

Effect of pressure on the $\text{Cl}^- \rightarrow \text{Cu}^{2+}$ charge transfer in A_2CuCl_4 layer perovskites ($\text{A} = \text{C}_n\text{H}_{2n+1}\text{NH}_3$, $n = 2, 3$) and (3-Chloroanilinium) $_8[\text{CuCl}_6]\text{Cl}_4$: structural correlations

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Abstract

The dependence of the $\text{Cl}^- \rightarrow \text{Cu}^{2+}$ charge transfer (CT) band at 26000 cm^{-1} with the local structure of the Jahn–Teller elongated CuCl_6^{4-} unit is investigated. For this purpose we report hydrostatic pressure experiments performed on the title compounds. The results indicate that the first CT band experiences a pressure-shift of -1000 and $+1200\text{ cm}^{-1}$ in the $0\text{--}80\text{ kbar}$ range for each compound, respectively. This different shift in behaviour is explained by the distinct anisotropic compression of CuCl_6^{4-} related to the crystal dimensionality. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The $\text{X}^- \rightarrow \text{M}^{2+}$ charge transfer (CT) transitions in transition metal (TM) complexes, MX_6^{4-} (M: divalent TM; X: Halogen ligand), strongly depend on the symmetry and the M–X distance, R . For octahedral (O_h) complexes, a reduction of R leads to a blue-shift of the CT transitions as a consequence of the overlap increase between the ligand and metal orbitals [1,2]. Within a simple electrostatic description, this blue-shift can be explained by the higher repulsion experienced by the 3d-electrons of

the TM in comparison to the ligand p-electrons which are more stabilized by the positive net charge of the TM ion. A rough estimate of this shift on the basis of the different electrostatic potential seen by the ligand and metal electrons gives: $\partial E_{\text{CT}}/\partial R \approx \partial V_{\text{L-M}}/\partial R = -e^2/R^2(2.67Z_{\text{L}} + Z_{\text{M}}) = -87000\text{ cm}^{-1}/\text{\AA}$ for a typical M–Cl distance of $R = 2.5\text{ \AA}$, and ionic charges $Z_{\text{L}} = 1$ for ligand and $Z_{\text{M}} = 2$ for TM, respectively. Interestingly, this value which is similar to that obtained from quantum-mechanics calculations [2,3], suggests that application of hydrostatic pressure to materials containing O_h TM complexes can induce large blue-shifts of the $\text{X}^- \rightarrow \text{M}^{2+}$ CT bands. This high sensitivity of CT bands is worthwhile for exploring piezochromic properties of materials whose colour

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strongly depends on the CT bands like FeCl_n or FeBr_n ($n = 4$ or 6) based-compounds [4]. Furthermore, variations of metal–ligand distances can be detected through changes in the CT energy. This latter aspect has been exploited to investigate the effects of structural phase transitions around Cu^{2+} in NH_4Cl [5] and $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$ [6] doped with Cu^{2+} . Nevertheless, the expected pressure-induced CT blue-shift for O_h complexes may not occur in Jahn–Teller (JT) distorted CuCl_6^{4-} ($3d^9$ configuration). The usual CuCl_6^{4-} coordination corresponds to an elongated octahedron (D_{4h}) [1] and, consequently, two different distances, R_{ax} and R_{eq} , associated with the two Cu–Cl bonds along the fourfold axis, and the four perpendicular Cu–Cl bonds forming the equatorial plane, respectively, are required to describe its structure. The dependence of the $\text{Cl}^- \rightarrow \text{Cu}^{2+}$ CT energy upon compression is more difficult to predict for such complexes since it relies on the relative variation of R_{ax} and R_{eq} .

The aim of this work is to investigate the effect of hydrostatic pressure on the CT spectra of the CuCl_6^{4-} complexes formed in the 2-D PA_2CuCl_4 ($\text{PA} : \text{C}_3\text{H}_7\text{NH}_3$) perovskite layer and the 3-D $(3\text{-Cl-an})_8[\text{CuCl}_6]\text{Cl}_4$ crystal in order to establish correlations between the complex structure and the corresponding CT energies. The main difference between these two compounds lies on the CuCl_6^{4-} packing structure [7,8] (Fig. 1) that gives rise to a strong anisotropy for Cu^{2+} in the antiferrodistortive layer crystal and a weak interaction between CuCl_6^{4-} units in the 3-D crystal. Consequently, the effect of pressure on the CuCl_6^{4-} structure is expected to be rather different for the two investigated crystals. In this paper, we present the variation of the first CT band of CuCl_6^{4-} with hydrostatic pressure in the range 0–80 kbar in $(3\text{-Cl-an})_8[\text{CuCl}_6]\text{Cl}_4$ and PA_2CuCl_4 . The distinct behaviour exhibited by the CT spectra upon pressure in the two investigated compounds is

