Tetrahedron Letters, Vo..22, No.44, pp 4407 - 4408, 1981
Printed in Great Britain

0040-4039/81/444407-02$02.00/0

SYNTHETIC MACROCYCLIC LIGANDS. IV.1) LITHIUM ION-CHARACTERISTIC COLORATION OF A "CROWNED" DINITROPHENYLAZOPHENOL

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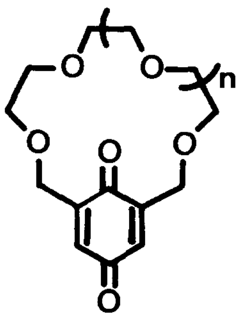
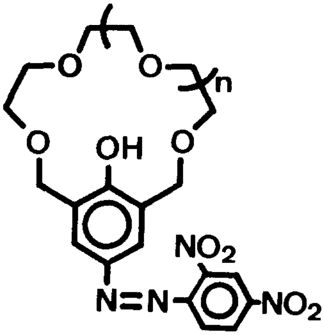
Summary: A "crowned" dinitrophenylazophenol shows a characteristic coloration only with lithium ion of alkali metal ions, as if an indicator.

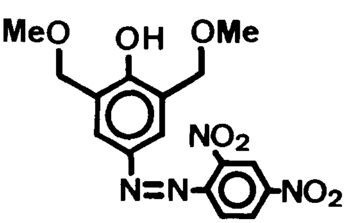
Recently we have reported the synthesis of "crowned" quinone-hydroquinone redox system **1n**.1) The 2,4-dinitrophenylhydrazones of **1n**, which were determined to exist only in another tautomer "crowned" dinitrophenylazophenols **2n**2) by NMR study, are of interest for the following reasons: 1) cation selectivity by cyclic polyethers with different size of cavity, 2) effect of azophenolate anion on the stability of resulting metal complexes, and 3) cation-dependent coloration.3) We now report on a characteristic coloration of 2_1 (**2n**, n=1) with lithium salts of various alkali metal salts.



1n



2n



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A number of preliminary examinations showed the coloration of 2_1 and a reference, non-crowned azophenol 32) with various salts to be very sensitive to the experimental conditions. The lithium-characteristic coloration was observed as follows. Thus, when crystalline lithium chloride or perchlorate was added to a yellow solution of 2_1 in chloroform in the presence of pyridine, dramatic color change to purple-red took place rapidly, as shown in the figure. On the other hand, the addition of other alkali metal salts showed no color change. Non-crowned azophenol 3 was ionically inactive with all alkali metal salts under the same conditions.

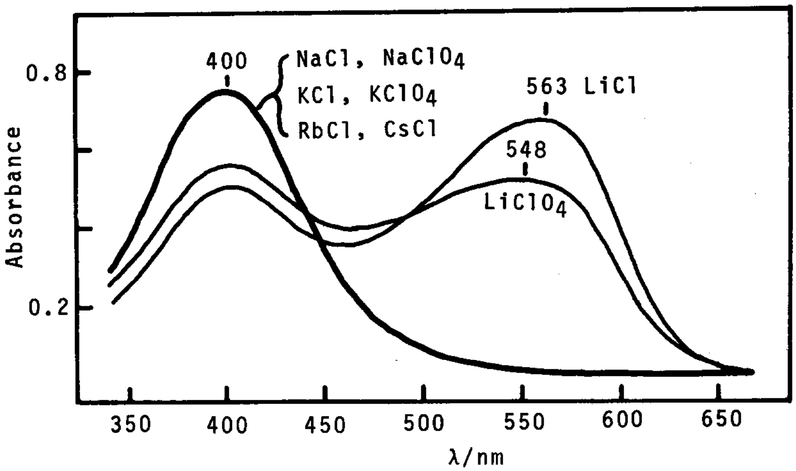

Figure Electronic spectra of 2_1-metal salt-pyridine systems (1:1300:800) in $CHCl_3$.

Since the phenol group of 2_1 shows no dissociation in chloroform-pyridine, the formation of colored lithium phenolate indicates that the dissociation of phenol 2_1 complexed with salts is assisted by coordination of the complexed metal cation. In other words, the observed lithium ion-characteristic coloration is strongly dependent on various factors, e.g., cavity of crown ether unit, acidity of azophenol, basicity of added amine, and polarity of solvent.

A series of alkaline earth metal salts were also examined and gave fairly complicated data. We will report this result elsewhere.

References and Note

1) Part III: K. Sugihara, H. Kamiya, M. Yamaguchi, T. Kaneda, and S. Misumi, Tetrahedron Lett., 22, 1619 (1981).

2) All new compounds show satisfactory elemental analyses and spectral properties. 2_1: reddish orange crystals from EtOH, mp 167.5-168.5 °C, λmax (log ε in $CHCl_3$) 400 nm (4.37). 2_2: orange long plates from MeOH, mp 109.5-110 °C. 3: purplish red needles from EtOH, mp 123-124.5 °C, 400 nm (4.37); azo/hydrazone forms = 58.8/41.2 in $CDCl_3$ by ^{1}H-NMR.

3) cf: J. P. Dix and F. Vögtle, Angew. Chem. Int. Ed. Engl., 17, 857 (1978); Chem. Ber., 113, 457 (1980); ibid., 114, 638 (1981).

(Received in Japan 16 July 1981)