Inorganica Chimica Acta, 22 (1977) 43–48

Comparison of Internal and External Pressure on the Symmetry of Tetrachloro Anions of Transition Metals*

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Received July 29, 1976

It has been established that the geometry of $CuCl_4^{2-}$ *is dependent on crystal field stabilization, extent of Cu 4s and 4p participation in bonding, ligand–ligand repulsion forces, extent of the hydrogen bonding of the counter ion to the chlorine atoms, and crystal packing forces. The geometry of the* $CuCl_4^{2-}$ *can be followed by examining several experimental parameters, such as the* trans *Cl–Cu–Cl angle, position of the "d–d" transitions and the nature of the Cu–Cl stretching vibration in the far infrared (FIR). It is not known to what extent similar considerations hold for the first-row transition metals in the (II) oxidation state* (e.g. Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+})*. A systematic study of the complexes involving counterions unable to provide hydrogen bonding to the chlorines of the* MCl_4^{2-} *entity, and to those complexes demonstrating a high degree of hydrogen bonding was started. The changes in the FIR and in the "d–d" transition spectrum were followed under ambient conditions and under high external pressures. Whenever it was possible comparisons of the effects of the internal pressure (hydrogen bonding) and high external pressure in changing the geometry of the* MCl_4^{2-} *ion were made.*

Introduction

The transformation from distorted tetrahedral to planar symmetry for copper complexes of the type M_2CuCl_4, where M = Cs^+ or alkylammonium ion, has been accomplished with high external pressure. The salts Cs_2CuCl_4 and Cs_2CuBr_4 were transformed at pressures in excess of 60–70 kbar [1]. The salt $[(CH_3)_2CHNH_3]_2CuCl_4$, existing in an environment of distorted tetrahedral and square planar [2], transformed at ~20 kbar [3]. The extent to which tetrachloro anions of the first-row transition elements transform from a distorted tetrahedral geometry to a planar symmetry with external pressure has not been investigated. For the tetrachloro cuprate salts it has been demonstrated that alkylammonium ions containing hydrogens capable of hydrogen bonding will distort the tetrahedral structure and increase the *trans* Cl–Cu–Cl bond angle [3–5]. Depending on the degree of hydrogen bonding the distortion can be considerable, and the Cl–Cu–Cl bond angle approaches 180° as is observed for $[C_2H_5NH_3]_2CuCl_4$ [6] and $(NH_4)_2CuCl_4$ [7]. The latter distortion, due to hydrogen bonding in the crystal, can be considered to involve internal pressure. In this work we have attempted to examine the extent that internal pressure can distort the geometry of tetrachlorometallate anions, where the metal is a first-row transition element. We have also examined the extent external pressure can modify the geometry, with and without internal pressure. The effects of pressure were monitored by observing the changes in the skeletal region of the far infrared and in the electronic spectra. The results of this study are presented.

Experimental Section

Preparation of Compounds

Two methods were used to prepare the compounds. When possible a solution preparation was used following the method of Cotton, Goodgame and Goodgame [8]. This method involves basically dissolving appropriate mol quantities of the organic amine hydrochloride in ethanol and the metal chloride in ethanol and mixing the two solutions and allowing crystal formation. When the solution technique was not successful the technique of Wiesner, *et al.* [9] was used. In this method 2 mol of the organic ammine hydrochloride were heated on a steam bath to approach melting, and then 1 mol of the metal chloride was added with stirring. After stirring, the compound was heated in an oven at 80 °C for at least

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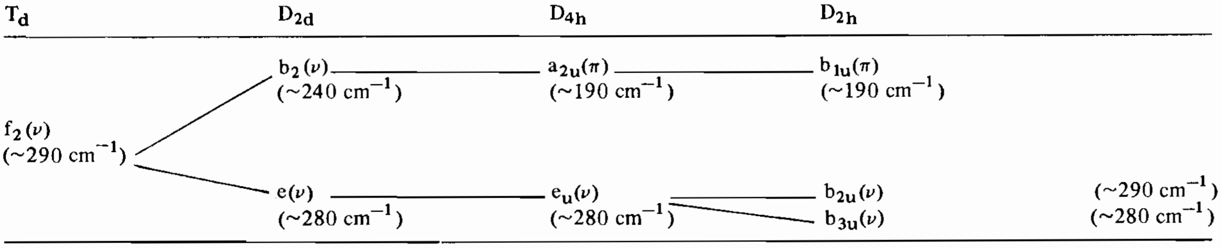
*Research performed under the auspices of the USERDA.

TABLE I. Analytical Data for R_2MCl_4 Complexes.

