Table III. Ligand Field Parameters for Chromium Complexes of EHPG and Transferrins

complex	10*Dq*, $cm^{-1} \times 10^3$	*B*, cm^{-1}
CrTr	16.26	650
CrLf	16.34	628
CrEHPG	19.57	642
CrEHPG	19.12	

of an evaluation of optical spectra. Unfortunately, there are a large number of iron complexes with moderately intense bands in the same region (~470 nm) as transferrin. Among them are complexes of the catechols, hydroxamates, simple phenols, and thiocyanate as well as EHPG. The plethora of iron complexes exhibiting a charge-transfer band in this region makes it difficult to substantiate any conclusions based solely on the optical spectra of these models. However, much more useful information about transferrin can be gained by extending these comparisons to metal ions other than iron.

The rather good qualitative if not quantitative similarity in the optical spectra of the Cr, Co, Mn, Cu, and Fe complexes of EHPG with their corresponding transferrin analogues seems to indicate that the donor groups in EHPG and transferrin are in fact quite similar. The spectra of the chromium complexes may be particularly informative as the lack of a CT band in the visible region allows the observation of the ligand field bands. For a d^3 ion such as Cr^{3+} in an octahedral or near-octahedral field, calculation of 10*Dq* is a trivial exercise. In addition, as long as at least two of the three expected transitions are observable, we may calculate values of *B* (the Racah parameter) rather accurately using tables such as those compiled by Lever.[24] These data are shown in Table III. The absorption peak maxima of transferrin and lactoferrin seem inconsistent with an N_2O_4 donor set. This question has been considered by Ainscough et al. They conclude that the donor set for CrTr or CrLf may be a N_2O_3Cl type, where a chloride is still bound to the chromium. Although our data would be consistent with this view, it is difficult to imagine the chromium ion being sufficiently inert that no aquation would occur over several weeks. In view of the sensitivity of the d–d bands in CrEHPG to isomer type, an alternative possibility would be to have two axial tyrosines, with somewhat lower pK_a's than those found in EHPG, in the transferrin complex. This combination would have the effect of shifting the absorption maxima to longer wavelength.

While the spectra of the metal EHPG complexes display all the characteristic features of the transferrin spectra, they are often shifted in energy or intensity (Table II). The *rac* iron and manganese complexes of EHPG display visible spectra that are nearly identical in band positions with those of their transferrin analogues, while the spectra of the cobalt, copper, and chromium complexes of EHPG are shifted to higher energy. The reasons for these differences may have several origins: The first is the negative charge on the EHPG complexes. This is expected to have the effect of increasing the energy of LMCT transitions. The second possibility is the steric strain associated with the five-membered carboxylate chelate rings. As has been pointed out by Martell, EHPG with its five-membered carboxylate chelate rings is strained upon metal binding. The position (axial or equatorial) of the strained ring system is seen to affect the optical spectra as demonstrated by the spectral differences between the meso and *rac* isomers. The third reason may be electronic effects and pK_a values. There appears to be evidence that the pK_a's of the tyrosines in conalbumin, at least, are unusually low with values of ~8.5 and 10.5 reported.[31] NMR work has shown that the histidine imidazoles have unusually high pK_a's: ~7.5 and 7.6.[32] The dissociation constants for EHPG are 6.3 and 8.6 for the amino nitrogens and 10.2 and 11.7 for the phenols.

Work in modifying the basic structure of EHPG to examine the electronic and steric effects discussed is under way, and it appears hopeful that some derivative of EHPG will be a very useful model in probing the binding site and mode of action of the transferrins.

Acknowledgment. This work was supported in part by a grant from the Research Corp. for which the authors are grateful. K.P.S. acknowledges the support of the NSF-URP program.

Registry No. *rac*-Na[Mn(EHPG)], 81654-79-7; *rac*-K[Cr(EHPG)], 81624-18-2; *rac*-$CoEHPG^-$, 81624-19-3; *rac*-$CuEHPG^{2-}$, 81602-76-8; *meso*-$MnEHPG^-$, 81602-70-2; *meso*-$CrEHPG^-$, 81654-77-5; *meso*-$CoEHPG^-$, 81654-78-6; *meso*-CuEHPG, 81702-29-6.

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Origin of the Red Color in Copper(II)-Doped Ethylenediammonium Tetrachloromanganate(II)

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Crystals of the two-dimensional antiferromagnets A_2MnCl_4 ($A = RNH_3$ or $A_2 = R(NH_3)_2$) doped with small amounts of copper(II) are deep red. The origin of the phenomenon is investigated by single-crystal absorption spectroscopy of a variety of copper(II)-doped manganese(II) compounds. An intense absorption band centered at 20 800 cm^{-1} and completely polarized in the plane of the two-dimensional lattice is responsible for the color. The band is interpreted as a Cl → Cu electron-transfer transition in a $CuCl_6$ center with a "strained" coordination.

