Synthesis, Characterization and Unusual Crystal Structures of two Cytosine Cadmium(II) Chloride Compounds†

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Two cytosine (Cyt) cadmium(II) chloride compounds have been prepared and their crystal structures determined: $[Cd(Cyt)_3Cl][Cd(Cyt)Cl_3]\cdot H_2O$ **1** and $[\{CdCl_2(H_2O)_2\cdot 2Cyt\}_n]$ **2**. Compound **1** is triclinic, space group $P\bar{1}$, $Z = 2$, $a = 7.243(2)$, $b = 13.860(3)$, $c = 14.113(3)$ Å, $\alpha = 95.07(2)$, $\beta = 90.79(2)$, $\gamma = 104.52(2)°$, $R = 0.027$; compound **2** is monoclinic, space group $C2/c$, $Z = 4$, $a = 22.355(6)$, $b = 3.853(1)$, $c = 18.645(5)$ Å, $\beta = 115.43(2)°$, $R = 0.038$. Both crystal structures are rather unusual. Compound **1** consists of two different ionic moieties, in both of which the cytosine molecules co-ordinate through N(3) and more weakly through O(2). Thus, taking into account only the stronger N(3) interaction, the cadmium(II) ions have a distorted-tetrahedral arrangement. When also the weaker interactions with the carbonyl oxygens are considered, in the first moiety the metal ion is seven- and in the second it is five-co-ordinated. Compound **2** is not a cytosine complex, as the Cyt molecules are not linked to the Cd^{II}; the metal atoms form a one-dimensional chain through bridging chlorine atoms along the *b* axis. The arrangement around the cadmium atoms is octahedral and each metal is linked to four equatorial Cl atoms and to two axial water molecules. The cytosine bases are hydrogen bonded to these water molecules in an arrangement allowing both inter-base stacking interactions and base pairing *via* hydrogen bonds. The structures are compared with that of $[CdCl_2(mcyt)_2]$ **3** (mcyt = 1-methylcytosine).

The interaction of metal ions with nucleic acids and their constituents (nucleotides, nucleosides and free bases) is a growing subject of extensive research.[1,2] Metal ions play a double role in organism physiology: some are indispensable for normal life, while most of them are toxic or cause chromosome damage with consequent mutagenic effects.

The binding of these dangerous metal ions to DNA is of interest because of the potential toxic effects of such interactions[3] and, above all, because they can induce DNA damage with permanent alteration of gene expression and consequent formation of neoplastic transformations.[4] Nucleic acids are ligands with a wide spectrum of binding possibilities: *via* nitrogen and oxygen donors on the bases, *via* hydroxyl groups on the ribose sugar and *via* the negatively charged oxygen atoms on the phosphate residues. The selectivity of metal binding and the factors influencing metal co-ordination sites are of prime interest,[1–4] and may depend on the preference of metal ions for one donor site over another according to their soft or hard character.

Several complexes of cytosine (Cyt; 4-amino-1*H*-pyrimidin-2-one) and of cytosine derivatives with a variety of metals have been studied and some structural data[5–10] reported. Cadmium(II) is one of the most active among the mutagenic metals. As a part of our studies concerning complexes of carcinogenic ions with nucleic acid components, the synthesis, infrared and thermogravimetric characterization, and the crystal and molecular structure of $[Cd(Cyt)_3Cl][Cd(Cyt)Cl_3]\cdot H_2O$ **1** and $[\{CdCl_2(H_2O)_2\cdot 2Cyt\}_n]$ **2** are reported and compared with that of $[CdCl_2(mcyt)_2]$ **3**[5] (mcyt = 1-methylcytosine).

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Experimental

Syntheses.—All the products were grade reagents used as received.

Compound **1** was prepared by dissolving separately equimolar amounts of Cyt and $CdCl_2\cdot 2.5H_2O$ in water at 80 °C and then mixing the two solutions, evaporating to a small volume, and finally cooling to room temperature. White crystals separated and were filtered off and dried in air. Compound **2** was prepared as previously reported[11] (Found: C, 23.10; H, 2.60, N, 20.60. Calc. for $C_{16}H_{22}Cd_2Cl_4N_{12}O_5$: C, 23.20; H, 2.65; N, 20.25. Found: C, 21.95; H, 3.20; N, 19.10. Calc. for $C_8H_{14}CdCl_2N_6O_4$: C, 21.75; H, 3.20; N, 19.05%).

Physical Techniques.—Thermogravimetric measurements were carried out on compounds **1**, **2** and on cytosine, using a Mettler TA 3000 system in a pure nitrogen atmosphere in the temperature range 30–410 °C. Infrared spectra were recorded on a Perkin Elmer 983G spectrophotometer, using CsI cells, in Nujol or hexachlorobutadiene mulls, in the wavenumber range 4000–200 cm^{-1}.

Crystallography.—Diffraction data were collected at 298 K on a Siemens R3m/V automatic four-circle diffractometer, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å). Lattice parameters were obtained from least-squares refinement of the setting angles of 25 reflections in the range $15 \leqslant 2\theta \leqslant 30°$. The details of data collection and structure refinement are summarized in Table 1.

