free induction decays were accumulated for Hg_3^{2+} and Hg_4^{2+} spectra recorded at 44.800 MHz and ca. 5000 for all other spectra. The decays were smoothed before being transformed into the frequency domain with use of a line-broadening parameter of 20 Hz for Hg_3^{2+} and Hg_4^{2+} at 44.800 MHz and 3-6 Hz for all other spectra.

Both spectrometers were equipped with variable-temperature controllers. The reported temperatures were measured by inserting a copper-constantan thermocouple directly into the probe and are accurate to ±1 °C.

Acknowledgment. We wish to thank Dr. D. P. Santry for useful discussions, the Natural Sciences and Engineering Research Council of Canada for financial support, and the Canada-France Exchange Program (administered jointly by the NSERC, Ottawa, Canada, and the CNRS, Paris, France) for a travel and subsistence grant to P.G.

Registry No. Hg^{2+}, 14302-87-5; Hg_2^{2+}, 12596-26-8; Hg_3^{2+}, 12596-27-9; Hg_4^{2+}, 51383-32-5; ^{199}Hg, 14191-87-8.

Contribution from the Department of Chemistry, The American University, Washington, D.C. 20016

pK_a and Isomer Determinations of Cobalt(III) Imidazole and Histidine Complexes by NMR and X-ray Crystallography

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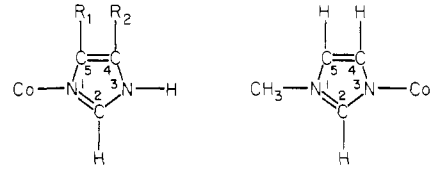
Received September 30, 1982

The pK_a's for *cis*-$Co(en)_2(H_2O)ImH^{3+}$, *cis*-$Co(en)_2(H_2O)(N\text{-MeIm})^{3+}$, *cis*-$Co(en)_2(H_2O)(4\text{-MeImH})^{3+}$, and $Co(en)(H_2O)HisH^{2+}$ are 5.85, 5.95, 5.95, and 6.20 for pK_{a_1}, respectively, at 25 °C and 10.5, ..., 10.8, and 10.8 for pK_{a_2}, respectively, as determined by potentiometric titration and ^1H NMR spectroscopy. pK_{a_1} represents the water ionization and pK_{a_2} the imidazole ionization. Changes in chemical shift for the acidic and basic forms of the coordinated imidazole were 0.6 ppm for the C(2)-H, 0.25 ppm for the C(4)-H, and about 0.16 ppm for the C(5)-H, which were similar to the changes found in $Co(NH_3)_5ImH^{3+}$. ^1H NMR titration behavior showed that the histidine was coordinated through an imidazole nitrogen, and ^{13}C NMR spectra indicated that this is N1. The single-crystal X-ray structure determination of the coordination environment of the complex showed that the histidine is tridentate. Crystal data for [Co(HisH)(en)Cl]Cl: space group $P\bar{1}$, $Z = 2$, $a = 7.939$ (2) Å, $b = 9.247$ (3) Å, $c = 11.021$ (4) Å, $\alpha = 118.75$ (3)°, $\beta = 97.76$ (3)°, $\gamma = 97.72$ (2)°, $R = 3.7\%$ for 3533 reflections. ^{13}C spectra also indicated the methyl group in the 4-methylimidazole complex was adjacent to the ionizable hydrogen. Changes in ligand, charge of the complex, substituents on the imidazole ring, and geometry of the complex all changed the C(2)-H chemical shift about 0.1 ppm. Ionization of coordinated water changed the C(2)-H chemical shift of coordinated imidazole less than 0.1 ppm and had less effect on the C(4)-H and C(5)-H resonances. Slow C(2) hydrogen exchange was found at pH 10.6 for *cis*-$Co(en)_2(OH)Im^+$. More rapid C(2)-H exchange was found for *cis*-$Co(en)_2(OH)(N\text{-MeIm})^{2+}$ at pH 12. In both cases the rates were slower than for the analogous methylated or protonated species.

Introduction

Histidine, the amino acid containing the aromatic side chain imidazole, is important in binding metal ions to proteins. NMR methods have been used to identify individual residues and determine which histidines are coordinated to metal ions.[2-4] In many cases it is difficult to tell whether an unusual imidazole pK_a is due to coordination or environmental effects. Because of our interest in coordinated imidazole, we used substitution-inert model complexes to examine some of the properties of coordinated imidazoles. In our model complexes, ligand changes, charge changes, geometry changes, pH titration behavior, C2-H exchange, and substitution effects could all be evaluated without the possibility of interference from environment effects.[3] In our studies we used *cis*-$Co(en)_2ClImH^{2+}$, *cis*-$Co(en)_2Cl(N\text{-MeIm})^{2+}$, *cis*-$Co(en)_2Cl(4\text{-MeImH})^{2+}$, $Co(en)ClHisH^+$ and their hydrolysis products in acidic and basic solution (en = ethylenediamine, Me = methyl, ImH = neutral imidazole, HisH = $NH_2CH(COO)CH_2ImH$). The aquated complexes contained a water molecule and an imidazole coordinated to the same metal center. The Zn^{2+} in carbonic anhydrase is coordinated to three histidines and a water molecule. An ionization occurs at pH 6-7, which is necessary for the catalytic reaction, but the mechanism for the reaction is not well understood.[5,6] Whether this ionization is due to a coordinated H_2O or coordinated histidine or some group in the cavity nearby is not known although recent evidence in the Co(II) enzyme shows that no imidazole N-H's are lost.[7] In the studies of the model complexes it was possible to observe the change in C(2)-H resonance during both the H_2O ionization and the imidazole ionization.



ligands:
imidazole (R_1, R_2 = H),
histidine (R_1 = $-CH_2CH(NH_2)$-(COOH), R_2 = H),
4-methylimidazole
(R_1 = H, R_2 = CH_3)

Experimental Section

Synthesis. *cis*-$[Co(en)_2ClImH]Cl_2$, *cis*-$[Co(en)_2Cl(N\text{-MeIm})]Cl_2$, and *cis*-$[Co(en)_2Cl(4\text{-MeImH})]Cl_2$ were all synthesized by the method of Kindred and House.[8] The complexes were recrystallized from a

