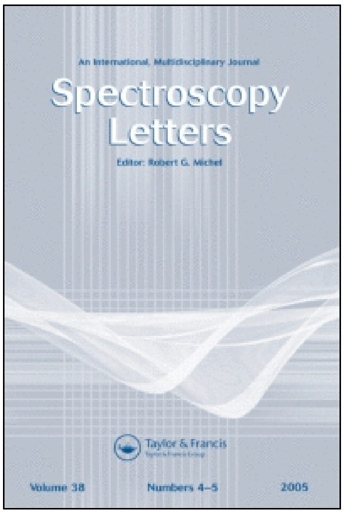

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Spectroscopic Evidence of The Formation of New Kryptand K22C2

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To cite this Article Salman, Salman R. , Petros, Amal G. and Jalhoom, Muayed G.(1992) 'Spectroscopic Evidence of The Formation of New Kryptand K22C2', Spectroscopy Letters, 25: 2, 163 — 174
To link to this Article: DOI: 10.1080/00387019208020684
URL: http://dx.doi.org/10.1080/00387019208020684

SPECTROSCOPY LETTERS, 25(2), 163-174 (1992)

Spectroscopic Evidence of The Formation of New Kryptand K22C2

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Abstract

Diaza-18-crown-6, K22, react with dichloroethane solvent to form a new Kryptand K22C2 with a bridge head. ^{13}C NMR and UV spectra give further evidence of the formation of the new Kryptand. It was found that K22 dissolved in dichloroethane react with the solvent to form a new kryptand K22C2 and a precipitate form which was identified as the salt of K22C2.

Introduction

Aza crown including kryptofix-22 (K22) were the subject of several studies(1-9). These compounds were used to prepare

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bicyclic and tricyclic cryptand$^{(10-16)}$. It was found that these compounds bind metal ions with higher ion selectivity. For this reason a considerable attention have been paid to these compounds$^{(17)}$. In recent communication$^{(18)}$ it was noticed that the distribution coefficient of TCO_4^- ions in the system K22-dichloroethane/$M^n(OH)_n$ increased in the aged solution. It was shown from preliminary IR, UV and mass spectra that K22 react with 1,2-dichloroethane to form K22O2.

Experimental

Kryptofix-22 (K22) was purchased from Fluka. All solvents used were spectrosol purchased from Fluka. The X-ray diffraction measurements were carried out on a Phillips PW 1480 horizontal diffractometer stabilized with generator with a 40 KV and 25 mA power, with a CU-K radiation (λ = 1.5418 A^o). The scan rate was 20^o/min.

The UV-Vis spectra were recorded on Pye-Unicam SP8-200 spectrometer using 1 cm quartz cell. The ^1H NMR spectra was recorded as 5 mole % solution in D_2O on a Brucker 200 operating at 200.132 MHz for ^1H NMR spectra and at 50.323 MHz for ^{13}C NMR spectra. The ^{13}C NMR proton decoupled spectra was recorded for the compound in $CDCl_3$ with TMS as an internal reference. Spectral width 10 KH_2. Pulse width 3.5 s aquisition time 1.3 sec. The proton coupled ^{13}C spectra was run with 10 KHz spectral width. Pulse width 5, aquisition time 4 sec, delay time 2 sec.

Table (1)

The Distribution coefficient (D) of TCO_4^- ions in the system 0.1 M K-22-DCE/Mn^n $(OH)_n$ (18).

Metal hydroxide	Cation Diameter A°	D	
		Fresh solution	Aged solution
0.004 M LiOH	1.20	0.001	0.63
0.004 M NaOH	1.96	0.011	2.11
0.004 M KOH	2.66	0.024	4.57
0.004 M RbOH	2.96	0.017	2.21
0.004 M CSOH	3.34	0.016	1.24

Results and Discussion

The distribution coefficient of TCO_4^- ions in the system 0.1 M K22-dichloroethane/M^n $(OH)_n$, where M = Li, Na, K, Rb and Cs, is given in Table 1 for fresh and aged solutions(18). The following experimental was carried out to prove the formation of a new Kryptand K22C2

a) X-ray:-

The precipitate formed in aged solution of K22 in 1,2-dichloroethane was powdered and its X-ray was recorded and compared with that of K22 (Fig. 1).

b) UV spectroscopy:-

Two solutions of K22 were prepared. The first was K22 in a centonitrile and the second was K22 in DCE. The UV

