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Supporting Information

SUPPORTING INFORMATION

Experimental

1. To a solution of a tetra(bromomethyl)cavitand[2a, 11] (1.0 g, 1.04 mmol) and diethyl iminodiacetate (1.6 g, 8.3 mmol) in freshly distilled THF (150 mL) was added potassium carbonate (3.0 g, 0.0217 mol) and the mixture heated under reflux (12 h). Upon cooling to room temperature it was filtered and the solution evaporated (under reduced pressure) to a viscous yellow oil. The addition of diethyl ether afforded a brown solid which was removed by filtration through a celite pad and discarded. Upon standing, white crystals of **1** were deposited (0.82 g, 56%). Crystals suitable for X-ray diffraction were grown by vapor diffusion of diethyl ether into a solution of **1** in chloroform, mp 159-162 °C. IR (KBr mull) cm^{-1}: 2977s, (CO) 1742vs, 1468s, 1192s, 979s, 585w. ^1H NMR (200 MHz, $CDCl_3$) δ 7.20 (s, 4 H, C_6H), 5.80 (d, 4 H, J = 7.2, outer OCH_2O), 4.98 (q, 4 H, J = 7.4, $CHCH_3$), 4.13 (m, 12 H, inner OCH_2O overlapped with ester CH_2CH_3), 3.71 (s, 8 H, benzyl CH_2), 3.49 (s,16 H, CH_2CO_2R), 1.73 (d, 12 H, J=7.2, $CHCH_3$), 1.14 (t, 12 H, J = 7.2, ester CH_2CH_3). MS (FAB) *m/e*: 1396 (M^+, 100 %). Anal. Calcd for $C_{72}H_{92}N_4O_{24}\cdot 0.5CHCl_3$: C, 59.70; H, 6.40; N, 3.84. Found: C, 59.70; H, 6.17; N, 3.57.

$Ba_4L\cdot 24H_2O$ **2**. A solution of 1 (0.40g, 0.29 mmol) in THF (75 cm3) was treated with a suspension of barium hydroxide octahydrate (0.81g, 2.6 mmol) in water (50 mL). The mixture was heated and stirred (14 h, 80 (C), cooled to room temperature and the precipitate thus formed was removed by filtration, washed with acetone and ether and left to dry, to yield **2** as a white powder (0.60 g, 96%). IR (KBr mull) cm^{-1}: 3400br,

1578vs, 1408, 974. ^{1}H NMR (500 MHz, D_2O/trifluoroacetic acid) δ 7.71 (s, 4 H, C_6H), 5.83 (d, 4 H, J = 7.0, outer OCH_2O), 4.36 (s, 8 H, benzyl CH_2), 4.21 (d, 4H, J = 7.0, inner OCH_2O), 4.04 (s,16 H, CH_2CO_2H), 1.79 (d, 12 H, J=7.0, $CHCH_3$). Anal. Calcd for $C_{56}H_{52}Ba_4N_4O_{24}\cdot 24H_2O$: C, 31.33; H, 4.70; N, 2.61. Found: C, 31.24; H, 4.07; N, 2.37.

$[Co_4L_2][Ba_{2.66}Co_{1.33}]\cdot 42H_2O$ **3**, Compound **2** (0.100g, 0.0465 mmol) was stirred in 1M hydrochloric acid (10 mL) until a clear solution was obtained. Water (10 mL), cobalt(II) chloride hexahydrate (80 mg, 0.336 mmol) and magnesium acetate (50 mg, 0.234 mmol) were added to the stirred pale orange/pink solution. Potassium carbonate was added until the solution became pink (pH 5), upon which it was filtered and layered with isopropyl alcohol. After two days pink prismatic crystals of **3** formed (0.054g, 61%). IR (KBr mull) cm^{-1}: 3436br, 1618s, 1387m, 1107m, 978m. Anal. Calcd for $C_{112}H_{104}Co_{5.33}Ba_{2.66}N_8O_{48}\cdot 42H_2O$: C, 35.71; H, 5.03; N, 2.97. Found: C, 35.65; H, 4.86; N, 2.92. The octaanionic complex **3** was crystallized as a mixed barium and cobalt salt. Analysis of crystals of **3** by ICP showed the only metal ions to be present were cobalt and barium in the molar ratio of two to one. The sodium salt of **3** can be obtained by disolving **2** in 1 M HCl, adding Na_2SO_4, removing the $BaSO_4$ precipitate, adding $CoCl_2$ and raising the solution pH with 1 M NaOH solution. The role of the magnesium or calcium acetate in the crystallization process is currently unknown.

