

Crown Ether Complexes of Potassium and Thallium(I) 2- and 4-Nitrophenoxides

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Abstract. 18-Crown-6 and dicyclohexano-18-crown-6 complexes of potassium 2- and 4-nitrophenoxide, and 18-crown-6 complexes of thallium(I) 2- and 4-nitrophenoxide have been synthesized. Solvent effects on the visible spectra of the nitrophenoxide anions are independent of the nature of the cation and the nature of the complexing agent. The 18-crown-6 complex of thallium(I) 2-nitrophenoxide is a 1:2 complex. All the other complexes are 1:1. X-ray crystallographic examination of the potassium dicyclohexano-18-crown-6 complexes showed the potassium ion is octacoordinated in the 2-nitrophenoxide and heptacoordinated in the 4-nitrophenoxide.

Key words. Nitrophenoxides, visible spectra, crown ethers.

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1. Introduction

The long wavelength electronic absorption band of 4-nitrophenol and of the 4-nitrophenoxide anion is an intramolecular charge-transfer band. Such bands are generally sensitive to solvent polarity. Kamlet and co-workers [1] have demonstrated that the wavenumber shift for alcoholic solutions of 4-nitrophenol, as compared with cyclohexane solutions, is a function of the inductive effect of the alkyl group of the alcohol. Parker and Brody [2] noted a sensitivity of the visible absorption band of the 4-nitrophenoxide anion to solvent polarity, but their work was limited to a very few solvents by the solubility of sodium 4-nitrophenoxide. This sensitivity was apparently confirmed by Ueji and Kitadani [3], who measured the spectrum of sodium 4-nitrophenoxide in solvents containing an excess of 15-crown-5 to complex the sodium ion and render the salt soluble. It was assumed in this work that the crown ether complexation had no effect on the wavelength of the absorption maximum.

The long-wavelength absorption band of 2-nitrophenol and its anion should also show solvent sensitivity. There are no reported investigations of this possibility. It has been reported, however, that the absorption spectrum of aqueous thallium(I)

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2-nitrophenoxide is significantly different from that of aqueous sodium 2-nitrophenoxide [4]. This difference was interpreted in terms of chelation of the thallium(I) ion, and raises a serious question concerning the comparability of spectra of these anions when measured in the presence of different cations. If such differences are real, then the comparability of spectra determined in the presence and absence of a crown ether must also be questioned.

The potassium and thallium(I) ions have similar ionic radii, 1.33 Å and 1.40 Å, respectively [5], allowing either of them to be tightly complexed in the cavity of 18-crown-6 [6]. A clearer picture of the solvent and counterion effects upon the spectra of nitrophenoxide anions should emerge from the use of these ions as counterions, both with and without 18-crown-6 complexation. Accordingly, we have undertaken the syntheses of the potassium and thallium(I) 2- and 4-nitrophenoxide and of their 18-crown-6 complexes in order to examine these effects.

2. Experimental

Crown ethers were purchased from Parish Chemical Company. Nitrophenols were obtained from Aldrich Chemical Company and were recrystallized from 95% ethanol before use. Thallium(I) ethoxide was purchased from Alfa Products. Microanalyses were done by Atlantic Microlab Inc.

2.1. PREPARATION OF POTASSIUM NITROPHENOXIDES

Mixtures of 13.9 g (0.100 mol) of the 2-nitrophenol or 4-nitrophenol, 13.8 g (0.100 mol) of anhydrous potassium carbonate and 50 mL of anhydrous acetone were refluxed with stirring for 1–2 h. The precipitate was transferred to a Soxhlet extractor and extracted with acetone until the residue in the thimble was no longer colored, 6–8 d. The extract was filtered to recover the product, 17.3 g (98%) of potassium 2-nitrophenoxide, bright orange crystals which decomposed without melting at 242–246°C, or 7.9 g (44%) of potassium 4-nitrophenoxide, pale yellow crystals which turned black at 240°C and exploded at 345°C. The potassium nitrophenoxides were used without further purification for the preparation of their crown ether complexes.

