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Note

Synthesis and characterization of the trimetaphosphate molybdenum tricarbonyl anion $[(P_3O_9)Mo(CO)_3]^{3-}$ as its *tris*(*bis*(triphenylphosphine)iminium) salt

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ABSTRACT

Treatment of $(CH_3CN)_3Mo(CO)_3$ with the trimetaphosphate salt $[PPN]_3[P_3O_9]\cdot H_2O$ ($[PPN]^+ = [Ph_3P{=}N\text{-}PPh_3]^+$) (acetonitrile, 25 °C) gave the trimetaphosphate-molybdenum complex $[(P_3O_9)Mo(CO)_3]^{3-}$ in 91% isolated yield. $[PPN]_3[(P_3O_9)Mo(CO)_3]$ was also obtained in 77% isolated yield by directly treating $Mo(CO)_6$ with $[PPN]_3[P_3O_9]\cdot H_2O$ in refluxing acetonitrile, presumably by generating $(CH_3CN)_3Mo(CO)_3$ *in situ*. Reported herein is the full characterization and structural determination of $[PPN]_3[(P_3O_9)Mo(CO)_3]$ and comparison to synthesized and calculated $[(P_3O_9)M(CO)_3]^{n-}$ (M = group 6–9) complexes.

1. Introduction

Trimetaphosphate ($P_3O_9^{3-}$) is an attractive, inorganic, tripodal ligand for transition-metal chemistry [1–15]. The first isolable metal trimetaphosphate complexes ($[N(n\text{-}Bu)_4]_2[(P_3O_9)M(CO)_3]$, M = Re, Mn) were reported by Klemperer and co-workers in 1981 (Fig. 1) [1]. Although not structurally characterized, the $[(P_3O_9)M(CO)_3]^{2-}$ anions were hypothesized to conform to C_{3v} symmetry based upon infrared spectroscopy. Since that initial report, there have been a handful of other reported trimetaphosphate transition-metal complexes – both from the Klemperer lab [2–7] and others [8–15]. Despite being a readily available, tridentate, trianionic ligand, $P_3O_9^{3-}$ seems to be underutilized as reflected by the chemical literature.

Perhaps one of the reasons trimetaphosphate coordination chemistry is underrepresented in the literature is due to its propensity to hydrolyze forming tripolyphosphate in water [16]. In seeking to introduce $P_3O_9^{3-}$ into molybdenum chemistry, we accordingly employed an anhydrous synthesis procedure modeled after that of Klemperer (Scheme 1). Reported herein is the synthesis and structure of $[PPN]_3[(P_3O_9)Mo(CO)_3]$ ($[PPN] = [Ph_3P{=}N\text{-}PPh_3]^+$), an example of a κ^3-trimetaphosphate, tricarbonyl, transition-metal complex.

2. Results and discussion

Initially, $(CH_3CN)_3Mo(CO)_3$ [17] was slurried in methylene chloride and treated with $[PPN]_3[P_3O_9]\cdot H_2O$ [18]. After stirring for 1 h, the golden-yellow mixture formed a homogeneous solution yielding $[PPN]_3[(P_3O_9)Mo(CO)_3]$ in 91% isolated yield by precipitation with diethyl ether. Alternatively, a streamlined synthesis has been developed by simply refluxing $Mo(CO)_6$ and $[PPN]_3[P_3O_9]\cdot H_2O$ in acetonitrile for 4 h (Scheme 2). $(CH_3CN)_3Mo(CO)_3$ is presumably generated *in situ* where it reacts with $[PPN]_3[P_3O_9]\cdot H_2O$ to form the desired product in 77% yield.

