PERKIN 2

Synthesis and spectroscopic studies of novel photochromic benzodithiacrown ethers and their complexes

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New styryl dyes containing the benzodithia-18-crown-6 fragment have been synthesized and their photoisomerization reactions and complexes with Hg^{2+} and Ag^{+} cations have been investigated by steady-state electronic and resonance Raman spectroscopy. (4-Formylbenzo)dithia-18-crown-6, *N*-carboxypropyl- and *N*-carboxybutyl-2-methylbenzothiazolium bromides have also been prepared as intermediates for the styryl dye syntheses. Changes in vibrational resonance Raman spectra observed on complexation with Ag^{+} and Hg^{2+} cations or on variation of solvent polarity have been correlated with changes in the UV–VIS absorption maxima of the dyes. Preliminary assignments of the observed Raman bands to particular vibrations are made.

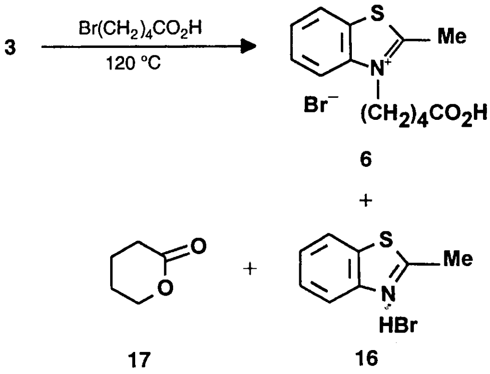
The molecular design and fine organic synthesis of artificial receptors with a capacity for photoswitching is a very active area of current research. From previous studies we have learned that the linking of a styryl dye fragment to a benzocrown ether results in novel photochromic compounds possessing interesting physico-chemical properties.[1] The dyes are intensely coloured and show significant hypsochromic shifts upon complexation with alkaline earth metal cations in acetonitrile solution. Reversible photochemical *trans–cis* isomerization is observed for both the dyes and their complexes. To continue our investigation, a novel class of photochromic dyes have been synthesized which contain *N*-methyl and *N*-carboxyalkyl substituents in the heterocyclic dye fragment linked to a benzodithia-18-crown-6 ether. As expected, the introduction of sulfur atoms into the crown moiety leads to novel photochromic crown ethers which form stable complexes with transition and other heavy metal ions, while their complexes with alkali and alkaline earth metal cations become less stable relative to the corresponding crown ethers containing only oxygen donors. UV–VIS and resonance Raman (RR) spectroscopy have been used to determine the stoichiometry of the metal–ligand complexes, to reveal intermolecular interactions,[2] and to provide information on the structures of these molecules and their complexes.[3,4]

Results and discussion

Synthesis

Styryl dyes **12–15**, shown in Scheme 1, have been prepared with yields of up to 73% by condensation of formyl derivatives of benzodithia- (**11**) or benzo-18-crown-6 ether (**2**) with *N*-methyl- (**4**) or *N*-carboxyalkyl-substituted (**5**, **6**) 2-methylbenzothiazolium in anhydrous ethanol using pyridine (Py) as a catalyst.

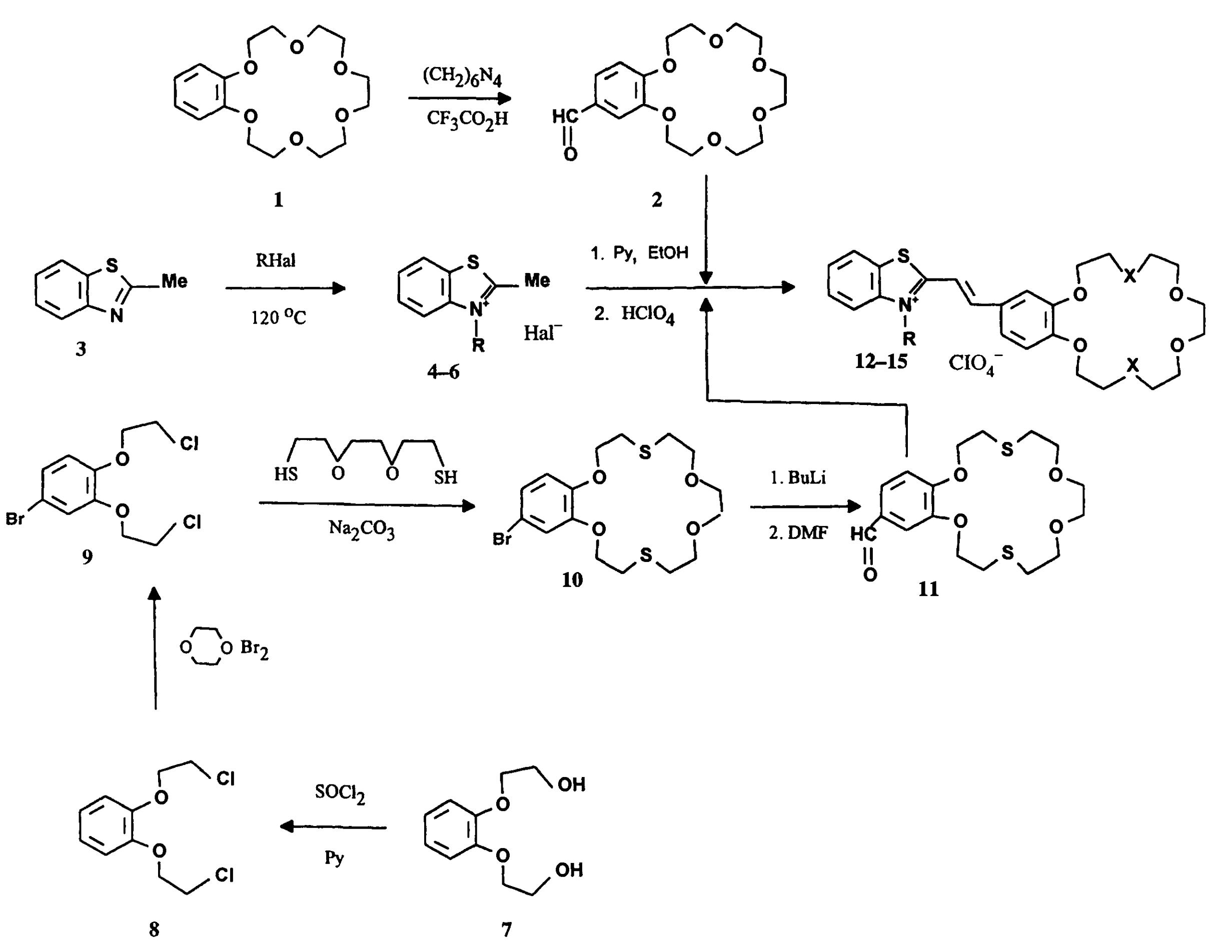
(4-Formylbenzo)-18-crown-6 (**2**) and the iodide of 2,3-dimethylbenzothiazolium (**4**) were obtained as described previously.[5,6] We have devised new synthetic routes to compounds **5**, **6** and **11**. To prepare the *N*-(hydroxycarbonylalkyl)-2-methylbenzothiazolium salts (**5**, **6**), 2-methylbenzothiazole was fused with the corresponding bromocarboxylic acid at 120 °C. In the case of 5-bromovaleric acid **6** was obtained, but the yield in this reaction was low because of a parallel reaction resulting in the formation of the corresponding lactone (**17**) and the hydrobromide of 2-methylbenzothiazolium (**16**) [reaction (1)].



