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Halogen Ordering in $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$: A Spectroscopic Study

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For the newly reported mixed-halide salt $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$, vibrational and electronic spectra are presented and interpreted on the basis of halogen ordering within the binuclear $\text{Cr}_2\text{Cl}_6\text{Br}_3^{3-}$ unit. The spectral studies support earlier structural findings that the bromine atoms occupy terminal halogen sites in the binuclear unit. Both the vibrational and electronic spectra are consistent with trigonal symmetry within the binuclear unit. Such symmetry exists for an ordered arrangement in which all three bromine atoms occupy terminal halogen sites at one end only of each binuclear unit but not for the alternative structure involving a statistical distribution of bromines over all terminal halogen sites available in the unit cell. The electronic spectrum can best be interpreted on the basis that transitions involving an excitation on the $\text{CrCl}_3\text{Br}_3^{3-}$ single ion center are dominant in intensity, and this again is consistent with the proposed structure model.

Introduction

In an earlier contribution we reported the X-ray structure refinement for the mixed-halide complex salt $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$.¹ This represents the first structural study of mixed-halogen complex salts of the type $\text{A}_3\text{M}_2\text{X}_n\text{Y}_{9-n}$.

The nonahalodimetalates $\text{A}_3\text{M}_2\text{X}_9$ are well-known and possess closely related hexagonal structures containing $\text{M}_2\text{X}_9^{3-}$ binuclear complex anions formed by pairs of octahedra sharing a common face. To understand structure-related properties exhibited by these systems, it is necessary to recognize two types of halogen coordination, terminal and bridging. The bridging halogens are particularly important in determining magnetic and spectroscopic properties.²⁻⁸ For mixed-halogen salts in the series $\text{A}_3\text{M}_2\text{X}_n\text{Y}_{9-n}$, it is of interest to determine whether structural ordering exists between the two kinds of halogens X and Y, and also, in the case where $n = 6$, whether halogens of type Y are confined to either bridging or terminal halogen sites or a combination of both. However, in the single-crystal structure refinement it was shown that the bromine atoms occupy terminal halogen sites only.¹ Each unit cell in the structure (space group $P6_3/mmc$) contains two formula units. The best structure refinement was obtained when all 12 terminal halogen sites were available to 6 bromine and 6 chlorine atoms.

Two structural possibilities arise as shown in Figure 1. An ordered arrangement where bromine atoms occupy all three terminal halogen sites at one end only of each binuclear unit (3-0 configuration), is possible if one considers ordering within microdomains over the entire crystal structure. In this "ordered" model the binuclear unit is unique and possesses C_{3v} pair symmetry as shown in Figure 1A. The other model involves a statistical distribution of bromine atoms over all terminal halogen sites at both ends of each binuclear unit. However, in the context of this statistical or "disordered" model, the binuclear unit is no longer necessarily unique since several possible geometries exist, all possessing a 2-1 type configuration (2 bromine atoms at one end and 1 at the other). As such, the local 3-fold axis is lost and the highest pair symmetry possible is that of C_2 when the odd halogen atoms at each end of the binuclear unit are in an eclipsed arrangement as shown in Figure 1B. From the X-ray data alone, it is not possible to distinguish between these two cases. The object of the spectroscopic studies now to be reported was to determine whether further evidence could be adduced in favor of one or the other of these models.

Experimental Section

Single crystals of $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$ were grown by high-temperature methods as detailed previously,¹ producing dark blue hexagonal plates and columns.

Infrared spectra were recorded at room temperature on a Digilab FTS 20E Fourier transform spectrometer with a resolution of 4 cm^{-1} . Raman spectra were recorded on a Cary 82 spectrometer at approximately 4 cm^{-1} resolution, using a Spectra Physics Model 164 argon laser and the 514.5-nm argon excitation line.

