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Complexes of 3-aminopyrazine-2-carboxylic acid with VO^{2+}, Pd(II), W(VI) and UO_2^{2+}; preparation and characterization

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ABSTRACT

Synthesis procedures are described for the new complexes of 3-aminopyrazine-2-carboxylic acid with VO^{2+}, W(VI), Pd(II) and UO_2^{2+}. These complexes were characterized by their spectral (IR, electronic, ^1H NMR and ESR), conductivity and magnetic measurements.

KEYWORDS

Hapc ;
IR;
Carboxyl
Amino;
ESR.

INTRODUCTION

It is known that pyrazines and their derivatives form quite important class of compounds present in many natural flavours and complicated organic molecules[1]. Also, few examples of pyrazine-carboxylic acid and its derivatives are known as good building blocks for construction of novel metal-organic frameworks that facilitate the formation of supramolecular architectures [2,3]. The dynamic pattern of 3-aminopyrazine-2-carboxylic acid by inelastic and incoherent neutron scattering, Raman spectroscopy and ab ignition calculations have been reported[4]. X-ray crystal structure of Mg(II) and Ca(II) 3-aminopyrazine-2-carboxylic acid complexes have been reported[5,6].

In this study, the chemistry of 3-aminopyrazine-2-carboxylic acid (Hapc, Figure 1; H ia the dissociable carboxylic proton) with some transition metal ions are reported. These complexes have been characterized on the bases of the spectral (IR, ^1H NMR, electronic and ESR), conductivity and magnetic measurements.

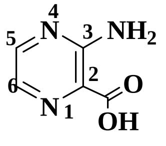

Figure 1: 3-Amino pyrazine-2-carboxylic acid (Hapc)

EXPERIMENTAL

Material and methods

All manipulations were performed under aerobic conditions using materials and solvents as received.[Pd(phen)Cl_2] was synthesized as we have been reported in previous paper[7].

Instrumentation

Microanalyses were determined by the Micro Analytical Unit of Cairo University. Magnetic moments at 25^{0}C were recorded using a Johnson Matthey magnetic susceptibility balance with $Hg[Co(SCN)_4]$ as calibrant. IR spectra were measured as KBr discs on a Matson 5000 FT-IR spectrometer. Electronic spectra were recorded using a Unicam UV_{2-100} U.V.-vis. Spectrometer. ^1H NMR spectra were measured on a

TABLE 1: Elemental and ^{1}H NMR spectral data of Hapc complexes

Compound	Elemenal	Analysis*	N	Cl	M	^{1}H NMR	SpectraH$_6^{(d)}$	NH$_2^{(s)}$
	C	H				H$_5^{(d)}$		
Cis-$[WO_2(apc)_2]$	24.7(24.4)	1.5(1.6)	16.8(17.1)			8.18	8.48	7.85
Trans-$[UO_2(apc)_2]$.MeOH	23.3(22.8)	2.1(2.1)	14.9(14.5)			8.24	8.50	7.77
[Pd(phen)(apc)Cl].$4H_2O$	37.9(38.4)	3.1(3.8)	13.0(13.2)	7.0(6.7)	20.2(20.0)	8.20	8.51	--**
$[VO(apc)_2]$	32.2(31.7)	3.8(2.9)	22.0(22.2)					

Calculated values in parentheses, **interference of NH_2 with phen protons

Varian Gemini WM-200 spectrometer (Laser Centre, Cairo University). Conductometric measurements were carried out at room temperature on a YSI Model 32 conductivity bridge. ESR spectrum was carried out on a Bruker EMX spectrometer working in the X-band (9.78 GHz) with 100 KHz modulation frequency. The microwave powder and modulation amplitudes were set at 1 mW and 4 Gauss, respectively. The low field signal was obtained after 4 scans with 10 fold in crease in the receiver again. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature.

Synthesis of complexes

Cis-$[WO_2(apc)_2]$

When a solution of $K_2[WO_4]$ (0.17 g, 0.5 mmol) in water (5 cm^3) was added to Hapc (0.07 g, 0.5 mmol) in ethanol (15 cm^3). The pale yellow precipitate was filtered off, washed with ethanol, diethyl ether and dried in vacuo. Conductivity data (10^{-3} M in DMSO): Λ_M = 5.0 ohm^{-1} cm^2 mol^{-1}. IR: $\nu_{as}(COO^-)$ 1653; $\nu_s(COO^-)$ 1394; $\nu_s(NH_2)$ 3419; ν_{as} (WO_2) 910; $\nu_s(WO_2)$ 935 cm^{-1}.

