

Stoichiometry and Conformation of the Azacrown Moiety in Sodium Complexes of Azacrown Ethers. A Raman/IR Spectroscopic Study. Part I: Complexes of 4,13-Diaza-18-crown-6

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Abstract. Three sodium complexes (bromide, iodide and thiocyanate) of 4,13-diaza-18-crown-6 were studied using Raman and IR spectroscopy and normal coordinate calculations to probe the stoichiometry of the complexes and the variation in the conformation of azacrown moiety on complex formation. Complex formation is accompanied by characteristic shifts of the bands, especially of those in the 800–900 cm⁻¹ region. Complexes of both 1 : 1 and 2 : 1 stoichiometry were observed. Normal coordinate calculations showed the reduction of symmetry of azacrown moiety to *C_i*, in contrast to the *C_{2h}* symmetry known for the parent azacrown and potassium thiocyanate complex.

Key words: Azacrown ether, sodium complex, conformation, Raman/IR spectra, normal mode calculations.

1. Introduction

Crown ethers constitute an important class of macrocyclic ligands [1–3]. Their peculiar properties originate from their ability to incorporate a wide variety of metal ions in their cavities, which causes a substantial conformational change of the cyclic oxyethylene chain. Raman spectroscopy has proved to be a very powerful means to probe these changes. Sato and Kusumoto [4] investigated Raman spectra of 1,4,7,10,13,16-hexaoxacyclooctadecane (18C6), 1,4,7,10,13-pentaoxacyclopentadecane (15C5), along with their complexes with Na and K salts, and found that the crown rings in these complexes have highly symmetric conformations in both crystalline and viscous liquid states. Fouassier and Lassegues [5] measured IR, Raman and neutron spectra of alkali metal complexes of 18C6 in

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the solid state. Takeuchi *et al.* [6] carried out a detailed study of the Raman spectra of 18C6, 15C5 and their complexes with Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} and Ba^{2+} with normal coordinate calculations. They concluded, among other things, that ring structures in 18C6 complexes are not much distorted from the highly symmetric D_{3d} configuration, while 15C5 complexes exhibit several types of ring structures, depending on the size and charge of the cation. Fukushima and Tamaki [7] studied the Raman spectra of 1,4,7,10-tetraoxacyclododecane (12C4) and its Li^+ , Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} and Pb^{2+} complexes. With the aid of normal vibration calculations they found that the conformation of the crown ring in these complexes depends to a remarkable degree on the cation. Khanna and Stranz [8] and Hilliard *et al.* [9] studied the IR and Raman spectra of counteranions (permanganate, dichromate and oxalate) in potassium complexes of 18C6. Zhelyaskov *et al.* [10] analysed Raman CH stretching spectra of 12C4, 15C5, 18C6 and their complexes with Li^+ , Na^+ , K^+ and Cu^+ , applying Fourier deconvolution to resolve the overlapped components due to intramolecular interactions and Fermi resonance. Benzo-15C5 and benzo-18C6 have been studied by Egyed and Izvekov [11] and by Takeuchi *et al.* [12], respectively.

In azacrown ethers, some of the oxygen donor atoms in crown ethers are substituted by NH or NR groups. The conformations of metal ion complexes of azacrown ethers are more interesting than those of crown ethers, in view of the different abilities of electron donation and hydrogen bond formation of NH and NR groups compared to O atoms. Although rather extensive studies have been performed on complexes of crown ethers, those on azacrown ethers are still very limited. Matsuura *et al.* [13] reported Raman and IR spectra of uncomplexed 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (4,13-diaza-18-crown-6, hereafter abbreviated as A_2 18C6) and analysed the data by normal coordinate calculations. This compound is known to crystallize in the C_{2h} conformation [14], as its KSCN complex does [15]. In the present paper, a Raman/IR spectroscopic study has been performed on sodium complexes of A_2 18C6. The stoichiometry of the complexes has been revealed. Normal mode calculations have been carried out to predict the conformations of the azacrown moiety in these complexes.

2. Experimental

A_2 18C6 from Merck was recrystallized from *n*-heptane. Sodium salts (bromide, iodide and thiocyanate) were G.R. reagents from Nacalai Tesque and recrystallized from methanol. Methanol (G.R. from Nacalai Tesque) was purified by distillation.

A_2 18C6 and an alkali metal salt were mixed in a known ratio with methanol in a screw-topped glass bottle, and allowed to react at room temperature for a few hours under sonication. Methanol was then evaporated off. Crystalline products obtained were dried under vacuum.

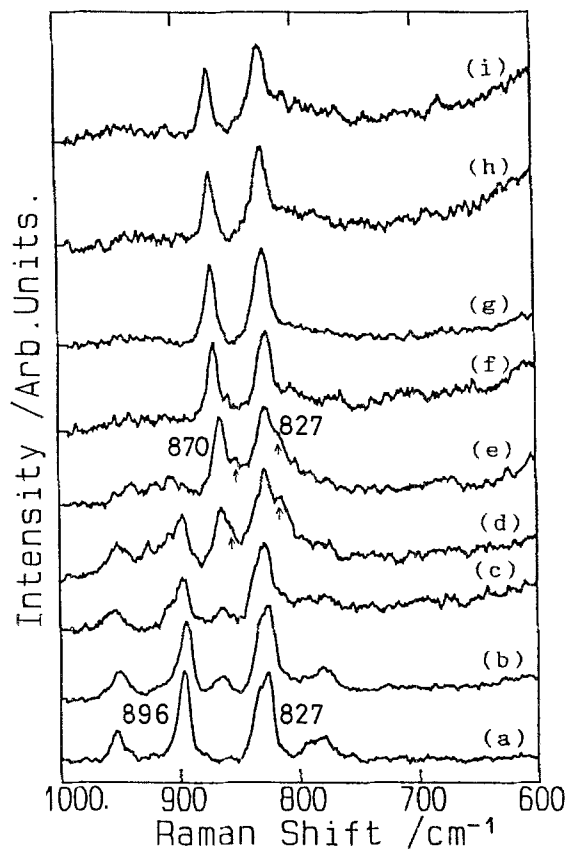


Fig. 1. Raman spectra of the NaBr-A₂18C6 system for various [NaBr]/[A₂18C6] ratios. (a) A₂18C6, (b)–(i) [NaBr]/[A₂18C6] = 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5 and 3.0, respectively. Small arrows: see Text.

