Structural characterization of the doubly cyclopalladated complex $[Pd_2L(-2H)(BTA)_2]$ derived from *N,N'*-diethylbenzene-1,3-dicarbaldimine (L) and benzoyltrifluoroacetone (HBTA)

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Abstract

Doubly cyclopalladated mixed chelates of the type $[Pd_2L(-2H)(\beta\text{-diket})_2]$ derived from *N,N'*-diethylbenzene-1,3-dicarbaldimine (L) and the unsymmetrical β-diketones (Hβ-diket) benzoyltrifluoroacetone (HBTA), benzoylacetone (HBA) and thenoyltrifluoroacetone (HTTA) have been synthesized and characterized. The crystal structure of $[Pd_2L(-2H)(BTA)_2]$ is reported. The complex $C_{32}H_{26}N_2O_4F_6Pd_2$ crystallizes in the triclinic space group $P\bar{1}$ with $a=10.872(1)$, $b=11.915(1)$, $c=13.525(1)$ Å, $\alpha=101.74(1)$, $\beta=112.78(1)$, $\gamma=97.77(1)°$, $V=1537.5(7)$ Å^3 and $Z=2$. The structure was solved by direct methods and refined by block-diagonal least-squares method to $R=0.034$ and $R_w=0.037$ based on 3535 observed reflections with $I>3\sigma(I)$.

Introduction

The ease with which palladium(II) undergoes cyclometallation reaction with heterosubstituted organic molecules has led to the synthesis of a variety of organopalladium intramolecular coordination compounds [1]. In particular there has been extensive studies with C^-,N chelated cyclopalladated compounds [1–8]. Notwithstanding wide occurrence of *ortho*-palladated compounds having one Pd–C bond per aromatic ring, similar dipalladiobenzene derivatives are quite sparse, albeit much earlier Trofimenko employed *N,N,N',N'*-tetraalkyl-*p*/*m*-xylene-α,α-diamines for cyclopalladation reaction [9]. We have recently reported [10, 11] a variety of reactions of the dipalladium metallacycles derived from *N,N*-dialkyl/dibenzylbenzene-1,3-dicarbaldimines with various nucleophiles, including the structure of $[Pd_2L(-2H)(py)_4](ClO_4)_2$ (L = *N,N'*-diethylbenzene-1,3-dicarbaldimine). Very recently Steel and co-workers [12, 13] have also studied double cyclopalladation reactions of diacetylbenzene dioximes and 4,6-diphenylpyrimidine. The present study is concerned with the formation of the doubly cyclopalladated mixed chelates $[Pd_2L(-2H)(\beta\text{-diket})_2]$ with the unsymmetrical β-diketones such as benzoyltrifluoroacetone (HBTA), benzoylacetone (HBA) and thenoyltrifluoroacetone (HTTA). The molecular structure of $[Pd_2L(-2H)(BTA)_2]$ is reported here.

Experimental

Preparation of the complexes

$[Pd_2L(-2H)(TBA)_2]$ (**1**). To a stirred suspension of $[Pd_4L(-2H)_2Cl_4]$ (0.94 g, 1 mmol) [10] in MeOH (40 cm^3) was added 0.86 g (4 mmol) of CF_3COCH_2COPh followed by the addition of an ethanol solution (10 cm^3) of KOH (0.22 g, 4 mmol) over a period of 0.5 h. After additional stirring of the mixture for 1 h the product was collected by filtration and washed successively with water and methanol. The compound was recrystallized from $CHCl_3$; yield 1.3 g (c. 80%). Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a CH_2Cl_2 solution. *Anal. Calc.* for $C_{32}H_{26}N_2O_4F_6Pd_2$: C, 46.33; H, 3.14; N, 3.38; Pd, 25.67. Found: C, 46.12; H, 3.18; N, 3.27; Pd, 25.82%.

The complexes $[Pd_2L(-2H)(BA)_2]$ (**2**) and $[Pd_2L(-2H)(TTA)_2]$ (**3**) were prepared in the same way as **1**. *Anal. Calc.* for $C_{32}H_{32}N_2O_4Pd_2$ (**2**): C, 53.26; H, 4.44; N, 3.88; Pd, 29.52. Found: C, 53.51; H, 4.52; N, 3.81; Pd, 29.62%. *Anal.* Calc. for $C_{28}H_{22}N_2O_4S_2F_6Pd_2$

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(**3**): C, 39.95; H, 2.61; N, 3.33; Pd, 25.31. Found: C, 40.30; H, 2.56; N, 3.21; Pd, 25.22%.

