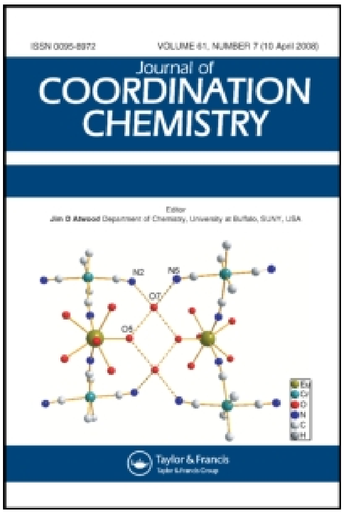

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Coordination Chemistry of Quinolyloxy Terminated Podands in the Solid and Solution States: The Crystal and Molecular Structures of Potassium Tosylate and Potassium Isothiocyanate Complexes of 1,8-*Bis*(Quinolyloxy)-3,6-Dioxaoctane

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COORDINATION CHEMISTRY OF QUINOLYLOXY TERMINATED PODANDS IN THE SOLID AND SOLUTION STATES: THE CRYSTAL AND MOLECULAR STRUCTURES OF POTASSIUM TOSYLATE AND POTASSIUM ISOTHIOCYANATE COMPLEXES OF 1,8-*BIS*(QUINOLYLOXY)-3,6-DIOXAOCTANE

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The crystal structures of 1,8-*bis*(quinolyloxy)-3,6-dioxaoctane complexes of potassium tosylate (I) and potassium isothiocyanate (II) have been determined and compared. Both complexes form monoclinic crystals belonging to the $P2_1/c$ space group with $a = 8.152(2)$, $b = 23.097(6)$, $c = 16.076(5)$ Å, $\beta = 102.14(2)°$, $Z = 4$ for (I), and $a = 11.172(2)$, $b = 22.177(2)$, $c = 9.960(2)$ Å, $\beta = 93.51(2)°$, $Z = 4$ for (II). In both cases the hexadentate podand wraps around the potassium ion in a helical fashion, while the isothiocyanate and tosylate anions strongly coordinate to the metal ion ($K^+ \ldots O(3) = 2.620(2)$Å (I); $K^+ \ldots N(3) = 2.737(7)$: (II)), the potassium ion having a coordination number of seven. As a consequence of strong ion-pair formation between the potassium ion and the isothiocyanate and tosylate anions, the podand adopts a subtly different conformation around the metal ion in the two complexes, presumably accommodating the different steric demands of the two anions. The marked differences in the ^1H NMR spectra of (I) and (II) in the non-coordinating solvent $CDCl_3$,suggests that the contact ion-pair between the complexed cation and anion persists in this solvent system. In contrast, in DMSO-d_6 the ^1H NMR spectra of (I) and (II) are essentially identical, showing that the DMSO-d_6 effectively displaces the anion from the coordination sphere of the potassium ion.

Keywords: Podands, 1,8-*bis*(quinolyloxy)-3,6-dioxaoctane, potassium tosylate, potassium isothiocyanate complexes, X-ray structure

INTRODUCTION

Synthetic acyclic oligoethers, with rigid donor terminal groups (*podands*), serve as models for naturally occurring acyclic ionophores.[1] Numerous crystal structures of, for example the 8-quinolyloxy terminated podands pioneered by Vögtle *et al.*,[2] show that these molecules tend to wrap around alkali metal cations in either a planar, helical or spherical arrangement, depending on the number of ethyleneoxy fragments in the backbone of the ligand.[1] For podands having two ethyleneoxy fragments, the span of the ligand does not allow for the complete encapsulation of the cation, leaving the metal cation coordinatively unsaturated. This is well illustrated by the hepta- and pentadentate quinolyloxy terminated podand complexes, *bis*[(8-quinolyloxy)ethoxyethyl]ether rubidium iodide[3] and *bis*(8-quinolyloxyethyl)-ether rubidium iodide.[4] The Rb^+ cation is completely encapsulated in the former case, while two I^- ions are coordinated to the Rb^+ cation in the latter complex.

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Furthermore, Laszlo *et al.* have shown that for podands in which the backbone chain is of insufficient length to completely engulf a Na^+ ion, the vacant coordination site may or may not be occupied by a solvent molecule, depending upon the Gutmann donicity of that solvent.[5] The enhanced stability of the sodium perchlorate complex of 1,11-*bis*(*o*-(methylamido)phenoxy)-3,6,9-trioxaundecane in pyridine ($K = 548$ M^{-1}, $T = 279$ K) compared to that of acetonitrile ($K = 34$ M^{-1}, $T = 273$ K) has been ascribed to the coordination of at least one pyridine molecule to the complexed cation. In the presence of strongly coordinating anions, it is conceivable that significant cation-anion interaction will compete with the solvation phenomenon, affecting the extent of *anion activation*[6] in such systems. The importance of specific anion association with crown ether complexed alkali metal cations has been found to influence anion reactivity,[7] cation-crown complex stability[8] and structure.[9–12] In the case of weakly coordinating anions, for example thiocyanate, the potassium ion of the (18-crown-6)K^+ complex is located exactly in the mean plane of the ring.[9] On the other hand, in the case of nitrate,[10] ethyl acetoacetate enolate,[11] and tosylate[12] anions, the K^+ cation is significantly displaced from the mean plane of the 18-crown-6 ligand as a consequence of strong contact ion-pair formation.

For podands, it is reasonable to expect that the geometrical arrangement of the ligating molecule around the alkali metal cation may be affected by contact ion-pair formation, both in the solid and the solution state. In solution the extent of contact ion-pair formation is expected to significantly depend upon the donor properties of the solvent. In order to investigate this proposition, we report the crystal and molecular structures of the potassium isothiocyanate and potassium tosylate complexes of the hexadentate podand 1,8-*bis*(quinolyloxy)-3,6-dioxaoctane (III). Surprisingly, no structural investigations of alkali metal complexes involving this ligand have been reported. The present study of this hexadentate podand thus contributes to a systematic examination of the effect of the number of ethyleneoxy fragments on the structure of alkali metal complexes of this series of quinolyloxy terminated podands. The extent of formation of contact ion-pairs or solvent separated ion-pairs in solution has been examined by means of ^1H NMR spectroscopy in selected solvents.

EXPERIMENTAL

The podand (III) was synthesized according to published methods.[13] All reagents and solvents were of Analytical reagent grade and used as received. Infrared spectra were measured in nujol mulls between KBr disks on a Perkin Elmer 983 Infrared spectrophotometer. ^1H NMR spectra at 25°C were obtained on a Varian VXR-200 Fourier transform spectrometer operating at 200.02 MHz.

