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Structural studies of unusually disordered diorganoplatinum(IV) complexes containing the cations $[PtIR_2(L\text{-}N,N',N'')]^+$, where the ligands L are facially coordinated

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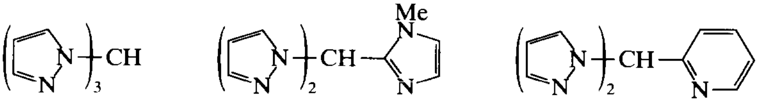
Abstract

The reaction of $[PtPh_2(SEt_2)]_2$ with tris(pyrazol-1-yl)methane $[(pz)_3CH]$ and iodine in dichloromethane gives the platinum(IV) complex $[PtIPh_2\{(pz)_3CH\text{-}N,N',N''\}]_2[I][I_3]$ (**1**). Complex **1**, and related complexes of the facially coordinated tridentate ligands $(pz)_2(mim)CH$ (mim = *N*-methylimidazol-2-yl) and $(pz)_2(py)CH$ (py = pyridin-2-yl) have octahedral geometry for platinum(IV), "$PtIC_2N_3$", and exhibit unusual disorder in the solid state. Complex **1** has two cations in the asymmetric unit, with one cation well ordered and the other showing disorder between the coordinated iodide and one phenyl group position. The complexes $[PtIMe_2\{(pz)_2(mim)CH\text{-}N,N',N''\}]I$ (**2a**) and $[PtIMe_2\{(pz)_2(py)CH\text{-}N,N',N''\}]I$ (**2b**) have coordinated iodide disordered with both methyl groups; in **2a** iodine is predominantly *trans* to the pz groups, and in **2b** iodine is predominantly *trans* to the py group.

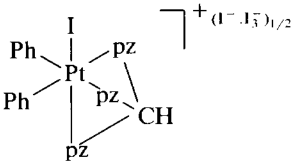
Introduction

The nitrogen donor polydentate ligands $(pz)_3CH$, $(pz)_2(mim)CH$, and $(pz)_2(py)CH$ form the platinum(IV) complexes $PtI_2Me_2(L\text{-}N,N')$, in which the ligands are *trans* to the methyl groups and act as bidentates with one uncoordinated ring [1].

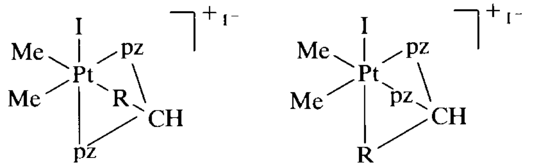


$(pz)_3CH$ $\qquad$ $(pz)_2(mim)CH$ $\qquad$ $(pz)_2(py)CH$

When heated in the solid state or in solution, the neutral complexes form cations, $[PtIMe_2(L\text{-}N,N',N'')]^+$, with displacement of one iodo group and coordination of the ligands as facial tridentates. ^{1}H NMR spectra indicate that a mixture of two isomers occurs for the cations containing unsymmetrical ligands, involving pz, mim, or py groups *trans* to methyl or iodo groups [1] (**2a**, **2b**). Crystals of $[PtIMe_2\{(pz)_2(mim)CH\text{-}N,N',N''\}]I$ (**2a**) and $[PtIMe_2\{(pz)_2(py)CH\text{-}N,N',N''\}]I$ (**2b**) have now been obtained, but for $(pz)_3CH$ as the ligand, crystals of suitable quality for X-ray diffraction could not be isolated. However, a highly crystalline complex (**1**) containing $(pz)_3CH$ has been obtained from the reaction of $[PtPh_2(SEt_2)]_2$ and $(pz)_3CH$ with the oxidant iodine, permitting structural studies of cationic complexes for the three tripod ligands.



(**1**)



(**2a**) R = mim

(**2b**) R = py

Experimental

The ligands [2], $[PtIMe_2\{(pz)_2(mim)CH\text{-}N,N',N''\}]I$ (**2a**) and $[PtIMe_2\{(pz)_2(py)\text{-}CH\text{-}N,N',N''\}]I$ (**2b**) [1], and $[PtPh_2(SEt_2)]_2$ [3] were prepared as described. ^{1}H NMR spectra were recorded with a Bruker AM 300 spectrometer, and chemical shifts are given in ppm relative to Me_4Si. Molar conductances were measured with a Philips PW 9504/00 conductivity meter using a Griffin and George conductivity cell for $\sim 10^{-3}$ *M* solutions in acetone at 25°C.