Raman measurements were performed at room temperature on the crystalline complex in a sealed glass tube. The excitation radiation at 514.5 and 488 nm was obtained from a Spectra Physics 165 argon ion laser. A Jasco CT 80D double monochromator equipped with a Hamamatsu R-649/C-1050 photomultiplier/photon counting unit was used in the measurements. IR measurements were made on KBr discs using a Jasco IR-700 spectrophotometer.

2.1. EXPERIMENTAL RESULTS

The Raman spectra of NaBr, NaI and NaSCN complexes are shown in Figures 1–3. Positions of the Raman and IR bands are given in Tables I–IV.

TABLE I. Observed and calculated wavenumbers (cm^{-1}) and vibrational assignments for NaBr and NaI (1 : 1) complexes of $\text{A}_2\text{18C6}$.

| NaBr(1 : 1) | | NaI(1 : 1) | | Calc. ^a (A) | Assignments |
|-------------|--------|------------|--------|---------------------------|----------------------|
| R | IR | R | IR | | |
| | 1350m | | 1349m | 1366u | CCO wag |
| | 1333s | | 1332s | 1327u | CCN wag |
| | 1319m | | 1318m | | CCN wag |
| | | 1301w | | 1292g | CCN wag |
| | | 1278w | | 1276g | CCO tw |
| 1269s | | 1269s | | 1265g | CCN tw |
| | 1263s | | 1261s | 1269u | CCN tw |
| 1240w | | 1243w | | 1241g | CCO tw |
| | 1218m | | 1219m | 1225u | CCN tw |
| | | 1210w | | 1219g | CCN tw |
| | 1199m | | 1198m | | CCN tw |
| 1179m | | 1167s | | 1160g | CC—NC str, CCO rock |
| | 1169sh | | 1159sh | 1159u | CC—NC str |
| 1136m | | 1138sh | | 1136g | OC—CO str, CC—OC str |
| | | 1094w | | 1099g | CCO rock |
| | 1092vs | | 1091vs | 1093u | CCO rock, CC—OC str |
| 1078m | | 1064m | | 1076g | CC—OC str |
| | 1058sh | | 1058sh | 1053u | CC—OC str |
| | | 1054sh | | 1056g | OC—CO str |
| | 1033w | | 1031w | 1044u | OC—CO str |
| | | | | 957g | CCO rock |
| | 957s | | 953s | 940u | CCN rock |
| | | | | 929g | OC—CO str, CCN rock |
| | 913w | 920w | | 919g | CCN rock |
| | | | 912w | 897u | OC—CN str, OC—CO str |
| | 882w | | 892sh | 879u | CNC bend, CC—NC str |
| 870s | | 867s | | 876g | CNC bend, CC—NC str |
| | 841sh | | 833m | 827u | CC—OC str |
| 827s | | 822s | | 837g | CC—OC str |
| | 825s | | 819m | 820u | CC—OC str |
| | | 810w | | 814g | CC—OC str |
| | | | 804sh | | |
| | | | 780sh | 780u | NH <i>para</i> bend |
| | | | | 776g | NH <i>para</i> bend |
| | | 577m | | 572u | COC bend |
| 553m | | 548m | | 559g | CCO def |
| | 530s | | 529s | 525u | CCN def |
| 370w | | | | 393g | CCO def |
| 281s | | 278s | | 269g | CCO def |

^aAll bands are listed for the 960–550 cm^{-1} range. Only those corresponding to the observed bands are listed for other ranges, while all bands are shown in Figure 4.

TABLE II. Observed and calculated wavenumbers (cm^{-1}) and vibrational assignments for NaI (2:1) complexes of $\text{A}_2\text{18C6}$.

| NaI(2:1) | | Calc. ^a (B) | Assignments |
|----------|--------|---------------------------|---------------------|
| R | IR | | |
| | 1352m | 1365u | CCO wag |
| | 1333s | 1331u | CCN wag |
| | 1319m | 1324u | CCO tw, CCN wag |
| 1293m | | 1297u | CCO tw |
| 1269s | | 1275g | CCN tw |
| | 1261s | 1259u | CCO tw, CCN tw |
| 1247m | | 1248g | CCO tw |
| 1223w | | 1233g | CCO tw |
| | 1218m | 1218u | CCN tw |
| | 1198m | 1213u | CCN tw |
| 1184w | | 1156g | CCN rock |
| | 1093vs | 1093u | CCO rock, CC—OC str |
| 1088w | | 1086g | CC—OC str |
| 1056sh | | 1062g | OC—CN str |
| 1046m | | 1060g | OC—CN str |
| | 1035s | 1023u | CC—OC str |
| | 1026w | 1019u | CC—OC str, CCO rock |
| 950w | | 955g | CCN rock |
| | 954s | 946u | CCN rock |
| 926m | | 935g | OC—CN str, CCO rock |
| | 922w | | |
| 915m | | 930g | OC—CN str, CCN rock |
| | 902w | 899u | CCO rock |
| | | 892u | CCN rock, CC—OC str |
| | | 873g | CNC bend |
| 866s | | 870g | CNC bend, CCO rock |
| | 836m | 858u | CC—OC str, CCN rock |
| | 820m | 832u | CC—OC str, CCO rock |
| 812s | | 778g | NH <i>para</i> bend |
| | 804m | 778u | NH <i>para</i> bend |
| | 800m | | |
| 668m | | 665g | COC bend, CCO def |
| | 648m | 666u | COC bend, CCO def |
| 602m | 618sh | | COC bend |
| | 592sh | 578u | CCO def, COC bend |
| | | 561u | CCO def |
| 547s | | 547g | CCO def, CNC bend |
| | 533w | 533u | CCN def, CCO def |
| 400m | | 403g | CCN def |
| 347m | | 353g | CCN def, CCO def |
| 282s | | 297g | CCO def, CNC bend |

^aSee footnote a of Table I.

