Inorganica Chimica Acta, *86* (1984) 165–168

Transition Metals Complexed to Ordered Mesophases. Synthesis and Crystal Structure of (8-Hydroxyquinolinato)[2-(4′-Methoxyphenylazo-N^2)-5-Methoxyphenyl]palladium(II)

ANNA MARIA MANOTTI LANFREDI*, FRANCO UGOZZOLI

Istituti di Chimica Generale ed Inorganica e di Strutturistica Chimica dell'Università, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. D'Azegli 85, 43100 Parma, Italy

MAURO GHEDINI and SILVIA LICOCCIA

Dipartimento di Chimica, Università della Calabria, 87030 Arcavacata di Rende, Cosenza, Italy

Received November 2, 1983

tometrica del C.N.R., Via M. D'Azeglio 85, 43100 Parma, Italy

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The synthesis and characterization of the complex [Pd(quin)(azbz)] are described (quin = 8-hydroxyquinolinate and azbz = 2-(4′-methoxyphenylazo)-5-methoxyphenyl ligands, the latter being a derivative of p,p′-dimethoxyazobenzene, which exhibits liquid crystalline behaviour). The structure of the complex was determined by X-ray methods. Crystals are triclinic, space group $P\bar{1}$, *with* $a = 10.225(5)$, $b = 11.092(4)$, $c = 9.365(3)$ Å; $\alpha = 105.65(2)$, $\beta = 94.08(3)$, $\gamma = 105.69(3)^\circ$ *and* $Z = 2$. *The structure was solved from diffractomer data by Patterson and Fourier methods and refined by full-matrix least-squares to* $R = 0.033$ *for 3395 independent observed reflections. The palladium atom is in a square planar arrangement involving nitrogen and carbon atoms from the azbz ligand [Pd–N(2) = 2.012(4) and Pd–C(10) = 1.939(5) Å] and oxygen and nitrogen atoms from the quin ligand [Pd–O(1) = 2.118(4) and Pd–N(1) = 2.118(4) Å]. In the crystals the* Pd^{II} *complexes are associated in pairs in columnar stacks (the stacking separation in each diadic units is of 3.304 Å with a metal–metal distance of 3.424 Å). These stacking interactions could be responsible for the different thermal behaviour of the complex (not exhibiting mesomorphic properties) with respect to the liquid crystalline p,p′-dimetoxyazobenzene.*

Introduction

Although liquid crystals are the subject of many studies because of their technological applications (*e.g.* semiconductor devices [1], membrane processes [2], catalytic systems [3]), very little has been published on transition metals complexed to ordered mesophases. A previous paper dealt with some binuclear Pd(II) complexes containing orthometalated p,p′-disubstituted azobenzenes and exhibiting liquid crystalline behaviour [4]. Since our interest is focused on the role played by the metal in determining the thermotropic behaviour of such complexes, we have examined other palladium complexes with an organic liquid crystal ligand containing the –N=N– moiety.

Experimental

Preparation of Compounds

4,4′-dimethoxyazobenzene (*1*) was prepared according to the literature method [5].

[PdCl(1 – H)]$_2$ (2)

This compound has been obtained in the conditions previously described by Cope and Siekman [6]. The orange precipitate that formed was collected by filtration, washed with ethanol and ethyl ether, and dried under vacuum; yield 45%. *Anal.* Calcd. $C_{28}H_{26}Cl_2N_4O_4Pd_2$: C, 43.83; H, 3.42; N, 7.31. Found: C, 43.35; H, 3.23; N, 7.49.

[Pd(quin)(1 – H)] (3)

In a typical preparation, to 10 ml of a methanolic suspension containing 0.1 mmol of *2*, was added 10 ml of a methanolic solution containing 0.02 mmol of 8-hydroxyquinoline (Hquin) and 0.2 mmol of potassium hydroxyde. The mixture was stirred at room temperature for 7 days. The resulting dark-red precipitate was filtered, washed with ethanol and recrystallized from chloroform and ethanol (yield 67%). *Anal.* Calcd. for $C_{23}H_{19}N_3O_3Pd$: C, 56.16; H, 3.89; N, 8.54. Found: C, 55.37; H, 3.70; N, 8.26.

