

- (17) Calculated C–C distances in ring 1 range from 1.29 to 1.78 Å. These, together with the unacceptable calculated value of 1.87 Å for the C–O distance in methanol, result from the crystallographic disorder in this region of the structure.
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## Synthesis, Characterization, and Crystal Structures of $[(\text{Ph}_3\text{P})_2\text{N}]_3^+\{\text{Na}[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})]_2\}^{3-}$ , an Unusual Organometallic Triple Ion, and $[\text{Me}_4\text{N}]^+[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-OCH}_3)]^-$

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**Abstract:** The compounds  $[(\text{Ph}_3\text{P})_2\text{N}]_3^+\{\text{Na}[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})]_2\}^{3-}$  (**1**) and  $[\text{Me}_4\text{N}]^+[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-OCH}_3)]^-$  (**2**) are synthesized by refluxing  $\text{Mo}(\text{CO})_6$ ,  $\text{NaNO}_2$ , and  $\text{NaOH}$  in methanol and adding the appropriate cation. X-ray diffraction studies reveal that **1** crystallizes in space group  $P\bar{1}$  [ $a = 15.057$  (6) Å,  $b = 15.689$  (6) Å,  $c = 17.079$  (7) Å,  $\alpha = 112.91$  (3)°,  $\beta = 65.90$  (3)°,  $\gamma = 112.50$  (3)°,  $V = 3270$  (2) Å<sup>3</sup>,  $\rho(\text{obsd}) = 1.49$  (1) g cm<sup>-3</sup>,  $\rho(\text{calcd}) = 1.499$  g cm<sup>-3</sup> for  $Z = 1$ ], while **2** crystallizes in space group  $P2_1/m$  [ $a = 9.678$  (4) Å,  $b = 11.763$  (7) Å,  $c = 13.162$  (5) Å,  $\beta = 119.30$  (2)°,  $V = 1307$  (1) Å<sup>3</sup>,  $\rho(\text{obsd}) = 1.89$  (1) g cm<sup>-3</sup>,  $\rho(\text{calcd}) = 1.891$  g cm<sup>-3</sup> for  $Z = 2$ ]. Data were collected with  $\text{Mo K}\alpha$  radiation to a  $2\theta$  limit of 50°. Standard Patterson, Fourier, and least-squares techniques resulted in final agreement factors:  $R = 9.5\%$ ,  $R_w = 10.9\%$  for 4674 reflections greater than  $3\sigma$  for **1**;  $R = 4.8\%$ ,  $R_w = 5.9\%$  for 2017 reflections greater than  $3\sigma$  for **2**. The anionic units of both **1** and **2** consist of equilateral triangles of molybdenum atoms; two carbonyl ligands and one nitrosyl ligand are terminally bonded to each Mo. The nonbonding Mo–Mo distances of 3.297 (2) Å for **1** and 3.428 (1) Å for **2** are bridged by methoxy ligands. **1** differs from **2** in that for **1** the Mo triangle is capped by a triply bridging oxygen atom, while **2** is capped by a triply bridging methoxy ligand. **1** exists as a triple ion in the solid state, with two  $\text{Mo}_3$  units "sandwiching" a sodium ion such that the  $\text{Na}^+$  ion is octahedrally coordinated by the six oxygen atoms of the methoxy ligands. **1** also contains an unusual example of a linear P–N–P linkage in the  $(\text{Ph}_3\text{P})_2\text{N}^+$  cation. Conductivity studies indicate that the triple ion of **1** persists in solution, and that additional ion pairing to the bulky counterions occurs.

### Introduction

Few metal carbonyl cluster compounds of the group 6B metals (Cr, Mo, W) are known,<sup>3</sup> due in part to the electron-deficient nature of transition metals on the left side of the periodic table. As an alternative to large charge buildup on these clusters, we hoped that the replacement of CO by the isoelectronic  $\text{NO}^+$  could produce stable clusters with reduced charge. In order to explore group 6B carbonyl nitrosyl compounds, we have synthesized and characterized  $(\mu_2\text{-H})\text{W}_2(\text{CO})_9(\text{NO})$  and  $(\mu_2\text{-H})\text{W}_2(\text{CO})_8(\text{NO})[\text{P}(\text{OCH}_3)_3]$ .<sup>4</sup>

To further our studies, an attempt was made to produce  $[\text{Mo}(\text{CO})_4(\text{NO})]^-$  by refluxing  $\text{Mo}(\text{CO})_6$ ,  $\text{NaNO}_2$ , and  $\text{KOH}$  in methanol, since an identical reaction using  $\text{Fe}(\text{CO})_5$  produced  $[\text{Fe}(\text{CO})_3\text{NO}]^-$ .<sup>5</sup> Instead of the expected product, two unusual molybdenum carbonyl cluster ions were isolated:  $[(\text{Ph}_3\text{P})_2\text{N}]_3^+\{\text{Na}[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})]_2\}^{3-}$

$[\text{Me}_4\text{N}]^+[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-OCH}_3)]^-$  (**1**) and  $[\text{Me}_4\text{N}]^+[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-OCH}_3)]^-$  (**2**). We report the synthesis, characterization, and crystal structures of these compounds here.

### Experimental Section

All operations were carried out in a prepurified nitrogen atmosphere using Schlenk techniques. Solvents were dried, deaerated, and stored under nitrogen over activated Linde 3A molecular sieves. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer and calibrated against polystyrene. Solution spectra were recorded using  $\text{CaF}_2$  cells with a 0.5-mm spacer and solid spectra were recorded using KBr disks. Room temperature <sup>1</sup>H NMR spectra were recorded on Varian A-60A and T-60 spectrometers using  $\text{Me}_4\text{Si}$  as internal standard. Conductivities were measured at 25 °C on a YSI-31 conductivity bridge. Melting points were determined in sealed capillaries and are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by PCR Inc., Gainesville, Fla. Metal carbonyls were purchased from Pressure Chemical Co., and

used without further purification.  $[(\text{Ph}_3\text{P})_2\text{N}][\text{Cl}]$  ( $[\text{PPN}][\text{Cl}]$ ) was prepared using published methods.<sup>6</sup>

**Preparation of  $[(\text{Ph}_3\text{P})_2\text{N}]_3^+[\text{Na}[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})_2]^{3-}]$  (1).** A mixture of  $\text{Mo}(\text{CO})_6$  (2.04 g, 7.71 mmol),  $\text{NaNO}_2$  (0.56 g, 8.05 mmol), and  $\text{KOH}$  (0.54 g, 8.24 mmol) was refluxed in 100 mL of methanol for 24 h. After the resultant red solution was cooled,  $[\text{PPN}][\text{Cl}]$  (4.43 g, 7.71 mmol) was added and the solvent removed under vacuum. Ethanol (40 mL) and 100 mL of acetone were added and the resultant solution was filtered. After concentration and cooling, the solution yielded orange crystals which were washed with ethanol and diethyl ether to give 2.46 g of  $[\text{PPN}]_3^+[\text{Na}[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})_2]^{3-}]$  (1, 65%); mp 202–207 °C;  $\nu_{\text{max}}$  ( $\text{CH}_3\text{CN}$ ) of 2100–1550- $\text{cm}^{-1}$  region 1996 s ( $\nu\text{CO}$ ), 1981 m ( $\nu\text{CO}$ ), 1889 vs ( $\nu\text{CO}$ ), 1595 m ( $\nu\text{NO}$ )  $\text{cm}^{-1}$ ;  $\nu_{\text{max}}$  ( $\text{KBr}$ ) of 4000–400- $\text{cm}^{-1}$  region excluding  $\text{PPN}^+$  absorptions 2910 m ( $\nu\text{CH}$ ), 2790 m ( $\nu\text{CH}$ ), 1965 vs ( $\nu\text{CO}$ ), 1850 vs ( $\nu\text{CO}$ ), 1565 vs ( $\nu\text{NO}$ ), 1395 m ( $\delta\text{CH}_3$ ), 1040 s ( $\nu\text{CO}$  methoxy), 632 m ( $\nu\text{Mo}-\mu_3\text{O}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  4.12, 4.35, 4.47 (3 s, 1 H,  $\text{OCH}_3$ ) 7.65 (m, 5 H,  $\text{PPN}^+$ ). Molar conductance [ $c \times 10^4$  (M),  $\Lambda$  ( $\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$ )] in  $\text{CH}_3\text{CN}$ : 9.33, 307; 4.67, 309; 2.33, 312; 1.17, 331; 0.585, 349; 0.293, 389; 0.146, 402; 0.0731, 407; in acetone 10.0, 230. The compound is slightly soluble in ethanol, methanol, acetonitrile, tetrahydrofuran, and acetone, but insoluble in diethyl ether, water, and nonpolar organic solvents. The solid is stable in air for extended periods of time, but moderately air sensitive in solution. Anal. Calcd for  $\text{C}_{126}\text{H}_{108}\text{N}_9\text{Mo}_6\text{O}_{26}\text{P}_6\text{Na}$ : C, 51.3; H, 3.7; N, 4.3; Mo, 19.6; P, 6.3; Na, 0.8. Found: C, 50.2; H, 3.5; N, 4.1; Mo, 20.2; P, 6.3; Na, 1.0.

**Preparation of  $[\text{Me}_4\text{N}]^+[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-OCH}_3)]^-$  (2).** A mixture of  $\text{Mo}(\text{CO})_6$  (2.9 g, 11 mmol),  $\text{NaNO}_2$  (0.83 g, 12 mmol), and  $\text{NaOH}$  (0.48 g, 12 mmol) was refluxed in 150 mL of methanol for 12 h. The resultant red solution was cooled,  $[\text{Me}_4\text{N}][\text{Cl}]$  (0.66 g, 6 mmol) added, and the solvent removed under vacuum. The tar was extracted with 200 mL of acetone and the red solution filtered. The volume of the acetone solution was reduced to 75 mL and 400 mL of diethyl ether was added to precipitate a mixture of 2 and 3 as an orange powder. The powder was fractionally recrystallized from warm methanol: usually the first two crops were 3 and subsequent crops 2. Alternatively, the orange powder can be separated by column chromatography using silica gel as the support material and acetonitrile as elutant. Only 2 was collected from the column under these conditions:  $\nu_{\text{max}}$  ( $\text{CH}_3\text{CN}$ ) of 2100–1550- $\text{cm}^{-1}$  region 2011 sh ( $\nu\text{CO}$ ), 1998 s ( $\nu\text{CO}$ ), 1907 vs ( $\nu\text{CO}$ ), 1628 s ( $\nu\text{NO}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.48 (s, 12 H,  $\text{Me}_4\text{N}^+$ ), 3.92 (1:3:1 t,  $J = 14.5$  Hz, 9 H,  $\text{OCH}_3$ ) 4.19 (s, 3 H,  $\text{OCH}_3$ ). Molar conductance [ $c \times 10^4$  (M),  $\Lambda$  ( $\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$ )] in acetone 115, 121; 82.3, 129; 61.0, 139; 38.1, 142; 19.9, 164; 12.6, 164; 7.12, 170,  $\Lambda_0 = 187$ . The compound is very soluble in acetone, soluble in acetonitrile, methanol, ethanol, and tetrahydrofuran, and insoluble in diethyl ether and nonpolar organic solvents. The solid is stable in air indefinitely, but solutions begin to show decomposition several hours after being exposed to air. Anal. Calcd for  $\text{C}_{14}\text{H}_{24}\text{N}_4\text{Mo}_3\text{O}_{13}$ : C, 22.60; H, 3.25; N, 7.53; Mo, 38.68. Found: C, 22.51; H, 3.34; N, 7.64; Mo, 38.56.

