

Structure of the Potassium Hydroxide– Dibenzo-18-crown-6 Complex

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Abstract—Dibenzo-18-crown-6 reacts with potassium hydroxide in methanol to give the $C_{20}H_{24}O_6 \cdot KOH \cdot MeOH$ complex which was characterized by the 1H NMR, UV, and IR spectra. Depending on the conditions, the reaction of the same compounds in toluene gave products with the compositions $4 C_{20}H_{24}O_6 \cdot KOH \cdot 3H_2O$ (3 h, reflux) and $11 C_{20}H_{24}O_6 \cdot KOH$ (1 h, $80^\circ C$, 1 h).

While studying the application of strong bases in the chemistry of acetylene [1] and developing concepts of superbases as systems in which the interaction between metal cation and anion is weakened due to coordination with a weakly basic ligand [2], we have encountered with the necessity of elucidating the structure of crown ether complexes with alkali metal hydroxides.

The synthesis of complexes formed by macrocyclic polyethers (crown ethers) with alkali metal salts [3–6], their properties, and application in organic chemistry are extensively discussed in the literature (see, e.g., [7, 8]). However, only a few data have been reported on the structure of complexes derived from crown ethers and alkali metal hydroxides: several short communications on this topic are available.

The dibenzo-18-crown-6–KOH complex was reported for the first time by Pedersen [3] who revealed reduction in the electric conductivity of a solution of potassium hydroxide in methanol in the presence of dibenzo-18-crown-6, synthesized complexes of KOH with dicyclohexyl-18-crown-6 and di(*tert*-butylbenzo)-18-crown-6 in toluene, and determined their solubility in benzene, toluene, DMF, and DMSO. No other parameters of the complexes were given.

Sam and Simmons [9] later showed that a toluene solution of the complex formed by dicyclohexyl-18-crown-6 and KOH, which was prepared in the presence of methanol [3], contains only 11% of hydroxide ions and that the fraction of methoxide ions (CH_3O^-) is 89%. This conclusion was drawn on the basis of the

1H NMR and potentiometric titration data which were not given in [9]. It was presumed that the presence of activated methoxide ions is confirmed by the formation of *o*-chloroanisole from *o*-dichlorobenzene on heating to $90^\circ C$ with the KOH–dicyclohexyl-18-crown-6 complex prepared in the presence of methanol [9]. Pedersen [10] also reported on the complex derived from sodium hydroxide and a sulfur-containing analog of dicyclohexyl-18-crown-6; its formation was proved by the data on sodium ion extraction. Lutz *et al.* [11] studied the IR spectra of solutions of dicyclohexyl-18-crown-6–KOH in methanol, chloroform, toluene, and heptane. The formation of the dibenzo-18-crown-6–KOH complex was also noted in [11], but no its parameters were given.

In the present work we made an attempt to isolate the dibenzo-18-crown-6–KOH complex and determine its structure. The complex was prepared by heating the components in methanol (with and without addition of toluene) or toluene, followed by filtration, removal of the solvent, and evacuation of the residue. The resulting amorphous powders were analyzed by IR, UV, and 1H NMR spectroscopy, and their elemental composition was determined.

The results showed that the complexes prepared under different conditions had different compositions and spectral parameters. They melted over a wide temperature range (142 – $158^\circ C$), as well as known dibenzo-18-crown-6 complexes with alkali metal salts [3, 4]. The complex obtained in methanol had the composition dibenzo-18-crown-6·KOH·MeOH.

Table 1. ^1H NMR spectra of dibenzo-18-crown-6 and dibenzo-18-crown-6·KOH·MeOH

Compound	Solvent	Chemical shifts δ , ppm			
		C_6H_4	CH_2	MeOH	MeOK
Dibenzo-18-crown-6	CDCl_3	6.87 m	4.16 t, 4.02 t		
	DMSO	6.91–6.86 m 6.92–6.87 m ^a	4.04 m, 4.07 t, 3.84 t ^a		
Dibenzo-18-crown-6·KOH·MeOH	CDCl_3	6.89–6.83 m	4.13 q	3.42 (10), ^b 3.42 (4) ^c	3.32 (1), ^b 3.32 (1) ^c
	DMSO	7.26–7.20 m	4.40 d, 4.18 d		

^a At 50°C.^b Relative intensity.^c Relative intensity after 10 days.

