olution of the racemic cation has been proposed and defended.[18] Supporting evidence can be found in stereospecific solute-solvent studies, in which preferred solubilities and packings were reported,[31] as well as in circular dichroism studies wherein a model was proposed in which two hydroxyl and one carboxyl oxygen of *d*-tartrate gave the best "fit" to the face of $Co(en)_3$.[32] Of course, *l*-tartrate is also capable of forming a three-membered bite, and the reason why *d*-tartrate preferentially resolves $\Lambda(\delta\delta\delta)$-$Co(en)_3$ is unclear. In published studies of the structures of *both* the preferred and nonpreferred diastereomeric salts of $Co(en)_2(ox)$ and $Co(en)(gly)_2$, it was found that the preferred (less soluble) salt was more tightly packed and included spiral chains of anions.[15] The spiraled chain of waters and chlorides may thus play an equally important role, combined with the handedness of the tartrate, in preferentially selecting $\Lambda(\delta\delta\delta)$-$Co(en)_3$ in the present case. It seems obvious, however, that this explanation of optical resolution may not necessarily be the dominant factor, as there are too many uncertain parameters involved to allow a definite conclusion from the relatively few investigations into this phenomenon which have so far been reported. A good example of an alternative method of resolution by *d*-tartrate can be found in the structure of $Co(tame)_2Cl(tart)\cdot5.4H_2O$, a portion of which is shown in Figure 5 (with permission of the authors).[20] In this case, the three axial hydrogens on each face of the cation, which allowed formation of the "local block" discussed earlier, are unavailable for bonding. The peripheral hydrogens are still available however, and the tartrates bind at these sites, but with only two-point attractions instead of three. The reason for this could be a more unfavorable angling of the equatorial hydrogens or a thermodynamically favorable arrangement by tartrate to take advantage of the greater number of equivalent "faces" presented by several neighboring cationic units. But whatever the rationale, it still demonstrates that resolution by *d*-tartrate is not limited to a single mechanism but instead is a complex and variable scheme which may have as many modes of interaction as there are resolved compounds containing tartrate, each being a unique energy minimum for the materials involved.

A final, interesting observation which has been made by many investigators who have resolved $Co(en)_3^{3+}$ with tartrate is that, after precipitation of large amounts of crystals of the preferred enantiomer, the solution thickens gradually until it forms what Sargeson refers to as the "nasty orange glue".[33] This presumably amorphous substance involving *d*-tartrate and $\Delta(\lambda\lambda\lambda)$-$Co(en)_3$ could conceivably be a polymeric chain involving pairs of two-point contacts as in $Co(tame)_2Cl(tart)\cdot5.4H_2O$. But for some reason, the opposite handedness of the cation prevents the degree of close packing found in the preferred enantiomer complex.

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Registry No. $[Co(en)_3](d\text{-tart})Cl\cdot5H_2O$, 71129-32-3.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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Metal-Metal Repulsion and Bonding in Confacial Bioctahedra. Crystal Structures of $Cs_3Y_2I_9$ and $Cs_3Zr_2I_9$ and Comparison with Related Phases

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The title compounds were synthesized by reaction of CsI_3 and Y or CsI, Zr, and ZrI_4 at 750-850 °C in welded Ta containers. Both were shown to have the $Cs_3Cr_2Cl_9$-type structure, space group $P6_3/mmc$. Positional and thermal parameters were established by full-matrix least-squares refinement of single-crystal diffractometer data. Data for the structures and the refinements of $Cs_3Y_2I_9$ and $Cs_3Zr_2I_9$ are respectively $a = 8.406$ (1) and 8.269 (1) Å, $c = 21.280$ (5) and 19.908 (3) Å, $R = 0.050$ and 0.082, and $R_w = 0.082$ and 0.077 for 328 and 610 independent reflections with $2\theta \leq 50$ and 60° collected with Mo $K\alpha$ radiation. The transition from the yttrium to the zirconium compound is accompanied by a decrease of the metal-metal distance in the $M_2I_9^{3-}$ confacial bioctahedra from 4.052 (9) to 3.129 (4) Å owing to the formation of a Zr-Zr bond. Correspondingly large changes occur in the internal angles in the M-I-M bridges. Parameters of five M_2X_9 groups in the $Cs_3Cr_2Cl_9$-type structure and of $CsCdCl_3$, all of which lack M-M bonds, are considered in terms of a model which recognizes the existence of both longer M-X bridge bonds and comprise bridge angles. Nonbonding repulsion between M atoms is concluded to not be a significant factor in these structures. The effects of packing and metal-metal bonding are also considered.

