

## A $^{13}\text{C}$ Cross-polarisation Magic-angle-spinning Nuclear Magnetic Resonance Study of Some Well Characterised Crown Ethers and their Complexes

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Solid crown ethers and crown ether complexes with well determined crystal structures have been examined by  $^{13}\text{C}$  cross-polarisation magic-angle-spinning (CPMAS) n.m.r. Certain carbon atoms in most of the compounds studied gave single lines in the solution-state spectra, but produced multiplets in the spectra of the solids. Such multiplicities depend on the conformation and packing adopted by the molecules in the solid state and a qualitative discussion is presented of the origins of such splittings in these compounds. The sensitivity of  $^{13}\text{C}$  CPMAS spectra to subtle structural differences is reflected in the differences between the spectra of two isomorphous complexes.

In recent years, there has been an increasing interest in the acquisition and interpretation of high-resolution solid-state n.m.r. spectra. Wasylishen *et al.*<sup>1</sup> and Yannoni<sup>2</sup> have recently reviewed this area.

A feature observed here, and in many other studies, is that solid-state spectra give rise to line multiplicities not observed in solution. In a single phase (not a mixture of polymorphic forms), peak multiplicities may arise through a number of different effects. The splitting observed in the solid-state  $^{13}\text{C}$  spectrum of 2,4-dinitrotoluene<sup>3</sup> arises from the presence of two independent molecules in the crystal whilst benzo-15-crown-5† shows splittings which arise because packing within the crystal renders chemically equivalent pairs of atoms magnetically inequivalent.<sup>4</sup> (The origins of splittings in this compound are discussed later.) Peak multiplicities may arise through the absence of exchange between different conformers; examples are provided by the  $^{13}\text{C}$  spectra of certain *trans*-azobenzenes<sup>5</sup> and *p*-alkoxybenzoic acids.<sup>6</sup> Splittings may also be observed when the resonant nucleus is very close to a quadrupolar nucleus. This phenomenon is often observed for  $^{13}\text{C}$  directly bonded to  $^{14}\text{N}$  and occurs because the quadrupole moment prevents magic-angle-spinning from eliminating the dipole-dipole interaction between the resonant and the quadrupolar nuclei.<sup>7,8</sup> The effect usually gives rise to asymmetric multiplets, is field-dependent (rarely being observed in fields of 7 T), and is thus often easily identified.

In this study cross-polarization (CP) magic-angle-spinning (MAS) techniques have been used to obtain high-resolution solid-state  $^{13}\text{C}$  spectra of some macrocyclic polyether ligands (shown in Figure 1) and their complexes formed with salts of alkali and alkaline earth metals. These compounds have been chosen, apart from their intrinsic chemical interest, because their crystal structures have been well characterised, enabling us to make direct comparisons of spectra and structure.

### Experimental

Details of the synthesis and crystal structure determinations of the crown ethers and their complexes studied here are provided in the references given in the Table.

High-resolution solid-state  $^{13}\text{C}$  spectra were obtained with two spectrometers; one home-built and operating at 4.7 T and the other a Bruker CXP300 instrument operating at 7 T. Cross-polarisation magic-angle spinning (CPMAS) was employed with single contact pulses of 5 ms duration and recovery times

