

Syntheses, Structures, and Electrochemical Properties of Inclusion Compounds of Cucurbit[8]uril with Cobalt(III) and Nickel(II) Complexes

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Inclusion compounds of a macrocyclic cavitand cucurbit[8]uril (CB[8]) with cobalt(III) and nickel(II) complexes of 1,3-diaminopropane (tn) and 1,3-diamino-2-propanol (tmOH) {*trans*-[Co(tn)₂Cl₂]@CB[8]}Cl · 14H₂O (**1**), {*trans*-[Co(tmOH)(tmO)]@CB[8]}Cl₂ · 22H₂O (**2**), and {*trans*-[Ni(tmOH)₂]@CB[8]}Cl₂ · 22H₂O (**3**) were synthesized and characterized by X-ray single crystal analysis, IR spectroscopy, ESI-MS, and by solid-state stripping voltammetry. The encapsulation of *trans*-[Co(tn)₂Cl₂]⁺ within the cavity of CB[8] stabilizes the complex toward ligand substitution reactions in aqueous solution. The electrochemical study demonstrates that CB[8] prefers the oxidized species in *trans*-[Co(tn)₂Cl₂]⁺/*trans*-[Co(tn)₂Cl₂]⁰ and *trans*-[Co(tmO)(tmOH)₂]²⁺/*trans*-[Co(tmO)(tmOH)₂]⁺ redox couples, but stabilizes the reduced form *trans*-[Ni(tmOH)₂]²⁺ against the oxidized species. The reversibility of voltammogram shapes evidence that for the inclusion compounds **1–3** electron transfer reactions proceed within the cavity of the host.

Introduction

Considerable attention paid to compounds obtained by inclusion of metal complexes into organic hosts (cyclodextrins, calixarenes, cucurbiturils) is essentially driven by unique microenvironment provided by the organic cavity to a transition metal. Such systems are reminiscent of metalloenzymes, where the substrate-binding site, spatially preorganizing catalyzing functional groups of an enzyme and a substrate, is located in a cavity.¹ Cucurbit[*n*]urils (C_{6*n*}H_{6*n*}N_{4*n*}O_{2*n*}, CB[*n*]; *n* = 5–10), macrocyclic cavitands comprising *n* glycoluril units, have hydrophobic cavities large enough for inclusion of metal complexes with organic ligands (for *n* ≥ 7).² Formation of highly stable inclusion compounds of transition-metal complexes with CB[7] and CB[8] has been

demonstrated during past few years,^{3–5} and some interesting and useful properties have been revealed. For instance, encapsulation of platinum complexes into CB[7] reduces their high cytotoxicity in cancer treatment,⁶ and several patents were obtained concerning the application of platinum, palladium, or gold complexes partly encapsulated by one or several cucurbit[*n*]urils as anticancer drugs.⁷

It was shown that the stability of cobaltocene and ferrocene inclusion complexes with the CB[7] host was generally higher than that of inclusion complexes with the cavitand β-cyclodextrin having a similar size; electrochemical studies revealed direct electron transfer to and from inclusion

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(1) Cram, D. J. *Science* **1983**, *219*, 1177.

(2) (a) Behrend, R.; Meyer, E.; Rusche, F. *Liebigs Ann. Chem.* **1905**, *339*, 1. (b) Freeman, W. A.; Mock, W. L.; Shih, N.-Y. *J. Am. Chem. Soc.* **1981**, *103*, 7367. (c) Day, A.; Arnold, P.; Blanch, R. J.; Snushall, B. *J. Org. Chem.* **2002**, *66*, 8094. (d) Lagona, J.; Mukhopadhyay, P.; Chakrabarti, S.; Isaacs, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4844. (e) Kim, K.; Selvapalam, N.; Young, H. K.; Kyeng, M. P.; Kim, D.; Kim, J. *Chem. Soc. Rev.* **2007**, *267*.

(3) Ong, W.; Kaifer, A. E. *Organometallics* **2003**, *22*, 4181.

(4) Jeon, W. S.; Moon, K.; Park, S. H.; Chun, H.; Ko, Y. H.; Lee, J. Y.; Lee, E. S.; Samal, S.; Selvapalam, N.; Rekharsky, M. V.; Sindelar, V.; Sobransingh, D.; Inoue, Y.; Kaifer, A. E.; Kim, K. *J. Am. Chem. Soc.* **2005**, *127*, 12984.

(5) (a) Sobransingh, D.; Kaifer, A. E. *Org. Lett.* **2006**, *8*, 3247. (b) Kim, S.-Y.; Jung, I.-S.; Lee, E.; Kim, J.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2121. (c) Lorenzo, S.; Day, A.; Craig, D.; Blanch, R.; Arnold, A.; Dance, I. *Cryst. Eng. Comm.* **2001**, *49*, 1.

(6) (a) Wheate, N. J.; Day, A. I.; Blanch, R. J.; Arnold, A. P.; Cullinane, C.; Collins, J. G. *Chem. Commun.* **2004**, 1424. (b) Wheate, N. J.; Buck, D. P.; Day, A. I.; Collins, J. G. *Dalton Trans.* **2006**, 451.

(7) (a) Kim, K.; Jeon, Y. J.; Kim, S.-Y.; Ko, Y. H. *POSTECH Foundation*, South Korea, PCT Int. Appl. 2003, 42. (b) Wheate, N. J.; Day, A. I.; Blanch, R. J.; Collins, J. G. *UNISEARCH Limited*, Australia, PCT Int. Appl. 2005, 63.

complexes of CB[7], whereas in the presence of β -cyclodextrin the electrochemical redox processes typically involve free guests escaped from the inclusion compounds.^{3,4} The electrochemical method is very attractive for controlling inclusion processes because the efficacy of the interaction is strongly affected by the oxidation states of the host or guest species, and thereby the gain or loss of an electron by the host or guest molecule will manifest itself in the stability of the host–guest complex.⁸ An interesting example of an artificial electrochemically switchable molecular machine driven by redox behavior of CB[7] inclusion compounds with bis-ferrocenyl derivatives was recently reported.^{5a} CV studies of a copper(II) complex with tetraazamacrocyclic ligand $[\text{Cu}(\text{cyclen})(\text{H}_2\text{O})_2]^{2+}$ included into CB[8] have demonstrated that encapsulation increases the stability of the Cu(I) state, but considerably slows down the electron transfer between an electrode and the redox center.^{5b} Similar behavior has been observed in electrochemistry of metalloproteins, where redox centers are embedded in protein coats.⁹

Our previous studies have demonstrated that nickel(II), copper(II), and cobalt(III) polyamine complexes are perfect guests for CB[8], and inclusion of $\text{trans-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ and $\text{trans-}[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ within the CB[8] cavity remarkably increases thermal stability of the metal complexes and blocks their tendency to isomerize into the cis form.¹⁰

Herein, we report syntheses, molecular and crystal structures, and electrochemical behavior of three new inclusion compounds derived from cobalt(III) and nickel(II) complexes with 1,3-diaminopropane (tn) or 1,3-diamino-2-propanol (tmOH) and a macrocyclic cavitand cucurbit[8]uril: $\{\text{trans-}[\text{Co}(\text{tn})_2\text{Cl}_2]@\text{CB}[8]\}\text{Cl}\cdot 14\text{H}_2\text{O}$ (**1**), $\{\text{trans-}[\text{Co}(\text{tmOH})(\text{tmO})]@\text{CB}[8]\}\text{Cl}_2\cdot 22\text{H}_2\text{O}$ (**2**), and $\{\text{trans-}[\text{Ni}(\text{tmOH})_2]@\text{CB}[8]\}\text{Cl}_2\cdot 22\text{H}_2\text{O}$ (**3**). Solid-state stripping voltammetry was applied for the first time to the investigation of electrochemical behavior of molecular host–guest complexes. The stability drops have been determined quantitatively for oxidized and reduced guests inside the macrocyclic cavitand CB[8].

