

Crystal Structure of (3-chloroanilinium)₈NiCl₁₀ and a Temperature-Dependent X-ray Diffraction Study of the Jahn–Teller Distortion in (3-chloroanilinium)₈CuCl₁₀

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The synthesis and crystal structure of (3-chloroanilinium)₈NiCl₁₀, C₄₈H₅₆N₈Cl₁₈Ni, are reported. Crystals of the compound are triclinic, *P* $\bar{1}$, with *a* = 8.682(1) Å, *b* = 13.900(2) Å, *c* = 14.128(2) Å, α = 81.77(1)°, β = 72.37(1)°, γ = 77.19(1)°, and *V* = 1579.1(5) Å³ (*Z* = 1). The final *R* value is 6.46%. The structure contains compressed octahedral NiCl₆⁴⁻ anions, with Ni–Cl_{eq(av)} = 2.490(3) Å and Ni–Cl_{ax} = 2.383(2) Å. This difference in bond length (0.11 Å) is due to an axial strain present in the structure. The structure of the isomorphous compound (3-chloroanilinium)₈CuCl₁₀ has been redetermined at room temperature and determined at three lower temperatures. Two models were used to refine the structure. Model 1 assumes no disorder of the anion. In this model, the geometry of CuCl₆⁴⁻ ion in (3-chloroanilinium)₈CuCl₁₀ appears to be a compressed octahedron. However, the anisotropic displacement parameters along the four long bond directions are anomalously large. The analyses of these anisotropic displacement parameters suggest the presence of 2-fold disorder for the Cl atoms involved in the four long Cu–Cl bonds. The refinement of this 2-fold disordered model (model 2) gave an elongated rhombic octahedral coordination the CuCl₆⁴⁻ ion with more reasonable displacement parameters and lower *R* values at all temperatures. The combination of lattice strain and Jahn–Teller distortion gives Cu–Cl bond lengths of approximately 2.29, 2.38, and 2.81 Å at –117 °C.

Introduction

Tetrahedral and octahedral Cu(II) species are subject to Jahn–Teller distortion due to the presence of orbitally degenerate ground states.¹ For six-coordinate complexes of Cu(II), this normally leads to a tetragonally elongated octahedral geometry.² The stabilization of the elongated geometry can be understood in terms of coupling of the ²E_g ground state with ϵ_g vibrational motions.³

Recently, the compound (3-chloroanilinium)₈CuCl₁₀ was reported⁴ to contain an unusual compressed tetragonal distortion of the CuCl₆⁴⁻ ion. Such geometry is extremely rare, although it has been shown to exist in KAlCuF₄⁵ and has also been observed for Cu(II) doped into NH₄Br.⁶ The original X-ray analysis showed the presence of unusual anisotropic displacement parameters for the four chloride ions involved in the “long” Cu–Cl bonds, in that the displacement parallel to the bond direction was anomalously large. EPR spectra were consistent with a dynamic and/or exchange-coupled average of two elongated CuCl₆⁴⁻ species.^{4a} Nevertheless, the authors chose to interpret the result in term of a species with a d_{x²-y²} ground state with vibronic coupling inducing a (dynamic) admixture of d_{x²-y²} character.

More recently, an EXAFS study of the title compound⁷ gave convincing evidence supporting the supposition that the observed apparent compressed geometry was indeed the superposition of two elongated configurations. Detailed analysis of the EXAFS data gave three distinct Cu–Cl distances of equal weight, 2.28(1), 2.38(1), and 2.83(5) Å. Thus the local geometry is described as a tetragonal elongated octahedral complex, with a substantial rhombic distortion. The observed compressed octahedral geometry is assumed to be the result of a disorder, either static or dynamic, within the crystal.

A further study involving the low-temperature EPR and electronic spectra of the title compound⁸ confirmed the above supposition. No direct evidence of a phase transition could be observed down to liquid He temperature, although a change in the angular dependence of the EPR *g* values was observed below 10 K. The existence of substantial magnetic exchange coupling complicates the interpretation of the EPR spectra, so it is not possible to draw definitive conclusion concerning the possible dynamic behavior. The “Mexican hat” potential surface was calculated on the basis of a vibronic coupling model, with an axial lattice strain³ introduced to account for the stabilization of two out of three potential minima. Thus only these two minima are populated at and below room temperature. Each minimum corresponds to an elongated rhombic octahedron which differs from the others only in the directions of the long and intermediate bonds.

