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Four novel nanometer-sized cobalt azametallacrown complexes†

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Four nanometer-sized cobalt azametallacrowns, $[Co_6(C_8H_6N_3O_3)_6(CH_3OH)_6]\cdot 10CH_3OH\cdot 2H_2O$ (**1**), $[Co_6(C_8H_5N_2O_3)_6(CH_3OH)_6]\cdot 5CH_3OH\cdot 0.5H_2O$ (**2**), $[Co_6(C_9H_7N_2O_3)_6(CH_3OH)_6]\cdot 6CH_3OH$ (**3**), and $[Co_6(C_{10}H_9N_2O_3)_6(CH_3OH)_6]\cdot 7CH_3OH\cdot 2H_2O$ (**4**) have been synthesized by the self-assembly reaction of cobalt ions with *N*-substituted salicylhydrazide ligands. The cobalt atoms in the four azametallacrowns adopt a propeller configuration. The chiralities of the cobalt atoms alternate between the Λ and Δ forms. In **1**, there are two encapsulated methanol solvent molecules in the 'host' cavity of the azametallacrown molecule, whereas in **2**–**4** there are no guest molecules in the 'host' cavities of the azametallacrowns.

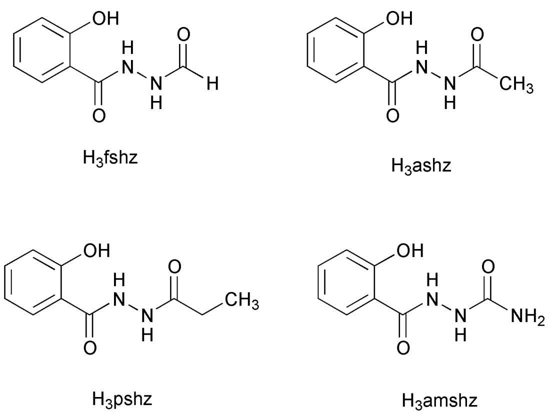
Introduction

Metallacrowns are among the first of a new class of molecule known as metallamacrocycles. Metallamacrocycles form cyclic structures as a consequence of key metal–heteroatom bonds that enforce a molecular architecture related to previously realized organic compounds. Interest in the metallacrowns stems not only from their high symmetry and aesthetic molecular frameworks, but also from the special magnetic properties associated with them.[1,2] The study of crown ethers and metallacrowns has, in fact, given rise to a new branch of chemistry known as "host–guest" or supramolecular chemistry.[3] Metallacrowns with a $[M–N–O]_n$ repeat unit have been reported,[4–17] utilizing hydroxamic acid ligands such as salicylhydroxamic acid (H_3shi) and β-alanine hydroxamic acid (H_2β-aha). A manganese 18-metallacrown-6 with a $[M–N–N]_n$ repeat unit has been prepared.[18] Recently, we have succeeded in synthesizing the first two manganese/iron 30-azametallacrowns-10,[19] several 24-azametallacrowns-8,[20] and 18-azametallacrowns-6,[20] in which cyclic structure is formed by linkage of $[M–N–N]_n$ repeat units. A few compounds with the metallacrown structure type have also been developed.[21] In this study, we expanded the core ring metal ions in the hexanuclear azametallacrowns from manganese to octahedral cobalt. We have synthesized and characterized a series of ligands H_3amshz (*N*-acylaminosalicylhydrazidate), H_3fshz (*N*-formylsalicylhydrazidate), H_3ashz (*N*-acetylsalicylhydrazidate), H_3psha (*N*-propionylsalicylhydrazidate) (Scheme 1) and the cobalt azametallacrowns $[Co_6(amshz)_6(CH_3OH)_6]\cdot 10CH_3OH\cdot 2H_2O$ (**1**), $[Co_6(fshz)_6(CH_3OH)_6]\cdot 5CH_3OH\cdot 0.5H_2O$ (**2**), $[Co_6(ashz)_6(CH_3OH)_6]\cdot 6CH_3OH$ (**3**), and $[Co_6(pshz)_6(CH_3OH)_6]\cdot 7CH_3OH\cdot 2H_2O$ (**4**) with *N*-substituted-salicylhydrazide ligands.

Experimental

Materials

All analytical grade chemicals and solvents were purchased commercially and used without further purification.



H_3fshz H_3ashz H_3pshz H_3amshz

Scheme 1 Ligands H_3amshz, H_3fshz, H_3ashz, and H_3pshz.

Physical measurements

Infrared spectra were measured on a Perkin-Elmer FT-IR 2000 spectrometer from KBr pellets in the 4000–400 cm^{-1} region. Electronic spectra were measured on a Perkin-Elmer λ 9 UV-vis-near IR spectrometer in CH_3OH solution and in the 200–700 nm range. The magnetic susceptibility data were obtained using a Quantum Design PPMS 6000 magnetometer in the temperature range 4 to 275 K at an applied magnetic field of 10 kG, whereby the diamagnetic contributions were estimated from Pascal's constants.

Preparations

Synthesis of ligand H_3amshz. Sodium cyanate (2.57 g, 39.5 mmol), glacial acetic acid (5 mL), and a solution of salicylhydrazide (5.0 g, 32.9 mmol) in chloroform (72 mL) were stirred at 0 °C for 4 h. A white precipitate was obtained after slowly warming the solution up to room temperature. This was filtered off and rinsed with chloroform and diethyl ether and dried at 120 °C in an oven (yield 4.7 g, 73.3%), mp: 179–181 °C. Anal. calc. for H_3amshz ($C_8H_9N_3O_3$): C, 49.23; H, 4.65; N, 21.53; found: C, 49.40; H, 4.52; N, 21.45%. IR (KBr pellet, cm^{-1}): 3409(s), 3290(s), 3232(s), 3169(s), 3055(s), 1677(s), 1638(s), 1600(s), 1534(s), 1497(s), 1457 (m), 1319 (m), 1263 (m), 752 (s), 532(m).

