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Divalent Metal Phenylphosphonates and Phenylarsonates

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Phenylphosphonates and phenylarsonates of divalent magnesium, manganese, iron, cobalt, nickel, zinc and cadmium having compositions $MPhRO_3\cdot H_2O$ *(M = all metals when R = P; M = all metals except iron and copper when R = As) and* $MPhRO_3$ *(M = metal; R = P and As) have been isolated and characterized. Structures are suggested for the complexes based on infrared and electronic spectra, magnetic and X-ray diffraction data.*

Introduction

Over this past decade there has been an ever increasing interest in a particular class of inorganic polymer, the so called coordination polymer and this interest initiated intensive studies of the structures and properties of metal phosphinates [1–8]. The emphasis on phosphinates stems from their good thermal stability and the degree to which other desirable properties can be introduced into the materials by varying the nature of the organic substituents on the phosphorus atoms. The potentially useful metal(II) and metal(III) phosphinates have skeletal backbone structures consisting of metal ions linked by bridging –O–P–O– groups thus giving rise to infinite single chain structures. In principle, metal(II) and metal(III) phosphonates could possess chain structures which might also exhibit useful properties. However, the structures and properties of these have not hitherto been examined. Whilst the corresponding metal arsonates are better known, arsonic acids having long been used as precipitants of many metal ions [9], the compositions and structures of these have received only limited attention [10, 11]. It seemed worthwhile, therefore, to extend solution studies of metal phosphonates and arsonates which have been carried out in this laboratory [12, 13] to include a study of the solid materials.

In this paper we describe the results of our investigations of the compositions and structures of phenylphosphonates and phenylarsonates of divalent magnesium, manganese, iron, cobalt, nickel, copper, zinc and cadmium.

Results and Discussion

Preparation, Composition and Physical Characteristics of Salts

The phenylphosphonates and phenylarsonates of all of the metals, with the exception of magnesium and iron, can be obtained in a straightforward manner by reacting the metal salt (chloride or sulphate) with the appropriate acid or with the mono- or disodium salt of the acid. The magnesium salts are most readily obtained from the reaction of freshly precipitated $Mg(OH)_2$ with the acids. In the case of the ferrous reactions preparations must be carried out in the absence of oxygen but the isolated dry salts are then stable towards oxidation (in contrast to ferrous bis diphenylphosphinate which oxidizes rapidly [5]).

While it has proved possible to prepare Fe(III) [14] and organotin(IV) [14, 15] phenylphosphonates and phenylarsonates containing either the singly or doubly charged anions $PhRO_2(OH)^-$ and $PhRo_3^{--}$ respectively (R = P or As) only those complexes containing $PhRO_3^{--}$ groups could be isolated for the divalent metals of this study. Apart from copper and ferrous phenylarsonates which are obtained only in anhydrous form all other salts precipitate from aqueous solution as highly insoluble hydrates of composition $MPhRO_3\cdot H_2O$ (M = metal, R = P or As). Anhydrous copper and zinc salts of composition $MPhRO_3$ (M = metal, R = P or As) can be obtained from the ethanolic reactions of the metal(II) bisacetylacetonates with the acids, but the other anhydrous complexes cannot be obtained in this manner. It is worth noting that reactions between iron trisacetylacetonate or organotin(IV) acetylacetonates and the acids [14] generally resulted in the formation of salts containing the singly charged anions $PhRO_3(OH)^-$.

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TABLE I. Analytical and Thermogravimetric Data for the Phenylphosphonate and Phenylarsonate Salts.