In the reaction of dibenzo-18-crown-6 with KOH in toluene we isolated soluble and insoluble fractions. The composition of the soluble products varied depending on the conditions. Amorphous compounds were isolated with the following compositions: 4(dibenzo-18-crown-6)·KOH·3H₂O and 11(dibenzo-18-crown-6)·KOH. Presumably, apart from the dibenzo-18-crown-6·KOH complex, the soluble fraction contained initial dibenzo-18-crown-6 which is soluble in hot toluene. The presence of crystallization water in the complexes dibenzo-18-crown-6·NaBr·2H₂O and benzo-15-crown-5·NaI·H₂O was proved by the X-ray diffraction data [6], although water was not specially added to methanol which was used as reaction medium. Probable sources of water present in the complexes isolated from toluene solution may be moist potassium hydroxide and atmospheric moisture (which is absorbed during filtration).

We performed a detailed analysis of the ^1H NMR, UV, and IR spectra of the dibenzo-18-crown-6·KOH·MeOH complex. Its ^1H NMR spectrum in CDCl_3 (Table 1) contained signals from aromatic (δ 6.89–6.83 ppm) and methylene protons (δ 4.13 ppm) and two singlets at δ 3.42 and 3.32 ppm with an intensity ratio of 10:1. These singlets were assigned to protons of the methyl group in methanol and potassium methoxide, respectively, by comparing with the spectrum of potassium methoxide recorded under comparable conditions. After 10 days, the ratio changed to

4:1, presumably due to reaction of the superbasic complex with the solvent. Thus the isolated complex is likely to exist in equilibrium between two forms with solvated HO^- (HOME) and MeO^- (H₂O) anions (Scheme 1). This conclusion is consistent with the data of [9, 11], where the authors also failed to isolate nonsolvated crown ether–potassium hydroxide complexes because of very strong basicity of free hydroxide ion.

From the above stated it follows that the generally accepted views on the formation of complexes with nonsolvated hydroxide ion in reactions of alkali metal hydroxides with crown ethers need to be revised. In keeping with published data [8, 12, 13], the ^1H NMR spectrum of dibenzo-18-crown-6 (CDCl_3 , Table 1) contains a multiplet from the aromatic protons and two triplets from the methylene protons. The spectrum of dibenzo-18-crown-6·KOH·MeOH in $\text{DMSO}-d_6$ is characterized by downfield positions of signals relative to those of dibenzo-18-crown-6. Analogous downfield shifts are typical of complexes formed by the same crown ether with alkali metal salts [14].

Like dibenzo-18-crown-6 complexes with potassium salts [3], dibenzo-18-crown-6·KOH·MeOH characteristically displayed in the UV spectrum two absorption maxima at λ 274 ($\epsilon = 3280$) and 280 nm ($\epsilon = 2835$) (methanol, $c = 1.8 \times 10^{-4}$ M). The UV spectrum of dibenzo-18-crown-6 contains only one absorption maximum at λ 275 nm ($\epsilon = 4190$; methanol, $c = 1.6 \times 10^{-4}$ M).

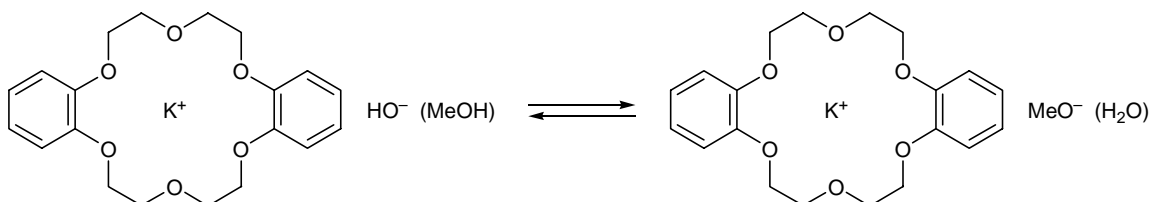
Scheme 1.

