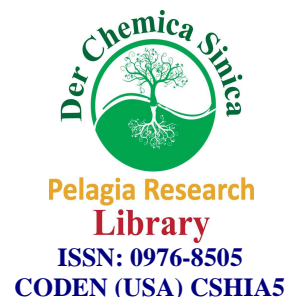




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Synthesis of Mn(II), Co(II), Cu(II) and Zn(II) complexes with (E)-N'-(pyridine-2-ylmethylene)nicotinohydrazide and their evaluation of antimicrobial activities

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ABSTRACT

Metal Complexes of (E)-N'-(pyridine-2-ylmethylene)nicotinohydrazide (PCNH) were prepared by treating it with various transition metal salts. The structure of the ligand was characterized by elemental, IR, ¹H NMR, ¹³C NMR and Mass spectral studies and the metal complexes were characterized by elemental, molar conductance, IR, UV, ¹H NMR and ESR studies. Magnetic studies and conductance measurements were also been carried out to establish the structure of the complexes. All the complexes have mononuclear structure and possess octahedral geometry. Redox behavior of the complexes has been investigated by Cyclic Voltametry at the glass carbon electrode in 0.1 M DMSO. Further, ligand and its metal complexes have been screened for in vitro to evaluate their activity against certain micro organisms.

Keywords: Antimicrobial, pyridine-2-carbaldehyde, Schiff base, azomethine, Overtone's theory.

INTRODUCTION

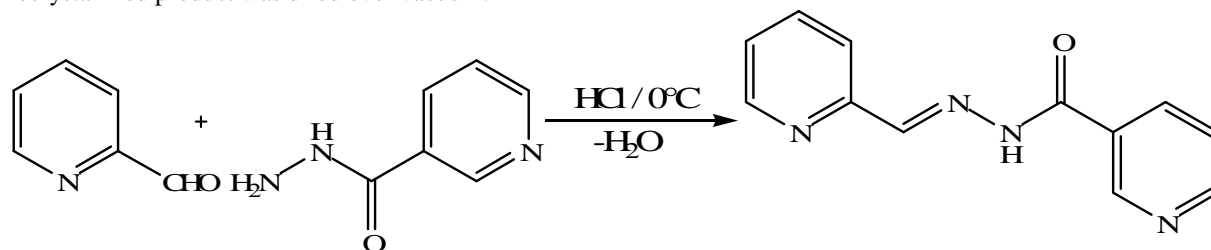
Finding of new compounds having pharmaceutical activities is an active field of research in recent years. It has been reported in the literature that antimicrobial and other biological properties of the metal complexes are found to be more than their parent ligand [1-3]. It is well known that metal ion present in complexes accelerate the drug action and the efficacy of the organic therapeutic agents [4]. The pharmacological efficiency of metal complexes depends on the nature of metal ions and the ligand [5]. Much more attention has been given on the synthesis of Schiff bases due to their wide spectra of biological and pharmaceutical activities such as antibacterial, antiviral, antifungal, anti-inflammatory, anti tubercular etc., So the synthesis of new ligand and their complexes would be an important step in the development of coordination chemistry. [6-8]. A probe into the literature on some transition metal complexes of the Schiff bases clearly reveals that they are act as neutral bidentate ligand and found to exhibit biological properties. In general the heterocyclic compounds having hetero atoms like N, O and S are found to possess more pharmaceutical activities [9]. Owing to the above said properties it is planned to synthesize a new Schiff by reacting compounds containing N, O and S atoms. (E)-N'-(pyridine-2-ylmethylene)nicotinohydrazide (PCNH) was prepared by treating pyridine-2-carboldehyde and nicotinic acid hydrazide. Using the synthesized compound as ligand, Manganese (II), cobalt (II), copper (II) and zinc (II) complexes were prepared both the ligand and complexes were characterized by elemental analyses, molar conductance, UV, IR, NMR, ESR, Cyclic Voltametry and Magnetic susceptibility. Further both the ligand and its metal complexes were screened for antimicrobial activities.

