Iron (II) and Iron(III) complexes of organophosphonic acids

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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"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), $Fe_5L_2.XH_2O$ (in case of ACEDP) $Fe_4L.XH_2O$, $Fe_2H_4L.XH_2O$ (in case of DAPTP), $Fe_5L.XH_2O$ (in case of DETAPMPO). The general formula of Iron(III) derivatives from elemental analysis is $Fe_2(OH)_2L.XH_2O$ (in case of AEDP, ABDP, DETBDMPO), $Fe_3L(OH)$(in case of DAPTP) $Fe_4L(OH)_2.H_2O$(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.

Key words: 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.[20] 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[9] EDBDMPO and DETAPMPO were more effective than DTPA in reducing the uranium content in rat organs[25]. Poly amine alkyl phosphonic acids may be used as effective ligands for binding and eliminating uranium and its fission products from the body [1].

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.

MATERIAL AND METHODS

All chemicals used were of AnalaR or reagent grade. 1-Amino ethylidene di-phosphonic acid (AEDP, H_4L) was prepared by the reaction reported by ploger et al.[18]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 Kottler were prepared by the method reported by Kabachnik et al. Diethylene triamine – N,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 by the method reported by Medved *et al* [13.]

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 is about 100 ml of water followed by dropwise 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), Na_2CO_3solution was not added.

Carbon and hydrogen in case of ligands were estimated by means of semi-micro analyzer, LG, VEB Laborgerate and Orthopadic Leipzig. Nitrogen was estimated by Duma's method. Metal and phosphorus contents were determined by standard procedures[23]. Chromium (III) and iron(III) were estimated gravimetrically as $BaCrO_4$ and iron Oxinate respectively.

Physical measurements
Diffused transmittance spectra were run on DMR-21 spectrophotometer in 200-2000 nm(50,000-5000 cm-1) region, diffused reflectance spectra were run on Cary 2390 spectrophotometer in 200-1800 nm (50,000-5555.5 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[16,]

RESULTS AND DISCUSSION

Infrared spectra
Infrared spectra of the free ligand , a characteristic band is observed at 1190 cm-1 (AEDP), 1230 cm-1 (ABDP), 1160 cm-1 (ACEDP),

1160 cm^{-1} (DAPTP), 1240 cm^{-1} DETAPMPO), 1190 cm^{-1} (DETBDMPO), which may be due to the phosphoryl v(P=O) vibrations. Corbridge[3], Bellamy, Ebstam and Ramadan[5] and others[14] have assigned 1320-1200 cm-1 region for v(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 cm^{-1} . The displacement of the band by 45-90 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 of khramov et al[11.]The two more bands at around 1130 and around 1020 cm^{-1} were observed in all the free ligands correspond to $v_{as}PO_2$ and V_sPO_2 vibrations in HPO_3 group In addition , V_{as} P-OH and V_s P-OH bands, corresponding to P-$(OH)_2$ also appeared at around 1000 and around 940 cm^{-1} In metal derivatives , the asymmetric and symmetric mode of stretching vibration of PO_3 group appeared at 1070-1020 and 1000-900 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 PO_3 group. In case of AEDP and ABDP the stretching and bending mode of –NH_3^+ group have been observed at 3400 cm^{-1} and 1580 cm^{-1} respectively. The bands at 3400 cm^{-1} and 3200 cm^{-1} may be due to the presence of OH/NH groups. Two more bands at 3060 cm^{-1} and 1450 cm^{-1} were present in ABDP and may be assigned due to aromatic grouping[19]In the infrared spectra of complexes the rocking and wagging vibrations appeared in the regions 880-860 cm^{-1} and 750-710 cm^{-1} suggesting the presence of coordinated water[7, 15, 22].

A medium sharp band due to v_{asym}(COO$^-$) group observed at 1660 cm^{-1} in the free ligand(ACEDP), shifted to lower frequency(1645-1630 cm^{-1})in all the complexes indicating that the carboxylic group is coordinated[8] to the metal atom of the same or another molecule. Another band found at 1300 cm^{-1} in the free ligand(ACEDP) spectrum was due to the presence of Vasy(COO$^-$) vibration. In the metal complexes, this band was found shifted to 1430-1400 cm^{-1} indicating the involvement of the carboxylic group in bond

formation with the metal[21].   The lowering of v_{asym} (COO$^-$) (mainly due to V(C=O) of the (COOH group) and the difference Δ =Vasym (COO$^-$) - V_{sym} (COO$^-$) is approximately equal to 200 cm^{-1} clearly suggested the coordinations of V(C=O) moiety to the metal atom[21.] The bands at 1090 and 1040 cm^{-1} were assigned to $v_{as}(PO_2)$ and $v_s(PO_2)$ vibrations in the group HPO_3^-. Two more bands were observed at 990 and 940 cm^{-1} which may be due to vasP-(OH)$_2$ and vs P-$(OH)_2$ vibrations of PO_3H_2 group in case of DETBDMPO. NH_2^+ group often gives two broad unresolved bands in the region of 3000-2750 cm^{-1}. In the Infrared spectrum of free DETBDMPO, there was a broad band in the region 3400-2600 cm^{-1} which may be due to masking of $v(NH_2^+$) bands by broad v(OH) band. A weak Band at 1620 cm^{-1} has been assigned to v (N-H) [4,19]. Two bands were present in the region of 450-410 cm^{-1} and 330-300 cm^{-1} in far infrared spectra of complexes and assigned to M-O and M-N linkages respectively.