In order to gain insight into the unusual (but not unknown⁹) behavior of this compound, we have determined the crystal structure of the isomorphous Ni(II) salt. This will allow a more direct determination of the effect of the lattice strain. We have also independently undertaken a temperature-dependent single-

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- (1) Jahn, H. A.; Teller, E. *Proc. R. Soc. London, Ser. A* **1937**, *161*, 220.
- (2) Reinen, D.; Friebel, C. *Struct. Bonding (Berlin)* **1979**, *37*, 1 and references therein.
- (3) Reinen, D.; Atanasov, M. *Magn. Reson. Rev.* **1991**, *31*, 167 and references therein.
- (4) (a) Tucker, D. A.; White, P. S.; Trojan, K. L.; Kirk, M. L.; Hatfield, W. E. *Inorg. Chem.* **1991**, *30*, 823. (b) Hatfield, W. E.; Trojan, K. L.; White, P. S.; Horner, O.; terHaar, L. W.; Nelson, D. J.; Cervantes-Lee, F.; Hoffmann, S. K.; Hilzler, W.; Gosler, J.; Hitchman, M. A. *Mol. Cryst. Liq. Cryst.* **1993**, *233*, 309.
- (5) Wingefeld, G.; Hoppe, R. Z. *Anorg. Allg. Chem.* **1984**, *516*, 223.
- (6) Riley, M. J.; Hitchman, M. A.; Reinen, D.; Steffen, G. S. *Inorg. Chem.* **1988**, *27*, 1924. Clayton, W. R.; Meyers, E. A. *Cryst. Struct. Comm.* **1976**, *5*, 61. Clayton, W. R.; Meyers, E. A. *Cryst. Struct. Comm.* **1976**, *5*, 63.

(7) Ellis, P. J.; Freeman, H. C.; Hitchman, M. A.; Reinen, D.; Wagner, B. *Inorg. Chem.* **1994**, *33*, 1249.

(8) Stratemeier, H.; Wagner, B.; Krausz, E. R.; Linder, R.; Schmidtke, H.; Pebler, J.; Hatfield, W. E.; ter Haar, L.; Reinen, D.; Hitchman, M. A. *Inorg. Chem.* **1994**, *33*, 2320.

(9) Joesten, M. D.; Takagi, S.; Lenhert, P. G. *Inorg. Chem.* **1977**, *16*, 2680.

Table 1. Parameters for the Data Collection and Structure Refinement for (3-chloroanilinium)₈NiCl₁₀

empirical formula	C ₄₈ H ₅₆ Cl ₁₈ NiN ₈	fw	1441.8
<i>a</i> , Å	8.682(1)	crystal system	triclinic
<i>b</i> , Å	13.900(2)	space group	<i>P</i> $\bar{1}$
<i>c</i> , Å	14.128(2)	temp, °C	23
α , deg	81.77(1)	λ (Mo K α), cm ⁻¹	0.710 73
β , deg	72.37(1)	ρ_{calcd} , g cm ⁻³	1.516
γ , deg	77.19(1)	μ (Mo K α), cm ⁻¹	110.9
<i>V</i> , Å ³	1579.1(5)	<i>R</i> ^a %	6.46
<i>Z</i>	1	<i>R</i> _w ^b %	5.79

$${}^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad {}^b R_w = \sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2.$$

crystal X-ray structure determination. If the observed structure is due to the static or dynamic average of two elongated structures, the anisotropic displacement parameters of the chloride ions involved in each of the four long Cu-Cl bonds would remain anomalously large at all temperatures. Conversely, if a ground state is truly present with a very weak force constant along the bond direction, the apparent thermal motion parallel to the bond direction should be strongly temperature dependent.

Experimental Section

(3-chloroanilinium)₈NiCl₁₀. Crystal samples of (3-chloroanilinium)₈NiCl₁₀ were prepared according to the literature method.^{4a} The yellow needles were found to belong to the triclinic crystal system, and the lattice constants were similar to those for the Cu(II) compound. The intensity data were collected on Siemens P2₁ spectrometer equipped with a graphite monochromator upgraded to P4 specification using the ω -scan technique in the range 3° < 2 θ < 50°. This and the subsequent data collection and data reduction were performed by utilizing the XSCANS program.¹⁰ Parameters for the data collection and structure refinement are given in Table 1. During the data collection three standards were checked every 97 reflections. Slow decay of the intensity standards was observed. When the data collection was complete, the standards reached about 80% of the initial values. The intensity data were scaled using the check reflection information and corrected for absorption utilizing empirical ψ -scan data. The Ni²⁺ compound is isostructural with (3-chloroanilinium)₈CuCl₁₀. The structure was refined by using the atomic positions of the Cu compound at -117 °C, replacing Cu by Ni, as starting parameters. Table 2 gives the positional and thermal parameters for (3-chloroanilinium)₈NiCl₁₀. This and all subsequent data structure refinements were performed with the SHELXTL-PLUS crystallographic package.¹¹ Full listings of data collection parameters, bond distances, and bond angles are available as supporting information.

