Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.848653

53 (2015) 709–717
January

Taylor & Francis
Taylor & Francis Group

Study of simultaneous complexation of heavy metals by a mixed heteropolyanion of dawson type

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Received 8 June 2012; Accepted 10 September 2013

ABSTRACT

In this work, the simultaneous complexation of the bivalent elements (Ni^{2+}, Pb^{2+}, Cd^{2+}) by a lacunar mixed heteropolyanion of Dawson type $(\alpha_2P_2W_{15}Mo_2O_{61}\cdot nH2O)^{10-}$ was studied. These elements are in couple (Ni^{2+}, Pb^{2+}), (Ni^{2+}, Cd^{2+}), and (Pb^{2+}, Cd^{2+}) in aqueous solutions. From the characterization of UV visible spectroscopy, the stability of the formed complexes $[NiPbP_2W_{15}\ Mo_2]^{6-}$, and $[CdNiP_2W_{15}\ Mo_2]^{6-}$, $[CdPbP_2W_{15}\ Mo_2]^{6-}$ according to the pH, the time, and the temperature of the reactional medium was studied. The stoechiometry and the constant of stability of these formed complexes were also given. From where it was noted that new mixed compounds having rather high constants of stability were ended, thus they could be steady to the elimination of heavy metals existing in water of industrial wastes.

Keywords: Heteropolyanions; Complexation; Heavy metals; Waters pollution; Spectrophotometric methods

1. Introduction

Heteropolyanions (HPAs) of Dawson type [1] have very remarkable structures and characteristics which enable them to be the object of many studies. They are of great interest in the catalysis as well in heterogeneous phase [2–4] as in homogeneous phase [5,6]. They are also used in chemical analysis, biochemistry [7], medicine [8], environment, and the science of materials [9,10]. It should be noted that these HPAs are not toxic and non-polluting; they are also employed for treatment of pollution [11] and electrocatalytic reduction in nitrogen oxide: NO^{2-}, NO, and NO_2 [12,13]. A great number of HPAs were employed like reagent chemicals in detection, separation, and the complexation of pharmaceutical and biological elementary materials [14,15]. To carry out one of these quoted uses (separation and complexation), various samples of aqueous solutions containing heavy metals like lead, nickel, and cadmium (Pb^{2+}, Ni^{2+}, Cd^{2+}) were separated from water and were complexed by a lacunar mixed HPA of Dawson type $(\alpha_2P_2W_{15}Mo_2O_{61}\cdot nH_2O)^{10-}$ in abrogated $(\alpha_2P_2W_{15}Mo_2)$.

These heavy metals (Pb^{2+}, Ni^{2+}, and Cd^{2+}) count among the most widespread agents of pollution in the areas with strong urban center and industry. Industrial water of rejections collects these various pollutants in notable quantities. These latter constitute the main issue for the environment. The difficulty in separately proportioning two heavy metals present in the same sample can be surmounted by calling upon the spectrophotometric method. This work

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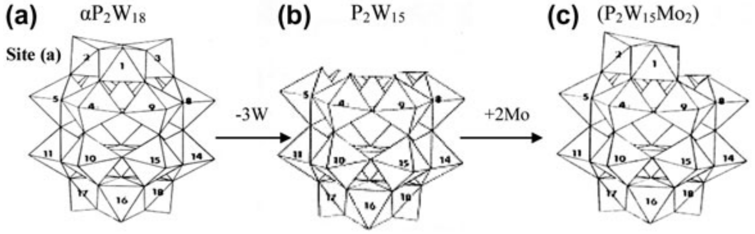

Fig. 1. Structures of HPAs.

studies the influence of the factors which control the stability and the reactivity of heavy metals (Pb^{2+}, Ni^{2+}, and Cd^{2+}) with the HPA $(\alpha_2P_2W_{15}Mo_2O_{61})^{10-}$ namely:

- pH of the reaction medium;
- Stability time of the complexes;
- Stability temperature of complexation reaction.

These various conditions made it possible to determine the analytical form of the complexes formed, such as the stoichiometry and the calculation of the constants of stability by using statistical methods of calculation.

2. Experimental

2.1 Preparation and structures of HPAs

HPA $(\alpha_2P_2W_{15}Mo_2)^{10-}$ was prepared according to the methods described in the literature [16–18]. This compound is obtained by elimination of a tritungstic group of site (a) of the saturated species αP_2W_{18} (Fig. 1(a)), then two ions molybdates $MoO_4^{2-}$are added on this site trivacant (Fig. 1(b)) so as to keep only one gap (Fig. 1(c)).

The various structures of these HPAs are presented in Fig. 1.

2.2 Characterization of HPAs by infrared spectroscopy

For better assessment of the purity of the compounds formed during the preparation, the characterization of these compounds by the IRTF was carried out. The spectra IR were recorded in solid phase in KBr (1 mg of sample for 300 mg of KBr) on a spectrophotometer (Shimadzu Japan). The recorded spectra are illustrated in Fig. 2.

In the spectrum of the lacunar compound $(\alpha_2P_2W_{15}Mo_2)^{10-}$, a PO band located at 1,110 cm^{-1} is noticed. Delcheff [19] showed that the existence of such a band represented an important disturbance in a direction of tetrahedron PO_4: direction of the gap in this case. This band disappears for the saturated compound αP_2W_{18}.

