

Structure of the Dimer Compounds $\text{Cs}_3R_2\text{Br}_9$ ($R = \text{Tb, Dy, Ho, Er, Yb}$) at 8 and 295 K Studied by Neutron Diffraction

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The structure of the dimer compounds $\text{Cs}_3R_2\text{Br}_9$ ($R = \text{Tb, Dy, Ho, Er, Yb}$) has been determined by powder neutron diffraction at 8 and 295 K. Rietveld refinements within the trigonal space group $R\bar{3}c$ show an anisotropic thermal expansion of the lattice parameters. With increasing temperature the dimeric units $R_2\text{Br}_9^{3-}$ become increasingly isolated and separated in the lattice. The intradimer distances can be rationalized with simple electrostatic arguments. © 1989 Academic Press, Inc.

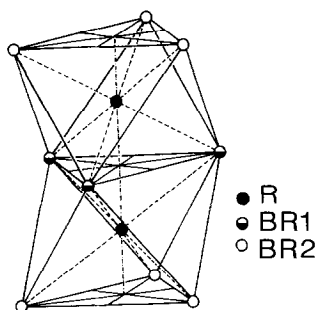
Introduction

Compounds of the general composition $\text{Cs}_3R_2\text{Br}_9$ ($R = \text{Tb, Dy, Ho, Er, Yb}$) have only recently become available for physical investigation. Their synthesis and structural characterization were reported in (1, 2). They form a very interesting class of dimer compounds which can be used as model systems for the study of exchange interactions. In the course of a systematic investigation of such interactions by inelastic neutron scattering in the above series of compounds (3, 4) we found it necessary to explore their structural properties at 295 and 8 K in some detail.

The title compounds all crystallize in the trigonal space group $R\bar{3}c$ with $Z = 6$, in the so-called $\text{Cs}_3\text{Tl}_2\text{Cl}_9$ structure (5). The structure contains the dimeric units $R_2\text{Br}_9^{3-}$, which are built up of two face-sharing

$R\text{Br}_6^{3-}$ octahedra as shown in Fig 1. The same type of dimer is found in the closely related $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ structure, space group $P6_3/mmc$ (6). Both these structure types can be considered as defect structures of the hexagonal CsNiF_3 structure (7), with only two-thirds of the trivalent sites occupied. This is shown in Fig. 2, and it is seen that the distribution of vacancies determines the dimer structure type.

The question of whether the dimeric $R_2\text{Br}_9^{3-}$ units can be considered as separate entities in these lattices is very interesting. The answer depends very much on the point of view and the experimental property under consideration. In the closely related compound $\text{Cs}_3\text{Cr}_2\text{Br}_9$, which was investigated in great detail by inelastic neutron scattering, a small interaction between adjacent dimers was found to dominate the magnetic properties below 2 K (8).

FIG. 1. The structure of the dimer $R_2Br_9^{3-}$.

At higher temperatures, however, the behavior was typical of a compound containing isolated $Cr_2Br_9^{3-}$ dimers. In the title compounds both intra- and interdimer exchange interactions are an order of magnitude smaller, so that any cooperative effects would be expected at much lower temperatures. In the present study the evolution of interatomic distances with temperature will be shown to be relevant to the question of the "molecular" nature of the $R_2Br_9^{3-}$ units. Powder neutron diffraction was the method of choice for this study, because both the preparation of polycrystalline samples and their cooling to 8 K are easily achieved.

Experimental

Polycrystalline samples of $Cs_3R_2Br_9$ ($R = Tb, Dy, Ho, Er, Yb$) were investigated at

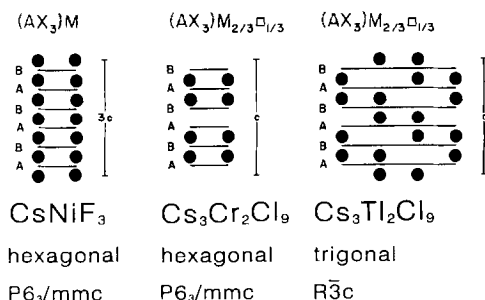


FIG. 2. $Cs_3Cr_2Cl_9$ and $Cs_3Tl_2Cl_9$ considered as defect structures of $CsNiF_3$. The (AX_3) sheets are piled up in the sequence $ABAB \dots$

