Inorg. Chem. **2003**, *42*, 3576–3581

Electronic Effects in 12-Metallacrown-3 Complexes. A Theoretical and Experimental Study

Marie-Line Lehaire,[†] Axel Schulz,[‡] Rosario Scopelliti,[†] and Kay Severin*[,†]

Institut de Chimie Moléculaire et Biologique, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Suisse, and Department Chemie, Ludwig-Maximilians Universität München, 81377 München, Germany

Received January 16, 2003

The Mulliken charges of the 12-metallacrown-3 complex $[(C_6H_6)Ru(C_5H_3NO_2)]_3$ were determined by a single point analysis at the HF level. For comparison, a Mulliken population analysis was carried out for the organic analogue 12-crown-3. The partial negative charges on the O-donor atoms of the metallamacrocycle were found to be larger than those on the O-donor atoms of 12-crown-3. The 12-metallacrown-3 complex $[(cymene)Ru(C_5H_2ClNO_2)]_3$ with chloro-substituents in position 5 of the pyridonate ligand was synthesized to determine the effect of electron withdrawing groups on the structure and the host–guest properties of the receptor. The chloro-substituents were found to have only a small influence on the structures, but they reduce the binding affinity for LiCl and NaCl by approximately 2 orders of magnitude.

Introduction

Metallacrown complexes are analogues of crown ethers, in which metal atoms constitute an integral part of the macrocyclic framework. Compounds of this kind were first reported in 1989 by Pecoraro et al.[1] Today, metallacrown complexes with ring sizes between 9 and 30 atoms are known.[2,3] They are generally obtained in self-assembly reactions using transition metal salts and suited multidentate ligands. Similar to their organic counterparts, metallacrown complexes can selectively bind metal ions with high affinity.

Recently, we reported the first example of a 12-metallacrown-3 complex (**1**),[4,5] which was obtained in good yield by reaction of $[(cymene)RuCl_2]_2$ with 2,3-dihydroxypyridine in the presence of base. The complex displays a concave geometry. Consequently, the three O-atoms of the 12-membered macrocycle are in close proximity to each other forming an ideal binding site for small cations (Scheme 1 and Figure 1). Lithium and sodium salts such as LiCl and NaCl are bound with extremely high affinity; in chloroform, the binding constants are comparable to those of cryptands. The potential of complex **1** to act as a host for alkali metal salts is underlined by the fact that it can be used to stabilize the elusive molecular form of LiF,[6,7] LiFHF,[6] and Na_2SiF_6.[8]

* To whom correspondence should be addressed. E-mail: kay.severin@epfl.ch. Fax: +41 21 6939305.

[†] École Polytechnique Fédérale de Lausanne.

[‡] Ludwig-Maximilians Universität München.

(1) (a) Lah, M. S.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1989**, *111*, 7258−7259. (b) Lah, M. S.; Kirk, M. L.; Hatfield, W.; Pecoraro, V. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1606−1608. (c) Pecoraro, V. L. *Inorg. Chim. Acta* **1989**, *155*, 171−173.

(2) For reviews see: (a) Pecoraro, V. L.; Stemmler, A. J.; Gibney, B. R.; Bodwin, J. J.; Wang, H.; Kampf, J. W.; Barwinski, A. *Progress in Inorganic Chemistry*; Karlin, K., Ed.; Pergamon Press: New York, 1997; Vol. 45, p 83−177. (b) Bodwin, J. J.; Cutland, A. D.; Malkani, R. G.; Pecoraro, V. L. *Coord. Chem. Rev.* **2001**, *216−217*, 489−512.

(3) For some selected recent references see: (a) Psomas, G.; Stemmler, A. J.; Dendrinou-Samara, C.; Bodwin, J. J.; Schneider, M.; Alexiou, M.; Kampf, J. W.; Kessissoglou, D. P.; Pecoraro, V. L. *Inorg. Chem.* **2001**, *40*, 1562−1570. (b) Dendrinou-Samara, C.; Psomas, G.; Iordanidis, L.; Tangoulis, V.; Kessissoglou, D. P. *Chem. Eur. J.* **2001**, *7*, 5041−5051. (c) Cutland, A. D.; Halfen, J. A.; Kampf, J. W.; Pecoraro, V. L. *J. Am. Chem. Soc.* **2001**, *123*, 6211−6212. (d) Liu, S.-X.; Lin, S.; Lin, B.-Z.; Lin, C.-C.; Huang, J.-Q. *Angew. Chem., Int. Ed.* **2001**, *40*, 1084−1087. (e) Mandal, S. K.; Young, G. V.; Que, L., Jr. *Inorg. Chem.* **2000**, *39*, 1831−1833. (f) Cutland, A. D.; Malkani, R. G.; Kampf, J. W.; Pecoraro, V. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2689−2692. (g) Stemmler, A. J.; Kampf, J. W.; Kirk, M. L.; Atasi, B. H.; Pecoraro, V. L. *Inorg. Chem.* **1999**, *38*, 2807−2817. (h) Saalfrank, R. W.; Löw, N.; Kareth, S.; Seitz, V.; Hample, F.; Stalke, D.; Teichert, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 172−175. (i) Saalfrank, R. W.; Löw, N.; Hampel, F.; Stachel, H.-D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2209−2210. (j) Rauter, H.; Hillgreis., E. C.; Erxleben, A.; Lippert, B. *J. Am. Chem. Soc.* **1994**, *116*, 616−624. (k) Gibney, B. R.; Stemmler, A. J.; Pilotek, S.; Kampf, J. W.; Pecoraro, V. L. *Inorg. Chem.* **1993**, *32*, 6008−6015.

