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Coordination Behaviour of Some New Schiff Bases Towards Co(II), Ni(II) and Cu(II)

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Some new Schiff bases are synthesised from 2-pyridinecarboxaldehyde with 2-aminobenzimidazole(L_1), 3-amino-1,2,4-triazole(L_2) and 2-amino-3-hydroxypyridine(L_3). Cobalt(II) chloride and nickel(II) chloride complexes of Schiff bases have the stoichiometry $[M(L)(H_2O)]Cl_2$(M = Co(II) and Ni(II), L = Schiff base) while copper(II) chloride complexes have the stoichiometry $[Cu(L)_2]Cl_2 . H_2O$. The complex compounds have been isolated and characterized by elemental analyses, electrical conductivity, magnetic measurements, and infrared spectral measurements. All Schiff bases act as tridentate ligand towards Co(II) and Ni(II), but in case of Cu(II) complexes, they behave as bidentate ligand.

INTRODUCTION

The main sphere of the coordination chemistry of Schiff bases which has as yet remained largely neglected is complexes of Schiff bases derived from heterocyclic amine and heterocyclic aldehydes. Thus there is a vast scope of synthetic work in this field. The present paper deals with the synthesis of some new Schiff bases derived from 2-pyridinecarboxaldehyde with 2-aminobenzimidazole(L_1), 3-amino-1,2,4-triazole(L_2), and 2-amino-3-hydroxypyridine(L_3) and their coordination behaviour towards Co(II), Ni(II) and Cu(II).

EXPERIMENTAL

2-Pyridinecarboxaldehyde, 2-aminobenzimidazole, 2-amino-3-hydroxypyridine (Fluka), and 3-amino-1,2,4-triazole (Koch & Light) were also used without further purification. $CoCl_2.6H_2O$, $CuCl_2.2H_2O$ (BDH), and $NiCl_2.6H_2O$ (Sarabhai M. Chemicals) were dehydrated at 120°C.

Preparation of the Schiff bases

10 mmol of amine was dissolved in *ca.* 20 c.c. dry acetone. The acetone solution of (10 mmol) 2-pyridinecarboxaldehyde was added to it with continuous stirring. The contents were refluxed for 1 hr. The yellow compound thus formed, was cooled, filtered, recrystallized from ethanol and dried under IR lamp.

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2-N-(2′-Pyridinecarboxaldimine) benzimidazole (L_1) (yield 91%, m.pt. 209°C), 3-N-(2′-pyridinecarboxaldimine)-1,2,4-triazole(L_2)(yield 80%, m.pt. 242°C), and 2-N-(2′-pyridinecarboxaldimine)-3-hydroxypyridine(L_3) (yield 72%, m.pt. 208°C) were prepared similarly. The products are soluble in methanol, ethanol, carbon tetrachloride, and insoluble in water and hexane. (TLC, Acetone: Methanol, 1 : 1 and 1 : 3) gave one spot.

Preparation of the complexes

An ethanol solution of 1 mmol anhydrous metal(II)chloride was added to the 2 mmol of the Schiff base dissolved in about 25 c.c. ethanol. The contents were mixed under mechanical stirring for ½ hr. followed by refluxing (water bath) for 1 hr. The solid complex thus formed, was filtered under suction and washed with water, ethanol, and ether. The complex was recrystallized from acetone and dried under IR lamp (yield *ca* 80–89%).

Microanalysis was performed at CDRI, Lucknow, and are in good agreement with the proposed structures. Sulphur and halogen were determined by conventional methods in our laboratories.

Infrared spectra were recorded on Perkin Elmer 577 spectrophotometer at CDRI, Lucknow, in the region 200–4000 cm^{-1} on CsI-disc. Electrical conductivity was measured with a Phillips Conductivity Meter, Model PR 9500/90, with a magic eye null detector. Magnetic susceptibility was measured on a Gouy balance using $Hg[Co(SCN)_4]$ as standard.

