Intercalation and Co-ordination of Ammonia and 1,2-Diaminoethane into Cobalt(II)-, Nickel(II)-, Copper(II)-, and Vanadium(IV)-exchanged α-Tin Phosphate

Lucilla Alagna and Anthony A. G. Tomlinson*
I.T.S.E., Area della Ricerca di Roma, C.N.R., C.P.10 Monterotondo Staz., 00016 Rome, Italy
Enrique Rodriguez-Castellon,* Pascual Olivera Pastor, and Sebastian Bruque
Departamento de Quimica Inorganica, Universidad de Malaga, 29071 Malaga, Spain

The reactions of gaseous ammonia and 1,2-diaminoethane (en) with α-$SnM(PO_4)_2{\cdot}H_2O$ (M = Co^{2+} Ni^{2+}, Cu^{2+}, or VO^{2+}) have been investigated. Reactions occur with retention of the layered phosphate structure, the NH_3-containing materials giving rise to an interlayer separation of 10.0 ± 0.05 Å. Co-ordination of NH_3 occurs in all cases except for VO^{2+} (as deduced from electronic absorption spectra); Co^{2+} is present in a tetrahedral, probably CoN_3O, environment not found in classical co-ordination chemistry, presumably as a consequence of the restricted space available in the interlayer. Ammonia co-ordinates to Ni^{2+} to give a *cis*-octahedral NiN_3O_3 environment and for Cu^{2+} a tetragonal octahedral environment, probably $CuN_2O_2O'_2$. An extensive surface and interlayer complex chemistry is displayed by low (2%) loaded Cu^{2+}-exchanged materials, for which e.s.r. studies have been made. The layer structure is retained on heating to 110 °C, stability to loss of ammonia being in the order: $Cu^{2+} > Co^{2+} > Ni^{2+}$, with the greatest change in geometry for the partially dehydrated products occurring in the case of Ni^{2+} which adopts a five-co-ordinate environment. 1,2-Diaminoethane co-ordinates to both Cu^{2+} and Co^{2+}, although only as a monodentate ligand; it does not appear to co-ordinate to either Ni^{2+} or VO^{2+}, instead showing a tendency to hydrogen-bond to phosphate groups in the interlayer.

A considerable intercalation chemistry has been developed recently by allowing transition-metal ions to co-ordinate to intercalated amine ligands.[1] α-Zirconium phosphate has been particularly fruitful as a matrix in these studies because it is the best characterised and most thermally stable member of the Group 4A phosphates.[2] In addition, it is also the only member of the series of known crystal structure.[3] Because of this it has been found possible to rationalise the very varied non-stoicheiometric materials obtained. More recently, attention has turned to other members of this series as intercalation matrices, despite the fact that they are (as yet) of unknown crystal structure. Thus, the intercalation of large aromatic amines into γ-zirconium phosphate leads to products of different stoicheiometry, interlayer amine orientation, and transition-metal complex pillar chemistry.[4]

Tin phosphate also forms a swellable, layered material of possible interest as a support, but was soon rejected for this use because of its relative instability to alkalis.[5] Despite this drawback it has recently been shown that α-tin phosphate and its n-butylamine intercalate give Co^{2+}-, Ni^{2+}-, and Cu^{2+}-exchanged phases[6] similar to those of the α-zirconium phosphate analogue.[7] The present paper describes the materials obtained when NH_3 and $NH_2C_2H_4NH_2$ (1,2-diaminoethane, en) are treated with bivalent transition-metal ion-exchanged forms of α-$Sn(HPO_4)_2$. The aim was to probe the interlayer region of the material in order to investigate whether it is different from that present in the α-zirconium phosphate analogue.

Experimental

The highly crystalline starting materials α-$Sn(HPO_4)_2{\cdot}H_2O$ (α-SnP; d_{002} = 7.8 Å, surface area 11.2 m^2 g^{-1}), α-$Sn(NH_2Bu^n)_2(HPO_4)_2{\cdot}H_2O$ (d_{002} = 19.5 Å, surface area = 25.7 m^2 g^{-1}), and the metal-ion exchanged phases were prepared and stored as reported previously.[6] In all cases, after filtering from the mother-liquors, the materials were washed well with hot water to remove any surface metal ion. Low-exchanged (nominally 2%) copper(II) forms were prepared by contacting with aqueous $CuCl_2$ solutions (10^{-3} mol dm^{-3}) for *ca.* 30 s, then quickly filtering and thoroughly washing with warm water. Samples containing the pure isotope $^{63}Cu^{2+}$ were also prepared, again from $^{63}CuCl_2$, with the aim of probing for the presence of *N*-superhyperfine effects in the e.s.r. spectra. The 20% VO^{2+}-exchanged phase of α-$Sn(NH_2Bu^n)_2(HPO_4)_2$ was obtained by shaking an aqueous suspension of the exchanger in a solution of $VO(SO_4){\cdot}5H_2O$ (1 × 10^{-3} mol dm^{-3}) for 2 d at 25 °C.

The ammonia complexes were obtained by placing the metal-exchanged phases in a desiccator in the presence of ammonia vapour for 1 d at 25 °C. The samples were then stored in a desiccator over H_2SO_4 to eliminate adsorbed surface ammonia. The en complexes were obtained similarly (en vapour at 50 °C for 1 d) and stored as for the ammonia analogues. All measurements were carried out on freshly prepared materials prior to any loss of amine.

Physical and Chemical Measurements.—Phase purities of all materials were checked throughout manipulations *via* x.r.d. patterns recorded on a Siemens D500 powder diffractometer (nickel-filtered Cu-K_α radiation, quartz calibrated patterns, 2θ accurate to ± 0.05°). The x.r.d. of the fully exchanged transition-metal ion species were as reported previously.[6] (The *X*-ray powder diagrams all showed lines corresponding to d_{002} and sometimes higher-order reflections. Throughout all manipulations, the reflections corresponding to *hk*0 planes persisted, indicating that the parent layer structure is retained.)

Metal-ion contents were estimated by atomic absorption spectrophotometry on a Varian 475 instrument and thermo-gravimetric analyses using a Du Pont 900 series instrument.

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* *Non-S.I. unit employed*: G = 10^{-4}T.