(4) Piotrowski, H.; Polborn, K.; Hilt, G.; Severin, K. *J. Am. Chem. Soc.* **2001**, *123*, 2699−2700.

(5) Piotrowski, H.; Hilt, G.; Schulz, A.; Mayer, P.; Polborn, K.; Severin, K. *Chem. Eur. J.* **2001**, *7*, 3196−3208.

(6) Lehaire, M.-L.; Scopelitti, R.; Severin, K. *Inorg. Chem.* **2002**, *41*, 5466−5474.

(7) For a related LiF complex see: Lehaire, M.-L.; Scopelitti, R.; Severin, K., *Angew. Chem., Int. Ed.* **2002**, *41*, 1419−1421.

10.1021/ic034042a CCC: $25.00
Published on Web 04/30/2003

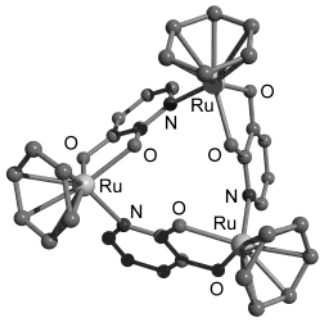
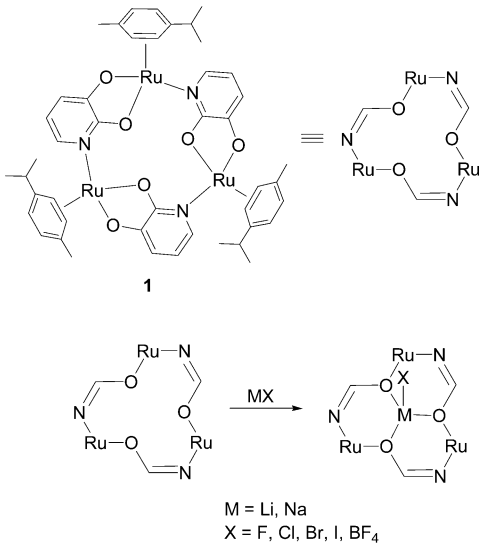
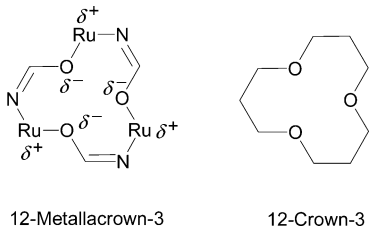


Figure 1. Ball and stick representation of the molecular structure of complex **2** as determined by a single-crystal X-ray analysis.[5] The hydrogen atoms are not depicted.

Scheme 1. A 12-Metallacrown-3 Complex with High Affinity for Lithium and Sodium Salts.



So far, three reasons for the exceptionally high affinity of **1** for Li^+ and Na^+ salts were discussed:[4,5] (a) The receptor **1** is very rigid with the three O-donor atoms being ideally preorganized to bind small cations. (b) The energetic costs for the desolvation of the donor atoms is very small because the binding site is well shielded by the cymene π-ligands. (c) The salts are bound as an ion pair with the anion occupying the fourth coordination site of the Li^+ or Na^+ ion. A fourth contribution is evaluated in this publication. It is known that metal−oxygen bonds can be very polar, even in complexes of the late transition metals.[9] If such a strong polarization is present in complex **1**, the affinity for cationic guests should be increased due to electrostatic reasons. To address this question, we have calculated the Mulliken charges in a 12-metallacrown-3 complex and, for comparison, in a classical 12-crown-3 ether.



The computational study was supplemented by experimental investigations, examining the effect of electron withdrawing groups, which reduce the partial negative charge of the O-donor atoms. The results, which will be discussed in the following section, point to the fact that electronic effects determine to a large extent the host−guest chemistry of 12-metallacrown-3 complexes. This is of general interest, because a similar behavior can be expected for other metallacrown complexes.