Introduction

Salts of the layer perovskite family, $(RNH_3)_2MX_4$, have been intensely studied during the past decade for a variety of reasons. They consist of layers of corner-sharing octahedra (or pseudooctahedra) sandwiched between layers of the monosubstituted ammonium ions.[1] When the metal ion is a paramagnetic center such as copper(II), manganese(II), or iron(II), the salts provide excellent realizations of two-di-

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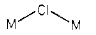
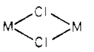
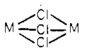
Table I. Structural Properties of Host Lattices (Literature) and Spectroscopic Results of the Copper(II)-Doped Crystals (20 K)

host	space group	metal coord	bridging geom	dimensionality	energies of Cu^{2+} abs, 10^3 cm^{-1}	ϵ_{max} (dominant polarizn)	assign
$Cs_2MnCl_4\cdot 2H_2O$[16]	$P\bar{1}$	*trans*-$MCl_4(H_2O)_2$	no bridge	isolated complexes	32.4	4800 (*c*)	CT
					38.2	9600 (*c*)	
$CsMnCl_3\cdot 2H_2O$[17]	*Pcca*	*cis*-$MCl_4(H_2O)_2$		1	6.6	3.4 (*a*)	d-d
					9.4	2.7 (*a*)	
					11.5	8.7 (*a*)	
					29.9	780 (*b*)	CT
					33.8	980 (*a*)	
					38.2	3000 (*b*)	
					42.6	1200 (*a*)	
$[(CH_3)_3NH]MnCl_3\cdot 2H_2O$[18]	*Pnma*	*trans*-$MCl_4(H_2O)_2$		1	35.4	8700 (*b*)	CT
					41.7	2200 (*b*)	
$[(CH_3)_4N]MnCl_3$(TMMC)[19]	$P6_3/m$	MCl_6		1	10.0	12.0 (*c*)	d-d
					12.0	26.3 (*c*)	
					27.5	11000 (*c*)	CT
					28.7	3100 (*ab*)	
					36.8	14000 (*c*)	
$(enH_2)MnCl_4$[15]	$P2_1/b$	MCl_6	M—Cl—M	2	9.0	14	d-d
					11.3	60	
					20.8	8000 (*bc*)	CT
					24.8	7000 (*bc*)	
					26.9	5000 (*a*)	
					31.9	2500 (*bc*)	
					35.0	3000 (*bc*)	
					36.0	8000 (*a*)	
$(enH_2)CuCl_4$[15]	$P2_1/b$	MCl_6	M—Cl—M	2	11.3	19	d-d
					13.3	25	

mensional magnetic systems.[2] This family also provides many examples of structural phase transitions,[3] including in at least one instance a transition to an incommensurate phase.[4] When R is a long-chain alkyl group, the systems become crystalline models for the behavior of lipid bilayers.[5]

An area of current interest in magnetism is the behavior of mixed-metal systems. Examples are the systems $K_2Mn_{1-x}M_xF_4$ (M = Fe, Co),[6,7] $Fe_{1-x}Co_xCl_2\cdot 2H_2O$,[8,9] and $CsMn_{1-x}Co_x\cdot 2D_2O$,[10] in which a "mixed-ordering" phase has been postulated. It has been a natural development, then, to seek to make mixed-metal salts in the layer perovskite family. Preliminary reports of anomalous EPR spectra in the $(RNH_3)_2Mn_{1-x}Cu_xCl_4$ systems have been given.[11] But the data do not allow the determination of the **g** tensor due to an overlap of copper(II) and manganese(II) lines. No evidence of dynamic Jahn–Teller effects has been found.

Crystals of the family A_2MnCl_4 doped with small amounts of copper(II) exhibit a very intense red color.[11] With copper(II) concentrations as low as 0.01 mol % the phenomenon is observed. Similar behavior has not been found to occur in other copper(II)-doped manganese chloride compounds. $[(CH_3)_4N]MnCl_3$ and $CsMnCl_3\cdot 2H_2O$ show drastic changes in their luminescent behavior on doping with copper(II), but their colors are not as greatly affected.[12,13] Pure A_2CuCl_4 compounds, which are structurally related to the corresponding compound A_2MnCl_4, are yellow with the first Cl → Cu charge-transfer (CT) band at 24 000 cm^{-1}.[14] The physical origin of the intense red color in $A_2Mn_{1-x}Cu_xCl_4$ is therefore not obvious. It may be a one-center effect, i.e., a chloride to copper electron transfer in a $CuCl_6$ unit with an unusual coordination. A cooperative effect involving an electron transfer from the nearest-neighbor manganese(II) ions to the copper(II) center is an alternative conceivable mechanism.

