X-Ray Crystal Structure of Bis(adeninium) *trans*-Bis(adenine)tetra-aquocobalt(II) Bis(sulphate) Hexahydrate: a Complex of Unidentate Adenine Containing Adenine–Adeninium Hydrogen-bonded Pairs

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The structure of the title compound has been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Crystals are monoclinic, with unit-cell dimensions: $a = 13{\cdot}971(2)$, $b = 7{\cdot}190(1)$, $c = 19{\cdot}900(3)$ Å, $\beta = 101{\cdot}82(2)°$, space group $P2_1/n$, $Z = 2$. Least-squares refinement, by use of 2275 independent reflections, has reached R 0·060.

The structure contains the centrosymmetric $[Co(H_2O)_4(adenine)_2]^{2+}$ ion, adeninium and sulphate ions, and molecules of water of solvation, held together by an intricate network of hydrogen bonds. In the complex cation the cobalt atom has octahedral co-ordination, and the co-ordinated adenine is unidentate, bonding *via* N(9). Co–N is 2·164 Å and the two independent cobalt–water distances are 2·073 and 2·114 Å.

The hydrogen-bond network contains the following types of linkage: O–H ··· O, N–H ··· O, O–H ··· N, N–H ··· N, and possibly C–H ··· O. A feature of the structure is the presence of adenine–adeninium pairs hydrogen-bonded together *via* N(1) ··· H–N(10) and N(10)–H ··· N(7).

THERE is a growing interest in the interaction of metal ions with nucleotides and nucleic acids.[1] As part of a programme of crystallographic studies on transition-metal complexes with nucleotides and nucleotide bases we have determined the structure of a new cobalt–adenine (ade) compound.[2] Although several cobalt–adenine complexes have been reported [3] this is the first whose crystal structure has been determined. This *X*-ray study has shown the compound to have the formula $(adeH)_2[Co(H_2O)_4(ade)_2](SO_4)_2,6H_2O$. The adenine ligand is unidentate, co-ordinating *via* N(9) as in $[Cu(adeH)_2Br_2]Br_2$,[4] while in $Zn(adeH)Cl_3$ [5] it bonds *via* N(7). In the other three metal–adenine complexes whose crystal structures are known, the inner complex $[Cu(C_5H_4N_5)_2(H_2O)]_2,6H_2O$,[6] $[Cu(ade)_2Cl]_2Cl_2,6H_2O$,[7] and $Cu_3Cl_8(adeH)_2,4H_2O$,[8] adenine acts as a bridging ligand co-ordinating *via* N(3) and N(9).

A preliminary account of this work has appeared.[2]

EXPERIMENTAL

Pale pink needles of the complex were obtained from aqueous solutions of adenine and cobalt(II) sulphate (2 : 1 mol ratio).

Crystal Data.—$C_{20}H_{42}CoN_{20}O_{18}S_2$, $M = 973{\cdot}8$, Monoclinic, $a = 13{\cdot}971(2)$, $b = 7{\cdot}190(1)$, $c = 19{\cdot}900(3)$ Å, $\beta = 101{\cdot}82(2)°$, $U = 1956{\cdot}6$ Å^3, $D_m = 1{\cdot}66$, $Z = 2$, $D_c = 1{\cdot}65$, $F(000) = 1010$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 52{\cdot}1$ cm^{-1}. Space group $P2_1/n$ (No. 14) from systematic absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$.

The crystals have b as the needle axis and twinning is very common. The space group was determined from preliminary Weissenberg photographs. The single crystal used for the collection of intensity data was *ca.* 0·10 × 0·03 × 0·02 mm, and was mounted about the b axis on a Siemens off-line four-circle diffractometer. Cu-K_α radiation at a take-off angle of 4·5°, a nickel β filter, and a Na(Tl)I scintillation counter were used. The intensities of 2275 independent reflections were measured (to θ 53°) by the θ—2θ scan technique with a 'five-value' measuring procedure.[9] Of these 429 were judged to be unobserved having $I < 2{\cdot}58\sigma(I)$ (*i.e.* <99% confidence level). The 008 reflection was measured as a reference every 50 reflections, and its net count did not vary noticeably during the data collection (*ca.* 8 days). Data were scaled by use of the reference reflection and Lorentz and polarisation corrections applied. In view of the small size of the crystal and the modest value of μ, data were not corrected for absorption.

Solution and Refinement of the Structure.—The crystal structure calculations system '*X*-ray '63' [10] and its updated version [11] were used to solve and refine the structure. Calculations were carried out on the Imperial College IBM 7094 and CDC 6400 and the University of London CDC 6600 and 7600 computers.

