Intercalative Ion Exchange of Polyamine Transition Metal Complexes into Hydrogen Uranyl Phosphate†

Daniel Grohol* and Elliott L. Blinn‡

Department of Chemistry and the Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403

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A series of derivatives of hydrogen uranyl phosphate (HUP) was prepared by displacing the butylammonium ions of butylammonium uranyl phosphate with the transition metal complexes $Cu(en)_2^{2+}$, $Cu(pn)_2^{2+}$, $Cu(trien)^{2+}$, $Cu(14\text{-}ane)^{2+}$, $Cu(15\text{-}ane)^{2+}$, $Ni(trien)^{2+}$, $Ni(14\text{-}ane)^{2+}$, and $Ni(diene)^{2+}$. X-ray powder patterns proved that the original tetragonal structure of the UP layers remained intact in all derivatives. The extent of the ion exchange and the interlamellar distances were found to depend mainly on the size and on the shape of a particular coordinating ligand. Electronic absorption spectra indicated that the intercalated complexes had four-coordinate square-planar geometry inside the UP lattice. Extents of hydration of the intercalates varied significantly, and they depended mostly on the shapes of the coordinating ligands and on their abilities to regularly pack between the UP layers. Results of the above-mentioned characteristics allow one to divide these transition metal complexes into two groups which differ from each other in their abilities to efficiently fill up the space between the UP layers. The steady-state luminescence spectra of intercalates showed a very weak uranyl emission which was partly due to quenching by the Cu^{2+} and Ni^{2+} guest complexes and partly to self-absorption.

Introduction

Inorganic layered materials have received considerable attention as hosts for intercalation of guest molecules and for intercalative ion exchange reactions.[1−3] The most investigated classes of layered hosts consist of divalent and tetravalent metal phosphates[4,5] and phosphonates,[6] clays,[7] layered double hydroxides,[8] and also other materials.

Hydrogen uranyl phosphate tetrahydrate (HUP), $HUO_2PO_4\cdot 4H_2O$ has a layered structure, and it can function as a cation exchanger. This compound has been investigated not only for its ion exchange properties but also for its luminescence[9] and ionic conductivity properties.[10,11] HUP is a layered inorganic, water insoluble polymer consisting of alternating lamellae built up by the UO_2^{2+} and PO_4^{3-} ions.[12] The interlamellar space is filled with four water molecules per molecular unit of HUP, one of which is protonated; the distance between the uranyl phosphate (UP) layers is 8.73 Å. HUP can exchange its protons for mono-, di- tri-, and tetravalent cations.[13,14] Upon ion exchange the electroneutrality of the compound is maintained, so a monovalent cation exchanges for one proton, a divalent cation for two protons, etc. The intercalating guest cations can be the main group metal cations (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}),[10,15] transition metal (TM) cations (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}),[16] transition metal complexes ($Cr(NH_3)_6^{3+}$, copper(I) bis(dimethylphenanthroline)),[17,18] lanthanides (La^{3+}, Pr^{3+}, Nd^{3+}, Eu^{3+}),[19,20] and organic cations (butylammonium, octylammonium, pyrazinium, pyridinium).[21−23]

HUP has also been investigated for its luminescence properties[21] and for the possibility of host−guest electron and energy transfer.[9] The strong green-yellow luminescence of HUP is caused by the uranyl cation,[24] and its excited state can be quenched by guest cations. If the guest cation is readily oxidizable, an electron-transfer quenching usually takes place because UO_2^{2+} in the excited state is a strong oxidant ($E° = +2.60$ V). The extent of such quenching is a function of the redox properties of the guest cation and of the distance between the photosensitizer and the quencher. On the other hand, if the guest cation has an electronic transition approximately matching the energy of one of the emission transitions of the uranyl ion, then energy-transfer quenching takes place.[21] In this case, the extent of quenching predominantly depends on the degree of the energy overlap of the two interacting moieties.

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* Author to whom correspondence should be addressed. Currently at Department of Chemistry, Texas A&M University, College Station, TX 77843. E-mail: gdaniel@chemvx.tamu.edu.

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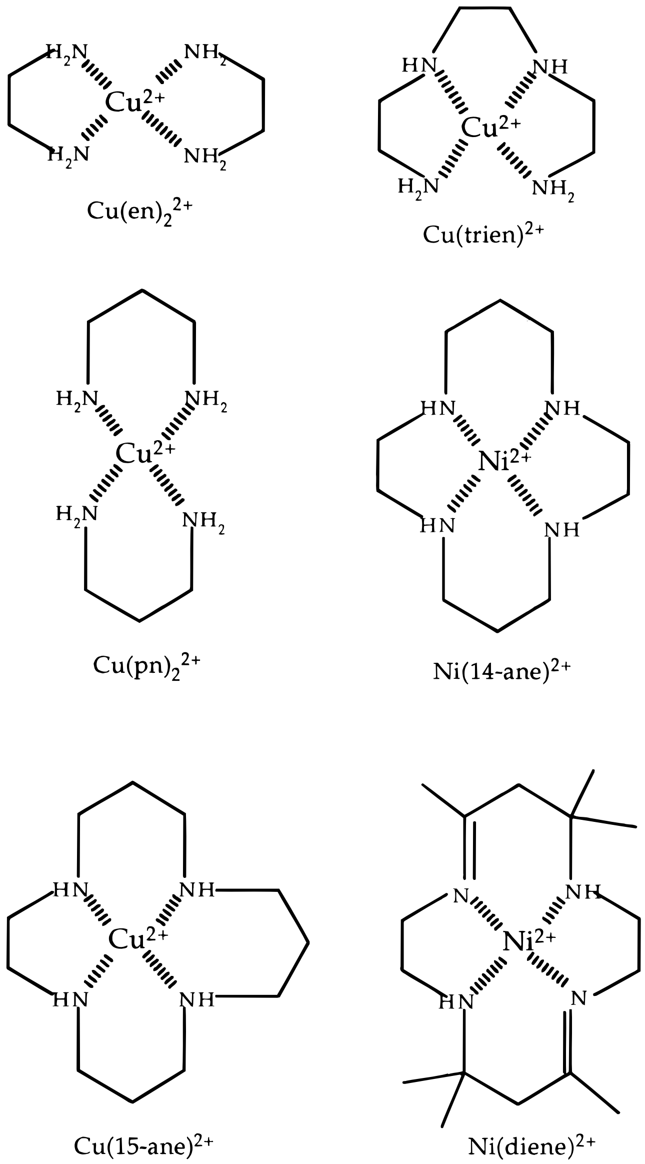

