Inorganic Chemistry

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Wheel-Shaped Icosanuclear Homo- and Heterometallic Complexes of Ni^{II}, Co^{II}, and Cu^{II} Ions Supported by Unsymmetrical Aminoalcohol Ligands

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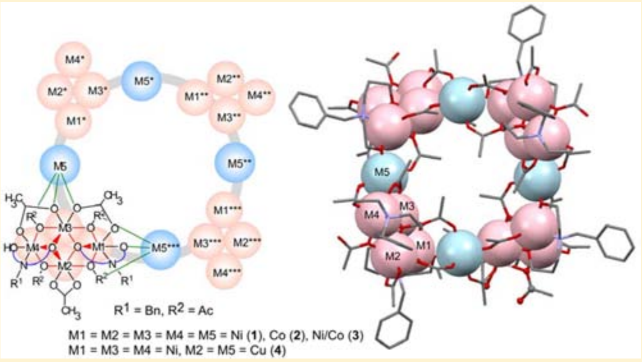
Supporting Information

ABSTRACT: Reactions of $M(OAc)_2{\cdot}4H_2O$ (M = Ni, Co) with 3-[benzyl(2-hydroxyethyl)amino]-1-propanol (H_2L) in the presence of pyridine or triethylamine afforded novel homometallic icosanuclear wheel-shaped complexes $[M_{20}L_4(HL)_4(OAc)_{28}]$ (M = Ni (**1**), Co (**2**)), which consist of a central M^{II}_{12} single-stranded, nearly planar loop with four peripheral $[M_2(HL)(OAc)_2]$ fragments attached in an S_4 symmetrical fashion. The complexes can alternatively be recognized as saddle-shaped wheel structures, in which four tetranuclear units of $[M_4L(HL)(OAc)_7]^{2-}$ are connected by four M^{2+} ions (M5). The tetranuclear unit itself can be derived from an ideal C_2 symmetrical $[M_4(HL)_2(\mu\text{-}\eta^2\text{-OAc})_4(\mu\text{-}\eta^1,\eta^1\text{-OAc})_2(\eta^1,\eta^1\text{-OAc})]^-$ structure through deprotonation of the HL^- ligand, and is composed of two plane-shared M_3O_4 incomplete cubanes in which the M2 and M3 atoms are involved in the central fused plane and the M1 and M4 atoms are disposed at the apex sites. Mixed-metal icosanuclear complexes $[Ni_xM_{20-x}L_4(HL)_4(OAc)_{28}]$ (**3**, M = Co, x = 9.5) and $[Ni_{12}M_8L_4(HL)_4(OAc)_{28}]$ (**4**, M = Cu) were also synthesized by using equimolar amounts of Ni^{II} and M^{II} ions, and were shown to have similar structures to **1** and **2**. X-ray crystallographic and fluorescent analyses revealed that complex **3** contains nonstoichiometric amounts of Ni^{2+} and Co^{2+} ions in the ratio of 9.5:10.5 and that these are disordered at every metal site. In striking contrast, complex **4** has a stoichiometric formula of $Ni_{12}Cu_8$, which was confirmed by the Jahn–Teller elongation of Cu^{2+} ions, and consequently, the M2 and M5 positions are occupied exclusively by the Cu^{2+} ions. The temperature-dependent direct current (dc) magnetic susceptibility data showed the presence of ferromagnetic exchange interactions in the Ni homometallic (**1**) and NiCu bimetallic (**4**) complexes, while the Co homometallic (**2**) and NiCo bimetallic (**3**) complexes exhibited antiferromagnetic interactions due to spin–orbit coupling effects of the octahedral Co^{II} ions. The present results demonstrate that the unsymmetrical aminoalcohol ligand H_2L is quite effective in organizing the homo- and heterometallic icosanuclear wheel-shaped metal arrangements.



■ INTRODUCTION

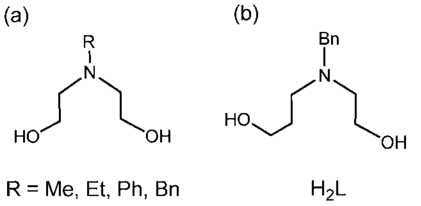
High-nuclearity metal complexes have attracted attention as nanoscaled functional materials in diverse applications such as catalysts and electronic, photochemical, and magnetic devices.[1] Among such complexes, wheel-shaped multinuclear complexes with 3d metal ions have continuously evoked synthetic interests because of their fascinating structures as molecule-based nanoparticles, and have recently been recognized as promising candidates for qubits used in quantum computation owing to their intriguing magnetic properties such as their infinite one-dimensional magnetism, spin frustration, and magnetic anisotropy relating to the single-molecule magnet (SMM).[2] While many homometallic wheel-shaped complexes with a variety of 3d metal ions have been synthesized with practical and theoretical advances,[3−11] the control of their sizes, shapes, and properties in such a topology remains an important subject for development.

