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COORDINATION COMPOUNDS OF Cu(II) AND Ni(II) WITH SCHIFF BASES DERIVED FROM FORMYLCARVONE AND o,p-AMINOBENZOIC ACID

Adalgiza Ciobanu*, Florica Zalaru**, D. Albinescu* and Christina Zalaru*

* Faculty of Chemistry, Organic Chemistry Dept., University of Bucharest, 90-92 Panduri Road, Romania.

** Faculty of Chemistry, Inorganic Chemistry Dept., University of Bucharest, 23 Dumbrava Rosie, Romania.

ABSTRACT

Copper(II) and nickel(II) complexes employing the Schiff bases derived from formylcarvone and ortho and para aminobenzoic acid (L) have been prepared. The complexes of general formula $CuL_2.2H_2O$ and $NiL_2.2L$ have been characterized by elemental analysis, infrared, visible and EPR spectra and thermodifferential analysis. The metallic ion has determined the type of the complex.

Keywords: Coordination compounds of Cu(II) and Ni(II), Schiff bases derived from formylcarvone.

RESUMO

Foram preparados complexos de cobre(II) e níquel(II) usando como ligantes bases de Schiff derivadas de formilcarvona e orto- e para- isômeros do ácido aminobenzoico. Os complexos tem a formula geral $CuL_2.2H_2O$ e $NiL_2.2L$ e foram caracterizados atraves de analise elementar, especroscopia no infravermelho, visível e REP e análise termodiferencial. O íon metalico determina o tipo de complexo formado.

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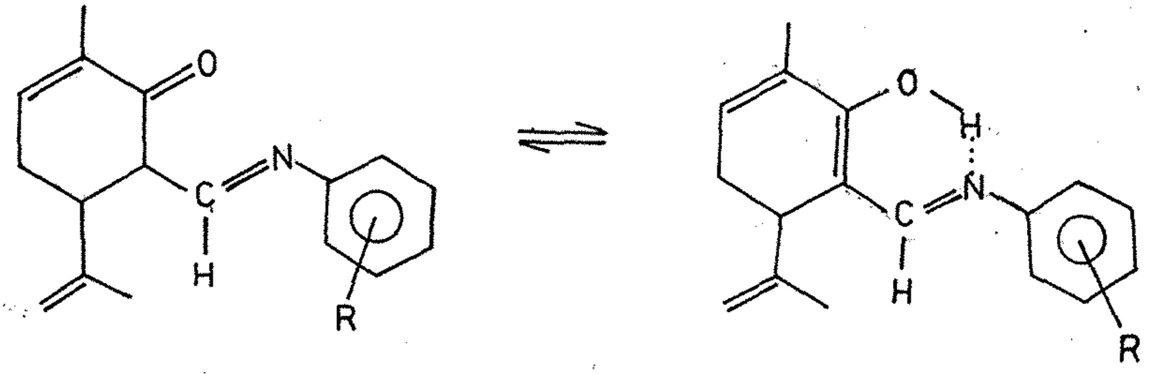
INTRODUCTION

Schiff bases represent a versatile series of ligands, the metal complexes of which have been widley studied /1-5/. Coordination compounds prepared by the reaction of some Schiff bases derived from formylcarvone and o,m,p-toluidine with Cu(II) and Ni(II) acetates have been previously described /6/.

This paper describs analogous compounds prepared by reaction of some Schiff bases derived from fromylcarvone and ortho and para benzoic amino acid by the type:

where R = -COOH, ortho and para



The presence of a >C=O group at the 2-position of the carvone ring of the ligand favours a keto-enolic tautomerism (scheme 1). NMR studies have been shown that these Schiff bases exist in solution as the enolic tautomer, and that the tautomer distribution was very strongly solvent dependent /7,8/. Such tautomerism has been atributed to intramolecular hydrogen bond formation. Since the oxygen is present as an OH group, these Schiff bases can act as chelating monoanion. The position of the -COOH substituent of the benzen ring and metallic ion might determine the type of the complex.

EXPERIMENTAL

The ligands were prepared according to the literature and $Cu(CH_3COO)_2.H_2O$ and $Ni(CH_3COO)_2.4H_2O$ p.a. were used. The complex compounds were prepared by mixing warm methanolic solutions 50% of metal acetate (1 mmole) and ligands (2 mmols and 4 mmols). The resulting precipitates were filtred and washed with aqueous methanol solution 50% and dried at room temperature.

