FREY, M., LELIGNY, H. & LEDÉSERT, M. (1971). *Bull. Soc. Fr. Minéral. Cristallogr.* **94**, 467–470.
FUESS, H., KÖRFER, M., AREND, H. & KIND, R. (1985). *Solid State Commun.* **56**, 137–139.
GAL, A. W., BEURSKENS, G., CRAS, J. A., BEURSKENS, P. T. & WILLEMSE, J. (1976). *Recl Trav. Chim. Pays-Bas*, **95**, 157–159.
HARRIS, G. S., INGLIS, F. & MCKECHNIE, J. (1967). *J. Chem. Soc. Chem. Commun.* pp. 442–444.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
KAMENAR, B. & NAGL, A. (1976). *Acta Cryst.* B**32**, 1414–1417.
KÖRFER, M., FUESS, H. & BATS, J. W. (1986). *Z. Anorg. Allg. Chem.* **543**, 104–110.
KÖRFER, M., FUESS, H., BATS, J. W. & KLEBE, G. (1985). *Z. Anorg. Allg. Chem.* **525**, 23–28.
LECHAT, J. R., FRANCISCO, R. H. P. & AIROLDI, C. (1980). *Acta Cryst.* B**36**, 930–931.
LELIGNY, H., FREY, M. & MONIER, J. C. (1972). *Acta Cryst.* B**28**, 2104–2109.
NORTH, A. C. T., PHILLIPS, D. & MATHEWS, F. S. A. (1968). *Acta Cryst.* A**24**, 351–359.
PABST, I. (1990). Thesis. Frankfurt Univ., Federal Republic of Germany.
PAKHOMOV, V. I., FEDOROV, P. M. & IVANOVA-KORFINI, I. N. (1979). *Coord. Chem.* (*USSR*), **5**, 1245–1248.
PAKHOMOV, V. I., FEDOROV, P. M. & SADIKOV, G. G. (1978). *Kristallografiya*, **23**, 615–616.
PAKHOMOV, V. I., FEDOROVA, N. M. & IVANOVA-KORFINI, I. N. (1978). *Coord. Chem.* (*USSR*), **4**, 1765–1766.
PODLAHOVÁ, J., KRATOCHVÍL, B., LOUB, J. & PAULUS, H. (1986). *Acta Cryst.* C**42**, 415–416.
PORTER, N. A., CUDD, M. A., MILLER, R. W. & MCPHAIL, A. T. (1980). *J. Am. Chem. Soc.* **102**, 404–416.
SCHOLTEN, W. & BIJVOET, J. M. (1941). *Z. Kristallogr.* **103**, 415–419.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.
SKOL'NIKOVA, L. M., PORAJ-KOŠIC, M. A., DJATLOVA, N. M., ZAVODNIK, V. E., BEL'SKIJ, V. K. & PODLAGA, J. (1980). *Koord. Khim.* **6**, 1281–1289.
SUBRAMANIAN, V. & SEFF, K. (1980). *Acta Cryst.* B**36**, 2132–2135.
TERZIS, A., FAUGHT, J. B. & POUSKOULELIS, G. (1980). *Inorg. Chem.* **19**, 1060–1063.
WHITE, J. G. (1963). *Acta Cryst.* **16**, 397–403.

Acta Cryst. (1990). B**46**, 508–519

Structures of Bis(4-aminopyridinium) Tetrachlorocuprate(II) Monohydrate, $[C_5H_7N_2]_2[CuCl_4].H_2O$, and Bis(2-amino-3-hydroxypyridinium) Tetrachlorocuprate(II), $[C_5H_7N_2O]_2[CuCl_4]$: Correlation of $CuCl_4^{2-}$ Geometry with Hydrogen Bonding and Electronic Structure

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Abstract

$[C_5H_7N_2]_2[CuCl_4].H_2O$, $M_r = 413{\cdot}62$, monoclinic, $C2/c$, $a = 8{\cdot}457\,(2)$, $b = 14{\cdot}318\,(2)$, $c = 14{\cdot}382\,(2)$ Å, $\beta = 95{\cdot}82\,(1)^\circ$, $V = 1732{\cdot}4\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}59$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 18{\cdot}79$ cm^{-1}, $F(000) = 836$, $T = 293$ K. The 1526 unique reflections ($2\theta \le 50^\circ$), of which 1288 had $F_o \ge 3\sigma(F_o)$, refined to a final R of 0·035 and $wR = 0{\cdot}038$. $[C_5H_7N_2O]_2[CuCl_4]$, $M_r = 427{\cdot}6$, triclinic, $P\bar{1}$, $a = 7{\cdot}554\,(1)$, $b = 7{\cdot}968\,(2)$, $c = 14{\cdot}578\,(3)$ Å, $\alpha = 103{\cdot}23\,(2)$, $\beta = 93{\cdot}30\,(2)$, $\gamma = 99{\cdot}59\,(2)^\circ$, $V = 838{\cdot}0\,(3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}69$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 19{\cdot}6$ cm^{-1}, $F(000) = 430$, $T = 293$ K. The 2185 unique reflections ($2\theta \le 45^\circ$), of which 1680 had $F_o \ge 3\sigma(F_o)$, refined to a final R of 0·047 and $wR = 0{\cdot}040$. The structures of both compounds consist of discrete $CuCl_4^{2-}$ anions and organic cations with the stoichiometric formulas indicated in the title. The geometry of both of the $CuCl_4^{2-}$ ions is intermediate between tetrahedral and square planar, with *trans* angles (average) of 134·6 and 137·8° respectively, and Cu—Cl distances (average) of 2·247 Å for both salts. The structural chemistry of 62 isolated $CuCl_4^{2-}$ anions is reviewed. The *trans* Cl—Cu—Cl angles in non-disordered $CuCl_4^{2-}$ anions range from 125 to 180°. Correlations of this *trans* Cl—Cu—Cl angle with hydrogen bonding to the cation, with the average Cu—Cl distance, and with the *d–d* electronic transition energy are examined. Finally, a review is given of structures in which the $CuCl_4^{2-}$ anion acts as a coordinating ligand.

Introduction

A major goal of the research program in this laboratory has been the synthesis and characterization of various copper(II) halide oligomers. A particularly fruitful approach has employed substituted pyridinium cations as counterions. In the process of these syntheses, the 4-aminopyridinium (4AP) and 2-

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amino-3-hydroxypyridinium (2A3HP) cations were used. The technique utilized in the syntheses involved the combination of various stoichiometric proportions of either 4APCl or 2A3HPCl with $CuCl_2$ in HCl solutions. This approach with 4AP has yielded two compounds, 4-aminopyridinium aquapentachlorodicuprate(II) monohydrate (Bond & Willett, 1987), and bis(4-aminopyridinium) tetrachlorocuprate(II) monohydrate. The structural characteristics of the latter compound are reported in this paper. In the 2A3HP system, synthesis of the bromide oligomer led to the formation of bis(2-amino-4-bromo-3-hydroxypyridinium) hexabromodicuprate(II) (Willett, 1987), the bromination of the pyridine ring occurring catalytically. An analogous synthesis, using 2A3HPCl yielded the compound bis(2-amino-3-hydroxypyridinium) tetrachlorocuprate(II).

The structural characteristics of these two salts are reported in this paper. A survey of the structural parameters of the 62 isolated $CuCl_4^{2-}$ anions structurally characterized to date is given. The correlation between the anion geometry and the energy of the *d–d* transition bonds (at both room and liquid-nitrogen temperatures) is reexamined. Finally, the role of the $CuCl_4^{2-}$ anion as a coordinating ligand is examined.

Data collection and structure solution

Yellow blocky crystals and red needles separated out upon evaporation of a saturated solution of 4-aminopyridine and $CuCl_2$ in a dilute HCl solution. The red crystals were shown to be the desired oligomeric species by crystallographic analysis (Bond & Willett, 1987). In order to determine the identity of the undesired yellow crystals, so that an improved synthetic procedure could be derived, its crystal structure was determined. A crystal of the yellow species of dimensions 0·5 × 0·5 × 0·25 mm was mounted on a glass fiber for data collection. Data were collected on a Syntex $P2_1$ diffractometer system upgraded to Nicolet $P3F$ specifications, with Mo $K\alpha$ radiation and a graphite monochromator (Campana, Shepherd & Litchman, 1981). The monoclinic unit cell and orientation matrix were defined by least-squares refinement of 25 accurately centered high-angle ($34 < 2\theta < 39°$) reflections. Empirical absorption corrections ($\mu = 18·70\ cm^{-1}$) assuming an ellipsoidally shaped crystal (minimum transmission = 0·617, maximum transmission = 0·762). Data collected for positive values of *h*, *k*, and all *l* ($0 \le h \le 11$, $0 \le k \le 18$, $-20 \le l \le 20$), with ω scans (scan width = 1·0°), and with scan speeds ranging from 3·9 to 29·3° min^{-1}. Two standards ($\bar{1}\bar{1}2$, $1\bar{3}\bar{3}$) monitored every 100 reflections, variation within counting statistics. 1751 reflections measured, $R_{merge} = 0·0266$. Systematic absences: *hkl*, *h* + *k* odd; *h*0*l*, *l* odd. Intensity statistics indicated the presence of a center of inversion, leading to the choice of *C*2/*c* as the preferred space-group selection. Direct methods yielded the positions of the Cu, Cl, C and N atoms. Subsequent difference maps, starting with these positions, yielded all other atom positions. Refinement on *F* *via* a cascading block-diagonal least-squares algorithm with anisotropic thermal parameters for the non-H atoms and isotropic thermal parameters for the H atoms (fixed values approximately 20% larger than the corresponding heavy atoms), gave a final value of $R = 0·0349$ and $wR = 0·0379$ for all observed reflections greater than 3σ (Sheldrick, 1986), where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$ and $w = [\sigma^2(F_o) + g|F_o|^2]$, $g = 0·00027$. Scattering factors, corrected for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974). A total of 117 parameters were refined with the maximum shift/e.s.d. = 0·059 on the last cycle of least squares. The goodness of fit was 1·315. The largest residual on the final difference map was approximately 0·39 e Å^{-3} near Cl(2) and the most negative peak was −0·27 e Å^{-3}. Final positional parameters are given in Table 1 with selected bond distances and angles reported in Table 2.*