We encountered considerable difficulty in interpreting the Patterson synthesis, because of uncertainty about the stoicheiometry of the compound and the unexpected location of the cobalt atom on a centre of symmetry at the origin. Eventually isotropic least-squares refinement of cobalt and sulphur atoms in their correct positions gave R 0·55 and the resulting difference-Fourier synthesis showed the positions of 15 further non-hydrogen atoms. A few cycles of refinement reduced R to 0·39, and the remaining atoms could then be located. Because of the number of atoms, block-diagonal matrix refinement was then used, and R was reduced to 0·100 for the 31 non-hydrogen atoms. When all atoms were allowed to refine with anisotropic thermal parameters R became 0·071. A difference-Fourier synthesis revealed the positions of the 11 hydrogen atoms

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attached to the adenine groups, and these were included in refinement as a fixed atom contribution with the isotropic temperature factors of their parent atoms (R 0·065). The ten somewhat less well defined water hydrogen atoms were then located and refinement as before gave the final R 0·060. In the final stages a weighting scheme of the type suggested by Hughes[12] was applied with $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geqslant F^*$, with $F^* = 45$ found to be optimum.

Atomic scattering factors were taken from ref. 13 except those for hydrogen which were taken from ref. 14. The real and the imaginary parts of the anomalous dispersion correction for cobalt were taken from ref. 15. Final fractional co-ordinates of non-hydrogen atoms are listed in Table 1, while Table 2 shows the coefficients in the expression for the anisotropic temperature factor $\exp\,[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and also the root-mean-square amplitudes of vibration along the principal axes of the thermal ellipsoid. Standard deviations have been estimated from block-diagonal matrix refinement and are, therefore, a slight underestimate of the true deviations. The co-ordinates of the hydrogen atoms are given in Table 3, and the observed structure amplitudes and the calculated structure factors are listed in Supplementary Publication No. SUP 20703 (8 pp., 1 microfiche).*

TABLE 1

Fractional co-ordinates with estimated standard deviation in parentheses. The atoms in the adenine groups have been given a number *mn*, where *m* agrees with the conventional numbering, and *n* = 1 for ade and 2 for adeH

Atom	x	y	z
Co(1)	0	0	0
O(1)	0·0404(3)	0·0121(8)	−0·0966(2)
O(2)	−0·0069(3)	0·2871(6)	0·0074(3)
N(11)	0·3992(4)	−0·1663(8)	−0·0053(3)
C(21)	0·3148(5)	−0·1488(9)	−0·0513(3)
N(31)	0·2284(4)	−0·0967(7)	−0·0405(2)
C(41)	0·2316(4)	−0·0509(8)	0·0259(3)
C(51)	0·3141(4)	−0·0574(8)	0·0768(3)
C(61)	0·4022(4)	−0·1202(8)	0·0610(3)
N(71)	0·2859(3)	−0·0009(8)	0·1362(2)
C(81)	0·1894(4)	0·0331(9)	0·1181(3)
N(91)	0·1519(3)	0·0040(7)	0·0522(2)
N(101)	0·4862(4)	−0·1429(8)	0·1066(3)
N(12)	0·1615(4)	−0·0296(7)	0·3805(3)
C(22)	0·2567(5)	0·0249(9)	0·3931(3)
N(32)	0·3163(4)	0·0152(8)	0·4529(3)
C(42)	0·2725(4)	−0·0569(8)	0·5022(3)
C(52)	0·1776(4)	−0·1174(8)	0·4949(3)
C(62)	0·1162(5)	−0·1017(9)	0·4303(3)
N(72)	0·1585(4)	−0·1783(8)	0·5565(3)
C(82)	0·2429(5)	−0·1535(10)	0·5993(3)
N(92)	0·3144(4)	−0·0821(8)	0·5690(3)
N(102)	0·0236(4)	−0·1410(8)	0·4154(3)
S(1)	0·47461(11)	0·0435(2)	0·29750(8)
O(11)	0·4921(4)	−0·0296(9)	0·3669(3)
O(12)	0·3727(4)	0·0804(10)	0·2691(3)
O(13)	0·5129(4)	−0·0813(10)	0·2516(3)
O(14)	0·5310(4)	0·2210(8)	0·3018(3)
O(3)	0·0748(4)	0·0508(7)	0·2534(2)
O(4)	0·1324(4)	0·1468(8)	0·7070(3)
O(5)	0·1772(4)	−0·2002(9)	0·7626(4)

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Determination of the crystal structure has shown that it contains four separate species: the $[Co(H_2O)_4(ade)_2]^{2+}$ complex cation, adeninium and sulphate ions, and molecules of water of solvation. These are shown in Figure 1, which also indicates the numbering used in the asymmetric unit. The more important bond lengths and bond angles are listed in Table 4.

