Binuclear Pyrazolato-bridged Platinum(II) Complexes: Synthesis, Characterization and Crystal Structure *

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Binuclear pyrazolato-bridged platinum(II) complexes of the type $[Pt_2Cl_2(\mu\text{-L–L})_2(PR_3)_2]$ [L–L = pz (pyrazolate) or dmpz (3,5-dimethylpyrazolate); PR_3 = PEt_3, PMe_2Ph or $PMePh_2$] have been prepared by the reaction of $[Pt_2Cl_2(\mu\text{-}O_2CMe)_2(PR_3)_2]$ with Hpz or Hdmpz. All the complexes were characterized by elemental analysis and ^1H and ^{31}P NMR data. A single-crystal structure analysis of a representative complex, $[Pt_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)_2]$, is also reported. Crystals are orthorhombic, with space group *Pbca* and unit-cell dimensions a = 17.701(9), b = 24.906(8), c = 16.976(7) Å. The structure was refined to final R = 0.040 for 3857 reflections with $I \geqslant 3.0\sigma(I)$.

Binuclear platinum-group complexes stabilized through pyrazolate bridges are of much current interest owing to their interesting structural features and rich reaction chemistry.[1–8] In these complexes two metal centres are bridged by the *exo*-bidentate pyrazolate ligands and the resulting metallacycle rings are usually puckered.

Attempts to synthesize complexes of the type $[Pt_2Cl_2(\mu\text{-L–L})_2(PR_3)_2]$ [L–L = pz (pyrazolate) or dmpz (3,5-dimethylpyrazolate)] by the reaction of $[Pt_2Cl_2(\mu\text{-Cl})_2(PR_3)_2]$ with Hpz or Hdmpz in the presence of methanolic sodium hydroxide yielded either chloropyrazolato-bridged complexes or chloro-bridged derivatives containing terminal pyrazolate ligands.[5,8] However, similar reactions with the analogous palladium complexes yield, exclusively, bis(pyrazolato)-bridged derivatives.[4] The results reported herein demonstrate that the bis(pyrazolato)-bridged platinum complexes of the type $[Pt_2Cl_2(\mu\text{-L–L})_2(PR_3)_2]$ may be isolated in high yield from the reaction of $[Pt_2Cl_2(\mu\text{-}O_2CMe)_2(PR_3)_2]$ with pyrazoles.

Experimental

The complexes $[Pt_2Cl_2(\mu\text{-}O_2CMe)_2(PR_3)_2]$ (PR_3 = PEt_3, PMe_2Ph or $PMePh_2$) were prepared according to the literature method.[9] Pyrazole, 3,5-dimethylpyrazole and the tertiary phosphines were obtained from commercial sources. Elemental analyses were carried out by the Analytical Chemistry Division, Bhabha Atomic Research Centre. Proton and $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded on a Bruker AMX-500 NMR spectrometer operating at 500 and 202.4 MHz, respectively. Chemical shifts are reported relative to the internal chloroform peak (δ 7.26) for ^1H and external 85% H_3PO_4 for the $^{31}P\text{-}\{^1H\}$ spectra.

Preparation of $[Pt_2Cl_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$.—To a dichloromethane solution (5 cm^3) of $[Pt_2Cl_2(\mu\text{-}O_2CMe)_2(PMe_2Ph)_2]$ (130 mg, 0.15 mmol), a solution (3 cm^3) of 3,5-dimethylpyrazole (31 mg, 0.32 mmol) was added. The reaction mixture was stirred for 6 h at room temperature. The solvent was removed *in vacuo* and further dried at 0.1 mmHg (*ca.* 13.3 Pa) for 6 h to remove the acetic acid that had formed. The residue was dissolved in dichloromethane (1 cm^3) and filtered. Hexane was added to the filtrate and the solution kept aside for crystallization. The crystals thus obtained were washed with hexane (2 × 2 cm^3) and dried (85 mg, 59% yield). The other complexes were prepared similarly; pertinent data are found in Table 1.

Crystallography.—Intensity data for a colourless crystal of $[Pt_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)_2]$ (0.34 × 0.36 × 0.52 mm) were measured at room temperature on a Rigaku AFC6R diffractometer fitted with Mo-Kα radiation, λ = 0.710 73 Å. A total of 7520 independent data (ω–2θ scan technique, $2\theta_{max}$ 50.0°) were corrected for Lorentz and polarization effects[10] and for absorption employing an empirical method[11] (range of transmission coefficients 0.892 to 1.278). The metric crystal data and systematic absences define unambiguously the space group *Pbca*.

