

The Vibrational Spectra and Force Constants of the Planar CuCl_4^{2-} Ion in Bis(2-aminobenzothiazolium)tetrachlorocuprate(II)

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Abstract

The vibrational analysis and a general valence force field are given for the square planar CuCl_4^{2-} anion of the complex $(\text{LH})_2\text{CuCl}_4$, where L = 2-aminobenzothiazole. The force constants have been compared with data obtained for other planar MCl_4^{n-} ions and interpreted in terms of the *trans*-influence and hydrogen bonding.

Introduction

The primary interest in the halogenocuprates(II) derives from the fact that they are able to assume, with great ease, very different geometries. Among the factors upon which this characteristic depends are the Jahn–Teller effect, crystal field stabilization, ligand–ligand repulsion, shape and size of the counter ions, van der Waals forces and hydrogen-bonding interactions [1]. In addition, copper(II) halide complexes have played an important role in the developments of magneto–structural correlations [2] and low-dimensional magnetism [3], in spectroscopic properties of copper(II) proteins [4], catalytic processes [5] and thermochromism [6].

The tetrachlorocuprate(II) ion has either a flattened tetrahedral geometry of D_{2d} symmetry or a tetragonally distorted octahedral arrangement of chloride ions about the copper(II) ion involving bridging ligands [1]. However, it is well known that the energy barrier to a displacement along the normal coordinate which transforms the complex ion from a tetrahedral ligand geometry toward a planar structure is very small [7]. This is indicated by the fact that with different counter ions the *trans* ClCuCl angle varies widely covering the range 180 to 129° [7]. A dynamic behaviour of this kind may be important in biologically active copper(II) complexes, by

providing low-energy pathways (it is noteworthy that the spectral properties of CuCl_4^{2-} have been proposed as a useful model of the ‘blue’ copper(II) proteins [8, 9]). To date, a truly four-coordinate planar geometry for the CuCl_4^{2-} ion, in which no axial ligation is present, has been found in only three compounds: bis(*N*-methylphenethylammonium)tetrachlorocuprate(II) ($(\text{N-mpH})_2\text{CuCl}_4$) [10], bis(creatininium)tetrachlorocuprate(II) ($(\text{creat})_2\text{CuCl}_4$) [11] and bis(methadonium)tetrachlorocuprate(II) ($(\text{metH})_2\text{CuCl}_4$) [12]. Very recently Riley and Hitchman [7] reported on the temperature dependence of the electronic spectrum of the planar CuCl_4^{2-} ion and discussed the role of the ground- and excited-state potential surfaces. In a previous article [13] Hitchman and Cassidy had studied the effects of vibronic coupling on the electronic spectrum of this complex anion.

We have recently synthesized [14] bis(2-aminobenzothiazolium)tetrachlorocuprate(II), abbreviated as $(\text{LH})_2\text{CuCl}_4$, which contains a strictly planar CuCl_4^{2-} ion; the structure of this compound is given in Fig. 1. The planar structure is thought to be stabilized through hydrogen bonds between the chloride atoms and the hydrogen atoms of the amino group and the protonated nitrogen of the thiazole ring. In spite of the great interest in halogenocuprates(II), complete vibrational analyses on these anions are rather scarce; this fact prompted us to a thorough infrared and Raman study of the planar CuCl_4^{2-} ion in $(\text{LH})_2\text{CuCl}_4$. This vibrational analysis can also be regarded as a valuable contribution in the better understanding of the force constants.

