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An Unprecedented Trinuclear Dawson Sandwich Complex with Internal Lacuna: Synthesis and ^{31}P NMR Spectroscopic Analysis of the Symmetrical $[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]^{17-}$ and $[CoNi_3(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ Anions

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The tri-nickel Dawson sandwich complex $[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]^{17-}$ has been obtained from $[P_2W_{15}O_{56}]^{12-}$ and Ni^{2+}. The X-ray crystal structure analysis is reported. This complex presents an unprecedented structure with the three transition metal ions in two external and one internal positions. Addition of 1 equiv. of Co^{2+} in the solution of $\{NaNi_3P_4W_{30}\}$ leads to the formation of the "saturated" mixed-metal sandwich complex $[CoNi_3(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$, which is characterized by microanalysis, IR and ^{31}P NMR spectroscopy. The electrochemical behaviour of $\{NaNi_3P_4W_{30}\}$ and $\{CoNi_3P_4W_{30}\}$ are also reported.

Introduction

Polyoxometalates (POMs) constitute a unique class of inorganic compounds due to the structural variety as well as interesting and often unexpected properties in fields as diverse as magnetochemistry, medicine, and catalysis.[1–4]

Since the first report of the synthesis of sandwich polyoxometalates derived from the trivacant anion α-$[P_2W_{15}O_{56}]^{12-}$ (abbreviated $\{P_2W_{15}\}$) by Finke et al.,[5] they have received increased attention because of their physicochemical and catalytical properties. It is well known that the reaction of the trivacant anion α-$[P_2W_{15}O_{56}]^{12-}$ with transition metal cations ($M^{n+} = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$, and Cd^{2+}) yields derived complexes $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{(24-4n)-}$ (abbreviated $\{M_4P_4W_{30}\}$) where a sheet of four M atoms is sandwiched between two $\{P_2W_{15}\}$ subunits.[6]

Lacunary di- and trinuclear sandwich complexes $[Na_2M_2(H_2O)_2(P_2W_{15}O_{56})_2]^{n-}$ and $[NaM_3(H_2O)_2(P_2W_{15}O_{56})_2]^{m-}$ ($M^{2+} = Mn^{2+}$ or Co^{2+}, $n = 18$, $m = 17$ and $M^{3+} = Fe^{3+}$, $n = 16$, $m = 14$)[7–9] have been also prepared. Actually, the structures of these trimetallic complexes may be considered as resulting from the fusion of one $\{M_3P_2W_{15}\}$ and one "lacunary" $\{M_2P_2W_{15}\}$ units with the lacuna in "external" position occupied by a Na^+ cation.

The present work reports on the synthesis and the full characterization, by FTIR and ^{31}P NMR spectroscopy and by X-ray structure analysis, of the trinickel derivative $[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]^{17-}$ which presents an unprecedented type of structure with the Na^+ cation located in an "internal" site.

We report also on the preparation of the "saturated" $\{CoNi_3P_4W_{30}\}$. The electrochemical behaviour of $\{NaNi_3P_4W_{30}\}$ and $\{CoNi_3P_4W_{30}\}$ are also reported.

Results and Discussion

Synthesis

The trinickel species $[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]^{17-}$ ($\{NaNi_3P_4W_{30}\}$) is readily formed by reaction of the trivacant anion $\{P_2W_{15}\}$ with Ni^{2+}. The sodium salt of $\{NaNi_3P_4W_{30}\}$ is obtained by crystallisation from the synthetic solution. In order to favour the formation of the "lacunary" species, it is necessary to operate with default of Ni^{2+}, that is about 1.2 equiv. Ni^{2+} per $\{P_2W_{15}\}$ instead of 1.5 as required [see Equation (1)].

$$2\,[P_2W_{15}O_{56}]^{12-} + 3\,Ni^{2+} + Na^+ + 2\,H_2O \rightarrow [NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]^{17-} \quad (1)$$

Actually, as already observed in the case of the cobalt or the manganese sandwich complexes,[8a,8d] using 1.5 equiv. of

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Ni^{2+} per $\{P_2W_{15}\}$ leads to a mixture of "lacunary" $\{NaNi_3P_4W_{30}\}$ and "saturated" $\{Ni_4P_4W_{30}\}$ species identified by ^{31}P solution NMR; these two species can not be isolated separately from the solution because of too close solubility.