Experimental Details for the Structure Determination of III

Single crystal data for **3** were collected using a Siemens R3m/V automated diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Lattice parameters were calculated using a least-squares procedure involving 38 (9.95°< 2θ < 31.78°) carefully centered reflections. The crystals of **3** lost solvent rapidly, so the crystal used for data collection was sealed in a quartz capillary and emersed in its mother liquor. Crystal data and experimental conditions are listed in the supporting data. An empirical absorption connection based on Ψ scans was applied to the data with minimum and maximum transmissions of 0.238 and 0.265. (Estimated range of transmission factors is between 0.55 and 0.75.)

A partial structure was obtained using direct methods and the structure was completed using Fourier methods. A difference map of the structure contained a large peak near **3** with a smaller peak about 1.5Å from the large peak. The stoichiometry of the compound required that an additional divalent cation must be included in the asymmetric unit . Because Ba^{2+} and Co^{2+} were used in the synthesis of **3** the larger peak was selected as the position of a partial Ba^{2+} and the smaller peak was assumed to be a partial Co^{2+}. Stoichiometry required that the sum of the population parameters of the disordered cations be 1.0 and imposing this restriction during the final cycles of refinements, the final occupancy factors of the Ba^{2+} and Co^{2+} were 0.63 and 0.37 respectively. The resulting ratio total of Co^{2+} to Ba^{2+} was 1.37/0.63 or 2.2 which agreed well with the ICP data which indicated that the Co/Ba ratio was 2. The Ba^{2+} is coordinated to two oxygen atoms of the ligand and seven water molecules. It was

possible to find only one ligand (O58) for the Co^{2+} in the difference maps because of the small scattering of the partial oxygen atoms (0.37) and the presence of the many oxygen atoms bound to Ba^{2+}. The positional parameters of the oxygen bound to Co2 (O58) were not refined but the oxygen was refined isotropically. It was possible to find one half of a methanol molecule and four additional water molecules in the difference maps. All non-hydrogen atoms with the exception of six of the water oxygen atoms were refined anisotropically. Several of those water molecules appeared to be disordered but only the disorder of O56 could be resolved. Positions for the hydrogen atoms bonded to the carbon atoms of **3** were calculated. The large R value can partially be attributed to the disorder of the counter cations and the inability to resolve the coordination of the Co^{2+} from that of the Ba^{2+}. The structure of **3** was refined to the appropriate structure with reasonable bond lengths and angles.

