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Tetraiododibenzoatodirhenium(III)

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The new compound $Re_2I_4(O_2CC_6H_5)_2$ has been isolated. In order to investigate the secondary dependence of Re–Re bond length on steric factors, the crystal and molecular structures of this compound, which was expected to be μ-dibenzoatotetraiododirhenium(III), have been determined from 2559 independent, nonzero reflections collected with a manual counter-diffractometer, using Mo Kα radiation. The compound crystallizes in the triclinic space group $C\bar{1}$ with four dinuclear molecules in a unit cell of dimensions: $a = 11.224 \pm 0.003$ Å, $b = 17.535 \pm 0.005$ Å, $c = 10.869 \pm 0.003$ Å, $\alpha = 91° 54' \pm 3'$, $\beta = 89° 10' \pm 5'$, $\gamma = 92° 45' \pm 5'$ ($\rho_{\text{calcd}} = 3.49$ g cm^{-1}, $\rho_{\text{obsd}} = 3.50 \pm 0.04$ g cm^{-1}). The structure was solved by conventional Patterson and Fourier methods and refined by the full-matrix least-squares procedure to final unweighted and weighted residuals of 0.040 and 0.048, respectively. The dinuclear molecular structure is formally derived from the $Re_2X_8^{2-}$ ion by replacement of four halide ions by two bridging benzoate ions. The remarkably short Re–Re distance of 2.198 (1) Å indicates the presence of quadruple metal–metal bonding, as has been proposed for other dinuclear compounds of Re(III) and Mo(II).

Introduction

The reaction of the dirhenium octahalide ions $Re_2X_8^{2-}$ (where X is Cl, Br) with carboxylic acids has been shown to produce mixed halide–carboxylate complexes of three distinct types: $Re_2(O_2CR)_4X_2$,[1] $Re_2(O_2CR)_3X_3 \cdot L$, and $Re_2(O_2CR)_2X_4 \cdot 2L$.[2] The first class with R = C_6H_5 and X = Cl has been shown to have a structure qualitatively analogous to that of copper acetate dihydrate, but differing quantitatively in the degree of metal–metal interaction.[3] The third class, represented by $Re_2(O_2CCH_3)_2Cl_4 \cdot 2H_2O$, is reported to have the same type of dinuclear structure with a short metal–metal distance (2.22 Å) and two chlorine atoms bonded to each atom,[4] but the report is preliminary in nature and contains no further details.

In the course of preparing $Re_2(O_2CC_6H_5)_4I_2$ to study the effect of the axial iodine atoms on the metal–metal bond length, crystals were obtained in small yield which differed visibly from the diiodide compound. Subsequent investigation indicated that these were the compound $Re_2(O_2CC_6H_5)_2I_4$, an example of the third type indicated above, with no L groups present. Since the parent $Re_2I_8^{2-}$ ion is presently unknown, a structural investigation of this compound was undertaken to determine the effect of the bulky iodine atoms upon the over-all geometry of the molecule and particularly upon the length of the Re–Re bond.

Experimental Procedure

Preparation.—In order to prepare $Re_2(O_2CC_6H_5)_4I_2$, a solution of $Re_2(O_2CC_3H_7)_4(H_2O)_2SO_4$[1] was allowed to react with 55% aqueous HI to produce a brown precipitate of "$Re_2(O_2CC_3H_7)_4I_2$." This material was then mixed with excess benzoic acid and the mixture was fused under nitrogen to exchange benzoate for butyrate. The excess benzoic acid was removed with ether, and the red-brown product was recrystallized from chloroform under nitrogen. Microscopic examination of the crystalline product revealed two different types of crystals: red-brown platelets which powdered soon after removal from the mother liquor and shiny black prisms which were air stable. The former product was demonstrated to be $Re_2(O_2CC_6H_5)_4I_2$ whose crystals immediately lose solvent in air. The latter was found to be $Re_2(O_2CC_6H_5)_2I_4$. Both compounds are soluble in polar halocarbons, the diiodide slightly more so than the tetraiodide, so that repeated fractional crystallization may be used to separate the two. Their solubilities are very close, however, so that manual crystal picking had to be employed to obtain an analytically pure sample.

Further investigation of the iodide-exchange reaction of the butyrate compound showed that the reaction is quite complex. Products containing rhenium and various proportions of iodine and carboxylate may be obtained by variation in the reaction time. The tetrabutyrate–diiodide dinuclear rhenium compound is obtained with very short reaction times, while an ionic, water-soluble rhenium iodide is obtained after prolonged reaction. Further study of this system is being carried out.

Both the tetrabenzoate–diiodide compound and the dibenzoate–tetraiodide compound may also be obtained by the direct reaction of $Re_2(O_2CC_6H_5)_4Cl_2$ with 55% HI. This reaction also yields several other products which have not been fully characterized.

A manually separated, crystalline sample of the black compound gave the following analytical results. *Anal.* Calcd for $Re_2(O_2CC_6H_5)_2I_4$: C, 14.98; H, 0.90; I, 45.23. Found: C, 15.2; H, 0.89; I, 45.4.