Figure 1. Examples of transition metal complexes intercalated between the uranyl phosphate layers: en, 1,2-ethanediamine; pn, 1,3-propanediamine; trien, triethylenetetramine; 14-ane, 1,4,8,11-tetraazacyclotetradecane; 15-ane, 1,4,8,12-tetraazacyclopentadecane, diene: 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

We have placed a variety of square-planar Cu^{2+} and Ni^{2+} complexes having different steric requirements (Figure 1) between the UP layers with the intention of determining the factors that influence the extent of ion exchange, as well as the spectral and emission properties of the intercalates as a function of the guest cations. On the basis of our data, we also suggest the geometry and the probable orientation of the guest cations in the UP interlayer space.

Experimental Section

Materials. All chemicals were of reagent or analytical grade, and they were used without further purification. All of the starting materials were purchased from commercial chemical companies. Copper turnings (J. T. Baker Chemical Co.) were used for preparation of standard AAS solutions, and the nickel standard AAS solution (1000 ppm) was supplied by Aldrich.

Caution. All uranyl compounds are toxic when ingested, and any contact with skin should also be avoided due to its radioactivity.

Syntheses. $HUO_2PO_4 \cdot 4H_2O$ (HUP) and $C_4H_9NH_3UO_2PO_4 \cdot 3H_2O$ (BAUP) were prepared by known literature procedures,[16] and the purity was checked by matching their X-ray diffraction powder patterns and IR spectra with previously published values.

Cu and Ni guest complexes were synthesized by established literature procedures as chloride salts,[25–30] and $Ni(diene)^{2+}$ was prepared as a perchlorate salt.[31] Purity of the prepared complexes was confirmed by comparing the electronic absorption spectra with literature data.

Ion Exchange. Typically, 10 mmol of each complex was dissolved in 50 mL of distilled water. The solution was poured into a 125 mL Erlenmeyer flask, and 1 g (2.0 mmol) of BAUP was added to the solution. This flask was shaken for a period of 2−6 days. Completeness of the ion exchange was checked by measuring and comparing the absorbance of filtered solutions at the wavelength maximum of the guest complex at different times. If the absorbance of a particular solution containing BAUP decreased with time, the ion exchange was assumed not to be complete; if, however, the absorbance remained constant, the reaction was considered complete. After the reaction was complete, each suspension was filtered on a frit and washed with distilled water. The product was spread on a dish and left to air-dry for about a day. Then it was ground with a mortar and pestle and stored in 55% humidity atmosphere.

Controlled Humidity Atmosphere (55% at 25 °C). Ion exchange samples were stored in the upper part of a desiccator in which the bottom part contained a saturated potassium dichromate solution.

Thermal analysis was carried out on Derivatograph System F. Paulik, J. Paulik, L. Erdey, MOM Budapest. Curves of the temperature, thermogravimetric analysis (TGA), and differential thermal analysis (DTA) were recorded simultaneously as functions of time. The rate of the temperature increase was 10 °C/min. The measurements were acquired in air, and the reference sample for DTA was alumina powder.

X-ray diffraction powder patterns were collected in the 2θ range 3−40° on a Phillips automatic powder diffractometer with the PW 1830 generator, using Cu Kα radiation and equipped with the Phillips PC-APD computer software.

IR spectra were acquired in KBr pellets on a Mattson Instruments Galaxy 6020 FTIR spectrometer in the range 400−4000 cm^{-1} with resolution of 4 cm^{-1} and with 16 background and 16 sample scans.

Electronic absorption spectra were measured on a Cary 219 spectrophotometer with a PC computer on-line to record the signal. The spectra of aqueous solutions of transition metal complexes were acquired in 1 cm optical glass cuvettes. Spectra of the solid HUP derivatives were acquired by suspending them in Nujol mull and by spreading the suspensions on Whatman no. 1 filter paper. The suspension was then placed into the sample beam, and another piece of filter paper which was moistened by several drops of Nujol mull was placed into the reference beam.

Steady-state electronic emission spectra were recorded on a spectrofluorometer system Spex Model 1680 with a Spex DM1B computer. All spectra were recorded front-face in the double-beam acquisition mode which gave the ratio of the sample and of the reference beam intensity as the output. The acquisition conditions were the same for all derivatives (except for HUP), so the relative emission intensities are comparable: sample/reference voltage 1000 V (600 V for HUP)/730 V, slits 0.4 mm on the excitation monochromator and 0.2 mm on the emission monochromator. The excitation wavelength was 460 nm.

