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Synthesis and Characterization of Polyoxometallate Compounds of Amine and Phosphine with Molybdovanadophosphoric Acid in Keggin Type

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Four novel compounds were synthesized by the reaction of tertiary amines (triphenyl amine, triethyl amine, tributyl amine) and triphenyl phosphine with freshly prepared molybdovanadophosphoric acid ($H_4PMO_{11}VO_{40}\cdot 32H_2O$). The products were characterized by elemental analysis, spectroscopic techniques (UV, IR, ICP-AES) and thermal analysis (TG/DTA). The experimental data indicated that the synthesized compounds retain the Keggin structure.

Key Words: Synthesis, Amine, Catalyst, Molybdovanadophosphoric acid, Keggin structure, Phosphine.

INTRODUCTION

Heteropoly acids (HPAs), in particular those of the Keggin structure $H_{8-x}[X^{n+}M_{12}O_{40}]$ ($X = P^{5+}$ or Si^{4+}, $M = W^{6+}$, MO^{6+}) and their salts are polynuclear complexes, which contain oxygen bridges and show strong acidity, oxidizing ability and high thermostability[1–10]. The acid strength of concentrated heteropoly acid in aqueous solutions in terms of Hammett acidity function is higher than that of constituent oxo-acids and ordinary inorganic acids. High-nuclear metal-oxo clusters (polyoxometallates) have attracted a great deal of interest as a result of their realized and potential applications in fields as diverse as catalysis, analysis, biochemistry, magnetism, medicine and material science[2–21]. Molybdoheteropoly acids are the most suitable species and are widely used for the preconcentration and determination of phosphorus. The liquid extraction of heteropoly acids in oxygen-containing or low-polar solvents as ion associates with high-molecular amines and basic dyes is the conventional method for their preconcentration[10].

Heteropoly compounds continue to display surprisingly novel structures, unexpected reactivity and applications. An interesting subarea of metal-oxo cluster chemistry is the small but growing family of molybdovanadates with a variety of structural features and interesting physico-chemical properties. Therefore, how to deliberately create some new-fangled oxomolybdovanadate novel compounds is still significant[3–9, 13]. In recent years, a variety of oxygen or nitrogen-containing organic derivatives of polyoxomolybdate anions have been synthesiz ed and structurally characterized[3–19]. However, to our knowledge, there is no report about amine and phosphine compounds of Keggin structure heteropoly anions. In this study, the first member of the Keggin-structured Mo-V-phosphoric acids of the 12th series $H_{3+X}PV^{V} \times MO_{12-X}O_{40}$ ($1 \leq X \leq 6$) is synthesized and characterized its salts with tertiary amines (triphenyl amine, triethyl amine, tributyl amine) and triphenyl phosphine.

EXPERIMENTAL

All chemicals were of reagent grade and were obtained from commercial sources. IR spectra were recorded on an MIDAC 1700 M FTIR spectrometer in the range of 4000–400 cm^{-1} at 2 cm^{-1} resolution and 50 scans using KBr pellets. UV spectra in acetonitrile were measured on a Shimadzu UV-160 automatic recording spectrometer employing 1 cm silica cells. Thermogravimetric investigations of the compounds were carried out with a Shimadzu TGA-50 thermal analyzer with *ca.* 20 mg samples being heated in dry from 20–800°C at a linear heating rate of 10°C min^{-1} with a nitrogen flow rate of 15 mL min^{-1}.

C, H and N analyses for studied heteropoly acid and its compounds with amine and phosphine were performed by a Carlo-Erba element analysis instrument model EA 1108. The elemental analyzer was calibrated with standard compounds using K factor calculation[22]. Vanadium, molybdenum and phosphorus were analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-AES, Jobin-Yvon JY 24) according to those described briefly in our previous report[20]. The results of elemental analysis are given in Table-1.

TABLE-1
MICRO-ANALYTICAL DATA FOR COMPOUNDS

Compound	Analysis: % Found (Calcd.)					
	C	H	N	Mo	V	P
I	25.54 (24.57)	2.03 (2.17)	—	38.54 (39.97)	1.95 (1.93)	4.62 (4.69)
II	24.22 (24.37)	2.39 (2.46)	1.50 (1.58)	38.91 (39.65)	1.89 (1.91)	1.12 (1.16)
III	13.10 (13.19)	2.73 (2.95)	2.44 (2.56)	48.10 (48.28)	2.13 (2.33)	1.49 (1.42)
IV	22.86 (22.85)	4.61 (4.48)	2.23 (2.22)	40.98 (41.83)	2.00 (2.02)	1.20 (1.23)

Preparation of Heteropoly acid and its amine and phosphine compounds

Molybdovanadophosphoric acid was prepared from initial substances such as Na_2HPO_4, $Na_2MoO_4 \cdot 2H_2O$, $NaVO_3$, H_2SO_4 and characterized according to literature[8, 9]. Starting from this freshly prepared heteropoly acid (orange crystal) we synthesized four new amine and phosphine compounds of Keggin structure polyoxometalates.

