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A New Series of Heptamolybdonickelate(IV) and Manganate(IV). Investigation of the Unusual Magnetic and Electronic Spectral Behavior of the Nickel(IV) Compound

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Two new heteropolymolybdates of nickel(IV) and manganese(IV) of composition $K_2H_8NiMo_7O_{28}\cdot 6H_2O$ and $K_2H_8MnMo_7O_{28}\cdot 4H_2O$ with a hitherto unknown 1 : 7 (Ni/Mn : Mo) stoichiometry are reported. X-Ray powder patterns show that they are isomorphous. The electronic spectrum of the nickel(IV) compound exhibits four absorption bands at 16.4, 17.5, 18.3, and 24×10^3 cm^{-1}, and the room temperature magnetic moment of the compound is abnormally high, 1.78 μB. The rationale for these observations is that there are Ni^{3+} impurity which occupy interstitial positions in the crystal lattice and as a consequence of dynamic Jahn-Teller distortion the high-spin $^4A_{2g}(^4T_{1g})$ state of the Ni^{3+} ion lies close to the low-spin ground state $^2A_{1g}(^2E_g)$ to get thermally populated to an appreciable extent leading to significant triplet state contribution.

Stabilization of higher oxidation states of nickel and manganese is a topic of current interest.[2,3] Most of the coordinating agents that stabilize the higher oxidation states of metal ions are organic molecules. Among the few inorganic ligands which are capable of forming higher valent metal complexes, isopolyanions are the prominent examples. Metal complexes of isopolymolybdates deserve special interest because of the diversity of their structural features. Crystal structure determinations have established their structures as hexa-, ennea-, deca-, and dodecamolybdometalates.[4–7]

Following the early discovery of nickel(IV) enneamolybdate by Hall,[8] several studies[5,9–11] have been reported on this and the analogous manganese(IV) species. However, to our knowledge, so far no hetero heptamolybdate has been reported in literature. This paper reports the preparation and characterization of nickel(IV) and manganese(IV) heptamolybdates.

Experimental

All chemicals were analytical grade and used without further purification.

Preparation of Dipotassium Octahydrogen Heptamolybdonickelate(IV), $K_2H_8NiMo_7O_{28}\cdot 6H_2O$. An aqueous solution (350 cm^3) of ammonium heptamolybdate (24.75 g, 20 mmol) was mixed with a solution (30 cm^3) of nickel(II) sulfate hexahydrate (2.65 g, 10 mmol). The solution was filtered, and to the filtrate 5.4 g (20 mmol) of potassium peroxodisulfate in small portions (addition required about 30 min) was added with constant stirring. During this addition the solution was maintained at 80 °C and stirred continuously. After $\approx$1 h a dark brown solution resulted which on standing overnight yielded dark brown shining crystals. The crystals were collected by filtration, washed several times with an aqueous solution of 0.1% $K_2S_2O_8$ followed by ice cooled water and finally dried over $CaCl_2$. Yield 6.3 g.

Dipotassium Octahydrogen Heptamolybdomanganate(IV), $K_2H_8MnMo_7O_{28}\cdot 4H_2O$. An aqueous solution (50 cm^3) of manganese(II) sulfate tetrahydrate (2.25 g, 10 mmol) was added to an aqueous solution (300 cm^3) of ammonium heptamolybdate (24.75 g, 20 mmol) with constant stirring. The solution turned yellowish in colour which was then filtered. The filtrate was heated on a steam bath and 5.4 g (20 mmol) of potassium peroxodisulfate was added in small portions (addition continued for 30 min) while stirring the solution vigorously. The colour of the solution gradually changed to orangeyellow. On standing at room temperature for $\approx$2 h, orangered shining crystals deposited. The product was collected on a glass frit and washed several times with 0.1% $K_2S_2O_8$ followed by ice cooled water and finally dried over $CaCl_2$. Yield 10.4 g.

Analyses. Chemical analyses were performed at least in triplicate. Manganese was estimated volumetrically by redox titration. Nickel and molybdenum were estimated gravimetrically using dimethylglyoxime and 8-quinolinol respectively as the reagents.[12] Water contents were determined thermogravimetrically.

Oxidation States†. About 30 mg of the compound was suspended in 25 cm^3 of water taken in an iodine flask. To this was added 2 g of iodate free potassium iodide and 10 ml of 2 mol dm^{-3} hydrochloric acid. 400 mg of sodium hydrogencarbonate was then added in small portions. The flask was stoppered immediately and the solution was stirred continuously for 2 h in dark with a magnetic stirrer. The solution was diluted to about 200 cm^3 and the liberated iodine was titrated with a standardized solution of sodium thiosulfate.

