THE CRYSTAL STRUCTURE OF Re2(02C.C3H7-n)4C12

AN INVESTIGATION OF THE CRYSTAL STRUCTURE

OF

DICHLORO-M-TETRA (N-BUTYRATO) DIRHENIUM(III)

By

RODERIC JOHN RESTIVO, B.Sc.

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TITLE: An Investigation of the Crystal Structure of dichloro- μ tetra(n-butyrato)dirhenium(III)

AUTHOR: Roderic John Restivo, B.Sc. (University of Toronto)

SUPERVISOR: Professor C. J. L. Lock

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SCOPE AND CONTENT:

Dichloro- μ -tetra(n-butyrato)dirhenium(III) was examined by x-rays and found to consist of a centrosymmetric dimeric unit in an eclipsed rotomeric configuration with a short rhenium-rhenium bond length of 2.20(2)Å. A long rhenium-chlorine bond 2.53(1)Å is present in the molecular unit.

The bonding in $\operatorname{Re}_2({}^0_2C.C_{}^H-n)_4Cl_2$ is discussed with reference to similar carboxylate dimer structures.

A preliminary report on the structure of $\operatorname{Re}_2O_4(O_2C.C_3H_7-n)_2$ is also presented.

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CHAPTER I: INTRODUCTION

The structures of many metal carboxylate complexes have been determined by single crystal x-ray diffraction methods. These include the known dimers: cupric acetate, chromous acetate, rhodium(II) acetate, π -allylpalladium acetate, and molybdenum(II) acetate (1, 2, 3, 4, 7). In the copper complex, it has been postulated that the copper-copper interaction results from a weak coupling of electron spins. The metal-metal bond (2.64A) is so weak that the configuration of the binuclear molecule can only be maintained by the four bridging acetate groups (5, 6). However, the molybdenum dimer, which is isostructural, contains a metal-metal distance of 2.11A, which is 0.8A shorter than the sum of two covalent radii of Mo²⁺. This suggests a very strong metal-metal interaction (7). Similar short metal-metal distances have been reported for the technetium-technetium distance (2.13A) in the octachloroditechnate(III) ion (8) as well as the rhenium-rhenium distance (2.24A) in the isoelectronic octachlorodirhenate(III) ion (3). These extremely short metal-metal distances suggest that multiple bonding is present and it seems likely that multiple bonding between d⁴ transition metal ions of the second and third row may be a fairly general occurrence. For the Cr(II) and Rh(II) compounds, the metal-metal distances, 2.46A and 2.45A respectively, are indicative of pronounced metal-metal interaction when compared with Pauling's estimates of single bond distances for the metals, 2.36A and 2.50A respectively (7). However, it is questionable whether multiple bonding exists in these compounds. A listing of these metal-metal distances is presented in Table 1.

Metal-Metal Distances in the Metal Carboxylate Complexes

NO.	COMPOUND	METAL ION	M- M	DISTANCE X	SINGLE BOND ^T DISTANCES FOR THE METAL IN ANGSTROMS Å	SUM OF O-BONDED COVALENT RADIUS OF THE METAL* A	REF
1.	Cu ₂ (0 ₂ C.CH ₃) ₄ 2H ₂ O	Cu ²⁺	4	2.64	2.34	2.64	1
2.	cr ₂ (0 ₂ c.cH ₃) ₄ 2H ₂ 0	Cr ²⁺		2.64	2.36		2
3.	Rh ₂ (0 ₂ C.CH ₃) ₄	Rh ²⁺		2.45	2.50		7
4.	Mo2(02C.CH3)4	M0 ²⁺		2.11	2.60	2.90	4
5.	(π-C ₃ H ₅) ₂ Pd ₂ (O ₂ C.CH ₃) ₂	Pd ²⁺		2.94		2.92	3
6.	(NH4)3 Te2 C18 2H20x	Tc ³⁺		2.13			8
7.	K2Re2C18.2H2 0	Re ³⁺		2.24			9

Estimated by Pauling's method.

The covalent radius of the metal can be estimated from the observed mean metal-oxygen bond length, subtracting the covalent radius of oxygen given a value of 0.65A, as judged from the available accurately determined carbon-oxygen bond length (10).

The charge of (-3) on the $Tc_2Cl_8^{3-}$ group is somewhat surprising. However, F. A. Cotton stated that there is analytical and magnetic susceptibility data consistent with the presence of oneunpaired electron per $Tc_2Cl_8^{3-}$ unit(8). There exists a series of dimeric rhenium carboxylate complexes which were prepared by F. Taha and G. Wilkinson (11) and which exhibit a change in the formal oxidation state of the rhenium metal. These dimeric complexes might possess metal-metal bond interaction and it is of interest to see if weaker metal-metal bond interaction results with increasing formal oxidation state of the rhenium metal.

The work initiated in this thesis is concerned with the butyrate complexes in which rhenium is in the (III), (IV), and (V), oxidation state. A single crystal structure has been determined for dichloro- μ tetra(n-butyrato(dirhenium(III)* as well as preliminary work being presented for oxorhenium(V)- μ -dioxo- μ -di(n-butryato)oxorhenium(V). The crystal structure of chlororhenium(IV)- μ -dioxo- μ -di(isobutyrato)chlororhenium(IV) is currently being determined (12).

> *In this thesis "the compound" refers to dichloro-µ-tetra(n-butyrato) dirhenium(III).

CHAPTER II: EXPERIMENTS

Microanalysis and molecular weight were performed by the Galbraith Laboratories, Inc., Knoxville, Tennessee. Infrared spectra were performed on KBr discs and recorded on a Beckmann model IR-10 infrared spectrometer. Nuclear magnetic resonance spectra were measured in deuterated chloroform on a Varian Associates A60 spectrometer at 60 Mc/sec with a chloroform reference. The mass spectrum was obtained on a crystalline sample at 150 - 160°C with voltages of 1 and 2KV using a Hitachi Perkin-Elmer mass spectrometer.

Rhenium metal was prepared by the reduction of ammonium perrhenate (lOg.NH₄ReO₄) (Johnson, Matthey and Co. Ltd.) brought about by heating to 420° C in a hydrogen atmosphere. Rhenium (2g) was heated to 550° C in a saturated chlorine atmosphere to convert it to rhenium pentachloride, a dark brown powder. The latter was thermally decomposed to rhenium trichloride (3g) which was a black crystalline powder.

I Dichloro-µ-tetra(n-butyrato)dirhenium(III)

Rhenium trichloride (2.5g) was refluxed in n-butryic acid (25 ml.) containing n-butyric anhydride (1 ml.) at just below the boiling point of the acid (163.6°C) for four days in a nitrogen atmosphere. The red solution changed slowly to dark brown and reddish orange crystals separated. After cooling, the crystals were removed, separated by

decantation from the less dense, insoluble black product, Re(HO₂C.C₃H₇-n)₂Cl₃, and washed with light petroleum (b.p. 40-60°C), and dried in vacuo (ca l.lg., ca 35% based on Re₃Cl₉). (Found C,24.0; H,3.3; Cl,9.1; Re,47.4%; M(in chloroform), 813. $C_{16}H_{28}Cl_2O_8Re_2$ requires C,24.3; H,3.5; Cl,9.0; Re,47.1%; M,791). The infrared spectrum of the compound in a KBr disc, showed absorptions at the frequencies expected for carboxylate groups (28). The nuclear magnetic spectrum gave independent information that the n-butyrate groups was present in the complex as opposed to a iso-butyrate group, and provided chemical shifts which were compared with n-butyric acid. The mass spectrum which was obtained gave information pertaining to the fragments which are obtained on vaporization of a crystalline sample, and which might be identified with a decomposition product. (m.p. 215°C with decomposition). The spectral information is listed in Table 2, Table 3 and Table 4.