Experimental Section

General Data. The starting compounds $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$, HCl (36%), and 1,3-diamino-2-propanol (95%) (tmOH) were of commercial quality and used without further purification; $\text{trans-}[\text{Co}(\text{tn})_2\text{Cl}_2]\text{Cl}$,¹¹ $\text{trans-}[\text{Co}(\text{tmO})_2]\text{Cl}\cdot 2\text{H}_2\text{O}$,¹² and cucurbit[8]uril^{2c} ($\text{C}_{48}\text{H}_{48}\text{N}_{32}\text{O}_{16}$) were synthesized according to the procedures published earlier. IR spectra were recorded using KBr pellets on an IFS-28 (Bruker) spectrophotometer in the range 4000–400 cm^{-1} . UV–vis spectra were measured on an Ultrospec 3300pro spectrophotometer. Mass spectra (ESI-MS) were obtained on Quattro LC

and QTOF I mass spectrometers (Micromass, Manchester, UK). Elemental analysis was carried out by the microanalytical services of the Institute of Inorganic Chemistry (Karlsruhe, Germany) and the Nikolaev Institute of Inorganic Chemistry (Novosibirsk, Russia).

All formulas of the compounds reported are given on the basis of X-ray crystal-structure analysis and include a large number of water molecules of crystallization. However, the crystals of **2** and **3** appeared to be prone to loss of some of the solvent molecules under ambient conditions, and, therefore, the data of elemental analysis for **2** and **3** were calculated with allowance for this dehydration. The number of lost water molecules calculated from elemental analysis data for **3** matches the results of thermogravimetric analysis.

Synthesis of $\{\text{trans-}[\text{Co}(\text{tn})_2\text{Cl}_2]@\text{CB}[8]\}\text{Cl}\cdot 14\text{H}_2\text{O}$ (1**).** Dry powders of $\text{trans-}[\text{Co}(\text{tn})_2\text{Cl}_2]\text{Cl}$ (0.038 g, 0.120 mmol) and cucurbit[8]uril $\cdot 20\text{H}_2\text{O}$ (0.020 g, 0.012 mmol) were mixed and added with water (7 mL). The resulting mixture was heated until CB[8] entirely dissolved, avoiding boiling. The resulting wine-red solution was cooled slowly resulting in precipitation of pale-green needle-shaped crystals within several hours. They were filtered off, washed with a small amount of cold water, and dried in air. Yield 0.015 g (67% based on cucurbit[8]uril). Crystals of **1** are moderately soluble in warm water, yielding a pale-green solution, which turns pink in several hours. Anal. Calcd for $\text{C}_{54}\text{H}_{96}\text{CoN}_{36}\text{O}_{30}\text{Cl}_3$: C, 34.23; H, 5.11; N, 26.61. Found: C, 34.03; H, 5.05; N, 26.45. IR (KBr, cm^{-1}): 3448(s), 2998(w), 2926(w), 1721(s), 1474(s), 1423(m), 1373(s), 1315(s), 1285(m), 1227(s), 1191(s), 1155(m), 1024(w), 995(w), 966(s), 828(m), 806(s), 756(m), 669(m), 632(w), 436(w). ESI-MS, m/z (I, %): 519.5 (25%) $\{\text{CB}[8] + [\text{Co}(\text{tn})_2]^{2+} + \text{Na}^+\}^{3+}$, 702.3 (30%) $\{\text{CB}[8] + \text{tn} + 2\text{H}^+\}^{2+}$, 767.8 (100%) $\{\text{CB}[8] + [\text{Co}(\text{tn})_2]^{2+}\}^{2+}$.

Synthesis of $\{\text{trans-}[\text{Co}(\text{tmOH})(\text{tmO})]@\text{CB}[8]\}\text{Cl}_2\cdot 22\text{H}_2\text{O}$ (2**).** Cucurbit[8]uril $\cdot 20\text{H}_2\text{O}$ (0.060 g, 0.036 mmol) was added to a solution of $\text{trans-}[\text{Co}(\text{tmO})_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ (0.096 g, 0.311 mmol) in 0.1 M HCl (21 mL). The resulting mixture was refluxed for 3 min until complete dissolution of CB[8], and then allowed to cool to room temperature in a closed beaker. In one day, wine-red crystals of **2** precipitated from the solution. They were filtered, rinsed with cold water, and dried in air. Yield: 0.064 g (88% based on cucurbit[8]uril). Crystals of **2** rapidly lose two water molecules of crystallization when kept in air. Anal. Calcd for $\{\text{trans-}[\text{Co}(\text{tmOH})(\text{tmO})]@\text{CB}[8]\}\text{Cl}_2\cdot 20\text{H}_2\text{O}$: C, 32.45; H, 5.40; N, 25.23. Found: C, 32.71; H, 5.22; N, 25.06. IR (KBr, cm^{-1}): 3429(s), 3003(w), 2930(w), 1721(s), 1474(s), 1425(m), 1373(s), 1318(s), 1290(m), 1232(s), 1190(s), 1153(m), 1027(w), 993(w), 968(s), 829(m), 807(s), 758(m), 673(m), 631(w), 372(m).

Synthesis of $\{\text{trans-}[\text{Ni}(\text{tmOH})_2]@\text{CB}[8]\}\text{Cl}_2\cdot 22\text{H}_2\text{O}$ (3**).** $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.113 g, 0.475 mmol) was dissolved in 0.0474 M aqueous solution of 1,3-diamino-2-propanol (20 mL), and then cucurbit[8]uril $\cdot 20\text{H}_2\text{O}$ (0.080 g, 0.047 mmol) was added. The resulting mixture was refluxed for 2 h, leading to almost complete dissolution of CB[8], then filtered and cooled slowly. Next day pale-violet rhombic platelets of **3** were filtered, washed with a small amount of cold water, and dried in air. Yield: 0.089 g (93% based on cucurbit[8]uril). Crystals of **3** rapidly lose eight water molecules of crystallization in air. Anal. Calcd for $\{\text{trans-}[\text{Ni}(\text{tmOH})_2]@\text{CB}[8]\}\text{Cl}_2\cdot 14\text{H}_2\text{O}$ ($\text{C}_{54}\text{H}_{88}\text{Cl}_2\text{N}_{36}\text{NiO}_{32}$): C, 34.44; H, 4.71; N, 26.78. Found: C, 34.71; H, 4.92; N, 27.11. IR (KBr, cm^{-1}): 3437(s), 3009(w), 2934(w), 1726(s), 1472(s), 1429(m), 1373(s), 1319(s), 1292(m), 1230(s), 1190(s), 1153(m), 1124(m), 1024(w), 993(w), 968(s), 829(m), 808(s), 758(m), 719(w), 673(m), 631(w), 447(w). ESI-MS, m/z (I, %): 523.86 (15%) $\{\text{CB}[8] + [\text{Ni}(\text{tmOH})_2]^{2+} + \text{Na}^+\}^{3+}$, 710.28 (100%) $\{\text{CB}[8] + \text{tmOH} + 2\text{H}^+\}^{2+}$.