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Table I. ^{1}H NMR Chemical Shifts[a]

compd	C(2)-H[b]	C(4)-H[b]	C(5)-H[b]	Me	compd	C(2)-H[b]	C(4)-H[b]	C(5)-H[n]	Me
ImH_2^+ [c]	8.75	7.56			*cis*-$Co(en)_2Cl(N\text{-}MeIm)^{2+}$ [f]	8.13	7.31	7.19	3.83
ImH [c]	7.76	7.19			*cis*-$Co(en)_2(H_2O)(N\text{-}MeIm)^{3+}$	8.14	7.46	7.21	3.87
$Co(NH_3)_5ImH^{3+}$ [c]	8.05	7.46	7.07		*cis*-$Co(en)_2(OH)(N\text{-}MeIm)^{2+}$	8.01	7.34	7.15	3.85
$Co(NH_3)_5Im^{2+}$ [c]	7.44	7.24	6.91		*cis*-$Co(en)_2Cl(4\text{-}MeImH)^{2+}$	8.08		6.92	2.31
	(−0.61)	(−0.22)	(−0.16)		*cis*-$Co(en)_2(H_2O)(4\text{-}MeImH)^{3+}$	8.07		6.94	2.34
cis-$Co(en)_2ClImH^{2+}$ [d,e]	8.26	7.41	7.26		*cis*-$Co(en)_2(OH)(4\text{-}MeImH)^{2+}$	7.97		6.88	2.32
cis-$Co(en)_2(H_2O)ImH^{3+}$	8.24	7.53	7.27		*cis*-$Co(en)_2(OH)(4\text{-}MeImH)^{+}$	7.44		6.72	2.23
cis-$Co(en)_2(OH)ImH^{2+}$	8.13	7.43	7.21			(−0.53)		(−0.16)	(−0.09)
cis-$Co(en)_2(OH)Im^{+}$	7.57	7.24	7.05		Co(en)ClHisH$^+$ [g]	8.18		7.25	
	(−0.56)	(−0.19)	(−0.16)		$Co(en)(H_2O)HisH^{2+}$	8.21		7.33	
trans-$Co(en)_2(H_2O)ImH^{3+}$	8.15	7.40	7.12		$Co(en)(OH)HisH^{+}$	8.01		7.23	
trans-$Co(en)_2(OH)ImH^{2+}$	8.13	7.43	7.21		$Co(en)(OH)His^{0}$	7.40		6.98	
trans-$Co(en)_2(OH)Im^{+}$	7.50	7.18	6.98			(−0.61)		(−0.25)	
	(−0.63)	(−0.25)	(−0.23)						

[a] In ppm from DSS (T = 29–30 °C). [b] Values in parentheses are differences in chemical shift from acidic to basic form. [c] From ref 35. [d] Reference 10 reports 8.24, 7.40, and 7.26 ppm, respectively, for this complex. [e] Reference 37 reports 8.20, 7.37, and 7.02 ppm for *cis*-$Pt(ImH)_2Cl_2$. [f] Methyl group at N(1); metal at N(3). [g] N adjacent to amino acid group is taken as N(1). Metal is attached to N(1); see text.

minimum amount of water, an equal volume of ethanol, and 1 mL of concentrated hydrochloric acid for every 100 mL of solution. [Co(en)ClHisH]Cl was synthesized by the method of Coulter and Krishnamurthy from 2.52 g of *trans*-$[Co(en)_2Cl_2]Cl$ dissolved in a minimum of water and 1.5 g of reagent grade *dl*-histidine hydrochloride added.[13] A color change to dark blue was observed after about 10 min, and a precipitate was obtained by cooling the solution in ice. The product was recrystallized by dissolving it in warm water and cooling the solution in ice. A crystal suitable for a single-crystal X-ray structure determination was grown by the vapor diffusion of ethanol into a concentrated aqueous solution of the complex.

The hydroxy complexes were produced by adjusting the pH of a solution of the chloro complexes to 12 and allowing the solution to stand for 0.5 h to allow for complete hydrolysis.[9,10] To prepare the aquo complexes, the pH of the solution was adjusted to 4 or less.[10,11]

To make crystalline $[Co(en)_2ImH(H_2O)]Cl_3$ 3 g of $[Co(en)_2ClImH]Cl_2$ was mixed with 0.1 N NaOH until almost dissolved. One drop of concentrated NaOH was then added, and the solution turned clear. It was allowed to stand for 0.5 h in order for hydrolysis to be complete, and then the pH was adjusted to 2.4 with HCl. The solution was put on a rotary evaporator until the volume was about 8 mL and then placed in the cold overnight. Large red crystals formed in the solution. They were filtered, washed with cold ethanol, and dried with ether.

Complex purity in all cases was determined by cobalt(II) analyses by the method of Kitson[12] after prereduction with stannochlorous acid ($SnCl_2$ + 6 M HCl). Extinction coefficients were also used when known to determine purity.

Potentiometric Titrations. Solutions of the hydroxy complexes were titrated with standard 0.10 M HCl. Solutions of the aquo complexes were titrated with standard 0.10 M sodium hydroxide. Constant temperature was maintained to within ±0.1 °C by using a thermostated beaker and a constant-temperature bath. A Fisher Accumet pH meter with a combination electrode was used to measure the pH. The electrode was standarized by using buffers at the temperature of the titration.

pK_a Determinations by NMR. The pK_a's of the complexes were determined also by ^{1}H and ^{13}C NMR spectroscopy. A 0.1 M solution of the respective chloro complex was made in D_2O, and the pH* was adjusted to 12.5 with NaOD. The solution was allowed to stand about 0.5 h in order to ensure complete hydrolysis. NMR spectra were obtained at half pH* increments beginning at pH* 12.5. (pH* is the pH reading from the electrode in the D_2O solutions, but the electrode was standardized with aqueous buffers.)

Adjustments downward were made with DCl administered with a micropipet. pH* was plotted against chemical shift, and the pK_a's were calculated from a nonlinear least-squares computer program for pH vs. δ.

The ^{1}H NMR titrations at 29–30 °C were done on a Bruker WP-80 spectrometer, and the ^{1}H NMR titration at 22 °C was done on a Nicolet NT 200 spectrometer, using a 5-mm probe and DSS as an internal standard. pH* values were obtained from a Fisher Accumet pH meter, Model 140A, using a Corning combination electrode. No adjustments for isotopes (pH vs. pD) were made.[2]

The ^{13}C NMR titration and other ^{13}C NMR spectra were taken on a Bruker WP-80 spectrometer with a 10-mm probe and with use of dioxane (δ 67.4) as an internal standard.