According to microanalysis data, the Ni/P/W ratio are 3:4:30 and these data are in full agreement with the formula $Na_{17}[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]$.

Spectroscopic Characterization

^{31}P NMR Characterization

The ^{31}P NMR spectra of the sandwich Dawson derivatives $\{NaNi_3P_4W_{30}\}$ and $\{Ni_4P_4W_{30}\}$ are presented in Figure 1, and all data are reported in Table 1.

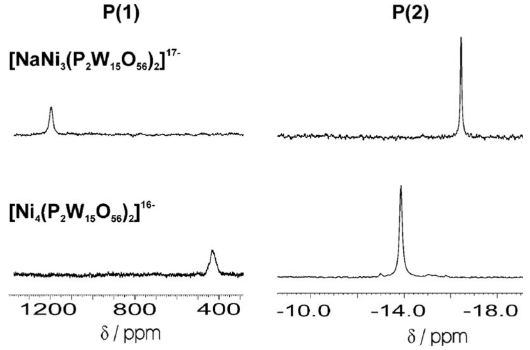

Figure 1. 121.5 MHz ^{31}P NMR spectra of $\{NaNi_3P_4W_{30}\}$ and of the parent compound $\{Ni_4P_4W_{30}\}$ in unbuffered D_2O/H_2O (1:1) solutions. Concentration: 0.005 mol L^{-1}. Note the different abscissa scale for the two regions.

Table 1. ^{31}P NMR spectroscopic data of the monolacunar trinickel, trimanganese and tricobalt sandwich species and of the parent saturated anions.[a]

Compounds	P(1)[b]		P(2)[b]	
	δ[c]	$\Delta\nu_{1/2}$[d]	δ[c]	$\Delta\nu_{1/2}$[d]
$\{NaNi_3P_4W_{30}\}$	+1223	2400	–16.4	7
$\{Ni_4P_4W_{30}\}$	+460	3400	–14.2	15
$\{CoNi_3P_4W_{30}\}$	+1115	550	–9.4	5
α_2-$[NiP_2W_{17}O_{61}]^{8-}$	+226.2[h]	750[h]	–13.46[h]	19[h]
$\{NaCo_3P_4W_{30}\}$	+1125[f]	450[f]	–9.3[f]	10[f]
	+1673[f]	450[f]	+22.0[f]	10[f]
$\{Co_4P_4W_{30}\}$	+1483[f]	420	+9.9[f]	20
$\{NaMn_3P_4W_{30}\}$	–[e]		–12.3[g]	220[g]
$\{Mn_4P_4W_{30}\}$	–[e]		–11.7[g]	180[g]

[a] Unbuffered D_2O/H_2O (1:1) solutions. Concentration: 0.005 mol L^{-1}. [b] P(1) and P(2) in the PW_6 and PW_9 subunits, respectively. [c] In ppm with respect to 85% H_3PO_4. [d] In Hz. [e] Not observed. [f] From ref.[8a]. [g] From ref.[8d]. [h] From ref.[11].

The ^{31}P NMR solution spectrum of $\{NaNi_3P_4W_{30}\}$ exhibits only two lines, at +1223 ppm ($\Delta\nu_{1/2}$ = 2400 Hz) for the two P(1) nuclei close to the Ni sheet and –16.4 ppm ($\Delta\nu_{1/2}$ = 7 Hz) for the two more remote P(2) nuclei.[10]

This clean spectrum is however distinct from that of the monosubstituted Dawson derivative α_2-$[NiP_2W_{17}O_{61}]^{8-}$ which could have result from the degradation of $[P_2W_{15}O_{56}]^{12-}$ and subsequent complexation with Ni^{2+} (see Table 1).

The spectrum of the trinickel compound differs also significantly from that of the tetranickel species (Figure 1) with the P(2) signal slightly shifted to low frequency ($\Delta\delta$ = –2.2 ppm) and the P(1) signal strongly shifted to high frequency ($\Delta\delta$ = +763 ppm).

