Crystal Structure and Nitrogen-15 NMR Solution Studies of a Purine Dication Copper(II) Chloro Complex

Einar Sletten, Jorunn Sletten and Nils Åge Frøystein

Department of Chemistry, University of Bergen, Allégt. 41, N-5007 Bergen, Norway

Sletten, E., Sletten, J. and Frøystein, N. Å., 1988. Crystal Structure and Nitrogen-15 NMR Solution Studies of a Purine Dication Copper(II) Chloro Complex. – Acta Chem. Scand., Ser. A 42: 413–420.

The structure of the copper(II) complex of purine, crystallized from concentrated HCl, has been determined by X-ray crystallographic methods. $[Cu_2(C_5H_6N_4)Cl_6]_n$, monoclinic, space group $P2_1/c$, $a = 12.724(1)$, $b = 6.104(2)$, $c = 17.223(1)$ Å, $\beta = 100.15(7)°$. The data were collected on a four-circle diffractometer using Mo$K\alpha$ radiation. The structure was solved by direct methods and refined to $R = 0.032$. The purine ligand is in the form of a dication, being protonated at N1, N7 and N9, with N3 as copper-binding site. One of the copper atoms has octahedral (4+2) coordination with four equatorial and one axial chlorine, the sixth position being occupied by purine, with Cu–N3 = 2.561 Å. The other copper atom has square-pyramidal coordination, all ligands being chlorine. The copper atoms are doubly bridged by two equatorially coordinated chlorines, and these dimers are linked through weak axial Cu–Cl bonds into a polymeric chain structure.

^{15}N NMR spectra of purine in 90% HCl solution show all nitrogen atoms except N3 to be protonated. The addition of Cu(II) ions to give a metal/purine ratio of 10^{-5} causes selective line broadening of the imidazole nitrogens only, indicating metal N7/N9 binding in solution. The small amount of metal-induced proton release from the imidazole ring is not sufficient to produce a detectable ^{15}N shift of the N3 signal.

Dedicated to Professor Otto Bastiansen on his 70th birthday

The purine molecule is one of the most exhaustively studied, biomolecules in nature. Its electronic structure has been investigated by practically all fundamental methods of quantum chemistry. The results of these calculations have been related to a multitude of experimentally determined physical properties, e.g. dipole moments, ionization potentials, electronic transitions, tautomerism and basicity.

Several of these parameters are closely related to the metal bonding properties of the pyrimidine and imidazole nitrogens in the purine ligand. The mechanism of metal binding is obviously related to which tautomer is predominant in solution at a particular pH (Scheme 1)[1a,b] and to what degree metal ions influence the tautomeric equilibrium.

In the crystal structure of a copper(II) complex with neutral purine ligands, a Cu–N7···N9–Cu bridging arrangement has been found.[2] A proton transfer from the imidazole ring to N1 has been induced by metallation (Scheme 2). A similar proton transfer has been observed for the cation of guanine (Scheme 3),[3] where addition of Cu^{2+} produces a shift from N9–H to N3–H. In this

Scheme 1.   p$K_a = -1.5$ p$K_a = 2.4$ p$K_a = 8.9$
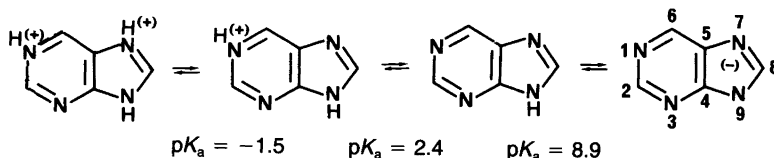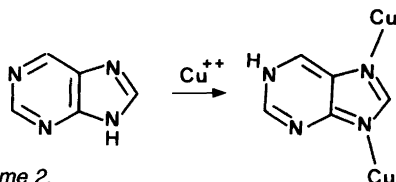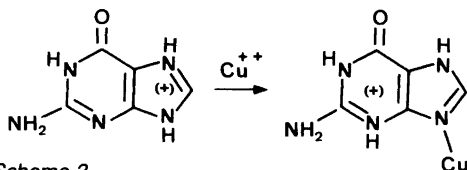
Scheme 2.