Physical measurements

^{1}H NMR spectra were recorded on $CDCl_3$ solutions on a Jeol FX-100 spectrometer using Me_4Si ($\delta = 0$ ppm) as the internal reference. IR spectra were carried out as KBr pellets using a Perkin-Elmer model 783 spectrophotometer. Electronic spectra were obtained with a Jasco 7850 UV–Vis spectrophotometer. C, H and N analyses were performed on a Perkin-Elmer model 240C elemental analyzer. Pd was estimated gravimetrically as the dimethylglyoximate.

Crystallographic studies

X-ray diffraction data of **1** were collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo Kα radiation. Cell dimensions were accurately determined by a least-squares fit of 25 arbitrarily chosen higher order reflections. Pertinent crystallographic data are given in Table 1. Lorentz polarization corrections were applied and absorption corrections were made empirically according to North *et al.* [14]. The structure was solved by direct methods using the program MULTAN 82 [15]. The E map computed with the highest combined figure of merit (2.997) gave the positions of the two Pd atoms. All the non-hydrogen atoms were located on a difference map after anisotropic refinement of the Pd atoms. The positions of the hydrogen atoms were obtained using stereochemical constraints. A mixed-mode refinement by block-diagonal least-squares methods, wherein the non-hydrogen atoms were refined anisotropically, while keeping the hydrogens fixed, resulted in convergence at $R = 0.034$ ($R_w = 0.037$). A unit-weighting scheme with Dunitz–Seiler weighting factor [16] was used in the final stages of the refinement. Hydrogen atoms were given an isotropic thermal factor 1.3 times those of the heavy atoms to which they are attached. At the end of the refinement the difference Fourier map was nearly featureless, except in the vicinity of the Pd atoms where ripples up to 0.92 e Å^{-3} were found. The scattering factors were taken from ref. 17. All the computations were carried out with SDP package of programs available on the PDP-11/73 system [18].

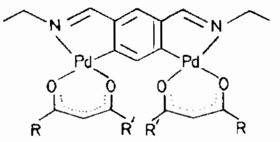
TABLE 1. Crystallographic data for $[Pd_2L(-2H)(BTA)_2]$

Formula	$C_{32}H_{26}N_2O_4F_6Pd_2$
Formula weight	829.35
Space group	$P\bar{1}$ (*triclinic*)
a (Å)	10.872(1)
b (Å)	11.915(1)
c (Å)	13.535(1)
α (°)	101.74(1)
β (°)	112.78(1)
γ (°)	97.77(1)
V (Å^3)	1537.5(7)
Z	2
F (000)	816
Crystal size (mm)	0.26×0.24×0.17
D_{calc} (g cm^{-3})	1.790
μ(Mo Kα) (cm^{-1})	12.302
Radiation	Mo Kα ($\lambda = 0.71068$ Å)
Data collection range (°)	$2 < 2\theta < 47$
Temperature (K)	293±1
Reflections measured	4532
Reflections observed ($I > 3\sigma(I)$)	3535
Parameters refined	415
R^a	0.034
$R_w{}^b$	0.037

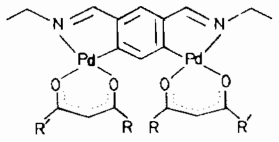
$^aR = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Results and discussion

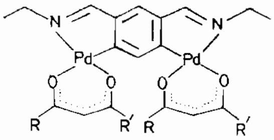
The reaction between the chloro-bridged tetracyclopalladate $[Pd_4L(-2H)_2Cl_4]$ and an unsymmetrical β-diketone $RCOCH_2COR'$ produces the mixed-chelate $[Pd_2L(-2H)(RCOCHCOR')_2]$, whose structure may be represented by I, II or III. Complexes **1–3** have been characterized by their IR, UV–Vis and ^{1}H NMR spectra. The IR spectra of the complexes are quite similar and four strong bands are observed in the range 1650–1500 cm^{-1}. For example, for **2** these bands appear at 1595, 1580, 1560 and 1515 cm^{-1} and may be assigned due to ν(C=N) and ν(C=C) of L, and combination vibrations due to ν(C$\cdots$O) and ν(C$\cdots$C) of the β-diketone. The electronic spectra of the complexes are also very similar. Typically for **1**, the absorption band observed at 295 nm ($\epsilon = 49\,000$ M^{-1} cm^{-1}) is followed by a shoulder at 340 nm ($\epsilon = 15\,000$ M^{-1} cm^{-1}). A dichloromethane solution of **1** on excitation at 360 nm



