

COMPLEXES WITH TRIAZOLE DERIVATIVES

II. MONONUCLEAR COMPLEXES OF Co(II) WITH 1-[METHYLAMINO-N-(O-TOLYL)]-1H-BENZOTRIAZOLE

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abstract: Three new mononuclear complexes with formula $[\text{CoL}_2(\text{H}_2\text{O})_2](\text{CH}_3\text{COO})_2$ (**1**), $[\text{CoL}_2]\text{Cl}_2$ (**2**) and $[\text{CoLCl}_2]$ (**3**) (L: 1-[methylamino-N-(o-tolyl)]-1H-benzotriazole) were synthesized and characterized as mononuclear species on the basis of elemental chemical analysis, electronic and infrared spectra. The IR spectra indicated the presence of benzotriazole derivative as chelate coordinated through one heterocyclic nitrogen atom and the nitrogen from the secondary amine group. In complex (**1**) Co(II) adopt octahedral stereochemistry while for the other two complexes the stereochemistry is tetrahedral.

Introduction

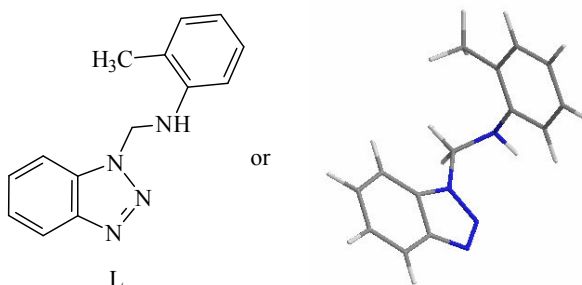
The chemistry of 1,2,3-triazole derivatives has received much attention due of their wide range of applications. They have been used as fungicided, herbicides, light stabilizers, fluorescent whiteners, optical brightening agents, corrosion inhibitors and photostabilizers for fibers, plastics or dyes [1, 2]. Some 1,2,3-triazole derivatives have seldom been found in nature as constituents of natural products. For a number of these compounds there have been found diverse uses in medicinal and pharmaceutical chemistry as cytostatic, virostatic, antiproliferative agents, synthetic intermediates for antibiotics, antihistaminic agents and polyheterocyclic compounds with neuroleptic activity [3-9].

There are few numbers of complexes with benzotriazole [10, 11] and 1,2,3- triazole derivatives [12]. We described elsewhere complexes of Ni(II) and Cu(II) with 1-[methylamino-N-(o-tolyl)]-1H-benzotriazole (L) [13].

The present note reports three new mononuclear complexes of Co(II) with 1-[methylamino-N-(o-tolyl)]-1H-benzotriazole (L).

The complexes were formulated as mononuclear species on the basis of elemental chemical analysis, electronic and infrared spectra.

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Experimental

All reagents used were p.a. grade.

The syntheses of the complexes

Compound $[\text{CoL}_2(\text{H}_2\text{O})_2](\text{CH}_3\text{COO})_2$ (**1**): 1 g (4 mmoles) $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 1.9 g (8 mmoles) 1-[methylamino-N-(o-tolyl)]-1H-benzotriazole were dissolved in 30 ml ethylic alcohol; the reaction mixture was refluxed for 30 minutes on air-bath. The sparingly soluble, pink colored product was filtered off and washed with ethanol. *Chemical analysis. Found:* Co, 9.23; C, 55.11; H, 5.82; N, 17.28 %, $\text{CoC}_{32}\text{H}_{38}\text{N}_8\text{O}_6$ requires: Co, 8.55; C, 55.73; H, 5.55; N, 16.25 %.

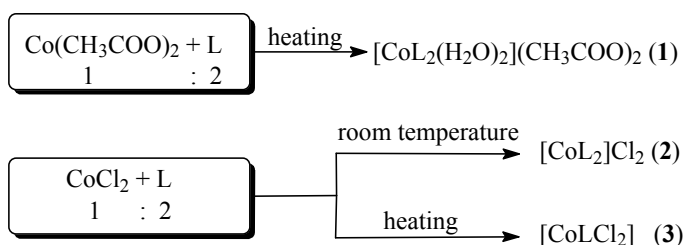
Compound $[\text{CoL}_2]\text{Cl}_2$ (**2**): By magnetic stirring at room temperature of 0.952 g (4 mmoles) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 1.9 g (8 mmoles) 1-[methylamino-N-(o-tolyl)]-1H-benzotriazole for 1 hour, a pink-grayish product, sparingly soluble in ethanol, is obtained. The compound was filtered off and washed several time with ethanol. *Chemical analysis. Found:* Co, 10.04; C, 55.32; Cl, 11.33; H, 4.45; N, 19.05 %, $\text{CoC}_{28}\text{Cl}_2\text{H}_{284}\text{N}_8$ requires: Co, 9.72; C, 55.46; Cl, 11.69; H, 4.65; N, 18.48 %.

