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Nickel(II) and palladium(II) complexes with acylhydrazone ligands of α-diketones: the electronic and steric factors affecting the formation of the dimeric palladium(II) complexes

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Abstract

Palladium(II) acetate reacts with butane-2,3-dione bis(octanoylhydrazone) (H_2oct) giving a dimeric [Pd_2(oct)$_2$] complex as main product; as shown by X-ray crystal analysis, the ligands are bideprotonated and in each of them one carbonyl oxygen and the two imine nitrogens are bonded to one palladium ion, whereas one hydrazide nitrogen is bonded to the second palladium, giving rise to a N_3O square planar coordination. The core of the complex is constituted by an unusual six-membered PdN_2PdN_2 ring. The same arrangement is also found in [Pd_2(ben)$_2$] (H_2ben, butane-2,3-dione bis(benzoylhydrazone)) where the alkyl chains of the ligand H_2oct are substituted by phenyl rings. On the contrary, the corresponding nickel(II) complexes are monomers and the coordination is N_2O_2 square planar. Monomers are also the nickel(II) and palladium(II) complexes with butane-2,3-dione bis(thiobenzoylhydrazone) and phthalic dicarboxaldehyde bis(benzoylhydrazone). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Hydrazone; Nickel complexes; Palladium complexes; Dimer complexes

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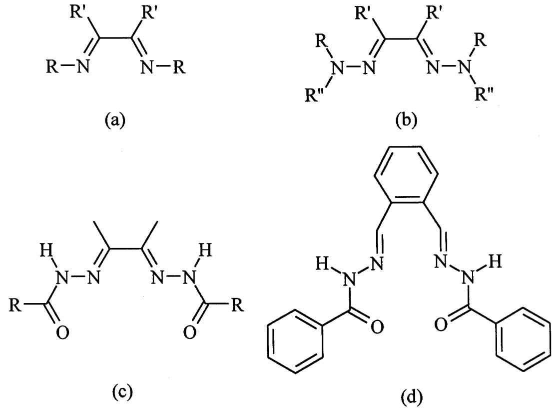
1. Introduction

The 1,4-disubstituted 1,4-diaza-1,3-butadiene (α-diimine) ligands (Scheme 1(a)) have been studied for their versatile coordination behaviour and the interesting properties of their metal complexes [1]. For example, they can be used as metallomesogens [2] or as homogeneous catalysts in the copolymerization of styrene and 4-methylstyrene with carbon monoxide [3], or in the hydrogenation of alkene or carbon–carbon cross-coupling reactions [4]. These ligands are generally prepared by condensation of a α-diketone with an amine, but *N*-mono- [5] and *N*,*N*-di-substituted [6] hydrazines (Scheme 1(b)) were also used. Less is known about the coordination abilities of the ligands obtained from condensation of α-diketones and hydrazides [7] (Scheme 1(c)) even if some studies on their analytical use are reported [8].

As an extension of our work on the chelating properties of polydentate ligands derived from 1,2-diketones



Scheme 1.

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[9], here we report the coordinating behaviour towards palladium(II) and nickel(II) of some hydrazonic ligands derived from 2,3-butadione (Scheme 1(c), $R = C_7H_{15}$, C_6H_5) and phthalic dicarboxaldehyde (Scheme 1(d)). The X-ray structure analysis of $[Pd_2(oct)_2]$ (H_2oct, butane-2,3-dione bis(octanoylhydrazone)), $[Pd_2(ben)_2]\cdot EtOH$ (H_2ben, butane-2,3-dione bis(benzoylhydrazone)), and Ni(tben) (H_2tben, butane-2,3-dione bis(thiobenzoylhydrazone)) are also reported.

2. Experimental

Reagents of commercial quality were used without further purification. Physical measurements were made as described elsewhere [10]. All new compounds gave satisfactory elemental analyses.

2.1. Crystal structure determination of $[Pd_2(oct)_2]$, $[Pd_2(ben)_2]\cdot EtOH$ and Ni(tben)

Well shaped single crystals suitable for X-ray diffractometric analysis were obtained for $[Pd_2(oct)_2]$ (orange plates), $[Pd_2(ben)_2]\cdot EtOH$ (red flat prisms) and Ni(tben) (dark green plates). Diffraction data for the compounds were measured at room temperature on a Philips PW1100 diffractometer, using Mo Kα ($\lambda = 0.71073$ Å) radiation, graphite monochromator, $\theta/2\theta$ scan. In all cases the intensity of one standard reflection was monitored every 100 measurements, and no significant crystal decay was observed throughout data collection. The intensity data were processed with a peak-profile procedure and corrected for Lorentz and polarization effects. Table 1 reports a summary of relevant parameters concerning data collection and structure refinement for the compounds. For $[Pd_2(ben)_2]\cdot EtOH$ data were corrected for absorption effects by using the ψ-scan method. The phase problem was solved by direct methods, using SHELXS86 [11], which allowed the retrieval of the molecular core; the structures were completed by a combination of least-squares refinement cycles and analysis of the Fourier difference maps. Neutral atomic scattering factors were employed, those for non-hydrogen atoms being corrected for anomalous dispersion. Structures were refined by full-matrix least-squares on F^2 with SHELXL97 [12] for $[Pd_2(oct)_2]$ and by least-

Table 1
Crystal data and structure determination parameters for compounds $[Pd_2(oct)_2]$, $[Pd_2(ben)_2]\cdot EtOH$ and Ni(tben)

