

³¹P NMR Studies on Sulfur/Oxygen-Bridged Incomplete Cubane-Type Molybdenum Cluster Compounds. X-ray Structures of [Mo₃OS₃(DTP)₄(CH₃CN)] and [Mo₃OS₃(OAc)(DTP)₂(Py)₂(OC₂H₅)][†]

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A series of sulfur/oxygen-bridged incomplete cubane-type molybdenum cluster compounds [Mo₃O_nS_{4-n}(DTP)₄(L)] (*n* = 0–3; DTP = diethyl dithiophosphate, L = monodentate ligand), and their ligand substitution derivatives were prepared by the reaction of the corresponding aqua ions with the ligand DTP. The crystallographic results obtained are as follows. [Mo₃OS₃(DTP)₄(CH₃CN)]: triclinic, *P* $\bar{1}$, *a* = 14.134(13) Å, *b* = 16.413(16) Å, *c* = 10.654(9) Å, α = 98.08(10)°, β = 112.23(6)°, γ = 77.03(9)°, *V* = 2225.3(37) Å³, *Z* = 2, no. of unique data ($|F_o| \geq 6\sigma|F_o|$) = 4810, *R* = 4.79%. [Mo₃OS₃(OAc)(DTP)₂(Py)₂(OC₂H₅)]: triclinic, *P* $\bar{1}$, *a* = 13.985(7) Å, *b* = 14.359(7) Å, *c* = 12.012(4) Å, α = 96.01(3)°, β = 104.37(3)°, γ = 114.20(3)°, *V* = 2072.3(17) Å³, *Z* = 2, no. of unique data ($|F_o| \geq 3\sigma|F_o|$) = 4944, *R* = 4.62%. Of four DTP ligands in [Mo₃OS₃(DTP)₄(CH₃CN)], three are terminal and one is bridging. Both DTP ligands in [Mo₃OS₃(OAc)(DTP)₂(Py)₂(OC₂H₅)] are terminal, and an acetato ligand is bridging. ³¹P NMR spectra of these cluster compounds were measured in a solution of *o*-dichlorobenzene and acetonitrile. The ³¹P NMR spectra of these cluster compounds presented much information about the structure, interaction between the ligands and the cluster core, solvent effect, lability of the ligands, and isomerization of this cluster compound series. The assignment of the chemical shifts to each distinct ligand under different circumstances was successfully accomplished. The site of the loosely-coordinated solvent ligand L was kinetically active and informative to the assignments of the spectra. The symmetry and chemical properties of the central trinuclear cluster core Mo₃O_nS_{4-n} (*n* = 0–3) were also well reflected in their spectral appearance.

Introduction

High attention has been paid to molybdenum–sulfur/oxygen species for chemical, structural and biochemical investigations in these three decades. Amongst them, the preparation, structure, and characterization of a series of sulfur/oxygen-bridged incomplete cubane-type molybdenum clusters, Mo₃O_nS_{4-n}⁴⁺(aq), (*n* = 0–4), have been reported, extensively.¹ These aqua ions showed very interesting properties toward the formation of multinuclear or heteropolynuclear cluster compounds and the reaction with many organic or inorganic small molecules.^{2,3} Multinuclear nuclear magnetic resonance measurements, along with the X-ray crystallography, are especially useful and powerful in the structural characterization of transi-

tion metal organometallic carbonyl clusters.⁴ However, when the NMR experiments are planned on Mo–S(O) clusters, those elements inside the cluster cores, Mo, O, and S, possess low natural abundance and the other deficiencies, and sophisticated NMR techniques are required to run the experiments. Several NMR studies were reported on cluster compounds.⁵ It is indisputable that ³¹P NMR spectra will be much more informative if the nucleus interested is bonded directly to the metal atom. But it is rather difficult to prepare such ideal samples with phosphorous atom directly bonded to Mo for the ³¹P NMR measurements. We report here the preparations and ³¹P NMR measurements of a series of new cluster compounds containing DTP ligands (diethyl dithiophosphate, Chart 1). The phosphorous nucleus, even not directly bonded to Mo, gave nuclear magnetic resonance that exhibited a lot of information on the labilities and ligating patterns of ligands, and solvent effect.

Experimental Section

All the compounds were prepared from their corresponding aqua clusters in aqueous solutions whose preparations were described in the literature.^{1a} Some of them were concentrated using a column of Dowex 50W-X2 resin before further preparation.

Preparation. [Mo₃S₄(DTP)₄(CH₃CN)]. All the reagents described below are directly used without further purification. Mo₃S₄⁴⁺(aq) (0.25

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[⊗] Instead of using the lengthy [Mo₃(μ₃-S)(μ-S)₃(μ-DTP)(DTP)₃(CH₃CN)], we preferred the concise one [Mo₃S₄(DTP)₄(CH₃CN)] for all the compounds appearing in this paper. Detailed structural information for these clusters is shown in Charts 2–5 in this paper.

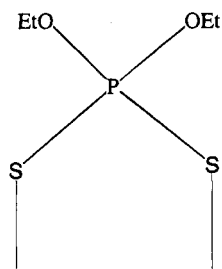
[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1994.

- (1) For example, (a) Mo₃O_nS_{4-n}⁴⁺(aq), *n* = 0–3: Shibahara, T.; Akashi, H. *Inorg. Synth.* **1992**, *29*, 254, 260. (b) Mo₃S₄⁴⁺(aq): Shibahara, T.; Yamasaki, M.; Sakane, G.; Minami, K.; Yabuki, T.; Ichimura, A. *Inorg. Chem.* **1992**, *31*, 640. (c) Mo₃O₄⁴⁺(aq): Richens, D. T.; Sykes, A. G. *Inorg. Synth.* **1985**, *23*, 130.
- (2) For example, (a) Sakane, G.; Yao, Y.-G.; Shibahara, T. *Inorg. Chim. Acta* **1994**, *216*, 13. (b) Shibahara, T.; Yamasaki, M.; Akashi, H.; Katayama, T. *Inorg. Chem.* **1991**, *30*, 2693.
- (3) For example: Shibahara, T.; Mochida, S.; Sakane, G. *Chem. Lett.* **1993**, 89.

(4) Heaton, B. T. *Pure Appl. Chem.* **1988**, *60*, 1757 and the references therein.

(5) For example, for ¹H: (a) Sola, M.; Cowan, J. A.; Gray, H. B. *J. Am. Chem. Soc.* **1989**, *111*, 6627. For ⁹⁵Mo: (b) Coddington, J. M.; Taylor, M. J. *J. Chem. Soc., Dalton Trans.* **1990**, 41. For ³¹P: (c) Ceconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Vacca, A.; Ramirez, J. A. *J. Chem. Soc., Dalton Trans.* **1990**, 773. (d) Carlin, R. T.; McCarley, R. E. *Inorg. Chem.* **1989**, *28*, 3432. For ³³S: (e) Kony, M.; Brownlee, R. T. C.; Wedd, A. G. *Inorg. Chem.* **1992**, *31*, 2281.

Chart 1. Schematic Views of Diethyl Dithiophosphate Ligand



M, per trimer 20 mL) in 2 M hydrochloric acid was mixed with HDTP solution of ethanol (1.0 M, 20 mL) which was prepared by dissolving P₄S₁₀ (diphosphorus pentasulfide, 10.0 g) in ethanol (100 mL) followed by filtration. A black oily material deposited immediately and solidified overnight. When separated, the solid was dissolved in acetonitrile (about 30 mL), forming a solution with dark brown color which was then kept in a freezer for 2 days until the sample recrystallized out of it. The product was collected and washed with a small amount of diethyl ether and air dried: yield 4.9 g (82%). Anal. Found (calcd): C, 17.27 (18.05); H, 3.58 (3.62); N, 0.76 (1.17). The result of elemental analysis shows that the crystals seem to lose some of the ligating acetonitrile. Further discussion will be described in the Results and Discussion.

