Contribution from the Departamento de Química Inorgânica,
Facultad de Ciencias, Universidad de Mãlaga, 29071 Mãlaga, Spain

Intercalation of Lanthanides into $H_3OUO_2PO_4{\cdot}3H_2O$ and $C_4H_9NH_3UO_2PO_4{\cdot}3H_2O$

Rafaela Pozas-Tormo, Laureano Moreno-Real,* Maria Martinez-Lara, and Sebastian Bruque-Gamez

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The ion-exchange reactions of La^{3+}, Pr^{3+}, and Nd^{3+} with $H_3OUO_2PO_4{\cdot}3H_2O$ (HUP) and $C_4H_9NH_3UO_2PO_4{\cdot}3H_2O$ (BAUP) involve a topotactic process that results in final products derived from HUP having a tetragonal structure. The infrared spectra show the gradual disappearance of the vibration band of the mobile H_3O^+ (1740 cm^{-1}) as the intercalation of the $Ln_{aq}{}^{3+}$ ions proceeds. The obtained solids conform to the following compositions: $La(UO_2PO_4)_3{\cdot}14H_2O$, $Pr(UO_2PO_4)_3{\cdot}14H_2O$, and $Nd(UO_2PO_4)_3{\cdot}13H_2O$. The diffuse-reflectance electron spectra for the lanthanum derivative show only the characteristic bands of the $UO_2{}^{2+}$ group, while in the cases of Pr^{3+} and Nd^{3+}, in addition to these bands, there are others in the 500–800-nm zone that correspond to these aqueous ions.

Introduction

Ion-exchange reactions of layered uranyl phosphates have been extensively studied.[1-3] Like intercalation reactions, ion-exchange reactions offer the possibility of systematically varying the chemical and physical properties of the host lattice. In electrochemical studies, uranyl hydrogen phosphate has been shown to have a high protonic conductivity (0.4 Ω^{-1} m^{-1} at 290 K).[4] This characteristic is due to the high mobility of the proton and also to the fact that there are hydrogen bridges in the solid interlaminar spaces; this conduction mechanism implies proton transference between H_3O^+ and H_2O. The solids derived from HUP by substituting metallic ions for protons show lower conductivity.[5] Other authors have systematically studied the effect that certain determined chemical substitutions of HUP have on its luminescence.[1]

Metallic uranyl phosphates can be prepared by direct synthesis at room temperature through precipitation reactions effected by mixing aqueous solutions of either metal nitrates or sulfates, uranyl nitrate, and phosphoric acid in appropriate molar amounts.[6,7] However, following this method, it is not always possible to avoid undesirable reactions, such as coprecipitation of other insoluble phosphates. In those cases where only one phosphate is isolated, it might not have high crystallinity. Consequently, in recent years, increasing experimentation with ion-exchange topotactic reactions has been done in order to prepare this type of compound. The starting material in these experiments is generally HUP.[1-3] Two mechanisms have been suggested for the HUP ionic exchange reactions, up to the time of writing this paper. Pekarek et al.[8] proposed the first, a process of evolutionary change through solution–reprecipitation, as there appeared to be a good correlation between the distribution coefficients of the metallic ions and the corresponding products of phosphate solubility. Howe,[9] however, proposed an ionic interdiffusion mechanism for the retention of the alkali-metal ions and alkaline-earth-metal ions by HUP, as this model is compatible with the results of kinetic results of the exchange process.

As previously mentioned,[1-3] a great number of synthetic compounds of the uranium mica group were prepared by ionic exchange with HUP, but all attempts to prepare lanthanide derivatives failed. Weigel and Hoffmann[2] could not effect the exchange of H^+/Ln^{3+} in HUP by employing lanthanum chlorides in aqueous media because the most stable products in this media are the lanthanide orthophosphates.