Preparation of [($C_{24}H_{24}N_2O_4$).*KTosylate*]

The [III.KTosylate] complex is one of the reaction products formed during the preparation of (III). Prior to the purification of the ligand by column chromatography, a chloroform solution containing the ligand and the other reaction products, including the potassium tosylate complex, was allowed to stand for several days whereupon the complex crystallized out as pale, pink-brown crystals. The analytically pure crystalline complex was collected by filtration, washed with chloroform and dried over silica gel *in vacuo*. The crystals were suitable for X-ray diffraction analysis without further recrystallization: mp 158–160°C. IR (KBr): 1614(m), 1594(m), 1572(m), 1498(s), 1467(s), 1432(s), 1426(m), 1315(s), 1281(m), 1254(s), 1217(vs), 1198(vs), 1182(s), 1130(s), 1115(vs), 1102(vs), 1087(vs), 1060(s), 1033(s), 1020(m), 1011(s), 950(s), 818(s), 789(m), 760(s), 750(m), 679(s) cm^{-1}. Anal.; Calcd. for $C_{31}H_{31}N_2O_7SK$: C, 60.0; H, 5.1; N, 4.6%. Found: C, 60.65, H, 5.15, N, 4.65%.

Preparation of [($C_{24}H_{24}N_2O_4$.KNCS]

The complex [III.KNCS] was prepared by combining equimolar (0.5 mmol) amounts of potassium thiocyanate in methanol (0.5 cm^3) and (III) in ethyl acetate (10 cm^3), followed by heating the mixture under reflux for 0.5 h. On standing, the analytically pure 1:1 complex crystallized out as yellow platelets. The crystals were collected by filtration, washed with ethyl acetate and dried over silica gel *in vacuo*. The crystals were suitable for X-ray diffraction analysis without further recrystallization: mp 158–160°C. IR (KBr): 2065(s, SCN^-), 1614(m), 1598(m), 1571(m), 1501(s), 1463(s), 1448(s), 1427(m), 1318(vs), 1294(m), 1257(vs), 1207(m), 1182(m), 1135(m), 1117(vs), 1104(vs), 1987(vs), 1075(vs), 1047(m), 945(s), 823(s), 795(s), 757(m), 744(s), 730(s), 624(s) cm^{-1}. Anal.; Calcd. for $C_{25}H_{24}N_3O_4SK$: C, 59.9; H, 4.8; N, 8.4%. Found: C, 59.8; H, 4.85; N, 8.4%.

X-ray Diffraction Data Collection

Preliminary cell dimensions and space group symmetry were determined from oscillation and Weissenberg photographs. For [III.KTosylate] and [III.KNCS] the systematic absences $0k0$, $k=2n+1$ and $h0l$, $l=2n+1$ indicated the space group $P2_1/c$.[14] Accurate cell parameters were obtained from a least-squares analysis of the setting angles of 24 reflections in the range $16° < \theta < 17°$ automatically located and centred on Enraf-Nonius CAD4 diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.7107$ Å). The intensities were collected at room temperature with an $\omega - 2\theta$ scan, with variable scan width and a maximum recording time of 40 s. The data were corrected for Lorentz and polarization effects but not for absorption.

Solution and refinement of structures

[III.KTosylate]: The structure was solved by direct methods using SHELXS-84[15] and refined using SHELX76.[16] In the final refinements, all the non-hydrogen atoms were treated anisotropically and hydrogen atoms isotropically. Quinoline and phenyl hydrogens were placed in calculated positions with a single temperature factor as were the methylene hydrogens on the ligand. The methyl hydrogens were treated as a rigid group with a single isotropic temperature factor constrained to $1.2 \times U_{11}$ of the parent carbon. A weighting scheme, $w = (\sigma^2 F)^{-1}$, was applied. In the final cycle of refinement the shift/e.s.d. was less than 0.05 and in the final difference map, maximum and minimum residual electron densities were 0.24 and -0.23 e/Å^3, respectively. Final $R = 0.038$, and $R_w = 0.037$. Attempts were made to model the charge separation between the complexed cation and anion by using scattering factors for K^+ and O^-. No improvement in the structure occurred and hence we report the result using complex neutral scattering factors obtained from Cromer and Mann[17] for non-hydrogen atoms and from Stewart *et al.*[18] for hydrogen atoms, with dispersion corrections from Cromer and Liberman.[19]

[III.KNCS]: The structure was solved by direct methods using SHELXS-84 and refined using SHELX76. In the final refinements, all the non-hydrogen atoms were treated anisotropically and hydrogen atoms isotropically. Quinoline and phenyl hydrogens were placed in calculated positions with a single temperature factor, as were the methylene hydrogens. A weighting scheme, $w=(\sigma^2F)^{-1}$, was applied. In the final cycle of refinement the shift/e.s.d. was less than 0.003 and in the final difference map, maximum and minimum residual electron densities were 0.52 and $-0.32\,e/Å^3$, respectively. Final $R=0.051$ and $R_w=0.049$. Complex neutral scattering factors were taken from Cromer and Mann[17] for non-hydrogen atoms and from Stewart *et al.*[18] for hydrogen atoms, with dispersion corrections from Cromer and Liberman.[19]

Full details of the data collection, structure solution and refinement are summarized in Table I. The final atomic coordinates and U_{eq} for [III.KTosylate] and the thiocyanate analogue are given in Tables II and III, respectively.

RESULTS AND DISCUSSION

Description of the structures

The molecular structures of [III.KTosylate] and [III.KNCS] are shown in Figures 1 and 2, respectively. The atom numbering scheme is arbitrary and not the same in the two structures.

In both structures the ligand adopts a helical arrangement around the K^+ ion, which is coordinated to all six heteroatoms of the ligand as well as to the anion associated with each complex: ([III.KTosylate]: K–O(3) (2.620(2) Å); [III.KNCS]: K–N(3) (2.737(7) Å)). The complexes are chiral and since both structures are centrosymmetric, both enantiomers of each complex are present in the crystal lattice.