For an investigation of the nature of the unusual color, a number of copper(II)-doped chloromanganate(II) compounds with different dimensionalities and bridging geometries (Table I) were prepared and investigated by polarized single-crystal absorption spectroscopy. $(NH_3C_2H_4NH_3)MnCl_4$ [abbreviated $(enH_2)MnCl_4$] was chosen as a representative of the class of A_2MnCl_4 compounds because it crystallizes in the same space group, $P2_1/b$, as $(NH_3C_2H_4NH_3)CuCl_4$ [abbreviated $(enH_2)CuCl_4$] with a very similar unit cell.[15]

Experimental Section

Preparations. The pure manganese compounds were first prepared as polycrystalline powders with use of literature procedures.[16-19] Single crystals of high optical quality containing copper concentrations of up to 10% were then grown by slow evaporation of aqueous solutions. All the compounds were identified by powder X-ray diffraction. The copper content of the crystals was determined by atomic absorption spectroscopy.

Single-Crystal Absorption Spectroscopy. A Bürger precession camera was used, when necessary, to orient the single crystals for the

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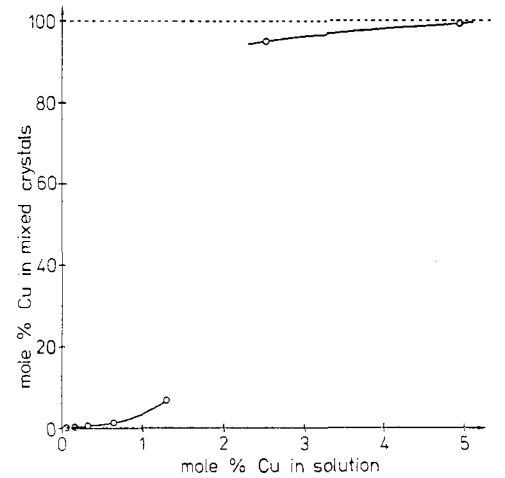

Figure 1. Composition of $(enH_2)Mn_{1-x}Cu_xCl_4$ mixed crystals obtained from aqueous solution. Mixed crystals for $0.07 \lesssim x \lesssim 0.95$ do not exist.

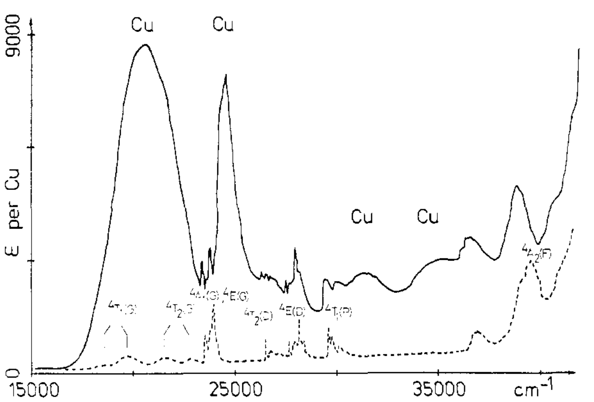

Figure 2. Absorption spectra at 20 K of $(enH_2)MnCl_4$ (---) and $(enH_2)Mn_{0.9986}Cu_{0.0014}Cl_4$ (—) with the light propagating perpendicular to the well-developed {100} faces. Dichroism within the *bc* plane was found to be very small. Assignments of manganese absorptions are included. Absorption bands related to Cu in the mixed crystals are indicated.

spectroscopic experiments. Most of the measurements were made with incident radiation perpendicular to the predominant crystal faces. For the experiments on $(enH_2)Mn_{1-x}Cu_xCl_4$ with the electric vector perpendicular to the layers, the light beam had to propagate parallel to the layers. Due to the platelike habit of the crystals and the easy cleavage, faces perpendicular to the principal face were obtained by careful grinding and polishing.

All the spectra were measured on a Cary 17 spectrometer. A matched pair of Glan-Taylor prisms was used for polarization. Cooling was achieved by a helium gas flow technique.

Results

Despite the fact that $(enH_2)MnCl_4$ and $(enH_4)CuCl_4$ crystallize in the same space group with very similar unit cells,[15] mixed crystals are only obtained in two very limited ranges of Cu/Mn ratios. As shown in Figure 1 mixed crystals $(enH_2)Mn_{1-x}Cu_xCl_4$ are obtained for $0 < x < 0.07$ and $0.95 < x < 1$. Products with compositions in the range $0.07 < x < 0.95$ were found by X-ray diffraction to consist of two distinct phases, a Mn-rich phase with the unit cell of pure $(enH_2)MnCl_4$ and a copper-rich phase with the $(enH_2)CuCl_4$ unit cell. Mixed crystals of $(CH_3NH_3)_2Mn_{1-x}Cu_xCl_4$ appear to have a similar behavior.[20] Reports in the literature of mixed crystals with *x* covering the whole range between 0 and 1 have to be viewed with caution.[11,21] The products used in these studies were not properly characterized by X-ray diffraction and elemental analysis.

