

Transition metal complexes with pyrazole-based ligands. Part 6. Synthesis, characterization and thermal decomposition of cadmium complexes with 3(5)-amino-5(3)-methylpyrazole

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Abstract

The synthesis, IR-spectra and thermal analysis of tetrahedral or octahedral Cd(II)-complexes of 3(5)-amino-5(3)-methylpyrazole (L), as represented by the general formula $CdX_2L_2 \cdot nH_2O$ ($X = NCS^-$, NCO^- , Cl^- , $n=2$; $1/2 SO_4^{2-}$, $n=1$), and of the complex $Cd(OAc)_2L_3 \cdot H_2O$ are described. Thermal decomposition of the acetato complex results in an intermediate, appearing in the 480–580 K range. On the basis of the IR-spectrum and the results of elemental analysis of the intermediate, a decomposition scheme is proposed. Because of the involvement of a different anion, the thermal decomposition of the other complexes differs from that of the acetato complex. © 1998 Elsevier Science B.V.

Keywords: 3(5)-Amino-5(3)-methylpyrazole; Cadmium complexes; Thermal decomposition

1. Introduction

Transition-metal complexes of pyrazole and its derivatives are widely used as components of herbicides and fungicides [1], and drugs (antipyretics, antirheumatics) [2]. Coordination of pyrazole to the metal center of various biologically active molecules modifies their activity. The inhibition effect of substituted pyrazoles has been investigated on Zn-, Co- and Ni-substituted horse liver ADH [3–6]. The binding site of the pyrazole in Cd-substituted horse liver ADH was also studied [7] and via perturbed correla-

tion spectroscopy, it was deduced that the geometry of the tetra-coordinated complexes is approximately tetrahedral, with Hpz present as a fifth ligand [8]. The coordination chemistry of the pyrazole-derived ligands has been extensively reviewed [1,2,9–11]. This paper reports the synthesis, IR-spectra and thermal analysis of cadmium(II)-complexes with 3(5)-amino-5(3)-methylpyrazole in the presence of various anions (OAc^- , NCS^- , NCO^- , Cl^- , SO_4^{2-}).

2. Experimental

IR spectra of the compounds were recorded in the 4000–450 cm^{-1} range on a Perkin–Elmer FT-IR

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spectrometer at ambient temperature using KBr pellet technique. The spectra were obtained with a resolution of 4 cm^{-1} and with the co-addition of 16 scans.

Thermal analysis was performed using a DuPont 1090 TA system. The sample masses were ca. 5 mg. For thermogravimetric measurements, samples were heated in a platinum crucible. DSC curves were recorded to 600 K using an open aluminum pan as sample holder and an empty aluminum pan as reference. The thermogravimetric curves for the complex with the chloride anion were recorded at heating rates of 5 and 10 K min^{-1} in both the argon and air atmospheres. The difference caused by the different heating rates was insignificant. Up to 600 K, the curves recorded at the same heating rate in the argon and air atmospheres were identical. However, the sample heating to 950 K in air resulted in a well-defined end product, whereas in argon the decomposition was not completed even up to 1300 K. Hence, all other measurements were conducted in a flowing air atmosphere at a heating rate of 10 K min^{-1} up to 950 K.

Molar conductivity of freshly prepared $10^{-3}\text{ mol dm}^{-3}$ solutions of the compounds in an appropriate solvent were measured at room temperature using a digital conductivity meter (Jenway 4010).

X-ray powder patterns for the acetate parent compound and its intermediate were recorded on a FPM HZG4 powder diffractometer using Ni filtered $\text{Cu } K_{\alpha}$ radiation.

3. Results and discussion

The crystalline solids (Table 1) were prepared by the reaction of warm aqueous solutions of the appro-

priate Cd(II)-salts ($\text{Cd(OAc)}_2 \cdot 2\text{H}_2\text{O}$; $\text{CdCl}_2 \cdot \text{H}_2\text{O}$; $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$; the pseudohalide Cd(II)-salts were prepared by the metathesis reaction of $\text{Cd(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with NaNCO and NH_4NCS) with a hot aqueous solution of 3(5)-amino-5(3)-methylpyrazole (L) in a mole ratio of 1 : 2. In spite of the 1 : 2 salt-to-ligand ratio, in the case of the reaction with $\text{Cd(OAc)}_2 \cdot 2\text{H}_2\text{O}$, a tris-ligand complex was obtained. The cyanato complex is insoluble, the sulfato complex is soluble only in water, and the acetato complex is soluble in MeOH. The chloro and thiocyanato complexes are soluble in DMF, less soluble in MeOH and EtOH, and insoluble in H_2O and Et_2O .

