Synthesis and Structure Studies of Complexes of Some Second Row Transition Metals with 1-(Phenylacetyl and Phenoxyacetyl)-4-phenyl-3-thiosemicarbazide

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The synthesis of the new complexes of 1-phenylacetyl-4-phenyl-3-thiosemicarbazide (H_2papts) and 1-phenoxyacetyl-4-phenyl-3-thiosemicarbazide (H_2p_xapts); [Ru(HL)$_2$(H_2O)$_2$], [Rh(HL)$_3$], [Ag(H_2L)(H_2O)$_2$](NO_3), *trans*-[UO_2(HL)(bipy)(AcO)(H_2O)$_2$] (H_2L=H_2papts, H_2p_xapts; bipy=2,2′-bipyridyl), [Ag(H_2papts)(bipy)]$^+$ and [Pd(Hpapts)(bipy)]$^+$ is described. Characterization of these complexes by IR, electronic and ^{1}H-NMR spectra, conductometric titrations and thermal analysis is included. The complexes [Ru(HL)$_2$(H_2O)$_2$] were found to be efficient catalysts for the oxidation of primary alcohols to aldehydes and acids, secondary alcohols to ketones and aryl halides to aldehydes and acids in the presence of $NaIO_4$ as co-oxidant.

Key words 1-(phenylacetyl or phenoxyacetyl)-4-phenyl-3-thiosemicarbazide; complexes; oxidation; spectra

Complexes of thiosemicarbazide and 1,4-substituted thiosemicarbazides are of general interest as models for bioinorganic processes.[1—3] In our laboratory, many studies on transition metal complexes with thiosemicarbazide derivatives have been reported.[4—9] As a part of continuing work on O, N[10] and O, N, S[4,9,11] donor ligands, complexes of 1-phenylacetyl-4-phenyl-3-thiosemicarbazide (H_2papts; Fig. 1a) and 1-phenoxyacetyl-4-phenyl-3-thiosemicarbazide (H_2p_xapts; Fig. 1b) with some second row transition elements are now reported.

We have earlier reported first row transition metal complexes of H_2papts[9] and H_2p_xapts[11] in which they behave as neutral or mononegative bidentate and binegative tetradentate ligands. Here we report the synthesis of the new complexes of H_2papts and H_2p_xapts with a number of second row transition elements. We also report their vibrational, electronic, ^{1}H-NMR spectral data, conductometric titrations and thermal analysis. The catalytic oxidation of alcohols and aryl halides by ruthenium complexes, [Ru(HL)$_2$(H_2O)$_2$] (HL=Hpapts, Hp$_x$apts), in the presence of $NaIO_4$ as co-oxidant is also discussed.

Experimental

H_2papts and H_2p_xapts were prepared by the reported methods.[9,11]

Instrumentation IR spectra were measured using KBr discs on a Mattson 5000 FT-IR spectrometer. The electronic spectra were measured on Unicam UV2-100 UV-VIS spectrophotometer. Microanalyses were carried out by the Microanalytical Unit, Cairo University, Egypt. ^{1}H-NMR spectra were measured on a Varian Gemini (200 MHz) spectrometer in National Research Centre, Cairo. Thermogravimetry (TG) measurements were made in a nitrogen atmosphere between 20 and 800 °C with a rate of 10 °C min^{-1} using α-Al_2O_3 as a reference on a Shimadzu thermogravimetric analyzer TGA-50 by The Analytical Unit, Mansoura University. Conductometric measurements were carried out at room temperature on YSI Model 32 conductance meter.

Preparation of Complexes [Ru(HL)$_2$(H_2O)$_2$]$\cdot n H_2O$ (HL=Hpapts, n=0; HL=Hp$_x$apts, n=1): Hydrated ruthenium trichloride (0.065 g, 0.25 mmol) in EtOH (25 ml) was added with stirring to H_2papts (0.285 g, 1 mmol) or H_2p_xapts (0.301 g, 1 mmol). The reaction mixture was boiled under reflux for 2 h and 1 M AcONa (5 ml) was added. The fine brown (H_2papts) or pale brown (H_2p_xapts) complexes were filtered off, washed with H_2O, EtOH, Et_2O and air-dried.

[Rh(HL)$_3$]$\cdot 2H_2O$ (HL=Hpapts, Hp$_x$apts): Hydrated rhodium trichloride (0.105 g, 0.4 mmol) in EtOH (10 ml) was added to H_2papts (0.43 g, 1.5 mmol) or H_2p_xapts (0.452 g, 1.5 mmol) in EtOH (20 ml). The mixture was boiled under reflux for 2 h to produce the yellow (H_2papts) or orange (H_2p_xapts) precipitates. These were filtered off, washed with EtOH, Et_2O and dried *in vacuo*.

