Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, U.S.A.

The Structure of Trimethylphenylammonium Nonachlorodirhodate(III) and a Survey of Metal-Metal Interactions in Confacial Bioctahedra

F. A. Cotton* and David A. Ucko

Received October 6, 1971

The structure of the $Rh_2Cl_9^{3-}$ ion has been determined by X-ray crystallographic study of $[(CH_3)_3C_6H_5N]_3Rh_2Cl_9$. The crystals are orthorhombic with dimensions $a = 32.487(14)$, $b = 9.274(5)$, and $c = 36.451(14)$, and the observed density (1.70 g/ml) requires $Z = 12$ (which gives $\rho = 1.69$ g/ml). Systematic absences were consistent with the space groups Pmma, Pma2 and $Pmc2_1$; the latter (in the form $P2_1ma$) was selected on the basis of the Patterson function. Difficulties were caused by disorder of the cation orientations. In the end, the structure was refined in the space group Pnma, with a c axis 1/3 the length of the c axis in $P2_1ma$. The reflections with $l \neq 3n$ in $P2_1ma$ were thus all omitted; these were almost entirely very weak ones, and omitting them was virtually a necessity in order to reduce the computing to tractable proportions. For the final refinement in Pnma, the asymmetric unit consisted of one $Rh_2Cl_9^{3-}$ ion, one ordered cation, all atoms of which were refined at full weight, one partially disordered cation, all atoms of which were refined in a single orientation at 2/3 weight and a third disordered cation of which the nitrogen and methyl carbon atoms were refined at full weight while each of two ring orientations were refined at 2/3 and 1/6 weight. The $Rh_2Cl_9^{3-}$ ion has virtual D_{3h} symmetry and shows symmetry-preserving distortions from the ideal bioctahedron structure which are indicative of Rh–Rh repulsion. The Rh–Rh distance is 3.121(5) A and the Rh–Cl–Rh angles have an average value of 81.3 (3)°. When the $Rh_2Cl_9^{3-}$ structure as well as those of 13 other M_2X_9 bioctahedra are analyzed in terms of various structure parameters which reflect the magnitude and sense (i.e., *attractive or repulsive*) *of the M–M interactions, systematic correlations with electronic structures and position in the periodic table are found.*

Introduction

An enormous number of solid state structures consist of hexagonal close-packed arrays of anions with metal atoms occupying octahedral interstices. In many cases, the metal atoms occupy adjacent sites in such a way that their respective octahedra share a triangular face. Among the familiar examples of this situation are substances with the corundum structure,[1,2] some of which are α–Al_2O_3, γ–Al_2S_3, Ti_2O_3, V_2O_3, Cr_2O_3, α–Fe_2O_3, α–Ga_2O_3, and Co_2As_3. There are also a number of A_2O_3 compounds,[2] including Rh_2O_3[3] which adopt this structure at higher pressures, even though they do not have it under normal conditions.

There are many other, less common, oxide systems in which metal ions lie in adjacent, face-sharing octahedra. Thus in hexagonal $BaTiO_3$ two-thirds of the titanium atoms occupy such pairs of positions,[4a] while in $BaMnO_3$ all manganese atoms are so situated.[4b] In $BaRuO_3$ there are linear sets of three Ru atoms in linear triplets of confacial octahedra.[5]

In a number of metal halides there are infinite linear chains of octahedrally coordinated metal atoms connected by shared triangular faces. Among these are β–$TiCl_3$,[6] $TiBr_3$,[7] and TiI_3,[7] the isotypic series[8] $ZrCl_3$, $ZrBr_3$, ZrI_3, HfI_3, $MoBr_3$,[9] MoI_3,[10], and β–$RuCl_3$.[11] Chains of this type are also found in $[(CH_3)_3NH]NiCl_3$[12] and $[(CH_3)_4N]MnCl_3$.[13]

In $ReCl_4$ there are relatively isolated pairs of Re atoms in face-sharing octahedra.[14]

In compounds of the stoichiometric type ABX_3 (*e.g.*, $CsMnCl_3$, $BaVS_3$), the structures are based on various forms of close-packed arrays of the X ions. When the packing sequence is hhhhh... (h = hexagonal) the B metal ions occur in infinite chains of face-sharing octahedra. When the stacking sequences are hhchhchhc... (c = cubic) and hcchcchcc... there are zigzag stacks of trioctahedra and zigzag stacks of alternating bioctahedra and single octahedra, respectively.[15,16]

---

* Address correspondence to this author at: Department of Chemistry, Texas A and M University, College Station, Texas 77843.

(1) For a general reference to this and other structure types to be mentioned, see R.W.G. Wyckoff, *Crystal Structures*, 2nd Edn., John Wiley-Interscience, N.Y., 1964.

(2) C.T. Prewitt, R.D. Shannon, D.B. Rogers and A.W. Sleight, *Inorg. Chem. 8*, 1985 (1969).

(3) R.D. Shannon and C.T. Prewitt, *J. Solid State Chem.*, *2*, 134 (1970).

(4) (a) Ref. 1, page 414; (b) Ref. 1, page 416.

(5) P.C. Donohue, L. Katz and R. Ward, *Inorg. Chem.*, *4*, 306 (1965).

(6) G. Natta, P. Corradini and G. Allegra, *J. Polymer Sci.*, *51*, 399 (1961).

(7) H.G. v. Schnering, Habilationsschrift, Munster, 1963.

(8) L.F. Dahl, T. Chiang, P.W. Seabaugh and E.M. Larson, *Inorg. Chem.*, 3, 1236 (1964).

(9) D. Babel and W. Rudorff, *Naturwissensch.*, *51*, 84 (1964).

(10) J. Lewis, D.L. Machin, R.S. Nyholm, P. Pauling and P.W. Smith, *Chem. Ind.* (*London*), 259 (1960).

(11) K. Brodersen, *Angew. Chem.*, *80*, 155 (1968).

(12) R.D. Willet, *J. Chem. Phys.*, *45*, 3737 (1966).

(13) B. Morosin and E.J. Graeber, *Acta Cryst.*, *23*, 766 (1967).

(14) M. J. Bennett, F.A. Cotton, B.M. Foxman and P.F. Stokely, *J. Amer Chem. Soc.*, 89, 2759 (1967).

(15) L. Katz and R. Ward, *Inorg. Chem.*, 3, 205 (1964).

Finally, there are a number of cases in which the pairs of metal atoms are completely isolated from each other, in the sense that the structure can be divided into separate M_2X_9 groups, with no shared anions. It is with the latter groups that we are specifically concerned in this paper, but their intrinsic interest is augmented by the fact that the structures mentioned previously can all be considered as overlapping arrays of M_2X_9 units. The X/M ratio in M_2X_9 is, of course, 4.5. As this ratio drops, sharing of X atoms between M_2X_9 units must occur and become more extensive. Thus, in $RcCl_4$, two of the terminal Cl atoms are shared between two Re_2Cl_9 units; the structure is catenated. In the infinite chain species, all terminal X groups may be thought of as shared. In the corundum structure the sharing is reticulated by a complex three-dimensional sharing pattern.

The foregoing discussion, which is intended to be only illustrative and not exhaustive, should demonstrate that the metal-metal interactions which occur in M_2X_9 confacial bioctahedra[17] have widespread importance. The study of such interactions can best be approached by first treating the simplest cases, *i.e.*, isolated M_2X_9 confacial bioctahedra. It is our purpose in this paper to report the structure of one such species, $Rh_2Cl_9^{3-}$, and to discuss the way in which M—M interactions affect the details and shape and dimensions in this and a number of other previously characterized confacial bioctahedral anions.