Measurements. The diffuse reflectance spectra were recorded (780—300 nm) on a Cary 14D spectrophotometer using magnesium oxide as the reference. Electronic spectra in solution were measured (800—200 nm) with a Pye Unicam SP8-150 spectrophotometer. Magnetic susceptibility measurements were made at room temperature on a Gouy balance with Co[Hg(SCN)$_4$] as calibrant. X-Ray powder data were recorded with a Philips X-ray generator PW 1130 coupled with a Counter Diffractometer PW 1050,51 with nickel filtered Cu *Ka* radiation. Thermal analyses were carried out on a Shimadzu DT-30 thermal analysis system in an atmosphere of nitrogen at a heating rate of 5 °C min^{-1}.

Results and Discussion

The analytical results of the compounds shown in Table 1 are compatible with the assigned formulations. Both manganese and nickel are shown by the analytical data to possess the +4 oxidation state. The equivalent weight measurements as shown in Table 1 also support the 7 : 1 stoichiometry. In solid state, both the heptamolybdo compounds are indefinitely stable. The manganese(IV) compound is insoluble in water but the

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† All solutions used in these measurements were prepared with deaerated water.

Table 1. Elemental analysis and equivalent weight of the compounds

Compound		$M^{a)}$	Mo	H_2O	Mo/M	Equivalent$^{b)}$ weight
$K_2H_8NiMo_7O_{28}\cdot 6H_2O$	Found(%)	4.18	48.29	7.51	7.06	$676\pm 4^{d)}$
$(1372.7)^{c)}$	Calcd (%)	4.28	48.95	7.57		
$K_2H_8MnMo_7O_{28}\cdot 4H_2O$	Found(%)	4.13	50.30	5.50	6.98	$663\pm 5^{d)}$
$((1333)^{c)}$	Calcd (%)	4.12	50.41	5.40		

a) M=Ni or Mn. b) With respect to reduction of the hetero atom to the +2 oxidation state. c) Molecular weight of the compound. d) Experimental mean of four determinations.

Table 2. Observed *d*-spacings and intensities of $K_2H_8NiMo_7O_{28}\cdot 6H_2O$ and K_2H_8 $MnMo_7O_{28}\cdot 4H_2O$

$K_2H_8NiMo_7O_{28}\cdot 6H_2O$		$K_2H_8MnMo_7O_{28}\cdot 4H_2O$	
d	Intensities	*d*	Intensities
5.63	9	5.57	10
4.70	16	4.76	14
3.92	44	3.93	43
3.60	72	3.61	70
3.22	100	3.25	100
3.00	43	2.99	41
2.82	43	2.82	42
2.49	10	2.51	10
2.40	61	2.41	65
2.03	42	2.04	42
1.97	25	1.99	24
1.79	20	1.69	19
1.63	13	1.65	15
1.42	30	1.42	31
1.41	20	1.41	19

Table 3. The diffuse reflectance spectra of $K_2H_8NiMo_7O_{28}\cdot 6H_2O$ and $K_2H_8MnMo_7O_{28}\cdot 4H_2O$

$K_2H_8NiMo_7O_{28}\cdot 6H_2O$		$K_2H_8MnMo_7O_{28}\cdot 4H_2O$	
Band position $\tilde{\nu}/10^3\ cm^{-1}$	Assignments	Band position $\tilde{\nu}/10^3\ cm^{-1}$	Assignments
16.4	$^1A_{1g}\rightarrow {}^1T_{1g}{}^{a)}$ or $^2A_{1g}\rightarrow {}^4A_{2g}{}^{b)}$	14.3	$^4A_{2g}\rightarrow {}^2E_g$
17.5	$^1A_{1g}\rightarrow {}^1T_{2g}{}^{a)}$	15.0	$^4A_{2g}\rightarrow {}^2T_{2g}$
18.3	$^2A_{1g}\rightarrow {}^4E_g{}^{b)}$	20.4	$^4A_{2g}\rightarrow {}^4T_{2g}$
24.0	$^2A_{1g}\rightarrow {}^2B_{1g}{}^{b)}$	27.9	$^4A_{2g}\rightarrow {}^4T_{1g}$ (F)

a) Due to Ni(IV). b) Due to Ni(III).

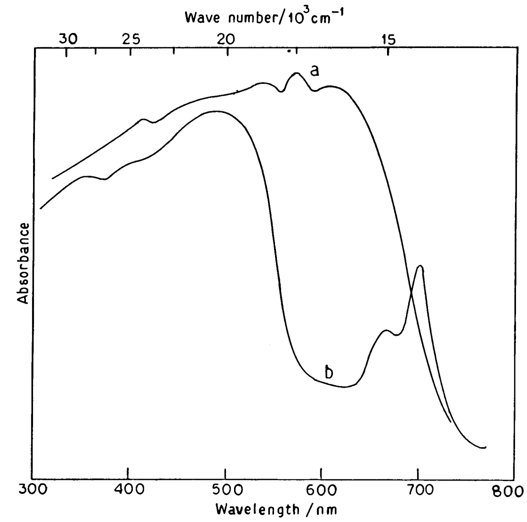

Fig. 1. Diffuse reflectance spectra of (a) $K_2H_8NiMo_7O_{28}\cdot 6H_2O$ and (b) $K_2H_8MnMo_7O_{28}\cdot 4H_2O$.

nickel(IV) compound is sparingly soluble in hot water (≈40 °C).

