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Synthesis and Characterization of *cis*-[$Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2$]·2THF

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Introduction

The chemistry of group 6 clusters of the type [$M_6Cl_8X_6$]$^{2-}$ (M=Mo, W; X = Br^-, Cl^-, I^-, OH^-, SCN^-, etc.) or [$M_6Cl_8L_6$]$^{4+}$ (M = Mo, L = phosphine oxide, pyridine *N*-oxide, DMF, etc.) has been well developed over the last 50 years as many groups have explored the ligand substitution chemistry and properties of this large family of compounds.[1] Recently, the preparation of a versatile starting material for the preparation of substituted $Mo_6Cl_8^{4+}$ clusters, $(Bu_4N)_2[Mo_6Cl_8(CF_3SO_3)_6]$, and a number of derivatives was reported.[2,3] The halide-substituted clusters have been thoroughly investigated, and compounds with a wide variety of donor ligands are also known.[4,5] In these compounds, similar to the majority of the known $Mo_6Cl_8^{4+}$ complexes, all the X ligands in [$M_6Cl_8X_6$]$^{2-}$ are identical, leading to complexes that approach octahedral symmetry. Relatively rare are examples where the X ligands are not identical, and most of these complexes are ligated in a *trans* fashion. For example, Saito et al. have prepared the *trans* phosphine ligated clusters *trans*-[$Mo_6Cl_8(Cl_4)(PR_3)_2$] (R = *n*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11}).[6] Moreover, Perchenek and Simon[7] have prepared the *trans* alcoholate ligated clusters *trans*-[$Mo_6Cl_{12}(OCH_3)_2$]$^{2-}$ and *trans*-[$Mo_6Cl_{12}(OCH_2C_{14}H_9)_2$]$^{2-}$. Saito et al. report the only known preparation of a *cis*-ligated [$Mo_6Cl_8X_6$]$^{2-}$ cluster, *cis*-[$Mo_6Cl_8(Cl_4)(P(n\text{-}C_3H_7)_3)_2$], in 3% yield. We report here a modification of Saito's preparation which allows the preparation of *cis*-ligated $Mo_6Cl_8^{4+}$ clusters in high (97%) yield.

Our motivation to prepare these complexes was not only to synthesize molecular complexes but also to link metal clusters by a bidentate ligand such as a diphosphine or diamine to form an extended crystalline structure. Precedents for such a material include [$Fe(pyrazine)_2(NCS)_2$]$_n$,[8−10] $Cu(pyrazine)Cl_2$,[11] $Co(pyrazine)_2Cl_2$,[12,13] and $Cu(pyrazine)(NO_3)_2$.[14] In all these examples, the metal atoms are linked by pyrazine. In the case of iron and cobalt two dimensional extended structures result, while in the case of copper the materials assume a one dimensional extended structure. We currently seek a general method by which crystalline extended structures may be grown from solution phase precursors. If such a method could be developed, a wide variety of both low- and high-dimensional materials could be prepared.

Experimental Section

All manipulations were carried out either in an Ar atmosphere or in vacuo. THF was distilled from sodium/benzophenone, DMSO, $CHCl_3$, and CH_2Cl_2 were dried with 3 Å Molecular Sieves, $CHCl_3$ and CH_2Cl_2 were distilled before use, and DMSO was syringe filtered before use.

Raman spectra were taken on a Dilor XY100 with a He−Ne laser, the spectra were smoothed with a binomial algorithm, and instrumental artifacts (spikes, peaks having no width) have been removed from the spectrum presented here. The Raman spectrum was acquired with a resolution of 4 cm^{-1}. Single crystal X-ray diffraction data was collected on a Rigaku AFC6S diffractometer using Mo Kα radiation. Microprobe analyses were performed on a JEOL 733 superprobe using the vendor supplied software SQ for standardless semiquantitative elemental analysis. Elemental analysis was performed by Oneida Research Services, Whitesboro, NY. IR spectra were collected on a Mattson Polaris FTIR, Model IR-10410. ^{31}P NMR spectra were acquired on a Varian VXR-400S spectrometer, and chemical shifts are reported in ppm downfield from 85% H_3PO_4.