1. Infrared spectra recorded on Beckmann IR-10 with KBr disc
For: Re₂(0₂C.C₃H₇-n)₄Cl₂ in cm⁻¹
3000 2955 2885m 1470vs 1375vs 1450s 1305s 1267s 1200s
1092s 1037m 955sh 933m 887s 861s 797vs 765m 723s 650vs

i.e. vs--very strong, s--strong, m--medium, sh--shoulder

1. n.m.r. spectra recorded in deuterated chloroform on a Varian A-60 with a chloroform reference for dichloro-µtetra(n-butyrato)dirhenium(III) (A) and n-butyric acid (B).

	A		B	
	T*(ppm)		r [*] (ppm)	7 ⁺ (ppm)
α-CH ₂	6.39(4)		7.69(4)	7.68
β-CH ₂	8.02(4)		8.34(4)	8.33
Y-CH3	9.99(4)	•	9.08(1)	9.01
	J (c.sec ⁻¹)		J (c.sec ⁻¹)
aCH2-BCH2	7.0(5)		7.0)(5)
BCH2-YCH3	7.0(5)		7.0)(5)

These values were calculated assuming the chloroform reference
 line lies 436 c.sec⁻¹ below tetramethylsilane.

+ Published values (26).

The mass spectra of $\operatorname{Re}_2(n-\operatorname{Bu})_4\operatorname{Cl}_2$

No.	Fragment Identified	Mass Numbers	Relative abundance
1	Re ⁺	185,187	250,500
2	ReCH ⁺	198,200	50,100
3	ReCl ⁺	220,222,224	650,1250,400
4	ReOCL+	236,238,240	700,1350,450
5	ReCl2+	255,257,259,261	880,1700,900,210
6	ReOC12+	271,273,275,277	800,1800,1000,220
7	ReCO2C12+	299,301,303,305	100,280,220,20
8	ReCO3C12+	315, 317, 319, 321	100,280,220,20
9	$\operatorname{Re}_{2}\operatorname{Cl}_{2}(n-\operatorname{Bu})^{+}$	527,529,531,533,535	180,450,450,200,250
10	$\operatorname{Re}_{2}Cl(n-Bu)_{2}^{+}$	579,581,583,585	100,210,200, 10
11	Re ₂ Cl ₂ (n-Bu) ₂ ⁺	614,616,618,620,622	10,20,100,100,20
12	$\operatorname{Re}_{2}(n-Bu)_{3}^{+}$	631,633,635	10,100,110

* Relative abundance measurements were made of peak heights instead of peak areas.

n-Bu = [O C C H -n]

Single crystals were prepared by dissolving the large red crystals (up to 3 mm. long) in dichloromethane (10 ml.). Petroleum ether (10 ml. b.p. 40-60°) was added and the solution was allowed to evaporate slowly. A yield of short orange needle-shaped crystals was obtained.

Crystals which showed complete extinction every 90° when viewed under a polarising microscope were chosen for study. A preliminary x-ray examination was carried out to determine the crystal system and space group. The single crystal was mounted so that the needle axis was parallel to the axis of the goniometer. A rotation photograph taken with MoKa radiation showed the needle axis, chosen as the crystallographic a, axis⁺, had a spacing of about 6.82Å. Equi-inclination Weissenberg photographs of the zero and first layers gave $\bar{b}_2 = 0.0844 A^{-1}$ perpendicular to $\bar{b}_3 = 0.0680 A^{-1}$. Systematic absences were observed for OkO reflections with k odd. This is characteristic of a two-fold screw axis along a ... The goniometer head and the crystal were transferred to a precession camera and the crystal was aligned so that the b, axis was parallel to the goniometer axis. A photograph was taken of the hOl zero layer reciprocal lattice and measurement gave $\beta = 107^{\circ}$. The hOl reflections with 1 odd were absent and this indicated the crystal had a c-glide plane. It was observed that only 2/m symmetry was present in these films and thus a monoclinic crystal system was chosen. The symmetry elements consisting of a two-fold screw axis directed along the a, direction and perpendicular to a glide plane along the a, direction were only found in the space group $P2_1/C$ (C_{2h}^5 - No. 14), so the crystal was assigned this space group. Measurements of all films combined gave the approximate cell constants of the monoclinic crystal as a = 6.82Å, b=11.85Å, c = 15.37Å and $\beta = 107^{\circ}$.

Notation used for crystallographic axes adopted above: $\bar{a}_1 = a$, $\bar{a}_2 = b$, $\bar{a}_3 = c$, $\bar{b}_1 = a^*$, $\bar{b}_2 = b^*$, $\bar{b}_3 = c^*$

The accurate unit cell parameters were obtained by the powder photograph method. The very finely powdered sample was inserted in fine capillaries and photographs were taken with the sample rotating using CuK radiation. Only two weakly scattered lines were obtained in the back reflection region. Since accurate values of their separations would be needed in order to make corrections for film shrinkage, an alternative technique was sought. This difficulty can be overcome by allowing for an effective camera rādius in the least square solution of the Bragg equation, $n\lambda=2d$ sin θ which relates the spacing d_{bkl} between successive planes of Miller indices hkl in the crystal lattice. The d value is related to interplanar spacings and, therefore, the unit cell parameters. The FORTRAN DESLS program, written by B. Robertson (1966) for a monoclinic system, was used and the observed theta values were compared to calculated theta values for thirty-eight powder data lines. Thirty-five lines were identified and of these, thirtyone which were in close agreement with the calculated values were used in a least square refinement of the approximate unit cell parameters. The relative measurement of the Bragg angle automatically corrects for the effects of film shrinkage and Debye-Scherrer camera radius used (114.83 mm) (29, 30). The observed theta values are tabulated together with those calculated from the lattice parameters found by least squares and put in Table 5. Four cycles of full matrix least squares refinement gave the parameters shown in Table 6. The estimated standard deviations for the unit cell parameters seemed unrealistically small since standard deviation in 0 were of the order of ±0.005 and hence were multiplied by three before listing in Table 6 as suggested by Webb (17).

The density of Re₂(0₂C.C₃H₇-n)₄Cl₂ was measured by flotation in a

diiodomethane-carbon tetrachloride mixture with a pycnometer of 10 ml. capacity. The volume of the unit cell is 1192^{10} . The measured density of 2.28 g ml.⁻¹ implies that there are two molecular units of $\text{Re}_2(0_2\text{C.C}_3\text{H}_7\text{-n})_4\text{Cl}_2$

(MW = 791.) per unit cell, which corresponds to a calculated density of 2.22 g.ml.⁻¹.

The single crystal chosen for the density data collection was 0.41 x 0.08 x 0.08 mm.³. The linear absorption coefficients for MoK_{α} and CuK_{α} radiation were calculated to be 113 and 220 cm.⁻¹ respectively, using the mass absorption coefficients found in the International Tables (16). This gives $\mu R = 0.45$ for Mok_{α} and 0.88 for CuK_{$\alpha} radiation.</sub>$

With these parameters in mind, it was decided to use CuK_{g} radiation with the Supper Weissenberg camera and Mok_{g} radiation with the Buerger precession camera to obtain the intensity data on Ilford Ilfex x-ray film. This combination allowed a reasonable amount of data to be collected with sufficient spacing of intensity spots on the films.

1. Observed and calculated diffraction angles, d spacings, and intensity data in the lattice parameter determination of $Re_2(O_2C.C_3H_7-n)_4Cl_2$ using CuK_x radiation.

