

# Vibrational and crystallographic studies of dioxohalogenomolybdenum(VI) complexes with crown ethers

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Crown ether adducts  $[\text{MoO}_2\text{X}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O} \cdot 18\text{-crown-6}$  ( $\text{X} = \text{Br}$  **1** or  $\text{Cl}$  **2**), obtained by combining solutions of  $\text{Mo}^{\text{VI}}$  in HBr or HCl with 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), were shown by X-ray crystallography to contain  $\text{MoO}_2\text{X}_2(\text{H}_2\text{O})_2$  units with *cis,trans,cis* ligand arrangement. Recrystallisation from methyl alcohol yielded  $[\text{MoO}_2\text{Cl}_2(\text{MeOH})_2] \cdot 18\text{-crown-6}$  **3** which was also characterised by X-ray analysis. Adding potassium ions to the HCl system gave  $[\text{K}(18\text{-crown-6})][\text{MoO}_2\text{Cl}_3(\text{H}_2\text{O})]$  **4** which was identified by studying Raman and IR spectra of the series.

## Introduction

The *cis*- $\text{MoO}_2$  unit is widespread in molybdenum(VI) chemistry. For example, it occurs at the active site in the molybdenum-containing oxotransferase enzymes which catalyse oxygen atom transfer to and from biological substrates in the nitrogen, sulfur and carbon cycles. Thus it is particularly important to understand the structural chemistry and ligand exchange behaviour of the  $\text{MoO}_2$  unit in relatively simple systems. Furthermore, dioxomolybdenum complexes with halogen ligands are on the borderline of stability between the +5 and +6 states of molybdenum, as shown by the fact that the  $\text{MoO}_2$  species with bromide ligands undergoes photoreduction. Such complexes are therefore potentially useful as model systems for the investigation of this redox process.

The nature of molybdenum(VI) species in aqueous solution is not well understood, especially for acidic solutions containing HCl or HBr. An object of the present work was to isolate dioxohalogenomolybdenum(VI) complexes from solution for X-ray and spectroscopic examination, in order to extend our earlier study of molybdenum(VI) solutions and solvent extracts.<sup>1</sup>

Molybdenum(VI) exists in alkaline solutions as the simple molybdate ion  $\text{MoO}_4^{2-}$  but on acidification this is converted into polyoxomolybdate complexes which separate as white solids of variable composition. The addition of an excess of hydrochloric or hydrobromic acid causes the white precipitate to dissolve yielding solutions in which halogen-containing molybdenum(VI) anions apparently exist. Previously we obtained <sup>95</sup>Mo NMR and Raman evidence indicating the presence of neutral  $[\text{MoO}_2\text{X}_2(\text{H}_2\text{O})_2]$  complexes in these HCl and HBr solutions, and showed that these species are the predominant form in which molybdenum(VI) undergoes solvent extraction into an ether phase.<sup>1</sup> The solid  $\text{Cs}_2[\text{MoO}_2\text{Cl}_4]$  is produced when CsCl is added to the HCl solution of  $\text{Mo}^{\text{VI}}$ , although the anion concerned,  $[\text{MoO}_2\text{Cl}_4]^{2-}$ , is not detected in the parent solution.<sup>2</sup> Molybdenum(VI) is efficiently extracted from its HCl or HBr solutions into an ether or ketone solvent phase, which provides a useful method of separation.<sup>3,4</sup>

In this investigation crown ethers are used to isolate the species  $[\text{MoO}_2\text{X}_2(\text{H}_2\text{O})_2]$  ( $\text{X} = \text{Br}$  or  $\text{Cl}$ ) within crystalline solids, enabling their structures to be characterised by vibrational spectroscopy and X-ray crystallography. Introduction of potassium ions to form  $[\text{K}(18\text{-crown-6})]^+$  allows the novel species  $[\text{MoO}_2\text{Cl}_3(\text{H}_2\text{O})]^-$  to be isolated and identified.

