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Crystallographic Studies on Metal–Nucleotide Base Complexes. VII. Di-9-methylguaninetriaquocopper(II) Sulphate Trihydrate

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$[(C_6H_7N_5O)_2Cu(H_2O)_3]SO_4.3H_2O$ is monoclinic, space group $P2_1/c$, with $a=11\cdot8733$, $b=6\cdot8057$, $c=28\cdot4534$ Å, $\beta=103\cdot423°$, $Z=4$. Most of the crystals are twinned and the single crystal used for data collection was very small. The structure determination is based on diffractometer data (Cu $K\alpha$ radiation) and the structure was refined by full-matrix least-squares calculations to a final R of 0·078. The Cu ion is octahedrally surrounded, the coordination spheres being linked in an infinite chain by one of the coordinated water molecules. Two guanine molecules, binding Cu through N(7), are arranged in a *syn* configuration with a water molecule in the coordination sphere bridging the two carbonyl groups *via* hydrogen bonds. The sulphate ion forms two hydrogen bonds to one of the guanine ligands. The 'bite' distance between the two donor H atoms at N(1) and the amino group is compatible with the distance between the acceptor atoms in the sulphate ion. The ability of guanine to form a di-hydrogen bond to certain anions is not paralleled by any other purines and pyrimidines.

Introduction

Cu^{II} complexes of neutral nucleoside analogues of hypoxanthine (Sletten, 1974) and adenine (Sletten & Thorstensen, 1974; Sletten & Ruud, 1975) have been examined by X-ray crystallography. In the present paper the corresponding complex of 9-methylguanine will be described. In $AdCuSO_4$ the anion is coordinated to Cu^{2+}, while in Ad_2CuCl_2 the anion forms a strong H-bond to adenine and has no contact with Cu^{2+}. The H-bond donor properties of the purines together with steric requirements may determine whether the anion will enter the coordination sphere or interact directly with the purine ring. The anions may thus have the ability to disrupt the complementary base-pairing scheme in DNA, producing denaturation. Usually, the anionic effect has not been dealt with explicitly in investigations of metal–nucleic acid interaction, even though several anions have been used in these studies, *e.g.* NO_3^-, Cl^-, ClO_4^-, SO_4^{2-}. It has been found that the denaturing power of anions on DNA follows the order Cl^-, $Br^- < CH_3COO^- < I^- < ClO_4^- < CNS^-$ (Hamaguchi & Geiduschek, 1962). Eichhorn & Shin (1968) have proposed a corresponding order for metal ions; $Mg^{II} < Co^{II} < Ni^{II} < Mn^{II} < Zn^{II} < Cd^{II} < Cu^{II}$. In this context it is important to be able to distinguish between the effect of anions and the effect of metal ions on DNA. Thus the investigation of metal–nucleic acid interaction should also include variation of the anionic environment.

Experimental

Equimolar amounts (10^{-3} mol) of 9-methylguanine and 1-methylcytidine were dissolved in 2 ml 1N H_2SO_4, and 4×10^{-3} mol $CuSO_4$ in 2 ml H_2O was added. The mixture was heated and the pH adjusted to 3 by the addition of 1N NaOH. A green precipitate was obtained and washed with methanol. The compound was dissolved in 1:1 dioxane–water and after 24 h at room temperature crystalline plates appeared. The complex synthesized might have guanine, cytidine, or both guanine and cytidine ligands, depending on the stability constants and the solubility of the different species.

The space group is $P2_1/c$. Most of the crystals were twinned, the twin plane being (100). Only minute single crystals could be found and the one used for data collection, $0\cdot01\times0\cdot03\times0\cdot37$ mm, was mounted along **b**. Cell dimensions were determined by measuring 2θ of the $K\alpha_1$ peak of 16 reflexions by an ω-scan technique (Maartmann-Moe, 1974). The experimental procedure is described elsewhere (Sletten, 1974). Within the sphere of reflexion limited at $\sin\theta/\lambda=0\cdot56$, 3299 unique reflexions were recorded with Cu $K\alpha$ radiation. Of these, 742 were less than the threshold value (Sletten, 1974).

