Characterisation and Electronic Properties of some Inorganic Ion Exchangers of the Zirconium Phosphate Type containing Transition-metal Ions [1]

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A series of transition-metal-ion forms of crystalline zirconium phosphate of general formula $ZrM(PO_4)_2 \cdot 4H_2O$ (M = Zn^{II}, Cu^{II}, Ni^{II}, Co^{II}, and Mn^{II}) has been characterised. The visible–near u.v. spectra of the copper, nickel, and cobalt species indicate the presence of an octahedral stereochemistry (tetragonally distorted in the case of Cu^{II}). The dehydration of the exchangers has been followed using thermal and *X*-ray powder techniques and electronic spectra. Magnetic-susceptibility measurements have also been used (where possible) to support structural assignment. Complete dehydration occurs only at *ca.* 450 °C with a change in stereochemistry for the compounds of Ni^{II} and Co^{II}. At higher temperature the layer structure is lost and the materials become double phosphates, $MZr(PO_4)_2$. Possible stereochemistries for the anhydrous forms are discussed.

SYNTHETIC inorganic ion exchangers of the zirconium phosphate type, such as $Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP) and the corresponding sodium-ion-containing phases, are of interest because of their possible practical applications.[2] More recently, attention has been focused on their use as catalysts when doped with varying amounts of transition-metal ions, especially Cu^{II},[3,4] although the isomerisation of, for example, cyclohexane using several ill defined zirconium phosphate type catalysts was reported as long ago as 1966.[5] Before any conclusions can be drawn as to the nature of the active sites in such materials and how they are involved in the catalysis mechanism, it is first necessary to characterise them in terms of their composition, dehydration behaviour, and structural modifications induced by chemical treatment and the possible structure types taken up by the transition-metal ions.

We report the first characterisation of the totally exchanged species of general formula $ZrM(PO_4)_2 \cdot 4H_2O$ (M = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}).† Reflectance spectra and magnetic moments, where these are likely to lead to conclusions as to the metal ion site, have been investigated. There are virtually no data of this kind in the literature and the difficulty of obtaining crystals suitable for *X*-ray work justifies the use of these methods.

EXPERIMENTAL

Preparation.—The materials were obtained by allowing the appropriate aqueous 0.01 mol dm^{-3} metal(II) acetate solution to percolate slowly (*ca.* 1—2 ml h^{-1}) over crystalline $ZrHNa(PO_4)_2 \cdot 5H_2O$ [6] at room temperature. Complete exchange was monitored by chemical analysis of the exchangers, until the M : PO_4^{3-} mole ratio reached 1 : 2. The products were then centrifuged, washed with water, and dried in air. All the completely converted forms have formula $ZrM(PO_4)_2 \cdot 4H_2O$.

Physical Methods.—The metals were analysed using a Varian Techtron 120 atomic absorption flame spectrophotometer. The phosphate content was determined colorimetrically.[7] All the elemental analyses were correct to within 2%. Differential thermal analysis (d.t.a.) curves were measured on a Du Pont 900 thermal analyser equipped with chromel–alumel thermocouples and platinum containers, using a heating rate of 2.5 °C min^{-1}. Thermal gravimetric (t.g.) measurements were made on a Stanton TG 750 thermobalance. Samples were heated in platinum crucibles in air and the heating rate was 1—5 °C min^{-1}. *X*-Ray powder spectra were obtained on a Philips diffractometer (Ni-filtered Cu-K_α radiation). An Italstructure AF 3 high-temperature attachment was used for recording high-temperature phases. The heating system consisted of an induction furnace with hemispherical graphite elements. The sample was held on a platinum support, in contact with Pt/Pt–Rh (10%) thermocouples.

Reflectance spectra were recorded on a Beckmann DK 2A spectrophotometer with standard reflectance attachment, against MgO as reference. Dynamic reflectance spectra were obtained using a sample furnace described previously.[8] The sample was first equilibrated for *ca.* 15 min at each temperature; the temperature was then held constant during registration of the spectrum. 'Static' spectra refer to samples first heated at a fixed temperature for 48 h; the spectrum was recorded immediately at room temperature.

Magnetic susceptibilities were measured using the Gouy method and tubes calibrated with $Hg[Co(SCN)_4]$.[9] E.s.r. spectra were obtained on a Varian E9 *X*-band spectrometer with standard liquid-nitrogen accessories.

RESULTS AND DISCUSSION

Thermal Measurements and X-Ray Powder Spectra.—The *X*-ray powder spectra of the tetrahydrates were all very similar and show that the interlayer distance between sheets containing Zr atoms, as measured by the

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† $ZrM(PO_4)_2 \cdot nH_2O$ and $ZrM(PO_4)_2$ denote layer-structured ion exchangers; $MZr(PO_4)_2$ denotes double-phosphate structures.

[1] Presented in part at the 8th Annual Meeting of the Associazone Italiana di Chim. Inorg., Jesolo (Italy), September 1975, communication A17.

