The Zinc Aqua Complex of a Tetrapodal Pentaamine Ligand and its Reactivity towards Carbon Dioxide

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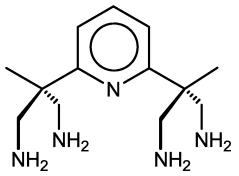
Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

In the context of derivatisation studies of the pentaamine ligand 2,6-$C_5H_3N[CMe(CH_2NH_2)_2]_2$ (2-(6-(1,3-diamino-2-methylpropan-2-yl)pyridin-2-yl)-2-methylpropane-1,3-diamine, **1**), we explored its zinc(II) coordination chemistry. With $ZnBr_2$ in hot aqueous ethanol, in the absence of Lewis acid, the aqua complex $[Zn(\mathbf{1})(H_2O)]Br_2$ (**2**) is obtained, in which the pentaamine ligand acts as a square-pyramidal coordination cap. Single crystal structure data for the dihydrate of **2** are reported. In methanol solution, the complex is reactive towards carbon dioxide, and spectroscopic data (IR, ^{13}C NMR) indicate the reversible formation of the dinuclear methyl carbonate complex $[(Zn(\mathbf{1}))_2(\mu_2\text{-}(\eta^1\text{-}O,\eta^1\text{-}O)O_2COCH_3)]Br_3$.

Key words: Tetrapodal Pentadentate Ligand, Zinc, Aqua Complex, Carbon Dioxide Fixation

Introduction

Our interest in the coordination chemistry of tetrapodal pentadentate ligands derives from the fact that such chelators provide a single "labile" coordination site in complexes of overall octahedral symmetry. The previously introduced pyridine-derived pentaamine "pyN_4" (**1**) exemplifies this approach and has been shown to have a versatile coordination chemistry (association, dissociation and transformation of small monodentate ligands) with metal ions such as cobalt(III), nickel(II), iron(II/III) or ruthenium(II) [1]. Current research attempts to diversify the donor set, both with respect to the introduction of peripheral groups, set up to modulate the reactivity of a small sixth ligand through secondary interactions, and with respect to a variation of the "teeth" in the pentadentate set (donor sets such as $pyN_2N'_2$, pyN_2S_2, etc.; N = primary amine; N' = secondary amine). The strategies we have been pursuing for secondary amine derivatives of **1** are twofold: a) introduction of different subsets (*e.g.*, combination of a pyN_2 precursor with an N'_2 synthon), and b) dissymmetrisation of an existing pyN_4 set trough selective or statistical derivatisation. It is in the context of the latter approach that we have become interested in the coordination chemistry of our pyN_4 ligand towards zinc, and we wish to report what is, to the best of our knowledge, a rare if not the only example to date of an octahedral zinc aqua complex of a polyamine ligand, as well as a summary of its reactivity towards carbon dioxide.



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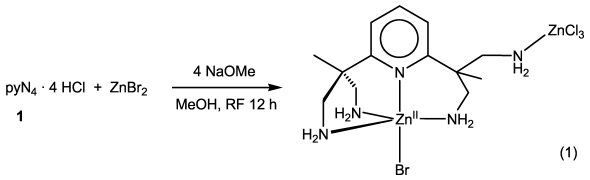
Results and Discussion

Zinc(II) has been shown to act as a "protective group" in selective derivatisation reactions of certain tetraazamacrocycles, since only three out of the four nitrogen atoms of the ligand bind to the zinc(II) cation. The nitrogen atom which remains uncoordinated can react with a suitable compound to afford, after demet-



(1)

allation, the desired mono-derivative [2]. Employing Zn^{2+} in this way would be a straightforward method for the selective synthesis of singly derivatised pyN_4 ligands of the type pyN_3N'. Previous work was encouraging, as it had shown that the hydrochloride adduct of the pyN_4 ligand ($pyN_4 \cdot 4\,HCl$) reacts in methanol with four equivalents of NaOMe and one equivalent of $ZnBr_2$ to yield the trigonal bipyramidal complex shown in eq. 1 [3]. Only the nitrogen atom of the pyridine ring and three equatorial amine nitrogen atoms coordinate to the central zinc(II) ion, whereas the fourth primary amine is bound to a trichlorozincate unit (preliminary X-ray data). The question arose whether with a different counterion the trigonal bipyramidal coordination geometry is maintained, so that one amino group is uncoordinated and thus available for selective derivatisation.

