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NOVEL LANTHANIDE COMPLEXES WITH DI-2-PYRIDYL KETONE-*p*-CHLORO-BENZOYLHYDRAZONE
Thermal investigation by simultaneous TG/DTG-DTA and IR spectroscopy

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The reaction of a hydrated nitrate salt of lanthanide(III) (*Ln*=Er, Ho, Tb, Gd) or yttrium(III) (Y) with the ligand di-2-pyridyl ketone-*p*-Cl-benzoylhydrazone (DpkClBH), afforded air stable solid compounds. The new complexes characterized by means of elemental analysis (C, H, N, Ln), magnetic moment determinations and spectroscopic data (IR, MS). It is proposed that they are cationic of the general type: $[Ln(DpkClBH)_2(NO_3)_2]NO_3{\cdot}nH_2O$, ($n$=2, 1, 1, 1, 1.5 for *Ln*=Y, Gd, Tb, Ho, Er, respectively).

Their thermal decomposition was studied in nitrogen atmosphere, between 25–980°C, by using simultaneous TG/DTG-DTA technique. The IR spectroscopy used to determine the intermediates and the final products. The anhydrous nitrate complexes decomposed to the intermediates $Ln(DpkClBH)(NO_3)_2$, which upon further heating give a carbonaceous residue of Ln_2O_3 at 980°C. The mass spectra revealed the molecular ions of the complexes and their possible fragmentation pattern.

Keywords: *hydrazone ligand, IR, lanthanide(III), MS, TG/DTG-DTA, yttrium complexes*

Introduction

Lanthanide complexes are of continuing interest mainly due to their structural and catalytic properties [1] and their applications in diagnostic pharmaceutical [2] and laser technology [3, 4]. Schiff-base ligands like hydrazones, are considered privileged ligands because they are easily prepared by a simple one-pot condensation of a carbonyl compound and primary amines in an alcohol solvent and are associated with various interesting types of biological effects, such as antiviral, antibacterial, and antimicrobial activity [5]. In the lanthanide complexes with various types of multidentate hydrazone ligands, the metal can achieve high coordination number giving structural differences responsible for their important properties [6]. Recently, there is an increasing research interest on the thermal properties of the lanthanide complexes with ligands having O and N donor ability, studied by TG-DTA techniques [7–9].

In the course of our studies on the high coordination number lanthanide chemistry [10–12], we report here the synthesis, spectral (IR, MS) and thermal studies (TG/DTG-DTA) of five new lanthanide complexes with the Schiff-base ligand di-2-pyridyl ketone-*p*-Cl-benzoylhydrazone (DpkClBH) (Fig. 1). As it is shown the ligand employs five potentially coordinated sites, one secondary amine nitrogen, one imine nitrogen, two pyridine nitrogens and one carbonyl oxygen to bind metal(III) ions.

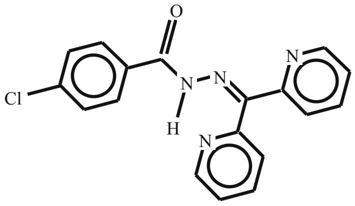

Fig. 1 Structural formula for the Schiff base ligand DpkClBH, derived from di-2-pyridylketone and *p*-chloro-benzoylhydrazide

Experimental

The hydrated nitrate salts of lanthanide ($Ln(NO_3)_3{\cdot}xH_2O$, where *Ln*=Y, Er, Ho, Tb, Gd and x=5 or 6) and the organic compounds *p*-Cl-benzoylhydrazide (*p*-ClBH) and di-2-pyridyl ketone (Dpk) were purchased from Aldrich and were used without further purification. All solvents were distilled prior to use.

Synthesis of the ligand DpkClBH

Preparation of the hydrazone ligand DpkClBH was carried out according to literature method [13], by refluxing a methanolic solution (500 mL) of *p*-chlorobenzoylhydrazide (8.53 g, 50 mmol) and di-2-pyridyl ketone (9.21 g, 50 mmol) for 48 h. After 24 h slow cooling of the reaction mixture at room temperature, a

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crude yellow product was filtered off, washed with cold methanol and recrystallized twice from hot methanol-water mixture.