It was considered of interest to study the structure of the $Rh_2Cl_9^{3-}$ ion because it contains metal ions with filled (t_{2g}^6) configurations. In such a case there should be a significant metal-metal repulsion. However, no species of this class had yet been studied structurally. It had been reported[18a] that the infrared spectrum of $[(C_2H_5)_4N]_3Rh_2Cl_9$ is consistent with the presence of the $Rh_2Cl_9^{3-}$ bioctahedron and that the electronic absorption spectrum differed noticeably from that of $RhCl_6^{3-}$, thus indicating a perturbation from simple octahedral ligand fields about each Rh^{3+} ion.

Experimental Section

Trimethylphenylammonium nonachlorodirhodate (III), $[(CH_3)_3C_6H_5N]_3Rh_2Cl_9$, was prepared using a modification of the method of Fraenkel.[18b] Rhodium (III) chloride trihydrate (0.25 g; 1 mmole) was dissolved in concentrated aqueous hydrochloric acid (40 ml) with gentle heating. The solution was then evaporated to a volume of about 5 ml. A solution of $[(CH_3)_3C_6H_5N]Cl$ (0.26 g; 1.5 mmole) in ethanol (20 ml) was added to the red solution with stirring. The precipitated brown product was removed by filtration. Small crystals of the product were obtained by allowing the red-brown filtrate to stand at room temperature for several days.

Anal. Calcd for $Rh_2Cl_9N_3C_{27}H_{42}$: C, 34.71; H, 4.50; Cl, 34.23. Found: C, 34.6; H, 4.54; Cl, 33.3.

A brown rectangular crystal with approximate dimensions 0.2×0.04×0.04 mm was mounted on a glass fiber with the longest dimension (later shown to coincide with the b axis of the unit cell) parallel to the ϕ axis. Rotation and Weissenberg (h0l, h1l) photographs taken with Cu Kα radiation ($\lambda(K\bar{\alpha})$ = 1.5418) showed that the crystal was orthorhombic. A further examination of reciprocal space was performed on a General Electric XRD-5 diffractometer using a CA-7 cobalt tube ($\lambda(K\bar{\alpha})$ = 1.7902). The only observed systematic absence was hk0, $h \neq 2n$, limiting the choice of space groups[19] to Pmma (D^5_{2h}, no. 51) Pm2a, a non-standard orientation of Pma2 (C^4_{2v}, no. 28), and $P2_1ma$, a non-standard orientation of $Pmc2_1$ (C^2_{2v}, no. 26). The cell dimensions were found to be a = 32.487(14), b = 9.274(5), c = 36.451(14) based on a least-squares refinement of 15 carefully centered reflections measured at 22°C. The value of ρ_{obs} = 1.70 g/ml, determined by flotation in $CHCl_3/CH_2Br_2$, compares favorably with ρ_{calc} = 1.69 for Z = 12.

The large size of the unit cell was discouraging. Moreover, Weissenberg photographs indicated that pseudosymmetry might be a problem since reflections for which $l = 3n$ were markedly and consistently stronger than those for which $l \neq 3n$. Finally, crystal quality, though acceptable, did not appear to be particularly good. Attempts were therefore made to obtain more suitable crystals using other solvents and crystal-growing techniques. When these efforts failed, we elected, with perhaps more valor than discretion, to tackle the structure using the crystal first obtained. As will be seen, it was in the end necessary to introduce an approximation (related to the pseudosymmetry) in order to make the problem tractable and to bring computing costs within tolerable limits.

Intensities were measured on the manually operated diffractometer equipped with a scintillation counter using Fe-filtered Co Kα radiation. A higher intensity CA-8 copper X-ray tube of suitable quality was unavailable and molybdenum radiation was inappropriate because of the large cell dimensions. The distances from the crystal to the source and from the crystal to the circular screening aperture (2°) were 14.6 cm and 17.9 cm respectively. The pulse height discriminator was set to receive 95% of the peak intensity, and the takeoff angle was 5°. A 20-second stationary count was employed with 10-second measurements of background at $2\theta \pm 1.1°$; the intensities (I) were obtained by subtracting the sum of the background counts (B_1+B_2) from the total number of counts (P) measured at the center of the peak, *viz.*, $I = P-(B_1+B_2)$. In the 2θ range 0-100°, 4,113 independent reflections were measured. Five standard reflections (020, 210, 013, 303, 400) were checked periodically during the data collection as a monitor of instrumental and crystal stability. A non-systematic fluctuation of less than ±3% was observed.

Structure factor amplitudes were calculated from

---

(16) J.M. Longo and J.A. Kafolas, *J. Solid State Chem.*, 3, 429 (1971).

(17) The explicit term « confacial bioctahedron » is used for clarity, since another important structure element, both in isolation and as part of a reticulated pattern, is the conlateral bioctahedron, which consists of two octahedra sharing an edge to give a unit whose ideal symmetry is D_{2h}.

(18) (a) R.A. Work, III, and M.L. Good, *Inorg Chem.*, 9, 956 (1970).

(18) (b) O. v. Fraenkel, *Monatsh. Chem.*, 35, 119 (1914).

(19) "International Tables for X-ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965.

corrected intensities as $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz-polarization factor. The estimated standard deviation of F_o, σ_F, is defined from the counting statistics as $[P+B_1+B_2+(0.05I)^2]^{1/2}/2LpF_o$. Since μ = 165.5 cm^{-1}, a correction for absorption was made using the intensity of the 020 reflection at 15° intervals of ø (at χ = 90°) as a check. The variation of intensity with ø was reduced from 27% to 7% and the transmission coefficients were in the range 0.49-0.67. Intensities were such that coincidence losses were negligible.

Solution and Refinement of the Structure[20]

A three-dimensional Patterson map was computed. The 12 rhodium atoms were found to lie in two mirror planes. These planes were separated by 1/2 in y and each one contained three pairs of atoms with the pairs separated by 1/3 in z, to within the accuracy with which the Patterson function could be evaluated. Six chlorine atoms, three of which lie on the mirror, were located around each pair of rhodium atoms. The positions of these atoms are inconsistent with the presence of a mirror perpendicular to the x axis as found in Pmma and Pm2a; $P2_1ma$ was therefore selected as the space group. The general equivalent positions are x,y,z; $x,\bar{y},z$; $\frac{1}{2}+x,y,\bar{z}$; $\frac{1}{2}+x,\bar{y},\bar{z}$ with the rhodium atoms and the in-plane chlorine atoms occupying special positions at y = 0 and y = ½.

The Patterson map, which had (0, 0, 1/3) as the largest non-origin peak (83% of origin height), confirmed the presence of pseudosymmetry along the z axis; the periodicity of the dinuclear units of 1/3 is not required crystallographically. This unfortunate circumstance had been suggested earlier by the Weissenberg photographs which showed that the intensities of $l = 3n$ reflections were very much greater than those which $l \neq 3n$.