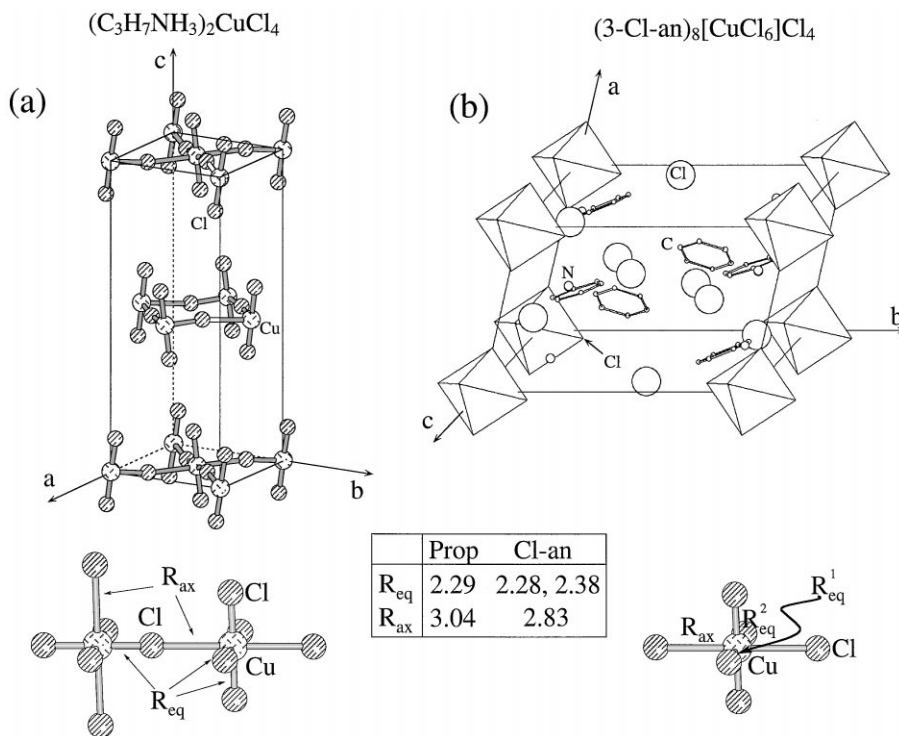


Fig. 1. Crystal structure of (a) PA_2CuCl_4 and (b) $(3\text{-Cl-an})_8[\text{CuCl}_6]\text{Cl}_4$. The CuCl_6^{4-} complex in each crystal is depicted below the unit cell. Note the antiferrodistortive structure formed by the complexes in the layer perovskite. Values of R_{ax} and R_{eq} [7,8] are given in Å.

explained on the basis of their respective crystal structures, and compared with results obtained in pure [9] and copper-doped materials [10,11].

2. Experimental

Single crystals of A_2CuCl_4 (A = Alkylammonium) and $(3\text{-Cl-an})_8[CuCl_6]Cl_4$ were grown from solutions as indicated elsewhere [6,8,12]. The hydrostatic pressure experiments were done in a Diamond Anvil Cell (High Pressure Diamond Optics, Inc), using Paraffin oil as pressure transmitter to prevent crystal hydration. The absorption spectra have been obtained with an implemented single beam spectrometer [13,14] able to measure optical densities in the 0–5 range. Microsamples of $80 \times 80 \times 30 \mu m^3$ were used for the chloroanilinum crystals, while a sample thickness of $2 \mu m$ was necessary for obtaining suitable CT spectra of the layer perovskites (absorption coefficient, $k \approx 5 \times 10^4 \text{ cm}^{-1}$ [15]). The pressure was measured through the R -line shift of Ruby chips introduced in the hydrostatic cavity. The Ruby luminescence was excited with the 568 nm line of a Coherent I-302 Krypton Laser.

3. Results and discussion

Fig. 1 depicts the crystal structure of the two investigated $(3\text{-Cl-an})_8[CuCl_6]Cl_4$ and PA_2CuCl_4 crystals. In both crystals the copper displays an elongated octahedral coordination. However, it must be noted that in the first crystal $CuCl_6^{4-}$ complexes are independent units, whereas in the latter crystal they share the four in-layer Cl ligands with the four neighbouring complexes, thus forming an antiferrodistortive structure in which the in-layer equatorial ligands of a complex act as axial ligands of the nearest complex [6]. This different packing exhibited by $CuCl_6^{4-}$ in these two structures must lead to a marked anisotropy of the complex deformation upon hydrostatic pressure. The use of pure crystals in this study is advantageous since they allow us to establish structural correlations through diffraction techniques.

