Cl(1)—V(1)—Cl(2)	90.80 (6)	Cl(1)—V(2)—Cl(5)	93.52 (6)
Cl(1)—V(1)—Cl(3)	172.68 (7)	Cl(1)—V(2)—O(1)	81.6 (1)
Cl(1)—V(1)—O(1)	79.2 (1)	Cl(1)—V(2)—O(4)	93.3 (1)
Cl(1)—V(1)—O(2)	90.8 (1)	Cl(1)—V(2)—O(5)	175.5 (1)
Cl(1)—V(1)—O(3)	89.1 (1)	Cl(4)—V(2)—Cl(5)	172.05 (7)
Cl(2)—V(1)—Cl(3)	96.44 (7)	Cl(4)—V(2)—O(1)	95.8 (1)
Cl(2)—V(1)—O(1)	170.0 (1)	Cl(4)—V(2)—O(4)	87.1 (1)
Cl(2)—V(1)—O(2)	89.8 (1)	Cl(4)—V(2)—O(5)	88.2 (1)
Cl(2)—V(1)—O(3)	89.0 (1)	Cl(5)—V(2)—O(1)	91.9 (1)
Cl(3)—V(1)—O(1)	93.6 (1)	Cl(5)—V(2)—O(4)	85.4 (1)
Cl(3)—V(1)—O(2)	90.3 (1)	Cl(5)—V(2)—O(5)	89.3 (1)
Cl(3)—V(1)—O(3)	89.9 (1)	O(1)—V(2)—O(4)	174.1 (2)
O(1)—V(1)—O(2)	90.1 (1)	O(1)—V(2)—O(5)	94.9 (2)
O(1)—V(1)—O(3)	91.0 (2)	O(4)—V(2)—O(5)	90.3 (2)
O(2)—V(1)—O(3)	178.8 (2)	V(1)—Cl(1)—V(2)	84.56 (6)
Cl(1)—V(2)—Cl(4)	89.40 (6)	V(1)—O(1)—V(2)	114.7 (2)

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

The weak reflections $[I < 10\sigma(I)]$ were rescanned (maximum of two rescans) and the counts accumulated to insure good counting statistics. The structure was solved by direct methods using the *SIR*88 program (Burla *et al.*, 1989) and expanded using Fourier techniques (*DIRDIF*; Beurskens *et al.*, 1992). The position of the H(1) atom was determined from the difference Fourier synthesis map and refined isotropically. Other H atoms were placed in calculated positions (C—H = 1.08 Å). The non-H atoms were refined anisotropically. All H atoms, except for H(1), were included but not refined. All calculations were performed using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985, 1992). *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) was used for data collection and cell refinement.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Allotropic Form of *trans*-Dichlorobis(creatinine)platinum(II) Dihydrate

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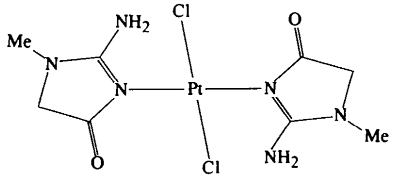
Abstract

The synthesis and crystal structure of a new allotropic form (violet crystals) of *trans*-bis(2-amino-1-methyl-1,5-dihydro-4*H*-imidazol-4-one-N^1)dichloroplatinum(II), $[PtCl_2(C_4H_7N_3O)_2].2H_2O$, are reported. This form differs from the two crystal forms (yellow and green crystals) studied previously in its intermolecular hydrogen-bonding scheme. The crystal structure of the new form is isomorphous with that reported for the corresponding palladium complex, *trans*-$[PdCl_2(C_4H_7N_3O)_2].2H_2O$.

Comment

The anticancer properties of the drug cisplatin, *cis*-$[PtCl_2(NH_3)_2]$, have motivated us to investigate the coordination chemistry of platinum–creatinine complexes. These compounds have potential antitumour activity and low nephrotoxicity compared with the anticancer drug cisplatin. Creatinine (2-amino-1-methyl-1,5-dihydro-4*H*-imidazol-4-one) plays an important role in protein metabolism and is of considerable biological interest. It has more than one site capable of coordinating to metal ions and, similar to adenine (Hodgson, 1977), can form cationic, neutral and anionic metal complexes. The syntheses of platinum–creatinine complexes and their properties have been described by Martín-Gil & Martín-Gil (1987). We have reported previously (Matos Beja, Paixão, Martín-Gil & Salgado, 1991) the crystal structures of two allotropic forms of $PtCl_2(creatinine)_2$, (I), corresponding to yellow and green crystals, formed by the reaction of K_2PtCl_4 and creatinine in aqueous solution at room temperature. The X-ray analyses have



(I)

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shown that in both the yellow and the green crystals the Pt^{II} ions are fourfold coordinated with square-planar geometry, the two Cl ions and the creatinine moieties being coordinated in a *trans* configuration. The same *trans* configuration is found in the violet crystals, but the structure differs from those of the yellow (monoclinic) and green (triclinic) crystals in its hydrogen-bonding scheme.

