Inorganica Chimica Acta, *119* (1986) 61–66

Bis{2-[(3-aminopropyl)amino] ethanolato} nickel(II) Chloride and Bromide: Crystal Structure and Magnetic Characterization

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(Received March 12, 1986)

Abstract

The title compounds, $Ni(C_5H_{14}N_2O)_2Cl_2$ and $Ni(C_5H_{14}N_2O)_2Br_2$, are isomorphous and crystallize in the orthorhombic space group *Pnna* with unit cell dimensions $a = 13.182(3)$, $b = 14.860(4)$, $c = 8.742(2)$ Å, and $a = 13.637(5)$, $b = 15.009(4)$, $c = 8.815(3)$ Å, respectively. The densities D_c and D_m are 1.42 and 1.425(4) g cm^{-3} for the chloride compound and 1.67 and 1.65(1) g cm^{-3} for the bromide; $Z = 4$. The data of both compounds were collected with an automatic four-circle diffractometer using ω-scan mode. The crystal structures were solved by direct methods, and the refinements, based upon 1388 and 1285 reflections with $F_o > 6.0\sigma(F_o)$, yielded conventional R factors of 4.0 and 7.5%, respectively.

The compounds are monomeric bischelates, where four nitrogen atoms and two oxygen atoms are coordinated octahedrally to a nickel(II) ion. The oxygen atoms are in *cis*-position to each other. The exact symmetries of the cations are C_2. The ligand molecules are not deprotonated and are coordinated tridentately to the central atom. The six-membered ring of the chelate is in chair conformation and the five-membered ring in antisymmetric skew conformation. The chloride and bromide ions are weakly bonded to the structure with hydrogen bridges.

The magnetic susceptibilities of the compounds were determined in the temperature range 93–303 K, and in both cases the magnetic data indicated octahedral nickel(II) coordination sphere with no interaction between the metal atoms.

Introduction

The diaminoalcohol 2-[(3-aminopropyl)amino]-ethanol (HL) forms one-to-one complexes with copper(II) chloride and nitrate salts in alcohol solutions [1]. X-ray structural analyses revealed the complexes to have tetranuclear structures with cubane-type Cu_4O_4 cores [2]. Further studies showed tetranuclear structures in $[Cu_4L_4]Br_4\cdot 3H_2O$ and $[Cu_4L_4](SO_4)_2\cdot 8H_2O$ [3] and dinuclear structures in $[Cu_2L_2]I_2\cdot 2H_2O$ and $[Cu_2L_2]_2[Cu(NCS)_4]NCS$ [4]. The structural details and the magnetic characterization of the complexes have been summarized in a publication examining the correlation between the magnetic behaviour and crystal structures of dinuclear and tetranuclear alkoxo-bridged copper(II) complexes [5]. An X-ray structural analysis was made of the monomeric biscomplex $[Cu(HL)_2](SCN)_2$ [6].

The study has now been extended to nickel metal. The stability constants of several Ni(II) complexes formed by 2-[(3-aminopropyl)amino]ethanol in aqueous solution have already been published, together with their crystal data in solid state [7]. In this paper the molecular structures of two nickel(II) complexes formed by HL are presented and their magnetic behaviour characterized.

Experimental

Starting Materials

2-[(3-aminopropyl)amino]ethanol was obtained from Aldrich-Europe (Belgium). The other chemicals were of reagent quality.

Preparation

The complex $[Ni(HL)_2]Cl_2$ was prepared by dissolving 0.025 mol $NiCl_2\cdot 6H_2O$ in 50 ml of absolute ethanol and adding this solution to a stirred solution of 0.050 mol amine in 25 ml of absolute ethanol. Evaporation of the liquid in a fume cupboard left a sticky remainder in the beaker. Dissolving of this in 1-propanol gave a green solution and dissolving of the insoluble residue in 1-propanol:water mixture (20:1) gave a blue solution. After several days at room temperature, well-developed blue crystals formed in the blue solution.

