$4e_1$ and $5a_1$ symmetry type, which are symmetry compatible to partake in bonding with the uppermost occupied orbitals of $C_2B_9H_{11}^{2-}$, i.e., MO's 8a″, 14a′, 9a″, and 15a′ which have masked e_1 symmetry. The three HOMO's of $C_5H_5Fe^+$, i.e., $4a_1(d_{z^2})$ and $3e_2(d_{xy}, d_{x^2-y^2})$, are symmetry incompatible; therefore, involvement in bonding with the HOMO's of the $C_2B_9H_{11}^{2-}$ moiety is disallowed, and, not surprisingly, they transform into MO's in the $[(C_2B_9H_{11})Fe(C_5H_5)]^-$ complex which possess very high metal orbital coefficients. The ordering of the frontier orbitals on $C_5H_5Fe^+$ agree with the description in Figure 2 of the paper of Hoffmann and coworkers.[16] Nevertheless, the essentially qualitative approaches have been and will continue to be of great use in rationalizing a large number of diverse structures.

Registry No. π-Cyclopentadienyl-(3)-1,2-dicarbollyliron, 37185-23-2; ferrocene, 102-54-5.

Supplementary Material Available: Lists of percentage atomic characters of the molecular orbitals of the cyclopentadienide anion, ferrocene, the dicarbollide dianion, and π-cyclopentadienyl-(3)-1,2-dicarbollyliron and interaction diagrams (11 pages). Ordering information is given on any current masthead page.

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Resonance Raman Spectra and Structure of the Vapor Complexes Formed by $CuCl_2(g)$ and $LCl_3(g)$ (L = Al, Ga, In)[1]

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The Raman spectra of the vapor complexes $CuAl_2Cl_8$, $CuGa_2Cl_8$, and $CuInCl_5$ are presented. Assignments of the Raman lines are obtained by isotopic substitution and by interpretation of the resonance Raman effect. On the basis of the spectral data, a structure containing a triply coordinated copper(II) ion is proposed for all three complexes.

Introduction

It is known that metal halides form complexes with group 3A metal halides in the vapor phase by reaction A,[2,3] where

$$MCl_2(s) + xLCl_3(g) \rightleftharpoons ML_xCl_{3x+2}(g) \qquad (A)$$

M is a bivalent metal ion and L is Al, Ga, or In. As a consequence of this complex formation, the volatility of the bivalent metal chloride is enhanced by several orders of magnitude. The thermodynamics and stoichiometry of this reaction have been studied by different techniques.[4] These studies showed that for L = Al, mainly 1:2 complexes are formed ($x = 2$).[2b,4] Only recently, detailed studies by visible spectroscopy revealed 1:1 ($MLCl_5$) and 1:2 (ML_2Cl_8) complexes for L = Ga and In.[5,6] The ratio between the two complexes is mainly controlled by the degree of dimerization of $LCl_3(g)$. As $AlCl_3$ exists below 500 °C mainly as a dimer, it is not surprising that only the 1:2 complexes could be observed.

The main experimental information on the structure of the vapor complexes has until now been the d–d transitions of the bivalent transition-metal ion. There is, however, no agreement on the interpretation of these spectra.[4,7–9] Emmenegger[2a] was able to rationalize the thermodynamic data of vapor complex formation assuming a structure with the transition-metal ion in a tetrahedral coordination sphere. Because Raman spectroscopy has already been used successfully to elucidate the structures of gaseous compounds at high temperatures,[10] we decided to use this method to determine the structure of the vapor complexes. One disadvantage of this method, however, is that the Raman spectrum of the vapor complex is overlapped by the spectrum of $LCl_3(g)$, always the major component of the equilibrium gas phase. As the transition-metal chloride complex is the only absorbing species in the visible and near-UV region, its Raman spectrum might under favorable conditions be largely enhanced by a resonance Raman effect. Therefore, the vapor complexes of $CuCl_2$, which show strong absorptions close to the lines of an argon ion laser, have been chosen to be studied first. A further advantage of this system is the high volatility of $CuCl_2$,[11,33] which allows one to observe the vapor complexes at temperatures of 250–350 °C for L = Al[2a] and Ga.[6]

Experimental Section

Chemicals. $CuCl_2 \cdot 6H_2O$ (p.a.) was dehydrated by refluxing in freshly distilled $SOCl_2$[12] and purified by chemical transport with $AlCl_3$. Anal. Calcd: Cu, 47.26; Cl, 52.74. Found: Cu, 47.12; Cl, 52.39. $AlCl_3$ was purified by sublimation from a mixture of 90% $AlCl_3$ (Fluka AG, purum) and 10% charcoal.[4] $InCl_3$ (Fluka AG, puriss) was sublimed under high vacuum before use. We thank Alusuisse AG, Neuhausen, Switzerland, for donating $GaCl_3$ (puriss). ^{63}CuO (^{63}Cu 97.8%) was purchased from Schenker Co.; ^{65}CuO (^{65}Cu 99.7%), from ORNL, Oak Ridge, Tenn. Professor E. Schumacher, University of Bern, Bern, Switzerland, generously provided 250 mg of $Al^{35}Cl_3$ (^{35}Cl 99%) and 250 mg of $Al^{37}Cl_3$ (^{37}Cl 99%).

