

## Transition Metal Coordination Compounds of 2-Aminoethylphosphonic Acid

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*Coordination compounds of 2-aminoethylphosphonic acid have been prepared with magnesium(II), chromium(III), manganese(II), iron(II), cobalt(II), nickel(II) and zinc(II). The complexes have been characterized by means of infrared spectra, visible spectra, magnetic susceptibilities and thermal analysis. Comparisons are made with analogous complexes of alanine.*

### Introduction

2-Aminoethylphosphonic acid ( $H_2AEP$ ) was the first phosphonic acid to be isolated and identified from a natural source, rumen ciliated protozoa.<sup>1</sup> It has subsequently been shown that  $H_2AEP$  is widely distributed in nature<sup>2</sup> and in humans.<sup>3</sup>

Coordination compounds of aminocarboxylic acids have been studied and comparisons made with aminophosphonic acids. In the case at hand, 2-aminoethylphosphonic acid is the phosphorus analog of  $\beta$ -alanine. Solid state complexes of phosphonic acids<sup>4</sup> and aminocarboxylic acids<sup>5</sup> have been reported; this is the first report of solid state complexes of an aminophosphonic acid. Stability constants in aqueous solution have been measured for aminophosphonic acid complexes<sup>6–9</sup> and comparisons made with aminocarboxylic acid complexes.<sup>9</sup> The results indicate that glycine forms more stable complexes than aminomethylphosphonic acid,  $\alpha$ -alanine forms more stable complexes than 1-aminoethylphosphonic acid but that 2-aminoethylphosphonic acid forms more stable complexes than  $\beta$ -alanine. This paper reports the synthesis and characterization of some solid complexes formed between 2-aminoethylphosphonic acid and first-row transition metal ions.

### Experimental

#### 2-Aminoethylphosphonic Acid

The ligand was prepared and characterized as previously reported.<sup>10</sup>

#### NaHAEP

To  $H_2AEP$  (1.25 g, 10.0 mmol) dissolved in 10 ml  $H_2O$ , 0.1M NaOH was added while heating until the

pH reached 9. Then 20 ml of 95% ethanol was added which resulted in two layers. The oil formed was removed, dissolved in water and ethanol added again. This was repeated twice and the final oil formed was placed in a rotary evaporator until a solid formed. The resulting white solid was dried at 100°C in 67% yield. Thermal analysis showed decomposition between 270 and 355°C.

#### $Mg(HAEP)_2 \cdot 5H_2O$

$H_2AEP$  (2.16 g, 17.3 mmol) and  $MgCl_2 \cdot 6H_2O$  (1.75 g, 8.61 mmol) were dissolved in 40 ml  $H_2O$  and the pH adjusted to 6.7 with 0.1M NaOH. Addition of 80 ml 95% ethanol resulted in the formation of an oil which formed a white precipitate after stirring with 100 ml 50% ethanol. The product, obtained in 65% yield, is soluble in  $H_2O$ . Thermal analysis showed weight loss equivalent to hydrated water between 38 and 180°C and decomposition above 225°C.

#### $[Cr(AEP)(OH)]_2 \cdot 4H_2O$

$H_2AEP$  (0.517 g, 4.14 mmol) and  $CrCl_3 \cdot 6H_2O$  (1.11 g, 4.16 mmol) were dissolved in 40 ml  $H_2O$  and the pH adjusted to 6.9 with 0.1M NaOH. As 40 ml 95% ethanol was added a dark green precipitate formed. After digestion for 5 minutes, the precipitate was filtered and washed with 50% ethanol. The product, obtained in 82% yield is not soluble in  $H_2O$  or in common organic solvents. Thermal analysis showed weight loss in three steps between 40 and 390°C and further decomposition above that temperature.

