Contribution from the Consiglio Nazionale delle Ricerche of Italy, Istituto di Chimica Generale,
Centro di Studio per la Strutturistica Diffrattometrica del CNR, University of Parma, 43100 Parma, Italy,
Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, 70126 Bari, Italy,
and Istituto di Chimica Generale ed Inorganica, University of Modena, 41100 Modena, Italy

Spectroscopic and Structural Investigation on the Trihalocuprates(II) of the 4-Benzylpiperidinium Cation. Crystal and Molecular Structure of Bis(4-benzylpiperidinium) Hexachlorodicuprate(II)

L. P. BATTAGLIA,[1a] A. BONAMARTINI CORRADI,[1a] G. MARCOTRIGIANO,[1b] L. MENABUE,[1c] and G. C. PELLACANI*[1c]

Received February 5, 1979

Some compounds of the type $(4BzpipdH)_2Cu_2X_mY_{6-m}$ (X = Cl; Y = Br; m = 6, 4, 2, 0; 4BzpipdH = 4-benzylpiperidinium cation) and $(4BzpipdH)_2CuBr_4$ complexes were prepared and characterized by means of X-ray powder, electronic, and infrared spectra and magnetic moments. For one of them, $(4BzpipdH)_2Cu_2Cl_6$, the crystal structure was also determined. The crystals are monoclinic, of space group $C2/c$, with a = 28.877 (8) Å, b = 8.440 (2) Å, c = 12.023 (2) Å, β = 101.9 (1)°, Z = 4, d_{calcd} = 1.60 g cm^{-3}, and d_{measd} = 1.61 g cm^{-3}. The structure, solved by the heavy-atom method and refined by least-squares calculations to a R = 3.1%, consists of 4-benzylpiperidinium cations and $Cu_2Cl_6^{2-}$ groups, weakly joined into infinite chains by Cu–Cl interaction (2.687 (3) Å). The copper atoms are five-coordinate with an average distance of 2.262 Å for the four shorter Cu–Cl bonds and a geometry intermediate between trigonal bipyramidal and tetragonal pyramidal. The magnetic and spectroscopic results for the $(4BzpipdH)_2Cu_2X_mY_{6-m}$ complexes indicate that they are isomorphous and isostructural, while those for the $(4BzpipdH)_2CuBr_4$ complex suggest a "distorted" tetrahedral symmetry. Hydrogen bonding interactions greater in the former than in the latter complexes are also evident from the infrared spectra.

Introduction

The trichlorocuprate salts containing $Cu_2Cl_6^{2-}$ anions show a variety of coordination numbers and configurations of Cl^- ions about the copper atom. In $KCuCl_3$ and NH_4CuCl_3,[2] the dimers, almost planar, are interconnected by two Cu–Cl long bonds, which make the coordination tetragonally distorted octahedral. In $Me_2NH_2CuCl_3$,[3] in $pqCu_2Cl_6$,[4] and in $PhCH_2CH_2NMeH_2CuCl_3$[5] the sixth octahedral position is vacant, producing a square-pyramidal or distorted trigonal-bipyramidal environment. In PPh_4CuCl_3[6] and in $AsPh_4CuCl_3$[7] there are discrete $Cu_2Cl_6^{2-}$ ions in which coordination around each copper atom is highly flattened tetrahedral.

In a previous study on chlorocuprates(II),[8] we have considered different geometries of tetrachlorocuprate ions in connection with the crystal-packing forces and hydrogen bonds involving the protonated cations. In this paper we have considered the halocuprates of 4-benzylpiperidinium cation in order to investigate the effects of the cation dimensions and of hydrogen bonding and inter- and intramolecular contacts on the geometry of the copper(II) complex anions.

Experimental Section

Preparation of the Hydrohalide Salts. The 4-benzylpiperidine hydrohalide salts were prepared by evaporating slowly and completely an aqueous amine solution neutralized with concentrated hydrogen halides. The salts were recrystallized from ethanol and diethyl ether.

Preparation of the Complexes. $(4BzpipdH)CuCl_3$ complex was prepared by mixing $CuCl_2{\cdot}2H_2O$ (1 mmol) and 4BzpipdHCl (1 mmol) in methanol, by adding diethyl ether and by cooling at 4 °C. The compound was recrystallized from methanol and 2-propanol (1:1).

$(4BzpipdH)CuCl_mBr_{3-m}$ (m = 0, 1, 2) complexes were prepared in ethanol by mixing stoichiometric amounts of the copper salts and the 4-benzylpiperidine hydrohalide ($CuCl_2{\cdot}2H_2O$ and 4BzpipdHBr, $CuBr_2{\cdot}3H_2O$ and 4BzpipdHCl, $CuBr_2{\cdot}3H_2O$ and 4BzpipdHBr for m = 2, 1, 0, respectively). The compounds instantaneously precipitated by cooling or by adding diethyl ether.

$(4BzpipdH)_2CuBr_4$ complex was separated by adding a 4BzpipdHBr (2 mmol) solution to a $CuBr_2{\cdot}3H_2O$ (1 mmol) solution in methanol and diethyl ether and by cooling at 4 °C.

Physical Measurements. The electronic spectra of the solid compounds were recorded as mull transmission spectra with a Shimadzu MPS 50L spectrophotometer in the temperature range 290–380 K. The infrared spectra of NaCl or KBr pellets (4000–250 cm^{-1}) and of Nujol mulls (400–60 cm^{-1}) were recorded with a Perkin-Elmer 180 spectrophotometer.