Conformation of oligoether chain

The bond distances, bond angles and torsion angles along the oligoether chain in [III.KTosylate] and [III.KNCS] are given in Tables IV and V, respectively. The bond distances are, on average, 1.47 Å for aliphatic C–C, 1.43 Å for (aliphatic)C–O and 1.36 Å for (aromatic)C–O bonds. The aliphatic C–C–O and C–O–C bond angles are approximately 109° and 114° respectively, whereas the (aromatic)C–O–C(aliphatic) bond angles are approximately 117°. These values correspond well with those reported for analogous podand metal ion complexes.[1,20]

It is interesting to note that the aliphatic C–C bond distances are much shorter than the observed mean value 1.524 Å reported for $C(sp^3)$–$C(sp^3)$ bonds in $-CH_2-CH_2-$ fragments,[21] an observation in keeping with that found in most of the crystal structures of cyclic and open-chain oligoethers and their complexes.[22] According to Hilgenfeld and Saenger, the short C–C bonds might result from the slightly polarized character of the adjacent C–O bonds which causes partially positive charges on the carbon atoms.[22]

The torsion angles about the C–C bonds are expectedly *gauche* (±60°) ([III.KTosylate]: mean 64.1°, range: 62.7(3)–66.9(3)° and [III.KNCS]: mean 61.4°, range: 56.5(5)–64.6(4)°), while those at the C–O bonds are in general *trans*(±180°) oriented ([III.KTosylate]: mean 171.8°, range: 166.2(3)–175.5(3)° and [III.KNCS]:

TABLE I
Summary of the crystal data, details of the data collection and final refinements for [($C_{24}H_{24}N_2O_4$).KTosylate] (I) and [($C_{24}H_{24}N_2O_4$).KNCS] (II).

	(I)	(II)
Crystal data		
Molecular formula	$C_{31}H_{31}N_2O_7SK$	$C_{25}H_{24}N_3O_4SK$
Molecular weight/g mol^{-1}	614.753	501.640
Space group	$P2_1/c$	$P2_1/c$
a/Å	8.152(2)	11.172(2)
b/Å	23.097(6)	22.177(2)
c/Å	16.076(5)	9.960(2)
α/°	90	90
β/°	102.14(2)	93.51(2)
γ/°	90	90
V/Å^3	2959(1)	2463(1)
z	4	4
D_c/g cm^{-3}	1.38	1.35
μ(MoK$_\alpha$)/cm^{-1}	2.54	3.29
F(000)	1288	1048
Data collection		
Crystal dimensions (mm)	0.22 × 0.25 × 0.31	0.22 × 0.25 × 0.47
Scan mode	$\omega-2\theta$	$\omega-2\theta$
Scan width (°)	$(0.69+0.35\tan\theta)$	$(0.95+0.35\tan\theta)$
Aperture width (mm)	$(1.11+1.05\tan\theta)$	$(1.12+1.05\tan\theta)$
θ Range scanned (°)	1–25	1–25
Number of unique reflections collected	4404	3704
Number of observed reflections, N, with $I_{rel}>2\sigma(I_{rel})$	3430	2924
Crystal stability (%)	<5	<5
Final refinement		
U_{iso}(H of CH_2)/Å^2	0.076(3)	0.111(5)
U_{iso}(H of CH)/Å^2	0.085(3)	0.091(4)
U_{iso}(H of CH_3)/Å^2	0.113(3)	
Number of parameters, N_P	384	309
$R=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.038	0.051
$R_w=\Sigma w^{1/2}\|\|F_o\|-\|F_c\|\|/\Sigma w^{1/2}\|F_o\|$	0.037	0.049

mean 171.3°, range: 163.3(3)–174.8(4)°). Similar values have been previously reported for closely related podand[1,20] and crown ether metal ion complexes.[22]

In the present structures the ligand is unable to wrap around the K^+ ion in a circular arrangement, adopting instead a helical configuration to avoid intramolecular interaction between the terminal quinoline moieties. This helical structure of the ligand molecule is achieved by the rotation of one C–O bond from *trans* to *gauche*, as observed in the [III.KTosylate] complex for the torsion angle C(61)–C(62)–O(7)–C(28) (−83.9(3)°) directly connected to the terminal group. On the other hand for [III.KNCS] complex, bond rotation from *trans* to *gauche* occurs

TABLE II

Fractional atomic coordinates (× 10^4) and thermal parameters (Å^2 × 10^3) of the non-hydrogen atoms with estimated standard deviations in parentheses for [($C_{24}H_{24}N_2O_4$).KTosylate].

Atom	*x/a*	*y/b*	*z/c*	U_{eq}*
O(7)	6822(2)	3580(1)	4437(1)	53(1)
K(1)	4705(1)	3160(0)	5426(0)	51(1)
S(1)	7454(1)	3243(0)	1128(0)	49(1)
N(1)	5026(3)	3191(1)	7216(1)	46(1)
N(2)	6590(3)	4249(1)	5742(2)	53(1)
O(1)	8211(3)	3153(1)	2004(1)	100(1)
O(2)	8512(2)	3547(1)	667(1)	71(1)
O(3)	6769(2)	2722(1)	699(2)	81(1)
O(4)	1948(2)	3159(1)	6288(1)	52(1)
O(5)	1177(2)	2989(1)	4511(1)	58(1)
O(6)	3786(3)	3047(1)	3666(1)	66(1)
C(1)	5698(3)	3705(1)	1118(2)	43(1)
C(2)	4102(3)	3482(1)	1014(2)	58(1)
C(3)	2743(4)	3838(1)	1023(2)	63(1)
C(4)	2959(4)	4422(1)	1136(2)	65(1)
C(411)	1473(5)	4819(2)	1145(3)	105(2)
C(5)	4565(4)	4642(1)	1252(3)	83(2)
C(6)	4521(4)	4285(1)	1235(2)	67(1)
C(11)	6564(4)	3190(1)	7696(2)	55(1)
C(12)	6980(4)	3432(1)	8506(2)	63(1)
C(13)	5765(4)	3697(1)	8836(2)	64(1)
C(14)	4102(4)	3710(1)	8355(2)	55(1)
C(15)	2763(5)	3972(1)	8650(2)	72(2)
C(16)	1191(5)	3956(1)	8156(2)	74(2)
C(17)	846(4)	3685(1)	7353(2)	62(1)
C(18)	2122(3)	3433(1)	7052(2)	48(1)
C(19)	3798(3)	3447(1)	7543(2)	45(1)
C(21)	6494(4)	4585(1)	6394(2)	67(1)
C(22)	6907(5)	5177(2)	6434(3)	79(2)
C(23)	7423(4)	5419(1)	5767(3)	78(2)
C(24)	7535(4)	5091(1)	5053(2)	61(1)
C(25)	8033(5)	5312(2)	4324(3)	81(2)
C(26)	8090(5)	4969(2)	3657(3)	85(2)
C(27)	7691(4)	4381(2)	3669(2)	69(1)
C(28)	7209(3)	4149(1)	4357(2)	49(1)
C(29)	7104(3)	4498(1)	5072(2)	47(1)
C(41)	264(3)	3051(1)	5820(2)	60(1)
C(42)	398(4)	2675(1)	5086(2)	64(1)
C(51)	1166(4)	2675(1)	3744(2)	66(1)
C(52)	2107(4)	3003(1)	3211(2)	64(1)
C(61)	4944(4)	3231(1)	3179(2)	65(1)
C(62)	6637(4)	3197(1)	3718(2)	64(1)

* U_{eq} = 1/3 (trace of the orthogonalized U_{ij} matrix).