Table 2. IR spectra of dibenzo-18-crown-6·KOH·MeOH, dibenzo-18-crown-6, and KOH

Compound	Conditions	IR spectrum, ν , cm^{-1}
Dibenzo-18-crown-6·KOH·MeOH	KBr	3428 s, 3236 m, 3065 w, 3039 w, 3009 w, 2949 m, 2926 m, 2883 m, 1650 br.m, 1596 m.sh, 1575 w, 1507 s, 1490 m, 1476 m, 1454 s, 1418 w, 1389 br.m, 1364 br.m, 1329 m, 1294 m, 1254 s, 1231 m, 1216 m.sh, 1197 w, 1129 s, 1081 m, 1061 m, 1047 m, 1030 m, 996 m, 958 m, 942 m, 933 m, 917 w, 902 w, 844 w, 820 w, 778 m.sh, 750 m, 741 s.sh, 728 m, 596 w, 496 w
Dibenzo-18-crown-6·KOH·MeOH	Mineral oil	3500–2700 br.m, 1650 br.w, 1596 m.sh, 1575 w, 1509 s, 1490 m.sh, 1418 w.sh, 1344 w, 1330 m, 1292 w, 1256 s, 1231 s.sh, 1217 m, 1131 s, 1081 m, 1061 m, 1047 m, 1030 w, 996 m, 958 w, 933 m, 915 w, 902 v.w, 843 w, 820 w, 778 m.sh, 750 m, 740 s.sh, 729 m, 596 w, 496 w
Dibenzo-18-crown-6	KBr	3428 s, 3064 w, 3036 w, 3012 w, 2949 m, 2924 m, 2884 m, 2867 m, 1596 s, 1507 s, 1490 m, 1476 m, 1454 s.sh, 1445 w, 1418 w, 1392 w, 1369 w.sh, 1344 m, 1329 m, 1294 m, 1256 s, 1231 s, 1132 s.sh, 1117 s, 1080 w, 1061 w, 1047 m, 1027 w, 996 s, 933 s, 916 w, 902 w, 844 v.w, 820 w, 779 m, 750 m, 740 s, 730 s, 595 w, 496 w
Dibenzo-18-crown-6	Mineral oil	1595 m, 1511 s, 1490 m, 1418 w, 1344 w, 1331 w, 1292 w, 1256 s, 1231 s, 1131 s.br, 1117 m, 1080 w, 1061 w, 1046 w, 1027 w, 996 m, 933 m, 915 w, 902 w, 844 w, 821 w, 778 m.br, 750 s, 740 s.br, 728 s, 595 w, 497 w
KOH ^a	KBr	3500 s.br, 3187 s.br, 2993 s.br, 2353 w.br, 1954 w.br, 1660 w.br, 1480 s, 1453 s, 1370 s.br, 1061 w, 920 w, 882 m, 722 m ^b
KOH ^a	Mineral oil	3500 m, 2449 w.br, 1954 s.br, 1660 m, 1304 w, 1148 w, 1073 m, 932 w, 882 s, 769 w, 722 s, 684 m, 667 s

^a According to the potentiometric titration data, the concentration of KOH was 97.4% (KOH·0.08H₂O).

^b K(H₂O)OH: 3503 s, 3430 br, 2700 s.br, 2450 s.br, 1960 m, 1660 m, 1405 m, 1070 m, 927 s, 878 s, 605 s [15].

The IR spectra of dibenzo-18-crown-6·KOH·MeOH, the initial crown ether, and KOH (KBr, mineral oil) are shown in Figs. 1 and 2 (see also Table 2). The formation of a complex by dibenzo-18-crown-6 and potassium hydroxide is confirmed by comparison with the spectra of the initial components, in particular by the following data:

(1) A shoulder appears at $\sim 1575 \text{ cm}^{-1}$ on the band with its maximum at 1596 cm^{-1} (stretching vibrations of the aromatic C–C bonds; Figs. 1, 2); medium-intensity bands at 1216 cm^{-1} with a shoulder at 1197 cm^{-1} (antisymmetric stretching vibrations of the C–O–C group; Fig. 1) and at 958 and 942 cm^{-1} also appear (C–H bending vibrations; Fig. 1);

(2) The shoulder at 1117 cm^{-1} on the strong band with its maximum at 1132 cm^{-1} (symmetric stretching vibrations of the C–O–C group) disappears (Figs. 1, 2);

(3) The intensity of absorption bands at 933, 996, 1061, 1081, 1364, and 1389 cm^{-1} (C–H bending vibrations, and C–C skeletal vibrations; Fig. 1) changes, and the bands at 1364 and 1389 cm^{-1} become considerably broadened and unresolved;

(4) Broad bands are observed at 3236 and 1650 cm^{-1} (KBr) due to stretching and bending vibrations of hydroxy group in the complex, while the narrow peak at 3500 cm^{-1} (mineral oil), belonging to the hydroxy group in potassium hydroxide, disappears.