(1)

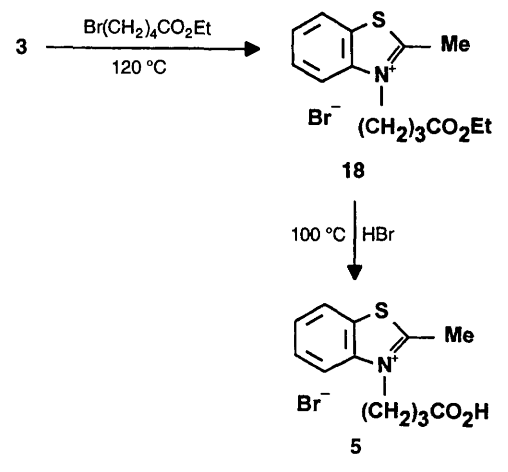
Due to the complication of lactone formation, we have attempted to obtain **5** by quaternization of 2-methylbenzothiazole with ethyl 4-bromobutyrate followed by hydrolysis of the ester in acid medium. In this way we have succeeded in obtaining **5** in 21% yield (Scheme 2).

The formyl derivative of benzo-18-crown-6 (**2**) has been prepared by electrophilic formylation using Duff's reaction conditions[5] (Scheme 1). However, both this method and Vilsmeir's reaction[7] appeared to be unsuccessful in the case of the crown ethers containing electron-donating sulfur atoms and a sharp resonification was observed, possibly arising from destruction of the crown ether ring. A preliminary attempt to transform these compounds into the corresponding sulfoxides also failed. However, it is known that oxygenous benzocrowns,[8] and 1,3-xylyl-18-crown-5[9] containing a bromine atom in the aromatic ring, can be metallated using BuLi, and that the lithium intermediates can readily react with various electrophiles. We hoped that such a reaction may be effective for preparing the formyl derivative of benzodithia-18-crown-6. The (bromobenzo)dithia-18-crown-6 (**10**) was obtained in high yield by condensation of 3,4-bis(2-chloroethoxy)bromobenzene (**9**) with 3,6-dioxaoctane-1,8-dithiol containing terminal SH groups, as described previously for the preparation of the corresponding unsubstituted benzocrowns[10] (Scheme 1).



4 R = CH$_3$, Hal$^-$ = I$^-$ **5** R = (CH$_2$)$_3$CO$_2$H, Hal$^-$ = Br$^-$ **6** R = (CH$_2$)$_4$CO$_2$H, Hal$^-$ = Br$^-$ **12** X = O, R = (CH$_2$)$_4$CO$_2$H **13** X = S, R = CH$_3$ **14** X = S, R = (CH$_2$)$_4$CO$_2$H **15** X = S, R = (CH$_2$)$_3$CO$_2$H

Scheme 1



Scheme 2

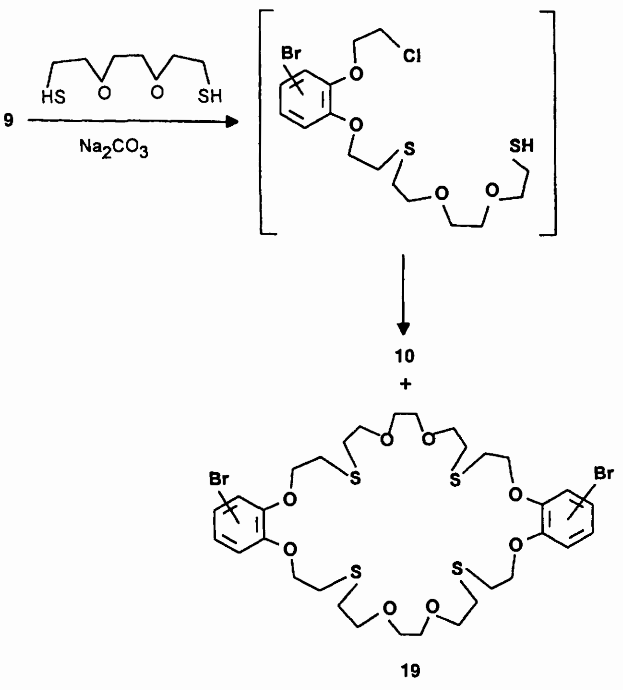
Compound **9** is unknown in the literature and was obtained by the reaction of **8** with dioxane dibromide (see Experimental section for details). In the condensation reaction, a mixture of isomers of the dibromo-derivative of dibenzotetrathia-36-crown-12 (**19**) was separated and the component structures were established by mass spectroscopy (Scheme 3). The presence of **19** indicates that the reaction between the bromo-derivative **9** and the dithiol is a two-step process. First, a nucleophilic substitution of one chlorine atom appears to occur and a linear intermediate forms. Then, either an intramolecular cyclization of the intermediate into **10** or an intermolecular dimerization to form **19** takes place.

The bromo substituent of benzodithia-18-crown-6 (**10**) was reacted with BuLi and subsequent treatment with DMF yielded the formyl derivative **11** at −100 °C, which is the optimum temperature for both stages of this reaction. The formation of unsubstituted benzodithia-18-crown-6 (**20**) together with **11** may be explained either by protonation of the carbanion by a solvent molecule, or by hydrolysis of the unreacted lithium intermediate when the reaction mixture is treated with HCl solution (Scheme 4).

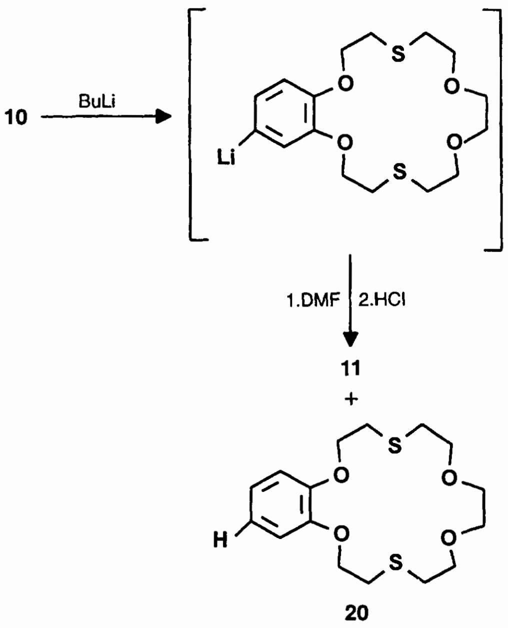
Thus, we have devised a new method of preparing formyl derivatives of benzocrown ethers containing S and O heteroatoms in the macrocycle. By using various electrophiles the synthesis of benzocrown ethers containing different substituents may be achieved.