MATERIALS AND METHODS

The ligand and complexes were prepared using commercially available chemicals of Merck and Sigma Alrich products. The purchased chemicals were used without any further purification. The synthesized compounds were identified by TLC using Silica-G coated glass plates and visualized by iodine vapor. Melting points were determined by open capillary and are uncorrected. The elemental analysis was performed using CHNO analyzer. ^1H NMR spectra were recorded on 300 MHz Bruker Spectrometer using DMSO- d_6 as the standard, chemical shifts are expressed in ppm. IR spectra were recorded on Shimadzu FT-IR spectrometer in the 400-4000 cm^{-1} region. UV spectra were recorded using UV visible Perkin Elmer model Arithmetic ranged from 200-1100 nm. Biological studies of the synthesized compounds were screened by disc diffusion method at EUMIC Laboratory, Tiruchirapalli.

Synthesis of PCNH

To the ethanolic solution of nicotinic acid hydrazide (3.4 g, 0.025 mol) is taken in a round bottom flask, pyridine-2-carboldehyde (2.6 mL, 0.025 mol) was added (Scheme 1). The reaction mixture was kept over a magnetic stirrer and stirred well in an ice cold condition for 3 hr. The colorless solid formed was filtered and washed several times with petroleum ether (40-60%). The crude solid obtained was dried and recrystallized using absolute alcohol. The recrystallized product was dried over vacuum.



Scheme 1. Synthesis of Nicotinic acid pyridine-2-ylmethylene-hydrazide

Synthesis of Metal complexes of PCNH

To the methanolic solution of PCNH (1.18 g, 0.005 M), each of the metal (Cu(II), Mn(II), Co(II) and Zn(II)) chloride (0.0025 M) was added. The reaction mixture was taken in a round bottom flask and kept over a magnetic stirrer cum hot plate and stirred well by maintaining a temperature at 60°C. After 2 h the product separated as a solid was washed, filtered and dried over vacuum.

Result and Discussion

The synthesized compound and complexes were characterized by elemental analysis and FT-IR. The results of elemental analysis of the ligand and its complexes, so in Table 1, are in good agreement with those required by the proposed formulae. The complexes are freely soluble in DMF and DMSO. The molar conductance of the soluble complexes is lying in the range $\lambda = 99-154 \times 10^{-3} \Omega^{-1} \text{mol}^{-1} \text{cm}^2$, in 10^{-3} DMSO, indicating their electrolytic nature. The metal content in the complexes were estimated by complexometry, while the geometry of the complexes was confirmed from elemental analysis, molar conductance, IR, electronic spectra, ESR, Cyclic Voltametry. The ligand and its complexes have been screened for the in vitro antimicrobial analysis.

Table 1. Elemental analysis and molar conductance of the ligand and its complexes

Compounds	Mol. Formula	Mol. Weight	Melt. Point	Elemental Analysis % Found [% Calc.]				Molar conductance $\Omega^{-1} \text{mol}^{-1} \text{cm}^2$
				C	H	N	O	
PCNH	$\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}$	226	146	63.61 [63.71]	4.46 [4.46]	24.7 [24.76]	7 [7.07]	--
PCNHMn	$\text{C}_{24}\text{H}_{24}\text{Cl}_2\text{MnN}_8\text{O}_4$	613	264	46.6 [46.92]	3.92 [3.94]	18.46 [18.24]	10.2 [10.42]	126
PCNHCo	$\text{C}_{24}\text{H}_{24}\text{Cl}_2\text{CoN}_8\text{O}_4$	617	268	46.6 [46.62]	3.88 [3.91]	18.12 [18.12]	10.15 [10.35]	154
PCNHCu	$\text{C}_{24}\text{H}_{24}\text{Cl}_2\text{CuN}_8\text{O}_4$	621	295	46.22 [46.26]	3.87 [3.88]	17.8 [17.9]	10.22 [10.27]	99
PCNHZn	$\text{C}_{24}\text{H}_{24}\text{Cl}_2\text{ZnN}_8\text{O}_4$	622	246	46.26 [46.16]	3.84 [3.87]	17.9 [17.93]	10.22 [10.24]	118

