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Structure and luminescence of a nitrate-bridged heterotrinnuclear $\text{Cu}_2\text{-Pr}$ complex with compartmental Schiff base ligand

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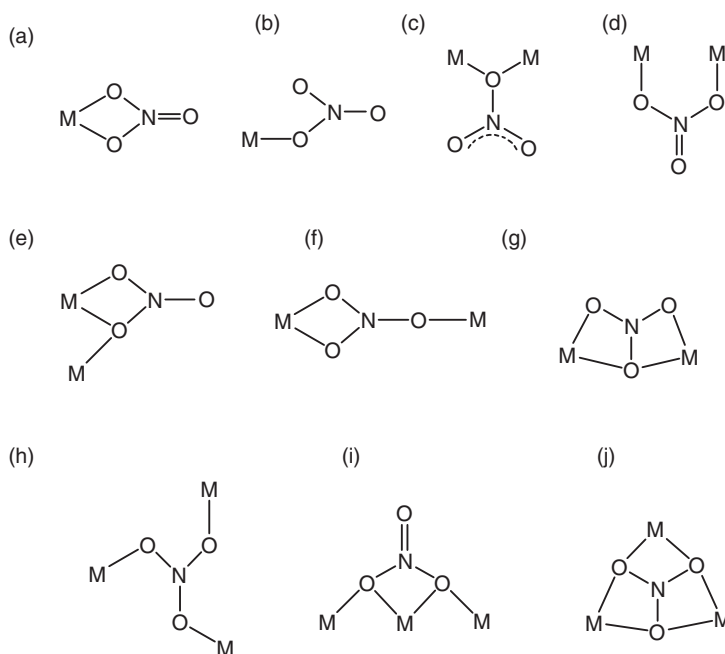
A unique heterotrinnuclear nitrate-bridged complex of hexanitrate praseodymium(III) and dicopper(II) compartmental species has been synthesized and characterized by X-ray single crystal structure analysis. The structure determination indicates that the dinuclear copper moiety undergoes a tilted deformation (with respect to the dicopper complex) upon connection to the lanthanide species *via* a rare nitrate bridge. The trinuclear species is highly fluorescent owing to the presence of praseodymium.

Keywords: Copper-lanthanide complex; Praseodymium(III) hexanitrate; Crystal structure, N-(3-Aminopropyl) morpholine

1. Introduction

Heterometallic complexes of transition metals, lanthanides, and mixed transition metal–lanthanide ions bridged by a connecting ligand continue to attract intense interest because of their importance in solid state technology [1–3], as models for magnetic studies [4–7], as stains for fluorescence imaging [8, 9], and their use as precursor complexes of magnetic materials in metal organic chemical vapor deposition (MOCVD). A search in the literature reveals a plethora of transition metals [10–12] and heterometallic transition metal–lanthanide (e.g., $\text{Cu}^{\text{II}}\text{-Ln}^{\text{III}}$) complexes with polydentate ligands coordinating the metal ions. On the other hand, structural studies showing these metals bridged by nitrate are scarce, although nitrate represents a very common bridging ligand acting through different coordination modes, as exemplified in scheme 1 [13]. Specifically, polynuclear Cu_4Ln_2 and Cu_2Ln salicylidene and Cu_4Ln_4

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Scheme 1. Different possible coordination modes of nitrate ligand.

derivatives [14–20] and more recently a Cu_2Gd_2 complex built by a substituted *bis* bidentate methylenedianiline ligand were reported [21]. All the cited examples contain a bridging nitrate between copper and the lanthanide. Jianmin *et al.* [22] described a unique compound where $[\text{La}(\text{NO}_3)_6]^{3-}$ connecting either a single or two $\text{Cu}(\text{bipy})_2$ units in the same compound. However, examples of $[\text{La}(\text{NO}_3)_6]^{3-}$ interacting with a dicopper core of an “end-off” compartmental ligand complex *via* nitrate bridge are not yet known. This study deals with the formation of a new heterotrinnuclear complex, where two copper(II) ions in close proximity are linked to the lanthanide through bridging nitrates, corresponding to coordination mode “(e)” of scheme 1.

