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Synthesis and Characterization of bis[salicylideneaminato] palladium(II) Complexes. Molecular Structure of Bis[*N*-(n-butyl)(3-benzyloxy)-2-salicylideneaminato]-palladium(II), [Pd($C_{18}H_{20}NO_2$)$_2$]

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Abstract

Transition metal compounds having liquid crystalline properties can be interesting materials for practical applications. Attempting to correlate mesomorphic properties with molecular structure and crystal packing mode, we have investigated some complexes obtained from Schiff bases of long chain aliphatic amines and salicylaldehyde or 2,3-dihydroxybenzaldehyde derivatives. The X-ray structural analysis of bis[*N*-(n-butyl)(3-benzyloxy)-2-salicylideneaminato] palladium[II] is also reported.

Introduction

Chemical species having anisotropic electric and/or magnetic properties are constantly required in many technological applications. Among these new compounds a prominent role is played by the liquid crystals [1, 2]. Therefore our interest was devoted to the synthesis of organometallic species or coordination transition metal complexes, having liquid crystalline properties.

In previous reports we described the mesomorphic behaviour of some palladium(II) complexes containing orthometallated *p,p'*-disubstituted azobenzenes [3, 4]. When the ligands reacted were liquid crystals, the compounds displayed mesomorphism in the region of 150–200 °C, at temperatures of some 100 °C higher than those of the free ligands and unfortunately close to the decomposition temperatures of the complexes. An extensive physical characterization of such new materials was therefore prevented.

In liquid crystals, organic in nature, the correlations among the molecular geometry, the different mesomorphic structures and the transition temperature are known [5, 6]. In particular, for systems in which the mesophases may be brought about by purely thermal processes (thermotropic liquid crystals), rodlike molecular structures containing a strong polar group near the center of the molecule and along the longest molecular axis appear to favor liquid crystallinity. Such features should be found in palladium(II) complexes with Schiff bases, L, formed from salicylaldehydes and aliphatic amines. From the literature it is known that complexes belonging to such a series are square-planar of the type PdL_2 [7–15] generally in a *trans* PdN_2O_2 configuration.

In this paper we report on the synthesis and thermal behaviour of the palladium(II) complexes obtained from Schiff bases formed from long chain aliphatic amines and salicylaldehyde or 2,3-dihydroxybenzaldehyde derivatives and the X-ray structural analysis of bis[*N*-(n-butyl)(3-benzyloxy)-2-salicylideneaminato] palladium(II).

Experimental

Physical Measurements

Infrared spectra were run on a Perkin-Elmer model 1330 spectrometer as KBr pellets. ^{1}H NMR spectra were recorded on a Varian XL-100 spectrometer in $CDCl_3$ solutions. The thermal behaviours were monitored by means of a Mettler FP 800 thermosystem equipped with a FP 84 Microscopy Cell, heating rate 4 °C/min. Elemental analyses were performed by the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Pisa, Italy.

X-ray Data Collection and Structure Refinement

Diffraction data were collected on a Siemens-Stoe-Four-Circle diffractometer using grafite-monochromated Mo Kα ($\lambda = 0.71069$ Å) radiation. Accurate

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TABLE I. Single-Crystal X-ray Crystallographic Analysis

A. Crystal parameters	
Formula	$C_{36}H_{40}N_2O_4Pd$
Formula weight	671.14
Color	yellow
Crystal size (mm)	0.20 × 0.15 × 0.15
Space group	$P\bar{1}$
Temperature (K)	293
Cell dimensions	
a (Å)	8.798(1)
b (Å)	10.431(2)
c (Å)	10.609(2)
α (°)	112.68(3)
β (°)	110.69(3)
γ (°)	98.21(2)
V (Å^3)	795.1(4)
Z (molecules/cell)	1
Density (g/cm^3)	1.401
Radiation	Mo Kα (λ = 0.71069 Å)
μ(Mo Kα) (cm^{-1})	11.2
Orientation reflections, number, range (2θ)	20, 15–30
Scan method	$\omega-2\theta$
Data collection range, 2θ (deg)	3–55
B. Refinement parameters	
Total number of reflections collected	4100
Number with $F_o^2 > 3\sigma(F_o^2)$	3379
Number of parameters refined	252
R[a]	0.039
R_w[b]	0.045
Largest shift/e.s.d., final cycle	−0.13
Largest peak (e/Å^3)	0.67

[a] $R = [\Sigma|F_o| - |F_c|]/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

unit-cell dimensions and crystal orientation matrices were obtained from least squares refinement of $2\theta,\omega,\chi$ and ϕ values of 20 strong reflections in the range $15 < \theta < 30°$. Crystallographic data and other pertinent informations are summarized in Table I. Lorentz and polarization corrections were applied to the intensity data. Adsorption was ignored. The data were collected using the ($\theta-2\theta$) scan technique with a speed of 0.03° s^{-1}. During the course of the intensity data collection, the crystals showed no loss in intensity of three standard reflections.

