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INVESTIGATIONS OF Co(II), Ni(II) AND Cu(II) (2,2′:6′,2"-TERPYRIDINE) COMPLEXES WITH SULFUR DONOR LIGANDS

A. M. Hammam, S. A. Ibrahim, M. A. El-Gahami and D. Fouad*

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

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Abstract

The ‘complexes as metal’ strategy has been used to prepare new mixed ligand complexes containing Co(II), Ni(II) and Cu(II) terpyridine (terpy) with dithiooxamide (dto) and thiosemicarbazide (tsc). Characterization of the complexes has been accomplished by elemental analysis, molar conductance, thermal analysis, as well as electronic and IR spectral measurements. It is deduced that the coordination mode of the terpyridine is changed from tridentate in the binary complex to bidentate in the ternary one where the uncoordinated pyridine exists in the protonated form. The dto and tsc act as neutral bidentate ligands coordinating through either sulfur or sulfur and nitrogen atoms respectively, forming chelate ring systems.

Keywords: spectroscopic investigations, sulfur donor ligands, 2,2′:6′,2"-terpyridine, thermal investigations

Introduction

Terpy is remarkably important form both the analytical and structural points of view [1, 2], the literature reveals very scarce data concerning ternary metal complexes with terpyridine and sulfur containing ligands [3–5]. On the other hand, metal complexes of thio-compounds were found to be important as antitumor [6], antimicrobial [7], and semiconducting compounds [8]. Accordingly, the work of the present paper is devoted to the synthesis and characterization of some new mixed ligand complexes involving divalent transition metal ions Co(II), Ni(II) and Cu(II); 2,2′:6′,2"-terpyridine as a primary ligand and the biologically active mono- and disulfur ligands (thiosemicarbazide and dithiooxamide) as secondary ones.

Experimental

All chemicals used metal salts ($CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$), 2,2′:6′,2"-terpyridine, thiosemicarbazide, dithiooxamide and the organic solvent methanol were

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* Author for correspondence: E-mail: elgahami@yahooo.com

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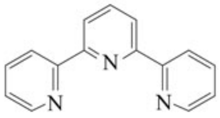
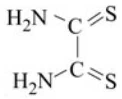
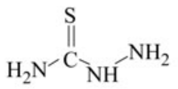
Analar grade (Fluka and Sigma chemicals), are used without further purification. The ligands used in the present study have the following structures:



I
2, 2':6', 1''-terpyridine (terpy)



II
dithiooxamide (dto)



III
thiosemicarbazide (tsc)

Preparation of the binary metal–terpy chelates

A methanolic solution (25 mL) containing 1.0 mmol of the metal salt was added slowly to an equimolar methanolic solution (25 mL) of the terpy, while stirring. The stirring was continued for about half an hour and then left at room temperature for 12–24 h. The solvent (methanol) was permitted to evaporate slowly at room temperature. For nickel complex, the solid was obtained after keeping the concentrated solution cold, in a fridge, for about 12 h.

Synthesis of the mixed ligand complexes

A hot methanolic solution (25 mL) of the previously prepared binary complexes (1.0 mmol) was mixed to a hot methanolic (25 mL) containing slightly more than 2.0 mmol of the secondary ligand dto or tsc. The mixture was boiled while stirring for ~10 min and then left to cool at room temperature whereby microcrystalline solid complexes were separated. In both cases the solid obtained was filtered, washed with methanol and dried in vacuo over P_4O_{10}.

Physical measurements

IR spectra were recorded on a Pye Unicam SP–1100 spectrophotometer as KBr discs. Electronic spectra were run in a Shimadzu UV 200S spectrophotometer, using 1 cm matched silica cells. Conductivity measurements were carried out using an LF Digi 55 conductivity bridge (10^{-3} M methanolic solutions were used). Thermogravimetry of the different complexes was carried out using a DuPont 2000 thermal analyzer, at heating rate of 10°C min^{-1} in a nitrogen atmosphere.

Results and discussion

Elemental analysis of the binary Co(II), Ni(II) and Cu(II) complexes with terpy and their mixed ligand complexes containing dto and tsc along with their colour, decomposition temperature and molar conductivity values are assembled in Table 1. The analytical data are consistent with 1:1 metal ion to ligand binary chelates having the formulas $[Cu(terpy)Cl_2]$, $[Ni(terpy)Cl]Cl\cdot4.5H_2O$ and $[Co(terpy)ClH_2O]Cl\cdot H_2O$, these formulations are in agreement with the reported binary complexes [9–11].

