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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL SCREENING OF 4-[4-PYRIDINECARBOXYLIC) DIAMINO]-4-CHLOROBENZOYL)-3-METHYL-1-PHENYLPYRAZOL-5-ONE AND ITS Ni (II), Cr (III), Cu (II) AND Co (II) COMPLEXES

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ABSTRACT

A 4-acylpyrazol-5-one Schiff base with isoniazide moiety; 4-[4-pyridinecarboxylic) diamino]-4-chlorobenzoyl)-3-methyl-1-phenylpyrazol-5-one was synthesized by condensation of 4-chlorobenzoyl-3-methyl-1-phenylpyrazol-5-one with pyridinecarboxylic acid hydrazide. The ligand was characterized on the basis of elemental analysis, infrared (IR), ^{1}H and ^{13}C NMR data. Ni (II), Cr (III), Cu (II) and Co (II) complexes of the ligand were also synthesized. The metal complexes were characterized by elemental analysis, molar conductance, magnetic measurements, IR and electronic spectral studies. All the synthesized compounds were screened for their *in vitro* antimicrobial activity against some Gram-positive and Gram-negative clinical bacterial strains. Antimicrobial activity test results revealed that the compounds showed better activity against the Gram-positive bacterial strains.

Key words: 4-acylpyrazol-5-one Schiff base, Isoniazide, Antimicrobial activity, Complexes.

INTRODUCTION

It is well documented that 4-acylpyrazol-5-ones are bidentate oxygen donor ligands[1-6]. In the last few decades considerable efforts have been made by various research groups to isolate derivatives with more potential coordination sites. Consequently a number of 4-acylpyrazol-5-one Schiff bases and their metal complexes have been synthesized by some workers[7-15]. 4-acylpyrazol-5-one Schiff bases have been reported as viable reagents in biological[16,17], clinical and analytical applications[18-21]. The tendency for 4-acylpyrazol-5-one derivatives to exist in various tautomeric forms also makes for an interesting study, because

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of several possible coordination modes that could be observed. Meanwhile, pyridine-carboxylic acid hydrazide and its derivatives are well known for their bactericidal action[22,23]. Pyridoxal isonicotinoyl hydrazone has been shown to mobilize iron from cells *in vitro* and *in vivo*[24-27], hence serves as a good iron chelator in biological system. In this report, we present a potential ONO donor 4-acylpyrazol-5-one Schiff base and some of its metallic derivatives. The antimicrobial activity of the ligand and its metal complexes is also discussed.

EXPERIMENTAL

4-chlorobenzoyl-3-methyl-1-phenylpyrazol-5-one was synthesized according to literature method[3]. All chemicals and solvents used were of analytical grade. 1-phenyl-3-methylpyrazol-5-one, 4-chlorobenzoylchloride and pyridinecarboxylic acid hydrazide were purchased from Fluka. Elemental analyses of C, H and N were performed using Carlo Erba Elemental analyzer EA 1108. Melting point was measured with a Fisher john melting point apparatus. IR spectra were recorded on a Perkin Elmer spectrum BX using the software package U.2.O. The molar conductance of the complexes was measured using Innolab conductivity meter Level 1. Magnetic moments of the metal complexes were done on a magnetic susceptibility balance-Sherwood Scientific Cambridge, Model No. MK-I. The % metals in complexes were determined using an Agilent KP-MS7500Ce. ^{1}H and ^{13}NMR were obtained from a Bruker AV 500 MHZ for ^{1}H and 125 MHZ for ^{13}C using a 5 mm Quadra Nuclei Probe (QNP).

Synthesis of 4-[4-pyridinecarboxylic)diamino]-4-chlorobenzoyl)-3-methyl-1-phenylpyrazol-5-one (ClBepINH)

A solution of 4-chlorobenzoyl-3-methyl-1-phenylpyrazol-5-one (3.31 g; 0.01 mol) in 30 mL ethanol was mixed with a solution of pyridine carboxylic acid hydrazide (1.36 g; 0.01 mol) dissolved in 20 mL ethanol, the resulting mixture was then refluxed for 2 hr. On cooling the resultant reddish solution, reddish product was obtained, filtered and recrystallized in ethanol to obtain reddish crystals.

