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Metal-substitution of 12-Heteropolymolybdate with Iron Atoms

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Synopsis. Triheteropolymolybdates of [$XFeMo_{11}O_{40}H_2$]- and [$XFeMo_{11}O_{40}H_3$]-type have been synthesised by the metal-substitution reaction of 12-heteropolymolybdate of [$XMo_{12}O_{40}$]-type (X is Si or P) and their properties have been investigated.

Although triheteropolymolybdate, a mixed-metal polyoxoanion, was expected to be a new catalyst of reversible oxidation in homogeneous system,[1] the compound, generally prepared in only a narrow pH range, is more easily hydrolyzed than the corresponding saturated heteropolymolybdate. We have examined the metal substitution of 12-heteropolymolybdate possessing well-known Keggin structure with Fe(II) and Fe(III) ions. We report on the isolation of the reaction products, the anions of [$XFeMo_{11}O_{40}H_2$]- and [$XFeMo_{11}O_{40}H_3$]-type as tetrabutylammonium salts, where X is Si or P. So far as Fe-ion substituted products derived from heteropolyanions of [$XMo_{12}O_{40}$]-type are concerned, no precedent has been reported except for [$SiFeMo_{11}O_{40}H_2$]$^{5-}$.[2]

The reaction of [$SiMo_{12}O_{40}$]$^{4-}$ with $FeCl_3$ in aqueous solution containing potassium acetate and glacial acetic acid gave mainly [$SiFeMo_{11}O_{40}H_2$]$^{4-}$, where Fe is tervalent and all Mo are sexivalent cations. The complex was isolated as a stable tetrabutylammonium salt. The reaction of [$SiMo_{12}O_{40}$]$^{4-}$ with $FeCl_2$ under similar conditions gave [$SiFeMo_{11}O_{40}H_3$]$^{5-}$, where Fe is also tervalent, only one Mo being quinquevalent and the others sexivalent cations. During the course of substitution, bivalent Fe ion turns into a tervalent cation by the intrinsic strong oxidation property of the parent anion. Such a compound has also been isolated as a tetrabutylammonium salt and purified by recrystallization from acetonitrile. By the reaction of [$PMo_{12}O_{40}$]$^{3-}$ with Fe(II) or Fe(III) ion, the corresponding one iron substituted derivatives were obtained. In these reactions no further substitution of Mo ion was observed.

The K^+, Na^+, and NH_4^+ salts of heteropolymolybdate containing an iron atom, once formed in aqueous solutions of limited pH range, are sparingly recrystallized from an aqueous solution because of their extremely low solubility and hydrolytic instability. However, by using tetrabutylammonium cation as precipitants, such unstable anions were converted into stable compounds for recrystallization from a nonaqueous solvent such as acetonitrile. The treatment makes the determination of anionic charge, elemental analysis, spectroscopic characterization easy, giving good yield of compounds. Furthermore, in a nonaqueous solvent, these compounds obtained as a tetrabutylammonium salt do not decompose even in the presence of an organic base such as pyridine and triphenylphosphine.

The heteropolyanions obtained are formulated as follows;

[$SiFe^{III}Mo^{VI}{}_{11}O_{40}H_2$]$^{5-}$	(yellow, **1**),
[$SiFe^{III}Mo^{V}Mo^{VI}{}_{10}O_{40}H_3$]$^{5-}$	(yellow-green, **2**),
[$PFe^{III}Mo^{VI}{}_{11}O_{40}H_2$]$^{4-}$	(pale yellow, **3**),
[$PFe^{III}Mo^{V}Mo^{VI}{}_{10}O_{40}H_3$]$^{4-}$	(dark green, **4**),

their analytical data being given in Table 1.