A total of 7733 and 1865 reflections were collected in the range $3 \leqslant 2\theta \leqslant 54°$ by ω–2θ and ω scan for complexes **1** and **2** respectively; 5998 and 1570 were unique and, from these, 5582 and 1504 were assumed as observed [$I > 3\sigma(I)$. Lorentz-

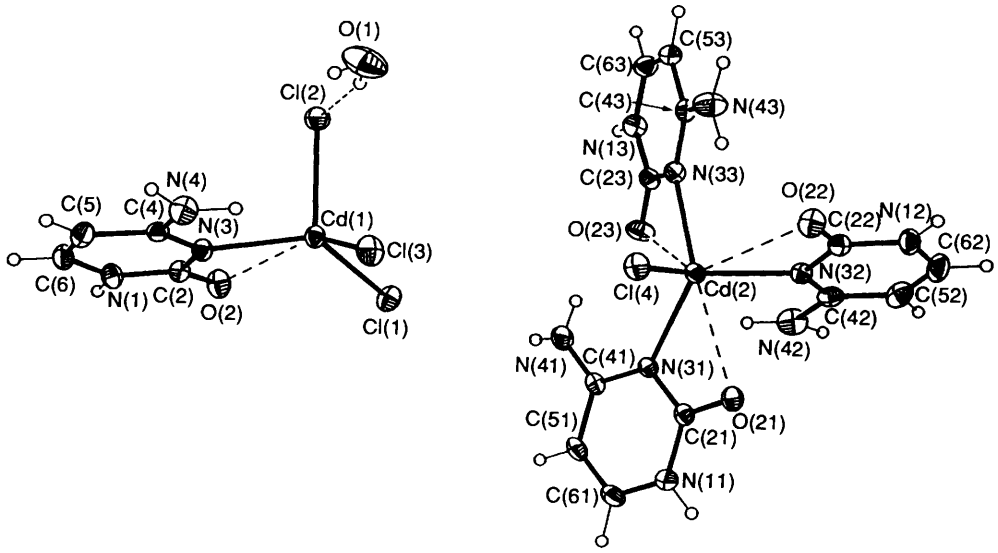

Fig. 1 View of the $[Cd(Cyt)_3Cl][Cd(Cyt)Cl_3]\cdot H_2O$ complex **1**, with the atom numbering scheme. Thermal ellipsoids are plotted at the 30% probability level. All hydrogen atoms are drawn with uniform isotropic thermal parameters

polarization and ψ-scan absorption corrections[12] were applied to the intensity data. The structures were solved by standard Patterson methods and subsequently completed by Fourier recycling. The full-matrix least-squares refinement was based on $|F_o|$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the amino groups and of the water molecules were located on a ΔF map and refined with constraints. All other hydrogen atoms were set in calculated positions and refined as riding atoms. A common thermal parameter was assigned to all hydrogen atoms. The final R values were 0.027 and 0.038, $R' = 0.035$ and 0.042, $S = 1.35$ and 1.13 for **1** and **2** respectively.

The weighting scheme used in the last refinement cycles was $w = [\sigma^2(F_o) + q(F_o)^2]$, with $q = 0.001\,258$ and 0.002 695 for compounds **1** and **2** respectively. Solutions and refinements were performed with the SHELXTL-PLUS program system.[13] The final geometrical calculations were carried out with the PARST program.[14] The graphical manipulations were performed using the XP utility of the SHELXTL-PLUS system and the MOLDRAW program.[15]

Final atomic coordinates for non-hydrogen atoms of compounds **1** and **2** are listed in Tables 2 and 3 respectively, selected bond distances and angles in Tables 4 and 5, and possible hydrogen bonds in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond distances and angles.

Results and Discussion

Description of the Structures.—We will compare the structure of compounds **1** and **2** with that of $[CdCl_2(mcyt)_2]$ **3**.[5] The structures of the three compounds differ considerably: in **1** and **3** the base molecules are directly linked to Cd^{II}, although with different arrangements, while **2** is not a cytosine complex, as the base is not directly connected to the metal ion. A comparison of the geometrical features of the five different Cyt molecules in the two compounds shows that the C(2)–N(1)–C(6)–C(5) part remains almost unaffected by the different crystal environments, while more significant variations are found in the rest of the molecule, which is directly involved in metal co-ordination and hydrogen-bond formation. In all moieties the trend of bond distances and angles is similar to that found in cytosine and cytosine monohydrate.[16]

Compound **1** consists of two different ionic moieties, represented in Fig. 1; one, positively charged, with three cytosine molecules and one chlorine atom linked to the metal, and the other, negatively charged, with one cytosine and three chlorines around the cadmium. The structure is completed by a water molecule hydrogen bonded to the two ions (*cf.* Table 6). This structure is completely different from that of the methylcytosine complex **3**, but our present data do not give any apparent reason for the different behaviour of the two similar ligands.