TABLE III. Observed and calculated wavenumbers (cm^{-1}) and vibrational assignments for NaSCN (1 : 1) complex of $\text{A}_2\text{18C6}$.

| NaSCN (1 : 1) | | Calc. ^a (C) | Assignments |
|---------------|--------|---------------------------|----------------------|
| R | IR | | |
| | 1349m | 1367u | CCO wag |
| | 1331s | 1356u | CCN wag |
| | 1318m | 1342u | CCN wag |
| 1299m | | 1291g | CCO tw |
| | 1283w | 1282u | CCO tw, CCN tw |
| 1275sh | | 1275g | CCO tw |
| 1263m | | 1256g | CCO tw, CCN tw |
| | 1263m | 1255u | CCO tw, CCN tw |
| 1242w | | 1239g | CCO tw |
| | 1220m | 1226u | CCN tw |
| | 1200w | 1222g | CCN tw |
| 1164w | | 1156g | CC—NC str |
| | 1168sh | 1152u | CC—NC str |
| 1134m | | 1133g | CC—OC str |
| | 1112sh | 1106u | CCO rock, OC—CO str |
| 1091w | | 1100g | CCO rock |
| | 1089vs | 1096u | CCO rock, CCN rock |
| 1065w | | 1067g | OC—CN str, OC—CO str |
| 1055w | | 1058g | OC—CN str |
| | 1043sh | 1047u | OC—CN str |
| 1044w | | 1037g | CC—OC str |
| 1017w | 1025sh | 1034u | CC—OC str, CCN rock |
| 942w | | 948g | CCO rock, CC—OC str |
| | 943s | 946u | CCO rock |
| | 937sh | 934u | CCO rock, CCN rock |
| 926w | | 932g | CCO rock |
| | 914sh | 919u | CC—OC str, CCO rock |
| 909w | | 912g | OC—CO str, CCO rock |
| 886w | 893sh | 871u | CC—OC str, CNC bend |
| 854s | | 867g | CNC bend |
| 835w | | 837g | CC—OC str, CCN rock |
| | 829s | 825u | CC—NC str |
| 816m | | 820g | CC—NC str |
| | 813w | 820u | CC—OC str |
| | 802w | | |
| 774w | | 792g | NH <i>para</i> bend |
| | 770sh | 794u | NH <i>para</i> bend |
| 740s | 751s | | SCN |
| | 726sh | | |
| | 612w | 605u | CCN def, CNC bend |
| 588m | | 605g | CCN def, CNC bend |
| | 583m | 543u | CCO def |
| 563m | | 541g | CCO def |
| | 530m | 498u | CCN def |
| 299w | | 285g | OCCN tors |

^aAll bands are listed for the 1060–500 cm^{-1} range. Only those corresponding to the observed bands are listed for other ranges, while all bands are shown in Figure 7.

TABLE IV. Observed and calculated wavenumbers (cm^{-1}) and vibrational assignments for NaSCN (2 : 1) complex of $\text{A}_2\text{18C6}$.

| NaSCN(2 : 1) | | Calc. ^a | Assignments |
|--------------|--------|--------------------|--------------------------------|
| R | IR | (D) | |
| | 1377w | 1381u | CCO wag |
| | 1354w | 1367u | CCO wag |
| | 1336s | 1344u | CCN wag |
| | 1320m | | CCN tw |
| 1295w | | 1294g | CCN tw |
| | 1280s | 1284u | CCO tw |
| 1279w | | 1281g | CCO tw |
| 1267m | 1268w | 1267g | CCO tw |
| | 1255w | 1255u | CCN tw, CCO tw |
| 1246w | | 1243g | CCO tw, CCN tw |
| | 1231w | 1227u | CCO tw |
| 1218w | 1213w | 1218g | CCN tw, CCO tw |
| 1176w | | | CCN tw |
| | 1161w | 1149u | CC—OC str |
| 1128m | | 1136g | CCO rock, OC—CO str |
| | 1124sh | 1132u | CC—OC str |
| | 1094sh | 1098u | CC—NC str |
| 1083w | | 1085g | CCO rock |
| | 1080vs | 1084u | CCO rock |
| 1060m | | 1065g | CC—NC str, CCN rock |
| | 1057sh | 1060u | CC—NC str |
| 1044m | | 1048g | CCN rock, CCO rock |
| | 1041w | 1043u | CC—NC str |
| | 1018w | 1016u | CC—OC str |
| | | 954g | OC—CN str |
| | 941vs | 947u | CCO rock, OC—CO str |
| | 929s | 937u | CCO rock |
| | 925sh | 928u | CC—OC str, CCO rock |
| | 901m | | OC—CO str |
| 862s | | 868g | CCO rock, NH <i>para</i> bend |
| | | 857g | CC—OC str, NH <i>para</i> bend |
| | 836m | 833u | CCN rock, CC—OC str |
| | 822s | 823u | CCN rock, CCO rock |
| 807m | 808sh | | ? |
| | 793s | 784u | NH <i>para</i> bend |
| | 769vs | 783g | NH <i>para</i> bend |
| 762s | 730s | | SCN |
| | | 697u | CCO def, CCN def |
| | | 686g | CCO def, CCN def |
| | 668sh | 668u | CCO bend, CCN def |
| | 612s | 650u | COC bend, CCN def |
| 593w | | 586g | CCO def, CCN def |
| | 583s | 580u | CCO def |
| | 538w | 498u | CCO def |
| | | 458g | CCN def, CCO def |
| 402w | | 369g | CCO def |
| 344w | | 328g | CCN def, CCO def |

^a All bands are listed for the 960–360 cm^{-1} range. For other remarks, see footnote a of Table III.

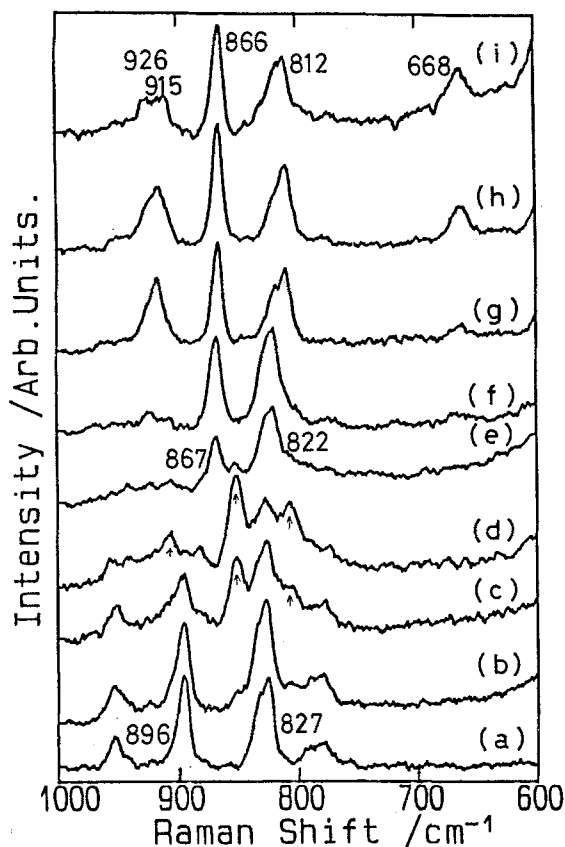


Fig. 2. Raman spectra of the NaI-A₂18C6 system for various [NaI]/[A₂18C6] ratios. (a) A₂18C6, (b)–(i) [NaI]/[A₂18C6] = 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0, respectively. Small arrows: see text.