Synthesis of $[PtIPh_2\{(pz)_3CH\text{-}N,N',N''\}]_2[I][I_3]$ *(1)*

Tris(pyrazol-1-yl)methane (0.03 mmol) and $[PtPh_2(SEt_2)]_2$ (0.05 mmol) were dissolved in dichloromethane (10 mL) and a solution of iodine (0.08 g, 0.32 mmol) in acetone (2 mL) was added dropwise with stirring until the colour of iodine persisted. The solution was taken to dryness by rotary evaporation and the excess iodine extracted from the residue with warm hexane (3 × 20 mL). The residue was dissolved in dichloromethane (10 mL), and hexane added until cloudiness developed. The product was obtained as black crystals in 79% yield. Anal. Found: C, 28.5; H, 2.3; N, 8.5. $C_{22}H_{20}N_6I_3Pt$ calc.: C, 28.0; H, 2.1; N, 8.9%. ^{1}H NMR ($CDCl_3$): δ 11.7 (1H, s, CH), 9.29 (1H, d, H(5), $J_{45} = 2.5$ Hz), 9.07 (2H, d, H(5), $J_{45} = 2.7$ Hz), 8.17 (2H, d, H(3), $J_{34} = 2.4$ Hz), 7.77 (1H, d, H(3), $J_{34} = 2.4$ Hz), 7.0–7.2 (10H, m, Ph), 6.65 (3H, m, H(4)) ppm. Molar conductance 209 Ω^{-1} cm^2 mol^{-1}.

Crystallography

For each complex a unique data set was measured at 295 K using an Enraf–Nonius CAD-4 diffractometer operating in conventional 2θ–θ scan mode with monochromatic Mo-K_α radiation ($\lambda = 0.71073$ Å), yielding N independent reflections, N_o, with $I > 3\sigma(I)$ considered observed and used in the full matrix least-squares refinement after analytical absorption correction, and solution of the

Table 1

Crystal data and refinement parameters for $[PtIPh_2\{(pz)_3CH\text{-}N,N',N''\}]_2[I][I_3]$ (**1**), $[PtIMe_2\{(pz)_2\text{-}(mim)CH\text{-}N,N',N''\}]I$ (**2a**), and $[PtIMe_2\{(pz)_2(py)CH\text{-}N,N',N''\}]I$ (**2b**)

	1 [a]	**2a**	**2b**
Formula	$C_{22}H_{20}N_6I_3Pt$	$C_{13}H_{17}N_6I_2Pt$	$C_{14}H_{17}N_5I_2Pt$
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$
a (Å)	18.614(4)	12.110(14)	21.520(3)
b (Å)	13.114(9)	9.809(6)	9.284(11)
c (Å)	11.794(11)	19.034(14)	19.797(5)
β (deg)	86.69(7)	120.52(8)	105.12(2)
V (Å^3)	2812	1948	3818
Z	4	4	8
Mol. wt.	944.3	706.2	704.2
$D_{calc.}$ (g cm^{-3})	2.23	2.41	2.45
Crystal size (mm)	$0.06 \times 0.13 \times 0.55$	$0.20 \times 0.10 \times 0.08$	$0.13 \times 0.14 \times 0.23$
μ (cm^{-1})	78.9	99.0	101
$F(000)$	1724	1284	2560
$2\Theta_{max}$ (deg)	50	50	47
$A^*_{min,max}$	1.59, 2.88	1.35, 1.54	2.81, 6.12
N	9512	3442	2826
N_o	5083	1398	1107
R	0.087	0.100	0.079
R_w	0.089	0.101	0.075

[a] $\alpha = 78.14(7)°$, $\gamma = 88.24(4)°$.

structures by vector methods. Residuals R and R_w are quoted on $|F|$ at convergence; statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were employed. Neutral-atom complex scattering factors were used [4]; computation used the XTAL 3.0 program system implemented by S.R. Hall [5]. Crystal data, coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms, and geometries of the cations are given in Tables 1–6, and views of the cations and unit cell contents are shown in Figs. 1 and 2. *

Abnormal features and variations in procedure

$[PtIPh_2\{(pz)_3CH$-N,N′,N″$\}]_2[I][I_3]$ (1). One of the two independent cations in the asymmetric unit is disordered, involving the coordinated iodide and one of the phenyl groups. Disordered phenyl components were refined as rigid bodies, with total site occupancy integrating to unity, and the iodine population totalling unity also after the initial refinement suggested these values to be reasonable. In this context, not all thermal parameters of the remaining atoms refined meaningfully with the anisotropic form, and thus N(11c), C(11a′) and C(25c) were refined in the isotropic mode. In view of the disorder, the possible presence of a superlattice or wrong space group assignment were explored and not found, a result which seems reasonable in the light of the normal behaviour of the other components of the structure.

