The Effect of Exchange Coupling on the Spectra of Transition Metal Ions.
The Crystal Structure and Optical Spectrum of CsCrBr₃*

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An X-ray study of the crystalline complex cesium chromium tribromide, $CsCrBr_3$, shows that it crystallizes in the space group $P6_3mc$; $a = 7\cdot588$ (3), $c = 6\cdot506$ (4) Å; $V = 324\cdot41$ Å³; $Z = 2$. The intensities of 164 reflections were measured by the θ–2θ scan technique on a four-circle Picker diffractometer and the corresponding structure factors were refined by full-matrix least-squares techniques to a final R index on F of $0\cdot074$ and a weighted R index of $0\cdot054$. $CsCrBr_3$ is isostructural with $CsCrCl_3$ and, like the latter compound, does not show any evidence of a static Jahn–Teller distortion as is observed in $CsCuCl_3$ and $CsCuBr_3$. The single-crystal optical absorption spectrum of $CsCrBr_3$ is presented and briefly compared with that of $CsCrCl_3$.

Introduction

Octahedral chromium(II) (^5E_g ground state) and copper (II) (^2E_g ground state) complexes are expected to display similar structural features, and in fact this is frequently true (Cotton & Wilkinson, 1972). It was therefore not surprising when Iberson, Gut & Gruen (1962) first reported $CsCrCl_3$ to be isostructural with $CsCuCl_3$. In a later report, however, Seifert & Klatyk (1964), using-single crystal diffraction data, suggested that $CsCrCl_3$ was isostructural with $CsNiCl_3$. A complete structural analysis of $CsCrCl_3$ (McPherson, Kistenmacher, Folkers & Stucky, 1972) showed that neither of the above reports was correct, and that $CsCrCl_3$ does not exhibit the static tetragonal distortion observed in $CsCuCl_3$ (Schlueter, Jacobsen & Rundle, 1966) and $CsCuBr_3$ (Li & Stucky, 1972). The results of the studies of $CsCrCl_3$, $CsCuCl_3$ and $CsCuBr_3$ raised several questions. The structures of the paramagnetic $CsCuCl_3$ and the strongly spin coupled $CsCuBr_3$ are markedly different. Is there any structural difference between $CsCrCl_3$ and $CsCrBr_3$? Is there any relation between the structures of $CsCuBr_3$ and $CsCrBr_3$? The single-crystal visible absorption studies of $CsMg_n(Cr)_{1-n}Cl_3$ (McPherson, Kistenmacher, Folkers & Stucky, 1972) showed a broad band at $\sim 22,000$ cm^{-1} which was due to exchange coupling. What is the effect of substituting Br for Cl on the energy and intensity of this transition? This paper presents the results of a single-crystal structural study of $CsCrBr_3$ and preliminary single-crystal optical absorption measurements in an attempt to answer the above questions.

Experimental section

Crystal preparation

$CsCrBr_3$ was obtained by melting equimolar mixtures of CsBr and $CrBr_2$ in a sealed, evacuated quartz

ampoule at 750 °C. $CrBr_2$ was prepurified by vacuum sublimation at 750 °C. The complex is brown in color and slowly oxidizes when exposed to air.

Analysis: Calculated for $CsCrBr_3$: $12\cdot23$% Cr; $56\cdot50$% Br. Found: $12\cdot01$% Cr; $56\cdot36$% Br.

Spectral measurements

The crystals for spectroscopic investigation were grown from melts by a vertical Bridgman method. Powdered samples sealed in evacuated quartz ampoules were lowered slowly (approximately 4″ per 24 hr) through a tube furnace maintained at 750 °C. Single-crystal samples for spectroscopic studies were prepared and spectroscopic measurements were made in the same manner as for $CsCrCl_3$ (McPherson, Kistenmacher, Folkers & Stucky, 1972).

Data collection and reduction

Optical examination in cross polarized light showed that the crystal system was uniaxial. Preliminary X-ray film data (precession and Weissenberg) were consistent with the previously reported hexagonal lattice (Seifert & Klatyk, 1964). Systematic absences were: $hh\bar{2}hl$, $l \neq 2n$. The possible space groups are $P6_3/mnc$ (D_{6h}^4), $P6_32c$ (D_{3h}^4), and $P6_3mc$ (C_{6v}^4). Lattice constants and standard deviations obtained from a least-squares refinement of the angular settings of 12 reflections carefully centered on a Picker four-circle diffractometer are: $a = 7\cdot588(3)$, $c = 6\cdot506(4)$ Å; $V = 324\cdot41$ Å³.