Compound	$[Pd_2(oct)_2]$	$[Pd_2(ben)_2]\cdot EtOH$	Ni(tben)
Chemical formula	$C_{40}H_{72}N_8O_4Pd_2$	$C_{38}H_{40}N_8O_5Pd_2$	$C_{18}H_{16}N_4S_2Ni$
Molecular weight	941.86	901.6	411.2
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	20.617(6)	10.525(6)	9.525(2)
b (Å)	16.856(5)	22.872(14)	13.853(5)
c (Å)	14.982(4)	8.700(4)	7.051(3)
α (°)		93.1(1)	91.83(4)
β (°)	103.49(2)	110.8(1)	96.30(3)
γ (°)		103.2(1)	97.85(2)
V (Å^3)	5063(2)	1885(2)	915.0(5)
Z	4	2	2
D_{calc} (g cm^{-3})	1.236	1.588	1.492
$F(000)$	1968	912	424
μ (Mo Kα) (cm^{-1})	7.51	10.1	13.0
Absorption T_{max}/T_{min}		1.000/0.707	
θ Range (°)	3–27	3–27	3–28
Index range	$-26 \leq h \leq 26$, $0 \leq k \leq 21$, $0 \leq l \leq 17$	$-13 \leq h \leq 13$, $-27 \leq k \leq 27$, $0 \leq l \leq 10$	$-12 \leq h \leq 12$, $-17 \leq k \leq 17$, $0 \leq l \leq 8$
Measured reflections	10 782	8205	4421
Independent reflections	10 373	8205	4421
Observed unique reflections [$I \geq 2\sigma(I)$]	2036	4115	1855
Parameters/restraints	495/464	630/0	290/0
R_1 (observed data)	0.0309 [a]	0.0400 [c]	0.0351 [c]
wR_2 (observed data), a, b	0.083, 0.15, 0.00 [b]	0.0415, 0.6885, 0.00225 [d]	0.0346, 0.3402, 0.00093 [d]
Goodness of fit	0.683	0.699	0.427

[a] $R_1 = \Sigma||F_o|^2 - |F_c|^2|/\Sigma|F_o|^2$.

[b] $wR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}\}$, $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$, $P = [2F_c{}^2 + \max(F_o{}^2, 0)]/3$.

[c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[d] $R_w = \Sigma|w|F_o| - |F_c||/\Sigma w|F_o|$, $w = a/(\sigma^2(F) + bF^2)$.

squares on F with SHELX76 [13] for $[Pd_2(ben)_2]\cdot EtOH$ (block-diagonal matrix) and Ni(tben) (full matrix). An $I > 2\sigma(I)$ cut off was applied on the reflections used in the refinement. In the last stages of the refinement anisotropic displacement parameters were used for all non-hydrogen atoms. For $[Pd_2(oct)_2]$ rigid-bond and similarity restraints were applied to displacement parameters of the alkyl chains, whose C–C bond distances were also restrained to be similar in all chains. Hydrogen atoms were introduced at calculated positions, riding on their carrier atoms, for $[Pd_2(oct)_2]$, and were localized on the Fourier difference maps and refined isotropically for $[Pd_2(ben)_2]\cdot EtOH$ and Ni(tben). The final geometry was analyzed by the program PARST95 [14] and the drawings were made with ZORTEP [15]. All calculations were performed on an Encore91 computer at the Centro di Studio per la Strutturistica Diffrattometrica del CNR in Parma. Besides referring to original literature, data for comparison with other compounds were retrieved and analyzed by the software packages of the Cambridge Structural Database [16] (release October 1998).

2.2. Synthesis and characterization

H_2ben and Ni(ben) [17], thiobenzoylhydrazine [18], butane-2,3-dione bis(thiobenzoylhydrazone) (H_2tben) and Ni(tben) [19] were obtained following literature findings.

2.2.1. Butane-2,3-dione bis(octanoylhydrazone) (H_2oct)

A total of 1.04 g (5.25 mmol) of octanoic hydrazide and 0.23 ml (2.62 mmol) of 2,3-butadione were refluxed for 24 h in 50 ml of ethanol with a few drops of glacial acetic acid as catalyst. The end of the reaction was confirmed by TLC (SiO_2; 2:8 hexane–ethyl acetate). Yield 95%; pale-yellow solid. M.p. 240°C. Mass spectrum (CI, *m*/*e*) 367 (MH^+, 60%). ^1H NMR ($CDCl_3$): δ 0.87 (t, 6H, $(CH_2)_6CH_3$), 1.24–1.33 (m, 16H, $(CH_2)_4CH_3$), 1.69 (m, 4H, $CH_2(CH_2)_4CH_3$), 2.07 (s, 6H, $CH_3C{=}N$), 2.69 (t, 4H, $CH_2(CH_2)_5CH_3$), 8.60 (s, 2H, NH). Selected IR bands (cm^{-1}, KBr): 3188m ν(NH), 2954–2851m ν(CH), 1668 vs ν(CO).

2.2.2. Butane-2,3-dione bis(benzoylhydrazone) (H_2ben)

^1H NMR (d_6-DMSO): δ 2.03 (s, 6H, CH_3), 7.48–7.59 (m, 6H, CH_{ar}), 7.85 (d, 4H, CH_{ar}), 10.78 (m, 2H, NH).

2.2.3. Butane-2,3-dione bis(thiobenzoylhydrazone) (H_2tben)

^1H NMR ($CDCl_3$): δ 1.90 (s, 6H, CH_3), 6.40 (s, 2H, NH), 7.35–7.38 (m, 6H, CH_{ar}), 7.58–7.61 (m, 4H, CH_{ar}).