#### $Na[Mn(HAEP)_2Cl(H_2O)]$

$H_2AEP$  (1.84 g, 14.7 mmol) and  $MnCl_2 \cdot 4H_2O$  (1.45 g, 7.34 mmol) were dissolved in 40 ml  $H_2O$  and the pH adjusted to 6 with 0.1M NaOH. As acetone was added an off-white precipitate formed. The solid was washed with 75% acetone and recovered in 88% yield. The solid is soluble in  $H_2O$ . Thermal analysis showed weight loss equivalent to hydrated water between 90° and 170°C with further decomposition above 215°C.

#### $Na[Fe(HAEP)_2Cl(H_2O)]$

This compound was prepared in the same manner as the manganese compound using  $FeCl_2 \cdot 4H_2O$ . The

green solid, obtained in 76% yield, is soluble in H<sub>2</sub>O but not soluble in common organic solvents. Thermal analysis showed weight loss equivalent to hydrated water between 38° and 180°C with further decomposition above 215°C.

#### *Co(HAEP)<sub>2</sub>*

H<sub>2</sub>AEP (1.78 g, 14.2 mmol) and CoCl<sub>2</sub>·6H<sub>2</sub>O (1.69 g, 7.10 mmol) were dissolved in 30 ml H<sub>2</sub>O. While heating, the pH was adjusted to 6.7 with 0.1M NaOH. Upon addition of 40 ml 95% ethanol the pink solution turned dark blue and a blue precipitate formed. The solid was heated in 50% ethanol to remove trapped chloride. After suction filtration, the product was dried at 110°C in a vacuum oven. The compound, obtained in 72% yield, decomposes above 315°C.

#### *NiAEP·2H<sub>2</sub>O*

H<sub>2</sub>AEP (0.721 g, 5.77 mmol) and NiCl<sub>2</sub>·6H<sub>2</sub>O (1.36 g, 5.74 mmol) were dissolved in 20 ml H<sub>2</sub>O and while heating the pH adjusted to 7 with 0.1M NaOH. The addition of acetone gave a green precipitate which was filtered and washed with water followed by acetone. The solid obtained in 84% yield is not soluble in H<sub>2</sub>O or in common organic solvents. Thermal analysis showed weight loss equivalent to hydrated water between 35° and 275°C with further decomposition above 275°C.

#### *Cu<sub>3</sub>(HAEP)<sub>2</sub>Cl<sub>4</sub>·2H<sub>2</sub>O*

H<sub>2</sub>AEP (1.25 g, 10.0 mmol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (1.70 g, 10.0 mmol) were dissolved in 20 ml H<sub>2</sub>O. Addition of 20 ml 95% ethanol gave a light green precipitate which was washed with 50% ethanol and recovered in 60% yield. The solid is soluble in H<sub>2</sub>O and not soluble in common organic solvents. Thermal analysis showed weight loss equivalent to hydrated water between 135° and 180°C with further decomposition above 180°C, changing from green to yellow to brown.

#### *Zn(HAEP)<sub>2</sub>*

H<sub>2</sub>AEP (1.10 g, 8.81 mmol) and ZnCl<sub>2</sub> (0.600 g, 4.37 mmol) were dissolved in 40 ml H<sub>2</sub>O and the pH adjusted to 6.7 with 0.1M NaOH. The addition of excess 95% ethanol gave an oil which was separated and allowed to dry. The white solid obtained was ground and washed by heating with H<sub>2</sub>O and recovered in 82% yield. Thermal analysis showed the compound to be stable up to 300°C.

Infrared spectra were obtained as KBr pellets, as mineral oil mulls and as fluorocarbon mulls over the range 4000–300 cm<sup>-1</sup> on a Perkin-Elmer Model 621 Recording Spectrophotometer. Visible spectra were obtained as mineral oil mulls or fluorocarbon mulls at room temperature and at liquid nitrogen temperature on a Cary Model 14 Recording Spectrophotometer.

Magnetic susceptibilities were measured at room temperature by the Gouy method using a permanent magnet developing approximately 5200 gauss with Hg[Co(NCS)<sub>4</sub>] as a standard. Magnetic moments were calculated using the Curie law. Thermogravimetric analysis was done on a Mettler Thermoanalyzer-2.