A cycle of least-squares refinement on the rhodium positions led to a conventional (unit-weighted) residual $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ of 0.419 and a weighted residual $R_2 = \Sigma w||F_o|-|F_c||^2/\Sigma w|F_o|^2$ (with $w = \sigma_F^{-1/2}$) of 0.467 using the 2,851 reflections for which the condition $F_o^2 \geqslant \sigma(F_o^2)$ was satisfied. Scattering factors were those of Cromer and Waber.[21] No correction for anomalous dispersion was made since values were not available for Co radiation. A difference Fourier map confirmed the chlorine positions previously found on the Patterson map. Subsequent refinement of the rhodium and chlorine atoms led to R_1 and R_2 values of 0.249 and 0.261 respectively. Attempts to determine completely the positions of the atoms constituting the cations from difference Fourier syntheses proved unsuccessful since the phasing provided by the heavy atoms had pseudosymmetry not present in the lighter cations. The cations appeared in positions with the nitrogen atoms lying in the mirror plane and the phenyl rings lying either in or perpendicular to the mirror planes. They were periodically distributed in the z direction at intervals of *c*/3. In all difference Fourier maps calculated while attempting to break the pseudosymmetry with an ordered set of cations at least some of the cations appeared to be superpositions of different orientations. We suspect that the cations may in fact be disordered, but an attempt to account in detail for both the pseudosymmetry and disorder would cause an alreadly inordinate number of variable parameters and correlation problems to proliferate to the point of absurdity.

After many fruitless attempts to resolve the cations it was decided to concentrate on the substructure consisting only of the complex anions. As Table I shows more than two-thirds of the reflections for which $l \neq 3n$ have $F_o^2/\sigma(F_o^2) < 2$, whereas more than three-quarters of the reflections with $l = 3n$ have $F_o^2/\sigma(F_o^2) > 2$. The approximation was therefore made that the structure has a periodicity in the *c* direction, $c' = c/3$, and only the 1,225 reflections for which $l = 3n$ and $F_o^2/\sigma(F_o^2) > 1$ were used in further computations. This approximation was considered tolerable since (1) the $Rh_2Cl_9^{3-}$ units seemed to be adequately described in terms of a subcell with $c' = c/3$, (2) these atoms account for about 86% of the electron density of the crystal, and (3) the information of primary interest, namely, the structure of the $Rh_2Cl_9^{3-}$ anion would still be obtained with useful accuracy.

Table I. Distribution of Intensities.

$F_o^2/\sigma(F_o^2)$	Number of Reflections, *hkl* $l=3n$	$l \neq 3n$
0-1	142	1119
1-2	167	823
2-3	133	458
3-4	120	184
4-5	64	76
5-6	87	34
6-7	55	18
7-8	50	17
8-9	48	9
>9	501	8
Total	1367	2746

The substructure was therefore refined using difference electron-density maps and least-squares refinement until the discrepancy indices converged to values of $R_1 = 0.095$ and $R_2 = 0.091$. In carrying the refinement to this stage, the cations were handled in the following manner. Of the six to be accounted for, 4 2/3 were located from difference Fourier syntheses and were oriented as follows; occupancy factors were chosen such that temperature factors for the atoms involved refined to reasonable values. Two were refined at full occupancy with their nitrogen atoms and phenyl rings lying in the mirror planes at y = 0 and y = 1/2. Two more were refined at 1/2 occupancy with nitrogen atoms and phenyl

---

(20) The principal computer programs used in the structure determination include: PICK2 (J.A. Ibers) for refining cell constants; MIXG2 (D.P. Shoemaker) for calculating diffractometer settings; DR69 (M.D. LaPrade) for data reduction; GONO9 (W.C. Hamilton) for the absorption correction; FORDAP (A. Zalkin) for Patterson and Fourier syntheses; SFIX (local version of SFLS5 by C.T. Prewitt) for least-squares refinement based on minimization of $\sum(w||F_o|-|F_c||^2)$; STAN1 (B.G. DeBoer) for distance and angle calculations; ORTEP (C.K. Johnson) for diagrams.

(21) D.T. Cromer and J.T. Waber, *Acta Cryst.*, *18*, 104 (1965).

rings perpendicular to the mirror planes. A fifth cation was also refined at 2/3 occupancy with the perpendicular orientation to the plane at y = 1/2. The sixth cation was refined at 1/3 occupancy each in both parallel and perpendicular orientations in the y = 0 plane. The remaining 4/3 cation could not be located with any certainty though presumably it is equally divided over the last four sites mentioned.

Pseudosymmetry beyond that already anticipated from the systematic intensity distribution (hkl, l = 3n strong; hkl, l $\neq$ 3n weak) now manifested itself very markedly in the correlation matrix. There were very strong correlations between coordinates of atoms in the anions at y = 0 and those of atoms in the anions at y = 1/4. A close examination of the anion arrangement indicated the presence of an n-glide at x = 1/4, and it was found that for the l = 3n data, the condition that 0kl′ be absent for k+l′ $\neq$ 2n (where l′ signifies only l = 3n) was rigorously satisfied. Therefore, the space group Pnma (D^{16}_{2h}, No. 62[19]) was adopted for all further work in the 1/3 cell. In making this change of space group, the origin was shifted so as to place the mirror planes at y = 1/4, 3/4, in accord with the standard arrangement. The heavy atom part of the asymmetric unit then became a single $Rh_2Cl_9^{3-}$ unit, with rhodium atoms and three of the chlorine atoms lying in the mirror planes at y = 1/4, 3/4. The complete asymmetric unit then also included three independent cations.

Refinement was resumed in the new space group using Fourier maps and full matrix least squares. The cation positions were again scrutinized using difference Fourier syntheses. Of the three cations, one (Cat-1) showed no disorder and all atoms in it were refined at full occupancy with isotropic temperature parameters. The second (Cat-2) was also refined, but all atoms were given occupancy factors of 0.67. Nc other interpretable features could be found at the location of Cat-2. Cat-3 was at first restricted to a single orientation at 2/3 occupancy for the ring and full occupancy at the nitrogen and methyl carbon atoms. From a later difference map, a second ring orientation at 1/6 occupancy seemed likely and was added. The final stages of refinement were performed on all of the above-mentioned cation positions as well as on the rhodium and chlorine atoms, which were assigned anisotropic temperature parameters of the form exp $[-1/4(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]$. This reduced R_1 to 0.132 and R_2 to 0.125. An empirical weighting scheme, setting $\sigma=[0.167\ F_o-7.0]^{1/2}$ for $F_o\leqslant 39$ and $\sigma=[0.778\ F_o-18.0]^{1/2}$ for $F_o>39$, removed the depen-

Table II. Observed and Calculated Structure Factors for l=3*n* Reflections in Units of 0.1 Electron

Table III. Observed Structure Factors for All Reflections (Unscaled).

H K L	FOBS	H K L	FOBS	H K L	FOBS	H K L	FOBS	H K L	FOBS	H K L	FOBS	H K L	FOBS	H K L	FOBS	H K L	FOBS	H K L	FOBS	H K L	FOBS
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table III. (continued)

H	K	L	FOBS	H	K	L	FOBS	H	K	L	FOBS	H	K	L	FOBS	H	K	L	FOBS	H	K	L	FOBS	H	K	L	FOBS	H	K	L	FOBS	H	K	L	FOBS	H	K	L	FOBS	H	K	L	FOBS	H	K	L	FOBS

dence of $w\Delta^2$ on F_o and reduced the standard deviation of an observation of unit weight to 1.05. The last cycle of refinement, which shifted no rhodium or chlorine atomic parameter by more than 1/3 of its e.s.d., gave $R_1=0.132$ and $R_2=0.140$. Inspection of a final correlation matrix revealed no correlations between atomic parameters of magnitude greater than 0.1. Since $|F_c|$ was not consistently larger than $|F_o|$ for the most intense reflections, an extinction correction was not deemed necessary.

