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Optically Active Chromium(III) Complexes.
VII*. Chiroptical and Kinetic Properties of Chloro(1,5-diazahexane)(1,4,7-triazaheptane)chromium(III) Tetrachlorozincate(II), [CrCl(N-Me-tn)(dien)]ZnCl$_4$

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Abstract

One isomer of [CrCl(N-Me-tn)(dien)]ZnCl$_4$ has been isolated from the reaction of CrCl$_3$·6H$_2$O, dehydrated in DMF, with the polyamines N-methyl-1,3-diaminopropane and diethylenetriamine. This complex is isomorphous with ΔΛ-(R,S)-*usft*-[CoCl(N-Me-tn)(dien)]ZnCl$_4$ and thus has the *unsym-fac-* configuration with the N-Me group *trans* to the *sec*-NH group of the coordinated triamine. The Cr(III) complex has been resolved with NH$_4$BCS and the chiroptical parameters of $(-)_{488}$-[CrCl(N-Me-tn)(dien)]-ZnCl$_4$, derived from the less soluble diastereoisomeride by metathesis, are similar to those obtained for the less soluble $(-)_{534}$-Λ-(S)-*a,cb,edf*-Co(III) analogue, of known absolute configuration. Kinetic parameters for the rates of thermal aquation (μ = 1.0 M, HClO$_4$) and Hg^{2+}-assisted chloride release (μ = 1.0 M) for *usft*-[CrCl(N-Me-tn)(dien)]ZnCl$_4$ are $k_H = 3.7 \times 10^{-6}$ s^{-1}, $E_a = 93 \pm 8$ kJ mol^{-1}, $\Delta S_{298}{}^{\#} = -45 \pm 16$ J K^{-1} mol^{-1} and $k_{Hg} = 2.01 \times 10^{-3}$ M^{-1} s^{-1}, $E_a = 64.2 \pm 3.3$, $\Delta S_{298}{}^{\#} = -89.5 \pm 7$, respectively at 298 K.

Introduction

We have previously described Cr(III) complexes of the type CrCl(AA)(dien)$^{2+}$ where AA** is one of en, R,S-pn or tn [1, 2]. These complexes adopt the *sym-fac-* configuration [1] which is an achiral arrangement of the chelate rings. The introduction of an unsymmetrical bidentate diamine increases the number of potential geometric isomers to seven [3] and the CoCl(N-Me-tn)(dien)$^{2+}$ system exhibits a rich and complex pattern of stereochemical interconversions [4]†, although the *sym-fac-* configuration has not been detected.

Thus the CrCl(N-Me-tn)(dien)$^{2+}$ cation is of interest as, by analogy with the previous diamines, this may provide a *sym-fac-* isomer which is unknown in Co(III) chemistry. This expectation was not realised, and the isolated Cr(III) isomer has the *unsym-fac-* configuration with a chiral arrangement of the chelate rings.

Nomenclature

The nomenclature used is that recommended by the Commission on the Nomenclature of Inorganic Chemistry, *Pure Appl. Chem.*, *28*, 1 (1971), *i.e.* the octahedral letter locant system. The convention adopted is that the polyamine ligands are coordinated stepwise from one end and in the order of the alphabetical letters. The prefixed lower case letters refer to the position of the donor atoms in the octahedron (*a* and *f* in the axial positions and *bcde*, clockwise about the octahedral plane) in the order in which they are written in the cation formula (Fig. 1). For unsymmetrical polyamine ligands, the site with the lowest number according to organic practice of naming the ligand is given the first letter. Thus, the systematic organic nomenclature of N-methyl-1,3-diaminopropane (CH$_3$NHCH$_2$CH$_2$CH$_2$NH$_2$) as 1,5-diazahexane would assign the primary amine site to the first alphabetical letter.

The octahedral letter locant system is cumbersome when dealing with racemic transition-metal complexes, as the enantiomeric forms have different letter locant combinations. On the other hand, individual chiral forms can be precisely designated (Fig. 1) and in this situation the nomenclature is extremely useful. To avoid the proliferation of letter locants in describing the racemic forms of the two possible unsym-

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*Part VI is ref. 14.