$T = 8$ K and $T = 295$ K with use of the multidetector powder diffractometer DMC at the reactor Saphir, Würenlingen. The samples were enclosed under He atmosphere into cylindrical vanadium containers of 50 mm height and diameters of 8 mm ($R = Tb, Ho, Er$) and 10 mm ($R = Yb$). For the highly neutron-absorbing compound $Cs_3Dy_2Br_9$ a similar annular container of 10 mm outer diameter and 6 mm inner diameter was used. The incident neutron wavelengths $\lambda = 1.713$ Å ($R = Ho, Er$) and $\lambda = 1.708$ Å ($R = Tb, Dy, Yb$) were obtained from a Ge(3,1,1) monochromator. The angular collimations were $10'/-12'$ from monochromator to detector. The samples were oscillated by $\pm 180^\circ$ during the measurements to reduce effects caused by preferred orientation.

The intensities were corrected for absorption according to the results from transmission experiments ($\mu R = 0.161, 0.176, 0.261, 0.217$ for $R = Tb, Ho, Er, Yb$, respectively, and $\mu = 0.217$ mm $^{-1}$ for $R = Dy$).

Results

Figure 3 shows as an example the diffraction pattern for $Cs_3Ho_2Br_9$ obtained at $T = 8$ K with a step width $\Delta(2\theta) = 0.1^\circ$. The diffraction patterns of the other compounds are very similar; they were analyzed by the Rietveld profile method using the following scattering lengths (10^{-12} cm): Cs 0.542, Br 0.679, Tb 0.738, Dy 1.690, Ho 0.808, Er 0.803, Yb 1.240 (9). The resulting structural parameters are listed in Tables I to III. Impurity phases were found to contribute less than 1% ($R = Tb, Ho, Er$) and less than 5% ($R = Dy, Yb$) to the total scattering. Their relative intensities increase strongly with increasing scattering length of the rare-earth ions, so that we only analyzed the lattice constants of the compounds $Cs_3Dy_2Br_9$ and $Cs_3Yb_2Br_9$. In all the observed neutron-diffraction patterns we were able