In the second compound, yellow blocky crystals separated out upon evaporation of a saturated solution of 2-amino-3-hydroxypyridine and $CuCl_2$ in dilute HCl solution. Data were collected on a Syntex $P2_1$ diffractometer system upgraded to Nicolet $P3F$ specifications, with Mo $K\alpha$ radiation and a graphite monochromator (Campana *et al.*, 1981). The triclinic unit cell and orientation matrix were defined by least-squares refinement of 25 accurately centered ($11 < 2\theta < 36°$) reflections. Empirical absorption corrections ($\mu = 19·6\ cm^{-1}$) assuming an ellipsoidally shaped crystal (minimum transmission = 0·252, maximum transmission = 0·273). Data collected for *h*, all *k*, and all *l* ($0 \le h \le 9$, $-10 \le k \le 9$, $-20 \le l \le 16$), with ω scans (scan width = 0·8°), and with scan speeds ranging from 3·9 to 29·3° min^{-1}. Two standards (202, $0\bar{1}\bar{2}$) monitored every 100 reflections, variation within counting statistics. 2386 reflections measured, $R_{merge} = 0·0220$. The space group $P\bar{1}$ was indicated by the analysis of intensity statistics. Direct methods yielded the positions of the Cu, Cl, C and N atoms. Subsequent difference maps, starting with these positions, yielded all other atom positions. Refinement on *F* with anisotropic thermal param-

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* Lists of observed and calculated structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52837 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *for* $[C_5H_7N_2]_2[CuCl_4].H_2O$

The equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu	0	5264 (1)	2500	37 (1)
Cl(1)	1942 (1)	6284 (1)	2984 (1)	51 (1)
Cl(2)	1455 (1)	4234 (1)	1782 (1)	59 (1)
N(1)	1140 (4)	2469 (2)	3584 (2)	51 (1)
N(2)	495 (5)	1035 (2)	5952 (2)	61 (1)
C(1)	1517 (5)	704 (3)	5377 (3)	57 (1)
C(2)	1770 (4)	1165 (2)	4581 (3)	45 (1)
C(3)	935 (4)	2000 (2)	4354 (2)	38 (1)
C(4)	−92 (5)	2312 (3)	4991 (3)	51 (1)
C(5)	−289 (5)	1833 (3)	5764 (3)	58 (1)
O(1)	0	103 (3)	2500	49 (1)

Table 2. *Bond distances* (Å) *and bond angles* (°) *for* $[C_5H_7N_2]_2[CuCl_4].H_2O$

Cu—Cl(1)	2·255 (1)	C(1)—C(2)	1·357 (6)
Cu—Cl(2)	2·239 (1)	C(2)—C(3)	1·411 (5)
N(1)—C(3)	1·323 (5)	C(3)—C(4)	1·397 (5)
N(2)—C(1)	1·341 (6)	C(4)—C(5)	1·332 (6)
N(2)—C(5)	1·335 (6)		
Cl(1)—Cu—Cl(2)	98·7 (1)	C(1)—C(2)—C(3)	119·3 (4)
Cl(1)—Cu—Cl(1*a*)	99·2 (1)	N(1)—C(3)—C(2)	121·3 (3)
Cl(2)—Cu—Cl(1*a*)	134·6 (1)	N(1)—C(3)—C(4)	122·0 (3)
Cl(2)—Cu—Cl(2*a*)	97·6 (1)	C(2)—C(3)—C(4)	116·7 (3)
C(1)—N(2)—C(5)	121·1 (4)	C(3)—C(4)—C(5)	121·4 (4)
N(2)—C(1)—C(2)	121·0 (4)	N(2)—C(5)—C(4)	120·5 (4)

eters for the non-H atoms and isotropic thermal parameters for the H atoms (fixed values approximately 20% larger than the corresponding heavy atoms), gave a final value of $R = 0{\cdot}0473$ and $wR = 0{\cdot}0389$ for all observed reflections greater than 3σ (Sheldrick, 1986), $g = 0{\cdot}00009$. Scattering factors, corrected for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974). A total of 190 parameters were refined, maximum shift/e.s.d. = 0·025 on the last cycle of least squares. The goodness of fit was equal to 1·477. The largest residual on the final difference map was 0·32 e $Å^{-3}$ near Cu and the most negative peak was $-0{\cdot}45$ e $Å^{-3}$. Final positional parameters are given in Table 3 with selected bond distances and angles reported in Table 4.*

Table 3. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *for* $[C_5H_7N_2O]_2[CuCl_4]$

The equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu	4304 (1)	5450 (1)	7532 (1)	46 (1)
Cl(1)	5259 (2)	3118 (2)	7921 (1)	52 (1)
Cl(2)	1385 (2)	4143 (2)	7109 (1)	52 (1)
Cl(3)	3839 (2)	8091 (2)	8270 (1)	64 (1)
Cl(4)	6715 (2)	6268 (2)	6822 (1)	64 (1)
O(18)	2543 (6)	11978 (5)	5265 (3)	61 (2)
N(11)	3333 (7)	9899 (7)	3708 (4)	63 (2)
C(12)	2820 (8)	9206 (8)	4427 (4)	46 (2)
N(13)	2713 (7)	7488 (6)	4388 (4)	54 (2)
C(14)	2126 (9)	6746 (8)	5084 (5)	64 (3)
C(15)	1636 (9)	7693 (8)	5868 (5)	68 (3)
O(28)	3163 (6)	3748 (6)	−226 (3)	70 (2)
N(21)	868 (7)	4258 (7)	1065 (4)	66 (3)
C(22)	332 (8)	3041 (8)	257 (4)	46 (3)
N(23)	−1323 (7)	2065 (7)	79 (4)	61 (3)
C(24)	−1899 (11)	769 (10)	−728 (7)	79 (4)
C(16)	1745 (8)	9509 (8)	5962 (4)	57 (3)
C(17)	2335 (8)	10259 (7)	5258 (4)	45 (2)
C(25)	−776 (12)	427 (10)	−1383 (6)	78 (4)
C(26)	978 (10)	1415 (8)	−1233 (5)	60 (3)
C(27)	1531 (8)	2691 (8)	−443 (4)	46 (3)

Table 4. *Bond distances* (Å) *and bond angles* (°) *for* $[C_5H_7N_2O]_2[CuCl_4]$

Cu—Cl(1)	2·276 (2)	C(15)—C(16)	1·410 (9)
Cu—Cl(2)	2·260 (2)	O(28)—C(27)	1·348 (7)
Cu—Cl(3)	2·228 (2)	N(21)—C(22)	1·336 (7)
Cu—Cl(4)	2·224 (2)	C(22)—N(23)	1·335 (8)
O(18)—C(17)	1·350 (7)	C(22)—C(27)	1·414 (9)
N(11)—C(12)	1·340 (9)	N(23)—C(24)	1·368 (9)
C(12)—N(13)	1·346 (8)	C(24)—C(25)	1·326 (13)
C(12)—C(17)	1·412 (8)	C(16)—C(17)	1·361 (9)
N(13)—C(14)	1·348 (10)	C(25)—C(26)	1·401 (11)
C(14)—C(15)	1·325 (10)	C(26)—C(27)	1·342 (8)
Cl(1)—Cu—Cl(2)	96·6 (1)	N(21)—C(22)—C(27)	120·9 (5)
Cl(1)—Cu—Cl(3)	137·9 (1)	N(23)—C(22)—C(27)	116·8 (5)
Cl(2)—Cu—Cl(3)	97·9 (1)	C(22)—N(23)—C(24)	123·9 (6)
Cl(1)—Cu—Cl(4)	96·1 (1)	N(23)—C(24)—C(25)	119·6 (7)
Cl(2)—Cu—Cl(4)	137·8 (1)	C(15)—C(16)—C(17)	120·3 (6)
Cl(3)—Cu—Cl(4)	99·0 (1)	O(18)—C(17)—C(12)	113·9 (5)
N(11)—C(12)—N(13)	122·0 (5)	O(18)—C(17)—C(16)	126·4 (5)
N(11)—C(12)—C(17)	120·9 (6)	C(12)—C(17)—C(16)	119·7 (6)
N(13)—C(12)—C(17)	117·1 (6)	C(24)—C(25)—C(26)	118·9 (6)
C(12)—N(13)—C(14)	123·1 (5)	C(25)—C(26)—C(27)	121·2 (7)
N(13)—C(14)—C(15)	121·3 (6)	O(28)—C(27)—C(22)	113·5 (5)
C(14)—C(15)—C(16)	118·5 (7)	O(28)—C(27)—C(26)	126·8 (6)
N(21)—C(22)—N(23)	122·3 (6)	C(22)—C(27)—C(26)	119·7 (6)

Structure descriptions

The structure of the first compound consists of discrete $CuCl_4^{2-}$ anions, 4AP cations and water molecules, with the amine and water molecule hydrogen bonding to the anion (Fig. 1). The copper ion and the water O atom sit on crystallographic twofold axes. The copper ion has a coordination geometry intermediate between tetrahedral and square planar with a *trans* bond angle of 134·6 (1)°. The Cu—Cl(1) bonds (2·255 Å) are longer than the Cu—Cl(2) bonds (2·239 Å) owing to their extensive involvement in hydrogen bonding. Cl(1) is hydrogen bonded to H(1*a*) (an amine H atom) and Cl(2) is hydrogen bonded to H(1*b*) (the second amine H atom) with distances of 2·582 and 2·586 Å, respectively. The water hydrogen bonds to Cl(1) and Cl(1*a*) of a neighboring molecule with a bond length of 2·457 Å.

The structure of the second compound consists of discrete $CuCl_4^{2-}$ anions and 2A3HP cations (Fig. 2). The copper ion again has a coordination geometry

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* See deposition footnote.

intermediate between tetrahedral and square planar. The *trans* bond angles are 137·9 (1)° for Cl(1)—Cu—Cl(3), and 137·8 (1)° for Cl(2)—Cu—Cl(4). The Cu—Cl bond lengths range from 2·224 (2) to 2·276 (2) Å. As above, two of the Cu—Cl distances, Cu—Cl(1) and Cu—Cl(2), are longer owing to their extensive involvement in hydrogen bonding. Cl(1) is hydrogen bonded to H(11*a*) (an amine hydrogen), Cl(2) is hydrogen bonded to H(O18) (a hydroxy H atom), and Cl(3) is hydrogen bonded to H(N23) (a pyridinium H atom), with Cl···H distances of 2·37 (1), 2·15 (1) and 2·26 (1) Å, respectively.

