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Characterization of Pd(II) and UO_2(VI) Complexes of some Schiff Base Ligands

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Abstract

Palladium(II) chloride and dioxouranium(VI) acetate complexes of some Schiff bases derived from 4-aminoantipyrine and certain carbonyl compounds such as salicylaldehyde (HL^1), 2-hydroxy-1-naphthaldehyde (HL^2), 2,4-dihydroxybenzaldehyde (HL^3) and acetylacetone (HL^4) have been prepared and characterized. Spectroscopic and other analytical studies reveal that the Schiff bases react with the metal ion as monobasic tridentates in the enolimine form, except HL^3 and HL^4 ligands coordinate with Pd(II) in the ketoenamine form as neutral tridentate and neutral bidentate respectively. IR spectra and conductance measurements of some metal complexes show the presence of coordinated chloride ion and acetate group. The IR spectra also reveal that the Pd(II) complex of ligand HL^4 has a square planar *cis*-configuration.

Introduction

Schiff base ligands derived from 4-aminoantipyrine and certain carbonyl compounds such as, salicylaldehyde (HL^1), 2-hydroxy-1-naphthaldehyde (HL^2), 2,4-dihydroxybenzaldehyde (HL^3) and acetylacetone (HL^4) are known as tridentate ligands [1–4] coordinating in two ways (depending upon the nature of metal ion and the type of substituent).

In the first one, the ligand is ionized by removal of the phenolic proton and coordination takes place through the negatively charged oxygen atom, the oxygen of the pyrazolone ring and the azomethine nitrogen atom. Typical examples are the Cu(II), Fe(III) and Th(IV) complexes of ligands HL^1 and HL^2 [1–3]. In the second one the Schiff base is unionized and coordination takes place through the phenolic oxygen, secondary nitrogen atom and the oxygen atom of the pyrazolone ring since, an enolimine to ketoenamine tautomeric conversion is possible. Examples are the Mn(II), Ni(II) and Co(II) complexes of HL^1–HL^3 ligands [4] and Fe(III) and Cu(II) complexes of HL^3 [2]. HL^4 ligand was found to react with Th(IV) ion in its keto-imine form as neutral tridentate [3].

It has been recently reported that some antipyrine Schiff bases undergo photochromism in the solid state [5]. The yellow enolic form gives the orange quinonoid structure upon photo-irradiation (λ_{ex} = 365 nm). As a part of our programme on the synthesis and characterization of metal complexes of Schiff bases derived from 4-aminoantipyrine, Pd(II) and UO_2(VI) complexes of the Schiff bases HL^1–HL^4 were prepared and characterized by a variety of spectral and analytical methods to identify the mode of bonding in these complexes.

Experimental

Materials

All chemicals were reagent grade. The ligands (HL^1–HL^4) were prepared according to the known method [1] by condensing equimolar amounts of 4-aminoantipyrine and the appropriate carbonyl compound in ethanol.

Preparation of the Complexes

The complexes were prepared by the addition of K_2PdCl_4 in distilled water or $UO_2(CH_3COO)_2\cdot 2H_2O$ in absolute ethanol to a hot ethanolic solution of the ligand, 1:1 molar ratio. The reaction solution was refluxed on a water bath for *c.* 30 min. The complexes of ligands HL^1–HL^3 were precipitated while the solution was hot but, the Pd(II) complex of HL^4 was precipitated after cooling. The precipitated complexes were filtered off, washed several times with ethanol and dried under vacuum over phosphorus pentoxide. The UO_2(VI) complex of the ligand HL^4 was difficult to separate as a solid.

The elemental analyses (C, H, Cl) were carried out at the analytical unit of the University of Cairo and nitrogen analysis was carried out at the analytical unit of the National Research Centre, Dokki, Cairo. The palladium content was estimated as bis(dimethylglyoximato)Pd(II) [6]. The uranium content in the complexes was determined by igniting a known weight of the complex to U_3O_8. IR spectra were measured as KBr discs using a Perkin-Elmer 598 (4000–200 cm^{-1}) spectrophotometer. ^{1}H NMR spectra were run on a Varian EM-390 90 MHZ NMR

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TABLE 1. Analytical and conductance data for ligands and their complexes