In the IR-spectrum of the ligand, broad overlapping bands were observed in the $3400\text{--}2700\text{ cm}^{-1}$ range, reflecting a complex hydrogen bonding pattern in the crystal. The IR-spectra of the complexes showed less expressive hydrogen bonding. The intense absorption bands around 1610 , 1590 and 1490 cm^{-1} appearing in the IR-spectra of all the compounds may be attributed to the $\delta(\text{NH}_2)$, $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{N}_a)$, respectively [12].

As there is no possibility for stabilization by ligand field stabilization energy (LFSE), the stereochemistry of the Cd-complexes depends on the cation size and on steric factors of the ligands. X-ray analysis [13] of the acetato complex revealed an octahedral arrangement around the metal center formed by coordination of three pyrazole ligands, two acetate groups and an NH_2 -group of the ligand of the neighboring molecule. In the IR-spectrum of the complex, the strong absorption at 1551 and 1526 cm^{-1} corresponds to the $\nu_{\text{as}}(\text{COO})$ vibration, whereas the other bands in this range (at 1588 and 1624 cm^{-1}) can be assigned to the $\nu(\text{C}=\text{N})$ and the $\delta(\text{NH}_2)$ vibrations of the ligand, respectively. The corresponding $\nu_{\text{s}}(\text{COO})$ band

Table 1
Some physico-chemical properties of the complexes

Complex	M g mol^{-1}	λ_{M}^* $\text{S cm}^2 \text{ mol}^{-1}$	Found (calculated), %		
			C	H	N
$[\text{Cd(OAc)}_2\text{L}_3] \cdot \text{H}_2\text{O}$	539.87	27.9^{a}	35.39 (35.59)	5.79 (5.41)	23.89 (23.35)
$[\text{Cd(NCO)}_2\text{L}_2(\text{H}_2\text{O})_2]$	426.72	insoluble	27.67 (28.14)	3.75 (4.25)	25.32 (26.26)
$[\text{Cd(NCS)}_2\text{L}_2]$	422.81	39.9^{b}	30.01 (28.40)	3.09 (3.34)	26.87 (26.51)
$[\text{CdCl}_2\text{L}_2]$	377.56	17.5^{b}	25.83 (25.45)	3.95 (3.74)	22.82 (22.26)
$[\text{CdSO}_4\text{L}_2] \cdot \text{H}_2\text{O}$	420.72	201.9^{c}	22.22 (22.84)	4.52 (3.83)	18.21 (19.97)

^a MeOH,

^b DMF,

^c H_2O

Table 2
Thermal decomposition data of the samples

Complex	Temperature range/K	Mass loss/%		Temperature range/K	Mass loss/%		Temperature range/K	Residue/%	
		found	calc.		found	calc.		found	calc.
[Cd(OAc) ₂ L ₃]·H ₂ O	410–480	46.0	45.25 ^a				580–750	21.0 ^b	23.82
[Cd(NCO) ₂ L ₂ (H ₂ O) ₂]	450–550	8.5	8.44	550–700	26.5	31.20	700–860	43.0	46.03
[Cd(NCS) ₂ L ₂]	—	—	—	450–630	22.0	22.97	630–930	61.0	54.05
[CdCl ₂ L ₂]	—	—	—	480–530	24.0	25.72	530–630	51.0	48.55
[CdSO ₄ L ₂]·H ₂ O	320–390	4.0	4.28				480–630	52.0	49.54
	Dehydration			–L			CdX ₂ , CdSO ₄		

^a According to the decomposition Scheme 1.