Spectroscopic studies

According to the ^{1}H NMR spectra, dyes **12–15** exist as the *trans*-isomers in CH$_3$CN. This conclusion can be reached with certainty from the high coupling constant, $^3J_{trans}$ = 16.0 Hz, observed for the olefinic protons. The *trans*-isomers of dyes **12–15** were found to have strong electronic transitions in the visible region, as shown for dye **14** in Fig. 1. The absorption spectra of dyes **12**, **13** and **15** are similar to that of **14**, the small differences in the positions of their absorption maxima and absorption coefficients are shown in Table 1.



Scheme 3



Scheme 4

Table 1 Observed long wavelength absorption maxima and absorption coefficients of dyes **12–14** and their complexes with Ag$^+$ and Hg^{2+} cations in CH$_3$CN

	λ/nm		
Ligand (L)	L (ε/10^3 m^2 mol^{-1})	LAg	LHg
12	431 (3.6)	431	421
13	429 (3.9)	421	411
14	430 (3.7)	422	412

Dyes **13** and **14** showed hypsochromic shifts of 8 and 18 nm, respectively, on complexation with Ag$^+$ or Hg^{2+} cations in CH$_3$CN (see Table 1). However, **12** gave no detectable shift of the long wavelength band on addition of Ag$^+$ and showed a shift of only 10 nm on complexation with Hg^{2+} cations. The shifts in the absorption bands observed on complexation of dyes **12–14** with Ag$^+$ or Hg^{2+} are much smaller than that observed for complexation of benzothiazolium styryl dye **21** with Mg^{2+} (43 nm), which was studied previously.[2]

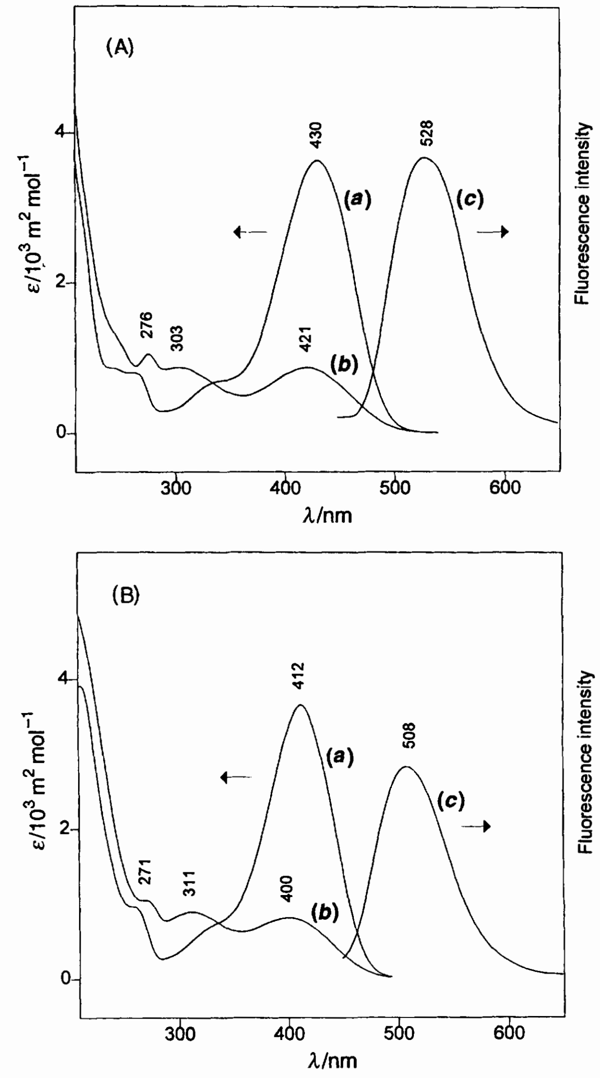
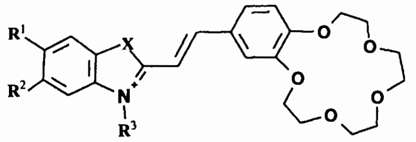


Fig. 1 Absorption and fluorescence spectra of *trans*- and *cis*-**14** (A) and their complexes with Hg^{2+} (B) in CH$_3$CN: (*a*) *trans*-**14** absorption; (*b*) *cis*-**14** absorption; (*c*) *trans*-**14** fluorescence



21 X = S, R^1 = R^2 = H, R^3 = (CH$_2$)$_3$SO$_3^-$
22 X = S, R^1 = R^2 = H, R^3 = C$_2$H$_5$
23 X = C(CH$_3$)$_2$, R^1 = R^2 = R^3 = CH$_3$

According to X-ray data,[11] the chromophore in **22** extends along the chain N$^+$=C–C=C–Ph–O. The strong hypsochromic shifts observed on complexation of **22** with cations of alkaline earth metals may be assigned to the electron-acceptor influence of the coordinated cations acting *via* the oxygen atom linked to the phenyl ring in the position *para* to the C=C double bond. For the complexes of **14** with Hg^{2+} and Ag$^+$, or of **12** with Hg^{2+}, the cations have only a small effect on the dyes, probably because the coordination to the oxygen atom is weaker. Indeed, for the complex of 18-crown-6 with Hg^{2+}, log K_1 is 2.42.[12] The log K_1 value for the complex of **12** with Hg^{2+} is expected to be similar, although for **22** complexed to Mg^{2+} it has been reported to be 6.60.[13] In the case of compounds with crown thioether ligands having a significant affinity for Ag^{I} and Hg^{II} (and also for Cu^{I}, Cu^{II}, Pd^{II}, Pt^{II} and Au^{III}), the stabilities of the complexes may be much higher due to the interaction of the ions with the sulfur atoms. For example, the high stability of the Hg^{II} complex with 5,14-dithia-18-crown-6 in 0.5 mol dm^{-3} HNO_3 is explained by the presence of the polarizable sulfur atoms and the stability of Hg^{2+}–S covalent bonds.[14]

The equilibrium constants for complex formation between Ag^+ cations and *trans*-**14** and *trans*-**13** were calculated from the dependence of the fractional complex formation, α, on the added $AgNO_3$ concentration, determined spectrophotometrically as $\alpha = (D_o - D)/(D_o - D_c)$, where D_o is the free ligand absorbance, D_c is the absorbance of the complex and D is the measured absorbance at a given cation concentration, all at 460 nm. The experimental dependences of α on the total $AgNO_3$ concentration, C_{Ag}, were fitted to eqn. (2), where C_L is the total

$$C_{Ag} = \alpha/[K_1(1 - \alpha)] + \alpha C_L \qquad (2)$$

ligand concentration and K_1 is the equilibrium constant for 1 : 1 complex formation.