Such a simple spectrum for a trimetallic sandwich complex is rather unexpected as for the analogous tricobalt anion $[NaCo_3(H_2O)_2(P_2W_{15}O_{56})_2]^{17-}$ ($\{NaCo_3P_4W_{30}\}$) four ^{31}P NMR signals (two for P(1) and two for P(2)) are observed (see Table 1).[8a,8c]

Then, contrary to $\{NaCo_3P_4W_{30}\}$ the two $\{P_2W_{15}\}$ moieties are equivalent in $\{NaNi_3P_4W_{30}\}$.

In the case of $\{NaCo_3P_4W_{30}\}$ the structure is built up from the fusion of one $\{P_2W_{15}Co_3\}$ and one $\{P_2W_{15}NaCo_2\}$ sharing two internal {Co} which results in C_s symmetry.[12] On the contrary, $\{NaNi_3P_4W_{30}\}$ anion should result from the fusion of 2 equiv. $\{P_2W_{15}NaNi_2\}$ sharing one {Na} and one {Ni} leading to C_2 symmetry.

The solid state ^{31}P MAS NMR spectrum is also in agreement with the virtual C_2 symmetry of $\{NaNi_3P_4W_{30}\}$. The spectrum exhibits two well-separated spinning side-band patterns with isotropic signals at ca. +1100 ppm ($\Delta\nu_{1/2}$ = 16 kHz) for the two P(1) nuclei and at –17 ppm ($\Delta\nu_{1/2}$ = 150 Hz) for the P(2) nuclei, respectively (Figure 2).[13]

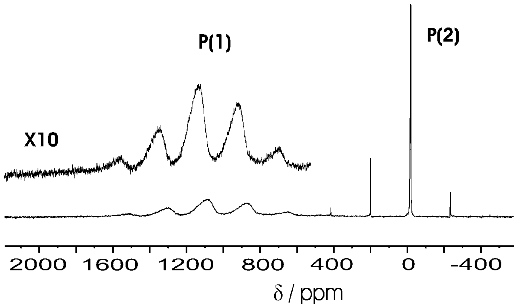

Figure 2. 161.9 MHz ^{31}P echo MAS solid-state NMR spectrum of $Na_{17}[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]$ recorded at 35 kHz.

This result is also at variance with the tricobalt sandwich compound which presents four signals in the ^{31}P MAS NMR spectrum.[8c]

From these ^{31}P NMR investigations, it should be concluded that the trinickel species exhibit the same anionic structure in the solid state and in solution where it is relatively stable.

IR Characterization

According to the close structures of $\{NaNi_3P_4W_{30}\}$ and $\{Ni_4P_4W_{30}\}$, their IR spectra are very similar (Figure S1); indeed they differ only by slight shifts in particular in the P–O stretching range between 1200 and 1000 cm^{-1}.

The relationships between infrared spectra of sandwich complexes and of their precursors have been already discussed in details in our previous papers.[7c,8a,8d,14] In tungstophosphates, the bands characteristic of the PO_4 stretch are located at relatively high wavenumbers ($\tilde{\nu} > 1000$ cm^{-1})

outside the range of the vibrational modes of the POM framework.[15] Three P–O bands are observed nearly at the same position for the two nickel compounds, at ca. 1084 cm^{-1} (strong), 1011 cm^{-1} (weak) and 998 cm^{-1} (weak). They are assigned to the PO_4 tetrahedron in the unperturbed PW_9 subunit.[15c] The additional P–O band observed in between may be assigned to the phosphate close to the metallic sheet as already noticed for cobalt and mixed cobalt–iron sandwich complexes.[8a,14] In the case of $\{NaCo_3P_4W_{30}\}$, there are two distinct bands at 1044 and 1035 cm^{-1} which were assigned to the "saturated" PW_6Co_3 and the "unsaturated" PW_6Co_2 moieties, respectively.[8a]

For the trinickel complex $\{NaNi_3P_4W_{30}\}$, however, the observation of a unique band (1037 cm^{-1}) again agrees with the equivalence of the two $\{P_2W_{15}\}$ moieties. It should be assigned to a PO_4 tetrahedron in unsaturated $\{P_2W_{15}NaNi_2\}$. This assignment is also consistent by the shift to low wavenumbers, with respect to $\{Ni_4P_4W_{30}\}$ (1058 cm^{-1}) according to the general trend observed on going from saturated to lacunary species.[16]

X-ray Structure Determination of $Na_{17}[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]\cdot 42H_2O$

Crystals of the sodium salt of $[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]^{17-}$ suitable for X-ray analysis were grown from their aqueous solutions at natural pH.[17]

