

Studies on N-(2-Thienylmethylidene)-2-aminothiophenol Complexes of Co(II), Ni(II) and Cu(II)

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Metal complexes ML_2 and ML_2Cl_2 , where M is Co(II), Ni(II), Cu(II) and L is Schiff base formed by condensation of 2-thiophenecarboxaldehyde and 2-aminothiophenol, N-(2-thienylmethylidene)-2-aminothiophenol (TNATPh), have been prepared and characterized by elemental analysis, magnetic and spectroscopic measurements. IR and NMR spectra show that the nitrogen of the azomethine group and sulphur of the thiophene ring take part in coordination in the ML_2Cl_2 complexes while in the ML_2 compounds the ligands act as tridentate coordinating through azomethine nitrogen and both sulphur atoms. Magnetic, ESR and electronic spectral studies show a distorted octahedral structure for the ML_2 and CoL_2Cl_2 complexes and a square-planar geometry for $Ni(TNATPh)_2Cl_2$ and $Cu(TNATPh)_2Cl_2$ complexes.

Key Words: Schiff base, N-(2-Thienylmethylidene)-2-aminothiophenol, NMR spectra, ESR spectra.

INTRODUCTION

Metal complexes of Schiff base are studied extensively due to synthetic flexibility of these compounds and their selectivity as well as sensitivity towards the central metal atom. Complexes with Schiff bases derived from 2-thiophenecarboxaldehyde were prepared and used for extracting some metal ions. In most complexes presented in previous works^{1,2}, the ligand coordination to the metal ions achieves both nitrogen and sulphur atoms.

In continuation of our work on metal complexes of Schiff bases³⁻⁶, the studies on the complexes of Schiff bases derived from 2-thiophenecarboxaldehyde (2-TFCA) and 2-aminothiophenol (2-ATPh), N-(thienylmethylidene)-2-aminothiophenol (TNATPh), with Co(II), Ni(II) and Cu(II) have been reported. Tentative structures have been proposed on the basis of analytical, spectral, magnetic and conductance data.

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EXPERIMENTAL

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck, 99.99%), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck, 99.99%), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck, 99.99%), 2-thiophenecarboxaldehyde (Merck, 98%), 2-aminothiophenol (Merck, 98%) were purchased and used as such. The ligand and the complexes were analyzed for M, S and Cl by conventional methods^{7,8}, while C and N by microanalytical methods. The IR spectra were obtained in KBr discs using a BIO-RAD FTS 135 spectrophotometer. Reflectance spectra were obtained with a Beckman DK2A spectrophotometer fitted with a standard reflectance attachment. 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 spectrometer. The ESR spectrum was recorded on an ART 5 spectrometer at room temperature. The magnetic moments were determined by the Faraday method. A digital conductivity meter K 612 was used to measure the molar conductivities in DMF solution.

Synthesis of bidentate Schiff base: An ethanolic solution of 2-TFCA (0.002 mol, 25 mL) was added to an ethanolic solution of 2-ATP (0.002 mol, 25 mL) and refluxed for 8 h 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 TNATPh ($M = 219$): C 60.27, H 4.11; N 6.39, S 29.22; Found: C 60.23; H 4.13, N 6.41, S 29.21; ^1H NMR (CDCl_3 δ -ppm): 8.7 (s, 1H, $\text{CH}=\text{N}$), 7.1 (d, 1H,); 3.8 (s, 1H, SH); ^{13}C NMR (CDCl_3 δ -ppm): 152.5 ($\text{CH}=\text{N}$), 135.3 (C-5), 111.2 (C-2).