Elemental Analyses. Contents of Cu and Ni in the HUP derivatives were determined by atomic absorption spectroscopy using a Jarrell-Ash Dial Atom III atomic absorption spectrophotometer. All intercalates prepared from chloride salts were tested for the chloride ion with an Ag^+ salt, and all the tests came out negative. This proved that no Cl^- anions entered the UP lattice along with the complex cations. Carbon and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, TN. Anal. Calcd for $\{Cu(en)_2\}_{0.38}BA_{0.24}UP \cdot 0.6H_2O$: Cu, 5.21; N, 5.32. Found: Cu, 5.20; N, 5.23. Anal. Calcd for $\{Cu(pn)_2\}_{0.21}BA_{0.58}UP \cdot 3.8H_2O$: Cu, 2.56; N, 3.82. Found: Cu, 2.55; N, 3.87. Anal. Calcd for $\{Cu(trien)\}_{0.47}BA_{0.06}UP \cdot 2.5H_2O$: Cu, 5.82;

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Table 1. Extents of Ion Exchange, Colors, and Interlayer Distances of HUP Derivatives

compound[a]	extent of ion exchange	color	interlayer distance (Å)
$[Cu(en)_2]_{0.38}BA_{0.24}UP{\cdot}0.6H_2O$	0.77	red-brown	8.59
$[Cu(pn)_2]_{0.21}BA_{0.58}UP{\cdot}3.8H_2O$	0.43	gray	11.53
$[Cu(trien)]_{0.47}BA_{0.06}UP{\cdot}2.5H_2O$	0.94	purple-blue	11.52
$[Cu(14\text{-}ane)]_{0.25}BA_{0.5}UP{\cdot}3.7H_2O$	0.52	red-orange	13.02
$[Cu(15\text{-}ane)]_{0.32}BA_{0.36}UP{\cdot}3.7H_2O$	0.67	blue	14.65
$[Ni(trien)]_{0.46}BA_{0.08}UP{\cdot}2.6H_2O$	0.92	yellow	10.95
$[Ni(14\text{-}ane)]_{0.29}BA_{0.42}UP{\cdot}4.0H_2O$	0.70	yellow	12.11
$[Ni(diene)]_{0.30}BA_{0.40}UP{\cdot}2.7H_2O$	0.65	yellow	17.91

[a] Since the complete formulas of intercalates are too long, they are abbreviated in Figure 1. The unexchanged butylammonium cations, the water molecules, and the stoichiometric ratio between the intercalated cation and the uranyl phosphate (UP) unit are omitted in the abbreviated form. For example, $[Ni(14\text{-}ane)_{0.34}BA_{0.42}UP{\cdot}4.0H_2O$ is abbreviated Ni(14-ane)UP.

N, 5.29. Found: Cu, 5.82; N, 4.90. Anal. Calcd for $\{Cu(14\text{-}ane)\}_{0.25}BA_{0.5}UP{\cdot}3.7H_2O$: Cu, 2.97; N, 3.95. Found: Cu, 2.94, N, 4.05. Anal. Calcd for $\{Cu(15\text{-}ane)\}_{0.32}BA_{0.36}UP{\cdot}3.7H_2O$: Cu, 3.72. Found: Cu, 3.70. Anal. Calcd for $\{Ni(trien)\}_{0.46}BA_{0.08}UP{\cdot}2.6H_2O$: Ni, 5.27; N, 5.25. Found: Ni, 5.25; N, 4.53. Anal. Calcd for $\{Ni(14\text{-}ane)\}_{0.29}BA_{0.42}UP{\cdot}4.0H_2O$: Ni, 3.64; N, 4.28. Found: Ni, 3.65; N, 4.35. Anal. Calcd for $\{Ni(diene)\}_{0.30}BA_{0.40}UP{\cdot}2.7H_2O$: Ni, 3.23; N, 4.11. Found: Ni, 3.26; N, 4.43.

Results

Extent of Ion Exchange. There are three commonly used methods of preparing HUP intercalates of transition metal complexes. One method requires that HUP is slurred in the water solution of the desired cations.[15] Another method requires solutions of UO_2^{2+} and PO_4^{3-} ions reacting to form the uranyl phosphate layers in the presence of the guest cations, which then become trapped in between the forming UP layers.[17] In yet another method, the interlamellar space of HUP is first expanded by intercalating an aliphatic amine, e.g. butylamine (BA), into the uranyl phosphate layers, and then BAUP is slurred in a solution of the guest cations which displace the BA ions.[16] The BAUP method was chosen for this research for the following reasons. Direct ion exchange of protons for large transition metal complexes having large steric requirements has been reported to be inefficient[18] due to a small interlayer distance of HUP. The precipitation of HUP in the presence of the guest ions was unsuccessful in our research.

The extent of ion exchange of the TM complexes in the UP lattice varied significantly (Table 1). The size and the shape of the coordinating ligand in the intercalating cation played an important role in the extent of ion exchange. The copper complex ions can be sequenced according to their ability to displace the BA cations of BAUP:

$$Cu(trien)^{2+} > Cu(en)_2^{2+} > Cu(15\text{-}ane)^{2+} > Cu(14\text{-}ane)^{2+} > Cu(pn)_2^{2+}$$

A similar sequence was observed for the nickel complexes:

$$Ni(trien)^{2+} > Ni(14\text{-}ane)^{2+} > Ni(diene)^{2+}$$

Thermogravimetric Analysis. TGA and DTA curves of all intercalates exhibit both an endothermic and an exothermic weight loss. The number of water molecules between the layers was determined by iterative fitting of the TGA data and the chemical analysis. As an example, thermal analysis of $Cu(pn)_2UP$ is shown in Figure 2.

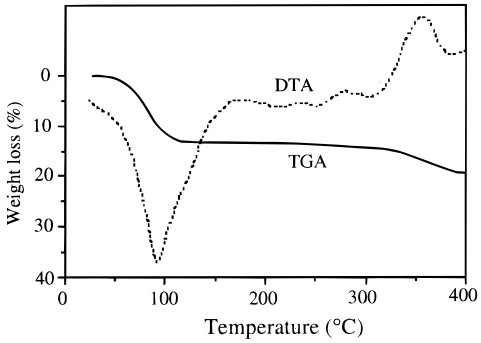


Figure 2. Thermal analysis of $Cu(pn)_2UP$.