The nickel and copper contents were determined gravimetrically analyses. The water content was calculated from the TG curve.

Diffuse reflectance spectra were obtained on VSU 2-P Zeiss Jena spectrophotometer using MgO as standard.

EPR spectra were recorded at room temperature on polycrystalline powders with an ART 5-IFA Spectrograph. The klystron frequency was 9060 MHz and the modulation of the magnetic field was 100 KHz. The EPR spectral parameters were calculated versus a Mn(II) standard.

Thermodifferential analyses were carried out with a Paulik-Paulik-Erdey derivatograph Q 1500 D MOM. Conditions of measurements: temperature range up to 1000°C, heating program 10 deg/min, sensivity DTA=1/10, s=50, m=0.0180 g; 0.0164 g; 0.024 g; 0.0190 g; atmosphere over sample-air.

IR spectra were recorded within 700-4000 cm^{-1} range on a Specord 75 Spectrophotometer in KBr pellet.

RESULTS AND DISCUSSION

The reaction of metallic acetates with the ligands in water-methanol mixture=1:1 and various M:L molar ratios (1:1; 1:2; and1:4) produces the complex compounds of formulas $CuL_2.2H_2O$ and $NiL_2.2L$ (table 1). The isolated compounds contain also molecules of water or ligand either as coordinated and/or as crystalline water.

Table 1: Results of the elemental and thermodifferential analyses.

No.	Ligand	Molar ratio M:L	Complex	M% found/ calcd.	H_2O% found/ calcd.	L% found/ calcd.	Colour
1.	R=ortho	1:2	$Cu(o\text{-}L)_2.2H_2O$	8.08/ 9.11	4.94/ 5.46	86.80/ 85.52	light-brown
2.	R=ortho	1:2 and 1:4	$Ni(o\text{-}L)_2.2(o\text{-}L)$	4.91/ 4.76	-	94.85/ 95.25	ochre
3.	R=para	1:2	$Cu(p\text{-}L)_2.2H_2O$	8.55/ 9.11	4.44/ 5.46	86.80/ 85.52	light brown
4.	R=para	1:2 and 1:4	$Ni(p\text{-}L)_2.2(p\text{-}L)$	4.66/ 4.76	-	94.39/ 95.25	ochre

It is noticed that, for nickel(II) ion is obtained the same compound for both Ni:L molar ratio (1:2 or 1:4).

The complex compounds are sparingle soluble in water and soluble in organic solvents (methanol, ethanol, chloroform).

The termodifferential analyses have been confirmed the formulas. Fig.1 and fig.2 show the decomposition of the compounds 1 and 2 in detail.

It is clear from the thermogravimetric data that, copper compounds contain water, while nickel compounds do not. The mass loss observed within 120-190°C range on TG curve corresponds to the loss of two water molecules per molecule of each of the copper compounds. The thermogravimetric (TG) curve for $Ni(o\text{-}L)_2.2(o\text{-}L)$ does not