A ^{31}P NMR spectrum of the product in methylene chloride shows two peaks at $\delta = 21.7$ and -11.3 ppm in a 2:1 ratio, corresponding to $[PPN]^+$ and $[(P_3O_9)Mo(CO)_3]^{3-}$, respectively. These spectroscopic data are in good agreement with trimetaphosphate ^{31}P NMR shifts of $[(P_3O_9)M(CO)_3]^{2-}$ complexes reported by Klemperer (M = Re, $\delta = -11.1$ ppm; M = Mn, $\delta = -9.8$ ppm). $[(P_3O_9)Mo(CO)_3]^{3-}$ gives the expected infrared spectrum for a C_{3v} symmetric tricarbonyl species with the A_1-carbonyl stretch at $\nu_{CO} = 1883\ cm^{-1}$ (s) and the E stretch at $\nu_{CO} = 1723\ cm^{-1}$ (s, br). Values for $[(P_3O_9)Mo(CO)_3]^{3-}$ differ from those for $[(P_3O_9)M(CO)_3]^{2-}$ (M = Re, $\nu_{CO} = 2018\ cm^{-1}$ (s), $1885\ cm^{-1}$ (s, br); M = Mn, $\nu_{CO} = 2034\ cm^{-1}$ (s), $1913\ cm^{-1}$ (s, br)) due to electronic differences between the group 6 trianion versus the group 7 dianions. The less energetic ν_{CO} stretches observed in $[(P_3O_9)Mo(CO)_3]^{3-}$ are expected from the more electron rich molybdenum center when compared to the group 7 congeners [20]. A recent article written by Earley reported calculated structural aspects and ν_{CO} stretching frequencies for a series of hypothetical $d^6[(P_3O_9)M(CO)_3]^{n-}$ compounds (where M = the 12 metals that make up group 6–9) [21]. The calculated ν_{CO} stretching frequencies for $[(P_3O_9)Mo(CO)_3]^{3-}$ were given as 1822 (A_1) and 1699 (E) cm^{-1}. The differences between calculated and experimental ν_{CO} frequencies in $[(P_3O_9)Mo(CO)_3]^{3-}$ are very similar to those for $[(P_3O_9)M(CO)_3]^{2-}$ where M = Mn and Re (Table 1).

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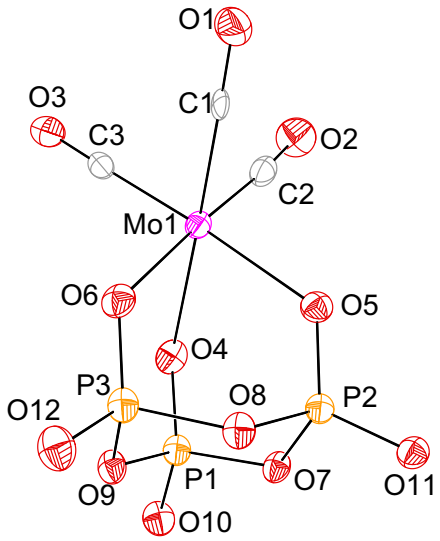


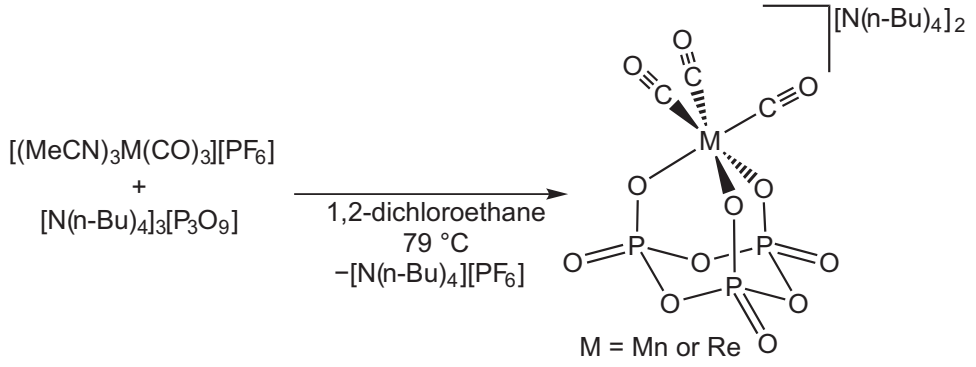
Fig. 1. Solid-state structure of anion $[(P_3O_9)Mo(CO)_3]^{3-}$ with thermal ellipsoids at the 50% probability level. Averaged bond lengths (Å): Mo–C 1.950(3), C–O 1.152(5), Mo—O_M 2.283(3), P—O_M 1.493(3), P—O_{ring} 1.625(3), P—$O_{terminal}$ 1.465(3).

