

Fig. 1. Structure of the [Zn(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> complex cation with the atomic numbering scheme.

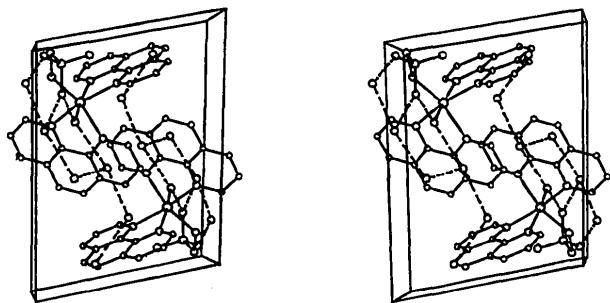


Fig. 2. Stereoview of the crystal packing as viewed down *b*. Broken lines denote hydrogen bonds.

phen(1) ligand makes contacts with one of its centrosymmetric partners on either side of the ring plane, with average spacings of 3.37 and 3.45 Å, thus forming a linear chain of stacking interactions running along the *a* axis. The two phen(2) ligands related by a center of symmetry stack themselves at an average spacing of 3.44 Å to create a discrete self dimer. An extensive hydrogen-bonding system forms involving the sulfate anions and all the water molecules. The coordinated O(*W*1) interacts with two sulfate anions through hydrogen bonds, while the O(*W*2) is hydrogen bonded to a sulfate anion and a hydrate water O(*W*3). The different packing environments may be responsible for non-equivalent Zn—O(water) bonds [2.043 (3) and 2.138 (3) Å].

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## Geometry of the Iminium Moiety. II. Structures of Four Cycloalkylidene Derivatives of a Dihydropyrazolium Salt

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**Abstract.** Compound (I; PENT), bis(1-cyclopentylidene-4,5-dihydro-3,5,5-trimethylpyrazolium) hexachlorostannate, [C<sub>11</sub>H<sub>19</sub>N<sub>2</sub>]<sub>2</sub>[SnCl<sub>6</sub>], *M<sub>r</sub>* = 690.0, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 13.363 (1), *b* = 11.857 (1), *c* = 9.572 (1) Å, β = 93.15 (2)°, *V* = 1514.3 (2) Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 1.50 (1), *D<sub>x</sub>* = 1.513 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 12.8 cm<sup>-1</sup>, *F*(000) = 700, *T* = 294 K, *R* = 0.026 for 1382 observed

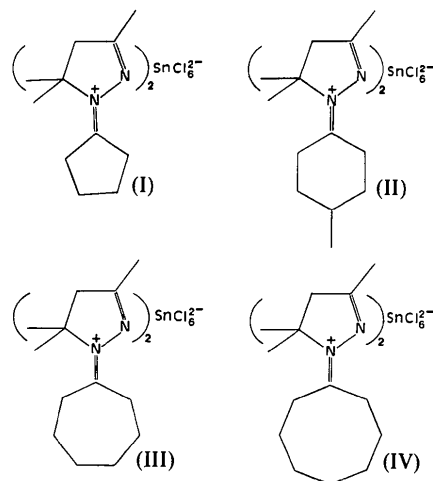
reflections. Compound (II; MHEX), bis[4,5-dihydro-3,5,5-trimethyl-1-(4-methylcyclohexylidene)pyrazolium] hexachlorostannate, [C<sub>13</sub>H<sub>23</sub>N<sub>2</sub>]<sub>2</sub>[SnCl<sub>6</sub>], *M<sub>r</sub>* = 746.1, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 19.223 (1), *b* = 10.803 (1), *c* = 16.990 (1) Å, β = 106.88 (2)°, *V* = 3376.2 (5) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.47 (1), *D<sub>x</sub>* = 1.468 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 11.52 cm<sup>-1</sup>, *F*(000) = 1528, *T* = 294 K, *R* = 0.035 for 3336 observed reflections. Compound (III; HEPT), bis(1-cycloheptylidene-4,5-dihydro-3,5,5-trimethyl-

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pyrazolium) hexachlorostannate,  $[C_{13}H_{23}N_2]_2[SnCl_6]$ ,  $M_r = 746.1$ , monoclinic,  $P2_1/n$ ,  $a = 13.462$  (1),  $b = 12.938$  (1),  $c = 9.744$  (1) Å,  $\beta = 100.91$  (2)°,  $V = 1666.5$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.48$  (1),  $D_x = 1.487$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 11.67$  cm<sup>-1</sup>,  $F(000) = 764$ ,  $T = 294$  K,  $R = 0.027$  for 2304 observed reflections. Compound (IV; OCTY), bis(1-cyclooctylidene-4,5-dihydro-3,5,5-trimethylpyrazolium) hexachlorostannate,  $[C_{14}H_{25}N_2]_2[SnCl_6]$ ,  $M_r = 774.1$ , monoclinic,  $P2_1/c$ ,  $a = 10.455$  (1),  $b = 12.246$  (1),  $c = 14.010$  (1) Å,  $\beta = 98.22$  (2)°,  $V = 1775.3$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.44$  (1),  $D_x = 1.448$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 10.97$  cm<sup>-1</sup>,  $F(000) = 796$ ,  $T = 294$  K,  $R = 0.035$  for 1717 observed reflections. The four structures are condensation products of a secondary amino function with carbocyclic five-, six-, seven- and eight-membered ring ketones. As in part I of this series, the existence of the ternary iminium ion was confirmed and its near-coplanarity with the mean dihydropyrazolium ring moiety established. Corresponding angles on the two sides of the iminium moiety show pronounced dissimilarities due to steric hindrance between the geminal methyl groups attached to the dihydropyrazolium rings and the neighbouring atoms in the carbocyclic rings.

