

COMPLEXES OF Fe(II), Co(II), Ni(II), Cu(II), Zn(II) AND Cd(II) WITH HETEROCYCLIC SCHIFF BASE N-[2-THIENYLMETHYLIDEN] METHANAMINE

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ABSTRACT: Iron(II), cobalt (II), nickel (II), copper (II), zinc(II) and cadmium(II) complexes of type 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 (TFCA) and methylamine (MA), N-[2-thienylmethylidene] methanamine (TNAM), have been prepared and characterised by elemental analysis, magnetic and spectroscopic measurements. Elemental analysis suggests the stoichiometry to be 1:2 (metal:ligand). Magnetic susceptibility data coupled with electronic and ESR spectra suggest a distorted octahedral structure for the Fe(II), Co(II) and Ni(II) complexes, a square-planar geometry for the Cu(II) compound and a tetrahedral geometry for Zn(II) and Cd(II) complexes. Infrared and NMR spectra of the complexes agree with the co-ordination to the central metal atom through nitrogen and sulphur atoms. Conductance measurements suggest the non-electrolytic nature of the complexes, except the Cu(II), Zn(II) and Cd(II) complexes which are 1:2 electrolytes.

Keywords: Schiff base, 2-thiophenecarboxaldehyde, N-[2-thienylmethylidene] methanamine

INTRODUCTION

Metal complexes of Schiff bases derived from 2-thiophenecarboxaldehyde are studied extensively due to synthetic flexibility of these compounds and their selectivity as well as sensitivity towards the central metal atom. In continuation of our work on these complexes^{1,2}, we report here the results of our studies on the complexes of Schiff base obtained through condensation of 2-thiophenecarboxaldehyde and methylamine, N[2-thienylmethylidene] methanamine, (TNAM). The presence of two potential donor atoms should render a TNAM a versatile ligand. We have synthesised and examined the donor characteristics of this new ligand towards chlorides of Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). Tentative structures have been proposed for the complexes on the basis of analytical, spectral, magnetic and conductance data.

EXPERIMENTAL

Reagents: $CoCl_2 \cdot 6H_2O$ (Merck, 99.99%), $NiCl_2 \cdot 6H_2O$ (Merck, 99.99%), $CuCl_2 \cdot 2H_2O$ (Merck, 99.99%), thiophenecarboxaldehyde (Merck, 98%), methylamine (Merck, 40% solution in water).

Synthesis of bidentate Schiff bases. The Schiff bases were prepared thus: an ethanolic solution of 2-thiophenecarboxaldehyde (0.001 mol, 25 ml) was added with an solution of methylamine (0.001 mol, 25 ml) and refluxed for 4h on a water-bath. After the concentration of the solution, the precipitate was separated, filtered, washed with ethanol and dried over $CaCl_2$ in vacuum. *Anal.* Calculated for C_6H_7NS : C, 57.60; H, 9.72; N, 19.44; S, 44.44. Found: C, 57.56; H, 9.75; N, 19.46; S, 44.40. ¹H NMR: δ_1 9.34, δ_2 7.12; ¹³C NMR: δ 161.5.

Synthesis of the ML_2Cl_2 complexes. A mixture of 2-thiophenecarboxaldehyde (0.002 mol, 50 ml), and methylamine (0.002 mol, 50 ml) in ethanol was added to an ethanolic solution of metal chlorides (0.001 mol, 50ml). The mixture of reaction was refluxed on a water-bath for 6-10 h. The excess of solvent was then distilled. The compounds separated were filtered, washed with ethanol and dried over $CaCl_2$ in vacuum. *Anal.* Calculated for $Fe(TNAM)_2Cl_2$: Fe, 14.82; C, 38.22; N, 7.43; S, 16.98; Cl, 18.81. Found: Fe, 14.85; C, 38.19; N, 7.50; S, 16.97; Cl, 18.77. Calculated for $Co(TNAM)_2Cl_2$: Co, 15.51; C, 37.91; N, 7.37; S, 16.84; Cl, 18.66. Found: Co, 15.48; C, 37.88; N, 7.40; S, 16.86; Cl, 18.64. Calculated for $Ni(TNAM)_2Cl_2$: Ni, 15.46; C, 37.93; N, 7.37; S, 16.85; Cl, 18.67. Found: Ni, 15.45; C, 37.90; N, 7.34; S, 16.82; Cl, 18.69. Calculated for $Cu(TNAM)_2Cl_2$: Cu, 16.53; C, 37.45; N, 7.28; S, 16.64; Cl, 18.44. Found: Cu, 16.56; C, 37.40; N, 7.31; S, 16.67; Cl, 18.41. Calculated for $Zn(TNAM)_2Cl_2$: Zn, 16.92; C, 37.28; N, 7.25; S, 16.57; Cl, 18.35. Found: Zn, 16.89; C, 37.25; N, 7.29; S, 16.61; Cl, 18.34; 1H NMR: δ_1 9.84, δ_2 7.52 ; ^{13}C NMR: δ 164.5. Calculated for $Cd(TNAM)_2Cl_2$: Cd, 25.94; C, 33.23; S, 14.77; Cl, 16.36. Found: Cd, 25.90; C, 33.21; S, 14.81; Cl, 16.33; 1H NMR: δ_1 9.94, δ_2 7.62 ; ^{13}C NMR: δ 166.5.

