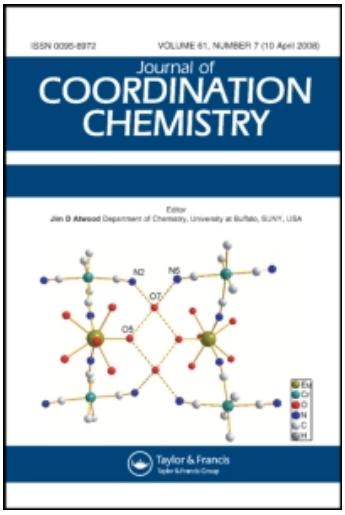

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Platinum(IV) and palladium(II) thiosemicarbazide and thiodiamine complexes: A spectral and antibacterial study

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Platinum(IV) and palladium(II) thiosemicarbazide and thiodiamine complexes: A spectral and antibacterial study

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Platinum(IV) and palladium(II) complexes $[Pt(L)_2Cl_2]$ and $[Pd(L)Cl_2]$, [where, L = 1,1-diphenyl-2-thiosemicarbazide (L^1) and (1,1-diphenyl-2-thio)-1,3-propanediamine (L^2) have been synthesized. The thiosemicarbazides and thiodiamines exist as the thione-thiol tautomer and coordinate as a bidentate N-S ligand. The ligands are monobasic bidentate. The complexes have been characterized by elemental analysis, IR, mass, electronic and 1H NMR spectroscopic studies. In vitro antibacterial studies have also been carried out for some complexes.

Keywords: Synthesis; Characterization; Spectral; Antibacterial

1. Introduction

Thiosemicarbazides and thiodiamines have aroused considerable interest in chemistry and biology due to their antibacterial, antimalarial, antineoplastic and antiviral activities [1–4]. Thiosemicarbazides and thiodiamines are significantly affected by substitution at the moiety's N(4) position [5–6]. The chemistry of transition metal complexes of thiosemicarbazides has received considerable attention largely because of their pharmacological properties [7]. The combination of thiosemicarbazides and thiohydrazones with metals like platinum(II) or palladium(II) that damage DNA produces synergistic inhibition of tumor growth and may lead to improvements in the effectiveness of cancer chemotherapy [8–10]. In view of the number of applications of thiosemicarbazides [3–6] and the clinical utility of platinum-metal complexes as antibacterial, antifungal, antitumour and cytotoxicity, we have prepared platinum(IV) and palladium(II) complexes of thiosemicarbazides and thiodiamines. These ligands and complexes were characterized by elemental analysis, IR, mass, electronic and ^{1}H NMR

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spectroscopic studies. In vitro antibacterial studies have also been carried out for some complexes.

2. Experimental

2.1. *General*

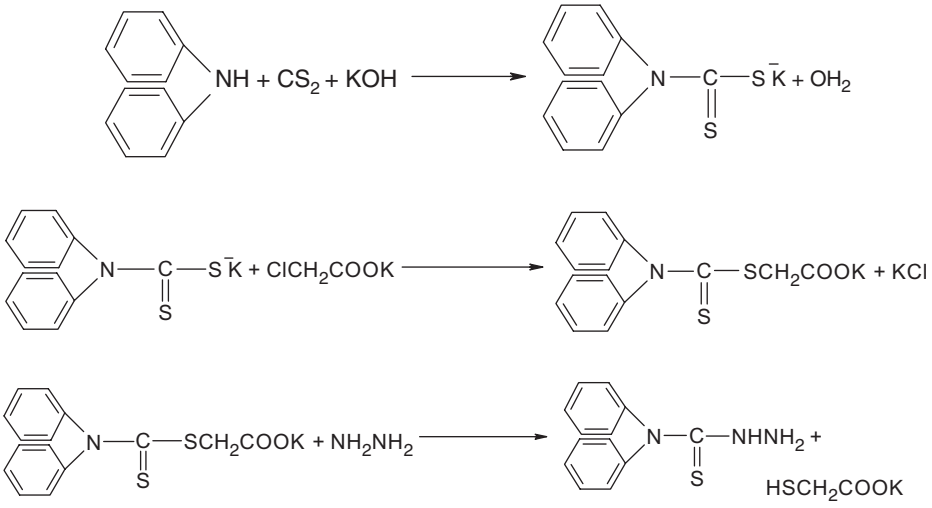
2.1.1. Materials and chemicals. All the reagents used were AR grade. The CHNS/O analysis of ligands and metal complexes were done on an Elementar Analysensysteme Gmbh Vario El-III. IR and far IR were recorded by using KBr pellets on a Perkin-Elmer spectrum 2000 FTIR spectrometer. Electronic spectra of the ligands in methanol solution and the complexes in DMSO solution were recorded on a Shimadzu UV-visible spectrophotometer Model 1601. Conductance measurements of the complexes in DMSO were carried out on a Digital Conductometer Model PT-827, India. Model JEOL SX102/DA-600 (KV 10MA) was used for recording mass spectra of the ligands in methanol solution. ^{1}H NMR spectra were recorded in d_6-DMSO on a Bruker Spectrospin 300 Spectrometer.