(3-chloroanilinium)₈CuCl₁₀. A sample of (3-chloroanilinium)₈CuCl₁₀ was prepared by a modified version of the published method.⁴ Crystals were grown by utilizing a temperature gradient method. Lattice constants, obtained on a Siemens R3 spectrometer upgraded to P4 specification equipped with a graphite monochromator, confirmed the identity of the compound. No evidence for superlattice reflection, indicating a larger unit cell than previously reported, was observed. Intensity data sets were collected using the ω -scan technique in the range 3° < 2 θ < 50° and corrected for absorption by utilizing empirical ψ -scan data at four temperatures: 23, -25, -59, and -117 °C. Temperature was controlled by a Siemens LT-2 device and calibrated by placing a small iron-constantan thermocouple at the crystal position. Parameters for the data collections and structure refinements are given in Table 3.

Analyses of the Cu(II) structure at each temperature were carried out with two models. Model 1 was basically that used in ref 1, in which no disorder was assumed. Thus the calculations for this model assume a single potential minimum for the equatorial Cl atoms with a very soft force constant along the in-plane Cu-Cl directions. The

Table 2. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for the NiCl₆⁴⁻ Anion In (3-chloroanilinium)₈NiCl₁₀

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Ni(1)	0	5000	5000	28(1)
Cl(1)	2746(2)	4982(1)	5010(1)	30(1)
Cl(2)	801(2)	3260(1)	4530(1)	34(1)
Cl(3)	669(2)	5630(1)	3212(1)	35(1)
Cl(4)	-3920(2)	2514(1)	4240(1)	41(1)
Cl(5)	3926(2)	4091(1)	7589(1)	43(1)
Cl(11)	1369(3)	903(2)	3581(2)	82(1)
N(11)	2729(7)	-2903(4)	3900(4)	44(3)
C(11)	1606(9)	-197(5)	3324(6)	45(3)
C(12)	1282(11)	-136(6)	2425(6)	66(4)
C(13)	1463(14)	-1015(7)	2020(7)	96(6)
C(14)	1916(12)	-1917(6)	2509(6)	72(5)
C(15)	2241(8)	-1935(5)	3394(5)	37(3)
C(16)	2084(8)	-1086(5)	3829(5)	39(3)
Cl(21)	617(3)	-1372(2)	-515(2)	75(1)
N(21)	1417(7)	-3937(4)	-2998(4)	40(2)
C(21)	199(9)	-2433(5)	-806(5)	45(3)
C(22)	-782(10)	-2980(6)	-120(5)	56(4)
C(23)	-1075(10)	-3842(6)	-356(6)	59(4)
C(24)	-352(9)	-4158(6)	-1293(5)	48(3)
C(25)	631(8)	-3587(5)	-1995(5)	34(3)
C(26)	918(8)	-2729(5)	-1785(5)	39(3)
Cl(31)	-7120(3)	-3823(2)	779(1)	58(1)
N(31)	-4098(6)	-4103(4)	-2941(4)	40(2)
C(31)	-5808(8)	-3415(5)	-329(5)	38(3)
C(32)	-5160(9)	-2584(5)	-365(5)	46(3)
C(33)	-4155(9)	-2268(5)	-1251(6)	53(4)
C(34)	-3821(9)	-2740(5)	-2105(5)	45(3)
C(35)	-4473(8)	-3580(5)	-2039(4)	30(3)
C(36)	-5483(8)	-3919(5)	-1173(5)	36(3)
Cl(41)	-3889(3)	-388(2)	929(2)	84(1)
N(41)	-2903(7)	-2883(4)	3843(4)	41(2)
C(41)	-3570(9)	-668(6)	2104(5)	46(3)
C(42)	-3567(11)	85(6)	2645(7)	66(4)
C(43)	-3306(12)	-161(6)	3580(7)	74(5)
C(44)	-3079(10)	-1123(6)	3964(6)	56(4)
C(45)	-3098(8)	-1855(5)	3411(5)	35(3)
C(46)	-3353(9)	-1643(5)	2478(5)	42(3)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

Table 3. Parameters for the Data Collection and Structure Refinement for (3-chloroanilinium)₈CuCl₁₀ at Different Temperatures^a

	23 °C	-25 °C	-59 °C	-117 °C
<i>a</i> , Å	8.557(2)	8.510(2)	8.473(2)	8.437(2)
<i>b</i> , Å	13.945(3)	13.918(3)	13.896(3)	13.875(3)
<i>c</i> , Å	14.203(2)	14.183(2)	14.171(2)	14.159(2)
α , deg	82.30(1)	82.20(1)	82.11(1)	81.99(1)
β , deg	72.87(1)	72.91(1)	72.94(1)	72.98(1)
γ , deg ^b	77.85(1)	77.94(1)	77.99(1)	78.07(1)
<i>V</i> , Å ³	1578.6(7)	1565.3(7)	1555.0(7)	1545.2(7)
<i>Z</i>	1			
ρ_{calcd} , g cm ⁻³	1.522	1.535	1.545	1.555
μ (Mo K α), cm ⁻¹	114.8	115.8	116.6	117.3
<i>R</i> ^c (for model 1), %	4.90	4.53	4.34	4.11
<i>R</i> _w ^c (for model 1), %	5.61	5.19	5.23	4.67
<i>R</i> ^c (for model 2), %	4.78	4.41	4.175	3.92
<i>R</i> _w ^c (for model 2), %	5.52	5.06	5.05	4.47

