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Potentiometric Study of the Complexing Ability of 2-Mono(Dihydroxyphosphonyl) Methyl 4-Nitro 6-Methyl Phenol (P2N4M6) and of 2-Mono(Dihydroxyphosphonyl) Methyl 4, 6-Dinitrophenol (P2N46) with Metal Cations Al(III), Cr(III) and Fe(III)

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Abstract: The interaction of ligands 2-mono(dihydroxyphosphonyl) methyl 4-nitro 6-methyl phenol (P2N4M6) and of 2-mono(dihydroxyphosphonyl) methyl 4,6-dinitrophenol (P2N4.6) with three metal ions, Al(III), Cr(III) and Fe(III) was studied . By means of potentiometry, the stability constants of the complexes formed were calculated at 25.0 ± 0.1°C. The ionic strength was maintained at 0.1 M with an aqueous solution of $NaClO_4$. Complexes of 1:1 metal to ligand ratio are formed and the logarithmic values of the stability constants of the model ML are: For P2N4M6: Al(III) = 7.99; Cr(III) = 6.30; Fe(III) = 6.70. For P2N4.6: Al(III) = 6.72; Cr(III) = 7.45; Fe(III) = 6.19. The stability of the two ligands is compared and a further comparison of the complexing ability with other ligands is attempted.

Key words: Dihydroxyphosphonyl phenols, P2N4M6, P2N4.6, potentiometry, stability constants, complexing ability

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INTRODUCTION

Metal phosphonates are a rich class of organic/inorganic hybrid materials and have been actively studied in recent years. The fact that the phosphonate group (RPO_3) contains both an inorganic moiety - which can form part of an inorganic framework, and an organic one, suggests that the preparation of novel materials is possible. Phosphonic acids (RPO_3H2) constitute a veritable class of compounds in which each phosphonate group can provide one, two or three oxygen atoms to coordinate metal ions. In practice, the most important are those associating a metallic cation to one or several complexing entities. The family of phenols substituted by the methylphosphonic groups comprises of a new generation of an important class of chelatants. Recently there has been an interest in the chemistry of calcium phosphonates due to the use of phosphonate-based drugs for diagonosis and therapy of various diseases of bones and for the study of calcium metabolism (Flesch, 1991, 1995; Francis *et al.*, 1983; Elford *et al.*, 1987; Schen *et al.*, 1988; Rubin *et al.*, 1985; Munday, 1987).

Bis(phosphonates) are an important class of drugs that have been reported to be active as anticalcification and antiresorption agents and have been used in the treatment of osteoporosis (Sietsema *et al.*, 1994). It was found that D.E.T.P.M.P. consisting of phosphonate groups ($-PO_3H_2$) is an effective crystal growth modifier in controlling the crystallization of $BaSO_4$ (Balestrieri *et al.*, 2005). The 9(R) [(2-phosphonomethoxy) propyl] adenine (teonofovir), is an acyclic neucloside phosphonate known to inhibit in vitro HIV replication and to reduce viremia in HIV-infected patients (Wang *et al.*, 2006).

Bentouhami *et al.* (Bentouhami *et al.*, 2002) studied by potentiometric and spectrophotometric means the complexing ability of ligands belonging to the same family of P2N4M6 and P2N4.6 with some lanthanides: Ce(III), Pr(III), Nd(III), Sm(III) and Eu(III). Recently, Benghanem *et al.* have reported the acid-base properties of a series of phenol methylenephosphonic acids (Benghanem *et al.*, 2001).

This study reports the results of complexation of ligands P2N4M6 and P2N4.6 with three metal cations: Al(III), Cr(III) and Fe(III). The number and the nature of the complexes present in solution are identified and their stabilities as well as their complexing abilities are compared. The structures of the ligands are given in Fig.1.

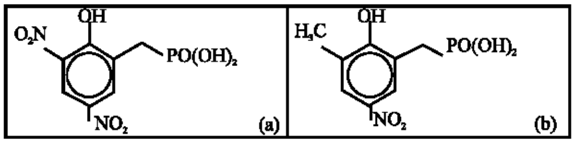

Fig. 1: Structure of ligands: (a) P2N4.6, (b) P2N4M6

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MATERIALS AND METHODS

For all analysis, sodium hydroxide 10-2 M was used as titrant, calibrated by using potassium hydrogenophtalate standard solution. Stock solutions of ligands P2N4M6 and P2N4.6 were prepared by weighing the required quantities of solid, synthesized at room temperature by (Vogt, 1990). These solutions are yellow in colour. Sodium perchlorate was used as supporting electrolyte because it is readily soluble and dissociates easily in water and thus assures good conductibility. Its solution was made from 99% $NaClO_4.H_2O$.