Experimental

The synthesis and structure of $(\text{LH})_2\text{CuCl}_4$ are fully discussed in another paper [14]. The Raman

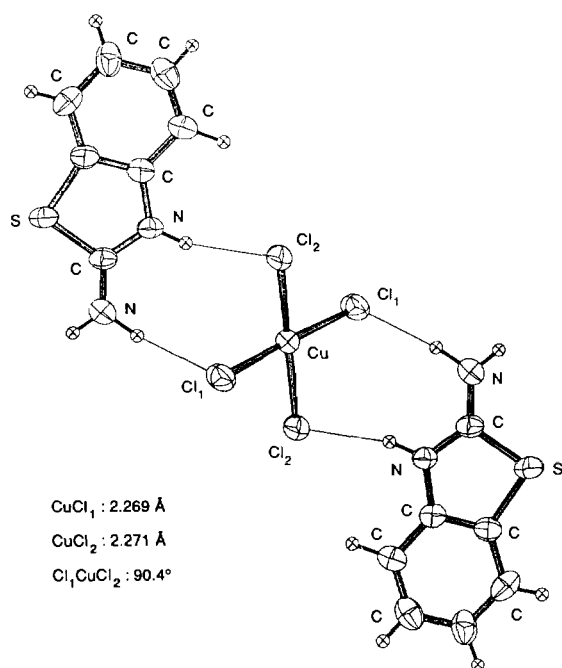


Fig. 1. The structure of bis(2-aminobenzothiazolium)tetrachlorocuprate(II).

spectrum was recorded on a SPEX 1403 spectrometer using the 488 nm line of a Spectra-Physics Ar⁺ laser; a spinning sample-cell was used to avoid thermal degradation of the coloured compound. Signal recording was done using photon counting with an integration time of 0.5 s, using a 2 cm⁻¹ slit width. The infrared spectra were recorded on a Bruker IFS 113v Fourier transform spectrophotometer with a global source, 6μ mylar beam splitter and a DTGS detector with polyethylene windows for the far-IR region and a KBr beam splitter and a DTGS detector with KBr windows for the mid-IR region, using KCl pellets in the 4000–500 cm⁻¹ region and polyethylene pellets in the 500–40 cm⁻¹ region.

For the description of the fundamental vibrations of the planar D_{4h} group we used the classification given by Nakamoto [15]. The GF matrix formulation, as presented by Wilson and co-authors [16], has been used in the calculation of the general valence force field. For the planar CuCl_4^{2-} ions known [10–12], a slight inequivalence of the Cu–Cl bond lengths and ClCuCl bond angles is generally observed. This inequivalence has also been observed in our compound (see Fig. 1). As no effects due to the above inequivalence could be detected in the infrared and Raman spectra of $(\text{LH})_2\text{CuCl}_4$, the D_{4h} point will be used to discuss the vibrational spectra of the compound. In our calculations we used an exact D_{4h} symmetry with a 2.270 Å Cu–Cl distance. The Cu–Cl bond length in square planar CuCl_4^{2-} ions is normally situated within the range 2.18–2.28 Å. The rather long bond distance in our complex must be

associated with the strong hydrogen bonding present, as the average hydrogen bonded NCl distance in $(\text{LH})_2\text{CuCl}_4$ (3.142 Å) is shorter than the corresponding distance observed for the other planar CuCl_4^{2-} systems with similar NHCl hydrogen bonds [10].

Results and Discussion

The IR and Raman spectra of 2-aminobenzothiazole (L), 2-aminobenzothiazolium chloride (LH^+Cl^-) and bis(2-aminobenzothiazolium)tetrachlorocuprate(II) ($(\text{LH})_2\text{CuCl}_4$) are, due to the fact that the complex is formed by hydrogen bonds, well comparable. Only minor changes, which are not significant for the study of the CuCl_4^{2-} ion, are observed in the regions of the NH₂ and NH⁺ vibrations. Consequently, as the high-frequency region is not relevant, only the low-frequency region will be discussed.