2.2. PREPARATION OF THALLIUM(I) NITROPHENOXIDES

A solution of 10.0 g (0.040 mol) of thallium(I) ethoxide in 25 mL of absolute ethanol was added slowly with stirring to a chilled solution of 5.8 g (0.041 mol) of 2-nitrophenol or 4-nitrophenol in 25 mL of absolute ethanol. After stirring for 15 min, solvent was removed under reduced pressure and the residue was washed with three 25 mL portions of absolute ether. The product was thallium(I) 2-nitrophenoxide, 10.5 g (80%), dark red, m.p. 215–216°C or thallium(I) 4-nitrophenoxide, 11.8 g (86%), bright orange, m.p. 263–265°C.

Anal. Calcd. for $C_6H_4HO_3Tl$: C, 21.04%; H, 1.18%; N, 4.09%. *Found* for thallium(I) 2-nitrophenoxide: C, 20.94%; H, 1.48%; N, 4.06%. *Found* for thallium(I) 4-nitrophenoxide: C, 20.96%; H, 1.48%; N, 4.03%.

2.3. PREPARATION OF CROWN ETHER COMPLEXES

A solution of 5.3 mmol of the crown ether in 25 mL anhydrous acetone was added to a suspension of 5.0 mmol of the nitrophenoxide in 25 mL of anhydrous acetone. The mixture was refluxed with stirring for 30 minutes, cooled to room temperature, filtered and evaporated to dryness under reduced pressure. The residue was washed with three 25-mL portions of cyclohexane and air-dried. The results of these preparations are summarized in Table I.

2.4. VISIBLE ABSORPTION SPECTRA

Visible absorption spectra were measured with a Cary Model 15 recording spectrophotometer using 1 cm cylindrical cells at ambient temperature. The results of these measurements are summarized in Tables II and III.

2.5. INFRARED ABSORPTION SPECTRA

Infrared absorption spectra were measured for Nujol mulls using a Pye-Unicam 3-200 infrared spectrophotometer with a 3-050 data processor system and a 3-080 data control console, which was programmed to subtract the Nujol spectrum. Table IV summarizes the data for the nitrogroup absorption frequencies.

2.6. X-RAY DATA COLLECTION AND STRUCTURE SOLUTION

Intensity data for *cis-syn-cis*-dicyclohexano-18-crown-6 potassium 4-nitrophenoxide were collected on an Enraf-Nonius CAD4 diffractometer equipped with MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) and a graphite monochromator, by $\omega-2\theta$ scans of variable speed. Crystals of $\text{C}_{26}\text{H}_{40}\text{KNO}_9$ are orthorhombic, space group P_{bca} , $a = 14.900(3)$, $b = 23.035(4)$, $c = 16.105(2) \text{ \AA}$, $V = 5527(3) \text{ \AA}^3$, $Z = 8$, $D_c = 1.321 \text{ g cm}^{-3}$ at 23°C , $\mu = 2.4 \text{ cm}^{-1}$. A yellow crystal of dimensions $0.28 \times 0.38 \times 0.43 \text{ mm}$, sealed in a glass capillary, was used for data collection. Cell dimensions were obtained from a least-squares fit to the setting angles of 25 reflections having $10^\circ < \theta < 11^\circ$. One octant of data having $1^\circ < \theta < 25^\circ$ was measured using scan rates $0.53-4.0^\circ \text{ min}^{-1}$. Data reduction included corrections for background, Lorentz, polarization and absorption. The small absorption corrections (minimum relative transmission 94.3%) were based on psi scans. Of 4850 unique reflections measured, 2374 had $I > 1\sigma(I)$, and were used in the refinement.