* Tables of thermal parameters and calculated hydrogen atom positions, details of ligand geometry, and a list of structure factors are available from the authors.

Table 2

Non-hydrogen atom coordinates and isotropic displacement parameters for $[PtIPh_2\{(pz)_3CH\text{-}N,N',N''\}]_2[I][I_3]$ (1)

Atom	x	y	z	U (Å^2)
Ordered cation				
Pt(1)	0.72412(7)	0.73576(9)	−0.0790(1)	0.0443(4)
I(1)	0.8229(1)	0.8630(2)	−0.0505(2)	0.070(1)
N(11a)	0.646(1)	0.865(2)	−0.116(2)	0.06(1)
N(12a)	0.609(1)	0.867(2)	−0.209(2)	0.05(1)
C(13a)	0.566(2)	0.956(2)	−0.224(3)	0.07(1)
C(14a)	0.576(2)	1.008(2)	−0.137(3)	0.09(2)
C(15a)	0.627(2)	0.950(2)	−0.080(3)	0.07(1)
N(11b)	0.745(1)	0.769(2)	−0.264(2)	0.051(9)
N(12b)	0.687(1)	0.788(2)	−0.330(2)	0.045(9)
C(13b)	0.708(2)	0.806(2)	−0.442(3)	0.06(1)
C(14b)	0.781(2)	0.801(3)	−0.453(3)	0.08(2)
C(15b)	0.803(2)	0.776(3)	−0.335(3)	0.08(2)
N(11c) [a]	0.644(1)	0.648(1)	−0.112(2)	0.05(1)
N(12c)	0.602(1)	0.689(2)	−0.206(2)	0.048(9)
C(13c)	0.547(2)	0.623(2)	−0.219(3)	0.07(1)
C(14c)	0.556(2)	0.537(2)	−0.126(3)	0.08(1)
C(15c)	0.614(2)	0.557(2)	−0.070(2)	0.05(1)
C(1)	0.617(2)	0.789(2)	−0.278(2)	0.05(1)
C(11a′) [a]	0.795(2)	0.609(2)	−0.069(3)	0.058(9)
C(12a′)	0.785(2)	0.543(2)	−0.141(3)	0.06(1)
C(13a′)	0.835(2)	0.457(2)	−0.132(3)	0.08(2)
C(14a′)	0.891(2)	0.439(2)	−0.062(3)	0.08(2)
C(15a′)	0.899(2)	0.503(3)	0.007(3)	0.09(2)
C(16a′)	0.852(2)	0.596(2)	0.005(3)	0.06(1)
C(11b′)	0.688(2)	0.708(2)	0.092(2)	0.05(1)
C(12b′)	0.618(2)	0.702(2)	0.118(3)	0.06(1)
C(13b′)	0.589(2)	0.678(2)	0.236(3)	0.07(1)
C(14b′)	0.637(2)	0.654(2)	0.323(3)	0.08(2)
C(15b′)	0.711(2)	0.659(3)	0.300(2)	0.09(2)
C(16b′)	0.735(2)	0.691(2)	0.182(3)	0.07(1)
Disordered cation				
Pt(2)	0.84633(8)	1.1226(1)	0.2896(1)	0.0795(7)
I(2) [b]	0.9360(2)	0.9841(3)	0.3405(4)	0.086(2)
I(2″) [c]	0.9602(4)	1.1934(5)	0.3233(7)	0.108(4)
N(21a)	0.755(1)	1.035(2)	0.282(2)	0.050(9)
N(22a)	0.692(1)	1.064(2)	0.330(2)	0.044(9)
C(23a)	0.639(2)	1.003(3)	0.318(2)	0.07(1)
C(24a)	0.666(2)	0.935(2)	0.253(3)	0.07(2)
C(25a)	0.736(2)	0.956(2)	0.235(3)	0.06(1)
N(21b)	0.806(1)	1.104(2)	0.470(2)	0.07(1)
N(22b)	0.738(1)	1.121(2)	0.491(2)	0.06(1)
C(23b)	0.719(2)	1.106(2)	0.606(3)	0.07(1)
C(24b)	0.781(2)	1.075(3)	0.661(3)	0.09(2)
C(25b)	0.834(2)	1.078(3)	0.573(3)	0.08(2)
N(21c)	0.773(2)	1.251(2)	0.263(2)	0.08(1)
N(22c)	0.711(1)	1.247(2)	0.321(2)	0.06(1)
C(23c)	0.673(2)	1.334(2)	0.297(3)	0.09(2)
C(24c)	0.712(2)	1.403(2)	0.223(3)	0.09(2)
C(25c) [a]	0.773(2)	1.351(3)	0.200(3)	0.10(1)
C(2)	0.689(2)	1.145(2)	0.395(2)	0.06(1)