Table 1 Analytical and physical data for the binary and mixed ligand complexes

No.	Complex	Decomp. temp./°C	Color	Elemental analysis/% found (calculated)					Λ_m/ Ω^{-1} cm^2 mol^{-1}
				C	H	N	S	Cl	
1	[Co(terpy)ClH$_2$O]Cl·H$_2$O	>360	green	45.81 (45.23)	2.97 (2.80)	11.19 (10.52)	– –	19.10 (18.60)	85.3
2	[Co(terpy)(dto)$_2$]Cl$_2$·4H$_2$O	360	dark green	33.68 (33.84)	3.66 (4.03)	14.65 (14.54)	18.28 (18.98)	10.84 (10.54)	162.0
3	[Co(terpy)(tsc)$_2$]Cl$_2$·2.5H$_2$O	195	dark green	35.07 (34.67)	5.01 (4.42)	20.90 (21.40)	11.00 (10.80)	12.40 (12.06)	164.0
4	[Ni(terpy)Cl]Cl·4.5H$_2$O	>360	yellow	40.11 (40.70)	4.39 (4.56)	9.38 (9.50)	– –	15.26 (15.99)	113.8
5	[Ni(terpy)(dto)$_2$]Cl$_2$·2H$_2$O	>360	brown	34.73 (35.60)	3.52 (3.60)	15.67 (15.36)	19.45 (19.50)	14.13 (13.70)	175.7
6	[Cu(terpy)Cl$_2$]	>360	green	48.96 (48.93)	2.84 (2.99)	11.41 (11.42)	– –	17.56 (17.30)	53.3
7	[Cu(terpy)(tsc)Cl]Cl·CH$_3$OH	>360	dark green	41.98 (41.88)	3.38 (3.51)	18.75 (18.36)	7.78 (6.97)	14.88 (15.47)	110.0
8	[Cu(terpy)(dto)Cl]Cl·3H$_2$O	>360	dark green	37.56 (37.67)	3.81 (3.53)	12.65 (12.92)	12.20 (11.80)	12.99 (13.10)	103.3

Examination of the microanalytical data of the different ternary complexes revealed the following formulas [Cu(terpy)LCl]Cl·$X$$H_2O$, [M(terpy)(L)$_2$]$Cl_2$·$X$$H_2O$ where M=Co(II) or Ni(II), L=dto or tsc and X=0–4.

In the Cu (II) mixed ligand complexes, only one molecule of the secondary ligand is coordinated together with a chloride ion where the molar conductance values are in the range of 1:1 electrolytes [12]. However the electronic spectra of Cu(II) ternary complexes indicate that they are five coordinates, the terpy molecule should be then bidentate. On the other hand, for Co(II) and Ni(II) mixed ligand complexes, two molecules of the secondary ligand are coordinated as the analytical data reveal. Since the coordination number of these metal ions does not, preferably, exceed six, the terpy molecule should be bidentate too. This suggests a change in the coordination mode of terpy from tridentate in the binary chelates to bidentate in the mixed-ligand complexes studied.

Molar conductivity values of $\sim10^3$ M methonalic solutions of complexes **1, 4, 7** and **8** are in the range 85.3–110 Ohm^{-1} cm^2 mol^{-1}. This indicates a 1:1 electrolyte nature. The complexes **2**, **3** and **5** have molar conductance values in the range of 1: 2 electrolytes [12] (Table 1). On the other hand, complex **6** is non-electrolyte indicating that both the two chlorine atoms are involved in coordination to the Cu(II) ion suggesting five coordinate formulation for the complex.

Infrared spectra

IR bands, which provide structural evidence for the coordination of the ligands to the metal ions, are reported in Table 2. The bands observed in the range 1620–1590 cm^{-1} in the IR spectra of binary chelates are assigned to the stretching vibration of the νC=N and νC=C of the pyridine ring [13]. The increase in the number of IR bands on going from a binary terpyridine complex to ternary one suggests non-equivalence of the three pyridine rings in the ternary complex. This is due to the change of the coordination mode of the terpyridine from tridentate in the binary chelates to bidentate in the corresponding ternary ones [14–16].