Complex synthesis and characterisation

In order to avoid the formation of $[ZnCl_3]^-$, the hydrobromide form of the ligand ($pyN_4 \cdot 4\,HBr$) was treated with 4 eq LiOMe and 1 eq $ZnBr_2$ in methanol under reflux. No precipitate formed during the reaction, and a colourless solution was obtained after cooling. The solvent was evaporated, and the crude product crystallised from hot aqueous ethanol. The product was identified by elemental analysis as a trihydrate (*cf.* Experimental Section). In solution, the ^1H and ^{13}C NMR spectra point to a C_{2v} symmetrical cation, with the pyN_4 ligand acting as a regular square-pyramidal coordination cap. The overall connectivity was established by an X-ray diffraction analysis, which revealed the presence of an octahedral aqua complex, $[Zn(pyN_4)(H_2O)]Br_2 \cdot 2\,H_2O$ (**2**$\cdot 2\,H_2O$). [In a separate experiment, single crystals of the solvate-free complex, $[Zn(pyN_4)(H_2O)]Br_2$, were obtained by recrystallisation from hot anhydrous ethanol, *cf.* Experimental Section]. A Lewis acid such as $[ZnCl_3]^-$ may be required to enforce a trigonal bipyramidal coordination mode for **1**; otherwise, all four primary amino groups of **1** coordinate to the zinc(II) cation. Selective protonation studies to decoordinate one amino group have so far been unsuccessful.

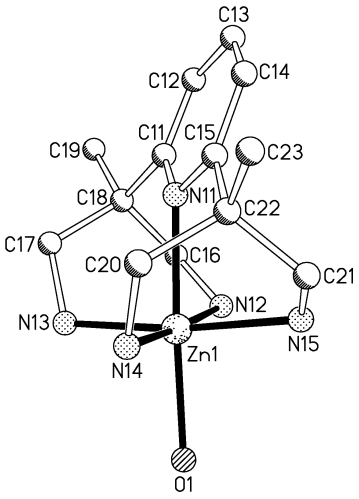


Fig. 1. Molecular structure of the dication in **2**$\cdot 2\,H_2O$ (hydrogen atoms omitted for clarity).

While zinc salts of very poorly coordinating anions (such as ClO_4^-) are normally used to synthesize zinc hydroxo and aqua complexes [4], we have found that the presence of bromide in solution does not inhibit the coordination of water. This observation supports the notion that a great excess of bromide is needed to promote the formation of the pentaamine *bromo* complex in the case of iron(II) as the central metal, and that otherwise the iron(II) aqua complex will form preferentially [5]. (In terms of chemical hardness, Zn^{II} and Fe^{II} are both on the borderline between hard and soft acids, and thus expected to show similar affinity for a given base) [6].

The aqua complex (dihydrate) crystallizes in the orthorhombic space group *Pbca* (No. 61). The molecular structure of the dication, which has no crystallographically imposed symmetry, is shown in Fig. 1. Two bromide anions balance the charge. Selected bond distances and angles are listed in Table 1. The complex crystallises with two water molecules per formula unit, which form hydrogen bonds with the counterions and the amine groups of the ligand. The Zn-N bond lengths are within the range 209.6(5)–218.2(4) pm, and are notably longer than the metal-nitrogen distances found in the related octahedral nickel-aqua complex $[Ni(pyN_4)(H_2O)]I_2$ (205.0(3)–211.0(4) pm) [7]. The Zn-O bond length is 217.9(4) pm, while in the nickel complex it is 213.3(3) pm. As shown in Fig. 1, the pyridine ring is tilted to one side of the $[Zn(pyN_4)]$ pyramid. This distortion may be quantified by the angle ε between the least-squares planes defined by the pyridine ring on the one hand and the quaternary and exocyclic methyl carbon atoms on the other; $\varepsilon = 30.0(4)^\circ$

Table 1. Selected bond lenghts and angles for $[Zn(pyN_4)(H_2O)]Br_2 \cdot 2\,H_2O$.