Thermal Ellipsoid Figure with the Asymmetric Unit Labeled for One Half of **3**

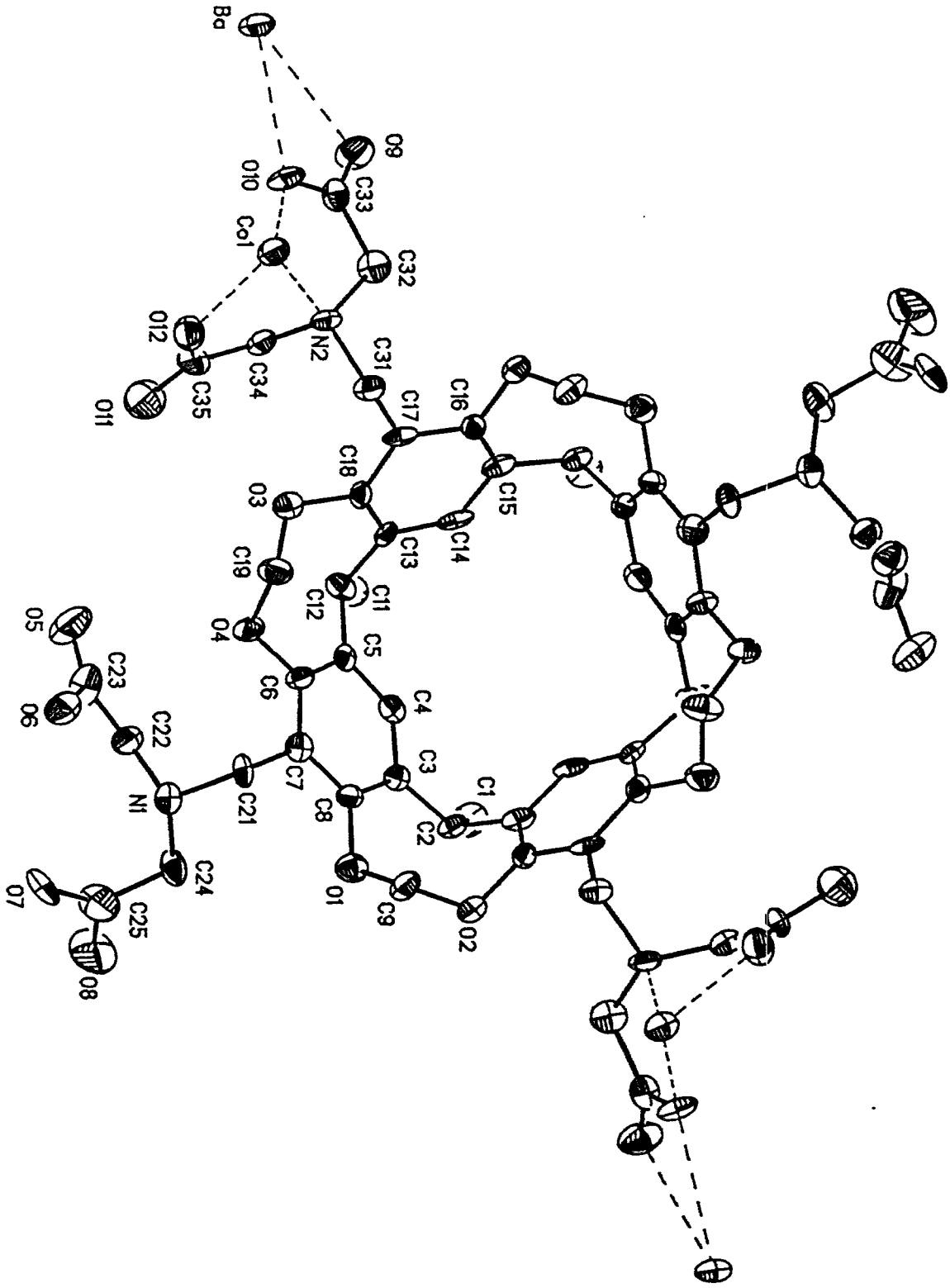

Table 1. Crystal data and structure refinement for III.

Identification code	co1
Empirical formula	C114 H104 Ba2.52 Co5.48 N8 O81.16
Formula weight	3553.56
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	tetragonal
Space group	I4(1)/a
Unit cell dimensions	a = 20.129(4) A alpha = 90 deg. b = 20.129(4) A beta = 90 deg. c = 54.399(18) A gamma = 90 deg.
Volume	22041(10) A^3
Z	4
Density (calculated)	1.071 Mg/m^3
Absorption coefficient	0.916 mm^-1
F(000)	7129
Crystal size	0.6 x 0.6 x 0.4 mm
Theta range for data collection	2.02 to 23.06 deg.
Index ranges	0<=h<=22, 0<=k<=22, -59<=l<=0
Reflections collected	7867
Independent reflections	7447 [R(int) = 0.0957]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7394 / 0 / 501
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.1113, wR2 = 0.2869
R indices (all data)	R1 = 0.2340, wR2 = 0.4226
Largest diff. peak and hole	0.765 and -0.527 e.A^-3