Introduction

The collection of enneahalodimetalates(III), $A_3M_2X_9$, has been growing with the development of new techniques for their preparation.[3,4] However, very little is known about iodides of this stoichiometry, and little quantitative data, i.e., on their crystal structures, are available. Only $Cs_3Bi_2I_9$[5,6] and $Cs_3Sb_2I_9$,[6,7] both crystallizing from aqueous solution, have been investigated by means of single-crystal X-ray techniques.

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These have the $Cs_3Cr_2Cl_9$-type structure[8] with (*chc*)$_2$ stacking of CsI_3 layers (alternative description: ABACBC). All the face-sharing I_6 octahedra are filled with bismuth or antimony to yield "isolated" confacial bioctahedra $Bi_2I_9^{3-}$ or $Sb_2I_9^{3-}$. Coulomb repulsion between the tripositive metal atoms in these and other $M_2X_9^{3-}$ groups has been said[9] to lead to enlarged M–X distances and angles at the bridging anions compared with those to the terminal ones.

In the series $Cs_3Cr_2Cl_9$, $Cs_3Mo_2Cl_9$,[10] $K_3W_2Cl_9$[11] only the principal quantum number of the transition metal changes and not the number of valence electrons (d^3). In this case the metal–metal distance within the bioctahedra is found to shorten from 3.12 (Cr) to 2.41 Å (W), indicating the presence of substantial metal-metal bonding in the latter case. In contrast nothing seems to be known about a simpler $Cs_3M_2X_9$ series in which one electron per M atom is added to a diamagnetic matrix to allow the formation of a metal bonded species. Therefore investigation of the pair $Cs_3Y_2I_9/Cs_3Zr_2I_9$, where the M^{3+} ions have $4d^0$ and $4d^1$ configuration, respectively, was undertaken after $Cs_3Zr_2I_9$ was found as a product in ongoing studies of reactions in the reduced part of the Cs/Zr/I ternary system. Binary reduced halides of zirconium are now known with formal oxidation states +1 to +3,[12-15] but only very recently have the first examples of ternary reduced halides been established, $CsZr_6I_{14}$ with $Zr_6I_{14}^-$ clusters[16] and $Cs_3Zr_2I_9$.

It has been predicted[4] from volume considerations that enneaiododimetalates(III) of the rare earth elements, yttrium, and scandium should crystallize with the $Cs_3Cr_2Cl_9$-type structure, and proof of this is found with $Cs_3Y_2I_9$ and $Cs_3Sc_2I_9$.[17]

Experimental Section

Starting Materials. Sintered yttrium metal powder was obtained by hydrogenation of metal strips at 450 °C followed by decomposition of the resulting YH_2 at 750 °C in a high vacuum ($<10^{-5}$ torr). Zirconium metal (reactor grade, <500 ppm Hf) was obtained in the form of strips by melting crystal bar material under a vacuum to form fingerlings which were then cold-rolled into strips 0.4–0.5 mm thick. The tetraiodide was prepared by reaction of the elements at 350–400 °C in sealed Pyrex container and was purified by vacuum sublimation ($<10^{-5}$ torr) through a coarse-grade Pyrex frit. Iodine (W. T. Baker) as resublimed while CsI was recrystallized from a 0.05 wt % aqueous HI solution and dried under vacuum at 350 °C; CsI_3 was obtained from reaction of stoichiometric amounts of CsI and I_2 to form the melt[18] (230 °C, Pyrex container sealed under vacuum).