[Mo₃S₄(OAc)(DTP)₃(Py)]. A similar compound [Mo₃S₄(C₂H₅CO₂)(DTP)₃(Py)] had been already prepared using a different starting material.^{6a} The route described below is an amendment of it. [Mo₃S₄(DTP)₄(CH₃CN)] (0.5 g), obtained as above, was mixed with ethanol (20 mL), acetic anhydride (1.0 mL) and pyridine (Py, 0.5 mL). This mixture was refluxed over a hot water bath for about 5 h until all the solid was dissolved. It was then filtered and cooled to room temperature. This dark clear solution, after standing for several days, gave good-shaped black crystals, which were collected by filtration and dried as above: yield 0.19 g (40%). Anal. Found (calcd): C, 20.56 (20.56); H, 3.46 (3.45); N, 1.29 (1.26).

[Mo₃OS₃(DTP)₄(CH₃CN)]. The preparation of this compound is like that of [Mo₃S₄(DTP)₄(CH₃CN)]. A black crystalline sample was obtained from Mo₃OS₃⁴⁺(aq) (0.18 M per trimer, 20 mL): yield 3.8 g (89%). Anal. Found (calcd): C, 18.14 (18.29); H, 3.62 (3.67); N, 1.16 (1.19).

[Mo₃OS₃(OAc)(DTP)₂(Py)₂(OC₂H₅)]. The main route of this preparation is like that of [Mo₃S₄(OAc)(DTP)₃(Py)]. [Mo₃OS₃(DTP)₄(CH₃CN)] (0.5 g), obtained as above, was mixed with ethanol (20 mL), acetic anhydride (1.0 mL), and pyridine (0.5 mL). This mixture was refluxed over a hot water bath for about 5 h until all the solid was dissolved. It was then filtered and cooled to room temperature. This dark clear solution, after standing for several days, gave good-shaped black crystals, which were collected by filtration and dried as above: yield 0.14 g (24%). Anal. Found (calcd): C, 25.53 (25.59); H, 3.55 (3.71); N, 2.77 (2.71).

[Mo₃OS₃(DTP)₄(H₂O)]. This compound was collected by picking the black crystals manually out of the solidified material before recrystallization from CH₃CN during the preparation of [Mo₃OS₃(DTP)₄(CH₃CN)]. Anal. Found (calcd): C, 16.55 (16.58); H, 3.53 (3.65).

[Mo₃O₂S₂(DTP)₄(Py)]. Mo₃O₂S₂⁴⁺(aq) (0.08 M per trimer, 40 mL) in 1 M HCl was reacted with 1 M HDTP solution in ethanol (20 mL). Following the same process as for [Mo₃S₄(DTP)₄(CH₃CN)], recrystallization from acetonitrile containing a small amount of pyridine gave a green crystalline product: yield 2.5 g (65%). Anal. Found (calcd): C, 21.79 (20.95); H, 3.52 (3.77); N, 1.43 (1.16).

[Mo₃O₃S(DTP)₄(H₂O)]. Black product was obtained from a Mo₃O₃S⁴⁺(aq) (0.04 M per trimer, 25 mL) in 1 M HCl by the method described for [Mo₃OS₃(DTP)₄(H₂O)]: yield 0.52 g (44%). Anal. Found (calcd): C, 17.66 (17.06); H, 3.54 (3.76).

Table 1. Crystallographic Data for [Mo₃OS₃(DTP)₄(CH₃CN)] and [Mo₃OS₃(OAc)(DTP)₂(Py)₂(OC₂H₅)]

	Mo ₃ S ₁₁ P ₄ O ₉ NC ₁₈ H ₄₃	Mo ₃ S ₇ P ₂ O ₈ N ₂ C ₂₂ H ₃₈
formula	Mo ₃ S ₁₁ P ₄ O ₉ NC ₁₈ H ₄₃	Mo ₃ S ₇ P ₂ O ₈ N ₂ C ₂₂ H ₃₈
fw	1181.98	1032.78
space group	P $\bar{1}$	P $\bar{1}$
a, Å	14.134(13)	13.985(7)
b, Å	16.413(16)	14.359(7)
c, Å	10.654(9)	12.012(4)
α, deg	98.08(10)	96.01(3)
β, deg	112.23(6)	104.37(3)
γ, deg	77.03(9)	114.20(3)
V, Å ³	2225.3(37)	2072.3(17)
Z	2	2
T, °C	18	18
λ(Mo Kα), Å	0.710 73	0.710 73
d _{obsd} , g/cm ³	unknown	1.65
d _{calcd} , g/cm ³	1.764	1.655
μ, cm ⁻¹	14.9	13.3
R, %	5.0	4.5
R _w , %	6.2	7.0

Structural Determinations. A dark red crystal (dimensions 0.45 × 0.28 × 0.28) of [Mo₃OS₃(DTP)₄(CH₃CN)] and a dark red crystal (dimensions 0.30 × 0.22 × 0.16) of [Mo₃OS₃(OAc)(DTP)₂(Py)₂(OC₂H₅)] were mounted in glass capillaries. The crystallographic data are given in Table 1. Cell constants and orientation matrices for the crystals were obtained from least-squares refinement, by using setting angles of 25 reflections in the range 20 < 2θ < 30° measured on a Rigaku AFC-6S diffractometer by use of Mo Kα radiation (λ = 0.710 73 Å). The intensities of standard reflections monitored after every 150 reflections did not show any appreciable decay. Intensities were corrected for polarization and Lorentz factors but not for absorption. All the structures were solved by SHELXS and refined by the block-diagonal least-squares method. Computations were performed on a FACOM M380 at Okayama University of Science using the programs in the CRYSTAN package. The atomic coordinates and thermal parameters for [Mo₃OS₃(DTP)₄(CH₃CN)] and [Mo₃OS₃(OAc)(DTP)₂(Py)₂(OC₂H₅)] are listed in Tables 2 and 3, respectively.

NMR Measurements. ³¹P NMR measurements were carried out using a 10 mm NMR tube on a JEOL GX400 NMR spectrometer at Analytical Center, Okayama University of Science, with external reference to 85% H₃PO₄. The reference sample was prepared by sealing a capillary containing 85% H₃PO₄ in a 5 mm NMR tube inside which a suitable amount of deuterated chloroform was inserted for field locking. The sample compounds were dissolved in the solvent DCB (*o*-dichlorobenzene) just before the measurements. Each spectrum was accumulated 128 times to secure adequate resolution.

Results and Discussion

Preparation. The ligand HDTP is very convenient for the preparation of trinuclear and tetranuclear molybdenum and tungsten cluster compounds. By direct reaction of HDTP with MoCl₃·3H₂O, several new clusters were prepared by Lu et al.⁶ The restriction of this spontaneous self-assembly method is that it cannot be used to synthesize all of the samples in this paper. Since a series of the incomplete cubane-type clusters, Mo₃-O_nS_{4-n}⁴⁺(aq), (n = 0–3), were synthesized by the present authors with a good yield and purity in aqueous hydrochloric acid solution,^{1a,b} it is possible to use HDTP to prepare the DTP compounds of this cluster series in crystalline form. The preparative methods described here turned out to be very successful in the both respects of simplicity and high yield. The number of μ-O and μ-S moieties in the core remained unchanged after these reactions.