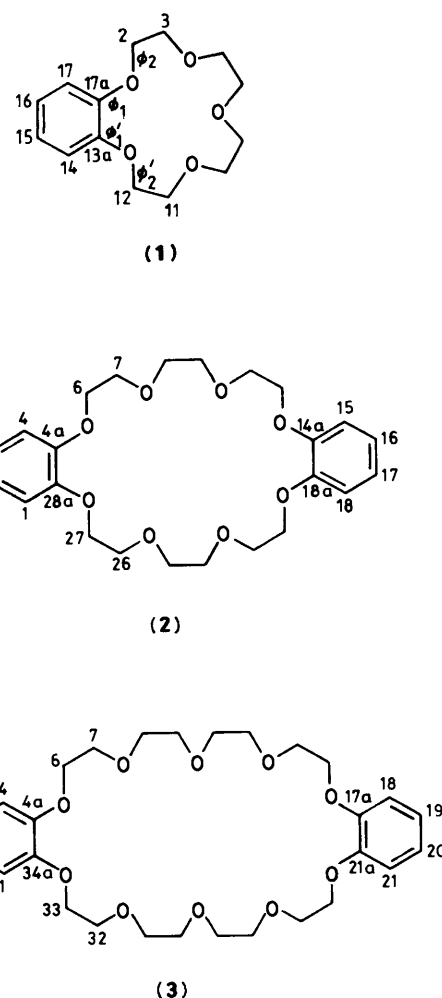


Figure 1. Structures of crown ether ligands: (1) benzo-15-crown-5 (2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine) [torsion angles  $\phi_1$  C(2)O(1)C(17a)C(13a),  $\phi_1'$  C(12)O(13)C(13a)C(17a),  $\phi_2$  C(3)C(2)O(1)C(17a),  $\phi_2'$  C(11)C(12)O(13)C(13a)], (2) dibenzo-24-crown-8 (6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[*b,n*][1,4,7,10,13,16,19,22]octaoxacyclotetrasine), and (3) dibenzo-30-crown-10 (6,7,9,10,12,13,15,16,23,24,26,27,29,30,32,33-hexadecahydrodibenzo[*b,q*][1,4,7,10,13,16,19,22,25,28]decaoxacyclotriacontine)

† Systematic names are given in the legend to Figure 1.

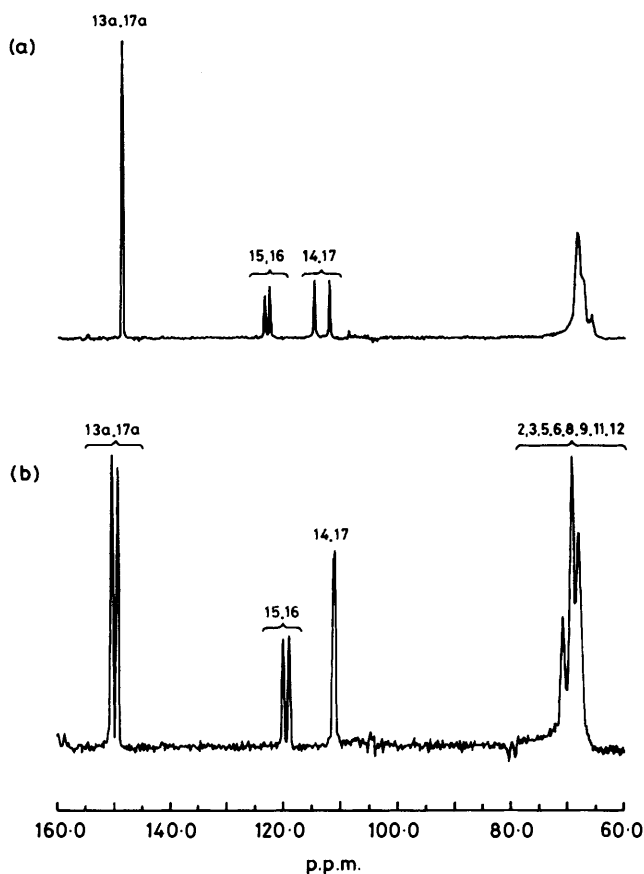


Figure 2. 75 MHz <sup>13</sup>C Spectra of (a) NaClO<sub>4</sub>(benzo-15-crown-5)<sub>2</sub>; (b) benzo-15-crown-5