2.3 Spectrophotometry study of the formed complexes

This study was carried out on three samples of aqueous solutions, one containing nickel and lead (Ni^{2+}, Pb^{2+}), the other nickel and cadmium (Ni^{2+}, Cd^{2+}) and the last lead and cadmium (Pb^{2+}, Cd^{2+}). HPA used as ligand is under form $(\alpha_2P_2W_{15}Mo_2O_{61})^{10-}$. However, the spectrophotometric proportioning of two heavy metals present in the same sample constitutes a certain difficulty. This difficulty consists in the

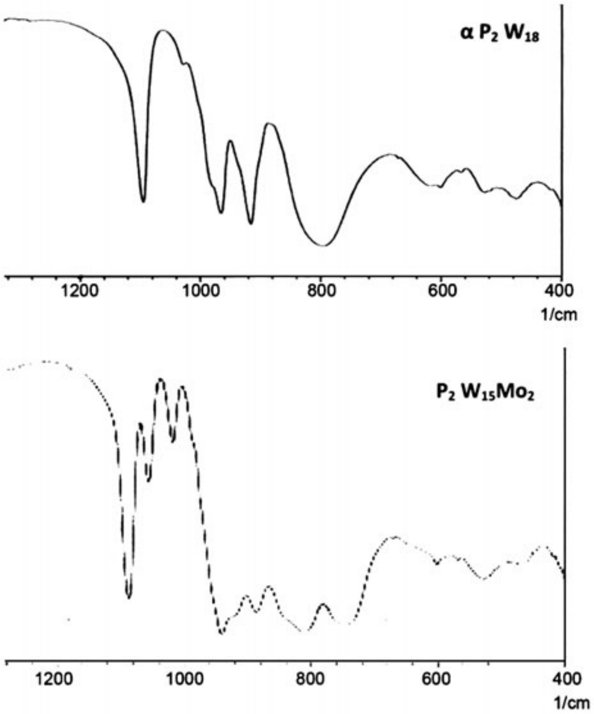

Fig. 2. Infra-red spectrums of HPAs.

possibility of interference wavelengths of heavy metals studied (problem of the awkward ions). To overcome this problem, a study of the complexation of each metal existing alone in solution (Ni^{2+}), (Cd^{2+}), and (Pb^{2+}) by the ($P_2W_{15}Mo_2$) was realized. In this intention, a UV–visible sweeping at different pH was carried out in a field wavelength [200–800 nm]. This has made it possible to determine the maximum and minimal wavelengths corresponding to the maximum and minimal absorbances of each metal with the selected pH. The mixtures of these solutions were prepared as follows:

The reference solution was made up of:

- Four millilitre of buffer solution;
- Two millilitre of ligand solution of concentration 5×10^{-5} M.

The solution to be analyzed consisted of:

- Two millilitre of buffer solution;
- Two millilitre of ligand solution of concentration 5×10^{-5} M;
- Two millilitre of metal solution to be complexed of concentration 5×10^{-5} M.

In addition, to study the complexation of two metals existing together in the same aqueous solution, the mixtures were prepared in the following way:

The reference solution was made up of:

- Six millilitre of buffer solution;
- Two millilitre of ligand solution of concentration 5×10^{-5} M.

The solution to be analyzed consisted of:

- Two millilitre of buffer solution;
- Two millilitre of ligand solution of concentration 5×10^{-5} M;
- Two millilitre of metal solution M_1 to be complexed of concentration 5×10^{-5} M;
- Two millilitre of metal solution M_2 to be complexed of concentration 5×10^{-5} M.

The solutions of metallic ions were prepared from commercial salts of quality for analysis: [$Cd(NO_3)_2,6H_2O$], [$Pb(NO_3)_2,6H_2O$], [$Ni(NO_3)_2,6H_2O$].

The analysis was realized with a spectrophotometer of type UV-1202 UV–vis (Shimadzu).

The stability study of the complexes formed by varying factors, such as pH, time, and temperature was carried out. On the basis of these parameters, the determination of stoechiometry and the constants of

Table 1

Influence of pH on the complexes $[NiP_2W_{15}Mo_2]^{-8}$ and $[PbP_2W_{15}Mo_2]^{-8}$

	$[NiP_2W_{15}Mo_2]^{-8}$		$[PbP_2W_{15}Mo_2]^{-8}$	
pH	Abs λ_{max} (nm)	Abs λ_{max} (nm)	Abs λ_{max} (nm)	Abs λ_{max} (nm)
3	0.347	0.055	0.205	0.000
	311	204	204	311
4	0.426	0.010	0.205	0.084
	308	231	231	308
5	0.522	0.000	0.135	0.049
	311	226	226	311
6	0.688	0.003	0.550	0.019
	311	301	244	311
7	0.788	0.031	0.575	0.010
	302	244	244	302
8	0.978	0.000	0.451	0.012
	302	205	205	302
9	**0.646**	**0.006**	**0.701**	**0.000**
	214	**209**	**209**	**214**
10	1.131	0.078	0.824	0.222
	247	202	202	247
11	0.924	0.019	0.731	0.337
	222	205	205	222

Note: Bold values represent the optimal pH for which we have the maximum or minimum absorbance for a given metal.

