Synthesis, Crystal Structure, and Thermal Decomposition of Two Co(II) Complexes with NNN Pyrazolyl Type Ligand and Pseudo-Halogen[1]

S. Öz[a],*, **N. Yılmaz[b], C. Arıcı[c], I. Svoboda[d], M. A. Akay[b],** and **O. Atakol[b]**

[a] Ahi Evran University, Faculty of Science and Arts, Department of Chemistry, Kırşehir, 40100 Turkey
[b] Department Chemistry, University of Ankara, Tandoğan, Ankara, 06100 Turkey
[c] Department of Engineering Physics, University of Hacettepe, Beytepe, Ankara, 06800 Turkey
[d] Darmstadt Technical University, Material Science, Darmstadt, 63287 Germany
*e-mail: sevioz@hotmail.com
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Abstract—The Co(II) complexes **I** and **II** were prepared in nonaqueous solvents containing cyanate with pyrazolylpyridine ligands, namely, bis-2,6-(pyrazol-1-yl) pyridine (Pp) and bis-2,6-(3,5-dimethyl-pyrazol-1-yl) pyridine (Dmpp), respectively. These complexes were characterized with elemental analysis, IR spectroscopy, and X-ray diffraction techniques. X-ray diffraction study revealed that complex **I** was mononuclear and complex **II** was dinuclear and ionic. The ionic complex **II** has an octahedral cationic coordination sphere and a tetrahedral anionic coordination sphere. Thermogravimetry results showed that the thermal decomposition is starting with the carbon content of the pyrazolyl rings.

INTRODUCTION

Pyrazolylpyridines act like NNN type ligands and they are often noticed in the coordination chemistry [1—3]. They form complexes with almost every transition element ions except soft metal ions [3—10]. The prepared ligands are shown below:
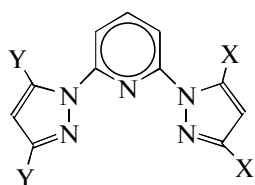
Pp: X = Y = H;
Dmpp: X = Y = CH$_3$.

In this study, Co(II) complexes were prepared in organic solvents containing OCN-groop by using bis-2,6-(3,5-dimethylpyrazol-1-yl) pyridine (Pp) and bis-2,6-(pyrazol-1-yl) pyridine (Dmpp) ligands. In a former study of ours, a cyanate containing complex was synthesized from Co^{2+} ion and bis-2,6-(3,5-di-methylpyrazol-1-yl) pyridine in a medium containing SCN, and its molecular structure was revealed [11]. The difference of this study is that the medium contains cyanate ion instead of thiocyanate. The crystals of both complexes were obtained and their molecular structures were determined by X-ray diffraction meth-ods. Also the thermal behaviour of the complexes were analysed by thermogravimetry.

Pyrazolylpyridines can form polynuclear complex-es depending on the nature of central ion and the an-ion content of the medium [12, 13]. At the beginning, the purpose of this study was to synthesize polynuclear complexes. However, it was revealed by the X-ray stud-ies that the complexes do not contain μ bridges.

EXPERIMENTAL

General apparatus. Elemental analysis was per-formed on a Eurovector 3018, C,H,N,S-analyzer in-strument. Co analyses were performed on a GBC Avanta PM atomic absorption spectrophotometer us-ing flame mode and IR spectra were recorded by Shi-madzu Infinity model device using an ATR attacha-ment. Mass spectra of the ligands were obtained by Shimadzu 2010 plus equipped with a DI unit and an electron impact ionizer. DI temperature was changed between 35 and 110°C and ionization was achieved with 70 eV electrons. ^{13}C NMR and ^{1}H NMR spectra were recorded on a Bruker ultrashield 300 MHz NMR spectrometer in DMSO-d$_6$. TGA—DTA thermograms were obtained using a Shimadzu TG-60H instrument. Aluminum pans were used for thermograms obtained at temperatures ranging from 25 to 450°C, whereas platinum pans were used for thermograms obtained at temperatures ranging between 25—750°C. All thermo-grams were obtained under nitrogen atmosphere with

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a flow rate of 100 mL/min. The heating rate was 10°C/min for the thermograms in the temperature range of 25−750°C.