**Introduction.** In Part I (Nassimbeni, Stephen & van Schalkwyk, 1991) of this series of papers on the geometry of the iminium ion, four crystal structures were reported for compounds containing a 4,5-dihydro-3,5,5-trimethylpyrazolium (=3,5,5-trimethylpyrazolinium) moiety with anions in the form of Cl<sup>-</sup> (I; PYCL) and SnCl<sub>6</sub><sup>2-</sup> (II; PYRA). Condensation of PYRA with acetone yielded (III; PYCS), containing the ternary iminium ion. By adding *m*-chloro- and *p*-hydroxybenzaldehyde to PYRA (Galloway, Nassimbeni & Stephen, 1979) large moieties were attached to the pyrazolinium ring and the crystallographic structures of the products were determined. A preliminary report (van Schalkwyk, Stephen & Hodgson, 1976) on the crystal structures of salts formed with PYRA and the ketones 4-methylcyclohexanone and cyclooctanone has now been completed together with structures formed with the ketones cyclopentanone and cycloheptanone. In this paper the structures of these four cycloalkylidene derivatives are reported, viz. (I; PENT; C<sub>22</sub>H<sub>38</sub>N<sub>4</sub><sup>2+</sup>·SnCl<sub>6</sub><sup>2-</sup>), bis(1-cyclopentylidene-4,5-dihydro-3,5,5-trimethylpyrazolium) hexachlorostannate; (II; MHEX; C<sub>26</sub>H<sub>46</sub>N<sub>4</sub><sup>2+</sup>·SnCl<sub>6</sub><sup>2-</sup>), bis[4,5-dihydro-3,5,5-trimethyl-1-(4-methylcyclohexylidene)pyrazolium] hexachlorostannate; (III; HEPT; C<sub>26</sub>H<sub>46</sub>N<sub>4</sub><sup>2+</sup>·SnCl<sub>6</sub><sup>2-</sup>), bis(1-cycloheptylidene-4,5-dihydro-3,5,5-trimethylpyrazolium) hexachlorostannate and (IV; OCTY; C<sub>28</sub>H<sub>50</sub>N<sub>4</sub><sup>2+</sup>·SnCl<sub>6</sub><sup>2-</sup>), bis(1-cyclooctylidene-4,5-dihydro-3,5,5-trimethylpyrazolium) hexachlorostannate, and are compared with the open-chain analogue PYCS described in Part I.

chlorostannate, and are compared with the open-chain analogue PYCS described in Part I.



**Experimental.** Condensation products of cyclic ketones, viz. cyclopentanone, cycloheptanone, cyclooctanone (Rathbone, Stephen, Schwersenski & Tyler, 1975) and 4-methylcyclohexanone with bis(4,5-dihydro-3,5,5-trimethylpyrazolium) hexachlorostannate (Pugh, 1954) in dry ethanol produced, after varying periods, stable prismatic crystals of compounds (I), (III), (IV) and (II), respectively. Measurements of crystal densities were made by flotation in mixtures of bromobenzene and bromoform, and by the use of a Paar DMA 35 density meter.

Crystals were each mounted on glass fibres for preliminary photographic measurement and standard intensity data collection on a four-circle PW 1100 diffractometer with graphite-monochromated Mo K $\alpha$  radiation. Accurate lattice parameters were obtained by least-squares analysis of 25 reflections measured in the range  $16 < \theta < 17^\circ$ . Intensity data collections were carried out at 294 K for all four crystals, with scans in the  $\omega$ - $2\theta$  mode, variable speeds and a maximum recording time of 30 s. Intensity variation of three standard reflections was monitored in each case and re-centring was carried out every 100 measured reflections. The range scanned was  $3 < \theta < 22^\circ$  and the data were corrected for Lorentz and polarization factors (North, Phillips & Mathews, 1968). No absorption corrections were applied. Additional experimental data and structure-refinement parameters are given in Table 1. The structures were solved by normal heavy-atom and direct methods, and refined by full-matrix least squares (based on  $F$ ) using the *SHELX76* (Sheldrick, 1976) program system. Final refinements were carried out with all non-H atoms treated anisotropically and the H atoms constrained to ride at 1.08 Å from the parent atom, with the methyl H atoms allowed to move as a rigid group. Separate common isotropic

Table 1. *Experimental data and structure-refinement parameters*

	(I)	(II)	(III)	(IV)
Crystal dimensions (mm)	0.10 × 0.10 × 0.15	0.25 × 0.20 × 0.15	0.25 × 0.20 × 0.10	0.12 × 0.15 × 0.20
Range of indices <i>h</i>	-14 → 14	-20 → 19	-14 → 14	-11 → 10
<i>k</i>	0 → 12	0 → 11	0 → 13	0 → 12
<i>l</i>	0 → 10	0 → 17	0 → 10	0 → 14
Standard reflections ( <i>h,k,l</i> )	7,3,2	4,2,3	8,6,1	8,1,1
	2,7,1	10,3,5	2,8,3	4,7,1
	1,3,6	0,7,6	1,2,8	0,7,9
Stability (%)	1.5	2.0	1.3	1.8
Scan width <sup>a</sup> (y)	0.95	0.80	0.80	0.90
Aperture width <sup>b</sup> (x)	1.15	1.20	1.25	1.20
Total No. of reflections	1805	4070	2754	2125
Total No. used in refinement <sup>c</sup>	1382	3336	2304	1717
No. of variables	162	360	180	189
$\Delta\rho$ (min., max.) (e Å <sup>-3</sup> )	-0.25, 0.23	-0.42, 0.65	-0.35, 0.69	-1.14, 0.59
$\Delta/\sigma$ (final)	< 0.05	< 0.06	< 0.03	< 0.09
<i>R</i>	0.026	0.035	0.027	0.035
<i>wR</i>	0.026	0.034	0.027	0.035
<i>S</i>	1.37	1.65	1.14	1.61
Weighting scheme, <i>w</i> <sup>d</sup> (g)	Unit	0.0001	Unit	Unit