2.1.a. NaBr complex

The Raman spectra of the NaBr complex for various [NaBr]/[A₂18C6] ratios are shown in Figure 1. The band characteristic of the complex appears near 870 cm⁻¹. When the intensity ratio of this band to the band near 827 cm⁻¹, which keeps a nearly constant intensity, is plotted against [NaBr]/[A₂18C6], it increases with the ratio and levels off at the ratio of unity. The 896 cm⁻¹ band of parent A₂18C6 decreases in intensity with the ratio and is no longer observable above the ratio of unity. These results indicate the shift of the 896-cm⁻¹ band to 870 cm⁻¹ and the formation of the 1 : 1 complex. A closer look at the spectra for the ratios 0.75 and 1.0 reveals some additional subtle features; small inflections are barely discerned near 810 and 850 cm⁻¹ (indicated by small arrows in the figure). We will touch on these small features later.

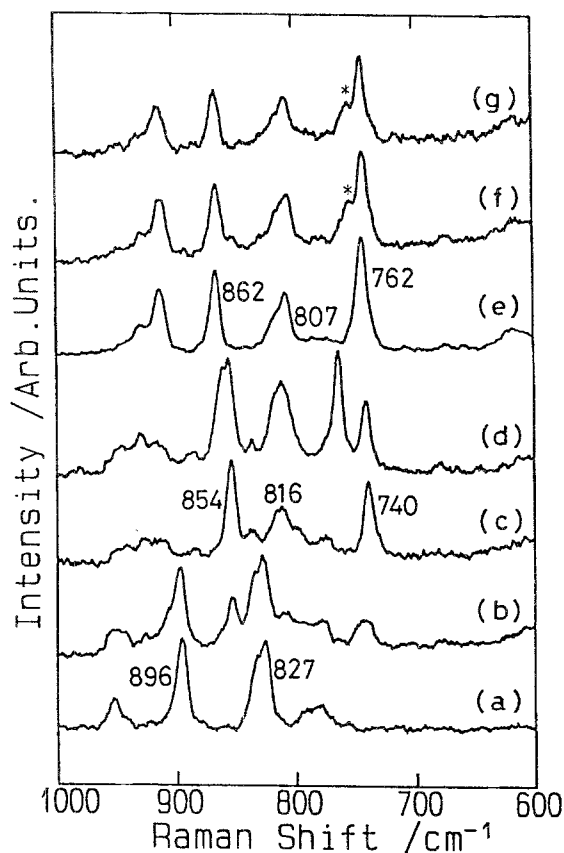


Fig. 3. Raman spectra of the NaSCN-A₂18C6 system for various [NaSCN]/[A₂18C6] ratios. (a) A₂18C6, (b)-(g) [NaSCN]/[A₂18C6] = 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0, respectively. *Excess SCN⁻.

2.1.b. NaI complex

The Raman spectra of the NaI complex (Figure 2) are more complex. For [NaI]/[A₂18C6] ratio of unity, the spectral feature is similar to that of the 1:1 complex of NaBr, and is characterized by the bands at 867 and 822 cm⁻¹. When this ratio approaches 2.0, however, a further change in the spectra is observed; the band at 812 cm⁻¹ appears in place of that at 822 cm⁻¹. Additional bands appear near 668 cm⁻¹ and 915 cm⁻¹. The spectra remain essentially the same above the ratio of 2.0 (until 3.0). This indicates the formation of the 2:1 complex besides the 1:1 complex. It should be noted that no band is observed in the 600-700 cm⁻¹ range for either the parent A₂18C6, its potassium complexes [16], and the NaBr and NaI (1:1) complexes. The conformation of the NaI complex (2:1) is therefore distinct from these complexes. A puzzling behavior is found in the spectra for the ratios 0.5 and 0.75; additional bands appear near 810, 850 and 920 cm⁻¹ (indicated by small arrows in the figure). It should be noted that the positions of these extra

bands nearly coincide with those of the bands observed for the 1 : 1 complex of NaSCN, as mentioned below. This strongly suggests the coexistence of a complex of another type, with the conformation of azacrown ring quite similar to that in the NaSCN (1 : 1) complex, for these ratios. The small inflections found for the NaBr case can be interpreted in a similar way. (The authors are grateful to the referee who pointed out these features.)

2.1.c. NaSCN complex

The Raman spectra of the NaSCN complex are given in Figure 3. The band characteristic of the complex formation appears at 854 cm^{-1} (for the $[\text{NaSCN}]/[\text{A}_2\text{18C6}]$ ratio 0.5–1.0) or 862 cm^{-1} (for the ratio 2.0–3.0). Both of these bands appear for the ratio 1.5. A band near 740 cm^{-1} must be due to the SCN moiety in the complex. In addition to this, the band of excess SCN (marked with an asterisk) is found at 754 cm^{-1} for the ratio larger than 2.5. Although the spectrum for the ratio 0.5 appears very complex, it can be reproduced by superposition of the spectra of parent azacrown and the 1 : 1 complex. Likewise, the spectrum for the ratio 1.5 can be reproduced by superposition of the spectra of the 1 : 1 and 2 : 1 complexes, except for an unexplainable band at 765 cm^{-1} . These analyses indicate that both 1 : 1 and 2 : 1 complexes exist for the NaSCN–azacrown system.

