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Structure of Polymeric Bis(benzimidazolium) Hexachlorodicuprate(II), $2C_7H_7N_2^+.Cu_2Cl_6^{2-}$

BY M. BUKOWSKA-STRZYŻEWSKA AND A. TOSIK

Institute of General Chemistry, Polytechnical University, 90–924 *Łódź, Poland*

AND T. GŁOWIAK AND J. WNĘK

Institute of Chemistry, Wrocław University, 50–383 *Wrocław, Poland*

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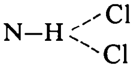
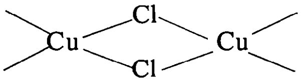
Abstract. $M_r = 578{\cdot}1$, monoclinic, $P2_1/n$, $a = 18{\cdot}567\,(6)$, $b = 6{\cdot}443\,(2)$, $c = 16{\cdot}810\,(5)$ Å, $\beta = 92{\cdot}93\,(4)°$, $V = 2008\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}911\,(1)$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo }K\alpha) = 2{\cdot}993$ mm^{-1}, $F(000) = 1144$, $T = 293$ K, final $R = 0{\cdot}032$, $wR = 0{\cdot}036$ for 2498 reflections $[I > 3\sigma(I)]$. The structure consists of polymeric $[Cu_2Cl_6{}^{2-}]_\infty$ chains and benzimidazolium cations, half of which form stacking columns, $(C_6H_4NHCHNH^+)_\infty$, surrounded by four parallel anionic chains. Benzimidazolium cations and anionic chains are linked by  $N—H\begin{smallmatrix}\cdot\cdot Cl\\ \cdot\cdot Cl\end{smallmatrix}$ and N—H···Cl hydrogen bonds. The Cu atoms are five-coordinated with one long and four short Cu—Cl bonds. Cu—Cu distances inside the polymeric chains indicate the possibility of magnetic exchange between metal atoms.

Introduction. Continuing our studies on the structure and magnetism of polymeric copper(II) complexes with  nuclei (Bukowska-Strzyżewska & Tosik, 1979; Mroziński & Bukowska-Strzyżewska, 1980) we have synthesized the new stable polynuclear chlorocuprate $(C_6H_4NHCHNH)_2\,[Cu_2Cl_6]$ and determined its molecular and crystal structure. The chlorocuprates containing $Cu_2Cl_6^{2-}$ dimers exhibit a large variety of copper(II) coordination polyhedra with coordination numbers 4, 5 and 6 (Smith, 1976). Their magnetic properties depend on the coordination number of the atoms and geometrical shape of the $Cu_2Cl_6^{2-}$ ions. The aim of this work was to investigate the influence of the large, planar, aromatic cations on the polymeric structure of the $Cu_2Cl_6^{2-}$ ions.

Experimental. The title compound was prepared by dissolving 1·70 g (0·01 mol) of $CuCl_2.2H_2O$ in 20 ml of 96% ethanol; 1·18 g (0·01 mol) of benzimidazole dissolved in 20 ml 96% ethanol and 1 ml of concentrated HCl were then added; dark-brown crystals suitable for X-ray analysis were obtained after 2 d by slow evaporation of the solvent. Crystal 0·18 × 0·20 × 0·45 mm. Syntex $P2_1$ diffractometer. 15 reflections with θ between 22 and 27° used for determination of lattice parameters. Two intensity and orientation control reflections measured every 50 reflections showed no significant drift in intensity. Scan rate 2–29·3° min^{-1} depending on intensity. $2° \le 2\theta \le 50°$, h 0–21, k 0–7, $l\ \bar{1}9$–19. 3559 data (all unique), 2498 with $I \ge 3\sigma(I)$. Syntex (1976) *XTL/XTLE* structure determination system. Lp correction, absorption ignored. *MULTAN* direct method (Germain, Main & Woolfson, 1971). H atoms located at expected positions and then found on the difference electron density map. Positional and anisotropic thermal parameters of non-hydrogen atoms refined on F with weights based on counting statistics. Coordinates of H atoms and their Debye–Waller temperature parameters ($B = 4{\cdot}5$ Å^2) were kept fixed. $R = 0{\cdot}032$, $wR = 0{\cdot}036$, $w = 1/\sigma^2(F)$, $S = 2{\cdot}39$, $(\Delta/\sigma)_{\max} = 0{\cdot}01$, maximum noise level in final difference Fourier map 0·5 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Refined parameters are listed in Table 1;* the numbering of the atoms is given in Fig. 2. The not exactly planar $Cu_2Cl_6^{2-}$ ions are situated at centres of symmetry. The polymeric chains $[Cu_2Cl_6^{2-}]_\infty$ elongated along the y axis are formed by stacking of $Cu_2Cl_6^{2-}$ dimers (Fig. 1). The coordination polyhedra around the Cu atoms in both crystallographically independent chains may be described as distorted square pyramids with four short and one long Cu—Cl bonds. As shown in Fig. 1, the bond lengths and angles in both crystallographically independent anionic chains are not identical. The bridging Cu(1)—Cl(3) and Cu(2)—Cl(6)