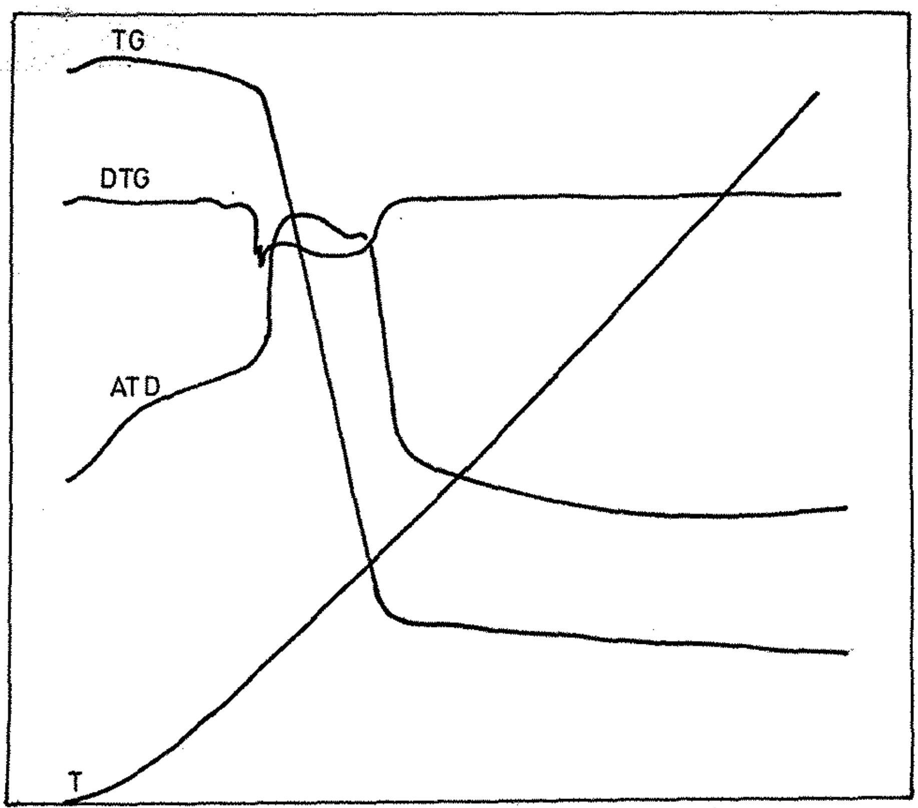


Fig. 1 Thermodifferential curve of $Cu(o\text{-}L)_2 . 2H_2O$.

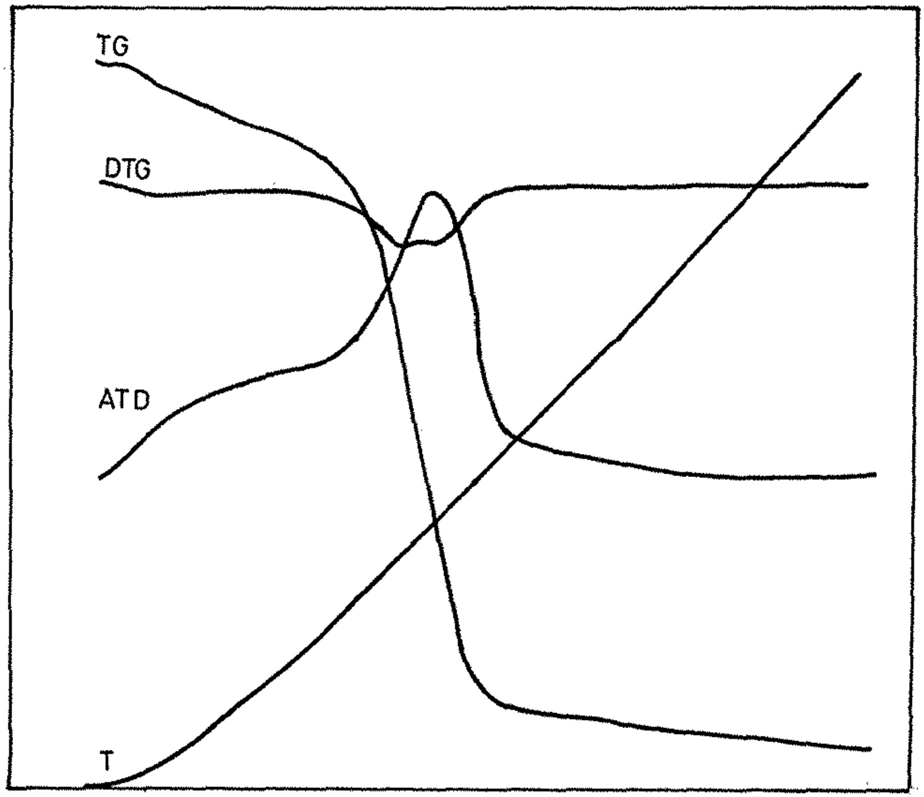


Fig. 2 Thermodifferential curve of $Ni(o\text{-}L)_2 . 2(o\text{-}L)$.

show whether or not the ligand molecules are liberated in steps (weight loss at 190°C, found: 10.98% calcd., for 2(o-L):47.62%.

Diffuse reflectance electronic spectra of Cu(II) complex compounds are similar; the broad band with a maximum at 700 nm can be assigned to a d-d transition (fig. 3).

