Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.yu • www.shd.org.yu/JSCS
J. Serb. Chem. Soc. 73 (4) 415–421 (2008) UDC 542.9+547.571+547.551:547.665:547.288.2:615.281
JSCS–3723
Original scientific paper

Biologically active new Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of *N*-(2-thienylmethylene)methanamine

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(Received 2 April, revised 22 November 2007)

Abstract: Iron(II), cobalt(II), nickel (II), copper (II), zinc(II) and cadmium(II) complexes of the type ML_2Cl_2, where M is a metal and L is the Schiff base *N*-(2-thienylmethylene)methanamine (TNAM) formed by the condensation of 2-thiophenecarboxaldehyde and methylamine, were prepared and characterized by elemental analysis as well as magnetic and spectroscopic measurements. The elemental analyses suggest the stoichiometry to be 1:2 (metal:ligand). Magnetic susceptibility data coupled with electronic, ESR and Mössbauer 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 the Zn(II) and Cd(II) complexes. The infrared and NMR spectra of the complexes agree with co-ordination to the central metal atom through nitrogen and sulphur atoms. Conductance measurements suggest the non-electrolytic nature of the complexes, except for the Cu(II), Zn(II) and Cd(II) complexes, which are 1:2 electrolytes. The Schiff base and its metal chelates were screened for their biological activity against *Escherichia coli, Staphylococcus aureus* and *Pseudomonas aeruginosa* and the metal chelates were found to possess better antibacterial activity than that of the uncomplexed Schiff base.

Keywords: Schiff base; 2-thiophenecarboxaldehyde; *N*-(2-thienylmethylene)-methanamine; antibacterial activity.

INTRODUCTION

A large number of Schiff bases and their complexes have been studied for their interesting and important properties, *e.g.*, catalytic activity[1] and transfer of the amino group,[2] photochromic properties[3] and the ability to complex some toxic metals.[4] In continuation of our work on these complexes,[5,6] the results of studies on the complexes of the Schiff base obtained through the condensation of 2-thiophenecarboxaldehyde and methylamine, *N*-(2-thienylmethylene)methanamine (TNAM), are reported herein. The presence of two potential donor atoms should render TNAM a versatile ligand. This new ligand was synthesized and its donor characteristics towards the chlorides of Fe(II), Co(II), Ni(II), Cu(II), Zn(II)

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doi: 10.2298/JSC0804415S

and Cd(II) were examined. Tentative structures are proposed for the complexes based on 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 %), 2-thiophenecarboxaldehyde (Merck, 98 %), methylamine (Merck, 98 %).

Synthesis of the bidentate Schiff base

The Schiff base was prepared by adding an ethanolic solution of 2-thiophenecaroxaldehide, 2-TFCA (0.001 mol, 25 ml) to an ethanolic solution of MA (0.001 mol, 25 ml) and refluxing for 4 h on a water bath. After the concentration of the solution, the precipitate was separated, filtered, washed with ethanol and dried over $CaCl_2$ under vacuum.

TNAM. Anal. Calcd. for C_6H_7NS: C, 57.6; H, 5.6; N, 11.2; S, 25.6. Found: C, 57.56; H, 5.70; N, 11.30; S, 25.40. ^{1}H-NMR: δ_1 9.34, δ_2 7.12. ^{13}C-NMR: δ 161.5.

Synthesis of the ML_2Cl_2 complexes

A mixture of 2-TFCA (0.002 mol, 50 ml), and MA (0.002 mol, 50 ml) in ethanol was added to an ethanolic solution of metal chlorides (0.001 mol, 50 ml). The reaction mixture was refluxed on a water bath for 6–10 h. The excess of solvent was then distilled and the compounds which separated were filtered, washed with ethanol and dried over $CaCl_2$ under vacuum.

Instruments

The ligand and complexes were analyzed for M, S and Cl by conventional methods,[7] and C, H and N by micro-analytical methods. The IR spectra were obtained in KBr discs 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 ^{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 Mössbauer spectrum of iron compound was measured at 293 K on an ECIL MBS 35 spectrometer using ^{57}Co in a Pd matrix as the source. The ESR spectra of polycrystalline samples were recorded on an ART 5 spectrophotometer at room temperature. The magnetic moments were determined by the Faraday method. A digital conductometer K 612 was used to measure the molar conductivities in DMF solution.

Antibacterial studies

The synthesized metal complexes, in comparison to the uncomplexed Schiff base ligand, were screened for their antibacterial activity against the pathogenic bacterial species: *Escherichia coli, Staphylococcus aureus* and *Pseudomonas aeruginosa*. The paper disc diffusion method[8] was employed for the determination of the antibacterial activity.