Table I. Band Positions and Assignments for the Vibrational Spectra of $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$

major vibrational coord	band position, cm^{-1}		C_{3v} sym assignt
	infrared	Raman	
$\nu(\text{Cr}-\text{Cl}_i)$	354	355	A_1
	340	335	E
$\nu(\text{Cr}-\text{Br}_i)$	308	306	A_1
	294	290	E
$\nu(\text{Cr}-\text{Cl}_b)$	273	268	A_1
	254		E
	237		E
	219	220	A_1
$\delta(\text{Cr}-\text{Cl}_i)$	192	190	A_1
	175		E
$\delta(\text{Cr}-\text{Br}_i)$	158	155	A_1
	150		E
$\delta(\text{Cl}_i-\text{Cr}-\text{Cl}_b) +$ $\delta(\text{Br}_i-\text{Cr}-\text{Cl}_b) +$		135	
		125	$A_1 +$
$\delta(\text{Cr}-\text{Cl}_b)$	100	105	3E
	95	90	
lattice	75	50	
	50	45	

Table II. Position, Polarization, and Assignment of Observed Transitions to the ${}^4A_2\text{-}{}^2T_1$ Pair State

position, cm^{-1}	polarization	assignt		label
		ground state	excited state	
14 438	σ	5A_1	${}^3A_1 ({}^4A_2\text{-}{}^2T_{10})^a$	a
14 481	π	5A_1	${}^3E ({}^4A_2\text{-}{}^2T_{1\pm})^a$	f
14 483	σ	3A_1	${}^3A_1 ({}^4A_2\text{-}{}^2T_{10})^a$	b
14 502	σ	1A_1	${}^3A_1 ({}^4A_2\text{-}{}^2T_{10})^a$	c
14 525	π	3A_1	${}^3E ({}^4A_2\text{-}{}^2T_{1\pm})^a$	g
14 550	π	1A_1	${}^3E ({}^4A_2\text{-}{}^2T_{1\pm})^a$	h
14 554	σ	1A_1	${}^3E ({}^4A_2\text{-}{}^2T_{1\pm})^a$	d
14 594	σ	1A_1	${}^3E ({}^4A_2\text{-}{}^2T_{1\pm})^b$	e
14 597	π	1A_1	${}^3E ({}^4A_2\text{-}{}^2T_{1\pm})^b$	i

^a Excitation on $\text{CrCl}_3\text{Br}_3^{3-}$ single ion center. ^b Excitation on CrCl_6^{3-} single ion center.

cm^{-1} resolution, using a Spectra Physics Model 164 argon laser and the 514.5-nm argon excitation line.

- Butler, S. E.; Grey, I. E.; Madsen, I. C.; Smith, P. W.; Stranger, R. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, in press.
- Black, J. D.; Dunsmuir, J. T. R.; Forrest, I. W.; Lane, A. P. *Inorg. Chem.* **1975**, *14*, 1257.
- Grey, I. E.; Smith, P. W. *Aust. J. Chem.* **1969**, *22*, 1627.
- Dean, N. J.; Maxwell, K. J.; Stevens, K. W. H.; Turner, R. J. *J. Phys. C* **1985**, *18*, 4505.
- Johnstone, I. W.; Maxwell, K. J.; Stevens, K. W. H. *J. Phys. C* **1981**, *14*, 1297.
- Dubicki, L.; Ferguson, J.; Harrowfield, B. V. *Mol. Phys.* **1977**, *34*, 1545.
- Briat, B.; Russel, M. F.; Rivoal, J. C.; Chapelle, J. P.; Kahn, O. *Mol. Phys.* **1977**, *34*, 1357.

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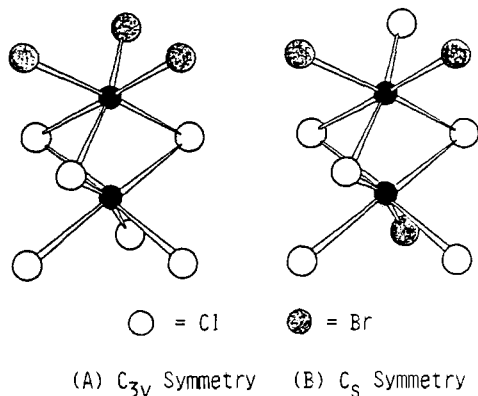


Figure 1. Halogen arrangement for ordered (A) and disordered (B) models.

