



## Polynuclear iron (II) and iron (III) complexes of organophosphonic acids and Identification by IR Spectroscopy

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### Abstract

Polynuclear Iron(II) and Iron(III) derivatives of 1-Aminoethylidenediphosphonic acid (AEDP,  $H_4L^1$ ), Alpha-Amino benzylidene diphosphonic acid (ABDP,  $H_4L^2$ ), 1-Amino-2-carboxyethane-1,1-diphosphonic acid (ACEDP,  $H_5L^3$ ), 1,3 Diaminopropane-1,1,3,3-tetraphosphonic acid (DAPTP,  $H_8L^4$ ), Diethylene triamine -N,N,N',N'',N'''-penta ( methylene phosphonic) acid (DETAPMPO,  $H_{10}L^5$ ), and Diethylene triamine -N,N''-bis (dimethyl methylene phosphonic) acid (DETBDMPO,  $H_4L^6$ ) have been prepared in aqueous medium. The general formula of Iron (II) derivatives from elemental analysis is  $Fe_2L.XH_2O$  (in case of AEDP, ABDP, DETBDMPO),  $Fe_3L_2.XH_2O$  (in case of ACEDP)  $Fe_2L.XH_2O$ ,  $Fe_3H_4L_2.XH_2O$  (in case of DAPTP),  $Fe_5L.XH_2O$  (in case of DETAPMPO). The general formula of Iron (III) derivatives from elemental analysis is  $Fe_4(OH)_4.L.XH_2O$  (in case of AEDP, ABDP, DETBDMPO),  $Fe_5L(OH)$  (in case of DAPTP)  $Fe_5L(OH)_5.H_2O$  (in case of DETAPMPO). The electronic spectra of Iron (II) complexes have shown them to have octahedral geometry. Antiferromagnetism has been inferred from magnetic moment data. Infrared spectral studies were carried out to determine coordination sites.

**Keywords:** Organophosphonic acids, metal organophosphonates, coordination sites, octahedral geometry, antiferromagnetism

### Introduction

Polydentate nature of the ligands may be due to availability of lone pairs of electrons at donor sites. Trivalent iron forms a large number of complexes, mostly octahedral ones and a few tetrahedral complexes. Iron (III) forms some definite complexes with chelating amines, for example,  $Fe(EDTA).H_2O$  ion in which iron is seven coordinated, and it has its greatest affinity for ligands that coordinate by oxygen. Iron (II) forms high spin, low spin octahedral and tetrahedral complexes. Aminoethylidenediphosphonic acid (AEDP) and alpha-amino benzylidenediphosphonic acid (ABDP) had a very strong herbicidal effect against Barnard grass, mustard and tomato seedlings and had fungicidal properties. 1-Amino-2-carboxyethane -1, 1 diphosphonic acid (ACEDP) has been used as water softner, for flask cleaning or as additive for dyeing baths for textiles [1]. An organophosphonic acid acts on a metal atom consisting of a labile linkage enabling it to remove the metal. Such property of alkylenebisnitrilodialkylphosphonic acid to form very stable complexes with bivalent metal, lead to the elimination of metal from the organism [2]. EDBDMPO and DETAPMPO were more effective than DTPA in reducing the uranium content in rat organs. Poly amine alkyl phosphonic acids may be used as effective ligands for binding and eliminating uranium and its fission products from the body [3].

From the survey of the literature above on the study of some organophosphonic acids and their metal derivatives, it is evident that except for the physico-chemical and biological studies, very little work seems to have been carried out on the synthetic and structural aspects of metal derivatives organo aminophosphonic acids. In view of this, it was thought of interest to attempt to study the reaction between Organo amino polyphosphonic acids and Iron salts in

aqueous medium to study and to make comparative study of their structure using different physico-chemical techniques.

### Materials and Method

All chemicals used were of Analytical reagent (AR) grade. 1-Amino ethylidene di-phosphonic acid (AEDP,  $H_4L$ ) was prepared by the reaction [4] reacting acetamide with Phosphorus trichloride and diethylphosphite in 1:3:1 molar ratio. Alpha-Amino benzylidene diphosphonic acid (ABDP,  $H_4L$ ), 1-Amino-2-carboxyethane-1,1-diphosphonic acid (ACEDP,  $H_5L$ ) and 1,3 Diaminopropane-1,1,3,3-tetraphosphonic acid (DAPTP,  $H_8L$ ) were prepared by the method used by Lerch and Kottlor were prepared by the method reported by Kabachnik *et al.* Diethylene triamine – N,N,N',N'',N'''-penta (methylene phosphonic) acid (DETAPMPO,  $H_{10}L$ ) has been prepared by the method used by Peck and Hudson Diethylene triamine – N,N''-bis (dimethyl methylene phosphonic) acid (DETBDMPO,  $H_4L$ ) have been prepared in aqueous medium [5].