The room-temperature magnetic moments were measured with the Gouy method by using $HgCo(NCS)_4$ as calibrants and correcting for diamagnetism with the appropriate Pascal constants.

Differential scanning calorimetric analysis was performed with a Perkin-Elmer DSC-1 instrument.

Crystallographic Data Collection. Preliminary cell dimensions and space groups were determined by rotation and Weissenberg photographs. A crystal of approximate dimensions 0.09 × 0.07 × 0.24 mm^3 was mounted with its c axis coincident with the ϕ axis of a Siemens on-line automated diffractometer. Cell dimensions, refined by a least-squares procedure of 2θ values for 20 high-angle reflections measured on the diffractometer using Cu Kα radiation, and other crystallographic data are as follows: $(C_{12}H_{18}N)_2Cu_2Cl_6$, formula weight 692.38; a = 28.877 (8), b = 8.440 (2), c = 12.023 (3) Å; β = 101.9 (1)°; V = 2867 (8) Å^3, d_{measd} = 1.61 g cm^{-3} (by flotation), Z = 4, d_{calcd} = 1.60 g cm^{-3}, $F(000)$ = 1400, μ = 71.1 cm^{-1} (Cu Kα); monoclinic, space group $C2/c$ (from systematic absences). The intensity data were collected to a maximum 2θ of 140° with Cu Kα radiation ($\bar{\lambda}$ = 1.541 78 Å) and ω–2θ scan technique. Of the 2877 independent reflections, 2388 were considered as observed having $I > 2\sigma(I)$ ($\sigma(I) = \lambda[(\text{total counts}) \times 0.05(\text{intensity})]^{1/2}$. A standard reflection was measured every 20 reflections to check the instrument stability and crystal stability and alignment; its intensity was practically constant during the data collection. The structure amplitudes were obtained after Lorentz and polarization reduction and the absolute scale was established first by Wilson's method and then by the least-squares refinement. Absorption corrections were deemed unnecessary in view of the low absorbance ($\mu\bar{r}$ = 0.3), the transmission factor ranging from 0.63 to 0.60, and the nearly cylindrical shape of the sample.

Solution and Refinement of the Structure. The structure was solved by Patterson and Fourier techniques, localizing first the copper atom from the Patterson synthesis and then the remaining nonhydrogen atoms from the successive Fourier maps. The refinement was carried out by means of full-matrix analysis minimizing the function $R = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ where w is the weight calculated as $w = 1/(\sum F_o)^2 + gF_o^2$ (g = 0.000 99) isotropically and anisotropically to R = 8.1%. At this stage a ΔF synthesis revealed all hydrogen atoms, which were refined with isotropic temperature factors: the im-

---

(1) (a) University of Parma. (b) University of Bari. (c) University of Modena.

(2) Willett, R. D.; Dwiggins, C.; Kruh, R. F.; Rundle, R. E. *J. Chem. Phys.* **1963**, *38*, 2429.

(3) Willett, R. D. *J. Chem. Phys.* **1966**, *44*, 39.

(4) Murray-Rust, P. *Acta Crystallogr., Sect. B* **1975**, *31*, 1771.

(5) Harlow, R. L.; Wells, W. J.; Watt, G. W.; Simonsen, S. H. *Inorg. Chem.* **1974**, *13*, 2860.

(6) Textor, M.; Dubler, E.; Oswald, H. R. *Inorg. Chem.* **1974**, *13*, 1361.

(7) Willett, R. D.; Chow, C. *Acta Crystallogr., Sect. B* **1974**, *30*, 207.

(8) Battaglia, L. P.; Bonamartini Corradi, A.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *Inorg. Chem.* **1979**, *18*, 148.

0020-1669/80/1319-0125$01.00/0

Table I. Fractional Coordinates ($\times 10^5$) for Cu and Cl and ($\times 10^4$) for N and C[a]

atoms	*x*	*y*	*z*
Cu	48240 (2)	38234 (7)	59918 (5)
Cl(1)	52806 (4)	35833 (11)	46357 (9)
Cl(2)	46316 (4)	12059 (11)	58189 (9)
Cl(3)	43973 (3)	41407 (13)	73572 (9)
N	4305 (1)	34 (6)	8153 (4)
C(1)	2513 (2)	−502 (6)	5942 (4)
C(2)	2254 (3)	451 (9)	5116 (6)
C(3)	1789 (3)	836 (10)	5117 (7)
C(4)	1583 (2)	367 (8)	5973 (6)
C(5)	1836 (2)	−525 (8)	6810 (6)
C(6)	2294 (2)	−965 (7)	6798 (5)
C(7)	3001 (2)	−1091 (8)	5852 (5)
C(8)	3381 (2)	−1052 (7)	6943 (5)
C(9)	3467 (2)	608 (6)	7414 (4)
C(10)	3867 (2)	673 (7)	8450 (4)
C(11)	4248 (2)	−1633 (7)	7729 (5)
C(12)	3841 (2)	−1746 (7)	6710 (4)

[a] Estimated standard deviations are in parentheses.