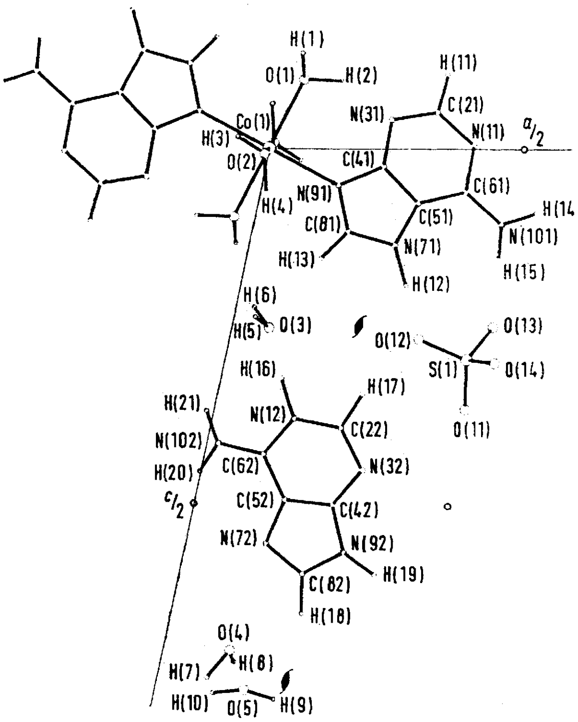

FIGURE 1 A fragment of the structure viewed down the *b* axis, showing the atom numbering scheme used in this analysis

In the complex cation the cobalt atom lies on a centre of symmetry and is co-ordinated to two *trans* unidentate adenine molecules and to four water molecules. The metal co-ordination is almost undistorted octahedral, consistent with the pale pink colour of the crystals. Figure 2 shows the complex cation, and also the thermal vibration ellipsoids[16] of the non-hydrogen atoms. The adenine is co-ordinated *via* N(9), as found in $[Cu(adeH)_2Br_2]Br_2$[4] and in two guanine (gua) complexes. $Cu_2Cl_6(guaH)_2,2H_2O$[17] and $Zn(guaH)Cl_3$,[5] whereas in $Zn(adeH)Cl_3$[5] it is co-ordinated *via* N(7). The other

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are supplied as full size copies).

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co-ordination mode of adenine is *via* N(3) and N(9) when it acts in a bridging role.[6-8]

TABLE 2

Anisotropic thermal parameters and root-mean-square amplitudes of vibration (Å)

	$10^5\beta_{11}$	$10^4\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$	Min.	Inter.	Max.
Co(1)	289(8)	62(3)	138(4)	34(13)	−1(4)	−6(9)	0·127	0·149	0·185
S(1)	302(9)	115(4)	108(4)	−53(15)	−18(5)	−65(10)	0·126	0·179	0·187
	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$			
N(11)	35(3)	137(13)	17(2)	11(5)	2(2)	−2(4)	0·166	0·180	0·206
C(21)	42(4)	109(14)	16(2)	3(6)	6(2)	−4(4)	0·162	0·180	0·200
N(31)	31(3)	124(12)	13(1)	2(5)	1(2)	−4(3)	0·152	0·175	0·188
C(41)	28(3)	72(13)	15(2)	−4(5)	1(2)	4(4)	0·133	0·155	0·186
C(51)	25(3)	72(13)	15(2)	−7(5)	2(2)	−1(4)	0·130	0·159	0·175
C(61)	35(4)	65(13)	16(2)	−5(6)	2(2)	3(4)	0·128	0·169	0·196
N(71)	28(3)	138(12)	15(2)	5(5)	0(2)	−7(4)	0·151	0·173	0·203
C(81)	33(4)	123(15)	20(2)	−1(6)	6(2)	−4(5)	0·175	0·177	0·200
N(91)	30(3)	103(11)	12(1)	4(5)	−2(2)	−5(3)	0·138	0·159	0·193
N(101)	28(3)	164(13)	18(2)	13(5)	−1(2)	−6(4)	0·151	0·185	0·224
N(12)	37(3)	105(12)	16(2)	−9(5)	3(2)	−1(3)	0·159	0·175	0·195
C(22)	35(4)	86(14)	25(2)	6(6)	7(2)	−2(5)	0·146	0·184	0·220
N(32)	37(3)	113(12)	20(2)	1(5)	1(2)	−1(4)	0·172	0·176	0·212
C(42)	27(3)	69(13)	21(2)	0(5)	1(2)	−2(4)	0·134	0·157	0·208
C(52)	34(4)	74(13)	20(2)	4(6)	2(1)	2(4)	0·137	0·176	0·205
C(62)	36(4)	81(13)	21(2)	10(6)	1(2)	−7(4)	0·137	0·177	0·221
N(72)	42(3)	120(12)	18(2)	0(5)	7(2)	2(4)	0·176	0·187	0·201
C(82)	45(4)	165(17)	17(2)	3(7)	−4(2)	−1(5)	0·163	0·207	0·234
N(92)	38(3)	136(12)	19(2)	−6(5)	−1(2)	8(4)	0·167	0·181	0·224
N(102)	29(3)	169(14)	21(2)	−16(5)	−4(2)	4(4)	0·146	0·201	0·236
O(1)	34(3)	252(13)	18(1)	13(5)	−1(1)	−3(4)	0·127	0·149	0·185
O(2)	43(3)	109(10)	29(2)	6(5)	0(2)	−4(3)	0·162	0·203	0·261
O(3)	65(3)	202(13)	21(1)	10(6)	−9(2)	1(4)	0·171	0·230	0·286
O(4)	59(3)	234(14)	25(2)	16(6)	8(2)	14(4)	0·206	0·230	0·264
O(5)	55(4)	267(17)	77(3)	17(7)	9(3)	71(6)	0·205	0·238	0·420
O(11)	75(4)	319(17)	22(2)	−25(7)	−2(2)	29(4)	0·185	0·252	0·326
O(12)	42(3)	480(21)	24(2)	15(7)	−6(2)	−7(5)	0·171	0·250	0·357
O(13)	70(4)	401(20)	30(2)	31(7)	5(2)	−45(5)	0·201	0·249	0·359
O(14)	85(4)	191(14)	40(2)	−42(6)	3(2)	−21(4)	0·186	0·286	0·309

