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Anhydrous 2,3,5,6-Tetramethylpyrazinium Tetraiodocadmate(II) and its Trihydrate, [C$_8$H$_{12}$N$_2$(H)$_2$][CdI$_4$].xH$_2$O (x = 0, 3)

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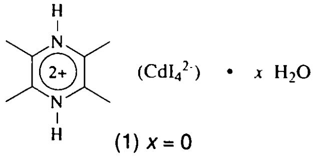
Abstract

The structures of diprotonated 2,3,5,6-tetramethylpyrazinium tetraiodocadmate(II) as an anhydrous salt, (C$_8$H$_{14}$N$_2$)[CdI$_4$], (1), and as a trihydrate, (C$_8$H$_{14}$N$_2$)[CdI$_4$].3H$_2$O, (2), have been determined. In both compounds the CdI$_4^{2-}$ anion has slightly distorted tetrahedral geometry with Cd—I bonds ranging from 2.755 (2) to 2.793 (2) Å for (1) and from 2.751 (2) to 2.795 (2) Å for (2). In (1), the cations and anions are joined through hydrogen bonds to form layers in the *ab* plane. In (2) the cations are linked through hydrogen bonds to strings of three hydrogen-bonded water molecules to form infinite chains; there are no significant interactions involving the anions.

Comment

We have shown recently that tetramethylpyrazinium cations crystallize with polyiodide anions to give a sheet structure, in which the polyiodide layers consist of a unique arrangement of interwoven branched chains of I$_3^-$ anions and I$_2$ molecules (Bailey & Pennington, 1995). In order to determine the extent to which this cation can influence the stoichiometry and structure of other anionic species, we have extended this work to iodocadmates. While not as structurally diverse as polyiodides (Tebbe, 1977; Coppens, 1982), the structures of iodocadmates have been shown to vary as a function of the counter cation: a tetrahedral CdI$_4^{2-}$ anion crystallizes with tetramethylammonium (Kallel, Bats & Daoud, 1981), methyltriphenylphosphonium (Couldwell & Prout, 1978) or alkali metal cations (Sjövall, 1989), and a Cd$_2$I$_6^{2-}$ anion, composed of two edge-sharing CdI$_4$ tetrahedra, crystallizes with a [tris(2-dimethylaminoethyl)amine]iodocadmium(II) cation (Orioli & Ciampolini, 1972). In order to determine the effect of a tetramethylpyrazinium cation on the structure of iodocadmate anions, we have prepared the compounds [tetramethylpyrazine(H)$_2$]CdI$_4$, (1), and [tetramethylpyrazine(H)$_2$]CdI$_4$.3H$_2$O, (2) (Fig. 1).



(1) x = 0
(2) x = 3

Both compounds crystallize with CdI$_4^{2-}$ anions. The Cd atom has distorted tetrahedral geometry [102.0 (1)–118.5 (1)°] in (1), while in (2) the range of the relevant angles is closer to the ideal [106.3 (1)–112.8 (1)°]. The Cd—I bond distances [2.755 (2)–2.793 (2) Å for (1); 2.751 (2)–2.795 (2) Å for (2)] lie within the range of those of known compounds.

H atoms could not be located, but the angles at the N atoms of the cations in both structures agree well with those of a protonated N atom [124.1 (5)°] in the tetramethylpyrazinium cation of a triiodide salt (Bailey & Pennington, 1995), indicating that the cations are protonated at both the N atoms of the pyrazine ring.

In the anhydrous compound, (1), the cations interact with the anions through bifurcated N—H···I hydrogen bonds; the N···I distances of 3.501 (6) and 3.540 (6) Å involving atom N(1) and those of 3.525 (6) and 3.534 (6) Å involving atom N(2) are significantly shorter than the nitrogen–iodine van der Waals distance of 3.65 Å (Pauling, 1960). Ion pairs participating in these interactions are related by 2$_1$ screw operations and by translation along the *a* and *b* axes, linking the ions into an extended two-dimensional network (Fig. 2). The strength of the Cd—I bond appears to be inversely related to the strength of N—H···I interaction, the I atom

