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Synthesis, spectroscopic characterization, pH-metric and thermal behavior on Co(II) complexes formed with 4-(2-pyridyl)-3-thiosemicarbazide derivatives

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ABSTRACT

Four new cobalt (II) complexes of some thiosemicarbazides have been synthesized and spectrochemically characterized. The thiosemicarbazides are prepared by the addition of 4-(2-pyridyl)-3-thiosemicarbazide to phenyl isothiocyanate (H_2PPS), benzoyl isothiocyanate (H_2PBO), phenyl isocyanate (H_2APO) and 2-pyridyl isothiocyanate (H_2PPY). The complexes are characterized by elemental analysis, spectral (IR, ^{1}H NMR and UV–Vis), thermal and magnetic measurements. The studies revealed that structures of complexes are of two types octahedral and tetrahedral. The octahedral complexes are of H_2PPS, which acts as di-anionic tetradentate SSNN and H_2APO acts as mono-anionic tridentate NON. The tetrahedral complexes are of H_2PBO, which acts as di-anionic tridentate NSO and H_2PPY acts as mono-anionic bidentate NS. From the modelling studies, the bond length, bond angle, HOMO, LUMO and dipole moment had been calculated to confirm the geometry of the ligands and their investigated complexes. From TG and DTA studies kinetic parameters are determined using Coats–Redfern and Horowitz–Metzger methods. From pH metric studies at 298, 303 and 308 K and μ (0.1, 0.15 and 0.2) in 50% dioxane–water mixture the protonation constants of the ligands, the stepwise stability constants of the complexes and their thermodynamic parameters are calculated.

1. Introduction

Heterocyclic thiosemicarbazones have aroused considerable interest in chemistry due to their remarkable coordination properties and in biology owing to a wide spectrum of potential biological activities [1–4]. The biological activity of thiosemicarbazone complexes is related to its chelating ability toward the transition metal ions, whether the bonding through nitrogen, and sulfur atoms [4] or oxygen, nitrogen and sulfur atoms [5–7]. The activity of heterocyclic thiosemicarbazones is affected by the presence of N(4) substitution [8,9]. We report here the preparation of Co(II) complexes of N^1-phenyl-N^2-(pyridin-2-yl)hydrazine-1,2-bis(carbothioamide) (H_2PPS), N-phenyl-2-(2-(pyridin-2-ylcarbamothioyl) hydrazinyl)-2-thioxoacetamide (H_2PBO), N-phenyl-2-(pyridin-2-ylcarbamothioyl)hydrazinecarboxamide (H_2APO) and 1-(aminoN-(pyridin-2-yl)methanethio)-4-(pyridin-2-yl)thiosemicarbazide (H_2PPY) with study the substituent effect on the thiosemicarbazidic moiety and its coordination behavior. Also, the thermal degradation kinetic parameters such as energy of activation (E_a) and the pre-exponential factor (A) and thermodynamic parameters like entropy (ΔS), enthalpy (ΔH) and activation energy (ΔG) for each step of degradation have been evaluated.

2. Experimental

2.1. Instrumentation and materials

All the chemicals were purchased from Aldrich and Fluka and used without further purification. Elemental analyses (C and H) were performed with a Perkin–Elmer 2400 series II analyzer. IR spectra (4000–400 cm^{-1}) for KBr discs was recorded on a Mattson 5000 FTIR spectrophotometer. Electronic spectra were recorded on an Unicam UV–Vis spectrophotometer UV2. Magnetic susceptibilities were measured with a Sherwood scientific magnetic susceptibility balance at 298 K. ^{1}H NMR measurements in d_6-DMSO at room temperature was carried out on a Varian Gemini WM-200 MHz spectrometer at the Microanalytical Unit, Cairo University. Thermogravimetric measurements (TGA, DTA, 20–800 °C) were recorded on a DTG-50 Shimadzu thermogravimetric analyzer at a heating rate of 10 °C/min and nitrogen flow rate of 20 ml/min.

2.2. Synthesis of the ligands

4-(2-Pyridyl)-3-thiosemicarbazide was synthesized as reported earlier [10]. Derivatives 1–4 were prepared by boiling ethanolic solution of 4-(2-pyridyl)-3-thiosemicarbazide (1.6 g, 100 mmol) with an equimolar amount of phenyl isothiocyanate, benzoyl isothiocyanate, phenyl isocyanate and 2-pyridyl isothiocyanate Fig. 1.

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2.3. Synthesis of metal complexes

All complexes were prepared by refluxing H_2PPS, H_2PBO, H_2APO or H_2PPY (1.0 mmol) and $CoCl_2{\cdot}6H_2O$ (1.0 mmol) in 30 ml ethanol for 2–3 h. The solid complexes were filtered off, washed with ethanol followed by diethyl ether and dried in a vacuum over $CaCl_2$.

2.4. Procedure for the pH-metric titration

The pH-metric readings were measured to 0.01 unit with Orion's research model 601A/digital Ionalyzer standardized before and checked after each titration with buffer solutions produced by Fischer (New Jersey, USA). The following mixtures were prepared and titrated potentiometrically at 298, 303 and 308 K against 9.2×10^{-3} M NaOH in 50% (v/v) dioxane–water at a constant ionic strength KCl (0.1, 0.15 and 0.2 M). The solution mixtures (i–iii) were prepared as follows:

(i) 1.25 ml (1.1×10^{-2} M) HCl + 1.25 ml (0.1, 0.15 and 0.2 M) KCl + 10 ml doubly-distilled H_2O.
(ii) 1.25 ml (1.1×10^{-2} M) HCl + 1.25 ml (0.1, 0.15 and 0.2 M) KCl + 2.5 ml (5×10^{-3} M) H_2PPS, H_2PBO, H_2APO and H_2PPY + 10 ml bi-distilled H_2O.
(iii) 1.25 ml (1.1×10^{-2} M) HCl + 1.25 ml (0.1, 0.15 and 0.2 M) KCl + 2.5 ml (5×10^{-3} M) H_2PPS, H_2PBO, H_2APO and H_2PPY + 0.5 ml (5×10^{-3} M) Co^{2+} in bi-distilled water + 9.5 ml H_2O.

