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(15) Although a 2:1 amide-Eu(DPM)$_3$ complex has been isolated from saturated solutions of Eu(DPM)$_3$ in DMF[3] and two-step equilibria involving Eu(fod)$_3$ have been shown to be of importance in solution[5], no evidence for such stoichiometry for Eu(DPM)$_3$ in solution has been presented.[3,6] It is therefore assumed that a 1:1 stoichiometry obtains under our experimental conditions.

Synthesis and Structure of Dilithium Octamethyldirhenate(III)

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Abstract: The interaction of rhenium pentachloride or the carboxylato bridged compound Re$_2$(O$_2$CC$_6$H$_5$)$_4$Cl$_2$ with methyllithium in diethyl ether produces Li$_2$Re$_2$(CH$_3$)$_8$·2(C$_2$H$_5$)$_2$O, a red crystalline air- and water-sensitive, but thermally stable, complex. The compound is diamagnetic and has a single sharp proton NMR line. Addition of *N,N,N′,N′*-tetramethylethylenediamine (tmed) or 1,10-phenanthroline (phen) yields the compounds Li$_2$Re$_2$(CH$_3$)$_8$·(tmed) and Li$_2$Re$_2$(CH$_3$)$_8$·(phen), respectively. The structure of the diethyl etherate has been determined by x-ray crystallography. Single crystals were formed from pentane and the following triclinic cell dimensions were obtained: $a = 8.343$ (4), $b = 10.436$ (3), $c = 7.551$ (2) Å, $\alpha = 106.91$ (2)°, $\beta = 96.59$ (3)°, $\gamma = 69.47$ (3)°, and $V = 589.0$ (4) Å^3. The space group is $P\bar{1}$ with $Z = 1$ and the Re$_2$(CH$_3$)$_8$$^{2-}$ anion is situated on a crystallographic center of inversion. The anion is very similar in structure to those in the compounds Li$_4$M$_2$(CH$_3$)$_8$·4C$_4$H$_{10}$O (M = Cr or Mo). Bond distances and angles of greatest interest are: Re(1)–Re(1)′, 2.178 (1); average Re–C, 2.19 (1); Li–O, 1.94 (2) Å; average Re(1)–Re(1)′–C angle, 105.7 (4)°. The short metal–metal bond and eclipsed configuration in this complex are consistent with the presence of a Re–Re quadruple bond. The Re–Re distance here is equal, within the esd's, to the shortest such distance previously reported. The effect of van der Waal's forces on the rotational configuration of Re$_2$X$_8$$^{2-}$ species is discussed in greater detail than has heretofore been possible.

In recent years the existence and, indeed, wide occurrence of strong, short multiple metal-to-metal bonds has been recognized and verified.[2,3] The thermally stable tetralithium salts of octamethyldichromate(II), Cr$_2$(Me$_8$)$^{4-}$, and octamethyldimolybdenate(II), Mo$_2$(Me)$_8$$^{4-}$, are known and their structures have been determined.[4,5]

The corresponding isoelectronic octamethyldirhenate(III) anion, Re$_2$(Me)$_8$$^{2-}$, has not previously been isolated despite the large number of known complexes derived from ligand substitution reactions carried out on the Re$_2$Cl$_8$$^{2-}$ ion, where chloride can be replaced by other monodentate ligands with retention of the Re–Re quadruple bond.[3] Only one alkylrhenate ion has been previously described, namely the paramagnetic octamethylrhenate(VI)[6,7] in Li$_2$[ReMe$_8$], obtained by action of methyllithium on hexamethylrhenium(VI). We have now found that the Re$_2$Me$_8$$^{2-}$ ion can be obtained either by action of MeLi on rhenium pentachloride in diethyl ether or by action of MeLi on the tetracarboxylato complex, Re$_2$(OCC$_6$H$_5$)$_4$Cl$_2$, which already has a rhenium–rhenium quadruple bond.

Experimental Section

Microanalyses were performed by Imperial College and Butterworth Analytical Laboratories. Direct analysis of methyl groups was accomplished by hydrolysis of the complexes with deoxygenated water; the methane evolved was measured by a gas buret. The rhenium in the residual solution was determined by plasma arc atomic absorption spectroscopy. NMR spectra were recorded on Perkin-Elmer R14 (60 MHz) and Varian HA 100 spectrometers.