Carbon, hydrogen and nitrogen analyses were performed by Chemalytics, Inc., Tempe, Arizona. Metal analyses were done by EDTA titration<sup>11</sup> except for chromium which was done gravimetrically as BaCrO<sub>4</sub>.<sup>12</sup> Chloride analyses were by the Volhard method.<sup>13</sup> Water was determined from the thermogravimetric analyses. These results are presented in Table I.

## Results and Discussion

The infrared spectrum of H<sub>2</sub>AEP has been reported<sup>14</sup> but not analyzed in detail. Studies on similar compounds are available<sup>15,16</sup> and our assignments will parallel these. The infrared absorptions of H<sub>2</sub>AEP, NaHAEP and the complexes over the range 1700 to 300 cm<sup>-1</sup> are listed in Table II. The zwitterion character of H<sub>2</sub>AEP is evident from its infrared spectrum which shows bands at 1655 and 1560 cm<sup>-1</sup> which have been assigned to NH<sub>3</sub><sup>+</sup> deformations. In the complexes, the absorptions in this region are much weaker and occur at lower frequencies indicating that a proton has been displaced from the NH<sub>3</sub><sup>+</sup> group and probable coordination of the nitrogen to the metal. The absorption of coordinated water in the 1600–1650 cm<sup>-1</sup> region was difficult to assign due to the NH<sub>2</sub> group absorption in this same region. In the free acid the bands between 900 and 1000 cm<sup>-1</sup> and between 1000 and 1200 cm<sup>-1</sup> are the symmetric and asymmetric stretching modes of the PO<sub>3</sub> group. In the complexes these bands occur over a narrower range of frequencies and are simpler in a manner similar to that previously observed for other complexes.<sup>4</sup> This indicates that the PO<sub>3</sub> group is coordinated to the metal in all the complexes.

The PO<sub>3</sub> deformation vibrations occur in the range 490–600 cm<sup>-1</sup>. In the free acid and in the magnesium complex there are only two absorptions in this region which must be these deformations. In the other complexes, except for copper, there are three or four bands in this region which may indicate that all PO<sub>3</sub> groups are not equivalent. It is reasonable to expect that bonding between metal centers will occur either by bridging oxygens as observed with phenylphosphonic acid<sup>4</sup> or by hydrogen bonding between an OH group of one ligand and an O of a neighboring ligand in a fashion analogous to that observed with some aminocarboxylic complexes.<sup>5,17</sup> With a trivalent metal such as chromium, the PO<sub>3</sub> deformations should be at higher frequencies; the two bands in this region for the chro-

TABLE I. Analytical Data.

Compound	C %		H %		N %		Metal %		H <sub>2</sub> O %		Cl %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
NaHC <sub>2</sub> H <sub>7</sub> NPO <sub>3</sub>	16.3	16.2	4.77	4.60	9.53	9.61						
Mg(HC <sub>2</sub> H <sub>7</sub> NPO <sub>3</sub> ) <sub>2</sub> ·5H <sub>2</sub> O	13.3	12.9	6.67	6.35	7.73	7.30	6.71	6.70	24.9	25.2		
[Cr(C <sub>2</sub> H <sub>7</sub> NPO <sub>3</sub> )(OH)] <sub>2</sub> ·4H <sub>2</sub> O	10.5	9.20	4.86	4.16	6.14	6.04	22.8	21.8	15.8	15.5		
Na[Mn(HC <sub>2</sub> H <sub>7</sub> NPO <sub>3</sub> ) <sub>2</sub> Cl(H <sub>2</sub> O)]	12.7	13.0	4.25	4.33	7.40	7.49	14.5	15.8	4.75	4.87	10.1	10.1
Na[Fe(HC <sub>2</sub> H <sub>7</sub> NPO <sub>3</sub> ) <sub>2</sub> Cl(H <sub>2</sub> O)]	12.6	12.8	4.24	4.20	7.37	7.22	14.7	16.1	4.76	5.43	9.32	9.57
Co(HC <sub>2</sub> H <sub>7</sub> NPO <sub>3</sub> ) <sub>2</sub>	15.7	15.5	4.60	4.48	9.13	8.42	19.2	19.4				
Ni(C <sub>2</sub> H <sub>7</sub> NPO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	11.0	11.5	4.63	4.25	6.43	6.17	27.0	26.0	15.6	15.1		
Cu <sub>3</sub> (HC <sub>2</sub> H <sub>7</sub> NPO <sub>3</sub> ) <sub>2</sub> Cl <sub>4</sub> ·2H <sub>2</sub> O	7.79	7.90	2.92	2.82	4.54	4.59	30.9	30.4	5.84	5.81	23.0	21.4
Zn(HC <sub>2</sub> H <sub>7</sub> NPO <sub>3</sub> ) <sub>2</sub>	15.3	14.9	4.50	4.08	8.94	8.39	20.9	23.2				

