

STUDIES ON *N*-[2-THIENYLMETHYLIDENE]-2-AMINOTHIAZOLE 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-aminothiazole, *N*-[2-thienylmethylidene]-2-aminothiazole (TNATZ), 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. Magnetic, Mössbauer, ESR and electronic spectral studies show a distorted octahedral structure for the Fe(II) complex, a square-planar geometry for $Ni(TNATZ)_2Cl_2$ and $Cu(TNATZ)_2Cl_2$ complexes and a tetrahedral geometry for Co(II), Zn(II) and Cd(II) complexes. Conductance measurements suggest the 1:2 electrolytic nature of the complexes, with the exception the of the $Fe(TNATZ)_2Cl_2$ compound.

Key words: Schiff base, *N*-[2-thienylmethylidene]-2-aminothiazole

Introduction

Investigation on metal complexes of thiazole derivatives, particularly the 2-substituted ones have received considerable attention,¹⁻³ owing to their importance in biological and industrial processes.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 Schiff base derived from 2-thiophenecarboxaldehyde (2-TFCA) and 2-aminothiazole (2-ATZ), *N*-[thienylmethylidene]-2-aminothiazole (TNATZ), 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.

Results and discussion

The complexes of Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with *N*-[2-thienylmethylidene]-2-aminothiazole (TNATZ) (Fig. 1) appear as powders with medium melting points. They are not soluble in methanole, ethanol, ethylether and chloroform but soluble in DMF.

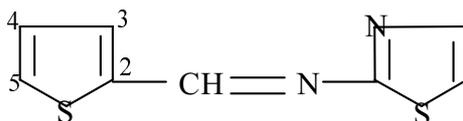


Figure 1. The structure of *N*-[2-thienylmethylidene]-2-aminothiazole

Based on the elemental analysis, the formula ML_2Cl_2 (Table 1) has been suggested for all compounds.

Table 1. Analytical and physical data of the complexes*

Compounds	Melting point °C	Colour	μ_{eff} (MB)	Λ_M^{**} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
Fe(TNATZ) ₂ Cl ₂	160	red	5.14	10.2
Co(TNATZ) ₂ Cl ₂	170	blue	4.41	125.8
Ni(TNATZ) ₂ Cl ₂	150	brownish	diam.	118.4
Cu(TNATZ) ₂ Cl ₂	130	brown	1.78	143.7
Zn(TNATZ) ₂ Cl ₂	210	yellowish	-	115.4
Cd(TNATZ) ₂ Cl ₂	145	white	-	120.6

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

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

Table 2. Characteristic infrared absorption frequencies (in cm^{-1}) of ligands and complexes

Compound	$\nu_{\text{C=N}}$ azomethine	$\nu_{\text{C=N}}$ thiophene	$\nu_{\text{C-S-C}}$	$\nu_{\text{C-S}}$	$\nu_{\text{M-N}}$
TNATZ	1656	1503	890	708	-
Fe(TNATZ) ₂ Cl ₂	1630	1504	892 860	710 638	430
Co(TNATZ) ₂ Cl ₂	1626	1505	894 854	711 626	425
Ni(TNATZ) ₂ Cl ₂	1620	1502	890 878	708 620	422
Cu(TNATZ) ₂ Cl ₂	1616	1503	895 879	703 667	428
Zn(TNATZ) ₂ Cl ₂	1618	1505	885 855	705 625	408
Cd(TNATZ) ₂ Cl ₂	1615	1501	889 868	704 635	410

The IR spectrum of the ligand shows a band at 1656 cm^{-1} which is assigned to the $\nu_{\text{C}=\text{N}}$ of the azomethyne group and an intense band at 1503 cm^{-1} corresponding to the C=N stretching of the thiazole ring. The comparison of the positions of these bands with those observed in the IR spectra of the complexes indicates that the band at 1656 cm^{-1} shifts towards lower frequencies, while that at 1503 cm^{-1} does not show a marked shift. This behaviour suggests that TNATZ is coordinated to the central metal ion through the azomethine nitrogen. The proof of the coordination to the N atom is provided by the occurrence of the bands in the $408\text{--}430\text{ cm}^{-1}$ region in the IR spectra of the compounds.

The band observed in the free ligand spectrum at 890 cm^{-1} can be ascribed to $\nu_{\text{C}-\text{S}-\text{C}}$ stretching vibration⁷. In the IR spectra of the complexes, two distinct bands appear in this region: the first one at $854\text{--}879\text{ cm}^{-1}$ (shifted to lower frequency side) and the second one at $885\text{--}895\text{ cm}^{-1}$ (which remains almost unchanged on complexation). These observations suggest that one of the two sulphur atoms takes part in coordination. The important canonical form of the TNATZ places a positive charge on the thiazole sulphur rendering it as a poor donor and we can suggest bonding of the ligand through the thiophene sulphur atom.