Syntheses. All syntheses and manipulations were carried out in oxygen-free nitrogen or argon. Solvents or reagents were freshly prepared, purified, dried, and degassed. Glass apparatus was dried by heating under vacuum before use. The rhenium used was reagent quality powder (99.9% BDH). Solutions of the products are extremely sensitive to air and moisture and the solid dietherate is pyrophoric. Rhenium pentachloride was freed from the volatile impurity ReOCl$_4$ by pumping under vacuum for several hours. Methyllithium was prepared in diethyl ether from lithium and methyl chloride or purchased from Ventron Corp., Beverly, Mass. Re$_2$(O$_2$CC$_6$H$_5$)$_4$Cl$_2$ was prepared as previously reported.[8]

Dilithium Octamethyldirhenate(III) Bis(diethyl ether). A. From Rhenium Pentachloride. To a solution of ReCl$_5$ (3.6 g. 0.01 mol) in diethyl ether (70 cm^3) was added at −78 °C, slowly and under rapid stirring, a solution of MeLi 0.9 M in ether (100 cm^3, 0.09 mol). The solution was prepared by cooling the ReCl$_5$ at −78 °C and by adding 70 cm^3 of melting diethyl ether previously frozen in liquid nitrogen. The reaction mixture was left to warm up slowly. The solution became red at −38 °C and bright red crystals precipitated. After warming to room temperature, the solution was filtered quickly, the filtrate reduced to a small volume (60 cm^3), and the product crystallized in the form of bright-red crystals by cooling at −78 °C. These were filtered at −78 °C, washed with successive 25-cm^3 portions of diethyl ether at −78 °C, and dried at −20 °C (10^{-3} mmHg) to give 2.2 g of the compound, yield 16%, based on ReCl$_5$: Re:Li determination, calcd 1.00; found 1.02; CH$_4$ determination, calcd Re:CH$_4$ 1:4; found 1:4.17; ^{1}H NMR (benzene) τ 9.21 (s, Re–CH$_3$), 6.58 (q, -O*CH*$_2$CH$_3$), 8.88 (t, -OCH$_2$*CH*$_3$).

B. From Re$_2$(O$_2$CC$_6$H$_5$)$_4$Cl$_2$. Re$_2$(O$_2$CC$_6$H$_5$)$_4$Cl$_2$ (0.5 g) and diethyl ether (30 ml) were placed in a round-bottom flask equipped with nitrogen inlets and immersed in liquid nitrogen, and LiCH$_3$ (20 cm^3 of a 1.7 M solution) was then introduced by means of a syringe. The reaction mixture was then allowed to warm to room temperature and stirred for an additional 2 h. The ether was removed by vacuum and four 20-cm^3 portions of pentane were used to extract the red Li$_2$Re$_2$(CH$_3$)$_8$·2Et$_2$O from the remaining solid. The resultant red solution was filtered through a fritted Schlenck tube, concentrated, and placed in a refrigerator at −40 °C in order to obtain a crystalline product.

The *N,N,N′,N′*-Tetramethylethylenediamine Salt, Li$_2$[Re$_2$Me$_8$]-(tmed). Into a red ethereal solution (35 cm^3) of Li$_2$[Re$_2$(Me)$_8$]·2Et$_2$O (0.5 g) of 0 °C was added slowly an ethereal solution of *N,N,N′,-N′*-tetramethylethylenediamine (tmed). A light blue-purple crystalline solid precipitated immediately. This was collected by filtration at −78 °C, washed with several 20-cm^3 portions of diethyl ether at

−20 °C, and dried at −10 °C in vacuo (10^{-3} mmHg) to give a purple pyrophoric powder: Re:Li determination, calcd 1.00; found 1.04; CH_4 determination, calcd CH_4:Re, 4:1; found 3.97:1. Elemental analysis. Calcd for $Re_2C_{14}H_{40}N_2Li_2$: Re, 35.63; Li, 1.34; C, 40.1; H, 9.4; N, 10.7. Found: Re, 36.9; Li, 1.37; C, 39.6: H, 8.9; N, 10.7. ^1H NMR (pyridine) at −30 °C, τ 8.9 (s, Re-CH_3), 7.9 (s, NCH_2CH_2N), 8.1 (s, -CH_2NMe_2).