Neutral cytosine is a versatile ligand, its preferred binding modes being *via* N(3)[8b,g,9b,10e,f] or through O(2),[6a,10a] chelation N(3), O(2),[6c,10b] bridging N(3), O(2),[7b,d,8e] and stronger N(3)–additional O(2) weaker interactions.[5,6d,7a,8d,9a] In compound **1** the base exhibits the last binding mode, indicated as the most favoured by electrostatic potential calculations.[17] The Cd–N(3) distances range from 2.252 to 2.289 Å with an average value of 2.273 Å, while the Cd–O(2) distances range from 2.680 to 2.981 Å; they are shorter than the sum of the van der Waals radii, 3.1 Å,[18] and are in the range found in **3** and in other cytosine derivatives. It is somewhat controversial whether a Cd ··· O distance greater than 2.9 Å should be regarded as a real non-bonding interaction. If the weak co-ordination with the exocyclic oxygens is overlooked, then, as in **3**, in both moieties of **1** Cd^{II} has a distorted-tetrahedral co-ordination (the tetrahedral angles vary from 93 to 134°). When the oxygen co-ordination is taken into account, then Cd^{II} becomes seven-co-ordinated (or six-co-ordinated if the longest Cd ··· O distance is not taken into account) in the positive ion, five-co-ordinated in the negative one and six-co-ordinated in **3**. Five-co-ordination for cadmium ion, especially in N- or O-donor complexes, is more common than it was once supposed; also several seven-co-ordinate complexes of Cd^{II} have been reported.[19] It is worth noting that the weak interaction with oxygen induces angular distortions in the tetrahedral geometry around the cadmium atom. This is most evident in the negative ion of **1** where the angle Cl(1)–Cd(1)–N(3) is widened to 131.3° to allow the interaction with O(2). In the positive ion the concomitant effect of three oxygen atoms complicates the pattern of the angular deformations.

All relevant hydrogen bonds are reported in Table 6. In the positive ion the amino group nitrogen N(41) is involved in an intramolecular hydrogen bond with O(23): N(41)–H(41A) ··· O(23). The formation of this bond may be the reason for the lengthening of the O(23) ··· Cd(2) distance to 2.981(2) Å.

The packing of the molecules, shown in Fig. 2, is governed by a network of intermolecular hydrogen bonds (*cf.* Table 6) in which also the water molecule takes part: as a donor towards a chloride of the negative ion and as an acceptor from an adjacent

Table 1 Crystallographic data for compounds **1** and **2**

	1	**2**
Formula	$C_{16}H_{22}Cd_2Cl_4N_{12}O_5$	$C_8H_{14}CdCl_2N_6O_4$
M	829.1	441.6
Colour	White	White
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a/Å	7.243(2)	22.355(6)
b/Å	13.860(3)	3.853(1)
c/Å	14.113(2)	18.645(5)
α/°	95.07(2)	90
β/°	90.79(2)	115.43(2)
γ/°	104.52(2)	90
U/Å^3	1365.2(5)	1450.2(7)
Z	2	4
D/g cm^{-3}	2.017	2.022
Crystal size (mm)	0.18 × 0.36 × 0.41	0.06 × 0.20 × 0.50
F(000)	812	872
μ(Mo-Kα)/cm^{-1}	20.0	19.0
h, k, l ranges	0–9, −17 to 17, −18 to 18	−28 to 25, 0–4, 0–23
No. parameters refined	382	108
Largest, mean Δ/σ	1.375, 0.077	0.252, 0.028
Data/parameter ratio	14.6:1	13.9:1
Maximum, minimum electron density/e Å^{-3}	0.55, −1.32	2.35, −0.98
Goodness of fit *	1.35	1.13

* $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$, where N_o, N_p = numbers of observations and parameters.

Table 2 Atomic coordinates (× 10^4) for compound **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	Atom	x	y	z
Cd(1)	405(1)	2 949(1)	8 457(1)	N(11)	6 322(3)	5 027(2)	3 545(2)
Cd(2)	2 444(1)	2 173(1)	3 254(1)	C(21)	5 055(3)	4 121(2)	3 330(2)
Cl(1)	3 487(1)	3 161(1)	7 716(1)	N(31)	4 930(3)	3 404(2)	3 945(1)
Cl(2)	−1 113(1)	1 160(1)	8 632(1)	C(41)	5 964(3)	3 613(2)	4 778(2)
Cl(3)	−1 445(1)	3 539(1)	7 242(1)	C(51)	7 232(4)	4 576(2)	5 011(2)
Cl(4)	−203(1)	2 882(1)	3 789(1)	C(61)	7 386(4)	5 249(2)	4 376(2)
O(1)	−4 871(4)	1 193(2)	7 393(3)	N(12)	1 976(4)	1 199(2)	287(2)
O(2)	2 540(3)	3 537(2)	10 132(2)	C(22)	1 808(4)	1 478(2)	1 230(2)
O(21)	4 036(3)	3 935(1)	2 594(1)	N(32)	3 392(3)	1 666(2)	1 812(2)
O(22)	282(3)	1 562(2)	1 550(2)	C(42)	5 065(4)	1 599(2)	1 463(2)
O(23)	4 421(3)	974(1)	4 371(2)	C(52)	5 260(5)	1 340(3)	495(3)
N(4)	−3 503(3)	3 770(2)	9 520(2)	C(62)	3 692(5)	1 156(2)	−76(2)
N(41)	5 736(4)	2 912(2)	5 366(2)	N(13)	2 543(3)	−568(2)	4 538(2)
N(42)	6 576(4)	1 801(2)	2 073(2)	C(23)	2 861(4)	353(2)	4 203(2)
N(43)	−1 550(4)	161(2)	3 033(2)	N(33)	1 477(3)	578(2)	3 693(2)
N(1)	916(3)	4 018(2)	11 369(2)	C(43)	−223(4)	−96(2)	3 514(2)
C(2)	1 080(4)	3 740(2)	10 431(2)	C(53)	−562(4)	−1 064(2)	3 849(2)
N(3)	−442(3)	3 663(2)	9 824(2)	C(63)	862(4)	−1 269(2)	4 346(2)
C(4)	−2 072(3)	3 841(2)	10 143(2)				
C(5)	−2 258(4)	4 102(2)	11 129(2)				
C(6)	−743(5)	4 179(2)	11 710(2)				

