Metal Complexes of 2-(*o*-Hydroxyphenyl)pyridine

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Abstract

Complexes of 2-(*o*-hydroxyphenyl)pyridine (PhOHpy) with group VIIIB metal ions were synthesized and characterized by elemental analysis and spectroscopic measurements. The crystal and molecular structures of $Co(PhOpy)_3$ and $Pd(PhOpy)_2$ were determined. The Co complex crystallizes in the orthorhombic space group *Fdd*2, with $a = 28.185(14)$, $b = 36.639(18)$, $c = 12.639(18)$ Å; $Z = 16$. The molecule has a *mer*-octahedral structure. Crystals of the Pd complex are orthorhombic, space group *Pbca*, with $a = 17.140(3)$, $b = 11.143(2)$, $c = 9.488(2)$ Å, $Z = 4$. The molecule is square-planar.

Introduction

2-(*o*-Hydroxyphenyl)pyridine (PhOHpy) is a very simple potentially chelating O,N-bidentate system. This ligand offers a coordinating environment similar to the one present in salicylaldimines. However, while the interest for the ligand properties of the latter species was prominent by far [1] and found recent reinforcement in catalytic processes [2] promoted by complexes of these ligands, very little is known about PhOHpy complexes. In fact, only a brief outline of the interaction of PhOHpy with Cu^{2+} and Be^{2+} in aqueous solution has been reported [3, 4]. A reason for this paucity of data could conceivably reside in the difficulty of preparing the ligand, since this involved cumbersome separation of substitution isomers. During a recent study on acetylcholinesterase, Riggio *et al.* [5] developed an easier synthetic procedure. Thus, the improved availability of PhOHpy makes easier the investigation of the coordination properties of this ligand toward transition ions. We report here the syntheses of Fe(III), Co(III), Cu(II) and Pd(II) complexes and the structural characterization of the Co(III) and Pd(II) complexes.

Experimental

The ^1H NMR spectra were obtained by use of a Brucker WH 270 spectrometer in $CDCl_3$ with Me_4Si as internal standard. Infrared spectra were recorded on a Perkin-Elmer model 457 spectrophotometer. Elemental analyses were performed, in part, by the Laboratorio di Microanalisi, Dipartimento di Chimica, Università di Padova and in part by EFI, Napoli. All solvents were reagent grade. The preparation and separation from isomeric products of 2-(*o*-hydroxyphenyl)pyridine were made according to a previous procedure [5]. All other chemicals were reagent grade and were used as received.

Synthesis of $(PhOpy)_3Co$ (I)

0.50 g (0.20 mmol) of $Co(OAc)_2 \cdot 4H_2O$ and 1.026 g (0.60 mmol) of PhOHpy were dissolved in a minimum amount of ethanol and 0.3 mmol of NaOAc were added. After 48 h stirring in air the green precipitate was filtered, washed with ethanol and dried *in vacuo*. Recrystallization from methylene chloride–heptane gave the product in 63% yield. The freshly crystallized compound contains one mole of solvent (CH_2Cl_2)/mole of Co. The analytical sample was dried *in vacuo* overnight in order to remove the crystallization solvent.

^1H NMR, δ: 8.74 d, 1H; 8.23 d, 1H; 7.91 d, 1H; 7.87 d, 1H; 7.7 m, 3H; 7.60 d, 1H; 7.45 t, 1H; 7.26 m, 2H; 7.20 d, 1H; 7.0 m, 4H; 6.8 m, 5H; 6.64 m, 1H; 6.46 t, 1H; 6.19 d, 1H.

Anal. Calc. for $C_{33}H_{24}CoN_3O_3$: C, 69.60; H, 4.25; N, 7.38. Found: C, 69.12; H, 4.26; N, 7.22%.

Reaction of PhOHpy with $FeCl_2$

$FeCl_2 \cdot 4H_2O$ (0.066 g, 0.33 mmol) was dissolved in a solution of PhOHpy (0.171 g, 1.0 mmol) in the minimum amount of ethanol. After stirring 24 h in air the dark violet crystals were filtered and dried, giving 0.146 g of crude product (62% yield).

Anal. Calc. for $C_{22}H_{16}ClFeN_2O_2$; C, 61.21; H, 3.74; N, 6.49; Cl, 8.21. Found: C, 59.77; H, 3.74; N, 6.14; Cl, 7.90%.