The spectra for the sodium salts (NaI and NaSCN) are rather complex; both 1 : 1 and 2 : 1 complexes are present, in contrast to the potassium salt systems which only form 1 : 1 complexes [16]. This is most probably due to the different size of sodium and potassium cations. While a potassium ion (diameter 2.66 \AA) fits the inner cavity of the azacrown ether ($2.6\text{--}3.2\text{ \AA}$), a sodium ion (1.94 \AA) is too small. This difference in size confers an extra freedom of conformational change on the azacrown ring in the sodium complexes. At least two conformations of azacrown ring were observed for the 1 : 1 complex of Na^+ ion: one is the NaBr/NaI type and the other the NaSCN type. Some small amount of the latter type was found to coexist with the former. The different conformations for different counteranions must have their origin in the subtle interplay of Na^+ –azacrown and Na^+ –counterion interaction.

2.2. NORMAL COORDINATE CALCULATIONS

Normal coordinate calculations were carried out with a computer program MVIB [17]. This program is capable of treating normal vibrations of chain molecules, open-chain or cyclic-chain, by simply inputting a molecular name, conformation (*trans* (T), *cis* (C), *gauche* (G) and *skew* (S)), and corrections for internal rotation angles. The initial force constants used in the calculation were those of uncomplexed $\text{A}_2\text{18C6}$ used by Matsuura *et al.* [13]. The calculations were carried out on a FACOM M-760 computer set up in the Information Processing Center of Mi'e

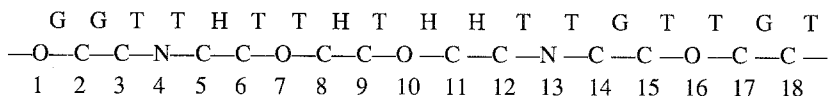
University. Normal modes of vibrations were drawn directly from the output of MVIB using the utility program reported in Ref. [13].

Comparison of the spectra of the sodium complexes with that of the parent azacrown indicates substantial changes in equilibrium conformation of the azacrown moiety on complex formation. No crystal structures have been reported for the sodium salt complexes. For the prediction of conformations of the azacrown moiety in these complexes, normal coordinate calculations were carried out for more than 120 conceivable molecular conformations. Some of them were constructed by referring to '190 ideal conformations of 18-crown-6' of Uiterwijk *et al.* [18]. We notice that a Raman-IR mutual exclusion principle is essentially obeyed in the sodium salt complexes, as is evident from Tables I-IV. This fact points to the presence of an inversion center in these complexes. Therefore, we consider possible conformations with an overall symmetry C_i . Positions of the bands, especially of those in the region below 1000 cm^{-1} , where many skeletal stretching and deformation modes appear, are found to be very sensitive to the change in conformation of the azacrown ring.

The conformations of the azacrown moiety for the complexes are discussed below on the basis of the normal coordinate calculations. The conformations predicted are, however, not conclusive, and further studies are necessary for their establishment.

2.2.a. 1 : 1 Complexes of NaBr and NaI

The distribution of the observed bands (Figure 4(a)) can be reproduced reasonably well (Figure 4(b)) with the conformation A depicted in Figure 5(a). This conformation corresponds to



where T, G and H stand for *trans*, *gauche*⁺, and *gauche*⁻, respectively. All oxygen and nitrogen atoms face inside. The *gauche* configurations at 1-2 and 10-11 positions distinguish this conformation from that of free azacrown. Inward rotation of the ring at these positions allows oxygen atoms at the 7 and 16 positions to approach the center of the ring. This seems to be favorable for the coordination of a sodium ion, which is smaller than the inner cavity of the azacrown.

In order to clarify the correlation between the bands of the NaBr or NaI (1 : 1) complex and those of the parent azacrown ether, vibrational modes in the $700\text{--}960\text{ cm}^{-1}$ region for the conformation A are depicted in Figure 6(a), in comparison with those of the parent azacrown in Figure 6(b). The *gerade* bands at 929 and 919 cm^{-1} correlate to the bands of the parent at 948 and 935 cm^{-1} , respectively; The *ungerade* band at 897 cm^{-1} correlates with the 903-cm^{-1} band (a_u) of the parent. The $780\text{-(}u\text{)}$ and $776\text{-(}g\text{)}\text{ cm}^{-1}$ bands of the complex can be correlated with

