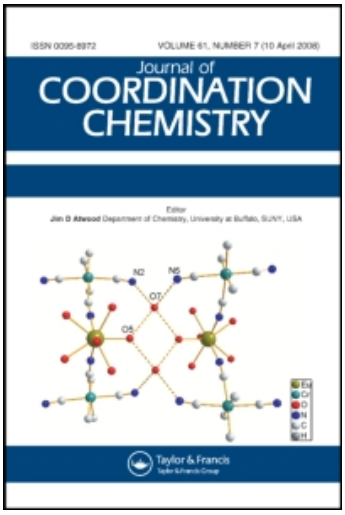

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M. Mitewa[a]; T. Todorov[b]; G. Gencheva[a]; O. Angelova[b]; T. N. Bakalova[a]
[a] Department of Chemistry, University of Sofia, Sofia, Bulgaria [b] Bulgarian Academy of Sciences, Central Laboratory of Mineralogy and Crystallography, Sofia, Bulgaria

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CRYSTAL STRUCTURE OF A NEW ALLOTROPIC FORM OF *TRANS*-$Pd(CREAT)_2Cl_2 \cdot 2H_2O$

M. MITEWA[a,*], T. TODOROV[b], G. GENCHEVA[a], O. ANGELOVA[b] and T.N. BAKALOVA[a]

[a]*Department of Chemistry, University of Sofia, J. Bourchier av. 1, Sofia, Bulgaria;*
[b]*Bulgarian Academy of Sciences, Central Laboratory of Mineralogy and Crystallography, Sofia, Bulgaria*

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$Pd(creat)_2Cl_2 \cdot 2H_2O$ crystallizes in space group $P\bar{1}$ with $a = 7.257(2)$, $b = 8.159(2)$, $c = 14.640(2)$ Å, $\alpha = 73.97(2)$, $\beta = 77.0(1)$, $\lambda = 72.22(2)^\circ$, $Z = 2$, and represents a new allotropic form of this compound. Pd atoms have planar fourfold coordination of *N* and Cl atoms in *trans* configuration. Creatinine moieties are coordinated to the Pd atoms *via* endocyclic *N* atoms and their essential planarity causes significant delocalization of electron density. The structure is stabilized by a system of weak hydrogen bonds involving interstitial water molecules and creatinine amino-groups.

Keywords: Creatinine; Allotropic form; Crystal structure

INTRODUCTION

The biological importance of creatine (*N*,*N*-acetylmethylguanidine) and its cyclic derivative creatinine (2-amino-1-methylimidazolinone) (creat) is well documented [1,2]. Both ligands are excellent complexing agents due to the presence of several donor groups and act either as monodentate or bridging ligands [2]. As part of a systematic study of the coordination properties of creatine and creatinine under different reaction conditions, we have studied the interaction of $PdCl_4^{2-}$ with creatine in neutral and basic aqueous media (pH 6–10). It should be noted that for these ligands it is already unambiguously proven [2] that variation of reaction conditions leads to the formation of different products. Here we report the crystal structure of *trans*-$Pd(creat)_2Cl_2.2H_2O$.

EXPERIMENTAL

Synthesis

Freshly prepared solutions of $(NH_4)_2PdCl_4$ (*Fluka*) and creatine (*Merck*) at a metal to ligand ratio of 1 : 6 (concentration 5×10^{-2} M) were mixed at ambient temperature and

*Corresponding author. E-mail: mmitewa@chem.uni-sofia.bg

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adjusted to pH 6 to 10 by adding 0.1 M KOH. After 3 days, precipitates were removed and from the yellow filtrate prismatic single crystals were obtained after several days. These were filtered off, washed with distilled water and dried in air.