(8) (a) Kaifer, A. E. *Acc. Chem. Res.* **1999**, *32*, 62. (b) Jing, L.; Yu, F. *Progr. Natur. Science* **2005**, *15*, 1057.

(9) (a) Frew, J. E.; Hill, H. A. O. *Eur. J. Biochem.* **1988**, *172*, 261. (b) Armstrong, F. A.; Hill, H. A. O.; Walton, N. J. *Acc. Chem. Res.* **1988**, *21*, 407.

(10) (a) Mitkina, T. V.; Naumov, D. Yu.; Gerasko, O. A.; Dolgushin, F. M.; Vicent, C.; Llusar, R.; Sokolov, M. N.; Fedin, V. P. *Russ. Chem. Bull.* **2004**, *53*, 2519. (b) Mitkina, T. V.; Naumov, D. Yu.; Kuratieva, N. V.; Gerasko, O. A.; Fedin, V. P. *Russ. Chem. Bull., Int. Ed.* **2006**, *1*, 26. (c) Mitkina, T. V.; Sokolov, M. N.; Naumov, D. Y.; Kuratieva, N. V.; Gerasko, O. A.; Fedin, V. P. *Inorg. Chem.* **2006**, *45*, 6950.

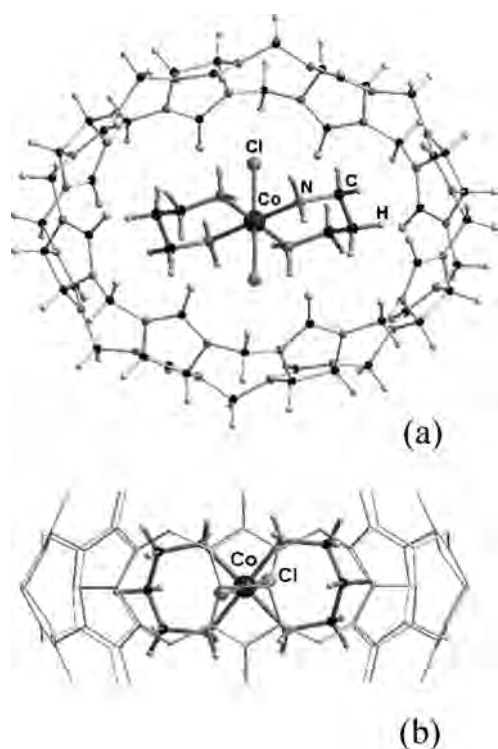
(11) Bailar, J. C.; Work, J. B. *J. Am. Chem. Soc.* **1946**, *68*, 232.

(12) Okamoto, M. S.; Barefield, E. K. *Inorg. Chem.* **1974**, *13*, 2611.

Table 1. Crystal Data and Structure Refinement for 1–4

	1	2	3	4
formula	C ₅₄ H ₉₆ Cl ₃ CoN ₃₆ O ₃₀	C ₅₄ H ₁₁₁ Cl ₂ CoN ₃₆ O ₄₀	C ₅₄ H ₁₀₄ Cl ₂ N ₃₆ NiO ₄₀	C ₆ H ₂₀ Cl ₂ N ₄ NiO ₁₀
fw	1894.95	2034.62	2027.34	437.87
T (K)	150(2)	150(2)	150(2)	150(2)
cryst syst	hexagonal	hexagonal	hexagonal	triclinic
space group	R3	R3	R3	P1
a (Å)	40.262(6)	29.144(4)	36.6870(6)	9.0219(2)
b (Å)				9.3988(2)
c (Å)	12.979(3)	26.515(5)	16.4927(6)	10.5601(3)
α (deg)				114.5390(10)
β (deg)				90.3990(10)
γ (deg)				104.3520(10)
V (Å ³)	18 221(6)	19 503(6)	19 224.1(8)	782.98(3)
Z	9	9	9	2
D _{calcd} (mg/m ³)	1.554	1.559	1.576	1.857
cryst size (mm ³)	0.10 × 0.08 × 0.08	0.40 × 0.34 × 0.28	0.38 × 0.34 × 0.32	0.42 × 0.32 × 0.30
no. of refls collected	18 609	34 364	37 425	5406
no. of independent refls	7687 [R(int) = 0.0378]	8232 [R(int) = 0.0423]	8103 [R(int) = 0.0340]	2902 [R(int) = 0.0127]
max. and min. transmission	0.9675 and 0.9597	0.9030 and 0.8654	0.8817 and 0.8618	0.6393 and 0.5463
GOF on F ²	1.330	1.257	1.124	1.034
final R indices [I > 2σ(I)] ^a	R1 = 0.0610, wR2 = 0.1369	R1 = 0.0650, wR2 = 0.0827	R1 = 0.0522, wR2 = 0.1613	R1 = 0.0251, wR2 = 0.0616
R indices (all data)	R1 = 0.1087, wR2 = 0.1384	R1 = 0.1161, wR2 = 0.0935	R1 = 0.0650, wR2 = 0.1712	R1 = 0.0261, wR2 = 0.0621

^a R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$; wR2 = $\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]\}^{1/2}$, w = σ_F^{-2} .

**Figure 1.** Structure of inclusion complex $\{trans-[Co(tm)_2Cl_2]@CB[8]\}^+$ in **1**: (a) top view and (b) side view (the CB[8] molecule is in gray-wire representation, hydrogen atoms are omitted for clarity).

Synthesis of *trans*-[Ni(tmOH)₂]Cl₂ (3a**).** The solution of 1,3-diamino-2-propanol (0.379 g, 4.206 mmol) in methanol (5 mL) was added to the solution of NiCl₂·6H₂O (0.500 g, 2.104 mmol) in methanol (5 mL) upon stirring. The resulting dark-blue solution was concentrated in air almost to dryness, and then ethanol (10 mL) was added under stirring, leading to the precipitation of a light-violet solid **3a**. The solid was filtered off and dried over P₂O₅. Yield: 0.650 g (99%) Anal. Calcd for NiCl₂N₄O₂C₆H₂₀: C, 23.26; H, 6.51; N, 18.08. Found: C, 22.97; H, 6.82; N, 17.99.

Synthesis of *trans*-[Ni(tmOH)₂](ClO₄)₂ (4**).** *Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should therefore be handled with appropriate care.* A solution of 1,3-diamino-2-propanol (0.250 g, 2.773 mmol) in

ethanol (5 mL) was added to a solution of Ni(ClO₄)₂·6H₂O (0.507 g, 1.386 mmol) in ethanol (3 mL) upon stirring. The resulting deep-violet solution was left for evaporation under ambient conditions. After 2 days, the first crop of violet crystals was collected, washed with diethyl ether, and dried over P₂O₅. The mother liquor was left to evaporate in air to dryness, and the solid residue (crop 2) was washed with diethyl ether and dried over P₂O₅. Overall yield (crop 1 + crop 2) was 0.433 g (71%). Anal. Calcd for C₆H₂₀Cl₂N₄NiO₁₀: C, 16.46; H, 4.60; N, 12.80. Found: C, 16.86; H, 4.77; N, 12.75. IR (KBr, cm⁻¹): 3372(s), 3318(s), 2945(m), 2616(w), 2495(w), 2217(w), 2017(w), 1617(m), 1592(m), 1456(w), 1410(w), 1382(w), 1346(w), 1256(m), 1110(s), 1082(s), 1022(s), 930(m), 915(m), 803(w), 784(w), 731(w), 623(s), 465(w), 437(w), 406 (w). UV-vis (190 – 1100 nm, aqueous solution), λ/nm (ε/mol⁻¹cm⁻¹): 969 (44), 572 (81), 357 (123), 309 (271). The crystals are well soluble in water and ethanol.