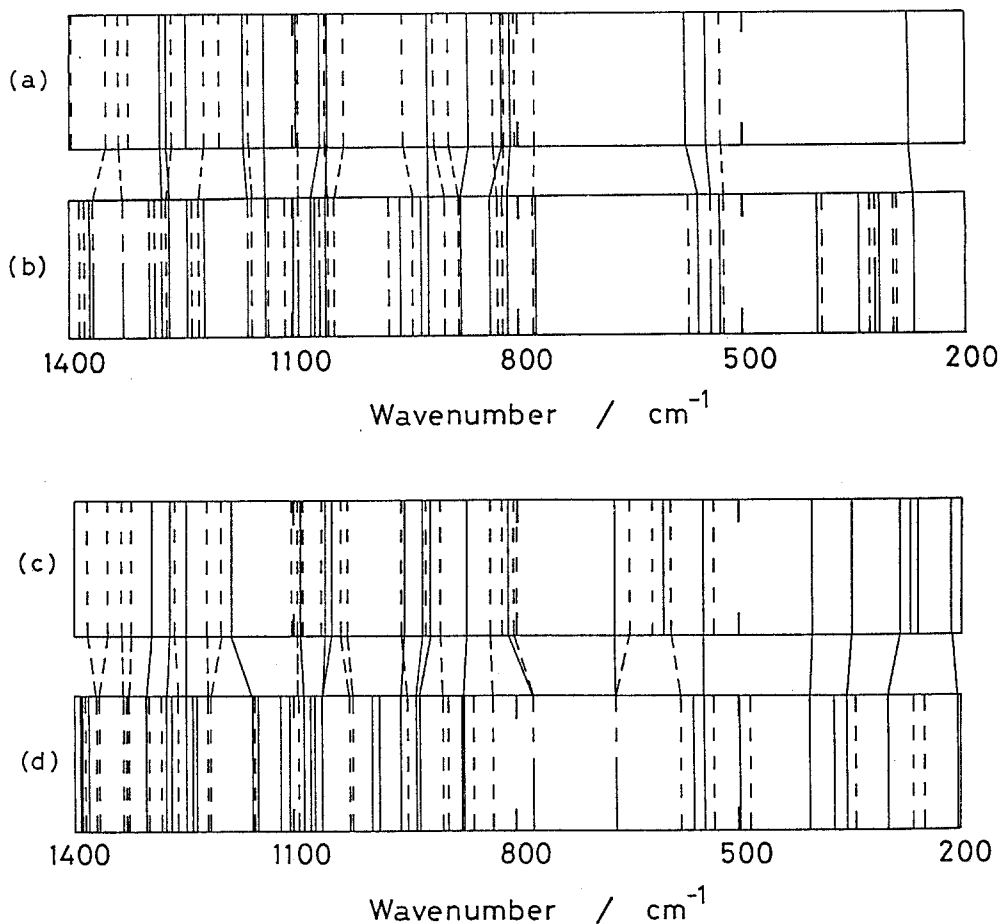


Fig. 4. Comparison of the experimental and calculated spectra for 1 : 1 and 2 : 1 complexes of NaI/A₂18C6. Positions of bands are indicated by vertical bars. (a) and (b): exp. and calc. of the 1 : 1 complex; (c) and (d): exp. and calc. of the 2 : 1 complex. Solid and broken lines in (a) and (c) show Raman and IR bands, and those in (b) and (d) are *g* and *u* bands, respectively. Half-way broken lines in (b) and (d) show *g* and *u* bands located close together.

the 783-(*b_u*) and 783-(*a_g*) cm⁻¹ bands of the parent with some admixture of the CC—NC stretching character. Extensive mixing of modes occurs for the bands at 814–879 cm⁻¹. The most peculiar is the 876-cm⁻¹ band (*g*) of the complex. Its vibrational mode is dominated by an admixture of the CNC bending and CC—NC stretching characters, appearing in the 783-(*a_g*) and 823-(*a_g*) cm⁻¹ bands of the parent, respectively.

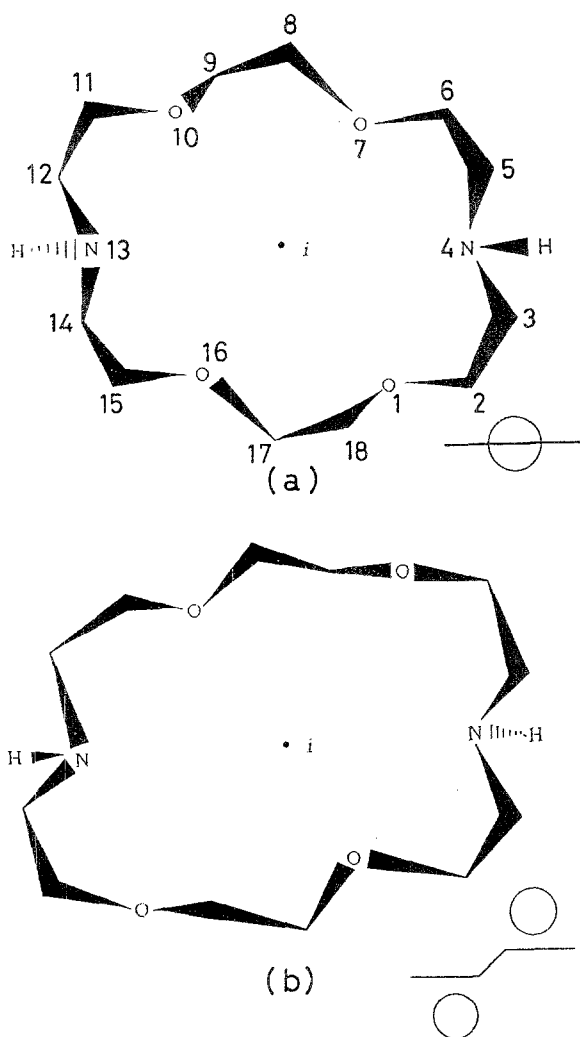


Fig. 5. Projected images of predicted molecular conformation of azacrown ring, 1 : 1 (a) and 2 : 1 (b) complex of NaI/A₂18C6, respectively. The probable location of a Na⁺ ion is shown by the circle. i: inversion center.

2.2.b. 2 : 1 Complex of NaI

This complex is characterized by the appearance of Raman and IR bands in the 600–700 cm⁻¹ region which is an open window for the parent azacrown and 1 : 1 complex. The calculation indicates that the occurrence of band(s) in this range is found only when *cis* and/or *skew* conformations are involved. The positions of the