Examination of the stereo plot of the 4AP salt (Fig. 3) reveals that the $CuCl_4^{2-}$ anion and water molecule form layers normal to the c^* direction (at $z = \frac{1}{4}$ and $\frac{3}{4}$) separated by layers of 4AP cations. The pyridine rings form stacks running in the (110) and $(1\bar{1}0)$ directions. The anionic and cationic layers are held together by the N—H···Cl and N—H···O hydrogen bonds discussed above. The O—H···Cl(1) hydrogen bonds tie the water molecules and $CuCl_4^{2-}$ anions together into chains running parallel to the *a* axis, while the hydrogen bonds from the amino groups to the $CuCl_4^{2-}$ anions unite the chains into the layers.

Examination of the stereo plot for $(2A3HP)_2CuCl_4$ (Fig. 4) shows that the cations and anions in this salt hydrogen bond to form layers normal to the c^* direction. The amine and hydroxy groups on two equivalent 2A3HP cations tie adjacent anions together by hydrogen bonds to Cl(1) and Cl(2). In addition, two equivalent 2A3HP cations hydrogen bond to Cl(3) through the pyridine N atom.

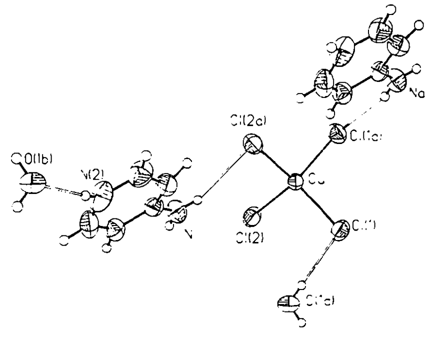


Fig. 1. View of the structure of $(4AP)_2CuCl_4.H_2O$, illustrating a portion of the hydrogen-bonding network. A twofold axis runs horizontally through the Cu and the O(*a*) atoms.

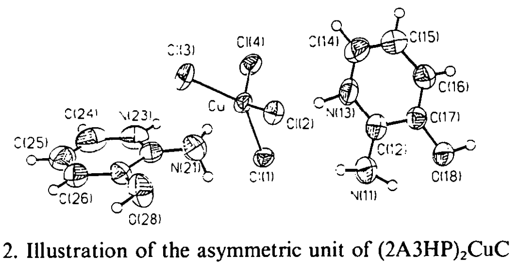


Fig. 2. Illustration of the asymmetric unit of $(2A3HP)_2CuCl_4$.

Structure correlations

Listed in Table 5 are structural data on the more than 60 $CuCl_4^{2-}$ anions whose structures have been reported in the literature. This certainly has to be one of the most intensively crystallographically studied transition-metal complex ions. In the following paragraphs, possible correlations are explored; specifically, between the average Cu—Cl bond distance and the average trans Cl—Cu—Cl angle, θ; between θ and the extent of hydrogen bonding; and between θ and the electronic transition energies. To facilitate the comparison, the data in Table 5 are listed in order of increasing values of θ.

Thermal motion and disorder

Care must be taken in interpreting the structural parameters in Table 5 because of the varying effects of thermal motion in different structures. This is most readily seen in the high-temperature determinations listed in Table 5, which show anomalously

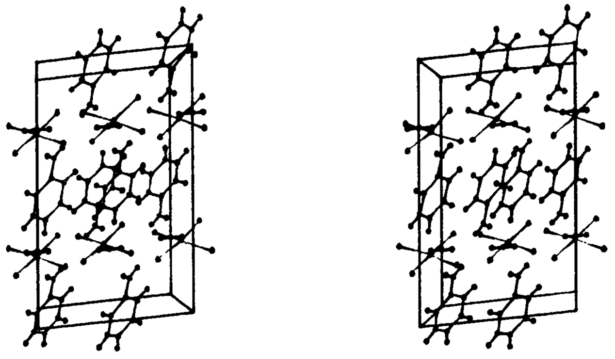


Fig. 3. Stereographic view of $(4AP)_2CuCl_4.H_2O$ as viewed parallel to the *b* axis.

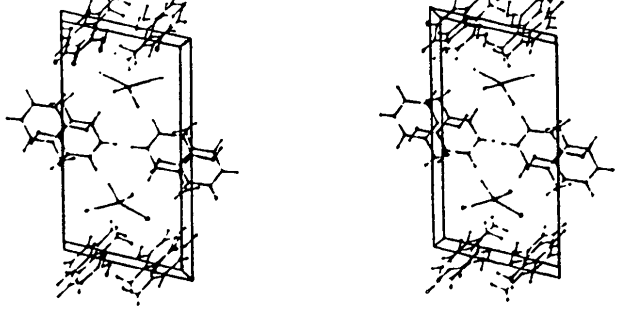


Fig. 4. Stereographic view of $(2A3HP)_2CuCl_4$ as viewed parallel to the *a* axis.

Table 5. *Structural parameters of isolated* $CuCl_4^{2-}$ *anions*

Compound	Acronym	N···Cl hydrogen bonding distance* (Å)	ΔU_{eq}† (Å^2)	Cu—Cl distance, av. (Å)	Cl—Cu—Cl *trans* angle, av. (°)	Ref.
$C_{42}H_{44}O_2P_2CuCl_4$	(2tbpo.H$^+$)$_2$	—	0·0313	2·225	105·2	*a*
$C_9H_{30}N_3Cl_3CuCl_4$	(Me$_3$NH)$_3$	—	0·0106	2·24	110·6	*b*
$C_{34}H_{40}N_4S_2Cl_2CuCl_8$	CPZ.H	—	0·0340	2·252	115·0	*c*
$C_{24}H_{72}N_{12}Cl_{14}Cu_3Cu_2Cl_8$	N(2amet)pipzH$_3$		0·0057	2·245	125·6	*d*
$C_{24}H_{28}N_{10}O_4CuCl_4$	DZH	3·136, 3·206, 3·432, 3·243	0·0178	2·246	125·8	*e*
$C_{30}H_{50}N_4O_2CuCl_4$	dietamacet	3·24		2·24	127·9	*f*
$C_{48}H_{40}P_2CuCl_4.H_2O$	TPhP	3·22, 3·21 (3·18, 3·33)		2·242	128·7	*g*
$C_6H_{13}N_3CuCl_4$	4(2amet)1Meimid	3·240, 3·274, 3·278, 3·335, 3·385	0·0068	2·242	120·0	*h*
Cs_2CuCl_4	(Cs)$_2$	—	0·0189	2·230	129·2	*i, j*
$C_{12}H_{14}N_2CuCl_4$	*N,N′*-DM-4,4′-BP	—	0·0108	2·247	129·2	*k*
$C_8H_{28}N_2CuCl_4$‡	[N(CH$_3$)$_4$]$_2$	—	0·0653	2·225	129·2	*l, m*
$C_{18}H_{28}N_2CuCl_4$‡	nmpH	3·55, 3·35, 3·45, 3·44	0·0215	2·208	130·6	*n*
$C_{22}H_{33}N_2O_6CuCl_4.H_2O$	(MescH)$_2$	3·311, 3·355, 3·221 (3·142, 3·190)		2·236	131·5	*o*
$C_{42}H_{44}O_2P_2CuCl_4$	(2tbpo.H$^+$)$_2$	—	0·0333	2·244	131·9	*p*
$C_{11}H_{14}N_2O_{0\cdot5}CuCl_4$	bzpipzn.H$_2$O	3·150 (3·225, 3·498)		2·251	132·2	*q*
$C_{20}H_{32}N_2CuCl_4$	TMBA	—	0·0223	2·256	132·4	*r*
$C_{68}H_{104}N_4Cl_2CuCl_4$	PCP	NR		2·264	132·6	*s*
$C_8H_{24}P_2CuCl_4$‡	Me$_4$P	—	0·1520	2·205	133·0	*t*
$C_{17}H_{21}N_2SCuCl_4$	PZH^{2+}	—	0·0110§	2·248	133·2	*u*
$C_{10}H_{34}N_5OP_5CuCl_4$	(NPMe$_2$)$_5$H$_2$	3·19 (3·31)	0·0142	2·255	133·4	*v*
$C_{10}H_{24}N_2CuCl_4$	pipdn	3·388, 3·395, 3·216, 3·265, 3·379, 3·260		2·249	133·5	*w*
$C_6H_{16}N_2OCuCl_4$	N(2amet)mfH$_2$	3·329, 3·304, 3·307, 3·357		2·250	133·8	*x*
$C_{11}H_{19}N_2O_{0\cdot5}CuCl_4$	bzpipzn.H$_2$O	3·155 (3·120)		2·249	133·8	*q*
$C_{12}H_{18}N_4OSCl_2CuCl_4$	Thianine	3·33, 3·44 (3·27)	0·0058	2·254	133·8	*y*
$C_{10}H_{14}N_4CuCl_4.H_2O$	4AP.H$_2$O	3·35, 3·35 (3·22, 3·31)	0·0180	2·247	134·6	This work
$C_6H_{20}N_2CuCl_4$‡	(IPA)$_2$	3·19, 3·26, 3·13, 3·28	0·0949	2·211	134·8	*z*
$C_{12}H_{32}N_2CuCl_4$	(TEA)$_2$	3·11	0·0140	2·241	134·8	*aa*
$C_{12}H_{26}N_2S_2CuCl_4$	(4-*N*-MPPD)S$_2$	3·14, 3·16		2·251	135·1	*bb*
$C_{11}H_{18}N_2CuCl_4$	bzpipzn	3·302, 3·249, 3·325, 3·278, 3·388		2·247	135·3	*q*
$C_6H_{24}N_3ClCuCl_4$§	(DMA)$_3$	3·124, 3·292, 3·240, 3·240	0·0404	2·230	135·8	*cc*
$C_8H_{24}P_2CuCl_4$‡	Me$_4$P	—	0·0417	2·240	135·8	*t*
$C_8H_{24}P_2CuCl_4$‡	Me$_4$P	—	0·0384	2·244	136·6	*t*
$C_{10}H_{14}N_4CuCl_4$	2A3HP	3·16, 3·33, 3·34, 3·36 (3·10, 3·19)	0·0122	2·247	137·8	This work
$C_{11}H_{18}N_2CuCl_4$	bzpipzn	3·372, 3·158, 3·330, 3·183, 3·322, 3·484		2·249	137·9	*q*
				2·249	137·9	*q*
$C_{20}H_{32}N_2CuCl_4$	dmampH	3·40, 3·31, 3·13, 3·45, 3·11, 3·28	0·0373	2·241	137·3	*dd*
$C_{34}H_{40}N_4S_2Cl_2Cu_2Cl_8$	CPZ.H	3·315, 3·318	0·0075	2·254	138·2	*c*
$C_4H_{12}N_2CuCl_4$	(DEA)$_2$	3·306, 3·269, 3·451, 3·225, 3·249		2·23	139	*ee*
$C_{20}H_{32}N_2CuCl_4$	dmampH	3·17, 3·26, 3·37, 3·31, 3·31	0·0368	2·236	139·2	*dd*
$C_8H_{12}N_6O_2CuCl_4$	Cytosinium	3·279, 3·372, 3·110, 3·352, 3·257		2·237	139·2	*ff*
$C_8H_{24}P_2CuCl_4$	Me$_4$P	—	0·0452	2·240	139·8	*t*
$C_{12}H_8N_4CuCl_4$	5-MAP	3·389, 3·249, 3·389, 3·249	0·0185	2·240	140·0	*gg*
$C_4H_{12}N_2CuCl_4$	(DEA)$_2$	3·266, 3·414, 3·274, 3·449, 3·383, 3·231, 3·370		2·20	141	*ee*
$C_{24}H_{36}N_{12}Cl_4Cu_3Cu_2Cl_8$	N(2amet)pipzH$_3$	3·492	0·0139	2·266	141·3	*d*
$C_{10}H_{16}N_2CuCl_4$	NPhpipzH$_2$	3·295, 3·368, 3·253, 3·228, 3·347		2·2498	142·0	*hh*
$C_{38}H_{48}N_{14}O_2Cu_2Cl_8.3H_2O$	cinH$_2$	3·17, 3·18 (3·26)	0·0110	2·251	142·1	*ii*
$C_{26}H_{38}N_4O_2S_2CuCl_4$	3,2-DEAMO	3·139, 3·139	0·0149	2·240	143·5	*jj*
$C_{10}H_{28}N_4CuCl_6$	1MepipzH$_2$Cl	3·17, 3·20, 3·47	0·0242	2·256	145·2	*kk*
$C_4H_{12}N_2CuCl_4$	(DEA)$_2$	NR		2·243	145·3	*ll*
$C_6H_{16}N_2OCuCl_4$	N(2amet)mfH$_2$	3·219, 3·242		2·267	146·2	*x*
$C_{12}H_{32}N_2CuCl_4$§	DPACC	3·28, 3·31, 3·36, 3·28, 3·22, 3·21	0·0295	2·248	146·4	*mm*
$C_{12}H_{32}N_2CuCl_4$	DPACC	3·28, 3·31, 3·36, 3·26, 3·22, 3·21	0·0183	2·252	146·6	*mm*
$C_{38}H_{48}N_4O_2Cu_2Cl_8.3H_2O$	cinH$_2$	(3·11, 3·19, 3·31)	0·0338	2·247	148·0	*ii*
$C_{11}H_{18}N_2CuCl_4$	bzpipzn	3·338, 3·156, 3·140, 2·940		2·230	150·9	*q*
$C_{11}H_{18}N_2CuCl_4$	bzpipzn	3·130, 3·132, 3·295, 3·174		2·227	151·8	*q*
$C_{10}H_{12}N_6Cl_4CuCl_4$	2,6-DA-3,5-DCP	3·077, 3·310, 3·392, 3·265, 3·126, 3·455, 3·351	0·0140	2·263	156·6	*nn*
$C_4H_{12}N_2CuCl_4$	(DEA)$_2$	NR		2·254	159·3	*ll*
$C_4H_{12}N_2CuCl_4$	(DEA)$_2$	NR		2·261	178·5	*ll*
$C_{42}H_{56}N_2O_2CuCl_4$	Methadone	—		2·263	180	*oo*
$C_{18}H_{28}N_2CuCl_4$	nmpH	3·349, 3·312, 3·223, 3·356	0·0153	2·265	180	*n*
$C_8H_{11}NO_2CuCl_4$	Creatinium	3·212, 3·337, 3·239	0·0299	2·251	180	*pp*
$C_6H_{16}N_2OCuCl_4$	N(2amet)mfH$_2$	3·271, 3·397, 3·219, 3·242		2·277	180	*x*
$C_{14}H_{14}N_4S_2CuCl_4$	(2AbtH)$_2$	3·15, 3·22	0·0130	2·270	180	*qq*