Scheme 3.

latter case the transfer may be caused by steric crowding of the N3 position by the amino group.

An efficient method for directly probing the environment of the bound nitrogen site is ^{15}N nuclear magnetic resonance. Over the past few years, the utility of ^{15}N NMR for detecting sites of nitrogen protonation and metallation has been amply demonstrated.[4]

In this paper we compare the results of a ^{15}N NMR study of interactions between Cu(II) ions and purine in 90 % HCl with the solid state structure of a Cu(II)−purine dication chloro complex.

Experimental

Materials. Purine was purchased from Sigma and used without further purification. The $CuCl_2$ used was purchased from Merck. The complex was synthesized by dissolving purine in aqueous HCl and adding an equimolecular amount of $CuCl_2$. The solution was left to slowly evaporate. After several weeks, crystals appeared in the strongly acidic solution.

Crystal data. $Cu_2Cl_6(C_5H_6N_4)$, F.W. 461.93, monoclinic, $P2_1/c$ (No. 14). Cell dimensions: $a = 12.724(1)$, $b = 6.104(2)$, $c = 17.223(1)$ Å, $\beta = 100.15(7)°$, $V = 1316.7(6)$ Å^3, $Z = 4$, $D_x = 2330$ kg m^{-3}, $\mu(MoK\alpha) = 4.452$ mm^{-1}.

Table 1. Final atomic parameters and their estimated standard deviations. Asterisks denote isotropic refinement. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter: $B_{eq} = 4/3 \Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i \cdot \mathbf{a}_j$.

Atom	x	y	z	$B_{eq}/Å^2$
Cu1	0.22950(4)	0.5795(1)	0.42815(3)	1.90(1)
Cu2	0.24582(4)	0.1018(1)	0.32700(3)	1.90(1)
Cl1	0.34285(8)	0.8656(2)	0.45618(6)	2.10(2)
Cl2	0.35253(9)	0.4070(2)	0.36066(6)	2.30(2)
Cl3	0.12175(8)	0.2907(2)	0.38209(7)	2.48(3)
Cl4	0.10917(8)	0.7143(2)	0.49730(6)	2.21(2)
Cl5	0.12252(9)	−0.1544(2)	0.28404(7)	3.30(3)
Cl6	0.35738(9)	−0.0241(2)	0.24768(6)	2.24(2)
N1	0.4434(3)	0.1429(7)	0.6217(2)	2.22(9)
N3	0.3031(3)	0.3468(6)	0.5493(2)	1.80(8)
N7	0.1872(3)	−0.0099(7)	0.6696(2)	2.39(9)
N9	0.1336(3)	0.2454(7)	0.5839(2)	2.35(9)
C2	0.4044(3)	0.2964(8)	0.5678(2)	2.1(1)
C4	0.2415(3)	0.2293(8)	0.5879(2)	1.52(9)
C5	0.2760(3)	0.0658(8)	0.6426(2)	1.78(9)
C6	0.3833(4)	0.0239(8)	0.6605(2)	2.2(1)
C8	0.1046(4)	0.0966(9)	0.6327(3)	2.7(1)
H1	0.505(3)	0.124(6)	0.625(2)	0.8(8)*
H2	0.459(3)	0.361(7)	0.542(2)	2.1(9)*
H6	0.409(3)	−0.66(7)	0.691(2)	1.6(9)*
H7	0.181(4)	−0.112(9)	0.699(3)	7(2)*
H8	0.036(4)	0.089(8)	0.640(3)	4(1)*
H9	0.095(3)	0.332(7)	0.555(2)	2.0(9)*

Crystallography. Cell parameters were determined at 20 °C from 25 centered reflections obtained on an Enraf-Nonius CAD-4 diffractometer. Intensity data were measured by the $\theta/2\theta$ scan technique. A total of 2085 unique reflections were recorded in the range $1° < \theta < 25°$. During data collection, three standard reflections were remeasured every 100 reflections; no indication of crystal deterioration was observed. The random error in any one reflection is calculated as $\sigma_I = [\sigma_c^2 + (0.02\ \sigma_c^2)^2]^{1/2}$. The usual corrections for Lorentz and polarization effects were made.