Two kinds of pretreatment were done for the elemental analysis of [Mo₃S₄(DTP)₄(CH₃CN)]. The first sample was dried in air and analyzed as described in the Experimental Section. The second sample was dried under vacuum since the first elemental analysis showed loss of some of the coordinated acetonitrile in the cluster. The result of the second elemental analysis was as follows: Anal. Found (calcd for [Mo₃S₄(DTP)₄]): C, 17.00 (16.61); H, 3.44 (3.48); N, 0.74 (0.00). These

(6) (a) Hu, J.; Zhuang, H.-H.; Huang, J.-Q.; Huang, J.-L. *Jiegou Huaxue (J. Struct. Chem.)* **1989**, 8, 6. (b) Huang, J.-Q.; Huang, J.-L.; Shang, M.-Y.; Lu, S.-F.; Lin, X.-T.; Lin, Y.-H.; Huang, M.-D.; Zhuang, H.-H.; Lu, J.-X. *Pure Appl. Chem.* **1988**, 60, 1185. (c) Lin, X.-T.; Lin, Y.-H.; Huang, J.-L.; Huang, J.-Q.; *Kexue Tongbao* **1986**, 509.

Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors for $[\text{Mo}_3\text{OS}_3(\text{DTP})_4(\text{CH}_3\text{CN})]^{2+}$

atom	x	y	z	$B_{\text{eq}}/\text{\AA}^2$
Mo1	0.6789(1)	0.78114(4)	0.8150(1)	3.88(2)
Mo2	0.6855(1)	0.61560(4)	0.8258(1)	3.78(2)
Mo3	0.7981(1)	0.67297(5)	0.7066(1)	3.69(2)
S1	0.6164(2)	0.6882(1)	0.6271(2)	4.0(1)
S2	0.7116(2)	0.7139(1)	1.0055(2)	4.5(1)
S3	0.8608(2)	0.5748(1)	0.8658(2)	4.2(1)
O	0.8223(4)	0.7684(3)	0.8277(5)	4.2(2)
S11	0.7128(2)	0.9108(2)	0.9762(3)	5.9(1)
S12	0.6240(2)	0.8963(2)	0.6507(2)	5.5(1)
S21	0.7096(2)	0.5090(2)	0.9967(2)	5.3(1)
S22	0.6400(2)	0.4848(2)	0.6734(3)	5.6(1)
S31	0.9871(2)	0.6585(2)	0.7171(2)	5.5(1)
S32	0.7724(2)	0.7443(2)	0.4966(2)	5.2(1)
S41	0.4911(2)	0.8359(2)	0.8145(3)	5.7(1)
S42	0.4936(2)	0.6316(2)	0.8148(3)	5.3(1)
P1	0.6762(2)	0.9733(2)	0.8125(3)	5.8(1)
P2	0.6839(2)	0.4241(2)	0.8413(3)	5.7(1)
P3	0.9258(2)	0.7188(2)	0.5472(3)	5.9(1)
P4	0.4166(2)	0.7408(2)	0.7409(3)	5.2(1)
O11	0.5987(6)	1.0585(4)	0.8113(8)	7.8(3)
O12	0.7691(6)	1.0100(4)	0.8105(8)	7.3(3)
O21	0.6029(6)	0.3704(4)	0.8360(8)	7.4(3)
O22	0.7786(6)	0.3512(5)	0.8558(9)	10.4(4)
O31	0.9595(6)	0.6755(6)	0.4281(7)	8.2(3)
O32	0.9730(7)	0.8023(5)	0.5685(8)	9.2(4)
O41	0.3767(5)	0.7299(4)	0.5821(6)	6.4(3)
O42	0.3102(5)	0.7629(4)	0.7668(7)	6.6(3)
C11	0.496(1)	1.0583(9)	0.820(2)	11.9(8)
C12	0.426(1)	1.111(2)	0.753(2)	20.1(1)
C13	0.8664(9)	0.9527(7)	0.807(1)	9.0(6)
C14	0.938(1)	1.0045(9)	0.799(2)	10.3(7)
C21	0.4921(9)	0.4114(9)	0.816(2)	9.8(7)
C22	0.432(1)	0.346(1)	0.780(1)	10.8(7)
C23	0.8781(8)	0.3516(8)	0.908(1)	9.8(6)
C24	0.9417(9)	0.2633(7)	0.904(1)	8.4(5)
C31	0.919(1)	0.6021(8)	0.354(1)	8.8(6)
C32	0.9596(9)	0.5810(8)	0.239(1)	8.2(5)
C33	0.996(2)	0.857(2)	0.479(2)	23.2(2)
C34	0.903(2)	0.878(2)	0.392(3)	21.2(2)
C41	0.318(2)	0.802(1)	0.495(1)	14.1(1)
C42	0.343(2)	0.806(1)	0.406(2)	15.1(1)
C43	0.3065(9)	0.781(1)	0.906(1)	9.8(6)
C44	0.209(1)	0.831(1)	0.897(2)	12.3(8)
N	0.7906(5)	0.5606(4)	0.5541(6)	4.2(2)
C1	0.7803(6)	0.5022(6)	0.4853(8)	4.7(3)
C2	0.7660(8)	0.4270(7)	0.395(1)	7.5(5)

^a Equivalent isotropic temperature factors ($B_{\text{eq}} = \frac{1}{3}\{\sum B_{ij}a_i a_j\}$).

results indicate that the cluster loses some of the coordinated acetonitrile in the air, but does not lose it thoroughly even under vacuum.

The coordinated water molecules of $[\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{H}_2\text{O})]^{6b,6c}$ and $[\text{Mo}_3\text{OS}_3(\text{DTP})_4(\text{H}_2\text{O})]$ are easily replaced on recrystallization from acetonitrile, but that of $[\text{Mo}_3\text{O}_3\text{S}(\text{DTP})_4(\text{H}_2\text{O})]$ is not replaced by the recrystallization: after recrystallization from the solution of CH_3CN the elemental analysis of the product matched only the formula with coordinated H_2O instead of CH_3CN . It seems that the presence of $\mu\text{-S}$ increases the lability of molybdenum atoms in the clusters.⁷ We failed in the preparation of the analogous compound of $\text{Mo}_3\text{O}_4^{4+}(\text{aq})$ in this series, for the oily material obtained after the reaction did not solidify even if it was kept under N_2 atmosphere to avoid air oxidation for a few weeks.

