



**SCHIFF BASES OF 3-[2-(1,3-BENZOTHAZOL-2-YL)HYDRAZINYLDENE]
PENTANE-2,4-DIONE WITH ALIPHATIC DIAMINES AND THEIR METAL
COMPLEXES**

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Received March 25, 2009. In final form August 8, 2009.

Abstract

The condensation of aliphatic diamines [1,2-diaminoethane, 1,3-diaminopropane and 1,6-diaminohexane] with 3-[2-(1,3-benzothiazol-2-yl) hydrazinylidene]pentane-2,4-dione under specified conditions yielded a new series of polydentate Schiff base ligands. Analytical, IR, ¹H NMR and mass spectral data showed the existence of the compounds predominantly in the intramolecularly hydrogen bonded keto-imine form. Dibasic tetradentate N₄ coordination of the compounds in their [ML] complexes [M = Ni(II), Cu(II) and Zn(II)] has been established on the basis of analytical and spectral data.

Keywords: 3-[2-(1,3-benzothiazol-2-yl)hydrazinylidene]pentane-2,4-dione; Schiff base; keto-imine; metal complexes

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Resumen

La condensación de diaminas alifáticas [1,2-diaminoetano, 1,3-diaminopropano y 1,6-diamino hexano] con 3-[2-(1,3-benzotiazol-2-il)hidrazinilideno]pentano-2,4-diona produjo bajo condiciones específicas una serie nueva de ligandos polidentados tipo bases de Schiff. Los datos analíticos y espectrales (IR, ^1H NMR y masas) mostraron la existencia de los productos predominantemente en la forma ceto-imina unida por enlace hidrógeno intramolecular. Sobre la base de los datos analíticos y espectrales se estableció la coordinación bibásica tetradentada N_4 en sus complejos [ML], con $\text{M} = \text{Ni(II)}$, Cu(II) y Zn(II) .

Palabras clave: 3-[2-(1,3-benzotiazol-2-il)hidrazinilideno]pentano-2,4-diona; bases de Schiff; ceto-imina; complejos metálicos

Introduction

Arylazo derivatives of 1,3-diketones have gained considerable importance in recent years because of their application in the laboratory as acid-base, redox, metallochromic and other indicators [1-3], as stains for bacteriological and histological investigations [2,4,5], and in the study of acid-base equilibrium and acidity constant values [2,6]. Although the coordination compounds of Schiff bases of 1,3-diketones have been extensively studied [7-10], reports are scanty on Schiff bases derived from arylazo derivatives of 1,3-diketones. As part of our investigation on arylazo derivatives of 1,3-diketones and their metal complexes [11-15], we report herein the synthesis and characterization of a new series of Schiff bases produced from 3-[2-(1,3-benzothiazol-2-yl)hydrazinylidene]pentane-2,4-dione with aliphatic diamines; 1,2-diaminoethane, 1,3-diaminopropane and 1,6-diaminohexane. Typical metal complexes of these ligand systems were also studied.

Experimental

Methods and instruments

Carbon, hydrogen and nitrogen percentages were determined by microanalyses (Heraeus Elemental analyzer) and metal contents of complexes by AAS (Perkin Elmer 2380). The electronic spectra of the compounds were recorded in methanol solution (10^{-4} M) on a 1601 Shimadzu UV-Vis. spectrophotometer, IR spectra (KBr discs) on an 8101 Shimadzu FTIR spectrophotometer, ^1H NMR spectra (CDCl_3 or DMSO-d_6) on a Varian 300 NMR spectrometer and mass spectra on a Jeol/SX-102 mass spectrometer (FAB using Argon and *meta*-nitrobenzyl alcohol as the matrix). Molar conductance of the complexes was determined in DMF at $28 \pm 1^\circ\text{C}$ using solution of about 10^{-3} M concentration. Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance.

Synthesis of the diazonium salt of 2-aminobenzothiazole

To a solution of NaNO_2 (1.4 g) in H_2SO_4 (12 M, 20 mL), kept cooled below 5°C , a cooled ($\sim 5^\circ\text{C}$) solution of 2-aminobenzothiazole (1.5 g, 0.01 mol) in 15 mL DMF was added slowly with stirring. Stirring was continued for ~ 1 h and filtered to get the clear yellow diazonium salt solution [16].