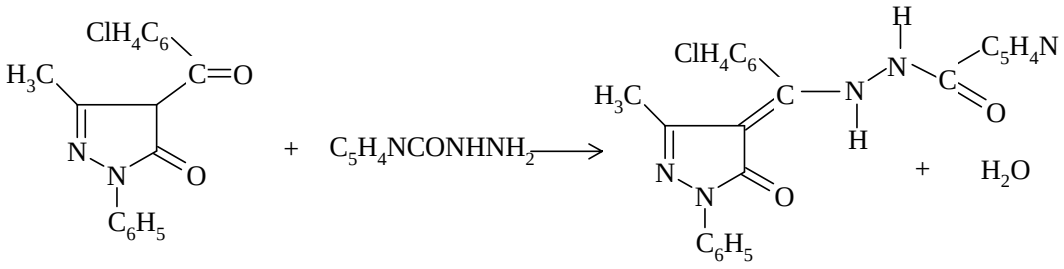


Fig. 1: Synthesis of ClBepINH

Synthesis of Ni (II), Cr (III), Cu (II) and Co (II) metal complexes of ClBepINH

To a dioxane solution (20 mL) of 4-[4-pyridinecarboxylic) diamino]-4-chlorobenzoyl)-3-methyl-1-phenylpyrazol-5-one (0.43 g, 0.001 mol), ethanolic solution (10 mL) of metal chloride (0.001 mol) was added with constant stirring. The coloured mixture was then refluxed for 4 hr. The resulting metal complex was filtered hot, washed several times with hot ethanol and hot water, drained under suction and kept in vacuum over $CaCl_2$.

Antimicrobial test

Escherichia coli, Pseudomonas aeruginosa, Klebsiella pneumoniae, Staphylococcus aureus and *Bacillus subtilis* were collected from clinical samples. The Gram positive and Gram negative bacteria were identified using bio-chemical methods[28]. Antimicrobial activity was studied by Agar well diffusion method[29]. Colonies of each test bacterium were suspended in sterile normal saline and adjusted to match 0.5 Macfarland turbidity standard. Each bacterial suspension was used to spread onto the surface of sterile Mueller Hinton agar plates. The surface of the plates were allowed to dry and a sterile cork borer of 6 mm diameter was used to bore wells in the agar plates. 50 μL of dilute solution (20 mg/mL) of each synthesized compound was delivered into each well. The plates were allowed to stand for 30minutes to aid diffusion and then incubated at 37^{o}C for 24 hrs. After incubation the zones of inhibition were measured and the mean recorded.

RESULTS AND DISCUSSION

All the complexes are coloured, soluble in dimethyl sulphoxide, dimethyl formamide and anhydrous ethanol but insoluble in hexane and carbon tetrachloride. Analytical and physical data of all the synthesized compounds are tabulated in Table 1. The molar conductivities of the complexes are in the range 6-13 $Ohm^{-1}cm^{2}mol^{-1}$ in DMSO, suggesting that the complexes are non-electrolytes in DMSO[30-32].

FT-Infrared spectra

The relevant stretching frequencies are tabulated in Table 2. The bands in the region ~ 3000-3270 cm^{-1} in the spectral of the ligand and the metal complexes have been assigned to NH stretching vibrations. Two strong *v* (C=O) bands are observable; one assignable to *v* (C=O) of the lateral chain comprising the hydrazide moiety and the other to the *v* (C=O) of pyrazolone ring[33-37]. These strong vibrational bands (cm^{-1}) have been presented as follows; 1610, 1585 (ClBepINH), 1590, 1574 (CuClBepINH), 1600, 1575 (NiClBepINH), 1598, 1561 (CoClBepINH), 1595, 1574 (CrClBepINH). The bands shifted to lower frequencies in the metal complexes, suggesting that the carbonyl oxygens are involved in coordination to the metal ions in the complexes[38-40].