Compound	C		H		N		Cl	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[(CH_3)_4N]_2MnCl_4$	27.5	27.8	6.9	7.2	8.0	8.1		
$[(C_2H_5)_4N]_2NiCl_4$	41.7	41.1	8.7	8.8	6.1	6.0		
$[(CH_3)_4N]_2NiCl_4$	27.5	29.3	6.9	7.4	8.0	8.5		
$[(C_2H_5)_4N]_2FeCl_4$	42.4	41.5	8.2	8.9	6.1	6.0		
$[(CH_3)_4N]_2FeCl_4$	17.7	17.8	4.4	4.6	5.2	5.2		
Cs_2CoCl_4							30.4	30.3
$[(CH_3)_4N]_2CoCl_4$	27.5	27.4	6.9	7.1	8.0	8.0		
$[(CH_3)_2CHNH_3]_2CoCl_4$	22.4	21.3	6.2	6.2	8.7	8.0		
$[(CH_3)_4N]_2CuCl_4$	27.2	27.4	6.8	6.9	7.9	7.9		
$[(CH_3)_2CHNH_3]_2CuCl_4$	22.2	22.4	6.1	6.3	8.6	8.8		

SCHEME.

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.

an hour. For details on the synthesis of tetrahedral nickel and iron complexes, see Gill [10] and Gill and Nyholm [11].

Analyses

The compounds were analyzed for carbon, hydrogen, and nitrogen. Table I compiles the analytical results, which were obtained from Micro Tech Laboratories, Inc., Skokie, Ill 60076.

Spectral Studies

The spectra in the electronic region (visible and near infrared) were obtained using a Cary Model 14R spectrophotometer. The far infrared spectra were obtained by using a Perkin–Elmer Model 301 far infrared spectrophotometer. Both spectrophotometers were equipped for use of the diamond anvil cell [12–13] and appropriate beam condensors to obtain the ambient and high pressure spectra of the solid compounds.

Results and Discussion

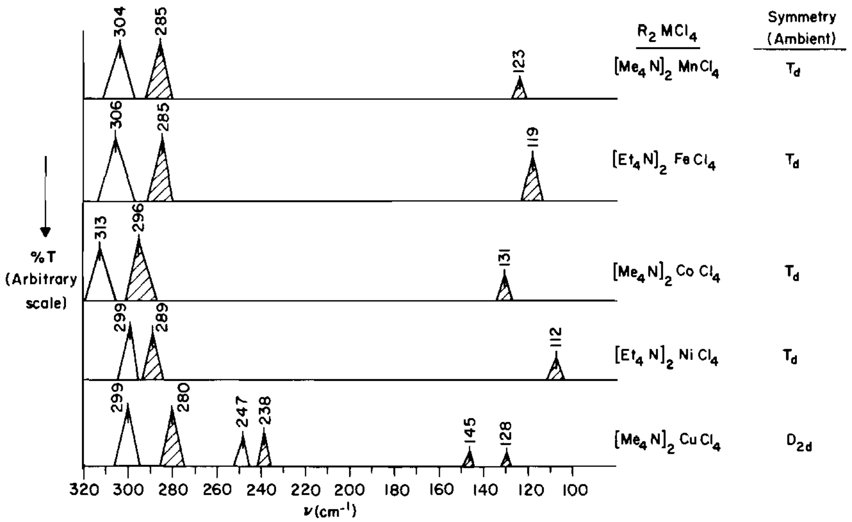
The low frequency infrared region shows some significant changes as the structure approaches square planar geometry from tetrahedral geometry. The scheme illustrates the correlation for the f_2 infrared active stretching mode in a tetrahedral symmetry, and its lower symmetry analogs (D_{2d}, D_{4h}, and D_{2h}). The triply degenerate f_2 stretching mode in the tetrahedral symmetry is split into 2 stretching modes in the D_{2d} geometry–b_2 and e with 40–50 cm^{-1} separation. With further symmetry degradation to the D_{4h} geometry, the stretch (b_2) becomes an out of plane bending mode of lower energy. The stretch (e) becomes a stretch (e_u) of approximately the same frequency. With further loss of symmetry to the D_{2h} geometry the (e_u) stretching mode is split into two stretching modes, (b_{2u}) and (b_{3u}), of almost equal energy (~285 cm^{-1}) and only minor changes in frequency will occur. The out-of-plane bending mode, (b_{1u}), appears at ~190 cm^{-1}. Thus it can be seen that when square planar symmetry is reached the degeneracy is completely removed and the triply degenerate f_2 stretching mode is split into three bands.