Table 3 Atomic coordinates (× 10^4) for compound **2** with e.s.d.s in parentheses

Atom	x	y	z
Cd(1)	0	−9 660(1)	2 500
Cl(1)	−9(1)	−14 653(2)	1 548(1)
O(1)	1 139(1)	−9 371(7)	3 077(2)
N(1)	3 147(2)	−14 348(8)	4 769(2)
C(2)	2 610(2)	−15 260(8)	4 085(2)
O(2)	2 037(1)	−14 433(6)	4 020(2)
N(3)	2 692(1)	−16 971(7)	3 513(1)
C(4)	3 310(1)	−17 841(8)	3 623(2)
N(4)	3 377(2)	−19 604(8)	3 055(2)
C(5)	3 883(1)	−16 905(9)	4 335(2)
C(6)	3 773(2)	−15 175(9)	4 892(2)

Table 4 Selected bond lengths (Å) and interbond angles (°) for compound **1**

Cd(1)–Cl(1)	2.440(1)	Cd(1)–Cl(2)	2.484(1)
Cd(1)–Cl(3)	2.478(1)	Cd(1)–O(2)	2.751(2)
Cd(1)–N(3)	2.253(2)	Cd(2)–Cl(4)	2.463(1)
Cd(2)–O(21)	2.681(2)	Cd(2)–O(22)	2.799(2)
Cd(2)–O(23)	2.981(2)	Cd(2)–N(31)	2.284(2)
Cd(2)–N(32)	2.266(2)	Cd(2)–N(33)	2.289(2)
Cl(1)–Cd(1)–Cl(2)	111.6(1)	Cl(1)–Cd(1)–Cl(3)	101.1(1)
Cl(2)–Cd(1)–Cl(3)	109.0(1)	Cl(1)–Cd(1)–N(3)	131.3(1)
Cl(2)–Cd(1)–N(3)	100.1(1)	Cl(3)–Cd(1)–N(3)	102.3(1)
Cl(4)–Cd(2)–N(31)	98.7(1)	Cl(4)–Cd(2)–N(32)	134.1(1)
N(31)–Cd(2)–N(32)	107.0(1)	Cl(4)–Cd(2)–N(33)	101.6(1)
N(31)–Cd(2)–N(33)	125.5(1)	N(32)–Cd(2)–N(33)	93.5(1)

amino group of the positive ion. Three pairs of bases face each other in different ways; the separations between the corresponding planes are A–A′ (x, y, 1 − z) 3.402, B–B′ (x, 1 − y, −1 + z) 3.381 and C–C′ (1 − x, 1 − y, 1 − z) 3.331 Å.

As already mentioned, in compound **2** the Cd^{II} is not directly linked to the cytosine molecules, similarly to what is found in

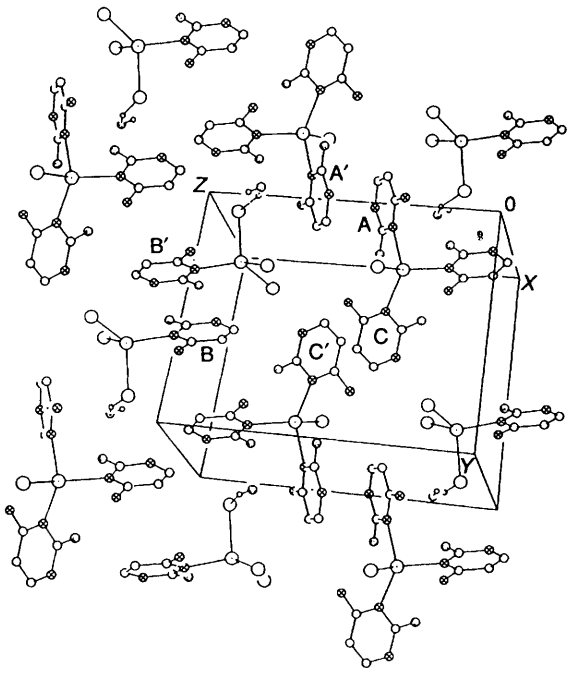

Fig. 2 View of the cell of complex **1**. Atoms are plotted with arbitrary atomic radii. Hydrogen atoms are omitted for clarity