Synthesis of the ML_2 complexes: An ethanolic solution of metal chlorides (0.002 mol, 50 mL) was added to an ethanolic solution of ligand (0.004 mol, 50 mL), at pH = 9.5–10. The mixture was refluxed on a water-bath for 6–8 h. The compounds separated were filtered, washed with ethanol and dried over CaCl_2 in vacuum. Anal. (%), Calcd. for $\text{Co}(\text{TNATPh})_2$ ($M = 494.93$): Co 11.90, C 53.34, N 5.66, S 25.86; Found: Co 11.94, C 53.30, N 5.69, S 25.81. Calcd. for $\text{Ni}(\text{TNATPh})_2$ ($M = 494.69$): Ni 11.86, C 53.36, N 5.66, S 25.87; Found: Ni 11.84, C 53.32, N 6.00, S 25.88. Calcd. for $\text{Cu}(\text{TNATPh})_2$ ($M = 499.54$): Cu 12.72, C 52.84, N 5.60, S 25.62; Found: Cu 12.75, C 52.81, N 5.63, S 25.59.

Synthesis of the ML_2Cl_2 complexes: A mixture of 2-TFCA (0.004 mol, 50 mL) and 2-ATP (0.004 mol, 50 mL) in ethanol was added to an ethanolic solution of metal chlorides (0.002 mol, 50 mL), at pH = 6.5. The mixture of reactants was refluxed on a water-bath for 4–6 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 $\text{Co}(\text{TNATPh})_2\text{Cl}_2$ ($M = 567.83$): Co 10.38, C 46.49, N 4.93, S 11.27, Cl 12.48; Found: Co 10.42, C 46.44, N 4.95, S 11.30, Cl 12.493; Calcd. for $\text{Ni}(\text{TNATPh})_2\text{Cl}_2$ ($M = 567.59$): Ni 10.34, C 46.51, N 4.93, S 11.27, Cl 12.49; Found: Ni 10.30, C 46.49, N 4.97, S 11.31, Cl 12.52; ^1H NMR (CDCl_3 δ -ppm): 8.9 (s, 1H, $\text{CH}=\text{N}$), 7.4 (d, 1H); 3.8 (s, 1H, SH); ^{13}C NMR (CDCl_3 δ -ppm): 155.3 ($\text{CH}=\text{N}$), 137.5 (C-5), 113.2 (C-2); Calcd. for $\text{Cu}(\text{TNATPh})_2\text{Cl}_2$ ($M = 572.44$): Cu 11.10, C 46.11, N 4.89, S 11.18, Cl 12.38; Found: Cu 11.15, C 46.07, N 4.92, S 11.21, Cl 12.39.

RESULTS AND DISCUSSION

The complexes of Co(II), Ni(II), Cu(II) with N-(2-thienylmethylidene)-2-aminothiophenol (TNATPh) (Fig. 1) appear as powders. They are not soluble in methanol, ethanol and ethylether but soluble in DMF and DMSO.

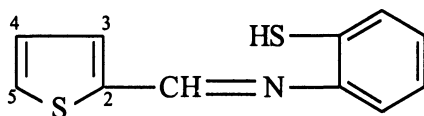


Fig. 1. The structure of N-[2-thienylmethylidene]-2-aminothiophenol

Based on the elemental analysis, the formulas ML_2 and ML_2Cl_2 (Table-1) has been suggested for the compounds.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES*

Compounds	Yield (%)	m.p. (°C)	Colour	μ_{eff} (BM)	Λ_M^{M} ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)
Co(TNATPh) ₂	60	180	Red	5.2	10.2
Ni(TNATPh) ₂	74	220	Yellow	3.1	6.5
Cu(TNATPh) ₂	77	240	Golden	1.96	8.7
Co(TNATPh) ₂ Cl ₂	58	250	Pink	4.9	15.3
Ni(TNATPh) ₂ Cl ₂	62	190	Brownish	diamag.	120.6
Cu(TNATPh) ₂ Cl ₂	84	250	Dark brown	1.86	112.4

*All the complexes give satisfactory metal, C, S, N and Cl analyses;

IR and NMR spectra. Some important IR bands of TNATPh and its complexes along with their assignments are presented in Table-2.