Compound	Colour	Theory		Found		Thermogravimetric Data[a]	
		%C	%H	%C	%H	Temp. of Water Loss/°C	Next Weight Loss/°C
$MgPhPO_3 \cdot H_2O$	White	36.1	3.5	36.2	3.6	25	550
$MgPhAsO_3 \cdot H_2O$	White	29.6	2.9	29.6	2.9	25	470
$MnPhPO_3 \cdot H_2O$	White	31.2	3.1	31.3	3.0	130	520
$MnPhAsO \cdot H_2O$	White	26.2	2.5	26.3	2.7	130	460
$MnPhAsO_3$	White	28.0	1.9	28.1	1.8	–	460
$FePHPO_3 \cdot H_2O$	Green	31.1	3.0	30.8	3.2	150	520
$FePhAsO_3$	Green	27.9	1.9	27.8	1.9	–	450
$CoPhPO_3 \cdot H_2O$	Violet	30.7	3.0	30.9	3.0	150	620
$CoPhAsO_3 \cdot H_2O$[b]	Violet	25.9	2.5	26.0	2.3	150	460
$CoPhAsO_3$	Violet	27.6	1.9	27.7	2.0	–	460
$NiPhPO_3 \cdot H_2O$	Yellow	30.7	3.0	30.9	3.1	160	560
$NiPhAsO_3 \cdot H_2O$[c]	Green	25.9	2.5	26.1	2.4	150	540
α-$CuPhPO_3 \cdot H_2O$	Pale Torquoise	30.1	2.9	30.1	2.9	150	360
β-$CuPhPO_3 \cdot H_2O$	Blue	30.1	2.9	29.9	2.8	120	360
γ-$CuPhPO_3 \cdot H_2O$	Blue	30.1	2.9	29.8	3.0	120	360
δ-$CuPhPO_3 \cdot H_2O$	Torquoise	30.1	2.9	30.2	2.9	100	360
$CuPhPO_3$	Green	32.5	2.3	32.4	2.3	–	360
$CuPhAsO_3$	Green	27.1	1.9	27.2	2.0	–	300
$ZnPhPO_3 \cdot H_2O$	White	29.8	2.9	29.9	3.0	80	540
$ZnPhPO_3$	White	32.2	2.2	32.3	2.1	–	540
$ZnPhAsO_3 \cdot H_2O$	White	25.2	2.5	25.2	2.7	70	440
$ZnPhAsO_3 \cdot 0.5H_2O$	White	26.0	2.2	26.1	2.3	140	440
α-$ZnPhAsO_3$[c]	White	26.9	1.9	27.0	2.0	–	440
$CdPhPO_3 \cdot H_2O$	White	25.0	2.4	24.9	2.3	160	520
$CdPhPO_3 \cdot 0.5H_2O$	White	25.8	2.1	25.9	2.2	160	520
$CdPhAsO_3 \cdot H_2O$[c]	White	21.7	2.1	21.9	2.2	120	440

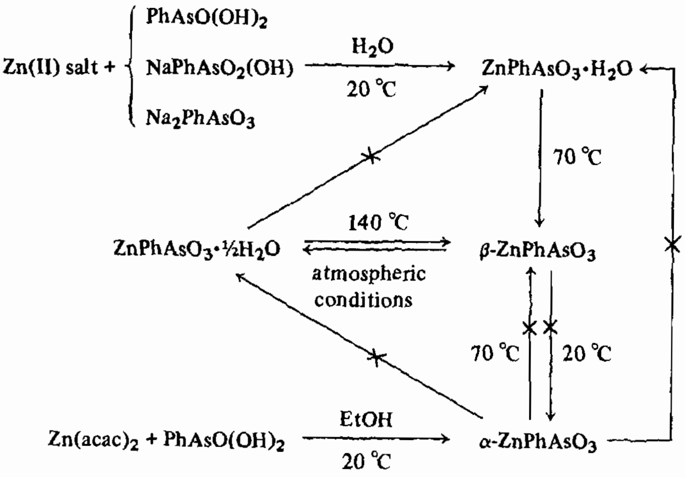
[a] Heating rate 10°/min in N_2. [b] A salt of composition $CoPhAsO_2 \cdot 0.5H_2O$ has been reported [10]. [c] Previously reported [10].

Thermogravimetric analysis of the hydrates reveals that in no case is water retained above 160 °C. The magnesium salts lose water most readily, losing water slowly from about 30 °C onwards and all other salts lose water rapidly at temperatures ranging from 70 °C to 160 °C (see Table I). The next weight loss in the thermograms probably indicates thermal decomposition. Thus, the phosphonates have a significantly greater thermal stability than the arsonates and in fact are also more stable than metal(II) bisdiphenylphosphinates [16]. A further feature of the thermogravimetric data is the relatively low thermal stability of the copper salts, paralleling the low thermal stability of copper bisdiphenylphosphinate compared to other metal bis diphenylphosphinates [16].