TABLE 3

Fractional co-ordinates of the hydrogen atoms

Atom	*x*	*y*	*z*
H(1)[O(1)] *	0·026	0·131	−0·133
H(2)[O(1)]	0·114	−0·045	−0·095
H(3)[O(2)]	−0·066	0·345	−0·017
H(4)[O(2)]	0·012	0·345	0·062
H(5)[O(3)]	0·043	0·168	0·238
H(6)[O(3)]	0·038	−0·054	0·225
H(7)[O(4)]	0·100	0·218	0·745
H(8)[O(4)]	0·145	0·023	0·723
H(9)[O(5)]	0·238	−0·264	0·775
H(10)[O(5)]	0·119	−0·300	0·767
H(11)[C(21)]	0·320	−0·181	−0·103
H(12)[N(71)]	0·324	0·009	0·193
H(13)[C(81)]	0·148	0·059	0·155
H(14)[N(101)]	0·548	−0·169	0·091
H(15)[N(101)]	0·495	−0·114	0·155
H(16)[N(12)]	0·121	−0·018	0·325
H(17)[C(22)]	0·285	0·059	0·347
H(18)[C(82)]	0·257	0·155	0·655
H(19)[N(92)]	0·383	−0·045	0·600
H(20)[N(102)]	0·000	−0·205	0·455
H(21)[N(102)]	−0·012	−0·150	0·370

* The atom to which each H is attached is listed in square brackets.

The Co–N distance is 2·164 Å. Cobalt is known to exhibit a rather wide range of Co–N distances, even in the same compound, *e.g.* 1·96—2·25 Å in the [Co(2-methylimidazole)$_4$NO$_3$]$^+$ ion.[18] The distance found in the title compound can, however, be regarded as normal compared to Cu–N distances of 2·01—2·04 Å found in copper–adenine complexes,[4,7,8] if one considers the metal–nitrogen distances of 2·02 and 2·14 Å respectively in the isostructural pair Cu(py)$_2$Cl$_2$ and Co(py)$_2$Cl$_2$.[19] The two independent Co–O(water) distances of 2·073 and 2·114 Å can also be regarded as unexceptional, *e.g.* 2·109 Å in [Co(H$_2$O)$_4$(C$_6$H$_4$NO$_2$)$_2$].[20] Since both ligand water molecules are involved in hydrogen bonding, it may be that the small, though statistically significant, difference in the two bond lengths is a consequence of differing constraints imposed by these linkages.

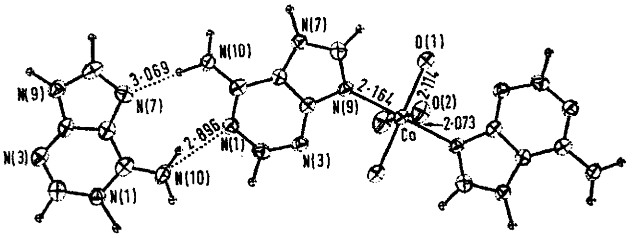

FIGURE 2 A centrosymmetric cation [Co(H$_2$O)$_4$(ade)$_2$]$^{2+}$ and an adeninium cation joined by N–H · · · N bonds. The hydrogen atoms of the ligand water molecules have been removed for sake of clarity. The thermal vibration ellipsoids have been scaled to enclose 50% probability; those of the hydrogen atoms are arbitrary. (Nitrogen atom labels show atom type and do not refer to atomic positions listed in Table 1)