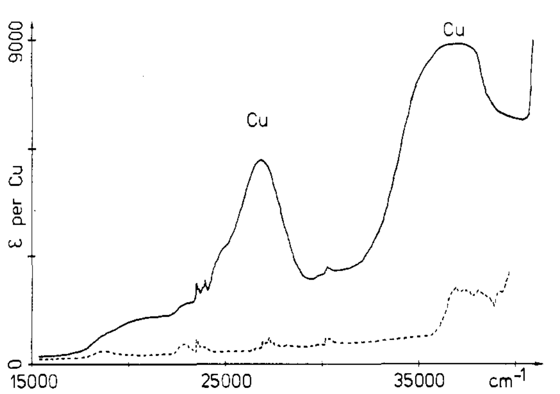

Figure 3. Spectra of the species in Figure 2, but with the light propagating approximately perpendicular to *a*. Due to the platelike habit of the crystals, faces containing the *a* axis were obtained by very careful grinding and polishing. The optical quality of the faces was not perfect, and the weak shoulders around 21 000 and 25 000 cm^{-1} are artifacts due to the intense absorptions in the other polarization.

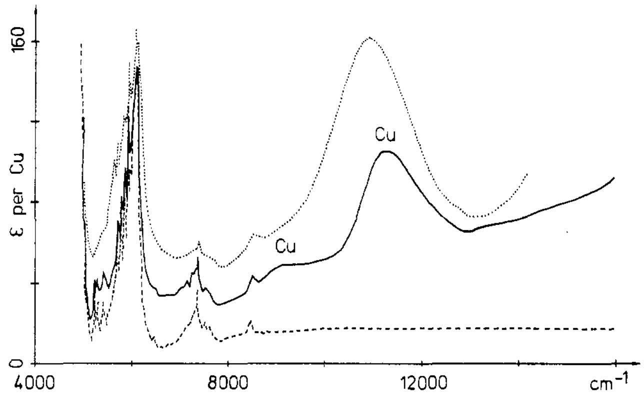

Figure 4. Absorption spectra of $(enH_2)MnCl_4$ at 20 K (---) and $(enH_2)Mn_{0.988}Cu_{0.012}Cl_4$ at 20 K (—) and 300 K (···) in the region of d–d transitions of copper(II). Light propagation is perpendicular to {100}. The sharp bands between 5000 and 8000 cm^{-1} are vibrational overtones of the host lattice.

Mixed crystals with *x* close to 0 are deep red while crystals with *x* close to 1 are yellow like the pure copper compound. Figures 2 and 3 show polarized single-crystal absorption spectra in the visible and near-UV region of pure and copper(II)-doped $(enH_2)MnCl_4$. The manganese absorptions show a great deal of fine structure. Their assignment to spin-forbidden d–d transitions, as indicated in Figure 2, is straightforward. In the following we shall only be concerned with those spectral features that are related to the copper in the mixed crystals. Thanks to the very low intensity of the manganese absorptions they are readily identified even with copper concentrations of less than 0.1 mol %. This transparency of the host lattices up to 45 000–50 000 cm^{-1} is a great advantage for the present work.

The prominent broad band at 20 800 cm^{-1} is clearly responsible for the red color of the doped material. The band is completely polarized in the {100} plane, i.e., within the layers of the two-dimensional lattice. Within {100} the optical spectroscopic anisotropy is negligible. The band shows no measurable variation of intensity for temperatures between 20 and 300 K. A number of polarized bands of higher energy with similar widths and comparable intensities are also related to the copper. The band at 24 800 cm^{-1}, completely polarized in-layer, is considerably sharper and must have a different physical origin. It may be a ${}^6A_1 \rightarrow {}^4E, {}^4A_1$ spin-flip excitation of manganese ions neighboring a copper ion in the crystal. Such a transition may be greatly enhanced by the overlapping

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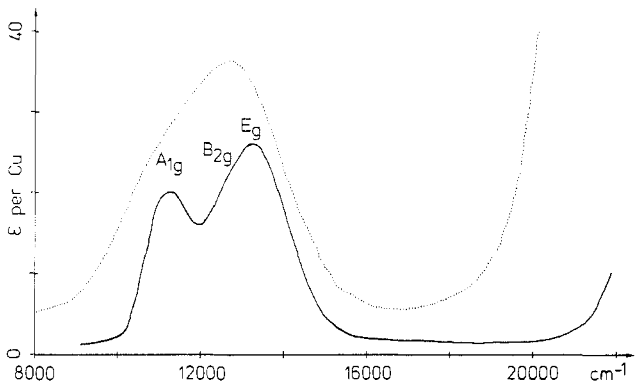

Figure 5. Absorption spectrum of (enH$_2$)CuCl$_4$ at 20 K (—) and 300 K (···) for light propagating perpendicular to {100}. The spectrum of (enH$_2$)Mn$_{0.014}$Cu$_{0.986}$Cl$_4$ is identical. The absorption bands are assigned as in the literature with D_{4h} symmetry assumed.