Table 2 (continued)

Atom	x	y	z	U (Å^2)
Disordered cation				
C(21a′) [a,b]	0.914(5)	1.267(5)	0.326(5)	0.13(3)
C(22a′) [a,b]	0.890(2)	1.339(7)	0.394(5)	0.28(6)
C(23a′) [a,b]	0.933(5)	1.424(5)	0.398(5)	0.31(7)
C(24a′) [a,b]	0.999(4)	1.437(5)	0.336(5)	0.17(4)
C(25a′) [a,b]	1.023(2)	1.365(7)	0.268(4)	0.11(3)
C(26a′) [a,b]	0.980(5)	1.280(5)	0.264(5)	0.13(3)
C(21a″) [a,c]	0.908(3)	0.938(3)	0.303(4)	0.03(2)
C(22a″) [a,c]	0.898(3)	0.859(5)	0.242(4)	0.19(6)
C(23a″) [a,c]	0.924(3)	0.758(4)	0.283(4)	0.08(3)
C(24a″) [a,c]	0.961(3)	0.736(3)	0.386(4)	0.07(2)
C(25a″) [a,c]	0.971(3)	0.814(5)	0.448(4)	0.07(2)
C(26a″) [a,c]	0.945(3)	0.915(4)	0.406(4)	0.11(3)
C(21b′)	0.873(1)	1.134(2)	0.118(3)	0.06(1)
C(22b′)	0.821(2)	1.155(3)	0.049(3)	0.08(2)
C(23b′)	0.829(2)	1.171(2)	−0.079(3)	0.08(2)
C(24b′)	0.902(2)	1.153(2)	−0.122(3)	0.08(2)
C(25b′)	0.952(2)	1.123(3)	−0.047(3)	0.10(2)
C(26b′)	0.939(2)	1.112(3)	0.077(3)	0.08(2)
I_3^- and I^-				
I(01)	0.5869(2)	0.2173(2)	0.0542(2)	0.097(1)
I(02)	0.6437(2)	0.3056(2)	−0.1854(2)	0.089(1)
I(03)	0.6992(3)	0.4066(3)	−0.4087(3)	0.212(3)
I(0)	0.4925(1)	0.8230(2)	−0.5124(2)	0.080(1)

[a] Isotropic thermal parameters. [b] Site occupancy factor = 0.589(4). [c] Site occupancy factor = 1.0–0.589(4).

Table 3

Non-hydrogen atom coordinates and isotropic displacement parameters for [PtIMe$_2${(pz)$_2$(mim)CH-N,N',N''}]I (**2a**)

Atom	x	y	z	U (Å^2)
Pt	0.3413(2)	0.4282(2)	0.6264(1)	0.075(1)
I(0)	0.1494(4)	0.9890(3)	0.3738(2)	0.086(2)
I [a]	0.1871(6)	0.2543(7)	0.6350(4)	0.114(5)
I(a) [a]	0.472(2)	0.407(3)	0.756(2)	0.22(2)
I(b) [a]	0.447(2)	0.232(1)	0.624(1)	0.15(1)
N(1a)	0.217(3)	0.454(4)	0.503(2)	0.055(9)
N(2a)	0.196(3)	0.580(4)	0.467(2)	0.059(9)
C(3a)	0.130(3)	0.588(4)	0.387(2)	0.05(1)
C(4a)	0.095(4)	0.464(5)	0.361(3)	0.08(2)
C(5a)	0.155(4)	0.385(4)	0.436(3)	0.06(1)
N(1b)	0.256(3)	0.605(3)	0.642(2)	0.06(1)
C(2b)	0.228(4)	0.705(4)	0.587(2)	0.05(1)
N(3b)	0.173(4)	0.806(5)	0.609(3)	0.10(1)
C(3b)	0.142(8)	0.92(1)	0.566(5)	0.22(4)
C(4b)	0.168(4)	0.765(5)	0.670(3)	0.08(1)
C(5b)	0.216(5)	0.639(6)	0.694(3)	0.10(2)
N(1c)	0.458(3)	0.575(4)	0.609(2)	0.053(9)
N(2c)	0.405(4)	0.678(5)	0.565(2)	0.09(1)
C(3c)	0.493(5)	0.766(5)	0.565(3)	0.07(1)
C(4c)	0.592(5)	0.704(6)	0.612(3)	0.10(2)
C(5c)	0.581(5)	0.583(6)	0.640(3)	0.09(2)
C	0.261(5)	0.693(5)	0.523(3)	0.08(2)

[a] Site occupancy factors: I, 0.68(1); I(a), 0.29(1); I(b), 0.31(1) (modelling I/CH_3 composites).