2.2. *Preparation of thiosemicarbazide*

Preparation of 1,1-diphenyl-2-thiosemicarbazide and (1,1-diphenyl-2-thio)-1, 3-propanediamine were prepared by modification of the literature methods [3–6,11].

2.2.1. Preparation of 1,1-diphenyl-2-thiosemicarbazide (L^1). In a three-necked round bottom flask 8.46 g (0.05 mol) of diphenylamine was dissolved in 40 mL methanol and chilled in an ice bath. To this, a chilled solution of 2.8 g (0.05 mol) potassium hydroxide in 1 mL water and 10 mL methanol was mixed with constant stirring. The mixed solution was treated with an ice-cold solution of 3.02 mL (0.05 mol) carbon disulfide (density 1.26 gcm^{-3}) in 3 mL methanol. The temperature of the reaction mixture was maintained below 10°C by the keeping flask in a freezing mixture of common salt and ice. During the process, a white crystalline precipitate of 1,1-diphenyl-2-dithiocarbamate separated. It was filtered, washed with ice-cold aqueous methanol. The product was then suspended in 10 mL methanol and treated with freshly prepared potassium chloroacetate [(0.05 mol){-potassium chloroacetate was obtained by dissolving 4.73 g chloroacetic acid in 3 mL ice cold water and mixing in 5 mL aqueous solution of 2.8 g potassium hydroxide}]. The temperature of the reaction mixture was kept at about 40°C on a water bath for an hour and the contents were left overnight at room temperature (25°C). After 24 h methanolic solution of 2.44 mL (0.05 mol) hydrazine hydrate (density 1.026 gcm^{-3}) was added to the reaction mixture and then heated on a water bath at 40°C for about 45 min. till the desired product began to separate. The solution was then cooled in ice for 24 h and filtered. 1,1-diphenyl-2-thiosemicarbazide thus obtained was recrystallized from methanol and dried under vacuum over $CaCl_2$ at room temperature.

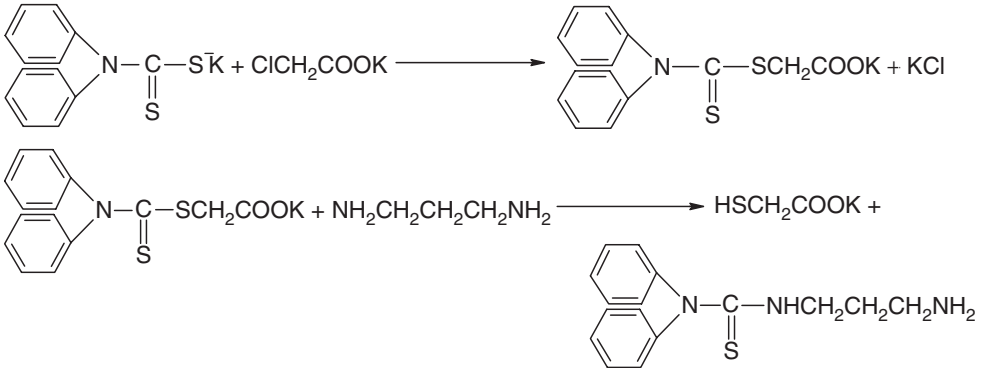
The reactions taking place in the preparation are shown below:



