

## METAL COMPLEXES WITH PYRAZOLE-DERIVED LIGANDS

### IV. Thermal decomposition of cobalt(II) complexes with 3(5)-amino-4-acetyl-5(3)-methylpyrazole

A. F. Petrović, S. R. Lukić, D. M. Petrović, E. Z. Ivegeš<sup>1</sup> and V. M. Leovac<sup>1</sup>

Institute of Physics, Faculty of Sciences, Trg D. Obradovića 4, 21000 Novi Sad

<sup>1</sup>Institute of Chemistry, Faculty of Sciences, Trg D. Obradovića 3, 21000 Novi Sad, Yugoslavia

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#### Abstract

The thermal decomposition of tetrahedral cobalt(II) complexes with 3(5)-amino-4-acetyl-5(3)-methylpyrazole (HL) of the general formula  $[\text{Co}(\text{HL})_2\text{X}_2]$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{NCO}, \text{NCS}$ ) and octahedral  $[\text{Co}(\text{HL})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$  and  $[\text{Co}(\text{HL})_2\{\text{N}(\text{CN})_2\}_2]$  complexes was investigated in air atmosphere in the interval from room temperature to 1000°C. Decomposition of the complexes occurred in several successive endothermic and exothermic processes, and the residue was in all cases CoO.

**Keywords:** complexes, cobalt(II), 3(5)-amino-4-acetyl-5(3)-methylpyrazole, thermal decomposition

#### Introduction

In our previous article [1] we have reported the synthesis and some physico-chemical characteristics (magnetic susceptibility, molar conductivity, IR, reflectance and absorption electronic spectra) of the tetrahedral Co(II) complexes with 3(5)-amino-4-acetyl-5(3)-methylpyrazole (HL) of the general formula  $[\text{Co}(\text{HL})_2\text{X}_2]$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{NCO}, \text{NCS}$ ) as well as the octahedral  $[\text{Co}(\text{HL})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$  and  $[\text{Co}(\text{HL})_2\{\text{N}(\text{CN})_2\}_2]$  complexes.

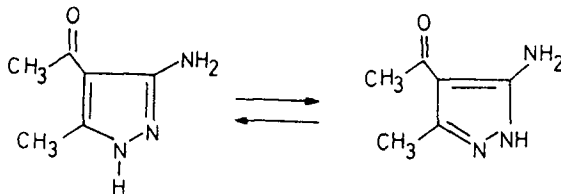


Fig. 1 Tautomeric forms of 3(5)-amino-4-acetyl-5(3)-methylpyrazole

The present article describe thermal decomposition of these complexes as well as of the ligand HL (Fig. 1).

## Experimental

Thermogravimetric measurements were carried out on a Paulik-Paulik-Erdey derivatograph (MOM, Hungary). Samples of 100 mg were heated up to 1000°C at a rate of 10°C min<sup>-1</sup>, in the air atmosphere in a Pt crucible, and using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as reference material.

Analysis of the final product was carried out with an automatic PW 1373 (Philips) powder diffractometer and by means of ASTM data.

## Results and discussion

Thermal decomposition of the ligand 3(5)-amino-4-acetyl-5(3)-methylpyrazole and its complexes takes place in several endo- and exothermic processes (Table 1). As the first endothermic effect for the ligand (Fig. 2) is not accompanied by a decrease in mass of the sample, it can be ascribed to its melting. The second endothermic effect of the ligand is accompanied by a decrease in mass too, and can be ascribed to elimination of NH<sub>3</sub>, what is confirmed by the appropriate qualitative reaction (litmus). It is interesting to notice that the process of melting is not observed with the complexes. Namely, with the halide-containing complexes, (Figs 3–5), the first endothermic effect is most probably related to elimination of HX (X=Cl, Br, I), whereby in the case of bromide and iodide complexes, only 50% of the HX eliminated. The endothermic effects accompanying the elimination of the rest of HX at higher temperatures are obscured by the exothermic effects due to elimination of the organic ligand. It should be noted that close temperature intervals of the endothermic effects accompanying elimination of these fragments have also been observed in decomposition of some other halogen-containing complexes [2, 3]. The NCS-complex behaves in similar way as bromide and iodide complexes (Fig. 6).

