

Synthesis, crystal structure and spectroscopic studies of copper(II) complex of *C*-meso-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane

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Abstract Copper(II) complex coordinated with cyclam-type macrocyclic tetramine, *C*-meso-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane (**2Cdmc**) has been synthesized and characterized by single crystal X-ray crystallographic analysis and UV–Vis absorption spectra. Solved molecular structure of [Cu(**2Cdmc**)(H₂O)]Cl₂·2H₂O (**1**) revealed that macrocyclic ligand **2Cdmc** was in the most stable *trans*-III structure, but the *C*-methyl groups of **2Cdmc** adopted energetically unfavorable axial configuration (*C*-axial). This complex **1** is the second example of complex of cyclam-type tetramine with only axially oriented *C*-methyl groups. This complex adopted five-coordinated square-pyramidal geometry with one water molecule occupying one of the two apical sites. Network of hydrogen bonds involving counter anions (Cl[−]), coordinating and non-coordinating water molecules, and N–H of **2Cdmc** was present. UV–Vis spectra in various solutions also indicated the formation of five-, or six-coordinated complex in methanol and DMSO, but four-coordinated complex in water.

Keywords Copper(II) · Tetraaza macrocycle · Crystal structure · Spectroscopic analysis · Coordination chemistry

Introduction

There are numerous reports concerned with the coordination chemistry of substituted derivative of tetraazamacrocycles, such as the 14-membered *cyclam* (1,4,8,11-tetraazacyclotetradecane). These macrocyclic ligands have provided ideal coordination sites for various metal ions and have been used in clinical application as metal ion binding sites for complex with DNA cleaving activity [1–3] and contrast agent for MRI [4, 5]. Furthermore, these metal complexes can be used as catalysis in redox reactions [6], such as nickel complexes which are used to produce CO through photochemical and electrochemical reduction of CO₂ [7, 8]. Because of intriguing chemical property that they exhibit, many structural analogues have been synthesized and investigated.

The stereochemistry and the coordination chemistry of *C*- and *N*-substituted derivative of tetraazamacrocycles and their metal complexes are complicated because of the presence of several asymmetric centres (carbon and nitrogen atoms) on their skeleton [9]. Thus macrocyclic ligand and its complex can have numerous diastereoisomeric forms [9–13]. The configurational isomerisation caused by the chiral nitrogen atoms was already classified into five configurational *trans* isomers of metal–cyclam adducts, which are designated as *trans*-I (RSRS), *trans*-II (RSRR), *trans*-III (RRSS), *trans*-IV (RSSR) and *trans*-V (RRRR) [10]. Among these five structures, although *trans*-III is the most stable form, tetra-*N*-alkylated cyclam such as *tmc* (*tmc* = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) tends to give complexes with *trans*-I configuration in which alkyl groups are directed to one side of the N₄-plane. This fact suggests that the number of *N*-methyl substituents produces a big difference on both structure and property of its complex. Although vast

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number of studies have been reported on the chemistry of *cyclam* with no *N*-substituent and fully *N*-substituted *tmc*, there are only small number of reports dealing the partially *N*-substituted complexes.

In our previous paper, we have reported the synthesis of *C*-meso-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane **2Cdmc** and its nickel(II) complex by non-template reaction, and succeeded in isolating and growing single-crystal of **2Cdmc** complex with only *C*-axial configuration for the first time [14]. Furthermore, we reported that the crystal structure and the spectral properties of this unusual *C*-axial nickel(II) complex were absolutely different from that of the *C*-equatorial nickel(II) complex. The results revealed that the axially oriented *C*-methyl groups strictly interfered the coordination of other ligands to apical sites [15]. Only square-planar four-coordinated complex could be found both in crystal and various solutions. Note that this ligand **2Cdmc** can be regarded as an intermediate of *cyclam* and *tmc* (Fig. 1).

In this paper, we report the coordination chemistry of copper(II) analogue in crystalline and solution state. We expected similar coordinating properties, but the result revealed the coordination of apical ligand to form five-coordinated species in crystal. Structural and spectral data are presented.

