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Full Paper

New Pt^{4+} complexes synthesized from $[Pt(FH.HCl)_2Cl_3(EtOH)]Cl.$ ½EtOH with alkali and alkaline earth metal salts by tribochemical reactions

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Abstract

Formylhydrazine (FH) reacts with H_2PtCl_6 in EtOH forming a new complex with the general formula, $[Pt(FH.HCl)_2Cl_3(EtOH)]Cl.1/2EtOH$. Tribochemical reaction of this complex with alkali and alkaline earth halides (KBr, KI and CaI_2) affords novel Pt (IV) complexes with the general formulae, $[Pt(FH)_2Br_4]3/2EtOH$, $[Pt(FH)_2I_2(EtOH)(H_2O)_{1/2}]I_2$ and $[Pt(FH)_2I_2(EtOH)_{3/2}]I_2$. The tribochemical reactions are always accompanied by color changes, substitution of chloride by bromide and/or iodide ions but no reduction for Pt(IV) has been occurred during grinding with KBr, KI and/or CaI_2. In all complexes the ligand (FH) coordinates to the Pt(IV) ion in a monodentate manner *via* the NH group. All the results suggest the existence of an octahedral geometry around the Pt(IV) complexes. The stereochemistry of the Pt(IV) complexes has been determined from the results of elemental analyses, conductance, spectral (IR., UV-Vis., ^{1}H-NMR), thermal (DTA, TGA) and magnetic measurements.

Keywords: Pt(IV) complexes; Tribochemical reactions; Spectroscopic studies.

1. Introduction

In our previous papers [1-8] we described the tribochemical reactions of some metal complexes derived from Girard's T with Cu^{2+} and Ru^{3+} salts as well as some crown ethers complexes containing $HgCl_2$ and KBr. The results showed that the complexes prepared by conventional chemical methods react directly with alkali and alkaline earth metal salts (KBr, KI and CaI_2) in the solid state. These reactions are always accompanied by color changes, substitution of chloride by bromide and/or iodide ions and reduction of the metal ion as in case of Cu^{2+} complexes [1]. But in our case, on grinding the Pt^{4+} complex with the general formula, $[Pt(FH.HCl)_2Cl_3(EtOH)]Cl.1/2EtOH$, with alkali and alkaline earth metals, the colors of the isolated complexes are changed and the substitution of chloride ions by bromide and/or iodide ions has been carried but no reduction of Pt^{4+} has been occurred. In an attempt to extend our earlier work, we prepared primarily a new Pt4+ solid complex with the general formula, [Pt(FH.HCl)2Cl3(EtOH)]Cl.1/2EtOH, derived from the reaction of formylhydrazine (FH) with H_2PtCl_6 in ethanolic solution by conventional chemical method. The geometries of the isolated solid complex are characterized by conventional physical and chemical methods. Reactions of this solid complex, $[Pt(FH.HCl)_2Cl_3(EtOH)]Cl.1/2EtOH$, with solid KBr, KI and/or CaI_2 using tribochemical technique were deeply investigated by chemical, spectral, magnetic and thermal measurements. The aim of this paper is to prepare novel complexes which are not easily prepared by direct chemical method and characterized by conventional chemical, spectral, thermal and magnetic measurements. Also, the tribochemical reactions are used to prepare of solid complexes as a type of Nano chemistry as well as a type of green chemistry.

2. Experimental

Formylhydrazine (FH) was prepared as reported earlier in literature [9].

2.1. Physical Measurements

IR spectra of the solid complexes were recorded in Nujol mull with a Mattson 5000 FTIR Spectrometer. ^{1}H-NMR spectra in d_6-DMSO were carried out on a Varian Gemini (200 MHz). The electronic spectra of the Pt(IV) complexes in Nujol and/or DMSO were recorded on Unicam UV-Vis. Spectrometer UV2. Molar conductance measurements were obtained with an YSI model 35 conductivity bridge using 10^{-3} M solution in DMSO at 25 ^oC. Thermal measurements (TGA, DTA) were obtained using a Shimadzu 50H at Mansoura University. The analyses of C and H were performed by the Microanalytical Unit at Cairo University.