TABLE II. Infrared Spectra.

Compound	Absorptions (cm <sup>-1</sup> )
H <sub>2</sub> AEP	1650 (s), 1635 (sh), 1560 (sh), 1555 (s), 1538 (sh), 1467 (m), 1422 (m), 1384 (m), 1335 (w), 1285 (s), 1220 (vs), 1163 (vs), 1135 (vs, br), 1096 (sh), 1078 (vs), 1037 (vs, br), 1016 (sh), 968 (m), 948 (s), 937 (s), 913 (vs), 807 (s), 781 (m), 738 (m), 550 (s), 490 (vs), 460 (sh), 364 (m), 344 (s), 303 (w)
NaHAEP	1632 (s), 1581 (s), 1528 (m), 1522 (sh), 1480 (m), 1468 (w), 1433 (w), 1383 (m), 1369 (m), 1267 (sh), 1252 (s), 1149 (s, br), 1070 (vs, br), 970 (sh), 960 (vs), 935 (sh), 861 (m), 770 (vs), 756 (sh), 742 (m), 680 (m), 590 (sh), 568 (vs), 508 (sh), 495 (vs), 380 (s), 336 (m), 325 (sh)
Mg(HAEP) <sub>2</sub> ·5H <sub>2</sub> O	1630 (s), 1539 (s), 1524 (sh), 1468 (m), 1414 (w), 1384 (m), 1262 (m), 1155 (s), 1107 (sh), 1087 (vs), 1050 (vs), 1047 (sh), 1014 (s), 970 (vs), 948 (sh), 928 (sh), 760 (m), 560 (m), 503 (m), 371 (m), 355 (m)
[Cr(AEP)(OH)] <sub>2</sub> ·4H <sub>2</sub> O	1620 (m), 1510 (m), 1468 (w), 1410 (w), 1383 (w), 1280 (w), 1093 (vs), 972 (vs), 720 (s), 555 (sh), 530 (s), 465 (s), 352 (m), 324 (w)
Na[Mn(HAEP) <sub>2</sub> Cl(H <sub>2</sub> O)]	1642 (m), 1608 (s), 1512 (sh), 1483 (s), 1470 (m), 1456 (m), 1433 (w), 1426 (w), 1420 (sh), 1390 (m), 1350 (w), 1332 (w), 1280 (sh), 1270 (s), 1220 (s), 1141 (vs), 1120 (vs), 1092 (vs), 1080 (sh), 1052 (vs), 1026 (vs), 990 (vs), 979 (sh), 932 (vs), 904 (vs), 787 (m), 774 (m), 754 (s), 745 (m), 719 (w), 575 (sh), 550 (s), 495 (sh), 488 (s), 482 (sh), 457 (s), 450 (sh), 378 (sh), 365 (s), 351 (s)
Na[Fe(HAEP) <sub>2</sub> Cl(H <sub>2</sub> O)]	1620 (m), 1608 (sh), 1480 (m), 1382 (w), 1283 (m), 1080 (sh), 1040 (vs), 1000 (vs), 895 (sh), 850 (sh), 721 (m), 565 (m), 514 (m), 362 (w)
Co(HAEP) <sub>2</sub>	1620 (m), 1505 (s), 1501 (sh), 1466 (m), 1411 (w), 1384 (m), 1342 (m), 1265 (s), 1165 (s), 1123 (vs), 1090 (sh), 1050 (vs), 1030 (sh), 991 (vs), 963 (s), 940 (s), 783 (s), 753 (w), 738 (m), 719 (m), 605 (vs), 520 (s), 486 (m), 407 (m), 360 (w), 338 (w)
NiAEP·2H <sub>2</sub> O	1605 (sh), 1595 (m), 1468 (vw), 1408 (w), 1384 (vw), 1320 (sh), 1283 (w), 1243 (m), 1117 (s), 1075 (vs), 1043 (vs), 1021 (vs), 995 (s), 980 (vs), 937 (s), 840 (vw), 812 (vw), 718 (s), 608 (w), 562 (s), 538 (sh), 500 (s), 376 (w), 370 (w)
Cu <sub>3</sub> (HAEP) <sub>2</sub> Cl <sub>4</sub> ·2H <sub>2</sub> O	1581 (sh), 1572 (m), 1564 (sh), 1498 (m), 1494 (sh), 1467 (w), 1460 (sh), 1416 (vw), 1383 (w), 1276 (w), 1115 (m), 1100 (sh), 1083 (vs), 1054 (vs), 1020 (vs), 1011 (sh), 985 (sh), 932 (vw), 882 (w), 828 (m), 778 (vw), 739 (m), 718 (w), 572 (s)
Zn(HAEP) <sub>2</sub>	1640 (sh), 1632 (m), 1622 (sh), 1599 (m), 1510 (sh), 1505 (s), 1480 (w), 1476 (sh), 1416 (m), 1412 (w), 1383 (m), 1379 (sh), 1341 (m), 1262 (m), 1240 (m), 1164 (s), 1125 (vs), 1085 (sh), 1074 (sh), 1065 (vs), 993 (vs), 963 (s), 940 (s), 784 (s), 751 (vw), 738 (m), 666 (w), 603 (vs), 539 (m), 521 (s), 486 (m), 395 (s), 370 (w), 335 (w)