In CH_3CN solution these constants were found to be 1.8×10^5 and 6.6×10^4 dm^3 mol^{-1} for **13** and **14**, respectively. Hg^{2+} was found to form complexes with **13** and **14** which were much more stable than the corresponding Ag^+ complexes. Unfortunately, it was impossible to determine the stability constants for these Hg^{2+} complexes by direct spectrophotometric titration because of their very high values. The log K value for the complex of 5,14-dithia-18-crown-6 with Hg^{2+} in 0.5 mol dm^{-3} HNO_3 is reported to be 19.5.[14] It is reasonable to expect that the stability constants of the Hg^{2+} complexes of the dyes studied here will be similar to this value. The spectrophotometric titration of the dyes with $Hg(NO_3)_2$ or $Hg(ClO_4)_2$ indicated only one kind of complex, of stoichiometry 1 : 1.

Photoisomerization

Irradiation of solutions of all of the dyes, and of dye complexes with Ag^+ or Hg^{2+}, resulted in a reversible *trans–cis* photoisomerization and a photostationary state containing both *cis*-and *trans*-isomers was formed, as shown previously for similar dyes.[2] Absorption spectra of *cis*-isomers were calculated by Fisher's method,[15] from the spectra of the *trans*-isomers and of the photostationary states obtained upon irradiating solutions with wavelengths $\lambda_1 = 365$ nm and $\lambda_2 = 436$ nm (Fig. 1). It was found that the absorption maxima of *cis*-**14** and *cis*-**14**·Hg^{2+} showed only small hypsochromic shifts (9–12 nm) in comparison with the corresponding *trans*-isomers. However, a very strong hypsochromic shift (70 nm) of the long wavelength absorption band of the *cis*-isomer from that of the *trans*-isomer has been reported upon complexation of **21** with Mg^{2+} in CH_3CN to form **24**.[2] This large shift was ascribed to intramolecular coordination between the anionic sulfonate group and the metal cation coordinated within the crown cavity in the case of the *cis*-isomer **24**. This additional intramolecular bond distorts the conjugation of the π-system of the dye molecule and as a result a strong hypsochromic shift is observed. For all of the dyes forming complexes with Ag^+ or Hg^{2+} the existence of only small hypsochromic shifts of the long wavelength absorption band of the *cis*-isomer from that of the *trans*-isomer indicates that the additional intramolecular bond between the COOH group and the Ag^+ or Hg^{2+} cations is not formed, possibly because of very weak dissociation of the COOH group in acetonitrile and a weak interaction of the COOH group with Ag^+ or Hg^{2+} in the crown cavity (structure **25**).

Fluorescence

The fluorescence spectra of *trans*-**14** and *trans*-**14**·Hg^{2+} recorded on irradiation at 365 nm are shown in Fig. 1. Upon complexation of *trans*-**14** with Hg^{2+}, a 20 nm hypsofluoric shift of the fluorescence band was observed and the quantum yield of fluorescence decreased from 0.027 for the free dye to 0.015 for the complex.

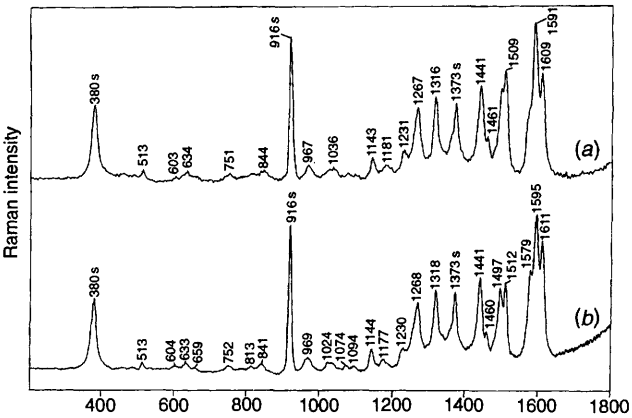
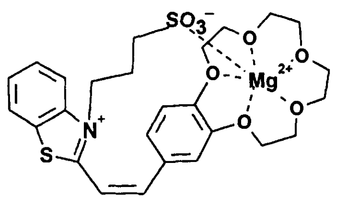


Fig. 2 Resonance Raman spectra of crown ether styryl dye **14** as a free ligand (*a*) and complexed with Hg^{2+} (*b*) in CH_3CN. Laser excitation wavelength 413.1 nm. Concentrations of the dye and its complex 3×10^{-4} mol dm^{-3}.



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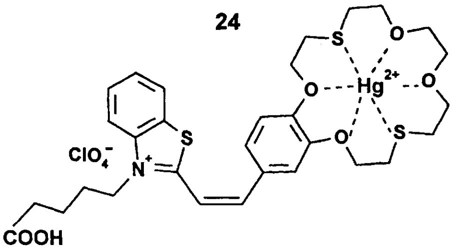

25

Resonance Raman spectroscopy

It was shown previously[3,16] that RR spectroscopy could be used to establish the structural changes occurring upon complex formation between Mg^{2+} and styryl dyes **21** and **22**. Some molecular vibrational modes were found to be sensitive to solvent polarity, to complexation with Mg^{2+} and to changes in molecular structure. In our present work, RR spectra of dyes **12**–**14** and their complexes with Ag^+ and Hg^{2+} in acetonitrile and in water–acetonitrile (9 : 1) have been recorded (Fig. 2 and Table 2). It should be noted that fluorescence emission precluded the recording of RR spectra of the dyes using excitation wavelengths of 514.5 or 457.9 nm. In order to decrease the fluorescence background, the RR spectra of the dyes were excited at 413.1 nm. Some bands in the RR spectrum of dye **14** were found to shift on complexation with Hg^{2+} or Ag^+ cations, though the magnitude of shifts is small, especially for the complex of **14** with Ag^+ (Table 3).

