

## Layered compounds based on molybdenum disulfide and ruthenium arene complexes

Alexandre S. Golub,<sup>\*a</sup> Inna B. Shumilova,<sup>a</sup> Yan V. Zubavichus,<sup>a</sup> Manfred Jahncke,<sup>b</sup> Georg Süss-Fink,<sup>b</sup> Michel Danot<sup>c</sup> and Yurii N. Novikov<sup>a</sup>

<sup>a</sup>Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov St. 28, 117813 Moscow, Russia

<sup>b</sup>Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

<sup>c</sup>Institut des Matériaux de Nantes, UMR 110, CNRS-Université de Nantes, 2 rue de la Houssinière, 44072 Nantes Cédex 03, France

Intercalation compounds of MoS<sub>2</sub> with monomeric or OH-bridged dimeric ruthenium arene cationic complexes have been obtained by interaction of MoS<sub>2</sub> single-layer dispersions with aqueous solutions of [(arene)Ru(H<sub>2</sub>O)<sub>3</sub>]SO<sub>4</sub> [arene = C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>2</sub>Me<sub>4</sub>-1,2,4,5, C<sub>6</sub>H<sub>4</sub>Me-1-Pr<sup>i</sup>-4]. The structural arrangement of these intercalation compounds is discussed on the basis of XRD and EXAFS data. The arene ligands are orientated roughly perpendicular to the MoS<sub>2</sub> slabs. Their nature determines the interlayer spacing as well as the intercalated cation content. Heating removes the organic ligands, while ruthenium-containing species remain in the van der Waals space of MoS<sub>2</sub>.

Intercalation compounds of molybdenum disulfide with metal arene complexes might be of great interest as model systems for studying the hydrogenation of aromatics in the presence of MoS<sub>2</sub>-based petrochemical catalysts.<sup>1</sup> Such intercalation compounds can also be used to design new hydrogenation catalysts, as in the case of layered aluminosilicates intercalated with ruthenium arene complexes.<sup>2</sup> The preparation of such layered systems can only be achieved using mild synthesis routes, for instance *via* single-layer aqueous dispersions of MoS<sub>2</sub>.<sup>3,4</sup> It was established recently that a freshly prepared MoS<sub>2</sub> dispersion contains single [S—Mo—S] layers retaining partial negative charge, lithium cations and hydroxide anions, according to the following formulation: [Li<sup>+</sup> + (MoS<sub>2</sub>)<sup>x-</sup> + (1-x)OH<sup>-</sup>]<sub>aq</sub>.<sup>5-7</sup> The ionic nature allows ion-exchange interactions with the various cations, which result in the precipitation of intercalation compounds. Depending on the nature of the cation, the MoS<sub>2</sub> interlayer space can thus accommodate cation monolayers (R<sub>4</sub>N<sup>+</sup>, for instance<sup>5</sup>) or, in the case of transition-metal cations, extended two-dimensional [M(OH)<sub>2-x</sub>(H<sub>2</sub>O)<sub>x</sub>]<sup>x+</sup> clusters.<sup>6,8</sup>

It is expected that organometallic [(arene)Ru(H<sub>2</sub>O)<sub>3</sub>]<sup>2+</sup> cations<sup>9</sup> could also interact with MoS<sub>2</sub> single-layer dispersions. They fill the interlayer space as monomeric cations or as OH-bridged fragments, depending on the medium characteristics. Mononuclear [(arene)Ru(H<sub>2</sub>O)<sub>3</sub>]<sup>2+</sup> cations are rather stable in acidic medium.<sup>9,10</sup> At basic pH values, they give condensation products. In the case of substituted benzene ligands, these products are dimeric [(arene)Ru(μ-OH)<sub>3</sub>Ru(arene)]<sup>+</sup> cations.<sup>11,12</sup> When the arene ligand is benzene, three different deprotonation products have been obtained in basic media: the dimeric [(C<sub>6</sub>H<sub>6</sub>)(OH)Ru(μ-OH)<sub>2</sub>Ru(H<sub>2</sub>O)(C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup>,<sup>11</sup> the tetranuclear cubane-like [(C<sub>6</sub>H<sub>6</sub>)Ru(μ<sub>3</sub>-OH)]<sub>4</sub><sup>4+</sup>,<sup>13</sup> and {(μ<sub>4</sub>-