2. Experimental

2.1. Methods

Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. Copper was estimated gravimetrically with α -benzoin oxime. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded at 27°C using a Shimadzu FTIR-8400S where KBr was used as medium. Electronic spectra ($800\text{--}200\text{ nm}$) were obtained at 27°C using a Shimadzu UV-3101PC where dry acetonitrile/dry methanol/nujol was used as a medium as well as a reference. Thermal analyses (TG–DTA;

thermal gravimetry–differential thermal analysis) were carried out on a Shimadzu DT-30 thermal analyzer in flowing dinitrogen (flow rate: $30\text{ cm}^3\text{ min}^{-1}$).

2.2. Materials

All materials were obtained from commercial sources and used as purchased. Solvents were dried according to standard procedure and distilled prior to use. 2,6-Diformyl-4-methylphenol was prepared according to the literature method [23]. N-3-(aminopropyl) morpholine, $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were purchased from Aldrich Chemical Company Inc. and used as received. All other chemicals were of AR grade.

2.3. Synthesis of L

2.3.1. 2,6-Bis(N-propylmorpholine-iminomethyl)-4-methylphenolato. An ethanolic solution (5 mL) of 1-(2-aminopropyl)morpholine (0.288 g, 2 mmol) was added dropwise to a heated ethanolic solution (10 mL) of 2,6-diformyl-4-methylphenol (0.164 g, 1 mmol) and the resulting deep yellow solution was stirred for 24 h. The solvent was removed under reduced pressure giving crude ligand (yellow liquid). Purification of L was done by column chromatography. Yield: 0.31 gm (87%). Anal. Calcd for L: C, 66.34; H, 8.65; N, 13.46. Found: C, 66.33; H, 8.66; N, 13.44. UV-Vis (CH_3OH)/nm: 452(sh, $\epsilon = 17,065$), 343($\epsilon = 3057$). $^1\text{H-NMR}$ 2.29(s, 3H) 1.87(m, 4H), 2.1–2.4(m, 15H), 3.4(m, 4H), 3.71(m, 8H), 7.68(s, 2H, Ar-H), 8.54(s, CH=N), 10.51 (s, Ph-OH). $^{13}\text{C-NMR}$ (δ , CDCl_3): 20.1, 30.7, 50.4, 56.8, 76.5, 127.0, 130.3, 132.1, 159.2, 165.00.

2.4. Synthesis of the complexes

2.4.1. $[\text{Cu}(\text{II})(\text{L})(\text{H}_2\text{O})(\text{NO}_3)]_2$ (1). The dinuclear copper(II) complex $[\text{Cu}(\text{II})(\text{L})(\text{H}_2\text{O})(\text{NO}_3)]_2$ was synthesized by adopting similar procedure as reported earlier [24].

2.4.2. $[\text{Cu}_2\text{L}'_2\text{Pr}(\text{NO}_3)_6]$ [$\text{L}' = 2\text{-formyl-4-methyl-6-propylmorpholine-imonomethyl phenolato}$] (2). The heterotrinary nuclear lanthanide copper complex was prepared by three methods as follows.

2.4.2.1. Method (a). 1 mmol of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 15 mL of acetonitrile was added to a heated suspension of 1 mmol of $[\text{Cu}(\text{L}')(\text{H}_2\text{O})(\text{NO}_3)]_2$ in 20 mL acetonitrile and stirred for 3 h at room temperature. Green microcrystals suitable for X-ray single diffraction analysis were obtained after a few days. Yield: 60%.

2.4.2.2. Method (b). To methanolic solution of 1 mmol of L (1 mmol), 1 mmol of 10 mL of methanolic solution of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.434 g) and 1 mmol of 10 mL copper nitrate trihydrate (0.241 g) were added and refluxed for 2 h. From the green filtrate, microcrystals suitable for X-ray single diffraction analysis were obtained. Yield: 70%.

Table 1. Crystallographic data and details of refinement for 1.

