

^{31}P NMR Studies on the Ligand Dissociation of Trinuclear Molybdenum Cluster Compounds

LI, Zhao-Ji^a(李兆基) QIN, Ye-Yan^a(覃业燕) TANG, Yan-Hong^a(唐艳红) KANG, Yao^a(康遥)
XIA, Ji-Bo^a(夏继波) CHEN, Zhong^b(陈忠) WU, Ling^a(吴凌) YAO, Yuan-Gen^{a*}(姚元根)

^a State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

^b Department of Chemistry, Xiamen University, Xiamen, Fujian 361005, China

A series of carboxylate-substituted trinuclear molybdenum cluster compounds formulated as $\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{RCO}_2)_2(\text{L})$, where $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2\text{Cl}, \text{CCl}_3, \text{R}^1\text{C}_6\text{H}_4$ (R^1 is the group on the benzene ring of aromatic carboxylate), $\text{L} = \text{pyridine}, \text{CH}_3\text{CN}, \text{DMF}$, have been synthesized by the ligand substitution reaction. The dissociation of the loosely-coordinated ligand L from the cluster core was studied by ^{31}P NMR. The dissociation process of L is related to the solvent, temperature, and acidity of carboxylate groups, so as to affect the solution structure and reactive properties of the cluster. The long-distance interaction between ligands RCO_2 and L is transported by Mo_3S_4 core.

Keywords ^{31}P NMR, molybdenum cluster, ligand dissociation

Introduction

It is recently demonstrated that the incomplete cuboidal trinuclear molybdenum clusters $\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{H}_2\text{O})_2(\text{I})$ ($\text{DTP} = \text{diethyl dithiophosphate}$) and $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{3+}(\text{II})$ are important precursors to synthesize their ligand substitution derivatives and heterometal cubane-type clusters. Compounds **I** and **II** can be prepared by the spontaneous self-assembly method¹ or by the rational synthesis.² Kinetic studies of compound **II** showed that the nine H_2O ligands are non-equivalent.³ H_2O in compound **I**, named as the loosely-coordinated ligand, can be replaced by a more nucleophilic ligand, even by a solvent molecule such as pyridine or acetonitrile.⁴ Those four DTPs in compound **I** have different reactivity towards the ligand substitution reactions. The bridging DTP ligand, which stretches across two Mo atoms, is more unstable than the terminal DTPs.

In this report, the ^{31}P NMR studies on a series of carboxylate-substituted trinuclear molybdenum cluster compounds $\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{RCO}_2)_2(\text{L})$ were carried out and the kinetic dissociation of the loosely-coordinated ligand L in

the solution was discussed based on the experimental results.

Experimental

The precursor $\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{H}_2\text{O})_2(\text{I})$ was prepared according to the reported method.⁵ A series of trinuclear molybdenum cluster compounds formulated as $\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{RCO}_2)_2(\text{L})$ (where $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2\text{Cl}, \text{CCl}_3, \text{R}^1\text{C}_6\text{H}_4$; $\text{L} = \text{pyridine}, \text{CH}_3\text{CN}, \text{DMF}$; $\text{R}^1 = o\text{-OH}, o\text{-OCH}_3, p\text{-NO}_2, p\text{-Cl}$) were synthesized by the ligand substitution reaction of $\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{H}_2\text{O})_2$ with corresponding aliphatic and aromatic acids according to the reported procedure.^{2, 6-8}

^{31}P NMR spectra of these cluster compounds were measured using a 10-mm tube on a JEOL GX400 NMR spectrometer, with external reference to 85% H_3PO_4 . The reference sample was prepared by sealing a capillary containing 85% H_3PO_4 in a 5-mm NMR tube inside which a suitable amount of deuterated chloroform was added for field locking. Other experimental details were similar to the reported method.²

Preparation of $\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{RCO}_2)_2(\text{Py})$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{Cl}$ or CCl_3)

In a flask, $\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{H}_2\text{O})_2$ (0.50 g) and 1.0 mL of acetic anhydride were added into 40 mL of mixed solvent of anhydrous ethanol and dichloromethane ($V/V = 1:1$). Pyridine (0.5 mL) was then added under stirring. The solution was refluxed over an oil bath for one hour and then filtered. The clear filtrate deposited prism dark-brown crystals of $\text{Mo}_3\text{S}_4(\text{DTP})_4(\text{CH}_3\text{CO}_2)_2(\text{Py})$ after few days. Yield 0.24 g (50.8%). Anal. calcd for $\text{C}_{19}\text{H}_{38}\text{O}_8\text{NM}_3\text{P}_3\text{S}_{10}$: C 20.56, H 3.45, N 1.26, S 28.89; found C

* E-mail: yyg@ms.fjirsm.ac.cn; Fax: 0591-3714946

Received November 16, 2002; revised March 11, 2003; accepted April 30, 2003.