Trans-$[UO_2(apc)_2]$.MeOH

$[UO_2(AcO)_2]$ (0.21 g, 0.5 mmol) in methanol (10 cm^3) was added to Hapc (0.07 g, 0.5 mmol) in methanol (15 cm^3). The yellow mixture was refluxed for 3h on a steam bath. Upon reducing the volume followed by cooling, a yellow complex separated out. It was washed with methanol and dried in *vacuo*. Conductivity data (10^{-3} M in DMSO): Λ_M = 7.0 ohm^{-1} cm^2 mol^{-1}. IR: $\nu_{as}(COO^-)$ 1672; $\nu_s(COO^-)$ 1358; $\nu_{as}(NH_2)$ 3260; $\nu_s(NH_2)$ 3495; ν_{as} (UO_2) 925 cm^{-1}.

[Pd(phen)(apc)Cl].$4H_2O$

To a stirred suspension of Hapc (0.07 g, 0.5 mmol) was added to NaOH (0.04 g, 1 mmol) in methanol-benzene (3:2, V/V) (15 cm^3) and$[Pd(phen)Cl_2]$ (0.5 mmol). The resulting solution was stirred with gentle heating for 9 h. Upon reducing the volume, precipitate was obtained. It was filtered off, washed with ice-cold H_2O and air-dried. Conductivity data (10^{-3} M in DMF): Λ_M = 7.0 ohm^{-1} cm^2 mol^{-1}. IR: $\nu_{as}(COO^-)$ 1651; $\nu_s(COO^-)$ 1362; $\nu_{as}(NH_2)$ 3358; $\nu_s(NH_2)$ 3470; ν(Pd-O) 581; ν(Pd-N) 427; ν(Pd-Cl) 327 cm^{-1}.

$[VO(apc)_2]$

$VO(SO_4)H_2O$ (0.083 g, 0.5 mmol) in ethanol (20 cm^3) was added to Hapc (0.07 g, 0.5 mmol) in ethanol. The reaction mixture was stirred under reflux for 4h to produce a green solid. It was filtered off, washed with little water, methanol, diethyl ether and dried in *vacuo*. Conductivity data (10^{-3} M in DMF): Λ_M = 3.0 ohm^{-1} cm^2 mol^{-1}. IR: $\nu_{as}(COO^-)$ 1600; $\nu_s(COO^-)$ 1383; $\nu_{as}(NH_2)$ 3290; $\nu_s(NH_2)$ 3367; ν(V-O) 970; ν(V-N) 400 cm^{-1}.

RESULTS AND DISCUSSION

The experimental section lists some new complexes of 3-aminopyrazine-2-carboxylic acid. The elemental analyses (TABLE 1) of the isolated complexes agree with the assigned formulae. The complexes were prepared by the reaction of Hapc with $K_2[WO_4]$,$[UO_2(AcO)_2]$,$[Pd(phen)Cl_2]$ and $VO(SO_4).H_2O$ in aqueous-ethanol, methanol, benzene-methanol in the presence of NaOH or ethanol media, respectively.

We had hoped to structurally characterize one of the complexes by single X-ray crystallography, but were thwarted on numerous occasions by very small crystal dimensions. Thus, the characterization of these complexes was based on physical and spectroscopic techniques.

IR spectra

The solid-state properties of 3-aminopyrazine-2-carboxylic acid (Hapc) were examined by IR. The spectra were compared with those of the complexes.

Tentative assignments of selected IR and Raman bands are reported in the experimental section. In the IR spectrum of Hapc, the stretching vibration of the carbonyl group ν(CO) is observed at 1719 cm^{-1} as a strong band[4,8,9]. The stretching vibration of the ν(OH) appears in the IR 3150 cm^{-1}[4,9,10]. Also, the bending frequency of the hydroxyl group appears as single band at 1318 cm^{-1}. The shift towards lower frequencies is observed in IR spectrum due to the participation of OH group in hydrogen bond[4]. The bands at 3329 and 3468 cm^{-1} arise from ν_s(NH$_2$) and $_{as}$(NH$_2$) stretches, respectively[11]. The frequencies due to the deformations of the pyrazine ring are overlapped with that assigned to -COOH, NH$_2$ and CH moieties[4]. The strong bands near 1650 and 1370 cm^{-1} are assigned to ν_{as}(COO$^-$) and ν_s(COO$^-$) vibration, respectively[8]. In the spectra of the complexes, the separation between these two bands $\{\Delta = \nu_{as}(COO^-) - \nu_s(COO^-) \sim 200\ cm^{-1}\}$ indicates a monodentate coordination of the carboxylic group[8]. The ν(OH) of the carboxylic group in the free ligand disappeared in the complexes indicating the deprotonation and subsequent coordination through the oxygen atom. The absence of any peak around 1700 cm^{-1} reveals that –COOH group is involved in coordination[9]. The bands at 3329 and 3468 cm^{-1} in Hapc assign to ν_s(NH$_2$) and $_{as}$(NH$_2$) stretches, respectively, are shifted to lower wave number in the complexes due to the coordination of the amino nitrogen atom to the metal ion[12]. The strong band near 1606 cm^{-1} assigns to δ(NH$_2$) in Hapc is shifted near 1618 cm^{-1} upon complexation[13]. Thus, the spectral data suggest N, O mononegative bidentate manner of Hapc (apc$^-$) except in the complex[Pd(phen)(apc)Cl].4H$_2$O. In this complex, the NH$_2$ group does not participate in coordination to Pd(II) and the spectroscopic data suggest the monodentate behaviour of apc$^-$ through –COO$^-$[9].