Analysis of the X-ray structure of $[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]^{17-}$ shows that the Na^+ cation is located in an "internal" site (contrary to the tricobalt[12] or trimanganese[18] anion where Na^+ cation is always located in an "external" site), and it is surrounded by six oxygen atoms of the two $\{P_2W_{15}\}$ units (Figure 3). Actually, the sandwich anion is located on an inversion centre which exchanges not only the two "external" Ni^{2+} but also the two "internal" sites statistically occupied by Na^+ and Ni^{2+}. However, the virtual symmetry of the anion $\{NaNi_3P_4W_{30}\}$ is C_2 instead of C_s for the other $\{NaM_3P_4W_{30}\}$ complexes reported until now. The lacuna position in $\{NaNi_3P_4W_{30}\}$ is rather unusual as in the other lacunary sandwich compounds the sodium cation is always located in the "external" site where it exchanges easily with other alkaline or transition metal cations.[7c,8a] The trinickel complex may therefore be described as resulting from the fusion of two $\{Ni_2P_2W_{15}\}$ units which exchange through a C_2 axis (Figure 3). Thus, at variance with the triiron, tricobalt and trimanganese derivatives, the two $\{P_2W_{15}\}$ moieties of $\{NaNi_3P_4W_{30}\}$ are therefore equivalent. The metrical parameters for these $\{P_2W_{15}\}$ units are in the usual range for tungsten POMs. The external Ni cation lies in the centre of a quasi regular NiO_6 octahedron with Ni–O distances ranging from 2.05 to 2.08 Å; the MO_6 internal octahedron is slightly more distorted with larger M–O distances from 2.17 to 2.23 Å ($M = 1/2\ Na^+ + 1/2\ Ni^{2+}$).

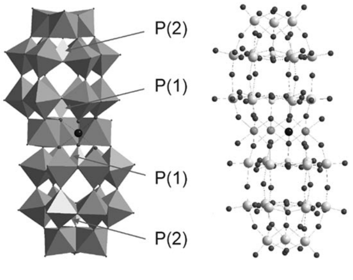

Figure 3. Polyhedral and ball-and-stick representations of $\{NaNi_3P_4W_{30}\}$.

Reactivity

The trinickel complex is stable in aqueous solution at relatively low pH. Moreover, according to ^{31}P NMR investigations, it adds rapidly first-row transition metal cations to form mixed saturated sandwich complexes $\{MNi_3P_4W_{30}\}$. For example, progressive addition of Co^{2+} to the solution of $\{NaNi_3P_4W_{30}\}$ shows the appearance of two new resonances (Figure 4). For 1 equiv. of Co^{2+} the lines from $\{NaNi_3P_4W_{30}\}$ disappear which shows that the addition of Co^{2+} to the trinickel anion is quantitative. The resulting spectrum consists of two lines at ca. +1115 ppm ($\Delta\nu_{1/2}$ = 550 kHz) for the two P(1) nuclei and at –9.4 ppm ($\Delta\nu_{1/2}$ = 5 Hz) for the more remote P(2) nuclei, respectively (Figure 4). This spectrum is also compatible with a symmetrical structure where the cobalt atom must have replaced the Na^+ cation in an internal position (Figure S2).

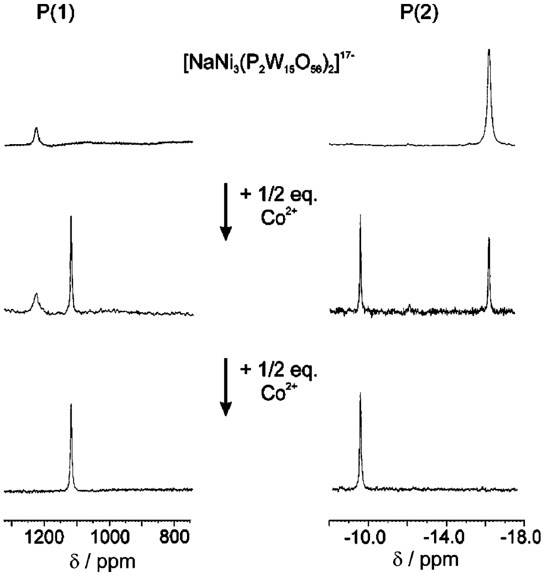

Figure 4. 121.5 MHz ^{31}P NMR study of the reactivity of $\{NaNi_3P_4W_{30}\}$ + two times 0.5 equiv. Co^{2+}: formation of the saturated sandwich complex $\{CoNi_3P_4W_{30}\}$ in unbuffered solutions in D_2O/H_2O (1:1). Concentration is 0.05 M in D_2O/H_2O (1:1). Left part: region of the P(1); Right part: region of the P(2). Note the different abscissa scale for the two regions.

