Organophosphonic acids as complexones, part III: o-phenylenediamine-N,N,N',N'-tetrakis- and ethylenediamine-N,N'-bis-(methylenephosphonic)acids as complexing agents

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Abstract. Polynuclear metal derivatives of o-phenylenediamine-N,N,N',N'-*tetrakis*-(methylenephosphonic)acid (PDTMP, H_8L) have been prepared in aqueous medium. The general formula of derivatives from elemental analysis is $M_4L \cdot x H_2O$ [M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II); x = 2–8]. Ethylenediamine-N,N'-*bis*(methylene-phosphonic)acid (EDBMP) complexes of iron(III) $Fe_3(OH)L_2 \cdot 9H_2O$, $Fe_2(OH)_2L \cdot H_2O$ have also been studied. The electronic spectra have shown them to be six coordinated with slight distortion from octahedral geometry. Antiferromagnetism has been inferred from magnetic moment data. Infrared spectral studies have been carried out to determine coordination sites.

Keywords. Metal organopolyphosphonates; coordination sites; six coordinate.

1. Introduction

Alkylenepolyaminepolyphosphonic acids have been reported to have potentialities for complex formation similar to their carboxylic analogues. This is due to the donor properties of nitrogen atoms of amine and oxygen atoms, their tendency to form chelate rings and their ability to adopt various conformations according to the configurational requirements of different metal ions. In addition to this, some special features have also been established (Kabachnik et al 1974) due to an increase in the number of donor atoms and the stereochemistry of the PO_3 group. However, literature includes very few studies of aminopolyphosphonic acid complexes. In view of this, in present work, complexes of a phenylenediamine*tetrakis*(methylenephosphonic)acid (PDTMP) with Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Pb^{II} and of ethylenediamine-N,N'-*bis*-methylene-phosphonic acid (EDBMP) with Fe^{III} have been synthesised and an attempt has been made to establish their stereochemistry.

2. Experimental

2.1 *Preparation of the ligand (PDTMP) and its sodium salt*

The ligand was prepared by the method of Peck and Hudson (1969). To 2·16 g (0·02 mole) o-phenylenediamine, 6 ml of formaldehyde (40%) and 2·88 ml of water were added. To this mixture was then added 7·1 ml (0·08 mole) of PCl_3 dropwise with stirring, and the whole refluxed for 10 hr. The solution was then made alkaline with

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sodium hydroxide and refluxed for 1 hr. On addition of acetone to this, two layers were formed. The lower layer was separated and worked up. Water was removed by evaporation and a white semisolid compound was obtained. The results of the analysis were as follows:

Found: C 17·92; H 1·71; N 4·20; and P 18·25.
Required for $Na_8C_{10}H_{12}O_{12}P_4$: C 18·19; H 1·82; N 4·25; and P 18·74%.

The free ligand was, however, prepared by replacing PCl_3 with diethylphosphite (Moedritzer and Irani 1965). The pure ligand was obtained by treating the glassy product with lead acetate and then passing H_2S gas through the lead salt solution (Westerback *et al* 1965). The result of the ligand analysis is given below:

Found: C 24·05; H 4·21; N 5·63; and P 24·85.
Required for $C_{10}H_{20}O_{12}P_4$: C 24·79; H 4·13; N 5·79 and P 25·62%.

2.2 *Preparation of complexes*

Bivalent metal salts (BDH AnalaR) were used as such. 0·002 moles of sodium salt of the ligand were added to an aqueous solution of 0·004 moles of a metal salt dropwise and with constant stirring. Immediate precipitation took place. The yield was improved by addition of acetone or methanol to the mixture. The precipitates were washed with 50% acetone to make the product free from metal ions and then dried at 60–70°C. The analytical data (table 1) shows the complexes as having the general formula $M_4L \cdot xH_2O$, where $x = 2$–8.

Reactions in the 1:1, 2:1 or 3:1 molar ratios of metal and ligand were also attempted without success. These always resulted in the formation of 4:1 metal-ligand complexes.