Received: September 1, 2012
Published: November 7, 2012

dx.doi.org/10.1021/ic3019106 | *Inorg. Chem.* 2012, 51, 12503−12510

By using high-valent oxygenophilic metal ions such as V,[4] Cr,[5] Mn,[6] and Fe,[7] a large number of wheels have been synthesized with the aid of oxo, alkoxo, and carboxylato bridging ligands; they include the Mn_{84} giant wheel as a symbolic example.[6e] In contrast, wheel-shaped clusters with softer 3d metal ions of Co[8] and Ni[9] are relatively rare in spite of the anisotropic magnetic properties derived from Co^{II} and Ni^{II} electronic states, and those compounds with a nuclearity higher than 20 are extremely limited to just four examples: $[Ni_{24}(OH)_8(mpo)_{16}(OAc)_{24}(Hmpo)_{16}]$ (Hmpo =3-methyl-3-pyrazolin-5-one),[9c] $[Ni_{24}(OAc)_{42}(mdaH)_6(EtOH)_6]$ ($mdaH_2$ = *N*-methyldiethanolamine),[9a] $[Co_4(TBSC)(trz)_2Cl_2\text{-}(MeOH)(H_2O)]_6$ (H_4TBSC = *p*-*tert*-butylthiacalix[4]arene, Htrz =1,2,4-triazole),[8e] and $[Co_{24}(TBSOC)_8(trz)_{16}\text{-}(MeOH)_8]$ (H_4TBSOC = *p*-tert-butylsulfonylcalix[4]arene).[8f] The structures and sizes of these soft 3d metal wheels could potentially be determined by the nature of the bridging ligands, and combinations of O and N donor systems have actually been employed. Various aminoalcohols have been prepared to support multinuclear centers through the N and O donor atoms. Among them, *N*-alkylated diethanolamine ligands $RN(CH_2CH_2OH)_2$ have been used widely in the preparation of ring-shaped complexes on account of their flexible bridging properties, and various *N*-substituent groups such as methyl, ethyl, phenyl, and benzyl groups were introduced with the aim of controlling the structures and properties of the wheel-shaped complexes (Scheme 1a).[6g−m,7b−e,9a,10b,12a−c] However, no attempt has been made to modify the aminoalcohols by tuning the lengths of the $N(CH_2)_nOH$ chelating arms, although such an alternation would have a significant influence on their bridging modes. With the hope of introducing some anisotropic factors in the wheel construction, we have recently synthesized a new NO_2-type ligand, 3-[benzyl(2-hydroxyethyl)amino]-1-propanol (H_2L), containing unsymmetrical NO chelating arms of hydroxyethyl and hydroxypropyl groups (Scheme 1b).

Scheme 1. Structures of *N*-alkylated Diethanolamine (a) and H_2L (b)



In the present report, we wish to describe the synthesis and characterization of novel homo- and heterometallic icosanuclear wheel-shaped clusters, $[M_{20}L_4(HL)_4(OAc)_{28}]$ (M = Ni (**1**), Co (**2**)), $[Ni_{9.5}Co_{10.5}L_4(HL)_4(OAc)_{28}]$ (**3**), and $[Cu_8Ni_{12}L_4(HL)_4\text{-}(OAc)_{28}]$ (**4**), created through the utilization of the unsymmetrical NO_2-donor aminoalcohol ligand. Both the homometallic complexes **1** and **2** have an unprecedented cyclic structure consisting of a central M^{II}_{12} single-stranded loop with four peripheral $[M_2(HL)(OAc)_2]$ fragments attached in an S_4 symmetrical fashion, or of four tetranuclear units of $[M_4L\text{-}(HL)(OAc)_7]^{2-}$ connected by four M^{2+} ions. Furthermore, by using equimolar amounts of Ni^{II} and M^{II} ions (M = Co, Cu), mixed-metal icosanuclear wheels of **3** and **4** were isolated. Interestingly, complex **3** involves nonstoichiometric amounts of Ni^{2+} and Co^{2+} (10.5/9.5) disordered at every metal position, and, in contrast, complex **4** has a stoichiometric formula of $Ni_{12}Cu_8$. The magnetic properties of **1** and **4** were measured to show their ferromagnetic exchange interactions, which are in contrast to the antiferromagnetic interactions for **2** and **3** with the incorporation of Co^{II} ions. The unsymmetrical aminoalcohol ligand has proven very useful for the organization of icosanuclear wheel-shaped homo- and heterometallic complexes, where the structure and magnetic properties are altered by varying the metal species.

■ EXPERIMENTAL SECTION

General Procedures. All chemicals were used as purchased, without further purification. ^1H and ^{13}C NMR spectra were recorded on a JEOL Lambda 500 spectrometer at 500 and 125 MHz, respectively. The chemical shifts were calibrated to TMS as an external reference. IR spectra were measured on KBr pellets with a JASCO FT/IR-410 spectrometer. Metal analysis was carried out on a Rigaku Supermini X-ray fluorescence spectrometer. Magnetic susceptibility measurements were performed using Quantum Design magnetometers PPMS-9 and MPMS-5S. The direct current (dc) measurements were carried out over the temperature range 2.0−300 K with a 5000 Oe dc field applied. Diamagnetic corrections for the samples were determined from Pascal's constants. The alternating current (ac) measurements were performed at various frequencies from 10 to 10000 Hz with an oscillating field amplitude of 3 Oe under zero dc field. Mass spectra were recorded on a JEOL JMS-GCmateII high-resolution mass spectrometer in FAB mode using an NBA matrix.

3-[Benzyl(2-hydroxyethyl)amino]-1-propanol (H_2L). A mixture of *N*-2-hydroxyethylbenzylamine (8.23 g, 60 mmol), 3-chloro-1-propanol (8.51 g, 90 mmol), and Na_2CO_3 (63.6 g, 600 mmol) in CH_3CN (300 mL) was heated at reflux for 7 d. The resultant solution was filtered and dried in vacuo. The residue was extracted with $CHCl_3$ and washed with water. The organic phase was then dried over $MgSO_4$, and the crude product was purified by silica gel column chromatography ($CHCl_3/CH_3OH$ = 9/1) to give the product in 49% yield (6.10 g). ^1H NMR (500 MHz, $CDCl_3$): δ 7.19−7.33 (5H, m), 3.65 (2H, t, *J* = 5.6 Hz), 3.61 (2H, t, *J* = 5.6 Hz), 3.59 (2H, s), 3.40 (2H, br), 2.64 (2H, t, *J* = 5.6 Hz), 2.59 (2H, t, *J* = 5.6 Hz), 1.69 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1, 128.6, 127.9, 126.7, 61.6, 58.9, 58.5, 55.0, 51.9, 28.3. MS calcd for $C_{12}H_{20}NO_2$ $[M + H]^+$: 210.1494; Found: 210.1495.

$[Ni_{20}L_4(HL)_4(OAc)_{28}]\cdot 4Et_2O\cdot 6MeCN$ ($1\cdot 4Et_2O\cdot 6MeCN$). A mixture of $Ni(OAc)_2\cdot 4H_2O$ (62 mg, 0.25 mmol), H_2L (52 mg, 0.25 mmol), and pyridine (39 mg, 0.5 mmol) in CH_3CN (15 mL) was stirred and heated at 60 °C for 4 h. The resulting solution was layered with diethyl ether to give lime crystals of $\mathbf{1}\cdot 4Et_2O\cdot 6MeCN$ (25 mg, 0.006 mmol, 45%). *Anal. Calcd.* for $C_{152}H_{224}N_8Ni_{20}O_{72}$: C, 40.67; H, 5.03; N, 2.50. Found: C, 40.51; H, 4.95; N, 2.41. Samples were dried under vacuum prior to elemental analysis and experimental data were consistent with the formula of $[Ni_{20}L_4(HL)_4(OAc)_{28}]$ without solvents. IR (KBr): ν 1598(s), 1558(s), 1464(m), 1412(s) cm^{-1}.