Compound	Found (calc.) (%)					Λ_M (ohm^{-1} cm^2 mol^{-1})	Colour	Effect of heat (℃)
	C	H	N	Cl	M			
HL^1	70.9(70.4)	5.9(5.5)	12.9(13.7)				yellow	
PdL^1Cl	48.7(48.3)	3.9(3.6)	8.8(9.4)	7.6(7.9)	23.1(23.7)	insoluble	yellow	267(melting)
$UO_2L^1(CO_2CH_3)$	38.2(37.8)	3.3(3.0)			37.8(37.5)	4.4	red	295(s.d.)[b]
HL^2	74.7(74.0)	5.8(5.3)	11.0(11.8)				yellow	
PdL^2Cl	52.9(53.1)	3.6(3.6)	8.6(8.4)	7.5(7.1)	21.8(21.3)	insoluble	orange	270(melting)
$UO_2L^2(CO_2CH_3)$	42.8(42.0)	3.2(3.1)			34.3(34.7)	4.5	crimison red	278(melting)
HL^3	67.0(66.9)	5.2(5.3)	12.9(13.0)				yellow	
$[PdHL^3Cl]Cl$	43.8(43.2)	3.7(3.4)	8.2(8.4)	13.9(14.2)	21.8(21.2)	insoluble	pale yellow	300(s.d.)
$UO_2L^3(CO_2CH_3)\cdot 2H_2O$	35.1(34.9)	3.6(3.4)			34.2(34.6)	4.5	brown	changed to red at 105 and darkness at 235
HL^4	66.8(67.4)	6.5(6.7)	14.9(14.7)				pale yellow	
$PdHL^4Cl_2$	41.3(41.6)	4.2(4.1)		15.3(15.4)	22.3(22.9)	17.8, 11.6[a]	orange	220(s.d.)

[a] In dimethylsulphoxide. [b] s.d. = start of decomposition.

spectrometer. The electronic spectra were carried out in dimethylformamide using a Perkin-Elmer 550 S spectrophotometer. The conductivity measurements were made in dimethylformamide solutions (10^{-3} M) using a Tacussel conductimeter type CD6N.

Results and Discussion

The analytical data (Table 1) show that the reactions of Pd(II) and $UO_2(VI)$ with the Schiff base ligands HL^1–HL^4 derived from 4-aminoantipyrine produce 1:1 metal complexes. These air stable metal complexes are non-hygroscopic and soluble in dimethylformamide and acetonitrile, except the Pd(II) complexes of ligands HL^1–HL^3 which are insoluble.

The conductance data (Table 1) show that the metal complexes behave as non-electrolytes [7, 8] indicating the coordination of the chloride ions or acetate groups. Unfortunately, the partial solubility of the Pd(II) complexes of HL^1–HL^3 ligands in most organic solvents precluded conductance measurements.

Infrared Spectra

Table 2 shows the more characteristic infrared spectral bands of the ligands and their metal complexes. The assignment of the infrared spectra of the ligands was discussed previously [3, 4]. The infrared spectra of the metal complexes of HL^1–HL^3, except that of the Pd(II) complex of HL^3, show bands at 1605–1600 and 1555–1530 cm^{-1}, assigned to νC=N [2, 4] and νC=O [9] respectively. The lowering of frequencies of these bands compared to those of the free Schiff bases indicates that the azomethine nitrogen and carbonyl oxygen of the pyrazolone ring are involved in coordination. The spectra of the metal complexes also reveal that the band corresponding to the stretching vibration of the o-O–H group disappeared due to its deprotonation through complex formation. The above arguments and analytical data (Table 1) indicate that the ligands HL^1–HL^3 [except HL^3 with Pd(II)] react as monobasic tridentates in the classical enolimine form as shown in Fig. 1.

The infrared spectrum of the $[PdHL^3Cl]Cl$ complex shows bands at 3230, 1615, 1535 and 1555 cm^{-1}, assigned to the coordinated secondary nitrogen atom (νN–H) [10–12], δN–H [11], coordinated νC=O [9] of the pyrazolone ring and coordinated νC=O [13] of the ketoenamine tautomer respectively. On the other hand, the bands characteristic of νo-OH and νC=N disappeared upon complex formation. This indicates that the ligand reacts with Pd(II) as a neutral tridentate in the ketoenamine form as shown in Table 3.

The infrared spectrum of the HL^4 ligand shows intramolecular hydrogen bonding (N–H...O) which gives rise to a broad absorption band at 3160 cm^{-1} [15]. The appearance of this band indicates ketoimine–ketoenamine tautomerism [14–17].

The spectrum of the $PdHL^4Cl_2$ complex shows a positive and a negative shift in νN–H and νC=O of the side chain respectively, compared to that of the ligand. This may be attributed to a metal (secondary) nitrogen coordination and carbonyl oxygen coordination [3]. On the other hand, the C=N stretching vibration disappears upon metal complexation which favours the ketoenamine tautomer formation. The band corresponding to νC=O of the pyrazolone ring does not change upon metal complexation. The above arguments and analytical data (Table 1) indicate that the ligand reacts with Pd(II) as a neutral bidentate in the ketoenamine form as shown in Table 3.