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles in the crystallographically independent $[Cu_2Cl_6^{2-}]_\infty$ chains and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42209 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^5$ *for* Cu *and* Cl *atoms*, $\times 10^4$ *for* N *and* C *atoms*) *and equivalent isotropic temperature factors* (Å$^2 \times 10^2$ *for* Cu *and* Cl *atoms*, $\times$ 10 *for* N *and* C *atoms*) *with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cu(1)	45726 (3)	26066 (11)	−634 (3)	227 (4)
Cu(2)	48398 (3)	23637 (11)	45329 (3)	218 (4)
Cl(1)	45735 (7)	−289 (23)	−9783 (8)	263 (10)
Cl(2)	35386 (7)	15352 (24)	4380 (8)	279 (10)
Cl(3)	45760 (9)	55683 (25)	7212 (9)	425 (14)
Cl(4)	40798 (7)	50608 (22)	47627 (7)	248 (10)
Cl(5)	50621 (7)	35351 (23)	33048 (7)	260 (10)
Cl(6)	55155 (8)	−6127 (22)	43546 (8)	307 (11)
N(11)	6685 (2)	5064 (7)	3543 (2)	25 (3)
N(13)	7861 (2)	5098 (7)	3623 (3)	26 (4)
N(21)	996 (3)	2779 (8)	1830 (2)	32 (4)
N(23)	959 (3)	5046 (8)	2779 (3)	33 (4)
C(12)	7275 (3)	5058 (9)	4033 (3)	26 (4)
C(14)	7651 (3)	5096 (8)	2811 (3)	22 (4)
C(15)	8059 (3)	5108 (9)	2134 (4)	31 (4)
C(16)	7661 (4)	5101 (9)	1416 (3)	35 (5)
C(17)	6906 (4)	5002 (10)	1363 (3)	35 (5)
C(18)	6508 (3)	4993 (9)	2042 (3)	31 (5)
C(19)	6907 (3)	5050 (8)	2767 (3)	21 (4)
C(22)	692 (3)	3270 (11)	2503 (3)	36 (5)
C(24)	1450 (3)	5774 (9)	2255 (3)	26 (4)
C(25)	1870 (4)	7550 (11)	2271 (4)	41 (5)
C(26)	2316 (4)	7791 (11)	1626 (4)	46 (6)
C(27)	2351 (3)	6293 (12)	1035 (4)	42 (6)
C(28)	1935 (3)	4559 (11)	1023 (3)	38 (6)
C(29)	1474 (3)	4340 (9)	1651 (3)	25 (4)