**Abbreviations used: en = NH$_2$(CH$_2$)$_2$NH$_2$; R,S-pn = NH$_2$CH(CH$_3$)CH$_2$NH$_2$; tn = NH$_2$(CH$_2$)$_3$NH$_2$; N-Me-tn = CH$_3$NH(CH$_2$)$_3$NH$_2$; dien = NH$_2$(CH$_2$)$_2$NH(CH$_2$)$_2$NH$_2$; NH$_4$BCS = ammonium α-bromocamphor-π-sulfonate; DMSO = dimethyl sulfoxide; DMF = dimethylformamide.

†The absolute configuration of the methyl group is incorrectly assigned in the optically active complexes described in this paper [5].

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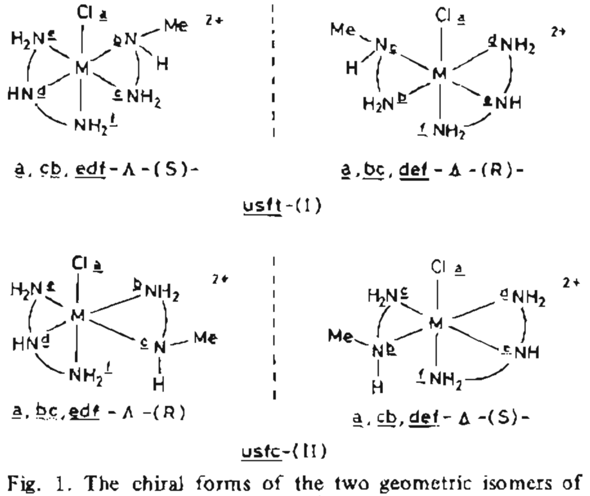

Fig. 1. The chiral forms of the two geometric isomers of *unsym-fac*-[MCl(*N*-Me-tn)(dien)]$^{2+}$ with the *N*-methyl group in the equatorial orientation.

metrical facial isomers of CrCl(*N*-Me-tn)(dien)$^{2+}$, the trivial abbreviation of *usft* will be used to describe the form with the two *sec*-NH donor groups in the *trans* arrangement (Fig. 1, I).

For optically active complexes, the sign of rotation, indicated by brackets, is for the sodium-D lines unless otherwise stated, e.g. $(-)_{488}$, and the sign of the CD will be indicated by braces at the appropriate wavelength, e.g. $\{-\}_{480}$.

Experimental

N-methyl-1,3-diaminopropane and diethylenetriamine were purchased from Fluka AG and used as supplied. All other chemicals were the best Reagent Grade available. The preparation of isomers of [CoCl(*N*-Me-tn)(dien)]ZnCl$_4$ used in this work has been previously described [4]. ORD and CD spectra were recorded in a 1.00 cm cell using a JASCO ORD/CD/UV-5 recording spectropolarimeter. Visible absorption spectra were recorded in matched 1.00 cm cells using a Varian DMS-100 recording spectrophotometer and the same instrument was used to determine the kinetic data. X-ray powder diffractograms were obtained using a Phillips PW-17 instrument.

Chloro(N-methyl-1,3-diaminopropane)(diethylenetriamine)chromium(III) Tetrachlorozincate(II), [CrCl(N-Me-tn)(dien)]ZnCl$_4$

A magnetically stirred mixture of hydrated chromium(III) chloride ($CrCl_3 \cdot 6H_2O$, 10 g) was dehydrated by boiling in DMF (50 ml) until a deep purple colour had developed and the volume was reduced to about 30 ml. The solution was allowed to cool to about 120 °C and *N*-methyl-1,3-diaminopropane (4 ml) was added to give a green solution (cooling to room temperature at this stage gives a green precipitate of unknown composition) and this was followed by a solution of diethylenetriamine (4 ml) in DMF (15 ml). A sticky purple oil formed and the mixture was reheated to boiling and then cooled to room temperature. The contents were dissolved in 300 ml of 6 M HCl containing 20 g of ZnCl$_2$ and the now purple solution was heated to 70 °C and then ice cooled. The solid that deposited (red crystals) was collected by filtration and washed successively with 2-propanol and ether and air dried. This was recrystallised by dissolving the solid in 0.1 M HCl at 60 °C (20 ml/1 g) and adding an equal volume of 12 M HCl and solid ZnCl$_2$ (2 g/1 g). The resulting crystalline solid (1.5 g, 8% yield) that formed from the ice cooled solution was washed and dried as above.