**Preparation of  $[\text{Me}_4\text{N}]_3^+[\text{Na}[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})_2]^{3-}]$  (3).** The compound was prepared in a manner identical with that used for 1, except that  $[\text{Me}_4\text{N}][\text{Cl}]$  (0.85 g, 7.71 mmol) was added in place of  $[\text{PPN}][\text{Cl}]$ :  $\nu_{\text{max}}$  ( $\text{CH}_3\text{CN}$ ) identical with that of 1;  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.45 (s, 2 H,  $\text{Me}_4\text{N}^+$ ), 4.09, 4.35, 4.42 (3 s, 1 H relative area 1:1:3.5,  $\text{OCH}_3$ ); (dimethyl- $d_6$  sulfoxide) 3.21 (s, 2 H,  $\text{Me}_4\text{N}^+$ ), 3.45, 3.79, 4.01, 4.23 (sh), 4.28 (4 s, 1 H relative area 1:1:2:10,  $\text{OCH}_3$ ). Molar conductance [ $c \times 10^4$  (M),  $\Lambda$  ( $\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$ )] in  $\text{CH}_3\text{CN}$  74.9, 253; 37.4, 301; 18.7, 317; 9.35, 342; 4.68, 352; 2.34, 372; 1.17, 393; 0.585, 421; 0.293, 438; in acetone 40.6, 168; 20.3, 185; 10.1, 224; 5.07, 245; 2.53, 280; 1.26, 317; 0.632, 345; in methanol 37.8, 260; 18.9, 279; 9.45, 301; 4.73, 313; 2.36, 346; 1.18, 358; 0.59, 371. The  $\text{Me}_4\text{N}^+$  salt is much more soluble than the  $\text{PPN}^+$  salt, but is less stable.

**Preparation of  $[\text{PPN}]_3^+[\text{Na}[\text{W}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})_2]^{3-}]$  (4).**  $\text{W}(\text{CO})_4(\text{CH}_3\text{CN})_2$  (5.86 g, 16.1 mmol)<sup>7</sup> was mixed with  $\text{NaNO}_2$  (1.14 g, 16.5 mmol) and  $\text{NaOH}$  (0.66 g, 16.5 mmol) and refluxed in 125 mL of methanol for 2.5 h. After the resultant red solution was cooled to room temperature,  $[\text{PPN}][\text{Cl}]$  (8.86 g, 15.4 mmol) was added, and the procedure used for the isolation of 1 followed to produce 1.50 g of red-orange crystals of  $[\text{PPN}]_3^+[\text{Na}[\text{W}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})_2]^{3-}]$  (16%);  $\nu_{\text{max}}$  ( $\text{CH}_3\text{CN}$ ) of 2100–1550- $\text{cm}^{-1}$  region 1987 s ( $\nu\text{CO}$ ), 1969 s ( $\nu\text{CO}$ ), 1876 vs ( $\nu\text{CO}$ ), 1585 s ( $\nu\text{NO}$ ); preliminary crystallographic photographs showed triclinic symmetry,  $V = 3250 \text{ \AA}^3$ ,  $\rho(\text{obsd}) = 1.78$  (1)  $\text{g cm}^{-3}$ , and  $\rho(\text{calcd}) = 1.77 \text{ g cm}^{-3}$  (for  $Z = 1$ ,  $M = 3480.7$ ). Anal. Calcd for

$\text{C}_{126}\text{H}_{108}\text{N}_9\text{W}_6\text{O}_{26}\text{P}_6\text{Na}$ : C, 43.5; H, 3.1; N, 3.6. Found: C, 41.5; H, 2.8; N, 3.4.

**Preparation of  $[\text{PPN}]_3^+[\text{citrate}]^{3-}$ .**  $[\text{PPN}][\text{Cl}]$  (1.86 g, 3.24 mmol) was dissolved in a minimum volume of hot 95% ethanol and added to sodium citrate,  $\text{Na}_3[\text{C}_6\text{H}_5\text{O}_7] \cdot 2\text{H}_2\text{O}$  (1.0 g, 1.08 mmol), that had been dissolved in a minimum amount of hot water. The solution was cooled, and the  $[\text{PPN}]_3^+[\text{citrate}]^{3-}$  crystals that formed were washed with water and dried under vacuum. The IR spectrum of the product showed characteristic absorptions: molar conductance,  $\Lambda_m = 380 \text{ cm}^2 \text{mol}^{-1} \Omega^{-1}$  at  $c 10^{-3} \text{ M}$ .

**Crystallographic Section for  $[\text{PPN}]_3^+[\text{Na}[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})_2]^{3-}]$  (1).** Suitable air and X-ray stable crystals of  $[\text{PPN}]_3^+[\text{Na}[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})_2]^{3-}]$  were formed from a slowly cooled solution of acetone–diethyl ether and one such crystal was mounted in air on a glass fiber. Preliminary precession photographs indicated a triclinic unit cell. The first data set was collected on a Nonius CAD-3 diffractometer in a manner similar to that described in an earlier publication.<sup>4b</sup>

The structural analysis was begun at a time when the correct chemical formulation was not yet known. It was thought, however, that the compound was an anionic molybdenum cluster (probably trimeric), containing both carbonyl and nitrosyl ligands. Because the salt behaved as a 3:1 electrolyte, it was postulated that the anion might be a trinegative species such as  $[\text{Mo}_3(\text{CO})_6(\text{NO})_3]^{3-}$ .

A three-dimensional Patterson map revealed an equilateral triangular array of molybdenum atoms related to another set by a center of symmetry. The two triangles were approximately 6 Å apart and disposed such that all Mo atoms were equidistant from the center of symmetry at  $(\frac{1}{2}, \frac{1}{2}, 0)$ . The three independent molybdenum positions were then used to phase a difference-Fourier map in space group  $P\bar{1}$ .

A series of  $\Delta F$  maps revealed the basic geometry around each molybdenum trimer unit: three edge-bridging ligands (believed initially to be nitrosyls), three terminal ligands on each molybdenum atom (believed to be carbonyls), and a single oxygen atom triply bridging (face bridging) each molybdenum triangle. The initial difference-Fourier maps also revealed the positions of the counterions: two bent  $\text{PPN}^+$  cations and a linear  $\text{PPN}^+$ , whose central nitrogen occupied a point of symmetry at  $(0, 0, \frac{1}{2})$ . Finally, also revealed was an area of significant electron density at the symmetry position  $(\frac{1}{2}, \frac{1}{2}, 0)$  midway between the two trimer units. Initially this position was not included in the model.

Although there was an obvious charge imbalance in the unit cell at this stage (the three  $\text{PPN}^+$  cations per unit cell required that each molybdenum trimer unit have a net negative charge of 1.5), a series of isotropic refinements was initiated on the assumption that the thermal parameters and geometry would indicate any incorrect assignments. The phenyl groups were treated as rigid bodies. Isotropic least-squares refinement indicated that the edge-bridging "nitrosyl" groups were misassigned. The isotropic thermal parameters for the "nitrogen" atoms became negative ( $B = -1.91, -2.28, -0.38 \text{ \AA}^2$ ) and the "oxygen" atoms became unreasonably large ( $B = 11.08, 9.45, 10.54 \text{ \AA}^2$ ). Moreover, the geometry of the nitrosyl ligands differed from that of other reported nitrosyl clusters: the "N–O" bond was much too long (approximately 1.45 Å) and the "NO group" was not coplanar with the two bridged molybdenum atoms. The observed trend of the thermal parameters and the geometry of the ligands, together with  $^1\text{H}$  NMR data, were compelling evidence for reassigning the edge-bridging ligands as methoxy groups.

At this stage it became necessary to resolve two questions about the model assignment: what was keeping the two trimer units together (they were separated by less than 6 Å), and what was the charge assignment per trimer? It was postulated that the area of electron density occupying the point of symmetry midway between the two trimer units (which persisted throughout the structure refinement) could be a sodium ion. This assignment was reasonable in three respects: (1) sodium ions were in the reaction mixture; (2) the electron density at this position was reasonable for a sodium atom; (3) the bridging ligands were not considered to be methoxy ligands so there was a structural precedent for this assignment (see Discussion). The charge balance for the unit cell was also resolved by this choice, since the 1+ charge the sodium cation together with the 3+ charge of the three  $\text{PPN}^+$  groups would support the reasonable charge assignment of 2– per molybdenum trimer. A subsequent elemental analysis confirmed the presence of a stoichiometric amount of sodium and no potassium.