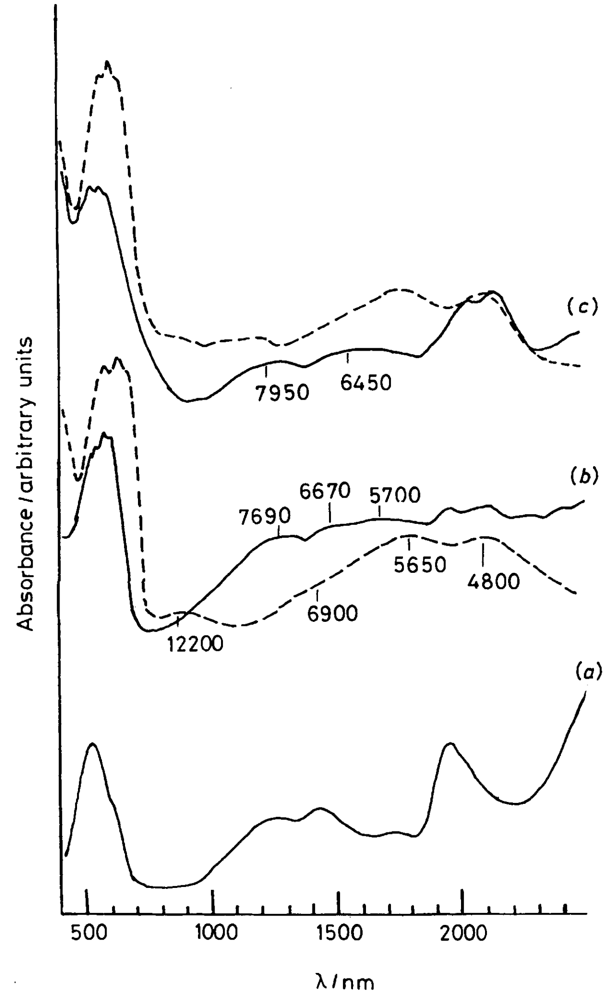


Figure 1. Electronic reflectance spectra for Co^{2+}-containing materials. (*a*) α-$SnCo(PO_4)_2 \cdot 6H_2O$, (*b*) α-$SnCo(en)_{0.9}(PO_4)_2 \cdot 2.9H_2O$, and (*c*) α-$SnCo(NH_3)_{2.85}(PO_4)_2 \cdot 3.7H_2O$; (—) as prepared; (- - -) after heating at 110 °C

Electronic reflectance spectra were measured on a Beckmann DK 2A spectrophotometer against MgO as reference, and e.s.r. spectra on a Varian E-9 instrument with a standard liquid-nitrogen attachment.

Results and Discussion

Metal-ion Exchanged Forms.—Before discussing the amine-treated materials, we first comment on the interlayer environment available to Co^{2+}-, Ni^{2+}-, Cu^{2+}- and VO^{2+}-exchanged α-SnP.

Apart from the bands at 16 000, 19 250, and 20 600 cm^{-1} in the electronic reflectance spectrum reported previously,[6] α-$SnCo(PO_4) \cdot 6H_2O$ shows a near-i.r. band at *ca.* 8 000 cm^{-1}, confirming that the environment present is pseudo-octahedral (CoO_6). There is a clear low-energy shift of the near-i.r. band envelope as the material loses water and anhydrous α-$SnCo(PO_4)_2$ contains pseudo-tetrahedral CoO_4 [bands at 8 000 and 5 800 cm^{-1}, attributable to components of the ${}^4T_1(F) \leftarrow {}^4A_2$ transition]. This behaviour is as for α-$ZrCo(PO_4)_2$, apart from a slight difference in the *Dq* value.

As prepared, α-$SnNi(PO_4)_2 \cdot 7H_2O$ gives bands in the visible-near u.v. region at 25 000, 15 100, and 13 650 cm^{-1}, from which it was concluded that the geometry of Ni^{2+} was octahedral.[6] However, the near-i.r. region reveals that there is a considerable splitting of the ${}^2T_1 \longleftarrow {}^3A_2$ transition into two clear components at 7 020 and 8 500 cm^{-1}, *i.e.* an indication that the environment is a tetragonally distorted rather than a regular octahedral one, and differs from that of the zirconium analogue.[7] This large splitting, together with the fact that on heating at 108 °C three water molecules are lost initially (although without change in the electronic spectrum), indicates the presence of a more highly strained site in the interlayer than exists in the zirconium analogue. However, despite this difference between α-$Sn(HPO_4)_2 \cdot 2H_2O$ and α-$Zr(HPO_4)_2 \cdot H_2O$, anhydrous α-$SnNi(PO_4)_2$ gives the same electronic absorbance spectrum, for which further support is being sought *via* extended *X*-ray absorption fine structure (EXAFS) spectroscopy.[8]

The electronic spectrum of α-$SnCu(PO_4)_2 \cdot 3H_2O$ shows a broad band at 12 350 cm^{-1} with an undefined shoulder at *ca.* 11 000 cm^{-1}, as for α-$ZrCu(PO_4)_2 \cdot 4H_2O$. The only difference between the two is the fact that although dehydration at 400 °C still gives rise to a layered material (as does the α-ZrP analogue) the *d*—*d* spectrum shows a major band at lower energy than that for the (α-ZrP) analogue: 11 400 *vs.* 12 500 cm^{-1}.

For all three cases, then, adsorption of NH_3 or en involves access to pseudo-octahedral sites in the interlayer, similar to, but not identical with, those of the zirconium analogue.

A further point of note is that when both Co^{2+} and Ni^{2+} adsorb NH_3 or en there is a large decrease in volume without change in mass, with d_{002} collapsing by *ca.* 6 (Co^{2+}) and *ca.* 7 Å (Ni^{2+}), see Table 1. We ascribe this to the presence of specific strong hydrogen bonds in the initial fully hydrated phases (in which the water molecules themselves act as 'pillars') which are subsequently destroyed by amine diffusion.

Co^{2+} *and* Ni^{2+}. Both α-$SnCo(PO_4)_2 \cdot 6H_2O$ and α-$SnNi(PO_4)_2 \cdot 7H_2O$ undergo layer contraction on adsorption of both NH_3 and en, and the colours of the materials change (Table 1). The electronic absorbance spectrum of α-$SnCo(NH_3)_3(PO_4)_2 \cdot 3.5H_2O$ shows that the characteristic near-i.r. combination bands of water at 1 440 and 1 950 cm^{-1} have been replaced by NH_3 combination bands at 2 050 and 2 150 cm^{-1}, an indication that the metal ion is co-ordinated to NH_3 ligands. Further, there are distinct changes in the *d*—*d* regions, the relative intensity of the visible band envelope being higher for the NH_3-containing material. The latter also contains further components in the near-i.r. region, at 6 500, 5 900 (sh), and *ca.* 4 000 cm^{-1}, pointing to the presence of a pseudo-tetrahedral species (Figure 1).[9] (A five-co-ordinate environment may be eliminated because the spectra do not contain the characteristic shoulder at 11 500—13 000 cm^{-1}.[10]) Further, the near-i.r. envelope lies at an energy lower and outside the range expected for a CoN_4 chromophore (barycentres in the range *ca.* 9 000—11 300 cm^{-1}, depending on the ligand-field strength of the *N*-donor[11,12]). It is, however, in the range expected for a CoN_2O_2 or CoN_3O[12] chromophore. The latter is more in line with the t.g.a. results and the changes in the spectra on dehydration.