Experimental Results

Table II lists the calculated and observed structure amplitudes of the reflections with $l=3n$. It will be noted that all reflections with $F_o^2/\sigma(F_o^2)<1$, which were omitted in the refinement, are calculated to be

Table IV. Atomic Parameters [a]

A. Positional Parameters

Atom	x	y	z
Rh(1)	0.0940(0)	1/4	1.1706(3)
Rh(2)	0.1447(1)	1/4	0.9524(3)
Cl(1)	0.0256(3)	1/4	1.1804(9)
Cl(2)	0.1007(2)	0.4279(9)	1.3023(7)
Cl(3)	0.1683(4)	1/4	1.1396(9)
Cl(4)	0.0967(2)	0.4202(9)	1.0230(7)
Cl(5)	0.1142(4)	1/4	0.7807(11)
Cl(6)	0.1902(3)	0.4298(9)	0.9023(7)

B. Anisotropic Temperature Parameters,[b] in A^2

Atom	B_{11}	B_{23}	B_{33}	B_{12}	B_{13}	B_{23}
Rh(1)	6.8(2)	4.8(2)	6.6(2)	0	0.2(2)	0
Rh(2)	7.0(2)	5.0(2)	6.5(2)	0	0.6(2)	0
Cl(1)	6.2(7)	4.9(7)	7.3(8)	0	0.7(6)	0
Cl(2)	7.9(5)	6.8(5)	7.9(5)	0.3(3)	0.0(4)	−1.2(5)
Cl(3)	8.0(8)	5.3(7)	5.9(8)	0	−0.3(6)	0
Cl(4)	7.9(5)	5.1(5)	7.5(5)	0.4(4)	1.1(4)	0
Cl(5)	7.9(9)	10.8(10)	7.5(9)	0	−0.3(7)	0
Cl(6)	8.9(5)	5.5(5)	8.7(6)	−0.8(4)	2.1(5)	0.7(5)

[a] Numbers in parentheses are estimated standard deviations, in the last significant digit, as obtained in the final cycle of refinement. [b] As defined in the text.

Table V. Interatomic Distances in $Rh_2Cl_9^{3-}$, Å

Rh-Rh	3.121(5)
Rh(1)-Cl(3)	2.442(12)
-Cl(4)	2.391(9)
Rh(2)-Cl(3)	2.400(12)
-Cl(4)	2.378(9)
Average Rh-Cl_{bridge}	2.397(10)
Rh(1)-Cl(1)	2.227(11)
-Cl(2)	2.309(9)
Rh(2)-Cl(5)	2.310(14)
-Cl(6)	2.310(9)
Average Rh-$Cl_{terminal}$	2.296(10)
Cl(3)-Cl(4)	3.147(13)
Cl(4)-Cl(4′)	3.158(17)
Average Cl_{bridge}-Cl_{bridge}	3.151(14)
Cl(1)-Cl(2)	3.299(13)
Cl(2)-Cl(2′)	3.300(18)
Cl(5)-Cl(6)	3.327(14)
Cl(6)-Cl(6′)	3.334(17)
Average $Cl_{term.}$-$Cl_{term.}$	3.314(15)

Table VI. Angles (Degrees) Within the $Rh_2Cl_9^{3-}$ Ion

Bridge-Rh-Bridge Angles		
Cl(3)-Rh(1)-Cl(4)		81.2(3)
Cl(4)-Rh(1)-Cl(4′)		82.6(4)
Cl(3)-Rh(2)-Cl(4)		82.4(3)
Cl(4)-Rh(2)-Cl(4′)		83.2(4)
	Average	82.2(3)
Terminal-Rh-Terminal Angles		
Cl(1)-Rh(1)-Cl(2)		93.3(3)
Cl(2)-Rh(1)-Cl(2′)		91.2(5)
Cl(5)-Rh(2)-Cl(6)		92.1(3)
Cl(6)-Rh(2)-Cl(6′)		92.4(4)
	Average	92.4(4)
Terminal-Rh-Bridge Angles		
Cl(1)-Rh(1)-Cl(4)		94.4(3)
Cl(2)-Rh(1)-Cl(3)		90.8(3)
Cl(2)-Rh(1)-Cl(4)		92.6(3)
Cl(3)-Rh(2)-Cl(6)		92.6(3)
Cl(4)-Rh(2)-Cl(5)		92.5(3)
Cl(4)-Rh(2)-Cl(6)		92.0(3)
	Average	92.5(3)
Rh-Bridge-Rh Angle		
Rh(1)-Cl(3)-Rh(2)		80.3(4)
Rh(1)-Cl(4)-Rh(2)		81.8(3)
	Average	81.3(3)

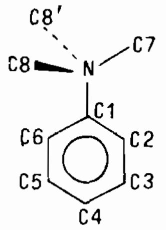
Table VII. Cation Atomic Parameters [a]

Atom	x	y	z	B
Cation-1 (full occupancy)				
N1	0.292(1)	1/4	0.660(4)	10(1)
C11	0.256(1)	1/4	0.580(4)	7(1)
C12	0.218(1)	1/4	0.628(3)	5(1)
C13	0.189(2)	1/4	0.549(5)	10(2)
C14	0.195(2)	1/4	0.442(5)	8(1)
C15	0.232(2)	1/4	0.394(4)	7(1)
C16	0.262(1)	1/4	0.468(4)	7(1)
C17	0.333(1)	1/4	0.593(4)	7(1)
C18	0.290(1)	0.392(5)	0.729(3)	13(1)
Cation-2 (2/3 occupancy)				
N2	0.392(2)	1/4	0.208(6)	8(1)
C21	0.351(1)	1/4	0.159(4)	2(1)
C22	0.336(1)	0.368(5)	0.118(4)	9(1)
C23	0.294(1)	0.382(6)	0.076(4)	8(1)
C24	0.280(2)	1/4	0.065(6)	8(2)
C25	0.388(3)	1/4	0.308(8)	7(2)
C26	0.417(2)	0.393(9)	0.165(7)	10(2)
Cation-3 (2/3 and 1/6 occupancy in each of two orientations)				
N3	0.485(1)	1/4	0.682(3)	6(1)
C31	0.500(2)	1/4	0.806(5)	6(2)
C32	0.506(2)	0.389(9)	0.860(6)	15(2)
C33	0.525(2)	0.354(8)	0.984(6)	15(2)
C34*	0.531	1/4	0.993	9
C35	0.441(1)	1/4	0.653(4)	8(1)
C36	0.506(1)	0.384(4)	0.630(3)	8(1)
C31′	0.470(6)	1/4	0.823(15)	5(4)
C32′*	0.510	1/4	0.870	5
C33′	0.493(7)	1/4	0.009(17)	1(4)
C34′	0.466(20)	1/4	0.024(47)	20(10)
C35′	0.443(5)	1/4	0.988(13)	0(4)
C36′	0.445(5)	1/4	0.874(15)	2(4)

* Not refined in final cycles. [a] In space group Pnma and in a unit cell with c′=c/3= 12.150(5) A.