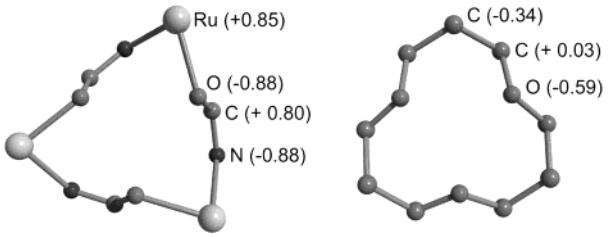


Figure 2. Left: Averaged Mulliken charges of the 12-membered metallamacrocycle of complex **2** as determined by a single point analysis on HF level. Right: Energy minimized geometry and Mulliken charges of 12-crown-3.

Results and Discussion

Theoretical Investigations. To investigate the polarity of metal−oxygen bonds in 12-metallacrown-3 complexes, we have carried out a Mulliken population analysis for the ruthenium complex $[(C_6H_6)Ru(C_5H_3NO_2)]_3$ (**2**). This complex has a structure very similar to that of **1**,[5] but the cymene π-ligands are replaced by benzene ligands to facilitate the calculations (Figure 1).

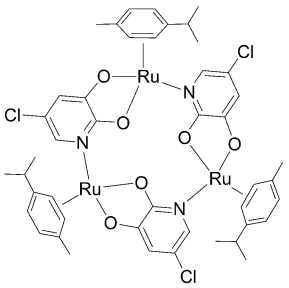
To determine the Mulliken charges, we have fixed the structure of **2** to the one that was determined by single crystal X-ray crystallography.[10] A single point analysis was then performed at the HF level. The averaged[11] charges on the metal and on the bridging pyridonate ligand are depicted in Figure 2. The data suggest that the Ru−O bond is highly polarized with a partial negative charge of −0.88 for the oxygen atom. It is interesting to note that the Ru−N bond is likewise very polar.

For comparison, we have performed a similar calculation for the classical crown ether 12-crown-3, which is known to have a lower affinity for Li^+ and Na^+ ions.[24] Prior to the Mulliken population analysis, a full geometry optimization was performed at the HF level, and the stationary point was characterized to be a minimum by a frequency analysis. The crown ether adopts a geometry where the three oxygen atoms point to the middle of the macrocycle, which is very similar to what was found for the adduct 12-crown-3·LiNCS (Figure 2).[12] The partial negative charge on the O-donor atoms (−0.59) is significantly lower than that found for the metallacrown complex **2**. A similar difference is expected

(8) Lehaire, M.-L.; Scopelitti, R.; Severin, K. *Chem. Commun.* **2002**, 2766−2767.
(9) (a) Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44−56. (b) Holland, P. L.; Andersen, R. A.; Bergman, R. G.; Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1997**, *119*, 12800−12814.
(10) Complex **2** cocrystallizes with one molecule of water, which was included in the calculations.
(11) In the crystal, there is no C_3 symmetry axis for complex **2**.
(12) Dale, J.; Eggestad, J.; Fredriksen, S. B.; Groth, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1391−1393.

for other ionophores such as larger crown ethers and cryptands which contain the same structural feature, that is $-(CH_2)_n-O-$ fragments. Since the O-donor atoms of the receptor **2** are ideally preorganized, the increased negative partial charge is most likely an important contribution to the high affinity of **2** for cationic guests such as Li^+ and Na^+ ions.

Experimental Investigations. In order to address the question of how electronic effects influence the host−guest chemistry of 12-metallacrown-3 complexes, we have synthesized chloro-derivative **3** using commercially available 5-chloro-2,3-dihydroxypyridine and $[(cymene)RuCl_2]_2$ as the starting materials. The electron withdrawing chloro-substituent was introduced because it was expected to slightly reduce the partial negative charge on the O-donor atoms in the *para* position without affecting the overall structure.[13]



3

The analytical data of complex **3** were in agreement with a trinuclear, pseudo-C_3 symmetric structure. As it was found for receptor **1**, complex **3** displays a high affinity for LiCl and NaCl. This was evidenced by the synthesis of adducts **3**·LiCl and **3**·NaCl, which were easily obtained by reaction of **3** with an excess of LiCl or NaCl in methanol. Of special interest, however, were the relative affinities of the receptor **1** and the chloro-substituted derivative **3**. To address this question, we have first performed a direct competition experiment using the two receptors and NaCl. To have precise control over the NaCl concentration, we have prepared the analytically pure adduct **3**·NaCl. This complex was subsequently dissolved in CD_3OD containing an equimolar amount of receptor **1** (3.6 mM each). The ^{1}H NMR spectrum of the resulting mixture showed that the NaCl guest molecule was slowly transferred from receptor **3** to receptor **1**. After equilibration at room temperature for 12 h, four sets of signals were observed which correspond to the two adducts **1**·NaCl and **3**·NaCl and the free receptors **1** and **3**. For one of the methyl groups of the cymene π-ligand, well separated signals were observed. Integration of these signals allowed the calculation of the concentration and therefore of the relative binding constant. It was found that receptor **1** binds NaCl 65 ± 10 times stronger than the chloro-substituted receptor **3**.