Table 4

Non-hydrogen atom coordinates and isotropic displacement parameters for [PtIMe$_2${(pz)$_2$(py)CH-*N,N′,N″*}]I (**2b**)

Atom	x	y	z	U (Å^2)
Pt	0.3293(1)	0.3886(2)	0.6956(1)	0.0734(9)
I(0)	0.4142(3)	−0.1869(4)	0.5276(2)	0.128(3)
I [a]	0.4029(3)	0.5655(6)	0.7808(3)	0.092(3)
C(0) [a]	0.409(7)	0.48(1)	0.752(7)	0.10(5)
I(a) [a]	0.263(3)	0.4(3)	0.766(3)	0.17(2)
C(a) [a]	0.26(5)	0.44(1)	0.766(4)	0.05
I(b) [a]	0.277(3)	0.59(7)	0.629(2)	0.11(2)
C(b) [a]	0.280(8)	0.61(2)	0.645(7)	0.05
N(1a)	0.392(2)	0.364(4)	0.633(2)	0.06(1)
N(2a)	0.402(2)	0.227(4)	0.613(2)	0.07(1)
C(3a)	0.447(2)	0.219(5)	0.575(2)	0.07(1)
C(4a)	0.469(2)	0.356(5)	0.573(2)	0.08(1)
C(5a)	0.435(2)	0.443(5)	0.612(2)	0.08(1)
N(1b)	0.374(2)	0.192(4)	0.751(2)	0.06(1)
C(2b)	0.387(2)	0.09(5)	0.704(2)	0.06(1)
C(3b)	0.415(3)	−0.04(6)	0.736(3)	0.10(2)
C(4b)	0.433(3)	−0.058(7)	0.808(3)	0.13(2)
C(5b)	0.415(4)	0.03(1)	0.833(4)	0.19(3)
C(6b)	0.390(2)	0.172(6)	0.818(3)	0.09(2)
N(1c)	0.262(2)	0.248(4)	0.623(2)	0.06(1)
N(2c)	0.296(2)	0.132(4)	0.607(2)	0.08(1)
C(3c)	0.247(3)	0.033(5)	0.561(2)	0.08(2)
C(4c)	0.187(3)	0.084(6)	0.551(2)	0.10(2)
C(5c)	0.198(3)	0.234(6)	0.592(2)	0.11(2)
C	0.367(2)	0.114(5)	0.632(2)	0.08(1)

[a] Site occupancy factors: I, 0.605; C(0), 0.395; I(a), 0.197; C(a,b), 0.803.

*[PtIMe$_2${(pz)$_2$(mim)CH-*N,N′,N″*}]I (2a).* Within the cation the coordinated iodide is distributed over three sites, one (I) dominant over the other two [I(a,b)] by a factor of about two. Associated methyl groups could not be resolved as independent fragments, not unexpectedly in view of the similar bulk of I and Me. The total coordinated iodide population refined to 1.28, again a reasonable outcome given that, in terms of Z, I + 2Me = 71 = 1.34 × 53 = 1.34I. Concerted effects of the disorder are evidenced in the apparent high thermal motion in the remainder of the cation, notably at the periphery. Some doubt remains as to whether the substituent methyl group on one ring is localized or also disordered with minor components distributed over alternative sites (i.e. disordering of pz and mim rings); difference maps did not resolve this question unambiguously. Platinum and iodine thermal parameters were refined with the anisotropic form, those of the remaining non-hydrogen atoms being refined anisotropically. The disposition of the cell contents is suggestive of higher pseudo-symmetry (Fig. 2(b)), but the possibility of an alternative cell or space group has been explored fruitlessly.

*[PtIMe$_2${(pz)$_2$(py)CH-*N,N′,N″*}]I (2b).* As found for **2a**, the iodine atom and methyl groups of the cation are disordered over three sites, with the dominant site for iodine trans to the pyridine donor. However, for this complex, the methyl groups were resolvable and were refined independently of iodine with constrained

Table 5

Coordination geometry for $[PtIPh_2\{(pz)_3CH\text{-}N,N',N''\}]_2[I][I_3]$ (**1**) [a]

