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Some Reactions of the Octahalodirhenate(III) Ions. VII. Structural Characterization of Dichlorotetrabenzoatodirhenium(III)^{1,2}

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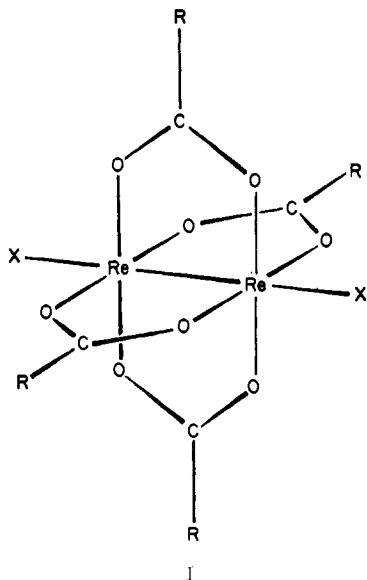
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The crystal and molecular structure of the chloroform adduct of chlororhenium(III)- μ -tetrabenzoato-chlororhenium(III), $\text{ClRe}(\text{O}_2\text{CC}_6\text{H}_5)_4\text{ReCl}\cdot 2\text{CHCl}_3$, has been determined by single-crystal X-ray diffraction methods. The crystal data are: space group $P2_1/c$, $a = 11.029 \pm 0.002 \text{ \AA}$, $b = 10.760 \pm 0.002 \text{ \AA}$, $c = 18.383 \pm 0.005 \text{ \AA}$, $\beta = 119.02 \pm 0.03^\circ$, $V = 1908 \text{ \AA}^3$, density $2.03 \pm 0.03 \text{ g cm}^{-3}$ (by flotation), 2.03 g cm^{-3} (calcd for $Z = 2$). The intensities of 1477 reflections above background were collected on a manually operated counterdiffractometer with $\text{Mo K}\alpha$ radiation. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares to final unweighted and weighted residuals of 0.049 and 0.050, respectively. The structure is analogous to that of copper acetate dihydrate, consisting of centrosymmetric molecules of virtual symmetry D_{4h} comprised of two rhenium atoms, four bridging benzoate groups, and two axial chlorine atoms. The short Re-Re distance of 2.235 \AA suggests quadruple metal-metal bonding, as has been proposed for the dinuclear molybdenum(II) acetate and the $\text{Re}_2\text{Cl}_8^{2-}$ ion. Two chloroform molecules per dimeric unit are enclosed in the lattice. They appear to be hydrogen bonded to the axial chlorine atoms.

Introduction

The preparation of $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$ compounds, albeit in poor yields, was first reported by Taha and Wilkinson,³ who obtained them by refluxing Re_2Cl_9 with RCOOH plus a trace of $(\text{RCO})_2\text{O}$. It was soon after discovered in this laboratory⁴ that the reaction of the $\text{Re}_2\text{X}_8^{2-}$ ions with RCOOH yielded $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$ compounds virtually quantitatively, and the scope of the reaction was later explored and the products were studied in some detail.⁵

Taha and Wilkinson³ suggested that the $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$ compounds were most likely to have the carboxylate-bridged structure I, although they were non-committal regarding the likelihood of Re-Re bonding.



Reports^{4,5} from this laboratory endorsed the suggestion of structure I and proposed unequivocally that strong Re-Re bonds should exist. It was specifically postulated that the Re-Re bonds should be essentially the same as those in the $\text{Re}_2\text{X}_8^{2-}$ species, where quadruple bonds are believed to exist.^{6,7}

Other investigations of the $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$ molecules, as well as the analogous $\text{Mo}_2(\text{O}_2\text{CR})_4$ compounds, are being carried out in this laboratory, but before proceeding further in these studies, it was considered wise to ascertain for certain, by means of an X-ray crystallographic study of the molecular structure, whether the $\text{Re}_2(\text{O}_2\text{CR})_4\text{X}_2$ molecules do indeed have structure I, and whether the Re-Re bond length is as short ($\sim 2.24 \text{ \AA}$) as those in the $\text{Re}_2\text{X}_8^{2-}$ ion⁸ and in $\text{Re}_2\text{Cl}_6(\text{P}(\text{C}_2\text{H}_5)_3)_2$.⁹

Since a structure of the type I was in fact found, the correct systematic name for the rhenium compound studied is chlororhenium(III)- μ -tetrabenzoato-chlororhenium(III).

Experimental Procedure

Preparation of Crystals.—Experiments with several $\text{Re}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ compounds were carried out ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{or } \text{C}_6\text{H}_7$). Each one was found to be unsatisfactory from a crystallographic point of view. The benzoate compound, $\text{Re}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{Cl}_2$, was next tried, and it afforded satisfactory crystals. The compound was prepared by literature methods⁵ from rhenium trichloride, Re_2Cl_9 , by way of the octachlorodirhenate(III) ion¹⁰ and $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$. The crude product was recrystallized from chloroform by slow evaporation under nitrogen at room temperature. The red crystals so obtained were stable in air for months but were observed visually to deteriorate under vacuum. Analyses indicated that the crystals which had not been subjected to pumping contained two molecules of chloroform per dinuclear molecule which can be removed at room temperature under vacuum.