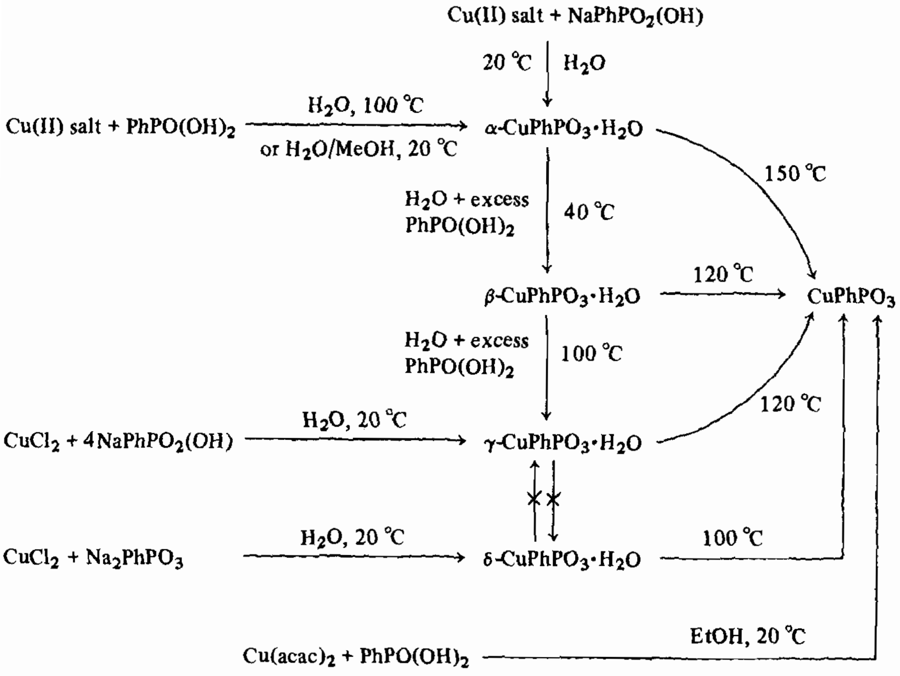
The stability of the anhydrous metal phenylphosphonates and phenylarsonates towards hydration varies considerably. Manganese, cobalt, iron and copper phenylarsonates and the α-modification of zinc phenylarsonate are completely stable towards hydration whereas the nickel, cadmium and magnesium analogs hydrate extremely rapidly to the monohydrate salts. β-zinc phenylarsonate hydrates rapidly to give a stable hemihydrate $ZnPhAsO_3 \cdot \frac{1}{2}H_2O$. Copper phenylphosphonate is the only phosphonate which is stable towards hydration. Zinc phenylphosphonate hydrates over the period of a few hours and all other phenylphosphonates hydrate immediately in the open atmosphere to give the monohydrated forms. Cadmium phenylphosphonate, like β-$ZnPhAsO_3$, hydrates to give a stable hemihydrate $CdPhPO_3 \cdot \frac{1}{2}H_2O$.

Several of the salts isolated exhibited polymorphism. For example, two crystal modifications of $ZnPhAsO_3$ and four crystal modifications of $CuPhPO_3 \cdot H_2O$ were isolated (see experimental and reaction schemes 1 and 2). It would appear from Mössbauer spectra that two modifications exist for both $FePhPO_3 \cdot H_2O$ and $FePhAsO_3$. The Mössbauer spectrum of $FePhPO_3 \cdot H_2O$ recorded at 20 °C consists of a doublet (typical of high-spin ferrous) in which component peaks have normal line widths. As the temperature is lowered a second doublet (also typical of high-spin ferrous) develops and increases in intensity relative to the original doublet with decreasing temperature. The effect is reversible. The

Reaction Scheme 1



Reaction Scheme 2



growth of the second doublet almost certainly corresponds to the growth of a new solid state phase. Two doublets are present in each of the Mössbauer spectra of $FePhAsO_3$ recorded at 20 °C and at −180 °C. While this may be indicative of a single phase in which there are two distinct ferrous sites it seems more probable, in view of the tendency of phosphonates and arsonates to exhibit polymorphism*, that two distinct phases of $FePhAsO_3$ have been precipitated from solution.

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*We have found an even greater tendency towards polymorphism among alkyltin(IV) phenylphosphonates and phenylarsonates.

TABLE II. Diffuse Reflectance Spectral Data for the Manganese, Cobalt and Nickel Salts and Tentative Band Assignments.