2.3 *Preparation of iron(III) complexes with* EDBMP

The ligand (EDBMP) was synthesized as reported earlier (Palta *et al* 1984).

(i) $Fe_3(OH)_2L \cdot 9H_2O$: To 5 ml of 0·1 M ligand solution were slowly added 5 ml of 0·1 M iron(III) chloride solution and then about 5–10 ml of acetone. The solution was stirred constantly throughout. A light yellow precipitate was formed. This was washed

Table 1. Analytical and magnetic moment data of the complexes.

| Complex | % Found (Reqd.) | | Colour | μ_{eff}(BM) at room temp. |
	Metal	P		
Mn_4(PDTMP)·$2H_2O$	30·64 (30·05)	16·60 (16·94)	White	3·02
Co_4(PDTMP)·$8H_2O$	26·92 (27·55)	14·75 (14·45)	Blue-violet	2·86
Ni_4(PDTMP)·$4H_2O$	29·63 (30·01)	15·43 (15·79)	Green	1·72
Cu_4(PDTMP)·$2H_2O$	34·02 (33·17)	15·52 (16·18)	Light-blue	0·91
Zn_4(PDTMP)·$2H_2O$	33·02 (33·82)	16·92 (16·04)	White	—
Cd_4(PDTMP)·$2H_2O$	47·85 (46·77)	12·70 (12·86)	White	—
Pb_4(PDTMP)·$2H_2O$	62·85 (61·85)	9·05 (9·25)	White	—
$Fe_3(OH)$(EDBMP)$_2$·$9H_2O$	19·80 (20·13)	14·50 (14·85)	Light yellow	2·54
$Fe_2(OH)_2$(EDBMP)·H_2O	27·05 (27·51)	15·50 (15·23)	Light yellow	3·12

with water till the filtrate was colourless and then dried on a water bath (50–60°C). (ii) $Fe_2(OH)_2L \cdot H_2O$: To 10 ml of 0·1 M iron(III) chloride solution 5 ml of ligand solution were added dropwise with constant stirring. 5 ml of 0·2 M Na_2CO_3 solution were then introduced. On working up, a light yellow solid was obtained.

The complexes were insoluble in water and common organic solvents and did not melt even up to 300°C. IR spectra in the form of KBr pellets were recorded on a Beckman IR-20 spectrophotometer. Mull spectra in the region 200–2000 nm were run on a DMR-21 spectrophotometer. Magnetic measurements at room temperature were made on a Gouy balance at the Panjab University, Chandigarh. Variable temperature magnetic measurements for Fe(III) EDBMP complexes were obtained from TIFR, Bombay. Thermal analyses were carried out on a Derivatograph Mom-Budapest, Hungary, type Paulik-Paulik-Erdey, OD-102. The specimens were heated at the rate of 10°/min in 20–1000° range and heated alumina was used as the standard.

The endothermic peak at about 80°C on the DTA curve shows the removal of water molecules, corresponding mass loss 2·5 % (theoretical $= 2·6 \%$). On further heating up to 800°C, the organic part starts decomposing. The total mass loss of 11·25 % indicates $4 PbO \cdot P_2O_5$ (theoretical requirement 12·20 %), as the composition of the residue.
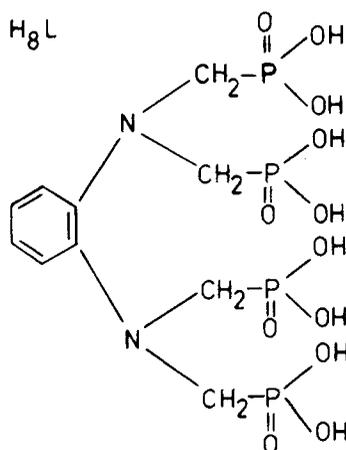

Chart 1.