[2] G. Alberti and U. Costantino, *J. Chromatog.*, 1974, **102**, 5.

[3] S. Allulli, A. La Ginestra, M. A. Massucci, M. Pelliccioni, and N. Tomassini, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 337.

[4] T. S. Kalman, M. Dudukovic, and A. Clearfield, *Adv. Chem. Ser.*, 1974, **133**, 654.

[5] N. Malemberg, A. I. Kukina, and T. N. Fadeeva, *Vestnik Moskov. Univ.*, 1966, 107.

[6] S. Allulli, A. La Ginestra, and M. A. Massucci, unpublished work.

[7] D. N. Bernart and A. R. Wreath, *Analyt. Chem.*, 1955, **27**, 400.

[8] A. Pupella, G. D'Ascenzo, and A. Marino, *Ann. Chim. (Italy)*, 1972, **62**, 144.

[9] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1958, 4190.

(002) reflection, is between 9.55 and 9.70 Å (Table 1) (*cf.* the similar *X*-ray patterns for the partially exchanged materials reported in ref. 3).

TABLE 1

X-Ray diffraction patterns of $ZrM(PO_4)_2\cdot 4H_2O$

Mn^{II}		Co^{II}		Ni^{II}		Cu^{II}		Zn^{II}	
d/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*
9.70	vs	9.60	m	9.55	m	9.60	m	9.60	m
4.85	s	4.80	s	4.78	vs	4.78	vs	4.79	vs
4.60	m	4.57	m	4.55	m	4.57	w	4.57	m
4.40	m	4.40	s	4.40	ms	4.41	mw	4.40	s
4.10	ms	4.10	vs	4.08	s	4.18	m	4.10	vs
4.03	mw	3.98	mw	3.97	w	3.92	w	3.98	mw
3.60	vw	3.57	mw	3.55	vw	3.58	w	3.57	mw
3.25	w	3.27	mw	3.24	vw	3.33	w	3.49	vw
3.20	m	3.15	m	3.14	w	3.18	vw	3.27	w
2.85	vw	2.80	w	2.78	vw	3.09	m	3.16	mw
2.68	vw	2.67	mw	2.65	mw	2.81	w	2.80	mw
2.65	vw	2.65	m	2.64	mw	2.69	vw	2.665	mw
2.26	vw	2.58	w	2.55	w	2.66	vw	2.655	mw
		2.47	vw	2.45	vw	2.62	m	2.58	w
		2.20	vw			2.47	vw	2.48	vw
						2.27	vw		
						2.24	vw		

vs = Very strong, s = strong, m = medium, mw = medium weak, w = weak, and vw = very weak.

The dehydration, followed by t.g. and d.t.a. methods, occurred between 40 and *ca.* 450 °C. Between 40 and 150—180 °C, hydrates containing 1 or 1.5 H_2O were produced and there was a decrease in the interlayer distance. The remaining water was eliminated much more slowly between 200 and 450 °C and this was accompanied by a further decrease in interlayer spacing (Table 2). The loss of the first water molecule(s) occurred in a single step for the compounds of Co^{II} and Ni^{II} (3 and 2.5 water molecules, respectively) and in several steps for those of Mn^{II} (2,1), Cu^{II} (1,1.5), and Zn^{II} (1.5,1.5). In this first dehydration phase the distance between layers of Zr atoms decreased from 9.6—9.7 to *ca.* 8 Å (Mn 8.11, Co 7.96, Ni 8.04, Cu 8.75, and Zn 8.07 Å). The first two dehydration processes in $ZrCu(PO_4)_2\cdot 4H_2O$ were quantitatively reversible and occurred below 160 °C. This made it necessary to carry out *X*-ray measurements at high temperature. The cobalt compound also rehydrated to some extent, but the process was very slow.

All the compounds began to lose the last 1 or 1.5 water molecules above 200 °C, with a further decrease in the interlayer distance ($d_{(002)}$ ranging from 7.6 to 6.7 Å). This dehydration was much slower than the first one and went to completion between 200 and 450 °C only for the compounds of Mn^{II} and Co^{II}. The nickel, copper, and zinc compounds were completely dehydrated only at much higher temperatures (700—900 °C) depending on the heating rate used (1—2 °C min^{-1}). This is presumably caused by the high interlayer contraction at temperatures higher than 200 °C for these compounds, which reaches values sufficient to slow down the diffusion of water molecules through the lattice. In addition, the water loss went through a plateau between 450 and 650 °C, during the phase change of the anhydrous form (see below). For the compounds of Co^{II} and Mn^{II}, decrease in the interplanar distance in steps also slowed down the loss of the last water molecule between 250 and 450 °C. This may account for the appearance of doubling in the endothermic peaks in this temperature range (Figure 1).

