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| 13. ABSTRACT (Maximum 200 words) Interaction of some 8-hydroxyquinoline-substituted and related ligands (see Figure 1) with various metal ions was evaluated by a calorimetric titration technique at 25 °C in MeOH. Bis-(8-hydroxyquinoline-2-ylmethyl)-substituted ligand 13 forms a very strong complex with Ba²⁺ (log K = 11.6 in MeOH) and is highly selective for Ba²⁺ over Na⁺, K⁺, Zn²⁺ and Cu²⁺ (selectivity factor > 10⁶). The ¹H NMR spectral studies of the Ba²⁺ complexes with bis-(8-hydroxyquinoline-2-ylmethyl)- and bis(5,7-dichloro-8-hydroxyquinoline-2-ylmethyl)-substituted diaza-18-crown-6 ligands (13 and 10) suggest that these complexes are cryptate-like structures with two overlapping hydroxyquinoline rings forming a pseudo second macroring. | | | | |
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Technical Report No. 15

**Metal Ion Complexation Studies of Novel 8-Hydroxyquinoline-Containing
Diaza-18-Crown-6 Ligands and Analogues**

by

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Table 1. Log K , ΔH (kJ/mol), and $T\Delta S$ (kJ/mol) Values for Interactions of Macrocyclic Ligands with Metal Ions in Methanol Solution at 25.0 °C

| ligand | cation | log K | ΔH | $T\Delta S$ |
|----------------------|------------------|------------------|-------------|-------------|
| 1^a | Na ⁺ | 2.89 | -14.1 | 2.4 |
| | K ⁺ | 3.39 | -24.4 | -5.0 |
| | Mg ²⁺ | 6.82 | -2.5 | 36.4 |
| | Ba ²⁺ | 3.60 | -11.6 | 8.9 |
| | Zn ²⁺ | 5.12 | -114 | -85 |
| | Cu ²⁺ | 10.1 | -92.5 | -34.9 |
| | Co ²⁺ | 5.14 | -91.1 | -61.8 |
| 2^a | Na ⁺ | 3.74 | -26.4 | -5.1 |
| | K ⁺ | 6.61 | -58.1 | -20.4 |
| | Mg ²⁺ | b | | |
| | Ca ²⁺ | 4.71 | -25.2 | 1.7 |
| | Sr ²⁺ | 4.67 | -24.6 | 2.1 |
| | Ba ²⁺ | 12.2 | -76.1 | -6.5 |
| | 4 | Mg ²⁺ | 5.7 ± 0.2 | 10.7 ± 0.9 |
| Co ²⁺ | | 3.91 ± 0.08 | -91.2 ± 0.5 | -68.9 |
| 5 | Mg ²⁺ | 5.02 ± 0.08 | 13.9 ± 0.9 | 42.6 |
| | Co ²⁺ | 3.96 ± 0.06 | -84.5 ± 0.5 | -61.9 |
| 6 | K ⁺ | b | | |
| | Ba ²⁺ | 3.57 ± 0.06 | -29.4 ± 0.7 | -9.0 |
| | Zn ²⁺ | 4.80 ± 0.08 | -64.8 ± 0.6 | -37.4 |
| | Cu ²⁺ | 5.01 ± 0.07 | -57.6 ± 0.6 | -29.0 |

...Continuation of Table 1

| ligand | cation | log K | ΔH | $T\Delta S$ |
|--------|------------------|--------------------------|--------------------------|-------------|
| 8 | Na ⁺ | ~3 ^c | ~-5 ^c | |
| | K ⁺ | 3.52 ± 0.03 | -31.2 ± 0.4 | -11.1 |
| | Ba ²⁺ | 4.22 ± 0.05 | -19.2 ± 0.8 | 4.9 |
| | Zn ²⁺ | > 5.5 | -19.0 ± 0.5 | > 12.4 |
| | Cu ²⁺ | 4.28 ± 0.09 | -55.3 ± 0.7 | -30.9 |
| 13 | Na ⁺ | 3.65 ± 0.01 | -25.3 ± 0.2 | -4.5 |
| | K ⁺ | 5.88 ± 0.04 ^d | -55.6 ± 0.7 ^d | -22.0 |
| | Ba ²⁺ | 11.6 ± 0.2 ^d | -73.0 ± 0.5 ^d | -6.8 |
| | Zn ²⁺ | 4.92 ± 0.07 ^c | -95.7 ± 0.6 | -67.6 |
| | Cu ²⁺ | 4.39 ± 0.09 | -100 ± 1 | -74.9 |
| 14 | Na ⁺ | 3.02 ± 0.05 | -20.0 ± 0.6 | -2.8 |
| | K ⁺ | 3.82 ± 0.02 | -47.8 ± 0.3 | -26.0 |
| | Ba ²⁺ | 4.87 ± 0.04 | -26.4 ± 0.4 | 1.4 |
| | Zn ²⁺ | 4.80 ± 0.08 | -64.8 ± 0.6 | -37.4 |
| | Cu ²⁺ | (Brown Precipitate) | | |

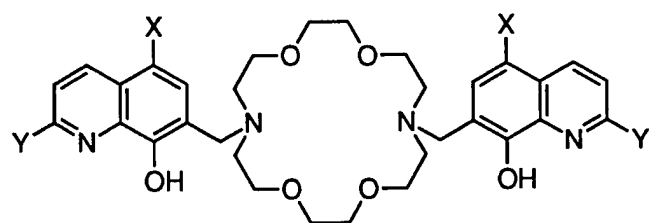
^a Bordunov, A. V.; Bradshaw, J. S.; Zhang, X. X.; Dalley, N. K.; Kou, X.-L.; Izatt, R. M. *Inorg. Chem.* 1996, 35, 7229.

^bNo measurable heat other than heat of dilution indicating that ΔH or/and log K is small.

^cEstimated by a competitive calorimetric titration with Zn²⁺.

^dDetermined by a competitive calorimetric titration.

^eWhen [Zn²⁺]/13 ≥ 2, a white precipitate formed.

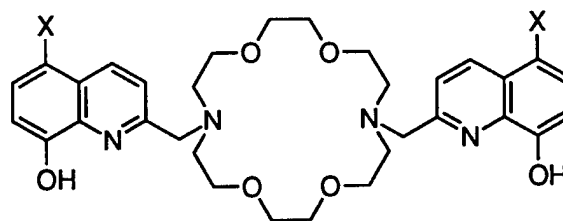


1 X = Cl, Y = H

4 X = Y = H

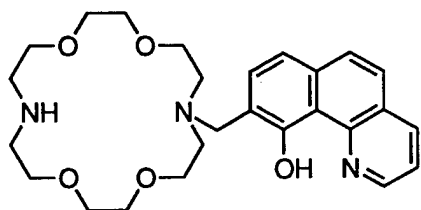
5 X = CH₃, Y = H

6 X = H, Y = OH

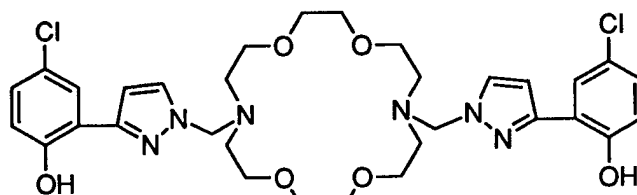


2 X = Cl

13 X = H



8



14

Figure 1. 5-Chloro-8-hydroxyquinoline(CHQ)-substituted Diaza-18-crown-6 Ligand Analogues of **1** and **2** Used in this Study