Uptake of en was expected to give rise to significant changes on co-ordination; however the spectrum obtained instead gave a similar *d*—*d* band envelope, with energies slightly lower than for the NH_3-containing material (Figure 1). The implication is that the en is not bonded in a bidentate fashion to the Co^{2+} within the layers but may be monodentate (Scheme 1).

Evidence for protonation of one end of the diamine is indicated from the i.r. spectrum, which shows a distinct sharp shoulder in the region expected for -NH_3^+ [Figure 2(*b*)].

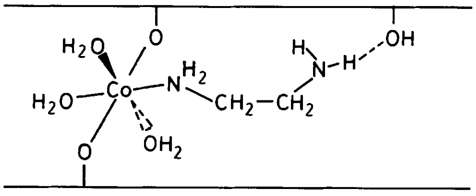
For neither NH_3 nor en was any evidence found for $[CoN_6]^{2+}$ species. This confirms that diffusion of the amines does not occur with partitioning between different cobalt(II) sites in the interlayer.

Both materials give the same electronic spectrum after losing

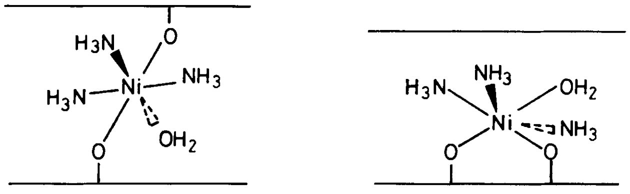
Table 1. Compositions and interlayer distances of the materials

Material as prepared	Colour	d_{002}/Å	Analysis^a/% C	H	N
α-$SnCo(NH_3)_{2.85}(PO_4)_2{\cdot}3.7H_2O$	Pale violet-brown	9.93(16.13)^b		3.30(3.30)	8.20(8.25)
α-$SnCo(NH_3)_{2.43}(PO_4)_2{\cdot}1.9H_2O^c$				2.50(2.50)	7.70(7.70)
α-$SnCo(en)_{0.9}(PO_4)_2{\cdot}2.9H_2O$	Pale violet	9.84	4.40(4.45)	2.70(2.70)	5.20(5.15)
α-$SnCo(en)_{0.9}(PO_4)_2{\cdot}2.1H_2O^c$			4.75(4.70)	2.45(2.50)	5.55(5.50)
α-$SnNi(NH_3)_{2.8}(PO_4)_2{\cdot}4.9H_2O$	Pale blue	9.99(17.23)		3.60(3.60)	7.70(7.70)
α-$SnNi(NH_3)_{1.16}(PO_4)_2{\cdot}3.0H_2O^c$				2.15(2.15)	3.65(3.70)
α-$SnNi(en)_{0.8}(PO_4)_2{\cdot}3.5H_2O$	Pale green	11.10	3.95(4.00)	2.80(2.80)	4.70(4.70)
α-$SnNi(en)_{0.42}(PO_4)_2{\cdot}2.7H_2O^c$			2.20(2.30)	2.00(2.00)	2.70(2.65)
α-$SnCu(NH_3)_{2.1}(PO_4)_2{\cdot}2.6H_2O$	Blue	9.98(9.94)		2.55(2.55)	6.50(6.50)
α-$SnCu(NH_3)_{1.93}(PO_4)_2{\cdot}1.5H_2O^c$				2.05(2.05)	6.30(6.25)
α-$SnCu(en)_{0.6}(PO_4)_2{\cdot}2.2H_2O$	Blue	9.40	3.25(3.20)	2.00(2.05)	3.70(3.75)
α-$SnCu(en)_{0.5}(PO_4)_2{\cdot}0.5H_2O^c$			2.95(2.90)	1.20(1.20)	3.35(3.40)
α-$SnVO(NH_3)_{3.1}(PO_4)_2{\cdot}3.4H_2O$	Pale green	10.04(14.24)		3.30(3.25)	8.80(8.80)
α-$SnVO(NH_3)_{2.0}(PO_4)_2{\cdot}2.8H_2O^c$				2.60(2.60)	6.15(6.20)
α-$SnVO(en)_{1.05}(PO_4)_2{\cdot}3H_2O$	Pale grey-green	14.10(diffuse)	3.10(3.10)	2.90(2.90)	5.95(5.95)
α-$SnVO(en)_{0.6}(PO_4)_2{\cdot}2.2H_2O^c$			3.15(3.20)	2.00(2.05)	3.70(3.70)

[a] Calculated values are given in parentheses. [b] Interlayer distance of the full hydrate phase. [c] The composition after heating at 110 °C for 24 h.



Scheme 1.



(I)

(II)

Scheme 2.

2 NH_3 and 1 en (plus molecules of H_2O) on heating at 110 °C (Figure 1). The spectra are again as expected for pseudo-tetrahedral geometry. There is evidence for the presence of two different tetrahedral species, the weak bands between 12 200 and 8 500 cm^{-1} being ascribed to a CoN_4 chromophore. More striking is the fact that the major near-i.r. band envelope has shifted to very low energy with the barycentre at *ca.* 5 800 cm^{-1}, considerably lower than expected for a CoN_2O_2 chromophore.[10] It is necessary to invoke either a very weakly bonded en molecule or a tetrahedral CoO_4 with all oxygen donor atoms being provided by interlayer phosphate, to rationalise this result.