Table VIII. Distances (A) and Angles (Deg.) for Cat-1

C(1)-C(2)	1.35(6)
C(2)-C(3)	1.36(7)
C(3)-C(4)	1.31(8)
C(4)-C(5)	1.34(7)
C(5)-C(6)	1.33(7)
C(6)-C(1)	1.37(7)
N-C(1)	1.54(6)
N-C(7)	1.56(6)
N-C(8)	1.56(5)
C(1)-N-C(7)	109(4)
C(1)-N-C(8)	107(3)
C(7)-N-C(8)	109(2)
C(8)-N-C(8′)	115(4)
C(6)-C(1)-C(2)	125(4)
C(1)-C(2)-C(3)	109(4)
C(2)-C(3)-C(4)	126(5)
C(3)-C(4)-C(5)	125(5)
C(4)-C(5)-C(6)	112(5)
C(5)-C(6)-C(1)	124(5)
N-C(1)-C(2)	115(4)
N-C(1)-C(6)	120(4)



weak. Table III is a complete list of observed structure amplitudes for all reflections. Table IV gives the atomic parameters for the $Rh_2Cl_9^{3-}$ anion and Table V and VI give the interatomic distances and angles in the anion.

Table VII gives the atomic parameters for the cations and Table VIII gives the bond lengths and angles for Cat-1, the only one of the three cations which appeared to be (and was treated as if) completely ordered.

The probable errors in the structure parameters for the $Rh_2Cl_9^{3-}$ ion, are of course larger than the e.s.d.'s quoted in Tables V and VI due to the systematic errors introduced by the approximations we have made in solving the structure using a subcell of the true unit cell. Nevertheless, the accuracy should be quite sufficient to make the structure useful in the discussion which is presented in the next section.

The $Rh_2Cl_9^{3-}$ ion has D_{3h} symmetry, within the probable uncertainties. It is a true confacial bioctahedron. The rhodium atoms evidently experience a mutually repulsive interaction since they lie off the approximate centers of their octahedra toward the extremities of the structure, and, as will be discussed more fully in the next section, the entire structure is distorted in a manner indicative of repulsion between the metal atoms.

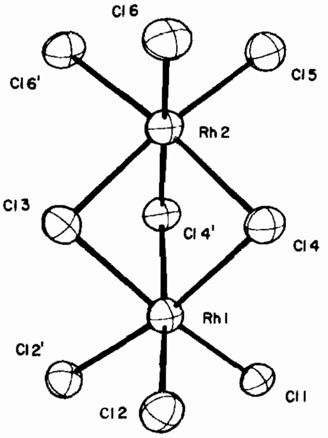


Figure 1. A projection of the $Rh_2Cl_9^{3-}$ ion, showing the atom numbering scheme. Each atom is represented by the ellipsoid of its thermal vibration parameters, drawn at the 75% probability level.

The $Rh_2Cl_9^{3-}$ ion is shown in Fig. 1, which defines the atom numbering scheme. Atoms which bear numbers differing only in the presence or absence of a prime are equivalent by reflection through the crystallographic mirror plane. The structure of cation-1, which was refined at full occupancy of a single orientation, is shown in Figure 2, with the numbering scheme.

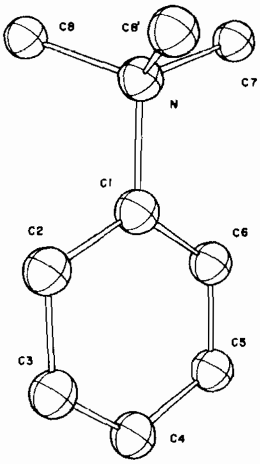


Figure 2. The structure and numbering scheme for Cat-1, the $(CH_3)_3(C_6H_5)N^+$ ion which was refined at full occupancy of a single orientation.

General Discussion of Confacial Bioctahedral Structures

Ideal and Axially Distorted Structures.[22] If two congruent regular octahedra share a face, the resulting figure is what we shall call the « ideal » confacial bioctahedron. The point symmetry is D_{3h}. There are, of course, several equalities of bond lengths and angles which symmetry requirements alone do not demand. Thus $M\text{-}X_t$ (t denotes terminal) and $M\text{-}X_{br}$ (br denotes bridge) bond lengths are equal, all X-M-X angles are equal to 90°, the $M\text{-}X_{br}\text{-}M$ angles are 70.53°, and each metal atom is precisely halfway between the planes defined by its set of terminal X atoms and the set of bridging X atoms.

Physically, this ideal structure has no exact significance. There is *no* set of chemically or physically significant preconditions which would necessarily cause this ideal geometry to be uniquely stable. Nevertheless, the ideal structure affords a useful reference point within the range of symmetry preserving distortions which are to be discussed.

---

(22) The arguments to be developed here in some detail were first adumbrated qualitatively and applied to a comparison of the $Cr_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$ bioctahedra several years ago. *Cf* F.A. Cotton, *Rev. Pure and Appl. Chem.*, *17*, 25 (1967); *idem*, *Accts. Chem. Res.*, *2*, 240 (1969).

Table IX. Structural Data and Moduli of Distortion from Ideal Confacial Bioctahedron[a,b]

Parameter or Modulus	$Ti_2Cl_9^-$	$Cr_2Cl_9^{3-}$	$Cr_2Br_9^{3-}$	$Mo_2Cl_9^{3-}$	$Mo_2Cl_8^{3-}$	$Mo_2Br_9^{3-}$	$W_2Cl_9^{3-}$	$Re_2Cl_9^-$	$Rh_2Cl_9^{3-}$	$Tl_2Cl_9^{3-}$	$Bi_2I_9^{3-}$	$Fe_2(CO)_9$	$Ru_2Cl_3(Et_2Ph)_6^+$	$Co_2(OH)_3(NH_3)_6^{3+}$
M–M(A), D	3.430 (7)	3.12	3.317 (21)	2.655 (11)	2.38 (1)	2.816 (9)	2.41 (10)	2.703 (13)	3.121 (5)	3.7	4.051 (5)	2.46 (5)	3.443 (4)	2.56 (2)
M–$_{br}$(A), r′	2.493 (6)	2.52	2.577 (9)	2.487 (12)	2.50 (2)	2.624 (5)	2.5 (2)	2.41 (2)	2.397 (10)	2.8	3.249 (5)	1.78 (5)	2.481 (6)	1.96 (7)
M–X_t(A), r″	2.133 (6)	2.34	2.417 (5)	2.384 (6)	2.38 (1)	2.544 (3)	2.4 (3)	2.29 (3)	2.296 (10)	2.5	2.923 (4)	1.87 (5)	2.318 (6)	2.00 (7)
X_{br}–X_{br}(A), R′	3.137 (9)	3.44	3.417 (5)	3.643 (8)	3.80 (6)	3.834 (4)	3.8 (3)	3.75 (6)	3.151 (14)	3.7	4.206 (10)	2.24 (5)	3.093 (7)	2.57 (9)
X_t–X_t(A), R″	3.343 (8)	3.41	3.527 (3)	3.401 (6)	3.46 (5)	3.620 (2)	3.4 (3)	3.59 (8)	3.314 (15)	3.7	4.193 (7)	2.74 (5)	3.467 (9)	2.88 (9)
∠ X_{br}–M–X_{br}, α′	78.1 (3)	85.8	83.0 (3)	94.2 (1)	99.2 (15)	93.89 (11)	98 (4)	91.6 (15)	82.2 (3)	82	85.25 (11)	78 (4)	77.2 (2)	82 (3)
∠ X_t–M–X_t, α″	98.1 (3)	93.3	93.7 (3)	91.0 (3)	93.1 (14)	90.73 (15)	91 (14)	92.7 (18)	92.4 (4)	97	94.13 (11)	94 (4)	96.8 (2)	92 (3)
∠ X_{br}–M–X_t, α‴	91.0 (2)	90.1	91.4 (1)	87.4 (2)	87.7 (9)	87.65 (7)	85 (8)	87.7 (16)	92.5 (3)	90	90.11 (11)	94 (4)	99.3 (2)	93 (3)
∠ M–X_{br}–M, β	86.7 (2)	76.4	80.0 (4)	64.5 (3)	56.8 (9)	64.88 (15)	58 (6)	68.2 (14)	81.3 (3)	81	77.12 (15)	87 (4)	87.9 (2)	76 (3)
M–X_{br}plane(A), d′	1.72	1.56	1.66	1.33	1.19	1.41	1.21	1.35	1.56	1.8	2.02	1.23	1.72	1.26
M–$X_t$plane(A),d″	1.06	1.27	1.30	1.35	1.33	1.45	1.35	1.25	1.23	1.5	1.56	1.01	1.17	1.11
d′/d″	1.62	1.23	1.28	0.98	0.89	0.97	0.90	1.08	1.27	1.2	1.29	1.22	1.47	1.14
90°–α′	11.9°	4.2°	7.0°	–4.2°	–9.2°	–3.9°	–8°	–1.6°	7.79°	8.0°	4.75°	12.0°	12.8°	8.0°
β–70.53°	16.2°	5.9°	9.5°	–6.0°	–13.7°	–5.6°	–12.5°	–2.3°	10.7°	10.5°	6.6°	16.5°	17.4°	5.5°

