibrational progression.

In summary, the experimental data and the calculation provide very strong evidence that the band in the near IR, with a vibrational progression beginning at 5900 cm^{-1} ($\Delta\nu \approx 320$ cm^{-1}), is the $^2B_{2g} \leftarrow {}^2B_{1u}$ $\delta \rightarrow \delta^*$ transition.

The extraordinarily good agreement between the calculated and observed energies of the $\delta \rightarrow \delta^*$ transition in this case is in contrast to the poor agreement in the $Re_2Cl_8^{2-}$ [15] and $Mo_2Cl_8^{4-}$ [18] ions and requires comment. It should be noted that for $Re_2Cl_8^{2-}$ the other transitions were also calculated appreciably lower than observed, but in $Mo_2Cl_8^{4-}$ the others were predicted rather accurately by the Xα calculation and only for the $\delta \rightarrow \delta^*$ transition was the discrepancy serious. For $Re_2Cl_8^{2-}$ the $\delta \rightarrow \delta^*$ transition was calculated[15] to occur at 4.5×10^3 cm^{-1}, but observed[14,15] at 14.18×10^3 cm^{-1}. For $Mo_2Cl_8^{4-}$ the calculated value[18] was 13.7×10^3 cm^{-1}, while the observed value is 18.08×10^3 cm^{-1}.

For $Re_2Cl_8^{2-}$ the calculation was based solely on spin-restricted configurations and this gives the weighted average of the energies for excitation to the singlet (S) and triplet (T) excited states, that is, $(S + 3T)/4$, whereas the observed energy is that for the singlet excitation (S) only. Since spin-orbit coupling for Re is large, one might expect the triplet state to lie well below the singlet and this could account for at least a considerable part of the discrepancy. In the case of $Mo_2Cl_8^{4-}$ a spin-restricted calculation was used to get the $(S + 3T)/4$ value and a spin-unrestricted calculation was used to get the value of T; from the two, the value of S (13.7×10^3 cm^{-1}) was obtained. While the agreement here is better there is still a sizable discrepancy. It has been pointed out by Bagus and Bennett[21] that there are inherent errors in all such calculations and that "the quantitative value of the $(S - T)$ splitting should be viewed with caution" when so calculated.

For $Tc_2Cl_8^{3-}$ the $\delta \rightarrow \delta^*$ transition must, by its nature, conserve spin multiplicity and thus a straightforward calculation of the doublet to doublet excitation should be free of the difficulties inherent in the rhenium and molybdenum cases. Our results bear this out.

The Band at 15.7×10^3 cm^{-1}. This band is noticeably unsymmetrical and, as Figure 1 shows, can be deconvoluted to show a second, very weak band at 13.6×10^3 cm^{-1} ($\epsilon_{max} \simeq 35$). The main peak is assigned to the $\delta^* \rightarrow \pi^*$ transition (no. 2, Table I) which is the only allowed transition expected anywhere near this energy. This transition, of course, has no counterpart in the spectra of $Mo_2Cl_8^{4-}$ and $Re_2Cl_8^{2-}$, since these have no δ^* electrons in their ground states.

The weak band at about 13.6×10^3 cm^{-1}, *if it is real*, can only be assigned to the $\pi \rightarrow \delta^*$ transition (no. 3, Table I). The corresponding $\pi \rightarrow \delta^*$ transitions have been assigned in $Mo_2Cl_8^{4-}$ at 23.8×10^3 cm^{-1} [18] and in $Re_2Cl_8^{2-}$ at 23.6×10^3 cm^{-1}.[16] It is not unreasonable for it to have a lower energy here, since the δ-δ^* splitting here is much lower than in the other two cases.

The Weak Band at 20.0×10^3 cm^{-1}. This is obviously a forbidden band, and there are four transitions that seem plausible assignments, as listed in Table II. We cannot rule out no. 4 (Table I), although it is calculated to be at too low an energy and might well be obscured on the high-energy side of the 15.8×10^3 cm^{-1} band. Transitions 5, 6, and 8 are not considered because, as explained earlier, these are CT transitions and thus expected to occur at much higher energies than those suggested by orbital energy differences. These three bands would probably be obscured under the lower edge of the rising near UV absorption. The same is probably true of transition no. 10, which has partial CT character, though we have not designated it as an unqualified CT transition. Besides transition 4, transitions 7, 9, and 11 must be considered possible assignments. We see no basis for selecting any one (or two) of them. The $\delta^* \rightarrow \sigma^*$ transition is, again, one with no previous counterpart, while the $\delta \rightarrow \pi^*$ assignment has been considered for a weak transition at 17.7×10^3 cm^{-1} in $Re_2Cl_8^{2-}$,[16] but was not discussed for $Mo_2Cl_8^{4-}$.[18] The $\delta \rightarrow d_{x^2-y^2}$ assignment was suggested for a band at 23.8×10^3 cm^{-1} in $Mo_2Cl_8^{4-}$ [18] and for a weak band at 20.9×10^3 cm^{-1} in $Re_2Cl_8^{2-}$ [16]

The Band at 31.4×10^3 cm^{-1}. There is no problem finding a way to assign this band. As Table II shows, there are four allowed transitions in the proper energy range. There are two, close Cl(π) $\rightarrow \delta^*$ transitions predicted at 28.3 and 29.1×10^3 cm^{-1} as well as a $\pi \rightarrow \pi^*$ transition calculated at 31.2×10^3 cm^{-1} and a $\pi \rightarrow d_{x^2-y^2}$ transition calculated at 32.5×10^3 cm^{-1}. The situation is very similar to those previously encountered in the $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$ ions. It is not possible to say with certainty in this case which of these possible assignments is appropriate for the particular resolved maximum shown in Figure 1. A comparable band in $Re_2Cl_8^{2-}$ has been assigned[16] to an $e_g \rightarrow b_{1u}$ transition. In this case there are two such transitions (nos. 14 and 15, Table I) very close together according to the calculation.

Ultraviolet Absorptions. There is a shoulder at 37.2×10^3 cm^{-1} and a maximum at about 43.5×10^3 cm^{-1}, the exact position of the latter being slightly doubtful, since the background is becoming very high in this part of the spectrum. Several charge-transfer bands are expected in this energy range and it is possible that no. 17 ($\pi \rightarrow \pi^*$) or no. 18 ($\pi \rightarrow d_{x^2-y^2}$) might occur at slightly higher than their calculated energies. Thus, in the absence of polarization information, which is not likely to become available because of the unfavorable orientations of the molecules in the crystal, we shall not attempt to be precise about the assignment of the near UV portion of the spectrum. Suffice it to say that nothing in the observed spectrum in this region is inconsistent with the calculated electronic structure or the predicted spectrum for the $Tc_2Cl_8^{3-}$ ion.

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