Variations on the above procedure, such as reversing the order of amine addition, varying the temperature at the time of amine addition or changing the solvent to DMSO, failed to improve the yield of product.

Anal. Calc. for $CrC_8H_{25}N_5ZnCl_5$: C, 19.66; H, 5.18; N, 14.41. Found: C, 19.70; H, 5.17; N, 14.41%.

Resolution of (±)-[CrCl(N-Me-tn)(dien)]ZnCl$_4$

The method of resolution was similar to that used for the corresponding Co(III) isomer (isomer V, [4]). The racemate and NH$_4$BCS (0.5 g each) were separately dissolved in 30 ml of H$_2$O at room temperature. Evaporation of the mixture under an air stream for 2 h produced a crystalline deposit of the less soluble diastereoisomeride (associated with the $(-)_{488}$ cation) and this was converted to $(-)_{488}$-[CrCl(*N*-Me-tn)(dien)]ZnCl$_4$ (0.2 g) by metathesis, following the above recrystallisation procedure. A second crop (0.05 g) of the less soluble BCS$^-$ salt, with the same chiroptical parameters, was obtained from the mother liquor overnight. An equal volume of 2-propanol was then added to the mother liquor and the $(+)_{488}$ ZnCl$_4$ salt (37% optically pure) deposited over 24 h. Addition of HCl (12 M) and ZnCl$_2$ gave a final crop of the inactive ZnCl$_4{}^{2-}$ salt. ORD, CD and visible absorption spectra were recorded in 0.1 M HClO$_4$ and the chiroptical parameters (Table I) were calculated from the visible absorption spectral parameters obtained for the racemate.

Similar data were obtained for (+)-Cr(*N*-Me-tn)(dien)(OH$_2$)$^{3+}$, by dissolving the $(-)_{488}$ chloro complex in 0.76 M HClO$_4$ containing 9.34×10^{-2} M Hg(NO$_3$)$_2$, and recording the spectra after 24 h at room temperature.

X-ray powder diffractograms of the racemic and enantiomeric [MCl(*N*-Me-tn)(dien)]ZnCl$_4$ salts (M = Co, isomer V [4]; M = Cr) show that all six are isomorphous (Table II).

TABLE I. Chiroptical Parameters for Λ-(*S*)-MX(*N*-Me-tn)(dien)$^{n+}$, (Fig. 1, I)

VIS λ (nm); ε (M^{-1} cm^{-1})		ORD λ (nm); [M] (deg M^{-1} m^{-1})		CD λ (nm); Δε (M^{-1} cm^{-1})	
M = Co, X = Cl, n = 2 (VIS^{a,b}, ORD^{c,b}, CD^{a,b})					
542max;	82.1	618;	+533	537;	+0.705
500sh;	~70	594;	0	530;	0
432min;	22.6	534;	−3360	480;	−0.785
375max;	112	472;	0	450sh;	~ −0.12
		448;	+661	385;	0
		410;	+101	355;	+0.336
		386;	+375	320;	0
		373;	0		
M = Co, X = H_2O, *n* = 3 (VIS^{a,d}, ORD and CD^{e,f})					
500max;	91.5	589;	+590	500;	+0.792
415min;	21.1	536;	+1320	458;	0
355max;	122	506;	0	435;	−0.16
		477;	−2470	405;	−0.11
		416;	−576	380;	−0.155
		400;	−667	345;	0
		355;	0		
		320;	−515		
M = Cr, X = Cl, *n* = 2^{e,b}					
521max;	66.6	589;	+220	530;	+0.242
480sh;	~50	555;	0	488;	0
436min;	25.8	488;	−1330	447;	−0.418
380max;	85.9	455;	0	395sh;	~ −0.05
		420;	+526	384;	0
		400;	+442	358;	+0.224
		385;	+526	300;	0
		355;	0		
		335;	−663		
M = Cr, X = H_2O, *n* = 3^{e,f}					
481max;	72.9	589;	+125	520;	−0.292
415 min;	23.4	496;	+2440	501;	0
361max;	67.7	470;	0	468;	+1.04
		440;	−2000	418;	0
		380sh;	~ −870	400sh;	~ −0.07
		340;	−187	360;	−0.218
				300;	0

[a] Ref. 4. [b] In 0.1 M $HClO_4$. [c] Ref. 15. [d] In 1.0 M $HClO_4$, 2 × 10^{-2} M $Hg(NO_3)_2$. [e] This research. [f] In 0.76 M $HClO_4$, 9.34 × 10^{-2} M $Hg(NO_3)_2$.