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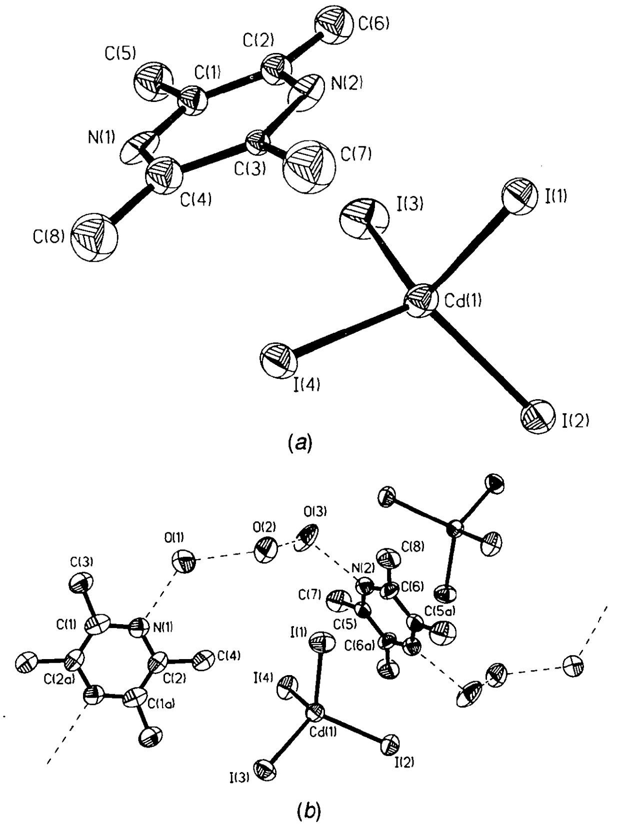

Fig. 1. Views showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level for (*a*) compound (1) and (*b*) compound (2); the hydrogen-bonded chains extend along [100].

with the longest Cd—I bond [atom I(1)] being involved in the strongest interaction [two N—H···I interactions of 3.501 (6)–3.540 (6) Å] and the I atom involved in no interaction [atom I(3)] having the shortest Cd—I bond distance. However, it should be noted that a similar range of Cd—I bond distances is observed in compound (2), in which no significant interionic interactions are observed. The layers stack along the *c* axis (Fig. 3), with adjacent layers related by inversion symmetry through the point ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$). The I atoms not involved in hydrogen bonding are oriented toward the surfaces of the layer.

In the hydrated compound, (2), there are two unique cations per asymmetric unit, each of which is situated about an inversion center [cation *A* at ($1\frac{1}{2}\frac{1}{2}$); cation *B* at ($0\frac{1}{2}0$)]. The cations are bridged through N—H···O hydrogen bonding by a chain of three hydrogen-bonded water molecules to form an extended chain along [100]. The CdI_4^{2-} anions occupy the kinks in the chains, with weak van der Waals interactions to the water molecules [O···I = 3.598 (6)–3.900 (6) Å].

The neutral parent molecule, tetramethylpyrazine, also crystallizes as an anhydrous form (Braam, Eshuis & Vos, 1981) and as a trihydrate (Braam, Eikelenboom, van Dijk & Vos, 1981).

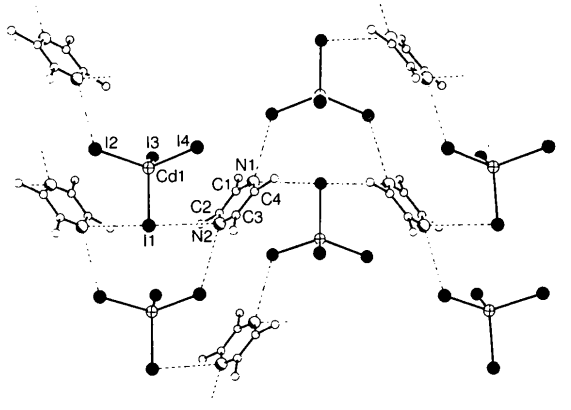

Fig. 2. Hydrogen-bonded layer of compound (1).

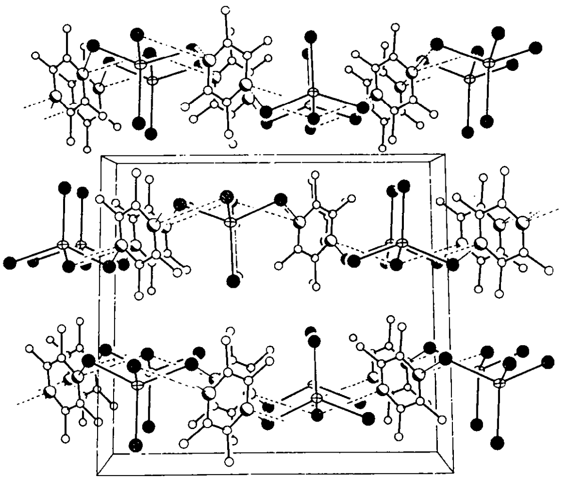

Fig. 3. Packing diagram of compound (1) viewed down the *a* axis; the origin is in the lower left, rear corner, positive *z* is up and positive *y* is to the right.