Syntheses. $Cs_3Y_2I_9$ was prepared from reaction at 750 °C of stoichiometric amounts of Y with CsI_3 or CsI plus I_2 in sealed tantalum capsules (welded with a He arc and jacketed in silica tubes under vacuum as previously described[12-15]). The product was in the form of colorless single crystals, slightly gray in bulk.

$Cs_3Zr_2I_9$ was obtained via a chemical transport reaction in sealed tantalum tubes about 10 cm long. Single crystals were selected from the products of a reaction of 400 mg of ZrI_4, 58 mg of CsI, and Zr metal strips in a temperature gradient of 750–850 °°C for 1 week. Black, lustrous crystals of $Cs_3Zr_2I_9$ were found in the hotter portion while some α-ZrI_2[16] occurred in the cooler region of the container. Powdered $Cs_3Zr_2I_9$ is very dark green. Its composition as established by the structural analysis.

Crystal Selection and Data Collection. A triangular platelet of $Cs_3Y_2I_9$ (0.16 × 0.20 × 0.08 mm) was mounted in a thin-walled glass capillary (0.2 mm o.d.) under dry N_2 with use of drybox techniques as previously described.[19] A gem-shaped crystal of $Cs_3Zr_2I_9$ (0.23 mm diameter) was selected and mounted in the same manner. Oscillation photographs were used to establish the quality of both crystals. The crystals were then transferred to a four-circle diffractometer designed and built in the Ames Laboratory. All procedures for indexing and orientation of the crystals were previously described.[20] Intensity data were collected at ambient temperature in the ω-scan mode with use of monochromatized Mo Kα radiation (graphite single crystal, $\lambda = 0.71002$ Å). Lattice constants and their estimated standard deviations were refined by least-squares techniques with use of 2θ values of about 12 reflections with $2\theta > 25°$ which had been tuned on both Friedel-related peaks.

Structure Determination and Refinement

$Cs_3Y_2I_9$. Intensity data for a total of 1115 reflections were collected for the indicated hexagonal cell within a sphere defined by $2\theta \le 50°$ for the *HKL* octant. Programs for data reduction, structure solution, and atomic scattering factors used were as referenced before.[19] The observed intensities were corrected for Lorentz and polarization effects and averaged to yield 328 observed ($I > 3\sigma(I)$) independent data. An empirical absorption correction was applied with use of a ϕ-scan method ($\phi = 0$–$350°$, $\Delta\phi = 10°$) at $\theta = 11.41°$ together with a program written by Karcher and Jacobson.[21]

Comparison of the observed powder pattern of $Cs_3Y_2I_9$ with that calculated from the positional parameters of $Cs_3Bi_2I_9$ gave a strong indication that $Cs_3Y_2I_9$ belonged to the $Cs_3Cr_2Cl_9$-type structure. Therefore the positional parameters of I1 and I2 in $Cs_3Bi_2I_9$[6] were initially assumed and refined by least-squares method. A difference Fourier map then yielded the positional parameters of Cs1, Cs2, and Y. After full-matrix least-squares refinement of positional and anisotropic thermal parameters values of $R = 0.050$ and $R_w = 0.072$ were obtained at convergence where $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with $w = \sigma_F^{-2}$.

$Cs_3Zr_2I_9$. All reflection data within a sphere defined by $2\theta \le 60°$ in the *HKL*, $\bar{H}KL$, and $H\bar{K}L$ octants were measured for the indicated cell. The 3826 observed reflections ($I > 3\sigma(I)$) were corrected for Lorentz–polarization effects and averaged to 610 independent reflections. The extinction $hh2\bar{h}l$ with l odd as observed from which the trigonal space group $P31c$ was assumed. This was later converted to the hexagonal space group $P6_3/mmc$ when the positional parameters were observed to have the higher symmetry. One iodine and the zirconium position were obtained from a Patterson map, and the remaining atom positions were located from a Fourier synthesis map. After full-matrix least-squares refinement of positional and isotropic thermal parameters R was 0.15. Refinement with anisotropic thermal parameters lowered this to $R = 0.083$ and $R_w = 0.137$. The diffraction data were then reweighted in groups sorted on F_o to give final residuals $R = 0.082$ and $R_w = 0.077$, where the shift/error values were ≤ 0.001 for all parameters. A Fourier difference map computed at this point as flat to $\le \pm 2$ e/Å^3 at the atoms and $\le \pm 1$ e/Å^3 elsewhere.