Empirical formula	C ₃₂ H ₄₆ Cu ₂ N ₁₀ O ₂₆ Pr
Formula weight, <i>M</i>	1254.78
Crystal system	Tetragonal
Space group	<i>P</i> 4 ₃ 2 ₁ 2 (no. 96)
Unit cell dimensions (Å)	
<i>a</i>	12.500(3)
<i>c</i>	30.837(5)
Volume (Å ³), <i>Z</i>	4818.3(18), 4
Calculated density (g cm ⁻³)	1.730
μ (Mo-K α) (mm ⁻¹)	1.967
<i>F</i> (000)	2532
Total data	15,703
Unique data	3365
<i>R</i> _{int}	0.1080
Parameters	320
Goodness-of-fit	0.778
Reflections [<i>I</i> > 2 σ (<i>I</i>)]	3863
<i>R</i> ₁	0.0554
<i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.1290
Flack parameter	-0.03(3)
Residuals (e Å ⁻³)	0.843 and -0.388

$$^a 1/[\sigma^2(F_o^2) + 0.0764P]^2 + 0.0000P], \text{ where } P = (F_o^2 + F_c^2)/3.$$

2.4.2.3. *Method (c)*. To a methanolic solution (10 cm³) of 2,6-diformyl-4-methylphenol (1 mmol, 0.164 g), 2 mmol (0.288 g) of N-3-aminopropylmorpholine (in 5 mL methanol) was added dropwise and refluxed for 2 h. Then 1 mmol of copper nitrate trihydrate (0.241 g) and 1 mmol of Pr(NO₃)₃ · 6H₂O (0.434 g) were mixed together in 5 mL methanol and the resulting mixture was added dropwise to the refluxing ligand solution and reflux was continued for 2 h. It was then filtered and the filtrate was kept in CaCl₂ desiccator. Green micro crystals were obtained after a few days (Yield 65%). Anal. Calcd for C₃₂H₄₆N₁₀O₂₆Cu₂Pr: C, 30.60; H, 3.60; N, 11.15%. Found: C, 30.40; H, 3.35; N, 11.20%. Selected IR data (KBr, cm⁻¹): 1633.7, 1560.3, 1457.1, 1323.7, 1384.3 ν (NO₃); UV-Vis (CH₃OH) nm: 373, 695.

2.5. X-ray data collection and structure determination

Diffraction data for the structure were collected at room temperature on a Nonius DIP-1030H system (Mo-K α radiation, $\lambda = 0.71073$ Å). Cell refinement, indexing, and scaling of the data sets were carried out using Denzo and Scalepack [24]. The structure was solved by direct methods and subsequent Fourier analyses and refined by full-matrix least-squares based on *F*² with all observed reflections [25]. The contribution of hydrogens at calculated position was introduced in the final cycles of refinement. In order to guarantee charge neutrality, a proton should be located on one of the morpholine amino nitrogens or on a lattice water molecule (hydronium ion), but the two-fold symmetry of the complex and the disordered solvent molecules complicated resolution. Two residuals in the ΔF map were interpreted as lattice water molecules at half occupancy (hydrogens not located). All the calculations were performed using the WinGX System, Version 1.70.01 [26]. Crystallographic data and experimental details are reported in table 1. Selected bond lengths and angles are shown in table 2.

Table 2. Selected coordination bond lengths (Å) and angles (°) for the copper in **1**.

1			
Cu–N(1)	1.913(11)	O(1)–Cu–O(2')	166.6(5)
Cu–O(1)	1.956(10)	O(1')–Cu–O(2')	89.1(5)
Cu–O(1')	1.970(11)	N(1)–Cu–O(4)	92.7(4)
Cu–O(2')	1.979(11)	O(1)–Cu–O(4)	80.5(4)
Cu–O(4)	2.493(8)	O(1')–Cu–O(4)	97.7(4)
Pr–O(4)	2.655(8)	O(2')–Cu–O(4)	92.7(4)
N(1)–Cu–O(1)	92.5(5)	Cu–O(1)–Cu'	99.6(5)
N(1)–Cu–O(1')	166.3(5)	C(9)–O(2)–Cu'	124.1(11)
O(1)–Cu–O(1')	80.4(5)	O(4)–Pr–O(4')	71.5(4)
N(1)–Cu–O(2')	99.4(5)		

Symmetry code: primed atoms at $x, -y+1/2, z$.