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The adeninium cations are connected to the ligand adenine groups by double N–H ··· N bonds of the type N(10)–H ··· N(1) and N(7) ··· H–N(10), with the former being the stronger (Figure 2). A similar linkage of adenine units is found in 9-methyladenine [21] and in deoxyadenosine,[22] forming an infinite zig-zag chain. In this structure, on the other hand, the direct linkage between ade and adeH is limited to a discrete pair because the N(1) site in adeH is protonated. The arrangements of these pairs is such that in the direction of the *b* axis they stack so that ade and adeH alternate (Figure 3). The nearest non-bonded contacts between the almost parallel planes of ade and adeH are *ca.* 3·3 Å.

TABLE 4

Bond lengths (Å) and bond angles (°) with standard deviations in parentheses

Cobalt co-ordination			
Co(1)–N(91)	2·164(4)	N(91)–Co(1)–O(1)	91·0(2)
Co(1)–O(1)	2·114(5)	N(91)–Co(1)–O(2)	90·5(2)
Co(1)–O(2)	2·073(4)	O(1)–Co(1)–O(2)	92·8(2)
Ade		AdeH	
N(11)–C(21)	1·342(7)	N(12)–C(22)	1·361(8)
C(21)–N(31)	1·323(9)	C(22)–N(32)	1·307(8)
N(31)–C(41)	1·352(8)	N(32)–C(42)	1·360(9)
C(41)–C(51)	1·372(7)	C(42)–C(52)	1·375(9)
C(51)–C(61)	1·405(9)	C(52)–C(62)	1·396(8)
C(61)–N(11)	1·352(8)	C(62)–N(12)	1·381(9)
C(61)–N(101)	1·338(7)	C(62)–N(102)	1·313(8)
C(51)–N(71)	1·382(8)	C(52)–N(72)	1·378(9)
N(71)–C(81)	1·344(8)	N(72)–C(82)	1·318(8)
C(81)–N(91)	1·325(8)	C(82)–N(92)	1·369(9)
N(91)–C(41)	1·382(8)	N(92)–C(42)	1·352(8)
C(21)–N(11)–C(61)	119·3(6)	C(22)–N(12)–C(62)	123·4(5)
N(11)–C(21)–N(31)	128·3(6)	N(12)–C(22)–N(32)	124·6(6)
C(21)–N(31)–C(41)	112·3(5)	C(22)–N(32)–C(42)	112·4(5)
N(31)–C(41)–C(51)	124·6(6)	N(32)–C(42)–C(52)	127·7(5)
C(41)–C(51)–C(61)	119·2(6)	C(42)–C(52)–C(62)	117·9(6)
C(61)–C(51)–N(71)	134·6(5)	C(62)–C(52)–N(72)	130·6(6)
C(51)–C(61)–N(11)	116·3(5)	C(52)–C(62)–N(12)	114·0(6)
C(51)–C(61)–N(101)	125·0(6)	C(52)–C(62)–N(102)	125·3(6)
N(11)–C(61)–N(101)	118·6(6)	N(12)–C(62)–N(102)	120·7(5)
C(51)–C(41)–N(91)	110·5(5)	C(52)–C(42)–N(92)	106·0(6)
N(31)–C(41)–N(91)	124·9(5)	N(32)–C(42)–N(92)	126·3(5)
C(41)–C(51)–N(71)	106·1(5)	C(42)–C(52)–N(72)	111·5(5)
C(51)–N(71)–C(81)	105·7(5)	C(52)–N(72)–C(82)	102·8(6)
N(71)–C(81)–N(91)	114·1(6)	N(72)–C(82)–N(92)	113·8(6)
C(81)–N(91)–C(41)	103·6(5)	C(82)–N(92)–C(42)	106·0(5)
Co(1)–N(91)–C(41)	126·9(4)		
Co(1)–N(91)–C(81)	128·9(4)		
Sulphate ion			
S(1)–O(11)	1·451(6)	S(1)–O(13)	1·458(7)
S(1)–O(12)	1·445(5)	S(1)–O(14)	1·494(6)
O(11)–S(1)–O(12)	113·5(4)	O(12)–S(1)–O(13)	109·1(3)
O(11)–S(1)–O(13)	111·2(4)	O(12)–S(1)–O(14)	109·4(4)
O)11)–S(1)–O(14)	105·7(3)	O(13)–S(1)–O(14)	107·8(4)

The bond lengths found in the ligand adenine are very similar to those recently reported for the adenine group in adenosine [23] (within 0·01 Å), except for the distances N(9)–C(8) and C(8)–N(7). The explanation for the difference lies almost certainly in the fact that in ade N(9) is linked to cobalt and N(7) is protonated, while in adenosine N(9) is linked to a glycosidic carbon atom and N(7) is not protonated. The angle C(61)–N(11)–C(21) is 119·3° and is somewhat larger than that predicted [24] for a non-protonated six-membered-ring nitrogen (125 ± 3° for protonated and 116 ± 3° for non-protonated nitrogen). In the accurate structure determination of adenosine, however the equivalent angle is similar [119·3(2)°] to that in the title compound.

