

Crystal Structure and Characterization of a Large Polyoxotungstate $(\text{NH}_4)_{21} \{ \text{La}(\text{H}_2\text{O})_5 [\text{Ni}(\text{H}_2\text{O})]_2 \text{As}_4 \text{W}_{40} \text{O}_{140} \} \cdot 53\text{H}_2\text{O}$

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The heteropolytungstate $(\text{NH}_4)_{21} \{ \text{La}(\text{H}_2\text{O})_5 [\text{Ni}(\text{H}_2\text{O})]_2 \text{As}_4 \text{W}_{40} \text{O}_{140} \} \cdot 53\text{H}_2\text{O}$ is obtained by the reaction of $\text{Na}_{27} [\text{NaAs}_4 \text{W}_{40} \text{O}_{140}] \cdot 60\text{H}_2\text{O}$ with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and NH_4Cl at pH ~ 4.5. The structure and chemical composition are determined by X-ray diffraction analysis and elemental analysis. The crystal data and main structure refinement are $a = 1.9551(3)$ nm, $b = 2.4156(4)$ nm, $c = 3.7068(6)$ nm, $\beta = 91.505(3)^\circ$, $V = 17.500(5)$ nm³, monoclinic crystal system with space group $P2_1/n$, $Z = 4$, $R_1 = 0.0573$, $wR_2 = 0.0717$ [$I > 2\sigma(I)$], $R_1 = 0.2463$ and $wR_2 = 0.1199$ (all data). $[\text{La}(\text{H}_2\text{O})_5 \{ \text{Ni}(\text{H}_2\text{O}) \}_2 \text{As}_4 \text{W}_{40} \text{O}_{140}]^{21-}$ has C_{2v} symmetry. IR spectra of the ligand $[\text{NaAs}_4 \text{W}_{40} \text{O}_{140}]^{27-}$ and its three complexes were discussed.

Keywords heteropolytungstate, crystal structure, tungsten, nickel, arsenic, lanthanum

Introduction

Polyoxometalates are metal-oxygen cluster species that exhibit a fascinating variety of structure and properties in catalysis, materials science and medicine.¹⁻⁴ The design and structure determination of novel large polyoxometalates and derivation of known polyoxometalates are interesting and remain a challenge. The big cyclic anion $[(B-\alpha-\text{AsO}_3\text{W}_9\text{O}_{30})_4(\text{WO}_2)_4]^{28-}$ "As₄W₄₀" can be viewed as a derivative of AsW₉, in which four AsW₉ units are linked by additional tungsten atoms. The properties of As₄W₄₀, especially its behavior in solution, have been studied in great detail in the past.⁵ Most of the knowledge is based on unambiguous spectroscopic data and the early crystal structural analysis obtained for the cobalt^{II}-substituted anion $\{ \text{NH}_4 [\text{Co}(\text{H}_2\text{O})]_2 \text{As}_4 \text{W}_{40} \text{O}_{140} \}^{23-}$.⁶ Liu *et al.*⁷ compared the emission spectrum of $[\text{Eu}^{\text{III}} \text{As}_4 \text{W}_{40} \text{O}_{140}]^{25-}$ with $\text{Eu}^{\text{III}}(\text{SiW}_{11})_2$, $\text{Eu}^{\text{III}}(\text{AsW}_{11})_2$ and $\text{U}^{\text{IV}}(\text{GeW}_{11})_2$, and concluded that the Ln^{III} occupied S1