Kinetics

The techniques for measuring the rate of loss of the chloro ligand from [CrCl(*N*-Me-tn)(dien)]ZnCl$_4$, both thermally (1.0 M HClO$_4$) and Hg^{2+} assisted (μ = 1.0 M) have been described previously [6]. Both reactions developed excellent isosbestic points at 508, 430 and 365 nm and gave the same final visible absorption spectrum which corresponds to Cr(*N*-Me-tn)(dien)(OH$_2$)$^{3+}$. Pseudo first-order rate constants were calculated from the rate of change of absorbance with time at 380 nm and activation parameters were computer calculated from the variation of k_H (s^{-1}) or k_{Hg} (M^{-1} s^{-1}) with temperature [7].

Results and Discussion

ΔΛ-(*R*,*S*)-[CrCl(*N*-Me-tn)(dien)]ZnCl$_4$ has been isolated in low yield from the reaction of CrCl$_3$·6H$_2$O (dehydrated in DMF) with *N*-Me-tn and dien. This complex is isomorphous with ΔΛ-(*R*,*S*)-*usft*-[CoCl(*N*-Me-tn)(dien)]ZnCl$_4$, one of the six known geometric isomers for the Co(III) system [4], and

TABLE II. Selected X-ray Powder Diffraction Data (2θ Values)[a]

Cr[b]	Co[c]
12.2vs	12.2s
13.5m	13.5m
15.7s	15.5s
16.9m	16.7m
17.2w	17.2m
19.2vw	19.4vw
19.9m	19.9m
21.2m	21.3m
22.0m	22.0w
22.9m	23.0w
23.7w	23.7m
24.5m	24.7m
25.1m	25.3m
27.3m	27.6m
28.7w	28.8w
29.3w	29.4w
31.2m	31.4m
33.0w	33.3w
36.8w	37.0w

[a] Abbreviations used: vs = very strong, s = strong, m = medium, w = weak, vw = very weak. [b] $(-)_{488}$-[CrCl(*N*-Me-tn)(dien)]$ZnCl_4$. Similar data are observed for the $(+)_{488}$- and (±)-$ZnCl_4^{2-}$ salts. [c] (±)-(*R*,*S*)-*usft*-[CoCl(*N*-Me-tn)(dien)]$ZnCl_4$. Similar data are observed for the $(-)_{534}$- and $(+)_{534}$-$ZnCl_4^{2-}$ salts.

thus has the *unsym-fac-* configuration with the *N*-Me group of the diamine *trans* to the *sec*-NH group of the triamine (Fig. 1, I). The Cr(III) complex has been resolved with NH_4BCS and the optically active $ZnCl_4^{2-}$ salt obtained from the less soluble diastereoisomeride is again isomorphous with the corresponding Co(III) analogue. Indeed, $ZnCl_4^{2-}$ salts of the racemates and the enantiomers are isomorphous for both Co(III) and Cr(III). This suggests that the racemates are equimolar mixtures of crystals of the Λ-(*S*)- and Δ-(*R*)- forms, technically known as 'conglomerates' [8], as the single crystal structure of the $ZnCl_4^{2-}$ salt from the less soluble Co(III) BCS diastereoisomeride has been determined as Λ-(*S*)- [5]. We note that the possible Λ-(*R*)- or Δ-(*S*)- forms both have the methyl group in the unfavourable axial orientation.