References: (*a*) Massabni *et al.* (1983), (*b*) Clay *et al.* (1973), (*c*) Obata *et al.* (1984), (*d*) Antolini *et al.* (1980), (*e*) Noren *et al.* (1989), (*f*) Shvelashvili *et al.* (1989), (*g*) Harlow & Simonsen (1976), (*h*) Głowka & Gilli (1989), (*i*) McGinnety (1972), (*j*) Helmholz & Kruh (1952), (*k*) Russell & Wallwork (1969), (*l*) Clay *et al.* (1975), (*m*) Morosin & Lingafelter (1961), (*n*) Harlow *et al.* (1974), (*o*) Buser & Watt (1979), (*p*) Halvorson (1989), (*q*) Antolini *et al.* (1981), (*r*) Bonamico *et al.* (1967), (*s*) Nelson & Simonsen (1981), (*t*) Pressprich (1989), (*u*) Von Dreele & Harris (1983), (*v*) Calhoun & Trotter (1974), (*w*) Fernandez *et al.* (1987), (*x*) Battaglia *et al.* (1982), (*y*) Caira *et al.* (1974), (*z*) Bloomquist *et al.* (1981), (*aa*) Lamotte-Brasseur *et al.* (1973), (*bb*) Brianso *et al.* (1988), (*cc*) Willett & Larsen (1971), (*dd*) Harlow *et al.* (1975), (*ee*) Bloomquist *et al.* (1988), (*ff*) Ogawa *et al.* (1979), (*gg*) Place & Willett (1987), (*hh*) Battaglia *et al.* (1979), (*ii*) Dyrek *et al.* (1987), (*jj*) Bonamartini-Corradi *et al.* (1971), (*kk*) Bonamartini-Corradi (1989), (*ll*) Simonsen & Harlow (1977), (*mm*) Bond *et al.* (1988), (*nn*) Willett & West (1987), (*oo*) Nelson *et al.* (1979), (*pp*) Udupa & Krebs (1979), (*qq*) Antolini *et al.* (1988).

* O—Cl bond distances are given in parentheses; NR, not reported.

† Defined as $\langle U_{eq,Cl}\rangle - U_{eq,Cl}$.

‡ High-temperature structure or disordered room-temperature structure.

§ Geometric average $(U_{11}U_{22}U_{33})^{1/3}$.

short apparent Cu—Cl distances because of large librational motion and/or disorder. Those undergoing large librations can be identified by large values of $\Delta U = \langle U_{\rm eq,Cl}\rangle - U_{\rm eq,Cu}$. Other types of motion (translational or screw-type motion, or disorder) may not be revealed by this parameter.

Before proceeding with an analysis of the structural data, it is appropriate to examine the structures where disorder is likely present. In a number of structures, identified by footnote ‡ in Table 5, disorder has been clearly identified in the structure determination. In all cases, these structures are characterized by large ΔU values and abnormally short Cu—Cl distances. This is most apparent in two compounds where the structures of both the high-temperature and low-temperature phases have been determined (Harlow, Wells, Watt & Simonsen, 1975; Simonsen & Harlow, 1977; Bloomquist, Pressprich & Willett, 1988), where a decided decrease in the *trans* angle occurs simultaneously with the increase in apparent thermal motion. One case where this does not occur is in $[(C_3H_7)_2NH_2]_2CuCl_4$ (Bond, Johnson & Willett, 1988). In this case, however, the major change involved in the phase transition is the onset of disorder in only one of the —C_3H_7 groups. Two of the structures reported, the $(CH_3)_4N^+$ salt (Morosin & Lingafelter, 1961) and the corresponding $(CH_3)_4P^+$ salt (Pressprich, 1989) exhibit a sequence of commensurately modulated/incommensurate/disordered phases. The high-temperature disordered phases clearly exhibit large ΔU values and shortened Cu—Cl bond lengths. The first three entries in Table 5, with $\theta < 125°$, probably also correspond to systems with disorder undetected by the authors. The tetragonal 2tbpo.H$^+$ salt (Massabni, Nascimento, De Almeida Santos, Francisco & Lechat, 1983) is reported to contain an elongated tetrahedral geometry, which does not remove the Jahn–Teller-type degeneracy for the $CuCl_4^{2-}$ anions. Our reinvestigation of this system has revealed that the stable crystalline material at room temperature is triclinic with $\theta = 131{\cdot}9°$ (Halvorson, 1989; Halvorson, Willett & Massabni, 1990). Thus, the original determination must have been carried out on a metastable phase, and the large ΔU value is consistent with the apparent elongated structure arising from disorder over two or more compressed tetrahedral orientations. The ΔU value for the $[(CH_3)_3NH]_3Cu_2Cl_7$ salt (Clay, Murray-Rust & Murray-Rust, 1973) is small, so disorder may not seem readily apparent. However, the magnitudes of the individual $U_{\rm eq}$ values for the Cu and Cl atoms are as large or larger than those for the C and N atoms. Thus disorder seems likely. The CPZ.H salt (Obata, Kawazura & Miyamae, 1984) contains two independent $CuCl_4^{2-}$, one with $\theta = 114{\cdot}95°$, and one with $\theta = 138{\cdot}25°$. The latter has a rather small ΔU value and $U_{\rm eq}$ values appear normal. For the nearly tetrahedral anion, however, the Cl $U_{\rm eq}$ values are abnormally large, as is evident from the ΔU value in Table 5. Disorder of the phenothiazine ring is observed so that disorder of the latter $CuCl_4^{2-}$ ion is not unreasonable. Examination of the thermal-ellipsoid parameters (or thermal-ellipsoid plots where parameters are not published) indicate that several other systems may have bond lengths affected by apparent shortening caused by libration or disorder. These include the Ph_4P^+ (Harlow & Simonsen, 1976), mescH$^+$ (Buser & Watt, 1979) and creatinium (Udupa & Krebs, 1979) salts. The lack of published or plotted thermal-ellipsoid plots prohibits comments on several other suspicious cases.