In the three crystal forms, each water molecule is involved in two intramolecular hydrogen bonds connecting the exocyclic amino and carbonyl groups of the creatinine moieties; details are given in Table 3 for the present structure. In the violet crystals, the water molecule forms an additional intermolecular hydrogen bond with a Cl atom of a neighbouring molecule. The structure is isomorphous with that reported for *trans*-Pd(creatinine)$_2$Cl$_2$ (Beurskens, Perales, Martín-Gil & Martín-Gil, 1988).

The bond distances and angles within the creatinine molecule are comparable to those of the two previously reported allotropes and also to those of the free base (Du Pré & Mendel, 1955) and the creatinium cation (Udupa & Krebs, 1979). They suggest extensive π-electron delocalization in the aromatic part of the molecule. This can account for the planarity of the creatinine ring, with a maximum deviation from the least-squares plane of the ring of 0.049 (3) Å. The dihedral angle between the Cl—Pt—N1 plane and the ring plane is 74.1 (2)°, a value intermediate between that found in the yellow form and that found in the green form [67.9 (5) and 83.5 (5)°, respectively]. Thus, the different crystal fields felt by the 5*d* electrons of the Pt^{2+} ions may possibly explain the different colours of the three allotropes.

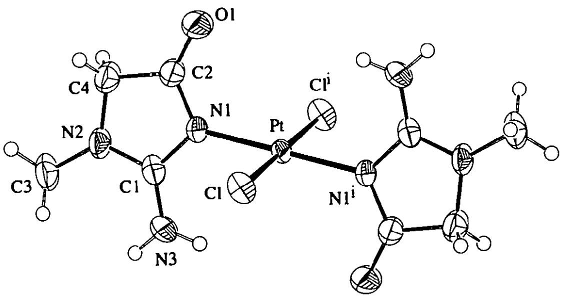

Fig. 1. The *trans*-dichlorobis(creatinine)platinum(II) molecule showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

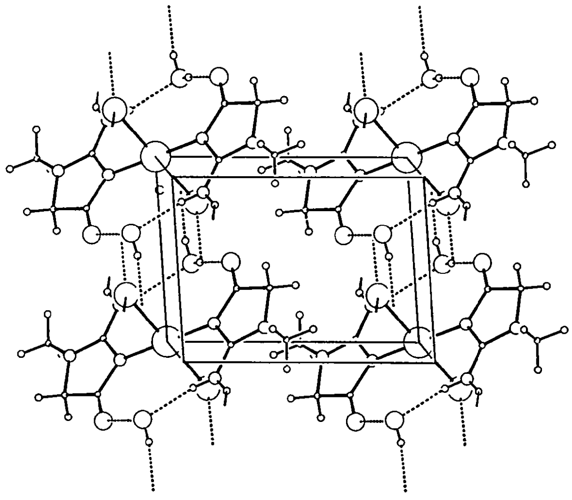

Fig. 2. Projection of the crystal structure along the [001] axis showing the hydrogen-bonding scheme.

Experimental

Violet crystals of *trans*-[PtCl$_2$(creatinine)$_2$].2H$_2$O were obtained by reaction of K$_2$PtCl$_4$ and creatinine (molar ratio 1:2) in the minimum amount of water at 313 K. Rapid cooling of the resulting solution resulted in a precipitate of yellow and green crystals (Matos Beja, Paixão, Martín-Gil & Salgado, 1991). Crystals of violet colour were formed when the solution was left in the dark for 1 h at 313 K and then allowed to cool slowly in a thermostatically controlled bath. Reducing the acidity of the solution and/or increasing the Cl$^-$ ion concentration also favoured crystallization of the violet crystals which have a strong absorption at λ = 550 nm and are stable in a dry atmosphere. Elemental analysis was in good agreement with the crystallographically determined stoichiometry.