Bond	[pm]	Angle	[°]
Zn1N11	218.2(4)	N12-Zn1-N11	85.12(16)
Zn1N12	217.7(5)	N13-Zn1-N11	89.64(17)
Zn1N13	212.2(5)	N14-Zn1-N11	91.36(17)
Zn1N14	209.6(5)	N15-Zn1-N11	83.92(17)
Zn1N15	215.9(5)	O1-Zn1-N11	175.53(17)
Zn1O1	217.9(4)		

for **2**, which is significantly greater than for the analogous nickel complex, $\varepsilon = 15.4(4)^\circ$ ($\varepsilon = 0$ if there is no such distortion).

There appears to be no precedent in the literature for a structurally characterised octahedral zinc aqua complex with a polyamine ligand. Related complexes with smaller coordination numbers show decreased bond lengths around Zn; for instance, the Zn-O distance in the pentacoordinated zinc aqua complex of tren (tris(2-aminoethyl)amine), $[Zn(tren)(H_2O)](ClO_4)_2$, is significantly shorter (212.1(4) pm), and the Zn-N equatorial distances are within the range 203.9(5)–207.0(5) pm [8]. In the case of tetrahedral zinc aqua complexes of aromatic amine ligands [9], the Zn-O distance (201.1(3) pm) is much shorter still than the corresponding bond in **2** (217.9(4) pm), in keeping with the observed decrease in ionic radius upon going from an octahedral to a tetrahedral coordination geometry [10]. The structural parameters (distances and angles) of the solvate-free complex, $[Zn(pyN_4)(H_2O)]Br_2$, are very similar, with deviations of not more than 2 pm and 3°, respectively; a single notable exception is the significantly shorter bond to the pyridine nitrogen atom (distance Zn1-N11 214.1(6) pm; *cf.* Experimental Section).

Fixation of CO_2 in methanolic solution

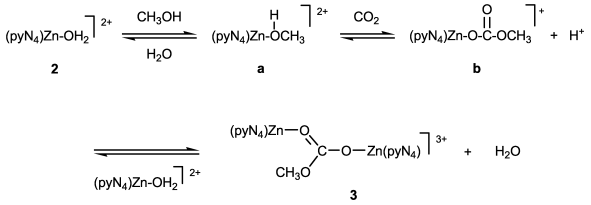
The zinc-aqua moiety is present in the active centre of several zinc-containing metalloenzymes. Probably the most representative of them is carbonic anhydrase, an enzyme which catalyses the reversible hydration of carbon dioxide, thereby playing an important role in respiration and intracellular CO_2/HCO_3^- equilibration. The zinc centre of the active site is coordinated by the imidazole groups of three histidine residues of the protein and a water molecule. It has been shown that the deprotonation of the coordinated water molecule is critical for the catalytic activity. Since the enzyme is characterized by a pK_a value of *ca.* 7, the deprotonation can be effected easily at physiological pH [11]. Synthetic models have shown that a low coordination number and a hydrophobic environment are prerequisites in order to lower the pK_a of a zinc-coordinated water molecule, so that it reaches values comparable to that of the enzyme. In the case of the octahedral complex **2**, the pK_a value is expected to be higher than 10.72, since this is the value determined for the pentacoordinated $[Zn(tren)(H_2O)](ClO_4)_2$, in which, as indicated by the short Zn–O bond (see above), the water molecule is more strongly bound than in **2** and, therefore, the protons may become more acidic. Thus, **2** is not expected to show carbonic anhydrase-like reactivity. However, in related tetraazamacrocyclic systems it has been shown that, upon substitution of coordinated H_2O by ROH, the alcohol is activated, so that the system can take up CO_2 to yield bridged carbonate complexes of the type $[Zn^{II}(L)(O_2COR)]ClO_4$ [12] or $[(Zn^{II}(L))_3(CO_3)](ClO_4)_4$ [4]. In this context, we set out to investigate the reactivity of **2** towards carbon dioxide in methanolic solution.