2.2.4. Phthalic dicarboxaldehyde bis(benzoylhydrazone) (H_2phben)

A total of 0.5 g (3.7 mmol) of phthalic dicarboxaldehyde and 1.0 g of benzoylhydrazine (7.4 mmol) were dissolved in 50 ml of ethanol and refluxed for 1 h. During the refluxing a white powder started to separate; on cooling an abundant white precipitate was obtained. Yield > 90%. M.p. 170–178°C. Mass spectrum (CI, *m*/*e*) 370 (MH^+, 100%). ^1H NMR (d_6-DMSO): δ 12.05 (s, D_2O exchangeable, 2H, NH), 8.96 (s, 2H, HC=N), 7.94–7.54 (m, 14H). Selected IR bands (cm^{-1}, KBr): 3263m,br ν(NH), 3065m $\nu(CH_{ar})$, 1657vs ν(CO), 1562m ν(CN).

2.2.5. Reaction of H_2oct with $Pd(CH_3COO)_2$

A total of 0.15 g (0.41 mmol) of the ligand in 30 ml methanol/chloroform and 0.092 g (0.41 mmol) of $Pd(CH_3COO)_2$ in methanol were refluxed for 24 h; the TLC (SiO_2, ethyl acetate) showed the presence of two products: a dark-green ($R_f = 0$) and an orange one ($R_f = 0.7$). They were separated by column chromatography using as eluents ethyl acetate (orange product) and then chloroform (green product). Well shaped crystals of the orange product, which turned out to have the formula $[Pd_2(oct)_2]$, were obtained by recrystallization from methanol/chloroform. Yield 45%. M.p. 115–116°C. Mass spectrum (CI, *m*/*e*): 940 (M^+, 100%), 470, 365. ^1H NMR ($CDCl_3$): δ 0.88 (m, 12H, $(CH_2)_6CH_3$), 1.28 (m, 24H, $(CH_2)_3CH_3$), 1.58 and 1.69 (m, 4H, $CH_2(CH_2)_4CH_3$), 1.94 and 2.16 (s, 6H, $CH_3C{=}N$), 2.20–2.59 (m, 8H, $CH_2(CH_2)_5CH_3$). Selected IR bands (cm^{-1}, KBr): 2954–2854s ν(CH), 1627vs,br ν(CO). Green product. Yield 20%. M.p. > 300°C. ^1H NMR ($CDCl_3$): δ 8.24, 8.65 (s, D_2O exchangeable, NH), 2.09 (m, $CH_3C{=}N$), 1.26 (m, $(CH_2)_6CH_3$), 0.88 (m, $(CH_2)_6CH_3$). Selected IR bands (cm^{-1}, KBr): 3100w,br ν(NH), 2924–2900s ν(CH), 1750–1612m ν(CO).

2.3. $[Pd_2(ben)_2]$

A total of 0.061 g (0.27 mmol) of $Pd(CH_3COO)_2$ dissolved in 10 ml of acetonitrile were added to 0.05 g (0.26 mmol) of the ligand suspended in 10 ml of absolute ethanol. The brown solution was stirred for 24 h at room temperature, filtered on Celite to remove some traces of black palladium and left to evaporate. The solid was recrystallized from chloroform thus obtaining red crystals useful for X-ray diffraction analysis. The same product was obtained starting from the ligand and Li_2PdCl_4; then the pH of the solution was adjusted to approximately pH 9 by adding NaOH. Yield 72%. M.p. 120°C. ^1H NMR ($CDCl_3$): δ 2.19 and 2.27 (s, 6H, $CH_3C{=}N$), 7.34–7.51 (m, 12H, H_{ar}), 7.94 (d, 4H, H_{ar}), 8.02 (d, 4H, H_{ar}). Selected IR bands (cm^{-1}, KBr): 3020w ν(CH), 1650m, 1613s ν(CO), 1598 ν(CN).

2.3.1. Ni(ben)

^{1}H NMR (CDCl$_3$): δ 1.87 (s, 6H, *CH*$_3$C=N), 7.18–7.34 (m, 6H, H$_{ar}$), 7.87 (d, 4H, H$_{ar}$).

2.3.2. Pd(tben)

A total of 0.107 g (0.3 mmol) of the ligand in 20 ml of absolute ethanol and 0.67 g (0.3 mmol) of Pd(CH$_3$COO)$_2$ in ethanol/acetonitrile were mixed and stirred for 1 h at room temperature; immediately the formation of a brown precipitate was observed. The solid was collected and dried. Yield 68%. M.p. > 300°C. ^{1}H NMR (CDCl$_3$): δ 2.17 (s, 6H, *CH*$_3$C=N), 7.28 (t, 4H, H$_{ar}$), 7.42 (t, 2H, H$_{ar}$), 8.01 (d, 4H, H$_{ar}$).

2.3.3. Ni(tben)

^{1}H NMR (CDCl$_3$): δ 2.05 (s, 6H, *CH*$_3$C=N), 7.31 (t, 4H, H$_{ar}$), 7.45 (t, 2H, H$_{ar}$), 8.01 (d, 4H, H$_{ar}$).

2.3.4. Pd(phben)

A total of 0.05 g (0.13 mmol) of the ligand were dissolved in boiling absolute ethanol, then 0.03 g (0.13 mmol) of Pd(CH$_3$COO)$_2$ in acetonitrile was added. During the refluxing (2 h) the clear solution became dark-green and some precipitate formed. The solvent was removed and the powder redissolved in 40 ml of chloroform; yellow microcrystals were obtained from the chloroform solution by adding 10 ml of absolute ethanol and leaving at −20°C for 1 week. Yield 75%. M.p. 164–170°C (dec.). ^{1}H NMR (d$_6$-DMSO): δ 9.41 (s, 2H, HC=N), 8.34 (dd, 2H, H$_{ar}$ α(C=N)), 8.10 (d, 4H, H$_{ar}$ α(C=O)), 7.95 (dd, 2H, H$_{ar}$ β(C=N)), 7.46–7.59 (m, 6H, H$_{ar}$). Selected IR bands (cm^{-1}, KBr): 3050m,br ν(CH$_{ar}$), 2990w,br ν(CH), 1592m ν(CN).