The structure was solved by direct methods and refined by full-matrix least-squares calculations. Hydrogen atoms were located in a Fourier difference map. After isotropic refinement an empirical absorption correction was carried out,[5] the maximum and minimum correction coefficients for F_{obs} obtained being 1.232 and 0.855, respectively. After absorption correction, non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. In the final cycles an extinction correction of the form $|F_{corr}| = |F_c|(1 + gI_c)^{-1}$ was included; g refined to 9.6×10^{-8}. The refinement converged at $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.032$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.032$, and with a standard deviation of an observation of unit weight $s = [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{var})]^{1/2} = 1.45$. The 1741 reflections with $|F_o| > 2\sigma_F$, where $\sigma_F = \sigma_I(ILp)^{-1/2}$, were included in the refinement with weight $w = 1/\sigma_F^2$. The scattering curves, with anomalous dispersion terms included, were those of Cromer and Waber.[6] All calculations were carried out on a PDP 11/55 computer using the Enraf-Nonius Structure Determination Programs.[7]

The refined coordinates and isotropic equivalent thermal parameters are listed in Table 1. Tables of anisotropic temperature factors have been deposited with the Cambridge Crystallographic Data Centre. Lists of structure factors may be obtained from one of the authors (J.S.) on request.

NMR. [15]NMR spectra were recorded on a Bruker AM-400 spectrometer at 40.55 MHz using 10 mm sample tubes. Typical spectral width was 8000 Hz with 32 K data points. The number of transients for the spectra in Figs. 1a, d were 3200 and in Figs. 1b, c 5000. To improve the signal-to-noise (S/N) ratio an exponential multiplication was applied to the FID, adding 4 Hz to the linewidth.

Different recording modes were adopted, depending on pH. At pH = 11 all four nitrogen atoms are deprotonated and a normal coupled spectrum was obtained with reasonable S/N ratio at 1 M concentration (Fig. 1a). At pH = 6 the tautomeric equilibrium N7–H/N9–H causes se-
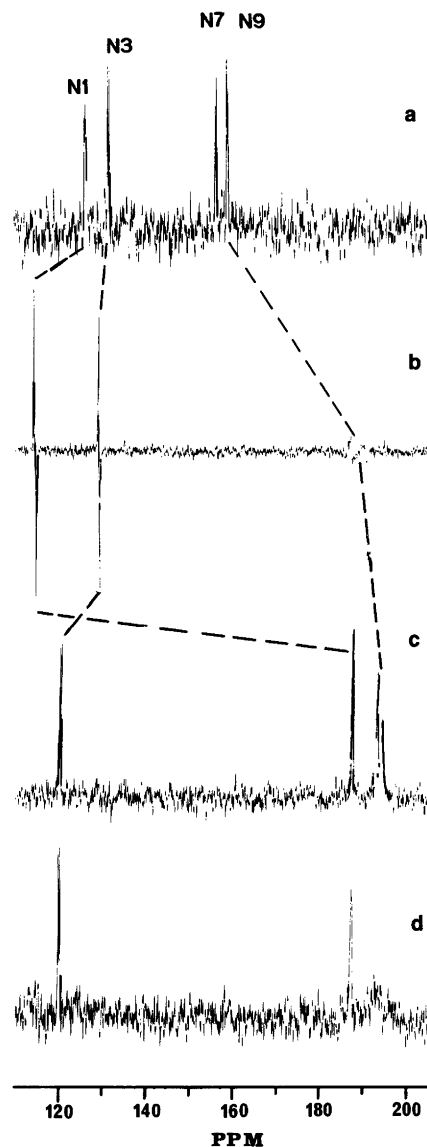