Physical Measurements

The transition temperatures and the textures of the various mesophases were observed by means of a Reichert Thermovar polarizing microscope equipped with a heating stage. Elemental analyses were

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*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

performed at the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Pisa, Italy.

X-ray Data Collection and Refinement

A red crystal of dimensions 0.20 × 0.22 × 0.30 mm was used for the X-ray analysis. The cell parameters were refined by a least-squares procedure applied to the θ values of 30 reflections accurately measured on a Siemens AED single crystal diffractometer. Crystal data are as follows: $C_{23}H_{19}N_3O_3$-Pd, $M = 491.82$, triclinic, $a = 10.225(5)$, $b = 11.092(4)$, $c = 9.365(3)$ Å, $\alpha = 105.65(2)$, $\beta = 94.08(3)$, $\gamma = 105.69(3)^\circ$; $V = 972.7(7)$ Å^3; $Z = 2$; $D_c = 1.679$ g cm^{-3}; Mo-Kα radiation ($\lambda = 0.71069$ Å), μ(Mo-Kα) = 9.70 cm^{-1}, space group: $P\bar{1}$ from structure determination. Intensity data were collected on the same diffractometer using the Nb-filtered Mo-Kα radiation and the $\theta/2\theta$ scan technique. The intensity of a standard reflection was measured after 50 reflections as a check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. A total of 4169 independent reflections were measured in the range $3 < \theta < 27^\circ$; of these, 3395 having $I > 2\sigma(I)$ were considered observed and were used in the analysis. The structure amplitudes were obtained after the usual correction for Lorentz and polarization factors and the absolute scale was established by Wilson's method. No correction for absorption was applied.

The structure was solved by Patterson and Fourier methods and refinement was carried out by least-squares full-matrix using the SHELX system of computing programs [7] with initially isotropic and then anisotropic thermal parameters for all the non-hydrogen atoms. All the hydrogen atoms were localized directly from a difference synthesis but not refined and included in the final structure factor calculation with isotropic thermal parameters (mean values of the thermal parameters of the atoms to which they are attached). The final R and R_w values were 0.033 and 0.037 respectively (observed reflections only).

The atomic scattering factors used (corrected for the anomalous dispersion of Pd atom) were taken from the International Tables [8]. The function minimized in the least-squares calculations was $\Sigma w(|F_o| - |F_c|)^2$. Unit weights were used in the first stages of the refinement, in the final cycles the weight used was calculated as $w = K/[\sigma^2(F_o) + gF_o^2]$ with K = 1.0000 and g = 0.005. Final atomic coordinates for the non-hydrogen atoms and for hydrogen atoms are given in Tables I and II respectively. The thermal parameters and a list of observed and calculated structure factors are available from the Authors on request. All the calculations were performed on the CYBER 76 Computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale,

TABLE I. Fractional Atomic Coordinates of the Non-hydrogen Atoms (×10^4) with E.s.d.'s in Parentheses.

	x/a	*y/b*	*z/c*
Pd	1566(1)	4878(1)	603(1)
O1	782(4)	5159(3)	2542(4)
O2	−2101(4)	413(4)	518(4)
O3	6157(4)	7216(4)	−3888(5)
N1	2723(4)	6864(4)	1674(5)
N2	2234(4)	4291(4)	−1362(4)
N3	1760(5)	3082(4)	−2161(4)
C1	1227(5)	6348(5)	3405(5)
C2	727(6)	6778(6)	4747(6)
C3	1255(6)	8089(6)	5622(6)
C4	2239(7)	9006(5)	5264(6)
C5	2798(6)	8618(5)	3926(6)
C6	3817(6)	9485(5)	3441(7)
C7	4282(6)	9023(5)	2136(7)
C8	3702(6)	7697(6)	1265(6)
C9	2286(5)	7308(5)	3017(5)
C10	479(5)	3045(5)	−144(5)
C11	785(5)	2390(5)	−1533(5)
C12	108(6)	1056(5)	−2262(6)
C13	−872(6)	349(5)	−1607(6)
C14	−1165(5)	1002(5)	−216(5)
C15	−489(5)	2323(5)	508(5)
C16	3281(5)	5053(5)	−1966(5)
C17	3042(6)	6037(6)	−2486(6)
C18	4008(6)	6747(5)	−3118(6)
C19	5258(6)	6468(5)	−3244(5)
C20	5524(6)	5483(5)	−2693(7)
C21	4500(6)	4780(6)	−2085(7)
C22	7390(7)	6891(6)	−4140(7)
C23	−2810(7)	−948(5)	−164(7)