Sample Preparation. A furnace fitting in the sample illuminator of the Spex Ramalog 4 was constructed (Figure 1).[13] The furnace can be closed at both ends by isolating stoppers fitted into the Pyrex tube (A). The temperature is controlled by a Eurotherm controller

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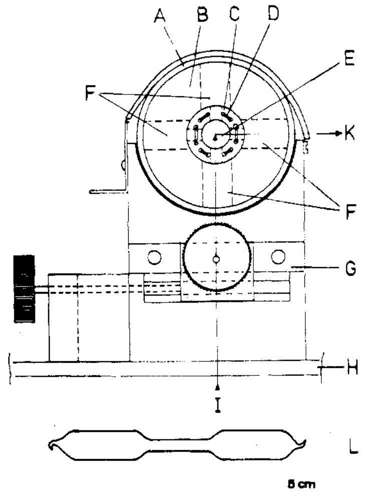


Figure 1. Furnace and ampule: (A) Pyrex tube (l = 180 mm, o.d. = 54 mm), (B) thermal isolation (Fiberfrax), (C) ceramic tube (l = 140 mm, o.d. = 22 mm, i.d. = 11 mm), (D) heating wire (Kantal o.d. = 0.7 cm, R = 152 Ω/cm), (E) sample, (F) windows for the beams, (G) transverse and longitudinal adjustable support, (H) cinematic platform, (I) exciting beam, (K) scattered light, (L) ampule.

(PIC/SCR 10A/FCO-1200 C DIN).

The temperature in the furnace is measured by a calibrated thermocouple (chromel/alumel). The temperature variations and the temperature gradient over the sample are smaller than 2 °C at 400 °C. The four windows and the adjustable support allow easy alignment of the samples. The ampules (L) containing the vapor complex are of dumbbell shape to avoid optical interference by the solid or liquid phases in equilibrium with the vapor complex and to minimize absorption by colored probes. The ampules were filled using the following method: Anhydrous $CuCl_2$ (1–5 mg) and LCl_3 (10–50 mg) were sealed under high vacuum in a tube attached to one end of the ampule. $CuCl_2$ was then transported in a temperature gradient (ΔT = 50 °C) by LCl_3 vapor into the ampule. The temperature at the cold end was 250 °C for $AlCl_3$ and $GaCl_3$ and 500 °C for $InCl_3$. LCl_3 was also condensed into the ampule and the latter sealed off. As CuO is completely converted to $CuCl_2$ by reaction with LCl_3 under transport conditions, CuO instead of $CuCl_2$ was used in some experiments. The isotopically pure samples have been prepared in the same way using isotopically pure starting materials.

Raman Spectra. The Raman spectra were recorded on an Spex Ramalog 4 Raman spectrometer. An argon ion laser (Spectra Pysics 164-01) was used as the exciting source. The spectral slit was 4 cm^{-1} in all measurements, if not indicated differently. An interference filter was used to filter off the spurious lines due to emission from the laser plasma at 19 430 and 20 450 cm^{-1}. The spectral response of the instrument was checked by comparing the experimental intensity ratio of Stokes and anti-Stokes lines in the spectrum of CCl_4 with the calculated one, using different exciting frequencies. The measurements using a krypton ion laser as exciting source were made on the Spex 1403 Raman spectrometer of the Institut de Chimie Minérale, University of Lausanne, Lausanne, Switzerland. The intensities of the Raman lines were measured as peak amplitudes, corrected for the spectral response of the instrument. The isotopic shifts were determined by recording the spectra of the isotopically pure samples at least ten times using different ampules. Whether the variances of two series of measurements were equal was checked by the F test.[14] Only isotopic shifts which by the t test[14] proved to be statistically significant by more than 99% were considered.

Absorption Spectra. The absorption spectra of the vapor complexes were measured with a Zeiss PMQ II single-beam spectrometer equipped with a Zeiss MM 12 double monochromator.[4]

Results

Raman Intensity. When the frequency (ν_0) of linear polarized incident light is removed from that of the lowest electronic transition, the intensity of vibrational Raman scattering in terms of the dependence of the ground-state polarizability on nuclear vibrations is given by expression 1.[15]

$$I_{mn} = \frac{(\nu_0 - \nu_{mn})^4 KM}{\nu_{mn}(1 - \exp(-hc\nu_{mn}/kT))}(45(\bar{\alpha}')^2 + 7(\gamma')^2) = f(\nu_{mn})KMI^\circ{}_{mn} \qquad (1)$$

$\bar{\alpha}'$ ($= \partial\bar{\alpha}/\partial Q_{mn}$) is the mean of the derived polarizability tensor and γ' its anisotropy. These quantities, on the right-hand side combined in $I^\circ{}_{mn}$, are characteristic properties of the scattering molecule. Within the approximation of the ground-state polarizability theory they are assumed in general to be independent of temperature, exciting frequency, and Raman shift (ν_{mn}). The left-hand side of eq 1 shows that the ratio $I_{mn}/f(\nu_{mn})$ is proportional to M, the concentration of the scattering molecules, analogous to the optical density. K is a constant largely dependent on the experimental setup. The measurement of absolute intensities is therefore difficult, and in general only relative intensities are measured. Under resonance conditions, i.e., when the exciting frequency (ν_0) approaches the frequency of the first electronic transition, the ground-state polarizability theory breaks down.[16] Under these conditions $I^\circ{}_{mn}$ becomes strongly dependent on the exciting frequency.[17] As long as the latter is kept constant, expression 1 holds. Consequently, the ratio $I_{mn}/f(\nu_{mn})$ is still proportional to the concentration of the scattering species. According to Albrecht and Hutley,[18] two different resonance processes, A type and B type, can be distinguished by their dependence of the intensity on the exciting frequency and the polarization ratio.[19] A-type resonance terms, due to interaction with only one single excited electronic state, are characteristic for totally symmetric vibrations. B-type terms, on the other hand, are due to interaction with two excited electronic states, which are coupled by the resonance-active vibration. A distinct feature which allows one to identify A-type resonance terms is the appearance of an intensified overtone and combination tone progression.[19] One is therefore able to assign totally symmetric vibrations based on the resonance enhancement. This provides, however, little information if one deals with larger molecules of unknown structure. Fortunately, some additional rules of thumb can be formulated which convert this rather complex theory into a useful tool. A very general rule states that the resonance-enhanced Raman lines are due to vibrations localized within the chromophore. This is very important because it allows one to study selectively vibrations in complex macromolecules or in mixtures. A second rule, only applicable to A-type resonance enhancement, states that the largest enhancement is shown by Raman lines due to normal coordinates along the largest distortion of the equilibrium conformation in the excited state.[20,21] This criterion obviously applies mainly to stretching vibrations. Therefore, mainly the totally symmetric metal–ligand vibrations will show a large resonance enhancement if the exciting line approaches charge-transfer transitions.