(13) To estimate the effect of the chloro-substituent, we have carried out a Mulliken population analysis for a model of ruthenium complex **3**. This model is based on the crystallographic data of **2** where we have substituted the hydrogen atoms in *para* position with Cl atoms using a fixed C−Cl bond length of 1.733 Å. The calculations indicate that the chloro-substituent reduces the partial negative charge of oxygen atoms, which are involved in guest binding, by less than 0.02 e^-.

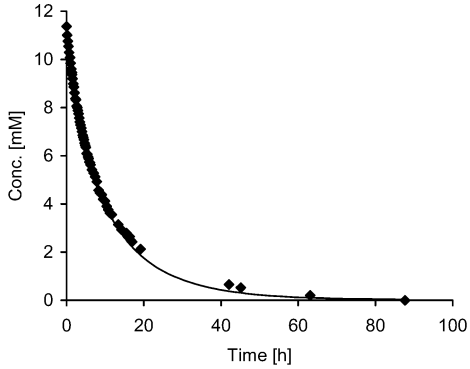


Figure 3. Time course of the concentration of receptor **1** (◆) for the reaction with LiCl to give adduct **1**·LiCl as determined by ^{1}H NMR spectroscopy (CD_3OD; [**1**] = 11.4 mM; [LiCl] = 22.8 mM).

For LiCl as the guest molecule, a similar competition experiment proved to be difficult because of very slow binding kinetics. To investigate this in more detail, we have determined the apparent second order rate constants for the formation of **1**·LiCl using NMR spectroscopy (Figure 3). Analysis of the data using the program *Optimiseur*[14] gave a value of $k_f = 1.6 \pm 0.3 \times 10^{-3}$ M^{-1} s^{-1}. This value is extremely low compared to what has been measured for other ionophores. For the Li^+ specific [2,1,1]-cryptand, for example, a formation rate constant of $k_f = 4.8 \times 10^5$ M^{-1} s^{-1} has been determined in methanol.[15] In view of the fact that the binding constant for **1**·LiCl in CD_3OD has a value of $K \geq 10^5$ M^{-1}, the dissociation rate constant can be estimated to be $k_d \leq 1 \times 10^{-8}$ s^{-1}. It is therefore not possible to perform a competition experiment with LiCl as is already described on a reasonable time scale.

The LiCl binding studies were therefore performed in the more polar solvent mixture CD_3OD/D_2O (5:1) since it is known that lower association constants and faster binding kinetics are observed in aqueous solutions.[16] When the adduct **3**·LiCl was dissolved in this solvent mixture, the slow formation of the free receptor **3** was observed by ^{1}H NMR spectroscopy (Figure 4). From the time course of the reaction, it was possible to deduce the rate constants as well as the binding constant. The following values were obtained: $k_f = 1.1 \times 10^{-1}$ M^{-1} s^{-1}, $k_d = 3.8 \times 10^{-5}$ s^{-1}, and $K = 2.9 \times 10^3$ M^{-1}.

When a similar experiment was performed with **1**·LiCl instead of **3**·LiCl, the dissociation of the guest could not be observed by ^{1}H NMR spectroscopy. This indicates that the stability of **1**·LiCl is significantly higher than that of **3**·LiCl. Given that the concentration of the free receptor under those conditions is less than 3%, the lower limit of the binding constant can be estimated: $K \geq 7.7 \times 10^5$ M^{-1}. The affinity of the chloro-substituted receptor **3** for LiCl is thus at least 270 times lower than that of **1**.

(14) Yerly, F. *Optimiseur 2.3.4*; ICMB, EPFL: Switzerland, 2001.
(15) Cox, B. G.; Garcia-Rosas, J.; Schneider, H. *J. Am. Chem. Soc.* **1981**, *103*, 1054−1059.
(16) Bartsch, R. A.; Ramesh, V.; Bach, R. O.; Shono, T.; Kimura, K. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, R., Eds.: John Wiley & Sons: New York, 1995; pp 393−476.

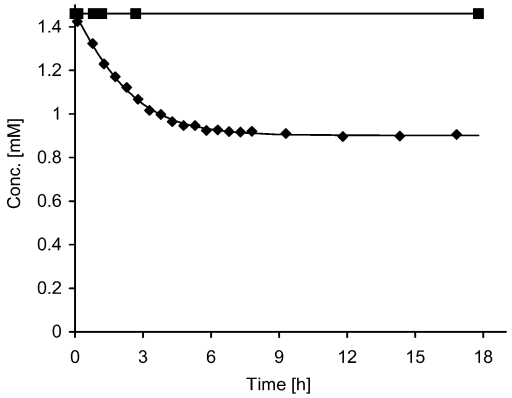


Figure 4. Time course of the concentration of the adducts **1**·LiCl (■) and **3**·LiCl (◆) after dissolving the compounds in CD_3OD/D_2O (5:1) (initial concentration = 1.4 mM).