^b CdO.

appears ca. 1415 cm⁻¹ (overlapped with the $\nu(\text{C}=\text{C})$ mode of the pyrazole ring). The difference, $\Delta\nu=130\text{ cm}^{-1}$, between the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ bands suggests the existence of an acetate bridge. As the acetate groups are coordinated to the central atom through only one oxygen atom, the other oxygen atom from the acetate group forms hydrogen bonds with the hydrogens of the NH- and NH₂-groups of the pyrazole ring and water, which explains the appearance of the characteristic bands for an acetate bridge. The low

molar conductivity suggests that the acetate group is also coordinated in the solution [15].

The characteristic absorption bands of the NCO-group ($\nu_{\text{as}}(\text{NCO})$ at 2257 and 2176 cm⁻¹, $\nu(\text{NCO})$ at 1384 cm⁻¹, $\delta(\text{NCO})$ at 638 and 625 cm⁻¹) in the IR-spectrum of the Cd(NCO)₂·2H₂O complex are in

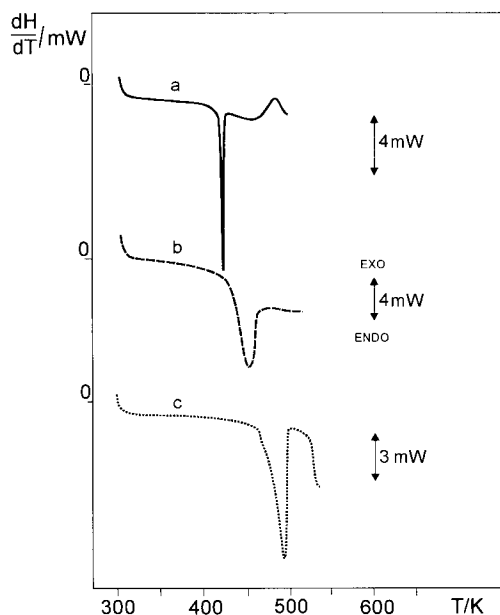


Fig. 1. DSC curves of the samples: (a) [Cd(NCS)₂L₂]; (b) [Cd(NCO)₂L₂(H₂O)₂]; and (c) [CdCl₂L₂].

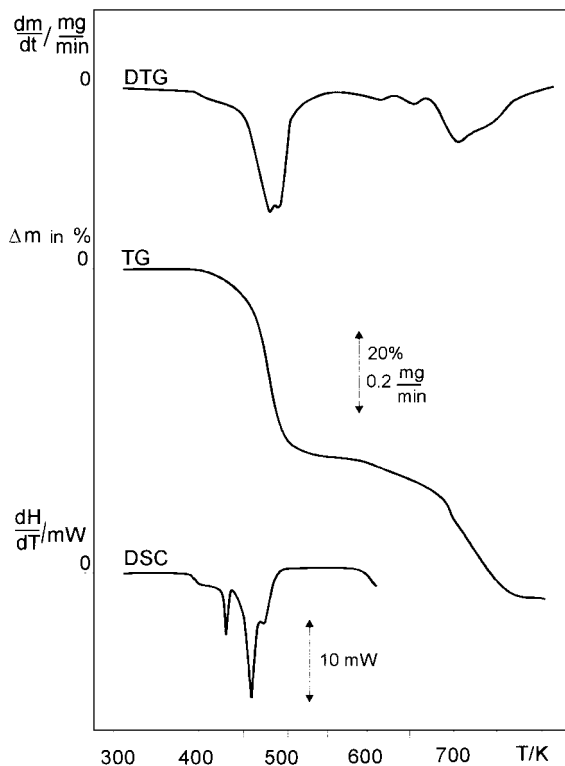


Fig. 2. TG, DTG and DSC curves for the [Cd(OAc)₂L₃]·H₂O complex.

agreement with literature data for the complexes with nitrogen as bonding atom [14]. The coordination of two ligands to the metal center suggests that the coordination number in this compound is four. However, the relatively high temperature of water evaporation (ca. 450 K) implies a coordination number of six.

The position of the $\nu(\text{CN})$ and $\nu(\text{CS})$ bands of the NCS-complex (2062 and 792 cm^{-1} , respectively) indicates that the NCS-group is coordinated through nitrogen [14] as in the case of the cadmium-thiocyanate complex with 3,5-dimethylpyrazole [16]. The value of the λ_{M} in DMF (Table 1) suggests that a partial dissociation of the complex takes place in the solution.