$[Co_{20}L_4(HL)_4(OAc)_{28}]\cdot 6Et_2O\cdot 6MeCN$ ($2\cdot 6Et_2O\cdot 6MeCN$). Portions of $Co(OAc)_2\cdot 4H_2O$ (125 mg, 0.50 mmol), H_2L (104 mg, 0.50 mmol), and NEt_3 (100 mg, 1.0 mmol) were stirred and heated in CH_3CN (15 mL) at 80 °C for 4 h. The resulting solution was layered with diethyl ether to afford purple crystals of $\mathbf{2}\cdot 6Et_2O\cdot 6MeCN$ (80 mg, 0.018 mmol, 72%). *Anal. Calcd.* for $C_{152}H_{224}N_8Co_{20}O_{72}$: C, 40.62; H, 5.02; N, 2.49. Found: C, 40.48; H, 5.01; N, 2.35. Samples were dried under vacuum prior to elemental analysis and experimental data were consistent with the formula of $[Co_{20}L_4(HL)_4(OAc)_{28}]$ without solvents. IR (KBr): ν 1577(s), 1417(s), 1340(m) cm^{-1}.

$[Ni_{9.5}Co_{10.5}L_4(HL)_4(OAc)_{28}]\cdot 5Et_2O\cdot 6MeCN$ ($3\cdot 5Et_2O\cdot 6MeCN$). A mixture of $Ni(OAc)_2\cdot 4H_2O$ (61 mg, 0.25 mmol), $Co(OAc)_2\cdot 4H_2O$ (62 mg, 0.25 mmol), H_2L (50 mg, 0.24 mmol), and pyridine (73 mg, 0.92 mmol) in CH_3CN (15 mL) was stirred and heated at 60 °C for 4 h. The resultant solution was crystallized from CH_3CN/Et_2O layered solvents to give purple crystals of $\mathbf{3}\cdot 5Et_2O\cdot 6MeCN$ (76 mg, 0.017 mmol, 81%). *Anal. Calcd.* for $C_{152}H_{224}Co_{10.5}N_8Ni_{9.5}O_{72}$: C, 40.64; H, 5.03; N, 2.49. Found: C, 40.32; H, 5.09; N, 2.47. Samples were dried under vacuum prior to elemental analysis, and experimental data were

Table 1. Crystallographic Data of Complexes **1**·$4Et_2O$·6MeCN, **2**·$6Et_2O$·6MeCN, **3**·$5Et_2O$·6MeCN, and **4**·$6Et_2O$

	1·$4Et_2O$·6MeCN	**2**·$6Et_2O$·6MeCN	**3**·$5Et_2O$·6MeCN	**4**·$6Et_2O$
formula	$C_{180}H_{282}N_{14}Ni_{20}O_{76}$	$C_{188}H_{302}N_{14}Co_{20}O_{78}$	$C_{184}H_{292}N_{14}Co_{10.5}Ni_{9.5}O_{77}$	$C_{164}H_{288}Cu_8N_8Ni_{12}O_{76}$
formula wt	5032.26	5185.16	5108.83	4800.86
cryst. syst	tetragonal	tetragonal	tetragonal	tetragonal
space group	$P4_2/n$	$P4_2/n$	$P4_2/n$	$I2_1/n$
a, Å	22.6978(6)	22.826(7)	22.724(11)	39.350(8)
c, Å	22.9284(8)	23.129(7)	22.778(12)	16.830(4)
V, Å^3	11812.5(6)	12051(6)	11762(11)	26060(10)
Z	2	2	2	4
temp, °C	−110	−120	−120	−120
D_{calcd}, g cm^{-1}	1.415	1.429	1.442	1.224
μ, mm^{-1} (Mo Kα)	1.632	1.417	1.541	1.550
2θ range, deg	6−55	6−55	6−55	6−55
R_{int}	0.026	0.031	0.044	0.058
no. of reflns collected	109303	108182	143364	157374
no. of unique reflns	13412	13468	13509	14957
no. of obsd reflns ($I > 2\sigma(I)$)	10168	11967	11858	12294
no. of variables	646	627	623	606
$R1^a$	0.052	0.048	0.066	0.064
$wR2^b$	0.146	0.140	0.207	0.195
GOF	1.138	1.092	1.072	1.094

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ (for obsd. refs with $I > 2\sigma(I)$). [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ (for all refs).

consistent with the formula of $[Ni_{9.5}Co_{10.5}L_4(HL)_4(OAc)_{28}]$ without solvents. IR (KBr): ν 1577(s), 1417(s), 1341(m), 1051(m), 669(m) cm^{-1}.

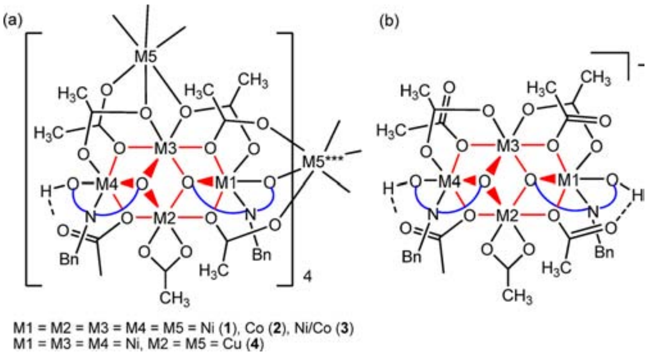
$[Ni_{12}Cu_8L_4(HL)_4(OAc)_{28}]$·$5CH_2Cl_2$ (4·$5CH_2Cl_2$). A mixture of $Ni(OAc)_2$·$4H_2O$ (125 mg, 0.50 mmol), $Cu(OAc)_2$·H_2O (100 mg, 0.50 mmol), H_2L (104 mg, 0.50 mmol), and NEt_3 (50 mg, 0.5 mmol) in CH_3CN (15 mL) was stirred at room temperature (r.t.) for 16 h. The solvent was removed to dryness under reduced pressure, and the residue was extracted with CH_2Cl_2, which was layered with diethyl ether to afford green crystals of **4**·$5CH_2Cl_2$ (80 mg, 0.018 mmol, 72%). *Anal. Calcd.* for $C_{157}H_{234}Cl_{10}Cu_8N_8Ni_{12}O_{72}$ ($[Ni_{12}Cu_8L_4(HL)_4(OAc)_{28}]$·$5CH_2Cl_2$): C, 38.07; H, 4.76; N, 2.26. Found: C, 38.10; H, 4.68; N, 2.35. IR (KBr): ν 1577(s), 1417(s), 1051(m), 669(m) cm^{-1}.