O)[(C<sub>6</sub>H<sub>6</sub>)Ru(μ-OH)]<sub>4</sub>}<sup>2+</sup> with a tetrahedrally coordinated oxide ion.<sup>13</sup> Variation of the nuclearity of the complex and the nature of the arene ligands may offer the possibility of modifying the interlayer spacing and structural arrangement of the resulting intercalate.

We report here the synthesis and structure of new layered materials obtained by interaction of MoS<sub>2</sub> single-layer dispersions with [(arene)Ru(H<sub>2</sub>O)<sub>3</sub>]<sup>2+</sup> cationic complexes.

### Experimental

Single-layer dispersions of MoS<sub>2</sub> (0.5 g dm<sup>-3</sup>, initial pH 11) were obtained by exfoliation of LiMoS<sub>2</sub> in water with the assistance of ultrasound, as described in ref. 5.

Solutions of [(arene)Ru(H<sub>2</sub>O)<sub>3</sub>]SO<sub>4</sub> (0.01 mol dm<sup>-3</sup>; Table 1) were prepared by *in situ* hydrolysis of the corresponding [(arene)RuCl<sub>2</sub>]<sub>2</sub> in an aqueous medium (acidified with H<sub>2</sub>SO<sub>4</sub> to pH 3 for synthesis of compound **1**) in the presence of a stoichiometric amount of Ag<sub>2</sub>SO<sub>4</sub>.<sup>9</sup> After stirring for 3 h, solid AgCl was removed by filtration.

The intercalation compounds (Table 1) were prepared at room temperature by addition of these solutions to single-layer dispersions (0.5 mol complex per mol MoS<sub>2</sub>) followed by stirring for 0.5 h (in the case of compound **1**, the dispersion was acidified with H<sub>2</sub>SO<sub>4</sub> to pH 4 before addition of the complex). The pH value of the reaction medium was measured with a pH meter after formation of the precipitates. The resulting precipitates were filtered off, washed with water and dried in vacuum.

The compositions of the intercalation compounds (Table 1) were determined from C, H contents (combustion) and Ru/Mo

**Table 1** Synthesis pH, composition, interlayer spacing and interlayer spacing expansion with respect to the host structure for MoS<sub>2</sub> intercalation compounds with arene-ruthenium cationic complexes

compound	arene	pH	cation nature <sup>a</sup>	composition found (calc.)			G/H <sup>b</sup>	c <sup>c</sup> /Å	Δc <sup>d</sup> /Å
				C (%)	H (%)	Ru/Mo			
<b>1</b>	C <sub>6</sub> H <sub>6</sub>	3.2	I	7.04 (6.97)	0.92 (1.16)	0.19 (0.20)	0.20	12.3	6.1
<b>2</b>	C <sub>6</sub> H <sub>6</sub>	8.5	II	8.27 (8.26)	1.01 (0.86)	0.21 (0.24)	0.12	12.2	6.0
<b>3</b>	C <sub>6</sub> H <sub>2</sub> Me <sub>4</sub> -1,2,4,5	8.5	II	12.50 (12.14)	1.71 (1.57)	0.22 (0.22)	0.11	16.8	10.6
<b>4</b>	C <sub>6</sub> H <sub>4</sub> Me-1-Pr <sup>i</sup> -4	8.5	II	7.58 (7.52)	0.99 (0.97)	0.12 (0.12)	0.06	12.0	5.8