Crystals of $[PPN]_3[(P_3O_9)Mo(CO)_3]$ were grown via vapor diffusion of tetrahydrofuran into a saturated acetonitrile solution at room temperature and subjected to an X-ray crystallographic study (Fig. 1). The trimetaphosphate salt crystallizes in $P2_1/c$ as a non-merohedral twin. The asymmetric unit consists of the salt as well as a disordered tetrahydrofuran molecule. There is also a positional disorder at the $[(P_3O_9)Mo(CO)_3]^{3-}$ anion caused by a C_2 rotation. The two components of the positional disorder exist in a *ca.* 95:5 ratio (see Supporting information for full crystallographic details).

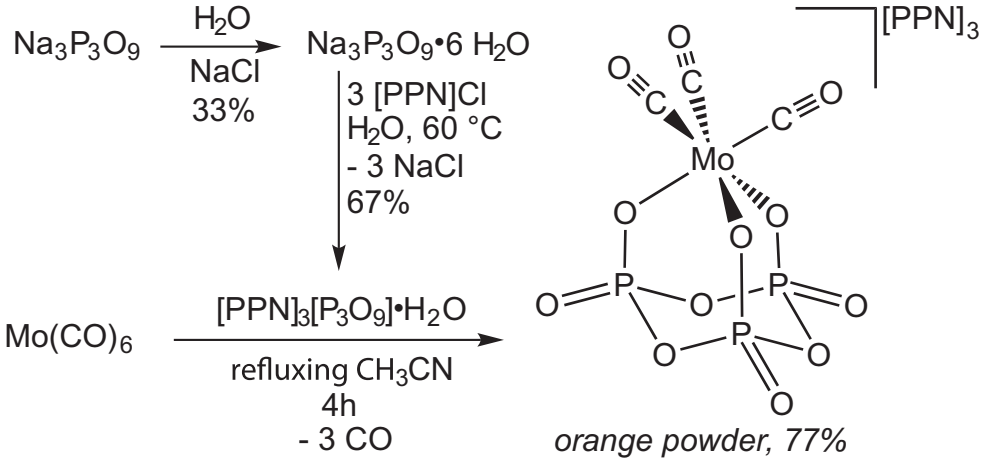
As expected from ^{31}P NMR and FT-IR spectroscopies, the solid-state structure of $[(P_3O_9)Mo(CO)_3]^{3-}$ exhibits near-perfect C_{3v} symmetry with all equivalent bond lengths varying by no more than 0.028 Å. To the best of our knowledge, $[PPN]_3[(P_3O_9)Mo(CO)_3]$ is the first example of a crystallographically characterized, transition metal $[(P_3O_9)M(CO)_3]^{n-}$ species. Other κ^3-trimetaphosphate complexes are known, but they are relatively rare. A search of the Cambridge Structural Database and the chemical literature only returns 13 such κ^3-$P_3O_9^{3-}$ complexes utilizing seven different transition metals (Hf [9], V [12], Fe [8], Ru [2,5,10,14,15], Rh [2], Ir [3], and Pt [11]).

We compared the experimentally derived metrical parameters from our structure of $[(P_3O_9)Mo(CO)_3]^{3-}$ to those predicted by Earley [21]. Earley has calculated the C–O, Mo–C, Mo—O_M and P—O_M bond lengths for complexes of the type $[(P_3O_9)M(CO)_3]^{n-}$ (where "O_M" refers to the oxygen atoms of the trimetaphosphate that are bound directly to the metal).

As shown in Table 2, with the exception of Mo–C bond lengths, the theoretical results overestimate the bond lengths that are revealed by the crystal structure. Earley contends [21] that as the $[(P_3O_9)M(CO)_3]^{n-}$ complexes become less electron rich (going from $n = 3$ to $n = 0$) that C–O bond lengths decrease in accordance with a decreasing amount of back bonding to the π^* orbital of CO. A



Scheme 1. Synthesis of $[N(n\text{-}Bu)_4]_2[(P_3O_9)M(CO)_3]$ [1].



Scheme 2. Syntheses of $Na_3P_3O_9 \cdot 6H_2O$ [19], $[PPN]_3[P_3O_9] \cdot H_2O$ [18] and $[PPN]_3[(P_3O_9)Mo(CO)_3]$.