Compound $[\text{CoLCl}_2]$ (**3**): Working as above, heating, a green product sparingly soluble in ethanol, is obtained. The compound was filtered off and washed several time with ethanol. *Chemical analysis. Found:* Co, 16.34; C, 45.45; Cl, 19.62; H, 3.57; N, 15.77 %, $\text{CoC}_{14}\text{Cl}_2\text{H}_{14}\text{N}_4$ requires: Co, 16.00; C, 45.68; Cl, 19.26; H, 3.83; N, 15.22 %.

The elemental chemical analyses were performed by usual micromethods. *The diffuse reflectance spectra* were recorded in the 24-14 kK (380-1200 nm) range, on a VSU2-P Zeiss-Jena spectrophotometer, using MgO as standard. *The IR spectra* were recorded on a Specord M80 spectrophotometer in the 200-4000 cm^{-1} range using KBr pellets. *The heating curves* (TG, T, ADT and DTG) were recorded in a MOM (Budapest) derivatograph, type Paulik-Paulik-Erdely, in a static air atmosphere.

Results and Discussion

Starting from Co(II) salts and 1-[methylamino-N-(o-tolyl)]-1H-benzotriazole (L) three new complexes was obtained as it showed in the scheme (1).



Scheme 1

The infrared spectra, offer information about the ligand and the donor atoms nature (Table 1). The assignments of the most important absorption bands, according to the literature data [14, 15] permit us to make the following remarks:

- the mean bands of the triazole derivative, $\gamma(\text{CH})$ (746 cm^{-1}) $\delta(\text{CH})$ ($1135\text{--}1220 \text{ cm}^{-1}$), $\delta(\text{CH}_2)$ (1445 cm^{-1}), $\delta(\text{CH}_3)$ (1390 cm^{-1}), $\nu(\text{C}=\text{C})$ ($1530\text{--}1535 \text{ cm}^{-1}$), $\nu_s(\text{CH}_2)$ ($2926\text{--}2949 \text{ cm}^{-1}$) indicate the presence of this ligand in all complexes;
- the band assigned to the $\nu(\text{N}\text{--}\text{N})$ vibration mode is shifted to lower energy in the spectra of complexes; that fact is in accord to a coordination of at least one nitrogen atom at the metallic ion;
- the $\nu(\text{N}=\text{N})$ band from the complexes spectra is shifted to higher energy from the one corresponding to the free ligand due to the coordination of at least one of the nitrogen atom to the metallic ion;
- the $\nu(\text{NH})$ band from the complexes spectra is shifted to lower energy which suggests the coordination of this nitrogen atom to the metallic ion;
- the additional bands which appear around 1415 and 1560 cm^{-1} for the complexes (1) is a proof for the presence of uncoordinated acetate ion [16];
- the presence of water molecules in compound (1) could be responsible for the appearance of a large strong band in the $3400\text{--}3500 \text{ cm}^{-1}$ range, assigned to $\nu(\text{OH})$ stretching vibrations; in addition, in the spectra of all complexes appear a band assigned to the coordinated water molecules ($\rho_w(\text{H}_2\text{O})$);
- in the $435\text{--}440 \text{ cm}^{-1}$ range, in all the complexes spectra it appears an absorption band assigned to the stretching vibration $\nu(\text{M}\text{--}\text{N}_{\text{alif}})$.

Thus, the infrared spectra suggest the chelate coordination of the triazole derivative through one heterocyclic nitrogen atom and the nitrogen from the secondary amine group; the complex (1) contains also water molecules coordinated while the acetate anion is uncoordinated.

The thermal degradation of the compound (1) occurs in two steps. The first step corresponds, in the TG curve, to the lost of the water molecules. The process occurs in the interval $150\text{--}190^\circ\text{C}$, with a maximum (endothermic effect in the DTG curve) at 170°C , which indicates that the water molecules are coordinated. This observation supports the conclusion of the spectral investigations. A second step, occurring between $420\text{--}750^\circ\text{C}$, is a non-single, exothermic one and corresponds, according to the DTA and DTG curves, to minimum two processes. The final residue of the thermal decomposition is Co_3O_4 .