TABLE 2

Dehydration steps and variations in the $d_{(002)}$ reflection (Å)

$$\underset{9.70\ (25\ ^{\circ}C)}{ZrMn(PO_4)_2\cdot 4H_2O} \xrightarrow[-2H_2O]{40—110\ ^{\circ}C} \underset{9.45\ (110\ ^{\circ}C)}{ZrMn(PO_4)_2\cdot 2H_2O} \xrightarrow[-H_2O]{110—180\ ^{\circ}C} \underset{8.11\ (180\ ^{\circ}C)}{ZrMn(PO_4)_2\cdot H_2O} \xrightarrow[-H_2O]{230—390\ ^{\circ}C} \underset{7.60\ (450\ ^{\circ}C)}{ZrMn(PO_4)_2}$$

$$\underset{9.60\ (25\ ^{\circ}C)}{ZrCo(PO_4)_2\cdot 4H_2O} \xrightarrow[-3H_2O]{40—180\ ^{\circ}C} \underset{7.96\ (180\ ^{\circ}C)}{ZrCo(PO_4)_2\cdot H_2O} \xrightarrow[-H_2O]{210—430\ ^{\circ}C} \underset{7.33\ (450\ ^{\circ}C)}{ZrCo(PO_4)_2}$$

$$\underset{9.55\ (25\ ^{\circ}C)}{ZrNi(PO_4)_2\cdot 4H_2O} \xrightarrow[-2.5H_2O]{40—190\ ^{\circ}C} \underset{8.04\ (200\ ^{\circ}C)}{ZrNi(PO_4)_2\cdot 1.5H_2O} \xrightarrow[-1.5H_2O]{250—700\ ^{\circ}C} \underset{7.02\ (450\ ^{\circ}C)}{ZrNi(PO_4)_2}$$

$$\underset{9.60\ (25\ ^{\circ}C)}{ZrCu(PO_4)_2\cdot 4H_2O} \xrightarrow[-H_2O]{40—100\ ^{\circ}C} \underset{9.30\ (100\ ^{\circ}C)}{ZrCu(PO_4)_2\cdot 3H_2O} \xrightarrow[-1.5H_2O]{100—160\ ^{\circ}C} \underset{8.75\ (160\ ^{\circ}C)}{ZrCu(PO_4)_2\cdot 1.5H_2O} \xrightarrow[-0.5H_2O]{160—240\ C}$$

$$\underset{\left.\begin{matrix}8.03\\7.00\end{matrix}\right\}(240\ ^{\circ}C)}{ZrCu(PO_4)_2\cdot H_2O} \xrightarrow[-H_2O]{250—900\ ^{\circ}C} \underset{\left.\begin{matrix}7.85\\6.78\end{matrix}\right\}(450\ ^{\circ}C)}{ZrCu(PO_4)_2}$$

$$\underset{9.60\ (25\ ^{\circ}C)}{ZrZn(PO_4)_2\cdot 4H_2O} \xrightarrow[-1.5H_2O]{40—80\ ^{\circ}C} \underset{9.56\ (80\ ^{\circ}C)}{ZrZn(PO_4)_2\cdot 2.5H_2O} \xrightarrow[-1.5H_2O]{80—125\ ^{\circ}C} \underset{8.07\ (200\ ^{\circ}C)}{ZrZn(PO_4)_2\cdot H_2O} \xrightarrow[-H_2O]{260—900\ ^{\circ}C} \underset{\left.\begin{matrix}7.66\\7.31\end{matrix}\right\}(450\ ^{\circ}C)}{ZrZn(PO_4)_2}$$

Copper and zinc forms of zirconium phosphate, at >400 °C, showed two *d*-line spacings indicating that two phases are present, one with $d_{(002)} < d$ (anhydrous) and the other with $d_{(002)} > d$ (hydrated). The latter line often appeared, depending on the heating rate, even at >600 °C. In order to obtain completely anhydrous transition-metal-ion forms of the crystalline zirconium phosphate, it was then necessary to carry out their dehydration for a prolonged time (at least 48 h) in an oven at 450 °C. Table 3 reports the *X*-ray powder patterns of these compounds obtained with the high-temperature camera at 450 °C. As seen from Figure 1, the (002) line was present in all the phases up to at least 450 °C, showing that the starting layer structure is retained up to this temperature.