CHNS-Analysis; Found (Calculated)%:
C; 63.89 (64.19), H; 5.33 (5.35), N; 18.68 (17.28), S; (12.67) 13.16
Mass spectrum; *m*/*z*: 243.59

2.2.2. Preparation of (1,1-diphenyl-2-thio)-1,3-propanediamine (L^2). 14.15 g (0.05 mol) 1,1-diphenyl-2-dithiocarbamate prepared as earlier was suspended in 25 mL methanol and treated with freshly prepared potassium chloroacetate [(0.05 mol). The temperature of the reaction mixture was kept at 40°C for an hour and the contents were left overnight at room temperature. After 24 h methanolic solution of 4.36 mL (0.05 mol) 1,3-propanediamine (density 0.85 gcm^{-3}) was added to the reaction mixture and then heated on a water bath for about 45 min when the desired product began to separate. It was cooled in ice for 24 h and filtered. (1,1-diphenyl-2-thio)-1,3-propanediamine thus obtained was recrystallized from methanol and dried under vacuum over $CaCl_2$ at room temperature.

The reactions taking place in the preparation are shown below:



CHNS-Analysis; Found (Calculated)%:

C; 68.23 (67.36), H; 6.53 (6.67), N; 16.23 (16.70), S; (10.61) 11.20.
Mass spectrum; *m*/*z*: 285.71.

3. Preparation of Complexes

3.1. *Preparation of [Pt(L)$_2$Cl$_2$] complexes where L = L^1 and L^2*

The corresponding ligand L [where L = L^1 (0.122 g, 0.5 mmol), L^2 (0.143 g, 0.5 mmol) in methanol was added to aqueous solution of H_2PtCl_6 (0.103 g, 0.25 mmol). The solution was stirred for 4–5 h and the colour changed from yellow to yellowish orange. The resulting yellowish orange precipitate was washed with double distilled water several times and dried in a desiccator over $CaCl_2$ under vacuum.

3.2. *Preparation of [Pd(L)Cl$_2$] complexes where L = L^1 and L^2*

The corresponding ligand L [where L = L^1 (0.122 g, 0.5 mmol), L^2 (0.143 g, 0.5 mmol) in methanol and added with constant stirring to a 1N HCl solution of palladium chloride (0.089 g, 0.5 mmol). The solution was stirred for 4–5 h. The brownish precipitate appeared immediately, was separated, washed with double distilled water several times and dried in desiccator over $CaCl_2$ under vacuum.

3.3. *In vitro antibacterial activity*

Most of the compounds have been screened in vitro against *Staphylococcus epidermidis* (*S. epidermidis*) and *Escherichia coli* (*E. coli*). Various methods [12–15] are available for the evaluation of the antibacterial activity of different types of drugs. However, the most widely used method [15] in determining the antibacterial activity of the drug is to add it in known concentrations to cultures of the test organisms.

3.4. *Disc diffusion assay*

The disc diffusion assay was used to determine antibacterial activity of the drug using gram positive and gram negative strains of *S. epidermidis* and *E. coli*. Base plates were prepared by pouring 10 mL of autoclaved Muller-Hinton agar (Biolab) into sterile Petri dishes (9 cm) and allowing them to settle. Molten autoclaved Muller-Hinton that had been kept at 48C was inoculated with a broth culture (10^6–10^8 mL^{-1}) of the test organism and poured over the base plate. The discs were air dried and placed on top of the agar layer. Four replicants of each drug tested (four discs per plate) with a gentamycin disc (0.5 μg disc^{-1}) as a reference. The plates were then incubated for 18 h at room temperature. Antibacterial activity is expressed as a ratio of the inhibition zone produced by the drug to the inhibition zone produced by the gentamycin standard.