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Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for III. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Co(1)	1475(1)	9129(1)	1246(1)	47(1)
O(1)	1403(5)	14510(5)	652(2)	53(3)
O(2)	317(5)	14934(5)	649(2)	43(3)
O(3)	1772(5)	11186(5)	720(2)	52(3)
O(4)	2196(5)	12274(5)	721(2)	51(3)
O(5)	3659(7)	12192(7)	916(3)	90(5)
O(6)	3511(5)	12958(5)	1205(2)	56(3)
O(7)	3932(6)	14533(6)	1004(3)	67(3)
O(8)	3815(8)	15174(9)	680(4)	128(7)
O(9)	1055(7)	7948(6)	654(2)	80(4)
O(10)	1511(6)	8353(5)	997(2)	55(3)
O(11)	2915(7)	10213(7)	914(3)	84(4)
O(12)	2274(6)	9773(6)	1201(2)	65(3)
N(1)	2867(6)	13785(6)	893(2)	45(3)
N(2)	1256(6)	9598(5)	891(2)	42(3)
C(1)	650(9)	14173(9)	-63(3)	57(5)
C(2)	664(7)	14213(7)	216(3)	39(4)
C(3)	1123(7)	13715(7)	334(3)	39(4)
C(4)	1186(8)	13058(8)	248(3)	46(4)
C(5)	1549(7)	12569(7)	367(3)	40(4)
C(6)	1841(7)	12744(7)	591(3)	43(4)
C(7)	1814(7)	13375(7)	684(3)	42(4)
C(8)	1443(7)	13853(7)	556(3)	33(3)
C(9)	835(8)	14664(8)	792(3)	50(4)
C(11)	1657(9)	11861(9)	-14(3)	64(5)
C(12)	1612(8)	11879(8)	262(3)	48(4)
C(13)	1101(7)	11408(6)	369(3)	40(4)
C(14)	501(7)	11303(7)	245(3)	40(4)
C(15)	6(8)	10851(7)	338(3)	44(4)
C(16)	143(8)	10536(7)	553(3)	46(4)
C(17)	753(8)	10621(7)	678(3)	41(4)
C(18)	1195(7)	11083(6)	594(3)	38(4)
C(19)	1817(9)	11790(7)	853(3)	54(5)
C(21)	2183(7)	13559(8)	926(3)	51(4)
C(22)	3287(8)	13255(8)	737(3)	50(4)
C(23)	3491(9)	12754(9)	983(4)	60(5)
C(24)	2966(8)	14410(8)	754(3)	56(5)
C(25)	3605(10)	14720(10)	812(4)	73(6)
C(31)	898(8)	10241(7)	918(3)	53(4)
C(32)	861(9)	9098(7)	748(3)	53(4)
C(33)	1171(8)	8420(9)	810(4)	54(4)
C(34)	1917(9)	9703(8)	789(3)	57(5)
C(35)	2394(8)	9920(9)	984(4)	62(5)
Ba	1707(1)	6948(1)	973(1)	64(1)
Co(2)	1914(3)	7227(3)	1214(1)	44(2)
O(51)	1336(8)	5846(7)	1255(3)	46(4)
O(52)	360(8)	6911(10)	1031(4)	78(7)
O(53)	2791(10)	6094(10)	1072(5)	91(8)
O(54)	1335(60)	7330(17)	1450(13)	577(90)
O(55)	2641(22)	7272(19)	632(7)	190(16)

O(56)	1781(28)	6039(28)	594(10)	120(18)
O(56A)	847(16)	6299(16)	579(6)	50(9)
O(57)	2602(20)	7525(20)	1270(7)	174(14)
O(58)	1765	6867	859	214(59)
O(59)	0	7500	366(4)	157(12)
O(60)	0	2500	734(6)	168(12)
O(61)	6592(18)	3818(18)	536(6)	264(15)
O(62)	3038(23)	6004(23)	388(8)	350(22)
C(63)	-28(20)	3468(14)	1155(6)	50(9)
O(64)	649(21)	3226(15)	1141(5)	114(14)

Table 3. Bond lengths (Å) for III. ("A" denotes a symmetry related atom.)

Co(1)-O(10)	2.068(11)	Co(1)-O(12)	2.080(13)
Co(1)-N(2)	2.192(13)	Co(1)-O(6A)	2.084(11)
Co(1)-O(7A)	2.095(12)	Co(1)-N(1A)	2.245(13)
O(2)-C(9)	1.41(2)	O(2)-C(16A)	1.42(2)
O(3)-C(18)	1.36(2)	O(3)-C(19)	1.42(2)
O(4)-C(6)	1.38(2)	O(4)-C(19)	1.43(2)
O(5)-C(23)	1.24(2)	O(6)-C(23)	1.28(2)
O(6)-Co(1A)	2.084(11)	O(7)-C(25)	1.29(2)
O(7)-Co(1A)	2.095(12)	O(8)-C(25)	1.23(2)
O(9)-C(33)	1.29(2)	O(9)-Ba	2.964(12)
O(10)-C(33)	1.24(2)	O(10)-Ba	2.858(9)
O(11)-C(35)	1.26(2)	O(12)-C(35)	1.24(2)
N(1)-C(21)	1.46(2)	N(1)-C(22)	1.48(2)
N(1)-C(24)	1.48(2)	N(1)-Co(1A)	2.245(3)
N(2)-C(31)	1.49(2)	N(2)-C(32)	1.50(2)
N(2)-C(34)	1.46(2)	C(1)-C(2)	1.52(2)
C(2)-C(3)	1.51(2)	C(2)-C(15A)	1.51(2)
C(3)-C(4)	1.41(2)	C(3)-C(8)	1.39(2)
C(4)-C(5)	1.39(2)	C(5)-C(6)	1.40(2)
C(5)-C(12)	1.51(2)	C(6)-C(7)	1.37(2)
C(7)-C(8)	1.40(2)	C(7)-C(21)	1.55(2)
C(11)-C(12)	1.50(2)	C(12)-C(13)	1.52(2)
C(13)-C(14)	1.40(2)	C(13)-C(18)	1.40(2)
C(14)-C(15)	1.44(2)	C(15)-C(16)	1.36(2)
C(15)-C(2A)	1.51(2)	C(16)-C(17)	1.42(2)
C(16)-O(2A)	1.42(2)	C(17)-C(18)	1.37(2)
C(17)-C(31)	1.54(2)	C(22)-C(23)	1.53(2)
C(24)-C(25)	1.46(2)	C(32)-C(33)	1.54(2)
C(34)-C(35)	1.50(2)	C(63)-O(64)	1.45(5)
Ba-O(51)	2.800(13)	Co(2)-O(58)	2.083(7)
Ba-O(52)	2.73(2)	Ba-O(53)	2.83(2)
Ba-O(54)	2.81(10)	Ba-O(55)	2.72(4)
Ba-O(56)	2.76(6)	Ba-O(57)	2.68(4)
Ba-O(56A)	3.05(3)		