Synthesis of the complexes $[Ln(DpkClBH)_2(NO_3)_2]NO_3\cdot nH_2O$

$[Ln(NO_3)_2(DpkClBH)_2]NO_3\cdot nH_2O$ complexes were prepared by the following general procedure: To a water solution (3 mL) of lanthanide nitrate (2 mmol) was added drop-wise a methanolic solution (10 mL) of DpkClBH (4 mmol). After 4 h stirring, microcrystalline products were obtained, filtered off, washed with small portions of methanol, and dried in vacuum over anhydrous calcium chloride.

Physical measurements

Stoichiometric analyses (C, H, N) were performed on a Perkin-Elmer 240B elemental analyzer. Metal content was determined by EDTA titration after decomposition with nitric acid, using as indicator xylenol orange and buffer hexamethylenetetramine [14].

Magnetic susceptibility measurements on powdered samples were performed at 25°C employing the Faraday method in instrument of Johnson Mathey, type MSB-MKI, calibrated against $Hg[Co(SCN)_4]$. Molar conductivities were measured in DMF solutions, employing a WTW conductivity bridge and a calibrated dip type cell.

Infrared spectra were recorded on a Perkin-Elmer FTIR 1650 spectrometer, in the region 4000-200 cm^{-1} using KBr pellets. Mass spectra were run on a RMU-6L Hitachi PerkinElmer, double focusing mass spectrometer, model TS 250 Fision, using direct probe insertion for the samples, operating at 70 eV.

The simultaneous TG/DTG-DTA curves were obtained on a SETARAM instrument, model SETSYS-1200. The samples were heated in platinum crucibles, in nitrogen atmosphere, within the temperature range 25–980°C. The heating rate was 10°C min^{-1} and the samples, about 10 mg, were weighted into a platinum crucible.

PXRD was performed using a Philips PW 1710 diffractometer with Ni-filtered CuK_{α} radiation on randomly oriented samples. The samples were scanned within the range $2\theta=3–63°$.

Results and discussion

The reaction of the lanthanide nitrate with the Schiff-base ligand DpkClBH afforded in good yield very stable in air solid compounds. The characterization of their molecular structure was made by elemental analyses, conductivity and magnetic measurements, as well as by infrared spectroscopy. Thermal analysis by TG-DTA technique was proved very useful in determining the crystal water content in the complexes and their thermal stability and decomposition mode under controlled heating rate. The fragmentation pattern of the complexes was studied with the aim of mass spectrometry.

The compounds prepared are pale colored, soluble in methanol, ethanol, acetonitrile and dimethylsulfoxide, but insoluble in chloroform, dichloromethane and diethylether. All the studied complexes possess 1:2 metal-to-ligand composition, as it is indicated from elemental analyses and exhibit corresponding conductivities (~80θ S cm^2 mol^{-1}) in DMF (Table 1), suggesting 1:1 electrolytic behavior. The room temperature magnetic moments (μ_{eff}) are characteristics of trivalent lanthanide ions, showing very close agreement with the theoretical values calculated from Van Vleck formula indicating minor participation of 4f electrons in the bond formation.

Table 1 Analytical and physicochemical data for the complexes $[Ln(DpkClBH)_2(NO_3)_2]NO_3\cdot nH_2O$ (n=2, 1, 1, 1, 1.5 for Ln=Y, Gd, Tb, Ho, Er, respectively)

Complex	Color	Yield/%	C/%	H/%	N/%	Ln/%	μ_{eff}/MB	Λ/S cm^2 mol^{-1}
Y	white	74	43.79	3.08	15.53	9.01	D	67.5
			(43.94)*	(3.05)	(15.65)	(9.05)		
Gd	white	82	41.53	2.46	14.99	15.06	7.63	68.4
			(41.78)	(2.71)	(14.89)	(15.28)		
Tb	yellow	59	41.92	2.63	15.14	15.49	9.59	81.7
			(41.74)	(2.70)	(14.88)	(15.36)		
Ho	yellow	79	41.99	2.55	14.90	15.83	10.32	73.3
			(41.49)	(2.69)	(14.79)	(15.85)		
Er	pink	87	41.27	2.60	14.96	15.87	9.29	80.0
			(41.10)	(2.76)	(14.65)	(15.79)		

*calculated values in parenthesis; D=diamagnetic

Similar values have been observed with substituted benzoate complexes of lanthanides [15, 16]. The complexes may be formulated as [Ln (DpkClBH)$_2$(NO$_3$)$_2$]NO$_3$·nH$_2$O, evidence also arisen from the interpretation of the IR data of the ligand and the complexes. Their physicochemical characteristics are listed in Table 1.