<sup>a</sup>Calculations have been made considering the cations to be mononuclear [(arene)Ru(H<sub>2</sub>O)<sub>3</sub>]<sup>2+</sup> (I) for compound **1** and dinuclear [(arene)Ru(μ-OH)<sub>3</sub>Ru(arene)]<sup>+</sup>, (II) for compounds **2-4**. <sup>b</sup>Guest/host molar ratio. <sup>c</sup>Interlayer spacing. <sup>d</sup>Interlayer spacing expansion.

atomic ratios (X-ray fluorescence analysis). The calculated contents of the elements given in Table 1 correspond to the guest/host ratio which leads to the best overall agreement with analytical results. X-Ray powder diffraction patterns were recorded with D5000 and Dron-3 (Ni-filter) diffractometers using Cu-K $\alpha$  radiation. Data processing, including background subtraction, was performed using DIFFRAC-AT V3-2 Siemens 1993 software. Thermogravimetry was performed under argon with a TGA 92 Setaram apparatus using a heating rate of 5 °C min<sup>-1</sup>.

The EXAFS spectrum (Ru K-edge) of MoS<sub>2</sub> intercalated by the ruthenium benzene complex (compound **2**) was recorded at the DCM beamline of the CAMD electron storage ring (Louisiana State University, Baton Rouge) operating at 1.5 GeV with the current in the range 80–100 mA. The sample was powdered finely and spread onto a Mylar film. The data were collected in transmission mode from 22 040 to 23 040 eV (Ru K-edge energy, *ca.* 22 130 eV) with an Si[220] double-crystal monochromator, 2 eV energy step and a counting time of 2 s per point. Standard Ar-filled ion chambers were used to measure the incident ( $I_0$ ) and transmitted ( $I$ ) X-ray intensities. The monochromator energy was calibrated with Mo foil (15  $\mu$ m). The background contribution was determined before and after the edge using linear and polynomial fits, respectively, and subtracted. The data were then converted from energy to  $k$  ( $\text{\AA}^{-1}$ ) space, Fourier-transformed and back Fourier-transformed (Hanning window) over a limited  $R$  interval (1.1–3.1  $\text{\AA}$ ) which included the maxima of interest. Fourier transform was restricted to the 2–11  $\text{\AA}^{-1}$   $k$  range because, owing to the presence of a significant amount of molybdenum in the compound, the signal to noise ratio was too low for higher  $k$  values.

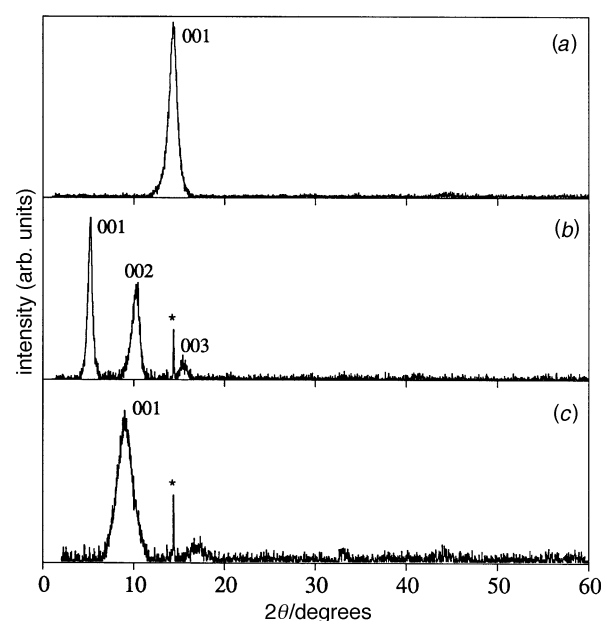
Curve fitting in the back Fourier-transformed space was carried out for structural parameters to be refined. Only single scattering on neighbouring atoms was taken into account. The number of neighbours ( $N$ ) and the many-body amplitude factor ( $S_0^2$ ) were fixed, and  $R$ ,  $\sigma^2$  and  $\Delta E_0$  were refined for each type of back-scatterer. Background subtraction, Fourier transformations and fitting were performed with Autobk and Feffit from the UWXAFS package.<sup>14</sup> Theoretical phases and amplitudes, and the electron mean free path,  $\lambda(k)$ , were calculated with FEFF.<sup>15</sup>