No.	h	k l	<u>a(A)</u>	O(obs) degrees	6(Calc) degrees	Ī
l	0	1 1	9.44	4.69	4.79	100
2	0	0 2	7.41	5.96	6.02	64
3	0	2 0	5.87	7.55	7.48	24
4	1	1 -2	5.24	8.46	8.52	29
5	0	1 3	4.55	9.76	9.80	33
6	1	12	4.10	10.83	11.01	16
7	l	2 1	3.94	11.28	11.13	28
8	0	31	3.79	11.74	11.66	12
9	0	04	3.72	11.95	12.11	9
10	1	30	3.41	13.09	13.19	21
11	2	1 -1	3.28	13.59	13.64	2
12	2	1 -3	3.06	14.59	14.56	7
13	2	0 -4	2.89	15.46	15.44	3
14	1	1 -4	2.77	16.19	16.08	10
15	2	2 -4	2.61	17.21	17.24	6
16	2	1 -5	2.52	17.84	17.72	9
17	0	06	2.44	18.39	18.34	8
18	2	13	2.37	18.96	19.06	4

No.	h	<u>k 1</u>	<u>d(Å)</u>	Q(obs) degrees	0(Calc) degrees	Ī
19	0	26	2.28	19.80	19.91	12
20	1	4 3	2.24	20.01	20.03	7
21	2	4 0	2.19	20.64	20.58	6
22	1	4 -5	2.13	21.36	21.33	6
23	1	16	2.06	21.99	21.89	4
24	2	1 -7	2.03	22.29	22.31	4
25	2	4 -2	2.01	22.61	22.71	2
26	3	3 -2	1.97	23.01	23.03	2
27	3	12	1.92	23.71	23.79	1
28	0	5 5	1,84	24.71	24.70	6
29	3	4 -3	1.79	25.56	25.52	5
30	2	5 -5	1.75	26.18	26.15	5
31	4	3 -1	1.54	29.99	29.99	6

Crystal Data on Re₂(0₂C.C₃H₇-n)₃Cl₂

System		monoclinic
Molecular Weight	t.	791
Space group		P21/C
a (Å)		6.32(0)+
b (Å)		11.89(1)
c (Å)		15.42(1)
β (°)		106.8 (0)
v (Å ³)		1192
Dm (Flotation	n) (g ml ⁻¹)	2.28
Dc	(g ml ⁻¹)	2.22
Z	·	2

+ Estimated standard deviations given in brackets

The x-ray radiations used in this study with their wavelengths, and the corresponding K_{β} filters, as listed in International Tables.

Radiation	Weighted mean values	Filter
CuKa	1.54178Å	Ni
MoKX	0.71069Å	Zr

With CuK_{α} radiation, equi-inclination Weissenberg photographs were taken of the nkl layers where n=0, 1, 2, &3. Precession photographs of the [O10] and [O01] zones were obtained with MoK_{α} radiation.

The intensity of all reflections were measured visually. Use was made of the Logarithmic Optical Method. If an ordered series of n films are exposed to a constant source of x-rays for y hrs., yx hrs... yxn hrs., then the relative intensities of a reflection on the successive films are given by $I_H(1) = I_H$, $I_H(z) = xI_H \dots I_H(n) = x^{n-1} I_H$. If a number, z=1 where z=ln x I_H is assigned to the weakest reflection on the first film, then on the jth film, $j = (1+Z) = Ln_X^{T}(j)$. Thus the measured intensities will be scaled according to an arbitrarily assigned intensity of x^Z to a given reflection. Values of $ln_X^{T}_H$ for other H were estimated by comparing its intensity with the standard reflection and any number of previously estimated intensities, and by continual cross checking to maintain a consistent and reliable scaling.

In all cases, three films of exposure times, four, twelve and thirty-six hours were taken for each layer. This established a film factor of x=3 so that the measured intensities were based on an assigned value of $x^{z} = 3^{1}$ for the lowest reflection.

All computations were carried out on the IBM 7040 computer. Initially all data was corrected for Lorentz and polarization factors, using the Fortran programs, WEILPC (Weissenberg) and PRELPC (precession) written in this laboratory. The measured intensity, Io_H , was related to the observed structure factor Fo_H by the expression $Fo_H = \sqrt{I_H/L.P.}$ where l/L.P. represents the Lorentz-polarization correction to intensity. Corrections for absorption were not applied since they were considered small assuming cylindrical

geometry for the crystal with radius equal to 0.04 mm. The corrected structure factors were then used to calculate Patterson projections. The Patterson Function is defined as

$$P(u,v,w) = \sqrt[4]{9} \int_{0}^{4} \int_{0}^{4} \int_{0}^{4} (x,y,z) \int_{0}^{4} (x^{+}u, y^{+}v, z^{+}w) dxdydz (1)$$
where $\int_{0}^{4} (x,y,z)$ and $\int_{0}^{4} (x^{+}u, y^{+}v, z^{+}w)$ are the electron densities at the point (x,y,z) and $(x^{+}u, y^{+}v, z^{+}w)$ respectively in the volume V of the unit cell. The electron density is defined as
$$f(x,y,z) = \frac{1}{V} \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} F(hkl) \exp\left(-2\pi i (hx + ky + lz)\right) (2)$$
where F(hkl) is the structure factor. Substituting in expression (1) the values obtained for $f(x,y,z)$ and $f(x + u, y + v, z + w)$ from (2), $f(u,v,w)$

$$= \frac{1}{V} \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} [F(hkl)]^{2} \exp\left(2\pi i (hu + kv + lw)\right) (3)$$
where the quantity
$$F^{2} \text{ is the square of the modulus of the structure factor. For structures which obey Friedel's law, this simplifies to
$$P(u,v,w) = \frac{1}{V} \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} [F(hkl)]^{2} \cos\left(2\pi (hu + kv + lw)\right) (4)$$
The projection of this function down one of the unit cell axis, say \bar{a}_{3} , is given by
$$P(uv) = \frac{1}{A} \sum_{n=0}^{\infty} [F(hk0)]^{2} \cos(2\pi (hu + kv)) (5)$$$$

where A is the area of the projection. P(u,v,w) will have peaks corresponding to interatomic vectors. In practice only the peaks caused by interactions of the heaviest atoms, that is, atoms with many electrons, can be resolved. Since the interatomic vector between any two heavy atoms will be represented on the Patterson Function as a large peak, this function will be extremely useful in positioning the heavy atoms relative to each other.

With two molecular units per unit cell and with the multiplicity of a general position in the space group, $P2_1/c$, being four, none of the atoms in the structure are constrained to lie in special positions. There will be four rhenium atoms per unit cell so that the Patterson Function will contain sixteen Re-Re peaks, four at the origin and twelve peaks dispersed throughout the function satisfying the required combined symmetry of the space group and the Patterson function. For $\text{Re}_2(0_2\text{C.C}_3\text{H}_2-n)_4\text{Cl}_2$, a double Re-Re peak should correspond to 44% of the peak height of the origin, while those corresponding to through center Re-Re vectors, that is, single peaks, and double Re-Cl peaks should correspond to 22% and 9% respectively. The rest of the Patterson Function is made up of interactions of Re and Cl with O and C, and O-O, C-O, and C-C interactions. The peaks corresponding to the "Rei-"Rej interactions were found at x=0.24 and y=0.12 in [001] zone, x=0.24 and z=0.07 in [010] zone; and y=0.11 and z=0.07 in [100] zone, while those for $r_{Re} - r_{Cli}$ were found at x=0.90 and y=.23 in [001] zone, x=0.52 and z=0.17 in [010] zone and y=0.23 and z=0.17 in [100] zone. These gave coordinates (0.12, 0.06, 0.04) for Re and (0.38, 0.17, 0.125) for Cl respectively. The [100] Patterson projection is shown in Figure 1 and the [001] projection is shown in Figure 2.