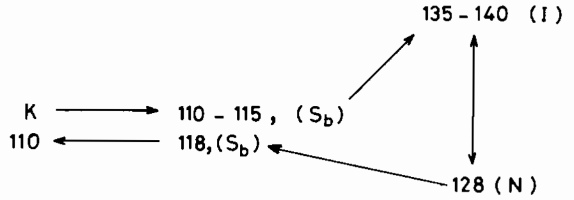
TABLE II. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3) of the Hydrogen Atoms.

	x/a	*y/b*	*z/c*	*U*
H2	38	6164	4998	56
H3	918	8345	6560	56
H4	2695	9996	5954	55
H6	4178	10381	4002	55
H7	5032	9595	1892	54
H8	4074	7354	308	53
H12	349	646	−3240	48
H13	−1436	−611	−2122	46
H15	−664	2666	1343	43
H17	2287	6240	−2307	60
H18	3909	7561	−3387	58
H20	6445	5241	−2830	55
H21	4710	4174	−1594	58
H221	7971	7005	−3264	65
H222	7881	7412	−4652	65
H223	7284	5952	−4710	65
H231	−3390	−1244	579	58
H232	−3313	−973	−1012	58
H233	−2163	−1379	−381	58

Casalecchio (Bologna), with the financial support from the University of Parma.

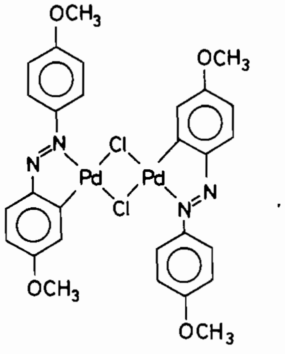
Results and Discussion

The ligand, 4,4′-dimethoxyazobenzene (*1*), in the solid phase, behaves like a polycrystalline system, optically uniaxial and partially ordered with a weak birifrangence. Increasing the temperature (Scheme I) causes melting over a large temperature range, showing a first order phase transition. A mosaic-like texture appears, probably a S_B phase, then the $S_B \rightarrow$ I transition occurs with a new first order phase transition. When the temperature is lowered a monotropic stable nematic phase is obtained [9].



Scheme I. Thermal behaviour (°C) of 4,4′-dimethoxyazobenzene.

By reacting *1* with K_2PdCl_4 orthometallation occurs and compound *2* is obtained:



Complex 2

Complex *2* reacts with 8-hydroxyquinoline and KOH to give the title compound *3*. Crystals suitable for X-ray analysis have been obtained by recrystallization from chloroform–ethanol.

The crystal structure of *3* consists of discrete palladium(II) complexes with metal atoms surrounded in a square-planar arrangement by the N(2) and C(10) atoms from the azbz ligand and by the N(1) and O(1) atoms from the quin ligand, with the nitrogen atoms of the two organic ligands in *cis* positions (Fig. 1). Bond distances and angles are given in Table III. Both azbz and quin act as chelate ligands forming five-membered rings with bite angles [N(2)–Pd–C(10) and N(1)–Pd–O(1)] of 78.3(2) and 80.9(2)°. The four coordinated atoms are strictly

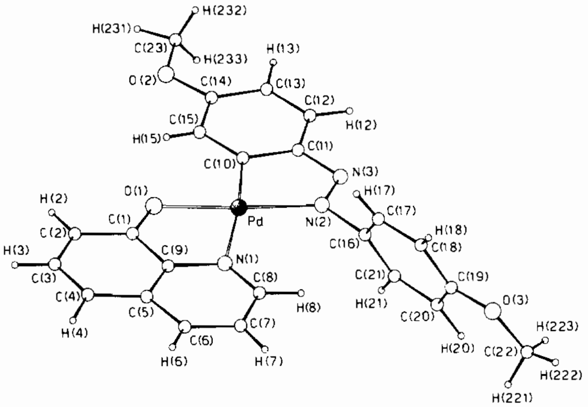


Fig. 1. View of complex *3* with the atomic numbering scheme.

