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Pressure Studies on the Thermochromic Salt $[(CH_3)_2CHNH_3]_2CuCl_4$, a Compound with Three Phases Containing Distinctly Different $CuCl_4^{2-}$ Stereochemical Configurations[1]

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The far-ir spectrum of $[(CH_3)_2CHNH_3]_2CuCl_4$ has been recorded at several temperatures and pressures. From the analysis of these data, three distinct phases were identified, each containing distinctly different $CuCl_4^{2-}$ stereochemistries. In the high-pressure phase, it has square-planar geometry and the high-temperature phase is characterized by nearly tetrahedral ions of D_{2d} symmetry. The ambient-temperature, ambient-pressure phase contains a mixture of planar and several distorted tetrahedral ions.

Introduction

Copper(II) halides show a wide variety of structural geometries ranging from square planar through tetrahedral and on to trigonal bipyramidal. That the first two geometries (if distorted) are rather close in energy is evidenced by the presence of thermochromic phase transitions[2] in two salts $[(C_2H_5)_2NH_2]_2CuCl_4$ (henceforth $(DEA)_2CuCl_4$) and $[(CH_3)_2CHNH_3]_2CuCl_4$ (henceforth $(IPA)_2CuCl_4$). In $(DEA)_2CuCl_4$, spectral evidence indicates the low-temperature phase contains nearly square-planar $CuCl_4^{2-}$ anions, while the high-temperature phase contains distorted tetrahedral $CuCl_4^{2-}$ anions. In $(IPA)_2CuCl_4$, a similar transition occurs at 56°. The crystal structure has been determined for the low- (room-) temperature phase of $(IPA)_2CuCl_4$.[3] In this structure, one-third of the $CuCl_4^{2-}$ anions have a planar geometry while the other two-thirds of the anions have a significant tetrahedral distortion superimposed upon them, so that the trans Cl-Cu-Cl angles are approximately 155°. These ions have approximately D_{2h} and D_{2d} symmetry, respectively. Spectral evidence indicates that the high-temperature phase contains solely distorted tetrahedral $CuCl_4^{2-}$ anions of approximate D_{2d} symmetry in which the trans Cl-Cu-Cl angles are roughly 135°.

The $(IPA)_2CuCl_4$ system attracted our attention for two reasons. First, in general, $(RNH_3)_2CuCl_4$ compounds crystallize into a layer structure[4] in which the interactions between adjacent anions lead to two-dimensional ferromagnetism at low temperature.[5] In $(IPA)_2CuCl_4$, the bulk of the isopropylammonium group apparently prohibits the formation of the layer structure, and the room-temperature structure can be envisioned as consisting of one-dimensional ribbons cut out from the two-dimensional layers. It was desired to obtain a clearer understanding of the interrelation between these two types of structures. Second, the striking analogy between the room-temperature structure of $(IPA)_2CuCl_4$ and the structure of $Ni(PBzPh_2)_2Br_2$ [$PBzPh_2 \equiv C_6H_5CH_2P(C_6H_5)_2$] intrigued us. As in $(IPA)_2CuCl_4$, the latter consists of metal chromophores, one-third in a planar configuration and two-thirds in a distorted tetrahedral configuration.[6] It had been observed by one of us that, under pressure, a phase transition is induced in which the nickel complex is converted solely to the planar stereochemistry.[7] It thus seemed reasonable to investigate the behavior of $(IPA)_2CuCl_4$ under high pressures. It is this study which is reported here. Subsequent to the initiation of our investigation, it has been shown that the distorted tetrahedral $CuCl_4^{2-}$ anion in Cs_2CuCl_4 converts to a planar geometry at high pressure.[8]

Experimental Section

The methods of preparation of the $(IPA)_2CuCl_4$ and $(DEA)_2CuCl_4$ salts were reported elsewhere.[2] The infrared experiments were conducted using a diamond-anvil cell and a 6X beam condenser. A Perkin-Elmer Model 301 far-infrared spectrophotometer was used to record the spectra at ambient and nonambient pressure. Further details of the technique are described in the literature.[9,10] For the low-temperature studies a special anvil cell containing an entry and exit port and a cooling element surrounding the diamonds was used. This allowed the entry of helium which was previously cooled in a liquid nitrogen trap. For the measurements recorded at temperatures higher than room temperature we used a cell which contained a heating element surrounding the diamonds. The higher temperatures were read with a standard chromel-alumel thermocouple with the reference junction at 273°K.