I



II



III

R	R'
Ph	CF_3
Ph	CH_3
C_4H_3S	CF_3

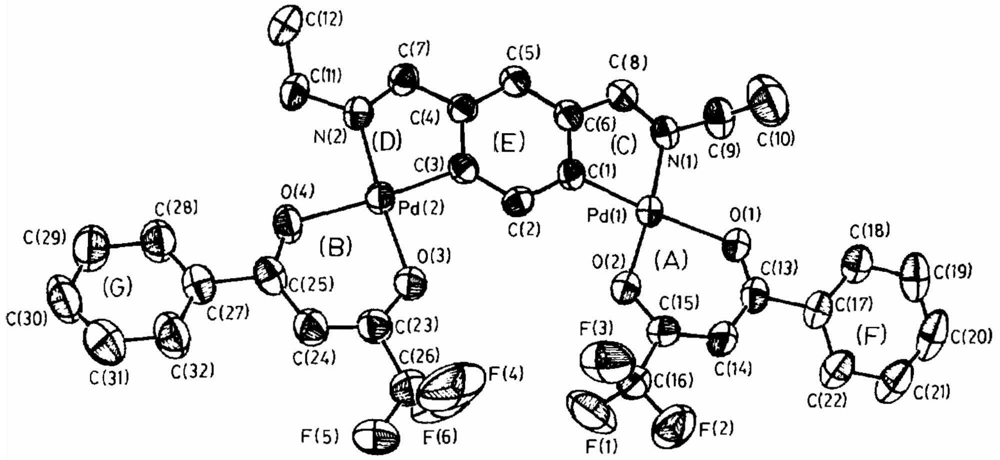


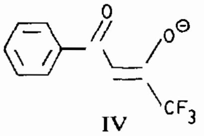
Fig. 1. ORTEP diagram of $[Pd_2L(-2H)(BTA)_2]$ along with the atom numbering scheme.

very weakly fluoresces at 430 nm. The ^1H NMR spectra of the complexes exhibit multiplets due to CH_3 and CH_2 substituents of the Schiff base at about 1.4 and 3.7 ppm, respectively. For **2** the methyl substituent of benzoylacetone is observed at 1.96 ppm. The resonance due to the CH proton of the β-diketones in complexes **1**, **2** and **3** are observed at 6.46, 5.98 and 6.32 ppm, respectively.

In order to establish which of the structures I–III is valid for the complexes, the X-ray crystal structure of **1** was determined. The ORTEP diagram of **1** is shown in Fig. 1, along with the numbering scheme. The final positional and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 2. Tables 3 and 4 give the selected bond lengths and bond angles, respectively.

The molecular structure shows that the two Pd atoms are in distorted square-planar environments. In the coordination planes Pd(1)O(1)O(2)C(13)C(14)C(15)-C(1)C(6)C(8)N(1) and Pd(2)O(3)O(4)C(23)C(24)C(25)-C(3)C(4)C(7)N(2) the deviations of the Pd atoms from the mean planes are −0.067(1) and −0.011(1) Å, respectively. These two planes are disposed more or less parallely, the dihedral angle between them is 7.3(2)°. The Pd–O distances *trans* to the carbon atoms (Pd(1)–O(1) 2.110(4), Pd(2)–O(4) 2.104(5) Å) are significantly longer than those *trans* to the nitrogen atoms (Pd(1)–O(2) 2.023(5), Pd(2)–O(3) 2.011(4) Å), illustrating the higher *trans*-effect of the aryl carbon. The Pd–C distances (1.957(5) and 1.965(6) Å) and the Pd–N distances (2.007(6) and 1.992(5) Å) are comparable to those of other related *ortho*-palladated compounds [11, 19–21]. The elongation of Pd(1)–O(1) and Pd(2)–O(4) bonds results in the contraction of the angles N(1)Pd(1)C(1) 81.1(2)°, N(2)Pd(2)C(3) 81.4(2)°, from the expected 90°. The OPdO angles, however, remain close to 90°. As a result of the significant difference between the two sets of opposing angles, the other angles in the coordination spheres are also affected (Table 4).