The object of the present work was to carry out a systematic and controlled study of the intercalation of lanthanides into the laminar uranyl phosphate. The intermediate exchange phases and the final products were studied by several different physical methods. Two isostructural uranyl phosphates with a laminar structure and different degrees of swelling were used as the starting products: $H_3OUO_2PO_4{\cdot}3H_2O$ (c = 17.48 Å); $C_4H_9NH_3UO_2PO_4{\cdot}3H_2O$ (c = 29.30 Å).

Experimental Section

$H_3OUO_2PO_4{\cdot}3H_2O$ (HUP) was prepared according to the method proposed by Schreyer and Baes.[10] $C_4H_9NH_3UO_2PO_4{\cdot}3H_2O$ (BAUP) was obtained by exposing HUP to a saturated atmosphere of *n*-butylamine vapor for 2 days in a desiccator.[11]

Table I. pH Values of the Initial Exchange Media and of the Exchange Media after 48-h Contact with HUP for Some Lanthanides (La, Pr, Nd)

Ln	pH (initial)	pH (48 h)
La	5.7	4.1
Pr	4.0	3.9
Nd	6.0	4.1

Aqueous ionic solutions of the lanthanide acetates (La, Pr, Nd) were prepared by treating the appropriate lanthanide oxide with acetic acid. The final pHs of the different acetate solutions were carefully regulated: pH $\simeq$6 for those of lanthanum and neodymium and pH 4 for praseodymium.

The retention processes of H^+/Ln^{3+} and $C_4H_9NH_3{}^+/Ln^{3+}$ were studied by preparing suspensions of the corresponding uranyl phosphate in 25 mL of lanthanide acetate aqueous solution and maintaining these for 48 h at 25 °C. Two experiments were carried out for each cation, both using 1 g of exchange compounds. The equivalent lanthanide ionic content of the solutions in one experiment was only 50% of the theoretical capacity of the exchanger; in the other, it was 300% of the exchange capacity. The reacted suspensions were centrifuged, and the solids were repeatedly washed to completely remove the acetates. They were then air-dried and stored in a controlled environment with 50% relative humidity.

The new materials were characterized by chemical analysis, infrared spectroscopy (Perkin-Elmer 580), X-ray diffraction (Siemens D-501), differential thermal and thermogravimetric analysis (Rigaku Thermoflex), and diffuse-reflectance and visible–UV spectroscopy (Kontron Uvikon 810).

Results and Discussion

When HUP comes into contact with aqueous solutions of lanthanide acetates (Ln^{3+} = La^{3+}, Pr^{3+}, Nd^{3+}) whose concentrations are in excess of 100% of the exchange capacity of the host, the exchange reaction is

$$3H_3OUO_2PO_4{\cdot}3H_2O + Ln_{aq}{}^{3+} \rightarrow Ln(UO_2PO_4)_3{\cdot}nH_2O + 3H_3O^+$$

The above ionic exchange is quite rapid, and a slight reduction of the solution pH is observed during the first 200 min. A constant pH is reached by 12 h. Table I shows the pH values of the initial

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* To whom correspondence should be addressed.

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Table II. Analytical Data for $Ln(UO_2PO_4)_3 \cdot nH_2O$

		% P	% U	% Ln	% H_2O
$La(UO_2PO_4)_3 \cdot 14H_2O$	calcd	6.25	48.06	9.35 (La)	16.96
	found	6.20	48.00	9.30	16.90
$Pr(UO_2PO_4)_3 \cdot 14H_2O$	calcd	6.09	46.86	9.25 (Pr)	16.54
	found	6.12	46.92	9.15	16.51
$Nd(UO_2PO_4)_3 \cdot 13H_2O$	calcd	6.31	48.47	9.79 (Nd)	15.88
	found	6.30	48.50	9.81	15.82