Notes: (a) Scan width,  $\Delta\omega = (y + 0.35 \tan\theta)^\circ$ . (b) Aperture width =  $(x + 1.05 \tan\theta)$  mm. (c)  $I > 2\sigma(I)$ . (d)  $w = (\sigma^2 F + gF^2)^{-1}$ .

thermal parameters were used for the methylene and methyl H atoms. Atomic scattering factors for non-H atoms were taken from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965). The final fractional atomic coordinates are listed in Table 2 for (I)–(IV), respectively.\*

**Discussion.** Figs. 1(a) and 1(b), Figs. 2(a) and 2(b), Figs. 3(a) and 3(b) and Figs. 4(a) and 4(b) show perspective views with atomic nomenclature and packing diagrams of molecules (I), (II), (III) and (IV), respectively. Observed bond lengths, selected angles and deviations of relevant atoms from mean planes for the four compounds, as well as for PYCS (Nassimbeni, Stephen & van Schalkwyk, 1991) for comparison, are shown in Table 3.

The endocyclic  $C_{sp^3}-C_{sp^3}$  bond lengths ( $-\text{CH}_2-\text{CH}_2-$ ) in the cycloalkylidene moieties of (I), (II), (III) and (IV) have mean values 1.515 (26), 1.531 (6), 1.533 (13) and 1.522 (16) Å, respectively. The mean value of all the  $C_{sp^3}-C_{sp^2}$  bond lengths ( $-\text{CH}_2-\text{C}=\text{C}-$ ) for these moieties is 1.491 (8) Å, in good agreement with 1.483 (4) Å for PYCS. Comparable mean values of C–C bond lengths from tables (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) are 1.524 (14) Å for substructure  $-\text{CH}_2-\text{CH}_2-$  in general, but 1.543 (18) Å for cyclopentane and 1.535 (16) Å for cyclohexane. For substructure  $-\text{CH}_2-\text{C}=\text{C}-$  the mean is 1.502 (13) Å.

The iminium bond length between the formally positively charged N(1) and the C(9) atoms shows

\* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, torsion angles, H-atom parameters and mean-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54255 (71 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

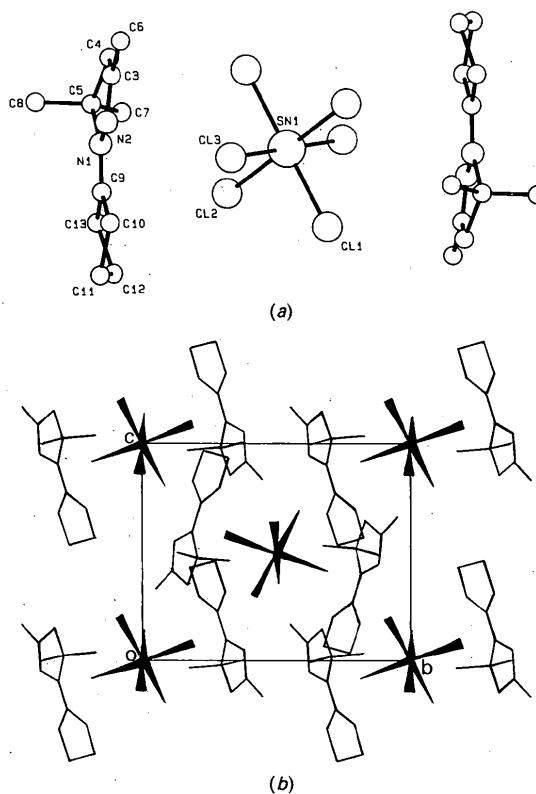


Fig. 1. (a) Perspective view of (I) with atomic nomenclature and (b) packing diagram of (I) viewed along the  $a^*$  axis.

small variation, with a mean of 1.293 (5) Å for the structures (I), (II), (III) and (IV), and 1.294 (5) Å for PYCS. Corresponding bond lengths in the dihydropyrazolium rings are in good agreement within the four structures and with those derived from previously published work (Nassimbeni, Stephen & van Schalkwyk, 1991; Galloway, Nassimbeni & Stephen,

Table 2. Fractional atomic coordinates ( $\times 10^4$ ) and thermal parameters ( $\text{\AA}^2 \times 10^3$ ), with e.s.d.'s in parentheses

