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TRANSITION METAL COMPLEXES WITH HYDRAZIDES AND HYDRAZONES

III. Thermal decomposition of octahedral Co(II) complexes with 1-naphthylacetic acid hydrazide

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A study was made of the thermal decomposition of octahedral Co(II) complexes of the type $CoL_nX_2 \cdot mH_2O$, where $n = 2$ and 3, $m = 1$, 2 and 5 and X = Cl, Br, I, NCS, OAc and $½SO_4$, in both air and nitrogen atmospheres. It was established that the complexes are completely decomposed below 800° and CoO is formed as final product. The most probable decomposition mechanism was proposed. The tris(ligand) complexes were characterized by elemental analysis, and spectral and magnetic measurements, and all the data suggested the presence of a point group symmetry of type O_h.

The work presented here is a continuation of our studies on transition metal complexes with different hydrazides and hydrazones [1-4]. The syntheses, and spectroscopic and magnetic properties of octahedral Co(II) bis(ligand) complexes with 1-naphthylacetic acid hydrazide (L) of the general formula $[CoL_2X_2] \cdot nH_2O$ (X = Cl, NCS, OAc, $½SO_4$), and the tris(ligand) complex $[CoL_3]I_2 \cdot H_2O$, have already been described [1].

With the aim of supplementing the physico-chemical characterization of the bis(ligand) complexes, this article presents the results of their elemental analysis and thermal decomposition. In addition, the analogous physical and chemical characteristics are presented for the newly-synthesized complex $[CoL_3]Br_2 \cdot H_2O$.

Experimental

Thermogravimetric investigations were carried out with a derivatograph. Each sample was heated from room temperature to 1000° at a rate of 10 deg/min. The processes were carried out in both air and nitrogen atmospheres. Al_2O_3 was used as the reference.

Reflection spectra were recorded in the range 10000-45000 cm^{-1} at room temperature with an SPM-2 monochromator (VEB Zeiss, Jena) with an R-45/0 reflection cell. MgO served as "white" reference.

Magnetic susceptibilities were measured by Faraday's method at room temperature, with $Hg[Co(NCS)_4]$ as calibrant.

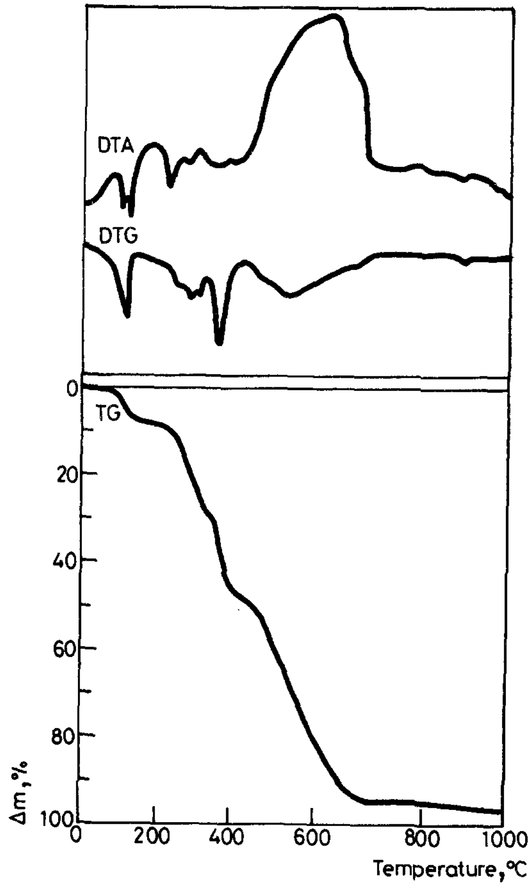

Fig. 1 TG, DTA and DTG curves of $[CoL_2Cl_2]\cdot 2H_2O$ complex

$[CoL_3]Br_2 \cdot H_2O$ was obtained by reaction with an ethanolic solution of the ligand in the molar ratio 1:3. Analysis: C 53.12 (found), 51.60 (calcd), H 4.69 (found), 4.57 (calcd), N 10.48 (found), 10.03 (calcd), H_2O 2 (found), 2.1 (calcd), %.