IR Spectra

The selected vibrational frequencies for the Schiff base ligand and its complexes are presented in Table 2. The IR spectrum of ligand showed characteristic band at 3381cm^{-1} can be attributed to the $\nu(\text{-NH-})$ group. A band appeared at 2854cm^{-1} can be attributed to the $\nu(\text{C-H})$ group. A sharp band appeared at 1658cm^{-1} can be attributed to the $\nu(\text{C=O})$ group of the ligand has been shifted to $1640\text{-}1624\text{cm}^{-1}$ in the spectra of the complexes indicate the involvement of oxygen atom of carbonyl group in binding with metal ions [10-12]. This is further confirmed by the appearance of band at $420\text{-}441\text{cm}^{-1}$ assignable to $\nu[\text{M-O}]$ [13]. The band appeared at 1153cm^{-1} due to $\nu(\text{C=N})$ of azomethine group of ligand has been shifted to lower frequency by $21\text{-}50\text{cm}^{-1}$ in the complexes suggest that the coordination is through N-atom of nicotinic acid ring. This is further supported by the appearance of band at $518\text{-}528\text{cm}^{-1}$ assignable to $\nu(\text{M-N})$ [14 & 15]. The above discussion indicates the nature of the free Schiff base is bidentate and shows the coordination through N and O atoms to the metal ion.

Table 2. Characteristic IR bands of the PCNH and its metal complexes (cm^{-1})

Compounds	$\nu(\text{NH})$	$\nu(\text{CH})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
PCNH	3381	2854	1658	1153	-	-
PCNHMn	3377	2854	1642	1132	528	426
PCNHCo	3371	2856	1624	1130	520	441
PCNHCu	3370	2776	1629	1103	520	414
PCNHZn	3215	2852	1640	1112	518	420

UV Spectral Studies

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The electronic spectral measurements were used for assigning the stereochemistry of metal ions in the complexes based on the position and number of d-d transitions. The electronic absorption spectra of the PCNH and its Mn(II), Co(II), Cu(II) and Zn(II) complexes are recorded in DMSO solution in the wavelength range $200\text{-}1100\text{nm}$ and their corresponding data are given in Table 3 and Fig 1. The UV-Vis spectra of the free ligand (PCNH) shows two absorption bands in the Ultra Violet region $\lambda_{\text{max}} = 39370, 33225\text{cm}^{-1}$ the first high intensity bands appeared at $\lambda_{\text{max}} = 39370\text{cm}^{-1}$. It follows from the literature that the band at 39370cm^{-1} is related to the $\pi \rightarrow \pi^*$ transitions of the benzene rings [16]. The second absorption band at $\lambda_{\text{max}} = 33225\text{cm}^{-1}$ may correspond to the $n \rightarrow \pi^*$ transition of the azomethine group [17].

Table 3. Electronic spectral bands, transition assignments and magnetic moment values of PCNH and its metal complexes (cm^{-1})

Compounds	Magnetic Moment B.M	Absorption Maxima		Transition Assignment	Geometry
		nm	cm^{-1}		
PCNH	-	254	39370	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	---
		301	33225		
PCNHMn	5.89	314	31847	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$	Octahedral
		375	26666		
PCNHCo	3.94	272	36765	$n \rightarrow \pi^*$ $n \rightarrow \pi^*$	Octahedral
		366	27322		
PCNHCu	2.78	283	35335	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$	Octahedral
		370	27027		
		406	24630		
PCNHZn	1.9	314	31847	$n \rightarrow \pi^*(\text{M-L, CT})$ $n \rightarrow \pi^*(\text{L-M, CT})$	Octahedral
		374	26738		

The electronic spectrum of manganese(II) complex has two bands one at $\lambda_{\text{max}} = 31847$ and other at 26666cm^{-1} , these can be attributed to charge transfer transitions ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$, these transition are the characteristic for a manganese(II) ion in an octahedral environment. In the spectra of the cobalt complexes two bands appeared at 36764 and 27322cm^{-1} , are assigned to charge transfer transitions $n \rightarrow \pi^*$ and $n \rightarrow \pi^*$, indicate octahedral geometry of the cobalt complex. This is further supported by the magnetic moment measured at 5.89 and 3.94BM [18, 19].