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
<b>(I) (PENT)</b>				
Sn(1)	0	0	0	31 (1)
Cl(1)	958 (1)	-849 (1)	1970 (1)	57 (1)
Cl(2)	-1469 (1)	68 (1)	1395 (1)	50 (1)
Cl(3)	444 (1)	1875 (1)	834 (2)	52 (1)
N(1)	-2402 (3)	3125 (4)	966 (5)	45 (2)
N(2)	-1620 (4)	3798 (4)	508 (5)	58 (2)
C(3)	-1751 (5)	3876 (6)	-825 (7)	65 (3)
C(4)	-2621 (5)	3295 (7)	-1471 (6)	70 (3)
C(5)	-3222 (4)	2945 (5)	-207 (6)	53 (2)
C(6)	-1014 (7)	4497 (8)	-1659 (9)	105 (4)
C(7)	-3577 (6)	1729 (6)	-337 (8)	82 (3)
C(8)	-4087 (4)	3759 (5)	37 (6)	55 (2)
C(9)	-2353 (4)	2799 (5)	2266 (6)	46 (2)
C(10)	-1485 (5)	3107 (6)	3231 (6)	67 (3)
C(11)	-1812 (6)	2723 (8)	4660 (7)	84 (3)
C(12)	-2499 (7)	1763 (7)	4334 (8)	89 (4)
C(13)	-3084 (5)	2083 (6)	2972 (7)	67 (3)
<b>(II) (MHEx)</b>				
Sn(1)	2602 (1)	4560 (1)	2815 (0)	37 (1)
Cl(1)	3553 (1)	4122 (1)	4071 (1)	65 (1)
Cl(2)	1654 (1)	5086 (2)	1571 (1)	69 (1)
Cl(3)	2111 (1)	6078 (2)	3565 (1)	77 (1)
Cl(4)	3060 (1)	2964 (2)	2096 (1)	90 (1)
Cl(5)	1823 (1)	2994 (2)	3164 (1)	83 (1)
Cl(6)	3386 (1)	6093 (2)	2484 (1)	101 (1)
N(1)	899 (2)	-33 (4)	1134 (2)	43 (2)
N(2)	646 (2)	1107 (4)	715 (3)	54 (2)
N(16)	4046 (2)	9362 (4)	5327 (2)	38 (2)
N(17)	4521 (2)	10331 (4)	5716 (2)	46 (2)
C(3)	1139 (3)	1487 (6)	402 (3)	56 (3)
C(4)	1791 (3)	682 (6)	552 (4)	67 (3)
C(5)	1628 (3)	-428 (6)	1012 (3)	52 (2)
C(6)	1050 (4)	2678 (6)	-42 (4)	81 (3)
C(7)	2196 (3)	-559 (7)	1844 (4)	80 (3)
C(8)	1518 (3)	-1609 (6)	491 (4)	71 (3)
C(9)	513 (3)	-558 (5)	1549 (3)	47 (2)
C(10)	-141 (3)	44 (5)	1662 (3)	57 (2)
C(11)	-23 (3)	256 (5)	2586 (4)	56 (2)
C(12)	181 (3)	-923 (5)	3091 (3)	49 (2)
C(13)	838 (3)	-1525 (5)	2916 (3)	55 (3)
C(14)	715 (3)	-1745 (5)	1993 (3)	55 (2)
C(15)	331 (3)	-688 (6)	4011 (4)	69 (3)
C(18)	4159 (3)	11338 (5)	5602 (3)	48 (2)
C(19)	3388 (3)	11220 (5)	5103 (4)	68 (3)
C(20)	3301 (3)	9874 (5)	4815 (3)	47 (2)
C(21)	4497 (4)	12510 (5)	5970 (3)	65 (3)
C(22)	3255 (3)	9768 (7)	3910 (3)	70 (3)
C(23)	2675 (3)	9251 (6)	5026 (4)	62 (3)
C(24)	4281 (3)	8241 (5)	5436 (3)	42 (2)
C(25)	5006 (2)	7939 (5)	6013 (3)	46 (2)
C(26)	4891 (3)	7164 (5)	6717 (3)	51 (2)
C(27)	4430 (3)	6005 (5)	6414 (3)	51 (2)
C(28)	3711 (3)	6363 (5)	5778 (3)	49 (2)
C(29)	3838 (3)	7127 (5)	5074 (3)	48 (2)
C(30)	4295 (3)	5323 (6)	7141 (3)	67 (3)
<b>(III) (HEPT)</b>				
Sn(1)	0	0	0	29 (1)
Cl(1)	134 (1)	1700 (1)	1080 (1)	49 (1)
Cl(2)	1639 (1)	-465 (1)	1400 (1)	46 (1)
Cl(3)	864 (1)	657 (1)	-1803 (1)	48 (1)
N(1)	1773 (2)	-2841 (2)	-3855 (3)	34 (1)
N(2)	1285 (2)	-3757 (2)	-4466 (3)	38 (1)
C(3)	1259 (3)	-3708 (3)	-5783 (4)	41 (1)
C(4)	1750 (4)	-2788 (3)	-6269 (4)	57 (2)
C(5)	1931 (3)	-2066 (3)	-4992 (4)	40 (1)
C(6)	779 (3)	-4542 (3)	-6740 (4)	51 (2)
C(7)	1115 (3)	-1244 (3)	-5102 (4)	50 (1)

Table 2 (cont.)

	x	y	z	$U_{eq}$
C(8)	3005 (3)	-1635 (3)	-4748 (5)	52 (2)
C(9)	1946 (3)	-2754 (3)	-2509 (4)	35 (1)
C(10)	1709 (3)	-3659 (3)	-1668 (4)	47 (1)
C(11)	2066 (3)	-3585 (3)	-77 (4)	53 (2)
C(12)	3211 (3)	-3483 (3)	410 (4)	57 (2)
C(13)	3603 (3)	-2380 (3)	414 (4)	52 (2)
C(14)	3483 (3)	-1882 (3)	-1026 (4)	45 (1)
C(15)	2365 (3)	-1785 (3)	-1793 (3)	36 (1)
<b>(IV) (OCTY)</b>				
Sn(1)	0	0	0	39 (1)
Cl(1)	726 (1)	732 (1)	1609 (1)	54 (1)
Cl(2)	-165 (2)	1852 (1)	-628 (1)	57 (1)
Cl(3)	2243 (1)	-54 (2)	-307 (1)	55 (1)
N(1)	4707 (4)	3349 (4)	2074 (3)	42 (2)
N(2)	5600 (5)	2974 (4)	1450 (4)	49 (2)
C(3)	6733 (6)	3095 (5)	1914 (5)	53 (2)
C(4)	6827 (6)	3582 (7)	2882 (5)	68 (3)
C(5)	5417 (6)	3820 (5)	3019 (4)	49 (2)
C(6)	7920 (6)	2777 (7)	1488 (6)	72 (3)
C(7)	5176 (7)	5034 (6)	3058 (5)	73 (3)
C(8)	5070 (7)	3220 (7)	3895 (5)	71 (3)
C(9)	3491 (5)	3244 (5)	1772 (4)	42 (2)
C(10)	3048 (6)	2782 (5)	785 (4)	53 (2)
C(11)	3096 (7)	3604 (6)	-29 (5)	69 (3)
C(12)	2167 (9)	4571 (7)	-69 (6)	92 (4)
C(13)	2452 (10)	5344 (6)	781 (6)	102 (4)
C(14)	1533 (8)	5231 (8)	1544 (6)	96 (4)
C(15)	1289 (6)	4100 (8)	1876 (6)	80 (3)
C(16)	2482 (6)	3521 (6)	2391 (5)	60 (3)