2.2.Synthesis of $[Pt(FH.HCl)_2Cl_3(EtOH)]Cl.1/2EtOH$ by conventional chemical method

An equimolar amounts of H_2PtCl_6 (0.01 mmol) in absolute EtOH (25 mL) and formylhydrazine (FH) dissolved in absolute EtOH (25 mL) were mixed thoroughly where a yellow precipitate was formed at once. The reaction mixture was heated under reflux for 1h to get a high yield of the product. The precipitate was filtered off hot, washed successively with EtOH and Et_2O and finally dried in a vacuum desiccator over silica gel (yield: 68.4%).

2.3. Synthesis of Pt^{4+} complexes by tribochemical reaction Reaction of $[Pt(FH.HCl)_2Cl_3(EtOH)]Cl.1/2EtOH$ with KI

0.5 g of $[Pt(FH.HCl)_2Cl_3(EtOH)]Cl.1/2EtOH$ was added to KI (1.5 g) in the solid state and the mixture was grinded in agate mortar for 1.5 h till the color of the original complex changes from yellow to deep red. A solution of EtOH/MeOH (15/85 V/V) was added to the reaction mixture and then the solution was refluxed for 2h on a hot plate. The product, $[Pt(FH)_2I_2(EtOH)(H_2O)_{1/2}]_2I_4$, was filtered off, washed with a mixture of EtOH/Et_2O (15/ 85 V/V) and finally dried in an oven at 110 ^oC for 1h (yield: 37.2 %). The same technique was used in the reactions of $[Pt(FH.HCl)_2Cl_3(EtOH)]Cl.1/2EtOH$ with CaI_2 and KBr giving the complexes with the general formulae, $[Pt(FH)_2I_2(EtOH)_{3/2}]_2I_4$ and $[Pt(FH)_2Br_4].3/2EtOH$, respectively.

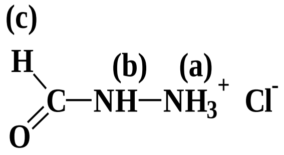
3. Results and Discussion

All the isolated solid complexes are stable towards air and moisture. Also, the complexes are easily soluble in DMSO and DMF, partially soluble in H_2O and insoluble in all other common organic solvents. The molar conductance values of the complexes in DMSO (10^{-3} M) solution suggest the electrolytic nature of all complexes [10] except the bromide complex (Table 1). Elemental analyses suggest that the complexes have 1:2 ratio (M: L). The low melting points of the chloride and bromide complexes suggest the existence of weak covalent bonding. On the other hand, the high melting points of the iodide complexes (> 300 ^{o}C) suggest the existence of a comparatively strong covalent bonding. The IR spectra of the three solid Pt^{4+} complexes, derived from the tribochemical reactions in KBr and/or Nujol mulls, are more or less the same while the IR spectrum of the parent complex in Nujol is quite different from that observed in KBr. This suggests that the parent solid complex, [Pt(FH.HCl)2Cl3(EtOH)]Cl.1/2EtOH, reacts easily with KBr during the preparation of the disc for IR measurements. Consequently, the IR spectrum in KBr disc differs from that carried out in Nujol mull. In order to gets a nice IR spectrum characterizing the original complex only without any reaction it prefers to avoid the use of KBr as mulling agent and hence Nujol is considered as a good and trustable medium for IR measurements. The IR spectrum of the parent complex, [Pt(FH.HCl)2Cl3(EtOH)]Cl.1/2EtOH, in Nujol shows three strong bands at 3299, 3139 and 3218 with a shoulder at 3260 cm-1 assigned to νas(NH$_2$), νs(NH$_2$), ν(NH) and ν(NH) (hydrogen-bonded) vibrations, respectively. Also, the bands observed at 1738, 1626, 1528, 974 and 544 cm-1 are assigned to ν(CO), β(NH2), ν[N⋯C⋯O) [11, 12], ν(N-N) [13] and ν(Pt-O) vibrations, respectively. Furthermore, two new bands at 495 and 456 are observed and assigning to ν(Pt-N) vibration in cis-form. Moreover, two bands observed at 360 and 331 cm-1 are assigned to ν(Pt-Cl) [14] vibration in the cis-form. The value of molar conductance in DMSO (57.3 Ω^{-1}.cm^{2}.mol^{-1}) suggests 1:1 electrolyte [10] of this complex. The low pH value of the complex solution in H$_2$O (pH = 2.5) as well as the positive test for acidity by using NaHCO$_3$ solution and the observation of the effervescence of CO$_2$ confirms the existence of HCl within the complex. The amount of HCl is determined quantatively using acid-base titration in the presence of ph. ph. as indicator. The results prove the existence of two molecules of HCl within the parent Pt^{4+} complex, [Pt(FH.HCl)$_2$Cl$_3$(EtOH)]Cl.1/2EtOH. Those two HCl molecules are probably react with the NH$_2$ groups forming NH$_3^+$Cl$^-$ molecules as shown in structure 1. Thermal analysis measurements (TGA, DTA) show four steps of decomposition at 215, 267.6, 352.7 and 521 ^{o}C corresponding to the loss of 1/2EtOH and steps of decomposition of this complex. The final residue corresponds to the formation of PtO$_2$ (Calcd. 37.9%; exp. 37.6%).