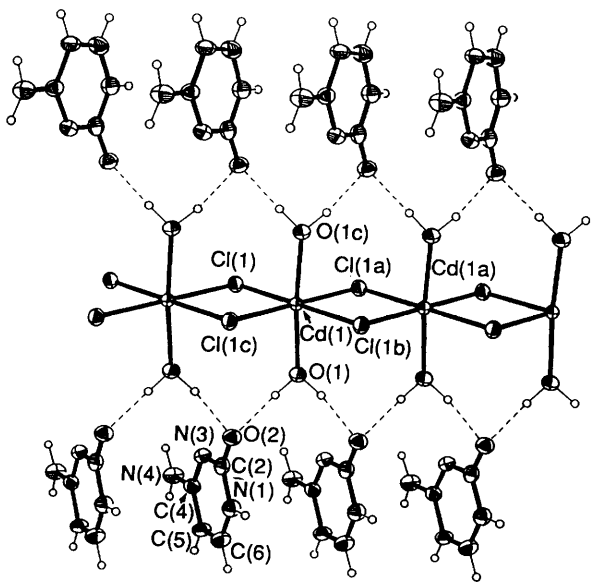

Fig. 3 View of the $[\{CdCl_2(H_2O)_2{\cdot}2Cyt\}_2]$ complex **2**, with the atom numbering scheme. Thermal ellipsoids are plotted at the 50% probability level. All hydrogen atoms are drawn with uniform isotropic thermal parameters

ephedrinium {[1-(α-hydroxybenzyl)ethyl]dimethylammonium} *catena*-aqua-di-μ-chloro-cadmium(II).[20d] Cadmium(II) has a distorted-octahedral co-ordination, linking four equatorial chlorine atoms and two axial water oxygens. The crystal structure, illustrated in Fig. 3, may be described as a one-dimensional polymer extending along the *b* axis. A similar arrangement was also found in other $CdCl_2$ complexes,[20] but in all but the ephedrinium complex the metal is directly linked to the ligand.

The link to the cytosine molecules is through water molecules hydrogen bonded to the exocyclic oxygen of the base. Each water molecule links two adjacent cytosines *via* medium-strength hydrogen bonds: O(1)–H(2w)···O(2) and O(1)–H(1w)···O(2) (x, 1 + y, z) (*cf.* Table 6). As shown in Fig. 4, cytosines are in turn linked one to another by two equivalent

Table 5 Selected bond lengths (Å) and interbond angles (°) for compound **2***

Cd(1)–Cl(1)	2.612(1)	Cd(1)–O(1)	2.303(3)
Cd(1)–Cl(1a)	2.616(1)	N(1)–C(2)	1.370(4)
N(1)–C(6)	1.354(6)	C(2)–O(2)	1.274(6)
C(2)–N(3)	1.332(5)	N(3)–C(4)	1.349(4)
C(4)–N(4)	1.319(5)	C(4)–C(5)	1.439(3)
C(5)–C(6)	1.343(6)		
Cl(1)–Cd(1)–Cl(1a)	95.0(1)	Cl(1)–Cd(1)–Cl(1b)	180.0(1)
Cl(1)–Cd(1)–Cl(1c)	85.1(1)	Cl(1)–Cd(1)–O(1)	92.1(1)
Cl(1)–Cd(1)–O(1c)	91.9(1)	O(1)–Cd(1)–Cl(1a)	88.1(1)
Cl(1a)–Cd(1)–O(1c)	87.9(1)	O(1)–Cd(1)–O(1c)	174.5(1)
Cd(1)–Cl(1a)–Cd(1a)	95.0(1)		

* Symmetry codes: (a) x, 1 + y, z; (b) $-x$, 1 + y, 0.5 − z; (c) $-x$, y, 0.5 − z.

hydrogen bonds N(1)–H(1)···O(2) (0.5 − x, 1.5 − y, 1 − z) (*cf.* Table 6). This base pairing is highlighted in the inset of Fig. 4 and it is an example of a resonance-assisted hydrogen bond,[21] as is indicated by the shortening of the C–N single-bond distance and the lengthening of the C=O and N=C double-bond distances. As is clearly shown in the same inset, oxygen O(2) acts as an acceptor for three hydrogen bonds; one lone pair is involved in the bond with H(1)–N(1), following the Legon–Millen rules,[22] while the two water hydrogens approach the other lone pair in a rather unusual tetrahedral arrangement. These interactions of O(2) may be the cause of the lengthening of the C(2)–O(2) distance and of the related angular distortions around C(2) with respect to the values found in the four cytosines of compound **1**.