Since the edge-bridging groups were no longer considered to be

**Table I.** Experimental Data for the X-ray Diffraction Study of  $[(\text{PPN})_3]^+ \{ \text{Na}[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})]_2 \}^{3-}$  (**1**)

A. Crystal and Lattice Parameters	
$a = 15.057(6) \text{ \AA}$	space group $P\bar{1}$
$b = 15.689(6) \text{ \AA}$	$Z = 1$
$c = 17.079(7) \text{ \AA}$	$V = 3270(2) \text{ \AA}^3$
$\alpha = 112.91(3)^\circ$	mol wt = 3733
$\beta = 65.90(3)^\circ$	$\rho(\text{obsd})^a = 1.49(1) \text{ g cm}^{-3}$
$\gamma = 112.50(3)^\circ$	$\rho(\text{calcd}) = 1.499 \text{ g cm}^{-3}$
	$\mu = 6.675 \text{ cm}^{-1}$ for Mo $K\alpha$ X-rays
B. Details of Data Measurement	
diffractometer:	Syntex P2 <sub>1</sub>
radiation:	Mo $K\alpha$ X-rays ( $\bar{\lambda} = 0.7107 \text{ \AA}$ )
monochromator:	highly oriented graphite ( $2\theta = 12.2^\circ$ )
reflections measured:	$h, \pm k, \pm l$ (one asymmetric unit)
$2\theta$ range:	$[2.5, 50.0]^\circ$
scan type:	$2\theta$ (counter)/ $\omega$ (crystal)
scan width:	$\Delta 2\theta = (1.2 + 0.69 \tan \theta)^\circ$ , $\Delta\omega = 0.5(\Delta 2\theta)$
scan speed:	max of $29.3^\circ/\text{min}$ ; min of $3.9^\circ/\text{min}$ according to intensity

<sup>a</sup> Measured by flotation in  $\text{ZnCl}_2/\text{H}_2\text{O}$ .

nitrosyls, and the infrared and elemental analyses were consistent with one nitrosyl equivalent per molybdenum atom, the terminal ligands were reexamined. It was noticed at this time that the three axial "carbonyl carbons" had abnormally small isotropic temperature factors ( $B = 1.19, -1.28, 1.27 \text{ \AA}^2$ ) compared to the average of the equatorial carbonyls ( $B = 6.78 \text{ \AA}^2$ ). These three ligands were then reassigned as nitrosyls and subsequent refinement gave normal temperature factors for three ligands.

The model at this stage was assumed to be complete. Several additional cycles of least-squares refinement were completed in two blocks: (1) the phosphorus and nitrogen atoms of  $\text{PPN}^+$  were refined with anisotropic temperature factors and the phenyl carbons were refined as rigid groups with isotropic temperature factors; (2) the hexamer cluster was refined with anisotropic temperature factors. The resulting  $R$  factor was 9.5%. However, the anisotropic temperature factors of several atoms in the hexamer cluster were nonpositive definite. Further refinement did not correct this problem.

In an attempt to obtain better results, a new data set was collected. Fresh crystals were grown, this time from moderate cooling of an acetone-ethanol mixture. These crystals were, as expected, isomorphous with those used previously. A suitable specimen (dimensions  $0.20 \times 0.37 \times 0.55 \text{ mm}$ ) was mounted on a glass fiber and placed on a Syntex P2<sub>1</sub> diffractometer. Precise unit cell parameters, obtained by centering 15 reflections on the diffractometer, are given together with other relevant crystal data in Table I. For data collection, a take-off angle of  $4^\circ$  was used and the upper and lower level discriminators of the pulse height analyzer were set to obtain a 90% window centered on the Mo  $K\alpha$  peak. As a check on the stability of the diffractometer and the crystal, the  $(\bar{2}, 1, \bar{1})$ ,  $(1, 1, 10)$ , and  $(0, 1, 2)$  reflections were measured at 50-reflection intervals during the data collection. No significant variation was found. An empirical absorption correction was carried out, based on the variation of intensity of  $(\bar{4}, 4, \bar{7})$  around the scattered beam ( $\psi$  scan).<sup>8a</sup> The standard deviation of each intensity reading was estimated using the expression<sup>8b</sup>  $\sigma(I) = [( \text{peak} + \text{background counts} ) + (0.04)^2 (\text{net intensity})^2]^{1/2}$ . Out of the total of 8922 reflections collected, 4674 independent reflections with intensities  $> 3\sigma$  were retained for the subsequent structure analysis. Their intensities were further corrected for Lorentz and polarization effects.

Again the parameters were blocked into two groups: (1) the hexamer unit with anisotropic temperature factors, and (2) the  $\text{PPN}^+$  cations with anisotropic temperature factors for the P and N atoms and isotropic temperature factors for the C atoms. Several cycles of least-squares refinement resulted in the final agreement factors  $R = 9.5\%$  and  $R_w = 10.9\%$ . Although the  $R$  factors did not improve significantly from those of the earlier analysis, the overall results (e.g., the standard deviations of the distances and angles) are better, partly because a larger data set was used [ $2\theta(\text{max}) = 50^\circ$ , as opposed to  $2\theta(\text{max}) = 45^\circ$ ]. This time, none of the atoms converted to nonpositive definitive anisotropic temperature factors.

**Crystallographic Section for  $[(\text{CH}_3)_4\text{N}]^+[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-OCH}_3)]^-$  (**2**).** A sample of approximate dimensions  $0.22$

**Table II.** Experimental Data for the X-ray Diffraction Study of  $[(\text{CH}_3)_4\text{N}]^+[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-OCH}_3)]^-$  (**2**)

A. Crystal and Lattice Parameters	
$a = 9.678(4) \text{ \AA}$	space group $P_1/m$
$b = 11.763(7) \text{ \AA}$	$Z = 2$
$c = 13.162(5) \text{ \AA}$	mol wt = 744
$\beta = 119.30(2)^\circ$	$\rho(\text{obsd})^a = 1.89(1) \text{ g cm}^{-3}$
	$\rho(\text{calcd}) = 1.891 \text{ g cm}^{-3}$
$V = 1307(1) \text{ \AA}^3$	
$\mu = 7.704 \text{ cm}^{-1}$ for Mo $K\alpha$ X-rays	
B. Details of Data Measurement	
diffractometer:	Nonius CAD-3
radiation:	Zr-filtered Mo $K\alpha$ X-rays ( $\bar{\lambda} = 0.7107 \text{ \AA}$ )
monochromator:	none
reflections measured:	$h, \pm k, \pm l$ (two asymmetric units)
$2\theta$ range:	$[10.0, 50.0]^\circ$
scan type:	$2\theta$ (counter)/ $\omega$ (crystal)
scan width:	$\Delta 2\theta = 1.2^\circ$ , $\Delta\omega = 0.6^\circ$
scan speed:	$10^\circ/\text{min}$ ; from 2 to 10 scans/reflection <sup>b</sup>

<sup>a</sup> Measured by flotation in  $\text{CH}_3\text{Br}/\text{CCl}_3$ . <sup>b</sup> Zirconium foil attenuators were automatically inserted into the detector to prevent the counting rate from exceeding 2500 counts/s.

$\times 0.17 \times 0.30 \text{ mm}$  was mounted on the tip of a glass fiber. Preliminary precession photographs revealed a monoclinic crystal system. Systematic extinctions were consistent with either space group  $P2_1$  or  $P2_1/m$ . Accurate lattice constants, obtained by centering 27 reflections on a Nonius CAD-3 automated diffractometer, are given together with other relevant crystal data in Table II. A take-off angle of  $4^\circ$  was used during data collection and the upper and lower level discriminators of the pulse height analyzer were set to obtain a 90% window centered on the Mo  $K\alpha$  peak. As a check on the stability of the diffractometer and crystal, the  $(2, 1, 1)$ ,  $(2, 6, 0)$ , and  $(3, 0, 4)$  reflections were measured at 50-reflection intervals during data collection. No significant variation was found. The standard deviation of each intensity measurement was estimated as before. Out of the total of 4392 reflections collected, 2017 independent reflections with intensities greater than  $3\sigma$  were retained for the subsequent structure analysis. An empirical absorption correction was carried out, based on the variation in intensity of the  $(4, \bar{1}, \bar{4})$  reflection around the scattered beam. Intensities were further corrected for Lorentz and polarization effects.

A three-dimensional Patterson map revealed the locations of the molybdenum atoms. From the symmetry of the Patterson vectors, the space group was taken to be  $P2_1/m$ . Successive difference Fourier synthesis revealed the remaining nonhydrogen atoms. Initially the nitrosyl group of Mo(1) (which lies on a mirror plane) was also placed on the mirror plane. However after several cycles of least-squares refinement, the average Mo(1)-C and Mo(1)-N distances converged to values of 1.882 and 1.990  $\text{\AA}$  respectively, a result which is opposite to that expected on the basis of known metal nitrosyl and carbonyl bond lengths. The nitrosyl and carbonyl ligands of Mo(1) were therefore interchanged and the nitrogen position was given a 50:50 carbon/nitrogen scattering factor. Taking this to be the complete model, four cycles of full-matrix least-squares refinement with anisotropic temperature factors resulted in the final agreement factors  $R = 0.048$  and  $R_w = 0.059$ . A final difference Fourier synthesis revealed no significant electron density.

## Results and Discussion

The final atomic parameters of **1** and **2** are given in Tables III and IV. Bond lengths and angles for **1** and **2** are collected in Tables V and VI, respectively. Structure factor tables are available.<sup>9</sup>

**Molecular Structure of 1.** The numbering scheme is shown in Figure 1. ORTEP plots showing the anion, bent  $\text{PPN}^+$  cation, and linear  $\text{PPN}^+$  cation are given in Figures 2, 3, and 4, respectively. Figure 5 shows a different view of the hexameric unit while Figure 6 illustrates the spherical shape of the molecule.

The unit cell (Figure 7) consists of the cluster of six octahedrally coordinated molybdenum atoms, whose central  $\text{Na}^+$

Table III. Final Atomic Parameters for  $[(\text{Ph}_3\text{P})_2\text{N}]_3^+[\text{Na}[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})]_2]^{3-}$  (1)