2.3.5. Ni(phben)

A total of 0.1 g of the ligand (0.26 mmol) and a slight excess of Ni(CH$_3$COO)$_2$·4H$_2$O in hot absolute ethanol were refluxed for 1 h. On standing an orange powder formed that was dried and characterized. Yield 70%. M.p. 261–262°C. ^{1}H NMR (CDCl$_3$): δ 9.07 (s, 2H, HC=N), 8.11 (d, 4H, H$_{ar}$ α(C=O)), 7.79 (d, br 4H, H$_{ar}$), 7.45–7.35 (m, 6H, H$_{ar}$). Selected IR bands (cm^{-1}, KBr): 3050m,br ν(CH$_{ar}$), 2993w,br ν(CH), 1595m ν(CN).

3. Results and discussion

The potentially quadridentate ligands H$_2$oct (Scheme 1(c), R = C$_7$H$_{15}$) and H$_2$ben (Scheme 1(c), R = C$_6$H$_5$) are obtained by condensation of 2,3-butadione and the opportune hydrazide in 1:2 molar ratio. In solution they are symmetric (in the ^{1}H NMR spectrum there is only one peak for the two methyl groups and the two hydrazone hydrogens), probably with the two arms in the less hindered *E,E* configuration around the imine bonds. In solid state the situation seems to be the same, in fact only one ν(C=O) band is observable. The *E,E* configuration for the two imine bonds and the *anti* conformation around the central C–C bond were found in all the butane-2,3-dione dihydrazones which have been characterized by X-ray diffraction [20].

After the work-up of the reaction between palladium(II) acetate and H$_2$oct (see Section 2), two different products are obtained, one orange and the other green. The elemental analysis of the orange compound suggests the formula Pd(oct); in the mass spectrum the molecular peak is twice the value of Pd(oct). In the IR spectrum a strong band at 1627 cm^{-1} attributable to an uncoordinated C=O group is still present, whereas in the ^{1}H NMR spectrum the peaks of the hydrazone hydrogens are absent but there are two sets of signals for the two arms of the ligand thus suggesting an asymmetric coordination mode.

The single-crystal X-ray determination made clear the structure of the complex: a perspective view of [Pd$_2$(oct)$_2$] is shown in Fig. 1, along with the labelling scheme. Table 2 reports the most relevant molecular geometric parameters. The complex is a dinuclear dimer, where two bideprotonated oct^{2-} molecules act as asymmetric tridentate ligands towards one metal and as monodentate ligands towards the other metal. Each metal is coordinated in a square planar fashion by one carbonyl and both iminic nitrogen atoms belonging to one ligand (O1, N2 and N3 for Pd1, and O3, N6 and N7 for Pd2), and by the remaining amidic nitrogen belonging to the other ligand (N8 for Pd1 and N4 for Pd2). Both the coordination arrangements do not deviate significantly from planarity. Thus, five chelation rings are present, two five-membered pairs formed by the tridentate arrangement of each ligand around the metals, and one six-membered dipalladacycle defined by the two N–N bridging units between the two metals (N3–N4 and N7–N8). The amidic nitrogen atoms adjacent to the coordinated carbonyls (N1 and N5) are not involved in coordination, as well as the carbonyl oxygens adjacent to the coordinated amidic nitrogens (O2 and O4). The four five-membered chelation rings are all

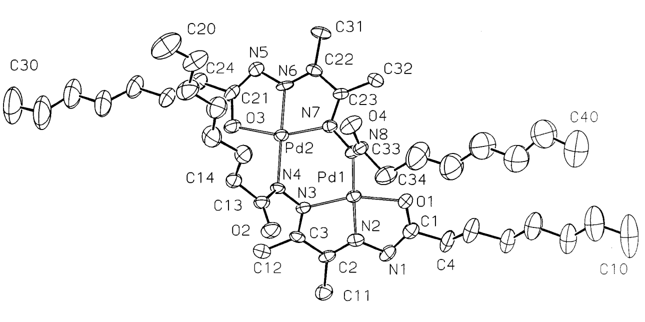

Fig. 1. ORTEP view of [Pd$_2$(oct)$_2$], with thermal ellipsoids drawn at 30% probability level. For clarity, hydrogen atoms are omitted and labelling of alkyl chains is not reported.

Table 2
Selected bond distances (Å) and angles (°) with s.u.s in parentheses for [$Pd_2(oct)_2$]