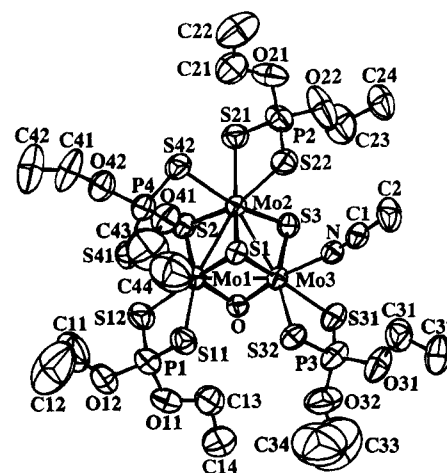
Structural Characterization. The X-ray structure of $[\text{Mo}_3\text{OS}_3(\text{DTP})_4(\text{CH}_3\text{CN})]$ is shown in Figure 1 and the selected bond distances and angles were shown in Table 4. The structure analysis revealed the existence of the Mo_3OS_3 core with four

Table 3. Atomic Coordinates and Equivalent Isotropic Temperature Factors for $[\text{Mo}_3\text{OS}_3(\text{OAc})(\text{DTP})_2(\text{Py})_2(\text{OC}_2\text{H}_5)]^{2+}$

atom	x	y	z	$B_{\text{eq}}/\text{\AA}^2$
Mo1	-0.1590(1)	0.12224(4)	0.18255(5)	2.92(2)
Mo2	-0.26741(4)	0.18620(4)	0.31093(5)	2.78(2)
Mo3	-0.28525(4)	-0.01199(4)	0.27663(5)	2.68(2)
S1	-0.3522(1)	0.0623(1)	0.1291(1)	3.2(1)
S2	-0.0854(1)	0.2754(1)	0.3211(1)	3.6(1)
S3	-0.2348(1)	0.1008(1)	0.4563(1)	3.2(1)
O1	-0.1316(3)	0.0374(3)	0.2838(3)	3.2(2)
P1	-0.0017(2)	0.2419(1)	0.0425(2)	4.3(1)
P2	-0.2808(2)	0.4037(1)	0.3478(2)	4.9(1)
S11	0.0385(2)	0.1758(1)	0.1717(2)	4.5(1)
S12	-0.1614(2)	0.2064(1)	0.0064(2)	4.6(1)
S21	-0.2259(2)	0.3417(1)	0.4756(2)	4.6(1)
S22	-0.3327(2)	0.3006(1)	0.1952(2)	4.5(1)
O11	0.0287(4)	0.2123(4)	-0.0680(4)	5.0(2)
O12	0.0753(5)	0.3636(4)	0.0683(5)	7.1(3)
O21	-0.3728(5)	0.4360(4)	0.3662(5)	6.6(3)
O22	-0.1960(5)	0.5161(4)	0.3479(5)	6.7(3)
C11	-0.0197(7)	0.0976(6)	-0.1233(7)	6.1(4)
C12	-0.0049(8)	0.1000(7)	-0.2459(7)	7.0(4)
C13	0.085(1)	0.436(1)	0.159(1)	14.7(9)
C14a	0.143(2)	0.546(2)	0.142(2)	14.7(8) ^b
C14b	0.196(3)	0.496(3)	0.224(3)	12.1(1) ^b
C21	-0.4795(8)	0.3587(8)	0.372(1)	9.0(5)
C22	-0.561(1)	0.400(1)	0.337(2)	11.1(1)
C23	-0.0934(8)	0.5332(7)	0.321(1)	9.2(5)
C24	-0.0550(9)	0.6279(9)	0.281(1)	15.5(6)
N2	-0.4478(4)	0.1247(4)	0.3234(5)	3.4(2)
N3	-0.2457(4)	-0.1221(4)	0.3778(4)	3.2(2)
Cp21	-0.5403(5)	0.0891(5)	0.2262(6)	3.9(3)
Cp22	-0.6456(6)	0.0534(6)	0.2316(7)	5.0(3)
Cp23	-0.6580(6)	0.0564(6)	0.3441(8)	5.8(3)
Cp24	-0.5629(6)	0.0921(6)	0.4498(7)	5.0(3)
Cp25	-0.4595(6)	0.1258(5)	0.4334(6)	3.9(3)
Cp31	-0.1470(6)	-0.0881(5)	0.4621(6)	3.8(3)
Cp32	-0.1144(6)	-0.1590(6)	0.5179(6)	4.8(3)
Cp33	-0.1902(7)	-0.2667(6)	0.4849(7)	5.0(3)
Cp34	-0.2900(7)	-0.3008(6)	0.3958(8)	6.1(4)
Cp35	-0.3160(6)	-0.2262(5)	0.3436(7)	4.9(3)
O31	-0.4334(3)	-0.1117(3)	-0.1117(3)	3.7(2)
C31	-0.5386(6)	-0.1567(6)	0.1726(7)	5.9(3)
C32	-0.6175(9)	-0.241(1)	0.191(1)	18.3(8)
Ob1	-0.2042(4)	-0.0170(3)	0.0416(3)	3.8(2)
Ob2	-0.3080(3)	-0.1305(3)	0.1307(4)	3.8(2)
Cb1	-0.2634(6)	-0.1092(6)	0.0496(6)	3.9(3)
Cb2	-0.2838(6)	-0.2005(5)	-0.0431(6)	5.0(3)

^a Equivalent isotropic temperature factors ($B_{\text{eq}} = \frac{1}{3}\{\sum B_{ij}a_i a_j\}$).

^b Isotropic temperature factors were used. The following occupancy factors were used for the disordered atoms: C14a, 0.6; C14b, 0.4.

**Figure 1.** Perspective view of $[\text{Mo}_3\text{OS}_3(\text{DTP})_4(\text{CH}_3\text{CN})]$ showing the atom-labeling scheme.

DTP ligands together with an acetonitrile ligand. The structure of $[\text{Mo}_3\text{OS}_3(\text{OAc})(\text{DTP})_2(\text{Py})_2(\text{OC}_2\text{H}_5)]$ is also shown in Figure 2 and the selected bond distances and angles were shown in

(7) Richens, D. T.; Pittet, P. -A.; Merbach, A. E.; Humanes, M.; Lamprecht, G. J.; Ooi, B. -L.; Sykes, A. G. *J. Chem. Soc. Dalton Trans.* **1993**, 15, 2305.

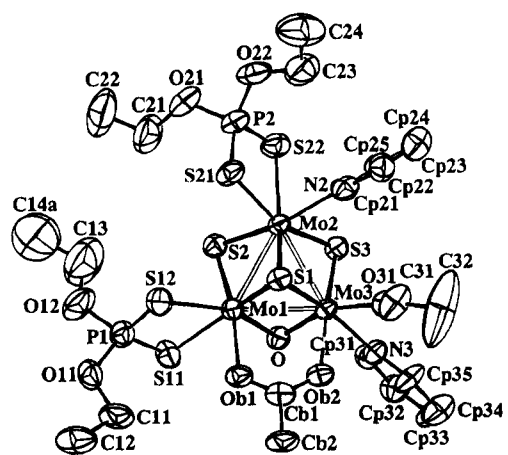


Figure 2. Perspective view of $[\text{Mo}_3\text{OS}_3(\text{OAc})(\text{DTP})_2(\text{Py})_2(\text{OC}_2\text{H}_5)]$ showing the atom-labeling scheme.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) in $[\text{Mo}_3\text{OS}_3(\text{DTP})_4(\text{CH}_3\text{CN})]$