Experimental

Materials

All chemicals were of reagent grade and used without further purification. The ligand, *C*-meso-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane (**2Cdmc**), was synthesized by a previously reported procedure [15]. Complex **1** was obtained by complexation of **2Cdmc** with copper(II) perchlorate, and anion exchanged to chloride using anion-exchange resin (AG3-X4A). Red-violet crystals of $[\text{Cu}(\mathbf{2Cdmc})(\text{H}_2\text{O})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ was obtained. Yield 34%. Single crystal suitable for X-ray diffraction measurement was obtained by slow evaporation of aqueous

solution. Formation and purity of the product were confirmed by IR and elemental analyses. (**1**): Anal. Calc. for $\text{C}_{14}\text{H}_{38}\text{Cl}_2\text{CuN}_4\text{O}_3$: C, 37.79; H, 8.61; N, 12.59%. Found: C, 37.08; H, 8.60; N, 12.02%. IR (KBr pellet, cm^{-1}): 3468, 3426, 3342 [$\nu(\text{O-H})$ s], 3132, 3101 [$\nu(\text{N-H})$ m], 2965, 2890, 1632 [$\nu(\text{C-N})$ m].

Measurements

IR spectra were measured with a JASCO FT/IR-410 spectrophotometer. Elemental analysis was performed by a Perkin-Elmer 2400II Analyzer. UV-Vis-NIR spectra were recorded with a JASCO V-570 UV/VIS/NIR spectrophotometer, with the sample concentration of 1.0×10^{-3} mol/L.

X-ray crystallography

Single crystal was mounted on a glass capillary. Intensity data were collected by a Bruker AXS SMART diffractometer equipped with CCD area detector and MoK α ($\lambda = 0.71073$ Å) radiation. The structure of **1** was solved and refined with the SHELX-97 [16] software using direct method and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically by the full-matrix least-square method. Some hydrogen atoms were found from experimental data directly, and their position and isotropic thermal parameters were refined. Selected crystallographic data are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2. Crystallographic data have been deposited on Cambridge Crystallographic Data Centre: Deposit numbers CCDC-763930 for compound **1**. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; mail: deposit@ccdc.cam.ac.uk).

Results and discussion

Synthesis and structural analysis

In our previous paper [15], convenient and selective synthetic paths to isolate nickel(II) complex of **2Cdmc** with either *C*-equatorial or *C*-axial configuration were reported. Even when central metal ion is replaced from nickel(II) to copper(II), isolating and growing single crystal of the complex of **2Cdmc** with only *C*-axial configuration was accomplished using similar procedures. However, the coordination structure obtained was different from that of the nickel(II) analogue. A water molecule was found to

