

## A Novel Organic-Inorganic Complex: Synthesis and Crystal Structure of $[\text{Ca}(\text{DMSO})_5(\text{H}_2\text{O})]_2\text{SiMo}_{12}\text{O}_{40}$

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**Abstract:** A novel organic-inorganic complex  $[\text{Ca}(\text{DMSO})_5(\text{H}_2\text{O})]_2\text{SiMo}_{12}\text{O}_{40}$  was synthesized from  $\text{CaCl}_2$ , DMSO and  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$  in mixed solvent of acetonitrile and water. Its structure was characterized with elemental analysis, IR and X-ray diffraction analysis.

**Keywords:** Synthesis, crystal structure, organic-inorganic complex.

It is becoming a focus to synthesize and assemble organic-inorganic materials, especially, to synthesize charge-transfer complexes formed by polyoxometalate and organic donors. They have attracted much attention because such complexes are active in their electric, magnetic and optic properties<sup>1-4</sup>, many investigations about them have been done and some crystal structures of them were reported<sup>5-6</sup>. But, the disadvantage of these crystals is instability at room temperature. According to the viewpoint of molecular design, we attempt to introduce some metal ions to coordinate with the organic groups to make the organic-inorganic complex stable. In this paper, we synthesized a novel complex  $[\text{Ca}(\text{DMSO})_5(\text{H}_2\text{O})]_2\text{SiMo}_{12}\text{O}_{40}$  and characterized its structure with elemental analysis, IR and X-ray diffraction analysis. The results of IR and X-ray diffraction show that there is strong interaction between polyoxometalate and organic donors.

### Experimental

*Preparation of  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ :* This compound was prepared according to the literature<sup>7</sup> and checked by IR spectra.

*Preparation of the title compound:*  $\text{CaCl}_2$  (0.24 g, 2.2 mmol) and  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$  (2 g, 1.1 mmol) in the molar ratio of 2:1 were dissolved in 10 mL of water and stirred below 90°C until some solids were isolated (2.11 g, in 96% yield). After dried under vacuum, 2 g of the product was dissolved in 10 mL mixed solvent of acetonitrile and water in the volume ratio of 5:2, and then, 1 mL DMSO was added slowly. The mixture was stirred 15 min at 70°C, then, cooled and filtered off. The filtrate was set at dark place and evaporated at room temperature. The yellow crystals were obtained five days later (1.77 g, in 71% yield based on  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ ). Anal. Calcd. for  $[\text{Ca}(\text{DMSO})_5(\text{H}_2\text{O})]_2\text{SiMo}_{12}\text{O}_{40}$ : C, 8.8%; H, 2.3%; S, 11.7%; Found. C, 9.03%; H, 2.22%; S, 11.7%. IR (KBr,  $\text{cm}^{-1}$ ): 1017.2, 947.4, 900.2, 860.8, 793.7.

### Structure Determination and Results

A single crystal with dimension of  $0.32 \times 0.28 \times 0.20 \text{ mm}^3$  was selected for the crystal structure analysis. The data for the crystal structure of the title complex were collected at room temperature on a Rigaku RAXIS-IV image plate area detector with Mo K $\alpha$  ( $\lambda=0.7103 \text{ \AA}$ ) radiation. The crystal is triclinic, space group P1, with unit cell dimensions  $a=12.030(2) \text{ \AA}$ ,  $b=12.870(3) \text{ \AA}$ ,  $c=13.324(3) \text{ \AA}$ ,  $\alpha=83.53(3)^\circ$ ,  $\beta=68.94(3)^\circ$ ,  $\gamma=87.36(3)^\circ$ ,  $V=1912.9(7) \text{ \AA}^3$ ,  $Z=1$ ,  $D_{\text{calc}}=2.358 \text{ g/cm}^3$ . The final  $R=0.0629$ ,  $R_w=0.1700$  for 7876 unique reflections.

The structures were solved by direct methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 program. The maximum and minimum residual peaks on the final difference Fourier map were  $1.523$  and  $-1.330 \text{ e/ \AA}^3$ , respectively.

