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Two Allotropic Forms of *trans*-Dichlorobis(creatinine)platinum(II) Dihydrate

BY ANA MATOS BEJA AND J. A. CARVALHO PAIXÃO

Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3000 Coimbra, Portugal

AND J. MARTIN GIL AND M. ARAGON SALGADO

Escuela Técnica Superior de Ingenieros Industriales, Paseo del Cauce, s/n Valladolid, Spain

Abstract. [PtCl$_2$(C$_4$H$_7$N$_3$O)$_2$.2H$_2$O, $M_r = 528\cdot27$, λ(Mo $K\alpha$) = 0·71073 Å, $T = 291$ (1) K. Crystal *M*: monoclinic, $P2_1/n$, $a = 6\cdot584$ (1), $b = 7\cdot538$ (1), $c = 15\cdot511$ (2) Å, $\beta = 93\cdot92$ (1)°, $V = 768\cdot0$ Å^3, $Z = 2$, $D_x = 2\cdot284$ g cm^{-3}, $\mu = 96\cdot039$ cm^{-1}, $F(000) = 504$, $R = 0\cdot013$ for 2014 independent reflections with $I > 3\sigma$ out of 3580 total unique data and 13 661 measured reflections. Crystal *T*: triclinic, $P\bar{1}$, $a = 7\cdot123$ (2), $b = 7\cdot370$ (2), $c = 8\cdot140$ (1) Å, $\alpha = 96\cdot84$ (1), $\beta = 106\cdot33$ (1), $\gamma = 104\cdot25$ (1)°, $V = 389\cdot2$ Å^3, $Z = 1$, $D_x = 2\cdot253$ g cm^{-3}, $\mu = 94\cdot743$ cm^{-1}, $F(000) = 252$, $R = 0\cdot025$ for 1046 independent reflections with $I > 3\sigma$ out of 1356 total unique data and 2434 measured reflections.

Introduction. The synthesis of *trans*-dichlorobis(creatinine)platinum(II) dihydrate constitutes an intermediate stage in the preparation of *cis*-dichlorobis(creatinine)platinum(II). The synthesis of 'Platinum Creatinine Blues' complexes and their properties have been described in a previous paper (Martin-Gil & Martin-Gil, 1987). Now we report the preparation, crystal structures and thermal behaviour of *trans*-Pt(creat)$_2$Cl$_2$.2H$_2$O (creat = crea-

tinine) monoclinic yellow (*M*), and triclinic green (*T*) crystals, in order better to understand this interesting class of compounds. The reason for this interest is their potential antitumour activity and low nephrotoxicity compared with the anticancer drug *cis*-platin.

Experimental. Yellow crystals *M* were obtained by reaction of K$_2$PtCl$_4$ and creatinine (2:1) in the minimum amount of water at room temperature. Some green crystals *T* were obtained together with yellow ones from the same reaction. Hydrolysis of the *trans*-dichlorobis(creatinine)platinum(II) complexes produces blue products.

A thermal study of the yellow crystals *M* was performed. The TG and DTG curves of *trans*-Pt(creat)$_2$Cl$_2$.2H$_2$O in air and N$_2$ from 303 to 803 K show that after dehydration the complex is stable between 348 and 573 K, the range of stability being 50 K wider than that of *trans*-Pd(creat)$_2$Cl$_2$.2H$_2$O (Beurskens, Perales, Martin-Gil & Martin-Gil, 1988). Above 573 K a decomposition starts in two consecutive stages: 583–628 K and 628–673 K, *versus* 523–663 K and 663–823 K in the palladium complex.

The DTA (differential thermal analysis) curve in air shows that the decomposition of M is exothermic and occurs at 659 K, whereas in N_2 it is endothermic. The measurements were carried out with a Perkin–Elmer 3600, using a heating rate of 5 K min^{-1}.

Monoclinic M: A prismatic crystal with dimensions $0.21 \times 0.16 \times 0.13$ mm was mounted on a glass fibre for data collection. The crystal was analysed at 291 (1) K with a CAD-4 Enraf–Nonius diffractometer, using graphite-monochromated Mo $K\alpha$ radiation.