Crystal data. $C_{36}H_{40}Cl_2N_4P_2Pt_2$, M = 1051.8, orthorhombic, space group *Pbca*, a = 17.701(9), b = 24.906(8), c = 16.976(7) Å, U = 7484(5) Å^3, D_c = 1.867 g cm^{-3}, Z = 8, $F(000)$ = 4032, μ = 76.97 cm^{-1}, 3857 data with $I \geqslant 3.0\sigma(I)$, R = 0.040, R' = 0.042.

The structure was solved by direct methods[12] and refined by a full-matrix least-squares procedure based on F.[10] All non-H atoms were refined anisotropically and the H atoms were included in the model at their calculated positions (C–H 0.97 Å). Disorder in the molecule is noted for the phenyl group with atoms C(231)–C(236) as seen in the thermal motion associated with these atoms and derived interatomic parameters; see Fig. 1. A weighting scheme based on sigma weights was applied and the refinement on 415 parameters converged with R = 0.040 and R' = 0.042. The analysis of variance showed no special features and the maximum and minimum excursions in the final difference map were 1.19 and −1.07 e Å^{-3}, respectively. Fractional atomic coordinates are listed in Table 2 and the numbering scheme employed is shown in Fig. 1 drawn with the ORTEP program at 30% probability ellipsoids.[13] Scattering factors for all atoms were as incorporated in the TEXSAN[10] package installed on an Iris Indigo workstation.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The reaction of $[Pt_2Cl_2(\mu\text{-}O_2CMe)_2(PR_3)_2]$ with 2 molar equivalents of pyrazole in dichloromethane solution at room

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical and physical data for $[Pt_2Cl_2(\mu\text{-L–L})_2(PR_3)_2]$

Complex	Yield (%)	M.p./°C	Analysis (%)* C	H	N
$[Pt_2Cl_2(\mu\text{-pz})_2(PEt_3)_2]$	57	168–170	27.1 (26.0)	4.5 (4.4)	6.5 (6.7)
$[Pt_2Cl_2(\mu\text{-dmpz})_2(PEt_3)_2]$	58	195	29.7 (29.8)	5.0 (5.0)	6.2 (6.3)
$[Pt_2Cl_2(\mu\text{-pz})_2(PMe_2Ph)_2]$	66	182–183	30.2 (30.3)	3.2 (3.2)	6.5 (6.4)
$[Pt_2Cl_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$	59	217	33.6 (33.7)	3.9 (3.9)	5.9 (6.0)
$[Pt_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)_2]$	61	285–287	40.9 (41.1)	3.8 (3.8)	5.2 (5.3)

*Calculated values in parentheses.

Table 2 Fractional atomic coordinates for $[Pt_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)_2]$

