Co(II), Ni(II) and Cu(II) COMPLEXES OF BIDENTATE SCHIFF BASES

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Abstract

Cobalt (II), nickel (II) and copper (II) complexes of type ML_2Cl_2, where M is Co^{II}, Ni^{II} and Cu^{II}, and L is Schiff base formed by condensation of 2-thiophenecarboxaldehyde and propylamine, *N*-[2-thienylmethylidene]-1-propanamine (TNAP), or ethylamine, *N*-[2-thienylmethylidene]ethanamine (TNAE), 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 Cu(II) and $Ni(TNAE)_2Cl_2$ complexes, a tetrahedral geometry for $Ni(TNAP)_2Cl_2$ and a D_{4h} symmetry for the Co(II) complexes. Infrared and NMR spectra of the complexes agree with the co-ordination to the central metal atom through nitrogen and sulfur atoms. Conductance measurements suggest the non-electrolytic nature of the complexes and the 1:2 electrolytic nature of the $Ni(TNAP)_2Cl_2$.

Keywords: Schiff base, *N*-[2-thienylmethylidene]ethanamine, *N*-[2-thienylmethylidene]-1-propanamine

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[1-3], the ligand co-ordination to the metal ions achieves both nitrogen and sulphur atoms.

In the present study, a series of new Schiff bases have been synthesised using 2-thiophenecarboxaldehyde (2-TFCA) and propylamine (PA) or ethylamine (EA). These bidentate ligands form 1:2 complexes with Co(II), Ni(II) and Cu(II) ions.

Results and discussion

The complex combinations of Co(II), Ni(II) and Cu(II) with *N*-[2-thienylmethylidene]-1-propanamine (TNAP) and *N*-[2-thienylmethylidene]ethanamine (TNAE) (fig. 1) appears as powders with high melting points. They are not soluble in ethanol, ethyl ether and chloroform but soluble in acetone and more soluble in DMF.

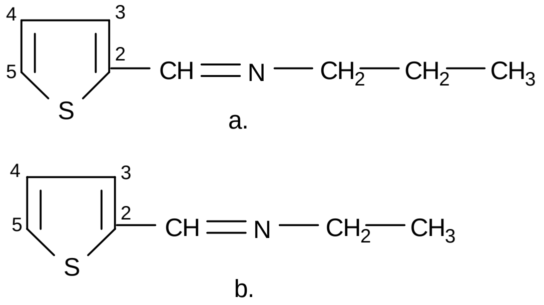


Figure 1. The structure of: a. *N*-[2-thienylmethylidene]-1-propanamine ($C_8H_{11}NS$) (TNAP)
b. N-[2-thienylmethylidene]ethanamine (C_7H_9NS) (TNAE)

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 1).

Table 1. Analytical and physical data of the complexes*

Compounds	Melting point °C	Colour	μ_{eff} (MB)	Λ_M** ($\Omega^{-1}cm^2mol^{-1}$)
$Co(TNAP)_2Cl_2$	220	purple	4.59	12.1
$Ni(TNAP)_2Cl_2$	150	blue	3.52	130.2
$Cu(TNAP)_2Cl_2$	128	green	1.92	10.4
$Co(TNAE)_2Cl_2$	250	pink	4.75	22.5
$Ni(TNAE)_2Cl_2$	215	yellow	3.02	7.8
$Cu(TNAE)_2Cl_2$	180	greenish	1.93	8.9

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

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 2) have been carried out.

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

Compound	$\nu_{C=N}$	ν_{CSC}	$\nu_{Chtiophen}$	$\nu_{C\text{-}Ctiophen}$	$\nu_{CSsym.}$	$\nu_{Csasym.}$	$\nu_{M\text{-}N}$
TNAP	1670	850	3070	1520	690	640	-
$Co(TNAP)_2Cl_2$	1632	822	3068	1511	-	620	418
$Ni(TNAP)_2Cl_2$	1615	830	3071	1518	-	617	420
$Cu(TNAP)_2Cl_2$	1620	825	3063	1520	-	625	415
TNAE	1656	845	3060	1523	680	650	-
$Co(TNAE)_2Cl_2$	1611	815	3063	1522	-	615	422
$Ni(TNAE)_2Cl_2$	1618	820	3065	1520	-	608	425
$Cu(TNAE)_2Cl_2$	1625	825	3058	1515	-	610	428

I.R. and NMR spectra. The IR spectra of the ligands exhibits a band at 1656-1670 cm^{-1} assignable to $\nu_{C=N}$ of the azomethyne group. This band shift to lower region by about 38-

60 cm^{-1} in case of the all complexes, suggesting co-ordination through N atom of the azomethyne group.