Anal. Calcd for $\text{Re}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{Cl}_2\cdot 2\text{CHCl}_3$: C, 30.89; H, 1.90; Cl, 24.31. Found: C, 31.2; H, 2.03; Cl, 23.7. Calcd

(1) This work was supported in part by the U. S. Atomic Energy Commission.

(2) Preceding paper in this series, part VI: F. Bonati and F. A. Cotton, *Inorg. Chem.*, **6**, 1353 (1967).

(3) F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).

(4) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).

(5) F. A. Cotton, C. Oldham, and R. A. Walton, *ibid.*, **5**, 1798 (1966).

(6) F. A. Cotton, *ibid.*, **4**, 334 (1965).

(7) F. A. Cotton and C. B. Harris, *ibid.*, **6**, 924 (1967).

(8) F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965).

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

(10) R. A. Bailey and J. A. McIntyre, *Inorg. Chem.*, **5**, 1940 (1966).

for $\text{Re}_2(\text{O}_2\text{CC}_6\text{H}_5)_4\text{Cl}_2$: C, 36.24; H, 2.17; Cl, 7.68. Found (after vacuum drying): C, 36.1; H, 2.28; Cl, 7.68.

Collection and Reduction of X-Ray Data.—The rhenium benzoate crystallized in the form of hexagonal or rhomboidal plates with well-developed $\{100\}$ faces. The systematic absences, $h0l$, for $l \neq 2n$, and $0k0$, for $k \neq 2n$, observed on Weissenberg and precession films of $hk0$, $h0l$, and $h1l$, uniquely determined the space group as $P2_1/c$ (no. 14). The unit cell dimensions, determined on a General Electric XRD-5 manual diffractometer at 20° by the method outlined by Bennett, Cotton, and Takats,¹¹ are $a = 11.029 \pm 0.002 \text{ \AA}$, $b = 10.760 \pm 0.002 \text{ \AA}$, $c = 18.383 \pm 0.005 \text{ \AA}$, and $\beta = 119.02 \pm 0.03^\circ$. The uncertainties quoted represent maximum estimated error. Copper radiation [λ ($K\alpha_1$) 1.5405 \AA , λ ($K\alpha_2$) 1.5443 \AA] was used for the determination of cell constants.

The density measured by flotation in an aqueous solution of zinc iodide was $2.03 \pm 0.03 \text{ g cm}^{-3}$, while the density calculated for two formula units per unit cell ($V = 1908 \text{ \AA}^3$) is 2.03 g cm^{-3} .

Intensity data were collected on a rhomboidal platelet $0.150 \times 0.075 \times 0.055 \text{ mm}$ in size, mounted along b on a glass fiber and coated with a thin layer of shellac to avoid possible oxidation and loss of chloroform. Mo $K\alpha$ radiation, filtered by zirconium foil, was used to measure 1998 independent reflections with $(\sin \theta)/\lambda$ less than 0.5. Intensities were measured by a scintillation counter with the pulse height discriminator set to accept 95% of the peak with the window centered on the $K\alpha$ peak. The distances from crystal to source and crystal to circular screening aperture (2°) were 5.73 and 7.05 in., respectively, while the take-off angle was 2° . A coupled θ - 2θ moving-crystal, moving-counter technique with a scan rate of $2^\circ/\text{min}$ was used to scan a range of 1.33° in 2θ centered on the calculated position¹² of the $K\alpha$ peak. Stationary background counts were taken for 20 sec at each end of the scan range. A periodic check of several reflections showed no systematic variation in intensity indicative of crystal decomposition.

Experimental data were corrected for background, assuming linear variation over the scan range, and the integrated intensities so obtained¹³ were corrected for Lorentz and polarization effects and for absorption¹⁴ ($\mu = 73.01 \text{ cm}^{-1}$, transmission factors 0.45–0.73), using an idealized rhomboidal prism as an approximation to the experimental crystal. Of the experimental intensities, 1477 were found to be statistically significant using the dual criteria: $I > 0$, and $I/[P + (t_p/t_b)^2(B_1 + B_2)]^{1/2} \geq 2$, where t_p and t_b are total counting time for peak and background, and P , B_1 , and B_2 are total counts in the peak and two backgrounds, respectively. Only these statistically significant reflections were used in subsequent refinement.

A weighting scheme of $w = 1/\sigma^2(|F_o|)$ was used throughout the refinement, with standard deviations derived from the standard deviation of the experimental intensities according to Doedens and Ibers,¹⁶ using an uncertainty factor, p , of 0.045.

