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Jørgensen Complex within a Molecular Container: Selective Encapsulation of *trans*-$[Co(en)_2Cl_2]^+$ into Cucurbit[8]uril and Influence of Inclusion on Guest's Properties

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The unprecedented selective encapsulation of *trans*-$[Co(en)_2Cl_2]^+$ from the mixture of trans and cis isomers into the cavity of macrocyclic cavitand cucurbit[8]uril ($C_{48}H_{48}N_{32}O_{16}$, CB[8]) leads to the inclusion compound {*trans*-$[Co(en)_2Cl_2]$@CB[8]}$Cl\cdot 17H_2O$ (**1**). Single-crystal X-ray analysis, ^1H NMR, and ESI-MS spectra confirm the formation of host–guest complex **1** in both solid state and solution. The geometry of the complex cation alters significantly upon inclusion, which causes appreciable hypsochromic shifts of the absorption bands of the guest complex. According to TGA data, inclusion of *trans*-$[Co(en)_2Cl_2]^+$ dramatically stabilizes the complex toward thermal decomposition. Encapsulation of *trans*-$[Co(en)_2Cl_2]^+$ into the CB[8] cavity also increases the stability of the metal complex toward isomerization into the cis form. The supramolecular adduct {*cis*-$[Co(en)_2(H_2O)_2](CB[8])_6$}$Cl_3\cdot$ca109.5$H_2O$ (**2**) was isolated only after prolonged heating of an aqueous solution of **1** at 120 °C in an evacuated tube; it was characterized by X-ray crystallography, IR, and elemental analysis.

1. Introduction

Inclusion of transition metal complexes into various molecular containers (cyclodextrins, calixarenes, cucurbiturils) represents a rare phenomenon in supramolecular chemistry. The first examples of such host−guest complexes, the inclusion compounds of ferrocene within the cavity of α-, β-, and γ-cyclodextrins, were reported in the 1980s.[1−3] The majority of inclusion compounds with metal complexes known to date exhibits an organometallic complex (metallocenes,[4−6] olefin metal complexes,[7−9] metal alkyls,[10,11] carbonyls[12,13]) encapsulated inside the cavity of a macrocyclic host. Investigation of these types of compounds is very important, because encapsulation can substantially affect the geometry of the guest, its thermal stability,[1,2,8,9,14−19] magnetic

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(1) Harada, A.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 645−646.
(2) Harada, A.; Hu, Y.; Yamamoto, S.; Takahashi, S. *J. Chem. Soc., Dalton Trans.* **1988**, 729−732.
(3) Odagaki, Y.; Hirotzu, K.; Higuchi, T.; Harada, A.; Takahashi, S. *J. Chem. Soc., Perkin Trans.* **1990**, 1230−1231.
(4) Zhang, L.; Macias, A.; Lu, T.; Gordon, J. I.; Gokel, G. W.; Kaifer, A. E. *J. Chem. Soc., Chem. Commun.* **1993**, 1017−1019.
(5) Klingert, B.; Rihs, G. *J. Inclusion Phenom. Macrocyclic Chem.* **1991**, *10*, 255−265.
(6) Turel, I.; Demsar, A.; Kosmrlj, J. *J. Inclusion Phenom. Macrocyclic Chem.* **1999**, *35*, 595−604.
(7) Fornasier, R.; Marcuzzi, F.; Marton, D.; Favero, G.; Russo, U. *J. Organomet. Chem.* **2000**, *605*, 127−133.
(8) Braga, S. S.; Gonçalves, I. S.; Lopes, A. D.; Pillinger, M.; Rocha, J.; Romro, Q. C. C.; Teixeira-Dias, J. J. C. *J. Chem. Soc., Dalton Trans.* **2000,** 2964−2968.
(9) Lima, S.; Gonçalves, I. S.; Ribeiro-Claro, P.; Pillinger, M.; Lopes, A. D.; Ferreira, P.; Teixeira-Dias, J. J. C.; Rocha, J.; Romao, C. C. *Organometallics* **2001**, *20*, 2191−2197.
(10) Luo, L.-B.; Chen, H.-L.; Tang, W. X.; Zhang, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1996**, 4425−4430.
(11) Chen, Y.; Chen, H.-L.; Yang, Q.-C.; Song, X.-Y.; Duan, C.-Y.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1999**, 629−633.
(12) Canuto, H. C.; Heyes, S. J.; Aime, S.; Gobetto, R.; Napolitano, F. *J. Chem. Soc., Dalton Trans.* **2000**, 4075−4077.
(13) Aime, S.; Canuto, H. C.; Gobetto, R.; Napolitano, F. *Chem. Commun.* **1999**, 281−282.
(14) Cunha-Silva, L.; Gonçalves, I.; Pillinger, M.; Xue, W.-M.; Rocha, J.; Teixiera-Dias, J. J. C.; Kuhn, F. E. *J. Org. Chem.* **2002**, *656*, 281−287.
(15) Harada, A.; Yamamoto, S.; Takahashi, S. *Organometallics* **1989**, *8*, 2560−2563.
(16) Harada, A.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1229−230.
(17) Song, L.; Meng, Q.; You, X. *J. Organomet. Chem.* **1995**, *498*, C1−C5.
(18) Chen, Y.; Luo, L.-B.; Chen, H.-L.; Hu, C.; Chen, J.; Zheng, P. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1375−1378.