Fig. 1. The natural abundance 40.55 MHz ^{15}N NMR spectra of aqueous solutions of purine. (a) pH = 11, (b) INEPT, pH = 6, (c) 90 % HCl, (d) effect of added $CuCl_2$.
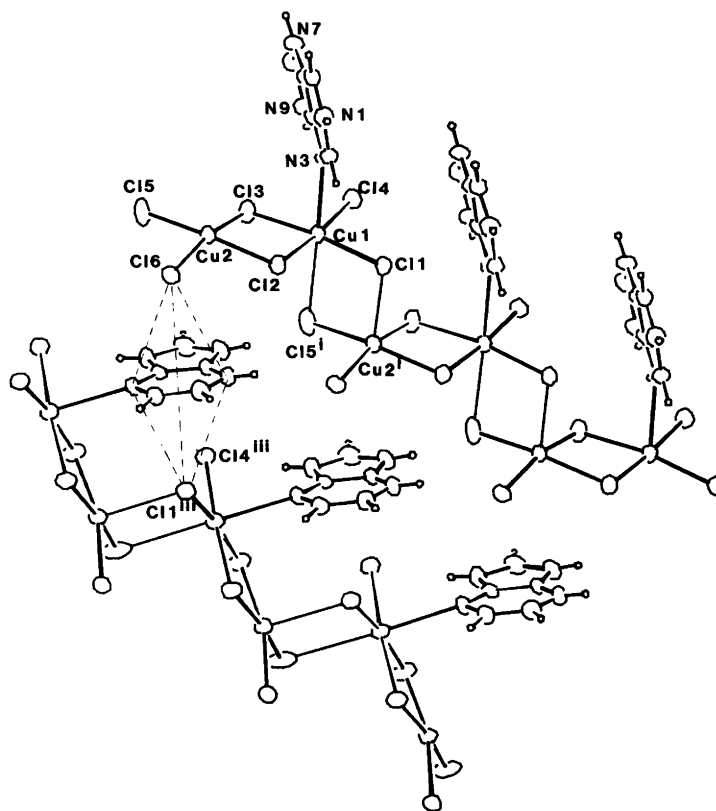
Fig. 2. Chains built of (Pu)Cu$_2$Cl$_6$ units. The units within a single chain are related by a unit cell translation along *b*. Two neighbouring chains related by the *c*-glide are shown.

Table 2. Bond distances with estimated standard deviations in parentheses.

Bond	Distance/Å	Bond	Distance/Å
Cu1—Cl1	2.262(2)	N3—C4	1.324(4)
Cu1—Cl2	2.356(2)	N7—C5	1.376(5)
Cu1—Cl3	2.288(1)	N7—C8	1.303(5)
Cu1—Cl4	2.254(2)	N9—C4	1.365(4)
Cu1—Cl5^{i,a}	3.076(1)	N9—C8	1.333(5)
Cu1—N3	2.561(3)	C4—C5	1.390(6)
Cu2—Cl1^{ii}	2.754(2)	C5—C6	1.371(5)
Cu2—Cl2	2.318(1)	N1—H1	0.78(3)
Cu2—Cl3	2.291(2)	N7—H7	0.82(5)
Cu2—Cl5	2.246(1)	N9—H9	0.83(4)
Cu2—Cl6	2.271(2)	C2—H2	0.97(3)
N1—C2	1.351(5)	C6—H6	0.79(4)
N1—C6	1.318(5)	C8—H8	0.90(4)
N3—C2	1.309(5)		

^{a}Symmetry operations: i: *x*, 1+*y*, *z*; ii: *x*, *y*−1, *z*.

Table 3. Bond angles (°) with estimated standard deviations in parentheses.