A consideration of the β-diketonate chelate rings reveals that while the bond C(15)–O(2), 1.276(6) Å, is longer than C(13)–O(1), 1.242(8) Å, the difference between the corresponding C–O distances for the Pd(2) center (1.256(9) and 1.249(8) Å), however, is very small. Nevertheless, shortening of the C(14)–C(15) bond (1.37(1) Å) relative to the C(13)–C(14) bond (1.42(2) Å), as well as the C(23)–C(24) bond (1.38(2) Å) being shorter than the C(24)–C(25) bond (1.41(1) Å), suggests that the β-diketonate ring has a significant contribution from the resonance structure (IV).



IV

All the chelate and aromatic rings marked A–F (Fig. 1) are planar; the maximum deviation of the constituent atoms from their mean planes does not exceed 0.035 Å. Table 5 lists some of the important dihedral angles between these planes. Both the CF_3 groups are oriented nearly perpendicularly (87°) to the planes of the β-diketones and thus shorter intermolecular contacts are avoided.

It seems logical to conclude that complexes **2** and **3** have the same structure (I) as observed for **1**. The overall structure for these complexes appears to be favoured by a combination of electronic and steric effects associated with the chelating unsymmetrical β-diketones.

TABLE 2. Positional and equivalent isotropic thermal parameters of non-hydrogen atoms for [Pd$_2$L($-$2H)(BTA)$_2$] with e.s.d.s. in parentheses

	x	y	z	B (Å^2)
Pd1	0.65674(5)	0.04691(4)	1.00463(4)	3.83(1)
Pd2	0.35280(5)	0.05459(4)	0.52831(4)	3.56(1)
F1	0.6094(6)	0.4397(5)	1.0151(5)	9.8(2)
F2	0.8114(6)	0.5116(4)	1.1363(4)	8.8(2)
F3	0.7760(7)	0.4188(4)	0.9757(4)	8.8(2)
F4	0.5538(6)	0.4511(5)	0.7407(6)	13.9(3)
F5	0.379(1)	0.5042(5)	0.6630(5)	16.5(4)
F6	0.3874(9)	0.4024(6)	0.7652(6)	13.4(3)
O1	0.7631(4)	0.1050(4)	1.1803(3)	4.3(1)
O2	0.6675(4)	0.2157(4)	0.9976(3)	4.5(1)
O3	0.4073(5)	0.2196(4)	0.6291(4)	4.8(1)
O4	0.2538(4)	0.1140(4)	0.3883(3)	4.6(1)
N1	0.6434(6)	−0.1254(5)	0.9929(4)	4.5(2)
N2	0.3047(5)	−0.1136(4)	0.4404(4)	3.6(1)
C1	0.5619(6)	−0.0160(5)	0.8420(5)	3.5(2)
C2	0.5117(6)	0.0473(5)	0.7653(5)	3.6(2)
C3	0.4411(6)	−0.0125(5)	0.6518(5)	3.4(2)
C4	0.4254(6)	−0.1336(5)	0.6161(5)	3.4(2)
C5	0.4763(6)	−0.1977(5)	0.6919(5)	4.0(2)
C6	0.5428(6)	−0.1376(5)	0.8045(5)	3.8(2)
C7	0.3500(6)	−0.1856(5)	0.4973(5)	3.9(2)
C8	0.5895(7)	−0.1937(6)	0.8924(5)	4.6(2)
C9	0.6864(8)	−0.1751(7)	1.0897(6)	6.2(3)
C10	0.836(1)	−0.158(1)	1.1411(9)	9.1(4)
C11	0.2240(7)	−0.1502(6)	0.3194(5)	4.7(2)
C12	0.209(1)	−0.2761(8)	0.2613(6)	7.2(3)
C13	0.8044(6)	0.2096(6)	1.2374(5)	4.0(2)
C14	0.7912(7)	0.3094(6)	1.1956(5)	4.4(2)
C15	0.7297(6)	0.3034(5)	1.0844(5)	4.0(2)
C16	0.7327(8)	0.4186(6)	1.0527(6)	5.2(2)
C17	0.8813(6)	0.2326(6)	1.3611(5)	4.2(2)
C18	0.9418(7)	0.1476(6)	1.4026(6)	5.2(2)
C19	1.0195(8)	0.1708(8)	1.5175(6)	6.7(3)
C20	1.0292(9)	0.2756(8)	1.5887(6)	6.9(3)
C21	0.9663(9)	0.3586(7)	1.5479(6)	6.5(3)
C22	0.8934(8)	0.3377(6)	1.4350(6)	5.4(2)
C23	0.3794(7)	0.3066(6)	0.5933(6)	4.5(2)
C24	0.3136(7)	0.3154(6)	0.4870(6)	5.0(2)
C25	0.2546(6)	0.2193(6)	0.3897(5)	4.2(2)
C26	0.4252(9)	0.4183(6)	0.6857(6)	6.6(3)
C27	0.1816(6)	0.2410(6)	0.2792(5)	4.3(2)
C28	0.0980(8)	0.1481(7)	0.1888(6)	5.7(3)
C29	0.0258(9)	0.1661(8)	0.0849(6)	6.6(3)
C30	0.0413(9)	0.2766(8)	0.0733(7)	6.9(3)
C31	0.127(1)	0.3695(8)	0.1614(8)	8.0(4)
C32	0.1949(9)	0.3524(7)	0.2637(7)	6.7(3)