## Results and discussion

Solids were isolated from  $\text{Mo}^{\text{VI}}\text{-HCl}$  and  $\text{-HBr}$  systems by introducing crown ethers which formed air-stable crystalline adducts with the molybdenum complexes. The ethers 18-crown-6, 15-crown-5 and 12-crown-4 gave similar products, as indicated by the Mo–O and Mo–X bands in the infrared spectra. The compounds involving 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) were chosen for particular study.

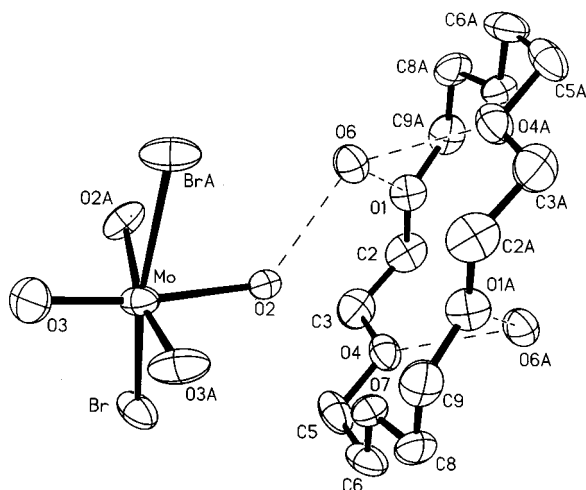
Three preparative methods were employed: (i) diethyl ether extraction of the  $\text{Mo}^{\text{VI}}\text{-HCl}$  or  $\text{-HBr}$  solution, followed by addition of crown ether to the separate extract phase, (ii) solvent extraction of the  $\text{Mo}^{\text{VI}}\text{-HX}$  solution using a solution of the crown ether in  $\text{Et}_2\text{O}$ , (iii) direct addition of the crown ether to a solution of the molybdenum complexes in HCl or HBr. The source of  $\text{Mo}^{\text{VI}}$  was potassium molybdate or ammonium molybdate. In the case of HCl solutions methods (ii) and (iii) gave a product which incorporated  $\text{K}^+$  ions. Crystalline samples **1–4** were obtained (Experimental section) and investigated by X-ray diffraction and by their vibrational spectra.

## X-Ray crystallography

Fig. 1 gives the structure of  $[\text{MoO}_2\text{Br}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O} \cdot 18\text{-crown-6}$  **1**, consisting of the uncharged molybdenum complex  $[\text{MoO}_2\text{Br}_2(\text{H}_2\text{O})_2]$  accompanied by a molecule of 18-crown-6 and two extraneous water molecules. The  $\text{H}_2\text{O}$  ligands take part in hydrogen bonds measuring 1.86(2) and 1.79(2) Å to the extra water molecules which form hydrogen bonds of 2.07(2) Å directed towards oxygens of the crown ether.

Table 1 contains the principal interatomic distances and angles of the  $[\text{MoO}_2\text{Br}_2(\text{H}_2\text{O})_2]$  structure which consists of the expected *cis*- $\text{MoO}_2$  group, with the  $\text{H}_2\text{O}$  ligands *trans* to the Mo=O bonds, and a pair of mutually *trans*-Br atoms making up an octahedral complex. Bromide is an uncommon ligand for molybdenum(VI) as such systems are prone to photoreduction and few structures are available for comparison.<sup>5</sup> (2,2'-bipyridyl)dibromodioxomolybdenum(VI)<sup>6</sup> has *cis*-M=O bonds of 1.643(17) and 1.826(18) Å, and *trans*-Mo–Br bonds of 2.461(3) and 2.781(3) Å with Br–Mo–Br angle of 159.7(1)° which may be compared with the dimensions of the present, less distorted structure. The Mo=O distance of 1.695 Å in **1** is slightly shorter than the average value of 1.704 Å derived from a large number of dioxomolybdenum structures.<sup>7</sup>

Crystals of  $[\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}\cdot 18\text{-crown-6}$  **2** were also investigated and found to have a kindred structure in which the pattern of hydrogen bonding resembles that of complex **1**. This compound contains the octahedral complex  $[\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2]$  which has been encountered before in  $[\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2]\cdot \text{H}_2\text{O}\cdot \text{NEt}_4\text{Cl}$ <sup>8</sup> and  $[\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2]\cdot 2\text{C}_3\text{H}_5\text{NHCl}$ .<sup>9</sup> The geometries are similar, and the average dimensions of our earlier study<sup>8</sup> are given in parentheses in the following comparison with the present bond lengths (Å) and angles (°): Mo=O 1.677 (1.687), Mo–O 2.210 (2.272) and Mo–Cl 2.368 (2.346); O=Mo=O 103.5 (103.5), O–Mo–O 75.8 (78.5) and Cl–Mo–Cl 159.9 (157.9).