Collection and Reduction of X-Ray Data.—Crystallographically suitable crystals of $Re_2(O_2CC_6H_5)_2I_4$ were obtained by slow evaporation in air of a chloroform solution of the compound. Weissenberg and precession photographs suggested a triclinic space group, and the systematic extinction $h + k \neq 2n$ for hkl indicated space groups C1 or $C\bar{1}$. Unit cell dimensions, determined[5] on a General Electric XRD-5 manual diffractometer at 22° with Cu Kα radiation, $\lambda(K\alpha_1)$ 1.5405 Å and $\lambda(K\alpha_2)$ 1.5443 Å, are as follows: $a = 11.224 \pm 0.003$ Å, $b = 17.535 \pm 0.005$ Å, $c = 10.869 \pm 0.003$ Å, $\alpha = 91° 54' \pm 3'$, $\beta = 89° 10' \pm 5'$, $\gamma = 92° 45' \pm 5'$. The angles β and γ were derived from measurements of precession photographs, and their uncertainties reflect the estimated precision of these measurements. The corresponding reduced, primitive cell has the following dimensions: $a = 10.869$ Å, $b = 11.224$ Å, $c = 14.937$ Å, $\alpha = 113° 9'$, $\beta = 134° 39'$, $\gamma = 90° 50'$. The density measured by flotation in aqueous thallium formate–thallium malonate solution was 3.50 ± 0.04 g cm^{-3}, while the density calculated for four di-

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[1] F. A. Cotton, C. Oldham, and W. R. Robinson, *Inorg. Chem.*, **5**, 1798 (1966).

[2] F. A. Cotton, C. Oldham, and R. A. Walton, *ibid.*, **6**, 214 (1967).

[3] M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *ibid.*, **7**, 1570 (1968).

[4] P. A. Koz'min, M. D. Surazhkaya, and V. G. Kuznetsov, *Zh. Strukt. Khim.*, **8**, 1107 (1967); *J. Struct. Chem.*, **8**, 983 (1967).

[5] M. J. Bennett, F. A. Cotton, and J. Takats, *J. Am. Chem. Soc.*, **90**, 903 (1968).

nuclear molecules per C-centered unit cell (V = 2135.3 Å^3) is 3.49 g cm^{-3}.

A crystal with well-formed {010}, {001}, {$1\bar{1}1$}, and {$11\bar{1}$} faces, approximately 0.14 × 0.07 × 0.11 mm in size, was mounted on a glass fiber and aligned with a^* coincident with the diffractometer ϕ axis. Mo Kα radiation filtered through zirconium foil was used to measure 2972 independent reflections with (sin θ)/λ less than 0.55. 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 Kα peak. The distances from crystal to source and crystal to circular screening aperture (2°) were 5.73 and 7.05 in., respectively, while the takeoff angle was 2°. A coupled θ–2θ moving-crystal, moving-counter technique with a scan rate of 4°/min was used to scan a range of 2.66° in 2θ centered on the calculated[6] position of the Kα peak. Stationary background counts were taken for 20 sec at each end of the scan range. Periodic checks of the intensity of several strong reflections showed no systematic variation in intensity.

Experimental data were corrected for background, assuming linear variation over the scan range, and the integrated intensities (I) so obtained were tested for statistical significance, using the dual criteria: $I > 0$ and $I \geq 2(P + B_1 + B_2)^{1/2}$, where P, B_1, and B_2 are total counts in the peak and two backgrounds, respectively. A total of 413 reflections violating either of these two conditions were excluded from further consideration. The remaining intensities were corrected for Lorentz and polarization effects[7] and for absorption,[8] using the equations for the faces of the crystal (μ = 178.13 cm^{-1}, transmission factors 0.21–0.41). The weighting scheme previously described[3] was used throughout the refinement, with an uncertainty factor, p, of 0.045.

Solution and Refinement of the Structure.—From a three-dimensional map of the Patterson function[9] the positions of two independent rhenium atoms were determined, one at x = 0.06, y = 0.03, z = 0.06; the second at x = 0.06, y = 0.55, z = 0.44. These were consistent with the presence of two independent, centrosymmetric dinuclear molecules located on the centers of $C\bar{1}$ at the origin and 0, $^1/_2$, $^1/_2$. These positional parameters, together with an over-all scale factor and isotropic temperature factors, were subjected to two cycles of full-matrix least-squares refinement[10] in $C\bar{1}$, and were used to obtain signs of structure factors for a difference Fourier map, from which the positions of the four independent iodine atoms were determined. These positions, as well as independent isotropic temperature factors, were included in two further cycles of refinement, after which a second difference Fourier map was calculated. The residuals R_1 and R_2 at this point were 0.14 and 0.18, respectively ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$).

The second difference Fourier map clearly indicated the positions of the carbon and oxygen atoms of the two independent benzoate groups. After four cycles of isotropic refinement, convergence was achieved with R_1 = 0.077 and R_2 = 0.097. The rhenium and iodine atoms were next assigned anisotropic temperature factors, and refinement was continued for four more cycles, after which R_1 and R_2 were 0.040 and 0.048, respectively. Examination of a difference Fourier map calculated from these parameters showed some peaks near positions calculated for the hydrogen atoms of the phenyl rings, but there were also peaks of about the same size (*ca.* 1 e$^-$/Å^3) which could only be attributed to random noise, as well as peaks of 1.6 e$^-$/Å^3 near the rhenium and iodine atoms.