Potentiometric measurements were carried out on solutions prepared by dilution of the stock solutions. Metal solutions were added at the end, after those of the supporting electrolyte and of the ligand. This procedure is followed to avoid all contact of metal and ligand at higher concentrations which may result in precipitation. Preliminary assays showed the formation of precipitates at the concentration of 10^{-3} M for all the systems [L-Al(III), L-Cr(III) and L-Fe(III) where L = P2N4.6 or P2N4M6]. Consequently, 10^{-4} M was chosen as the optimal concentration for this potentiometric study in aqueous solution.

The experiments were made in a double-jacketed glass cell, thermoregulated at 25.0±0.1°C with the help of polysta CCI thermostat. The glass cell is purged and maintained under an atmosphere of nitrogen at atmospheric pressure to avoid any carbonation.

The potentiometric titrations were done by an automatic system, Titralab 90. This is basically composed of an efficient titrator, Tim 900, a burette of great precision, ABU 901 and a compact measuring stand, SAM 7. In order to realise the titration, the continuous inflection detection method was chosen as it is best adapted to elucidate the different significant points of the neutralisation curve and the numerical interpretation was done with the SUPERQUAD program (Gans *et al.*, 1983).

All pH measurements were carried out in sodium perchlorate medium with the help of a combined glass electrode to minimise the junction potential. The standardisation of the system was done with two solutions of hydrochloric acid of pH = 2 and pH = 3. The variations of the junction potential with respect to pH follows the exponential law of Haeringer and Schwing (1967), which expresses the real value of pH according to the relation:

$$pH_{true} = pH_{read} + a + b.10\text{-}pH_{read}$$

The stability constants of the different identified complexes were determined by pH-metric titrations of 20 ml samples at 25.0±0.1°C and at 0.1 M ($NaClO_4$). The ligand concentration was 0.02 M and the metal to ligand ratio was 1:1.

RESULTS AND DISCUSSION

Ligand P2N4M6: The system P2N4M6/Al(III) was titrated against NaOH 10^{-2} M. The solution turns bright yellow for pH values superior to 6.24. The same phenomena of colour change is observed for systems P2N4M6/Cr(III) (pH = 5.39) and P2N4M6/Fe(III) (pH = 5.75). The different titration curves, reported in Fig. 2, show that the quantity of protons liberated by the ligand, in the presence of Fe(III), is more important than that liberated by the ligand in the presence of Al(III) and Cr(III). These curves also indicate the formation of new species in the solutions under study.

The numerical analysis of the potentiometric data and testing of different models was done with the program SUPERQUAD (Gans *et al.*, 1983). This program calculates the electromotive force corresponding to each measured pH value, the measured and the calculated potentials and their difference, and the analytical and the free concentrations of all the species. According to this program the mathematical criteria for the best model are $S < 12.6$ and $1 < \delta < 3$, where S is the sum of squares of the absolute errors of observed and calculated concentration and δ is the standard deviation obtained for N measured values of pH, and defines the precision with which the whole set of measurements is interpreted.

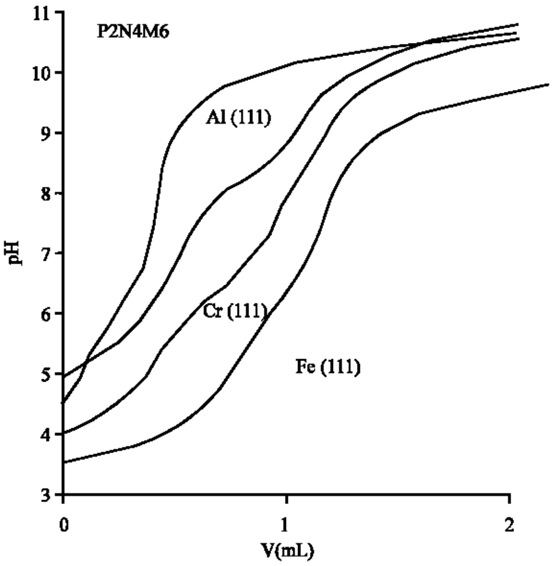

Fig. 2: Neutralisation curves of P2N4M6, P2N4M6/Fe(III), P2N4M6Al(III), P2N4M6/Cr(III). [L] = [M] = 10-4 M, I = 0.1 M, 25.0±0.1°C