Table 1: Analytical and physical data of the ligand and complexes

Compd.	Colour	MF	MW	Yield %	Elemental analysis % found (calculated)				μeff B.M	λ_M ohm^{-1} cm^2 mol^{-1}	M.P. °C
					C	H	N	M			
ClBepINH	Red	$C_{23}H_{19}N_5O_2Cl$	432.93	68.68	63.12 (63.81)	3.98 (4.44)	6.75 (7.39)	-	-	-	140
CoClBepINH	Orange	$C_{46}H_{38}N_{10}O_4Cl_2Co$	924.79	65.51	59.10 (59.74)	3.75 (4.14)	7.20 (6.92)	6.85 (6.37)	4.75	12.11	239
NiClBepINH	Light green	$C_{46}H_{38}N_{10}O_4Cl_2Ni$	924.55	60.21	59.98 (59.76)	4.77 (4.14)	6.40 (6.92)	6.10 (6.35)	3.02	9.34	250
CuClBepINH	Brown	$C_{46}H_{38}N_{10}O_4Cl_2Cu$	929.41	62.55	59.10 (59.44)	4.67 (4.12)	6.95 (6.89)	6.63 (6.84)	1.97	7.10	190
CrClBepINH	Brown	$C_4H_{38}N_{10}O_4Cl_2Cr$	917.85	61.55	60.87 (60.19)	3.86 (4.17)	6.54 (6.97)	5.12 (5.67)	3.72	6.25	200

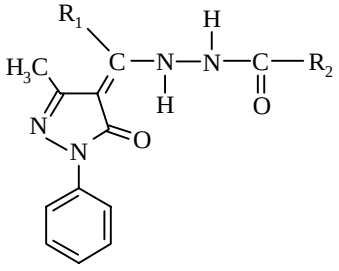
Table 2: Relevant IR band assignments for the ligand and metal complexes

Compound	ν N-H	ν C=O	ν N-N	ν M-O	ν M-N
ClBepINH	3056	1610 1585	1140	-	-
CuClBepINH	3185	1590 1574	1088	514	435
NiClBepINH	3266	1600 1575	1055	511	460
CoClBepINH	3223	1598 1561	1060	521	488
CrClBepINH	3238	1595 1574	1050	514	447

The bands in the region ~ 1050-1140 cm^{-1} in the ligand and the metal complexes have been assigned to ν (N-N). Bands in the range 511-521 cm^{-1} in the metal complexes were assigned to ν (M-O) while bands in the range 435-488 cm^{-1} were assigned to ν (M-N)[41-44].

^{1}H and ^{13}C NMR spectra

A number of tautomeric forms are possible for the study compound (Fig.2). The keto forms I-III, the keto-enol forms IV-VI and the enol form VII. The absence of peak assignable to *ν*OH in the IR spectral of the compound coupled with absence of bands downfield around the region 12-14 ppm in the ^{1}H NMR spectra[7] eliminates any of the enol forms as the possible isolate. Jensen[3] reported that recrystallization of crude 4-acylpyrazolones in aqueous solvents often result in the keto form of the 4-acylpyrazolone.



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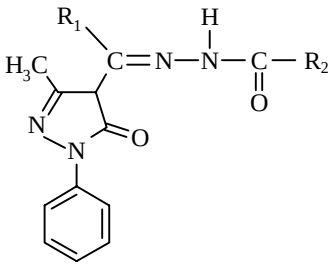

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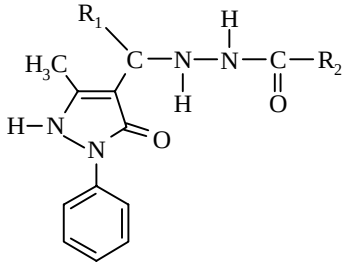