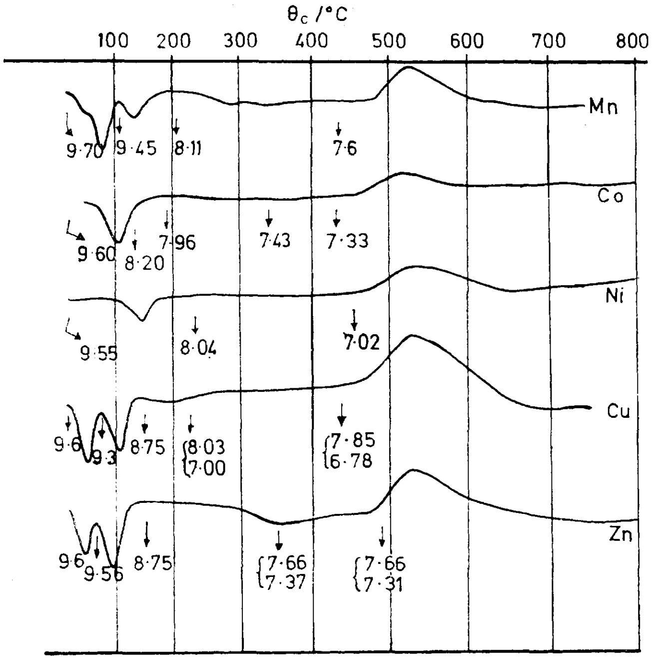

FIGURE 1 D.t.a. curves (heating rate 2 °C min^{-1}) and variations in the $d_{(002)}$ reflection (Å)

TABLE 3

High-temperature (450°C) *X*-ray diffraction patterns of $ZrM(PO_4)_2$

Mn^{II}		Co^{II}		Ni^{II}		Cu^{II}		Zn^{II}	
d/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*
7.60	vs	7.33	s	7.02	s	7.85	w	7.66	w
4.56	ms	4.50	s	4.42	m	6.78	m	7.31	ms
4.24	vw	4.22	w	4.29	mw	4.62	mw	4.52	vs
3.88	m	3.79	ms	3.91	mw	4.28	s	4.21	w
3.73	m	3.66	s	3.77	s	3.94	w	4.01	w
3.00	w	3.49	w	3.64	mw	3.66	vs	3.87	vw
2.65	vw	2.99	m	2.92	m	3.48	w	3.77	s
		2.64	m			3.45	vw	3.66	w
		2.49	vw			2.90	ms	3.59	w
						2.55	m	3.23	w
								2.99	w
								2.63	w

Between 470 and 650 °C the d.t.a. curves of all the compounds show that an exothermic reaction occurs. The anhydrous phases rearrange to form double phosphates, $MZr(PO_4)_2$, with consequent loss of the layer structure. The *X*-ray powder diagrams (Figure 2) confirm this and show that all the compounds have *d*-line spacings very similar to those[10] of $CaZr(PO_4)_2$. As expected, the compounds are no longer ion exchangers and it is not possible to release the transition-metal ion with dilute acids, in contrast to the case for the phases obtained at temperatures up to 450 °C.

Spectra and Magnetism.—Before suggesting stereochemistries from these data, two difficulties should be borne in mind: (*i*) the large amount of literature information available on transition-metal ions, and especially Co^{II} and Ni^{II}, in oxides,[11] zeolites,[12] and adsorbed on silica gel[13] shows that quantitative estimates of the geometries present (*e.g.* tetrahedral–octahedral in the case of Co^{II}) from reflectance measurements are hazardous because of the very different intensities for the electronic transitions characteristic of each geometry; (*ii*) although this difficulty can be partially overcome by extracting information from bulk susceptibility measurements,[14] the presence of bridging oxygen atoms in dehydrated products would invalidate the diagnostic use of such data.

$ZrCo(PO_4)_2{\cdot}4H_2O$. The reflectance spectrum of the room-temperature (r.t.) phase clearly shows that octahedral Co^{II} is present (Figure 3), undiluted with other stereochemistries. There was a broad low-intensity band centred at 1 200 nm followed by a maximum at 515 nm having shoulders at 620 and 475 nm. This spectrum is very similar to that[15] of $[Co(OH_2)_6]^{2+}$ and virtually superimposable on that of $Co_{0.1}Mg_{0.9}O$ (ν_1 at 1 180, ν_2 at 625, and ν_3 at 518 nm; shoulder at higher energy).[16] Susceptibility measurements are in agreement with this structure, $\mu_{eff.}$ = 5.2 B.M.* (Figure 4) being characteristic of the $^4T_1$ ground state of O_h Co^{II}.[15] A new species

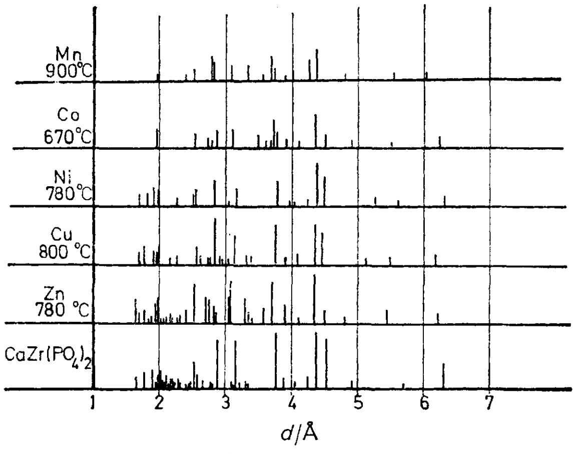

FIGURE 2 *X*-Ray powder data for the double phosphates, $MZr(PO_4)_2$. The data for $CaZr(PO_4)_2$ are shown for comparison

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* 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

[10] C. Bettinali, A. La Ginestra, and M. Valigi, *Atti Accad. naz. Lincei. Sez. VIII*, 1962, **33**, 472.