Results and Interpretation

Figure 1 shows the spectra of $(IPA)_2CuCl_4$ at ambient pressure and room temperature (β phase), at 20-kbar pressure and room temperature (α phase), and at ambient pressure and 343°K (γ phase). It may be observed that the distorted starting phase demonstrates two absorptions (301, 271 cm^{-1}) in the region of the copper-chlorine stretching vibrations ($\sim$300 cm^{-1}). With the application of pressure the spectrum collapses into one intense peak at 281 cm^{-1} and a shoulder at $\sim$295 cm^{-1}. The pressure effect is reversible. Only one absorption at 290 cm^{-1} is seen in the spectrum of $(IPA)_2CuCl_4$ at ambient pressure and 343°K.

Table I lists the correlation table for the ir-active stretching vibrational modes for $CuCl_4^{2-}$ ions of different geometries. An important feature is that the triply degenerate t_2 mode in T_d (tetrahedral) symmetry splits into an e and a b_2 mode when compressed along one of the S_4 axes to form a species of D_{2d} symmetry. The amount of splitting will be propor-

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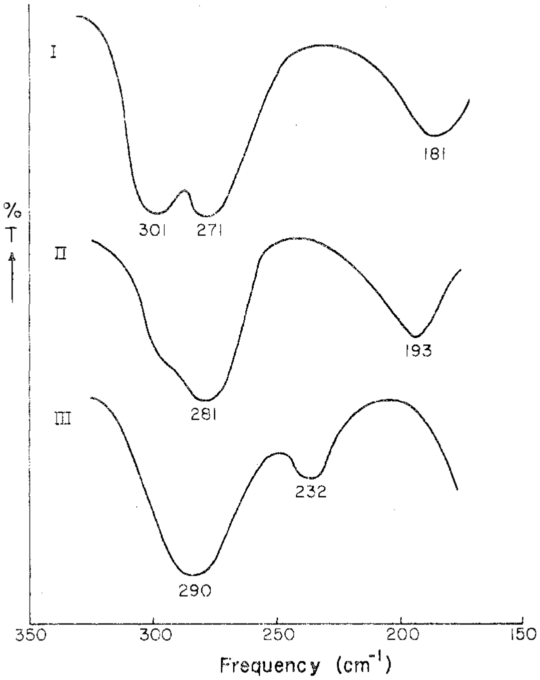
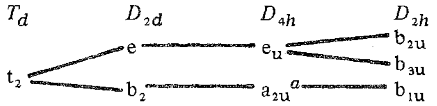


Figure 1. Far-ir spectra for $(IPA)_2CuCl_4$ at (I) ambient pressure and room temperature, (II) 20 kbars and room temperature, and (III) ambient pressure and 343°K.

Table I. Correlation of Ir-Active Stretching Anodes for CuX_4^{2-} Ions



[a] It should be noted that the b_2 stretching mode in D_{2d} becomes an out-of-plane bend in D_{4h}.

tional to the extent of the compression. This is experimentally confirmed by those data on the first two entries of Table II. In Cs_2CuCl_4, where the trans Cl–Cu–Cl angle is 124°, the splitting is 35 cm^{-1}.[11] This splitting has increased to 60 cm^{-1} at the trans angle of 135° found in $[(CH_3)_2NH_2]_3Cl\cdot CuCl_4$. The e stretching mode remains at a frequency typical of T_d ions.[11-14] As the ion is compressed further to a square-planar configuration, the b_2 mode takes on a_{2u} symmetry. This is a bending mode in D_{4h} symmetry and hence should be of a lower frequency than the e vibration. This confirms the assignment of the lower frequency absorption as the b_2 mode in D_{2d} geometry. Finally, it should be noted that the degeneracy of the e mode in D_{4h} will be removed when the geometry becomes D_{2h} (or lower). Thus, the planar $CuCl_4^{2-}$ ion in $(C_2H_5NH_3)_2CuCl_4$ shows a peak at approximately 278 cm^{-1} with a shoulder at 294 cm^{-1}, corresponding to the b_{2u} and b_{3u} bands in D_{2h}, and a weaker absorption at 182 cm^{-1}, corresponding to the out-of-plane b_{1u} bend.

With this information available, we then can proceed to make assignments and determine the geometry of the various phases of the compounds studied. The high-temperature phases of both $(IPA)_2CuCl_4$ and $(DEA)_2CuCl_4$ have been assigned a D_{2d} geometry with a trans Cl–Cu–Cl angle of approximately 135° based on their electronic absorption spectra.[2]

Table II. Geometries, Ir Frequencies, and Assignments for Various $CuCl_4^{2-}$ Ions

Compd	Trans Cl–Cu–Cl angle, deg	Approx geometry	Freq of e vibration (D_{2d}) or b_{2u}, b_{3u} vibrations (D_{2h}), cm^{-1}	Freq b_2 vibration (D_{2d}) or b_{1u} vibration (D_{2h}), cm^{-1}
Cs_2CuCl_4 [a]	124 [b]	D_{2d}	292	257
$[(CH_3)_2NH_2]_3Cl\cdot CuCl_4$ [c]	135 [d]	D_{2d}	295	235
$(IPA)_2CuCl_4$ (γ)	~135 [e]		290	232
$(DEA)_2CuCl_4$ (high T)	~135 [e]		295	220 sh
$(IPA)_2CuCl_4$ (β)	155 (2/3) [f] 180 (1/3)	D_{2d} D_{2h}	301, 279	181
$(DEA)_2CuCl_4$ (low T)	~162 [e]		282, 287 sh	186
$(IPA)_2CuCl_4$ (α)			281, 295 sh	193
$(C_2H_5NH_3)_2CuCl_4$ [g]	180 [h]	D_{2h}	278, 294 sh	182

[a] Reference 11. [b] L. Helmholz and R. F. Kruh, *J. Amer. Chem. Soc.*, **74**, 1176 (1952). [c] Reference 2. [d] R. D. Willett and M. L. Larsen, *Inorg. Chim. Acta*, 5, 175 (1971). [e] Estimated in ref 2. [f] Reference 3. [g] Reference 1 and this work. [h] Reference 4.

As can be seen from the data in Table II, this is confirmed by the position of the b_2 band in the far-ir spectra for these two salts.

In the β phase of $(IPA)_2CuCl_4$ (the stable phase at ambient temperature and pressure), a complex spectrum is expected due to the coexistence of ions of different geometries in the solid. The splitting in the e band of the ir spectrum of the low-temperature phase of $(DEA)_2CuCl_4$ indicates that some distortion from D_{2d} symmetry must be present. We anticipate a similar splitting to occur in the β phase of $(IPA)_2CuCl_4$, since the crystal structure analyzed shows significant distortion from D_{2d} symmetry. Thus, the two discrete peaks found in the 270-300-cm^{-1} region are a result of the overlap of a $(DEA)_2CuCl_4$ type spectrum and a $(C_2H_5NH_3)_2CuCl_4$ type spectrum. Since both species present in the β phase of $(IPA)_2CuCl_4$ are close to planar, the lower frequency band will be primarily a bending mode, and thus the frequency has dropped down below 200 cm^{-1}. The width of the band is indicative that it is a superposition of two spectra.

By comparison of the data for $(C_2H_5NH_3)_2CuCl_4$ and the α phase of $(IPA)_2CuCl_4$, the latter obviously contains planar or nearly planar $CuCl_4^{2-}$ ions. If the structure is isomorphous with that of the $(RNH_3)_2CuCl_4$ salts (a logical assumption since the β phase consists of ribbons cut out from that structure type), the $CuCl_4^{2-}$ ion will have effective D_{2h} symmetry. In these salts, the cis Cl–Cu–Cl bond angles are ~90°, but one pair of trans chloride ions bridge to adjacent $CuCl_4^{2-}$ ions. This explains the appearance of the shoulder in the 280-300-cm^{-1} range for the α phase.

Figure 2 illustrates spectra of $(IPA)_2CuCl_4$ obtained with pressures applied at liquid nitrogen temperatures. The overall effect of liquid nitrogen temperatures appears to be that of retardation of the pressure effects (see Figure 2-II). The change in intensities in the 280-200-cm^{-1} range upon cooling may be associated with an order–disorder transition in the N-H· · ·Cl hydrogen bonding.[2] The spectrum produced at 343°K and 12-kbar pressure is similar to that observed at 343°K and ambient pressure except that the 232-cm^{-1} absorption is missing in the latter spectrum. Experience with the diamond-anvil cell and weak absorptions has provided extensive evidence that such weak absorption may wash out with pressure. Thus, it is fairly reasonable to assume that

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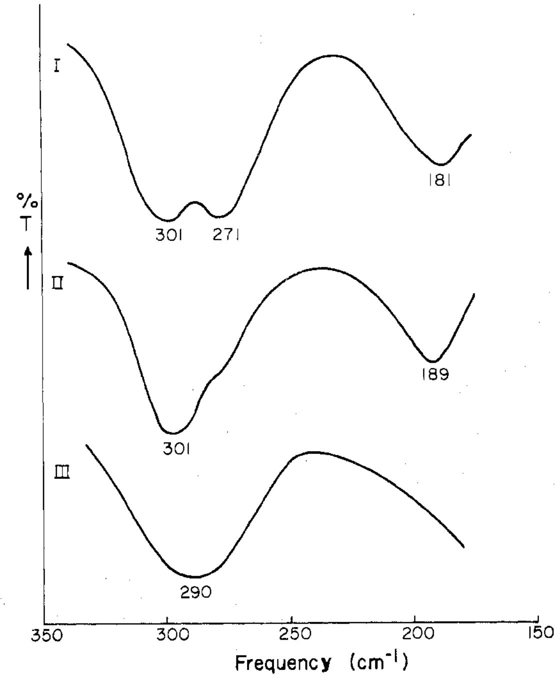

Figure 2. Far-ir spectra for $(IPA)_2CuCl_4$ at (I) ambient pressure and 78°K, (II) 16 kbars and 78°K, and (III) 12 kbars and 343°K.

the spectra obtained for $(IPA)_2CuCl_4$ at 343°K at ambient and at 12-kbar pressure are the same and indicate a conversion to nearly T_d symmetry as one increases the temperature.

Figure 3 shows a qualitative chart depicting the stabilities of $(IPA)_2CuCl_4$ as a function of pressure and temperature. Three distinct phases, each containing a different $CuCl_4^{2-}$ stereochemical configuration, are stable. The starting phase (β) (labeled as a distorted phase (D.P.) in Figure 3) is stable from room temperature to liquid nitrogen temperatures. The pressure-stable phase at room temperature is the square-planar configuration. The D_{2d} phase is stable only at elevated temperatures, at both ambient and 12-kbar pressures. This is the first report of a copper salt system involving three phases containing distinct and different $CuCl_4^{2-}$ stereochemical configurations.

Discussion

Several solid-state transformations of coordination complexes with the central metal atom possessing a coordination number (CN) of 4 or 5 have been induced by the application of high external pressures.[7,15-20] A review of the subject will shortly appear in the literature.[21] In complexes with CN 4 and a nearly regular T_d geometry, the transformation to a different stereochemical configuration requires considerable energy.[22-24] Such transformations have not been observed to date, with application of pressures to 50 kbars. For complexes with CN 4 or 5 it has been observed that a starting material with a distorted geometry will be nonrigid and convert more readily than a nondistorted configuration. Less energy is required to cause these conversions if the starting material contains a structure distorted in the direction of the pressure-stable phase.

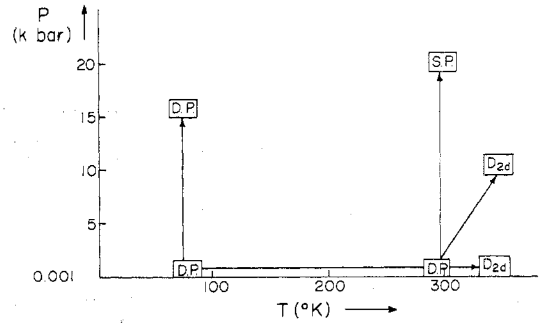

Figure 3. Stabilities of $(IPA)_2CuCl_4$ as a function of temperature and pressure: D.P., distorted phase–$^1/_3$ square planar + $^2/_3$ D_{2d} (β phase); S.P., square planar (α phase); D_{2d}, tetrahedral (γ phase).

The compound $(IPA)_2CuCl_4$ contains distorted $CuCl_4^{2-}$ anions (one-third planar and two-thirds distorted D_{2d}).[2] The system is analogous to $Ni(PBzPh_2)_2Br_2$, which possesses a similar structure[7] and which is converted in the solid state with pressure to a planar configuration. Application of pressure to solid $(IPA)_2CuCl_4$ has also transformed the distorted $CuCl_4^{2-}$ anions into a planar configuration. The skeletal infrared results are consistent with such an interpretation, as are the dta and the ligand field spectral results.[2] Recently, the $CuCl_4^{2-}$ and $CuBr_4^{2-}$ ions in Cs_2CuCl_4 and Cs_2CuBr_4 have been converted under pressure from flattened tetrahedra to planar ions,[8] lending further support to this interpretation.

The ir data for $(DEA)_2CuCl_4$ are consistent with the previous structural assignments.[2] From the electronic spectrum of the room-temperature phase, it was deduced that the trans Cl-Cu-Cl band angle was ~162°. The existence of the b_2 mode at 186 cm^{-1}, nearly identical with that observed for $(C_2H_5NH_3)_2CuCl_4$ and for the α and β phases of $(IPA)_2CuCl_4$, strengthens this assignment. Similarly, in the high-temperature phase, a structure much closer to tetrahedral was postulated, with a trans angle of ~135°. In this phase, the b_2 mode has increased to 220 cm^{-1}. By comparison with the data in Table II, it is evident that this angle is slightly larger, probably about 140°.

In contrast to $(IPA)_2CuCl_4$, however, no pressure effect is observed in the ir spectrum of the room-temperature phase of $(DEA)_2CuCl_4$. However, it may be that the transition to the phase with strictly planar ions occurs at pressures above 20 kbars. This is reasonable from a structural point of view. There are two structural characteristics which favor the planar geometry: strong N-H· · ·Cl hydrogen bonding and the formation of intermolecular Cu· · ·Cl interactions between the $CuCl_4^{2-}$ ions. In $(IPA)_2CuCl_4$, a prototype structure exists in which both of these effects contribute,[4] and so the transformation from the β to α phase is particularly facile. In $(DEA)_2CuCl_4$, the stereochemistry of the DEA ion does not allow the formation of this structure type, so that it is only the N-H· · ·Cl hydrogen bonding which contributes to the stabilization of the planar geometry. Thus, the absence of a phase transition in $(DEA)_2(CuCl_4$ below 20-kbar pressure is not particularly surprising.

Registry No. $(IPA)_2CuCl_4$ (α phase), 17950-18-4; $(IPA)_2CuCl_4$ (β phase), 52699-16-8; $(IPA)_2CuCl_4$ (δ phase), 52699-17-9; $(DEA)_2$-$CuCl_4$, 51961-58-1.

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