From 4100 independent measured reflections ($3 < 2\theta < 55°$) 3379 were considered unique, having $I > 3\sigma(I)$, and were used to refine 252 parameters to a final residual of $R = 0.039$ and $R_w = 0.045$. The weighting scheme used in the last refinement cycles was $w = 1.0000/\sigma^2(F_o) + 0.004254\, F_o^2$.

The structure was solved by using standard Patterson and Fourier methods and refined by a full-matrix least-squares technique. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, were w was taken as σ^{-2} (F_o) All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were assigned in the scattering model in calculated idealized positions with a thermal parameter U of 0.07 Å^2 and not refined. Scattering factors, for non-hydrogen atoms were taken from ref. 16 and for hydrogen atoms from ref. 17. Anomalous dispersion corrections from ref. 18.

All calculations were performed with SHELX 76 [19] and PARST [20] set of programs on the IBM 4341 computer (Università di Messina) or on the VAX/VMS computer (Università della Calabria). The refined structure was plotted using the ORTEP program. See also 'Supplementary Material'.

Reagents

The reagents n-butylamine, n-octylamine, n-dodecylamine, salicylaldehyde, 2,3-dihydroxybenzaldehyde and benzylbromide, were Fluka A.G. reagent grade and were used without further purification. The starting complex $Pd(PhCN)_2Cl_2$ was prepared as described in the literature [21].

All the reactions involving palladium complexes were performed in on oxygen-free nitrogen atmosphere.

Preparation of the Ligands L1–L4

In a typical preparation, to 30 ml of an ethanolic solution containing 15 mmol of salicylaldehyde (for **L1** and **L2**), alternatively 2,3-dihydroxybenzaldehyde (for **L3** and **L4**), was added 15 mmol of the appropriate amine (namely n-$C_8H_{17}NH_2$ for **L1** and **L4**, n-$C_{12}H_{25}NH_2$ for **L2**, n-$C_4H_9NH_2$ for **L3**). The solution was stirred under reflux for 1 h. After cooling the solvent was removed under vacuum. Recrystallization from diethylether–hexane at −20 °C afforded the ligands in quantitative yields. The Schiff bases **L1**–**L4** were characterized by IR and ^{1}H NMR spectroscopy.

Preparation of Complexes 1–4

In a typical preparation, to 30 ml of an ethanolic solution containing 10 mmol of the appropriate ligand **L** and 10 mmol of KOH, was added 5 mmol of $Pd(PhCN)_2Cl_2$. The resulting dark yellow solution was stirred at room temperature for 48 h. The yellow air-stable precipitate which forms was collected by filtration, washed with water, ethanol then hexane and dried under vacuum. Compound **1**, $(\mathbf{L1}-H)_2Pd$, yield 60% (Found C, 63.35; H, 7.98; N, 5.07. Calc. for $C_{30}H_{44}N_2O_2Pd$ C, 63.09; H, 7.76; N, 4.90 %). Compound **2** $(\mathbf{L2}-H)_2Pd$, yield 55% (Found C, 66.68, H, 8.76, N, 4.14. Calc. for $C_{38}H_{60}N_2O_2Pd$ C, 66.79; H, 8.85, N, 4.09%). Compound **3**, $(\mathbf{L3}-H)_2Pd$, yield 70% (Found. C, 53.98; H, 5.86, N, 5.67. Calc. for $C_{22}H_{28}N_2O_4Pd$: C, 53.83, H, 5.74, N, 5.70%). Compound **4**, $(\mathbf{L4}-H)_2Pd$· yield 65% (Found: C, 59.42, H, 7.29, N, 4.58. Calc. for $C_{30}H_{44}N_2O_4Pd$· C, 59.74, H, 7.35; N, 4.64%)

Preparation of Complexes 5 and 6

In a typical preparation, to 30 ml of an ethanolic solution containing 2 mmol of complex **3** or **4** and 4 mmol of KOH was added 5 mmol of benzylbromide. The resulting mixture was stirred at room temperature for 15 h. The yellow air-stable solid formed was collected by filtration, washed with water then ethanol and dried under vacuum. Recrystallization from pentane at –20 °C afforded to **5** or **6**. Compound **5**, [3-benzyloxy(L3–2H)]$_2$Pd, yield 30% (Found: C, 64.50; H, 6.06; N, 4.12. Calc. for $C_{36}H_{40}N_2O_4Pd$: C, 64.42; H, 6.00; N, 4.17%). Compound **6**, [3-benzyloxy(L4–2H)]$_2$Pd, yield 50% (Found: C, 67.58; H, 7.27; N, 3.13. Calc. for $C_{44}H_{56}N_2O_4Pd$: C, 64.46; H, 7.20; N, 3.57%).