The typical low-frequency IR and Raman 2-aminobenzothiazole vibrations, which are not influenced on complex formation, are listed in Tables 1 and 2, respectively; they all must arise in the same regions for L, LH^+Cl^- and $(\text{LH})_2\text{CuCl}_4$. In this region six bands can be located. These bands must entail some skeletal modes of 2-aminobenzothiazole and are indicated as 'ligand skeletal modes 1 to 6'; the six 'ligand

TABLE 1. The Far-IR (cm⁻¹) 'Ligand Bands'

Assignment	L	LH^+Cl^-	$(\text{LH})_2\text{CuCl}_4$
Ligand skel. mode 1	322w		
Ligand skel. mode 2	304s	310s	305s
Ligand skel. mode 3	214m	203m	211sh
	182sb	185s	$\nu_7(\text{E}_g)^a$
Ligand skel. mode 4	157 w		$\nu_3(\text{A}_{2g})^a$
			120m ^b
Ligand skel. mode 5	110vw		94vw ^b
Ligand skel. mode 6	88vw		79w

^a See text and Table 3. ^b Lattice modes. s = strong; m = medium; w = weak; b = broad; v = very; sh = shoulder.

TABLE 2. The low-frequency Raman (cm⁻¹) 'Ligand Bands'

Assignment	L	LH^+Cl^-	$(\text{LH})_2\text{CuCl}_4$
Ligand skel. mode 1	323(3)	313(sh)	[320]
Ligand skel. mode 2	301(3)	305(3)	300(3)
Ligand skel. mode 3	214(3)	208(2)	$\nu_2(\text{B}_{1g})^a$
Ligand skel. mode 4	159(1)	168(1)	
Ligand skel. mode 5	114(3)	113(2)	116(2)
Ligand skel. mode 6	87(10)		85(4)

^a See text and Table 3.

TABLE 3. The Vibrational Fundamentals (cm^{-1}) for the Square Planar CuCl_4^{2-} Ions

Mode (D_{4h})	Activity	Mode description	(<i>N</i> -mpH) $_2\text{CuCl}_4^a$	(metH) $_2\text{CuCl}_4^b$	(creat) $_2\text{CuCl}_4^b$	(LH) $_2\text{CuCl}_4^c$
$\nu_1(A_{1g})$	R	$\nu_s(\text{CuCl})$	276s	275s	290s	274s
$\nu_2(B_{1g})$	R	$\nu_{as}(\text{CuCl})$	209vw	195w	not-observed	200mb
$\nu_3(A_{2u})$	IR	π	158s	159s	150s	158s
$\nu_4(B_{2g})$	R	$\delta(\text{ClCuCl})$	182s	181s	202s	180s
$\nu_5(B_{2u})$	inactive	π				87.8 ^d
$\nu_6(E_u)$	IR	$\nu_d(\text{CuCl})$	{ 314s 285s	{ 303s 281s	{ 308s 290s	291s
$\nu_7(E_u)$	IR	$\delta_d(\text{ClCuCl})$	193s	{ 179s 177s	188s	185s

^a Refs. 13 and 17. ^b Ref. 17. ^c This work. ^d Calculated value. ν = stretching; δ = in-plane bending; π = out-of-plane bending; R = Raman-active; IR = IR-active; subscripts as, s and d denote antisymmetric, symmetric and degenerate modes, respectively.

TABLE 4. The Vibrational Frequencies for Some Planar MCl_4^{2-} Ions

Mode (D_{4h})	AuCl_4^{-a}	PdCl_4^{2-a}	PtCl_4^{2-a}	CuCl_4^{2-b}
$\nu_1(A_{1g})$	349	304.3	331.3	274
$\nu_2(B_{1g})$	326	278.3	311	200
$\nu_3(A_{2u})$	142	150	147	158
$\nu_4(B_{2g})$	170	165.5	164.5	180
$\nu_6(E_u)$	361	321	313	291
$\nu_7(E_u)$	166	161	165	185

^a Ref. 18; similar data have also been given by Goggin and Mink [19]. ^b This work.

bands' are not relevant in the description of the CuCl_4^{2-} fundamentals and will consequently not be discussed.

