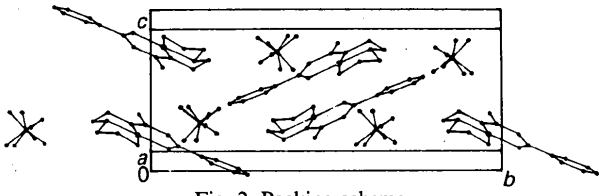

Fig. 2. Packing scheme.

for C12 to 0·004 (4) Å for C13. The O atoms of the perchlorate anion (O11, O22, O33 and O44) are disordered. The *R*-factor value decreased for a model in which each O atom assumes two positions, *A* and *B*, with refined occupancy factors. According to this model the ClO_4 unit apparently oscillates between these two states in the structure.

Fig. 2 shows the crystal packing. No hydrogen bonds are indicated in the structure, which is held together predominantly by electrostatic interactions.

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Synthesis and Structure of Cytosine Dichloride Cuprate: Direct Binding of Copper to Cytosine

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Abstract. Dichlorobis(cytosine)copper(II), $[CuCl_2(C_4H_5N_3O)_2]$, $M_r = 356{\cdot}65$, monoclinic, $P2_1/n$, $a = 8{\cdot}399$ (2), $b = 13{\cdot}773$ (2), $c = 10{\cdot}775$ (2) Å, $\beta = 90{\cdot}8$ (2)°, $V = 1246{\cdot}3$ (9) Å^3, $Z = 4$, $D_x = 1{\cdot}901$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 2{\cdot}195$ mm^{-1}, $F(000) = 716$, $T = 298$ K, $R = 0{\cdot}032$, $wR = 0{\cdot}037$ for 2313 reflections $> 2\sigma(F)$. The crystal structure of the title compound consists of two crystallographically independent cytosine molecules attached together through the direct bonding of a Cu^{2+} ion with two N atoms of the pyrimidine rings. In addition to the N atoms, the Cu ions are coordinated to two Cl atoms forming approximately a square-planar environment. The bond distances of Cu to Cl(1), Cl(2), N(3) and N(3′) atoms are 2·299 (1), 2·267 (1), 1·985 (4) and 1·996 (3) Å, respectively. Packing of the Cyt(I)–$CuCl_2$–Cyt(II) complex in the crystal is ensured by an extensive extramolecular N—H···Cl and N—H···O network. Hydrogen bonds involving Cl, O and H atoms of the neighboring Cyt(I) and Cyt(II) induce a slight distortion in Cu—Cl, C=O distances but do not significantly affect intramolecular bond lengths and angles in the cytosine rings and their flatness.

Introduction. It is established that the stability of the DNA structure is affected by the interaction of a 3*d* transition metal with polynucleic acids by binding to their phosphate groups and/or to their base moieties. Thus, it was reported that Mg^{2+}, Co^{2+}, Ba^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} act as stabilizers of the calf-thymus DNA macromolecule while Cu^{2+} has a reverse effect (Eichhorn, 1962). The binding of metal ions to biomolecules is therefore of interest in helping to understand this mechanism.

Selective binding of an alkaline ion to a GC-rich DNA fragment was first suggested by kinetic studies (Eichhorn & Shin, 1968) and later confirmed by

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Table 1. *Final atomic coordinates and equivalent isotropic thermal factors*

Standard deviations are in parentheses.