Monodentate coordination of the acetate in $UO_2(VI)$ acetate complexes of HL^1 and HL^2 is suggested since ν_{as} and ν_{sym} of the carboxylate were detected at comparable frequencies to those reported [18] for the monodentate acetates of $UO_2(VI)$. Whereas the $UO_2(VI)$ complex of the HL^3 ligand shows a bidentate coordination of the acetate since the ν_{as} and ν_{sym} of the carboxylate were detected at comparable frequencies to those reported for the bidentate acetates of $UO_2(VI)$ [18]. The infrared spectra of the $UO_2(VI)$ complexes show a strong absorption band near 910–895 cm^{-1} that is assigned to antisymmetric ν_3(O–U–O) [19]. Vidali *et al.* [18] have reported that if the $UO_2(VI)$ ion is linear the bending ν_2(O–U–O) band will appear in the range 268–249 cm^{-1}. The infrared spectra of $UO_2(VI)$ complexes of HL^1 and HL^2 show a medium absorption band at 265 and 255 cm^{-1} respectively, whereas the spectrum of $UO_2(VI)$ complex of HL^3 does not show this band. This indicates that the $UO_2(VI)$ ion is linear in the complexes of HL^1 and HL^2, while in the complex of HL^3 the linearity is perturbed. This perturbation may be due to the chelation effect of the acetato group. The infrared spectra of metal complexes show new bands at 545–510 and 500–405 cm^{-1}, assigned to νM–N [20–23] and νM–O [24–26] respectively. The IR spectra of the Pd(II) complexes show a band in the region 330–305 cm^{-1} which may be associated with νM–Cl [27–32]. This band is splitted into two bands at 330 and 305 cm^{-1} in the spectrum of the $PdHL^4Cl_2$ complex. This can be taken as evidence for the square planar *cis*-configuration of this complex [33]. The spectrum of the $UO_2(VI)$ complex of HL^3 shows a broad absorption band near 3540 cm^{-1}, assigned to uncoordinated water molecules.

Proton NMR Spectra

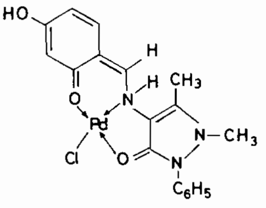
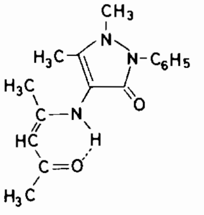
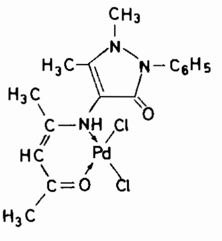
The chemical shifts observed in the ^1H NMR spectra of $[PdHL^3Cl]Cl$, HL^4 and $PdHL^4Cl_2$ are listed in Table 3. The data further indicate that the above

TABLE 2. Infrared spectral data of ligands and their metal complexes[a]

Compound	νO–H	νN–H	νC=O of the side chain	νC=O of pyrazolone ring	δN–H	νC=O of phenyl ring	νC=N	νCOO (ν_{as} and ν_{sym})	Pyrazolone ring	ν_3O–U–O	ν_2O–U–O	νM–N	νM–O	νM–Cl
HL^1	3420(br)			1655(s)			1625(sh)		1595(vs)					
PdL^1Cl				1530(s)			1600(s)		1580(s)			510(s)	415(s)	330(s)
$UO_2L^1(CO_2CH_3)$				1555(s)			1605(sh)	1620(s), 1330(s)	1590(s)	907(s)	265(m)	545(s)	480(s)	
HL^2	3420(br)			1640(s)			1618(s)		1590(s), 1570(m)					
PdL^2Cl				1532(s)			1600(s)		1575(s), 1560(sh)			510(s)	410(s)	325(s)
$UO_2L^2(CO_2CH_3)$				1543(m)			1600(m)	1615(m), 1340(s)	1590(w), 1563(s)	910(s)	255(m)	535(s)	482(s)	
HL^3	3430(s) 3120(br)			1630(s)			1612(s)		1585(s), 1575(sh)					
$[PdHL^3Cl]Cl$	3440(br)	3230(br)		1535(s)	1615(sh)	1555(m)			1590(s), 1580(s)			505(s)	405(m)	325(w)
$UO_2L^3(CO_2CH_3)\cdot 2H_2O$	3540(br), 3440(br)			1535(s)			1600(s)	1545(s), 1410(m)	1590(m)	895(s)		535(br)	500(m)	
HL^4		3160(splitted)	1670(vs)	1620(vs)	1618(sh)		1570(s)		1555(sh)					
$PdHL^4Cl_2$		3200(br)	1590(s)	1620(s)	1615(sh)				1555(m)			545(w)	430(w)	330(s) 305(s)

[a] br = broad; s = strong; sh = shoulder; m = medium; vs = very strong.