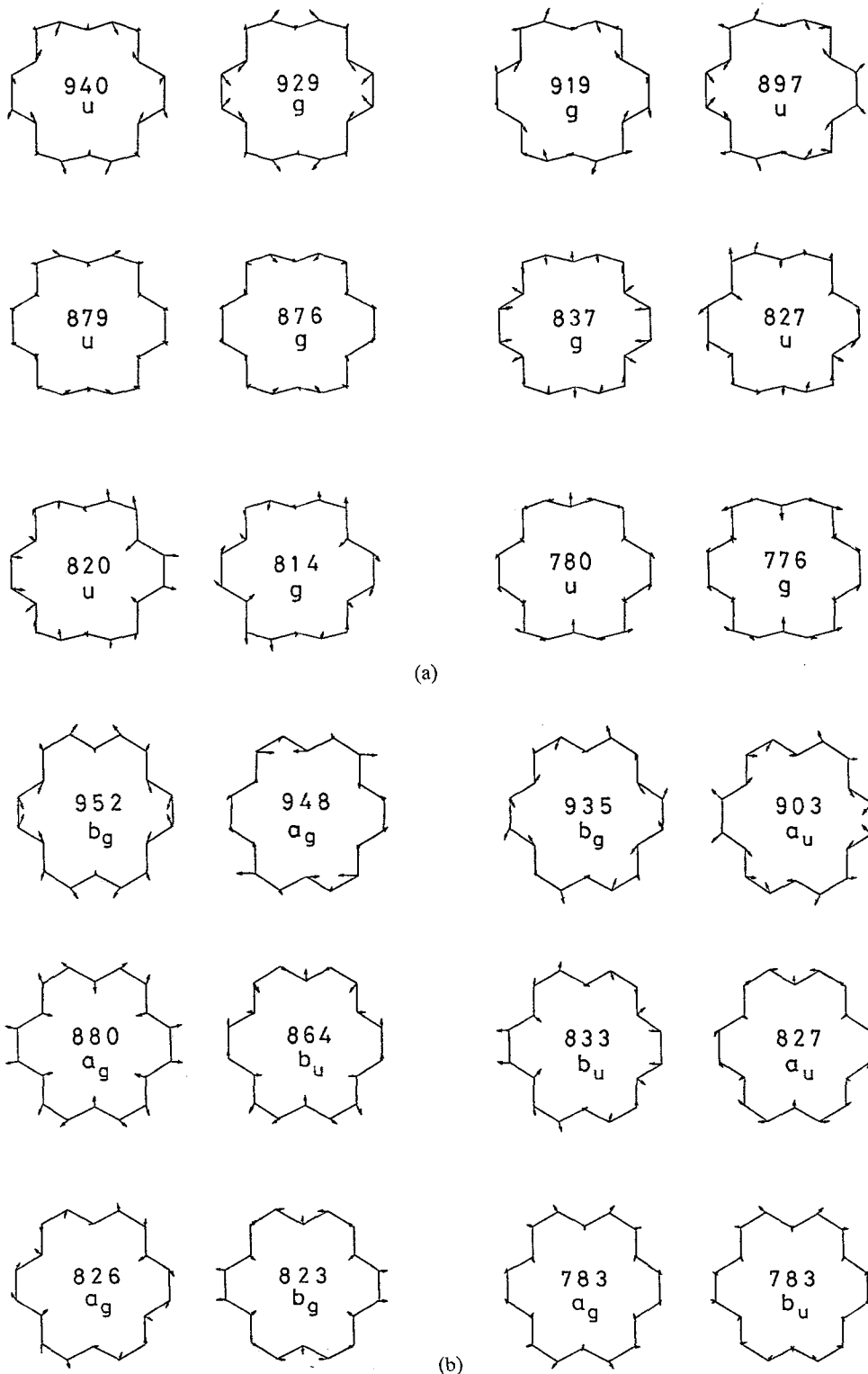


Fig. 6. Graphic representation of normal modes of NaBr and NaI (1 : 1) complexes (a), in comparison with those of parent azacrown (b).

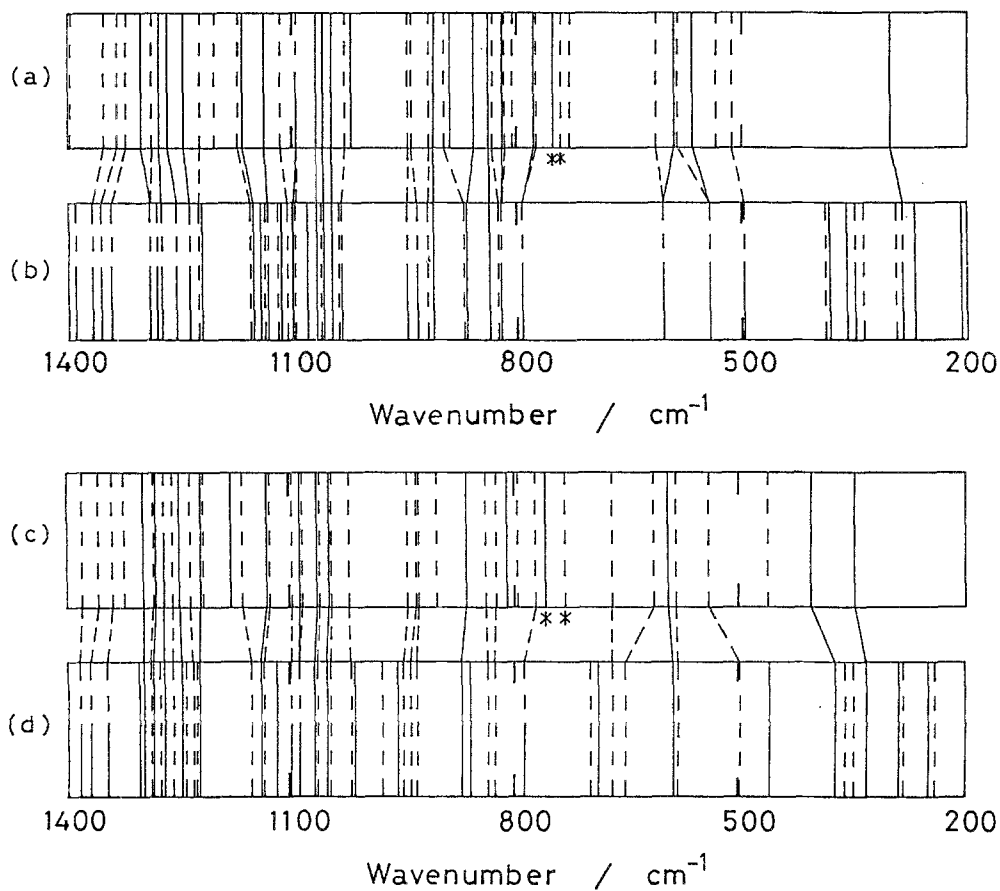
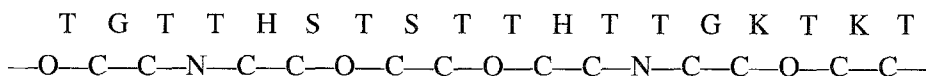


Fig. 7. The same as Fig. 4 for 1:1 and 2:1 complexes of NaSCN/A₂18C6. (a) and (b): exp. and calc. of the 1:1 complex; (c) and (d): exp. and calc. of the 2:1 complex. Asterisks indicate bands of SCN.

observed bands (Figure 4(c)) can be fitted reasonably well (Figure 4(d)) with the conformation B shown in Figure 5(b), which corresponds to



where S and K stand for *skew* with opposite directions. The azacrown ring assumes a chair form; two sodium ions are most probably located above and below the ring, as depicted schematically in the figure.