Yellow compounds **1** and **3** are written as [$XFeMo_{11}O_{40}H_2$] (X=Si, P), where "H_2" is included in the formula not only to make the total oxidation number consistent; X (+4 or +5 corresponding to Si or P), Fe (+3), Mo (+6), O (−2) and two H (+1), but is arised from the hydrogen part of coordinating water molecule. Existence of a coordinating water molecule was determined by IR study. The complexes were recrystallized several times from dry acetonitrile in order to remove solvated water molecules entirely. In this case, the characteristic bands of coordinating water at *ca.* 3400 and 1630 cm^{-1} were observed, but not in the case of parent anion [$XMo_{12}O_{40}$]-type. Thus if Fe ion is considered as a central ion, the compounds obtained are considered to be a hexa-coordination complex of Fe coordinated by quinquedentate ligand "$XMo_{11}O_{39}$" and unidentate ligand H_2O.

The green compounds **2** and **4** with the formula [$XFeMo_{11}O_{40}H_3$]-type also possess the water molecule coordinated to tervalent Fe ion and one hydroxyl group coordinated to one quinquevalent Mo ion in quinquedentate ligand "$XMo_{11}O_{39}$." The presence of the coordinating hydroxyl group is strongly suggested from the reduction of parent anion [$SiMo_{12}O_{40}$]$^{4-}$ by alcohols leading to the formation of the blue anion of [$SiMo_{12}O_{40}H_n$]-type, where n=2—4 and Mo ions of the corresponding numbers are quinquevalent.[3]

IR and electronic spectral data of heteropoly anion obtained together with parent molybdosilicate and molybdophosphate, are given in Tables 2 and 3,

Table 1. Analytical data

Formula		Found (%)				Calcd (%)			
		C	H	N	Fe	C	H	N	Fe
K[$(C_4H_9)_4N$]$_4$[$SiFeMo_{11}O_{40}H_2$]·CH_3CN	**1**	28.09	5.57	2.17	1.41	27.99	5.27	2.47	1.97
K[$(C_4H_9)_4N$]$_4$[$SiFeMo_{11}O_{40}H_3$]	**2**	26.90	5.23	2.10	1.64	27.53	5.27	2.01	2.00
[$(C_4H_9)_4N$]$_4$[$PFeMo_{11}O_{40}H_2$]·$12H_2O$	**3**	25.89	5.04	1.87	1.82	25.89	5.73	1.89	1.88
[$(C_4H_9)_4N$]$_4$[$PFeMo_{11}O_{40}H_3$]·$9H_2O$	**4**	26.46	5.19	1.81	1.63	26.34	5.66	1.92	1.92

Table 2. IR data (KBr)

$[(C_4H_9)_4N]_4$ $[SiMo_{12}O_{40}]$	**1**	**2**	$[(C_4H_9)_4N]_3$ $[PMo_{12}O_{40}]$	**3**	**4**
			1057s	1053s	1053s
980m	980m	980m			
			960s	970w(sh)	970w(sh)
			950vs	950vs	948vs
940s	937s	936s		940vs	938vs
898vs	894vs	887vs			
863m	863m	860m	875s	863s	868s
800vs	800vs	788vs	804vs	803vs	805vs
730m(sh)	730m(sh)	730m(sh)	735w	735w	735m(sh)
633m	633m	633m		710w	
			605w	588w	590w
527m	527m	525m			
503m	505m	500m	495w	495w	500w

respectively. Typical electronic spectra are dominated by two or three bands in the 240—500 nm region, which are based on the charge transfer transition of intra-ligand, *viz.* intra-"$XMo_{11}O_{39}$" moiety. The absorption due to the low spin Fe(III) complex under such ligand fields is extremely weak, the whole spectral aspect resembling that of the parent anion. However, the intensity at near 300 nm strongly reflects the effect of metal substitution and/or the degree of reduction of molybdenum atom. The characteristic spectra of compounds **2** and **4** containing a reduced molybdenum ion have weak intensity bands in a longer wave-length region than 700 nm. The data (Table 2) reveal that the metal substitution and/or heteroatom substitution directly influence the IR bands due to the M–O–M, X–O and M–O stretching modes.[4] All such bands are shifted to the low frequency region on replacement of one Mo ion in $[XMo_{12}O_{40}]$ with one Fe ion.