Table 1: Logarithms of overall stability constants, log β, calculated for different models and different systems in aqueous solutions. [L] = [M] = 10-4 M, I = 0.1 M, 25.0±0.1°C

System	Model	Logβ	δ	S	pH formation range	Percentage formation
P2N4M6/Fe(III)	1,1,0	6.70±0.03	2.17	10.16	4.19-10.74	89.83
	1,1,-1	-2.96±0.12			7.16	12.42
	1,1,-2	-11.72 ±0.06			7.74	98.95
	2.17	10.16				
P2N4.6/Fe(III)	1,1,0	6.19±0.05	2.86	11.75	3.58-9.91	55.06
	1,1,-1	-1.6±0.07			5.31-11.37	65.27
	1,1,-2	-9.88±0.13			6.50-11.52	99.40
P2N4M6/Al(III)	1,1,0	7.99±0.04	2.23	3.75	3.53-9.84	88.00
	1,1,-1	0.08±0.05			5.43	45.82
	1,1,-2	-8.49±0.08			7.05	99.18
P2N4.6/Al(III)	1,1,0	6.72±0.05	2.89	5.65	3.68-8.66	41.76
	1,1,-1	0.12±0.07			4.16-9.60	82.27
	1,1,-3	-16.33 ±0.09			6.59-10.58	100
P2N4M6/Cr(III)	1,1,0	6.30±0.01	1.91	10.02	4.2	94.00
P2N4.6/Cr(III)	1,1,0	7.45±0.04	1.04	7.99	2.73-8.64	59.69
	1,1,-1	1.19±0.08			3.90-10.36	77.43
	1,1,-2	-6.37±0.09			5.99-10.66	8.66
	1,1,-3	-14.68±0.10			5.98-11.10	99.88

In order to determine the stability constants of the complexes formed with an acid ligand, it is necessary to know, a priori, its acidity constants. The values used in this work are those determined by Böhmer *et al.* (Bohmer *et al.*, 1993). These values of pKa1, pKa2 and pKa3 are, respectively, for: P2N4M6: 1.53; 5.88; 10.12 and for P2N4.6: 1.10; 4.22, 7.96.

For different models, overall stability constants βx,y,z were calculated where x pertains to metal (M), y is for ligand (L) and z for proton (H). In the case of hydroxo species, z is negative. With the ferric ions, the testing of different models led to the retention of model [(1,1,0), (1,1,-1) and (1,1,-2)] corresponding to [FeL], [FeL(OH)]- and FeL(OH)2]2-, where L is the ligand P2N4M6. The logarithm of the stability constants, β, are calculated as log β1,1,0 = 6.70±0.03; log β1,1,-1 = -2.96±0.12; and log β1,1,-2 = -11.72±0.06 for which the parameters δ = 2.17 and S = 10.16. The complete results of the numerical analysis have been summarized in Table 1.

These stability constants were used to calculate the degree of formation of the species with the help of the HALTAFALL program (Ingri *et al.*, 1967), which in turn were used for the drawing of the formation curves, α% = f (pH), presented in Fig. 3.

It can be seen that the formation of the complex ML is between pH 4.19 and 10.74 with maximum formation of 89.83% at pH = 7.81. The ML (OH) complex is detectable from pH = 7.16 onwards and attains its maximum formation of 12.42% at pH = 9.23. Finally, ML (OH)^2 begins to form at pH = 7.74 with maximum formation, 98.95%, at pH = 10.99.

When Al (III) is the central metal ion the best model is also [(1,1,0), (1,1,-1) and (1,1,-2)] and the three complexes in solution are [AlL], [AlL(OH)]$^-$ and [AlL (OH)$_2$]$^{2-}$ for which the logarithm of stability constants are, respectively 7.99±0.04, 0.08±0.05 and -8.49±0.08. For these values, δ = 2.23 and S = 3.75. The distribution curves of these species are given in Fig. 4.