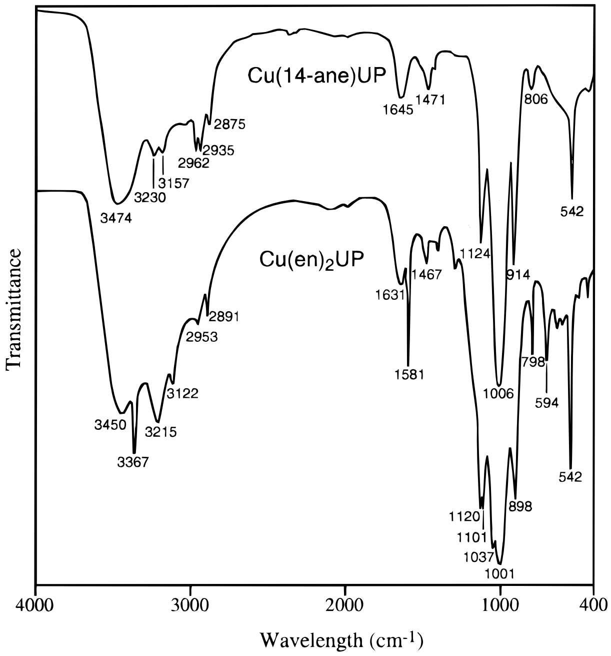


Figure 3. IR spectra of Cu(14-ane)UP and of $Cu(en)_2UP$.

Dehydration of the intercalates occurs at relatively low temperatures (40−200 °C), whereas the exothermic weight loss at higher temperatures (220−500 °C) is due to combustion of organic ligands of the guest complexes.

Infrared Spectra. The IR spectra of HUP and of BAUP were consistent with the literature.[14,16] Spectra of the other HUP derivatives have many similar features arising from the common vibrations of the uranyl and phosphate groups and from organic groups (e.g. CH_2, CH_3, NH or NH_2) of the guest complexes and from interlayer water molecules (Figure 3).

The most distinct pattern in the IR spectra of all HUP derivatives is a group of three very strong peaks of which the strongest peak at about 1000 cm^{-1} is attributed to the symmetric P−O stretch, and another peak at about 1120 cm^{-1} is attributed to the antisymmetric P−O stretch. In the spectra of $Cu(en)_2UP$ and Ni(diene)UP, both of these P−O peaks are split (Figure 3), which indicates a $P{-}O{-}M(L)^{2+}$ interaction. The U−O antisymmetric stretch appears around 900 cm^{-1}, and the weak U−O symmetric stretch is at approximately 800 cm^{-1}. A strong and sharp peak at 542 cm^{-1} is due to the O−P−O bending mode of the PO_4^{3-} anion. The water O−H stretching mode shows as a very broad and strong band at approximately 3450 cm^{-1}, and the H−O−H bending mode as a weak and broad peak at 1640 cm^{-1}. The region between 3250 and 3150 cm^{-1} contains the butylammonium N−H stretching mode from the unexchanged BA cations, and an amine N−H stretch from some of the organic ligands. Weak peaks between 3000 and 2870

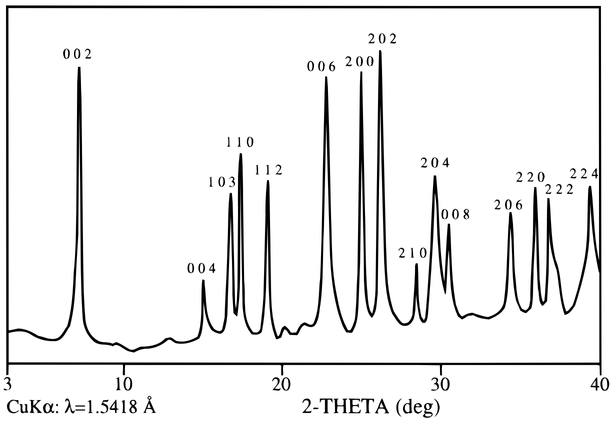


Figure 4. X-ray diffraction powder pattern of Cu(trien)UP.

cm^{-1} belong to the stretching modes of CH_2, and CH_3 groups in BA cations and in the organic ligands.

X-ray Diffraction Powder Patterns. Most powder patterns exhibited broad peaks and relatively high baselines that indicated low crystallinity of the intercalates. As an example, the X-ray powder pattern of Cu(trien)UP is shown in Figure 4.

Despite the low crystallinity, powder patterns of all derivatives could be indexed in the tetragonal system, which proves that the original layered structure remained the same as that of the parent compound HUP. HUP crystallizes in the space group $P4/ncc$ ($a = b = 6.995$ Å, $c = 17.491$ Å).[12] The UP layers constitute planes perpendicular to the c-axis at $c = 0, {}^1/_2$, so the interlayer distance is half the c-value. Peaks of the planes independent of the interlayer distance (*hk0*) were found in the patterns of all prepared intercalates virtually at the same positions as those of HUP. However, the positions of peaks for which $l \neq 0$ varied significantly.

In all patterns, the peak found at the lowest 2θ angle (the 002 reflection) corresponds to the interlayer distance of the particular derivative. Interlayer distances of the derivatives containing incorporated complexes range from 8.59 Å for $Cu(en)_2UP$ to 17.91 Å for Ni(diene)UP (Table 1). Interlayer distances do not appear to depend on the nature of the central metal ion in the complex; however, they significantly depend on the nature of the size and shape of the coordinating ligand. The copper derivatives can be sequenced according to their increasing interlayer distances:

$$Cu(en)_2UP < Cu(trien)UP < Cu(pn)_2UP < \\ Cu(14\text{-}ane)UP = Cu(15\text{-}ane)UP$$

The same trend for the nickel series is

$$Ni(trien)UP < Ni(14\text{-}ane)UP << Ni(diene)UP$$

Electronic Absorption Spectra. Electronic absorption spectra of almost all HUP derivatives contain a characteristic pattern of vibronic peaks in the region 340−500 nm, which is associated with the uranyl chromophore.[24] The individual peaks in this uranyl pattern are found at virtually constant wavelengths in all of the spectra where bands of the guest transition metal complexes do not interfere with the uranyl band. This indicates that the guest complex cations do not directly influence the absorption properties of the uranyl ion in the visible region.