^a Empirical formula C₄₈H₅₆Cl₁₈CuN₈; crystal system triclinic; fw 1446.6; space group *P* $\bar{1}$; λ (Mo K α) 0.710 73 Å. ^b The matrix (100, 010, 101) transforms the unit cell to the one reported in ref 1. ^c See Table 1 for definition.

results for the room-temperature structure, which show the existence of an apparent compressed octahedron, are essentially identical with those reported in ref 1. Specifically, the two chloride ions, Cl(2) and Cl(3), involved in the "long" Cu-Cl bonds show anomalously large displacement parameters parallel to the Cu-Cl bond directions. Model 2 incorporated a 2-fold disorder for the Cl(2) and Cl(3) atoms. This

(10) XSCANS, Version 2.0a; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1992.

(11) Sheldrick, G. M. SHELXTL-PLUS, Release 4.0; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1990.

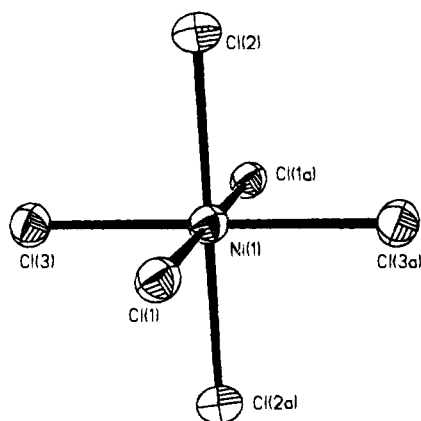


Figure 1. ORTEP diagram of the NiCl_6^{4-} anion at room temperature.

Table 4. The M-Cl bond distances (\AA) and bond angles ($^\circ$) from model 1 for $(3\text{-chloroanilinium})_8\text{CuCl}_{10}$ at each temperature and for $(3\text{-chloroanilinium})_8\text{NiCl}_{10}$

$T, ^\circ\text{C}$	M = Ni		M = Cu		
	23	23	-25	-59	-117
M(1)-Cl(1)	2.383(2)	2.278(1)	2.281(1)	2.284(1)	2.286(1)
M(1)-Cl(2)	2.492(2)	2.603(1)	2.593(1)	2.586(1)	2.579(1)
M(1)-Cl(3)	2.487(2)	2.608(1)	2.607(1)	2.605(1)	2.605(1)
Cl(1)-M(1)-Cl(2)	90.5(1)	90.6(1)	90.6(1)	90.6(1)	90.5(1)
Cl(2)-M(1)-Cl(3)	90.6(1)	90.9(1)	91.0(1)	91.1(1)	91.2(1)
Cl(1)-M(1)-Cl(3)	90.2(1)	90.5(1)	90.5(1)	90.5(1)	90.6(1)

model assumed a double minimum potential, with an unspecified potential barrier between the two minima. Initially the Cu-Cl distances at each site were loosely constrained to 2.3 \AA (for Cl(2) and Cl(3)) and 2.8 \AA (for Cl(2') and Cl(3')) with site occupancies fixed at 0.5. The distance constraints proved unnecessary. Subsequently, the site occupancy factors were varied, with the constraints

$$S(\text{Cl}(2)) = S(\text{Cl}(3'))$$

$$S(\text{Cl}(3)) = S(\text{Cl}(2'))$$

$$S(\text{Cl}(2)) + S(\text{Cl}(2')) = 1$$

The refinements for model 2 were always significantly better than those for model 1. However, without the above constraints for model 2, the correlation between the site occupancy parameters and the components of the displacement ellipsoids precluded sensible refinement of the data. Full listings of data collection parameters, atomic coordinates, anisotropic displacement parameters, bond distances, and bond angles for both models at each temperature are available as supporting information.

Results

(3-chloroanilinium) $_8$ NiCl $_{10}$. The crystal structures of $(3\text{-chloroanilinium})_8\text{NiCl}_{10}$ and $(3\text{-chloroanilinium})_8\text{CuCl}_{10}$ are isomorphous. The NiCl_6^{4-} anions have compressed octahedral geometry with the shortest Ni-Cl bonds parallel to the a axis and a Ni-Cl bond length of 2.383(2) \AA . The two long Ni-Cl bonds have lengths of 2.492(2) and 2.487(2) \AA , respectively, a difference that is not significant and suggests that a compressed tetragonal-octahedral geometry is present (see Figure 1). Bond distances and bond angles for the NiCl_6^{4-} anion are given in Table 4. Since the NiCl_6^{4-} anion has the $^3A_{2g}$ ground state and is Jahn-Teller stable, the NiCl_6^{4-} geometry solely reflects the strain effects imposed by the steric packing effects in the unit cell. The strain of the axial compression has been confirmed and the orthorhombic lattice strain, if it exists, must be very small. The difference between the long Ni-Cl bond (average) and the short Ni-Cl bond is 0.11 \AA ; it is about the same as that between the intermediate Cu-Cl bond and short Cu-Cl bond obtained by EXAFS⁷ or refined by model 2 (see below).