Manganese Salts	$^4T_{1g}(G) \leftarrow {}^6A_{1g}$	$^4T_{2g}(G) \leftarrow {}^6A_{1g}$	$^4A_{1g}, {}^4E_g(G) \leftarrow {}^6A_{1g}$	$^4T_{2g}(D) \leftarrow {}^6A_{1g}$	$^4E_g(D) \leftarrow {}^6A_{1g}$	$^4T_{1g}(P) \leftarrow {}^6A_{1g}$
$MnPhPhO_3 \cdot H_2O$	19,417	–	24,570	27,624	29,154	33,330
$MnPhAsO_3 \cdot H_2O$	18,691	–	23,810	27,397	29,240	33,220
$MnPhAsO_3$	18,000	21,980	24,250	27,150	29,250	30,250
Cobalt Salts	$^4T_{2g} \leftarrow {}^4T_{1g}$	$^4A_{2g} \leftarrow {}^4T_{1g}$	$^4T_{1g} \leftarrow {}^4T_{1g}$			
$CoPhPO_3 \cdot H_2O$	6,349, 7270	13,890	18,620, 20,000			
$CoPhAsO_3 \cdot H_2O$	6,670, 7270	13,990	18,520, 20,000			
$CoPhAsO_3$	8000	–	19,100, 21,050			
Nickel Salts	$^3T_{2g} \leftarrow {}^3A_{2g}$	$^1E_g \leftarrow {}^3A_{2g}$	$^3T_{1g} \leftarrow {}^3A_{2g}$	$^1T_{1g} \leftarrow {}^3A_{2g}$	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$	
$NiPhPO_3 \cdot H_2O$	7,480	14,390	13,070	20,830	23,990	
$NiPhAsO_3 \cdot H_2O$[a]	7,410	14,390	13,250	20,620	23,530	
	(8,000)	(14,000)	(13,400)	(20,800)	(23,800)	

[a] Values in parenthesis are from ref. 10.

Structures of Monohydrate Salts

X-ray powder diffraction patterns of the metal(II) phenylphosphonate hydrates $MPhPO_3 \cdot H_2O$ (M = Fe, Co, Ni, Zn, Cd and Mg) and of α-$CuPhPO_3 \cdot H_2O$ strongly suggest that they form an isomorphic series and furthermore that this series and the series of arsonates $MPhAsO_3 \cdot H_2O$ (M = Mg, Mn, Co, Ni, Zn, Cd) are isomorphous. Unfortunately we have not been able in any case to obtain crystals suitable for a full X-ray crystal structure analysis even though in some preparations visibly crystalline materials were obtained (see experimental).

Diffuse reflectance spectra of the manganese, nickel, cobalt and copper phenylphosphonate and phenylarsonate hydrates are consistent with approximately octahedral geometry about the metal ions. In fact the very pale colour of the manganese salts is in itself suggestive of octahedral manganese(II). Band assignments of the reflectance spectra of the nickel, cobalt and manganese salts are given in Table II. Room temperature magnetic moments of the cobalt and nickel salts (see Table III) also support the octahedral assignments.

TABLE III. Magnetic Data for Phenylphosphonate and Phenylarsonate Salts.

Compound	Magnetic Moment/B.M.		θ-values
	20 °C	−180 °C	
$MnPhPO_3 \cdot H_2O$	5.28	4.75	42
$MnPhAsO_3 \cdot H_2O$	5.49	4.93	54
$MnPhAsO_3$ [a]	4.32	2.07	624
$FePhPO_3 \cdot H_2O$	5.18	4.53	–
$CoPhPO_3 \cdot H_2O$	5.11	4.39	40
$CoPhAsO_3 \cdot H_2O$	4.84	4.11	50
$NiPhPO_3 \cdot H_2O$	3.27	2.93	54
$NiPhAsO_3 \cdot H_2O$	3.13 (3.13)[b]	2.91 (2.86)	35
α-$CuPhPO_3 \cdot H_2O$	2.16	2.18	–4
β-$CuPhPO_3 \cdot H_2O$	2.07	2.01	7
γ-$CuPhPO_3 \cdot H_2O$	2.07	1.98	7
δ-$CuPhPO_3 \cdot H_2O$	2.00	1.94	2

[a] A sharply defined Curie point is observed for $MnPhA_5O_3$ at −123 °C. [b] Values in parenthesis are from ref. 10.