The hydrogen atoms were introduced into the refinement but failed to refine satisfactorily. They were therefore fixed at their calculated positions ($R_{\text{C-H}}$ = 1.0 Å) with temperature factors 0.5 Å^2 higher than the carbon atoms to which they are attached. Two final cycles of refinement brought convergence, with no parameter changing by more than one-tenth of its estimated standard deviation in the final cycle.

Atomic scattering factors used for structure factor calculations were from Cromer and Waber[11] for Re and I, from Ibers[12] for C and O, and from Mason and Robertson[13] for H. Anomalous dispersion corrections[14] for Re and I were included in the calculations according to Ibers and Hamilton.[15]

The value for the estimated standard deviation of an observation of unit weight in this structure determination is 0.77, indicating an overestimation of the standard deviations of the intensity data. Variation in the value of $w\Delta^2$ ($\Delta = |F_o| - |F_c|$) for different ranges of $|F_o|$ and (sin θ)/λ was satisfactorily small.[16]

Results

The molecular structure of $Re_2(O_2CC_6H_5)_2I_4$ is shown in Figure 1. The numbering scheme shown is used for both independent centrosymmetric molecules, an additional subscript 1 or 2 differentiating between the two. Centrosymmetrically related atoms are denoted by a prime. Figure 2 shows the crystal packing of half of the unit cell. The molecules light-lined in the figure are located on centers in the $xy0$ plane and bear subscript 1 in the following tables; those heavy-lined lie at 0.5 in z and are denoted by subscript 2. In Table I are reported the final calculated and observed structure amplitudes. Table II contains final positional parameters and isotropic temperature factors for the atoms of the asymmetric unit. Anisotropic thermal parameters and amplitudes of vibration for the heavy atoms are presented in Table III. Tables IV and V contain molecular bond lengths and angles, while Table VI describes some molecular planes.

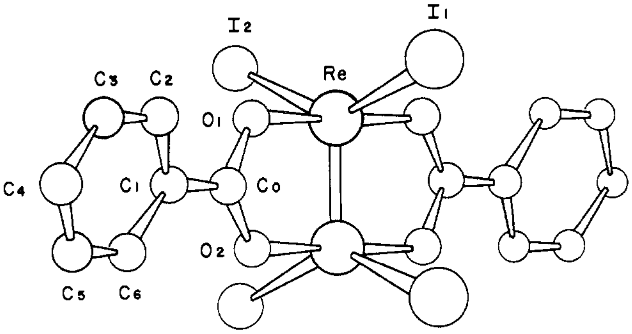

Figure 1.—A perspective view of the $Re_2I_4(O_2CC_6H_5)_2$ molecule. Unlabeled atoms are related to labeled ones by inversion centers located midway between the rhenium atoms.

Discussion

The crystal structure of $Re_2(O_2CC_6H_5)_2I_4$ is built of two independent, centrosymmetric dinuclear molecules packed together as shown in Figure 2. The two dinuclear molecules are virtually identical in every dimension, as may be determined from Tables IV–VI;

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[6] D. P. Shoemaker, MIXG2-A, an IBM 360 version of MIXG2.

[7] M. J. Bennett, PMMO, an X-ray crystallographic data reduction program.

[8] W. C. Hamilton, GONO9, extinction and absorption correction for goniostat data on polyhedral crystals.

[9] A. Zalkin, FORDAP, Fourier data processing program, extensively modified by B. M. Foxman.

[10] C. T. Prewitt, SFLS5, a full-matrix crystallographic program for the IBM 360. This program minimizes $\Sigma w(|F_o| - |F_c|)^2$.

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

[12] J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

[13] R. Mason and C. B. Robertson, *Advan. Struct. Res. Diffraction Methods*, **2**, 57 (1966).