Table 1
Experimental and calculated ν_{CO} stretching frequencies (cm^{-1}) for $[(P_3O_9)M(CO)_3]^{n-}$.

		Observed[a]	Calculated[b]	Difference
$[(P_3O_9)Mo(CO)_3]^{3-}$	A_1	1883	1822	61
	E	1723	1699	24
$[(P_3O_9)Mn(CO)_3]^{2-}$	A_1	2034	1973	61
	E	1918	1886	32
$[(P_3O_9)Re(CO)_3]^{2-}$	A_1	2018	1960	58
	E	1885	1848	37

[a] $[(P_3O_9)Mn(CO)_3]^{2-}$ and $[(P_3O_9)Re(CO)_3]^{2-}$ data taken from Ref. [1].
[b] Calculated data taken from Ref. [21].

Table 2
Experimental and calculated bond lengths (Å) for $[(P_3O_9)Mo(CO)_3]^{3-}$.

	Experimental	Calculated[a]
C–O	1.152(5)	1.210
Mo–C	1.950(4)	1.942
Mo–O_M	2.283(3)	2.348
P–O_M	1.493(3)	1.521

[a] Calculated data taken from Ref. [21].

second reason for this effect stems from decreasing *d*-orbital energies going from group 6 to group 9 leading to poorer overlap with the CO π^* orbitals [21]. M—O_M bond lengths are simply predicted to be dependent upon the atomic radius of the metal. Predictions of M–C bond lengths were more complicated as they are dependent upon all of the aforementioned factors. M–C bond lengths show an increase within a period for second- and third-row metals versus first-row as well as a local minimum within each row at group 7.

3. Conclusions

Reported here is the synthesis and characterization of the first trimetaphosphate molybdenum complex. $[PPN]_3[(P_3O_9)Mo(CO)_3]$ is synthesized in a total of three steps from commercially available materials. The structure of the $[(P_3O_9)Mo(CO)_3]^{3-}$ anion exhibits C_{3v} symmetry as inferred from ^{31}P NMR and FT-IR spectroscopic data. The species is also the first structurally characterized example of a complex of the type $[(P_3O_9)M(CO)_3]^{n-}$.

4. Experimental details

4.1. General considerations

Unless stated otherwise, all operations were performed in a Vacuum Atmospheres drybox under an atmosphere of purified nitrogen or using Schlenk techniques under an argon atmosphere. $Mo(CO)_6$ was purchased from Strem and used without further purification. $[PPN]_3[P_3O_9]\cdot H_2O$ was prepared as previously reported [18]. $(CH_3CN)_3Mo(CO)_3$ was prepared as previously reported [17]. Diethyl ether, acetonitrile and methylene chloride were dried and deoxygenated by the method of Grubbs [22] using a system built by SG Water USA, LLC (www.glasscontoursolvent-systems.com). $CDCl_3$ was purchased from Cambridge Isotope Labs, purified by distillation off of CaH_2 and stored over 4 Å molecular sieves. Celite, alumina and 4 Å molecular sieves were dried under reduced pressure overnight at a temperature above 200 °C. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Varian Mercury-300, Varian INOVA-500 or Bruker AVANCE-400 spectrometers. ^1H and ^{13}C chemical shifts are reported with respect to internal solvent ($CDCl_3$, $\delta = 7.24$ and 77.23 ppm, respectively). ^{31}P NMR chemical shifts are reported with respect to an external reference (85% H_3PO_4, $\delta = 0.0$ ppm). Infrared spectra were recorded on a Bruker TENSOR37 FT-IR Spectrophotometer. X-ray data collections were carried out on a Siemens Platform three-circle goniometer with a CCD detector using MoKα radiation, $\lambda = 0.71073$ Å. Combustion analyses were performed by Midwest Microlabs LLC, Indianapolis, IN.