In the spectrum of[WO$_2$(apc)$_2$] shows bands characteristic of the cis-WO$_2^{2+}$ unit. The IR bands at 930 and 912cm^{-1} are assigned to the ν_s(WO$_2$) and ν_{as}(WO$_2$) modes, respectively[14], the appearance of two stretching bands is indicative of the cis configuration[14]. The IR spectrum of[UO$_2$(apc)$_2$] shows only one U=O stretching band, i.e. ν_{as}(UO$_2$), at 927 cm^{-1} indicating its linear trans-dioxo configuration[7,11]. The IR spectrum of[VO(apc$_2$] shows only one V=O stretching band, ν(VO) at 970 cm^{-1}, characteristic for monomeric square-pyramidal oxovanadium(IV) complexes[15], this data is supported by the absence of band near 860 cm^{-1} (for polymeric oxovanadium(IV) complexes)[15]. The region of the complex spectra between 520 and 400cm^{-1} contains several weak bands; these may assign to ν(M-O), ν(M-N) stretches, respectively[14,16].

Electronic spectra

The electronic spectrum of Hapc in DMSO shows three absorption bands near 295, 330 and 400 nm. The electronic spectra the complexes in DMSO in the 200-900 nm regions contain intense bands due to ligand to metal charge transfer (LMCT) transitions and weaker bands assigned to d-d transitions[17]. The transition below 400 nm are assigned to intra-ligand charge transfer ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$).

In the electronic spectrum of[WO$_2$(apc)$_2$], bands at 450 and 345 (shoulder) nm are observed, the later band is assigned to $O^{2-} \rightarrow W^{VI}$ transition and is characteristic of the WO$_2^{2+}$ moiety in octahedral geometry[18].

The electronic spectrum of *trans*-[UO$_2$(apc)$_2$], (3), in DMSO shows two bands at 460 and 390 nm may be due to $\Sigma_g^{1+} \rightarrow {}^2\pi_u$ and n π^* charge transfer, respectively[18].

The electronic spectrum of the diamagnetic[Pd (phen)(apc)Cl] complex in DMSO is typical of square planar. The ground state of Pd(II) is $^1A_{1g}$ and the excited states corresponding to three transitions are $^1A_{2g}$, $^1B_{1g}$ and ^1E_g in order of increasing energy. Strong charge transfer transitions interfere and prevent the observation of the expected bands. The absorption band at 384 nm is assigned to combination of charge transfer transition from platinum or palladium d-orbital to π^* orbital of phen[19] while the band at 488 nm due to a combination of ligand (π) to metal charge transfer and M(II) d-d bands[19].

The electronic spectrum of[VO(apc)$_2$] complex shows bands at 730, 605 and 490 nm due to $^2B_2(d_{xy}) \rightarrow {}^2E(d_{xz},d_{yz})$, $^2B_2(d_{xy}) \rightarrow {}^2B_1(d_{x2-y2})$ and charge transfer (LMCT) transitions in a square-pyramidal configuration[15]. The magnetic moment is1.66 B. M corresponding to only one electron[15].