The 1,10-Phenanthroline Salt, $Li_2[Re_2Me_8]$phen. The phenanthroline complex was prepared similarly to produce a thermally stable, pyrophoric, purple crystalline solid: Re:Li determination, Calcd 1.00; found 1.05. Elemental analysis. Calcd for $Re_2C_{10}H_{34}N_2Li_2$: C, 43.6; H, 4.6; N, 6.4. Found: C, 44.6; H, 4.0; N, 6.60.

Structure Determination. The red crystals obtained from pentane were placed in Nujol and inspected under a microscope. Several of the most promising ones were covered with a thick hydrocarbon grease and sealed into capillaries which had been previously flushed with N_2. One of these crystals, having approximate dimensions 0.16 × 0.38 × 0.20 mm, was subsequently used for data collection.

Collection of the Data. Data were collected on a Syntex $P\bar{1}$ autodiffractometer at 23° using Mo Kα radiation. The positions of 15 intense reflections that were automatically centered by the computer were used to derive an orientation matrix from which cell constants and setting angles were calculated. The ω scans of the brightest reflections had peak widths at half height of about 0.2°. Cell constants for the triclinic crystal are: 8.343 (4), 10.436 (3), 7.551 (2) Å, 106.91 (2)°, 96.59 (3)°, 69.47 (3)°, and $V = 589.0$ (4) Å^3.

Data in the range $0 < 2\theta < 45°$ were obtained using the θ-2θ scan technique. The scan range was from 1.0° above Kα_1 to 1.0 below Kα_2 with scan rates varying from 4 to 24° min^{-1} depending upon reflection intensity. The intensities and profiles of three strong reflections were periodically monitored during data collection. In this way crystal decomposition, which was linear with time, was followed and the data were corrected accordingly. The intensity decrease of the standards was 69% at the termination of the data collection. An absorption correction was also made, since the linear absorption coefficient is 108 cm^{-1} and the transmission factors vary from 0.146 to 0.294. The crystal was carefully measured on an optical goniometer. Programs for data reduction, absorption correction, and structure analysis were from standard sources.[9]

Solution of the Structure. From the unit cell volume it was evident that only one formula unit, $Li_2Re_2(CH_3)_8$, could be present and that, probably, several molecules of ether were also present. The space group $P\bar{1}$ was assumed at the outset and the successful refinement shows it to be correct. A three-dimensional Patterson map was used to determine the position of the rhenium atom. One cycle of refinement of the positional coordinates and of a scale factor gave agreement indices of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.24$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.28$. All other atoms in the asymmetric unit were then found in a subsequent difference Fourier synthesis. These were refined isotropically to convergence and the corrections for absorption and linear decomposition were then made to the data. After two more cycles of isotropic refinement all atoms were anisotropically refined. A difference Fourier synthesis then revealed all of the methyl hydrogen atoms and a few hydrogen atoms of the ether molecule. The former were included in the structure factor calculations, but were not refined, while the latter were not used.

During the refinement it was found that the Re_2Me_8 unit is disordered in such a way that, while the majority of them have one orientation, a small number lie perpendicular to this. Disorder of this type was first observed for $Mo_2Cl_8^{4-}$ ions[10] and more recently for $Re_2Cl_8^{2-}$ ions.[11] Both disordered rhenium atoms were included in the refinements. A total occupancy of 100% for the metal complex was assumed. The occupancy factor of Re(1) was refined in the last cycles and that of Re(2) was reset after each cycle to one minus the occupancy factor of Re(1). The final values are 86.5 (1)% and 13.5%, respectively. Only one of each pair of disordered carbon atoms was found in a difference Fourier synthesis. The positions of the missing carbon atoms, representing ca. 0.8 electrons each (0.135 × 6), were geometrically determined from consideration of the expected bond distances and angles, but these assigned positions raised the discrepancy factors and would not refine. Consequently, the four carbon atoms having expected occupancy factors of 0.135 were not included in the structure and the other four methyl carbon atoms were given unit weight.