Preparations of the Pp and Dmpp ligands were made according to literature [1].

Synthesis of Pp ligand. Pyrazol (6.8 g, 0.1 mol) was solved within diglym (150 mL) at room temperature. To this solution, newly-cut metallic sodium (3.9 g, 0.1 mol) was added under N_2 atmosphere and reflux, and the solution was stirred for 3−4 h to dissolve solid sodium. Subsequently, solid 2,6-dichloropyridine (7.4 g, 0.05 mol) was added to this solution, and it was dissolved by heating. Temperature of the solution was raised to 110−120°C and the solution was stirred for about 12 h. Formation of solid NaCl was observed. After this period, the cooled solution was poured onto water-ice mixture (500 mL), and NaCl was dissolved by agitating. The white precipitate was filtered and dried in air. M.p. = 136°C.

IR data (ν, cm^{-1}): 1583 ν(C=C)$_{ring}$; 1603 ν(C=N)$_{ring}$; 3110−3165 ν(C−H)$_{Ar}$; 1479−1458 δ(CH$_3$); 763 δ(C−H). ^{1}H NMR (DMSO-d$_6$; δ, ppm): 6.63 m. (2H), 7.82 d.d. (4H), 8.15 t. (1H), 8.95 d. (2H). ^{13}C NMR (DMSO-d$_6$; δ, ppm): 108.0, 109.4, 127.3, 142.0, 143.1, 151.2. MS (m/z): 211 (base peak and molecular peak), 144, 117.

Synthesis of Dmpp ligand was carried out from 3,5-dimethyl pyrazole (0.1 mol) and 2,6-dichloropyridine (0.05 mol) following the same procedure for the synthesis of Pp. M.p. = 106−107°C.

IR data (ν, cm^{-1}): 1587 ν(C=C)$_{ring}$; 1596 ν(C=N)$_{ring}$; 2880−2958 ν(C−H)$_{aliph}$; 3102−3130 ν(C−H)$_{Ar}$; 1473−1425 δ(CH$_3$); 791 δ(C−H). ^{1}H NMR (DMSO-d$_6$; δ, ppm): 2.20 s. (6H), 2.55 s. (6H), 6.15 s. (2H), 7.68 d. (2H), 8.05 t. (1H). ^{13}C NMR (DMSO-d$_6$; δ, ppm): 14.0, 14.5, 109.0, 115.4, 140.1, 141.1, 150.1, 156.0. MS (m/z): 267 (base peak and molecular peak), 252, 225, 211, 173, 147, 95.

Synthesis of Co(Pp)(OCN)$_2$ complex (I). 0.01 mol was dissolved in 50 mL MeCN−MeOH (1 : 2) mixture by heating. The solution of CoCl$_2$·6H$_2$O (0.01 mol) in hot MeOH (20 mL) and the solution of KOCN (0.01 mol) in hot H$_2$O (10 mL) were added to Pp solution. The crystals in the resulting solution were allowed to grow for 24 h. The precipitate was filtered and air-dried.

For C$_{13}$H$_9$N$_7$O$_2$Co (**I**)

anal. calcd., %:   C, 44.09; H, 2.56; N, 27.69; Co, 16.64.
Found, %:   C, 43.65; H, 3.1;   N, 27.86; Co, 16.34.

IR data (ν, cm^{-1}): 1586 ν(C=C)$_{ring}$; 1612 ν(C=N)$_{ring}$; 2193 ν(OCN); 2880−2958 (C−H)$_{aliph}$; 781 δ(C−H).

Synthesis of [Co(Dmpp)(OCN)$_2$]$_2$ complex (II). 0.01 mol Dmpp was dissolved in 50 mL MeCN−

MeOH (1 : 2) mixture by heating. The solution of CoCl$_2$·6H$_2$O (0.01 mol) in hot MeOH (20 mL) and the solution of KOCN (0.01 mol) in hot H$_2$O (10 mL) were added to Dmpp solution. The crystals in the resulting solution were allowed to grow for 24 h. The precipitate was filtered and air-dried.