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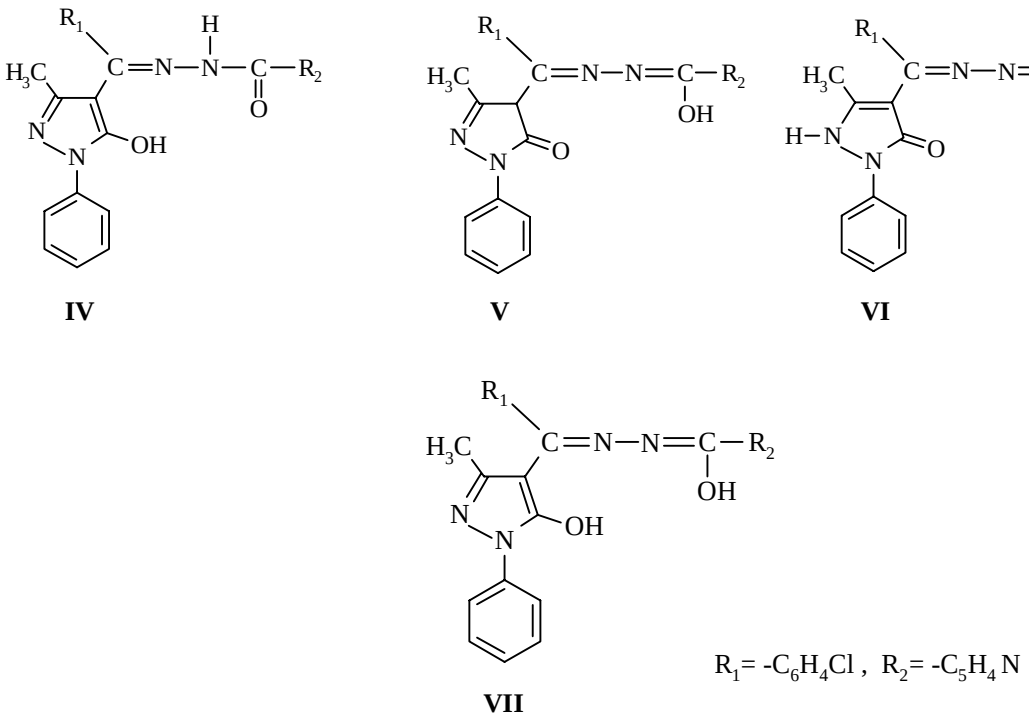


Fig. 2: Possible tautomeric forms of ClBePINH

Spectroscopic evidence in the present study suggest that the study compound was isolated in the keto-amine form (I) and reacted with the metal salts as a neutral molecule.

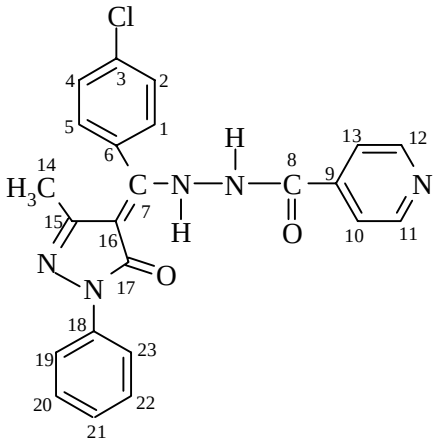


Fig. 3: Structure of ClBePINH

Assignments done by workers on related studies[5,45-48] have been considered in assigning the ^{1}H and ^{13}C NMR of the ligand. In the ^{1}H NMR spectrum the 3-methyl protons signal was observed as singlet up field at 2.50 ppm, The absence of signal assignable to pyrazolone ring C-H further substantiate the existence of the compound in the keto form.