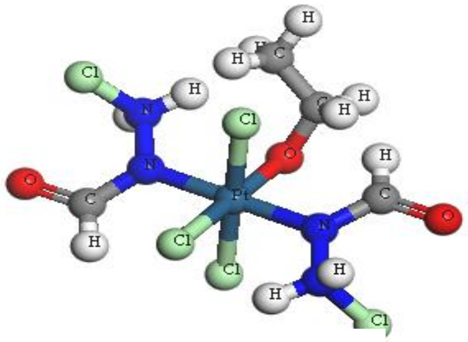
Table 1. Analytical data and some physical properties of the isolated Pt(IV) complexes

Compound	color	M.p.; ^{o}C	% Found (calcd.)		
			C	H	Cl
[Pt(FH.HCl)$_2$.Cl$_3$.(EtOH)]Cl.1/2EtOH	Yellow	210	10.1 (10.0)	3.2 (3.2)	36.0 (35.5)
[Pt(FH)$_2$.I$_2$.(EtOH)$_{3/2}$]$_2$I$_4$	Brown	>300	6.3 (6.7)	2.6 (1.9)	56.8 (56.9)
[Pt(FH)$_2$.I$_2$.(EtOH)(H$_2$O)$_{1/2}$]$_2$I$_4$	Chocolate-brown	>300	5.1 (5.5)	2.2 (1.7)	57.2 (57.8)
[Pt(FH)$_2$.Br$_4$].3/2EtOH	Reddish-orange	240	8.6 (8.5)	2.4 (3.0)	45.8 (45.4)