These values give a calculated density of $4\cdot35$ g cm⁻³ for 2 $CsCrBr_3$ molecules per unit cell as compared to an average observed density of $4\cdot29(5)$ g cm⁻³ measured by the pycnometric method using bromobenzene.

A crystal, with the approximate shape of a hexagonal cylinder 0·32 mm in height and a base diameter of 0·22 mm, was sealed in a soft glass capillary in order to prevent air oxidation and mounted for the measurement of intensity data with the long dimension, [0001], parallel to the Picker 4-circle φ axis. Molybdenum radiation, $\lambda K\alpha = 0\cdot71069$ Å, with a graphite monochromator was used to collect the data. All positive $hkil$ intensity data

$h \geq k$ were measured as described previously (McPherson, Kistenmacher, Folkers & Stucky, 1972; Li & Stucky, 1972) to 85° in 2θ. Of these observations, 164 were used in subsequent least-squares analysis. Nine faces were used in the program $ORABS2$ (Wehe, Busing & Levy, 1962) to correct for absorption. The scattering factors for Cs^+, Cr^{2+} and Cl^- were those of Hanson & Pohler (1966). Anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) for Cs^0, Cr^0 and Cl^0 were taken from the compilation of Cromer (1965) and applied to the calculated structure factors.

Solution and refinement of the structure

The unit-cell space-group data and film data suggested that $CsCrBr_3$ was isomorphous with $CsCrCl_3$ (McPherson, Kistenmacher, Folkers & Stucky, 1972). A three-dimensional Patterson function was calculated and confirmed this configuration. The same considerations and structural ambiguities which were found for $CsCrCl_3$ also accordingly apply to $CsCrBr_3$. The following models were refined by the full-matrix least-squares method for the data set $hkil$; $h \geq k$. Counting statistics weights were used with $P = 0.04$.

Table 1. *Positional and anisotropic temperature parameters for* $CsCrBr_3$

	Cs	Cr	Br
x	⅓	0	0·1614 (5)
y	⅔	0	−0·1614
z	¼	−0·0046 (25)	0·2715 (18)
β_{11}	0·0090 (9)†	0·0080 (18)	0·0133 (15)
β_{22}	0·0090	0·0080	0·0133
β_{33}	0·03170 (23)	0·0049 (20)	0·0262 (14)
β_{12}	0·0045	0·0040	0·0077 (8)
β_{13}	0·0	0·0	0·0021 (18)
β_{23}	0·0	0·0	−0·0021

* Restrictions on the thermal parameters:
(i) for Cs and Cr, $\beta_{11} = \beta_{22} = 2\beta_{12}$; $\beta_{13} = \beta_{23} = 0$
(ii) for Br, $\beta_{11} = \beta_{22}$; $\beta_{23} = -\beta_{13}$.
The form of the anisotropic thermal ellipsoid is
exp $[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$.
† Numbers in parentheses here and in succeeding tables are the estimated standard deviations in the least significant digit.

(1) Ordered, space group $P6_3/mmc$.
(2) Disordered, space group $P6_3/mmc$.
(3) Ordered, space group $P\bar{6}2c$.
(4) Ordered, space group $P6_3mc$.
(5) Ordered, Br and Cr reflected through the mirror plane at $m = 0$, space group $P6_3mc$.

Because of the high correlation of the x and y parameters of the bromine atoms, it was not possible to refine model (3). The results of the refinement of the other four models are:

Model	$R_2 = \dfrac{(\sum w\lvert F_o - F_c\rvert^2)^{1/2}}{\sum wF_o^2}$	ERF (Standard deviation in an observation of unit weight)
(1)	0·068	2·02
(2)	0·068	1·97
(4)	0·054	1·82
(5)	0·056	1·84

As in the case of $CsCrCl_3$, the application of Hamilton's R-value test (Hamilton, 1965) suggests that model (4), $P6_3mc$ with h, k, l indexing, gives the best fit to the experimental data. Statistical tests suggested that the space group was centric; however, this is not surprising since the cesium atoms are related by a center of inversion in all models and the deviation from a centrosymmetric configuration is small for the Cr and Br atoms. Table 1 gives the final positional and thermal parameters. Table 2 gives a summary of the bond distances, bond angles and near-neighbor distances. Fig. 1 is a view of the anionic chain of octahedra, sharing faces. The observed and calculated structure factor amplitudes are compared in Table 3. The reflections which were judged as unobserved are marked with an asterisk.