Crystal data

$[(C_6H_7N_5O)_2Cu(H_2O)_3]SO_4.3H_2O$, F.W. 598·0, Space group: $P2_1/c$, $Z=4$, $a=11\cdot8733$ (9), $b=6\cdot8057$ (7), $c=28\cdot4534$ (16) Å, $\beta=103\cdot423$ (7)°, $V=2263\cdot4$ (3) Å^3. $D_m=1\cdot80$ (3), $D_x=1\cdot81$ (2) g cm^{-3}. λ(Cu $K\alpha$) = 1·5418 Å, $\mu=30\cdot1$ cm^{-1}.

The structure was solved by the heavy-atom method and the refinement by full-matrix least squares proceeded satisfactorily for all crystallographically ordered non-hydrogen atoms. However, some of the crystal water is disordered. From peaks in the disordered region four different sites were allocated fractional O atoms and the occupancy factors were refined, keeping the isotropic thermal parameters fixed at the average value for the ordered crystal water. The data, not extending beyond $\sin\theta/\lambda=0{\cdot}56$, did not allow simultaneous refinement of thermal and occupancy parameters.

All H atoms attached to ordered atoms were located in a difference map. In the subsequent refinement some of the water H atoms moved to unreasonable positions, and so were fixed from the difference map. The least-squares refinement converged at a relatively high $R=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}078$, partly due to poor quality of the data from the minute crystal and partly due to the inadequate model for the disordered water molecules.

Atomic parameters are listed in Table 1.* Scattering factors and computer programs are mentioned elsewhere (Sletten, 1974). All drawings were made by *ORTEP* (Johnson, 1970).

Results and discussion

Coordination geometry

The molecular dimensions of the complex and the sulphate ion are shown in Fig. 1 and Table 2. Cu is octahedrally surrounded by two guanine N(7) atoms and two water molecules [O(6), O(7)] in the equatorial plane and two water molecules in axial positions [O(5), O(7)′]. The complex units are linked together *via* O(7) forming an infinite chain running along the screw axis [Fig. 2(*a*)]. The guanine ligands are arranged in a *syn* configuration with water molecule O(7) serving as an H-bond bridge between the carbonyl groups. The array N(7*A*)–Cu–N(7*B*) is almost linear, the angle at Cu being 176·7°. Both guanine ligands are tilted so as to accommodate the bridging water molecule, the angles between Cu–N(7) and ring planes *A* and *B* being 15·6° and 15·9°, respectively [Fig. 2(*b*)].

In the chloro complex of 9-methylhypoxanthine the purine ligands are arranged *anti* and the intra-complex hydrogen bond is found between the carbonyl group and a water molecule in equatorial position. The axial positions are occupied by Cl^- ions (Sletten, 1974). The corresponding sulphato complex is now

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31224 (22 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *The final atomic parameters*

(*a*) Non-hydrogen atoms (temperature parameters $\times 10^3$). Standard deviations are in parentheses. Anisotropic temperature factor $=\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{23}klb^*c^*+2U_{13}hla^*c^*)]$.

