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Interaction of Transition-Metal-Substituted Heteropolytungstates with Adenosine and Determination of the Site Coordination

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The complexes of Keggin and Dawson structures of transition-metal-substituted heteropolytungstates ($Cs_5[PW_{11}O_{39}M\text{-}OH_2]\cdot xH_2O$ and $K_8[P_2W_{17}O_{61}M\text{-}OH_2]\cdot yH_2O$ where M is Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}) with adenosine have been synthesized and characterized. The UV-visible Fourier transform IR, ^{1}H-NMR spectra show an interaction between transition-metal-substituted heteropolytungstates and adenosine. Our spectroscopic data show transition-metal-substituted heteropolytungstates coordinated with adenosine molecule through N(7) of imidazole ring and have a direct interaction in solid phase. It seems the interaction of $Cs_5[PW_{11}O_{39}M\text{-}OH_2]\cdot xH_2O$ with adenosine is indirect in solution.

Key words: Adenosine, Binding sites, Heteropolytungstates, Metal ion.

INTRODUCTION

The antiviral and antitumour properties of polyoxometalates have been an important research field for several years due to their redox ability.[1–4] The possibility of incorporating transition metal cations into octahedral binding sites on the surfaces of lacunary heteropolyanions such as $[PW_{11}O_{39}]^{7-}$ (Fig. 1)[5] and $[P_2W_{17}O_{61}]^{10-}$, results in the formation of complexes $[PW_{11}O_{39}M\text{-}L]^{n-}$ or $[P_2W_{17}O_{61}M\text{-}L]^{m-}$ and probably also can show the same behaviour in viruses and cancerous cells *via* interaction with the donor basic molecules. Ko and co-workers[6, 7] studied imidazole, L-histidine and their derivatives with undecatungstatometalto(II) silicate (metal ion is Ni^{2+} or Co^{2+}). Pope[5], Weakley[8–10], Zonnevijlle[11] and Ahmadabadi[12] studied transition-metal-substituted heteropolytungstates (SLH) with different ligands. The purpose of this work is to report the coordination of adenosine with transition-metal-substituted heteropolytungstates which has an important role as building blocks in the construction of living structures of DNA and RNA.

EXPERIMENTAL

All compounds were reagent grade and used without purification. The IR spectra were taken on a Shimadzu FT-IR Model 4300 spectrometer as a KBr plate. The ^{1}H-NMR spectra were recorded on a FT- NMR, Brucker Aspect 3000

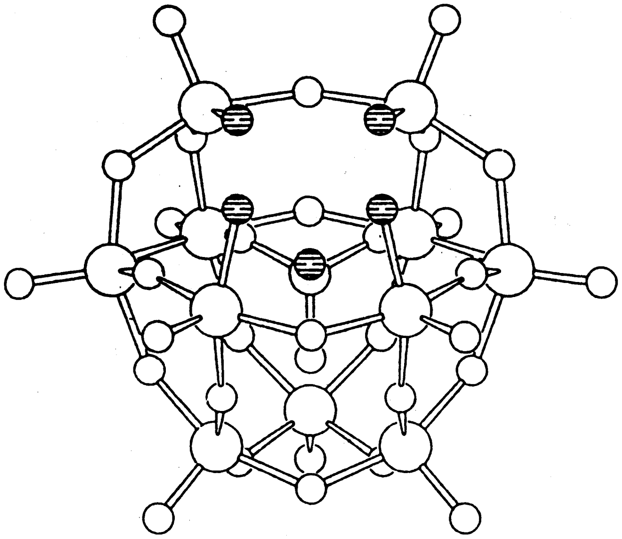


Fig. 1. Lacunary heteropolyanion $[PW_{11}O_{39}]^{7-}$ (Ref. 5)

spectrometer AC-100 instrument. The cyclic voltammograms were performed on EG&G Model 384B polarographic analyzer. The working electrode was SMDE and Ag/AgCl as a reference electrode. The electronic spectra were obtained on a Beckman Du-6 spectrophotometer in 0.1 M $NaClO_4$ solution.

Preparation: The α and a-2 isomers of both lacunary and transition-metal-substituted heteropolytungstates were prepared according to known procedures, identified by electronic spectroscopy and cyclic voltammetry and compared to literature[10–15].

Adenosine (0.0001 mol) was dissolved in double distilled hot water (75–80°C) and mixed with a solution of transition-metal-substituted heteropolytungstates (molar ratio is 1 : 1). The resulting clear solution (5 mL) was reduced in volume to 1 mL leaving a sticky liquid. This residue was treated with acetone and the solution was cooled. The resulting precipitates of $K_8[a_2\text{-}P_2W_{17}O_{61}M\text{-ado}]\cdot yH_2O$ and $Cs_5[\alpha\text{-}PW_{11}O_{39}M\text{-ado}]\cdot xH_2O$ (M is Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} and ado is adenosine) were filtered, washed with ethanol and dried *in vacuo* for 24 h.