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TABLE 1. Crystal Data and Details of Measurements for I and II

	I	II
Molecular formula	$Co(C_{11}H_8NO)_3 \cdot CH_2Cl_2$	$Pd(C_{11}H_8NO)_2$
Molecular weight	654.4	446.9
Space group	*Fdd*2	*Pbca*
a (Å)	28.185(4)	17.140(3)
b (Å)	36.639(18)	11.143(2)
c (Å)	12.489(6)	9.488(2)
V (Å^3)	12897.0	1812.1(4)
Z	16	4
D_{calc} (g cm^{-3})	1.347	1.64
Radiation	graphite monochromatized Mo Kα (λ = 0.7107 Å)	
Crystal size (mm)	0.02 × 0.2 × 0.3	0.2 × 0.2 × 0.5
μ (cm^{-1})	6.8	11.4
Diffractometer	Philips PW 100	
2θ range (°)	0–45	2–35
Scan mode	$\theta-2\theta$	$\theta-2\theta$
Collected reflections	3105	1599
Reflections $\|F\| > 3\sigma(\|F\|)$	1802	829
R	0.068	0.029
R_w	0.062	0.035

The product could not be recrystallized owing to extensive decomposition in solution.

Synthesis of Cu(PhOpy)$_2$

The complex was prepared from $Cu(OAc)_2 \cdot H_2O$ and PhOHpy with a procedure similar to that reported above, giving a crude product in 67% yield. The product could be recrystallized by evaporation of a methylene chloride solution.

Anal. Calc. for $C_{22}H_{16}CuN_2O_2$: C, 65.42; H, 3.99; N, 6.94. Found: C, 66.12; H, 4.04; N, 6.78%.

Synthesis of Pd(PhOpy)$_2$ (II)

To a solution of 0.171 g (1.0 mmol) of PhOHpy in ethanol (5 ml) 0.088 g (0.5 mmol) of $PdCl_2$ and 0.178 g (1 mmol) of finely powdered $NaOAc \cdot 2H_2O$ were added. After 24 h stirring the yellow precipitate was collected, washed with water and ethanol and dried *in vacuo*. The product was recrystallized from chloroform–heptane giving 0.195 g of product (75% yield).

^{1}H NMR, δ: 8.88 d, 2H; 7.78 t, 2H; 7.67 d, 2H; 7.41 d, 2H; 7.26 t, 2H; 7.14 t, 2H; 6.97 d, 2H; 6.72 t, 2H.

Anal. Calc. for $C_{22}H_{16}N_2O_2Pd$: C, 59.14; H, 3.61; N, 6.27. Found: C, 58.72; H, 3.57; N, 6.11%.

X-ray Data Collection and Structure Determination

Dark brown crystals of $Co(PhOpy)_3 \cdot CH_2Cl_2$ (**I**) and needle-shaped yellow crystals of $Pd(PhOHpy)_2$ (**II**), suitable for X-ray analysis were obtained from methylene chloride. Selected crystals were mounted on a Philips PW 100 computer controlled four-circle diffractometer equipped with a graphite monochromator. Standard centering and auto-indexing procedures [6] indicated a face-centered orthorhombic lattice for **I** and a primitive orthorhombic lattice for **II**. The orientation matrix and accurate unit cell dimensions were determined from a least-square fit of 25 symmetry-related reflections (10° $< 2\theta <$ 23°).

Intensity data were collected at 24 °C using the $\theta-2\theta$ scan method; two standard reflections, monitored every 150 reflection measurements, fluctuated within ±3% for **I**, and ±1% for **II**, of their mean value. Empirical absorption correction was applied for **II** by a pseudoellipsoidal treatment of intensities of selected strong reflections measured at various azimutal angles [7–9]; no absorption corrections have been applied for **I**. The intensities were corrected for Lorentz and polarizations factors and scaled to give 1802 independent F_{hkl} values with $I > 3\sigma(I)$ for **I** and 829 for **II**. Crystal data and details of data collection are listed in Table I.

In the case of **I** the position of the Co atom was determined from a three-dimensional Patterson synthesis. In the case of **II**, it turned out that the molecular units $(C_{11}H_8NO)_2Pd$ must lie on inversion centers, which fact allowed us to phase almost all the Fourier coefficients. All the carbon atoms were located from subsequent Fourier maps and refined anisotropically. The hydrogen atoms were located from the final difference Fourier synthesis; they were included in the calculations but not refined. Blocked-cascade least-square refinements were used; they converged to the conventional R index of 0.068 for **I** and 0.029 for **II**.