Results and discussion

The important conclusions obtained from this structural investigation are as follows: (1) In contrast to the very significantly different structures found for $CsCuCl_3$ and $CsCuBr_3$, the environment of the Cr(II) ion is basically the same in $CsCrBr_3$ and $CsCrCl_3$. (2) There

Table 2. *Selected distances and angles of* $CsCrB_3$ *for model* (IV) *and of* $Cs_3Cr_2Br_9$

	Bond distances (Å)				Angles (°)	
	$CsCrBr_3$	$Cs_3Cr_2Br_9$			$CsCrBr_3$	$Cs_3Cr_2Br_9$
Cr–Br	2·574 (12)	2·417 (6)*		Br–Cr–Br	82·7 (6)	83·0 (3)
Cr–Br'	2·780 (13)	2·577 (9)†		Br'–Cr–Br'	91·1 (5)	91·4 (1)
				Br–Cr–Br'	92·9 (8)	93·7 (3)
				Cr–Br–Cr	74·7 (9)	

	Near-neighbor distances within an ion			Near-neighbor distances between ions	
	$CsCrBr_3$	$Cs_3Cr_2Br_9$			
Br–Br'	3·884 (6)	3·573 (3)*		Cs–Br	3·797 (10)
Br–Br	3·675 (5)	3·417 (5)†		Cs–Br'	4·076 (10)
Cr–Cr	3·253	3·417 (5)			

* Terminal
† Bridge

Table 3. *Observed and calculated structure factor amplitudes for* CsCrBr$_3$

K	L	OBS	CAL	K	L	OBS	CAL	K	L	OBS	CAL
		H= 0						2	0	30.4	28.6
0	6	50.7	48.4	0	0	69.6	62.2	2	1	68.3	70.4
0	8	27.7	29.4	0	1	153.8	148.6	2	2	48.2	47.9
0	10	10.4	10.9	0	2	110.6	99.2	2	3	52.3	52.2
0	12	10.3	6.7*	0	3	110.5	106.2	2	4	14.6	15.0
		H= 1		0	4	35.9	31.2	2	5	23.2	29.2
0	0	33.5	34.7	0	5	57.6	56.9	2	6	16.3	18.1
0	1	35.0	35.3	0	6	36.0	33.2	3	0	20.5	26.6
0	2	46.6	48.6	0	7	20.8	23.5	3	4	14.6	20.1
0	3	26.1	28.4	1	0	49.4	48.6	3	5	9.5	7.1*
0	4	20.8	22.9	1	1	15.0	13.2	4	0	14.0	18.1
0	5	16.6	18.4	1	3	14.3	11.2	4	1	39.8	45.3
0	6	24.6	23.0	1	4	33.9	35.3	4	2	24.8	32.4
0	7	12.0	9.4*	2	0	50.4	47.6	4	3	26.9	33.7
1	2	14.5	13.9	2	1	113.9	112.8	4	5	12.9	19.0
1	4	58.9	48.6	2	2	80.0	76.5	5	1	11.6	5.8*
1	6	9.6	11.2	2	3	86.0	82.3	5	2	15.8	20.1
1	8	17.3	18.7	2	4	21.2	24.8	5	6	9.7	11.7
1	10	10.6	7.4*	2	5	38.5	44.9	5	0	30.8	38.4
		H= 2		2	6	21.8	27.2	6	2	14.9	21.7
0	1	212.2	213.3	2	7	14.6	18.8	6	4	17.0	22.9
0	2	145.1	138.4	3	0	11.3	6.7*			H= 7	
0	3	146.2	142.0	3	2	34.6	38.0	0	0	25.5	19.7
0	4	41.2	40.7	3	6	15.7	20.7	0	1	23.0	23.7
0	5	79.3	72.6	4	0	96.8	105.0	0	3	17.8	19.3
0	6	45.2	41.8	4	2	59.0	65.4	0	4	20.8	17.0
0	7	25.8	29.2	4	4	14.7	19.7	1	0	27.5	28.3
1	1	25.6	20.9			H= 5		1	1	9.9	6.4*
1	2	62.5	55.9	0	0	10.4	7.4*	1	4	20.3	22.4
1	3	19.3	18.8	0	2	50.7	47.1	2	2	24.3	28.0
1	5	12.2	13.3	0	6	20.7	24.4	2	6	13.3	15.6
1	6	23.1	26.9	1	1	13.7	15.3	4	1	11.8	9.4*
2	0	234.9	230.3	1	2	34.4	33.8	6	0	10.5	6.2*
2	2	128.3	119.6	1	6	16.5	19.2			H= 8	
2	6	31.4	38.3	2	8	10.1	11.5	0	0	21.6	23.3
2	8	19.4	23.9	2	0	28.8	36.5	0	1	55.9	55.9
		H= 3		2	1	16.9	17.7	0	2	40.6	39.8
0	0	64.0	63.5	2	3	17.9	15.2	0	3	44.2	41.5
0	1	21.5	18.0	2	4	22.4	26.3	0	4	15.9	12.7
0	3	15.6	14.5	2	5	10.6	10.7	0	5	23.3	23.2
0	4	43.3	42.7	3	2	17.6	19.5	1	2	21.1	22.3
1	0	25.0	20.7	3	5	11.3	10.8	2	0	51.5	56.0
1	1	28.8	26.6	4	0	18.2	15.4	2	2	32.9	33.2
1	2	36.6	35.4	4	3	11.3	16.6	2	4	26.0	32.9
1	3	24.1	23.2	4	4	12.2	13.7	4	1	15.3	25.1
1	4	14.2	16.5	5	4	14.0	18.6	4	2	18.6	18.4
1	5	13.7	16.0			H= 6		4	3	13.7	18.9
1	6	15.1	19.3	0	0	138.8	132.5			H= 9	
2	0	32.5	28.8	0	2	82.3	82.9	0	0	16.4	21.9
2	1	34.1	30.9	0	4	75.4	74.4	0	7	9.5	4.4*
2	2	19.8	20.3	0	6	21.6	24.4	3	4	12.3	12.1
2	3	24.7	25.7	0	8	12.0	16.3			H= 10	
2	4	23.5	22.6	1	0	17.8	15.8	0	1	27.6	30.6
2	5	15.5	16.9	1	1	19.4	21.7	0	2	19.1	21.7
3	0	47.4	43.3	1	2	13.0	14.5	0	3	21.4	23.0
3	4	26.0	33.0	1	3	14.5	18.7	1	1	9.9	4.8*
3	8	10.7	14.6	1	4	15.1	13.9			H= 11	
3	10	9.8	5.4*	1	6	10.4	10.3	0	2	13.2	15.1
										H= 12	
								0	0	18.8	22.8