site and was coordinated by eight O_d in $[\text{Eu}^{\text{III}} \text{As}_4 \text{W}_{40} \text{O}_{140}]^{25-}$. During last years, the synthesis and crystallographic characterization of polyoxometalate anions related with large cyclic ligand $[(B-\alpha-\text{As}_3\text{W}_9\text{O}_{30})_4(\text{WO}_2)_4]^{28-}$ have made some progresses, some novel structures of large polyoxometalate anions were reported, $[\text{Ln}(\text{Ln}_2\text{OH})(\text{H}_2\text{O})_{10} \text{As}_4 \text{W}_{40} \text{O}_{140}]^{20-}$ (Ln^{III} = Ce, Nd, Sm, Gd), $[\text{M}^m(\text{Ln}_2\text{OH})_2(\text{H}_2\text{O})_{10} \text{As}_4 \text{W}_{40} \text{O}_{140}]^{(18-m)-}$ (M = Ba^{II}, K⁺, none, and Ln^{III} = La, Ce, Gd),⁸ and $[\text{Ce}^{\text{III}}(\text{H}_2\text{O})_5 \text{As}_4 \text{W}_{40} \text{O}_{140}]^{25-}$.⁹ We here report the synthesis and structural characterization of derivative of As₄W₄₀ with La^{III} and Ni^{II} cations, the single-crystal X-ray analysis located all the cations and nonhydrogen atoms of anion $\{ \text{La}(\text{H}_2\text{O})_5 [\text{Ni}(\text{H}_2\text{O})]_2 \text{As}_4 \text{W}_{40} \text{O}_{140} \}^{21-}$ in $(\text{NH}_4)_{21} \{ \text{La}(\text{H}_2\text{O})_5 [\text{Ni}(\text{H}_2\text{O})]_2 \text{As}_4 \text{W}_{40} \text{O}_{140} \} \cdot 53\text{H}_2\text{O}$, this is the first report about crystal structure of heteropolyoxometalate of ligand As₄W₄₀ simultaneously with lanthanide and transition metal ions.

Experimental

Syntheses

All the reagents for the preparation were used without further purification. The $\text{Na}_{27} [\text{NaAs}_4 \text{W}_{40} \text{O}_{140}] \cdot 60\text{H}_2\text{O}$ was prepared according to the reported procedure.¹⁰ $\text{Na}_{27} [\text{NaAs}_4 \text{W}_{40} \text{O}_{140}] \cdot 60\text{H}_2\text{O}$ (6.97 g, 0.6 mmol) was dissolved in 20 mL of water under mild heat; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.29 g, 1.2 mmol) dissolved in 5 mL of water was then added dropwise with stirring. The mixture was warmed at 50 °C for 5 min, then $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.26 g, 0.6 mmol) dissolved in 5 mL of water was added dropwise with stirring. The mixture was warmed at 50 °C for 15 min, and then NH_4Cl (3.0

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g, 56 mmol) was added dropwise, a small amount of precipitate was filtered off. The clear green filtrate (at pH 4.5) was kept at room temperature. With a few days pale-green crystals were formed. The yield was 6.5 g (94%). Anal. calcd (Found) for $(\text{NH}_4)_{21} \{ \text{La}(\text{H}_2\text{O})_5 [\text{Ni}(\text{H}_2\text{O})_2 \text{As}_4 \text{W}_{40} \text{O}_{140}] \cdot 53\text{H}_2\text{O}$: W 63.36 (63.01), As 2.58 (2.50), La 1.20 (1.12), Ni 1.01 (1.08), N 2.53 (2.46), H_2O 9.30 (9.25).

X-Ray Crystallography

A pale-blue crystal of $(\text{NH}_4)_{21} \{ \text{La}(\text{H}_2\text{O})_5 [\text{Ni}(\text{H}_2\text{O})_2 \text{As}_4 \text{W}_{40} \text{O}_{140}] \cdot 53\text{H}_2\text{O}$ with approximate $0.14 \text{ mm} \times 0.06 \text{ mm} \times 0.06 \text{ mm}$ was mounted on a glass fiber capillary which was put on a Bruker Smart-1000 CCD diffractometer equipped with graphite monochromatic radiation $\text{Mo K}\alpha$ ($\lambda = 0.071069 \text{ nm}$). A total of 77374 (24501 independent, $R_{\text{int}} = 0.2782$) reflections were collected at temperature 293(2) K. The crystal structure belongs to monoclinic, space group $P2_1/n$, with cell dimensions $a = 1.9551(3) \text{ nm}$, $b = 2.4156(4) \text{ nm}$, $c = 3.7068(6) \text{ nm}$, $\beta = 91.505(3)^\circ$, $V = 17.500(5) \text{ nm}^3$, $Z = 4$, $D_{\text{calcd}} = 4.092 \text{ g/cm}^3$, $F(000) = 18784$. The structure was solved by direct methods (SHELXTL-97) and refined by the full-matrix-block least-squares method on F^2 .

Anisotropic temperature factors were applied to all nonhydrogen atoms. Structure solution and refinement based on 6618 reflections with $I > 2\sigma(I)$ and on 1999 parameters gave $R_1 = 0.0573$, $wR_2 = 0.0717$. In the final difference map, the maximum and minimum residuals were 1.575×10^3 and $-1.781 \times 10^3 \text{ e/nm}^3$, respectively.