X-ray Crystallography. The crystals of **1**−**4** were quickly coated with Paratone N oil and mounted on top of a loop fiber at room temperature. The crystal and experimental data are summarized in Table 1. All data were collected at −110 °C (**1**) or −120 °C (**2**−**4**) on a Rigaku AFC8R/Mercury CCD diffractometer equipped with graphite-monochromated Mo Kα radiation using a rotating-anode X-ray generator (50 kV, 180 mA) and a Rigaku VariMax Mo/Saturn CCD diffractometer equipped with graphite-monochromated Mo Kα radiation using a rotating-anode X-ray generator (RA-Micro7, 50 kV, 24 mA). A total of 1440−2160 oscillation images, covering a whole sphere of 6° < 2θ < 55°, were collected by the ω-scan method. The crystal-to-detector (70 × 70 mm) distance was set at 45 or 60 mm. The data were processed using the Crystal Clear 1.3.5 program (Rigaku/MSC)[13] and corrected for Lorentz−polarization and absorption effects.[14] The structures of complexes were solved by direct methods with SHELXS-97[15] (**2**−**4**) and SIR-92[16] (**1**), and were refined on F^2 with full-matrix least-squares techniques with SHELXL-97[15] using the Crystal Structure 4.0 package[17] All non-hydrogen atoms were refined with anisotropic thermal parameters, and the C−H hydrogen atoms were calculated at ideal positions and refined with riding models. All calculations were carried out on a Windows PC running the Crystal Structure 4.0 package.[17]

■ RESULTS AND DISCUSSION

Synthesis and Structures of Homometallic Icosanuclear Complexes. When $M(OAc)_2$·$4H_2O$ (M = Ni, Co) was treated with 1 equiv of H_2L in the presence of pyridine for $Ni(OAc)_2$·$4H_2O$ or NEt_3 for $Co(OAc)_2$·$4H_2O$ in acetonitrile, cyclic icosanuclear complexes $[M_{20}L_4(HL)_4(OAc)_{28}]$ (M = Ni (**1**), Co (**2**)) were obtained in 45 and 72% yields, respectively (Scheme 2). The structures of **1** and **2** were determined by X-ray crystallography to be isomorphous with each other; ORTEP views of **1** and **2** are given in Figure 1a and Supporting Information, Figure S1a, respectively. Complexes **1** and **2** are the first icosanuclear and the third largest wheel-shaped nickel and cobalt complexes reported to date.[8,9,18] The molecules are disposed around a crystallographically imposed S_4 axis; the asymmetric unit contains a neutral unit of $\{[M_4L(HL)(OAc)_7]$-$M\}$ consisting of five independent metal ions (M1−M5) (Figure 1b and Supporting Information, Figure S1b, Scheme 2a). The unit involves two deprotonated aminoalcohol ligands L^{2-} and HL^- together with seven acetate anions; the O4 atom is revealed by X-ray crystallography to bear a proton making a hydrogen-bonding interaction with the acetate oxygen atom of O14 (O(4)···O(14) = 2.539(3) Å (**1**), 2.532(3) Å (**2**)). Charge-valence considerations suggested that all the metal ions are divalent. The wheel-shaped structures of **1** and **2** involve a

Scheme 2. Schematic Structures of 1, 2, 3, and 4



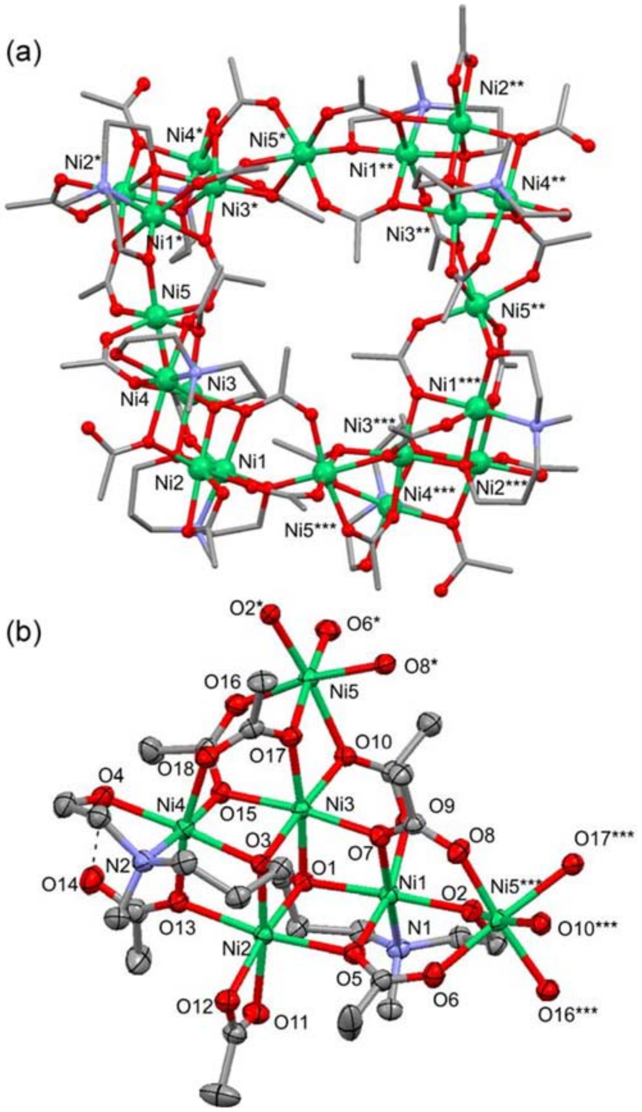


Figure 1. (a) Perspective diagram of **1**; Ni, O, and N atoms are drawn with arbitrary spheres and C atoms are illustrated by stick modes for clarity. Phenyl rings and hydrogen atoms are omitted for clarity. (b) ORTEP diagram for the asymmetric unit of **1** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40% probability level. Phenyl rings and hydrogen atoms are omitted for clarity. A hydrogen bond is shown as dashed line (O4−O14).

