SYNTHESIS AND CHARACTERIZATION OF POLYOXOMETALLATES

$Na_{18}[(\alpha_2P_2W_{17}O_{61})_2M],nH_2O$(M = Co^{2+}, Ni^{2+}, Cu^{2+})

Nawel Nadji[1], *Robila Belghiche*[1*], *Mostefa Abbessi*[1]

Département de Génie des procédés, Faculté des Sciences de l'Ingénieur

Université d' Annaba, BP 12,23000 Annaba,

E-mail: robuniv@yahoo.fr Tel/fax : 038 87 65 60

ABSTRACT

Three novel polyoxometallates Na_{18} $[M(\alpha_2\text{-}P_2W_{17}O_{61})_2]$,(M = Co, Ni, Cu) have been synthesized from the Dawson lacunaria precursor $Na_{10}[\alpha_2P_2W_{17}O_{61}].20H_2O$ and characterized by elementary analysis, UV, IR and ^{31}P NMR spectroscopy, and by an electrochemical method. The compounds consist of two $[\alpha_2P_2W_{17}O_{61}]^{10-}$ Dawson moieties linked through one metallic ion. The ^{31}P NMR spectra exhibit one line for the three compounds at -12.991, -12.985 and -13.004 ppm respectively.

INTRODUCTION

Polyoxometalates (POMs) are metal-oxygen cluster species with versatile structures and interesting properties in medicine (Holclaijtner-Antunovic, 2004), catalysis (Ryul Park, 2010), and materials science (Coronado, 1998).

The ability to modify the redox and chemical properties of heteropolyanions by replacing one or more elements renders them particularly interesting in catalysis. The Dawson $[P_2W_{18}O_{62}]^{6-}$ polyoxoanion may be hydrolyzed into lacunary species containing one α_2-$[P_2W_{17}O_{61}]^{10-}$, or more lacuna (Contant, 1981; Massart, 1977).

It is reported by Nebebech and al the synthesis and characterization of Dawson sandwich complexes $[Ce\{X(H_4)W_{17}O_{61}\}_2]^{19-}$ (X = P, As) (Belai, 2005) . Ostuni and al have described the synthesis of three other sandwiches type from monolacunary Dawson species $K_{16}[U(\alpha_2\text{-}P_2W_{17}O_{61})_2].22H_2O$, $K_{16}[Th(\alpha_2\text{-}P_2W_{17}O_{61})_2].H_2O$ and $(NH_4)_{17}[Ce(\alpha_2\text{-}P_2W_{17}O_{61})_2].H_2O$(Ostuni, 2003)

The present study concerns the synthesis and spectroscopic characterization (IR, UV, RMN^{31}P) of the Dawson-derived sandwich-type complexes $Na_{18}[(\alpha_2P_2W_{17}O_{61})_2M].nH_2O$(M = Co^{2+}, Ni^{2+}, Cu^{2+}). They have been obtained by the dissolution of solid Na_{10} $[\alpha_2P_2W_{17}O_{61}].20H_2O$ in an aqueous solution at pH ≤3 with metallic ions. An electrochemical characterization was carried out by cyclic voltammetry in order to study the redox comportment of the obtained compounds and confirm their structure.

EXPERIMENTAL

Synthesis of heteropolyanions

The heteropolyanion $K_6P_2W_{18}O_{62}$ et α_2-$K_{10}P_2W_{17}O_{61}$ were synthesized according to the published procedures (Massart, 1977; Contant, 1977) and their purity was confirmed by infrared spectroscopy and ^{31}P NMR spectroscopy.

$Na_{18}[(\alpha_2P_2W_{17}O_{61})_2M],nH_2O$: 1.25 mmole of $M(NO_3)_2.nH_2O$ (M = Co^{2+}, Ni^{2+}, Cu^{2+}) was dissolved in 50 ml of 1M NaCl solution. Solid α_2-$K_{10}P_2W_{17}O_{61}$ (2.5 mmole) was then added in small portions and dissolved under vigorous stirring. The solution was heated between 40 and 60 °C until complete dissolution of α_2-$K_{10}P_2W_{17}O_{61}$, then filtered hot and the filtrate was left to stand in air for about two week at room temperature. A crystalline powder was recuperated for each compound.

M = Co^{2+}; n = 17; IR (KBr pellet, cm^{-1}): 1083(s), 1065(w), 1013 (w), 939(s), 912(s). ^{31}PNMR: δ =13.004 ppm. Anal.Calcd.(found): P 1.36(1.33); W 68.66(67); Co 0.65(0.58); Na 4.54(4.30)

M = Ni^{2+}; n = 9; IR (KBr pellet, cm^{-1}): 1084(s), 1013(w), 959(s), 914(s). ^{31}PNMR: δ =-12.991 ppm. Anal. Calcd.(found): P 1.38(1.31); W 68.91(68.10); Ni 0.66(0.60); Na 4.63(4.49).