Results

The compounds $Cs_3Y_2I_9$ and $Cs_3Zr_2I_9$ both crystallize in space group $P6_3/mmc$ with two formula units per cell and are isotypic with $Cs_3Cr_2Cl_9$.[8] Final positional and thermal parameters are given in Table I. Distances and angles in both are listed in Table II while the observed and calculated structure factors are available as supplementary material. The lattice constants determined from least-squares refinement of tuned 2θ values from the data crystals are $a = 8.406$ (1) Å, $c = 21.280$ (5) Å, and $c/a = 2.532$ for $Cs_3Y_2I_9$ and $a = 8.269$ (1) Å, $c = 19.908$ (3) Å, and $c/a = 2.408$ for $Cs_3Zr_2I_9$. The molar volumes are 392.2 ($Cs_3Y_2I_9$) and 355.0 cm^3 ($Cs_3Zr_2I_9$).

In this structure, layers of close-packed atoms of compositions CsI_3 are stacked in the c lattice direction with relative ordering ABACBC or, alternatively, (*chc*)$_2$. Two-thirds of the octahedral interstices are filled with M^{3+} in pairs so that

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Table I. Crystallographic Data and Atom Parameters for $Cs_3Y_2I_9$ and $Cs_3Zr_2I_9$[a]

atom	Wyckoff notation	x	y	z	B_{11}[b]	B_{22}	B_{33}	B_{23}
$Cs_3Y_2I_9$								
Cs1	4f	1/3	2/3	0.0715 (2)	5.65 (10)	B_{11}	5.97 (16)	0
Cs2	2b	0	0	1/4	4.26 (10)	B_{11}	6.29 (25)	0
Y	4f	2/3	1/3	0.1548 (2)	2.95 (8)	B_{11}	3.43 (17)	0
I1	12k	0.8371 (1)	$2x$	0.08422 (7)	5.33 (7)	3.37 (7)	5.16 (9)	1.29 (6)
I2	6h	0.5032 (1)	$2x$	1/4	3.67 (7)	2.07 (7)	3.94 (9)	0
$Cs_3Zr_2I_9$								
Cs1	4f	1/3	2/3	0.0699 (1)	4.30 (6)	B_{11}	2.77 (6)	0
Cs2	2b	0	0	1/4	3.64 (7)	B_{11}	2.68 (8)	0
Zr	4f	2/3	1/3	0.17142 (9)	2.00 (5)	B_{11}	1.50 (6)	0
I1	12k	0.83187 (8)	$2x$	0.08990 (4)	3.85 (4)	2.39 (4)	2.48 (4)	0.72 (2)
I2	6h	0.4950 (1)	$2x$	1/4	4.39 (6)	2.82 (6)	2.53 (6)	0

[a] $Cs_3Y_2I_9$: $a = 8.406$ (1) A, $c = 21.280$ (5) A, $c/a = 2.532$, $R = 0.050$, $R_w = 0.072$ (321 reflections, $2\theta \leqslant 50°$). $Cs_3Zr_2I_9$: $a = 8.269$ (1) A, $c = 19.908$ (3) A, $c/a = 2.408$, $R = 0.082$, $R_w = 0.077$ (610 reflections, $2\theta \leqslant 60°$). [b] $T = \exp[4^{-1}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. $B_{12} = B_{22}/2; B_{13} = B_{23}/2$.