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) for the Non-hydrogen Atoms of $Co(PhOpy)_3$ (I)[a]

Atom	*x/a*	*y/b*	*z/c*
Co	1549(1)	488(1)	0
O	1688(3)	531(2)	−1426(8)
N	1365(3)	−26(2)	−265(9)
C(1)	1461(3)	−280(2)	539(9)
C(2)	1407(3)	−652(2)	337(9)
C(3)	1256(3)	−771(2)	−668(9)
C(4)	1159(3)	−517(2)	−1472(9)
C(5)	1214(3)	−145(2)	−1270(9)
C(6)	1095(4)	126(2)	−2062(8)
C(7)	737(4)	45(2)	−2796(8)
C(8)	652(4)	278(2)	−3658(8)
C(9)	924(4)	593(2)	−3786(8)
C(10)	1282(4)	674(2)	−3052(8)
C(11)	1367(4)	441(2)	−2190(8)
O′	1762(3)	968(2)	250(11)
N′	920(2)	680(2)	−220(10)
C(1)′	543(2)	468(2)	146(10)
C(2)′	77(2)	584(2)	−14(10)
C(3)′	−12(2)	913(2)	−541(10)
C(4)′	365(2)	1125(2)	−907(10)
C(5)′	831(2)	1009(2)	−747(10)
C(6)′	1240(3)	1240(3)	−1023(11)
C(7)′	1171(3)	1501(3)	−1821(11)
C(8)′	1542(3)	1734(3)	−2110(11)
C(9)′	1981(3)	1705(3)	−1600(11)
C(10)′	2049(3)	1444(3)	−801(11)
C(11)′	1679(3)	1212(3)	−513(11)
O″	1389(4)	446(3)	1412(13)
N″	2194(3)	335(3)	319(11)
C(1)″	2440(3)	159(3)	−501(11)
C(2)″	2895(3)	24(3)	−315(11)
C(3)″	3104(3)	64(3)	691(11)
C(4)″	2858(3)	239(3)	1511(11)
C(5)″	2402(3)	375(3)	1325(11)
C(6)″	2151(5)	563(4)	2134(13)
C(7)″	2420(5)	716(4)	2956(13)
C(8)″	2195(5)	892(4)	3808(13)
C(9)″	1701(5)	913(4)	3838(13)
C(10)″	1432(5)	760(4)	3015(13)
C(11)″	1657(5)	585(4)	2163(13)
Cl(1)	2652(4)	1243(3)	6502(10)
Cl(2)	3120(4)	810(3)	8004(10)
C	2573(9)	819(6)	7193(20)

[a] e.s.d.s given in parentheses.

The weighting scheme used in the final calculations was of the form $w^{-1} = a_j|F_o|^j$. The a_j parameters were calculated using the program PESO [10]. Scattering factors for the atoms were taken from Cromer and Waber [11], the scattering factor for Pd and Co were corrected for the real and imaginary parts of the anomalous dispersion using Cromer's values [12].

All computations were carried out on a CDC cyber 76 computer using the programs of ref. 13. The positional parameters of the non hydrogen atoms are listed in Tables II and III, the atom numbering scheme being shown in Figs. 1 and 2.

TABLE III. Fractional Atomic Coordinates ($\times 10^4$) for the Non-hydrogen Atoms of $Pd(PhOpy)_2$ (II)[a]

Atom	*x/a*	*y/b*	*z/c*
Pd	0	0	0
O	−1141(2)	267(3)	41(6)
N	166(3)	1746(4)	582(6)
C(1)	815(4)	2286(6)	41(10)
C(2)	984(5)	3454(7)	350(8)
C(3)	460(5)	4111(6)	1130(9)
C(4)	−218(4)	3586(6)	1605(8)
C(5)	−366(4)	2368(6)	1322(6)
C(6)	−1429(4)	790(6)	1184(7)
C(7)	−2138(4)	354(6)	1699(8)
C(8)	−2475(5)	846(8)	2922(8)
C(9)	−2120(5)	1307(8)	3194(9)
C(10)	−1438(4)	2266(7)	3055(8)
C(11)	−1080(4)	1793(6)	1854(7)

[a] e.s.d.s given in parentheses.