When a stream of CO_2 is passed through a methanolic solution of **2**, a white precipitate forms immediately. If the stream of gas is interrupted and the suspension is allowed to stand for a few minutes, the white solid redissolves. It can be rapidly regenerated if CO_2 is again passed into the solution. The process thus seems to be reversible. The solution IR spectrum after reaction with CO_2 shows two prominent bands at 1643 and 1312 cm^{-1} which point to the formation of the bridged methyl carbonate dinuclear complex $[(Zn(\mathbf{1}))_2(\mu_2\text{-}(\eta^1\text{-}O,\eta^1\text{-}O)O_2COCH_3)]Br_3$ (**3**). A 1 : 3 salt such as this is expected to be sparingly soluble, and hence precipitate from solution. The isolated solid shows a very strong absorption at 1320 cm^{-1} which is assigned to the symmetric stretching vibration of the methyl carbonate bridge, while the asymmetric vibration may be overlapped with the pyridine stretching vibration of the pyN_4 ligand, resulting in a broad, very strong absorption around 1577 cm^{-1}. The ^{13}C NMR spectrum of **3** (*cf.* Experimental Section) points to a C_{2v} symmetrical cation, since 6 signals are observed for the skeleton of the pyN_4 ligand (three are assigned to the pyridine ring (C2/6, C3/5, C4); the quaternary and exocyclic methyl carbon atoms of the ligand backbone are pairwise equivalent; finally, there is a set of four equivalent methylene carbon atoms). The methyl carbonate bridge is characterized by two signals, at 159.6 ($-O_2\mathit{C}OCH_3$) and 49.6 ($-O_2CO\mathit{C}H_3$) ppm, which are consistent with the values found for related, structurally characterised complexes (see Table 2).

Table 2. Spectroscopic data for methyl carbonate-bridged dinuclear zinc complexes.

Complex	IR [cm^{-1}]	^{13}C NMR [ppm]	Ref.
$[Zn([14]aneN_4)(O_2COCH_3)]ClO_4$	1638, 1316 [a]	—	[12]
$[Zn([15]aneN_4)(O_2COCH_3)]ClO_4$	1635, 1306 [a]	160.6, 53.7 [c]	[12]
$[(Zn(\mathbf{1}))_2(O_2COCH_3)]Br_3$	1643, 1312 [b]	159.6, 49.6 [d]	this work

[a] Solvent not indicated; [b] MeOH; [c] $CDCl_3$; [d] DMSO-d_6.



Scheme 1. Proposed mechanism for the uptake of CO_2 by **2** in methanolic solution. For clarity, the counterions of **2** and **3** are not shown.

The formation of **3** (Scheme 1) can be rationalised if one assumes the initial solvolysis of **2** to form the methanol adduct (**a**). This reacts with CO_2 to give the mononuclear methyl carbonate zinc complex (**b**). The existence of neither **a** nor **b** could be proved, but related complexes of certain tetraazamacrocycles have been isolated and characterised [4, 12]. Furthermore, the activation of methanol by zinc coordination is required, since when CO_2 is passed into methanol alone no reaction occurs. The reaction of **b** with the aqua complex **2** would finally yield the dinuclear complex $[(Zn(\mathbf{1}))_2(\mu_2\text{-}(\eta^1\text{-}O,\eta^1\text{-}O)O_2COCH_3)]Br_3$, which is stable only in the presence of an excess of CO_2.

Conclusion

The reaction of pyN_4 with zinc(II), in the absence of chloride, leads to the formation of the octahedral complex $[Zn(pyN_4)(H_2O)]Br_2$ (**2**), which thwarts the use of zinc(II) as a potential "protective group" for selective condensation reactions of pyN_4 with carbonyl compounds, since there is no discrimination amongst the amine functions upon coordination. The reaction of **2** with CO_2 in methanol leads to the reversible formation of the methyl carbonate-bridged dinuclear complex $[(Zn(pyN_4))_2(\mu_2\text{-}(\eta^1\text{-}O,\eta^1\text{-}O)O_2COCH_3)]Br_3$ (**3**), as indicated by ^{13}C NMR and IR spectroscopic data. The use of uniformly derivatised pentaamine ligands with sterically demanding substituents R ($py(NR)_4$) is expected to prevent the formation of dinuclear complexes. Such studies are currently in progress.