For C$_{34}$H$_{34}$N$_{14}$O$_4$Co$_2$ (**II**)

anal. calcd., %: C, 49.77; H, 4.18; N, 23.88; Co, 14.36.
Found, %:   C, 49.39; H, 3.89; N, 23.51; Co, 14.02.

IR data (ν, cm^{-1}): 2181 ν(OCN); 2889−2957 (C−H)$_{aliph}$; 3106−3139 ν(C−H)$_{Ar}$; 783 δ(C−H).

X-ray structure determination. The single crystals of compound **I** were analysed on an Oxford Diffraction Xcalibur (TM) Single Crystal X-ray Diffractometer with Sapphire CCD Detector [14] and the crystals of compound **II** were analysed on an Enraf-Nonius CAD 4 diffractometer [15] with MoK_α radiation using ω−2θ scan mode low-temperature facilities in order to define their crystal structure. For complex **I**, diffraction measurements were done at room temperature on an Oxford Diffraction Xcalibur (TM) Single Crystal X-ray Diffractometer [14] with Sapphire CCD Detector using MoK_α radiation (λ = 0.71073 Å) and ω−2θ scan mode. Unit-cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in 2.78° ≤ θ ≤ 26.37° range. The empirical absorption corrections were applied by the semiempirical method via CrysAlis CCD software [14].

For complex **II**, the X-ray diffraction intensity data were collected at room temperature using an Enraf-Nonius CAD 4 diffractometer [15] working with MoK_α radiation and on ω−2θ scan mode. The cell parameters were determined from least squares of 16 centred reflections in the range of 2.12° ≤ θ ≤ 25.76°. Three standard reflections for every 120 min were periodically measured during data collection and showed no significant intensity variations. It was revealed that the non-hydrogen atoms were anisotropic and all hydrogen atom positions were refined in an isotropic approximation in the riding model with the $U_{iso}(H) = 1.5U_{eq}(C,H)$ for methyl groups and $U_{iso}(H) = 1.2U_{eq}(C,H)$ for other carbon atoms.

The disordered N(13) atom with suffix *A* has an occupancy of 0.48(8) and that with suffix *B* has an occupancy of 0.52(8). Both models were obtained from the results of the cell refinement and the data reductions were carried out using the solution software SHELXL-97 [16]. The structures of each compound were revealed by direct methods using SHELXS-97 in the WinGX package [17].

The crystal and the experimental data are given in Table 1 and the bond angles and bond lengths obtained from the X-ray diffraction study are given in Table 2. The hydrogen bonding geometry is given in Table 3.

Table 1. Crystal data and structure refinement for the complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	354.20	820.61
Temperature, K	293(2)	293(2)
Crystal system,	Monoclinic	Orthorombic
Space group	$C2/c$	$Pbca$
Unit cell dimensions:		
a, Å	14.469(2)	16.5704(12)
b, Å	9.1610(10)	18.6340(13)
c, Å	12.6580(10)	23.5781(14)
β, deg	122.100(10)	90
Volume, Å^3	1421.3(3)	7280.3(9)
Z	4	8
ρ_{calcd}, g cm^{-3}	1.655	1.497
μ, mm^{-1}	1.229	0.971
$F(000)$	716	3376
Crystal size, mm	$0.70 \times 0.16 \times 0.14$	$0.40 \times 0.30 \times 0.25$
θ_{max}, deg	52.7	51.5
Index range	$-18 \le h \le 17, -11 \le k \le 11, -15 \le l \le 15$	$-20 \le h \le 0, -22 \le k \le 0, -28 \le l \le 0$
Reflection collected	5996	11344
Independent reflections (R_{int})	1459 (0.016)	6234 (0.001)
Reflections with $I \ge 2\sigma(I)$	1265	4121
Number of parameters	106	487
R	0.037	0.053
R_w	0.122	0.136
GOOF	1.14	1.18
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	$-0.40/0.68$	$-0.36/0.48$