Fig. 1. A perspective view of the anionic chain in CsCrBr$_3$.

is no evidence of a static Jahn–Teller distortion in CsCrBr$_3$. The crystallographic site symmetry of the Cr(II) ion is required to be no lower than C_{3v} in all the models, so that the degeneracy of the e_g orbitals is not removed. (3) In all the models tested, there is a large component of the bromine atom anisotropic thermal motion which is nearly parallel to the c axis (Fig. 1). The E_{1g} vibration of the anionic chain involves motions of the bromide ions parallel to the c axis (Adams & Smardzewski, 1970) and is Jahn–Teller active (Moffitt & Thorson, 1957). This could explain both the anisotropic motion of the Br ions and the apparent absence of static Jahn–Teller distortion. (4) Model 4 suggests that there are two sets of halogen–Cr distances, a result also obtained for CsCrCl$_3$ and discussed previously. As in CsCrCl$_3$, we do not feel that we have conclusively demonstrated the physical reality of interacting CrBr$_3^-$ units and, in fact, favor instead some variation of the dynamical model suggested by (3) above. The difference between the two different Cr–Br distances, 0·206 Å, is approximately the same as the difference between the two different Cr–Cl distances, 0·199 Å, It is clear that CsCrBr$_3$ is not isostructural with CsNiBr$_3$ or CsMgBr$_3$, both of which have the CsNiCl$_3$ structure (Tishchenko, 1955).

The only other bromide compound of chromium(II) for which a structure has been reported is Cs$_2$Cr$_3$Br$_9$ (Saillant, Jackson, Streib, Folting & Wentworth, 1971) which consists of discrete units of [Cr$_2$Br$_9$]$^{2-}$. Table 3 compares some bond distances and bond angles of these two compounds.