The next endothermic effect, registered with all tetrahedral complexes, including the NCO-complex (Fig. 7), (for which this is the first and only endothermic effect), is most probably due to elimination of the NH<sub>2</sub>-group. An indication for this is the nitrogen content (Found 14.6%, Calc. 18.6%) in the residue of the chloride complex (CoL<sub>2</sub><sup>\*</sup>) after its isothermal heating (420°C, 2 h). Namely, a qualitative test on the presence of chlorine in this residue gave a negative result, which confirms the supposition that the chlorine was completely eliminated at lower temperatures (ca. 400°C). This is in contrast to the literature report [4] that the complex Co(3,5-DMP)<sub>2</sub>Cl<sub>2</sub> (3,5-DMP=3,5-dimethylpyrazole) loses first the whole organic ligand, so that the residue (570°C) is CoCl<sub>2</sub>.

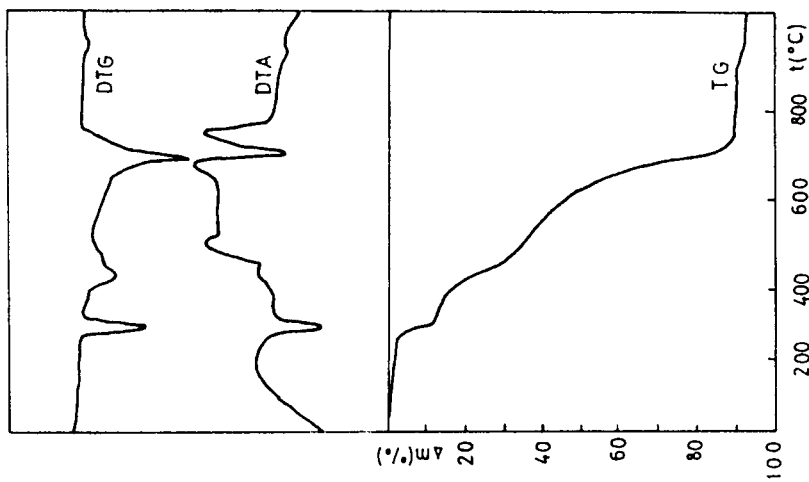


Fig. 3 TG, DTG and DTA curves of  $[\text{Co}(\text{HL})_2\text{Cl}_2]$

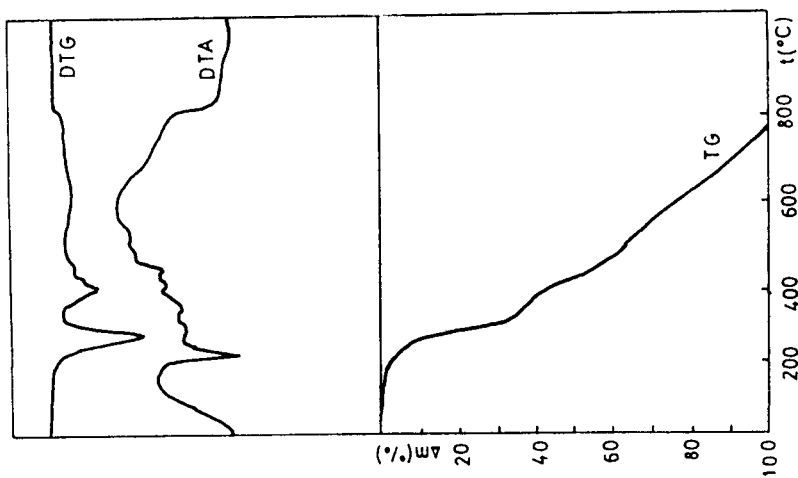
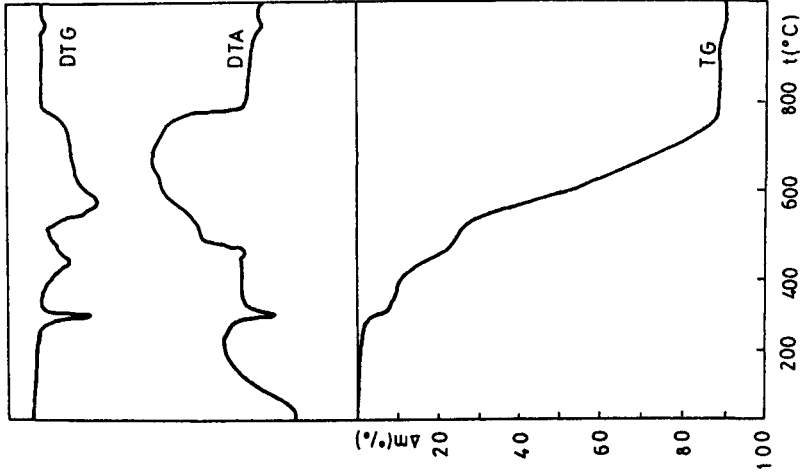
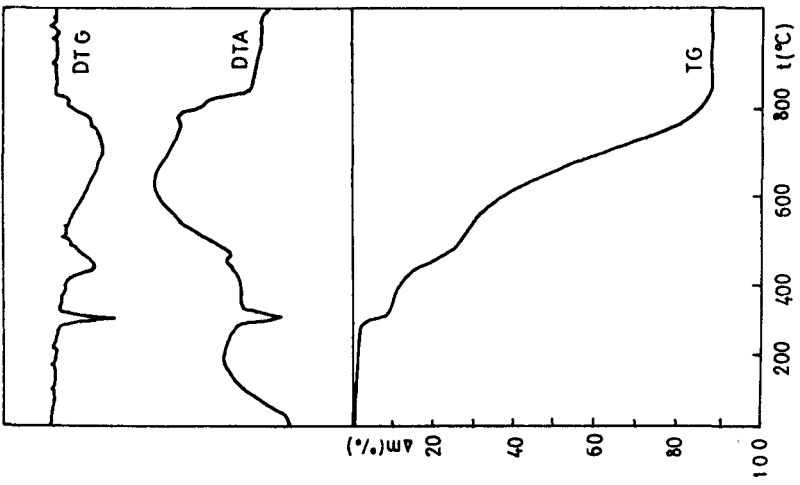


Fig. 2 TG, DTG and DTA curves of HL

Fig. 5 TG, DTG and DTA curves of  $[\text{Co}(\text{HL})_2\text{I}_2]$ Fig. 4 TG, DTG and DTA curves of  $[\text{Co}(\text{HL})_2\text{Br}_2]$

