(This change is very rapid for the blue isomer, but relatively slow for the purple isomer.) The weight gained in the formation of the yellow complex, which is identical with the weight loss when the yellow complex is dehydrated to re-form the original blue or purple complexes, corresponds to three molecules of water per Ni(II) ion (Calcd: 14.11. Found: 13.9). This yellow complex can be tentatively formulated as (I)$NiCl_4(H_2O)_2 \cdot H_2O$. It is significant that in the vibrational spectrum of this complex, the water absorptions are more intense and much broader than those observed in the complex formed in ethanol solution, (I)$NiCl_4(H_2O)_2$, which contains two molecules of coordinated water only.

**Characterization of the Complexes.** The complexes prepared were characterized by analysis, visible and infrared spectra (30,000–250 $cm^{-1}$), and magnetic susceptibility measurements. For details, see ref 15.

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# Electronic Energy Levels in Hexahalotellurate(IV) Complexes

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**Abstract:** The electronic spectra of the octahedral $TeCl_6{}^{2-}$ and $TeBr_6{}^{2-}$ complexes are reported and assigned. The s → p transition $a_{1g}\sigma^* \rightarrow t_{1u}\sigma^*$ gives rise to three spin-allowed bands in $TeCl_6{}^{2-}$ (32,880; 34,480; 35,680 $cm^{-1}$) and $TeBr_6{}^{2-}$ (28,470; 29,730; 30,850 $cm^{-1}$). These data are taken as evidence that the excited singlet states are distorted to lower symmetry, probably $C_{2v}$. The lowest allowed halide → Te(IV) charge transfer transitions are at 44,170 $cm^{-1}$ and somewhat higher than 52,000 $cm^{-1}$ in $TeCl_6{}^{2-}$; analogous transitions appear at 37,000 and 42,600 $cm^{-1}$ in $TeBr_6{}^{2-}$. The observed spectral data indicate that the "inert" $5s^2$ Te(IV) electrons, which reside in the $a_{1g}\sigma^*$ level, are partially delocalized to the halide ligands.

The elucidation of electronic structure in hexahalo complexes of post-transition metals through electronic spectroscopic means has primarily been directed at the $d^{10}$ systems represented by the central metals Sn(IV) and Sb(V).[1,2] Of the relatively few studies on the interesting complexes of $d^{10}s^2$ metals, a recent investigation[1] has shown that the interpretation of absorption spectra of halo complexes of Sb(III) and Bi(III) is complicated by uncertainties in the structure of the species under investigation. Furthermore, the most extensive spectral studies[3] on halo complexes of Se(IV) and Te(IV) have been in aqueous media where hydrolysis is a serious problem.[4,5]

We have begun an investigation of the electronic spectra and structures of $TeX_6{}^{2-}$ complexes. This choice of $d^{10}s^2$ systems is appropriate because the complexes can be studied in media where sufficient structural information is at hand to allow a detailed interpretation of the results. In particular, the anions $TeCl_6{}^{2-}$ and $TeBr_6{}^{2-}$ in various solid samples have been shown from X-ray diffraction,[6,7] infrared,[4,5,8] Raman,[4,5] and nuclear quadrupole resonance[9] studies to possess regular octahedral structures. Furthermore, two independent Raman spectral studies[4,5] are in agreement that these anions retain octahedral structure in acetonitrile solution. In the present paper we report absorption spectra of $TeCl_6{}^{2-}$ and $TeBr_6{}^{2-}$ as thin films ($n$-$Bu_4N^+$ salts) and in various nonaqueous solvents, in an effort to establish a basis for serious discussion of their electronic structures.

## Experimental Section

**Preparation of Compounds. $(NH_4)_2[TeCl_6]$.** This compound was prepared by a modification of a method due to Fernelius.[10] Tellurium dioxide, freshly prepared from 99.999% tellurium, was dissolved in hot, concentrated hydrochloric acid. A saturated solution of ammonium chloride in hydrochloric acid was added, and yellow crystals of the complex formed immediately. The solution was evaporated down to about one-third its original volume and cooled. The crystals were collected on a sintered glass filter and washed with hydrochloric acid. The complex was recrystallized from concentrated hydrochloric acid, washed thoroughly, and dried under vacuum.