TABLE-2
CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES
(IN cm^{-1}) OF LIGAND AND COMPLEXES

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{SH})$	$\nu(\text{C}-\text{S}-\text{C})$	$\nu(\text{C}-\text{Ssym})$	$\nu_{\text{asym}}(\text{C}-\text{Sasym})$	$\nu(\text{M}-\text{N})$
TNATPh	1655	2550	870	680	630	—
Co(TNATPh) ₂	1620	—	840	—	590	423
Ni(TNATPh) ₂	1618	—	833	—	607	417
Cu(TNATPh) ₂	1614	—	825	—	605	422
Co(TNATPh) ₂ Cl ₂	1625	2542	820	—	609	420
Ni(TNATPh) ₂ Cl ₂	1622	2545	825	—	602	425
Cu(TNATPh) ₂ Cl ₂	1615	2552	840	—	600	418

The IR spectrum of the ligand shows a band at 1635 cm^{-1} which is assigned to the $\nu(\text{C}=\text{N})$ of the azomethyne group. The comparison of the positions of these bands with those observed in the IR spectra of the complexes indicates that the band shifts towards lower frequencies ($\Delta\nu = 15\text{--}40\text{ cm}^{-1}$). This behaviour suggests that TNATPh is coordinated to the central metal ion through the azomethyne nitrogen.

The band observed in the free ligand spectrum at 870 cm^{-1} can be ascribed to $\nu(\text{C—S—C})$ stretching vibration⁹. This band is shifted to lower values with $30\text{--}50\text{ cm}^{-1}$, for all compounds, suggesting the involvement of sulphur atom in the bonding with the metal's ions. The band observed at 630 cm^{-1} in the ligand spectrum, assigned to the $\nu_{\text{asym}}(\text{C—S})$ stretching vibration, is similarly shifted and the symmetric $\nu_{\text{sym}}(\text{C—S})$ (from 685 cm^{-1}) completely disappears after complexation. This also confirms that the thiophene ring sulphur is a donor atom¹⁰.

Also, the band at 2550 cm^{-1} [$\nu(\text{SH})$] in the ligand disappears in the spectra of the ML_2 complexes indicating deprotonation of —SH group, while in the spectra of ML_2Cl_2 does not show a marked shift. On the basis of these data, it can be concluded that in ML_2 compounds the ligand coordinates through sulphur atom. The proof of the coordination to the N atom is provided by the occurrence of the bands in the $430\text{--}417\text{ cm}^{-1}$ region in all the compounds. From the infrared spectral studies it is obvious that the ligands act as tridentate coordinating through azomethyne N and both S atoms in the ML_2 complexes, while in the ML_2Cl_2 complexes act as bidentate co-ordinating through azomethyne N and thiophene S.

In the ^1H NMR spectrum of the ligand, the thiophene ring proton 5-H appears at δ_1 7.1 ppm and the azomethyne proton ($\text{—CH}=\text{N—}$) at δ_2 8.7 ppm¹¹. The proton present on the —SH group gives a signal at δ_3 3.8 ppm. In the ^1H NMR spectra of the NiL_2Cl_2 complex the downfield shift of the signals δ_1 and δ_2 is $0.2\text{--}0.3$ ppm. These observations support the bonding of TNATPh through nitrogen and sulphur atoms of the thiophene ring.

The ^{13}C NMR spectra provide further support for the mode of coordination of TNATPh. In the complex spectra, the signals due to azomethyne carbon, 2-C and 5-C (thiophene ring), show a distinct downfield shift by nearly $2.2\text{--}2.8$ ppm clearly demonstrating the coordination of the ligand *via* the nitrogen and sulphur of the thiophene ring atoms.

Electronic and ESR spectra: The electronic spectrum of the ligand exhibits three intense bands at 41518 cm^{-1} ($\epsilon = 7300$), 37340 cm^{-1} ($\epsilon = 6500$) and 32560 cm^{-1} ($\epsilon = 3000$). The absorptions at 41518 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 chromophore $\text{C}=\text{N}$.