Results and discussion

Structure of $(\text{NH}_4)_{21} [\text{La}(\text{H}_2\text{O})_5 \{ \text{Ni}(\text{H}_2\text{O})_2 \text{As}_4 \text{W}_{40} \text{O}_{140}] \cdot 53\text{H}_2\text{O}$

The crystal structure of the title compound is shown in Fig. 1 with the atomic numbering scheme; the coordination circumstances of La^{III} , Ni^{II} , N(1) and N(2) are shown in Fig. 2 (top view, two $\text{AsW}_9\text{O}_{33}$ have been omitted for clarity in the bottom drawing). Oxygen atoms relating cyclic ligand $[\text{As}_4 \text{W}_{40} \text{O}_{140}]^{28-}$ are O(1) through O(140) and the coordination water molecules are O(141)—O(147). Tungsten atoms relating four $\text{AsW}_9\text{O}_{33}$ subunits are W(1) through W(36) and four bridging tungsten atoms are W(37) through W(40). Selected bond lengths and bond angles are shown in Table 1.

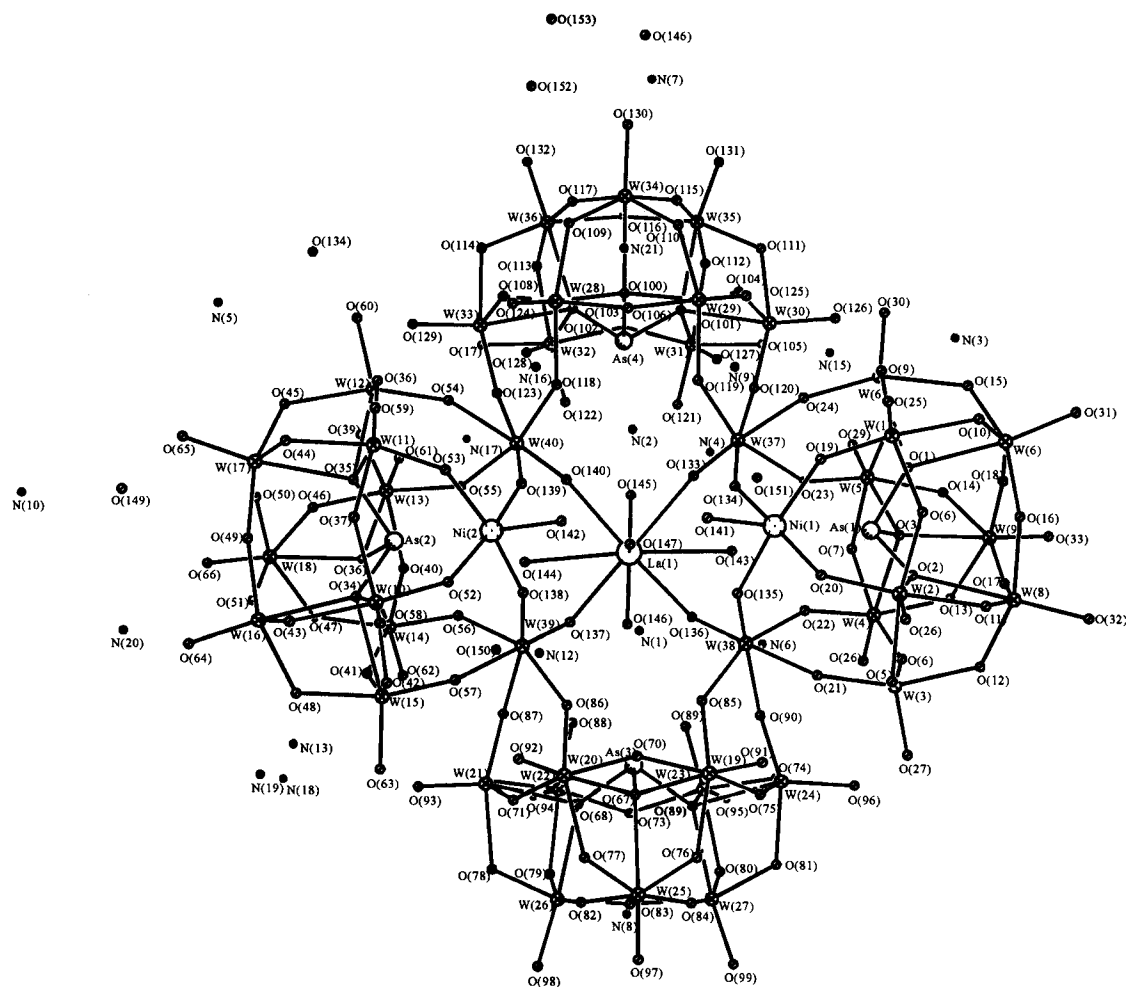


Fig. 1 The structure of the title compound.

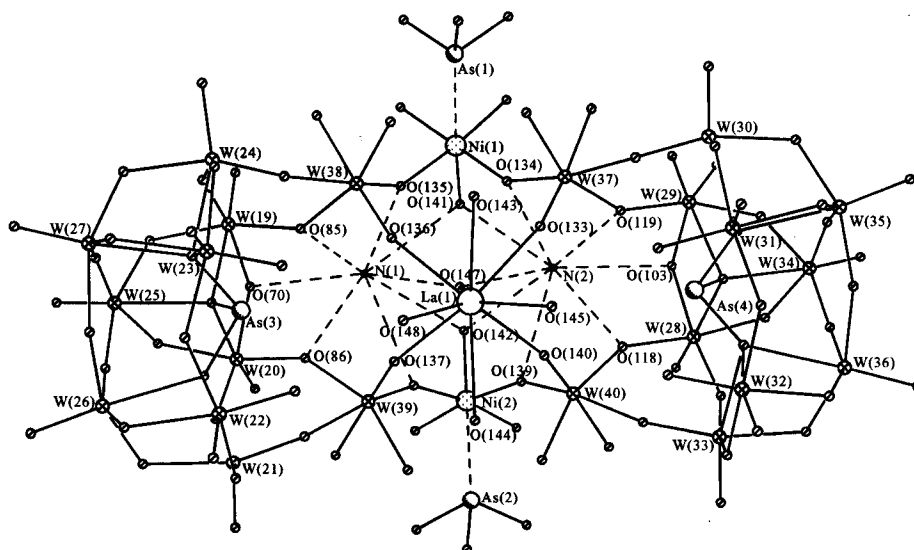


Fig. 2 The coordination circumstances of La^{III} , Ni^{II} , $\text{N}(1)$ and $\text{N}(2)$ in $[\text{La}(\text{H}_2\text{O})_5[\text{Ni}(\text{H}_2\text{O})_2]_2\text{As}_4\text{W}_{40}\text{O}_{140}]^{21-}$ (top view, two $\text{AsW}_9\text{O}_{33}$ were omitted for clarity in the bottom drawing).

Table 1 Selected bond lengths (nm) and bond angles ($^\circ$)