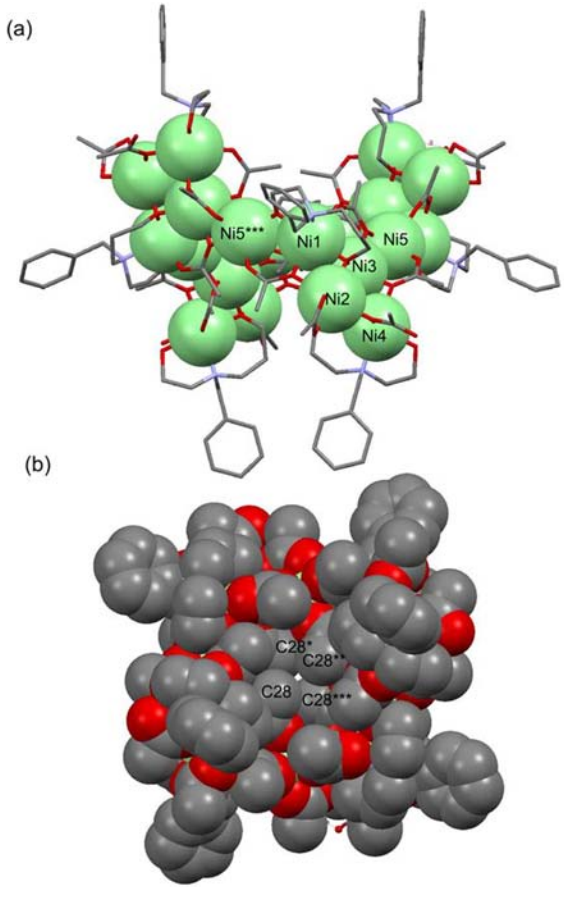


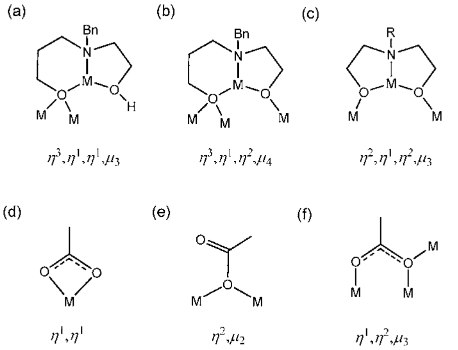
Figure 2. (a) Side view of **1** showing the saddle-like structure; Ni atoms (green) are drawn with space-filling model and O (red), N (blue), and C (gray) atoms are illustrated by stick modes for clarity. Hydrogen atoms are omitted for clarity. (b) Space-filling representation of **1** viewed perpendicular to the ring.

nearly planar M^{II}_{12} single-stranded loop (containing M1, M3, M5, and symmetry equivalents (s.e.)) to which four peripheral $[M_2(HL)(OAc)_2]$ fragments are attached (M2, M4, and s.e.) in an S_4 symmetrical fashion, resulting in a saddle-shaped conformation (Figure 2a). The M···M distances across the M_{12} loop vary from 10.4476(5) (Ni5···Ni5**) Å to 12.1095(5) (Ni1···Ni1**) Å and from 10.605(3) (Co5···Co5**) Å to 12.216(4) (Co1···Co1**) Å, indicating a wheel with a diameter of approximately 1 nm. The central cavities of **1** and **2** are mostly filled with four methyl groups (C28 and s.e.) of the acetate ligands (Figure 2b).

The structures of **1** and **2** can also be viewed as four tetranuclear fragments $[M_4L(HL)(OAc)_7]^{2-}$ (containing M1−M4) alternately connected by four M^{2+} ions (M5) via six O-donor atoms (Scheme 2). The tetranuclear unit comprises a plane-shared M_4O_6 incomplete double cubane, in which the M2 and M3 atoms are involved in the central fused plane and the M1 and M4 atoms are disposed at the apex sites. The M_4O_6 tetranuclear fragment itself is not unusual, and can be derived from an ideal C_2 symmetrical $[M_4(HL)_2(\mu\text{-}\eta^2\text{-OAc})_4(\mu\text{-}\eta^1,\eta^1\text{-OAc})_2(\eta^1,\eta^1\text{-OAc})]^-$ structure (Scheme 2b) through deprotonation of the HL^- ligand. The neighboring Ni···Ni distances (Ni1···Ni2 = 3.2396(6), Ni1···Ni3 = 2.9950(5), Ni1···Ni5*** = 3.3391(4), Ni2···Ni3 = 3.0671(6), Ni2···Ni4 = 3.2117(6), Ni3···Ni4 = 2.9536(6), Ni3···Ni5 = 3.1224(5) Å) are slightly shorter than the corresponding Co···Co distances (Co1···Co2 = 3.311(1), Co1···Co3 = 3.0373(9), Co1···Co5*** = 3.351(1), Co2···Co3 = 3.1182(9), Co2···Co4 = 3.269(1), Co3···Co4 = 3.0049(9), Co3···Co5 = 3.1790(9) Å); such a tendency is ascribable to the smaller ionic radius of Ni^{2+} (0.84 Å) than of high-spin Co^{2+} (0.88 Å), and is also observed in the case of isomorphous Ni_{12} and Co_{12} wheel-shaped complexes.[8a,9e]

All the metal centers in the complexes are six-coordinate with approximately octahedral geometry. The Ni1 and Ni4 atoms are bound to one N and five O atoms, and the Ni2, Ni3, and Ni5 atoms are ligated by six O atoms. The two aminoalcohol ligands exist as monodeprotonated HL^- and doubly deprotonated L^{2-} forms. The former supports three metal ions (M2, M3, M4) with the $\eta^3,\eta^1,\eta^1,\mu_3$-bridging mode (Scheme 3a); the deprotonated O3 atom triply bridges the M2, M3, and M4 atoms (Ni2−O3 = 2.030(2), Ni3−O3 = 2.068(2), Ni4−O3 = 2.009(2); Co2−O3 = 2.057(2), Co3−O3 = 2.155 (2), Co4−O3 = 2.030(2) Å), and the aminoethanol moiety (N2, O4)