The normal modes appearing in the planar CuCl_4^{2-} ion are assigned in comparison with the data obtained for planar CuCl_4^{2-} groups [13, 17] and other planar MCl_4^{2-} ions [15, 18, 19]. These data are given in Tables 3 and 4. If the slight difference between the Cu—Cl bond lengths is neglected, the planar CuCl_4^{2-} ion has seven normal vibrations [15]. The out-of-plane bending mode of B_{2u} symmetry is both IR and Raman inactive.

The intense 291 cm^{-1} band appearing in the IR spectrum of (LH) $_2\text{CuCl}_4$ is absent in the spectra of L and LH^+Cl^- and is situated in the region of the $\nu_6(E_u)$ mode. This band is split in the far-IR spectra of (*N*-mpH) $_2\text{CuCl}_4$, (metH) $_2\text{CuCl}_4$ and (creat) $_2\text{CuCl}_4$ (see Table 3) [17], perhaps indicating its doubly degenerate nature. The higher-wavenumber component is not clearly seen in our spectrum and is probably overlapped by the intense ligand skeletal mode 2.

Strong IR bands appear at 182 and 185 cm^{-1} in the spectra of L and LH^+Cl^- , respectively. We

expect both this band and the $\nu_7(E_u)$ mode at ca. 195–185 cm^{-1} [13, 17]. We observe only one very strong band at 185 cm^{-1} , so we must conclude that these vibrations coincide at the same frequency.

In the 150 cm^{-1} region, a weak band is observed in the far-IR spectrum of L at 157 cm^{-1} . In the spectrum of the complex we observe an intense band at 158 cm^{-1} ; as the $\nu_3(A_{2u})$ mode appears in this region for similar square planar CuCl_4^{2-} ions [13, 17] we ascribe the strong 158 cm^{-1} band to this fundamental, overlapping the weak ligand skeletal mode 4.

The bands arising in the far-IR spectrum of the complex at 120 and 94 cm^{-1} are absent in the spectra of L and LH^+Cl^- and can, in agreement with literature data [20], be ascribed to the $\nu_8(A_{2u})$ and $\nu_9(E_u)$ lattice modes of the complex.

The 274 cm^{-1} band appears as the most intense band in the Raman spectrum of the complex. No bands are observed in this region for L and LH^+Cl^- . This fact and literature reports [13, 17] let us conclude that the Raman band at 274 cm^{-1} must have a high $\nu_1(A_{1g})$ character. The A_{1g} stretching mode occurs at slightly lower energy in (LH) $_2\text{CuCl}_4$ than in creatininium salt (290 cm^{-1}) [17], and this may reflect the shorter Cu—Cl bond lengths in the later compound (225 pm as opposed to 227 pm). If the energy of the stretching vibration were to vary as about the sixth power of the bond length, a shift of the above amount would be expected.

In the 205–170 cm^{-1} region two Raman bands are observed in the spectrum of the complex. In this region we expect the $\nu_2(B_{1g})$ and $\nu_4(B_{2g})$ modes; the ν_2 mode is generally situated at a higher frequency as a stretching vibration and appears less intense [17]. So we can state that the less intense Raman band at 200 cm^{-1} has $\nu_2(B_{1g})$ character, probably overlapping the ligand skeletal mode 3 as this band appears rather broad in the spectrum of the complex. The strong band at 180 cm^{-1} must then be assigned to the $\nu_4(B_{2g})$ mode.