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† Electronic supplementary information (ESI) available: space filling diagrams of compounds **1** (Fig. S1) and **3** (Fig. S2). See http://www.rsc.org/suppdata/dt/b1/b109517j/

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Synthesis of ligand H_3fshz. This ligand was synthesized according to ref. 18 with the following improvements. Benzoyl chloride (3.91 mL, 33.4 mmol) was added to a solution of formic acid (1.31 mL, 33.4 mmol) and triethylamine (4.66 mL, 33.4 mL) in chloroform (60 mL) at 0 °C. The reaction mixture was slowly warmed to 25 °C. Upon addition of salicylhydrazide (4.238 g, 27.9 mmol) a white suspension was obtained. This was filtered and the solid rinsed with chloroform and diethyl ether (yield 4.568 g, 91.0%), mp 171–172 °C.

Synthesis of ligand H_3ashz. Acetic anhydride (3.41 g, 33.4 mmol) and salicylhydrazide (4.24 g, 27.9 mmol) were added to chloroform (60 mL) at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 4 h, then left overnight in a refrigerator (*ca.* 5 °C). The resulting white precipitate was filtered off and rinsed with chloroform and diethyl ether (yield 5.1 g, 95.0%), mp 179–181 °C. Anal. calc. for H_3ashz ($C_9H_{10}N_2O_3$): C, 55.67; H, 5.15; N, 14.43; found: C, 55.82; H, 5.06; N, 14.28%. IR (KBr pellet, cm^{-1}): 3319(s), 3196(s), 3040(s), 2963(s), 2870(s), 1671(s), 1632(s), 1606(s), 1527(s), 1490(s), 1457 (m), 1369 (m), 1311(m), 1255(m), 1236(s), 748(s), 520(m).

Synthesis of ligand H_3pshz. Benzoyl chloride (3.91 mL, 33.4 mmol) was added to a solution of propionic acid (2.73 mL, 33.4 mmol) and triethylamine (4.66 mL, 33.4 mmol) in 60 mL of chloroform at 0 °C. The reaction mixture was then slowly warmed to room temperature. When salicylhydrazide (4.238 g, 27.9 mmol) was added to the reaction mixture, a white suspension was obtained. The resulting suspension was filtered off and rinsed with chloroform and diethyl ether (yield 1.8 g, 27.2%), mp 150~153 °C. Anal. calc. for H_3pshz ($C_{10}H_{12}N_2O_3$): C, 57.69; H, 5.77; N, 13.46; found: C, 57.86; H, 5.63; N, 13.25%. IR (KBr pellet, cm^{-1}): 3305(s), 3057(s), 2975(s), 2935(s), 2873(s), 1675(s), 1640(s), 1607(s), 1544(s), 1484(s), 1456(s), 1416(m), 1380(s), 1311(m), 1261(m), 1237(s), 754(s), 525(m).

Synthesis of $[Co_6(amshz)_6(CH_3OH)_6]\cdot10CH_3OH\cdot2H_2O$ (1). Diacetylacetonato cobalt (29.3 mg, 0.1 mmol) was dissolved in 10 mL of methanol and H_3amsha (9.5mg, 0.1 mmol) was dissolved in 10 mL of methanol in another flask. The two solutions were mixed and stirred for 5 min. A dark violet–red solution was obtained and then filtered. After the filtrate had stood for 4 days in air, at room temperature, the dark brown rectangular crystals which had formed were separated out (yield 20.6 mg, 60.1%). Anal. calc. for $[Co_6(amshz)_6(CH_3OH)_6]\cdot10CH_3OH\cdot2H_2O$ ($Co_6C_{64}H_{104}N_{18}O_{36}$): C, 37.40; H, 5.10; N, 12.27; O, 28.03; found: C, 36.53; H, 3.94; N, 13.08; O, 28.89%. IR (KBr pellet, cm^{-1}): 3461(s), 3340(s), 1618(s), 1555(s), 1519(s), 1472 (m), 1432(m), 1398 (s), 1318 (m), 1241(m), 753(m), 621(m), 583(m), 446(m). UV-Vis (λ/nm): 204(m), 246(w), 278(s), 356(m), 496(vw).

Synthesis of $[Co_6(fshz)_6(CH_3OH)_6]\cdot5CH_3OH\cdot0.5H_2O$ (2). H_3fshz (0.180 g, 1.0 mmol) was dissolved in 20 mL of methanol and cobalt nitrate hexahydrate (0.291g, 1.0 mmol) was dissolved in 20 mL of methanol in another flask. The two solutions were mixed and stirred and the colour of the mixture changed to dark violet–red. After the filtrate had stood for 4 days in air, at room temperature, the quite air-sensitive dark violet–red rectangular crystals which had formed were separated out. The yield of the title compound was approximately 67% based on cobalt. Anal. calc. for $[Co_6(fshz)_6(CH_3OH)_6]\cdot5CH_3OH\cdot0.5H_2O$ ($C_{59}H_{75}Co_6N_{12}O_{29.5}$): C, 39.86; H, 4.25; N, 9.46; O, 26.55; found: C, 39.86; H, 4.06; N, 9.32; O, 26.40%. IR (KBr pellet, cm^{-1}): 1649(s), 1609(s), 1556(s), 1522(s), 1491 (m), 1377 (s), 1316 (m), 1259(m), 1229(m), 749(m), 641(m), 578(m), 524(m), 446(m). UV-Vis (λ/nm): 201(m), 241(w), 276(s), 350(m), 498(w).