Synthesis of 3-[2-(1,3-benzothiazol-2-yl)hydrazinylidene]pentane-2,4-dione

After destroying the excess nitrous acid with urea, the diazonium salt solution was added drop by drop with stirring to an ice-cold ($< 5^\circ\text{C}$) solution of acetylacetone (0.01 mol, 20 mL ethanol). Cooled ($< 5^\circ\text{C}$) NaOH solution (1 M, 20 mL) was added drop-wise to adjust the pH of the mixture around 5. Stirring was continued for about half an hour and the precipitated compound was

filtered, washed several times with water and recrystallized twice from hot methanol to get chromatographically (TLC) pure compound [Yield: 75%; M.P.: 192°C; elemental analysis (found/calcd.): C (55.28/55.17), H (4.19/4.21), N (15.98/16.09); UV (λ_{\max} , nm): 280, 385; IR (cm^{-1}): 3500-2500 (hydrogen bonded NH), 1676 (conjugated free carbonyl), 1645 (chelated carbonyl), 1620, 1605 (C=N), 1270 (C-N); ^1H NMR (δ , ppm): 14.25 (NH, singlet, broad), 6.80-7.35 (aryl, multiplet), 2.58 (CH_3 , singlet), 2.35 (CH_3 , singlet). The compound is crystalline in nature and is soluble in common organic solvents.

Synthesis of Schiff bases, H_2bte , H_2btp and H_2bth

An ethanolic solution of the diamine (0.01 mol in 20 mL) was added to an ethanolic solution of 3-[2-(1,3-benzothiazol-2-yl)hydrazinylidene]pentane-2,4-dione (0.02 mol, 20 mL) and stirred for ~5 h in a closed vessel maintaining the temperature at 60-65°C. Evaporated at reduced pressure and the crystalline compound formed was filtered. The solid was recrystallized from hot methanol to get chromatographically (TLC) pure compound.

Synthesis of Ni(II), Cu(II) and Zn(II) complexes

An ethanolic solution of metal(II)acetate (0.01 mol, 20 mL) was added to an ethanolic solution of the ligand (0.01 mol, 20 mL) and the mixture refluxed on a water bath for ~2 h. The solution was kept overnight at room temperature and added to crushed ice, containing ~1 g sodium acetate to maintain the pH around 6. The precipitated complex was filtered, washed with excess of water, recrystallized from hot ethanol and dried in vacuum.

