

Synthesis and Spectroscopic Characterization of Transition Metal Complexes of Maleionitriledithiolene and 1,10-Phenanthroline

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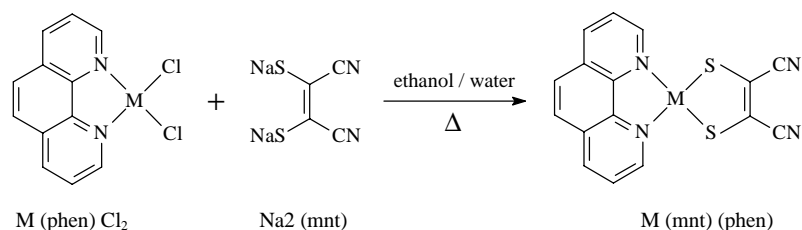
Abstract: The title complex $M(mnt)(phen)$, $M=Fe^{II}$, Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , was respectively synthesized by reaction of disodium maleionitriledithiolate ($Na_2(mnt)$) with corresponding metal complex $M(phen)Cl_2$. Charge transfer transitions in the absorption and emission spectra have been studied.

Keywords: Maleionitriledithiolene, 1, 10-phenanthroline, transition metal complex, synthesis.

The dithiolenes and diimines and their metal complexes are an important research field in the organic and coordination chemistry¹⁻⁵. Metal complexes of a dithiolene and a diimine have excellent electronic functions due to the intramolecular charge transfer from a ligand to other ligand (LL'CT)³⁻⁵. Our interest is in transition metal complexes of the mixture ligands dicyanodithiolene and some diimine such as substituted and unsubstituted phenanthrolines and bipyridines^{6,7}. Recently we studied synthesis, characterization, photo-physical and photochemical properties of the title complexes $M(mnt)(phen)$, $M=Fe^{II}$, Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} . In the present paper we report briefly their synthesis and spectroscopic characterization.

As the starting materials, the metal complex $M(phen)Cl_2$ of 1, 10-phenanthroline and two chlorine ions and the disodium *cis*-1, 2-dicyanoethylene-1,2-dithiolate, *i.e.*, disodium maleionitriledithiolate ($Na_2(mnt)$) was respectively synthesized and characterized according to the literature method^{8,9}. The complex $M(mnt)(phen)$ was respectively synthesized by reaction of $Na_2(mnt)$ with corresponding metal complex $M(phen)Cl_2$ in a mixed solvent of ethanol / water (3 : 1) as showed in **Scheme 1**.

Scheme 1



The yield, color and elemental analysis data of the M (mnt) (phen) have been given in **Table 1**. Where analyses of element C, H and N were performed on a Foss Heraeus CHN-O-rapid elemental analyzer. Metal content was determined by titration with EDTA. The M (mnt) (phen) is thermostable in the range $T < 574$ K. The stability is increased in the metal order $Fe < Cu < Co < Zn < Ni$. They are not solvable in water and are solvable in DMF, DMSO and pyridine. Molar conductivity in DMF is in the range $7.29-18.36 \times 10^{-3} \text{ S cm}^{-1} \text{ mol}^{-1}$ and is decreased in the metal order $Fe > Co > Cu > Ni > Zn$. The results showed that these metal complexes are electrically neutral.

Table 1. Color, yield (%) and elemental analysis (calcd. for M (C₂N₂S₂) (C₁₂H₈N₂)) of the MLL' (L = mnt²⁺, L' = phen)

Complex	Color	Yield	C %	H %	N %	M %
FeLL'	Amaranth	60.52	50.62 (51.08)	2.55 (2.13)	14.67 (14.90)	14.48 (14.89)
CoLL'	Bottle green	70.44	49.68 (50.23)	2.59 (2.11)	14.40 (14.78)	15.12 (15.55)
NiLL'	Wine	67.16	51.22 (50.69)	2.30 (2.13)	14.46 (14.79)	15.02 (15.46)
CuLL'	Yellow green	55.74	49.82 (49.98)	2.20 (2.10)	14.35 (14.57)	15.99 (16.51)
ZnLL'	Buff	58.83	50.27 (49.82)	2.55 (2.07)	14.36 (14.53)	16.48 (16.85)