The electronic spectrum of the original complex, $[Pt(FH.HCl)_2Cl_3(EtOH)]Cl.1/2EtOH$, in Nujol mull shows two bands at 310 nm (32360 cm^{-1}) and 338 nm (29585 cm^{1}) which may be assigned to $\pi\rightarrow\pi^*$ (C=O) and $n\rightarrow\pi^*$ (C=O) transitions, respectively. Also, the spectrum shows another three bands at 252 (39680 cm^{-1}), 381 (26250 cm^{-1}) and 451 nm (22175 cm^{-1}) attributed to charge-transfer (L→M), $\pi \rightarrow eg$ [15], spin-allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ and spin-forbidden $^1A_{1g} \rightarrow {}^3T_{2g}$ [16, 17] transitions, respectively, in an octahedral geometry around the Pt^{4+} ion. All these foundations suggest that the complex has structure 2. The IR spectrum of $[Pt(FH)_2I_2(EtOH)(H_2O)_{1/2}]_2I_4$ in Nujol mull shows several bands at 3450, 3305, 3196, 3247, 1730, 1614, 1524 972 and 540 cm^{-1} assigned to ν(OH) (solvent), $\nu_{as}(NH_2)$, $\nu_s(NH_2)$, ν(NH) [11], ν(C=O), $\beta(NH_2)$, $\nu(N\overset{...}{-}C\overset{...}{-}O)$ [12,13], ν(N-N) [11], and ν(Pt-O) [14] vibrations, respectively. Also, two bands at 441 and 389 cm^{-1} are observed and assigning to ν(Pt-N) [14] vibration in cis-form. This suggests that FH coordinates in a monodentate fashion via the NH group as shown in structure 3. The electronic spectrum of this complex in Nujol mull shows four bands at 329 nm (30395 cm^{-1}), 369 nm (27100 cm^{-1}), 432 nm (23150 cm^{-1}), 510 nm (19570 cm^{-1}) and assigned to $\pi\rightarrow\pi^*$ (C=O), spin-allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ [15, 16] and spin-forbidden $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^3T_{1g}$ [15, 16] transitions, respectively in octahedral geometry around the Pt^{4+} ion. The high value of molar conductance in DMSO (173 $\Omega^{-1}.cm^2.mol^{-1}$) suggests 1:4 electrolyte [10]. This structure is achieved by dimerization of two units of the monomer complex through one H_2O molecule as shown in structure 3. The ^{1}H-NMR spectrum of $[Pt(FH)_2I_2(EtOH)(H_2O)_{1/2}]_2I_4$ in d_6-DMSO shows three singlet signals at 8.9, 6.7 and 3.2 ppm, downfield with respect to TMS, assigned to the protons of CH, NH and NH_2 groups, respectively. Thermal analysis measurements (TGA, DTA) show four steps of decomposition at 218, 518, 801 and 840 °C (Figure 1). The first step correspond to the loss of two EtOH and one H_2O molecules while the other steps correspond to the steps of decomposition of this complex. The residue corresponds to the formation of PtO_2 (Calcd. 25.9%; exp. 25.4%). The electronic spectrum of the Pt^{4+} complex, $[Pt(FH)_2I_2(EtOH)_{3/2}]_2I_4$, in Nujol shows four bands at 330 nm (30300 cm^{-1}), 374 nm (26740 cm^{-1}), 428 nm (23360 cm^{-1}) and 512 nm (19530 cm^{-1}) assigned to $n \rightarrow \pi^*$ (C=O), spin-allowed of the type $^1A_{1g}\rightarrow{}^1T_{1g}$ [15,16] and spin- forbidden $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^3T_{1g}$ [15,16] transitions, respectively, in octahedral geometry around the Pt^{4+} ion.



Structure 1



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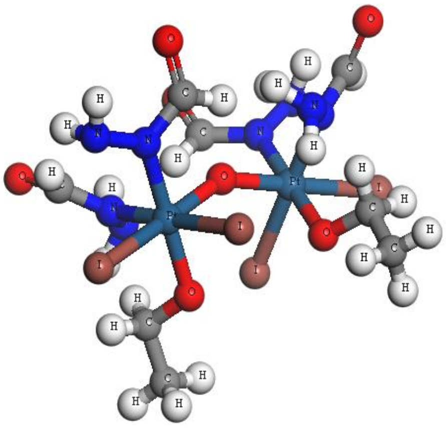