TABLE III

Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\text{Å}^2 \times 10^3$) of the non-hydrogen atoms with estimated standard deviations in parentheses for [($C_{24}H_{24}N_2O_4$).KNCS].

Atom	x/a	y/b	z/c	U_{eq}*
K(1)	3597(1)	1178(1)	2112(1)	53(1)
N(1)	4589(2)	29(1)	3009(3)	50(1)
C(11)	5736(3)	−80(2)	2884(4)	63(1)
C(12)	6339(3)	−591(2)	3451(4)	70(2)
C(13)	5724(4)	−987(2)	4160(4)	70(2)
C(14)	4501(3)	−895(2)	4332(3)	57(1)
C(15)	3814(4)	−1291(2)	5082(4)	71(2)
C(16)	2641(4)	−1178(2)	5223(4)	80(2)
C(17)	2091(3)	−674(2)	4626(4)	69(2)
C(18)	2729(3)	−279(2)	3883(4)	51(1)
C(19)	3969(3)	−377(1)	3724(3)	46(1)
N(2)	5720(2)	1320(1)	740(3)	51(1)
C(21)	6005(4)	861(2)	−8(4)	65(2)
C(22)	7159(4)	734(2)	−389(4)	78(2)
C(23)	8059(4)	1112(2)	21(4)	79(2)
C(24)	7822(3)	1622(2)	821(4)	62(2)
C(25)	8712(4)	2035(2)	1282(5)	84(2)
C(26)	8418(4)	2498(2)	2064(5)	88(2)
C(27)	7238(3)	2593(2)	2435(4)	70(2)
C(28)	6349(3)	2203(2)	1988(4)	51(1)
C(29)	6626(3)	1701(2)	1164(3)	48(1)
O(1)	2258(2)	220(1)	3267(3)	62(1)
C(31)	1019(3)	359(2)	3530(5)	87(2)
C(32)	632(3)	849(2)	2745(6)	101(2)
O(2)	1331(2)	1385(1)	2905(3)	83(1)
C(41)	1228(3)	1727(2)	4074(5)	84(2)
C(42)	1789(3)	2324(2)	3881(5)	84(2)
O(3)	3046(2)	2246(1)	3704(3)	67(1)
C(51)	3531(3)	2778(2)	3139(5)	73(2)
C(52)	4858(3)	2736(2)	3137(4)	66(2)
O(4)	5168(2)	2251(1)	2260(2)	54(1)
S(3)	613(1)	1089(1)	−2357(1)	82(1)
C(3)	1585(4)	979(2)	−1101(4)	66(2)
N(3)	2295(4)	913(2)	−231(4)	110(2)

* $U_{eq} = 1/3$ (trace of the orthogonalized U_{ij} matrix).

two bonds earlier at C(31)-C(32)-O(2)-C(41) (−74.4(5)°). A similar helical arrangement of 1,11-*bis*(quinolyloxy)-3,6,9-trioxaundecane (abbreviated to (**IV**)) is adopted in the KNCS and RbI complexes,[3,22] the helical conformation of (**IV**) being achieved by the rotation of one C–O bond from *trans* to *gauche*. The dihedral angle of this bond in the [**IV**.KNCS] complex is 75° and for the [**IV**.RbI] complex 69°.

In the [**III**.KTosylate] complex the heteroatoms N(1), O(4), O(5) and O(6) are essentially coplanar (deviation from mean plane <0.02 Å), the O(7) and N(2) atoms located 1.08 and 2.49 Å respectively above this plane. The K^+ ion lies 0.08 Å above the plane described by the atoms mentioned above. The geometrical arrangement of

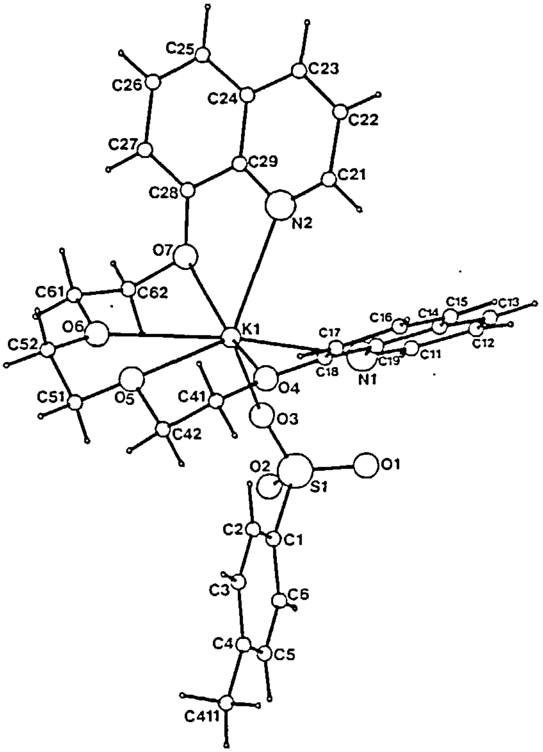

FIGURE 1 Perspective view of the molecular structure of [III.KTosylate] showing the atom numbering scheme for all non-hydrogen atoms.

the heteroatoms of the ligand results in a nearly perpendicular orientation of the heterocycles with respect to each other. The dihedral angle between the planes of the quinoline rings is 82.9°. On the other hand, in the [III.KNCS] complex, the N(2), O(4), O(3) and O(2) atoms are coplanar within 0.05 Å. The O(1) and N(1) atoms and K^+ ion lie 1.97, 2.89 and 0.46 Å respectively out of this plane. The dihedral angle between the planes of the terminal groups is 65.2°, considerably smaller than that observed in the [III.KTosylate] complex. In the corresponding KNCS and RbI complexes of (IV), the K^+ and Rb^+ ions are situated 0.66 and 0.75 Å above the planar part of the ligand.[1,20]

Coordination to potassium

In both structures, one of the K^+–N bond distances ([III.KTosylate]: K^+–N(1), 2.835(2) Å and [III.KNCS]: K^+–N(2), 2.829(3) Å) is close to the sum of the ionic and van der Waals radii 2.83 Å,[23] while the second K^+–N bond distance is extended somewhat ([III.KTosylate]: K^+–N(2), 2.936(3) Å and [III.KNCS]: K^+–N(1), 2.896(2) Å). These distances compare with those observed in the [IV.KNCS] complex (K^+–N: mean 2.81 Å)[22] and in the KNCS coronand complex of tetraoxa-1,7,10,16-diaza-4,13-cyclooctadecane (K^+–N distances are 2.856(3) Å.)[24]