Table 5. Comparison of Rms Displacement Amplitudes (\AA) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for Cl Atoms in $(3\text{-chloroanilinium})_8\text{CuCl}_{10}$ and $(3\text{-chloroanilinium})_8\text{NiCl}_{10}$

$T, ^\circ\text{C}$	Ni complex		Cu complex		
	23	23	-25	-59	-117
$U_{11}^{1/2}(\text{Cl}(1))^a$	0.170(3)	0.184(2)	0.163(2)	0.158(2)	0.133(2)
$U_{11}^{1/2}(\text{Cl}(2))^a$	0.161(3)	0.293(2)	0.288(2)	0.282(2)	0.278(2)
$U_{11}^{1/2}(\text{Cl}(3))^a$	0.170(3)	0.313(2)	0.304(2)	0.297(2)	0.295(2)
$U_{\text{eq}}(\text{Cl}(1))^b$	30(1)	34(1)	28(1)	24(1)	19(1)
$U_{\text{eq}}(\text{Cl}(2))^b$	34(1)	38(2)	30(2)	26(2)	20(2)
$U_{\text{eq}}(\text{Cl}(2'))^b$		38(2)	34(2)	26(2)	20(2)
$U_{\text{eq}}(\text{Cl}(3))^b$	35(1)	42(2)	33(2)	26(2)	22(2)
$U_{\text{eq}}(\text{Cl}(3'))^b$		41(2)	33(2)	27(2)	22(2)

^a Model 1 for the Cu complex. ^b Model 2 for the Cu complex.

However, the calculations of Stratemeier et al.⁸ predict a compression of only 0.05 \AA for closed-shell Zn^{2+} and Mg^{2+} ions.¹² It is only about half of what is observed for the Ni compound. Thus the lattice strains present in $(3\text{-chloroanilinium})_8\text{NiCl}_{10}$ appear to be larger than those from the theoretical model for $(3\text{-chloroanilinium})_8\text{CuCl}_{10}$. The anisotropic displacement parameters for the atoms in the NiCl_6^{4-} anion appear normal, with the U_{eq} values for the Cl atoms only slightly larger than those for the Ni atom.

(3-chloroanilinium) $_8$ CuCl $_{10}$, Model 1. The crystal structure at room temperature is essentially the same as reported previously and consists 3-chloroanilinium cations, discrete CuCl_6^{4-} anions, and Cl^- anions. Except for the displacement parameters, there are no significant differences between the room-temperature and -117 $^\circ\text{C}$ structures. Table 4 gives the Cu-Cl bond distances and bond angles of the CuCl_6^{4-} anion at the different temperatures. Table 5 gives the rms displacements of the Cl atoms along the Cu-Cl bond directions.

The coordination about the discrete CuCl_6^{4-} anion appears to be a tetragonally compressed octahedron, as shown in Figure 2, at room temperature and at -117 $^\circ\text{C}$. It is observed in Figure 2 that the displacement parameters of the two Cl atoms involved in the long Cu-Cl bond are drastically elongated along the bond directions and their longest principal axes nearly coincide with the long Cu-Cl bond directions. The components of the displacement parameters of all atoms have shrunk by 40–50% between room temperature and -117 $^\circ\text{C}$, except for those along the bond direction for Cl(2) and Cl(3). In the latter cases, the displacement parameters decreased by less than 20%. The mean square displacement parameters for the Cl atoms along the bond directions are plotted as a function of temperature in Figure 3. The displacement amplitudes of the Cl(1) atom show a significant decrease with decreasing temperature, while the amplitudes for the Cl(2) and Cl(3) atoms along the Cu-Cl bond directions show a very slight decrease.

If it is assumed that the abnormally large displacement parameters of the Cl(2) and Cl(3) atoms along the Cu-Cl bond directions are due to disorder (static or dynamic) over two sites, the distance, Δd , between the two sites can be calculated from the equation¹³

$$(\Delta d/2)^2 = U_{\text{ll,obs}} - U_{\text{ll,normal}}$$

The value of $U_{\text{ll,normal}}$ can be approximated by the observed value for Cl(1). Table 6 gives the results of this analysis. The calculated values for Δd are nearly the same for both Cl atoms and agree well with the value (0.48 \AA) deduced from the

- (12) The value for the axial compression cited in ref 8 was 0.02 \AA , but converted to 0.05 \AA in a private communication from M. A. Hitchman.
 (13) Ammeter, J. H.; Burgi, H. B.; Gamp, E.; Meyer-Sandrin, V.; Jensen, W. P. *Inorg. Chem.* **1979**, *18*, 733.

