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Crystal Structure of 2:1 Molecular Complexes of Caffeine with Hexaaquamagnesium(II) Bromide and Hexaaquamanganese(II) Triiodide Iodide

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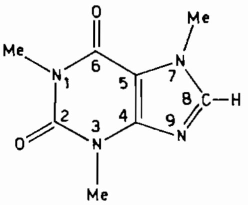
The crystal structures of $(C_8H_{10}N_4O_2)_2Mg(OH_2)_6Br_2$ *(I) and* $(C_8H_{10}N_4O_2)_2Mn(OH_2)_6I\cdot I_3$ *(II) have been determined by X-ray diffraction methods; crystals of I are triclinic, space group* $P\bar{1}$, *with* $Z = 1$, *in a unit cell of dimensions:* $a = 9.620(7)$, $b = 10.779(8)$, $c = 7.645(6)$ Å, $\alpha = 107.03(7)$, $\beta = 108.88(7)$, $\gamma = 72.71(8)^\circ$; *crystals of II are monoclinic, space group* $P2_1/n$, *with* $Z = 4$, *in a unit cell of dimensions* $a = 12.406(8)$, $b = 29.652(12)$, $c = 9.419(6)$ Å, $\beta = 108.39(7)^\circ$. *The structures of I and II have been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to* $R = 0.046$ *for I and 0.090 for II. Both compounds contain octahedral hexaaquametal(II) cations, uncoordinated caffeine molecules and bromide anions in I and triiodide and iodide anions in II, held together by a network of hydrogen bonds. The triiodide anions are unsymmetrical* $[I(1)–I(2) = 2.89$, $I(2)–I(3) = 2.95$ Å, $I(1)–I(2)–I(3) = 178^\circ]$, *arranged in linear systems with a weak 'head-to-tail' interaction, the distance being of 3.62* Å.

Introduction

Influence of caffeine (cf) on both animal and vegetable cells behaviour in normal and abnormal situation is under continuous investigation. Generally cf is dissolved in aqueous solutions of sodium aromatic organic salts, frequently benzoate [1].

It is known that solubility of cf in water is increased on addition of metal salts. The preparation of some complexes in the solid state [2] or in aqueous solutions [3] has been reported. With sodium benzoate cf can also be dosed complexometrically [4]. Recently we prepared some cf copper(II) complexes in the course of a research program on the ligand behaviour of purine derivatives [5]. cf coordinates to the metal through the N(9) atom in $[CuNO_3(cf)(H_2O)_3]NO_3$ [6] and in $[CuCl_2(cf)H_2O]$ [7], as shown by structural X-ray determinations. cf shows a considerable bent for coordinating to copper giving stable complexes. However, it does not seem to coordinate either to other transition metals, or to typical metals. Nevertheless, cf forms stable crystal compounds with some salts of divalent metals; examples are the two structures here reported, $2cf\cdot[Mg(OH_2)_6]Br_2$ (I) and $2cf\cdot[Mn(OH_2)_6]I\cdot I_3$ (II).



Experimental

By slow evaporation at room temperature of aqueous solutions containing $MgBr_2$ or MnI_2 in excess and caffeine, colourless crystals of the compound $(C_8H_{10}N_4O_2)_2Mg(OH_2)_6Br_2$ (I) and of the compound $(C_8H_{10}N_4O_2)_2(OH_2)_8I_2$ were obtained, respectively. From the mother liquors (which in the air became brown) of the latter compound at pH 4, small green-brown crystals of the compound $(C_8H_{10}N_4O_2)_2\cdot Mn(OH_2)_6I\cdot I_3$ (II) separated. Crystals having the same stoichiometry were always obtained from CoI_2 and NiI_2 with caffeine solutions: $(C_8H_{10}N_4O_2)_2Co(OH_2)_6I\cdot I_3$ (III) and $(C_8H_{10}N_4O_2)_2Ni(OH_2)_6I\cdot I_3$ (IV).