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and photochemical[20−22] properties, electrochemical behavior,[23−28] and reactivity. Inclusion into macrocyclic hosts may be the best way to stabilize unusual coordination environments and unstable oxidation states of metals, trap short-living reaction intermediates, and solubilize metal complexes in required reaction media. This is highly promising for applications in bioinorganic chemistry[10,11] and pharmaceuticals[29,30] (model systems for biological processes and drug delivery), for selective molecular separation[31,32] (on the basis of shape, size, and charge selectivity of the host along with its hydrophobic−hydrophilic affinity toward various types of guests), and for creation of new homogeneous and heterogeneous catalytic systems.[16,33−35]

The field of our particular interest represents the inclusion of transition metal complexes into large cavitand cucurbit[*n*]uril ($C_{6n}H_{6n}N_{4n}O_{2n}$, CB[*n*]; $n \geq 7$).[29,36] Recent reports in this field have been related to the encapsulation of copper(II) and zinc(II) complexes with the tetraazamacrocyclic ligands cyclen and cyclam in the CB[8] cavity and the investigation of their electrochemical behavior and ligand-substitution reactions;[37] the synthesis and crystal-structure characterization of the host−guest complex between cucurbit[7]uril and *cis*-$[Sn(H_2O)_2Cl_4]$;[38] comprehensive NMR and CV studies of the formation and reactivity of inclusion compounds of ferrocene and its derivatives with CB[7] and their X-ray crystallography.[27,28] A patent was obtained for application of platinum inclusion complex $\{[Pt(1,2\text{-}(NH_2)_2C_6H_{10}\text{-}(C_2O_4)]@CB[7]\}$ as an anticancer drug.[29,30]

Here, we report the synthesis and full characterization of a new compound formed by the inclusion of *trans*-dichlorobis-ethylenediaminecobalt(III) complex into the rigid macrocyclic cavitand cucurbit[8]uril, $\{$*trans*-$[Co(en)_2Cl_2]@CB[8]\}Cl\cdot 17H_2O$ (**1**). Reactivity and thermal properties of compound **1** are also discussed.

2. Experimental Section

General Data. The starting compounds *trans*-$[Co(en)_2Cl_2]Cl$ [39] and cucurbit[8]uril ($C_{48}H_{48}N_{32}O_{16}\cdot 20H_2O$)[40] were synthesized according to procedures published earlier. The IR spectra were recorded using KBr pellets on a Scimitar FTS 2000 spectrophotometer in the 4000−400 cm^{-1} region. The UV−vis spectra were measured on an Ultrospec 3300pro spectrophotometer. The NMR spectra were collected on a Bruker DPX/250 spectrometer. The mass spectra (ESI-MS) were obtained on Quattro LC and QTOF I mass spectrometers (Micromass, Manchester, U.K.). Thermogravimetric studies were done in an argon atmosphere on a Derivatograph Q-1000 (Paulik & Paulik, Hungary) apparatus at a rate of 10 °C min^{-1}. Elemental analysis was carried out by the Novosibirsk Institute of Organic Chemistry's microanalytical service.