This band can be associated with a distorted octahedron axially/9,10/. The strong broad absorption which occurs at ~ 400 nm is assigned to the ligand. Its "tails off" strongly into the visible range.

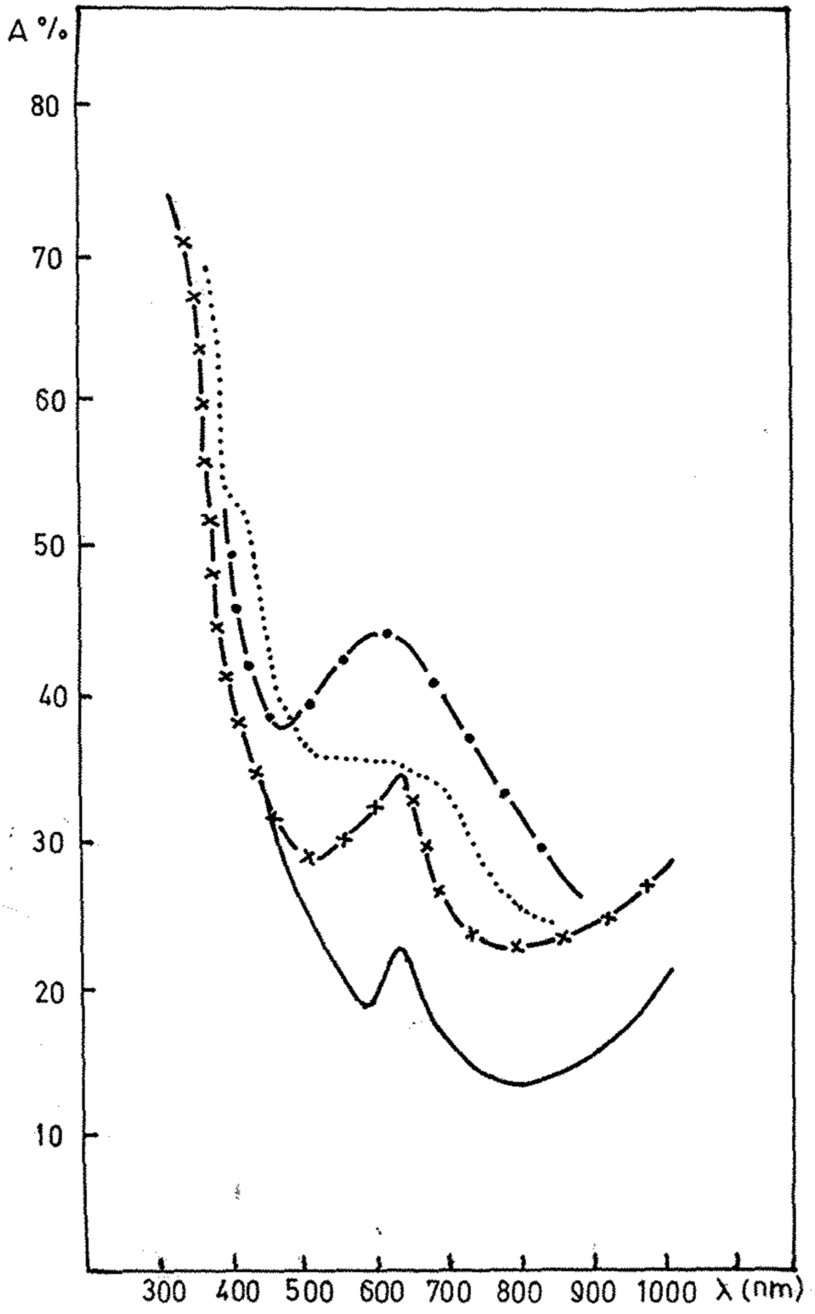


Fig. 3 Electronic reflectance spectra of the compounds:
-.-.- $Cu(p-L)_2 . 2H_2O$; . . . . . $Cu(o-L)_2 . 2H_2O$;
-x-x- $Ni(p-L)_2 . 2(p-L)$; —— $Ni(o-L)_2 . 2(o-L)$.

The EPR spectra of both Cu(II) complex compounds present a similar EPR signal with two g factors characteristic for the elongated tetragonal octahedral stereochemistry supporting the electronic spectra (fig. 4). The numerical g factors: $g_{//} >> g_{\perp} > 2.0$ suggests a bigger distorsion for $Cu(p\text{-}L)_2 \cdot 2H_2O$ compound.