Table II. Fractional Coordinates ($\times 10^3$) for Hydrogen Atoms[a]

atoms	*x*	*y*	*z*
H(11)	455 (2)	11 (6)	872 (4)
H(12)	438 (2)	62 (7)	768 (5)
H(2)	240 (2)	67 (8)	451 (7)
H(3)	160 (2)	154 (8)	450 (5)
H(4)	123 (2)	71 (7)	592 (5)
H(5)	166 (2)	−91 (7)	734 (6)
H(6)	247 (2)	−163 (7)	740 (5)
H(71)	312 (9)	−43 (8)	522 (5)
H(72)	300 (2)	−215 (7)	543 (5)
H(8)	328 (2)	−168 (8)	752 (5)
H(91)	353 (2)	132 (6)	675 (5)
H(92)	320 (2)	96 (6)	764 (5)
H(101)	393 (2)	173 (7)	883 (5)
H(102)	380 (2)	5 (7)	910 (5)
H(121)	390 (2)	−121 (7)	603 (5)
H(122)	379 (2)	−287 (7)	634 (4)
H(111)	417 (2)	−226 (6)	836 (4)
H(112)	453 (2)	−200 (7)	753 (5)

[a] Estimated standard deviations are in parentheses.

provement of the *R* index was 3.1%. No evidence for secondary extinction was found. Scattering factors for Cu, Cl, N, and C were those of Cromer and Mann[9] and for hydrogen atoms were those of Stewart, Davidson, and Simpson.[10] The effects of anomalous dispersion were corrected by including the values of $\Delta f'$ and $\Delta f''$ in the calculations for Cu and Cl atoms. The final positional parameters are given in Tables I and II. A listing of the observed and calculated structure factors for the reflections used in the refinement with thermal parameters are available as supplementary material. All calculations were performed on the Cyber 7600 computer of the Centro di Calcolo dell'Italia Nord-Orientale, Casalecchio (Bologna).

Analyses. Nitrogen, carbon, and hydrogen were analyzed by Mr. Giuseppe Pistoni using a Perkin-Elmer 240 elemental analyser. The halogens were directly determined on aqueous solutions of the complexes, by the Volhard method. The copper was determined by complexometric titration with EDTA.

Results and Discussion

The conventional chemical analysis results are reported in Table III. All the complexes have a Cu:X:cation stoichiometric ratio of 1:3:1; a 1:4:2 ratio is only observed for the tetrabromocuprate(II) complex.

A sharp endothermic peak, corresponding to the melting point, was observed in the differential scanning calorimetric analysis for all the compounds, indicating that there is no thermochromic behavior and that they are true compounds, in particular the (mixed halo)cuprates(II), and not a mixture of $CuCl_3^-$ and $CuBr_3^-$ anions.

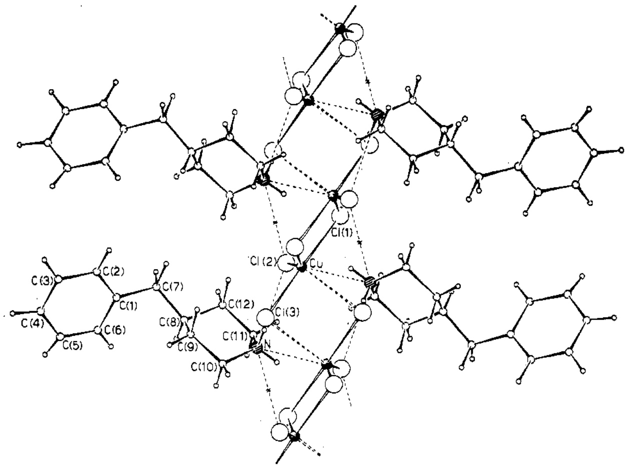

Figure 1. Projection of the structure along [010].

Crystal Structure of $(4BzpipdH)_2Cu_2Cl_6$. As shown in Figure 1, the structure consists of chlorocuprate anions and 4-benzylpiperidinium cations. In Table IV bond distances and angles in the structure are given. Copper is surrounded by five chlorine atoms, four of them more strictly bonded to it. Two adjacent copper atoms are bridged by two chlorine atoms, so that the anions are linked in $(Cu_2Cl_6)^{2-}$ dimers forming, through weak interaction (2.687 (3) Å), infinite chains running along the *c* axis. In this way the coordination around each copper atom in the dimer is distorted trigonal bipyramidal. The least-squares mean plane through equatorial atoms, $CuCl(2)Cl(1)^{i}Cl(3)^{ii}$ (for i and ii see Table IV), is $0.74092X - 0.14070Y - 0.65669Z + 6.46342 = 0$ (X, Y, Z are the orthogonal coordinates), the distances of each atom from this plane being Cu 0.04 Å, Cl(2) −0.02 Å, Cl(1)^{i} −0.02 Å, Cl(3)^{ii} −0.003 Å, Cl(1) −2.26 Å, and Cl(3) 2.30 Å.