Project supported by the Major State Basic Research and Development Program of China (No. 001CB108906), the National Natural Science Foundation of China (Nos. 29733090 and 20173063), and the Natural Science Foundation of Fujian Province (Nos. B97015 and E0020001).

20.29, H 3.46, N 1.29, S 28.23. The preparation of $\text{Mo}_3\text{S}_4(\text{DTP})(\text{CH}_2\text{ClCO}_2)(\text{Py})$ and $\text{Mo}_3\text{S}_4(\text{DTP})(\text{CCL}_3\text{CO}_2)(\text{Py})$ is similar to that of $\text{Mo}_3\text{S}_4(\text{DTP})(\text{CH}_3\text{CO}_2)(\text{Py})$ with yields 0.20 g (41.1%) and 0.32 g (62.0%), respectively. Anal. calcd for $\text{C}_{19}\text{H}_{37}\text{O}_8\text{NM}_3\text{P}_3\text{S}_{10}\text{Cl}$: C 19.94, H 3.26, N 1.22, S 28.02; found C 19.66, H 3.50, N 1.46, S 28.24. Anal. calcd for $\text{C}_{19}\text{H}_{35}\text{O}_8\text{NM}_3\text{P}_3\text{S}_{10}\text{Cl}_3$: C 18.81, H 2.91, N 1.15, S 26.43; found C 19.08, H 3.55, N 1.45, S 26.04.

Results and discussion

The schematic structure of carboxylate-substituted molybdenum cluster compounds is shown in Fig. 1. T1, T2 and T3 represent different ^{31}P NMR environments in the molecule. T1 and T2 from the horizontal terminal DTP ligands are almost the same as shown in the structural scheme. Experimentally, they will merge into one peak in many complexes at r. t., as reported in the literature.⁶ When the temperature decreased, they split from each other, for example, in the case of $\text{Mo}_3\text{S}_4(\text{DTP})(\text{CCL}_3\text{CO}_2)(\text{Py})$ in *o*-dichlorobenzene (DCB).

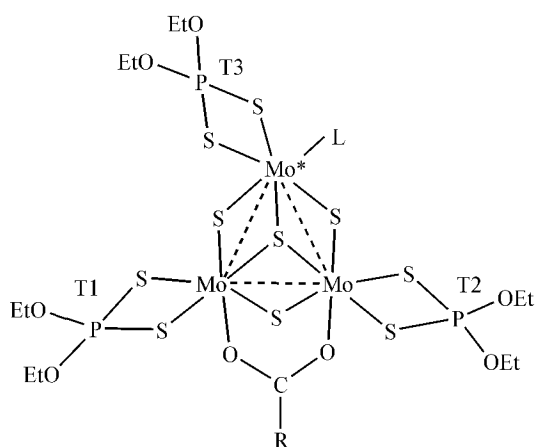


Fig. 1 Structure scheme of carboxylate-substituted cluster compounds $\text{Mo}_3\text{S}_4(\text{DTP})(\text{RCO}_2)(\text{L})$ ($\text{L} = \text{Py}$; $\text{R} = \text{CH}_3$, CH_2Cl and CCL_3 , etc.).

^{31}P NMR experiments showed that the structures of these clusters in the solution are much more complicated than those in the crystalline form. $\text{Mo}_3\text{S}_4(\text{DTP})_3$ of this series of clusters is a quite stable moiety in the solution. However, the loosely-coordinated ligand L, the bridging RCO_2 as well as the terminal DTP will dissociate from the core. At r. t., severe dissociation was encountered in more polar solvents such as CH_3CN and CH_2Cl_2 . At the first stage, the loosely-coordinated ligand is replaced by the solvent molecule. The further dissociation occurs when the bridging RCO_2 group also dissociates from the cluster core. There are too many unexpected NMR peaks and heavy linewidth broadening at this stage. When the dissociation of terminal DTP occurred, ^{31}P NMR spectra measured at this stage will not give convincing information.