The absorption bands of all the intercalated copper(II) complexes are found at wavelengths higher than those of the uranyl band, and they are blue-shifted with respect to the water solution spectra (Figure 5). The extent of the blue shift, however, varies depending on the guest complex (Table 2).

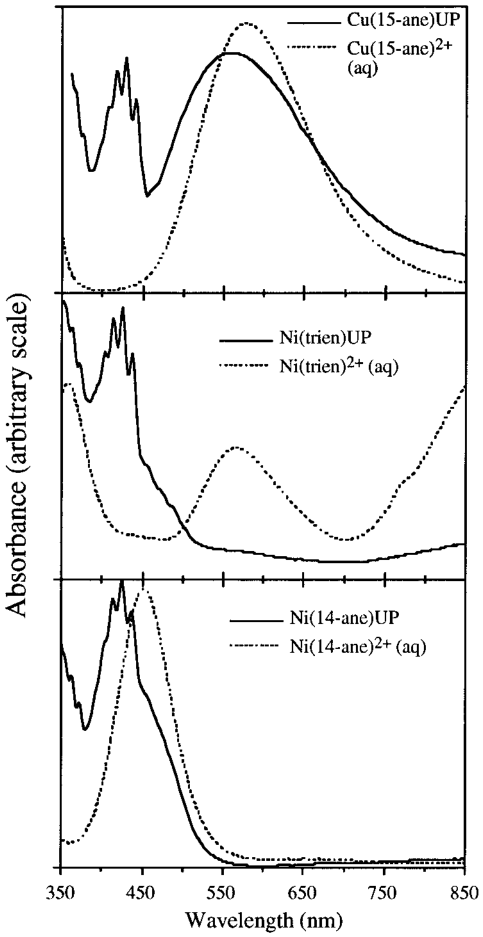


Figure 5. Electronic absorption spectra of HUP intercalates containing transition metal complexes compared to the spectra of aqueous solutions of those complexes.

Table 2. Comparison of the Absorption Maxima in the Electronic Spectra of the Cu^{2+} Complexes in Aqueous Solutions and Inside the UP Lattice

	absorption maximum (nm)	
complex cation	water soln	UP layers
$Cu(en)_2^{2+}$	550	501
$Cu(pn)_2^{2+}$	572	543
$Cu(trien)^{2+}$	576	546
$Cu(14\text{-}ane)^{2+}$	506	490
$Cu(15\text{-}ane)^{2+}$	580	554

The absorption bands of all of the intercalated nickel(II) complexes interfere with the uranyl absorption band, which results in a sloping shoulder on the low-energy edge of the uranyl band. Consequently, the maxima cannot be discerned (Figure 5). Even though the exact wavelength of the maximum of the intercalated $Ni(trien)^{2+}$ cannot be discerned, it is also clearly blue-shifted with respect to the water solution spectrum.

The absorption bands of the intercalated $Ni(14\text{-}ane)^{2+}$ and $Ni(diene)^{2+}$ are at approximately the same wavelengths as found for these complexes in aqueous solutions (Figure 5). Whether any band shift upon intercalation occurred in these complexes cannot be determined with certainty because of the interference with the uranyl absorption band.

Electronic Emission Spectra. Emission spectra ($\lambda_{exc} = 460$ nm) of BAUP and of all other intercalates maintain the original vibronic pattern which is found in HUP.[21] The positions of individual peaks (501, 523, 547, 573, 602 nm) are at the same wavelengths as those of HUP, but the intensities are much smaller (10^2−10^5 times) and the relative intensities of individual peaks vary (Figure 6).

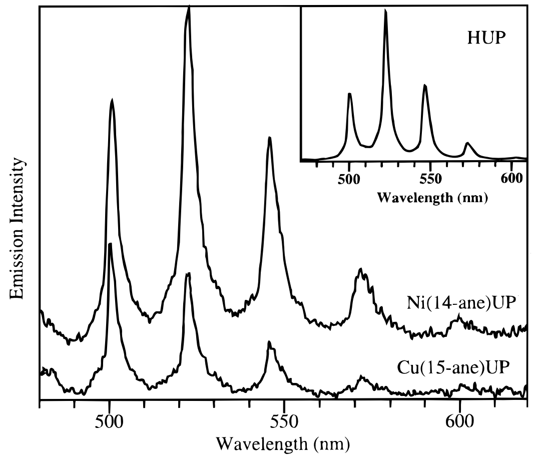


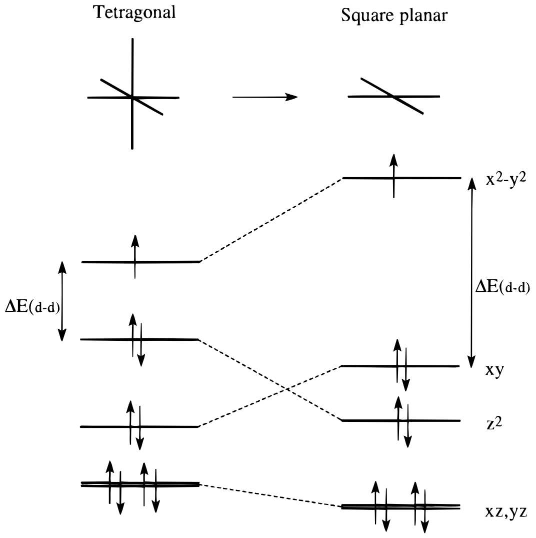
Figure 6. Electronic emission spectra of Cu(15-ane)UP, Ni(14-ane)-UP, and HUP (inset).