Instruments. The ligand and complexes were analysed for M, S and Cl as follow: Fe was spectrophotometrically determined with o-phenanthroline; Co and Ni were volumetrically determined with EDTA; Cu was volumetrically determined with thiosulphate; Zn and Cd were volumetrically determined with $(NH_4)HPO_4$; C and N were determined by combustion; S and Cl were gravimetrically determined after precipitation with $BaCl_2$ and $AgNO_3$, respectively. The IR spectra were obtained in KBr disc using a BIO-RAD FTS 135 spectrophotometer. The UV-VIS spectra were recorded on a UNICAM UV-VIS UV-4 spectrophotometer in DMF solution. The 1H -NMR spectra (in $CDCl_3$) were recorded on a Varian T60 and the ^{13}C -NMR spectra were obtained using a Bruker WH 270 spectrophotometer. The ESR spectra of the were recorded on a ART 5 spectrophotometer, in a polycrystalline sample 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 complex combinations of Co(II), Ni(II) and Cu(II) with TNAM (fig.1) appears as powders with high melting points. They are not soluble in ethanol, ethylether and chloroform but soluble in acetone and more soluble in DMF.

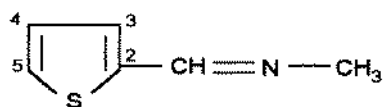


Figure 1. The structure of: N-[2-thienylmethylidene] methanamine (C_6H_7NS) (TNAM)

Elemental analysis data suggest that the complexes have 1:2 (metal-ligand) stoichiometry. Based on the elementary chemical analysis has been suggested, for all compounds, the formula ML_2Cl_2 (table I).

Table I. Analytical and physical data of the complexes*

Compounds	Melting point (°C)	Colour	μ_{eff} (MB)	Λ_M^{**} ($\Omega^{-1}cm^2mol^{-1}$)
$Fe(TNAM)_2Cl_2$	210	red	5.14	10.7
$Co(TNAM)_2Cl_2$	170	pink	4.88	11.6
$Ni(TNAM)_2Cl_2$	145	greenish	3.19	19.2
$Cu(TNAM)_2Cl_2$	230	purple	1.82	120.3
$Zn(TNAM)_2Cl_2$	215	pale yellow	-	134.5
$Cd(TNAM)_2Cl_2$	185	brownish	-	128.7

*All the complexes give satisfactory metal, C, H, S, N and Cl analyses; ** in DMF solution (10^{-3} M)

In order to get data conceiving the ligand way of co-ordination to the metal ions, the IR spectra on the 400-4000 cm^{-1} range (table II) have been carried out.

Table II. Characteristic infrared absorption frequencies in (cm^{-1}) of ligands and complexes

Compound	$\nu_{\text{C-N}}$	$\nu_{\text{C-S-C}}$	$\nu_{\text{C-Ssym}}$	$\nu_{\text{C-Sasym}}$	$\nu_{\text{CH thiophene}}$	$\nu_{\text{C thiophene}}$	$\nu_{\text{M-N}}$
TNAM	1665	860	690	640	3075	1520	-
$\text{Fe(TNAM)}_2\text{Cl}_2$	1622	821	-	620	3071	1520	420
$\text{Co(TNAM)}_2\text{Cl}_2$	1618	826	-	617	3074	1517	422
$\text{Ni(TNAM)}_2\text{Cl}_2$	1620	828	-	625	3069	1525	415
$\text{Cu(TNAM)}_2\text{Cl}_2$	1615	811	-	615	3078	1515	419
$\text{Zn(TNAM)}_2\text{Cl}_2$	1619	817	-	605	3068	1510	424
$\text{Cd(TNAM)}_2\text{Cl}_2$	1624	825	-	610	3070	1512	427

IR and NMR spectra. The IR spectrum of the ligand exhibits a band at 1665 cm^{-1} assignable to $\nu_{\text{C-N}}$ of the azomethyne group. This band shift to lower region by about 35-50 cm^{-1} in case of the all complexes, suggesting co-ordination through N atom of the azomethyne group.