Table 1. IR spectra (cm⁻¹)

L	(1)	(2)	(3)	Assignments
–	437 w	437 w	437 w	v(M–N _{ait})
–	617 m	–	–	ρ _w (H ₂ O)
750 vs	750 m	750 vs	750 vs	γ(CH)
980 m	990 w	995 w	996 w	v(N–N)
1154 s	1134 w	1134 m	1135 w	δ(CH)
1229 m	1220 w	1200 m	1191 w	
–	1414 s	–	–	v _s (COO)
1435 s	1438 s	1445 m	1445 s	δ(CH ₂)
1525 vs	1535 s, sh	1534 m	1530 m	v(C=C)
–	1562 vs	–	–	v _{as} (COO)
1605 s	1646 m	1647 s	1616 s 1661 s	v(N=N)
2949 m	2928 m	2932 m	2926 m	v _{as} (CH ₂)
3394 s	3427 s	3377 vs	3425 s	v(NH)
–	3480 m, sh	–	–	v(OH)

The diffuse reflectance spectra were assigned, in order to obtain information about the coordination number and the complexes stereochemistry (Table 2) [17].

Table 2. Electronic spectra

Compound	Absorption maxima [cm ⁻¹]	Assignments
[CoL ₂ (H ₂ O) ₂](CH ₃ COO) ₂ (1)	{ 20408 17065 13890 8764	⁴ T ₁ → ⁴ T ₁ (P) ⁴ T ₁ → ⁴ A ₂ ⁴ T ₁ → ⁴ T ₂
[CoL ₂]Cl ₂ (2)	{ 18832 15823 8511	⁴ A ₂ → ⁴ T ₁ (P) ⁴ A ₂ → ⁴ T ₁ (F)
[CoLCl ₂] (3)	{ 24570 15823 11364 8780	CT ⁴ A ₂ → ⁴ T ₁ (P) ⁴ A ₂ → ⁴ T ₁ (F)

The spectrum of the complex (1) is consistent with an octahedral distorted environment of the Co(II) ion, being assigned the three spin-allowed transitions (Fig. 1).

For the complexes (2) and (3) the electronic spectra indicate a tetrahedral environment (Figs. 2 and 3) for the metallic ion.

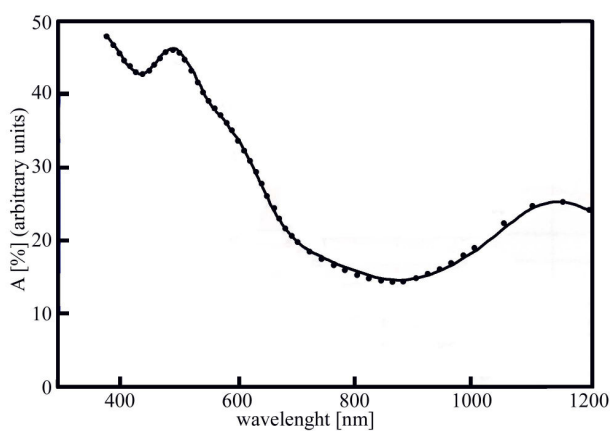


Fig. 1. The electronic spectrum of $[\text{CoL}_2(\text{H}_2\text{O})_2](\text{CH}_3\text{COO})_2$