Mo1–Mo2	2.715(2)	S2–Mo2–S3	93.0(1)
Mo1–Mo3	2.621(2)	S2–Mo1–O	97.5(2)
Mo2–Mo3	2.751(2)	S3–Mo3–O	97.7(2)
Mo1–S1	2.350(2)	S1–Mo2–S2	107.2(1)
Mo2–S1	2.339(1)	S1–Mo2–S3	105.5(1)
Mo3–S1	2.343(2)	S1–Mo1–S2	107.0(1)
Mo1–S2	2.291(2)	S1–Mo3–S3	105.7(1)
Mo2–S2	2.294(2)	S1–Mo1–O	100.7(2)
Mo2–S3	2.303(3)	S1–Mo3–O	102.5(2)
Mo3–S3	2.291(2)	Mo1–S1–Mo2	70.7(1)
Mo1–O	1.944(3)	Mo2–S1–Mo3	71.9(1)
Mo3–O	1.890(4)	Mo1–S1–Mo3	67.9(1)
Mo1–S11	2.552(3)	Mo1–S2–Mo2	72.6(1)
Mo1–S12	2.546(3)	Mo2–S3–Mo3	73.6(1)
Mo2–S21	2.578(5)	Mo1–O–Mo3	86.3(2)
Mo2–S22	2.550(3)	S1–Mo1–S11	164.8(1)
Mo3–S31	2.588(5)	S1–Mo2–S21	160.1(1)
Mo3–S32	2.537(3)	S1–Mo3–S31	162.6(1)
Mo1–S41	2.603(4)	S1–Mo1–S12	88.3(1)
Mo2–S42	2.624(3)	S1–Mo2–S22	86.9(1)
S11–P1	1.984(3)	S1–Mo3–S32	86.6(1)
S12–P1	1.988(3)	S1–Mo1–S41	90.4(1)
S21–P2	1.985(4)	S1–Mo2–S42	87.1(1)
S22–P2	1.991(4)	S1–Mo3–N	84.9(2)
S31–P3	1.979(3)		
S32–P3	1.983(4)		
S41–P4	1.982(4)		
S42–P4	1.973(4)		
Mo2–Mo1–Mo3	62.0(1)		
Mo1–Mo2–Mo3	57.32(4)		
Mo1–Mo3–Mo2	60.6(1)		

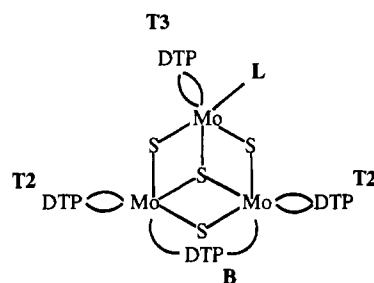
Table 5. The carbon atom C14 is disordered. Since two peaks were disclosed by fourier synthesis, we assigned the peaks to C14a and C14b. The occupancy factors of C14a and C14b are 0.6 and 0.4 respectively. Only C14a is included in ORTEP drawing (Figure 2) of $[\text{Mo}_3\text{OS}_3(\text{DTP})_4(\text{CH}_3\text{CN})]$ for clarity. The Mo_3OS_3 core remained unchanged after ligand substitution of Py for CH_3CN , and of bridging OAc for DTP. This cluster is very informative for the assignment of chemical shifts as described in the “NMR Measurements” section below. The ethyl groups in the DTP ligands have statistical disorder, and the B_{eq} values of the ethyl carbon atoms become high in these two cluster compounds.

Before the assignment of chemical shifts to each DTP ligand, it is necessary to make some definitions on the DTP positions

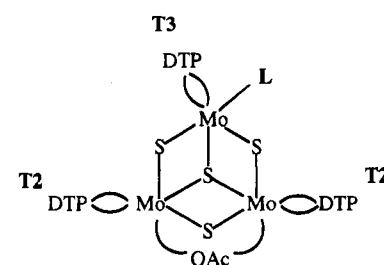
Table 5. Selected Interatomic Distances (Å) and Angles (deg) in $[\text{Mo}_3\text{OS}_3(\text{OAc})(\text{DTP})_2(\text{Py})_2(\text{OC}_2\text{H}_5)]$

Mo1–Mo2	2.743(1)	S2–Mo1–O	98.4(1)
Mo1–Mo3	2.601(1)	S3–Mo3–O	91.6(1)
Mo2–Mo3	2.730(2)	S1–Mo1–S2	104.7(1)
Mo1–S1	2.359(2)	S1–Mo3–S3	106.8(1)
Mo2–S1	2.348(2)	S1–Mo2–S2	104.5(1)
Mo3–S1	2.354(2)	S1–Mo2–S3	107.6(1)
Mo1–S2	2.279(2)	S1–Mo1–O	104.0(1)
Mo2–S2	2.296(2)	S1–Mo3–O	102.5(1)
Mo2–S3	2.296(2)	Mo1–S1–Mo2	71.3(1)
Mo3–S3	2.314(2)	Mo1–S1–Mo3	67.0(1)
Mo1–O	1.890(5)	Mo2–S1–Mo3	71.0(1)
Mo3–O	1.943(4)	Mo1–S2–Mo2	73.7(1)
Mo1–S11	2.589(3)	Mo2–S3–Mo3	72.6(1)
Mo1–S12	2.544(2)	Mo1–O–Mo3	85.4(2)
Mo2–S21	2.584(2)	S1–Mo1–S11	162.4(1)
Mo2–S22	2.558(3)	S1–Mo2–S21	159.9(1)
Mo1–Ob1	2.233(5)	S1–Mo1–S12	88.1(1)
Mo3–Ob2	2.174(5)	S1–Mo2–S22	84.8(1)
Mo2–N2	2.357(6)	S1–Mo1–Ob1	84.0(1)
Mo3–N3	2.252(6)	S1–Mo3–Ob2	85.4(1)
S11–P1	1.984(3)	S1–Mo3–O31	91.8(1)
S12–P1	1.994(3)	S1–Mo2–N2	85.1(1)
S21–P2	2.000(3)	S1–Mo3–N3	164.5(1)
S22–P2	1.993(3)		
Mo2–Mo1–Mo3	61.38(4)		
Mo1–Mo2–Mo3	56.75(3)		
Mo1–Mo3–Mo2	61.87(4)		
S2–Mo2–S3	95.4(1)		

Chart 2. Schematic Views of (a) $[\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{CH}_3\text{CN})]$ and $[\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{H}_2\text{O})]$ and (b) $[\text{Mo}_3\text{S}_4(\text{OAc})(\text{DTP})_3(\text{Py})]$



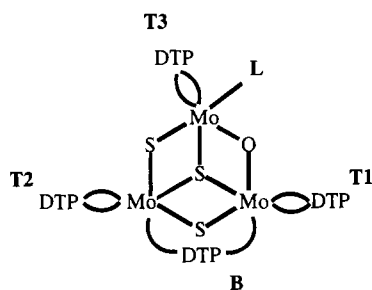
a, L = CH_3CN , H_2O



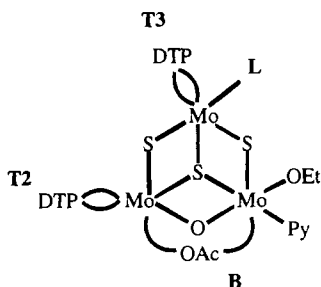
b, L = Pyridine

in the molecule. The schematic views of all samples were shown in Charts 2–5. The crystal structures of the $[\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{H}_2\text{O})]$ and $[\text{Mo}_3\text{S}_4(\text{OAc})(\text{DTP})_3(\text{Py})]$ (in Chart 2) have been reported.⁶ The structures $[\text{Mo}_3\text{OS}_3(\text{DTP})_4(\text{CH}_3\text{CN})]$ and $[\text{Mo}_3\text{OS}_3(\text{OAc})(\text{DTP})_2(\text{Py})_2(\text{OC}_2\text{H}_5)]$, whose schematic views are drawn in Chart 3, are reported in this paper. The schematic views of $[\text{Mo}_3\text{O}_2\text{S}_2(\text{DTP})_4(\text{Py})]$ and $[\text{Mo}_3\text{O}_3\text{S}(\text{DTP})_4(\text{H}_2\text{O})]$ in Charts 4 and 5 were assumed, the correctness of which was

Chart 3. Schematic Views of (a) $[\text{Mo}_3\text{OS}_3(\text{DTP})_4(\text{CH}_3\text{CN})]$, $[\text{Mo}_3\text{OS}_3(\text{DTP})_4(\text{H}_2\text{O})]$, and $[\text{Mo}_3\text{OS}_3(\text{DTP})_4(\text{Py})]$ and (b) $[\text{Mo}_3\text{OS}_3(\text{OAc})(\text{DTP})_2(\text{Py})_2(\text{OC}_2\text{H}_5)]$