The single-crystal electronic spectra of CsCrBr$_3$ are shown in Fig. 2 and the corresponding band assignments (McPherson, Kistenmacher, Folkers & Stucky, 1972) are given in Table 4. There appear to be only minor differences in the absorption spectra of CsCrBr$_3$ and CsCrCl$_3$. Polarization effects are enchanced in CsCrBr$_3$ and spin-forbidden bands are somewhat broader, probably as a result of a relaxation of the $\Delta S = 0$ selection rule in CsCrBr$_3$ due to the greater covalency of the Cs–Br bond. Single-crystal spectroscopic studies of CsNiCl$_3$ and CsNiBr$_3$ (McPherson & Stucky, 1972) clearly show a shift to lower energies for the
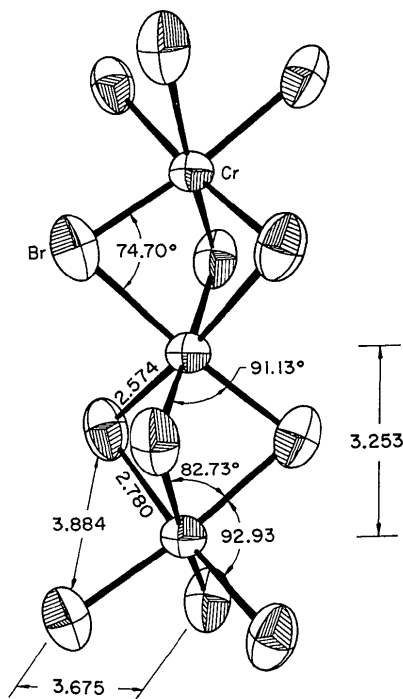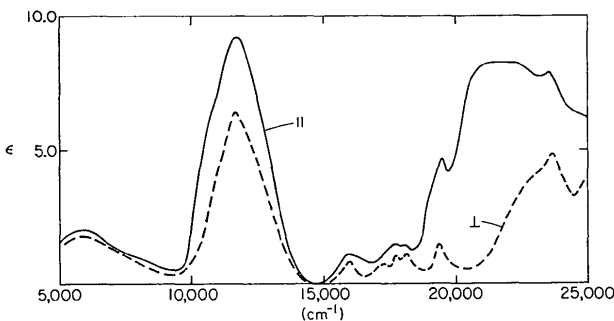

Fig. 2. Near infrared–visible spectra of CsCrBr$_3$ at liquid nitrogen temperature.

bands of $CsNiBr_3$ compared to those of $CsNiCl_3$. This was not observed for $CsCrCl_3$ and $CsCrBr_3$.

Table 4. *Band assignments for* $CsCrBr_3$

Observed energies		Excited states
$CsCrBr_3$	$CsCrCl_3$	
5·900 cm⁻¹	6·500 cm⁻¹	$^3T_{1g}(H)$
11·500	11·450	$^5T_{2g}(D)$
15·800	15·900	$^3E_g(H)$
17·100	16·900	$^3T_{1g}(P), {}^1E_g(I)$
17·600	17·500	$^3T_{2g}(H)$
18·100		$^3A_{2g}(F)$
19·300	18·700	$^3A_{1g}(G)$
20·900*	21·000	
22·000 (sh)†	21·000	$^1A_{1g}(I), {}^3E_g$ $^3E_g(G)$
23·400	23·200	$^1A_{2g}(I), {}^1T_2(D)$

* Strongly polarized.

† *sh* designates a shoulder.

The broad strongly polarized band around 22·000 cm⁻¹ is assigned as a double excitation of the allowed ($^5E_g{\rightarrow}^5T_{2g}$) transition. The somewhat greater breadth and intensity of this band indicates that exchange coupling is stronger in $CsCrBr_3$ than in $CsCrCl_3$, despite the fact that the Cr–Cr distance is longer in $CsCrBr_3$ (3·253 Å) than in $CsCrCl_3$ (3·112 Å). This suggests that, in this one-dimensional complex, the coupling mechanism is *via* a superexchange process through the halogen bridges.

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Structure de NdSBr et des Sulfobromures de Terres Rares Isotypes*

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Sulfobromides of Pr (β form), Nd, Sm, Gd and Tb are monoclinic. On account of a twinning the structure must be described in a cell whose a parameter is three times smaller than the ones first proposed. Cell dimensions of NdSBr are: $a = 6·94$; $b = 6·91$; $c = 7·05$ Å; $\gamma = 99·28°$; space group is $P2_1/b$. There are four formula units in the unit cell. The intensities have been collected with a counter diffractometer using Mo $K\alpha$ radiation. The structure was solved by the heavy-atom method using Patterson and Fourier calculations and refined by least-squares methods with anisotropic thermal parameters to an R index of 0·062. The neodymium atom is coordinated to seven atoms (4S and 3Br). The structure consists of layers of bromine atoms alternating with layers of Nd_4S tetrahedra.

Le sulfobromure de néodyme a été préparé pour la première fois en 1967 au laboratoire de chimie minérale de la Faculté de Pharmacie (Dagron, Etienne & Laruelle, 1967). Il fait partie d'un groupe de 5 sulfobromures monocliniques isotypes: PrSBr (β), NdSBr, SmSBr, GdSBr et TbSBr (Dagron & Thevet, 1970).

La préparation et les paramètres de ces sulfobromu-