Table 3. Relative Emission Intensities of HUP and Its Derivatives

compound	rel amt of emitted light
HUP	1
BAUP	2.5×10^{-3}
$Cu(en)_2UP$	1.6×10^{-4}
$Cu(pn)_2UP$	3.9×10^{-5}
Cu(trien)UP	1.7×10^{-5}
Cu(14-ane)UP	2.6×10^{-5}
Cu(15-ane)UP	8.2×10^{-5}
Ni(trien)UP	1.3×10^{-4}
Ni(14-ane)UP	2.2×10^{-4}
Ni(diene)]UP	1.8×10^{-4}

The emission spectrum of Ni(14-ane)UP retains the original shape of the parent HUP, but the spectrum of Cu(15-ane)UP does not. The most intense peak in the emission spectrum of Cu(15-ane)UP appears at 501 nm, and the other peaks at longer wavelengths gradually diminish. The reason for this difference becomes apparent when the emission spectrum is compared with the respective electronic absorption spectrum. The first and the strongest emission peak of Cu(15-ane)UP appears at a wavelength of approximately 501 nm, where the absorbance of the intercalated complex is relatively low. The second emission peak at 523 nm is weaker, because the absorbance of the guest complex at this wavelength is higher. The intensity of the third peak at 547 nm is even lower because at this wavelength the absorbance of the intercalated complex is highest. The decreased intensity at the wavelengths of a higher absorbance is evidence for a self-absorption of the emitted light by the intercalate. This fact hinders the measurement of luminescence quantum yields. The luminescence quantum yield is defined as the ratio of the total number of emitted photons by a chromophore to the total number of absorbed photons by the same chromophore.[32] Since our samples absorb light in the luminescence region of the uranyl ion, it is difficult to determine what fraction of light emitted by the uranyl ion was absorbed by the guest cations. Consequently, this prevented us from ascertaining how much of the decreased emission intensity is due to quenching by the guest cations via electron transfer and how much is due to self-absorption of sample. Nevertheless, integrating the areas under the emission curves of different samples measured under the same conditions can provide an approximate idea about the relative emission intensities of intercalates (Table 3).

Scheme 1. Orbital Energy Level Diagram Rationalizing the Increase in Ligand Field Splitting of Cu(II) (and Ni(II)) Complexes upon Their Intercalation between the Uranyl Phosphate Layers



Discussion

It has been reported earlier that the absorption spectrum of $H_{0.7}\{Cr(NH_3)_6\}_{0.1}UP{\cdot}6H_2O$ was virtually identical with the spectrum of a physical mixture of HUP and of the nitrate salt of octahedral hexaaminechromium(III).[17] A similar result was observed when two spacious tetrahedral bis(phenanthroline)-Cu(I) complexes were inserted into the UP lattice; the absorption maximum of the intercalated complexes remained the same compared to the spectrum measured in the CH_2Cl_2 solution.[18] In contrast to the mentioned results, the maxima of all of our intercalated Cu(II) complexes and at least of one Ni(II) complex ($Ni(trien)^{2+}$) were significantly blue-shifted with respect to the water solution spectra. The degree of the blue shift varied from 16 nm for $Cu(14\text{-}ane)^{2+}$ to 49 nm for $Cu(en)_2^{2+}$ (Table 2). The mentioned band shifts can be explained by a changing of geometry of the TM complexes which occurs upon intercalation.

In water solutions, the copper(II) and nickel(II) complexes containing four nitrogen donor atoms (Figure 1) equilibrate between the square-planar and the octahedral, tetragonally distorted form:[33-36]

$$ML(H_2O)_2^{\ 2+} \rightleftarrows ML^{2+} + 2H_2O$$

The four equatorial positions are occupied by the ligand nitrogen atoms, and the two axial positions are occupied by weakly bound water molecules. The blue shift of the d−d transition in the visible spectra of the intercalated ML^{2+} complexes compared to the respective aqueous solution spectra indicates an increased ligand-field splitting as the geometry of the TM complexes changes from an equilibrium mixture of distorted octahedral and square-planar species in solution to the predominantly square-planar species in the UP lattice (Scheme 1).

Apparently, the less sterically demanding square-planar complexes can more readily enter the interlamellar space

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between the UP layers than the six-coordinate complexes. This geometric selectivity is an excellent example of a thermodynamic template effect since the BAUP lattice sequesters only the square-planar ML^{2+} species from the equilibrium, and in doing so, it shifts the equilibrium to the right.

This finding is consistent with the temperature-dependent band shifts in a water solution containing $Ni(en)_2{}^{2+}$.[37] At room temperature, the solution was blue with the visible absorption band at 570 nm, and the complex had the octahedral tetragonally distorted geometry with water molecules in the axial positions. At 77 °C the solution turned yellow, and the absorption band shifted to 450 nm. This was attributed to the loss of the coordinated water molecules and the shifting of equilibrium to the square-planar species. Similar band shifts were observed in the absorption spectra of $Cu(13\text{-ane})^{2+}$, $Cu(14\text{-ane})^{2+}$, $Cu(15\text{-ane})^{2+}$, and $Cu(16\text{-ane})^{2+}$, where bands of the complexes dissolved in nitromethane were blue-shifted with respect to the water solution spectra.[38] The shifts were explained by the inability of nitromethane to coordinate the square-planar complexes in the axial sites, whereas the water molecules were capable of such coordination.