Anal. Calcd. for I, $C_{16}H_{32}Br_2MgN_8O_{10}$: C, 28.24; H, 4.74; Br, 23.48; Mg, 3.57; N, 16.46; Found: C, 27.9; H, 4.8; Br, 23.4; Mg, 3.5; N, 16.3. D_m =

1.62 g cm^{-3}. Calcd for II, $C_{16}H_{32}I_4MnN_8O_{10}$: C, 18.15; H, 3.05; I, 47.93; Mn, 5.19; N, 10.58. Found: C, 17.7; H, 2.9; I, 47.8; Mn, 5.2; N, 10.5. D_m = 2.13 g cm^{-3}. Calcd for III, $C_{16}H_{32}CoI_4N_8O_{10}$: C, 18.08; H, 3.04; Co, 5.54; I, 47.75; N, 10.54. Found: C, 18.2; H, 3.0; Co, 5.5; I, 47.7, N, 10.5. D_m = 2.08 g cm^{-3}. Calcd. for IV, $C_{16}H_{32}I_4N_8NiO_{10}$: C, 18.08; H, 3.03; I, 47.76; N, 10.54; Ni, 5.52. Found: C, 18.0; H, 3.0; I, 47.7; N, 10.1; Ni, 5.5. D_m = 2.15 g cm^{-3}.

C, H and N were determined by a C. Erba Elemental Analyzer Mod. 1106, metal by a Perkin-Elmer Atomic Absorption Spectrophotometer Mod. 303, halogen as silver halide. Measured density was determined by flotation.

The crystals of II, III and IV are insulating, their resistivity being between 10^{10} and 10^{13} Ω cm; they are slightly photoconducting.

Crystal Data

Compound I, $C_{16}H_{32}Br_2MgN_8O_{10}$, M = 680.6. Triclinic, a = 9.620(7), b = 10.779(8), c = 7.645(6) Å, α = 107.03(7), β = 108.88(7), γ = 72.71(8)°, U = 699(1) Å^3, Z = 1, D_c = 1.617 g cm^{-3}, $F(000)$ = 346. Cu-Kα radiation, $\bar{\lambda}$ = 1.54178 Å; μ(CuKα) = 44.69 cm^{-1}. Space group $P\bar{1}$ from structure determination.

Compound II, $C_{16}H_{32}I_4MnN_8O_{10}$, M = 1059.0. Monoclinic, a = 12.406(8), b = 29.652(12), c = 9.419(6) Å, β = 108.39(7)°, U = 3288(4) Å^3, Z = 4, D_c = 2.14 g cm^{-3}, $F(000)$ = 2004. Mo-Kα radiation, $\bar{\lambda}$ = 0.71069 Å; μ(Mo-Kα) = 41.56 cm^{-1}. Space group $P2_1/n$ from systematic absences.

Cell parameters were first determined from photographs and then refined from diffractometer data.

Intensity Data

Intensities of I and II were collected on Siemens AED single-crystal diffractometers of the Centro di Studio per la Strutturistica Diffrattometrica dell' Università di Parma and of Istituto di Chimica Generale dell'Università di Padova respectively, using Cu-Kα radiation for I and Mo-Kα radiation for II, with the ω–2θ scan technique. All the reflections in the range of $6 < 2\theta < 140°$ for I and $3 \leqslant 2\theta \leqslant 40°$ for II were collected, the intensities of reflections of II decreasing very rapidly with the diffraction angle. Of 2624 (I) and 3052 (II) independent measured reflections, 2440 (I) and 1068 (II), having $I > 2\sigma(I)$ and $I > 3\sigma(I)$ respectively, were considered observed and used in the analyses. The large portion (65%) of very weak reflections of II may be attributed to the small crystal used, to large thermal motion of the heavy atoms and to some possible disorder in the lattice of the triiodide sites. The intensity data were corrected for Lorentz and polarization factors, but no absorption correction was applied.