Single-crystal Experiment

A suitable prismatic crystal was mounted on the goniometer head of an Enraf-Nonius CAD4 X-ray diffractometer [3] (MoKα, $\lambda = 0.71073$ Å, graphite monochromator). The title compound crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. Lattice constants were obtained from a least-squares fit of 22 reflections within $20 < \theta < 22°$. Intensity data were collected with the $\omega/2\theta$ scan mode at 292 K. Within the collection limits (h 0 to 10, $k - 11$ to 11, $l - 20$ to 20; $\sin\theta/\lambda < 0.703$) were measured 4892 reflections, 2258 of which with $I > 3\sigma(I)$ were used for structure refinement. Three check reflections monitored every 2 h revealed no intensity decay. A ψ-scan-based empirical absorption correction was applied to the data set [4]. The structural motif was solved by direct methods using *SHELXS*86 [5] and difference Fourier syntheses. The final anisotropic model of all non-hydrogen atoms was refined by full-matrix least-squares on F_0. Atom coordinates are listed in Table I. More detailed information for data collection and structure refinement is presented in Table II.

Hydrogen atoms of the creatinine ligand were placed at calculated positions (C–H = 0.95 Å), while water hydrogen coordinates were extracted from a difference map. All H-atoms were refined as riding with fixed isotropic $U = 0.05$ Å^2. Atomic scattering factors and anomalous dispersion coefficients were taken as quoted in the *SDP*/*PDP V*3.0 package [6].

TABLE I Fractional atomic coordinates and equivalent isotropic thermal displacement parameters for the non-hydrogen atoms in $Pd(creat)_2Cl_2.2H_2O$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Pd1	0	0	0	0.03068 (9)
Pd2	1/2	0	1/2	0.02633 (8)
Cl1	0.1821 (2)	0.1366 (1)	−0.13908 (7)	0.0388 (2)
Cl2	0.6789 (2)	0.1223 (2)	0.36757 (8)	0.0444 (3)
OW1	0.4252 (6)	−0.3111 (5)	0.0670 (3)	0.059 (1)
OW2	0.0586 (5)	0.3194 (4)	0.4517 (2)	0.0586 (9)
O18	−0.2535 (5)	0.3791 (5)	0.0774 (3)	0.0503 (9)
O28	0.2711 (5)	0.3826 (4)	0.5540 (2)	0.0491 (8)
N1	0.0360 (4)	0.1447 (4)	0.0827 (2)	0.0252 (7)
N13	0.1957 (5)	0.2596 (4)	0.1568 (3)	0.0393 (9)
N16	0.3823 (4)	−0.0015 (4)	0.0966 (2)	0.0320 (8)
N2	0.5521 (4)	0.1687 (4)	0.5660 (2)	0.0257 (8)
N23	0.6972 (5)	0.2609 (5)	0.6553 (2)	0.0416 (8)
N26	0.8464 (4)	0.0023 (4)	0.6133 (2)	0.0277 (7)
C12	0.2208 (4)	0.1276 (4)	0.1096 (2)	0.0204 (6)
C14	−0.0115 (5)	0.3720 (4)	0.1559 (3)	0.0360 (9)
C15	−0.0774 (7)	0.3107 (7)	0.0958 (4)	0.054 (1)
C17	0.3278 (5)	0.2742 (5)	0.2130 (3)	0.0348 (9)
C22	0.6957 (6)	0.1419 (5)	0.6159 (3)	0.037 (1)
C24	0.5206 (5)	0.3936 (4)	0.6479 (3)	0.0322 (8)
C25	0.4144 (5)	0.3101 (4)	0.5911 (2)	0.01318 (8)
C27	0.8637 (6)	0.2681 (6)	0.6964 (3)	0.042 (1)

TABLE II Experimental parameters and single-crystal data

Formula	$C_8H_{16}Cl_2N_6O_4Pd$
Crystal size (mm)	$0.22 \times 0.15 \times 0.08$
Formula weight	437.56
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	2
a (Å)	7.257 (2)
b (Å)	8.159 (2)
c (Å)	14.640 (2)
α (°)	73.97 (2)
β (°)	77.04 (1)
γ (°)	72.22 (2)
V (Å^3)	784.0 (4)
Temperature (K)	292
$F(000)$	436
Calculated density (g cm^{-3})	1.853
Absorption coeff. μ (cm^{-1})	1.51
λ (MoKα) (Å)	0.71073
Scan mode	$\omega/2\theta$
Scan width (°)	$0.90 + 0.35\,\mathrm{tg}\theta$
Total number of reflections	4892
Independent reflections	4560
R_{int}	0.017
No. $I > 3\sigma(I)$	2258
Absorption correction type	Ψ-scan
Transmission limits	0.824–0.998
Refinement on	F
Weighting scheme	$1/[\sigma^2(F) + (0.022F)^2]$
Least-squares parameters	193
R	0.027
R_w	0.037
Goodness of fit	1.321
$\Delta/\sigma_{\max}$	0.020
$\Delta/\rho_{\max}$ (e Å^{-3})	− 1.087