EXPERIMENTAL

The IR spectra were recorded in KBr and mineral oil on a Bruker IFS-25 spectrometer. The UV spectra were measured on a Specord UV-Vis spectrophotometer from solutions in methanol with a concentration c of $1.6\text{--}1.8 \times 10^{-4} \text{ M}$. The ¹H NMR spectra were obtained on a Bruker DPX-400 instrument (400.13 MHz) in DMSO-*d*₆ and CDCl₃ using hexamethyldisiloxane as internal reference.

The solvents were purified and dehydrated according to the procedures described in [16] and were distilled just before use; dibenzo-18-crown-6 (Cherkassy Chemicals Plant; TU 6-09-20-19-83) was recrystallized from benzene (mp 164°C); potassium hydroxide (Merck) was calcined at $400\text{--}450^\circ\text{C}$ (97.4% of KOH).

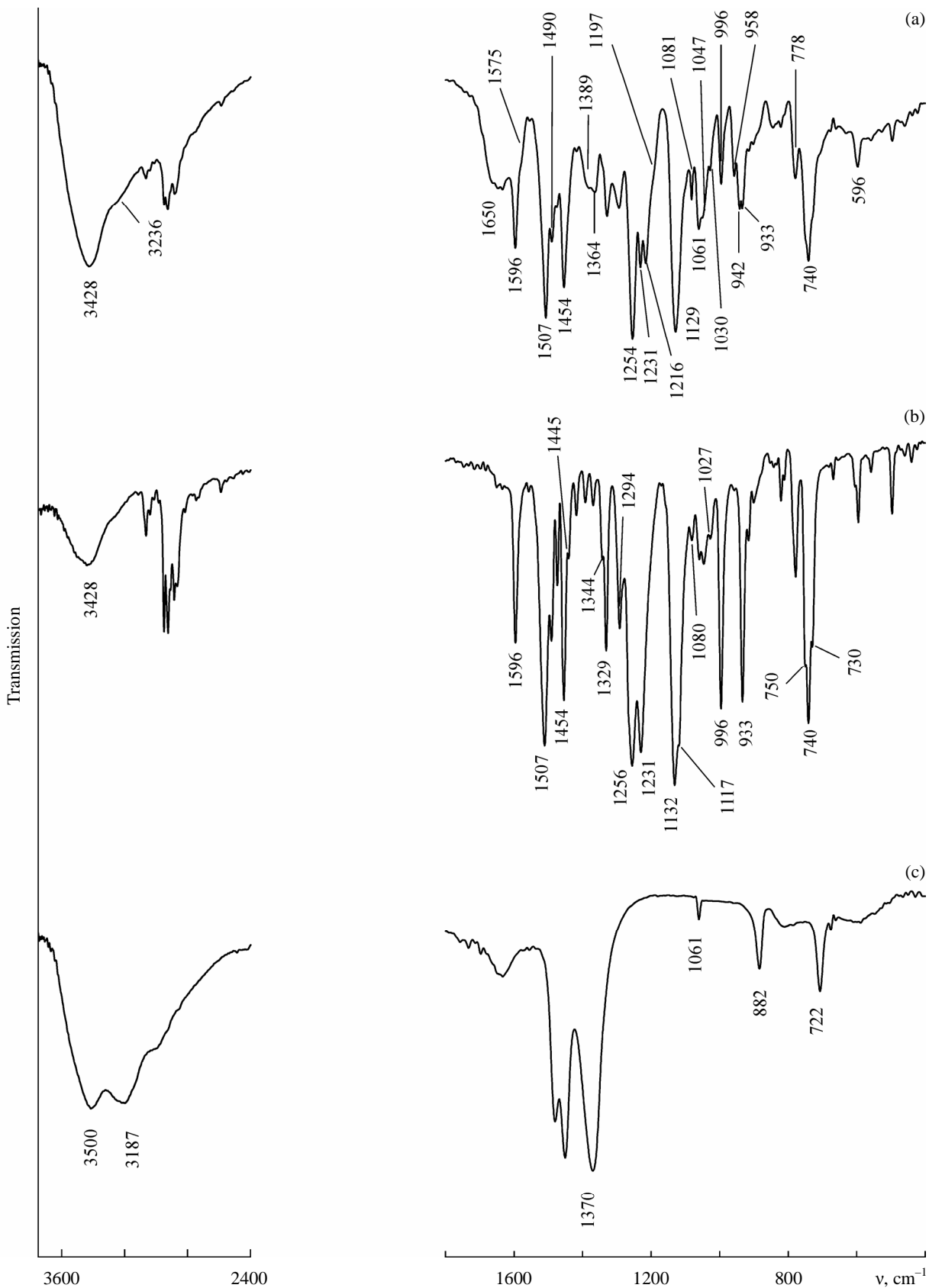


Fig. 1. IR spectra (KBr) of (a) dibenzo-18-crown-6-KOH complex, (b) dibenzo-18-crown-6, and (c) KOH.

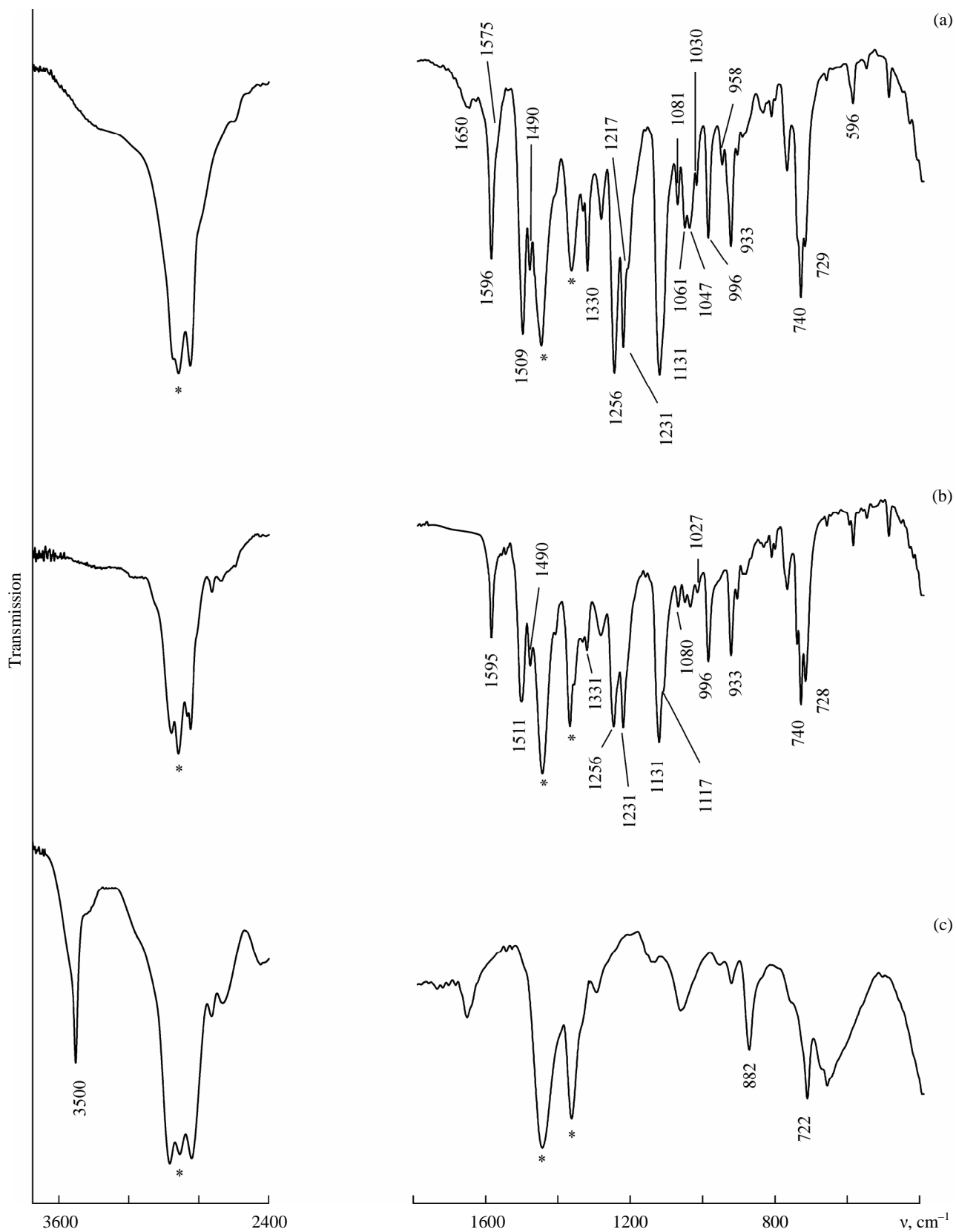


Fig. 2. IR spectra (mineral oil) of (a) dibenzo-18-crown-6-KOH complex, (b) dibenzo-18-crown-6, and (c) KOH. Absorption bands of mineral oil are marked with asterisks.