atom	x	y	z	atom	x	y	z				
A. Coordinates of the Anion				C. Coordinates of the Linear $[(\text{Ph}_3\text{P})_2\text{N}]^+$ Cation							
Mo(1)	0.62430(12)	0.47313(12)	0.76584(12)	N(5)	0.0000(0)	0.0000(0)	0.5000(0)				
Mo(2)	0.39572(12)	0.33277(12)	0.82560(12)	P(3)	0.0700(4)	0.0011(4)	0.5451(4)				
Mo(3)	0.58573(12)	0.29454(13)	0.84352(12)	C(46)	1.0826(15)	0.7436(15)	0.5402(15)				
C(1)	0.7517(18)	0.4494(17)	0.6752(16)	C(47)	0.9839(18)	0.7055(17)	0.5860(18)				
C(2)	0.5977(19)	0.4728(14)	0.6614(15)	C(48)	0.9114(20)	0.7550(20)	0.6129(19)				
C(3)	0.3675(19)	0.3396(21)	0.7248(19)	C(49)	0.9405(17)	0.8492(17)	0.6041(17)				
C(4)	0.3394(14)	0.1923(16)	0.7827(14)	C(50)	1.0397(14)	0.8883(13)	0.5632(14)				
C(5)	0.5199(14)	0.1529(16)	0.8039(14)	C(51)	1.1098(15)	0.8348(15)	0.5297(15)				
C(6)	0.7187(16)	0.2681(16)	0.7571(18)	C(52)	0.9141(15)	0.8428(16)	0.2018(16)				
C(7)	0.4358(13)	0.5583(13)	0.8674(14)	C(53)	0.9500(16)	0.7721(16)	0.1905(17)				
C(8)	0.3760(14)	0.2741(14)	0.9905(15)	C(54)	0.9823(17)	0.7610(17)	0.2489(18)				
C(9)	0.7399(14)	0.4944(14)	0.8940(14)	C(55)	0.9775(14)	0.8366(14)	0.3355(15)				
N(1)	0.6909(12)	0.6005(14)	0.7815(11)	C(56)	0.9401(13)	0.9086(13)	0.3451(13)				
N(2)	0.2646(12)	0.3433(10)	0.8936(12)	C(57)	0.9108(14)	0.9237(14)	0.2844(16)				
N(3)	0.6142(14)	0.2665(12)	0.9200(17)	C(58)	0.6762(15)	0.9900(14)	0.6701(15)				
O(1)	0.8273(12)	0.4451(13)	0.6230(12)	C(59)	0.6017(15)	0.9292(15)	0.6271(16)				
O(2)	0.5868(15)	0.4772(12)	0.6017(12)	C(60)	0.6224(15)	0.8863(14)	0.5364(16)				
O(3)	0.3472(15)	0.3297(16)	0.6648(13)	C(61)	0.7238(13)	0.9075(13)	0.4818(13)				
O(4)	0.3015(12)	0.1130(11)	0.7578(12)	C(62)	0.7984(13)	0.9688(13)	0.5199(14)				
O(5)	0.4856(11)	0.0757(10)	0.7865(12)	C(63)	0.7790(15)	1.0124(15)	0.6134(16)				
O(6)	0.7908(11)	0.2497(13)	0.7104(13)	D. Thermal Parameters <sup>a</sup>							
O(7)	0.7345(12)	0.6834(11)	0.7887(11)	atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$	
O(8)	0.1819(10)	0.3476(11)	0.9356(11)	Mo(1)	67(1)	69(1)	32(1)	21(1)	-4(1)	-6(1)	
O(9)	0.6302(16)	0.2454(13)	0.9733(14)	Mo(2)	59(1)	65(1)	39(1)	24(1)	-16(1)	-13(1)	
O(10)	0.4758(8)	0.4847(9)	0.8638(8)	Mo(3)	66(1)	67(1)	44(1)	37(1)	-13(1)	-13(1)	
O(11)	0.4440(8)	0.3318(8)	0.9288(8)	C(1)	85(20)	101(20)	57(16)	18(16)	43(14)	2(14)	
O(12)	0.6429(8)	0.4495(8)	0.8775(8)	C(2)	170(25)	57(15)	22(13)	51(15)	-12(15)	6(11)	
O(13)	0.5455(8)	0.3346(8)	0.7636(8)	C(3)	103(21)	146(26)	69(20)	54(18)	-19(17)	47(19)	
Na	0.5000(0)	0.5000(0)	0.0000(0)	C(4)	49(14)	81(17)	50(14)	15(13)	-21(11)	-24(12)	
B. Coordinates of the Bent $[(\text{Ph}_3\text{P})_2\text{N}]^+$ Cation				C(5)	48(14)	64(16)	47(14)	23(12)	7(11)	-6(12)	
N(4)	0.7425(11)	0.1940(10)	0.2177(10)	C(6)	49(16)	77(18)	108(22)	22(14)	-24(15)	-8(15)	
P(1)	0.6937(4)	0.2635(4)	0.3099(4)	C(7)	59(14)	53(13)	67(15)	29(11)	-16(11)	8(11)	
P(2)	0.8222(4)	0.2004(4)	0.1253(4)	C(8)	70(15)	68(15)	51(14)	16(12)	5(12)	18(12)	
C(10)	0.9874(16)	0.4735(16)	0.1206(16)	C(9)	60(15)	79(16)	60(14)	23(12)	-40(12)	-3(11)	
C(11)	0.9270(16)	0.5049(15)	0.1012(16)	N(1)	72(13)	94(15)	38(11)	30(12)	6(9)	15(11)	
C(12)	0.8375(15)	0.4446(15)	0.0837(15)	N(2)	57(13)	52(11)	69(13)	0(10)	-44(11)	-15(9)	
C(13)	0.8082(14)	0.3501(15)	0.0874(15)	N(3)	107(16)	64(13)	124(21)	72(12)	-40(15)	4(12)	
C(14)	0.8688(13)	0.3172(12)	0.1053(13)	N(4)	78(12)	58(11)	19(8)	8(9)	1(8)	0(8)	
C(15)	0.9583(15)	0.3797(15)	0.1251(15)	N(5)	52(16)	115(21)	45(15)	64(14)	-17(13)	-11(14)	
C(16)	1.0924(22)	0.1376(21)	0.0290(23)	O(1)	80(13)	163(18)	68(13)	26(12)	18(10)	14(12)	
C(17)	1.0958(21)	0.1175(19)	0.0965(23)	O(2)	245(23)	111(14)	43(11)	92(14)	-39(13)	10(10)	
C(18)	1.0168(23)	0.1139(20)	0.1671(22)	O(3)	170(20)	200(21)	66(14)	42(15)	-65(14)	27(14)	
C(19)	0.9318(18)	0.1391(17)	0.1806(18)	O(4)	109(14)	74(12)	120(15)	35(11)	-70(12)	-38(10)	
C(20)	0.9245(14)	0.1642(13)	0.1158(15)	O(5)	91(13)	46(10)	102(14)	15(10)	9(10)	-16(9)	
C(21)	1.0084(20)	0.1621(18)	0.0325(20)	O(6)	61(12)	133(16)	122(16)	53(11)	-11(11)	-8(12)	
C(22)	0.6390(17)	-0.0257(17)	-0.0091(19)	O(7)	149(16)	66(12)	78(12)	-23(11)	-33(11)	28(10)	
C(23)	0.6859(20)	-0.0110(19)	-0.0977(20)	O(8)	31(9)	124(14)	80(12)	41(9)	-10(8)	-14(9)	
C(24)	0.7664(20)	0.0591(20)	-0.1198(20)	O(9)	242(24)	125(16)	103(17)	132(16)	-82(16)	-20(12)	
C(25)	0.8086(16)	0.1312(16)	-0.0476(18)	O(10)	44(8)	70(9)	24(7)	25(7)	4(6)	-7(6)	
C(26)	0.7638(13)	0.1162(13)	0.0395(14)	O(11)	43(8)	71(9)	28(7)	31(7)	0(6)	8(7)	
C(27)	0.6841(15)	0.0428(15)	0.0602(16)	O(12)	48(8)	60(9)	32(8)	26(7)	-3(6)	-5(6)	
C(28)	0.9227(17)	0.4896(18)	0.3795(17)	O(13)	44(8)	60(8)	43(8)	32(6)	-15(6)	-15(6)	
C(29)	0.8983(16)	0.5633(16)	0.3789(16)	Na	56(6)	49(6)	28(6)	26(5)	-8(5)	-8(5)	
C(30)	0.8144(16)	0.5555(16)	0.3620(16)	P(1)	58(4)	45(3)	31(3)	8(3)	-12(3)	-6(2)	
C(31)	0.7491(14)	0.4612(14)	0.3376(14)	P(2)	65(4)	63(4)	25(3)	18(3)	-10(3)	6(3)	
C(32)	0.7719(13)	0.3857(12)	0.3396(13)	P(3)	50(4)	75(4)	32(3)	25(3)	-8(3)	2(3)	
C(33)	0.8582(15)	0.3933(15)	0.3585(15)	C(10)	6.5(5)	C(24)	9.7(8)	C(37)	4.2(4)	C(51)	6.1(5)
C(34)	0.6297(12)	0.0652(12)	0.4349(13)	C(11)	7.2(6)	C(25)	7.2(6)	C(38)	3.4(4)	C(52)	6.3(5)
C(35)	0.6110(13)	0.1190(14)	0.5277(14)	C(12)	6.4(5)	C(26)	4.7(4)	C(39)	3.7(4)	C(53)	7.1(6)
C(36)	0.6191(13)	0.2165(13)	0.5497(13)	C(13)	5.9(5)	C(27)	6.1(5)	C(40)	7.6(6)	C(54)	7.6(6)
C(37)	0.6498(13)	0.2637(13)	0.4859(14)	C(14)	4.1(4)	C(28)	7.9(6)	C(41)	8.2(6)	C(56)	5.7(5)
C(38)	0.6666(11)	0.2081(11)	0.3930(12)	C(15)	6.0(5)	C(29)	7.1(6)	C(42)	7.2(6)	C(57)	4.5(4)
C(39)	0.6555(12)	0.1123(12)	0.3716(12)	C(16)	10.9(9)	C(30)	6.9(6)	C(43)	4.9(4)	C(58)	5.8(5)
C(40)	0.4238(17)	0.3244(17)	0.3946(18)	C(17)	9.6(7)	C(31)	5.3(4)	C(44)	5.6(5)	C(59)	6.1(5)
C(41)	0.3967(18)	0.2899(18)	0.3218(20)	C(18)	9.7(8)	C(32)	4.3(4)	C(45)	6.1(5)	C(60)	5.9(5)
C(42)	0.4574(17)	0.2498(16)	0.2389(17)	C(19)	7.9(6)	C(33)	6.4(5)	C(46)	6.1(5)	C(61)	6.2(5)
C(43)	0.5478(14)	0.2373(13)	0.2350(14)	C(20)	5.2(4)	C(34)	4.6(4)	C(47)	7.8(6)	C(62)	5.0(4)
C(44)	0.5781(15)	0.2720(14)	0.3116(16)	C(21)	9.4(7)	C(35)	4.8(4)	C(48)	9.3(7)	C(63)	4.8(4)
C(45)	0.5141(15)	0.3163(15)	0.3962(15)	C(22)	7.9(6)	C(36)	4.3(4)	C(49)	7.3(6)	C(64)	6.1(5)
				C(23)	8.7(7)			C(50)	4.8(4)		

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

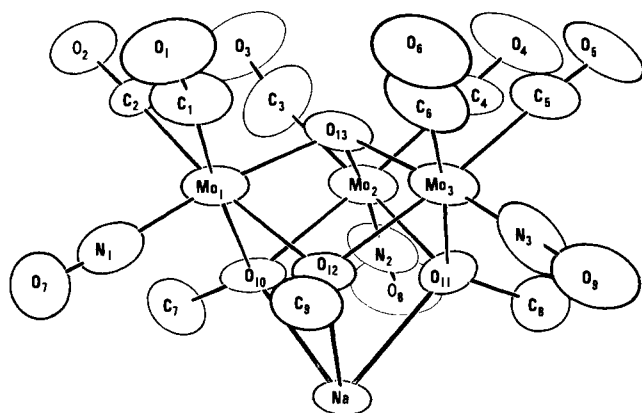
**Table IV.** Final Atomic Parameters for  $[Me_4N]^+[Mo_3(CO)_6(NO)_3(\mu_2-OCH_3)_3(\mu_3-OCH_3)]^-$  (**2**)