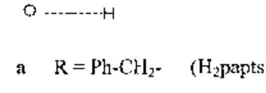
[Ag(H_2L)(H_2O)$_2$](NO_3)$\cdot H_2O$ (H_2L=H_2papts, H_2p_xapts): Silver nitrate (0.087 g, 0.5 mmol) in H_2O (1 ml) was added to H_2papts (0.143 g, 0.5 mmol) or H_2p_xapts (0.151 g, 0.5 mmol) in EtOH (10 ml) to give yellow (H_2papts) or orange-brown (H_2p_xapts) solids. These were left in the dark for 3 h, filtered off, washed with little H_2O, EtOH, Et_2O and dried in the dark *in vacuo*.

Trans-[UO_2(HL)(bipy)(AcO)(H_2O)$_2$]$\cdot n H_2O$ (HL=Hpapts, n=3; HL=Hp$_x$apts, n=0; bipy=2,2′-bipyridyl): Hydrated uranyl acetate (0.21 g, 0.5 mmol) in MeOH (10 ml) was added to a MeOH solution of 2,2′-bipyridyl (0.078 g, 0.5 mmol) and H_2papts (0.143 g, 0.5 mmol) or H_2p_xapts (0.151 g, 0.5 mmol). The resulting solution was boiled under reflux for 3 h in a steam bath. The red-orange (H_2papts) or yellow (H_2p_xapts) solutions were reduced in volume until the precipitates separated out. These were filtered off, washed with little MeOH and dried in a desicator over silica gel.

[Ag(H_2papts)(bipy)]BPh_4: $AgNO_3$ (0.087 g, 0.5 mmol) in H_2O (0.5 ml) was added to 2,2′-bipyridyl (0.078 g, 0.5 mmol) in MeOH (25 ml) to form a colorless solution, to which H_2papts (0.143 g, 0.5 mmol) in MeOH (10 ml) was added to produce a red-brown solution. $NaBPh_4$ (0.17 g, 0.5 mmol) in MeOH (5 ml) was added and the precipitate was separated out. This was filtered off, washed with a little H_2O, MeOH, Et_2O and dried in the dark *in vacuo*.

[Pd(Hpapts)(bipy)]BPh_4: The complex [Pd(bipy)Cl_2] was prepared by the literature method.[12] To a stirred suspension of [Pd(bipy)Cl_2] (0.17 g, 0.5 mmol) in acetone (10 ml), H_2papts (0.143 g, 0.5 mmol) and KOH (0.056 g, 1 mmol) in MeOH (10 ml) was added. The mixture was stirred overnight. $NaBPh_4$ (0.17 g, 0.5 mmol) in MeOH (5 ml) was added to the resulting brown solution. The complex was filtered off, washed with MeOH, Et_2O and dried *in vacuo*.

Catalytic Oxidation For the catalytic oxidation by [Ru(HL)$_2$(H_2O)$_2$] (HL=Hpapts, Hp$_x$apts) complexes, the organic substrate (1.0 mmol) was added to $NaIO_4$ (2.5 mmol) in CCl_4–CH_3CN–H_2O (1 : 1 : 2; 20 ml) and the catalyst (0.02 mmol). The reaction mixture was stirred under reflux at 70 °C, then cooled and extracted with diethyl ether (3×20 ml). The ethereal layer was then dried with anhydrous Na_2SO_4 and the aldehyde or ketone content quantified as its 2,4-dinitrophenylhydrazone derivatives. The aqueous layer



a R = Ph-CH_2- (H_2papts)

b R = Ph-O-CH_2- (H_2p_xapts)

Fig. 1. Structure of 1-(Phenylacetyl and Phenoxyacetyl)-4-phenyl-3-thiosemicarbazide

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Table 1. Analytical and Spectroscopic Data of H$_2$papts, H$_2$p$_x$apts and their complexes