The overall IR spectra of $\{CoNi_3P_4W_{30}\}$ and $\{Ni_4P_4W_{30}\}$ are similar, which indicates a structural similarity.

Crystallization of $\{CoNi_3P_4W_{30}\}$ from the solution further requires the addition of NaCl in order to lower the solubility by ionic strength and common cation effects. In this condition, in order to obtain $\{CoNi_3P_4W_{30}\}$ free from $\{NaNi_3P_4W_{30}\}$, it is necessary to use a fourfold excess of Co^{2+} to displace the Na^+ cation from the central $NaNi_3O_{14}(H_2O)_2$ cluster. Actually, by using less than four equivalents of Co^{2+}, a mixture of $\{CoNi_3P_4W_{30}\}$ and $\{NaNi_3P_4W_{30}\}$ is always obtained.

Analysis of the crystallized solid confirms the Co/Ni/P/W ratio as 1:3:4:30 in full agreement with the formula $Na_{16}[CoNi_3(H_2O)_2(P_2W_{15}O_{56})_2]$.

Unfortunatly, the crystals of $Na_{16}[CoNi_3(H_2O)_2(P_2W_{15}O_{56})_2]$ were not suitable for crystallographic X-ray structure determination.

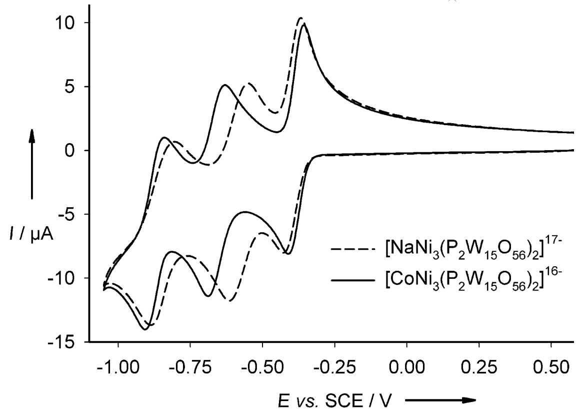

Figure 6. Cyclic voltammograms of 0.5 mmol L^{-1} $\{CoNi_3P_4W_{30}\}$ (full line) and of $\{NaNi_3P_4W_{30}\}$ (dotted line) in 0.5 mol L^{-1} $Na_2SO_4 + H_2SO_4$ solution (pH 3.00). Scan rate 20 mV s^{-1}.

Electrochemistry

The electrochemical behaviour of complexes $\{NaNi_3P_4W_{30}\}$ and $\{CoNi_3P_4W_{30}\}$ was studied in aqueous solution (pH 3.0) by cyclic voltammetry (CV) and compared to that of $\{Ni_4P_4W_{30}\}$.[7c] All electrochemical data are gathered in Table 2, and typical cyclic voltammograms are presented in Figures 5 and 6.

Table 2. Electrochemical data of the sandwich complexes of formula $\{NaNi_3P_4W_{30}\}$ and $\{Ni_4P_4W_{30}\}$.[a]

Compound	W centres		
$\{NaNi_3P_4W_{30}\}$	–0.40 (4e, 60)	–0.58 (4e, 64)	–0.85 (4e, 80)
$\{CoNi_3P_4W_{30}\}$	–0.36 (4e, 38)	–0.63 (4e, 66)	–0.87 (4e, 87)
$\{Ni_4P_4W_{30}\}$	–0.49 (4e, 69)	–0.55 (4e, 69)	–0.83 (4e, 144)

[a] All redox potentials $E°'$, approximated by $(E_p^a + E_p^c)/2$ for the reversible steps, are given in V vs. SCE as obtained from cyclic voltammetry (v = 20 mV s^{-1}) in Na_2SO_4 0.5 mol L^{-1} + H_2SO_4 (pH 3.0). In parentheses: number of electrons exchanged, n; $\Delta E_p = |E_p^a - E_p^c|$ in mV.