RESULTS AND DISCUSSION

All compounds are isolated in solid form. The data on elemental analyses of the Schiff bases and their complexes are listed in Table 1. All complexes behave as 1 : 2 electrolytes in methanol or acetone (240–260 ohm^{-1} $mole^{-1}$ cm^2), which indicate that both chloride ions are uncoordinated. The magnetic moment of the Co(II), Ni(II), and Cu(II) are in the range of 4.25 to 4.76, 3.74 to 3.90 and 1.73 to 1.78 B.M. corresponding to four, three, and one unpaired electron respectively. This data also corresponds to the Co^{2+} Ni^{2+} and Cu^{2+} oxidation state. The elemental analyses and conductivity data also suggest a probable four coordinated structure for these complexes.

The prominent infrared bands of the ligands and complexes are listed in Tables 2–4.

2-N-(2′-Pyridinecarboxaldimine)benzimidazole complexes

In the spectrum of 2-pyridinecarboxaldehyde, the strong and sharp bands at 1710 cm^{-1} and 1585 cm^{-1} ascribed to the $\nu(C{=}O)$ and $\nu(C{=}N)$ vibrations, respectively. There are bands at 1425 cm^{-1} (s, sp). 1645 cm^{-1}

TABLE 1

ANALYTICAL DATA FOR THE SCHIFF BASES AND THEIR COMPLEXES DERIVED FROM 2-PYRIDINECARBOXALDEHYDE AND HETEROCYCLIC AMINES

Compound	% Found (Calcd.)			
	C	H	N	Cl
L_1	70.13 (70.27)	4.58 (4.50)	25.73 (25.20)	— —
$[Co(L_1)(H_2O)]Cl_2$	42.69 (42.16)	3.36 (3.24)	15.77 (15.13)	19.74 (19.18)
$[Ni(L_1)(H_2O)]Cl_2$	42.47 (42.16)	3.51 (3.24)	15.11 (15.13)	19.02 (19.18)
$[Cu(L_1)_2]Cl_2.H_2O$	52.81 (52.26)	3.68 (3.68)	18.61 (18.76)	11.10 (11.89)
L_2	54.60 (54.60)	4.22 (4.02)	40.18 (40.00)	— —
$[Co(L_2)(H_2O)Cl_2$	29.77 (29.90)	2.81 (2.80)	21.49 (21.80)	22.27 (22.11)
$[Ni(L_2)(H_2O)]Cl_2$	29.99 (29.90)	2.98 (2.80)	21.67 (21.80)	22.40 (22.11)
$[Cu(L_2)_2]Cl_2.H_2O$	38.21 (38.55)	3.96 (3.21)	28.28 (28.11)	14.17 (14.25)
L_3	66.60 (66.20)	4.39 (4.55)	21.05 (21.01)	— —
$[Co(L_3)H_2O]Cl_2$	38.36 (38.04)	3.12 (3.17)	12.38 (12.10)	20.57 (20.46)
$[Ni(L_3)(H_2O)]Cl_2$	38.41 (38.04)	3.19 (3.17)	12.19 (12.10)	20.58 (20.46)
$[Cu(L_3)_2]Cl_2.H_2O$	48.28 (48.00)	3.38 (3.63)	15.65 (15.27)	12.68 (12.90)

TABLE 2

ASSIGNMENT OF THE MAIN INFRARED BANDS (cm^{-1}) OF 2-N-(2′PYRIDINE-CARBOXALDIMINE)BENZIMIDAZOLE AND THEIR COMPLEXES

Assignment	L_1	$[Co(L_1)(H_2O)]Cl_2$	$[Ni(L_1)(H_2O)]Cl_2$	$[Cu(L_1)_2]Cl_2.H_2O$
νOH(H_2O) νNH	3200 ms,br	3400–3070 s,br	3450–3120 ms,v.br	3400–3110 s,v.br
νCH=N) (azomethine)	1610 m,br	1640–1570 vs,v.br	1660 s,br	1663 s,br
νC=N (Pyridine ring)	1585 m,sp	1640–1570 vs,v.br	1600 s.br	1625 s,br
νC=N (benzimidazole ring)	1550 m,br	1640–1570 vs,v.br	1575 s,br	1580 s,br
νM-O	—	420 w,br	415 m,br	
νM-N	—	305 mw,v.br	365 m.br	250 mw,br