**Fig. 1** The structure of  $[\text{MoO}_2\text{Br}_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}\cdot 18\text{-crown-6}$  **1**, showing the atomic labelling.

**Table 1** Selected bond distances (Å) and angles (°) for  $[\text{MoO}_2\text{Br}_2(\text{H}_2\text{O})_2]\cdot 18\text{-crown-6}$  **1**,  $[\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}\cdot 18\text{-crown-6}$  **2** and  $[\text{MoO}_2\text{Cl}_2(\text{MeOH})_2]\cdot 2\text{H}_2\text{O}\cdot 18\text{-crown-6}$  **3**

	<b>1</b>	<b>2</b>	<b>3</b>
Mo=O	1.695(2)	1.677(3)	1.696(3)
Mo–O	2.204(2)	2.210(3)	2.240(3)
Mo–X*	2.5310(3)	2.3682(9)	2.3730(10)
O=Mo=O	103.2(2)	103.5(3)	102.8(2)
O–Mo–O	76.1(1)	75.8(2)	76.9(1)
X–Mo–X*	161.47(2)	159.90(5)	160.81(6)

\* X = Br in complex **1** or Cl in **2** and **3**.

**Table 2** Vibrational spectral data ( $\text{cm}^{-1}$ ) and assignments for crystalline solids  $[\text{MoO}_2\text{X}_2(\text{H}_2\text{O})_2]$  (X = Br **1** or Cl **2**) and  $[\text{MoO}_2\text{Cl}_3(\text{H}_2\text{O})]^-$  \*

<b>1</b>		<b>2</b>		<b>4</b>		Vibration
Raman	IR	Raman	IR	Raman	IR	
948vs	957s	951vs	957s	946vs	957s	$\nu_{\text{sym}}(\text{MoO}_2)$
914m	948s	919m	951s	896s	944s	
	907s		909vs		894vs	$\nu_{\text{asym}}(\text{MoO}_2)$
	425m	435vw	433m	391s	390m	$\nu_{\text{sym}}(\text{Mo–OH}_2)$
372m	372m	378m	376w	327m	329s	$\nu_{\text{asym}}(\text{Mo–OH}_2)$
			332s		320 (sh)	$\nu_{\text{asym}}(\text{Mo–Cl})$
		318s		300m		$\nu_{\text{sym}}(\text{Mo–Cl})$
247m	248vs	262s	260m	253s	251s	$\rho(\text{MoO}_2)$
205vs	205w					$\nu_{\text{asym}}(\text{Mo–Br})$
185vs	180w					$\nu_{\text{sym}}(\text{Mo–Br})$
		146m	146w	146w	147m	$\delta(\text{MoCl}_2)$
		92s	125m	113m		$\delta(\text{Cl–Mo–OH}_2)$
103m	118m					$\delta(\text{MoBr}_2)$
87m						$\delta(\text{Br–Mo–OH}_2)$

\* The spectrum of complex **3** is almost identical to that of **2** except for an additional IR band, 1002w  $\text{cm}^{-1}$ , due to MeOH.

Previously the distances to the pair of  $\text{H}_2\text{O}$  ligands differed significantly, but in the present instance these bonds are equal.