$(Cu_2Cl_6)^{2-}$ dimeric anions containing five-coordinated copper(II) have been also found in $(CH_3)_2NH_2CuCl_3$,[3] in $pqCu_2Cl_6$,[4] and in $PhCH_2CH_2NMeH_2CuCl_3$,[5] where the coordination geometry is tetragonal pyramidal in the first case, trigonal bipyramidal in the last, and intermediate in the second, the Cu–Cl longest distances being 2.773, 2.668, and 2.528 Å in ref 3–5, respectively. The corresponding value in the present compound, 2.687 (3) Å, places it in an intermediate situation between $(CH_3)_2NH_2CuCl_3$ and $pqCu_2Cl_6$. A similar kind of coordination is also found in $[Co(en)_3]CuCl_5{\cdot}H_2O$, in which the structure has been found as consisting of distorted square-planar $CuCl_4^{2-}$ ions linked in pair by long Cu–Cl bonds to form $Cu_2Cl_8^{4-}$ dimers, with five-coordinated copper.[11]

The coordination geometry of chlorocuprates can be also described by considering only the four chlorine ions more strictly coordinated to copper and using the two greatest Cl–Cu–Cl angles as indicative of distortion from the planarity of the anion.[12] In Table V are quoted these angles for some trichlorocuprates. In complexes with large cations, as $AsPh_4CuCl_3$ and PPh_4CuCl_3, these angles are approximately equal but less than 180° and the coordination symmetry is approximately D_{2d}. With smaller cations two different cases are found: if the two greatest angles are close to 180°, the coordination symmetry may be considered as D_{4h} ($KCuCl_3$ and NH_4CuCl_3[2]), while if one angle is close to 180° and the other to 120°, the coordination geometry is square pyramidal ($MeNH_2CuCl_3$[3]) or distorted trigonal bipyramidal ($pqCu_2Cl_6$[4] and $PhCH_2CH_2NMeH_2CuCl_3$[5]).

---

(9) Cromer, D. J.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321.
(10) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
(11) Hodgson, D. J.; Hale, P. K.; Hatfield, W. E. *Inorg. Chem.* **1971**, *10*, 1061.
(12) Smith, D. W. *Coord. Chem. Rev.* **1976**, *21*, 93.

Table III. Conventional Chemical Analysis Results, Melting Points, and Magnetic Moments

		Cu, %		C, %		H, %		N, %			
	color	calcd	found	calcd	found	calcd	found	calcd	found	mp, °C	μ_{eff}, μ_B
$(4BzpipdH)CuCl_3$[a]	red-orange	18.36	18.40	41.61	41.60	5.24	5.27	4.05	4.16	212–216	1.88
$(4BzpipdH)CuCl_2Br$	red	16.27	16.14	36.87	37.18	4.64	4.55	3.58	3.42	193–197	1.77
$(4BzpipdH)CuClBr_2$	red-brown	14.61	14.83	33.11	33.20	4.17	4.59	3.22	3.42	175–179	1.85
$(4BzpipdH)CuBr_3$[b]	brown	13.28	13.21	30.03	29.92	3.87	3.81	2.92	2.95	161–165	1.79
$(4BzpipdH)_2CuBr_4$[c]	violet	8.64	8.56	39.16	39.55	4.94	4.91	3.81	3.80	130–134	1.78

[a] % Cl = 30.74 (31.11) (found values are in parentheses). [b] % Br = 50.01 (49.98). [c] % Br = 43.46 (43.50).

Table IV

(1) Bond Distances (Å) and Angles (deg)

(a) In the Chlorocuprate Anion[a]

Cu–Cl(1)	2.308 (3)	Cu–Cl(1)^{i}	2.314 (1)
Cu–Cl(2)	2.277 (2)	Cu–Cl(3)^{ii}	2.687 (3)
Cu–Cl(3)	2.261 (3)		
Cl(1)–Cu–Cl(2)	90.8 (1)	Cl(2)–Cu–Cl (3)	91.3 (1)
Cl(1)–Cu–Cl(3)	177.5 (1)	Cl(2)–Cu–Cl(1)^{i}	151.0 (1)
Cl(1)–Cu–Cl(1)^{i}	84.8 (1)	Cl(2)–Cu–Cl(3)^{ii}	108.4 (1)
Cl(1)–Cu–Cl(3)^{ii}	91.0 (1)	Cl(3)–Cu–Cl(1)^{i}	94.1 (1)
Cl(1)^{i}–Cu–Cl(3)^{ii}	100.4 (1)	Cl(3)–Cu–Cl(3)^{ii}	87.1 (1)

(b) In the Benzylpiperidinium Cation

C(1)–C(2)	1.373 (9)	C(7)–C(8)	1.527 (8)
C(1)–C(6)	1.371 (8)	C(8)–C(9)	1.512 (8)
C(2)–C(3)	1.382 (12)	C(8)–C(12)	1.529 (8)
C(3)–C(4)	1.350 (11)	C(9)–C(10)	1.515 (7)
C(4)–C(5)	1.345 (10)	C(11)–C(12)	1.516 (7)
C(5)–C(6)	1.378 (11)	N–C(10)	1.485 (7)
C(1)–C(7)	1.519 (8)	N–C(11)	1.494 (7)
C(2)–C(1)–C(6)	116.3 (6)	C(7)–C(8)–C(12)	109.4 (5)
C(1)–C(2)–C(3)	121.4 (7)	C(7)–C(8)–C(9)	112.0 (5)
C(2)–C(3)–C(4)	120.8 (7)	C(9)–C(8)–C(12)	110.0 (5)
C(3)–C(4)–C(5)	118.5 (7)	C(8)–C(9)–C(10)	112.3 (5)
C(4)–C(5)–C(6)	121.2 (7)	N–C(10)–C(9)	109.4 (4)
C(1)–C(6)–C(5)	121.6 (6)	N–C(11)–C(12)	110.3 (5)
C(2)–C(1)–C(7)	121.0 (6)	C(8)–C(12)–C(11)	112.7 (4)
C(6)–C(1)–C(7)	122.6 (5)	C(10)–N–C(11)	112.6 (4)
C(1)–C(7)–C(8)	116.4 (5)		