Results and discussion

Figures 1-7 show the diagrams for the thermal decomposition of the investigated complexes in air atmosphere, while Fig. 4b shows the corresponding curves for $[CoL_2SO_4] \cdot 5H_2O$, for the process of thermal decomposition taking place in nitrogen atmosphere. The thermal decomposition of the ligand has been described elsewhere [2].

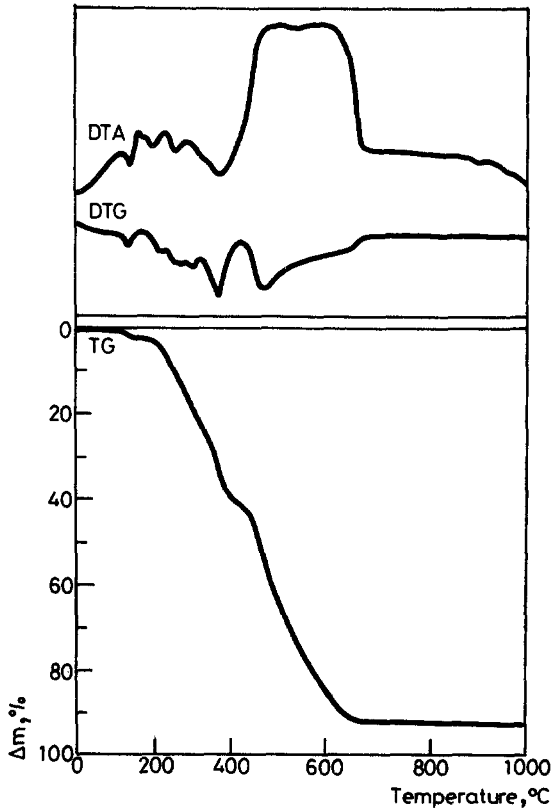

Fig. 2 TG, DTA and DTG curves of $[CoL_3]Br_2 \cdot H_2O$ complex

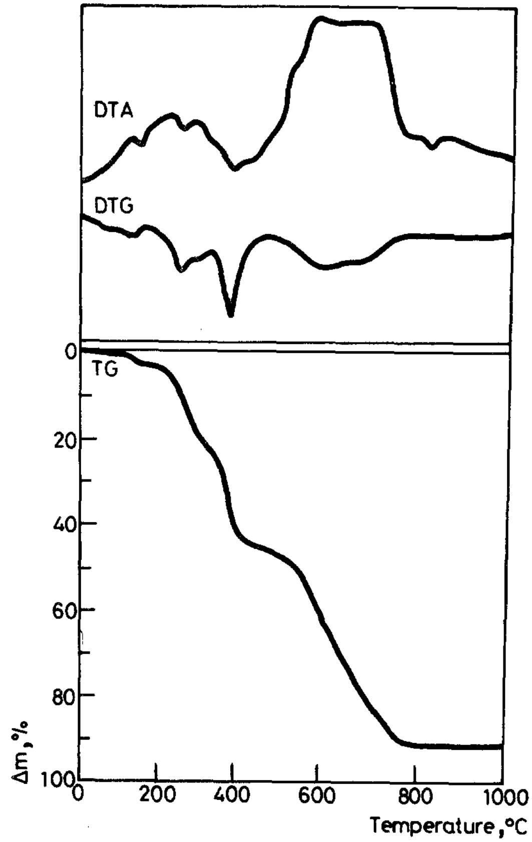

Fig. 3 TG, DTA and DTG curves of $[CoL_3]I_2 \cdot H_2O$ complex

In the case of the hydrated complexes (Table 1), the first endothermic peak corresponds to the elimination of the appropriate number of water molecules. It can be concluded that the dehydration processes of $(CoL_2Cl_2] \cdot 2H_2O$ and $[CoL_2SO_4] \cdot 5H_2O$ take place in two steps. The dehydration temperatures of the bis(ligand) complexes are lower than those of the tris(ligand) complexes, for which the involvement of the crystal (and not coordinated) water is beyond doubt. The octahedral configuration of the tris(ligand) complexes, which can be postulated on the basis of the positions of the maxima in their electronic spectra and the effective magnetic moments [1], is established via the N and O atoms of the bidentate ligand. Therefore, it can be concluded, that, apart from the two molecules of the bidentate ligand, 1-naphthyl-acetic acid hydrazide, the octahedral coordina-