C–2H Exchange. All samples were dissolved in D_2O, adjusted to pH* 12 with NaOD, and allowed at least 30 min to hydrolyze completely. They were then brought to the desired pH* with DCl. ^{1}H NMR spectra were taken immediately and at various time intervals. The samples were kept at 25 °C. The C(2)–H, C(4)–H, and C(5)–H resonances were integrated and compared. The C(4)–H and C(5)–H resonances were taken as standards.

Data Collection for the Single-Crystal Structure Determination. Cell dimensions and space group data for [Co(en)(HisH)Cl]Cl were determined by standard methods[14,15] on a Nicolet P3m microprocessor-controlled four-circle X-ray diffractometer.

The θ–2θ technique, with scans 1.2° above and below $K\alpha_1$ and $K\alpha_2$, was used to collect the intensities for all nonequivalent reflections for which $3.8° < 2\theta < 60°$. The intensities of four standard reflections monitored every 96 reflections showed no greater fluctuations during the data collection than that expected from Poisson statistics. The 4714 raw intensity data collected were corrected for Lorentz–polarization effects and absorption, and those 3533 reflections for which $I > 3\sigma(I)$[16] were used in the final refinement of the structural parameters.

Structure Solution and Refinement. A three-dimensional Patterson synthesis was used to determine the heavy-atom positions, which phased the data sufficiently well to permit the location of the remaining non-hydrogen atoms from difference Fourier syntheses. Full-matrix least-squares refinement of the model was carried out as previously described.[17] Anisotropic temperature factors were introduced for all non-hydrogen atoms. Further difference Fourier calculations enabled the location of the hydrogen atom positions, which were included in the refinement for four cycles of least-squares refinement and then held fixed. The model converged with R = 3.7% and R_w = 4.3%. A final Fourier difference map was featureless. Scattering factors and anomalous dispersion term values were taken from standard sources.[18–20]

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Table II. ^{13}C NMR Chemical Shifts[a]

complex	C(2)	C(4)	C(5)	en	Me
cis-$Co(en)_2ClImH^{2+}$ [b]	140.7	120.6	128.3	46.2, 45.0	
cis-$Co(en)_2(H_2O)ImH^{3+}$	139.8	121.5	127.9	3 peaks	...
cis-$Co(en)_2(OH)ImH^{2+}$	139.3	120.9	127.7	3 peaks	...
cis-$Co(en)_2(OH)ImH^{+}$	145.4	129.2	126.5	3 peaks	...
$Co(en)ClHiSH^{+}$	139.9	117.7	133.9[c]	45.8, 45.1	26.3[d]
$Co(en)(OH)His^{0}$	143.9	124.4	133.4	45.0, 44.5	26.2[d]
cis-$Co(en)_2Cl(4\text{-}MeImH)^{2+}$	140.7	132.1[c]	125.5	45.9, 44.9	9.13
cis-$Co(en)_2(OH)(4\text{-}MeIm)^{+}$	145.4	139.5	124.5	45.0, 43.9	12.2
cis-$Co(en)_2Cl(N\text{-}MeIm)^{2+}$	143.6	129.7	125.7	45.9, 44.9	35.1

[a] In ppm from dioxane at 67.4 ppm. [b] From ref 22. [c] NOE shows this is the quaternary carbon. [d] $-CH_2-$.

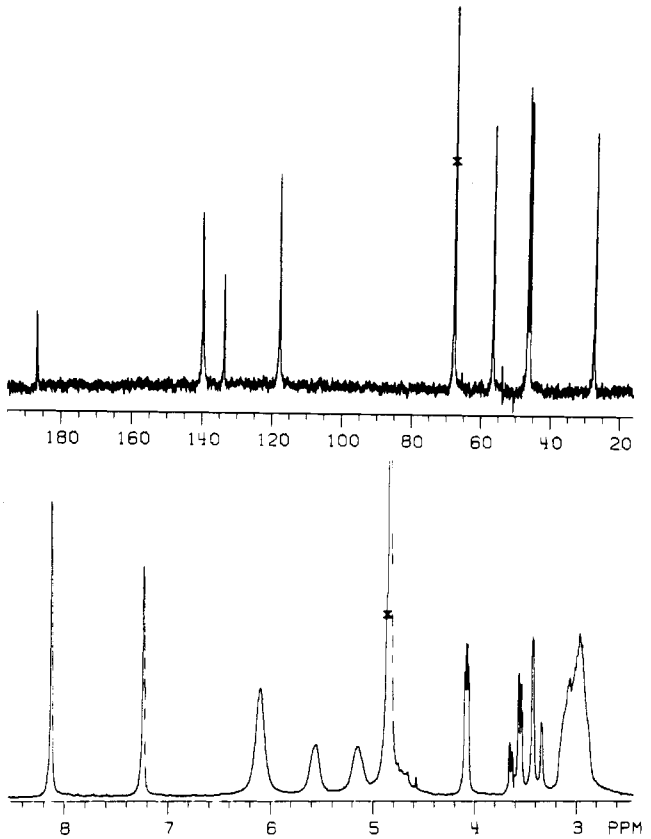

Figure 1. ^{13}C (upper) and ^1H (lower) NMR spectra of [Co(en)ClHisH]Cl. The peaks marked with an × are for reference dioxane (δ 67.4) (^{13}C) and solvent HOD (^1H). The pH of the solution was 6.2.

Listings of the observed and calculated structure factors, thermal parameters, and selected least-squares planes through groups of atoms are available.[21] The principal programs used are as described previously.[17]

Results and Discussion

The *cis*-$Co(en)_2ClImH^{2+}$ and *cis*-$Co(en)_2Cl(N\text{-}MeIm)^{2+}$ complexes had Co(II) analyses that indicated that the complexes were pure, and their UV–vis, IR, and NMR data agreed with previously reported data.[9-11,13] The $Co(en)_2Cl(4\text{-}MeImH)^{2+}$ had a cobalt analysis that indicated that the complex was pure (within 1% of the calculated value). Its UV–vis,[21] IR, and NMR spectra were similar to those for both the imidazole and *N*-methylimidazole complexes (Tables I and II), and therefore the complex is assumed to be the 4-methylimidazole complex and to have the cis configuration. The ^1H and ^{13}C NMR spectra of the complex also show that only one isomer of the two possible for this cis complex is present and no H-containing impurities were detectable in the ^1H NMR spectrum.