X-ray Structure Determinations. Data collection was performed on a STOE IPDS II diffractometer (for **1** and **2**) and Bruker Nonius X8 Apex diffractometer (for **3** and **4**) (Mo Kα, λ = 0.71073 Å) equipped with a CCD area detector. The diffraction frames were integrated with subsequent constrained cell refinement using the SAINT package and corrected for absorption with SADABS.¹³ Further experimental details are described in Table 1. The crystals did not degrade during data collection. The structures were solved by the direct methods and refined by full-matrix least-squares method with SHELXTL.¹³ The positions of hydrogen atoms of cucurbit[8]uril and organic ligands were calculated geometrically and refined using the riding model. The hydrogen atoms of the water molecules of crystallization were not located because of their high disordering. The hydrogen bonds are not revealed because of the absence of these hydrogen atoms; and it is the reason for observed shot contacts with the participation of water oxygen atoms and for the absence of values of X–H bonds and X–Y–H and H–Y–H angles in CIF files. CCDC-676273 to -676276 (for **1–4**, respectively) contain supplementary crystallographic data for this article.

Electrochemical Experiments. All voltammetric measurements were performed with an electrochemical analyzer 797 VA Com-

(13) Bruker Advanced X-ray Solutions (APEX2, version 1.08; SAINT, version 7.03; SHELXTL, version 6.12; SADABS, version 2.11); Bruker AXS Inc.: Madison, WI, 2004.

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for Complexes Encapsulated into CB[8] **1–3** and Free Complexes **1a**, **2a**, and **4**

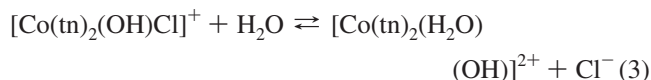
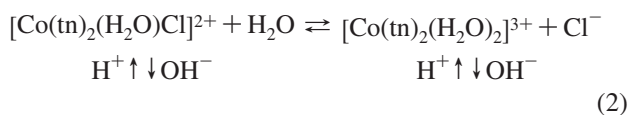
	<i>trans</i> -[Co(tn) ₂ Cl ₂] ¹⁺		<i>trans</i> -[Co(tmOH)(tmO)] ²⁺		<i>trans</i> -[Ni(tmOH) ₂] ²⁺			
	1	1a ¹⁸	2	2a ^{19b}	3	4		4
M–Cl	2.246(2)	2.26						
M–N	1.972(4), 1.981(4)	2.00	1.945(4), 1.954(4)	1.956(2), 1.960(2)	2.093(3), 2.103(2)	2.090(2), 2.106(2)	2.087(2), 2.108(2)	
M–O			1.939(3)	1.898(2)	2.095(2)	2.098(2)	2.110(2)	
N–M–Cl	89.97(13), 90.54(13)	90.0						
N–M–N ^a	95.15(16)	95.4	85.10(16)	85.42(6)	83.11(10)	84.62(6)	84.43(6)	
N–M–O			83.81(15), 85.89(15)	84.01(5), 86.68(5)	81.69(10), 82.61(9)	79.40(6), 82.91(6)	80.23(6), 82.05(6)	

^a Concerning one tn or tmOH ligand.

putrace (Metrohm, Switzerland). A three-electrode glass cell of 10 mL capacity was used. A graphite or glassy carbon rod was used as the counter electrode, and Hg₂I₂/Hg electrode (+0.02V vs NHE) filled with saturated KCl solution (Metrohm, Switzerland) served as the reference electrode. The butt-end of a 3 mm platinum rod modified with a mixture containing 5×10^{-2} to 1.2×10^{-1} mmol of the analyzed compound per 1 g of graphite powder and 2–3 wt % of Nafion polymer was utilized as the working electrode. This electrode is referred hereafter as the modified platinum electrode (MPTE). Solutions were deaerated with high-purity argon gas for 20 min prior to measurements. Experiments were carried out at ambient temperature (22 ± 2 °C).

Results and Discussion

Synthesis and Structure of {*trans*-[Co(tn)₂Cl₂]@CB[8]}·Cl·14H₂O (1**).** A reliable synthetic procedure for *trans*-[Co(tn)₂Cl₂]Cl (where tn is trimethylenediamine, or 1,3-diaminopropane) employing anhydrous medium was published by Bailar and Work in 1946,¹¹ although the earliest report about this compound was made by Werner in 1912.¹⁴ Green trimethylenediamine complex undergoes extremely rapid aquation in water (rate constant $k = 10^{-2} \text{ s}^{-1}$, eq 1) giving a red solution, which contains complexes listed in eqs 1–3.¹⁵



In contrast to the ethylenediamine homologue *trans*-[Co(en)₂Cl₂]Cl,¹⁶ the trimethylenediamine compound *trans*-[Co(tn)₂Cl₂]Cl does not tend to isomerize into the *cis*-complex.

Mixing powders of cucurbit[8]uril and *trans*-[Co(tn)₂Cl₂]Cl (10-fold molar excess of the latter) followed by addition of water and subsequent gentle heating of the mixture led to a wine-red solution, which yielded green needle-like crystals of {*trans*-[Co(tn)₂Cl₂]@CB[8]}·Cl·14H₂O (**1**) upon cooling. X-ray crystal structure analysis revealed that in **1** *trans*-[Co(tn)₂Cl₂]⁺ is included into the cavity of cucurbit[8]uril (Figure 1). Encapsulation inside the cavity of CB[8] hinders aquation of the cation *trans*-[Co(tn)₂Cl₂]⁺. Similar behavior was described for an encapsulated ethylenediamine complex *trans*-[Co(en)₂Cl₂]⁺: the guest is stabilized toward isomerization and ligand exchange reactions within the cavity of the host.^{10c} Thus, CB[8] acts as a molecular container for

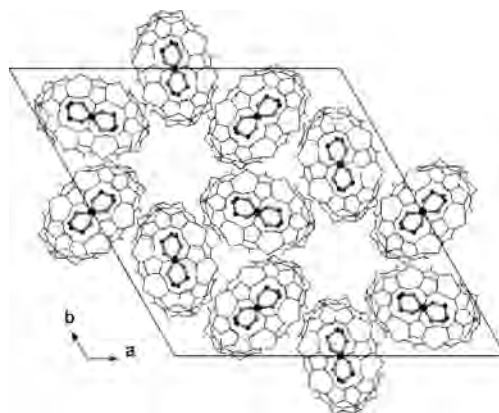


Figure 2. Crystal packing of inclusion compound {*trans*-[Co(tn)₂Cl₂]@CB[8]}·Cl·14H₂O (**1**) (the CB[8] molecule is in gray-wire representation; hydrogen, chlorine atoms and crystallization water molecules are omitted for clarity).

complexes, which are unstable in aqueous solution in the absence of the host.