solutions and the pH after 48-h contact with HUP. The observed pH variations of the solutions are minimal, as the aqueous acetates are buffer media and so impede the structural modifications that might occur as a result of the hydrolysis of the phosphate. Weigel and Hoffmann,[3] employing chloride solutions of lanthanide ions with HUP, did not succeed in effecting the H^+/Ln^{3+} exchange because the salts employed generated a final pH that was too acidic, so that the most stable product after dissolution of the exchange compound was $LnPO_4$. When the intercalated solid BAUP is used as the starting substance for the ionic exchange, the pH of the exchange media is not appreciably modified; the exchange process is faster than that with HUP, and the equivalents of the lanthanides observed to disappear from the solutions correspond to the equivalents of butylammonium ion that appear in the supernatant of the solution in equilibrium. The final products are identical with those obtained by direct H^+/Ln^{3+} exchange and confirm that the process is effected by a substitution reaction of the $C_4H_9NH_3^+$ ions by means of the interdiffusion mechanism noted by Howe.[9] At the same time, it contradicts the solubilization–reprecipitation process proposed by Pekarek et al.[8] The percentage of hydrolysis occurring at any moment in the exchange process is negligible, as repeated measurements of soluble phosphate never exceed 1%.

When amounts of lanthanide ions equivalent to 50% of the theoretical exchange capacity of HUP are added to suspensions of the latter, the retentions are practically quantitative and the products have Ln^{3+} ions occupying 50% of the hydrogen positions of the starting product. When quantities of salt in excess of the exchange capacity of the HUP are present (cec = 2.28 mequiv/g), the amounts of metallic ion remaining in solution correspond to the equivalent excess of the original solution. The elemental analyses of the solids obtained in this way are given in Table II. From this data, the following stoichiometric formulas were calculated: $La(UO_2PO_4)_3 \cdot 14H_2O$, $Pr(UO_2PO_4)_3 \cdot 14H_2O$, and $Nd(UO_2PO_4)_3 \cdot 13H_2O$. The degrees of hydration are very much higher than those observed for other intercalated ions[2,11] and relate to the ionic charge and the tendency for the Ln^{3+} ions to form superior hydrates.

The mixed phases of hydrogen–lanthanide–uranyl phosphate complicate the DTA diagram of the starting compound: the two endothermic effects seen in HUP (Figure 1A) become four endothermic dehydration processes in a sample with 50% of available hydrogens substituted (Figure 1B). The homoionic lanthanide compounds lose between 10 and 11 water molecules per formula below 170 °C through the endothermic processes centered at 60 and 85 °C (Figure 1C). The three last water molecules may be strongly retained because a high temperature (230 °C) is required to expel them.

When followed by X-ray diffraction, the evaluation of the crystal parameters in the exchange process indicates that the *hk*0 reflections of the HUP parent persist (Figure 2). At the same time, several *hkl* reflections, notably those of 00*l*, vary. The basal spacings increase for the fully exchanged materials because of the inclusion of Ln_{aq}^{3+} ions, which have a large hydration sphere. However, for the intermediate phases, the 00*l* reflections of the original HUP persist. This excludes the existence of an intermediate phase with a structure different from both that of the starting material and that of the final product. Consequently, by inference, it appears that the retention of the Ln^{3+} ions is by a topotactic process, and so the structure of the final product is predetermined from the outset and is detectable at the beginning of the process. On the other hand, when the LnUP materials are obtained from BAUP, the basal spacing (d_{002}) decreases from 14.65 Å (BAUP parent) to ca. 11 Å (LnUP): the butylammonium ions are arranged perpendicularly to the layers;[11] when these are exchanged by hydrated Ln^{3+} ions (of lesser thickness), the interlaminar space is reduced.