Table 2 summarizes the powder diffraction data of both $K_2H_8MnMo_7O_{28}\cdot 4H_2O$ and $K_2H_8NiMo_7O_{28}\cdot 6H_2O$. The identical *d*-spacings as well as intensities confirm that they are isomorphous. Similar isomorphism in other heteropolymetalates of Ni(IV) and Mn(IV) is well documented in literature.[11,13,14]

The number of water molecules present in the nickel(IV) and manganese(IV) compounds were determined from TGA and DTA. $K_2H_8NiMo_7O_{28}\cdot 6H_2O$ loses the six water molecules between 60 and 190 °C. The DTA shows that the water molecules are lost in two overlapping steps having the endothermic peaks at 105 and 135 °C. The observed weight loss, 7.51% agrees well with the calculated value, 7.58%. The thermolysis product arrested at 190 °C have the composition $K_2H_8NiMo_7O_{28}$ and the iodometric assay shows +4 oxidation state of nickel. On further heating, $K_2H_8NiMo_7O_{28}$ decomposes between 240—500 °C in a complicated way with the evolution of water along with oxygen as indicated by the appearance of two consecutive exotherms in the DTA. In $K_2H_8MnMo_7O_{28}\cdot 4H_2O$ the four water molecules are lost between 50 and 200 °C in a single step (DTA peak temperature, 120 °C). Above 230 °C further decomposition takes place in a way similar to the nickel(IV) compound. From the thermal analysis it may be stated that both the compounds contain two types of water, *viz.* the water of crystallization and the constitutional water which evolve at a considerably higher temperature (between 230—500 °C) compared to the water of crystallization.

Electronic Spectra and Magnetic Moments. The electronic spectrum of $K_2H_8NiMo_7O_{28}\cdot 6H_2O$ in saturated aqueous solution contains two bands at 17.8 and $47.4\times 10^3\ cm^{-1}$. The first one has also been observed in enneamolybdonickelate(IV)[11] and is assigned to nickel(IV) d-d ($^1A_{1g}\rightarrow {}^1T_{2g}$) transition. The other band at $47.4\times 10^3\ cm^{-1}$ is most likely due to a charge transfer transition.

The diffuse reflectance spectra of the compounds with probable assignments are listed in Table 3. The electronic spectrum of the nickel(IV) compound in solid state as shown in Fig. 1 exhibits four bands at 16.4, 17.5, 18.3, and $24\times 10^3\ cm^{-1}$. The band at $17.5\times 10^3\ cm^{-1}$ which is also observed in solution is the most intense one, while the other three are of comparable intensities. It seems likely that due to their lower intensities they were not observed in the spectrum obtained with saturated aqueous solution.

In interpreting the electronic spectra of the nickel(IV) and manganese(IV) compounds we have considered that these metal ions are present in an octahedral array of oxygen atoms which is consistent with the structural information available for the heteropolymolybdates.

A common feature for most of the spin paired octahedral d^6 metal ions like nickel(IV) is that they give rise to two allowed ($^1A_{1g}\rightarrow{}^1T_{1g}$ and $^1A_{1g}\rightarrow{}^1T_{2g}$) and two spin forbidden ($^1A_{1g}\rightarrow{}^3T_{1g}$ and $^1A_{1g}\rightarrow{}^3T_{2g}$) ligand field transitions of which the $^1A_{1g}\rightarrow{}^1T_{2g}$ transition is of highest energy and maximum intensity.[15)] Thus the most intense ligand field band observed at 17.5×10^3 cm^{-1} in the solid state spectrum of $K_2H_8NiMo_7O_{28}\cdot6H_2O$ can safely be assigned to $^1A_{1g}\rightarrow{}^1T_{2g}$ nickel(IV) transition. Since of the remaining three bands, two appear at still higher energies relative to the one at 17.5×10^3 cm^{-1}, their origin cannot be due to d-d transition of nickel(IV). However, the band at 16.4×10^3 cm^{-1} can tentatively be assigned to the second spin allowed nickel(IV) d-d transition, *viz.* $^1A_{1g}\rightarrow{}^1T_{1g}$.