**$(NH_4)_2[TeBr_6]$, $[n\text{-}Bu_4N]_2[TeCl_6]$, and $[n\text{-}Bu_4N]_2[TeBr_6]$.** These compounds were prepared by methods analogous to the above.

**Solvents.** Acetonitrile was distilled eight times off phosphorus pentoxide and fractionated; the fraction boiling at 82.0° was collected. Precautions were taken to prevent access of moisture at all stages in handling the solutions. Dichloromethane was washed with dilute sulfuric acid and sodium carbonate solution, dried over calcium chloride, and fractionated; the fraction boiling at 39.6° was collected.

**Spectral Measurements.** Absorption spectra were recorded on Beckman DK-2A, Cary 14CMRI, and Cary 15 spectrophotometers. Thin films were prepared by evaporating dichloromethane solutions of tetra-$n$-butylammonium salts of $TeCl_6{}^{2-}$ and $TeBr_6{}^{2-}$

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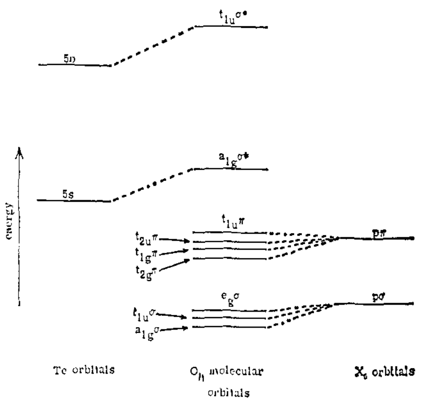

Figure 1. Relative orbital energies estimated for $TeX_6^{2-}$ complexes.

on a silica plate, as described by Bird and Day.[11] Spectra at 18°K were obtained with a Cary L He dewar.

## Theory for $d^{10}s^2$ Systems in $O_h$ Symmetry

Atomic spectra reveal[12] that the order of orbital energies for the uncomplexed $d^{10}s^2$ atoms and ions is $nd \ll (n + 1)s < (n + 1)p$. The lowest electronic excited states are derived from the $s^2 \rightarrow sp$ transition, which gives $^3P$ and $^1P$ upper states. In constructing a useful diagram of molecular orbital energies for $MX_6^{n-}$ complexes (where M is a $d^{10}s^2$ central atom), we shall assume that the levels derived primarily from the very low-lying $nd$ orbitals are nonvalence in a spectroscopic sense. The order of coulomb energies of the valence orbitals for hexahalo complexes will be taken as $(n + 1)p > (n + 1)s > p\pi(X) > p\sigma(X)$. The halide order $p\pi > p\sigma$ is observed in charge transfer spectra of hexahalo complexes of transition metals and is interpreted as the "crystal field" splitting of pπ and pσ orbitals;[13] the pσ orbitals are oriented more favorably insofar as the attractive potential of the positively charged metal is concerned. The order of $(n + 1)s > p\pi(X)$ is reasonable, considering that charge transfer spectra in $d^{10}s^0$ complexes have been assigned[1,2] to transitions of the $L\pi_u \rightarrow a_{1g}(s)$ type. Furthermore, previous interpretations of the electronic spectra of $d^{10}s^2$ complexes have assumed[1,3] that the lowest observed excitations are not $L\pi_g \rightarrow t_{1u}\sigma^*$, but rather $a_{1g}\sigma^* \rightarrow t_{1u}\sigma^*$.

The diagram of molecular orbital energies appropriate for our discussions of $d^{10}s^2$ systems is shown in Figure 1. The order of $L\pi_u$ levels derived from $p\pi(X)$ is taken from recent work[2,14,15] on the magnetic circular dichroism associated with electronic transitions in a variety of hexahalometalate complexes, whereas the placement of the $L\pi_g$ levels anticipates experimental results to be dealt with in the present report.

The ground state for the $d^{10}s^2$ complexes is $(a_{1g}\sigma^*)^2 \equiv {}^1A_{1g}$. From a theoretical point of view, two types of electronic transitions are expected: those that are derived from the free ion $s \rightarrow p$ transition and therefore should be more localized on the central atom, and those that involve strong charge transfer from halide to the central atom. Thus, the overall pattern expected is somewhat analogous to that of a $d^6$ low-spin transition metal complex $MX_6^{n-}$, where the "internal" $a_{1g}\sigma^* \rightarrow t_{1u}\sigma^*$ transition has taken the place of the $t_{2g} \rightarrow e_g$ excitation; an important difference, however, is that $a_{1g}\sigma^* \rightarrow t_{1u}\sigma^*$ is Laporte allowed.