Electronic spectra and magnetic moments

Since $Fe_2(L^1)(OH)_2.2H_2O$, $Fe_2(L^2)(OH)_2$. H_2O, $Fe_3(L^4)(OH)$, $Fe_4(L^5)(OH)_2.H_2O$ and $Fe_2(L^6)(OH)_2.6H_2O$ have d^5 configuration similar to Manganese(II), the stereochemistry cannot be assigned to it in the absence of oscillator strength of various bands. $Fe_2(L^1).3H_2O$, $Fe_2(L^2).2H_2O$, $Fe_5(L^3)_2.5H_2O$, $Fe_4H_4(L^4).7H_2O$, $Fe_4(L^4).10H_2O$, $Fe_5(L^5).12H_2O$ and $Fe_2(L^6).14H_2O$ gave absorption bands(Table I) which are due to spin-allowed transition ^5T2_g ^5E_g or charge transfer phenomenon suggesting octahedral geometry[10,18]. The magnetic moment values of $Fe_2(L^1)(OH)_2.2H_2O$, $Fe_2(L^2)(OH)_2$. $H2O$, $Fe_3(L^4)(OH)$, $Fe_4(L^5)(OH)_2.H_2O$ and $Fe_2(L^6)(OH)_2.6H_2O$ have been found to be in the range of 2.1-3.87(Table I) which are lower than the expected value 5.65—6.10B.M for d^5 system. In case of $Fe_2(L^2)(OH)_2.H2O, Fe_3(L^4)(OH)$, $Fe_4(L^5)$ $(OH)_2. H_2O$ and $Fe_2(L^6)(OH)_2.6H_2O$ complexes , the magnetic moment at 296K(Table II) decreased with the decrease in the temperature. From the cryomagnetic data, a graph was plotted (1/ x M vs. temperature) from which Weiss- constant (θ) value was calculated. The Curie-Weiss law is obeyed with θ = -86°, -79^0, -92°,and -120° respectively for the above metal complexes. Klemm and Roddatz[12] have reported the weiss constant (θ = -90°) for their complex Fe (HN: $CH.C_6H_4O)_3$ in the temperature range 90-290K. It is due to antiferromagnetism,

which may have arisen due either to metal-metal interactions or to super exchange through hydroxyl or phosphonic bridges. The magnetic moment values of $Fe_2(L^1).3H_2O$, $Fe_2(L^2).2H_2O$, $Fe_5(L^3)_2.5H_2O$, $Fe_4H_4(L^4).7H_2O$, $Fe_4(L^4).10H_2O$, $Fe_5(L^5).12H_2O$ and $Fe_2(L^6).14H_2O$ 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 (θ = -180^0). Foex has reported θ value for his tutton salt (-22^0) in the temperature range of 200-300K[6]. Welo[24] has reported the negative value of θ (-26^0) for Fe (Oxalate).$2H_2O$ in the temperature range of 200-300K. The large è value in case of $Fe_2 (L^2).2H_2O$ and $Fe_4(L^4).10H_2O$, complex further confirms the

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

Complex	Colour	Bands in Electronic Spectrum	µeff (B.M.)
$Fe_2(L^1)(OH)_2. 2H_2O$	Dirty white	23,700;20,000;15,380;9,950	2.88
$Fe_2(L^1).3H_2O$	Dirty white	18,020;14,810,	4.20
$Fe_2(L^2)(OH)_2.H2O$	White	15,630;20,830;24,390	3.77
$Fe_2(L^2).2H_2O$	Dirty white	17,860;23,810	2.88
$Fe_5(L^3)_2.5H_2O$	Pale brown	15,150;20,830;24,100	2.00
$Fe_4H_4(L^4).7H_2O$	Dirty white-	-3.66	
$Fe_4(L^4).10H_2O$	Dirty white	8,930;13,700;22,220;24,100	2.23
$Fe_3(L^4)(OH)$	Dirty white	13,330;21,740;23,260;34,480;41,670	2.46
$Fe_4(L^5)(OH)_2.H_2O$	Dirty white	11,000;18,180;24,100;21,980	2.1
$Fe_5(L^5).12H_2O$	Dirty white	7,290;7,630;15,380;24,270	1.76
$Fe_2(L^6)(OH)_2.6H_2O$	brown	-	3.87
$Fe_2(L^6).14H_2O$	Brown	16,670;31,250(sh)	3.9