trans-[$Mo_6Cl_8(Cl_4)(P(C_5H_{11})_3)_2$] was prepared by the method of Saito et al.[6] by the reaction of Mo_6Cl_{12}[15] (20 g) and $P(C_5H_{11})_3$[16] (11.7 g) in THF, yield 14.8 g (50%). Chemical analysis [found wt % (calcd wt % for [$Mo_6Cl_8(Cl_4)(P(C_5H_{11})_3)_2$])]: Cl, 26.12 (28.55); P, 4.14 (4.16); C, 24.35 (24.18); H, 4.37 (4.465); N, 0.17 (0). Microprobe analysis [found at % (calcd at % for $Mo_6Cl_{12}P_2$)]: Mo, 28.9 (30); Cl, 60.9 (60); P, 10.2 (10). IR (KBr): 2955 (s), 2929 (s), 2868 (m), 1458 (s), 1412 (w), 1379 (w), 1103 (s), 1062 (w), 1021 (w), 965 (w), 824 (w), 720 (m), and 464 (w) cm^{-1}. One resonance was observed in the ^{31}P NMR spectrum at δ 3.8. Triethylphosphine (Aldrich) was distilled before use.

Preparation of *cis*-[$Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2$]·2THF. In a two neck flask, a solution of *trans*-[$Mo_6Cl_8(Cl_4)(P(C_5H_{11})_3)_2$] (0.2982 g, 200.1 μmol) in THF (25 mL) was formed at 35 °C and an excess of $P(C_2H_5)_3$ (0.4 mL, 2.6 mmol) added by syringe. The mixture was allowed to stand, and yellow crystals, some platelike and others acicular in appearance, grew from the yellow solution in 48 h. After 5 days the crystalline product was collected: yield 0.268 g, 194 μmol, 97.0%; mp >260 °C. The product was observed to be insoluble in THF, $CHCl_3$, and CH_2Cl_2 and only sparingly soluble in DMSO. No discoloration was observed upon exposure to air. Microprobe analysis confirmed the presence of Mo, Cl, and P in the product. Chemical analysis [found wt % (calcd wt % for *cis*-[$Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2$]·2THF)]: P; 4.71 (4.48), C; 17.49 (17.38); H, 3.38 (3.35); N, 0 (0). IR (KBr): 2969 (s), 2962 (s), 2933 (s), 2978 (s), 1457 (m), 1419 (m), 1383 (m), 1258 (m), 1063 (m), 1035 (s), 910 (w), 762 (s), and 725 (s) cm^{-1}. The Raman spectrum of *cis*-[$Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2$]·2THF is shown in Figure 1.

When trimethyl phosphine was used in place of triethylphosphine, small platelike crystals resulted. When larger phosphines such as tributylphosphine were used, a yellow clear solution resulted; no crystals formed in the solvents used. In the case where a bidentate phosphine such as 1,2-bis(dialkylphosphino)ethane (alkyl = methyl, ethyl) or 1,2-bis(diphenylphosphino)butane was used in place of triethylphosphine, yellow amorphous powders resulted.

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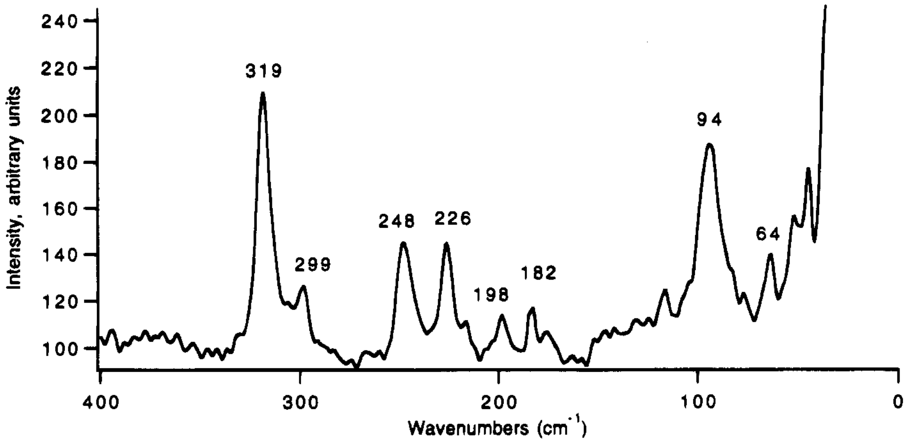

Figure 1. Raman spectrum of *cis*-[$Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2$]·2THF, with bands observed at 319 (s), 299 (w), 248 (s), 226 (s), 198 (w), 182 (w), 175 (w), 115 (w), 94 (s), and 64 (w) cm^{-1}. For reference, the Raman spectrum of $(Bu_4N)_2[Mo_6Cl_{14}]$ shows bands at 315 (s), 246 (s), 236 (s), 215 (w), 196 (w), 176 (s), 94 (s), and 64 (w) cm^{-1}.

