

Ligational Behaviour of a Bridging Tetradentate NONO Donor Ligand Towards Co(II), Ni(II), Cu(II), Zn(II) & Cd(II)

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Synthesis of a new bridging tetradentate NONO donor ligand, 1-acetylpyridiniumchloride-4-phenyl-3-semicarbazide, [APPS]Cl, and preparation and characterization of its complexes with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are described. Elemental analyses, spectroscopic (NMR, visible, IR), magnetic and conductivity measurements have been used to characterize the complexes.

In continuation of our earlier work¹ on 1-acetylpyridiniumchloride-4-phenyl-3-thiosemicarbazide, [APTS]Cl, we report here the preparation and characterization of the complexes of the analogous ligand, 1-acetylpyridiniumchloride-4-phenyl-3-semicarbazide, [APPS]Cl, with some dipositive metal ions.

All the chemicals used were of AR grade. 1-Acetylpyridiniumchloride-4-phenyl-3-semicarbazide, [APPS]Cl, was prepared by adding slowly phenyl isocyanate (11.9 ml, 0.1 mol) to 150 ml of an alcoholic solution of Girard-P reagent (acetylhydrazide pyridinium chloride) (18.5 g, 0.1 mol). The mixture was refluxed on a water bath for 15 min. On cooling, white crystals were separated. The product was filtered off, washed, recrystallized from absolute ethanol and dried *in vacuo* over anhydrous calcium chloride; yield: 24 g (80%); m.p., 191°C.

Preparation of the complexes

[APPS]Cl (3.06 g) dissolved in absolute ethanol (50 ml) was added to the metal salt solution [2.37 g of CoCl₂·6H₂O, 2.37 g NiCl₂·6H₂O, 1.71 g CuCl₂·2H₂O, 1.4 g ZnCl₂ or 2.01 g CdCl₂·H₂O] dissolved in 50 ml of absolute ethanol. The mixtures were refluxed for 1 hr. The solid complexes precipitated on adding sodium acetate as a buffering agent. The isolated complexes were filtered off, washed several times with ethanol and finally dried *in vacuo* over anhydrous calcium chloride. Several attempts to isolate the solid complexes in absence of sodium acetate failed. The results of elemental analysis together with some physical properties of the complexes are listed in Table 1.

The analyses for the metals and halide were carried out by the standard methods². Carbon and hydrogen contents were determined at the Microanalytical Unit of the Mansoura University. Magnetic moments were obtained at room temperature (25°C) by Gouy balance using Hg[Co(NCS)₄] as the calibrating agent at Alexandria University. Infrared spectra were recorded in nujol on a Pye Unicam SP 2000 spectrophotometer (4000-200 cm⁻¹). Proton magnetic resonance spectra were recorded on a Perkin-Elmer R 12B (60 MHz) spectrometer. Electronic spectra were recorded in DMF on a Perkin-Elmer 330 spectrophotometer at the Illinois State University, USA. Molar conductivities were measured in DMF at room temperature using a Tacussel conductivity bridge type CD6 NG.

Complexes having the composition [M(APPS-2H)2H₂O]Cl where M = Cu(II), Co(II), Ni(II), Zn(II) and Cd(II) have been isolated and characterized (Table

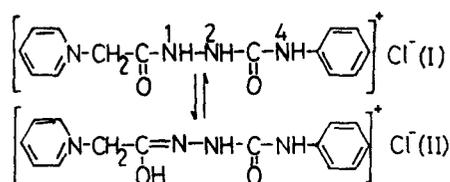
Table 1—Analytical and Physical Data of [APPS]Cl and Its Metal Complexes

Compound	M.P. (°C)	Colour	Found (Calc.), %				Λ _M ^o in DMF
			C	H	M	Cl	
2[APPS]Cl	191	White	54.8 (54.8)	5.2 (4.9)	— (—)	11.6 (11.6)	34
[Cu(APPS-2H)]Cl·2H ₂ O	216	Green	39.7 (41.6)	4.6 (4.2)	15.9 (15.7)	9.2 (8.8)	38
[Co(APPS-2H)2H ₂ O]Cl	> 300	Brown	42.7 (42.1)	4.1 (4.3)	15.3 (14.7)	9.2 (8.9)	26
[Ni(APPS-2H)2H ₂ O]Cl	> 300	Yellowish green	41.8 (42.1)	3.9 (4.3)	14.5 (14.9)	8.9 (8.9)	41
[Zn(APPS-2H)2H ₂ O]Cl	210	Yellow	40.9 (41.4)	3.8 (4.2)	16.8 (16.1)	9.1 (8.7)	26
[Cd(APPS-2H)2H ₂ O]Cl	142	Yellow	36.7 (37.1)	3.3 (3.8)	24.1 (24.8)	8.1 (7.8)	30