TABLE 3

ASSIGNMENT OF THE MAIN INFRARED BANDS (cm^{-1}) OF 3-N-(2′-PYRIDINECARBOXALDIMINE)-1,2,4-TRIAZOLE AND THEIR COMPLEXES

Assignment	L_2	[Co(L_2)(H_2O)]Cl_2	[Ni(L_2)(H_2O)]Cl_2	[Cu(L_2)$_2$]Cl_2.H_2O
νOH(H_2O) νNH	3240 s,br	3320 s,v.br	3390 s,br	3400 s,br 3340 sh
νC=N (azomethine)	1580 vs.v.br 1540 sh	1600 ms,sp	1610 ms,sp	1620 ms,sp
νC=N (pyridine ring)	1580 vs,v.br 1540 sh	1590 s,sp	1595 ms,sp	1595 s,sp
νC=N (triazole)	1580 vs,v.br 1540 sh	1555 ms,sp	1545 s,br	1530 s,br
νM-O	—	412 w,br	420 w,br	—
νM-N	—	295 w,br	290 w,br	255 w,br

TABLE 4

ASSIGNMENT OF THE MAIN INFRARED BANDS (cm^{-1}) OF 2-N-(2′PYRIDINECARBOXALDIMINE)-3-HYDROXYPYRIDINE AND THEIR COMPLEXES

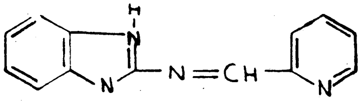
Assignment	L_3	[Co(L_3)(H_2O)]Cl_2	[Ni(L_3)(H_2O)]Cl_2	[Cu(L_3)$_2$]Cl_2.H_2O
νOH(H_2O) (phenolic)	3360 m,br	3410 s,br	3105 s,br	3400 m,br
νCH=N (azomethine)	1600 s, sp	1615 s,sp	1620 s,sp	1615 s,br
νC=N (rings)	1590 s,sp	1500 ms,sp	1580 ms,sp	1585 ms,sp
νC-OH	1190 m,br	1200 m,sp	1200 m,sp	1190 m,br
νM-O	—	405 m,br	415 m,br	—
νM-N	—	300 mw,br	305 m,br	250 m,br

(ms, sp), 1540 cm^{-1}, 1550 cm^{-1} (mw, sp) corresponding to other ring vibrations. The out-of-plane wagging vibrations are also indicated at 780 cm^{-1}, 755 cm^{-1} and 730 cm^{-1} corresponding to four adjacent hydrogens bonds.[1]

2-Aminobenzimidazole contains one NH_2 and one NH groups. A broad and very strong band occurs at 3360 – 3380 cm^{-1} (3300) cm^{-1} sh and two medium intensity bands appear at 3120 and 3360 cm^{-1}. These are attributable to ν(NH). A medium strong and sharp band at 1655 cm^{-1} with shoulder at 1640 cm^{-2} is assigned to δ(NH_2) vibrations.

In 1600–1400 cm^{-1} region, a medium strong and sharp band at 1560 cm^{-1} (1590 cm^{-1} (sh); 1572 cm^{-1} (sh); 1565 cm^{-1} (sh)), a medium intensity band at 1475 cm^{-1}, a strong and sharp band at 1455 cm^{-1}, and a weak band at 1383 cm^{-1} are corresponding to the ν(C=N) (ring) and imidazole ring vibrations.

In the spectrum of this Schiff base(I), a broad envelope of medium intensity appears at 3200 cm^{-1}. The band due to δ(NH_2) of the amine and band due to ν(C=O) of the aldehyde are observed to disappear. These indicate the reaction of NH_2 group with carbonyl group of the aldehyde and broad envelope at 3200 cm^{-1} is assigned to NH group of benzimidazole. A medium and slightly broad band appears at 1610 cm^{-1}, which is attributed to ν(CH=N) (azomethine). The broad band of medium intensity and multiple nature are observed at 1550 cm^{-1}, which can be attributed to the ν(C=N) (benzimidazole ring) vibration. A medium, sharp band at 1585 cm^{-1} is ascribed to the ν(C=N) (pyridine ring), and bands at 1570 cm^{-1}(m, sp), 1450 cm^{-1}(ms, sp), 1425 cm^{-1}(m, sp), 1390 cm^{-1} (mw, br), and 1360 cm^{-1}(mw, br) are attributed to the 2-substituted pyridine ring vibrations and imidazole ring vibrations. Four adjacent hydrogens of pyridine and benzimidazole rings are assigned by the medium strong, sharp band at 740 cm^{-1} with shoulders at 755 cm^{-1} and 775 cm^{-1}. Benzimidazole and pyridine ring vibrations are not distinguished because both are heterocyclic rings and bands appear in the same region. This Schiff base has four potential donor sites; nitrogens of the pyridine ring, two of benzimidazole ring, and azomethine.