(a) $(Ph_3P)_3HPMo_{11}VO_{40} \cdot 4H_2O$ (I): To a solution of triphenyl phosphine (4×10^{-2} M) in acetic acid (25 mL) was added 25 mL of $H_4PMo_{11}VO_{40} \cdot 32H_2O$ (10^{-2} M) that was dissolved in acetic acid. The mixture was stirred at room temperature and the green product was filtered and then dried in air.

(b) $(Ph_3NH)_3HPMo_{11}VO_{40} \cdot 8H_2O$ (II): To a solution of triphenyl amine (4×10^{-2} M) in acetic acid (25 mL) was added 25 mL of $H_4PMo_{11}VO_{40} \cdot 32H_2O$ (10^{-2} M) that was dissolved in acetic acid. The mixture was stirred at room temperature and the dark green solid obtained was filtered and then dried in air.

(c) $(Et_3NH)_4PMo_{11}VO_{40}$ (III): To a solution of triethyl amine (4×10^{-2} M) in acetic acid (25 mL) was added 25 mL of $H_4PMo_{11}VO_{40} \cdot 32H_2O$ (10^{-2} M) that was dissolved in acetic acid. The mixture was stirred at room temperature and the yellow product was filtered and then dried in air.

(d) $(Bu_3NH)_4PMo_{11}VO_{40}$ (IV): To a solution of tributylamine (4×10^{-2} M) in acetic acid (25 mL) was added 25 mL of $H_4PMo_{11}VO_{40} \cdot 32H_2O$ (10^{-2} M) that was dissolved in acetic acid. The mixture was stirred at room temperature and the dark yellow product was filtered and then dried in air.

RESULTS AND DISCUSSION

The Keggin-structured vanadomolybdophosphoric heteropoly acid, $H_2PMo_{11}VO_{40} \cdot 32H_2O$, was prepared with a high degree of purity according to the previously described procedure[8, 9]. Pure molybdovanadophosphoric heteropoly acid ($H_4PMo_{11}VO_{40} \cdot 32H_2O$) exhibits IR absorption bands at 3407, 1620 and 1060–595 cm^{-1}. The bands at 3407 and 1620 cm^{-1} correspond to ν(O—H) and δ(O—H), respectively. There are 5 bands in the 595–1060 cm^{-1} region which are characteristic peaks of the Keggin structure. Frequencies at 1060, 960, 866, 792 and 595 cm^{-1} were assigned to $\nu(P—O_a)$, $\nu(Mo{=}O_d)$, $\nu(Mo—O_b—Mo)$, $\nu(Mo—O_c—Mo)$ and $\delta(P—O_a)$ or δ(Mo—O) vibrations, respectively, where O_a = inner oxygen atoms forming P—O bonds, O_b = bridging oxygen atoms on the common corners of neighbouring MoO_6 octahedra, O_c = bridging oxygen atoms situated on common edges within structural triple subunits and O_d = terminal oxygen atoms, frequently considered as double- bonded as in Mo=O. In the IR spectra of the compounds prepared from $H_3PMo_{11}VO_{40} \cdot 32H_2O$, the five characteristic vibration frequencies mentioned above are only slightly changed compared to the starting material. IR absorption frequencies of the HPA and the prepared compounds are given in Table-2. As can be seen from Table-2, among the prepared compounds only triphenyl phosphine and triphenyl amine salts contain crystal water. This finding was also supported by TGA results.

TABLE-2
IR AND UV-Vis DATA FOR THE PREPARED COMPOUNDS

Compd.	Colour	ν(O–H), δ(O–H)	ν(P—O)	ν(Mo═O)	ν(Mo–O–Mo)	ν(Mo–O)	λ_{max} (nm)
I	Green	3502, 1615	1123, 1058	958	727	691, 538	232, 249, 305
II	Dark green	3495, 1602	1054	999, 951	874, 793	591	230, 256, 308
III	Yellow	—	1056	950	870, 785	597	234, 256, 310
IV	Dark yellow	—	1074, 1057	960	874, 783	597	213, 269, 311

The number of molecules of crystallization water in the prepared compounds and the temperature at which thermal decomposition of the samples takes place were determined by TGA measurements[23, 24]. The TGA measurements showed that the per cent of weigh loss for the compounds $(Ph_3PH)_3HPMo_{11}VO_{40}$ and $(Ph_3NH)_3HPMo_{11}VO_{40}$ are 2.73 and 5.41%, which indicates that these compounds consist of 4 and 8 molecules of water, respectively. The second stage decomposition was observed for the compounds **I–IV** in the range 275–634°, 288–596°, 295–800° and 285–718°C, respectively. This broad region of decomposition may be attributed to different kinds of simple compounds and polyoxometallates.

The UV absorption bands of HPA and the prepared compounds are almost similar. The intense absorption bands near 200 and 270 nm are assigned to the charge-transfer of the terminal oxygen and bridge-oxygen to metal atoms, respectively. The UV-Vis spectra of the prepared compounds also show a characteristic absorption of molybdovanadophosphoric acid at 310 nm.

The results of this study demonstrate that the prepared species show distorted Keggin-type structure[25–28]. Our observations suggest that these compounds can be tested as environmentally friendly catalysts in common organic reactions in the regular temperature region for HPA catalysts is below 300°C.

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