between acquisitions of at least 5 s. All spectra were recorded at room temperature (*ca.* 293 K). Decoupling strengths of *ca.* 50 kHz were used with the 7 T spectrometer and 60 kHz on the lower field instrument. Spectra obtained with the CXP300 instrument were acquired by using a modest spinning rate of 3 kHz, and a modified version<sup>4</sup> of the pulse sequence TOSS (developed by Dixon<sup>9</sup>) was required to suppress spinning sidebands. As the TOSS pulse sequence contains relatively long delays prior to data acquisition, the intensities of peaks arising from the use of this sequence will almost certainly not be quantitative. Many of the spectra in this study give rise to multiplets, particularly symmetric doublets. The relative peak intensities within a given multiplet, are, however quantitative (allowing for distortion due to peak overlap). Evidence for this proposition comes from spectra acquired with and without sideband suppression where the relative peak heights within a multiplet are found to be identical. Chemical shifts are quoted with respect to tetramethylsilane and were obtained relative to the shifts of adamantane, which were measured prior and subsequent to each acquisition. The shift values quoted are somewhat inaccurate, owing to differences in bulk magnetic susceptibility between samples; however, the values are believed to be accurate to within *ca.* ±1 p.p.m. Chemical shift differences within a spectrum, however, are reliable to within ±0.1 p.p.m.

### Results and Discussion

The solid-state high-resolution <sup>13</sup>C spectra of benzo-15-crown-5 (1) and its 2:1 complex with NaClO<sub>4</sub> are shown in Figure 2. Certain peaks in the aromatic region of these spectra are split into symmetric doublets, whereas the corresponding peaks in

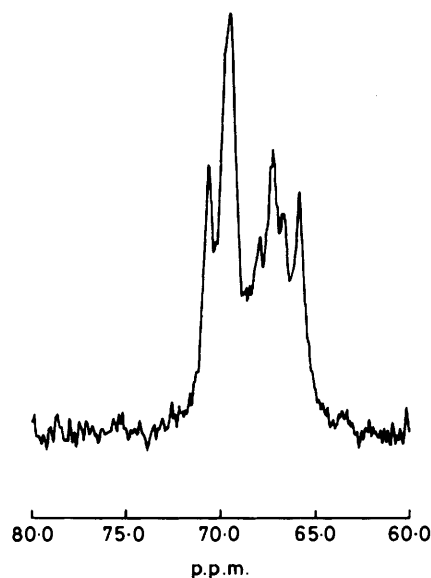


Figure 3. 75 MHz <sup>13</sup>C Spectrum of aliphatic region of Mg(NCS)<sub>2</sub>(benzo-15-crown-5)

the solution-state spectra are singlets. Carbon atoms 15 and 16 give rise to symmetric doublets in both spectra; carbon atoms 13a and 17a give a doublet in the ligand but a singlet in the complex, and carbon atoms 14 and 17 give rise to a singlet in the ligand and a doublet in the complex.

The problems of assignment of the aliphatic region of spectra of the crown ethers and their complexes are illustrated in Figure 3. This shows six lines in the aliphatic region of the <sup>13</sup>C spectrum of Mg(NCS)<sub>2</sub>(benzo-15-crown-5) which we were unable to assign to individual CH<sub>2</sub> groups within the heterocyclic ring. We have observed a complex structure in the aliphatic region of all the spectra obtained. This is due in part to crystallographic disorder present in the heterocyclic ring in a number of compounds [*e.g.* KSCN(dibenzo-30-crown-10) monohydrate and NaClO<sub>4</sub>(benzo-15-crown-5)<sub>2</sub>], resulting in either line multiplicities due to differing conformations, and/or chemical shift distributions leading to broad lines. Another complicating feature is that spectra obtained on the 7 T instrument had aliphatic resonances that were relatively weak in intensity and often poorly resolved relative to the lower field instrument. This difference in resolving power arises from a combination of the lower decoupling power of the 7 T instrument and the enhanced off-resonance proton irradiation effect (ORPI) occurring at high magnetic fields.<sup>10</sup>

Because of the problems encountered with the aliphatic region we have concentrated on the aromatic region, where there are relatively large chemical shift differences between the <sup>13</sup>C resonances. The aromatic peaks were not so sensitive to decoupling power (possibly as a result of the lower local dipolar field at the aromatic carbon atoms) and we were able to resolve a splitting of only 0.3 p.p.m. in the peaks centred at *ca.* 148 p.p.m. in KI(benzo-15-crown-5)<sub>2</sub> only when working at the higher field.