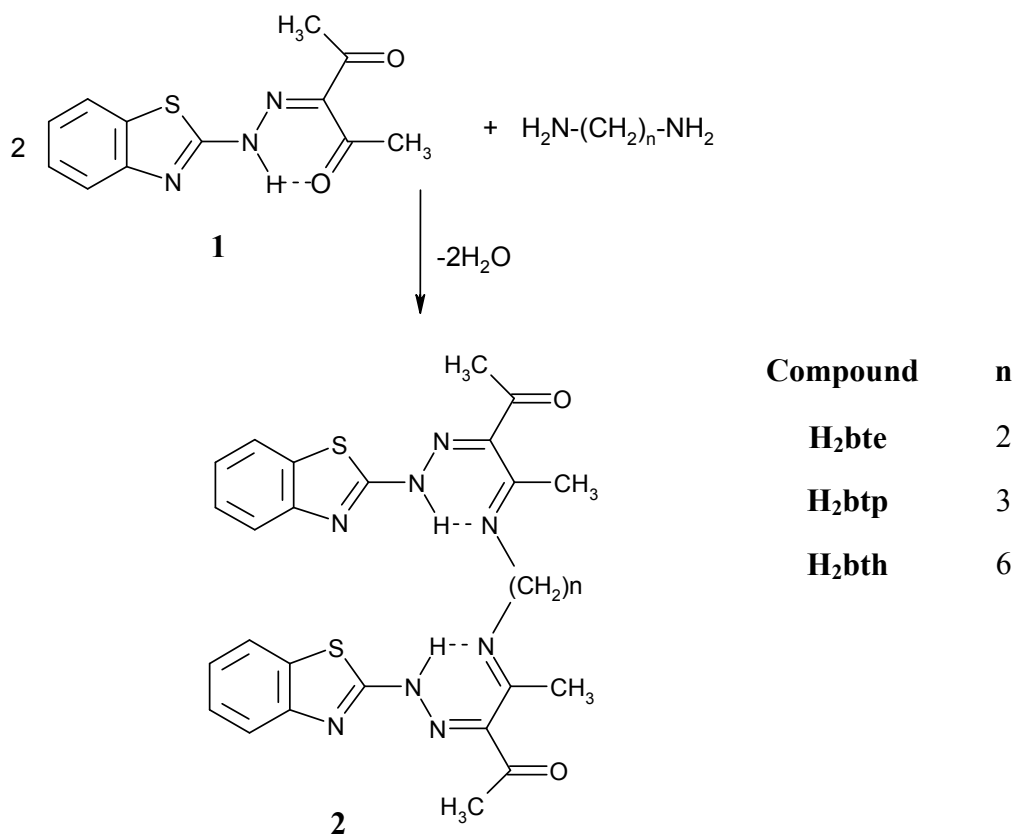
Results and Discussion

The Schiff bases H_2bte , H_2btp and H_2bth are formed in good yield by the condensation of 3-[2-(1,3-benzothiazol-2-yl)hydrazinylidene]pentane-2,4-dione (structure **1**) with 1,2-diaminoethane, 1,3-diaminopropane and 1,6-diaminohexane. Elemental analytical data (Table 1) of the compounds suggest that the condensation of 3-[2-(1,3-benzothiazol-2-yl)hydrazinylidene]pentane-2,4-dione with diamines occurred in the 2:1 ratio as in structure **2** (Scheme 1). The compounds are crystalline in nature and are soluble in common organic solvents. They formed well defined and crystalline complexes with Ni(II), Cu(II) and Zn(II) ions. The analytical data (Table 1) together with non-electrolytic nature in DMF (specific conductance $<10\Omega^{-1}\text{cm}^{-1}$; 10^{-3} M solution) suggest [ML] stoichiometry of the complexes. The Ni(II) and Zn(II) chelates are diamagnetic while Cu(II) complexes showed normal paramagnetic moment. The observed electronic, IR, ^1H NMR and mass spectral data of the complexes are fully consistent with structure **3** (Scheme 2).

Infrared spectra

The IR spectra of the Schiff bases in the 1600-1800 cm^{-1} region showed four strong bands at ~1670, 1630, 1620 and 1615 cm^{-1} . The band at ~1670 cm^{-1} is due to conjugated free acetyl carbonyl [17]. The remaining three bands are due to C=N of hydrazone, imine and benzothiazole groups [18]. A prominent band appeared at ~1540 cm^{-1} is due to NH deformation vibration. Several medium intensity bands appeared in the 1580-1600 cm^{-1} region of the spectra are due to the stretching of various C=C vibrations. That the compounds exist in the intramolecularly hydrogen bonded form [19] as in structure **2** is clearly evident from the broad band appeared in the region 2300-3500 cm^{-1} . In the IR spectra of all the complexes the strong band at ~1670 cm^{-1} due to conjugated free acetyl carbonyl group of the ligand remain unaffected indicating its non-involvement in complexation. The strong band at ~1620 cm^{-1} of the free ligand due to $\nu\text{C}=\text{N}$ (imine) shifted to low wave number and appeared as a prominent band in the 1550-1600 cm^{-1} region. The hydrazone and benzothiazole

$\nu\text{C}=\text{N}$ are only marginally affected in the spectra of all the complexes. These indicate that the imine and one of the hydrazone nitrogens are involved in bonding with the metal ion [20] as in structure **3**. The replacement of the NH proton by metal ion is clearly indicated from the disappearance of the NH deformation band of the free ligand at $\sim 1540\text{ cm}^{-1}$ in the spectra of all the complexes. The broad band in the region $2300\text{--}3500\text{ cm}^{-1}$ cleared up in the spectra of all the complexes confirming the replacement of the hydrogen bonded NH proton by metal ion. The presence of new medium intensity bands appeared in the $500\text{--}550\text{ cm}^{-1}$ region assignable to $\nu\text{M}\text{--}\text{N}$ in the spectra of all the complexes [19] also support structure **3**. Since the spectra of all the complexes are of similar nature only important bands that appeared in the spectra of the Schiff bases and their Cu(II) complexes are given in Table 2.