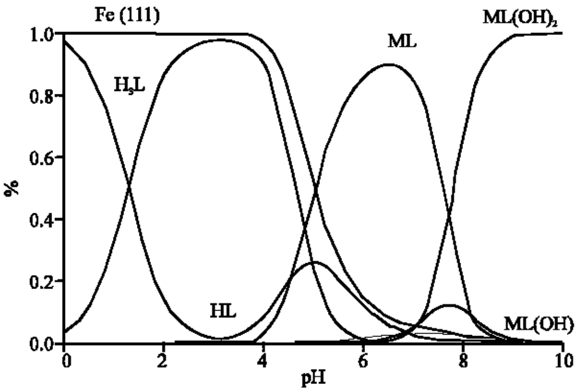

Fig. 3: Formation curves of system P2N4M6/Fe (III). [L] = [M] = 10-4 M, I = 0.1 M, 25.0±0.1°C

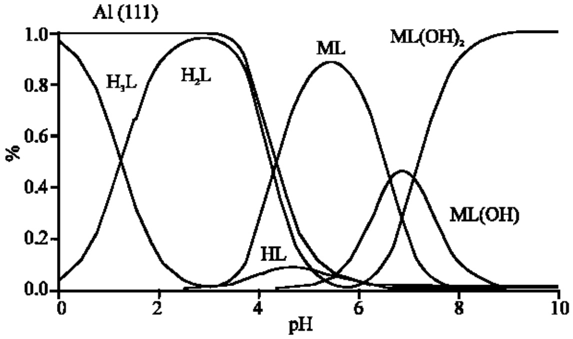

Fig. 4: Formation curves of system P2N4M6/Al(III). [L] = [M] = 10-4 M, I = 0.1 M, 25.0±0.1°C

However, in case of Cr (III), the best model is that of only one complex, namely, [CrL] for which log β = 6.30±0.01, δ = 1.91 and S = 10.02. The distribution

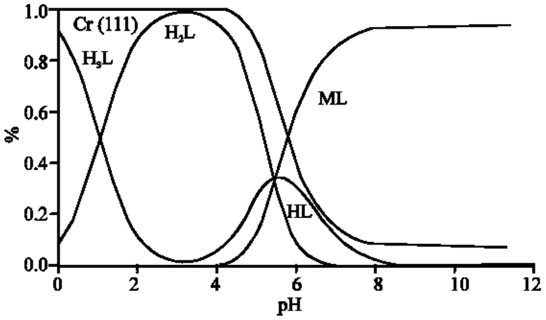

Fig. 5: Formation curves of system P2N4M6/Cr(III). [L] = [M] = 10-4 M, I = 0.1 M, 25.0±0.1°C

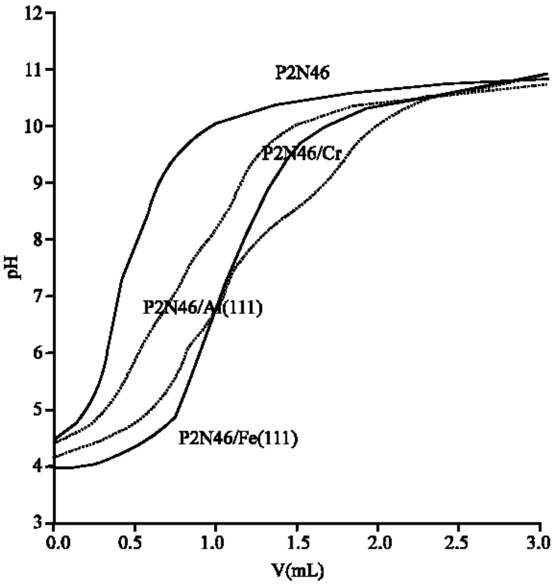

Fig. 6: Neutralisation curves of P2N4.6, P2N4.6/Fe(III), P2N4.6/Al(III) and P2N4.6/Cr(III). [L] = [M] = 10-4 M, I = 0.1 M, 25.0±0.1°C

curve of this complex, given in Fig. 5, shows that [CrL] begins to form at pH = 4.2 and reaches its maximum formation, around 94%, at pH = 8.3.

Ligand P2N4.6: The titration curves of the ligand P2N4.6 in absence and in presence of the three metal cations are reported in Fig. 6.

The study with this ligand was undertaken under identical conditions as those of the ligand P2N4M6 and the Table 1 resumes the different results obtained. The formations curves for each system are drawn from Haltafall program (Fig. 7-9) which takes into consideration the stability constants of each complex reported in Table 1.