These transitions are to be found also in the spectra of the complexes, but they are shifted to lower frequencies ($\Delta\nu = 2500\text{--}2000\text{ cm}^{-1}$), confirming the coordi-

nation of the ligand to the metal ions. The relevant electronic spectral data are reported in Table-3.

TABLE-3
ELECTRONIC SPECTRA OF THE COMPLEXES (d-d TRANSITIONS)

Compound	Absorption maxima (cm ⁻¹)
[Co(TNATPh) ₂]	20 620 16 390 9479
[Ni(TNATPh) ₂]	23 018 14 840 9986
[Cu(TNATPh) ₂]	16 280
[Co(TNATPh) ₂ Cl ₂]	18 850 18 120 15 750 9400 8509
[Ni(TNATPh) ₂ Cl ₂]	21 540 18 010
[Cu(TNATPh) ₂ Cl ₂]	18 140 15 210

The reflectance spectrum of the Co(TNATPh)₂ compound consists of three bands at 9479, 16390 and 20620 cm⁻¹. For octahedral Co(II) complexes three bands are expected corresponding to the three spin-allowed transitions ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (ν_3).

However, it has been pointed out¹² that the transition ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$ corresponds to a two-electron jump and as such will have a much lower oscillator strength than the other two bands and will be much weaker. The band at 9479 cm⁻¹ can therefore be assigned to the ν_1 transition and the band at 20620 cm⁻¹ to the ν_3 transition.

Using the equations which are derived from the energy matrix of the two ${}^4T_{1g}$ levels¹³ we obtain the values of D_q and B from the position of the ν_1 and ν_3 bands which are 1069 and 823 cm⁻¹, respectively.

Using the relationship $\nu_2 = \nu_1 + 10D_q$, the ν_2 band would be expected to occur at about 20100 cm⁻¹, very close to the ν_3 band. The calculation does suggest that the shoulder at 16390 cm⁻¹ is not due to the ν_2 transition and is likely to be the spin-forbidden ${}^4T_{1g} \rightarrow {}^2T_{2g}(G)$ transition.

The reflectance spectrum clearly shows the compound to be octahedral and this is supported by the magnetic moment which lies in the range normally observed for cobalt(II) octahedral complexes.

The reflectance spectrum of the Co(TNATPh)₂Cl₂ complex exhibits five bands. By analogy with the assignments of Ferguson¹⁴, the bands at 18850 and 18120 cm⁻¹ arise from the ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition which is split in complexes of D_{4h} symmetry.

That at 15750 cm⁻¹ arises from the ${}^4T_{1g} \rightarrow {}^4A_{2g}$ transition and those at 9400 and 8509 cm⁻¹ arise from the ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$ transition.

For octahedral nickel(II) complexes, having d⁸ electronic configuration three transitions are expected: ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1), ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and

${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3). In the Ni(TNATPh)₂ spectrum the spin allowed transition of the lowest energy (ν_1) may be assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ consisting band at 9986 cm^{-1} . The second band observed near 14840 cm^{-1} can be assigned to ν_2 transition, while the highest energy transition obtained at 23018 cm^{-1} may probably be due to ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$. These complexes exhibit magnetic moment in the range expected for octahedral geometry.

The Ni(TNATPh)₂Cl₂ complex is diamagnetic suggesting an essentially square-planar environment about Ni(II), which is also supported by their visible spectrum in the regions 21540 and 18010 cm^{-1} assignable to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transitions, respectively, in a planar arrangement of ligand molecules around Ni(II) atoms¹⁵.