Synthesis of $[Co_6(ashz)_6(CH_3OH)_6]\cdot6CH_3OH$ (3). H_3ashz (0.097 g, 0.5 mmol) was dissolved in 10 mL of DMF and triacetylacetonato cobalt (0.176 g, 0.5 mmol) was dissolved in 10 mL of DMF in another flask. The two solutions were mixed and stirred. The colour of the mixture changed to dark green and was then filtered. After the filtrate had stood for 2 days in air, at room temperature, the quite air-sensitive black–brown rhombohedral crystals which had formed were separated out. The yield of the title compound was approximately 64% based on cobalt. Anal. calc. for $[Co_6(ashz)_6(CH_3OH)_6]\cdot6CH_3OH$ ($C_{66}H_{90}Co_6N_{12}O_{30}$): C, 42.05; H, 4.81; N, 8.92; O, 25.46; found: C, 41.81; H, 4.50; N, 8.74; O, 25.60%. IR (KBr pellet, cm^{-1}): 2972(s), 2825(s), 1662(s), 1602(s), 1512(s), 1563(s), 1472(m), 1408(m), 1390(s), 1256(m), 760(m), 664(m), 628(m), 589(m), 446(m). UV-Vis (λ/nm): 203(m), 246(w), 289(s), 325(m), 498(w).

Synthesis of $[Co_6(pshz)_6(CH_3OH)_6]\cdot7CH_3OH\cdot2H_2O$ (4). H_3psha (41.6 mg, 0.20 mmol) was dissolved in methanol (5 mL) and methylene chloride (5 mL) and triacetylacetonato cobalt (58.6 mg, 0.20 mmol) was dissolved in methanol (10 mL) in another flask. The two solutions were mixed and stirred. The light pink solution obtained was then filtered. After the filtrate had stood for one day in air, at room temperature, the red–brown rhombohedral crystals which had formed were separated out. The yield of the title compound was approximately 62% based on Cobalt. Anal. calc. for $[Co_6(pshz)_6(CH_3OH)_6]\cdot7CH_3OH\cdot2H_2O$ ($C_{73}H_{110}Co_6N_{12}O_{33}$): C, 43.03; H, 5.44; N, 8.25; O, 25.92; found: C, 42.03; H, 4.24; N, 9.26; O, 27.17%. IR (KBr pellet, cm^{-1}): 2976(s), 2930(s), 2871(s), 1657(s), 1602(s), 1564(s), 1468(s), 1406(m), 1392(s), 1245(m), 759(m), 586(m), 446(m). UV-Vis (λ/nm): 205(m), 249(w), 306(s), 344(m), 500(w).

Crystal structure determination

Suitable crystals of the four title compounds were mounted in glass capillaries with the mother liquor to prevent the loss of structural solvents during data collection. The diffraction intensities were collected with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and the ω scan mode, using a Siemens Smart CCD 1000 area-detector diffractometer for **1**, **3**, and **4**, and a Rigaku R-AXIS RAPID Weissengberg IP diffractometer for **2**. The structures were solved by direct methods using SHELXS-86[22] and refined by full-matrix least-squares calculations with SHELXL-97.[23] All non-hydrogen atoms were refined with anisotropic thermal parameters. Most of the hydrogen atoms were located in calculated positions and/or in positions found from difference Fourier maps. The crystallographic data are collected in Table 1.

CCDC reference numbers 141232, 157263, 157264 and 172706.

See http://www.rsc.org/suppdata/dt/b1/b109517j/ for crystallographic data in CIF or other electronic format.

Results and discussion

Spectroscopy and magnetic properties

The IR spectra of the ligands show stretching bands at 1650–1680, 3050–3268, and *ca.* 3300 cm^{-1}, which attributed to C=O, PhO–H (phenolic, including intramolecular and intermolecular hydrogen bonding) and N–H bonds, respectively.[24] In addition, the strong bands found at 3340 and 3461 cm^{-1} in the spectrum of H_3amshz are assigned to the asymmetric and symmetric stretching bands of the NH_2 group, respectively. The infrared spectra for compounds **1**–**4** are quite similar. The absence of the N–H and C=O stretching vibration bands is consistent with the deprotonation of the CONH groups and coordination to the metal ions. This is confirmed by the bands at 583–699 cm^{-1}, attributed to M–O linkages (phenolic and enolic oxygen), and

Table 1 Summary of crystallographic data for $[Co_6(amshz)_6(CH_3OH)_6]\cdot10CH_3OH\cdot2H_2O$ (**1**), $[Co_6(fshz)_6(CH_3OH)_6]\cdot5CH_3OH\cdot0.5H_2O$ (**2**), $[Co_6(ashz)_6(CH_3OH)_6]\cdot6CH_3OH$ (**3**), and $[Co_6(pshz)_6(CH_3OH)_6]\cdot7CH_3OH\cdot2H_2O$ (**4**)

Complex	**1**	**2**	**3**	**4**
Formula	$C_{64}H_{104}Co_6N_{18}O_{36}$	$C_{59}H_{75}Co_6N_{12}O_{29.5}$	$C_{66}H_{90}Co_6N_{12}O_{30}$	$C_{73}H_{110}Co_6N_{12}O_{33}$
Formula weight	2055.23	1777.89	1885.08	2037.31
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	11.510(3)	10.157(2)	13.265(2)	11.7567(7)
b/Å	13.970(3)	13.025(3)	19.280(2)	14.4971(8)
c/Å	15.748(6)	14.969(5)	16.266(2)	16.4840(9)
α/°	111.40(2)	85.22(2)	90	65.149(1)
β/°	90.63(3)	85.60(2)	108.264(3)	73.935(1)
γ/°	105.62(2)	68.24(2)	90	74.937(1)
V/Å	2254(1)	1830.5(8)	3950.4(7)	2416.4(2)
Z	1	1	2	1
T/K	296(2)	293(2)	293(2)	296(2)
μ/mm^{-1}	1.171	1.418	1.321	1.089
R_{int}	0.0339	0.0360	0.0561	0.0535
Total reflections measured	11802	8892	8944	12760
No. of independent reflections	7868	6032	8944	8419
No. of observed reflections	4838	3600	5776	4419
R_1[a]	0.0499	0.0620	0.0472	0.0918
wR_2[b]	0.1237	0.1685	0.1305	0.2150