A. Atomic Coordinates							
	x	y	z		x	y	z
Mo(1)	0.40206(11)	0.25	0.84649(8)	O(13)	0.7370(10)	0.25	1.0661(9)
Mo(2)	0.06237(8)	0.39736(6)	0.76370(6)	C(20)	0.0005(11)	0.5151(8)	0.8427(8)
O(4)	0.2910(6)	0.1306(4)	0.9062(5)	C(21)	-0.0435(8)	0.5816(6)	0.8823(6)
C(5)	0.3475(16)	0.0906(14)	1.0118(11)	C(22)	0.1544(11)	0.5255(8)	0.7167(8)
O(6)	-0.0011(10)	0.25	0.8211(7)	O(23)	0.1990(10)	0.6001(6)	0.6869(8)
C(7)	-0.1141(16)	0.25	0.8590(13)	N(24)	-0.1226(8)	0.4291(6)	0.6328(6)
O(8)	0.1523(8)	0.25	0.7061(6)	O(25)	-0.2360(7)	0.4596(7)	0.5486(6)
C(9)	0.1165(15)	0.25	0.5875(10)	C(40)	0.4269(16)	0.1443(11)	0.3412(10)
X <sup>a</sup>	0.4787(8)	0.1394(6)	0.7837(6)	C(41)	0.2188(22)	0.25	0.3555(19)
O(11)	0.5334(7)	0.0743(5)	0.7436(5)	C(42)	0.4820(30)	0.25	0.5190(15)
C(12)	0.6158(14)	0.25	0.9873(11)	N(43)	0.4040(16)	0.25	0.3908(10)

B. Thermal Parameters $\times 10^4$							
Mo(1)	121(2)	59(1)	55(1)	0	86(2)	0	
Mo(2)	134(1)	52(1)	56(1)	10(1)	76(1)	-3(1)	
O(4)	108(8)	58(4)	51(4)	-7(10)	66(10)	13(7)	
C(5)	218(22)	255(22)	74(10)	-210(36)	12(25)	154(24)	
O(6)	153(14)	42(6)	83(8)	0	140(18)	0	
C(7)	175(24)	84(12)	109(15)	0	178(33)	0	
O(8)	110(11)	52(6)	35(6)	0	52(13)	0	
C(9)	174(21)	73(10)	50(9)	0	121(24)	0	
X	139(12)	69(6)	77(7)	-2(13)	118(15)	14(10)	
O(11)	202(11)	78(5)	111(6)	35(12)	216(15)	-37(9)	
C(12)	120(19)	77(11)	80(12)	0	122(27)	0	
O(13)	105(14)	120(11)	105(11)	0	51(21)	0	
C(20)	176(15)	66(7)	69(8)	2(18)	59(18)	-6(12)	
O(21)	208(12)	93(6)	102(7)	70(14)	168(16)	-44(10)	
C(22)	184(16)	60(7)	78(8)	12(17)	108(19)	4(12)	
O(23)	328(18)	76(6)	154(10)	-37(16)	286(24)	46(11)	
N(24)	128(10)	75(6)	82(7)	17(13)	106(15)	-19(10)	
O(25)	168(11)	138(8)	74(6)	83(15)	-20(13)	-6(11)	
C(40)	304(27)	120(13)	103(12)	45(29)	178(31)	-53(19)	
C(41)	250(34)	99(17)	172(25)	0	191(49)	0	
C(42)	436(55)	192(28)	53(14)	0	102(48)	0	
N(43)	295(27)	57(9)	74(10)	0	178(29)	0	

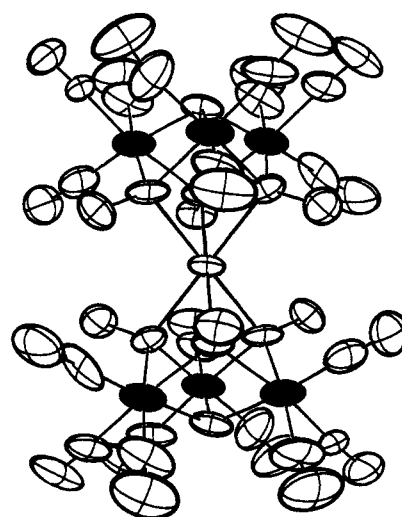
<sup>a</sup> X denotes the position which is disordered (50% C, 50% N).



**Figure 1.** A plot of the trinuclear fragment in  $\{Na[Mo_3(CO)_6(NO)_3(\mu_2-OCH_3)_3(\mu_3-O)]_2\}^{3-}$  (**1**), indicating the atomic numbering scheme used.

ion occupies a center of symmetry at  $(\frac{1}{2}, \frac{1}{2}, 0)$ , and three bis(triphenylphosphine)iminium counterions. Two of the PPN<sup>+</sup> cations are bent  $[143(1)^\circ]$ , while the third, which is situated at the inversion center  $(0, 0, \frac{1}{2})$ , is crystallographically constrained to be linear.

The molybdenum hexamer cluster may be visualized as two trimeric units coordinated to a central sodium ion. Each molybdenum trimer forms an equilateral triangle of molybdenum atoms held together on each edge by bridging methoxy ligands and capped by a triply bridging oxygen atom. Two equatorial carbonyls and one axial nitrosyl complete the octahedral geometry around each molybdenum atom. The coordination of



**Figure 2.** A plot of the full hexameric unit  $\{Na[Mo_3(CO)_6(NO)_3(\mu_2-OCH_3)_3(\mu_3-O)]_2\}^{3-}$  (**1**), showing the two  $Mo_3$  clusters sequestering a  $Na^+$  ion through the O atoms of the bridging methoxy groups. This "triple ion" remains predominantly intact in solution.

the methoxy oxygen atoms around the central sodium ion is octahedral and trigonally distorted along two opposing faces (Figure 8).

**Molecular Structure of 2.** An ORTEP plot of the anion of **2**, as well as a numbering scheme, is shown in Figure 9. Figure 10 shows another view. The  $[Me_4N]^+$  cations and  $[Mo_3(CO)_6(NO)_3(\mu_2-OCH_3)_3(\mu_3-OCH_3)]^-$  anions are well sep-

Table V. Distances and Angles in  $[(\text{Ph}_3\text{P})_2\text{N}]_3^+\{\text{Na}[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})]_2\}^{3-}$  (1)

		A. Distances (Å)			
atoms	distance	atoms	distance	atoms	distance
Mo(1)-Mo(2)	3.290(2)	C(3)-O(3)	1.12(4)	Mo(2)-O(10)	2.19(1)
Mo(1)-Mo(3)	3.312(3)	C(5)-O(5)	1.09(3)	Mo(2)-O(13)	2.06(1)
Mo(1)-C(1)	1.97(2)	O(10)-C(7)	1.47(3)	Mo(3)-C(6)	2.03(2)
Mo(1)-N(1)	1.83(2)	O(11)-C(8)	1.46(3)	Mo(3)-O(11)	2.19(1)
Mo(1)-O(12)	2.22(1)	Na-O(10)	2.41(1)	Mo(3)-O(13)	2.06(1)
Mo(2)-C(3)	1.98(3)	Na-O(11)	2.41(1)	N(3)-O(9)	1.21(3)
Mo(2)-N(2)	1.87(2)	P(1)-N(4)	1.59(2)	C(2)-O(2)	1.13(3)
Mo(2)-O(11)	2.17(1)	P(2)-N(4)	1.56(2)	C(4)-O(4)	1.14(3)
Mo(3)-C(5)	2.02(2)	P(3)-N(5)	1.53(1)	C(6)-O(6)	1.12(3)
Mo(3)-N(3)	1.77(2)	Mo(2)-Mo(3)	3.288(3)	O(12)-C(9)	1.45(2)
Mo(3)-O(12)	2.17(1)	Mo(1)-C(2)	1.98(2)	Na-O(12)	2.44(1)
N(1)-O(7)	1.20(3)	Mo(1)-O(10)	2.20(1)	P(1)-C(av)	1.79(2)
N(2)-O(8)	1.17(2)	Mo(1)-O(13)	2.03(1)	P(2)-C(av)	1.80(2)
C(1)-O(1)	1.13(3)	Mo(2)-C(4)	1.98(2)	P(3)-C(av)	1.81(2)
		B. Angles (deg)			
atoms	angle	atoms	angle	atoms	angle
Mo(2)-Mo(1)-Mo(3)	59.74(6)	C(1)-Mo(1)-N(1)	85.8(10)		
C(1)-Mo(1)-C(2)	82.1(11)	C(1)-Mo(1)-O(10)	174.6(9)		
C(1)-Mo(1)-O(13)	98.3(9)	C(1)-Mo(1)-O(12)	97.8(8)		
N(1)-Mo(1)-C(2)	89.5(10)	N(1)-Mo(1)-O(10)	99.6(7)		
N(1)-Mo(1)-O(13)	173.5(6)	N(1)-Mo(1)-O(12)	99.3(7)		
C(2)-Mo(1)-O(13)	97.7(8)	C(2)-Mo(1)-O(13)	96.0(9)		
C(2)-Mo(1)-O(12)	171.2(9)	O(10)-Mo(1)-O(13)	76.3(5)		
O(10)-Mo(1)-O(12)	81.6(5)	O(13)-Mo(1)-O(12)	75.3(5)		
Mo(1)-(Mo(2)-Mo(3))	60.46(6)	C(3)-Mo(2)-N(2)	86.7(10)		
C(3)-Mo(2)-C(4)	85.1(12)	C(3)-Mo(2)-O(11)	173.7(9)		
C(3)-Mo(2)-O(13)	97.9(9)	C(3)-Mo(2)-O(10)	95.7(10)		
N(2)-Mo(2)-C(4)	88.8(8)	N(2)-Mo(2)-O(11)	98.9(6)		
N(2)-Mo(2)-O(13)	172.9(6)	N(2)-Mo(2)-O(10)	98.1(7)		
C(4)-Mo(2)-O(11)	97.8(8)	C(4)-Mo(2)-O(13)	97.0(7)		
C(4)-Mo(2)-O(10)	173.1(7)	O(11)-Mo(2)-O(13)	76.3(5)		
O(11)-Mo(2)-O(10)	80.7(5)	O(13)-Mo(2)-O(10)	76.1(5)		
Mo(1)-Mo(3)-Mo(2)	59.81(6)	C(5)-Mo(3)-N(3)	86.3(10)		
C(5)-Mo(3)-C(6)	88.1(10)	C(5)-Mo(3)-O(12)	171.6(8)		
C(5)-Mo(3)-O(13)	96.1(8)	C(5)-Mo(3)-O(11)	94.5(7)		
N(3)-Mo(3)-C(6)	85.4(11)	N(3)-Mo(3)-O(12)	101.6(8)		
N(3)-Mo(3)-O(13)	175.1(9)	N(3)-Mo(3)-O(11)	99.8(8)		
C(6)-Mo(3)-O(12)	95.5(8)	C(6)-Mo(3)-O(13)	98.9(9)		
C(6)-Mo(3)-O(11)	174.3(9)	O(12)-Mo(3)-O(13)	75.8(5)		
O(12)-Mo(3)-O(11)	81.3(5)	O(13)-Mo(3)-O(11)	75.8(5)		
Mo(1)-N(1)-O(7)	178(2)	Mo(2)-N(3)-O(9)	178(2)		
Mo(2)-N(2)-O(8)	178(2)	Mo(1)-C(2)-O(2)	176(2)		
Mo(1)-C(1)-O(1)	173(3)	Mo(2)-C(4)-O(4)	175(2)		
Mo(2)-C(3)-O(3)	170(3)	Mo(3)-C(6)-O(6)	177(2)		
Mo(3)-C(5)-O(5)	177(2)				
Mo(1)-O(10)-C(7)	117.0(11)	Mo(2)-O(10)-C(7)	119.9(10)		
Mo(1)-O(10)-Mo(2)	97.0(5)	Mo(2)-O(11)-C(8)	119.8(10)		
Mo(3)-O(11)-C(8)	116.6(12)	Mo(2)-O(11)-Mo(3)	98.0(5)		
Mo(1)-O(12)-C(9)	117.8(11)	Mo(3)-O(12)-C(9)	119.9(12)		
Mo(1)-O(12)-Mo(3)	101.9(5)				
Mo(1)-O(13)-Mo(2)	107.1(6)	Mo(2)-O(13)-Mo(3)	105.8(5)		
Mo(1)-O(13)-Mo(3)	107.9(5)				
O(10)-Na-O(11)	71.9(5)	O(10)-Na-O(12)	73.1(4)		
O(10)-Na-O(10') <sup>a</sup>	180.0(6)	O(10)-Na-O(11') <sup>a</sup>	108.1(5)		
O(10)-Na-O(12') <sup>a</sup>	106.9(4)	O(11)-Na-O(12)	71.5(4)		
O(11)-Na-O(10') <sup>a</sup>	108.1(5)	O(11)-Na-O(11') <sup>a</sup>	180.0(13)		
O(11)-Na-O(12') <sup>a</sup>	108.5(4)	O(12)-Na-O(10') <sup>a</sup>	106.9(4)		
O(12)-Na-O(11') <sup>a</sup>	108.5(4)	O(12)-Na-O(12') <sup>a</sup>	180.0(0)		
P(1)-N(4)-P(2)	139.1(12)				