Table II. Bond Distances (A) and Angles (Deg) in $Cs_3Y_2I_9$ and $Cs_3Zr_2I_9$[a]

	$Cs_3Y_2I_9$	$Cs_3Zr_2I_9$
M*c*–M*c*	4.052 (9)	3.129 (4)
M*c*–I1*A*	2.901 (2)	2.869 (1)
M*c*–I2*B*	3.126 (3)	2.914 (2)
I1*A*–I1*A*	4.108 (1)	4.098 (1)
I1*A*–I1*C*	4.298 (1)	4.314 (1)
I1*A*–I2*B*	4.285 (3)	3.998 (1)
I2*B*–I2*B*	4.122 (1)	4.010 (2)
Cs1*A*–I1*A*	4.212 (1)	4.154 (1)
Cs1*A*–I1*C*	4.140 (4)	3.965 (2)
Cs1*A*–I2*B*	4.533 (4)	4.267 (2)
Cs2*B*–I2*B*	4.203 (1)	4.135 (1)
Cs2*B*–I1*A*	4.251 (2)	3.995 (1)
I1*A*–M*c*–I1*A*	95.6 (1)	91.15 (5)
I1*A*–M*c*–I2*B*	90.58 (3)	87.47 (2)
I2*B*–M*c*–I2*B*(α)	82.52 (9)	93.88 (4)
M*c*–I2*B*–M*c*(β)	80.8 (1)	64.93 (7)

[a] Italicized letters refer to the different layers in the stacking sequence:□AcBcA□CaBaC□. . . (*a*, *c* for M; *A*, *B*, *C* for CsI_3 layers).

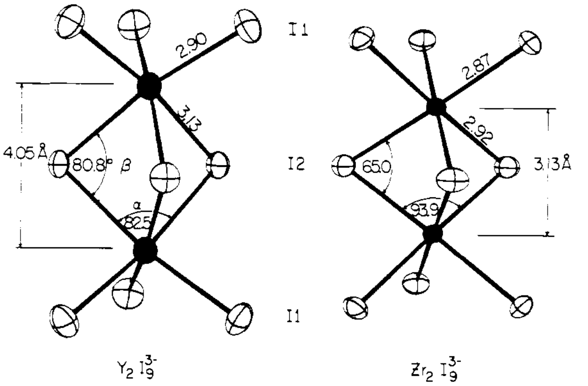

Figure 1. Perspective views of the $Y_2I_9^{3-}$ (left) and $Zr_2I_9^{3-}$ (right) groups in their $Cs_3M_2I_9$ salts (drawn with same linear scale and view distance and 50% probability thermal ellipsoids).

confacial bioctahedra $Y_2I_9^{3-}$ and $Zr_2I_9^{3-}$ are formed, as shown in Figure 1. The structure is closely related to that of hexagonal $BaTiO_3$[22] or $CsCdCl_3$;[23] in the latter all octahedral sites between $CsCl_3^{2-}$ layers stacked in the same manner are occupied by Cd^{2+} to generate zig-zag chains of $CdCl_6$ octahedra in which single octahedra share corners with confacial bioctahedra. In the $Cs_3Cr_2Cl_9$-type defect structure the single octahedral sites are left vacant.

Discussion

The marked differences in configuration between $Cs_3Y_2I_9$ and $Cs_3Zr_2I_9$ that are so evident in Figure 1 must be ascribed essentially entirely to the formation of a zirconium–zirconium bond in the latter through overlap of two $d_{z^2}^1$ orbitals through the shared face. This feature is reflected in many differences in the two structures even though they are formally isotypic. For example, the lattice constants themselves would ordinarily show a small and more or less uniform decrease with increasing atomic number in such a homologous series, but the 6.4% contraction in the c axis parallel to the principal axis of the M_2X_9 bioctahedron on transition from yttrium to zirconium vs. only a 1.6% reduction in a within the layers is noteworthy. Similar decreases in molar volume (9.5%) and the c/a ratio (4.9%) are also diagnostic of the change in bonding.[6]

The most direct evidence for the change in bonding is also the most striking, a shortening of the metal–metal distance across the shared face from 4.052 (9) (Y) to 3.129 (4) Å (Zr), a 22.8% decrease. Such a large change naturally affects not only distances and angles in the $M_2I_9^{3-}$ bioctahedron but also positions of neighboring atoms as well. Internal angles defined by the metal atoms and I2 atoms in the shared face are affected most, a 15.8% decrease from 80.8 to 65.0° in the angle β at the bridging iodine (M–I2–M) and an 11.4° increase from 82.5 to 93.9° in the internal angle α at the metal (I2–M–I2) (see Figure 1). Small changes also occur in the external angles to atoms I1 and in the M–I distances. The latter distances appear to be particularly significant and will be considered shortly.

