SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 9 , N° 10, 2001

STUDIES ON N-[2-THIENYLMETHYLIDENE]-2-AMINOPYRIDINE COMPLEXES OF Fe(II), Co(II), Ni(II), Cu(II), Zn(II) AND Cd(II)

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ABSTRACT

Metal complexes ML_2Cl_2, where M is Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} and L is Schiff base formed by condensation of 2-thiophenecarboxaldehyde and 2-aminopyridine, N-[2-thienylmethylidene]-2-aminopyridine (TNAPY), have been prepared and characterized by elemental analysis, magnetic and spectroscopic measurements. IR and NMR spectra show that the nitrogen of the azomethyne group and the sulphur of the thiophene ring take part in coordination. Magnetic, ESR and electronic spectral studies show a distorted octahedral structure for the Fe(II), Co(II), Ni(II) and Cu(II) complexes and a tetrahedral geometry for the Zn(II) and Cd(II) complexes. Conductance measurements suggest the nonelectrolytic nature of the complexes, with the exception of the $Zn(TNAPY)_2Cl_2$ and $Cd(TNAPY)_2Cl_2$ compounds which are 1:2 electrolytes.

KEYWORDS: Schiff base, N-[2-thienylmethylidene]-2-aminopyridine, NMR, ESR, Transition Metal Complexes

RESUMO

Complexos metálicos do tipo ML_2Cl_2 [M = Fe(II), Co(II), Ni(II), Cu(II), Cd(II) e L é o ligante N- [2-tienilmetilideno] -2-aminopiridina (TNAPY)] foram preparados e caracterizados usando análise elementar e métodos espectroscópicos e magnéticos. Espectros de ressonância magnética nuclear (RMN) e infravermelho (IV) demonstraram que o nitrogênio do grupo azometina e o enxofre do tiofeno participam da coordenação. Estudos de espectros eletrônicos, magnéticos e ressonância de spin do elétron (RSE) idicam uma estrutura octaédrica distorcida para os complexos de Fe(II), Co(II), Ni(II) e Cu(II) e geometria tetraédrica para os complexos de Zn(II) e Cd(II). Medidas de condutância sugerem que a maioria dos complexos não são eletrólitos, com exceção de $Zn(TNAPY)_2Cl_2$ e $Cd(TNAPY)_2Cl_2$ que são eletrolitos 2:1 .

DOI: 10.48141/SBJCHEM.v9.n10.2001.20_2001.pdf

INTRODUCTION

The pyridine ring occurs in molecules of many natural and synthetic biologically active compounds. Pyridine derivatives have also found application in hydrometallurgy and metal complexes with pyridine bases have been used as catalysts in a number of technological processes[1-4].

In continuation of our work on a metal complexes of Schiff bases[5,6] we report here the results of our studies on the complexes of a Schiff base derived from 2-thiophenecarboxaldehyde (2-TFCA) and 2-aminopyridine (2-APy), N-[thienylmethylidene]-2-aminopyridine (TNAPY), with Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

Tentative structures have been proposed on the basis of analytical, spectral, magnetic and conductance data.

EXPERIMENTAL

Reagents: $FeCl_2{\cdot}4H_2O$ (Merck, 99%), $CoCl_2{\cdot}6H_2O$ (Merck, 99.99%), $NiCl_2{\cdot}6H_2O$ (Merck, 99.99%), $CuCl_2{\cdot}2H_2O$ (Merck, 99.99%), 2-thiophenecarboxaldehyde (Merck, 98%), 2-aminopyridine (Merck, 98%).

Synthesis of bidentate Schiff base. An ethanolic solution of 2-TFCA (0.002 mol, 25 ml) was added to an ethanolic solution of 2-APy (0.002 mol, 25 ml) and refluxed for 6h on a water-bath. After the concentration of the solution, the precipitate was filtered, washed with ethanol and dried over $CaCl_2$ in vacuum. *Anal.* Calcd. for TNAPY : C, 63.83; H, 4.25; N, 14.89; S, 17.02. Found: C, 63.79; N, 14.96; S, 17.43. ^{1}H NMR: δ_1 8.7; δ_2 7.4; ^{13}C NMR: $\delta_1$162.7; δ_2 132.5; δ_3 111.2.