Table 2

Influence of pH on the complexes $[NiP_2W_{15}Mo_2]^{-8}$ and $[CdP_2W_{15}Mo_2]^{-8}$

	$[NiP_2W_{15}Mo_2]^{-8}$		$[CdP_2W_{15}Mo_2]^{-8}$	
pH	Abs λ_{max} (nm)	Abs λ_{max} (nm)	Abs λ_{max} (nm)	Abs λ_{max} (nm)
3	0.347	0.055	0.320	0.000
	311	204	204	311
4	0.426	0.010	0.331	0.091
	308	231	231	308
5	0.522	0.000	0.246	0.000
	311	226	226	311
6	0.688	0.003	0.341	0.064
	311	301	301	311
7	0.788	0.031	0.524	0.123
	302	244	244	302
8	0.978	0.000	0.857	0.248
	302	205	205	302
9	**0.646**	**0.013**	**0.941**	**0.000**
	214	**220**	**220**	**214**
10	1.302	0.078	1.241	0.363
	217	260	260	217
11	0.924	0.019	0.910	0.000
	222	205	205	222

Note: Bold values represent the optimal pH for which we have the maximum or minimum absorbance for a given metal.

stability were also studied by using the following methods of calculation: isomolaires series, saturation, and balance displacement [20].

3. Results and discussion

3.1 Influence of pH on the complexes formation

A UV–visible sweeping with different pH (acido-basic) was carried out in order to choose the optimum pH which gives the maximum of absorbance to a fixed wavelength for a given metal (M_1) at pH and the same wavelength that gives the minimum of absorbance or null absorbance for another metal (M_2). In this manner, the proportioning of two metals (M_1 and M_2) existing together in the same solution being able to be carried out without one gene the other (Tables 1–3).

Results presented in Tables 1–3 show that the formation of the complexes is very weak in acid medium; but the basic medium is more favorable for their formation. This may be due to the possibility of dimerization of HPA in acid medium as mentioned in research paper [21]. The experimental results showed that the favorable pH for the formation of the complexes $[M_1M_2P_2W_{15}Mo_2]^{-6}$ is pH equal to 9 (Table 4).

Table 3
Influence of pH on the complexes $[PbP_2W_{15}Mo_2]^{-8}$and $[CdP_2W_{15}Mo_2]^{-8}$

	$[PbP_2W_{15}Mo_2]^{-8}$		$[CdP_2W_{15}Mo_2]^{-8}$	
pH	Abs λ_{max}(nm)	Abs λ_{max}(nm)	Abs λ_{max}(nm)	Abs λ_{max}(nm)
3	0.205	0.000	0.153	0.060
	204	311	311	204
4	0.205	0.084	0.169	0.011
	231	308	308	231
5	0.135	0.049	0.110	0.001
	226	311	311	226
6	0.550	0.019	0.398	0.069
	301	311	311	301
7	0.575	0.010	0.507	0.020
	244	302	302	244
8	0.451	0.012	0.339	0.089
	205	302	302	205
9	**0.701**	**0.000**	**0.941**	**0.000**
	209	**220**	**220**	**209**
10	0.824	0.222	1.241	0.049
	208	260	260	208
11	0.731	0.337	0.501	0.000
	205	222	222	205

Note: Bold values represent the optimal pH for which we have the maximum or minimum absorbance for a given metal.

The results obtained are illustrated better in Figs. 3–5.

3.2 Influence of time on the complex formation

In order to determine the time for which the complexes are stabilized, variation of absorbance of these complexes according to time was followed, while operating with the same solutions and with the optimum pH found (pH 9).

The results illustrated if Figs. 6–8 show that formation of complexes $[NiPbP_2W_{15}Mo_2]^{-6}$, $[CdNiP_2W_{15}Mo_2]^{-6}$, and $[CdPbP_2W_{15}Mo_2]^{-6}$ was instantaneous and fast, from where their absorbances increased with time until a maximum was reached, then they decreased appreciably, to reach a minimal value. It is deduced that these complexes are stable in a rather broad time interval which can last 25 min. Generally, HPAs of Dawson type are usually stable over time in basic medium. The findings of this study are consistent with other results reported in the literature [22].

3.3 Influence of temperature on the complex formation

To determine favorable temperature for the formation of the complexes, the variation of the absorbance of the complexes according to the temperature was followed. The results obtained are illustrated in Figs. 9–11.

The study of the influence of temperature on the formation of bimetallic complexes $[NiPbP_2W_{15}\ Mo_2O_{61}]^{6-}$, and $[CdNiP_2W_{15}Mo_2O_{61}]^{6-}$, $[CdPbP_2W_{15}Mo_2O_{61}]^{6-}$ showed that their absorbances increased slightly with the increase in the temperature. However, it is preferable to work at room temperature, because the reaction is realizable at this temperature.