TABLE I. Fractional Atomic Coordinates of the Non-hydrogen Atoms (×10^4) for I with e.s.d.s in Parentheses.

	x/a	y/b	z/c
Mg	0	0	5000
Br	2059(1)	1580(1)	2032(1)
O2	1783(5)	3579(5)	−1869(7)
O6	6689(6)	2481(5)	1596(9)
OW1	293(5)	1880(4)	5218(6)
OW2	1422(6)	−141(5)	7652(6)
OW3	1785(6)	−827(5)	3732(8)
N1	4243(6)	3028(5)	−120(8)
N3	2685(6)	5181(5)	545(7)
N7	6163(6)	5343(5)	3884(8)
N9	3895(6)	6731(5)	3206(8)
C1	4360(9)	1647(7)	−1291(12)
C2	2834(7)	3917(6)	−553(9)
C3	1246(7)	6183(7)	133(11)
C4	3879(7)	5534(6)	1981(9)
C5	5253(7)	4647(6)	2347(9)
C6	5504(8)	3320(6)	1308(10)
C7	7772(8)	4865(8)	4837(11)
C8	5308(8)	6578(7)	4346(10)

Structure Determination and Refinement

The structures were solved by Patterson and Fourier methods and the refinements were carried out by means of SHELX [8] for I and X-RAY system [9] for II. Some cycles of full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms were computed for I: the subsequent $|\Delta F|$ maps revealed the positions of all the hydrogen atoms which were introduced in the final structure factor calculations but not refined. As for the compound II the number of observations was inadequate to give a good observation-to-parameter ratio, only thermal parameters of the iodine and manganese atoms were allowed to vary anisotropically. At the termination of the refinement unexplained electron density of up to 1.5 eÅ^{-3} was observed, mainly around the heavy atoms, which is assumed to have arisen from a great variety of errors. Unit weights were used at each stage of the refinement of both compounds, by analyzing the variations of $|\Delta F|$ as a function of $|F_o|$. The final R was 0.046 for I and 0.090 for II (observed reflections only). Final atomic coordinates for I and II are given in Tables I, II and III respectively. Thermal parameters of the atoms and a list of calculated and observed structure factors for I and II are available from the authors on request. The accuracy of the atomic coordinates in the organic part of II is not high, as the major part of the intensity of most reflections is determined by the contribution of iodine and manganese atoms. Inspection of the Tables of positional and thermal parameters of II shows some unrealistic thermal parameters and

TABLE II. Fractional Atomic Coordinates of the Hydrogen Atoms ($\times 10^4$) for I.

	x/a	*y/b*	*z/c*
H1	759	2325	6089
H2	585	1908	4273
H3	1376	420	8683
H4	1964	−790	7841
H5	2391	−1555	3596
H6	2167	−301	3156
H8	5718	7241	5326
H11	4111	1554	−2684
H12	5195	1218	−753
H13	3554	1205	−1126
H31	1443	7004	−220
H32	635	6405	1066
H33	585	5844	−888
H71	7829	3951	5125
H72	8430	4777	3899
H73	7925	5419	6050

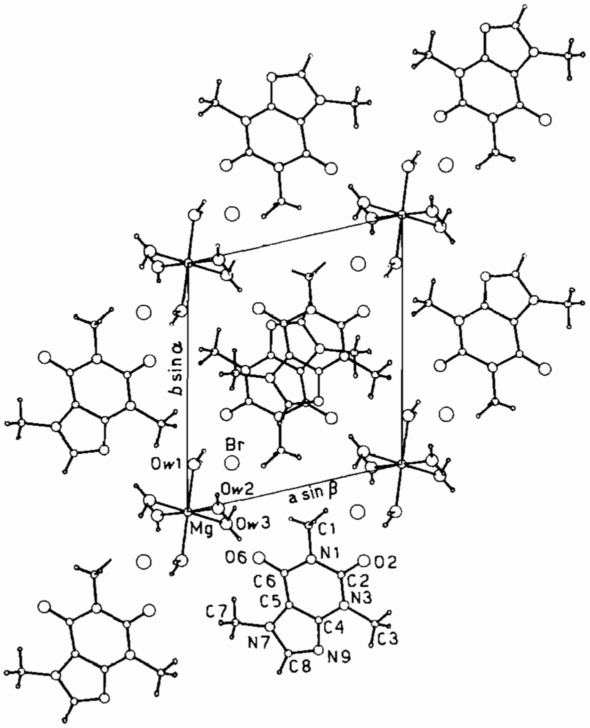


Fig. 1. Projection along *c* of the structure of compound I.