Synthesis of the ML_2Cl_2 complexes. A mixture of 2-TFCA (0.004 mol, 50 ml) and 2-APy (0.004 mol, 50 ml) in ethanol was added to an ethanolic solution of metal chlorides (0.002 mol, 50ml), at pH=8-8.5. The mixture of reactants was refluxed on a water-bath for 6-8 h. The excess of solvent was then distilled. The compounds separated were filtered, washed with ethanol and dried over $CaCl_2$ in vacuum. *Anal.* Calcd. for $Co(TNAPY)_2Cl_2$: Co, 11.63; C, 47.35; N, 11.05; S, 12.63; Cl, 14.18. Found: Co, 11.71; C, 47.29; N, 11.28; S, 12.60; Cl, 14.67. Calcd. for $Ni(TNAPY)_2Cl_2$: Ni, 11.59; C, 47.37; N, 11.05; S, 12.63; Cl, 14.19. Found: Ni, 11.31; C, 47.05; N, 10.86; S, 12.76; Cl, 14.38. Calcd. for $Cu(TNAPY)_2Cl_2$: Cu, 12.42; C, 41.92; N, 10.95; S, 12.51; Cl, 14.06. Found: Cu, 12.11; C, 41.72; N, 11.15; S, 12.52; Cl, 14.11. Calcd. for $Zn(TNAPY)_2Cl_2$: Zn, 12.47; C, 46.76, N, 10.91; S, 12.47; Cl, 14.00. Found: Zn, 12.44; C, 46.58, N, 10.66; S, 12.45; Cl, 13.56. ^{1}H NMR: δ_1 9.1; δ_2 7.5; ^{13}C NMR: $\delta_1$165.7; δ_2 137.2; δ_3 116.7. Calcd. for $Cd(TNAPY)_2Cl_2$: Cd, 20.06; C, 42.83, N, 9.99; S, 11.42; Cl, 12.83. Found: Cd, 20.41; C, 42.56, N, 9.40; S, 11.73; Cl, 13.03. ^{1}H NMR: δ_1 9.1; δ_2 7.6; ^{13}C NMR: $\delta_1$166.6; δ_2 138.7; δ_3 114.8. Calcd. for $Fe(TNAPY)_2Cl_2$: Fe, 11.08; C, 47.64, N, 11.11; S, 12.70; Cl, 14.27. Found: Fe, 11.64; C, 47.98, N, 11.03; S, 12.92; Cl, 14.11.

Instruments. The ligand and the complexes were analysed for M, S and Cl by conventional methods[7,8] , while C and N by microanalytical methods. The IR spectra were obtained with KBr pellets using a BIO-RAD FTS 135 spectrophotometer. The UV-VIS spectra were recorded on an UNICAM UV-VIS UV-4 spectrophotometer in DMF solution. The reflectance spectra were recorded on a VSU-2P spectrometer at room temperature.

The ^{1}H-NMR spectra (in $CDCl_3$) were recorded on a Varian T60, and the ^{13}C-NMR spectra were obtained using a Bruker WH 270 spectrometer. The ESR spectrum was recorded on an ART 5 spectrometer at room temperature.

The magnetic moments have been determined by the Faraday method. A digital conductivity meter K 612 was used to measure the molar conductivities in DMF solution.

RESULTS AND DISCUSSION

The complexes of Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with N-[2-thienylmethylidene]-2-aminopyridine (TNAPY) (Fig. 1) appear as powders. They are not soluble in methanol, ethanol and ethyl ether but soluble in DMF.

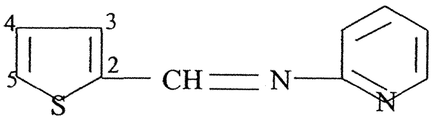


Figure 1. The structure of N-[2-thienylmethylidene]-2-aminopyridine

Based on the elemental analysis, the formula ML_2Cl_2 (Table I) has been suggested for all compounds.

Table I. Analytical and Physical Data of the Complexes*

Compounds	Melting point (°C)	Colour	μ_{eff} (BM)	Λ_M** ($\Omega^{-1}cm^2mol^{-1}$)
$Fe(TNAPY)_2Cl_2$	160	red	5.20	9.5
$Co(TNAPY)_2Cl_2$	180	pink	4.88	5.2
$Ni(TNAPY)_2Cl_2$	175	greenish	3.10	19.8
$Cu(TNAPY)_2Cl_2$	220	blue	1.88	13.5
$Zn(TNAPY)_2Cl_2$	240	white	-	126.9
$Cd(TNAPY)_2Cl_2$	210	yellowish	-	133.2

**All the complexes give satisfactory metal, C, S, N and Cl analyses*
*** in DMF solution*

IR and NMR spectra. Some important IR bands of TNAPY and its complexes along with their assignments are presented in Table II.