TABLE III. Bond Distances (Å) and Angles (°).

i) In the coordination polyhedron			
Pd–N(1)	2.118(4)	Pd–O(1)	2.018(4)
Pd–N(2)	2.012(4)	Pd–C(10)	1.939(5)
N(1)–Pd–N(2)	107.7(2)	N(2)–Pd–C(10)	78.3(2)
N(1)–Pd–O(1)	80.9(2)	O(1)–Pd–C(10)	93.0(2)
N(1)–Pd–C(10)	173.3(2)	O(1)–Pd–N(2)	170.9(2)
ii) In the 8-hydroxyquinolinate ligand			
O(1)–C(1)	1.284(5)	C(1)–C(9)	1.442(7)
C(1)–C(2)	1.403(8)	C(5)–C(6)	1.406(8)
C(2)–C(3)	1.395(8)	C(6)–C(7)	1.363(9)
C(3)–C(4)	1.356(9)	C(7)–C(8)	1.412(7)
C(4)–C(5)	1.423(9)	C(8)–N(1)	1.322(7)
C(5)–C(9)	1.403(7)	C(9)–N(1)	1.374(7)
C(2)–C(1)–C(9)	117.0(5)	C(5)–C(6)–C(7)	119.3(6)
O(1)–C(1)–C(2)	122.7(5)	C(6)–C(7)–C(8)	119.7(6)
O(1)–C(1)–C(9)	120.3(4)	C(7)–C(8)–N(1)	122.4(6)
C(1)–C(2)–C(3)	119.4(6)	N(1)–C(9)–C(5)	122.4(5)
C(2)–C(3)–C(4)	124.2(6)	C(1)–C(9)–C(5)	122.1(5)
C(3)–C(4)–C(5)	118.7(5)	C(8)–N(1)–C(9)	118.3(5)
C(4)–C(5)–C(9)	118.6(5)	C(8)–N(1)–Pd	132.2(4)
C(6)–C(5)–C(9)	117.9(5)	C(9)–N(1)–Pd	109.5(4)
C(4)–C(5)–C(6)	123.6(5)	C(1)–O(1)–Pd	113.5(4)
N(1)–C(9)–C(1)	115.5(4)		
iii) In the 2-(4′-methoxyphenylazo)-5-methoxyphenyl ligand			
N(2)–N(3)	1.284(5)	O(2)–C(23)	1.426(6)
N(2)–C(16)	1.427(7)	C(16)–C(17)	1.379(9)
N(3)–C(11)	1.357(7)	C(17)–C(18)	1.364(9)
C(10)–C(11)	1.410(7)	C(18)–C(19)	1.400(9)
C(11)–C(12)	1.403(7)	C(19)–C(20)	1.407(9)
C(12)–C(13)	1.385(8)	C(20)–C(21)	1.383(9)
C(13)–C(14)	1.405(7)	C(21)–C(16)	1.365(9)
C(14)–C(15)	1.391(6)	C(19)–O(3)	1.354(7)
C(15)–C(10)	1.384(7)	C(22)–O(3)	1.420(9)
O(2)–C(14)	1.347(7)		
N(3)–N(2)–C(16)	113.4(4)	N(2)–C(16)–C(21)	120.3(5)
N(2)–N(3)–C(11)	111.4(4)	C(17)–C(16)–C(21)	119.8(6)
C(11)–C(10)–C(15)	118.0(5)	C(16)–C(17)–C(18)	121.0(6)
C(10)–C(11)–C(12)	121.5(5)	C(17)–C(18)–C(19)	119.4(6)

(continued overleaf)