M = Cu^{2+} $^{+}$; n = 15; IR (KBr pellet, cm^{-1}): 1084(s), 1060(w), 1016(w), 941(s), 918(s). ^{31}P NMR: δ =-12.985ppm. Anal. Calcd.(found): P

1.37(1.34); W 68.90(67.95); Cu 0.7(0.66); Na 4.56(4.44).

Spectroscopic characterization

The IR spectra were recorded on KBr pellets using a spectrophotometer shimadzu FTIR-8400s. The UV-Visible spectra were recorded on spectrophotometer Jenway 6705 UV/Vis in a quartz tank.

^{31}P NMR spectra were recorded on Bruker 400 MHz Ascend. The ^{31}P shifts were measured for 10^{-3}M solution of polyanions in D_2O solution and were referenced to H_3PO_4 85%.

Cyclic voltammetry analysis

The electrochemical study was carried out by a cyclic voltammetry on PGZ 100 voltalab controlled by voltamaster 4 software. The experiments were performed in a cell of 20 ml at pH 3 (0.5 M Na_2SO_4 + H_2SO_4) with a concentration $4x10^{-4}$ of polyoxometallate. The working electrode used was glassy carbon (GC), a saturated calomel reference electrode as reference electrode (SCE) and a platinum wire is used as auxiliary electrode. All experimental solutions were deaerated thoroughly by bubbling pure N_2 through the solutions for 10 min. all cyclic voltammograms were recorded at a scan rate of 20 mVs^{-1}. All experiments were performed at room temperature.

RESULTS AND DISCUSSION

The precursor tungstophosphate $\alpha_2K_{10}P_2W_{17}O_{61}$, $20H_2O$, is monolacunary specie of Dawson $K_6P_2W_{18}O_{62}$ anion from which one of the cap tungsten octaedra has been removed. The $Na_{18}[(\alpha_2P_2W_{17}O_{61})_2M],nH_2O$ compounds were obtained in acid middle of NaCl 1 M, HCl 0.1M solution at pH ≤3 with stœchiometric amount (1:2) of M^{2+} ions (M = Co, Ni, Cu) and $\alpha_2K_{10}P_2W_{17}O_{61}$, $20H_2O$ at about 60°C; while the$[\alpha_2P_2W_{17}O_{61}M]^{8-}$ compounds were synthesized from 1:1 ratio of M^{2+} and $\alpha_2K_{10}P_2W_{17}O_{61}$, $20H_2O$ at pH between 6 and 7 and ambient temperature(Lyon, 1991). The metallic cations of $Na_{18}[(\alpha_2P_2W_{17}O_{61})_2M],nH_2O$ are incorporate between two monolacunary species. The compounds belong to the known class of sandwich type structures.

The UV electronic spectra of Cu- and Co-derivatives in aqueous solution (Fig.1) are nearly similar and exhibit two characteristic bands at 210 and 273 nm. The spectrum of Ni-derivative exhibits a slight shift of the first band to 215 nm.

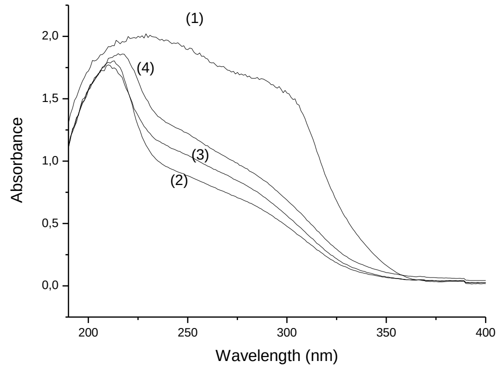


Fig. 1: UV spectra of spectra of $\alpha_2P_2W_{17}$ (1), Cu- (2), Co- (3) and Ni-derivatives (4) species

The first absorption bands of polyoxometallates could be assigned to dπ – pπ electronic transition in W=O bond and the second band could be assigned to dπ – pπ electronic transition in W-O-W bonds (Rusu, 1999). In the obtained polyoxometallates these bands are shifted in comparison with the ligand frequencies because of the coordination with the metallic ions (Co^{2+}, Ni^{2+}, Cu^{2+}).

The IR spectrum Dawson compound $K_6P_2W_{18}O_{62}$ is characterized by the elongation of P-O bands at 1100 cm^{-1} and W-O terminal and inter- and intra-W-O-W bands at 960, 910, and 780 cm^{-1}, respectively (Rocchiccioli – Deltcheff, 1979, 1976). The spectrum of lacunary substrate $\alpha_2K_{10}P_2W_{17}O_{61}$ shows three bands between 1100 and 1010 cm^{-1} assigned to stretching of P-O.