## Results and Discussion

Interaction of MoS<sub>2</sub> single-layer dispersions with solutions of cationic ruthenium arene complexes leads to the rapid formation of layered intercalation compounds as flake-like precipitates. XRD data allow only the  $c$  periodicity to be determined since only a limited number of low-angle 00 $l$  lines can be observed in the patterns. As shown in Table 1, this intercalation reaction results in a significant increase ( $\Delta c$ ) of the interlayer distances of MoS<sub>2</sub>. Only small amounts of non-intercalated MoS<sub>2</sub> can be detected in the precipitates by XRD [Fig. 1(a)(b)].

### Nature of the intercalated complexes

As shown in Table 1, the filling of the interlayer space of molybdenum disulfide by the ruthenium benzene complex proceeds in both acidic and basic media. The two resulting intercalates (compounds **1** and **2**) exhibit nearly identical interlayer distance expansions ( $\Delta c$ ). However, the linewidth of the diffraction peaks is 4–5 times larger for compound **1** than for **2**. This fact can probably be related to a difference in the nature of the intercalated species. The synthesis of **1** used an acidic medium, where the monomer  $[(C_6H_6)Ru(H_2O)_3]^{2+}$  is stable. The geometry of this cation allows a set of orientations in the interlayer space, which leads to a set of intercalated layer thicknesses and, consequently, to a set of MoS<sub>2</sub> slab-to-slab distances. For compound **2** in which a basic medium was used (where condensation can occur), the appearance of OH-



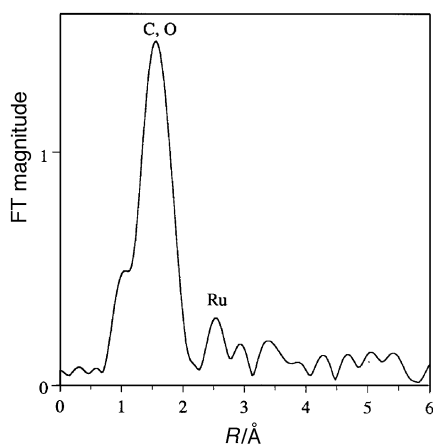
**Fig. 1** Background-subtracted X-ray diffractograms of MoS<sub>2</sub> restacked without intercalation (a), intercalation compound **3** (b), and the product of its decomposition under TG conditions (argon atmosphere, heating rate 5 °C min<sup>-1</sup>) at 700 °C (c). Small amounts of non-intercalated MoS<sub>2</sub> are indicated in (b) and (c) by asterisks.

bridges between two ruthenium arene fragments may result in the formation of the dimeric species with a more significant shape anisotropy, which can limit the number of possible orientations. Under these conditions, the distribution of the MoS<sub>2</sub> interlayer distances should be broader, and the linewidth effectively larger, for compound **1** than for compound **2**. It can thus be thought that the reaction carried out in acidic medium (compound **1**) results in the intercalation of mononuclear cations, while binuclear species are intercalated in basic media (compounds **2–4**). The next condensation step, tetrameric cations, need not be considered since, whatever their orientation, such cations should give interlayer distances greater than those we measured.