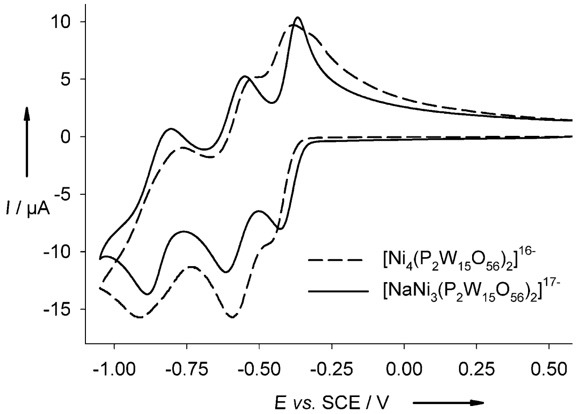

Figure 5. Cyclic voltammograms of 0.5 mmol L^{-1} $\{NaNi_3P_4W_{30}\}$ (full line) and of $\{Ni_4P_4W_{30}\}$ (dotted line) in 0.5 mol L^{-1} $Na_2SO_4 + H_2SO_4$ solution (pH 3.00). Scan rate 20 mV s^{-1}.

These complexes exhibit three successive reduction processes involving the W centres. For these three couples, the cathodic (and anodic) peak currents are almost proportional to the square root of the scan rate up to 250 mV s^{-1}, which indicates that the reduction (and oxidation) processes are both diffusion-controlled.

For all species, controlled-potential coulometry at –0.45 V shows that the solution turns deep blue and consumes between 4.1 and 4.2 electrons per sandwich complex. At –0.70 V, the number of exchanged electrons is between 8.2 and 8.4. This shows that both the first and the second processes involve four electrons.

The voltammograms of $\{NaNi_3P_4W_{30}\}$ are very similar to those of $\{Ni_4P_4W_{30}\}$ (Figure 5) as expected owing to the similarity of overall structures (Table 2).

There are still some differences: by comparison with $\{Ni_4P_4W_{30}\}$, the first tungsten centered ($W^{VI/V}$) wave of $\{NaNi_3P_4W_{30}\}$ is shifted to more positive potential (90 mV) while the two other $W^{VI/V}$ waves appear at slightly more negative potentials (30 mV and 20 mV respectively, see Table 2). The shift observed for the first wave is rather surprising: actually according to the global charges of the two complexes, it is expected that $[Ni_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ should be more easily reduced than $[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]^{17-}$.[19] Completely reverse experimental behaviour might be tentatively explained by the formation of ion pairs and/or protonation of the anions, resulting in the inversion of the charge order of the species travelling to the electrode.

An inverse trend is observed when comparing the voltammograms of the monolacunary $\{NaNi_3P_4W_{30}\}$ and saturated complex $\{CoNi_3P_4W_{30}\}$ (Figure 6 and Table 2). By comparison with $\{CoNi_3P_4W_{30}\}$, the first tungsten centered ($W^{VI/V}$) wave of $\{NaNi_3P_4W_{30}\}$ is shifted to more negative potential (40 mV) while the two other $W^{VI/V}$ waves appear at slightly more positive potentials (50 mV and 20 mV respectively, see Table 2).

In recent report, for $[P_2W_{18}O_{62}]^{6-}$ and its molybdenum analog $[P_2Mo_{18}O_{62}]^{6-}$ Dawson compounds, both electrochemistry experiments[20] and theoretical calculations[21] support the hypothetis that the first reduction process involves tungsten or molybdenum on the equatorial belts.

For the present sandwich complexes there are two inequivalent belts that is the crowns close to the central metallic sheets and those in PW_9 moieties. Because the second reduction wave is highly affected by the presence of cobalt, it could tentatively be assigned to the belt close to the central $\{NaNi_3\}$ or $\{CoNi_3\}$ cluster while the first reduction wave should correspond to a process occurring on the more remote belt.