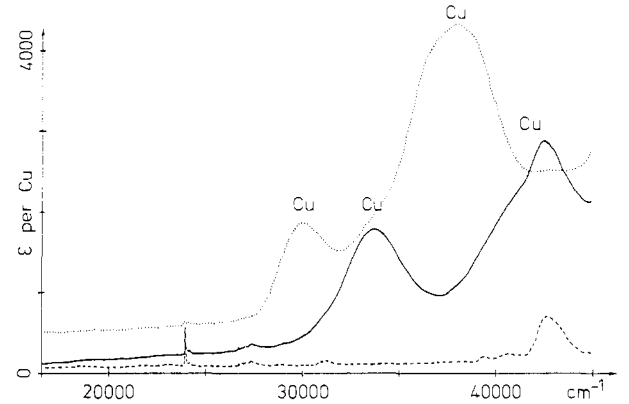

Figure 6. Polarized visible and near-UV absorption spectra at 20 K of CsMnCl$_3$·2H$_2$O (- - -, $\vec{E}$ parallel to *a*) and CsMn$_{0.993}$Cu$_{0.007}$Cl$_3$·2H$_2$O (—, $\vec{E}$ parallel to *a*; ···, $\vec{E}$ parallel to *b*). Bands related to Cu in the mixed crystals are indicated.

electron-transfer transition through an exchange-intensity mechanism.[22] Its polarization is expected to be in-layer as observed.

The region of d–d transitions of copper(II) is shown in Figure 4. The strong temperature dependence of intensity of the 9000- and 11 000-cm^{-1} bands demonstrates the vibronic character of parity-forbidden transitions. The highly structured bands below 8000 cm^{-1} are vibrational overtones. For comparison the absorption spectrum of pure (enH$_2$)CuCl$_4$ is shown in Figure 5. The spectrum of (enH$_2$)Mn$_{0.014}$Cu$_{0.987}$Cl$_4$ is identical. There is no absorption at 20 800 cm^{-1}, and there is, consequently, no drastic color effect.

Spectra of CsMn$_{1-x}$Cu$_x$Cl$_3$·2H$_2$O are shown in Figures 6 and 7. They serve as examples to illustrate the types of effects observed with all the other copper-doped manganese compounds: broad intense bands appear in the near-UV and some weak transitions are found in the near-IR. The number of observed transitions as well as their positions show some variations from one lattice to another. But with the exception of (enH$_2$)Mn$_{1-x}$Cu$_x$Cl$_4$ the range of intense absorptions never extends below 27 000 cm^{-1}. This is, of course, the reason that the (enH$_2$)Mn$_{1-x}$Cu$_x$Cl$_4$ system is the only one exhibiting a deep red color. Positions and intensities of all the copper-related absorptions are listed in Table I together with structural information for the various lattices.

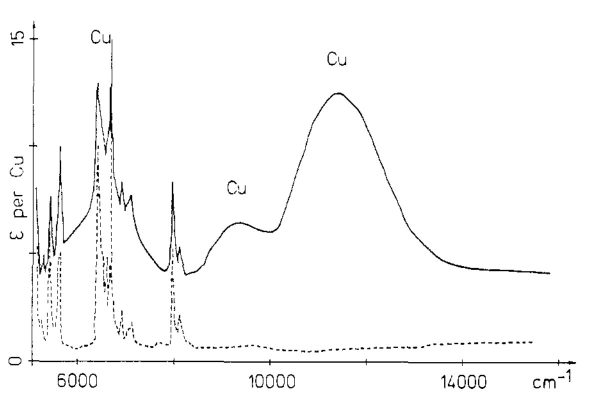

Figure 7. Near-IR absorption spectrum at 20 K of CsMnCl$_3$·2H$_2$O (- - -) and CsMn$_{0.955}$Cu$_{0.045}$Cl$_3$·2H$_2$O (—) with the electric vector parallel to *a*. d–d transitions of copper(II) are indicated. The sharp structure is due to vibrational overtones of the host lattice.