In one sense the magnitude of the contraction in the M–M distances seems very remarkable since it is 0.2 Å greater than that accompanying the transition from the paramagnetic $Cs_3Cr_2Cl_9$ to the diamagnetic $K_3W_2Cl_9$ and the formation of a triple bond. On the other hand the percentage decrease is nearly the same. But further interpretation and comparison with the latter series becomes complex owing to substantial changes in both halide and metal bonding radii let alone because of any restraints provided by the close-packed M^IX_3 matrix. The simpler horizontal relationship between $Cs_3Y_2I_9$ and $Cs_3Zr_2I_9$ allows a considerably more straightforward consideration of some factors which appear important in determining the configurations of the $M_2X_9^{3-}$ groups, particularly the questions of ideal geometry and metal–metal repulsion.

Previous considerations[8,24] of $M_2X_9^{3-}$ ions and the effect of metal–metal interactions on their configuration have particularly emphasized an ideal bioctahedral geometry, to the neglect of structural considerations. The geometrically ideal

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Table III. Comparison of Structural Parameters in Some $Cs_3M_2X_9$ and Related Phases[a]

Nonbonding

	$Cs_3Y_2I_9$	$Cs_3Cr_2Cl_9$	$Cs_3Cr_2Br_9$	$Cs_3Sb_2I_9$	$Cs_3Bi_2I_9$	$CsCdCl_3$	$Cs_3In_2Cl_9$[c]	$Ti_2Cl_9^-$[d]
c/a	2.53	2.48	2.49	2.51	2.52	2.49		
d'/d''	1.35	1.23	1.28	1.28	1.29	1.16	1.33	1.62
α, deg	82.5	~86	83.0	85.6	85.2	84.4	78.6	78.1
β, deg	80.8	~76	80.0	76.7	77.2	78.3	86.0	86.7
d_{M-X_2}/d_{M-X_1}[b]	1.078	~1.08	1.066	1.116	1.111	1.020	1.098	1.127
ref	this work	8	10	6, 7	6	23	25	26

Bonding

	$Cs_3Zr_2I_9$	$Cs_3Mo_2Cl_9$	$Cs_3Mo_2Br_9$	$K_3W_2Cl_9$[e]	$W_2Br_9^{2-}$[f]
c/a	2.41	2.38	2.40	2.27	
d'/d''	0.97	0.98	0.97	0.90	0.90
α, deg	93.9	94.2	93.9	~98	97.1
β, deg	65.0	64.5	64.9	~58	60.0
d_{M-X_2}/d_{M-X_1}	1.016	1.043	1.031	~1.04	1.026
ref	this work	10	10	27	28

[a] $Cs_3Cr_2Cl_9$-type structure up to the dividing line. The parameters are defined in Figure 1 and in the text. [b] X2 is bridging; X1 is terminal. [c] $Cs_3Tl_2Cl_9$-type structure, $R\bar{3}c$. [d] Average of two independent anions in $PCl_4^+Ti_2Cl_9^-$. [e] Lower symmetry version ($P6_3/m$) of $Cs_3Cr_2Cl_9$ structure type.[6] [f] Tetrapropylammonium cation.

confacial bioctahedron taken as a reference was assumed to retain 90° angles at the metal (α) and equal M–X distances. These constraints then require an angle of 70.53° at the bridging halide (β) and equal spacings between planes normal to the principal axis which are defined by (a) M and bridging halide X2 (cB in the stacking sequence) with separation d' and (b) M and terminal halide X1 (cA) with separation d''. Thus in the ideal figure the ratio d'/d'' is unity, and metal bonding is inferred when values of this ratio are significantly less than 1.0 while metal–metal nonbonding repulsion, presumably closed shell and/or coulombic in character, has been assumed for values well above 1.0. Corresponding changes have been shown to occur in the angles α and β accompanying these classes of metal–metal interactions. All three moduli are said to have the advantage of being insensitive to halide or metal radius. The angles α and β are of course interrelated in M_2X_9 species with full D_{3h} symmetry.

