

Synthesis and Spectral Investigations of Some Platinum Metals Ions Coordination Compounds of 4[N-(Furan-2'-carboxalidene)Amino]Antipyrine Thiosemicarbazone and 4[N-(3',4',5'-Trimethoxybenzalidene)Amino]Antipyrine Thiosemicarbazone

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Received 04.05.2004

The present work describes the synthesis and spectral properties of some platinum metals chlorides coordination compounds of 4[N-(furan-2'-carboxalidene)amino]antipyrine thiosemicarbazone (FFAAPTS) and 4[N-(3',4',5'-trimethoxybenzalidene)amino]antipyrine thiosemicarbazone (TMBAAPTS). All the compounds have the general composition $MCl_2(L)$ ($M = Pd^{2+}$ or Pt^{2+} ; $L = FFAAPTS$ or $TMBAAPTS$) or $MCl_3(L)$ ($M = Ru^{3+}$, Rh^{3+} or Ir^{3+} ; $L = FFAAPTS$ or $TMBAAPTS$). All the complexes were characterized by elemental analyses, molar conductance, molecular weight, magnetic measurements, and infrared and electronic spectra. The infrared spectra suggest that both the thiosemicarbazones behave as neutral tridentate (N,N,S) ligands. The magnetic and electronic spectra suggest that Pd^{2+} and Pt^{2+} complexes are square planar, while Ru^{3+} , Rh^{3+} and Ir^{3+} complexes have octahedral geometry.

Key Words: Platinum metals, Thiosemicarbazones, Coordination compounds.

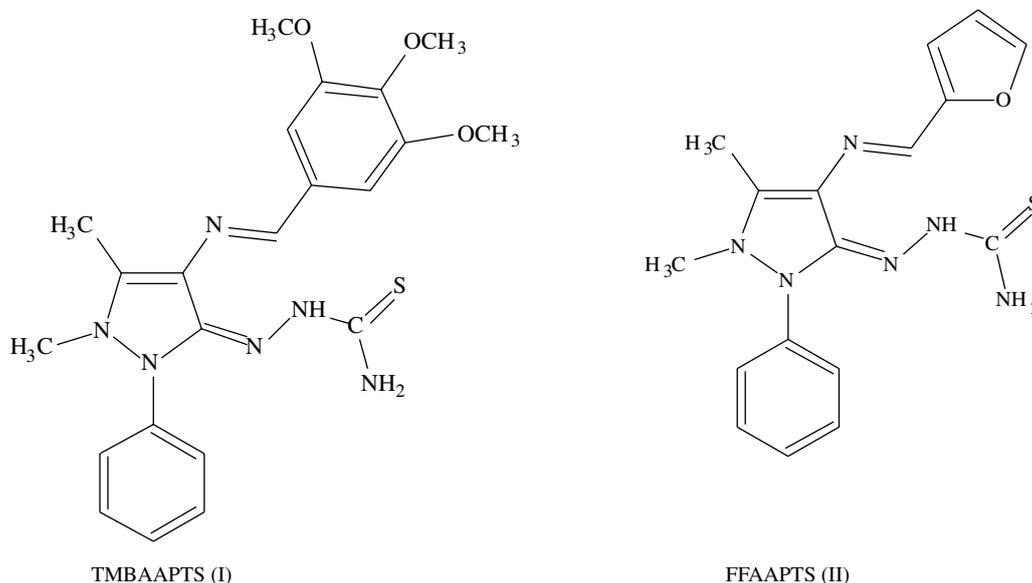
Introduction

Ruthenium, osmium, rhodium, iridium, palladium and platinum are the heaviest members of group VIII in the periodic table and are rare elements on a terrestrial scale. The chemistry of these elements frequently exhibits common features, but wide variations are also frequent. Interest in the interactions of platinum metals with biologically important molecules began about 35 years ago when Rosenberg et al.¹ published their discovery that certain platinum complexes exhibit anticancer activity. Cisplatin is the parent compound in this group. It is widely used for the treatment of testicular and ovarian cancers and, to a lesser extent,

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head and neck tumors. The prognosis of this treatment against testicular cancer is usually very good, with 5 year disease free survivals for disseminated disease approaching 90%^{2,3}. However, the efficacy of the drug is hampered by severe side effects, principally nephrotoxicity, severe nausea and vomiting.