Copper(II) complex shows magnetic moments corresponding to one unpaired electrons, i.e. 1.82BM, electronic spectrum displays bands at 35460, 27027 and 24360 cm^{-1} . These bands may be assigned charge transfer transitions $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively. It is suggest that octahedral geometry of copper(II) complex [20]. The Zn(II) complex exhibits absorptions at 31847 and 26737 cm^{-1} , which are assigned to $n \rightarrow \pi^*(\text{M-L,CT})$ and $n \rightarrow \pi^*(\text{L-M,CT})$ respectively. This is further supported by the measured magnetic moment at 0 BM diamagnetic [21].

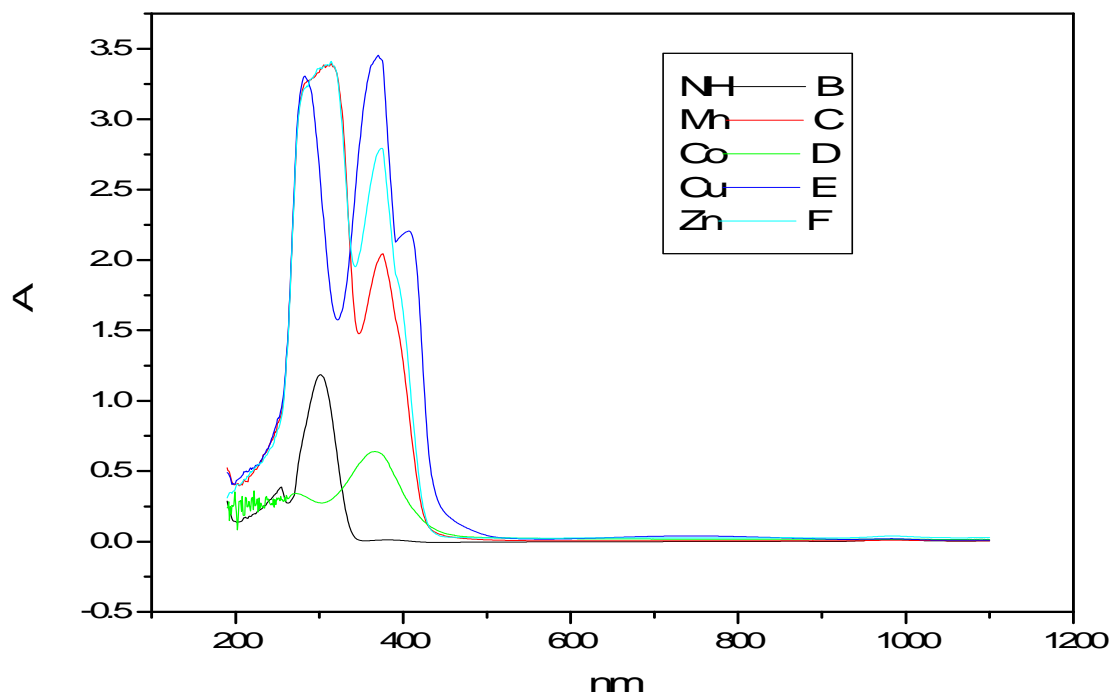
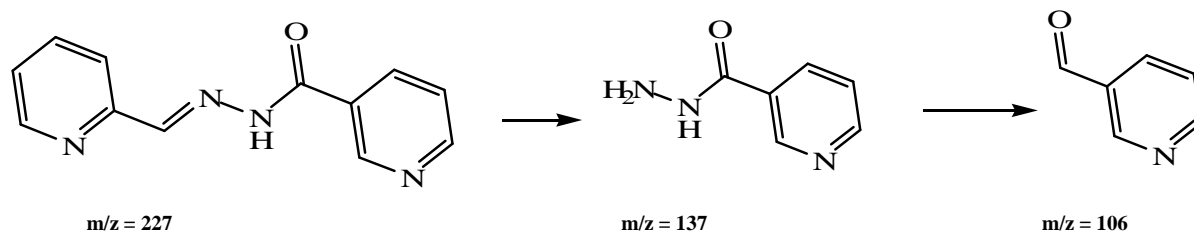