Comparing the IR spectra of the title compound with that of  $\alpha\text{-H}_4\text{SiMo}_{12}\text{O}_{40}$ <sup>7</sup>, the vibration peak of the Mo=Od bond shifted from  $957$  to  $947 \text{ cm}^{-1}$ ; the Mo-Ob bond shifted from  $855$  to  $860 \text{ cm}^{-1}$ ; the Mo-Oc bond shifted from  $770$  to  $793 \text{ cm}^{-1}$ ; the X-Oa bond is nearly unchangeable. The results indicated that the polyanions of the title compounds still maintained basic Keggin structure, but their structures were distorted due to the influence of coordination effect produced by metal ions bound with organic groups and coordinated water. In addition, the resonance at  $1024 \text{ cm}^{-1}$  and  $706 \text{ cm}^{-1}$  in the title compound were assigned to  $\nu_{\text{as}}(\text{S}=\text{O})$  and  $\nu_{\text{as}}(\text{C}-\text{S})$  asymmetrical stretching vibration of DMSO. Comparing the IR spectra of the title compound with that of free DMSO<sup>8</sup>, the  $\nu_{\text{as}}(\text{S}=\text{O})$  decreased approximately  $30 \text{ cm}^{-1}$ , from  $1055$  to  $1024 \text{ cm}^{-1}$ . The result verified that the DMSO as ligands were coordinated with metal ion at its oxygen atom<sup>9</sup> and its sulfur atom is not involved in coordination. The  $\nu_{\text{as}}(\text{C}-\text{S})$  increased approximately  $8 \text{ cm}^{-1}$ , from  $698$  to  $706 \text{ cm}^{-1}$ . It can be explained that the decrease of the charges density over the oxygen and sulfur atoms due to O atoms of the S=O bonds coordinated with the metal ions, leads to the increase of electron-donating effect of methyl, accordingly, the  $\nu_{\text{as}}(\text{C}-\text{S})$  was enhanced slightly.

The molecular structure and the coordination environment diagram of  $\text{Ca}^{2+}$  are depicted in **Figure 1** and **Figure 2**, respectively. It can be seen from **Figure 1** that the title complex consisted of two  $\text{Ca}^{2+}$  lattices and  $\text{SiMo}_{12}\text{O}_{40}^{4-}$  anion. As shown in **Figure 2**, each of  $\text{Ca}^{2+}$  ions is surrounded by five DMSO molecules and one water molecule with the distorted octahedra. In the structure of polyanion,  $\text{SiO}_4$  tetrahedron is nearly regular, the O-Si-O bond angles are in the range of  $108.2(6)$ - $111.4(6)^\circ$ . But the  $\text{MoO}_6$  octahedra are severely distorted. The longest Mo-O distances involving O atoms of the central tetrahedron are in the range of  $2.342(11)$ - $2.382(11) \text{ \AA}$ ; The shortest Mo-O distances for the unshared oxygen atoms are in the range of  $1.617(15)$ - $1.707(14) \text{ \AA}$ ; The Mo-O distances for the bridging oxygen atoms vary from  $1.765(14)$  to  $2.085(12) \text{ \AA}$ . The results indicated that there is strong interaction between outer cationic groups and polyanion. The present paper focuses primarily on solid-state structural aspects of organic-inorganic complexes and reveals novel structure. The manner may serve as a useful model for the design of functional molecular assemblies.