Solution and Refinement of the Structure.—The positions of the rhenium atoms and the chlorine atoms bound to them were determined by examination of a three-dimensional map of the Patterson function.¹⁶ These atom parameters were subjected to one cycle of least-squares refinement¹⁷ and used to determine the signs of structure factors for the calculation of a difference Fourier map, which showed the positions of the carbon and oxygen atoms of the two independent benzoate groups but failed to resolve clearly the atoms of the chloroform molecule. After two cycles of refinement of the over-all scale factor and the positional and isotropic thermal parameters of all atoms in the dimer, a structure factor calculation was carried out; this gave

a discrepancy index, R_1 , of 0.11 ($R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$). A second difference Fourier map at this point clearly showed the position of the chloroform molecule, but the diffuse nature of the peaks indicated either a small rotational disorder or a large amplitude of vibration about the C_3 axis of the molecule. The carbon and chlorine atoms of the chloroform molecule were included in four cycles of isotropic refinement, after which anisotropic temperature factors were assigned to the rhenium and chlorine atoms of the dimer and the four heavy atoms of the chloroform molecule. At this point the residuals R_1 and R_2 were 0.052 and 0.069, respectively ($R_2 = \{\Sigma w[|F_o| - |F_c|]^2 / \Sigma w|F_o|^2\}^{1/2}$). Two cycles of mixed anisotropic and isotropic refinement, followed by a difference Fourier calculation, produced an electron density map showing the locations of some of the hydrogen atoms of the phenyl rings. Since all of the hydrogen atoms were not resolved, they were introduced isotropically at positions calculated from the phenyl ring carbon positions, and the entire asymmetric unit was subjected to two cycles of refinement. The hydrogen atom positions did not refine satisfactorily and were therefore fixed at their calculated values with temperature factors 0.5 larger than those of the carbon atoms to which they are attached. Two final cycles of refinement lowered the unweighted and weighted residuals, R_1 and R_2 , to 0.049 and 0.050, respectively. In the final cycle of refinement, no parameter changed by more than one-fifth its estimated standard deviation. A final difference Fourier map showed no peaks higher than $0.8 \text{ e}^-/\text{\AA}^3$.

The inclusion of the phenyl hydrogen atoms, even though they failed to refine satisfactorily, is considered justified by the marked improvement which thereby results in fitting the intensities of low-angle reflections to which these atoms would be expected to contribute most heavily.

Although the vibrational ellipsoids of the chloroform chlorine atoms showed significant rotational components about the C_3 axis of the molecule, the final difference Fourier synthesis showed peaks approximately one-sixth the size of the originally assigned chlorine peaks between the assigned chlorine positions. No evidence was found for more complex disorder, however, and, since rotational motion of this type would have little effect on the molecular parameters of interest, we felt our approximation of hindered rotation through anisotropic thermal motion to be justified.

The correctness of the weighting scheme chosen is reflected by the lack of dependence of $w\Delta^2$ ($\Delta = |F_o| - |F_c|$) on $|F_o|$ and $(\sin \theta)/\lambda$, in accordance with Cruickshank's criterion,¹⁸ and the approximate value of unity (0.985) obtained for the estimated standard deviation of an observation of unit weight. Our value indicates a slight overestimation of the standard deviations of the intensity data.

Results

The molecular structure and the position of the chloroform molecules relative to the axial chlorine atoms are shown in Figure 1. Figure 2 shows the packing of the chloroform molecule in the lattice. In Table I are the final calculated and observed structure amplitudes. Table II reports fractional coordinates and isotropic temperature parameters for the

(11) M¹ J. Bennett, F. A. Cotton, and J. Takats, *J. Am. Chem. Soc.*, **90**, 903 (1968).

(12) D. P. Shoemaker, MIXG2-A, an IBM 360 version of MIXG2.

(13) M. J. Bennett, FMMO, an X-ray crystallographic data-reduction program.

(14) W. C. Hamilton, GONOR, extinction and absorption correction for goniostat data on polyhedral crystals.

(15) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(16) FORDAP II, a highly modified version of Zalkin's original Fourier program written by B. M. Foxman of MIT for the IBM 360.

(17) (a) SFLS5, "A Full-Matrix Crystallographic Program for the IBM 360," by C. T. Prewitt (modified by B. M. Foxman), 1966. This program minimizes $\Sigma w(|F_o| - |F_c|)^2$. (b) Structure factors were calculated using atomic scattering factors from the following sources. Re, Cl: D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965); C, O: J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202; H: R. Mason and C. B. Robertson in "Advances in Structure Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1966, p 57. For Re and Cl the real and imaginary parts of anomalous scattering were included in the calculation according to J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964). These values were from D. T. Cromer, *ibid.*, **18**, 17 (1965).

(18) D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press Inc., New York, N. Y., 1965, p 113.

TABLE I
OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (X10) (IN ELECTRONS) FOR Re2Cl2(O2CC6H5)2·2CHCl3

Table with multiple columns containing numerical data representing structure amplitudes. The data is organized into groups, likely corresponding to different reflections or symmetry-equivalent positions. Each group contains observed and calculated values.

atoms of the asymmetric unit. Anisotropic thermal parameters for Re, Cl, and the heavy atoms of the chloroform molecule are shown in Table III. Tables IV-VI contain data on molecular bond lengths, angles, and planes, respectively. The numbering system shown in Figure 1 is used throughout, with centrosymmetrically related atoms (lighter lined in Figure 1) indicated by the subscript "i."