The isomorphic salt hydrates all show bands typical of water in the higher regions of their infrared spectra. For example, all of the phenylphosphonate hydrates exhibit two reasonably sharp intense bands in their spectra between 3000 and 3500 cm^{-1} while the phenylarsonate hydrates show a broad intense band in this region, and for all salts a band is observed at approximately 1600 cm^{-1}. More significant, however, is the fact that in the spectra of several of the metal phenylphosphonate hydrates (*e.g.* α-$CuPhPO_3 \cdot H_2O$) bands are found in the 600–800 cm^{-1} region which disappear on dehydration of the salts and thus almost certainly owe their origin to water. This is a region of the spectrum in which coordinated water typically absorbs [17].

Structures consisting of non-interacting polymeric chains in which metal ions are linked by bridging phosphonate and arsonate groups (as found in many metal(II) phosphinates) could not, even with the assumption of coordinated water, account for the octahedral coordination of the metal ions. This coordination could only be achieved as a result of the acid groups being involved in more extensive bridging giving probably either two or three dimensional polymeric networks. Where crystals of phosphonates were obtained these were plate-like in appearance and exhibited extremely pronounced cleavage, characteristics of crystals resulting from layer-type lattices where only weak van der Waal's forces hold layers together. Thus, the structure most strongly suggested for the isomorphic series of phosphonates and arsonate hydrates is one in which layers consisting of octahedrally coordinated metal ions linked by multibridging acid groups are held together by weak van der Waal's forces.

X-ray diffraction patterns and infrared spectra suggest that β- and γ-$CuPhPO_3 \cdot H_2O$ have very similar structures. Their diffraction patterns differ only in the positions of the weaker lines and the positions of the three most intense reflections exactly coincide with those of the three most intense reflections in the diffraction pattern of α-$CuPhPO_3 \cdot H_2O$. Crystals of β- and γ-$CuPhPO_3 \cdot H_2O$ exhibit the same plate-like appearance and pronounced cleavage of crystals of α-$CuPhPO_3 \cdot H_2O$ and in all cases the three most intense reflections in the diffraction patterns are from planes parallel to the cleavage planes. Thus, it would appear that both the β- and γ-phases also possess layer lattice structures in which layer separations are similar to the layer separation in the structure of the α-phase. The striking similarity in the infrared spectra (4000–250 cm^{-1}) of β- and γ-$CuPhPO_3 \cdot H_2O$ is strongly suggestive of structures which merely differ in the stacking sequence of layers. This would also account for the extreme ease with which the β-form is transformed to the γ-phase (see experimental). The infared spectra of these phases differ most strikingly from that of α-$CuPhPO_3 \cdot H_2O$ in the positions of the water bands in the higher region of the spectrum. In contrast to the two sharp bands exhibited by α-$CuPhPO_3 \cdot H_2O$ above 3000 cm^{-1} the β- and γ-modifications show two very broad bands at much lower frequencies, thus indicating a much stronger participation in hydrogen bonding by water in these solids.

Magnetic measurements were made on the transition metal phenylphosphonate and phenylarsonate hydrates in the range 20–−180 °C. In all cases Curie–Weiss law behaviour was closely observed over this temperature range. Some relevant data are in Table III. The data for the copper salts do not reveal antiferromagnetic behaviour and in the case of the cobalt and nickel salts the temperature dependent magnetic moments and θ-values are probably explicable in terms of orbital contributions to the magnetic moments. However, in the case of the manganese salts where no orbital contributions are expected the low room temperature magnetic moments (compared to the spin-only value), their temperature dependence, and the reasonably large θ-values are all indicative of antiferromagnetic interactions which of course, are not unexpected in the proposed polymeric structures.

Structures of the Anhydrous Salts

The anhydrous phenylphosphonates and phenylarsonates are less crystalline than the hydrated salts and their diffraction patterns are consequently of very poor quality. Thus, it is not possible to positively establish isomorphic behaviour, if it exists, from diffraction data. However, it is clear that while α-$ZnPhAsO_3$, $MnPhAsO_3$ and $CoPhAsO_3$ may not be isomorphous they are at least very closely structurally related and their structures definitely differ from that of $CuPhAsO_3$. β-$ZnPhAsO_3$ appears to have a similar structure to $ZnPhPO_3$ but $CuPhAsO_3$ is not structurally related to $CuPhPO_3$.