Infrared spectra

The relevant infrared vibration bands of the free ligand and the complexes, in the region 4000–250 cm^{-1}, are given in Table 2. The broad band at 3457 cm^{-1} of the free ligand DpkClBH, attributable to ν(N–H), is observed at the region 3234–3377 cm^{-1} for all the complexes. A strong band at 1675 cm^{-1} in the DpClBH (due to ν(C=O)), upon complexation is shifted by ~50–60 cm^{-1} to lower frequencies due to the coordination of the carbonyl oxygen with lanthanide. The appearance of the ν(N–H) and ν(C=O) bands, in the spectra of all complexes, is an evidence for the coordination of the hydrazone with the metal as neutral ligand [17]. For the complexes the ν(C=N) band appears at the region ~1560 cm^{-1}, which is ~25 cm^{-1} lower in frequency than the corresponding band of the free DpkClBH. This indicates that the azomethine nitrogen is coordinated to the metal. The low energy pyridine ring in-plane and out-of-plane vibrations observed in the spectrum of the ligand at 613 and 403 cm^{-1} respectively, but the corresponding bands for the complexes are shifted to higher frequencies at 625–637 and 414–429 cm^{-1} respectively, which is a indication of the coordination of the heterocyclic nitrogen [18]. The appearance of a strong band at ~1384 cm^{-1} in the spectra of all complexes indicates the presence of ionic nitrates (D$_{3h}$ symmetry, free NO$_3^-$ ion). All the spectra demonstrate also the presence of coordinated nitrates. Two strong bands observed at 1288–1302 and 1488–1502 cm^{-1} assigned to the ν_4 and ν_1 vibrations modes of the nitrate group, respectively (C$_{2V}$ symmetry, coordinated nitrate group). The magnitude of the splitting (ν_4–ν_1) is ~180 cm^{-1} in all complexes and it is typical of bidentate bonding of nitrates [19]. This value is confirmed in absolutely related hydrazone–lanthanide complexes with both spectral and structural data [11]. The existence of crystal water is inferred from the bands at 3460 cm^{-1}, while the bands due to the coordination bonds Ln–N and Ln–O at ~480 and 380 cm^{-1} respectively. A representative IR spectrum for the Ho complex is given in Fig. 2.

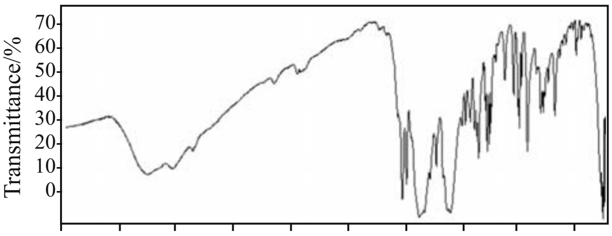

Fig. 2 Infrared spectrum of the Ho complex

Mass spectra

The electron impact (EI) mass spectral data for four of the investigated complexes are listed in Table 3. The molecular ion [Ln(NO$_3$)$_2$L$_2$]NO$_3$$^{-+}$ is detected for the complexes of Y(III), Er(III) and Tb(III) at m/e=947, 1024 and 1017 respectively, but not for the Ho(III) one. The observed peaks due to the fragment [Ln(NO$_3$)$_2$(L)$_2$]$^+$ are formed from the expulsion of the radical –NO$_3$ from the molecular ion. Further removal of nitrate ion as HNO$_3$ resulted in the formation of the fragments [Ln(NO$_3$)L$_2$]$^+$.

It is worthwhile to be mentioned that for the erbium complex, [Er(NO$_3$)$_2$(L)$_2$]NO$_3$·nH$_2$O, a set of four peaks was detected for each fragment containing the metal, due to the different isotopes of erbium. For example, there are four peaks at m/e 1024, 1025, 1026 and 1028 corresponding to the molecular ion [Er(NO$_3$)$_2$L$_2$]NO$_3$$^{-+}$ due to the ^{166}Er, ^{167}Er, ^{168}Er and ^{170}Er isotopes, respectively.