Discussion

The crystal structure of Re2Cl2(O2CC6H5)2·2CHCl3, as shown in Figure 1, consists of discrete dinuclear units composed of two rhenium atoms, four bridging benzoate

groups, and two axial chlorine atoms. A full calculation of intermolecular contacts indicates no irregularities except for the abnormally short distance between the axial chlorine atoms and the chloroform molecules to which they appear to be hydrogen bonded. Although crystallographically the molecule possesses only a center of symmetry, the dimer has an eclipsed rotomeric configuration of virtual symmetry D4h with only minor distortions which are attributable to crystalline forces. Each rhenium atom is thus at the center of a square set of oxygen atoms, with the other rhenium and an axial chlorine atom completing the axially distorted octahedral coordination about the metal.

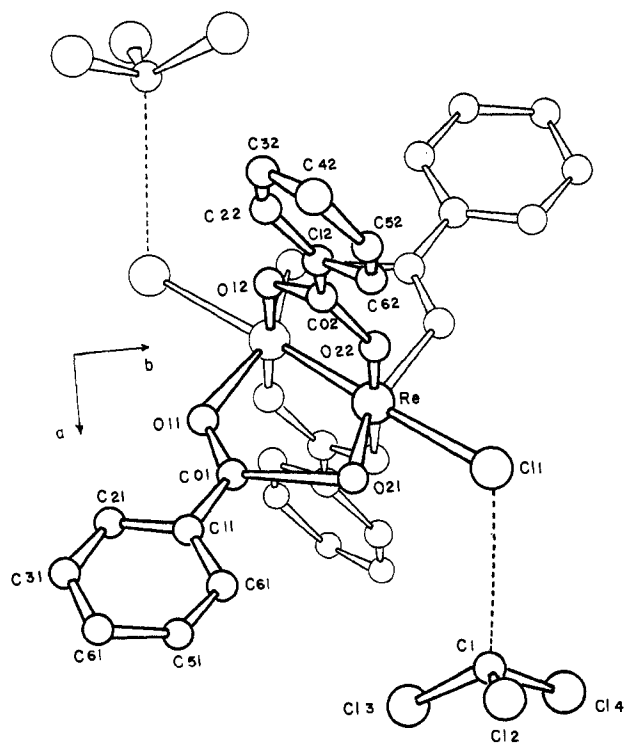


Figure 1.—The $\text{Re}_2\text{Cl}_2(\text{O}_2\text{C}_6\text{H}_5)_4 \cdot 2\text{CHCl}_3$ moiety projected on the (001) plane. Atoms in light outline are related to labeled atoms by an inversion center located at the cell origin, midway between the two rhenium atoms.

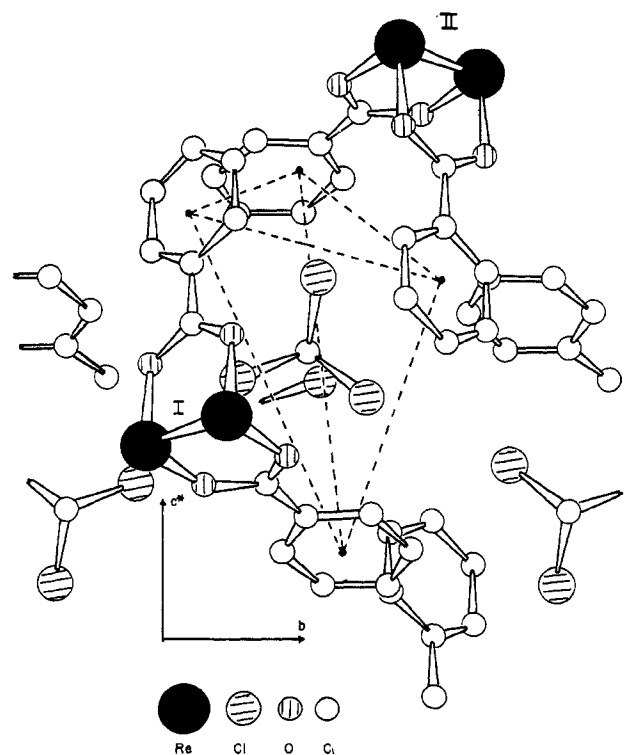


Figure 2.—A view down the a axis showing the immediate environment of the chloroform molecule. The cell origin lies at the center of dirhenium molecule I. Parts of the two dirhenium molecules have been omitted for clarity.

Despite the fact that the structure is of the type found in $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$, in which metal-metal interaction is weak and not such as to constitute bonding, the specific dimensions here,