X-ray Diffraction. A yellow elongated platelike crystal with the approximate dimensions 0.15 × 0.02 × 0.33 mm was mounted in a glass capillary with a small amount of Apiezon H grease and mineral oil. All measurements were made on a Rigaku AFC6S four circle diffractometer with graphite-monochromated Mo Kα radiation generated at 2 kW. The diffractometer was operated by the MSC-AFC diffractometer control software.[17] Unit cell parameters were obtained from least-squares analysis of the setting angles of 16 high-angle reflections ($40° < 2\theta$ (Mo Kα) $< 49°$) in which the 90° angles were constrained to their ideal value. Intensity data in the range $3° < 2\theta < 50°$ were collected with $\omega-2\theta$ scans of constant speed (8°·min^{-1} in ω) with reflections having $I < 10\sigma(I)$ scanned up to a maximum of four times. The intensities of three standard peaks measured at 150 reflection intervals remained unchanged within counting statistics. Crystallographic computations were performed on a VAXStation 3100/76 computer with the TEXSAN[18] series of programs. Atomic scattering factors[19] and anomalous dispersion terms[20] were taken from standard sources. Data were corrected for Lorentz and polarization effects, and an empirical absorption correction, based on azimuthal scans of three reflections, was applied to the data (transmission factors 0.83–1.00). The space group was determined on the basis of systematic absences ($0k0$, $k \neq 2n$) and intensity statistics and was confirmed by a satisfactory refinement. The Mo atoms were located on an *E*-map calculated by the program MITHRIL,[21] and the remaining non-hydrogen atoms were revealed by direct methods phase refinement (DIRDIF[22]) or difference electron density maps. No H atoms were found during refinement, and none were included in the model. Final refinement was performed on those data with $I > 3\sigma(I)$ and included anisotropic thermal parameters for all non-hydrogen atoms. The position of the oxygen atom in the THF molecule could not be distinguished from that of the carbon atoms so all five ring positions were refined as carbons. The final difference electron density map contained only small, random features (maximum and minimum heights ±0.65 e·Å^{-3}). No unusual trends were revealed by an analysis of F_o vs F_c as a function of F_o, $(\sin\theta)/\lambda$, and Miller indices. Crystal parameters are reported in Table 1, final atomic positions and equivalent isotropic thermal parameters are reported in Table 2, and selected bond lengths and angles are reported in Table 3. Full crystallographic details (Table SI), additional bond distances and angles (Table SII), and anisotropic thermal parameters (Table SIII) are provided as supplementary material.

Table 1. Crystallographic Details

[$Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2$]·2THF	space group $P2_1/m$ (No. 11)
$a = 10.342(3)$ Å	$T = -21$ °C
$b = 15.176(3)$ Å	$\lambda = 0.71069$ Å
$c = 13.515(3)$ Å	ϱ(calc) = 2.17 g cm^{-3}
$\beta = 93.55$ (2)°	$\mu = 25.47$ cm^{-1}
$V = 2117.1(9)$ Å^3	$R(F_o)^a = 0.037$
$Z = 2$	$R_w(F_o)^b = 0.039$
fw 1381.6	

[a] $R(F_o) = \sum (F_o - F_c)/\sum(F_o)$. [b] $R_w(F_o) = [\sum w(F_o - F_c)^2/\sum(F_o)^2]^{1/2}$.