The band observed at 708 cm^{-1} in the ligand spectrum assigned to the $\nu_{\text{C}-\text{S}}$ stretching vibration is similarly shifted. This also confirms that the thiophene ring sulphur is a donor atom.⁸

In the $^1\text{H-NMR}$ spectrum of the ligand, the thiophene ring proton 5-H appears at $\delta\ 7.2$ ppm and the azomethine proton ($-\text{CH}=\text{N}-$) at 8.7 ppm. These signals register downfield shifts ($0.4\text{--}0.6$ ppm) in the Ni(II), Zn(II) and Cd(II) complexes. These observations support the bonding of TNATZ through nitrogen and sulphur atoms.

The $^{13}\text{C-NMR}$ spectra provide further support for the mode of coordination of TNATZ. In the complexes spectra, the signals due to azomethine carbon, 2-C and 5-C (thiophene ring) show a distinct downfield shift by nearly $5\text{--}6.2$ 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 $40\ 310$ and $36\ 180\text{ cm}^{-1}$, respectively, has been observed. These transitions are to be found also in the

spectra of the complexes, but they are shifted to lower frequencies ($\Delta\nu=1500-2000\text{ cm}^{-1}$), 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 3) and from values of the magnetic moments.

Table 3. Electronic spectra of the complexes

Compound	Absorption maxima (cm^{-1})
[Fe(TNATZ) ₂ Cl ₂]	12 600 10 200
[Co(TNATZ) ₂ Cl ₂]	15 000 8 330
[Ni(TNATZ) ₂ Cl ₂]	20 276 15 973
[Cu(TNATZ) ₂ Cl ₂]	19 157 15 280
[Zn(TNATZ) ₂ Cl ₂]	25 260 (C.T.)
[Cd(TNATZ) ₂ Cl ₂]	24 320 (C.T.)

The electronic spectrum of the iron(II) complex consists of a pair of low intensity bands at 12600 and 10200 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.⁹ The room temperature magnetic moment (5.14 BM) corresponds with the octahedral symmetry. Also, in the Mössbauer spectrum, the value of isomer shift ($0.874\text{ mm}\cdot\text{s}^{-1}$) indicates a high spin variety for iron(II) complex. Further, the somewhat lower value of the isomer shift than expected for perfect octahedral structure suggests a distortion from octahedral geometry.¹⁰

The solid state electronic spectral bands of the Co(II) complex around 8330 (ν_2) and 15000 cm^{-1} (ν_3), the value of Dq (487 cm^{-1}), B (725 cm^{-1}), β (0.75) and ν_2/ν_1 (1.71) calculated using Underhill and Billing equation¹¹ as well as the magnetic moment value 4.41 B.M., all reveal the tetrahedral coordination of ligands around the Co(II) ion.

The diamagnetism of the Ni(II) complex indicates an essentially square-planar environment about Ni(II), which is in agreement with the reflectance spectrum of the Ni(TNATZ)₂Cl₂ compound. The bands at 20276 and 15973 cm^{-1} can be assigned to the transitions ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}$, respectively.

The electronic spectrum of Cu(II) complex shows absorption bands at 19157 and 15280 cm^{-1} assignable to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition, supporting square-

planar configuration. The ESR spectrum for this compound, measured in polycrystalline sample at room temperature, gives g_{\parallel} and g_{\perp} values about 2.15 and 2.07, respectively.

The value $g_{\parallel} > g_{\perp}$ is well consistent with a primarily $d_{x^2-y^2}$ ground state having an elongated square-planar structure¹². 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 state.

From stoichiometry and other physicochemical evidences, four-coordinated tetrahedral geometry is suggested for Zn(II) and Cd(II) complexes.

The molar conductance of the complexes in DMF (10^{-3} M) are in the range 115.4–143.7 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ indicating their 1:2 electrolytic nature, with the exception of the Fe(TNATZ)₂Cl₂ compound ($\Lambda_M = 10.2 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$).

Conclusions

In this paper we report about preparation, isolation and characterisation of a new bidentate Schiff base ligand derived from 2-thiophenecarboxaldehyde and 2-aminothiazole, 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. Correlating the experimental data, one can estimate the stereochemistry of the prepared complexes: distorted octahedral for the [Fe(TNATZ)₂Cl₂], square-planar for the [M(TNATZ)₂]Cl₂ (M=Ni^{II} and Cu^{II}) and tetrahedral for the [M(TNAP)₂]Cl₂ (M=Co^{II}, Zn^{II} and Cd^{II}) compounds. The proposed structural formulas of these compounds are presented in Figure 2.