Angular distortion

The bulk of the systems have θ values between 125 and 145°; in addition, five compounds have planar $CuCl_4^{2-}$ anions ($\theta = 180°$). A smattering of structures with anion *trans* angles between 148 and 180° have been reported. Unfortunately, most of these structures contain two or more anions with substantially different *trans* angles. The 2,6-diamino-3,5-dichloropyridinium salt (Willett & West, 1987) is the only exception. Thus, unique interpretation of physical properties is difficult. Several nonisolated $CuCl_4^{2-}$ anions are known which have $150 < \theta < 175°$ (Antolini, Menabue, Pellacani, Saladini & Marcotrigiano, 1982; Larson, Hazell, Toftland, Anderson, Bisgard, Edlund, Eliasen, Herskind, Laurensen & Peterson, 1975; Anderson & Willett, 1974; Willett, Place & Middleton, 1988). In these, other ligands (usually chloride ions) occupy axial coordination sites at long distances (>3·2 Å). It has been argued (McDonald, Riley & Hitchman, 1988) that these interactions do not seriously perturb the *d–d* transitions. This will be true only when these axial distances are extremely long.

A feeling for the shape of the potential curve for the angular deformation of the isolated $CuCl_4^{2-}$ anion can be obtained from the distribution of the values of θ. From the histogram in Fig. 5, it can be deduced that the minimum occurs at 135 ± 5°, with a secondary minimum at 180°. The local minimum at $\theta = 180°$ must be attributable to interactions with its crystalline environment, since such a minimum is not predicted for the free ion (Lohr & Lipscomb, 1963). A broad maximum appears to cover the range from 160 to 175°, and again for $\theta < 125°$. The three entries in Table 5 with $\theta < 120°$ certainly correspond to systems with disordered orientations of the pseudo-C_4 axes, although the disorder was not identified in the publications.

A correlation between geometry and hydrogen bonding has previously been postulated (Willett, Haugen, Lesback & Morrey, 1974). This was based on the observation that when little or no hydrogen bonding occurs to the $CuCl_4^{2-}$ ion, the *trans* bond angle, θ, is usually less than 132°, with the anion generally becoming more planar as the extent of hydrogen bonding increases. As is usual, as more data becomes available, some simplistic arguments must be modified. The geometry of a truly isolated $CuCl_4^{2-}$ ion represents a balance between crystal-field stabilization effects, favoring a square-planar geometry, and ligand–ligand electrostatic repulsion, favoring the tetrahedral coordination. In a crystal, the anion is subjected to other influences, some of electrostatic origins, and others which are simply steric in nature. In general hydrogen bonds tend to remove charge from the Cl atoms. This reduces the electrostatic repulsions between the Cl atoms and allows the $CuCl_4^{2-}$ ion to move toward a square-planar geometry. The data in Table 5 generally support this correlation, with shorter and/or more hydrogen-bonding interactions present as the anion approaches planarity. Additionally, the reduction of the θ angle when hydrogen-bonding interactions are broken or weakened by onset of disorder supports this contention. However, it is clear from Fig. 5 that the potential surface is rather flat and that other crystal forces (*e.g.* packing) can have a substantial effect upon the observed geometries. This is most evident in examination of the five reported planar ions, where the methadone salt shows little or no hydrogen bonding in contrast to the other four salts.

Cu—Cl *distances*

It has also been suggested that a correlation exists between the average Cu—Cl distance and the average *trans* angle, θ (Smith, 1976). The reduced electrostatic repulsion in the planar limit should lead to a slight shortening of the bonds. When the data is plotted (omitting the high-temperature structures), a diagram is obtained with a nominal slope for a linear fit of 0·00039 Å $\deg^{-1}$. However, the slope is unduly influenced by the values at the extreme ends of the range of θ, and the scatter of values found for $130 < \theta < 150°$ is nearly as large as the total scatter. Thus, no conclusive correlation exists from this simple analysis. Part of the problem, of course, is the fact that the bond lengths are uncorrected for thermal motion and thus the bond lengths will be anomalously short when large librational motions are present. In the frequent absence of published anisotropic thermal parameters, it is impossible to make these corrections systematically. In the limited number of cases where we were able to make librational corrections, no substantial decrease in the amount of scatter was obtained. A feel for the effect of thermal motion can be obtained however, from a three-dimensional plot of θ *versus* the average Cu—Cl distance (Fig. 6), where the third coordinate is ΔU. It is seen that a majority of the compounds with short (< 2·24 Å) Cu–Cl distances undergo quite large librational motions. Examination of those data points in Fig. 6 with small ΔU values lends support to the idea that the average Cu—Cl distance shortens by a maximum of 0·02 Å as θ decreases from 180 to 125°, but a quantitative estimate is impossible to make. The earlier statement regarding the significant shortening of the Cu—Cl distance as θ decreased was probably biased by structural results on disordered systems.

Electronic spectra

Table 6 compares the *d–d* electronic absorption energy, ΔE_{dd}, with the average *trans* angle. At room temperature, a single broad band is normally observed in the near-IR region of the spectrum. At liquid-nitrogen temperature, this is generally resolved into several overlapping bands. The band positions have been correlated with the *trans* Cl—Cu—Cl angle, θ (Harlow *et al.*, 1975) or the dihedral angle, Δ, between the $CuCl_2$ planes which do not contain θ (Battaglia, Bonamartini-Corradi, Marcotrigiano, Menabue & Pellacani, 1979). When the energy of the band maximum, ΔE_{dd}, at room temperature is plotted against the *trans* angle, the relationship seen in Fig. 7 is obtained. A monotonic relation between ΔE_{dd} and θ clearly exists. A plot of the energy of the highest energy transition *versus* θ yields a similar plot that is nearly linear. The linearity is undoubtably fortuitous, and since the maximum energy transition

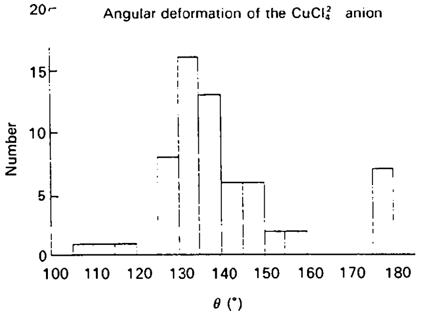


Fig. 5. Distribution of θ values for the 62 known $CuCl_4^{2-}$ anions.

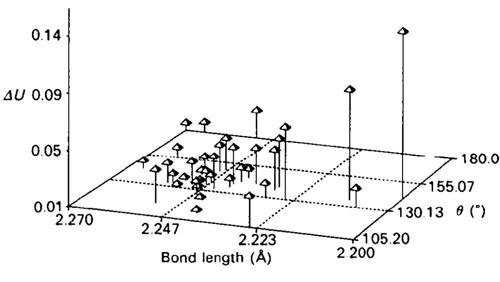


Fig. 6. Cu—Cl distance and *trans* bond angle *versus* ΔU.

Table 6. *Electronic spectra of* $CuCl_4^{2-}$ *anions*

Acronym*	Av. *trans* angle (°)	Band maximum	Electronic spectra (cm^{-1}) $^2B_2\rightarrow{}^2E$	$^2B_2\rightarrow{}^2B_1$	$^2B_2\rightarrow{}^2A_1$	Ref.
$(2tbpo.H^+)_2$	105·2		6250		9520	*a*
$N(2amet)pipzH_3$	125·6, 141·8	8890, 10990				*b*
DZH	125·8	7900				*c*
TPhP	128·7	9110				*d*
$(Cs)_2$	129·2	9050†	4800, 5500	7900	9050†	*e*
$[N(CH_3)_4]_2$	129·4	9000	6000		9000	*f, g*
nmpH	130·6	9100‡				*h*
$bzpipzn.H_2O$	132·2, 133·8		6350		9390	*i*
TMBA	132·4	8850	5900		9200	*j, g*
pipdn	133·5		6620		9710	*k*
$N(2amet)mfH_2$	133·8		6250		9620	*l*
$4AP.H_2O$	134·6		6750	8850	9730	*m*
$(TEA)_2$	134·8	9390		8000	9400	*n, g*
$(IPA)_2$	134·8	9500‡				*o*
(4-*N*-MPPD)S_2	135·1	9800	7000		10300	*p*
bzpipzn	135·3, 137·9	10200				*i*
$(DMA)_3$	135·8	9520	7400		10800†	*o*
dmampH	137·3, 139·2	10200	7500		10800†	*q*
$(DEA)_2$	138·9, 141·0		7300		10200‡	*r*
5-MAP	139·9		7200	8900	9900	*m*
$NPhpipzH_2$	142·0	10750		8930	10750	*l*
$cinH_2$	142·1, 148·2	11100		9100	11100	*g*
3,2-DEAMO	143·5	10810				*s*
$1MepipzH_2Cl$	145·2	10420		~9000	~11000	*t*
$(DEA)_2$	145·3, 159·3, 178·8		(9900, 12900, 15300 – unassigned)			*o*
$N(2amet)mfH_2$	146·2		9300		11500	*l*
DPACC	146·6	11200	9800		12700	*u*
bzpipzn	150·9, 151·8	12500				*i*
$(2AbtH)_2$	180	13500	13500	11500	15500	*v*
nmpH	180	13600	14300	12500	16900†	*h, w*
Methadone	180	13200	14000	12200	16600	*x, y*
$N(2amet)mfH_2$	180		14290	11500	16400	*z*
Creatinium	180	~13500	14000	12300	16500	*y*

References: (*a*) Massabni *et al.* (1983), (*b*) Antolini *et al.* (1980), (*c*) Noren *et al.* (1989), (*d*) Harlow & Simonsen (1976), (*e*) Ferguson (1964), (*f*) Willett *et al.* (1967), (*g*) Dyrek *et al.* (1987), (*h*) Harlow *et al.* (1974), (*i*) Antolini *et al.* (1981), (*j*) Furlani *et al.* (1967), (*k*) Doadrio & Gutierrez Rios (1979), (*l*) Battaglia *et al.* (1982), (*m*) Gaura *et al.* (1982), (*n*) Lamotte-Brasseur (1974), (*o*) Willett *et al.* (1974), (*p*) Brianso *et al.* (1988), (*q*) Harlow *et al.* (1975), (*r*) Hill & Smith (1973), (*s*) Bonamartini-Corradi *et al.* (1971), (*t*) Marcotrigiano *et al.* (1979), (*u*) Bond *et al.* (1988), (*v*) Antolini *et al.* (1988), (*w*) Cassidy & Hitchman (1975), (*x*) Riley & Hitchman (1987), (*y*) McDonald & Hitchman (1986), (*z*) McDonald *et al.* (1989).