Experimental Section

Materials and instrumentation

Reagents were AR grade or better and were purchased from Merck, Fluka, and Aldrich. The ligand $pyN_4 \cdot 4\ HBr \cdot CH_3OH$ was prepared as described previously [1]. IR (KBr pellets or methanol solutions) were recorded on a Perkin Elmer 16PC FT-IR instrument. NMR spectra were measured on a JEOL JNM-EX 270 spectrometer, and mass spectra were obtained on a JEOL MSTATION 700 spectrometer. Elemental analyses were performed using Carlo Erba Elemental Analysers 1106 and 1108.

*$[Zn(pyN_4)(H_2O)]Br_2 \cdot 2\ H_2O$ (**2** $\cdot$ 2 H_2O)*

To a suspension of $pyN_4 \cdot 4HBr \cdot MeOH$ (0.53 g, 0.87 mmol) in methanol (8 ml) was added LiOMe (3.48 ml of a 1 M stock solution in MeOH, 3.48 mmol). The resulting solution was stirred at room temperature for 5 min. A solution of $ZnBr_2$ (0.20 g, 0.87 mmol) in methanol (3 ml) was added, and the resulting colourless solution was refluxed for 2 h. The solvent was then evaporated and the remaining pale yellow oil taken up in an ethanol : water mixture (8 : 2, v/v, 15 ml) and refluxed for 10 min. The mixture was filtered hot and allowed to cool. From the filtrate there formed a batch of colourless crystals of **2** $\cdot$ 2 H_2O, which were collected by filtration and dried in air overnight. $C_{13}H_{27}Br_2N_5OZn \cdot 2\ H_2O$ (530.6): calcd. C 29.43, H 5.89, N 13.20; found C 29.49, H 5.77, N 13.16. IR (KBr, cm^{-1}): 3262vs, 3232vs, 3159vs, 2962s, 2937s, 2866m, 1607s, 1586s, 1575vs, 1463vs, 1394m, 1239m, 1159m, 1132s, 1111s, 1082s, 1025vs, 1014vs, 822m, 768w, 655w, 611s, 561s, 530m. MS (FD): m/z (%) = 314 [$Zn(pyN_4) - 2H$] (80). ^{1}H NMR (DMSO-d_6, r.t.): $\delta = 7.95$ [AB_2, t, $^3J(HH) = 8.04$ Hz, 1 H, H^4]; 7.49 [AB_2, d, $^3J(HH) = 8.01$ Hz, 2 H, $H^{3,5}$]; 3.29 [s(br), -NH_2, 8H]; 3.20 [m, 4H, -CHH-]; 2.85 [m, 4H, -CHH-]; 1.20 [s, 6H, -CH_3]. (+ D_2O, r.t.): $\delta = 7.94$ [AB_2, t, $^3J(HH) = 8.04/8.01$ Hz, 1 H, H^4]; 7.48 [AB_2, d, $^3J(HH) = 8.04$ Hz, 2 H, $H^{3,5}$]; 3.15 [d; $^2J(HH) = 13.59$ Hz, 4H, -CHH-]; 2.84 [d (br), $^2J(HH) = 13.46$ Hz, 4H, -CHH-]; 1.18 [s, 6H, -CH_3]. ^{13}C NMR (D_2O, r.t.): $\delta = 163.7$ (s, py-C2/6), 140.2 (s, py-C4), 120.0 (s, py-C3/5), 50.2 (s, -CH_2-), 38.7 (s, $> C <$), 23.3 (s, -CH_3). (DMSO-d_6, r.t.): $\delta = 165.7$ (s, py-C2/6), 141.5 (s, py-C4), 121.1 (s, py-C3/5), 51.8 (s, -CH_2-), 40.2 (s, $> C <$), 24.6 (s, -CH_3).

Reaction of $[Zn(pyN_4)(H_2O)]Br_2 \cdot 2\ H_2O$ with CO_2

The zinc aqua complex **2** (0.21 g, 0.40 mmol) was dissolved in methanol (10 ml), and a vigorous stream of CO_2 was passed through the solution. After a few seconds a white precipitate started to form. After 5 min. the gas stream was stopped and the mixture was rapidly filtered. The reaction

Table 3. Crystallographic data for compound **2**.