Table 4
Maximum wavelength for each complex $(M_1M_2P_2W_{15}Mo_2)^{-6}$ with the optimal pH equal to 9

Complexes	$[NiPbP_2W_{15}Mo_2O_{61}]^{6-}$	$[CdNiP_2W_{15}Mo_2O_{61}]^{6-}$	$[CdPbP_2W_{15}Mo_2O_{61}]^{6-}$
λ (nm)	214_{Ni} 209_{Pb}	220_{Cd} 214_{Ni}	220_{Cd} 209_{Pb}

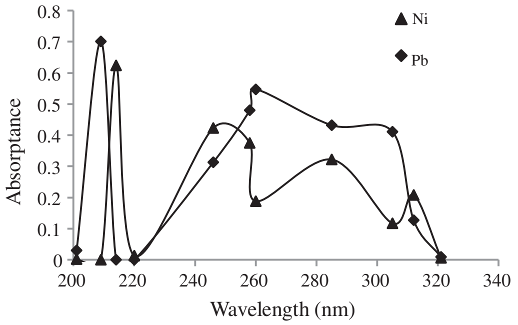

Fig. 3. Variation of the absorptance of the formed complexe $[NiPbP_2W_{15}Mo_2O_{61}]^{6-}$ according of the wavelength for pH 9.

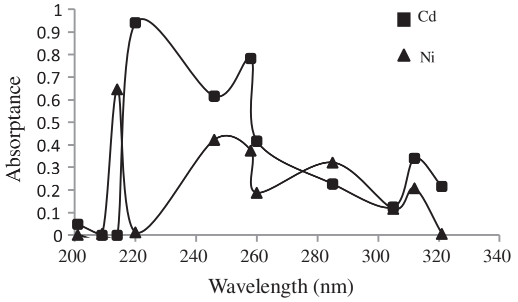

Fig. 4. Variation of the absorptance of the formed complexe $[NiCdP_2W_{15}Mo_2O_{61}]^{6-}$ according of the wavelength for pH 9.

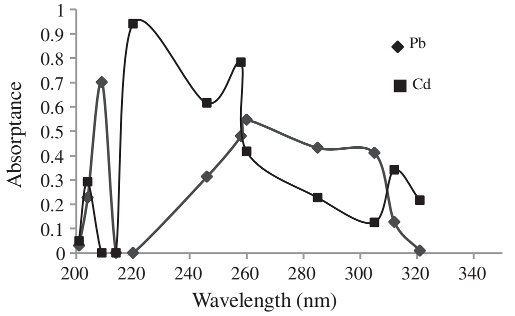

Fig. 5. Variation of the absorptance of the formed complexe $[CdPbP_2W_{15}Mo_2O_{61}]^{6-}$ according of the wavelength for pH 9.

3.4 *Study of the analytical form of the formed complexes*

3.4.1 *Determination of stoechiometry by the isomolaire series method*

The isomolaires series method is exploited starting from the metal ions and the ligand solutions of respective concentrations C_M and C_L, such as $C_M = C_L = 5 \times 10^{-5}$M.

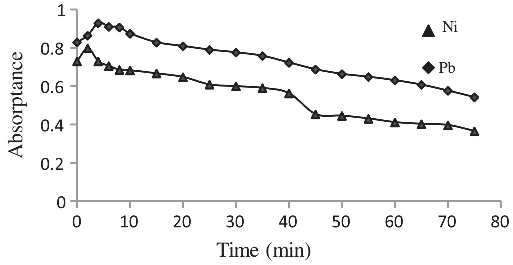

Fig. 6. Variation of the absorptance of the formed complexe $[NiPbP_2W_{15}Mo_2O_{61}]^{6-}$ according to time.

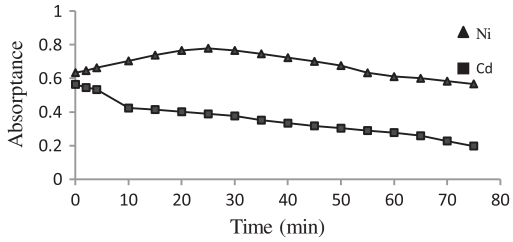

Fig. 7. Variation of the absorptance of the formed complexe $[NiCdP_2W_{15}Mo_2O_{61}]^{6-}$ according to time.

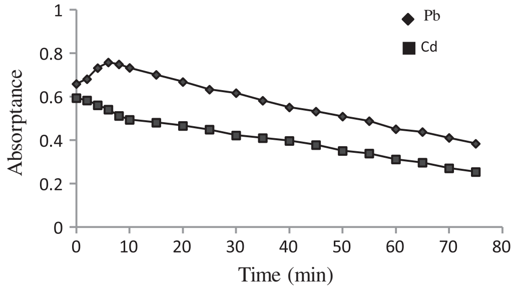

Fig. 8. Variation of the absorptance of the formed complexe $[CdPbP_2W_{15}Mo_2O_{61}]^{6-}$ according to time.

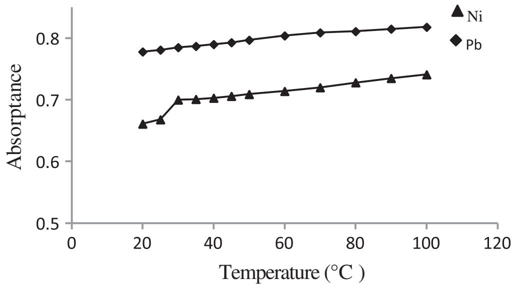

Fig. 9. Variation of the absorptance of the formed complexe $[NiPbP_2W_{15}Mo_2O_{61}]^{6-}$ according to the temperature.