	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cu	0·86346 (9)	0·20613 (15)	0·23657 (3)	45·4 (6)	38·8 (6)	27·2 (4)	4·9 (6)	0·8 (6)	13·4 (4)
S	0·45521 (15)	0·0828 (3)	0·11562 (7)	18·6 (10)	30·1 (13)	26·7 (10)	−0·2 (10)	0·7 (10)	7·0 (9)
O(6*A*)	0·1417 (4)	0·2292 (7)	0·19729 (14)	27 (3)	36 (3)	10 (2)	1 (3)	−8 (2)	1 (2)
O(6*B*)	0·1341 (4)	0·2225 (8)	0·32645 (15)	29 (3)	38 (3)	17 (2)	2 (3)	4 (3)	13 (2)
O(1)	0·3684 (4)	0·0762 (9)	0·14512 (17)	19 (3)	73 (5)	30 (3)	3 (3)	−3 (3)	6 (2)
O(2)	0·3963 (4)	0·0528 (9)	0·06484 (17)	39 (3)	69 (4)	24 (3)	2 (3)	0 (3)	5 (3)
O(3)	0·4563 (4)	0·4312 (8)	0·36795 (17)	28 (3)	32 (3)	40 (3)	−6 (3)	1 (3)	2 (3)
O(4)	0·5139 (4)	0·2751 (8)	0·12259 (22)	29 (3)	31 (4)	95 (5)	2 (3)	4 (4)	13 (3)
O(5)	0·3049 (5)	0·5070 (11)	0·27788 (24)	33 (4)	63 (5)	22 (4)	8 (4)	1 (4)	1 (3)
O(6)	0·7663 (4)	0·4436 (8)	0·22319 (17)	13 (3)	53 (4)	39 (3)	16 (3)	3 (3)	−1 (2)
O(7)	0·0471 (4)	0·4525 (7)	0·25356 (15)	21 (3)	35 (3)	19 (3)	−3 (3)	2 (2)	7 (2)
O(8)	0·3836 (7)	0·4055 (13)	0·00851 (28)	51 (5)	72 (6)	40 (4)	17 (4)	16 (4)	20 (4)
O(10)	0·3768 (6)	0·1030 (13)	0·40873 (27)	47 (4)	38 (5)	54 (5)	7 (4)	16 (4)	26 (4)
N(1*A*)	0·1349 (5)	0·1216 (9)	0·12133 (19)	10 (3)	25 (4)	17 (3)	−2 (3)	−2 (3)	3 (3)
N(2*A*)	0·1469 (6)	0·0246 (11)	0·04537 (23)	25 (4)	53 (5)	15 (4)	−1 (4)	−13 (4)	8 (3)
N(3*A*)	0·9648 (4)	0·0692 (9)	0·05969 (18)	20 (3)	25 (4)	11 (3)	−1 (3)	−3 (3)	9 (3)
N(7*A*)	0·8714 (4)	0·2034 (9)	0·16658 (18)	14 (3)	20 (3)	20 (3)	3 (3)	1 (3)	6 (3)
N(9*A*)	0·7941 (4)	0·1304 (8)	0·08962 (17)	18 (3)	30 (4)	10 (3)	2 (3)	−1 (3)	3 (2)
N(1*B*)	0·1319 (5)	0·1224 (9)	0·40236 (19)	24 (4)	22 (4)	12 (3)	−6 (3)	−2 (3)	1 (3)
N(2*B*)	0·1433 (7)	0·0234 (11)	0·48089 (23)	23 (4)	46 (5)	17 (4)	1 (4)	2 (3)	4 (3)
N(3*B*)	0·9630 (5)	0·0711 (9)	0·43196 (18)	24 (3)	26 (5)	13 (3)	3 (3)	2 (3)	5 (3)
N(7*B*)	0·8655 (4)	0·2062 (9)	0·30776 (17)	20 (3)	15 (3)	18 (3)	−3 (3)	−1 (3)	6 (3)
N(9*B*)	0·7911 (5)	0·1320 (8)	0·37003 (18)	23 (3)	23 (4)	17 (3)	−5 (3)	2 (3)	10 (3)
C(2*A*)	0·0789 (6)	0·0735 (10)	0·07491 (22)	22 (4)	16 (4)	13 (4)	−2 (3)	−1 (3)	6 (3)
C(4*A*)	0·9113 (5)	0·1173 (10)	0·09558 (22)	16 (4)	20 (4)	15 (4)	−2 (3)	−2 (3)	2 (3)
C(5*A*)	0·9598 (6)	0·1641 (10)	0·14267 (22)	26 (4)	17 (5)	15 (3)	1 (3)	−5 (3)	11 (3)
C(6*A*)	0·0804 (5)	0·1750 (10)	0·15781 (22)	14 (4)	22 (4)	14 (4)	7 (3)	3 (3)	6 (3)
C(8*A*)	0·7754 (6)	0·1814 (11)	0·13341 (23)	17 (4)	19 (5)	26 (4)	5 (4)	1 (3)	9 (3)
C(9*A*)	0·7054 (8)	0·0926 (17)	0·04600 (30)	20 (5)	53 (7)	26 (5)	−10 (5)	−5 (5)	5 (4)
C(2*B*)	0·0758 (6)	0·0729 (11)	0·43905 (23)	32 (4)	22 (4)	13 (4)	−3 (3)	1 (3)	5 (3)
C(4*B*)	0·9017 (5)	0·1205 (10)	0·38715 (22)	17 (4)	14 (4)	16 (4)	−5 (3)	−1 (3)	6 (3)
C(5*B*)	0·9546 (6)	0·1669 (10)	0·34806 (22)	26 (4)	12 (4)	11 (3)	3 (3)	2 (3)	2 (3)
C(6*B*)	0·0750 (6)	0·1744 (10)	0·35586 (22)	24 (4)	18 (4)	15 (3)	6 (3)	1 (3)	2 (3)
C(8*B*)	0·7702 (6)	0·1808 (12)	0·32263 (23)	22 (4)	30 (5)	15 (4)	2 (4)	2 (4)	−1 (3)
C(9*B*)	0·7034 (8)	0·0871 (17)	0·3981 (3)	28 (5)	52 (7)	32 (5)	−10 (5)	1 (5)	15 (5)