Compound	Found (Calcd) % C	H	N	S	IR data (cm^{-1}) ν(C=O)	ν(C=S)+ν(C−N) & ν(C=S)
H$_2$papts					1687	1230, 760
[Ru(Hpapts)$_2$(H$_2$O)$_2$]	51.03 (51.06)	4.66 (4.54)	11.63 (11.91)	8.93 (9.08)	—	2125, 730
[Rh(Hpapts)$_3$]·2H$_2$O	55.00 (54.54)	4.50 (5.65)	12.61 (12.73)	9.56 (9.70)	—	1230, 760
[Ag(H$_2$papts)(H$_2$O)$_2$]NO$_3$·H$_2$O	36.59 (36.66)	3.78 (3.87)	11.30 (11.41)	6.30 (6.52)	1649	1240, 745
[UO$_2$(Hpapts)(bipy)(AcO)(H$_2$O)$_2$]·3H$_2$O	37.53 (37.72)	3.95 (4.07)	8.06 (8.15)	3.80 (3.70)	—	1230, 750
[Ag(H$_2$papts)(bipy)]BPh$_4$	67.71 (67.74)	4.78 (4.95)	8.00 (8.06)	3.71 (3.69)	1650	1235, 750
[Pd(Hpapts)(bipy)]BPh$_4$	67.90 (67.95)	4.79 (4.85)	8.01 (8.09)	3.73 (3.70)	—	1215, 750
H$_2$p$_x$apts					1670	1225, 747
[Ru(Hp$_x$apts)$_2$(H$_2$O)$_2$]·2H$_2$O	47.63 (47.68)	4.51 (4.50)	11.10 (11.13)	8.50 (8.48)	—	1230, 745
[Rh(Hp$_x$apts)$_3$]·2H$_2$O	51.54 (51.98)	4.47 (4.43)	12.05 (12.13)	9.34 (9.24)	—	1225, 740
[Ag(H$_2$p$_x$apts)(H$_2$O)$_2$]NO$_3$·H$_2$O	35.50 (35.50)	3.75 (3.75)	10.81 (11.04)	6.08 (6.31)	1650	1235, 748
[UO$_2$(Hp$_x$apts)(bipy)(AcO)(H$_2$O)$_2$]	39.42 (39.46)	3.86 (3.76)	8.59 (8.53)	3.85 (3.90)	—	1230, 760

Compound	ν(C=N)	ν(C−O)	ν(N−N)	ν(M−O)	ν(M−N)	^{1}H-NMR data (δ/ppm)$^{a)}$ CH$_2$ (s)	Ph-ring (m)	N^{1}H (s)	N^{2}H (s)	N^{4}H (s)
H$_2$papts	—	—	990	—	—	3.55	7.1—7.5	10.15	9.85	9.75
[Ru(Hpapts)$_2$(H$_2$O)$_2$]	1610	1080	1000	530	400	3.60	7.1—7.5	—	10.0	9.85
[Rh(Hpapts)$_3$]·2H$_2$O	1600	1080	1010	520	340	3.55	7.15—7.6	—	9.95	9.85
[Ag(H$_2$papts)(H$_2$O)$_2$]NO$_3$·H$_2$O	—	1380^{b}	1020	490	410	3.80	7.2—7.6	10.60	10.2	10.0
[UO$_2$(Hpapts)(bipy)(AcO)(H$_2$O)$_2$]·3H$_2$O	1600	1065	1015	910^{c}	330					
[Ag(H$_2$papts)(bipy)]BPh$_4$	—	—	1020	495	415	3.74	d	10.40	10.2	10.05
[Pd(Hpapts)(bipy)]BPh$_4$	1610	1067	1020	515	350	3.63	d	—	10.0	9.9
H$_2$p$_x$apts	—	—	970	—	—	3.50	6.9—7.4	10.25	9.7	9.6
[Ru(Hp$_x$apts)$_2$(H$_2$O)$_2$]·2H$_2$O	1605	1070	1020	500		3.55	7.1—7.5	—	9.9	9.65
[Rh(Hp$_x$apts)$_3$]·2H$_2$O	1610	1075	1020	500	415	3.68	7.1—7.6	—	9.9	9.7
[Ag(H$_2$p$_x$apts)(H$_2$O)$_2$]NO$_3$·H$_2$O	—	1383^{b}	1020	495		3.72	7.0—7.4	10.43	10.1	9.8
[UO$_2$(Hp$_x$apts)(bipy)(AcO)(H$_2$O)$_2$]	1260	1060	1005	900^{c}	400					

a) ^{1}H-NMR spectra in CDCl$_3$ solution. *b*) ν(NO$_3$). *c*) ν^{as}(UO$_2$) and *d*) ^{1}H-NMR band interferes with the tetraphenyl protons (complicated multiplet).

was acidified with 5 M H$_2$SO$_4$ to pH 2, extracted with diethyl ether (3×20 ml), dried and evaporated to give the acid.

Conductometric Titration To determine the stoichiometric ratios of some of the studied complexes, conductometric titrations were carried out at room temperature. 25 cm^3 of 10^{-3} M RuCl$_3$ or RhCl$_3$ in EtOH, AgNO$_3$ or AgNO$_3$–bipy (1 : 1) in 99% EtOH , and K$_2$PdCl$_4$–bipy (1 : 1) in 80% EtOH were titrated against 10^{-2} M H$_2$papts or H$_2$p$_x$apts in EtOH. The titrations were carried out twice to test the reproducibility.