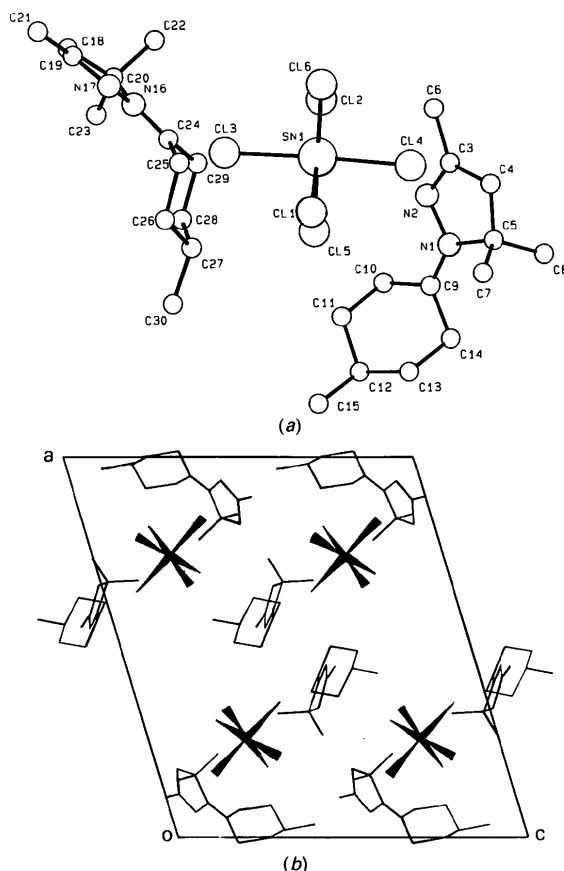


Fig. 2. (a) Perspective view of (II) with atomic nomenclature and (b) packing diagram of (II) viewed along [010].

1979). The mean value of the N(1)—N(2) bond length of 1.426 (15) Å is, like that of PYCS [1.414 (4) Å], significantly shorter than the mean for PYCL and PYRA (Part I) *viz.* 1.459 (4) Å, confirming, as for PYCS (Part I), the presence of a conjugate system C(9)=N(1)—N(2)=C(3) in (I), (II), (III) and (IV). The length of the double bond N(2)=C(3) is practically constant with a mean value of 1.279 (3) Å, which is close to the values for PYCL and PYRA (Part I).

The sum of the bond angles about both N(1)<sup>+</sup> and C(9) is remarkably constant with a mean value of 360.0 (1)°. Furthermore, the torsion angles N(2)—N(1)—C(9)—C(10) and C(5)—N(1)—C(9)—C(13) for (I) and the corresponding angles for (II), (III),

(IV) and PYCS range from 1.4 (8) to 5.7 (7)° and 0.2 (6) to 5.0 (9)°, respectively (Table 3), demonstrating the extent of coplanarity of the iminium moiety with the mean dihydropyrazolium ring. The mean angle between the mean planes of these moieties is 5.9 (18)°.

The angle C(5)—N(1)—C(9) in (I), (II), (III), (IV) and PYCS, which brings C(9) into close proximity with the geminal groups C(7) and C(8), is always greater than its adjacent angle N(2)—N(1)—C(9) on the other side of the iminium double bond. Similarly, but to a lesser extent, angle N(1)—C(9)—C(13) in (I) and the corresponding angles in (II), (III) and (IV) are always greater than the adjacent angle N(1)—C(9)—C(10), although this is not the case for PYCS. This is a result of the steric interaction between atom

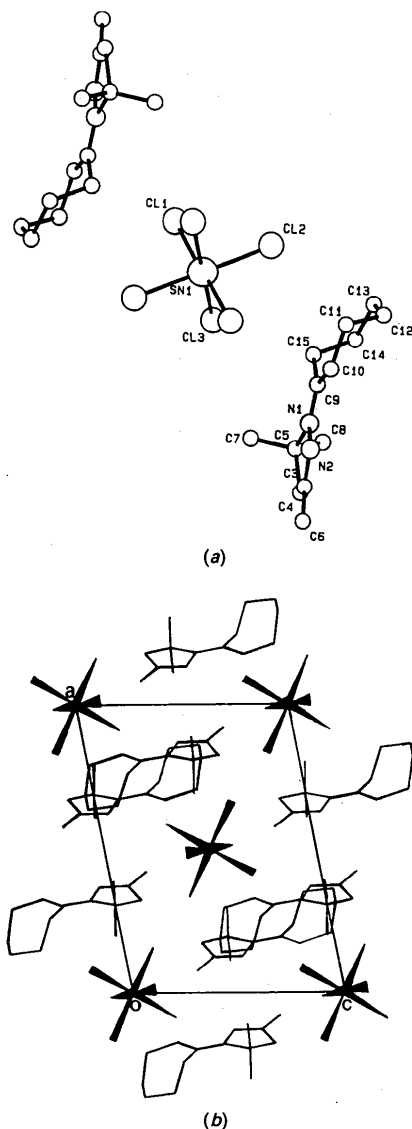


Fig. 3. (a) Perspective view of (III) with atomic nomenclature and (b) packing diagram of (III) viewed along [010].

