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Ni^{II}, Pd^{II} and Pt^{II} Complexes Containing N,N′-bis(2-pyridylmethyl)oxamide as Ligand

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Although several works [1–4] have been previously devoted to the N,N′-bis(2-pyridylalkyl)oxamidato copper(II) complexes, to the best of our knowledge there is still no report on similar nickel(II), platinum(II) and palladium(II) complexes.

We have prepared four compounds which, according to analytical and spectrographic data, can be formulated as (1) $PdCl_2(LH_2)$; (2) $PtCl_2(LH_2)2H_2O$; (3) $Pt(LH_2)(H_2O)_2(NO_3)_2$; (4) $PdL2H_2O$, LH_2 being N,N′-bis(2-pyridylmethyl)oxamide. The presence of two bonded water molecules in 4 has been checked by thermogravimetric analysis.

The palladium and platinum complexes are diamagnetic and show a strong band (370–400 nm) in the near uv region of their electronic spectra which is usually observed for the square planar compounds. The nickel complex 4 exhibits a magnetic moment (μ = 2.85 BM) very close to the spin only value for two unpaired electrons consistent with an octahedral arrangement of ligands around the Ni(II). The electronic spectrum of such a complex is expected [5] to show three bands due to $^3A_{2g} \rightarrow {}^3T_{2g}$; $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions. The observation of the last two bands at 270 and 600 nm gives further evidence of an octahedral structure.

The main infrared absorption bands of the free ligand and the various complexes in the solid state are listed in Table I. In the case of the free ligand, the tentative assignments based on previous work [6–11] have been checked by deuteration. From the IR spectra patterns, the complexes can be divided into two classes: class A (1, 2 and 3), class B (4 and 5).

The main characteristic of the A compounds is that their spectra display almost all the bands observed in the free ligand. On complexation the amide I band (mainly ν_{CO}) moves to higher frequency by about 20 cm^{-1}, amide II (ν_{CN}) to lower frequency by about 20 cm^{-1} while the amide III (δ_{NH}) and amide IV bands are scarcely affected. This trend indicates that the amide group is not involved in coordination [4, 7, 12]. On the contrary, appreciable perturbations of the pyridine part (ν_{CC}, ν_{CN} and in and out of plane deformation) of the spectra have to be noticed. These shifts support conclusively that coordination to the metal ions occurs through the pyridine ring nitrogen [13]. Concerning the ν_{MCT}, a medium intensity band is observed at 320 (1) and 315 cm^{-1} (2). The observation of a unique absorption cannot be taken as a definitive evidence of *trans* configuration [14] but this configuration is strongly suggested by molecular models. The Pt–Cl band is lacking in the far infrared spectrum of 3 which instead displays three of the four fundamental absorptions of ionic nitrates (1380, 825, 720 cm^{-1}).

The IR spectra of the B compounds show no band attributable to ν_{NH} (or to ν_{ND}) in deuterated species which, on the other hand, has been located near 3300 cm^{-1} (2500 cm^{-1} for ν_{ND}) in the A compounds. Furthermore the amide II, III and VI bands are no longer observable; instead, a new band at 1370 cm^{-1} is observed to show the N-coordination of the

TABLE I. Infrared Spectra. Tentative Assignments for the Main Absorptions (cm^{-1}).

	LH_2	$PdCl_2(LH_2)$	$PtCl_2(LH_2)\cdot 2H_2O$	$Pt(LH_2)(H_2O)_2(NO_3)_2$	$NiL(H_2O)_2$	$PdL\cdot 2H_2O$
ν_{NH}	3275 s	3320 br	3300 sbr	3240 sbr		
Amide I	1645 s	1660 s	1665 s	1670 s	1620 sh	1655 s
Pyridine	1585 m	1610 ms	1605 ms	1610 ms	1594 s	1605 s
	1565 m	–	1575 m	–	1555 m	1555 w
Amide II	1520 s	1500 s	1495 s	1480 s	(1380 w)[a]	(1370 m)[a]
	1470 m	1480 sh	1400 sh	1470 sh	1470 m	1480 m
Pyridine	1430 ms	1435 sh	1435 ms	[b]	1420 m	1435 w
	1345 ms	1365 ms	1355 ms	[b]	–	–
Pyridine	1320 m	1280 m	1280 m	1320 m	1310 s	1290 w
	1240 s	1265 w	1240 sh	1260 sh	1275 w	–
Amide III	1220 s	1230 m	1225 m	1225 w	–	–
ν_{MCl}		320 ms	315 m	–	–	–