In the adeH moiety the bond lengths and bond angles are very like those found in the adenine group in adenosine 3′-phosphate (3′-AMP),[25] and slightly less so compared to those in the less-accurate structure of adenosine 5′-phosphate (5′-AMP).[26] These groups have similar protonation sites except that adeH has a proton at N(9) whereas the other two have a glycosidic carbon atom.

When comparing bond lengths and bond angles found in compounds where adenine is protonated at N(1) we pointed out [4] that the biggest differences in terms of angles between a pair of copper complexes and two AMP molecules were centred at C(4) and C(5). In this structure, quite apart from angular changes at N(1) due to protonation, we find the same situation. Thus in ade N(9)–C(4)–C(5) > C(4)–C(5)–N(7) (110·5 and 106·1°), whereas in adeH N(9)–C(4)–C(5) < C(4)–C(5)–N(7) (106·0 and 111·5°). Clearly such differences are associated with, on one hand, a metal atom bonding to N(9), and on the other, a hydrogen or a glycosidic carbon atom.

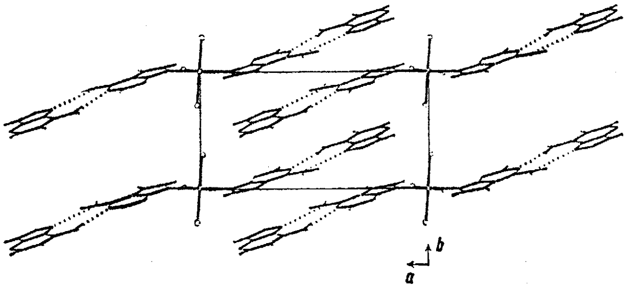

FIGURE 3 A view of a layer, centred about $z \approx 0$, of complex and adeH cations, showing the alternate stacking of ade and adeH in the *b* direction

The three-dimensional packing of the four species in the unit cell is shown as a stereoscopic pair of drawings in Figure 4. It can be seen that the cationic species are concentrated in layers centred about $z \approx 0$ and $\frac{1}{2}$, while the sulphate ions and water molecules occupy the region of $z \approx \frac{1}{4}$ and $\frac{3}{4}$. All these groups are joined together by a complicated network of hydrogen bonds. Of the 21 independent hydrogen atoms in the structure the 17 which are attached to oxygen or nitrogen atoms are all involved in forming hydrogen bonds. The remaining four hydrogen atoms are attached to ring carbon atoms, and of these two may also be involved in weak interactions. The interatomic distances in the 19 cases and the angles involved are given in Table 5.

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[23] T. F. Lai and R. E. Marsh, *Acta Cryst.*, 1972, **B28**, 1982.

[24] C. Singh, *Acta Cryst.*, 1965, **19**, 861.

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[26] J. Kraut and L. H. Jensen, *Acta Cryst.*, 1963, **16**, 79.

Apart from the two N–H···N bonds which hold together the ade–adeH pairs, the ligand adenine forms two N–H···O bonds to the sulphate ion, in a similar manner to that reported in the structure of an adenine *N*^{1}-oxide–sulphuric acid complex.[27] There is also an intramolecular hydrogen bond between a ligand water molecule O(1) and N(31). The adeH group also forms three N–H···O bonds to the sulphate ion and to water molecules. Both the ligand water molecules are involved in two hydrogen bonds each, while the three free water molecules form either three or four such linkages. The strongest hydrogen bond in the structure is N(12)–H···O(3), 2·636 Å, shorter than any of the O–H···O bonds. In every adenine complex we have studied we find that N(1) is involved in the strongest bond. Judging from the lengths of like bonds in Table 5 the following sequence of hydrogen-bond strength is suggested for the nitrogen atoms in adenine: N(1) > N(7) > N(10) ≈ N(3) ≈ N(9).