The electronic region also demonstrates important changes as the symmetry is lowered from T_d. The "d–d" transitions in square planar copper complexes occur at higher energies than those in T_d. [5, 14]. As illustrated by this work results for cobalt complex transitions are similar.

TABLE II. Effects of Pressure on Infrared and Electronic Transitions of R_2MCl_4 Complexes (R = tetrasubstituted ammonium cations).[a]

	← Ambient Pressure →			← High Pressure →		
Compound	Cl–M–Cl *Trans* Angle (°)	IR Absorptions (cm^{-1})	Electronic Absorptions (cm^{-1})	IR Absorptions (cm^{-1})	Electronic Absorptions (cm^{-1})	Ambient Symmetry
$[Me_4N]_2MnCl_4$		285; 123	23; 256 (vvw)	$304(25)^b$	Too weak to follow with pressure	T_d
$[Et_4N]_2FeCl_4$		285; 119	34, 013; 32, 258	305(25)	34, 480(40)	T_d
$[Me_4N]_2CoCl_4$	109	296; 131	15, 750; 14, 925 6061; 5495; 5195	313(20)	Sl. blue shifts (38)	T_d
$[Et_4N]_2NiCl_4$	110	289; 112	15, 152; 14, 184	299(25)	14, 925; 14, 130 (40)	T_d
$[Me_4N]_2CuCl_4$	128	280; 145 238; 128	6000; 8333 (w, br)	299; 247(20)	too weak to follow with pressure	D_{2d}

[a] All results obtained at room temperature. [b] Numbers in parenthesis represent pressures applied in kbar.



Crosshatched indicates ambient pressure spectra

Figure 1. Far infrared spectra of R_2MCl_4 complexes where R is a tetrasubstituted ammonium ion and M = transition element.

Thus, one can use the changes noted in the skeletal region of the infrared in combination with those observed in the electronic region to determine if any conversion in geometry is occuring. These spectroscopic techniques were used diagnostically to follow the effects of pressure on the R_2MCl_4 complexes.

Non-Hydrogen Bonded R_2MCl_4 Complexes

Figure 1 shows the spectra of the R_2MCl_4 complexes where R is a tetrasubstituted ammonium ion, and contains no hydrogen available for hydrogen bonding to the chlorines in the MCl_4^{2-} entity. Thus, no internal pressure exists in these complexes. The first-row transition elements (except Cu) all crystallize in a tetrahedral geometry at ambient conditions [9, 15, 16, 16a]. The far infrared spectra and Raman scattering data have been obtained and assignments made [17, 18]. The metal–chlorine stretching vibration (f_2) has been assigned at ~290 cm^{-1}. Table II summarizes the infrared and electronic data to ~50 kbar. When external pressure is applied to the Mn, Fe, Co and Ni complexes, the only changes that are noted are those involving a blue shift of the stretching vibration due to the shortening of interatomic distances [19, 20]. The electronic transitions for these complexes also show a slight blue shift with pressure, except for Ni which manifests a slight red shift.

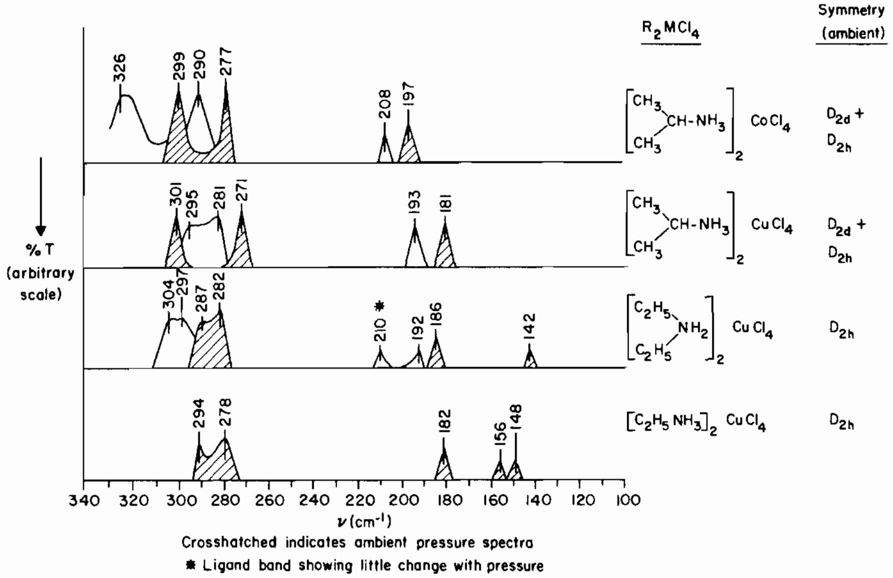


Figure 2. Comparison of far infrared spectra of cobalt(II) and copper(II) complexes.