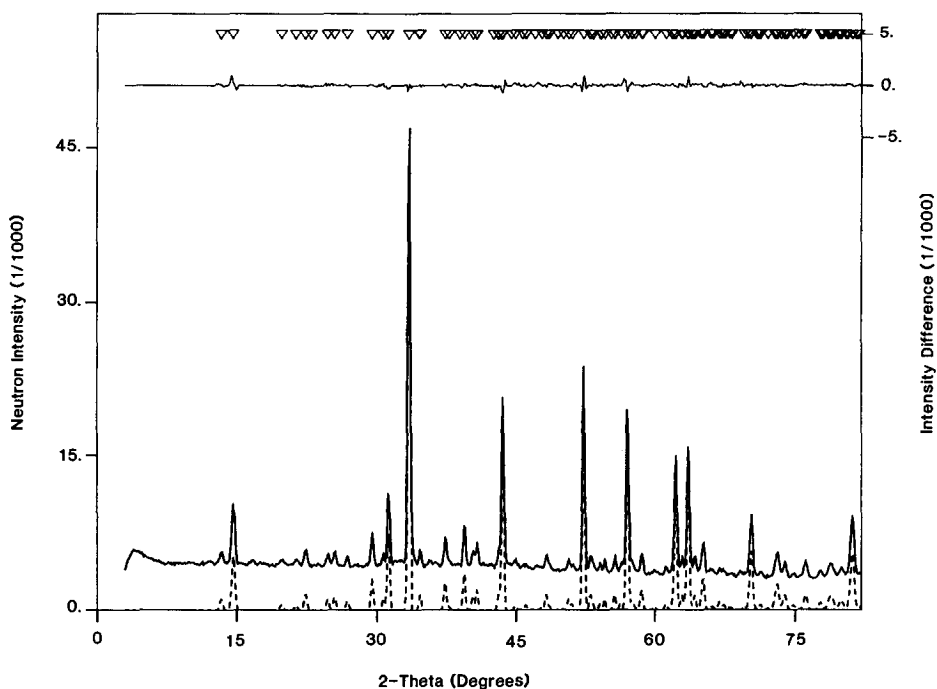


FIG. 3. Observed (full line) and calculated (dashed line) neutron-diffraction pattern of $\text{Cs}_3\text{Ho}_2\text{Br}_9$ at 8 K for $\lambda = 1.713 \text{ \AA}$. The difference between observed and calculated intensities is shown at the top of the figure. Peak positions are marked by triangles. Because of an impurity phase contribution the reflections $(3, 1, 2)$, $(1, 3, -2)$ ($2\theta = 32.47^\circ$), and $(0, 4, 2)$ ($2\theta = 35.78^\circ$) with calculated intensities of less than 0.05% of the strongest peak were not included in the fit.

TABLE I
LATTICE CONSTANTS AND MOLAR VOLUMES (V_M) OF $\text{Cs}_3R_2\text{Br}_9$ AT 8 AND 295 K
(SPACE GROUP $R\bar{3}c$, $Z = 6$)

R:	Tb	Dy	Ho	Er	Yb
$T = 8 \text{ K}$					
a (Å)	13.541(9)	13.489(9)	13.467(9)	13.440(9)	13.382(9)
c (Å)	19.07 (2)	19.09 (2)	19.09 (2)	19.07 (2)	19.07 (2)
c/a	1.408(3)	1.415(3)	1.418(3)	1.419(3)	1.425(3)
V_M (cm ³)	304.0 (8)	301.9 (8)	301.0 (8)	299.5 (8)	296.8 (8)
$T = 295 \text{ K}$					
a (Å)	13.668(9)	13.623(9)	13.603(9)	13.571(9)	13.515(9)
c (Å)	19.36 (2)	19.36 (2)	19.36 (2)	19.35 (2)	19.33 (2)
c/a	1.416(3)	1.421(3)	1.423(3)	1.426(3)	1.430(3)
V_M (cm ³)	314.3 (8)	312.3 (8)	311.4 (8)	309.8 (8)	306.8 (8)
Δa (%) ^a	0.93(14)	1.00(14)	1.01(14)	0.97(14)	0.99(14)
ΔC (%)	1.50(21)	1.40(21)	1.41(21)	1.45(21)	1.36(21)
ΔV_M (%)	3.39(54)	3.44(54)	3.46(54)	3.44(54)	3.37(54)

^a $\Delta = 295 - 8 \text{ K}$.

TABLE II

ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS OF Cs₃R₂Br₉ (*R* = Tb, Ho, Er) AT *T* = 8 K OBTAINED FROM A RIETVELD ANALYSIS OF NEUTRON POWDER DATA

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Cs ₃ Tb ₂ Br ₉				
(18e) Cs	0.6607(14)	0	0.25	0.6
(12c) Tb	0	0	0.6479(6)	0.1
(18e) Br1	0.1589(9)	0	0.25	0.6
(36f) Br2	0.1820(6)	0.1747(7)	0.0851(6)	0.6
<i>R</i> _{wp} = 0.076,	<i>R</i> ₁ = 0.048,	<i>R</i> _{exp} = 0.038		
Cs ₃ Ho ₂ Br ₉				
(18e) Cs	0.6618(14)	0	0.25	0.6
(12c) Ho	0	0	0.6490(5)	0.1
(18e) Br1	0.1578(8)	0	0.25	0.6
(36f) Br2	0.1809(5)	0.1742(8)	0.0849(6)	0.6
<i>R</i> _{wp} = 0.071,	<i>R</i> ₁ = 0.037,	<i>R</i> _{exp} = 0.037		
Cs ₃ Er ₂ Br ₉				
(18e) Cs	0.6610(17)	0	0.25	0.6
(12c) Er	0	0	0.6490(6)	0.1
(18e) Br1	0.1588(11)	0	0.25	0.6
(36f) Br2	0.1791(7)	0.1737(10)	0.0856(7)	0.6
<i>R</i> _{wp} = 0.089,	<i>R</i> ₁ = 0.045,	<i>R</i> _{exp} = 0.046		

Note. The *R* values are defined in Ref. (11).

to identify the intense (001) and (200) reflections of the impurity phase ROBr (tetragonal PbFCl-type structure, space group *P4/nmm*, Ref. (10)). The structural data obtained for Cs₃Tb₂Br₉ have an inherent uncertainty due to the almost identical scattering lengths of Tb and Br.