The number of platinum complexes that show antitumor activity is still rapidly growing, because of attempts to find complexes with greater potency and less toxicity than the existing clinical drugs. As a consequence of , attention has turned to the other platinum group metals, like ruthenium, rhodium, palladium, osmium and iridium. Recently several groups of researchers⁴⁻¹⁰ became interested in various platinum and palladium metal complexes and studied their antitumor activity. A careful literature survey indicated that very little is known about platinum metal complexes of thiosemicarbazone having a pyrazolone ring¹¹. Thus in the present work, we describe the synthesis and characteristic properties of Pd²⁺, Pt²⁺, Ru³⁺, Rh³⁺ and Ir³⁺ complexes of 4[N-(3', 4', 5'-trimethoxybenzylidene)amino]antipyridine thiosemicarbazone (TMBAAPTS) (I) and 4[N-(furan-2-carboxalidene)amino]antipyridine thiosemicarbazone



Experimental

Palladium(II) chloride, tetrachloroplatinous acid(H₂PtCl₄), ruthenium(III) chloride, rhodium(III) chloride and iridium(III) chloride were obtained from Loba Chemicals and were dried prior to use. Both thiosemicarbazones were synthesized from 4-aminoantipyridine in the laboratory by a known method¹². All the solvents were obtained from standard sources such as BDH and E. Merck.

Synthesis of the complexes

Palladium(II) complexes

A solution of PdCl₂ (1 mmol) and the respective ligand (1.1 mmol) in ethanol containing a few drops of HCl were mixed and refluxed for ~1-2 h. The precipitate obtained was filtered, washed with ethanol and dried in vacuo over P₄O₁₀ (yield 60%).

Platinum(II) complexes

A hot aqueous solution (10 mL) of the $\text{H}_2[\text{PtCl}_4]$ (1.1 mmol) was added to a hot ethanolic solution (10 mL) of the respective ligand (1.2 mmol). The reaction mixture was refluxed on a water bath for ~ 2 h. On cooling the desired complex was precipitated out. The complex was filtered, washed with 50% aqueous ethanol and dried in vacuo over P_4O_{10} (yield 50%).

Ruthenium(III), rhodium(III) and iridium(III) complexes

Hot ethanolic solution of MCl_3 ($\text{M} = \text{Ru}, \text{Rh}$ or Ir) (1 mmol) was mixed with a hot ethanolic solution of the respective ligand (1.1 mmol). The reaction mixture was refluxed for $\sim 2-3$ h, and the volume of reaction mixture was reduced by evaporation. On cooling the contents, the required crystalline products were separated out. The complexes were filtered, washed with hot ethanol and dried as above (yield 55% - 65%).

Analysis

The percentages of platinum metals were determined by a standard method using EDTA as titrant and employing Erichrome Black T or xylenol orange as indicator, after decomposing the complexes with H_2SO_4 and H_2O_2 and dissolving the residue in water and by making the necessary volumes¹³. The chloride content was estimated by Volhard's method¹⁴. C, H and N analyses were carried out by the Microanalytical Laboratory of the Central Drug Research Institute, Lucknow, India.

The molecular weight of the complexes was determined in the laboratory cryoscopically in freezing nitrobenzene using a Beckmann thermometer of accuracy $\pm 0.01^\circ\text{C}$. The conductivity measurements were carried out using a conductivity bridge and dip type cell. All the measurements were obtained at room temperature in PhNO_2 . The magnetic measurements of the powder form of the complexes were carried out at room temperature on an Evan's balance using anhydrous copper(II) sulfate as calibrant. The infrared spectra of the complexes were obtained on a Perkin Elmer FT-IR Spectrometer model Spectrum 1000 in KBr. Electronic spectra were measured at room temperature on a GBC (Australia) UV-visible spectrophotometer Cintra 5.