TABLE III. Fractional Atomic Coordinates of the Non-hydrogen Atoms ($\times 10^4$) for II with e.s.d.s in Parentheses.

	x/a	*y/b*	*z/c*
I1	4380(5)	1759(2)	6138(7)
I2	4208(4)	1795(2)	9129(7)
I3	4076(5)	1854(2)	12193(7)
I4	3881(4)	4388(2)	1261(5)
Mn	5609(8)	4095(3)	6901(11)
O10	6305(40)	4704(15)	6184(53)
O11	6448(31)	3701(14)	5613(37)
O12	4910(32)	3528(17)	7746(50)
O13	4861(34)	4513(14)	8234(39)
O14	4102(30)	4191(16)	5013(30)
O15	7216(36)	4080(20)	8805(48)
N1	−1460(51)	4518(20)	3321(72)
C1	−2700(65)	4533(27)	2347(83)
C2	−809(72)	4513(26)	2491(95)
O2	−1216(44)	4548(16)	1039(59)
N3	317(52)	4448(22)	3141(71)
C3	1000(64)	4453(29)	1901(84)
C4	819(62)	4386(28)	4626(83)
C5	127(49)	4409(24)	5515(67)
C6	−1145(62)	4476(26)	4947(86)
O6	−1697(38)	4514(16)	5744(51)
N7	714(53)	4292(21)	6891(73)
C7	437(70)	4372(31)	7993(93)
C8	1849(69)	4256(28)	6942(90)
N9	1861(42)	4342(18)	5123(53)
N11	6923(52)	2303(23)	3299(71)
C11	7245(50)	2009(21)	4848(67)
C21	6245(63)	2715(29)	3074(97)
O21	6159(37)	2825(16)	4368(52)
N31	6103(46)	2950(22)	2036(72)
C31	5464(60)	3338(25)	1720(77)
C41	6426(66)	2740(29)	827(98)
C51	7061(48)	2310(22)	897(74)
C61	7335(52)	2087(23)	2148(73)
O61	7943(37)	1705(16)	2631(48)
N71	7142(44)	2240(20)	−408(62)
C71	7686(69)	1917(30)	−1165(91)
C81	6726(62)	2565(29)	−1244(87)
N91	6282(42)	2851(19)	−535(61)

high estimated standard deviations. This is probably due to a lack of crystal quality and, as a result of the long *b* axis, complete resolution of reflection spots was not always possible. However, the general trends observed in the structure are consistent and appear reliable. All the calculations were carried out on a CYBER 76 computer of Centro di Calcolo Elettronico Interuniversitario dell'Italia-Nord Orientale, Casalecchio (Bologna).

Discussion

The crystal structures of I and II, depicted in Fig. 1 and Fig. 2, respectively, consist of octahedral hexaaquametal(II) cations, of uncoordinated cf molecules and of bromide counter-ions in I and of triiodide and iodide anions in II. The Mg–OH_2 (2.07–2.08 Å) (Table IV) and the Mn–OH_2 distances (2.16–2.22 Å) (Table V) show the same pattern as in the other previously reported Mg–O and Mn–O bond lengths respectively, in particular in magnesium

TABLE IV. Bond Distances (Å) and Angles (°) with e.s.d.s in I.