The cobalt atom in the structure of **1** has an octahedral coordination environment, which consists of two bidentate trimethylenediamine ligands (in the equatorial plane of the guest complex) and two axial chloride ligands (Figure 1). The plane defined by the four nitrogen atoms of the guest cation is almost orthogonal (84.4°) to the equatorial plane of CB[8], so that the axial chlorides are situated within the cavity (part b of Figure 1). Similar orientation has been found in the inclusion compound of CB[8] with *trans*-[Co(en)₂Cl₂]⁺.^{10c} Six-membered *tn*-Co chelate rings in **1** adopt usual chair conformation, as in the free guest complex.¹⁷ Similar to *trans*-[Co(en)₂Cl₂]⁺, the *trans*-[Co(tn)₂Cl₂]⁺ guest exhibits slight shortening of the Co–Cl and Co–N bonds upon inclusion into CB[8] (by ~0.02 Å) (Table 2). Encapsulation of the guest having bulkier trimethylenediamine ligands, as compared to the ethylenediamine complex,^{10c} causes a more significant elliptical distortion of the host molecule from the ideal round shape: the difference between the shortest and longest diameters, measured between opposite CH carbon atoms (Δ_{CH}), is 2.43 Å. The arrangement of CB[8] molecules in the crystal structure of **1** leaves channels running along the *c* axis (approximate diameter of 5.4 Å) (Figure 2), filled with chloride counterions and crystallization water molecules. The water molecules

(14) Werner, A.; Lindenberg, A. *Annalen* **1912**, *386*, 265.

(15) Pearson, R. G.; Boston, C. R.; Basolo, F. J. *Am. Chem. Soc.* **1946**, *75*, 3089.

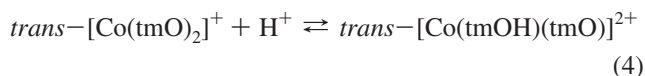
(16) Haworth, D. T.; Neuzil, E. F.; Kittsley, S. L. *J. Am. Chem. Soc.* **1955**, *77*, 6198.

form complicated system of hydrogen bonds with each other and with carbonyl groups of CB[8] portals.

Electrospray mass spectrum of a freshly prepared aqueous solution of **1** proves that the guest complex remains encapsulated inside CB[8] in solution: the spectrum contains intensive peaks of $\{\text{CB}[8] + [\text{Co}(\text{tm})_2]^{2+} + \text{Na}^+\}^{3+}$ and $\{\text{CB}[8] + [\text{Co}(\text{tm})_2]^{2+}\}^{2+}$. The loss of chloride may be caused by high cone voltage under experimental conditions, which caused partial fragmentation of the guest in the ionization gas. The guest complex charge of 2+ can be attributed to possible reduction in the ionization gas.

Synthesis and Structure of $\{\text{trans}[\text{Co}(\text{tmOH})(\text{tmO})]@ \text{CB}[8]\} \text{Cl}_2 \cdot 22\text{H}_2\text{O}$ (2**).** 1,3-diamino-2-propanol (tmOH) displays a great versatility of coordination modes, forming various mono- and polynuclear metal complexes and acting as a tridentate or bidentate ligand with deprotonated or intact OH group.^{18,19} An extensive study of pH-dependent equilibria between different cobalt(III) complexes with 1,3-diamino-2-propanol was reported by Okamoto and Barefield.^{19a}

The initial compound for the syntheses is $\text{trans}[\text{Co}^{\text{III}}(\text{tmO})_2]\text{Cl} \cdot 2\text{H}_2\text{O}$, where the ligand is coordinated to cobalt atom in the tridentate fashion. It is worthwhile to mention that the attempt to dissolve cucurbit[8]uril in aqueous solution of $\text{trans}[\text{Co}(\text{tmO})_2]\text{Cl}$ failed, even when refluxed under a 10-fold excess of the guest complex. However, CB[8] can be completely dissolved in 0.1 M HCl solution of $\text{trans}[\text{Co}(\text{tmO})_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (10-fold molar excess of the guest complex) upon slight heating, which leads to the precipitation of the crystalline compound $\{\text{trans}[\text{Co}(\text{tmOH})(\text{tmO})]@ \text{CB}[8]\} \text{Cl}_2 \cdot 22\text{H}_2\text{O}$ (**2**). It is well established that one ligand in $\text{trans}[\text{Co}(\text{tmO})_2]^+$ in diluted acids recovers H^+ (eq 4).^{19a}



Therefore, it was not unexpected that **2** appeared to be an inclusion compound containing $\text{trans}[\text{Co}(\text{tmOH})(\text{tmO})]^{2+}$ in the cavity of cucurbit[8]uril. The presence of one tmOH ligand was deduced from the charge 2+ of the guest cation (two chloride ions per one guest complex).

The cobalt atom in **2** has a slightly distorted octahedral environment of one tridentate 1,3-diamino-2-propanol and one tridentate 1,3-diamino-2-propanolato-ligand (Figure 3). As site symmetry of the cobalt atom is -1 and the alcoholic hydrogen atom is disordered over two positions, it is impossible to distinguish between tmOH and tmO^- in the crystal structure. The same problem was observed during refinement of the crystal structure of the free $\text{trans}[\text{Co}(\text{tmOH})(\text{tmO})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$.^{19b} The shape of the guest cation resembles a dumbbell, whose main axis (the line through the cobalt atom and tertiary carbon atoms of tmOH mol-

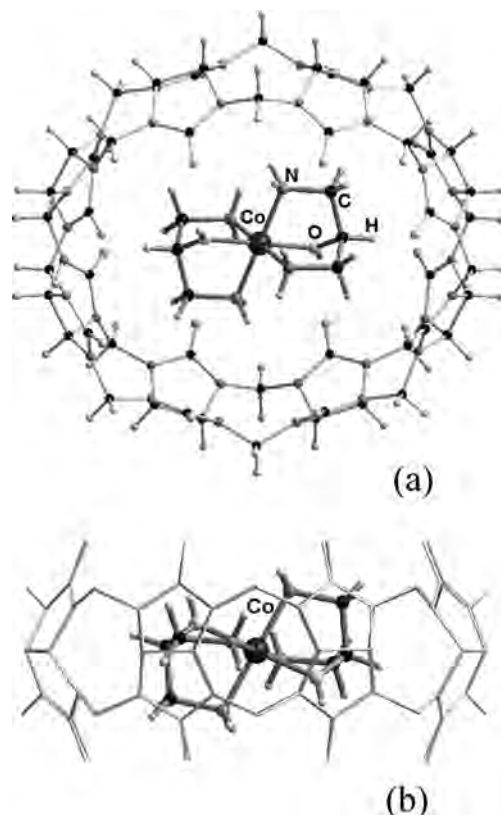


Figure 3. Structure of inclusion complex $\{\text{trans}[\text{Co}(\text{tmOH})(\text{tmO})]@ \text{CB}[8]\}^{2+}$ in **2** (both positions of disordered hydrogen atom are shown): (a) top view and (b) side view (the CB[8] molecule is in gray-wire representation, hydrogen atoms are omitted for clarity).

ecules) virtually coincides with the equatorial plane of the host (the angle between them is 3° , so the dumbbell is completely hidden inside the host cavity). The encapsulation brings slight changes in the geometry of the guest and the host molecules of the complex: two Co–N bonds are slightly contracted (by $<0.01 \text{ \AA}$), Co–O bond becomes longer by $\sim 0.04 \text{ \AA}$ upon inclusion (Table 2), and ellipsoidal distortion of CB[8] is $\Delta_{\text{CH}} = 0.93 \text{ \AA}$.