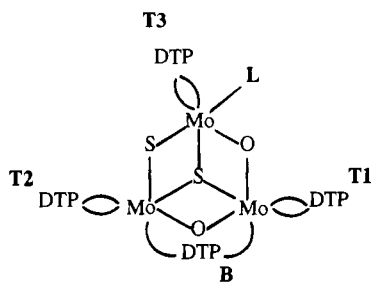


a, L = CH_3CN , H_2O and Py

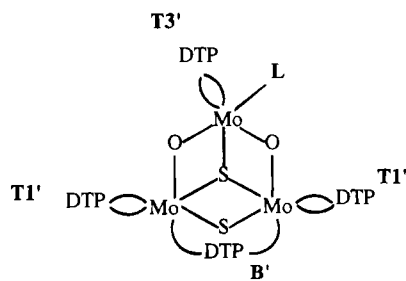


b, L = Py

Chart 4. Two Isomers of $[\text{Mo}_3\text{O}_2\text{S}_2(\text{DTP})_4(\text{Py})]$ Derived from the Different Ligand Distributions around the Cluster Core



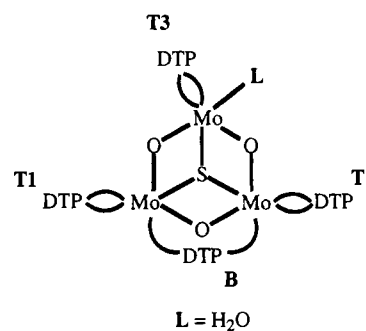
a, isomer 1, L = Pyridine



b, isomer 2, L = Pyridine

supported by the NMR studies as we shall see later in the discussion section. In Charts 2a, 3a, 4, and 5, the four DTP ligands are coordinated to the each cluster core with two modes—that is, three of terminal and one of bridging. The terminal ones are divided into two kinds—with or without the solvent ligand L to the same Mo atom. The two DTP's without L, situated along the horizontal line in Charts 3a and 4 also differ in their relative position to $\mu\text{-O}$. In the following discussion we named the bridging DTP by B, the terminal DTP with L by T3. The two DTP ligands without L were named T1 and T2, respectively—so that there was a $\mu\text{-O}$ between T1 and T3 and a $\mu\text{-S}$ between T2 and T3, instead.

Chart 5. Schematic View of $[\text{Mo}_3\text{O}_3\text{S}(\text{DTP})_4(\text{H}_2\text{O})]$



^{31}P NMR. The coordinated ligand L and the bulk solvent have a great influence on the ^{31}P NMR appearance of DTP ligands.

At first stage, several solvents were tested to prepare the NMR solution for the measurement. It was found that the chemical shifts and their relative positions were very sensitive to the kinds of solvents. Those solvents with high nucleophilicity, such as CH_3CN , tended to shift the whole spectra considerably, to change the peak intensities, and to decompose the cluster samples. It is of importance to minimize the complexity of the investigation system, so DCB was selected at last as the main solvent of the measurements because most samples have a good stability in it at room temperature and their chemical shifts do not seem to have a very intense solvent effect due to it, for only a small shift difference of $\sim\pm 0.1$ ppm was experienced when measuring an identical sample in different concentrations.

The bulk solvent played a dual role with respect to the absolute chemical shift and the ligand exchange with the coordinated molecule, so that the NMR measurements in different solvents presented important information for the spectrum assignments and structural descriptions as demonstrated below.

Clusters with Mo_3S_4 Cores. In Figure 3, spectra 1 and 2 are of $[\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{CH}_3\text{CN})]$ (see Chart 2a) and $[\text{Mo}_3\text{S}_4(\text{OAc})(\text{DTP})_3(\text{Py})]$ (see Chart 2b), respectively. In the latter, only two peaks appeared as shown in spectrum 2, which is due to the loss of the bridging DTP. The latter is the derivative of the former through the ligand substitutions of Py for CH_3CN , and of bridging OAc for DTP, so the peak at lower field with the relative intensity of 2 in spectrum 2 was assigned to T2, the remaining one in spectrum 2 was assigned to T3. As a matter of fact, T2, the horizontal DTP, is a collection of two sterically distinct DTP's, but they were indistinguishable in the spectrum. At lower temperature, -20°C , the phosphorus, however, showed the static spectrum consisting of three signals (spectrum 3). These data indicate that the stereochemical nonequivalence of the DTP (T2)'s observed in the solid state is retained even in the solution at low temperatures. They, however, equalized somewhat at 20°C by the effect of dynamic behavior of terminal DTP (T3) and loosely-coordinated ligand L. Spectra 2 and 3 gave broad peak appearances. It is the effect from the substituted bridging OAc ligand which made the two horizontal terminal ligands more dynamically active.

The peak with relatively double intensity in spectrum 1 was assigned to T2 in the same way as it was done with spectrum 2. We assigned the other two peaks to T3 and B based on the comparison between these two spectra. The terminal DTP's should have similar shifts, so that the bridging DTP was located at the highest field. As it is shown afterwards, this feature that T2 always situated at the lower field, and B at the higher field in the spectra of these clusters with Mo_3S_4 cores will remain in most spectra of the other clusters.

Clusters with Mo_3OS_3 Cores. Spectra of $[\text{Mo}_3\text{OS}_3(\text{DTP})_4(\text{L})]$, where L = CH_3CN , H_2O , or Py in the solvents of

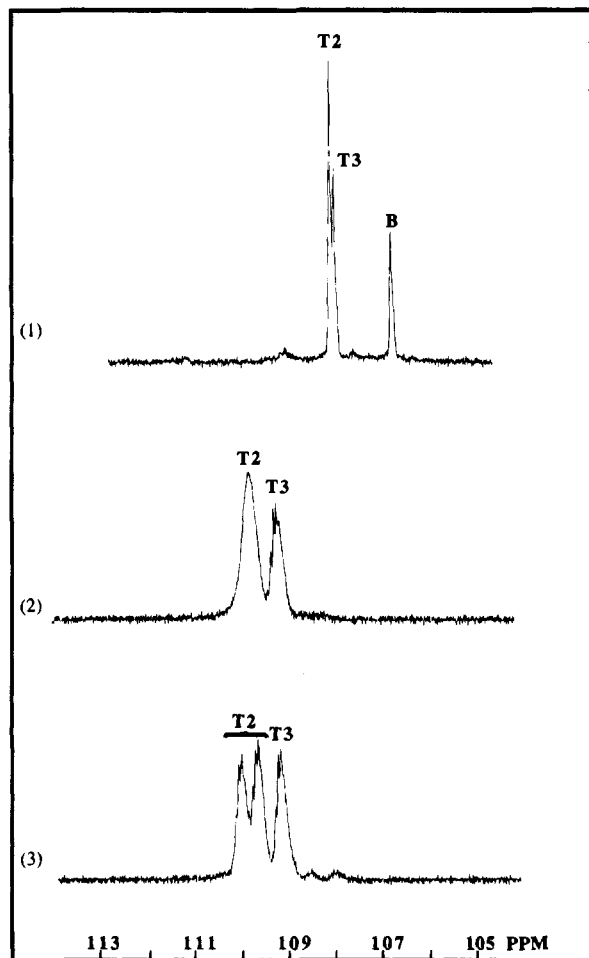


Figure 3. Decoupled ³¹P NMR spectra of the cluster compounds: (1) [Mo₃S₄(DTP)₄(CH₃CN)] in DCB (*o*-dichlorobenzene), at 20 °C, δ 108.20 (T₂), 108.6 (T₃), 106.92 (B); (2) [Mo₃S₄(OAc)(DTP)₃(Py)] in DCB, at 20 °C, δ 109.79 (T₂), 109.21 (T₃); (3) [Mo₃S₄(OAc)(DTP)₃(Py)] in DCB, at -20 °C, δ 110.03 (T₂), 109.68 (T₂), 109.20 (T₃).