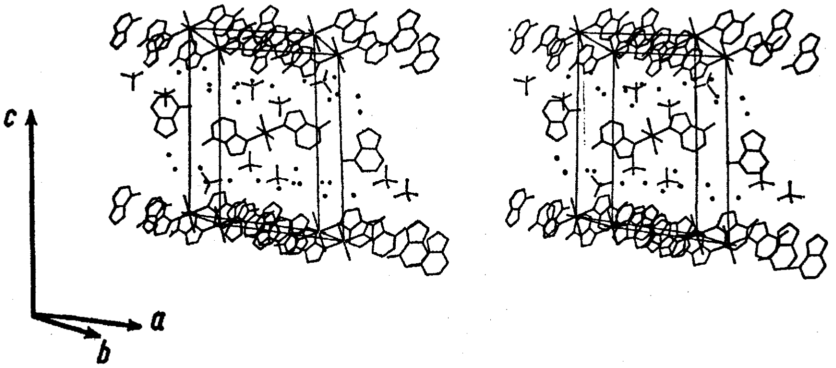

FIGURE 4 A stereoscopic view of the structure. For sake of clarity only one complex cation is shown in the layer $z \approx \frac{1}{2}$; this layer is of the same complexity as those at $z \approx 0$ and 1

TABLE 5

Interatomic distances (Å) and angles (°) defining hydrogen bonds and possible C–H···O interactions

N(71)–H(12)···O(12)	2·737	N(71)–H(12)–O(12)	165
C(81)–H(13)···O(3)	3·405	C(81)–H(13)–O(3)	165
N(101)–H(14)···N(72$^{\mathrm{I}}$)	3·069	N(101)–H(14)–N(72$^{\mathrm{I}}$)	159
N(101)–H(15)···O(13)	2·868	N(101)–H(15)–O(13)	175
N(12)–H(16)···O(3)	2·636	N(12)–H(16)–O(3)	165
C(22)–H(17)···O(12)	3·241	C(22)–H(17)–O(12)	165
N(92)–H(19)···O(11$^{\mathrm{II}}$)	2·857	N(92)–H(19)–O(11$^{\mathrm{II}}$)	166
N(102)–H(20)···N(11$^{\mathrm{III}}$)	2·896	N(102)–H(20)–N(11$^{\mathrm{III}}$)	152
N(102)–H(21)···O(4$^{\mathrm{IV}}$)	2·917	N(102)–H(21)–O(4$^{\mathrm{IV}}$)	157
O(1)–H(1)···O(14$^{\mathrm{V}}$)	2·770	O(1)–H(1)–O(14$^{\mathrm{V}}$)	162
O(1)–H(2)···N(31)	2·749 *	O(1)–H(2)–N(31)	144
O(2)–H(3)···O(11$^{\mathrm{VI}}$)	2·797	O(2)–H(3)–O(11$^{\mathrm{VI}}$)	162
O(2)–H(4)···N(32$^{\mathrm{V}}$)	2·863	O(2)–H(4)–N(32$^{\mathrm{V}}$)	168
O(3)–H(5)···O(13$^{\mathrm{VI}}$)	2·908	O(3)–H(5)–O(13$^{\mathrm{VI}}$)	156
O(3)–H(6)···O(14$^{\mathrm{VII}}$)	2·889	O(3)–H(6)–O(14$^{\mathrm{VII}}$)	163
O(4)–H(7)···O(14$^{\mathrm{VIII}}$)	2·750	O(4)–H(7)–O(14$^{\mathrm{VIII}}$)	165
O(4)–H(8)···O(5)	2·748	O(4)–H(8)–O(5)	173
O(5)–H(9)···O(4$^{\mathrm{IX}}$)	2·827	O(5)–H(9)–O(4$^{\mathrm{IX}}$)	170
O(5)–H(10)···O(13$^{\mathrm{III}}$)	2·753	O(5)–H(10)–O(13$^{\mathrm{III}}$)	162

Roman numeral superscripts refer to atoms in the following positions:

I $\frac{1}{2} + x, -\frac{1}{2} - y, z - \frac{1}{2}$
II $1 - x, -y, 1 - z$
III $x - \frac{1}{2}, -\frac{1}{2} - y, \frac{1}{2} + z$
IV $-x, -y, 1 - z$
V $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$
VI $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
VII $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$
VIII $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$
IX $\frac{1}{2} - x, y - \frac{1}{2}, 1\frac{1}{2} - z$

* Intramolecular.

The bond lengths in the sulphate ion vary from 1·445 to 1·494 Å, an almost identical range to that found in adenine *N*^{1}-oxide–sulphuric acid complex.[27] As in that compound we also find that there is a correlation between the length of the S–O bond and the number and strength of the hydrogen bonds in which each sulphate oxygen is involved. Thus O(14) forms three O···H–O bonds, O(13) forms two O···H–O and one O···H–N bonds, O(11) forms one O···H–O and one O···H–N bond, and O(12) forms one O···H–N and one possible O···H–C bond. As can be seen from Table 4, S–O(14) is the longest and S–O(12) the shortest sulphur–oxygen bond.