FIGURE ! (Re2(m-Bu)4 Cl2)



0,1/2

THE PATTERSON SYNTHESIS OF HKO PROJECTION

The coordinates obtained for rhenium and chlorine were used to calculate structure factors for 212 (Okl), 141 (hOl) and 109 (hkO) reflections. The preliminary scale factor K, and overall temperature factor B defined by

$$KF_{o} = F_{c} \exp\left(\frac{-B \sin^2\theta}{\lambda^2}\right)$$

were determined for these data. F_{o} is the observed structure factor and F_{c} the calculated structure factor determined by

$$F_{c} (hkl) = 2 \sum_{i=1}^{N} f_{i} (hkl) \cos 2\pi (hx_{i} + ky_{i} + lz_{i})$$

The atomic coordinates are x_i , y_i , and z_i and the scattering factors for the ith species is f_i . The scattering factors were interpolated from $\sin \theta/\lambda$ = 0.0 to 1.75 using values quoted in the International Tables. The values for rhenium were corrected for anomolous dispersion effects, using the relation

$$|\mathbf{f}| = \mathbf{f}_{0} + \Delta \mathbf{f}^{*} + 1/2 \frac{(\Delta \mathbf{f}^{*})^{2}}{\mathbf{f}_{0} + \Delta \mathbf{f}^{*}}$$

where f^{1} and $\Delta f^{"}$ were the real and imaginary dispersion correction coefficients. These dispersion correction coefficients were obtained from the International Tables (Vol. III, p. 216).

The trial coordinates gave an overall temperature factor, B, of 0.65^{0^2} and an unweighted overall reliability factor, R_1 , of 0.40. R_1 , also called the unweighted R factor, is defined as $R_1 = \frac{\sum(|F_0| - |F_0|)}{\sum|F_0|}$ with the summation over all the measured reflections. Refinements were then made with individual isotropic temperature and scale constant variations together with the positional parameters; R_4 was reduced to 0.32.

Electron density and electron difference maps were then prepared for the (x,y), (x,z) and y,z) projections. From these projections, a suitable position was indicated for one of the oxygen atoms O(AC), bonded

to the rhenium atom. The positions of oxygen atoms O(AC), O(BD), O(CA) and O(DB) were found in the following manner. A four-fold axis was set up along the Re(1) - Cl(1) vector. This generated three other oxygen atoms positions from the coordinates of O(AC). A rotation transformation was performed on the entire group about this axis; the angle of rotation was chosen as $\Theta=0^{\circ}$, 30° , and 60° from the original orientation. The positional parameters obtained in this way were used in a three-dimensional least squares refinement of the positions. Isotropic temperature factors and unit weights were used in the calculation. The lowest R factor was obtained with $\Theta=0^{\circ}$ confirming the validity of the original chosen oxygen O(AC) position. The R factor was 0.26.

An electron difference synthesis was prepared using the calculated structure factors. Carbon atoms C(1A) and C(1B) were obtained by choosing suitable peaks, which conformed to the geometrical condition that the carbon atoms and related oxygen atoms are coplanar; that is, carbon atom C(1A) lies in the plane of O(AC), the centrosymmetrically related oxygen atom of O(AC), namely O(\overline{AC}), Re(1) and its centrosymetrically related atom, namely Re(\mathbf{T}). The refinement was made using these positional parameters and R dropped to 0.20. Further electron density and electron difference maps were calculated. The positions of the known carbon atoms C(1A) and C(1B) were then used as a guide in locating the three chain carbons attached to C(1A) and C(1B) respectively. Peaks in the electron difference were used which fit the conditions that the carbon-carbon vectors would be defined as 1.5 and that the carbon chains for different dimers in the crystal were not closer than 3.0Å. After least squares refinement, the R_{i} factor dropped to 0.19.

During the refinements, the temperature factors of the oxygen and carbon atoms were not varied, and only a fraction, usually 1/2, of the calculated shifts of the coordinates were actually applied. After each cycle of refinement, the geometries of the carboxylate groups were inspected and the carbon atom positions readjusted if the geometries of the carboxylate groups were not those which would be expected (1-7). At several stages, the temperature factors of the oxygen and carbon atoms were allowed to vary, in order to determine if the orientations of the carboxylate groups were correct. If a group was incorrectly oriented, the temperature factors of all its atoms would increase sharply effectively eliminating these atoms from the trial structure in an attempt to provide better agreement with the measured data. When this happened, the atoms in error were removed, and a difference synthesis calculated. The atoms were replaced as indicated by this synthesis, and further cycles of least squares refinements undertaken.

The isotropic temperature factor of the rhenium atom was converted to anisotropic temperature factors introduced in the form

$$\exp\left[-(\beta_{11}h^{2} + \beta_{22}k^{2} + \beta_{33}l^{2} + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\right].$$

The anisotropic temperature factor of rhenium as well as the isotropic temperature factors of the oxygen and carbon atoms were varied. A Hughes (18) weighting scheme was used in which the weight w, equals $\frac{1}{\sigma^2}$. The estimated standard deviation of a given reflection equals 0.1 F_o if F_o > 75, and equals 7.5 if F < 75. R_b for all reflections was 0.18 and R_b = 0.20,

where R₂, the weighted R factor is defined as

$$R_{2} = \left(\frac{\sum W^{2} ||F_{0}| - |F_{c}||^{2}}{W^{2} ||F_{0}|^{2}}\right)^{1/2}$$

The positions were refined until no further improvement in the residual R_2 could be obtained. After convergence had been obtained new weights, W, were calculated so as to satisfy a criterion suggested by Cruickshank, et. al. (19) that $W^{-1*} = C_0 + C_1 F_0^2 + C_2 F_0^3$ where the C's were chosen so that the average value of $W\Delta^2$ would be independent of F_0 with Δ defined as $\Delta = 1F_0^1 - 1F_c^1$. Unobserved reflections whose calculated value was less than the minimum observed value were considered to be in agreement and left out of the refinement; otherwise, F_0 was taken as 0.70 x (minimum F_0). The final value of the crystallographic discrepancy index was 0.15. Table 7 shows the agreement between the observed and calculated structure factors for 1655 independent reflections.

TABLE 7 · OBSERVED AND CALCULATED STRUCTURE FACTORS (XIO)

UNOBSERVED REFLECTIONS ARE MARKED WITH AN ASTERISK (+), AND UNRELIABLE REFLECTIONS WITH THE SYMBOL (0).

FOBS FCALC	FOBS FCALC	FOBS FCALC	FOBS FCALC	FOBS FCALC
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2. Oxorhenium(V)-µ-dioxo-µ-di(n-butyrato)oxorhenium(V)

Rhenium trichloride (2 g) was heated with n-butyric acid (25 ml) for four days at just below the b.p. $(163.6^{\circ}C)$ with a slow stream of dry air passing through the solution. Purple needles separated slowly from an orange solution and were filtered off while the solution was hot. The crystals were recrystallized from chloroform and dried in vacuo. This gave chlororhenium(IV)- μ -dioxo- μ -di(n-butyrato)chlororhenium(IV), (0.5 g, 20%) (based on Re₃Cl₉), m.p. 210°. (Found C, 15.6; H, 2.3; 0,14.8%. C₈H₁₄Cl₂O₆Re₂ requires C, 14.8; H, 2.2; 0, 14.8%).

From the original filtrate, on cooling, orange crystals were obtained. These were recrystallized from hot n-butyric acid, washed with petroleum ether until they were acid-free, and then dried in vacuo. The compound obtained was oxorhenium(V)-adioxo- μ (di(n-butyrato)oxorhenium(V), (ca 0.4 g), m.p. 260°C. (Found C, 15.9; H, 2.3%; $C_8H_{14}O_8Re_2$ requires C, 15.7; H, 2.3%). The infrared spectrum of $Re_2O_4(O_2C.C_3H_7-n)_2$ in a Nujol mull gave, in addition to the usual carboxylate bands a very strong band at ca 930 cm^{-1⁺}. This indicates that a Re = 0 bond is present (31). In addition, a broader band at ca 830 cm⁻¹ was seen suggesting the presence of a Re-O-Re bond (32).