There is no observable colour change associated with the removal of the coordinated water from either $CoPhAsO_3 \cdot H_2O$ or $MnPhAsO_3 \cdot H_2O$ and the electronic spectra are still consistent with the presence of octahedrally coordinated metal ions in the anhydrous salts (see Table II). It is clear that the removal of coordinated water must be accompanied by a structural change resulting in more extensive oxygen bridging if the approximately octahedral geometry is retained about the metal ions. The striking difference in magnetic behaviour between $MnPhAsO_3 \cdot H_2O$ and $MnPhAsO_3$ (see data in Table III) probably reflects this structural change. The sharply defined Curie point observed for $MnPhAsO_3$ is characteristic of an extensive antiferromagnetic interaction in the solid [18]. It is thus highly probable that the anhydrous manganese, cobalt and zinc arsonates have three-dimensional polymeric structures in which the metal ions occupy octahedral sites.

Due to the extreme sensitivity of $MnPhPO_3$ to moisture no attempt was made to obtain a diffraction pattern or electronic spectrum of the solid. The material is practically colourless and this favours the presence of manganese ions in octahedral sites as is the case in $MnPhAsO_3$. However, the marked difference in stabilities (towards hydration) between $MnPhPO_3$ and $MnPhAsO_3$ does strongly suggest that they are not isostructural.

In contrast to the violet colour of $CoPhPO_3 \cdot H_2O$ and its room temperature magnetic moment of 5.11 B. M. $CoPhPO_3$ has an intense blue colour and a room temperature magnetic moment of 4.73 B.M. It is clear therefore that the removal of water is accompanied by a decrease in the coordination of cobalt from six to either five or four. Thus, $CoPhPO_3$ cannot be isostructural with $CoPhAsO_3$ which contains six coordinate cobalt.

The particularly intense absorption (centred at 10,130 cm^{-1} with a shoulder at approximated 11,500 cm^{-1}) in the electronic spectrum of $CuPhAsO_3$ is rather suggestive of trigonal bipyramidal copper. Unfortunately, supporting data could not be obtained from the e.s.r. spectrum as lines were extremely broad due to exchange coupling within the unit cell. It is noteworthy, however, that the suggestion of five coordinate copper in $CuPhAsO_3$ is not inconsistent with diffraction data which clearly indicate that $CuPhAsO_3$ is not isomorphous with the manganese and cobalt analogs, both of which contain six coordinate metal ions. The diffuse reflectance spectrum of $CuPhPO_3$ is also suggestive of the presence of five coordinate copper but as in the case of the arsonate salt the e.s.r. spectrum was totally uninformative.

Experimental

Preparation of Magnesium Phenylarsonate and Magnesium Phenylphosphonate

An excess of freshly prepared magnesium hydroxide was added to aqueous solutions of the acids. After stirring for half an hour at room temperature and centrifuging to remove unreacted magnesium hydroxide the solutions were evaporated to dryness. The white solids ($MgPhPO_3 \cdot H_2O$ and $MgPhAsO_3 \cdot H_2O$) were washed with methanol and dried under vacuum at room temperature for six hours. Elemental analyses are in Table I.

The Preparation of Manganese(II), Cobalt(II), Nickel(II), Zinc and Cadmium Phenylphosphonates and -arsonates

Reactions (i)–(iv) below were carried out using the following procedure. Aqueous solutions of the metal salts (chlorides, sulphates) were added to aqueous solutions of the acids or their sodium salts. The compositions of the precipitates obtained were independent of the mol ratios of reactants. All solids were isolated by centrifuging solutions and after washing with methanol they were dried under vacuum at room temperature for not less than six hours. Elemental analyses of products are in Table I.

(i) Reactions of metal salts with phenylarsonic acid

$ZnPhAsO_3 \cdot H_2O$ and $CdPhAsO_3 \cdot H_2O$ precipitate immediately at room temperature. $MnPhAsO_3 \cdot H_2O$ precipitates very slowly at room temperature but rapidly at 100 °C. Nickel and cobalt salts do not precipitate even on prolonging refluxing.

(ii) Reactions of metal salts with phenylphosphonic acid

$ZnPhPO_3 \cdot H_2O$ precipitates immediately at room temperature. $CdPhPO_3 \cdot H_2O$ and $MnPhPO_3 \cdot H_2O$ precipitate very slowly at room temperature but rapidly at 100 °C. Nickel and cobalt salts are not precipitated at any temperature.

(iii) Reactions of metals salts with mono- and disodium salts of phenylarsonic acid

$ZnPhAsO_3 \cdot H_2O$, $CdPhAsO_3 \cdot H_2O$ and $MnPhAsO_3 \cdot H_2O$ precipitate immediately at room temperature and $CoPhAsO_3 \cdot H_2O$ precipitates in good yield after approximately one hour. $NiPhAsO_3 \cdot H_2O$ does not precipitate at room temperature but fairly rapidly at 100 °C.