### Preparative Method for the Complexes

**Reaction between AEDP and Ferric Chloride (For Iron (III) salts):** To 0.005 moles of ligand solution were added 0.010 mole of Ferric chloride solution. Immediate precipitation of a white solid was observed. The precipitate was filtered, washed with water, aqueous acetone, acetone (90%) and finally dried on water bath. Yield, 76%.

**Reaction between AEDP and Ferrous ammonium sulphate (For Iron (II) salts):** 0.005 mole of ligand were slowly introduced into 0.01 mole of ferrous ammonium sulphate solution to about 100 ml of water followed by drop wise addition of 20ml of 0.01M  $Na_2CO_3$  solution with constant stirring. A dirty white precipitate was obtained. The precipitate was filtered, washed with water, aqueous

acetone, acetone (90%) and finally dried on water bath. Yield, 75%.

**General method of preparation of Metal complexes:** The above procedure may be taken as a general procedure for remaining complexes. In case of Reaction between ABDP and Ferric Chloride, the procedure used for this is same as above but acetone is added to complete the precipitation. In case of Reaction between AEDP and Ferrous ammonium sulphate (For Iron (II) salts),  $\text{Na}_2\text{CO}_3$  solution was not added. Carbon and hydrogen in case of ligands were estimated by means of semi-micro analyzer, LG, VEB Laborgerate and Orthopedic Leipzig. Nitrogen was estimated by Duma's method Metal and phosphorus contents were determined by standard procedures. Chromium (III) and iron (III) were estimated gravimetrically as  $\text{BaCrO}_4$  and iron Oxinate respectively.

**Physical Measurements:** Diffused transmittance spectra were run on DMR-21 spectrophotometer in 200-2000 nm (50,000-5000  $\text{cm}^{-1}$ ) region, diffused reflectance spectra were run on Cary 2390 spectrophotometer in 200-1800 nm (50,000-5555.5  $\text{cm}^{-1}$ ) region at RSIC, Madras India. Magnetic susceptibility measurements were carried out using a Princeton Applied Research Model 155 Vibrating Sample Magnetometer incorporating a digital read out. The electromagnet was fed from a polytronic constant current regulator (Type CP 200). A pure nickel pellet was used as calibrant, cross checking against Hg [Co (CNS)  $_4$ ]. The instruments and methods used for the remainder of the analyses were the same as described earlier.

## Results and Discussion

**Infrared Spectra:** Infrared spectra of the free ligand, a characteristic band is observed at 1190  $\text{cm}^{-1}$  (AEDP), 1230  $\text{cm}^{-1}$  (ABDP), 1160  $\text{cm}^{-1}$  (ACEDP), 1160  $\text{cm}^{-1}$  (DAPTP), 1240  $\text{cm}^{-1}$  (DETAPMPO), 1190  $\text{cm}^{-1}$  (DETBDMPPO), which may be due to the phosphoryl  $\nu$  (P=O) vibrations. Scientists [6, 7] have assigned 1320-1200  $\text{cm}^{-1}$  region for  $\nu$  (P=O) stretching frequency from the survey of a large number of phosphorus compounds having free phosphoryl group. Stretching vibrations of phosphoryl group in case of metal derivatives have been observed at 1110-1155  $\text{cm}^{-1}$ . The displacement of the band by 45-90  $\text{cm}^{-1}$  towards lower region has been attributed to the formation of coordination bond between phosphoryl oxygen and metal ion. Such observations are also in agreement with the observations [8]. The two more bands at around 1130 and around 1020  $\text{cm}^{-1}$  were observed in all the free ligands correspond to  $\nu_{\text{as}}\text{PO}_2$  and  $\nu_{\text{s}}\text{PO}_2$  vibrations in  $\text{HPO}_3$  group. In addition,  $\nu_{\text{as}}$  P-OH and  $\nu_{\text{s}}$  P-OH bands, corresponding to P-(OH) $_2$  also appeared at around 1000 and around 940  $\text{cm}^{-1}$ . In metal derivatives, the asymmetric and symmetric mode of stretching vibration of  $\text{PO}_3$  group appeared at 1070-1020 and 1000-900  $\text{cm}^{-1}$  ranges, respectively and splitting of these bands was observed. Such splitting is expected in view of the covalent character of M-O bond due to lowering of the symmetry of  $\text{PO}_3$  group. In case of AEDP and ABDP the stretching and bending mode of  $-\text{NH}_3^+$  group have been observed at 3400  $\text{cm}^{-1}$  and 1580  $\text{cm}^{-1}$  respectively. The bands at 3400  $\text{cm}^{-1}$  and 3200  $\text{cm}^{-1}$  may be due to the presence of OH/NH groups. Two more bands at 3060  $\text{cm}^{-1}$  and 1450  $\text{cm}^{-1}$  were present in ABDP and may be assigned due to aromatic grouping [9]. In the infrared spectra of complexes the rocking