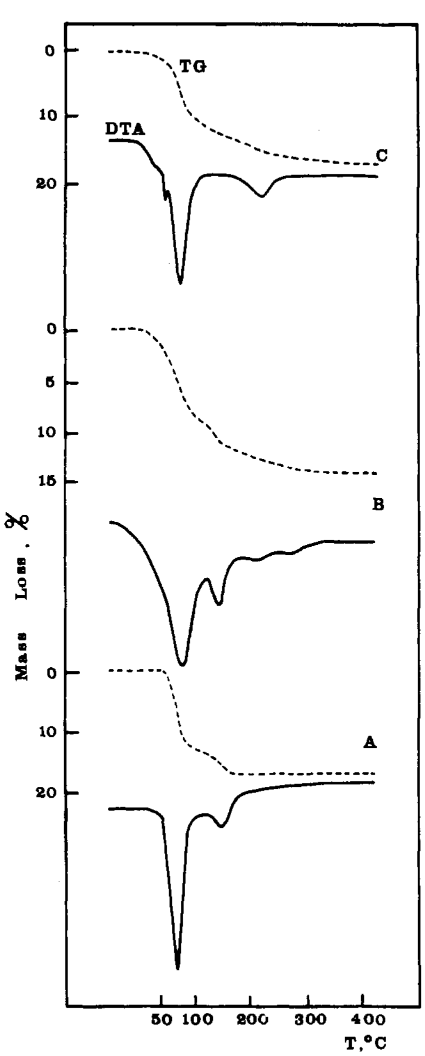

Figure 1. Thermal analyses (TGA and DTA) and (A) HUP, (B) a mixed phase with 50% hydrogens substituted by Nd^{3+}, and (C) a phase fully exchanged with Nd^{3+}. TGA and DTA were obtained with a heating rate of 10 °C/min and with alumina as reference.

The intermediate stage could contain three different types of crystallites: (1) those of the original HUP; (2) those formed by a partially exchanged phase containing both hydrogen and lanthanide; (3) the crystallites of fully exchanged phases.

This model fits perfectly the X-ray diffraction diagrams and the infrared spectra of the partially exchanged phases. When, in the latter, the degree of substitution of hydrogen by lanthanide is equal to or less than 20%, a band toward 1740 cm^{-1} may be seen (Figure 3B) due to the mobile H_3O^+ vibration[12] of the class 1 crystallites, although it is attenuated in comparison with that of the starting product (Figure 3A). This band decreases considerably in intensity as the percentage of substituted hydrogens increases, and in those phases more than 50% exchanged, it is not seen (Figure 3C) but the *hk*0 diffraction reflection of the HUP compound persists. It is thought that the proton mobility of HUP strongly decreases because of the slight distortion of the crystal lattice, such as might be caused by the presence of a number of metal ions in each crystallite. Such specimens must have a diffraction diagram similar to that for pure HUP; however, the protons remain linked to the phosphate groups of the sheets.[13]

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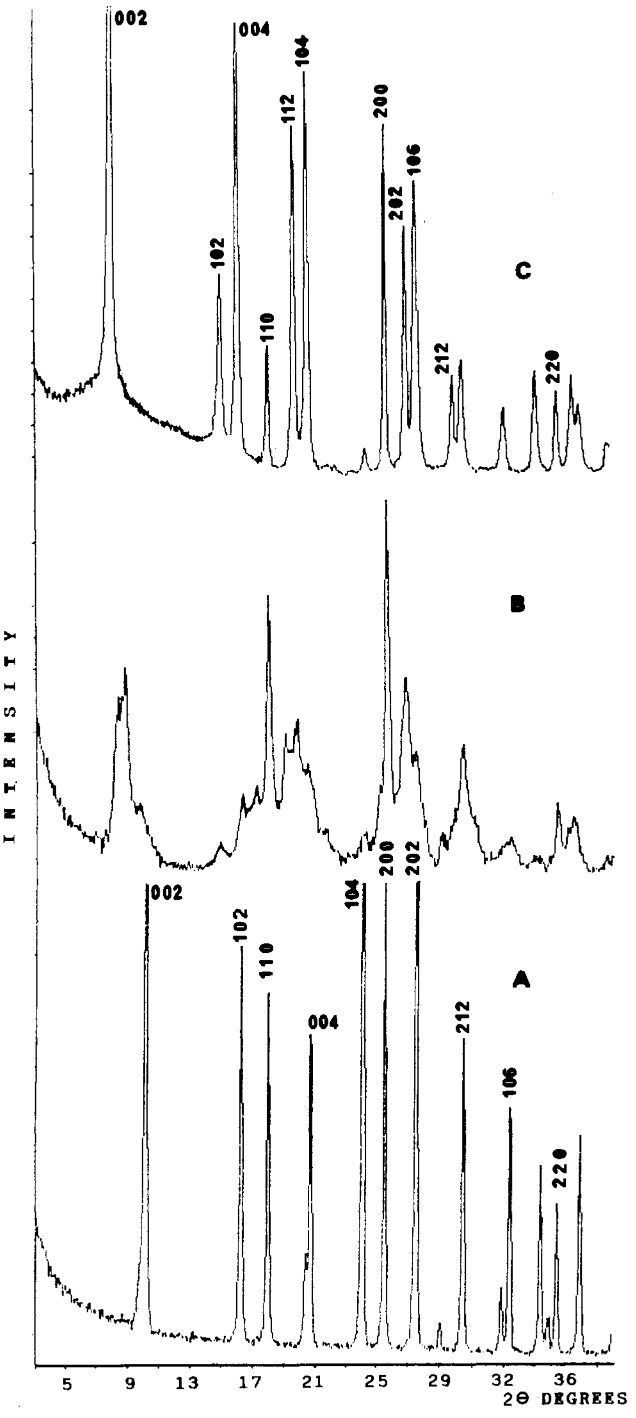