Table II. Characteristic Infrared Absorption Frequencies (in cm^{-1}) of Ligand and Complexes

Compound	$\nu_{C=N\ azomethyne}$	$\nu_{C=N\ pyridine}$	$\nu_{C\text{-}S\text{-}C}$	$\nu_{C\text{-}S}$	$\nu_{M\text{-}N}$
TNAPY	1675	1456	920	673	-
Fe(TNAPY)$_2$Cl$_2$	1635	1449	843	640	423
Co(TNAPY)$_2$Cl$_2$	1621	1455	841	654	419
Ni(TNAPY)$_2$Cl$_2$	1626	1456	859	650	430
Cu(TNAPY)$_2$Cl$_2$	1625	1450	851	645	420
Zn(TNAPY)$_2$Cl$_2$	1640	1451	860	635	418
Cd(TNAPY)$_2$Cl$_2$	1630	1453	835	630	415

The IR spectrum of the ligand shows a band at 1675 cm^{-1} which is assigned to the $\nu_{C=N}$ of the azomethyne group and an intense band at 1456 cm^{-1} corresponding to the C=N stretching of the pyridine ring. The comparison of the positions of these bands with those observed in the IR spectra of the complexes indicates that the band at 1675 cm^{-1} shifts towards lower frequencies ($\Delta\nu$=35-55 cm^{-1}) , while that at 1456 cm^{-1} does not show a marked shift. This behaviour suggests that TNAPY is coordinated to the central metal ion through the azomethyne nitrogen. The proof of the coordination to the N atom is provided by the occurrence of the bands in the 415-430 cm^{-1} region in the IR spectra of the compounds.

The band observed in the free ligand spectrum at 920 cm^{-1} can be ascribed to $\nu_{C\text{-}S\text{-}C}$ stretching vibration[9]. This band shifted to lower values with 60-85 cm^{-1}, for all compounds, suggesting the involvement of the sulphur atom in bonding with the metal ions. The band observed at 673 cm^{-1} in the ligand spectrum, assigned to the $\nu_{C\text{-}S}$ stretching vibration, is similarly shifted. This also confirms that the thiophene ring sulphur is a donor atom[10].

In the ^{1}H-NMR spectrum of the ligand, the thiophene ring proton 5-H appears at δ 7.4 ppm and the azomethyne proton (-CH=N-) at 8.7 ppm. These signals register downfield shifts (1-2 ppm) in the Zn(II) and Cd(II) complexes. These observations support the bonding of TNAPY through nitrogen and sulphur atoms.

The ^{13}C-NMR spectra provide further support for the mode of coordination of TNAPY. In the complexes spectra, the signals due to azomethyne carbon, 2-C and 5-C (thiophene ring) show a distinct downfield shift by nearly 3-6 ppm clearly demonstrating the coordination of the ligand via the nitrogen and sulphur atoms.

Electronic and ESR spectra. Within the UV spectrum of the ligand, the existence of two absorption bands assigned to the transition $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ at 41 518 and 37 340 cm^{-1}, respectively, has been observed.

These transitions are to be found also in the spectra of the complexes, but they are shifted to lower frequencies ($\Delta\nu$=2000-2500 cm^{-1}), confirming the coordination of the ligand to the metal ions. The relevant electronic spectral data are reported in the Table III.

Table III. Electronic Spectra of the Complexes

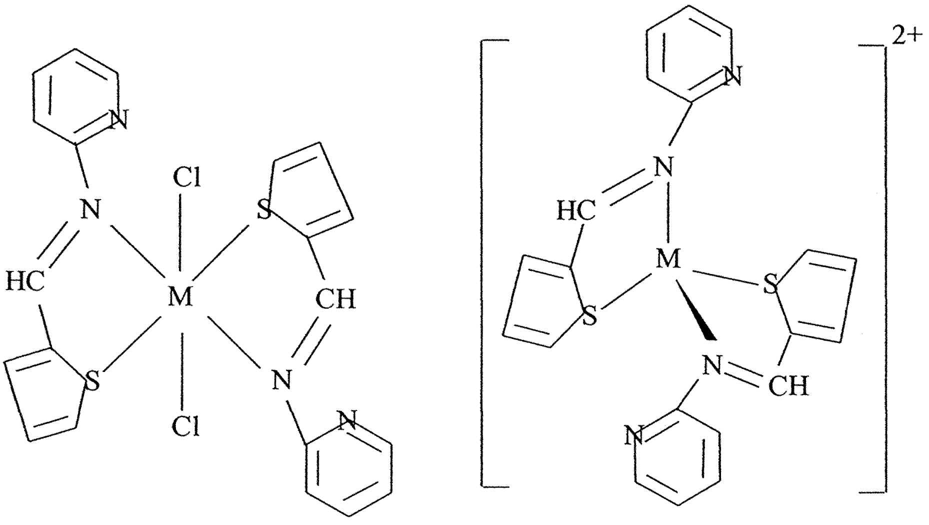
Compound	Absorption maxima (cm^{-1})
$[Fe(TNAPY)_2Cl_2]$	12 800 11 200
$[Co(TNAPY)_2Cl_2]$	21 270 19 040 15 600 9 210 8 330
$[Ni(TNAPY)_2Cl_2]$	22 320 17 000 9 200
$[Cu(TNAPY)_2Cl_2]$	16 500