[a] See text for further explanations. [b] Obscured by the $\nu_{(NO_3)}$ at 1380 cm^{-1}.

TABLE II. Analytical Data.

No.	Compound	C %		H %		N %		M %		Cl %	
		found	calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.
1	$PdCl_2(LH_2)$	37.05	37.57	3.27	3.15	12.06	12.51	23.62	23.77	15.54	15.84
2	$PtCl_2(LH_2)\cdot 2H_2O$	29.89	29.38	3.12	3.15	9.65	9.79	33.43	34.09	12.15	12.39
3	$(Pt(LH_2)(H_2O)_2)(NO_3)_2$	28.65	26.89	2.66	2.90	13.26	13.43	31.31	31.20	–	–
4	$NiL(H_2O)_2$	47.30	46.33	4.29	4.44	15.41	15.43	16.27	16.18	–	–
5	$PdL\cdot 2H_2O$	40.94	40.71	3.91	3.71	13.64	13.61	25.90	25.32	–	–

deprotonated amide groups [15]. Coordination of pyridine N-atoms is confirmed by the higher frequency shifts of the bands located at 1585, 1470, 995 and 400 cm^{-1} in the free ligand. The absorptions observed at 3420 and 1640 cm^{-1} in the spectrum of 4 may be attributed to coordinated water molecules [16]. All these data strongly suggest that, in class B compounds, N,N'-bis(2-pyridylmethyl)oxamide is acting as a tetradentate ligand through both the pyridine N-atoms and the deprotonated amide groups, coordination around the nickel (4) being achieved through two water molecules.

Further characterization of the diamagnetic complexes (1, 2, 3 and 5) could be gained from NMR experiments. Due to solubility limitation DMSO is the only solvent which can be used but side-reactions take place leading to new species and also to free a ligand, which reasonably implies substitution of metal–ligand by metal–DMSO bonds. Presently the ^1H NMR spectra relating to freshly prepared solutions firmly establish the presence of the ligand in the form LH_2 in the compounds 1, 2 and 3 and in a deprotonated form L in the compound 5. They also suggest a modification of the C=O anisotropy effects through a change in the ligand conformation when it becomes coordinated. Further studies of these phenomena are in progress.

Experimental

N,N'-bis(2-pyridylmethyl)oxamide (LH_2) was prepared according to the method of Ojima and coworkers [3].

Synthesis of the Complexes

1

To a solution of $PdCl_2$ (1.69 mmol) and NaCl (5.12 mmol) in 10 cm^3 of water was added 1.69 mmol of LH_2. The orange red ($PdCl_2$ + 2NaCl) dissolved and slowly crystals precipitated.

2

To 0.62 mmol of K_2PtCl_4 in 10 cm^3 of water was added 0.62 mmol of LH_2 with vigorous stirring. The mixture became clear and then yellow crystals precipitated.

3

An aqueous solution of 3 was obtained from the 2 complex by precipitating the chloride ions using two equivalents of $AgNO_3$.

4

To an aqueous solution (10 cm^3) of $NiCl_2\cdot 6H_2O$ (0.81 mmol) was added an aqueous solution of LH_2 (0.84 mmol). The solution was stirred for 48 hours and blue crystals slowly precipitated.

5

0.84 mmol of Na_2PdCl_4 dissolved in a small amount of water was mixed with 0.84 mmol of LH_2. By adding 2.4 mmol of NaOH, yellow crystals precipitated.

All the products but 3 were washed with water and dried in vacuum. Analytical data are reported in Table II.

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