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Crystal and Molecular Structure of Bis(creatinine)silver(I) Perchlorate Dihydrate

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The crystal and molecular structure of bis(creatinine)silver(I) perchlorate dihydrate, $[Ag(C_4H_7N_3O)_2]ClO_4 \cdot 2H_2O$, was determined from single crystal three-dimensional X-ray data collected by counter methods. The compound belongs to the monoclinic system, the space group being P2/c. *The unit cell parameters are* a = *11.405(2),* b = *6.052(2),* c = *12.325(2) Å, β = 95.95(1)° and* Z = *2. The structure was solved by direct methods and was refined by least-squares methods to a conventional* R *factor of 0.035 for 1509 observed reflections.*

The $[Ag(C_4H_7N_3O)_2]^+$ molecule is centrosymmetric with Ag being linearly coordinated through the cyclic imino nitrogen atoms of two creatinine ligands at a distance (Ag–N) of 2.100(3) Å. The H atom of the cyclic imino group in free creatinine is found to be transferred to the exocyclic imino group in the complex. The creatinine molecules are planar. There is an extensive intermolecular hydrogen bonding system in the complex involving the water molecules, the perchlorate groups and the carbonyl and the exocyclic NH_2 groups of the ligands.

Introduction

Creatinine, $\mathrm{H_3C{-}\overline{N{-}C(NH){-}NH{-}CO{-}C}H_2}$, plays an important role in protein metabolism and is as such of considerable biological interest. It has more than one bonding site towards metal ions and is capable of forming cationic, neutral and anionic metal complexes [1] similar to adenine [2]. Recently we have investigated [3] the crystal structure of creatinium tetrachlorocuprate(II), and in this paper the preparation and crystal and molecular structure of bis(creatinine)silver(I) perchlorate dihydrate is reported.

Experimental

Bis(creatinine)silver(I) perchlorate dihydrate, $[Ag(C_4H_7N_3O)_2]ClO_4 \cdot 2H_2O$ was prepared by interacting an aqueous solution of silver perchlorate with a 1 *N* solution of creatinine in perchloric acid, taken in 1:2 molar ratio. The resultant solution was filtered and concentrated on a water bath, whereby plate-like colourless crystals of the complex separated out. The crystals were collected on a filter and washed with ether. *Anal.* Found: C, 20.68; H, 3.36; N, 18.24; Ag, 22.85. Calcd. for $C_8H_{18}N_6O_8ClAg$: C, 20.46; H, 3.86; N, 17.90; Ag 22.97%. The crystals are light-sensitive.

Crystal Data

Preliminary Weissenberg and precession photographs of the crystals suggested that they belong to the monoclinic system. The systematic absences noticed from the photographs, h0l with l = 2n + 1, indicated the space group *P2/c* (C^4_{2h}, no. 13). Using a crystal of approximate dimensions 0.09 × 0.08 × 0.35 mm^3, the cell dimension were refined by least-squares from the diffractometer coordinates of 15 high-order reflections. The refined unit cell dimensions are a = 11.405(2), b = 6.052(2), c = 12.325(2) Å, β = 95.95(1)°, V = 846.1 $Å^3$. There are two formula units of the complex per unit cell, giving a calculated density of 1.843 $g \cdot cm^{-3}$ compared with the measured density of 1.82(2) $g \cdot cm^{-3}$.