(2) Bond Distances (Å) Involving Hydrogen Atoms

C(2)–H(2)	0.92 (7)	C(9)–H(92)	0.92 (5)
C(3)–H(3)	1.03 (7)	C(10)–H(101)	1.00 (6)
C(4)–H(4)	1.05 (7)	C(10)–H(102)	0.99 (6)
C(5)–H(5)	0.95 (7)	C(11)–H(111)	0.99 (5)
C(6)–H(6)	0.97 (6)	C(11)–H(112)	0.94 (6)
C(7)–H(71)	1.05 (6)	C(12)–H(121)	0.99 (6)
C(7)–H(72)	1.03 (6)	C(12)–H(122)	1.05 (6)
C(8)–H(8)	0.97 (6)	N–H(11)	0.87 (5)
C(9)–H(91)	1.05 (5)	N–H(12)	0.82 (6)

[a] Key: superscript i, $1-x$, $1-y$, $1-z$; ii, $1-x$, y, $^3/_2-z$.

Table V. The Values of the Two Greatest Cl–Cu–Cl Angles in Some Trichlorocuprate(II) Complexes

	θ, deg		ref
PPh_4CuCl_3	143.3 (1)	143.6 (1)	6
$AsPh_4CuCl_3$	145.2 (1)	144.6 (1)	7
$Me_2NH_2CuCl_3$	156.0 (2)	176.0 (2)	3
$(4BzpipdH)_2Cu_2Cl_6$	151.0 (1)	177.5 (1)	this work
$PhCH_2CH_2NMeH_2CuCl_3$	133.0 (1)	176.7 (1)	5
$KCuCl_3$	173.2 (1)	175.8 (1)	2
NH_4CuCl_3	172.8	176.2	2

In the present compound the values of the two greatest angles 177.5 (1)° and 151.0 (1)° enable copper coordination to be described as distorted trigonal bipyramidal, with one of the equatorial positions occupied by a long-bonded chlorine atom from a neighboring dimer. The following hydrogen bonds involving the nitrogen atom and the nonbridging Cl(2) atoms of adjacent anions justify the distortion of the bipyramid: N···Cl(2) = 3.292 (5) Å, NH(12)Cl(2) = 154 (6)°, H(12)···Cl(2) = 2.54 (6) Å; N···Cl(2)^{iii} = 3.219 (5) Å, NH(11)-Cl(2)^{iii} = 141 (6)°, H(11)···Cl(2)^{iii} = 2.49 (6) Å; N···Cl(2)^{iv} = 3.319 (5) Å, NH(11)Cl(2)^{iv} = 127 (6)°, H(11)···Cl(2)^{iv} = 2.72 (6) Å (iii = $1-x, y, {}^3/_2-z$; iv = $x, \bar{y}, {}^1/_2+z$). N···Cl(2)^{iii} and N···Cl(2)^{iv} can be considered as a bifurcated hydrogen bond. The structures of Willett[3] and Harlow et al.[5] both contain hydrogen bonds involving the N atoms of the cation and the nonbridging chlorine atoms; in the $pqCu_2Cl_6$ there is only a contact N···Cl.[4]

Table VI. Room-Temperature Solid Electronic Spectra (cm^{-1}) of the Complexes

	d–d bands	charge-transfer bands
$(4BzpipdH)_2Cu_2Cl_6$	9520 sh, 11 110	18 690 sh, 24 110, 27 470 sh, 35 710, 46 080
$(4BzpipdH)_2Cu_2Cl_4Br_2$	9710 sh, 11 430	18 180 sh, 20 530 sh, 29 410, 38 460, 46 510
$(4BzpipdH)_2Cu_2Cl_2Br_4$	9800 sh, 11 770	17 390 sh, 20 530 sh, 27 170, 38 170, 46 510 sh
$(4BzpipdH)_2Cu_2Br_6$	10 000 sh, 12 000	16 670 sh, 20 280 sh, 26 530, 37 740
$(4BzpipdH)_2CuBr_4$	6130, 8930	15 873 sh, 18 690, 22 570 sh, 28 570, 37 880, 44 840

The values of the Cu–Cu distances, 3.415 (2) Å in the dimers (Cu–Cu^{i}) and 3.558 (2) Å between different dimers (Cu–Cu^{ii}), agree quite well with the corresponding values found in $Me_2NH_2CuCl_3$[3] (3.44 (1), 3.57 (1) Å) and in $PhCH_2CH_2NMeH_2CuCl_3$ (3.453 (1), 3.550 (1) Å).[5] The bridging Cu–Cl–Cu angles are CuCl(1)Cu^{i} = 96.7° in the dimers and CuCl(3)Cu^{ii} = 92.2° between the different dimers. These values are in the range of those found in other five-coordinated complexes with two halogen bridges, e.g., $Cu_2Cl_8^{4-}$ (Cl–Cu–Cl = 95.2°),[11] $[Cu(DMG)Cl_2]_2$ (Cl–Cu–Cl = 88.0°),[15] and $CuCl_2\cdot 2(CH_2)_4SO$ (Cl–Cu–Cl = 88.5°).[14]

Packing is determined along the *c* and *b* axes by hydrogen bonds and along the *a* axis by normal van der Waals contacts.