The nickel(II) analogues also give electronic spectra indicative of non-partitioned amine and, as expected, clearer diagnostic evidence for stereochemistry. The *d*—*d* spectra (Figure 3) clearly show that a pseudo-octahedral geometry is present in α-$SnNi(NH_3)_3(PO_4)_2{\cdot}3.7H_2O$, with absence of considerable splitting on the ν_1 band ($^3T_1 \longleftarrow {}^3A_2$) pointing to a *cis* rather than *trans* geometry.[13] Applying the classic average environment rule[14] {and recalling that ν_1 $[Ni(NH_3)_6]^{2+}$ 10 750 cm^{-1} and ν_1 $[Ni(OH_2)_6]^{2+}$ 8 500 cm^{-1}[14]} leads to the conclusion that the species present contains a NiN_3O_3 chromophore [ν_1(calc.) 9 600 cm^{-1}]. The similar position of OH_2 and $PO_4{}^{3-}$ in the spectrochemical series[15] means that it is not possible to conclude which oxygen atoms derive from water and which from layer phosphate. Nevertheless, combining the above results with the interlayer distance of d_{002} = 10 Å suggests that the interlayer complex is present as in (I) rather than in (II).

As for Co^{2+}, diffusion of en does not follow expectations. Not only is there no high-energy shift of the *d*—*d* bands as would be expected for *N*-co-ordination, but the *d*—*d* bands of this material lie at energies *lower* than for the starting α-$SnNi(PO_4)_2{\cdot}7H_2O$. We conclude that the en does not bond to the Ni^{2+}. On intercalation it presumably hydrogen-bonds to the phosphate groups. The i.r. spectrum shows a strong band at 3 500 cm^{-1} [Figure 2 (*c*)] in agreement with this suggestion. These results and the considerable layer contraction (to 11.10 Å) found on intercalating en may be rationalised by suggesting that the hydrogen bonding involving the en occurs through bridging water molecules.

Both materials give almost identical electronic spectra after removal of molecules of water, the drastic change in band shapes and energies clearly showing that the species present are not pseudo-octahedral (Figure 3). Band energies are very close to those expected for a trigonal bipyramidal geometry.[7]

Cu^{2+} *and* VO^{2+}. Adsorption of gaseous NH_3 by α-$SnCu(PO_4)_2{\cdot}3H_2O$ gives rise to an immediate colour change from pale to intense blue. The *d*—*d* band (Figure 4) shifts from 12 350 to 14 800 cm^{-1} (plus an unclear shoulder at *ca.* 11 000 cm^{-1}), clear evidence that NH_3 bonds to the exchanged Cu^{2+}. Less clear is how many NH_3 molecules are bonded [although analysis provides a guide, the possibility exists that the ammonia may form ammonium ion and/or the diffusion dynamics may be such as to give rise to partitioning of NH_3 co-ordination between different copper(II) sites].

Five-co-ordinate-type species may be discounted (square-based pyramidal because the *d*—*d* band energy is too low and trigonal bipyramidal because it is too high, and because the e.s.r. spectrum does not show $g_{\parallel} < g_{\perp}$[14]). The spectrum is very similar to that expected for a distorted tetragonal octahedral geometry, having close axial oxygen donor atoms.

Similarly, the en-containing analogue also gives a shift to higher energy of the *d*—*d* band envelope, indicating that co-ordination occurs, although ambiguity exists as to whether a monodentate en ligand is involved [the stoicheiometry agrees with one en per two Cu^{2+}, suggesting partitioning of the en between copper(II) sites in the interlayer, yet the width of the *d*—*d* band is as expected for a single complex in the interlayer].

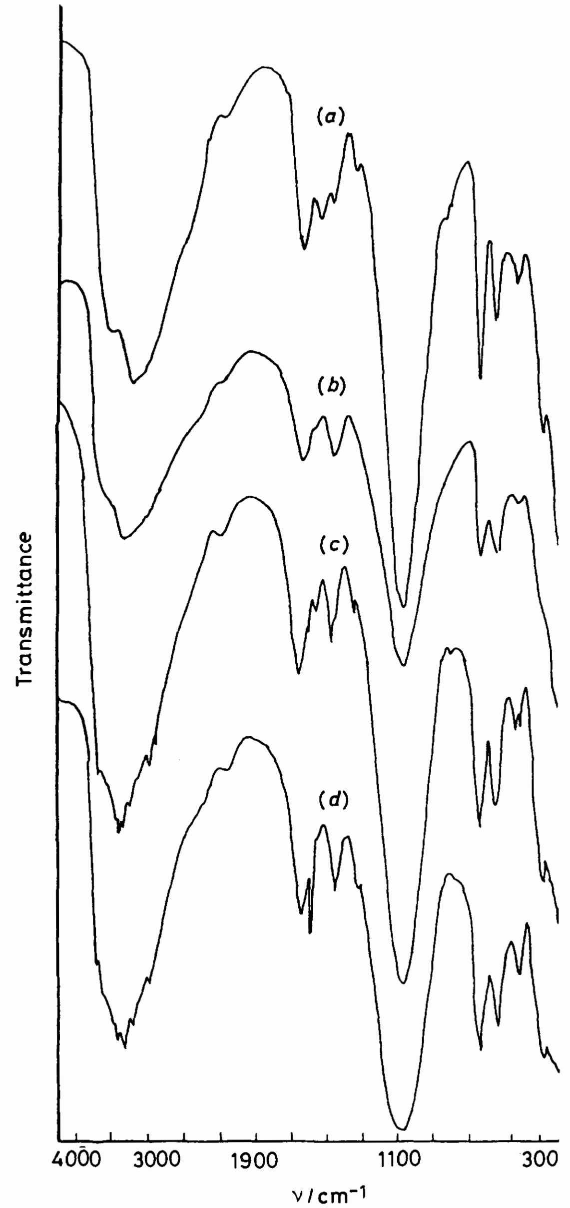


Figure 2. I.r. (KBr disks) spectra of (*a*) α-SnVO(en)$_{0.6}$(PO$_4$)$_2$$\cdot$2.2H$_2$O, (*b*) α-SnCo(en)$_{0.9}$(PO$_4$)$_2$$\cdot$2.9H$_2$O, (*c*) α-SnNi(en)$_{0.8}$(PO$_4$)$_2$$\cdot$3.5H$_2$O, and (*d*) α-SnCu(en)$_{0.6}$(PO$_4$)$_2$$\cdot$2.2H$_2$O

As expected, the fully exchanged Cu^{2+}-containing materials gave e.s.r. spectra characteristic of magnetic exchange coupling, from which little information can be extracted.[16] The spectra of 2% Cu^{2+}-loaded materials gave more resolved *g* and *A* tensors, although at such low loadings the possibility arises that surface, rather than interlayer, species are involved. First, we note that throughout for all manipulations the highly crystalline (*i.e.* low surface area) α-Sn(HPO$_4$)$_2$$\cdot$H$_2$O was utilised. Secondly, we note that ^{63}CuCl$_2$ was utilised to exchange the protons in attempts to observe ^{63}Cu^{2+}–N superhyperfine structure, whereas Cu(O$_2$CMe)$_2$ was used previously. (Although in no case was such structure observed, the figures indicate the isotopically pure materials, because they gave slightly more resolved e.s.r. spectra.) Now, uptake of Cu^{2+} from CuCl$_2$ solutions by both α-SnP and α-Sn(NH$_2$Bu^n)$_2$(HPO$_4$)$_2$$\cdot$H$_2$O occurs at pH 3—4 with a slow-rise isotherm, *i.e.* at very low uptake considerable distribution between the surface and interlayer occurs. Conversely, uptake of Cu^{2+} from Cu(O$_2$CMe)$_2$ solution, occurring at pH 5—6, gives a more normal Langmuir uptake curve and consequently mainly interlayer exchange of Cu^{2+} is expected.