The chemical shifts of the crown ether aromatic carbon atoms are shown in the Table. It is clear that a majority of the compounds studied have at least one aromatic carbon atom that gives rise to only a single line in the solution-state spectrum, but to a multiplet in the spectrum of the solid. These peak multiplicities do not arise from the quadrupolar nature of certain nuclei in the complexes (*e.g.* Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, I<sup>-</sup>) as the chemical shifts in the spectra do not vary significantly on the two spectro-

Table.  $^{13}\text{C}$  Chemical shifts of various crown ethers and crown ether complexes

Compound	Carbon atoms (see Figure 1 for numbering)						Crystal structure ref.
	17a,13a		15,16		14,17		
Benzo-15-crown-5 (1)	150.4	149.4	120.0	119.0	111.2		a
	(149.2) <sup>†</sup>	(150.3) <sup>‡</sup>	(121.4) <sup>†</sup>	(122.0) <sup>‡</sup>	(114.2) <sup>†</sup> (115.2) <sup>‡</sup>		
NaI(benzo-15-crown-5)·H <sub>2</sub> O	147.9	147.3	125.9	124.1 <sup>§</sup>	118.0 <sup>§</sup> 115.0		b
	(146.5) <sup>†</sup>	(148.2) <sup>‡</sup>	(122.0) <sup>†</sup>	(123.0) <sup>‡</sup>	(112.6) <sup>†</sup> (114.6) <sup>‡</sup>		
NaClO <sub>4</sub> (benzo-15-crown-5)	147.0		124.7	123.4	114.8		c
	(146.6) <sup>†</sup>	(148.3) <sup>‡</sup>	(122.2) <sup>†</sup>	(123.0) <sup>‡</sup>	(112.6) <sup>†</sup> (114.6) <sup>‡</sup>		
Mg(NCS) <sub>2</sub> (benzo-15-crown-5)	143.8		124.7	122.1	111.0		d
Ca(NCS) <sub>2</sub> (benzo-15-crown-5)·H <sub>2</sub> O	150.2	147.3	127.7	122.9 <sup>§</sup>	113.0 <sup>§</sup>		d
Ca(NCS) <sub>2</sub> (benzo-15-crown-5)·MeOH	148.2	147.6	125.0	120.4 <sup>§</sup>	113.6 <sup>§</sup>		d
NaClO <sub>4</sub> (benzo-15-crown-5) <sub>2</sub>	149.1		123.8	122.9	115.0 112.5		c
KI(benzo-15-crown-5) <sub>2</sub>	148.0	147.7	125.5	122.2	115.8 114.4		e
	(147.7) <sup>†</sup>		(121.9) <sup>†</sup>		(113.7) <sup>†</sup>		
	Carbon atoms						
	4a,14a,18a,28a		2,3,16,17		1,4,15,18		
Dibenzo-24-crown-8 (2)	149.5		119.7		111.8		f
	(149.1) <sup>†</sup>		(121.4) <sup>†</sup>		(114.7) <sup>†</sup>		
	Carbon atoms						
	4a,17a,21a,34a		2,3,19,20		1,4,18,21		
Dibenzo-30-crown-10 (3)	150.1		121.3 119.8		115.4 114.4		g
	(149.0) <sup>†</sup>		(121.5) <sup>†</sup>		(114.6) <sup>†</sup>		
KI(dibenzo-30-crown-10)	149.6	147.7	121.8	120.3 <sup>§</sup>	118.0 <sup>§</sup> 110.0		g
	(148.8) <sup>†</sup>		(123.0) <sup>†</sup>		(116.6) <sup>†</sup>		
KSCN(dibenzo-30-crown-10) anhydrous	151.6	147.6	126.6	122.8	120.1 116.2		h
	(148.8) <sup>†</sup>		(123.0) <sup>†</sup>		(116.5) <sup>†</sup>		
KSCN(dibenzo-30-crown-10)·H <sub>2</sub> O	151.8	148.8 148.0	123.4	122.6 119.7	119.3 112.8 111.4*		h
RbSCN(dibenzo-30-crown-10)·H <sub>2</sub> O	151.7	148.6 147.8	123.5	123.1 119.7	113.1 111.6 111.0*		i