<sup>a</sup> A prime indicates an atomic position generated by the inversion center.

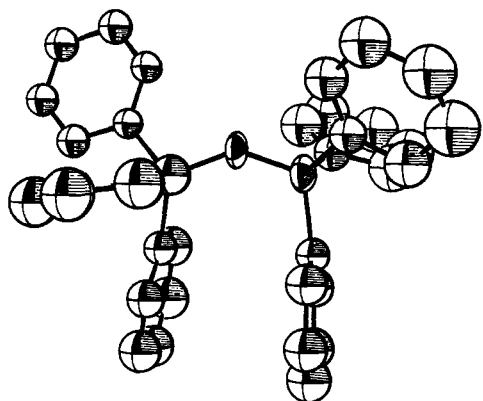
arated in the unit cell, as can be seen in Figure 11. The anions of **1** and **2** are quite similar, except that (a) the  $\mu_3\text{-O}$  of **1** is replaced by the  $\mu_3\text{-OCH}_3$  of **2**; (b) the oxygen-sodium interactions of **1** are absent in **2**; (c) the nitrosyl ligands occupy axial positions in **1**, but occupy equatorial positions in **2**. However, in order to maintain the crystallographically required mirror plane of **2**, the nitrosyl ligand bonded to Mo(1) is disordered about two equatorial positions.

**Discussion of the Solid-State Structures.** The average Mo-Mo distances, 3.297 (2) Å for **1** and 3.428 (1) Å for **2**, are larger than that observed for the longest unbridged Mo-Mo bond, 3.235 (1) Å in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ .<sup>10</sup> Moreover, no metal-metal bonding is required for either cluster to obey the 18-electron rule.<sup>11</sup> Although metal-metal interactions are postulated for a variety of group 6B carbonyl compounds with M-M distances that vary from 3.33 to 3.53 Å,<sup>12</sup> these com-

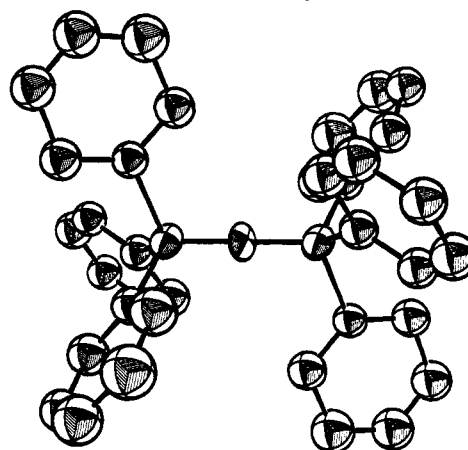
**Table VI.** Distances and Angles in  $[Me_4N]^+[Mo_3(CO)_6(NO)_3(\mu_2-OCH_3)_3(\mu_3-OCH_3)]^-$  (2)

A. Distances (Å)					
Mo(1)-Mo(2)	3.3901(13)	Mo(2)-C(20)	1.992(10)	O(4)-C(5)	1.307(14)
Mo(2)-Mo(2') <sup>b</sup>	3.4668(10)	Mo(2)-O(21)	3.122(8)	O(6)-C(7)	1.407(20)
Mo(1)-X <sup>a</sup>	1.878(8)	Mo(2)-C(22)	1.997(10)	O(8)-C(9)	1.424(14)
Mo(1)-O(11)	3.067(7)	Mo(2)-O(23)	3.125(9)	X-O(11)	1.191(10)
Mo(1)-C(12)	1.990(14)	Mo(2)-N(24)	1.815(7)	C(12)-O(13)	1.123(17)
Mo(1)-O(13)	3.113(10)	Mo(2)-O(25)	2.981(6)	C(20)-O(21)	1.132(13)
Mo(1)-O(4)	2.138(6)	Mo(2)-O(4)	2.112(6)	C(22)-O(23)	1.130(13)
Mo(1)-C(5)	3.107(15)	Mo(2)-C(5)	3.079(13)	N(24)-O(25)	1.170(6)
Mo(1)-O(8)	2.210(8)	Mo(2)-O(8)	2.232(5)	N(43)-C(40)	1.470(16)
Mo(1)-C(9)	3.168(12)	Mo(2)-C(9)	3.137(11)	N(43)-C(41)	1.617(30)
		Mo(2)-O(6)	2.099(6)	N(43)-C(42)	1.473(21)
		Mo(2)-C(7)	3.097(14)		
B. Angles (deg)					
Mo(1)-Mo(2)-Mo(2') <sup>b</sup>	59.25(2)	Mo(1)-X-O(11)	175.9(7)		
Mo(2)-Mo(1)-Mo(2') <sup>b</sup>	61.50(3)	Mo(1)-C(12)-O(13)	179.3(13)		
X-Mo(1)-X' <sup>b</sup>	87.7(3)	O(11)-Mo(1)-O(13)	86.7(2)		
X-Mo(1)-C(12)	87.4(4)	O(11)-Mo(1)-O(11') <sup>b</sup>	84.7(2)		
X-Mo(1)-O(4)	94.8(3)	O(11)-Mo(1)-O(4)	96.4(2)		
X-Mo(1)-O(8)	98.0(3)	O(11)-Mo(1)-O(8)	98.7(2)		
X'Mo(1)-O(4) <sup>b</sup>	174.1(3)	O(11')-Mo(1)-O(4) <sup>b</sup>	175.1(2)		
X'Mo(1)-O(8) <sup>b</sup>	98.0(3)	O(13)-Mo(1)-O(4)	98.1(2)		
C(12)-Mo(1)-O(4)	97.9(3)	O(13)-Mo(1)-O(8)	172.7(3)		
C(12)-Mo(1)-O(8)	172.5(5)				
O(4)-Mo(1)-O(8)	76.5(2)	O(21)-Mo(2)-O(23)	85.8(2)		
C(20)-Mo(2)-C(22)	86.0(3)	O(21)-Mo(2)-O(25)	84.4(8)		
C(20)-Mo(2)-N(24)	86.8(4)	O(21)-Mo(2)-O(4)	97.0(5)		
C(20)-Mo(2)-O(4)	95.6(4)	O(21)-Mo(2)-O(6)	99.6(3)		
C(20)-Mo(2)-O(6)	99.8(4)	O(21)-Mo(2)-O(8)	170.6(2)		
C(20)-Mo(2)-O(8)	169.7(3)	O(23)-Mo(2)-O(25)	82.6(6)		
C(22)-Mo(2)-N(24)	86.2(4)	O(23)-Mo(2)-O(4)	88.9(3)		
C(22)-Mo(2)-O(4)	87.7(4)	O(23)-Mo(2)-O(6)	172.4(3)		
C(22)-Mo(2)-O(6)	171.2(4)	O(23)-Mo(2)-O(8)	100.7(2)		
C(22)-Mo(2)-O(8)	100.0(3)	O(25)-Mo(2)-O(4)	171.3(4)		
N(24)-Mo(2)-O(4)	173.3(3)	O(25)-Mo(2)-O(6)	103.1(5)		
N(24)-Mo(2)-O(6)	100.7(3)	O(25)-Mo(2)-O(8)	103.0(7)		
N(24)-Mo(2)-O(8)	101.8(3)				
O(4)-Mo(2)-O(6)	85.2(3)	Mo(1)-O(4)-Mo(2)	105.8(2)		
O(4)-Mo(2)-O(8)	76.6(2)	Mo(1)-O(4)-C(5)	127.1(8)		
O(6)-Mo(2)-O(8)	73.3(3)	Mo(1)-O(8)-Mo(2)	99.5(2)		
		Mo(1)-O(8)-C(9)	119.7(8)		
Mo(1)-N(10)-O(11)	175.9(7)	Mo(2)-O(6)-Mo(2') <sup>b</sup>	111.3(4)		
Mo(1)-C(12)-O(13)	179.3(13)	Mo(2)-O(6)-C(7)	122.9(3)		
Mo(2)-C(20)-O(21)	176.0(9)	Mo(2)-O(8)-Mo(2') <sup>b</sup>	101.9(3)		
Mo(2)-C(22)-O(23)	176.6(10)	Mo(2)-O(8)-C(9)	116.5(4)		
Mo(2)-N(24)-O(25)	173.6(11)	C(41)-N(43)-C(42)	101.7(17)		
C(40)-N(43)-C(40') <sup>b</sup>	113.1(9)				
C(40)-N(43)-C(41)	105.0(10)				
C(40)-N(43)-C(42)	113.8(8)				

<sup>a</sup> X denotes the position which is 50:50% C:N. <sup>b</sup> A prime indicates an atomic position generated by the mirror plane.