The structure was solved by direct methods using MULTAN [7] and refined by full-matrix least-squares minimizing $\sum w(|F_0| - |F_c|)^2$, where $w = 4F_0^2[\sigma^2(I) + (0.02F_0^2)^2]^{-1}$, using Enraf-Nonius SDP programs [8]. Scattering factors were those of Cromer and Waber [9], and anomalous coefficients were those of Cromer [10]. Nonhydrogen atoms were refined anisotropically, while hydrogen atoms were included as fixed contributions in calculated positions. Convergence was achieved with maximum shift $< 0.01\sigma$, $R = 0.068$, $R_w = 0.050$, $\text{GOF} = 1.560$ for 335 variables, maximum residual density 0.45 e \AA^{-3} , minimum -0.23 e \AA^{-3} . An extinction coefficient refined to $g = 3.2(7) \times 10^{-8}$, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c .

Table I. Crown ether complexes of nitrophenoxides

Isomer	Cation	Crown ether	Yield, %	Melting point, °C	Color	C			H			N		
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
2	K ⁺	18C6	76	214–215	yellow orange	49.04	48.92	6.39	6.42	3.17	3.15			
2	K ⁺	DiCyl18C6 ^a	27	170–172	yellow orange	56.81	57.19	7.33	7.19	2.55	2.65			
2	K ⁺	DiCyl18C6 ^b	33	128–130	yellow orange	56.81	56.75	7.33	7.34	2.55	2.55			
2	Tl ⁺	18C6 ^c	66	182–183	bright orange	30.37	30.32	3.40	3.28	2.95	2.98			
4	K ⁺	18C6	53	161–162	greenish yellow	49.04	48.95	6.39	6.39	3.17	3.15			
4	K ⁺	DiCyl18C6 ^b	76	188–189	greenish yellow	56.81	56.75	7.33	7.34	2.55	2.55			
4	Tl ⁺	18C6	64	96–98	yellow	35.63	35.52	4.65	4.69	2.31	2.35			

^a*cis-anti-cis* Isomer.^b*cis-syn-cis* Isomer.^c1:2 Complex.

Table II. Absorption spectra of 2-nitrophenoxides^a

Solvent	Cation							
	K ⁺		18C6K ⁺		Tl ⁺		18C6Tl ⁺	
	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}
Methanol	403.5	6870	406	6120	402	3550	406	4290
Water	416	4650			414	3640		
Chloroform		^b	443	5500		^b	443	2840
Carbon Tetrachloride		^b	443	9100		^b	443.5	4920
Acetone	445	7510	446	7300	442.5	5260	445	6510
Benzene, anhydrous		^b	448 ^c	6040		^b	448	4200
Acetonitrile	448	7250	449	7660	443	^d	448	8040
<i>N,N</i> -Dimethylformamide	446	6250	452	8030	446	5160	450	7250

^a λ_{\max} values are in nanometers.^bInsoluble.^cIn water-saturated benzene, 441 nm.^dSaturated solution.Table III. Absorption spectra of 4-nitrophenoxides^a

Solvent	Cation							
	K ⁺		18C6K ⁺		Tl ⁺		18C6Tl ⁺	
	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}
Methanol	389	9790	388	7230	389	8150	388	6440
Carbon Tetrachloride		^b	389	7240		^b	392	16800
Benzene, water-saturated		^b	390			^b	387	
Water	400	16600			401	9720		
Benzene, anhydrous		^b	403	15900	404	^c	401	11800
Chloroform		^b	421	17400		^b	417	18800
Acetone	428	20000	428	24800	428	24700	428	28200
Acetonitrile	431	25000	430	28000	425	^c	425	17200
<i>N,N</i> -dimethylformamide	434	33400	434	31400	434	38500	433	42300

^a λ_{\max} values are in nanometers.^bInsoluble.^cSaturated solution.