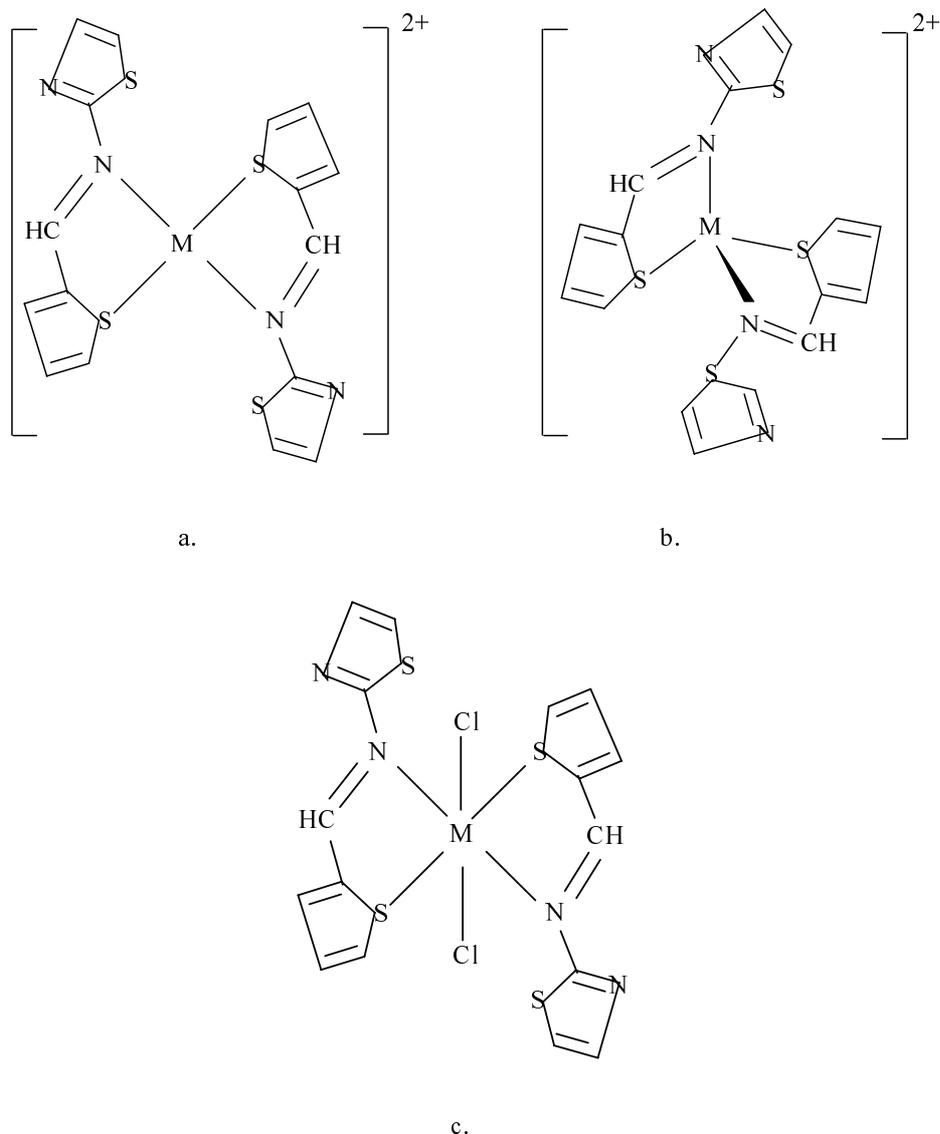


Figure 2. The proposed formulae of the complexes: a. $[M(\text{TNATZ})_2]\text{Cl}_2$ ($M = \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}$);
 b. $[M(\text{TNATZ})_2]\text{Cl}_2$ ($M = \text{Co}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}$); c. $[M(\text{TNATZ})_2]\text{Cl}_2$ ($M = \text{Fe}^{\text{II}}$)

Experimental

Reagents: $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck, 99.9%), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (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%), thiophenecarboxaldehyde (Merck, 98%), 2-aminothiazole (Merck, 98%).

Synthesis of bidentate Schiff bases. An ethanolic solution of 2-TFCA (0.002 mol, 25 ml) was added to an ethanolic solution of 2-ATZ (0.002 mol, 25 ml) and refluxed for 3h 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.* Calculated for $\text{C}_8\text{H}_6\text{N}_2\text{S}_2$: C, 49.46; H, 3.11; N, 14.43; S, 33.01. Found: C, 49.45; N, 14.46; S, 33.02. ^1H NMR: δ_1 8.7; δ_2 7.2; ^{13}C NMR: δ_1 150.7; δ_2 133.3; δ_3 111.7.