$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}/B_{iso}(Å^2)
Cu	0·56515 (6)	0·38488 (5)	0·69498 (6)	2·28 (1)
Cl(1)	0·5393 (1)	0·3591 (1)	0·5006 (1)	3·01 (3)
Cl(2)	0·6649 (2)	0·4495 (1)	0·8733 (1)	3·13 (3)
N(1)	1·0167 (4)	0·3654 (3)	0·5509 (4)	2·7 (1)
C(2)	0·8731 (5)	0·3998 (4)	0·5957 (4)	2·5 (1)
N(3)	0·7755 (4)	0·3318 (3)	0·6478 (4)	2·30 (9)
C(4)	0·8162 (6)	0·2371 (4)	0·6564 (4)	2·6 (1)
C(5)	0·9665 (6)	0·2035 (4)	0·6068 (5)	2·9 (1)
C(6)	1·0584 (6)	0·2725 (4)	0·5543 (5)	2·9 (1)
O(2)	0·8353 (4)	0·4853 (3)	0·5894 (3)	3·33 (9)
N(4)	0·7181 (5)	0·1742 (4)	0·7096 (4)	3·3 (1)
N(1′)	0·1621 (5)	0·3055 (3)	0·8754 (4)	2·8 (1)
C(2′)	0·3040 (5)	0·3103 (4)	0·8108 (4)	2·4 (1)
N(3′)	0·3450 (4)	0·3959 (3)	0·7608 (3)	2·11 (9)
C(4′)	0·2497 (6)	0·4744 (4)	0·7674 (5)	2·4 (1)
C(5′)	0·1048 (6)	0·4693 (5)	0·8361 (5)	3·1 (1)
C(6′)	0·0680 (5)	0·3852 (5)	0·8872 (5)	2·9 (1)
O(2′)	0·3886 (4)	0·2354 (3)	0·7984 (3)	2·80 (8)
N(4′)	0·2907 (5)	0·5547 (4)	0·7089 (4)	3·4 (1)

X-ray analysis of the structure of a cytosine calcium chloride complex in which the alkali ion is found directly coordinated to the cytosine base (Ogawa, Kumihashi, Tomita & Shirotake, 1980). However, direct cytosine–metal–cytosine binding is rather an exceptional case. Previous structural investigations of 3*d* metal cytosine complexes, $[C_4H_6N_3O_2]_2[ZnCl_4].(C_4H_5N_3O)$ (Fujinami, Ogawa, Arakawa, Shirotake, Fujii & Tomita, 1979) and cytosine tetrachlorocuprate (Ogawa, Nishitani, Fujiwara, Shirotake & Tomita, 1979), indicated no direct interaction between metal and pyrimidine base.

Recently we have succeeded in isolating a new copper complex in which direct binding of the Cu^{2+} ion to cytosine molecules has been evidenced by X-ray study. We report here its crystal structure. (See also *Note from the authors*.)

Experimental. A solution of 1:2 of $CuCl_2.2H_2O$ and cytosine was stirred in an aqueous solution, slightly acidified by HCl, at room temperature for 2h and then heated overnight at 323 K. A very slow evaporation at ambient temperature of this mixture produces three visually different types of crystals: (*a*) plate-like transparent crystals, (*b*) green-brown crystals and, (*c*), in addition to two dominant previous species some tiny blue crystals. Replacing HCl by ethanol seems to favor the growth of the blue species. Preliminary X-ray studies permitted one to identify the (*a*) and (*b*) species as cytosine monohydrate (Weber, Craven & McMullan, 1980) and dicytosine tetrachlorocuprate (Ogawa *et al.*, 1979), respectively. The blue crystals, (*c*), generally tend to be badly twinned or exhibit large mosaic spread. Several crystals were however picked up and some satisfactory single crystals, checked by precession-camera photographs, were obtained for X-ray data collection.

Nicolet *P*3 diffractometer, crystal size 0·09 × 0·04 × 0·12 mm, random orientation, no absorption correction, ω scan; 2° min^{-1}, scan range = 1·1°, $2\theta_{max}$ = 35°, $-8 \le h \le 8$, $-12 \le k \le 12$, $-10 \le l \le 10$. Unit-cell parameters from 24 reflections with $9 \le 2\theta \le 24°$. 3352 reflections measured, averaged to 2711 unique reflections of which $2313 \ge 2\sigma(F)$, internal agreement factors were 3·4 and 4·3 % for observed and all measured reflections, respectively. Three standard reflections, no intensity variation.

The structure was solved by direct methods by application of the *MULTAN* program (Main, Fiske, Hull, Lessinger, Germain, Delclercq & Woolfson, 1980), which revealed the position of Cu and two Cl atoms and part of the cytosine rings. The remaining non-H atoms were located by successive refinements alternated with difference Fourier syntheses. Final difference maps based on the last anisotropic refinement including Cu, Cl, O, N and C atoms successfully revealed the presence of 10 H atoms.