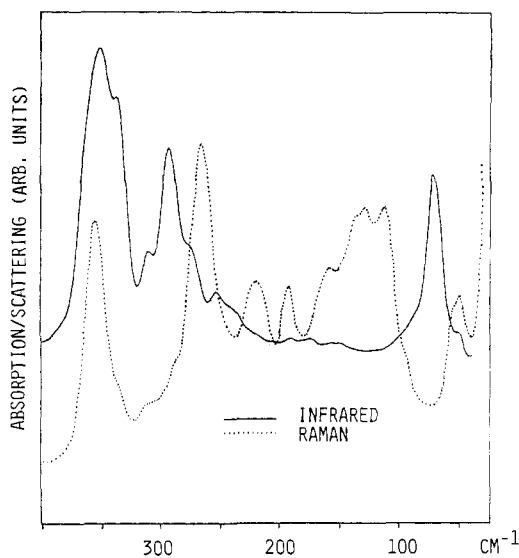


Figure 2. Vibrational spectra of $Cs_3Cr_2Cl_6Br_3$.

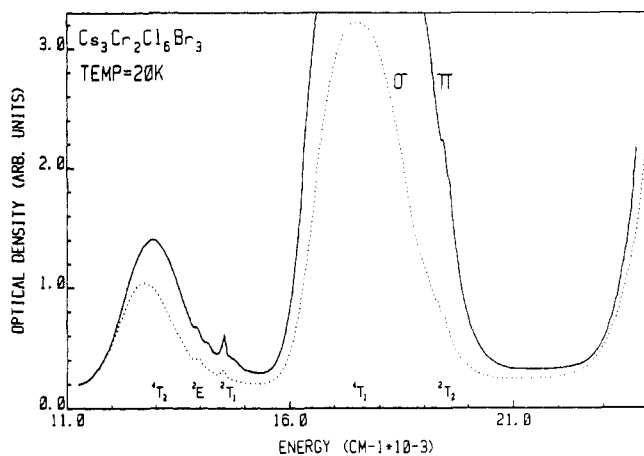


Figure 3. Polarized single-crystal electronic spectra of $Cs_3Cr_2Cl_6Br_3$.

Electronic spectra were measured on a Cary 17 spectrophotometer, on both axial plates (unpolarized) and orthoaxial rods (xy and z polarizations) of $Cs_3Cr_2Cl_6Br_3$. The crystals were cooled to temperatures down to 20 K with a Cryodyne Model 21 cryostat fitted with an Oxford Instruments temperature controller and sensor.

Results

The infrared and Raman spectra measured at room temperature on powdered samples of $Cs_3Cr_2Cl_6Br_3$ are shown in Figure 2 while the positions of observed vibrational bands and their tentative

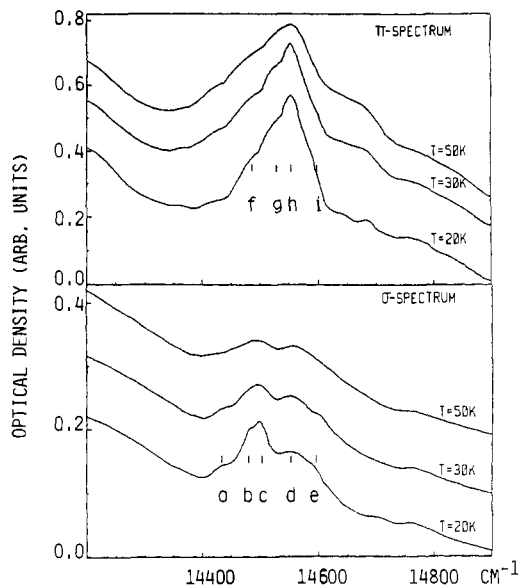


Figure 4. Temperature dependence of the ${}^4A_2\text{-}{}^2T_1$ pair state.