The known chemistry of ruthenium–arene aqua complexes indicates that in the case of substituted arene ligands the dimeric ruthenium–arene complexes are the only deprotonation products of  $[(\text{arene})Ru(H_2O)_3]^{2+}$ ,<sup>11,12</sup> but the pH dependence of this condensation process is not known. However, a recent NMR study of the isoelectronic complex  $[(C_5Me_5)Rh(H_2O)_3]^{2+}$  showed that dimeric species are formed above pH 7.<sup>16</sup> In the case of ruthenium–benzene cations, the existence of dimeric species in solution has been proven.<sup>11</sup> However, the hydrolysis of  $[(C_6H_6)Ru(H_2O)_3]^{2+}$  was found to be more complicated, and to result, with an excess of alkali, in the formation of tetranuclear cations as crystalline products,<sup>13</sup> probably due to the rather basic conditions.<sup>17</sup> On the other hand, the ruthenium–benzene dimeric complex  $[(C_6H_6)Ru(\mu-OH)_3Ru(C_6H_6)]^+$  was isolated as a stable product upon hydrolysis of  $[(C_6H_6)Ru(\mu-OC_6H_5)_3Ru(C_6H_6)]^+$  without the addition of alkali.<sup>17</sup> We can therefore suggest that weakly basic conditions used for the synthesis of **2–4** may also be favourable for the formation of dimeric complexes which can further fill the interlayer space of MoS<sub>2</sub>. However, we cannot exclude the possibility that, along with dimers, some monomers may also be trapped between the MoS<sub>2</sub> slabs.

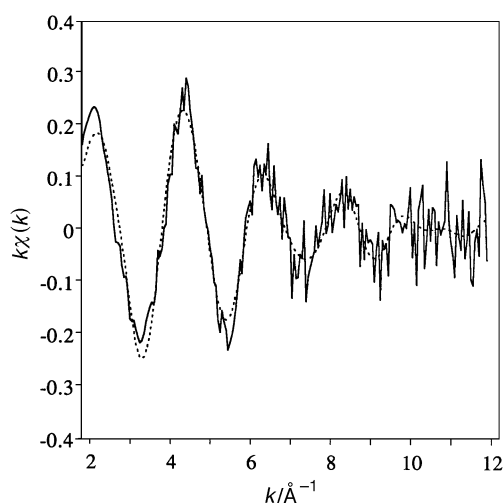
### EXAFS study

An EXAFS study (Ru K-edge) of the intercalation compound **2** with benzene ligands was undertaken in order to obtain further proof of the dimeric nature of the intercalated complexes. The pseudo-radial distribution function (RDF) around the absorb-



**Fig. 2** Radial distribution function around ruthenium in the MoS<sub>2</sub> intercalation compound **2**

ing atom (Fig. 2), obtained by Fourier transformation of the spectrum, exhibits a first maximum related to unresolved Ru—O and Ru—C contributions. The second maximum corresponds to Ru—Ru contacts. Its intensity is weaker, consistent with the greater distance and with the small expected number of ruthenium neighbours. The refined interatomic distances (Fig. 3, Table 2) are in good agreement with those derived from X-ray diffraction data for the dimeric complex [(C<sub>6</sub>H<sub>6</sub>)Ru(μ-OH)<sub>3</sub>Ru(C<sub>6</sub>H<sub>6</sub>)]Cl·2H<sub>2</sub>O obtained recently by hydrolysis of the corresponding triphenoxo-bridged binuclear complex.<sup>17</sup> Note that, despite the weakness of the corresponding peak in the RDF, the Ru—Ru contribution refinement yields satisfactory results and thus provides proof that most of intercalated species are dimeric. However, it does not allow the presence of some monomeric complexes in the compound to be completely excluded. A third, very weak, maximum can be detected in the RDF at  $R \approx 3.5$  Å (value without phase-shift



**Fig. 3** Normalized EXAFS spectrum at the Ru K-edge (solid line) and its fit (dotted line) for the MoS<sub>2</sub> intercalation compound **2**

**Table 2** Structural parameters obtained for the compound **2** from EXAFS data {single-crystal X-ray data for [(C<sub>6</sub>H<sub>6</sub>)Ru(μ-OH)<sub>3</sub>Ru(C<sub>6</sub>H<sub>6</sub>)]Cl·2H<sub>2</sub>O (A)<sup>17</sup> are given in parentheses for comparison}

	<i>N</i>	<i>R</i> /Å	$\sigma^2/\text{Å}^2$	$\Delta E/\text{eV}$
Ru—C	6 (6)	2.18 (2.14–2.17)	0.0048	–6.23
Ru—O	3 (3)	2.05 (2.07–2.10)	0.0029	–7.52
Ru···Ru	1 (1)	2.98 (2.98)	0.0037	–6.59

$S_0^2 = 0.75$ ;  $R_f = 0.028$

correction). If significant, it can probably be attributed to long-range van der Waals Ru···O contacts with hydrate water molecules co-intercalated with the complex. This type of contact (3.8–4.2 Å) was also observed in the crystal structure of the salt mentioned above.