Results and Discussion

Preparations The ruthenium complexes [Ru(HL)$_2$(H$_2$O)$_2$] (HL=Hpapts, Hp$_x$apts) were prepared from hydrated ruthenium trichloride and the corresponding ligand in EtOH under basic conditions while the rhodium complexes [Rh(HL)$_3$] (HL=Hpapts, Hp$_x$apts) were obtained from the reaction of hydrated rhodium trichloride and H$_2$L in EtOH. The complexes [Ag(H$_2$L)(H$_2$O)$_2$](NO$_3$) (H$_2$L=H$_2$papts, H$_2$p$_x$apts) were produced from very concentrated aqueous solution of AgNO$_3$ and H$_2$L in EtOH while the *trans*-[UO$_2$(HL)(bipy)(AcO)(H$_2$O)$_2$] complexes were prepared from the reaction of uranyl acetate, bipy and H$_2$L in MeOH. The [Ag(H$_2$papts)(bipy)]$^+$ complex was made from AgNO$_3$, bipy and H$_2$papts in aqueous-EtOH solution while [Pd(Hpapts)(bipy)]$^+$ was isolated from the reaction of [Pd(bipy)Cl$_2$] and H$_2$papts in acetone–MeOH solution in the presence of KOH.

Vibrational Spectra The IR spectral data of H$_2$papts and H$_2$p$_x$apts and a number of their complexes have been reported.[9,11] In Table 1, the IR spectra of H$_2$papts, H$_2$p$_x$apts and their complexes are listed with provisional assignments of selected vibrations. As expected, the free ligands exhibit broad absorption bands near 2200 and 1950 cm^{-1} assigned to the stretching and bending vibrations of intramolecular hydrogen bonding ν(N(2)H..........O);[13] these are not observed in the spectra of any of the complexes, indicating the involvement of the N(2) center in coordination.[4,9,11] This view is further supported by the slight shift of the bands at *ca.* 3300—3150 cm^{-1} region and 990 cm^{-1} in the free ligands and complexes owing to ν(NH) and ν(N–N) vibrations, respectively.[5]

In the case of Ag(I) complexes, [Ag(H$_2$L)(H$_2$O)$_2$]$^+$ (H$_2$L=H$_2$papts, H$_2$p$_x$apts) and [Ag(H$_2$papts)(bipy)]$^+$, the strong bands near 1680 cm^{-1} in the free ligands arising from

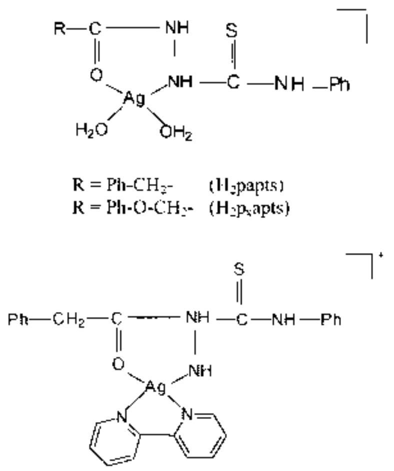

Fig. 2. Structure of $[Ag(H_2L)(H_2O)_2]^+$ ($H_2L=H_2papts$, H_2p_xapts) and $[Ag(H_2papts)(bipy)]^+$ Complexes

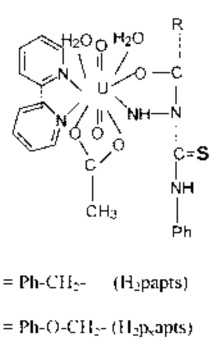

Fig. 3. Structure of $[UO_2(HL)(bipy)(AcO)(H_2O)_2]$ ($HL=Hpapts$, Hp_xapts) Complexes