W(1)—O(25)	0.166(3)	W(8)—O(32)	0.176(3)	W(38)—O(135)	0.174(3)
W(1)—O(19)	0.172(3)	W(8)—O(12)	0.182(3)	W(38)—O(136)	0.177(2)
W(1)—O(4)	0.194(3)	W(8)—O(11)	0.189(3)	W(38)—O(85)	0.193(2)
W(1)—O(9)	0.196(3)	W(8)—O(16)	0.194(3)	W(38)—O(22)	0.195(3)
W(1)—O(10)	0.204(2)	W(8)—O(17)	0.197(3)	W(38)—O(21)	0.210(3)
W(1)—O(1)	0.223(3)	W(8)—O(2)	0.239(3)	W(38)—O(90)	0.217(3)
As(1)—O(3)	0.164(2)	As(4)—O(102)	0.173(3)	La(1)—O(143)	0.281(3)
As(1)—O(2)	0.166(3)	As(4)—O(100)	0.174(3)	Ni(1)—O(141)	0.188(3)
As(1)—O(1)	0.178(4)	As(4)—O(101)	0.186(2)	Ni(1)—O(134)	0.192(3)
As(1)—Ni(1)	0.2648(8)	La(1)—O(136)	0.243(2)	Ni(1)—O(20)	0.198(3)
As(2)—O(34)	0.176(4)	La(1)—O(140)	0.247(3)	Ni(1)—O(135)	0.207(3)
As(2)—O(36)	0.176(3)	La(1)—O(137)	0.252(2)	Ni(1)—O(19)	0.207(3)
As(2)—O(35)	0.179(3)	La(1)—O(133)	0.255(3)	Ni(2)—O(138)	0.191(3)
As(2)—Ni(2)	0.2617(8)	La(1)—O(146)	0.255(3)	Ni(2)—O(142)	0.196(3)
As(3)—O(67)	0.170(3)	La(1)—O(145)	0.259(3)	Ni(2)—O(53)	0.196(2)
As(3)—O(68)	0.181(3)	La(1)—O(147)	0.260(4)	Ni(2)—O(52)	0.200(3)
As(3)—O(69)	0.190(3)	La(1)—O(144)	0.279(3)	Ni(2)—O(139)	0.202(3)
O(25)—W(1)—O(19)	102.7(14)	O(32)—W(8)—O(12)	103.5(14)		
O(25)—W(1)—O(4)	100.4(17)	O(32)—W(8)—O(11)	102.3(13)		
O(19)—W(1)—O(4)	94.8(12)	O(12)—W(8)—O(11)	93.5(13)		
O(25)—W(1)—O(9)	101.7(14)	O(32)—W(8)—O(16)	99.2(15)		
O(19)—W(1)—O(9)	92.4(12)	O(12)—W(8)—O(16)	154.8(15)		
O(4)—W(1)—O(9)	154.6(14)	O(11)—W(8)—O(16)	92.0(16)		
O(1)—As(1)—Ni(1)	102.1(9)	O(135)—W(38)—O(136)	95.8(13)		
O(34)—As(2)—O(36)	89.8(16)	O(135)—W(38)—O(85)	93.9(14)		
O(34)—As(2)—O(35)	102.8(16)	O(136)—W(38)—O(85)	97.7(13)		
O(36)—As(2)—O(35)	100.6(14)	O(135)—W(38)—O(22)	101.6(14)		
O(34)—As(2)—Ni(2)	105.7(12)	O(136)—W(38)—O(22)	93.7(12)		
O(36)—As(2)—Ni(2)	146.4(10)	O(85)—W(38)—O(22)	159.7(10)		
O(35)—As(2)—Ni(2)	104.5(9)	O(135)—W(38)—O(21)	88.3(12)		
O(67)—As(3)—O(68)	99.3(13)	O(136)—W(38)—O(21)	173.5(11)		
O(67)—As(3)—O(69)	97.4(11)	O(20)—Ni(1)—O(19)	82.9(12)		
O(68)—As(3)—O(69)	97.0(12)	O(135)—Ni(1)—O(19)	174.2(11)		
O(102)—As(4)—O(100)	93.1(18)	O(141)—Ni(1)—As(1)	174.9(10)		
O(102)—As(4)—O(101)	96.5(13)	O(134)—Ni(1)—As(1)	92.9(8)		
O(100)—As(4)—O(101)	94.6(15)	O(20)—Ni(1)—As(1)	82.0(7)		
O(136)—La(1)—O(140)	136.7(9)	O(135)—Ni(1)—As(1)	94.1(8)		
O(136)—La(1)—O(137)	73.3(9)	O(19)—Ni(1)—As(1)	80.3(7)		

The single-crystal X-ray analysis revealed the structure of $\{La(H_2O)_5[Ni(H_2O)]_2As_4W_{40}O_{140}\}^{21-}$. The four AsW_9O_{33} subunits through four WO_2 connection form the large cyclic ligand $[(B-\alpha-AsO_3W_9O_{30})_4(WO_2)_4]^{28-}$, in which two of four lacunary S2 sites are respectively occupied by two nickel cations, the central cryptate site S1 is occupied by a lanthanum cation. The anion $\{La(H_2O)_5[Ni(H_2O)]_2As_4W_{40}O_{140}\}^{21-}$ has approximately C_{2v} symmetry.