Bond lengths			
Pd1–O1	2.05(1)	N3–N4	1.41(2)
Pd1–N2	2.04(1)	N3–C3	1.38(2)
Pd1–N3	2.02(1)	N4–C13	1.38(2)
Pd1–N8	2.14(1)	N5–N6	1.37(2)
Pd2–O3	2.040(9)	N5–C21	1.32(2)
Pd2–N4	2.08(1)	N6–C22	1.31(2)
Pd2–N6	1.97(1)	N7–N8	1.42(2)
Pd2–N7	2.01(1)	N7–C23	1.33(2)
O1–C1	1.36(3)	N8–C33	1.43(2)
O2–C13	1.24(2)	C1–C4	1.51(3)
O3–C21	1.34(2)	C2–C3	1.50(3)
O4–C33	1.26(3)	C13–C14	1.54(2)
N1–N2	1.40(3)	C21–C24	1.50(2)
N1–C1	1.36(2)	C22–C23	1.49(2)
N2–C2	1.31(2)	C33–C34	1.53(3)
Bond angles			
O1–Pd1–N2	79.0(6)	Pd1–N3–N4	123.2(9)
O1–Pd1–N3	159.0(5)	Pd1–N3–C3	112(1)
O1–Pd1–N8	99.7(5)	Pd2–N4–N3	116.0(8)
N2–Pd1–N3	79.9(6)	N6–N5–C21	107(1)
N2–Pd1–N8	177.8(5)	Pd2–N6–N5	117.4(9)
N3–Pd1–N8	101.3(5)	Pd2–N6–C22	118(1)
O3–Pd2–N4	99.2(4)	Pd2–N7–N8	124.9(9)
O3–Pd2–N6	80.7(5)	Pd2–N7–C23	116(1)
O3–Pd2–N7	159.7(4)	Pd1–N8–N7	113.5(8)
N4–Pd2–N6	178.7(4)	Pd1–N8–C33	130(1)
N4–Pd2–N7	101.0(5)	O1–C1–N1	129(2)
N6–Pd2–N7	79.1(6)	N2–C2–C3	110(2)
Pd1–O1–C1	108(1)	N3–C3–C2	119(1)
Pd2–O3–C21	105(1)	O3–C21–N5	130(2)
N2–N1–C1	105(2)	N6–C22–C23	114(2)
Pd1–N2–N1	119(1)	N7–C23–C22	113(1)
Pd1–N2–C2	119(1)		

planar within 0.04 Å, whereas the six-membered dipalladacycle has a butterfly shape with the hinge along the N4–N8 bond; consequently, the two square planar coordination systems make a dihedral angle of 133°, and the Pd1···Pd2 distance is 3.724(2) Å (Fig. 2). A great number of six-membered dimetallacycles M–N–N–M–N–N are structurally known, but in almost all of them the bridging groups belong to aromatic heterocycles such as pyridazine, pyrazole or triazole; some others contain bridging ethylendiaminic ligands. Only in five complexes is the bridging performed by acyclic N–N systems, like those present in [$Pd_2(oct)_2$]. In general, it is observed that the ligands of the former class induce a boat conformation for the dimetallacycle, with metals at the flaps, or in some cases a planar ring is found. On the contrary, ligands similar to the present one induce the butterfly folding described above. Of particular interest is the comparison between [$Pd_2(oct)_2$] and bis(μ^2-acetophenone *N*-phenylhydrazone-*C*,*N*,*N*′)-bis(trimethylphosphite)-dipalladium [21], and bis(trimethoxyphosphine - (μ^2 - 2 - (1 - (4 - nitrophenylhydrazono)ethyl) phenyl-*C*,*N*,*N*′)-palladium) [22], the only other palladium complexes containing acyclic N–N bridges in the six-membered dimetallacycle. In both cases the span of the butterfly wings (118 and 117°) is narrower than in [$Pd_2(oct)_2$], whereas the metals are slightly farther apart (Pd···Pd = 3.788 and 3.803 Å). The presence of the five condensed chelation rings in the dinuclear unit induces major angular distortion in the square coordination around the metals, mostly by reducing to about 80° the angles between *cis* donors belonging to the five-membered rings, and by widening to about 100° the angles belonging to the six-membered ring. The analysis of bond distances of the hydrazonic skeleton of [$Pd_2(oct)_2$] shows variations difficult to rationalize completely on the basis of electronic delocalization and steric strains, and probably mostly due to statistical fluctuations. The most remarkable feature is that there are no relevant differences between the bond length of the bridging (1.36(4) Å) and non-bridging (1.34(4) Å) N–N systems, probably due to the possibility of charge delocalization on the central molecular core — in the other two palladium complexes [21,22], the bridging N–N distances are slightly longer than here, 1.38 and 1.40 Å, respectively, due to the presence of aromatic substituents instead of the C(O)-alkyl groups. The whole complex has a rough two-fold symmetry around the central dipalladacycle Pd1–N3–N4–Pd2–N7–N8. The alkyl chains involved in the carbonyl coordination (C4–C10 and C24–C30) are extended and roughly contained in the planes of the butterfly wings, whereas the free carbonyl protrude almost orthogonally out of the hinge, as shown by the torsion angles C3–N3–N4–C13 = 71(2)° and C23–N7–N8–C33 = 69(2)°. The chains C33–C40 and C13–C20 extend in different directions, perturbing the approximate overall two-fold molecular symmetry (Fig. 1). The crystal packing shows no relevant interaction below 3.40 Å, with the exception of the contacts C31···O4(*i*) = 3.35(2) Å, C31–H···O4(*i*) = 136(1)° and C32···O4(*i*) = 3.35(2) Å, C32–H···O4(*i*) = 129(1)° ($i = -x, 1-y, 2-z$); the extended alkyl chains of adjacent molecules face each other.

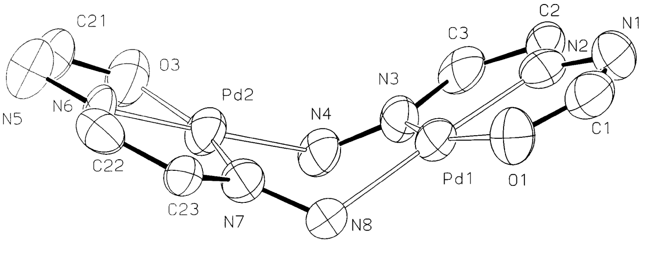

Fig. 2. Butterfly geometry for five fused chelation rings in [$Pd_2(oct)_2$]. A similar arrangement is found in [$Pd_2(ben)_2$].