and wagging vibrations appeared in the regions 880-860  $\text{cm}^{-1}$  and 750-710  $\text{cm}^{-1}$  suggesting the presence of coordinated water [10,11,12].

A medium sharp band due to  $\nu_{\text{asym}}(\text{COO}^-)$  group observed at 1660  $\text{cm}^{-1}$  in the free ligand (ACEDP), shifted to lower frequency (1645-1630  $\text{cm}^{-1}$ ) in all the complexes indicating that the carboxylic group is coordinated [10] to the metal atom of the same or another molecule. Another band found at 1300  $\text{cm}^{-1}$  in the free ligand (ACEDP) spectrum was due to the presence of  $\nu_{\text{sym}}(\text{COO}^-)$  vibration. In the metal complexes, this band was found shifted to 1430-1400  $\text{cm}^{-1}$  indicating the involvement of the carboxylic group in bond formation with the metal [21]. The lowering of  $\nu_{\text{asym}}(\text{COO}^-)$  (mainly due to  $\nu(\text{C=O})$  of the (COOH group) and the difference  $\Delta = \nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)$  is approximately equal to 200  $\text{cm}^{-1}$  clearly suggested the coordinations of  $\nu(\text{C=O})$  moiety to the metal atom [13]. The bands at 1090 and 1040  $\text{cm}^{-1}$  were assigned to  $\nu_{\text{asym}}(\text{PO}_3)$  and  $\nu_{\text{sym}}(\text{PO}_3)$  vibrations in the group  $\text{HPO}_3^-$ . Two more bands were observed at 990 and 940  $\text{cm}^{-1}$  which may be due to  $\nu_{\text{as}}\text{P}-(\text{OH})$  and  $\nu_{\text{s}}\text{P}-(\text{OH})_2$  vibrations of  $\text{PO}_3\text{H}_2$  group in case of DETBDMPPO.  $\text{NH}_2^+$  group often gives two broad unresolved bands in the region of 3000-2750  $\text{cm}^{-1}$ . In the infrared spectrum of free DETBDMPPO, there was a broad band in the region 3400-2600  $\text{cm}^{-1}$  which may be due to masking of  $\nu(\text{NH}_2^+)$  bands by broad  $\nu(\text{OH})$  band. A weak Band at 1620  $\text{cm}^{-1}$  has been assigned to  $\nu(\text{N-H})$  [14]. Two bands were present in the region of 450-410  $\text{cm}^{-1}$  and 330-300  $\text{cm}^{-1}$  in far infrared spectra of complexes and assigned to M-O and M-N linkages respectively.