Atom	*x*	*y*	*z*
Pt(1)	0.144 25(3)	0.650 26(2)	0.077 33(3)
Pt(2)	0.153 08(3)	0.631 54(2)	−0.107 14(3)
Cl(1)	0.047 2(2)	0.606 5(2)	0.137 7(2)
Cl(2)	0.247 6(2)	0.574 9(2)	−0.143 8(3)
P(1)	0.222 0(2)	0.599 3(2)	0.147 1(3)
P(2)	0.070 7(2)	0.572 6(2)	−0.152 0(2)
N(11)	0.071 5(6)	0.692 0(5)	0.007 4(6)
N(12)	0.075 7(6)	0.683 8(5)	−0.071 3(7)
N(21)	0.223 1(6)	0.691 0(5)	0.022 1(7)
N(22)	0.228 5(6)	0.683 0(5)	−0.057 5(8)
C(11)	0.000 6(10)	0.745 5(8)	0.101 1(10)
C(12)	0.020 6(9)	0.729 7(7)	0.018 6(10)
C(13)	−0.011 0(9)	0.745 0(7)	−0.050 8(10)
C(14)	0.026 7(8)	0.715 7(6)	−0.105 5(9)
C(15)	0.019 5(9)	0.718 3(7)	−0.192 8(9)
C(21)	0.276 7(8)	0.750 1(7)	0.122 3(9)
C(22)	0.270 1(9)	0.729 5(6)	0.040 1(8)
C(23)	0.306 1(9)	0.748 8(7)	−0.024 4(9)
C(24)	0.280 9(9)	0.716 5(7)	−0.085 2(9)
C(25)	0.300 3(9)	0.716 4(7)	−0.170 9(9)
C(111)	0.210 6(10)	0.529 7(6)	0.126 8(10)
C(121)	0.322 5(8)	0.608 5(6)	0.129 4(9)
C(122)	0.371 7(11)	0.618 8(7)	0.189 3(10)
C(123)	0.448 7(12)	0.624 9(7)	0.168 3(13)
C(124)	0.471 7(11)	0.619 5(9)	0.088 6(14)
C(125)	0.422 0(11)	0.609 6(9)	0.035 8(12)
C(126)	0.348 8(11)	0.605 9(6)	0.051 6(9)
C(131)	0.209 5(9)	0.606 1(7)	0.251 6(9)
C(132)	0.224 4(11)	0.564 6(8)	0.301 8(11)
C(133)	0.215 1(14)	0.570 7(11)	0.381 4(15)
C(134)	0.194 1(13)	0.616 6(13)	0.408 5(12)
C(135)	0.178 6(10)	0.659 2(8)	0.363 5(13)
C(136)	0.185 5(10)	0.653 2(8)	0.278 8(10)
C(211)	0.084 5(8)	0.508 9(6)	−0.111 5(10)
C(221)	−0.023 9(8)	0.585 6(6)	−0.132 4(9)
C(222)	−0.046 0(9)	0.592 6(6)	−0.053 4(11)
C(223)	−0.117 0(11)	0.603 2(7)	−0.028 1(10)
C(224)	−0.172 4(10)	0.608 2(7)	−0.085 0(12)
C(225)	−0.152 7(11)	0.602 9(7)	−0.163 9(10)
C(226)	−0.079 9(9)	0.590 9(6)	−0.185 7(9)
C(231)	0.072 1(9)	0.560 5(7)	−0.257 0(9)
C(232)	0.106 9(10)	0.597 6(8)	−0.303 5(12)
C(233)	0.102 2(11)	0.583 7(13)	−0.391 7(14)
C(234)	0.065 6(21)	0.542 7(13)	−0.406 5(20)
C(235)	0.036 2(29)	0.510 7(12)	−0.371 4(28)
C(236)	0.041 1(15)	0.519 7(8)	−0.291 5(12)

temperature gives exclusively the bis(pyrazolato)-bridged complexes $[Pt_2Cl_2(\mu\text{-L–L})_2(PR_3)_2]$ (L–L = pz or dmpz; PR_3 = PEt_3, PMe_2Ph or $PMePh_2$). All the complexes are white crystalline solids and can be recrystallized from dichloromethane–hexane (50 : 50 v/v) in 57–66% yield.

Unlike the $[Pt_2R_2(\mu\text{-L–L})_2(PR_3)_2]$ (R = methyl or aryl) complexes, which exist as a mixture of *cis* and *trans* isomers,[7,14] the $[Pt_2Cl_2(\mu\text{-L–L})_2(PR_3)_2]$ complexes could be isolated only in one isomeric form. The NMR data (Table 3) can be best interpreted in terms of a *sym-trans* configuration. The $^{31}P\text{-}\{^1H\}$ NMR spectra displayed only one resonance flanked with platinum satellites $[^1J(^{195}Pt–^{31}P)$ *ca.* 3400 Hz]. The magnitude of $^1J(Pt–P)$ has been reduced significantly from the values reported for $[Pt_2Cl_2(\mu\text{-}O_2CMe)_2(PR_3)_2]$[15] and $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$.[16] The observed magnitude of $^1J(Pt–P)$ for the new complexes is consistent with the values reported for complexes containing phosphine ligands in positions *trans* to nitrogen atoms.[17]

The ^1H NMR spectra of the $[Pt_2Cl_2(\mu\text{-L–L})_2(PR_3)_2]$ complexes were recorded at 500 MHz and exhibited the expected integration and peak multiplicities (Table 3). The C^4 proton of the pyrazolate ring showed only a single resonance indicating the equivalence of the rings. This result suggests that the complexes adopt a *trans* configuration; in the *cis* isomer two signals would be anticipated as the two rings would be magnetically non-equivalent. The substituents at the 3 and 5 positions (H or Me) are non-equivalent owing to the different groups (*i.e.*, PR_3 or Cl) *trans* to the bridging nitrogen atom. The complexes containing the PMe_2Ph ligand showed two doublets for the PMe protons indicating the non-equivalence of these groups. Unambiguous structure assignment for the new complexes has been afforded by a single-crystal structure analysis of a representative derivative, namely $[Pt_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)_2]$.