TABLE II

FINAL POSITIONAL AND ISOTROPIC THERMAL PARAMETERS ^{a,b}				
Atom	x	y	z	$B, \text{\AA}^2$
Re	0.07356 (8)	0.08017 (7)	0.01969 (4)	2.60
Cl ₁	0.2296 (5)	0.2645 (4)	0.0655 (2)	4.03
O ₁₁	0.0888 (12)	-0.1972 (9)	0.0339 (6)	2.80 (23)
O ₂₁	0.2353 (13)	-0.0352 (10)	0.0739 (7)	3.39 (25)
O ₁₂	-0.0752 (11)	-0.0720 (10)	0.0900 (6)	2.84 (21)
O ₂₂	0.0707 (11)	0.0893 (10)	0.1290 (6)	2.89 (21)
C ₀₁	0.2107 (20)	-0.1583 (16)	0.0713 (10)	3.14 (36)
C ₁₁	0.3284 (17)	-0.2386 (16)	0.1155 (9)	3.04 (34)
C ₂₁	0.3069 (22)	-0.3657 (18)	0.1114 (12)	4.89 (45)
C ₃₁	0.4190 (21)	-0.4456 (17)	0.1601 (11)	4.77 (44)
C ₄₁	0.5513 (23)	-0.4002 (20)	0.2085 (12)	5.42 (48)
C ₅₁	0.5705 (24)	-0.2707 (22)	0.2060 (12)	6.10 (52)
C ₆₁	0.4619 (20)	-0.1903 (16)	0.1625 (11)	3.85 (40)
C ₀₂	-0.0021 (17)	0.0093 (14)	0.1437 (10)	2.71 (33)
C ₁₂	0.0037 (18)	0.0114 (15)	0.2251 (10)	3.19 (35)
C ₂₂	-0.0745 (20)	-0.0689 (19)	0.2408 (11)	4.84 (40)
C ₃₂	-0.0656 (21)	-0.0674 (20)	0.3223 (11)	4.89 (43)
C ₄₂	0.0248 (24)	0.0140 (20)	0.3790 (13)	5.70 (50)
C ₅₂	0.1009 (22)	0.0946 (20)	0.3637 (12)	5.33 (45)
C ₆₂	0.0908 (19)	0.0961 (17)	0.2844 (10)	3.75 (38)
Cl ₁	0.5880 (32)	0.2380 (28)	0.1076 (15)	9.37
Cl ₂	0.7176 (13)	0.2599 (13)	0.2046 (7)	16.89
Cl ₃	0.6100 (14)	0.1023 (10)	0.0695 (7)	17.59
Cl ₄	0.5759 (17)	0.3538 (11)	0.0448 (8)	18.87
H ₂₁	0.203	-0.402	0.075	5.8
H ₃₁	0.400	-0.545	0.158	6.0
H ₄₁	0.638	-0.462	0.243	6.9
H ₅₁	0.675	-0.234	0.246	7.1
H ₆₁	0.478	-0.091	0.161	4.8
H ₂₂	-0.143	-0.131	0.192	5.4
H ₃₂	-0.127	-0.132	0.335	6.2
H ₄₂	0.033	0.016	0.440	6.8
H ₅₂	0.170	0.157	0.413	6.0
H ₆₂	0.154	0.158	0.269	4.9

^a Numbers in parentheses here and in the following tables are esd's in the last figure(s) quoted. ^b Equivalent isotropic B 's are quoted here for the anisotropically refined atoms. B 's for hydrogen atoms are derived from those of the carbon atoms to which they are attached, as described in the text.

as in the case of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, show that strong metal-metal bonding exists. The basic rationale of this argument and characteristics of the structures mentioned have been discussed recently.¹⁹ It is of particular interest that in this carboxylato-bridged molecule, the Re-Re distance (2.235 Å) is identical within the experimental uncertainties with those found^{8,9} in the non-bridged species $\text{Re}_2\text{Cl}_8^{2-}$ and $\text{Re}_2\text{Cl}_6[\text{P}(\text{C}_2\text{H}_5)_3]_2$. In the latter species the existence of quadruple Re-Re bonds is strongly indicated,^{6,7} and hence the suggestion that such multiple bonds prevail also in the carboxylato-bridged molecules receives considerable support.

A most interesting and significant feature of the structure is the length of the Re-Cl bond, 2.49 Å. This is considerably longer than the Re-Cl bonds normally observed for rhenium in its III and IV oxidation states,^{8,9,20} viz., 2.35 Å, and is reminiscent of the long bonds in the centrifugal positions of $\text{Re}_3\text{Cl}_{12}^{3-}$ (2.52 Å) and Re_3Cl_9 (2.66 Å). It indicates a bond considerably weaker than normal and is thus consistent with the

(19) F. A. Cotton, *Rev. Pure Appl. Chem.*, **17**, 25 (1967).

(20) See the forthcoming review by B. R. Penfold in "Perspectives in Structural Chemistry," J. D. Dunitz and J. A. Ibers, Ed., Academic Press, New York, N. Y., 1968, for a tabulation of data.