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/[\Sigma\, w(F_o^2)^2]\}^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) for **1**

Co(1)–O(1)	1.869(4)	Co(1)–O(3)	1.913(3)
Co(1)–O(6)	1.896(3)	Co(1)–N(1)	1.846(4)
Co(1)–O(4)	1.932(4)	Co(1)–N(5)	1.900(4)
N(1)–N(2)	1.423(5)	Co(1)–Co(2)	4.460(2)[a]
Co(1)–Co(1A)[b]	8.768(3)[c]		
O(1)–Co(1)–O(3)	177.5(2)	O(1)–Co(1)–O(6)	91.2(2)
O(1)–Co(1)–N(1)	94.3(2)	O(1)–Co(1)–O(4)	90.3(2)
O(1)–Co(1)–N(5)	91.2(2)	O(3)–Co(1)–O(6)	91.2(2)
O(3)–Co(1)–N(1)	83.3(2)	O(3)–Co(1)–O(4)	89.5(2)
O(3)–Co(1)–N(5)	89.4(2)	N(1)–Co(1)–O(6)	174.1(2)
N(1)–Co(1)–N(5)	98.3(2)	N(1)–Co(1)–O(4)	89.7(2)
O(6)–Co(1)–N(5)	83.9(2)	O(6)–Co(1)–O(4)	87.9(2)
N(5)–Co(1)–O(4)	171.7(2)	Co(1)–Co(2)–Co(3)	115.60(3)[d]

[a] This is an average of the Co(1)–Co(2), Co(2)–Co(3), and Co(3)–Co(1a) interatomic distances. [b] Symmetry code: (A) $-x + 1, -y, -z$. [c] This is an average value of the Co(1)–Co(1a), Co(2)–Co(2a), and Co(3)–Co(3a) interatomic distances. [d] This is an average of the Co(1)–Co(2)–Co(3), Co(2)–Co(3)–Co(1a), and Co(3)–Co(1a)–Co(2a) interatomic angles.

the bands at 410–600 cm^{-1} assigned to M–N linkages.[25] The >C=N–N=C< framework absorption band is found at *ca.* 1603 cm^{-1}.[24,26] The bands at *ca.* 1410 and 1560 cm^{-1} are assigned to ν(C=N) and ν(CO).[27]

The electronic spectra recorded in methanol for the four title compounds are also quite similar, displaying absorption peaks at 204, 240–250, 270–350 and 490–505 nm . The bands at 204 and *ca.* 230 nm can be attributed to internal ligand π–π* or n–π* transitions of the benzene rings and π conjugation. The absorption maxima at *ca.* 300 nm can be assigned to metal to ligand M(dπ) ⟶ O(π) charge transfer (MLCT) transitions. The d–d transition of the cobalt(III) ion in the ligand field is observed at 498 nm.

Variable temperature magnetic susceptibility measurements (4–275 K) for complex **3** indicate that $[Co_6(ashz)_6(CH_3OH)_6]\cdot6CH_3OH$ is diamagnetic. This shows that there are six d electrons of Co^{III} filling the three t_{2g} orbitals, paired due to the strong field and low-spin state. This is also associated with ideal octahedral coordination of the Co(III) ion and with good planarity of three least-squares planes around the Co(III), shown by the crystal structure analysis.

Structures

$[Co_6(amshz)_6(CH_3OH)_6]\cdot10CH_3OH\cdot2H_2O$ (1). The structural representation of the hexanuclear azametallacrown molecule is shown in Fig. 1, selected bond distances and angles are given in Table 2. Six Co(III) ions and six *N*-acylaminosalicylhydrazidate (amsz^{3-}) ligands construct a planar 18-membered ring based on the M–N–N–M linkage. One of the characteristics of the azametallacrown ring with a $[Co–N–N]_6$ repeat unit is that the Co–N–N–Co torsion angles are in the range 174.45–176.65° and the N–Co–N–N torsion angles alternate between 82.74–83.80 and 166.53–168.11°.

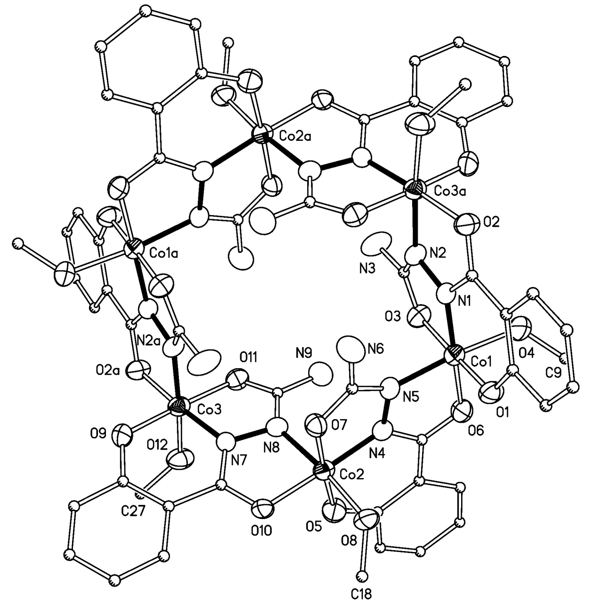

Fig. 1 Molecular structure of complex **1**, showing the atom numbering, with 50% probability displacement ellipsoids.