Results and Discussion

All the platinum metals [Pd(II) , Pt(II) , Ru(III) , Rh(III) and Ir(III)] chlorides react with FFAAPTS and TMBAPTS to form complexes of the general composition $\text{MCl}_2\cdot\text{L}$ ($\text{M} = \text{Pd}^{2+}$ or Pt^{2+}) and MCl_3L ($\text{M} = \text{Ru}^{3+}$, Rh^{3+} or Ir^{3+} ; $\text{L} = \text{FFAAPTS}$ or TMBAPTS). The analytical data of these complexes are presented in Table 1. All the complexes are quite stable and can be stored for months without any appreciable change. These complexes are generally soluble in common organic solvents.

The molar conductances of the present complexes in nitrobenzene are presented in Table 1. The molar conductance values of $\text{PdCl}_2(\text{L})$ and $\text{PtCl}_2(\text{L})$ indicate that these complexes to be 1:1 electrolytes and thus one chloro ion is present outside the coordination sphere. In the case of Ru^{3+} , Rh^{3+} and Ir^{3+} complexes, the molar conductance values are too low to account for any dissociation; therefore, we consider that all these complexes are non-electrolytes.

Table 1. Analytical conductivity, molecular weight and magnetic moment data of Pd²⁺, Pt²⁺, Ru³⁺, Rh³⁺ and Ir³⁺ complexes of FFAAPTS and TMBAAPTS.

Complex	Analysis: Found (calcd.) %						m.wt. Found (calcd.)	Ω_m ohm ⁻¹ cm ² mol ⁻¹	μ eff (B.M.)
	Yield (%)	Metal	C	H	N	Cl			
PdCl ₂ (FFAAPTS)	70	19.84 (19.96)	38.14 (38.41)	3.32 (3.38)	15.73 (15.81)	13.20 (13.37)	267 (531)	25.2	Diamag
PdCl ₂ (TMBAAPTS)	72	16.67 (16.79)	41.67 (41.83)	4.09 (4.12)	13.26 (13.31)	11.14 (11.25)	318 (631)	23.9	Diamag
PtCl ₂ (FFAAPTS)	68	31.34 (31.45)	32.73 (32.90)	2.87 (2.90)	13.45 (13.54)	11.33 (11.45)	313 (620)	24.3	Diamag
PtCl ₂ (TMBAAPTS)	70	26.90 (27.08)	36.52 (36.66)	3.57 (3.61)	11.60 (11.66)	19.78 (19.86)	364 (720)	25.6	Diamag
RuCl ₃	60	17.79 (17.89)	36.18 (36.33)	3.16 (3.20)	14.83 (14.95)	18.79 (18.96)	558 (661.5)	3.3	1.87
RhCl ₃ (FFAAPTS)	65	18.16 (18.27)	36.06 (36.20)	3.16 (3.19)	14.80 (14.90)	18.76 (18.89)	560 (563.5)	2.9	Diamag
RhCl ₃ (TMBAAPTS)	62	15.40 (15.52)	39.62 (39.78)	3.86 (3.91)	12.53 (12.66)	15.93 (16.05)	659 (663.5)	2.8	Diamag
IrCl ₃ (FFAAPTS)	65	29.28 (29.42)	31.11 (31.26)	2.70 (2.75)	12.76 (12.87)	16.20 (16.32)	649 (652.5)	3.1	Diamag
IrCl ₃ (TMBAAPTS)	65	25.34 (26.51)	34.95 (35.08)	3.40 (3.45)	11.85 (11.16)	14.04 (14.15)	748 (752.5)	3.3	Diamag

The molecular weights determined cryoscopically in nitrobenzene are also given in Table 1. The results are in broad agreement with the conductance data.

A study and comparison of infrared spectra of free ligands (FFAAPTS and TMBAAPTS) and their platinum metal complexes (Table 2) imply that both ligands behave as neutral tridentate and the metals are coordinated through N and N of the 2 azomethine groups and of S of the thio-keto group.

Table 2. Infrared absorption frequencies (cm^{-1}) of Pd^{2+} , Pt^{2+} , Ru^{3+} , Rh^{3+} and Ir^{3+} complexes of FFAAPTS and TMBAAPTS.