TABLE III
ANISOTROPIC TEMPERATURE PARAMETERS^a ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	68.5 (9)	61.3 (7)	23.4 (3)	-12.4 (9)	19.5 (4)	-2.5 (5)
Cl ₁	110 (7)	82 (5)	38 (2)	-39 (5)	27 (3)	-5 (3)
C ₁	367 (62)	196 (37)	57 (13)	51 (44)	83 (24)	-4 (20)
Cl ₂	519 (29)	413 (21)	123 (7)	85 (24)	131 (12)	-34 (12)
Cl ₃	529 (32)	230 (15)	163 (8)	27 (18)	72 (13)	-40 (9)
Cl ₄	842 (45)	316 (18)	204 (11)	121 (23)	337 (20)	90 (11)

^a Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE IV

INTRAMOLECULAR DISTANCES^a

Atoms	Distance, Å	Atoms	Distance, Å
Re-Re ₁	2.235 (5)	C ₆₁ -C ₁₁	1.40 (3)
Re-Cl ₁	2.489 (5)	O ₁₂ -C ₀₂	1.27 (2)
Re-O ₁₁	2.01 (1)	O ₂₂ -C ₀₂	1.29 (2)
Re-O ₂₁	2.00 (1)	C ₀₂ -C ₁₂	1.47 (2)
Re-O _{12₁}	2.03 (1)	C ₁₂ -C ₂₂	1.35 (3)
Re-O ₂₂	2.03 (1)	C ₂₂ -C ₃₂	1.45 (3)
O ₁₁ -C ₀₁	1.25 (2)	C ₃₂ -C ₄₂	1.36 (3)
O ₂₁ -C ₀₁	1.35 (2)	C ₄₂ -C ₅₂	1.33 (3)
C ₀₁ -C ₁₁	1.44 (2)	C ₅₂ -C ₆₂	1.41 (3)
C ₁₁ -C ₂₁	1.38 (3)	C ₆₂ -C ₁₂	1.39 (2)
C ₂₁ -C ₃₁	1.41 (3)	C ₁ -Cl ₂	1.68 (3)
C ₃₁ -C ₄₁	1.38 (3)	C ₁ -Cl ₃	1.69 (3)
C ₄₁ -C ₅₁	1.41 (3)	C ₁ -Cl ₄	1.66 (3)
C ₅₁ -C ₆₁	1.38 (3)		

^a Distances, angles, and planes calculated with MGEOM, by J. S. Wood.

TABLE V

BOND ANGLES

Atoms	Angle, deg	Atoms	Angle, deg
Re ₁ -Re-Cl ₁	177.1 (1)	O ₁₂ -C ₀₂ -C ₁₂	120 (1)
Re ₁ -Re-O _{11₁}	89.5 (3)	O ₂₂ -C ₀₂ -C ₁₂	119 (1)
Re ₁ -Re-O ₂₁	90.8 (3)	C ₀₁ -C ₁₁ -C ₂₁	119 (2)
Re ₁ -Re-O _{12₁}	90.0 (3)	C ₀₁ -C ₁₁ -C ₆₁	121 (2)
Re ₁ -Re-O ₂₂	90.0 (3)	C ₀₂ -C ₁₂ -C ₂₂	120 (2)
O _{11₁} -Re-O ₂₂	91.0 (4)	C ₀₂ -C ₁₂ -C ₆₂	119 (1)
O ₂₂ -Re-O ₂₁	88.6 (5)	C ₆₁ -C ₁₁ -C ₂₁	120 (2)
O ₂₁ -Re-O _{12₁}	91.8 (5)	C ₁₁ -C ₂₁ -C ₃₁	120 (2)
O _{12₁} -Re-O ₁₁	88.6 (4)	C ₂₁ -C ₃₁ -C ₄₁	121 (2)
Cl ₁ -Re-O _{11₁}	88.4 (3)	C ₃₁ -C ₄₁ -C ₅₁	117 (2)
Cl ₁ -Re-O ₂₂	88.1 (3)	C ₄₁ -C ₅₁ -C ₆₁	122 (2)
Cl ₁ -Re-O ₂₁	91.3 (4)	C ₅₁ -C ₆₁ -C ₁₁	119 (2)
Cl ₁ -Re-O _{12₁}	91.9 (3)	C ₆₂ -C ₁₂ -C ₂₂	122 (2)
Re ₁ -O ₁₁ -C ₀₁	122 (1)	C ₁₂ -C ₂₂ -C ₃₂	119 (2)
Re-O ₂₁ -C ₀₁	118 (1)	C ₂₂ -C ₃₂ -C ₄₂	117 (2)
Re ₁ -O ₁₂ -C ₀₂	120 (1)	C ₃₂ -C ₄₂ -C ₅₂	124 (2)
Re-O ₂₂ -C ₀₂	119 (1)	C ₄₂ -C ₅₂ -C ₆₂	119 (2)
O ₁₁ -C ₀₁ -O ₂₁	120 (2)	C ₅₂ -C ₆₂ -C ₁₂	119 (2)
O ₁₂ -C ₀₂ -O ₂₂	121 (1)	Cl ₂ -C ₁ -Cl ₃	110 (2)
O ₁₁ -C ₀₁ -C ₁₁	123 (2)	Cl ₃ -C ₁ -Cl ₄	110 (2)
O ₂₁ -C ₀₁ -C ₁₁	117 (2)	Cl ₄ -C ₁ -Cl ₂	112 (2)

indications of weakness provided by the lability of such axial ligands^{5,21} and suggested by far-infrared data.²²

The structure of the rhenium benzoate chloride dimer is remarkably regular, approaching quantitative D_{4h} symmetry. As shown in Tables IV-VI, the four independent Re-O bond lengths are statistically equal at 2.02 Å, the four O-Re-O angles are 90° within experimental error, the ReO₄ and Re₂O₂C groupings are rigorously planar and orthogonal to one another,

(21) B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.*, 5683 (1964); J. H. Hickford and J. E. Fergusson, *ibid.*, 113 (1967).