The green product of the reaction between H_2oct and palladium(II) acetate has not been unambiguously characterized. The spectroscopic data are not clear

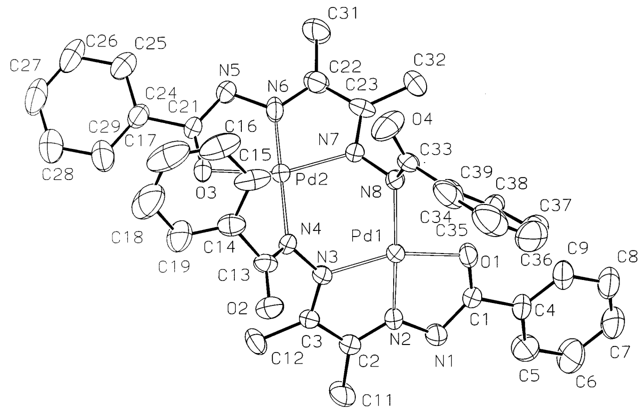

Fig. 3. ORTEP view of $[Pd_2(ben)_2]$, with thermal ellipsoids drawn at 50% probability level. For clarity, hydrogen atoms are omitted.

enough to rule out the presence of the acetate as counterion. The band at 1750 cm^{-1} in the IR region and the D_2O exchangeable signals in the NMR spectrum imply that at least one arm of the ligand is not deprotonated and its carbonyl group is not coordinated to the metal. The complexing ability of the ligand in the neutral form is in fact very poor: in the reaction between $NiCl_2{\cdot}4H_2O$ and H_2oct in methanol, free ligand is clearly visible in the TLC (SiO_2, 1:1 hexane–ethyl acetate) after 4 h at refluxing but if the pH is risen above 9 by adding aqueous NaOH, the complex forms immediately.

It is known [23] that the coordinating ability of the carbonyl group in the acylhydrazones is deeply influenced by the R substituents (Scheme 1(c)) and in particular it becomes greater as the conjugating ability of R increases. With the aim to force the N_2O_2 coordination around the palladium ion by increasing the donor ability of the C=O groups, the alkyl chains of H_2oct are substituted by phenyl rings thus obtaining the H_2ben ligand. It reacts with palladium(II) acetate giving a dimeric complex, $[Pd_2(ben)_2]$ with the same spectroscopic peculiarities of $[Pd_2(oct)_2]$. Contrary to the above reaction with H_2oct, now only the dimeric product formed: H_2ben is easily deprotonated because the negative charge can be delocalized in the phenyl rings. The reaction was also made in high dilution conditions (10^{-6} M), but the dimer was, again, the only product.

A perspective view of the $[Pd_2(ben)_2]$ molecule is shown in Fig. 3, while relevant geometric parameters are listed in Table 3. $[Pd_2(ben)_2]$ is a dimeric dinuclear complex like $[Pd_2(oct)_2]$, in which two doubly deprotonated ben^{2-} ligands bridge two metals by two N–N systems. Each ligand acts as a N_2O tetradentate donor towards one metal and as a N monodentate donor towards the other metal to complete the square coordination, which in both cases is planar within 0.10 Å. The five-membered chelated rings are planar within 0.02 Å, and the six-membered dipalladacycle has a butterfly conformation with a dihedral angle of 121° around the hinge at N4–N8 (133° in $[Pd_2(oct)_2]$). The smaller width of the butterfly span determines a shorter Pd1···Pd2 distance for $[Pd_2(ben)_2]$ (3.669(3) Å) than for $[Pd_2(oct)_2]$ (3.724(2) Å). The angular distorsions induced by the chelation strains on the coordination geometry are comparable with those observed above, whereas the metal–donor distances, more precisely determined than for $[Pd_2(oct)_2]$, reveal that the bonds to N2 and N6 are significantly shorter than the others, due to the fact that the formal negative charge resonating along the N–N and CO systems is donated to only one metal, whereas for N3, N4, N7 and N8 it is shared by two metals. The analysis of bond distances along the hydrazonic core shows that the bridging N–N bonds are longer than the non-bridging ones (1.413(7) and 1.37(1) Å, respectively), in contrast with the findings for $[Pd_2(oct)_2]$.

Table 3
Selected bond distances (Å) and angles (°) with s.u.s in parentheses for $[Pd_2(ben)_2]{\cdot}EtOH$

Bond lengths			
Pd1–O1	2.051(5)	N3–N4	1.414(7)
Pd1–N2	1.904(6)	N3–C3	1.295(8)
Pd1–N3	1.995(5)	N4–C13	1.35(1)
N8–Pd1	2.032(5)	N5–N6	1.363(7)
Pd2–O3	2.055(5)	N5–C21	1.334(8)
Pd2–N4	2.057(6)	N6–C22	1.295(7)
Pd2–N6	1.920(6)	N7–N8	1.412(7)
Pd2–N7	2.017(5)	N7–C23	1.301(9)
O1–C1	1.277(8)	N8–C33	1.320(8)
O2–C13	1.22(1)	C1–C4	1.481(9)
O3–C21	1.286(9)	C2–C3	1.47(1)
O4–C33	1.237(8)	C13–C14	1.51(1)
N1–N2	1.380(7)	C21–C24	1.480(9)
N1–C1	1.327(8)	C22–C23	1.46(1)
N2–C2	1.303(7)	C33–C34	1.52(1)
Bond angles			
O1–Pd1–N2	79.5(2)	Pd1–N3–N4	125.0(4)
O1–Pd1–N3	159.7(2)	Pd1–N3–C3	113.7(5)
N8–Pd1–O1	100.2(2)	Pd2–N4–N3	108.9(4)
N2–Pd1–N3	80.3(2)	N6–N5–C21	108.7(5)
N8–Pd1–N2	176.1(2)	Pd2–N6–N5	118.5(4)
N8–Pd1–N3	100.1(2)	Pd2–N6–C22	117.6(5)
O3–Pd2–N4	100.6(2)	Pd2–N7–N8	124.1(4)
O3–Pd2–N6	79.1(2)	Pd2–N7–C23	113.4(5)
O3–Pd2–N7	159.2(2)	N7–N8–Pd1	112.1(4)
N6–Pd2–N4	173.8(3)	C33–N8–Pd1	130.2(4)
N7–Pd2–N4	99.9(2)	O1–C1–N1	127.0(7)
N6–Pd2–N7	80.1(2)	N2–C2–C3	111.8(6)
Pd1–O1–C1	107.4(4)	N3–C3–C2	115.6(6)
Pd2–O3–C21	107.9(4)	O3–C21–N5	125.8(7)
N2–N1–C1	107.6(5)	N6–C22–C23	113.9(6)
Pd1–N2–N1	118.5(4)	N7–C23–C22	114.8(6)
Pd1–N2–C2	118.7(5)		