$CuCl_2/AlCl_3$. Figure 2 shows the Raman spectra of the vapor in an ampule containing $AlCl_3$ and $CuCl_2$ at different temperatures. The spectrum at 220 °C is identical with the one of pure Al_2Cl_6(g).[22,23] It shows clearly the split peak at 328 and 338 cm^{-1} characteristic of Al_2Cl_6. At 250 °C, two new bands are observed, one at 444 cm^{-1} and the other at 289 cm^{-1}. Comparison with the Raman spectrum of pure Al_2Cl_6(g) shows that these two lines cannot be due to any aluminum chloride species. On the basis of the thermodynamics of the vapor complex formation,[2a] the two lines undoubtedly have to be assigned to $CuAl_2Cl_8$(g). At 300 °C the two bands dominate the whole spectrum, and the relative intensity of the line at 444 cm^{-1} is exceptionally large because the vapor phase consists of less than 20% of $CuAl_2Cl_8$. Furthermore, a distinct series of overtones and combination tones of the 444-cm^{-1} line is observed. These characteristics suggest an enhancement of this band by a resonance Raman effect. Similar observations

Table I. Raman Spectra of $CuAl_2Cl_8(g)$, $CuGa_2Cl_8(g)$, and $CuInCl_5(g)$

$CuAl_2Cl_8$					
ν, cm^{-1}	$\Delta\nu(^{35}Cl, ^{37}Cl)$, cm^{-1}	$\Delta\nu(^{63}Cu^{65}Cu)$, cm^{-1}	$CuGa_2Cl_8$ ν, cm^{-1}	$CuInCl_5$ ν, cm^{-1}	Assign
87 m	*a*	*a*	80 m		L[e]
130 w	2.6	0.0	108 w	90 m	L
154 m	0.5	1.3	140 w	130 m	$\nu(Cu-Cl_t) - \nu(Cu-Cl_b)$
			165 w		L
289 s (0.32)[c]	5.7	0.0	278 s (0.30)[c]	275 sh (0.32)[c]	$\nu(Cu-Cl_b)$
330[d]			315	312	L
372 m	11.5	0.0	*b*	*b*	L
444 ss (0.30)[c]	5.3	2.1	443 ss (0.28)[c]	442 s (0.29)[c]	$\nu(Cu-Cl_t)$
490 w	*a*	*a*	401 w	400 w	L
590 w	*a*	*a*	560 w	550 w	$2\nu(Cu-Cl_b)$
735 m	10.7	1.7	724 m	720 m	$\nu(Cu-Cl_t) + \nu(Cu-Cl_b)$
770 w	*a*	*a*	758 w	750 w	$\nu(Cu-Cl_t) + L$
888 m	13.7	3.8	885 m	884 m	$2\nu(Cu-Cl_t)$
950 w	*a*	*a*			$\nu(Cu-Cl_t) + 2\nu(Cu-Cl_b)$
1180 w	17.0	4.3	1180 w	1170 w	$2\nu(Cu-Cl_t) + \nu(Cu-Cl_b)$
1325 w	*a*	*a*	1320 w	1328 w	$3\nu(Cu-Cl_t)$

[a] Too weak to observe isotopic shift. [b] Overlapped by Raman lines of L_2Cl_6 or LCl_3. [c] Depolarization ratio. [d] Extrapolated from the combination band at 735 cm^{-1}. [e] $L_xCl^-{}_{3x+1}$.

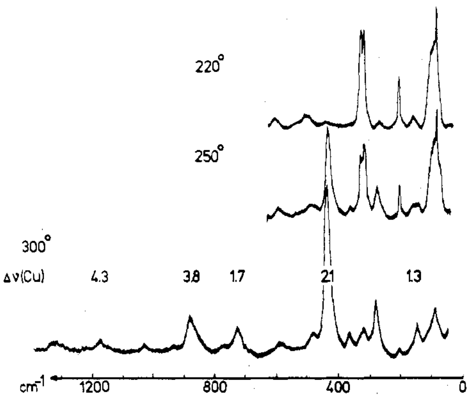


Figure 2. Raman spectrum of the vapor phase over $CuCl_2/AlCl_3$ at 220, 250, and 300 °C (ν_0 = 20 487 cm^{-1}, 1 W, slit 200 μ).

Table II. Excitation Profile of $CuAl_2Cl_8$

	$CuAl_2Cl_8$			Al_2Cl_6			
ν_0, cm^{-1}	I_{888}[a]	I_{444}[a]	I_{289}[a]	I_{328}[a]	I_{217}[a]	Av I_cf_d/f_cI_d[b]	I_{888}/I_{444}[b]
21 830	8	64	33	45	16	2.54	1.36
20 980	14	*c*	22	31	14	2.03	1.29
20 487	10	40	25	50	19	1.44	1.19
20 135	9	39	20	52	20	1.21	1.17
19 430	7	36	19	58	23	1.00	1.00

[a] Peak amplitude in mm, corrected for spectral response of the instrument. [b] Value at 19 430 cm^{-1} arbitrarily scaled to 1.00. [c] Overlapped by spurious emission lines of the laser.