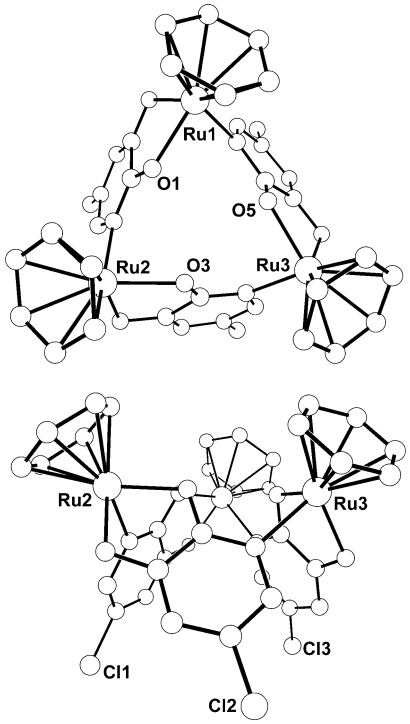


Figure 5. Molecular structure of **3** in the crystal. Top: View along the pseudo-C_3 symmetry axis. Bottom: View from the side. Hydrogen atoms and the side chain of the π-ligand have been omitted for clarity.

To confirm that the changes in affinity of the chloro-substituted receptor **3**, as compared to receptor **1**, are really due to electronic effects and not the result of structural changes, we have carried out single crystal X-ray analyses of complex **3** (Figure 5) and the corresponding adducts **3**·LiCl and **3**·NaCl (Figure 6).

Receptor **3** shows the expected trinuclear, concave geometry with three pyridonate O-atoms positioned in close proximity to each other. The bond length and angles are very similar to those found for **1**, confirming that the chloro-substituent has only a minor influence on the structure (Table 1).

For the LiCl and the NaCl adducts, the alkali metal ion is coordinated to the three adjacent O-atoms of the metallamacrocycle with the fourth coordination site being occupied by the chloride counterion (Figure 6). Again, the structures are very similar to those of **1**·LiCl and **1**·NaCl (Table 1).

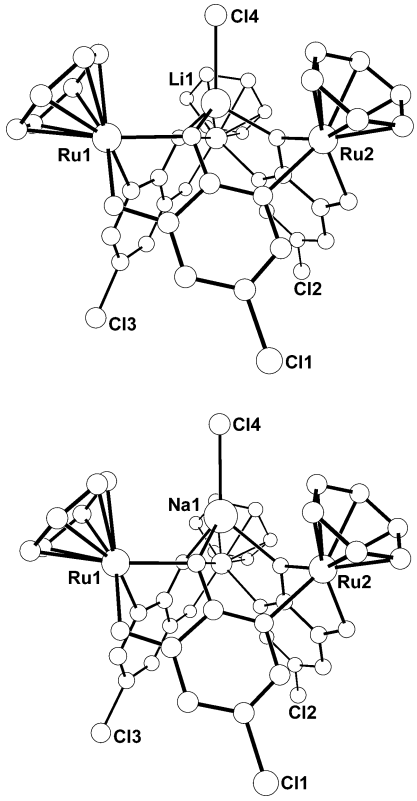


Figure 6. Molecular structure of **3**·LiCl (top) and **3**·NaCl (bottom) in the crystal. Hydrogen atoms and the side chain of the π-ligand have been omitted for clarity.

Although the overall structure of **3**·LiCl resembles that of **3**·NaCl, the geometries around the alkali metal ions show characteristic differences. Whereas the O−Na−O′ angle is relatively small (88.1°), the O−Li−O′ angle (100.1°) is closer to that of a perfect tetrahedral geometry. This is a direct consequence of the longer Na−O bond length (2.24 Å) as compared to the Li−O bond length (1.96 Å). It is interesting to note that the LiCl guest molecule leads to a slight contraction of the binding site as indicated by the reduced O···O′ distances of **3**·LiCl when compared to **3**. The NaCl guest molecule, on the other hand, hardly affects the geometry of the receptor.

Conclusions

A computational study was performed to determine the partial negative charge on the O-donor atoms of a 12-metallacrown-3 complex. On average, a value of −0.88 was obtained which is significantly different from what was determined for a classical 12-crown-3 compound (−0.59). The high negative charge on the donor atoms of the metallamacrocyclic receptor favors the binding of cationic guests such as Li^+ and Na^+ due to electrostatic reasons. This result could be of general importance. It is expected that the M−O bonds of other metallacrown complexes are likewise more polar than the CH_2−O bonds of classical ionophores such as crown ethers and cryptands. If this were the case, metallacrown complexes would have an additional intrinsic advantage: a highly polarized binding site.