Single crystals were prepared by dissolving the large orange crystals in dichloromethane(10 ml) to form an orange solution and then benzene (10 ml) was added. The solution was allowed to evaporate slowly and a yield of light orange thin plates were obtained.

Only crystals which showed complete extinction every 90° when viewed under a polarising microscope were chosen for crystallographic examination to determine the crystal system and space group. The single crystal (0.3 mm. long and .08 mm. thick) was mounted so that its needle axis was

+ The strong band between 900-1000 cm⁻¹ has been assigned to the Re=O stretching mode.

parallel to the axis of the goniometer head. A rotation photograph taken with CuK_X radiation showed the needle axis, chosen as the crystallographic \bar{a}_1 axis, had a spacing of 9.19Å. Equi-inclination Weissenberg photographs of the zero layer (0kl) gave $\bar{b}_2 = 0.0914 \text{Å}^{-1}$, $\bar{b}_3 = 0.1362 \text{Å}^{-1}$, and $\alpha^* = 96.9^\circ$. Precession photographs were then taken of the (hk0) and (h01) zones, and, as the crystal was aligned with the \bar{b}_1 axis parallel to the camera spindle axis, the α' angle could be determined directly from the spindle settings for these two photographs. This measurement gave α' as 86.3° verifying the value obtained from the (0kl) Weissenberg photograph. The axis lengths and angles obtained from all the data combined are a = 9.19Å, b = 11.16Å, C = 7.79Å, $\alpha' = 86.3^\circ$, $\beta = 108.3^\circ$ and $\Lambda' = 81.0^\circ$. Crystal data shown in Table 8.

The density of $\text{Re}_2\text{O}_4(\text{O}_2\text{C.C}_3\text{H}_7-\text{n})_2$ was measured by flotation in a diiodomethane-carbon tetrachloride mixture with a pycnometer of 25 ml. capacity. The volume of the unit cell is 744.³. The measured density of 2.76 g ml⁻¹ implies that there are two molecular units of $\text{Re}_2\text{O}_4(\text{O}_2\text{C.C}_3\text{H}_7-\text{n})_2$, (MW = 594), per unit cell, which corresponds to a calculated density of 2.73 g ml⁻¹.

No systematic absences were observed. Therefore, the crystal must have triclinic symmetry with the space group either Pl or Pl rather than any oddly oriented crystal of higher symmetry. The Patterson synthesis using (0kl) data showed the double Re-Re peaks characteristic of Pl. The suggested space group then is Pl although only a complete structure resolution will confirm this.

The same crystal with dimensions 0.3 x 0.08 x 0.08 mm³ was used in collecting the intensity data. Equi-inclination Weissenberg photographs

Crystal Data on $\operatorname{Re}_2O_4(O_2C.C_3H_7-n)_4Cl_2$

System	triclinic
Molecular Weight	594.
Space group	PĪ
a (Å)	9.19 (5)+
ь (Å)	11.16 (5)
c (Å)	7.79 (5)
≪ (°)	86.3 (3)
β ([°])	108.3 (3)
४ (°)	81.0 (3)
V (Å ³)	744.
Dm(Flotation) (g ml ⁻¹)	2.76
Dc	2.73
Z	2

+ e.s.d's in parentheses.

were taken of the nkl layers where n=0, to 3 using $\operatorname{CuK}_{\alpha}$ radiation and the multiple film technique. Three films were loaded in the camera at one time and an exposure of fity-four hours was taken. Each film of the pack acts as a uniform absorber and reduces the x-ray reflection intensities which arrive at the film underneath it by a constant factor called the film factor. Ilford Ilfex x-ray film was used providing a film factor of 2.75. The [OlO] and [OOl] zones were recorded with the precession camera using MoK_{α} radiation. Each zone was photographed for periods of 4, 12 and 36 hours. The intensities of the (Okl) reflections were estimated by visual intercomparison, using the logarithmetic method. The usual Lorentz and polarization corrections (16) were made to the data, but no corrections for absorption were applied.

A [100] Patterson projection was obtained using the 139 (0kl) reflections. The peaks corresponding to the $r_{Rej} - r_{Rej}$ interactions were found at y = 0.23 & z = 0.46 while those corresponding to the r_{Rej} + r_{Rej} interactions were found at y = 0.13 & z = 0.29. These gave coordinates (0.18, 0.37) for Re_i and (-0.06, -0.08) for Re_j respectively. The residual discrepancy factor, R₁, obtained using these values was 0.40 showing that the positionschosen for the two Re atoms seem reliable. Table 9 lists the observed and calculated structure factors. The [100] Patterson projection is shown in Figure 3.



FIGURE 3 (Re. O. (n-Bu)))

TABLE 9 . OBSERVED AND CALCULATED STRUCTURE FACTORS (XIO)

UNOBSERVED REFLECTIONS ARE MARKED WITH AN ASTERISK (=), AND UNRELIABLE REFLECTIONS WITH THE SYMBOL (Ø).

	FOBS FCALC	FOBS	FCALC	IF0	BS FCALC		FOBS	FCALC	FOBS FCALC
K 2345678901120000000000123456	L $H = 0$ 0 113 -23 0 790 -624 0 563 -75 0 558 476 0 590 307 0 673 -695 01363 -1533 01078 -1312 0 977 -461 0*89 53 1 516 -39 2 824 446 31169 1037 4*776 -1403 5 641 -299 61075 -735 71351 -938 8 269 174 9*158 -228 1*245 -287 1 131 527 1 704 868 1 738 500 1 763 -567 11689 -1737	7 11850 8 1 469 9 1* 99 10 1*1025 12 1 3075 12 1 3075 12 1 3075 12 2 2497 3 2 5660 4 214666 6 2 541 7 2 301 8 2 391 9 2 4425 11 2* 987 12 3 3453 3 31502 4 3 3670 5 3 323 6 3 712 8 3 780 9 3*102	$\begin{array}{r} -1728\\ -633\\ 147\\ -469\\ -544\\ -738\\ 857\\ 3207\\ -14445\\ -1445\\ -1445\\ -1445\\ -1843\\ -2868\\ -736\\ -8688\\ -735\\ -648\\ -735\\ -648\\ -1213\\ -1213\\ -1209\\ -55\\ 648\end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} 08 & -1228 \\ -415 \\ 78 & -575 \\ 28 & -1458 \\ -1458 \\ -1458 \\ -1352 \\ -249 \\ 8511 \\ 13 & -496 \\ 29 & 4930 \\ -602 \\ 29 & 4930 \\ -604 \\ 29 & 4930 \\ -604 \\ 20 & -602 \\ 29 & 4930 \\ -604 \\ -1120 \\ 669 \\ 26 \\ 10 \\ -1026 \\ 40 & -120 \\ -609 \\ 10 \\ -609 \\ 10 \\ -1026 \\ -609 \\ 10 \\ -1026 \\ $	90123456789012345671234561111	6**5402 773861 1195 88062 1960 1960 8818 1960 8818 1960 1978 1960 1978 1960 1978 1960 1978 1960 1978 1978 1978 1978 1978 1978 1978 1978	$\begin{array}{c} 723\\ 897\\ -369\\ 2428\\ -71\\ -3630\\ 855\\ 1057\\ -3162\\ -214\\ 7943\\ -3059\\ 84755\\ -3059\\ 84755\\ -3059\\ 84755\\ -3059\\ 84755\\ -3059\\ 84755\\ -3059\\ 84755\\ -3153\\ -3452\\ -386\end{array}$	 52067 - 1039 6262 55 71156 - 1019 8257 - 334 9*59 82 268 41 309 906 41515 902 52139 - 1303 6206 132 7*507 - 510 8*339 - 852 9* 52 165 21484 1327 3*72 29 41951 1128 5416 - 408 6492 - 534 7*98 86 8*257 - 948 9*230 - 176 3397 150 -1 411 - 11 -1 253 491 -1*95 265

CHAPTER II: DISCUSSION

It was proposed originally by Taha and Wilkinson (11) that the compound, dichloro- μ -tetra(n-butyrato)dirhenium(III), was a bridged carboxylate dimer in which the carboxylate groups held the rhenium atoms together, and spinspin coupling of the rhenium d electrons was proposed to explain the diamagnetism of the complex. They did not suggest that metal-metal bonding held the group together. The work initiated in this thesis, has confirmed that carboxylate groups do bridge the two rhenium atoms. However, the short rhenium-rhenium distance (2.20(2)Å) can only be interpreted as showing considerable metal-metal bonding.