(I)

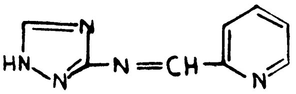
(a) The spectrum of cobalt(II)chloride complex of this Schiff base shows a very broad and strong envelope centered in 3400 cm^{-1} to 3070 cm^{-1} region due to the NH group of imidazole and the presence of water molecule. The greatly increased intensity and very broad nature of this band seems to be indicative of the presence of water molecule at 1620 cm^{-1} (vs, br). The ν(C=N) (imidazole ring) band also shows shift in positive direction and merges into the higher energy band. Other ring vibrations also appear at 1465 cm^{-1} (s, sp); 1432 cm^{-1} (m, sp), 1400 cm^{-1} (m, br) and 1372 cm^{-1} (m, br) with 10 to 15 cm^{-1} positive shift. Medium and sharp band at 1585 cm^{-1} of ν(C=N) (pyridine ring) vibration also merges into the very broad band of azomethine linkage at 1620 cm^{-1} (1640–1570 cm^{-1}). The shifting of azomethine band and ring vibrational bands seem to be indicative of the involvement of the nitrogens of azomethine, pyridine, and imidazole ring system in complexation. Imidazole ring has two nitrogens, one (C-N) linkage and other (C=N) linkage. Nitrogen of (C=N} linkage is coordinated to the metal atom because ν(C=N) (ring) band is shifted in higher frequency region. New weak, broad bands at 420 cm^{-1} and medium weak, very broad band at 305 cm^{-1} (with shoulders) are attributed to the ν(M-O) and ν(M-N) vibrations, respectively. This is another evidence for the metal-ligand linkage and metal-aquo linkage. Thus this Schiff base probably acts as tridentate ligand through (N,N,N) donor set.

(b) In nickel(II) chloride complex of this Schiff base, medium strong and very broad envelope in 3450 cm^{-1} to 3120 cm^{-1} region, indicates NH group of imidazole ring and water molecule within the complex. The strong and broad band at 1660 cm^{-1} due to ν(CH=N)(azomethine) appears with 50 cm^{-1} positive shift and band 1575 cm^{-1} with 25 cm^{-1} positive shift is attributed to the ν(C=N) (benzimidazole ring). Other skeletal vibrations of benzimidazole and pyridine ring also appear at 1470 sm^{-1} (ms,sp) and medium strong, very broad envelope at 1400 cm^{-1} (1440–1360). The strong and broad band at 1600 cm^{-1} with 15 cm^{-1} positive shift is attributed to the νC=N (pyridine ring). Four adjacent hydrogens of pyridine and imidazole are assigned at 740 cm^{-1} (ms,br) with shoulders at 765 cm^{-1}, 780 cm^{-1} and 790 cm^{-1}. Now medium, broad band at 415 cm^{-1} and medium, sharp band at 365 cm^{-1} correspond to the ν(M-O) and ν(M-N) vibrations respectively[2]. Shifting of azomethine band, ν(C=N)(ring) bands and skeletal vibrations of pyridine and imidazole ring and appearence of νM-N band indicate the linkage of three nitrogens with the metal. Thus this Schiff base is probably tridentate ligand through (N,N,N) donor set. The strong and very broad band in 3300 cm^{-1} region and appearence of νM-O band also indicate coordination through water molecule.