Table III. Positional Parameters for [Co(en)Cl(His)]Cl

atom	*x*	*y*	*z*
Co	0.22067 (4)	0.23915 (4)	−0.03393 (3)
Cl(1)	0.23405 (9)	0.47414 (7)	−0.04852 (7)
Cl(2)	0.47653 (10)	0.76795 (8)	0.37561 (7)
O(10)	0.2208 (2)	0.0398 (2)	−0.0203 (2)
O(11)	0.3353 (2)	−0.1860 (2)	−0.0958 (2)
N(1)	0.0560 (3)	0.1008 (3)	−0.2176 (2)
N(3)	−0.1876 (4)	−0.0157 (3)	−0.3805 (3)
N(8)	0.4082 (3)	0.1779 (2)	−0.1310 (2)
N(E1)	0.3782 (3)	0.3639 (3)	0.1536 (2)
N(E4)	0.0361 (3)	0.2851 (3)	0.0703 (2)
C(2)	−0.1057 (4)	0.1142 (4)	−0.2542 (3)
C(4)	−0.0760 (5)	−0.1181 (4)	−0.4311 (3)
C(5)	0.0767 (4)	−0.0452 (3)	−0.3305 (3)
C(6)	0.2479 (4)	−0.0985 (3)	−0.3393 (3)
C(7)	0.3819 (3)	−0.0082 (3)	−0.1976 (3)
C(9)	0.3127 (3)	−0.0573 (3)	−0.0965 (3)
C(E2)	0.2829 (4)	0.3569 (4)	0.2586 (3)
C(E3)	0.1098 (4)	0.3939 (4)	0.2248 (3)
H(2)	−0.145 (4)	0.187 (4)	−0.206 (3)
H(3)	−0.286 (5)	−0.039 (4)	−0.430 (4)
H(4)	−0.110 (5)	−0.212 (4)	−0.516 (3)
H(61)	0.287 (5)	−0.085 (4)	−0.412 (3)
H(62)	0.234 (4)	−0.210 (4)	−0.379 (3)
H(7)	0.479 (4)	−0.040 (4)	−0.215 (3)
H(81)	0.516 (4)	0.221 (4)	−0.078 (3)
H(82)	0.409 (5)	0.196 (4)	−0.198 (3)
H(E11)	0.404 (6)	0.470 (5)	0.183 (4)
H(E12)	0.470 (5)	0.315 (4)	0.146 (3)
H(E21)	0.267 (5)	0.242 (4)	0.247 (4)
H(E22)	−0.039 (4)	0.332 (4)	0.047 (3)
H(E31)	0.121 (5)	0.500 (4)	0.252 (3)
H(E32)	0.049 (6)	0.382 (5)	0.265 (4)
H(E41)	−0.015 (5)	0.201 (4)	0.054 (3)
H(E42)	0.342 (4)	0.436 (4)	0.350 (3)

Although the procedure of Coulter and Krishnamurthy yielded *cis*-$Co(en)_2LCl^{2+}$ complexes, where L = imidazole and substituted pyridines, the products were always red. The complex formed when *dl*-histidine is used is blue (λ_{max} = 580 and 360 nm, ϵ = 68 and 179 M^{-1} cm^{-1}, respectively). ^1H NMR and ^{13}C NMR showed that, of many isomers possible for the product, only one is present in solution (Tables I and II, Figure 1). The ^1H NMR shows that there are no H-containing impurities, the integrated spectrum shows that there are only four ethylenediamine protons instead of the expected eight, and the ^{13}C NMR shows eight carbons although only eight peaks would be observed for *cis*-$Co(en)_2ClHisH^{+}$ as well.[22]

Consequently, a single-crystal X-ray structure determination of this product was done.

Crystal Structure. The structure showed that the correct formula for the product is [Co(en)ClHisH]Cl. The final positional parameters for the atoms are given in Table III. Table IV contains the most important interatomic distances and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures

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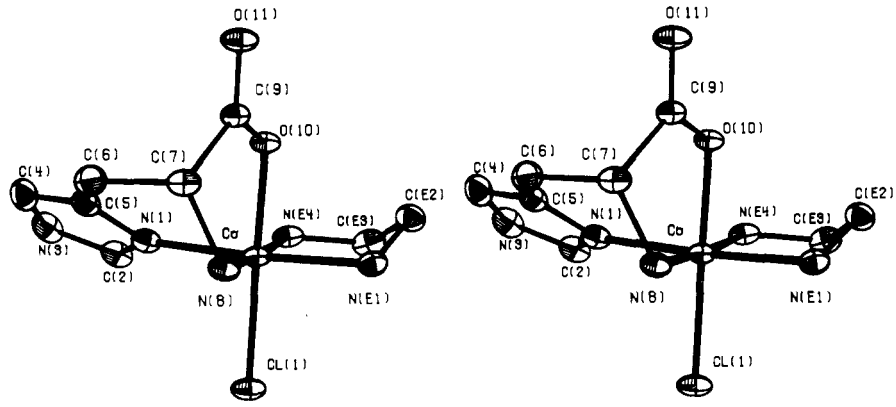

Figure 2. Atomic arrangement of the $[Co(en)ClHisH]^{2+}$ cation and the numbering scheme for the complex.

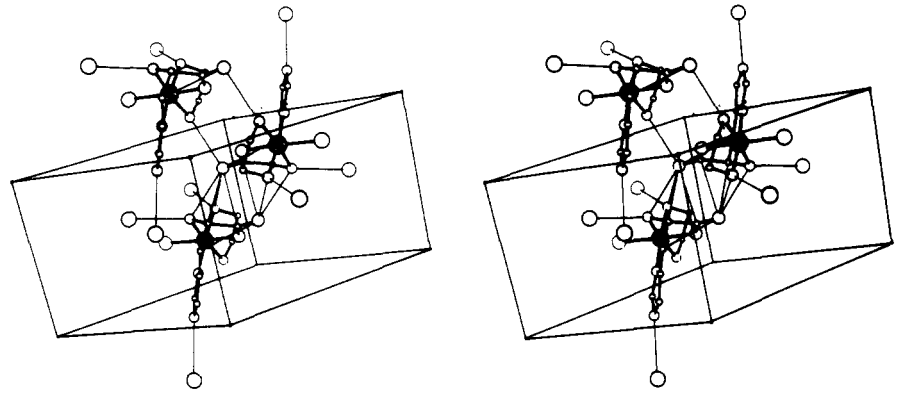

Figure 3. Ionic packing diagram in the unit cell of [Co(en)ClHisH]Cl.

quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figure 2 shows a stereoview of the cation and also gives the numbering scheme for the atoms, while Figure 3 shows the ionic packing in the unit cell. As is evident from the packing diagram, the complex consists of complex cations and Cl^- anions connected via extensive hydrogen-bonding interactions as described below.