Figure 2. X-ray powder patterns of (A) HUP, (B) an intermediate phase with 50% hydrogens exchanged by Nd^{3+}, and (C) a phase fully exchanged with Nd^{3+}.

This phenomena may be seen in the infrared spectrum (Figure 3B) at 1170 cm^{-1}, which is due to the P–OH groups in the class 2 crystallites. The PO_4 group loses symmetry and the ν_3 mode develops into two or three components ($\nu_{as}(PO_3)$, $\nu_s(PO_3)$, and ν_{as}(P–OH)); the first is seen clearly in the monohydrogen phosphates toward 1170 cm^{-1}.

The disappearance from the LnUP infrared spectra of the vibration band corresponding to the mobile H_3O^+ is due to the protons having been entirely substituted by the Ln^{3+} ions, whose coordinated water may be seen in the OH group stretching region (toward 3420 cm^{-1}) and in the bending region $\delta(H_2O)$ (1630 cm^{-1}). The strong absorption of the PO_4 group can be seen in the 1000-cm^{-1} ($\nu_{as}(PO_4)$), 1125-cm^{-1} ($\nu_s(PO_4)$), and 550-cm^{-1} ($\delta(PO_4)$) regions. The uranyl group shows vibration bands at 910 cm^{-1} ($\nu_{as}(UO_2)$) and 790 cm^{-1} ($\nu_s(UO_2)$). The bands appearing at 615 and 305 cm^{-1} may be assigned to U–O– valence vibration and to that of uranium–oxygen[6] in the UO_2^{2+}. However, other authors[15] assign the bands to the $(H_2O)_n$ libration modes whose