In the low mass-number region, an intense peak at m/e 336, corresponding to the coordinated ligand L$^+$, is apparent for all the complexes. The elimination

Table 2 Selected IR bands/cm^{-1} for the ligand DpkClBH and its lanthanide complexes

Comp.	ν(N–H)	ν(C=O)	ν(C=N)	ν_4 (NO$_3$) (C$_{2v}$)	ν_3 (NO$_3$) (D$_{3h}$)	ν_1 (NO$_3$) (C$_2$)	Pyridine ring in plane	Pyridine ring out of plane
ligand	3457	1675	1586	–	–	–	613	403
Y	3365	1616	1561	1488	1384	1302	625	429
Gd	3234	1615	1560	1485	1384	1293	636	428
Tb	3234	1623	1560	1502	1384	1288	637	428
Ho	3234	1615	1562	1488	1384	1300	636	420
Er	3377	1615	1561	1488	1384	1301	625	414

Table 3 Relative abundances of the most significant ions in the mass spectra of the complexes $[Ln(DpkClBH)_2(NO_3)_2]NO_3 \cdot nH_2O$

Chemical species	*m*/*e*, Intensity/%			
	Ln=Y	*Ln*=Tb	*Ln*=Ho	*Ln*=Er
$[Ln(NO_3)_2L_2]NO_3^+$	947 (6)	1017 (9)	–	1024 (9)
$[Ln(NO_3)_2L_2]^+$	885 (4)	955 (7)	–	962 (8)
$[Ln(NO_3)L_2]^+$	823 (5)	893 (5)	–	890 (8)
$[LnL_2]^+$	760 (7)	830 (7)	–	837 (5)
$[Ln(NO_3)_2L]NO_3^+$	611 (5)	681 (7)	687 (8)	688 (5)
$[Ln(NO_3)_2L]^+$	549 (3)	619 (10)	625 (11)	626 (6)
$[LnNO_3L]$	487 (7)	557 (4)	–	564 (6)
L^+	336 (9)	336 (100)	336 (15)	336 (11)

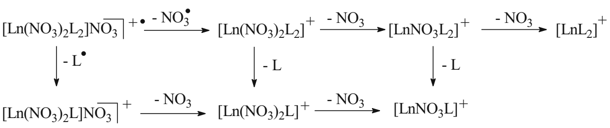

Fig. 3 Fragmentation pattern of the lanthanide complexes $[Ln(NO_3)_2(DpkClBH)_2]NO_3$

of a chloride ion of the ligand DpkClBH forms the base peak at 301 *m*/*e*. A possible fragmentation pattern for the lanthanide complexes under investigation, is given in Fig. 3.

Thermal behavior

The yttrium and the lanthanide complexes were subjected to TG/DTA-DTA analysis from ambient up to 980°C in nitrogen atmosphere. The temperature ranges, the determined percentage mass losses and the thermal effects accompanying the decomposition are given in Table 4. For all the investigated complexes, the thermal decomposition mode seems to follow the same model. Representative thermal curves are depicted for the yttrium complex $[Y(DpkClBH)_2(NO_3)_2]NO_3 \cdot 2H_2O$ in Fig. 4.

The elimination of the crystal water molecules at ~200°C suggests that these are strongly kept in the crystal lattice of the complexes, due to the strong hydrogen bonds network, as it has been found in the crystal structure of other analogous hydrazone lanthanide complexes [11].