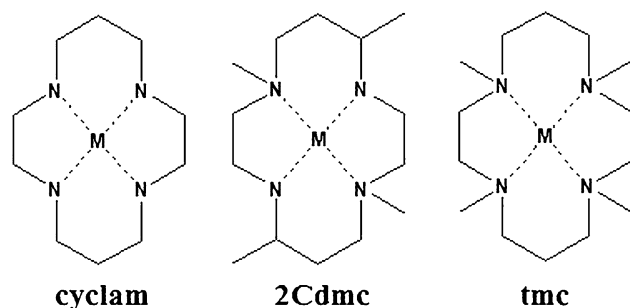


Fig. 1 Molecular structure of *cyclam*, **2Cdmc** and *tmc* complexes

Table 1 Crystallographic data

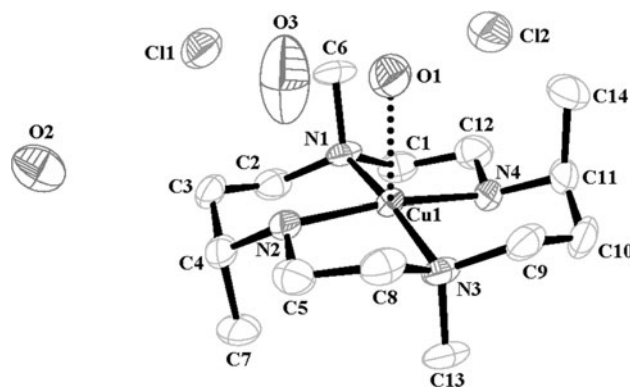
	1
Formula	C ₁₄ H ₃₈ Cl ₂ CuN ₄ O ₃
Formula weight	444.92
Crystal size (mm)	0.33 × 0.33 × 0.15
<i>T</i> (K)	296
Crystal system	Monoclinic
Space group	P2(1)/n
<i>a</i> (Å)	9.9996(8)
<i>b</i> (Å)	15.9313(12)
<i>c</i> (Å)	13.5643(10)
β (°)	105.9490(10)
Volume (Å ³)	2077.7(3)
<i>Z</i>	4
<i>D_c</i> (g cm ⁻³)	1.422
μ (mm ⁻¹)	1.328
GOF	0.998
R1	0.0670
wR2	0.1956

Table 2 Selected bond lengths (Å) and angles (°)

Cu1–N1	2.054(3)	Cu1–N2	2.010(3)
Cu1–N3	2.043(3)	Cu1–N4	2.013(3)
Cu1–O1	2.518(3)	–	–
N1–Cu1–N2	95.00(13)	N1–Cu1–N4	85.69(13)
N2–Cu1–N3	85.67(13)	N3–Cu1–N4	92.54(14)
Cu1–N1–C6	108.9(2)	Cu1–N3–C13	109.2(2)
N1–Cu1–O1	95.99(11)	N2–Cu1–O1	84.12(12)
N3–Cu1–O1	92.46(11)	N4–Cu1–O1	103.37(12)

coordinate to copper(II) ion to form square-pyramidal five coordinated complex.

The ORTEP drawing with atom numbering scheme of **1** and its crystal packing are shown in Figs. 2 and 3. Macrocyclic tetramine **2Cdmc** coordinates to copper(II) as a quadridentate ligand, and its four nitrogen-donor atoms occupy the planar coordination sites. The configuration of the cyclam moiety of **2Cdmc** is stable *trans-III* where all four chelate rings are in the stable skew (five-membered ring) or chair (six-membered ring) forms. This structure is often found in nickel(II) and/or copper(II) complexes of cyclam derivatives [17, 18]. Four N atoms of **2Cdmc** are coplanar with the deviation from their average plane of within ± 0.008 Å, and Cu sits in the middle of N₄ plane with the deviation of 0.14(15) Å [Cu1] towards coordinated water. Note that two *C*-methyl and two *N*-methyl groups adopt axial configuration.

**Fig. 2** ORTEP drawing of *C*-axial complex (**1**). H atoms were omitted for clarity

In the case of nickel(II) complex reported previously [15], the influence of the axial *C*-methyl groups towards apical coordination was discussed. Although both *C*-equatorial and *C*-axial complexes adopted *trans-III* structure, nickel(II) complex with *C*-equatorial orientation adopted six coordinated octahedral geometry where two water molecules occupied the apical sites, while nickel(II) complex with *C*-axial orientation strictly adopted four coordinated square-planar geometry with no water molecule coordinated both in crystal and solution. Furthermore, according to the report of Chung and his co-worker [18], *C*-equatorial copper(II) complex also adopted six coordinated octahedral geometry but with largely elongated Cu–O (H₂O) bonds due to Jahn–Teller effect. In this case, the geometry of copper(II) analogue is described as tetragonally elongated octahedral. Metal–ligand bond length of the related complexes are summarised in Table 3.

In **1**, however, copper ion is coordinated by four nitrogen atoms of **2Cdmc**, and only one water molecule occupied one of the two apical sites to adopt five coordinated square pyramidal geometry as a whole. Cu–O(1) bond length (2.518(3) Å) for coordinated water molecule of **1** is still longer than those of Cu–N, but is apparently shorter than that of *C*-equatorial complex (2.692 Å). This fact indicates a strong bonding of water molecule in **1**, despite the steric hindrance possibly caused by *C*-axial methyl groups. On the other hand, other parameters such as bond angles and C–N bond lengths are almost the same as those of *C*-equatorial complex. The reason of such a short Cu–O(1) bond length is attributable to the difference in the number of coordinating water molecules at apical sites. Decrease in the number of coordinating ligand decreases the electron density around central metal ion, which leads to a stronger binding of coordinating ligand as a whole. This applied to the *C*-axial nickel(II) complex of **2Cdmc**, where Ni–N bond lengths were 1.9375(13)–1.9533(12) Å, apparently shorter than those of *C*-equatorial complex