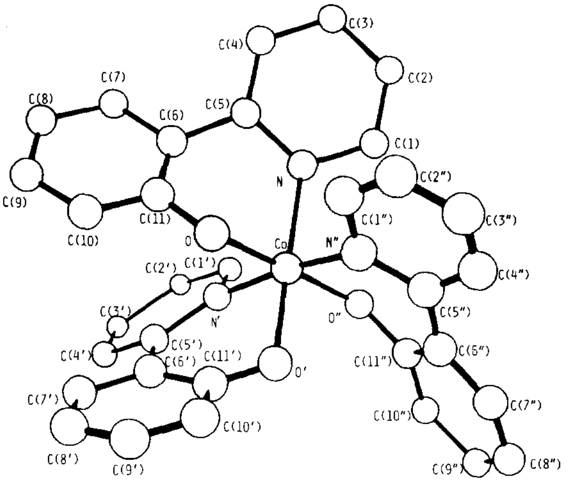

Fig. 1. Perspective view of the molecular structure of $Co(PhOpy)_3$ (I) showing the atom numbering scheme.

Results and Discussion

Synthetic Aspects and Physical Measurements

The complexes were prepared by procedures similar to those previously reported for N-substituted salycilaldimine derivatives. We found that the same Fe(III) compound was obtained either using $FeCl_3$ or $FeCl_2$ in aerobic conditions. Easy aerial oxidation also allowed the synthesis of $Co(PhOpy)_3$ from Co(II) acetate.

In all complexes the ligand is present as a chelating anion. The Co(III) and the Pd(II) complexes (**I** and **II** respectively) are diamagnetic as expected. These were characterized by elemental analysis, ^1H NMR

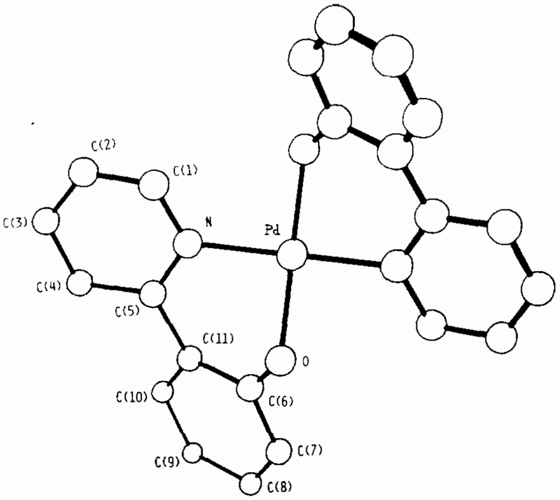

Fig. 2. Perspective view of the molecular structure of Pd(PhOpy)$_2$ (**II**) showing the atom numbering scheme.

spectroscopy and X-ray diffraction studies. The multiplicity of signals observed in the ^1H NMR spectrum of the Co complex **I** indicates that the three ligand molecules are not symmetry related. This points to an unsymmetrical *mer* structure, as usually observed for analogous octahedral complexes [14], and confirmed in the solid state by the X-ray structure.

The crude iron complex is a poorly soluble material, which resisted attempts to recrystallization. The analytical data are approximately consistent with the formula Fe(PhOpy)$_2$Cl. The magnetic moment is 6.9 BM, outside the range (5.8, 6.0) of the observed values for magnetically diluted complexes of the same type [1]. Further investigations are required on an analytically pure product in order to explain this finding.

The copper complex has a magnetic moment of 1.97 BM, which points to a somewhat distorted planar structure, in analogy with analogous salicylaldimine complexes [1].

Structure Description

I. The internal geometrical parameters of $(C_{11}H_8NO)_3Co{\cdot}CH_2Cl_2$ are shown in Table IV with reference to Fig. 1. The coordination geometry about Co is nearly undistorted octahedral and corresponds to the unsymmetrical *mer* isomer.