The least-squares refinement, involving 110 variables and 1370 observations, converged to final R_1 and R_2 values of 0.048 and 0.064. The hydrogen atoms were assigned B values of 5.0 Å^2. The final error in an observation of unit weight was 1.801. The value of the parameter p used in the expression for $\sigma(I)$ was 0.060. A final difference Fourier map contained no peaks higher than those for the hydrogen atoms other than several ripples very close to the metal atoms. The rhenium atom was treated as an anomalous scatterer using corrections taken from the tabulations of Cromer and Liberman.[12] Ordinary scattering factors were those of Cromer and Waber[13] for neutral atoms. The scattering factor for hydrogen was taken from Stewart, Davidson, and Simpson.[14]

Table I. Atomic Positional Parameters[a]

	x	y	z
Re(1)	−0.00149 (7)	0.03205 (6)	−0.12529 (8)
Re(2)	−0.1214 (5)	0.0828 (4)	0.0430 (6)
C(1)	0.069 (2)	−0.165 (2)	−0.349 (2)
C(2)	0.261 (2)	0.028 (2)	−0.151 (2)
C(3)	−0.264 (2)	0.072 (1)	−0.234 (2)
C(4)	−0.079 (2)	0.264 (2)	−0.041 (2)
O	0.275 (1)	0.295 (1)	0.314 (1)
C(5)	0.265 (2)	0.423 (2)	0.263 (3)
C(6)	0.427 (2)	0.412 (2)	0.194 (3)
C(7)	0.365 (2)	0.275 (2)	0.491 (3)
C(8)	0.253 (3)	0.364 (2)	0.653 (3)
Li	0.165 (3)	0.162 (2)	0.162 (4)
H(1)	−0.034	−0.198	−0.388
H(2)	0.096	−0.141	−0.438
H(3)	0.163	−0.241	−0.311
H(4)	0.268	0.123	−0.018
H(5)	0.275	0.048	−0.270
H(6)	0.348	−0.066	−0.146
H(7)	−0.277	0.115	−0.344
H(8)	−0.347	0.143	−0.139
H(9)	−0.287	−0.016	−0.277
H(10)	−0.106	0.298	−0.155
H(11)	0.013	0.293	0.032
H(12)	−0.176	0.304	0.028

[a] Positions without esd's were not refined.

Table II. Anisotropic Temperature Factors,[a] β (× 10^3)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re(1)	14.5 (1)	11.0 (1)	15.2 (1)	−9.9 (1)	0.5 (2)	7.3 (1)
Re(2)	16.4 (6)	10.7 (4)	17.2 (8)	−10.3 (7)	−0.9 (12)	4.7 (9)
C(1)	32 (3)	16 (2)	13 (2)	−21 (3)	10 (4)	−4 (3)
C(2)	22 (2)	18 (2)	22 (3)	−19 (3)	0.3 (5)	2 (4)
C(3)	15 (2)	15 (2)	28 (3)	−9 (3)	−8 (5)	17 (4)
C(4)	21 (2)	16 (2)	32 (4)	−14 (3)	−8 (5)	19 (4)
O	27 (2)	20 (1)	25 (2)	−27 (2)	−11 (3)	14 (2)
C(5)	30 (3)	22 (2)	46 (5)	−29 (3)	−14 (7)	25 (5)
C(6)	30 (4)	31 (3)	43 (5)	−28 (4)	2 (7)	26 (6)
C(7)	28 (4)	22 (2)	35 (5)	−16 (4)	−14 (7)	8 (6)
C(8)	52 (5)	31 (3)	25 (4)	−38 (6)	17 (8)	−1 (6)
Li	35 (4)	14 (2)	34 (6)	−32 (4)	−18 (9)	17 (6)

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

Results

Structural. A list of structure factors expressed as 10(FOBS) and 10(FCALC) is available.[15] Tables I, II, and III contain atomic positional parameters, anisotropic temperature factors, and root-mean-square amplitudes of thermal vibration. Interatomic distances and angles are given in Tables IV and V. An ORTEP representation of the contents of one unit cell is shown in Figure 1.

Chemical. The interaction of an excess of methyllithium with rhenium pentachloride in diethyl ether at −78 °C gives immediately a brown solution which at −50 °C changes to red; at −30 °C bright red crystals separate from the solution. The

Table III. Root-Mean-Square Amplitudes of Thermal Vibrations (Å)

Atom	Min	Intermediate	Max
Re(1)	0.198	0.206	0.224
Re(2)	0.202	0.226	0.229
C(1)	0.171	0.253	0.338
C(2)	0.212	0.285	0.302
C(3)	0.213	0.240	0.287
C(4)	0.208	0.266	0.317
O	0.226	0.263	0.320
C(5)	0.245	0.304	0.368
C(6)	0.266	0.333	0.377
C(7)	0.259	0.306	0.359
C(8)	0.252	0.338	0.422
Li	0.183	0.275	0.364