Crystal packing of **2** is similar to that of **1** (both belong to the same space group $R\bar{3}$) with channels of approximately 2.5 \AA in diameter running along the c axis and filled with chloride ions and crystallization water molecules (Figure 1S in the Supporting Information). These water molecules make a complicated system of hydrogen bonds also involving, besides the water molecules, carbonyl groups of CB[8] molecules, NH_2^- and OH^- groups of diaminopropanol of the guest cations.

Synthesis and Structure of $\{\text{trans}[\text{Ni}(\text{tmOH})_2]@ \text{CB}[8]\} \text{Cl}_2 \cdot 22\text{H}_2\text{O}$ (3**).** Refluxing the mixture of NiCl_2 , tmOH, and CB[8] (molar ratio 10:20:1) in water followed by slow cooling leads to precipitation of pale-violet rhombic platelets of the inclusion compound $\{\text{trans}[\text{Ni}(\text{tmOH})_2]@ \text{CB}[8]\} \text{Cl}_2 \cdot 22\text{H}_2\text{O}$ (**3**).

X-ray crystallographic study revealed that **3** is isotypical to **2**. The cation $\text{trans}[\text{Ni}(\text{tmOH})_2]^{2+}$ is encapsulated into the cavity of CB[8] (Figure 4). The nickel atom is surrounded by two tridentate tmOH molecules, where OH-groups are in the *trans*-position to each other. The dumbbell-shaped guest cation is oriented within the cavity of CB[8] in the

(17) Matsumoto, K.; Ooi, S.; Kuroya, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1903.

(18) Mario, E.; Bolton, S. M. *J. Pharm. Sci.* **1968**, *57*, 418.

(19) (a) Okamoto, M. S.; Barefield, E. K. *Inorg. Chem.* **1974**, *13*, 2611. (b) Kivekas, R. *Acta Chem. Scand. A* **1987**, *41*, 441. (c) Ribas, J.; Monfort, M.; Costa, R.; Solans, X. *Inorg. Chem.* **1993**, *32*, 695. (d) El Fallah, M. S.; Rentschler, E.; Caneschi, A.; Sessoli, R.; Gatteschi, D. *Inorg. Chem.* **1996**, *35*, 3723.

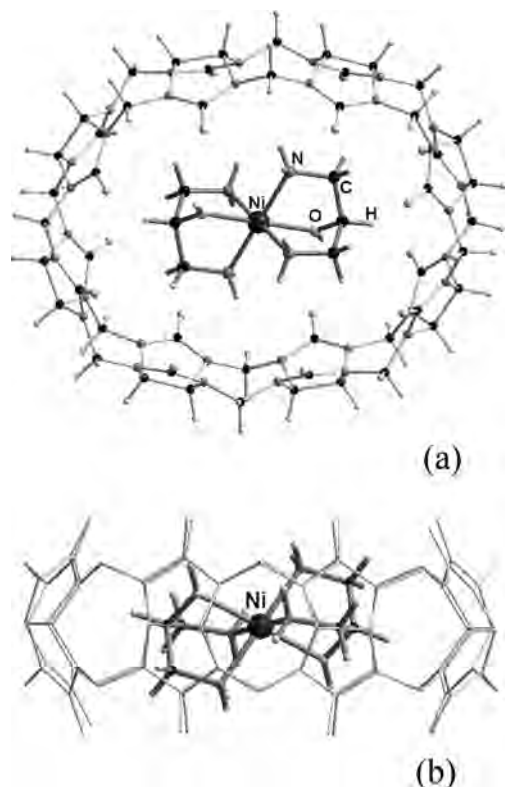


Figure 4. Structure of inclusion complex $\{trans-[Ni(tmOH)_2]@CB[8]\}^{2+}$ in **3**: (a) top view and (b) side view (the CB[8] molecule is in gray wire representation, hydrogen atoms are omitted for clarity).

same manner as in **2**. Encapsulation does not lead to any significant changes in the guest geometry (Table 2), in contrast to dramatic ellipsoidal distortion of the host: $\Delta_{CH} = 2.58 \text{ \AA}$, what, however, is smaller than in the inclusion compound of CB[8] with $trans-[Ni(en)_2(OH)_2]^{2+}$ ($\Delta_{CH} = 2.92 \text{ \AA}$).^{10b} This distortion (in **3**) is significantly larger than that in **2** ($\Delta_{CH} = 0.93 \text{ \AA}$). The reason for this fact cannot be explained solely by the difference in sizes of the guest complexes (the largest van der Waals dimensions of guests are 9.53 and 9.74 \AA for **2** and **3**, respectively).

Crystal packing of **3** is analogous to that of **2** (Figure 2S in the Supporting Information), but the channels are wider in the former case (estimated diameter is 4 \AA) in accordance with larger cell parameters. These channels are occupied by hydrogen-bonded crystallization water molecules and chloride counterions.

According to ESI-MS data, $\{[Ni(tmOH)_2]@CB[8]\}^{2+}$ cations are observed in aqueous solution of **3** (the peak $\{CB[8] + [Ni(tmOH)_2]^{2+} + Na^+\}^{3+}$), revealing high stability of the inclusion compound.

Synthesis and Structure of $trans-[Ni(tmOH)_2](ClO_4)_2$ (4**).** Surprisingly, no X-ray crystal structure investigation of the cation $trans-[Ni(tmOH)_2]^{2+}$ with tmOH performing the tridentate coordination mode has been published, although tetra-^{19c} and heptanuclear^{19d} nickel complexes with bridging 1,3-diamino-2-propanol and other ligands have been reported. We have grown crystals of **4** to compare distances and angles in the free $trans-[Ni(tmOH)_2]^{2+}$ to those in the complex enclathrated within the cucurbit[8]uril cavity. In the crystal structure of **4**, there are two symmetrically independent

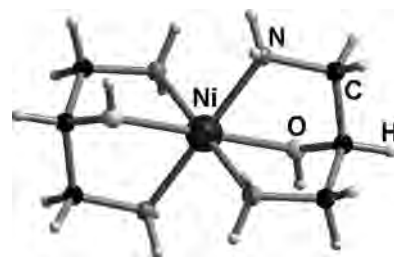


Figure 5. Structure of the cation $trans-[Ni(tmOH)_2]^{2+}$ in **4**.

complex cations (one of them is shown in Figure 5) having minor differences in geometrical parameters (Table 2). The synthetic procedure, crystal packing, UV-vis, and IR spectra for **4** are given in the Supporting Information.

Electrochemical Investigations. Cyclic voltammetry in the solid state is a modern trend in electroanalytical chemistry and is mostly used for investigation of solid films and composite materials.²⁰ This method ideally suits for studying electrochemical behavior of host-guest **1–3** because of their moderate solubility in water and absolute insolubility in other solvents. To the best of our knowledge, this is the first case of using solid state cyclic voltammetry for electrochemical investigation of molecular inclusion compounds.