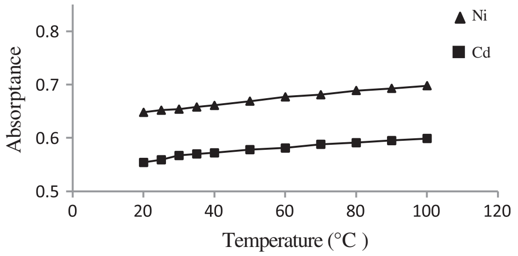

Fig. 10. Variation of the absorptance of the formed complexe $[NiCdP_2W_{15}Mo_2O_{61}]^{6-}$ according to the temperature.

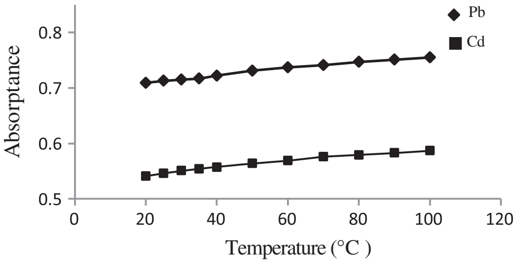

Fig. 11. Variation of the absorptance of the formed complexe $[CdPbP_2W_{15}Mo_2O_{61}]^{6-}$ according to the temperature.

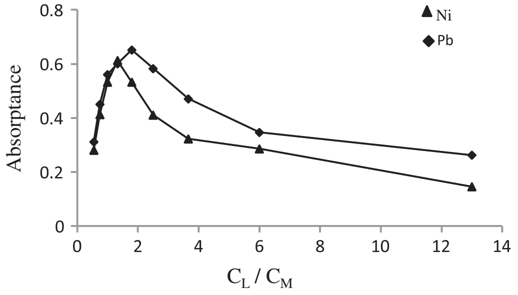

Fig. 12. Variation of the absorptance of the formed complexe $[NiPbP_2W_{15}Mo_2O_{61}]^{6-}$ according to report C_L/C_M by the serie isomolaire method.

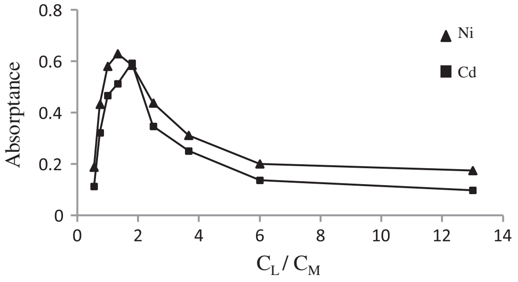

Fig. 13. Variation of the absorptance of the formed complexe $[NiCdP_2W_{15}Mo_2O_{61}]^{6-}$ according to report C_L/C_M by the serie isomolaire method.

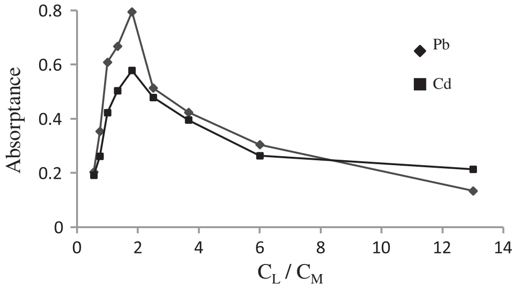

Fig. 14. Variation of the absorptance of the formed complexe $[CdPbP_2W_{15}Mo_2O_{61}]^{6-}$ according to report C_L/C_M by the series isomolaire method.

These solutions are mixed in different volumetric proportions for the same final volume from the mixture, so as to maintain the sum (C_M + C_L) constant. The absorbances are measured with wavelengths and a pH corresponding to each complex (Table 1). The curves of absorption A = f (C_L/C_M) are represented in Figs. 12–14.

According to the principle of the method of the isomolaires series, the stoechiometry of the formed complexes corresponds to the maximum of the absorbance on the curve of absorption $A = f\ (C_L/C_M)$. It was noted that the stoechiometry of the three formed complexes is higher than 1, it varies between 1.33 and 1.88.

3.4.2 Determination of stoechiometry by the method of saturation

In this method the concentration of metal is fixed, so that the concentration of the ligand is varied, while maintaining a total volume of solution constant.

According to the principle of the saturation method, the stoechiometry of the formed complexes is obtained by the intersection of the tangents traced in two parts of the curve of saturation (ascending part and stage of saturation). The curves of absorption $A = f\ (C_L/C_M)$ are illustrated in Figs. 15–17. These fig-

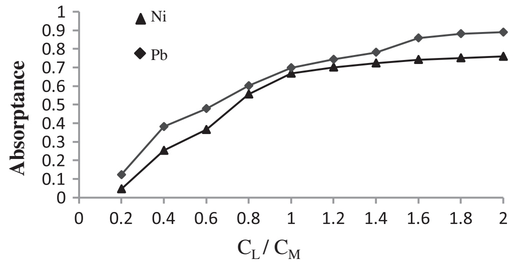

Fig. 15. Variation of the absorptance of the formed complexe $[NiPbP_2W_{15}Mo_2O_{61}]^{6-}$ according to report C_L/C_M by the saturation method.

ures show that the stoechiometry of the three complexes formed is slightly higher than 1.