Remarkable is the fact that the bond lengths Co–N and Co–O are sensibly shorter (~0.05 Å) when the oxygen and nitrogen are *trans* to each other with respect to Co. The three ligands, which obviously are not structurally equivalent in the molecule, have virtually identical conformations, and also the torsion angles about the C(5)–C(6) bonds in the three ligands are almost the same (absolute values = 29°, 26° and 22° respectively). The structure shows a partial disorder due to the solvent molecules CH_2Cl_2. These are randomly placed between complex molecules approximately in the *c* direction; hence the components U_{33} of the thermal factors are relatively higher and the conventional *R* factor is not very low. The solvent molecules themselves are intrinsically disordered, but we did not try any accurate calculation in order to elucidate such particular structural features.

TABLE IV. Selected Geometrical Parameters for Co(PhOPy)$_3$ (I)

Bond lengths (Å)			
Co–N	1.983(7)	Co–O	1.830(10)
Co–N′	1.928(7)	Co–O′	1.885(9)
Co–N″	1.942(9)	Co–O″	1.827(10)
Bond angles (°)			
O–Co–N	88.6(4)	N–Co–O″	90.9(5)
O–Co–N′	91.4(4)	N′–Co–O′	88.5(4)
O–Co–N″	91.4(5)	N′–Co–O″	86.6(5)
O–Co–O′	90.8(5)	N′–Co–N″	174.3(5)
O–Co–O″	178.1(5)	O′–Co–O″	89.8(5)
N–Co–N′	94.7(4)	O′–Co–N″	86.5(4)
N–Co–N″	90.3(4)	O″–Co–N″	90.5(6)
N–Co–O′	176.7(4)		
Torsion angles (°)			
C(4)–C(5)–C(6)–C(7)	29		
C(4)′–C(5)′–C(6)′–C(7)′	–26		
C(4)″–C(5)″–C(6)″–C(7)″	22		

TABLE V. Selected Geometrical Parameters for Pd(PhOpy)$_2$ (II)

Bond distances (Å)			
Pd–O	1.979(2)	O(–C(6)	1.327(5)
Pd–N	2.042(2)	C(6)–C(7)	1.397(5)
N–C(1)	1.364(5)	C(7)–C(8)	1.407(6)
C(1)–C(2)	1.366(6)	C(8)–C(9)	1.387(7)
C(2)–C(3)	1.376(6)	C(9)–C(10)	1.374(7)
C(3)–C(4)	1.376(6)	C(10)–C(11)	1.398(5)
C(4)–C(5)	1.407(5)	C(11)–C(6)	1.418(5)
C(5)–N(1)	1.344(5)	C(11)–C(5)	1.471(5)
Bond angles (°)			
O–Pd–N	89.4(2)	Pd–N–C(1)	115.6(4)
Pd–O–C(6)	116.7(4)	Pd–N–C(5)	122.5(4)
O–C(6)–C(7)	117.2(5)	C(5)–N–C(1)	121.5(5)
O–C(6)–C(11)	123.7(5)	N–C(1)–C(2)	120.9(5)
C(7)–C(6)–C(11)	119.0(6)	C(1)–C(2)–C(3)	118.9(6)
C(8)–C(7)–C(6)	120.7(6)	C(2)–C(3)–C(4)	120.1(7)
C(9)–C(8)–C(7)	120.0(6)	C(3)–C(4)–C(5)	120.6(6)
C(10)–C(9)–C(8)	119.3(5)	C(4)–C(5)–N	118.3(6)
C(11)–C(10)–C(9)	122.5(6)	C(4)–C(5)–C(11)	120.3(5)
C(6)–C(11)–C(10)	118.5(6)	N–C(5)–C(11)	121.3(5)
C(6)–C(11)–C(5)	122.7(6)	C(10)–C(11)–C(5)	118.8(6)
Torsion angles (°)			
C(6)–C(11)–C(5)–N	[26]		

II. The internal geometrical parameters of $(C_{11}H_8NO)_2Pd$ are listed in Table V with reference to Fig. 2. The coordination about Pd is almost exactly square-planar: both the nitrogen atoms and the oxygen atoms are *trans* to each other with respect to Pd. The conformation of the ligand is almost the same as in the complex **I**; even the torsion angle about the bond C(5)–C(6) is almost unchanged (~26°). All the remaining molecular parameters and in particular the bond lengths Pd–N and Pd–O are within the average values reported in the literature for similar complexes (see for instance ref. 1).

Supplementary Material

Lists of hydrogen atom coordinates (Tables VI and VII), of thermal parameters (Tables VIII and IX), and the observed and calculated structure factors (Tables X and XI) are available from the authors on request.

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