(c) Copper(II) chloride complex of this Schiff base shows strong and very broad band in 3400 to 3100 cm^{-1} region, which is indicative of NH group and water molecule within the complex. The azomethine band appears at 1660 cm^{-1} (s,br) with 50 cm^{-1} (s,br), which is unaffected by complexation. ν(C=N)(pyridine ring) appears at 1625 cm^{-1} (s,br) with 40 cm^{-1} positive shift. The skeletal vibrations of 2-substituted pyridine ring and imidazole ring show 5 to 25 cm^{-1} positive shift and appear at 1500 cm^{-1} (s,br), 1470 cm^{-1} (s,sp), 1460 cm^{-1} (s,sp) and 1420 cm^{-1} (m,br). The strong slightly broad band at 740 cm^{-1} with shoulders is attributed to the four adjacent hydrogens on both the rings. A new band appears at 250 cm^{-1} (mw,br) due to ν(M-N) vibrations[2]. Shifting of azomethine band, ν(C=N)(pyridine ring) band, and skeletal vibrations of 2-substituted pyridine ring are assigned to the coordination through azomethine and pyridine ring nitrogens.

3-N-(2′-Pyridinecarboxaldimine)-1,2,4-triazole complexes

3-Amino-1,2,4-triazole contains one NH_2 and one NH groups. Infrared bands occur at 3380 cm^{-1}, 3305 cm^{-1}, 3180 cm^{-1}, and 3040 cm^{-1}. The $\delta(NH_2)$ and $\nu(C{=}N)$ can be attributed bands at 1640 cm^{-1}, 1585 cm^{-1} and 1535 cm^{-1} with the aromatic ring vibrations as 1420 cm^{-1} and 1365 cm^{-1}. In the spectrum of Schiff base(II) the multiplet in 3100 to 3400 cm^{-1} region is much simplified only leaving one band at 3240 cm^{-1} and very weak shoulders at 3180 cm^{-1}, 3080 cm^{-1} and 3050 cm^{-1}. This band may be due to the $\nu(NH)$, which suggests that the NH_2 group has reacted with the aldehyde. The absence of the aldehyde band at 1712 cm^{-1} further indicates the formation of the azomethine linkage in the 1600 cm^{-1} to 1500 cm^{-1} region. The condensation product shows a very strong and broad band at 1580 cm^{-1}, and the band at 1640 cm^{-1} of the triazole has also vanished. The band at 1580 cm^{-1} with shoulder at 1540 cm^{-1}, therefore, be taken as the $\nu(CH{=}N)$ of azomethine stretching mode and $\nu(C{=}N)$(ring). Bands also appeared at 1475 cm^{-1} and 1440 cm^{-1} due to the pyridine ring vibrations. Therefore, it can be safely proposed that the Schiff base formation has taken place. The presence of several C=N linkages mostly in the conjugated positions appear to give rise to very strong and broad band at 1580 cm^{-1}.



(II)

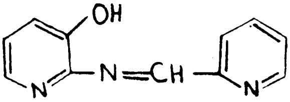
In the chloride complexes of Co(II), Ni(II), and Cu(II) of Schiff base show a very broad and strong envelope centered in 3400–3300 cm^{-1} region, which is to be attributed to the presence of water along with NH grouping. In the 1600–1500 cm^{-1} region, the very strong and broad band of the ligand at 1580 cm^{-1} is modified and bands appear at 1600 cm^{-1} (ms,sp) with 10–20 cm^{-1} positive shift due to the azomethine linkage. $\nu C{=}N$ (pyridine ring) bands appear at 1590 cm^{-1} (ms.sp) with 5–10 cm^{-1} shifting. The spectra of cobalt and nickel complexes show shifting of triazole ring vibrations but spectrum of copper complex does not show shifting. This indicates the involvement of azomethine nitrogen, and nitrogens of both rings in cobalt and nickel complexes, whereas in copper complex nitrogens of azomethine and pyridine ring involve in coordination. The skeletal bands due to triazole and pyridine ring vibrations also get reduced in intensity, particularly the band at 1420 cm^{-1} of the ligand in cobalt and nickel complexes. New bands appear in 250 cm^{-1} (w,br) region, probably due to the ν(N-M-N) vibrations. In cobalt and nickel complexes $\nu(M{-}O)(H_2O)$ bands appear in 400 cm^{-1} (w,br) region which indicate coordination through water molecule. Copper complex does not show ν(M-O) band.

The ligand behaves as tridentate with Co(II) and Ni(II), whereas with Cu(II) as bidentate through nitrogens of azomethine and pyridine ring as evidenced by infrared.