Table III. Vibrational Coordinates and Wavenumber Ranges for $Cs_3Cr_2X_9$ ($X = Cl, Br$)

major vibrational coord	wavenumber range, cm^{-1}	
	$Cs_3Cr_2Cl_9$	$Cs_3Cr_2Br_9$ ^a
$\nu(Cr-X_a)$	380-335	305-270
$\nu(Cr-X_b)$	285-200	235-180
$\delta(Cr-X_a) + \delta(X_a-Cr-X_b)$	200-160	180-110
$\delta(Cr-X_b)$	145-100	110-75

^a Range based on A_{1g} phonon energies observed for ${}^4A_1\text{-}{}^2T_1$ pair state in $Cs_3Cr_2Br_9$.⁴

assignments relative to C_{3v} pair symmetry are given in Table I. The single-crystal polarized electronic spectra of $Cs_3Cr_2Cl_6Br_3$ at 20 K are shown in Figure 3 for both σ - and π -polarizations. Figure 4 shows the temperature dependence in both polarizations of excitations belonging to the ${}^4A_2\text{-}{}^2T_1$ singly excited pair state for $Cs_3Cr_2Cl_6Br_3$, while the assignment of observed pair lines is detailed in Table II, again on the basis of C_{3v} pair symmetry.

Discussion

Vibrational Spectra. Before applying the symmetry arguments applicable to the ordered and disordered models, it is of use to tabulate the known ranges of band positions for the various vibrational coordinates as observed in the pure chloro and bromo complexes.^{2,3} The relevant wavenumber ranges found for the cesium salts of $Cr_2X_9^{3-}$ ($X = Cl, Br$) are shown, together with the major vibrational coordinate involved, in Table III. For $Cs_3Cr_2Br_9$, only the positions of the terminal bromine stretching bands have been reported.³ However, it is possible to obtain an approximate energy range for each coordinate based on the reported A_{1g} phonon coupling energies in the ${}^4A_2\text{-}{}^2T_1$ pair state spectra of $Cs_3Cr_2Br_9$.⁴ For the bromide complex, the A_{1g} phonon associated with each vibrational coordinate is assumed to lie highest in energy since this applies to all analogous coordinates in the chloride salts, with the exception of bridging chlorine deformation modes in the latter. Although the A_{1g} terminal bromine stretching phonon was reported at 290 cm^{-1} , the equivalent chloride phonon was reported over 10 cm^{-1} lower in energy than that observed in the Raman spectra of $Cs_3Cr_2Cl_9$.⁵ As such, the true position of the A_{1g} terminal bromine stretch is likely to be closer to 305 cm^{-1} , as given in Table III.

The positions and associated vibrational coordinates for the observed infrared and Raman bands in $Cs_3Cr_2Cl_6Br_3$ are given in Table I. With one exception, the coordinates assigned to the observed bands fall within the ranges specified in Table III. The band located at 308 cm^{-1} is slightly outside the range for terminal bromine stretching vibrations, but since its position is too low to be associated with terminal chloride stretching modes, there is

no alternative but to assign it to the former type of vibration. In any case, mixing effects between chlorine and bromine stretching vibrations should result in a shift to higher energy for the terminal bromine stretching modes. In this respect, the observed vibrational spectra are consistent with structural findings detailed earlier in that both terminal and bridging chlorine stretching vibrations are present while for the bromine atoms only terminal stretching vibrations are observed. Furthermore, deformation modes associated with both terminal and bridging chlorines are observed whereas only the terminal bromine deformation modes appear to be present.

For the ordered arrangement, the internal modes belonging to $\text{Cr}_2\text{Cl}_6\text{Br}_3^{3-}$ span $7A_1 + 2A_2 + 9E$ representations for C_{3v} molecular symmetry, giving a total of 16 infrared- and Raman-active fundamentals. For the disordered case all degeneracy is removed, and in addition, all inactive modes become allowed. Unit cell analysis for the ordered case shows that again only 16 infrared-active internal modes are expected while 25 Raman-active modes are allowed, although in the latter case 9 of these result from factor group splittings and are not likely to be resolved.

In either model there are three terminal chlorine and three terminal bromine stretching vibrations to assign, all six vibrations being both Raman and infrared active. In the disordered model all degeneracy is lost so that in theory it is possible to observe all six bands mentioned. With the ordered model on the other hand, the degeneracies are such that only two chlorine stretching and two bromine stretching bands should be seen in both the Raman and infrared spectra of $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$.