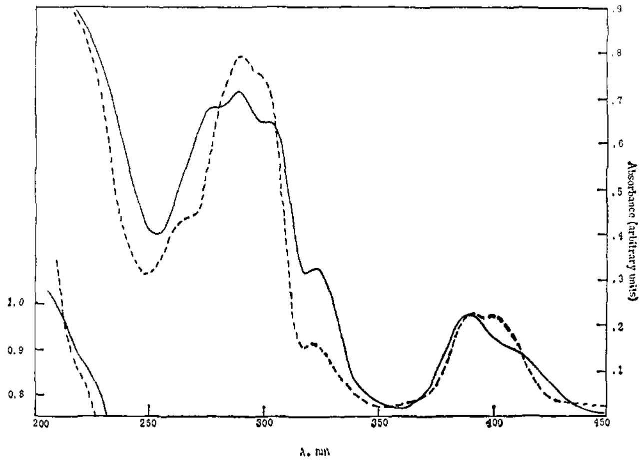

Figure 2. Electronic absorption spectra of a thin film of $[n\text{-}Bu_4N]_2[TeCl_6]$: ———, 300°K; - - - -, 18°K.

The $a_{1g}\sigma^* \rightarrow t_{1u}\sigma^*$ transition gives rise to excited states $^3T_{1u}$ and $^1T_{1u}$. The transition to the $^1T_{1u}$ state is fully electric-dipole allowed, whereas transitions to components of the spin-forbidden $^3T_{1u}$ state should be prominent only when the spin-orbit coupling associated with the central atom p orbitals is large. The latter requirement is met[12] in Te(IV).

There are two allowed charge transfer transitions of the type $L\pi_g \rightarrow t_{1u}\sigma^*$, namely $t_{1g}\pi \rightarrow t_{1u}\sigma^*$ and $t_{2g}\pi \rightarrow t_{1u}\sigma^*$. Bands due to transitions to these excited states are likely to appear close together and may be difficult to resolve. At considerably higher energy, we expect the two allowed $L\sigma_g \rightarrow t_{1u}\sigma^*$ transitions, $e_g\sigma \rightarrow t_{1u}\sigma^*$ and $a_{1g}\sigma \rightarrow t_{1u}\sigma^*$.

## Electronic Spectra of $TeX_6^{2-}$ Complexes

The electronic absorption spectra of $TeCl_6^{2-}$ measured at 300 and 18°K from a thin film of $[n\text{-}Bu_4N]_2[TeCl_6]$ are shown in Figure 2. We have also measured the spectrum at 77°K and found it to be essentially identical with the 18°K spectrum. Below 40,000 cm$^{-1}$ at 300°K, two band systems are clearly evident; the first system has peaks at 24,240, 25,740, and 30,670 cm$^{-1}$ whereas the second system consists of a principal maximum at 34,530 cm$^{-1}$ and two side bands at 32,680 and 36,510 cm$^{-1}$. As set out in Table I, spectra of $TeCl_6^{2-}$ in acetonitrile and methylene chloride solutions are very similar to the thin film spectrum, and we may conclude that the octahedral structure of the anion is preserved in these solvents.

At 18°K, the maxima of the bands in the first system occur at 24,650, 25,560, and 30,750 cm$^{-1}$. It is reasonable to assign these three bands as components of the $^3T_{1u}$ excited state derived from the $a_{1g}\sigma^* \rightarrow t_{1u}\sigma^*$ excitation. The relatively large separation of the two higher energy bands in this system presumably is due to the large spin-orbit coupling of Te(IV). It may be recalled that the analogous $^3P$ excited state in uncomplexed

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[12] C. E. Moore, "Atomic Energy Levels," Vol. III, National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1958.

[13] See, for example, W. R. Mason and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5721 (1968).

[14] G. N. Henning, A. J. McCaffery, P. N. Schatz, and P. J. Stephens, *J. Chem. Phys.*, **48**, 5656 (1968).

[15] A. J. McCaffery, P. N. Schatz, and T. E. Lester, *ibid.*, **50**, 379 (1969).