Dichloro- μ -tetra(n-butyrato)dirhenium(III) has been shown to belong to the monoclinic space group P2₁/C. The geometrical features of the molecule as seen in the a-c projection are shown in Figure 4 as well as structural features in Figure 5. The final atomic parameters are shown in Table 10. The bond lengths and bond angles are given in Table 11.

With only two molecules in the unit cell, a crystallographic center of symmetry is imposed on the molecule. The molecule, $\text{Re}_2(O_2\text{C.C}_3\text{H}_7-n)_4\text{Cl}_2$ has bridging n-butyrate groups and a terminal chlorine on each rhenium atom. The four oxygen atoms bonded to each rhenium atom form roughly a square planar configuration and are essentially coplanar with the rhenium atom. The average rhenium-oxygen bond length is $2.05(4)^{\text{A}}$ Since the Re-O bond lengths quoted in Table 11 have not been corrected for thermal effects, the bond lengths may be somewhat short. The bond angles of the oxygens around the rhenium atom lie between $84(1)^{\circ}$ and $98(1)^{\circ}$ while those for Cl-Re-O lie between $83(7)^{\circ}$ and $98(6)^{\circ}$. It would appear, considering the error limits, that therhenium atom is close to coplanar with the four oxygen atoms bonded to it. The crystallographic axis, \bar{a}_2 , bisects the rhenium-rhenium bond which lies approximately along the body diagonal [111] of the unit cell. Viewing down the Re(1)-Re($\bar{1}$) bond, it is observed that the Re(1)-O bond will make a slight dihedral angle (5°) with respect to the similar Re($\bar{1}$)-O bond. This is the only indication of any staggered conformation in this molecule. Thus, within the error limits of the refinement, the dimer sits in an eclipsed rotomeric configuration.

The $O(AC)-C(1A)-O(\overline{CA})$ angle and the $O(BD)-C(1B)-O(\overline{DB})$ angle are $124(8)^{\circ}$ and $127(9)^{\circ}$, respectively, so that the bridging carbon atoms, C(1A) and C(1B), can be regarded as essentially trigonal carbon atoms. These values are close to the corresponding angle values in molybdenum acetate(4) as well as those quoted for lithium acetate dihydrate $(119.4(2)^{\circ})$ (36). The bond lengths of oxygen atoms to this central carbon atom have an average value of $1.26(10)^{\circ}$ which can be compared to the corresponding bond length $(1.27(10)^{\circ})$ in molybdenum acetate (4) as shown in Figure7.

The chain carbon atoms are essentially tetrahedral with an average bond length $(1.52(14)^{\text{A}})$ between carbon neighbours. When the structure is viewed down the \bar{a}_3 axis, it is noted that the Re(1)-Re(1) vector is alternately 90° out of phase at every translation $(\bar{a}_3)_{/2}$. The structure is restricted mainly by the packing of the carbon stoms which fit as a zigzag chain in the space neighbouring four propeller carboxylate groups. This stacking of molecules can be seen in the a-c projection, Figure 4, where there are close contacts between the carbon chain of the rhenium binuclear unit at y=0, Z=0 and those at y=1/2,7-1/2. The closest contact distances are the sum of the van der Waal radii of the atoms involved. The distance of carbon atom, C(4B) at $\langle x, y, z \rangle$ to carbon atom C(4B) at $\langle x, 1/2-y, 1/2+z \rangle$ is 4.0Å. The sum of the van der Waal's radii for two methyl groups is 4.0Å

Atomic Coordinates and Temperature Factors of Re2(02C.C3H7-n)4Cl2

Atom		Atomic Coordi	Temperature Factors	
	x=x/a	y=y/b	Z=z/c	
Re(1)	0.1239(0.0003)	0.0563(0.0002)	0.0384(0.0001)	B ⁺
C1(1)	0.4175(0.0020)	0.1826(0.0009)	0.1223(0.0007)	5.53* (0.29)
O(AC)	0.0292(0.0038)	0.0218(0.0018)	0.1541(0.0013)	5.0
O(BD)	0.3267(0.0040)	0.9366(0.0016)	0.0837(0 0014)	5.0
O(CA)	0.2241(0.0037)	0.0867(0.0018)	0.9339(0.0013)	5.0
O(DB)	0.9065(0.0039)	0.1848(0.0018)	0.9821(0.0013)	5.0
C(1A) C(2A)	0.8592(0.0077) 0.8380(0.0077)	0.9524(0.0033) 0.9488(0.0032)	0.1349(0.0027) 0.2292(0.0028)	5.0 5.0
C(3A)	0.7897(0.0071)	0.0001(0.0040)	0.3130(0.0026)	5.0
C(4A)	0.6503(0.0076)	0.9562(0.0033)	0.3697(0.0027)	5.0
C(1B)	0.2527(0.0080)	0.8375(0.0037)	0.0423(0.0027)	5.0
C(2B)	0.4180(0.0067)	0.7459(0.0036)	0.0707(0.0026)	5.0
C(3B)	0.5313(0.0071)	0.7192(0.0035)	0.1697(0.0027)	5.0
C(4B)	0.4332(0.0066)	0.7277(0.0036)	0.2442(0,0026	5.0

 \vec{B} = Anisotropic temperature factor consisting of: V_{11} = 0.0177, V_{22} = 0.0079, V_{33} = 0.0067, V_{12} =-0.0012, V_{13} = 0.0038, V_{23} = -0.0001

* = Isotropic

Bond lengths and bond angles in Re2(02C.C3H7-n)4Cl2

In the Re(1) so	luare planar			
Bond leng	gths		Angles	
Re(1) - O(AC)	2.11(2)Å	O(AC) - Re	(1) - O(BD)	85(1)°
- O(BD)	1.96(2)	O(BD) -	- O(CA)	93(1)
- O(CA)	1.96(2)	0(CA) -	- O(DB)	84(1)
- O(DB)	2.13(2)	O(DB) -	-0(AC)	98(1)

2. Rhenium binuclear unit Bond length Re(1) - Re(1) 2.20(2)A

1.

3. Rhenium-terminal chlorine

Bond length

			0		
Re(1)	_	$C_{1}(1)$	2 53	(1)8	

		An	gle	s	
Re(1)	-	Re(1)	-	Cl(1)	178(1)°
C1(1)	-	Re(1)	-	O(AC)	94.2(6)
			-	O(BD)	82.7(7)
			-	O(CA)	84.2(7)

- O(DB) 98.2(6)

⁺The numbers in parenthesis indicate the standard errors in the last figures quoted.