The concentration of KOH was determined by titration of complexes in methanol with 0.1 N HClO₄; initial potassium hydroxide was titrated in water with 0.1 N hydrochloric acid; the titration was performed using an Ionomer EV-74 universal potentiometer.

Reaction of potassium hydroxide with dibenzo-18-crown-6 in methanol. A suspension of 7.2 g (20 mmol) of dibenzo-18-crown-6 and 1.12 g (20 mmol) of KOH in 60 ml of anhydrous methanol was stirred for 1 h at 60°C (at 30°C, a light brown transparent solution was formed). The solution was filtered while hot, the filtrate was cooled and concentrated by partial removal of methanol (45 ml) under reduced pressure, and 5 ml of anhydrous toluene was added to the residue. The solvent was removed, and the tarry residue was evacuated at a residual pressure of 1–2 mm until constant weight (40–50°C, 3 h). We thus obtained 8.75 g (97.9%) of the complex dibenzo-18-crown-6·KOH·MeOH; concentration of potassium hydroxide 12.58% (potentiometric titration), mp 142–156°C. Found, %: C 55.83; H 6.56; K 8.73. C₂₁H₂₉KO₈. Calculated, %: C 56.23; H 6.52; K 8.72.

A parallel run afforded 8.68 g (97.2%) of dibenzo-18-crown-6·KOH·MeOH, KOH concentration 12.06% (potentiometric titration), mp 142–156°C. Found, %: C 56.69; H 6.52; K 8.81.

In an analogous experiment performed without addition of toluene we isolated 8.89 g (99.6%) of the same product, mp 142–158°C. Found, %: C 56.98; H 6.87; K 8.56.

Reaction of potassium hydroxide with dibenzo-18-crown-6 in toluene. *a.* Potassium hydroxide, 0.38 g (6.7 mmol), was added to a suspension of 2.4 g (6.7 mmol) of dibenzo-18-crown-6 in 30 ml of anhydrous toluene. The mixture was stirred and was heated for 3 h under reflux in a flask equipped with a Dean–Stark trap. The solution was filtered while hot, the filtrate was cooled and concentrated by removal of the solvent under reduced pressure, and the residue was evacuated at a residual pressure of 1–2 mm until constant weight (40–50°C, 3 h). We thus obtained 0.71 g of a product with the composition 4(dibenzo-18-crown-6)·KOH·3H₂O, mp 140–156°C. Found, %: C 60.91; H 6.42; K 2.43. C₈₀H₁₀₃KO₂₈. Calculated, %: C 61.92; H 6.69; K 2.52.

The precipitate separated by filtration was evacuated at a residual pressure of 1–2 mm until constant weight (40–50°C, 3 h); yield 2.03 g.

b. A suspension of 7.2 g (20 mmol) of dibenzo-18-crown-6 and 1.12 g (20 mmol) of KOH in 60 ml of

toluene was heated for 1 h at 80°C under stirring. The resulting light brown transparent solution was filtered while hot, the filtrate was cooled and concentrated by removal of the solvent under reduced pressure, and the residue was evacuated at a residual pressure of 1–2 mm until constant weight (20–25°C, 20 h). We thus obtained 5.76 g of a product with mp 152–158°C whose elemental composition corresponded to 11(dibenzo-18-crown-6)·KOH, KOH concentration 1.39% (potentiometric titration). Found, %: C 65.97; H 6.29; K 0.93. C₂₂₀H₂₆₅KO₆₇. Calculated, %: C 65.72; H 6.64; K 0.97. The precipitate separated by filtration was evacuated at a residual pressure of 1–2 mm until constant weight (40–50°C, 3 h) to obtain 2.34 g of a product with mp 142–156°C (begins to flow at 130°C), whose elemental composition corresponded to dibenzo-18-crown-6·6KOH·6H₂O. Found, %: C 29.37; H 5.39; K 30.26. C₂₀H₄₂K₆O₁₈. Calculated, %: C 29.84; H 5.26; K 29.14.

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