The $[Ni(HL)_2]Br_2$ complex was prepared essentially by the method of Lukkari [7]. 0.025 mol $NiBr_2\cdot 3H_2O$ was dissolved in 50 ml of absolute ethanol and the resulting solution was added to a stirred solution of 0.075 mol amine in 12 ml of absolute ethanol. The blue precipitate was separated, washed with ethanol and recrystallized from boiling

0020-1693/86/$3.50

TABLE I. Crystallographic Data

Compound	$Ni(C_5H_{14}N_2O)_2Cl_2$	$Ni(C_5H_{14}N_2O)_2Br_2$
M_r	365.97	454.87
a (Å)	13.182(3)	13.637(5)
b (Å)	14.860(4)	15.009(4)
c (Å)	8.742(2)	8.815(3)
$\alpha = \beta = \gamma$ (°)	90	90
U (Å^3)	1712.3(8)	1804.2(9)
Z	4	4
D_c (g cm^{-3})	1.42	1.67
D_m (g cm^{-3})	1.425(4)	1.65(1)
Space group	*Pnna* (No. 52)	*Pnna* (No. 52)
Radiation (Å)	Monochromated Mo Kα; $\lambda = 0.71069$	Monochromated Mo Kα; $\lambda = 0.71069$
$F(000)$	776	920
μ (cm^{-1})	13.7	53.8
Diffractometer	Nicolet P3F	Nicolet P3F
Scan mode	ω	ω
Scan range (°)	1.0	1.0
Scan speed (° min^{-1})	2.5–29.3	2.5–29.3
2θ range (°)	5.0–55.0	5.0–55.0
Total data	2272	2077
$F_o > 6.0\sigma(F_o)$	1388	1265
R	0.040	0.075
R_w	0.046	0.074
w	$1.000/(\sigma^2(F_o) + 0.0027\ F_o^2)$	$1.000/(\sigma^2(F_o) + 0.0111\ F_o^2)$

absolute ethanol. After a few days blue rectangular crystals were formed.

Magnetic Susceptibility

The magnetic susceptibilities of the complexes were measured over the temperature range 93–303 K by the Gouy method using a Newport Instrument variable-temperature Gouy balance. $CuSO_4 \cdot 5H_2O$ was used for calibration [8]. Diamagnetic corrections were applied with Pascal's constants for the atoms of the amine, and calculated corrections were applied for Cl^- and Br^- ions [9].

Crystal Structure Analysis

The crystal $[Ni(HL)_2]Cl_2$ used for data collection was a sphere of diameter 0.46 mm, and the crystal of $[Ni(HL)_2]Br_2$ had approximate dimensions of 0.45 × 0.45 × 0.20 mm. Relevant crystal data of both complexes are listed in Table I. Systematic absences $0kl$ for $k + l = 2n + 1$, $h0l$ for $l + h = 2n + 1$ and $hk0$ for $h = 2n + 1$ indicated the space group *Pnna* (D_{2h}^6, No. 52). The intensities of two standard reflections recorded after every fiftieth reflection varied about 4% in the data of $[Ni(HL)_2]Cl_2$ and about 9% in the data of $[Ni(HL)_2]Br_2$ and intensity data were corrected for Lorentz and polarization effects. A check of the ϕ-scan data for possible absorption showed an essential drop in the intensities only for $[Ni(HL)_2]Br_2$ and an absorption correction was made only for this compound.

The structure of $[Ni(HL)_2]Cl_2$ was solved by direct methods using the MULTAN 80 program system [10]*. An E-map based upon 238 reflections with $|E| \geqslant 1.47$ revealed the positions of nine non-hydrogen atoms. The other non-hydrogen atoms were located from a successive Fourier map and the hydrogen atoms from a difference map. The full-matrix refinement yielded a conventional R factor of 4.0%.

Because the structures of $[Ni(HL)_2]Cl_2$ and $[Ni(HL)_2]Br_2$ are isomorphous, the structure of the latter complex was refined using the atomic coordinates of $[Ni(HL)_2]Cl_2$ The refinement converged to a conventional R factor of 7.5%.

Final atomic parameters for non-hydrogen atoms of the complexes are presented in Table II. The atomic parameters of the hydrogen atoms of $[Ni(HL)_2]Cl_2$ are shown in Table III. The hydrogen atoms of $[Ni(HL)_2]Br_2$ were located in calculated positions using the routine method included in the SHELX-76 program system [10]. These parameters are not published, see also 'Supplementary Material'.