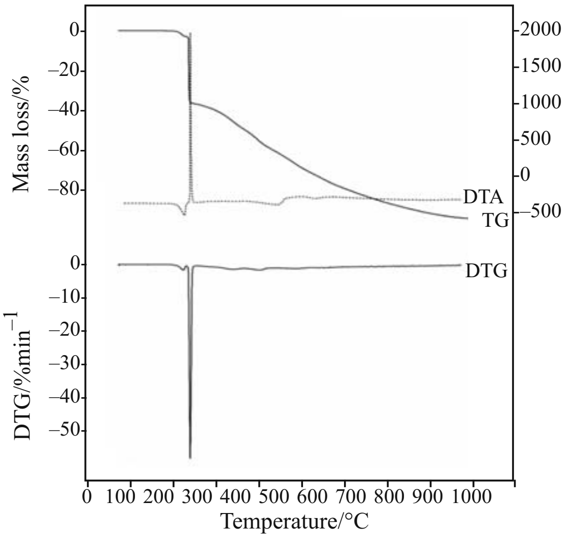

Fig. 4 TG/DTG-DTA curves for the yttrium complex in nitrogen

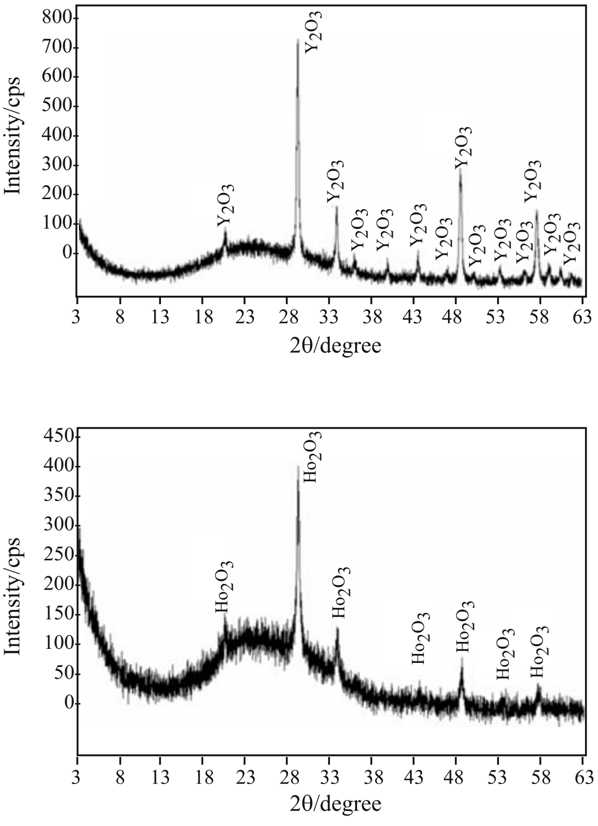

Fig. 5 Powder XRD of the residues at 980°C for the a – Y and b – the Ho compounds

Table 4 Thermoanalytical results (TG/DTG-DTA) for the complexes $[Ln(DpkClBH)_2(NO_3)_2]NO_3\cdot nH_2O$ in nitrogen

Complex	Temp. range/ °C	Evolved compounds	DTG_{max}/ °C	DTA/ °C	Mass loss/% (calc./%)
$[Y(DpkClBH)_2(NO_3)_2]NO_3\cdot 2H_2O$	175–210	$2H_2O$	210	210 endo	3.3 (3.65)
	210–300	DpkClBH+HNO_3	230	230 exo	38.3 (34.20+6.41)
	300–495	DpkClBH	400	–	32.0 (34.20)
	495–850	$2NO_2$+1/4O_2	–	–	9.3 (9.84)
	Res.>900	Y_2O_3+C			17.1 (11.48+x)
$[Gd(DpkClBH)_2(NO_3)_2]NO_3\cdot H_2O$	179–197	H_2O	197	197 endo	2.0 (1.70)
	197–310	DpkClBH+HNO_3	223	223 exo	37.0 (32.50+6.00)
	310–450	–DpkClBH	415	–	31.20 (32.50)
	450–830	$2NO_2$+1/4O_2	–	–	9.5 (9.67)
	Res.>900	Gd_2O_3+C			20.3 (17.5+x)
$[Tb(DpClBH)_2(NO_3)_2]NO_3\cdot H_2O$	175–195	H_2O	194	194 endo	2.0 (1.70)
	195–305	DpkClBH+HNO_3	220	220 exo	37.7 (32.50+6.10)
	305–442	DpkClBH	400	–	31.3 (32.50)
	495–850	$2NO_2$+1/4O_2	–	–	9.3 (9.65)
	Res.>900	Tb_2O_3+C			19.7 (17.66+x)
$[Ho(DpkClBH)_2(NO_3)_2]NO_3\cdot H_2O$	182–195	H_2O	195	195 endo	1.9 (1.70)
	195–320	DpkClBH+HNO_3	250	250 exo	36.6 (32.30+6.00)
	320–495	DpkClBH	400	–	30.9 (32.30)
	495–840	$2NO_2$+1/4O_2	–	–	9.9 (9.59)
	Res.>900	Ho_2O_3+C			20.7 (18.14+x)
$[Er(DpkClBH)_2(NO_3)_2]NO_3\cdot 1.5H_2O$	180–190	$1.5H_2O$	188	188 endo	2.6 (2.60)
	190–330	DpkClBH+HNO_3	240	240 exo	37.2 (31.90+5.90)
	330–497	DpkClBH	400	–	30.4 (31.90)
	497–830	$2NO_2$+1/4O_2	–	–	9.7 (9.50)
	Res.>900	Er_2O_3+C			20.1 (18.14+x)