Table 1 TG analysis octahedral Co(II) complexes with L

Effect	Fragment eliminated	$\lvert CoL_2Cl_2\rvert \cdot 2H_2O$ T, °C	 Δm_{exp}, %	 Δm_{calc}, %	$\lvert CoL_3\rvert Br_2 \cdot H_2O$ T, °C	 Δm_{exp}, %	 Δm_{calc}, %	$\lvert CoL_3\rvert I_2 \cdot H_2O$ T, °C	 Δm_{exp}, %	 Δm_{calc}, %
endo	H_2O	90	3.5	3.1	130	2	2.1	140	2	1.9
	H_2O	100	3.5	3.1						
endo	melting							210		
endo	HX*	240	13	12.8	270	19	19.1	270	27	27.5
exo	acetic acid hydrazide	240-380	26	25.8	270-410	26	26	270-480	22	22.5
exo	naphthalene ring	380-700	44	44.9	410-760	44	44.5	480-680	40	40.1
Residue	CoO		10	10.3		9	8.3		9	8

X* = Cl, Be, I

Table 1 TG analysis octahedral Co(II) complexes with L (continued)

Effect	Fragment eliminated	|$CoL_2(NCS)_2$| T, °C	Δm_{exp}, %	Δm_{calc}, %	|$CoL_2(OAc)_2$| T, °C	Δm_{exp}, %	Δm_{calc}, %	|CoL_2SO_4| $\cdot 5H_2O$ T, °C	Δm_{exp}, %	Δm_{calc}, %
endo	$5H_2O$							90 120	14	13.95
endo	CH_3COO				210	20.5	20.4			
endo	melting							260	-	-
endo	NCS									
exo	naphthalene ring	260	20	20.1	210-415	43	44	300-400	41	39.5
exo	acetic acid hydrazide + + SO_4	300-420	25	25.3	415-610	25.5	25.3	300-400	36	37.5
exo	naphthalene ring	420-800	42	42.1						
Residue	CoO		13	13		11	10.3		9	9.1

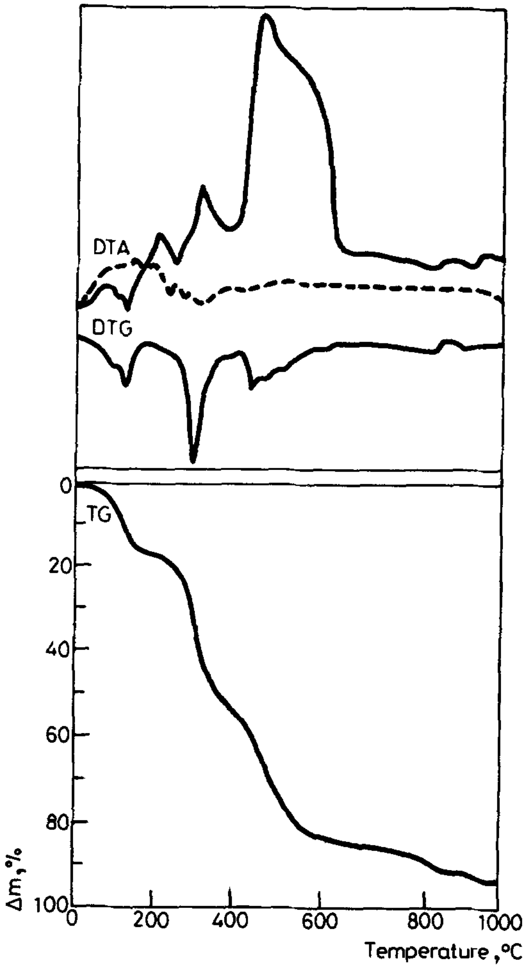

Fig. 4 TG, DTA and DTG curves of $[CoL_2SO_4]\cdot5H_2O$ complex (— air,- - - nitrogen)

tion in the bis(ligand) complexes also involves two chloride ions and the SO_4 group.