Table IV. Interatomic Distances[a] (Å)

	Bond Distances		
Re(1)-Re(1)′	2.178 (1)	Re(2)-Re(2)′	2.169 (7)
-C(1)	2.19 (1)	-C(1)	2.27 (1)
-C(2)	2.21 (1)	-C(2)	2.26 (1)
-C(3)	2.19 (1)	-C(3)	2.28 (1)
-C(4)	2.19 (1)	-C(4)	2.30 (1)
Li-O	1.94 (2)	C(2)-H(4)	1.20
O-C(5)	1.47 (2)	-H(5)	1.00
O-C(7)	1.49 (2)	-H(6)	1.00
C(5)-C(6)	1.46 (2)	C(3)-H(7)	1.03
C(7)-C(8)	1.49 (2)	-H(8)	0.99
C(1)-H(1)	1.02	-H(9)	0.96
-H(2)	0.86	C(4)-H(10)	1.00
-H(3)	0.99	-H(11)	0.98
		-H(12)	0.91
	Nonbonded Distances		
C(1)····C(2)	2.97 (2)	Li····C(1)′	2.52 (3)
C(1)····C(3)	3.02 (2)	Li····C(2)	2.45 (3)
C(1)····C(4)′	3.34 (2)	Li····C(3)′	2.49 (2)
C(2)····C(4)	3.04 (2)	Li····C(4)	2.53 (3)
C(2)····C(3)′	3.36 (2)	Li····Re(1)	2.74 (2)
C(3)····C(4)	2.91 (2)	Li····Re(2)	2.76 (2)

[a] Atoms with primed numbers are related by the center of symmetry to atoms of the same unprimed number.

Table V. Bond Angles[a] (degrees)

	M = Re(1)	M = Re(2)
M-M′-C(1)	105.6 (3)	100.1 (4)
-C(2)	105.7 (4)	102.8 (4)
-C(3)	105.6 (3)	100.5 (4)
-C(4)	106.1 (4)	99.2 (4)
C(1)-M-C(2)	85.1 (5)	82.2 (5)
-C(3)	87.0 (5)	158.4 (5)
-C(4)	148.2 (5)	95.1 (5)
C(2)-M-C(3)	148.8 (5)	95.7 (5)
-C(4)	87.6 (5)	158.0 (5)
C(3)-M-C(4)	83.3 (5)	78.8 (5)

Li-O-C(5)	122 (1)	O-C(5)-C(6)	112 (1)
-C(7)	121 (1)	O-C(7)-C(8)	111 (1)
C(5)-O-C(7)	117 (1)		

[a] Bond angles involving the unrefined hydrogen atoms ranged from 100 to 113°.

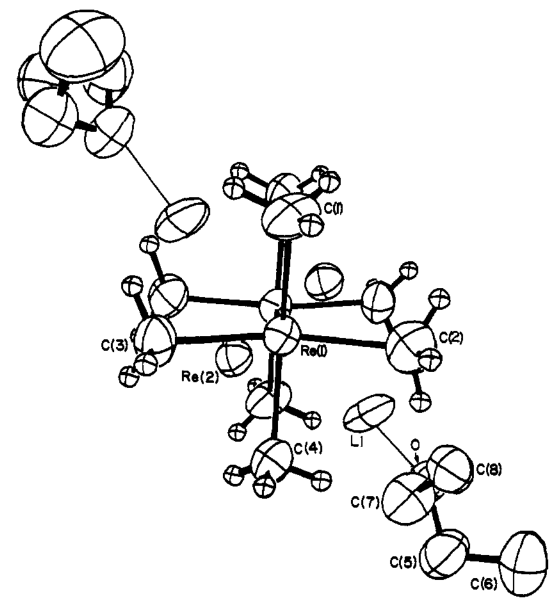

Figure 1. The structure of $Li_2Re_2(CH_3)_8{\cdot}2C_4H_{10}O$. The hydrogen atoms have been reduced for clarity, while the other atoms are represented by 50% ellipsoids. Unlabeled atoms are related to labeled atoms by a center of symmetry.

yield of $Li_2[Re_2(CH_3)_8]{\cdot}2(C_2H_5)_2O$ is quite high if the $ReCl_5$:LiMe ratio is 1:9; the red solutions are quite stable at room temperature. However, if lower ratios are used, e.g., 1:5, the reaction is very much slower, although some product can be obtained at −30 °C after 3 h stirring. If the solutions are quickly allowed to warm to room temperature the initially red solutions become brown and little or no product can be isolated.