3. Results and discussion

Reaction between *o*-phenylenediamine-N,N,N′,N′-*tetrakis*(methylenephosphonic)-acid above and the different bivalent metal salts in different molar ratios in aqueous solution has always resulted in the formation of complexes containing four metal atoms attached to one ligand. The elemental analysis (table 1) has shown these complexes to have the general formula $M_4^{II}L \cdot xH_2O$ ($x = 2–8$; M = Mn, Co, Ni, Cu, Zn, Cd and Pb). Ethylenediamine-N,N′-*bis*(methylenephosphonic)acid formed two complexes with iron(III) $Fe_3OHL_2 \cdot 9H_2O$ and $Fe_2(OH)_2L \cdot H_2O$. These compounds do not melt even up to 300°, nor do they dissolve in any common organic solvent. These two properties suggest that they are polymeric in nature. To establish their structure further, their infrared and electronic spectral, and magnetic measurement studies have been carried out.

3.1   Infrared spectra

The literature data have been used for assigning the absorption wave number (Dolphin and Wick 1977; Zhadanov and Dyatlova 1969; Kireeva *et al* 1973; Grayson and Griffith 1969).

The presence of two absorption bands at $1160 \, \text{cm}^{-1}$ and $1035 \, \text{cm}^{-1}$ corresponding to $v_{as}(PO_2)$ and $v_s(PO_2)$ respectively suggest that the free ligand exists as a zwitterion. In addition to this $v_{as}(P–OH)$ and $v_s(P–OH)$ absorptions corresponding to $-P(OH)_2$ also appear at 1000 and $950 \, \text{cm}^{-1}$. The absorption bands at $2840 \, \text{cm}^{-1}$ and $1580 \, \text{cm}^{-1}$ are assigned to the stretching and bending modes of vibration of $\overset{+}{N}–H$. The characteristic band of the free phosphoryl group appears at $1230 \, \text{cm}^{-1}$.

In the IR spectra of complexes, the phosphoryl frequency gets shifted to lower values of $1105–1100 \, \text{cm}^{-1}$ due to the coordination of the phosphoryl oxygen to the metal ion (Khramov and Kol'tsov 1973). The stretching vibrations of the deprotonated phosphonic group $PO_3(C_{2v})$ give rise to two bands v_{as} ($1080 \, \text{cm}^{-1}$) and v_s ($980 \, \text{cm}^{-1}$). When M–O bonds are formed with considerable contribution from covalent forces, the v_{as} band should undergo marked perturbation and split into two components because the symmetry of the PO_3 group is disturbed (Grigor'ev *et al* 1974). In these complexes, the two bands appear in the 1020–1070 and 960–980 cm^{-1} region. The bands observed for $\overset{+}{N}–H$ in the free ligand disappear in the spectra of metal derivatives.

3.2   Electronic spectra

The PDTMP derivative of manganese(II) is almost white and does not absorb in the 200–2000 nm range. The cobalt(II) complex $(Co_4L \cdot 8H_2O)$ is blue-violet and its electronic spectrum gives a weak band at $7168 \, \text{cm}^{-1}$ and two at 16 000 and 19 420 cm^{-1}, corresponding to $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F) \, (v_1)$; $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F) \, (v_2)$; $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F) \, (\bar{v}_3)$ transitions respectively. There is some splitting in the latter two and shoulders at 17 800 and 22 220 cm^{-1} are observed. This splitting is generally assumed to be due to spin-forbidden transitions. The green coloured nickel(II) complex $Ni_4L \cdot 4H_2O$) exhibits three absorption bands at $8330 \, \text{cm}^{-1}$ $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F) \, (v_1)$, 14 290 cm^{-1} $(^3T_{1g}(F) \leftarrow {}^3A_{2g}(F), \, v_2)$, 25 970 cm^{-1} $(^3T_{1g}(P) \leftarrow {}^3A_{2g}(F), \, v_3)$ for octahedral geometry. A band at 18 520 cm^{-1} can be assigned to a spin forbidden transition $^1E_g \leftarrow {}^3A_{2g}$. The absorption spectrum of blue coloured $Cu_4L \cdot 2H_2O$ consists of a broad band at 13 330 cm^{-1} and is attributed to the transition $^2T_{2g} \leftarrow {}^2E_g$. The band is asymmetric on account of splitting by a low symmetry ligand field component.