Compound	$\nu(\text{N-H})$	$\nu(\text{C=N})$	$\nu(\text{C=S}) + \nu(\text{C=N}) + \nu(\text{C-N})$	$\delta(\text{N-C-S}) + \text{C=S bending}$	$\nu(\text{N-N})$	$\nu(\text{C=S})$	$\nu(\text{M-N})/\nu(\text{M-S})$
FFAAPTS	3440 s 3280 s	1600 vs	1315 s 1185 m	1122 m 1095 m	1040 m	840 s 820 m 780 s	—
$\text{PdCl}_2(\text{FFAAPTS})$	3342 m 3282 m	1560 s	1370 s 1205 m	1160 m 1130 m	1052 m	810 s 792 m	530 m 432 m
$\text{PtCl}_2(\text{FFAAPTS})$	3440 m 3280 m	1560 s	1370 s 1275 m	1160 m 1135 m	1050 m	808 s 785 m	525 m 435 m
$\text{RuCl}_3(\text{FFAAPTS})$	3342 m 3280 m	1565 s	1372 s 1218 m	1165 m 1130 m	1058 m	810 s 775 m	530 m 425 m
$\text{RhCl}_3(\text{FFAAPTS})$	3440 m 3282 m	1562 s	1365 s 1210 m	1165 m 1130 m	1052 m	812 m 780 m	525 m 440 m
$\text{IrCl}_3(\text{FFAAPTS})$	3442 m 3280 m	1558 s	1370 s 1210 m	1162 s 1130 m	1055 m	808 m 782 m	530 m 425 m
TMBAAPTS	3320 m 3200 m	1602 vs	1305 s 1280 m	1125 m 1085 m	1060 m	840 m 770 s	—
$\text{PdCl}_2(\text{TMBAAPTS})$	3320 m 3200 m	1550 s	1330 s 1303 m	1152 m 1120 m	1070 m	810 m 755 m	515 m 435 m
$\text{PtCl}_2(\text{TMBAAPTS})$	3325 m 3205 m	1552 s	1335 s 1315 m	1145 m 1122 m	1072 m	815 m 750 m	520 m 435 m
$\text{RuCl}_3(\text{TMBAAPTS})$	3312 m 3202 m	1570 s	1342 s 1310 m	1150 m 1125 m	1080 m	810 m 740 m	535 m 440 m
$\text{RhCl}_3(\text{TMBAAPTS})$	3315 m 3202 m	1572 s	1340 s 1315 m	1140 m 1120 m	1078 m	807 m 735 m	525 m 435 m
$\text{IrCl}_3(\text{TMBAAPTS})$	3320 m 3200 m	1575 s	1360 s 1310 m	1145 m 1125 m	1075 m	815 m 730 m	530 m 430 m

Strong bands in the $3440\text{-}3270\text{ cm}^{-1}$ region in both ligands were observed due to $\nu(\text{N-H})$ vibrations. The negligible effect on these frequencies after complexation precludes the possibility of complexation at this group.

The absorptions at $\sim 1600\text{ cm}^{-1}$ in free ligands can be attributed to (C=N) stretching vibrations of imine nitrogen, which is in agreement with previous observations^{15,16}. On complexation these frequencies were observed to be shifted to a lower wave number (Table 2). These observations suggest the involvement of unsaturated nitrogen atoms of the 2 azomethine groups in bonding with the metal ions.

In substituted thioureas, the (C=S) stretching vibrations contributed much with some other vibrations as (C-N) stretching and bending as well as (N-C-S) bending modes¹⁷. In the spectra of the present

ligands, the bands observed in the 1300-1185 cm^{-1} , 1120-1085 cm^{-1} and 840-770 cm^{-1} regions are assigned to $[\nu(\text{C}=\text{S}) + \nu(\text{C}=\text{N}) + \nu(\text{C}-\text{N})]$, $[\delta(\text{N}-\text{C}-\text{S}) + \delta(\text{C}=\text{S})]$ and $\nu(\text{C}=\text{S})$ stretchings, respectively^{18,19}. Coordination of sulfur with the metal ion would result in the displacement of electrons towards the latter, thus resulting in the weakening of the (C=S) bond. Hence, on complexation (C=S) stretching vibrations should decrease and those of (C-N) should increase¹⁹. In all the present complexes of Pd^{2+} , Pt^{2+} , Ru^{3+} , Rh^{3+} and Ir^{3+} the FFAAPTS and TMBAAPTS frequencies in the range 1315-1185 cm^{-1} increase by nearly 50-60 cm^{-1} . Similarly, bending modes of (N-C-S) and (C=S) also increase but by lesser amounts. On the other hand, on complexation the frequencies in 840-770 cm^{-1} are shifted to lower wave numbers and the intensity of the bands are also reduced. All these peculiar changes on complexation confidently preclude any unambiguous ascertainment of the metal-sulfur bond. The possibility of thione-thiol tautomerism ($\text{H}-\text{N}-\text{C}=\text{S} \rightleftharpoons \text{C}=\text{N}-\text{SH}$) in these ligands has been ruled out for no bands around 2700-2500 cm^{-1} , characteristics of the thiol group, are displayed in the infrared absorption^{20,21}.