Mass spectra of the M (mnt) (phen) were measured on a ZAB 3F HF-HF model mass spectrometer. The peaks of the M (mnt) (phen), M (phen)²⁺ and phen+1, *etc.*, have been found, for example, Co (mnt) (phen) in m/e 380, Co (phen) in 239 and phen+1 in 181. Infrared spectra were obtained from KBr pellets on a Nicolet 170 SX model FT IR spectrometer. **Table 2** gave character IR absorption frequencies of the complexes and material Na₂ (mnt) and Cu (phen) Cl₂. The data in **Table 1** and **Table 2** and the results of the mass spectra showed that the general chemical formula of the M (mnt) (phen) is consisted with M (C₂N₂S₂) (C₁₂H₈N₂).

Table 2. Character IR absorption bands (cm⁻¹) of the MLL' (L = mnt, L' = phen) at room temperature (in KBr)

Compd.	ν (C-H)	ν (C \equiv N)	ν (C=C), ν (C=N)	ν (C-C)	ν (C-C), ν (C-S)
FeLL'	3057w, 2995w	2195vs	1631w, 1491ms, 1425vs	1146s	990w, 898w
CoLL'	3045w, 2988w	2210vs	1624w, 1482vs, 1418vs	1147s	1001m, 874w
NiLL'	3056w, 2980w	2193vs	1624m, 1476s, 1425vs	1150s	990m, 877w
CuLL'	3059w, 2971w	2202vs	1627m, 1481s, 1426vs	1150s	981w, 908m
ZnLL'	3061w, 2999w	2195vs	1624m, 1483s, 1424vs	1152s	996m, 894w
CuL'Cl ₂	3070w, 2980w		1625mw, 1495mw, 1425vs	1152s	990vw, 862s
Na ₂ L		2194vs	1639s, 1427s	1155s	1002m, 861s

Electronic spectra of the complexes in DMF, DMSO, acetone, acetonitrile and benzonitrile have been studied in detail by using a Shimadzu UV-240 and U-3100 model spectrophotometer and by using a Shimadzu FR-5000 spectrofluorophotometer. It has been found that the emission intensity of the complexes in these solvents is increased in the metal order Cu~Ni < Fe < Co. As example, **Table 3** gave the absorption, emission (Em) and excitation (Ex) bands of them and some starting materials in DMF. And fluorescence spectra of Co (mnt) (phen) in DMF are illustrated in **Figure 1**. Quenching study of these complexes in DMF have been performed using the electronic donor N, N-dimethylaniline (DMA) and the electronic acceptor *o*-nitrobenzaldehyde (ONB). The ratios of no quenching emission intensity (I_0) to quenching emission intensity (I) have been calculated in various concentrations of the quenchers. The dependence of the ratios (I_0 / I) on concentrations of the quencher DMA and ONB are respectively illustrated in **Figure 2**. The results showed that effect of the quenchers on the emission intensity of Fe (mnt) (phen) is most. The quencher DMA effects not almost on the fluorescence of the Co (mnt) (phen) in DMF.

Table 3. Electronic spectra of the MLL', NiL'Cl₂ and Na₂L (L = mnt, L' = phen) in DMF at room temperature

Compd.	Absorption band λ_{\max} (log ϵ) (nm)	Fluorescence band (nm)	
		Em	Ex (intensity I)
FeLL'	512 (3.34) 477 (3.42) 382 (3.73), 268 (4.53)	478	370 (208) 390 (139)
CoLL'	648 (2.31) 434 (3.33) 268 (4.28)	472	415 (920)
NiLL'	569 (3.20) 480 (3.63) 358 (3.71) 271 (4.52)	510	365 (79) 370 (71) 473 (98)
CuLL'	484 (3.08) 365 (3.73) 286 (4.28) 272 (4.15)	514	435 (86) 445 (95) 475 (113)
ZnLL'	378 (4.05) 368 (4.03) 267 (4.45)		
NiL'Cl ₂	367 (2.45) 269 (4.32)		
Na ₂ L	392 (3.76) 266 (3.59)		

Figure 1. Fluorescence spectra of Co (mnt) (phen) in DMF at room temperature
--- Excitation band for emission wavelength 472 nm,
—Emission band under excitation light of wavelength 415 nm.