These findings can be compared with those observed for the cation *trans*-diammine[2,3-butanedione bis-(4-methoxybenzoylhydrazonato)]cobalt(III) [24], where both the ligand arms are deprotonated and coordinate the metal by the hydrazonic N and the carbonyl O. This is the only other known crystal structure containing a butane-2,3-dione hydrazonic ligand [25][1]: C=N = 1.307(1), N–N = 1.37(1), N–C(O) = 1.325(6), C=O = 1.295(4), C(O)–$C_6H_4OCH_3$ = 1.47(1) Å. These values are in good agreement with those observed for the NO donor systems in $[Pd_2(ben)_2]$ and indicate that both the Pd–N–N–CO chelation ring and the terminal aromatic groups are involved in a certain degree of charge delocalization. The situation is significantly different for the ligand arms containing the NN bridging groups and the free carbonyls: the coordination of the second N withdraws electronic density from the N–N bond and from the bond between the first N and Pd, which both elongate. The N–C(O) length is practically unaffected by the different coordination mode, and its partial multiple bond character is built at the expense of the Pd2–N4 and Pd1–N8 bonds, which are practically equivalent to Pd1–N3 and Pd2–N7. The shortening of the uncoordinated C=O bonds is accompanied by a slight lengthening of the C–C_6H_5 bonds. Even if the structural data for $[Pd_2(oct)_2]$ are less reliable, they seem to suggest that the lack of resonance for the C(O)-alkyl system shifts the electronic delocalization more towards the N–C(O) and N–N bonds, the former becoming sensitive to the CO coordination, the latter increasing the bond order.

As observed for $[Pd_2(oct)_2]$, the free carbonyls in $[Pd_2(ben)_2]$ point away from the condensed chelation rings, as shown by torsion angles C3–N3–N4–C13 = 80(1)° and C23–N7–N8–C33 = 64(1)°. The phenyl rings bonded to the coordinated carbonyls are almost coplanar with the C=O groups (O1–C1–C4–C9 = −12° and O3–C21–C24–C29 = 11°), whereas the phenyls bonded to the free carbonyls C13 and C33 are rotated by 35° and −58°, respectively.

The crystal packing is characterized by the presence of an ethanol molecule, which is strongly hydrogen-bonded to O4 (O30···O4 = 2.761(9) Å, O30–H···O4 = 166(9)°). The only other relevant interaction below 3.40 Å is: C6···O2(i) = 3.353(9) Å, C6–H···O2(i) = 130(7)° ($i = 1 - x, 1 - y, 2 - z$).

From the literature [17] it is known that the corresponding Ni(II) complex, Ni(ben), has a N_2O_2 square planar structure: in the IR spectrum there are no ν(C=O) bands and in ^{1}H NMR the two arms of the ligand are equivalent and give rise to only one set of signals.

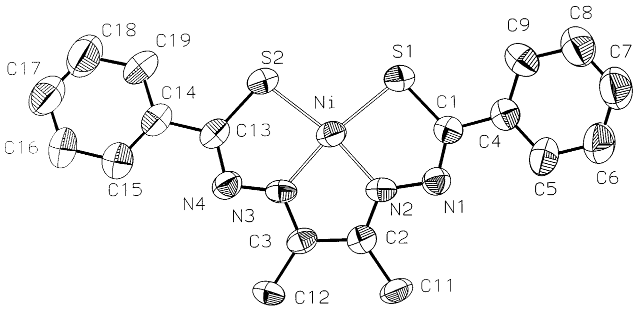

Fig. 4. ORTEP view of Ni(tben), with thermal ellipsoids drawn at 50% probability level. For clarity, hydrogen atoms are omitted.