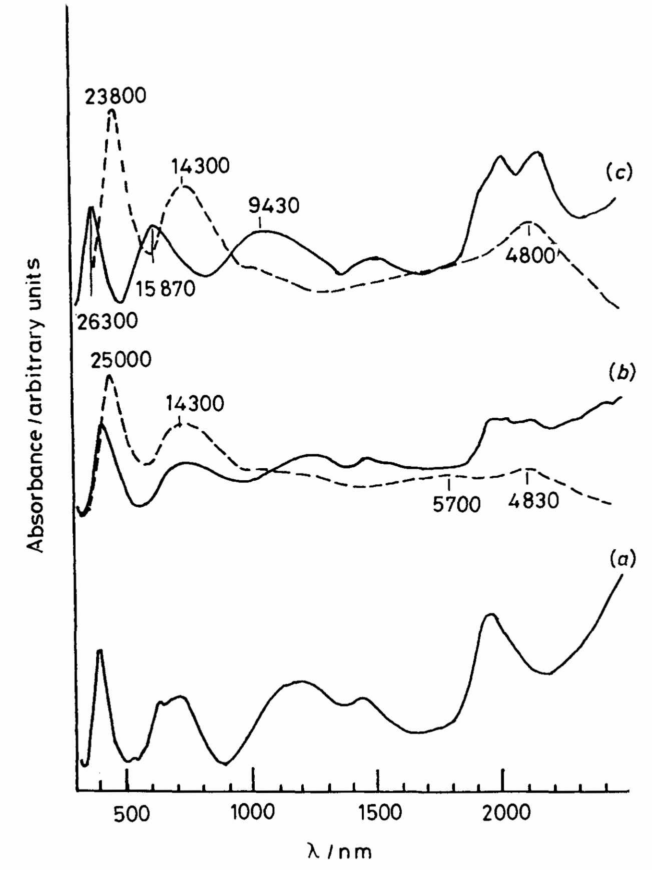


Figure 3. Electronic reflectance spectra for Ni^{2+}-containing materials. (*a*) α-SnNi(PO$_4$)$_2$$\cdot$7H$_2$O, (*b*) α-SnNi(en)$_{0.8}$(PO$_4$)$_2$$\cdot$3.5H$_2$O, and (*c*) α-SnNi(NH$_3$)$_{2.8}$(PO$_4$)$_2$$\cdot$4.9H$_2$O; (—) as prepared; (– – –) after heating at 110 °C

The spectra of Figures 5—7 can then be readily interpreted keeping these two points in mind. α-SnCu$_{0.02}$H$_{1.96}$(HPO$_4$)$_2$$\cdot$H$_2$O itself shows a single e.s.r. signal with *g* parameters slightly higher ($g_\parallel$ 2.44, $g_\perp$ 2.07$_6$) than those found previously for the α-zirconium phosphate analogue.[15] Thus, although the environment available in both is a tetragonally distorted axial geometry, the covalent bonding is lower in the case of Sn$^{\text{IV}}$.[16] Conversely, low exchange of Cu^{2+} into the n-butylamine analogue clearly gives two species, for both ^{63}CuCl$_2$ and Cu(O$_2$CMe)$_2$ exchange (Figure 5). Again, the spectra are characteristic of tetragonally distorted axial species except for species (**B**) arising in the former experiment, for which the lower $g_\parallel$ value of 2.32$_4$ presumably reflects higher covalent bonding with matrix phosphate oxygen atoms compared with species (**A**).

The distinction between surface and interlayer copper(II) complexation is clear when NH$_3$ is adsorbed by both Cu^{2+}-exchanged forms (Figure 6) α-SnCu$_{0.02}$H$_{1.96}$(PO$_4$)$_2$$\cdot$H$_2$O and the n-butylamine analogue. Each gives a spectrum showing one signal, the former with $g_\parallel$ and $A_\parallel$ parameters expected for all-*O* tetragonal octahedral axial geometry. However, the latter, with $g_\parallel$ 2.29$_6$, $g_\perp$ 2.06$_9$ and $A_\parallel$ 170 G, clearly is indicative of coordination by NH$_3$ (whether two or three is not clear, there is a spread in e.s.r. parameters for diamines of known crystal structure[17]). This signal is presumably mainly due to a surface species since partial dehydration provides evidence for the

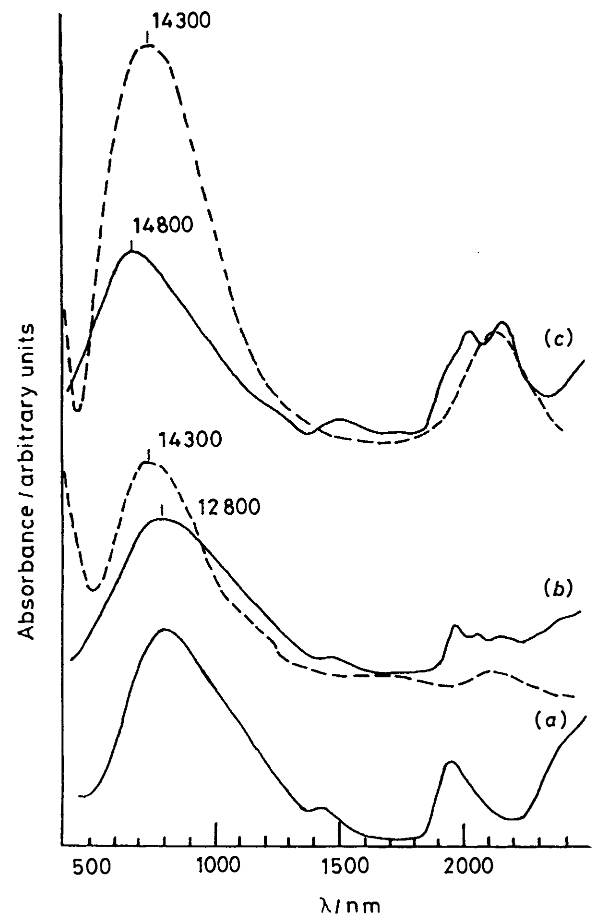


Figure 4. Electronic reflectance spectra of (*a*) α-$SnCu(PO_4)_2 \cdot 3H_2O$, (*b*) α-$SnCu(en)_{0.6}(PO_4)_2 \cdot 2.2H_2O$, and (*c*) α-$SnCu(NH_3)_{2.1}(PO_4)_2 \cdot 4.9H_2O$; (—) as prepared; (– – –) after heating at 110 °C