The medium intensity band at ~850 cm^{-1} observed in free ligand ascribed to $\nu_{CSC\ (ring)}$ stretching vibration[4] is shifted to lower values with 28-30 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 $\nu_{C\text{-}S}$ is shifted to lower frequency after complexation and the symmetric $\nu_{C\text{-}S}$ is completely disappears in all the complexes. This also confirms that the sulphur atom is taking part in the complex formation[2,5]. The proof of coordination to the N atom is provided by the occurrence of the bands from 415-428 cm^{-1} in the I.R. spectra of the compounds.

In the ^{1}H-NMR spectra of the ligands the formation of Schiff bases is supported by the presence of a singlet at δ 9.54 and 9.72 ppm respectively, corresponding to the azomethyne proton (-CH=N-) and a peak at δ 159.7 and 162.3 ppm respectively, in the ^{13}C-NMR spectra.

Electronic and ESR spectra. Within the UV spectrum of the ligand has been observed the existence of two absorption bands assigned to the transition $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ at 42 522 and 35 100 cm^{-1} respectively. These transitions are to be found also in the spectra of the complexes, but they are shifted to lower frequencies ($\Delta\nu$=1100-3000 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})				
[Co(TNAP)$_2$Cl$_2$]	19 870	19 020	15 600	9 500	7 300
[Co(TNAE)$_2$Cl$_2$]	20 030	19 130	16 200	10 100	8 070
[Ni(TNAP)$_2$]Cl$_2$	17 300	9 650			
[Ni(TNAE)$_2$Cl$_2$]	25 800	14 100	8 560	7 200	
[Cu(TNAP)$_2$Cl$_2$]	11 760				
[Cu(TNAE)$_2$Cl$_2$]	16 670				

The reflectance spectra of the Co(II) complexes are similar. In the spectra appear bands at 19870, 19020, 15600, 9500 and 7300 cm^{-1} and 20030, 19130, 16200, 10100 and 8070 cm^{-1} respectively. By analogy with the band assignments of Ferguson[6], the bands at 19870, 19020 cm^{-1}, in the spectrum of Co(TNAP)$_2$Cl$_2$, and 20030, 19130 cm^{-1}, in the spectrum of Co(TNAE)$_2$Cl$_2$, arise from the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition which is split in complexes of D_{4h} symmetry. That at 15600 cm^{-1} and 16200 cm^{-1} respectively, arise from $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition, and those at 9500, 7300 cm^{-1} and 10100, 8070 cm^{-1} respectively, from the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions. This geometry is confirmed by the values of the effective magnetic moment too (4.59 and 4.75 BM respectively).

Within the spectrum of Ni(TNAP)$_2$Cl$_2$ compound, the presence of the absorption bands at 17 300 and 9650 cm^{-1} ascribed to the transitions $^3T_1(F) \rightarrow {}^3T_1(P)$ and $^3T_1(F) \rightarrow {}^3A_2$, can be notice. These transition are characteristic to the tetrahedral environment around the Ni^{2+} ion. The value of the magnetic moment, 3.52 BM, confirmed that structure. Using the method of Ballhausen[7] we calculate values Dq = 450 cm^{-1} and B = 772.

The electronic spectrum of the Ni(TNAE)$_2$Cl$_2$ 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 8560 and 7200 cm^{-1}) indicating tetragonal distortion. The magnetic moment (3.02 MB) lie in the region expected for octahedral complexes.