Fig. 3 Packing diagram for C-axial copper(II) complex (**1**)

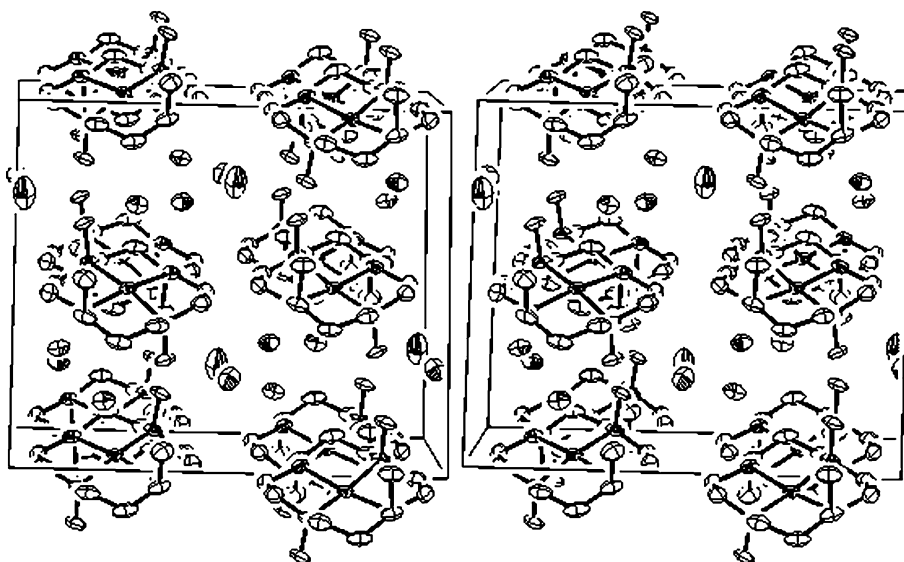


Table 3 Metal-O and Metal-N bond lengths of related complexes (Å)

Complexes	Configuration		M–N (Å)	M–O (Å)	T (K)	Reference
Cu						
[Cu(2Cdmc)(H ₂ O)]Cl ₂	<i>Trans-III</i>	/C-a	2.010(3)–2.054(3)	2.518(3)	296	–
[Cu(2Cdmc)(H ₂ O) ₂]Cl ₂	<i>Trans-III</i>	/C-e	2.032(2)–2.055(2)	2.692(2)	295	[15]
[Cu(cyclam)(H ₂ O) ₂]F ₂	<i>Trans-III</i>	–	2.012(5)	2.484(6)	300	[17]
[Cu(tmc)(H ₂ O)](ClO ₄) ₂	<i>Trans-I</i>	–	2.041(6)–2.095(6)	2.398(5)	296	[16]
Ni						
[Ni(2Cdmc)](H ₂ O) ₂ Cl ₂	<i>Trans-III</i>	/C-a	1.93(13)–1.95(12)	–	294	[12]
[Ni(2Cdmc)(H ₂ O) ₂]Cl ₂	<i>Trans-III</i>	/C-e	2.06(14)–2.11(12)	2.21(12)	294	[12]
[Ni(cyclam)(H ₂ O) ₂]Cl ₂	<i>Trans-III</i>	–	2.065(3)–2.072(2)	2.176(2)	300	[23]
[Ni(tmc)(H ₂ O) ₂]Cl ₂	<i>Trans-III</i>	–	2.136(2)–2.148(2)	2.141(2)	300	[5]

Note C-a, and C-e represents C-axial, and C-equatorial configuration of C-methyl groups, respectively

(2.06(14)–2.11(12) Å) with two extra water molecules coordinated [15].