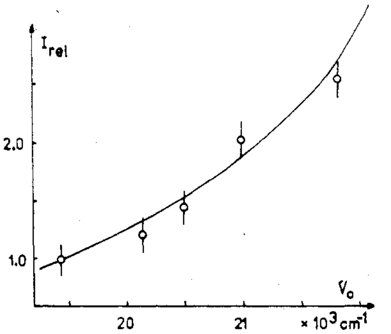


Figure 3. Excitation profile of $CuAl_2Cl_8$. The relative intensity at 19 430 cm^{-1} is arbitrarily scaled to 1.00. The solid line is calculated from eq 4 in ref 19 (ν_e = 30.3 × 10^3 cm^{-1}).

can be made for the band at 289 cm^{-1}, but the enhancement is not so strong. Several weaker Raman lines of the vapor complex can be identified by comparison with the Raman spectrum of pure Al_2Cl_6 if both spectra are observed under the same experimental conditions. They are compiled in Table I. The isotopic substitution technique[24,25] allows one to obtain direct experimental information on the symmetry of the complex and to assign the Raman and IR bands. We therefore prepared the isotopically pure vapor complexes $^{63}CuAl_2Cl_8$, $^{65}CuAl_2Cl_8$, $^{65}CuAl_2{}^{35}Cl_8$, and $^{65}CuAl_2{}^{37}Cl_8$ and measured their spectra. The observed isotopic shifts are given in Table I. As expected, all Raman lines shift upon ^{35}Cl, ^{37}Cl substitution, which confirms experimentally that the complex contains no Cu–Al structural element with isolated vibrations. A ^{63}Cu, ^{65}Cu isotopic shift is observed for five Raman lines. Three of these lines have to be assigned to overtones and combination tones because their frequencies are larger than 650 cm^{-1}. The intense line at 444 cm^{-1}, which shifts by 2.1 cm^{-1}, is undoubtedly due to a vibration within the coordination sphere of Cu^{2+}. As Cu^{2+} moves in the course of this vibration, a centrosymmetric structure can be ruled out. In a centrosymmetric structure, the unique Cu^{2+} ion would have to be located at the center of inversion. The mass point located there, however, moves only in vibrations of ungerade representations, which are not Raman active. The fifth line, at 154 cm^{-1}, is in the frequency region of deformation modes. Because the observed isotopic shift is too large for such a mode, it is tentatively assigned to the difference (hot band) of the two intense lines at 444 and 289 cm^{-1}. This assignment is confirmed qualitatively by the temperature dependence of its intensity.

The relative intensities of the Raman lines at 444 and 289 cm^{-1} (assigned to the vapor complex) have been measured for various exciting frequencies using Al_2Cl_6 as an internal standard (Table II). The Raman intensities observed with the 19 430-cm^{-1} line of the argon ion laser as exciting beam are arbitrarily scaled to 1.00. The frequency dependence of the intensities (Figure 3) and the depolarization ratio of 0.32 indicate clearly an A-type, resonance enhancement by an electronic transition in the near-UV region.[18] A value of (30.2 ± 1.0) × 10^3 cm^{-1} is found for the effective absorption frequency ν_e by nonlinear regression using expression 4 in ref 19. The absorption spectra of the vapor complexes are given in Figure 4. $CuAl_2Cl_8(g)$ shows an intense absorption at 30 × 10^3 cm^{-1} in agreement with the value found using the excitation profile. Owing to its high absorption coefficient (ca. 8000), this absorption band is assigned to the lowest ligand to metal

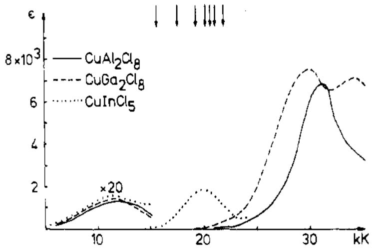


Figure 4. Absorption spectra of $CuAl_2Cl_8$ (300 °C), $CuGa_2Cl_8$ (300 °C), and $CuInCl_5$ (550 °C). The arrows indicate the positions of the laser lines.

Table III. Relative Raman Intensities of $CuCl_2/AlCl_3$ at Different Temperatures ($\nu_0 = 20\,487$ cm^{-1})

	$CuAl_2Cl_8$		Al_2Cl_6			
T, °C	$I_{444}{}^a$	$I_{289}{}^a$	$I_{217}{}^a$	ln ($I_{444}f_{217}/f_{444}I_{217}$)	ln ($I_{289}f_{217}/f_{289}I_{217}$)	ln K(B)^b + const
240	11	7	41	−0.107	−1.323	−0.71
250	80	26	30	2.195	0.303	1.25
260	122	42	21	2.977	1.146	2.06
270	157	51	18	3.392	1.490	2.44
280	172	57	17	3.541	1.661	2.60
290	177	57	15	3.699	1.786	2.74
300	177	57	14	3.772	1.856	2.81
320	177	55	10	4.115	2.160	3.14
340	172	52	9	4.199	2.210	3.20

[a] Peak amplitude in mm, corrected for spectral response of the instrument. [b] [ln ($I_{444}f_{217}/f_{444}I_{217}$) + ln ($I_{289}f_{217}/f_{289}I_{217}$)]/2.

charge-transfer transition. In the excited state, the Cu(II) is formally reduced to Cu(I). The metal to ligand bond length will, therefore, be different in the excited state, causing resonance enhancement primarily of the Cu–Cl stretching vibrations. The fact that one observes two such bands at 444 and 289 cm^{-1} strongly suggests a structure in which the coordination sphere of Cu^{2+} is composed of two sets of chemically nonequivalent chlorides.

$$CuCl_2(s) + Al_2Cl_6(g) \rightleftarrows CuAl_2Cl_8(g) \qquad \text{(B)}$$

The temperature dependence of the ratio $I_{mn}/f(\nu_{mn})$ allows one to determine directly the enthalpy of the vapor complex formation (reaction B) by expression 2, where I_c is the observed

$$\ln\left[\frac{I_c}{f(\nu)_c}\frac{f(\nu)_d}{I_d}\right] = \ln K(B) + \text{const} = -\frac{\Delta H(B)}{R}\frac{1}{T} + \text{const}' \qquad (2)$$

relative intensity of an isolated Raman line of the complex, I_d the intensity of an isolated Raman line of $Al_2Cl_6(g)$, K(B) the equilibrium constant, and ΔH(B) the enthalpy of reaction B. f(ν) is defined in expression 1. The observed values for I_c and I_d are given in Table III. Calculation of ln K(B) + const and linear regression in the temperature interval 270–340 °C yield 31.3 ± 4.0 kJ/mol for ΔH(B). This value is in agreement with the value given by Emmenegger[2a] (33.9 ± 0.3 kJ/mol) and thus confirms that the Raman spectrum of $CuAl_2Cl_8(g)$ has indeed been observed. The much higher slope at temperatures below 270 °C indicates that the system probably contains liquid $AlCl_3$.[2a]