Table 4. Bond angles (°) for III. ("A" denotes a symmetry related atom.)

O(10)-Co(1)-O(12)	111.5(5)	O(10)-Co(1)-N(2)	75.3(6)
O(12)-Co(1)-N(2)	77.5(5)	O(10)-Co(1)-O(6A)	90.9(5)
O(12)-Co(1)-O(6A)	149.3(5)	N(2)-Co(1)-O(6A)	88.5(5)
O(10)-Co(1)-O(7A)	89.9(5)	O(12)-Co(1)-O(7A)	89.9(5)
N(2)-Co(1)-O(7A)	155.7(5)	O(6A)-Co(1)-O(7A)	111.8(5)
O(10)-Co(1)-N(1A)	156.9(4)	O(12)-Co(1)-N(1A)	87.4(5)
N(2)-Co(1)-N(1A)	122.8(4)	O(6A)-Co(1)-N(1A)	77.4(5)
O(7A)-Co(1)-N(1A)	76.5(5)	C(8)-O(1)-C(9)	116.7(11)
C(9)-O(2)-C(16A)	115.3(11)	C(18)-O(3)-C(19)	116.0(11)
C(6)-O(4)-C(19)	116.5(12)	C(23)-O(6)-Co(1A)	115.6(11)
C(25)-O(7)-Co(1A)	114.0(10)	C(33)-O(9)-Ba	92.1(10)
Co(1)-O(10)-C(33)	116.0(10)	Co(1)-O(10)-Ba	141.5(5)
C(33)-O(10)-Ba	98.5(10)	Co(1)-O(12)-C(35)	114.3(11)
C(21)-N(1)-C(22)	111.3(12)	C(21)-N(1)-C(24)	117.0(12)
C(22)-N(1)-C(24)	109.7(13)	C(21)-N(1)-Co(1A)	111.8(9)
C(22)-N(1)-Co(1A)	101.9(9)	C(24)-N(1)-Co(1A)	103.9(9)
Co(1)-N(2)-C(31)	112.8(9)	Co(1)-N(2)-C(32)	106.0(9)
C(31)-N(2)-C(32)	112.1(12)	Co(1)-N(2)-C(34)	102.5(9)
C(31)-N(2)-C(34)	110.6(11)	C(32)-N(2)-C(34)	112.3(12)
C(1)-C(2)-C(3)	113.8(12)	C(1)-C(2)-C(15A)	114.7(13)
C(3)-C(2)-C(15A)	105.3(16)	C(2)-C(3)-C(4)	122.5(14)
C(2)-C(3)-C(8)	121.3(13)	C(4)-C(3)-C(8)	115.7(13)
C(3)-C(4)-C(5)	123.9(15)	C(4)-C(5)-C(6)	116.8(14)
C(4)-C(5)-C(12)	121.3(14)	C(6)-C(5)-C(12)	122.0(13)
O(4)-C(6)-C(5)	119.2(13)	O(4)-C(6)-C(7)	118.0(14)
C(5)-C(6)-C(7)	122.7(14)	C(6)-C(7)-C(8)	118.2(14)
C(6)-C(7)-C(21)	121.0(14)	C(8)-C(7)-C(21)	120.9(13)
O(1)-C(8)-C(3)	118.5(13)	O(1)-C(8)-C(7)	118.8(12)
C(3)-C(8)-C(7)	122.7 13)	O(1)-C(9)-O(2)	112.7(13)
C(5)-C(12)-C(11)	114.1(13)	C(5)-C(12)-C(13)	111.9(12)
C(11)-C(12)-C(13)	114.2(14)	C(12)-C(13)-C(14)	119.4(14)
C(12)-C(13)-C(18)	122.5(13)	C(14)-C(13)-C(18)	118.0(13)
C(13)-C(14)-C(15)	121.4(14)	C(14)-C(15)-C(16)	117.2(15)
C(14)-C(15)-C(2A)	121.2(13)	C(16)-C(15)-C(2A)	121.3(14)
C(15)-C(16)-C(17)	122.3(15)	C(15)-C(16)-O(2A)	119.6(14)
C(17)-C(16)-O(2A)	118.0(14)	C(16)-C(17)-C(18)	119.1(14)
C(16)-C(17)-C(31)	120.8(14)	C(18)-C(17)-C(31)	119.9(14)
O(3)-C(18)-C(13)	118.9(13)	O(3)-C(18)-C(17)	119.3(14)
C(13)-C(18)-C(17)	121.5(14)	O(3)-C(19)-O(4)	111.2(13)
N(1)-C(21)-C(7)	114.9(13)	N(1)-C(22)-C(23)	111.0(13)
O(5)-C(23)-O(6)	124.5(18)	O(5)-C(23)-C(22)	118.1(17)