The PLATON drawings [18] of complexes **I** and **II** are given in Fig. 1. Note that the displacement ellipsoids were drawn for the probability level of 50% in the PLATON drawings. Supplementary material for the complexes has been deposited with the Cambridge Crystallographic Data Centre (nos. 832248 (**I**) and 832249 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Complex **I** was found to be mononuclear where complex **II** was found to be cationic and anionic dinuclear. In complex **I**, there is a five membered coordination sphere around Co^{2+} ion. The Co^{2+} ion was coordinated by the three nitrogen donors of the organic ligand and two oxygens of the cyanate ions. Nevertheless, the coordination sphere seems to be quite distorted that it is not clear if the coordination was square pyramidal or trigonal bipyramidal [19]. The level of

the distortion is clearly seen when the angles for complex **I** are taken into consideration.

Complex **II** constitutes of two complexes one of which is cationic and the other one is anionic. In the cationic complex, the central Co^{2+} ion is surrounded by two bis-2,6-(3,5-dimethyl-pyrazol-1-yl) ligands and is coordinated by three nitrogen atoms of the ligands. Coordination sphere is octahedral where the six nitrogen atoms of the ligands are at the corners. Although the coordination seems symmetrical, the data given in Table 2, shows that the octahedron is deformed and far from ideal. The largest angles around Co^{2+} ion are N(10)Co(1)N(6) 145.31(14)°, N(3)Co(1)N(8) 168.20(12)°, and N(5)Co(1)N(1) 149.48° which are notably narrower than 180°. In addition to that, almost all other angles ranging in between 73.64° and 99.29° are found to be quite different than 90°.

Due to the deformation of the octahedral geometry, it is very difficult to tell which nitrogen donors are at the axial positions and which constitute the basal

Table 2. Selected bond distances (Å) and angles (deg) for structures **I** and **II**

Bond	d, Å	Bond	d, Å
		I	
Co–N(1)	2.162(2)	Co–N(3)	2.066(3)
Co–O(1)	1.957(3)	N(1)–N(2)	1.359(3)
O(1)–C(7)	1.157(4)	C(7)–N(4)	1.180(4)
		II	
Co(1)–N(1)	2.144(4)	Co(1)–N(3)	2.084(4)
Co(1)–N(5)	2.122(4)	Co(1)–N(6)	2.147(3)
Co(1)–N(8)	2.088(4)	Co–N(10)	2.111(4)
Co(2)–O(1)	1.988(6)	Co(2)–O(2)	2.007(8)
Co(2)–O(3)	1.967(6)	Co(2)–O(4)	1.925(6)
Angle	ω, deg	Angle	ω, deg
		I	
O(1)CoO(1)^i	113.41(17)	O(1)CoN(3)	123.29(9)
O(1)CoN(1)	95.52(10)	O(1)CoN(1)^i	101.04(10)
N(3)CoN(1)	74.81(6)	N(1)CoN(1)^i	149.62(13)
O(1)C(7)N(4)	178.2(4)		
		II	
N(3)Co(1)N(8)	168.26(14)	N(8)Co(1)N(6)	73.67(14)
N(3)Co(1)N(10)	114.13(16)	N(10)Co(1)N(6)	145.24(16)
N(8)Co(1)N(10)	74.71(16)	N(5)Co(1)N(6)	91.06(15)
N(3)Co(1)N(5)	74.90(14)	N(1)Co(1)N(6)	99.58(14)
N(8)Co(1)N(5)	114.06(14)	O(4)Co(2)O(3)	113.1(3)
N(10)Co(1)N(5)	88.87(16)	O(4)Co(2)O(1)	106.9(3)
N(3)Co(1)N(1)	75.15(15)	O(3)Co(2)O(1)	109.9(2)
N(8)Co(1)N(1)	96.44(14)	O(4)Co(2)O(2)	113.3(3)
N(10)Co(1)N(1)	97.92(16)	O(3)Co(2)O(2)	107.2(3)
N(5)Co(1)N(1)	149.45(15)	O(1)Co(2)O(2)	106.1(3)
N(3)Co(1)N(6)	99.32(14)		