The CT absorption spectra of $CuCl_6^{4-}$ in the investigated crystal family and their dependence with pressure are shown in Figs. 2 and 3. The two main intense bands at about 26000 and 36000 cm^{-1} correspond to CT transitions involving electronic jumps from the mainly π - and σ -bonding e_u ligand orbitals, mostly constructed from the equatorial Cl^- p-orbitals, to the antibonding mainly Cu^{2+} $d(x^2 - y^2)$ orbital of b_{1g} symmetry, respectively [6,12]. These transitions are electric-dipole allowed in D_{4h} and therefore their oscillator strength ($f \sim 0.1\text{--}0.01$) is higher than the corresponding d–d transitions ($f \sim 10^{-4}$) [4,6]. This makes it difficult to obtain the CT spectrum of pure crystals from an absorption experiment. Although this difficulty can be overcome by diluting Cu^{2+} into the PA_2CdCl_4 and $(3\text{-Cl-an})_8[CdCl_6]Cl_4$ isomorphous [14], this procedure however precludes any structural correlation.

As regards the variation of the first $e_u(\pi) \rightarrow b_{1g}(x^2 - y^2)$ CT band with hydrostatic pressure, it is worth pointing out the different behaviour exhibited by this band in the investigated crystals. Whereas a red-shift of -1000 cm^{-1} is observed upon pressure for PA_2CuCl_4 , an opposite variation is observed for $(3\text{-Cl-an})_8[CuCl_6]Cl_4$, whose CT band shifts $+1200 \text{ cm}^{-1}$ towards higher energies. According to findings in the pure EA_2CuCl_4 compound [9] and in Cu^{2+} -doped

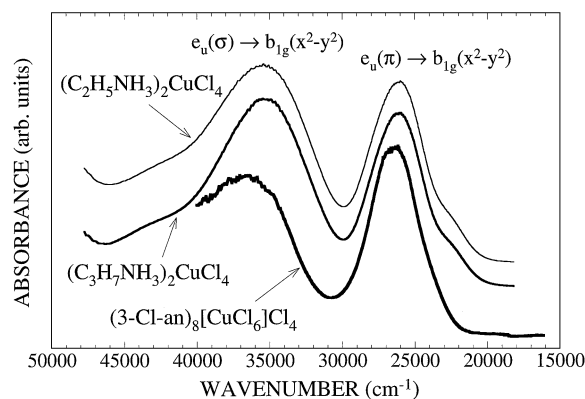


Fig. 2. Polarized optical absorption spectra of the 2D PA_2CuCl_4 and EA_2CuCl_4 perovskites and the 3D $(3\text{-Cl-an})_8[CuCl_6]Cl_4$ crystal at room temperature and atmospheric pressure.