Table 1 (*cont.*)

(*b*) Oxygen ($U=0\cdot05$) and hydrogen atoms. Isotropic temperature factor $=\exp[-8\pi^2U\sin^2\theta/\lambda^2]$ ($U\times10^3$).

	X/a	*Y/b*	*Z/c*	Occupancy
O(91)	0·4321 (10)	0·2931 (20)	0·2291 (4)	0·501 (10)
O(92)	0·4250 (28)	−0·014 (7)	0·2466 (11)	0·212 (19)
O(93)	0·4999 (11)	0·4537 (20)	0·2133 (5)	0·463 (10)
O(94)	0·4017 (13)	0·098 (3)	0·2420 (5)	0·454 (19)

	X/a	*Y/b*	*Z/c*	*U*
H(1*A*)	0·211 (5)	0·125 (8)	0·1296 (19)	6 (16)
H(21*A*)	0·242 (6)	0·033 (10)	0·0545 (23)	33 (20)
H(22*A*)	0·877 (6)	0·495 (10)	0·4795 (23)	13 (23)
H(8*A*)	0·703 (4)	0·208 (8)	0·1373 (16)	−9 (12)
H(91*A*)	0·646 (6)	0·062 (11)	0·0467 (25)	23 (24)
H(92*A*)	0·275 (7)	0·450 (13)	0·4655 (29)	65 (30)
H(93*A*)	0·710 (6)	0·193 (11)	0·0249 (26)	39 (24)
H(1*B*)	0·211 (6)	0·133 (11)	0·4075 (25)	47 (26)
H(21*B*)	0·204 (4)	0·030 (8)	0·4866 (18)	−19 (15)
H(22*B*)	0·888 (7)	0·526 (14)	−0·004 (3)	70 (35)
H(8*B*)	0·702 (5)	0·203 (9)	0·3064 (19)	10 (17)
H(91*B*)	0·645 (6)	0·110 (11)	0·3823 (24)	22 (24)
H(92*B*)	0·315 (8)	0·443 (14)	0·104 (3)	83 (35)
H(93*B*)	0·718	0·165	0·427	60
H(51)	0·313 (7)	0·437 (12)	0·2592 (26)	32 (29)
H(52)	0·360 (6)	0·497 (11)	0·3012 (26)	32 (26)
H(61)	0·710	0·450	0·220	60
H(62)	0·820	0·440	0·239	60
H(71)	0·067	0·387	0·230	60
H(72)	0·067	0·387	0·278	60
H(81)	0·404 (7)	0·323 (11)	0·0226 (26)	18 (26)
H(82)	0·415 (6)	0·096 (11)	0·4908 (23)	14 (22)
H(101)	0·390 (7)	0·168 (11)	0·3961 (25)	2 (25)
H(102)	0·418 (8)	0·005 (14)	0·404 (4)	87 (43)

being investigated to determine whether SO_4^{2-} will replace Cl^- in the coordination sphere or whether the geometry will be analogous to that of the guanine complex.

In the present compound SO_4^{2-} does not interact with Cu^{2+} but participates in a strong di-hydrogen bond to guanine. The 'bite' distances between the donors, N(1)···N(2), and the acceptors, O(1)···O(2),

Table 2. *Angles* (°) *around* Cu *and* S ($\sigma=0\cdot2°$ *and* 0·3° *respectively*)