Table 3. Geometric parameters of hydrogen bonds for complexes **I** and **II***

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
I				
C(1)–H(1)···N(4)	0.93	2.35	3.268	170
II				
C(2)–H(2)···N(8)	0.96	2.47	3.347(6)	152
C(2)–H(2)···N(13)^i	0.96	2.39	3.196(12)	141
C(3)–H(3)···N(11)^{ii}	0.93	2.46	3.373(7)	166
C(8)–H(8)···N(11)^{iii}	0.93	2.49	3.392(7)	165
C(22)–H(22)···N(12)^{iv}	0.96	2.45	3.392(10)	166
C(30)–H(30)···N(4)	0.96	2.60	3.488(7)	154

* Symmetry codes: ^{i} $-1 + x, y, z$; ^{ii} $1/2 - x, -1/2 + y, z$; ^{iii} $1 - x, -1/2 + y, 1/2 - z$; ^{iv} $-1/2 + x, 1/2 - y, 1 - z$.

plane. The largest angle around Co(1) ion is 168.20°. According to this information, N(3)−Co(1)−N(8) is the axial axis of the octahedron. On the other hand, in order to define the basal plane, the possible axes around Co(1) were determined with the help of the software PARST [20] and the following results were obtained (Table 4).

If N(3) and N(8) are at the axial positions, the basal plane should be N(1)N(5)N(6)N(10) (plane 3) but the above calculations suggest otherwise. If the least deviation from the average plane is taken into consideration, the most appropriate candidate for the basal plane would be N(1)N(3)N(5)N(8). However, in this case, N(6) and N(10) should be at the axial positions which seem unlikely since the deviation from 180° of N(6)Co(1)N(10) angle (145.31°) is too much.

In the anionic complex, a second Co^{2+} ion is coordinated between four OCN-ions and the coordination
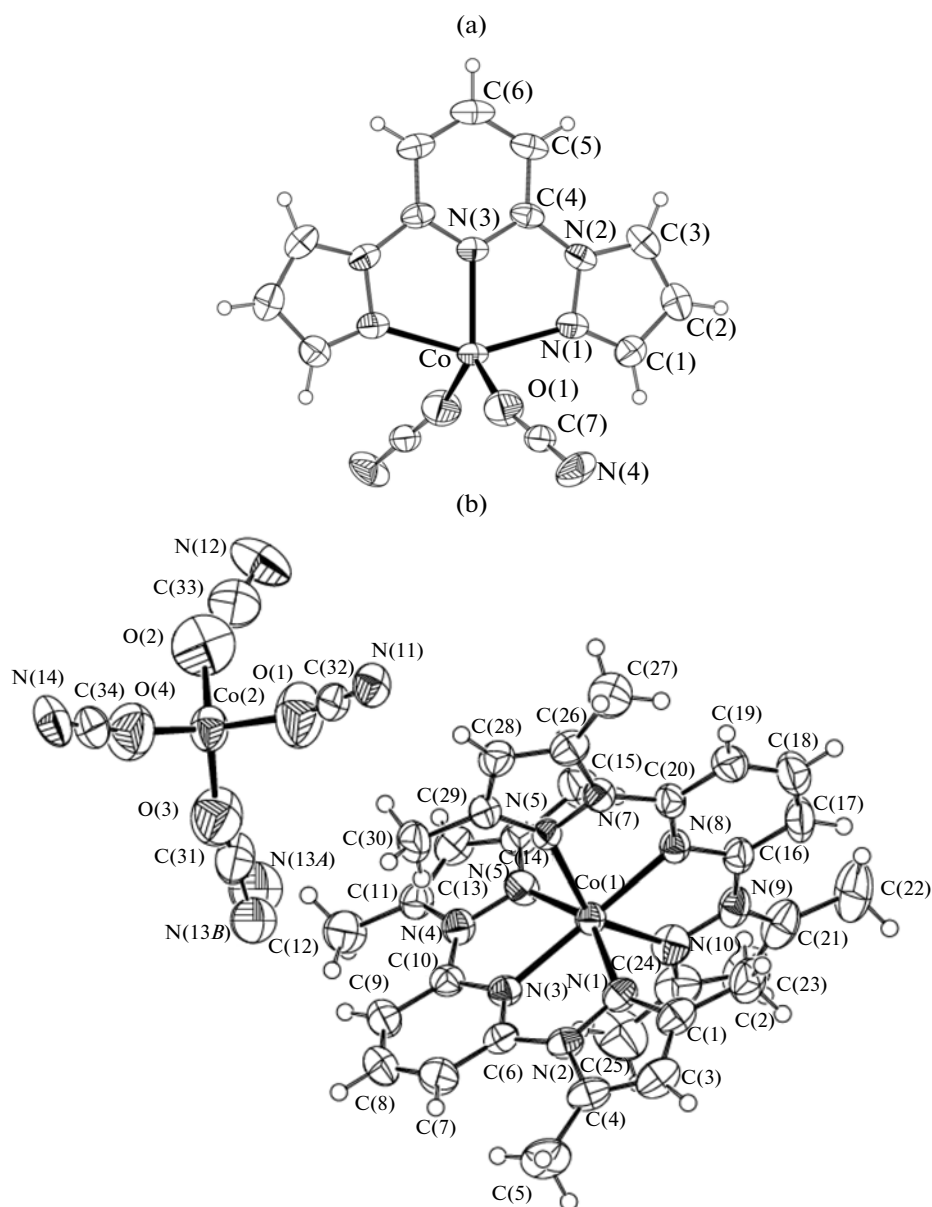
Fig. 1. PLATON [18] drawing of **I** (a) and **II** (b) with the atomic numbering scheme.