Angle		Angle	
Cl1—Cu1—Cl2	89.78(4)	Cl3—Cu2—Cl5	89.69(4)
Cl1—Cu1—Cl3	171.69(4)	Cl3—Cu2—Cl6	165.68(4)
Cl1—Cu1—Cl4	94.15(5)	Cl5—Cu2—Cl6	92.32(4)
Cl1—Cu1—Cl5[i,a]	86.54(3)	Cu1—Cl1—Cu2[i]	93.06(3)
Cl1—Cu1—N3	97.26(7)	Cu1—Cl2—Cu2	94.11(4)
Cl2—Cu1—Cl3	83.93(4)	Cu1—Cl3—Cu2	96.71(4)
Cl2—Cu1—Cl4	174.77(5)	Cu1[ii]—Cl5—Cu2	85.27(4)
Cl2—Cu1—Cl5[i]	94.35(3)	C2—N1—C6	123.8(4)
Cl2—Cu1—N3	88.54(7)	Cu1—N3—C2	122.1(3)
Cl3—Cu1—Cl4	92.47(4)	Cu1—N3—C4	123.0(2)
Cl3—Cu1—Cl5[i]	88.51(4)	C2—N3—C4	113.3(3)
Cl3—Cu1—N3	88.05(8)	C5—N7—C8	107.9(4)
Cl4—Cu1—Cl5[i]	89.33(3)	C4—N9—C8	107.9(4)
Cl4—Cu1—N3	87.54(7)	N1—C2—N3	123.8(4)
Cl5[i]—Cu1—N3	175.24(7)	N3—C4—N9	128.0(4)
Cl1[ii]—Cu2—Cl2	93.39(4)	N3—C4—C5	125.8(3)
Cl1[ii]—Cu2—Cl3	99.93(4)	N9—C4—C5	106.2(3)
Cl1[ii]—Cu2—Cl5	95.13(4)	N7—C5—C4	106.9(3)
Cl1[ii]—Cu2—Cl6	94.02(3)	N7—C5—C6	135.0(4)
Cl2—Cu2—Cl3	84.73(4)	C4—C5—C6	118.0(4)
Cl2—Cu2—Cl5	170.51(5)	N1—C6—C5	115.3(4)
Cl2—Cu2—Cl6	91.25(4)	N7—C8—N9	111.0(4)

[a]Symmetry operations: i: x, $1+y$, z; ii: x, $y-1$, z.

vere line broadening due to rapid exchange. To alleviate this problem an INEPT sequence was used.[8] Fig. 1b shows the spectrum with doublets in antiphase. In a solution in 90 % HCl the decoupler was difficult to tune properly owing to the large ionic strength. Thus, only a coupled spectrum was recorded for the acidic solution.

Aliquots of 1 M CuCl$_2$ were added to an acidic 2 M purine solution. The spectrum in Fig. 1d corresponds to a metal/purine ratio of 10^{-5}. The spectra are referenced on a relative scale which corresponds to that published for purine in sulfuric acid.[9] For the present study this is adequate since only the relative shifts between the different nitrogen atoms are required. All spectra were recorded at 298 K.

Results

Crystallographic data. The structure is shown in Fig. 2, and bond distances and bond angles are listed in Tables 2 and 3. Each asymmetric unit consists of a $[Cu_2Cl_6]^{2-}$ moiety with the doubly protonated purine axially coordinated to one of

the Cu atoms at N3. These binuclear chloro-bridged units are linked through long out-of-plane Cu—Cl bonds to polymeric chains running along the crystallographic *b*-axis. Cu1 is (4+2) coordinated, with four short equatorial bonds to chlorine atoms and two long axial bonds, one to N3 and the other to Cl5($x,1+y,z$). The coordination at Cu2 is square-pyramidal, with four short equatorial Cu—Cl bonds and a weaker axial bond to Cl1($x,-1+y,z$). The sixth position
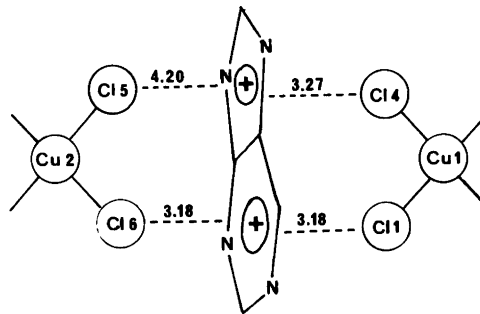

Fig. 3. Chlorine—purine interaction.

Table 4. Hydrogen bonds.