The unit-cell parameters were determined on the basis of 24 well centered reflections in the angular range $23 \leq 2\theta \leq 48°$. A preliminary data collection indicated the systematic absences $h0l$: $h + l = 2n + 1$, $0k0$: $k = 2n + 1$ of the monoclinic system, uniquely determining the space group $P2_1/n$ ($P2_1/c$ on a non-standard setting). The intensity data were collected in the $\omega/2\theta$ scan mode, with scan speed 0.2–$5.0° $ min^{-1}, in the range $4 \leq 2\theta \leq 70°$. The scan range was determined as a function of θ to correct for the separation in the $K\alpha$ doublet, the scan width in ω being $(1.0 + 0.34\tan\theta)°$ and the background/scan time ratio 0.5. The counter aperture was also adjusted as a function of θ.

A total of 13 661 reflections was measured, in the ranges $h = -10$ to 10, $k = -12$ to 12, $l = -25$ to 25. Four standard reflections ($\overline{3}52$; $\overline{2}59$; $\overline{2}5\overline{3}$; $\overline{1}41$) were measured every 3 h and exhibited a uniform intensity decay which amounted to a total of 10·2% during the total measuring time of 530·9 h; accordingly, a linear decay correction was applied. Data were corrected for Lorentz and polarization effects; a ψ-scan absorption correction was applied, based on ψ-scan data of nine reflections obtained at the conclusion of intensity data collection; the range of transmission factors was 61·5–99·8%, with an average value of 82·6%. Uncertainties were assigned to each reflection using the formula $\sigma_I^2 = \sigma_{cs}^2 + (0.04I)^2$, where σ_{cs} is based on counting statistics and I is the integrated intensity. The symmetry-related reflections were averaged to give a final set of 3580 independent reflections, of which 2014 had $I > 3\sigma$, and the remainder had been rejected. After averaging, the internal agreement factors of the accepted reflections were $R(F) = 0.015$ and $R(F^2) = 0.024$.

The size of the unit cell and the empirical formula of the compound indicated the existence of no more than two Pt atoms per unit cell. Accordingly, Pt atoms were placed at special positions $(0,0,0; \frac{1}{2},\frac{1}{2},\frac{1}{2})$. The positions of all the other non-H atoms were determined by direct methods, using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and *DIRDIF* (Beurskens, Bosman, Doesburg, van den Hark, Prick, Noordik, Beurskens, Gould & Parthasarathi, 1983). Full-matrix least-squares refinements of positional and anisotropic thermal parameters of non-H atoms for 2014 observed reflections (125 variables) converged to $R = 0.017$, $wR = 0.029$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F_o)$.

H atoms were located by difference electron density maps, and their positional parameters refined with an isotropic thermal parameter $B_{iso} = 5.0$ Å^2; an empirical extinction parameter g (Stout & Jensen, 1968) was refined simultaneously [g: $|F_o|_{corr} = |F_o|/(1 + gI_c)$, where I_c is the calculated intensity], converging to 3.32×10^{-7}. Final residual factors for 125 variables were $R = 0.013$, $wR = 0.017$; the maximum Δ/σ in the last full-matrix least-squares refinement cycle was 0·01. The final difference Fourier map against the spherical model showed $-1.05 \leq \Delta\rho \leq +0.86$ e Å^{-3}.

Triclinic T: Experimental set-up and data analysis performed as for monoclinic crystal M. Dimensions of the approximately prismatic crystal: $0.14 \times 0.12 \times 0.07$ mm.

The unit-cell parameters were determined on the basis of 25 well centered reflections in the angular range $12 \leq 2\theta \leq 41°$. Intensity data collected in $\omega/2\theta$ scan mode, in the range $4 \leq 2\theta \leq 50°$. Scan width in ω: $(0.9 + 0.34\tan\theta)°$, background/scan time ratio 0·5. A total of 2434 reflections were measured, in the ranges $h = -8$ to 8, $k = -8$ to 8, $l = -9$ to 9. Four standard reflections (200; $21\overline{1}$; $\overline{1}3\overline{1}$; 301) measured every 3 h exhibited a uniform intensity decay of 4·5% during the total measuring time of 243·7 h; a linear decay correction was applied. Data were corrected for Lorentz and polarization effects, no absorption correction was applied.