Results and Discussion

Both structures contain monomeric bischelate cations $[Ni(HL)_2]^{2+}$ with the nickel(II) ion on a

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*All crystallographic calculations were carried out on a UNIVAC 1108 computer.

TABLE II. Fractional Atomic Coordinates and the Equivalent Isotropic Temperature Factors[a] (× 10^3) for the Non-hydrogen Atoms of $[Ni(HL)_2]Cl_2$ and $[Ni(HL)_2]Br_2$. Estimated Standard Deviations are Given in Parentheses

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
$Ni(HL)_2Cl_2$				
Ni	0.38156(3)	0.2500	0.2500	26
Cl1	0.2500	0.0000	0.0652(2)	51
Cl2	0.0364(1)	0.2500	0.2500	70
O	0.5007(2)	0.2895(2)	0.4075(3)	40
N1	0.2698(2)	0.2246(2)	0.0853(3)	38
N2	0.3969(2)	0.3848(2)	0.1911(3)	36
C1	0.2723(3)	0.2763(3)	−0.0581(4)	49
C2	0.2803(3)	0.3760(3)	−0.0331(5)	57
C3	0.3814(3)	0.4086(3)	0.0284(5)	49
C4	0.4960(3)	0.4174(3)	0.2490(4)	49
C5	0.5116(3)	0.3856(2)	0.4089(5)	50
$Ni(HL)_2Br_2$				
Ni	0.3823(1)	0.2500	0.2500	32
Br1	0.2500	0.0000	0.0356(3)	66
Br2	0.0396(2)	0.2500	0.2500	111
O	0.4973(7)	0.2891(6)	0.4014(11)	54
N1	0.2758(8)	0.2259(7)	0.0869(12)	46
N2	0.3958(8)	0.3850(7)	0.1934(13)	52
C1	0.2744(11)	0.2786(13)	−0.0552(15)	64
C2	0.2846(14)	0.3777(11)	−0.0276(19)	72
C3	0.3771(11)	0.4107(10)	0.0340(16)	61
C4	0.4941(11)	0.4164(10)	0.2454(18)	60
C5	0.5085(12)	0.3843(10)	0.4024(20)	64

[a] $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

TABLE III. Fractional Atomic Coordinates and Isotropic Thermal Parameters (× 10^3) for the Hydrogen Atoms of $[Ni(HL)_2]Cl_2$. Estimated Standard Deviations are Given in Parentheses

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
H1(N1)	0.268(2)	0.166(3)	0.064(4)	38(9)
H2(N1)	0.208(3)	0.233(2)	0.135(4)	34(9)
H1(C1)	0.210(2)	0.266(2)	−0.117(4)	32(9)
H2(C1)	0.344(4)	0.258(2)	−0.119(6)	55(12)
H1(C2)	0.222(4)	0.393(3)	0.058(6)	76(14)
H2(C2)	0.251(5)	0.412(4)	−0.144(8)	126(24)
H1(C3)	0.385(2)	0.477(2)	0.020(4)	37(9)
H2(C3)	0.448(4)	0.380(3)	−0.039(6)	83(14)
H1(N2)	0.351(3)	0.412(3)	0.256(4)	37(10)
H1(C4)	0.499(3)	0.487(3)	0.240(3)	50(11)
H2(C4)	0.544(4)	0.400(3)	0.175(5)	61(12)
H1(C5)	0.578(3)	0.401(3)	0.447(5)	52(10)
H2(C5)	0.455(4)	0.417(3)	0.478(6)	75(14)
H(1)O	0.517(4)	0.269(3)	0.476(6)	64(15)

TABLE IV. Interatomic Distances (Å) and Angles (°) of Non-hydrogen Atoms in the $[Ni(HL)_2]^{2+}$ cations of $[Ni(HL)_2]Cl_2$ and $[Ni(HL)_2]Br_2$. Estimated Standard Deviations are Given in Parentheses