Table 4. Bond angles (°) for III. (continued)

O(6)-C(23)-C(22)	117.3(15)	N(1)-C(24)-C(25)	111.7(14)
O(7)-C(25)-O(8)	120.7(19)	O(7)-C(25)-C(24)	120.0(16)
O(8)-C(25)-C(24)	119 (2)	N(2)-C(31)-C(17)	116.4(13)
N(2)-C(32)-C(33)	105.4(13)	O(9)-C(33)-O(10)	124.0(16)
O(9)-C(33)-C(32)	115.8(16)	O(10)-C(33)-C(32)	120.2(15)
N(2)-C(34)-C(35)	110.8(15)	O(11)-C(35)-O(12)	121.1(19)
O(11)-C(35)-C(34)	117.1(19)	O(12)-C(35)-C(34)	118.7(15)
O(9)-Ba-O(10)	45.1(3)	O(9)-Ba-O(51)	137.8(4)
O(10)-Ba-O(51)	136.2(4)	O(9)-Ba-O(52)	69.3(4)
O(10)-Ba-O(52)	83.4(5)	O(56)-Ba-O(57)	134.4(14)
O(51)-Ba-O(52)	69.5(5)	O(9)-Ba-O(53)	149.9(5)
O(10)-Ba-O(53)	134.4(6)	O(51)-Ba-O(53)	67.7(5)
O(52)-Ba-O(53)	136.6(5)	O(9)-Ba-O(54)	103.7(13)
O(10)-Ba-O(54)	69.5(7)	O(51)-Ba-O(54)	68.8(8)
O(52)-Ba-O(54)	69(2)	O(53)-Ba-O(54)	101.3(17)
O(9)-Ba-O(55)	75.1(9)	O(10)-Ba-O(55)	83.7(9)
O(51)-Ba-O(55)	138.4(9)	O(52)-Ba-O(55)	140.5(10)
O(53)-Ba-O(55)	75.1(9)	O(54)-Ba-O(55)	138.6(19)
O(9)-Ba-O(56)	92.1(12)	O(10)-Ba-O(56)	134.2(12)
O(51)-Ba-O(56)	84.2(12)	O(52)-Ba-O(56)	97.0(13)
O(53)-Ba-O(56)	72.4(13)	O(54)-Ba-O(56)	152.4(16)
O(55)-Ba-O(56)	67.1(15)	O(9)-Ba-O(57)	110.9(9)
O(10)-Ba-O(57)	68.8(9)	O(51)-Ba-O(57)	101.9(9)
O(52)-Ba-O(57)	127.5(10)	O(53)-Ba-O(57)	68.3(10)
O(54)-Ba-O(57)	60(2)	O(55)-Ba-O(57)	81.0(13)