Synthesis of $\{$*trans*-$[Co(en)_2Cl_2]@CB[8]\}Cl\cdot 17H_2O$ (1). The solution of *trans*-$[Co(en)_2Cl_2]Cl$ (0.027 g, 0.095 mmol) in water (6.5 mL) was refluxed for 5 min until the color of the solution changed from green to wine red. After cucurbit[8]uril (0.020 g, 0.012 mmol) was added, the resulting solution was refluxed for 2 h and then cooled slowly. The next day, the green rod-shaped crystals of **1** were separated from the solution. They were filtered, washed with a small amount of cold water, and dried in air. Yield: 0.022 g (97% on the basis of cucurbit[8]uril). Product **1** can be recrystallized from hot aqueous solution. Crystals of **1** slowly lose crystallization water into the air. Anal. Calcd for $C_{52}H_{98}Cl_3CoN_{36}O_{33}$: C, 32.52; H, 5.14; N, 26.25; Cl, 5.54. Found: C, 32.48; H, 4.88; N, 26.24; Cl, 5.75. ^1H NMR (250 MHz, D_2O, 25 °C) δ 5.81 (d, 16H), 5.55 (s, 16H), 4.49 (s, broad, 8H), 4.23 (d, 16H), 2.39 (m, 8H). UV−vis (200−1100 nm, aqueous solution), λ (nm) (ϵ (L mol^{-1} cm^{-1})): 383 (17), 454 (11), 602 (15). ESI-MS *m/z* (I): 511 (100%) $[CB[8] + Co(en)_2 + Na]^{3+}$, 517 (13%) $[CB[8] + Co(en)_2 + Na + H_2O]^{3+}$, 523 (15%) $[CB[8] + Co(en)_2 + Na + 2H_2O]^{3+}$, 687 (37%) $[CB[8] + 2Na]^{2+}$, 754 (36%) $[CB[8] + Co(en)_2]^{2+}$, 763 (25%) $[CB[8] + Co(en)_2 + H_2O]^{2+}$, 801 (12%) $[CB[8] + Co(en)_2 + Na]^{2+}$. IR (cm^{-1}): 3524 (s), 3436 (s), 2921 (w), 1723 (s), 1594 (w), 1472 (s), 1426 (m), 1376 (s), 1319 (s), 1228 (s), 1190 (s), 1153 (m), 1051 (w), 1028 (w), 993 (w), 970 (s), 830 (m), 808 (s), 757 (m), 673 (m), 631 (w), 444 (w).

Synthesis of $\{$*cis*-$[Co(en)_2(H_2O)_2](CB[8])_6\}Cl_3\cdot$ca$109.5H_2O$ (2). A solution of **1** (0.0275 g, 0.014 mmol) in water (5 mL) in an evacuated sealed glass ampule was heated for 46 h at 120 °C. Subsequent cooling led to deposition of orange octahedral crystals of **2**. They were filtered, washed with a small amount of cold water, and dried in air. Compound **2** is not soluble in water and slowly loses crystallinity in air. Yield: 0.011 g (45% on the basis of cucurbit[8]uril).

Anal. Calcd for $C_{292}H_{519}Cl_3CoN_{196}O_{207.50}$: C, 34.18; H, 5.10; N, 26.76; Cl, 1,04. Found: C, 34.05; H, 5.00; N, 26.85; Cl, 1.15. IR (cm^{-1}): 3437 (s), 3004 (w), 2923 (w), 1717 (s), 1643 (m), 1475

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(19) Shimada, M.; Harada, A.; Takahashi, S. *J. Organomet. Chem.* **1992**, *428*, 199−205.

(20) Braga, S. S.; Ferreira, R. S.; Goncalves, I. S.; Ribeiroclaro, P.; Pillinger, M.; Rocha, J.; Teixeira-Dias, J. J. C.; Carlos, L. D. *J. Phys. Chem. B* **2002**, *106*, 11430−11437.

(21) Braga, S. S.; Ferreira, R. S.; Goncalves, I. S.; Ribeiroclaro, P.; Pillinger, M.; Rocha, J.; Teixeira-Dias, J. J. C.; Carlos, L. D. *J. Inclusion Phenom. Macrocyclic Chem.* **2002**, *44*, 261−265.

(22) Yang, T.; Qin, W.; Liu, W. *Talanta* **2004**, *62*, 451−456.

(23) Isnin, R.; Salam, C.; Kaifer, A. *J. Org. Chem.* **1991**, *56*, 35−41.

(24) Wang, Y.; Mendoza, S.; Kaifer, A. E. *Inorg. Chem.* **1998**, *37*, 317−320.

(25) Castro, R.; Cuadrado, I.; Alonso, B.; Casado, C. M.; Moran, M.; Kaifer, A. E. *J. Am. Chem. Soc.* **1997**, *119*, 5760−5761.

(26) Gonzalez, B.; Casado, C. M.; Alonso, B.; Cuadrado, I.; Moran, M.; Wang, Y.; Kaifer, A. E. *J. Chem. Soc., Chem. Commun.* **1998**, 2569−2570.

(27) Ong, W.; Kaifer, A. E. *Organometallics* **2003**, *22*, 4181−4183.

(28) D. 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*, 12984−12989.

(29) Lee, J. W.; Samal, S.; Selvapalam, N.; Kim, H.-J.; Kim, K. *Acc. Chem. Res.* **2003**, *36*, 621−630.

(30) Kim, K.; Jeon, Y. J.; Kim, S.-Y.; Ko, Y. H. POSTECH Foundation, South Korea, PCT Int. Appl. 2003, 42.

(31) Li, Y.-M.; Yao, X.-J.; Feng, X.; Wang, X.-M.; Wang, J.-T. *J. Organomet. Chem.* **1996**, *509*, 221−224.

(32) Shimada, M.; Harada, A.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1991**, 263−264.

(33) Alston, D. R.; Slawin, A. M. Z.; Stoddart, S. F.; Williams, D. J. *Angew. Chem., Int. Ed.* **1985**, *24*, 786.