**Figure 3.** The bent  $[(Ph_3P)_2N]^+$  cation in 1. Two of the three PPN<sup>+</sup> cations in the compound have the bent configuration, which is the usual geometry found in PPN<sup>+</sup> salts.



**Figure 4.** The linear  $[(Ph_3P)_2N]^+$  in 1. This, and the cation found in  $[PPN]^+[V(CO)_6]^-$  (ref 16), represents the only known example of the linear form of PPN<sup>+</sup>.

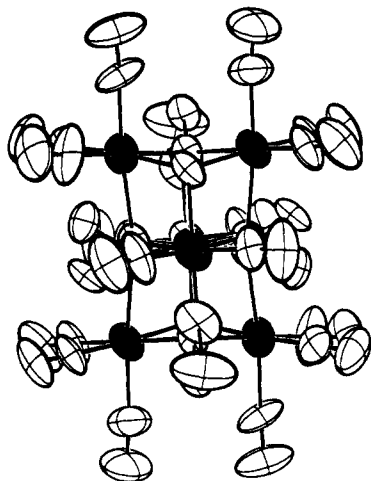


Figure 5. A plot of the entire hexameric unit showing the arrangement of shared edges of the Mo and Na octahedron. Five of the six molybdenum atoms have been shaded, and the sixth is partially hidden. The equatorial plane of the Na octahedron is perpendicular to the page.

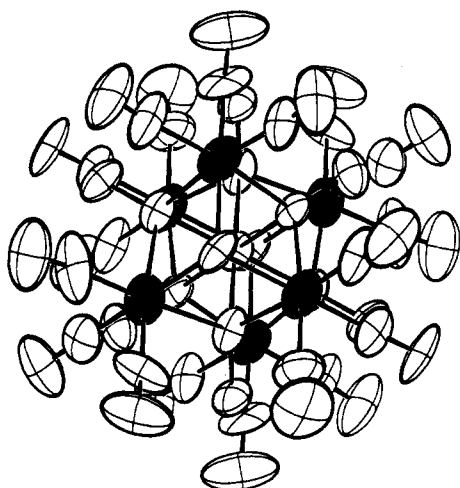


Figure 6. A view down the axis of the anion **1** showing the spherical shape of the hexamer. The molybdenum atoms have been shaded, and the sodium ion is quite evident in the center of the figure.

pounds all contain an electron-deficient M-H-M bridge bond. On the other hand, group 6B carbonyl compounds with electron-precise bridging hydroxyl ligands have M-M distances between 3.23 and 3.48 Å and are thought to be nonbonding.<sup>13</sup> Mason and Mingos have argued<sup>14</sup> that only electron-deficient compounds have filled bridge orbitals that are bonding with respect to the metals; it seems likely that neither **1** nor **2**, which are bridged by electron-precise methoxy ligands, has appreciable metal-metal bonding, and that neither compound is, therefore, a true metal cluster.

Organometallic reactions in methanol have occasionally

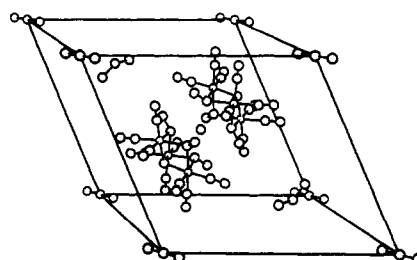
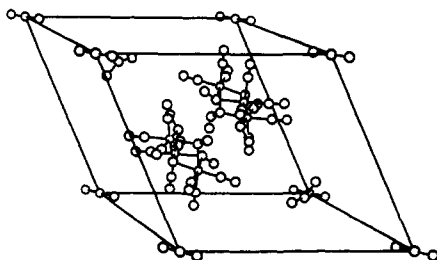


Figure 7. A stereoscopic view of the unit cell of **1** with the phenyl groups removed for clarity. The *cb* plane is parallel to the page, with *c* in the horizontal direction.

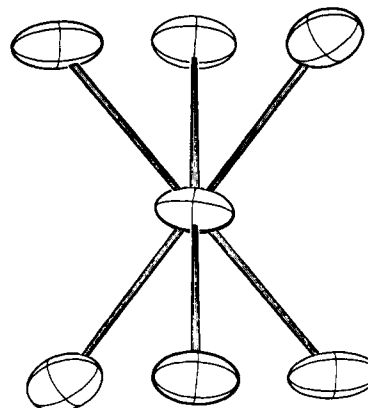


Figure 8. The geometry about the central Na<sup>+</sup> ion in [Na[Mo<sub>3</sub>(CO)<sub>6</sub>(NO)<sub>3</sub>(μ<sub>2</sub>-OCH<sub>3</sub>)<sub>3</sub>(μ<sub>3</sub>-O)]<sub>2</sub><sup>3-</sup> (**1**). The distorted octahedral coordination of methoxy oxygen atoms about the sodium ion is reminiscent of that found in some Na<sup>+</sup>/crown ether complexes.

produced compounds with bridging methoxy ligands.<sup>15,16</sup> In **1** and **2**, the methoxy groups are noncoplanar with the Mo atoms they bridge, as has been observed in other bridging chalcogen structures.<sup>14,17</sup> The Mo-O methoxy distances, 2.19 (1) Å for **1** and 2.16 (1) Å for **2**, compare favorably to other Mo-O bridged distances.<sup>13</sup> The triply bridging oxygen atom of **1** symmetrically bridges the metal triangle at an average Mo-O distance of 2.05 (1) Å, close to that found in H<sub>3</sub>Re<sub>3</sub>(CO)<sub>9</sub>(μ<sub>3</sub>-O)<sup>2-</sup>, 2.12 Å.<sup>18</sup> It is thought not to be a hydroxyl ligand because of the absence of either a suitable resonance in the <sup>1</sup>H NMR or an O-H stretch in the IR, and because a bridging hydroxyl group would cause each trimer unit to be paramagnetic.

The assignment of the nitrosyl ligands, indicated by the thermal parameters (see Experimental Section), is confirmed by bond distances. The unique Mo-N distances average 1.827 (11) Å in **1** and 1.815 (7) Å in **2**, while the Mo-C distances average 1.995 (9) Å in **1** and 1.994 (6) Å in **2**. In the mixed carbonyl nitrosyl complex HW<sub>2</sub>(CO)<sub>8</sub>(NO)[P(OCH<sub>3</sub>)<sub>3</sub>], the axial W-C distance, 1.980 (4) Å, is 0.162 Å longer than the axial W-N distance of 1.818 (4) Å.<sup>4</sup> It is gratifying to note that the disordered Mo-X (X = 50% C, 50% N) distance of 1.878 (8) Å in **2** is close to the average of the Mo-C and Mo-N distances in the same compound, 1.914 (5) Å. We can offer no explanation at this time as to why the nitrosyl ligands of **1** occupy axial positions while those of **2** occupy equatorial positions. In **1** the NO groups are trans to the μ<sub>3</sub>-O ligand and cis to the μ<sub>2</sub>-OCH<sub>3</sub> group, while in **2** the NO groups are cis to μ<sub>3</sub>-OCH<sub>3</sub> and trans to μ<sub>2</sub>-OCH<sub>3</sub>, even though this arrangement involves the disordering of one NO group in the solid state. The reason for this preference is not clear.

Two features of **1** are of particular interest. The first is the linear P-N-P geometry found in one of the bis(triphenylphosphine)iminium cations. The central nitrogen of this linear PPN<sup>+</sup> occupies the special symmetry position at (0, 0, 1/2). The only other linear PPN<sup>+</sup>, found in [PPN]<sup>+</sup>[V(CO)<sub>6</sub>]<sup>-</sup>, also



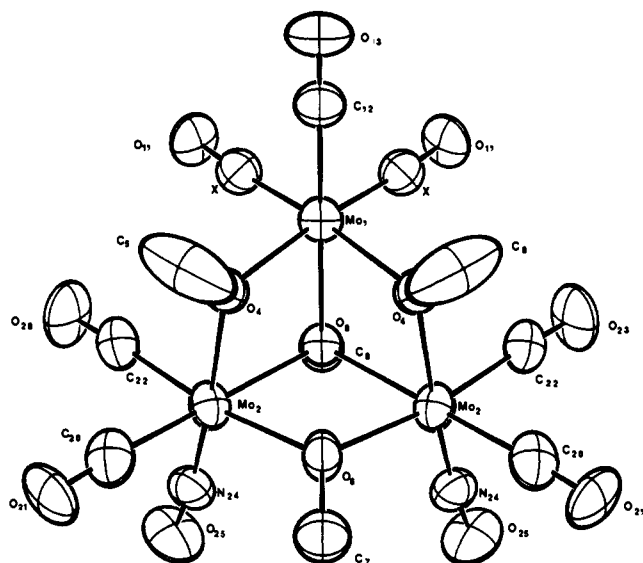


Figure 9. A plot of the anion in  $[Me_4N]^+[Mo_3(CO)_6(NO)_3(\mu_2-OCH_3)_3(\mu_3-OCH_3)]^-$  (2) showing the mirror symmetry of the anion. X marks the position of the disordered N/C atom.