X-ray Data Collection

The X-ray intensity data were collected on a Syntex $P2_1$ four-circle diffractometer at 22 °C, using graphite-monochromated MoKα radiation (Kα_1 = 0.70926 Å, Kα_2 = 0.71354 Å, θ–2θ scan, scintillation counter, take-off angle 6°). The sampling interval for each reflection was (in 2θ) 1.0° below the calculated MoKα_1 maximum to 1.0° above the calculated MoKα_2 maximum. The scan rate varied from 2 to 15° per min., depending on the intensity of the

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TABLE I. Coordinates of the Atoms in the Structure of Bis(creatinine)silver(I) Perchlorate Dihydrate.[a]

	x	y	z
Ag	0.5	0.39129(8)	0.25
Cl	0.0	0.40905(27)	0.75
O1	0.41775(26)	0.71180(50)	0.44793(23)
O2	0.08287(47)	0.28900(91)	0.81039(43)
O3	−0.05346(51)	0.54080(95)	0.81878(43)
O4	0.40596(34)	−0.00399(66)	0.12239(29)
N1	0.36183(25)	0.39972(53)	0.35007(23)
N2	0.21643(28)	0.27882(57)	0.44407(26)
N3	0.26030(33)	0.07683(65)	0.29271(31)
C1	0.35619(34)	0.54647(66)	0.43162(32)
C2	0.26103(40)	0.47463(78)	0.50095(38)
C3	0.12327(47)	0.14143(91)	0.47856(46)
C4	0.27738(31)	0.24372(63)	0.35975(30)
H1	0.2983(33)	0.4432(61)	0.5781(31)
H2	0.2043(35)	0.5739(65)	0.4915(31)
H3	0.1519(36)	0.0478(71)	0.5169(33)
H4	0.0649(35)	0.1041(65)	0.4160(30)
H5	0.0752(33)	0.2245(65)	0.5162(30)
H6	0.2074(35)	−0.0092(72)	0.2948(31)
H7	0.3056(35)	0.0512(65)	0.2482(32)
H8	0.4073(41)	0.0678(71)	0.0770(33)
H9	0.4506(37)	−0.0955(68)	0.1104(33)

[a] Estimated standard deviations are given in all tables in units of the last significant digits.

reflection. Background measurements with the total time for background counts being equal to the scan time were made at the start and end of each scan with the counter stationary. A standard reflection was measured for every 50 reflections. A complete set of 1674 unique reflections was measured up to $(\sin\theta)/\lambda = 0.62$ Å^{-1} of which 1509 reflections were accepted at statistically above background on the basis that $I > 1.96\sigma(I)$. The linear absorption coefficient was found to be 13.8 cm^{-1}, and no absorption correction was made. The reduction of data was done by applying Lorentz and polarization corrections, and a Wilson plot.

Determination and Refinement of the Structure

The structure was solved by direct methods using the MULTAN program system [4]. The program was allowed to select, besides the origin-defining reflections, four starting phases to be permuted, and the combined figure of merit values readily suggested the correct solution. Most of the non-hydrogen atoms were located from the first E map. The other nonhydrogen atoms were obtained from the subsequent Fourier and difference Fourier syntheses. All the hydrogen atoms were located from a subsequent difference Fourier map after the isotropic refinement of the nonhydrogen atoms. The atomic scattering factors for Ag, Cl, O, N, C and H were taken from the International Tables [5]. Full-matrix least-squares refinement with anisotropic temperature factors for all nonhydrogen atoms and a fixed isotropic temperature factor of 5.0 Å^2 for the hydrogen atoms converged to residuals of $R_1 = 0.035$ (including unobserved data 0.040), $R_2 = 0.034$ where $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2]^{1/2}$. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$. The weighting scheme was based on counting statistics of the intensities. The shifts in the final cycle were below 0.02σ, and the final difference Fourier map had no significant features. The final positional and thermal parameters of the atoms are given in Tables I and II. A table of the calculated and observed structure factors is available from the Editor.