(34) Lewis, L. N.; Sumpter, C. A. *J. Mol. Catal. A: Chem.* **1996**, *104*, 293−297.

(35) Lewis, L. N.; Sumpter, C. A. Proceedings of the 6th International Symposium on Cyclodextrins, Chicago, April 21−24, 1992; Hedges, A. R., Ed.; Ed Santé: Paris, 1993; p 351.

(36) Lagona, J.; Mukhopadhyay, P.; Chakrabarti, S.; Isaacs, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4844−4870.

(37) Kim, S.-Y.; Jung, I.-S.; Lee, E.; Kim, J.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2119−2121.

(38) Lorenzo, S.; Day, A.; Craig, D.; Blanch, R.; Arnold, A.; Dance, I. *CrystEngComm* **2001**, *49*, 1−7.

(39) Jørgensen, S. M. *J. Prakt. Chem.* **1889**, *39*, 18.

(40) Day, A.; Arnold, A. P.; Blanch, R. J.; Snushall, B. *J. Org. Chem.* **2001**, *66*, 8094−8100.

Table 1. Crystal Data and Structure Refinement for **1** and **2**

	1	**2**
empirical formula	$C_{52}H_{98}Cl_3CoN_{36}O_{33}$	$C_{292}H_{519}Cl_3CoN_{196}O_{207.50}$
fw	1920.94	10261.31
T (K)	210(2)	150(2)
cryst syst	monoclinic	tetragonal
space group	$P2_1/c$	$I4_1/a$
a (Å)	22.8936(7)	28.2264(6)
b (Å)	16.4505(5)	28.2264(6)
c (Å)	24.9447(8)	21.7921(8)
β (deg)	105.6930(10)	
V (Å^3)	9044.3(5)	17362.4(8)
Z	4	1.3333
D_{calcd} (Mg/m^3)	1.411	1.308
cryst size (mm^3)	0.30 × 0.24 × 0.20	0.30 × 0.24 × 0.20
no. of reflns collected	64 686	52 479
no. of independent reflns	17 083 [R(int) = 0.0549]	8222 [R(int) = 0.0475]
max. and min. transmission	0.9288 and 0.8958	0.9695 and 0.9547
GOF on F^2	1.163	1.088
final R indices [$I > 2\sigma(I)$]^a	R1 = 0.0596, wR2 = 0.0814	R1 = 0.0546, wR2 = 0.2104
R indices (all data)	R1 = 0.1277, wR2 = 0.0963	R1 = 0.1168, wR2 = 0.2901

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

(s), 1425 (m), 1376 (s), 1319 (s), 1292 (m), 1232 (s), 1192 (s), 1156 (m), 1055 (w), 1028 (w), 993 (w), 970 (s), 831 (m), 809 (s), 759 (m), 675 (m), 631 (w), 445 (w).

X-ray Structure Determinations. The data collection for **1** and **2** was performed on a Bruker Nonius X8Apex diffractometer (MoKα, $\lambda = 0.71073$ 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.[41] Further experimental details are described in Table 1. Decomposition of the crystals did not occur during data collection. The structures were solved by direct methods and refined by the full-matrix least-squares method with SHELXTL.[41] 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 water molecules were not located.

3. Results and Discussion

Synthesis and Structure of {*trans*-[Co(en)$_2$Cl$_2$]@CB-[8]}Cl·17H$_2$O (1). The synthesis of *trans*-$[Co(en)_2Cl_2]^+$ was described for the first time by Jørgensen in 1889.[39] It is well-known that *trans*-$[Co(en)_2Cl_2]^+$ strongly tends to isomerize into the cis form in neutral aqueous solution; this process is especially rapid upon heating. The kinetics of isomerization has been extensively studied by absorption spectroscopy.[42] Besides it, the resulting *cis*-$[Co(en)_2Cl_2]^+$ undergoes ligand substitution of chlorine atoms by aqua ligands, which is substantially faster than it is for the trans isomer.[43] It means that when [*trans*-$Co(en)_2Cl_2]^+$ is heated, the solution will contain the mixture of the forms from eqs 1−3. When, in our experimental conditions, CB[8] is added to the mixture of isomers, the cis forms already predominate. The transformations are accompanied by color changes from emerald green (trans forms) to wine red (cis forms)