Figure 1. UV-Vis spectrum of the PCNH and its metal complexes

NMR and Mass Spectra

^1H NMR spectrum of the PCNH was recorded in DMSO-d_6 (300 MHz). The PCNH shows a singlet at δ 12.2 is due to may be enolic OH proton. The signals appeared in the region of δ 9.0 (s, 1H) 8.8 (d, 1H) 8.6 (d, 1H) 7.4 (q, 1H) due to nicotinic acid ring protons. A sharp absorption peak around δ 8.4 azomethine proton ($\text{HC}=\text{N}$ -). The pyridine ring proton signals appeared in the region of 8.2 (d, 1H) 8.0 (d, 1H) 7.9 (t, 1H) 7.5 (q, 1H). The ^{13}C NMR spectrum of the PCNH was recorded in DMSO-d_6 (100 MHz). The signals appeared in the region of 152 to 124 is due to pyridine and nicotinic acid ring carbons. The carbonyl carbon and the azomethine ($-\text{CH}=\text{N}$ -) carbon appeared at δ 168 and 154 respectively. The mass spectrum of the PCNH exhibits a molecular ion peak ($\text{M}+1$) at m/z 227, which is equivalent to its molecular weight. This ligand shows a fragment ion peak with loss of pyridine ring at 137 (Scheme 2). This fragment on further losing hydrazine group given fragment ion peak at m/z 106. The ^1H NMR and Mass spectra are shown in Fig 2 & 3.