Uncertainties on the intensities were assigned in the same way as for M. The Friedel pairs were averaged to give a final set of 1356 independent reflections, 1046 with $I > 3\sigma$ accepted. The internal agreement factors of the accepted reflections were $R(F) = 0.016$, $R(F^2) = 0.026$. Atomic positions determined as for M. Non-H atoms refined anisotropically; H atoms located by difference Fourier maps, positional parameters refined with $B_{iso} = 5.0$ Å^2. Extinction parameter refined as for M gave $g = 7.77 \times 10^{-7}$. Final residual factors for 125 variables were $R = 0.025$, $wR = 0.029$; the maximum $\Delta\sigma$ in the last full-matrix least-squares refinement cycle was 0·01. Final difference Fourier map was featureless, $-1.36 \leq \Delta\rho \leq +1.08$ e Å^{-3}.

Atomic scattering factors including the anomalous-dispersion correction factors for both crystals were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a MicroVAX II computer, using the *SDP* (V3.0) package (Frenz, 1985).

Discussion. The molecular structure and atom numbers are shown in Fig. 1. The final atomic

coordinates with their e.s.d.'s and equivalent iso-tropic thermal parameters are given in Tables 1 and 2.* Intramolecular bond lengths and angles are listed in Tables 3 and 4. Figs. 2 and 3 show molecular packing indicating the network of hydrogen bonds which play an important role in the crystal stability (Table 5 shows the hydrogen-bonding geometry). The crystal structure consists of chains of coordinated creatinine molecules, hydrogen bonded by water molecules. No interactions other than van der Waals appear to occur between chains. The main difference between the two allotropic forms lies in the intermolecular bonding. In the triclinic structure the planes of the creatinine moiety are parallel; however, this does not occur in the monoclinic structure due to the presence of the glide plane.

In both compounds the Pt atoms are four coordinated in a square-planar geometry, the two Cl atoms and the two N(1) creatinine atoms are coordinated to Pt in a *trans* configuration. The bond distances in the molecule agree well with previous studies of related compounds (Beurskens *et al.*, 1983) and suggest an extensive delocalization of the charge in the creatinine moiety, with the exceptions C(2)—C(4), N(2)—C(3) and N(2)—C(4). This delocalization can account for the observed planarity of the creatinine ring [N(1), C(1), N(2), C(4) and C(2) atoms]; the maximum deviations from the least-squares plane of

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* TG, DTG and DTA curves for crystal *M*, lists of structure factors, H-atom coordinates and displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53917 (39 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
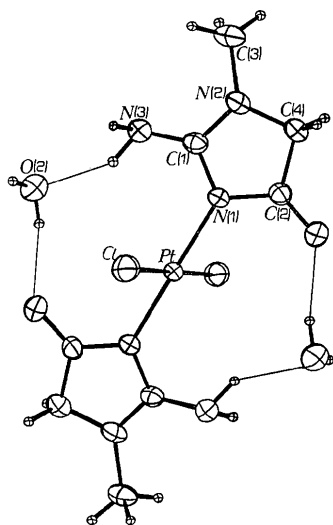
the ring ('ring plane') are 0·021 Å for C(1) in crystal *M* and −0·022 and 0·022 Å for C(4) and C(2) respectively, in crystal *T*. The bond C(2)—O(1) in compound *M* lies in the 'ring plane', but both N(3) and C(3) atoms lie out of it (deviations are 0·087 and 0·211 Å respectively). The Pt—N(1) bond is bent out of the plane also, the Pt atom deviating by −0·126 Å from it. In crystal *T* the N(3) atom lies well within the 'ring plane' and the deviations of both C(3) and Pt from the least-squares plane are also reduced (0·023 and −0·043 Å respectively). On the other hand, we observe in this crystal form a pronounced bending of the carbonyl bond [O(1) is 0·110 Å out of the 'ring plane'].

Fig. 2. A *PLUTO* (Motherwell, 1976) view of the molecular packing in crystal *M* projected onto the (010) plane. Hydrogen bonds are shown by thin lines.