* See Table 5 for identification of acronyns.
† Low-temperature data.
‡ High-temperature data.

may not be readily resolvable at room temperature, the former plot seems preferable.

The structure of the 4AP salt corresponds well with the spectroscopic properties previously reported (Gaura, Stein, Willett & West, 1982). The maximum in the electronic absorption band caused by the *d–d* transitions occurs at 9730 cm^{-1}. This would predict a *trans* angle of approximately 135°, close to the observed value of 134·6°. Conversely, the crystal-field model developed to predict the *trans* angle (Gaura *et al.*, 1982), predicted a value of about 131° for the 4AP salt. For the 2-amino-5-methylpyridinium salt, $(5MAP)_2CuCl_4$, recently reported by Place & Willett (1987), the band maximum occurs at 9900 cm^{-1} and the average *trans* angle is predicted to be about 137°, somewhat less than the observed value of 139·8°.

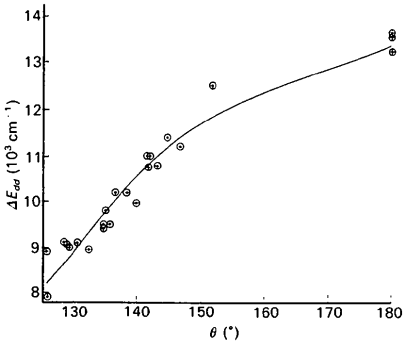


Fig. 7. Bond energy for the maximum of the *d–d* transitions at room temperature *versus trans* bond angle.

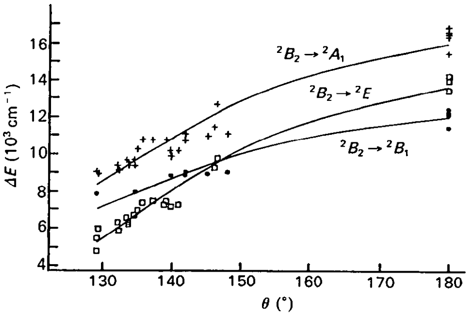


Fig. 8. Transition energies, ΔE, of the *d–d* bands at low temperature *versus* average *trans* bond angle, θ. Filled circles are the reported values cited in Table 7. The curves show calculated energies from angular overlap model equations.

Table 7. *Geometry of coordinated* $CuCl_4^{2-}$ *anions*

Cu denotes the Cu atom in the $CuCl_4^{2-}$ anion, Cu′ denotes the Cu atom in the other moiety. Cl_b denotes the bridging chloride ion.

Compound	Cu′—Cl_b (Å)	Cu′—Cl_b—Cu (°)	Cu—Cl, av. (Å)	Cu—Cl_b (Å)	Cl—Cu—Cl, av. (°)	Ref.
CuL^4CuCl_4	2·507	110·67	2·243	2·266	134·3	*a*
$[Cu(dapdo)Cl]_2CuCl_4$	2·604	138·84	2·246	2·273	133·85	*b*
$Cu(TIM)CuCl_4$	2·676	115·8	2·249	2·309	127·14	*c*
	3·163	122·0		2·227		
$(1,4DMP)_4Cu_5Cl_{14}$	2·457	129·5	2·249	2·235	133·2	*d*
	2·868	125·1		2·316		
$[Cu(L^3)(H_2O)]$-$[Cu_2(L^3)_2](CuCl_4)_2$	3·011	135·0	2·250	2·252	133·22	*e*
	3·407	165·0		2·279		
	3·736	108·5		2·228		
$Cu^I_3Cu^{II}L_3Cl_5$	2·372, 2·373	85·85, 85·64	2·256	2·263, 2·273	141·4	*f*
	2·340	108·79		2·280		
	2·514	125·1		2·223		
$Et_4NCu_2Cl_4$	2·342	87·2	2·254	2·254	133·9	*g*
$(Et_4N)_4Cu_4Cl_{12}$	2·316, 2·662	95·5, 88·3	2·250	2·324, 2·250	141·4	*h*
$A_2Cu_2Cl_6$	2·290–2·319	92·9–94·6		2·290–2·319	124·8–147·6	*i, j*
	(2·303 av.)	(93·4 av.)	(2·254 av.)	(2·303 av.)	(142 av.)	
$Cu(TSMO)_4Cu_2Cl_6$	2·894	112·3	2·250	2·213	142·8	*i*

References: (*a*) Comba *et al.* (1988), L^4 = 12-methyl-12-nitro-1,4,7,10-tetraazacyclotridecane. (*b*) Vasilevesky, Rose *et al.* (1989), dapdo = 2,6-diacetylpyridine dioxime. (*c*) Vasilevesky, Stenkamp *et al.* (1989), TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclohexadec-1,3,8,11-tetraene. (*d*) Bond & Willett (1990), 1,4DMP = 1,4-dimethylpyridinium. (*e*) Schlemper *et al.* (1989), L^3 = 2-methyl-1,3-di-2-pyridyl-2-propanol. (*f*) Ainscough *et al.* (1985), *L* = tetrahydrothiophene. (*g*) Willett (1987). (*h*) Willett & Geiser (1986). (*i*) See Landee *et al.* (1988). (*j*) Reported values are averages for eight structures.

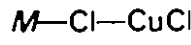
When the individual *d–d* transitions are resolvable, a more quantitative analysis of the angular dependence of the spectra can be made. Fig. 8 shows the correlation of the resolved spectra ($^2B_2 \rightarrow {}^2A_1$, $^2B_2 \rightarrow {}^2B_1$, $^2B_2 \rightarrow {}^2E$), with average *trans* angle. In this case, the angular overlap model (AOM) was used to generate the solid curves (Smith, 1976; McDonald *et al.*, 1988) since it provides a convenient method to predict the change in transition energies as a function of anion geometry. The equations for the transition energies of any complex of general D_{2d} symmetry as a function of distortion angle θ are

$$
\begin{aligned}
{}^2B_2 \rightarrow {}^2E &= 3e_\sigma(\sin^4\alpha - \tfrac{1}{2}\sin^2 2\alpha) \\
&\quad + e_\pi(\sin^2 2\alpha - 2\cos^2 2\alpha - \cos^2\alpha) \\
{}^2B_2 \rightarrow {}^2A_1 &= 3e_\sigma \sin^4\alpha - 4e_\sigma(\cos^2\alpha - \tfrac{1}{2}\sin^2\alpha)^2 \\
&\quad - 2e_\pi \sin^2 2\alpha + 16e_{ds}(\cos^2\alpha - \tfrac{1}{2}\sin^2\alpha)^2 \\
&\quad - 13{\cdot}3e_{dp}(\sin^4\alpha\cos^2\alpha) \\
{}^2B_2 \rightarrow {}^2B_1 &= 3e_\sigma \sin^4\alpha + e_\pi(\sin^2 2\alpha - 4\sin^2\alpha) \\
&\quad - 13{\cdot}3e_{dp}(\sin^4\alpha\cos^2\alpha)
\end{aligned}
$$

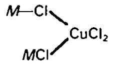
where $\alpha = \theta/2$. The parameters e_σ and e_π represent the σ- and π-bonding effects of the ligands, e_{ds} takes into account the lowering of the d_{z^2} orbital caused by configuration interaction, and e_{dp} represents the possible effects of the mixing of metal *d* and *p* orbitals. Calculated parameters using the AOM are $e_\sigma = 5100$, $e_\pi = 820$, $e_{ds} = 1450$ and $e_{dp} = 550\ \text{cm}^{-1}$. This is in fair agreement with the previously reported values of $e_\sigma = 5030$, $e_\pi = 900$, $e_{ds} = 1320$ and $e_{dp} = 160\ \text{cm}^{-1}$ (McDonald *et al.*, 1988). The larger value for e_{dp} suggests that the metal 4*p* orbitals mix into the d_{z^2} orbital to a greater extent than was previously thought (McDonald *et al.*, 1988).

The $CuCl_4^{2-}$ anion as a ligand

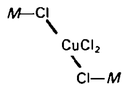
In addition to existing as an isolated anion, the $CuCl_4^{2-}$ ion can act as a coordinating ligand to other metal(II) ions. Possible coordination modes of $CuCl_4^{2-}$ anions to other metal ions, *M*, are structures (I*a*)–(I*c*) and (II). In all cases reported to date, *M* is another copper ion. Because of the very flexible nature of the copper(II) coordination sphere, this coordination can take a variety of forms, either as a monodentate or bidentate ligand which can interact with one, two, or more additional copper(II) ions. Some of the important structural parameters are summarized in Table 7.



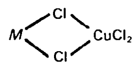
(I*a*)



(I*c*)



(I*b*)



(II)

Included are several structures which have been reported where the $CuCl_4^{2-}$ anion acts as a simple monodentate ligand, occupying the axial coordination site of a square-pyramidal complex, as denoted in (I*a*). In the macrocyclic complex involving (12-methyl-12-nitro-1,4,7,10-tetraazacyclotridecane)-copper(II) (Comba, Curtis, Lawrence, O'Leary, Skelton & White, 1988), the basal plane contains the four N ligands of the macrocycle, while one Cl atom from the $CuCl_4^{2-}$ anion occupies the axial position with a short axial Cu—Cl distance of 2·507 Å. The bridging Cu′—Cl—Cu angle is extremely small at 110·67°, where Cu′ denotes the Cu atom to which the

$CuCl_4^{2-}$ anion is bridging, and Cl_b denotes the bridging chloride ion. The $CuCl_4^{2-}$ ion acts as a bridging group in a trimeric complex involving two CuL^3Cl^+ cations, where L^3 = 2,6-diacetylpyridine dioxime, which symmetrically sandwiches a $CuCl_4^{2-}$ anion, as in (I*b*). The basal plane of each cation is occupied by the three N atoms of the bidentate ligand and a chloride ion (Vasilevsky, Stenkamp, Lingafelter, Schomaker, Willett & Rose, 1989). For each cation, the fifth, axial, site of the coordination sphere is occupied by a Cl atom of the $CuCl_4^{2-}$ anion at 2·604 Å. This distance is 0·1 Å longer than in the first complex discussed, and the $Cu'—Cl_b—Cu$ angle is opened up to 138·8°. This type of unit is linked together into infinite chains in CuL^4CuCl_4, $L^4 = C_{14}H_{24}N_4$ (Vasilevsky, Rose, Willett & Stenkamp, 1989). The L^4 ligand forms the basal plane for a 4 + 2 coordinated copper(II) ion, while the fifth site is occupied by a Cl atom from an anion at distances of 2·676 Å. The back of the macrocycle is relatively open, and a Cl atom from an adjacent $CuCl_4^{2-}$ ion forms a long semicoordinate bond of 3·163 Å. The bridging is thus quite asymmetric, with the bridging $Cu'—Cl_b—Cu$ angles equal to 115·8 and 122·0°, respectively.