### Packing of dimeric complexes in the interlayer space

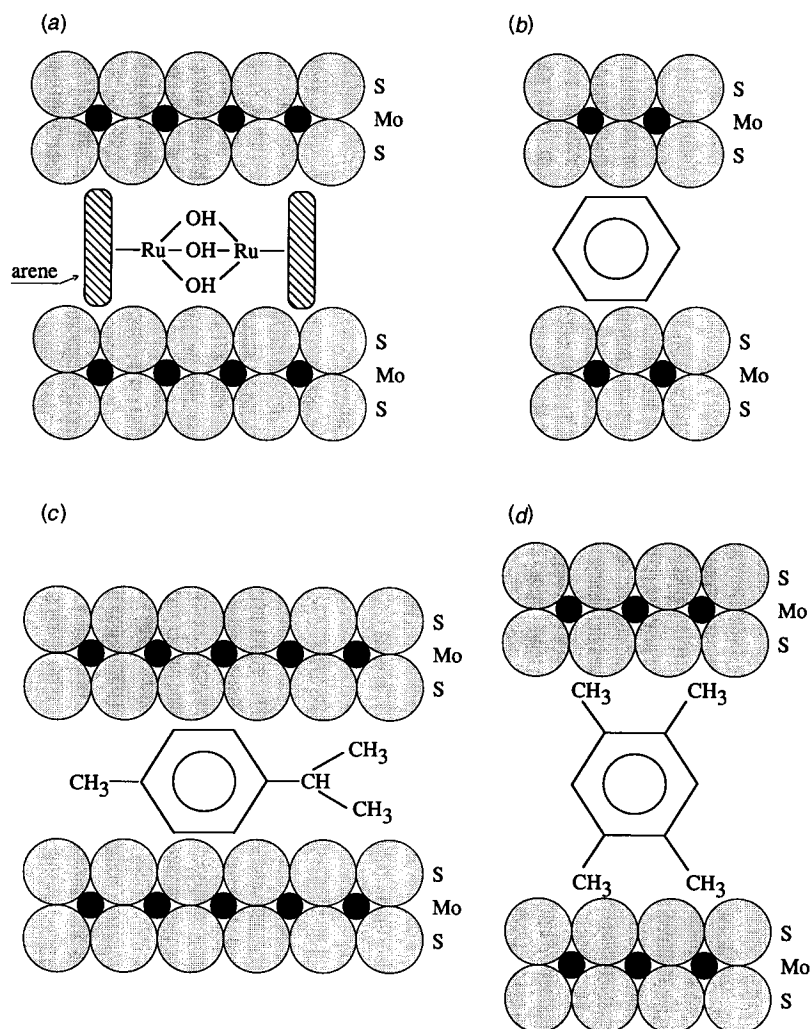
Table 1 shows that intercalation of ruthenium–benzene and ruthenium–*para*-methylisopropylbenzene dinuclear cations (compounds **2–4**) induces very similar expansions ( $\Delta c$ ) of the interlayer distance. In contrast, the presence of four methyl substituents results in a much larger  $\Delta c$  value (compound **3**).