3.4.3 Determination of the stoechiometry and the constant of stability by displacement of balance method

The determination of stoechiometry (n) and the constant of stability (β) of the formed complexes were carried out starting from the linearization of the results obtained by the method of saturation according to the following equation:

$$\log(A_i/A_{\max} - A_i) = n\log C_{\text{Li}} + \log\beta \tag{1}$$

where A_i is absorbance of the complex corresponding to the increasing part of the curve of saturation; $A_{\max}$—maximum absorbance corresponding to the stage of the curve of saturation; n—stoechiometric report (C_L/C_M); $C_{\text{L}i}$–concentration of the ligand correspondent to each value of A_i; β–constant of stability.

By tracing log ($A_\text{i}/A_{\max}$–A_i) according to log $C_{\text{L}i}$ for some points of the ascending part of the curves of saturation, Figs. 18–20 were obtained.

It was noted that the stoechiometries obtained by this method are also higher than 1. This confirms the results found by the two other methods. The stability

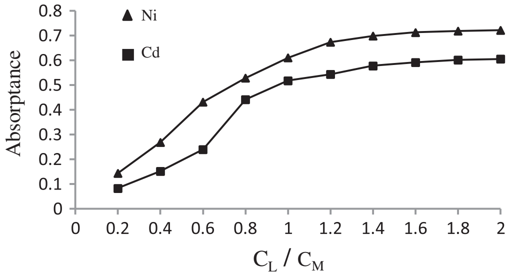

Fig. 16. Variation of the absorptance of the formed complexe $[\text{NiCdP}_2\text{W}_{15}\text{Mo}_2\text{O}_{61}]^{6-}$ according to report C_L/C_M by the saturation method.

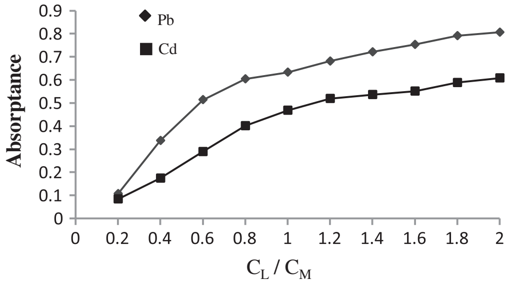

Fig. 17. Variation of the absorptance of the formed complexe $[\text{CdPbP}_2\text{W}_{15}\text{Mo}_2\text{O}_{61}]^{6-}$ according to report C_L/C_M by the saturation method.

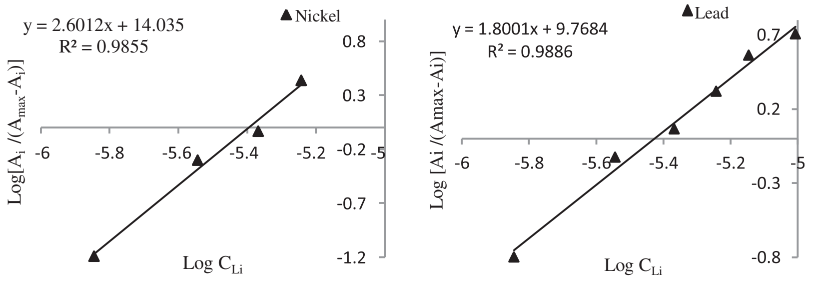

Fig. 18. Variation of log ($A_\text{i}/A_{\max}$–A_i) according to log $C_{\text{L}i}$ For the complexe $[\text{NiPbP}_2\text{W}_{15}\text{Mo}_2\text{O}_{61}]^{6-}$.

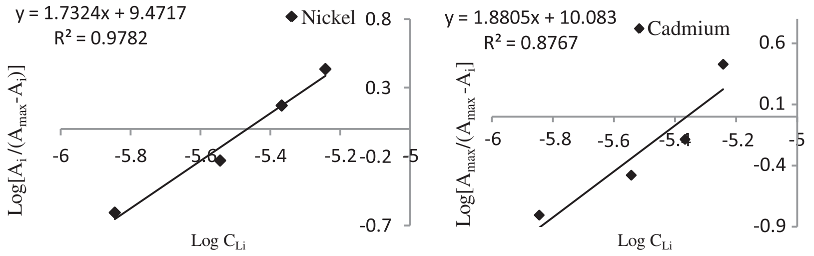

Fig. 19. Variation of log ($A_\text{i}/A_{\max}$–A_i) according to log $C_{\text{L}i}$ For the complexe $[\text{NiCdP}_2\text{W}_{15}\text{Mo}_2\text{O}_{61}]^{6-}$.

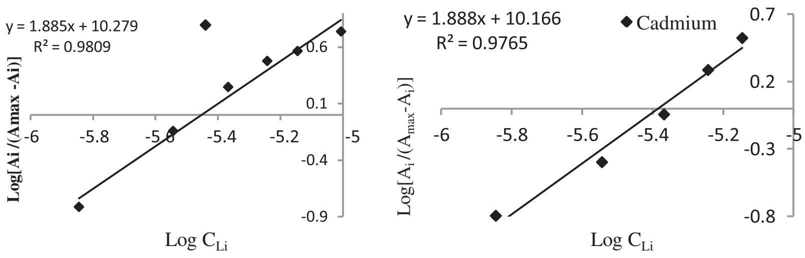

Fig. 20. Variation of log ($A_i/A_{max}-A_i$) according to log C_{Li} For the complexe $[CdPbP_2W_{15}Mo_2O_{61}]^{6-}$.