Recrystallisation of complex **2** from methanol results in the replacement of both the co-ordinated  $\text{H}_2\text{O}$  ligands by MeOH molecules, forming the compound  $[\text{MoO}_2\text{Cl}_2(\text{MeOH})_2]\cdot 18\text{-crown-6}$  **3** which was also investigated by X-ray crystallography. The structure reveals that the extra water molecules (those linked to the crown ether in the structure of **2**) have been lost. The pair of *cis*-MeOH ligands of **3** form Mo–O bonds of 2.240(3) Å which is significantly longer than the Mo–O bond distance of 2.210(3) Å to the  $\text{H}_2\text{O}$  ligands of **2**. The C–O bond length of the co-ordinated methanol molecule is 1.467(5) Å and the bond angle Mo–O–C measures 133.9(2)°. Other bond distances and angles are given in Table 1 where it will be noted that the Mo=O and Mo–Cl bonds of **3** are slightly longer than those of **2**.

The O–H bond of each methanol ligand measures 0.73(5) Å. These hydrogens are involved in hydrogen bonds of 1.97(5) Å to oxygen atoms of the 18-crown-6 molecule. The angle O–H...O is 167(5)°.

### Vibrational spectroscopy

Table 2 compares the vibrational data for complex **1** with those of **2** and **4**. Bands due to the 18-crown-6 component do not interfere with those of the molybdenum species and are omitted. Strong bands from the *cis*- $\text{MoO}_2$  unit are characteristic, and are accompanied by a number of other bands, including those of the Mo–Br or Mo–Cl stretching modes, assigned in Table 2. The spectrum of **2** gives frequencies for  $[\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2]$  closely matching those of  $[\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2]\cdot \text{H}_2\text{O}\cdot \text{NEt}_4\text{Cl}$  where  $\text{Et}_4\text{N}^+$  and  $\text{Cl}^-$  ions accompany the diaquadiochlorodioxomolybdenum(vi) complex.<sup>8</sup>

The present spectra of  $[\text{MoO}_2\text{X}_2(\text{H}_2\text{O})_2]$  (X = Br **1** or Cl **2**) closely resemble those given by acidic molybdenum(vi) solutions and solvent extracts,<sup>1</sup> supporting the earlier conclusion these are the principal complexes involved. The <sup>95</sup>Mo NMR spectra of the molybdenum(vi) solutions have also been attributed to  $[\text{MoO}_2\text{X}_2(\text{H}_2\text{O})_2]$ ,<sup>1</sup> although the presence of other halogeno-complexes was not ruled out. Thus complexes such as  $[\text{MoO}_2\text{X}_3(\text{H}_2\text{O})]^-$  and  $[\text{MoO}_2\text{X}_4]^{2-}$  may coexist with  $[\text{MoO}_2\text{X}_2(\text{H}_2\text{O})_2]$ . In species such as these, bonds opposed to the oxo-groups are expected to be weak because of strong *trans* influence, allowing facile exchange of the ligands (water molecules or halide ions).

**[K(18-crown-6)][MoO<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)]**. Initially we thought that the molybdenum(vi) compound from HCl solution might be of

**Table 3** Data collection and processing parameters for complexes 1–3

	<b>1</b>	<b>2</b>	<b>3</b>
Formula	C <sub>12</sub> H <sub>32</sub> Br <sub>2</sub> MoO <sub>12</sub>	C <sub>12</sub> H <sub>32</sub> Cl <sub>2</sub> MoO <sub>12</sub>	C <sub>14</sub> H <sub>32</sub> Cl <sub>2</sub> MoO <sub>10</sub>
<i>M</i>	624.14	535.22	527.24
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>C2/c</i>	<i>Pbcn</i>	<i>C2/c</i>
<i>a</i> /Å	8.6690(1)	8.3364(2)	8.7118(1)
<i>b</i> /Å	19.7867(2)	19.2115(6)	19.0183(3)
<i>c</i> /Å	13.5329(1)	14.3430(4)	13.6617(2)
$\beta$ /°	94.284(1)		94.949(1)
<i>V</i> /Å <sup>3</sup>	2314.82(4)	2297.10(11)	2255.08(6)
<i>Z</i>	4	4	4
$\mu$ /mm <sup>-1</sup>	4.069	0.854	0.862
<i>T</i> /K	203	203	203
Reflections collected/unique ( <i>R</i> <sub>int</sub> )	10949/2567 (0.0176)	13297/2026 (0.0316)	6451/2481 (0.0218)
No. observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	2445	1619	2191
Goodness of fit on <i>F</i> <sup>2</sup>	1.075	1.073	1.131
<i>R</i> (observed data)	0.0267	0.0374	0.0456
<i>wR2</i> (all data)	0.0632	0.0933	0.1335