The theoretical investigations were supplemented by experiments, performed to determine the effects of electron

Table 1. Selected Bond Lengths [Å] and Angles [deg] for the Complexes **3**, **3**·LiCl, and **3**·NaCl[a]

	Ru−N	Ru−O1	Ru−O2	O1···O1′	Ru···Ru′	M−Cl	M−O1	O1−M−O1′
1[b]	2.13	2.08	2.05	3.09	5.38			
3	2.13	2.08	2.07	3.09	5.27			
1·LiCl[b]	2.14	2.10	2.06	2.97	5.36	2.42	1.95	99.3
3·LiCl	2.14	2.11	2.06	3.01	5.39	2.38	1.96	100.1
1·NaCl[b]	2.14	2.09	2.04	3.11	5.36	2.53	2.23	88.4
3·NaCl	2.15	2.09	2.06	3.13	5.37	2.57	2.24	88.8

[a] For comparison, the corresponding values for complex **1** and its MCl adducts are given (M = Li, Na). Averaged values are given. [b] Values from ref 5.

withdrawing substituents in 12-metallacrown-3 complexes. A rather conservative change,[13] a chloro atom instead of a hydrogen atom in position 5 of the bridging pyridone ligand, was shown to reduce the affinity of the receptor for LiCl and NaCl by approximately 2 orders of magnitude although only very small structural differences were observed. For future applications of metallacrown complexes as specific receptors (e.g., as chemosensors[17]), electronic effects should thus be considered as a powerful tool to modulate the binding affinities.

Experimental Section

General. The synthesis of all complexes was performed under an atmosphere of dry dinitrogen, using standard Schlenk techniques. All solvents (analytical grade purity) were degassed and stored under a dinitrogen atmosphere. The complex [(cymene)Ru($C_5H_3NO_2$)]$_3$ (**1**) was prepared according to literature procedures.[4] 5-Chloro-2,3-dihydroxypyridine was purchased from Lancaster and Cs_2CO_3 from Aldrich. The ^{1}H, ^{13}C, and ^{7}Li spectra were recorded on a Bruker Advance DPX 400 or a Bruker Advance 200 spectrometer using the residual protonated solvents (^{1}H, ^{13}C) as internal standards and LiCl/D_2O (^{7}Li) as the external standards. The spectra were recorded at room temperature.

[(Cymene)Ru($C_5H_2ClNO_2$)]$_3$ (3). A suspension of [(cymene)$RuCl_2$]$_2$ (150 mg, 0.24 mmol), 5-chloro-2,3-dihydroxypyridine (73 mg, 0.49 mmol), and Cs_2CO_3 (399 mg, 1.22 mmol) in methanol (40 mL) was stirred for 2 h at room temperature. During that time, a brown-orange solution was obtained. After evaporation of the solvent under reduced pressure, the product was extracted with dichloromethane (60 mL). Evaporation of the solvent under reduced pressure gave an orange powder (yield: 183 mg, 96%). Crystals were obtained by slow diffusion of pentane into a solution of **1** in benzene. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.33 (d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$), 1.38 (d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$), 1.94 (s, 9 H, CH_3), 2.80 (sept, ^3J = 7 Hz, 3 H, CH(CH_3)$_2$), 5.04 (d, ^3J = 6 Hz, 3 H, CH, cymene), 5.27 (d, ^3J = 6 Hz, 3 H, CH, cymene), 5.49 (d, ^3J = 6 Hz, 3 H, CH, cymene), 5.74 (d, ^3J = 6 Hz, 3 H, CH, cymene), 6.19 (d, ^4J = 2 Hz, 3 H, CH, pyridone), 6.61 (d, ^4J = 2 Hz, 3 H, CH, pyridone). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 18.39, 22.43, 23.69 (CH_3), 31.49 (CH(CH_3)$_2$), 75.54, 79.29, 82.38, 82.61 (CH, cymene), 97.34, 98.20 (C, cymene), 116.24, 117.45, 128.88, 156.89, 170.00 (pyridone). Anal. Calcd (%) for $C_{45}H_{48}N_3O_6Cl_3Ru_3$: C 47.56, H 4.26, N 3.70. Found: C 47.44, H 4.00, N 3.44.