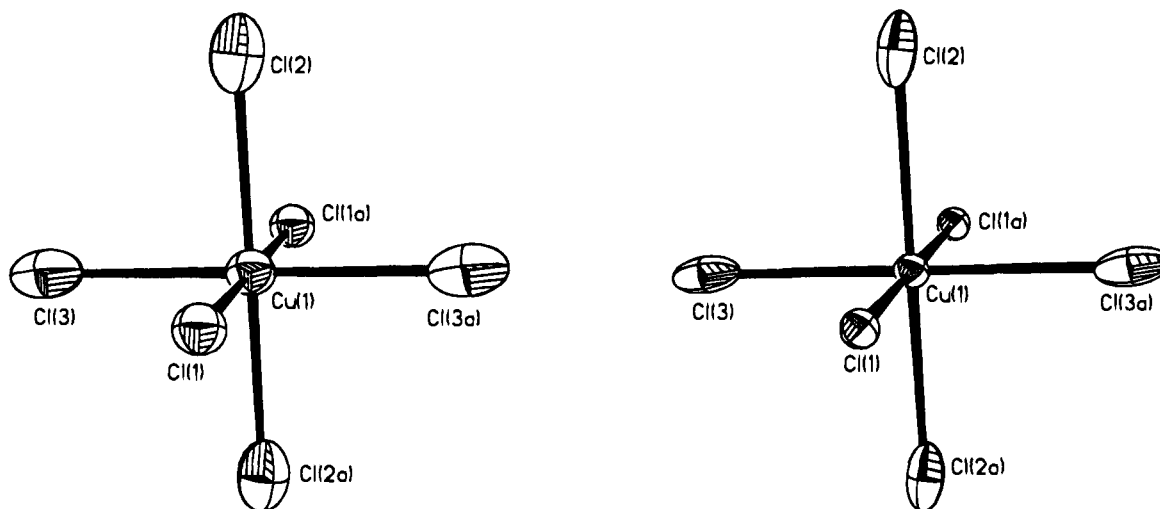


Figure 2. ORTEP diagrams of the CuCl_6^{4-} anion at room temperature (left) and -117°C (right).

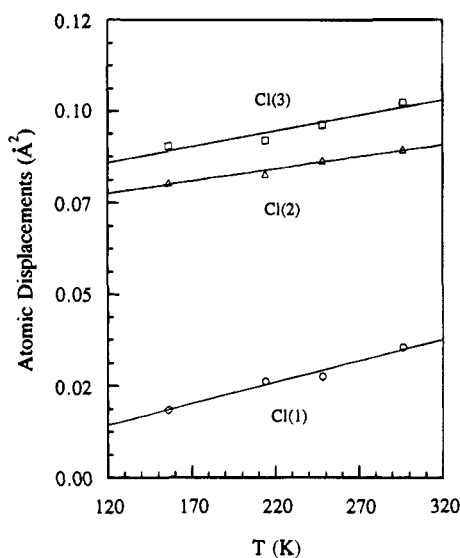


Figure 3. Mean square displacement amplitudes of Cl atoms along bond directions as a function of temperature.

Table 6. The Differences between the Long and Short Cu—Cl Bond Distances As Derived from X-ray Diffraction Data at Different Temperatures

	$\Delta d, \text{\AA}$			
	23 $^\circ\text{C}$	-25 $^\circ\text{C}$	-59 $^\circ\text{C}$	-117 $^\circ\text{C}$
using $\Delta U^{1/2}(\text{Cl}(2))^a$	0.450	0.475	0.466	0.488
using $\Delta U^{1/2}(\text{Cl}(3))^a$	0.500	0.513	0.502	0.525
$\text{Cl}(2)-\text{Cl}(2')^b$	0.43(3)	0.42(3)	0.43(3)	0.44(3)
$\text{Cl}(3)-\text{Cl}(3')^b$	0.43(3)	0.44(3)	0.45(3)	0.44(3)

^a Model 1. ^b Model 2.

EXAFS⁷ data. The fact that the Δd values remain nearly constant as a function of temperature lends credibility to the analysis.

The shortest Cu—Cl distance, Cu—Cl(1), increases slightly as the temperature is lowered, consistent with decreased thermal shortening of the apparent Cu—Cl distance at lower temperature. While one of the longer Cu—Cl distances remains essentially constant, it is observed that the Cu—Cl(2) distance decreases significantly. There is no obvious structural reason for the temperature dependence of the Cu—Cl(2) bond distance.