Scheme 1

¹H NMR spectra

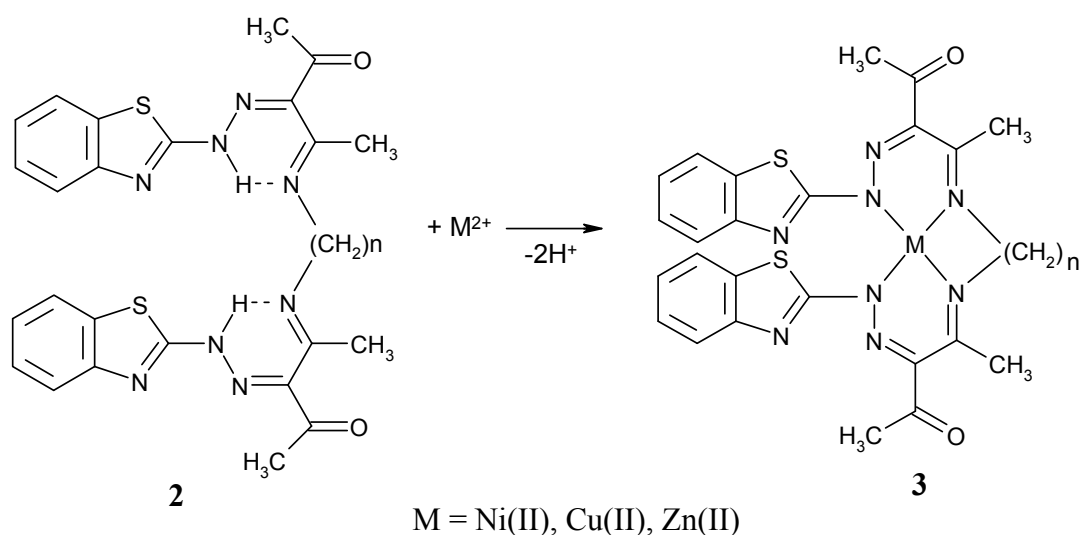
In the ¹H NMR spectra of the Schiff bases no signals were observed above $\delta 10$ ppm assignable to intramolecularly hydrogen bonded $\text{N}\text{--}\text{H}\dots\text{O}=\text{C}/\text{O}\text{--}\text{H}\dots\text{N}$ groups of the keto-hydrazone/ azo-enol forms typical of arylazo derivatives of acetylacetone [12-15]. The spectra of all the compounds show a two proton signal at $\sim \delta 9.50$ ppm due to the intramolecularly hydrogen bonded $\text{N}\text{--}\text{H}\dots\text{N}$ protons [21]. The methylene proton signals are observed at $\delta 2.80\text{--}3.95$ ppm. The benzothiazolyl protons appear in the range $\delta 7.00\text{--}7.80$ ppm as a complex multiplet. The spectra showed two six-proton singlets at $\delta 2.20\text{--}2.60$ ppm due to methyl groups. The integrated intensities of all the signals agree well with the structure **2** of the compounds. In the ¹H NMR spectra of the diamagnetic Ni(II) and Zn(II) complexes, signal due to the NH protons of the free ligand disappeared indicating their replacement by metal ions. Integrated intensities of all other protons agree well with 1:1 metal-ligand stoichiometry of complexes as in structure **3** (Table 3).

Table 1. Physical and analytical data of **H₂bte**, **H₂btP**, **H₂bth** and their metal complexes