(22) W. K. Bratton and F. A. Cotton, to be submitted for publication.

TABLE VI

Weighted Mean Molecular Planes^a

Type of plane	No.	Equation
ReO ₄	1	0.5614x + 0.7794y + 0.2782z = 1.1179
Re ₂ O ₂ C (1)	2	-0.5110x + 0.0615y + 0.8574z = 0.0003
Re ₂ O ₂ C (2)	3	0.6586x - 0.6340y + 0.4053z = 0.0000
C ₆ H ₅ (1)	4	-0.6186x + 0.0883y + 0.7807z = -0.3996
C ₆ H ₅ (2)	5	0.6680x - 0.6731y + 0.3173z = -0.2571
Re ₂ O ₂ CC ₆ H ₅ (1)	6	-0.5357x + 0.0895y + 0.8397z = -0.0031
Re ₂ O ₂ CC ₆ H ₅ (2)	7	0.6747x - 0.6338y + 0.3782z = -0.0022

Dihedral Angles

Planes	Angle	Planes	Angle	Planes	Angle
1-2	90° 14'	2-3	91° 37'	3-5	5° 33'
1-3	90° 40'	2-4	7° 44'	6-7	95° 46'

Distances of Atoms from Planes (Å)^b

Plane 1:	Re, -0.0007; O _{11₁} , 0.004; O ₂₁ , 0.005; O _{12₁} , -0.0002; O ₂₂ , -0.0003.
Plane 2:	Re, -0.0006; Re, 0.00006; O ₁₁ , -0.010; O ₂₁ , 0.005; C ₀₁ , 0.015.
Plane 3:	Re, 0.00002; Re ₁ , -0.00007; O ₁₂ , 0.003; O ₂₂ , -0.013; C ₀₂ , 0.014.
Plane 4:	C ₁₁ , 0.019; C ₂₁ , -0.028; C ₃₁ , 0.009; C ₄₁ , 0.026; C ₅₁ , -0.029; C ₆₁ , 0.003.
Plane 5:	C ₁₂ , 0.009; C ₂₂ , 0.001; C ₃₂ , -0.015; C ₄₂ , 0.014; C ₅₂ , 0.004; C ₆₂ , -0.013.
Plane 6:	Re, 0.006; Re ₁ , 0.0005; O ₁₁ , -0.09; O ₂₁ , -0.07; C ₀₁ , -0.09; C ₁₁ , -0.06; C ₂₁ , -0.13; C ₃₁ , 0.02; C ₄₁ , 0.17; C ₅₁ , 0.14; C ₆₁ , 0.06.
Plane 7:	Re, 0.004; Re ₁ , 0.0003; O ₁₂ , -0.06; O ₂₂ , -0.07; C ₀₂ , -0.07; C ₁₂ , -0.03; C ₂₂ , -0.07; C ₃₂ , -0.007; C ₄₂ , 0.11; C ₅₂ , 0.13; C ₆₂ , 0.04.

^a The orthogonal coordinate system x, y, z corresponds to the crystal a, b, c* axes. ^b Average esd's in atom positions derived from uncertainties in fractional coordinates are as follows (Å): Re, 0.0008; O, 0.013; C, 0.023.

and the molecule is in strictly eclipsed rotational configuration. The only significant deviations from strict D_{4h} symmetry are the noncolinearity of the Re-Re and Re-Cl bonds and the slight twist of the phenyl rings with respect to the mean planes of the carboxylate-rhenium rings. These deviations are small and it seems entirely reasonable that they should be attributed to crystalline packing forces rather than to any inherent characteristics of the dinuclear molecule.

As shown in Figure 2, the chloroform molecule occupies a distorted tetrahedral cage formed by four phenyl rings, with other contacts coming from adjacent chloroform molecules and other phenyl rings. The most interesting contact occurs with the axial chlorine atom of a dimer located one translation unit behind

the one labeled I in the figure. The view shown coincides with the C_3 axis of the molecule so that the chloroform hydrogen atom lies directly behind the carbon atom shown, the C-H bond making an angle of $14 \pm 3^\circ$ with the C-Cl vector. Using this angle and the C-Cl contact distance of $3.65 \pm 0.03 \text{ \AA}$, together with an assumed C-H bond length of 1.07 \AA , the H...Cl contact between the chloroform hydrogen atom and the axial chlorine atom of the dimer may be calculated as 2.6 \AA , suggesting an appreciable degree of hydrogen-bonding interaction.²³ McGinney, *et al.*,

(23) (a) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968, Table 1-1, p 16. Calculated and observed values for H...Cl in N-H...Cl of 3.0 and 2.4 \AA , respectively, suggest that 2.6 \AA for H...Cl in C-H...Cl is a reasonable value. (b) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman Co., San Francisco, Calif., 1960, Table 9-XXV, pp 290, 291. Extension of tabulated N-H...Cl contacts by 0.1 \AA predicts C-H...Cl hydrogen-bonding contacts up to about 3.6 \AA .

report similar evidence for C-H...I hydrogen bonding between methylene chloride and iodine in a recent paper.²⁴ Although considerable spectroscopic and calorimetric data indicate that C-H...B hydrogen bonding can occur when the carbon atom bears electronegative substituents,²⁵ there is little structural evidence available to support these findings. Observation of intensity or frequency changes in the infrared C-H stretching mode of the chloroform molecule which would support the presence of hydrogen bonding in the present instance is precluded by the C-H vibrations of the phenyl rings, which occur in the same region of the spectrum.