Hereafter, the relationships of the dissociation process of L with the solvent, the temperature and the acidity of bridged carboxylates are discussed.

Solvent influence on the spectra

Spectra of these clusters are sensitive towards the solvent used. In order to run the NMR measurements to the lower temperature, toluene and PCl_3 , instead of *o*-dichlorobenzene and H_3PO_4 , were selected as the NMR solvent and the external reference. But an overall different NMR spectrum was experienced. The dissociation of L in toluene is much faster than that in DCB (separate T1 and T2 were detected).² The spectra of $\text{Mo}_3\text{S}_4(\text{DTP})_3(\text{CCL}_3\text{CO}_2)(\text{Py})$ in toluene at room temperature showed that T1 and T2 are coalesced into a single peak. The dissociation of L in *o*-dichlorobenzene is very slow if the temperature is reduced enough.

The bridging ligand (DTP or RCO_2) is more stable than the loosely-coordinated ligand L towards the ligand exchange. In *o*-dichlorobenzene, the dissociation stops for both the bridging DTP and RCO_2 , only the dissociation of L can be detected. In CH_3CN , DTP dissociates but RCO_2 does not. R group in RCO_2 also affects the dissociation: in CH_2Cl_2 , the NMR spectra of the aromatic carboxylate-substituted clusters give clear peaks of T1, T2 and T3 (T1 and T2 merge into one peak at r. t.), while the spectra of the aliphatic carboxylate-substituted clusters give many unexpected peaks, indicating that the bulky aromatic carboxylate improves the stability of the clusters.⁶⁻⁸

Ligand acidity influence on the spectra

The ^{31}P NMR spectra of $\text{Mo}_3\text{S}_4(\text{DTP})(\text{RCO}_2)(\text{Py})$ ($\text{R} = \text{CCL}_3$, CH_2Cl and CH_3 , respectively) (Fig. 2) show that the ^{31}P NMR spectral appearance of these compounds in the ambient temperature is sensitive to the acidity of the carboxylate ligands. Fig. 2(a) and (b) exhibit three peaks T1, T2 and T3, however, Fig. 2(c) exhibits only two peaks, T1 and T2 merge into a single peak. The sequence of acidity is: $\text{CCL}_3\text{CO}_2\text{H} > \text{CH}_2\text{ClCO}_2\text{H} > \text{CH}_3\text{CO}_2\text{H}$. The sequence of electron pulling capability is: $\text{CCL}_3 > \text{CH}_2\text{Cl} > \text{CH}_3$. And the sequence of ligands dissociation rate of L is: $\text{Mo}_3\text{S}_4(\text{DTP})(\text{CCL}_3\text{CO}_2)(\text{Py}) < \text{Mo}_3\text{S}_4(\text{DTP})_3(\text{CH}_2\text{ClCO}_2)(\text{Py}) < \text{Mo}_3\text{S}_4(\text{DTP})_3(\text{CH}_3\text{CO}_2)(\text{Py})$. The electron delocalization from RCO_2 group to the loosely-coordinated ligand is shown in Fig. 3. This gives an experimental evidence that the trinuclear cluster core Mo_3S_4 has the quasi-aromaticity⁹ and transports the ligands interaction around the trinuclear Mo_3S_4 core.

Dependence of ^{31}P NMR spectra on temperature

Temperature-dependent ^{31}P NMR experiments have been studied on these carboxylate-substituted cluster compounds, and the representative results are shown in Fig. 4