	Ordered cation (n = 1)	Disordered cation (n = 2)
Distances (Å)		
Pt(n)–N(n1a,b,c)	2.20(2), 2.15(2), 2.01(2)	2.10(2), 2.18(3), 2.12(3)
Pt(n)–C(n1a′,b′)	2.09(3), 2.05(3)	2.43(7), 2.03(3)
Pt(n)–I(n)	2.601(3)	2.434(5)
Pt(n)–C(21a″), I(2″)		2.63(4), 2.425(8)
Angles (°)		
C(n1a′)–Pt(n)–N(n1a,b,c)	171(1), 89(1), 90(1)	157(2), 86(2), 76(2)
C(n1a′)–Pt(n)–C(n1b′)	98(1)	100(2)
C(n1b′)–Pt(n)–N(n1a,b,c)	89(1), 171(1), 89(1)	92(1), 173(1), 94(1)
I(n)–Pt(n)–C(n1a′,b′)	93.9(9), 93.8(9)	99(2), 91.2(8)
I(n)–Pt(n)–N(n1a,b,c)	90.8(7), 92.0(6), 174.8(5)	100.6(6), 91.7(7), 172.9(8)
N(n1a)–Pt(n)–N(1b,c)	83.9(8), 84.8(9)	80.9(9), 84(1)
N(n1b)–Pt(n)–N(n1c)	84.7(9)	84(1)
C(21a″)–Pt(2)–N(21a,b,c)		81(1), 98(1), 164(1)
C(21a″)–Pt(2)–C(21a′,b′)		120(2), 82(1)
I(2″)–Pt(2)–C(21a′,b′)		31(1), 92.5(8)
I(2″)–Pt(2)–N(21a,b,c)		168.7(6), 94.3(7), 105.7(8)

[a] I_3^-: I(02)–I(01,03) = 2.972(4), 2.846(5)Å; I(01)–I(02)–I(03) = 175.1(1)°.

Table 6

Coordination geometry for $[PtIMe_2\{(pz)_2(mim)CH\text{-}N,N',N''\}]I$ (**2a**) and $[PtIMe_2\{(pz)_2(py)CH\text{-}N,N',N''\}]I$ (**2b**)

	2a [a]	**2b**
Distances (Å)		
Pt–N(1a,b,c)	2.07(3), 2.11(4), 2.16(4)	2.08(4), 2.21(3), 2.19(3)
Pt–C(a,b,0)		2.3(1), 2.4(2), 2.0(1)
Pt–I, I(a,b)	2.595(8), 2.15(2), 2.32(2)	2.581(6), 2.24(6), 2.39(6)
Angles (°)		
I–Pt–N(1a,b,c)	91(1), 97(1), 175.2(7)	94.4(9), 95.1(8), 176(1)
I–Pt–I(a,b)	90.0(8), 83.0(5)	87(1), 89(1)
I(a)–Pt–N(1a,b,c)	179(1), 93(1), 95(1)	176(1), 90(1), 91(2)
I(a)–Pt–I(b)	81.1(9)	91(2)
I(b)–Pt–N(1a,b,c)	100(1), 174.0(9), 98(1)	93(2), 176(1), 88(2)
N(1a)–Pt–N(1b,c)	86(1), 84(1)	86(1), 88(1)
N(1b)–Pt–N(1c)	83(2)	88(1)
I–Pt–C(a,b)		82(2), 82(3)
I(a)–Pt–C(b,0)		87(4), 103(5)
I(b)–Pt–C(a,0)		84(3), 101(4)
C(a)–Pt–N(1a,b,c)		175(2), 98(2), 95(2)
C(a)–Pt–C(b,0)		79(4), 100(5)
C(b)–Pt–C(0)		95(5)
C(b)–Pt–N(1a,b,c)		97(4), 176(4), 95(4)
C(0)–Pt–N(1a,b,c)		78(5), 83(4), 163(5)

[a] For this complex, iodine atoms and methyl group carbon atoms are not resolved, and the atoms listed as I, I(a), and I(b) represent iodine/carbon coordinate positions obtained directly from the least squares refinement.