TABLE II. Coefficients of the Anisotropic Temperature Factors.[a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ag	2.62(2)	3.98(2)	3.63(2)	0.0	1.08(1)	0.0
Cl	3.61(6)	3.83(7)	3.41(6)	0.0	0.45(5)	0.0
O1	4.57(15)	3.55(14)	4.49(14)	−1.41(13)	1.17(12)	−0.61(12)
O2	10.37(35)	9.22(33)	14.11(41)	4.93(30)	−3.22(32)	0.73(31)
O3	11.72(42)	14.11(45)	10.60(35)	3.43(36)	3.22(31)	−5.14(32)
O4	5.29(18)	4.65(19)	4.53(17)	1.01(15)	2.15(15)	0.41(15)
N1	2.44(12)	2.91(14)	2.92(12)	−0.22(12)	0.74(10)	−0.13(12)
N2	3.04(14)	3.34(16)	3.47(15)	−0.71(13)	1.22(12)	−0.12(13)
N3	3.54(17)	3.62(19)	4.20(17)	−0.75(14)	1.29(14)	−0.80(15)
C1	2.75(16)	3.16(19)	3.29(17)	0.06(15)	0.51(14)	0.29(14)
C2	3.57(19)	3.39(19)	3.66(18)	0.09(17)	1.19(16)	−0.30(17)
C3	4.37(24)	4.76(28)	5.29(27)	−1.03(21)	2.14(21)	0.47(22)
C4	2.38(15)	2.86(18)	3.04(16)	0.16(14)	0.31(13)	0.25(14)

[a] The temperature factors are defined as $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$; the isotropic temperature factors for the hydrogen atoms are fixed at 5.0 Å^2.

TABLE III. Interatomic Distances and Bond Angles in the Structure of Bis(creatinine)silver(I) Perchlorate Dihydrate.

Distances (Å)			Angles (°)	
Ag Coordination				
Ag–N1(N1′)	2.100(3)		N1–Ag–N1′	177.2(1)
Creatinine Molecule				
C1–C2	1.513(6)		C1–N1–Ag	123.4(3)
C1–N1	1.348(5)		C1–N1–C4	107.6(3)
C1–O1	1.227(5)		C4–N1–Ag	128.0(2)
C2–N2	1.443(6)		C2–C1–N1	108.9(3)
C3–N2	1.447(6)		C2–C1–O1	125.0(4)
C4–N1	1.363(5)		N1–C1–O1	126.1(4)
C4–N2	1.326(5)		C1–C2–N2	101.5(3)
C4–N3	1.307(5)		C2–N2–C3	124.2(4)
			C2–N2–C4	109.0(3)
C2–H1	1.02(4)		C3–N2–C4	126.8(4)
C2–H2	0.88(4)		N1–C4–N2	113.0(3)
C3–H3	0.79(4)		N1–C4–N3	122.7(4)
C3–H4	0.99(4)		N2–C4–N3	124.3(4)
C3–H5	0.91(4)			
N3–H6	0.80(4)			
N3–H7	0.81(4)			
Perchlorate Ion				
		corrected		
Cl–O2(O2′)	1.353(5)	1.454	O2–Cl–O2′	115.0(3)
Cl–O3(O3′)	1.354(6)	1.472	O2–Cl–O3	107.8(3)
			O2–Cl–O3′	109.1(3)
			O3–Cl–O3′	107.8(4)
Water Molecule				
O4–H8	0.71(4)		H8–O4–H9	103(5)
O4–H9	0.78(4)			

Results and Discussion

The structure is ionic and consists of $[Ag(N{-}CO{-}CH_2{-}N(CH_3){-}C(NH_2))_2]^+$ cations and perchlorate anions, both on twofold axes within the cell, and of water molecules. Silver(I) is strongly coordinated through the nitrogen atoms of two cyclic imino groups, resulting in a linear N–Ag–N arrangement. A SHELXTL plot of one formula unit within the structure is shown in Fig. 1. The interatomic distances and bond angles are given in Table III.

It is well established that Ag(I) generally assumes linear, triangular planar, trigonal pyramidal and tetrahedral geometries in complex compounds, of which the linear coordination is more common. Among the N-ligated linear Ag(I) complexes, the structures of which are crystallographically determined, the Ag–N distances are found to be in the range 2.12–2.20 Å [6–10]. The bond length of 2.100(3) (Ag–N1) found in the present study clearly suggests strong covalent interaction between Ag and creatinine. The value is comparable to the sum of the covalent radii (2.09 Å) given by Pauling [11]. When Ag is linearly bonded, the angle at the metal centre is observed to vary from 158 to 177° in typical Ag(I) complexes [6, 7, 12, 13]. In the present case, the configuration is almost as ideally linear as the AgN_2 species reported [7] for the polymeric glycinatosilver(I) complex.