O(5)—Cu-N(7*A*)	93·1
O(5)—Cu-N(7*B*)	89·3
O(5)—Cu-O(6)	90·2
O(5)—Cu-O(7)	86·0
O(6)—Cu-N(7*A*)	88·6
O(6)—Cu-N(7*B*)	93·7
O(7)—Cu-N(7*A*)	89·2
O(7)—Cu-N(7*B*)	88·7
O(7)′—Cu-N(7*A*)	87·8
O(7)′—Cu-N(7*B*)	90·0
O(7)′—Cu-O(7)	97·4
O(7)′—Cu-O(6)	86·4
O(5)—Cu-O(7)′	176·5
O(6)—Cu-O(7)	175·5
N(7*A*)-Cu-N(7*B*)	176·7
O(1)—S—O(2)	108·7
O(1)—S—O(3)	109·9
O(1)—S—O(4)	108·8
O(2)—S—O(3)	111·0
O(2)—S—O(4)	111·0
O(3)—S—O(4)	107·5

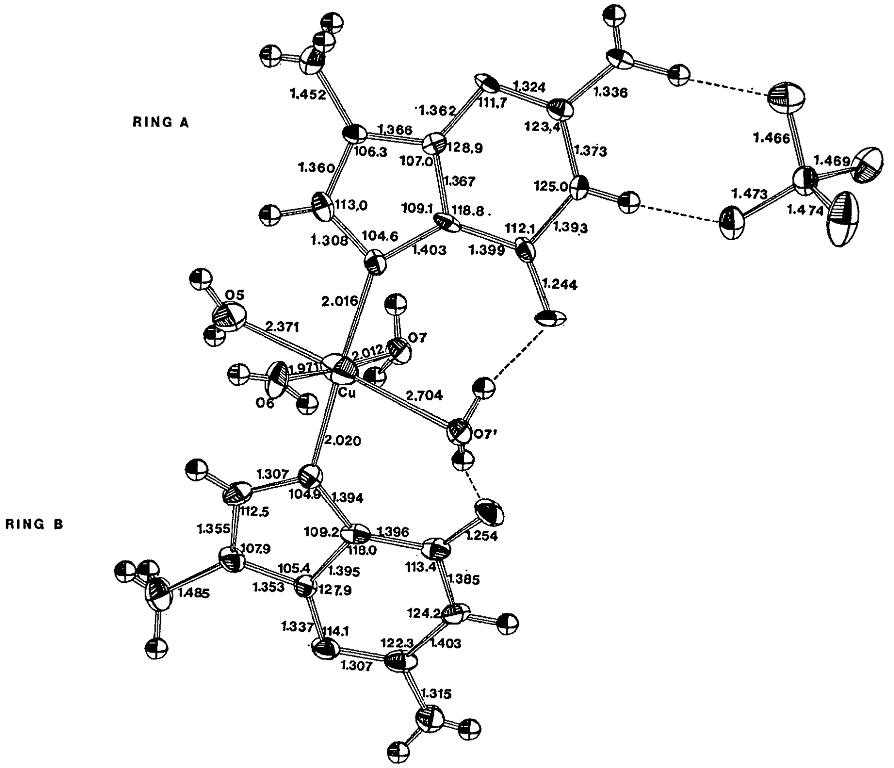

Fig. 1. Interatomic distances and angles in the complex unit. The σ's in bond lengths are in the range 0·005–0·012 Å, and in angles 0·2–0·6°.

are 2·296 (9) and 2·388 (7) Å, respectively. This unique H-bond arrangement is probably of importance in determining electrolyte activity on nucleic acids. In this respect, guanine is different from all other purines and pyrimidines by having *two* donor groups which are able to establish strong 'bidentate' H-bonds to *e.g.*