a) In the caffeine molecule			
N(1)–C(2)	1.410(9)	C(8)–N(7)	1.355(9)
C(2)–N(3)	1.369(9)	N(7)–C(5)	1.385(9)
N(3)–C(4)	1.367(8)	C(2)–O(2)	1.230(8)
C(4)–C(5)	1.381(9)	C(6)–O(6)	1.228(9)
C(5)–C(6)	1.410(9)	N(1)–C(1)	1.488(9)
C(6)–N(1)	1.390(9)	N(3)–C(3)	1.487(9)
C(4)–N(9)	1.355(9)	N(7)–C(7)	1.486(9)
N(9)–C(8)	1.349(9)		
C(6)–N(1)–C(2)	126.0(6)	C(6)–N(1)–C(1)	117.8(6)
N(1)–C(2)–N(3)	117.2(6)	C(2)–N(1)–C(1)	116.1(6)
C(2)–N(3)–C(4)	119.9(6)	C(2)–N(3)–C(3)	120.1(5)
N(3)–C(4)–C(5)	121.5(6)	C(4)–N(3)–C(3)	120.0(6)
C(4)–C(5)–C(6)	122.5(6)	C(8)–N(7)–C(7)	125.8(6)
C(5)–C(6)–N(1)	112.8(6)	C(5)–N(7)–C(7)	127.7(6)
C(5)–C(4)–N(9)	111.8(6)	C(5)–C(6)–O(6)	125.4(7)
C(4)–N(9)–C(8)	104.1(6)	N(1)–C(6)–O(6)	121.8(7)
N(9)–C(8)–N(7)	112.5(6)	N(1)–C(2)–O(2)	121.7(6)
C(8)–N(7)–C(5)	106.5(6)	N(3)–C(2)–O(2)	121.2(6)
N(7)–C(5)–C(4)	105.2(6)		
b) In the hexaaquamagnesium cation			
Mg–O_w(1)	2.080(5)	Mg–O_w(3)	2.084(6)
Mg–O_w(2)	2.066(5)		
O_w(1)–Mg–O_w(2)	93.0(2)	O_w(2)–Mg–O_w(3)	91.8(2)
O_w(1)–Mg–O_w(3)	88.8(2)		
c) Hydrogen bonds			
O_w(1)–H(2)···Br	3.288(5)	O_w(1)–H(2)–Br	164
H(2)···Br	2.53	H(2)–O_w(1)–Br	12
O_w(1)–H(1)···O(2^{i})	2.734(7)	O_w(1)–H(1)–O(2^{i})	174
H(1)···O(2^{i})	1.95	H(1)–O_w(1)–O(2^{i})	4
O_w(2)–H(3)···Br^{i}	3.277(5)	O_w(2)–H(3)–Br^{i}	161
H(3)···Br^{i}	2.47	H(3)–O_w(2)–Br^{i}	14
O_w(2)–H(4)···O(6^{ii})	2.728(8)	O_w(2)–H(4)–O(6^{ii})	177
H(4)···O(6^{ii})	1.97	H(4)–O_w(2)–O(6^{ii})	2
O_w(3)–H(5)···N(9^{iii})	2.818(8)	O_w(3)–H(5)–N(9^{iii})	177
H(5)···N(9^{iii})	1.99	H(5)–O_w(3)–N(9^{iii})	2
O_w(3)–H(6)···Br	3.331(6)	O_w(3)–H(6)–Br	155
H(6)···Br	2.39	H(6)–O_w(3)–Br	18

Asymmetric units:	i	$x, y, 1+z$
	ii	$1-x, -y, 1-z$
	iii	$x, -1+y, z$

ammonium sulfate hexahydrate [10] and in manganese(II) ammonium sulfate hexahydrate [11], two members of the isomorphous series of Tutton's salts. The triiodide anion is unsymmetrical and its dimensions [I(1)–I(2) = 2.89, I(2)–I(3) = 2.95 Å, I(1)–I(2)–I(3) = 178°] are well within the range normally found for this anion [12, 13]. When no crystallographic symmetry is imposed on the anion, invariably two unequal I–I distances have been found. The distance between triiodide and iodide anions is *ca.* ¼ *b*, longer than corresponding van der Waals contact. The I_3^- ions are arranged in linear systems parallel to the *c* axis (Fig. 3); moreover, the 'head-to-tail' I(3)··· I(1) distance of 3.62 Å, represents an interaction rather weak so that the I_3^- species can be considered as discrete anions.