Table 5
Determination of the stoechiometries and the stabilities constants of formed complexes by different methods: isomolaire series, saturation and balance displacement

Complexes	Metallic elements		Isomolaires series	Saturation	Balance displacement
$[NiPbP_2W_{15}Mo_2O_{62}]^{6-}$	Ni^{2+}	$n = C_L/C_M$	1.33	1	2.60
		β	–	–	1.07×10^{14}
	Pb^{2+}	$n = C_L/C_M$	1.80	1.15	1.80
		β	–	–	5.86×10^{9}
$[CdNiP_2W_{15}Mo_2O_{62}]^{6-}$	Ni^{2+}	$n = C_L/C_M$	1.33	1.15	1.73
		β	–	–	2.95×10^{9}
	Cd^{2+}	$n = C_L/C_M$	1.80	1	1.88
		β	–	–	1.20×10^{10}
$[CdPbP_2W_{15}Mo_2O_{62}]^{6-}$	Pb^{2+}	$n = C_L/C_M$	1.80	1.15	1.88
		β	–	–	1.86×10^{10}
	Cd^{2+}	$n = C_L/C_M$	1.80	1.10	1.88
		β	–	–	1.44×10^{10}

constants found for the three formed complexes are high enough; they are about 10^9–10^{14}.

To make the distinction between these three methods of calculation, the results were compared and are represented in Table 5. The results obtained by the three methods are rather close; they show that stoechiometries or the ratio ligand-metal (C_L/C_M) are practically higher than 1 for all the complexes formed. Also the calculation of stabilities constants gave considerably high values. It proves that HPA $[P_2W_{15}Mo_2]$ used as a ligand has a very important complexing capacity on two heavy metals existing together in the same in aqueous solution.

4. Conclusion

The molybdo-tungsto-phosphoric mixed lacunar HPA of Dawson type $(\alpha_2P_2W_{15}Mo_2O_{61})^{10-}$ seems to have remarkable properties of complexation on the bivalent metal ions (Ni^{2+}, Pb^{2+}, Cd^{2+}) being present in form of couples in the same aqueous solution. These metal ions are likely to be present in water of industrial waste like polluting agents of the first degree. So, heteropolyanion can be used in the field of water treatment to fix toxic metals in homogenous catalysis, and it can also be proposed in chemical analysis. The study by UV–visible spectrophotometry for the formation of the complexes $[NiPbP_2W_{15}Mo_2O_{61}]^{6-}$, $[CdNiP_2W_{15}Mo_2O_{61}]^{6-}$, and $[CdPbP_2W_{15}Mo_2O_{61}]^{6-}$ revealed satisfactory results. The study showed the stability of these complexes. The basic medium is more favorable for their formation, more precisely with a pH equal to 9. The proportioning of these metal ions in bi-simultaneous presence with various found wavelengths was carried out successfully without having the problem of awkward ions. These complexes are stable in a rather broad time interval which can last up to 25 min. The increase in the temperature supports the formation of these complexes, but it is preferable to work at room temperature because the reaction is realizable at this temperature. The study of the stoechiometry and the constant of stability of these complexes by the three methods of calculating showed that the mixed lacunar HPA $[P_2W_{15}Mo_2O_{61}]^{10-}$ forms the bimetallic complexes with the metal ions (Ni^{2+}, Pb^{2+}, Cd^{2+}) with a stoechiometry (report ligand-metal) near to two. The constants of stabilities of the formed complexes are high enough, they are about 10^9–10^{14}, which makes it possible to deduce that these complexes are sufficiently stable thus indicating the use potential of this compound $[P_2W_{15}Mo_2O_{61}]^{10-}$, in particular in aqueous media, without risk of decomposition. The results obtained starting from this work show that the HPA used as ligand $[K_{10}P_2W_{15}Mo_2O_{61}]^{10-}$ constitutes aninteresting sequestering agent on only one metal ion, as on two metal ions being together in aqueous solution. Consequently, it leads to the development of a new compound for the proportioning of heavy metals (lead, nickel, and cadmium) simultaneously present in the same sample, without having recourse to other methods of analysis, by using like method of analysis UV–visible spectrophotometry.

References

[1] B. Dawson, The structure of the 9(18)-heteropolyanion in potassium 9(18)-tungstophosphate, K_6 $(P_2W_{18}O_{62})$. $14H_2O$, Acta Crystallogr. 6 (1953) 113.

[2] J.M. Galownia, A.P. Wight, A. Blanc, J.A. Labinger, M.E. Davis, Partially reduced heteropolyanions for the oxidative dehydrogenation of ethane to ethylene and acetic acid at atmospheric pressure, J. Catal. 236 (2005) 356–365.

[3] F. Ragaini, M. Macchi, S. Cenini, Carbonylation of nitrobenzene catalysed by palladium and heteropolyanions: A mechanistic approach, J. Mol. Catal. A: Chem. 127 (1997) 33–42.