TABLE III *(continued)*

C(10)–C(11)–N(3)	118.4(5)	C(18)–C(19)–C(20)	120.2(6)
C(12)–C(11)–N(3)	120.1(5)	C(18)–C(19)–O(3)	115.6(5)
C(11)–C(12)–C(13)	119.9(5)	C(20)–C(19)–O(3)	124.3(6)
C(12)–C(13)–C(14)	118.4(5)	C(19)–C(20)–C(21)	118.0(6)
C(13)–C(14)–C(15)	121.6(5)	C(20)–C(21)–C(16)	121.7(6)
C(13)–C(14)–O(2)	123.4(5)	C(19)–O(3)–C(22)	117.0(5)
C(15)–C(14)–O(2)	115.0(4)	N(3)–N(2)–Pd	119.1(3)
C(14)–O(2)–C(23)	117.3(4)	C(16)–N(2)–Pd	127.4(3)
N(2)–C(16)–C(17)	119.9(5)	C(15)–C(10)–Pd	129.3(4)
C(10)–C(15)–C(14)	120.6(5)	C(11)–C(10)–Pd	112.7(4)

planar with the palladium atom out of the plane passing through them of 0.051(2) Å. As regards the bond distances involving the azbz ligand, the Pd–C(10) bond length of 1.939(5) Å is shorter than the predicted one of 2.05 Å [10] and suggests some multiple-bond character of the Pd–C(aryl) linkage, while the Pd–N(2) bond length of 2.012(4) Å is in good agreement with the predicted value of 2.01 Å for the Pd–N(sp^2) distance [11]. As regards the bond lengths involving the quin ligand, the Pd–O(1) distance of 2.018(4) Å can be compared with the corresponding value found for the 8-hydroxyquinolinate complexes of palladium(II) [12, 13], while the Pd–N(1) distance of 2.118(4) Å, *trans* to the carbon atom, shows a significant lengthening with respect to that *trans* the oxygen and with respect to those generally found in the other 8-hydroxyquinolinate palladium(II) complexes. This could be attributed to the *trans*-lengthening effect of the σ-bonded carbon atom.

The five-membered chelate rings, both nearly planar (the maximum deviations from the corresponding mean plane being 0.020(5) and 0.038(6) Å for N(3) and C(1) atoms respectively) lie on the same plane, the dihedral angles between them being 2.9(6)°. As a result the main portion of the complex can be considered planar, except for the un-coordinated methoxyphenyl portion of the azbz ligand which is rotated by 109.3° with respect to the coordination plane. A characteristic feature of the crystal structure is the presence of stacks of Pd(II) complexes which are associated in pairs, the spacing between the planar moieties of the complexes in the diadic unit being 3.304(5) Å with a metal–metal distance of 3.424(1) Å (Fig. 2). The stacks, located along the direction parallel to [100] at $y = 1/2$, are arranged in a columnar system by Pd- - -H interactions [Pd–H(20)(1 – x, 1 – y, –z) = 2.86 Å] involving palladium and hydrogen atoms from two adjacent diadic units. The un-coordinated methoxyphenyl moieties of the azbz ligands seem to show a 'head to tail' type overlap in the direction parallel to [010] at $x = 1/2$ even if the interplanar spacing between these moieties is rather longer (3.6 Å).

Complexes *2* and *3* are lacking thermotropic mesophases: they only show decomposition at 299–302 °C and 174–176 °C respectively. It has been suggested [14] that metal–metal interaction may inhibit the formation of mesophases; so the interactions present in the complex *3* could indeed be responsible for the observed different thermal behaviour of *3* with respect to the liquid crystalline compound *1*.

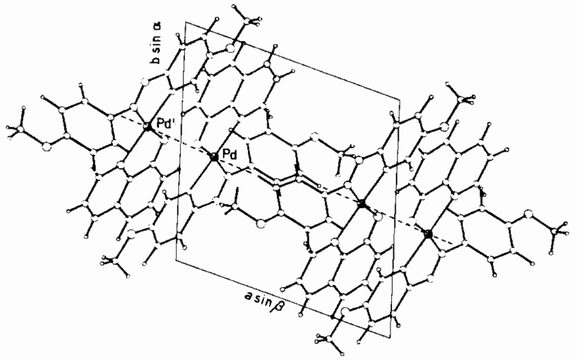


Fig. 2. Projection along *c* of the structure of *3*.

Acknowledgments

The authors are indebted to Dr. R. Bartolino for the characterization of the textures of the various mesophases. Thanks are due to Mr. S. Armentano for his laboratory assistance. This work was supported by the CNR project 'Chimica Fine e Secondaria'.

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