Interaction of methyllithium with $Re_2(O_2CC_6H_5)_4Cl_2$ in ether also gives $Li_2Re_2(CH_3)_8{\cdot}2(C_2H_5)_2O$, but the yields are somewhat lower. The corresponding acetate is not a convenient starting material because it is difficult to separate the product from lithium acetate.

The use of dimethylmagnesium or methylmagnesium chloride with $ReCl_5$ in ether or toluene-ether also leads to red solutions, but from these, only oxotetramethylrhenium(VI)[16] can be isolated.

The etherate $Li_2Re_2(CH_3)_8{\cdot}2(C_2H_5)_2O$ is extremely air sensitive, to the extent of being pyrophoric. However, it is thermally quite stable, decomposing only over a period of weeks at room temperature. The etherate is readily soluble in ethers and is soluble in aromatic hydrocarbons and alkanes such as pentane, from which it can be crystallized at low temperatures.

The solutions of the compound vary in color depending on the solvent. They are red in pentane or ether, but purple-blue in dioxane or tetrahydrofuran. Solutions in the latter solvents are unstable at room temperature and decomposition occurs rapidly in acetone, chlorinated solvents, carbon disulfide, and acetonitrile. Solvolysis to give methane occurs rapidly in alcohols and in water.

The solvent molecules can be removed from $Li_2Re_2(CH_3)_8{\cdot}2(C_2H_5)_2O$ by pumping under vacuum at room temperature for about 8 h. The resulting brown powder $Li_2Re_2(CH_3)_8$ is insoluble in ethers or hydrocarbons.

The fresh etherate in benzene or deuteriobenzene gives a single sharp resonance due to Re-CH_3 at τ 9.24 together with peaks due to diethyl ether in the correct ratio. If a benzene solution is refluxed under nitrogen for ca. 30 min and solvent periodically removed, a new peak appears at τ 9.61. We attribute this to the methyl resonance of the ion pair $[Li^+]_2[ReMe_8{}^{2-}]$, since the addition of a little ether results in disappearance of the τ 9.61 line and an increase in intensity of the τ 9.24 line. By contrast, heating of a benzene solution in a sealed tube (35-85 °C) or exposure to ultraviolet light for several hours produces no change in the original spectrum.

Replacement of diethyl ether in $Li_2[Re_2(CH_3)_8]{\cdot}$

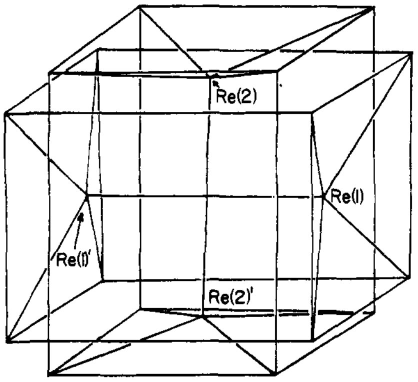

Figure 2. A representation of the disorder in the orientation of the $Re_2(CH_3)_8{}^{2-}$ anions. Methyl groups are located at the corners of the parallelepipeds.

$2(C_2H_5)_2O$ by *N,N,N',N'*-tetramethylethylenediamine (tmed) or 1,10-phenanthroline (phen) yields the blue-purple pyrophoric adducts $Li_2Re_2(CH_3)_8$·tmed and $Li_2Re_2(CH_3)_8$·phen. *N,N'*-Dimethylpiperazine or 2,2'-bipyridyl react with the etherate to give green-brown solutions, but the 1:1 complexes could not be isolated.

The tmed complex is sparingly soluble in diethyl ether and tetrahydrofuran and decomposes slowly at room temperature (turns dark brown after several hours), while the phen complex is totally insoluble and thermally stable up to 90 °C. Addition of pyridine to $Li_2Re_2(CH_3)_8$·tmed at −35 °C gives a blue solution whose NMR spectrum has a singlet at τ 8.9 (methyl resonance of $Re_2Me_8{}^{2-}$) and a doublet at τ 7.9, 8.1 due to the methylene and methyl protons of the tmed ligand, respectively. When the temperature is raised to −15 °C the blue color changes to brown, but the spectrum remains unchanged, suggesting that ligand displacement by the solvent occurs. The phen adduct also reacts with pyridine at −40 °C to give a brown solution which at that temperature gives a complex NMR spectrum consisting of several single resonances.