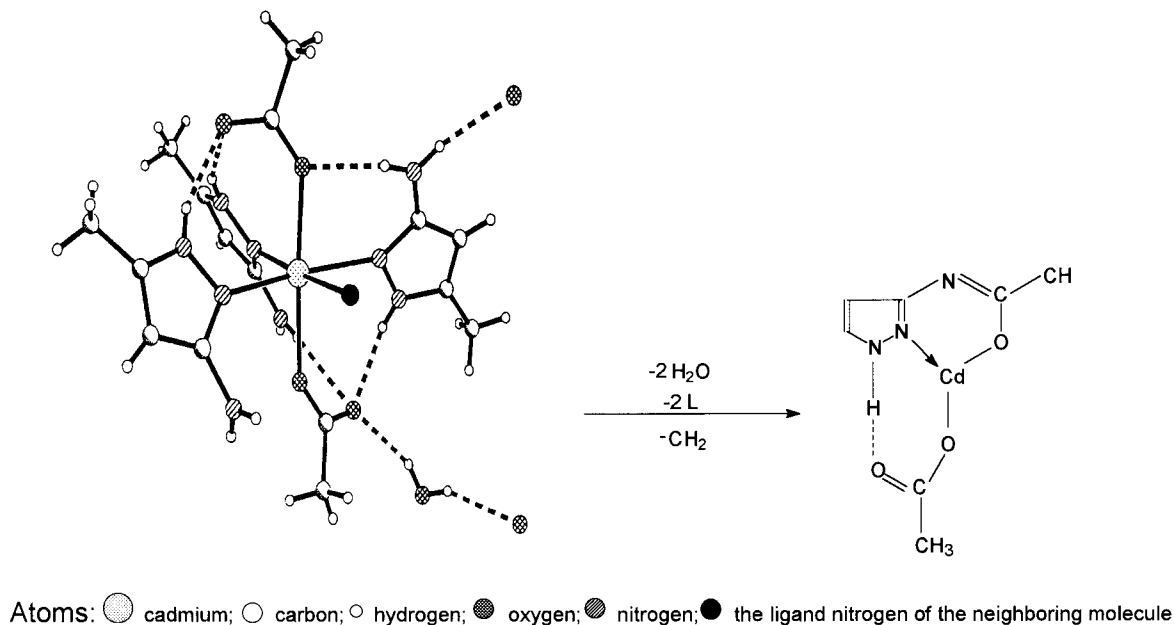
The broad, very strong and unresolved $\nu(\text{SO}_4)$ band at 1108 cm^{-1} along with another strong band at 618 cm^{-1} in the IR-spectrum of the sulfato-complex suggests the presence of an uncoordinated sulfate group [14]. The low temperature of water removal (ca. 330 K, Table 2) from this complex indicates the absence of its coordination. However, as the smallest coordination number for cadmium is four, irrespective of the character of the $\nu(\text{SO}_4)$ band, we supposed that the sulfate group is still coordinated as a bidentate ligand. The position and characteristics of the $\nu(\text{SO}_4)$

bands indicate also the presence of strong hydrogen bonding in the crystal with the uncoordinated oxygen atoms, which suggests that the original T_d symmetry of the sulfate ion in the complex has been preserved.

Spectral data and composition of the complexes suggest a tetrahedral configuration for the thiocyanato, sulfato and chloro compounds, while in the case of the acetato and cyanato complexes an octahedral geometry is apparent.

The thermal decomposition curves indicate involvement of different decomposition schemes, depending on the nature of the anion. The DSC curves (Figs. 1, 2 and 4) show a complex endothermic decomposition process for all the samples. The very sharp endotherm for the thiocyanato complex at 425 K is due to melting of the sample (Fig. 1(a)).

The thermogravimetric data of the compounds are presented in Table 2. Thermal decomposition of the acetato complex is accompanied by formation of an intermediate (Fig. 2). The decomposition starts at ca. 410 K with evaporation of the water which is followed immediately by elimination of two ligand molecules. In the 410–480 K interval, in addition to the dehydration and ligand elimination, an intramolecular amide formation and the loss of a methylene group from the



Scheme 1.