Figure 1 The molecular structure of the title complex

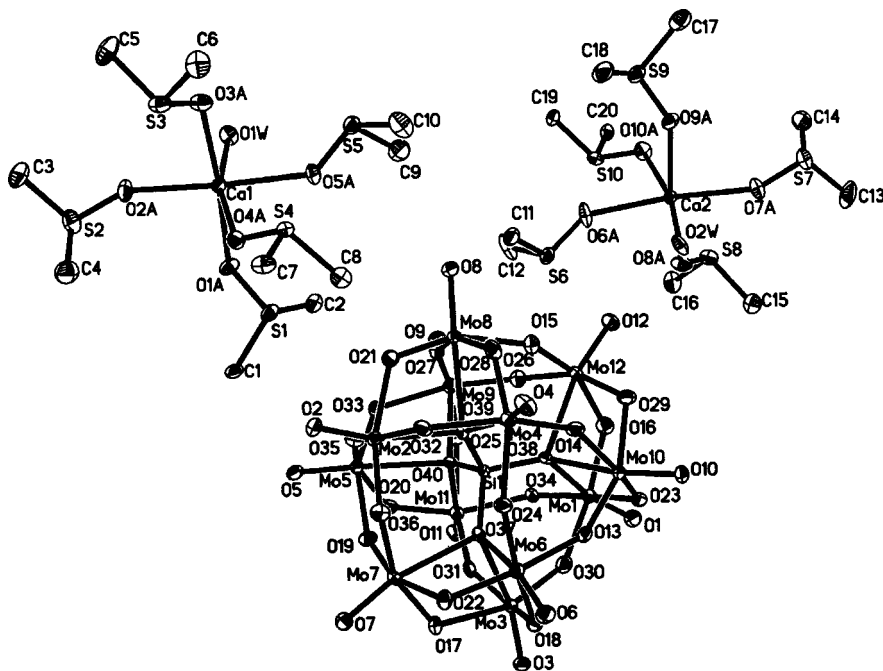
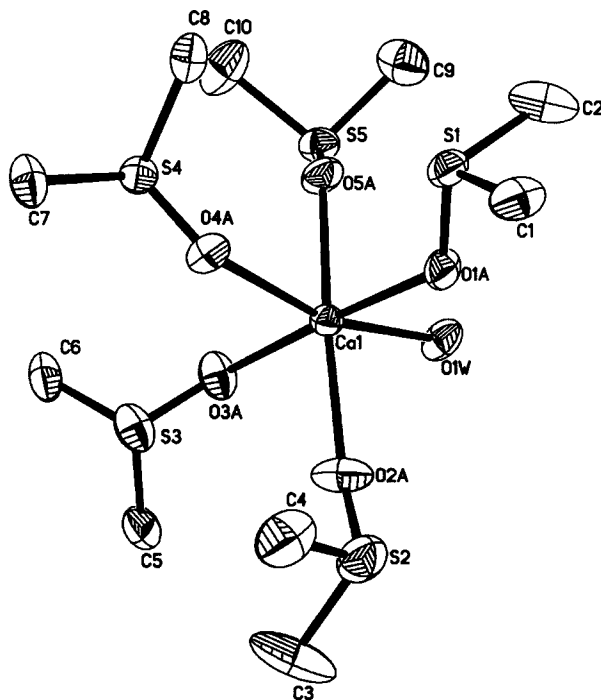


Figure 2 The coordination environment of  $\text{Ca}^{2+}$



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### References

1. E. Coronado, C. Gomez-Garcia, *J. Chem. Rev.*, **1998**, 98, 273.
2. A. Mhanni, L. Ouahab, O. Pena, D. Grandjean, C. Garrigou-Lagrange, P. Delhaes, *Synth. Met.*, **1991**, 41-43, 1703.
3. A. Davidson, K. Boubekeur, A. Penicaud, P. Auban, C. Lenoir, P. Batail, G. Herve, *J. Chem Soc, Chem Commun.*, **1989**, 1373.
4. P. Le Magneres, L. Ouahab, S. Golben, D. Grandjean, O. Peha, J. C. Jegaden, C. J. Gomez-Garcia, P. Delhaes, *Inorg. Chem.*, **1994**, 33, 5180.
5. J. Y. Niu, J. P. Wang, X. Z. You, W. Chen, *J. Coord. Chem.*, **2001**, 2, 153.
6. D. Attanasio, M. Bonamico, V. Fares, *et al.*, *J. Chem. Soc. Dalton*, **1990**, 3221.
7. Rocchiccioli-Deltcheer, M. Fournier, R. Franck and R.Thouvenot. *Inorg. Chem.*, **1983**, 22, 207.
8. R.Thomas, C. B. Shoemaker, K. Eriks, *Acta Crystallogr.*, **1966**, 21, 12.
9. F. A. Cotton, E. V. Dikarev, M. A. Petrukhina, S. -E Stiriba, *Inorg. Chem.*, **2000**, 39, 1748.

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