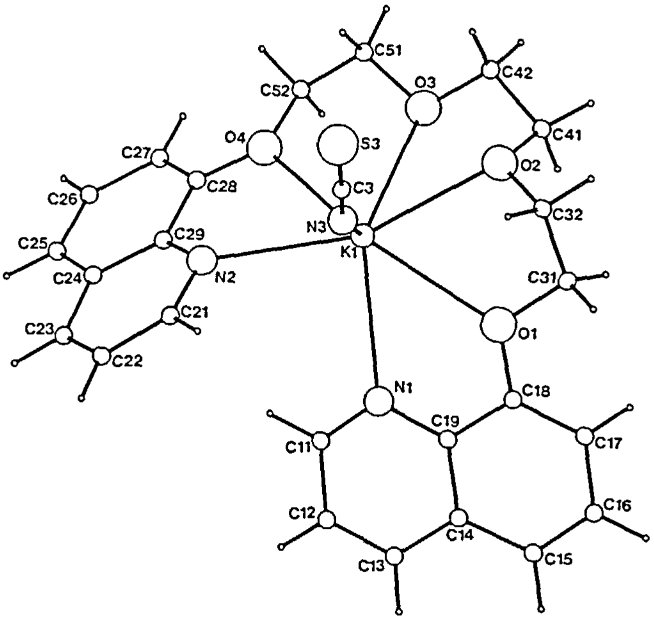

FIGURE 2 The molecular structure of [III.KNCS] showing the atom numbering scheme for all non-hydrogen atoms.

TABLE IV

Bond distances (Å), bond angles (°) and torsion angles (°) along the oligoether chain of $[(C_{24}H_{24}N_2O_4.KTosylate]$ with estimated standard deviations in parentheses.

A	B	C	D	B–C (Å)	A–B–C (°)	A–B–C–D* (°)
C(11)	N(1)	C(19)	C(18)	1.360(4)	117.3(3)	−177.6(3)
N(1)	C(19)	C(18)	O(4)	1.427(3)	118.2(3)	−0.4(4)
C(19)	C(18)	O(4)	C(41)	1.362(4)	114.5(3)	170.7(3)
C(18)	O(4)	C(41)	C(42)	1.442(3)	117.3(2)	−171.6(3)
O(4)	C(41)	C(42)	O(5)	1.488(4)	107.1(2)	−66.9(3)
C(41)	C(42)	O(5)	C(51)	1.425(4)	109.5(2)	−173.2(3)
C(42)	O(5)	C(51)	C(52)	1.429(4)	112.3(2)	−175.5(3)
O(5)	C(51)	C(52)	O(6)	1.474(5)	109.3(2)	62.7(3)
C(51)	C(52)	O(6)	C(61)	1.413(4)	107.6(3)	166.2(3)
C(52)	O(6)	C(61)	C(62)	1.413(4)	115.0(2)	−174.3(3)
O(6)	C(61)	C(62)	O(7)	1.470(4)	108.1(3)	−62.7(3)
C(61)	C(62)	O(7)	C(28)	1.438(4)	111.6(3)	−83.9(3)
C(62)	O(7)	C(28)	C(29)	1.364(3)	120.3(3)	170.8(3)
O(7)	C(28)	C(29)	N(2)	1.422(4)	114.6(3)	−2.1(4)
C(28)	C(29)	N(2)	C(21)	1.363(5)	118.7(3)	−179.5(3)

*The torsion angles are defined as follows: in a molecular fragment –A–B–C–D–, the torsion angle about the B–C bond is the dihedral angle between the planes defined by A–B–C and B–C–D. The strain free values of these angles are ±180° (*trans*) or ±60° (*gauche*).

TABLE V
Bond distances (Å), bond angles (°) and torsion angles (°) along the oligoether chain of [$(C_{24}H_{24}N_2O_4)$.KNCS] with estimated standard deviations in parentheses.

A	B	C	D	B–C (Å)	A–B–C (°)	A–B–C–D* (°)
C(11)	N(1)	C(19)	C(18)	1.365(4)	117.0(3)	−177.3(3)
N(1)	C(19)	C(18)	O(1)	1.421(5)	119.2(3)	1.0(5)
C(19)	C(18)	O(1)	C(31)	1.360(5)	115.2(3)	−174.2(3)
C(18)	O(1)	C(31)	C(32)	1.457(4)	115.9(3)	−174.8(4)
O(1)	C(31)	C(32)	O(2)	1.392(7)	109.3(3)	−56.5(5)
C(31)	C(32)	O(2)	C(41)	1.426(5)	116.0(4)	−74.4(5)
C(32)	O(2)	C(41)	C(42)	1.400(6)	118.1(3)	−166.6(3)
O(2)	C(41)	C(42)	O(3)	1.483(6)	108.5(4)	−63.1(4)
C(41)	C(42)	O(3)	C(51)	1.435(4)	109.5(3)	163.3(3)
C(42)	O(3)	C(51)	C(52)	1.429(5)	110.3(3)	171.8(3)
O(3)	C(51)	C(52)	O(4)	1.485(5)	110.6(4)	64.6(4)
C(51)	C(52)	O(4)	C(28)	1.439(5)	109.0(3)	171.0(3)
C(52)	O(4)	C(28)	C(29)	1.368(3)	116.7(3)	177.3(3)
O(4)	C(28)	C(29)	N(2)	1.428(6)	114.8(3)	−0.5(5)
C(28)	C(29)	N(2)	C(21)	1.365(4)	118.6(3)	−179.6(4)

* As defined in Table IV.

TABLE VI
Relevant bond lengths (Å) and bond angles (°) in [$(C_{24}H_{24}N_2O_4)$.KTosylate] with estimated standard deviations in parentheses.

Bond lengths		Bond angles	
K(1)–N(1)	2.835(2)	N(1)–K(1)–N(2)	82.5(1)
K(1)–N(2)	2.936(3)	N(1)–K(1)–O(4)	55.0(1)
K(1)–O(4)	2.878(2)	O(4)–K(1)–O(5)	57.7(1)
K(1)–O(5)	2.969(2)	O(5)–K(1)–O(6)	57.2(1)
K(1)–O(6)	2.783(2)	O(6)–K(1)–O(7)	60.9(1)
K(1)–O(7)	2.757(2)	O(7)–K(1)–N(2)	55.3(1)
K(1)–O(3)	2.620(2)		

The K^+–O bond distances in both complexes display a large variation, and are, on average, greater than the sum of the ionic and van der Waals radii (2.73) Å.[23] The K^+–O bond distances in the [III.KTosylate] complex range from 2.757(2) to 2.969(2) Å (mean 2.85 Å), while in [III.KNCS] the K^+–O bond distances range from 2.736(3) to 2.957(3) Å (mean 2.88 Å) (see Table VII and VII). These distances are significantly longer than those observed for the [(dibenzo-18-crown-6).KNCS] (2.71–2.80 Å, mean 2.76 Å)[22] and [(18-crown-6).KNCS] (range: 2.77–2.83 Å, mean: 2.81 Å)[9] complexes. A similar variation and extension in the K^+–O bond distances is observed in the [IV.KNCS] complex (range: 2.80–2.93 Å, mean: 2.86 Å)[22] as well as in some potassium-18-crown-6 complexes which have strongly coordinating anions, for example: [(18-crown-6).potassium ethylacetoacetate enolate] (range: 2.83 to

TABLE VII
Relevant bond lengths (Å) and bond angles (°) in [$C_{24}H_{24}N_2O_4$).KNCS] with estimated standard deviations in parentheses.