sphere is tetrahedral. Nevertheless, there found to be a disorder in the molecular structure, probably due to excessive symmetry. So, the tetrahedral geometry is not ideal despite the symmetric placement of the anions. The bond angles around the central atom Co(2) are in between 106.3° and 113.3°. Like the other coordination types, Dobson parameters were defined for tetrahedral coordination to represent ideality [21]. These parameters were calculated considering the angles around Co(2) and the following results were found:

$$\theta_x = 91.57°; \quad \theta_y = 88.21°; \quad \theta_z = 92.93°.$$

According to these results, the anionic complex is tetrahedral and is very close to ideal. Probably, the lit-

tle deviations from ideality are due to the disorder in the complex.

The thermal decomposition curves for complexes **I** and **II** were given in Fig. 2. A distinct mass loss is not detected in the TG curves of neither complex. As can be seen in the Fig. 2, both complexes decompose gradually with increasing temperature up to 700°C indicating a pyrolysis-like thermal reaction. Still, the decomposition reactions being two or three stepped can be noted in the TG curves. The thermoanalytical data for both complexes is given in Table 5. The only accountable points in the TG curves are the first thermal reactions and there is no conclusive evidence even for those, the explanations can only be based on inter-

Table 4. The possible axes around Co(1) using PARST [20]

Plane 1		Plane 2		Plane 3	
Atom	d, Å*	Atom	d, Å	Atom	d, Å
Co(1)	−0.0042	Co(1)	−0.0002	Co(1)	−0.0006
N(1)	−0.0780	N(3)	−0.1132	N(1)	0.4931
N(3)	0.1624	N(6)	0.1647	N(5)	0.6122
N(5)	−0.0589	N(8)	−0.2074	N(6)	−0.4127
N(8)	0.1170	N(1)0	0.2369	N(1)0	−0.7931

* Distance from average plane.