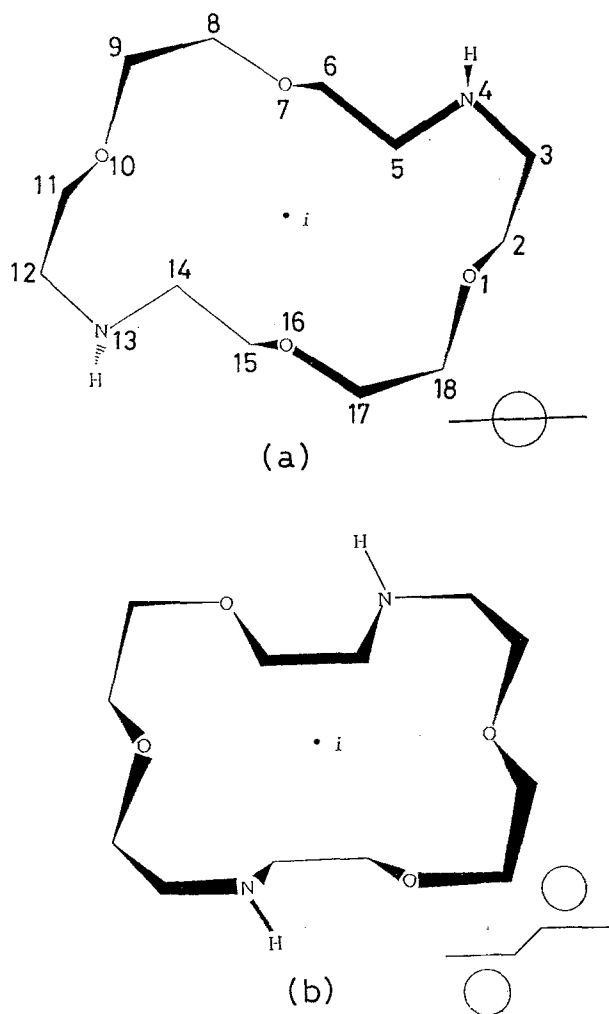
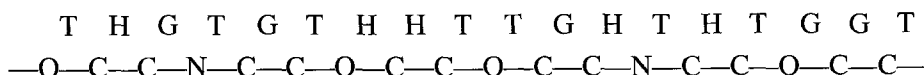


Fig. 8. The same as Fig. 5 for the 1:1 (a) and 2:1 (b) complex of NaSCN/A₂18C6.

2.2c. 1:1 Complex of NaSCN

The positions of the observed bands (Figure 7(a)) can be fitted (Figure 7(b)) with the conformation C



shown in Figure 8(a). The azacrown ring is somewhat elongated in the C₃—C₁₂ direction. The two nitrogen atoms are now located a little far away from the central metal cation compared to four oxygen atoms. Vibrational modes in the 700–960 cm⁻¹ region are depicted in Figure 9. Mixing among the modes is extensive

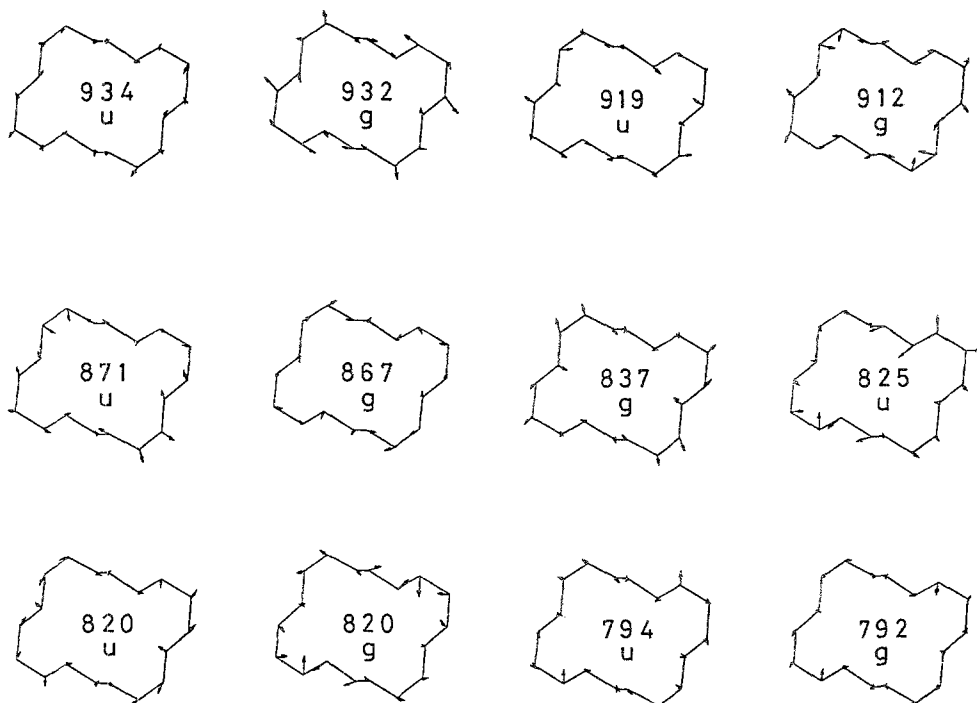
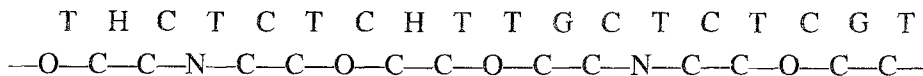


Fig. 9. The same as Fig. 6(a) for the 1 : 1 complex of NaSCN/A₂18C6.

compared to the parent azacrown. The 867-cm⁻¹ band (*g*) is again dominated by an admixture of the CNC bending and CC—NC stretching characters.

2.2d. 2 : 1 Complex of NaSCN

The positions of the observed bands (Figure 7(c)) can be fitted as in Figure 7(d) by the chair-form conformation D



depicted in Figure 8(b).

3. Conclusions

Three sodium complexes (bromide, iodide and thiocyanate) of 4,13-diaza-18-crown-6 (A₂18C6) have been studied by Raman/IR spectroscopy and normal coordinate calculations. The sodium ion gave both 1 : 1 and 2 : 1 stoichiometry, in contrast to the 1 : 1 stoichiometry of the potassium complexes. Normal coordinate calculations reveal that the symmetry of the azacrown moiety in sodium complexes is lowered to *C_i*, in contrast to the higher symmetry, *C_{2h}*, of the parent azacrown and KSCN complex. This can be understood by the smaller size of a

Na⁺ ion compared to the inner cavity of the azacrown, which gives extra freedom of displacement of the azacrown ring.

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