Bond lengths		Bond angles	
K(1)-N(1)	2.896(2)	N(1)-K(1)-N(2)	86.1(1)
K(1)-N(2)	2.828(3)	N(1)-K(1)-O(1)	55.0(1)
K(1)-O(1)	2.877(3)	O(1)-K(1)-O(2)	59.8(1)
K(1)-O(2)	2.736(3)	O(2)-K(1)-O(3)	58.7(1)
K(1)-O(3)	2.937(3)	O(3)-K(1)-O(4)	57.8(1)
K(1)-O(4)	2.957(3)	O(4)-K(1)-N(2)	54.6(1)
K(1)-N(3)	2.737(7)	N(1)-K(1)-N(3)	104.3(1)
		N(2)-K(1)-N(3)	91.7(1)
		O(1)-K(1)-N(3)	85.5(1)
		O(2)-K(1)-N(3)	80.2(1)
		O(3)-K(1)-N(3)	121.1(1)
		O(4)-K(1)-N(3)	119.9(1)

3.02 Å, mean 2.93 Å)[11] and [(18-crown-6).potassium tosylate] (range: 2.78 to 2.94 Å, mean: 2.87 Å).[12]

The bond angles formed by two adjacent donor sites with K^+ as apex are similar in both complexes and can be divided into three categories: (i) The O–K^+–O angles (range: 57.7(1)–60.9(1)°, mean 58.7°) which are determined by the specific geometry of the –O-CH_2CH_2-O– fragments within the oligoether chain. (ii) The N–K^+–O angles of 54.6(1)° to 53.(1)° (mean 55°) which are laid down by the atomic arrangement in the 8-quinolyloxy moiety and (iii) the N–K^+–N angles 82.5(1)° and 86.1(1)° for the [III.KTosylate] and [III.KNCS] complexes respectively, which result from the acyclic structure of the ligand.

The most interesting aspect of the molecular structures of [III.KTosylate] and [III.KNCS] is that the hexadentate podand, although still adopting a helical conformation about the K^+ ion, leaves a vacant coordination site, which is occupied by the tosylate and isothiocyanate anions respectively. By comparison, the structures of [IV.KNCS] and [IV.RbI] show that the K^+ and Rb^+ ions are completely engulfed by the (IV) ligand, the anion being effectively excluded from the coordination sphere of the complexed metal ion.[3,22] This observation is in keeping with the finding that the majority of the K^+ complexes tend to be 7 or 8 coordinate. In the present study the K^+–O(3) (tosylate) and K^+–N(3) (isothiocyanate) distances (2.620(2) Å and 2.737(7) Å, respectively) are significantly shorter than the sum of the corresponding ionic and van der Waals radii (2.73 and 2.83 Å, respectively[23]), confirming the formation of strong contact ion-pairs. By contrast, in the [(18-crown-6).KTosylate] complex, the tosylate anion interacts strongly with the K^+ ion in a bidentate mode in the solid state (K^+–O: 2.69 and 2.93 Å)[13], while in the [(18-crown-6).KNCS] compound, only *weak* anion-cation interaction is evident (K^+–N: 3.19 Å).[9] This interesting observation presumably reflects the differing stabilities of the K^+ ion complexes of 18-crown-6 and the (III) podand studied here. In methanol solution, the alkali metal complex formation constants for podates are typically two orders of magnitude smaller than those for corresponding coronates.[1] Hence the nature of the

TABLE VIII

Proton chemical shift data (ppm) for [III_4.KTosylate] and [III_4.KNCS] in various solvents. The total shifts, $\Delta\delta H^*_{(n)}$, relative to the free ligand are given in parentheses (for numbering of H atoms see Figure 3).

Solvent	H_2	H_4	H_3	$H_{5,6}$	H_7	$H_{AA'}$	$H_{BB'}$	$H_{CC'}$
III_4-KTosylate								
$CDCl_3$	8.83 (0.07)	8.09 (0)	7.38 (0)	5.32–7.38	7.08 (0)	4.39 (0)	4.05 (0)	3.80 (0)
CD_3NO_2	8.17 (0.58)	8.28 (−0.05)	7.32 (0.20)	7.55–7.59	7.27 (−0.10)	4.47 (−0.17)	4.09 (−0.07)	3.90 (−0.08)
CD_3CN	8.28 (0.54)	8.23 (−0.03)	7.30 (0.15)	7.51–7.54	7.21 (−0.09)	4.37 (−0.08)	3.96 (−0.03)	3.78 (−0.04)
CD_3COCD_3	8.58 (0.27)	8.29 (−0.05)	7.42 (0.03)	7.51–7.54	7.26 (−0.07)	4.44 (−0.08)	4.05 (−0.05)	3.86 (−0.06)
DMSO-d_6	8.60 (0.28)	8.31 (0)	7.44 (0.12)	7.49–7.55	7.21 (−0.03)	4.29 (0)	3.89 (0.04)	3.70 (0.04)
III_4-KNCS								
$CDCl_3$	8.27 (0.63)	8.06 (0.03)	7.17 (0.22)	7.41–7.45	7.09 (−0.02)	4.42 (−0.03)	4.07 (−0.01)	3.86 (−0.07)
CD_3NO_2	8.10 (0.65)	8.30 (−0.07)	7.31 (0.20)	7.57–7.61	7.28 (−0.11)	4.50 (−0.20)	4.10 (−0.08)	3.92 (−0.10)
CD_3CN	8.13 (0.68)	8.25 (−0.05)	7.27 (0.19)	7.53–7.56	7.22 (−0.11)	4.39 (−0.10)	3.98 (−0.04)	3.79 (−0.05)
CD_3COCD_3	8.37 (0.48)	8.34 (−0.10)	7.39 (0.07)	7.56–7.59	7.33 (−0.14)	4.51 (−0.15)	4.10 (−0.10)	3.91 (−0.10)
DMSO-d_6	8.59 (0.29)	8.31 (0)	7.45 (0.12)	7.49–7.52	7.21 (−0.03)	4.30 (0)	3.90 (0.03)	3.71 (0.03)

*The total shifts $\Delta\delta H_{(n)} = \delta H_{(L)} - \delta H_{(C)}$, $\delta H_{(L)}$ and $\delta H_{(C)}$ representing the ^1H chemical shifts for a particular proton for the ligand and complex, respectively the negative values designate a downfield shift and the positive values an upfield shift relative to the free ligand.

ligating podand or coronand has a significant influence on the extent of the cation-anion interaction. As illustrated in this study the weaker nature of the (III)-K^+ interaction requires the stabilizing effect of the K^+-SCN^- contact ion-pair formation in contrast to the 18-crown-6 case. Furthermore the flexibility of the (III) podand allows for the accommodation of the different steric demands of the coordinating isothiocyanate and tosylate anions, as reflected in the subtle differences in the two structures presented here.