Fig. 1. An *ORTEP* (Johnson, 1965) view of the molecule (crystal *M*) showing the atomic numbering scheme (thermal ellipsoids at the 50% probability level; hydrogen bonds are shown by thin lines).
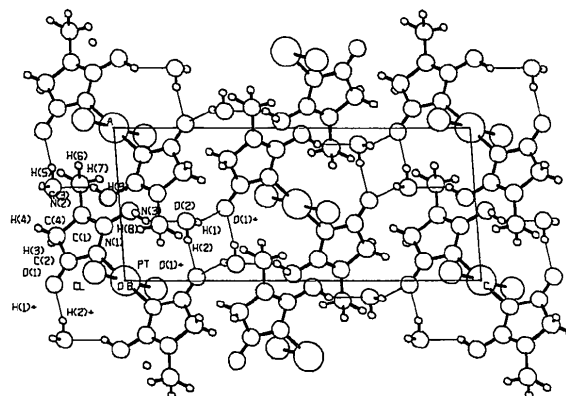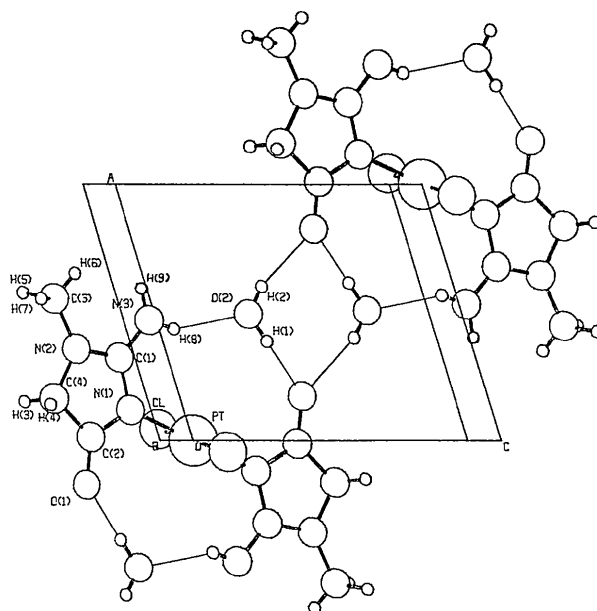

Fig. 3. A *PLUTO* (Motherwell, 1976) projection of the structure of crystal *T* onto the (010) plane. Hydrogen bonds are shown by thin lines.

Table 1. *Positional and equivalent isotropic thermal parameters for non-*H *atoms and their e.s.d.'s in parentheses for crystal M*

	x	y	z	B (Å^2)
Pt	0·0000	0·0000	0·0000	1·636 (1)
Cl	0·05379 (9)	0·24468 (9)	−0·08515 (4)	2·632 (9)
O(1)	−0·0259 (3)	−0·1608 (3)	−0·20263 (11)	2·83 (3)
O(2)	0·3910 (4)	−0·0293 (2)	0·18498 (24)	3·26 (4)
N(1)	0·1747 (3)	−0·15098 (25)	−0·0736 (1)	1·95 (3)
N(2)	0·4286 (3)	−0·3293 (3)	−0·10904 (14)	2·48 (3)
N(3)	0·45499 (32)	−0·1942 (3)	0·02695 (15)	2·50 (3)
C(1)	0·3593 (3)	−0·2247 (3)	−0·04843 (14)	2·00 (3)
C(2)	0·1266 (3)	−0·2029 (3)	−0·15704 (15)	2·15 (4)
C(3)	0·6333 (4)	−0·4056 (4)	−0·10768 (19)	3·06 (5)
C(4)	0·2923 (4)	−0·3232 (3)	−0·18528 (2)	2·65 (4)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta) \times \beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 2. *Positional and equivalent isotropic thermal parameters for non-*H *atoms and their e.s.d.'s in parentheses for crystal T*

	x	y	z	B (Å^2)
Pt	0·0000	0·0000	0·0000	2·392 (7)
Cl	0·0438 (3)	−0·2737 (3)	−0·1316 (2)	3·58 (4)
O(1)	−0·1727 (7)	0·1259 (9)	−0·3836 (6)	4·8 (1)
O(2)	0·4937 (8)	0·1152 (9)	0·3192 (6)	5·3 (1)
N(1)	0·1183 (7)	0·1466 (8)	−0·1596 (6)	2·8 (1)
N(2)	0·3552 (8)	0·3138 (8)	−0·2612 (6)	3·2 (1)
N(3)	0·4672 (8)	0·2124 (9)	−0·0005 (6)	3·3 (1)
C(1)	0·3212 (9)	0·2243 (9)	−0·1351 (7)	2·5 (1)
C(2)	0·0122 (9)	−0·1842 (9)	−0·3141 (8)	3·1 (1)
C(3)	0·5529 (10)	−0·4117 (12)	−0·2737 (9)	4·0 (2)
C(4)	0·1619 (11)	0·3040 (11)	−0·3851 (8)	3·7 (2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta) \times \beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 3. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses for crystal M*