$CuCl_2/GaCl_3$. Figure 6 shows the Raman spectrum of the vapor in an ampule containing $CuCl_2$ and $GaCl_3$ at different temperatures. The Raman spectrum at 200 °C is identical with the one of the vapor phase over pure $GaCl_3$. In contrast to aluminum chloride, the Raman lines of both $Ga_2Cl_6(g)$ and $GaCl_3(g)$ are observed,[13,23] indicating some dissociation of Ga_2Cl_6. The Raman line at 380 cm^{-1} must be assigned to the totally symmetric ν(Ga–Cl) in $GaCl_3(g)$.[13,26] At 250 °C, two new bands appear in the spectrum, one at 443 cm^{-1} and the other at 278 cm^{-1}. They are assigned to the vapor complex $CuGa_2Cl_8$ by analogy to the $CuCl_2/AlCl_3$ system. A detailed equilibrium study by absorption spectroscopy proves that the complex formed under the experimental conditions is indeed $CuGa_2Cl_8(g)$.[6] The increased relative intensity of the line at 380 cm^{-1} indicates increased dissociation of $Ga_2Cl_6(g)$. At 300 °C, the general features of the Raman spectrum are very similar to those observed for the $CuCl_2/AlCl_3$ system. The high intensity of the Raman line at 443 cm^{-1} and the progression of its overtones and combination tones dominate the shape of the spectrum. The weaker lines assigned to the vapor complex are identified by comparison with the spectrum of the vapor over pure $GaCl_3$ at the same temperature and are given in Table I. In contrast to the lines at 443 and 278 cm^{-1}, they are shifted compared with $CuAl_2Cl_8$ and are, therefore, assigned to vibrations outside the coordination sphere of Cu^{2+}. The nearly identical absorption spectrum (Figure 4) and the similar position of the Raman lines assigned to vibrations within the coordination sphere of the Cu^{2+} indicate clearly that the environment of the Cu^{2+} must be identical in the two vapor complexes.

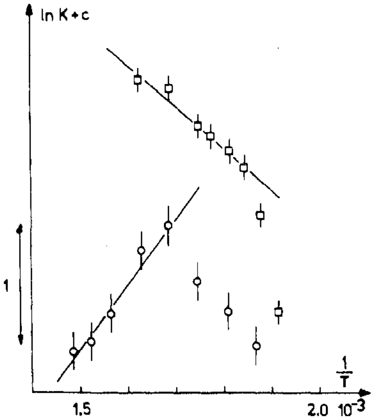


Figure 5. ln K + const as a function of $1/T$ for the reactions $CuCl_2(s) + Al_2Cl_6(g) \rightleftarrows CuAl_2Cl_8(g)$ (□) and $CuCl_2(s) + 2\,GaCl_3(g) \rightleftarrows CuGa_2Cl_8(g)$ (○). The solid lines have been obtained by linear regression (see text).

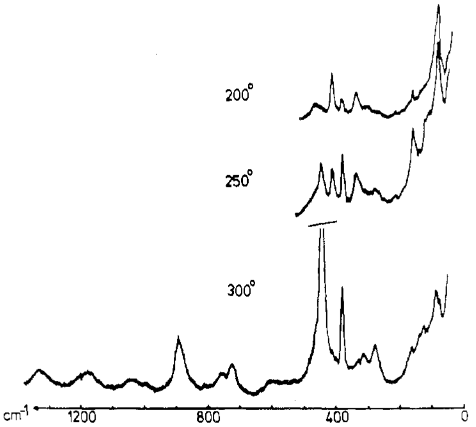


Figure 6. Raman spectrum of the vapor phase over $CuCl_2/GaCl_3$ at 200, 250, and 300 °C ($\nu_0 = 20487$ cm^{-1}, 1 W, slit 200 μ).

$$CuCl_2(s) + 2GaCl_3(g) \rightleftarrows CuGa_2Cl_8(g) \qquad \text{(C)}$$

$$CuCl_2(s) + Ga_2Cl_6(g) \rightleftarrows CuGa_2Cl_8(g) \qquad \text{(D)}$$

The enthalpy of the vapor complex formation by reaction C can be determined using the temperature dependence of the relative intensity of the Raman line at 443 cm^{-1} of the complex

Table IV. Raman Intensities of $CuCl_2/GaCl_3$ at Different Temperatures

	$CuGa_2Cl_8(g)$		$GaCl_3$	ln	ln	ln
T, °C	$I_{443}{}^a$	$I_{278}{}^a$	$I_{380}{}^a$	$(I_{443}f_{380}{}^2/f_{443}I_{380}{}^2T)$	$(I_{278}f_{380}{}^2/f_{278}I_{380}{}^2T)$	$K(C)^b$ + const
265	67	14	67	−10.842	−13.193	−12.02
280	146	27	82	−10.476	−12.953	−11.71
300	217	51	94	−10.367	−12.610	−11.49
320	180	40	66	−9.857	−12.616	−11.01
340	164	38	70	−10.079	−12.346	−11.21
365	137	28	84	−10.636	−13.034	−11.84
380	112	22	80	−10.747	−13.188	−11.97
400	83	17	72	−10.845	−13.258	−12.05

[a] Peak amplitude in mm, corrected for spectral response of the instrument. [b] $[\ln(I_{443}f_{380}{}^2/f_{443}I_{380}{}^2T) + \ln(I_{278}f_{380}{}^2/f_{278}I_{380}{}^2T)]/2$.