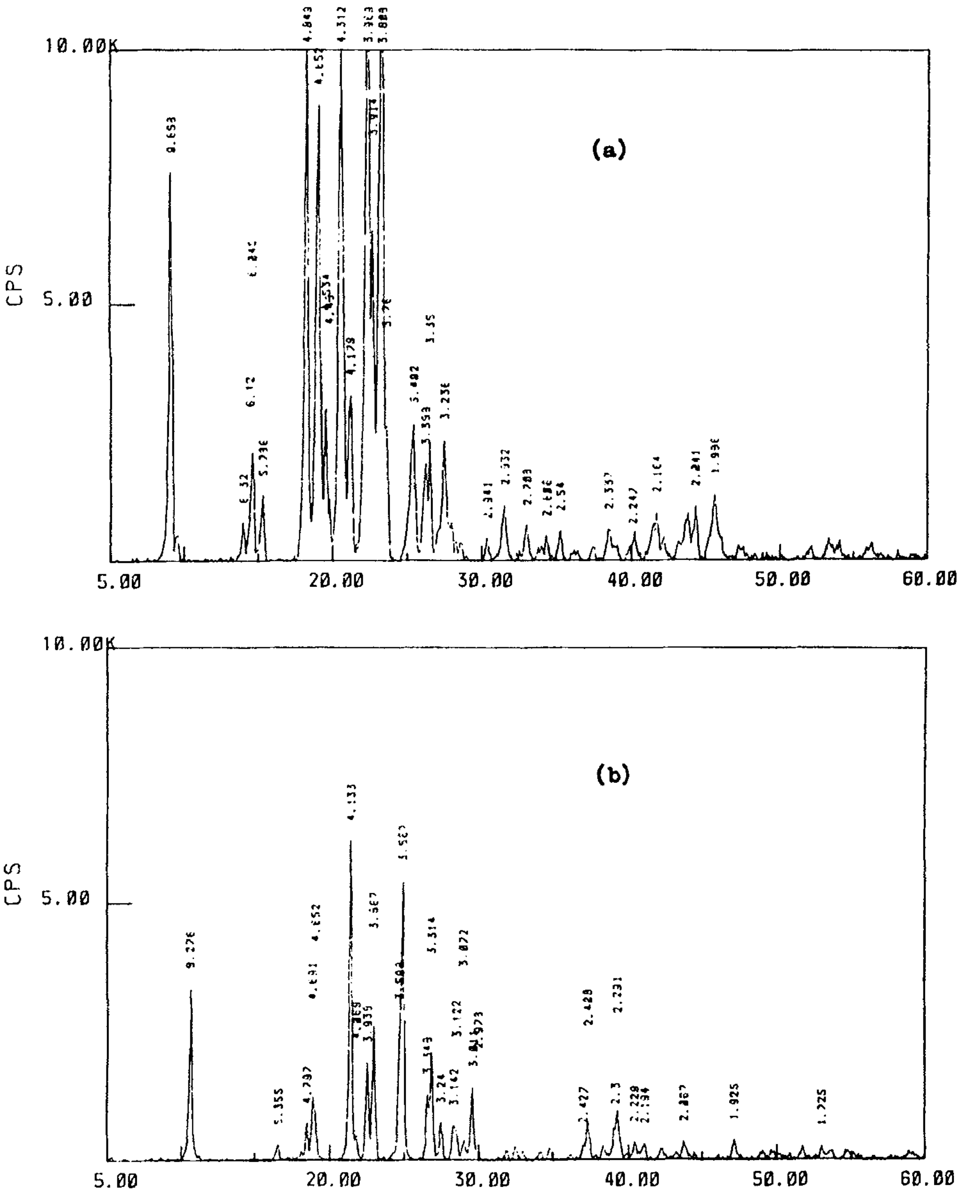


Fig. 1: X-ray spectra of (a) K22, (b) K22C2 Salt.