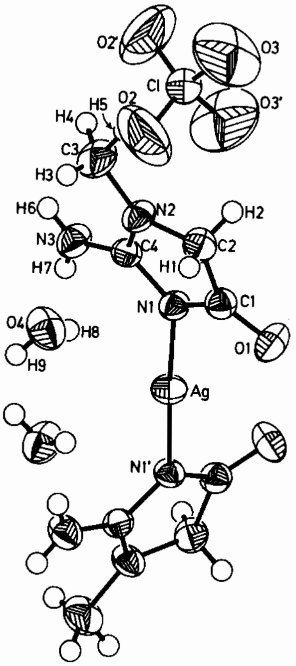

Fig. 1. Bis(creatinine)silver(I) Perchlorate Dihydrate: plot of one formula unit of the structure (50% probability ellipsoids, horizontal twofold axes through Ag and Cl).

The bond distances and the bond angles within the creatinine molecule are comparable to those obtained earlier for the free base [14] and to those of the creatininium cation [3]. The results suggest an extensive π electron delocalization in the creatinine molecule with the exception of the N2–C3, N2–C2 and C1–C2 bonds. Thus, the molecule is essentially planar, and the least-sqares equation containing the atoms N1, O1, C1, C2, N2, C3, C4 and N3 is $-0.6094x + 0.5415y - 0.5791z + 3.4085 = 0$ where x, y and z are related to the monoclinic axes of the crystal. The maximum deviations from the mean plane are 0.02 Å for C2, 0.01 Å for N2 and C3.

The geometry of the perchlorate ion is close to the regular tetrahedron, the O–Cl–O angles ranging from 108 to 115°. However, the observed bond distance of 1.353(5) Å is significantly shorter than the expected value of 1.42 to 1.44 Å [15, 16] due to the high thermal librational motion of the anion around its center of mass. Application of a rigid body correction [17] for the tetrahedral anion results in librational tensor elements of 0.095(19) (L_{11}), 0.090(17)

TABLE IV. Intermolecular Hydrogen Bonding in the Structure of Bis(creatinine)silver(I) Perchlorate Dihydrate.

Distances (Å)				Angles (°)	
N3–H6···O2^{ii}	2.23(4)	N3···O2^{ii}	3.022(7)^a	N3–H6···O2^{ii}	171(4)
N3–H7···O4	2.05(4)	N3···O4	2.851(5)	N3–H7···O4	174(4)
O4–H8···O1^{iii}	2.09(4)	O4···O1^{iii}	2.798(5)	O4–H8···O1^{iii}	177(5)
O4–H9···O1^{iv}	2.09(4)	O4···O1^{iv}	2.848(5)	O4–H9···O1^{iv}	167(4)

Symmetry code: ii: x, –y, –½ + z; iii: x, 1 – y, –½ + z; iv: 1 – x, –1 + y, ½ – z.

[a] Uncorrected.

(L_{22}), 0.058(18) (L_{33}), 0.022(8) (L_{13}) rad^2 and in corrected Cl–O bond lengths of 1.454 (Cl–O2) and 1.472 Å (Cl–O3). The hydrogen bond distances and bond angles are given in Table IV. It is clearly seen that the water molecules are hydrogen-bonded to two neighbouring carboxyl oxygen atoms (O4····O1 2.80 and 2.85 Å) and the exocyclic NH_2 group (O4····N3 2.85 Å) of creatinine. Further, the exocyclic NH_2 group is hydrogen-bonded to one perchlorate oxygen atom (N3····O2 3.02 Å).

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