Representative cyclic voltammetric responses (CVs) for inclusion compounds **1–3** and free guest complexes **1a–3a** ($trans-[Co(tn)_2Cl_2]Cl$, $trans-[Co(tmO)_2]Cl \cdot 2H_2O$, and $trans-[Ni(tmOH)_2](Cl)_2$, respectively) are depicted in Figure 6. It is noteworthy that CVs for inclusion compounds remain undistorted and fully reversible from cycle to cycle, contrary to the free complexes. For the latter, the overall current decreases already after the second cycle, indicating their low stability in the redox processes. In other respects, inclusion into CB[8] does not cause significant changes to the Nernstian (reversible) character of CVs of the free guest complexes, as can be seen from Figure 6. However, overall current levels are almost halved for these three systems upon encapsulation (Table 3), it can be deduced from the ratio of response sensitivities S_a/S for the free (S_a) and encapsulated (S) complexes ($S = I_p/C$, where I_p is the peak current, C is concentration of complex in graphite powder (mmol/g)). This current attenuation is due to the interactions between the host and the guests, leading to the decrease of diffusion coefficients of electroactive forms.

It is worth mentioning that effective diffusion coefficients of electroactive complexes always decrease upon inclusion into macrocyclic cavitands because host-guest complexes diffuse slower to electrode than the free guests.²¹ Such current decrease was observed, for example, upon oxidation of functionalized ferrocene encapsulated within calix[6]-arenesulphonate²² and β -cyclodextrine,²³ and also for reduction of CB[7] inclusion compounds with ferrocenium, cobalticenium^{3,4} and copper complex $\{[Cu(cyclen)(H_2O)$

(20) (a) Scholz, F.; Meyer, B. In *Electroanalytical Chemistry, a Series of Advances*; Bard, A. J., Rubinstein, I., Eds.; Dekker: New York, 1998, p 86. (b) Scholz, F.; Meyer, B. *Chem. Soc. Rev.* **1994**, 23, 341. (c) Zakcharchuk, N. F.; Meyer, B.; Henning, H.; Scholz, F.; Jaworski, A.; Stojek, Z. *J. Electroanal. Chem.* **1995**, 398, 23.

(21) *Comprehensive Supramolecular Chemistry. Physical Methods in Supramolecular Chemistry*, Davies, J. E. D., Ripmeester, J. A., Eds.; Pergamon Press: Oxford, 1996, Vol. 8, pp 512–531.

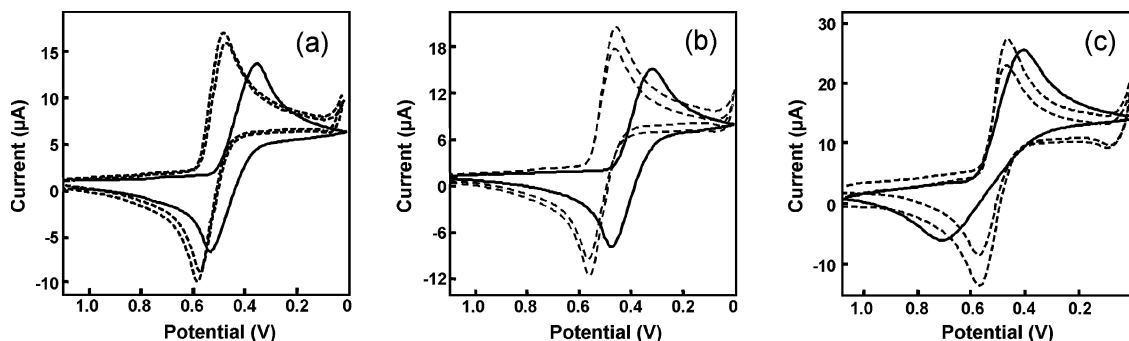


Figure 6. Cyclic voltammograms of inclusion compounds **1–3** (solid lines, second and sixth cycles) and free complexes **1a–3a** (dashed lines, first and second cycles) immobilized at the MPTE surface: (a) 0.70 mmol/g (mmol in 1 g graphite powder, further mmol/g) *trans*-[Co(tn)₂Cl₂]Cl and 1.06 mmol/g *trans*-{[Co(tn)₂Cl₂]@CB[8]}Cl·14H₂O; (b) 0.75 mmol/g *trans*-[Co(tmO)₂]Cl·2H₂O and 1.05 mmol/g *trans*-{[Co(tmO)(tmOH)]@CB[8]}Cl₂·22H₂O; (c) 0.75 mmol/g [Ni(tmOH)₂]Cl₂ and 1.04 mmol/g {[Ni(tmOH)₂]@CB[8]}Cl₂·22H₂O. Electrolyte 0.1 M HCl; scan rate 0.1 V·s⁻¹.

Table 3. Main Electrochemical Parameters for Inclusion Compounds **1–3** and for Free Complexes **1a–3a** (Experimental Conditions are the Same as in Figure 6)^a

System	Parameters					
	S _a /S	E _p ^c	E _p ^a	E _{1/2}	ΔE _{1/2}	K'/K
1/1a	1.87	350/463	530/575	440/519	-79	4.6 × 10 ⁻²
2/2a	2.01	309/457	464/557	368.5/507	-120.5	9.1 × 10 ⁻³
3/3a	1.77	400/458	700/562	550/510	40	4.75

^a Response sensitivity ratio (S_a/S); cathodic (E_p^c), anodic (E_p^a) peak potentials, half-wave potential (E_{1/2}), and shift in the E_{1/2} values (ΔE_{1/2}) in mV; association constants ratio (K'/K).

@CB[8]]²⁺.^{5b} In some cases, inclusion of an electroactive form into the macrocyclic host totally suppresses redox activity of the guest, as it was found for an anthraquinone derivative within the CB[7] cavity,²⁴ and also for a manganese(II) porphyrin complex encapsulated into β-cyclodextrin.²⁵ Nevertheless, for the latter the electrode process can be accelerated using an electron mediator.

The apparent half-wave potential E_{1/2} for the encapsulated *trans*-[Co(tn)₂Cl₂]^{+/0}/*trans*-[Co(tn)₂Cl₂] redox couple (calculated as the mean of the anodic and cathodic peak potentials) is shifted by ΔE_{1/2} = -79 mV to more negative values in comparison with the free redox couple. This significant cathodic shift reveals that the oxidized form of the guest in the redox couple {*trans*-[Co(tn)₂Cl₂]@CB[8]}^{+/0} is more stabilized by encapsulation into the cavity of CB[8]. In other words, reduction of *trans*-[Co(tn)₂Cl₂]⁺ substantially weakens the stability of the host–guest complex. This stability drop can be determined quantitatively from the eq 5:

$$K'/K = \exp(F\Delta E_{1/2}/RT) \quad (5)$$

where K' and K are association constants of the reduced form {*trans*-[Co(tn)₂Cl₂]@CB[8]}⁰ and the oxidized form {*trans*-[Co(tn)₂Cl₂]@CB[8]}⁺, respectively, and ΔE_{1/2} is the shift in the E_{1/2} values for the free and encapsulated complexes. The value K'/K for **1** is 4.6 × 10⁻², thus the oxidized form of the guest is almost 20 times more stable within CB[8].