The azametallacrown molecule has non-crystallographic pseudo-C_{3i} symmetry and is in the crystallographic inversion centre. The neighbouring Co ··· Co interatomic distances are 4.454(2)–4.464(2) Å. The Co ··· Co ··· Co interatomic angles in the 18-membered core ring range from 115.07(3) to 116.48(3)°. These values are quite close to value for the interior angles in an n-hexagon (120°). This was also observed in some 18-azametallacrowns-6, for example, the Fe ··· Fe ··· Fe interatomic angles range from 111.73(4) to 121.42(4)° in $[Fe_6(C_9H_6ClN_2O_3)_6(CH_3OH)_6]\cdot6CH_3OH\cdot3H_2O$[20] and the Mn ··· Mn ··· Mn interatomic angles range from 107.20(1) to 115.57(1)° in $[Mn_6(C_9H_7N_2O_3)_6(C_3H_7NO)_6]\cdot3C_3H_7NO$.[20]

Table 3 Hydrogen bond geometry in complex **1** (Å, °)[a]

D–H ··· A	D–H	H ··· A	D ··· A	D–H ··· A
N3–H(03A) ··· N(7a)	0.86	2.32	3.036(6)	141
N6–H(06A) ··· N(1)	0.86	2.31	3.030(6)	141
N9–H(09B) ··· N(4)	0.86	2.33	3.042(6)	141
N6–H(06B) ··· O(16a)	0.86	2.23	3.056(6)	161
N9–H(09A) ··· O(16)	0.86	2.27	3.099(6)	164
O(4)–H(44A) ··· O(15)	0.96	1.76	2.546(6)	136
O(8)–H(48A) ··· O(13b)	1.13	1.55	2.618(6)	155
O(12)–H(52A) ··· O(14c)	1.03	1.57	2.564(6)	160
O(13)–H(53A) ··· O(1d)	1.00	1.67	2.664(5)	170
O(14)–H(54A) ··· O(5c)	1.05	1.73	2.725(6)	157
O(15)–H(55A) ··· O(9a)	1.00	1.68	2.681(6)	177
O(16)–H(56A) ··· O(17)	1.00	1.71	2.69(1)	163
O(17)–H(57A) ··· O(7d)	0.98	2.08	3.044(9)	167

[a] Symmetry codes: (a) $-x + 1, -y, -z$; (b) $x + 1, y, z$; (c) $-x + 1, -y + 1, -z$; (d) $x - 1, y, z$.

The flexibility around the N–N single bond and the conformational adaptability of the pentadentate ligand allow for the formation of the multinuclear complex and for the propeller configuration of the cobalt(III) ions. The chiralities of the cobalt atoms alternate between the Λ and Δ forms.[18–20a] The three methanol molecules coordinated at the Co centres with the Λ configuration are in one face of the azametallacrown and the remaining three methanol molecules coordinated at the other Co centres with the Δ configuration are in the other face of the azametallacrown. The two faces of each azametallacrown have opposite chiralities.

The peripheral diameter of the core ring in $[Co_6(amshz)_6(CH_3OH)_6]\cdot 10CH_3OH\cdot 2H_2O$ (**1**), measured between the opposite carbon atoms (C23–C23A, plus 0.77 Å for the van der Waals radius of carbon), is 18.63 Å. The approximate dimensions of the oval-shaped cavity are about 4.74 Å internal diameter at the entrance, measured between the opposite nitrogen atoms (N6–N6A, less 0.70 Å for the van der Waals radius of nitrogen), about 6.30 Å in diameter, measured between the opposite cobalt atoms (Co3–Co3a, less 1.25 Å for the van der Waals radius of cobalt), at its widest point, and about 3.52 Å in depth.

The cobalt(III) ion has an octahedral configuration of the Co(ONO)(NO)(O) type. The equatorial plane is formed by a phenolate oxygen [O(1)], a diazine nitrogen [N(1)], an acyl oxygen [O(3)] of a trianionic pentadentate ligand, and an acyl oxygen [O(6)] of an adjacent trianionic ligand. The atom O(4) of a coordinated neutral methanol molecule lies *trans* to the diazine nitrogen N(5) of the adjacent trianionic ligand. The bond distances Co–N(diazine), Co–O(phenolate), and Co–O(acyl) are in the ranges 1.841–1.852, 1.862–1.869, and 1.907–1.913 Å, respectively. The Co(III)–O(CH_3OH) bond distances in complex **1** range from 1.932 to 1.967 Å.

A remarkable structural feature in $[Co_6(amshz)_6(CH_3OH)_6]\cdot 10CH_3OH\cdot 2H_2O$ **1** is that two of the solvent methanol molecules, C(31)H_3OH and C(32)H_3OH, are encapsulated into the cobalt azametallacrown cavity (Fig. S1, ESI). These two solvent molecules are not only connected with each other through hydrogen bonds, but also bound to carbonyl oxygen atoms from the ligands through hydrogen bonds (Table 3). There are also other intramolecular and intermolecular hydrogen bonds in **1**. They are between the N–H of the terminal NH_2 group and the diazine N atom or the oxygen atom of a solvent methanol molecule, between the O–H of coordinated methanol molecules and the oxygen atom of solvent methanol molecules, and between the O–H of solvent methanol molecules and phenol oxygen atoms.