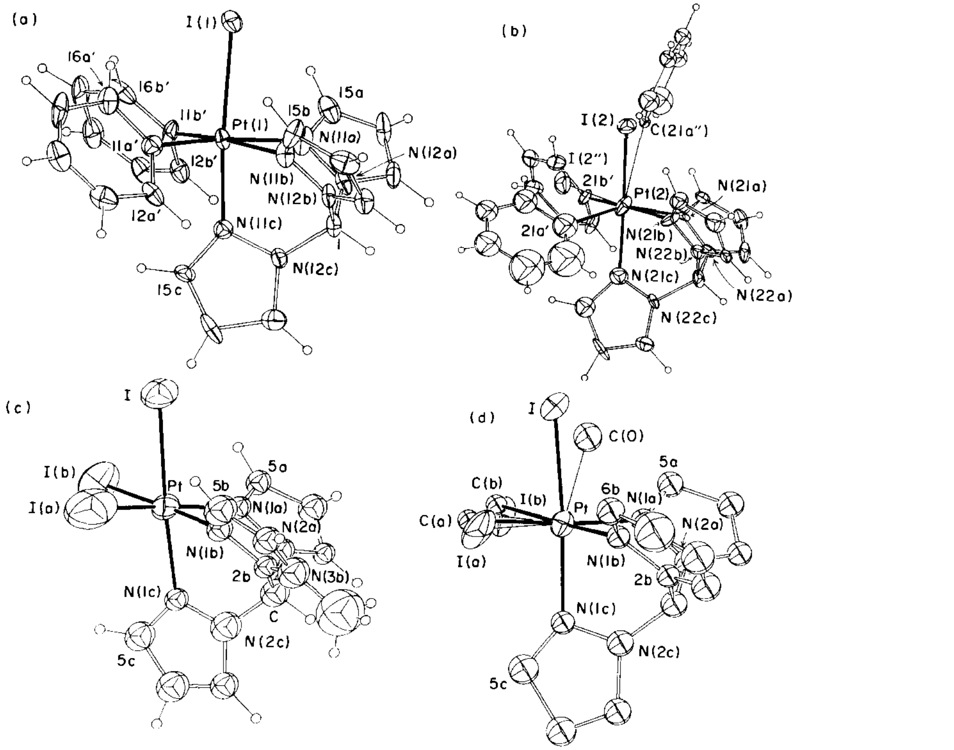


Fig. 1. The molecular structures of the cations $[PtIR_2(L)]^+$, showing partial atom numbering. (a) The well ordered cation $[PtIPh_2\{(pz)_3CH\text{-}N,N',N''\}]^+$; (b) the disordered cation $[PtIPh_2\{(pz)_3CH\text{-}N,N',N''\}]^+$, occurring together with the ordered cation in the asymmetric unit of $[PtIPh_2\{(pz)_3CH\text{-}N,N',N''\}]^+[I][I_3]$ (**1**), showing disorder in the position of iodine and one of the phenyl groups; (c) $[PtIMe_2\{(pz)_2(mim)CH\text{-}N,N',N''\}]^+$ in **2a**, showing disorder in the iodine and methyl group positions such that the iodine atom is about 60% trans to a pyrazole ring, and the lack of resolution of methyl and iodine positions; (d) $[PtIMe_2\{(pz)_2(py)CH\text{-}N,N',N''\}]^+$ in **2b**, showing disorder in the position of the iodine and methyl groups such that the iodine is about 50% trans to a pyridine group, and showing resolution of iodine and methyl group positions. Twenty percent thermal envelopes are shown for the non-hydrogen atoms, and hydrogen atoms are shown with an arbitrary radius of 0.1 Å.

isotropic thermal parameter estimates and occupancies totally constrained to unity at each site. Isotropic thermal parameters were refined for all other atoms, except for platinum and iodine atoms which carried the anisotropic form. Fourier difference maps did not reveal whether there is any minor disordering of the pyridine ring positions. The structure shows pseudo-symmetry, e.g. as illustrated by the disposition of cell contents relative to the cell diagonals which intersect at approximately 90° (Fig. 2(c)).

Results and discussion

The complex $[PtIPh_2\{(pz)_3CH\text{-}N,N',N''\}]_2[I][I_3]$ was obtained by a procedure similar to that reported for the neutral complex $PtI_2Me_2\{(pz)_3CH\text{-}N,N'\}$ [1]. Reaction of $[PtPh_2(SEt_2)]_2$ with $(pz)_3CH$ and iodine in dichloromethane gave the complex at ambient temperature. Oxidation of platinum(II) by iodine is assumed