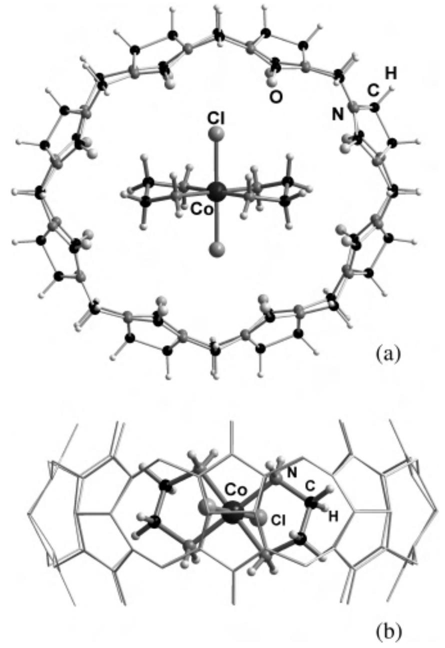

Figure 1. Structure of inclusion complex {*trans*-$[Co(en)_2Cl_2]$@CB[8]}$^+$ (**1**): (a) top view and (b) side view (the CB[8] molecule is in gray wire representation for clarity).

$$\textit{trans}\text{-}[Co(en)_2Cl_2]^+ \rightleftarrows \textit{cis}\text{-}[Co(en)_2Cl_2]^+ \qquad (1)$$

$$\textit{cis}\text{-}[Co(en)_2Cl_2]^+ + H_2O \rightleftarrows \textit{cis}\text{-}[Co(en)_2(H_2O)Cl]^{2+} + Cl^- \qquad (2)$$

$$\textit{cis}\text{-}[Co(en)_2(H_2O)Cl]^{2+} + H_2O \rightleftarrows \textit{cis}\text{-}[Co(en)_2(H_2O)_2]^{3+} + Cl^- \qquad (3)$$

The dissolution of CB[8] in this mixture of isomers followed by 2 h of refluxing and subsequent cooling results in the precipitation of green crystals of {*trans*-$[Co(en)_2Cl_2]$@CB-[8]}Cl·17H$_2$O (**1**) with quantitative yield. The crystals were studied by single-crystal X-ray crystallography and proved to be the compound resulting from the inclusion of cationic complex *trans*-$[Co(en)_2Cl_2]^+$ into the cavity of cucurbit[8]uril (Figure 1). This led us to the assertion that the unprecedented selective encapsulation of only *trans*-$[Co(en)_2Cl_2]^+$ by cucurbit[8]uril occurred from a mixture of both isomers (cis and trans) that contained a large excess of cis forms (see eqs 1 −3). This remarkable selectivity must be due to the excellent matching between the geometries of the host cavity and the trans guest rather than the cis complexes.

The coordination environment of the cobalt atom in **1** exhibits a distorted octahedron (Co atom occupies position with symmetry −1) that is built of four nitrogen atoms of ethylenediamine ligands (in the equatorial plane of the guest complex) and two axial chloride ligands. The plane of the four nitrogen atoms of the guest complex is almost orthogonal to the equatorial plane of the host, so that the axial chlorides are also within the cavity (Figure 1b). This orientation is completely different from those observed in

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(41) *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.

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

(43) Pearson, R. G.; Boston, C. R.; Basolo, F. *J. Phys. Chem.* **1955**, *59*, 304−308.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex *trans*-[Co(en)$_2$Cl$_2$]$^+$ in **1** (types **1A** and **1B**) and "Free" *trans*-[Co(en)$_2$Cl$_2$]Cl·HCl·2H$_2$O

	1A	**1B**	*trans*-[Co(en)$_2$Cl$_2$]Cl·HCl·2H$_2$O [46]
Co−Cl	2.2402(9)	2.2087(11)	2.257(16)
Co−N	1.925(3), 1.920(3)	1.892(3), 2.004(3)	1.951(1), 1.959(2)
N−C	1.461(4), 1.478(4)	1.443(5), 1.451(5)	1.479(1), 1.485(1)
C−C	1.386(5)	1.447(5)	1.505(1)
Cl−Co−Cl	180	180	180
Cl−Co−N	89.73(10)−90.27(10)	89.34(11)−90.66(11)	88.80(1)−91.20(2)
N−Co−N^a	85.77(13)	85.89(15)	85.89(2)
Co−N−C	108.9(2), 108.5(2)	110.6(3), 104.6(3)	108.89(3), 109.83(3)
N−C−C	109.4(3), 110.4(4)	108.9(4), 108.8(4)	106.91(3), 108.08(3)

^{a} Concerning one en ligand.

the inclusion compounds of CB[8] with *trans*-[Cu(en)$_2$(H$_2$O)$_2$]$^{2+}$ and *trans*-[Ni(en)$_2$(H$_2$O)$_2$]$^{2+}$.[44,45] In the latter, the plane of the four nitrogen atoms of the guest almost coincides with the equatorial plane of CB[8] and the axial aqua ligands are directed to the portals. This orientational diversity may be explained by implying that different guests are different sizes and by the fact that the M−Cl and M−H$_2$O bonds have different polarities: whereas chloride is a H-bond acceptor, water is a H-bond donor. Hence, the coordinated water molecules display a weaker affinity toward the hydrophobic CB[8] cavity than the chloride ligands in the encapsulated *trans*-[Co(en)$_2$Cl$_2$]$^+$.