3. Results and discussion

3.1. Synthesis and characterization

The “end-off” compartmental ligand **L** was synthesized by conventional Schiff-base condensation maintaining aldehyde–amine ratio as 1:2 in ethanol. The ligand was characterized by spectroscopic techniques. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectral data of the ligand (Supplementary material), with their corresponding assignments, are reported in section 2 and the data are consistent with the proposed structure. The heterotrinnuclear lanthanide–copper complex was prepared by sequential reaction as well as by applying template synthesis. The composition and the structure of the complex are determined by routine physico-chemical techniques, such as elemental analysis, IR and UV-Vis methods, and X-ray single crystal structure analysis. During complexation **L** was converted to **L'**.

The IR stretching frequencies of nitrates of this heterotrinnuclear complex differ significantly from those of the corresponding dicopper and $\text{Pr}(\text{NO}_3)_6$, species (Supplementary material). In $\text{Pr}(\text{NO}_3)_6$ a highly intense broad band with maxima at 1447 and 1330 cm^{-1} and in dicopper complex highly intense band with only one band maxima at 1378 cm^{-1} corresponding to nitrate are observed. The heterotrinnuclear copper–lanthanide complex exhibits highly intense band split into three, well-resolved sharp bands at 1457, 1384, and 1324 cm^{-1} .

IR and UV-Vis stretching frequencies, attributed to azomethine $\nu(\text{C}=\text{N})$, skeletal vibrations, and nitrates $\nu(\text{NO}_3^-)$ were observed at 1634, 1560, 1324, and 1384 cm^{-1} for the heterotrinnuclear lanthanide–copper complex, respectively. Electronic spectra of ligand and heterotrinnuclear lanthanide–copper complexes have been studied in the solid state (dispersed in Nujol mull) as well as in solution using CH_3OH as solvent. The absorption bands for the ligand are observed from 343 to 452 nm. Bands at 370–380 nm for the complex are due to both phenoxido–Cu(II) and hydroxido–Cu(II) LMCT as a single band. For a d^9 system, the $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$ transition is expected to take place at 800 nm for octahedral geometry and this band will undergo a significant blue shift on distortion of octahedral coordination to square-pyramidal and square-planar structure [27]. In **1**, the band at $\sim 690\text{ nm}$ due to the d–d transition is in agreement with a square pyramidal geometry around copper. Bands at $\sim 1400\text{ nm}$ for the mixed lanthanide–copper complex are due to f–f transitions. Since no significant shifting in

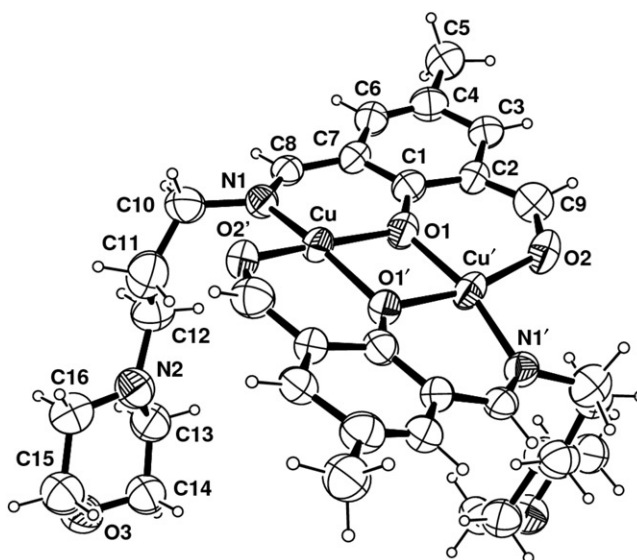


Figure 1. ORTEP drawing of the copper moiety of **1** with atom labeling of the crystallographic independent part (primed atoms at $y, x, -z + 1$).

band positions is observed in solid state electronic spectra compared to the corresponding spectra recorded in solution, it may be assumed that solution and solid state structures are very similar.