Table 4 Selected bond lengths (Å) and angles (°) for **2**

Co(1)–O(1)	1.879(5)	Co(1)–O(3)	1.916(5)
Co(1)–O(6)	1.920(5)	Co(1)–N(1)	1.851(6)
Co(1)–O(4)	1.955(5)	Co(1)–N(4)	1.875(6)
N(1)–N(2)	1.400(7)	Co(1)–Co(2)	4.435(2)[a]
Co(1)–Co(1A)[b]	8.634(3)[c]		
O(1)–Co(1)–O(3)	176.6(2)	O(1)–Co(1)–O(6)	90.6(2)
O(1)–Co(1)–N(1)	93.5(2)	O(1)–Co(1)–O(4)	90.6(2)
O(1)–Co(1)–N(4)	91.1(2)	O(3)–Co(1)–O(6)	92.8(2)
O(3)–Co(1)–N(1)	83.2(2)	O(3)–Co(1)–O(4)	88.5(2)
O(3)–Co(1)–N(4)	90.1(2)	N(1)–Co(1)–O(6)	175.4(2)
N(1)–Co(1)–N(4)	93.9(2)	N(1)–Co(1)–O(4)	91.4(3)
O(6)–Co(1)–N(4)	83.9(2)	O(6)–Co(1)–O(4)	90.8(2)
N(4)–Co(1)–O(4)	174.4(2)	Co(1)–Co(2)–Co(3)	108.40(3)[d]

[a] This is an average of the Co(1)–Co(2), Co(2)–Co(3), and Co(3)–Co(1a) interatomic distances. [b] Symmetry code: (A) $-x + 1, -y, -z$. [c] This is an average of the Co(1)–Co(1a), Co(2)–Co(2a), and Co(3)–Co(3a) interatomic distances. [d] This is an average of the Co(1)–Co(2)–Co(3), Co(2)–Co(3)–Co(1a), and Co(3)–Co(1a)–Co(2a) interatomic angles.

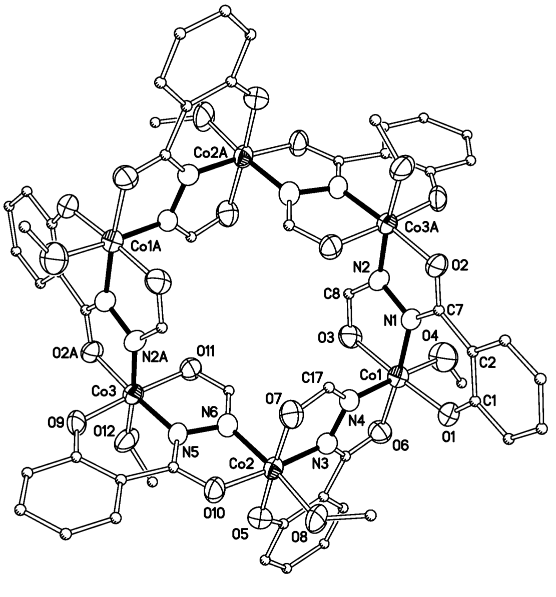

Fig. 2 Molecular structure of complex **2**, showing the atom numbering, with 50% probability displacement ellipsoids.

$[Co_6(fshz)_6(CH_3OH)_6]\cdot 5CH_3OH\cdot 0.5H_2O$ 2. The molecular structure of the complex **2** is illustrated in Fig. 2, selected bond distances and angles are listed in Table 4. The structure of complex **2** is similar to that of **1**. The azametallcrown molecule lies on a crystallographic inversion center at (1/2, 0, 0). The azametallacrown core ring is a hexanuclear ring of six cobalt ions linked by six hydrazide N–N groups of the six *N*-acetylsalicylhydrazide ($ashz^{3-}$) ligands, the core ring has Co–N–N–Co torsion angles of 171.47–179.43° and N–Co–N–N torsion angles alternating between 86.07–89.55° and 174.81–178.09°. The neighbouring Co ··· Co interatomic distances in the 18-membered core ring are 4.432(2)–4.436(2) Å. The Co ··· Co ··· Co interatomic angles range from 106.00(3) to

Table 5 Hydrogen bond geometry (Å, °) in **2**[a]

D–H ··· A	D–H	H ··· A	D ··· A	D–H ··· A
O(8)–H(08) ··· O(13)	0.99	1.76	2.699(9)	157
O(12)–(012) ··· O(9A)	1.00	1.64	2.626(7)	168
O(1) ··· O(13B)[b]			2.857(8)	

[a] Symmetry codes: (A) $1 - x, 1 - y, -z$; (B) $1 - x, -y, 1 - z$. [b] Not all hydrogen atoms were found in the refinement of the crystal structure. According to the O(1)–O(13B) distance, there may be an intermolecular hydrogen bond between O(1) and O(13B).

Table 6 Selected bond lengths (Å) and angles (°) for **3**

Co(1)–O(1)	1.870(3)	Co(1)–O(3)	1.895(3)
Co(1)–O(6)	1.895(3)	Co(1)–N(1)	1.849(3)
Co(1)–O(4)	1.945(3)	Co(1)–N(4)	1.909(3)
N(1)–N(2)	1.417(4)	Co(1)–Co(2)	4.4768(8)[a]
Co(1)–Co(1A)[b]	8.824(1)[c]		
O(1)–Co(1)–O(3)	177.1(1)	O(1)–Co(1)–O(6)	91.6(1)
O(1)–Co(1)–N(1)	94.1(1)	O(1)–Co(1)–O(4)	89.4(1)
O(1)–Co(1)–N(4)	89.9(1)	O(3)–Co(1)–O(6)	91.3(1)
O(3)–Co(1)–N(1)	83.0(1)	O(3)–Co(1)–O(4)	90.1(1)
O(3)–Co(1)–N(4)	91.0(1)	N(1)–Co(1)–O(6)	173.4(1)
N(1)–Co(1)–N(4)	99.7(1)	N(1)–Co(1)–O(4)	88.4(1)
O(6)–Co(1)–N(4)	83.6(1)	O(6)–Co(1)–O(4)	88.4(1)
N(4)–Co(1)–O(4)	171.9(1)	Co(1)–Co(2)–Co(3)	116.31(1)[d]

[a] This is an average of the Co(1)–Co(2), Co(2)–Co(3), and Co(3)–Co(1a) interatomic distances. [b] Symmetry code: (A) $1 - x, -y, -z$. [c] This is an average of the Co(1)–Co(1a), Co(2)–Co(2a), and Co(3)–Co(3a) interatomic distances. [d] This is an average of the Co(1)–Co(2)–Co(3), Co(2)–Co(3)–Co(1a), and Co(3)–Co(1a)–Co(2a) interatomic angles.