[11] See, for example, F. S. Stone, *J. Solid State Chem.*, 1975, **12**, 271.

[12] See, for example, M. A. Heilbron and J. G. Vickerman, *J. Catalysis*, 1974, **33**, 434.

[13] B. J. Hathaway and C. E. Lewis, *J. Chem. Soc.* (*A*), 1969, 1176, 1182.

[14] T. A. Egerton, A. Hagan, F. S. Stone, and J. G. Vickerman, *J.C.S. Faraday I*, 1972, 723.

[15] R. L. Carlin, *Transition Metal Chem.*, 1965, **1**, 1.

[16] O. Schmitz-Du Mont, H. Brokopf, and K. Bukhandt, *Z. anorg. Chem.*, 1958, **295**, 7.

began to form before 200 °C, in which range the three water molecules of the same energy were lost and there

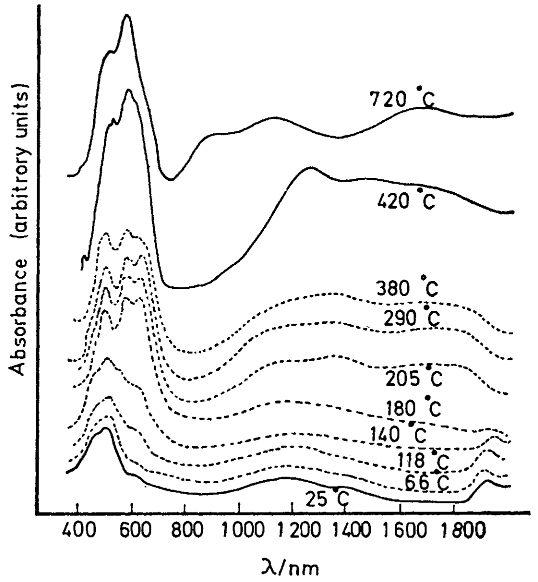

FIGURE 3 Reflectance spectra of the cobalt(II) form: (——) static conditions; (– – –) dynamic conditions

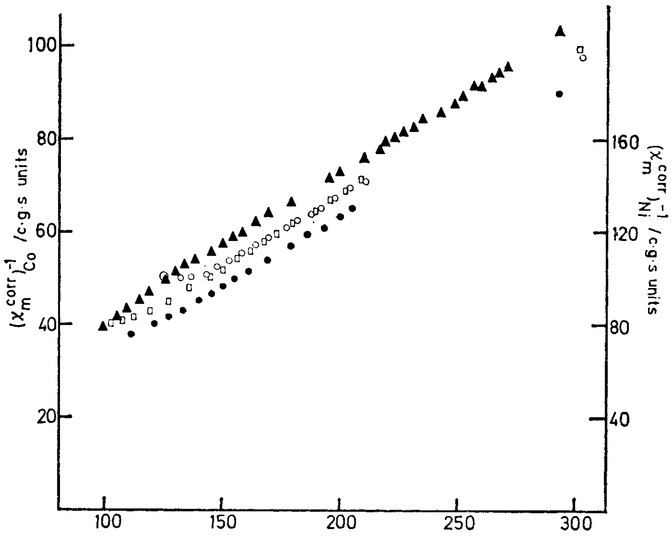

FIGURE 4 Magnetic susceptibility: (○) $ZrCo(PO_4)_2\cdot4H_2O$, $\mu = 5.21$ B.M. at 303 K, $\theta = -28 \pm 3$ K; (□) $ZrCo(PO_4)_2$, $\mu = 4.47$ B.M. at 99 K, 4.77 B.M. at 293 K, $\theta = -25 \pm 3$ K; (▲) $CoZr(PO_4)_2$, $\mu = 5.03$ B.M. at 302 K, $\theta = -14 \pm 3$ K; (●) $NiZr(PO_4)_2$, $\mu = 3.69$ B.M. at 293 K, $\theta = -12 \pm 4$ K

was a further change in spectrum at the final loss of water. This is a clear indication that all the four water molecules in the r.t. tetrahydrate are bonded to the cobalt.

There was a relatively smooth increase in tetrahedral species up to the anhydrous phase $ZrCo(PO_4)_2$. The latter had a static reflectance spectrum (see Figure 3) with bands at 1 665, 1 495, and 1 235 nm in the near i.r. and a peak at 580 nm with shoulders at 615, 525, and 510 nm in the visible region. The band wavenumbers are somewhat closer to those in $[Co(OH)_3(OH_2)]^-$, present in 65% Na[OH] [17] (apart from the shoulder at 510 nm which presumably is caused by a spin-forbidden transition), than in the only slightly C_{3v}-distorted tetrahedron present in Co^{II}–ZnO.[18] This suggests that a tetrahedral structure of the type $[CoO'_3O'']$ is present. There is no convincing evidence for octahedral species, there being no shoulder towards the lower-frequency side of the ν_2 transition. (Since $PO_4^{3-} < H_2O$ in the spectrochemical series,[19] a $[CoO_6]$ chromophore might be expected to have a $^4T_{2g}(F) \leftarrow {}^4T_{1g}$ transition at a slightly higher frequency which would make it unobservable.) As expected, the magnetic moment is lower than that for the hydrate (see Figure 4).