An examination of Figure 2 in conjunction with Tables I and III shows that the observed spectra are in agreement with the predictions of the ordered model above in that both the Raman and infrared spectra reveal only two bands associated with each of the chlorine and bromine stretching vibrations. Similar arguments can also be applied to the bridging chlorine stretching modes as well as both terminal chlorine and bromine deformation modes with results consistent with the ordered model, though in general, these vibrations are much weaker and therefore less well resolved.

One final comment regarding the Raman spectra of $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$ is that vibrations involving largely movement of the terminal bromine atoms are very much weaker in intensity than those of the corresponding chlorine vibrations, and in general, the totally-symmetric vibrations associated with movement of the chlorine atoms are dominant in intensity. Raman polarization data for $\text{Cs}_3\text{Cr}_2\text{Cl}_6$ showed that the A_{1g} terminal chlorine stretching and bridging chlorine stretching modes were the dominant scatterers, particularly the latter.² As such, the assignment of the vibrational band at $\sim 270\text{ cm}^{-1}$ in both the Raman and infrared spectra of $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$ to the A_{1g} bridging chlorine stretching vibration rather than as a third terminal bromine stretching band seems justifiable on the basis of the large scattering intensity observed for this band.

Electronic Spectra. (a) Spin-Allowed Transitions. In general, the gross features of the polarized crystal spectra of $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$, as seen in Figure 3, have certain features in common with the spectra of the pure chloro and bromo complexes,⁴⁻⁷ particularly the former. First, the π/σ intensity ratio of approximately 1.3 as well as the half-widths for 4T_2 are very similar to those occurring in $\text{Cs}_3\text{Cr}_2\text{Cl}_6$. Second, the first-order trigonal field splitting⁹ of 4T_2 gives a value of $K = -115\text{ cm}^{-1}$ for $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$, which is quite close to $K = -130\text{ cm}^{-1}$ found for both $\text{Cs}_3\text{Cr}_2\text{Cl}_6$ and $\text{Cs}_3\text{Cr}_2\text{Br}_6$.⁶ As is apparent from Figure 3, the 4T_1 (4F) state could not be penetrated in π -polarization, making an exact determination of K for this state impossible. However, on the assumption of a symmetric Gaussian band shape, a value of $K \sim -200\text{ cm}^{-1}$ seems reasonable.

For $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$ $10Dq = 12790\text{ cm}^{-1}$, which is intermediate between $10Dq$ values for $\text{Cs}_3\text{Cr}_2\text{Cl}_6$ and $\text{Cs}_3\text{Cr}_2\text{Br}_6$ at 13095 and 12335 cm^{-1} , respectively. The latter two values were obtained

on the assumption of a first-order trigonal field splitting of the 4T_2 state. However, the most significant difference between the spectra of $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$ and $\text{Cs}_3\text{Cr}_2\text{Cl}_6$ is the dipole strengths associated with the spin quartet states. At approximately 300 K the pure chloro complex has a value of $D_0 = 2.3 \times 10^{-2}\text{ D}^2$ for 4T_2 , whereas for $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$ the value of $D_0 = 8.5 \times 10^{-2}\text{ D}^2$ was obtained, this being almost four times as large.

Against these observations, spectral features predicted on the basis of the two structural models considered may be examined. For the disordered case, the presence of several nonequivalent single ion centers possessing at most C_3 symmetry should lead to rather broad bands associated with transitions to 4T_2 and 4T_1 excited states. Not only this, but the trigonal field splitting normally associated with single ion centers of C_{3v} symmetry should effectively be swamped since a significant rhombic field component will be present. The fact that symmetric Gaussian band shapes are observed with half-widths similar to those found in the pure halide complexes, as well as an almost identical splitting between σ - and π -components of 4T_2 , is consistent with trigonal symmetry being retained in the single ion centers of $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$ as predicted for the ordered case. However, the intermediate value of $10Dq$ as well as the anomalously high dipole strengths of 4T_2 and 4T_1 states compared to that of $\text{Cs}_3\text{Cr}_2\text{Cl}_6$ still need to be explained.