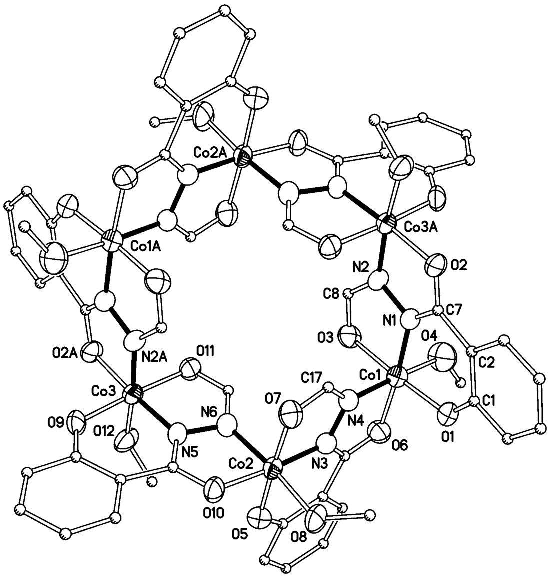

Fig. 3 Molecular structure of complex **3**, showing the atom numbering, with 50% probability displacement ellipsoids.

110.70(3)°. The peripheral diameter of the cobalt azametallacrown, measured between the opposite carbon atoms (C23–C23A, plus 0.77 Å for the van der Waals radius of carbon), is 18.13 Å. The approximate dimensions of the oval-shaped cavity are about 3.78 Å (C26–C26A, less 0.77 Å for the van der Waals radius of carbon) in internal diameter at the entrance, about 6.13 Å in diameter (Co1–Co1A, less 1.25 Å for the van der Waals radius of cobalt) at its widest point, and about 4.06 Å in depth. No guest molecules are encapsulated within the cobalt metallacrown 'host' cavity in **2**. As shown in Table 5, there are several intermolecular and intramolecular hydrogen bonds between the O–H of coordinated methanol molecules and oxygen atoms of solvent methanol molecules or phenol oxygen atoms, and between the O–H of solvent methanol molecules and phenol oxygen atoms.

$[Co_6(ashz)_6(CH_3OH)_6]\cdot 6CH_3OH$ 3. Complex **3** was synthesized using cobalt(II) acetate tetrahydrate as the metal source and ashz^{3-} as a trianionic pentadentate ligand. An ORTEP diagram of the crystal structure of **3** is shown in Fig. 3, selected bond distances and angles are given in Table 6. Complex **3** has a hexanuclear cobalt azametallacrown structure similar to **1** and **2**. The molecule has non-crystallographic pseudo-C_{3i} symmetry and lies on a crystallographic inversion centre at (1/2, 0, 0). Six ashz^{3-} ligands act as bridges between the adjacent Co(III) centres and support the cyclic skeleton of the compound. The 18-membered ring with the $[Co–N–N]_6$ repeat unit is also illustrated by the Co–N–N–Co torsion angles of 174.28–176.92°; the N–Co–N–N torsion angles alternate between 84.99–88.50 and 164.79–165.57°. All of the cobalt ions are in the +3 oxidation state and are related by pseudo-C_{3i} symmetry. The six cobalt ions have chiralities alternating between the Λ and Δ forms, as was observed in complexes **1** and **2**. The coordination spheres of the six cobalt ions are occupied by four oxygen donors and two nitrogen donors. The average neighbouring Co ··· Co interatomic distances are 4.4768(8) Å. The average Co ··· Co ··· Co interatomic angles are 116.31(1)°. The peripheral diameter of the cobalt azametallacrown, measured between the opposite carbon atoms (C25–C25A, plus 0.77 Å for the van der Waals radius of carbon), is 18.86 Å. The approximate dimensions of the oval-shaped cavity are about 4.75 Å (C18–C18A, less 0.77 Å for the van der Waals radius of carbon) in internal diameter at the entrance, about 6.45 Å in diameter (Co3–Co3A, less 1.25 Å for the van der Waals radii of cobalt) at its widest point, and about 3.48 Å in depth.

In contrast to **1**, there are no guest molecules in the azametallacrown cavity of **3** (Fig. S2, ESI). However, there are several intermolecular and intramolecular hydrogen bonds between the O–H of coordinated methanol molecules and oxygen atoms of solvent methanol molecules, and between the O–H of solvent methanol molecules and phenol oxygen atoms (Table 7).

$[Co_6(pshz)_6(CH_3OH)_6]\cdot 7CH_3OH\cdot 2H_2O$ 4. The molecular structure of the complex **4** is illustrated in Fig. 4, selected bond distances and angles are listed in Table 8. The hexanuclear molecule consists of six octahedral Co(III) centres bridged by six N–N groups of the six pshz^{3-} ligands. The azametallacrown structure is quite close to that observed for **3**. The azametallcrown molecule lies on a crystallographic inversion center at (0, 1/2, 1/2). Five coordination sites of the cobalt ion are filled by the heteroatoms from two neighbouring pentadentate ligands, the remaining sixth site is filled with an oxygen atom from one coordinated methanol molecule. The Co–N–N–Co torsion angles are in the range 173.94–177.82° and the N–Co–N–N torsion angles alternate between 86.85–88.21 and 162.37–164.23°. The average neighbouring Co ··· Co interatomic distances are 4.478 (8) Å. The Co ··· Co ··· Co interatomic angles range from 115.30 to 117.73°. The peripheral diameter of the cobalt azametallacrown, measured between the opposite carbon atoms (C16–C16A, plus 0.77 Å for the van der Waals radius of carbon), is 18.83 Å. The approximate dimensions of