3. Results and Discussion

The yields, melting points and colors of the 18-crown-6 complexes of the potassium and thallium(I) 2- and 4-nitrophenoxides and the dicyclohexano-18-crown-6 complexes of the potassium salts are summarized in Table I. The analytical data correspond to 1:1 complexes for all compounds except the 18-crown-6 complex of thallium(I) 2-nitrophenoxide, which has one mole of crown ether to two moles of the thallium salt. Tables II and III summarize the data for the visible absorption spectra of the uncomplexed and complexed salts. The molar absorptivities given in

Table IV. Nitrogroup infrared absorption frequencies

Compound	Unsymmetric $\nu_{\text{NO}}, \text{cm}^{-1}$	Symmetric $\nu_{\text{NO}}, \text{cm}^{-1}$
2-Nitrophenol	1540	1381 1337
Potassium 2-nitrophenoxide	1539	1374 1333
18-Crown-6-potassium 2-nitrophenoxide	1550	1358 1329
Thallium(I) 2-nitrophenoxide	1546	1359 1330
18-Crown-6 bis[thallium(I) 2-nitrophenoxide]	1539	1369 1330
4-Nitrophenol	1547	1335
Potassium 4-nitrophenoxide	1558	1310
18-Crown-6 potassium 4-nitrophenoxide	1558	1357
Thallium(I) 4-nitrophenoxide	1543	1383
18-Crown-6 thallium(I) 4-nitrophenoxide	1555	1360

Table II for 18-crown-6 bis[thallium(I) 2-nitrophenoxide] is the value per mole of nitrophenoxide ion. The structure of the *cis-syn-cis*-dicyclohexano-18-crown-6 complex with potassium 4-nitrophenoxide was determined by X-ray crystallography, and the fractional coordinates are given in Table V.

Inspection of the spectral data clearly shows that neither variation of the cation nor complexation of the cation has a significant effect on the visible absorption of either of the nitrophenoxide ions in a given solvent. The absorption maxima for aqueous solutions are in agreement with those reported elsewhere [2, 3, 11–15] for the sodium salts. The maxima of the 4-nitrophenoxides in methanol, carbon tetrachloride, chloroform, acetonitrile and *N,N*-dimethylformamide are also in agreement with those reported [5] for 15-crown-5 sodium 4-nitrophenoxide in these solvents. There are no reports in the literature of spectra of the nitrophenoxides with inorganic cations other than sodium, potassium and thallium(I).

The spectrum of the 2-nitrophenoxide ion (Table II) is not greatly affected by variation of the solvent in aprotic solvents, and such variation that is observed cannot be correlated with solvent polarity. On the other hand, the spectrum of the 4-nitrophenoxide ion (Table III) shows a fairly regular redshift with increasing solvent polarity in aprotic solvents, in agreement with the observations for the 15-crown-5 sodium complex [5]. The spectra of both anions are strongly blueshifted in hydroxylic solvents.

For comparison, the spectra of the parent nitrophenols show only end absorption in the visible range. In aqueous solution the absorption maxima are 351 and 317.5 nm, respectively, for the 2- and 4-isomers [12]. The spectrum of 4-nitrophenol is redshifted with increasing solvent polarity in both protic and aprotic solvents [1–3]. Solvent effects on the spectrum of 2-nitrophenol have not been investigated.

The 2-nitrophenoxides showed a reversible thermochromism in the solid state. The most extreme case was that of the uncomplexed thallium(I) salt, which was white at liquid nitrogen temperature and black at 120°. The complexed compounds

Table V. Coordinates and equivalent isotropic parameters for *cis-syn-cis*-dicyclohexano-18-crown-6 potassium 4-nitrophenoxide