Above the phase transition, the spectrum changed markedly, although still remaining tetrahedral in type. The clearest change was in the near i.r., bands appearing at 2 220, 1 615, 1 110, and 915 nm. Bands in the visible region changed less. It is believed that the splitting observed in ν_2 is a more reliable measure of distortion from tetrahedral symmetry than that in ν_3.[20] The possibility that the component of ν_2 at 915 nm is, in fact, the $^4T_{2g} \leftarrow {}^4T_{1g}$ transition of an octahedral chromophore is discounted on the basis of its high energy and relatively high intensity, and the fact that $\mu_{eff.} = 4.72$ B.M. (0°C) is even lower, as expected, than that of $ZrCo(PO_4)_2$. The ν_2 splitting appears to be much larger than any previously reported for a $[CoO_4]$ chromophore. We suggest that a C_{2v}-distorted tetrahedral geometry is present, caused by two very different Co–O distances and/or a compression along the C_2 axis.

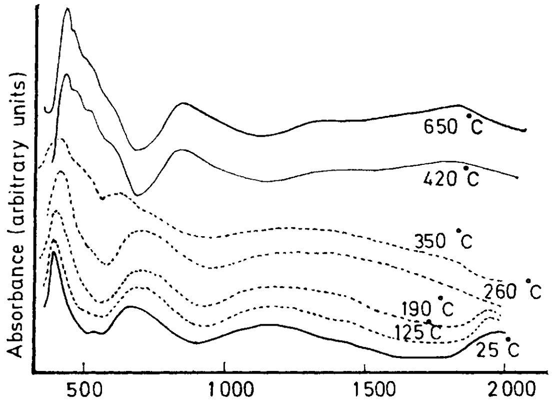

FIGURE 5 Reflectance spectra of the nickel(II) form: (——) static conditions; (— — —) dynamic conditions

$ZrNi(PO_4)_2\cdot4H_2O$. The reflectance spectrum of this compound leaves little doubt that the Ni^{II} is in an octahedral site. Three bands were observed at 1 140, 680,

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[17] S. Gordon and J. M. Screyer, *J. Amer. Chem. Soc.*, 1952, **74**, 3169.

[18] F. Pepe, M. Schiavello, and G. Ferraris, *J. Solid State Chem.*, 1975, **12**, 63.

[19] C. K. Jørgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' Pergamon, London, 1962.

[20] A. B. P. Lever and S. M. Nelson, *J. Chem. Soc.* (*A*), 1966, 859.

and 395 nm, which compare well with those[19] at 1 177, 725, and 395 nm in $[Ni(OH_2)_6]^{2+}$. An octahedral species is still present at *ca.* 260 °C (*i.e.* when 2.5 water molecules have been lost), the very small changes in the spectrum (see Table 4) being in agreement with P–O–Ni bonding, *i.e.* it is again probable that all the four water molecules in the r.t. tetrahydrate are bound to the nickel. From 200—430 °C a new species is evident, characterised by bands at 1 785, 1 350, and 860 nm in the near i.r. and a strong peak at 440 nm with clear shoulders at 614 and 490 nm in the visible. Since there was virtually no absorption between 700 and 680 nm, it seems reasonable to suppose that the initial octahedral structure is destroyed on dehydration. The spectrum changed little on going to temperatures beyond the exothermic phase change. The magnetic moment of 3.69 B.M. for $NiZr(PO_4)_2$ is somewhat lower than that of NiO–ZnO ($\mu_{eff.}$ 4.1 B.M.).[21]