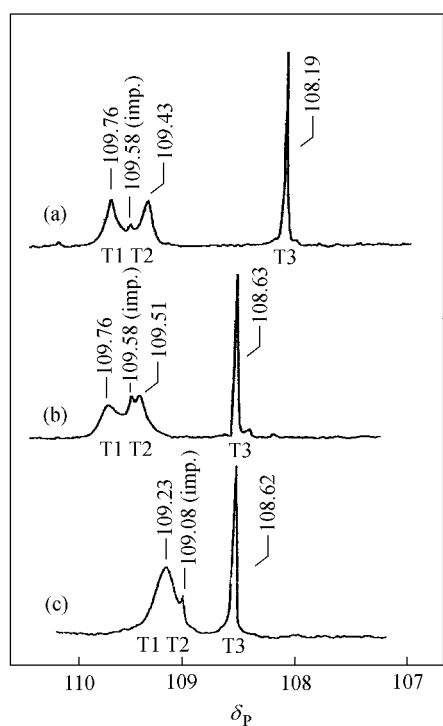


Fig. 2 ^{31}P NMR spectra of 1.0×10^{-3} mol/L, r.t., in DCB, showing the effect from different substituents: (a) $\text{Mo}_3\text{S}_4(\text{DTP})_3(\text{CCl}_3\text{CO}_2)_3(\text{Py})$; (b) $\text{Mo}_3\text{S}_4(\text{DTP})_3(\text{CH}_2\text{ClCO}_2)_3(\text{Py})$; (c) $\text{Mo}_3\text{S}_4(\text{DTP})_3(\text{CH}_3\text{CO}_2)_3(\text{Py})$.

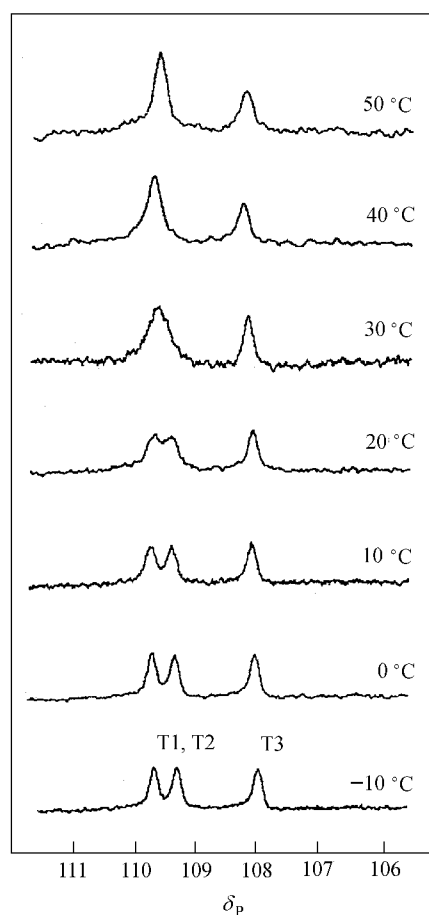


Fig. 4 Temperature-dependent ^{31}P NMR spectra of $\text{Mo}_3\text{S}_4(\text{DTP})_3(\text{CCl}_3\text{CO}_2)_3(\text{Py})$, 1.0×10^{-3} mol/L, in DCB.

for the compound $\text{Mo}_3\text{S}_4(\text{DTP})_3(\text{CCl}_3\text{CO}_2)_3(\text{Py})$. Spectra for these aliphatic carboxylate-substituted compounds in *o*-dichlorobenzene show reversibility that at higher temperature, the NMR signals of T1 and T2 tend to merge into a single one. When the temperature is reduced enough, the two peaks will recover with equal height and linewidth.

Conclusion

The ligand exchange process at the first stage can be expressed by Scheme 1. In this stage only the loosely-coordinated ligand L dissociates from the cluster, and no disso-