Solution-state chemical shifts where available given in parentheses; superscript <sup>†</sup> indicates shifts measured in CDCl<sub>3</sub>; superscript <sup>‡</sup> indicates shifts measured in (CD<sub>3</sub>)<sub>2</sub>CO. An asterisk (\*) indicates that the assignment of carbons 2, 3, 19, and 20 and 1, 4, 18, and 21 is uncertain. The sign § indicates that this assignment may be reversed. <sup>a</sup> I. R. Hanson, *Acta Crystallogr., Ser. B*, 1978, **34**, 1026. <sup>b</sup> M. A. Bush and M. R. Truter, *J. Chem. Soc., Perkin Trans. 2*, 1972, 341. <sup>c</sup> J. D. Owen, *J. Chem. Soc., Dalton Trans.*, 1980, 1066. <sup>d</sup> J. D. Owen, *J. Chem. Soc., Dalton Trans.*, 1978, 1418. <sup>e</sup> P. R. Mallinson and M. R. Truter, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1818. <sup>f</sup> I. R. Hanson, D. L. Hughes, and M. R. Truter, *J. Chem. Soc., Perkin Trans. 2*, 1976, 972. <sup>g</sup> M. A. Bush and M. R. Truter, *J. Chem. Soc., Perkin Trans. 2*, 1972, 345. <sup>h</sup> J. D. Owen, M. R. Truter, and J. N. Wingfield, *Acta Crystallogr., Ser. C*, 1984, **40**, 1515. <sup>i</sup> J. Hasek, K. Huml, and D. Hlavata, *Acta Crystallogr., Ser. B*, 1979, **35**, 330.

meters operating at different field strengths. Detailed examination of the crystal structures of both ligand and complexes shows that the peak multiplicities have their origins in both inter- and intra-molecular interactions.

An important intramolecular source of splitting must arise as a consequence of differences in the torsion angles,  $\phi_1$ ,  $\phi'_1$ ,  $\phi_2$ , and  $\phi'_2$ , defined in Figure 1. Changes in  $\phi_1$  and  $\phi'_1$  affect the extent of resonance delocalisation of the oxygen *p* electrons into the aromatic  $\pi^*$  orbitals; if  $\phi_1 \neq \phi'_1$  the electron densities at the carbon atoms on the two sides of the ring will be different. There is also a steric effect; interaction between the  $\alpha$ -CH<sub>2</sub> of the heterocyclic ring and the 'ortho' aromatic CH will depend upon the values of  $\phi_1$  and  $\phi_2$  and of  $\phi'_1$  and  $\phi'_2$ , and will primarily affect the chemical shifts of the carbon atoms involved. If  $\phi_1 \neq \phi'_1$ , the equivalence amongst the members of the three pairs of aromatic carbon atoms is lost, and, in contrast to the solution state, these conformational differences will not be dynamically averaged; thus in principle three pairs of lines may be observed.

Important intermolecular contributions to splitting include intermolecular steric interactions, electrostatic interactions of

C–O dipoles with aromatic hydrogen atoms from neighbouring molecules, and through-ring-current effects analogous to those observed in solution (see later). In addition there may be non-specific intermolecular effects which arise because small distortions in molecular geometry could be traded off against the overall reduction in crystal free energy resulting from some preferred packing arrangement.