Results and Discussion

Ligands

In order to have available compounds with an elongated molecular shape, we have synthetized Schiff bases formed from long chain aliphatic amines. Among the aldehydes, beside the salicylaldehyde, SA, we have selected the 2,3-dihydroxybenzaldehyde, DBA (see discussion below).

The ligands, synthetized following the usual procedures and characterized by IR and ^1H NMR spectroscopy, will be indicated as L1–L4, in the text, according to the order reported in Table II.

For the sake of clarity, in the following discussion the synthetized bis-[ligand]Pd(II) compound will be divided in two groups: (i) complexes containing ligands with one hydrocarbon chain, named two tail complexes and (ii) complexes containing ligands with two hydrocarbonic chains, named four tail complexes.

TABLE II. Numbering Order of the Synthetized Ligand L

Ligand	Aldehyde	Amine
L1	SA[a]	n-$C_8H_{17}NH_2$
L2	SA[a]	n-$C_{12}H_{25}NH_2$
L3	DBA[b]	n-$C_4H_9NH_2$
L4	DBA[b]	n-$C_8H_{17}NH_2$

[a] Salicylaldehyde. [b] 2,3-Dihydroxybenzaldehyde.

Two Tail Complexes

The set of ligands L1–L4 reacts with Pd(PhCN)$_2$Cl$_2$ (2:1 molecular ratio in ethanol) giving rise to the corresponding yellow products **1**–**4** (see Table III). The complexes, obtained in good yields, were characterized by elemental analysis, IR and ^1H NMR spectroscopy (Table III).

The elemental analyses of **1**–**4** are in agreement with a Pd(L–H)$_2$ stoichiometry. Their spectroscopic data, in comparison with the data of the parent free ligands, show shifts of the ν(C=N) and δ(N–CH$_2$–) values as expected by a PdN_2O_2 complexation.

Remarkably for **3** and **4**, derived from ligands containing either $\widehat{NO}$ or $\widehat{OO}$ chelating sites, the IR spectra show a sharp ν(O–H) stretch (3460 cm^{-1} and 3480 cm^{-1} respectively) attributable to an uncomplexed OH group, while no bands indicating $\widehat{OO}$ chelation are present [22].

Four Tail Complexes

The solid state geometry of compounds prepared from unsubstituted salicylaldimines (e.g. ref. 15) shows that the longest axis of the molecule may be profitably increased by a second tail in the position adjacent to the complexed oxygen atom. Furthermore there is a simple synthetic route for preparing the proper ligands, the Williamson synthesis with activated RX halogenide. These two reasons singlet out the DBA as starting material.

The synthesis of the four tail complexes, performed reacting complexes **3** and **4** with benzylbromide (see 'Experimental'), affords the yellow products **5** and **6** (Table III). These compounds were characterized by elemental analysis, IR and ^1H NMR spectroscopy. Particularly, in the IR spectra no bands in the ν(OH) region were present, while the ^1H NMR spectra showed singlets, at δ = 5.08 for **5**

TABLE III. Physical Properties of the Schiff Bases Palladium(II) Complexes

Compound		ν(C=N)[a] (cm^{-1})	ν(O–H)[a] (cm^{-1})	δ(–O–CH_2–)[b]	δ(–N–CH_2–)[b]	Melting point (°C)
1	(L1–H)$_2$Pd	1620			3.74	139
2	(L2–H)$_2$Pd	1615			3.80	116
3	(L3–H)$_2$Pd	1620	3460		3.66	223 (dec.)
4	(L4–H)$_2$Pd	1615	3480		3.56	119
5	[3-benzyloxy(L3–H)]$_2$Pd	1615		5.08	3.82	110
6	[3-benzyloxy(L4–H)]$_2$Pd	1620		5.12	3.82	123

[a] KBr pellets. [b] ^1H NMR spectra are reported in δ units (ppm downfield from Me_4Si) in $CDCl_3$ solutions.