mium complex are undoubtedly of different origin (*vide infra*).

The absorptions in the region 2500–3500 cm<sup>-1</sup> have not been reported because the spectra in this region

are poorly resolved. Attempts at obtaining better resolution, particularly in the case of the chromium complex, were unsuccessful. This region of the spectrum would have given valuable structural information. We

TABLE III. Visible-Near Infrared Spectra.

Compound	Absorptions (cm <sup>-1</sup> )
[Cr(AEP)(OH)] <sub>2</sub> · 4H <sub>2</sub> O	16900 (1.00), 23500 (0.82)
Co(HAEP) <sub>2</sub>	5920 (0.37), 6760 (0.37), 7460 (0.35), 17130 (1.00)
NiAEP · 2H <sub>2</sub> O	8700 (0.39), 13070 (0.35), 14500 (0.45), 25300 (1.00)
Cu <sub>3</sub> (HAEP) <sub>2</sub> Cl <sub>4</sub> · 2H <sub>2</sub> O	13100 (0.38), 25600 (1.00)

suggest that this poor resolution is due, at least in part, to extensive hydrogen bonding in the crystals.

For the visible-near infrared spectra listed in Table III, relative absorbance values are given with the strongest absorption in each case assigned a value of 1.0.

The blue color and the room temperature magnetic moment of 4.69 B.M. for [Co(HAEP)<sub>2</sub>] indicate a tetrahedral environment around the cobalt. The splitting of the spectral band near 7000 cm<sup>-1</sup> into three components and a band centered near 16,000 cm<sup>-1</sup> confirm this.<sup>18</sup> Assigning the band at 17,125 cm<sup>-1</sup> as the <sup>4</sup>A<sub>2</sub> ← <sup>4</sup>T<sub>1</sub>(P) transition and the weighted average<sup>19</sup> of 6862 cm<sup>-1</sup> from the other three bands as the <sup>4</sup>A<sub>2</sub> ← <sup>4</sup>T<sub>1</sub>(F) transition we obtained by the method of Lever<sup>20</sup> adapted to a computer a Dq value of 395 cm<sup>-1</sup> and B equal to 809 cm<sup>-1</sup>. The infrared spectrum of [Zn(HAEP)<sub>2</sub>] is very similar to that of [Co(HAEP)<sub>2</sub>] and thus it is expected that the structures of these two complexes are similar.

The results for Ni(AEP) indicate a regular octahedral environment around the nickel. The room temperature magnetic moment of 3.40 B.M. is typical of octahedral nickel(II). The three absorption bands in the visible-near infrared region are expected and the fact that there is little change in the spectrum when measured at liquid nitrogen temperature suggests<sup>21</sup> that there is little or no tetragonal distortion. Using the method of Lever for an octahedral *d*<sup>8</sup> system and using  $\nu_1$  and  $\nu_3$  we have calculated a value of  $\nu_2$  of 14,400 cm<sup>-1</sup> which agree well with the experimental value of 14,500 cm<sup>-1</sup>. This same calculation gives a Dq value of 870 cm<sup>-1</sup> and B equal to 908 cm<sup>-1</sup>. These values of Dq and B are typical of weak field complexes and are similar to those for the phenylphosphonic acid complex previously reported.