The histidine moiety acts as a tridentate ligand occupying one face of the cobalt(III) octahedron, which is the only way the molecule can readily fit as a tridentate ligand in an octahedral complex. The coordination of the histidine moiety to the cobalt center is via the amine nitrogen atom, one of the carboxylate oxygen atoms, and one of the imidazole nitrogen atoms. It is deprotonated only at the carboxylate group and not at the imidazole ring. One bidentate ethylenediamine group and one chloride ion complete a six-coordinate environment about the cobalt atom. As the chloride ion is the most electronegative donor atom, it is bonded trans to the coordinated carboxylate oxygen atom as stability is conferred by placing these donor atoms on opposite sides of the metal.

The two $[Co(en)ClHisH]^+$ ions in the unit cell are related by an inversion center and therefore are enantiomers, not only because one must contain *d*-histidine and one *l*-histidine but also because the cobalt center itself is chiral.

The uncoordinated carboxylate oxygen atom, the uncoordinated (and protonated) imidazole nitrogen atom, and the ethylenediamine nitrogen atoms are involved in an extensive hydrogen-bonding network that may be summarized into three classes:

(1) The two cations within the unit cell are linked together by hydrogen bonding via the uncoordinated carboxylate oxygen atom of each, O(11), which is linked through H(E41) to one of the nitrogen atoms of the ethylenediamine group, N(E4), of the other; O(11)–N(E4) = 3.059 (3) Å.

(2) Each cation is also paired with an enantiomer of the adjacent unit cell in the *a* direction. The O(11) atoms of each are linked via H(81) and H(E1) to the N(8) and N(E1) atoms of the other; O(11)–N(8) = 2.968 (4) Å, O(11)–N(E1) = 2.945 (4) Å.

Table IV. Interatomic Distances and Bond Angles for [Co(en)Cl(His)]Cl[a]

Co-Cl(1)	2.244 (1)	C(9)-O(10)	1.288 (4)
Co-N(1)	1.946 (3)	C(9)-O(11)	1.231 (3)
Co-N(8)	1.938 (3)	N(E1)-C(E2)	1.487 (5)
Co-O(10)	1.921 (2)	C(E2)-C(E3)	1.502 (6)
Co-N(E1)	1.946 (3)	C(E3)-N(E4)	1.476 (6)
Co-N(E4)	1.949 (3)	Cl(2)-N(3)	3.130 (4)[a]
N(1)-C(2)	1.333 (4)	Cl(2)-N(8)	3.193 (3)[b]
N(1)-C(5)	1.377 (5)	C(7)-O(11)	3.177 (4)[c]
C(2)-N(3)	1.319 (6)	N(8)-O(11)	2.968 (4)[c]
N(3)-C(4)	1.358 (6)	C(9)-C(9)	3.125 (6)[c]
C(4)-C(5)	1.360 (5)	C(9)-O(11)	3.080 (4)[c]
C(5)-C(6)	1.507 (5)	O(10)-N(E4)	3.154 (4)[d]
C(6)-C(7)	1.525 (5)	O(11)-N(E1)	2.945 (4)[c]
C(7)-N(8)	1.480 (4)	O(11)-N(4)	3.059 (3)[e]
C(7)-C(9)	1.529 (4)		

Cl(1)-Co-N(1)	92.31 (8)	C(2)-N(3)-C(4)	108.2 (3)
Cl(1)-Co-N(8)	92.69 (8)	N(3)-C(4)-C(5)	106.9 (4)
Cl(1)-Co-O(10)	177.34 (7)	N(1)-C(5)-C(4)	108.1 (3)
Cl(1)-Co-N(E1)	91.93 (9)	N(1)-C(5)-C(6)	123.3 (3)
Cl(1)-Co-N(E4)	92.78 (9)	C(4)-C(5)-C(6)	128.4 (4)
N(1)-Co-N(8)	88.34 (12)	C(5)-C(6)-C(7)	114.1 (3)
N(1)-Co-O(10)	89.18 (11)	C(6)-C(7)-N(8)	110.7 (3)
N(1)-Co-N(E1)	175.38 (12)	C(6)-C(7)-C(9)	108.8 (3)
N(1)-Co-N(E4)	93.15 (13)	N(8)-C(7)-C(9)	107.4 (3)
N(8)-Co-O(10)	85.15 (10)	Co-N(8)-C(7)	106.4 (2)
N(8)-Co-N(E1)	93.28 (12)	C(7)-C(9)-O(10)	114.8 (3)
N(8)-Co-N(E4)	174.27 (12)	C(7)-C(9)-O(11)	121.6 (3)
O(10)-Co-N(E1)	86.65 (11)	O(10)-C(9)-O(11)	123.4 (3)
O(10)-Co-N(E4)	89.34 (11)	Co-O(10)-C(9)	114.2 (2)
N(E1)-Co-N(E4)	84.82 (13)	Co-N(E1)-C(E2)	108.9 (2)
Co-N(1)-C(2)	127.7 (3)	N(E1)-C(E2)-C(E3)	105.1 (3)
Co-N(1)-C(5)	125.8 (2)	C(E2)-C(E3)-N(E4)	108.1 (3)
C(2)-N(1)-C(5)	106.0 (3)	Co-N(E4)-C(E3)	111.1 (2)
N(1)-C(2)-N(3)	110.8 (4)		

[a] Symmetry transformations: (a) $1+x, 1+y, 1+z$; (b) $1-x, 1-y, -z$; (c) $1-x, -y, -z$; (d) $-x, -y, -z$.

Together, these two classes of hydrogen bonding serve to link the cations into a chain in the *a* direction, the chain links being of alternating chirality.

(3) The anion chains are hydrogen bonded together by the intervening chloride ions. The chloride anion is held in a pocket consisting of the N(3), N(8), and N(E1) atoms of different anion chains, to which it is linked via H(3), H(82), and H(E11), respectively; Cl(2)–N(3) = 3.130 (4) Å, Cl(2)–N(8) = 3.193 (3) Å, Cl(2)–N(E1) = 3.234 (4) Å.