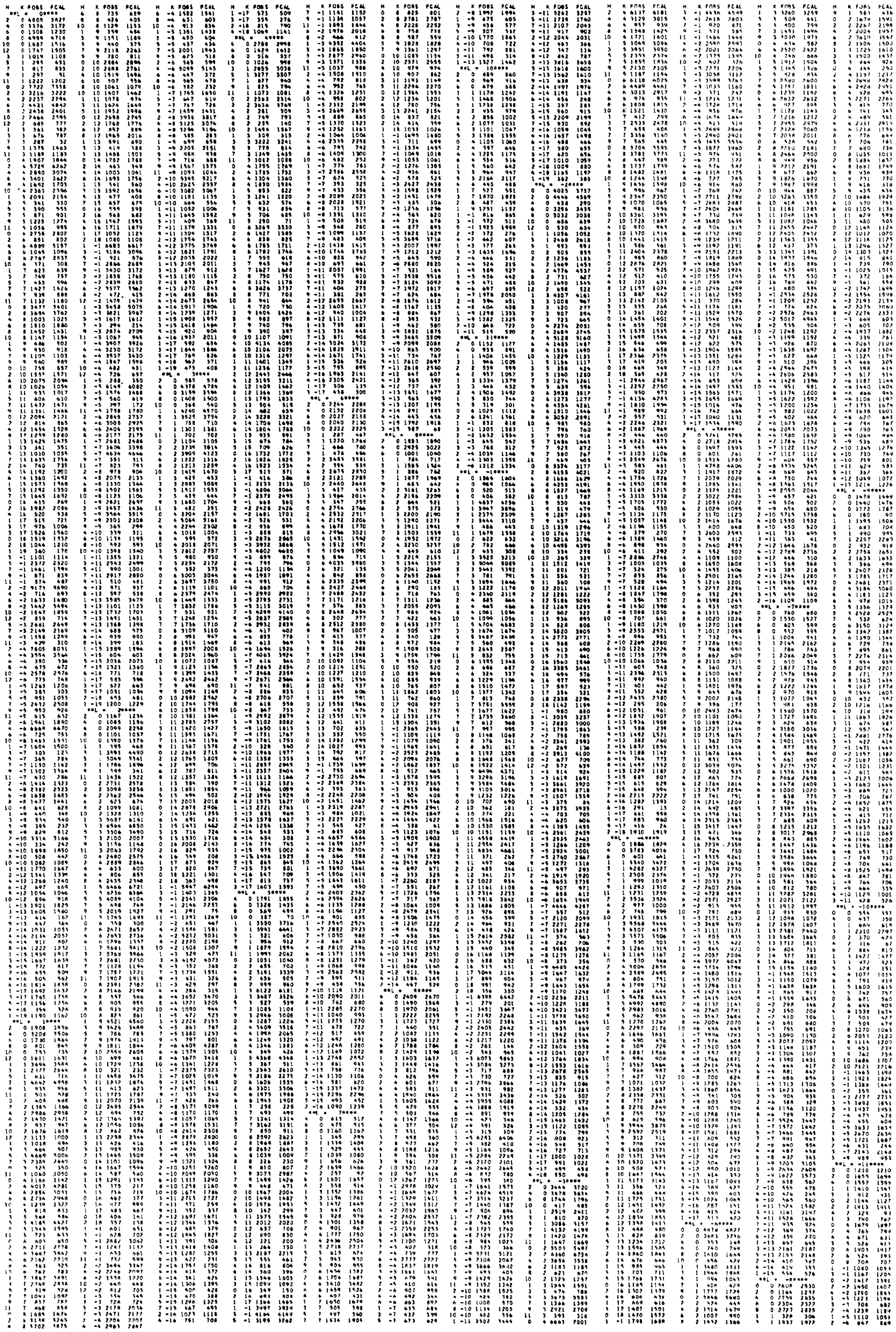
[14] D. T. Cromer, *Acta Cryst.* **18**, 17 (1965).

[15] J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

[16] 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 (×10) (IN ELECTRONS) FOR $Re_2(O_2CC_6H_5)_2I_4$



and their over-all geometry is shown in Figure 1 where the line of view bisects the Re–Re bond and the angle between the Re_2I_4 and the Re_2O_2C planes. With the exception of the benzoate phenyl rings, which are significantly tilted out of carboxylate–rhenium planes, the symmetry of the molecule is D_{2h}. The two ends are rigorously eclipsed, and the metal–metal distance is very short, as would be expected for a compound with a quadruple bond joining the metal atoms.

It is evident from Figure 1 that the $Re_2(O_2CC_6H_5)_2I_4$ molecule is structurally related to the $Re_2X_8^{2-}$ ions[17]

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[17] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965).

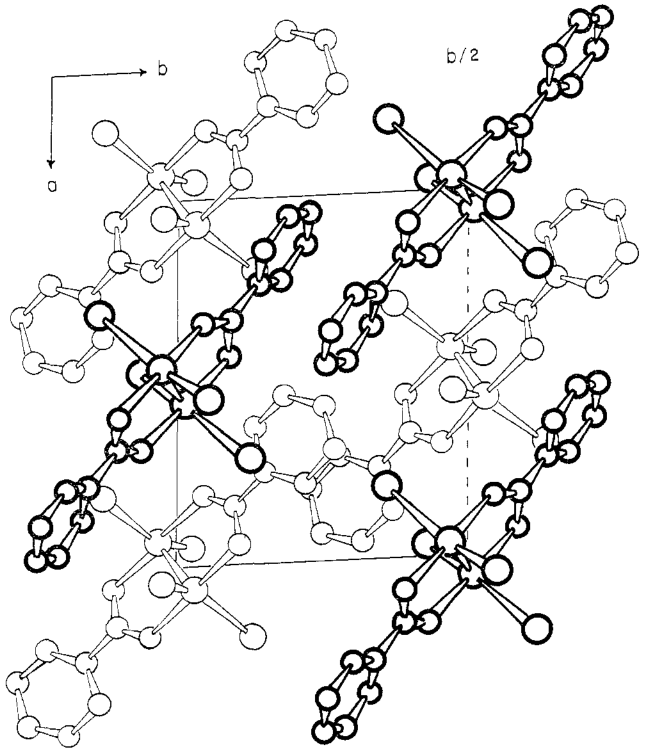

Figure 2.—The contents of half of the unit cell projected on the (001) plane. Molecules in light outline lie on centers at z = 0.0; those in heavy outline are at z = 0.5. The two sets are not related by symmetry.