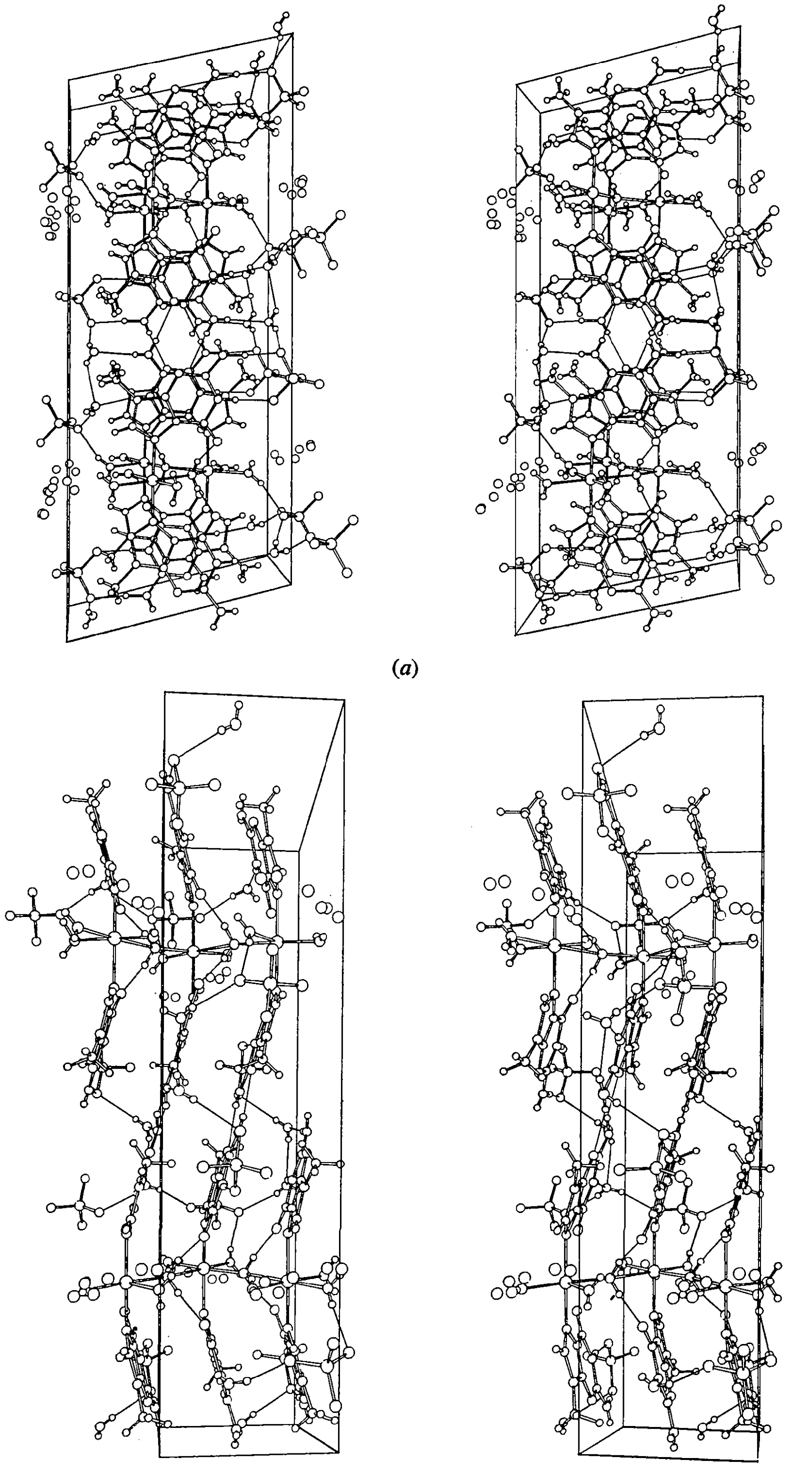

Fig. 2. Stereoscopic drawings of the crystal packing viewed (*a*) along **b** with **a** along the interocular line, and (*b*) along **a** with **b** along the interocular line.

Table 3. *Hydrogen-bond distances and angles*

D–H$\cdots A$	Position of acceptor atom			Distance (Å) $D\cdots A$	Distance (Å) H$\cdots A$	Angle (°) D–H–A
O(5)—H(51) ····O(91)	x,	y,	z	2·700 (14)	2·06 (9)	146 (6)
O(5)—H(52) ····O(3)	x,	y,	z	2·816 (8)	2·03 (7)	161 (6)
O(7)—H(71) ····O(6A)	x,	y,	z	2·640 (7)	1·79	162
O(7)—H(72) ····O(6B)	x,	y,	z	2·612 (6)	1·81	168
O(8)—H(81) ····O(2)	x,	y,	z	2·871 (10)	2·21 (8)	158 (7)
O(8)—H(82) ····O(10)	x,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$	2·822 (11)	2·27 (6)	137 (5)
O(10) -H(101) ···O(3)	x,	y,	z	2·781 (10)	2·18 (8)	166 (7)
O(10) -H(102) ···O(4)	$1-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$	2·827 (10)	2·00 (10)	165 (7)
N(1A)-H(1A)····O(1)	x,	y,	z	2·714 (7)	1·85 (6)	168 (4)
N(2A)-H(21A)···O(2)	x,	y,	z	2·890 (9)	1·80 (7)	176 (4)
N(2A)-H(22A)···N(3A)	$1-x$,	$-y$,	$-z$	3·043 (8)	2·32 (6)	174 (6)
N(1B)-H(1B)····O(10)	x,	y,	z	2·875 (10)	1·97 (7)	167 (5)
N(2B)-H(21B)···O(8)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	2·820 (11)	2·13 (5)	171 (5)
N(2B)-H(22B)···N(3B)	$1-x$,	$-y$,	$1-z$	3·100 (10)	2·31 (10)	162 (7)