The Debye–Waller factors were kept fixed at the values listed in Tables II and III; they represent the average of the Debye–Waller factors determined for each sample individually. More precise values require neutron diffraction experiments with increased *Q*-resolution in an extended 2θ-range. At 295 K the Debye–Waller factors determined in the present work are in reasonable agreement with the results obtained for trigonal Cs₃In₂Cl₉ (space group *R3c*) by X-ray diffraction on a single crystal (12) which gave the following *B* values (in

Å²): Cs 2.3, In 1.5, C11 1.9, C12 2.2. In this study the thermal parameters of In and C11 turned out to be strongly anisotropic.

The room-temperature lattice constants *a* and *c* are in excellent agreement with the X-ray data (2). The lanthanide contraction results in a decrease of the lattice constants with increasing atomic number, which is more pronounced for *a* than for *c*; see Table I. The thermal expansion is anisotropic. Upon raising the temperature from 8 to 295 K the lattice constants *a* and *c* increase typically by 1.0 and 1.4%, respectively.

Discussion

The R₂Br₃³⁻ dimer units are of particular interest. Table IV reveals that the distances to the bridging bromide ions *R*–Br1 are typically 0.2 Å bigger than the terminal *R*–Br2

TABLE III

ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS OF Cs₃R₂Br₉ AT *T* = 295 K OBTAINED FROM A RIETVELD ANALYSIS OF NEUTRON POWDER DATA

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Cs ₃ Tb ₂ Br ₉				
(18e) Cs	0.6561(20)	0	0.25	2.2
(12c) Tb	0	0	0.6477(7)	0.4
(18e) Br1	0.1551(13)	0	0.25	2.2
(36f) Br2	0.1798(9)	0.1729(11)	0.0871(6)	2.2
<i>R</i> _{wp} = 0.110,	<i>R</i> ₁ = 0.081,	<i>R</i> _{exp} = 0.049		
Cs ₃ Ho ₂ Br ₉				
(18e) Cs	0.6605(18)	0	0.25	2.2
(12c) Ho	0	0	0.6499(5)	0.4
(18e) Br1	0.1557(11)	0	0.25	2.2
(36f) Br2	0.1780(7)	0.1708(10)	0.0869(7)	2.2
<i>R</i> _{wp} = 0.089,	<i>R</i> ₁ = 0.062,	<i>R</i> _{exp} = 0.051		
Cs ₃ Er ₂ Br ₉				
(18e) Cs	0.6593(21)	0	0.25	2.2
(12c) Er	0	0	0.6497(7)	0.4
(18e) Br1	0.1558(12)	0	0.25	2.2
(36f) Br2	0.1769(9)	0.1706(12)	0.0876(7)	2.2
<i>R</i> _{wp} = 0.105,	<i>R</i> ₁ = 0.081,	<i>R</i> _{exp} = 0.055		

Note. The *R* values are defined in Ref. (11).