Model 2. The temperature dependencies of the Cu—Cl bond distances and atomic displacement amplitudes of Cl atoms along bond directions may be rationalized in a disordered model—two

almost equally weighted elongated octahedra misaligned by 90° with the short bonds of the two octahedra coincident. Thermal ellipsoid plots of the disordered CuCl_6^{4-} anions at room temperature and -117°C are given in the left and right diagrams of Figure 4 respectively. It is observed that the ellipsoids are approximately the same size for all Cl atoms and have the same orientations with respect to the Cu—Cl bond directions. The rms displacement parameters for Cu and Cl atoms have normal values between 0.16 and 0.22 \AA at room temperature. Furthermore, the displacement parameters of all atoms show roughly the same temperature dependency. Thus, the model gives physically realistic results. The Cu—Cl distances obtained are listed in Table 7. The rhombic octahedral geometry of the CuCl_6^{4-} anions is the consequence of a static Jahn—Teller elongation along the Cu(1)—Cl(2) or Cu(1)—Cl(3) bond direction and a lattice strain compression along the Cu(1)—Cl(1) direction. The two elongated rhombic octahedra are almost identical within the experimental errors at all temperatures. The refined $\Delta d = \text{Cl}(n)-\text{Cl}(n')$ distances are also tabulated in Table 6 for comparison of those values calculated using the displacement amplitudes of the Cl atoms in model 1. The average of the long (2.82 \AA) and intermediate (2.38 \AA) bond distances refined in the disordered model (model 2) is almost exactly equal to the long Cu—Cl bonds (2.60 \AA) refined in model 1. The observed distances (approximately 2.28, 2.38, and 2.82 \AA) are in excellent agreement with the EXAFS results.⁷

Comparison of the Displacement Parameters. The relevant displacement parameters of (3-chloroanilinium)₈CuCl₁₀ for the two models at different temperatures and of (3-chloroanilinium)₈-NiCl₁₀ are summarized in Table 5. The root mean square displacement amplitudes for the two Cl atoms, refined by model 1, along the long Cu—Cl bond directions are considerably larger than those along the long Ni—Cl bond directions, while they are of comparable magnitude perpendicular to the bond directions. For the short Cu—Cl bonds, the displacement parameters of the Cl atoms are similar to the parameters for the Cl atoms in the Ni complex. In general, the displacement parameters for the CuCl_6^{4-} anion, refined by model 2, and the NiCl_6^{4-} anion show that the largest root mean square amplitudes are perpendicular to the bond directions. However, the differences between the different directions are not large. Hence, only the U_{eq} values are listed in Table 5 for comparison purpose. At room temperature, it is seen that the displacement parameters for (3-chloroanilinium)₈CuCl₁₀ are a little bit larger than those for the Ni complex. This is consistent with the existence with

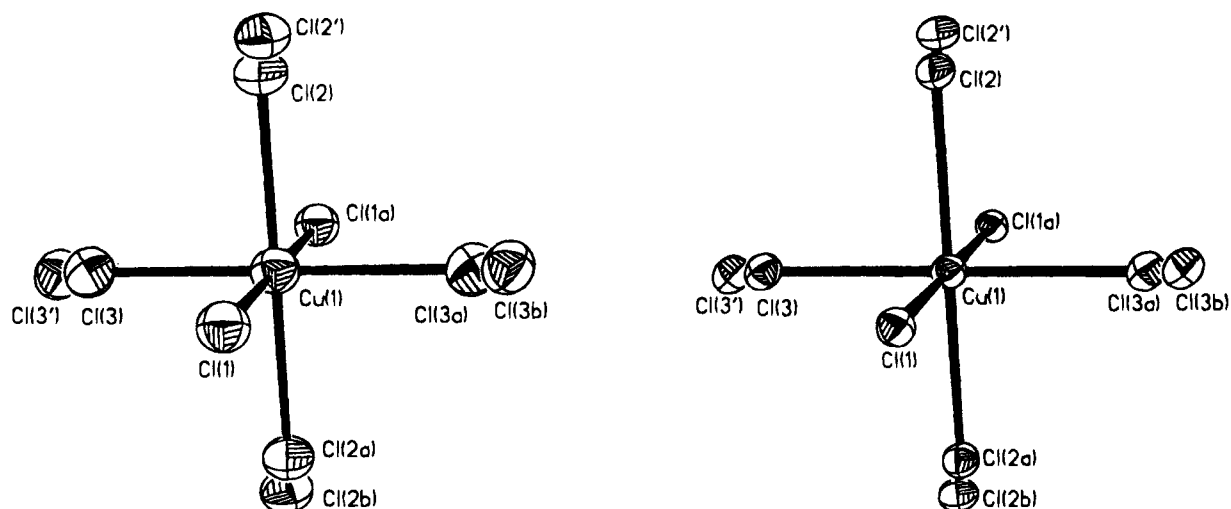


Figure 4. Apparent compressed octahedron as the average over two elongated octahedra at room temperature (left) and $-117\text{ }^{\circ}\text{C}$ (right). One octahedron is composed of Cu(1), Cl(2), Cl(2a), Cl(3), Cl(3a), Cl(4'), and Cl(4b) and the other of Cu(1), Cl(2), Cl(2a), Cl(3'), Cl(3b), Cl(4), and Cl(4a), where the atoms labeled with an "a" or a "b" are generated as follows: Cl(na), coordinates of Cl(n) transformed by $(-x, -y, -z)$; Cl(nb), coordinates of Cl(n') transformed by $(-x, -y, -z)$.