Table II

Final Positional and Isotropic Thermal Parameters[a,b]

Atom	x	y	z	B, Å^2
Re_1	0.06594 (5)	0.03144 (3)	0.05864 (6)	2.57
I_{11}	0.19552 (9)	0.13144 (6)	−0.06694 (12)	4.21
I_{21}	0.04708 (10)	−0.01907 (6)	0.28203 (10)	4.04
O_{11}	0.1881 (8)	−0.0458 (5)	0.0132 (10)	3.00 (19)
O_{21}	0.0540 (8)	−0.1102 (5)	−0.1016 (9)	2.84 (18)
C_{01}	0.1597 (12)	−0.1015 (8)	−0.0645 (14)	3.01 (27)
C_{11}	0.2521 (12)	−0.1545 (7)	−0.1003 (14)	2.76 (25)
C_{21}	0.3701 (14)	−0.1322 (9)	−0.0827 (16)	4.03 (32)
C_{31}	0.4557 (15)	−0.1838 (9)	−0.1204 (17)	4.50 (35)
C_{41}	0.4254 (14)	−0.2532 (9)	−0.1753 (17)	4.20 (33)
C_{51}	0.3058 (14)	−0.2736 (9)	−0.1923 (16)	4.16 (33)
C_{61}	0.2183 (13)	−0.2243 (8)	−0.1554 (15)	3.41 (29)
Re_2	0.04682 (5)	0.51761 (3)	0.41536 (5)	2.51
I_{12}	0.20597 (9)	0.62788 (6)	0.46640 (11)	3.93
I_{22}	−0.03588 (10)	0.43511 (6)	0.22714 (10)	4.04
O_{12}	0.1721 (8)	0.4411 (5)	0.4412 (9)	2.70 (17)
O_{22}	0.0768 (8)	0.4065 (5)	0.6133 (9)	2.72 (18)
C_{02}	0.1689 (12)	0.4009 (7)	0.5401 (14)	2.80 (26)
C_{12}	0.2660 (12)	0.3526 (8)	0.5630 (14)	2.94 (26)
C_{22}	0.3571 (12)	0.3413 (8)	0.4802 (14)	3.21 (28)
C_{32}	0.4490 (14)	0.2992 (9)	0.5041 (16)	3.99 (32)
C_{42}	0.4567 (15)	0.2667 (10)	0.6154 (18)	4.61 (35)
C_{52}	0.3662 (15)	0.2761 (9)	0.7061 (17)	4.32 (34)
C_{62}	0.2695 (13)	0.3196 (8)	0.6780 (15)	3.44 (29)
H_{21}	0.393	−0.081	−0.043	4.6
H_{31}	0.544	−0.168	−0.107	5.1
H_{41}	0.488	−0.289	−0.203	4.7
H_{51}	0.283	−0.327	−0.233	4.7
H_{61}	0.132	−0.239	−0.168	4.0
H_{22}	0.353	0.366	0.394	3.7
H_{32}	0.517	0.292	0.440	4.5
H_{42}	0.526	0.233	0.637	5.2
H_{52}	0.370	0.253	0.789	4.8
H_{62}	0.205	0.327	0.742	3.9

[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 given here for the anisotropically refined atoms. B's for hydrogen atoms are set 0.5 Å^2 higher than those of the carbon atoms to which they are attached.

and may be formally derived from the unknown $Re_2I_8^{2-}$ ion by substitution of two bridging carboxylate ions for four of the iodide ions. The Re–O bond lengths are equal to those observed in $Re_2(O_2CC_6H_5)_4Cl_2$[3] and the Re–I bond lengths are very similar to the nonbridging Re–I distances reported for Re_3I_9[18] (2.580–2.635 Å). The two iodine atoms bound to each rhenium atom are swept back with respect to a plane perpendicular to the Re–Re bond and containing the rhenium and oxygen atoms so that the coordination around each rhenium atom may be better described as trigonal bipyramidal, rather than square pyramidal as is the case for the $Re_2X_8^{2-}$ ions. In this description the oxygen atoms of the carboxylate groups occupy the axial positions while the two iodine atoms and the other rhenium atom lie in the equatorial positions. The angles in the equatorial plane are 110, 110, and 140°, with the smaller angles adjacent to the Re–Re bond.

The length of the Re–Re bond is remarkably short in this compound, 2.198 (1) Å, significantly shorter than those observed in the $Re_2Cl_8^{2-}$ ion[17,19] and $Re_2(O_2CC_6H_5)_4Cl_2$ (2.241 (7) and 2.235 (2) Å, respectively), and slightly shorter than that reported[20] for $Re_2Cl_6[P(C_2H_5)_3]_2$ (2.222 (3) Å). A report of uncertain reliability[21] claims an Re–Re bond length of 2.207 (3) Å in $Re_2Br_8^{2-}$, which is not significantly different from the one in this structure. The presence of the iodine atoms in an eclipsed configuration in this molecule might have been expected to result in a slight lengthening of the metal–metal bond because of the steric repulsion of the iodine atoms. However, the lack of steric interaction on the ends of the molecule allows the iodine atoms to move away from this contact, thereby permitting the metal atoms to move closer together. In the more sterically crowded $Re_2X_8^{2-}$ ions a slight lengthening of the metal–metal bond in $Re_2Br_8^{2-}$ over that in $Re_2Cl_8^{2-}$ might have been expected. The reported[21] result is the opposite, however.