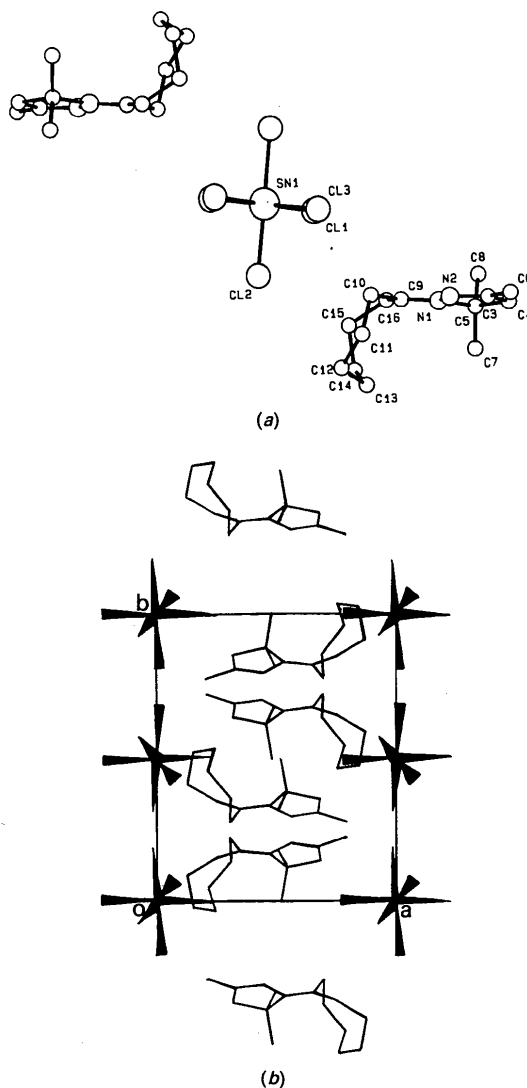


Fig. 4. (a) Perspective view of (IV) with atomic nomenclature and (b) packing diagram of (IV) viewed along the  $c^*$  axis.

Table 3. Bond distances (Å), selected bond angles (°), torsion angles (°) and interplanar angles (°) of relevant atoms from the dihydropyrazolium and iminium mean planes (planes 1 and 2 respectively) for structures (I), (II), (III) and (IV), as well as for PYCS (from Part I), with *e.s.d.*'s in parentheses