TABLE IV

TEMPERATURE EVOLUTION OF INTERATOMIC DISTANCES r WITHIN THE $R_2\text{Br}_9^{3-}$ SUBUNITS ($R = \text{Tb, Ho, Er}$)

	$T = 8 \text{ K} (\text{Å})$	$T = 295 \text{ K} (\text{Å})$	$\Delta r/r^a (\%)$
$\text{Cs}_3\text{Tb}_2\text{Br}_9$			
Tb–Tb(1×)	3.894(19)	3.963(28)	+1.8
Tb–Br1(3×)	2.903(11)	2.902(16)	0.0
Tb–Br2(3×)	2.697(9)	2.682(13)	–0.6
Br1–Br1(2×)	3.728(20)	3.673(30)	–1.5
Br1–Br2(2×)	3.853(11)	3.853(16)	0.0
–Br2(2×)	3.934(11)	3.931(16)	0.0
Br2–Br2(2×)	4.185(11)	4.178(17)	–0.2
$\text{Cs}_3\text{Ho}_2\text{Br}_9$			
Ho–Ho(1×)	3.858(17)	3.874(22)	+0.4
Ho–Br1(3×)	2.870(10)	2.870(13)	0.0
Ho–Br2(3×)	2.687(8)	2.669(11)	–0.7
Br1–Br1(2×)	3.680(19)	3.667(25)	–0.4
Br1–Br2(2×)	3.848(11)	3.841(11)	–0.2
–Br2(2×)	3.921(10)	3.921(13)	0.0
Br2–Br2(2×)	4.144(11)	4.111(14)	–0.8
$\text{Cs}_3\text{Er}_2\text{Br}_9$			
Er–Er(1×)	3.852(21)	3.881(26)	+0.7
Er–Br1(3×)	2.875(13)	2.870(15)	–0.1
Er–Br2(3×)	2.662(10)	2.647(12)	–0.6
Br1–Br1(2×)	3.697(24)	3.662(29)	–0.9
Br1–Br2(2×)	3.837(14)	3.828(15)	–0.3
–Br2(2×)	3.896(13)	3.898(15)	–0.1
Br2–Br2(2×)	4.108(14)	4.085(17)	–0.6

^a $\Delta r = r(295 \text{ K}) - r(8 \text{ K})$.

Note. The relative uncertainties are typically one-third of the standard deviations given in parentheses.

distances. The R –Br1 bonds, which are 2.90, 2.87, and 2.87 Å at 295 K for the Tb^{3+} , Ho^{3+} , and Er^{3+} compounds, respectively, are very close to the respective sums of ionic radii (13): 2.88, 2.85, and 2.84 Å. The R –Br2 bond lengths, on the other hand, are only 93% of the sum of ionic radii. This can be rationalized with simple electrostatic arguments as follows. The anions X^- provide a shielding between the positive charges of the A^+ and M^{3+} ions. But within the $M_2X_9^{3-}$ bioctahedra the M^{3+} – M^{3+} repulsion is insufficiently shielded by the three $X1^-$ ions and, as a consequence, there is a shift of the M^{3+} ions toward the terminal $X2^-$ ions. This is in contrast to $\text{Cs}_3M_2\text{Cl}_9$ compounds in which the M^{3+} ion has 5d or 6d electrons such as $M = \text{Mo, W}$. These are well-docu-

mented examples of direct metal–metal bonds in the dimers (15, 16).

A comparison of the temperature dependence of intradimer (Table IV) and interdimer (Table V) distances in the title compounds is very revealing. Within the $R_2\text{Br}_9^{3-}$ dimers there is a slight overall contraction between 8 and 295 K. In contrast the shortest distances between terminal Br^- ions on neighboring dimers increase by 2.2% (Ho) and 2.4% (Tb, Er). In addition the mean distance between the Cs^+ ion and the 12 Br^- neighbors increases by 1.4% (Tb, Ho, Er) between 8 and 295 K. This means that with increasing temperature the $R_2\text{Br}_9^{3-}$ units become increasingly isolated and separated in the lattice, or, in other words, their “molecular” character increases. Although the temperature variation of the above distances is almost within the standard deviation reflecting absolute errors, consideration of possible systematic errors in our measurements would lead to smaller relative errors and thus a strengthening of our arguments.