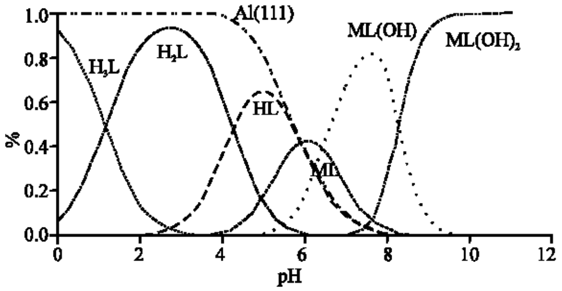

Fig. 7: Formation curves of system P2N4.6/Al (III). [L] = [M] = 10-4 M, I = 0.1 M, 25.0±0.1°C

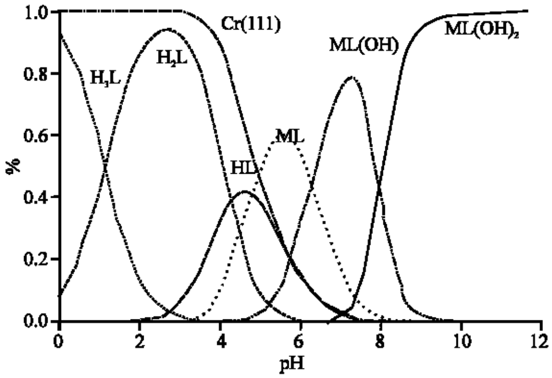

Fig. 8: Formation curves of system P2N4.6/Cr (III). [L] = [M] = 10-4 M, I = 0.1 M, 25.0±0.1°C

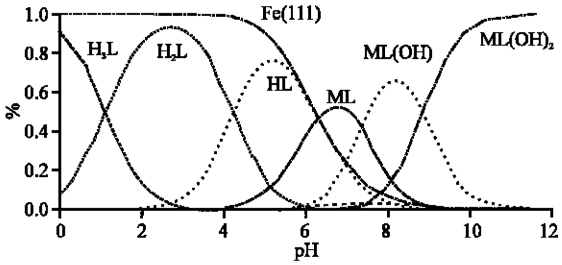

Fig. 9: Formation curves of system P2N4.6/Fe (III). [L] = [M] = 10-4 M, I = 0.1 M, 25.0±0.1°C

In the range of pH between 0 and 12, in case of Al(III), the formation of the complex ML begins at pH = 2.73, whereas $ML(OH)_3$ attains its maximum, 99.88%, at pH = 11.10. For the ferric complexes, ML(OH) is formed between the pH values of 5.31 and 11.37. At pH = 11.52, the complex $ML(OH)_2$ is formed to the extent of 99.40%.

Stability comparison of the two ligands: A study of the stability constants for the identified complexes between the two ligands and the three metals shows that the stability of the two ligands with ML complex follow the

Table 2: Comparison of stability constants with different ligands reported in the literature

	Metal			
Ligand	Reference	Fe(III)	Al(III)	Cr(III)
Tenoxicam	18			5.1
IDA	19	10.99		
MIDA		10.99		
EIDA		11.53		
PIDA		12.09		
OX^{-2}	20		5.96	
HEDP	21	24.20	22.70	19.00
ATMP		21.10		20.67
GlcHNA	22	11.45		
GlcHN		8.01		
O-TRENSOX	23	30.9	21.40	
TRENCAMS		43.60	39.97	
^{1}L	24		18.5	
^{4}L			19012	
P2N4M6	This work	6.7	7.99	6.3
P2N46		6.19	6.72	7.45

pattern as given below. This comparison was undertaken with ML complex only as it is the only type which is common in all the systems.

With P2N4M6: Al(III)> Fe(III)> Cr(III)
With P2N4.6: Cr(III)> Al(III)>Fe(III)

The results from the formation curves of the different complexes obtained with the two ligands are also given in Table 1. It can be remarked that the percentage formation for the ML complex is higher for the ligand P2N4M6 than for P2N4.6. It is further noted that the percentage formation is always higher for the complex with chromium and the least with that of aluminium.

Cr(III)/P2N4M6> Fe(III)/P2N4M6> Al(III)/P2N4M6
Cr(III)/P2N4.6>Fe(III)/P2N4.6>Al(III)/P2N4.6

Comparison of complexing abilities: In order to situate the complexing ability of the identified complexes, a comparison of the stability constants is made in the case of complex of the type ML, where M = Fe(III), Cr(III), Al(III) and L is different type of ligands. This comparison is presented in Table 2.

According to this Table, P2N4M6 and P2N4.6 with the cation Fe(III) give complexes less stable than with other ligands. The same observation is made with cation Al(III) with the exception of the oxalate ligand. On the other hand, in case of Cr(III) cation, the two ligands give complexes which are less stable than those with HEDP and ATMP, but higher in stability than those with TENOXICAM.

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