Table 7. Cu–Cl Distances Calculated by the Disordered Model (Model 2) at Different Temperatures

	R, Å			
	23 °C	-25 °C	-59 °C	-117 °C
Cu(1)–Cl(1)	2.278(1)	2.281(1)	2.284(1)	2.286(1)
Cu(1)–Cl(2)	2.39(2)	2.40(2)	2.39(2)	2.38(2)
Cu(1)–Cl(2')	2.82(3)	2.82(3)	2.81(3)	2.81(3)
Cu(1)–Cl(3)	2.40(2)	2.38(2)	2.37(2)	2.37(2)
Cu(1)–Cl(3')	2.83(3)	2.82(3)	2.81(3)	2.81(3)

residual disorder of the cations in the lattice due to the disorder of the CuCl_6^{4-} species.

The rigid-body motion analyses for the NiCl_6^{4-} and CuCl_6^{4-} groups in both models 1 and 2 at different temperatures were performed using a generalized TLS procedure¹⁴ given in the SHELXTL-PLUS program. The root mean square deviations between the observed displacement parameters and those calculated from T, L, and S were compared with the average experimental standard deviations over all tensor components of all atoms in the MCl_6^{4-} anions (Table 8). On the basis of these values, we concluded that the NiCl_6^{4-} anion and the CuCl_6^{4-} anions refined by model 2 at all temperatures may be considered to be rigid. However, the CuCl_6^{4-} anion described by model 1 cannot be considered rigid at all experimental temperatures. The differences are attributed to the presence of dynamic or static Jahn–Teller disorder in the Cu complex.

Conclusion

The structure determination of $(3\text{-chloroanilinium})_8\text{NiCl}_{10}$ revealed that the NiCl_6^{4-} octahedron shows tetragonal compression. The geometry of the NiCl_6^{4-} anion reflects the presence of an axial lattice strain which induces a tetragonal compression. The displacement parameters of the Cl atoms in the CuCl_6^{4-} anion and NiCl_6^{4-} anion are compared. The observed displacement parameters and bond distances in the apparent compressed CuCl_6^{4-} octahedron strongly support a disordered model for

Table 8. Root Mean Square Deviations between $(U_{ij})_{\text{obsd}}$ and $(U_{ij})_{\text{calcd}}$

	Ni complex 23 °C	Cu complex			
		23 °C	-25 °C	-59 °C	-117 °C
rms $\Delta_{ij}U^a$ Å ²	0.0014	model 1 0.0183	0.0185	0.0187	0.0195
$\sigma(U_{ij})_{\text{obsd}}^b$ Å ²	0.0008	0.0005	0.0005	0.0004	0.0004
rms $\Delta_{ij}U^{a,c}$ Å ²		model 2 0.0029	0.0019	0.0015	0.0017
$\sigma(U_{ij})_{\text{obsd}}^b$ Å ²		0.0018	0.0017	0.0015	0.0014

^a rms $\Delta_{ij}U = \sum((U_{ij})_{\text{obsd}} - (U_{ij})_{\text{calcd}})^2 / (\text{observations} - \text{parameters})$, where observations are the number of all tensor components of all atoms in a MCl_6^{4-} anion and parameters are the number of independent parameters used in the TLS calculation. ^b $\sigma(U_{ij})_{\text{obsd}}$ is the experimental standard deviation averaged over all tensor components of all atoms in a MCl_6^{4-} anion. ^c The rms $\Delta_{ij}U$ for model 2 are the average of the values for the two orientations for the CuCl_6^{4-} groups.

the CuCl_6^{4-} anion in $(3\text{-chloroanilinium})_8\text{CuCl}_{10}$, although single-crystal X-ray diffraction cannot distinguish between static and dynamic disorder. The apparent compressed geometry is interpreted as an average of two elongated anions. This is in agreement with the published EXAFS⁷ and EPR⁸ spectroscopic results, as well as the theoretical calculations. The lattice strain induces a shortening of the Cu–Cl(1) bonds. When combined with the normal Jahn–Teller distortion, this forces an elongation of the octahedron in a direction perpendicular to the Cu–Cl(1) bond direction. The combination of these two effects leads to the observed rhombic distortion of the Cu(II) coordination.

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Supporting Information Available: Tables of structure determination parameters, bond distances, bond angles, anisotropic thermal parameters, and H atom positions for $(3\text{-chloroanilinium})_8\text{NiCl}_{10}$ and tables of structure determination parameters, positional parameters, bond distances, bond angles, anisotropic thermal parameters, and H atom positions for models 1 and 2 of $(3\text{-chloroanilinium})_8\text{CuCl}_{10}$ at four temperatures (71 pages). Ordering information is given on any current masthead page.

(14) Shomaker, V.; Trueblood, K. N. *Acta Crystallogr.* **1968**, B24, 63.