$\nu(C=O)$ are affected upon coordination and shifted to lower wave number, as expected since the carbonyl oxygen centers are involved in coordination.[14,15] This means that both H_2papts and H_2p_xapts behave as neutral bidentate ligands as shown in Fig. 2. In the other reported complexes, the stretching vibrations $\nu(C=O)$ of the free ligands are missing in the complexes indicating the participation of the deprotonated enolic carbonyl oxygen ($=C–O^-$) in coordination. This feature is further supported by the observation of new bands near 1600 and $1075\,cm^{-1}$ due to $\nu(C=N)$[16] and $\nu(C–O)$[17] vibrations, respectively. In the uranyl complexes, *trans*-$[UO_2(HL)(bipy)(AcO)(H_2O)_2]$ ($HL=Hpapts$, Hp_xapts), (Fig. 3) two extra bands are observed near 1540 and $1400\,cm^{-1}$ attributed to $\nu^{as}(OCO)$ and $\nu^{s}(OCO)$ of the acetato group, respectively, indicating asymmetric bidentate coordination of the acetato group[18] ($\Delta(OCO)$ between $\nu^{as}(OCO)$ and $\nu^{s}(OCO)$ is in the $140\,cm^{-1}$ region[18]). Also, the uranyl complexes show strong IR bands near $900\,cm^{-1}$ assigned to $\nu^{as}(UO_2)$ of the *trans*-O=U=,O group.[14,19] When the hydro complexes, $[Ru(HL)_2(H_2O)_2]$, $[Ag(H_2L)(H_2O)_2]^+$ and *trans*-$[UO_2(HL)(bipy)(AcO)(H_2O)_2]$ ($HL=Hpapts$, Hp_xapts) were heated up to 120 °C, no water molecules were removed indicating their presence in the coordination sphere.[9] The IR band near $750\,cm^{-1}$ in the free ligands arising from $\nu(C=S)$ vibrations remain more or less in the same position in the complexes indicating that the thione group is not taking part in complexation.[9]

Table 2. Electronic Spectral Data for H_2papts and H_2p_xapts Complexes

Compound	Electronic spectra[a) (λ_{max}/nm (ε_o $dm^3\,mol^{-1}\,cm^{-1}$))
H_2papts	
$[Ru(Hpapts)_2(H_2O)_2]$	518 (532), 430 (885), 305 (7075)
$[Rh(Hpapts)_3]\cdot 2H_2O$	610 (490), 520 (5636), 410 (15760)
$[Ag(H_2papts)(H_2O)_2]NO_3$	520 (661), 315 (18352)
$[Ag(H_2papts)(bipy)]^+$	515 (338), 308 (6916)
$[Pd(Hpapts)(bipy)]^+$	480 (225), 330 (20067)
H_2p_xapts	
$[Ru(Hp_xapts)_2(H_2O)_2]\cdot H_2O$	525 (437), 428 (1195), 310 (6877)
$[Rh(Hp_xapts)3]\cdot 2H_2O$	595 (65), 490 (250), 400 (1755)
$[Ag(H_2p_xapts)(H_2O)_2]NO_3$	534 (207), 300 (14010)

a) Spectra in DMSO solutions.

Most of the reported complexes show new bands near 510 and $380\,cm^{-1}$ which may arise from $\nu(M–O)$[14,20,21] and $\nu(M–N)$[10,22,23] stretching, respectively. The complexes, $[Ag(H_2L)(H_2O)_2](NO_3)$ ($H_2L=H_2papts$, H_2p_xapts) show new strong band at $1385\,cm^{-1}$, which may be assigned to $\nu(NO_3^-)$ proving the presence of NO_3^- as a free ion in these complexes.[24]

Electronic Spectra The electronic spectra in dimethyl sulphoxide for some complexes are given in Table 2. The electronic spectra of $[Ru(HL)_2(H_2O)_2]$ ($HL=Hpapts$, Hp_xapts) show three bands near 520, 430 and 300 nm which may arise from ${}^1A_{1g}\rightarrow{}^1T_{1g}$, ${}^1A_{1g}\rightarrow{}^1T_{2g}$ and ligand (π–dπ) to metal transitions, respectively, this indicates a low-spin octahedral arrangement around the diamagnetic Ru(II).[23,25] The electronic spectra of $[Rh(HL)_3]$ ($HL=Hpapts$, Hp_xapts) exhibit three bands observed in the regions 610—595, 520—490 and 410—400 nm which may be assigned to ${}^1A_{1g}\rightarrow{}^3T_{1g}$, ${}^1A_{1g}\rightarrow{}^1T_{1g}$ and ${}^1A_{1g}\rightarrow{}^1T_{2g}$ transitions, respectively, due to the octahedral geometry around Rh(III).[14,26,27] The electronic spectra of $[Pd(Hpapts)(bipy)]^+$ shows two bands at 480 and 330 nm due to ${}^1A_{1g}\rightarrow{}^1B_{1g}$ and ${}^1A_{1g}\rightarrow{}^1E_g$, transitions, respectively, in a square planar configuration.[9,25,28] The electronic spectra of silver(I) complexes show bands in the 540—510 and 330—300 nm regions, which may be attributed to square planar stereochemistry.[29]