3.2. Structure description of **1** and **2**

X-ray structural analysis confirms the formation of the trinuclear complex. An ORTEP view of the phenoxido-bridged copper dimer of **1** with atom labeling scheme of the independent part is shown in figure 1, while the entire complex is depicted in figure 2. The compound can be described as an adduct formed by a dinuclear copper cationic part bound to $[\text{Pr}(\text{NO}_3)_6]^{3-}$. The lanthanide resides on a crystallographic two-fold axis. The copper ions, chelated by unsymmetrical tridentate ligands, possess a distorted square pyramidal coordination sphere. Two phenoxido-bridged oxygens, an imine nitrogen, and a carbonyl oxygen are located in the basal plane. The Cu–N bond distance [1.913(11) Å] appears slightly shorter than the Cu–O bond lengths which range from 1.956(10) to 1.979(11) Å and the apical distance Cu–ONO₂ is, as expected, significantly elongated (2.493(8) Å). The bond angle Cu–O1–Cu' of 99.6(5)° leads to an intermetallic separation of 2.998(4) Å. The praseodymium is chelated by six nitrates with Pr–O distances between 2.585(9) and 2.655(8) Å, the longest value is that pertaining to O₄ bound to copper. In fact, O₄ bridges the metals with a Cu–O4–Pr angle of 138.7(4). Conversely, making allowance for the esd.'s, the nitrate N–O4 bond length (1.308(14) Å) is the longest among the nitrates. The intermetallic Pr–Cu distance is 4.817(2) Å. The morpholine moieties assume the usual chair conformation and are pendant from the copper–phenolate dimer surface, opposite to $[\text{Pr}(\text{NO}_3)_6]$.

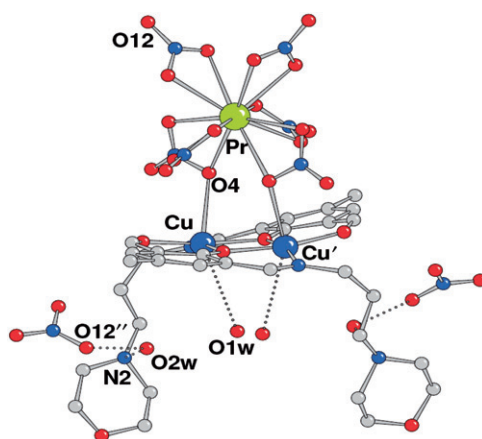


Figure 2. Molecular structure of **1**, showing the disordered lattice water molecules O1w and O2w interacting with the copper center and through H-bond to nitrates and morpholine nitrogens.

Two residuals in the electron density map were attributed to disordered lattice water (occupancy 0.5). One bridges at H-bond distance the morpholine nitrogen ($Ow2 \cdots N2 = 2.86 \text{ \AA}$) and a nitrate oxygen of a symmetry related complex ($Ow2 \cdots O12 = 2.87 \text{ \AA}$). The other (O1w) is located at 3.259 \AA from the copper-ion to indicate possible six-coordination. The molecular structure of the dinuclear copper derivative $[Cu(L')(H_2O)(NO_3)]_2$ [28] showed octahedral Cu(II) coordinated at axial positions by an aquo and a nitrate (axial distances of $2.450(7)$ and $2.484(10) \text{ \AA}$, respectively). However, it is worth noting that the centrosymmetric copper-phenolato dimer has practically coplanar atoms, contrary to the propeller-like twisted conformation assumed here by the phenolato units that seem to wrap the $[Pr(NO_3)_6]$ moiety. Nevertheless, the intermetallic copper distances ($2.998(4) \text{ \AA}$ in **1** and $3.015(1) \text{ \AA}$ in the dicopper precursor) appear comparable within 3σ . A selection of bond lengths and angles is given in table 2.