	$[Ni(HL)_2]Cl_2$	$[Ni(HL)_2]Br_2$
Coordination sphere		
Distances		
Ni–N1	2.094(3)	2.078(10)
Ni–N2	2.078(3)	2.094(11)
Ni–O	2.170(2)	2.143(9)
Angles		
N1–Ni–N2	94.1(1)	93.8(4)
N1–Ni–O	173.9(1)	172.8(4)
N2–Ni–O	80.0(1)	79.5(4)
Amine molecule		
Distances		
N1–C1	1.471(4)	1.48(2)
C1–C2	1.501(6)	1.52(2)
C2–C3	1.516(5)	1.46(2)
C3–N2	1.481(5)	1.48(2)
N2–C4	1.482(4)	1.49(2)
C4–C5	1.490(5)	1.47(2)
C5–O	1.435(5)	1.43(2)
Angles		
Ni–N1–C1	118.4(2)	119.9(9)
N1–C1–C2	113.1(3)	112.9(12)
C1–C2–C3	115.4(3)	117.9(13)
C2–C3–N2	112.7(3)	114.9(13)
C3–N2–Ni	117.1(2)	117.5(9)
C4–N2–Ni	108.4(2)	108.2(8)
C4–N2–C3	111.8(3)	111.6(11)
N2–C4–C5	109.8(3)	107.9(11)
C4–C5–O	107.1(3)	108.0(12)
C5–O–Ni	110.3(2)	110.7(9)

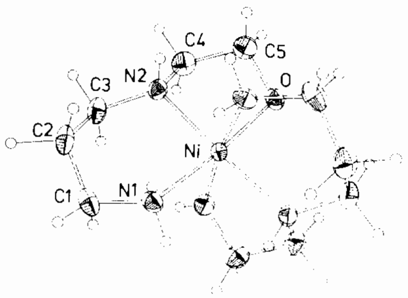

Fig. 1. View of the cation $[Ni(C_5H_{14}N_2O)_2]^{2+}$ (thermal ellipsoids with 50% probability).

2-axis (*x*, ¼, ¼). The cation (presented in Fig. 1) has C_2-symmetry and bond lengths and angles as shown in Table IV. The Cl^- and Br^- ions are non-coordinated.

TABLE V. Least-squares Planes through Four of the Six Donor Atoms in the Nickel(II) Coordination Spheres of $[Ni(HL)_2]Cl_2$ and $[Ni(HL)_2]Br_2$ and Distances (Å) of Donor Atoms from these Planes. Estimated Standard Deviations are Given in Parentheses

$[Ni(HL)_2]Cl_2$							
Plane 1:	N1	N2	O	$N2^a$	Ni	O^a	$N1^a$
N1, N2, O, $N2^a$	0.048(2)	−0.055(3)	0.055(2)	−0.049(3)	0.089(1)	−2.066(3)	2.183(3)
Plane 2:	N1	$N1^a$	O	O^a	Ni	N2	$N2^a$
N1, $N1^a$, O, O^a	0.110(3)	−0.110(3)	0.109(3)	−0.109(3)	0.000(2)	2.062(3)	−2.062(3)
$[Ni(HL)_2]Br_2$							
Plane 1′:	N1	N2	O	$N2^a$	Ni	O^a	$N1^a$
N1, N2, O, $N2^a$	0.035(10)	−0.041(11)	0.030(8)	−0.036(11)	0.089(5)	−2.033(12)	2.165(13)
Plane 2′:	N1	$N1^a$	O	O^a	Ni	N2	$N2^a$
N1, $N1^a$, O, O^a	0.138(11)	−0.138(11)	0.109(9)	−0.109(9)	0.000(5)	2.077(12)	−2.077(12)

[a] Equivalent position x, ½ − y, ½ − z.

The coordination sphere around the nickel(II) ion is distorted octahedron. The distortion from regularity is evidently due to steric reasons, as was found earlier in the copper(II) complexes of the amine [5]. The set of donor atoms is N_4O_2, with the oxygen atoms lying in *cis*-position to each other. The coordination bond lengths are normal for octahedral Ni(II) complexes [11], varying from 2.078 to 2.094 Å for Ni–N bonds and from 2.143 to 2.170 Å for Ni–O bonds.

Least-squares planes were calculated through four of the six donor atoms and the deviations of the central atom and the six donor atoms from these planes are presented in Table V. According to the symmetry the Ni(II) ion lies in the least-squares plane [N1, $N1^a$, O, O^a] (^{a} is equivalent position x, ½ − y, ½ − z). The location of these four atoms crosswise above and below the least-squares plane, indicates slight tetrahedral distortion.