[a] All data taken from following literature sources: $[PCl_4][Ti_2Cl_9]$: T. J. Kistenmacher and G. D. Stucky, *Inorg. Chem., 10,* 122 (1971); $Cs_3Cr_2Cl_9$: G. J. Wessel and D.J.W. Ijdo, *Acta Cryst., 10,* 466 (1957); $Cs_3Cr_2Br_9$, $Cs_3Mo_2Cl_9$, $Cs_3Mo_2Br_9$: R. Saillant, R.B. Jackson, W.E. Streib, K. Folting, and R.A.D. Wentworth, *Inorg. Chem., 10,* 1453 (1971); $Rb_3Mo_2Cl_8$: M.J. Bennet, J.V. Brencic, and F.A. Cotton, *Inorg. Chem., 8,* 1060 (1969); $K_3W_2Cl_9$: W.H. Watson, Jr. and J. Waser, *Acta Cryst., 11,* 689 (1958); $[n\text{-}C_4H_9)_4N][Re_2Cl_9]$: P.F. Stokely, Ph.D. Thesis, M.I.T., 1969; $[(CH_3)_3C_6H_5N]_3R_2Cl_9$: This paper; $Cs_3Tl_2Cl_9$: H.M. Powell and A.F. Wells, *J. Chem. Soc.,* 1008 (1935), and J.L. Hoard and L. Goldstein, *J. Chem. Phys., 3,* 199 (1935); $Cs_3Bi_2I_9$: O. Lindquist, *Acta Chem. Scand., 22,* 2943 (1968); $Fe_2(CO)_9$: H.M. Powell and R.V.G. Ewens, *J. Chem Soc.,* 286 (1939); $[Ru_2Cl_3(Et_2PhP)_6][RuCl_3(Et_2PhP)_3]$: K.A. Raspin, *J. Chem. Soc. (A),* 461 (1969); $[Co(OH)_3(NH_3)_6]Br_3$: P. Anderson, *Acta, Chem. Scand., 21,* 243 (1967).

[b] Estimated standard deviations in structure parameters, occuring in least significant figure, are given in parentheses. These e.s.d.'s are either those given in the original publications or estimates made by the present authors. In two cases there seemed to be no basis for assessing e.s.d.'s and therefore none are listed.

While the confacial bioctahedron may be distorted in many ways, we are interested here in only one type of distortion: elongation or contraction along the C_3 axis such that D_{3h} symmetry is preserved. The resulting general (as opposed to the « ideal ») bioctahedron can be described by a number of structure parameters, some, but not all, of which are independent of each other. Figure 3 shows a number of structure parameters which might, in various combinations, be used to specify the structure of a general bioctahedron. The entire set shown is, of course, redundant, and we now wish to consider which parameters might be considered most useful for practical discussion.

Since our principal concern is to be with the effects of direct M to M forces, either attractive or repulsive, depending on the electron configuration of M, the displacement of the M atoms from the centroids of their own « octahedra » is an obvious modulus of distortion from the ideal structure. This displecement can be expressed conveniently using the ratio d′/d″, where d′ and d″ are defined in Fig. 3. This ratio is unity in the ideal bioctahedron. As Table IX shows, d′ and d″ are not equal in any of the known structures, and the ratio d′/d″ varies from as little as 0.89 to as much as 1.62.

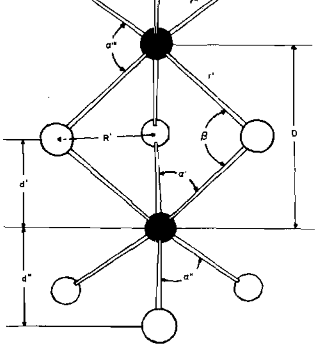


Figure 3. A sketch of a general confacial bioctahedron in which a number of structure parameters are defined.

Two other parameters which must be coupled to the variation in M–M distance, though not necessarily in a simple or exact way, are the angles α′ and β. Instead of dealing with these angles, as such, we again invoke the concept of the ideal bioctahedron and define the following moduli: 90°-α′ and β-70.53°. The former gives the amount by which the X_{br}–M–X_{br} angles deviate from the ideal value of 90° and the latter gives the amount by which the angles at the X_{br} atoms deviate from the ideal value of 70.53°. The expressions for these parameters are so written that each should increase algebraically with an algebraic increase in d′/d″, if we assume that a drawing together of the M atoms will (a) decrease the M–X_{br}–M angles, and (b) increase the X_{br}–M–X_{br} angles, while an increase in d′/d″ would affect each of these angles oppositely. The question then arises: Are there consistent, well-correlated, variations in all three of these distortion moduli?

To answer this question, each of the angular moduli has been plotted against the ratio d′/d″ in Fig. 4. It can be seen that there is a high degree of consistency. The only serious discrepancy is in the case of

$Fe_2(CO)_9$, a species chemically very unlike the others. There are smaller deviations in the case of OH–bridged $(NH_3)_3Co(OH)_3Co(NH_3)^{3+}$ and in the case of $Tl_2Cl_9^{3-}$ where the accuracy of the structure parameters is very low. It is interesting that the species with X = Br, I fit the correlation as well as those with X = Cl. This is not accidental; the moduli used were, in fact, chosen to be insensitive to absolute dimensions and thus to keep all M_2X_9 species on a common basis regardless of changes in size of X and M. Figure 4 justifies the conclusion that there is a well-correlated set of structural variations which, individually and conjointly, afford a measure of the sign and strength of the M–M interaction.