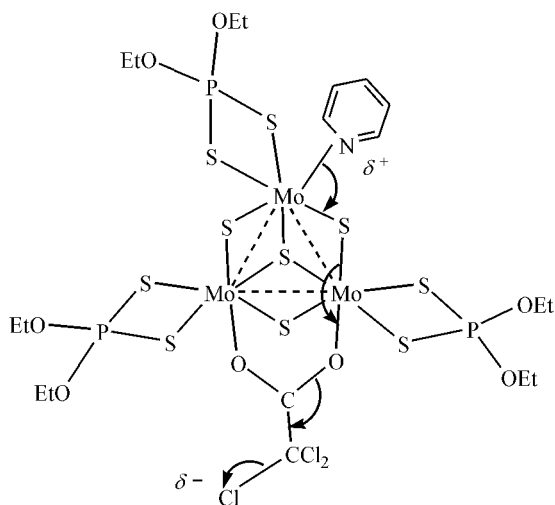
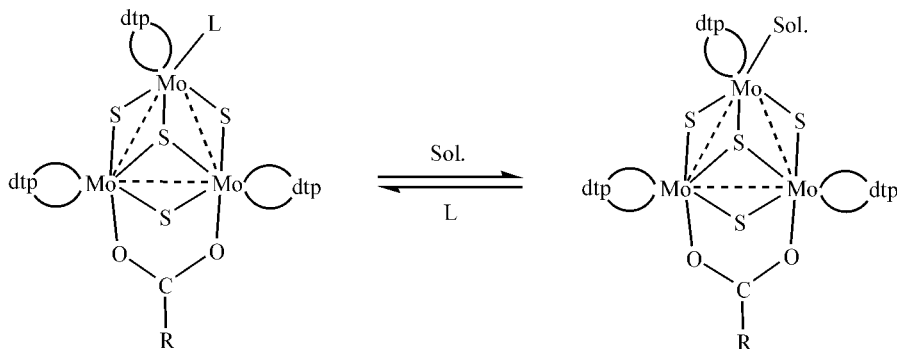


Fig. 3 Scheme of electron delocalization between the RCO_2 and L.

Scheme 1



ciation of the bridging ligand RCO_2 occurs.

At low temperature, the dissociation of L is slow enough or stops completely, making the whole cluster molecule asymmetric. So well-separated ^{31}P NMR resonances for T1 and T2 were observed. When the temperature is raised, the dissociation of L begins, and the solvent molecule will enter the empty site left by L from random directions. If this process is fast enough, T1 and T2 will be sterically equivalent. So a coalesced NMR resonance for T1 and T2 was observed. In Fig. 4, the spectrum of compound $\text{Mo}_3\text{S}_4(\text{DTP})_2(\text{CCl}_3\text{CO}_2)_2(\text{Py})$ measured at $-10\text{ }^\circ\text{C}$ can be assigned to the configuration on the left side in Scheme 1. The pyridine is coordinated to the Mo atom; the two DTPs, T1 and T2 are sterically non-equivalent. On the other hand, the spectrum measured at $50\text{ }^\circ\text{C}$ is assigned to the configuration on the right side in Scheme 1. The two DTPs are sterically identical.

Acknowledgement

We gratefully acknowledge Prof. T. Shibahara, Dr. H. Akashi and Dr. G. Sakane from Okayama University of Science, Japan, for their contribution to the measure-

ment and explanation of ^{31}P NMR spectra.

References

- 1 Lin, X.-T.; Lin, Y.-H.; Huang, J.-L.; Huang, J.-Q. *Chin. Sci. Bull.* **1986**, 509 (in Chinese).
- 2 Yao, Y.-G.; Akashi, H.; Sakane, G.; Shibahara, T.; Ohtaki, H. *Inorg. Chem.* **1995**, 34, 42.
- 3 Richens, D. T.; Pittet, P.-A.; Merbach, A. E.; Humaned, M.; Lamprecht, G. J.; Ooi, B.-L.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1993**, 2305.
- 4 Huang, J.-Q.; Huang, J.-L.; Shang, M.-Y.; Lu, S.-F.; Lin, X.-T.; Lin, Y.-H.; Huang, M.-D.; Lu, J.-X. *Pure Appl. Chem.* **1988**, 60, 1185.
- 5 Yao, Y. G.; Wu, L.; Zhu, Y. B.; Lu, S. F. *Chin. J. Struct. Chem.* **1996**, 15, 117.
- 6 Wu, L.; Xia, J.; Chen, C.; Huang, X.; Yao, Y.; Lu, J. *Polyhedron* **1998**, 17, 4203.
- 7 Tang, Y.-H.; Qin, Y.-Y.; Wu, L.; Li, Z.-J.; Kang, Y.; Yao, Y.-G. *Polyhedron* **2000**, 20, 2911.
- 8 Xia, J.-B.; Yao, Y.-G.; Wu, L.; Huang, X.-Y.; Lu, J.-X. *Acta Cryst.* **1998**, C54, 1612.
- 9 Lu, J.-X. *Chin. J. Struct. Chem.* **1989**, 8, 327 (in Chinese).

(E0211261 SONG, J. P.; DONG, L. J.)