The coordination geometry of the amine resembles the geometries found in the one-to-one copper(II) complexes [5]. The N1 atom and O atom lie on opposite sides of the Ni(II) ion. Likewise, the angle N1–Ni–N2 of 94.1° is similar to that in the polynuclear copper(II) complexes (92.9–94.4°) rather than to that in $[Cu(HL)_2](SCN)_2$ (87.3°) [6]. As expected for nickel(II) complexes, the elongation of the apical coordination bonds is lacking, and may be the reason why no polynuclear nickel(II) complex is formed by the amine.

The amine molecule coordinates tridentately and is deprotonated. The bond lengths and angles presented in Table IV are normal for the amine [5].

The six-membered chelate ring is in chair conformation. The puckering of the ring can be characterized by applying the principles used by Gollogly and Hawkins [12] in their conformational analysis of the six-membered diamine ring. Thus the distances Z_1, Z_2 and Z_3 of the atoms C1, C2 and C3 from the plane NiN_2 (Fig. 2) are 0.668(5), 0.240(5) and 0.712(5) Å in $[Ni(HL)_2]Cl_2$, and 0.64(2), 0.23(2) and 0.66(2) Å in $[Ni(HL)_2]Br_2$, and the differences $Z_1 - Z_2$ and $Z_3 - Z_2$ are 0.43 and 0.47 Å in $[Ni(HL)_2]Cl_2$, and 0.41 and 0.43 Å in $[Ni(HL)_2]Br_2$. Comparison with the values for the copper(II) complexes shows the degree of the puckering to be similar to that in tetranuclear copper(II) complexes (0.38–0.49 Å). The $Z_1 - Z_2$ and $Z_3 - Z_1$ values for the dinuclear copper(II) complexes are only 0.32–0.35 Å and those for the mononuclear complex 0.10 Å [5].

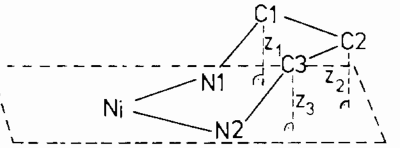

Fig. 2. Labelling and configuration of structural parameters in the six-membered NiC_3N_2 ring.

In the five-membered ring the C4 and C5 atoms deviate from the plane 0.437(4) and −0.259(5) Å in $[Ni(HL)_2]Cl_2$, and 0.48(2) and −0.24(2) Å in $[Ni(HL)_2]Br_2$. In their study on five-membered rings, Corey and Bailar [13] describe the conformation as symmetric skew when the two carbon atoms are equidistant. Thus the conformation in this complex, as in most of the copper(II) complexes formed by 2-[(3-aminopropyl)amino]ethanol studied this far [5], is unsymmetric skew. The degree of the puckering of the five-membered ring is characterized by the dihedral angle between the planes NC_2 and OC_2. The angle is 55.0(3)° in $[Ni(HL)_2]Cl_2$ and 56.7(13)° in $[Ni(HL)_2]Br_2$, and comparable to the angles found in the one-to-one copper(II) complexes of the amine [5]. The corresponding angle in the biscomplex $[Cu(HL)_2](SCN)_2$ is 60.9° [6].

The Cl^- and Br^- ions occupy special positions (x, ¼, ¼) and (¼, 0, z), and the hydrogen bonding

TABLE VI. Hydrogen Bonding Details for Cl^- and Br^- Ions in $[Ni(HL)_2]Cl_2$ and $[Ni(HL)_2]Br_2$ Estimated Standard Deviations are Given in Parentheses

X–H···Y	Position of acceptor atom	X···Y (Å)	X–H (Å)	H···Y (Å)	X–H···Y (°)
$[Ni(HL)_2]Cl_2$					
N1–H1(N1)···Cl1	¼, 0, *z*	3.352(3)	0.92(4)	2.44(4)	168(3)
N2–H1(N2)···Cl1	¼, ½, ½ – *z*	3.353(3)	0.92(4)	2.44(4)	172(3)
N1–H2(N1)···Cl2	*x*, ¼, ¼	3.418(3)	0.93(4)	2.49(4)	175(3)
O–H1(O)···Cl2	½ + *x*, ¼, ¾	3.088(3)	0.69(5)	2.44(4)	158(3)
$[Ni(HL)_2]Br_2$					
N1–H1(N1)···Br1	¼, 0, *z*	3.435(10)	1.04(5)	2.63(11)	134(14)
N2–H1(N2)···Br1	¼, ½, ½ – *z*	3.555(10)	1.03(4)	2.59(10)	173(16)
N1–H2(N1)···Br2	*x*, ¼, ¼	3.546(11)	1.02(2)	2.57(7)	160(15)
O–H1(O)···Br2	½ + *x*, ¼, ¼	3.184(10)	1.08(2)	2.46(8)	137(15)