Scheme 3. Coordination Modes of L^{2-} (a), LH^- (b), $\{RN(CH_2CH_2O)_2\}^{2-}$ (c), and Acetate Ligands (d)−(f)



chelates to the M4 center (Ni4−N2 = 2.104(3), Ni4−O4 = 2.075(3); Co4−N2 = 2.176(3), Co4−O4 = 2.091(3) Å). The latter L^{2-} ligand gathers four metal ions (M1, M2, M3, M5***) in the $\eta^3,\eta^1,\eta^2,\mu_4$-bridging mode (Scheme 3b). Both the alcohol groups are deprotonated with the O1 atom triply bridging the M1, M2, and M3 atoms (Ni1−O1 = 2.042(2), Ni2−O1 = 2.008(2), Ni3−O1 = 2.050(2); Co1−O1 = 2.073(2), Co2−O1 = 2.048 (2), Co3−O1 = 2.092 (2) Å) and the O2 atom bridging the M1 and M5*** atoms (Ni1−O(2) = 1.978(2), Ni5***−O2 = 1.954(2); Co1−O2 = 1.971(2), Co5***−O2 = 1.981(2) Å). The N1 atom is attached to the M1 center with Ni1−N1 = 2.137(3) and Co1−N1 = 2.195(3) Å. The unsymmetrical $\eta^3,\eta^1,\eta^1,\mu_3$- and $\eta^3,\eta^1,\eta^2,\mu_4$-bridging structures found in **1** and **2** are very rare with *N*-alkylated diethanolamine ligands,[9a] which are likely to act in the symmetric $\eta^2,\eta^1,\eta^2,\mu_3$-bridge of the doubly deprotonated forms (Scheme 3c).[6g−k,m,7b−e] These unusual coordination behaviors can be ascribed to the unsymmetrical hydroxyethyl and hydroxypropyl arms of H_2L, and may lead to the formation of high-nuclear wheel-shaped complexes.[19]

The seven acetate ligands adopt three different binding modes (Scheme 3d−f). One acetate ligand binds to Ni2 with the η^1,η^1-chelating mode (Ni2−O11 = 2.079(3), Ni2−O12 = 2.090(3); Co2−O11 = 2.123(3), Co2−O12 = 2.134(3) Å). Another acetate group adopts the η^2,μ_2-bridging mode between Ni2 and Ni4 via the O13 atom (Ni2−O13 = 2.175(3), Ni4−O13 = 2.091(2); Co2−O13 = 2.227(2), Co4−O13 = 2.142(2) Å). The remaining five acetate ligands bridge the M1/M2/M5***, M1/M3/M5***, M1/M3/M5, and M4/M3/M5 trinuclear sets in η^1,η^2,μ^3-fashion.

Synthesis and Structures of Heterometallic Icosanuclear Complexes. With the aim of synthesizing heterometallic wheel-shaped clusters, reactions were examined by using equimolar amounts of $Ni(OAc)_2{\cdot}4H_2O/Co(OAc)_2{\cdot}4H_2O$ and $Ni(OAc)_2{\cdot}4H_2O/Cu(OAc)_2{\cdot}H_2O$. Reaction of a 1:1 mixture of $Ni(OAc)_2{\cdot}4H_2O$ and $Co(OAc)_2{\cdot}4H_2O$ with H_2L in the presence of pyridine afforded single crystals of the bimetallic icosanuclear complex $[Ni_{9.5}Co_{10.5}L_4(HL)_4(OAc)_{28}]$ (**3**) in 81% yield. The ratio of Ni to Co ions was determined as 9.5:10.5 by X-ray fluorescence (XRF) analysis, and the structure of **3** was characterized by X-ray crystallography at −120 °C as being isomorphous with **1** and **2** (Supporting Information, Figure S2). Population analysis of the Ni^{2+} and Co^{2+} ions at the metal sites of M1−M5 indicated that all M sites are occupied by disordered populations, and in addition, the ratios of Ni and Co metal ions vary depending on the M sites (M1 = $Ni_{0.42}/Co_{0.58}$; M2 = $Ni_{0.24}/Co_{0.76}$; M3 = $Ni_{0.76}/Co_{0.24}$; M4 = $Ni_{0.69}/Co_{0.31}$; M5 = $Ni_{0.26}/Co_{0.74}$). On the whole, the populations of Co^{2+} ions are apt to be high at the M2 and M5 positions. The M−O/N bond lengths of **3** are, in most cases, between the corresponding values for **1** and **2** (Supporting Information, Table S1). These results suggested that the Ni^{2+} and Co^{2+} ions dispersed at more or less every metal site of **3** in a nonstoichiometric manner.

The similar reaction of equimolar amounts of $Ni(OAc)_2{\cdot}4H_2O$ (1 equiv) and $Cu(OAc)_2{\cdot}H_2O$ (1 equiv) with H_2L (1 equiv) in the presence of Et_3N in CH_3CN afforded a mixed-metal complex $[Ni_{12}Cu_8L_4(HL)_4(OAc)_{28}]$ (**4**) in 72% yield. Interestingly, complex **4** has a stoichiometric metal formula of $Ni_{12}Cu_8$, in striking contrast to the NiCo complex **3**. The solid-state structure of **4** (Figure 3 and Table 1) is very similar to that of **1**, with the Ni^{2+} ions at the M2 and M5 sites replaced by Cu^{2+} ions site-selectively, as clearly confirmed by X-ray crystallography in the light of the Jahn−Teller elongation around the Cu2 and Cu5 ions. The bond lengths of Cu2−O5 =