The ligand environment about the cobalt atom conforms quite closely to that of an octahedron. The adjacent ligand angles range from 84.8 (1) to 93.3 (1)°, while the trans ligand angles range from 175.4 (1) to 177.34 (7)° instead of the 90 and 180°, respectively, required for a regular octahedron. The greatest deviations occur for the ethylenediamine moiety, whose bite only allows a N–Co–N angle of 84.8 (1)° instead of 90°. A similar distortion occurs for the coordinated amine nitrogen and carboxylate oxygen atoms of the histidine molecule, N–Co–O being 85.1 (1)°.

Least-squares planes through selected groups of atoms also indicate small deviations from octahedral symmetry in the cation, with angles 86.7, 89.2, and 89.5° between the three equatorial planes of donor atoms. The only strong deviation from orthogonality, 86.7°, is a direct result of the small bite of the ethylenediamine ligand. The plane of the imidazole ring of the histidine ligand is rotated by 32.4° from the ligand plane containing the imidazole nitrogen, the amine nitrogen, and the ethylenediamine nitrogen atoms, to allow the carboxylate oxygen atom to also participate in bonding to the cobalt atom.

There have been two reports of X-ray structures of histidine complexes of cobalt(III): (*d*-histidinato)(*l*-histidinato)cobalt(III) bromide[23] and bis(*l*-histidinato)cobalt(III) perchlorate dihydrate.[24] Of the five possible configurations, trans amine nitrogen, trans carboxylate oxygen, trans imidazole nitrogen, all trans, and all cis, the former structure has an all cis configuration while the latter has a trans amine configuration. A comparison of the bond lengths and angles found in the present structure with those found previously shows that there are very little significant differences between these structures.[21] The largest difference is found for the cobalt imidazole nitrogen bond length and even this is only marginally significant (2.1σ). The bond lengths and angles found for the chelated ethylenediamine moiety are similar to those found in other mixed-ligand chelates of cobalt(III).[25]

pK_a Determinations. Previous kinetic results show that leaving a solution of the chloroimidazole or the chloro-*N*-methylimidazole complex at pH 12 for 0.5 h is sufficient time for complete Cl^- hydrolysis to occur and some cis–trans isomerization.[10,11] pH titration of the chloro-4-methylimidazole and chlorohistidine complexes shows similar behavior as indicated by a decrease in pH with time in the 9–11 range and the consumption of more than 1 mol of OH^-/mol of complex. Stability studies, where changes in the UV–vis spectrum were monitored, showed that the imidazole, *N*-methylimidazole, and 4-methylimidazole complexes were stable in both acidic and basic solution after hydrolysis to the aquo or hydroxy species for at least 3 weeks and longer for the imidazole complex. Consequently, there was no deterioration of the complexes during the titration and exchange experiments. However, the histidine complex was completely destroyed in 2 days at 25 °C at pH 12.

All four complexes were titrated potentiometrically at various temperatures (Table V). The histidine, 4-methylimidazole, and imidazole complexes all consumed 2 mol of acid/mol of complex. Each had a pK_a at approximately 10.8 and 6. The titration of the amine H and the carboxyl H was not found because of coordination in the histidine complex. The pK_a at about 10.8 is due to the ionization of the imidazole hydrogen. NMR results given below show this ionization more clearly. The pK_a at 6 is the pK_a for the coordinated water. The *N*-methylimidazole complex has only the pK_a at 6 because it has only a titratable water. Because there is no way to determine the amount of isomerization during the titration and because the amount of cis–trans isomerization varies with pH,[10,11] the pK_a's reported for the potientiometric titration in Table V are those for isomeric mixtures. For the substituted imidazoles, the free 4-methylimidazole has the highest pK_a (7.61),[26] but after coordination this does not seem to make a difference as all four complexes have about the same pK_a values.

Table V. Potentiometric Titrations of $Co(en)_2H_2ORImH^{3+}$

complex	pK_{a_1} [a]	pK_{a_2} [a]	T, °C
$Co(en)_2(H_2O)ImH^{3+}$ [b]	5.6 (cis 6.56)	10.5 (cis 11.0; trans 10.6)	30
	5.8	10.5	25
	6.3	10.7 (cis 10.8; trans 10.40)	22
	5.9	10.7	16
$Co(en)_2(H_2O)(4\text{-MeImH})^{3+}$	5.7	10.6 (cis 11.24)	30
	5.9	10.8	26
	6.1	11.1	15
$Co(en)_2(H_2O)(N\text{-MeIm})^{3+}$	5.8		30
	5.9		25
	6.2		15
$Co(en)(H_2O)HisH^{2+}$	6.0	10.7	35
	6.1	10.8	30
	6.2	10.8 (11.3)	25
	6.2	10.9	20

[a] Values in parentheses determined by ^{1}H NMR. [b] Reference 11 reports pK_{a_1} = 6.40 at 50.6 °C. Reference 10 reports pK_{a_1} = 6.28 and pK_{a_2} = 10.52 at 25 °C and μ = 0.1. Reference 9 reports pK_{a_2} = 9.29 determined kinetically.

^{1}H NMR. As in previous work it is assumed the metal coordinates to the pyridine nitrogen and can be compared to CH_3^+ and H^+ in *N*-methylimidazolium and imidazolium. We have called this coordination site N(1) in all complexes except the *N*-methylimidazole complex where the methyl group is bonded to N(1) and the metal to N(3). The imidazole chemical shifts in the ^{1}H NMR were assigned as they were in the imidazolepentaaminecobalt(III) complex with the C(2)–H farthest downfield, the C(4)–H in the center, and the C(5)–H farthest upfield. The peak assignments in Table I reflect these assumptions. Isomerization studies show that the cis isomer seem to predominate, at least initially, at all pHs. Therefore, if a second set of peaks due to the trans isomer was present, then the larger set of peaks was assigned to the cis isomer.

In metalloproteins where metal ions are bound to proteins by the imidazole side chain, it is impossible to tell whether the change in imidazole behavior from free imidazole is due to microenvironment effects or coordination. Cass and Hill et al. suggest that the following information from the ^{1}H NMR of model systems would be useful for application to metalloproteins.[3] In the model systems there is no question that the effects are due to coordination. The information needed includes (1) changes in pH titration behavior for the C(2)–H resonances in the holoprotein as compared to the apoprotein, (2) a change in the chemical shift of the C(2)–H resonance on binding to metal ion, (3) the observation of nuclear spin–spin coupling between the metal ion nucleus and histidine C(2) and C(4) resonances in proteins, (4) changes in the chemical

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shifts of C(2)–H resonances on addition of anions or molecules that can act as ligands and/or a change in charge or geometry of the complex, and finally (5) a decrease in rate of C(2)–H exchange in neutral and basic solutions.[3] With the model systems in this work we were able to evaluate each of the above points except for 3.