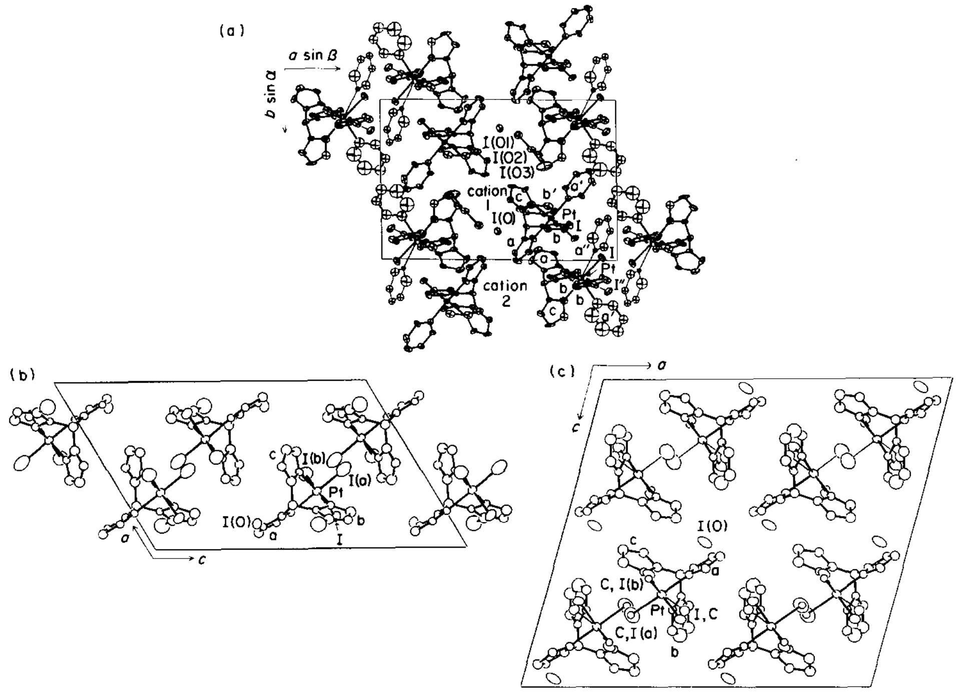


Fig. 2. Unit cell contents of the complexes, showing fragment labelling. (a) $[PtIPh_2\{(pz)_3CH\text{-}N,N',N''\}]^+[I][I_3]$ (**1**) viewed down the *c* axis, showing the ordered and disordered cations; (b) $[PtIMe_2\{(pz)_2(mim)CH\text{-}N,N',N''\}]I$ (**2a**) viewed down *b*, showing the disordered cations; (c) $[PtIMe_2\{(pz)_2(py)CH\text{-}N,N',N''\}]I$ (**2b**) viewed down *b*, showing the disordered cations.

to occur prior to coordination of the ligand, since the reaction of $[PtPh_2(SEt_2)]_2$ to form $PtPh_2\{(pz)_3CH\}$ requires heating [6].

All three structures exhibit disorder (Fig. 1), and indications of higher pseudo-symmetry, although evidence for alternative cells or space groups could not be found. Complex **1** is a remarkable structure, possessing two independent $[PtIPh_2\{(pz)_3CH\text{-}N,N',N''\}]^+$ cations in the asymmetric unit, in association with iodide and triiodide ions. One of the cations is well ordered, and the other cation exhibits a disorder similar to that of the cations in **2a** and **2b**. In **1**, the coordinated iodide is disordered with one of the phenyl groups (approx. 60% in one site), and in both **2a** and **2b** the iodide is disordered with methyl groups. In **2a** the coordinated iodide is predominantly (approx. 60%) in the site *trans* to a pyrazole group, and in **2b** it is predominantly (approx. 50%) *trans* to the pyridine group. Presence of disorder in **2a** and **2b** confirms the indication from ^1H NMR spectra that the complexes contain isomers with iodine *trans* to pz and mim or py groups [1].

The complexes $[M\{(pz)_2(py)CH\text{-}N,N',N''\}_2][NO_3]_2$ (M = Fe, Co, Ni, Zn) exhibit disordering of pyrazole and pyridine ring positions in the centrosymmetric cations [7]. Minor disorder of this kind might occur in **2a** and **2b**, but difference maps could not confirm this possibility. The structural studies of the transition metal complexes, and **1**, **2a** and **2b**, illustrate well the potential for disorder in complexes containing ligands with three-fold symmetry $[(pz)_3CH]$ or approximate three-fold symmetry [$(pz)_2$(mim)CH and $(pz)_2$(py)CH] in conjunction with other ligands in octahedral complexes.

Bond lengths and angles for all of the cations show considerable variation, even for the well ordered cation in **2a** (Tables 5 and 6). In view of the disorder exhibited by the complexes, and the resulting imprecise complex geometries, a detailed comparison of geometries for the cations with those reported for the related complexes $PtIMe_3\{(3,5\text{-}Me_2pz)_2CH_2\text{-}N,N'\}$ [8], $PtI_2Me_2\{(pz)_2CH_2\text{-}N,N'\}$ [9], $PtI_2Me_2\{(3,5\text{-}Me_2pz)_2CH_2\text{-}N,N'\}$ [9], and $PtI_2Me_2\{(pz)_2$(thien-2-yl)CH-$N,N'\}$ [1] is not warranted.

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