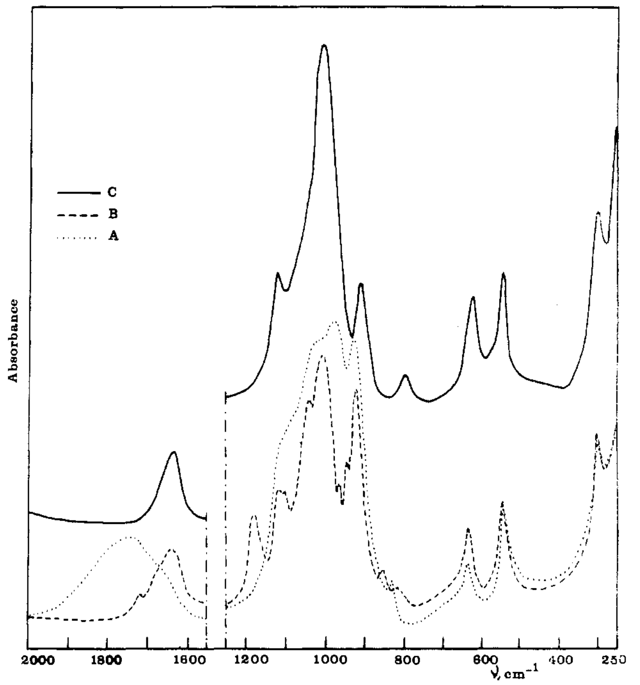

Figure 3. Infrared spectra of (A) HUP, (B) an intermediate phase with 18% hydrogens substituted, $Nd_{0.06}H_{0.82}UP$, and (C) a phase fully exchanged with Nd^{3+}. All spectra were obtained with use of Nujol.

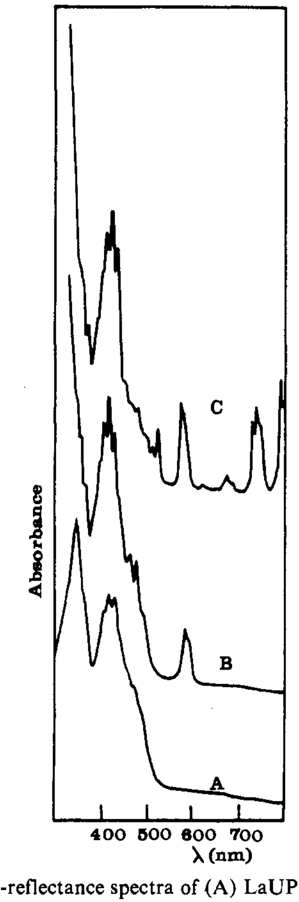

Figure 4. Diffuse-reflectance spectra of (A) LaUP, (B) PrUP, and (C) NdUP. All spectra were obtained at 283 K with use of $BaSO_4$ as reference.

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Table III. X-ray Crystallographic Data for $Ln_{1/3}UO_2PO_4\cdot nH_2O$ (Cu Kα_1, Kα_2; $\lambda = 1.5418$ Å; 20 °C; $Z = 4$)

compd[a]	color	fw	*a*, Å	*c*, Å
$La_{1/3}UO_2PO_4\cdot 4.7H_2O$	yellow	495.90	6.966 (5)	22.36 (8)
$Pr_{1/3}UO_2PO_4\cdot 4.7H_2O$	pale yellow-green	496.57	6.970 (7)	22.23 (8)
$Nd_{1/3}UO_2PO_4\cdot 4.3H_2O$	pale yellow-orange	490.48	6.986 (6)	22.08 (9)

[a] All compounds belong to the tetragonal system.

rotational oscillations remain, restricted by strong interactions with the neighboring atoms.[16]

The X-ray diffraction of the lanthanide uranyl phosphates can be indexed in the tetragonal system. Table III contains the crystallographic data of these solids.

The diffuse-reflectance spectra reveal that the absorption maxima of the LnUP hydrates are similar to the absorption spectra of the hydrated salts of the lanthanides and of the ions present in the aqueous solutions.[17] Figure 4 shows the LaUP, PrUP, and NdUP spectra. The lanthanum derivative does not show absorption maxima in the visible region, as is appropriate for a metallic ion with a complete electron shell; the uranyl group vibration bands, however, appear to be attenuated, probably because of the interaction between the uranyl group and $La(OH_2)_n^{3+}$. Olken et al.[1] also report alterations in the emission characteristics of the uranyl phosphates when they contain several intercalated ions, but the behavior observed in the present work could correspond to any correlation and further investigation is required to classify the system.