TABLE 4

Reflectance spectra

Compound	Colour	λ^a/nm	Comments ^{b}
$ZrCo(PO_4)_2 \cdot 4H_2O$	Pink	1 200b, 620 (sh), 515, 475 (sh)	Probably $[CoO'_2O_4]$ *ca.* O_h
$ZrCo(PO_4)_2$	Blue	1 665 (sh), 1 495 (sh), 1 235, 615 (sh), 580 525 (sh)	$[CoO'_4]$ *ca.* T_d
$CoZr(PO_4)_2$	Blue-purple	2 220 (sh), 1 615, 1 110, 915, 654, 578, 515	$[CoO'_3O'']$ (see text)
$ZrNi(PO_4)_2 \cdot 4H_2O$	Pale green	1 140, 680, 395	$[NiO'_2O_4]$ *ca.* O_h
$ZrNi(PO_4)_2 \cdot 1.5H_2O$	Pale green	1 165, 680, 395	*ca.* O_h
$ZrNi(PO_4)_2$	Brown	1 785, 1 350, 860, 615 (sh), 490 (sh), 440	see text
$NiZr(PO_4)_2$	Brown	as for $ZrNi(PO_4)_2$	
$ZrCu(PO_4)_2 \cdot 4H_2O$	Pale blue	765b	g_1 2.071, g_2 2.189, g_3 2.283
$ZrCu(PO_4)_2$	Turquoise	845vb	g_1 2.076, g_2 2.198, g_3 2.288
$CuZr(PO_4)_2$	Turquoise	1 050 (sh), 860	g_1 2.063, g_2 2.121, g_3 2.294
$Cu^{2+}(2\%)$–$ZrZn(PO_4)_2 \cdot 4H_2O$			$g_{\parallel}$ 2.395, $g_{\perp}$ 2.077, $A_{\parallel} = 140 \times 10^{-4}$ cm^{-1}

^{a} Static spectra (see text); b = broad, sh = shoulder, vb = very broad. ^{b} O′ and O″ signify oxygen atoms from PO_4; e.s.r. spectra recorded at *ca.* 125 K.

Comparison with literature data so as to arrive at some conclusion on the stereochemistry present is not as straightforward as for Co^{II}. The near-i.r. bands are close in frequency to those found for Ni^{2+} in ZnO,[22] but the structured peak in the visible region is at considerably lower frequency than that found for the ${}^3bT_{1g} \leftarrow {}^3aT_{1g}$ transition in (tetrahedral) $Ni_xZn_{1-x}O$ (650 and 615 nm)[22] and in nickel(II) spinel (588 nm).[23] This suggests that a plausible stereochemistry for $NiZr(PO_4)_2$ and, by implication, $ZrNi(PO_4)_2$, is a very distorted tetrahedron. Against this is the rather similar spectrum found for Ni^{2+}–$GaInO_4$, in which matrix the Ni^{2+} is octahedrally co-ordinated.[24] There seems little possibility of choosing between these alternatives since there are few data on tetrahedral $[NiO_4]$ species. Nevertheless, we prefer the first alternative since it would better explain the three shoulders on the 440 nm band (crystal-field energy-level diagrams predict that the ${}^3T_{1g}$, ${}^1E_g$, and ${}^1T_{2g}$ levels should lie close together)[23] and the high magnetic moment compared to octahedral co-ordination.

$ZrCu(PO_4)_2 \cdot 4H_2O$.—The reflectance spectrum of this compound and the changes on dehydration are shown in Figure 6. The room-temperature spectrum consisted of a broad band centred at 765 nm with no further absorption ascribable to *d–d* transitions at higher and lower energies. Much information is available in the literature on copper–oxygen systems to allow comparison.[25] Thus the much lower frequency than is found for Cu^{2+}–ZnO (*d–d* transitions at 1 680 and 1 560 nm at r.t. according to ref. 26) and for dodecatungstocuprate(II) anion (tetrahedral environment; *d–d* band at 1 430 nm)[27] excludes the presence of tetrahedral $[CuO_4]$. Similarly, highly tetragonally distorted $[CuO_4 + 2O]$ or square planar $[CuO_4]$ systems are known to give absorptions at frequencies in the range 500—650 nm[25] which also does not fit the present spectrum. Comparison with correlations between tetragonality and band position[25] suggest a moderately tetragonally distorted octahedral chromophore. Unfortunately, the e.s.r. spectra are uninformative, both the tetrahydrate and $ZrCu(PO_4)_2$ giving signals characteristic of exchange narrowing[25] (Figure 7). The smooth

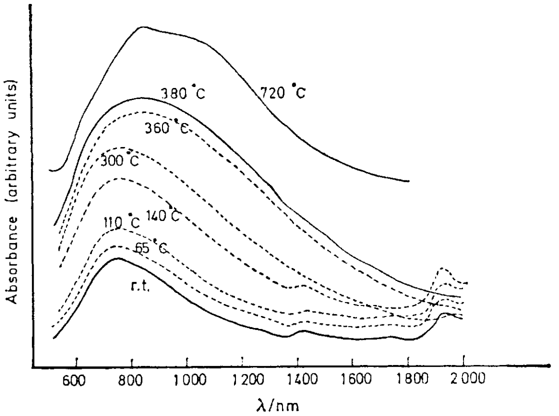

FIGURE 6 Reflectance spectra of the copper(II) form: (——) static conditions; (– – –) dynamic conditions

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changes in spectrum up to $ZrCu(PO_4)_2$ indicate that the stereochemistry remains essentially the same. As there was no drastic change in energy of the absorption band after the exothermic phase change (at 720 °C), it seems reasonable to again suggest a tetragonal structure. There was no evidence to suggest that a tetrahedral $[CuO_4]$ chromophore is present at >380 °C. A significant change in e.s.r. spectrum occurred only at >650 °C when a three-*g* value signal was obtained and little evidence of exchange narrowing. This is presumably caused by a rhombic octahedral, or grossly misaligned tetragonal octahedral, stereochemistry.[25] In agreement with this, there was a slight splitting in the *d–d* band, not sufficiently pronounced to indicate a gross change in symmetry or the presence of different site symmetries.