The molecular structure of $[Pt_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)_2]$ is illustrated in Fig. 1 and selected interatomic bond distances and angles are listed in Table 4. The molecule features two square-planar platinum centres that are bridged by two dmpz ligands with a Pt $\cdots$ Pt separation of 3.170(1) Å. The molecule has non-crystallographic two-fold symmetry with the approximate two-fold axis passing through the central Pt_2N_4 chromophore as can be seen from Fig. 1. The lattice is comprised of discrete molecules there being no significant intermolecular interactions; the closest non-H atom contact is 3.32(4) Å which occurs between the C(124) and C(235′) atoms (symmetry operation: $0.5 - x, 1 - y, 0.5 + z$).

The square-planar geometry about each of the Pt atoms is defined by two N atoms, a Cl atom and a P atom of the $PMePh_2$ ligand such that the two N atoms occupy *cis* positions. The mean deviation from the least-squares plane through the four donor atoms defining the square-plane about the Pt(1) atom is 0.043 Å [0.034 Å for the Pt(2) atom] and the metal atom lies 0.040 Å (0.044 Å) out of the plane. There is a disparity in the Pt–N bond distances that may be related to the different *trans* influences of the Cl and P atoms. The Pt(1)–N(21) bond, with the N atom occupying a position approximately *trans* to the Cl atom, of 1.96(1) Å is significantly shorter than the Pt(1)–N(11) distance of 2.04(1) Å where the N atom is approximately *trans* to the P atom; for the second platinum atom, Pt(2), the same trend occurs, however, the derived parameters lie within their 3σ limits.

The bridging dmpz ligands (including the methyl substituents) are each planar to ±0.030(2) Å. The Pt(1) atom lies 0.099(1) and −0.156(1) Å out of the two planes, respectively and the

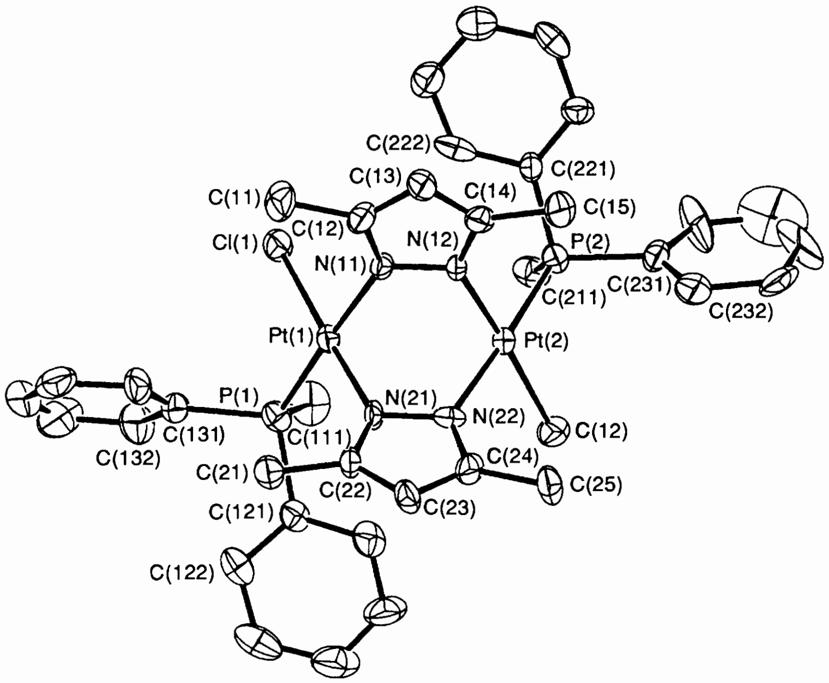

Fig. 1 Molecular structure and crystallographic numbering scheme for $[Pt_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)_2]$