Conclusion

HUP and BAUP are formed by $(UO_2PO_4)_n^{n-}$ layers, which can be easily separated to permit the intercalation of ions by the respective exchange of H_3O^+ and $C_4H_9NH_3^+$ cations. The pH of the exchange media must be carefully controlled to avoid the hydrolysis of the host compound to that precipitation of insoluble and highly stable lanthanide orthophosphate does not occur. The lanthanide acetate solutions provide a buffer media appropriate to prevent host dissolution. The ionic interdiffuison mechanism proposed by Howe[9] is in agreement with the evolution of the X-ray diffractograms and IR spectra of the exchange process. The retention of Ln_{aq}^{3+} ions is caused by a topotactic process because the *ab* plane is preserved during intercalation.

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Registry No. $La(UO_2PO_4)_3\cdot 14H_2O$, 107453-28-1; $Pr(UO_2PO_4)_3\cdot 14H_2O$, 107453-29-2; $Nd(UO_2PO_4)_3\cdot 13H_2O$, 107453-30-5; $H_3O(UO_2PO_4)\cdot 3H_2O$, 107453-31-6; $C_4H_9NH_3(UO_2PO_4)\cdot 3H_2O$, 102566-09-6; La, 7439-91-0; Pr, 7440-10-0; Nd, 7440-00-8; $(H_3O)_3Nd(UO_2PO_4)_6\cdot xH_2O$, 107453-32-7.

Supplementary Material Available: Listings of observed and calculated *d* spacings, relative intensities, and Miller indices from the X-ray powder diffraction diagram (6 pages). Ordering information is given on any current masthead page.

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Contribution from the ISSECC, CNR, Firenze, Italy, and Departments of Chemistry, University of Modena, Modena, Italy, and University of Firenze, Firenze, Italy

Anisotropic Exchange in Dinuclear Complexes with Polyatomic Bridges. Crystal and Molecular Structure and EPR Spectra of (μ-Oxalato)bis(1,10-phenanthroline)dicopper(II) Dinitrate

Alessandro Bencini,*[1a] Antonio C. Fabretti,[1b] Claudia Zanchini,[1c] and Paolo Zannini[1b]

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The X-ray crystal structure of (μ-oxalato)bis(1,10-phenanthroline)dicopper(II) dinitrate was determined at room temperature. The crystals are triclinic, space group $P\bar{1}$, with $a = 9.977$ (6) Å, $b = 9.658$ (6) Å, $c = 7.036$ (3) Å, $\alpha = 108.03$ (4)°, $\beta = 95.40$ (4)°, $\gamma = 90.22$ (4)°, and $Z = 2$. The least-squares refinement of the structure led to a conventional R factor of 0.036. Single-crystal EPR spectra were recorded at X-band (9-GHz) frequency at 77 K. The measured zero-field splitting tensor was found to be largely misaligned from the **g** tensor, showing that exchange contributions to the anisotropic spin–spin interaction are operative. The relative influences of the dipolar magnetic and the anisotropic exchange interactions in determining the zero-field splitting in oxalato-bridged copper(II) dimers are discussed.

Introduction

Anisotropic exchange interactions between couples of transition-metal ions have been extensively studied in the last few years since they allow one to estimate exchange interactions between ground and excited states of the dinuclear unit.[2] The mechanisms that determine the anisotropic exchange interactions[3] are not related to those responsible for the isotropic exchange interaction, which often control the magnetic properties of dinuclear species, and involve exchange interactions between the ground states of the magnetic ions.[4,5] As a matter of fact, in a series of μ-hydroxo-bridged copper(II) complexes the isotropic exchange coupling between the unpaired electrons can be ferro- or antiferromagnetic according to the value of the Cu–O–Cu bridging angle[4] while the anisotropic magnetic interaction remains always ferromagnetic.[6]

Dinuclear copper(II) complexes are still the simplest systems to investigate, and since they can be found in a number of different geometries, they are ideal candidates for systematic investigations on correlations between structural and magnetic parameters. The anisotropic exchange interactions in copper(II) couples determine, together with direct magnetic interactions,[3] the zero-field splitting of the triplet state arising from the isotropic exchange interactions

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