Scheme 2. Mass fragmentation pattern of PCNH

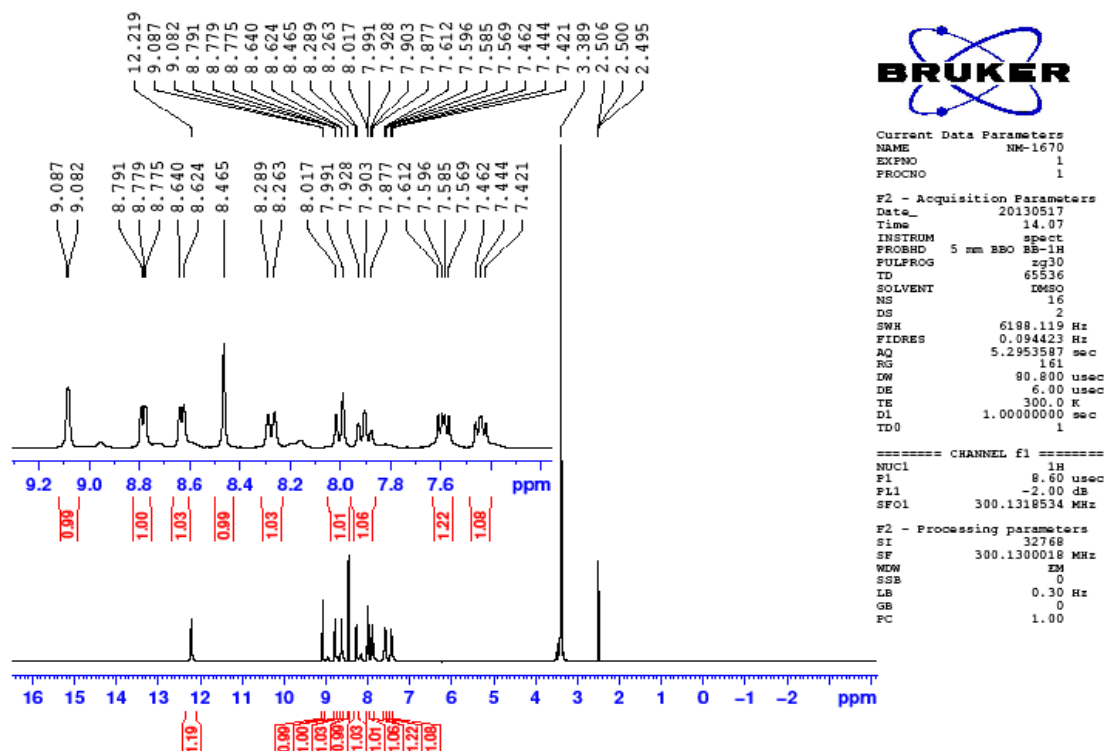
Figure 2. ^1H NMR spectrum of PCNH

Figure 3. Mass spectrum of PCNH

ESR Studies

The X-band EPR spectra of copper(II) complex have been recorded in the solid state at room temperature. The measure of symmetry of these complexes is in terms of g values, that is $g > 2.04$ indicates that indicates that the ground state copper(II) ion is predominantly the dx^2-y^2 orbital [22, 23]. The g values of these complexes are found to be less than 2.3 indicating the covalent nature of the complexes. This has been further supported by spin-orbit coupling constant value of -460cm^{-1} . The in-plane σ -bonding covalency parameter, α_2 is found to be 0.80 indicates that the complex has covalent character. The ESR spectra gives $g_{\parallel} = 2.23$ and $g_{\perp} = 2.03$. The trend $g_{\parallel} > g_{\perp} > 2.0023$, observed for the complex, under study, indicates that the unpaired electron is localized in dx^2-dy^2 orbital of the Cu(II) ion and the axial symmetry. The elongated octahedral geometry of the complexes have been established from the relation $g_{\parallel} > g_{\perp} > 2.04$ [24].

standard. This means that the activity of the newly prepared Schiff base against different microorganisms is enhanced with chelation with different biological active metals. The antimicrobial activities are shown in Table 4.

Table 4. Antimicrobial activity of PCNH and its metal complexes

S. No	Organism	Antibacterial		Antifungal
		<i>S. Aureus</i>	<i>E. Coli</i>	<i>A. Niger</i>
1	PCNH	20	15	15
2	PCNH-Mn	28	22	24
3	PCNH-Co	36	43	40
4	PCNH-Cu	22	31	15
5	PCNH-Zn	30	30	30
6	DMSO	0	0	0
7	Standard	31	36	15

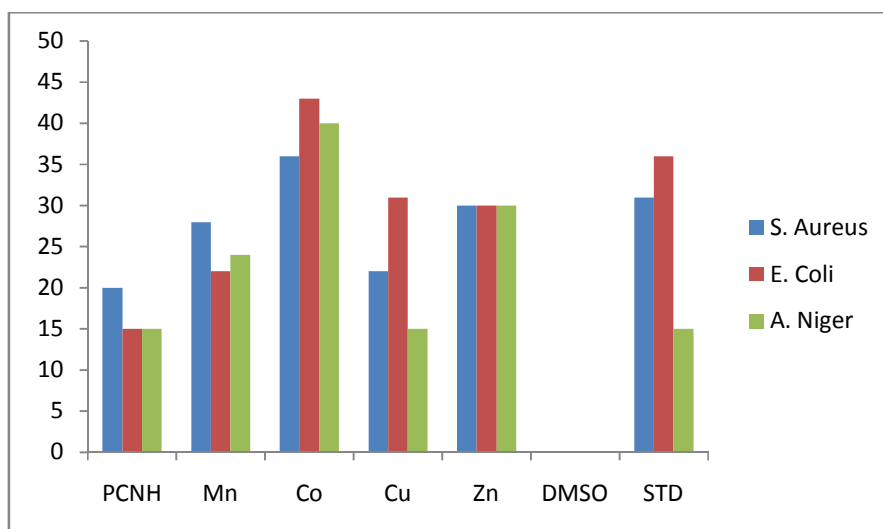


Figure 5. Antimicrobial activity of PCNH and its metal complexes

CONCLUSION

Synthesis and characterization of complexes containing NO donor bidentate Schiff base ligand have been described in this paper. The spectroscopic data of the complexes are in good agreement with proposed structure. The PCNH coordinates through azomethine nitrogen atom and hydrazide carbonyl oxygen (NO) to the metal ion acts as a neutral bidentate ligand. All the complexes exhibit octahedral geometry. Further, the cobalt complex has more biological active than the standard. Hence the cobalt complex is used in medicinal field.

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