Donor	Acceptor	D---A/Å	H---A/Å	∠D−H---A/°
N1	Cl1(1−x, 1−y, 1−z)	3.238(3)	2.58(3)	142(3)
N1	Cl6(1−x, −y, 1−z)	3.162(3)	2.62(3)	128(3)
N7	Cl5(x, −1/2−y, 1/2+z)	3.054(4)	2.25(5)	165(5)
N9	Cl4(−x, 1−y, 1−z)	3.168(3)	2.61(4)	126(3)
N9	Cl4(x, y, z)	3.218(4)	2.56(9)	138(3)

is screened by the proximity of an imidazole ring in a symmetry-related chain, Cu2···N7 (x,1/2−y,z−1/2) being 3.66 Å.

Willett[10] classifies polymeric Cu(II)−halogen complexes as planar, twisted or bifolded according to the dihedral angles τ and σ at Cu. In the present structure the dimers are essentially planar, the twist angles at Cu1 and Cu2 being $\tau_1 = 6.8°$ and $\tau_2 = 12.5°$, respectively, and the bifold angles being $\sigma_1 = 5.9°$ and $\sigma_2 = 4.1°$.

The Cu···Cu distance within the dimer is 3.422 (1) Å, the bridging angles (φ) at Cl2 and Cl3 being 94.1° and 96.7°, respectively. The distance Cu1···Cu2(x,1+y,z) between neighbouring dimers in the chain is 3.656(1) Å.

The purine molecule is approximately planar, the maximum atomic deviation from the plane being 0.026 Å; the dihedral angle between the purine plane and the least-squares plane through the atoms constituting the $[Cu_2Cl_6]^{2-}$ unit is 75°. The purine ring is "sandwiched" between four chlorine atoms (Figs. 2 and 3). Cl1 and Cl6 are positioned on either side of the centre of the pyrimidine ring. Cl4 is positioned above the imidazole ring, while Cl5 is displaced somewhat to the side of the ring.

The chains are held together through interchain hydrogen bonds. All the potential hydrogen-bonding donor sites on purine are involved, and the terminal chlorine atoms in $[Cu_2Cl_6]^{2-}$ are acceptors. H1 and H9 are bifurcated. Distances and angles of hydrogen bonds are listed in Table 4. Packing of chains in the crystal is depicted in the stereo plot of Fig. 4.

NMR data. Natural-abundance ^{15}N NMR spectra of purine at basic, neutral and acidic pH are shown in Figs. 1a, b, c. The spectra are coupled, showing ^{15}N, ^1H spin−spin splitting. The assignments of the N1, N3, N7 and N9 resonances correspond to those published by Schumacher and Günther.[9] At pH = 11 the purine molecule is in the mono-anionic form with all four nitrogen atoms unprotonated. In neutral solution the N7/N9 signals are severely broadened due to tautomeric N7−H/N9−H exchange. In a solution in
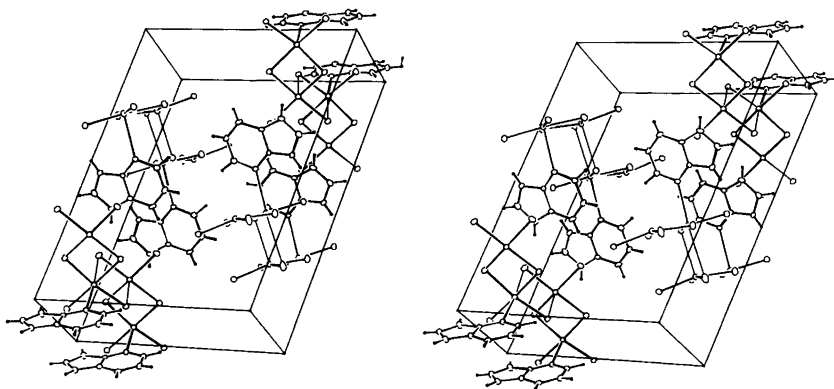

Fig. 4. Stereo plot showing the packing in the crystal. The a-axis runs left to right, and the c-axis top to bottom.

90 % HCl the purine molecule is a dication, N1, N7 and N9 being fully protonated, preventing any exchange broadening.