The S1 site supplies four O_d coordinating to La^{III} , and other five water molecule coordinate to La^{III} , the coordination number of La^{III} is nine, the coordination circumstance of La^{III} in $\{La(H_2O)_5[Ni(H_2O)]_2As_4W_{40}O_{140}\}^{21-}$ is similar to that of Ce^{III} in $[Ce^{III}(H_2O)_5As_4W_{40}O_{140}]^{25-}$,⁹ the four bonding lengths of $La-O_d$ are among 0.243(2)—0.255(3) nm, five bonding lengths of $La-O_w$ among 0.255(3)—0.281(3) nm. The structure of $\{La(H_2O)_5[Ni(H_2O)]_2As_4W_{40}O_{140}\}^{21-}$ is different from those of $[M^m(Ln_2^{III}OH)_2(H_2O)_{10}As_4W_{40}O_{140}]^{(18-m)-}$ ($M = Ba, K, none, and Ln^{III} = La, Ce, Gd$) in which all four Ln^{III} occupy S2 sites and the coordination number of Ln^{III} is eight, M occupies site S1, and a little similar to $[Ln(Ln_2OH)(H_2O)_{10}As_4W_{40}O_{140}]^{20-}$ ($Ln^{III} = Ce, Nd, Sm, Gd$)⁸ in which two Ln^{III} occupy S2 sites, one same Ln occupies S1 site, and the coordination number of Ln^{III} is also nine. Based on the structure knowledge of the anion $\{La(H_2O)_5[Ni(H_2O)]_2As_4W_{40}O_{140}\}^{21-}$ and other related anions^{8,9} it can be concluded that site S1 only supplies four but not eight oxygens coordinating to Ln^{III} ion in the similar anions $[Ln^{III}As_4W_{40}O_{140}]^{25-}$ and $[LnM_2As_4W_{40}O_{140}]^{21-}$.⁶

Two Ni coordination situations are generally same, S2 site supplies four O_d coordinating to Ni, and another water molecule coordinates to Ni. The bonding lengths of four $Ni(1)-O_d$ [$O(134), O(20), O(135), O(19)$] are 0.192(3), 0.198(3), 0.208(3) and 0.207(3) nm, respectively, $Ni(1)-O_w$ [$O(141)$] is 0.188(3) nm, and the bonding lengths of four $Ni(2)-O_d$ [$O(52), O(53), O(138), O(139)$] are 0.200(3), 0.196(2), 0.191(3) and 0.202(3) nm, respectively, $Ni(2)-O_w$ [$O(142)$] is 0.188(3) nm, therefore the five coordination oxygens to Ni are definite. Owing to the $Ni(1)-As(1)$ and $Ni(2)-As$

(2) distance are respectively 0.2648(8) and 0.2617(8) nm, which are both greater than the usual covalent ones (from 0.23 to 0.24 nm) but considerably less than the non-bonded one (sum of the van der Waals radii of As and Ni is about 0.39 nm), only a weak interaction can be assumed, and considering that $Ni(1)$ and $Ni(2)$ are out of the plane formed by four-coordinate O_d 0.004 and 0.017 nm respectively toward the coordination water, much less than 0.03—0.06 nm in most five-coordinate pyramid complexes, and the direction for the lone pair of As is consistent with an interaction between Ni and As, a six-coordinate Ni appears more suitable than five.

All bridging tungsten atoms [$W(37)$ through $W(40)$] each has four O_b connecting with neighboring two AsW_9O_{33} subunits, and two O_d respectively coordinates to La and Ni cations, and the average $W-O_d$ bond length in $W-O_d-Ni$ is 0.178 nm, the average $W-O_d$ bond length in $W-O_d-La$ is 0.169 nm, and the difference is 0.009 nm, which means the reaction force between O_d-Ni is stronger than that between O_d-La , the former have more covalent ingredient than the later.

Table 2 lists possible hydrogen-bond distances between $N-O$. $N(1)$ and $N(2)$ locate near other two S2 sites not occupied by Ni^{II} , but not occupy the two S2 sites as two NH_4^+ in $(NH_4)_{23}[NH_4[Co(H_2O)]_2As_4W_{40}O_{140}] \cdot nH_2O$ ($18 \leq n \leq 20$).⁶ $N(1)$ [or $N(2)$] forms weak hydrogen bonds with neighboring eight O (five O_b and three O_w), the hydrogen bond lengths between $N-O$ are from 0.294 to 0.323 nm, other NH_4^+ distribute irregularly in or surrounding the anion. Most of lattice water molecules except five which indicate in analysis could not be located. It is possible that these unlocated water molecules forming hydrogen bonds with the anion and NH_4^+ are disordered.¹¹⁻¹⁴ In certain other types of heteropolyanion salts, for example, salts of $XW_{12}O_{40}^{n-}$ and $XM_{12}O_{40}^{n-}$, both the cation and lattice water sites may be disordered.¹⁵

IR spectra

Characteristic IR absorptions of the ligand $[NaAs_4W_{40}O_{140}]^{27-}$ and its three complexes are shown in Fig. 3.