The ultimate volume (25 ml) was adjusted by adding dioxane in each case and after adding of each increment of the titrant, the solution was stirred for about two minutes and the pH-reading is then recorded. For converting the pH-meter reading (B) in 50% (v/v) dioxane–water and 0.1, 0.15 and 0.2 M KCl to $[H^+]$ values, the equation of Van Uitert and Hass [11] was applied,

$$-\log[H^+] = B + \log U_H$$

where $\log U_H$ is the correction factor for the solvent composition and ionic strength for which B is read.

2.5. Molecular modeling

An attempt to gain better insight on the molecular structure of the ligand and its complexes, geometric optimization and conformational analysis has been performed using PM3 [12] forcefield as implemented in hyperchem 8 [13]. The low lying obtained from MM+ was then optimized at PM3 using the Polak–Ribiere algorithm in RHF–SCF, set to terminate at an RMS gradient of 0.01 kcal mol^{-1}.

3. Results and discussion

The physical and analytical data of each ligand and their Cobalt complexes are listed in Table 1.

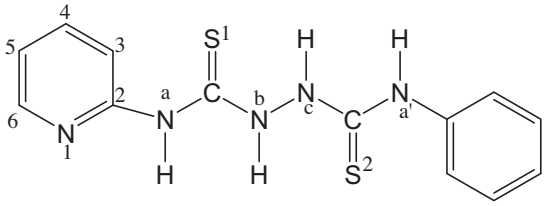
3.1. Infrared and ^1H NMR spectra of ligands

The most important IR bands of ligands are recorded in Table 2. The spectra exhibit three bands between 3234 and 3100 cm^{-1} due to ν(NH) groups. The ν/δ modes of (CN) group of pyridyl ring are found at ≈1560 and 620–635 cm^{-1}.

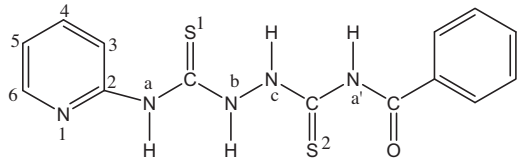
An inspection on the Table 2 describing the IR spectra of H_2PPS, H_2PBO, and H_2PPY indicates that the appearance of strong bands assigned to ν(C═N) (azomethine), ν(C—S) and ν(SH) as well as (C═S) modes suggested that these ligands exist in thione–thiol form. As these ligands contain two C═S groups, $(C{=}S)^1$ and $(C{=}S)^2$, we proposed that $(C{=}S)^1$ is in thione form and $(C{=}S)^2$ in thiol form. This assumption is confirmed by the absence of bands due to ν(C═N) (azomethine), ν(C—S) and ν(SH) vibrational modes in the IR spectrum of the start (4-pyridyl thiosemicarbazide) [14] and the missing of SH signal in the ^1H NMR spectrum of H_2APO.

In the IR spectrum of H_2PPY, the band due to ν(C═N) mode was difficult to recognize because it is overlapped with ν(C═C) of pyridyl ring. Furthermore, the appearance of ν(C—S) at higher wavenumber, 683 cm^{-1} than that of other ligands may be due to the presence of pyridyl groups at the extremes of H_2PPY structure, which act as electron withdrawing groups. The IR spectrum of H_2APO exhibits a sharp band at 3521 cm^{-1} due to ν(OH) in addition to the ν(CO) band at 1675 cm^{-1} suggested the keto–enol tautomerism.

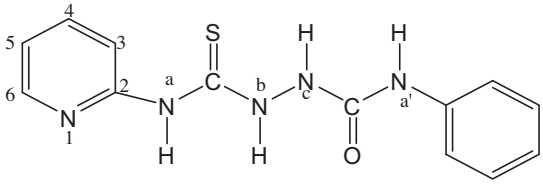
The ^1H NMR spectra of H_2PPS, H_2PBO and H_2PPY (Figs. 2–4) derivatives in DMSO-d6 show two signals at approximately δ═11.10 and 15.4 ppm relative to TMS that disappear upon adding D_2O. These signals are attributed to the amide ($NH_{a,a'}$) and thiol (SH) protons. The signal at δ = 8.29 ppm is due to the (NH_b), while the multiplets at 7.00–7.86 ppm are characteristic of the pyridine ring protons [15]. The appearance of signal at δ 15.4 ppm in the



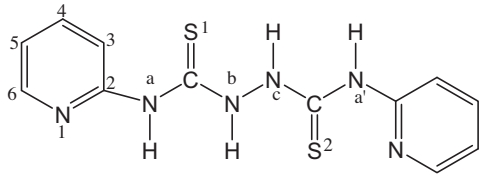
N^1-phenyl-N^2-(pyridin-2-yl)hydrazine-1,2-bis(carbothioamide)
(H_2PPS)



N-phenyl-2-(2-(pyridin-2-ylcarbamothioyl)hydrazinyl)-2-thioxoacetamide
(H_2PBO)



N-phenyl-2-(pyridin-2-ylcarbamothioyl)hydrazinecarboxamide
(H_2APO)



1-(amino*N*-(pyridin-2-yl)methanethio)-4-(pyridin-2-yl)thiosemicarbazide
(H_2PPY)

Fig. 1. Structure of H_2PPS, H_2PBO, H_2APO and H_2PPY.