Structure in Solution

The ^1H NMR data for complexes [III.KTosylate] and [III.KNCS] in various solvents are given in Table VIII. Assignments of the various ^1H resonances are consistent with reported values for related podands[1] as well as 8-hydroxyquinoline in $CDCl_3$.[25,26] Inspection of the data in Table VIII shows that on complexation with potassium, most of the ^1H resonances of (III) experience a slight downfield shift, with the striking exception of H_2 and H_3. The chemical shifts of the hydrogen atoms attached to the 8-quinolyloxy termina have been proposed to be sensitive probes for the average conformation that the podand assumes around the alkali metal cation.[1] The pronounced *upfield* shift of the H_2 and H_3 resonances may be ascribed to the partial stacking of the quinolyloxy termina as a consquence of the helical conformation adopted by the ligand upon complexation. The ^1H NMR spectra for the $-OCH_2CH_2O-$ fragments remain characteristic of a four spin AA'BB' system with average vicinal coupling constants of $J_{AB}=J_{A'B'}$ ranging from 4.3 to 5.2 Hz, and $J_{A'B}=J_{AB'}$ ranging from 1.7 to 3.5 Hz, when comparing solutions in chloroform with DMSO-d_6 respectively. These values are typical of those observed for a XCH_2CH_2Y fragment undergoing rapid conversion between *syn-* and *anti-gauche* rotamers.[27]

The dependence of the ^1H NMR spectra of [III.KTosylate] and [III.KNCS] on the solvent is illustrated in Figure 3. The ^1H NMR spectra of [III.KTosylate] and [III.KNCS] are essentially identical in DMSO-d_6, while significantly different in $CDCl_3$. These marked differences in the H_2 chemical shifts in the non-coordinating, low dielectric $CDCl_3$ solvent ($\varepsilon=4.7$), may clearly be ascribed to contact ion-pair formation. As observed in the molecular structures described above, the nature and steric demands of the coordinated anion affects the overall conformation of the ligand (III) around the K^+ ion. By contrast in DMSO-d_6, (high Gutmann donicity, DN=29.8, and dielectric constant, $\varepsilon=45.0$) the tosylate and isothiocyanate anions are clearly displaced from the coordination sphere of the ligated cation. The chemical shift trends observed in nitromethane-d_3, acetonitrile-d_3 and acetone-d_6 are, however, more difficult to interpret unambiguously. Since these solvents have relatively high dielectric constants ($\varepsilon=35.9$, 38.0, 20.7, respectively), a degree of ionization of both complexes may be expected. The extent of the dissociation of the contact ion-pair presumably depends on the nature of the anion as well as on the relative Gutmann donicity of these solvents, suggesting competing cation-anion and cation-solvent interactions. These processes are evidently rapid on the NMR time-scale as in all cases only a single set of ^1H resonances is observed at 25°C. Our observations are consistent with the solvent dependence of the complexation enthalpies and entropies in the sodium perchlorate complex of 1,11-*bis*(*o*-(methylamido)phenoxy)-3,6,9-trioxaundecane, in pyridine and acetonitrile,[5] as already indicated above.

The ^1H NMR spectrum of uncomplexed (III) in chloroform (see Figure 3) shows an interesting similarity to the corresponding [III.KTosylate] complex, which

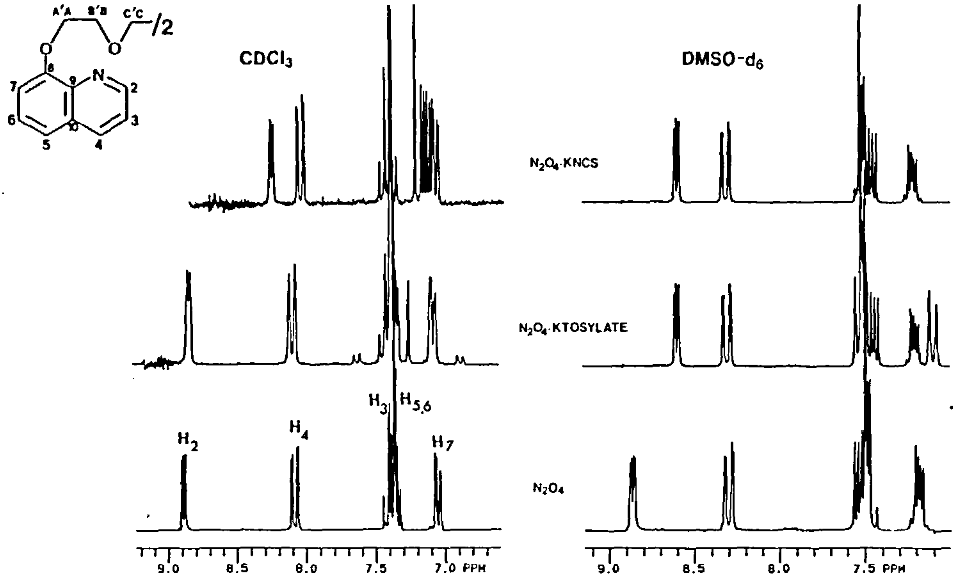

FIGURE 3 ^1H NMR spectra (showing only the quinoline termina) of (III), [III.KTosylate] and [III.KNCS] in $CDCl_3$ and DMSO-d_6 at 25°C. ($N_2O_4 \equiv$ III).

suggests that the average conformation of the uncomplexed ligand resembles that in the [III.KTosylate] complex. Hence it may not be unreasonable to conclude that the podand (III) in chloroform solution adopts a non-extended conformation, the quinolyloxy moieties being *intra*molecularly stacked to some extent. This conclusion is supported by the relative insensitivity of the ^1H NMR spectrum of (III) in $CDCl_3$ to variations in concentration. Given the possibility of *inter*molecular as well as *intra*molecular stacking between the 8-quinolyloxy moieties, ^1H chemical shifts are expected to show significant concentration dependence in the former case.[28] Experiments in which the concentration of (III) in $CDCl_3$ was varied in the range of $0.3-1.5 \times 10^{-4}$ M show that *all* the ^1H chemical shifts remain essentially invariant (<0.05 ppm) over this concentration range.[29] This observation corroborates the possibility of only *intra*molecular stacking of the 8-quinolyloxy moieties of (III) in $CDCl_3$.