Table 2. Positional Parameters and B_{eq} Values (Å^2) for *cis*-[$Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2$]·2THF

atom	x	y	z	B_{eq}
Mo(1)	0.2818(2)	1/4	0.7687(1)	3.09(9)
Mo(2)	0.1998(2)	1/4	0.5827(1)	2.72(8)
Mo(3)	−0.0385(2)	1/4	0.6328(1)	2.74(8)
Mo(4)	0.0413(2)	1/4	0.8208(1)	2.98(8)
Mo(5)	0.1198(1)	0.12797(7)	0.7020(1)	2.92(5)
Cl(1)	0.3457(3)	0.1332(2)	0.6531(3)	3.7(2)
Cl(2)	0.0444(3)	0.1344(2)	0.5247(2)	3.5(2)
Cl(3)	−0.1082(3)	0.1369(2)	0.7496(2)	3.8(2)
Cl(4)	0.1987(3)	0.1361(2)	0.8793(2)	3.9(2)
Cl(5)	0.1137(4)	−0.0308(2)	0.7057(3)	5.1(2)
Cl(6)	0.3061(5)	1/4	0.4284(4)	4.6(3)
Cl(7)	0.4974(5)	1/4	0.8485(4)	5.6(3)
P(1)	−0.2557(5)	1/4	0.5282(4)	3.8(3)
P(2)	−0.0660(6)	1/4	0.9907(4)	4.8(3)
C(1)	−0.226(2)	1/4	0.394(1)	4(1)
C(2)	−0.350(2)	1/4	0.325(2)	6(1)
C(3)	−0.362(1)	0.155(1)	0.551(1)	5.1(8)
C(4)	−0.301(2)	0.063(1)	0.525(1)	6.0(9)
C(5)	0.059(2)	1/4	1.093(1)	5(1)
C(6)	0.008(2)	1/4	1.202(1)	7(1)
C(7)	−0.189(2)	0.156(2)	1.009(2)	10(2)
C(8)	−0.119(3)	0.074(2)	1.010(2)	12(2)
C(9)	0.307(2)	0.080(2)	0.209(2)	11(2)
C(10)	0.324(2)	0.111(2)	0.120(2)	11(2)
C(11)	0.457(3)	0.107(2)	0.101(2)	13(2)
C(12)	0.503(2)	0.035(2)	0.157(2)	12(2)
C(13)	0.413(2)	0.018(1)	0.234(2)	10(2)

Discussion

The starting cluster *trans*-[$Mo_6Cl_8(Cl_4)(P(C_5H_{11})_3)_2$] was prepared by the method of Saito et al.[6] The chemical and microprobe analyses of the starting cluster are consistent with the proposed stoichiometry. Only one peak was observed in the ^{31}P NMR spectrum at δ 3.8 suggesting only one isomer was present. Saito et al. determined the structure of the $P(C_4H_9)_3$ analog and showed it to be ligated in a *trans* fashion. They report it shows one peak in the ^{31}P NMR spectrum at δ 3.8.

The synthesis of the title compound, *cis*-[$Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2$]·2THF, is straightforward and reliable. When *trans*-

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(17) MSC/AFC Diffractometer Control Software, Molecular Structure Corp., The Woodlands, TX, 1988 (revised).

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Table 3. Selected Bond Distances (Å) and Angles (deg) in *cis*-$[Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2]\cdot 2THF$