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR2 = \frac{[\sum w(F_o^2 - F_c^2)^2]}{[\sum w(F_o^2)^2]}$$

the form [H<sub>3</sub>O(18-crown-6)]<sup>+</sup>[MoO<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)]<sup>-</sup> since ionic complexes of this kind are known for other elements.<sup>10–13</sup> However, this possibility was ruled out when vibrational and crystallographic evidence for **2** showed it to be a molecular adduct containing [MoO<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].

A different complex, namely [K(18-crown-6)][MoO<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)] **4**, was obtained when the synthetic procedures (as above) employed potassium molybdate, instead of ammonium molybdate. The IR and Raman spectra of **4** are given in Table 2 and provide firm support for the presence of the [MoO<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)]<sup>-</sup> anion. The stretching frequencies of the *cis*-MoO<sub>2</sub> group drop from 909 and 951 cm<sup>-1</sup> in the molecular complex **2** to 894 and 944 cm<sup>-1</sup> in **4**, while that of the MoO<sub>2</sub> rocking mode falls from 260 to 251 cm<sup>-1</sup>. The Mo–Cl stretching frequencies of **4**, 300, 320 and 329 cm<sup>-1</sup>, are lower than those of **2** which displays  $\nu_{\text{sym}}$  at 318 cm<sup>-1</sup> and  $\nu_{\text{asym}}$  at 332 cm<sup>-1</sup>. This comparison also suggests that the molybdenum(vi) species in **4** is anionic. The spectra of Cs<sub>2</sub>[MoO<sub>2</sub>Cl<sub>4</sub>]<sup>1,2</sup> confirm the trend to lower frequencies, with *cis*-MoO<sub>2</sub> bands at 883 and 919 cm<sup>-1</sup> and Mo–Cl stretches at 308 and 325 cm<sup>-1</sup>.

The formation of [K(18-crown-6)][MoO<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)], rather than the [MoO<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex, is attributable to replacement of one of the H<sub>2</sub>O ligands by Cl<sup>-</sup> under the *trans* influence of the MoO<sub>2</sub> oxygen atoms, aided by the tendency of 18-crown-6 to accommodate K<sup>+</sup> as the necessary counter ion.<sup>14</sup> Unfortunately, attempts to solve the structure of **4** by X-ray crystallography were defeated by severe disorder problems.

Rather surprisingly, the addition of a crown ether to the Mo<sup>VI</sup>-HBr systems in the presence of potassium ions yields crystals of the molecular [MoO<sub>2</sub>Br<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] adduct **1**, with no sign of a bromide complex analogous to **4**. In like vein, efforts to prepare Cs<sub>2</sub>[MoO<sub>2</sub>Br<sub>4</sub>], by adding CsBr to Mo<sup>VI</sup>-HBr solutions, were also unsuccessful.

## Experimental

### Preparations

The compounds 18-crown-6, 15-crown-5 and 12-crown-4 were obtained from Acros Organics. Molybdenum(vi) solutions were prepared using ammonium or potassium molybdate and analytical grade acids, HBr or HCl.

The compound K<sub>2</sub>MoO<sub>4</sub>·5H<sub>2</sub>O was added to 6 mol dm<sup>-3</sup> HBr or 8 mol dm<sup>-3</sup> HCl to prepare solutions which were 0.5 mol dm<sup>-3</sup> in Mo<sup>VI</sup>. The solution (10 ml) was shaken with an equal volume of diethyl ether and the upper, ether-extract phase was withdrawn. Crown ether (0.15 g in 1 ml Et<sub>2</sub>O) was added to 2 ml of the ether extract in which molybdenum(vi) complexes were present. Each extract gave crystals with 18-crown-6, 15-crown-5 and 12-crown-4 which were pale yellow

for the bromide samples and colourless for the chlorides. The samples were collected, rinsed with ether and dried in a stream of nitrogen. The IR spectra suggested that the products were likely to be crown ether adducts of [MoO<sub>2</sub>X<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (X = Cl or Br). Further samples were prepared using 18-crown-6 and characterised, as follows.