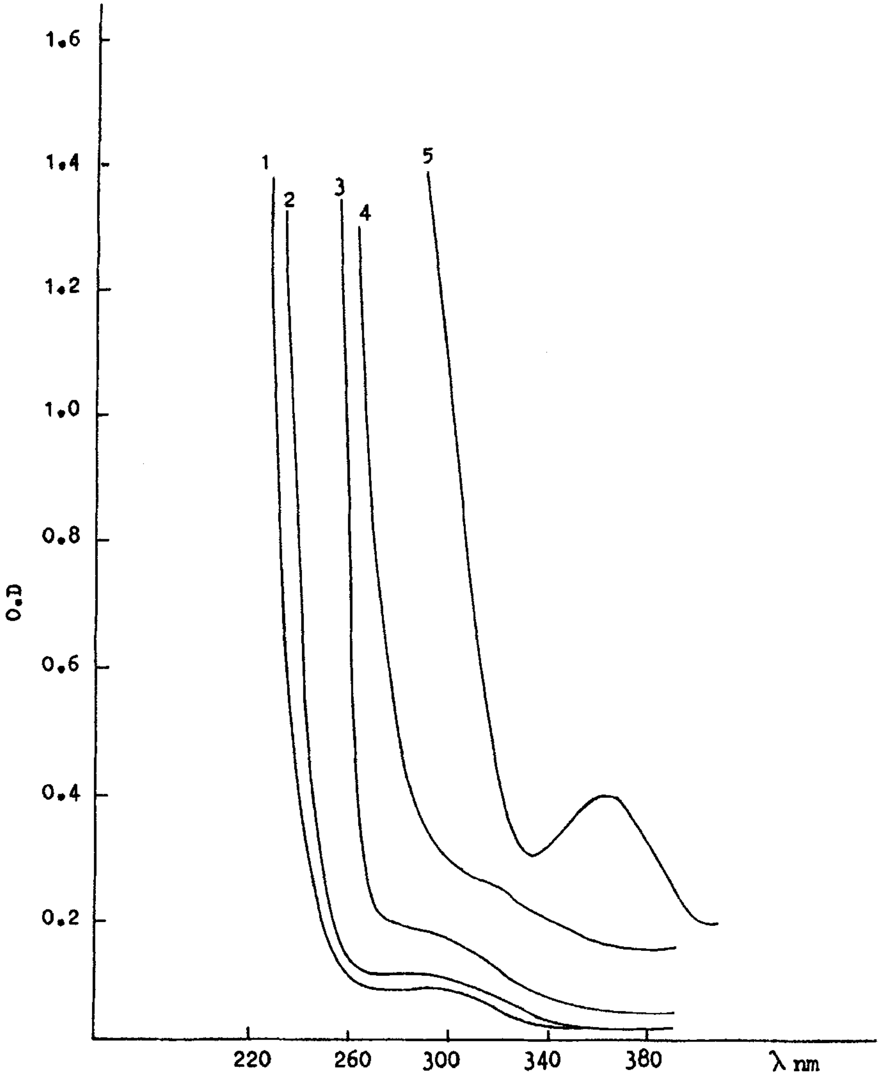


Fig. 2: UV spectra of K22 in DCE (1) Fresh, (2) after two days (3) after 3 days, (4) KI + K22 after six days, (5) KI + K22 in DCE after eight days.

Table (2)

UV-Visible Absorption wavelength in nm and their molar extinction coefficient ε in

K22 in DCE			K22 in DCE (Fresh) + KI				K22 in DCE (aged for two days) + KI			
Time days	λ_{240} ε	λ_{300} ε	Time days	λ_{280}	λ_{300}	λ_{360}	Time days	λ_{280}	λ_{300}	λ_{360}
1	27	7	1	13	13	5	1	14	12	3
2	63	9	3	89	50	25	3	23	20	8
4	108	10	5	136	61	31	5	60	36	18
8	112	14	8	249	196	112	8	137	72	33
			10	309	180	136	10	146	72	69

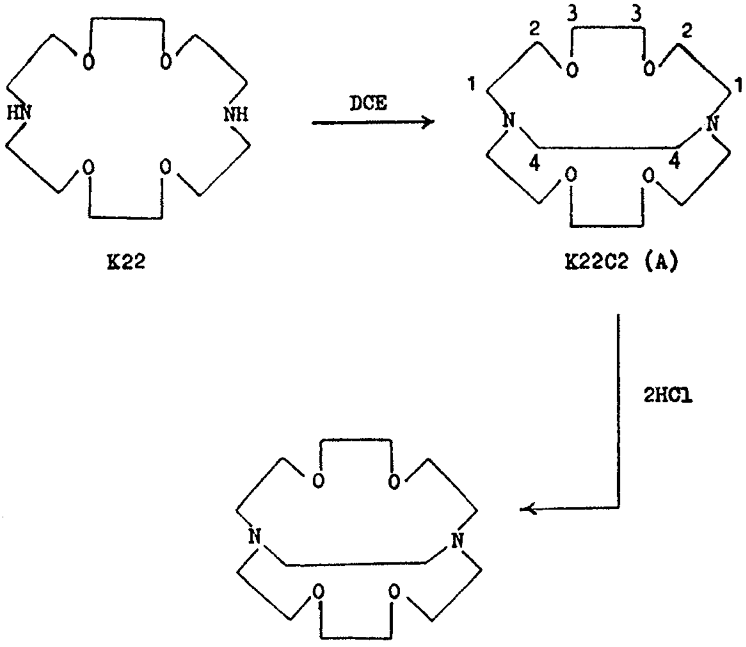
Table (3)

Change of pH values with time for K22 in DCE.