The positions of the maxima in the spectra of $[CoL_3]Br_2\cdot H_2O$ and $[CoL_3]I_2\cdot H_2O$, as well as the respective values of the effective magnetic moments of 5.22 and 5.21 BM (298 K), suggest the presence of an approximate point group symmetry O_h and an octahedral environment around the metal ion. As we have a d^7 system in this case, the transitions at 11.3, 17.2 and $20.4.10^3$ cm^{-1} for $[CoL_3]Br_2\cdot H_2O$, and at 11.5, 17.2 and $20.0.10^3$ cm^{-1} for

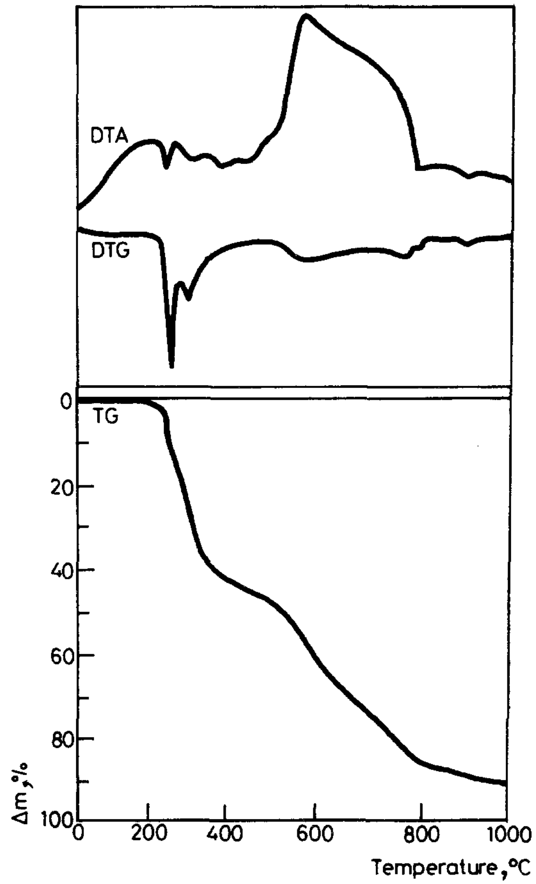

Fig. 5 TG, DTA and DTG curves of [$CoL_2(NCS)_2$]

[CoL_3]$I_2 \cdot H_2O$ (Fig. 7), can be identified as $^4T_{1g} \rightarrow {}^3E_g$, $^4T_{1g} \rightarrow {}^4A_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{1g}$ (P), respectively [5].

The process of sample melting was observed for the sulphate- and iodide-containing complexes, the corresponding endothermic peaks being observed at 210 and 260° (Figs 3 and 4).

In the cases of the halide, acetate and cyanate complexes, the next endothermic peak corresponds to the elimination of the halogen, acetate and cyanate group, which is in agreement with the literature data [6-8]. The decomposition of the sulphate complex most probably takes place in parallel with the decomposition of the acetic acid hydrazide part of the ligand.