*ohm⁻¹cm²mol⁻¹

1). The solid complexes are quite stable in air and insoluble in common organic solvents, but are soluble in dimethylformamide (DMF) and dimethyl sulphoxide (DMSO). The molar conductivity of uncomplexed [APPS]Cl ($35 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in DMF at 25°C falls in the range reported for univalent electrolytes³, indicating that the chloride ion is readily ionized in DMF. The molar conductivities of the metal complexes in DMF are found in the range which have been reported for 1:1 electrolytes³.

1-Acetylpyridiniumchloride-4-phenyl-3-semicarbazide [APPS]Cl can be represented by two tautomeric forms (I, II).



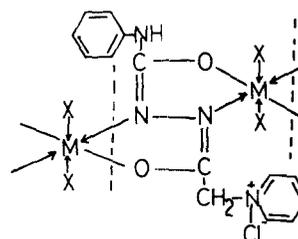
IR spectral studies show that the ligand [APPS]Cl exists in a tautomeric equilibrium of the keto and enol forms according to the following evidences: (i) Three bands are observed at 3456 , 3250 and 3160 cm^{-1} due to $\nu(\dot{\text{N}}\text{H})$, $\nu(\ddot{\text{N}}\text{H})$ and $\nu(\ddot{\text{N}}\text{H})$, respectively⁴. (ii) A sharp and strong band is observed at 3548 cm^{-1} which could be due to $\nu(\text{OH})$. (iii) Two strong bands occurring at 1715 and 1675 cm^{-1} are assigned to stretching vibrations of the carbonyl groups of the hydrazide and urea moieties, respectively. (iv) The band at 1000 cm^{-1} is assigned to $\nu(\text{N}-\text{N})$ vibration. The NMR spectrum of the ligand [APPS]Cl in $\text{DMSO}-d_6$ shows three signals at 10, 8.7 and 7.9 ppm which are downfield from TMS and disappear upon adding D_2O . The signals at $\delta 8.7$ and $\delta 7.9$ ppm are assigned to the protons of $\dot{\text{N}}\text{H}$ and $\ddot{\text{N}}\text{H}$, respectively, while the signals at $\delta 10.0$ ppm is attributed to the proton of $\dot{\text{N}}\text{H}$ or OH .

Our previous work¹ on the ligand containing thiocarbonyl group, [APTS]Cl, showed that it coordinates in the keto form via thioketo and $\dot{\text{N}}\text{H}$ groups. On the contrary, the IR spectra of all the present metal complexes show that [APPS]Cl behaves as a bridging tetradentate ligand coordinating through the enolic oxygen atom ($=\text{C}-\text{OH}$) of the hydrazide moiety and nitrogen atom of $\dot{\text{N}}\text{H}$ group from one end and the enolic oxygen atom ($=\text{C}-\text{OH}$) of the urea moiety and nitrogen atom of $\dot{\text{N}}\text{H}$ group on the other with the replacement of the hydrogen atoms from the enolized carbonyl groups. Steric factors prevent the coordination of all the donors to a single metal ion, which therefore acts as a bridging unit between the donor sites of the ligand, and thus the polymeric chain grows through consecutive ligand-metal linkages⁵ as shown in structure III. This mode of complexation is

suggested on the basis of the following observations: (i) the disappearance of the $\nu\text{C}=\text{O}$ bands of the hydrazide and urea moieties with simultaneous appearance of new bands in the regions 1630 - 1640 and 1170 - 1185 cm^{-1} due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})$ ⁶, respectively, (ii) the disappearance of both $\nu\dot{\text{N}}\text{H}$ and $\nu\ddot{\text{N}}\text{H}$ bands, (iii) the $\dot{\text{N}}\text{H}$ band remains at the same position, (iv) the positive shift in $\nu(\text{N}-\text{N})$, and (v) the appearance of new bands in the low frequency region at 475 - 500 and 330 - 350 cm^{-1} which are assigned to $\nu(\text{M}-\text{O})$ ⁷ and $\nu(\text{M}-\text{N})$ ⁸, respectively.