Table 2 Hydrogen bond lengths between $N-O$ (nm)

$N(1)-O(85)$	0.304	$N(2)-O(147)$	0.323	$N(12)-O(52)$	0.278
$N(1)-O(86)$	0.319	$N(2)-O(141)$	0.288	$N(13)-O(48)$	0.310
$N(1)-O(70)$	0.294	$N(2)-O(142)$	0.301	$N(13)-O(93)$	0.318
$N(1)-O(135)$	0.301	$N(2)-O(134)$	0.304	$N(13)-O(41)$	0.263
$N(1)-O(138)$	0.322	$N(2)-O(139)$	0.317	$N(13)-O(47)$	0.323
$N(1)-O(147)$	0.323	$N(3)-O(15)$	0.322	$N(14)-O(127)$	0.321
$N(1)-O(142)$	0.314	$N(3)-O(30)$	0.299	$N(15)-O(127)$	0.296
$N(1)-O(141)$	0.305	$N(10)-O(149)$	0.263	$N(16)-O(124)$	0.270
$N(2)-O(118)$	0.309	$N(11)-O(72)$	0.297	$N(19)-O(48)$	0.266
$N(2)-O(119)$	0.306	$N(11)-O(62)$	0.294	$N(21)-O(103)$	0.269
$N(2)-O(103)$	0.299	$N(12)-O(92)$	0.292		

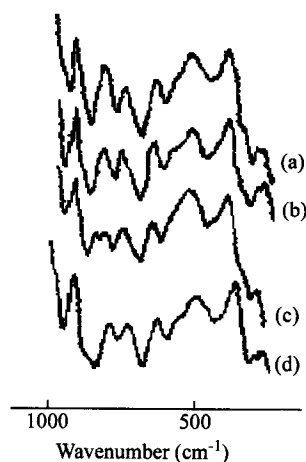


Fig. 3 IR spectra of several related heteropolyoxometalates. (a) $[\text{NaAs}_4\text{W}_{40}\text{O}_{140}]^{27-}$, (b) $[\text{Co}_2(\text{H}_2\text{O})_2\text{As}_4\text{W}_{40}\text{O}_{140}]^{24-}$, (c) $[\text{Ce}(\text{H}_2\text{O})_5\text{As}_4\text{W}_{40}\text{O}_{140}]^{25-}$, (d) $[\text{LaNi}_2(\text{H}_2\text{O})_7\text{As}_4\text{W}_{40}\text{O}_{140}]^{21-}$.

The following points can be drawn from the IR spectra:

- (i) The large cyclic ligand $[\text{NaAs}_4\text{W}_{40}\text{O}_{140}]^{27-}$ and its derivatives have 5 characteristic peaks [absorptions at *ca.* 950, 879, 797, 707 and 630 cm^{-1} respectively attributed to $\nu(\text{W}-\text{O}_d)$, $\nu(\text{O}_b-\text{W}-\text{O}_b)$, $\nu(\text{As}-\text{O})$, $\nu(\text{W}-\text{O}_d)$] among the region 960–620 cm^{-1} , and their relative absorption ratio are not changed in the ligand and complexes. (ii) When rare earth ion occupy S1 in the ligand, O_b characteristic peaks at about 879 cm^{-1} split into 2 peaks.

UV-vis spectra

UV spectra have two absorption bands, the lower energy bond at *ca.* 214 nm is attributed to the charge transfer of O_d-W , and the higher energy bonds at *ca.* 260 nm is attributed to that of $\text{O}_b/\text{O}_c-\text{W}$. Among visible region,

$(\text{NH}_4)_{21} \{ \text{La}(\text{H}_2\text{O})_5 [\text{Ni}(\text{H}_2\text{O})_2\text{As}_4\text{W}_{40}\text{O}_{140}] \cdot 53\text{H}_2\text{O}$ has three absorption bands, maximum absorption are respectively at 421, 712 and 809 nm, attributed d-d transitions of Ni^{II} .

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