	Distances		
Mo(1)−Mo(2)	2.603(3)	Mo(3)−Cl(2)	2.471(3)
Mo(1)−Mo(4)	2.627(3)	Mo(3)−Cl(3)	2.469(4)
Mo(1)−Mo(5)	2.620(2)	Mo(3)−P(1)	2.578(5)
Mo(1)−Cl(1)	2.479(4)	Mo(4)−Mo(5)	2.614(2)
Mo(1)−Cl(4)	2.475(4)	Mo(4)−Cl(3)	2.466(4)
Mo(1)−Cl(7)	2.416(6)	Mo(4)−Cl(4)	2.470(4)
Mo(2)−Mo(3)	2.596(2)	Mo(4)−P(2)	2.611(6)
Mo(2)−Mo(5)	2.622(2)	Mo(5)−Cl(1)	2.467(4)
Mo(2)−Cl(1)	2.479(4)	Mo(5)−Cl(2)	2.475(3)
Mo(2)−Cl(2)	2.474(3)	Mo(5)−Cl(3)	2.487(4)
Mo(2)−Cl(6)	2.416(5)	Mo(5)−Cl(4)	2.487(4)
Mo(3)−Mo(4)	2.623(3)	Mo(5)−Cl(5)	2.412(3)
Mo(3)−Mo(5)	2.607(2)		
	Angles		
Cl(1)−Mo(1)−Cl(1)	91.3(2)	Cl(3)−Mo(3)−P(1)	94.1(1)
Cl(1)−Mo(1)−Cl(4)	89.8(1)	Cl(3)−Mo(4)−Cl(3)	88.2(2)
Cl(1)−Mo(1)−Cl(4)	175.1(1)	Cl(3)−Mo(4)−Cl(4)	91.3(1)
Cl(1)−Mo(1)−Cl(7)	90.4(1)	Cl(3)−Mo(4)−Cl(4)	175.5(1)
Cl(4)−Mo(1)−Cl(4)	88.7(2)	Cl(3)−Mo(4)−P(2)	93.0(1)
Cl(4)−Mo(1)−Cl(7)	94.4(1)	Cl(4)−Mo(4)−Cl(4)	88.8(2)
Cl(1)−Mo(2)−Cl(1)	91.3(2)	Cl(4)−Mo(4)−P(2)	91.5(1)
Cl(1)−Mo(2)−Cl(2)	89.0(1)	Cl(1)−Mo(5)−Cl(2)	89.2(1)
Cl(1)−Mo(2)−Cl(2)	175.4(1)	Cl(1)−Mo(5)−Cl(3)	175.0(1)
Cl(1)−Mo(2)−Cl(6)	91.9(1)	Cl(1)−Mo(5)−Cl(4)	89.8(1)
Cl(2)−Mo(2)−Cl(2)	90.3(2)	Cl(1)−Mo(5)−Cl(5)	93.7(1)
Cl(2)−Mo(2)−Cl(6)	92.7(1)	Cl(2)−Mo(5)−Cl(3)	90.1(1)
Cl(2)−Mo(3)−Cl(2)	90.5(2)	Cl(2)−Mo(5)−Cl(4)	174.9(1)
Cl(2)−Mo(3)−Cl(3)	90.6(1)	Cl(2)−Mo(5)−Cl(5)	93.0(1)
Cl(2)−Mo(3)−Cl(3)	175.9(1)	Cl(3)−Mo(5)−Cl(4)	90.4(1)
Cl(2)−Mo(3)−P(1)	89.9(1)	Cl(3)−Mo(5)−Cl(5)	91.3(1)
Cl(3)−Mo(3)−Cl(3)	88.1(2)	Cl(4)−Mo(5)−Cl(5)	92.1(1)

$[Mo_6Cl_8(Cl_4)(P(C_5H_{11})_3)_2]$ was allowed to stand with a variety of concentrations of $P(C_2H_5)_3$ in THF, yellow-orange crystals of *cis*-$[Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2]\cdot 2THF$ grew from the solution in high (97%) yield. In the case where a large excess of phosphine was used, the product was recovered by filtration and the excess phosphine was washed away with hexane.

The *cis* phosphine ligated cluster *cis*-$[Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2]\cdot 2THF$ is remarkably insoluble in THF, $CHCl_3$, and CH_2Cl_2 and is only sparingly soluble in DMSO. Because of the lack of solubility, solution NMR spectra could not be obtained. In sharp contrast, *trans*-$[Mo_6Cl_8(Cl_4)(P(C_5H_{11})_3)_2]$ is soluble in many organic solvents of moderate polarity such as THF, $CHCl_3$, and CH_2Cl_2 and is very soluble in DMSO.

Platelike crystals were selected for X-ray single crystal analysis. The platelike and acicular crystals were of the same color, gave identical results by microprobe analysis, and exhibited similar solubilities. Further, X-ray diffraction analysis of multiple crystals gave the same unit cell, thus we presume that the acicular crystals are an exaggerated platelike morphology.

The structure of the compound is shown in Figure 2. It consists of six molybdenum atoms in an octahedral arrangement with eight face-capping chlorides. To four of the molybdenum atoms are bound chlorine atoms, and to two of the molybdenum atoms are bound triethylphosphine ligands such that the phosphine ligands are in a *cis* geometry. A mirror plane containing Mo(1)−Mo(4), Cl(6), Cl(7), P(1), and P(2) and C(1), C(2), C(5), and C(6) bisects the molecule. Included in the crystal structure but not bound to the $Mo_6Cl_8^{4+}$ cluster core are two molecules of THF per cluster. The $Mo_6Cl_8^{4+}$ cluster in this compound is a well-known structural motif; however, this is the only known method by which a *cis* isomer may be prepared in high yield and is the first single crystal structural determination of such a cluster ligated in a *cis* geometry. The preparation of the *cis*-ligated cluster *cis*-$[Mo_6Cl_8(Cl_4)(P(n\text{-}C_3H_7)_3]_2$ has been reported previously in 3% yield.[6]