The 4-benzylpiperidinium cations show the usual "chair" conformation, as indicated by the puckering parameters calculated according to Cremer and Pople:[15] $q_2 = 0.03$ Å, $q_3 = 0.56$ Å, $\varphi_2 = 47.5°$, $Q = 0.56$ Å. Similar values are found in other piperidinium cations, e.g., in piperidinium *p*-toluate[16] in which the same parameters are $q_2 = 0.01$ Å, $q_3 = 0.58$ Å, $\varphi_2 = 44.6°$, and $Q = 0.58$ Å. The distances of N and C(8) from the mean plane through C(9), C(10), C(11), C(12) are 0.66 (1) and −0.64 (1) Å, respectively; the corresponding values in piperidinium *p*-toluate are 0.672 and 0.688 Å.

The phenyl ring is planar and forms a dihedral angle of 112° with the mean plane through C(9), C(10), C(11), C(12). The enlargement of the C(1)–C(7)–C(8) angle = 116.4 (5)°, with respect to theoretical tetrahedral value, can be attributed to overcrowding between the phenyl and the piperidinium rings as indicated by the contact H(6)···H(8) = 2.32 (8) Å.

---

(13) Svedung, D. H. *Acta Chem. Scand.* **1969**, *23*, 2865.
(14) Swank, D. D.; Needham, G. F.; Willett, R. D. *Inorg. Chem.* **1979**, *18*, 761.
(15) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.
(16) Kashino, S. *Acta Crystallogr., Sect. B* **1973**, *29*, 1836.

Table VII. Solid Far-IR Spectra (400-60 cm^{-1}) of the Hydrohalide Salts and the Complexes

	ν(CuCl), cm^{-1}	ν(CuBr), cm^{-1}	other bands below 400 cm^{-1}
4BzpipdHCl			340 w, 276 m, 243 w, 223 m, 210 s, 150 s, 139 sh, 100 ms
4BzpipdHBr			345 m, 333 m, 269 m, 240 vw, 219 w, 190 sb, 124 m, 100 w, 76 w
$(4BzpipdH)_2Cu_2Cl_6$	295 vs, 275 sh, 263 vs		336 m, 182 s, 150 s, 110 m
$(4BzpipdH)_2Cu_2Cl_4Br_2$	275 vs, b, 258 sh	232 m, 216 w	335 m, 176 ms, 128 ms, 104 vw
$(4BzpipdH)_2Cu_2Cl_2Br_4$	274 vs, b	229 sb, 215 sh	335 m, 317 w, 177 ms, 123 ms, 102 sh
$(4BzpipdH)_2Cu_2Br_6$		226 vs, 214 vs	333 m, 317 w, 275 w, 179 s, 123 m, 102 m
$(4BzpipdH)_2CuBr_4$		239 vs, 224 vs	325 m, 271 m, 178 m, 152 m, 115 ms, 89 m

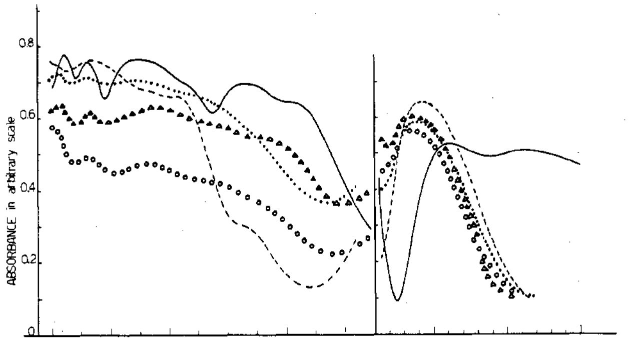

Figure 2. Electronic spectra of $(4BzpipdH)_2Cu_2Cl_6$ (---), $(4BzpipdH)_2Cu_2Cl_4Br_2$ (···), $(4BzpipdH)_2Cu_2Cl_2Br_4$ (O), $(4BzpipdH)_2Cu_2Br_6$ (Δ), and $(4BzpipdH)_2CuBr_4$ (—) complexes.

Solid Powder and Electronic Spectra and Magnetic Moments. The room-temperature powder X-ray spectra of the $(4BzpipdH)_2Cu_2X_mY_{6-m}$ (m = 6, 4, 2, 0) complexes are very similar to one another, suggesting that these compounds are isomorphous. Furthermore, as their room-temperature electronic spectra (Table VI) are practically identical with one another, we may also consider these compounds as isostructural.

The electronic absorption spectra (Figure 2) show a broad unresolved band at 11 110–12 000 cm^{-1} with a shoulder on the low-energy side at 9500–10 000 cm^{-1}, which may be assigned to d–d transitions. In addition there is a weak but distinct shoulder at 16 000–18 600 cm^{-1} on a more intense charge-transfer band. This band, which is absent in monomeric complexes[3,5,17,18] and explains the pronounced pleochroism of these complexes, when examined with polarized light, may be considered indicative of the presence of dimeric or polymeric $Cu_2Cl_6^{2-}$ anions, independently of their coordination geometry, as has its maximum absorption in the Cu–Cu direction.[12]

For previously reported Cu–Cl coordination geometries found in similar trichlorocuprates(II), the following maximum energy d–d transition bands at 25 °C are observed: distorted square pyramid[3] 10 800 (sh), 12 900 cm^{-1},[17] distorted trigonal bipyramid 7690, 10 600 cm^{-1},[5] and, by comparison, rigorous trigonal-bipyramidal symmetry, as found in $(Cr(NH_3)_6)CuCl_5$,[19] 8330, 10 000 (sh) cm^{-1}.[20] The shape and positions of the d–d bands in the spectra of our trichlorocuprate(II) complex compared with those reported above are indicative of an intermediate stereochemistry between distorted trigonal bipyramidal and distorted square pyramidal. As this effect is paralleled in angular changes, it suggests that for a series of complexes involving the same ligands there may be an electronic criterion of stereochemistry.