When the Cu–N bond lengths with Ni–N bond lengths of six coordinated complexes are compared, Cu–N tends to be shorter than Ni–N probably due to the weaker electronic effect of the apical coordination of water molecules. Presence of extra d-electron in d_{z^2} orbital strongly repels the apical ligand, and elongates the Cu–N bond length. This relaxes the steric hinderance by C-axial methyl groups to enable the coordination of water molecule. However, according to the crystallographic data of [Cu(tmc)(H₂O)](ClO₄)₂ [19], in which tmc ligand adopted *trans-I* structure, this complex adopted five coordinated square pyramidal geometry with Cu–O bond length of 2.398 Å much shorter than that of **1**. Furthermore, Cu–O bond length of [Cu(cyclam)(H₂O)₂]F₂ [20] was also shorter than that of **1**, although it was six coordinated complex. These facts indicate that C-axial methyl groups sticking out towards apical sites have

weak but not negligible steric effect towards apical coordination of water molecules.

In crystal, N–H⋯O hydrogen bond was present. The crystal packing and hydrogen bonded network of **1** is shown in Figs. 4, 5, and their parameters are tabulated in Table 4. Coordinated water molecule (O1) is hydrogen bonded to the non-coordinated chloride ions, and the chloride ion is hydrogen bonded to the two non-coordinated water molecules (O2 and O3). O–H⋯Cl hydrogen bonds form a one-dimensional chain along *a* axis as shown in Fig. 4. Furthermore, complexes are connected by N–H⋯Cl and complementary C–H⋯Cl [21] hydrogen bonds in the direction perpendicular to the CuN₄ planes of **1**.

UV–Vis spectra

UV–Vis spectra of **1** in three different solvents (DMSO, methanol, and water) are given in Fig. 6. They exhibit only

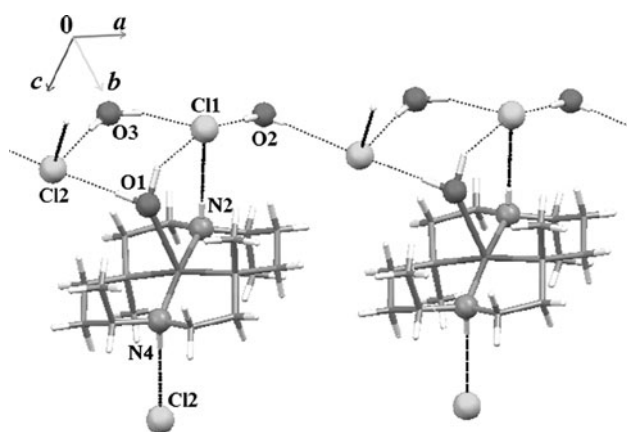


Fig. 4 Hydrogen bond network between anion proton (N2-H) of complexes, water molecules (O1, O2, and O3), and chloride ions (Cl1, Cl2) along the *a* axis. Dashed and thin lines indicate O-H...Cl and N-H...X (X = Cl or O) hydrogen bonds, respectively

Table 4 Geometries (Å, °) of N-H...O, N-H...Cl, O-H...Cl and C-H...O hydrogen bonds

D-H...A	D-H	H...A	D...A	(D-H...A)
N2-H2...O1	0.89(4)	2.62(4)	3.057(4)	111
N2-H2...Cl1	0.89(4)	2.47(4)	3.355(3)	170
N4-H4...Cl2 ⁱ	1.00(5)	2.36(5)	3.307(3)	157
O1-H15...Cl1	0.97(3)	2.39(7)	3.132(3)	133
O1-H16...Cl2	0.97(3)	2.19(3)	3.147(3)	168
O2-H18...Cl1	0.97(3)	2.27(3)	3.235(4)	173
O2-H17...Cl2 ⁱⁱ	0.97(3)	2.27(3)	3.225(4)	171
O3-H19...Cl1	1.02(8)	2.24(8)	3.225(4)	162
O3-H20...Cl2	0.89(7)	2.33(7)	3.196(4)	164
C2-H2A...Cl1 ⁱ	0.97	2.94	3.871(4)	160