3.3. Absorption and fluorescence properties

The complex exhibits strong fluorescence in methanol (figure 3). The dinuclear copper(II) complex is nearly non-fluorescent, as is evidenced from figure 3 (excitation was done at λ_{max} 386 nm, since the dinuclear copper(II) complex exhibits absorption λ_{max} at 386 nm). However, when the dinuclear copper complex is combined with the praseodymium species, an intense fluorescence band, nearly twice as intense as the fluorescence exhibited by pure $Pr(NO_3)_3 \cdot 6H_2O$ (figure 4), was observed upon excitation at λ_{max} 371 nm in methanol (the complex shows a UV-Vis band at $\lambda_{\text{max}} = 371 \text{ nm}$) with quantum yield ($\varphi = 0.0155$). The above-mentioned data suggest that **1** exhibits luminescence owing to the presence of Pr, whereas dinuclear copper(II) complex is non-fluorescent due to deactivation of excited state *via* non-radiative channel owing to the presence of paramagnetic copper(II).

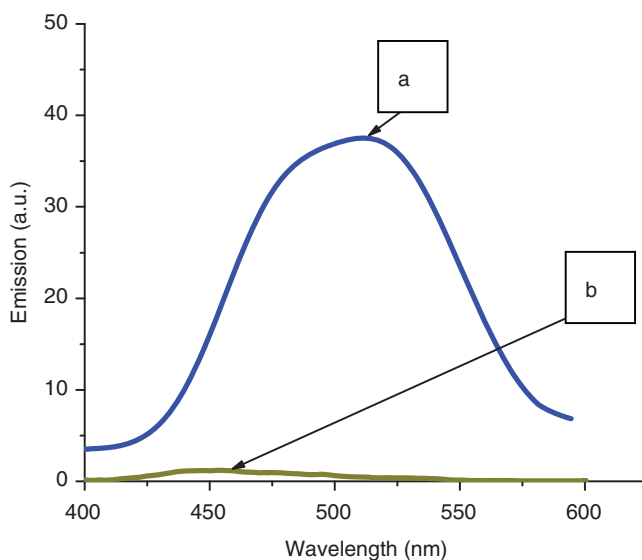


Figure 3. Luminescence spectra (a) of **1** and (b) of [Cu(L')(H₂O)(NO₃)₂] in methanol.

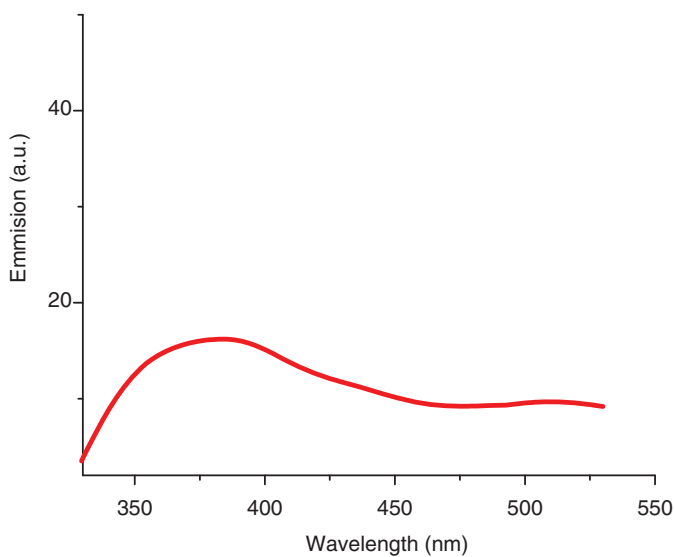


Figure 4. Luminescence of pure Pr(NO₃)₃·6H₂O in methanol.

4. Conclusions

A heterotrimeric copper(II)-praseodymium complex was synthesized, where the praseodymium connected with both dinuclear copper(II) centers simultaneously through a rare nitrate bridge. The fluorescence spectra of the dinuclear copper complex and heterotrimeric copper-lanthanide complex were investigated in methanol, where

the former remains non fluorescent and the latter exhibits good fluorescence due to the presence of Pr(III).

Supplementary material

CCDC reference number for **1** is 730014. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

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