Table 3. Electronic spectral data[a)]

	λ_{max}/nm($\varepsilon_{max} \times 10^{-4}$)
$[(C_4H_9)_4N]_4[SiMo_{12}O_{40}]$	250sh (7.26), 292 (2.40)
1	245sh (4.45), 300 (1.64), 420sh (0.04)
2	245sh (5.35), 300 (2.06), 420sh (0.08)
$[(C_4H_9)_4N]_4[PMo_{12}O_{40}]$	307 (2.24), 400sh (0.19)
3	307 (6.30), 360sh (2.54)
4	307 (3.24), 360sh (1.29)

a) In acetonitrile.

Experimental

IR spectra (KBr and Nujol) were recorded with a JASCO IR-G spectrophotometer and electronic spectra with a Hitachi 124-Model spectrophotometer. In the measurements of the tetraalkylammonium salts of heteropolyanions, both the KBr pellet method and the Nujol mull method gave the same results. $[SiMo_{12}O_{40}]^{4-}$ was prepared according to the method of North and Haney.[5] Its tetrabutylammonium salt was obtained by adding excess tetrabutylammonium halide. Commercial $[PMo_{12}O_{40}]^{3-}$ (Wako Pure Chemicals Co., Ltd.) was used. Its tetrabutylammonium salt was prepared by a similar work-up. The contents of Fe in the heteropolymolybdates was determined by the analytical method in the presence of Mo.[6]

Preparation. $K[(C_4H_9)_4N]_4[SiFeMo_{11}O_{40}H_2]\cdot CH_3CN$, ***1***: A solution of 1 g (0.478 mmol) $H_4[SiMo_{12}O_{40}]\cdot 15H_2O$ dissolved in 3 ml water was gently heated to 60 °C. To this were added in succession a 1 ml solution mixture of 15 g (0.15 mol) CH_3COOK and 25 ml water containing 1 ml glacial acetic acid, and a 2 ml solution of 1.2 g (7.39 mmol) $FeCl_3$ dissolved in 20 ml water. The mixture was refrigerated overnight. The white precipitate produced was filtered off. The filtrate was evaporated under 50 °C until some crystal appeared, and then refrigerated overnight. The resulting yellow needle compound of $K_5[SiFeMo_{11}O_{40}H_2]$ was dissolved in a small amount of warm water, and then an aqueous solution containing excess tetrabutylammonium bromide was added. The product was washed several times with water, dried *in vacuo*, and recrystallized from dry acetonitrile (yield 35%, pale yellow).

$K[(C_4H_9)_4N]_4[SiFeMo_{11}O_{40}H_3]$, ***2***: 0.94 g (7.39 mmol) of $FeCl_2$ was dissolved in 20 ml water containing 0.5 ml concd HCl. Except for use of this solution instead of the $FeCl_3$ aqueous solution in the preparation of **1**, the product was obtained by a similar work-up (yield 38%, yellow-green).

$[(C_4H_9)_4N]_4[PFeMo_{11}O_{40}H_2]\cdot 12H_2O$, ***3***: A solution of 1 g $H_3[PMo_{12}O_{40}]$ in 3 ml water was gently heated to 65 °C. A 1 ml solution of 15 g (0.15 mol) CH_3COOK in 25 ml water containing 1 ml glacial acetic acid was added and stirred thoroughly. A 2 ml solution of 1.2 g (7.39 mmol) $FeCl_3$ in 20 ml water was then added and refrigerated overnight. The precipitate was dissolved in water. To this yellow clear solution was added a small amount of solution containing excess tetrabutylammonium bromide. The product was thoroughly washed with water and dried *in vacuo* (yield 95%, pale yellow).

$[(C_4H_9)_4N]_4[PFeMo_{11}O_{40}H_3]\cdot 9H_2O$, ***4***: 0.94 g (7.39 mmol) of $FeCl_2$ was dissolved in 20 ml water containing 0.5 ml concd HCl. Except for use of the solution mixture instead of the $FeCl_3$ aqueous solution in the preparation of **3**, the product was obtained by a similar work-up (yield 62%, dark green).

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