Composition	**2** · 2 H_2O
Empirical formula	$C_{13}H_{31}Br_2N_5O_3Zn$
Formula weight	530.62
Crystal system	orthorhombic
Space group (no.)	*Pbca* (No. 61)
a [Å]	12.154(1)
b [Å]	17.406(1)
c [Å]	19.042(2)
Z	8
V [Å^3]	4028.4 (6)
ρ_{calcd} [g cm^{-3}]	1.750
Diffractometer	Siemens P4
λ[a] [Å]	0.71073
Crystal size [mm^3]	$0.60 \times 0.50 \times 0.28$
T [K]	220(2)
Absorption correction	Psi-scan
T_{min}/T_{max}	0.006/0.028
Scan	ω
2θ Range	$4.2 \leq 2 \leq 54.0$
Measured reflections	5420
Unique reflections	4396
Observed reflections[b]	2889
μ(Mo-K$_\alpha$) [mm^{-1}]	5.208
Refined parameters	217
Data/parameter ratio	20.3
$wR2$ (all data)[c]	0.1272
$R1$ (obs. data)[d]	0.0503
ρ_{fin}(max/min) [e Å^{-3}]	0.600/−0.473

[a] Mo-K$_\alpha$, graphite monochromator; [b] with $F_o \geq 4\sigma(F)$; [c] $wR2 = (\{\Sigma[w(F_o^2 - F_c^2)^2]\}/\{\Sigma[w(F_o^2)^2]\})^{0.5}$; [d] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o = 4\sigma(F)$.

was monitored by IR spectroscopy, which indicated the formation of the bridged methyl carbonate dinuclear adduct $[(Zn(pyN_4))_2(\mu_2\text{-}(\eta^1\text{-}O,\eta^1\text{-}O)O_2COCH_3)]Br_3$ (**3**) (1643, 1312 cm^{-1}, methanol). $C_{28}H_{53}Br_3N_{10}O_3Zn_2$ (948.28): calcd. C 35.46, H 5.63, N 14.77; found C 32.16, H 5.14, N 12.34. The deviations point to the presence of an impurity, possibly occluded carbonobromidic acid (bromoformic acid), BrC(=O)OH, from the reaction of CO_2 with HBr; the corresponding adduct of **3**, $C_{28}H_{53}Br_3N_{10}O_3Zn_2 \cdot CHBrO_2$, has $C_{29}H_{54}Br_4N_{10}O_5Zn_2$ (1073.20): calcd. C 32.46, H 5.07, N 13.05. IR (KBr, cm^{-1}): 3321br, 2966s, 2936s, 2885m, 1577vs(br), 1466vs, 1379s, 1321vs, 1155m, 1093m, 1023m, 812m, 757m. The colourless solid was dissolved in DMSO-d_6, and CO_2 was briefly passed into the solution before the ^{13}C NMR spectrum (r.t.) was recorded, which was consistent with the formation of $[(Zn(pyN_4))_2(\mu_2\text{-}(\eta^1\text{-}O,\eta^1\text{-}O)\ O_2COCH_3)]Br_3$: ^{13}C NMR (DMSO-$d_6$.): δ = 164.9 (s, py-C2/6), 159.6 (s, -O_2COCH_3), 141.1 (s, py-C4), 125.2 (BrC(=O)OH or CO_2), 121.1 (s, py-C3/5), 51.8 (s, -CH_2-), 49.6 (s, -O_2COCH_3), 45.4 (s, $> C <$), 24.7 (s, -CH_3).

Crystallography

Crystal data for compound **2** are given in Table 3, and selected bond distances and angles are listed in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 using SHELXTL NT 5.10 (Bruker AXS, 1998). The compound crystallizes with 2 molecules of H_2O per formula unit. All non-hydrogen atoms were refined anisotropically. All hydrogen atom positions were obtained from a difference Fourier synthesis, and both positional and common isotropic displacement parameters were kept constant during refinement. Crystallographic data (excluding structure factors) for this structure as well as the solvate-free complex (which is very similar, and therefore not discussed in detail) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 250714 and 250713. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44 (1223) 336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgement

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