In contrast to the changing geometry of most of our complexes upon intercalation, the mentioned octahedral complex $Cr(NH_3)_6{}^{3+}$ and tetrahedral complex bis(phenanthroline)Cu(I) described in the literature could not lose any ligands or significantly alter their geometry upon intercalation, and thus no shift in their spectra was observed or expected. The absorption bands of the intercalated $Ni(14\text{-ane})^{2+}$ and of $Ni(diene)^{2+}$ are obscured by the uranyl band, which makes it impossible to determine whether any shift occurred, compared to the respective water solution spectra.

The electronic absorption spectra thus suggest that all guest complexes have the square-planar geometry inside the UP lattice, and therefore the water molecules found in the interlamellar space are not coordinated to the intercalated complexes. The most likely reason for this is that there is not sufficient space between the UP layers to achieve a maximum extent of ion exchange if the water molecules are bonded to the metal complexes. As a result, these water molecules thus occupy void cavities in the interlamellar UP space.

The extent of ion exchange of the complexes is incomplete in all intercalates, and it varies from 0.43 for $Cu(pn)_2{}^{2+}$ to 0.94 for $Cu(trien)^{2+}$. The nature of the central metal ion has only a minor influence on the extent of ion exchange. For example, $Cu(trien)^{2+}$ and $Ni(trien)^{2+}$ intercalate into the UP lattice almost to the same degree (Table 1); however $Ni(14\text{-ane})^{2+}$ intercalates in between the layers to a larger extent than $Cu(14\text{-ane})^{2+}$. We have no explanation for this difference.

Steric requirements of the guest complexes play a more important role than the nature of the transition metal in determining the extent of ion exchange. Generally, the larger the complex, the less ion exchange occurs (Table 1). This observation is reasonable given the fact that the interlayer volume is limited, and larger guest cations occupy more space than the small ones. However, some results on the extent of ion exchange cannot be explained by the relative sizes or relative molecular volumes of complexes alone. For example, the amount of $Cu(pn)_2{}^{2+}$ found in the UP lattice is much smaller than one might expect based on the size of the transition metal complex and on the amount of space available within the UP lattice. It is apparent that the way the guest complexes are arranged in between the UP layers has a significant consequence on the extent of ion exchange.

Table 4. Approximate Sizes of Intercalated Complexes[a]

complex[b]	*x* (Å)	*y* (Å)	*z* (Å)
$M(en)_2{}^{2+}$	7.6	4.6	3.4
$M(pn)_2{}^{2+}$	9.2	5.1	3.7
$M(trien)^{2+}$	6.8	5.2	2.3
$M(14\text{-ane})^{2+}$	9.4	7.7	3.8
$M(15\text{-ane})^{2+}$	9.4	8.1	4.6
$M(diene)^{2+}$	8.8	7.4	5.6

[a] The sizes were estimated from published crystal structures using the Cambridge Structural Database. The *x*- and *y*-dimensions constitute the plane containing the four relatively planar nitrogens, and the *z*-dimension is perpendicular to this plane. [b] M = Cu or Ni.

The arrangement of ions or molecules intercalated in layered solids is often obvious from the acquired data,[39−41] but in many cases the orientation of the guest ion must be deduced.[42−44] The IR spectra provide a hint about the orientation of the square-planar complexes relative to the UP layers. In BAUP, the antisymmetric P−O stretch is positioned at 1124 cm^{-1}, and also in most intercalates this peak is located between 1124 and 1118 cm^{-1} . This indicates that there is no interaction or a very weak interaction between the TM complex and the $PO_4{}^{3-}$ group, and these complexes thus are arranged perpendicular to the UP layers. However, in the spectrum of $Cu(en)_2UP$ the P−O antisymmetric peak splits into 1120 and 1101 cm^{-1} (Figure 3) and in Ni(diene)UP into 1122 and 1105 cm^{-1}. The peaks at the lower wavenumber indicate a weakened P−O stretch due to a $(P-O)-M(L)^{2+}$ interaction, and thus in $Cu(en)_2UP$ and in Ni(diene)UP the TM complexes are arranged parallel to the UP layers.

From the crystal structure of HUP, one proton occupies approximately 24.5 $Å^2$ of the UP layer area.[12] Therefore, one divalent cation in a monolayer will occupy the area of two protons and will have a maximum of 49.0 $Å^2$ of the layer area. The approximate sizes of the intercalated complexes (Table 4) indicate that the bis(en), bis(pn), and trien complexes are small enough to be able to reside in the UP interlayer space in a monolayer parallel to the UP layers at 100% ion exchange.

In such a case, the interlayer distance would consist of the thickness of the UP layer (4.7 Å) plus the *z*-dimension of the complex (up to 3.7 Å), yielding very small interlayer distances of approximately 8.4 Å. This indeed happens in $Cu(en)_2UP$ (d = 8.59 Å), and thus a monolayer parallel to the UP layers is the most likely explanation. This, however, is not true for the bis(pn) and trien complexes, as both the IR spectra and the interlayer distances indicate. The IR spectra and the observed interlayer distance (17.91 Å) of Ni(diene)UP indicate a bilayer of complexes arranged parallel to the UP layers. The remaining intercalates, $Cu(pn)_2UP$, Cu(trien)UP, Cu(14-ane)UP, Cu(15-ane)UP, Ni(trien)UP, and Ni(14-ane)UP, appear to have the intercalated complexes oriented in monolayers which are perpendicular to the UP layers, or they may be slightly tilted. In such a case, the interlayer distances should consist of the thickness of the UP layer and of the *x*- or *y*-dimension of the particular guest cation (Table 4), and the observed interlayer distances indeed correlate with this prediction (Figure 7).