pretation. The boundaries of the first mass loss in the 1st thermal reaction can just be noticed. Nonetheless, mass losses in both complexes seem to correspond to the carbon content of the pyrazol groups of the organic ligands. Pyridine rings remain unharmed at around 300°C since they are more stable than the pyrazol groups. Over 330°C, where the first reaction is complete, the complexes decompose at particular pace and lose most of their masses until 700°C. The remainings are Co_3O_4 and some carbon. The exothermic peak at around 700°C is due to the combustion of the remain-
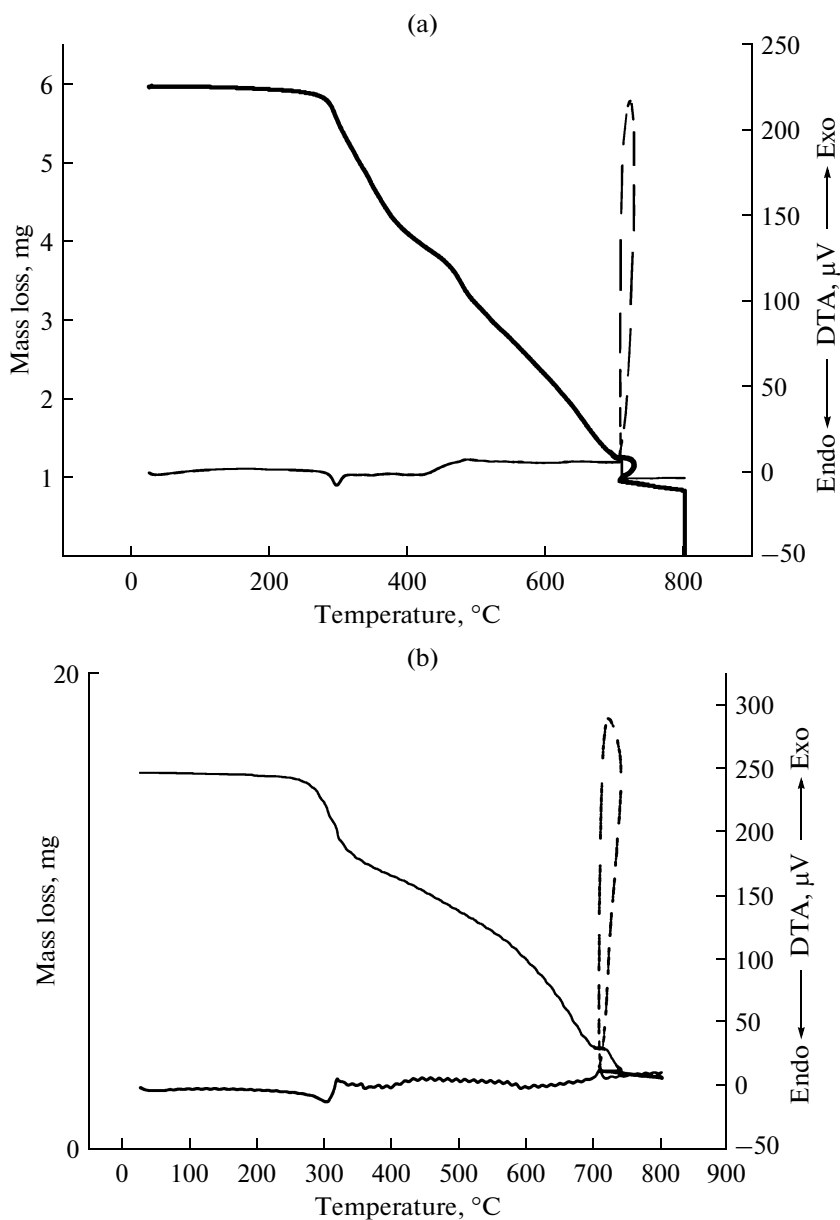

Fig. 2. The TG curves of complexes **I** (a) and **II** (b).

Table 5. Thermoanalytical data for the complexes **I** and **II**

Com-plex	The 1st thermal reaction			The following thermal reaction		Co$_3$O$_4$	
	temperature interval, °C	observed mass loss, %	expected mass loss, %	temperature interval, °C	observed mass loss, %	observed mass loss, %	expected mass loss, %
I	260−340	22.41 ± 1.09	22.09	Indistinguishable	Indistinguishable	21.37 ± 0.24	22.70
II	280−330 DTA peak: 297	32.70 ± 1.10	32.66	405−500	16.18 ± 1.96	19.20 ± 0.82	18.31

ing carbon content under oxygen atmosphere. The only remaining mass over this temperature is of Co$_3$O$_4$.

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