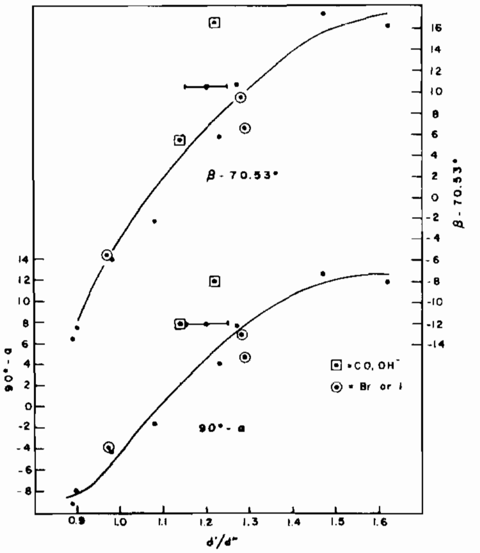


Figure 4. A plot of the angular moduli, 90°-α' and β-70.53° *vs.* the ratio d'/d".

The Probable Origins of Axial Variations. Real confacial bioctahedra should always deviate from the ideal for two main reasons. First, the $M–X_{br}$ bond lengths and $M–X_{br}–M$ angles will both probably tend to have values greater than the ideal, even in the absence of other stresses. Second, there will be some direct interaction between the metal atoms. The M–M interaction may be repulsive, thus tending to elongate the bioctahedron, or it may be attractive, thus tending to contract the central $M(X_{br})_3M$ groups. Regardless of the electron configuration of the metal atoms, there will always be an underlying repulsive potential between the metal atoms, attributable at least partly to overlapping of their electron clouds, and in part to Coulombic repulsion of their positive charges. For appropriate electron configurations an attractive potential will be superimposed. It would be sheer accident if the repulsive and attractive forces happened to cancel exactly in a given case, so as to result in an ideal bioctahedron. It is likely that, in general, a net attraction or net repulsion will prevail.

Summary of Structure Parameters for Isolated Bioctahedra. The dimensions of a considerable number of isolated bioctahedral M_2X_9 units have been reported. These data, in terms of the various structure parameters defined in Figure 3, and also in terms of the ratios and differences between these and corresponding parameters for the ideal bioctahedron are summarized in Table IX. The upper rows of Table IX give actual dimensions, *i.e.*, interatomic distances and angles; the lower part gives various differences and ratios which are useful moduli of the type and degree of distortion from the ideal structure. In particular, the moduli d'/d", 90°–α' and β–70.53°, discussed above, are listed.

Interpretation of Data. We now consider the question of whether, and now, the M–M interaction, as implied by the direction and magnitude of structural variations from the ideal bioctahedron, is related to the electronic structure of the metal atoms. In a few cases, it seems safe to assume that no attractive M–M interaction is possible since the metal atoms have completely filled or completely empty valence orbital subshells after formation of metal-ligand bonds. For $Ti_2Cl_9^-$ the 3d subshells are vacant and for $Tl_2Cl_9^{3-}$ and $Bi_2I_9^{3-}$ the underlying 5d subshells are filled. In these three species the bioctahedra are distinctly elongated, as expected, since the M–M interactions must be exclusively repulsive. It is notable that the magnitude of the elongation (d'/d" = 1.62) in $Ti_2Cl_9^-$ is greater than that in any other species. This may reflect the fact that the formal Ti^{4+} ions bear a considerable positive charge, which may lead to a large electrostatic repulsion between them.

The $Rh_2Cl_9^{3-}$ ion, whose structure is reported in this paper, also exhibits significant elongation (d'/d" = 1.27). Although the metal ions have formal charges of only 3+, and the d shell is neither vacant nor full, a repulsive Rh–Rh interaction is to be expected. The metal ions have low-spin d^6 configurations. Thus, all of the regions of space other than those along metal-ligand bond directions are filled with electron density, much as they would be if the metal ions had filled d shells. In the $Ru_2Cl_3(Et_2PtP)_6^+$ ion we again have d^6 ions, and again there is a repulsive M–M interaction. The repulsive force seems to be even greater here than in the $Rh_2Cl_9^{3-}$ case, since d'/d" = 1.47 as compared to 1.27 for the $Rh_2Cl_9^{3-}$ ion. This may be due to the fact that the lower nuclear charge and lower formal oxidation number for Ru^{3+} should permit the d^6 charge clouds to expand, thereby increasing repulsive overlap.

We shall next discuss the six cases in which the metal ions have d^3 configurations, namely the $Cr_2X_9^{3-}$, $Mo_2X_9^{3-}$, $W_2Cl_9^{3-}$, and $Re_2Cl_9^-$ species. These species are especially interesting since a pair of ions with d^3 configurations have the potentiality of interacting quite strongly. With the three-fold axis of the bioctahedron as the axis of quantization, that set of d orbitals which would be t_{2g} orbitals of each individual octahedron are subdivided into an *a* or σ orbital and a degenerate pair of *e* or π orbitals. Those on each metal ion may then interact to give M–M bonding orbitals of σ and π types. With three electron pairs present, these three bonding orbitals could be just filled to give a bonding $\sigma^2\pi^4$ configuration. The extent to which this actually occurs, however, varies considerably from one case to another.

For both $Cr_2Cl_9^{3-}$ and $Cr_2Br_9^{3-}$, magnetic data down to ~70°K show[23] that there is no bonding interaction between the metal atoms; these species bebave magnetically as though they contain two independent d^3 ions, although presumably at very low temperatures the magnetic behavior would reveal weak interactions. In the absence of a bonding interaction there must be a net repulsive Cr—Cr interaction and this should be evidenced by the structure. As the data in Table IX show, all three of the moduli discussed above confirm this. In fact, the structures themselves would have led to the conclusion that there is a net repulsive Cr—Cr interaction and thus little or no metal-metal bonding.

The $W_2Cl_9^{3-}$ ion stands at the opposite extreme, having a pronounced bonding interaction between the metal atoms which is clearly evident in the structure. The structural moduli indicative of interaction all have the most extreme values in the ranges characteristic of contraction of the bioctahedron. This accords perfectly with magnetic susceptibility, which indicates that there are no unpaired electrons in the ground state, nor is there any paramagnetic excited state thermally accessible at 300°K. The small temperature-independent paramagnetism observed in the range 90°K to 300°K is attributable to a second order Zeeman effect according to Saillant and Wentworth.[23]

The $Mo_2X_9^{3-}$ species appear to be intermediate between the $Cr_2X_9^{3-}$ and $W_2Cl_9^{3-}$ extremes, according to the structural moduli. Thus, using the d′/d″ ratio, we have for the two chromium species (with X = Cl, Br) values between 1.2 and 1.3, while for $W_2Cl_9^{3-}$ the d′/d″ ratio is 0.90. For $Mo_2Cl_9^{3-}$ and $Mo_2Br_9^{3-}$ the ratios are 0.98 and 0.97, respectively. Thus there is a net contraction. Even though the contraction is small relative to the idealized bioctahedron (where d′/d″ = 1), a more relevant comparison is to species in which there is no attractive M—M interaction. As we have seen, for such species, with +3 ions, the d′/d″ modulus lies in the range 1.2-1.5. When the $Mo_2X_9^{3-}$ species are compared to these cases, it is evident that there must be a substantial attractive force between the metal atoms. This conclusion is in good accord with the magnetic susceptibility data,[24] which show that $Cs_3Mo_2Cl_9$ has only temperature-independent paramagnetism, though $Cs_3Mo_2Br_9$ does possess weak, temperature-dependent paramagnetism, indicative of a spin-singlet ground state with one or more paramagnetic excited states slightly thermally populated at 300°K. The fact that the actual Mo—Mo distance in $Mo_2Br_9^{3-}$ is 0.16 Å longer than that in $Mo_2Cl_9^{3-}$ would be consistent with the lower energy of a paramagnetic excited state.