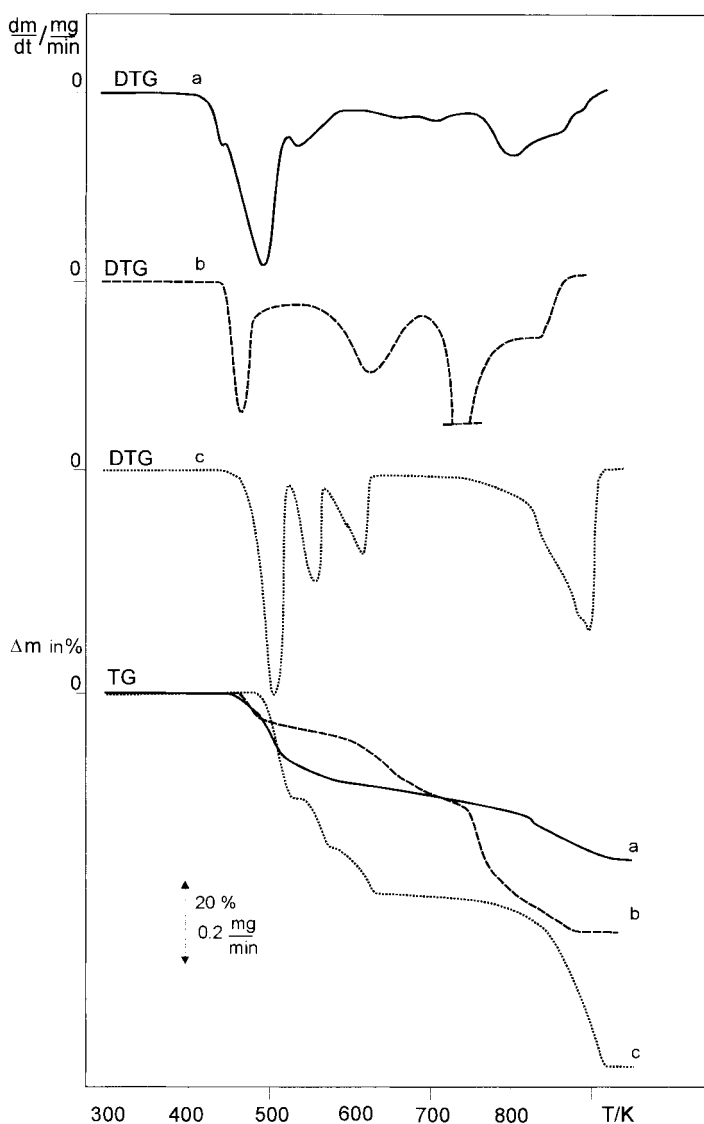


Fig. 3. TG and DTG curves of the samples: (a) $[\text{Cd}(\text{NCS})_2\text{L}_2]$; (b) $[\text{Cd}(\text{NCO})_2\text{L}_2(\text{H}_2\text{O})_2]$; and (c) $[\text{CdCl}_2\text{L}_2]$.

remaining ligand takes place. The total mass loss in this temperature range corresponds to the decomposition process shown in Scheme 1. The compound formed is stable over a 100 K range. The IR spectrum of the intermediate does not show the characteristic bands of the NH_2 -group, while the sharp absorption band at 3320 cm^{-1} indicates the presence of a ring NH -group. Also, several characteristic absorption bands of the pyrazole ring (e.g. 953 , 652 , 618 cm^{-1}) reveal that the intermediate contains at

least one ligand. The $\nu(\text{COO})$ bands of the acetate group (1526 and 1551 cm^{-1}) are still present. This means that the IR spectrum is consistent with the proposed decomposition scheme. The results of the elemental analysis of the intermediate compound also confirm the proposed composition of the intermediate (calculated for $\text{C}_7\text{H}_9\text{N}_3\text{O}_3\text{Cd}$ ($M_r=295.60$): C, 28.44; H, 3.07; N, 14.22%; found: C, 28.91; H, 3.72; N, 18.66%). The X-ray pattern of the intermediate refers to a crystalline product, but none of the known phases

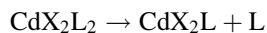
is matching with it. It indicates the appearance of a new phase at this stage of decomposition. Further decomposition at ca. 750 K results in CdO as final product (calc.: 23.78%; found: 21.0%).