Five final cycles including all atoms without any constraints on H-atom positions showed significant improvement in *R*, *wR* and *S* factors, 3·2, 3·7% and 1·1 respectively (compared to 3·9, 4·2% and 1·2 for hydrogen-excluded model). Function minimized $\sum w|F_o - |KF_c||^2$, $w[\sigma^2(F_o) + 0{\cdot}01|F_o|^2]^{-1}$; *f*, *f′* and *f″* from *International Tables for X-ray Crystallography* (1974). $(\Delta/\sigma)_{max} = 0{\cdot}03$, $|\Delta\rho|_{max} = 0{\cdot}3$ e Å^{-3} on final difference Fourier map. *SDP-Plus* package of programs was used on MicroVAX II for structure solution and refinement (Frenz, 1983).

Discussion. Table 1 contains final positional parameters while selected interatomic distances, bond angles and hydrogen bonds appear in Table 2.* The complex of Cyt/copper and its molecular packing are depicted in Figs. 1 and 2, respectively.

Unlike $[C_4H_6N_3O].\frac{1}{2}[ZnCl_4].(C_4H_5N_3O)$ (Fujinami *et al.*, 1979) and $[C_4H_6N_3O]_2.[CuCl_4]$ (Ogawa *et al.*, 1979), the Cu^{2+} ion in the title compound is directly coordinated to the ring N(3) and N(3′) of two crystallographically independent cytosine molecules. Two additional Cl atoms are also found bonded to the Cu^{2+} ion completing a rough square-planar coordination around the copper site (Fig. 1).

As a result of direct Cu^{2+} ion binding with the pyrimidine rings the molecular structure of $[CuCl_2(C_4H_5N_3O)_2]$ consists of Cyt(I)–$CuCl_2$–Cyt(II)

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52705 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond distances* (Å) *and angles* (°)

Standard deviations are in parentheses.

$CuCl_2N_2$ group			
Cu—Cl(1)	2·299 (1)	Cl(1)—Cu—Cl(2)	165·74 (6)
Cu—Cl(2)	2·267 (1)	Cl(1)—Cu—N(3)	92·17 (12)
Cu—N(3)	1·985 (4)	Cl(1)—Cu—N(3′)	89·66 (12)
Cu—N(3′)	1·996 (3)	Cl(2)—Cu—N(3)	92·40 (12)
Cl(2)—Cu—N(3′)	90·14 (12)	N(3)—Cu—N(3′)	162·11 (16)
Cyt(I)		Cyt(II)	
N(3)—C(2)	1·369 (6)	N(3′)—C(2′)	1·343 (7)
N(3)—C(4)	1·352 (7)	N(3′)—C(4′)	1·348 (7)
C(4)—C(5)	1·446 (7)	C(4′)—C(5′)	1·435 (7)
C(5)—C(6)	1·357 (8)	C(5′)—C(6′)	1·321 (8)
C(6)—N(1)	1·327 (7)	C(6′)—N(1′)	1·359 (7)
N(1)—C(2)	1·389 (6)	N(1′)—C(2′)	1·391 (6)
N(4)—C(4)	1·331 (7)	N(4′)—C(4′)	1·321 (7)
O(2′)—C(2′)	1·221 (7)	O(2′)—C(2′)	1·260 (6)
C(2)—N(3)—C(4)	122·4 (4)	C(2′)—N(3′)—C(4′)	121·8 (4)
C(2)—N(3)—Cu	113·2 (3)	C(2′)—N(3′)—Cu	108·7 (3)
C(4)—N(3)—Cu	124·2 (3)	C(4′)—N(3′)—Cu	129·3 (3)
N(3)—C(2)—N(1)	115·9 (4)	N(3′)—C(2′)—N(1′)	117·9 (4)
C(2)—N(1)—C(6)	123·3 (4)	C(2′)—N(1′)—C(6′)	120·8 (4)
N(1)—C(6)—C(5)	122·2 (5)	N(1′)—C(6′)—C(5′)	122·0 (5)
C(6)—C(5)—C(4)	115·7 (5)	C(6′)—C(5′)—C(4′)	117·5 (5)
N(3)—C(4)—C(5)	120·4 (4)	N(3′)—C(4′)—C(5′)	119·8 (4)
N(3)—C(4)—N(4)	120·0 (4)	N(3′)—C(4′)—N(4′)	119·2 (5)
C(5)—C(4)—N(4)	119·8 (5)	C(5′)—C(4′)—N(4′)	121·0 (5)