The charge-transfer bands of the complexes (Table VI and Figure 2), which agree with previous reports,[18,21] show bathochromic shifts in the sequence $Cu_2Br_6^{2-} < Cu_2Cl_2Br_4^{2-} < Cu_2Cl_4Br_2^{2-} < Cu_2Cl_6^{2-}$ as a consequence of the lower optical electronegativity of bromine with respect to chlorine. As these bands are characteristic of the ligands bonded to the Cu^{2+}, they further confirm that the mixed complexes are true compounds and not mixtures of $CuCl_3^-$ and $CuBr_3^-$ ions.

A "distorted" tetrahedral symmetry may be suggested for the $(4BzpipdH)_2CuBr_4$ complex by comparing their d–d and charge-transfer bands (Table VI and Figure 2) with those reported for other known $CuBr_4^{2-}$ anions.[18,22]

The room-temperature magnetic moments of the complexes (Table I) suggest the presence of weak interactions between the copper atoms.

Far-Infrared Spectra. The far-infrared spectra for the complexes and the appropriate starting hydrohalide salts are listed in Table VII. Their comparison shows that the internal vibrations of the cations do not hamper the assignment of the metal–halogen vibrations, as they disappear on complexation, except for a cation band at 180 cm^{-1}, or are masked by the more intense vibrations of the haloanions.

The spectra of our complexes are of interest in light of their unusual structural properties. As we consider a series of isostructural compounds, it is possible to observe the variation of the infrared frequencies with changes in halogen. In fact the frequency of the bands increases in the order Cl > Br, as is expected, considering the masses of the different halide ions. This permits an unambiguous assignment of the metal–halogen stretching vibrations, as reported in Table VII, but the lack of any symmetries in our compounds does not enable terminal metal–halogen vibrations to be distinguished from bridging metal–halogen vibrations. We may tentatively assign the bands at 263 and 224 cm^{-1} in the $Cu_2Cl_6^{2-}$ and $Cu_2Br_6^{2-}$ anions, respectively, to the Cu–halogen stretching modes, possibly associated with the longer axial Cu–X bond (2.668 Å) and the bands at higher energies at 295, 275, and 239 cm^{-1} to the Cu–halogen stretching modes, associated with the shortest equatorial Cu–X bonds. The positions of these bands agree with the literature data.[5,23,24]

In the $(4BzpipdH)_2CuBr_4$ complex the well-resolved splitting of the e vibration at 239, 224 cm^{-1} and of the bending mode at 152, 115 cm^{-1} indicates that some distortion from D_{2d} symmetry must be present.

Hydrogen Bonding. In the amine hydrohalides the N–H motions are assigned to the bands which appear at 2950–2900 (vs, b) and 2790–2750 (s, b) cm^{-1} which are shifted at lower energies and attenuated in intensity on deuteration, in agreement with secondary amine hydrohalides.[25,26]

In the trihalo complexes these bands are shifted at 3129–3110 (vs) and 3055–3045 (s) cm^{-1}, while that in the

---

(17) Willett, R. D.; Liles, O., Jr. *Inorg. Chem.* **1967**, *6*, 1666.
(18) Ludwig, W.; Textor, M. *Helv. Chim. Acta*, **1971**, *54*, 1143.
(19) Raymond, K. N.; Meek, D. W.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 1111.
(20) Allen, G. C.; Hush, N. S. *Inorg. Chem.* **1967**, *6*, 4.
(21) MacFarlane, A. J.; Williams, R. J. P. *J. Chem. Soc. A* **1969**, 1517.
(22) Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *Inorg. Chem.* **1976**, *15*, 2333 and references therein.
(23) Adams, D. M.; Lock, P. J. *J. Chem. Soc. A* **1967**, 620.
(24) Heyns, A. M.; Schutte, C. J. H. *J. Mol. Struct.* **1971**, *8*, 339.
(25) Colthrum, N. B.; Daly, L. H.; Wiberley, S. E. "Introduction to Infrared and Raman Spectroscopy"; Academic Press: New York, 1964; p 282.
(26) Bellamy, L. J. "The Infrared Spectra of Complex Molecules"; Chapman and Hall: London, 1975; p 267.

tetrabromocuprate(II) appears at $\sim$3000 (s, b) cm^{-1}. This indicates that the presence of hydrogen bonding in the former complexes is stronger than in the latter, as electron density is removed from $N—H\cdots X$ interaction and into the Cu–X bond, and as in all trihalo complexes the NH_2^+ bands appear to be shifted by the same amount, the same hydrogen bonding strength may also be suggested.

As a consequence, hydrogen bonding interactions may be considered to be one of the principal factors responsible for the stereochemistry of our trihalocuprates(II), but the size effect of the cation must also contribute to the reduction of the chlorine–chlorine repulsions. In fact when the dimension and hydrogen bonding ability of the cation are negligible, as in the case of the piperidinium cation,[27] CuX_4^{2-} anions were obtained having "flattened" tetrahedral geometries, while when the hydrogen bonding ability of the cation prevails on its size effect, as in the case of the *N*-phenylpiperazinium dication,[8] $CuCl_4^{2-}$ ion was obtained having strongly distorted tetrahedral symmetry.