[4] C. Travers, N. Essayem, M. Delage, S. Quelen, Heteropolyanions based catalysts for paraffins isomerization, Catal. Today 65 (2001) 355–361.

[5] S. Hocine, C. Rabia, M. Fournier, M.M. Bettahar, Études cinétique et mécanistique de la déshydrogénation oxydante du cyclohexane sur $Cs_{2,5}Fe_{0,08}H_{0,26}PMo_{12}O_{40}$, C.R. Chim. 10 (2007) 637–643.

[6] Y. Leng, J. Wang, D. Zhu, Y. Wu, P. Zhao, Sulfonated organic heteropolyacid salts: Recyclable green solid catalysts for esterifications, J. Mol. Catal. A: Chem. 313 (2009) 1–6.

[7] X. Wang, F. Li, S. Liu, M.T. Pope, New liposome-encapsulated-polyoxometalates: synthesis and antitumoral activity, J. Inorg. Biochem. 99 (2005) 452–457.

[8] F. Bussereau, M. Picard, C. Majik, A. Teze, J. Blancon, Efficacy of heteropolyanions against rabies virus infection in mice, Ann. de l'Inst. Pasteur/Virologie 137 (1986) 391–400.

[9] N. Zabat, M. Abbessi, R. Kherrat, N. Jaffrezic-Renault, S. Zougar, A. Grid, Elaboration of Impedancemetric sensor for cobalt detection by polymeric membrane incorporating a heteropolyanion of Dawson type, Mater. Sci. Eng., C 28 (2008) 1006–1009.

[10] J. Modesto Clemente-Juan, Mi. Clemente-Leon, L. Coronado, J. R. Galán-Mascarós, C. Giménez-Saiz, C.J. Gómez-García, Magnetic clusters and conducting molecular materials from polyoxometalates, C.R. Acad. Sci., Ser. IIc: Chim. 1 (1998) 305–317.

[11] D. Soogund, P. Lecour, A. Daudin, B. Guichard, C. Legens, C. Lamonier, E. Payen, New Mo–V based oxidic precursor for the hydrotreatment of residues, Appl. Catal., B 98 (2010) 39–48.

[12] B. Keita, F. Girard, L. Nadjo, R. Contant, R. Belghiche, M. Abbessi, Chemistry, cyclic voltammetric evidence of facilitation of the reduction of nitrite by the presence of molybdenum in Fe-or Cu-substituted heteroplytungstates, J. Electroanal. 508 (2001) 70–80.

[13] B. Keita, E. Abdeljalil, L. Nadjo, R. contant, R. Belghiche, First examples of efficient participation of selected metal-ion-substituted heteropolyanions in in electrocatalytic nitrate reduction, Electrochem. Commun. 3 (2001) 56–62.

[14] M.N. Sokolova, G.B. Andreev, A.B. Yusov, Structural peculiarities of actinylcomplexation with monolacunarypolyoxometalates, Inorg. Chem. Commun. 14 (2011) 466–469.

[15] J. Li, F. Zhai, X. Wang, E. Li, S. Zhang, Q. Zhang, X. Du, Synthesis and biological activity of triorganogermanium substituted heteropolytungstates, Polyhedron 27 (2008) 1150–1154.

[16] J.P. Ciabrini, R. Contant, Mixed heteropolyanions: Synthesis and formation constants of Cerium(III) and Cerium(IV) complexes with lacunary tungstophosphates, J. Chem. Res. 10 (1993) 2720–2744.

[17] M. Abbessi, Synthèse et propriétés d'hétéropolyanions vanado-molybdo-tungsto-phosphoriques en vue d'une application en catalyse d'oxydation, Thèse de doctorat Université de Paris 1989.

[18] M. Abbessi, R. Contant, R. Thouvenot, G. Hervé, Dawson type hétéropolyanions. 1. Multinuclear $(^{31}P,^{51}V,^{184}W)$ NMF structural investigations of octadeca (molybdotungstovanado)diphosphate, Inorg. Chem. 30 (1991) 1695–1702.

[19] C. Rocchiccioli-Deltcheff, R. Thouvenot, Vibrational studies of heteropolyanions related to $\alpha P_2W_{18}O_{62}{}^{6-}$ I-Infrared Evidence of the structure of α_1 and $\alpha_2P_2W_{17}O_{61}{}^{10-}$. Spectrosc. Lett. 12 (1979) 127–138.

[20] M.L. Hamlaoui, K. Vlassenko, D. Messadi, Constante de stabilité des complexes de quelques métaux de transition avec l'hétéropolyanion non saturé $[P_2W_{17}O_{61}]^{10-}$, C.R. Acad. Sci. Paris 311 (1990) SérieII 795–798.

[21] B. Keita, F. Girard, L. Nadjo, R. Contant, J. Canny, M. Richet, Metal ion complexes derived from the α_1 isomer of $(P_2W_{17}O_{61})^{10-}$: Comparison with the corresponding α_2 species. J. Electroanal. Chem, 478 (1999) 76–82.

[22] Ouhiba Béchiri, Mostefa Abbessi, M. Elhadi Samar, Robila Belguiche, Extraction du complexe $(\alpha_1P_2W_{17}O_{61}Fe)^{7-}$ par membrane liquide émulsionnée, Afr. Sci. 3 (2007) 90–108.