The $Re_2Cl_9^-$ ion shows slight elongation (d′/d″ = 1.08) but still, as compared to the cases of pure M—M repulsion, where the elongations are far greater, it would seem that there is a substantial Re—Re bonding force present. This somewhat unstable species[25] requires more study, especially of its magnetic properties before it can profitably be discussed further.

It is perhaps unjustified to include the $Mo_2Cl_8^{3-}$ ion in this discussion since its structure is unique in one critical respect. One of the bridging Cl atoms of a complete $Mo_2Cl_9^{3-}$ bioctahedron is absent from each anion in a statistically random way, so that each $Mo_2Cl_8^{3-}$ ion lies on a position of crystallographic D_{3h} symmetry. In effect the structure has three 2/3 Cl atoms instead of three full Cl atoms in bridging positions. There appears to be only a single unpaired electron per $Mo_2Cl_8^{3-}$ and thus a triple Mo—Mo interaction presumably exists, as in $Mo_2Cl_9^{3-}$. The greater contraction of this structure as compared to the contraction in $Mo_2Cl_9^{3-}$ (e.g., d′/d″ = 0.89 *vs.* 0.98) most likely reflects the fact that the X_{br} atoms in a bioctahedron oppose contraction along the threefold axis and, thus, with only two instead of three of them present, a greater degree of contraction can be achieved.

$Fe_2(CO)_9$. The diamagnetism of this substance requires that there be a pairing of the spins of two electrons, one on each iron atom. The molecule is often described as having an iron-iron bond. The two statements are not necessarily synonymous, though it appears that they are often so used. The pairing of spins could be through an Fe—Fe bond, but it could also be the result of only a very weak direct interaction, just sufficient to give a diamagnetic ground state. It could even result from an indirect interaction through the bridging CO groups. Let us see if the structural parameters, interpreted in the context of the present discussion, afford any indication of the mechanism of spin-spin coupling. Unfortunately, the uncertainties in bond lengths and angles are quite large and any deductions must be correspondingly insecure.

The structure shows a degree of elongation comparable to that seen in the $Cr_2X_9^{3-}$, $Rh_2Cl_9^{3-}$, $Bi_2I_9^{3-}$, and $Tl_2Cl_9^{3-}$, where a strictly repulsive M—M interaction would be expected. However, we do not think this necessarily suggests that the Fe—Fe interaction is repulsive in $Fe_2(CO)_9$. Indeed it is not unlikely that the structure is consistent with the presence of at least a weak Fe—Fe bond, for two reasons. With the very small bridging atom, C, the maintenance of acceptable M—X_{br} distances necessitates some elongation of the central $Fe(CO)_3Fe$ unit in order to avoid excessive Fe—Fe repulsions, even when an Fe—Fe two-electron bond is formed. Second, the actual value of the Fe—Fe separation, ~2.46 Å, is sufficiently short that one can scarcely doubt that direct overlap of metal orbitals must occur, thus giving an electron distribution which can legitimately be described as an Fe—Fe single bond.

$Co_2(OH)_3(NH_3)_6^{3+}$. Here each metal ion should have a $3d^6$ configuration and hence a purely repulsive Co—Co interaction is expected. The distortion moduli indicate elongation though not to an extreme degree, and the Co—Co distance is relatively short, *viz.*, 2.56 A. The d^6 electron clouds of Co^{3+} may be relatively contracted due to the high nuclear charge and the formal degree of ionization, but even so, some mingling of the d^6 configurations of the two ions might be expected at this distance. Presumably only a close examination of the electronic spectra could

---

[23] R. Saillant and R.A.D. Wentworth, *Inorg Chem.*, *7*, 1606 (1968).

[24] R. Saillant and R.A.D. Wentworth, *Inorg. Chem.*, *8*, 1226 (1969).

[25] F. Bonati and F.A. Cotton, *Inorg. Chem.*, *6*, 1353 (1967).

reveal whether this is so. Such a study would seem to be worthwhile undertaking.

The Structure of $BaRuO_3$. An interesting application of the ideas developed here can be made to the $BaRuO_3$ structure in which there are linear *confacial trioctahedral* groupings. Essentially the same structural criteria for assessing the nature and degree of M–M interactions can be used here. There will be an additional restriction, however, since the central metal atom will be subject to equal and opposite forces, either attractive or repulsive, from each of the end metal atoms. Thus the central metal atom should remain in the center of its octahedron and the resultant distortions must all be accomplished by the movement of one metal atom toward or away from the other, rather than by the combined movements of two metal atoms. This might well have the consequence that a given change in the d′/d″ modulus would imply a greater M–M interaction in the trioctahedron than in the bioctahedron. Another way of describing the situation in the trioctahedron is that a certain amount of the M–M force is nullified in its effect on structure by cancellation at the central metal atom.

Table X. Structure Parameters[a] for Ru_3O_{12} Trioctahedron[b] in $BaRuO_3$

Ru-Ru	2.55(1) A	O_{br}–Ru–O_{br}	84(1)°
Ru-O_{br}	2.00(1) A	O_t–Ru–O_t	94(1)°
	2.02(1) A	Ru–O_{br}–Ru	79(1)°
Ru-O_t	1.96(1) A	d′	1.27 A
O_{br}–O_{br}	2.69(3) A	d″	1.05 A
O_t–O_t	2.87(3) A		
d′/d″	1.21		
90°-α′	6°		
β-70.53	8°		

[a] Some of these are given explicitly in Ref. 25; others have been calculated from the atomic positional coordinates. [b] An ideal confacial trioctahedron has D_{3d} symemtry.

From the reported structure[5] of $BaRuO_3$ the quantities in Table X have been calculated. It can be seen that an appreciable net repulsion between the metal ions is suggested by these figures. Donohue, Katz and Ward proposed that the face sharing of the octahedra occupied by ruthenium atoms implies Ru–Ru bonding, and noted that the Ru–Ru distance here (2.55 A) is shorter than the closest approach distance in ruthenium metal (2.65 A).

We suggest that this may not be so. Metal-to-metal distance in itself may not always provide a criterion for evaluating the M–M interaction, unless, of course, there are no bridging groups. In the present case, and in others comparable to it, the *entire* structure should be analyzed. For $BaRuO_3$ the structure of the Ru_3O_{12} trioctahedron as a whole could be taken to imply that there is no Ru–Ru bond, and that the relatively short Ru–Ru distance is maintained only by the bridging oxygen atoms. We cannot say, and are not saying, that the proposal of Ru–Ru bonding is definitely wrong, but we believe that the occurrence of such bonding is a much more debatable question than previously[5] implied. Since there are a number of other structures[26] related to that of $BaRuO_3$, we believe that the question we have raised here is not a picayune one.

Acknowledgments. This work was supported in part by the National Science Foundation under Grant No. GP-24264. D. A. Ucko is grateful to the Board of Regents of the State of New York for a fellowship. We wish to thank Drs. V. Day, B. G. DeBoer, M. D. LaPrade, and G. Rusholme for their interest and for helpful discussions, and Professor R. A. D. Wentworth of Indiana University for communicating data prior to publication.

(26) P.C. Donohue, L. Katz and R. Ward, *Inorg. Chem.*, 5, 335, 339 (1966).