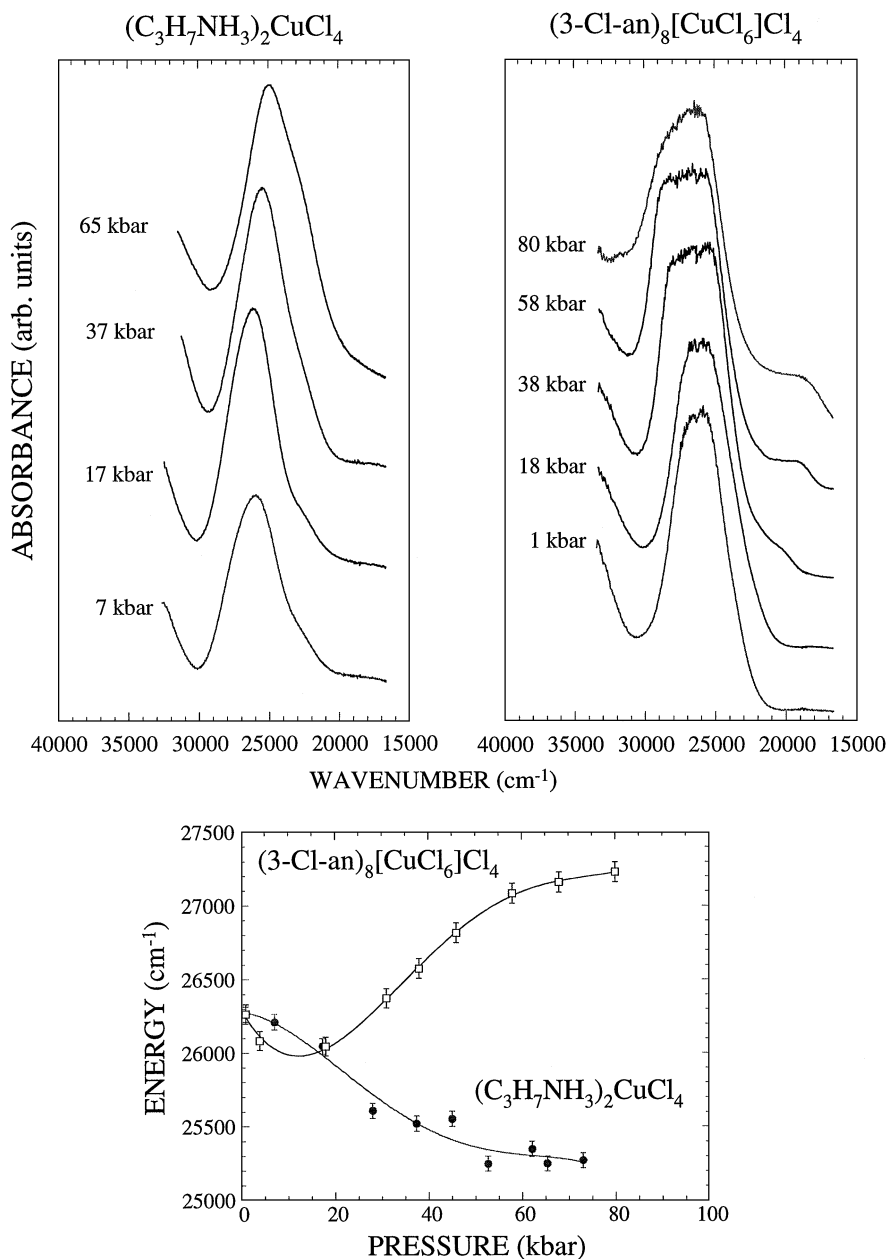


Fig. 3. Variation of the first $\text{Cl}^- \rightarrow \text{Cu}^{2+}$ CT band with hydrostatic pressure in PA_2CuCl_4 and $(3\text{-Cl-an})_8[\text{CuCl}_6]\text{Cl}_4$. Note the different shift in behaviour exhibited by the two crystals.

EA_2MCl_4 (M : Cd, Mn) [10,11], the present results confirm that the pressure-induced red-shift experienced by the first CT band in pure and Cu^{2+} -doped perovskite series is not associated with any pres-

sure-induced phase transition of the host crystal, but with changes of local structure around the Cu^{2+} . In particular, we interpret the distinct CT shift exhibited by the title compounds by a different

structural deformation of the CuCl_6^{4-} complex upon pressure imposed by the crystal anisotropy (Fig. 1). While a nearly isotropic decrease of R_{ax} and R_{eq} is expected in $(3\text{-Cl-an})_8[\text{CuCl}_6]\text{Cl}_4$ as a consequence of the isolated character of CuCl_6^{4-} , the bond length reduction in the antiferrodistortive A_2CuCl_4 family must be not only different for R_{ax} and R_{eq} but also of opposite sign. The reason for this behaviour is due to the layer structure of the crystal. In fact, this structure can be regarded as an interconnected sequence of square-planar CuCl_4^{2-} complexes, in which the two in-plane equatorial ligands act as axial ligands of the neighbouring CuCl_4^{2-} complexes. Taking into account that $R_{\text{Cu-Cu}} = R_{\text{ax}} + R_{\text{eq}}$, a reduction of $R_{\text{Cu-Cu}}$ induced by pressure should affect R_{ax} more than R_{eq} since the long axial Cu–Cl bond is much weaker than the equatorial bond, as deduced from their respective vibrational frequencies [16]. In conclusion, the observed CT blue-shift in $(3\text{-Cl-an})_8[\text{CuCl}_6]\text{Cl}_4$ is interpreted by a nearly isotropic reduction of the Cl–Cu distances upon pressure. By contrast, the CT red-shift in PA_2CuCl_4 is explained by an anisotropic reduction of R_{ax} and R_{eq} . The complex compression is presumably attained by a larger reduction of the weak axial Cu–Cl bond and a slight increase of the equatorial distance. This variation leads necessarily to a diminution of the tetragonal distortion of the complex (Q_θ decrease) towards an octahedral [9] or a more compressed rhombic [10,11] situation. In either case, the structural modification reduces the JT splitting of the parent octahedral $3p\text{-Cl } t_{1u}$ and $3d\text{-Cu } e_g$ orbitals that can lead to a red-shift of the CT band if the JT contribution is higher than the blue-shift contribution due to an average bond-length reduction. Recent MS-X α and Extended Hückel calculations carried out for CuCl_6^{4-} around its equilibrium geometry [17] indicate that a pressure-induced red-

shift of the first CT band is possible whenever the complex compression is accomplished in such a way that $|\Delta R_{\text{ax}}| \geq 4|\Delta R_{\text{eq}}|$ with $\Delta R_{\text{ax}} < 0$ and $\Delta R_{\text{eq}} > 0$. The interpretation proposed in this work is based on the fact that this condition is favoured in layered perovskites, whereas it does not apply in the 3D structure due to the isolated character of the CuCl_6^{4-} units.

Preliminary XANES experiments carried out on the pure A_2CuCl_4 support this interpretation.

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