Table 3 Proton and $^{31}P\text{-}\{^1H\}$ NMR data for $[Pt_2Cl_2(\mu\text{-L-L})_2(PR_3)_2]$ in $CDCl_3$ solution

	^{31}P NMR		
Complex	δ	^1J(Pt-P)/Hz	^{1}H NMR
$[Pt_2Cl_2(\mu\text{-pz})_2(PEt_3)_2]$	−1.7	3389	1.22 (m, 18 H, PCH_2CH_3), 1.77 (m, 12 H, PCH_2), 6.16 (d, 2 H, NCH of pz, *J* 1.8), 7.25 (s, 2 H, H^4 of pz), 7.48 (d, 2 H, NCH of pz, *J* 1.5 Hz)
$[Pt_2Cl_2(\mu\text{-dmpz})_2(PEt_3)_2]$	−3.6	3400	1.18 (m, 18 H, PCH_2CH_3), 1.77 (m, 12 H, PCH_2), 2.20 (s, 6 H, Me of dmpz *trans* to P), 2.35 (s, 6 H, Me of dmpz *trans* to Cl), 5.68 (s, 2 H, H^4 of dmpz)
$[Pt_2Cl_2(\mu\text{-pz})_2(PMe_2Ph)_2]$	−23.7	3433	1.63 (d, 6 H, PMe, *J* 11.2), 1.83 (d, 6 H, PMe, *J* 11.4), 5.94 (d, 2 H, NCH of pz, *J* 1.9 Hz), 6.76 (s, 2 H, H^4 of pz), 7.42 (br), 7.81–7.86 (m, 12 H, Ph + NCH of pz)
$[Pt_2Cl_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$	−22.6	3441	1.58 (d, 6 H, PMe, *J* 11.2), 1.82 (s, 6 H, Me of dmpz *trans* to P), 1.91 (d, 6 H, PMe, *J* 11.3), 2.34 (s, 6 H, Me of dmpz *trans* to Cl), 5.55 (s, 2 H, H^4 of dmpz), 7.35–7.41 (m, 10 H, Ph)
$[Pt_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)]$	−10.8	3495	1.70 (s, 6 H, Me of dmpz *trans* to P), 2.01 (d, 6 H, PMe, *J* 10.9 Hz), 2.42 (s, 6 H, Me of dmpz *trans* to Cl), 5.39 (s, 2 H, H^4 of dmpz), 7.22–8.00 (m, 20 H, Ph)

Table 4 Selected bond distances (Å) and angles (°) for $[Pt_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)_2]$

Pt(1)–Cl(1)	2.279(4)	Pt(2)–Cl(2)	2.276(4)
Pt(1)–P(1)	2.216(4)	Pt(2)–P(2)	2.206(4)
Pt(1)–N(11)	2.04(1)	Pt(2)–N(22)	2.03(1)
Pt(1)–N(21)	1.96(1)	Pt(2)–N(12)	1.99(1)
Cl(1)–Pt(1)–P(1)	87.4(2)	Cl(2)–Pt(2)–P(2)	88.8(2)
Cl(1)–Pt(1)–N(11)	91.7(3)	Cl(2)–Pt(2)–N(22)	91.2(3)
Cl(1)–Pt(1)–N(21)	176.3(4)	Cl(2)–Pt(2)–N(12)	176.2(3)
P(1)–Pt(1)–N(11)	175.4(3)	P(2)–Pt(2)–N(22)	175.5(4)
P(1)–Pt(1)–N(21)	96.3(4)	P(2)–Pt(2)–N(12)	95.0(3)
N(11)–Pt(1)–N(21)	84.7(4)	N(22)–Pt(2)–N(12)	85.0(4)

corresponding values for the Pt(2) atom are 0.059(1) and −0.262(1) Å; the dihedral angle between the two dmpz ligands is 89.0°. The remaining geometric parameters in the molecule are as expected.

To a first approximation, the structure reported here for $[Pt_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)_2]$ resembles closely that reported recently for $[Pd_2Cl_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$ which was formed exclusively as the *sym-trans* isomer in which the two platinum atoms lie above the approximate plane defined by the four nitrogen atoms.[4]

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