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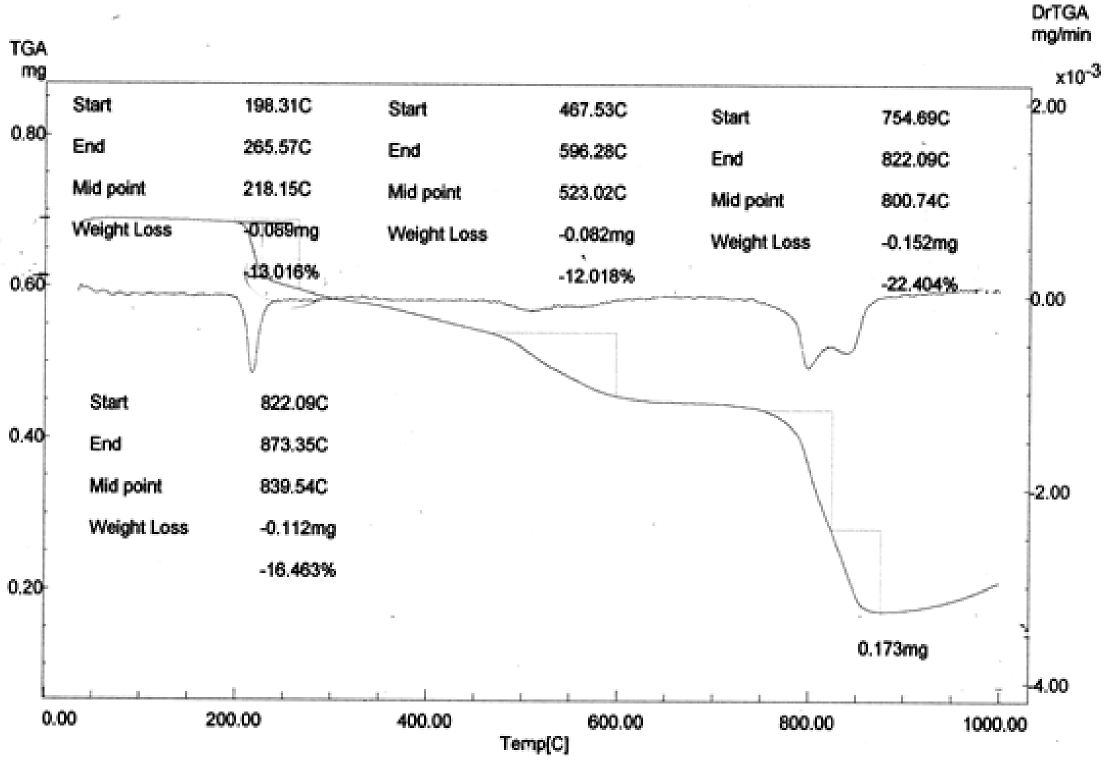
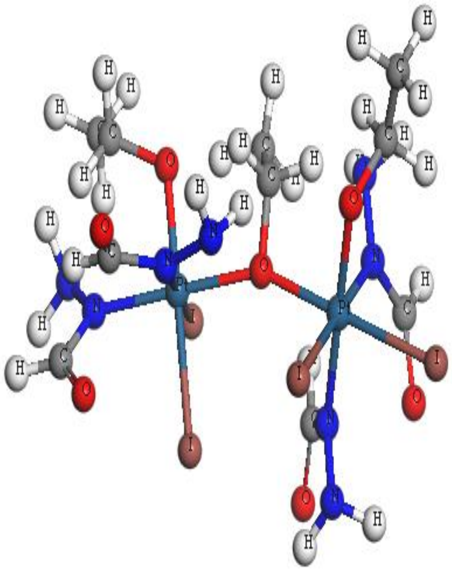
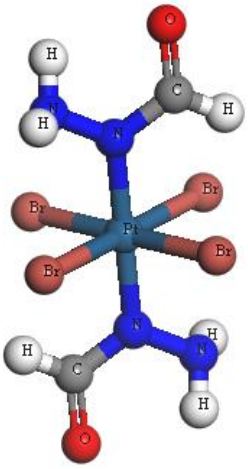


Fig. 1: TGA of $[Pt(FH)_2I_2(EtOH)(H_2O)_{1/2}]I_2$.