**Electronic spectra and magnetic moments:** Since  $\text{Fe}_2(\text{L}^1)(\text{OH})_2.2\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{L}^2)(\text{OH})_2.\text{H}_2\text{O}$ ,  $\text{Fe}_3(\text{L}^3)(\text{OH})_5$ ,  $\text{Fe}_3(\text{L}^4)(\text{OH})_5.\text{H}_2\text{O}$  and  $\text{Fe}_3(\text{L}^6)(\text{OH})_5.6\text{H}_2\text{O}$  have  $d^5$  configuration similar to Manganese(II), the stereochemistry cannot be assigned to it in the absence of oscillator strength of various bands.  $\text{Fe}_2(\text{L}^1).3\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{L}^2).2\text{H}_2\text{O}$ ,  $\text{Fe}_3(\text{L}^3).5\text{H}_2\text{O}$ ,  $\text{Fe}_3\text{H}_4(\text{L}^4).7\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{L}^6).10\text{H}_2\text{O}$ ,  $\text{Fe}_3(\text{L}^5).12\text{H}_2\text{O}$  and  $\text{Fe}_3(\text{L}^6).14\text{H}_2\text{O}$  gave absorption bands (Table-1) which are due to spin-allowed transition  $^5\text{T}_{2g} \rightarrow ^5\text{E}_g$  or charge transfer phenomenon suggesting octahedral geometry [15]. The magnetic moment values of  $\text{Fe}_2(\text{L}^1)(\text{OH})_2.2\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{L}^2)(\text{OH})_2.\text{H}_2\text{O}$ ,  $\text{Fe}_3(\text{L}^3)(\text{OH})_5$ ,  $\text{Fe}_3(\text{L}^4)(\text{OH})_5.\text{H}_2\text{O}$  and  $\text{Fe}_3(\text{L}^6)(\text{OH})_5.6\text{H}_2\text{O}$  have been found to be in the range of 2.1-3.87 (Table-I) which are lower than the expected value 5.65–6.10 B.M for  $d^5$  system. In case of  $\text{Fe}_2(\text{L}^2)(\text{OH})_2.\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{L}^1)(\text{OH})$ ,  $\text{Fe}_3(\text{L}^3)(\text{OH})_5.\text{H}_2\text{O}$  and  $\text{Fe}_3(\text{L}^6)(\text{OH})_5.6\text{H}_2\text{O}$  complexes, the magnetic moment at 296K (Table-II) decreased with the decrease in the temperature. From the cryomagnetic data, a graph was plotted ( $1/\chi_M$  vs. temperature) from which Weiss- constant ( $\theta$ ) value was calculated. The Curie-Weiss law is obeyed with  $\theta = -86^\circ$ ,  $-79^\circ$ ,  $-92^\circ$ , and  $-120^\circ$  respectively for the above metal complexes. The Weiss constant ( $\theta = -90^\circ$ ) for their complex  $\text{Fe}(\text{HN:CH.C}_6\text{H}_4\text{O})_3$  in the temperature range 90-290K. It is due to antiferromagnetism [16], which may have arisen due either to metal-metal interactions or to super exchange through hydroxyl or phosphonic bridges. The magnetic moment values of  $\text{Fe}_2(\text{L}^1).3\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{L}^2)(\text{OH})_2.2\text{H}_2\text{O}$ ,  $\text{Fe}_3(\text{L}^3).5\text{H}_2\text{O}$ ,  $\text{Fe}_3\text{H}_4(\text{L}^4).7\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{L}^6).10\text{H}_2\text{O}$ ,  $\text{Fe}_3(\text{L}^5).12\text{H}_2\text{O}$  and  $\text{Fe}_3(\text{L}^6).14\text{H}_2\text{O}$  have been found to be in the range of 1.76-4.20 B.M. These values are much lower than the normal range suggesting the presence of an appreciable antiferromagnetic character (Table-1) which is

further confirmed by studying magnetic moments at different temperatures. The magnetic moments of the complex decreased significantly as the temperature is lowered (Table-2) obeying the curie-weiss law ( $\theta = -180^\circ$ ). The reported <sup>[17]</sup>  $\theta$  value for this tutton salt ( $-22^\circ$ ) in the

temperature range of 200-300K<sup>6</sup>. The negative value of  $\theta$  ( $-26^\circ$ ) for Fe(Oxalate).2H<sub>2</sub>O in the temperature range of 200-300K. The large  $\theta$  value in case of Fe<sub>2</sub> (L<sup>2</sup>).2H<sub>2</sub>O and Fe<sub>2</sub>(L<sup>4</sup>).10H<sub>2</sub>O, complex further confirms the presence of strong antiferromagnetic interactions <sup>[18]</sup>.