In order to explain the appearance of two higher energy bands at 18.3 and 24×10^3 cm^{-1}, we invoke the presence of Ni^{3+} ion in the crystal lattice of $K_2H_8NiMo_7O_{28}\cdot6H_2O$. This assumption is based on the observation made from magnetic moment measurements (see later). It is conjectured that during the preparation of $K_2H_8NiMo_7O_{28}\cdot6H_2O$, some of the nickel(IV) sites are occupied by nickel(III) in the crystal lattice. These Ni^{3+} ions present in an octahedral array of oxygen should ordinarily have a low-spin ^2E_g ground state. It is well known[16)] that for a ground state of E symmetry the octahedral environment undergoes tetragonal distortion by interaction with the ε_g vibrational mode leading to either elongation or compression along the four fold axis together with appreciable ground-state splitting. Reinen *et al.*[17,18)] have shown from EPR and ligand field data that for a Ni^{3+} ion in an octahedral site, Jahn-Teller distortion sharply splits ^2E_g into $^2B_{1g}+{}^2A_{1g}$ while $^4T_{1g}$ undergoes a much smaller splitting into ^4E_g and $^4A_{2g}$. In effect, $^2A_{1g}$ becomes the ground state with $^4A_{2g}$ lying only slightly above it. The result is the equilibrium $^2A_{1g}\rightleftharpoons{}^4A_{2g}$. Similar tetragonal ground state splitting has also been considered by Warren *et al.*[19)] during their attempt to explain the electronic spectrum of $[NiF_6]^{3-}$ ion.

Thus following the energy level diagram as proposed by Reinen,[18)] the bands at 18.3 and 24×10^3 cm^{-1} can be assigned to ($^2A_{1g}\rightarrow{}^4E_g$) and ($^2A_{1g}\rightarrow{}^2B_{1g}$) transitions respectively. The lowest energy band at 16.4×10^3 cm^{-1} which has been previously indicated as due to $^1A_{1g}\rightarrow{}^1T_{1g}$ of nickel(IV) can alternatively be assigned to $^2A_{1g}\rightarrow{}^4A_{2g}$ nickel(III) d-d transition.

Table 3 shows that the spectrum of Mn(IV) compound contains four bands (also shown in Fig. 1). The ruby band observed at 14.3×10^3 cm^{-1} was also observed by Baker *et al.*[11)] in enneamolybdomanganate(IV) and was assigned to $^4A_{2g}\rightarrow{}^2E_g$ transition. The next higher energy band at 15×10^3 cm^{-1} was also observed in the spectrum of hexamolybdochromate(III) and was interpreted as due to $^4A_{2g}\rightarrow{}^2T_{2g}$ transition.[11)] The remaining two higher energy bands appeared at 20.4 and 27.9×10^3 cm^{-1} are considered to be due to first and second spin allowed transitions to excited $^4T_{2g}$ and $^4T_{1g}(F)$ states respectively following the arguements made by Jϕrgensen.[20)]

The room temperature magnetic moment of the Mn(IV) compound is 3.95 BM which is in agreement with the value 3.88 BM calculated for a high-spin d^3 Mn(IV) configuration. Although on the basis of analytical and X-ray powder data one would expect that $K_2H_8NiMo_7O_{28}\cdot6H_2O$ should be diamagnetic; however, it is paramagnetic having a room temperature magnetic moment of 1.78 BM. This unusually high magnetic moment for a nickel(IV) compound can not be explained on the basis of its temperature independent paramagnetism which at the most can have a contribution of ≈0.6 BM.[21)] Such unusual paramagnetic behavior was also observed in nickel(IV) periodate[22)] and was explained from EPR studies as due to nickel(III) impurities.[23)] The presence of nickel(III) impurity has been already considered in order to explain the electronic spectrum of $K_2H_8NiMo_7O_{28}\cdot6H_2O$. Obviously the concentration of nickel(III) is very low as the chemical composition indicates and literature[2)] shows that nickel(III) species are almost invariably low-spin with one unpaired electron. Thus a small concentration of nickel(III) ion with a low-spin ground state (^2E_g) having no orbital contribution can not alone explain such a high room temperature magnetic moment. Hoppe *et al.*[24,25)] in order to explain the unusually high magnetic moments of Ni^{3+} ion in alkali metal hexafluoronickelates considered thermal equilibrium between the high and low-spin forms. We also propose that because of the dynamic Jahn-Teller effect, the high-spin $^4A_{2g}$ ($^4T_{1g}$) state of the nickel(III) lies close enough to the low-spin ground state $^2A_{1g}(^2E_g)$ to get thermally populated to an appreciable extent leading to significant triplet state contribution towards the room temperature magnetic moment.

In conclusion we emphasize that the Ni^{3+} ion that is present as impurity in $K_2H_8NiMo_7O_{28}\cdot6H_2O$ provides a rare example of spin state equilibrium of nickel(III). To our knowledge such example is restricted only to alkalimetal hexafluoronickelates(III).

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