RESULTS AND DISCUSSIONS

The complex combinations of Co(II), Ni(II) and Cu(II) with *N*-(2-thienylmethylene)methanamine (TNAM) (Fig. 1) appeared as powders with high melting points. They were not soluble in ethanol, diethyl ether or chloroform but were soluble in acetone and more soluble in DMF.

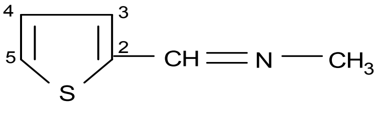

Fig. 1. The structure of *N*-(2-thienylmethylene)methanamine (C_6H_7NS) (TNAM).

Elemental analysis data

Anal. Calcd. 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. Anal. Calcd. 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. Anal. Calcd. 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. Anal. Calcd. 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. Anal. Calcd. 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; Anal. Calcd. 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.

The elemental analysis data suggest that all the complexes have a 1:2 (metal–ligand) stoichiometry. Based on the elementary chemical analysis, the formula ML_2Cl_2 (Table I) is suggested for all the prepared complexes.

TABLE I. Analytical and physical data of the complexes[a]

Compounds	Melting point, °C	Colour	μ_{eff} / μ_B	$\Lambda_M{}^b$ / Ω^{-1} cm^2 mol^{-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

[a]All the complexes give satisfactory metal, C, H, S, N and Cl analyses; [b]in DMF solution

IR and NMR spectra

In order to obtain data revealing the manner in which the ligand were coordinated to the metal ions, IR spectra in the 400–4000 cm^{-1} range (Table II) were recorded.

TABLE II. Characteristic infrared absorption frequencies, in cm^{-1}, of the ligand and the complexes

Compound	ν(C=N)	ν(C–S–C)	ν(C–S_{sym})	ν(C–S_{asym})	Other bands		ν(M–N)
TNAM	1665	860	690	640	3075	1520	–
$Fe(TNAM)_2Cl_2$	1622	821	–	620	3071	1520	420
$Co(TNAM)_2Cl_2$	1618	826	–	617	3074	1517	422
$Ni(TNAM)_2Cl_2$	1620	828	–	625	3069	1525	415
$Cu(TNAM)_2Cl_2$	1615	811	–	615	3078	1515	419
$Zn(TNAM)_2Cl_2$	1619	817	–	605	3068	1510	424
$Cd(TNAM)_2Cl_2$	1624	825	–	610	3070	1512	427

The IR spectra of the ligands exhibit a band at 1665 cm^{-1}, assignable to the ν(C=N) of the azomethine group. This band shifted by about 35–50 cm^{-1} to a lower wavenumber region in the case of all the complexes, suggesting coordination through the N atom of the azomethine group.

The medium intensity band at ≈ 880 $\mathrm{cm^{-1}}$ observed in the spectrum of the free ligand, ascribed to ν(C–S–C) (ring) stretching vibration,[9] shifted to lower values by 30–40 $\mathrm{cm^{-1}}$ for all complexes, suggesting the involvement of the sulphur atom in the bonding with the metal ions. The band assigned to the asymmetric ν(C−S) shifted to lower frequency after complexation and the symmetric ν(C−S) completely disappeared in all the complexes. This also confirms that the sulphur atom is participating in the complex formation.[10]

Proof of coordination to the N atom is provided by the occurrence of new bands in the range 419–427 $\mathrm{cm^{-1}}$ in the IR 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 9.34 and δ 7.12 ppm, corresponding to the azomethine proton (−CH=N−) and to the H-5 proton of the thiophene ring, respectively, and a peak at δ 161.5 in the ^{13}C-NMR spectra, corresponding to the azomethine carbon. In the spectra of the $\mathrm{ZnL_2Cl_2}$ and $\mathrm{CdL_2Cl_2}$ complexes, these signals showed distinct downfield shifts of nearly 0.4–0.6 ppm in the ^{1}H-NMR spectrum and 3–5 ppm in the ^{13}C-NMR spectrum, clearly demonstrating the coordination of TNAM *via* the nitrogen and sulphur atoms.

Electronic, Mössbauer and ESR spectra

Two absorption bands at 40300 and 31560 $\mathrm{cm^{-1}}$, assigned to the transitions $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$, respectively, were observed in the UV spectrum of the ligand. These transitions were also found in the spectra of the complexes but they were shifted to lower frequencies ($\Delta\nu$ = 1500–2200 $\mathrm{cm^{-1}}$), confirming the coordination of the ligand to the metal ions.