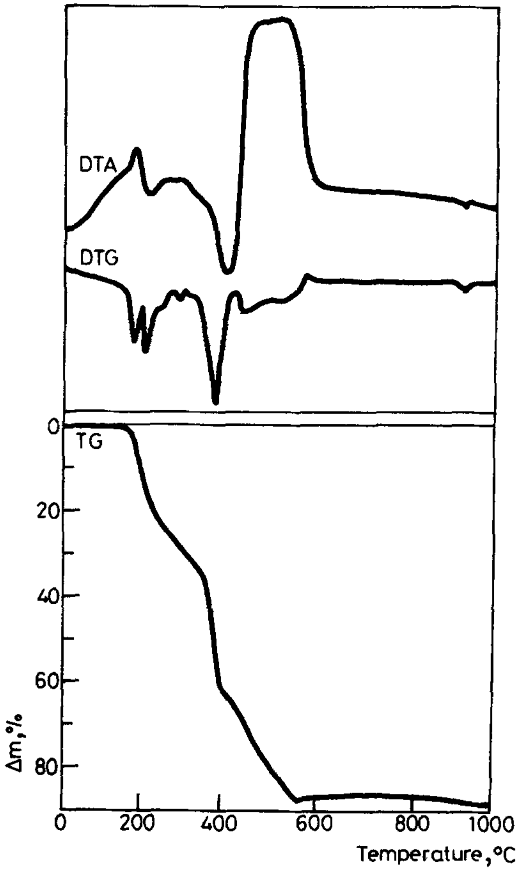

Fig. 6 TG, DTA and DTG curves of $[CoL_2(OAc)_2]$ complex

Taking into account the decomposition of the ligand in both air and nitrogen atmospheres [2], the broader peak which appears in the range 400-800° for all complexes corresponds to the decomposition of the naphthalene ring. The assumption is that the ligand itself is decomposed first in an endothermic process, and the ligand fragments are then oxidized by the atmospheric oxygen.

An X-ray analysis of the decomposition residue showed that CoO is formed as the final product of thermal decomposition of all the investigated complexes.

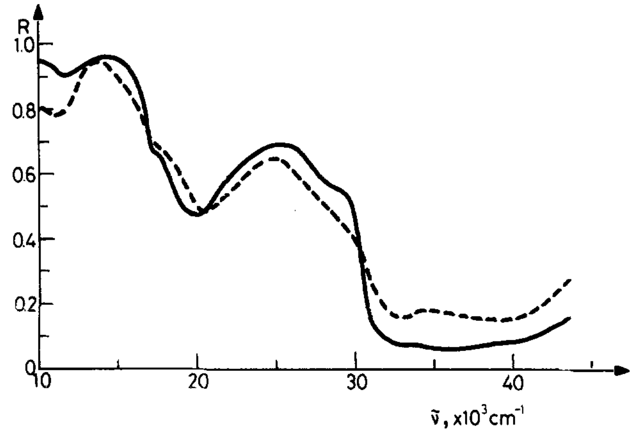

Fig. 7 Reflection spectra of $[CoL_3]I_2 \cdot H_2O$ (——) and $[CoL_3]Br_2 \cdot H_2O$ (- - -)

References

1 S. Yu. Chundak, V. M. Leovac, D. Z. Obadovic and D. M. Petrovic, Trans. Met. Chem., 11 (1986) 308.
2 V. M. Leovac, D. Z. Obadovic, A. f. Petrovic and S. Yu. Chundak, J. Thermal Anal., 34 (1988) 1263.
3 D. Z. Obadovic, D. M. Petrovic, V. M. Leovac and S. Caric, J. Thermal Anal., 36 (1990) 99.
4 D. Z. Obadovic, A. F. Petrovic, V. M. Leovac and S. Yu. Chundak, J. Phys. C, 2 (1990) 3611.
5 A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam 1968.
6 E. Jona, M. Jaminsky and M. Zenlicka, J. Thermal Anal., 30 (1985) 913.
7 G. Liptay, T. Wadsten and A. Borbély-Kuszman, J. Thermal Anal., 31 (1986) 845.
8 J. Zsakó, G. Liptay and Cs. Várhely, J. Thermal Anal., 31 (1986) 1027.

Zusammenfassung — Sowohl in Luft als auch in Stickstoffatmosphäre wurde die thermische Zersetzung von oktaedrischen Co(II)-Komplexen der allgemeinen Formel $CoL_nX_2 \cdot mH_2O$ ($n = 2$ und 3, $m = 1$, 2 und 5, X = Cl, Br, I, NCS, OAc und SO_4) untersucht. Es wurde festgestellt, daß sich die Komplexe unterhalb 800°C vollkommen zu CoO als Endprodukt zersetzen. Der wahrscheinlichste Zersetzungsmechanismus wurde unterbreitet. Die tris-Ligandenkomplexe wurden mittels Elementaranalyse sowie Spektral- und magnetischen Untersuchungen charakterisiert, alle Angaben deuten auf eine Punktsymmetriegruppe vom Typ O_h hin.