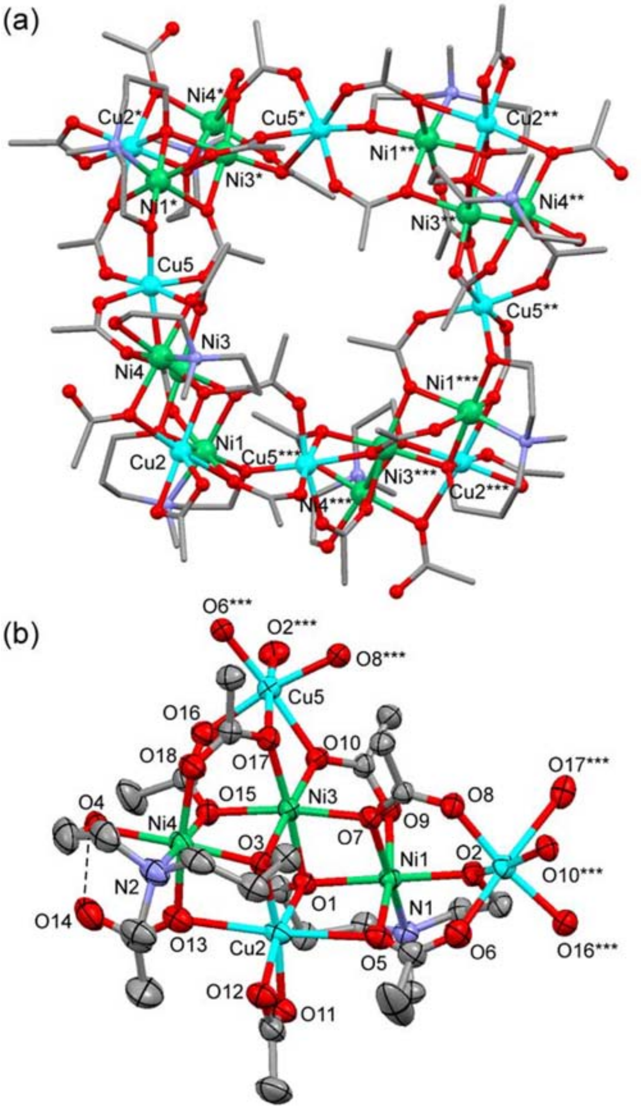


Figure 3. (a) Perspective diagram of **4**; Ni, Cu, O, and N atoms are drawn with arbitrary spheres and C atoms are illustrated by stick modes for clarity. (b) ORTEP diagram for the asymmetric unit of **2** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40% probability level. A hydrogen bond is shown as dashed line (O4−O14).

2.430(3), Cu2−O13 = 2.438(3), and Cu5−O17 = 2.384(3) Å are significantly longer by about 0.2 Å than the corresponding distances in **1** (Ni2−O5 = 2.196(2), Ni2−O13 = 2.175(3), Ni5−O17 = 2.196(2) Å), and the Cu2 and Cu5 metal centers are described, respectively, as having axially elongated four-coordinate square-planar geometry and five-coordinate square-pyramidal geometry rather than the six-coordinate octahedral structure. The octahedral geometries around the Ni1, Ni3, and Ni4 metal centers in **4** are retained, as found in **1**. The Ni−O/N bond lengths of **4** are comparable to the corresponding bond lengths of **1** (Supporting Information, Table S1). Although it is not clear why Cu ions are exclusively incorporated at the M2 and M5 sites, the site-selectivity of Cu^{2+} observed in **4** roughly coincides with the metal sites of **3** at which the populations of Co^{2+} ions are relatively high. Cu^{2+} and Co^{2+} ions have larger ionic radii than Ni^{2+} and are more likely to be distorted, which might explain the preference for Co^{2+} or Cu^{2+} ions to be located at the M2 and M5 sites. It is noteworthy that heterometallic wheel-shaped clusters are very scarce, and such structures containing more than 20 metal ions have not yet been reported,[12] and complex **4** is the largest 3d heterometal wheel and is one of only a few examples of NiCu heterometallic wheel-shaped complexes.[20]

Magnetic Properties. Temperature-dependent dc magnetic susceptibility data for complexes **1**−**4** were collected on polycrystalline samples in the temperature range 2−300 K (Figure 4). The $\chi_M T$ value of **1** at 300 K (27 cm^3 K mol^{-1}) is slightly higher than the spin-only value of 24.2 cm^3 K mol^{-1} calculated for 20 uncoupled Ni^{II} ions with an appropriate g value of 2.2. As the temperature is lowered below 50 K, the $\chi_M T$ value increases markedly and reaches a maximum value of 47.3 cm^3 K mol^{-1} at 4.5 K, then decreases rapidly upon further cooling to 2 K. The low-temperature increase in the $\chi_M T$ value is characteristic of ferromagnetic interactions within the cluster. The maximum value of 47.3 cm^3 K mol^{-1} at 4.5 K corresponds to a total spin of $S = 17/2$ (calculated value is 48.9 cm^3 K mol^{-1} with $g = 2.2$). The sudden drop at the lowest temperature is probably due to the effect of zero-field splitting or the presence of intermolecular antiferromagnetic interactions. Magnetization measurements for **1** were performed at 2 K under a dc field up to 9 T. The curve for reduced magnetization M versus H did not show clear saturation up to 9 T (Supporting Information, Figure S7), which is caused by the gradual population of closely lying, higher-energy states, and therefore, does not help to determine the spin ground state. The temperature dependence of the molar susceptibility in the range 50−250 K is well described by a Curie−Weiss term, $\chi = C/(T - \theta)$, with C = 25.2 cm^3 K mol^{-1} and θ = 11.2 K (Supporting Information, Figure S3), which is consistent with ferromagnetic coupling between the Ni^{II} ions.

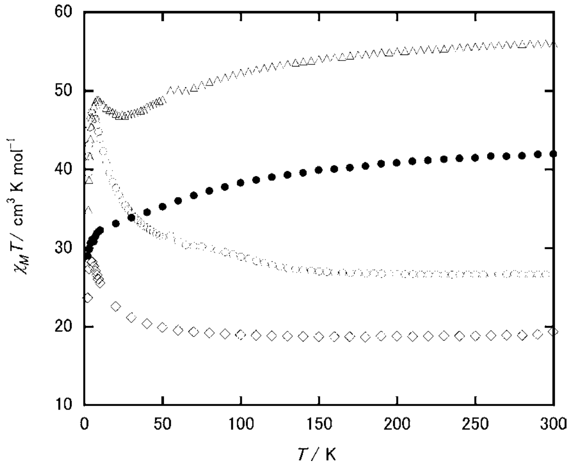


Figure 4. Plots of $\chi_M T$ versus T for complexes **1** (○), **2** (△), **3** (●), and **4** (◇).