The etherate $Li_2Re_2(CH_3)_8 \cdot 2(C_2H_5)_2O$ reacts rapidly with acetic anhydride at −78 °C evolving gas, but we have been unable to isolate any well defined product from the solution. Attempts to delithiate the salt by interaction with *tert*-butyl hypochlorite (in toluene), methyl chloride (in ether), methylfluorosulfonic acid (in toluene), tetramethylphosphonium chloride (in ether), or *N,N'*-dichlorocyclohexylamine (in ether, tetrahydrofuran, or toluene) have not been successful. There is usually no apparent reaction below 20 °C, but at higher temperatures gas evolution is often observed and black or brown residues are obtained from which no characterizable rhenium complexes have been isolated. Reliable vibrational spectra of the compounds have not yet been obtained because of their extreme sensitivity to oxygen and water.

Discussion

The preparation of $Re_2Me_8{}^{2-}$, as described in this paper, is of importance in two respects. The existence of the anion provides further evidence to show that quadruply bonded M–M species are capable of forming highly covalent bonds to ligands, and, in particular, to carbon, as well as more ionic ones to ligand atoms such as Cl or O. This adds impetus to the effort to expand the organometallic chemistry of these species, which at present is limited to the preparation and structural characterization of only a few species derived from $Cr_2{}^{4+}$ and $Mo_2{}^{4+}$, in addition to the anion reported here. Second, the formation of the quadruply bonded $Re_2{}^{6+}$ unit from the pentachloride, which may be present as the chlorine-bridged, but not Re–Re bonded, dimer[17] or as a solvated monomer, is of interest, since the discovery of reactions in which multiple M–M bonds are generated is important in the development of this field.

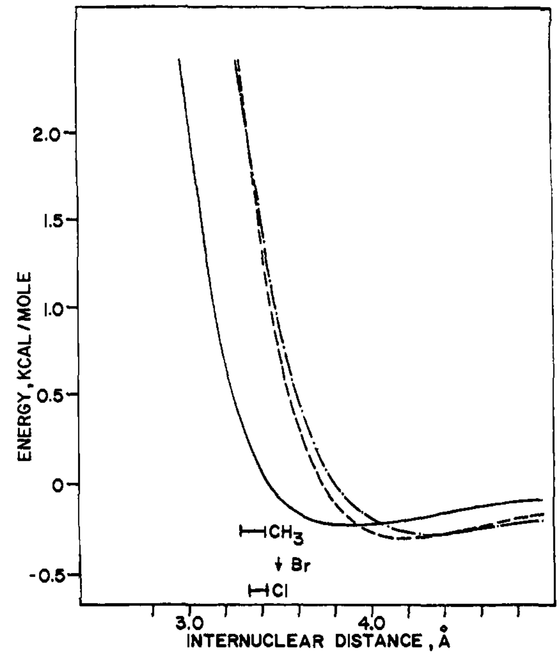

Figure 3. Plots of the X····X van der Waals energies for X = Cl(—), Br(- - -), and CH_3(- · - ·) with indications of the X···X distances actually observed in $M_2X_8{}^{n-}$ species.

The overall structure of the compound is remarkably similar to those of the analogous $Li_4Cr_2Me_8 \cdot 4THF$ and $Li_4Me_2Me_8 \cdot 4THF$, except that there are Li^+ ions centered over only two opposite "vertical" faces of the $M_2Me_8{}^{n-}$ ion instead of over all four and, of course, the ether molecule coordinated to each Li^+ ion is $(C_2H_5)_2O$ instead of THF. The close relationship of the Li^+ ion to four methyl groups and even, perhaps, to the electron density of the M–M bond is analogous to that observed in the chromium and molybdenum cases.

Two other similarities to the Mo and Cr compounds are the absence of any axial coordination, however weak, and the relatively loose crystal packing. The volumes per nonhydrogen atom, in cubic angstroms, for the Cr, Mo, and Re compounds are 26, 26, and 27, respectively, as compared to values in the range 18–22 Å that are typically observed.

The presence of only one $Re_2Me_8{}^{2-}$ ion in the unit cell, residing on a center of inversion, is in itself an auspicious circumstance, since it would allow very easy measurement of the polarization of absorption bands (a correction for the disorder would be easy to make), as well as eliminate factor group effects in the vibrational spectrum. Unfortunately, the extreme air sensitivity of the compound will make it difficult to take advantage of this structural feature.