It was found by Wilbrandt *et al.*[17] that the Raman spectrum of (*E*,*E*)-diphenylbutadiene can be considered to be a superposition of the modified benzene ring and butadiene vibrational bands. Similarly, the spectra of the styryl dyes studied here can be considered to consist of benzothiazolium, benzocrown and ethylene fragment vibrations. For this reason, an assignment of the RR bands of the dyes has been made by comparison with a normal mode analysis of structurally similar compounds: 2-methyl-3-ethylbenzothiazolium iodide,[18] 3,4-dimethoxybenzaldehyde,[19] benzocrown ethers[20] and alkyl sulfides[21] (Table 2). In order to explain the magnitudes of band shifts for dye **14** on complexation with Hg^{2+} or Ag^+ cations the results obtained previously[16] for dye **23** can be used. It was shown for **23** that an increase in the solvent polarity or complexation with Mg^{2+} cations resulted in a hypsochromic shift in the absorption spectrum and a wavenumber increase for several of the Raman bands assigned to both C=C stretching and some phenyl ring vibrations. The size of these changes of band position was approximately proportional to the magnitude of the hypsochromic shifts in the absorption spectra. In the case of the dyes studied here, the small shifts observed for Raman bands on variation of the solvent polarity or on complexation with Ag^+ and Hg^{2+} cations are similarly correlated with small shifts in the absorption bands (see Table 3).

In summary, the novel styryl dyes containing a benzodithiacrown ether group have been found to show only slight changes in their electronic and vibrational spectra on complexation with Ag^+ or Hg^{2+}, or on photoisomerization. In such complexes, the sulfur atoms play the most important role in metal binding, but the sulfur–metal interaction does not cause large changes in the chromophore because the sulfur atoms are not conjugated into it.

Table 2 Observed resonance Raman bands of 3×10^{-4} mol dm^{-3} solutions of styryl dyes **12–14** in CH_3CN at the excitation wavelength 413.1 nm, along with their assignments[a]

$\bar{\nu}$/cm^{-1}			
12	**13**	**14**	Assignment
1609s	1611s	1609s	ν(C=C)
1592vs	1590vs	1591vs	8b, BCR
1576sh	1576sh	1576sh	8a, BCR
1509s	1511s	1509s	$\nu(N^+{=}C)$
1498s	—	1498s	19b, BCR
1460m	1460m	1461m	$\delta(CH_2)$, BCR, BT
1442s	1440s	1441s	19a, BCR
—	1413m	—	asym. $\delta(CH_3)$
—	1349s	—	$\omega(CH_2)$, BCR
1317s	1316s	1316s	3, BCR
1268s	1270s	1267s	14, BCR
1229m	1227m	1231m	7a, BCR
1182w	1168w	1181w	18a, BCR
1147m	1143m	1143m	ν(C–Ph)
1097w	1128m	—	asym. ν(COC), BCR
—	—	1036w	18b, BT
967m	967m	967m	$\nu(CO) + \nu(CC) + \delta(CH_2)$
845w	836w	844w	‘Breathing’ of BCR
—	—	751w	11, BCR
637w	626m	634w	ν(CS), BCR or 1, BCR
611w	—	603w	$\delta(CCO) + \delta(COC)$, BCR
513w	513w	513w	δ(CSC), BT

[a] ν, δ and ω denote stretching, bending and wagging vibrations of various functional groups, respectively. BT = benzothiazolium, BCR = benzocrown; vs = very strong, s = strong, m = medium, w = weak and asym. = antisymmetric.

Experimental

Synthesis

The numbering of the compounds is as given above. Chromatographic purification was performed on silica gel [Type A: Kieselgel 60, 70–230 mesh ASTM (Merck); Type B: Silicagel L 40/100 (Chemapol)]. Thin layer chromatography (TLC) was performed on 2 × 5 cm DC-Alufolien plates with a 0.2 mm layer of Kieselgel 60 F_{254} (Merck). ^1H NMR spectra were recorded on a Bruker AC-200p (200 MHz) spectrometer. Tetramethylsilane was used as standard; J values are given in Hz. IR spectra were measured on a Shimadzu IR-470 spectrophotometer using KBr disks. Mass spectra were recorded on a Varian MAT 311A spectrometer.

1,2-Bis(2-hydroxyethoxy)benzene, 3-oxa-1,5-pentanedithiol, 3,6-dioxaoctane-1,8-dithiol, 5-bromovaleric acid, ethyl 4-bromobutyrate, 2-methylbenzothiazole and benzo-18-crown-6 were purchased from the Aldrich Chemical Company.

4-Formylbenzo-18-crown-6 (2). 4-Formylbenzo-18-crown-6 (**2**) was obtained as described previously,[5] yield 58%, mp 62–63 °C (lit.,[5] 63 °C).

1,2-Bis(2-chloroethoxy)benzene (8). 1,2-Bis(2-chloroethoxy)-benzene (**8**) was synthesized according to the established method[22] using benzene as the solvent; yield 88%; mp 53–55 °C (lit.,[22] 50–52 °C).

3,4-Bis(2-chloroethoxy)bromobenzene (9). Freshly prepared dioxane dibromide [23.5 g, 95 mmol, prepared by adding Br_2 to dioxane (1 : 1) to form an orange precipitate] was added to a solution of **8** (22.1 g, 94 mmol) in diethyl ether (120 cm^3) and the mixture was stirred for 1 h at room temperature. Water (100 cm^3) was added and the ether layer was separated, washed with aqueous sodium sulfite and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue was purified by column chromatography [silica gel column (Type A) with benzene as the eluent]; the product **9** (22.7 g, 96%) was isolated: mp 61–62 °C, R_F 0.79 (benzene) (Found: C, 38.39; H, 3.47%. Calc. for $C_{10}H_{11}BrCl_2O_2$: C, 38.25; H, 3.53); $\delta_H(CDCl_3)$ 3.86 (4 H, m, CH_2Cl), 4.29 (4 H, m, CH_2O), 6.83 (1 H, d, J 8.2, ArH), 7.06 (1 H, s, ArH) and 7.09 (1 H, d, J 8.2, ArH).

1^4-Bromo-2,8,11,17-tetraoxa-5,14-dithia-1(1,2)-benzenaheptadecaphane (10) and 1^4,18^4-dibromo-2,8,11,17,19,25,28,34-octaoxa-5,14,22,31-tetrathia-1,18(1,2)-dibenzenacyclotetratriacontaphane (19). To a boiling solution of $Na_2CO_3{\cdot}10H_2O$ (30.5 g, 107 mmol) in ethanol (420 cm^3) and water (380 cm^3), a solution of 3,6-dioxaoctane-1,8-dithiol (3.88 g, 21.3 mmol) and **9** (6.69 g, 21.3 mmol) in ethanol (75 cm^3) and benzene (10 cm^3) were added over 1 h. The reaction mixture was

Table 3 Observed resonance Raman bands of dye **14** in CH_3CN, and shifts observed on complexation with Hg^{2+} and Ag^+ and on changing the solvent to H_2O:CH_3CN (9:1)

$\bar{\nu}$(**14**)/cm^{-1} 430[a]	$\Delta\bar{\nu}$(**14**·Hg^{2+} − **14**)/cm^{-1} 412[a]	$\Delta\bar{\nu}$(**14**·Ag^+ − **14**)/cm^{-1} 422[a]	$\Delta\bar{\nu}$(**14**, H_2O:CH_3CN (9:1) − **14**, CH_3CN)/cm^{-1} 415[a]
1609	+2	+1	+3
1591	+4	+1	+2
1576	+3	+2	+1
1509	+3	+1	0
1441	0	0	+2
1316	+2	+2	+2
1267	+1	+1	+2
1231	−1	−1	−2
1181	−4	—	−4
967	+2	+2	+3

[a] Absorption maxima in nm.

refluxed for 14 h and ethanol was removed from the mixture. The aqueous solution was extracted with benzene–chloroform (10:1), the organic extracts were dried (K_2CO_3) and the solvent was removed *in vacuo*. The residue was purified by column chromatography [silica gel column (Type A) with benzene–ethyl acetate (5:1) as the eluent]. Recrystallization from benzene yielded product **10** (7.8 g, 75%) and product **19** (0.78 g, 9%).