Pt—Cl	2·3098 (6)	N(2)—C(1)	1·332 (3)
Pt—N(1)	2·025 (2)	N(2)—C(3)	1·465 (3)
O(1)—C(2)	1·229 (3)	N(2)—C(4)	1·435 (3)
N(1)—C(1)	1·369 (3)	N(3)—C(1)	1·3101 (31)
N(1)—C(2)	1·369 (3)	C(2)—C(4)	1·507 (3)
Cl—Pt—N(1)	90·64 (6)	N(1)—C(1)—N(2)	112·32 (19)
Pt—N(1)—C(1)	126·52 (15)	N(1)—C(1)—N(3)	123·15 (20)
Pt—N(1)—C(2)	126·16 (14)	N(2)—C(1)—N(3)	124·5 (2)
C(1)—N(1)—C(2)	107·29 (18)	O(1)—C(2)—N(1)	126·7 (2)
C(1)—N(2)—C(3)	125·6 (2)	O(1)—C(2)—C(4)	124·6 (2)
C(1)—N(2)—C(4)	109·73 (19)	N(1)—C(2)—C(4)	108·75 (19)
C(3)—N(2)—C(4)	123·2 (2)	N(2)—C(4)—C(2)	101·8 (2)

The small $\Delta\rho$ values observed in the difference Fourier maps show no special features for crystal *T*. However, for crystal *M* they are located on the lone pair regions and on the covalent bonds of the creatinine ring. This is likely to be of some significance, as for crystal *M* the $h + k + l = 2n + 1$ reflections have no contribution from Pt atoms. Although no conclusion can be drawn, this suggests that a low-temperature electron density study should be carried out. This work is being undertaken.

Table 4. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses for crystal T*

Pt—C(1)	2·302 (2)	N(2)—C(1)	1·330 (9)
Pt—N(1)	2·016 (6)	N(2)—C(3)	1·454 (9)
O(1)—C(2)	1·218 (8)	N(2)—C(4)	1·439 (8)
N(1)—C(1)	1·365 (8)	N(3)—C(1)	1·310 (7)
N(1)—C(2)	1·372 (8)	C(2)—C(4)	1·50 (1)
Cl—Pt—N(1)	90·0 (2)	N(1)—C(1)—N(2)	113·1 (5)
Pt—N(1)—C(1)	126·1 (4)	N(1)—C(1)—N(3)	123·2 (6)
Pt—N(1)—C(2)	127·1 (4)	N(2)—C(1)—N(3)	123·7 (6)
C(1)—N(1)—C(2)	106·9 (5)	O(1)—C(2)—N(1)	125·3 (7)
C(1)—N(2)—C(3)	126·8 (5)	O(1)—C(2)—C(4)	125·9 (6)
C(1)—N(2)—C(4)	109·1 (5)	N(1)—C(2)—C(4)	108·8 (5)
C(3)—N(2)—C(4)	124·1 (6)	N(2)—C(4)—C(2)	102·0 (6)

Table 5. *Hydrogen-bonding geometry* (Å, °)

	D—H···A	D···A	D···H	D—H—A
Crystal *M*				
	O(2)—H(2)···O(1)^i	2·828 (3)	0·90 (8)	155 (4)
	O(2)—H(1)···O(1)^{ii}*	2·943 (4)	0·88 (7)	155 (3)
	N(3)—H(8)···O(2)	2·807 (4)	0·97 (6)	144 (3)
Crystal *T*				
	O(2)—H(2)···O(1)^{iii}	2·749 (8)	0·91 (11)	170 (11)
	O(2)—H(2)···O(1)^{iv}*	2·853 (7)	0·80 (10)	161 (11)
	N(3)—H(8)···O(2)	2·749 (8)	0·89 (11)	146 (7)

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

* Intermolecular hydrogen bond.

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