4.2. Synthesis of $[PPN]_3[(P_3O_9)Mo(CO)_3]$ from $(CH_3CN)_3Mo(CO)_3$.

In the glovebox, $(CH_3CN)_3Mo(CO)_3$ (1.176 g, 3.880 mmol) was dissolved in 10 mL of acetonitrile and stirred. $[PPN]_3[P_3O_9]\cdot H_2O$ (7.257 g, 3.879 mmol) was dissolved in 20 mL of acetonitrile and added to the stirring, greenish-brown $(CH_3CN)_3Mo(CO)_3$ solution over a period of 5 min. Upon addition of the trimetaphosphate salt, the reaction mixture attained a golden-brown color. The mixture was stirred for 1 h, after which time an aliquot was taken for analysis by ^{31}P NMR spectroscopy. The ^{31}P NMR (202.5 MHz, CH_3CN) spectrum showed complete consumption of starting material with concomitant formation of the desired product: δ 22.12 (s, 6P, $[PPN]^+$), −10.70 (s, 3P, $P_3O_9{}^{3-}$). The reaction mixture was filtered through a bed of Celite. The filtrate was reduced in volume to *ca.* 10 mL under reduced pressure. The golden-yellow reaction mixture was then added dropwise to 100 mL of diethyl ether while stirring. The desired product initially precipitated out of solution, forming a flocculent, yellow solid before oiling out to a dark-orange tar. All volatile materials were then removed under reduced pressure forming a foamy, bright-orange solid. The solids were slurried in *ca.* 50 mL of diethyl ether and the larger chunks crushed with a spatula. The material was isolated on a medium-porosity, fritted-glass filter and washed with diethyl ether (2×20 mL). The bright-orange product was stored under reduced pressure for 24 h yielding the desired product as an orange powder (7.170 g, 3.527 mmol, 90.9%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (br s, 6H, phenyl), 7.45–7.36 (m, 24H, phenyl) ppm. ^{13}C NMR (125.8 MHz, $CH_3CN/CDCl_3$) δ 230.57 (s, 3C, *CO*), 133.04 (m, 6C, *para*), 131.44 (m, 6C, *ortho*), 128.76 (m, 6C, *meta*), 126.33 (dd, $^1J_{PC} = 107.7$ Hz, $^3J_{PC} = 1.7$ Hz, 6C, *ipso*) ppm. ^{31}P NMR (202.5 MHz, $CH_2Cl_2/CDCl_3$) 21.81 (s, 6P, $[PPN]^+$), −11.08 (s, 3P, $P_3O_9{}^{3-}$) ppm. FT-IR (KBr, thin film) $\nu_{CO} = 1883$ (s, A_1), 1723 (s, (E) cm^{-1}. FT-IR (CH_2Cl_2 solution) $\nu_{CO} = 1884$ (s, A_1), 1724 (s, (E) cm^{-1}. *Anal.* Calc. for $C_{111}H_{90}N_3P_9O_{12}$-Mo: C, 65.59; H, 4.46; N, 2.07; P, 13.71. Found: C, 63.92; H, 4.68; N, 1.96; P, 13.20%.

4.3. Synthesis of $[PPN]_3[(P_3O_9)Mo(CO)_3]$ from $Mo(CO)_6$

$Mo(CO)_6$ (685 mg, 2.59 mmol) and $[PPN]_3[P_3O_9]\cdot H_2O$ (4.857 g, 2.596 mmol) were suspended in 40 mL MeCN and stirred at reflux for 4 h. Upon reaching reflux temperature, the reaction mixture went from a colorless suspension to a homogeneous, light yellow solution. All volatile materials were removed under reduced pressure. The resulting golden-yellow solid was dissolved in 10 mL CH_2Cl_2 and the solution filtered through a bed of Celite. The Celite pad was washed with 5 mL CH_2Cl_2; the filtrates were combined and added dropwise to 75 mL Et_2O producing a pale yellow precipitate. All volatile materials were again removed under reduced pressure. The bright-orange solids were slurried in 30 mL diethyl ether, isolated on a medium-porosity, fritted-glass filter and washed with 3×20 mL diethyl ether. The solids were stored under reduced pressure for 12 h yielding the desired product as a free-flowing, orange powder (4.056 g, 1.995 mmol, 77.0%). Spectroscopic data for the sample prepared in this manner were identical to those obtained according to Section 4.2.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.11.060.

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