It is difficult to assign any stereochemistry to iron(III) (d^5 system) in EDBMP complexes in the absence of the oscillator strength of various bands as is the case with Mn^{II} EDBMP complexes (Palta *et al* 1984).

3.3   Magnetic moments

The magnetic moment of the Mn(II) complex is 3·02 BM (297°K). This value is much lower than the spin only value for a d^5 system (5·92 BM) and suggests the presence of antiferromagnetic exchange. The direct orbital-orbital overlap of neighbouring metal ions is also possible, because the polymeric character can bring these metal ions to distances close enough for interaction. However, the possibility of super exchange via PO_3 bridges is not ruled out. The magnetic moment of the cobalt(II) complex at room temperature (2·86 BM) as compared to the normal moments (4·30–5·20 BM) again

shows the presence of an appreciable antiferromagnetic exchange interaction. The anomalous magnetic moment value of 1·72 BM for the nickel(II) complex (spin only value of d^8-2·83 BM) indicates that the system is magnetically concentrated $Cu_4L \cdot 2H_2O$ has the magnetic moment value of 0·91 BM at 297°K, which is much lower than the normal value (1·70–2·20 BM) and is probably due to antiferromagnetic exchange arising from Cu–Cu interaction or via super exchange.

Magnetic moments at different temperatures for the iron complexes with ethylenediamine-N,N'-*bis*(methylenephosphonic acid) were determined. It was observed that there was decrease in magnetic moments with decrease in temperature as is also expected for antiferromagnetic complexes (table 2) (Ranbore *et al* 1982). From this observation antiferromagnetism may be inferred for other complexes also.

$Zn_4L \cdot 2H_2O$, $Cd_4L \cdot 2H_2O$ and $Pb_4L \cdot 2H_2O$ are diamagnetic as expected. The corresponding mercuric complex could not be prepared as the addition of the ligand to $HgCl_2$ solution first reduces it to Hg_2Cl_2 and then to Hg.

4. Thermal analyses

Thermal behaviour of these complexes is almost the same, hence, only that of $Pb_4L \cdot 2H_2O$ is being discussed here in detail. There is a broad endothermic peak at about 80°C and corresponds to a mass loss of 2·5 % due to removal of water molecules (theoretical required 2·6 %). The DTG curve shows a sharp peak at 170° paralleled by a strong exothermic peak. The compound undergoes a further mass loss of 5 %, perhaps due to the decomposition of organic part. The DTG curve shows no more clear steps and mass loss is also gradual upto 800°C. However, a large number of peaks with exothermic effects are seen on DTA curve—360°, 400°, 420°, 490° and 570°C. At 640°C, there is a slight endothermic effect. The total mass loss of 11·25% indicates the formation of $2PbO \cdot P_2O_5$ as the composition of the residue (theoretical required: 12·20%). Such conclusions have also been drawn by Khramov and Kol'tsov (1973) in case of rare earth element complexes with 1-hydroxyethylidenediphosphonic acid.

Table 2. Magnetic moment data at different temperatures for EDBMP complexes of iron(III).

Temperature (K)	Magnetic moment μ_{eff}(B.M.) of $Fe_3(OH)(EDBMP)_2 \cdot 9H_2O$	Temperature (K)	Magnetic moment μ_{eff}(B.M.) of $Fe_2(OH)_2(EDBMP)_2 \cdot H_2O$
14·0	1·259	14·4	1·5685
14·6	1·266	15·0	1·585
20·6	1·5123	20·8	1·738
24·0	1·5416	24·2	1·7605
28·0	1·578	27·8	1·8345
31·2	1·5823	31·4	1·8795
41·4	1·58	41·0	1·9325
86·0	1·908	86·0	2·25
110·0	2·047	105·0	2·455
295	2·53	295	3·10

Acknowledgements

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