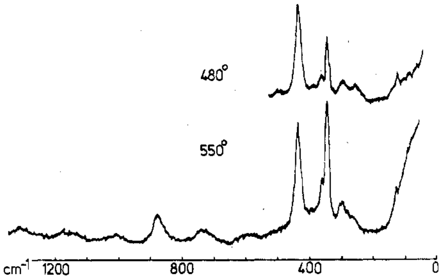


Figure 7. Raman spectrum of the vapor phase over $CuCl_2/InCl_3$ at 480 and 550 °C (ν_0 = 20 487 cm⁻¹, 1 W, slit 200 μ).

and the line at 380 cm⁻¹ of $GaCl_3$. Expression 2, however, has to be modified to expression 3, where the meaning of the

$$\ln\left[\frac{I_c}{f(\nu)_c}\frac{f^2(\nu)_m}{I_m{}^2T}\right] = \ln K(C) + \text{const} = -\frac{\Delta H(C)}{R}\frac{1}{T} + \text{const}' \qquad (3)$$

symbols is the same as in expression 2. The observed intensities are given in Table IV. By linear regression (Figure 5) in the temperature interval 320–400 °C, one obtains −48 ± 9 kJ/mol for the enthalpy $\Delta H(C)$. Adding the enthalpy of the dimerization of $GaCl_3$,[27] one calculates 42 ± 9 kJ/mol for the enthalpy of reaction D, which is in satisfactory agreement with 37 ± 3 kJ/mol, the value given by Dienstbach and Emmenegger.[6] If the observed temperature dependence is interpreted assuming formation of $CuGaCl_5$, the enthalpy found is much too small.

$CuCl_2/InCl_3$. Figure 7 shows the Raman spectrum of the vapor in an ampule containing $CuCl_2$ and $InCl_3$ at 480 and 550 °C. Ampules with additional Cl_2 to prevent decomposition of $CuCl_2$[11] give identical spectra, indicating that, for this experiment, the decomposition can be neglected. In both spectra shown in Figure 7, the Raman lines of $InCl_3(g)$, $In_2Cl_6(g)$, and the vapor complex are observed. The spectrum of the complex was assigned by comparison with the spectrum of the vapor over pure $InCl_3$.[13,23] The Raman line of greatest intensity assigned to the vapor complex appears at 443 cm⁻¹, very close to the frequency of the analogous lines in $CuAl_2Cl_8$ and $CuGa_2Cl_8$, and, as before, a distinct progression of overtones and combination tones of this fundamental is observed. A second, weaker band from the vapor complex is observed at 275 cm⁻¹.

It is, therefore, reasonable to conclude that the coordination sphere of Cu^{2+} is very similar in all these vapor complexes studied, although it is then surprising that the absorption spectrum of the complex with $InCl_3$ differs considerably from those of the $AlCl_3$ and $GaCl_3$ complexes (Figure 4). In the spectrum of the complex with $InCl_3$, the charge-transfer band near 30 × 10³ cm⁻¹ is missing and a medium-intense band (ϵ ca. 1800) at 20 × 10³ cm⁻¹ is observed instead. In the region of 20 × 10³ cm⁻¹ are the lines of an Ar ion laser. Therefore, the excitation profile of the Raman line at 443 cm⁻¹ can be obtained using different lines of the Ar ion laser. It matches this absorption band closely as shown in Figure 8. This fact and the depolarization ratio of 0.30 indicate a resonance effect of A type.[18] Because we assign the enhanced Raman lines in the same way as in the complexes with $AlCl_3$ and $GaCl_3$, we have to assign this absorption band as well to the first charge-transfer transition.

Table V. Excitation Profile of $CuInCl_5(g)$

ν_0, cm⁻¹	$CuInCl_5$ $I_{442}{}^a$	$InCl_3$ $I_{350}{}^a$	$I_{442}f_{350}/f_{442}I_{350}{}^b$
21 830	51	50	0.508
20 980	57	39	0.732
20 487	58	31	0.936
20 135	57	29	0.983
19 430	28	14	1.000
17 600[c]	64	50	0.639
15 434[c]	15	16	0.467

[a] Peak amplitude in mm, corrected for spectral response of the instrument. [b] Value at 19 430 cm⁻¹ arbitrarily scaled to 1.00. [c] Krypton ion laser.

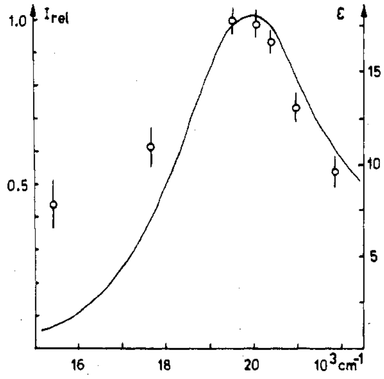


Figure 8. Excitation profile of $CuInCl_5(g)$. The intensity at 19 430 cm⁻¹ is arbitrarily scaled to 1.00. The solid line gives the absorption spectrum.

Thermodynamic studies have shown that $InCl_3$ forms mainly 1:1 complexes (x = 1) with $CoCl_2$[5] and $NiCl_2$.[28] An estimate based on the temperature dependence of the formation constants of $CuGaCl_5$ and $CuGa_2Cl_8$[6] and the dissociation of In_2Cl_6[29] (i.e., assuming the ratio of the formation constant of the 1:1 complex to the formation constant of the 1:2 complex to be the same for $GaCl_3$ and $InCl_3$) shows that, at 550 °C, about 80% of the vapor complex is $CuInCl_5$. The spectra have, therefore, to be assigned to $CuInCl_5$ and not to $CuIn_2Cl_8$, as in the systems with $AlCl_3$ and $GaCl_3$. Unfortunately, it was not possible to observe a Raman spectrum under the conditions of reaction A (solid $CuCl_2$) at different temperatures in this system. It is thus not possible to measure any thermodynamic quantity comparable with a known value.