The uniqueness of the binuclear unit in the ordered model necessarily implies the presence of exactly two nonequivalent single ion centers, CrCl_6^{3-} and $\text{CrCl}_3\text{Br}_3^{3-}$. The value of $10Dq$ for the former ion should be very close to that observed for $\text{Cs}_3\text{Cr}_2\text{Cl}_6$ at 13095 cm^{-1} , whereas $10Dq$ for the latter ion, in the cubic approximation, should be close to 12720 cm^{-1} . In this respect, the value of $10Dq$ at 12790 cm^{-1} for $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$ is almost exactly that expected for a $\text{CrCl}_3\text{Br}_3^{3-}$ single ion center. This puzzling result can be explained on the basis of the relative single ion intensities for the two inequivalent centers in $\text{Cr}_2\text{Cl}_6\text{Br}_3^{3-}$. The "static" intensity associated with the 4T_2 and 4T_1 ligand field states is derived from the single ion odd-parity ligand field potential. This will be much larger in $\text{CrCl}_3\text{Br}_3^{3-}$ than in CrCl_6^{3-} , as in the former ion the "trans" halide ions differ. Moreover, d-d transitions within $\text{CrCl}_3\text{Br}_3^{3-}$ can acquire intensity from both metal-chlorine and -bromine charge-transfer transitions, whereas the analogous transitions in CrCl_6^{3-} can only obtain intensity from the former. Since charge-transfer transitions involving bromine ligands are lower in energy than the corresponding chloride transitions, it can be anticipated that d-d transitions within $\text{CrCl}_3\text{Br}_3^{3-}$ will be further intensified in relation to the equivalent transitions in CrCl_6^{3-} .

With respect to spin-allowed transitions, the electronic spectra of the mixed-halide complex can be rationalized on the basis of an ordered model where transitions within the $\text{CrCl}_3\text{Br}_3^{3-}$ single ion center dominate in intensity. This interpretation carries with it certain implications regarding the fine structure and intensity of pair lines belonging to the singly excited ${}^4A_2, {}^2T_1$ pair state as is discussed below.

(b) Spin-Forbidden Transitions. The analysis of fine structure associated with pair transitions to the spin doublet states in $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$ is limited to the ${}^4A_2, {}^2T_1$ singly excited pair state since the ${}^4A_2, {}^2E, {}^2T_2$ pair state transitions are much too broad. Since $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$ and $\text{Cs}_3\text{Cr}_2\text{Cl}_6$ both possess a chlorine bridge unit as well as a similar metal-metal separation (cf. Table II in ref 1), it may be anticipated that pair interactions in $\text{Cs}_3\text{Cr}_2\text{Cl}_6\text{Br}_3$, with regard both to the mechanism and magnitude of exchange, should be quite similar to that of $\text{Cs}_3\text{Cr}_2\text{Cl}_6$.

On the assumption that the exchange processes operative in $\text{Cs}_3\text{Cr}_2\text{Cl}_6$ apply in the mixed-halide complex, certain predictions can be made regarding transitions to the ${}^4A_2, {}^2T_1$ pair state based on the detailed assignments for the former.⁵ First, as occurs for both $\text{Cs}_3\text{Cr}_2\text{Cl}_6$ ⁵ and $\text{Cs}_3\text{Cr}_2\text{Br}_6$ ⁴, pair transitions to ${}^4A_2, {}^2T_{10}$ will lie lowest in energy. Second, pair transitions to ${}^4A_2, {}^2T_{10}$ will be more intense in σ -polarization while transitions to ${}^4A_2, {}^2T_{1\pm}$ will in general be more intense in π -polarization. This in particular applies to the so called "cold" band transitions emanating from the ${}^4A_2, {}^4A_2(S=0)$ ground-state level. Also, as occurs for $\text{Cs}_3\text{Cr}_2\text{Cl}_6$,⁵ it may be expected that transitions to the ${}^4A_2, {}^2T_{1\pm}$ pair state will be broader and less well resolved, particularly in π -

(9) Sugano, S.; Tanabe, Y.; Kamimura, H. *Multiplets of Transition-Metal Ions in Crystals*; Academic: New York, 1970.

polarization, and transitions to ${}^4A_2\text{-}{}^2T_1(S = 2)$ levels will not be observed. Finally, cold transitions to ${}^4A_2\text{-}{}^2T_1$ were dominant in intensity for the pure halide complexes, implying that single ion electric dipole processes are more important than exchange-induced electric dipole ones.