The far i.r. spectral bands in both the ligands are practically unchanged in the complexes, but show some new bands with medium to weak intensity in the 530-425 cm^{-1} region tentatively assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$, which are in agreement with previous works^{22,23}. $\nu(\text{M}-\text{Cl})$ is tentatively assigned in the 380-360 cm^{-1} region^{22,23}.

Palladium(II) complexes

The magnetic moment data of Pd^{2+} complexes indicate that these complexes are diamagnetic. The complexes may have a square-planar coordination of the central metal ion by the surrounding ligands. Pd^{2+} having a d^8 configuration favors the formation of complexes with square-planar geometry. In the electronic spectra of the present Pd^{2+} complexes, 2 spin allowed d-d bands in the 26,000-29,000 cm^{-1} region along with 2 charge-transfer bands were observed. The spin allowed transitions were assigned as a combination of both $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{E}_g$ transitions by assuming the difference in the energies of both b_{2g} (xy) and e_g (xz, yz) levels is very little. The other spin allowed bands for these Pd^{2+} complexes were assigned to the $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ transition. The charge transfer bands were observed as a combination of $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2u}$, $^1\text{A}_{1g} \rightarrow a^1\text{E}_u$ and $^1\text{A}_{1g} \rightarrow b^1\text{E}_u$ transitions, respectively. The reason for taking the combination of these transitions is that the resolution of the lower transitions was not observed in the spectra of Pd^{2+} complexes at room temperature. The electronic spectra of these complexes are indicative of planar geometries and our data are in good agreement with previous reports²⁴⁻²⁶. Assuming $C = 3500 \text{ cm}^{-1}$ and $B = 500 \text{ cm}^{-1}$, the values of Δ_1 , Δ_2 and Δ_3 were evaluated²⁷. The value of Δ_1 can also be obtained by taking a value of $F_2 = 10 F_4 = 600 \text{ cm}^{-1}$ for the Slater-Condon interelectronic repulsion parameter²⁸ and using a relation $\Delta_1 = \nu_1 + 3.5 F_2$ for the first $d-d$ spin allowed transition. The values of Δ_1 , Δ_2 and Δ_3 are presented in Table 3.

Table 3. Electronic spectral bands (cm^{-1}) and relevant ligand field parameters in Pd^{2+} complexes of FFAAPTS and TMBAAPTS.

Complex	ν_1 $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}, ^1\text{E}_g$	ν_2 $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$	C.T.	C.T.	Δ_1 (cm^{-1})	Δ_2 (cm^{-1})	Δ_3 (cm^{-1})
$\text{PdCl}_2(\text{FFAAPTS})$	26,100	28,000	35,300	47,250	29,600	3600	2100
$\text{PdCl}_2(\text{TMBAAPTS})$	27,000	28,100	35,900	46,350	30,500	3100	1600

Platinum(II) complexes

Pt²⁺ complexes are diamagnetic and have a *d*⁸-configuration implying a square-planar geometry of these complexes. Further, the electronic spectra of these complexes positively affirm the presence of square-planar geometry^{29,30}. Three *d* – *d* spin allowed transitions are expected corresponding to the transitions from the 3 lower lying *d*-levels to the empty *d*_{x²-y² orbitals. The ground state is ¹A_{1g} and the excited states corresponding to these transitions are ¹A_{2g}, ¹B_{1g} and ¹E_g in increasing order of energy. The electronic spectral bands (Table 4) appearing at ~25,000 cm⁻¹ in the present complexes may be assigned to the ¹A_{1g} → ¹B_{1g} transition. Other electronic spectral bands appearing at ~28,500 cm⁻¹ and above are due to charge transfers.}

Table 4. Electronic spectral bands (cm⁻¹) and their assignments in Pd²⁺ complexes of FFAAPTS and TMBAPTS.