Experimental

Crystalline products of both (1) and (2) were obtained from the reaction of equimolar quantities of tetramethylpyrazine and cadmium iodide in excess aqueous hydrogen iodide solution.

Compound (1)

Crystal data

$(C_8H_{14}N_2)[CdI_4]$
M_r = 758.21
Monoclinic
$P2_1/c$
a = 7.057 (2) Å
b = 16.595 (4) Å
c = 15.192 (5) Å
β = 100.01 (2)°
V = 1752.0 (8) Å^3
Z = 4
D_x = 2.87 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 33 reflections
θ = 14.0–19.2°
μ = 8.27 mm^{-1}
T = 294 (1) K
Parallelepiped
0.51 × 0.27 × 0.21 mm
Red

Data collection

Nicolet *R3m/V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.68$, $T_{\max} = 1.00$
3108 measured reflections
2737 independent reflections
1849 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.063$
$\theta_{\max} = 24.0°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 19$
$l = -18 \rightarrow 18$
3 standard reflections monitored every 97 reflections intensity decay: ±2%

Refinement

Refinement on F
$R = 0.0559$
$wR = 0.0750$
$S = 2.14$
1849 reflections
96 parameters
H atoms were not located
$w = 1/[\sigma^2(F) + 0.0005(F^2)]$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.76$ e Å^{-3}
$\Delta\rho_{\min} = -1.35$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (2)

Crystal data

$(C_8H_{14}N_2)[CdI_4].3H_2O$
$M_r = 812.26$
Monoclinic
$P2_1/c$
$a = 8.549$ (2) Å
$b = 17.564$ (5) Å
$c = 14.401$ (3) Å
$\beta = 105.35$ (2)°
$V = 2085.2$ (8) Å^3
$Z = 4$
$D_x = 2.59$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 46 reflections
$\theta = 14.0$–$19.5°$
$\mu = 6.97$ mm^{-1}
$T = 294$ (1) K
Parallelepiped
0.37 × 0.25 × 0.23 mm
Orange

Data collection

Nicolet *R3m/V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.76$, $T_{\max} = 1.00$
3658 measured reflections
3285 independent reflections
2362 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.071$
$\theta_{\max} = 24.0°$
$h = 0 \rightarrow 10$
$k = -21 \rightarrow 0$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 97 reflections intensity decay: ±2%

Refinement

Refinement on F
$R = 0.0677$
$wR = 0.0900$
$S = 2.50$
2362 reflections
164 parameters
$w = 1/[\sigma^2(F) + 0.0005(F^2)]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.61$ e Å^{-3}
$\Delta\rho_{\min} = -2.79$ e Å^{-3}