It is interesting to speculate, from a strictly steric point of view, on the possibility of preparing the $Re_2I_8^{2-}$ ion. If the Re–I bond length observed in the present structure is assumed to be a normal distance

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[18] M. J. Bennett, F. A. Cotton, and B. M. Foxman, *Inorg. Chem.*, **7**, 1563 (1968).

[19] V. G. Kuznetzov and P. A. Koz'min, *Zh. Strukt. Khim.*, **4**, 55 (1965), reported for $(C_5H_6N)_2Re_2Cl_8$ an Re–Re distance of 2.22 ± 0.02 Å, obtained by "trial and error" refinement. Their data were refined by least squares (*cf.* W. R. Robinson, Ph.D. Thesis, MIT, 1965) giving Re–Re = 2.244 ± 0.015 Å. Other distances, *viz.*, Re–Cl and Cl···Cl, changed somewhat from those reported but esd's are so large that the changes have no clear significance. There are no significant differences between the dimensions of $Re_2Cl_8^{2-}$ in the two compounds $(C_5H_6N)_2Re_2Cl_8$ and $K_2Re_2Cl_8 \cdot 2H_2O$.

[20] F. A. Cotton and B. M. Foxman, *Inorg. Chem.*, **7**, 2135 (1968).

[21] P. A. Koz'min, V. G. Kuznetzov, and Z. V. Popova, *Zh. Strukt. Khim.*, **6**, 651 (1965).

TABLE III

Anisotropic Temperature Parameters[a] (×10⁴)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re_1	52.0 (5)	18.9 (2)	58.4 (6)	−0.9 (2)	−5.0 (4)	0.2 (3)
I_{11}	73 (1)	32.2 (4)	105 (1)	−9.7 (5)	7.1 (9)	13.9 (6)
I_{21}	109 (1)	29.2 (4)	65 (1)	−2.8 (5)	−5.5 (9)	6.3 (5)
Re_2	52.5 (5)	22.3 (2)	46.6 (6)	1.2 (2)	3.5 (4)	8.3 (3)
I_{12}	72.5 (9)	30.4 (4)	93 (1)	−11.5 (5)	−3.6 (8)	13.5 (5)
I_{22}	100 (1)	34.1 (4)	60 (1)	−1.4 (5)	−9.2 (9)	−1.1 (5)

Root-Mean-Square Amplitudes of Vibration and Their Orientation[b]

	Minor axis	Medium axis	Major axis
Re_1	0.167	0.181	0.192
	(61.7, 35.9, 74.9)	(51.3, 125.0, 54.2)	(128.2, 83.2, 39.8)
I_{11}	0.180	0.241	0.264
	(50.6, 49.0, 111.4)	(40.2, 121.8, 63.5)	(96.6, 57.3, 35.2)
I_{21}	0.190	0.215	0.266
	(89.2, 118.4, 26.5)	(76.5, 32.4, 64.2)	(12.6, 104.2, 95.9)
Re_2	0.151	0.184	0.197
	(101.0, 121.2, 32.7)	(14.6, 106.7, 84.7)	(80.6, 36.3, 57.8)
I_{12}	0.177	0.224	0.261
	(53.9, 43.9, 108.3)	(48.8, 105.4, 43.0)	(117.8, 50.2, 52.8)
I_{22}	0.186	0.229	0.257
	(79.1, 81.5, 14.9)	(76.7, 19.9, 103.1)	(17.4, 107.9, 97.0)

[a] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Amplitudes given are in angströms; angles in parentheses are with respect to the crystallographic *a*, *b*, *c* axes, respectively.

TABLE IV

INTRAMOLECULAR DISTANCES (Å)[a]

Molecule 1	Atoms	Molecule 2
2.199 (1)	Re–Re′	2.197 (1)
2.629 (1)	$Re–I_1$	2.620 (1)
2.614 (1)	$Re–I_2$	2.621 (1)
2.018 (9)	$Re–O_1$	2.018 (9)
2.014 (9)	$Re'–O_2$	2.003 (9)
1.30 (2)	$O_1–C_0$	1.30 (2)
1.26 (2)	$O_2–C_0$	1.30 (2)
1.47 (2)	$C_0–C_1$	1.44 (2)
1.38 (2)	$C_1–C_2$	1.37 (2)
1.40 (2)	$C_2–C_3$	1.33 (2)
1.37 (2)	$C_3–C_4$	1.36 (3)
1.39 (2)	$C_4–C_5$	1.42 (3)
1.39 (2)	$C_5–C_6$	1.40 (2)
1.38 (2)	$C_6–C_1$	1.40 (2)

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

TABLE V

INTERBOND ANGLES (DEG)