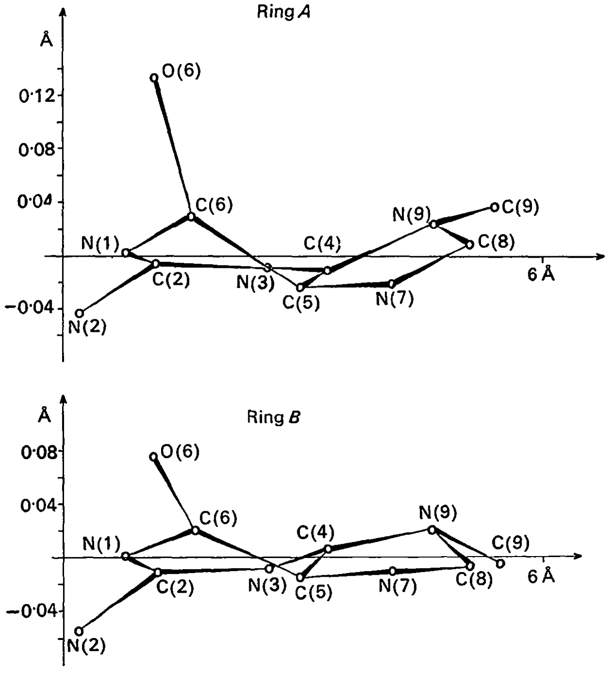

Fig. 3. The puckering of the guanine ligands. The scale of the ordinate is expanded relative to the abscissa.

SO_4^{2-}, NO_3^-, ClO_4^-. The influence on the melting temperature of DNA by varying salt concentration is found to be dependent on the base composition (Hamaguchi & Geiduschek, 1962). However, it is not clear whether the denaturing action of electrolytes is due to effects on the structure of the solvent or due to the breaking of hydrogen bonds between complementary bases.

The formation constants for Cu^{2+} nucleoside complexes are reported to be much larger for guanosine than for adenosine (Fiskin & Beer, 1965). Comparing adenine and guanine, we find that only the latter has the ability to accommodate a strong intra-purine H-bond bridge *via* a coordinated water molecule. It is not evident, however, to what extent different anions in the coordination sphere may alter this H-bond arrangement.

Geometry of the 9-methylguanine ligands

The bond lengths and angles of the two crystallographically independent guanine ligands are given in Fig. 1. The agreement between chemically equivalent dimensions is satisfactory, taking into account the high standard deviations. Any changes in molecular dimensions due to metal binding are expected to be less than the limit of error in this investigation. The guanine rings are appreciably puckered (Fig. 3). In particular the carbonyl and the amino groups exhibit large deviations from the mean molecular planes. The deformation of the two ligands is remarkably similar considering the differences in ionic environment.

Molecular packing and hydrogen bonding

The crystal packing is shown in stereo drawings viewed along **b** [Fig. 2(*a*)] and **a** [Fig. 2(*b*)]. Hydrogen-bond distances and angles are listed in Table 3. The complexes are arranged in an infinite helical chain running along the screw axis. *A* and *B* rings are stacked on top of each other with almost identical interplanar distances (3·27 Å) between alternate rings [Fig. 2(*b*)]. The orientation of *A* relative to *B* is such as to leave the carbonyl O almost exactly on top of N(7) when projected perpendicular to the ring plane.