Discussion

Charge-transfer transitions corresponding to an electron transfer from a weakly bonding ligand orbital to the singly occupied orbital at the copper have been observed for many chlorocuprate(II) species of various coordination geometries in the energy range 24 000–50 000 cm^{-1}.[23,24] Cl → Cu transfer is therefore the most likely assignment for the intense absorptions observed in this energy range in all the copper-doped manganese compounds (Table I). For Cs$_2$MnCl$_4$·2H$_2$O, which contains discrete molecular MnCl$_4$(H$_2$O)$_2$ complexes,[16] there is no other plausible assignment. With the exception of (enH$_2$)Mn$_{1-x}$Cu$_x$Cl$_4$ the spectra of the bridged systems are quite similar. The origin of the extraordinary 20 800-cm^{-1} band in copper-doped (enH$_2$)MnCl$_4$ will be discussed below. We conclude that the other manganese compounds act as genuine host lattices taking no active part in the intense electronic transitions. The differences in band positions of the order of 3000 cm^{-1} between the various lattices reflect different coordinations of the copper centers. The actual coordination of a copper(II) ion in a given manganese host lattice is not known; it is the result of a compromise between the requirements and flexibilities of guest and host. While manganese(II) usually shows small deviations from regular octahedral geometry, hexacoordinated copper(II) prefers a pronounced tetragonal elongation of the nominally octahedral geometry, which, in fact, approaches square-planar coordination. From the fact that, with the exception of (enH$_2$)Mn$_{1-x}$Cu$_x$Cl$_4$, both d–d and CT absorptions lie in the expected energy ranges, we conclude that the copper(II) ions are reasonably well accommodated in their host environments.

We now turn to a detailed discussion of the spectrum of copper-doped (enH$_2$)MnCl$_4$. The intense 20 800-cm^{-1} absorption band is the most striking feature. While its intensity is comparable to that of the lowest energy CT transition in other host lattices, e.g., [(CH$_3$)$_4$N]MnCl$_3$, its energy is exceptionally low: more than 6000 cm^{-1} lower than that in any of the other lattices studied here (Table I). It is therefore tempting to postulate a different mechanism, e.g., a Mn → Cu electron transfer, to explain this low-lying absorption. The observed pure in-layer polarization of the band is in favor of such a mechanism. Mn–Cl–Cu connections only occur within the layers, and such electron-transfer excitations have to be polarized parallel to the metal–metal connection. However, there is strong experimental evidence against this interpretation: no corresponding absorption is observed in manganese(II)-doped (enH$_2$)CuCl$_4$. If neighboring manganese(II) and copper(II) ions in (enH$_2$)Mn$_{1-x}$Cu$_x$Cl$_4$ were involved in the transition, it should occur for all values of *x*. With a Mn → Cu assignment the absence of a corresponding absorption

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in the other systems containing Cu–Mn bridges would also be difficult to explain.

The likely origin, therefore, of the 20 800-cm^{-1} band is an electron-transfer transition within the $CuCl_6$ entity. This conclusion requires careful analysis, since it is generally found that the positions of CT transitions in naturally occurring copper(II) complexes are not greatly affected by changes in coordination geometry.[23] In our mixed crystals the copper ions are forced into an artificial environment. The low energy of the first CT band in $(enH_2)Mn_{1-x}Cu_xCl_4$ is therefore very likely the result of a "strained" copper coordination with unusual distances.

This follows not only from a comparison of spectra but also from the observations summarized in Figure 1. It is not possible to incorporate more than a few percent of copper into the $(enH_2)MnCl_4$ lattice. With higher copper concentrations in the solutions $(enH_2)Mn_{1-x}Cu_xCl_4$ crystals are obtained with x very close to 1. The $(enH_2)MnCl_4$ lattice thus cannot be an ideal host lattice for copper. There must be a lack of sufficient flexibility to properly accommodate the guest. This relative rigidity compared to that of the other systems studied (Table I) must be due to the two-dimensional character of the lattice. All the chloride ions within the layers are involved in M–Cl–M bridges. The range of possible M–Cl distances is therefore restricted.

Table II provides a comparison of structural properties of pure $(enH_2)MnCl_4$ and $(enH_2)CuCl_4$. While the lengths of the unit cell axes are very similar, interatomic distances are quite different.[15] The principal axis of crystal field anisotropy of the copper ions, i.e., the axis of tetragonal elongation, is *within* the layers (*bc* plane) of the two-dimensional lattice. The relative orientation of principal axes on neighboring copper ions is (approximately) rectangular, a so-called antiferrodistortive arrangement. The ferromagnetic interactions[2] between neighboring copper centers are an immediate consequence of the antiferrodistorted structure. The exact site symmetry for copper in $(enH_2)CuCl_4$ is C_i,[15] but D_{4h} is a good approximation (Table II). Possible ligand donor orbitals for allowed electron-transfer transitions in square-planar coordination are b_{2u} (nonbonding), e_u ($\pi + \sigma$), and e_u ($\pi + \sigma$) (cf. Figure 9). The likely acceptor orbital is b_{1g} ($3d_{x^2-y^2}$). No assignments based on polarized crystal spectra have been offered for the CT transitions in $(enH_2)CuCl_4$ so far.[23] The $b_{2u} \rightarrow b_{1g}$ one-electron transition is formally allowed with axial polarization. However, from a mechanistic point of view it is not expected to carry much charge-transfer intensity. An experimental confirmation comes from the related square-planar $PdCl_4^{2-}$ complex. By specular reflectance the two lowest-energy electron-transfer transitions in the complex were found to be of predominant equatorial polarization.[25] We neglect the $b_{2u} \rightarrow b_{1g}$ transition in the following, thus assuming that the first CT absorption at 24 000 cm^{-1} in $(enH_2)CuCl_4$ has equatorial polarization. Experimental support for this assumption is given by the observation that there is no observable dichroism in-layer/out-of-layer in $(enH_2)CuCl_4$ when the crystal is viewed parallel to the layers under the polarizing microscope. For the d–d spectral region there appears to be a generally accepted interpretation,[14] which is included in Figure 5.