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

TABLE III. Electronic spectra of the complexes

Compound	Absorption maxima, $\mathrm{cm^{-1}}$
$\mathrm{Fe(TNAM)_2Cl_2}$	12600; 10200
$\mathrm{Co(TNAM)_2Cl_2}$	19520; 18140; 15200; 10020
$\mathrm{Ni(TNAM)_2Cl_2}$	26100; 15200; 10000; 9150
$\mathrm{Cu(TNAM)_2Cl_2}$	18500; 15400
$\mathrm{Zn(TNAM)_2Cl_2}$	26000
$\mathrm{Cd(TNAM)_2Cl_2}$	24500

The electronic spectrum of the iron(II) complex consisted of a pair of low intensity bands at 12600 and 10200 $\mathrm{cm^{-1}}$, arising from $^5T_{2g}\rightarrow{}^5E_g$ transitions, similar to those found for distorted octahedral complexes. The doublet is attributed to a Jahn–Teller distortion in the excited state.[5] The room temperature magnetic moment (5.14 μ_B) corresponded to octahedral symmetry. In addition, in the Mössbauer spectrum, the value of isomer shift (0.871 mm s^{-1}) indicates a high spin variety for the iron(II) complex. Furthermore, the somewhat lower value of the isomer shift than expected for a perfect octahedral structure suggests distortion from octahedral geometry.[11] The lower value of the quadrupole splittings (1.72 mm s^{-1}) lead to a similar conclusion.

The electronic spectrum of the Co(II) compound exhibited three bands (Table III). 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 that at 10020 cm^{-1} from the $^4T_{1g}\rightarrow{}^4T_{2g}$ transition.[12,13] These transitions correspond to a distorted octahedral geometry, which was also supported by the magnetic moment value (4.88 μ_B).

The electronic spectrum of the $Ni(TNAM)_2Cl_2$ could be assigned assuming pseudo-octahedral stereochemistry. The energies represent the following electronic transitions from the $^3A_{2g}(F)$ ground state to the $^3T_{2g}(F)$ (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 into two components (at 10000 and 9150 cm^{-1}), indicating tetragonal distortion. The magnetic moment (3.19 μ_B) lies in the region expected for octahedral complexes.

The $Cu(TNAM)_2Cl_2$ complex displays 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 stereochemistry.[14] The ESR spectrum of a polycrystalline sample of the complex measured at room temperature gave $g_{||}$ and $g_{\perp}$ values in the range of 2.147 and 2.083, respectively. The value $g_{||} > g_{\perp}$ is well consistent with a primarily $d_{x^2-y^2}$ ground state having a square-planar structure.[14] The G parameter determined as $G = [(g_{||}-2)/(g_{\perp}-2)]$ was found to be much less than 4, suggesting considerable interaction in the solid state.

The electronic spectra of the Zn(II) and Cd(II) complexes exhibit a sharp band of high intensity at 26000 and 24500 cm^{-1}, respectively, which may be due to ligand–metal charge transfer. The preference of the TNAM for bidentate chelation in the Zn(II) and Cd(II) complexes may due to the preference of these ions for tetrahedral coordination.

The molar conductance of the complexes in DMF (10^{-3} M) are in the range 10.7–15.2 Ω^{-1} cm^2 mol^{-1} for the Fe(II), Co(II) and Ni(II) complexes, indicating their non-electrolytic nature and 120.3–134.5 Ω^{-1} cm^2 mol^{-1} for the Cu(II), Zn(II) and Cd(II) complexes, which are 1:2 electrolytes.

In light of the above discussion, octahedral structures for the Fe(II), Co(II) and Ni(II) complexes, square-planar for the Cu(II) compound and tetrahedral for the Zn(II) and Cd(II) complexes is proposed. It is tentatively proposed that the Schiff base ligands coordinate through the nitrogen of the azomethine group and the sulphur of the thiophene ring, forming a stable chelate ring structure (Fig. 2).