Time days	pH	Time days	pH
Fresh	9.22	10	7.96
2	8.92	14	7.33
4	8.55		
6	8.32		

spectra were recorded for the two samples at different intervals. The UV of both solutions show one absorption band at 240 nm. The extinction coefficient of this band for the first solution did not change with time. The band at 240 nm in the UV spectra of solution two increase in intensity with time and a broad band start to appear round 300 nm and increase in intensity with time (Fig. 2). This might indicate that K22 undergo a structural changes when it is aged in DCE.

A solution of K22 in DCE (0.8×10^{-3} M) was prepared. This solution was aged for two days and 0.01 gm of KI was added. The UV spectra was recorded for this solution at different intervals. It was noticed that after the addition of KI the intensity of the 240 nm band increases while the band at 300 nm start to disappear. After eight days a new



K22C2 Salt (B)

Fig. 3

Table (4)

^{13}C chemical shift (ppm) of K22C2 in $CDCl_3$.

K22C2	
^{13}C chemical shift	
δ_1	53.08
δ_2	67.43
δ_3	70.60
δ_4	55.18

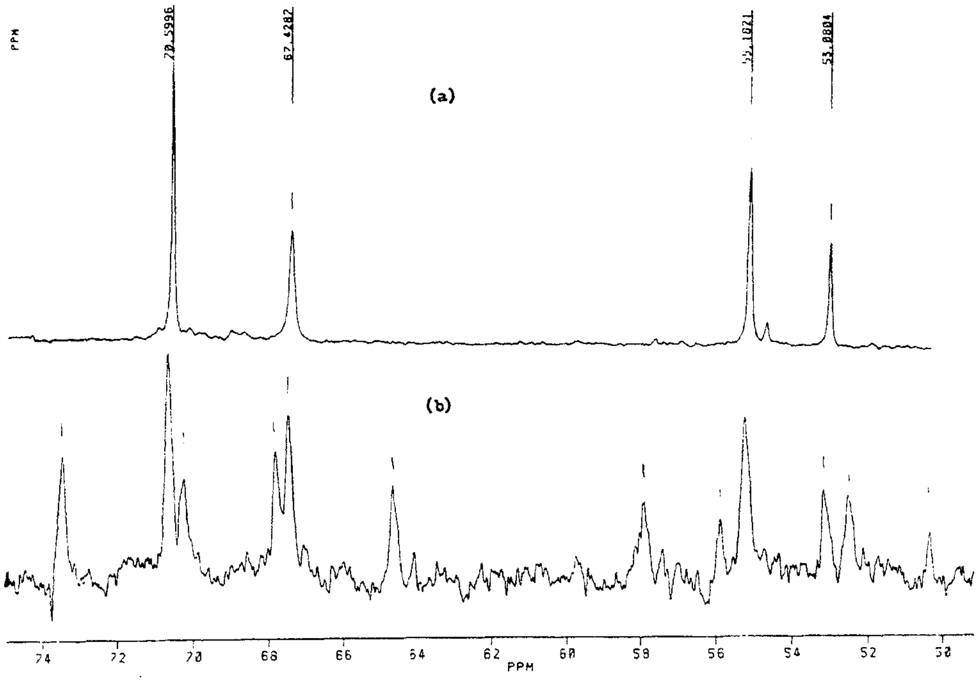


Fig. 4: ^{13}C NMR Spectra of K22C2 in $CDCl_3$ (a) Proton decoupled ^{13}C spectrum (b) Proton coupled ^{13}C spectrum.

band at 360 nm start to grow indicating the formation of a complex (Table 2) (Fig. 2).

A new solution of K22 in DCE was prepared and its pH was recorded at different intervals (Table 3). The pH of the aged sample start to become neutral indicating a reaction between K22 and the solvent. From this solution a few crystals start to ppt. These crystals were isolated and it was found that they are soluble in water. The C,H,N analysis indicate that the found values were 46.1, 8.36 and 7.77 respectively while the calculated values 46.5, 8.31 and 7.75 respectively. This suggest the formation of a salt (part B, Fig. 3). The aged solution was evaporated and the residue (part A, Fig. 3) was purified, dissolved in $CDCl_3$ and its ^{13}C NMR spectra was recorded.

c) NMR Spectra:-

The proton decoupled ^{13}C NMR spectra of part B show four lines (Table 4). The quantitative ^{13}C NMR spectra gave a ratio of the carbons 1:2:3:4 as 2:2:2:1. In the proton-decoupled ^{13}C NMR spectra each line was split to a triplet (Fig. 4) with J_{C-H} = 141.3 Hz.

All these results indicates that K22 undergo the following reaction.

More work is needed to study the solvent effect, chlorinated and non chlorinated, on the extraction of different ions using K22, and this work is in progress.

Acknowledgment

The authors like to thank Dr. John C. Lindon, Wellcome foundation for recording the NMR spectra.

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Date Received: 09/16/91
Date Accepted: 10/18/91