X—H···*Y*	*X*—H(Å)	*X*···*Y*(Å)	*X*—H···*Y*(°)
N(4′)—H(2N4′)···Cl(1)	0·84 (5)	2·938 (5)	141 (5)
N(4′)—H(1N4′)···O(2′)	0·93 (5)	2·909 (6)	173 (4)
N(4)—H(1N4)···O(2′)	0·78 (5)	3·059 (5)	162 (5)
N(1′)—H(2N4′)···Cl(1)	0·88 (7)	2·840 (5)	170 (6)
N(4)—H(2N4)···Cl(2)	1·01 (7)	3·371 (5)	147 (5)
N(1)—H(N1)···O(2)	0·71 (4)	2·848 (5)	168 (4)
C(6′)—H(C6′)	0·93 (4)	No bond	
C(6)—H(C6)	0·90 (5)	No bond	
C(5′)—H(C5′)	0·90 (5)	No bond	
C(5)—H(C5)	0·97 (6)	No bond	

entities which are attached together by H bonding to form a three-dimensional network of Cyt(I)–Cu–Cyt(II). Two types of relatively strong H bonds are observed (Table 2): N—H···O and N—H···Cl, considering a strong N—H···Cl bond as one where the interatomic distance between a Cl and an H atom is less than 2·6 Å (Hamilton & Ibers, 1968). All Cl atoms are participating in H bonds but not in the same way: Cl(1) accepts two H bonds from N(1′) and N(4′) donors while Cl(2) has only one contact with N(4). This results in a slight lengthening of the Cu—Cl(1) bond with respect to that of Cu—Cl(2). In a similar manner, the discrepancy in carbonyl bonds, C(2)═O(2) and C(2′)═O(2′), may be attributed to the same origin. It is worth noting that the two nitrogens, N(3) and N(3′), which are not involved in any H bonds are nearly equidistant from the Cu^{2+} ion.

H bonding seems have little effect on the geometry of the two cytosine molecules. As listed in Table 2, the C—C and C—N intraring distances are similar for Cyt(I) and Cyt(II) and are in agreement with those observed for the neutral deuterated cytosine monohydrate (Weber *et al.*, 1980). The cytosine ring including the exocyclic O(2) and amino N(4) atoms is practically planar with a maximum deviation from the least-squares plane of less than 0·03 Å except for N(3) and N(4) (0·04 and 0·05 Å, respectively). The angle between the two cytosine planes is 7·3 (6)°, close to the value found in a cytosine calcium polymer (Ogawa *et al.*, 1980).

According to previous structural studies, direct binding of a 3*d* transition metal to base moiety rings is rather unusual, it may be a result of competition between H bonds to form direct Cyt–Cyt pairing or a Cu—Cyt bond. In the case of copper/cytosine a neutral medium seems to favor the direct Cu–cytosine chelation, other syntheses extended to thymine and guanine bases are under way to verify this assumption.

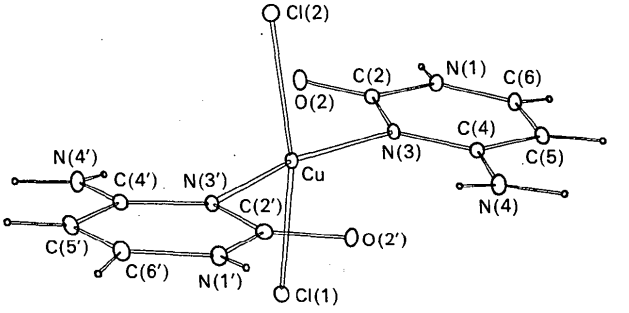

Fig. 1. *ORTEP* (Johnson, 1965) plot of $[CuCl_2(C_4H_5N_3O)_2]$ complex.