Compared to those in the pure copper compound the d–d transitions in $(enH_2)Mn_{1-x}Cu_xCl_4$ are shifted to lower energy by approximately 2000 cm^{-1}. In the region of the first CT absorption we observe a band with out-of-layer polarization at 26 900 cm^{-1} and the low-energy 20 800-cm^{-1} band with in-layer polarization. For a rationalization of these findings the following two models may be considered: (1) (Figure 8) The copper coordination is a compressed octahedron (approximate D_{4h} symmetry) with the principal axis of anisotropy

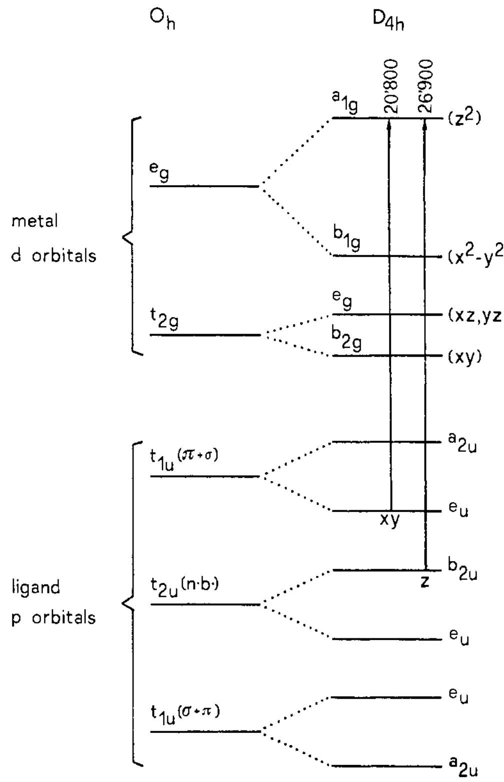

Figure 8. Schematic orbital energy diagram for a tetragonally compressed $CuCl_6$ octahedron (D_{4h} symmetry notation). The two lowest energy CT transitions according to model 1 (see text) are indicated by arrows.

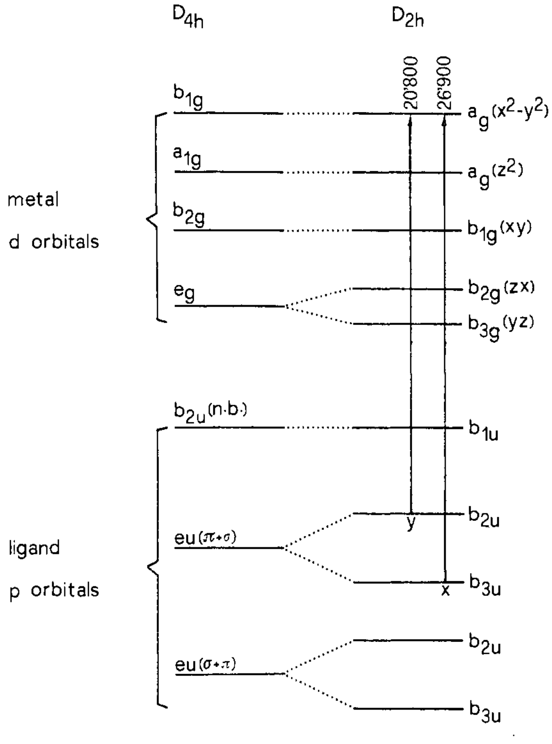

Figure 9. Schematic orbital energy diagram for a tetragonally elongated $CuCl_6$ octahedron with additional rhombic distortion (D_{2h} symmetry). The two lowest energy CT transitions according to model 2 (see text) are indicated by arrows. x is chosen along the shortest Cu–Cl bond, i.e., perpendicular to the layers.