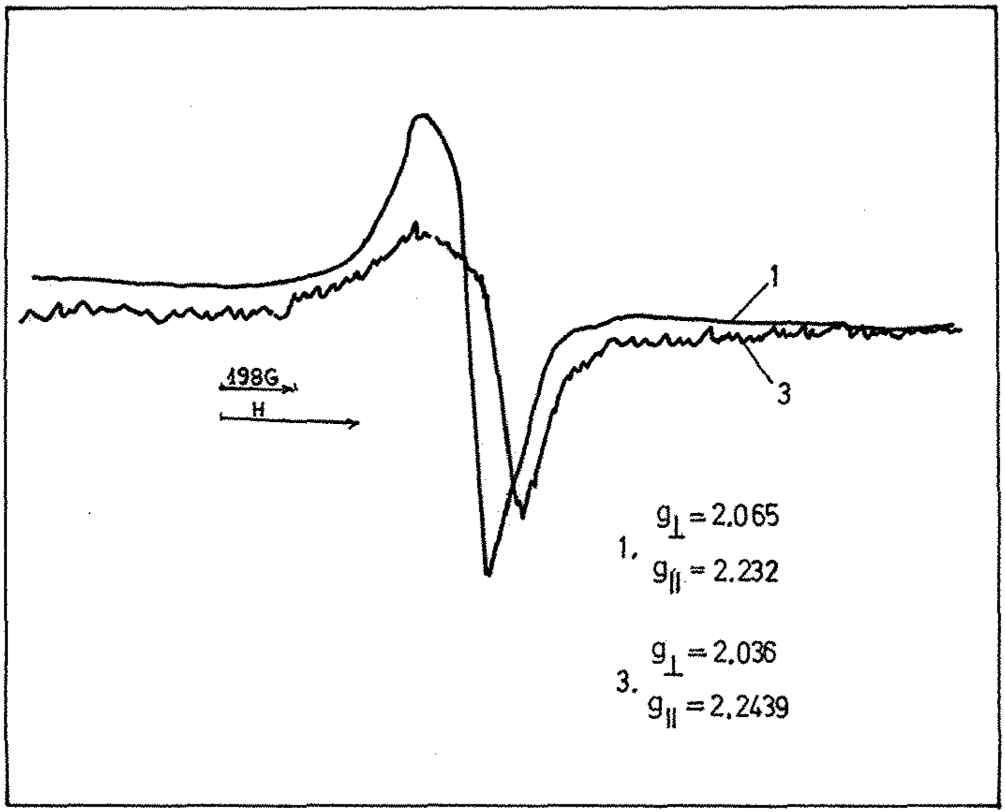


Fig. 4 EPR spectra of the compounds and EPR spectral parameters:
1. $Cu(o\text{-}L)_2 . 2H_2O$; 3. $Cu(p\text{-}L)_2 . 2H_2O$;

The electronic spectra of the Ni(II) complex compounds are similar and are consistent with the postulation that Ni(II) ion is essentially hexacoordinate/11/. The spectra present a band (λmax=730 nm, 740 respectively), ν_2, that could be assigned to $^3A_{2g} \dashrightarrow {}^3T_{1g}(F)$ transition. The band ν_3 (λmax~400 nm) assigned to $^3A_{2g} \dashrightarrow {}^3T_{1g}(P)$ transition could be covered by the very strong ligand band.

Infrared spectra. The most relevant absorption bands in the IR spectra of the free ligands and their complex compounds are shown in table 2.

The keto-enolic tautomerism is suported by presence of the bands due to ν_{OH} and $\nu_{C=O}$. The spectra of the free ligands are different within 1700-1000 cm^{-1} range. Thus, the stretching frequencies $\nu_{C=O}$(1700 cm^{-1}) and $\nu_{C=N}$(1610 cm^{-1}) appear as a strong and broad band with two unresolved peaks (1665 and 1610 cm^{-1}) for the ortho substituted ligand, but as a very strong band (1610 cm^{-1}) structured in some peaks (1680, 1650, 1550 cm^{-1}) for the para substituted ligand.