(24) J. A. McGinney, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 2243 (1967).

(25) Reference 23b, Section 6.2, pp 197-201.

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The Crystal Structure of Aluminum Tetrahydroborate-Trimethylamine at 25 and -160°

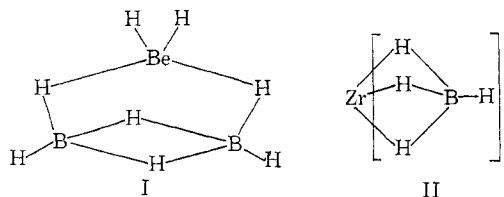
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Aluminum tetrahydroborate-trimethylamine, $(\text{CH}_3)_3\text{N} \rightarrow \text{Al}(\text{BH}_4)_3$, forms orthorhombic crystals with unit cell parameters $a = 13.02 \text{ \AA}$, $b = 7.53 \text{ \AA}$, $c = 11.33 \text{ \AA}$, $Z = 4$, $\rho_{\text{calcd}} = 0.781 \text{ g/cc}$ at 25° and $a = 12.88 \text{ \AA}$, $b = 7.15 \text{ \AA}$, $c = 11.40 \text{ \AA}$, $Z = 4$ at -160° ; the space group is Pnam at both temperatures. The room- and low-temperature structure determinations, from data collected by photographic methods, have converged to discrepancy indices of 0.103 and 0.091 based on 388 and 597 independent reflections, respectively; in the low-temperature structure, hydrogen atoms were located. In the monomeric complex, the coordination of the aluminum atom is approximately tetrahedral at room temperature, but at low temperature the coordination is asymmetric; the nitrogen atom shows near-tetrahedral coordination in both structure determinations. At room temperature the mean skeletal bond lengths (in \AA) are: N-C, 1.59 ($\sigma = 0.02$); Al-N, 2.00 ($\sigma = 0.01$); Al-B, 2.19 ($\sigma = 0.02$); at low temperature these become: N-C, 1.52 ($\sigma = 0.01$); Al-N, 1.99 ($\sigma = 0.01$); Al-B, 2.24 ($\sigma = 0.01$); and the two distinct N-Al-B bond angles are 121.8° ($\sigma = 0.4^\circ$) and 100.8° ($\sigma = 0.3^\circ$). The relationship between the two structures is discussed in the light of disordering and exchange mechanisms and the room-temperature structure is compared with those of related molecules.

Introduction

Several metal tetrahydroborates which exhibit a high degree of covalent character (*e.g.*, $\text{Be}(\text{BH}_4)_2$, $\text{Al}(\text{BH}_4)_3$, $\text{Zr}(\text{BH}_4)_4$, etc.) are now known,¹ and it has been suggested² that in these compounds the metal and boron atoms are linked by bridging hydrogen atoms. However, recent structure determinations by X-ray and electron diffraction methods have indicated that the type of bridging system may vary. Thus it has been suggested that $\text{Be}(\text{BH}_4)_2$ ³ and $\text{Zr}(\text{BH}_4)_4$ ⁴ possess structures I and II, respectively, although the precise positions of the hydrogen atoms have not yet been unambiguously determined. The infrared spectra and other physical



properties of $\text{Hf}(\text{BH}_4)_4$ and $\text{U}(\text{BH}_4)_4$ are closely similar to those of $\text{Zr}(\text{BH}_4)_4$,⁵ and it might therefore be inferred that they have similar structures. It would therefore be of interest to compare these structures with those of other metal tetrahydroborates.

Although $\text{Al}(\text{BH}_4)_3$ is a liquid at ambient temperatures, many of its derivatives, *e.g.*, $(\text{CH}_3)_3\text{N} \cdot \text{Al}(\text{BH}_4)_3$, are crystalline solids,⁶ and a detailed study of this adduct by X-ray diffraction was undertaken at both 25 and -160° to determine the AlB_3 skeletal arrangement and the

(1) H. G. Heal, "Recent Studies in Boron Chemistry," Royal Institute of Chemistry Monograph, No. 1, London, 1960.

(2) W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949).

(3) A. Almennigen, G. Gundersen, and A. Haaland, *Chem. Commun.*, 557 (1967).

(4) P. H. Bird and M. R. Churchill, *ibid.*, 403 (1967).

(5) B. D. James and M. G. H. Wallbridge, to be submitted for publication.

(6) P. H. Bird and M. G. H. Wallbridge, *J. Chem. Soc.*, 3923 (1965).