The $\chi_M T$ product of **2** at 300 K (56.0 cm^3 K mol^{-1}) is significantly higher than the value calculated for 20 magnetically uncoupled Co^{II} ($S = 3/2$) centers with a g value of 2.0 (37.5 cm^3 K mol^{-1}). This is due to the large orbital contribution of Co^{II}, which is well-known to be significant for a Co^{II} ion located in an octahedral environment with the $^4T_{1g}$ ground state. A more realistic g value is in the range 2.4 to 2.6, which corresponds to $\chi_M T$ values ranging from 54.0 to 63.4, in close agreement with the experimental data. The continuous decrease in the $\chi_M T$ value below 50 K may be due to the depopulation among the Kramers doublets of $S_z = \pm 1/2$ and $\pm 3/2$ states caused by spin−orbit coupling in each Co^{II} ion.[21] The slight increase in the $\chi_M T$ value below 25 K may be due to ferromagnetic interactions between adjacent Co(II) ions within the cluster. A fit of the susceptibility data to the Curie−Weiss equation in the temperature range 50−250 K gives C = 2.89 cm^3 K mol^{-1} per Co^{II} and θ = −10.2 K (Supporting Information, Figure S4). The Curie constant is typical for high-spin octahedral Co^{II} ions[21] and comparable to those found in other high-nuclear Co complexes.[8e,22] The negative value of the Weiss constant may correlate to the spin−orbit coupling effect of Co^{II}.

The $\chi_M T$ value of **3** at 300 K is 42.0 cm^3 K mol^{-1}, which is in good agreement with the calculated spin-only value of 42.2 cm^3 K mol^{-1} for a molecule composed of 9.5 Ni^{II} ($S = 1$, $g = 2.2$) and 10.5 Co^{II} ($S = 3/2$, $g = 2.5$) noninteracting ions. The $\chi_M T$ value gradually decreases with decreasing temperature to reach a value of 29.0 cm^3 K mol^{-1} at 2 K. The data suggest that antiferromagnetic exchange interactions exist predominantly within the cluster, which is consistent with the negative value of the Weiss constant (θ = −12.8 K) obtained by the Curie−Weiss plot (Supporting Information, Figure S5). As for **4**, the $\chi_M T$ product of 19.4 cm^3 K mol^{-1} at 300 K is in good agreement with the spin-only value of 17.5 cm^3 K mol^{-1} calculated for uncoupled 12 Ni^{II} ($S = 1$, $g = 2.2$) and 8 Cu^{II} ions ($S = 1/2$, $g = 2$). Over the temperature range of 50−300 K, the $\chi_M T$ remains essentially constant. Upon further lowering of the temperature, the $\chi_M T$ increases gradually, and reaches a maximum value of 28.4 cm^3 K mol^{-1} at 4 K. The maximum $\chi_M T$ value corresponds to a total spin of $S = 7$ (calculated $\chi_M T$ value is 28.0 cm^3 K mol^{-1} with $g = 2$). Upon further lowering of the temperature, it drops sharply to a value of 23.6 cm^3 K mol^{-1} at 2 K. This type of magnetic behavior indicates the presence of dominant ferromagnetic interactions within the cluster. The data over the temperature range 30−250 K are fitted nicely to the Curie−Weiss equation with C = 19.1 cm^3 K mol^{-1} and θ = 1.1 K (Supporting Information, Figure S6). The positive value of the Weiss constant is consistent with ferromagnetic coupling between neighboring metal centers. In addition, the M versus H data at 2 K without obvious saturation ($M/N\beta$ = 23.5 at 9 T) indicate the presence of appreciable zero-field splitting, which should influence the thermal population at low temperatures (Supporting Information, Figure S9).

Variable-frequency ac magnetic susceptibility experiments for **1**−**4** were carried out at low temperatures down to 2 K

(Supporting Information, Figures S10−S13), and no signal of out-of-phase susceptibility suggested the absence of slow magnetic relaxation in **1**−**4**.

■ CONCLUSION

A novel class of icosanuclear wheel-shaped complexes $[M_{20}L_4(HL)_4(OAc)_{28}]$ (M = Ni (**1**), Co (**2**)), $[Ni_{9.5}Co_{10.5}L_4(HL)_4(OAc)_{28}]$ (**3**), and $[Cu_8Ni_{12}L_4(HL)_4(OAc)_{28}]$ (**4**) were synthesized by utilizing 3-[benzyl(2-hydroxyethyl)-amino]-1-popanol (H_2L). The icosanuclear wheels are composed of four tetranuclear units of M_4O_6 incomplete double cubanes connected by four M^{2+} ions in an alternate S_4 symmetrical fashion. The unsymmetrical bis-alcohol amine ligand with hydroxyethyl and hydroxypropyl arms has proven very suitable to support the M_{20} wheel aggregation in the unusual $\eta^3,\eta^1,\eta^1,\mu_3$- and $\eta^3,\eta^1,\eta^2,\mu_4$-bridging modes. In the thermodynamically stabilized structure, some nickel sites of **1** can be replaced by Co^{2+} or Cu^{2+} ion to afford the heterometallic icosanuclear complexes **3** and **4**. The site-selectivity or distribution preference for the heterometal depends on the nature of the heterometal ions. In spite of the lack of SMM behavior for the icosanuclear complexes, the dc magnetic property is delicately altered by changing the metal species from Ni_{20} to Co_{20}, $Ni_{9.5}Co_{10.5}$, and $Ni_{12}Cu_8$ arrays. The present results are useful for the development of systematic syntheses of homo- and heterometallic giant wheels with magnetically active 3d metal ions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables, figures, and CIF files giving the structural parameters of **1**−**4**, ORTEP diagrams of **2** and **3**, plots of the temperature dependence of χ_M^{-1} for **1**−**4**, plots of magnetization versus H for **1**, **3**, and **4**, ac magnetic susceptibility data of χ_M' and χ_M'' for **1**−**4**, and crystallographic data of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org..

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research and on Priority Area 2107 (no. 22108521, 24108727) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. T.N. is grateful to Tokuyama Science Foundation, Kurata Memorial Hitachi Science and Technology Foundation, and Nara Women's University for a research project grant.

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