Table 2 Tentative assignment of the important infrared bands of M(II)–terpy and M(II)–terpy–sulfur containing complexes

Complex	Frequency/cm^{-1}		
	υ C=N+υ C=C	υ C=S	Ring deformation
[Co(terpy)ClH_2O]Cl·H_2O	1585, 1560	–	640
[Co(terpy)(tsc)$_2$]Cl_2·2.5H_2O	1680, 1645, 1620, 1600, 1560	830	640, 660
[Co(terpy)(dto$_2$)]Cl_2·4H_2O	1665, 1580, 1500	825	635, 690
[Ni(terpy)Cl]Cl·4.5H_2O	1620, 1585, 1560	–	640
[Ni(terpy)(dto)$_2$]Cl_2·2H_2O	1625, 1580, 1560	815	640, 665
[Cu(terpy)Cl_2]	1585, 1560, 1435	–	640
[Cu(terpy)(tsc)Cl]Cl·CH_3OH	1585, 1560, 1485, 1460, 1440	825	640–660
[Cu(terpy)(dto)Cl]Cl·3H_2O	1585, 1520, 1485, 1440	825	645–665

The bands assigned to the pyridine ring vibrations are shifted to lower frequencies, which is a good indication of the coordination of the heterocyclic nitrogen atoms.

The IR spectra of the mixed ligand complexes show a shift to a higher frequency for δNCS appearing in the range 1275–1290 cm^{-1}. Such shift strongly suggests that the donor atoms in these mixed ligand complexes have to be the sulfur atoms [17]. On the other hand, the ligands dto and tsc display a strong band at 835 and 760 cm^{-1} respectively. This band is assignable to νC=S [18] and again indicates that these two ligands exist in the ketothione form (structures II and III). This band suffers a significant lowering in its frequency upon coordination of the ligand to the metal ions. This is in confirmation to the conclusion that complexes are formed through coordination of the sulfur atoms of the secondary ligands [17, 19].

The bands observed at 3280 and 1575 cm^{-1} in the IR spectrum at the dto ligand are due to νNH_2 and δNH_2 respectively [18]. These bands were found to locate in the IR spectra of the different mixed ligand complexes, at almost the same frequencies as in the spectra of the free dto ligand. This indicates that the NH_2 group does not participate in complexes formation. In case of the free tsc ligand, the band observed at 3200 cm^{-1} due to νNH_2 is found at higher frequencies in the spectra of the corresponding mixed ligand complexes. This indicates coordination of the NH_2 group of tsc to the metal ions [20].

The spectrum of the aquo complexes showed in addition to the O–H stretching vibration at 3500–3300 cm^{-1} a broad band of moderate intensity at ~640 cm^{-1} which is usually assigned to wagging or rocking modes of coordinated water.

Electronic spectra

The electronic spectra of methanolic solutions of the Co(II), Ni(II) and Cu(II) complexes were recorded in the wavelength range 300–800 nm. υ_{max} and ε_{max} values of the different absorption bands are recorded in Table 3. The first band that appeared with υ_{max} in the range 29.7–48.4 kK, are attributable to intraligand electronic transition [21] (mainly π–π^* and n–π^* transitions) [22]. The bands having υ_{max} in the range 24.80–28.0 kK are attributable to an L$\rightarrow$MCT transition.

The third set of bands was found to have υ_{max} at the 14.20 kK in the spectra of both binary and ternary Cu(II) complexes. This band corresponds to a distorted trigonal bipyramidal stereochemistry of the Cu(II) complexes [23]. The results of UV, elemental analysis and conductivity measurements again reflect the ambidentate behavior of terpy molecule and confirm the decoordination of one pyridine ring during the formation of the mixed ligand complexes.

Binary Ni(II) chelate has a symmetric band at 16.82 kK assignable to the transition $^3T_1\rightarrow{}^3T_1(p)$ that is indicative of a tetrahedral sterochemical configuration of the complexes [24, 25]. The shift of the band to lower υ_{max} in the spectra of the mixed ligand complex relative to the binary chelate clearly indicates a change in the stereochemical configuration around the Ni(II) ion. Therefore, the band observed at 12.98 kK in the mixed ligand Ni(II)–dto complex can be assigned to the $^3A_{2g}\rightarrow{}^3A_{1g}$ transition of distorted octahedral geometry.