The suggested model makes it easier to understand why the very flat metal−trien complexes were able to intercalate into

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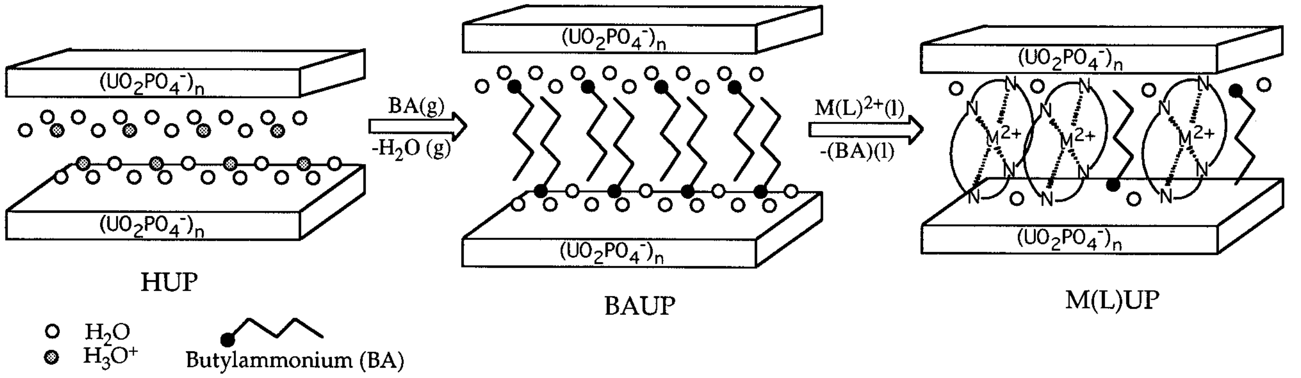

Figure 7. Arrangement of molecules and ions in the interlayer uranyl phosphate space during incorporation of transition metal complexes. Cu(pn)$_2^{2+}$, Cu(trien)$^{2+}$, Cu(14-ane)$^{2+}$, Cu(15-ane)$^{2+}$, Ni(trien)$^{2+}$, and Ni(14-ane)$^{2+}$ arrange in this way. Cu(en)$^{2+}$ forms a monolayer and Ni(diene)$^{2+}$ forms a bilayer which are parallel to the UP sheets.

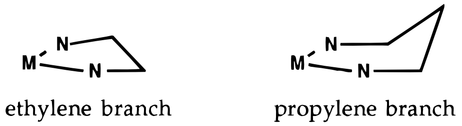

Figure 8. Types of aliphatic branches in transition metal complexes. The ethylene branch is much flatter than the propylene branch.

the UP lattice with such a high efficiency. The small size and a relative flatness of the trien and of the ethylenediamine complexes is given by the fact that they contain only ethylene branches. The trien complexes are able to efficiently stack "face to face" in the UP interlayer space, whereas the bis(en) complexes reside in a parallel sandwich-like arrangement. As observed in the TGA results, these intercalates contain little water. The low water content in this group of intercalates results from the fact that the small, square-shaped, well-ordered, and tightly stacked bis(ethylenediamine) and tris(ethylenetetramine) complexes leave little free space for water molecules.

On the other hand, all other complexes contain propylene branches in which the additional CH_2 group considerably protrudes out of the $x-y$ plane, significantly adding to their z-dimension (Figure 8). This additional CH_2 group diminishes the ability of these complexes to regularly stack in between the UP layers. This explains why complexes with ligands containing aminopropylene branches (pn, 14-ane, 15-ane) generally intercalate to a lesser degree than the complexes containing only the ethylene groups in the ligands. The less regular stacking of all of the other complexes thus leaves more open space for water molecules. The positions of the interlayer water molecules is random, mostly filling cavities in the irregular stacking of complexes.

Orientation of the aliphatic chains of unexchanged BA cations can also be estimated. In intercalates with perpendicular stacking as in Figure 7, the 5.8 Å long BA cations probably remain oriented perpendicularly to the UP sheets, as it is in BAUP.[45] The sum of the thickness of a UP layer and of the BA cation length is less (10.5 Å) than the interlayer distance of any of these intercalates (Table 1), and such a perpendicular orientation is both possible and likely. It is more questionable how the BA cations are arranged in Cu(en)$_2$UP and in Ni(diene)-UP in which the planar complexes are stacked parallel to the UP layers. One possibility is a parallel arrangement of the BA cations to the UP layers, and the other is a random bent arrangement. From the known data, it is impossible to distinguish which option of these two is preferred.

The ion exchange derivatives of HUP prepared in this study can thus be divided into two groups. The first group includes Cu(en)$_2$UP, Cu(trien)UP, and Ni(trien)UP. These intercalates are typical for high extents of ion exchange, low extents of hydration, and small UP interlayer distances. The three mentioned characteristics reveal a high ability of these complexes to efficiently stack themselves into the interlayer uranyl phosphate space which is due to their small sizes and regular squarelike shapes. The second group includes all derivatives other than those in the above group. These compounds contain relatively lower amounts of intercalated complexes and high amounts of water, and their UP interlayer distances are large. These characteristics reflect a poor ability of the complexes to closely and efficiently stack themselves in the UP interlayer space, which is due to their large sizes and to their irregular shapes.

Conclusions

Several conclusions can be drawn from the reported results. The Cu^{2+} and Ni^{2+} complexes known to predominantly have an octahedral, tetragonally distorted symmetry in water solutions lost the axial water molecules upon their intercalation into the uranyl phosphate interlayer space. Most of the square-planar complexes intercalated into the interlayer UP space oriented their planes perpendicularly to the UP layers and parallel to the alkyl chains of unexchanged BA cations. The Cu(en)$_2^{2+}$ complexes formed a monolayer parallel to the UP layers and Ni(diene)$^{2+}$ formed a parallel bilayer. Finally, the degree of intercalation of a particular square-planar complex depended very little on the central metal, but very significantly on the size and on the shape of the ligands of the particular complex. This research thus contributes to an understanding of how planar transition metal complexes behave in layered hosts as HUP and how this behavior influences properties of the intercalate such as its electronic spectroscopy, luminescence, interlayer distance, and hydration.

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