Atom	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
K	0.79607(7)	0.12804(4)	0.62689(8)	4.10(2)
O(1)	0.9277(2)	0.2014(1)	0.6949(2)	3.55(7)
O(2)	0.9578(2)	0.1606(1)	0.5356(2)	4.45(8)
O(3)	0.8736(2)	0.0544(2)	0.5111(2)	6.5(1)
O(4)	0.6873(2)	0.0693(1)	0.5077(2)	3.89(8)
O(5)	0.6430(2)	0.1827(1)	0.5655(2)	3.67(7)
O(6)	0.7486(2)	0.2353(1)	0.6949(2)	3.35(7)
C(1)	0.9752(3)	0.2344(2)	0.6348(3)	4.8(1)
C(2)	1.0229(3)	0.1928(2)	0.5796(3)	4.8(1)
C(3)	0.9965(3)	0.1165(2)	0.4864(4)	6.1(2)
C(4)	0.9304(4)	0.0762(2)	0.4567(4)	7.0(2)
C(5)	0.8151(3)	0.0088(2)	0.4841(3)	4.6(1)
C(6)	0.7975(3)	-0.0280(2)	0.5593(3)	5.2(1)
C(7)	0.7387(4)	-0.0800(2)	0.5385(4)	6.6(2)
C(8)	0.6515(4)	-0.0581(2)	0.5001(4)	6.4(2)
C(9)	0.6675(3)	-0.0199(2)	0.4244(4)	5.6(1)
C(10)	0.7282(3)	0.0321(2)	0.4456(3)	4.4(1)
C(11)	0.6147(3)	0.1022(2)	0.4748(3)	4.3(1)
C(12)	0.5785(3)	0.1399(2)	0.5429(3)	4.3(1)
C(13)	0.6093(3)	0.2206(2)	0.6277(3)	3.9(1)
C(14)	0.6793(3)	0.2642(2)	0.6504(3)	4.0(1)
C(15)	0.8124(3)	0.2728(2)	0.7341(3)	3.3(1)
C(16)	0.7738(3)	0.3040(2)	0.8097(3)	4.4(1)
C(17)	0.7451(4)	0.2613(2)	0.8767(4)	5.4(1)
C(18)	0.8239(3)	0.2229(2)	0.9037(3)	5.0(1)
C(19)	0.8623(3)	0.1915(2)	0.8282(3)	3.8(1)
C(20)	0.8906(3)	0.2346(2)	0.7614(3)	3.1(1)
O(1A)	0.6884(2)	0.0919(2)	0.7481(3)	8.0(1)
O(2A)	0.3683(2)	-0.0805(1)	0.7543(3)	6.6(1)
O(3A)	0.4776(3)	-0.1401(1)	0.7395(3)	8.3(1)
N(1A)	0.4492(3)	-0.0896(2)	0.7470(3)	4.9(1)
C(1A)	0.6333(4)	0.0501(2)	0.7506(3)	4.9(1)
C(2A)	0.5380(3)	0.0588(2)	0.7600(3)	4.8(1)
C(3A)	0.4792(3)	0.0141(2)	0.7587(3)	3.8(1)
C(4A)	0.5106(3)	-0.0426(2)	0.7475(3)	3.4(1)
C(5A)	0.6013(3)	-0.0536(2)	0.7399(3)	4.4(1)
C(6A)	0.6611(3)	-0.0090(2)	0.7427(3)	5.0(1)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

showed much less color variation, ranging from light yellow to red. No thermochromism could be detected for these compounds in solution. The thermochromism thus appears to be a property of the crystal structure, possibly a temperature-dependent charge-transfer effect.

The wavenumbers of the symmetric and unsymmetric N—O stretching vibrations for the nitrophenols and their salts are listed in Table IV. In 2-nitrophenol, the classic case of intramolecular hydrogen bonding, the hydroxylic hydrogen atom may be said to be chelated between the hydroxyl oxygen and one of the oxygens of