The $CuCl_4^{2-}$ anion can also bridge between neighboring atoms in oligomeric or polymeric species, as in (I*c*). The structure of tetrakis(1,4-dimethylpyridinium) tetradecachloropentacopper(II) contains bibridged $CuCl_2$ chains in which the copper(II) ions have either distorted square-pyramidal or 4 + 2 coordination geometries. The $CuCl_4^{2-}$ anion appended to this chain bridges two such adjacent coordination sites: one Cl atom occupies the fifth coordination site of square-pyramidal geometry at an extremely short distance of 2·457 Å, while a second chloride atom is semicoordinated to the neighboring copper(II) ion at a distance of 2·868 Å. The bridging $Cu'—Cl_b—Cu$ angles are 125·1 and 129·5°, respectively. Both the (I*b*) and (I*c*) types of bridging features are incorporated in the compound $[Cu_2(L^3)_2][Cu_2(L^3)_2(H_2O)_2][CuCl_4]_2$, where L^3 = 2-methyl-1,3-di-2-pyridyl-2-propanol (Schlemper, Patterson & Stunkel, 1989). Two of the Cl atoms of each $CuCl_4^{2-}$ anion occupy the two semicoordinate sites on one side of the centrosymmetric nonhydrated dimer. These $Cu'\cdots Cl$ distances are 3·011 and 3·736 Å. A third Cl atom then links to one of the semicoordinate sites on the hydrated dimer ($Cu\cdots Cl$ = 3·407 Å, $Cu'—Cl—Cu$ = 165·0°), while the final Cl atom is involved in a hydrogen bond to a semicoordinated water molecule. This links the dimeric units together into infinite chains.

It is also possible for the distorted tetrahedral $CuCl_4^{2-}$ species to act as a bidentate ligand, as in (II). In one sense the simplest examples are the isolated $Cu_2Cl_6^{2-}$ dimer, composed of two edge-shared, distorted tetrahedra (see Landee, Djili, Mudgett, Newhall, Place, Scott & Willett, 1988, and references therein). Here the edge sharing may be viewed as mutual bidentate coordination. In $Cu(TMSO)_4Cu_2Cl_6$, two of the terminal Cl atoms (one per copper ion) also are involved in monodentate bridges to the square $Cu(TMSO)_4^{2+}$ cations, yielding an infinite chain structure (Landee *et al.*, 1988). Bidentate coordination is also observed in $(Et_4N)_4Cu_4Cl_{12}$ (Willett & Geiser, 1986) where two Cl atoms on each of two terminal $CuCl_4^{2-}$ species coordinate to an axial ($Cu'—Cl$ = 2·662 Å) and an equatorial ($Cu'—Cl$ = 2·316 Å) site on each of two central five coordinate copper(II) ions. Similar bidentate coordination occurs in the mixed-valence salt $Cu^I_3Cu^{II}L_3Cl_5$, where L = tetrahydrothiophene. In this structure, an identifiable $CuCl_4^{2-}$ anion acts as a bidentate ligand coordinating to a copper(I) ion in a central Cu_3L_3 core. In addition, the other two Cl atoms form mondentate bridges to adjacent Cu_3L_3 cores (Ainscough, Brodie, Husbands, Gainsford, Gabe & Curtis, 1985). Finally, in $Et_4NCu_2Cl_4$ (Willett, 1987), the alternating mixed-valence $(Cu^ICu^{II}Cl_4)_n^-$ chain can be viewed as $CuCl_4^{2-}$ anions serving as a double-bidentate ligand which coordinate to pairs of Cu^I ions.

The examples given here involve coordination of the $CuCl_2^{4-}$ anion to other copper ions. There is, in principle, no reason why this could not involve other metal ions. With paramagnetic metal ions, bridging coordination of type (I*b*) can lead to the formation of alternating-spin magnetic chain systems; systems which are of considerable interest at present in low-dimensional physics. One of the features substantiated again by the data in Table 7 is the flexibility of the $CuCl_4^{2-}$ potential surface, this time in the form of the variability of the Cu—Cl bond lengths. The Cu—Cl distances involved in bridge formation can stretch out to 2·325 Å. Concomitantly, the nonbridging distances shorten down as far as 2·181 Å [see Table VI in Landee *et al.* (1988)]. The net result is that the average Cu—Cl distance is nearly invariant at 2·251 ± 0·004 Å. A similar effect has been observed in stacked planar $Cu_nCl_{2n+2}^{2-}$ anions (Willett, 1988).

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References

Ainscough, E. W., Brodie, A. M., Husbands, J. M., Gainsford, G. J., Gabe, E. J. & Curtis, N. F. (1985). *J. Chem. Soc. Dalton Trans.* pp. 151–158.

Anderson, D. N. & Willett, R. D. (1974). *Inorg. Chim. Acta*, **8**, 167–175.

Antolini, L., Benedetti, A., Fabretti, A. C. & Giusti, A. (1988). *Inorg. Chem.* **27**, 2192–2194.

Antolini, L., Marcotrigiano, G., Menabue, L. & Pellacani, G. C. (1980). *J. Am. Chem. Soc.* **102**, 5506–5510.

Antolini, L., Menabue, L., Pellacani, G. C., Saladini, M. & Marcotrigiano, G. (1982). *Inorg. Chim. Acta*, **58**, 193–200.

Antolini, L., Menabue, L., Pellacani, G. C., Saladini, M., Marcotrigiano, G. & Porzio, W. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1753–1758.

Battaglia, L. P., Bonamartini-Corradi, A., Marcotrigiano, G., Menabue, L. & Pellacani, G. C. (1979). *Inorg. Chem.* **18**, 148–152.

Battaglia, L. P., Bonamartini-Corradi, A., Marcotrigiano, G., Menabue, L. & Pellacani, G. C. (1982). *Inorg. Chem.* **21**, 3919–3922.

Bloomquist, D. R., Pressprich, M. R. & Willett, R. D. (1988). *J. Am. Chem. Soc.* **110**, 7391–7398.

Bloomquist, D. R., Willett, R. D. & Dodgen, H. W. (1981). *J. Am. Chem. Soc.* **103**, 2610–2615.

Bonamartini-Corradi, A. (1989). Private communication.

Bonamartini-Corradi, A., Nardelli, M., Palmieri, C. & Pelizzi, C. (1971). *Acta Cryst.* **B27**, 1775–1779.

Bonamico, M., Dessy, G. & Vaciago, A. (1967). *Theor. Chim. Acta*, **7**, 367–374.

Bond, M. R., Johnson, T. J. & Willett, R. D. (1988). *Can. J. Chem.* **66**, 963–973.

Bond, M. R. & Willett, R. D. (1987). *Acta Cryst.* **C43**, 2304–2309.

Bond, M. R. & Willett, R. D. (1990). *Inorg. Chem.* Submitted.

Brianso, M. C., Brianso, J. L., Gaete, W. & Ros, J. (1988). *Inorg. Chim. Acta*, **49**, 263.

Buser, H. J. & Watt, G. W. (1979). *Acta Cryst.* **B35**, 91–95.

Caira, M. R., Fazakerley, P. W., Linder, P. W. & Nassimbeni, L. R. (1974). *Acta Cryst.* **B30**, 1660–1666.

Calhoun, H. P. & Trotter, J. (1974). *J. Chem. Soc. Dalton Trans.* pp. 382–386.

Campana, C. F., Shepherd, D. F. & Litchman, W. N. (1981). *Inorg. Chem.* **20**, 4039–4044.

Cassidy, P. & Hitchman, M. A. (1975). *J. Chem. Soc. Chem. Commun.* pp. 837–838.

Clay, R., Murray-Rust, J. & Murray-Rust, P. (1975). *Acta Cryst.* **B31**, 289–290.

Clay, R., Murray-Rust, P. & Murray-Rust, J. (1973). *J. Chem. Soc. Dalton Trans.* pp. 595–599.

Comba, P., Curtis, N. F., Lawrence, G. A., O'Leary, M. A., Skelton, B. & White, A. H. (1988). *J. Chem. Soc. Dalton Trans.* pp. 497–502.

Doadrio, A. & Gutierrez Rios, M. T. (1979). *An. Quim.* **75**, 228–231.

Dyrek, K., Goslar, J., Hodorowicz, S. A., Hoffmann, S. K., Oleksyn, B. J. & Weselucha-Birczynska, A. (1987). *Inorg. Chem.* **26**, 1481–1487.

Ferguson, J. (1964). *J. Chem. Phys.* **40**, 3406–3410.

Fernandez, V., Moran, M., Gutierrez-Rios, M., Foces-Foces, C. & Cano, F. H. (1987). *Inorg. Chim. Acta*, **128**, 239–243.

Furlani, C., Cervone, E., Calzona, F. & Baldanza, B. (1967). *Theor. Chim. Acta*, **7**, 375–382.

Gaura, R. M., Stein, P., Willett, R. D. & West, D. X. (1982). *Inorg. Chim. Acta*, **60**, 213–218.

Głowka, M. C. & Gilli, G. (1989). *Acta Cryst.* **C45**, 408–410.

Halvorson, K. E. (1989). MS Thesis, Washington State Univ., USA.

Halvorson, K. E., Willett, R. D. & Massabni, A. C. (1990). *J. Chem. Soc. Chem. Commun.* pp. 346–348.