TABLE V. Bond Distances (Å) and Angles (°) in II.

a) Selected Bond distances (Å) and angles (°)

I(1)–I(2)	2.89(1)	Mn–O(12)	2.16(5)
I(2)–I(3)	2.95(1)	Mn–O(13)	2.17(4)
Mn–O(10)	2.20(5)	Mn–O(14)	2.15(3)
Mn–O(11)	2.17(4)	Mn–O(15)	2.22(4)
I(1)–I(2)–I(3)	178.4(3)	O(13)–Mn–O(10)	89(2)
O(10)–Mn–O(11)	88(2)	O(14)–Mn–O(15)	173(2)
O(11)–Mn–O(12)	96(2)	O(10)–Mn–O(12)	176(2)
O(12)–Mn–O(13)	86(2)	O(11)–Mn–O(13)	177(2)

b) Relevant intermolecular distances (Å)

O(11)–I(3^{i})	3.53(4)	O(11)–O(21)	2.83(6)
O(14)–I(4)	3.51(3)	O(12)–N(91^{ii})	2.79(7)
O(13)–I(4^{ii})	3.45(4)	O(12)–O(61^{v})	2.51(6)
O(13)–I(4^{iii})	3.58(4)	O(14)–N(9)	2.85(7)
O(10)–O(6^{iv})	2.70(7)	O(15)–O(2^{vi})	2.75(7)

Asymetric units:

i	$\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$	iv	$1+x, y, z$
ii	$x, y, 1+z$	v	$-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
iii	$1-x, 1-y, 1-z$	vi	$1+x, y, 1+z$

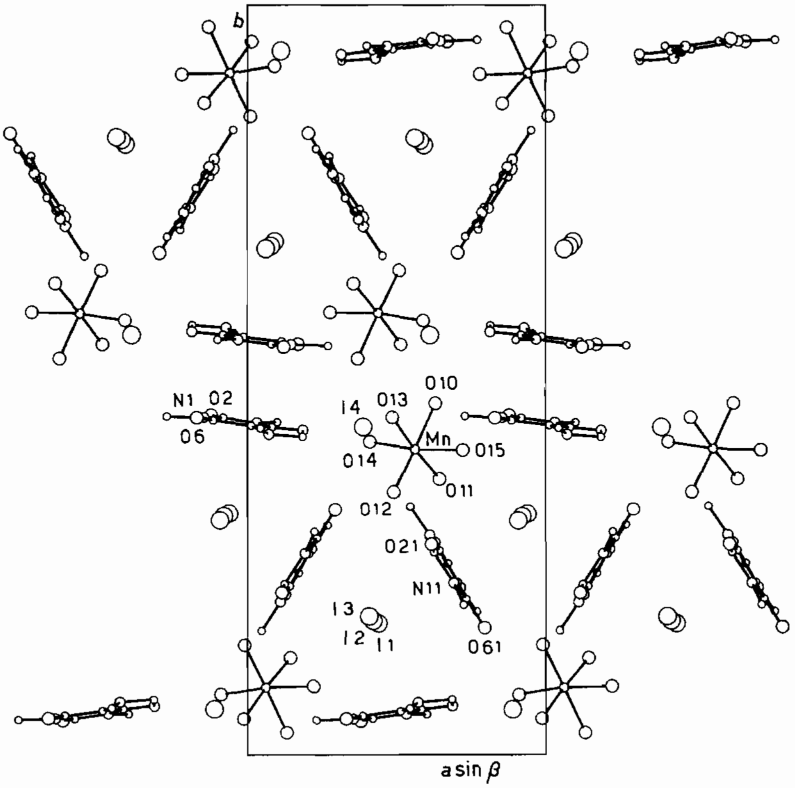


Fig. 2. Projection along *c* of the structure of compound II.