Addition of $CuCl_2$ to the acidic purine solution produces a selective, paramagnetic line-broadening of the imidazole nitrogens N7 and N9 (Fig. 1d). The pyrimidine nitrogens N1 and N3 show no sign of paramagnetic influence. Furthermore, there are no significant ^{15}N shift changes induced by the addition of metal ions. From the acidic copper–purine solution a reddish-brown precipitate was formed overnight. The ^{15}N spectra recorded before and after precipitation appeared to be qualitatively the same.

Discussion

Metal coordination in the crystal. The chains formed by approximately planar $[Cu_2Cl_6]^{2-}$ dimers joined by relatively weak out-of-plane Cu–Cl bonds, are similar to those observed in the trichlorocuprate(II) salts with ethanolammonium,[10] dimethylammonium,[11] lithium,[12] potassium[13] and ammonium[13] cations. In these compounds, examples of 6-coordinated as well as 5-coordinated tetragonal pyramidal copper are found, the bridging Cl atoms within the dimers being in each case situated in equatorial positions.

Other types of doubly chlorine-bridged Cu dimers comprise tetragonal pyramidal coordination with bridging chlorine atoms in axial and equatorial positions,[14] and trigonal bipyramidal geometries in which the dimers share an equator-to-apex edge.[15] This latter type is found in a copper complex of monoprotonated guanine.[3]

The various types of chloro-bridged Cu(II) dimers and polymers have been shown to exhibit interesting magnetic behaviour.[10,16,17] Structural factors assumed to influence exchange coupling are: the role of ligand-to-metal charge-transfer energies and the effect of distortion of the $Cu_2X_6^{2-}$ dimer from planarity.[10] In this context the electronic interaction with axial Y ligands, e.g. purine, may be of importance.

A comparison between structural parameters in the purine complex and a closely related ethanolammonium complex, $(EOA)_2Cu_2Cl_6$,[10] shows remarkable consistency in the dimer dimensions. Average $Cu-Cl_{eq} = 2.288$ Å and 2.286 Å in $(Pu)Cu_2Cl_6$ and $(EOA)_2Cu_2Cl_6$, respectively. The average bridging angle at Cl, φ, is 95.4° in (Pu) Cu_2Cl_6 and 95.9° in $(EOA)_2Cu_2Cl_6$. The differ-

ences in geometry appear in the axial bonding, wherein the purine complex Cu–N = 2.561 Å is relatively short and exerts a strong *trans* effect on the axial chlorine ligand: $Cu-Cl_{ax} = 3.076$ Å. The relatively long $Cu-O_{ax}$ of 3.128 Å in $(EOA)_2$ Cu_2Cl_6 exhibits no *trans* effect, the axial chlorine distances of 2.739 Å being comparable to $Cu-Cl_{ax}$ for the pentacoordinated copper in (Pu) Cu_2Cl_6.

A weak antiferromagnetic interaction is found in $(EOA)_2Cu_2Cl_6$.[10] The structural similarities between the ethanolammonium and the purine complexes suggest comparable magnetic properties. A susceptibility study of the latter might reveal whether the indicated charge-transfer between chlorine atoms and the purine ligand has any effect on the magnetic properties.

Metal coordination in solution. Previously, selective paramagnetic line broadening of ^{15}N resonances has not been utilized for determination of ligand binding sites. The spectrum recorded following addition of Cu(II) ions to the acidic purine solution (Fig. 1d) clearly indicates that the metal ions are attached to the imidazole nitrogens N7/N9 rather than to the pyrimidine nitrogen N3. At a metal/ligand ratio of 10^{-5} there is no indication of interaction between Cu(II) and N3.

Partial protonation of N7/N9 is seen to be accompanied by a large upfield shift, viz. 33–34 ppm (Figs. 1a, b). The spectrum obtained following reduction in pH (90 % HCl) clearly indicates complete N1 protonation (Fig. 1c). At this acid concentration sharp N7/N9 resonances are observed, which are indicative of a change from tautomeric exchange to almost complete N7/N9 protonation. However, in this scheme a somewhat larger protonation-induced upfield shift might be expected. Protonation of N3 as observed in a solution of SbF_5/FSO_3H produces an upfield shift of ca. 60 ppm.[18] No evidence of a metal-induced N7–H/N9–H → N3–H tautomeric shift is observed. However, this is not surprising considering the extremely low metal-to-ligand ratio used in the line broadening experiment. Only a minute fraction of protons is expelled from the imidazole ring due to metal binding. This proton release is not sufficient to produce a detectable ^{15}N shift.