Table 2. E.s.r. parameters of low-loaded Cu^{2+}-exchanged materials (*X*-band, 77 K)

Material		g_{11}	$g_{\perp}$	A/G
α-$SnCu_{0.02}H_{1.96}(PO_4)_2 \cdot H_2O$		2.442	2.076	116
α-$SnCu_{0.02}H_{1.96}(PO_4)_2 \cdot H_2O$ + NH_3(g, 25 °C)		2.379	2.069	128
α-$SnCu_{0.02}H_{1.96}(PO_4)_2 \cdot H_2O$	**(A)**	2.451		103
+ en(vap., 50 °C)	**(B)**	2.401	2.08	121
α-$SnCu_{0.02}(NH_2Bu^n)_{1.96}(HPO_4)_2 \cdot H_2O$	**(A)**	2.385	2.073	125
	(B)	2.421	2.053	125
	(C)		2.018	
$Sn^{63}Cu_{0.02}(NH_2Bu^n)_{1.96}(HPO_4)_2 \cdot H_2O$	**(A)**	2.31	2.074	180
+ NH_3(g)	**(B)**	2.262	2.05	180
	(C)	2.20		205
$^{63}Cu_{0.02}(NH_2Bu^n)_{1.96}(HPO_4)_2 \cdot H_2O$		2.30	2.07	170
$Cu_{0.02}(NH_2Bu^n)_{1.96}(HPO_4)_2 \cdot H_2O$ + en(vap.,50 °C)		2.202	2.015	190

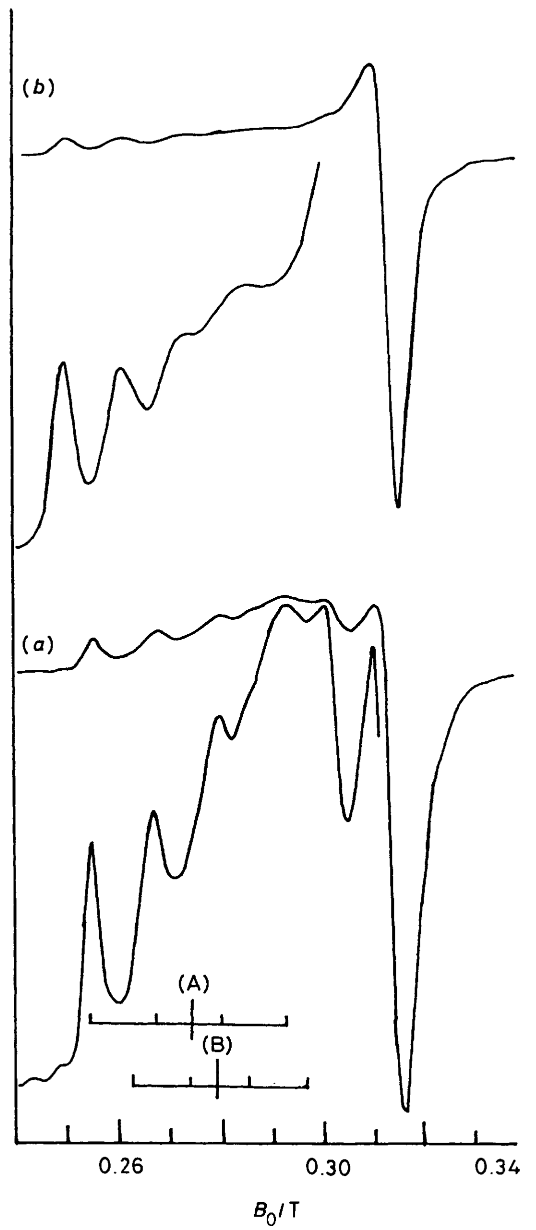


Figure 5. E.s.r. spectra of (*a*) $Sn^{63}Cu_{0.02}(NH_2Bu^n)_{1.96}(HPO_4)_2 \cdot H_2O$ and (*b*) $Sn^{63}Cu_{0.02}H_{1.96}(PO_4)_2 \cdot H_2O$

growth of a second signal with $A_{\parallel}$ 160 G, as expected for some loss of surface NH_3. In the analogous case, but for exchange with $Cu(O_2CMe)_2$, at least three species are visible (as confirmed by measurement of the spectrum at *Q*-band), all of which can be imputed to NH_3-co-ordinated complexes (see Figure 6). It is tempting to assign species (**A**) as due to a complex with two NH_3, and species (**B**) to one with three or four NH_3.[18] Of particular interest is species (**C**), having a very low *g*, 2.19_7, and high $A_{\parallel}$, 205 G, diagnostic of a non-tetragonal octahedral geometry. Partial dehydration simplifies the $g_{\perp}$ region, a signal at *ca.* 2.0 disappearing (the component of a fourth species, having only very weak $A_{\parallel}$ structure?) and the hyperfine lines of species (**B**) decrease significantly in intensity. This provides further evidence that species (**B**) indeed contains three or four co-ordinated NH_3 molecules (unstable to ammonia loss) and is a surface species; (**A**) is then also a surface species (and is identical with that present in the $CuCl_2$-exchanged analogue). We then suggest that species (**C**) is within the interlayer; although it is clearly co-ordinated to NH_3, and the e.s.r. parameters are close to those expected for a distorted $Cu(NH_3)_5{}^{2+}$ moiety,[19] unfortunately the overlap in the $g_{\perp}$ region prevents quantitation of the $g_{\perp}$ value.