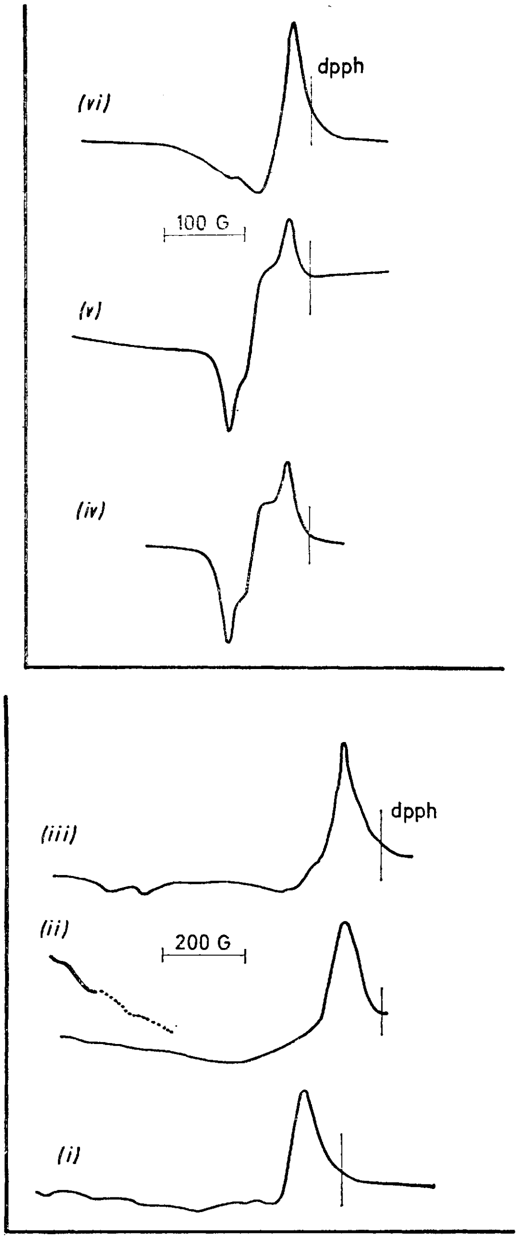

FIGURE 7 E.s.r. spectra: (*i*) Cu–$ZrZn(PO_4)_2{\cdot}4H_2O$; (*ii*) Cu–$ZrZn(PO_4)_2$; (*iii*) Cu–$ZnZr(PO_4)_2$; (*iv*) $ZrCu(PO_4)_2{\cdot}4H_2O$; (*v*) $ZrCu(PO_4)_2$; (*vi*) $CuZr(PO_4)_2$. dpph = Diphenylpicrylhydrazyl

An attempt was also made to obtain some indication as to the zinc(II) site in $ZrZn(PO_4)_2{\cdot}4H_2O$ using the e.s.r. spectrum of Cu^{2+} (2%) as a probe. The spectrum of the r.t. form (Figure 7) is, indeed, indicative of an axial, probably tetragonal, system, being very close to that of $Cu_xMg_{1-x}O$.[28] A similar site was still present after dehydration, but beyond the exothermic phase change (750 °C) the spectrum changed entirely. Although an unambiguous attribution is not possible, the indications are that the high-temperature zinc(II) double phosphate is different in stereochemistry from that of Cu^{II}.

Conclusions.—Despite the limitations of the data obtainable on powder specimens, several points have arisen from this work: (*i*) 100% exchange of Na^+ and H^+ ions in $ZrHNa(PO_4)_2{\cdot}5H_2O$ by transition-metal ions is possible; (*ii*) a layer structure similar to that of zirconium phosphate itself is retained by all the $ZrM(PO_4)_2{\cdot}4H_2O$ materials obtained, as also are the cation-exchange properties; (*iii*) there is evidence that the water molecules are all bound to the transition-metal ions; and (*iv*) the compounds of Co^{II}, Ni^{II}, and Cu^{II} appear to have similar stereochemistries in their hydrates. On dehydration, especially after the last loss of water, the transition-metal ions behave differently: Co^{II} and Ni^{II} markedly change whilst Cu appears to retain a tetragonal stereochemistry. This may be due prevalently to the flexible nature of the zirconium phosphate matrix which adapts itself to the preferred stereochemistry of the transition-metal ions.

It is not yet possible to fully define the site available to the transition-metal ions. Work on partially exchanged materials and on exchange with metal–ammine species (which may allow conclusions to be drawn as to which oxygen atoms in the lattice are involved in bonding to the transition-metal ions) is under way.

[6/399 *Received, 27th February*, 1976]

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