The medium intensity band at $\sim 880 \text{ cm}^{-1}$ observed in free ligand ascribed to ν_{CSC} (ring) stretching vibration³ is shifted to lower values with 30-40 cm^{-1} for all compounds, suggesting the involvement of sulphur atom in the bonding with the metal's ions. The band assigned to the asymmetric $\nu_{\text{C-S}}$ is shifted to lower frequency after complexation and the symmetric $\nu_{\text{C-S}}$ is completely disappears in all the complexes. This also confirms that the sulphur atom is taking part in the complex formation⁴.

The prove of coordination to the N atom is provided by the occurrence of the new bands from 419-427 cm^{-1} in the I.R. spectra of the compounds.

In the $^1\text{H-NMR}$ spectra of the ligand the formation of Schiff bases is supported by the presence of a singlet at $\delta 9.34$ and $\delta 7.12$ ppm, corresponding to the azomethyne proton ($-\text{CH}=\text{N}-$) and to the H-5 proton of the thiophen's ring respectively, and a peak at $\delta 161.5$ in the $^{13}\text{C-NMR}$ spectra corresponding to the azomethyne carbon. In the ZnL_2Cl_2 and CdL_2Cl_2 spectra these signals shows a distinct downfield shifts by nearly 0.4-0.6 ppm, in $^1\text{H-NMR}$ spectrum, and 3-5 ppm, $^{13}\text{C-NMR}$ spectrum, clearly demonstrating the coordination of TNAM via the nitrogen and sulphur atoms.

Electronic and ESR spectra. The electronic spectrum of the ligand exhibits three intense bands at 44053 cm^{-1} ($\epsilon=7300$), 40300 cm^{-1} ($\epsilon=6500$) and 31560 cm^{-1} ($\epsilon=3000$). The absorption at 44053 cm^{-1} are assigned to the $\pi \rightarrow \pi^*$ transition of the thiophene ring and the remaining two bands to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the chromophor $\text{C}=\text{N}$. These transitions are to be found also in the spectra of the complexes, but they are shifted to lower frequencies ($\Delta\nu=1500-2200 \text{ cm}^{-1}$), confirming the coordination of the ligand to the metal ions.

The information referring to the geometry of these compounds is obtained from the electronic spectra (table III) and from values of the magnetic moments.

Table III. Electronic spectra of the complexes (d-d transitions)

Compound	Absorption maxima (cm^{-1})			
$[\text{Fe(TNAM)}_2\text{Cl}_2]$	12 600	10 200		
$[\text{Co(TNAM)}_2\text{Cl}_2]$	19 520	18 140	15 200	10 020
$[\text{Ni(TNAM)}_2\text{Cl}_2]$	26 100	15 200	10 000	9 150
$[\text{Cu(TNAM)}_2]\text{Cl}_2$	18 500	15 400		

The electronic spectrum of the iron(II) complex consist of a pair of low intensity bands at 12600 and 10200 cm^{-1} arising from a $^5\text{T}_{2g} \rightarrow ^5\text{E}_g$ transitions, similar to those found for distorted octahedral complexes. The doublet is attributed to Jahn-Teller distortion in the excited state⁵. The

room temperature magnetic moment (5.14 BM) corresponding to octahedral symmetry. Also, this spectrum exhibits a band at 25200 cm^{-1} which may be due to the metal-ligand charge transfer.

The electronic spectrum of the Co(II) compound exhibits three bands (table 3). The bands at 19520 and 18140 cm^{-1} arise from the ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition which is split in complexes of D_{4h} symmetry. That at 15200 cm^{-1} arises from the ${}^4T_{1g} \rightarrow {}^4A_{2g}$ transition, and those at 10020 cm^{-1} from the ${}^4T_{1g} \rightarrow {}^4T_{2g}$ transition⁶. These transitions correspond to a distorted octahedral geometry, which also supported by the magnetic moment value (4.88 BM).