Compound **10**: mp 118–119 °C; R_F 0.67 (benzene–ethyl acetate, 5:1) (Found: C, 45.20; H, 5.58%. Calc. for $C_{16}H_{23}BrO_4S_2$: C, 45.39; H, 5.48); $\delta_H(CDCl_3)$ 2.96 (4 H, m, CH_2S), 3.12 (4 H, m, CH_2S), 3.63 (4 H, s, CH_2O), 3.76 (4 H, m, CH_2O), 4.18 (4 H, m, CH_2O), 6.71 (1 H, d, *J* 8.5, ArH), 6.95 (1 H, s, ArH) and 7.01 (1 H, d, *J* 8.5, ArH); *m*/*z* 424 (M^+ with ^{81}Br, 16%), 422 (M^+ with ^{79}Br, 16), 216 (31), 214 (27), 149 (29), 89 (39), 87 (61), 79 (27), 61 (62), 60 (100) and 59 (21).

Compound **19**: mp 104–108 °C; R_F 0.36 (benzene–ethyl acetate, 5:1) (Found: C, 45.13; H, 5.60%. Calc. for $C_{32}H_{46}Br_2O_8S_4$: C, 45.39; H, 5.48); $\delta_H(CDCl_3)$ 2.87 (8 H, m, CH_2S), 2.97 (8 H, m, CH_2S), 3.63 (8 H, s, CH_2O), 3.70 (8 H, m, CH_2O), 4.13 (8 H, m, CH_2O), 6.73 (2 H, d, *J* 8.4, ArH), 6.99 (2 H, s, ArH) and 7.01 (2 H, d, *J* 8.4, ArH); *m*/*z* 848 (M^+ with two ^{81}Br, 2%), 846 (M^+ with ^{81}Br and ^{79}Br, 4), 844 (M^+ with two ^{79}Br, 2), 235 (40), 216 (62), 214 (64), 207 (46), 175 (46), 149 (100), 118 (35) and 105 (37).

1^4-Formyl-2,8,11,17-tetraoxo-5,14-dithia-1(1,2)-benzenaheptadecaphane (11). A solution of **10** (0.508 g, 1.2 mmol) in abs. diethyl ether (25 cm^3) and abs. THF (15 cm^3) under excess pressure of dried argon was cooled to −100 °C, and a 1.2 mol dm^{-3} solution of butyllithium in hexane (3 cm^3) was added. The mixture was stirred at −100 °C for 2.5 h and abs. DMF (0.26 cm^3, 3.3 mmol) was added. The reaction mixture was stirred for 1 h, and the temperature was slowly raised to room temperature for 4 h. A 5% aqueous solution of HCl (40 cm^3) was added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with chloroform (3 × 15 cm^3) and the solvent was removed *in vacuo*. The residue was purified by column chromatography [silica gel column (Type A) with benzene–ethyl acetate (5:1) as the eluent] and 2,8,11,17-tetraoxa-5,14-dithia-1(1,2)-benzenaheptadecaphane (**20**) (0.107 g, 26%) and the product **11** (0.260 g, 58%) were separated.

Unsaturated crown ether **20**: mp 90–91 °C (lit.,[10] 90–91 °C); R_F 0.71 (benzene–ethyl acetate, 5:1).

Compound **11**: mp 131–132 °C; R_F 0.50 (benzene–ethyl acetate, 5:1) (Found: C, 54.89; H, 6.54%. Calc. for $C_{17}H_{24}O_5S_2$: C, 54.82; H, 6.49); $\delta_H(CDCl_3)$ 2.97 (4 H, m, CH_2S), 3.15 (4 H, m, CH_2S), 3.62 (4 H, s, CH_2O), 3.75 (4 H, m, CH_2O), 4.27 (4 H, m, CH_2O), 6.95 (1 H, d, *J* 8.2, ArH), 7.38 (1 H, s, ArH), 7.45 (1 H, d, *J* 8.2, ArH) and 9.84 (1 H, s, CH=O); *m*/*z* 372 (M^+, 49%), 175 (24), 164 (47), 163 (27), 149 (98), 105 (43), 89 (37), 87 (88), 61 (84), 60 (100) and 59 (51); $\bar{\nu}_{max}/cm^{-1}$ 1683 (C=O).

Iodide of 2,3-dimethylbenzothiazolium (4). The iodide of 2,3-dimethylbenzothiazolium (**4**) was synthesized according to the published method;[6] yield 65%; mp 189 °C (lit.,[6] 188–189 °C).

Bromide of 3-[3-(hydroxycarbonyl)propyl]-2-methylbenzothiazolium (5). A mixture of ethyl 4-bromobutyrate (0.70 cm^3, 4.89 mmol) and 2-methylbenzothiazole (1.25 cm^3, 9.79 mmol) was heated at 120 °C for 6 h. The resulting product was cooled and washed with benzene. To the benzene insoluble residue an aqueous solution of HBr (1:1) (4 cm^3) was added and the mixture was heated at 50–55 °C for 6 h. The solvent was evaporated *in vacuo* and the residue was purified [silica gel column (Type B) with acetonitrile–ethanol (20:1) as the eluent]. The hydrobromide of 2-methylbenzothiazolium (**16**) (1 g, 67%) and product **5** (0.33 g, 21%) were isolated. Compound **5**, mp 218–219 °C (decomposition) (Found: C, 45.44; H, 4.56; N, 4.48%. Calc. for $C_{12}H_{14}BrNO_2S$: C, 45.58; H, 4.46; N, 4.43); $\delta_H([^2H_6]DMSO)$ 2.10 (2 H, m, NCH_2CH_2), 2.55 [2 H, t, $C(O)CH_2$], 3.27 (3 H, s, CH_3), 4.77 (2 H, m, NCH_2), 7.80 (1 H, m, ArH), 7.91 (1 H, m, ArH), 8.40 (1 H, d, *J* 8.1, ArH), 8.48 (1 H, d, *J* 8.1, ArH) and 12.38 (1 H, br s, COOH); $\bar{\nu}_{max}/cm^{-1}$ 3440 (O–H) and 1718 (C=O).