bonds [from 2·298 (2) to 2·320 (2) Å] are similar to similar bonds in other known dimeric square-pyramidal chlorocuprates [from 2·305 (3) to 2·346 (6) Å (Willet, 1966; Murray-Rust, 1975)] but the bridge angles Cu—Cl—Cu of 97·42 (6) and 96·92 (6)° give a Cu—Cu separation within dimers of 3·464 (1) and 3·470 (1) Å, a little greater than the 3·410 (5) and 3·444 (6) Å found in the papers cited above. The terminal Cu—Cl bonds, shorter than the bridging ones, are not equal. The Cu(1)—Cl(1) and Cu(2)—Cl(4) bonds of 2·291 (2) and 2·284 (2) Å linking adjacent dimers are significantly longer than the Cu(1)—Cl(2) and Cu(2)—Cl(5) bonds of 2·245 (1) and 2·256 (1) Å. The Cu—Cu distances between adjacent dimers are 3·716 (1) and 3·777 (1) Å. The most important structural parameters in the magnetic exchange process for $\mathrm{Cu_2Cl_6^{2-}}$ complexes are the planarity of the $\mathrm{Cu_2Cl_6^{2-}}$ group, the Cu—Cu distances and the bridging Cu—Cl—Cu angles. The bond lengths and angles of the benzimidazolium rings are equal within $\sim 3\sigma$ for both crystallographically independent rings. The partly double $\mathrm{N}\overset{\mathrm{C}}{\diagup\,\diagdown}\mathrm{N}$ bonds, in accordance with the literature data (Craven, McMullan, Bell & Freeman, 1977, and references cited therein), are identical in one of the imidazolium ions [C(22)—N(21) 1·328 (7), C(22)—N(23) 1·322 (9) Å]. In the other they are a little different [C(12)—N(11) 1·337 (7), C(12)—N(13) 1·318 (7) Å] and equal to those in the imidazole molecule [1·337 (2) and 1·316 (2) Å (Craven, McMullan, Bell & Freeman, 1977)]. Perhaps this difference in the length of the bonds C(12)—N(11) and C(12)—N(13) in the benzimidazolium ions is caused by the inequivalence of the hydrogen bonds formed by the N(11) and N(13) atoms: bifurcated $\mathrm{N(11)—H(11)}\begin{smallmatrix}\cdots\mathrm{Cl(4)}\\ \cdots\mathrm{Cl(5)}\end{smallmatrix}$ and nearly linear and considerably shorter N(13)—H(13)···Cl(1). The scheme of hydrogen bonds in the unit cell is shown in Fig. 2. Their geometry with unrefined H-atom positions is illustrated in Table 2. The H(11), H(21) and H(23) atoms form inequivalent bifurcated hydrogen bonds, the shorter of which range from 2·33 to 2·45 Å, the longer from 2·64 to 2·73 Å. The H(13) atom forms only one, short (2·24 Å) and almost linear [∠N(13)—H(13)—Cl(1) 164°] hydrogen bond. As shown in Fig. 2, half of the benzimidazolium ions which lie almost

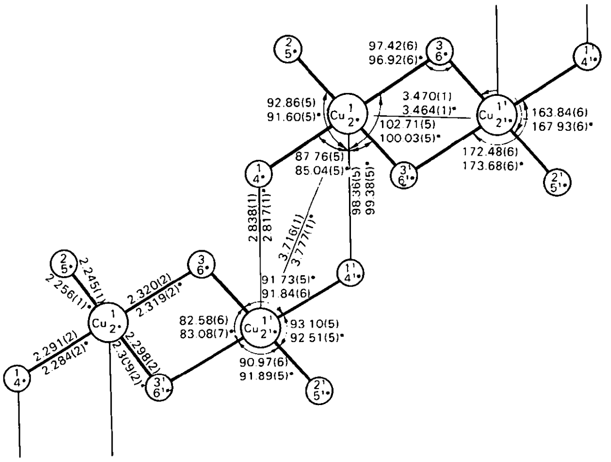

Fig. 1. Bond lengths (Å) and angles (°) in the two crystallographically independent $[\mathrm{Cu_2Cl_6^{2-}}]_\infty$ chains.

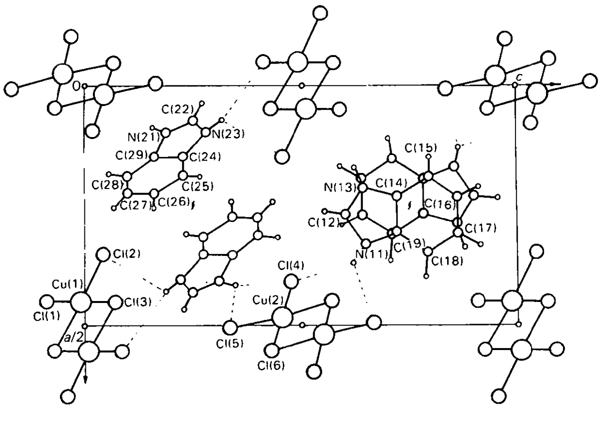

Fig. 2. A projection of the structure viewed along the y axis.