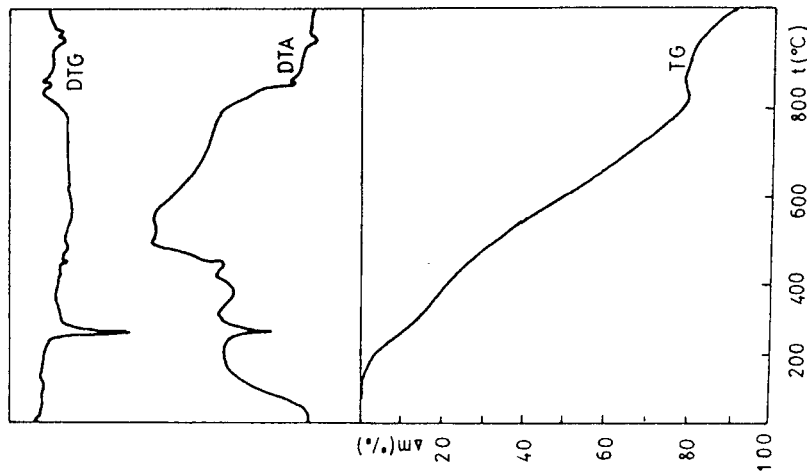


Fig. 7 TG, DTG and DTA curves of  $[\text{Co}(\text{HL})_2(\text{NCS})_2]$

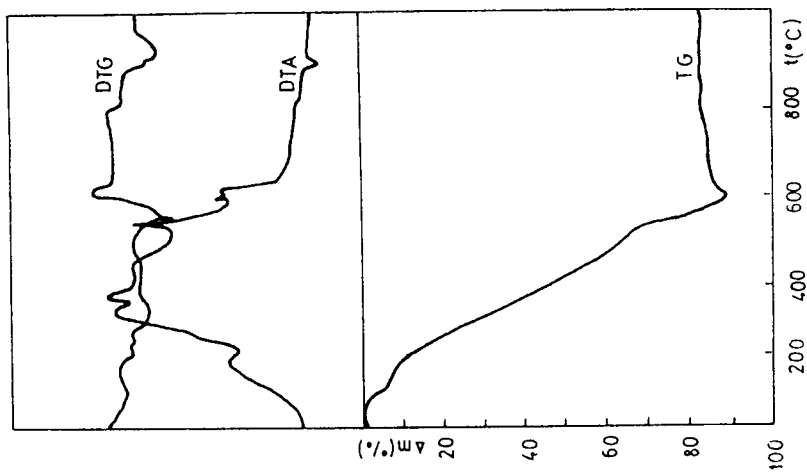


Fig. 6 TG, DTG and DTA curves of  $[\text{Co}(\text{HL})_2(\text{NCO})_2]$

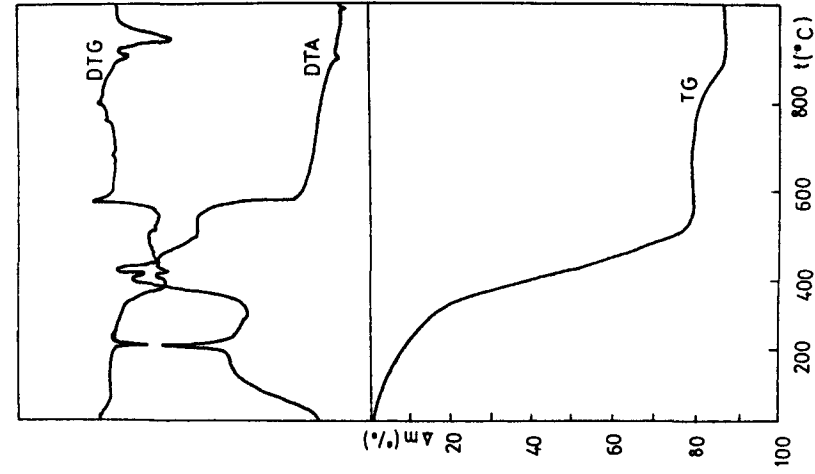


Fig. 9 TG, DTG and DTA curves of  $[\text{Co}(\text{HL})_2(\text{N}(\text{CN})_2)_2]$