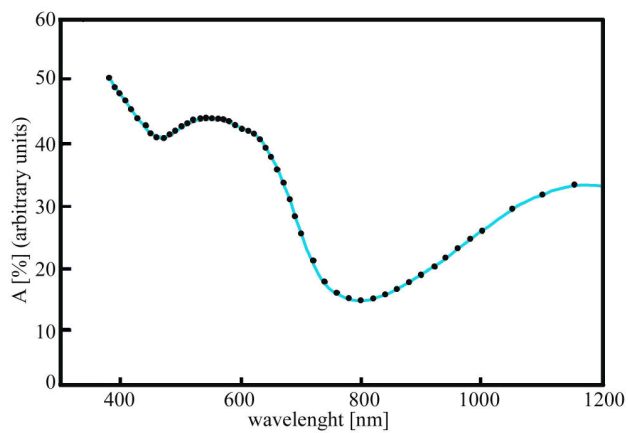


Fig. 2. The electronic spectrum of $[\text{CoL}_2]\text{Cl}_2$

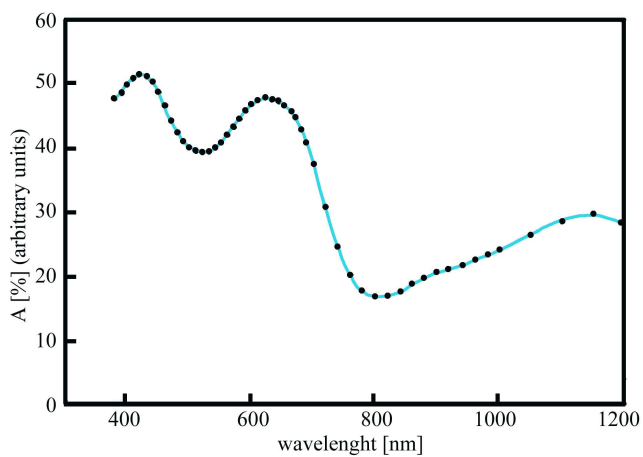


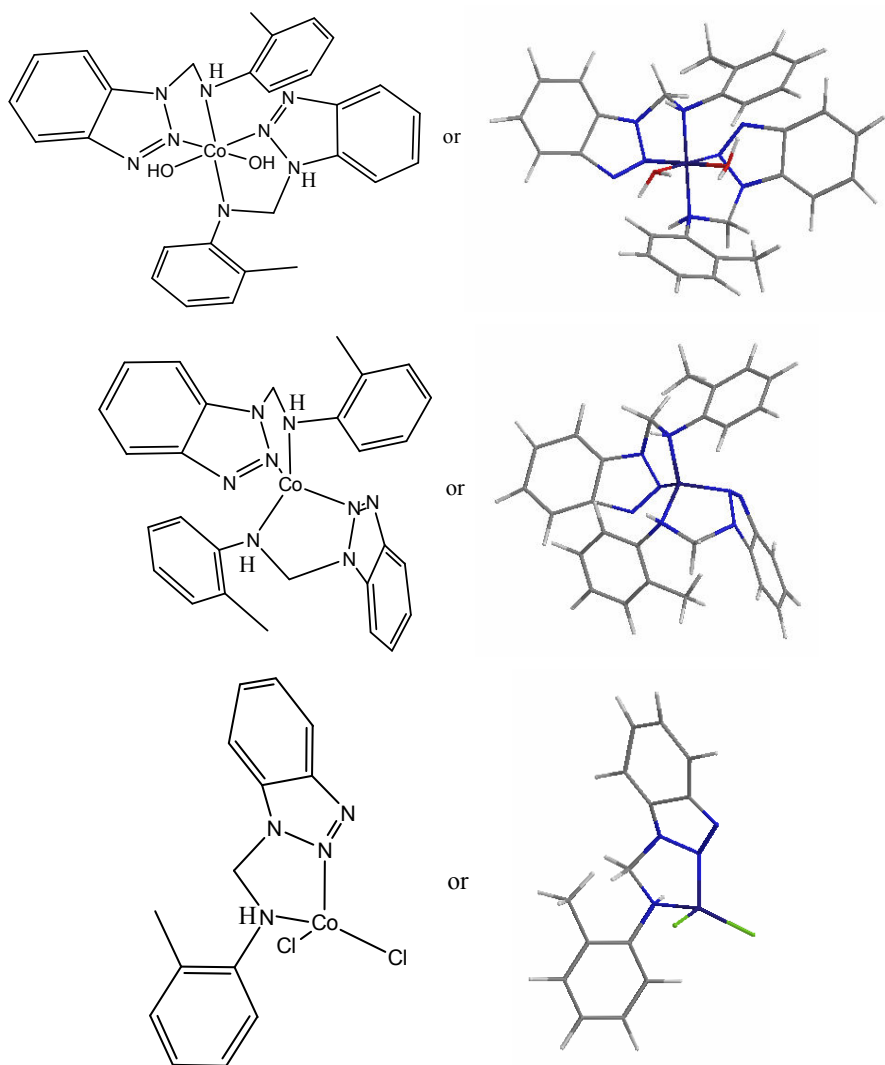
Fig. 3. The electronic spectrum of $[\text{CoLCl}_2]$

Conclusions

Three new Co(II) complexes of 1-[methylamino-N-(o-tolyl)]-1H-benzotriazole have been synthesized and characterized on the basis of elemental chemical analysis, electronic and infrared spectra.

According to the IR spectra, all the complexes contain the triazole derivative as chelate ligand. The electronic spectra agree with an octahedral stereochemistry for complex (1) and tetrahedral one for the complexes (2) and (3).

By correlating all these experimental data, we propose the following molecular formula for the complexes:



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