Bonds	PYCS	(I)	(II <sup>R</sup> )*	(II <sup>S</sup> )*	(III)	(IV)
N(1)—N(2)	1.414 (4)	1.404 (7)	1.435 (6)	1.420 (6)	1.429 (4)	1.442 (7)
N(2)—C(3)	1.274 (5)	1.282 (8)	1.282 (8)	1.276 (7)	1.279 (5)	1.276 (8)
C(3)—C(4)	1.474 (5)	1.459 (10)	1.486 (8)	1.484 (7)	1.482 (6)	1.471 (10)
C(4)—C(5)	1.531 (5)	1.545 (9)	1.513 (9)	1.528 (8)	1.538 (5)	1.541 (9)
C(5)—N(1)	1.529 (5)	1.540 (7)	1.535 (7)	1.545 (6)	1.539 (5)	1.535 (7)
C(3)—C(6)	1.489 (5)	1.495 (12)	1.476 (9)	1.478 (8)	1.491 (5)	1.504 (10)
C(5)—C(7)	1.514 (5)	1.520 (9)	1.521 (7)	1.518 (8)	1.518 (6)	1.510 (10)
C(5)—C(8)	1.527 (5)	1.534 (8)	1.531 (9)	1.513 (9)	1.526 (6)	1.518 (10)
N(1)—C(9)	1.294 (5)	1.301 (8)	1.294 (7)	1.287 (7)	1.292 (5)	1.288 (7)
C(9)—C(10)	1.485 (5)	1.488 (8)	1.477 (8)	1.489 (6)	1.498 (6)	1.503 (8)
C(10)—C(11)		1.528 (10)	1.537 (9)	1.528 (8)	1.537 (5)	1.528 (9)
C(11)—C(12)		1.485 (12)	1.522 (8)	1.534 (8)	1.530 (6)	1.528 (12)
C(12)—C(13)		1.531 (10)	1.525 (9)	1.536 (7)	1.521 (6)	1.517 (12)
C(13)—C(14)			1.535 (7)	1.530 (8)	1.525 (6)	1.543 (14)
C(14)—C(15)					1.554 (4)	1.495 (14)
C(15)—C(16)						1.523 (10)
C(9)—C(X)†	1.480 (5)	1.485 (9)	1.481 (7)	1.499 (7)	1.493 (5)	1.497 (9)
C(12)—C(15)			1.526 (8)	1.524 (8)		
<b>Endocyclic angles</b>						
N(2)—N(1)—C(5)	110.9 (3)	111.3 (4)	111.3 (4)	111.3 (4)	110.8 (3)	111.6 (4)
N(2)—N(1)—C(9)	118.5 (3)	117.9 (4)	118.8 (4)	118.4 (4)	118.4 (3)	117.6 (5)
C(5)—N(1)—C(9)	130.5 (3)	130.7 (5)	130.0 (4)	130.3 (4)	130.6 (3)	130.9 (5)
N(1)—N(2)—C(3)	107.6 (3)	106.8 (5)	107.2 (4)	108.0 (4)	107.5 (3)	106.7 (5)
N(2)—C(3)—C(4)	115.5 (3)	116.7 (6)	115.5 (5)	115.1 (5)	115.6 (3)	116.9 (6)
C(3)—C(4)—C(5)	103.7 (3)	103.4 (5)	105.2 (5)	105.2 (5)	104.0 (3)	104.6 (5)
N(1)—C(5)—C(4)	99.6 (3)	98.9 (4)	100.6 (5)	99.4 (4)	99.5 (3)	100.1 (5)
N(1)—C(9)—C(10)	122.3 (3)	121.2 (5)	121.5 (5)	121.6 (5)	118.1 (3)	120.0 (5)
N(1)—C(9)—C(X)	120.8 (3)	127.3 (5)	123.4 (5)	124.2 (5)	121.8 (3)	122.1 (5)
C(10)—C(9)—C(X)	116.9 (3)	111.6 (5)	115.0 (5)	113.9 (5)	120.1 (3)	117.9 (5)
C(9)—C(10)—C(11)		103.4 (5)	108.6 (5)	108.4 (4)	116.5 (3)	113.7 (5)
C(10)—C(11)—C(12)		104.1 (6)	112.9 (5)	112.7 (4)	115.0 (3)	116.7 (6)
C(11)—C(12)—C(13)		105.7 (6)	109.8 (5)	110.2 (4)	114.2 (3)	113.7 (7)
C(12)—C(13)—C(14)			112.0 (5)	111.7 (5)	114.7 (3)	114.7 (7)
C(13)—C(14)—C(15)					113.7 (3)	116.6 (7)
C(14)—C(15)—C(16)						114.5 (7)
C(9)—C(13)—C(12)		102.2 (6)				
C(9)—C(14)—C(13)			109.0 (4)	108.2 (4)		
C(9)—C(15)—C(14)					113.8 (3)	
C(9)—C(16)—C(15)						115.3 (6)
<b>Torsion angles</b>						
N(2)—N(1)—C(9)—C(10)	-177.3 (3)	-1.4 (8)	-5.7 (7)	5.5 (7)	5.4 (5)	-2.2 (8)
C(5)—N(1)—C(9)—C(X)	175.6 (3)	3.7 (9)	-2.0 (9)	-1.5 (9)	0.2 (6)	-5.0 (9)
C(10)—C(9)—C(13)—C(12)		-11.8 (7)				
C(10)—C(9)—C(14)—C(13)			-58.0 (6)	60.4 (6)		
C(10)—C(9)—C(15)—C(14)					72.3 (5)	
C(10)—C(9)—C(16)—C(15)						-43.0 (8)
C(X)—C(9)—C(10)—C(11)		-10.2 (7)	57.1 (6)	-59.5 (6)	-8.9 (5)	104.1 (6)
C(9)—C(10)—C(11)—C(12)		28.8 (7)	-54.3 (6)	55.0 (6)	-61.1 (5)	-66.5 (8)
C(10)—C(11)—C(12)—C(13)		-37.1 (8)	54.0 (6)	-53.4 (6)	85.1 (4)	66.0 (9)
C(11)—C(12)—C(13)—C(9)		30.1 (7)				
C(11)—C(12)—C(13)—C(14)			-54.1 (6)	53.9 (6)	-65.4 (4)	-103.5 (9)
C(12)—C(13)—C(14)—C(9)			55.1 (6)	-56.2 (6)		
C(12)—C(13)—C(14)—C(15)					61.5 (4)	47.9 (10)
C(13)—C(14)—C(15)—C(9)					-81.7 (4)	
C(13)—C(14)—C(15)—C(16)						63.4 (10)
C(14)—C(15)—C(16)—C(9)						-67.4 (9)
<b>Angles between planes (1) and (2)</b>						
	5.8 (1)	8.3 (2)	4.9 (2)	6.9 (2)	5.7 (1)	3.5 (2)

\* The structure (II<sup>R</sup>) refers to the organic moiety with atoms numbered from 1 to 16 and structure (II<sup>S</sup>) refers to the organic moiety with atoms numbered from 16 to 30, in the same order as in (II<sup>R</sup>).

† X is 11 in PYCS, 13 in (I), 14 in (II<sup>R</sup>) and (II<sup>S</sup>), 15 in (III) and 16 in (IV).

C(13) of (I) [or C(14), C(15) and C(16) of (II), (III) and (IV), respectively] and the two geminal methyl groups attached to atom C(5) which have non-

bonded contact distances varying from 3.164 (6) to 3.637 (9) Å [van der Waals distance for C...C is 3.5 Å (Bondi, 1964)].

Table 4. Conformations of puckered cycloalkylidene rings

(a) Asymmetry parameters								
Molecule	Ring				Asymmetry parameters (°)			
(I)	C(9)—C(10)—C(11)—C(12)—C(13)				$\Delta C_2(11-12) = 1.5$			
(IIR)	C(9)—C(10)—C(11)—C(12)—C(13)—C(14)				$\Delta C_1(9) = 0.7; \Delta C_1(10) = 2.9;$ $\Delta C_1(11) = 2.4; \Delta C_2(9-10) = 2.7;$ $\Delta C_2(10-11) = 3.5; \Delta C_2(11-12) = 1.4$			
(IIS)	C(24)—C(25)—C(26)—C(27)—C(28)—C(29)				$\Delta C_1(24) = 0.9; \Delta C_1(25) = 6.1;$ $\Delta C_1(26) = 4.1; \Delta C_2(24-25) = 6.1;$ $\Delta C_2(25-26) = 6.3; \Delta C_2(26-27) = 2.6$			
(III)	C(9)—C(10)—C(11)—C(12)—C(13)—C(14)—C(15)				$\Delta C_1(13) = 7.1$			
(IV)	C(9)—C(10)—C(11)—C(12)—C(13)—C(14)—C(15)—C(16)				$\Delta C_1(11) = 3.3$			