Turning to adsorption by en, it seems clear that accessibility differences between NH_3 and en must be taken into account. Both $CuCl_2$ and $Cu(O_2CMe)_2$ give identical e.s.r. spectra, which remain virtually unchanged on dehydration. The single

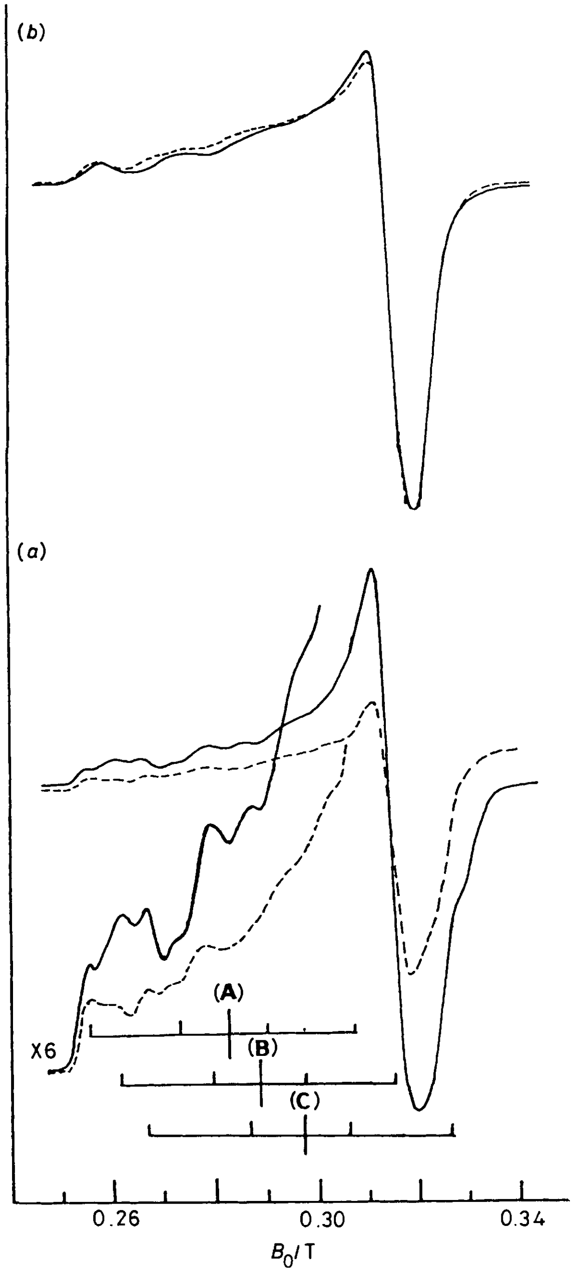


Figure 6. E.s.r. spectra for (*a*) α-$SnCu_{0.02}(NH_2Bu^n)_{1.96}(HPO_4)_2 \cdot H_2O + NH_3(g)$; (—) as prepared, (- - -) after heating at 110 °C, (*b*) $Sn^{63}Cu_{0.02}(NH_2Bu^n)_{1.96}(HPO_4)_2 \cdot H_2O + NH_3(g)$

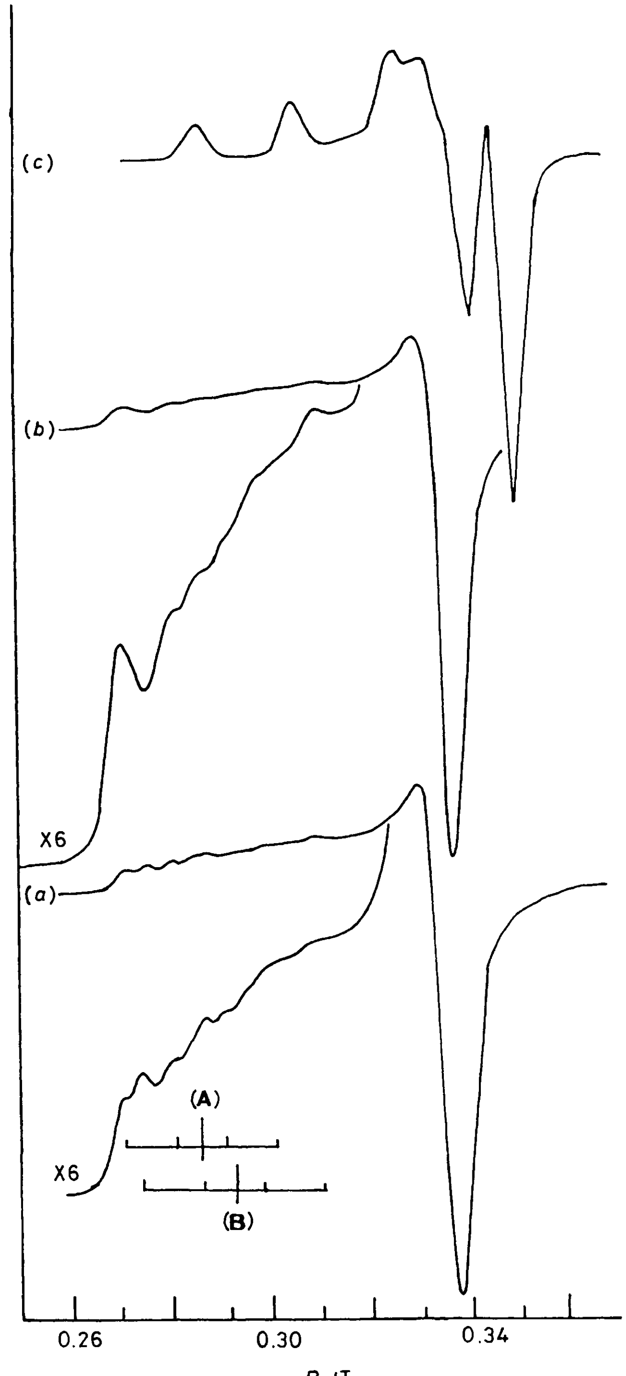


Figure 7. E.s.r. spectra of (*a*) $Sn^{63}Cu_{0.02}H_{1.96}(PO_4)_2 \cdot H_2O$ + en(vap.) at 50 °C, (*b*) $SnCu_{0.02}H_{1.96}(PO_4)_2 \cdot H_2O$ + en(vap.) at 50 °C, and (*c*) $Sn^{63}Cu_{0.02}(NH_2Bu^n)_{1.96}(HPO_4)_2 \cdot H_2O$ + en(vap.) at 50 °C

signal is of a NH_3-co-ordinated species: g_1 2.20_6, g_2 2.01, $A_{\parallel}$ 195 G, parameters pointing to the presence of a geometry giving a d_{z^2} ground state.[20] We suggest that by contrast with the fully exchanged material en co-ordinates to give a *cis*-CuN_2O_4 chromophore.[21,22] There was no evidence for any all-O site, indicating that, at these loading levels at least, all Cu^{2+} ions are saturated by en. Figure 7 also shows the e.s.r. spectra of species obtained by adsorbing en onto α-$SnCu_{0.02}H_{1.96}(PO_4)_2 \cdot H_2O$. For both $CuCl_2$- and $Cu(O_2CMe)_2$-derived materials, different species than for the n-butylamine analogue are observed. We ascribe signal (**B**) to a surface species and in neither case is there clear evidence for *N*-co-ordination of the en ligand.