We now proceed to compare some structural features of hexagonal and trigonal $A_3M_2X_9$ -type compounds. Analyzing X-ray powder data Stranger *et al.* (16) investigated the effects of changing relative sizes of A and X in the hexagonal compounds

TABLE V
TEMPERATURE EVOLUTION OF SOME SELECTED INTERDIMER DISTANCES

	$T = 8 \text{ K} (\text{Å})$	$T = 295 \text{ K} (\text{Å})$	$\Delta r/r^a (\%)$
Mean distance Cs–Br(12×)			
$\text{Cs}_3\text{Tb}_2\text{Br}_9$	3.886(25)	3.942(32)	+1.4
$\text{Cs}_3\text{Ho}_2\text{Br}_9$	3.877(21)	3.932(22)	+1.4
$\text{Cs}_3\text{Er}_2\text{Br}_9$	3.872(16)	3.927(21)	+1.4
Terminal Br2–Br2(2×)			
$\text{Cs}_3\text{Tb}_2\text{Br}_9$	4.047(18)	4.145(25)	+2.4
$\text{Cs}_3\text{Ho}_2\text{Br}_9$	4.030(17)	4.118(14)	+2.2
$\text{Cs}_3\text{Er}_2\text{Br}_9$	4.035(21)	4.130(23)	+2.4

^a $\Delta r = r(295 \text{ K}) - r(8 \text{ K})$.

A₃Mo₂X₉ (A = K, Rb, Cs, Me₄N; X = Cl, Br). In Cs₃Mo₂Cl₉ (*P6₃/mmc*) the cesium and chloride ions are similar in size, with ionic radii 1.88 and 1.81 Å, respectively (13). They form an almost perfect hexagonal closed-packed layer. In (Me₄N)₃Mo₂Cl₉ with increased size of the cation relative to the anion the space group *P6₃/mmc* is maintained. Decreasing the cation size relative to the anion lowers the space group symmetry from *P6₃/mmc* to *P6₃/m* for K₃Mo₂Cl₉. A rotation of the Mo₂Cl₃²⁻ dimers about the Mo–Mo axis reduces the K(1)–Cl bond lengths. The same observations apply to the bromide series.

In the following we restrict our discussion to A = Cs and X = Cl, Br. Within a range of similar sizes of cations A and anions X we can investigate the effects of changing the relative sizes of M and X. The decisive factor for the occurrence of the hexagonal (*P6₃/mmc*) or trigonal (*R3c*) phase in the Cs₃M₂Cl₉ and Cs₃M₂Br₉ compounds is the ratio of the ionic radii *I_M/I_X*. According to Table VI hexagonal compounds have an *I_M/I_X* ratio smaller than a critical value of about 0.40. An *I_M/I_X* value of 0.50 might be an upper limit for stability of the trigonal compounds. Attempts to produce compounds like Cs₃Dy₂Cl₉ and Cs₃Tb₂Cl₉ failed so far.

TABLE VI

I_M/I_X RATIOS FOR SEVERAL HEXAGONAL AND TRIGONAL Cs₃M₂Cl₉ AND Cs₃M₂Br₉ COMPOUNDS^a

Hexagonal (<i>P6₃/mmc</i>)			Trigonal (<i>R3c</i>)		
Ref.	Compounds	<i>I_M/I_X</i>	Ref.	Compounds	<i>I_M/I_X</i>
(14)	Cs ₃ Cr ₂ Br ₉	0.31	(2)	Cs ₃ Sc ₂ Cl ₉	0.40
(6)	Cs ₃ Cr ₂ Cl ₉	0.34	(12)	Cs ₃ In ₂ Cl ₉	0.44
(14)	Cs ₃ Mo ₂ Br ₉	0.34	(2)	Cs ₃ Rl ₂ Br ₉ ^b	0.44–0.49
(17)	Cs ₃ V ₂ Cl ₉	0.35	(2)	Cs ₃ R2 ₃ Cl ₉ ^c	0.47–0.49
(14)	Cs ₃ Mo ₂ Cl ₉	0.37	(5)	Cs ₃ Tl ₂ Cl ₉	0.49
(2)	Cs ₃ Sc ₂ Br ₉	0.37	(2)	Cs ₃ Y ₂ Cl ₉	0.49
(12)	Cs ₃ In ₂ Br ₉	0.40			

^a Ionic crystal radii from Ref. (13).

^b R1 = Lu, Yb, Tm, Er, Ho, Dy, Tb, Gd, Sm.