**[MoO<sub>2</sub>Br<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O·18-crown-6 1.** The addition of 18-crown-6 to the diethyl ether extract from a solution of potassium molybdate in 6 mol dm<sup>-3</sup> HBr gave pale yellow crystals which were rinsed with ether and dried under nitrogen, mp 115–118 °C (Found: C, 23.1; H, 4.90. C<sub>12</sub>H<sub>32</sub>Br<sub>2</sub>MoO<sub>12</sub> requires C, 23.1; H, 5.16%).

**[MoO<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O·18-crown-6 2.** The addition of 18-crown-6 to the ether extract from a solution of potassium molybdate in 8 mol dm<sup>-3</sup> HCl gave colourless crystals. A further sample, with identical IR spectrum, was obtained when 18-crown-6 was added directly to an aqueous solution of ammonium molybdate in 8 mol dm<sup>-3</sup> HCl. The crystals were rinsed with acetone and dried under nitrogen, mp 112–114 °C (Found: C, 30.5; H, 6.52. C<sub>12</sub>H<sub>32</sub>Cl<sub>2</sub>MoO<sub>12</sub> requires C, 26.2; H, 5.86%). The discrepancy in the analytical results may be due to adherence of some crown ether to the crystals which were identified as **2** by their IR and Raman spectra, and by X-ray crystallography.

**[MoO<sub>2</sub>Cl<sub>2</sub>(MeOH)<sub>2</sub>]·18-crown-6 3.** A sample of complex **2** was recrystallised from hot methanol which yielded colourless crystals, mp 105 °C (decomp.) (Found: C, 29.8; H, 6.18. C<sub>14</sub>H<sub>32</sub>Cl<sub>2</sub>MoO<sub>10</sub> requires C, 31.9; H, 6.11%). The constitution of this product was established by X-ray crystallography.

**K[MoO<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)]·18-crown-6 4.** Extraction of a solution of potassium molybdate in 8 mol dm<sup>-3</sup> HCl with diethyl ether containing 18-crown-6 led to the formation of colourless crystals with a different IR spectrum from that of complex **2** (whose preparation had involved separating the ether extract from the aqueous phase before introducing the crown ether). The same product **4** was obtained by adding 18-crown-6 directly to the aqueous solution of potassium molybdate in 8 mol dm<sup>-3</sup> HCl, mp 228–230 °C (Found: C, 26.1; H, 5.35. C<sub>12</sub>H<sub>26</sub>Cl<sub>3</sub>KMoO<sub>9</sub> requires C, 25.9; H, 4.71%).

### Spectroscopy

Infrared spectra were recorded as pressed discs in Polythene or KBr, using Bio-Rad FTS6000 or Perkin-Elmer Paragon 1000PC spectrometers. Raman spectra were obtained with a Bio-Rad FT Raman spectrometer, which gave data above 70

cm<sup>-1</sup>, supplemented by scanning the range 10–1200 cm<sup>-1</sup> using a Jobin–Yvert U1000 system with a Spectra Physics 2016 argon-ion laser tuned to the green line of wavelength 514 nm.

### Crystal structure determinations

Crystallographic data for complexes **1** to **3** are summarised in Table 3. Suitable crystals were mounted in Paratone oil on glass fibres and frozen to -70 °C for data collection on a Siemens SMART diffractometer. Data collection covered a nominal hemisphere of reciprocal space. Lorentz-polarisation corrections were applied and absorption corrections using the program SADABS.<sup>15</sup> The structures were solved by Patterson and Fourier techniques and refined by full matrix least squares. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms of 18-crown-6 were placed in calculated positions and refined as riding atoms with isotropic thermal parameters fixed at 20% greater than those of the host atom. Structures were determined using SHELXS<sup>16</sup> for the solution and SHELXL<sup>17</sup> for refinement.

CCDC reference number 186/1104.

See <http://www.rsc.org/suppdata/dt/1998/3195/> for crystallographic files in .cif format.

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