Bromide of 3-[4-(hydroxycarbonyl)butyl]-2-methylbenzothiazolium (6). A mixture of 5-bromovaleric acid (1.00 g, 5.53 mmol) and 2-methylbenzothiazole (2.1 cm^3, 16.6 mmol) was heated at 120 °C for 5.5 h. The resulting mixture was cooled and washed with benzene–acetonitrile, 2:1 (3 × 20 cm^3). The insoluble residue was purified by column chromatography on a silica gel column (Type B) with acetonitrile to remove the hydrobromide of 2-methylbenzothiazolium (**16**), and the crude product **6** was obtained by eluting with acetonitrile–methanol (2:1). The solvent was evaporated *in vacuo* and the residue was washed with hot acetonitrile to obtain product **6** (0.689 g, 38%), mp 208–209 °C (decomposition) (Found: C, 47.41; H, 4.96; N, 4.06%. Calc. for $C_{13}H_{16}BrNO_2S$: C, 47.28; H, 4.88; N, 4.24); $\delta_H([^2H_6]DMSO)$ 1.68 [2 H, m, $C(O)CH_2CH_2$], 1.90 (2 H, m, NCH_2CH_2), 2.31 [2 H, t, $C(O)CH_2$], 3.21 (3 H, s, CH_3), 4.74 (2 H, m, NCH_2), 7.79 (1 H, m, ArH), 7.88 (1 H, m, ArH), 8.32 (1 H, d, *J* 8.5, ArH), 8.44 (1 H, d, *J* 8.2, ArH) and 12.20 (1 H, br s, COOH); $\bar{\nu}_{max}/cm^{-1}$ 3440 (O–H) and 1714 (C=O).

General procedure for preparation of styryl dyes 12–15

A solution of the heterocyclic salt **4**–**6** (0.111 mmol) and the crown ether **2** or **11** (0.122 mmol) in abs. ethanol (2 cm^3) and dried pyridine (0.3 cm^3) was refluxed for 6 h. The solvent was evaporated *in vacuo* and the residue was washed with benzene (3 × 10 cm^3) to remove the unreacted crown ether. The residue was dissolved in a minimum quantity of hot methanol and conc. $HClO_4$ (0.05 cm^3) was added. The solution was cooled and a precipitate was filtered to obtain the product **12**–**15** as orange crystals.

Perchlorate of 2-[2,8,11,17-tetraoxa-5,14-dithia-1(1,2)benzenaheptadecaphan-1^4-yl]ethen-1-yl-3-[(hydroxycarbonyl)-butyl]benzothiazolium (12). **12** was prepared in 83% yield, mp 146 °C (Found: C, 50.48; H, 5.27; N, 1.96%. Calc. for $C_{30}H_{38}ClNO_{12}S$: C, 50.52; H, 5.22; N, 2.27); $\delta_H([^2H_6]DMSO)$ 1.72 [2 H, m, $C(O)CH_2CH_2$], 1.96 (2 H, m, NCH_2CH_2), 2.32 [2 H, t, $C(O)CH_2$], 3.60 (12 H, m, OCH_2), 3.85 (4 H, m, OCH_2), 4.25 (4 H, m, OCH_2), 4.98 (2 H, t, NCH_2), 7.16 (1 H, d, *J* 8.9, ArH), 7.65 (2 H, m, ArH), 7.8 (3 H, m, α-H, ArH), 8.15 (1 H, d, *J* 15.7, β-H), 8.25 (1 H, d, *J* 8.1, ArH) and 8.39 (1 H, d, *J* 7.6, ArH).

Perchlorate of 2-[2,8,11,17-tetraoxa-5,14-dithia-1(1,2)benzenaheptadecaphan-1^4-yl]ethen-1-yl-3-methylbenzothiazolium (13). **13** was prepared in 65% yield, mp 232–233 °C (decomposition) (Found: C, 50.48; H, 5.27; N, 1.96%. Calc. for $C_{26}H_{32}ClNO_8S_3$: C, 50.52; H, 5.22; N, 2.27); $\delta_H(CD_3CN)$ 2.96 (4 H, m, CH_2S), 3.12 (4 H, m, CH_2S), 3.59 (4 H, s, CH_2O), 3.71 (4 H, m, CH_2O), 4.27 (3 H, s, NCH_3), 4.31 (4 H, m, CH_2O), 7.08 (1 H, d, *J* 8.1, ArH), 7.43–7.50 (2 H, m, ArH), 7.56 (1 H, d, *J* 15.8, α-H), 7.77 (1 H, m, ArH), 7.87 (1 H, m, ArH), 7.98–8.09 (2 H, m, β-H and ArH) and 8.20 (1 H, d, *J* 8.5, ArH).

Perchlorate of 2-[2,8,11,17-tetraoxa-5,14-dithia-1(1,2)benzenaheptadecaphan-1^4-yl]ethen-1-yl-3-[4-(hydroxycarbonyl)-butyl]benzothiazolium (14). **14** was prepared in 72% yield, mp 185–187 °C (decomposition) (Found: C, 55.21; H, 5.97; N, 2.28%. Calc. for $C_{29}H_{38}ClNO_{10}S$: C, 55.45; H, 6.09; N, 2.23); $\delta_H([^2H_6]DMSO)$ 1.67 [2 H, m, $C(O)CH_2CH_2$], 1.89 (2 H, m, NCH_2CH_2), 2.30 and 2.40 [2 H, 2 t, $C(O)CH_2$], 2.90 (4 H, t, CH_2S), 3.10 (4 H, m, CH_2S), 3.54 (4 H, s, CH_2O), 3.65 (4 H, t, CH_2O), 4.25 (4 H, m, CH_2O), 4.95 (2 H, m, NCH_2), 7.16 (1 H, d, *J* 8.6, ArH), 7.61–7.92 (5 H, m, ArH and α-H), 8.19 (1 H, d, *J* 16.0, β-H), 8.27 (1 H, d, *J* 8.6, ArH) and 8.40 (1 H, d, *J* 8.9, ArH); $\bar{\nu}_{max}/cm^{-1}$ 3424 (O–H) and 1722 (C=O).