3.5. *Micro dilution antibacterial assay*

The serial dilution technique was performed using 96 well micro plates to determine the minimum inhibitory concentration (MIC) of the drugs for antibacterial activity. Two milliliter cultures of two bacterial strains of *S. epidermidis* and *E. coli* were prepared and placed in a water bath overnight at 37C. The overnight cultures were diluted with Muller-Hinton broth. The drugs were suspended to a concentration of $60\,\mu g\,disc^{-1}$ (in dmso) with sterile distilled water in a 96 well micro plate. A similar two fold serial dilution of gentamycin (Sigma) was used as positive control against each bacterium. One hundred microliters of each bacterial culture was added to each well. The plates were covered and incubated overnight at 37°C. To indicate bacterial growth p-iodonitrotetrazolium violet was added to each well and the plates incubated at 37°C for 30 min. Bacterial growth in the wells was indicated by a red colour, whereas clear wells indicated inhibition.

4. Result and discussion

4.1. *Elemental analysis*

Elemental analysis table 1 indicates pure complexes. All complexes are soluble in DMSO. The molar conductance values of the isolated complexes measured in DMSO are found to be less than $15\,Ohm^{-1}\,cm^2\,mol^{-1}$ suggesting their non-electrolytic nature.

4.2. *Electronic spectra*

The electronic spectra table 2 of the thiosemicarbazides (L^1) and thiodiamines (L^2) show spectral bands because of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. In the present study, the complexes are diamagnetic. The platinum(IV) complexes must be octahedral and palladium(II) complexes square planar. Their geometries are supported by their electronic spectra. The ground state of platinum(IV) is $^1A_{1g}$ and four bands can be expected corresponding to $^1A_{1g} \rightarrow {}^3T_{1g}$ (23,900–24,200 cm^{-1}), $^1A_{1g} \rightarrow {}^3T_{2g}$ (17,200–18,250 cm^{-1}), $^1A_{1g} \rightarrow {}^1T_{1g}$ (38,300–28,000 cm^{-1}), and $^1A_{1g} \rightarrow {}^1T_{2g}$ (27,500–25,000 cm^{-1}) transitions [16]. Palladium (II) is a d^8 system and three spin allowed singlet–singlet d–d transitions are predicted [17–18]. The ground state is $^1A_{1g}$ and the predicted transitions are $^1A_{1g} \rightarrow {}^1A_{2g}$ (16,800–12,000 cm^{-1}), $^1A_{1g} \rightarrow {}^1B_{1g}$ (17,500–23,100 cm^{-1}) and $^1A_{1g} \rightarrow {}^1E_g$ (21,000–26,500 cm^{-1}).

Strong charge transfer transitions may interfere and prevent the observation of all the expected bands [19–21]. Strong bands between 340 and 400 nm (25,000–29,000 cm^{-1}) are assignable to a combination of metal ligand charge transfer ($M \rightarrow LCT$) and d–d bands. The very intense band at ~400 is assignable to combination of sulfur → metal charge transfer ($L\pi \rightarrow MCT$) and d–d bands.

Solutions of thiosemicarbazide and thiodiamines in DMSO feature a strong band at ca. 340 nm ($\log \varepsilon = 2.80$) because of the $n \rightarrow \pi^*$ transition for the azomethine fuction with shoulders at higher and lower energy. These values show very little shift in complexes but the intensity is enhanced. One absorption band observed at ca. 285 nm, is assigned to the $\pi \rightarrow \pi^*$ intraligand electron transition, N=C=S. This band shifts on

Table 1. Elemental analysis of the complexes.

Complexes	Molar conductance	Colour	Found (calculated)%					
			C	H	N	S	Cl	Metal
$Pt(L^1)_2Cl_2$	12.6	Yellowish orange	41.85 (41.49)	3.49 (3.46)	10.98 (11.17)	8.66 (8.51)	9.50 (9.44)	26.25 (25.93)
$Pd(L^1)Cl_2$	11.4	Brownish	37.44 (37.14)	3.03 (3.09)	9.89 (10.00)	7.43 (7.62)	17.05 (16.90)	25.50 (25.34)
$Pt(L^2)_2Cl_2$	13.8	Yellowish orange	46.17 (45.93)	4.52 (4.54)	10.19 (10.05)	7.92 (7.65)	9.02 (8.49)	23.50 (23.33)
$Pd(L^2)Cl_2$	14.5	Brownish	41.35 (41.56)	4.09 (4.11)	9.33 (9.09)	7.13 (6.93)	15.20 (15.37)	23.25 (22.94)

complexation, revealing involvement of the C=S group in complexation in all the complexes. Additional bands appear in the complexes from d–d and charge transfer transitions.