Thermal analysis measurements (TGA, DTA) show four steps of decomposition at 219, 555, 808 and 842 °C. The first step corresponds to the loss of three EtOH molecules while the other steps correspond to the steps, of decomposition of this complex. The residue corresponds to the formation of PtO_2. The behavior of this complex during thermal analysis measurements is quite similar to the above complex except that the former complex contains 2EtOH and H_2O while this complex involves 3 EtOH molecules. The four steps of decomposition in the complex, $[Pt(FH)_2I_2(EtOH)_{3/2}]_2I_4$ (structure 4) is a little bite higher than that observed in case of $[Pt (FH)_2I_2(EtOH)(H_2O)_{1/2}]_2I_4$. This may suggest that the EtOH molecule links between the two units more strongly (structure 4) than the H_2O molecule in structure 3. The IR spectrum of $[Pt(FH)_2I_2(EtOH)_{3/2}]_2I_4$ in Nujol mull shows bands at 3448, 3304, 3196, 3248, 1731, 1615, 1524, 973, 541, 441 and 388 cm^{-1} assigned to ν(OH) (EtOH), $\nu_{as}(NH_2)$, $\nu_s(NH_2)$, ν(NH), ν(C=O), $\beta(NH_2)$, $\nu(N\overset{...}{-}C\overset{...}{-}O)$ [11,12], ν(N-N) [13], ν(Pt-O), and ν(Pt-N) [14] vibrations, respectively. All these foundations suggest that FH coordinates to the Pt^{4+} ion in a monodentate fashion via the NH group. The molar conductance value in DMSO (171 $\Omega^{-1}cm^2mol^{-1}$) suggests 1:4 electrolyte and the existence of a dimeric structure through the EtOH molecule as shown in structure 4. Finally, the IR spectrum of $[Pt(FH)_2Br_4].3/2EtOH$ in Nujol mull shows bands at 3435, 3308, 3208, 3257, 1715, 1622, 1536, 967, and 540 cm^{-1} assigned to ν(OH) (EtOH), $\nu_{as}(NH_2)$, $\nu_s(NH_2)$, ν(NH), ν(C=O), $\beta(NH_2)$, $\nu(N\overset{...}{-}C\overset{...}{-}O)$ [11, 12], ν(N-N) [13], and ν(Pt-O) [14] vibrations, respectively. Also, the spectrum shows two bands at 470 and 429 assigned to ν(Pt-N) vibration in cis-form [14]. Moreover, two new bands at 238 and 218 are observed and assigned to ν(Pt-Br) vibration in cis-form [14]. This spectrum is quits similar to the above spectra of the Pt^{4+} complexes indicating that formylhydrazine behaves in a monodentate fashion ***via*** the NH group. The electronic spectrum in Nujol mull shows four bands at 310 nm (32155 cm^{-1}), 335 (29940 cm^{-1}), 386 nm (25910 cm^{-1}), 428 nm (23365 cm^{-1}) and 357 nm (28010 cm^{-1}) assigned to $\pi \rightarrow \pi^*$ (C=O), $n \rightarrow \pi^*$ (C=O) spin-allowed $^1A_{1g} \rightarrow {}^1T_{1g}$, spin-forbidden $^1A_{1g} \rightarrow {}^3T_{2g}$ and charge-transfere (L → M) $\pi \rightarrow e_g$ [15, 16] transitions, respectively in an octahedral structure around the Pt^{4+} ion. Thermal analysis measurements (TGA, DTA) show four steps of decomposition at 250, 428, 490 and 579 °C corresponding to the loss of 3/2EtOH and the steps of decomposition. The final residue corresponds to the formation of PtO_2 (Calcd. 32.3%; exp. 32.1%). All the above foundations suggest structure 5 for this complex. The low value of molar conductance in DMSO (23 $\Omega^{-1}.cm^2.mol^{-1}$) suggests a non-electrolytic nature [10]. Finally, the diamagnetic nature of all Pt^{4+} complexes suggests the existence of d^6-configuration and are similar to these reported in literature for all Pt^{4+} complexes [15].



Structure 4



Structure 5

Conclusion

Novel metal complexes derived from the reaction of formylhydrazine with H_2PtCl_6 in EtOH have been synthesized by both chemical and tribochemical reactions. The complexes derived by tribochemical reactions are always accompanied by color changes; substitution of chloride by bromide and/or iodide ions but no reduction for Pt^{4+} has been occurred during grinding with KBr, KI and/or CaI_2. In all complexes the ligand coordinates to the Pt^{4+} ion in a monodentate manner ***via*** the NH group. Octahedral geometry is suggested for the Pt^{4+} complexes. The stereochemistry of the Pt^{4+} complexes has been determined from the results of elemental analyses, conductance, spectral (IR., UV-Vis., ^{1}H-NMR), thermal (DTA, TGA) and magnetic measurements.

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