The electronic spectrum of the iron(II) complex consists of a pair of low intensity bands at 12800 and 11200 cm^{-1} arising from $^5T_{2g} \rightarrow {}^5E_g$ transitions, similar to those found for distorted octahedral complexes. The doublet is attributed to Jahn-Teller distortion in the excited state[11]. The room temperature magnetic moment (5.2 BM) corresponds with the octahedral symmetry.

The reflectance spectrum of the $Co(TNAPY)_2Cl_2$ complex exhibits five bands. The bands at 21270 and 19040 cm^{-1} arise from the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition which is split in complexes of D_{4h} symmetry. That at 15600 cm^{-1} arise from the $^4T_{1g} \rightarrow {}^4A_{2g}$ transition and those at 9210 and 8549 cm^{-1} from the $^4T_{1g} \rightarrow {}^4T_{2g}(F)$ transition.

The ligand field spectrum of the Ni(II) compound could be assigned assuming that the stereochemistry is pseudo-octahedral. The bands may be assigned to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), respectively. The low energy band is broad indicating (tetragonal) distortion and the room temperature. A magnetic moment (3.1 BM) in the region is expected for the octahedral complexes of the Ni(II) ion.

The proposed structural formulas of Fe(II), Co(II), Ni(II) and Cu(II) complexes is given in figure 2a and those of the Zn(II) and Cd(II) complexes is show in figure 2b.



a. b.

Figure 2. The proposed formulas of the complexes:
a.$[M(TNAPY)_2Cl_2]$ (M = Fe^{II}, Co^{II}, Ni^{II} and Cu^{II});
b.$[M(TNAPY)_2]Cl_2$ (M = Zn^{II} and Cd^{II}).

The electronic spectrum of $Cu(TNAPY)_2Cl_2$ complex shows only one broad absorption band at 16500 cm^{-1} indicating probably a distorted octahedral configuration. The magnetic moment value is 1.88 BM. The ESR spectrum for this compound, measured in a polycrystalline sample at room temperature, gives the following values: g_{II} =2.067 and $g_{\perp}$ =2.146. The value $g_{II} < g_{\perp}$ is well consistent with a primarily d_{z2} ground state and the spectrum is characteristic of axial (compressed octahedral) symmetry. The parameter G, determined as $G =(g_{II}-2)/(g_{\perp}-2)$, is found to be much less than 4 suggesting a considerable interaction in the solid state[12].

Zinc(II) and cadmium(II) complexes do not show d-d transitions hence their stereochemistry can not be determined from UV and visible reflectance spectra. From stoichiometry and other physicochemical evidence, a four-coordinated tetrahedral geometry is suggested for Zn(II) and Cd(II) complexes (see figure 2b).

The molar conductance of the complexes, in DMF (10^{-3} M) solution, is in the range 5.2-19.8 $\Omega^{-1}cm^2mol^{-1}$ indicating their nonelectrolytic nature, with the exception of the Zn(II) and Cd(II) compounds which are 1:2 electrolytes.

CONCLUSIONS

In this paper we report the preparation, isolation and characterisation of a new bidentate Schiff base ligand derived from 2-thiophenecarboxaldehyde and 2-aminopyridine, and its complexes with Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

The products were characterised by elemental analysis, magnetic and spectroscopic measurements.

From the infrared and NMR spectral studies of the ligand and complexes it is obvious that the ligand act as bidentate coordinating through the azomethine nitrogen and the thiophene sulphur.

Correlating the experimental data, one can predict the stereochemistry of the prepared complexes: distorted octahedral for the $[M(TNATZ)_2Cl_2]$ (M = Fe^{II}, Co^{II}, Ni^{II} and Cu^{II}) and tetrahedral for the $[M(TNATZ)_2]Cl_2$ (M= Zn^{II} and Cd^{II}) compounds.

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