The phenyl protons appeared as multiplets in the range 7.15-8.02 ppm while the signal due to –NH was observed at 8.80 ppm. The ^{13}C NMR spectrum of Cl Bep INH exhibited 17 carbons comprising 16 sp^2 and one sp^3 ($-CH_3$) carbons, the signal at δ 16.06 has been assigned to carbon of 3-methyl. Carbons of benzene rings are present at δ 118.47-165.18. The most deshielded carbons have been assigned relevant signals downfield. The assignments are as follows C_1= 128.87, C_2 = 124.56, C_3= 162.13, C_4 = 124.56, C_5 = 128.87, C_6 = 130.35, C_7 = 153.07, C_8 =165.18, C_9 = 147.79, C_{10} = 139.23, C_{11} = 150.66, C_{12} = 150.66, C_{13} = 139.23, C_{14} = 16.06, C_{15} =161.22, C_{16} = 148.13, C_{17} = 164.21, C_{18}=163.22, C_{19} = 118.47, C_{20} = 129.28, C_{21} = 121.58, C_{22} = 129.28, C_{23} = 118.47 ppm.

Electronic spectra and magnetic studies

The significant electronic absorption bands in the spectra of the ligand and the metal complexes recorded in DMSO solution are presented in Table 3. The ligand show high frequency bands at 32, 258, 30, 113 and 28, 169 cm^{-1} which were assigned to n → π* and π → π* transitions[49-51]. The electronic spectral of Cr (III) complexes in an octahedral environment will show three spin allowed d-d transitions $^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(\nu_1)$, → $^{4}T_{1g}(\nu_2)$ and $^{4}T_{1g}(P)$ (ν_3). The ν_2 and ν_3 bands have been observed above 25,000 cm^{-1} [52,53]. Cr (III) complex show bands at 20, 354, 22, 722 and 25, 364 cm^{-1} assignable to $^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$, $^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$ and $^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(P)$, respectively[54]. The observed magnetic moment of 3.72 BM suggests an octahedral geometry[55]. Octahedral Cu^{2+} complexes have either D_{4h} or C_{4v} symmetry, the ground state ^{2}D in the electronic spectral is split into $^{2}E_g$ and $^{2}T_{2g}$ which are further split into B_{1g}, A_{1g}, B_{2g} and E_g levels. Three spin allowed transitions are expected in the visible and near IR region which are often difficult to resolve because of the low energy difference between them. The Cu (II) complex studied here show bands at 15, 338, 12, 823 and 21, 175 cm^{-1} which have been assigned to $^{2}B_{1g} \rightarrow {}^{2}A_{1g}$, $^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ and $^{2}B_{1g} \rightarrow {}^{2}E_g$ transitions, respectively[56-60]. The observed magnetic moment of 1.97 B.M. is suggestive of an octahedral geometry for Cu (II) complex[56], which is expectedly distorted as a result of symmetry-lowering Jahn-Teller effect[61]. The ground state for Ni (II) with d^8 configuration in an octahedral field has a ground state of ^{3}F and the excited state of ^{3}P, which is not split and designated as $^{3}T_{1g}(P)$. ^{3}F state is split into three states $^{3}A_{2g}$, $^{3}T_{2g}$ and $^{3}T_{1g}(F)$. The Ni (II)

complex display three bands at 24, 292, 14, 674 and 12, 735 cm^{-1} assignable to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively[62]. The magnetic moment of 3.02 B.M. for Ni (II) complex is an indication of its octahedral geometry. The three bands observed at 21, 502, 14, 651 and 10, 454 cm^{-1} for Co (II) complexes have been assigned to $^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$ (P), $^4T_{1g}$ (F) $\rightarrow {}^4A_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{2g}$ (P) transitions, respectively[56]. The magnetic moment of 4.75 B.M and the observed electronic transitions indicate high spin octahedral geometry of the complex.