TABLE 5. Comparison of General Force Field Constants (10^2 N m^{-1}) for Planar MCl_4^{n-} Ions

Internal coordinate representation	PdCl_4^{2-a}	PtCl_4^{2-a}	AuCl_4^{-a}	CuCl_4^{2-b}
f_r	1.558	1.822	2.205	1.017
f_{rr}	0.079	0.068	0.081	0.183
$f_{rr'}$	0.218	0.334	0.177	0.185
$f_{\alpha}-f_{\alpha'}$	0.193	0.230	0.228	0.248
$f_{r\alpha}-f_{r'\alpha}$	0.025	0.044	0.038	0.039
f_{β}	0.069	0.054	0.054	0.073
$f_{\beta\beta}$	0.050	0.065	0.061	0.160

^a Ref. 18. ^b This work. f_r = bond stretching; f_{rr} = stretch-stretch (*cis*-bonds) interaction; $f_{rr'}$ = stretch-stretch (*trans*-bonds) interaction; f_{α} = in-plane bending; $f_{r\alpha}$ = stretch-bend (adjacent in-plane angle) interaction; $f_{\alpha\alpha}$ = bend-bend (adjacent in-plane angles) interaction; $f_{r'\alpha}$ = stretch-bend (non-adjacent in-plane angle) interaction; $f_{\alpha\alpha'}$ = bend-bend (non-adjacent in-plane angles) interaction; f_{β} = out-of-plane bending.

By comparing the fundamentals obtained for the square planar CuCl_4^{2-} ion of $(\text{LH})_2\text{CuCl}_4$ with other MCl_4^{2-} planar complex ions (Table 4) we observe a shift to lower frequencies for the stretching modes ν_1 , ν_2 and ν_6 , as the CuCl bonding is expected to have less covalent character compared with the MCl bonding ($\text{M} = \text{Pd}, \text{Pt}$).

The calculated force constants for the planar CuCl_4^{2-} ion are summarized in Table 5 and compared with the corresponding published values [18, 19] for planar $d^8 \text{MCl}_4^{2-}$ ions.

Since we had only one experimental frequency (ν_3) to determine two out-of-plane bending force constants, we assumed $f_{\beta\beta}$ (bend-bend (out-of-plane angles) interaction) to be negligible in order to obtain the value f_{β} and to calculate the frequency of the inactive $\nu_5(\text{B}_{2u})$ mode; the result of our calculation was 87.8 cm^{-1} . Force-field calculations [13] gave an energy of $150 \pm 30 \text{ cm}^{-1}$ in PdCl_4^{2-} and PtCl_4^{2-} and suggested an even lower value in planar CuCl_4^{2-} . The energy of the $\nu_5(\text{B}_{2u})$ was recently estimated by normal coordinate analysis [17]; the calculated energy of $\bar{\nu}(\text{B}_{2u}) = \sim 75 \text{ cm}^{-1}$ is similar to the value obtained by analysis of the optical spectrum (62 cm^{-1}) [17]. So we can conclude that the frequency for this mode at 87.8 cm^{-1} is situated in the region predicted and calculated in literature. This out-of-plane bending normal ν_5 mode carries the complex from a planar toward a distorted tetrahedral geometry [7].

The sensitivity of the deformation modes to the counter ion in the solid state has been explained by assuming a coupling of the fundamentals with the lattice modes of the same symmetry [21]. As the complex under investigation is stabilized by inter-

molecular hydrogen bonds, only solid state spectra could be obtained; so, a profound discussion of the deformation force constants and a comparison with the data obtained for other planar MCl_4^{n-} ions in solution is not meaningful. However, our calculated f_{β} value is considerably higher than those obtained for other planar MCl_4^{n-} ($\text{M} = \text{Pd}, \text{Pt}, \text{Au}$) ions in solution [18, 19]. This high f_{β} value can be explained by the strong hydrogen bonds which keep the chloride ligands strictly in the plane of the complex anion.

The slight difference between our calculated value and the published value for the ν_5 mode can be due to the high f_{β} value as obtained for $(\text{LH})_2\text{CuCl}_4$.

The f_r values follow the expected order $\text{Cu(II)} < \text{Pd(II)} < \text{Pt(II)} < \text{Au(III)}$. The 'softer' metals have higher values for the $f_{rr'}$ constant. For the interaction stretching force constants f_{rr} and $f_{rr'}$, we calculated approximately the same values. The order $f_{rr'} > f_{rr}$ was observed for the planar MCl_4^{n-} ions [18, 19]. The greater value of the *trans*- than the *cis*-interaction constant has been explained by the well known importance of the *trans*-influence in the d^8 square-planar chemistry.