RESULTS AND DISCUSSION

There are two crystallographically non-equivalent Pd atoms in the structure. Both have planar, centrosymmetric, fourfold coordination, constituted by two Cl atoms and the endocyclic N atoms from two creatinine ligands in a *trans* configuration (Fig. 1). Pd–Cl and Pd–N distances are similar to the corresponding distances in its allotropic form **I** with known structure [7]. However, there is a difference concerning central angles – the two Cl–Pd–N angles in **I** are 89.98(2) and 90.02(2)°, while the corresponding angles at the Pd1 [Pd2] atoms in the title structure **II** are 86.49(8) and 93.51(8)° [86.28(8) and 93.72(8)°]. In both Pd1 and Pd2 molecules creatinine moieties are planar with maximum deviations of 0.165(3) Å and 0.096(4) Å for N1 and C25, respectively. The angles between coordination and ligand planes are 78.93(8)° and 82.83(8)° for Pd1 and Pd2, respectively. Bond lengths within creatinine ligands show delocalization of electron density over N1–C12 [N2–C22], C12–N13 [C22–N23] and C12–N16 [C22–N26] bonds of Pd1 [Pd2] molecules. As can be seen from Table III, the delocalization is more extensive in the Pd2 molecule. This phenomenon can be ascribed to the better planarity of this molecular fragment. In the structure of **I**, where the planarity of creatinine is commensurable with that of the same ligand in the Pd2 molecule, the

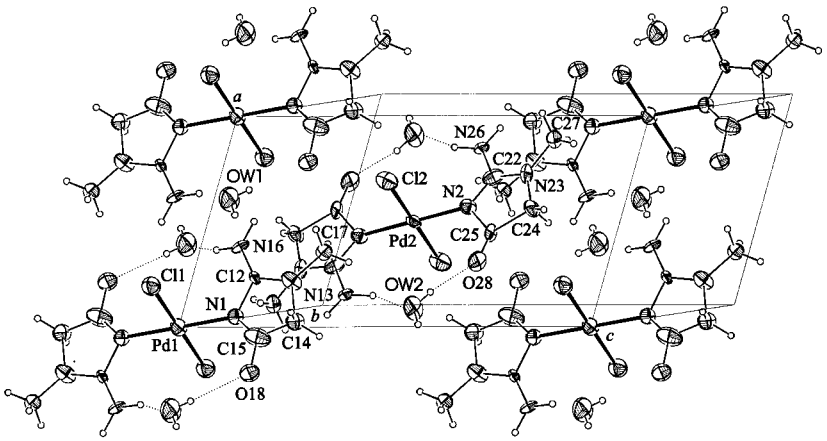

FIGURE 1 An *ORTEP* [13] view of the complex showing 50% probability displacement ellipsoids and the atom labelling scheme. H atoms are shown as spheres of arbitrary radii. Intramolecular hydrogen bonds are also shown.

TABLE III Selected interatomic distances (Å) and angles (°); estimated standard deviations are given in parentheses