(iv) Reactions of metal salts with mono- and disodium salts of phenylphosphonic acid

$ZnPhPO_3 \cdot H_2O$ and $CdPhPO_3 \cdot H_2O$ precipitate immediately and $MnPhPO_3 \cdot H_2O$ slowly at room temperature. $NiPhPO_3 \cdot H_2O$ and $CoPhPO_3 \cdot H_2O$ precipitate only on refluxing.

Solids obtained from reactions (i)–(iv) carried out at room temperature were not visibly crystalline. More crystalline samples of $MnPhPO_3 \cdot H_2O$, $ZnPhPO_3 \cdot H_2O$ and $CdPhPO_3 \cdot H_2O$ are obtained when aqueous solutions of the metal salts (1 mol) at 100 °C are added to aqueous solutions of phenylphosphonic acid (1 mol) at 100 °C. The crystals are platelike in appearance and show very pronounced cleavage. They appear to be orthorhombic or pseudo-orthorhombic.

(v) Reactions of zinc, nickel and cobalt bisacetylacetonates with phenylphosphinic and phenylarsonic acids

The method consisted of adding an ethanolic solution of the metal bisacetylacetonate (1 mol) to an ethanolic solution of the acid (1 mol). Solids were isolated by filtration, washed with ethanol, and dried under vacuum at room temperature for several hours.

$ZnPhAsO_3$ and predominantly $ZnPhPO_3 \cdot H_2O$ (when alcohol is not dried) precipitate fairly rapidly at room temperature and much more rapidly when a two- or three-fold excess of the acid is present. $ZnPhPO_3$ precipitates from solution when the alcohol is previously dried and the reaction carried out under anhydrous conditions. Due to its sensitivity towards hydration this latter salt must be handled under anhydrous conditions.

In reactions involving nickel and cobalt bisacetylacetonates precipitates are obtained only on refluxing. Solid products from phenylarsonic acid solutions give slightly variable elemental analyses. The elemental analyses are fairly consistent with formulations $NiPhAsO_3 \cdot 0.5EtOH$ and $CoPhAsO_3 \cdot 0.5EtOH$. Infrared spectra of the solids verify the presence of alcohol and diffraction patterns indicate that $NiPhAsO_3 \cdot H_2O$ and $CoPhAsO_3 \cdot H_2O$ are absent. $NiPhPO_3 \cdot H_2O$ is obtained exclusively from phenylphosphonic acid solution but we have not been able to characterise the nature of the product from the reaction between cobalt bisacetylacetonate and phenylphosphonic acid. The product shows very variable carbon and hydrogen analyses.

The Preparation of Copper Phenylarsonate, Copper Phenylphosphonate and the Polymorphs of Copper Phenylphosphonate Hydrate

Copper phenylarsonate, $CuPhAsO_3$, is obtained in anhydrous form from all reactions (i–v) described for the preceding metals. Copper phenylphosphonate hydrate, $CuPhPO_3 \cdot H_2O$, is obtained from reactions i–iv and copper phenylphosphonate, $CuPhPO_3$, is obtained from reaction v.

Four crystal modifications of $CuPhPO_3 \cdot H_2O$ were identified. These can be separately isolated by adhering to the following reaction conditions a–d. (all solid products are isolated by filtration, washed with water and alcohol, and dried under vacuum at room temperature for approximately six hours. Elemental analyses are in Table I).

(a) The formation of α-$CuPhPO_3 \cdot H_2O$

Three preparative procedures were found to yield this modification.

(i) An aqueous solution (75 ml) containing 1.7 g (1 mol) $CuCl_2 \cdot 2H_2O$ is added to an aqueous solution (75 ml) containing 1.80 g (1 mol) monosodium phenylphosphonate. Pale turquoise α-$CuPhPO_3 \cdot H_2O$ precipitates immediately.

(ii) If the acid is used in place of its monosodium salt in the above reaction no precipitate is formed. However, addition of methanol results in the slow precipitation of the α-modification.

