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SYNTHESIS AND PROPERTIES OF A NOVEL CAVITY-FORMING LIGAND-SYSTEM
BASED ON DIPHENYLGLYCOLURIL

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Abstract: The synthesis of a tetraimidazoly1 ligand is described. Coordination to a metal centre affords a metallocryptand.

Enzymes are able to bind substrates selectively in an intramolecular cavity and position them favourably to an active centre. There is considerable interest in the design and construction of artificial systems which mimic these properties.1

In the present paper, we describe the synthesis of a molecule containing a cavity that is formed by coordination of a tetrapus ligand to a metal ion. The ligand is based on a glycoluril unit which has a rigid, bent configuration. Two phenyl substituents shield the convex side of this unit (la).

Reaction of diphenylglycoluril (la)2 with paraformaldehyde in DMSO, using base as catalyst, yields the tetrahydroxymethyl derivative lb (85%). The latter compound was reacted with 2-(2-chloroethoxy)ethanol in toluene using p-toluenesulfonic acid as catalyst. Subsequently, the product of this reaction was treated with sodium imidazolate in DMF to give the macroligand lc as an oil (80%).3

\[ a, R = H \]
\[ b, R = CH_2OH \]
\[ c, R = CH_2(OCH_2CH_2)_2N \]
Treatment of 1c with RhCl₃·3H₂O in methanol gave the metallocryptand [Rh(lc)Cl₂]Cl (2) in 57% yield. The proposed structure of this compound is confirmed by elemental analysis (C₄₈H₆₂N₁₂O₁₀Cl₃Rh), FAB mass spectroscopy (m/e 1162 (M - Cl + Na⁺)⁺), conductivity measurements (1:1 electrolyte, Λ = 72 ohm cm mol⁻¹)⁴ and ¹H NMR analysis. The presence of two covalently bound trans chlorines is in agreement with the structure of [RhL₄Cl₂]ClO₄ (L = N-methylimidazole)⁶.

Addition of 2, dissolved in methanol to an excess of diethylether caused the complex to precipitate as a yellowish solid. According to ¹H NMR the precipitate contained exactly one equiv. of diethylether, which could not be removed by heating under vacuum (0.01 Torr) for 15 hours. We propose that the ether molecule is trapped inside the cavity which is defined by the glycoluril unit, the four ligating side arms, and the metal centre. Also a CPK model of 2 demonstrates that an ether molecule can be accommodated in the cavity. Complexation experiments in methanol indicate that charged guest molecules such as Li⁺, Na⁺, NH₄⁺, etc. are not bound by complex 2, probably because of electrostatic repulsion by the rhodium centre.

Reaction of the macroligand 1c with Pd(CH₃CN)₂Cl₂ in methanol yields a complex (78%) analyzing as C₄₈H₆₂N₁₂O₁₀Cl₂Pd. The structure [Pd(lc)]Cl₂ (3) is supported by FAB and FD mass spectroscopy (m/e 1107 (M - Cl)⁺, 1072 (M - 2Cl⁺)⁺), conductivity measurements (1:2 electrolyte, Λ = 116 ohm cm⁻¹ mol⁻¹),⁵ and ebulliometry (1:2 electrolyte, M = 1125 ± 75 in methanol).
The spectroscopic properties of complex 3 differ appreciably from those of complex 2. For instance, in the $^1$H NMR spectrum of 3, the CH$_2$Im-protons appear as an AB quartet split into triplets, implicating the protons to be chemically non-equivalent. In the rhodium complex these methylene protons show the expected AA'BB' pattern (Fig. 1). Another remarkable difference is that complex 3 does not bind guest molecules. We explain these features by the fact that in 3 no coordinated chloride is present in the cavity. The tetrapus ligand now has the possibility to stabilize the Pd(II) ion internally. CPK-models indicate that such an internal stabilization forces the molecule to take on a twisted conformation. In this structure the Pd(Im)$_4$-part is rotated either clockwise or counter-clockwise, with respect to the glycoluril unit. In this way a chiral structure is created. The $^1$H NMR spectrum of 3 remains unaltered even at temperatures as high as 60 °C, indicating this twisted chiral structure to be relatively stable. It also shows that the two enantiomeric forms do not interconvert rapidly.
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References

(c) J.M. Lehn, Science, 227, 849 (1985)
3. All new compounds gave spectroscopic and analytical data consistent with their structures.
5. Conductivity measurements were performed in dry methanolic solutions (10^{-3} \text{ mol.dm}^{-3}) at 25^\circ\text{C}. Under these conditions the conductivity of the Cl^{-} ion is 41 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}; \text{cf. R.A. Robinson and R.M. Stokes, "Electrolyte Solutions"}, Butterworths, London 1959, p. 162.

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