The Re–Re bond length is taken to be 2.178 (1) Å, which is that observed in the molecule having the most highly populated orientation. The apparent bond length of 2.169 (7) Å in the molecule with the minor orientation is much less accurate, but not significantly different ($<2\sigma$), and it has accordingly been neglected. The distance of 2.178 (1) Å is equal, within the experimental errors, to that in $Re_2Cl_4(HN_2CPh_3)_2$, 2.177 (2) Å, which is the shortest Re–Re distance previously reported.[18]

An attempt to determine the "best" values of the Re–C distance and the Re–Re'–C angles by analyzing the effects of near superposition of methyl groups in the major and minor orientations (see Figure 2), following the procedure described and successfully applied earlier to $Re_2Cl_8{}^{2-}$ in its $(\eta\text{-}C_4H_9)_4N^+$ salt[11] was ineffectual here. This is not surprising in view of the lightness of CH_3 compared to Cl and the fact that the minor orientation here has only about half the occupancy as did the minor orientation in the $Re_2Cl_8^{2-}$ case. Thus, the values for the Re–C bond length and the Re–Re′–C angle found in the major orientation are taken to be the "best" values, just as for the Re–Re′ bond distance.

It should be noted that no occupation of the third possible orientation of $Re_2Me_8^{2-}$ is observed. This is readily understood because in this case the Li^+ ions would have to be over basal edges of the $Re_2Me_8^{2-}$ parallelepiped, or else be disordered too. There is no indication of any electron density at the positions appropriate to such a minor set of Li^+ ions.

Interpretation of the Eclipsed Configuration in $M_2X_8{}^{n-}$ Species. In the earliest publications[2,3] describing the evidence for, and the nature of, the quadruple bond, the eclipsed configuration of $Re_2Cl_8^{2-}$ was invoked as evidence for the δ component of the bonding. It was proposed that nonbonded repulsions (Cl···Cl) would favor a staggered configuration and that only a δ component to the metal–metal bond could oppose this tendency by favoring an eclipsed configuration. This argument is in principle correct, but its forcefulness is diminished because the chlorine atom has a relatively small van der Waals radius. The same reasoning, when applied to species such as $Re_2Br_8^{2-}$ and $Re_2(CH_3)_8^{2-}$, is more cogent, since the Br and CH_3 groups have larger packing radii.

It is even more useful to examine the entire van der Waals energy curve for Cl···Cl, Br···Br and $CH_3\cdots CH_3$ in relation to this problem. In Figure 3 these curves, according to the equations of Mason and Kreevoy,[19] are shown. Also indicated on the plot are the values, or small ranges of values, for the X···X distances that have been observed experimentally in $M_2X_8{}^{n-}$ species with D_{4h} configurations. It is evident that while the Cl case may be near the minimum in the Br and, especially, the CH_3 cases, the eclipsed configuration puts the X···X distances well into the repulsive region. Thus, the occurrence of the eclipsed configuration must be taken as evidence that the δ component of the quadruple bond is strong enough to overcome significant nonbonded repulsion effects.

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Supplementary Material Available: A listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Rate Controlling Proton Transfer in the Complexing of Copper(II) and Nickel(II) by 2-Aminomethylpyridine

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Abstract: The kinetics of complexation of 2-aminomethylpyridine (amp) with Cu(II) and Ni(II) in aqueous solution has been studied as a function of pH and total buffer concentration at 25 °C in 0.5 M $NaClO_4$. In both systems the reaction was found to be catalyzed by the basic component of the buffer. This observation demonstrates that the complexation reaction is controlled (at least in part) by proton loss from the protonated intermediate M-ampH^+ where M = Cu(II) and Ni(II).

In spite of the added complication of a multiplicity of steps, the overall rate for complexation of multidentate ligands by bivalent metal ions in aqueous solution has, in many cases, been assumed to be governed by the rate of formation of the first bond which, in turn, triggers a rapid sequence of ring closures.[1] Reactions for which first bond formation is rate determining are commonly referred to as "normal" substitutions. In these cases, the first bond formation can be described in terms of the generally accepted Eigen mechanism of complex formation[2] which proceeds by a fast preequilibrium to yield an outer-sphere complex followed by rate limiting elimination of a water molecule from the first coordination sphere