Harlow, R. L. & Simonsen, S. H. (1976). *Cryst. Struct. Commun.* **5**, 265–270.

Harlow, R. L., Wells, W. J., Watt, G. W. & Simonsen, S. H. (1974). *Inorg. Chem.* **13**, 2106–2111.

Harlow, R. L., Wells, W. J., Watt, G. W. & Simonsen, S. H. (1975). *Inorg. Chem.* **14**, 1768–1773.

Helmholz, L. & Kruh, R. F. (1952). *J. Am. Chem. Soc.* **74**, 1176–1181.

Hill, D. R. & Smith, D. W. (1973). *J. Inorg. Nucl. Chem.* **36**, 466–467.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Lamotte-Brasseur, P. J. (1974). *Acta Cryst.* **A30**, 487–489.

Lamotte-Brasseur, P. J., Dideberg, O. & Dupont, L. (1973). *Acta Cryst.* **B29**, 241–246.

Landee, C. P., Djili, A., Mudgett, D. F., Newhall, M., Place, H., Scott, B. & Willett, R. D. (1988). *Inorg. Chem.* **27**, 620–627.

Larson, K. P., Hazell, R. G., Toftlund, H., Anderson, P. R., Bisgard, P., Edlund, K., Eliasen, M., Herskind, C., Laurensen, T. & Peterson, P. M. (1975). *Acta Chem. Scand. Ser. A*, **29**, 499–504.

Lohr, L. L. & Lipscomb, W. N. (1963). *Inorg. Chem.* **2**, 911–917.

McDonald, R. G. & Hitchman, M. A. (1986). *Inorg. Chem.* **25**, 3273–3281.

McDonald, R. G., Riley, M. J. & Hitchman, M. A. (1988). *Inorg. Chem.* **27**, 894–900.

McDonald, R. G., Riley, M. J. & Hitchman, M. A. (1989). *Inorg. Chem.* **28**, 752–758.

McGinnety, J. A. (1972). *J. Am. Chem. Soc.* **94**, 8406–8413.

Marcotrigiano, G., Menabue, L. & Pellacani, G. C. (1979). *J. Coord. Chem.* **9**, 141–149.

Massabni, A. C., Nascimento, O. R., De Almeida Santos, R. H., Francisco R. H. P. & Lechat, J. R. (1983). *Inorg. Chim. Acta*, **72**, 127–131.

Morosin, B. & Lingafelter, E. C. (1961). *J. Phys. Chem.* **65**, 50–51.

Nelson, H. C. & Simonsen, S. H. (1981). *Acta Cryst.* **A37**, C-168.

Nelson, H. C., Simonsen, S. H. & Watt, G. W. (1979). *J. Chem. Soc. Chem. Commun.* pp. 632–633.

Noren, B., Oskarsson, A., Svensson, C., Soto, L., Ruiz, J. & Colacio, E. (1989). *Acta Chem. Scand.* **43**, 368–372.

Obata, A., Kawazura, H. & Miyamae, H. (1984). *Acta Cryst.* **C40**, 45–48.

Ogawa, K., Nishitani, K., Fujiwara, T., Shirotake, S. & Tomita, K. (1979). *Acta Cryst.* **B35**, 965–967.

Place, H. & Willett, R. D. (1987). *Acta Cryst.* **C43**, 1050–1052.

Pressprich, M. R. (1989). Private communication.

Riley, M. J. & Hitchman, M. A. (1987). *Inorg. Chem.* **26**, 3205–3215.

Russell, J. H. & Wallwork, S. C. (1969). *Acta Cryst.* **B25**, 1691–1695.

Schlemper, E. O., Patterson, C. & Stunkel, J. (1989). *Acta Cryst.* **C45**, 199–201.

Sheldrick, G. (1986). *SHELXTL Users Manual.* Revision 5.1. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

Shvelashvili, A. E., Metrevili, L. A., Sobolev, A. N. & Vardosanidze, T. D. (1989). *Russ. J. Inorg. Chem.* **33**, 1640–1645.

Simonsen, S. H. & Harlow, R. L. (1977). *Am. Crystallogr. Assoc. Abstr. Ser.* 2, **5**, HN5.

Smith, D. W. (1976). *Coord. Chem. Rev.* **21**, 93–158.

Udupa, M. R. & Krebs, B. (1979). *Inorg. Chim. Acta*, **33**, 241–244.

Vasilevsky, I., Rose, N. J., Willett, R. D. & Stenkamp, R. E. (1989). *Am. Crystallogr. Assoc. Abstr. Ser.* 2. **17**, PB91.

Vasilevsky, I., Stenkamp, R. E., Lingafelter, E. C., Schomaker, V., Willett, R. D. & Rose, N. J. (1989). *Inorg. Chem.* **28**, 2619–2623.

Von Dreele, R. B. & Harris, J. (1983). *Acta Cryst.* **C39**, 170–173.

Willett, R. D. (1987). *Inorg. Chem.* **26**, 3424–3426.

Willett, R. D. (1988). *Acta Cryst.* **B44**, 503–508.

Willett, R. D. & Geiser, U. (1986). *Inorg. Chem.* **25**, 4558–4561.

Willett, R. D., Haugen, J. A., Lesback, J. & Morrey, J. (1974). *Inorg. Chem.* **13**, 2510.

WILLETT, R. D. & LARSEN, M. L. (1971). *Inorg. Chim. Acta*, **5**, 175–179.
WILLETT, R. D., LILES, O. L. & MICHELSON, C. (1967). *Inorg. Chem.* **6**, 1885–1889.
WILLETT, R. D., PLACE, H. & MIDDLETON, M. (1988). *J. Am. Chem. Soc.* **110**, 8639–8649.
WILLETT, R. D. & WEST, D. X. (1987). *Acta Cryst.* C**43**, 2300–2303.

Acta Cryst. (1990). B**46**, 519–524

Structure of 3,4,5-Trihydroxybenzoic Acid Octyl Ester (Octyl Gallate) Dihydrate at 123 K. A Non-Mesogenic Amphiphilic Molecule

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Abstract

The crystal structure of 3,4,5-trihydroxybenzoic acid octyl ester (octyl gallate) dihydrate, $C_{15}H_{22}O_5.2H_2O$, is triclinic, $P\bar{1}$, with $a = 6\cdot617\,(1)$ [6·648 (1)], $b = 9\cdot956\,(2)$ [9·995 (3)], $c = 14\cdot088\,(4)$ [14·327 (7)] Å, $\alpha = 79\cdot08\,(2)$ [79·78 (3)], $\beta = 85\cdot58\,(3)$ [86·59 (4)], $\gamma = 70\cdot80\,(2)$ [70·99 (3)]°, $V = 860\cdot5$ Å^3, $Z = 2$, $D_x = 1\cdot229$ [1·183] g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0\cdot7093$ Å, $\mu = 0\cdot58$ cm^{-1}, $F(000) = 344$ at 123 K [290 K]. The structure was solved by direct methods and refined to $R(F^2) = 0\cdot059$ for 302 parameters and 3655 observations. The alkyl chain of the molecule is in the fully extended conformation. The molecular packing is head-to-head bilayer with interdigitizing alkyl chains. The gallate head groups are hydrogen bonded with the water molecules to form a strong system of intra- and intermolecular hydrogen bonds consisting of finite and infinite chains. The crystals undergo crystal-to-crystal phase transitions at 365 K on heating and at 333 K on cooling, but despite the molecular packing which is analogous to that of the mesogenic alkyl glycosides, there is no thermotropic liquid crystal phase prior to the formation of the isotropic liquid phases at 376 K. Similary, no lyotropic liquid crystal phases are observed at room temperature in contact with a mixture of water and propanediol in which the crystals are soluble.

Introduction

The amphiphilic carbohydrates such as the *n*-alkyl 1-*O*- or 1-*S*-pyranosides (Jeffrey, 1984, 1986), *n*-alkyl gluconamides (Pfannemüller, Welte, Chin & Goodby, 1986) and the 1-deoxy-1-(*N*-methylalkamido)-D-glucitols (MEGA-*N*) (Goodby, Marcus, Chin, Finn & Pfannemüller, 1988) are mesogens when the alkyl chain length exceeds seven C atoms. They also undergo one or more crystal-to-crystal phase transitions prior to forming thermotropic liquid crystals of the smectic type in the temperature range 333–463 K. When sufficiently soluble, they form lyotropic liquid crystals at room temperature with water or water–alcohol mixtures. The β-alkyl glucosides, especially *n*-octyl-β-D-glucopyranoside, and the glucitol derivatives (MEGA-8 to MEGA-12) are well known surfactants used in the crystallization of membrane proteins (Baron & Thompson, 1975; Hildreth, 1982). *n*-Octyl-1-*O*-β-glucopyranoside has also been shown to have a beneficial effect on the crystal growth of soluble proteins (McPherson, Koszelak, Axelrod, Day, Williams, Robinson, McGrath & Cascio, 1986).

The crystal structures have been determined for anhydrous *n*-octyl-1-*O*-α-D-glucopyranoside (van Koningsveld, Jansen & Straathof, 1988) and its hemi- and monohydrate (Jeffrey, Yeon & Abola, 1987), *n*-decyl-l-*O*-α-D-glucopyranoside (Moews & Knox, 1976), *n*-heptyl-*S*-α-D-mannopyranoside (Carter, Ruble & Jeffrey, 1982), *n*-octyl-l-*O*-β-D-xylopyranoside (Bhattacharjee & Jeffrey, 1983), *n*-octyl-D-gluconamide (Bhattacharjee, Jeffrey & Goodby, 1985; Zabel, Müller-Fahrnow, Hilgenfeld, Saenger, Pfannemüller, Enkelmann & Welte, 1986), 1-deoxy-(*N*-methylnonamido)-D-glucitol (Müller-Fahrnow, Zabel, Steifa & Hilgenfeld, 1986) and 1-deoxy-(*N*-methyloctanamido)- and 1-deoxy-(*N*-methylundecanamido)-D-glucitol (Jeffrey & Maluszynska, 1989).

Two types of molecular packing are observed: hydrogen-bonded 'head-to-head' bilayers with interdigitizing alkyl chains in the alkyl pyranosides and alkyl gluconamides, and 'head-to-tail' monolayers with interdigitizing alkyl chains in the glucitol alkamide derivatives. In both types of structure, the hydrogen bonding is extensive, linking the head

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