Table 7 Hydrogen bond geometry for complex **3** (Å, °)[a]

D–H ··· A	D–H	H ··· A	D ··· A	D–H ··· A
O(4)–H(04) ··· O(33A)	0.99	1.62	2.607(5)	176
O(8)–H(08) ··· O(31)	1.11	1.56	2.609(4)	156
O(12)–H(012) ··· O(32)	1.05	1.62	2.559(5)	147
O(31)–H(031) ··· O(1)	0.93	1.76	2.678(4)	169
O(32)–H(032) ··· O(5)	1.00	1.72	2.710(5)	171
O(33)–H(033) ··· O(9B)	0.96	1.80	2.746(5)	169

[a] Symmetry codes: (A) $x + 1, y, z$; (B) $-x, -y, -z$.

Table 8 Selected bond lengths (Å) and angles (°) for **4**

Co(1)–O(1)	1.870(6)	Co(1)–O(3)	1.895(6)
Co(1)–O(6)	1.906(6)	Co(1)–N(1)	1.852(7)
Co(1)–O(4)	1.964(6)	Co(1)–N(4)	1.916(7)
N(1)–N(2)	1.431(9)	Co(1)–Co(2)	4.478(8)[a]
Co(1)–Co(1A)[b]	8.836(1)[c]		
O(1)–Co(1)–O(3)	177.1(3)	O(1)–Co(1)–O(6)	91.3(3)
O(1)–Co(1)–N(1)	94.3(3)	O(1)–Co(1)–O(4)	90.8(3)
O(1)–Co(1)–N(4)	90.6(3)	O(3)–Co(1)–O(6)	91.3(3)
O(3)–Co(1)–N(1)	83.1(3)	O(3)–Co(1)–O(4)	87.9(3)
O(3)–Co(1)–N(4)	91.1(3)	N(1)–Co(1)–O(6)	173.6(3)
N(1)–Co(1)–N(4)	99.2(3)	N(1)–Co(1)–O(4)	88.2(3)
O(6)–Co(1)–N(4)	83.8(3)	O(6)–Co(1)–O(4)	87.7(3)
N(4)–Co(1)–O(4)	171.4(3)	Co(1)–Co(2)–Co(3)	116.56(3)[d]

[a] This is an average of the Co(1)–Co(2), Co(2)–Co(3), and Co(3)–Co(1a) interatomic distances. [b] Symmetry code: (A) $-x, -y + 1, -z + 1$. [c] This is an average of the Co(1)–Co(1a), Co(2)–Co(2a), and Co(3)–Co(3a) interatomic distances. [d] This is an average of the Co(1)–Co(2)–Co(3), Co(2)–Co(3)–Co(1a), and Co(3)–Co(1a)–Co(2a) interatomic angles.

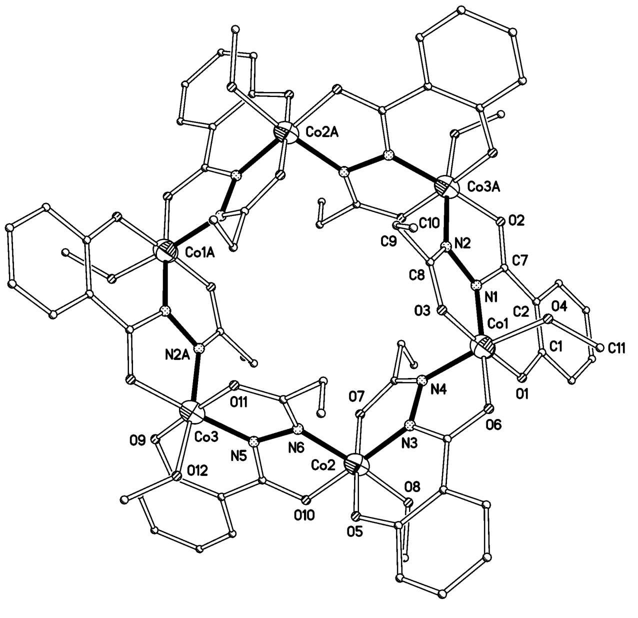

Fig. 4 Molecular structure of complex **4**, showing the atom numbering, with 50% probability displacement ellipsoids.

the oval-shaped cavity are about 4.75 Å (C19–C19A, less 0.77 Å for the van der Waals radius of carbon) in internal diameter at the entrance, about 6.43 Å (Co3–Co3A, less 1.25 Å for the van der Waals radius of cobalt) at its largest diameter and about 3.41 Å in depth. Again, there are no guest molecules in the azametallacrown cavity of **4**. This is similar to **3**, but different from the situation in **1**. Several O(phenol) ··· O(solvent methanol molecule) distances and O(Coordinated methanol molecule) ··· O(solvent methanol molecule) distances are in the range 2.58(1)–2.70(1) Å, indicating that hydrogen bonds may exist.

Conclusion

There is a hexanuclear 18-membered ring of six cobalt ions linked by the six hydrazide N–N groups of the six N-substituted salicylhydrazide pentadentate ligands in these four cobalt metallacrowns. All of the four title azametallacrown complexes possess non-crystallographic pseudo-C_{3i} symmetry and lie on crystallographic inversion centres. The chiralities of the cobalt atoms alternate between the Λ and Δ forms. One of the characteristics of the azametallacrown core ring is that Co–N–N–Co torsion angles are in the range 171.47–179.43° and the N–Co–N–N torsion angles alternate between 82.74–89.55 and 162.37–178.09° in the four title complexes. Two solvent methanol molecules are incorporated in the nanometer-sized cavity of the azametallacrown molecule in compound **1**.

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