^{1}H-NMR Spectra The ^{1}H-NMR spectroscopic data of H_2papts and H_2p_xapts and some of their complexes in $CDCl_3$ are given in Table 1, and are in close agreement with the reported data.[9,11] In the free ligands, the aromatic protons appear in the δ 7.1—7.5 ppm region.[25,30] The CH_2 protons give a singlet at δ 3.55 ppm while the N(1)H, N(2)H and N(4)H protons appear as singlets in the regions δ 10.40—10.15, 10.2—9.85 and 10.05—9.75 ppm, respectively; similar features have been observed for the 1-morpholineacetyl-4-phenyl-3-thiosemicarbazide (MPTSC).[31]

In the complexes, the resonance arising from the N(1)H proton disappears, whereas that arising from the N(2)H proton shifts to downfield[9] values indicating the chelation of the ligands through the deprotonated enolic carbonyl oxygen ($=C–O^-$) and the N(2) centers to the metal ion. The ^{1}H-NMR of $[Ag(H_2L)(H_2O)_2](NO_3)$ ($H_2L=H_2papts$, H_2p_xapts) and $[Ag(H_2papts)(bipy)]^+$ are of particular interest since the N(1)H and N(2)H protons are shifted downfield indicating a decrease in the electron density caused by the withdrawing of electrons by Ag(I) from the coordinating centers.[19]

Conductometric Titrations The conductance of a solu-

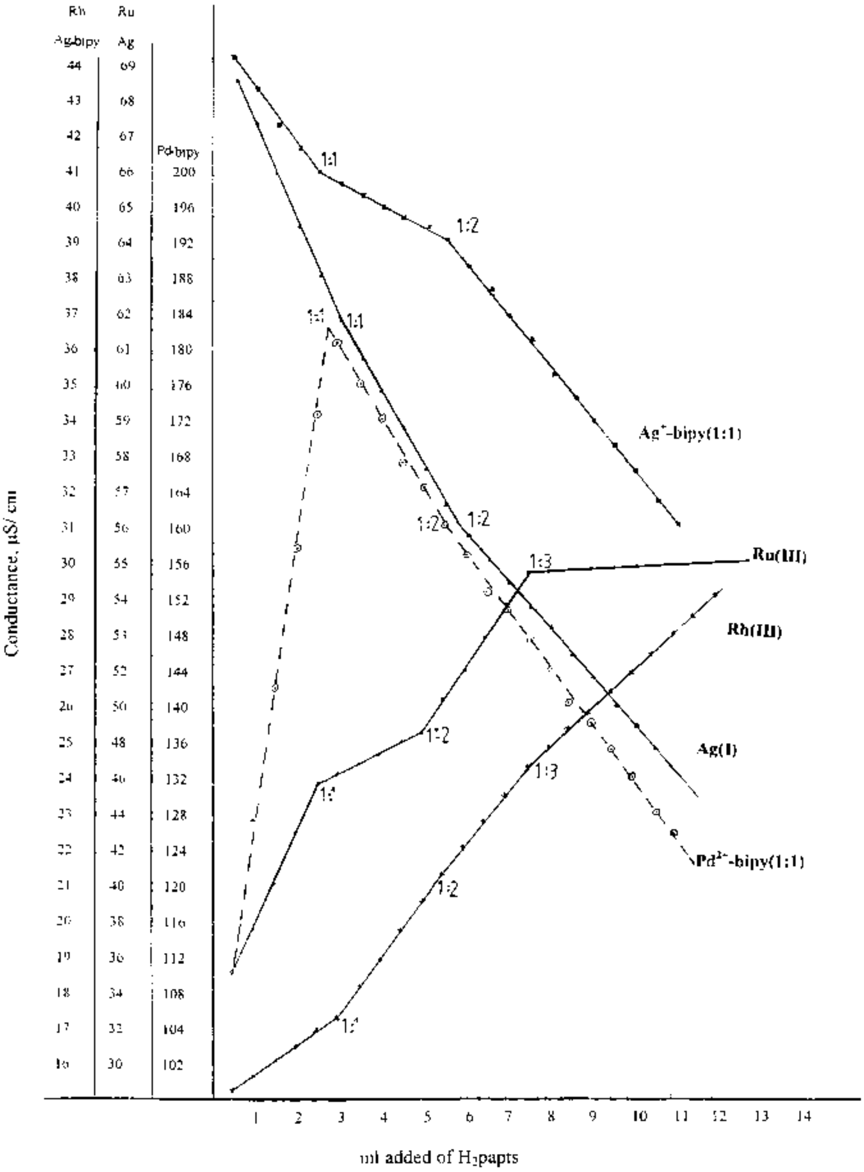

Fig. 4. Conductograms of the Metal Salts with H_2papts

tion, at a certain temperature, is affected by the mobility of the ions present. Thus, the formation of a complex in a solution can be characterized by using conductometric titrations.[32)] The composition of the complexes can be determined by studying the relation between the conductance measured and the volume of ligand added to the metal ion solution. The plots consist of some lines with different slopes, each intersection gives a certain molar ratio of complex formation.[33)]