(iii) A more crystalline product is obtained by adding an aqueous solution of $CuSO_4 \cdot 5H_2O$ (2.5 g/30 ml) at 100 °C to an aqueous solution of the acid (6.32 g/30 ml) at 100 °C. Plate-like crystals of α-$CuPhPO_3 \cdot H_2O$ form rapidly. These must be filtered from solution immediately in order to avoid phase change. The crystals appear to be orthorhombic.

(b) The formation of β-$CuPhPO_3 \cdot H_2O$

This modification is the most difficult to isolate in a pure state. α-$CuPhPO_3 \cdot H_2O$ is heated in an aqueous phenylphosphoric acid solution with constant stirring at approximately 40 °C until the solid has changed from pale turquoise to a blue colour. Complete phase change takes about eight hours but the time is somewhat unpredictable and sometimes the γ-form is mainly obtained. As the β- and γ-modifications have the same colour they are most readily identified by their infrared spectra. A water band which occurs at 3340 cm^{-1} in the spectrum of β-$CuPhPO_3 \cdot H_2O$ occurs at 2280 cm^{-1} in the spectrum of γ-$CuPhPO_3 \cdot H_2O$. The reaction of cupric sulphate with phenylphosphonic acid in water at approximately 80 °C often yields a mixture of crystalline α- and β-$CuPhPO_3 \cdot H_2O$. Crystals of β-$CuPhPO_3 \cdot H_2O$ have the plate-like appearance and pronounced cleavage of crystals of α-$CuPhPO_3 \cdot H_2O$. They have lower than orthorhombic symmetry.

(c) The preparation of γ-$CuPhPO_3 \cdot H_2O$

This modification can be conveniently formed by either of two methods.

(i) α-$CuPhPO_3 \cdot H_2O$ is heated in an aqueous solution of phenylphosphonic acid with constant stirring at 100 °C. Phase change to γ-$CuPhPO_3 \cdot H_2O$ is complete within four hours.

(ii) An aqueous solution (50 ml) containing 1.7 g (1 mol) $CuCl_2 \cdot 2H_2O$ is added to an aqueous solution (150 ml) containing 7.2 g (4 mol) monosodium phenylphosphonate. γ-$CuPhPO_3 \cdot H_2O$ precipitates immediately at room temperature.

(d) Preparation of δ-$CuPhPO_3 \cdot H_2O$

An aqueous solution (75 ml) containing 1.7 g (1 mol) $CuCl_2 \cdot 2H_2O$ is added to an aqueous solution (75 ml) containing 2.02 g (1 mol) disodium phenylphosphonate. δ-$CuPhPO_3 \cdot H_2O$ precipitates immediately. This modification does not undergo phase change when stirred in an aqueous solution of phenylphosphonic acid at 100 °C for two days.

The Preparation of Ferrous Phenylphosphonate Hydrate and Ferrous Phenylarsonate

A freshly prepared ferrous sulphate aqueous solution at 80 °C was added to a disodium phenylphosphonate aqueous solution at 80 °C under oxygen free conditions. A white precipitate of $FePhPO_3 \cdot H_2O$ was rapidly formed. This was separated by filtration under nitrogen, washed with deoxygenated water and alcohol and dried under vacuum for several hours at room temperature. Analytical data for the product are in Table I. The Mössbauer spectrum of this product indicates the presence of ferrous ions. If the reaction is carried out without the exclusion of oxygen the product contains mainly iron(III) (as indicated by its Mössbauer spectrum). Despite all efforts to exclude oxygen in reactions between ferrous sulphate and either phenylphosphonic acid or monosodium phenylphosphonate products were always obtained which were contaminated with iron(III).

The reaction of ferrous sulphate with disodium phenylphosphonate in water did not yield a pure ferrous salt (as it did with disodium phenylarsonate). Initially a pale yellow solid was obtained which despite all precautions darkened to a green colour in the course of filtration and drying. The Mössbauer spectrum of the green solid indicates the presence of both iron(II) and iron(III). When the same reaction was carried out in the open atmosphere a green precipitate formed which was found to contain only iron(III). Elemental analyses of this product are consistent with its formulation as $(FePhAsO_3)_2O$.

Ferrous phenylarsonate, $FePhAsO_3$, free of iron(III) was obtained from the reaction of ferrous sulphate (freshly prepared) with phenylarsonic acid in water under oxygen free conditions. At approximately 80 °C a light green precipitate formed, ($FePhAsO_3$) which was separated by filtration under nitrogen, washed with water and alcohol and dried under vacuum at room temperature for several hours. Analytical data for the salt are in Table I.

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