DCB or CH₃CN, are shown in Figure 4 and the schematic view of the structure was shown in Chart 3a. Spectra 4 and 7 show that changing the bulk solvent from DCB to CH₃CN shifts all peaks in the spectrum down to the lower field about 1 ppm. When the loosely-coordinated ligand L changed from CH₃CN to H₂O, two peaks shifted while the other two peaks remained almost unchanged as can be seen from spectra 4 and 5. The second peak from the left in spectrum 4 shifted significantly to the lowest field in spectrum 5. The identification of this peak was accomplished by comparing spectra 4 and 5 together with spectrum 6, which was obtained by adding a drop of Py into the same NMR tube containing the sample solution of spectrum 5 and then measuring the spectrum immediately. Furthermore, when the bulk solvent changed to CH₃CN, the peak shifted closer to the first peak from the left in spectrum 4, coalescing into one peak as a result in spectrum 7. Spectrum 8 is the corresponding decoupled one of spectrum 7 in which two peaks at low field merged into one because of proton coupling.

All the above facts showed that the loosely-coordinated ligand L can be easily replaced by other stronger ligands. The ligand site is kinetically active for ligand exchange, so the nucleophilic solvents, like CH₃CN or pyridine, will exchange with it, even the less nucleophilic solvents like DCB to some extent. The consequence of these processes will effect the nearby T₃ ligand most, causing it to rotate or fluctuate around its coordination site. So we assigned that peak, which changed most in the four spectra of Figure 4, to T₃. The remaining three peaks in spectra 4–6 in Figure 4 have a similar pattern, so they will be allocated

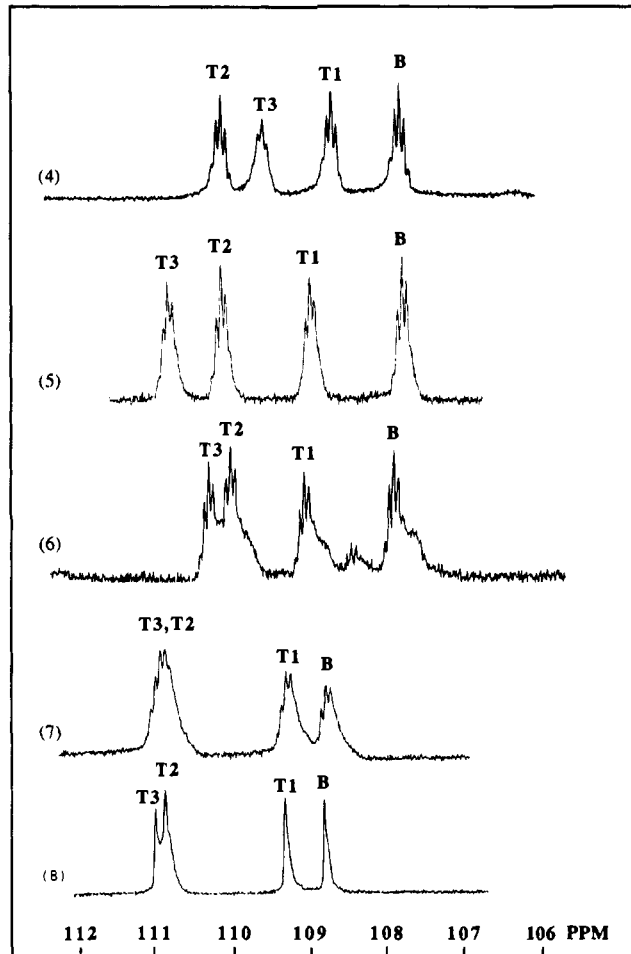


Figure 4. Nondecoupled ³¹P NMR spectra of [Mo₃OS₃(DTP)₄(L)] in different solvents: (4) L = CH₃CN in DCB, at 20 °C, δ 110.13 (T₂), 109.59 (T₃), 108.63 (T₁), 107.74 (B); (5) L = H₂O in DCB, at 20 °C, δ 110.86 (T₃), 110.16 (T₂), 109.01 (T₁), 107.80 (B); (6) solution from spectrum 5 with a drop of pyridine added, at 20 °C δ 110.33 (T₃), 110.05 (T₂), 109.07 (T₁), 107.89 (B); (7) L = CH₃CN in CH₃CN, at 20 °C, δ 110.89 (T₂ and T₃), 109.32 (T₁), 108.08 (B); (8) sample from spectrum 7 with decoupling mode, at 20 °C, δ 111.02 (T₃), 110.89 (T₂), 109.32 (T₁), 108.80 (B).

in the same way for each spectrum. As in the case of the clusters with Mo₃S₄ cores, the peak at the highest field was assigned to the bridging DTP B, the peak at the lower field to the horizontal DTP T₂, and the remaining peak to T₁. The peaks corresponding to the two horizontal ligands, T₁ and T₂, are no longer one peak, and they are well split apart about 1.4 ppm. This is the effect of μ-O, which makes T₁ shift up the field relative to T₂, causing the chemical shift of T₁ close to B. That is to say, spectrum 4 was assigned in the sequence of T₂, T₃, T₁, and B from the left.

We are not concerned here with the NMR spectrum of [Mo₃-OS₃(OAc)(DTP)₂(Py)₂(OC₂H₅)]. Because it needs further consideration since that cluster compound gives very complicate spectrum. The magnetic susceptibility measurements showed that these are diamagnetic species.

[Mo₃O₂S₂(DTP)₄(C₅H₅N)]. Spectra of [Mo₃O₂S₂(DTP)₄(Py)] in the solvents DCB or CH₃CN are shown in Figure 5. The features in spectrum 9 are perplexing. The spectrum showed five peaks instead of two to four peaks in the other spectra. These five peaks had a rough intensity ratio of 4:1:1:1:1. In order to explain this complexity, we assume the existence of two isomers of the cluster compound in the solution in the proportion of 1:1 as illustrated in Chart 4. There will be eight different DTP ligands in this system correspondingly. If the number of sulfur and oxygen atoms ligated to molybdenum is