Conclusions

In conclusion, the “monolacunar” trinickel sandwich complex $[NaNi^{II}_3(H_2O)_2(P_2W_{15}O_{56})_2]^{17-}$ $\{NaNi_3P_4W_{30}\}$ was obtained in isomerically pure form where the Na^+ cation is located in an “internal” site. Addition of Co^{2+} in the solution of $\{NaNi_3P_4W_{30}\}$ leads to the formation of the “saturated” mixed-metal sandwich complex $[CoNi_3(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ which was fully characterized by ^{31}P NMR spectroscopy. The electrochemical behaviour of $\{NaNi_3P_4W_{30}\}$ was investigated and compared with $\{CoNi_3P_4W_{30}\}$. Both compounds exhibit three couples of W-centered reversible reduction processes.

These results open the route to the preparation of mixed-metal sandwich complexes $\{MNi_3P_4W_{30}\}$, where we expect to modulate the electrochemical as well as electrocatalytic properties with the nature of M.

Experimental Section

General: Most common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification.

Preparation of Compounds: The tetranuclear complex $[Ni_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$, $\{Ni_4P_4W_{30}\}$ was prepared as described previously.[7c]

Synthesis of $\{NaNi_3P_4W_{30}\}$: $Na_{17}[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]$ ($\{NaNi_3P_4W_{30}\}$) was prepared as follows: $NiCl_2{\cdot}6H_2O$ (1.00 g; 4 mmol) was dissolved in 360 mL of a 0.4 mol L^{-1} NaCl aqueous solution. α-$[Na_{12}P_2W_{15}O_{56}]{\cdot}24H_2O$ (15.00 g; 3.4 mmol) was then added with vigorous stirring. The solution was heated at 60 °C until complete dissolution (≈ 40 min). The solution was filtered hot and was left cooling in air. The filtrate was left in open vessel at 4 °C, and pale yellow crystals ($\{NaNi_3P_4W_{30}\}$) appear after ca. 4 d; they were collected on a sintered glass frit after 30 d and dried in air (yield 1.98 g, 0.226 mmol, 17% calculated from Ni). $Na_{18}Ni_3O_{112}P_4W_{30}{\cdot}42H_2O$ (8777.92): calcd. Ni 1.98, Na 4.71, P 1.41, W 62.87, H_2O 8.62; found Ni 2.01, Na 4.67, P 1.39, W 62.31, 8.62 H_2O. ^{31}P NMR (121.5 MHz, D_2O/H_2O (1:1)): $\delta = +1223$ ppm ($\Delta\nu_{1/2} = 2400$ Hz) and $\delta = -16.4$ ppm ($\Delta\nu_{1/2} = 7$ Hz). IR (KBr): $\tilde{\nu} = 1084$ (s), 1037 (s), 1011 (w), 998 (w), 945 (s), 933 (s), 918 (s), 890 (s), 797 (s), 757 (s), 735 (s) cm^{-1}.

Synthesis of $\{CoNi_3P_4W_{30}\}$: $Na_{17}[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]$ ($\{NaNi_3P_4W_{30}\}$) (0.50 g; 0.057 mmol) was dissolved in 50 mL of water. By addition of $Co(NO_3)_2{\cdot}6H_2O$ (66 mg; 0.227 mmol) with vigorous stirring, the solution turned immediately from yellow to brown. The resulting neutral solution (pH ≈ 6.5) was stirred for 2 h after which 1.46 g of NaCl was added. The solution was left to evaporate in air in open vessel and a greenish brown precipitate appeared after ca. 1 d; it was collected on a sintered glass-frit (porosity 4) after 2 d and dried in air (yield 0.43 g; 85%). $CoNi_3Na_{16}P_4W_{30}O_{112}{\cdot}46H_2O$ (8862.87): calcd. Co 0.66, Ni 1.99, Na 4.15, P 1.40, W 62.23, H_2O 9.35; found Co 0.65, Ni 1.99, Na 4.12, P 1.38, W 62.11, H_2O 9.35. ^{31}P NMR (121.5 MHz, D_2O/H_2O (1:1)): $\delta = +1115$ ppm ($\Delta\nu_{1/2} = 550$ Hz) and $\delta = -9.4$ ppm ($\Delta\nu_{1/2} = 5$ Hz). IR (KBr): $\tilde{\nu} = 1083$ (s), 1049 (w), 1010 (w), 1000 (w), 936 (s), 912 (s), 883 (s), 819 (s), 735 (s) cm^{-1}.