Complex	Spectral bands (cm ⁻¹)	Assignments	Δ ₁ (cm ⁻¹)
PtCl ₂ (FFAPTS)	25,100 28,610 37,300 41,900	¹ A _{1g} → ¹ B _{1g} Charge-transfer bands	27,200
PtCl ₂ (TMBAPTS)	24,700 28,590 36,900 42,000	¹ A _{1g} → ¹ B _{1g} Charge-transfer bands	26,800

Ruthenium(III) complexes

Ruthenium(III) belongs to the *d*⁵ system and as such has 5 electrons in the outer orbital. Ru³⁺ complexes show magnetic moments of 1.83-1.87 B.M. at room temperature, which are lower than the spin only value. The lowering of μ_{eff} values may arise due to the effect of the ligand-field, metal-metal interaction of considerable delocalization. These values ruled out the possibility of square-planar or square-bipyramidal type complexes. The only possible stereochemistry on the basis of magnetic data is inner orbital octahedral geometry around the metal ion due to a donor atom in all the Ru³⁺ complexes³⁰⁻³³.

Rhodium(III) complexes

All the complexes of Rh³⁺ are diamagnetic. From this observation, we expect octahedral stereochemistry of the ligand around the metal ion, forming sp³d² hybridization³⁰⁻³³.

Iridium(III) complexes

The complexes of Ir³⁺ are diamagnetic, as expected, for the complexes are of low spin type (*t*_{2g})⁶. Electronic spectra of the complexes positively affirm an octahedral configuration around the central metal ion^{34,35}. In all the Ir³⁺ complexes the bands appear at 17,500-17,700 cm⁻¹, 23,250-23,365 cm⁻¹ and few bands above 30,000 cm⁻¹. The bands may be assigned to ¹A_{1g} → ¹T_{1g} and ¹A_{1g} → ¹T_{2g} transitions in increasing order of energy. The bands above 30,000 cm⁻¹ may be assigned to charge transfer bands.

On the basis of above studies, we tentatively assigned the following structures of the present complexes (Figures 1 and 2).

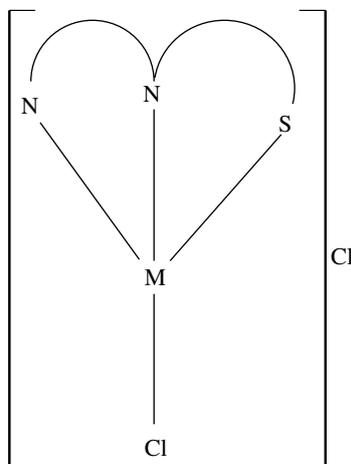


Figure 1. Probable structure of platinum metals complexes of thiosemicarbazone; $[M(L)Cl]Cl$; ($M = Pd^{2+}$ or Pt^{2+} ; $L = TMBAAPTS$ or $FFAAPTS$).

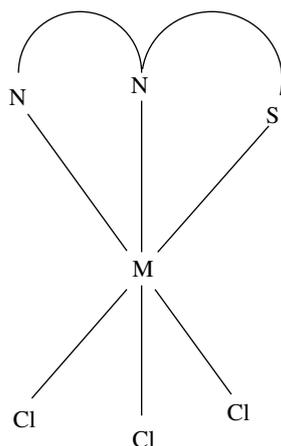


Figure 2. Probable structure of platinum metals complexes of thiosemicarbazone; $[M(L)Cl_3]$; ($M = Rh^{3+}$, Rh^{3+} or Ir^{3+} ; $L = TMBAAPTS$ or $FFAAPTS$).

Acknowledgment

The authors are grateful to the University of the South Pacific, Suva, Fiji, for the financial support in the form of a research project (6395-1321) from, URC grant.

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