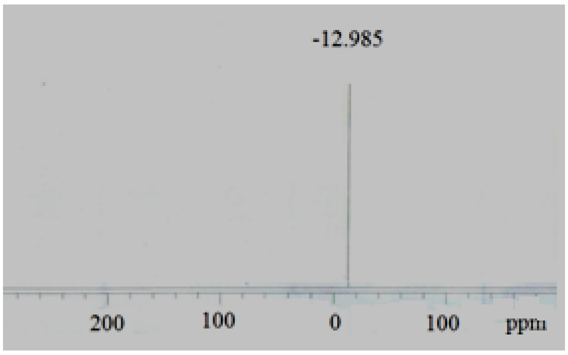
The IR spectra of the three compounds present the characteristic peaks of Dawson structure (Table 1). The intensities bands at 1058.85 cm^{-1} in Cu-derivative and at 1064.63 cm^{-1} for Co-derivative characteristic of a lacuna in the structure decreases and disparate for Ni-derivative compared to the spectrum of $\alpha_2K_{10}P_2W_{17}O_{61}$ precursor.

Table1. Selected I.R. data (cm^{-1}) of $Na_{18}[(\alpha_2P_2W_{17}O_{61})_2M],nH_2O$; M = Cu, Co, Ni

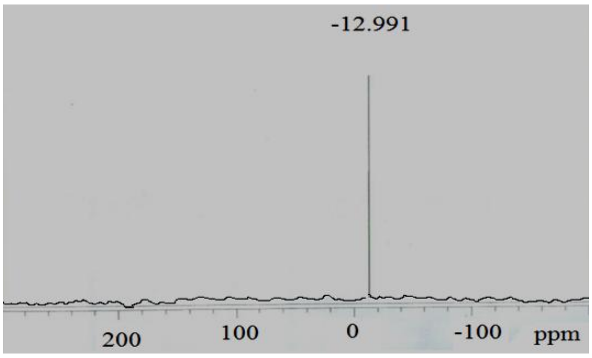
POM	$\nu_{as}(P\text{-}O_a)$	$\nu_{as}(W\text{-}O_d)$
α_2 $K_{10}P_2W_{17}O_{61}$	1086	959
		914
$[(\alpha_2P_2W_{17}O_{61})_2Cu]^{18-}$	1084	941
	1059	918
	1016	
$[(\alpha_2P_2W_{17}O_{61})_2Co]^{18-}$	1083	939
	1065	912
	1013	
$[(\alpha_2P_2W_{17}O_{61})_2Ni]^{18-}$	1084	959
	1013	914

The IR spectra of Cu and Co derivatives are nearly identical, indicating a structural similarity. In the IR spectrum of Ni derivative no band is present at around 1060 cm^{-1}. This indicates that both PO_4 groups in PW_9 and PW_8 moieties are becoming nearly equivalent, probably, because of the d (dε & dγ) orbital symmetry of Ni^{2+}.

^{31}PNMR spectroscopy is particularly suitable for checking the purity of polyoxometallates. ^{31}PNMR spectrum of precursor specie shows two lines at -7 and -13.6 ppm (Massart, 1977). This is compatible with two non equivalents phosphorus atoms. The NMR study of paramagnetic elements containing POMs reveals that the chemical shift of the P atom noted P(2) far from the paramagnetic element was practically unaffected by the presence of this element, while P(1) resonance is shifted radically and broadened. This shift and broadening might be important enough to make the corresponding signal hardly or not at all observed (Contant, 2000; Belghiche, 2002). In the same way, the spectra of Ni and Cu derivatives (Fig. 2b, 2a) show one line at -12.991 and -12.985 ppm respectively. The spectrum of Co compound shows one line at -13.004 ppm with traces (<9%) at -24.04 ppm (Fig. 2c).



(a)



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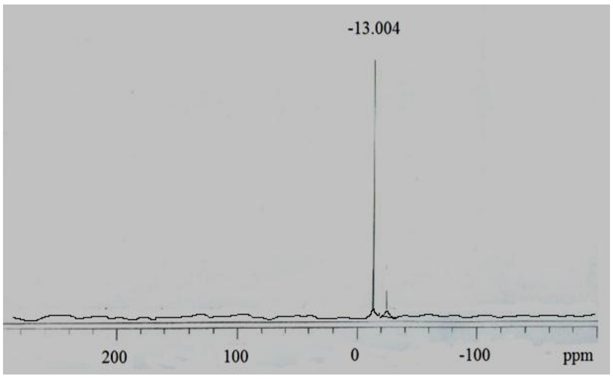


(c)