The shift of metal binding site between solution and the crystalline state is difficult to rationalize. In the copper(II) complex of protonated

guanine[3] a N9−H → N3−H transfer is induced by the metal ion. In a neutral copper−purine complex a similar proton transfer from imidazole is observed.[2]

In the competition between protons and metal ions for the most basic ligand site, the metal ion is generally seen to prevail. However, in the present solid state structure this general rule is not obeyed, presumably due to the presence of a stabilizing copper−chloro matrix in the crystal, exerting a strong influence on the overall coordination geometry. In particular one may notice that the purine ligand is "sandwiched" between chlorine atoms, providing an unusual charge-transfer stabilization (Figs. 2 and 3). A similar strong attraction between chlorine and the π-electron system of the pyrimidine ring has also been observed in the Cu(II) complex of protonated guanine.[3] Streitwiser and Smith have introduced the concept of "inverse sandwiches" to describe compounds where an electron-rich central atom interacts with cationic π-ring ligands.[19] In the present structure an analogous electronic configuration is established, but the geometry is inverted, the electron-deficient π-ring being sandwiched between electron-rich atoms.

References

1. (a) Schumacher, M. and Günther, H. *J. Am. Chem. Soc. 104* (1982) 4167; (b) Albert, A. and Brown, D. J. *J. Chem. Soc.* (1954) 2060.
2. Vestues, P. I. and Sletten, E. *Inorg. Chim. Acta 52* (1981) 269.
3. Carrabine, J. A. and Sundaralingam, M. *J. Am. Chem. Soc. 92* (1970) 369.
4. Buchanan, G. W. and Bell, M. G. *Magn. Reson. Chem. 25* (1987) 864.
5. Walker, N. and Stuart, D. *Acta Crystallogr., Sect. A 39* (1983) 159.
6. Cromer, D. T. and Waber, J. T. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1974, Vol. IV, p. 99, Table 2.2 B.
7. Frez, B. A. *The SDP-User's Guide,* Enraf-Nonius, Delft, The Netherlands 1983.
8. Morris, G. A. and Freeman, R. *J. Am. Chem. Soc. 101* (1979) 760.
9. Schumacher, M. and Günther, H. *Chem. Ber. 116* (1983) 2001.
10. Scott, B. and Willett, R. *Inorg. Chim. Acta 141* (1988) 193.
11. Willett, R. D. *J. Chem. Phys. 44* (1966) 39.
12. Vossos, P. H., Jennings, L. D. and Rundle, R. E. *J. Chem. Phys. 32* (1960) 1590.
13. Willett, R. D., Dwiggings, C., Jr., Kruh, R. F. and Rundle, R. E. *J. Chem. Phys. 38* (1963) 2429.
14. Marsh, W. E., Patel, K. C., Hatfield, W. E. and Hodgson, D. J. *Inorg. Chem. 22* (1983) 511.
15. Hodgson, D. J., Hale, P. K. and Hatfield, W. E. *Inorg. Chem. 10* (1971) 1061.
16. Hatfield, W. E. In: Willett, R. D., Gratteschi, D. and Kahn, O., Eds, *Magneto-Structural Correlations in Exchange Coupled Systems, NATO ASI Series C: 140* (1985) 555.
17. Willett, R. D. In: Willett, R. D., Gratteschi, D. and Kahn, O., Eds, *Magneto-Structural Correlations in Exchange Coupled Systems, NATO ASI Series C: 140* (1985) 389.
18. Benedikt, G. M., Dissertation, Case Western Reserve Univ. 1979; *Diss. Abstr. Int. 40* (1980) 5689-B.
19. Streitwiser, A. and Smith, K. A. *J. Mol. Struct. 163* (1988) 259.