Metal coordination changes the pK_a of imidazolium from 7 to anywhere between 9 and 12.[27] In this work the pK_a's of all of the complexes were between 10.5 and 11.4; see Table V. Coordination affects not only the pK_a but also the change in chemical shift ($\Delta\delta$) from acidic to basic form. In free imidazole or histidine this change is about 1 ppm upfield for C(2)–H, about 0.6 ppm upfield in the complexes (Table I), about 0.4 ppm for the free C(4)–H and C(5)–H resonances, and 0.25 and 0.16 ppm for the complexed C(4)–H and C(5)–H resonances, respectively. Coordination also causes the C(2)–H resonance to be shifted upfield from the C(2)–H resonance in imidazolium and protonated histidine. The exact position of the C(2)–H resonance depends on the charge on the complex, the other ligands in the complex, and the geometry of the complex, but none of these factors cause as large a change as coordination (about 0.1 ppm as opposed to about 0.5 ppm) (Table I). In superoxide dismutase the effect of a change in ligand was as high as 0.4 ppm.[28] Table I also shows that the ionization of a coordinated water molecule caused almost no change in chemical shift for any of the imidazole resonances, and the imidazole resonances could not be used to determine the pK_a of the H_2O in a specific isomer. This is further evidence to show that the ionization that occurs between pH 6 and 7 in carbonic anhydrase is probably not one of the coordinated imidazoles but could be the coordinated water. The reported ^1H NMR data for the imidazoles in the enzyme either show almost no change in chemical shift or show changes in chemical shift of 1 ppm.[29,30] Small changes ($\simeq$0.1 ppm) in chemical shifts of bound imidazoles were observed for the addition of anions.[29,31]

C(2)–H exchange was investigated under a variety of conditions. $Co(en)_2(OH)ImH^{2+}$ and imidazole at pH 8.4 were allowed to exchange for 62 days at room temperature in the presence and absence of added base such as 0.1 M acetate and 0.1 M borate. The coordinated imidazole did not exchange at all, and the imidazole exchanged at the same rate in all solutions. $Co(en)_2(OH)Im^+$ and imidazole were compared at pH 10.6 and 11.1, and it was found that the imidazole exchanged more rapidly by a factor of about 12. But at this pH the coordinated imidazole did exchange, with a half-life of about 20 days at room temperature. These results can be explained by the presence of a small amount of imidazolium in free imidazole for exchange and none in the coordinated imidazole. *cis*-$Co(en)_2(OH)(N\text{-MeIm})^{2+}$, *cis*-$Co(en)_2(OH)(4\text{-MeIm})^+$, and *cis*-$Co(en)_2(OH)His^0$ were allowed to exchange at 25 °C at pH 12. At this pH the histidine complex decomposed, the 4-methylimidazole complex isomerized so that some trans isomer was present but did not exchange, and the *N*-methylimidazole complex exchanged with a half-life of about 16 h but did not isomerize. These results are consistent with previous work that proposes an ylide intermediate for the exchange.[3,27,32,33] The imidazolate ion is inert to C(2)–H exchange, neutral imidazole exchanges very slowly, and imidazolium, which stabilizes the negative charge on the intermediate, is the fastest. The exchange rate for imidazole and *N*-methylimidazole is constant in the 7–11 region because the increasing OH^- concentration is offset by the decreasing $RImH^+$ (R = CH_3 or H)[33] concentration. Martin et al. have shown that a metal is a poorer Lewis acid by a factor of 10^5 than H^+ or CH_3^+ but still catalyzes exchange.[32] If we compare 1,3-dimethylimidazolium,[34] the *N*-methylimidazole complex, and *N*-methylimidazole all at pH 12 and 25 °C, rate constants for exchange are 1×10^{-1}, 2×10^{-4}, and 2×10^{-5} s^{-1}, respectively, again showing that a metal is a poorer Lewis acid than a methyl cation by a factor of about 10^3. At this pH apparently enough CH_3ImH^+ is gone so that the complex exchanges more rapidly than *N*-methylimidazole.

^{13}C NMR. The carbon-13 NMR spectra of all four chloro complexes showed two peaks of approximately equal intensity at about δ 45, where dioxane was the internal standard at δ 67.4 in each spectrum. This information had already been reported for the chloroimidazole complex. House and Blunt have shown that cis isomers should have two types of ethylenediamine carbons while the trans isomers have only one ^{13}C peak in this region.[22] Consequently, we have assumed that our complexes have the cis configuration. This has been shown for $Co(en)HisHCl^+$.

A pH titration of the aquoimidazole complex at 32 °C using ^{13}C NMR showed that the cis imidazole complex had a pK_a of 10.9 from both the C(2) and C(4) behavior with $\Delta\delta$ of 6.1 and 8.3 ppm, respectively. Because the sample was so dilute, only the cis chemical shifts were apparent in the imidazole region. In the ethylenediamine region there were three peaks, two for the cis isomer and one between the cis peaks for the trans isomer. The peak positions and changes in peak position with pH for the aquoimidazole complex agreed with the results reported for the imidazolepentaamminecobalt(III) complex.[35] No further ^{13}C pH titrations were done.

The ^{13}C chemical shifts for the complexes are reported in Table II. The ^{13}C NMR spectrum shows where the methyl group or amino-acid group is in relation to the metal in the 4-methylimidazole and histidine complexes. The ^{13}C spectrum of the acidic form and basic form shows which carbon is adjacent to the N(3)–H ($\Delta\delta$ 6–7) and which is adjacent to the metal ($\Delta\delta$ 1–2).[35,36] The diminished NOE and longer T1 for the quaternary carbon make this peak the smallest one in the imidazole region of the ^{13}C spectrum; in both cases this was the middle peak. From these results in the histidine complex, the quaternary carbon is adjacent to the metal (confirmed by the crystal structure), and in the 4-methylimidazole complex, the carbon with the methyl group is adjacent to the N(3)–H. The C(4) resonance in the 4-methyl complex is shifted further downfield than expected, but the shift may be due to the combined effect of the metal and methyl group. The ^1H NMR spectra of the acidic and basic forms help confirm these assignments as the change in chemical shift for the C(5)–H in the 4-methylimidazole complex is 0.16 ppm, similar to that found for the C(5)–H in the imidazole complexes, and $\Delta\delta$ of 0.25 ppm for the C(4)–H in the histidine complex, which is similar to the change in chemical shift for the C(4)–H in the imidazole complexes.