**Table 1:** Electronic Spectral, Magnetic Moment Data and Colour of Metal Derivatives

| Complex                                                                | Colour       | Bands In Electronic Spectrum       | $\mu_{\text{eff}}$ (B.M.) |
|------------------------------------------------------------------------|--------------|------------------------------------|---------------------------|
| Fe <sub>4</sub> (L <sup>1</sup> )(OH) <sub>4</sub> . 2H <sub>2</sub> O | Dirty white  | 23,700;20,000;15,380;9,950         | 2.88                      |
| Fe <sub>2</sub> (L <sup>1</sup> ).3H <sub>2</sub> O                    | Dirty white  | 18,020;14,810,                     | 4.20                      |
| Fe <sub>2</sub> (L <sup>2</sup> )(OH) <sub>2</sub> .H <sub>2</sub> O   | White        | 15,630;20,830;24,390               | 3.77                      |
| Fe <sub>2</sub> (L <sup>2</sup> ).2H <sub>2</sub> O                    | Dirty white  | 17,860;23,810                      | 2.88                      |
| Fe <sub>5</sub> (L <sup>3</sup> )(OH) <sub>5</sub>                     | Pale brown   | 15,150;20,830;24,100               | 2.00                      |
| Fe <sub>3</sub> H <sub>4</sub> (L <sup>4</sup> ).7H <sub>2</sub> O     | Dirty white- | -3.66                              |                           |
| Fe <sub>2</sub> (L <sup>4</sup> ).10H <sub>2</sub> O                   | Dirty white  | 8,930;13,700;22,220;24,100         | 2.23                      |
| Fe <sub>5</sub> (L <sup>4</sup> )(OH)                                  | Dirty white  | 13,330;21,740;23,260;34,480;41,670 | 2.46                      |
| Fe <sub>5</sub> (L <sup>5</sup> )(OH) <sub>5</sub> .H <sub>2</sub> O   | Dirty white  | 11,000;18,180;24,100;21,980        | 2.1                       |
| Fe <sub>5</sub> (L <sup>5</sup> ).12H <sub>2</sub> O                   | Dirty white  | 7,290;7,630;15,380;24,270          | 1.76                      |
| Fe <sub>5</sub> (L <sup>6</sup> )(OH) <sub>5</sub> .6H <sub>2</sub> O  | brown        | -                                  | 3.87                      |
| Fe <sub>2</sub> (L <sup>6</sup> ).14H <sub>2</sub> O                   | Brown        | 16,670;31,250(sh)                  | 3.9                       |

Sh=shoulder

**Table 2:** Temperature Dependent Magnetic moment Data of Metal Derivatives

| T(°K) | A     | B     | C     | D    | E    | F     | G     |
|-------|-------|-------|-------|------|------|-------|-------|
| 296   | 2.88  | 3.77  | 2.33  | 2.23 | 2.46 | 2.118 | 3.87  |
| 261   | 2.787 | 3.68  | 2.787 | 2.19 | 2.39 | 2.059 | 3.85  |
| 237   | 2.702 | 3.58  | 2.702 | 2.17 | 2.38 | 2.027 | 3.73  |
| 213   | 2.624 | 3.51  | 2.624 | 2.11 | 2.36 | 1.99  | 3.59  |
| 189   | 2.516 | 3.425 | 2.516 | 2.03 | 2.31 | 1.96  | 3.50  |
| 165   | 2.391 | 3.35  | 2.391 | 1.98 | 2.25 | 1.903 | 3.38  |
| 141   | 2.258 | 3.208 | 2.258 | 1.92 | 2.17 | 1.845 | 3.26  |
| 117   | 2.163 | 3.07  | 2.163 | 1.86 | 2.12 | 1.78  | 3.146 |
| 93    | 2.038 | 2.92  | 2.038 | 1.76 | 2.02 | 1.704 | 2.99  |
| 77    | 1.94  | 2.82  | 1.94  | 1.70 | 1.96 | 1.629 | 2.91  |

- A = Fe<sub>2</sub>(L<sup>1</sup>).3H<sub>2</sub>O
- B = Fe<sub>2</sub>(L<sup>2</sup>)(OH)<sub>2</sub>.H<sub>2</sub>O
- C = Fe<sub>2</sub>(L<sup>2</sup>).2H<sub>2</sub>O
- D = Fe<sub>2</sub>(L<sup>4</sup>).10H<sub>2</sub>O
- E = Fe<sub>5</sub>(L<sup>4</sup>)(OH)
- F = Fe<sub>5</sub>(L<sup>5</sup>)(OH)<sub>5</sub>.H<sub>2</sub>O
- G = Fe<sub>5</sub>(L<sup>6</sup>)(OH)<sub>5</sub>.6H<sub>2</sub>O

## Conclusion

All these complexes were insoluble in water as well as other common organic solvents and did not melt even up to 270-280°C. The properties indicated them to be polymeric in nature. Polymeric nature has also been established on the basis of phosphoryl oxygen coordinated to metal atom which is assigned from the IR data of metal derivatives. Stereochemistry of complexes was found to have hexa-coordinated and octahedral geometry. The magnetic moments of the complexes have been found to be subnormal at room temperature. Those low magnetic moment values may be due to the presence of antiferromagnetism which can arise due to polymeric nature of the complexes and thus bring the metal ions at distance close enough to interact or through super exchange via phosphoric acid or hydroxo bridges (in case of trivalent metal compounds). The magnetic moments have decreased with decreasing temperature. A straight line was obtained when  $1/\chi_M$  was plotted against temperature. Curie-Weiss law is also obeyed with the  $\theta$  values ranging from 77 to  $-297^\circ\text{K}$ .

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