Table I. Electronic Absorption Spectra of $TeCl_6^{2-}$ and $TeBr_6^{2-}$

| Complex | Exptl | $\lambda_{max}$, nm | $\bar{\nu}_{max}$, cm$^{-1}$ | $\epsilon_{max}$ |
|---|---|---|---|---|
| $(NH_4)_2[TeCl_6]$ | $CH_3CN$ soln, 300°K | 410 | 24,400 (sh) | 700 |
| | | 385 | 26,000 | 1,900 |
| | | 323 | 31,000 | 3,000 |
| | | 304 | 32,900 (sh) | 8,000 |
| | | 287 | 34,900 | 9,000 |
| | | 277 | 36,100 | 8,600 |
| | | 227 | 44,100 (sh) | 1,200 |
| $[n\text{-}Bu_4N]_2[TeCl_6]$ | $CH_2Cl_2$ soln, 300°K | 410 | 24,400 (sh) | 1,350 |
| | | 385 | 26,000 | 3,700 |
| | | 321 | 31,200 | 6,000 |
| | | 301 | 33,200 (sh) | 15,500 |
| | | 288 | 34,700 | 21,000 |
| | | 276 | 36,200 | 19,000 |
| $[n\text{-}Bu_4N]_2[TeCl_6]$ | Thin film, 300°K | 412.6 | 24,240 | |
| | | 388.5 | 25,740 | |
| | | 326.0 | 30,670 | |
| | | 306.0 | 32,680 | |
| | | 289.6 | 34,530 | |
| | | 273.9 | 36,510 | |
| | | 228.0 | 43,860 (sh) | |
| $[n\text{-}Bu_4N]_2[TeCl_6]$ | Thin film, 18°K | 405.7 | 24,650 | |
| | | 391.2 | 25,560 | |
| | | 325.2 | 30,750 | |
| | | 304.1 | 32,880 | |
| | | 290.0 | 34,480 | |
| | | 280.3 | 35,680 | |
| | | 261.7 | 38,210 | |
| | | 226.4 | 44,170 | |
| $(NH_4)_2[TeBr_6]$ | $CH_3CN$ soln, 300°K | 467 | 21,400 (sh) | 1,500 |
| | | 447 | 22,400 | 3,900 |
| | | 381 | 26,200 (sh) | 1,200 |
| | | 330 | 30,300 | 19,000 |
| | | 268 | 37,300 (sh) | 5,500 |
| | | 225 | 44,400 | 77,000 |
| $[n\text{-}Bu_4N]_2[TeBr_6]$ | $CH_2Cl_2$ soln, 300°K | 467 | 21,400 (sh) | 1,000 |
| | | 446 | 22,400 | 2,600 |
| | | 381 | 26,200 (sh) | 1,500 |
| | | 323 | 31,000 | 19,000 |
| | | 275 | 36,400 (sh) | 28,000 |
| $[n\text{-}Bu_4N]_2[TeBr_6]$ | Thin film, 300°K | 473 | 21,100 | |
| | | 449.2 | 22,260 | |
| | | 384 | 26,000 | |
| | | 355.4 | 28,140 | |
| | | 336.3 | 29,730 | |
| | | 320.5 | 31,200 | |
| | | 272 | 36,760 | |
| | | 237 | 42,200 | |
| $[n\text{-}Bu_4N]_2[TeBr_6]$ | Thin film, 77°K | 462 | 21,600 | |
| | | 451 | 22,200 | |
| | | 381 | 26,200 | |
| | | 351.2 | 28,470 | |
| | | 336.4 | 29,730 | |
| | | 324.2 | 30,850 | |
| | | 270 | 37,000 | |
| | | 235 | 42,600 | |

$Te^{4+}$ has components $^3P_0$, $^3P_1$, and $^3P_2$ at 75,109, 78,023, and 85,997 cm$^{-1}$, respectively, above the ground state.[12] Thus the 25,560- and 30,750-cm$^{-1}$ bands in $TeCl_6^{2-}$ are assigned to transitions to the components of $^3T_{1u}$ related to $^3P_1$ and $^3P_2$, respectively. The transition to the component derived from $^3P_0$ is severely forbidden and thus we prefer *not* to associate it with the band at 24,650 cm$^{-1}$. In the opinion of the authors, it seems more likely that this band arises as a result of a distortion of the excited $^3T_{1u}$ ($^3P_1$) state from $O_h$ to lower symmetry; several models, including ones of $D_{4h}$ and $C_{3v}$ symmetries, could be postulated to account for the appearance of two bands. Further development of this point, however, will not be attempted, because the experimental evidence does not merit it. Instead, the discussion will proceed to an interpretation of the $^1A_{1g} \rightarrow {}^1T_{1u}$ region, where the evidence for distorted excited states is less ambiguous.