RESULTS AND DISCUSSION

Optical Spectra Analysis: The positions and assignments of the absorption maximum of our synthetic material are given in Table-1. The spectra assignments for transition-metal-substituted heteropolytungstates are made on the basis of O_h symmetry, though the true site symmetry around metal ion in lacunary heteropolytungstates is probably lower. In heteropolyanions containing cobalt a broad relatively weak band is superimposed on the ultraviolet absorption edge. Malik and Weakley[9] have ascribed this to the charge transfer between cobalt and polytungstate, either from cobalt or tungsten.

Our results confirm the previous reports that SLH have also, at least, a water molecule bound to the outer (transition metal) heteroatom and replaceable by other ligands. The changes in the position and shape of the ligand field band were observed in the interaction of potential ligands and cobalt in the heteropolyanions[8–11].

When adenosine interacts with cobalt in the heteropolyanion, the absorption maximum shift to higher wavenumbers and this shift is accompanied by a broadening of the band (Table-1).

In the previous report, the spectrum of $[PNiW_{11}]^{5-}$ was interpreted in terms of slightly distorted NiO_6 octahedron[10].

The small changes in the position of the $^3T_{1g}(P)$ and the $^3T_{1g}(F)$ bands were observed in the presence of potential ligand[8–11].

The interaction of adenosine with nickel in heteropolyanion shows a slight shift in wave number of the $^3T_{1g}(P)$ band (Table-1).

TABLE-1
[a]UV-VISIBLE SPECTRA OF $[PW_{11}O_{39}M(L)]^{5-}$

Compound	d → d band (nm)		Charge transfer band
$(Cs_5[PW_{11}O_{39}Co\text{-}OH_2]$	539	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	366 $(Co^{2+} \rightarrow W^{6+})$
	528		251 $(O^{2-} \rightarrow W^{6+})$
	506		
$(Cs_5[PW_{11}O_{39}Co\text{-}ado]$	526	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	363 $(Co^{2+} \rightarrow W^{6+})$
	503		250 $(O^{2-} \rightarrow W^{6+})$
$(Cs_5[PW_{11}O_{39}Ni\text{-}OH_2]$	418	$^3A_{1g} \rightarrow {}^3T_{1g}(P)$	250 $(O^{2-} \rightarrow W^{6+})$
	> 800	$^3A_{1g} \rightarrow {}^3T_{1g}(F)$	
$(Cs_5[PW_{11}O_{39}Ni\text{-}ado]$	416	$^3A_{1g} \rightarrow {}^3T_{1g}(P)$	250 $(O^{2-} \rightarrow W^{6+})$
	> 800	$^3A_{1g} \rightarrow {}^3T_{1g}(F)$	
$(Cs_5[PW_{11}O_{39}Mn\text{-}OH_2]$	no observed maximum		250 $(O^{2-} \rightarrow W^{6+})$
$(Cs_5[PW_{11}O_{39}Mn\text{-}ado]$	no observed maximum		250 $(O^{2-} \rightarrow W^{6+})$
$(Cs_7[PW_{11}O_{39}]$	—		239 $(O^{2-} \rightarrow W^{6+})$

[a]L is ligand and M is Mn^{2+}, Ni^{2+} or Co^{2+}.

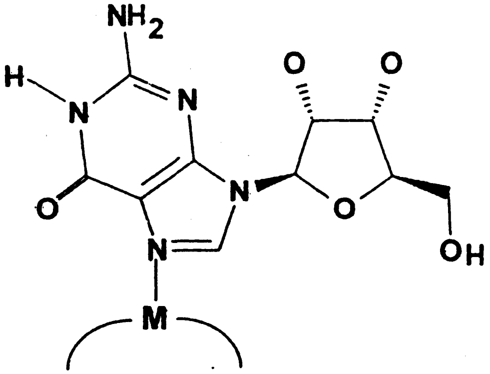
The absorption maxima in manganese in the heteropolyanion are not observed due to the overlapping of strong charge transfer with ligand field bands.

There exist similar results for the interaction of adenosine with Ni^{2+}, Co^{2+} and Mn^{2+} in Dawson lacunary heteropolyanion.

IR Spectra Analysis: The band frequencies and assignments to the appropriate vibrations of ado and interaction of ado with transition-metal-substituted heteropolytungstates are shown in Table-2. Fig. 2 shows the interaction of ado with SLH.

The strong absorption band in 1668 cm^{-1} has been assigned to bending vibration of NH_2 deformation in accordance with previous report[16], by interaction of metal ion with ring shift to lower wavenumbers. This shift is due to change in hydrogen bonding structure of $—NH_2$ group. The determination of precise position of this group is difficult because of overlapping with bending vibration of H_2O.

Absorption bands at 1508, 1576 and 1604 cm^{-1} in the free ado spectrum, assigned to pyrimidine and imidazole skeletal vibration, show no drastic change in interaction with SLH (Table-2). Absorption band 1476 cm^{-1} in free ado spectrum assigned to stretching vibration of N(7)—C(8) and bending vibration of C(8)—H of imidazole ring. Beauchamp[16–19] analyzed the positions of these bands and determined the crystal structure with one, two and three $MeHg^+$ moieties with adenine. Skeletal vibrations of pyrimidine and imidazole have been found at the frequencies as in adenine bonded with two methylmercury cations *via* N(9) and N(7). This can be caused by the M^{2+}—N(7) and N(9)—C(1) in adenosine[20–22]. Although the N(1) atom in adenosine is characterized by much greater basicity compared to N(7), the latter is the preferred site of metallation[23, 24].



M = Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}

Fig. 2. Interaction of adenosine with SLH

When metal ion interacts to N(7) adenosine site, the absorption band of 1476 cm^{-1} shifts to higher frequencies (Table-2).

Other pyrimidine vibrations in the range of 1350 to 1200 cm^{-1} in the free ado spectrum and in the compound resulting from the interaction of adenosine with each of SLH do not show any considerable change.

The IR spectrum of structurally characterized divalent metal ion shows a direct metal ion-N(7) coordination[22–27]. Our results confirm the previous reports.

The strong absorption bands in the frequency range of 1200 to 500 cm^{-1} are due to SLH vibration. Other absorption bands related to ado in this region could not be observed. The absorption region related to P—O and W—O stretching of heteropolytungstates with ado interaction shows no drastic changes.

Similar results have been seen for the interactions of $[P_2W_{17}O_{61}Co\text{-}OH_2]^{8-}$ and $[P_2W_{17}O_{61}Ni\text{-}OH_2]^{8-}$ (Dawson structure of SLH) with adenosine (Table-2).

^{1}H-NMR Spectra Analysis: The ^{1}H-NMR spectrum of $Cs_5[PW_{11}O_{39}Zn\text{-}ado]\cdot xH_2O$ was studied in deuterium oxide solution and provided useful information about the structural properties of the $Cs_5[PW_{11}O_{39}Zn\text{-}ado]\cdot xH_2O$ complex.

The observed ^{1}H- NMR signals have been assigned to particular atoms on the

TABLE-2
INFRARED SPECTRA FREQUENCIES (cm^{-1})

Adenosine	$Cs_5[PW_{11}O_{39}Co\text{-}ado]$ xH_2O	$Cs_5[PW_{11}O_{39}Ni\text{-}ado]$ xH_2O	$Cs_5[PW_{11}O_{39}Mn\text{-}ado]$ xH_2O	$Cs_5[PW_{11}O_{39}Zn\text{-}ado]$ xH_2O	$K_6[P_2W_{17}Co\text{-}ado]$ yH_2O	$K_6[P_2W_{17}Ni\text{-}ado]$ yH_2O	Assignments
1712 (s)	1692 (s)	1694 (s)	1692 (s)	1683 (m)	1688 (s)	1692 (s)	—
1668 (s)	1640 (vs)	1640 (vs)	1637 (vs)	1642 (vs)	—	—	NH_2 & H_2O def.
1604 (s)	1608 (vs)	1608 (sh)	1616 (br)	1608 (vs)	1616 (s)	1601 (s)	pyrimidine ring
1576 (s)	1582 (sh)	1583 (sh)	1580 (sh)	1583 (sh)	1580 (sh)	—	pyrimidine ring
1508 (w)	1508 (w)	1508 (w)	1508 (w)	1508 (w)	1508 (w)	—	Imidazole ring
1476 (s)	1484 (s)	1492 (br)	1479 (br)	1479 (s)	1483 (s)	1479 (s)	Imidazole ring sk.
—	1460 (sh)	1458 (w)	1448 (br)	1458 (sh)	1466 (sh)	—	imidazole ring sk.
1428 (s)	1424 (vs)	1425 (s)	1420 (s)	1425 (s)	1425 (s)	1422 (s)	imidazole ring plane
1334 (s)	1336 (s)	1339 (s)	1338 (s)	1340 (s)	1336 (s)	1333 (s)	purine
1304 (s)	1304 (s)	1308 (b)	1305 (w)	1308 (br)	1308 (br)	1301 (br)	purine

s: strong; vs: very strong; w: weak; m: medium; br: broad; sh: shoulder; sk: skeletal; def: deformation.

basis of literature data. The H-2 and H-8 proton chemical shifts of adenosine have been observed at 8.11 and 8.26 ppm, respectively[24, 27–29]. The H-2 and H-8 chemical shifts of the $Cs_5[PW_{11}O_{39}Zn\text{-ado}]\cdot xH_2O$ has been observed at 8.10 and 8.35 ppm respectively . The slight downfield shift of H-8 chemical shift of $Cs_5[PW_{11}O_{39}Zn\text{-ado}]\cdot xH_2O$ could be indicative of the indirect Zn-N(7) binding through an H_2O molecule. This kind of chemical shift has also been observed in similar complexes[23, 29].

The analysis of the IR, NMR and UV-visible spectra leads to the conclusion that transition-metal-substituted heteropolytungstates interact with N(7) of ado. However, it seems that $Cs_5[PW_{11}O_{39}Zn\text{-}OH_2]\cdot xH_2O$ has a bond to N(7) of ado *via* a solvent in solution.

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