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Table II. Comparison of Structural Properties of $(enH_2)MnCl_4$ and $(enH_2)CuCl_4$[13] [a]

	unit cell parameters				M–Cl dist, Å		M–M dist, Å
	a, Å	*b*, Å	*c*, Å	γ, deg	in-layer	out-of-layer	
$(enH_2)MnCl_4$	8.61	7.13	7.19	92.7	2.56, 2.58	2.49	5.06
$(enH_2)CuCl_4$	8.11	7.16	7.36	92.4	2.29, 2.88	2.29	5.13

[a] The *a* axis corresponds to the tetragonal *c* axis in the undistorted K_2NiF_4 structure.

out-of-layer. A small in-layer anisotropy may be possible. Plausible Cu–Cl distances are ~2.2–2.3 Å (out-of-layer) and ~2.5–2.6 Å (in-layer). (2) (Figure 9) The copper coordination is an elongated octahedron with the principal axis in-layer and an additional substantial rhombic distortion in the equatorial plane (approximate D_{2h} symmetry). Plausible Cu–Cl distances are ~2.2–2.3 Å (out-of-layer) and ~2.4 and ~2.7–2.8 Å (in-layer).

A definite answer to the question of copper coordination can only come from a diffraction experiment. The very limited range of copper concentrations makes a determination by X-ray diffraction very difficult. The chances are greater if there is a large difference between host and guest geometry. In principle, EXAFS[19] is an ideal method for this purpose, because the structural environment of the guest can be probed without too much perturbation by the host. We are presently engaged in a study of copper coordinations in A_2MnCl_4 host crystals by EXAFS. In addition high-frequency EPR experiments are planned to separate the overlapping copper(II) and manganese(II) signals.

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Registry No. $(enH_2)MnCl_4$, 68370-07-0; $(enH_2)CuCl_4$, 9088-46-4; $CsMnCl_3{\cdot}2H_2O$, 30444-42-9; $Cs_2MnCl_4{\cdot}2H_2O$, 31173-79-2; $[(CH_3)_3NH]MnCl_3{\cdot}2H_2O$, 56115-72-1; $[(CH_3)_4N]MnCl_3$, 30442-52-5; Cu, 7440-50-8.

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Electrochemistry of $(TPP)Mo(O)(OCH_3)$ and $(TPP)Mo(O)$ in Dichloromethane

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The electrochemical reduction of the (5,10,15,20-tetraphenylporphinato)oxomolybdenum(V)–methoxy complex, (TPP)-$Mo(O)(OCH_3)$, was investigated in TBAP–dichloromethane solution by dc polarography, cyclic voltammetry, coulometry, and controlled-potential electrolysis. Five redox couples were found in the potential range +0.3 to −1.8 V. Two of these couples at −1.15 and −1.53 V corresponded to formation of the five-coordinate anion radical $[(TPP)Mo(O)]^-$ and dianion $[(TPP)Mo(O)]^{2-}$. The other three couples involved six-coordinated complexes of Mo(V) and Mo(IV) containing either ClO_4^- or OCH_3^- as the sixth axial ligand. An overall reduction mechanism involving both covalent and ionic forms of $(TPP)Mo(O)(OCH_3)$ and $[(TPP)Mo(O)(OCH_3)]^-$ is proposed.

Introduction

In the last several years, the synthesis, structural characterization, and chemical reactivity of molybdenum metalloporphyrins have received considerable attention in the literature. Among several different types of porphyrin complexes, these studies have included porphyrins containing Mo^{IV}, Mo^{V}, or Mo^{VI} as central metals.[2-12] Our interest in this paper is to report initial results concerning the electrochemistry of Mo^{IV} and Mo^{V} complexes of TPP^{2-}. Until recently there has been no systematic study of molybdenum porphyrin electrochemistry. This is unusual since thermodynamic potentials and electrochemical reactivity should have a direct correlation with the chemical and photochemical reactivity of these complexes.

The first electrochemistry of a molybdenum porphyrin was published in 1973 by Fuhrhop, Kadish, and Davis.[2] In this study potentials for 25 representative complexes were reported, which included those for (OEP)Mo(O)(OH) in Me_2SO and butyronitrile. A later ESR and electron-transfer kinetic study by Newton and Davis[10] in 1975 gave results for the reduction and oxidation of (TPP)Mo(O)(OH) in four nonaqueous solvents but did not discuss what were considered complex data.

In this study we have limited our discussion to the reactions of (TPP)Mo(O) and $(TPP)Mo(O)(OCH_3)$ in CH_2Cl containing varying concentrations of supporting electrolyte. Our interest was to determine the effect of the sixth axial ligand OCH_3^- and the possible counterion ClO_4^- on the reversible potentials and to define any existing equilibria which existed in solution. This data would then serve as a needed reference for interpreting the electrochemistry of solutions containing Mo^{IV} and Mo^{V} porphyrins which have been reacted with dioxygen. The electrochemistry of these solutions is complex and is now the object of intense investigation in our laboratories.

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