There are two types (**1A** and **1B**) of inclusion complexes of CB[8] with *trans*-[Co(en)$_2$Cl$_2$]$^+$ in the structure of **1**. They have slight differences in the inclination angle of the CoN4 plane toward the equatorial plane of CB[8] (85° for **1A** and 87° for **1B**) and in some geometrical parameters of the encapsulated complex and the CB[8] molecule. For comparison, the data for the free *trans*-[Co(en)$_2$Cl$_2$]Cl·HCl·2H$_2$O[46] complex are shown in Table 2. Upon inclusion into the host cavity, the bond lengths in the first coordination sphere of *trans*-[Co(en)$_2$Cl$_2$]$^+$ distort in two different ways: in **1A**, the Co−N bonds undergo contraction (by ∼ 0.03 Å), whereas in **1B**, two Co−Cl and two Co−N bonds contract by ∼0.06 Å and the other two Co−N bonds are elongated by ∼0.05 Å. The inclusion of the guest is also accompanied by an ellipsoidal distortion of the cavitand molecule; the largest differences in the distances between the opposite carbon atoms of the CH groups of cucurbit[8]uril are 1.43 and 0.78 Å for **1A** and **1B**, respectively, which correlates with the longer Co−Cl distance of the encapsulated complex in **1A**. Such deformation upon the inclusion of guests molecules is typical of cucurbit[*n*]urils when the van der Waals size of the guest is comparable with the size of the host cavity and amounts to 2.92 Å in the inclusion complex of CB[8] with [Ni(en)$_2$(H$_2$O)$_2$]$^{2+}$.[45]

In the crystal structure of **1**, the cations {*trans*-[Co(en)$_2$Cl$_2$]@CB[8]}$^+$ form a two-layer packing, in which the layers from **1A** and **1B** types alternate along the *a* axis (see the Supporting Information, Figure 1S). The equatorial planes of the CB[8] molecules in one layer are parallel to each other, and the angle between the planes of the CB[8] molecules from the adjacent layers is about 56°. The space between the inclusion compounds is occupied by the crystallization water molecules and chloride ions, which unite all structural units of a crystal by an intricate hydrogen-bonding system.

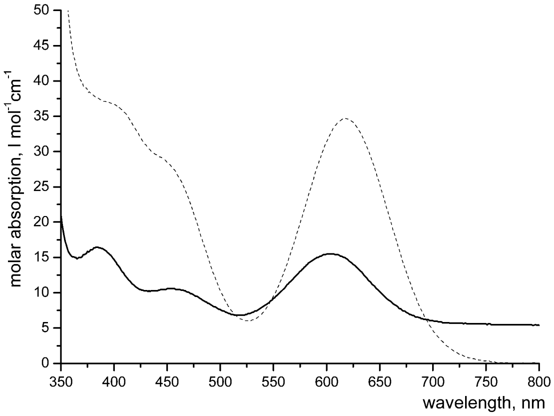

Figure 2. UV−vis spectra comparison of inclusion compound {*trans*-[Co(en)$_2$Cl$_2$]@CB[8]}Cl·17H$_2$O (**1**) and free complex *trans*-[Co(en)$_2$Cl$_2$]Cl (dashed line).

Spectroscopic Characterization and Thermolysis of 1. The electrospray ionization mass spectrum of **1** (see the Supporting Information, Figure 2S) reveals an intense peak assigned to the molecular ion [CB[8] + Co(en)$_2$]$^{2+}$, which shows unequivocally that the metal complex remains encapsulated within CB[8] in aqueous solution. The chloride loss may be due to the high cone voltage at the experimental conditions, which caused partial fragmentation of the guest in the ionization gas. The charge of this fragment is 2+, not 3+, because of possible reduction processes in the ionization gas.

The UV−vis spectrum of the aqueous solution of **1** shows the three absorption bands of the d−d transitions of the guest complex that are typical for octahedral low-spin *trans*-[Co(en)$_2$Cl$_2$]$^+$ (Figure 2).[47] However, the spectrum of **1** reveals a significant hypsochromic shift of the $^1E_g-^1A_{1g}$ band (from 617 to 602 nm), which can be explained by the crystal field enforcement caused by the shortening of Co−N and Co−Cl bonds upon inclusion of the complex. Therefore, it can be concluded that encapsulation into the CB[8] cavity changes the electronic structure of the guest complex. In addition,

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(44) 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., Int. Ed.* **2004**, *53*, 2519−2524.

(45) Mitkina, T. V.; Naumov, D. Yu.; Kuratieva, N. V.; Gerasko, O. A.; Fedin, V. P. *Russ. Chem. Bull., Int. Ed.* **2006**, *55*.