TABLE 3. ^1H NMR data

Compound	Chemical shifts (δ (ppm))^a (dmso-d_6)
 $[PdHL^3Cl]Cl$	2.35(S, 3H, =C–CH_3), 3.2(S, 3H, N–CH_3), 6.05–6.4(q, 3H, C_6H_3), 7.3–7.58(q, 5H, C_6H_5), 7.9 (S, 1H, =CH), 8.25(S, 1H, OH), 9.7 (br, 1H, NH).
 HL^4	1.8(S, 3H, =C–CH_3), 1.9(S, 3H, N–C–CH_3), 2.13(S, 3H, $COCH_3$), 3.03(S, 3H, N–CH_3), 5.16(S, 1H, –CH=), 7.35(q, 5H, C_6H_5), 11.15(br, 1H, HN…O).
 $PdHL^4Cl_2$	1.93(t, 3H, =C–CH_3), 1.95(t, 3H, N–C–CH_3), 2.2(t, 3H, $COCH_3$), 3.1(t, 3H, N–CH_3), 5.3(S, 1H, –CH=), 7.5 (q, 5H, C_6H_5).

^{a}s = singlet, t = triplet, q = quartet, br = broad. In spectrum of HL^4 there is a very weak intensity signal at 3.3 (CH_2) due to the presence of a keto-imine tautomer.

PdL^1Cl: R = H, M = Pd(II), X = Cl
$UO_2L^1(CO_2CH_3)$: R = H, M = UO_2(VI), X = CO_2CH_3
$UO_2L^3(CO_2CH_3)$: R = OH, M = UO_2, X = bidentate acetate.

M = Pd, X = Cl,
M = UO_2, X = CO_2CH_3

Scheme 1.

compounds exist almost entirely as the ketoenamine tautomer, although a very weak signal assignable to the presence of the ketoimine tautomer (HL^4) was detected. The disappearance of the signal corresponding to (H, NH) in the spectrum of $PdHL^4Cl_2$ may be due to the strong deshielding effect of the Pd(II) ion.

The above arguments indicate that the contribution of the structures indicated in Scheme 1 and Table 3 is more significant.

Electronic Spectra

The electronic spectral features of the complexes are summarized in Table 4. The broad shoulder

TABLE 4. Electronic spectral data of the metal complexes in dimethylformamide[a]

Complex	λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1}))
PbL^{1}Cl	460(sh); 405(sh); 365(sh); 350(s); 320(w).
UO$_2$L^1(CO$_2$CH$_3$)	490(sh)(160); 470(sh)(210); 410(sh)(1500); 365(sh)(20600); 355(s)(22600); 340(s)(17500).
PbL^{2}Cl	455(sh); 405(s); 380(w); 335(sh); 325(s).
UO$_2$L^2(CO$_2$CH$_3$)	465(w)(110); 408(sh)(22300); 390(s)(28700); 370(sh)(21800); 340(w)(8500).
[PdHL^{3}Cl]Cl	450(sh); 390(sh); 370(s); 316(s).
UO$_2$L^3(CO$_2$CH$_3$)$\cdot$2H$_2$O	535(w)(200); 365(sh)(27200); 355(s)(31900); 340(sh)(25200).
PdHL^{4}Cl$_2$	460(sh)(615); 404(w)(649); 380(br)(1948); 350(sh)(3247).

[a]br = broad; sh = shoulder; s = strong; w = weak.

appearing at about 460 nm appears to be a $^1A_{1g} \rightarrow {}^1A_{2g}$ ($d_{xz} \rightarrow d_{x^2-y^2}$) transition in square planar Pd(II) complexes [34]. The UO$_2$(VI) complexes exhibit two absorption bands at 410–390 and 535–465 nm that are ascribed to the apical oxygens → f transition of the uranyl moiety [18] and a charge-transfer transition from the equatorial ligands to the uranium atom [18] respectively. The higher energy bands displayed by all metal complexes are due to charge transfer(s) and internal ligand transitions. Determination of the exact geometries of the UO$_2$(VI) complexes requires single crystal X-ray analysis which is not available.

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