Molecule 1	Atoms	Molecule 2
111.50 (4)	$Re'–Re–I_1$	109.98 (4)
109.05 (4)	$Re'–Re–I_2$	109.72 (4)
90.3 (3)	$Re'–Re–O_1$	90.5 (3)
90.1 (3)	$Re–Re'–O_2$	90.4 (3)
87.8 (3)	$I_1–Re–O_1$	89.1 (3)
91.1 (3)	$O_1–Re–I_2$	90.3 (2)
90.0 (3)	$I_2–Re–O_2'$	89.1 (3)
90.9 (3)	$O_2'–Re–I_1$	91.0 (3)
119.1 (8)	$Re–O_1–C_0$	120.1 (8)
120.5 (9)	$Re'–O_2–C_0$	121.1 (9)
120 (1)	$O_1–C_0–O_2$	118 (1)
118 (1)	$O_1–C_0–C_1$	119 (1)
122 (1)	$O_2–C_0–C_1$	123 (1)
119 (1)	$C_0–C_1–C_6$	118 (1)
119 (1)	$C_0–C_1–C_2$	123 (1)
122 (1)	$C_6–C_1–C_2$	119 (1)
117 (2)	$C_1–C_2–C_3$	123 (1)
122 (2)	$C_2–C_3–C_4$	120 (2)
119 (1)	$C_3–C_4–C_5$	120 (2)
121 (2)	$C_4–C_5–C_6$	118 (2)
119 (1)	$C_5–C_6–C_1$	119 (1)

TABLE VI

Type of plane	No.	Directional cosines[a]			Origin dist, Å
			m	*n*	
$Re_2I_2(1)$	1	−0.6599	0.7164	0.2265	−0.0001
$Re_2O_2C(1)$	2	−0.2948	−0.5556	0.7775	−0.0001
$C_6H_5(1)$	3	−0.0316	−0.4380	0.8984	0.1585
$Re_2I_2(2)$	4	0.6870	−0.7127	0.1418	−5.3012
$Re_2O_2C(2)$	5	0.5405	0.6568	0.5258	8.5340
$C_6H_5(2)$	6	0.5000	0.7851	0.3655	8.3488

Dihedral Angles

Planes	Angle	Planes	Angle
1–2	91° 34′	4–5	91° 16′
2–3	17° 59′	5–6	12° 1′

Distances of Atoms from Planes, Å[b]

Plane 1: Re_1, 0.005; Re_1', −0.005; I_{11}, −0.012; I_{21}', 0.011
Plane 2: Re_1, 0.002; Re_1', 0.0000; O_{11}, −0.005; O_{21}, 0.038; C_{01}, −0.046
Plane 3: C_{11}, 0.004; C_{21}, −0.007; C_{31}, 0.006; C_{41}, −0.002; C_{51}, 0.0005; C_{61}, −0.002
Plane 4: Re_2, −0.002; Re_2', 0.002; I_{12}, 0.004; I_{22}', −0.004
Plane 5: Re_2, 0.0000; Re_2', −0.0001; O_{12}, −0.022; O_{22}, −0.010; C_{02}, 0.045
Plane 6: C_{12}, −0.0006; C_{22}, 0.006; C_{32}, −0.008; C_{42}, 0.003; C_{52}, 0.004; C_{62}, −0.004

[a] The directional cosines are with respect to the Cartesian axis system *x*, *y*, *z*, which corresponds to the crystallographic axes ($b \times c^*$), *b*, c^*. [b] Average esd's in atom positions derived from uncertainties in fractional coordinates are as follows (Å): Re, 0.0006; I, 0.001; O, 0.01; C, 0.02.

and a nonbonded I–I contact is assumed to have a lower limit of 3.50–3.60 Å as in Re_3I_9,[18] it is a simple matter to calculate the minimum Re–Re bond length compatible with an eclipsed D_{4h} type of structure. For a limiting I–I contact of 3.5 Å, the Re–Re bond length is 1.78 Å, and the Re–Re–I angle is 109° 9′. If the I–I contact must be no less than 3.6 Å, the minimum Re–Re bond length is 2.36 Å, and the Re–Re–I angle decreases to 103° 41′. For a metal–metal bond length of 2.25 Å, the I–I contacts are about 3.58 Å and the Re–Re–I angle is 104° 45′, quite close to the Re–Re–Cl angle of 103.7 ± 2.1° observed in $Re_2Cl_8^{2-}$. It is evident that the calculated minimum Re–Re bond length is extremely sensitive to the assumed limiting, nonbonded I–I contact. However, from the information presently available, it appears that the $Re_2I_8^{2-}$ ion may be sterically feasible. Further work on this question is presently under way in this laboratory.