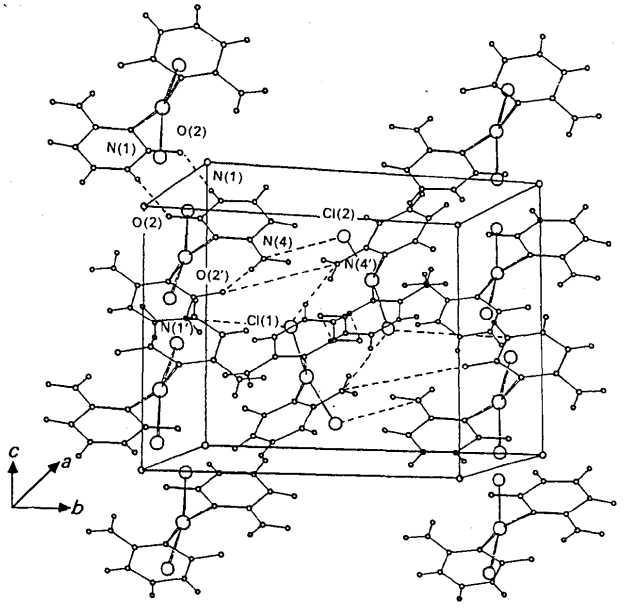

Fig. 2. Packing of molecular structure of $[CuCl_2(C_4H_5N_3O)_2]$, viewed nearly along the *a* axis.

Note from the authors: After this manuscript was ready for publication we realized that the crude structure of this compound was actually solved by Sundaralingam & Carrabine (1971), from photographic data. The H-atom locations in this referenced work were unknown. Therefore we think it is useful to publish this new and more precisely determined structure in which the H-atom positions are determined.

The authors wish to thank Dr Bagieu in our Laboratory for her help in tracing the bibliographic data related to the interaction of metal ions with nucleic acids and their constituents.

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Structure of the Silver Salt of *N*-(*p*-Aminophenylsulfonyl)acetamide (Silver Sulfacetamide)

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Abstract. $Ag^+.C_8H_9N_2O_3S^-$, $M_r = 321{\cdot}1$, monoclinic, $P2_1/n$, $a = 5{\cdot}849\ (2)$, $b = 7{\cdot}720\ (5)$, $c = 22{\cdot}573\ (5)$ Å, $\beta = 83{\cdot}16\ (1)°$, $V = 1012\ (1)$ Å^3, $Z = 4$, $D_x = 2{\cdot}107$ g cm^{-1}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 21{\cdot}57$ cm^{-1}, $T = 295$ K, $F(000) = 632$, final $R = 0{\cdot}0413$ for 1522 observed reflections. Each Ag atom is coordinated to two O atoms and one N atom of two sulfacetamide molecules with Ag—O distances 2·408 (4) and 2·336 (5) Å and Ag—N distance 2·218 (5) Å. Thus a silver sulfacetamide polymer is formed along **a** showing Ag–Ag interaction [3·102 (1) Å] about alternate centres of inversion. The molecules are linked by N—H···O-type hydrogen bonds.

Introduction. Sulfacetamide, a highly soluble sulfonamide which does not cause crystalluria, and its sodium salt are extensively used in opthalmic infections, giving solutions which are non-irritating to the delicate tissues of the eye. Crystal structures of sulfacetamide (Basak, Mazumdar & Chaudhuri, 1982) and sulfacetamide sodium monohydrate (Ghosh, Basak & Mazumdar, 1987) have already been reported.

Sulfonamides are selective inhibitors of animal and bacterial carbonic anhydrase and this is partially due to the ionization of this molecule by deprotonation at the amido nitrogen, upon coordination to the metalloenzyme. The present structural analysis was undertaken in order to study the complex as a model sulfonamide–metal ion complex and also to see the structural changes in the ligand as a result of coordination to the metal.

Experimental. Reddish square-shaped plate-like crystals obtained by slow evaporation from a 10% ammonia solution at room temperature in the dark. Crystal size 0·15 × 0·25 × 0·40 mm, $\omega/2\theta$ scan, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, lattice parameters from least-squares fit with 25 reflections up to $2\theta = 50°$, three standard reflections ($\bar{2}\bar{2}4$, $22\bar{2}$, $2,\bar{1},10$) moni-

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