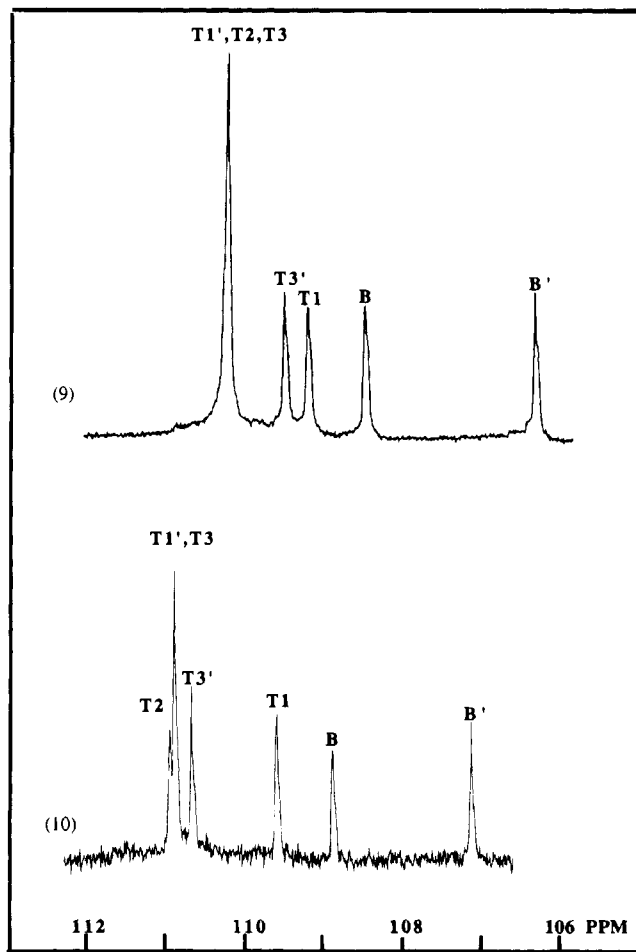


Figure 5. Nondecoupled ^{31}P NMR spectra of $[\text{Mo}_3\text{O}_2\text{S}_2(\text{DTP})_4(\text{Py})]$ in different solvents: (9) $[\text{Mo}_3\text{O}_2\text{S}_2(\text{DTP})_4(\text{Py})]$ in DCB, at 20 °C, δ 110.27 (T1, T1', and T2), 109.53 and 109.23 (T3 and/or T3'), 108.50 and 106.35 (B and/or B'); (10) $[\text{Mo}_3\text{O}_2\text{S}_2(\text{DTP})_4(\text{Py})]$ in CH_3CN : at 20 °C, δ 110.91 (T2), 110.85 (T1 and T1'), 110.64 and 109.56 (T3 and/or T3'), 108.86 and 107.11 (B and/or B').

the most important factor used to determine the chemical shifts, T2, T3 in isomer 1 (Chart 4a), and two T1' in isomer 2 (Chart 4b) have a likely chemical shift, they are subject to the peak at 110.27 ppm of the highest intensity in spectrum 9. The remaining four peaks were assigned (from the left) to T3', T1, B, and B' from a consideration of the influence of the $\mu\text{-O}$ or $\mu\text{-S}$, as is already encountered in the case of Mo_3OS_3 core. That is, the peak positions were always shifted to higher field by the substitution of $\mu\text{-O}$ for $\mu\text{-S}$.

Spectrum 10 in Figure 5 was measured in CH_3CN solution instead of in DCB as shown in spectrum 9. With the bulk solvent effects, all the peaks in spectrum 9 shifted to the lower field. The peak of highest intensity in spectrum 9 was split into two peaks in spectrum 10 with a ratio of 1:3. Since the T2 always situated at the lower field relative to T1 as shown in Figure 4, we assigned the peak at the lowest field to T2.

It should be pointed out that the isomerization of $[\text{Mo}_3\text{O}_2\text{S}_2(\text{DTP})_4(\text{C}_5\text{H}_5\text{N})]$ is the only example in this trinuclear cluster compound series. For example, there was also possibility of isomerization of $[\text{Mo}_3\text{OS}_3(\text{DTP})_4(\text{CH}_3\text{CN})]$, but only one isomer of the cluster has been observed by ^{31}P NMR.

$[\text{Mo}_3\text{O}_3\text{S}(\text{DTP})_4(\text{H}_2\text{O})]$. All the above spectra showed similar pattern of relative chemical shifts for the different DTP ligands. Nevertheless, the result from $[\text{Mo}_3\text{O}_3\text{S}(\text{DTP})_4(\text{H}_2\text{O})]$, with the structure shown in Chart 5, was an exception. Spectra of $[\text{Mo}_3\text{O}_3\text{S}(\text{DTP})_4(\text{H}_2\text{O})]$ in the solvents DCB and CH_3CN are shown in Figure 6. When all three $\mu\text{-S}$'s were replaced by

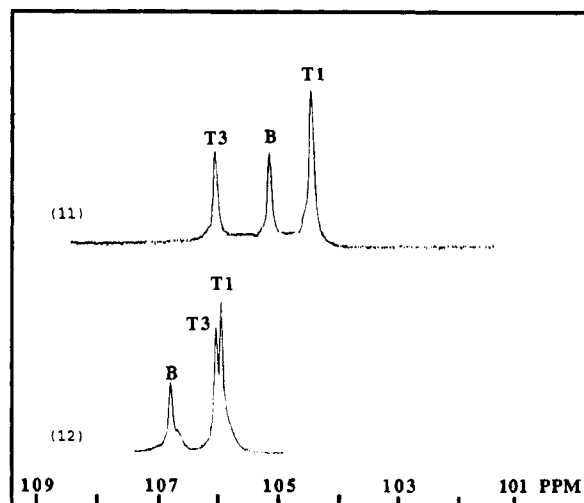


Figure 6. Nondecoupled ^{31}P NMR spectra of $[\text{Mo}_3\text{O}_3\text{S}(\text{DTP})_4(\text{H}_2\text{O})]$ in different solvents: (11) $[\text{Mo}_3\text{O}_3\text{S}(\text{DTP})_4(\text{H}_2\text{O})]$ in DCB, at 20 °C, δ 106.27 (T3), 105.38 (B), 104.69 (T1); (12) $[\text{Mo}_3\text{O}_3\text{S}(\text{DTP})_4(\text{H}_2\text{O})]$ in CH_3CN , at 20 °C, δ 106.78 (B), 106.10 (T3), 106.02 (T1).

$\mu\text{-O}$'s, spectrum 11 of $[\text{Mo}_3\text{O}_3\text{S}(\text{DTP})_4(\text{H}_2\text{O})]$ no longer has the pattern. The peaks shift upfield very much compared with spectrum 5, and the peak sequence also changed. At first sight, T1 was assigned to the peak with a relative intensity of 2. For the assignment of T3 and B, we need the solvent effect information of this compound as shown in spectrum 12 of $[\text{Mo}_3\text{O}_3\text{S}(\text{DTP})_4(\text{H}_2\text{O})]$ measured in CH_3CN . The peak with relatively large shift from T1 was assigned to T3. The peak position of B appeared at the lower field than that of T1 in spectrum 11, while the peak positions of B of all the other clusters appeared at the highest field.

Summary

After the assignment and discussion above, we can summarize the main result for the ^{31}P NMR study on this series of incomplete cubane-type molybdenum cluster compounds. Even though the P nucleus was not directly bonded to the metal Mo, its NMR spectra did give much information about the ligands and the cluster cores when a suitable solvent was selected for the measurements. ^{31}P NMR chemical shifts and the peak intensity of these trinuclear clusters are very sensitive to the structure and dynamic processes so that the properties of these four DTP ligands together with the loosely-coordinated solvent ligand L were well demonstrated in their spectra. Among those ligands coordinated to the core, the solvent ligand L is the most labile ligand in the system so that not only can the other ligands replace it but also the bulk solvent can also exchange with it in the solution. This lability of the solvent ligand L makes the T3 DTP ligand fluctuate around the coordination site, and the chemical shift of T3 is very sensitive to the solvent ligand L. The two horizontal ligands, T1 or T2, are relatively stable in the system, but its ^{31}P NMR signals well reflected the symmetry of the cluster core. The chemical shift of T2 always was situated at the lower field than that of T1.

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Supplementary Material Available: Listings of crystallographic data, thermal parameters, bond distances, and angles (Tables SI–SVIII) (23 pages). Ordering information is given on any current masthead page.