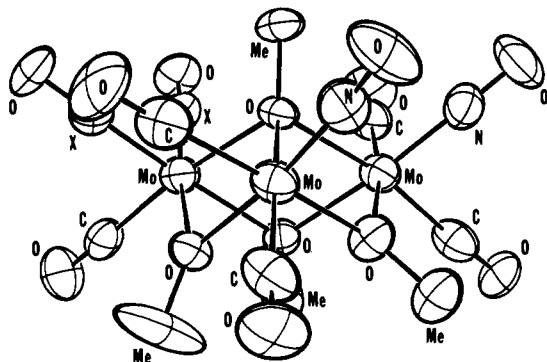


Figure 10. A plot of the anion in 2 showing the similarity in structure to 1. In 1, which is capped by  $\mu_3-O$ , the NO groups on each Mo are opposite this position, while in 2, which is capped by  $\mu_3-OCH_3$ , the NO groups are cis to the triply bridging positions. X marks the position of the disordered N/C atom.

occupies a special position on a  $\bar{3}(S_6)$  axis.<sup>19</sup> A discussion of the geometries and bonding of  $PPN^+$ , as well as a comparison with other  $PPN^+$  structures, can be found in the  $[V(CO)_6]^-$  paper.<sup>19</sup>

The second novel (and perhaps most interesting) feature of the solid-state structure of 1 is the interaction between the oxygen atoms of the six methoxy ligands and the central sodium ion. As previously noted, the sodium ion is surrounded

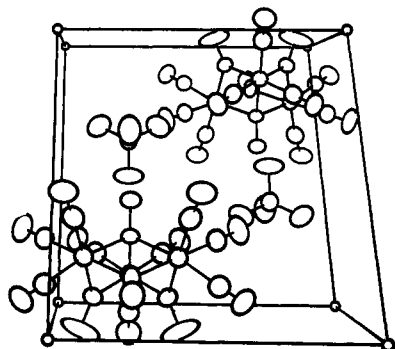
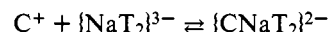


Table VII. Molar Conductivities at 25 °C

compd	solvent	$\Lambda_m$ ( $10^{-3}$ M)	$\Lambda_m$ lit. <sup>27</sup>
1		310	
3	acetonitrile	330	340-420
$[PPN]_3$ [citrate]		380	
1	acetone	230	
3		230	270
3	methanol	300	290-350

by the six bridging methoxy atoms in a trigonally distorted octahedral coordination (Figure 8), with O-Na-O angles that deviate about  $18^\circ$  from  $90^\circ$ . The Na-O distances average 2.419 (7) Å, and both geometry and distances are quite similar to those found in crown ether complexes of sodium.<sup>20</sup> Other Na-O distances, such as 2.326 (3) Å in  $Na_2Fe(CO)_4 \cdot 1.5(\text{dioxane})$ <sup>21</sup> and 2.40 (2) Å in  $[Na(DMF)_3]^+$ ,<sup>22</sup> are also quite similar to those of 1. The anion unit of 1 can be thought of as a solid-state triple ion, with the sodium cation "sandwiched" by two molybdenum trimer dianions. The triple ion persists in solution (vide infra). It is interesting to note that the sum of the ionic radii of  $Na^+$  and  $O^{2-}$  is 2.35<sup>23</sup> or 2.40 Å,<sup>24</sup> while the sum of the ionic radius<sup>24</sup> of  $Na^+$  and the van der Waals radius<sup>25</sup> of O is 2.66 Å, although neither bonding analogy is exact.

**Discussion of Solution Behavior.** In order to examine the ion pairing of 1 in solution, conductivity and  $^1H$  NMR studies of 1 and its more soluble  $Me_4N^+$  salt 3 were initiated. Conductivity measurements on 1 and 3 in a variety of solvents at concentrations as low as  $10^{-4}$  M yielded plots of equivalent conductance vs. the square root of the equivalent concentration that show hyperbolic curves typical of weak electrolytes.<sup>26</sup> Because of the nonlinearity of the plots, no exact values of the slope or limiting conductance,  $\Lambda_0$ , could be obtained. Although  $\Lambda_0$  values were not obtained, Table VII collects values of  $\Lambda_m$ , the molar conductance at  $10^{-3}$  M. For both 1 and 3 in several solvents, the values of  $\Lambda_m$  fall slightly below those typical of a 1:3 electrolyte.<sup>27</sup> The association of a bulky cation with the anionic triple ion could explain the conductance measurements:



where  $C^+$  = bulky cation and  $T = [Mo_3(CO)_6(NO)_3(\mu_2-OCH_3)_3(\mu_3-O)]^{2-}$ . No molar conductivity values greater than those of a 1:3 electrolyte were observed,<sup>28</sup> indicating that at concentrations as low as  $10^{-4}$  M the  $Na^+$  must be ion paired in some manner.<sup>29</sup>

Routine  $^1H$  NMR studies of 1 and 3 revealed unusually complicated solution behavior. 1 was expected to display a singlet for the  $\mu_2$ -methoxy ligands and a multiplet for the  $PPN^+$  cation, and, although the  $PPN^+$  protons gave the ex-

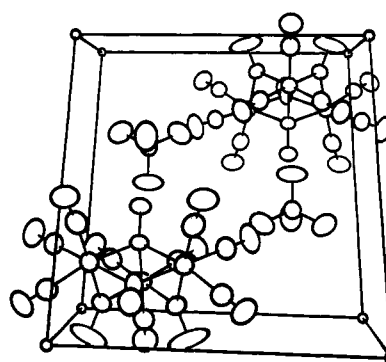


Figure 11. A stereoscopic view of the unit cell contents of 2, looking down the  $c$  axis to the  $ab$  plane, showing the mirror symmetry. On the forward anion, the nitrosyl groups are aimed toward the viewer and up.

pected peaks and the methoxy region integrated properly vs. the cation, the methoxy resonances were more complex than anticipated (see Experimental Section). The  $^1\text{H}$  NMR spectrum of **3** in acetone- $d_6$  displayed the  $\text{Me}_4\text{N}^+$  resonance at  $\delta$  3.45. However, instead of a singlet for the six  $\mu_2\text{-OCH}_3$  ligands, a singlet at 4.42, a poorly resolved shoulder at  $\delta$  4.35, and a singlet at  $\delta$  4.09 were observed. The combination of these three resonances integrated correctly vs. the  $\text{Me}_4\text{N}^+$  cations, indicating that the three peaks are all due to the methoxy ligands. Since the conductivity studies indicate that both **1** and **3** are extensively ion paired at concentrations of  $10^{-3}$  M, it is possible that the complex  $^1\text{H}$  NMR methoxy resonances are due to some form of ion pairing.<sup>30</sup>

**2**, in contrast to **1** and **3**, does not seem to ion pair in solution or the solid state, presumably because of the smaller anionic charge. Conductivity measurements for **2** indicate behavior typical of a 1:1 electrolyte, and no sodium ions are located in the solid-state structure. The  $^1\text{H}$  NMR spectrum, on the other hand, exhibits complexity in the methoxy region typical of **1** and **3**. Further studies on the ion pairing of **1**, **2**, and **3** and related species have been initiated.

## Conclusions

The crystal structure of **1** strongly indicates a tight, contact triple ion between two  $[\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu_2\text{-OCH}_3)_3(\mu_3\text{-O})]^{2-}$  dianions and a sodium cation. The geometry and bonding of the methoxy oxygens coordinated about the central sodium ion are suggestive of crown ether complexes. Like the sodium ion coordinated by a crown ether, the sodium ion of **1** is completely removed from its solvation shell. Moreover, preliminary experiments using sodium-free reactants such as  $\text{KOH}/\text{KNO}_2$  or  $\text{CsOH}/[\text{PPN}]\text{NO}_2$  have failed to produce **1**,<sup>31</sup> a possible indication of a selectivity toward  $\text{Na}^+$  reminiscent of crown ether complexes. Further such indications are the lack of  $\text{K}^+$  incorporation in the mixed  $\text{NaNO}_2/\text{KOH}$  system and the lack of exchange of the central  $\text{Na}^+$  for  $\text{Me}_4\text{N}^+$  or  $\text{PPN}^+$ . Solution studies indicate tight pairing of the  $\text{Na}^+$  to the dianions similar to the tight ion pairing found between  $[\text{Fe}(\text{CO})_4]^{2-}$  and  $\text{Na}^+$ ,<sup>21,27</sup> although the sites for ion pairing are obviously different. More relevant analogues of the type of chelation described in this paper are the very interesting compounds of the type  $\{[(\text{C}_5\text{H}_5)\text{Co}[\text{P}(\text{O})(\text{OR})_2]_3]_2\text{M}\}^{n+}$  ( $n = 0$  or  $1$ ), prepared recently by Kläui and co-workers.<sup>32</sup> In these complexes, which have been synthesized with a wide range of  $\text{M}^{2+}$  and  $\text{M}^{3+}$  ions, two  $\{[(\text{C}_5\text{H}_5)\text{Co}[\text{P}(\text{O})(\text{OR})_2]_3]^{-}$  moieties sequester a central metal ion in a manner much like that exhibited by the structure of **1**.

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**Supplementary Material Available:** A listing of structure factor amplitudes for the X-ray data sets (Tables VII and VIII) (31 pages). Ordering information is given on any current masthead page.

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- (28) The overall dissociation  $[\text{Me}_4\text{N}]_3^+ [\text{NaT}_2]_3^{3-} \rightleftharpoons 3[\text{Me}_4\text{N}]^+ + \text{Na}^+ + 2[\text{T}]^{2-}$  would yield an effective 1:4 electrolyte if an equivalent weight equal to the molecular weight is assumed.
- (29) Conductivity studies would not be sensitive to the following equilibrium:  $[\text{NaT}_2]_3^{3-} \rightleftharpoons [\text{NaT}]_1^{1-} + \text{T}^{2-}$ .
- (30) It is certainly reasonable to assume that a nominal 1:3 electrolyte such as **3** will ion pair with its bulky  $\text{Me}_4\text{N}^+$  cation in solvents such as acetone, especially at high NMR concentrations. Such pairing, however, probably could not account for the various methoxy resonances, since the ion pairing that caused methoxy shifts would be likely to cause  $\text{Me}_4\text{N}^+$  shifts as well. It is possible that ion pairing between  $\text{Me}_4\text{N}^+$  and **3** occurs through the  $\mu_3$  oxygens or through solvent-separated ion pairs. The carbonyl and nitrosyl oxygen atoms appear not to be sites for ion pairing, since infrared spectra in the carbonyl and nitrosyl regions are invariant to changes in cation and/or solvent. Different forms of ion pairing between the trimer dianions and the sodium cation might explain the methoxy region, but the spectrum of sodium-free **2** is also complex.
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