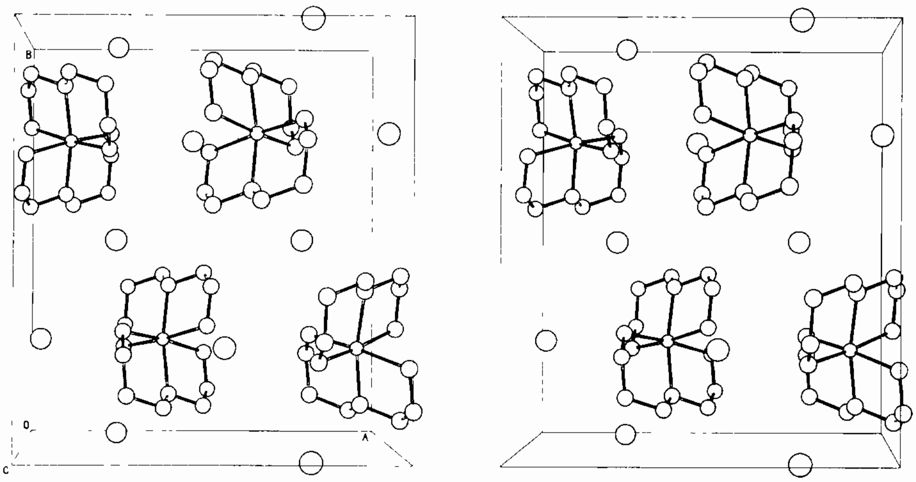

Fig 3 Stereoview of the packing of $[Ni(C_5H_{14}N_2O)_2]Cl_2$

details (Table VI) indicate that they are attached to the structure by weak hydrogen bridges. There are no other non hydrogen ions within a distance of 3.6 Å of the halide ions. The stereoview of the packing of $[Ni(HL)_2]Cl_2$ is shown in Fig. 3.

The susceptibility data of both complexes obey the Curie–Weiss law $\chi'_M = C/(T - \theta) + N\alpha$, where C is the Curie constant, θ the Weiss constant and $N\alpha$ the temperature-independent paramagnetism. The refined constants are $C = 1.114(8)$, $\theta = 0.7(5)$ K and $N\alpha = 240(2) \times 10^{-6}$ cm^3 mol^{-1} for $[Ni(HL)_2]Cl_2$ and $C = 1.29(2)$, $\theta = 2.6(13)$ K and $N\alpha = 350(70) \times 10^{-6}$ cm^3 mol^{-1} for $[Ni(HL)_2]Br_2$. The residuals R to the goodness of the fits ($R = [\Sigma(\chi'_M(\text{obs}) - \chi'_M(\text{calc}))^2/\Sigma\chi'_M(\text{obs})^2]^{1/2}$ are 0.0016 and 0.0042, respectively. The almost zero values of the Weiss constants indicate that there is no interaction between the nickel(II) ions.

The magnetic moment μ_{eff} (20 °C) is 3.017(7) BM for $[Ni(HL)_2]Cl_2$ and 3.229(8) BM for $[Ni(HL)_2]Br_2$ ($\mu_{eff} = 2.828\sqrt{(\chi'_M - N\alpha)T}$). The values are normal for Ni(II) complexes with octahedral ligand field [14]. The temperature independence of the magnetic moment is typical for octahedral mononuclear complexes [5, 14] In the tetrahedral ligand field, the μ_{eff} value is greater (about 3.8 BM) and temperature dependent.

Supplementary Material

Anisotropic temperature parameters and observed and calculated structure factors have been deposited with the Editor-in-Chief.

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