Table III lists these and some other parameters for the principal examples of the $Cs_3Cr_2Cl_9$ structure together with data for the related $CsCdCl_3$,[23] $Cs_3In_2Cl_9$,[25] and $K_3W_2Cl_9$[27] and for $PCl_4^+Ti_2Cl_9^-$[26] and $(NPr_4)_2W_2Br_9$.[28] It will be noted that the distribution of d'/d'' ratios is quite uneven, all compounds in which no metal–metal bonding is expected having ratios above 1.2 and those known to have such a bond having ratios between 0.90 and 0.98. The skewed character of the distribution is a reflection of some inadequacies of the ideal model.

Two well-known structural factors can be used to improve the model and to aid our consideration of the data in Table III: (1) the dependence of halogen radii on coordination number to the tripositive metal and (2) the necessity for some sort of compromise on the best bonding angles at the metal and bridging halogen. The applicability of these ideas to the present phases is favored by the presence of only the low-field countercation Cs^+ as long as it can be safely assumed that the close-packed matrix does not impose a severe restriction on response to metal–metal interactions. As far as the first factor it is well-known experimentally[29] that doubly bridging halide atoms have substantially longer bonds to metal than do terminal atoms, typically by amounts in the range of 0.12–0.3 Å. The success of the highly empirical bond order–distance relationships in oxides[30] in fact requires recognition of this factor; in this sense the difference should also vary with bond polarity. The differences in M–X terminal and bridging bond lengths in the examples classed in Table III as nonbonding, 8–11% or 0.16–0.33 Å, appear to be quite typical in this respect.

The formation of longer bridge bonds alone can be accommodated by motion of the metal atoms toward the outer AX_3 layers (A or C) thereby opening the external angle (X1–M–X1) at M and increasing d'/d'' to 1.05–1.10. The internal angles α and β, which at this hypothetical point remain 90 and 70.53°, respectively, are nearly optimal for the metal but far from that for the halide where 90° angles for good p-orbital bonding would appear to be the minimum reasonable value. Judging from the collection of nonbonding examples in Table III, the angular compromise which is evidently reached is quite analogous to that which occurs in M_2X_6 dimers,[29] the angle α at the metal decreasing 4–7° from the ideal 90° and β at the halogen, with the more diffuse bonding orbitals, decreasing 9–13° from the same value.

A remarkable feature of the wide range of nonbonding examples of the $Cs_3Cr_2Cl_9$-type shown in Table III is that there is indeed little change in parameters to distinguish between members of the entire collection. Furthermore, it seems plausible that neither the charges on the metal(III) atoms in $Cs_3Sb_2I_9$ and $Cs_3Bi_2I_9$ nor closed-shell repulsions at distances of 3.97 and 4.05 Å can be very significant and therefore that the metal–metal repulsions do *not* play a significant role in determining the configurations of those two and, by implication, in the remainder as well. The absence of a charge effect is further emphasized by the parameters for $CsCdCl_3$. As noted earlier this is derived from the $Cs_3Cr_2Cl_9$-type structure through filling of the isolated octahedra which share corners with the M_2X_9 groups, i.e., $Cs_3Cd_3Cl_9$. This makes the two types of halogen and their bond lengths to metal more nearly equal, and the interdependent d'/d'' ratio accordingly decreases to 1.16. Notwithstanding, the α and β angles show no difference whatsoever from the range already associated with "nonbonding" M_2X_9 groups, although this now involves a lower oxidation state. It would appear that nonbonding repulsion of cations in the $Cs_3Cr_2Cl_9$ structure type has been substantially overemphasized. It is difficult to understand these results

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solely in terms of close-packing considerations either.