The cytosine molecules are parallel and stacking interactions with base–base overlap are observed. The distance between equivalent ring atoms and therefore between the centroids of the rings equals the *b*-axis length, but the cytosine planes are tilted by 30° with respect to the *xz* plane and the distance between the planes is reduced to 3.34 Å. This is in agreement with the values reported for some free pyrimidines, where the distance between the planes of two adjacent bases ranges from 3.25 Å for mcyt, *via* 3.36 Å for Cyt, to 3.78 Å for pyrimidine.[23] It is interesting to compare these inter-base distances with the values of 3.4–3.5 Å reported[24] for double-stranded DNA. The base arrangement is very similar to that found in the nitrate–mcyt complex of Ag^I,[7b,d] where mcyt is bridge-linked between silver atoms, with both N and O involved in the binding. The inter-base distance is 3.34 Å and the distance between Ag atoms on different planes equals the *c*-axis length of 3.642 Å. Examples of different types of base–base overlap have been reported by Marzilli and co-workers[10d] for the zinc complexes of cytidine (4-amino-1-β-D-ribofuranosyl-1*H*-pyrimidin-2-one) and deoxycytidine. Another example of a cytosine–metal derivative in which there is no direct co-ordination of the base to the metal is that of the cytosinium hemitetrachlorozincate–cytosine.[6b] Also in this case the bases show stacking interactions of parallel molecules and base pairing by hydrogen bonds. Stacking interactions between the planar ligands were found also in the benzotriazole complex of $CdCl_2$,[20a] which is quite similar to our compound **2**, as is also shown by the short *b* axis (3.818 Å).

Besides the van der Waals forces, the molecular chains along the *y* axis are held together by a weak hydrogen-bond interaction N(4)–H(41)···N(3) (*cf.* Table 6), and a helical disposition of bases around this axis is obtained (Fig. 4). Altogether each base is involved in six hydrogen bonds with the surrounding molecules.

Thermogravimetric and Infrared Results.—Cytosine and compounds **1** and **2** gave different differential thermal gravimetry (DTG) curves. Both **1** and **2** show a lower-temperature water loss, in the range 182–210 °C for **1** and 110–160 °C for **2**; the other losses at higher temperatures may be attributed to cytosine. It is somewhat surprising that complex **1**, in which a water molecule

is only bound by a hydrogen bond (water of crystallization) shows a higher temperature loss than compound **2** where the water molecules are directly linked to Cd^{II}. This may be explained by considering that in the ionic complex **1** the packing is such (Fig. 2) as to hold the water molecules more strongly than in **2**.

The infrared spectral data for cytosine and of derivatives **1** and **2**, together with the three different band assignments proposed for cytosine by Susi *et al.*[25] Radchenko *et al.*[26] and Nishimura and Tsuboi[27] respectively, are reported in Table 7. The spectrum of compound **1** shows, in the 3600–3000 cm^{-1} region, two sets of bands due to NH_2 and NH vibrations, while cytosine and derivative **2** only show one set of bands in this region. Radchenko *et al.*[26] found that isolated cytosine molecules display NH_2 and NH vibrational bands at 3559, 3468 and 3438 cm^{-1} for $\nu_{asym}(NH_2)$, $\nu(NH)$ and $\nu_{sym}(NH_2)$ respectively; in crystalline cytosine where strong intermolecular interactions are present these bands fall at lower frequencies. The two sets of bands of compound **1** may be attributed to isolated and to interacting molecules; this is supported by the crystal structure which shows two different ionic units, one with a single cytosine molecule and the other with three mutually interacting cytosines (*cf.* Fig. 2).

In the 1700–1600 cm^{-1} region the IR spectra are complex and exhibit overtone and/or combination bands. The cytosine spectrum shows a very wide and intense band around 1660 cm^{-1}, with several shoulders; also the spectrum of compound **1** shows only one wide and intense band at 1630 cm^{-1}, with several shoulders. The absorption frequencies corresponding to these shoulders may be divided in two regions: the C=O stretching vibration region between 1668 and 1660 cm^{-1},[25,26] and the C=C vibration region at 1615–1612 cm^{-1}. No assignment has been made for the strong absorption around 1635 cm^{-1}. The position of the absorption maximum is obviously related to the relative intensities of the superposing bands. Following the assignments of Susi *et al.*[25] and of Radchenko *et al.*[26] we may infer that the shift of the maximum from 1660 cm^{-1} for cytosine to 1630 cm^{-1} for complex **1** corresponds to a decrease, in the latter, of the intensity of the C=O stretching band, while this stretching mode in compound **1** may be assigned to the shoulder at 1668 cm^{-1}. Compound **2** shows two very strong bands at 1646 and 1612 cm^{-1}. The second corresponds to the C=C stretching and its intensity is increased with respect to cytosine. The band at 1646 cm^{-1} corresponds to the unassigned band of cytosine at 1635 cm^{-1}, while the C=O stretching mode corresponds to the shoulder at 1670 cm^{-1}, which is shifted towards higher wavenumbers with respect to cytosine.