Figures 4 and 5 show the relation between the conductance of Ru(III), Rh(III), Ag(I), Ag(I)–bipy (1 : 1) and Pd(II)–bipy (1 : 1) and the added volumes of H_2papts and H_2p_xapts, respectively. It is clear that, the molar ratios M : L, M : 2L are formed in all cases as well as M:3L in the case of Rh(III) with both ligands and Ru(III) with H_2papts. The continuous increase in the conductance of the solution in successive additions of the ligand may be owing to the liberation of highly conducting hydrogen ions from the enolised hydroxyl center during complex formation[34,35)] as supported from the IR spectral data. The decrease in the conductance of metal ions solutions with the ligand additions may be attributed to the replacement of hydrogen ions of high conductivity by another species with low conductivity.

Thermal Studies The thermal decompositions of the complexes, $[Ru(Hpapts)_2(H_2O)_2]$, $[Rh(Hp_xapts)_3]\cdot 2H_2O$ and *trans*-$[UO_2(Hp_xapts)(bipy)(AcO)(H_2O)_2]$ were studied using the TG technique. The thermogram of the $[Ru(Hpapts)_2(H_2O)_2]$ complex shows firstly a weight loss endothermic step between 170 and 312 °C, which may be corresponding to the release of the coordinated water molecules and a phenylthiourido ($C_7H_7N_2S$) fragment[9,36)] (Found: 27.26; Calcd: 26.52%). The second weight loss step (Found: 22.93; Calcd: 21.42%) between 321 and 410 °C may be attributed to elimination of the phenylthiorido fragment from the second ligand species while between 410 and 451 °C, a weight loss (Found: 16.88; Calcd: 16.59%) may arise from the elimination of the phenylethylimio (C_8H_7N) fragment[11)] from one ligand species. The last decomposition step at 521 °C may consist of the formation of mixed carbide-RuO_2 residue (Found: 28.34%). The TG curve of [Rh