Synthesis of the ML_2Cl_2 complexes. A mixture of 2-TFCA (0.004 mol, 50 ml), 2-ATZ (0.004 mol, 50 ml) in ethanol was added to an ethanolic solution of metal chlorides (0.002 mol, 50ml), at pH=8.5-9. The mixture of reactants was refluxed on a water-bath for 10-12 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 $\text{Co}(\text{TNATZ})_2\text{Cl}_2$: Co, 11.38; C, 37.08; N, 10.81; S, 24.74; Cl, 13.68. Found: Co, 11.42; C, 37.05; N, 10.78; S, 24.75; Cl, 13.67. Calculated for $\text{Ni}(\text{TNATZ})_2\text{Cl}_2$: Ni, 11.34; C, 37.09; N, 10.82; S, 24.75; Cl, 13.68. Found: Ni, 11.31; C, 37.05; N, 10.86; S, 24.76; Cl, 13.68. Calculated for $\text{Cu}(\text{TNATZ})_2\text{Cl}_2$: Cu, 12.16; C, 36.75; N, 10.72; S, 24.52; Cl, 13.57. Found: Cu, 12.11; C, 36.72; N, 10.75; S, 24.52; Cl, 16.11. Calculated for $\text{Zn}(\text{TNATZ})_2\text{Cl}_2$: Zn, 12.47; C, 36.62, N, 10.68; S, 24.44; Cl, 13.59. Found: Zn, 12.44; C, 36.58, N, 10.66; S, 24.45; Cl, 13.56. ^1H NMR: δ_1 9.2; δ_2 7.5; ^{13}C NMR: δ_1 155.6; δ_2 134.7; δ_3 114.3. Calculated for $\text{Cd}(\text{TNATZ})_2\text{Cl}_2$: Cd, 19.67; C, 33.60, N, 9.80; S, 22.43; Cl, 12.41. Found: Cd, 19.71; C, 33.56, N, 9.40; S, 22.43; Cl, 12.38. ^1H NMR: δ_1 9.0; δ_2 7.6; ^{13}C NMR: δ_1 156.4; δ_2 135.2; δ_3 115.6. Calculated for $\text{Fe}(\text{TNATZ})_2\text{Cl}_2$: Fe, 10.84; C, 37.29, N, 10.86; S, 24.89; Cl, 13.76. Found: Fe, 10.64; C, 36.98, N, 11.03; S, 24.92; Cl, 13.11. ^1H NMR: δ_1 9.3; δ_2 7.6; ^{13}C NMR: δ_1 154.8; δ_2 137.2; δ_3 116.1.

Instruments. The ligand and the complexes were analysed for M, S and Cl by conventional methods,^{13,14} while C, H and N by microanalytical methods. The IR spectra were obtained in KBr discs 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 Mössbauer spectrum of iron compound was measured at 293 K on an ECIL MBS 35 spectrometer using ^{57}Co in Pd matrix as source. 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 of a polycrystalline sample 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.

References

1. J. A. Weaver, P. Hambrigh, *Inorg. Chem.* **1970**, *9*, 268.
2. E. J. Duff, M. N. Hughes, K. J. Rutt, *Inorg. Chim. Acta*, **1972**, *6*, 408.
3. W. E. Estes, D. P. Gavel, W. E. Hatfield, *Inorg. Chem.* **1978**, *17*, 1415.
4. M. M. Campbell, *Comprehensive Organic Chemistry*, vol. 4, Pergamon Press, Oxford, **1979**.
5. A. Kriza, C. Spinu, *J. Indian Chem. Soc.* **2000**, *76*, 84.
6. C. Spinu, A. Kriza, *Acta Chim. Slov.* **2000**, *47*, 179.
7. S. C. Mohapatra, D. V. R. Rao, *J. Indian Chem. Soc.* **1980**, *57*, 262.
8. S. Burman, D. N. Sathyanarayana, *J. Inorg. Nucl. Chem.* **1981**, *43*, 1940.
9. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, New York, **1984**.
10. T. G. Gibb, N. N. Greenwood, *Mössbauer Spectroscopy.*, Chapman & Hall, London, **1971**.
11. D. E. Billing, A. E. Underhill, *Nature (London)* **1966**, 843.
12. B. T. Hathaway, *Struct. Bonding* **1973**, *14*, 60.
13. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis* 3rd ed., ELBS, London., **1961**.
14. A. Steyemark, R. Calancertle, *J. Assoc. Anal. Chem.* **1972**, *55*, 680.

Povzetek

Pripravili in karakterizirali smo komplekse s sestavo ML_2Cl_2 , kjer je M Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} ali Cd^{II} in L je Schiffova baza, ki jo dobimo s kondenzacijo 2-tiofenkarboksaldehida z 2-aminotiazolom oziroma *N*-[2-tienilmetiliden]-2-aminotiazolom (TNATZ). Z merjenjem IR, NMR, magnetnih, Mössbauerjevih in EPR spektrov smo sklepali na geometrijo pripravljenih kompleksov.