The $[Me_4N]_2CuCl_4$ complex exists in a distorted tetrahedral (D_{2d}) geometry at ambient conditions as evidenced by the x-ray data [15, 16] and spectroscopic results [17, 18]. Two stretching vibrations are observed at 280 and 238 cm^{-1} following the predictions from the selection rules (Scheme). With application of external pressure no further change in symmetry are observed. Only blue shifts of the electronic and infrared transitions are seen.

The effect of external pressure in complexes with an absence of internal pressure is rather minimal. No changes in geometry are observed, and only changes in the vibrational and electronic regions (blue shifts), due to a decrease in bond lengths of the metal–chlorine distances or an increased ligand-field effect [19, 20], are manifested. The latter type of effects have been previously observed for other compounds.

It should be emphasized that other tetrahedral complexes may behave differently with pressure. The $M(CN)_4^{2-}$ tetrahedra in $K_2M(CN)_4$ compounds, where M = Zn, Cd or Hg, demonstrate a lowering of symmetry to D_{2d} with application of external pressures to 30 kbar [21]. The differences in behaviour from MCl_4^{2-} tetrahedral may reflect differences in ligand field effects on the central metal atom as well as differences in the ligand. Other contributing factors may involve differences in lattice energy and compressibilities.

Hydrogen Bonded R_2MCl_4 Complexes

In attempting to prepare the series of complexes of the type R_2MCl_4 where R = partially substituted ammonium ion and M = Mn, Fe, Co, Ni and Cu, synthetic problems were incurred. Complexes involving Co and Cu in a distorted T_d geometry could be readily prepared. However, in the case of Mn and Fe the complexes obtained were octahedral, and not distorted T_d. With R = $CH_3(CH_2)_2NH_3^+$ and i-C_3H_7-NH_3^+ cations, manganese gave pink complexes, which contained a two-dimensional metal–halogen framework formed by $MnCl_6$ octahedra sharing corners [22–24]. Similar structures are obtained for iron [23]. For nickel complexes syntheses attempted in solution gave complexes of the stoichiometry $RNiCl_3$ rather than R_2NiCl_4 [25–29]. As a result a comparison of the effects of external pressure on tetrahalometallates involving R groups capable of hydrogen bonding was only possible for the $CoCl_4^{2-}$ and $CuCl_4^{2-}$ anions. Table III summarizes these results.

The bis(isopropylammonium)tetrachlorocobaltate shows a distorted geometry approximating a symmetry of D_{2d} + D_{2h}. Hydrogen bonding or internal pressure has caused a distortion with a lowering of symmetry from the essentially T_d geometry in the $(Me_4N)_2CoCl_4$ complex. Application of external pressure to ~70 kbar failed to materially reduce the symmetry, and mostly blue shifts were observed.

Copper complexes of R_2CuCl_4 where R = i-$C_3H_7NH_3^+$, $(C_2H_5)_2NH_2^+$ and $C_2H_5NH_3^+$ were studied. At ambient pressures the bis(isopropylammonium)-tetrachlorocuprate $[(IPA)_2CuCl_4]$ crystallizes in a structure involving 1/3 D_{2h} and 2/3 distorted T_d geometry. The bis(diethylammonium)tetrachlorocuprate and the bis(ethylammonium)tetrachlorocuprate are already in a square planar configuration. The effect of internal pressure (hydrogen bonding) in the crystal is seen to have greater effect than is observed with the cobalt analogue. Application of external pressure (~20 kbar) converts the $(IPA)_2CuCl_4$ to a D_{2h} geometry [5].

TABLE III. Effects of Pressure on Infrared and Electronic Transitions of R_2MCl_4 Complexes (R = mono-di-substituted ammonium cation).[a]

		← Ambient Pressure →					← High Pressure[c] →		
Compound	Cl–M–Cl *Trans* Angle (°)	Density[b]	IR Absorptions (cm^{-1})		Electronic Absorptions (cm^{-1})	Ambient Geometry	IR Absorptions (cm^{-1})		Electronic Absorptions (cm^{-1})
$(i\text{-}C_3H_7NH_3)_2CoCl_4$			299; 277	197	16,393 14,286	$D_{2d} + D_{2h}$	326; 290 (20)	208	Sl. blue shifts (44)
$[i\text{-}C_3H_7NH_3]CuCl_4$	155 (2/3) 180 (1/3)	1.50	301; 279	181	12,048	$D_{2d} + D_{2h}$	281; 295(sh) (20)	193	12,578 (25)
$(C_2H_5NH_3)_2CuCl_4$	180	1.70	278; 294(sh)	182	12,800(b) 10,500(sh)	D_{2h}			12,987 (35)
$((C_2H_5)_2NH_2)_2CuCl_4$	162		282; 287(sh)	202(sh); 186	12,121(b)	D_{2h}	304; 297 (20)	210,192	12,500 (25)

[a] All results obtained at room temperature. [b] Obtained from X-ray measurements. [c] Numbers in parenthesis represent pressures applied in kbar.