Acknowledgment. The authors are grateful to Professor M. Nardelli for helpful discussion and to the Centro Strumenti of the University of Modena for the recording of the IR spectra.

Registry No. $(4BzpipdH)_2Cu_2Cl_6$, 71699-78-0; $(4BzpipdH)_2Cu_2Cl_4Br_2$, 71661-76-2; $(4BzpipdH)_2Cu_2Cl_2Br_4$, 71661-75-1; $(4BzpipdH)_2Cu_2Br_6$, 71661-74-0; $(4BzpipdH)_2CuBr_4$, 71661-73-9; 4BzpipdHCl, 23239-75-0; 4BzpipdHBr, 70659-34-6.

Supplementary Material Available: Listings of thermal parameters and structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

---

(27) Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *J. Coord. Chem.* **1976**, *5*, 189.

Contribution from Ames Laboratory—DOE and the Departments of Chemistry and Physics,
Iowa State University, Ames, Iowa 50011

Study of the Crystal Structures and Nonstoichiometry in the System $Cs_3Sc_2Cl_9$–$CsScCl_3$

KENNETH R. POEPPELMEIER,[1a] JOHN D. CORBETT,*[1a] TOM P. McMULLEN,[1b] DAVID R. TORGESON,[1b] and RICHARD G. BARNES[1b]

Received February 12, 1979

The phase $Cs_3Sc_2Cl_9$ has the $Cs_3Tl_2Cl_9$ type structure ($R\bar{3}c$, a = 12.707 (2) Å, c = 18.117 (4) Å) rather than the chromium(III) structure type common to the remainder of the 3d elements. The ^{45}Sc NMR spectra of $ScCl_3$ and of $Cs_3Sc_2Cl_9$, which has been slowly cooled in comparison with that quenched from the melt and annealed, establish that the ternary compound melts somewhat incongruently. Reduction of the scandium(III) phase at elevated temperatures by metal gives $CsScCl_3$ which has the $CsNiCl_3$ structure (hexagonal perovskite, $P6_3/mmc$, a = 7.350 (2) Å, c = 6.045 (3) Å). The close relationship between the two structures, strings of scandium pairs alternating with vacancies in $Cs_3Sc_2Cl_9$ and fully occupied strings of metal in the reduced limit, allows for an apparent region of nonstoichiometry between the two without X-ray evidence for superstructure ordering of vacancies. Values of R = 0.055 and R_w = 0.064 were obtained by least-squares refinement of 108 independent reflections from a single crystal with a refined average scandium occupancy of 0.79 (3). Limited refinement of $\bar{3}m$-symmetry diffraction data from the same crystal reveals that the scandium atoms are probably unevenly distributed, namely, as fully occupied pairs with random fractional occupancy of the third site. Precise Guinier powder diffraction data suggest that all scandium sites become crystallographically equivalent above about 87–90% average occupancy. The blue $CsScCl_3$ is probably a semiconductor rather than a metallic compound.

Introduction

As a class, ternary phases with the simple formula $A_xB_yX_{3x}$ include hundreds of compounds related by very useful structural concepts.[2] In particular, the compounds in which A is a large cation, B a transition-metal cation, and X halide or chalcide crystallize in the perovskite or a related structure. Here the large A cations together with the X atoms form close-packed layers in which A atoms are surrounded only by X atoms, and these layers are superimposed so as to generate X_6 octahedral sites for the B cation without bringing A cations into direct contact. When A is an alkali metal cation, X a halogen, and B a transition metal in the 2+ oxidation state, the composition is ABX_3 and all octahedra are filled. In a similar way the composition $A_3B_2X_9$ has two-thirds of the octahedral sites filled with B cations which carry a 3+ charge.

Scandium chemistry has traditionally been limited to the 3+ oxidation state, particularly in oxides where attempts to produce new reduced phases have all proven fruitless.[3] Accordingly halometalate(II) compounds ABX_3 with perovskite-related structures have been known for all first-row transition metals except scandium.[4–6] However, routes to a variety of reduced scandium chlorides have recently been found,[7] and the thought of an additional stabilization of the close-packed A + 3X layers combined with the possibility of enhanced metal–metal interactions because of a relatively large radial

---

(1) (a) Department of Chemistry. (b) Department of Physics.

(2) A. F. Wells, "Structural Inorganic Chemistry", 4th ed., Clarendon Press, Oxford, England, 1975, pp 150–4.

(3) J. E. Young and M. J. Sienko, *Natl. Bur. Stand.* (*U.S.*), *Spec. Publ.*, **No. 364**, 385 (1972).

(4) J. F. Ackerman, G. M. Cole, and S. L. Holt, *Inorg. Chim. Acta*, **8**, 323, (1974).

(5) J. Fernandez, M. J. Tello, and M. A. Arriandiagon, *Mater. Res. Bull.*, **13**, 477 (1978).

(6) P. Ehrlich and R. Schmitt, *Z. Anorg. Allg. Chem.*, **308**, 91, (1961).

(7) K. R. Poeppelmeier and J. D. Corbett, *J. Am. Chem. Soc.*, **100**, 5029 (1978), and earlier work cited therein.

0020-1669/80/1319-0129$01.00/0