4. Carboxylate unit

Bond	length	

C(1A)	-	O(AC)	1.38(5)Å
	-	O(CA)	1.15(3)
C(1B)	-	O(BD)	1.36(4)
	-	O(DB)	1.08(6)

	-		
nn.	Cr I	0	-
nu	61	- C	0

Re(1)	- (O(AC)	-	C(1A)	112(2)
Re(1)) -	O(BD)	-	C(1B)	119(3)
Re(1)) -	O(CA)	-	C(1A)	119(3)
Re(1)) -	O(DB)	-	C(2B)	107(1)
O(CA)) -	C(1A)	-	O(AC)	128(4)
O(DB)) _	C(1B)	-	O(BD)	125(4)

5. Chain carbons.

Bond length

C(1A)	-	C(2A)	1.50(3)A
C(2A)	-	C(3A)	1.55(4)
C(3A)	-	C(4A)	1.56(6)
C(1B)	-	C(2B)	1.53(6)
C(2B)	-	C(3B)	1.53(3)
C(3B)	-	C(4B)	1.49(5)

Angles

C(2A)	-	C(1A)	-	O(AC)	97(3)°
C(1A)	-	C(2A)	-	C(3A)	154(3)
C(2A)	-	C(3A)	-	C(4A)	131(3)
C(2B)	-	C(1B)	-	O(BD)	109(3)
C(1B)	-	C(2B)	-	C(3B)	123(3)
C(2B)		C(3B)	-	C(4B)	123(4)









so that no significant bonding between groups is taking place.

The mass spectrum of dichloro- μ -tetra(n-butyrato) dirhenium (III) obtained from the mass spectrograph is extremely complicated. The range of the mass spectrometer used does not allow observation of the parent ion peaks at 788 to 797 but the mass number as high as 695 have been observed. The entire range of peaks has not been identified but peaks caused by the fragments Re₂Cl (n-Bu)⁺₂, Re₂Cl₂(n-Bu)⁺₂, Re₂Cl₂(n-Bu)⁺, and Re₂(n-Bu)⁺₃ have been positively identified by mass number and isotopic pattern.

The middle mass region is of considerable interest (mass 180-320) since some of the fragments found would not be expected to come from the compound under study. Peaks caused by Re⁺(185,187), ReO⁺(201,203), Re CH⁺(198,200), Re Cl⁺(220,222,224), ReO Cl⁺(236,238,240), Re Cl⁺(255, 257, 259, 261) and ReO Cl⁺₂ (271,273,275,277) have been positively identified by mass number and isotopic pattern. The fragments containing two chlorine atoms would not be expected for the compound and the relative intensities are quite similar to those observed for mass spectra of rhenium oxochlorides (22) or mixtures of rhenium chlorides and oxygen(23,24).

It is possible that these latter peaks are caused by decomposition products of the compound under study. The compound melts at 215°C with decomposition, and temperatures of 150-160°C were necessary to give measurable amounts of material in the mass spectrometer. If this is the case, the thermodynamic stability of the compound and particularly the Re-Re core in the solid state is in marked contrast to the kinetic stability of the same species in solution where numerous ligand exchange reactions have been carried out without destroying the core (25).

* $n-Bu = [0_2C.C_3H_7-n]$

A further group of peaks in the spectrum also suggest decomposition. Three strong peaks at 359, 360 and 361 were observed in the spectra of all samples run. Such a pattern cannot arise from fragments containing rhenium or chlorine implying that the peak either comes from background in the instrument or that a relatively high mass organic material is formed in the decomposition reaction. Neither explanation is very satisfactory and this problem should be studied further when the larger mass spectrometer (Electrodynamics Consolidated) becomes available. Table 4 showed the results.

The H' n.m.r. spectrum of a solution of $\text{Re}_2(0_2\text{C.C}_3\text{H}_7-n)_4\text{Cl}_2$ in deuterochloroform was measured in order to see whether all the organic groups were equivalent. This was found to be the case. The spectrum was compared with that of n-butyric acid in deuterochloroform. The results were presented in Table 3. The resonace peaks caused by the q',β and δ protons were positively identified by the splitting pattern. Compared to n-butyric acid, the peaks of the compound are shifted to low field. The peak arising from the & protons show very little shift but those from the & protons are considerably shifted; that of the β protons shows an intermediate shift. The shift of the resonance to lower fields at fixed frequency is normally interpreted (27) as deshielding of the protons caused by removal of electron density from their environment. A comparison with the published spectra (27) for various substituted propyl derivatives shows that the shifts are very close to those for very strong electron-withdrawing groups (i.e.-OH, -0-,-NO2,-NO3).

The electron withdrawing power must arise from the rhenium-rhenium binuclear core and since this effect is transmitted over the carboxylate group, it must be considerable.

Other suggested sources of the shift may be neglected (27). Anisotropic shielding effects arising from the carboxyl to the propyl group will be present in n-butyric acid, and it seems unlikely that the other groups can make significant contribution since the nearest protons in the propyl group lie at least 4Å distant from the carboxyl of any other nbutyrate group. Intra-molecular electric field effects only arise in molecules with permanent electric dipoles which cannot be present in this centrosymmetric compound. "C-C" bond shifts as suggested by Dailey (26) will contribute both in n-butyric acid and in this molecule.

Multiple bonding between the two rhenium atoms is suggested by several features of the molecular structure. There is present in the molecule an extremely short rhenium-rhenium bond length of 2.20(2)A which can be compared to the rhenium-rhenium bond length (2.24 Å) found in dipotassium octachlorodirhenate dihydrate, K2Re2Cl8,2H2O, where multiple bonding was postulated (9). The terminal chlorine-rhenium bond length of 2.53(1) Å is very long. This can be compared to the chlorine-rhenium distances of 2.29(2) Å in $K_2 \text{Re}_2 \text{Cl}_8$. 2H₂O (9) and 2.37(3) Å in $K_2 \text{Re}$ Cl₆(34), in which the Re-Cl bond is assumed to be single as shown in Table 12. However, the long distance, 2,53(1)^A, is similar to that found in other compounds with a Re-Cl bond trans to a multiple bond. High values are found for the Re-Cl bond trans to nitrogen in nitridodichloro-tris(diethylphenylphosphine)rhenium(V), $(2.563(4)^{\text{A}})$ where multiple bonding was suggested for rhenium-nitrogen (13), as well as for the Re-Cl bond trans to oxygen in trans-oxotrichlorobis(diethylphenylphosphine)rhenium(V), $(2.47(3)^{\circ})$ where multiple bonding was suggested for rhenium-oxygen (14).

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It has been proposed that a short rhenium-rhenium distance in $\operatorname{Re}_2(O_2C.C._{3}H_7-n)_4\operatorname{Cl}_2$ might be indicative of quadruple bonding (15). Cotton has measured the electronic (UV-visible) spectrum of this compound and suggests that a $\delta - \delta$ * transition occurs (15). This information would confirm the existence of a quadruple bond in the molecule. This would consist of a σ bond, two π bonds, and a δ bond. Because the Re-Re σ and π bonds are symmetric about the fourfold rotation axis, they should not preferentially stabilize the molecule in D_{4h} (eclipsed) as opposed to D_{4d} (staggered) symmetry. Only the δ bond has the proper symmetry characteristics to stabilize the molecule in the observed D_{4h} symmetry. A δ bond is one which has two nodal planes that intersect along the internuclear axis, and in this case it is formed by the dxy orbitals of the rhenium atoms (taking the Re-Re line as the z axis) as shown in Figure 6. This type of bonding has been suggested in $K_2Re_2CL_8.2H_2O$ and the benzoate complex, $Re_2(O_2C.CH_2C_6H_5)_4Cl_2$ of Cotton (15).

Either oxidation or reduction of Re(III) creates a change in conformation of the molecule, thus there is a difference in conformation which is exhibited between rhenium in an oxidation state of three as opposed to a mixed, or mean fractional oxidation state. This mixed oxidation state for rhenium, namely, II and III, is observed in $\operatorname{Re_2Cl_5(DTH)_2}^*$ where the conformation is found to be staggered and a reduction in bond strength of the Re-Re bond was observed. There, the Re-Re bond more closely resembled a triple bond (20).