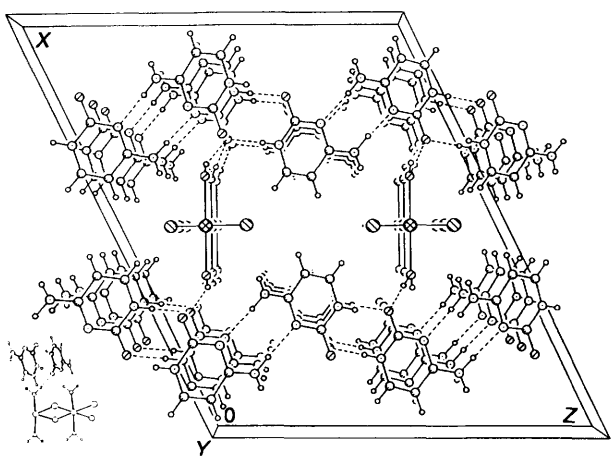

Fig. 4 View of the cell of complex **2**. Atoms are plotted with arbitrary atomic radii. Hydrogen atoms are omitted for clarity. The inset shows the hydrogen bonds involving atom O(2)

Below 1600 cm^{-1} the bands in the cytosine spectrum are mainly due to ring stretching and bending modes, but also to CH and NH bending and to C–NH_2 stretching and bending modes. All these bands change in frequency and intensity with respect to cytosine. These large variations suggest a ring involvement in the formation of the two derivatives. This is certainly true for complex **1**, where the ligand is co-ordinated to the metal *via* the ring nitrogen. The variations in **2** may be ascribed to the cytosine–water interactions *via* hydrogen bonding and to the stacking interactions between adjacent parallel rings. In keeping with the crystal structure, the two low-frequency bands at 260 and 238 cm^{-1}, found for compound **1**, may be attributed to the Cd–Cl stretching modes of the terminal chlorides. For compound **2** no bands are found above 200 cm^{-1}, since the absorptions due to bridging chloride fall below this value.[28]

Conclusion

The existence of three different types of molecules with a different number of bases and chlorine atoms linked to the Cd atom indicates that Cl and Cyt compete in binding the metal. For this reason we also undertook the crystal structure analysis of compound **2**, which is synthesised in an excess of Cl.[11] In **2** the Cl atoms compete with the cytosine molecules in the complexation reaction to the point of excluding them from the co-ordination sphere of the metal. The result is a polymeric $CdCl_2$ compound. Its linear chain geometry is quite rigid, and leaves only two axial co-ordination sites on opposite sides of the plane.

Table 6 Bond distances (Å) and angles (°) of possible hydrogen bonds (B · · · H–A) for compounds **1** and **2**

B · · · H–A	B · · · A	B · · · H	H–A	B · · · H–A
(*a*) Compound **1**[a]				
Cl(2) · · · H(1w)–O(1)	3.228(4)	2.33(3)	0.96(3)	155(3)
Cl(3a) · · · H(41B)–N(41)	3.240(3)	2.33(2)	0.94(3)	162(2)
Cl(1d) · · · H(11A)–N(11)	3.181(3)	2.29(2)	0.90(1)	169(3)
Cl(2e) · · · H(12A)–N(12)	3.199(3)	2.34(2)	0.90(1)	159(3)
O(23) · · · H(41A)–N(41)	2.847(3)	1.94(2)	0.95(2)	159(3)
O(22a) · · · H(42A)–N(42)	2.883(4)	2.01(3)	0.95(3)	152(3)
O(21c) · · · H(1A)–N(1)	2.858(3)	1.97(2)	0.90(1)	167(3)
O(1b) · · · H(43B)–N(43)	2.814(4)	1.87(2)	0.95(2)	174(2)
(*b*) Compound **2**[b]				
O(2) · · · H(2w)–O(1)	2.809(4)	1.88(3)	0.96(4)	163(4)
O(2a) · · · H(1w)–O(1)	2.776(4)	1.81(3)	0.97(3)	169(3)
O(2b) · · · H(1)–N(1)	2.862(5)	1.96(3)	0.90(1)	179(3)
N(3c) · · · H(41)–N(4)	3.015(4)	2.06(3)	0.96(3)	170(3)

[a] Symmetry codes: (a) $1 + x, y, z$; (b) $-1 - x, -y, 1 - z$; (c) $x, y, 1 + z$; (d) $1 - x, 1 - y, 1 - z$; (e) $x, y, -1 + z$. [b] Symmetry codes: (a) $x, 1 + y, z$; (b) $0.5 - x, 1.5 - y, 1 - z$; (c) $0.5 - x, -0.5 + y, 0.5 - z$.

Table 7 Some relevant infrared bands (cm^{-1}) of cytosine and its cadmium compounds **1** and **2***