Conclusions. In summary we have confirmed previous results that metal coordination changes the pK_a of imidazole by 3–4 pK_a units from imidazolium and changes the magnitude of the chemical shift change from about 1 to 0.6 ppm for the C(2)–H in coordinated imidazole. We have found that other

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ligands, charge on the complex, geometry of the complex, and ionization of coordinated water have a smaller effect (0.1 ppm) on the C(2)-H resonance of the coordinated imidazole than coordination with about a 0.5 ppm change from imidazolium. C(2)-H exchange was found for coordinated imidazole and *N*-methylimidazole, but the metalated imidazoles exchanged much more slowly than the analogous methylated (10^{-3}) or protonated species.[32] In neutral regions, coordination inhibits exchange but, in basic regions, may enhance exchange depending on the relative concentrations of positive species to metalated species in solution. Using ^{13}C NMR spectroscopy, we have been able to determine that in the 4-methyl complex the quaternary carbon is adjacent to the ionizable H. The histidine in the Co(en)HisHCl$^+$ complex is tridentate with the cis configuration. The information on these model systems should be useful in identifying histidines coordinated to metal in proteins, as well as helping to identify the source of the pH 6-7 ionization in carbonic anhydrase.

Acknowledgment. The authors gratefully acknowledge the financial support of the Petroleum Research Fund, administered by the American Chemical Society, and partial support from Grant RR08016 from the National Institutes of Health. They also thank Jerome Harris and Agnes Nguyenpho for their help with potentiometric titrations.

Registry No. *cis*-Co(en)$_2$(H$_2$O)ImH^{3+}, 71155-64-1; *cis*-Co(en)$_2$(OH)Im$^+$, 88657-79-8; *trans*-Co(en)$_2$(H$_2$O)ImH^{3+}, 88728-25-0; *trans*-Co(en)$_2$(OH)ImH^{2+}, 88728-26-1; *cis*-Co(en)$_2$Cl(*N*-MeIm)$^{2+}$, 60314-39-8; *cis*-Co(en)$_2$(H$_2$O)(*N*-MeIm)$^{3+}$, 60314-42-3; *cis*-Co(en)$_2$(OH)(*N*-MeIm)$^{2+}$, 88657-80-1; *cis*-Co(en)$_2$Cl(4-MeImH)$^{2+}$, 88657-81-2; *cis*-Co(en)$_2$(H$_2$O)(4-MeImH)$^{3+}$, 88657-77-6; *cis*-Co(en)$_2$(OH)(4-MeImH)$^{2+}$, 88657-82-3; [Co(en)(HisH)Cl]Cl, 88657-76-5; Co(en)(HisH)Cl$^+$, 88657-78-7; Co(en)(H$_2$O)HisH^{2+}, 88657-83-4; Co(en)(OH)HisH$^+$, 88657-84-5; ImH, 288-32-4; *cis*-Co(en)$_2$ClImH^{2+}, 60314-38-7.

Supplementary Material Available: Tables of UV-vis spectral data, selected bond lengths and angles, crystal data and parameters of data collection, least-squares planes data, thermal parameters, and structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Resolution of a Structural Disorder through Apparently Inconsistent X-ray Diffraction and EXAFS Data: Structure of the New Layered System $Mn_{1-x}Cu_{2x}PS_3$ (x = 0.13)

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Received May 19, 1983

The synthesis, characterization, and complete structural determination of the layered system $Mn_{0.87}Cu_{0.26}PS_3$ are reported. A room-temperature single-crystal X-ray diffraction (XRD) study and powder EXAFS measurements at the manganese and copper K edges (15 and 300 K spectra) have been performed. XRD shows the existence of disorder and leads to metal-sulfur distances inconsistent with EXAFS data. This puzzling difference has been overcome and has proved very helpful for leading to a detailed picture of the metallic sites. It is shown that besides the classical [S_3PPS_3] entities two distinct types of pseudooctahedra are randomly distributed within the layers: (a) [MnS_6] entities with the expected Mn-S = 2.61 Å distances and (b) [$S_3Cu\cdots CuS_3$] bimetallic entities with center-to-apex distances of 2.83 Å.

Introduction

In recent years, there has been an increasing interest in intercalated layered systems of the MPS_3 family (where M^{II} is a transition-metal ion), which exhibit promising electrical and magnetic properties.[2] The structural versatility of these layer-type systems is well illustrated by $In_{2/3}\square_{1/3}PS_3$ ($\square$ stands for a metal vacancy)[3] and $Cr_{1/2}Cu_{1/2}PS_3$,[4] for which it was established that the occupancy of all the pseudooctahedral intralayer metallic sites was not a strict requirement for the stability of these two-dimensional frameworks.

In other respects, quite high concentrations of intralamellar metallic vacancies were shown to be tolerable by the 2D structure in a series of intercalation compounds $M^{II}_{1-x}\square_xPS_3,2x[C^+]$, where M^{II} is Mn, Zn, and Cd and C^+ represents cationic species like alkali, metallocenium, and ammonium ions.[5] However, no evidence for a superstructure was ever found in the X-ray powder diffraction patterns of these new intercalates.

During the course of our search for ordered intercalated systems, we have prepared several lamellar compounds of general formula $M_{1-x}M'_{2x}PS_3$ with M^{II} = Mn and Cd and where M'^{I} = Cu and Ag monocations were supposed to be distributed in an ordered manner over interlamellar sites. The synthesis, characterization, and complete structural determination of the $Mn_{0.87}Cu_{0.26}PS_3$ compound are reported hereafter.

In the present work, the conjunction of X-ray diffraction (XRD) results with EXAFS data proved to be invaluable; consequently, special emphasis is given to the complementarity of these two techniques.

Experimental Section

Synthesis. When the pure (~99.9%) elements Mn, Cu, P, and S in $^5/_6$:$^2/_6$:1:3 ratios were heated at 750 °C for 2 weeks in evacuated quartz ampules, a polycrystalline powder of $Mn_{1-x}Cu_{2x}PS_3$ with x = 0.13 was obtained. Subsequent treatment by chemical transport led to small green monocrystalline platelets suitable for X-ray dif-

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