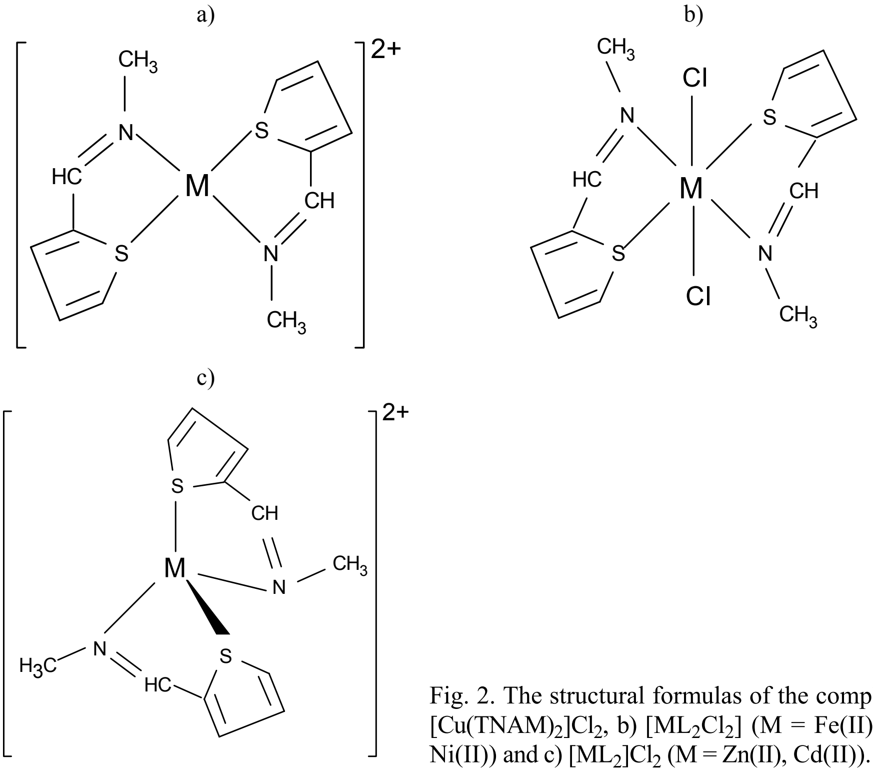

Fig. 2. The structural formulas of the complexes: a) $[Cu(TNAM)_2]Cl_2$, b) $[ML_2Cl_2]$ (M = Fe(II), Co(II), Ni(II)) and c) $[ML_2]Cl_2$ (M = Zn(II), Cd(II)).

Antibacterial activity

The antibacterial activity of the Schiff base and its complexes were studied against *Escherichia coli, Staphylococcus aureus* and *Pseudomonas aeruginosa* bacterial species. The antibacterial results are given in Table IV.

TABLE IV. Antibacterial activity data

Compound	Microbial species		
	Escherichia coli	*Staphylococcus aureus*	*Pseudomonas aeruginosa*
TNAM	+ +[a]	+	+
$Fe(TNAM)_2Cl_2$	+ + + +	+ + + +	+ + +
$Co(TNAM)_2Cl_2$	+ + + +	+ + +	+ + +
$Ni(TNAM)_2Cl_2$	+ + +	+ +	+ +
$Cu(TNAM)_2Cl_2$	+ + +	+ +	+ +
$Zn(TNAM)_2Cl_2$	+ + +	+ +	+ +
$Cd(TNAM)_2Cl_2$	+ +	+	+

[a] Inhibition zone diameter, mm (% inhibition): +, 6–10 (27–45 %); + +, 10–14 (45–64 %); + + +, 14–18 (64–82 %); + + + +, 18–22 (82–100 %). Percent inhibition values are relative to the inhibition zone (22 mm) of the most active compound with 100 % inhibition

The Schiff base and all its complexes individually exhibited varying degrees of inhibitory effects on the growth of the tested bacterial species. The biological activity of the complexes follows the order Co(II) = Fe(II) > Ni(II) = Zn(II) = = Cu(II) > Cd(II).

Furthermore, the data in Table IV show that *E. coli* were more inhibited by the Co(II) and Fe(II) complexes. The importance of this lies in the fact that these complexes could reasonably be used for the treatment of some common diseases caused by *E. coli*.

ИЗВОД

НОВИ БИЛОШКИ АКТИВНИ Fe(II), Co(II), Ni(II), Cu(II), Zn(II) И Cd(II) КОМПЛЕКСИ *N*-(2-ТИЕНИЛМЕТИЛЕН)МЕТАНАМИНА

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У раду су добијени гвожђе(II), кобалт(II), бакар(II), цинк(II) и кадмијум(II) комплекси типа ML_2Cl_2, где је M метал, а L Шифова база *N*-(2-тиенилметилен)метанамин (TNAM) добијен кондензацијом 2-тиофенкарбоксалдехида и метиламина, и окарактерисани елементалном анализом као и магнетним и спектроскопским мерењима. Елементалне анализе указују на стехиоментрију M:L = 1:2. Подаци за магнетну сусцептибилност, повезани са електронским, ESR и Mössbauer-овим спектрима, указују на извијену октаедарску структуру Fe(II), Co(II) и Ni(II) комплекса и квадратно-планарну за Cu(II), односно тетраедарску геометрију за Zn(II) и Cd(II) комплексе. Инфрацрвени и NMR спектри комплекса одговарају координацији централног металног атома преко атома азота и сумпора. Мерења проводљивости указују на то да су комплекси неелектролити, осим Cu(II), Zn(II) и Cd(II) комплекса који су 1:2 електролити. Испитивана је биолошка активност Шифове базе и њених металних хелатних комплекса према микроорганизмима *Escherichia coli, Staphylococcus aureus* и *Pseudomonas aeruginosa*, и нађено је да су комплекси активнији од некомплексиране Шифове базе.

(Примљено 2. априла, ревидирано 22. новембра 2007)

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