Considering these observations, the  $\Delta c$  values and the van der Waals dimensions of the intercalated cations, the only possibility is that the aromatic rings are approximately perpendicular to the MoS<sub>2</sub> slabs, as shown in Fig. 4. In this case, two substituents in the *para*-positions can be directed towards neighbouring cations and therefore do not increase the layer separation. If exactly perpendicular to the slabs, benzene ligands of dinuclear complexes in the orientation shown in Fig. 4 should induce an expansion of *ca.* 6.8 Å because of their van der Waals dimension. The difference between this value and measured  $\Delta c$  values (*ca.* 6 Å, Table 1) may indicate that the intercalated aromatic rings are tilted slightly with respect to the *c* axis of the MoS<sub>2</sub> slabs. Such a situation might result from structural strain due to the location of the intercalated complexes between two MoS<sub>2</sub> slabs. However, the van der Waals distance between the MoS<sub>2</sub> slabs and the H atoms of the aromatic rings is not known accurately. Besides, the sulfur environment of molybdenum has been reported to be octahedral in single-layer dispersions, and to return to the usual trigonal-prismatic geometry in restacked MoS<sub>2</sub>.<sup>18</sup> For this reason we determined the  $\Delta c$  values with respect to the slab thickness of pristine MoS<sub>2</sub> (trigonal-prismatic geometry, as shown in Fig. 4). Nevertheless, it cannot be excluded that the octahedral environment of Mo or local distortions of the MoS<sub>2</sub> layer structure could be retained in the present intercalates. It would slightly influence the MoS<sub>2</sub> slab thickness and, consequently, the  $\Delta c$  value. For these reasons, the existence of a tilt angle cannot be claimed.

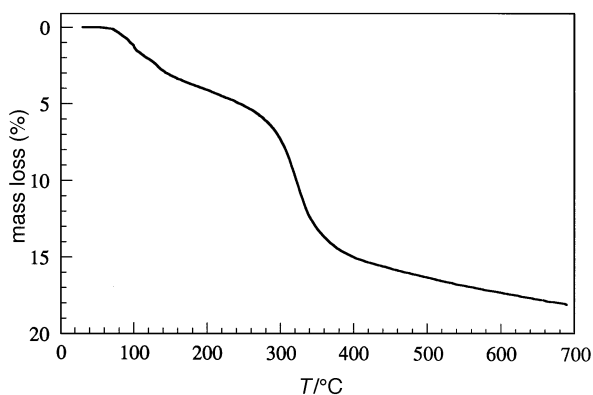
The maximum amount of intercalated cations can be evaluated from the van der Waals sizes of the complexes and the compositions of the intercalates. For instance, assuming the orientation shown in Fig. 4, the rectangular areas which must be attributed to each intercalated dimeric complex can be estimated as *ca.* 70 Å<sup>2</sup>, *ca.* 80 Å<sup>2</sup> and *ca.* 120 Å<sup>2</sup> respectively for the dimers with benzene (compound **2**), 1,2,4,5-tetramethylbenzene (compound **4**), and 1,4-methylisopropylbenzene (compound **3**) ligands. From these values, and attributing 8.6 Å<sup>2</sup> of the MoS<sub>2</sub> layer surface to each Mo atom, the maximum allowed contents for the complexes discussed are calculated to be *ca.* 0.12, *ca.* 0.11 and *ca.* 0.07 mol per mol MoS<sub>2</sub>, respectively. These values are very close to the contents reached upon intercalation of the complexes. It thus appears that the filling of the MoS<sub>2</sub> interlayer space with ruthenium arene complexes results in rather dense packing of intercalated species, as already reported in the case of phenanthroline intercalation.<sup>19</sup>

### Thermal behaviour

The thermal behaviour of the intercalated materials has been studied for the 1,2,4,5-tetramethylbenzene derivatives. The TG curve shows a two-step decomposition of the intercalation compound (Fig. 5). The mass loss (3–4%) which occurs at the first step (70–150 °C) can be attributed to the removal of water molecules formed upon decomposition of the complexes, and also of co-intercalated and absorbed water. Further heating (150 to *ca.* 500 °C) causes a further mass loss (*ca.* 13%) which



**Fig. 4** