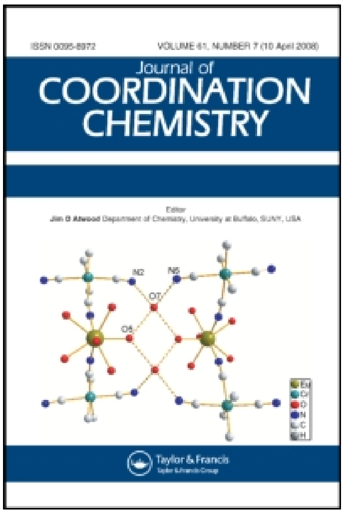

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SHORT COMMUNICATION

The Importance of a Distorted Structure in Solid-State Pressure Interconversions of Salts containing $CuCl_4^{2-}$ Ion†

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The importance of a distorted structure in the pressure interconversions of coordination compounds in the solid state has been recognized.[1,2] In $CuCl_4^{2-}$ salts involving a starting solid phase, distorted in the direction of the pressure stable phase, conversions to another structure occur more readily. In a recent publication[1] this was related to the lower energy necessary to transform a distorted structure, as compared to the higher energy required to convert a non-distorted structure. This short communication discusses the importance of a distorted structure in solid-state pressure interconversions of salts containing the $CuCl_4^{2-}$ ion.

It has recently been demonstrated that it was possible to convert by high external pressures the distorted tetrahedral $CuCl_4^{2-}$ ion in solid $(IPA)_2CuCl_4$, where IPA = $[(CH_3)_2CHNH_3]^+$, to a square configuration.[2] However, for solid $(DEA)_2CuCl_4$, where DEA = $[(C_2H_5)_2NH_2]^+$, and in which the $CuCl_4^{2-}$ ion exists in a square planar geometry, no pressure effects were observed. X-ray studies[3] have demonstrated that the starting phase of $(IPA)_2CuCl_4$ contains one copper in the $CuCl_4^{2-}$ ion in a square planar environment and two copper ions in distorted tetrahedral positions. The crystal is held together by hydrogen bonding from the isopropylammonium ions to the chlorine atoms in the $CuCl_4^{2-}$ ion.

The importance of hydrogen bonding in determining the degree of distortion in the R_2CuCl_4 salts, where R is an organic-ammonium cation, has been cited by Willett.[4] As the extent of the hydrogen bonding increases, the *trans* Cl–Cu–Cl angle increases, and the structure moves toward a square-planar geometry. Concurrent with this trend it is observed that the d–d transitions for the Cu^{2+} ion increase in energy (See Table I).

These trends can be correlated with the pressure effects on these salts. Since the pressure-stable phase is the square-planar configuration, it is this configuration that would be expected to have the smaller volume (larger density). It should be indicated that the density is determined by the bulk of the organic cation to a large extent, and only to a small degree by the geometry of the $CuCl_4$ anion. Unfortunately, an insufficient number of solids of this type, approaching a square-planar geometry are known that have an experimentally or calculated determined density. Thus, an appropriate comparison of density with volume cannot be made. However, it may be observed from Table I that a trend appears to exist, which indicates that an increase in density does occur, as the square-planar structure is approached. Only for square-planar, green $[\Phi(CH_2)_2NH(CH_3)H]_2CuCl_4$ does the density appear to be abnormally low. Reasons for this are not precisely known, although one would expect that a large spatially bulky $\Phi(CH_2)_2NH(CH_3)H^+$ cation might contribute in lowering the density.

The low-frequency infrared region manifests some significant changes as the structure approaches a square-planar geometry. Table II illustrates the correlation table for the infrared active stretching mode in T_d symmetry, and its lower symmetry analogs (D_{2d}, D_{4h}, D_{2h}). From Table I it may be observed that the strectching mode at ~290 cm^{-1} shows little change in frequency as one goes from a $T_d \rightarrow D_{2d} \rightarrow D_{4h} \rightarrow D_{2h}$ symmetry. This is to be expected as we are dealing with stretching modes in all of the symmetries, with only minor changes in energy occurring. In the D_{2h} symmetry the single stretching mode splits into b_{2u} and b_{3u} species, but again with only minor frequency changes occurring. However, in going from the stretching mode (b_2) in

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TABLE I
Several parameters for R_2CuCl_4 salts

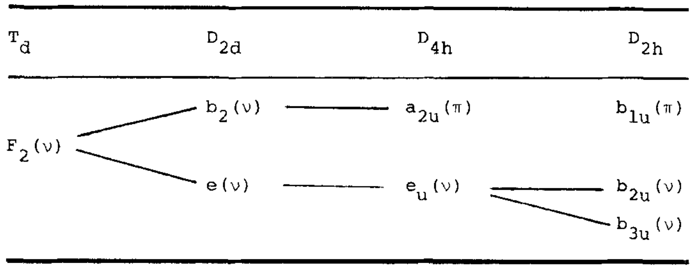
	Trans Cl-CuCl Angle (ave)°	Density	CuCl Infrared Modes (cm^{-1}) $D_{2d}(e)$	$D_{2d}(b_2)$	Electronic Absorptions (cm^{-1})	Ref.
Cs_2CuCl_4	124	-	292	257	9100	4,5,6
$[(CH_3)_4N]_2CuCl_4$	128	1.40			9000	4,5
$[\phi(CH_2)_2NH(CH_3)H]_2CuCl_4$ (yellow - 80°)	131	1.37			9100	7
$[\phi CH_2N(CH_3)_3]_2CuCl_4$	132	1.36				8
$[(CH_3)_2CHNH_3]CuCl_4$ $[(IPA)_2CuCl_4]$ (yellow - 60°)	135		290	232	10000	3,4
$[(C_2H_5)_2NH_2]_2CuCl_4$ $[(DEA)_2CuCl_4]$ (yellow - 43°C)	135		295	220(sh)	10200,7300	2-4
$[(C_2H_5)_3NH]_2CuCl_4$	137	1.33				10
$[C_6H_5CH_2CH(CH_3)NH_2CH_3]_2CuCl_4$	138	1.33			10200	15
$[C_{13}H_{19}N_2OS]_2CuCl_4$	143	1.43				11
			$D_{2h}(b_{2u},b_{3u})$	$D_{2h}(b_{1u})$		
$[(CH_3)_2CHNH_3]_2CuCl_4$ $[(IPA)_2CuCl_4]$ (green - RT)	155(2/3) 180(1/3)	1.50	301,279	181	11000-13000	2-4
$[(C_2H_5)_2NH_2]_2CuCl_4$ $[(DEA)_2CuCl_4]$ (green - RT)	162		282,287(sh)	186	15300,12900,9900	2-4
$[(CH_3)_2CHNH_3]_2CuCl_4$ $[(IPA)_2CuCl_4]$ (yellow - HP)	∿180[a]		281,295(sh)	193		2-4
$[C_2H_5NH_3]_2CuCl_4$	180	1.70	278,294(sh)	182		12
$[\phi(CH_2)_2NH(CH_3)H]_2CuCl_4$ (green - LT)	180	1.40(?)			16900,14300,12500	7
$Pt(NH_3)_4CuCl_4$	180[a]	-			14300	13

[a] estimated; Abbreviations: HT = high temperature; LT = low temperature; HP = high pressure.

D_{2d} symmetry, significant shifts are observed. This is again expected as a lowering of symmetry to D_{4h} and to D_{2h} converts the b_2 species of vibration to a_{2u} and b_{1u} respectively, and now the modes correspond to out-of-plane bending modes with lower energy than a stretching mode. These skeletal regions are a spectroscopic substantiation of the conversion of a distorted T_d structure into a square-planar configuration with an increase in hydrogen bonding and/or pressure.

In the systems where the *trans* Cl–Cu–Cl angle approaches 180° and hydrogen bonding is at a maximum, no further pressure effects are observed. This is consistent with the larger d–d transition energies observed. Gray has recently cited the importance of the magnitude of the d–d transition

TABLE II
Correlation of T_d symmetry with D_{2d}, D_{4h} and D_{2h} symmetries for the F_2 stretching vibration



ν = stretching mode; π = out-of-plane bending.

energy relative to the stability of five-coordinate complexes of Ni^{2+}.[9] It is observed that the green $(DEA)_2CuCl_4$ salt, in which the $CuCl_4^{2-}$ ion is already in a square-planar symmetry at room temperature, shows no pressure effect. The existence of the $CuCl_4^{2-}$ ion in this compound is a square-planar structure and the green $(IPA)_2CuCl_4$ in a distorted structure, is a reflection of the stronger hydrogen bonding in the former compound. Due to the stronger hydrogen bonding in green $(DEA)_2CuCl_4$, the compound is already under some internal pressure sufficient to allow a square-planar geometry. It is noted from Table I that the electronic absorptions for green $(DEA)_2CuCl_4$ are located at higher energy than those observed for green $(IPA)_2CuCl_4$ (see also the electronic transitions for yellow $(IPA)_2CuCl_4$ vs green $(IPA)_2CuCl_4$ and yellow $(DEA)_2CuCl_4$ vs green $(DEA)_2CuCl_4$).

The effect of higher temperature would be to decrease the hydrogen bonding, increase the volume and stabilize a nearly tetrahedral structure. Interestingly enough, both $(IPA)_2CuCl_4$ and $(DEA)_2CuCl_4$ have high temperature phases of D_{2d} symmetry (quasi-T_d).[4]

It should be emphasized that an asymmetric ligand field observed by the central metal atom (complex involving several different types of ligands) may also contribute to the conversion observed for these systems. The relative importance of an asymmetric field vs a distorted structure in facilitating an inter-conversion is as yet unknown. Although the distorted structure for salts containing $CuCl_4^{2-}$ ions provide a less energetic pathway to a square-planar geometry, the importance of the distorted structure for other transition metal salts containing MX_4^{2-} ions (e.g. M = Mn, Co, Ni, Fe), has not as yet been demonstrated. Preliminary data on distorted $(IPA)_2CoCl_4$ fail to indicate any structural transformation with pressure.[14] Further investigations on these factors are presently underway.

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