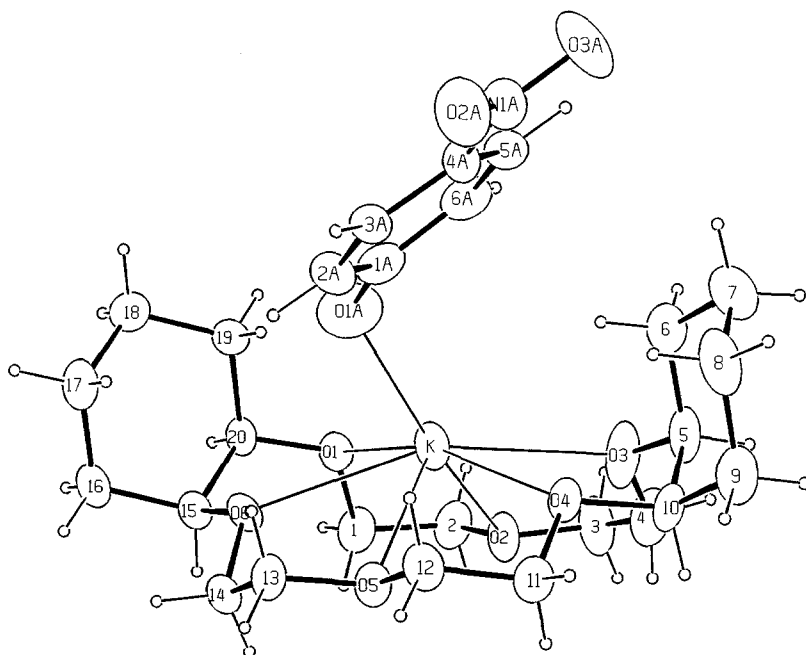


Fig. 1. Structure of *cis-syn-cis*-dicyclohexano-18-crown-6 potassium 4-nitrophenoxide.

the *ortho*-nitrogroup. One result of this chelation is to make the two N—O vibrations of the symmetric mode nonequivalent, and to split the symmetric absorption band into a doublet. This pattern is repeated with both the uncomplexed and complexed potassium and thallium(I) 2-nitrophenoxides, leading to the conclusion that both of these ions are similarly chelated.

The chelation of the potassium ion in the *cis-syn-cis*-dicyclohexano-18-crown-6 potassium 2-nitrophenoxide has been confirmed by determination of its crystal structure, which clearly shows the potassium ion to be octacoordinated with the six donor oxygens of the crown ether and two oxygens of the 2-nitrophenoxide [15]. Similar octacoordination exists in the crystal structure of the *cis-anti-cis*-isomer [16].

The crystal structure of the *cis-syn-cis*-dicyclohexano-18-crown-6 potassium 4-nitrophenoxide is illustrated in Figure 1. In this case, the cation is heptacoordinated, with the six K—O(crown) distances within the range 2.773(3)–2.920(3) Å, and the K—O(phenoxide) distance, 2.661(4) Å. While the latter is indicative of a strong interaction, it is longer than the 2.628(2) Å observed for the bidentate 2-nitrophenoxide [15]. The cavity size, R , of the crown ether is 1.42 Å, which is smaller than in the 2-nitrophenoxide complex, 1.45 Å. The smaller R reflects the change from octacoordinate in the 2-nitrophenoxide complex to heptacoordinate in this complex.

The strong visible absorption of the nitrophenoxide ions can be attributed to a strong contribution from the quinonoid form of the anions. The bond lengths determined in the crystal structure measurements are consistent with this conclusion [15]. The blue shifts produced by hydroxylic solvents must be the result of shifting

the electron distribution toward the benzenoid form through hydrogen-bonding of the solvent to the hydroxylic oxygen of the anion.

We have not been able to prepare crystals of the thallium compounds that are suitable for crystal structure measurements.

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16. The chloroform solvate crystallized in triclinic space group $P1$. Crystal data are: $C_{26}H_{40}KNO_9 \cdot CHCl_3$, $F_w = 669.1$, $a = 9.838(1)$, $b = 11.954(2)$, $c = 14.231(4)$ Å, $\alpha = 80.92(2)$, $\beta = 86.66(2)$, $\gamma = 84.03(1)^\circ$, $V = 1642.1(8)$ Å³, $Z = 2$, $C_c = 1.353$ g cm⁻³. Disorder of the solvent molecule and of the K⁺ ion above and below the best plane of the crown oxygens have prevented satisfactory refinement. At present, $R = 0.080$ for 3318 observed data collected with MoK α radiation. Preliminary coordination and a molecular drawing are included in the supplementary material.