Extinction correction: isotropic, modified Larson (1970)
Extinction coefficient: 0.0098 (5)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$U_{\rm iso}$ for C atoms of (1); $U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
Compound (1)				
I(1)	0.6429 (2)	0.1264 (1)	0.3571 (1)	0.032 (1)
I(2)	0.1338 (2)	−0.0209 (1)	0.3545 (1)	0.034 (1)
I(3)	0.1688 (2)	0.1150 (1)	0.0995 (1)	0.056 (1)
I(4)	0.1211 (2)	0.2672 (1)	0.3412 (1)	0.036 (1)
Cd(1)	0.2519 (2)	0.1216 (1)	0.2834 (1)	0.030 (1)
N(1)	0.3478 (23)	0.4234 (9)	0.2137 (9)	0.027 (5)
N(2)	0.6353 (22)	0.3251 (8)	0.2745 (9)	0.024 (5)
C(1)	0.4107 (24)	0.3706 (10)	0.1557 (11)	0.022 (4)
C(2)	0.5661 (25)	0.3200 (10)	0.1858 (12)	0.024 (4)
C(3)	0.5758 (21)	0.3754 (9)	0.3332 (10)	0.013 (3)
C(4)	0.4180 (27)	0.4282 (11)	0.3025 (12)	0.029 (4)
C(5)	0.3118 (30)	0.3749 (13)	0.0582 (14)	0.041 (5)
C(6)	0.6433 (29)	0.2594 (12)	0.1321 (14)	0.038 (5)
C(7)	0.6750 (34)	0.3711 (14)	0.4303 (16)	0.051 (6)
C(8)	0.3305 (33)	0.4864 (13)	0.3567 (14)	0.043 (5)
Compound (2)				
I(1)	0.1858 (2)	0.4625 (1)	0.2983 (1)	0.059 (1)
I(2)	−0.0664 (2)	0.6890 (1)	0.2081 (1)	0.054 (1)
I(3)	0.3804 (2)	0.6768 (1)	0.4630 (1)	0.057 (1)
I(4)	0.4171 (2)	0.6360 (1)	0.1544 (1)	0.056 (1)
Cd(1)	0.2327 (2)	0.6180 (1)	0.2842 (1)	0.043 (1)
O(1)	0.7810 (21)	0.3449 (11)	0.3091 (15)	0.081 (8)
O(2)	0.4432 (21)	0.3177 (10)	0.2407 (15)	0.078 (7)
O(3)	0.3538 (22)	0.3468 (11)	0.0400 (13)	0.081 (7)
N(1)	0.9163 (18)	0.4425 (9)	0.4511 (13)	0.042 (6)
N(2)	0.1060 (19)	0.4452 (9)	−0.0023 (12)	0.044 (6)
C(1)	1.0630 (25)	0.4269 (10)	0.5112 (16)	0.046 (7)
C(2)	0.8518 (22)	0.5124 (11)	0.4379 (15)	0.042 (7)
C(3)	1.1172 (27)	0.3475 (12)	0.5154 (19)	0.058 (9)
C(4)	0.6866 (31)	0.5201 (15)	0.3661 (22)	0.075 (10)
C(5)	0.1301 (22)	0.5111 (10)	−0.0391 (14)	0.041 (6)
C(6)	−0.0185 (22)	0.4304 (10)	0.0390 (16)	0.044 (7)
C(7)	0.2619 (32)	0.5192 (14)	−0.0888 (20)	0.069 (10)
C(8)	−0.0273 (30)	0.3510 (11)	0.0780 (19)	0.063 (9)

Table 2. *Selected geometric parameters* (Å, °)

Compound (1)			
I(1)—Cd(1)	2.793 (2)	I(2)—Cd(1)	2.786 (2)
I(3)—Cd(1)	2.755 (2)	I(4)—Cd(1)	2.784 (2)
N(1)—C(1)	1.37 (2)	N(1)—C(4)	1.36 (2)
N(2)—C(2)	1.35 (2)	N(2)—C(3)	1.34 (2)
C(1)—C(2)	1.39 (2)	C(1)—C(5)	1.53 (2)
C(2)—C(6)	1.46 (3)	C(3)—C(4)	1.43 (2)
C(3)—C(7)	1.52 (3)	C(4)—C(8)	1.47 (3)
I(1)—Cd(1)—I(2)	102.1 (1)	I(1)—Cd(1)—I(3)	115.4 (1)
I(2)—Cd(1)—I(3)	109.5 (1)	I(1)—Cd(1)—I(4)	102.0 (1)
I(2)—Cd(1)—I(4)	118.5 (1)	I(3)—Cd(1)—I(4)	109.3 (1)
C(1)—N(1)—C(4)	125 (2)	C(2)—N(2)—C(3)	127 (1)
N(1)—C(1)—C(2)	120 (1)	N(1)—C(1)—C(5)	117 (2)
C(2)—C(1)—C(5)	123 (2)	N(2)—C(2)—C(1)	115 (2)
N(2)—C(2)—C(6)	120 (2)	C(1)—C(2)—C(6)	126 (2)
N(2)—C(3)—C(4)	119 (1)	N(2)—C(3)—C(7)	118 (2)
C(4)—C(3)—C(7)	123 (2)	N(1)—C(4)—C(3)	115 (2)
N(1)—C(4)—C(8)	119 (2)	C(3)—C(4)—C(8)	127 (2)
N(1)$\cdots$I(1$^{\rm i}$)	3.540 (6)	N(1)$\cdots$I(2$^{\rm ii}$)	3.501 (6)
N(2)$\cdots$I(1)	3.525 (6)	N(2)$\cdots$I(4$^{\rm iii}$)	3.534 (6)

Symmetry codes: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1+x, y, z$.