(b) Puckering parameters								
	$Q_2$ (Å)	$Q_3$ (Å)	$Q_4$ (Å)	$\varphi_2$ (°)	$\varphi_3$ (°)	$QT^*$ (Å)	$\theta_2$ (°)	$\theta_3$ (°)
(I)	0.349 (8)			91 (1)				
(IIR)	0.009 (6)	-0.561 (6)		136 (34)		0.561 (6)	179.1 (6)	
(IIS)	0.031 (6)	0.575 (6)		339 (9)		0.576 (6)	3.1 (6)	
(III)	0.448 (4)	0.666 (4)		315 (1)	285.1 (4)	0.803 (4)	33.9 (3)	
(IV)	1.030 (8)	0.609 (8)	-0.336 (8)	183 (1)	273.0 (7)	1.243 (7)	59.4 (4)	118.9 (7)

(c) Conformational analysis of rings using computer program CONFOR			
	Assignment		Classic form
(I)	$a\varphi(E) + b\varphi(T)$ 8(6) + 92(5)		Twist
(IIR)	$a\varphi(B) + b\varphi(T) + c(\pm 1)$ 1(8) + 1(10) + 98(-1)		Chair
(IIS)	$a\varphi(B) + b\varphi(T) + c(\pm 1)$ 2(24) + 4(22) + 95(+1)		Chair
(III)	$a\varphi(B) + b\varphi(TB) + c\varphi(C) + d\varphi(TC)$ 19(24) + 21(25) + 49(22) + 10(23)		Mixed
(IV)	$a\varphi(BB) + b\varphi(BB) + c\varphi(TC) + d\varphi(TC) + e(\pm 1)$ 51(16) + 2(24) + 28(24) + 2(28) + 17(-1)		Boat-chair

\*  $QT$  = total puckering amplitude.

Intramolecular distances of 2.758 (8) Å for C(10)⋯N(2) and 2.744 (7) Å for C(25)⋯N(17) in (II) and even 3.192 (8) Å for C(11)⋯N(2) in (IV) are shorter than the van der Waals distance of 3.3 Å (Bondi, 1964). Possible H bonds are, however, ruled out since the bond angles vary from 106 to 110°.

The two independent organic halves of molecule (II) [Fig. 2(a)] are stereoisomers of opposite configuration. According to the Cahn and Ingold specification the half with lower numbering has configuration *R* and the other half has configuration *S* at chiral centres C(12) and C(27), respectively. Hence we refer to the two halves as (IIR) and (IIS) (see footnote in Table 3).

The molecular conformations of the cycloalkylidene rings are described in three different ways, (a), (b) and (c), in Table 4. In Table 4(a) the asymmetry parameters calculated from torsion angles (Duax & Norton, 1975) are given. In Table 4(b) the total degree of ring pucker is described in terms of polar coordinates  $Q$  and angular coordinates  $\varphi$  and  $\theta$  using deviations of ring atoms from the mean planes of the rings (Cremer & Pople, 1975; Boeyens, 1978; Nardelli, 1983).

Linear combinations of the normal atomic displacements, or modes, define the conformation of a

general puckered ring. In Table 4(c) the results obtained from program CONFOR (Evans & Boeyens, 1989) express each ring conformation as a linear combination of the standard primitive forms of puckered rings, such as envelope (*E*), twist (*T*), boat (*B*), chair (*C*), crown ( $\pm 1$ ) or mixtures such as twist-boat (*TB*), twist-chair (*TC*) and boat-boat (*BB*). The normalized numerical coefficients  $a$ ,  $b$ ,  $c$ , etc. indicate the relative contributions of each primitive form and appear in order of increasing mode  $m$  in the linear sum.  $\varphi_m$  are the phase angles of the relevant primitive form and are expressed as multiples of  $\pi/2N$ , for an  $N$ -membered polygon. The nomenclature is reported in order of increasing mode of displacement  $m$  at different values of phase angle  $\varphi$ . Where coefficients of a ring differ by less than 10% from a primitive form  $X$ , CONFOR reports the ring as an  $X$  form. If the difference is between 10 and 20% the ring is reported to be very similar to an  $X$  form. The cycloalkylidene rings in (IIR) and (IV) have been calculated as chair and boat-chair forms, respectively, and the rings in (I) and (IIS) as very similar to a twist and a chair form, respectively. Since the calculation for the ring in (III) indicates the difference of coefficients to be more than 20%, it can best be described as having a mixed form.

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

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**Abstract.** [PtCl<sub>2</sub>(C<sub>4</sub>H<sub>7</sub>N<sub>3</sub>O)<sub>2</sub>·2H<sub>2</sub>O, *M<sub>r</sub>* = 528·27, λ(Mo Kα) = 0·71073 Å, *T* = 291 (1) K. Crystal *M*: monoclinic, *P*2<sub>1</sub>/*n*, *a* = 6·584 (1), *b* = 7·538 (1), *c* = 15·511 (2) Å, β = 93·92 (1)°, *V* = 768·0 Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 2·284 g cm<sup>-3</sup>, μ = 96·039 cm<sup>-1</sup>, *F*(000) = 504, *R* = 0·013 for 2014 independent reflections with *I* > 3σ out of 3580 total unique data and 13 661 measured reflections. Crystal *T*: triclinic, *P*1̄, *a* = 7·123 (2), *b* = 7·370 (2), *c* = 8·140 (1) Å, α = 96·84 (1), β = 106·33 (1), γ = 104·25 (1)°, *V* = 389·2 Å<sup>3</sup>, *Z* = 1, *D<sub>x</sub>* = 2·253 g cm<sup>-3</sup>, μ = 94·743 cm<sup>-1</sup>, *F*(000) = 252, *R* = 0·025 for 1046 independent reflections with *I* > 3σ 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)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>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<sub>2</sub>PtCl<sub>4</sub> 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)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O in air and N<sub>2</sub> 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)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>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.