<sup>4</sup> The visible-near infrared spectrum of a solid  $\beta$ -alanine complex has been reported<sup>22</sup> from which we calculate a Dq value of 980 cm<sup>-1</sup> and B equal to 826 cm<sup>-1</sup>.

The chromium(III) complex is postulated to be a dimer with two hydroxo bridges on the basis of a sub-normal magnetic moment at room temperature,<sup>23-25</sup> 3.37 B.M. calculated on a per chromium basis, and two bands in the infrared spectrum between 500 and 550 cm<sup>-1</sup> which will be the stretching vibrations associated with the hydroxo bridges.<sup>25,26</sup> The visible-near infrared spectra at room temperature and at liquid

nitrogen temperature are nearly identical. Using the method of Lever for an octahedral *d*<sup>3</sup> system and assigning the two observed bands as  $\nu_1$  and  $\nu_2$  we obtain Dq equal to 1690 cm<sup>-1</sup> and B equal to 655 cm<sup>-1</sup>. For [Cr(L-alanine)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl using reported values<sup>27</sup> of  $\nu_1 = 17,860$  cm<sup>-1</sup> and  $\nu_2 = 24,100$  cm<sup>-1</sup> we calculate Dq = 1790 cm<sup>-1</sup> and B = 601 cm<sup>-1</sup>; these are similar to our complex.

The magnetic moments at room temperature of Na[Mn(HAEP)<sub>2</sub>Cl(H<sub>2</sub>O)] and Na[Fe(HAEP)<sub>2</sub>Cl(H<sub>2</sub>O)] are 5.91 and 5.17 B.M. respectively. These values are typical of high spin complexes of these metal ions. We were unable to obtain spectra in the visible and near infrared regions for these compounds. The copper(II) complex has a room temperature magnetic moment of 2.25 B.M. per copper. The absorption which has a center of gravity of 13,090 cm<sup>-1</sup> is the *d-d* transition expected for a *d*<sup>9</sup> system; this band is not symmetrical and can be resolved into two bands centered at 12,990 and 10,640 cm<sup>-1</sup>. The band at 25,640 cm<sup>-1</sup> is not found in many copper compounds and has been attributed to charge transfer from non-bonding orbitals of bridging oxygen atoms to vacant metal *d* orbitals.<sup>28,29</sup> With a magnetic moment of 2.25 B.M. it seems unlikely that there is any direct copper-copper interaction since that would decrease the moment below that of the spin-only moment for one unpaired electron.

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