The decomposition scheme for the other complexes involving a monovalent anion differs from that of the acetato complex. The TG and DTG curves of these compounds are presented in Fig. 3. In the cyanato complex, the thermal decomposition starts with evaporation of the water molecules at ca. 450 K. The high evaporation temperature suggests that the solvent molecules belong to the inner coordination sphere. The first minimum of the DTG curve corresponds to the water loss of 8.5%, which is in agreement with the supposed composition of the sample (calc., 8.44%). Further decomposition leads to another minimum on the DTG curve ca. 700 K, while at 860 K the decomposition is complete yielding Cd(NCO)₂ as an end product.

The thermal decomposition of the thiocyanato complex begins at a somewhat lower temperature than that of the cyanato complex. The mass loss up to the minimum on the DTG curve at 630 K amounts to 22.0%, involving at least three decomposition steps. The decomposition is completed at 930 K, with Cd(NCS)₂ being the end product.

The thermal decomposition of the chloro complex starts at a somewhat higher temperature (480 K). Above this temperature a rapid decomposition takes place in three well-separated steps. At ca. 630 K, the decomposition is completed with CdCl₂ as residue. Above 800 K, evaporation of chloride is observed.

As no stable intermediates are formed during the thermal decomposition of these compounds, it is difficult to give a decomposition scheme. The first mass loss, most probably, corresponds to the evaporation of one ligand molecule (L):



as in the case of copper(II)-complexes with pyrazole-type ligands [17]. In the case of the hydrate complex of cadmium–cyanate, this is the second decomposition step, assuming that the first step of the decomposition is the evaporation of water.

The decomposition of the sulfato complex (Fig. 4) begins with evaporation of water, almost at room temperature. The water content of the sample agrees with the composition given in Table 1. The dehy-

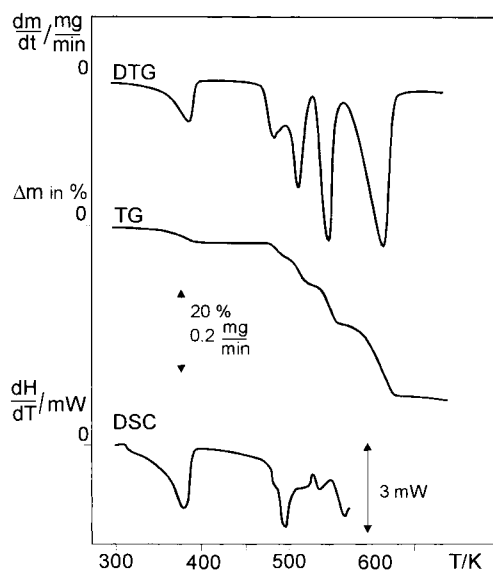


Fig. 4. TG, DTG and DSC curves for the [CdSO₄L₂]-H₂O complex.

drated sample is stable up to 480 K. Above this temperature a rapid decomposition proceeds in at least four steps. The decomposition is almost completed at 630 K. Above this temperature, the decomposition is very slow (0.03 mg min⁻¹). The final product is CdSO₄. A possible scheme for the cadmium sulfato complex decomposition may be deduced on the basis of decomposition of the Cu(II) and Co(II)-sulfato complexes with the same ligand, where an intermediate is formed [18]. It is possible that the decomposition of the dehydrated sulfato complex is also initiated by the formation of an N–H bridge, followed by a demethylation process.

4. Conclusion

The geometry of the investigated cadmium complexes with 3(5)-amino-5(3)-methylpyrazole depends on the steric factors determined by the anion: the thiocyanato, sulfato and chloro complexes have a tetrahedral geometry, whereas an octahedral geometry is characteristic for the acetato and cyanato complex. In the case of the hydrates, the first step of the decomposition is water evaporation. Thermal stability of the dehydrated complexes is approximately the

same for the complexes with the tetrahedral geometry (ca. 450 K). Thermal stability of the octahedral cyanato complex is significantly higher (ca. 550 K). In the case of the acetato complex, a stable intermediate compound forms. The decomposition of this intermediate also begins at a higher temperature (ca. 590 K) than in the case of the complexes with tetrahedral geometry.

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