Strong evidence for enolization comes from the NMR spectra of the diamagnetic complexes $[\text{Cd}(\text{APPS}-2\text{H})2\text{H}_2\text{O}]\text{Cl}$ and $[\text{Zn}(\text{APPS}-2\text{H})2\text{H}_2\text{O}]\text{Cl}$ which show the disappearance of the signals at $\delta 10.0$ and $\delta 8.7$ ppm assigned to $\dot{\text{N}}\text{H}$ and $\ddot{\text{N}}\text{H}$ protons while the signal at $\delta 7.9$ ppm due to $\dot{\text{N}}\text{H}$ proton remains unchanged.

All these observations confirm structure (III) for the complexes of [APPS]Cl.



M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

X = H_2O in Co(II), Ni(II), Zn(II) and Cd(II) only.

(III)

The existence of coordinated water in all the complexes, excepting the Cu(II) complex is supported by the observation of the bands at 3500 , 1610 , 890 and 770 cm^{-1} assigned to $\nu(\text{OH})$, $\nu(\text{H}_2\text{O})$, $\rho_r(\text{H}_2\text{O})$ and $\rho_w(\text{H}_2\text{O})$ vibrations⁹ respectively in the IR spectra of the solid complexes. On drying these complexes *in vacuo* or by heating in an oven up to 120°C , no water molecule is removed which indicates the presence of water molecules in the coordination sphere.

The magnetic moments and the electronic spectral data of the complexes are listed in Table 2. The spectrum of Ni(II) complex, $[\text{Ni}(\text{APPS}-2\text{H})2\text{H}_2\text{O}]\text{Cl}$, exhibits three absorption bands at 8.5, 14.3 and 25.64 kK which are assigned respectively to ${}^3A_{2g} \rightarrow {}^3T_{2g}(v_1)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(v_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(v_3)$ transitions in octahedral geometry¹⁰. The values of v_2/v_1 (1.68), $10Dq$, B and β (Table 2) lie in the same ranges as earlier reported¹¹. Also, the value of magnetic moment (3.18 B.M.) is an additional evidence for the octahedral structure. The electronic spectrum of the complex $[\text{Co}(\text{APPS}-2\text{H})2\text{H}_2\text{O}]\text{Cl}$ shows three bands at 8.4, 16.4 and 20.4 kK attributable to ${}^4T_{1g} \rightarrow {}^4T_{2g}(v_1)$, ${}^4T_{1g} \rightarrow {}^4A_{2g}(v_2)$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)(v_3)$ transitions, respectively¹². Moreover, the values of

Table 2—Spectral and Magnetic Properties of [APPS]Cl Complexes

Compound	Magnetic moment μ_{eff} (B.M.)	Electronic spectral bands (in $\text{cm}^{-1} \times 10^3$) and spectral parameters
[Ni(APPS-2H)2H ₂ O]Cl	3.18	8.5, 14.3, 25.64; $Dq = 850, B = 962, \beta = 0.92, \nu_2/\nu_1 = 1.68$
[Co(APPS-2H)2H ₂ O]Cl	4.83	8.4, 16.4, 20.4; $Dq = 957, B = 878, \beta = 0.9, \nu_2/\nu_1 = 1.95$
[Cu(APPS-2H)]Cl. 2H ₂ O	2.09	8.62, 14.28, 20.4

ν_2/ν_1 (1.95) and magnetic moment (4.83 B.M.) are in good agreement with the reported octahedral structure. The values of Dq, B, β (Table 2) are calculated from the values of ν_1 and ν_3 bands. ν_2 was then predicted on the basis of these values of B and Dq . The predicted position of ν_2 (17.97 cm^{-1}) corresponds closely to the observed band¹³.

The electronic spectral data and the magnetic moment value (Table 2) of the Cu(II) complex [Cu(APPS-2H)]Cl. 2H₂O suggest square planar or distorted octahedral structures for this complex. It is not possible to assign the absorption bands on the basis of the present studies.

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