The e.s.r. results cannot be directly related to those of the fully Cu^{2+}-exchanged materials. However, they do show that: (*i*) α-$Sn(HPO_4)_2 \cdot H_2O$ forms surface species different from those formed by the zirconium analogue, (*ii*) the counter ion has a dramatic effect on the environment adopted by the Cu^{2+}, (*iii*) the interlayer is less accessible to en than to NH_3 unless first expanded, as with n-butylamine, and (*iv*) unusual geometries can be adopted whenever complexes are formed in the interlayer.

Finally, Figures 8 and 9 show the reflectance and e.s.r. spectra of the 20% VO^{2+}-exchanged materials of Table 1. It is seen that the evidence for *N*-co-ordination both for NH_3 and en is not clear.

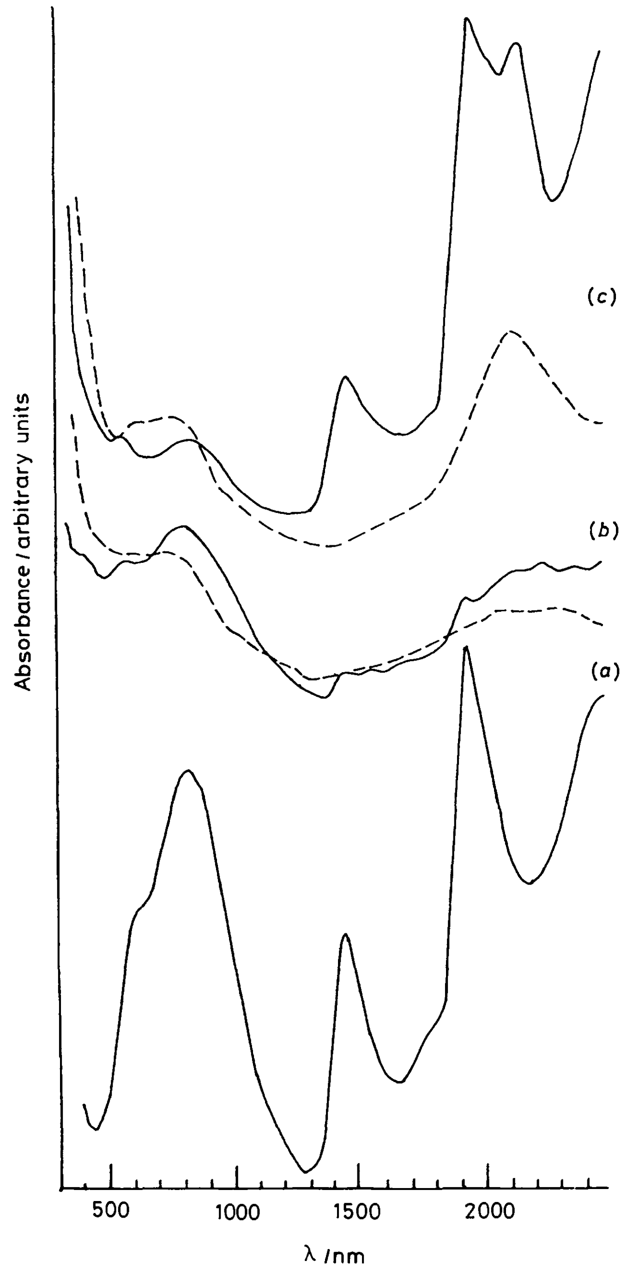


Figure 8. Electronic reflectance spectra of (*a*) α-$SnVO(PO_4)_2·4H_2O$, (—) as prepared, (*b*) α-$SnVO(en)_{1.05}(PO_4)_2·3H_2O$, and (*c*) α-$SnVO(NH_3)_{3.1}(PO_4)_2·3.4H_2O$, (- - - -) after heating at 110 °C

In conclusion, this paper has demonstrated that α-$Sn(HPO_4)_2·H_2O$ can give an extensive co-ordination chemistry both within the interlayer and on the surface. Further clarification of the precise geometries must await growth of single crystals of the starting material, attempts at which are underway.

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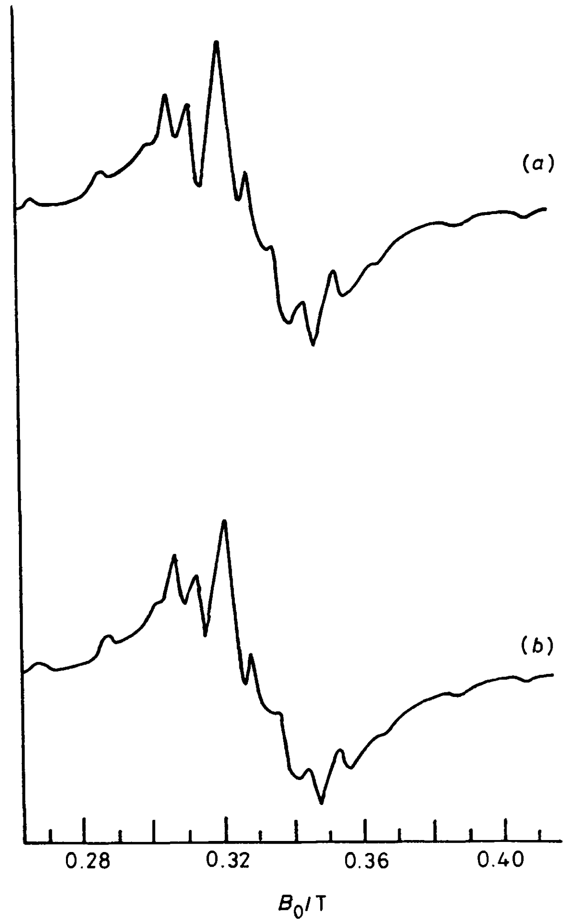

Figure 9. E.s.r. spectra of (*a*) $Sn(VO)_{0.2}H_{1.6}(PO_4)_2·nH_2O$ + en(vap.) at 50 °C, and (*b*) $Sn(VO)_{0.2}H_{1.6}(PO_4)_2·nH_2O$

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