Table 3 Electronic spectral data of binary and ternary complexes in methanolic solutions

Complexes	$\overline{\nu}_{Max}$/kK (ε_{max}/L mol^{-1} cm^2)
$[Co(terpy)ClH_2O]Cl\cdot H_2O$	20.28 (243); 30.35 (33 600); 31.53 (33 000) 25.68 (37 000); 48.44 (57 000)
$[Co(terpy)(dto)_2]Cl_2\cdot 4H_2O$	17.70 (250); 31.95 (30 000); 35.46 (30 000) 47.62 (51 400)
$[Co(terpy)(tsc)_2]Cl_2\cdot 2.5H_2O$	18.18 (247); 19.60 (347); 31.39 (13 240); 35.50 (15 150); 36.56 (14 750); 46.50 (27 200)
$[Cu(terpy)Cl_2]$	14.20 (103); 29.49 (1 2630); 30.67 (13 120); 34.96 (11 870); 38.75 (17 100)
$[Cu(terpy)(tsc)Cl]Cl\cdot CH_3OH$	14.23 (110); 29.63 (9 750); 30.72 (10 910); 35.10 (10 000); 37.80 (10 800)
$[Cu(terpy)(dto)Cl]Cl\cdot 3H_2O$	14.20 (160); 29.50 (25 800)); 30.72 (22 700)); 34.90 (22 400); 39.13 (25 600)
$[Ni(terpy)Cl]Cl\cdot 4.5H_2O$	16.83 (114); 24.87 (1 840); 29.76 (14 100); 31.25 (14 500)
$[Ni(terpy)(dto)_2]Cl_2\cdot 2H_2O$	12.98 (261); 23.800 (3 450); 29.80 (27 000); 30.93 (28 500); 36.76 (29 600)

The band appearing at 20.20 kK in the case of binary Co(II) complex was found previously for five coordinate Co(II) complex of terpy as an intense one [26]. In the case of ternary Co(II) complexes they show bands around 17.70–18.18 kK which are assigned to the transition $^4T_{1g}\rightarrow{}^4T_{1g}(p)$. This band is suggestive for a distorted octahedral geometry for Co(II) complexes [27]. The large molar absorptivity values of the *d–d* bands are in agreement with the low symmetry of the complexes.

Thermogravimetric analysis

The recorded TG curve of the ternary complex [Cu(terpy)(dto)Cl]Cl·3H_2O displays a gradual mass loss terminating at 192.78°C (Table 4). The magnitude of this mass loss through this temperature range amounts to 9.11% which is in accordance with the loss of three water molecules as indicated from the above suggested molecular formula of this ternary complex. The TG curve of [Cu(terpy)(tsc)Cl]Cl·CH_3OH shows a smooth mass loss over the temperature range 25–150°C followed by a fast one at 195.9°C. The first mass loss is corresponding to the removal of the physically absorbed CH_3OH molecule while the second fast step corresponds to the loss of a tsc molecule. This calculated total loss for these changes is 25.1% and the found value is 25.2%.

Table 4 TG data for binary and ternary complexes

Complex	Calc.	Found	Temp./°C	Change
[Co(terpy)ClH_2O]Cl·H_2O	95.5 90.98	96.13 91.10	46.2 188.04	Loss of one H_20 Loss of two H_2O
[Co(terpy)(tsc)$_2$]Cl_2·2.5H_2O	92.20 76.58	91.9 76.39	40.03 178.25	Loss of 2.5H_2O Loss of tsc molecule
[Co(terpy)(dto)$_2$]Cl_2·4H_2O	89.34 71.55	90.59 69.40	48.3 196.74	Loss of four H_2O Loss of dto molecule
[Ni(terpy)Cl]Cl·4.5H_2O	81.16	81.27	70.98	Loss of 4.5H_2O
[Ni(terpy)(dto)$_2$]Cl_2·2H_2O	94.36 75.56	93.65 75.02	87.76 195.93	Loss of 2H_2O Loss of dto molecule
[Cu(terpy)Cl_2]		No mass-loss up to decomposition		
[Cu(terpy)(dto)Cl]Cl·3H_2O	90.04	90.89	192.78	Loss of 3H_2O
[Cu(terpy)(tsc)Cl]Cl·CH_3OH	96.08 74.91	96.32 74.81	161.98 195.91	Loss of CH_3OH Loss of tsc molecule

The recorded TG curves of the ternary complex [Ni(terpy)(dto)$_2$]Cl_2·2H_2O display two successive mass loss steps (Fig. 1), the first extends between room temperature up to 87.76°C with a mass loss of 6.36%. This process corresponds to the loss of two water molecules. The second step extends between 87.76 to195.93°C with a mass loss of 24.98%. The observed mass loss of this step is due to the removal of a dto molecule.