Figure 2 compares far infrared spectra with and without pressure for cobalt and copper complexes.

Conclusions

Table IV summarizes the results obtained. The $(R_4N)_2MCl_4$ complexes are of T_d geometry except for M = Cu, where a D_{2d} symmetry ensues. As one increases the internal pressure (increased hydrogen bonding from mono-, di- and tri-substituted ammonium cations to Cl in MCl_4^{2-} anion), two-dimensional sheets are obtained for the manganese and iron complexes, which involve $MnCl_6$ or $FeCl_6$ octahedra. Thus, the hydrogen bonding stabilizes an octahedral geometry rather than a quasi square-planar structure, indicating the reluctance of Mn(II) and Fe(II) to form square-planar complexes. With nickel, preparations in solutions give $RNiCl_3$ complexes, which have $NiCl_6$ octahedra.

For the $(i\text{-}C_3H_7NH_3)_2CoCl_4$ complex, which shows a distorted structure (D_{2d}) due to the internal pressure caused by hydrogen bonding, an increase in external pressures to ~70 kbar does not demonstrate a change in geometry.

However, for $(i\text{-}C_3H_7NH_3)_2CuCl_4$ crystallizing in D_{2d} and D_{2h} symmetry due to internal pressure, an increase in external pressure converts the complex to D_{2h} geometry at 20 kbar. Thus, considerably less energy is necessary to convert the copper complex as opposed to the cobalt complex. It should be emphasized that $((C_2H_5)_2NH_2)_2CuCl_4$ and $(C_2H_5NH_3)_2CuCl_4$ exist in a square-planar configuration at ambient pressures, illustrating the effectiveness of internal pressure in distorting the geometry of copper complexes.

It would be anticipated that the tendency to convert a distorted T_d geometry to square-planar would decrease as one went to Fe(II) and Mn(II) systems.

If conversion to a square-planar configuration involves a transformation from high-spin to low-spin with the pairing of electrons, it would be expected that more electrons would have to be paired as we proceed to the left-hand side of the first-row elements, making any change in geometry increasingly more difficult to achieve. The enhancement provided to any external pressure conversion of geometry, by starting with already distorted structures, distorted toward the pressure-stable phase, has recently been cited [3, 4]. However, even if the distortion is minor, as for Cs_2CuCl_4 and Cs_2CuBr_4, it should be possible to convert the distorted T_d geometry to square-planar, if sufficient pressure is utilized [1]. Thus, in principle, it should be possible to convert $(i\text{-}C_3H_7NH_3)_2CoCl_4$ to a square-planar configuration if sufficiently high external pressures are applied (>70 kbar).

Pearson's [30–31] symmetry rules predict that for MX_4 systems, d^5 through d^9 low-spin systems should

TABLE IV. Summary of Pressure Effects on R_2MCl_4 Complexes.

Counterion	Mn(II) d^5	Fe(II) d^6	Co(II) d^7	Ni(II) d^8	Cu(II) d^9
R_4N^+	T_d	T_d	T_d	T_d	D_{2d}
R_3NH^+	Increasing Internal Pressure				
$R_2NH_2^+$					
$R NH_3^+$ ↓	O_h	O_h	D_{2d}	O_h[a]	D_{2d} and D_{2h}
R_3NH^+	Increasing External Pressure				
$R_2NH_2^+$					
$R NH_3^+$ ↓	–	–	D_{2d}	–	D_{2h}
	R = alkyl group				

[a] Stoichiometry involves $NiCl_3^-$ anion; all others involve MCl_4^{-2} anions.

be stable in a square-planar geometry. Molecular orbital and ligand field theories essentially predict similar results; with d^5 and d^6 systems being stable in a distorted T_d geometry (D_{2d}) for low-spin complexes. Where comparisons are possible, the experimental results are in substantial agreement with such predictions.

Acknowledgment

The authors would like to thank Dr. Gary J. Long of University of Missouri, Rolla for the supply of $[(CH_3)_4N]_2$ $CoCl_4$ and Dr. Louis J. Basile of Argonne National Laboratory for helpful discussions.

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