[(Cymene)Ru($C_5H_2ClNO_2$)]$_3$·LiCl. To a solution of an excess of LiCl (131 mg, 3.08 mmol) in methanol (30 mL) was added **3** (70 mg, 62 μmol). The resulting orange solution was stirred for 1 h at room temperature. After evaporation of the solvent under reduced pressure, the product was extracted with dichloromethane (35 mL). Evaporation of the solvent under reduced pressure gave an orange powder (yield: 57 mg, 79%). Crystals were obtained by slow diffusion of pentane into a solution of **3**·LiCl in chloroform. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.25−1.32 (m, br, 18 H, CH(CH_3)$_2$), 1.77 (s, br, 9 H, CH_3), 2.81 (m, br, 3 H, CH(CH_3)$_2$), 5.01 (m, br, 3 H, CH, cymene), 5.81 (d, br, ^3J = 6 Hz, 3 H, CH, cymene), 6.09 (s, br, 3 H, CH, cymene), 6.40 (d, ^4J = 2 Hz, 3 H, CH, pyridone), 6.74 (d, ^4J = 2 Hz, 3 H, CH, pyridone), 6.90 (m, br, 3 H, CH, cymene). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 21.12, 24.87, 26.90 (CH_3), 34.39 (CH(CH_3)$_2$), CH and C (cymene) not detected, 121.70, 122.86, 132.48, 159.03, 169.70 (pyridone). ^{7}Li NMR (156 MHz, $CDCl_3$): δ (ppm) = − 0.1. Anal. Calcd (%) for $C_{45}H_{48}N_3O_6Cl_3Ru_3$·$CHCl_3$·1.5$H_2O$·LiCl: C 41.69, H 3.95, N 3.17. Found: C 41.51, H 3.82, N 2.79.

[(Cymene)Ru($C_5H_2ClNO_2$)]$_3$·NaCl. To a solution of an excess of NaCl (154 mg, 2.64 mmol) in methanol (20 mL) was added **1** (60 mg, 53 μmol). The resulting orange solution was stirred for 1 h at room temperature. After evaporation of the solvent under reduced pressure, the product was extracted with dichloromethane (30 mL). Evaporation of the solvent under reduced pressure gave an orange powder (yield: 51 mg, 81%). Crystals were obtained by slow diffusion of pentane into a solution of **3**·NaCl in chloroform. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.28 (d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$), 1.31 (d, ^3J = 7 Hz, 9 H, CH(CH_3)$_2$), 1.84 (s, 9 H, CH_3), 2.81 (sept, ^3J = 7 Hz, 3 H, CH(CH_3)$_2$), 5.20 (d, ^3J = 6 Hz, 3 H, CH, cymene), 5.75 (d, ^3J = 6 Hz, 3 H, CH, cymene), 5.77 (d, ^3J = 6 Hz, 3 H, CH, cymene), 6.35 (d, ^4J = 2 Hz, 3 H, CH, pyridone), 6.51 (d, ^3J = 6 Hz, 3 H, CH, cymene), 6.69 (d, ^4J = 2 Hz, 3 H, CH, pyridone). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 18.37, 22.03, 23.76 (CH_3), 31.40 (CH(CH_3)$_2$), 75.36, 78.54, 82.90, 83.76 (CH, cymene), 98.77, 99.17 (C, cymene), 118.37, 119.72, 129.46, 156.00, 167.89 (pyridone). Anal. Calcd (%) for $C_{45}H_{48}N_3O_6Cl_3Ru_3$·$CHCl_3$·2$H_2O$·NaCl: C 40.93, H 3.99, N 3.06. Found: C 40.92, H 3.96, N 3.11.

Competition Experiment. An equimolar mixture of **3**·NaCl and **1** (3.6 mM each) in CD_3OD was allowed to equilibrate for 12 h at room temperature. The amount of the free receptors and the corresponding NaCl adducts was determined by integration of the signals for the methyl group of the cymene ligand which are distinguishable and appear at 1.79 (**1**·NaCl), 1.86 (**3**·NaCl), 2.02 (**1**), and 2.08 (**3**) ppm, respectively.

Kinetic Study of the Formation of 1·LiCl. The time course of adduct formation for a mixture of LiCl (22.8 mM) and **1** (11.4 mM) in CD_3OD was followed by ^{1}H NMR spectroscopy. The relative amounts of **1**·LiCl and of the free receptor **1** were determined by integration of suitable signals. To fit the resulting kinetic profile, the program *Optimiseur*[14] was used assuming that the reaction can be described as a reversible complexation of LiCl to **1**. For LiCl, a stock solution was used.

Kinetic Study of the Dissociation of 3·LiCl. The time course of dissociation of **3**·LiCl (1.4 mM) in a mixture of CD_3OD/D_2O (5:1) was followed by ^{1}H NMR spectroscopy. The relative amounts of **3**·LiCl and of the free receptor **3** were determined by integration

(17) For a highly specific 12-metallacrown-3 receptor for Li^+ see: Piotrowski, H.; Severin, K. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4997−5000.