Compound/ Empirical formula	Yield %	M.P. °C	Elemental Analysis: Found (Calculated)%			
			C	H	N	M
H ₂ bte C ₂₂ H ₂₄ N ₈ O ₂ S ₂	72	102	53.48 (53.23)	4.82 (4.84)	22.68 (22.58)	-
H ₂ btP C ₂₃ H ₂₆ N ₈ O ₂ S ₂	70	98	53.98 (54.12)	5.16 (5.10)	22.18 (21.96)	-
H ₂ bth C ₂₆ H ₃₂ N ₈ O ₂ S ₂	68	112	56.48 (56.52)	5.74 (5.80)	20.20 (20.29)	-
[Ni(bte)] C ₂₂ H ₂₂ N ₈ NiO ₂ S ₂	70	238	47.70 (47.76)	3.94 (3.98)	20.19 (20.26)	10.52 (10.62)
[Ni(btP)] C ₂₃ H ₂₄ N ₈ NiO ₂ S ₂	72	266	48.94 (48.70)	4.22 (4.23)	19.82 (19.76)	10.44 (10.36)
[Ni(bth)] C ₂₆ H ₃₀ N ₈ NiO ₂ S ₂	68	202	51.34 (51.23)	5.02 (4.93)	18.12 (18.40)	9.60 (9.64)
[Cu(bte)] C ₂₂ H ₂₂ CuN ₈ O ₂ S ₂	72	288	47.68 (47.35)	3.94 (3.95)	20.32 (20.29)	11.42 (11.40)
[Cu(btP)] C ₂₃ H ₂₄ CuN ₈ O ₂ S ₂	70	268	48.51 (48.29)	4.21 (4.20)	19.35 (19.60)	11.28 (11.12)
[Cu(bth)] C ₂₆ H ₃₀ CuN ₈ O ₂ S ₂	66	278	50.71 (50.85)	4.91 (4.89)	18.05 (18.25)	10.34 (10.36)
[Zn(bte)] C ₂₂ H ₂₂ N ₈ O ₂ S ₂ Zn	74	198	47.36 (47.20)	3.91 (3.93)	19.92 (20.02)	11.61 (11.69)
[Zn(btP)] C ₂₃ H ₂₄ N ₈ O ₂ S ₂ Zn	70	210	48.28 (48.14)	4.12 (4.19)	19.30 (19.53)	11.64 (11.40)
[Zn(bth)] C ₂₆ H ₃₀ N ₈ O ₂ S ₂ Zn	68	214	50.98 (50.70)	4.82 (4.88)	18.06 (18.20)	10.74 (10.62)

Mass spectra

The mass spectra of all the compounds show the molecular ion peak corresponding to their formulation. Peaks due to the elimination of CH₃CO⁺ and benzothiazole groups from the molecular ion are observed in all the spectra [12,22]. The FAB mass spectra of the Cu(II) complexes showed molecular ion peaks of appreciable intensity corresponding to [CuL] stoichiometry. Peaks correspond to L⁺ and fragments of L⁺ are also present in the spectra. Other prominent peaks are due to the elimination of CH₃CO⁺ and benzothiazole groups from the parent ion. The spectra of all the chelates contain a number of fragments containing copper in the 3:1 natural abundance of ⁶³Cu and ⁶⁵Cu isotopes. Important fragments appeared in the spectra are given in Table 4.



Scheme 2

Table 2. Characteristic IR stretching frequencies (cm^{-1}) of **H₂bte**, **H₂btp**, **H₂bth** and their Cu(II) complexes.

Compound	C=O	C=N	M-N
H ₂ bte	1676	1632, 1622, 1617	-
[Cu(bte)]	1675	1627, 1616, 1572	555, 536
H ₂ btp	1678	1630, 1621, 1612	-
[Cu(btp)]	1674	1625, 1613, 1574	546, 535
H ₂ bth	1666	1625, 1616, 1612	-
[Cu(bth)]	1664	1620, 1617, 1566	528, 510

Electronic spectra

The UV spectra of the Schiff bases show two broad bands with maxima at ~ 370 nm and ~ 260 nm due to the various $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. In complexes these absorption maxima shifted appreciably to low wave numbers. The Cu(II) complexes showed a broad visible band, λ_{max} at $\sim 15,000$ cm^{-1} . This, together with the measured μ_{eff} values (~ 1.74 BM) suggests the square-planar geometry [23]. In agreement with this, spectra recorded in pyridine, a broad band centered at $\sim 11,000$ cm^{-1} was observed which indicates the formation of octahedral pyridine adducts. The observed diamagnetism and broad medium-intensity band at $\sim 17,500$ cm^{-1} in the spectra of the Ni(II) chelates suggest their square-planar geometry. In conformity, the spectra of the chelates in pyridine solution (10^{-3} M) showed three bands corresponding to configurational change to octahedral due to the association of pyridine. The three well-separated absorption bands at λ_{max}

$\sim 8,300$, $\sim 13,500$ and $\sim 24,300$ cm^{-1} correspond to the transitions; ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$; ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ respectively [8,24].