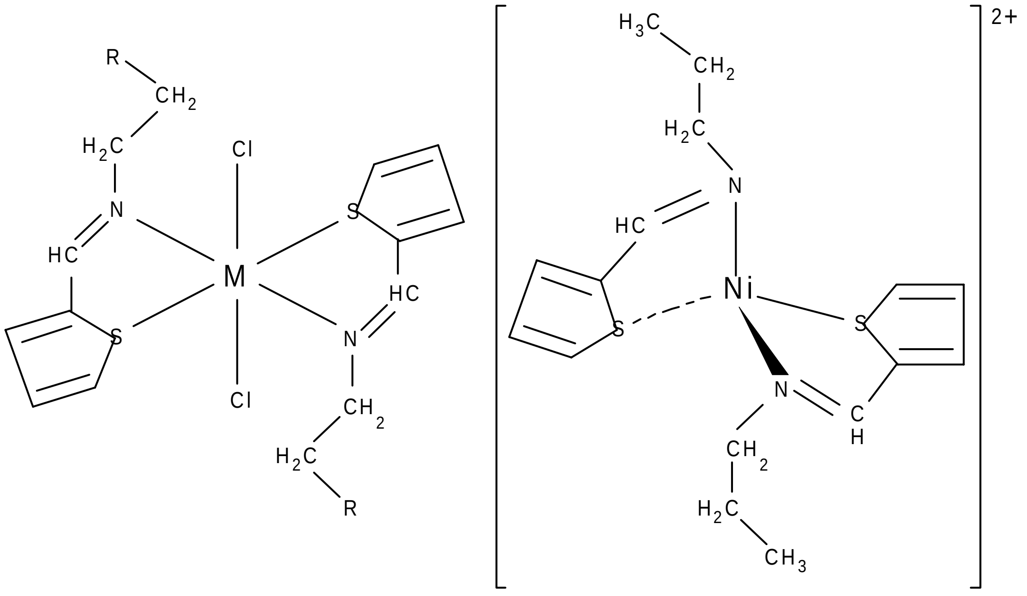
The Cu(II) complexes exhibit only one broad asymmetric band at 11760 - 16670 cm^{-1}. The calculated values of Dq (1400 cm^{-1}), LFSE (24.7 – 25 kcal/mol) and the effective magnetic moments (1.92 and 1.93 BM) suggest a distorted octahedral geometry[8].

The ESR spectra for copper compounds, measured in polycrystalline sample at room temperature, give the following values: $g_{II} = 2.0577$, $g_{\perp} = 2.1419$ for the Cu(TNAP)$_2$Cl$_2$ and $g_{II} = 2.0827$, $g_{\perp} = 2.1514$ for the Cu(TNAE)$_2$Cl$_2$. The trend, $g_{II} < g_{\perp}$ showed that the electron is delocalised in d_{z^2} orbital of the ground state of Cu^{II} and the spectra are 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 considerable interaction in the solid state[9].

The molar conductance of the complexes in DMF (10^{-3} M) are in the range 7.8-22.5 $\Omega^{-1}cm^2mol^{-1}$ indicating their nonelectrolytic nature, excepting the $Ni(TNAP)_2Cl_2$ compound which is an 1:2 electrolyt (Λ = 130.2 $\Omega^{-1}cm^2mol^{-1}$).

Conclusions

In this paper we report the isolation and characterisation of two new bidentate Schiff base ligands derived from 2-thiophenecarboxaldehyde and propylamine or ethylamine and their complexes with Co^{II}, Ni^{II} and Cu^{II}. The products were characterized by elemental analysis, magnetic and spectroscopic measurements. Correlating the experimental data one can estimate that the stereochemistry of the prepared complexes belong to the octahedral symmetry group, with the formula $[ML_2Cl_2]$ (M = Co^{II}, Ni^{II} and Cu^{II}; L = TNAP and TNAE), excepting the $[Ni(TNAP)_2]Cl_2$ compound which has a tetrahedral geometry. The proposed structural formulas of these compounds are presented in the figure 2.



a. b.

Figure 2. The structural formulas of the complexes:
a.$[ML_2Cl_2]$ (M = Co^{II}, Ni^{II}, Cu^{II}; L = TNAP and TNAE); R=CH_3, H
b.$[Ni(TNAP)_2]Cl_2$

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%), propylamine (Merck, 98%), ethylamine (Merck, 98%).