Table 3: Electronic spectra data of ligand and metal complexes

Compounds	Bands (cm^{-1}) (ε, $Lmol^{-1}\,cm^{-1}$)	Assigned transition
ClBepINH	30, 113 (4360)	$n \rightarrow \pi^*$
	30, 169 (3184)	$n \rightarrow \pi^*$
	28, 169 (3184)	$\pi \rightarrow \pi^*$
CoClBepINH	21, 502 (154)	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	14, 651 (235)	$^4T_{1g}(F) \rightarrow {}^4A_{2g}$
	10, 454 (175)	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$
CrClBepINH	20, 354 (135)	$^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$
	22, 722 (255)	$^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$
	25, 364 (351)	$^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$
NiClBepINH	24, 292 (351)	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$,
	14, 694 (178)	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$
	12, 735 (185)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
CuClBepINH	15, 338 (172)	$^2B_{1g} \rightarrow {}^2A_{1g}$,
	12, 823 (134)	$^2B_{1g} \rightarrow {}^2B_{2g}$
	21, 175 (147)	$^2B_{1g} \rightarrow {}^2E_g$

Antimicrobial activity

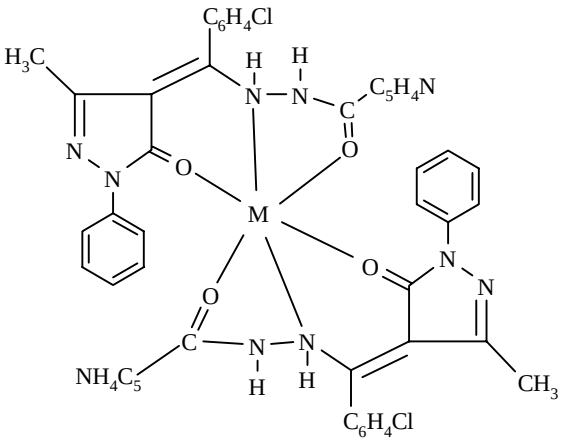
All the synthesized compounds were tested *in vitro* for their antimicrobial activity against *Escherichia coli, Pseudomonas aeruginosa, Klebsiella pneumoniae, Staphylococcus aureus* and *Bacillus subtilis*

Table 4: Antimicrobial data of synthesized compounds (zone of inhibition in mm)

Compound	*K. pneumonial*	*E. coli*	*P. aeruginosa*	*S. aureus*	*B. subtilis*
ClBepINH	+	+	+	+++	+++
CoClBepINH	+	+	+	+++	+++
CrClBepINH	+	+	+	+++	++
NiClBepINH	+	+	+	++	++
CuClBepINH	+	+	+	++	++

+ low activity (inhibition zone 2-5 mm), ++ moderate activity (inhibition zone 6-14 mm), +++ high activity (15-30 mm)

The results of antimicrobial screening showed that the synthesized compounds exhibited better activity against Gram positive *S. aureus and B. subtilis* compared to the low activity observed against Gram negative *K. pneumonia, E. coli and P. aeruginosa*. In order for these compounds to exert their bacteriostatic or bactericidal actions, they must access intracellular targets[63]. The observed variation in activity may be attributed to the protective lipopolyssacharide (LPS) in the outer membrane of the cell walls of Gram negative bacteria, which protects the sensitive inner membrane and the cell wall from drugs and dyes[64]. Therefore in Gram negative bacteria, drugs must cross the outer membrane, a substantial permeability barrier and thus a major determinant of antimicrobial resistance in these bacteria[65]. These protective lipopolyssacharide is absent in Gram positive bacteria[64]. Cr, Ni and Cu complexes showed moderate activity against *B. subtilis,* while Ni and Cu complexes showed moderate activity against *S. aureus*.



M= Co, Cu, Ni, Cr

Fig. 4: Proposed structure of the metal complexes

On the basis of microanalytical data, magnetic moments, conductivity measurements and spectral analysis, the above structure has been proposed for the metal complexes.

CONCLUSION

A pyrazoloimine and some of its metallic derivatives have been synthesized and characterized. The spectra data showed that the ligand exist in the keto-amine form, and coordinated as a neutral tridentate ONO donor ligand. The analytical data show that the metal: ligand ratio is 1:2 in all complexes studied. The electronic data and magnetic moments are in favour of octahedral geometry for all the complexes. The compounds exhibited better antimicrobial activity against Gram positive bacterial strains studied.

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