Perchlorate of 2-[2,8,11,17-tetraoxa-5,14-dithia-1(1,2)benzenaheptadecaphan-1^4-yl]ethen-1-yl-3-[3-(hydroxycarbonyl)-propyl]benzothiazolium (15). **15** was prepared in 64% yield, mp 203–205 °C (decomposition) (Found: C, 50.50; H, 5.27; N, 1.77%. Calc. for $C_{29}H_{36}ClNO_{10}S_3$: C, 50.46; H, 5.26; N, 2.03);

$\delta_H(CD_3CN)$ 2.34 (2 H, m, NCH_2CH_2), 2.63 [2 H, t, $C(O)CH_2$], 2.95 (4 H, t, CH_2S), 3.13 (4 H, m, CH_2S), 3.59 (4 H, s, CH_2O), 3.70 (4 H, m, CH_2O), 4.32 (4 H, m, CH_2O), 4.76 (2 H, m, NCH_2), 7.09 (1 H, d, J 8.5, ArH), 7.47 (1 H, d, J 8.4, ArH), 7.58 (1 H, s, ArH), 7.68–7.92 (3 H, m, ArH and α-H), 8.03–8.17 (2 H, m, β-H and ArH) and 8.20 (1 H, d, J 7.9, ArH); $\tilde{\nu}_{max}/cm^{-1}$ 3408 (O–H) and 1724 (C=O).

Spectroscopy

Raman spectra were recorded using a Jobin Yvon Ramanor HG2 spectrometer equipped with an RCA C31034A02 photomultiplier tube. A Vig III PC with PRISM software provided instrumental control and data processing. Excitation was provided by Spectra-Physics 2020-05 Ar^+ (457.9, 488.0 and 514.5 nm) or 170 Kr^+ (413.1 and 647 nm) lasers. Typically, spectra were recorded using a laser power of 0.1 W (413.1 nm), 0.2 W (457.9, 488 and 514.5 nm) or 0.7 W (647 nm). The spectra were accumulated using a spectral slitwidth of 6 cm^{-1}, with 1 cm^{-1} steps and an accumulation time of 1 s per spectral point. Each spectrum is the average of 3–6 individual scans. The liquid samples were held in a capillary tube for normal Raman and in a spinning cell for resonance Raman experiments.

UV–VIS spectra of dye solutions were recorded using a Perkin-Elmer Lambda 15 UV–VIS spectrophotometer.

Steady-state fluorescence spectra were recorded using a Shimadzu RF-5000 spectrofluorimeter. The fluorescence quantum yields for the styryl dyes and their complexes were determined relative to rhodamine B in 0.01 mol dm^{-3} NaOH with excitation at 365 nm.

A glass-filtered 100 W high pressure Hg lamp was used for irradiation to induce photoisomerization.

Acknowledgements

The authors thank Mr R. B. Girling for his technical assistance. This work was supported by the Royal Society in the framework of the joint project between the University of York, York, UK, and the N. N. Semenov Institute of Chemical Physics of the Russian Academy of Sciences, Moscow, Russia. Y. V. F., O. A. F. and V. P. O. gratefully acknowledge the Royal Society for support of their stay in York and travel expenses. J. N. M. acknowledges EPSRC Advanced Fellowship support.

References

1 S. Gromov, O. Fedorova and M. Alfimov, *Mol. Cryst. Liq. Cryst.*, 1994, **246**, 183.

2 A. V. Barzykin, M. A. Fox, E. N. Ushakov, O. B. Stanislavsky, S. P. Gromov, O. A. Fedorova and M. V. Alfimov, *J. Am. Chem. Soc.*, 1992, **114**, 6381.

3 I. K. Lednev, S. P. Gromov, E. N. Ushakov, M. V. Alfimov, J. N. Moore and R. E. Hester, *Spectrochim. Acta, Part A*, 1992, **48**, 799.

4 I. K. Lednev, O. A. Fedorova, S. P. Gromov, M. V. Alfimov, J. N. Moore and R. E. Hester, *Spectrochim. Acta, Part A*, 1993, **49**, 1055.

5 F. Wada, H. Hirayama, H. Namiki, K. Kikukawa and T. Matsuda, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1473.

6 M. Koral, D. Bonis, A. J. Fusco, P. Dougherty, A. Leifer and J. E. LuValle, *J. Chem. Eng. Data*, 1964, **9**, 406.

7 E. M. Hyde, B. L. Shaw and I. Shepherd, *J. Chem. Soc., Dalton Trans.*, 1978, 1696.

8 L. N. Markovski, D. M. Rudkevich and V. I. Kalchenko, *J. Org. Chem. USSR*, 1990, **26**, 426.

9 J. van Gent, E. J. R. Sudholter, P. V. Lambeck, T. J. A. Popma, G. J. Gerritsma and D. N. Reinhoudt, *J. Chem. Soc., Chem. Commun.*, 1988, 893.

10 C. Pedersen, *J. Org. Chem.*, 1971, **36**, 254.

11 S. P. Gromov, O. A. Fedorova, M. V. Alfimov, V. V. Tkachev and L. R. Atovmyan, *Dokl. Akad. Nauk SSSR*, 1991, **319**, 1141.

12 R. M. Izatt, R. E. Terry, L. D. Hansen, A. G. Avondet, J. S. Bradshaw, N. K. Dalley, T. E. Jensen and J. J. Christensen, *J. Inorg. Chim. Acta*, 1978, **30**, 1.

13 S. P. Gromov, O. A. Fedorova, E. N. Ushakov, O. B. Stanislavsky, I. K. Lednev and M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1991, **317**, 1134.

14 R. M. Izatt, G. Wu, W. Jiang and N. K. Dalley, *Inorg. Chem.*, 1990, **29**, 3828.

15 E. Fisher, *J. Phys. Chem.*, 1967, **71**, 3704.

16 I. K. Lednev, M. V. Fomina, S. P. Gromov, O. B. Stanislavsky, M. V. Alfimov, J. N. Moore and R. E. Hester, *Spectrochim. Acta, Part A*, 1992, **48**, 931.

17 R. Wilbrandt, W. E. L. Grossman, P. M. Killough, J. E. Bennett and R. E. Hester, *J. Phys. Chem.*, 1984, **88**, 5964.

18 H. Sato, M. Kawasaki, K. Kasatani and M. Katsumata, *J. Raman Spectrosc.*, 1988, **19**, 129.

19 G. Varsanyi, *Assignments for vibrational spectra of seven hundred benzene derivatives*, vol. 1, Akademiai Kiado, Budapest, 1974.

20 A. Yu. Tsivadze, A. A. Varnek and V. E. Khutorsky, *Coordination compounds of metals with crown-ligands*, Nauka, Moscow, 1991.

21 F. R. Dollish, W. G. Fateley and F. F. Bentley, *Characteristic Raman frequencies of organic compounds*, Wiley-Interscience, New York, 1974.

22 E. Weber, H.-J. Köhler, K. Panneerselvam and K. X. Chacko, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1599.

Paper 5/08070C
Received 11*th December* 1995
Accepted 8*th March* 1996