Crystal data

$[PtCl_2(C_4H_7N_3O)_2].2H_2O$
$M_r = 528.27$
Triclinic
$P\bar{1}$
$a = 7.313\ (2)$ Å
$b = 9.057\ (2)$ Å
$c = 6.994\ (2)$ Å
$\alpha = 107.63\ (2)°$
$\beta = 117.60\ (2)°$
$\gamma = 74.810\ (2)°$
$V = 387.2\ (2)$ Å^3
$Z = 1$
$D_x = 2.266$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.18$–$25.72°$
$\mu = 9.429$ mm^{-1}
$T = 293\ (2)$ K
Good quality prism
0.116 × 0.098 × 0.085 mm
Violet

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.38$, $T_{max} = 0.45$
3385 measured reflections
2260 independent reflections

1639 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.044$
$\theta_{max} = 29.96°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -3 \rightarrow 9$
4 standard reflections
frequency: 120 min
intensity decay: 10.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0388$
$wR(F^2) = 0.0551$
$S = 0.995$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.323$ e Å^{-3} (adjacent to Pt)
$\Delta\rho_{min} = -0.99$ e Å^{-3}

2260 reflections
104 parameters
H atoms riding, except for those of the water molecule
$w = 1/[\sigma^2(F_o^2) + (0.0195P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Pt	0	0	0	0.02928 (10)
Cl	0.2426 (2)	0.14633 (14)	0.0609 (2)	0.0449 (3)
O1	−0.4189 (6)	0.2777 (4)	−0.0870 (6)	0.0575 (10)
O2	0.3679 (6)	−0.1445 (5)	0.4703 (7)	0.0602 (11)
N1	−0.1187 (5)	0.1796 (4)	0.1844 (6)	0.0333 (9)
N2	−0.1296 (6)	0.3599 (4)	0.4820 (6)	0.0413 (10)
N3	0.1382 (6)	0.1485 (5)	0.5359 (6)	0.0481 (11)
C1	−0.0291 (7)	0.2262 (5)	0.4091 (7)	0.0363 (11)
C2	−0.2970 (7)	0.2810 (5)	0.1065 (8)	0.0403 (12)
C3	−0.0892 (9)	0.4291 (6)	0.7130 (8)	0.0544 (14)
C4	−0.3222 (8)	0.4011 (5)	0.2997 (8)	0.0462 (13)

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

Pt—N1	2.022 (3)	N2—C1	1.332 (5)
Pt—Cl	2.2968 (13)	N2—C4	1.448 (6)
O1—C2	1.224 (5)	N2—C3	1.460 (6)
N1—C2	1.363 (6)	N3—C1	1.304 (6)
N1—C1	1.366 (5)	C2—C4	1.510 (6)
$N1^i$—Pt—N1	180.0	C4—N2—C3	123.2 (4)
N1—Pt—Cl	89.95 (11)	N3—C1—N2	124.3 (4)
Cl^i—Pt—Cl	180.0	N3—C1—N1	123.2 (4)
C2—N1—C1	107.6 (4)	N2—C1—N1	112.5 (4)
C2—N1—Pt	126.2 (3)	O1—C2—N1	126.7 (4)
C1—N1—Pt	126.1 (3)	O1—C2—C4	124.6 (4)
C1—N2—C4	109.0 (4)	N1—C2—C4	108.7 (4)
C1—N2—C3	125.5 (4)	N2—C4—C2	101.5 (4)

Symmetry code: (i) $-x, -y, -z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1···$O1^i$	0.85 (8)	1.91 (8)	2.741 (5)	167 (7)
O2—H2···Cl^{ii}	0.78 (8)	2.48 (7)	3.197 (4)	152 (7)
N3—H3A···Cl^{iii}	0.86	2.65	3.391 (4)	146
N3—H3B···O2	0.86	1.97	2.778 (6)	157

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1117). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Tetrahydrofuran-*O*)bis(η^5-1,2,4-triisopropylcyclopentadienyl)strontium

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Abstract

The title compound, $[Sr(C_{14}H_{23})_2(C_4H_8O)]$, has twofold crystallographic symmetry and possesses a bent geometry with a *Cp*—Sr—*Cp* angle of 139.4 (1)°, where *Cp* indicates a cyclopentadienyl ring (Cp) centroid. The Sr—O distance is 2.571 (3) Å and the average Sr—C_{Cp} distance is 2.838 (7) Å.

Comment

We have reported previously the synthesis and characterization of a series of alkaline earth metallocenes containing the 1,2,4-triisopropylcyclopentadienyl ligand, $[X\{(C_3H_7)_3C_5H_2\}_2(thf)_n]$ (X = Mg–Ba; n = 0–2; thf is tetrahydrofuran) (Burkey, Williams & Hanusa, 1993; Burkey, Hanusa & Huffman, 1994). During the course of related work, we obtained X-ray quality crystals of one of these complexes, namely $[Sr\{(C_3H_7)_3C_5H_2\}_2(thf)]$,