The bands due to ν_{OH} and $\nu_{C\text{-}OH}$ from the carvone ring and -COOH group (3400 and 1200 cm^{-1} respectively) are different, too. These bands are broad for ortho substituted ligand. The electronic and steric effects of the -COOH substituent may be transmitted to affect the strength of the hydrogen bond O-H. . . N modifying the capacity of the nitrogen atom for participating in hydrogen bonding/8/. The changes noticed in the infrared spectra of the complex compounds $Cu(o\text{-}L)_2.2H_2O$ and $Ni(o\text{-}L)_2.2(o\text{-}L)$ are similar and involve the ν_{OH} and $\nu_{C=N}$ stretching frequencies. The broad band with two peaks (1665 and 1610 cm^{-1}) is shifted to lower values (1600 cm^{-1}).

Table 2: The main bands in IR(cm^{-1}) and their assignements

Ligand/ Complex compound	ν_{OH}	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{C\text{-}OH}$
R=ortho	3000-3400 br	-	1610 s $\}^*$ 1665	1200 m, br
$Cu(o\text{-}L)_2 . 2H_2O$	3410 s	-	1600 br	1200 vw
$Ni(o\text{-}L)_2 . 2(o\text{-}L)$	3350-3405 s	-	1600 br	1200 w
R=para	3405 m	1700 vw	1550 $\}^*$ 1610 vs 1650 1680	1160 m 1230 vw 1260 s
$Cu(p\text{-}L)_2 . 2H_2O$	3410 s	1700 vw	1560 sh 1600 s 1650 sh	1160 w 1230 vw 1260 s
$Ni(p\text{-}L)_2 . 2(p\text{-}L)$	3410 s	1700 vw	1580 sh 1600 s 1650 sh	1160 m 1230 sh 1270 s

vs = very strong; s = strong; m = medium; w = weak; vw = very weak; br = broad; sh = shoulder.

$\}^*$ = multiplet structure of the band.

It is due to M <--N bond formation. The band ν_{OH}(3400-3000 cm^{-1}) lost its broad character and is shifted to higher values suggesting that upon coordination intramolecular hydrogen bond O-H. . .N from the ligand (scheme 1) is destroyed and O-M < - - N bond is formed in the metal chelates.

The IR spectrum of both compounds: $Cu(p-L)_2.2H_2O$ and $Ni(p-L)_2.2(p-L)$ presents the changes that involve the ν_{OH} and $\nu_{C=N}$ stretching frequencies suggesting the same donor atoms. Very strong band (1610 cm^{-1}) appears as a strong band (1600 cm^{-1}) with two shoulders (1650 and 1560 cm^{-1}).

These Schiff bases containing an N,O donor atoms set, upon coordination to metal ion through both O and N, a decrease of the $\nu_{C=N}$ frequency and a increase of the ν_{OH} frequency are generally noticed/8/.

These changes correlated with analytical data, electronic and EPR spectra could suggest that ligands are acted bidentately through both O and N donor atoms by the deprotonation of the OH group making evident participation of the ligands in the enolic tautomeric form. Cu(II) coordinates with four strong bond N and O donor atoms in a plane and with weaker bond to axial two molecules of water (Fig. 5).

Octahedral environment of the Ni(II) ion suggested by electronic spectrum could be achieved by the participation of para-substituted ligand to coordination both bidentately in a plane (through both O and N donor atoms) and monodentately axial (through O atom of the -COOH group).

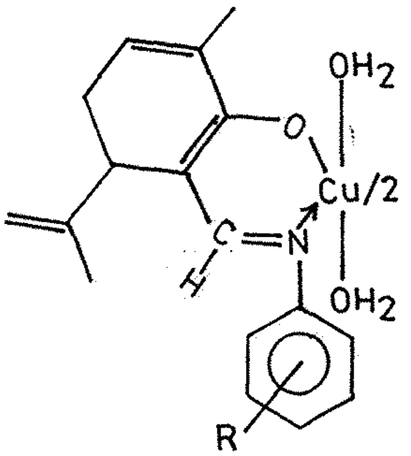


Fig. 5 Structural formula proposed for $Cu(o-L)_2 . 2H_2O$

CONCLUSION

Metallic ion determines the type of the compounds and different coordination behaviours of the ligands.

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