The electronic spectrum of the Ni(TNAE)₂Cl₂ could be assigned assuming that the stereochemistry pseudo-octahedral. The energies represent the next electronic transitions from the ${}^3A_{2g}(F)$ ground state to ${}^3T_{2g}(F)$ (ν_1), ${}^3T_{1g}(F)$ (ν_2) and ${}^3T_{1g}(P)$ (ν_3) excited states for nickel (II). The low energy band of this complex is broad and split in two components (at 10000 and 9150 cm^{-1}) indicating tetragonal distortion. The magnetic moment (3.19 MB) lie in the region expected for octahedral complexes.

The molar conductance of the Fe(II), Co(II) and Ni(II) complexes in DMF (10^{-3} M) are in the range $10.7 - 15.2\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ indicating their nonelectrolytic nature and supporting six-coordination.

The Cu(TNAM)₂Cl₂ complex display electronic spectral bands in the region 18500 and 15400 cm^{-1} which may be assigned to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions in a square-planar stereochemistry⁷. The ESR spectrum of the complex measured in polycrystalline sample at room temperature gives g_{\parallel} and g_{\perp} values in the range of 2.147 and 2.083 respectively. The value $g_{\parallel} > g_{\perp}$ is well consistent with a primarily $d_{x^2-y^2}$ ground state having a square-planar structure⁸. The G parameter determined as $G = (g_{\parallel}-2) / (g_{\perp}-2)$ is found to be much less 4 suggesting considerable interaction in the solid state. The molar conductance of this complex in DMF solution are $120.3\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ indicating their 1:2 electrolytic nature and supporting four coordination.

Electronic spectra of Zn(II) and Cd(II) complexes exhibit a sharp band of high intensity at 26000 and 24500 cm^{-1} respectively, and it may be due to ligand-metal charge transfer. 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. The molar conductance of these complexes indicates their 1:2 electrolytic nature.

Because the ligand is bidentate and due to the preference of Zn(II) and Cd(II) ions for tetrahedral coordination it should be conferred such geometry. From stoichiometry and other physicochemical evidences, four-coordinated tetrahedral geometry is suggested for Zn(II) and Cd(II) complexes.

CONCLUSION

In this paper we report the isolation and characterisation of a new bidentate Schiff base ligand derived from 2-thiophenecarboxaldehyde and methylamine and their complexes with Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II}. The products were characterized by elemental analysis, magnetic and spectroscopic measurements.

Correlating the experimental data one can estimate that the following stereochemistry: distorted octahedral for the Fe(II), Co(II) and Ni(II) complexes, square-planar for the Cu(II) compound and tetrahedral for Zn(II) and Cd(II) complexes.

The proposed structural formulas of these compounds are presented in the figure 2.

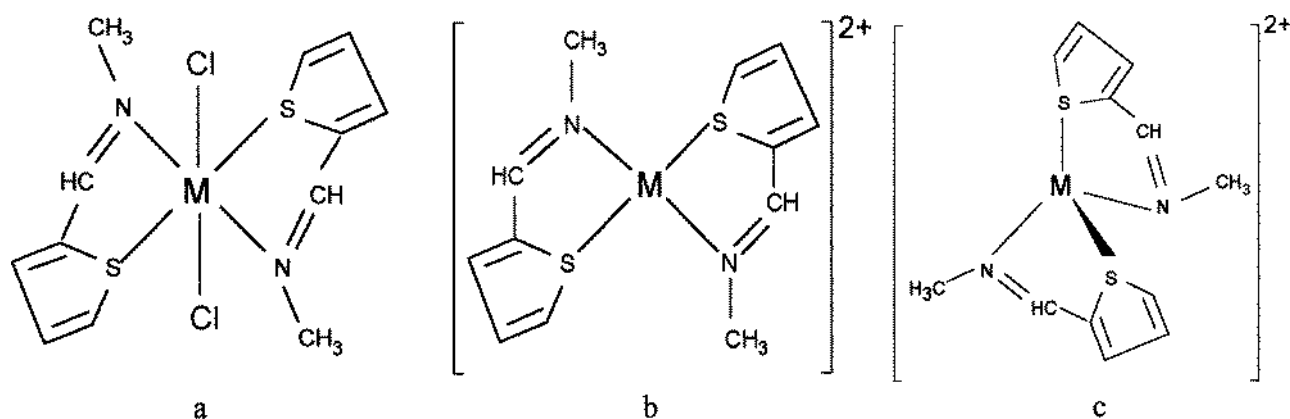


Figure 2. The structural formulas of the complexes:

a. $[ML_2Cl_2]$ ($M = Fe^{II}, Co^{II}, Ni^{II}$)

b. $[CuL_2]Cl_2$

c. $[ML_2]Cl_2$ ($M = Zn^{II}, Cd^{II}$)

L = TNAM

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