The two guanine ligands are each hydrogen bonded in centrosymmetrical pairs involving N(3) and the amino group. Each H-bonded pair is approximately planar. As mentioned above guanine has the rare ability to form di-hydrogen bonds to certain oxy anions. In the present structure ligand *A* is H-bonded to SO_4^{2-} through N(1) and the amino group, N(1)–H(1)$\cdots$O(1) $=2·714$ and N(2)–H(21)$\cdots$O(2)$=2·890$ Å. The corresponding hydrogen-bond donors on ligand *B* are not interacting with sulphate, but participate in H-bonding to water molecules O(10) and O(8). The hydrogen-bonding network of the disordered water is difficult to clarify.

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The Crystal and Molecular Structure of Dipotassium *trans*-Dicarbonatotetraaquocobalt(II), *trans*-$K_2[Co(CO_3)_2(H_2O)_4]$

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The crystal structure of the salt *trans*-$K_2[Co(CO_3)_2(H_2O)_4]$ has been determined by single-crystal, X-ray diffraction methods. The crystals are monoclinic, space group $P2_1/n$, with a = 11·450 (1), b = 6·184 (1), c = 6·817 (1) Å, β = 99·46 (1)°, Z = 2, at 23°C. At −40°C, the temperature at which the intensities were collected, the unit-cell parameters were: a = 11·424 (1), b = 6·173 (1), c = 6·809 (1) Å, β = 99·40 (1)°. Full-matrix least-squares refinement of 2219 intensities $[I > 2\sigma(I)]$ collected by θ–2θ scans on a Syntex $P2_1$ diffractometer (Mo $K\alpha$ radiation) converged at a conventional R of 0·024. All non-hydrogen atoms were refined with anisotropic thermal parameters, H atoms with isotropic parameters. The Co atom (located on a crystallographic inversion center) is octahedrally coordinated with two monodentate carbonate groups to form a *trans*-$[Co(CO_3)_2(H_2O)_4]^{2-}$ complex anion, in agreement with predictions made on the basis of infrared and electronic spectra. The Co–O bond lengths are: Co–O (carbonate) = 2·068 (1); Co–O(water) = 2·121 (1) and 2·130 (1) Å. The carbonate group, with C–O distances of 1·291 (1), 1·291 (1) and 1·284 (1) Å, shows almost no distortion from D_{3h} symmetry. The complex ions are interconnected by a network of hydrogen bonds from the H atoms of the water molecules to the O atoms of the carbonate groups.

Introduction

The infrared spectrum of a carbonatometallate complex may often be used to discern the presence of a bidentate and/or monodentate carbonate ligand. From an analysis of the infrared spectrum, Scott (1967) and Blumentritt (1967) concluded that the title compound contained monodentate carbonate ions. From the electronic spectrum, they additionally deduced that the cobalt atom was octahedrally coordinated, forming a $[Co(CO_3)_2(H_2O)_4]^{2-}$ species. The crystal structure was undertaken to verify these predictions, to assist in further correlations between the infrared spectrum and the bonding of the carbonate ion, and to continue our investigation into the distortion (from D_{3h} symmetry) of the carbonate ion when coordinated to transition metal ions.

Experimental

Crystals of the title compound were prepared according to the method of Reynolds (1898). Preliminary unit-cell parameters and space-group information were obtained from Weissenberg photographs. The lattice parameters at 23 °C were refined by the least-squares method from the Bragg angles of 23 reflections ($135 < 2\theta < 147$°, Cu $K\alpha_1$, λ = 1·54050 Å) measured on a G.E. XRD-5 diffractometer. The lattice parameters at −40 °C were refined with 60 low-angle reflections ($24 < 2\theta < 30$°, Mo $K\alpha$, λ = 0·71069 Å) measured on a Syntex $P2_1$ diffractometer using the Syntex centering routine. Table 1 summarizes the crystal data.

A crystal with dimensions of 0·13 × 0·15 × 0·35 × 0·39 mm perpendicular to (100), $(10\bar{1})$, $(1\bar{1}0)$ and (110),

Table 1. *Crystal data*

trans-$K_2[Co(CO_3)_2(H_2O)]_4$, F.W. 329·2
Monoclinic, $P2_1/n$, Z = 2

	at 23 °C	at −40 °C
a	11·450 (1) Å	11·424 (1) Å
b	6·184 (1)	6·173 (1)
c	6·817 (1)	6·809 (1)
β	99·46 (1)	99·40 (1)°
V	476·1 Å^3	473·7 Å^3
D_m	2·293 g cm^{-3}	
D_x	2·296	