As it is obvious there is a relation between the $f_{rr'}/f_{rr}$ ratio (Cu^{2+} , 1.01; Au^{3+} , 2.18; Pd^{2+} , 2.76; Pt^{2+} , 4.91) and the *trans*-influence, and as there is also a direct relation between the softness of the metal ion and the *trans*-influence, it might be possible that the values of the interaction stretching force constants could be useful in making quantitative predictions about the absolute hardness of metal ions in planar MX_4^{n-} complex ions. The determination of absolute hardness and softness still remains a problem in chemistry [22, 23].

References

- 1 D. W. Smith, *Coord. Chem. Rev.*, 21 (1976) 93.
- 2 R. D. Willett, D. Gatteschi and O. Kahn, (eds.), *Magneto-Structural Correlations in Exchange Coupled Systems*, NATO ASI Series, Plenum, New York: R. D. Willett, p. 389; W. E. Hatfield, p. 555.
- 3 L. J. de Jongh and A. R. Miedema, *Adv. Phys.*, 23 (1974) 1.
- 4 E. I. Solomon, J. W. Hare, D. M. Dooley, J. H. Dawson, P. J. Stephens and H. B. Gray, *J. Am. Chem. Soc.*, 102 (1980) 168.
- 5 G. Davies and M. A. El-Sayed, *Inorg. Chem.*, 22 (1983) 1257.
- 6 R. D. Bloomquist and R. D. Willett, *Coord. Chem. Rev.*, 47 (1982) 125.
- 7 M. J. Riley and M. A. Hitchman, *Inorg. Chem.*, 26 (1987), 3205, and refs. therein.
- 8 S. R. Desjardins, K. W. Penfield, S. L. Cohen, R. L. Musselman and E. I. Solomon, *J. Am. Chem. Soc.*, 105 (1983) 4590.
- 9 E. I. Solomon, K. W. Penfield and D. E. Wilcox, *Struct. Bonding (Berlin)*, 53 (1983) 1.
- 10 R. L. Harlow, W. J. Wells III, G. W. Watt and S. H. Simonsen, *Inorg. Chem.*, 13 (1974) 2106.

- 11 M. R. Udupa and B. Krebs, *Inorg. Chim. Acta*, **33** (1979) 241.
- 12 H. C. Nelson, S. H. Simonsen and G. W. Watt, *J. Chem. Soc., Chem. Commun.*, (1979) 632.
- 13 M. A. Hitchman and P. J. Cassidy, *Inorg. Chem.*, **18** (1979) 1745.
- 14 L. Antolini, A. Benedetti, A. C. Fabretti and A. Giusti, *Inorg. Chem.*, **27** (1988) 2192.
- 15 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 3rd edn., 1978, pp. 147–149.
- 16 E. B. Wilson, J. C. Decius and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955.
- 17 R. G. McDonald and M. A. Hitchman, *Inorg. Chem.*, **25** (1986) 3273.
- 18 A. N. Pandey, D. K. Sharma, U. P. Verma and V. Kumar, *J. Raman Spectrosc.*, **6** (1977) 163.
- 19 P. L. Goggin and J. Mink, *J. Chem. Soc., Dalton Trans.*, (1974) 1479.
- 20 J. R. Ferraro, *J. Chem. Phys.*, **53** (1970) 117.
- 21 J. Hiraishi and T. Shimanouchi, *Spectrochim. Acta*, **22** (1966) 1483.
- 22 R. G. Parr and R. G. Pearson, *J. Am. Chem. Soc.*, **105** (1983) 7512.
- 23 R. G. Pearson, *J. Am. Chem. Soc.*, **107** (1985) 6801.