The system **2/2a** displays electrochemical behavior similar to that of **1/1a**. Electrochemical waves for **2/2a** are shifted toward more cathodic potentials. The value E_{1/2} for the couple *trans*-[Co(tmO)₂]^{+/0}/*trans*-[Co(tmO)₂] undergoes considerable cathodic shift of ΔE_{1/2} = -120.5 mV upon inclusion into CB[8], proving that the oxidized guest *trans*-[Co(tmO)(tmOH)₂]²⁺ in **2** gains considerably larger stabilization on inclusion in cucurbit[8]uril than the reduced guest *trans*-[Co(tmO)(tmOH)₂]⁺. According to (5), K'/K in this case is 9.1 × 10⁻³, therefore the oxidized form of the guest is by almost 100 times more stable within CB[8] than the reduced one.

The complex *trans*-[Ni(tmOH)₂]²⁺, encapsulated within CB[8], undergoes reversible oxidation and the apparent half-wave potential for **3** is also shifted from the value for the free guest **3a**. However, in contrast to the cobalt compounds, inclusion of *trans*-[Ni(tmOH)₂]²⁺ into cucurbit[8]uril leads to anodic shift of ΔE_{1/2} = 40 mV. It means that the inclusion compound with the reduced guest complex *trans*-[Ni(tmOH)₂]²⁺ has a higher stability than that involving the oxidized form. The value K'/K is 4.75 (from the eq 5), showing that both reduced and oxidized form of redox-couple **3** are of about the same order of stability.

It is interesting to compare our results with some electrochemical data for inclusion compounds with CB[n] obtained by cyclic voltammetry in aqueous solutions. Inclusion complexation with cucurbit[n]urils is not solely governed by hydrophobic interactions between the macrocyclic cavitand and a guest. Along with negatively charged areas concentrated around the carbonyl oxygens of the portals, the inner cavity surface of cucurbit[n]urils also bears some negative charge, and this explains strong affinity of cucurbit[n]urils to positively charged guests.⁴ The cathodic shifts for **1** and **2** demonstrate an essential increase in stability of the oxidized form of the guest included in CB[8]. The cathodic shift was observed also for ferrocenium/ferrocene (Fc⁺/Fc, ΔE_{1/2} = -22 mV) and cobaltocenium/cobaltocene (Cob⁺/Cob, ΔE_{1/2} = -9 mV) redox couples in the presence of CB[7], but in these cases the half-wave potential values evidence only minor differences in the stabilities of both forms.³ An anodic shift, similar to that in **3** but of larger magnitude ΔE_{1/2}, was observed for positively charged ferrocene derivatives (Fc*) encapsulated into CB[7] (Fc*²⁺/

(22) Zhang, L.; Macias, A.; Lu, T.; Gordon, J. I.; Gokel, G. W.; Kaifer, A. E. *J. Chem. Soc., Chem. Comm.* **1993**, 1017.

(23) (a) Isnin, R.; Salam, C.; Kaifer, A. *J. Org. Chem.* **1991**, 56, 35. (b) Matsue, T.; Evans, D. H.; Osa, T.; Kobayashi, N. *J. Am. Chem. Soc.* **1985**, 107, 3411.

(24) Sindelar, V.; Parker, S. E.; Kaifer, A. E. *New J. Chem.* **2007**, 31, 725.

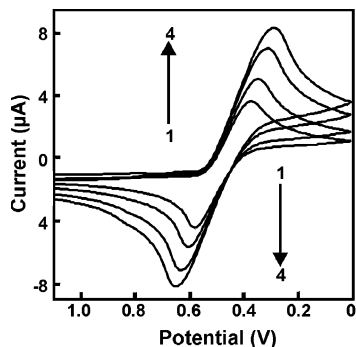


Figure 7. CVs of the inclusion compound **2** (0.4 mmol/g) at scan rates of 0.05 (1), 0.10 (2), 0.20 (3), and 0.30 (4) $\text{V}\cdot\text{s}^{-1}$, electrolyte 0.1 M HCl.

Fc^{*+} , $\Delta E_{1/2} > 100$ mV), indicating that the oxidized species are considerably less stable inside the cavity than the reduced ones.⁴ The decrease in binding ability of the Fc^{*+} form upon oxidation to the Fc^{*2+} form is believed to be related to greater hydrophilicity of the oxidized form or to the failure of the host to get adjusted to spatial arrangement of the two charges of the guest. CV studies of a copper(II) complex $[\text{Cu}(\text{cyclen})]^{2+}$ included into CB[8] also demonstrate a decrease in the stability of the oxidized species upon encapsulation as compared to the reduced form $[\text{Cu}(\text{cyclen})]^{1+}$.^{5b} All these data demonstrate that electrochemical behavior of the inclusion metal complexes with CB[n] is complicated, and the strength of binding between a host and a guest depends on different factors.

CVs for **1/1a**, **2/2a**, and **3/3a** were recorded at variable scan rates. The example of such experiment for the inclusion compound **2** is illustrated in Figure 7. Taking into account that the shape of CV curves for host–guest complexes **1–3** remains fully reversible and undistorted irrespective of the scan rate, in contrast to **1a–3a**, we concluded that electron transfer (et) reactions of **1–3** proceed inside the cavity of cucurbit[8]uril. Such an electron transfer mechanism was observed for cucurbit[7]uril inclusion compounds with metal complexes^{3,4} and with organic guest methylviologen;²⁶ however, it is uncommon for inclusion compounds of other macrocyclic hosts, for instance, cyclodextrins.²³ Electron transfer typically takes place to and from the guest released due to dissociation of an inclusion compound. At shorter

time scales, the inclusion compound cannot dissociate sufficiently fast to produce enough free guests for the et process, thus the resulting voltammograms are distorted. In the case of **1–3**, voltammograms remain reversible and undistorted.

Conclusions

This work shows that cobalt(III) and nickel(II) complexes with 1,3-diaminopropane (tn) and 1,3-diamino-2-propanol (tmOH) form inclusion compounds with the macrocyclic host cucurbit[8]uril. Encapsulation of *trans*- $[\text{Co}(\text{tn})_2\text{Cl}_2]^+$ within the CB[8] cavity preserves the guest cation from the ligand substitution reaction characteristic of its aqueous solutions. Low solubility of obtained inclusion compounds prompted us to investigate their electrochemical behavior by solid-state stripping voltammetry. This is the first attempt to apply stripping solid-state CV to examination of inclusion compounds. The electrochemical study demonstrates that CB[8] prefers the oxidized species in *trans*- $[\text{Co}(\text{tn})_2\text{Cl}_2]^+/\text{trans}$ - $[\text{Co}(\text{tn})_2\text{Cl}_2]^0$ and *trans*- $[\text{Co}(\text{tmO})(\text{tmOH})_2]^{2+}/\text{trans}$ - $[\text{Co}(\text{tmO})(\text{tmOH})_2]^+$ redox couples, but stabilizes the reduced form *trans*- $[\text{Ni}(\text{tmOH})_2]^{2+}$ better than the oxidized species. Reversible and undistorted nature of voltammograms at variable scan rates evidence that electron transfer reactions for the inclusion compounds **1–3** proceed within the cavity of the host.

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Supporting Information Available: Detailed description of experimental procedure for **4** and crystallographic data of **1–4** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(25) Kano, K.; Kitagishi, H.; Sone, Y.; Nakazawa, N.; Kodera, M. *Eur. J. Inorg. Chem.* **2006**, 20, 4043.

(26) Kim, H.-J.; Jeon, W. S.; Ko, Y. H.; Kim, K. *Proc. Nat. Acad. Sci. U.S.A.* **2002**, 99, 5007.