Discussion

The Raman spectra of the vapor complexes of $CuCl_2$ and LCl_3 (L = Al, Ga, In) are all characterized by a strongly resonance-enhanced Raman lines between 442 and 445 cm⁻¹ and a distinct progression of overtones and combination tones of the latter. This line is assigned to a totally symmetric ν(Cu–Cl) vibration by its isotopic shift and by interpretation of its resonance behavior. A second, weaker Raman line, shifting to smaller energies in the complexes of the heavier group 3A metals, is also observed in all the complexes and, by the same arguments, is also assigned to a totally symmetric ν(Cu–Cl) vibration. As the vibrational spectrum is very sensitive to changes in the coordination sphere,[30] the close

Table VI. ν(Cu–Cl) and Coordination Number (CN) in Copper Compounds[a]

	CN	ν, cm^{-1}	Assign[b]	Ref
$CuCl_2$	2	496	ν(Cu–Cl) [Σ_u]	34
		370	ν(Cu–Cl) [Σ_g]	33
Cu_2Cl_4	3	445	ν(Cu–Cl$_t$) [A_{1g}]	33
		315	ν(Cu–Cl$_b$) [A_{1g}]	
$CuAl_2Cl_8$	3	444	ν(Cu–Cl$_t$) [A_1]	This work
		289	ν(Cu–Cl$_b$) [A_1]	
Cu(2-pic)$_2$Cl$_2$	4	308	ν(Cu–Cl) [B_{2u}]	44
$CuCl_4^{2-}$	4	297	ν(Cu–Cl) [A_1]	45
Cu(py)$_2$Cl$_2$	6	294	ν(Cu–Cl$_t$) [B_{2u}]	44
		236	ν(Cu–Cl$_b$) [B_{1u}]	
Cu(3,4-lut)$_4$Cl$_2$	6	184	ν(Cu–Cl) [A_{2u}]	44

[a] 2-pic = 2-picoline, 3,4-lut = 3,4-lutidine, py = pyridine.
[b] Irreducible representation is given in brackets.

similarity of the Raman spectra indicates that the Cu^{2+} has a similar coordination sphere in all three complexes. The copper isotopic shift proves that the complexes have no center of inversion. The two different totally symmetric ν(Cu–Cl) vibrations indicate that the coordination sphere is composed of two chemically different sets of chlorides.

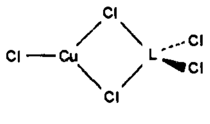
The frequency of metal–ligand stretching vibrations is strongly influenced by the coordination number and the oxidation state of the central metal ion.[31] In Table VI, frequencies of ν(Cu–Cl) for copper complexes with different coordination numbers are compiled for comparison. The values show that the frequency decreases with increasing coordination number (similar frequencies are reported by Smith[32] in his review on chlorocuprates). By comparison with these values, the high frequency (444 cm^{-1}) of the intense line found in the vapor complexes indicates that the coordination number is smaller than 4, most probably 3. For the following reasons, this 444-cm^{-1} line must be assigned to the stretching vibration of a terminal chloride attached to the copper:

(i) The observed frequency is much to high for a vibration between copper and a bridging chloride. Considering that the ratio ν(Cu–Cl$_b$)/ν(Cu–Cl$_t$) is in general 0.8,[30] the highest possible frequency for such a vibration is estimated to be below 400 cm^{-1}.

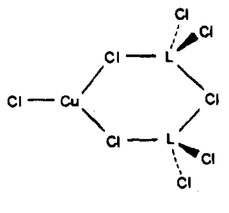
(ii) The position of this line in the spectrum is not influenced by the mass of the group 3A metal, indicating that the latter does not move in the normal coordinate of this vibration.

(iii) The isotopic shifts (Table I) can be calculated satisfactorily using a simple Cu–Cl two-atom model.

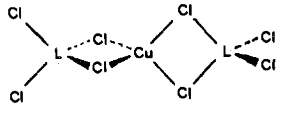
Structure A is obviously the most reasonable structure for the 1:1 complex containing a terminal Cu–Cl bond in accordance with the requirements deduced from the Raman spectrum, while we think structure B to be the most reasonable for the 1:2 complexes. The coordination sphere of Cu^{2+} is similar in both structures, as required by the similarity of the Raman spectra of CuL_2Cl_8 (L = Al, Ga) and $CuInCl_5$. In both structures, Cu^{2+} is surrounded by one terminal and two bridging chlorides. In structure A the anion LCl_4^- acts as a bidentate ligand forming a four-membered chelate ring, but in structure B the anion $L_2Cl_7^-$ acts as a bidentate ligand forming a six-membered chelate ring. Other less symmetrical structures with a bond between a third terminal chlorine of the anion and Cu^{2+} cannot be excluded, but they seem unlikely in view of the ν(Cu–Cl) frequencies. Structure C can be eliminated, having no terminal chloride attached to the Cu^{2+}.



(A)



(B)



(C)

By the arguments developed before, the line at 444 cm^{-1} is assigned to the terminal ν(Cu–Cl$_t$). In Cu_2Cl_4(g), which contains Cu^{2+} in a similar coordination sphere, the analogous vibration is observed at 442 cm^{-1}.[33] The IR-active vibration (ungerade) assigned to ν(Cu–Cl$_t$) is reported at 417 cm^{-1}.[34] The Raman line near 280 cm^{-1}, slightly influenced by the group 3A metal, is assigned to the totally symmetric ν(Cu–Cl$_b$), the line due to this vibration in Cu_2Cl_4(g) being at 307 cm^{-1}.[33] If these assignments are accepted, it is at first sight surprising that the line at 289 cm^{-1} shows no Cu isotope shift. However, ν(Cu–Cl$_b$) is coupled to other vibrations within the chelate ring, and the atomic masses of aluminum and chlorine are small compared with that of copper. The Cu^{2+}, therefore, moves only slightly in this vibration, and the expected isotope shift is small. This was confirmed by model calculations of the totally symmetric vibrations in $CuAl_2Cl_8$.[13]

The large energy differences between ν(Cu–Cl$_t$) and ν(Cu–Cl$_b$) shows that the terminal Cu–Cl$_t$ bond is considerably stronger than the bridging Cu–Cl$_b$ bond, and the orbital overlap between the terminal chloride and Cu^{2+} must also be larger. Hence, the different electron distribution of the excited state, which is active in the resonance enhancement, will affect this bond more than that between the bridging chloride and the copper. Consequently, we expect the resonance enhancement to be larger for ν(Cu–Cl$_t$) than for ν(Cu–Cl$_b$),[35] and this is in accordance with our results.