Cotton has prepared the complex $\operatorname{Re}_2\operatorname{Cl}_9[(C_6H_5)_4]$ As 2, which is believed to be binuclear and to contain rhenium in the mixed oxidation states of III and IV. It is uncertain at present whether this results in an eclipsed or staggered conformation (21).

DTH = 2,5 dithiahexane



(1) OVERLAP OF day OF Re() AND Re() SHOWING THE FORMATION OF A QUADRUPLE BOND WITH AN ECLIPSED CONFIGURATION



(2) IN A STAGGERED CONFIGURATION THERE IS NO NET BONDING IN THE

OVERLAPPING OF dayORBITALS

FIGURE 6

TJ

Re-O and Re-Cl bond lengths in various compounds.

No.	COMPOUND	Re-Cl bond length (Å)	Re-O bond length (Å)	Reference
1.	Re(acac) ⁺ ₂ Cl ₂	2.33(2)	2.08(5)	33
2	K2ReCl6	2.37(3)		34
3	(TH) [*] 2 ^{ReCl} 6	2.35(3)		35
4	K2Re2C18.2H20	2.29(2)		9
5	ReNC12[P(C2H5)2C6H5]3	2.563(4)		13
6	ReOC13[P(C2H5)2C6H5]3	2.47(3)		14

- + acac = acetylacetonate group
- * TH = p-toluidinium group



(1) $(Re_2 C1_8)^{2-1}$ ION



(2) Mo2 (02 C. CH3)4 MOLECULE

The rather long Re-Cl bond seem to be because it is trans to the multiple Re-Re bond. However, an interpretation of the character of this bonding is dependent on the determination of the actual length of a Re-Cl single bond distance. Values of $2.37(3)^{\text{A}}$ and $2.35(3)^{\text{A}}$ have been quoted for $K_2 \text{ReCl}_6(34)$ and $(\text{Th})_2 \text{ReCl}_6(35)$ in which the rhenium atom has a formal oxidation state of four. If the Re-Re bond is defined as the z axis, then, $K_2 \text{Re}_2 \text{Cl}_8.2\text{H}_20$ contains a Re-Cl equatorial bond distance of $2.29(2)^{\text{A}}$ where the rhenium is in a formal oxidation state of three. Since it is known that Re(III) would have a larger covalent radius than Re(IV), it can be seen that the Re-Cl bond distance in $K_2 \text{Re}_2 \text{Cl}_8.2\text{H}_20$ is anamolously small.

It is suggested that an explanation of these anamolous bond distances is that as well as strong trans effects taking place in these molecules, $K_2Re_2Cl_8.2H_2O$ and also $Re_2(O_2C.C_3H_7-n)_4Cl_2$ there are also strong equatorial effects occurring. The Re-Re binuclear core might be considered as an electron sink which is collecting π electron density from the equatorial Re-Cl bond in $K_2Re_2Cl_8.2H_2O$ and the Re-O bond in $Re_2(O_2C.C_3H_7-n)_4Cl_2$. A slight shortening of the Re-Cl bond distance is certainly evident in $K_2Re_2Cl_8.2H_2O$ compared to K_2ReCl_6 . Analogous shortening of the Re-O bonds may occur in $Re_2(O_2C.C_3H_7-n)_4Cl_2$ but the error limits are too large to draw any definitive conclusion.

Changes in the distribution of electron density in $\text{Re}_2(O_2\text{C.C}_3\text{H}_7-n)_4\text{Cl}_2$ where the Re-Cl bond is 2.53(1)Å and in $\text{Re}(\text{acac})_2\text{Cl}_2$ where the Re-Cl bond is 2.33(2)Å could be detected by performing a nuclear quadrupole resonance experiment on chlorine to determine the different shifts present in the two compound. However, this spectrum would be complex since rhenium has two isotopes, Re^{185} and Re^{187} , both with nuclear spin I=5/2 and abundance

of approximately 1:2 and chlorine has two isotopes, Cl^{35} and Cl^{37} , both with I=3/2 and abundances approximately 3:1, and interpretation would be difficult.

Mass spectra and nmr spectra taken of the compound $\operatorname{Re}_2(O_2C.C_3H_7-n)_4Cl_2$ show some very interesting effects. The Re-Re binuclear core seems to be acting as a strong electron withdrawing or electronegative group on \checkmark -CH₂ as witnessed by the large shift to low field of the \checkmark -CH₂ group in the nmr spectra. The mass spectra results suggest that a decomposition product is being produced and it would be of interest to continue work into the thermodynamics of this interconversion.

The n.m.r. spectrometer has proved to be a good tool in exposing the electronegative effect of the Re-Re binuclear core and certainly studies should be continued with the other compounds in this series, namely, $\operatorname{Re}_2O_4(O_2C.C_3H_7-n)_2$ and $\operatorname{Re}_2O_2Cl_2(O_2C.C_3H_7-n)_2$ to see whether this electronegative effect is continued or not.

The crystal structure study of $\operatorname{Re}_2O_4(O_2C.C_3H_7-n)_2$ was only just started but because the Re-Re bond distance is at least 3.0Å the binuclear core in this compound is not going to exert as much effect on the structural framework of the compound as in $\operatorname{Re}_2(O_2C.C_3H_7-n)_4Cl_2$ where the Re-Re bond distance is 2.20(2)Å

In the crystal structure refinement of $\operatorname{Re}_2(O_2C.C_3H_7-n)_4\operatorname{Cl}_2$ the positions of the carboxylate groups were found with a fair degree of accuracy. However, there was pronounced bending, observed in the $\operatorname{Cl}(1)$ - $\operatorname{Re}(1)$ - $\operatorname{O}(AC)$ angles (>90°) as compared with the equivalent $\operatorname{Cl}-\operatorname{Re}(1)$ - $\operatorname{O}(\overline{CA})$ (<90°). It is uncertain at this point, whether this bending is significant. Further refinement of the positions of these groups as well as the orientation of the n-butyrate groups will be undertaken since a more accurate set of intensity data will be obtained. Probably, counter x-ray techniques will have to be employed in order to obtain this data. Then, Re-O bonds lengths could be accurately calculated and quoted in discussing slight distortions present in the molecular structure of the compound, $\operatorname{Re}_2(O_2C.C_3H_7-n)_4Cl_2$.

CONCLUSIONS

The structure proposed for $\operatorname{Re}_2(O_2C\cdot C_3H_7-n)_4Cl_2$ by Taha and Wilkinson (11) is basically correct, but the diamagnetism of the compound arises from strong metal-metal bonding rather than a weak internal anti-ferromagnetic coupling as originally proposed. The compound is another in the series of compounds first discovered by Cotton (8) in which there is a stable binuclear core where the metalmetal bond lengths are so short that it has been necessary to postulate quadruple bonding to explain them.

The long Re-Cl distance trans to the Re-Re bond is not unexpected and correlates with the empirical observation that halogenmetal bonds trans to multiple bonds are longer than usual (14). We have obtained some evidence of abnormal bonding effects to ligands equatorial to the Re-Re core. The C(1A)-O(AC) bond distance of 1.38(5)Å and the C(1A)-O(\overline{CA}) bond distance of 1.15(3)Å have too large an error limit on them to say whether these bond distances are significant. However, if they are significant, then it can be seen that the n-butyrate groups are preferentially stabilized in an asymmetric symmetry on bonding to the rhenium atoms. Previously, in discussing bonding in these compounds any equatorial contribution to bonding other than single σ -bonds has been ignored. Our results suggest that these theories may have to be re-examined.

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