^c R2 = Lu, Yb, Tm, Er, Ho.

TABLE VII

COMPARISON OF INTRADIMERIC DISTANCES IN RELATIVE UNITS FOR TRIGONAL A₃M₂X₉ COMPOUNDS AT 295 K

	Cs ₃ Tb ₂ Br ₉ ^a	Cs ₃ Ho ₂ Br ₉ ^a	Cs ₃ Er ₂ Br ₉ ^a	Cs ₃ In ₂ Cl ₉ ^b
<i>M–M</i> ^c (1×)	1.01	0.99	0.99	1.00
<i>M–X1</i> ^d (3×)	1.01	1.01	1.10	1.02
<i>M–X2</i> ^d (3×)	0.93	0.93	0.93	0.93
<i>X1–X1</i> ^d (2×)	0.94	0.93	0.93	0.93
<i>X1–X2</i> ^d (2×)	0.98	0.98	0.98	0.98
(2×)	1.00	1.00	0.99	0.99
<i>X2–X2</i> ^d (2×)	1.07	1.05	1.04	1.03

^a Neutron powder diffraction (this work).

^b X-ray single crystal measurement (12).

^c Distances in units of 2*I_X* (13).

^d Distances in units of the sum of the ionic radii (13).

The trigonal compounds Cs₃Tb₂Br₉, Cs₃Ho₂Br₉, Cs₃Er₂Br₉, and Cs₃In₂Cl₉ (12) exhibit chirality in the sense that the X2 planes are twisted around the *M–M* axis by 2.0°, 2.0°, 1.8°, and 1.0°, respectively. This reduces the Cs–X(2) bond lengths and increases the interdimeric X(2)–X(1) distances without changing the intradimeric *M–X*(1) and *M–X*(2) bond lengths. For the hexagonal compounds with space group *P6₃/mmc* chirality is forbidden by symmetry.

Intradimer distances for the trigonal compounds Cs₃R₂Br₉ (R = Tb, Ho, Er) and Cs₃In₂Cl₉ at 295 K are compared in Table VII. The *M–M* distances turn out to be almost independent of *I_M*. Empirically we find that the relationships

$$d_{M-M} = 2 \cdot I_X \quad (1)$$

and

$$d_{M-X1} = I_M + I_X \quad (2)$$

are valid within 2%. *X1–X1* and *M–X2* distances amount to 93% of the sum of the ionic radii. Equations (1) and (2) suggest that only the lattice parameter *a* should be sensitive to the well-known lanthanide contraction, which is nicely substantiated by the experiments; see Table I.

No temperature dependence of the *R–*

Br1 distances (Eq. (2)) is observed for the title compounds. With increasing temperature the $R-R$ separation increases and produces a decrease of the $R-Br2$, $Br1-Br1$, and $Br2-Br2$ distances (Table IV).

For the hexagonal compounds $Cs_3M_2Cl_9$ ($M = Cr, Mo, W$) (15, 16) Eq. (2) is still valid, whereas the $M-M$ separations are significantly smaller than expected from Eq. (1): in units of $2I_X$ they are 0.87, 0.74, 0.69, respectively. The intradimer distances $M-X2$, $X1-X1$, and $X2-X2$ are very sensitive to changes of the $M-M$ separations.

In $Cs_3W_2Cl_9$ and $Cs_3Mo_2Cl_9$, with $M-M$ separations of 2.50 and 2.66 Å, respectively, there are genuine metal-metal bonds and the compounds are diamagnetic due to a pairing of all the electrons (16, 14). In contrast, there is a slight repulsion of the two M ions in $Cs_3Cr_2Cl_9$ as well as the title compounds. As a consequence they can be treated as weakly exchange-coupled dimers. It is not a priori clear whether the exchange is due to direct overlap of the magnetic orbitals on the metal ions or whether a superexchange pathway through the bridging halide ions is more efficient.

Temperature-dependent structural information for other trigonal $Cs_3R_2X_9$ ($X = Cl, Br$) compounds would be highly desirable for a rigorous check of the empirical laws derived in the present work as well as an extension of the above considerations.

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