(46) Roziere, J.; Williams, J. M. *Inorg. Chem.* **1976**, *15*, 1174−1178.

(47) Jørgensen, C. K. *Adv. Chem. Phys.* **1963**, *5*, 33.

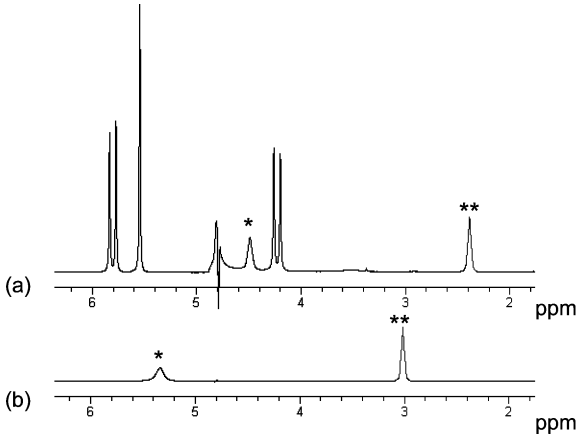

Figure 3. ^{1}H NMR spectra comparison of (a) inclusion compound $\{trans\text{-}[Co(en)_2Cl_2]@CB[8]\}Cl \cdot 17H_2O$ (**1**) and (b) free complex $trans\text{-}[Co(en)_2Cl_2]Cl$ (* = NH_2(en) signals, ** = CH_2(en) signals).

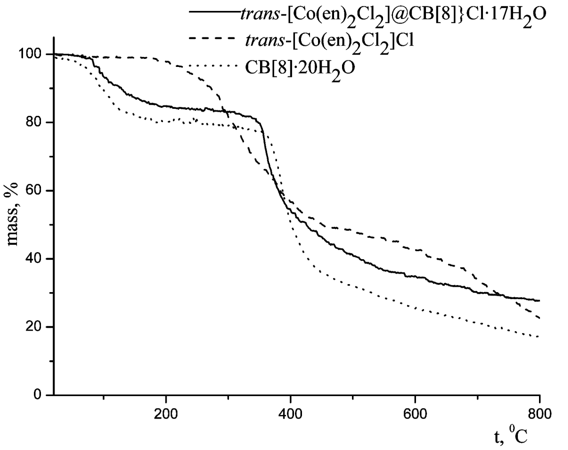

Figure 4. Thermogravimetric analysis in argon of $\{trans\text{-}[Co(en)_2Cl_2]@CB[8]\}Cl \cdot 17H_2O$ (**1**), $trans\text{-}[Co(en)_2Cl_2]Cl$, and CB[8] hydrate.

the inclusion causes an overall considerable decrease in the molar absorption. As there is a correlation between the extinction coefficient of a chromophore and the polarizability of a medium,[48] it can be assumed that for the enclosed cation $trans\text{-}[Co(en)_2Cl_2]^+$, the CB[8] cavity exhibits a significantly less polarizable environment than water, approaching that of the gas phase.

The aqueous solutions of $trans\text{-}[Co(en)_2Cl_2]Cl$ and **1** have been studied by ^{1}H NMR spectroscopy. The resonances of the amine and methylene protons of ethylenediamine ligands are remarkably upfield-shifted upon inclusion ($\Delta_\delta = -0.87$ and -0.63 ppm for NH_2 and CH_2 groups, respectively); the scale of the shifts are among the highest published for inclusion compounds of metal complexes,[4,27,49] which means a considerable host–guest interaction in the case of **1** (Figure 3).

The thermolysis in argon atmosphere was studied for **1** in comparison with that of $trans\text{-}[Co(en)_2Cl_2]Cl$ and CB[8] hydrate (Figure 4). The first step of the mass loss on the thermogravimetric curves for **1** and CB[8] hydrate (beginning at <100 °C) can be ascribed to the total loss of crystallization water molecules. Decomposition of free $trans\text{-}[Co(en)_2Cl_2]Cl$ begins at approximately 220 °C, whereas decomposition of both **1** and CB[8] after the water loss does not start below ~360 °C and is due to the destruction of the cucurbit[8]uril molecule. Hence, the decomposition temperature of the complex increases by at least 140 °C upon inclusion. The encapsulated guest does not undergo thermolysis until its host remains intact, so the host functions here as a "body armor" for the guest. Although a substantial gain in thermal stability of the metal complexes upon inclusion into cyclodextrines was observed in many cases,[1,2,8,9,15–19,34] compound **1** displays the highest increase in decomposition temperature.

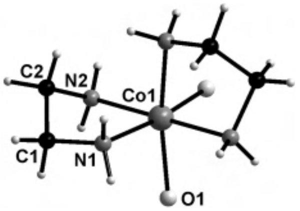

Figure 5. Coordination arrangement of the Co(III) atoms in **2**. Only one of the two disordered position is shown.