4.3. *Infrared spectra*

The IR spectra table 3 of the thiosemicarbazide and thiodiamine contain −NH−C=S groups as a potential bond forming site. The IR band of ν(C=S) is observed at 750–900 cm^{-1}. The ν(C=S) shifted to lower frequency on complexation indicating coordination to metal through the thioamide sulfur. This shift is 80–140 cm^{-1} [22].

Table 2. Electronic spectra of the complexes.

Complexes	λ_{max} (nm)	log ε ($L\,mol^{-1}\,cm^{-1}$)
L^1	209	3.54
	283	2.65
$Pt(L^1)_2Cl_2$	290	3.49
	346	2.79
	416	2.18
$Pd(L^1)Cl_2$	286	3.77
	351	2.83
	413	2.56
L^2	211	4.02
	284	3.59
$Pt(L^2)_2Cl_2$	287	3.70
	344	2.56
	403	2.17
$Pd(L^2)Cl_2$	299	3.35
	343	2.49
	398	2.26

Table 3. IR spectra of the complexes.

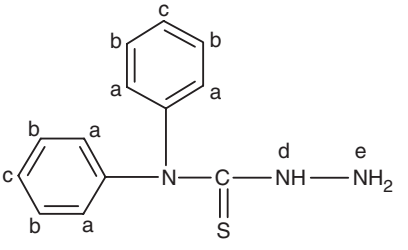
Complexes	ν_{N-H}	Thioamide I	Thioamide II	ν_{N-N}	$\nu_{C=S}$	ν_{M-N}	ν_{M-S}	ν_{M-Cl}
L2	2924							
	3249	1460	1307	1023	875	–	–	–
Pt(L2)2Cl2	2923							
	3229	1491	1323	1027	786	470	381	307
Pd(L2)Cl2	2922							
	3120	1500	1314	1025	766	463	385	295
L5	2929							
	3135	1462	1301	1025	882	–	–	–
Pt(L5)2Cl2	2919							
	3194	1493	1303	1020	780	460	389	285
Pd(L5)Cl2	2923							
	3173	1508	1307	1022	807	465	383	302

In all complexes with thiosemicarbazide and thiodiamine ligands, no band for ν(S–H) in the region 2600–2800 cm^{-1} is observed indicating the absence of any thiol (–SH) tautomer in the solid state. However, in solution and in the presence of certain metal ions, the ligands may exist in equilibrium with the tautomeric thiol form.

In all Pt(IV) and Pd(II) complexes the metal nitrogen vibrations, ν(M–N) are observed [23] in the far IR between 460–490 cm^{-1}, while 350–390 cm^{-1} shows metal–sulfur, ν(M–S) band stretching [24]. The band at ~330–270 cm^{-1} is assigned due to $\nu_{(Pt–Cl)}$ and $\nu_{(Pd–Cl)}$ stretching vibrations.

4.4. *NMR spectra*

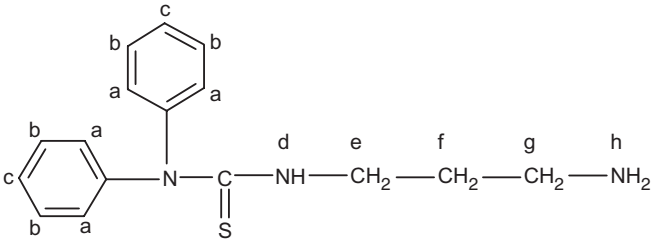
^{1}H NMR spectra of ligands and complexes were recorded in d_6-DMSO taking TMS as an internal standard.