TABLE IV. Bond Lengths (Å) and Interbond Angles (°)

Pd–O(1)	1.961(2)	O(2)–C(7)	1.417(4)
Pd–N	2.001(3)	C(7)–C(8)	1.499(4)
N–C(18)	1.275(4)	C(8)–C(9)	1.376(4)
C(18)–C(2)	1.440(4)	C(9)–C(10)	1.389(5)
O(1)–C(1)	1.298(4)	C(10)–C(11)	1.358(6)
C(1)–C(2)	1.397(4)	C(11)–C(12)	1.364(7)
C(2)–C(3)	1.408(4)	C(12)–C(13)	1.378(6)
C(3)–C(4)	1.354(5)	C(13)–C(8)	1.366(5)
C(4)–C(5)	1.385(6)	N–C(14)	1.471(4)
C(5)–C(6)	1.373(5)	C(14)–C(15)	1.513(5)
C(6)–C(1)	1.433(4)	C(15)–C(16)	1.479(7)
C(6)–O(2)	1.356(4)	C(16)–C(17)	1.545(7)
O(1)–Pd–N	91.6(1)	C(4)–C(5)–C(6)	120.6(3)
O(1)–Pd–N′	88.4(1)	C(1)–C(6)–O(2)	113.5(3)
C(1)–C(2)–C(18)	122.1(3)	C(5)–C(6)–O(2)	125.9(3)
Pd–N–C(18)	123.4(2)	C(5)–C(6)–C(1)	120.6(3)
C(18)–N–C(14)	116.9(3)	C(8)–C(7)–O(2)	114.2(3)
Pd–N–C(14)	119.7(2)	C(7)–C(8)–C(9)	122.3(3)
N–C(18)–C(2)	127.4(3)	C(7)–C(8)–C(13)	119.1(3)
Pd–O(1)–C(1)	124.2(2)	C(9)–C(8)–C(13)	118.6(3)
O(1)–C(1)–C(2)	125.9(3)	C(8)–C(9)–C(10)	120.4(3)
O(1)–C(1)–C(6)	116.7(3)	C(9)–C(10)–C(11)	120.2(4)
C(2)–C(1)–C(6)	117.4(3)	C(10)–C(11)–C(12)	119.6(4)
C(1)–C(2)–C(18)	122.1(3)	C(11)–C(12)–C(13)	120.4(4)
C(3)–C(2)–C(1)	120.3(3)	C(12)–C(13)–C(8)	120.9(4)
C(18)–C(2)–C(3)	117.5(3)	N–C(14)–C(15)	111.5(3)
C(2)–C(3)–C(4)	120.7(3)	C(14)–C(15)–C(16)	114.3(4)
C(3)–C(4)–C(5)	120.3(3)	C(15)–C(16)–C(17)	112.5(5)
Torsion angles (°)			
C(6)–O(2)–C(7)–C(8)	78.0(4)		
Pd–O(1)–C(1)–C(6)	160.6(3)		
Pd–N–C(18)–C(2)	2.8(4)		
N–C(18)–C(2)–C(1)	10.3(4)		
C(18)–C(2)–C(1)–O(1)	–0.6(4)		
C(2)–C(1)–O(1)–Pd	–20.6(4)		
C(1)–O(1)–Pd–N	25.0(3)		
Pd–N–C(14)–C(15)	–70.7(3)		
O(1)–Pd–N–C(18)	–16.4(2)		

TABLE V. Fractional Coordinates ($\times 10^4$) for Non-Hydrogen Atoms

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Pd	5000	0	5000	371(2)
O(1)	4954(3)	1971(3)	5310(3)	484(11)
O(2)	5662(3)	4762(2)	6593(3)	498(10)
N	2440(3)	–0835(3)	3826(3)	428(10)
C(18)	1455(4)	–0050(3)	3851(3)	441(12)
C(1)	3651(4)	2422(3)	5299(3)	406(12)
C(2)	1951(4)	1528(3)	4635(3)	416(13)
C(3)	645(4)	2157(4)	4679(4)	515(16)
C(4)	1018(5)	3633(4)	5399(5)	574(18)
C(5)	2685(5)	4551(4)	6048(4)	502(16)
C(6)	3990(4)	3978(3)	6010(3)	426(13)
C(7)	6125(5)	6310(4)	7225(4)	524(15)
C(8)	6249(4)	7077(3)	8796(4)	457(13)
C(9)	6339(5)	6394(4)	9689(4)	529(16)
C(10)	6506(5)	7159(5)	11157(4)	598(19)
C(11)	6598(5)	8594(5)	11728(4)	620(17)
C(12)	6528(7)	9280(4)	10854(5)	696(20)
C(13)	6355(6)	8524(4)	9395(5)	620(19)
C(14)	1614(4)	–2432(3)	2862(4)	502(13)
C(15)	1929(5)	–2978(4)	1462(4)	579(16)
C(16)	1148(7)	–2415(6)	391(5)	749(23)
C(17)	1368(9)	–3103(9)	8917(6)	1057(36)

and $\delta = 5.12$ for **6**, which are fingerprints of the expected –O–CH_2– protons.