The Raman spectrum of *cis*-$[Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2]\cdot 2THF$ exhibits bands characteristic for $Mo_6Cl_8^{4+}$ clusters. The Raman spectra of $Mo_6Cl_8X_6^{2-}$ clusters have been previously examined by Preetz et al. In an idealized octahedral geometry, one expects the A_{1g}, E_g, and T_{2g} modes to be Raman active. There are 10 such modes total. In the case of $(Bu_4N)_2[Mo_6Cl_{14}]$, Preetz et al.[4] report bands at 67, 100, 106, 181, 201, 219, 239, 251, and 320 cm^{-1}. They assign the band at 320 cm^{-1} to a Mo_6Cl_8 breathing mode and the band at 239 cm^{-1} to a symmetric Mo−X vibration. Similar bands are observed in the Raman spectrum of *cis*-$[Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2]\cdot 2THF$, shown in Figure 1, with bands observed at 64, 94, 182, 198, 226, 248, 299, and 319 cm^{-1}. The absorption observed at 319 cm^{-1} may be assigned to a Mo_6Cl_8 breathing mode, and the band at 226 cm^{-1}, to a symmetric Mo−X vibration; the broad absorption near 94 cm^{-1} is characteristic for $Mo_6Cl_8^{4+}$ clusters.

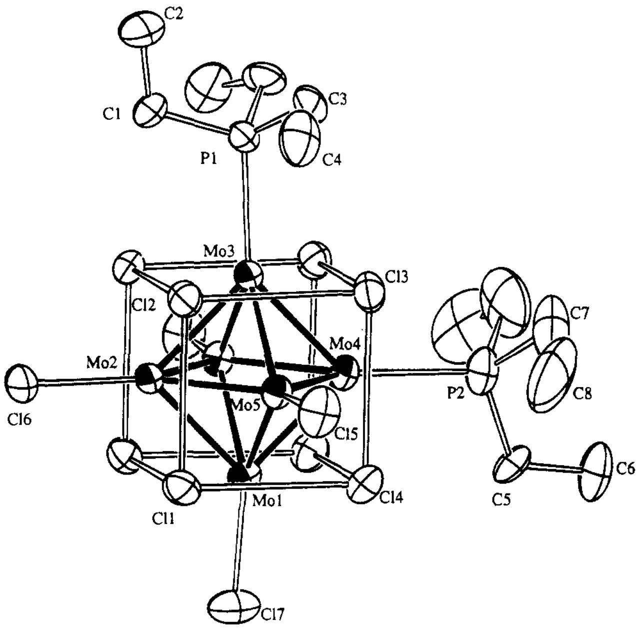

Figure 2. ORTEP diagram of the molecular structure of *cis*-$[Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2]$ (ellipsoids shown at 35% probability level).

Preliminary experiments suggest that materials with extended structures may be prepared by the reaction of *trans*-$[Mo_6Cl_8(Cl_4)(P(C_5H_{11})_3)_2]$ with bidentate ligands although crystalline products have not yet been prepared. We find that, upon standing, a solution of *trans*-$[Mo_6Cl_8(Cl_4)(P(C_5H_{11})_3)_2]$ and a bidentate ligand such as 1,2-bis(dialkylphosphino)ethane (alkyl = methyl or ethyl) or 1,2-bis(diphenylphosphino)butane yields a yellow amorphous powder over 48 h that is remarkably insoluble in organic solvents. We are currently investigating methods to crystallize this material which we propose assumes an extended structure.

Conclusion

The reaction of *trans*-$[Mo_6Cl_8(Cl_4)(P(C_5H_{11})_3)_2]$ with $P(C_2H_5)_3$ in THF yields *cis*-$[Mo_6Cl_8(Cl_4)(P(C_2H_5)_3)_2]\cdot 2THF$ in 97% yield. Presumably an equilibrium exists between the phosphine ligands present in the reaction mixture although attempts to utilize this equilibrium to grow crystals of a material where the *trans* phosphine ligated metal clusters are linked by a bidentate phosphine have not yet yielded single crystals but only powders.

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Supplementary Material Available: Table SI, experimental crystallographic details, Table SII, additional bond distances and angles, and Table SIII, anisotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.

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