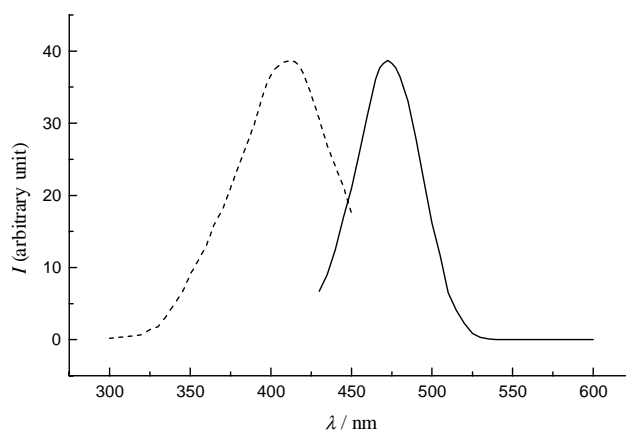
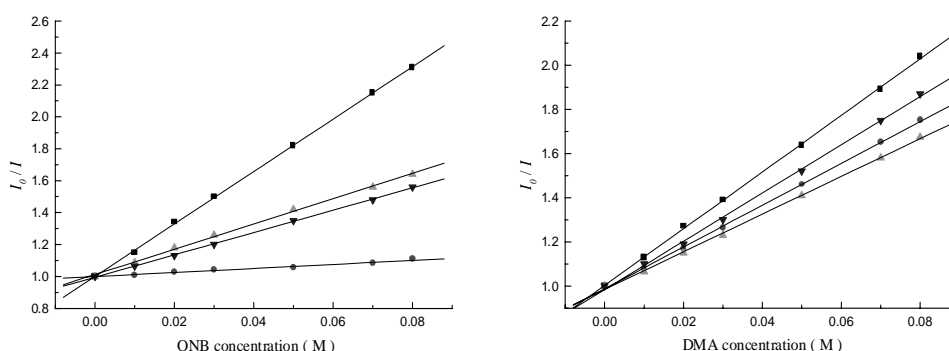


Figure 2. dependence of fluorescence intensity of M (mnt) (phen) in DMF on concentrations of the quencher (I_0 : no quenching emission intensity, I : quenching emission intensity)

■ Fe (mnt) (phen), Ex = 370 nm, Em = 478 nm; ● Co (mnt) (phen), Ex = 415 nm, Em = 472 nm;
▲ Ni (mnt) (phen), Ex = 473 nm, Em = 510 nm; ▼ Cu (mnt) (phen), Ex = 475 nm, Em = 514 nm;



To study an authenticity of the LL'CFs and their dependence on the metal ions for electronic spectra of the complexes M (mnt) (phen), the molecular orbital calculations have been performed by using ZINDO/1 method. The calculation results of geometry optimization show the dependence of both the highest occupied molecular orbital (HOMO) mostly composed of the ligand mnt^{2-} orbitals and the lowest unoccupied molecular orbital (LUMO) mostly composed of the ligand phen orbitals on the metal ion is decreased in the metal order $\text{Fe} > \text{Co} > \text{Ni} > \text{Cu} > \text{Zn}$. The first and second single electron transitions are this so-called LL'CFs. Theoretic energies of the Zn (mnt) (phen) are higher than those of other complexes. The calculation results lead to the conclusion that the first and second columns of absorption bands and the fluorescence bands of the M (mnt) (phen) in **Table 3** belong substantially to LL'CFs.

Acknowledgments

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