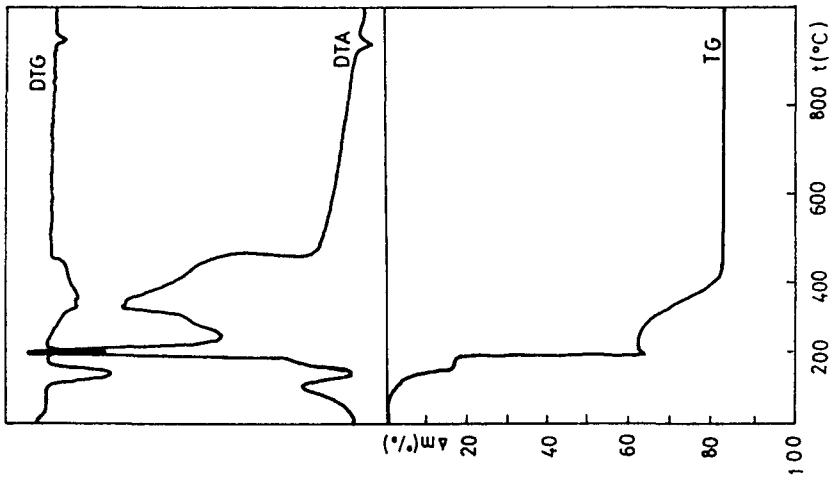


Fig. 8 TG, DTG and DTA curves of  $[\text{Co}(\text{HL})_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$

**Table 1** Thermal decomposition of the ligand and its Co(II) complexes

Effect	T/K	Mass loss		Fragment eliminated
		found/%	calc./%	
HL				
endo	503	–	–	melting
endo	503–623	36.0	36.6	3NH <sub>3</sub>
exo	623–1093	64.0	63.4	HL-residue
[Co(HL) <sub>2</sub> Cl <sub>2</sub> ]				
endo	553–683	19.0	17.9	2HCl
endo	683–718	8.0	8.3	2NH <sub>3</sub>
exo	718–1023	58.0	55.4	2L*
residue CoO	1023	15.0	18.4	
[Co(HL) <sub>2</sub> Br <sub>2</sub> ]				
endo	553–683	16.0	16.3	HBr
endo	683–743	9.0	7.0	2NH <sub>3</sub>
exo	743–1063	63.0	61.7	2L* + HBr
residue CoO	1063	12.0	15.0	
[Co(HL) <sub>2</sub> I <sub>2</sub> ]				
endo	538–693	20.0	21.6	HI
endo	693–753	5.0	5.8	2NH <sub>3</sub>
exo	753–1013	63.0	60.0	2L* + HI
residue CoO	1013	12.0	12.6	
[Co(HL) <sub>2</sub> (NCO) <sub>2</sub> ]				
endo	473	8.0	8.0	2NH <sub>3</sub>
exo	473–813	59.0	58.0	HL-residue
exo	813–1063	15.0	16.1	2OCN–O
residue CoO	1063	18.0	17.9	
[Co(HL) <sub>2</sub> (NCS) <sub>2</sub> ]				
endo	513	14.0	12.8	NCS
endo	513–673	7.0	7.5	2NH <sub>3</sub>
exo	673–1073	61.0	63.2	2L* + NCS
residue CoO	1073	18.0	16.5	
[Co(HL) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub>				
endo	403	13.0	13.5	4H <sub>2</sub> O
exo	503–593	48.0	49.2	2NL–O
endo	593–713	25.0	23.3	2NO <sub>3</sub>
residue CoO	713	14.0	14.0	

Table 1 Continued

Effect	T/K	Mass loss		Fragment eliminated
		found/%	calc./%	
		[Co(HL) <sub>2</sub> {N(CN) <sub>2</sub> }] <sub>2</sub>		
exo	503	5.0	5.1	2CO
exo	583–853	71.0	67.8	2HL–O + 2N <sub>2</sub>
endo	1193	8.0	11.0	(CN) <sub>2</sub>
residue CoO	1193	16.0	16.0	

*L\** = residue of pyrazole without 2NH<sub>3</sub> groups and oxygen

The first endothermic effect (130°C) with the octahedral aqua-complex is undoubtedly the elimination of the coordinated water (Fig. 8), whereas the subsequent exo- and endothermic effects correspond to elimination of the organic molecule and NO<sub>3</sub> group respectively. In contrast to the previous complexes, the first two endothermic effects observed for the dicyanamide complex are due to elimination of CO and pyrazole, whereas the subsequent endothermic process is the formation and elimination of dicyanogen (Fig. 9).

As can be seen from Table 1, the least stable compound is the aqua-complex (decomposition is completed at 440°C), and the most stable is dicyanamide complex, which is decomposed not before 920°C. The final decomposition product of all the complexes is CoO.

## References

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