The examples in which there is clear metal–metal bonding (Table III) might then be better judged relative to a nonbonding reference ratio *d'/d''* of ~1.2. Strong metal–metal bonding in this structure appears to put a greater strain on the surrounding matrix, and although bridge angles at the metal open from the ideal 90° by ~4°, those at the bridging halide fall to ~65°. The M–X2 bridging bonds in fact may be under some compression (or the bond order has dropped substantially) since their lengths are now only a few percent larger than those to terminal halogen. The yttrium–zirconium pair suggest that both compression of M–X2 and elongation of the terminal M–X1 bond may occur during the formation of the M–M bond when the observed changes are compared with a reduction in metal size of ~0.17 Å indicated by empirical crystal radii.[31] The closer approach of the bridging iodine atoms to one another (4.01 Å relative to 4.12 Å before) also supports the notion of a compression at the bridging atoms. A substantial shortening of the Cs–I distance between both the AB planes which contain intervening tripositive metal and the AC planes which contain the vacant octahedra are also reflections of the strong metal–metal bonding.

It should be admitted that there are two other factors which might be responsible, at least in part, for the absence of a more significant lengthening of the metal–metal distance in the more polar "nonbonding" examples with the $Cs_3Cr_2Cl_9$ structure. One is the rationale that the Cs^+ atoms which lie directly along the metal–metal axis in the next (C) layer resist motion of the M atoms; however, the lack of any apparent response to probable differences in M–X polarity among the M_2X_9 groups still remains a problem. A possible restraint from the more or less close-packed CsI_3 layers has also been noted. The last two entries in the nonbonding category in Table III suggest these problems may merit further study, the $In_2Cl_9^{3-}$ group in its cesium salt which now occurs in the $Cs_3Tl_2Cl_9$ structure and the $Ti_2Cl_9^-$ ion which is unconstrained by a regular packing (but which also has a higher oxidation state). In the former the dimer units now alternate with the vacant octahedra in a confacial mode so that the outward motion of the trivalent metals might be less restrained. Both of these bioctahedra do exhibit a significant elongation, especially as represented by the α and β angles, although the *d'/d''* ratio changes significantly only ith the higher charged titanium ion. Presumably the restraint of close-packed layers is still significant in the indium phase. The ratio of bridging to terminal M–Cl bond lengths in both remain in a region termed "normal" in the above discussion. Some idea of the effect which packing with even low-field cations can have on what appears to be a "soft" anion in fairly unconstrained circumstances is shown by a 3.1° range of α for $Sb_2Br_9^{3-}$ in its $N(CH_3)_4^+$ and $C_5NH_6^+$ salts[32] even though *d'/d''* and d_{M-X_t}/d_{M-X_b} are scarcely affected (1.34 and 1.15, respectively; $\bar{\alpha} = 81.8°$).

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Registry No. $Cs_3Y_2I_9$, 76173-83-6; $Cs_3Zr_2I_9$, 76173-84-7; CsI, 7789-17-5; CsI_3, 12297-72-2; ZrI_4, 13986-26-0.

Supplementary Material Available: Listings of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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Stereochemical Perturbations of the Cobalt–Methyl Bond. An X-ray Structural Study of $[Co(d,l(N)\text{-}Me_6[14]4,11\text{-}dieneN_4)(OH_2)CH_3](ClO_4)_2$[1]

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An X-ray structural study has been performed of axial steric interactions in the title compound. The compound crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$. The coordination sphere bond lengths are reasonably typical of a cobalt–methyl complex, but a torsion angle analysis indicates that there is some strain in the equatorial macrocyclic ligand, apparently a consequence of axial $CoOH_2$–geminal methyl repulsive interactions. The unit cell dimensions are $a = 11.368$ (5) Å, $b = 11.611$ (4) Å, $c = 21.660$ (9) Å, $\beta = 93.05$ (3) °, and $V = 2855$ (2) Å^3. The structure has been refined to final discrepancy factors $R_1 = 0.050$ and $R_2 = 0.065$.

Introduction

A variety of studies of organocobalt complexes have suggested that the cobalt–carbon bond is very susceptible to stereochemical perturbations.[2-5] Thus bulky alkyl ligands have been shown to have relatively long[2] and easily cleaved[3] Co–C bonds. Further, various stereochemical interactions of adenosylcobalamin with the apoenzyme have been suggested[4,5] as possible means for sufficiently weakening the cobalt–alkyl bond to make thermal homolysis of this bond a feasible mechanistic step in some enzymatic reactions.[6-8]

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