Compound (2)			
I(1)—Cd(1)	2.776 (2)	I(2)—Cd(1)	2.795 (2)
I(3)—Cd(1)	2.751 (2)	I(4)—Cd(1)	2.764 (3)
N(1)—C(1)	1.35 (2)	N(1)—C(2)	1.34 (2)
N(2)—C(5)	1.31 (2)	N(2)—C(6)	1.38 (3)
C(1)—C(3)	1.47 (3)	C(1)—C(2$^{\rm ii}$)	1.39 (3)
C(2)—C(4)	1.52 (3)	C(5)—C(7)	1.49 (4)
C(5)—C(6$^{\rm i}$)	1.40 (3)	C(6)—C(8)	1.51 (3)

I(1)—Cd(1)—I(2)	109.4 (1)	I(1)—Cd(1)—I(3)	109.9 (1)
I(2)—Cd(1)—I(3)	110.2 (1)	I(1)—Cd(1)—I(4)	106.3 (1)
I(2)—Cd(1)—I(4)	108.1 (1)	I(3)—Cd(1)—I(4)	112.8 (1)
C(1)—N(1)—C(2)	124 (2)	C(5)—N(2)—C(6)	124 (2)
N(1)—C(1)—C(3)	117 (2)	N(1)—C(1)—C(2^{i})	117 (2)
C(3)—C(1)—C(2^{i})	126 (2)	N(1)—C(2)—C(4)	117 (2)
N(1)—C(2)—C(1^{i})	119 (2)	C(4)—C(2)—C(1^{i})	124 (2)
N(2)—C(5)—C(7)	120 (2)	N(2)—C(5)—C(6^{ii})	118 (2)
C(7)—C(5)—C(6^{ii})	122 (2)	N(2)—C(6)—C(8)	117 (2)
N(2)—C(6)—C(5^{ii})	118 (2)	C(8)—C(6)—C(5^{ii})	125 (2)
N(1)···O(1)	2.684 (7)	O(1)···O(2)	2.834 (7)
O(2)···O(3)	2.833 (7)	N(2)···O(3)	2.676 (7)

Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $-x, 1 - y, -z$.

The structures were solved by direct methods and refined by full-matrix least squares. Corrections were applied for Lorentz and polarization effects, and real and imaginary anomalous dispersion (Cromer, 1974). Structure solution, refinement and the calculation of derived results were performed by using *SHELXTL* (Sheldrick, 1985). All non-H atoms were refined anisotropically except for the C atoms of (1); H atoms were not located. For (1), the asymmetric unit contains one diprotonated tetramethylpyrazinium cation and one CdI_4^{2-} anion, each occupying general positions in the cell. For (2), the asymmetric unit contains two unique cations, each situated about inversion centers [cation *A* at $(1\,\frac{1}{2}\,\frac{1}{2})$; cation *B* at $(0\,\frac{1}{2}\,0)$], three water molecules and a CdI_4^{2-} anion, all occupying general positions.

Lists of structure factors and anisotropic displacement parameters, along with a packing diagram of compound (2), have been deposited with the IUCr (Reference: HR1003). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Forms of (5,5-Dimethyl-4,7-diazadecane-1,10-diamine)nickel(II) Diperchlorate

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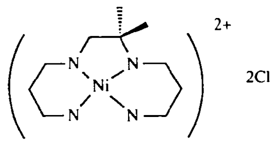
Abstract

The title Ni^{II} complex, $[Ni(C_{10}H_{26}N_4)](ClO_4)_2$, crystallizes in yellow and orange forms. In both crystals, the stereochemistry and conformation of the complex cations are identical. Small differences arise from packing effects, differences in the orientations of the perchlorate groups and hydrogen bonding. The Ni^{II} atom has square-planar coordination with the four tetraamine N atoms in equatorial positions. In each complex, the two chiral N-atom centres are in the (4*RS*,7*RS*) configuration. The tetraamine binds to the Ni^{II} atom in a relatively strain-free planar manner; the central six-membered ring exhibits a stable chair conformation and the two terminal five-membered rings adopt stable skew forms.

Comment

The crystal structures of open-chain tetraamine complexes containing secondary amine groups have been studied extensively. Anichini, Fabbrizzi, Paoletti & Clay (1977) pointed out that tetraaza complexes of Ni^{II} exist in equilibrium as a mixture of blue (paramagnetic, octahedral) and yellow (diamagnetic, square planar) forms. However, complexes containing methyl groups on the C(5) atom (see Fig. 1 for numbering) of the tetraamine ligand have received very little attention in the solid state. In this study, the structures of two different crystal forms, yellow and orange, of (5,5-dimethyl-4,7-diazadecane-1,10-diamine)nickel(II) diperchlorate, (I), have been determined.



(I)

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