Table I lists the measured chiroptical parameters for the analogous Cr(III) and Co(III) systems. The correspondence between the ORD (and CD) spectra of the $ZnCl_4^{2-}$ salts derived from the less soluble BCS^- salts indicate that the absolute configuration of $(-)_{488}$-[CrCl(*N*-Me-tn)(dien)]$ZnCl_4$ is the same as that for $(-)_{534}$-[CoCl(*N*-Me-tn)(dien)]$ZnCl_4$ *viz.*, Λ-(*S*)- [5]. The racemic-[CrCl(*N*-Me-tn)(dien)]$ZnCl_4$ is thus unique for Cr(III) in that the bidentate–tridentate ligand combination is arranged in the unsymmetrical facial configuration. All previously reported CrCl(bidentate)(tridentate)$^{2+}$ cations having the symmetrical facial arrangements [1, 2].

TABLE III. Pseudo-first-order Rate Constants for the Thermal Aquation of *usft*-CrCl(*N*-Me-tn)(dien)$^{2+}$ in 1.0 M $HClO_4$[a]

T (°C [K])	10^4 k_H(obs.) (s^{-1})	10^4 k_H(calc.)[b] (s^{-1})
64.0 [337.2]	2.99 ± 0.04 3.16 ± 0.15	2.97
69.6 [342.8]	4.83 ± 0.11 4.45 ± 0.16	4.93
75.5 [348.7]	9.09 ± 0.09	8.57

[a] Using the $ZnCl_4^{2-}$ salt. [b] Calculated from the activation parameters cited in Table IV.

Although the kinetics of both the thermal and Hg^{2+}-assisted chloride release reactions of *usft*-CrCl(*N*-Me-tn)(dien)$^{2+}$ have been measured (Tables III–VI) it is difficult to decide if the approximately 10-fold decrease in reaction rate, relative to other CrCl(bidentate)(tridentate)$^{2+}$ complexes, is due to the change in stereochemistry or the introduction of the *N*-Me group. In terms of the generally accepted more associative nature for the mechanism of aquation of Cr(III) complexes [9] we suspect the latter effect is more pronounced. For Co(III) systems, where more isomers are available, *usf* complexes generally aquate more rapidly than the *sf* analogues. Consequently, if the same trends were to continue for Cr(III), we would expect the present *usf* system to aquate more rapidly than the *sf* analogues, which is opposite to that observed.

The introduction of *N*-Me substituents has a pronounced effect for $MCl(MeNH_2)_5^{2+}$ systems relative to $MCl(NH_3)_5^{2+}$ and the change in relative rates is one of the major pieces of experimental evidence in support of a more associative aquation mechanism for Cr(III), [3] assuming a dissociative mechanism for Co(III).

Data from systems with less *N*-Me substitution are more ambiguous. *trans*-$CoCl_2$(*N*-Me-en)$_2^+$ aquates about 2X more slowly than *trans*-$CoCl_2(en)_2^+$ [10] and there is a slight decrease in aquation rate for *usft*- or *usfc*-CoCl(*N*-Me-tn)(dien)$^{2+}$ relative to *usf*-CoCl(tn)(dien)$^{2+}$ [4].

We have argued previously [11] that, assuming a dissociative mechanism, the relative rates of aquation of $CoCl(N_5)^{2+}$ complexes can be correlated with the ease of distortion of the N_5 polyamine systems to a trigonal bipyramid intermediate. Consequently *N*-Me substitution appears to have little influence on the chelate ring deformations required to affect the change.

However, *N*-Me substitution is expected to have an inhibitory effect for a more associative mechanism,

TABLE IV. Activation Parameters for the Thermal Aquation of some MCl(N$_5$)$^{2+}$ Complexes (μ = 1.0 M) at 298.2 K

M	N$_5$	Configuration	$10^6\ k_H$ (s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ (J K^{-1} mol^{-1})	Reference
Cr	(NH$_3$)$_5$		9.5	89.3	−50	a
Cr	(MeNH$_2$)$_5$		0.63	97	−47	a
Cr	(en)(dien)	*sf*	22.4	89.2	−43	a
Cr	(*R*,*S*-pn)(dien)	*sf*	19.2	93.7	−29	a
Cr	(tn)(dien)	*sf*	21.8	91.0	−37	a
Cr	(*N*-Me-tn)(dien)	*usft*	3.7	93 ± 8	−45 ± 16	b, e
Co	(NH$_3$)$_5$		1.76	96.7	−39	a
Co	(MeNH$_2$)$_5$		36.7	91.8	−30	a
Co	(en)(dien)	*sf*	0.094	113	−7	a
		usf	0.256	110	−8	c
Co	(tn)(dien)	*sf*	0.216	110	−10	a
		usf	4.30	73	−111	c
Co	(*N*-Me-tn)(dien)	*usft*	3.07	107	+3	d, e
		usfc	3.34	97	−33	d, f

[a] Ref. 2. [b] This research. [c] Ref. 6. [d] Ref. 4. [e] *usft*-isomer (Fig. 1, I). [f] *usfc*-isomer (Fig. 1, II).