Synthesis and Structure of $\{cis\text{-}[Co(en)_2(H_2O)_2](CB[8])_6\}Cl_3 \cdot ca109.5H_2O$ (2). In fact, the behavior of $trans\text{-}[Co(en)_2Cl_2]^+$ changes abruptly upon inclusion into CB[8] not only in the crystalline state but also in solution, for example, toward the isomerization reaction into the $cis\text{-}[Co(en)_2Cl_2]^+$ isomer. As mentioned above, heating an aqueous solution of the free trans isomer leads to a rapid color change from green to red (minutes), whereas **1** is stable in aqueous solution during prolonged refluxing (several hours) and can be recrystallized from such solution; therefore, inclusion into CB[8] strongly reduces the tendency of guest complex $trans\text{-}[Co(en)_2Cl_2]^+$ to isomerize. The transformation of **1** into the cis isomer requires more severe conditions than that of the free complex: only heating an aqueous solution of **1** in an evacuated ampule for 46 h at 120 °C and subsequent cooling leads to the deposition of orange crystals of $\{cis\text{-}[Co(en)_2(H_2O)_2](CB[8])_6\}Cl_3 \cdot ca109.5H_2O$ (**2**). When **1** was heated for only 36 h, a mixture of green crystals of **1** and orange crystals of **2** precipitated, which also confirms the exceptional stability of **1** in aqueous solution.

The formation of supramolecular adduct **2** from inclusion compound **1** can be presumably divided into three main steps: dissociation of **1** (slow; eq 4), followed by the isomerization of released trans complex into cis form (eq 1) and subsequent rapid exchange of chloride ligands to water molecules in cis isomers (eqs 2 and 3)

$$\{trans\text{-}[Co(en)_2Cl_2]@CB[8]\}^+ \rightarrow trans\text{-}[Co(en)_2Cl_2]^+ + CB[8] \quad (4)$$

According to X-ray single-crystal analysis of **2**, the cobalt atom in cationic complex $cis\text{-}[Co(en)_2(H_2O)_2]^{3+}$ has a distorted octahedral environment of four nitrogen atoms of en ligands and two H_2O molecules in the cis position (Figure 5). The N1(O), C1, and C2 atoms of the ligands are disordered over two positions. The average Co–N(O)

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(48) Marquez, C.; Nau, W. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4387–4390.

(49) Mustafina, À. R.; Skripacheva, V. V.; Elistratova, Yu. G.; Kazakova, E. H.; Burilov, À. R.; Konovalov, À. I. *Koord. Khim. (Russ. J. Coord. Chem.)* **1997**, *23*, 609–612.

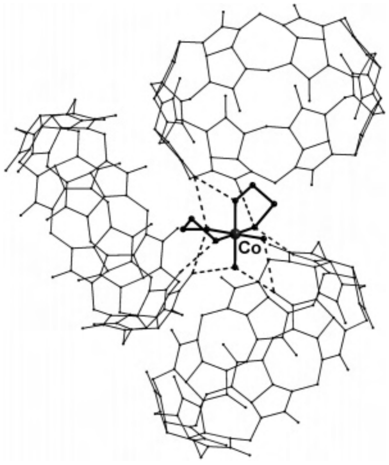

Figure 6. Fragment of the crystal structure of **2**. Only three of the four surrounding CB[8] molecules are shown for clarity. The hydrogen atoms, water solvate molecules, and chloride anions are omitted for clarity. Hydrogen bonds are shown as dashed lines.

distance is 1.99[1] Å. Complex *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ is no longer able to enter the cavity of CB[8]; the crystal structure of **2** represents a packing of cucurbit[8]uril molecules with huge cavities of a nearly tetrahedral geometry between them, which accommodate cation *cis*-$[Co(en)_2(H_2O)_2]^{3+}$. Thus, supramolecular adduct **2** can be referred to as the type of lattice clathrates. An additional stabilizing factor of the structure is the hydrogen bonds between amine ligands, coordinated water molecules of the cobalt complex, and oxygen atoms of the four cucurbit[8]uril molecules that surround the cation (OCB[8]···O(N)Co = 2.53−2.96 Å) (Figure 6).

4. Conclusions

In conclusion, we present here an example of selective isolation of a minor isomer (*trans*-$[Co(en)_2Cl_2]^+$) from the mixture of isomers (cis and trans) via the formation of an inclusion compound with a macrocyclic host (cucurbit[8]uril). The encapsulation within the CB[8] cavity significantly alters the properties of guest cation *trans*-$[Co(en)_2Cl_2]^+$ in both the solid state and solution. Inclusion remarkably increases the thermal stability of the metal complex and blocks its tendency to isomerize into the cis form.

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Supporting Information Available: Figures 1S and 2S, and crystallographic data of **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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