In conclusion, the subtle differences in the helical conformation adopted by the hexadentate podand (III) as it wraps around the spherical potassium ion in the two complexes [III.KTosylate] and [III.KNCS] in the solid state, may be ascribed to the differences in the nature and steric demands of the two coordinated anions. Evidently, the span of the podand is insufficient to completely engulf the K^+ ion, necessitating coordination of the anions to stabilize the usually preferred coordination number of 7–8 of the potassium ion.

The significant differences between the ^1H NMR spectra of [III.KTosylate] and [III.KNCS] in non-coordinating $CDCl_3$ reflect the difference in the conformation of the podand around the potassium ion in the solid state, suggesting the persistence of strong contact ion-pair formation in this solvent system. In strongly coordinating solvents with high dielectric constants, such as DMSO-d_6, the anions are effectively displaced from the coordination sphere of the K^+ ion, resulting in identical podand conformations for both complexes as is evident from the ^1H NMR spectra.

The present study clearly illustrates that in podand metal ion complexes with vacant coordination sites, the anion and solvent have a significant influence on the podand-cation interactions and therefore on the overall structure of the complex in solution and solid state.

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SUPPLEMENTARY MATERIAL

A listing of anisotropic temperature factors for non-hydrogen atoms, hydrogen atom coordinates, equations of least-squares planes, tables of calculated and observed structure factors, complete bond lengths, angles and torsion angles, is available from KRK. Arrangements to deposit this material in the Cambridge Crystallographic Data Centre will be made.

REFERENCES

1. F. Vögtle and E. Weber, *Angew. Chem. Int. Ed. Engl.*, **18**, 753 (1979); *Angew. Chem.*, **91**, 813 (1979).
2. F. Vögtle and E. Weber, *Tetrahedron Lett.*, 2415 (1975).
3. W. Saenger and B.S. Reddy, *Acta Cryst.*, **B35**, 56 (1979).
4. (a) W. Saenger and H. Brand, *Acta Cryst.*, **B35**, 838 (1979). (b) W. Saenger, H. Brand, F. Vögtle and E. Weber, Proceedings of the 9th Jerusalem Symposia on Quantum Chemistry and Biochemistry in *Metal-Ligand Interactions in Organic Chemistry and Biochemistry*; B. Pullman and N. Goldblum, Eds.; D. Riedel: Dortrecht, Vol. 9, Part 1, p. 363 (1977).
5. J. Grandjean, P. Laszlo, W. Offernan and P.L. Rinaldi, *J. Am. Chem. Soc.*, **103**, 1380 (1981).
6. J. Grandjean, P. Laszlo, F. Vögtle and H. Sieger, *Angew. Chem. Int. Ed. Engl.*, **17**, 856 (1978); *Angew. Chem.*, **90**, 902 (1978).
7. D. Landini, A. Maia, F. Montanari and P. Tundo, *J. Am. Chem. Soc.*, **101**, 2526 (1979).
8. (a) N.S. Poonia and A.V. Bajaj, *Chem. Rev.*, **79**, 389 (1979); (b) A.I. Popov, *Pure Appl. Chem.*, **51**, 101 (1979); (c) C.J. Pedersen and H.K. Frensdorff, *Angew. Chem. Int. Ed. Engl.*, **11**, 16 (1972); *Angew. Chem.*, **84**, 16 (1972); (d) R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen and D. Sen, *Chem. Rev.*, **85**, 271 (1985).
9. P. Sieler, M. Dobler and J.D. Dunitz, *Acta Cryst.*, **B30**, 2744 (1974).
10. R.B. Dyer, R.G. Ghirardelli, R.A. Palmer and E.M. Holt, *Inorg. Chem.*, **25**, 3184 (1986), and references therein.
11. C. Riche, C. Pascard-Billy, C. Cambillau and G. Gram, *J. Chem. Soc., Chem. Comm.*, 183 (1977).
12. P. Groth, *Acta Chem. Scand.*, **25**, 3189 (1971).
13. E. Weber, W. Saenger, F. Vögtle and H. Sieger, *Angew. Chem. Int. Ed. Engl.*, **18**, 226 (1979); *Angew. Chem.*, **91**, 234 (1979).
14. *International Tables for X-ray Crystallography*, T. Hahn (Ed.), (D. Riedel; Dortrecht, 1983), Vol. A.
15. G.M. Sheldrick, SHELXS-84. Direct Methods Program; Preliminary Version; private communication (1983).
16. G.M. Sheldrick. SHELX76. *Computing in Crystallography*, H. Schenk, R. Olthof-Hazenkamp, H. von Koningsveld and G.C. Bassi (Eds.), (Delft University Press, Delft, 1978), p. 34.
17. D.T. Cromer and J.B. Mann, *Acta Cryst.*, **A24**, 321 (1968).
18. R.F. Stewart, E.R. Davidson and W.T. Simpsom, *J. Chem. Phys.*, **42**, 3175 (1965).
19. D.T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
20. W. Saenger, I.-H. Suh and G. Weber, *Isr. J. Chem.*, **18**, 253 (1979).

21. F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans.* **II**, S1 (1987).
22. R. Hilgenfeld and W. Saenger, *Host-Guest Complex Chemistry—Macrocycles—Synthesis, Structures, Applications*, F. Vögtle and E. Weber (Eds.), (Springer-Verlag, Berlin, 1985), pp. 43–124.
23. J.E. Huheey, *Inorganic Chemistry. Principles of Structure and Reactivity* (Harper and Row, New York, 1978), 2nd Edition.
24. D. Moras, B. Metz, M. Herceg and R. Weiss, *Bull. Soc. Chim. France*, 551 (1972).
25. A. Corsini, W.J. Louch and M. Thompson, *Talanta*, **21**, 252 (1974).
26. J.L. Nieto and A.M. Gutierrez, *Polyhedron*, **2**, 987 (1985).
27. R. J. Abraham and G. Gatti, *J. Chem. Soc. B*, 961 (1969).
28. (a) P.J. Black and M.L. Heffernan, *Aust. J. Chem.*, **17**, 558 (1964); (b) T. Schaefer, *Can. J. Chem.*, **39**, 1864 (1961); (c) L.W. Reeves and K.O. Stromme, *Can. J. Chem.*, **39**, 2318 (1961).
29. (a) C. Sacht, *Ph.D. Thesis*, University of Cape Town (1990); (b) No bulk susceptibility corrections were undertaken, although all shifts were measured relative to internal TMS at 25±0.1°C.