Symmetry codes: *i* $x-1/2$, $-y+1/2$, $z+1/2$; *ii* $x-1$, y , z

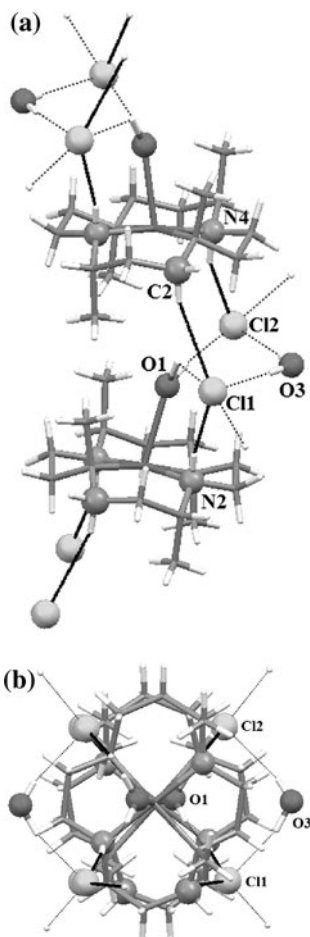


Fig. 5 Hydrogen bond network perpendicular to the CuN4 plane of complexes. **a** Side view, and **b** top view. Thin lines indicate N-H...Cl and C-H...Cl hydrogen bonds

one broad absorption band in the range from 13,000 to 26,000 cm^{-1} typical for d^9 complexes with apparent blue-shift in aqueous solution. Since UV-Vis spectra of square

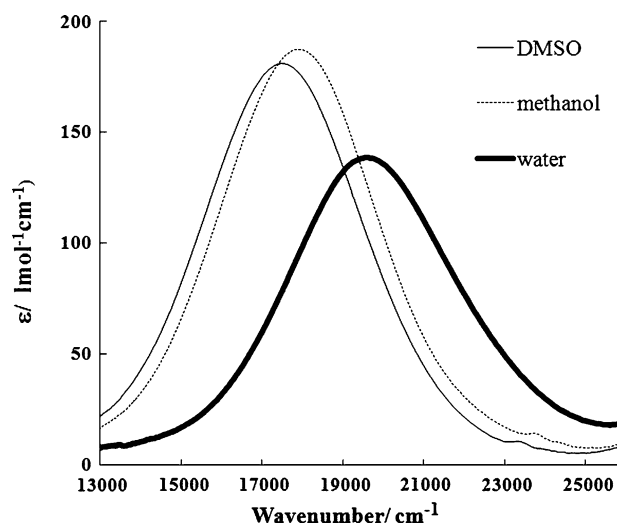


Fig. 6 UV-Vis absorption spectra of **1** in various solvents

planar four coordinated complexes usually exhibit maxima at around 20,000 cm^{-1} [22], and also a blue-shift from those of five or six coordinated complexes [23, 24], the data show that water molecules do not coordinate to **1** in aqueous solution. In the case of nickel(II) complex reported previously [15], this type of solvatochromism is explained by the difference in acceptor number (AN) of the solvents, which is a measure of electron pair accepting ability. In some case, the shift in UV-Vis is proportional to ANs' value. ANs are in the order DMSO (19.3) < methanol (41.3) < water (54.8) [25]. Although the absorption maxima of copper(II) complex shifted according to the ANs' order, shift is not proportional to AN. Due to the high AN of water molecule, water molecules form hydrogen bond network by themselves, and does not coordinate to **1** in aqueous solution. Based on these results, the complex **1** is

concluded to adapt the same five- or six-coordination geometry as crystalline state in DMSO and methanol, but in aqueous solution, **1** adopts four-coordination structure due to the high AN of water molecule.

Conclusion

We have prepared chloride salts of **1**, and found that the configuration of **2Cdmc** adopted *trans-III* structure. Unlike nickel(II) analogue, copper(II) complex with *C*-axial orientation (**1**) adopted five-coordinated square pyramidal geometry where one water molecule occupied one of the two apical sites. In addition, complexes, water molecules, and chloride ions were connected by network of hydrogen bonds. Furthermore, UV–Vis spectra exhibited that *C*-axial complex adopted square–planar four-coordinated geometry in aqueous solution, while five- or six-coordinated species in DMSO and methanol solution.

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