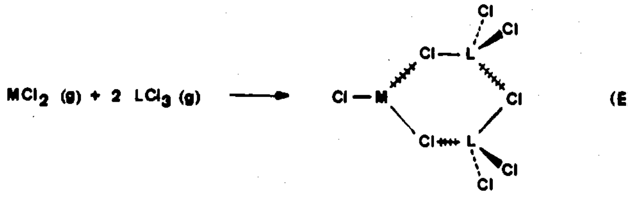
An open question concerns the differences between the absorption spectra of the 1:1 A and 1:2 B complexes. The lowest charge-transfer band, which is at different wavelengths in the two vapor complexes, is assigned (by analogy with $Cu_2Cl_6^{2-}$) to the transition of an electron from a pπ in-plane orbital localized mainly on the bridging chlorines to a dπ* orbital.[36] The π in-plane orbital is more (α = 90°) or less (α = 120°) involved in the L–Cl σ bond depending on the bond angle α on the bridging chloride. Hence, it is obvious that the energy of the lowest charge-transfer transition will be influenced by this angle, which is different in structures A and B. This qualitative consideration is supported by the observation that the absorption spectra of the 1:1 complex and Cu_2Cl_4 are similar.

The Raman shifts of the other weaker bands of the vapor complexes, which are strongly influenced by the group 3A metal, are assigned to vibrations localized mainly within the $L_2Cl_7^-$ or LCl_4^- moiety. The frequencies observed for the $L_2Cl_7^-$ ions are in agreement with the frequencies given by Rytter,[37] who identified these anions in melts of metal and group 3A metal chlorides. The frequencies assigned to vibrations of $InCl_4^-$ are similar to those given by Clark and Hester.[38]

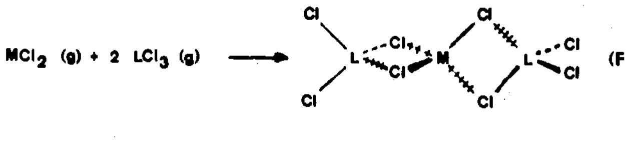
The cyclic structure B has never been proposed so far for vapor complexes[2] and might therefore seem strange. There are, however, chemical arguments in favor of this structure. As mentioned above, the anions $L_2Cl_7^-$ were identified spectroscopically in melts of LCl_3 and metal chlorides.[37,39] Furthermore, the crystal structures of $Pd_2(C_6H_6)_2(Al_2Cl_7)_2$[40] and $Te_4(Al_2Cl_7)_2$[41] are shown to contain the anion $Al_2Cl_7^-$. The analogous anion $Al_2Br_7^-$ was found in KAl_2Br_7 and $NH_4Al_2Br_7$

by Rytter[37,42] and independently by Schumann.[43] Therefore, we see no reason why $L_2Cl_7^-$ should not also be found in the vapor-phase complexes. In addition, the six-membered chelate ring in structure B is practically strain-free, in contrast to the four-membered rings in structure C.

Whether the cyclic structure B is particular to the vapor complexes of $CuCl_2$ or is of more general significance may be clarified by comparing the energetics of reactions E and F.



(B)



(C)

++++ new bond

To the first approximation, the entropies of the two reactions are the same since, in both reactions, one molecule of similar symmetry is formed from identical starting materials. The enthalpy of reaction F may be approximated by the sum of the enthalpies of dimerization of LCl_3 and MCl_2,[2a] in which value the conformational strain of the four-membered rings is included. It is more difficult to estimate the enthalpy of reaction E, in which only one new M–Cl bond is formed but the chelate ring is strain-free, in contrast to the four-membered rings formed in reaction F. Hence, the energy difference between structures B and C is determined by the energy gain due to the formation of a second bond M–Cl and the energy loss due to the conformational strain. It is reasonable to assume that the conformational strain is not much influenced by the metal ion M^{2+}. Therefore, comparing various M^{2+}, the energy of the second M–Cl bond is the only variable parameter. If this energy is larger than the conformational strain, structure C will be favored; if it is smaller, B will be preferred. The energy of the second M–Cl bond is difficult to estimate because it depends not only on the dissociation energy of a M–Cl bond but also on the tendency of the metal ion to increase its coordination number. A thermodynamic study of $CuCl_2(g)$[33] showed that the sublimation temperature of the latter is lower than for other bivalent transition-metal chlorides. This shows that the difference of the energy content of the condensed and the vapor phases is rather small and thus indicates that the metal ion cannot gain much energy by increasing the coordination number, even if the local concentration of ligands is high. It therefore seems that under these conditions the cyclic structure B of the vapor complex is favored. It would thus be reasonable from this point of view if, of all the ML_2Cl_8 species, only the $CuCl_2$ vapor complexes show cyclic structure B. These arguments, however, do not exclude the cyclic structure for vapor complexes of other metal chlorides but rather indicate that further studies are necessary before the structures in this class of compounds are completely understood.

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Registry No. $CuAl_2Cl_8$, 58915-60-9; $CuGa_2Cl_8$, 65589-60-8; $CuInCl_5$, 66197-67-9; $AlCl_3$, 7446-70-0; $InCl_3$, 10025-82-8; $GaCl_3$, 13450-90-3; $CuCl_2$, 7447-39-4.

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