The anhydrous compounds are very unstable upon heating, and decomposed suddenly with a mass loss corresponding to the elimination of one HNO_3 molecule and one hydrazone ligand. Fig. 4 shows that the melting is accompanied by the decomposition. The strong exothermic effect at 230°C on the DTA curve causes evidence that an oxidation of the sample takes place along with the decomposition. As it was deduced from the TG findings and from the elemental analysis and IR spectrum of the intermediate at ~300°C (the peak at 1384 cm^{-1}, due to the uncoordinated nitrate ion is absent), this compound could be assigned as $Ln(NO_3)_2(DpkClBH)$.

Beyond 300°C, the continuous mass loss is possibly due to successive elimination of the second hydrazone ligand, to be followed by degradation of the nitrate groups with the evolution of $2NO_2$ plus 1/4 O_2 [20]. This speculation can be enhanced from the composition of the final residues. The residues at 980°C for all the studied complexes are carbonaceous solids consisting of the lanthanide oxide Ln_2O_3 plus carbon in a ratio of ~10% of the complex, evidence arisen from the TG/DTG curves and IR peak at ~370 cm^{-1}, attributable to Ln–O bond, in agreement with other analogous lanthanide compounds [7, 12]. The formation of the oxides Ln_2O_3 was observed at ~750°C as it was expected [21].

Powder XRD diagrams for the final residue of the Y and Ho compounds are given in Figs 5a and b, confirming the existence of Y_2O_3 and the lanthanide oxide as Ho_2O_3 respectively.

Finally, from the thermoanalytical data (TG/DTG-DTA) it is deduced that the thermal decomposition mode of the titled complexes is in good agreement with their fragmentation pattern derived from mass spectral data.

Conclusions

The characterization of the newly synthesized lanthanide complexes with the hydrazone ligand DpkClBH was made by stoichiometric analysis, molar conductivity and magnetic at RT measurements. The infrared spectral data gave evidence for the coordination of the keto form of the hydrazone to the lanthanide ion via azomethine nitrogen, pyridine nitrogen and carbonyl oxygen, thus making the DpkClBH behaving as tridentate neutral ligand. The infrared spectra also demonstrate the presence of bidentate and ionic nitrates in the complexes. The TG-DTA measurements gave evidence for the existence of crystal water, strongly kept in the crystal lattice of the complexes. Conclusively, the formula of the complexes is $[Ln(DpkClBH)_2(NO_3)_2]NO_3 \cdot nH_2O$, with a metal coordination number of ten.

The molecular ions are also proved by the EI mass spectral data. The thermal data gave as intermediates the $\{Ln(DpkClBH)(NO_3)_2\}$ and as residues the carbonaceous oxides Ln_2O_3.

The proposed structure of the complexes is shown in Fig. 6.

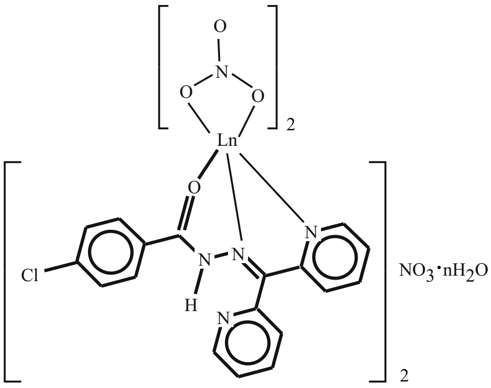

Fig. 6 Proposed structure of the $[Ln(NO_3)_2(DpkClBH)_2]NO_3 \cdot nH_2O$ complexes

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