The electronic spectrum of Cu(TNATPh)₂ complex shows only one broad absorption band at 16280 cm^{-1} indicating probably a distorted octahedral configuration. The magnetic moment value is 1.96 BM. The ESR spectrum for this compound, measured in polycrystalline sample at room temperature, gives the following values: $g_{\parallel} = 2.032$ and $g_{\perp} = 2.216$. The value $g_{\parallel} < g_{\perp}$ is well consistent with a primarily d_{z^2} ground state and the spectrum is characteristic of axial (compressed octahedral) symmetry¹⁶.

The electronic spectrum of Cu(TNATPh)₂Cl₂ compound shows absorption bands at 15210 and 18140 cm^{-1} assignable to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively, supporting square-planar configuration¹⁷. The room temperature magnetic moment value (1.86 BM) indicates the presence of one free electron. The ESR spectrum recorded on the powdered sample revealed two g-values $g_{\parallel} = 2.198$ and $g_{\perp} = 2.070$. A comparison of the g_{\parallel} and g_{\perp} indicates that $g_{\parallel} > g_{\perp} > 2$ and so the unpaired electron lies predominantly in the metal $d_{x^2-y^2}$ orbital with ${}^1B_{1g}$ ground state and the spectrum is characteristic of axial symmetry¹⁸. The parameter G, determined as $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, is found to be much less than 4 suggesting a considerable interaction in the solid state¹⁹.

The molar conductance of the complexes, in DMF (10^{-3} M) solution, are in the range 113.5–119.8 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating their 1 : 2 electrolytic nature, with the exception of the ML₂ and CoL₂Cl₂ complexes which are nonelectrolytes.

Conclusions

In this paper we report about preparation, isolation and characterization of a new Schiff base derived from 2-thiophenecarboxaldehyde and 2-aminothiophenol, and its complexes with Co(II), Ni(II), Cu(II). The products were characterized by elemental analysis, magnetic and spectroscopic measurements. Correlating the experimental data, one can estimate the stereochemistry of the prepared complexes: distorted octahedral for the [M(TNATPh)₂] (M = Co(II), Ni(II), Cu(II)) and [Co(TNATPh)₂Cl₂] and square-planar for the [M(TNATPh)₂]Cl₂ (M = Ni(II) and Cu(II)).

The predicted structural formulas of these compounds are presented in Fig. 2.

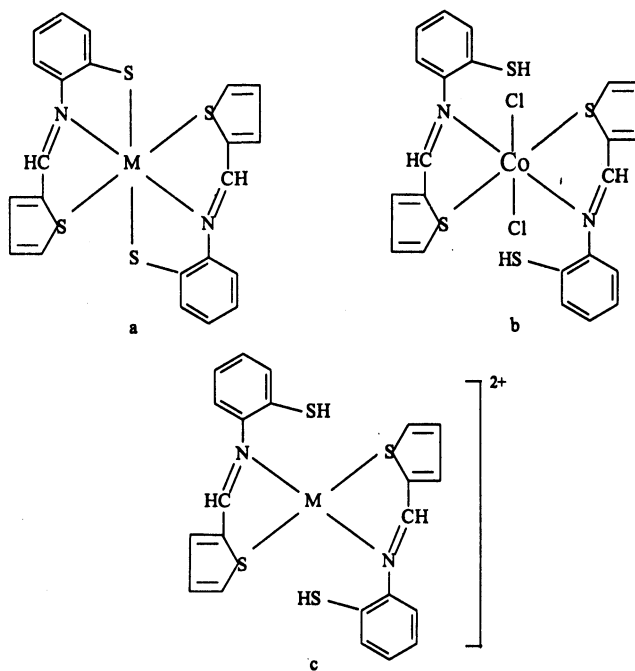


Fig. 2. The proposed formulas of the complexes:

- (a) $[M(TNATPh)_2]$ ($M = Co(II), Ni(II)$ and $Cu(II)$); (b) $[Co(TNATPh)_2Cl_2]$;
 (c) $[M(TNATPh)_2]Cl_2$ ($M = Ni(II)$ and $Cu(II)$)

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