Crystal Data: $H_{108}Na_{18}Ni_3O_{166}P_4W_{30}$, *F*w = 8994.19, an air- and/or moisture-sensitive crystal ($0.16 \times 0.12 \times 0.06$ mm^3) was rapidly selected, mounted onto a glass fiber, and transferred into a cold nitrogen gas stream. Triclinic, space group $P\bar{1}$, $a = 12.5042(16)$, $b = 13.1074(8)$, $c = 24.600(3)$ Å, $\alpha = 87.202(9)$, $\beta = 75.545(14)$, $\gamma = 73.720(7)°$, $V = 3746.7(8)$ Å^3, $T = 250$ K, $2\theta_{max} = 30°$, $Z = 1$, $\rho_{calcd} = 3.986$ g cm^{-3}, $\mu = 23.511$ mm^{-1}, $F(000) = 3998$, 58930 reflections collected, 25831 unique [$R_{int} = 0.0526$], final R indices [$I > 2\sigma(I)$] $R_1 = 0.0609$, $wR_2 = 0.1076$, $\rho_{max/min} = +2.938/-2.924$ e Å^{-3}. The occupation factor for Ni^{2+} on the disordered site Ni^{2+}/Na^+ was refined to a value 0.485(16) and then fixed at 0.5. The present chemical formula $Na_{17}[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]{\cdot}52H_2O$, differs from the one given by the elemental analysis because of a higher number of identified water molecules of crystallization.

Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de], on quoting the depository number CSD-419428.

NMR and IR Measurements: ^{31}P NMR spectra were recorded in 5 mm o.d. tubes on a Bruker AC 300 or a Bruker AvanceII 300 spectrometer operating at 121.5 MHz. The NMR spectra were obtained at 300 K on 0.005–0.05 M solutions in D_2O/H_2O (1:1) and were referenced to external 85% H_3PO_4 (IUPAC convention) by the substitution method. The ^{31}P chemical shift are pH-dependent and some slight differences may be observed between the synthetic solution and those obtained after redissolution of the solid samples. IR spectra were recorded on a Bio-Rad FTS 165 FTIR spectrophotometer on KBr pellets.

Electrochemical Experiments: Water used for all electrochemical measurements was obtained by passing through a Milli-RO_4 unit and subsequently through a Millipore Q water purification set. H_2SO_4 solutions and solid Na_2SO_4 were commercial products (Prolabo). The electrolyte was made up from 0.5 M Na_2SO_4 aqueous solution and its pH was precisely adjusted to 3.5 by addition of 0.5 M (H_2SO_4 + Na_2SO_4) aqueous solution. The solutions were deaerated thoroughly for at least 30 min by bubbling argon (Ar-U from Air Liquide) and kept under argon atmosphere during the whole experiment.

The glassy carbon working electrode (Tokai, Japan) had a diameter of 3 mm. The counter electrode was platinum gauze of large surface area. Potentials were measured on an EG&G 273A potentiostat and quoted against a saturated calomel electrode (SCE). All experiments were carried out at room temperature.

Controlled potential coulometry experiments were conducted by using a large-surface (6 cm^2) glassy carbon plate under continuous argon bubbling and strirring.

Analyses: Elemental analyses were performed by the Service Central d’Analyse du CNRS, Vernaison (France). The water content was determined by thermogravimetric analysis.

Supporting Information (see also the footnote on the first page of this article): Comparison of the IR spectra of $\{NaNi_3P_4W_{30}\}$,

{$Ni_4P_4W_{30}$}, α-[$P_2W_{15}O_{56}$]$^{12-}$ and α-[$P_2W_{18}O_{62}$]$^{6-}$ (Figure S1). Schematic representation of the formation of {$CoNi_3P_4W_{30}$} from {$NaNi_3P_4W_{30}$} (Figure S2).

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[18] Preliminary crystallographic data for $Na_{17}[NaMn_3(H_2O)_2(P_2W_{15}O_{56})_2]\cdot 43H_2O$: triclinic space group $P\bar{1}$ with a = 12.9979(19) Å, b = 15.2232(26) Å, c = 22.8211(36) Å, α = 88.66(2), β = 75.01(2), γ = 66.114(9)°, V = 3971(1) Å^3. The {$NaMn_3P_4W_{30}$} presents a ββ connectivity. The complete crystallographic report will be published later.
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