An analysis of the fine structure belonging to the ${}^4A_2\text{-}{}^2T_1$ pair state in the context of the disordered model is difficult and will not be attempted here due to the statistical problem inherent in this model. For the ordered case all transitions from ${}^4A_2\text{-}{}^4A_2(S = 0, 1, 2)$ to ${}^4A_2\text{-}{}^2T_{1\pm}(S = 1)$ and ${}^4A_2\text{-}{}^2T_{10}(S = 1)$ are allowed in both σ - and π -polarization, the only exception being the ${}^4A_2\text{-}{}^4A_2({}^1A_1)$ to ${}^4A_2\text{-}{}^2T_{10}({}^3A_1)$ transition, which is not allowed in π -polarization. Similarly, all transitions from ${}^4A_2\text{-}{}^4A_2(S = 1, 2, 3)$ to ${}^4A_2\text{-}{}^2T_{1\pm}(S = 2)$ and ${}^4A_2\text{-}{}^2T_{10}(S = 2)$ are allowed in both polarizations. In general, the number of allowed pair transitions to ${}^4A_2\text{-}{}^2T_1$, as a consequence of the lower pair symmetry, greatly exceeds that for D_{3h} pair symmetry appropriate to $Cs_3Cr_2X_9$ ($X = Cl, Br$). Consequently, it is anticipated that pair transitions to ${}^4A_2\text{-}{}^2T_{1\pm}$ and ${}^4A_2\text{-}{}^2T_{10}$ pair states will be less resolved than those associated with the pure halide complexes due to the overlap of several pair lines, particularly at higher temperatures.

Finally, there exists a distinct difference in the description of pair states resulting for a C_{3v} pair compared to those applicable to a D_{3h} pair. In the latter, excitation to either metal ion in the pair is formally equivalent so that it is not possible to distinguish on which metal ion the excitation resides. In any case, excitation transfer transfers the excitation from one metal ion to the other. For a C_{3v} pair however, the single ion excitations are no longer equivalent so that it is possible to define states in which the excitation is largely localized on either metal ion.

Examination of the temperature dependence of the σ - and π -spectra for the ${}^4A_2\text{-}{}^2T_1$ pair state shown in Figure 4 reveals certain features in common with the corresponding spectra of $Cs_3Cr_2Cl_9$, as was anticipated in the discussion above. In particular, the σ - and π -polarized cold bands c and h are dominant in intensity and appear similar to the pair lines assigned to transitions from ${}^4A_2\text{-}{}^4A_2(S = 0)$ to ${}^4A_2\text{-}{}^2T_{10}({}^3A_2'')$ and ${}^4A_2\text{-}{}^2T_{1\pm}({}^3E')$, respectively, in $Cs_3Cr_2Cl_9$. However, the analogous bands (c and h) in $Cs_3Cr_2Cl_6Br_3$ are around 40 cm^{-1} lower in energy, if account is taken of excitation transfer occurring in $Cs_3Cr_2Cl_9$, and this discrepancy is too large to be the sole consequence of differing ground-state exchange. Rather this energy difference is the more likely result of cold bands c and h corresponding to transitions to ${}^4A_2\text{-}{}^2T_{10}(S = 1)$ and ${}^4A_2\text{-}{}^2T_{1\pm}(S = 1)$ respectively, where in each case the excitation resides on the $CrCl_3Br_3^{3-}$ single ion center. Calculations in the cubic approximation, assuming the same ground-state exchange, predict a shift to lower energy of approximately 60 cm^{-1} for $CrCl_3Br_3^{3-}$ in relation to the $CrCl_6^{3-}$ single ion center occurring in $Cs_3Cr_2Cl_9$, and this value is in reasonable agreement with that observed. The analogous transitions, where the excitation is located on the $CrCl_6^{3-}$ center, should lie at approximately 14535 and 14595 cm^{-1} , respectively, again assuming a similar ground-state exchange to $Cs_3Cr_2Cl_9$. The former line will occur in the middle of pair transitions to ${}^4A_2\text{-}{}^2T_{1\pm}(S = 1, 2)$ and so is not a good candidate. The latter line, however, may well be observable since it should occur as the highest energy pair line associated with transitions to ${}^4A_2\text{-}{}^2T_1$. Indeed, a cold-band shoulder is observed around 14595 cm^{-1} in both σ - and π -polarization corresponding to bands e and i, respectively, in Figure 4. Since these cold-band transitions are