$\delta_{(ppm)}$7.16 (d, 2H^a, Ar–H), 7.75 (t, 4H^b, Ar–H), 6.57 (t, 4H^c, Ar–H), 9.09 (br s, 1H^d, –NH), 3.26 (br s, 2H^e, –NH_2)

[Pt(L^1)$_2$$Cl_2$] $\delta_{(ppm)}$ 8.32 (d, 4H^a, Ar–H), 7.95 (t, 8H^b, Ar–H), 7.26 (t, 8H^c, Ar–H), 9.23 (br s, 2H^d, –NH), 4.34 (br s, 4H^e,–NH_2)

[Pd(L^1)Cl_2] $\delta_{(ppm)}$ 8.21 (d, 2H^a, Ar–H), 7.86 (t, 4H^b, Ar–H), 7.35 (t, 4H^c, Ar–H), 9.18 (br s, 1H^d, –NH), 4.12 (br s, 2H^e,–NH_2)



$\delta_{(ppm)}$7.19 (d, 2H^a, Ar–H), 7.71 (t, 4H^b, Ar–H), 6.46 (t, 4H^c, Ar–H), 8.92 (br s, 1H^d, –NH), 1.52 (t, 2H^e, –CH_2), 1.42 (m, 4H^f, –CH_2), 1.47 (t, 2H^g, –CH_2), 3.8 (br s, 2H^h, –NH_2)

[Pt(L^2)$_2$$Cl_2$] $\delta_{(ppm)}$ 8.32 (d, 4H^a, Ar–H), 7.96 (t, 8H^b, Ar–H), 7.12 (t, 8H^c, Ar–H), 9.1 (br s, 2H^d, –NH), 3.28 (t, 4H^e, –CH_2), 3.2 (m, 8H^f, –CH_2), 3.06 (t, 4H^g, –CH_2), 4.33 (br s, 4H^h, –NH_2)

[Pd(L^2)Cl_2] $\delta_{(ppm)}$ 8.18 (d, 2H^a, Ar–H), 7.85 (t, 4H^b, Ar–H), 7.16 (t, 4H^c, Ar–H), 8.97 (br s, 1H^d, –NH), 1.82 (t, 2H^e, –CH_2), 1.73 (m, 4H^f, –CH_2), 1.66 (t, 2H^g, –CH_2), 4.02 (br s, 2H^h, –NH_2)

Table 4. Antibacterial study of the complexes.

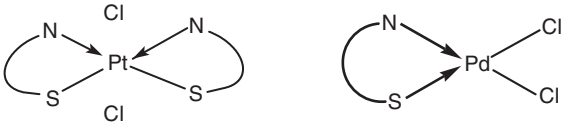
S. No.	Complexes	Zone of inhibition (mm)		MIC ($\mu g\,disc^{-1}$)	
		S. epidermidis	*E. coli*	*S. epidermidis*	*E. coli*
3	$Pt(L^1)_2Cl_2$	8	8	60.0	60.0
4	$Pt(L^2)_2Cl_2$	8	8	60.0	60.0
Gentamycin		16	16	1.0	1.0

The ^1H NMR spectrum of thiosemicarbazides and thiodiamines [25–27] shows signals at $\delta \sim 9.0$ and $\delta \sim 4.0$ ppm, due to the presence of NH protons which are lost on D_2O exchange. This is observable in the complexes also, suggesting that hydrogen bonding to the solvent occurs in the complexes as well as free ligands. Two signals at $\delta \sim 3.0$ and $\delta \sim 1.5$ ppm show the presence of different $-CH_2$ groups in the complex. Other signals due to aromatic ring (Ar–H) are observed.

4.4.1. Antibacterial study. In the current study some compounds were tested against pathogenic bacterial strains such as *S. epidermidis* and *E. coli* using the disc diffusion method. Gentamycin was used as reference drug for bacteria. The zone of inhibition was 8 mm at minimum inhibitory concentration (MIC) of 60.0 $\mu g\,disc^{-1}$.

5. Conclusion

All the complexes are diamagnetic; Pt(IV) complexes must be octahedral with four bands expected corresponding to $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions. Palladium(II) has three predicted transitions, $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_g$. The ν(C=S) shift towards lower frequency on complexation, indicating coordination to the metal ion is through azomethine nitrogen and thioamide sulphur. On the basis of these spectroscopic studies the probable structure of the complexes is:



The antibacterial study of the complexes compared with the standard drug gentamycin shows significant activity.

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