Synthesis of bidentate Schiff bases. The Schiff bases were prepared thus: an ethanolic solution of 2-TFCA (0.002 mol, 25 ml) was added with an ethanolic solution of PA or EA (0.002 mol, 25 ml) and refluxed for 12h 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 $C_8H_{11}NS$: C, 62.74; H, 7.19; N, 9.15; S, 20.19. Found: C, 62.76; H, 7.22; N, 9.13; S, 20.14. ^1H NMR: δ_1 9.54; δ_2 7.25; δ_3 6.9; δ_4 6.92. ^{13}C NMR: δ_1 159.7; δ_2 133.28; δ_3 112.08. Calculated for C_7H_9NS: C, 60.43; H, 6.47; N, 10.07; S, 23.02. Found: C, 60.39; H, 6.50; N, 10.11; S, 22.98. ^1H NMR: δ_1 9.72; δ_2 7.22; δ_3 6.85; δ_4 6.88. ^{13}C NMR: δ_1 162.3; δ_2 133.41; δ_3 112.23.

Synthesis of the ML_2Cl_2 complexes. A mixture of 2-TFCA (0.004 mol, 50 ml), and PA or EA (0.004 mol, 50 ml) in ethanol was added to an ethanolic solution of metal chlorides (0.002 mol, 50ml). The mixture of reaction was refluxed on a water-bath for 16-18h. 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 $Co(TNAP)_2Cl_2$: Co, 13.52; C, 44.05; H, 5.05; N, 6.42; S, 14.68; Cl, 16.27. Found: Co, 13.55; C, 44.01; H, 5.09; N, 6.47; S, 14.66; Cl, 16.25. Calculated for $Ni(TNAP)_2Cl_2$: Ni, 13.47; C, 44.08; H, 5.05; N, 6.43; S, 14.69; Cl, 16.27. Found: Ni, 13.50; C, 44.06; H, 5.08; N, 6.47; S, 14.67; Cl, 16.24. Calculated for $Cu(TNAP)_2Cl_2$: Cu, 14.43; C, 43.60; H, 5.00; N, 6.36; S, 14.53; Cl, 16.10. Found: Cu, 14.40; C, 43.57; H, 5.05; N, 6.40; S, 14.50; Cl, 16.11. Calculated for $Co(TNAE)_2Cl_2$: Co, 14.45; C, 41.19, N, 6.86; S, 15.69; Cl, 17.38. Found: Co, 14.40; C, 41.22, N, 6.83; S, 15.68; Cl, 17.43. Calculated for $Ni(TNAE)_2Cl_2$: Ni, 14.40; C, 41.22, N, 6.87; S, 15.70; Cl, 17.39. Found: Ni, 14.43; C, 41.19, N, 6.88; S, 15.65; Cl, 17.43. Calculated for $Cu(TNAE)_2Cl_2$: Cu, 15.41; C, 40.73, N, 6.72; S, 15.52; Cl, 17.19. Found: Cu, 15.40; C, 40.70, N, 6.78; S, 15.70; Cl, 14.41.

Instruments. The ligand and complexes were analysed for M, S and Cl by a conventional methods[10,11] , while C, H and N by microanalytical methods. 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 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 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.

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Povzetek

Kobaltovi(II), nikljevi(II) in bakrovi(II) kompleksi ML_2Cl_2 in ML'_2Cl_2, kjer je M oznaka za Co^{II}, Ni^{II} in Cu^{II} , L in L’ pa oznaka za Shciffove baze dobljene s kondenzacijo 2-tiofenkarboksaldehida in propilamina oziroma etilamina., so bili pripravljeni in karakterizirani z elementno analizo, magnetnimi in spektroskopskimi meritvami. Mag netna susceptibilnost, elektronski in ESR spektri kažejo na popačeno oktaedrično geometrijo pri Cu^{II} in Ni^{II} L'_2Cl_2 kompleksih, na tetraedrično geometrijo pri $Ni^{II}L_2Cl_2$ in na D_{4h} simetrijo pri Co(II) kompleksih. Infrardeči in NMR spektri so v skladu s koordinacijo dušikovih in žveplovih donorskih atomov na centralni kovinski atom. Na osnovi meritev prevodnosti predpostavljamo, da je $Ni^{II}L_2Cl_2$ 1:2 elektrolit, ostali kompleksi pa niso elektroliti.