A further potential source of splitting in the complexes arises as a consequence of the polarisation of filled molecular orbitals by electric fields originating at the ions. The most polarisable orbitals will be the delocalised  $\pi$  orbitals on the aromatic ring(s). The crystal structures of the complexes indicate that even where there are marked differences between  $\phi_1$  and  $\phi'_1$ , the complexed metal ion is, to a good approximation, symmetrically disposed with respect to the aromatic ring. (C...M<sup>+</sup> distances for all pairs of aromatic carbon atoms differ by less than 0.1 Å.) Thus although the presence of the metal ion may affect the absolute values of chemical shifts it will not be a major source of peak multiplicities. The intermolecular contribution of the metal ion to splitting will also generally be small because it is either partially or completely encapsulated by the crown ether

part of the ligand. In contrast, in a number of complexes (*e.g.* the iodides) the anions lie close to and asymmetrically disposed with respect to the aromatic ring and may thus be an important source of splitting.

Some of the compounds shown in the Table [*e.g.* benzo-15-crown-5, dibenzo-24-crown-8,  $\text{NaClO}_4(\text{benzo-15-crown-5})_2$ , and  $\text{NaI}(\text{benzo-15-crown-5})$  monohydrate] contain ligand and cation units which possess an approximate plane of symmetry; therefore the splittings observed in the spectra of these compounds are unlikely to arise from intramolecular interactions and indicate the importance of interactions with species outside the local unit. For benzo-15-crown-5, inspection of the crystal structure reveals a lack of symmetry in that one side of each benzene ring points towards the benzene ring of a neighbouring molecule whilst the other side points towards a heterocyclic ring. Calculations on the effect of ring currents using the Johnson-Bovey approach<sup>11</sup> predict splittings of *ca.* 1 p.p.m. in benzo-15-crown-5, but do not reproduce the observed pattern of splittings.<sup>12</sup> Similar ring-current contributions have been calculated to be present in a number of complexes; however, as the observed peak multiplicities are generally larger than 1 p.p.m., factors other than ring currents must be contributing to the observed splittings.

The ligands dibenzo-24-crown-8 and dibenzo-30-crown-10 possess crystallographic centres of symmetry relating pairs of carbon atoms in the two aromatic rings. Consequently a maximum of three pairs of lines may be expected in the aromatic regions of the spectra of these compounds. The splittings encountered (Table) are consistent with this expectation. The spectra of  $\text{KI}(\text{dibenzo-30-crown-10})$  and  $\text{KSCN}(\text{dibenzo-30-crown-10})$  (anhydrous) show three sets of doublets in the aromatic region. For the KI complex this is also consistent with the crystal structure, which shows the potassium ion to lie on a two-fold symmetry axis and the carbon atoms of the ligand to be related thereby. The spectrum of the anhydrous KSCN complex lends support to a recent reinterpretation of the crystal structure of this compound, which also suggests the presence of a two-fold axis of symmetry at the cation position.<sup>13</sup> The absence of splitting is not conclusive evidence for the absence of interactions that might be expected to cause splittings however, as broad lines and/or the addition of effects of opposite sign could mask such interactions.