Table 2. Crystallographic Data for Complex **3** and the Adducts **3**·NaCl and **3**·LiCl

	3	**3**·NaCl·$CHCl_3$·$2H_2O$	**3**·LiCl·$CHCl_3$·$1.5H_2O$
empirical formula	$C_{45}H_{48}Cl_3N_3O_6Ru_3$	$C_{46}H_{53}Cl_7N_3NaO_8Ru_3$	$C_{46}H_{52}Cl_7LiN_3O_{7.5}Ru_3$
MW [g mol^{-1}]	1136.42	1350.26	1325.21
cryst size, m^3	0.24 × 0.20 × 0.17	0.25 × 0.22 × 0.15	0.28 × 0.23 × 0.19
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	*C*2/*c*	*C*2/*c*
a [Å]	10.210(5)	19.957(5)	20.041(3)
b [Å]	12.254(3)	16.444(4)	16.332(3)
c [Å]	18.749(10)	32.834(4)	33.167(4)
α [deg]	88.36(3)	90	90
β [deg]	75.90(5)	105.586(15)	106.455(11)
γ [deg]	84.55(3)	90	90
V [$Å^3$]	2264.9(18)	10379(4)	10411(3)
Z	2	8	8
D [g cm^{-3}]	1.666	1.728	1.691
T [K]	140(2)	140(2)	140(2)
abs coeff [mm^{-1}]	1.215	1.284	1.270
Θ range [deg]	3.24 to 24.40	3.21 to 24.41	3.29 to 25.03
index ranges	−11 → 11, −14 → 14, −21 → 21	−23 → 23, −19 → 19, −37 → 38	−23 → 23, −19 → 19, −39 → 39
reflns collected	12818	27887	29623
indep reflns	6998 (R_{int} = 0.1023)	8436 (R_{int} = 0.0598)	8639 (R_{int} = 0.0353)
abs correction	empirical	empirical	empirical
max and min transm	0.6250 and 0.1520	0.5720 and 0.1070	0.3870 and 0.0230
data/restraints/params	6998/0/541	8436/1/628	8639/0/619
GOF on F^2	0.947	1.151	1.150
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0892, wR2 = 0.2269	R1 = 0.0613, wR2 = 0.1656	R1 = 0.0652, wR2 = 0.1727
R indices (all data)	R1 = 0.1380, wR2 = 0.2668	R1 = 0.0875, wR2 = 0.1858	R1 = 0.0807, wR2 = 0.1917
largest diff peak/hole [e $Å^{-3}$]	1.881/−0.994	0.720/−1.413	1.068/−1.934

of suitable signals. When a similar experiment was performed with **1**·LiCl instead of **3**·LiCl, the formation of **1** could not be detected by ^1H NMR spectroscopy.

Crystallographic Investigations. The relevant details of the crystals, data collection, and structure refinement are listed in Table 2. Diffraction data were collected at 140 K, using the Mo Kα radiation, with a mar345 imaging plate detector system. Data reduction was performed with CrysAlis RED 1.6.9.[18] Absorption correction was applied to all data sets using an empirical method (DIFABS).[19] Structure solutions were determined with ab initio direct methods.[20] All structures were refined using full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the "riding model" with $U_{iso} = aU_{eq}(C)$ (where *a* is 1.5 for methyl hydrogen atoms and 1.2 for others, C is the parent carbon atom). Space group determination, structure refinement, and geometrical calculations were carried out on all structures with the SHELXTL software package, release 5.1.[21] Complex **3**·NaCl crystallizes with two molecules of water, both of which are disordered, and one molecule of chloroform. The terminal chloride ion shows close contacts to the $CHCl_3$ molecule and to one of the water molecules (Cl···O = 3.11(2) Å; Cl···$HCCl_3$ = 2.32 Å; Cl···H−C = 170.0°).

Computational Methods. Computations have been carried out using the Gaussian98 program suite.[22] A 6-31G(d,p) standard basis set was applied for all atoms, except for ruthenium, for which a multielectron adjusted quasirelativistic effective core potential (electronic configuration Ru: [Ar]$3d^{10}$) and a (8s7p6d)/[6s5p3d] valence basis set (311111,22111,411) were used. Both the pseudopotentials and the corresponding basis sets were those of the Stuttgart group (ECP28MWB).[23] For 12-crown-3, a full geometry optimization was carried out at the HF level, and the stationary point was characterized by a frequency analysis. Mulliken population analysis for ruthenium complex **2** was carried out with the structure fixed at that determined by single crystal X-ray analysis (single point at HF level). Mulliken population analysis for the 12-crown-3 ether was carried out with the optimized geometry.

Acknowledgment. This work was initiated by a discussion with Prof. R. G. Bergman, and we are grateful for his comments. The project was supported by the Swiss National Science Foundation and by OMG.

Supporting Information Available: Crystallographic data in CIF format of the complexes **3**, **3**·LiCl, and **3**·NaCl. This material is available free of charge on the Internet at http://pubs.acs.org.

IC034042A

(18) *CrysAlis RED 1.6.9*; Oxford Diffraction Ltd: Abingdon, Oxfordshire, U.K., 2001.
(19) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158−166.
(20) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.
(21) Sheldrick, G. M. *SHELXTL*; University of Göttingen: Göttingen, Germany, 1997; Bruker AXS, Inc.: Madison, WI, 1997.
(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.
(23) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.
(24) Fredriksen, S. B.; Dale, J. *Acta Chem. Scand.* **1992**, *46*, 1188−1194.