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The Crystal and Molecular Structures of a Toluene-Containing Form of Di-μ-aquo-di-μ_3-hydroxo-deca(1,1,1-trifluoropentane-2,4-dionato)hexanickel(II)[1]

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The crystal and molecular structures of di-μ-aquo-di-μ_3-hydroxo-deca(1,1,1-trifluoropentane-2,4-dionato)hexanickel(II)–toluene (an enclosure compound) have been determined. The compound crystallizes in space group $P2_1/c$ with unit cell dimensions $a = 14.268 \pm 0.006$ Å, $b = 17.519 \pm 0.006$ Å, $c = 16.862 \pm 0.006$ Å, $\beta = 107.57 \pm 0.05°$, and $Z = 2$. Of 4215 reflections collected by counter methods 2559 above background were used to solve and refine the structure by least-squares methods to a conventional R factor of 8.4%. The molecule is composed of two trinuclear units joined by two bridging water molecules. Each nickel atom in the trinuclear unit is octahedrally coordinated by oxygen atoms of the ligands. The octahedra share a common vertex occupied by a hydroxide ion which bridges three nickel atoms. The toluene molecules lie on symmetry centers between the hexanickel units and are disordered about an axis perpendicular to the phenyl ring.

Introduction

In the course of attempts to prepare polymeric nickel and cobalt complexes with unsymmetrically substituted acetylacetones (*e.g.*, $RCOCH_2COCH_3$, with R = C_6H_5, $C(CH_3)_3$, and CF_3), which were suitable for single-crystal X-ray diffraction studies, a complex of nickel(II) with the anion 1,1,1-trifluoropentane-2,4-dione (TFA) was isolated. A preliminary investigation suggested that the complex was either a trimer or a centrosymmetric hexamer of $Ni(TFA)_2$ in the solid phase. The complete structural determination was therefore undertaken with the hope of finding a possible relationship with the structures of $Ni_3(DEPAM)_6$[3,4] and $Ni_3(AA)_6$.[5] However, the substance was found to be far more complicated, chemically and structurally, as the following report will explain.

Experimental Section

Preparation.—A solution of 11.9 g (0.0774 mol) of 1,1,1-trifluoropentane-2,4-dione (HTFA; Peninsular ChemResearch, Inc., Gainesville, Fla.) in 50 ml of benzene was refluxed in the presence of 4.0 g (0.0337 mol) of $NiCO_3$ (J. T. Baker Chemical Co., Phillipsburg, N. J.) for 20 hr. The resulting suspension, containing a light green solid (presumably $Ni(TFA)_2 \cdot 2H_2O$) which formed after 3 hr, was filtered; the solid was washed with four 40-ml portions of petroleum ether (bp 40–60°) and dried in air. In an attempt to remove the water of hydration, the compound was dried under vacuum at 108° (0.05 mm) for 24 hr. The intense, broad band at 3400 cm^{-1} in the ir spectrum of the original solid (in Nujol) disappeared after the compound was heated to 108° under vacuum. A weak, sharp absorption, not present in the original solid, appeared at 3560 cm^{-1}. This vacuum-dried material was then recrystallized from toluene and analyzed. *Anal.* Calcd for $Ni_6(TFA)_{10}(H_2O)_2(OH)_2 \cdot C_6H_5CH_3$ ($Ni_6C_{57}H_{54}O_{24}F_{30}$): C, 29.75; H, 2.37; F, 29.18; Ni, 18.04. Found: C, 30.6; H, 2.21; F, 28.4; Ni, 17.8. Calcd for $Ni(CF_3COCHCOCH_3)_2$: C, 32.92; H, 2.21; F, 31.24; Ni, 16.09.

X-Ray Crystallography.—Crystals of the complex suitable for X-ray crystallographic examination were grown by slow cooling in a nitrogen atmosphere of a hot toluene solution. Monoclinic prisms mounted on glass fibers and coated with a thin layer of shellac to prevent exposure to atmospheric moisture were used for reciprocal lattice photography and collection of data. Precession photographs with Cu Kα radiation of the $0kl$, $1kl$, $h0l$, $h1l$, and $hk0$ levels indicated the systematic extinctions $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, uniquely characteristic of the space group[6] $P2_1/c$ (no. 14, C_{2h}^5). Preliminary cell constants were measured from the precession films. The density calculated for two hexanuclear molecules with two toluene molecules of crystallization is 1.69 g/cm^3. Attempts to measure the density by flotation in a mixture of ethyl iodide and carbon tetrachloride gave an approximate value of 1.73 ± 0.05 g/cm^3. Two molecules per unit cell in space group $P2_1/c$ requires that each molecule lie at a center of symmetry. The two toluene molecules must occupy a different set of centers and must be disordered.

Accurate unit cell dimensions were measured on a General Electric XRD-5 manual diffractometer. The cell parameters are $a = 14.268 \pm 0.006$ Å, $b = 17.519 \pm 0.006$ Å, $c = 16.862 \pm$

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[1] Research supported by the National Science Foundation under Grant No. GP 7034X.

[2] NIH Predoctoral Fellow, 1965–1968.

[3] F. A. Cotton and B. H. C. Winquist, unpublished work. It has been found that $Ni_3(DEPAM)_6$ (where DEPAM is the anion $(C_2H_5O)_2P(O)CHC(O)CH_3^-$) is crystallographically isomorphous and apparently isostructural with $Co_3(DEPAM)_6$ which has been reported to have an unusual structure.[4]

[4] F. A. Cotton, R. Hugel, and R. Eiss, *Inorg. Chem.*, **7**, 18 (1968).

[5] G. J. Bullen, R. Mason, and P. Pauling, *ibid.*, **4**, 456 (1965).

[6] "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.