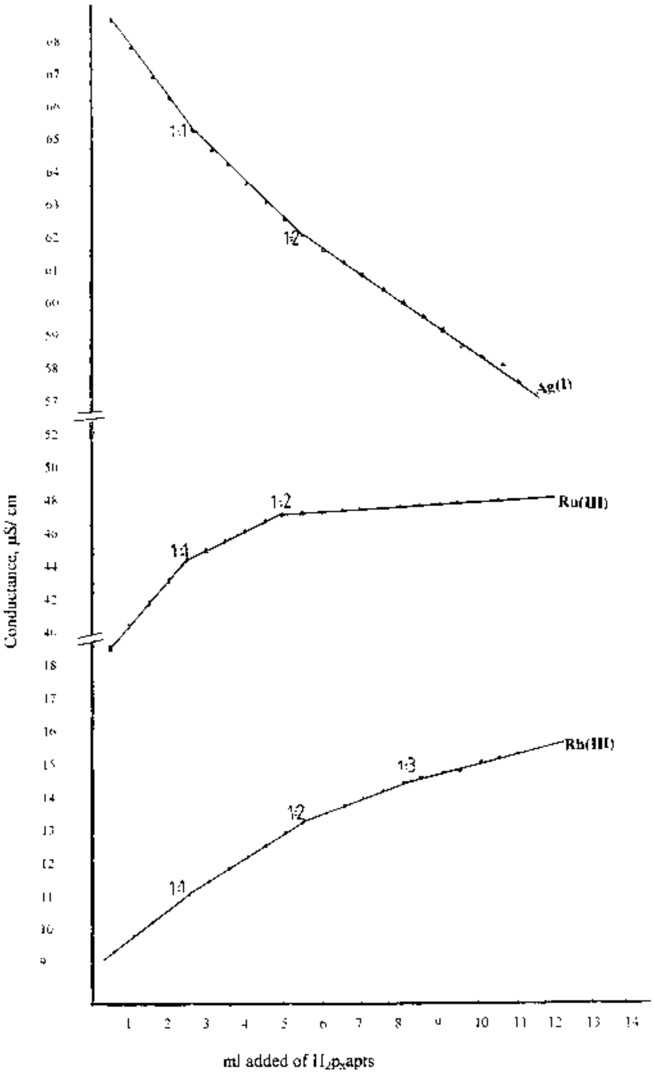

Fig. 5. Conductograms of the Metal Salts with H_2p_xapts

$(Hp_xapts)_3]\cdot 2H_2O$ shows the first weight loss between 80 and 170 °C, which may be due to the release of water molecules (Found: 3.38; Calcd: 3.47%) while the endothermic weight loss between 170 and 308 °C, which may be due to the release of two phenylthiourido fragments[9,36] (Found: 29.63; Calcd: 29.07%). There are two other TG inflections in the ranges 308—332 and 351—404 °C, the first weight loss in these inflections may arise from the release of the third phenylthiourido (Found: 14.95; Calcd: 14.53%). The last decomposition step may consist of the elimination of two phenoxyethylimio fragments[11] (Found: 25.63; Calcd: 25.60%), leaving Rh_2O_3 representing (Found: 22.79; Calcd: 24.43%).[26] The thermogram of *trans*-$[UO_2(Hp_xapts)(bipy)(AcO)(H_2O)_2]$ shows three TG inflections in the ranges 161—345, 345—406 and 406—497 °C. The first weight loss may arise from the release of the coordinated water molecules and the phenylthiourido fragment[11,36] (Found: 22.46; Calcd: 22.77%) while the second step is attributed to the removal of the acetate species[37,38] (Found: 6.98; Calcd: 7.18%). The last TG inflection may be corresponding to the release of a half of the bipy molecule[39] (Found: 9.08; Calcd: 9.50%) followed by mixed carbide-U_3O_8 residue formation at 505 °C (Found: 63.70%) of the initial weight of the complex.

Table 3. Catalytic Oxidations by $[Ru(HL)_2(H_2O)_2]$ (HL=Hpapts, Hp_xapts) Complexes[a]

Substrate	$[Ru(Hpapts)_2(H_2O)_2]$ Yield %	Turn Over	$[Ru(Hp_xapts)_2(H_2O)_2]$ Yield %	Turn Over
Benzyl alcohol	60^{ald}, 14^{ac}	40.5	82^{ald}, 19^{ac}	52
3,4-Dimethoxybenzyl alcohol	68^{ald}, 12^{ac}	40	73^{ald}, 14^{ac}	51
α-Tetralol	90^{k}	45.5	93^{k}	47
Benzohedrol	64^{k}	33	70^{k}	36
Benzylchloride	42^{ald}, 14^{ac}	29	46^{ald}, 10^{ac}	29
p-Methoxybenzylchloride	80^{ald}, 16^{ac}	49	84^{ald}, 16^{ac}	51

a) Oxidation of alcohols were carried out for 3 h, those of aryl halides for 4 h, all at 70 °C by using 0.02 mmol of catalyst, 2.5 mmol of $NaIO_4$ (co-oxidant) in CCl_4–CH_3CN–H_2O (1 : 1 : 2, 20 cm^3), ^{ald}corresponding aldehyde, ^{ac}corresponding acid, ^{k}corresponding ketone

Catalytic Oxidations We reported that the $[Fe^{III}(papts)Cl(H_2O)]$ complex could oxidize primary alcohols to aldehydes and secondary alcohols to ketones stoichiometrically in dichloromethane at room temperature.[9] The catalytic oxidation of alcohols by $[Ru^{III}Cl_2(NQ)(EPh_3)_2]$ (E=P, As)[40] and $[Ru^{III}Cl_2(acac)(PPh_3)_2]$[41] using *N*-methylmorpholine-*N*-oxide (NMO) as co-oxidant in dichloromethane have been reported. Furthermore, the catalytic oxidation of lower valent ruthenium complexes in the presence of NMO[42] or hydroquinones–Co(salophen)(PPh_3) (H_2salophen=*N*,*N′*-bis(salicylidene-*o*-phenylenediamine)[43] as co-oxidants towards the oxidation of primary and secondary alcohols has been investigated. It was found that primary and secondary alcohols were oxidised to the corresponding carbonyl compounds. We tested the reported ruthenium complexes $[Ru(HL)_2(H_2O)_2]$ (HL=Hpapts, Hp_xapts) for possible organic catalytic oxidations by taking 0.02 mmol of the catalyst in CCl_4–CH_3CN–H_2O (1 : 1 : 2) solution with $NaIO_4$ (2.5 mmol) as co-oxidant with 1.0 mmol of substrate, the reactions being carried out for 3 h in the case of alcohols and 4 h in the case of aryl halides, all at 70 °C. Aldehydes and ketones were detected and quantified as 2,4-dinitrophenylhydrazone derivatives and acids isolated and weighed as such, as shown in Table 3. Blank experiments were conducted under similar conditions, but in the absence of complexes; in all cases very small amounts of oxidation products were found.

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