Supplementary material

Tables of thermal parameters, remaining bond lengths and angles, and H atom coordinates may be obtained from author K.N.

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TABLE 3. Selected bond lengths (Å) for [Pd$_2$L($-$2H)(BTA)$_2$]

Pd(1)–C(1)	1.957(5)	Pd(2)–C(3)	1.965(6)
Pd(1)–N(1)	2.007(6)	Pd(2)–N(2)	1.992(5)
Pd(1)–O(1)	2.110(4)	Pd(2)–O(4)	2.104(5)
Pd(1)–O(2)	2.023(5)	Pd(2)–O(3)	2.011(4)
C(13)–O(1)	1.242(8)	C(25)–O(4)	1.249(8)
C(15)–O(2)	1.276(6)	C(23)–O(3)	1.256(9)
C(13)–C(14)	1.42(2)	C(24)–C(25)	1.412(8)
C(14)–C(15)	1.37(1)	C(23)–C(24)	1.38(2)
C(13)–C(17)	1.498(8)	C(25)–C(27)	1.49(1)

TABLE 4. Selected bond angles (°) for [Pd$_2$L($-$2H)(BTA)$_2$]

N(1)–Pd(1)–C(1)	81.2(2)	N(2)–Pd(2)–C(3)	81.4(2)
O(1)–Pd(1)–O(2)	90.7(2)	O(3)–Pd(2)–O(4)	90.5(2)
O(1)–Pd(1)–N(1)	95.6(2)	O(4)–Pd(2)–N(2)	94.4(2)
O(2)–Pd(1)–C(1)	92.6(2)	O(3)–Pd(2)–C(3)	93.6(3)
N(1)–Pd(1)–O(2)	173.2(2)	N(2)–Pd(2)–O(3)	175.1(3)
O(1)–Pd(1)–C(1)	176.5(2)	O(4)–Pd(2)–C(3)	175.9(2)
Pd(1)–O(1)–C(13)	125.2(4)	Pd(2)–O(4)–C(25)	125.3(4)
Pd(1)–O(2)–C(15)	122.5(4)	Pd(2)–O(3)–C(23)	122.9(4)
O(1)–C(13)–C(14)	125.8(5)	O(4)–C(25)–C(24)	124.9(6)
O(2)–C(15)–C(14)	131.5(7)	O(3)–C(23)–C(24)	131.4(6)
C(13)–C(14)–C(15)	124.2(5)	C(23)–C(24)–C(25)	124.7(7)

TABLE 5. Selected dihedral angles between the planes for [Pd$_2$L($-$2H)(BTA)$_2$]

Plane	Plane	Angle (°)
A	B	7.8(0.3)
A	C	4.9(0.4)
B	D	1.8(1.7)
C	D	6.9(0.4)
A	F	23.8(0.3)
B	G	15.7(0.3)
E	F	16.2(0.5)
E	G	16.1(0.3)
F	G	31.1(0.3)

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