2-N-(2′-Pyridinecarboxaldimine)-3-hydroxypyridine complexes

In 2-amino-3-hydroxypyridine strong and sharp bands occur at 3420 cm^{-1}, 3320 (s,br) cm^{-1}, 3195 (w,sp) and 3060 cm^{-1} (m,br), in the 3600 cm^{-1} region. These may be attributed to νNH and νOH. There is a band at 1630 cm^{-1} (δNH_2) with shoulder at 1640, 1650 cm^{-1} and three characteristic ring vibrations at 1560 cm^{-1}, 1470 cm^{-1} and 1410 cm^{-1}. McWhinnie[3] reported spectrum for 2-aminopyridine recorded as nujol mull in NaCl. However we could not obtain a well resolved spectrum in CsI disc through bands occurs at 3410 (s,br), 3300 (s,br), and 1620 (s,br) cm^{-1}.

In the Schiff base(III), the strong, sharp bands at 3420 and 3320 cm^{-1} are replaced. There is a broad, medium intensity band at 3360 cm^{-1} which show that reaction has occurred between amine and 2-pyridinecarboxaldehyde. The 1630 cm^{-1} band also disappears and the band at 1560 cm^{-1} present in the amine also disappears completely. The strong bands at 1600 cm^{-1} and 1590 cm^{-1} are attributed to the νCH=N (azomethine) and νC=N (ring) vibrations, respectively. In the 700 cm^{-1} to 800 cm^{-1} region, strong and sharp band at 780 cm^{-1} with shoulders completely disappears in the spectrum of Schiff base. There is a broad and medium band at 3360 cm^{-1} appears due to the νOH (phenolic) vibrations. Medium and slightly broad band at 1190 cm^{-1} is attributed to the νC-OH vibrations.



(III)

In the chloro complexes of Co(II), Ni(II), and Cu(II), of the Schiff base exhibit a very broad and medium intensity and at 3400 cm^{-1} correspond to the νOH(phenolic and water) vibrations. Broadness of the band indicates the presence of phenolic group and water molecules within the complex. A medium strong and slightly broad band in 1610 cm^{-1} with 5–10 cm^{-1} negative shift are ascribed to the νCH=N of azomethine linkage. The νC=N (ring) band appears in 1585 cm^{-1} (ms,sp) with 5 cm^{-1} negative shift. The νC-OH vibrations band appears at 1190 cm^{-1} (m,sp) in Cu(II) complex and does not show any shift on complexation. New weak and broad band appears at 255 cm^{-1} probably due to the νN-M-N vibrations. The spectra of Co(II) and Ni(II) complexes show νM-O bands appear in 400 cm^{-1} region indicate coordination through hydroxy and aquo group. The spectrum of Cu(II) complex does not show νM-O band. The ligand appeared to behave as tridentate nature with Co(II) and Ni(II) through hydroxy group, azomethine nitrogen, and nitrogen of aldehyde ring but in Cu(II) complex, the ligand acts as bidentate ligand through nitrogens of azomethine and aldehyde ring.

The inference drawn from these data, in the present work, it is observed, is that all the three ligands, L_1, L_2, and L_3 behave as tridentate towards Co(II) and Ni(II). In L_1 and L_2, coordination site is 'N,N,N' type through nitrogens of azomethine, pyridine and benzimidazole or triazole system, whereas in L_3 it is 'N,N,O' type, with nitrogens of azomethine, aldehyde ring and oxygen of hydroxy group of amine part as coordinating sites. These Schiff bases act as bidentate ligand in Cu(II) complexes, through azomethine nitrogen and nitrogen of aldehyde ring. Cu(II) complexes have the Schiff base ligands and four coordination sites are occupied by the bidentate behaviour of two Schiff base ligands. Different behaviours of the same ligand in Co(II) and Ni(II) complexes are probably due to the partial hydrolysis of the complexes. One Schiff base ligand is eliminated and remaining one Schiff base acts as a tridentate ligand. The coordination behaviour of the same Schiff base towards different metals has been found to be different from metal to metal.[4,5]

Copper(II) chloride complexes of these Schiff bases were also prepared in *in situ* reaction in methanol [copper(II) chloride (1 mmol), amine (2 mmol) and aldehyde (2 mmol)]. Results of all complexes are similar, either prepared by the preformed Schiff base and metal chloride reaction or prepared by *in situ* reaction. Comparison of infrared spectra in both cases showed almost complete superimposition.

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