X-ray Crystal Structure of Bis[N-(n-butyl)(3-benzyloxy)salicylideneaminato]palladium(II), $[Pd(C_{18}H_{20}NO_2)_2]$, *5*

Crystals suitable for X-ray analysis have been obtained by recrystallization from chloroform –ethanol.

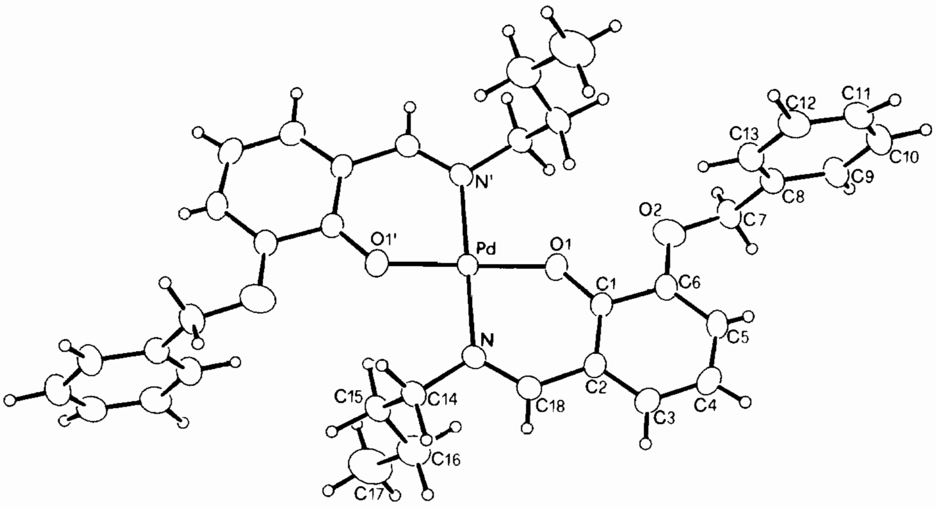

Fig. 1. Perspective view of the complex which the atomic numbering scheme.

Interatomic distances, bond angles and relevant torsion angles with their standard deviations are listed in Table IV. Non-hydrogen coordinates are shown in Table V.

The crystal structure consists of discrete molecules (Fig. 1) in which the palladium atom, lying on a center of symmetry, is square-planar coordinated in the usual *trans* PdN_2O_2 configuration. Bond distances and angles (Table IV) are in agreement with the previously reported data [10–15]. The plane containing the benzyloxy group is tilted with respect to the coordination plan by 99.19(5)°. Finally, complex **5** can be considered 'stepped' [15], the height of the step being 1.00(2) Å.

Conclusions

Concerning the preparation of the new compounds, while the syntheses of **1**–**4** appear straightforward, of note is the success in the Williamson reactions performed on the coordination compounds **3** or **4** giving rise to complexes **5** and **6** respectively.

The molecular structure of **5** has been determined by X-ray diffraction, therefore if we assume that **5** is representative of the whole series of compounds, some considerations about its molecular shape and crystal packing might be roughly extended to complexes **1**–**6**. In particular, the complexation plane, the two salicylideneamine moieties and the N-bonded aliphatic chains are nearly coplanar. Therefore the overall geometry of complexes **1**–**4** is probably planar. Moreover, in **5** and likely in **6**, the benzylic groups are nearly perpendicular and are placed above and below the previously mentioned molecular plane.

Complexes **1**–**6** melt or decompose at temperatures ranging from 110 °C (**5**) to 223 °C (**3**) and none of them display mesomorphic properties. Increasing the length of the aliphatic chains from n-C_8H_{17} in **1** to n-$C_{12}H_{25}$ in **2** as well as from n-C_4H_9 in **3** to n-C_8H_{17} in **4** the observed effect is the lowering of the melting or decomposition temperatures, while a similar behaviour is lacking in the benzyloxy derivatives **5** and **6**.

The salicylideneaminato palladium(II) complexes reported in this paper have been studied in order to gain some insight into the connection between molecular shape and thermotropic properties in coordination compounds. These results suggest further investigations on a different series of complexes, that are now in progress.

Supplementary Material

Hydrogen coordinates, anisotropic temperature factors, and calculated and observed structure factors are available as supplementary material.

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