only able to acquire intensity through single ion electric dipole processes, it is anticipated that, analogous to the spin-allowed states, transitions involving an excitation on the $CrCl_3Br_3^{3-}$ single ion center will be more intense than the corresponding transitions where the excitation is located on the $CrCl_6^{3-}$ single ion center. Comparison of cold bands h and i in Figure 4 shows that indeed this is the case.

From the above discussion, bands c, d, and h can be assigned to cold-band transitions to ${}^4A_2\text{-}{}^2T_{10}(S = 1)$ and ${}^4A_2\text{-}{}^2T_{1\pm}(S = 1)$ where the excitation is on the $CrCl_3Br_3^{3-}$ single ion center. It now remains to assign bands a and b in σ -polarization and bands f and g in π -polarization. These four bands are not cold transitions (cf. Figure 4) and therefore must emanate from the ${}^4A_2\text{-}{}^4A_2(S = 1, 2, 3)$ ground-state exchange levels. Since bands a and b occur to the lower energy side of cold band c, they can only be assigned as transitions to ${}^4A_2\text{-}{}^2T_{10}(S = 1)$ from the ground-state $S = 1$ and $S = 2$ spin levels, respectively, where the excitation is on the $CrCl_3Br_3^{3-}$ single ion center. This assignment excludes the possibility of transitions to ${}^4A_2\text{-}{}^2T_1(S = 2)$ exchange levels, but analogous to the pure halide complexes, these transitions are expected to be very weak if at all observed. Similarly, bands f and g in π -polarization can be assigned to transitions from the ground-state $S = 1$ and $S = 2$ spin levels, respectively, to the ${}^4A_2\text{-}{}^2T_{1\pm}(S = 1)$ excited pair state where again the excitation is on the $CrCl_3Br_3^{3-}$ single ion center. From the band assignments of a, b, and c in σ -polarization, the ground-state exchange is antiferromagnetic with $J_{ab} = -21 \pm 3\text{ cm}^{-1}$. Bands f, g, and h in π -polarization give a similar ground-state exchange with $J_{ab} \sim -23\text{ cm}^{-1}$; however, considering the broadness of these bands in π -polarization, the former value is more reliable. The increase in ground-state exchange for $Cs_3Cr_2Cl_6Br_3$ in relation to $Cs_3Cr_2Cl_9$ (cf. $J_{ab} = -13\text{ cm}^{-1}$) is not surprising since the presence of terminal bromine ligands will increase slightly the dilation of the t_{2g} orbitals, thus facilitating direct overlap and, as a consequence, antiferromagnetic exchange.

Conclusion

The infrared and Raman spectra for the mixed-halide complex $Cs_3Cr_2Cl_6Br_3$ are in agreement with structural findings that the bromine atoms occupy terminal halogen sites only in the binuclear unit. Furthermore, on the basis of symmetry arguments, the position and number of vibrational bands, particularly with regard to terminal halogen stretching modes, are consistent with an ordered arrangement of bromine atoms at one end only of each binuclear unit such that trigonal symmetry is retained. The gross features as well as the fine structure of the single-crystal polarized electronic spectra of $Cs_3Cr_2Cl_6Br_3$ can be rationalized on the basis that transitions involving an excitation on the $CrCl_3Br_3^{3-}$ single ion center are dominant in intensity. In this respect, the electronic spectra are in accord with the above ordered arrangement of bromine atoms.

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