Table 2. *Geometry of the hydrogen bonds* (*e.s.d.'s in parentheses*)

It is assumed that e.s.d.'s for H atoms in calculated positions are 10 times those of the atoms to which they are attached.

N–H···Cl	N–H (Å)	H···Cl (Å)	N···Cl (Å)	N–H···Cl (°)
N(11)–H(11)···Cl(4^{i})	1·00 (4)	2·64 (5)	3·248 (4)	119 (3)
N(11)–H(11)···Cl(5^{i})		2·36 (4)	3·175 (4)	138 (3)
N(13)–H(13)···Cl(1^{ii})	1·00 (4)	2·24 (4)	3·216 (5)	164 (4)
N(21)–H(21)···Cl(4^{iii})	1·00 (5)	2·33 (5)	3·196 (5)	144 (4)
N(21)–H(21)···Cl(5^{iii})		2·64 (5)	3·368 (5)	130 (4)
N(23)–H(23)···Cl(1^{iv})	1·00 (5)	2·73 (5)	3·396 (5)	124 (4)
N(23)–H(23)···Cl(2^{v})		2·45 (5)	3·238 (5)	135 (4)

Symmetry code: (i) $1-x$, $1-y$, $1-z$; (ii) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (iii) $\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$; (iv) $x-\frac{1}{2}$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (v) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$.

exactly on the $y=0$ and $y=\frac{1}{2}$ planes form stacking columns running along the 2_1 axis. The distances between the rings are 3·221 (7) Å, which are thus markedly shorter than in the graphite structure (3·35 Å). Short C···C van der Waals contacts of 3·189 (8), 3·263 (8), 3·285 (8) and 3·339 (8) Å are observed. Research on the magnetic properties of these crystals and comparison with the magnetism of other polymeric chlorocuprates is planned.

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Structure of Hexacarbonyl-μ-ethoxymethylidyne-μ-[σ:1–2-η-(1-phenyl-1-propenyl)]-diiron(*Fe–Fe*), $C_{18}H_{14}Fe_2O_7$

By X. Solans and M. Font-Altaba

Departamento de Cristalografía y Mineralogía, Universidad de Barcelona, Gran Via 585, 08007-*Barcelona, Spain*

J. Ros and R. Yañez

Departamento de Química Inorgánica, Universidad Autónoma de Barcelona, Bellaterra (*Barcelona*), *Spain*

and R. Mathieu

Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 205 *route de Narbonne,* 31400-*Toulouse, France*

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Abstract. $[Fe_2(CO)_6(C_9H_9)(C_3H_5O)]$, $M_r = 454·0$, monoclinic, $P2_1/a$, $a = 16·591$ (2), $b = 17·140$ (3), $c = 6·948$ (2) Å, $\beta = 100·83$ (2)°, $V = 1941$ (1) Å^3, $Z = 4$, $D_x = 1·55$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 1·566$ mm^{-1}, $F(000) = 920$, room temperature, $R = 0·049$ for 1235 observed reflections. The structure consists of an $Fe_2(CO)_6$ unit with 1-phenyl-1-propenyl and ethoxymethylidyne bridging groups. The first is σ bonded to an iron atom and unsymmetrically π bonded to the other iron atom, while the ethoxymethylidyne is symmetrically bonded to the two iron atoms. The methyl and phenyl groups attached to the vinyl group are in *cis* configuration. The Fe—Fe length is 2·549 (2) Å.

Introduction. A systematic study of carbon–carbon bond formation at diiron centres is being carried out by the authors' departments. In this paper it is shown that the reaction of $[Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}C(C_6H_5)\text{-}C(CH_3)H\}][P(C_6H_5)_4]$ (Lourichi & Mathieu, 1982)

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