			Band assignment for cytosine		
Cyt	Compound **1**	Compound **2**	Ref. 25	Ref. 26	Ref. 27
	3528m			$\nu_{asym}(NH_2)$	
	3470(sh)m			$\nu(NH)$	
	3428m			$\nu_{sym}(NH_2)$	
3370vs	3400ms	3396vs	$\nu_{asym}(NH_2)$	$\nu_{asym}(NH_2)$	$\nu_{asym}(NH_2)$
	3324vs(br)	3300s(br)			
	3220(sh)vs		$\nu_{sym}(NH_2)$		
3165vs(br)	3180vs(br)	3145vs(br)	$\nu(NH)$	$\nu(NH)$	$\nu_{sym}(NH_2)$
	3095(sh)s	3089vs	$\nu_{sym}(CH)$	$\nu_{sym}(CH)$	
3000w(br)	3010(sh)m	2990s(br)	$\nu_{asym}(CH)$	$\nu_{asym}(CH)$	
1700(sh)m	1685(sh)ms	1685(sh)ms	$\delta(NH_2)$	$\delta(NH)_2$	$\nu(C{=}O)$
1660vs(br)	1668(sh)s	1670(sh)s	$\nu(C{=}O)$	$\nu(C{=}O)$	$\nu(C{=}C)$
1635(sh)vs	1630vs(br)	1646vs(br)			
1615(sh)s	1612(sh)vs	1612vs(br)	$\nu(C{=}C)$	$\nu(C{=}C)$, ν_r	$\delta(NH_2)$
1540ms	1524s		$\delta(NH)$, ν_r	$\nu(C{=}N)$, ν_r	$\nu_a{}^6$
1504ms	1510s	1501s	ν_r, $\delta(NH)$	ν_r	$\nu(C{-}NH_2)$
1465vs	1455s		$\delta(CH)$, $\nu(C{-}N)$	$\delta(CH)$, ν_r	$\delta(NH)$
	1443s	1444s			
	1383mw				
1362s	1360m	1370ms	$\nu(C{-}N)$, $\delta(CH)$	$\nu(C{-}N)$, $\delta(NH)$	$\delta_{sym}(CH)$
1307vw	1303mw				
1275s	1286m	1304m	$\delta_{asym}(CH)$	ν_r, $\delta(CH)$	Kekulé
	1245m				
1232s	1228(sh)m	1233s	ν_r	ν_r	$\delta_{asym}(CH)$
	1216s				
	1155w	1168vw			
1152w	1142w		ν_r, $\rho(NH_2)$	ν_r, δ_r	$\rho(NH_2)$
	1108w	1118w		ν_r, δ_r	$\nu_{\delta a}{}^6$
965mw	976w	974mw	ν_r, $\rho(NH_2)$	ν_r, $\rho(NH_2)$	tr
820m(br)	850vw(br)	853m	$\gamma(NH)$		$\gamma(NH)$
	811(sh)m	806s			
	801(sh)s				
792s	792s	787vs	ν_r, δ_r	ν_r, δ_r	Breathing
780(sh)ms	780(sh)s				
	779s				
	751ms				
600s	609s	600s	δ_r	δ_r	$\delta_a{}^6$
565(sh)mw	578mw	572ms	$\delta(C{=}O)$, $\delta_{sym}(C{-}N)$	$\delta(C{=}O)$, $\delta_{sym}(C{-}N)$	
548ms	560(sh)ms	551ms			$\delta_b{}^6$
534ms	542ms		δ_r	δ_r	$\delta(C{=}O)$
510ms(br)			$\tau(NH)$		$\tau(NH)$
440ms	438(sh)ms	438w	sk		
420ms	422ms	415w			
	400(sh)m	401w			
390(sh)vw	390ms		$\delta(C{=}O)$, $\delta_{asym}(C{-}N)$		
	260m				
	238m				

* ν = Stretching mode, δ = bending mode, ρ = rocking mode, γ = out-of-plane bending mode, τ = out-of-plane wagging mode, sk = skeletal mode, r = ring, $\nu_a{}^6$, Kekulé, $\nu_{\delta a}{}^6$, tr, breathing, $\delta_a{}^6$, $\delta_b{}^6$ = stretching and bending ring vibrational modes.

Cytosine could be co-ordinated on these sides only as a mono- and not as a bi-dentate ligand, since eight-co-ordination would require a distortion of the planar chloride co-ordination, which we have seen to be rigid. Cytosine can indeed behave as a monodentate ligand *via* O(2), as found in the complexes of Mn [10a] and Ni [6a] but, as we have seen, the preferred mode of complexing with Cd^{II} is *via* both N and O. Since the reaction occurs in an aqueous medium, the water molecules seem to be the favoured ligands, with respect to cytosine. Furthermore, the adopted arrangement is favoured by the realization of inter-base stacking interactions and of base pairing.

Finally, the ability of cadmium to co-ordinate different numbers of cytosine molecules, with easy interchange of Cl and cytosines, is clearly indicated. The unexpected ionic complex (no other similar structure in base complexes has been reported) contains the two extreme substitution schemes, $[Cd(Cyt)_3Cl]^+$ and $[Cd(Cyt)Cl_3]^-$, while the intermediate neutral scheme, found in $[Cd(mcyt)_2Cl_2]$, is not adopted, under our experimental conditions, by the cytosine complex.

It may be concluded that the reaction between $CdCl_2$ and cytosine strongly depends on the reaction conditions and this may be relevant in defining the ligand properties of cytosine in aqueous solutions.

Acknowledgements

This work was supported by the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica. We are grateful to Dr. Piero Ugliengo of the University of Torino for critical reading of the manuscript and helpful discussion.

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Received 3rd *September* 1992; *Paper* 2/04753E