In the low-temperature film spectrum, the three bands in the second system appear at 32,880, 34,480, and 35,680 cm$^{-1}$. These bands are logically due to components of the $^1T_{1u}$ excited state of the $a_{1g}\sigma^* \rightarrow t_{1u}\sigma^*$ transition. The observed splitting is too large to be a vibrational progression and again suggests that distorted excited states result on promotion of an electron to the strongly antibonding $t_{1u}\sigma^*$ orbitals. The fact that three bands are resolved suggests that the symmetry of the excited singlet states is even lower than apparently is the case for the triplet states derived from $^3T_{1u}(^3P_1)$. If the symmetry becomes as low as $C_{2v}$, for example, three allowed transitions, to excited states of $^1A_1$, $^1B_1$, and $^1B_2$ symmetries, are expected. A plausible model for the $C_{2v}$ excited state would involve a nonlinear structure for one of the three Cl–Te–Cl groupings.

We next turn to a consideration of the charge transfer bands of $TeCl_6^{2-}$. There is strong absorption in the region above 40,000 cm$^{-1}$, which does not peak below 52,000 cm$^{-1}$. Both acetonitrile and film spectra show a distinct shoulder on this intense system; at 18°K the shoulder is placed at 44,170 cm$^{-1}$. Furthermore, a weak band at 38,210 cm$^{-1}$ is revealed in the film spectrum when the $^1A_{1g} \rightarrow {}^1T_{1u}$ system narrows at 18°K. Although several assignments are possible, we suggest that the weak band at 38,210 cm$^{-1}$ represents the forbidden $t_{1u}\pi \rightarrow t_{1u}\sigma^*$ transition, whereas the moderately intense 44,170 cm$^{-1}$ shoulder and the very intense maximum (>52,000 cm$^{-1}$) should be designated $t_{1g}\pi \rightarrow t_{1u}\sigma^*$ and $e_g\sigma \rightarrow t_{1u}\sigma^*$, respectively. Since some support for this interpretation may be developed from the $TeBr_6^{2-}$ spectrum, it is appropriate at this point to turn in that direction.

The spectra of $TeBr_6^{2-}$ in a film at 300 and 77°K and in solution at 300°K are given in Table I. Again, the spectral data do not suggest any change in the ground state octahedral structure of the anion in the solutions studied. As in the case of $TeCl_6^{2-}$, the lower energy portion of the $TeBr_6^{2-}$ spectrum shows the $^1A_{1g} \rightarrow {}^3T_{1u}$ and $^1A_{1g} \rightarrow {}^1T_{1u}$ systems. Components of the $^1A_{1g} \rightarrow {}^3T_{1u}$ system in acetonitrile solution appear at 21,400, 22,400, and 26,200 cm$^{-1}$. In the film spectra, the splitting of the $^1A_{1g} \rightarrow {}^1T_{1u}$ band into three components is again evident, but is less pronounced than in $TeCl_6^{2-}$. From the discussion above, this suggests that $TeBr_6^{2-}$ is more nearly octahedral in the excited states derived from the $a_{1g}\sigma^* \rightarrow t_{1u}\sigma^*$ transition.