^{1}H NMR spectra

The ^{1}H NMR assignments of Hapc and some of

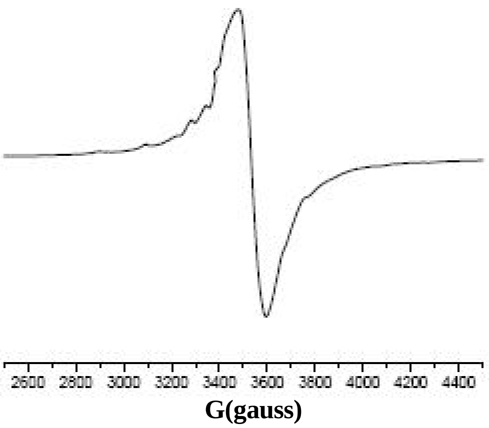

Figure 2: ESR spectrum of[VO(apc)$_2$]

the representative complexes (in DMSO-d$_6$) are listed in TABLE 1. The ^{1}H NMR spectrum of the free Hapc exhibits two doublets at δ 7.90 and 8.26 ppm assigned to H(5) and H(6), respectively (see figure 1 for numbering scheme). The protons of the carboxylic group and the amino group appear as singlets at δ 13.06 (broad) and 7.41 ppm, respectively. In the complexes, the resonance arising from the carboxylic group is not observed, whereas that arising from NH$_2$, H(5) and H(6) are shifted to lower field indicating the chelation of Hapc via the deprotonated carboxylic oxygen and amino1 centres to the metal ion[11]. This feature is probably due to the decrease in the electron density caused by the withdrawing of electrons by the metal ions from the pyrazine ring coordination centres[11].

ESR spectra

The ESR spectra of vanadyl complexes provide information about hyperfine and superhyperfine structures which are important in studying the metal ion environment in the complexes, i.e, the geometry, nature of the ligation sites from the ligand to the metal and the degree of covalency of the metal ligand bonds.

To obtain further information about the stereochemistry and the site of the metal ligand bonding and to determine the magnetic interaction in the metal complexes, ESR spectra of the complexes were recorded in the solid state.

Generally, the mononuclear VO^{+2} ion (S = 1/2, I = 7/2) has a characteristic octet ESR spectrum showing the hyperfine coupling to the ^{51}V nuclear magnetic moment. Upon the existence of two vanadyl ions, the two electron spins may combine to a non-magnetic spin singlet (S = 0) or a paramagnetic spin triplet state (S = 1); only the latter is ESR detectable. The super-exchange interaction between the two vanadium ions lead to a configuration in which the two electron spins have an antiferromagnetic character, i.e. the singlet state is energetically favored. Therefore, the ESR spectrum of strongly coupled pairs has the form of a single broad line with inhomogeneous broadening.

The room temperature (300K) solid state ESR spectrum of[VO(apc)$_2$] (Figure 2) shows a typical broad single line with poorly resolved eight-line pattern. The obtained data is similar to those reported for mononuclear vanadyl complex. In the powdered samples, the spectrum showed the parallel and the perpendicular features which indicate axially symmetric anisotropy with poorly resolved sixteen-lines hyperfine splitting characteristic for the interaction between the electron and the vanadium nuclear spin (I = 7/2). The spin Hamiltonian parameters for the complex are $g_{//} = 1.93$, $g_{\perp} = 1.96$ and the hyperfine coupling $A_{//} = 195 \times 10^{-4}$ (cm^{-1}), $A_{\perp} = 55$. The calculated ESR parameters indicate that the unpaired electron (d^1) of complex 1 is present in the d$_{xy}$-orbital with square-pyramidal geometry[20]. The values obtained for this complex agree well with those reported for square pyramidal configuration around the vanadyl ion[21].

The molecular orbital coefficients α^2 and β^2 for vanadyl complex was calculated using the following equations[22].

$$A_{//} = -PK - 4\beta^2P/7 - (ge - g_{//})P - 3/7(ge - g_{\perp})P$$

$$A_{\perp} = -PK - 4\beta^2P/7 - 11/14(ge - g_{\perp})P$$

$$ge - g_{//} = 8\,\alpha^2\beta^2\lambda/E$$

Neglecting the second order effects and taking the negative values for $A_{//}$ and $A_{\perp}$ and solving the last equations to obtain α^2 and β^2, where the dipolar interaction constant "P" between magnetic moment of the electron and vanadium nucleus can be calculated from the following equation[23]:

$$p = 7/6(A_{//} - A_{\perp})$$

The spin-orbit coupling coefficient, λ, is assumed to be 170cm^{-1} for VO^{2+}þ ion and E is the electronic transition energy of $^2B_2 \rightarrow {}^2E$ and k is the Fermi contact term which is directly related to the isotropic hyperfine coupling and represents the amount of unpaired electron density at the nucleus.

The lower value of β^2 (0.83) compared to α^2 (0.87) indicates that the in-plane σ-bonding is less covalent. The values of α^2 and β^2 for most of the oxovanadium complexes indicate that the in-plane σ-bonding and in-plane and π-bonding are appreciably ionic. These data are well consistent with other reported data[20].

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