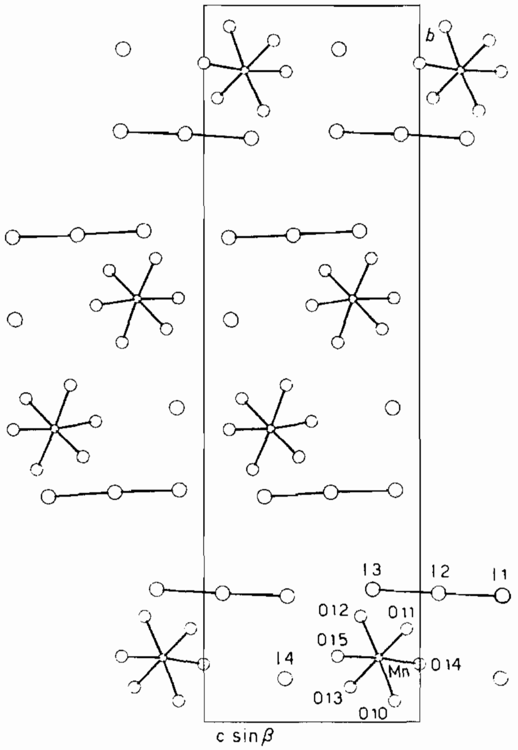


Fig. 3. Projection along *a* of II showing the linear arrangements of the I_3^- anions. The caffeine molecules are omitted for clarity.

In both compounds the geometry of the cf units is in good agreement with that found in other cf compounds even though the high e.s.d.s of the light atoms of II do not allow an accurate comparison. As observed in other xanthine derivatives, the purine moiety is not strictly planar (the maximum deviation being of 0.02 in I and of 0.07 and 0.11 Å respectively for the two crystallographically independent cf molecules in II); the dihedral angles between the mean planes through the pyrimidine and imidazole rings of the cf units are of 1.6° in I and 4.4 and 3.8° in II. In this last compound the I(1)–I(2)–I(3) best line makes angles of 82.2 and 89.2° with the normals to mean planes passing through the nine-atom framework of the two independent of molecules.

In I (Fig. 1) the cf molecules are arranged, through the symmetry centers at ½ ½ 0 and ½ ½ ½, parallel to each other and in an infinite stack running along *c* with distances between successive purine moieties of 3.35 and 3.37 Å, alternately. In II (Fig. 2) half of the cf molecules arranged in pairs through the symmetry centres at y = 0 and ½ (with interplanar distance of 3.38 Å) form double layers parallel to (010). The other cf molecules, having the barycentres at y ≅ 1/4 and 3/4, are disposed in a zig-zag way forming layers, always parallel to (010). The I_3^- ions interpose between different layers at y ≅ 1/6, 1/3, 2/3 and 5/6, while the $Mn(OH_2)_6^{2+}$ and I^- ions interpose at y ≅ 1/12, 5/12, 7/12 and 11/12.

In I (Table IV) the water molecules form O_w–H···N, O_w–H···O, O_w–H···Br hydrogen bonds involving the imidazole nitrogen N(9), the exocyclic pyrimidine oxygens O(2) and O(6), and the bromide anions. The intermolecular distances reported in Table V suggest also that in II the packing is determined by intermolecular O_w–H···N, O_w–H···O and O_w–H···I hydrogen bonds, so that in both structures all the water molecules are involved in a hydrogen bond network with all the acceptor sites of the cf molecule. In I there also is a C–H···Br interaction involving the hydrogen at C(8) of the cf molecule [H(8)···Br (1 – *x*, 1 – *y*, 1 – *z*) = 2.75 Å] which seems to play a significant role in determining the packing. There are numerous examples in the recent literature showing the acidic nature of this proton generally found participating in hydrogen bonds with carbonyl oxygens. In the structure of I, the H···Br distance (much less than the sum of the van der Waals radii (3.15 Å)) and the geometry of the C–H···Br interaction [C(8)–H(8)–Br (1 – *x*, 1 – *y*, 1 – *z*) = 157°] suggest that attractive H···Br forces are present, appreciably stronger than the usual van der Waals effects.

For II we can add that the polyiodide salts may be classified into four categories: (i) large-cation polyiodides; (ii) neutral organic alkali-metal triiodides; (iii) protonated organic heterocycles with polyiodides and (iv) radical-cation polyiodides [13]. The true identity of II has been revealed by the structural characterization, which established the compound as a 2:1 crystal complex of cf and $[Mn(OH_2)_6]^{2+}I_3^-\cdot I^-$. Thus the compound is of particular interest as it does not fall into any of the previous four categories and represents the first example of a polyiodide salt containing an unprotonated organic heterocycle and an aqua 3*d* transition metal complex as the cation. Moreover, together with $KI\cdot KI_3\cdot 6(CH_3CONHCH_3)$ [14], it is, to date, the only example of a structure with both I_3^- and I^- ions present.

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