The charge transfer spectrum of $TeBr_6^{2-}$ in acetonitrile solution consists of a shoulder at 37,300 cm$^{-1}$ of moderate intensity ($\epsilon$ 5500) and an intense peak at 44,500 cm$^{-1}$. Similar bands are revealed in the film spectrum at 77°K. These two features clearly correspond to the shoulder and strongly rising absorption (>52,000 cm$^{-1}$) observed for $TeCl_6^{2-}$, with the band positions substantially red shifted. The large shift to lower energy in going from $TeCl_6^{2-}$ to $TeBr_6^{2-}$ pinpoints these bands as of the halide → Te(IV) charge transfer type. The enormous intensity of the 44,500-cm$^{-1}$ band ($\epsilon$ 77,000) of $TeBr_6^{2-}$ suggests that it be assigned as a $\sigma_g \rightarrow \sigma_u^*$ transition, namely $e_g\sigma \rightarrow t_{1u}\sigma^*$. This means that the allowed $t_{1g}\pi \rightarrow t_{1u}\sigma^*$ transition

**Table II.** Positions of Excited Electronic States in $TeX_6^{2-}$ Complexes[a]

| | $a_{1g}\sigma^* \rightarrow t_{1u}\sigma^*$ transitions; $^1A_{1g} \rightarrow$ | | | Charge transfer transitions | | |
|---|---|---|---|---|---|---|
| Complex | $^3T_{1u}(^3P_1)$[d] | $^3T_{1u}(^3P_2)$ | $^1T_{1u}$[d] | $t_{1u}\pi \rightarrow t_{1u}\sigma^*$ | $t_{1g}\pi \rightarrow t_{1u}\sigma^*$ | $e_g\sigma \rightarrow t_{1u}\sigma^*$ |
| $TeCl_6^{2-}$[b] | 24.65; 25.56 | 30.75 | 32.88; 34.48; 35.68 | 38.21 | 44.17 | *e* |
| $TeBr_6^{2-}$[c] | 21.6; 22.2 | 26.2 | 28.47; 29.73; 30.85 | *e* | 37.0 | 42.6 |

[a] Band maxima given in units of $10^3$ cm$^{-1}$. [b] For film spectrum at 18°K. [c] For film spectrum at 77°K. [d] Band splitting interpreted as a result of the lower symmetry of the excited states. [e] Not observed.

must give rise to the moderately intense shoulder at 37,300 cm$^{-1}$.

## Discussion

A summary of band positions and transition assignments for the low-temperature film spectra of $TeCl_6^{2-}$ and $TeBr_6^{2-}$ is presented for comparison purposes in Table II. The most interesting point to explore is the extent to which these electronic spectral studies shed light on the question[16] of the bonding involvement of the "inert" pair of s electrons in these $d^{10}s^2$ complexes. At the very least, it may be concluded that the $a_{1g}\sigma^*$ electrons are not spectroscopically "inert," because relatively low-energy transitions are observed involving them. Furthermore, several lines of evidence, including the rather substantial variation in the positions of $^1A_{1g} \rightarrow {}^3T_{1u}$ and $^1A_{1g} \rightarrow {}^1T_{1u}$ with halide, and the variation in the $(^1A_{1g} \rightarrow {}^3T_{1u}) - (^1A_{1g} \rightarrow {}^1T_{1u})$ *separation*, suggest very strongly that some delocalization of $a_{1g}\sigma^*$ occurs in the $TeX_6^{2-}$ complexes. The fact that the observed shifts in the charge transfer transitions in going from $TeCl_6^{2-}$ to $TeBr_6^{2-}$ are not unusually large means that the *ca.* 5000 cm$^{-1}$ lower energy of $^1A_{1g} \rightarrow {}^1T_{1u}$ in $TeBr_6^{2-}$ cannot be explained on the basis of some special stabilization of $t_{1u}\sigma^*$. Indeed, there is a clear indication that $a_{1g}\sigma^*$ is involved in bonding with the halides.

The final point of this discussion will be a brief consideration of how the results obtained in this work influenced the choice expressed in Figure 1 of the L$\pi$ level order in hexahalometalates. The fact that magnetic circular dichroism measurements on several $MX_6^{n-}$ complexes have positioned[2,14,15] $t_{1u}\pi$ slightly above $t_{2u}\pi$ has already been noted. The charge transfer assignments here, particularly the identification of the weak band at 38,210 cm$^{-1}$ in $TeCl_6^{2-}$ as the $t_{1u}\pi \rightarrow t_{1u}\sigma^*$ transition, make it probable that $t_{1g}\pi$ is even further below $t_{1u}\pi$ than is $t_{2u}\pi$. Thus the available experimental spectroscopic data are consistent with the relative energies $t_{1u}\pi > t_{2u}\pi > t_{1g}\pi > t_{2g}\pi$ in hexahalometalate complexes.

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