Figure 4 shows spectra of the aromatic region of the  $\text{KSCN}(\text{dibenzo-30-crown-10})$  monohydrate and  $\text{RbSCN}(\text{dibenzo-30-crown-10})$  monohydrate complexes. These two complexes are of particular interest in that they have isomorphous crystal structures. They possess neither a centre of symmetry nor a two-fold axis at the cation; consequently the spectra shown are more complicated than those of the other complexes or ligands. The 'non-quaternary suppression' (NQS) experiment<sup>14</sup> shows that four peaks arise from quaternary carbon atoms. One of these (at *ca.* 130 p.p.m.) is tentatively assigned to the thiocyanate carbon atom. Although spectra obtained at the lower applied magnetic field (4.7 T) did not result in this peak splitting into the characteristic asymmetric doublet (often encountered in lower field spectra for carbon atoms directly bonded to nitrogen<sup>8</sup>), broadening indicative of unresolved splitting was observed. No analogous resonances were observed in spectra of the other thiocyanate complexes studied here. The other three peaks in Figure 4 that remain when the NQS pulse sequence was used are those occurring at highest frequency (*ca.* 147–152 p.p.m.) and are assigned to the aromatic quaternary carbon atoms. Consideration of crystal structures shows that the torsion angles in these complexes are very similar at one aromatic ring ( $\phi_1 \approx \phi_1' = 170\text{--}180^\circ$ ) but differ substantially at the second ring (105–110° and 170–175°). This enables a tentative assignment of the most intense peak (at *ca.* 148 p.p.m.) to the two quaternary carbon atoms in the ring with the similar  $\phi_1$  and

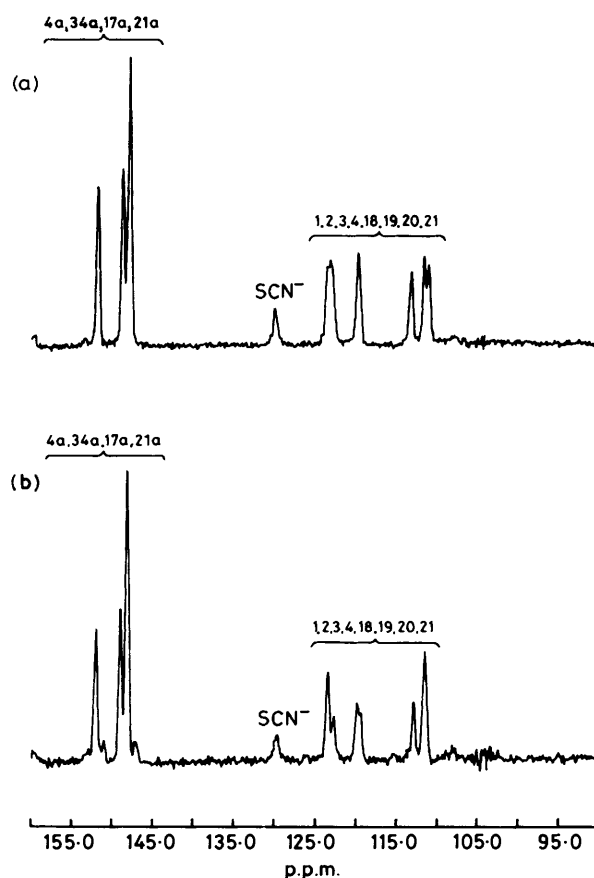


Figure 4. 75 MHz  $^{13}\text{C}$  Spectra of aromatic regions of (a)  $\text{RbSCN}(\text{dibenzo-30-crown-10})$  monohydrate; (b)  $\text{KSCN}(\text{dibenzo-30-crown-10})$  monohydrate

$\phi_1'$  values; the two less intense peaks are due to the two quaternary carbon atoms having different  $\phi$  values in the second ring. Assignment of the remaining protonated aromatic resonances is considerably more difficult, requiring consideration of the factors discussed earlier. Both inter- and intra-molecular effects are important in contributing to their chemical shifts. As a result of the very high resolution obtained (in some cases splittings resolved are in the region of 30 Hz), differences can be seen between the spectra of the rubidium and potassium complexes. A resolution of about 1 p.p.m. would result in the two spectra shown in Figure 4 having very similar appearance, consistent with the isomorphous crystal structures. At the level of resolution achieved here therefore, CPMAS  $^{13}\text{C}$  n.m.r. is a sensitive probe for very subtle structural differences (*e.g.* metal-oxygen distances vary by  $<0.2\text{\AA}$  and the torsion angles within the heterocyclic ring vary by  $<15^\circ$ ). We believe that the data given here together with the details of crystal structures represent a challenge to the theoretical interpretation of chemical shifts in solids.

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