TABLE V. Observed and Calculated Rate Constants for the Hg^{2+}-assisted Aquation of *usft*-[CrCl(dien)(*N*-Me-tn)]ZnCl$_4$ (μ = 1.0 M)

T (°C[K])	[H$^+$] (M)	[Hg^{2+}]$_i$ [a] (mM)	$10^4\ k_{obs}$ [b] (s^{-1})	$10^3\ k_{Hg}$ [c] (M^{-1} s^{-1})	$10^3\ k_{Hg}$(calc.) [d] (M^{-1} s^{-1})
25.0[298.2]					2.01
33.9[307.1]	0.76	93.4	4.01 ± 0.16	4.29 ± 0.17	4.26
38.2[311.4]	0.76	93.4	5.55 ± 0.06	5.94 ± 0.06	6.03
42.4[315.6]	0.76	93.4	7.92 ± 0.08	8.84 ± 0.09	8.39
48.4[321.6]	0.76	93.4	11.8 ± 0.3	12.6 ± 0.3	13.2
	0.76	93.4	11.9 ± 0.07	12.7 ± 0.08	
	0.82	64.5	9.38 ± 0.04	14.5 ± 0.06	

[a] Initial Hg^{2+} concentration as Hg(NO$_3$)$_2$. Initial [Cr(III)] ~2.10 mM. [b] Observed pseudo-first-order rate constant measured at 380 nm. [c] $k_{Hg} = k_{obs}[Hg^{2+}]_i^{-1}$. [d] Calculated from the activation parameters cited in Table VI.

TABLE VI. Activation Parameters for the Hg^{2+}-assisted Chloride Release from some MCl(N$_5$)$^{2+}$ Complexes (μ = 1.0 M) at 298.2 K

M	N$_5$	Configuration	$10^2\ k_{Hg}$ (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S_{298}^{\#}$ (J K^{-1} mol^{-1})	Reference
Cr	(NH$_3$)$_5$		8.73[a]	62	−56	a
Cr	(en)(dien)	*sf*	2.36			b
Cr	(*R*,*S*-pn)(dien)	*sf*	2.26			b
Cr	(tn)(dien)	*sf*	2.16			b
Cr	(*N*-Me-tn)(dien)	*usft*	0.201	64.2 ± 3.3	−89 ± 7	c, f
Co	(NH$_3$)$_5$		12.2			b
Co	(en)(dien)	*sf*	0.495			b
		usf	1.49	58	−93	d
Co	(*R*,*S*-pn)(dien)	*sf*	0.448			b
Co	(tn)(dien)	*sf*	4.74			b
		usf	12.6	64	−56	e

[a] Ref. 16; (μ = 2.0 M). This value is incorrectly cited in Table III of ref. 2. [b] Ref. 2. [c] This research. [d] Ref. 6. [e] Ref. 17. [f] *usft*-isomer (Fig. 1, I).

and this is precisely what is observed for *usft*-CrCl(*N*-Me-tn)(dien)$^{2+}$ relative to *sf*-CrCl(tn)(dien)$^{2+}$, where the rate decreases by a factor of 6 for the thermal aquation and 11 for the Hg^{2+}-assisted aquation.

The extensive data available for both the thermal and Hg^{2+}-assisted chloride release reactions [12] of CoCl(N)$_5$$^{2+}$ systems has allowed a linear correlation of k_H with k_{Hg}, *viz.*, $\log k_{Hg} = 0.96 \log k_H + 4.36$ at 298.2 K [13]. No such correlation appears to exist for the five CrCl(N)$_5$$^{2+}$ systems where comparisons are available, but more data are needed.

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