Table 3. ${}^1\text{H}$ NMR spectral data (δ , ppm) of H₂bte, H₂btp, H₂bth and their Ni(II) and Zn(II) complexes.

Compound	NH	Benzothiazolyl	(CH ₂) _n	CH ₃
H ₂ bte	9.49 (2H)	7.28-7.78 (8H)	3.85 (4H)	2.25 (6H) 2.47 (6H)
H ₂ btp	9.61 (2H)	7.20-7.72 (8H)	2.87 (2H) 3.82 (4H)	2.22 (6H) 2.57 (6H)
H ₂ bth	9.55 (2H)	7.32-7.76 (8H)	2.94-3.40 (12H)	2.35 (6H) 2.56 (6H)
[Ni(bte)]	-	7.22-7.68 (8H)	3.92 (4H)	2.29 (6H) 2.54 (6H)
[Ni(btp)]	-	7.28-7.70 (8H)	2.91 (2H) 3.87 (4H)	2.28 (6H) 2.58 (6H)
[Ni(bth)]	-	7.24-7.66 (8H)	2.98-3.46 (12H)	2.37 (6H) 2.60 (6H)
[Zn(bte)]	-	7.22-7.70 (8H)	3.88 (4H)	2.26 (6H) 2.56 (6H)
[Zn(btp)]	-	7.20-7.70 (8H)	2.93 (2H) 3.84 (4H)	2.28 (6H) 2.57 (6H)
[Zn(bth)]	-	7.26-7.64 (8H)	3.04-3.45 (12H)	2.36 (6H) 2.67 (6H)

Conclusions

Three new Schiff base ligands have been prepared by the condensation of 3-[2-(1,3-benzothiazol-2-yl)hydrazinylidene]pentane-2,4-dione with 1,2-diaminoethane, 1,3-diaminopropane and 1,6-diaminohexane. Analytical, IR, ${}^1\text{H}$ NMR and mass spectral data revealed a 2:1 product in which one of the carbonyl group of the diketone is involved in Schiff base formation. Analytical, physical and spectral data of the [ML] complexes of Ni(II), Cu(II) and Zn(II) showed the dibasic tetradentate N₄ coordination involving the imino and hydrazone nitrogens while the carbonyl groups are excluded from coordination.

Table 4. Mass spectral data of **H₂bte**, **H₂btp**, **H₂bth** and their Cu(II) complexes.

Compound	Mass spectral data (m/z)
H ₂ bte C ₂₂ H ₂₄ N ₈ O ₂ S ₂	496, 453, 410, 362, 319, 276, 228, 185, 142, 134
H ₂ btp C ₂₃ H ₂₆ N ₈ O ₂ S ₂	510, 467, 424, 376, 333, 290, 242, 199, 156, 134
H ₂ bth C ₂₆ H ₃₂ N ₈ O ₂ S ₂	552, 509, 466, 418, 375, 332, 284, 241, 198, 134
[Cu(bte)] C ₂₂ H ₂₂ CuN ₈ O ₂ S ₂	559, 557, 516, 514, 496, 473, 471, 453, 425, 423, 382, 380, 339, 337, 291, 289, 246, 203, 134
[Cu(btp)] C ₂₃ H ₂₄ CuN ₈ O ₂ S ₂	573, 571, 530, 528, 510, 487, 485, 467, 439, 437, 396, 394, 353, 351, 305, 303, 260, 217, 134
[Cu(bth)] C ₂₆ H ₃₀ CuN ₈ O ₂ S ₂	615, 613, 572, 570, 552, 529, 527, 509, 481, 479, 438, 436, 393, 347, 345, 302, 259, 134

Acknowledgement. The authors are thankful to University Grants Commission, New Delhi, India for financial assistance [Research Project No. MRP(S)-313/2005(XPlan) KLCA012/UGC-SWRO].

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