Pd1–Cl1	2.361 (1) × 2	Cl1–Pd1–N1	93.51 (8)
Pd1–N1	2.013 (4) × 2	Cl1–Pd1–N1	86.49 (8)
Pd2–Cl2	2.244 (1) × 2	Cl2–Pd2–N2	86.28 (8)
Pd2–N2	2.046 (4) × 2	Cl2–Pd2–N2	93.72 (8)
O18–C15	1.286 (6)	C12–N1–C15	104.57 (37)
C14–C15	1.353 (9)	C12–N13–C14	108.16 (36)
N1–C12	1.437 (5)	C12–N13–C17	127.43 (29)
N1–C15	1.393 (6)	C14–N13–C17	123.55 (35)
N13–C12	1.380 (5)	N1–C12–N13	107.84 (25)
N13–N14	1.504 (5)	N1–C12–N16	125.12 (34)
N13–C17	1.445 (6)	N13–C12–N16	126.89 (35)
N16–C12	1.333 (4)	N13–C14–C15	102.60 (35)
O28–C25	1.194 (5)	O18–C15–N1	124.39 (58)
C24–C25	1.635 (6)	O18–C15–C14	119.83 (48)
N2–C22	1.335 (6)	N1–C15–C14	113.04 (40)
N2–C25	1.353 (4)	C22–N2–C25	104.69 (35)
N23–C22	1.263 (7)	C22–N23–C24	108.95 (39)
N23–C24	1.406 (4)	C22–N23–C27	126.00 (34)
N23–C27	1.488 (7)	C24–N23–C27	124.91 (39)
N26–C22	1.319 (4)	N2–C22–N23	119.35 (34)
		N2–C22–N26	119.54 (44)
		N23–C22–N26	120.54 (44)
		N23–C24–C25	99.53 (31)
		O28–C25–N2	123.77 (40)
		O28–C25–C24	127.24 (32)
		N2–C25–C24	105.67 (30)

charge delocalization is of the same extent. Planes of creatinine ligands in symmetrically-independent molecules are almost parallel with a dihedral angle of 6.7° and are oriented along ($\bar{1}02$).

$Pd(creat)_2Cl_2$ molecules are stitched into a three-dimensional structure by a system of weak hydrogen bonds involving N16, N26 and water oxygen atoms (Table IV). The water molecules are not coordinated to the metal atom. They represent interstitial

TABLE IV Proposed hydrogen bonding geometry

$D-H\cdots A$	$D-H$ (Å)	$H\cdots A$ (Å)	$D\cdots A$ (Å)	$D-H\cdots A$ (°)
N16–H161···Cl1[i]	0.95	2.29	3.158 (3)	151
N16–H162···OW1	0.95	1.70	2.594 (6)	156
N26–H26···Cl2[ii]	0.95	2.58	3.334 (3)	136
N26–H262···OW2[iii]	0.95	2.01	2.872 (5)	150
OW1–HW11···O18[iv]	0.73 (1)	2.20	2.930 (7)	179
OW1–HW12···O18[v]	0.73 (1)	2.14	2.863 (4)	178
OW2–HW21···O28	0.77 (1)	1.85	2.615 (6)	169
OW2–HW22···O28[vi]	0.72 (1)	2.12	2.841 (4)	178

Symmetry codes: (i) $1-x, -y, -z$; (ii) $2-x, -y, 1-z$; (iii) $1-x, -y, 1-z$; (iv) $-x, -y, -z$; (v) $1+x, y-1, z$; (vi) $-x, 1-y, 1-z$.

species and are donors for two hydrogen bonds (inter- and intramolecular) and acceptors of one from N16 and N26 *via* H162 and H262 atoms, respectively. Cl atoms participate in structure stabilization as acceptors in intermolecular N–H···Cl hydrogen bonds. Although the H···Cl and N···Cl distances for the C12 atom are considerably longer than corresponding C11-distances they are in the range reported for such H-bonds [8,9].

It was shown that at pH > 6 immediately after mixing the reagents $PdCl_4^{2-}$ and creatine, paramagnetic, dimeric and oligomeric palladium complexes are formed and these precipitate simultaneously [10]. Their formation is connected with an increase in acidity to pH ~ 3.5 and a colour change of the reaction mixture from greenish-brown to yellow. Some 3 days after the reaction starts the precipitates are removed and in the course of the next several days yellow, prismatic crystals of *trans*-$Pd(creat)_2Cl_2 \cdot 2H_2O$ (**II**) are formed. Their formation is not surprising as it is well documented that in acidic media creatine is readily cyclized to creatinine [11,12].

A possible reason for the existence of allotropic modification **II** is the use of creatine instead of creatinine in the preparation of **I**. There are some differences in the packing role of the hydrogen bonds. In **I**, the Cl atoms are acceptors in hydrogen bonds of OW···Cl type. The corresponding contacts in the title structure of 3.989(5) and 4.052(3) Å are far from accepted hydrogen bond limits. This fact, as well as the presence of shorter and consequently stronger (in a view of their Coloumbic nature) H-bonds, are responsible, from the structural point of view, for the existence of this second allotropic form.

Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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