Sundaralingam,[25,27] among others, has suggested the existence of weak C–H···O hydrogen bonds in this type of compound. In our structure two of the C–H bonds point more or less directly at oxygen atoms and produce a sensible hydrogen-bonding geometry at these atoms. Although the C···O distances of 3·24 for C(22)···O(12) and 3·40 Å for C(81)···O(3) are unexceptional, the H···O distances of 2·17 and 2·39 Å respectively are shorter than the 2·6 Å suggested by Pauling [28] for O···H van der Waals contact distance. If, however, one takes the value of 2·4 Å for the van der Waals distance as suggested by Ramachandran *et al.*,[29] then only one of these distances is shorter than expected. At best, therefore, these may represent extremely weak interactions.

Table 6 shows details of the planarity of the ade and adeH moieties, and also the displacement from these planes of the various atoms which are either directly or hydrogen bonded. The ligand adenine is not strictly planar, being hinged about an approximate line N(71), C(51), C(21), and the slight distortion can be correlated with the pull of the various external bonds. Both

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TABLE 6

Planarity of the adenine and adeninium groups

(*a*) Ade

Plane equation: $3{\cdot}74x + 6{\cdot}80y - 4{\cdot}68z = 0{\cdot}39$

Devations (Å) of plane atoms: N(11) −0·004, C(21) 0·014, N(31) −0·006, C(41) 0·008, C(51) 0·034, C(61) 0·011, N(71), 0·035, C(81) −0·011, N(91) −0·040, N(101) −0·042

Deviations of other atoms: N(102^{I}) −0·416, O(1) −0·392, O(12) 0·291, O(3) −0·952, Co(1) −0·392, N(72^{I}) −0·379, O(13) −0·202

(*b*) AdeH

Plane equation: $-4{\cdot}48x + 6{\cdot}63y + 5{\cdot}49z = 1{\cdot}17$

Deviations of plane atoms: N(12) 0·001, C(22) 0·005, N(32) 0·003, C(42) −0·009, C(52) −0·025, C(62) −0·001, N(72) −0·005, C(82) 0·017, N(92) 0·003, N(102) 0·011

Deviations of other atoms: O(3) 0·224, O(12) −0·827, O(2^{X}) 0·822, N(101^{III}) −0·123, O(11^{II}) 0·230, O(4^{IV}) 0·064, N(11^{III}) −0·215

Superscripts have the same meaning as in Table 5, in addition: X $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

these features can be seen in Figure 5. The extent of this distortion is slightly greater than that observed in 6-mercaptopurine monohydrate.[30] A lesser amount of bending may also affect the adeH group, but here the deviations from the plane are in general not significant. In a hydrogen-bonded pair ade–adeH the two planes are almost parallel (angle between them is 3·7°), and if a common plane is calculated all atoms are within 0·16 Å of that plane. Within the complex cation the O(1) · · · Co(1) · · · O(1′) vector makes a minimum angle of 18·9 with the ade plane, while for vector O(2) · · · Co(1) · · · O(2′) this angle is 65·8°.

The formation of discrete ade–adeH hydrogen-bonded pairs may be of interest in relation to biological systems. Clearly great caution should be exercised in extrapolating these results to complex biological molecules; however, it is conceivable that if, under certain conditions, an individual adenine base in a nucleic acid becomes protonated, then this may lead to an abnormal adenine–adenine pairing. Protonation of a nucleotide base would prevent normal pairing in the Watson-Crick [31] double-helix structure of DNA (ade–thy and gua–cyt), and is the basis of the most commonly accepted Löwdin theory of mutations.[32] This suggests that owing to proton tunnelling during replication, normal pairing becomes impossible and pairs of type ade–cyt and gua–thy may be formed. Adenine–adenine pairing would be geometrically rather less likely in the double-helix structure, although there is much evidence [33] that the DNA molecule undergoes considerable internal deformation in a continuous manner. The very rare and transient formation of such a linkage followed by normal replication would provide one simple mechanism for a mutation where a single thy is substituted for ade in the DNA base sequence. The formation of this abnormal pairing may be easier (though still very rare) in the transcription stages involving the less-rigid RNA species.

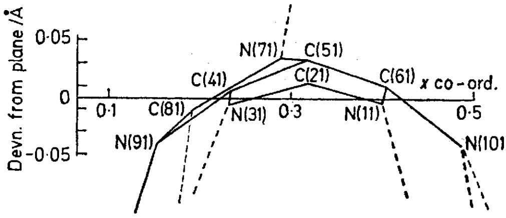

FIGURE 5 A diagram showing the bending of the ade group and the direction of the external bonds. The standard deviations of the atoms in a direction normal to the least-squares plane are 0·005—0·007 Å. *N.B.* Scale much exaggerated in the vertical direction

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[3/026 *Received, 5th January*, 1973]

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