Sh=shoulder

Table 2: Temperature Dependent Magnetic moment Data of Metal Derivatives

T(^{0}K)	µeff (B.M.)						
	A	B	C	D	E	F	G
296	2.88	3.77	2.88	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=$Fe_2(L^1).3H_2O$,B=$Fe_2(L^2)(OH)_2.H2O$,C=$Fe_2(L^2).2H_2O$,D=$Fe_4(L^4).10H_2O$,E=$Fe_3(L^4)(OH)$,F= $Fe_4(L^5)(OH)_2.H_2O$,G= $Fe_2(L^6)(OH)_2.6H_2O$

presence of strong antiferromagnetic interactions. Conclusion:

Al these complexes were insoluble in water as well as other common organic solvents and did not melt even upto 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 I.r. data of metal derivatives. Stereochemistry of complexes was found to have hexa-coordinated and octahedral geometry. T h e magnetic moments of the complexes have been found to be subnormal at room temperature. These 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 $1/xM$ was plotted against temperature. Curie-Weiss law is also obeyed with the θ values ranging from 77 to -297 ^{0}k.

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REFERENCES

1. Balabukha, V.S., Irannikov,A.I., Razhitnaya, L.I., Razamovskii, N.C., Tikhonaya, L.I., Baranovskaya, L.M, Eur.Congr. Radiat.Prot.2nd, 1972(pub.1973), 293-8 (Eng.); Chem.Abstr., **80**: 45278 (1974).

2. Benckiser-K., G.m.b.h., Ger.offen. 2, 211, 578 (cl.D.061), 13 sept., 1972, 13 pp;' *Chem. Abstr*., **80**: 16372K (1974).

3. Corbridge, D.E.C., 'Topics in Phosphorus Chemistry', edited by Crayson, M. and Griffith, E.J, Interscience publishers, New York, **6**: 235 (1969).

4. Dyer,J.R., 'Applications of Absorption Spectroscopy of Organic Compounds' Prentice Hall of India, New Delhi, 37.(1978).

5. Ebstam A. Saad and Ramadan M Ramadan, Bull.Chem. Soc.,Jpn., **62**: 3697-3700 (1989).

6. Foex,G. Ann.Phys.(Paris), **16**: 174(1921)

7. Fujita, J., Nakamoto, K. and Kobayashi, M., *J. Am. Chem. Soc.,* **78**: 3963(1956)

8. Joshi, R.N. and Patel, M.N., *Indian J.Chem.,* **21**A: 637(1982).

9. Kabachnik, M.I., Medved, T.Ya. Dyatlova, N.M,Arkhipova,O.G and Rudomino, M.V., Russ.Chem.Rev., **7**: 503 (1968).

10. Kapadia, R.N. *Indian J.Chem.*,**20**A: 525 (1981)

11. Khramov, V.P., and Kol'tsov, A>A., *Russ. J. Inorg. Chem.*, 18(11): 1567(1973)

12. Klemm,W. and Rodatz, K.H., Z. *Anorg. Allgem. Chem.*, **250**: 207 (1942)

13. Medved,T.Ya., Rudomino,M.V., ., Mironova, E.A BalaBukha, V.S and Kabachnik, M.I., Izv. Akad. Nauk. Ser.Khim., 351-6 (1967).

14. Mohd Helmy Bin Hashim"Preparation and Properties Characterisation of P_2O_5-KNO_3-K_2O Glass" A Thesis of Universiti Teknologi, Malaysia (2005)

15. Patel, M.M. and Patel, R.P., *J.Indian Chem. Soc.,* 52: 1046 (1975).

16. Puri,D.M and Neelam Palta, *Indian J. Chem.,* **21**A: 624(1982)

17. Ploger, W., Schindler, N., Wollmann, K and Woras, K.N., *Z.Anorg. Allg.Chem.,* **119**: 389 (1972).

18. Rana, A.K and Shah, J.R., *Indian J.Chem.* **20**A: 924 (1981).

19. Scheinmann (Editor). 'An Introduction to Spectroscopy Methods for the Identification of Organic compounds', Pergamon Press

(1970).

20. Schindler,N., Ploeger, W., Ger Offen., 2, 048, 913(13 Apr. 1972) Appl.P. 2048 913-8; *Chem.Abstr.*, **77**: 19799d(1972)

21. Sengupta, S.K., Sahni, S.K. and Kapoor, R.N., *Polyhedron,* **2**: 317 (1983).

22. Shukla, P.R., Singh, O.K., Jaiswal, A.M. and Narayan, G., *J. Indian Chem. Soc.,* 60: 321 (1983).

23. Vogel. A.I., Quantitative Inorganic analysis, Longmans, Green, 4th edition (1978).

24. Welo,L.A., Phil.Mag., **6**: 481 (1928).

25. Zablotna, R., Zylicz, E., Szot, Z., Peskorska, c., Anna, G., Nukleonika, **22**(8): 703-11 (1977) (Eng.); *Chem. Abstr.*, **88**: 59775h (1978).