The TG curve of [Co(terpy)(dto)$_2$]Cl_2·4H_2O displays two successive mass loss steps. The first at 48.30°C with a mass loss amounting to 9.41% in accordance with

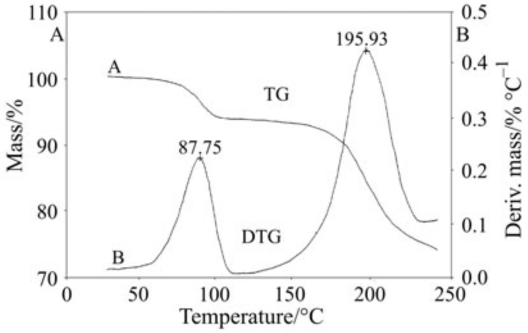


Fig. 1 TG and DTG curves of mixed Ni(II)-trpy-dto complex

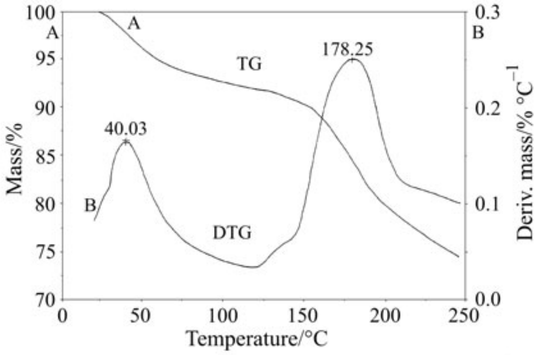
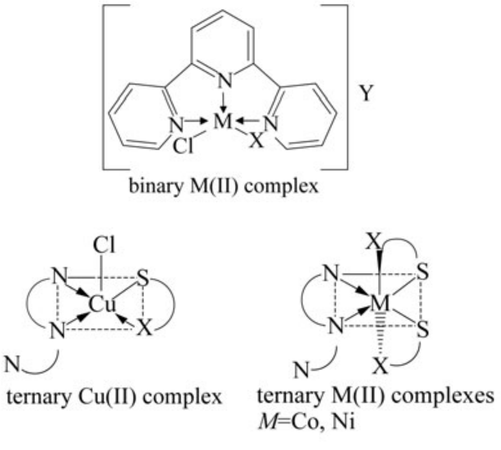


Fig. 2 TG and DTG curves of mixed Co(II)-trpy-tsc complex



X=S, dithiooxamide; *X*=N, thiosemicarbazide

the loss of four water molecules. These four water molecules exist as hydration water. The second one at 196.74°C with a mass loss 30.50% which is in accordance with the loss of a dto molecule.

The TG and DTG curves of $[Co(terpy)(tsc)_2]Cl_2{\cdot}2.5H_2O$ display two successive mass loss steps (Fig. 2). The first at 40.03°C with a mass loss of 8.10% corresponding to the loss of 2.5 hydration water molecules. The second one occurring at 178.25°C corresponds to a mass loss of 23.61%. According to the above molecular formula this observed mass loss is due to the removal of one tsc molecule (calculated mass loss 25.97%).

Based on the foregoing discussion the proposed structures of the complexes can be formulated as follows:
where M=Cu(II), X=Cl, Y=nothing; M=Co(II), X=H_2O, Y=Cl; M=Ni(II), X=nothing, Y=Cl

Conclusions

By examination of chemical analysis as well as infrared and electronic spectra and thermogravimetric analysis of the synthesized different ternary complexes, the following conclusions are achieved.

i) The terpyridyl ligand is changed from tridentate in the binary metal terpyridyl complexes to bidentate in the ternary complexes.

ii) The sulfur containing compounds used as secondary ligands are coordinated to the metal ions as neutral bidentate ligands. The bonding sites are the thioketone sulfur atoms in dto and both the thione sulfur and the amine nitrogen in tsc.

iii) The coordination geometry around the divalent metal ions used is changed from five-coordinate (square-pyramidal) or four-coordinate (tetrahedral) in the binary complexes to distorted octahedral in the mixed ligand complexes.

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