The ligand H_2tben is synthesized starting from butane-2,3-dione and thiobenzoylhydrazine with the aim to substitute oxygen with sulfur, that has more affinity for palladium(II); the reactions with Ni(II) and Pd(II) acetates give only one product. Considering that the ^{1}H NMR spectra are highly symmetric, the signals of the hydrazone hydrogens are absent and in mass spectra there is the molecular peak of the monomer, it is possible to conclude that both complexes are monomeric and square planar, with the bideprotonated ligand that coordinates to the metal with the two imine nitrogens and the two sulfur atoms. This arrangement is confirmed by the X-ray structure analysis carried on the Ni(tben) complex. The molecular structure and labelling scheme of Ni(tben) are viewed in Fig. 4, and relevant geometric parameters are listed in Table 4. The neutral complex is monomeric and the doubly deprotonated tben^{2-} ligand behaves as a symmetric N_2S_2 donor, by coordinating the Ni atom in a square planar

Table 4
Selected bond distances (Å) and angles (°) with s.u.s in parentheses for Ni(tben)

Bond lengths			
Ni–S1	2.160(2)	N2–C2	1.311(6)
Ni–N2	1.865(3)	C2–C3	1.488(6)
Ni–N3	1.862(4)	C3–N3	1.309(6)
Ni–S2	2.168(1)	N3–N4	1.377(5)
C1–S1	1.750(5)	N4–C13	1.296(6)
C1–C4	1.481(7)	C13–S2	1.768(5)
C1–N1	1.317(6)	C13–C14	1.467(6)
N1–N2	1.368(6)		
Bond angles			
S1–Ni–N2	86.4(1)	Ni–N2–C2	115.7(3)
S1–Ni–N3	169.8(1)	N1–N2–C2	119.7(4)
S1–Ni–S2	103.44(5)	N2–C2–C3	112.6(4)
N2–Ni–N3	83.4(2)	C2–C3–N3	111.9(4)
N2–Ni–S2	170.1(1)	Ni–N3–C3	116.3(3)
N3–Ni–S2	86.8(1)	Ni–N3–N4	123.7(3)
S1–C1–N1	123.2(4)	N3–N4–C13	111.7(4)
Ni–S1–C1	95.3(1)	N4–C13–S2	123.1(4)
C1–N1–N2	110.6(4)	Ni–S2–C13	94.8(2)
Ni–N2–N1	124.5(3)		

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[1] The crystal structure of [Ni(o-phen)(ethoxy)(Hben)] is reported, but structural parameters are not deposited or published.

geometry. The strain of the penta-atomic chelation rings together with the steric hindrance of sulfur atoms induce a substantial angular deformation in the square coordination geometry, by widening the S1–Ni–S2 angle (103.44(5)°) and narrowing the remaining ones, which range from 83.4(1) to 86.8(1)°. The molecular core, comprising the three fused chelation rings, methyls C11 and C12, and atoms C4 and C14, is planar within 0.07 Å, and the phenyl groups C4–C9 and C14–C19 form with it dihedral angles of 16 and 2°, respectively. The electronic delocalization along the system C=N–N–C(S)–C_6H_5 is similar to the one observed for the non-bridging arm of the ligand in $[Pd_2(ben)_2]$. The coordination is described by the averaged bond distances: Ni–S = 2.164(6), Ni–N = 1.863(4), C–S = 1.76(1) Å. In the crystallographic literature, only one complex containing the ligand tben — diacetyl-bis-(thiobenzoylhydrazonato)-dioxo-(3,6-diphenyl-9-methyl-4,5,7,8-tetraza-2-thiabicyclo(4.4.0)dec-3,6,8-trien-10-olato)-uranium(ii) [26] — and one closely related nickel complex — butane-2,3-dione-di(phenylthioacetyl-hydrazonato) nickel(ii) [27] — are known. The nickel complex is identical to Ni(tben), except for the fact that the terminal –CH_2–C_6H_5 substituents do not allow the extension of the resonance beyond the –C(S)– groups. The reported average bond distances are: Ni–N = 1.853(1), Ni–S = 2.151(1), C–S = 1.746(6), C=N = 1.301(5), N–N = 1.39(1), N–C(S) = 1.294(8) Å. It is seen that the larger electron-withdrawing capabilities of terminal phenyls in Ni(tben) determine an elongation of the metal–donor and C–S distances.

The crystal packing of Ni(tben) shows no relevant features apart from van der Waals interactions.

The dimerization of the palladium(II) complexes could be prevented by introducing a soft donor such as sulfur, as in H_2tben, but probably also by removing the ligand strains which make the N_2O_2 coordination unfavourable. This last approach directs the synthesis of the ligand H_2phben (Scheme 1(d)), obtained from phthalic dicarboxaldehyde and benzohydrazide. As the butane-2,3-dione derivatives in the coordination H_2phben can use two imine nitrogens and two carbonyl oxygens, but instead of three five-membered chelate rings, it forms two five-membered and one seven-membered rings as observed in [acetonylacetone bis(benzoylhydrazone)]-Ni(II), that was X-ray characterized [28]. In this compound the N–M–N angle becomes larger (106.1°) and, accordingly, the opposite O–M–O angle smaller (87.9°). The reaction between $Pd(CH_3COO)_2$ and H_2phben gave an orange microcrystalline powder which was effectively characterized as the monomer Pd(phben). The ligand results not only in being bideprotonated (in the IR the C=O band and in the ^{1}H NMR the peaks of the hydrazonic protons disappear) but also symmetric as expected for a N_2O_2 square planar coordination around palladium. The corresponding nickel(II) derivative, Ni(phben), is diamagnetic and has the same spectroscopic features as Pd(phben) therefore the same coordination is proposed.

It is possible to conclude that the palladium atom preference for nitrogen donors instead of oxygen and the ligand constrains lead to dimerization in $[Pd_2(oct)_2]$ and $[Pd_2(ben)_2]$. On the contrary, when the carbonyl oxygens of the ligand are substituted by the softer and larger sulfur atoms, the high affinity between palladium(II) and sulfur stabilizes the monomeric Pd(tben) form. If the ligand is obtained from a 1,4-diketone instead of a 1,2-diketone, the central chelation ring is seven-membered and correspondingly the O–M–O angle narrows: this seems to release the ligand strains that destabilize the N_2O_2 square planar coordination and, as a result, the monomer Pd(phben) is obtained as the only product.

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