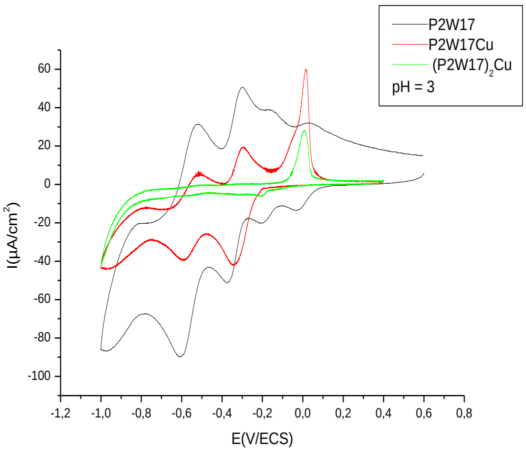
Fig. 2: ^{31}PNMR spectrum of a: Cu-compounds; b: Ni-compound; c: Co-compound

Characterization by cyclic voltammetry access to the redox peak of different metallic elements present in the structure (Keita, 2007).The study was effected at pH 3. The voltammograms of compounds $P_2W_{17}O_{61}^{10-}$, $P_2W_{17}CuO_{61}^{8-}$ and $[Cu(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{18-}$ (Fig.3a) are clearly different, which reveals the structure difference of the three compounds.

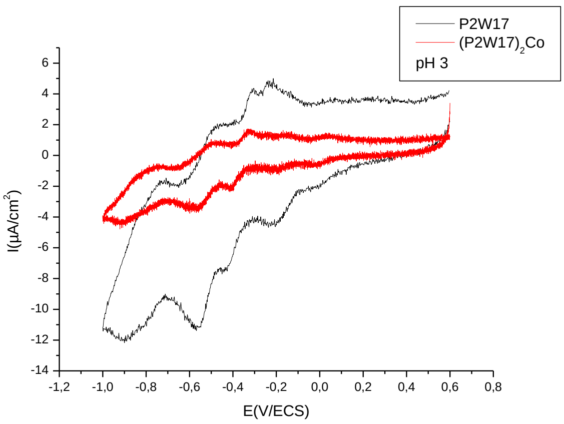
A pair of redox process is observed for Cu-compound at potential of -0.192V for oxidation and 0.013V for reduction. The anodic peak should correspond to the reoxidation of Cu^0 to

Cu^{2+}, the same shape of oxydoreduction wave of copper was observed in Dawson polyoxometallates and similar results have reported elsewhere for sandwich compound $[Cu_4(OH)_2(P_2W_{15}O_{56})_2]^{18-}$(Rhulmann, 2002).

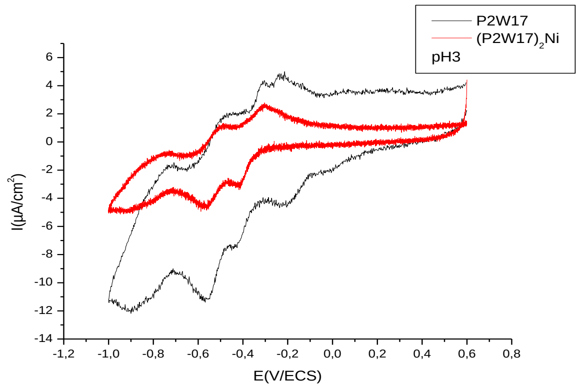
The voltammograms of $[M(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{18-}$, M = Co^{2+}, Ni^{2+},(Fig. 3b, 3c) are different from precursor's voltammogram, with less redox systems. The insertion of metallic ions in the structure affected the number and the potential of different redox systems. The intensities of waves in precursor or synthesized compounds are almost close. The oxydoreduction of Co^{2+} or Ni^{2+} ions, not observed at explored potential (Rhulmann, 2002).



(a)



(b)



(c)

Fig. 3: Voltammograms of a: Cu-compounds; b: Co-compound; c: Ni-compound

CONCLUSION

Three new compounds $Na_{18}[M(\alpha_2\text{-}P_2W_{17}O_{61})_2]$ (M = Co, Ni, Cu) were obtained from monolacunary Dawson polyoxometallate specie in acidic medium at about 60°C. The UV spectra for the three compounds are nearly equivalent and exhibit the specific absorption of Dawson polyoxometallates. The IR spectra show the similarity of Co- and Cu-derivatives with the decreases of the lacuna band. This band disparate for Ni compound. The insertion of Ni metallic ions seems to have saturated the gap with respect to the results obtained at IR spectroscopy. The purity of compounds was cheeked by ^{31}PNMR. The apparition of one line at ^{31}PNMR spectra is due to the insertion of paramagnetic elements in the structure.
The electrochemical study reveals the difference of precursor from compounds; substrate: metal (1:1) and substrate: metal (2:1).

Acknowledgement

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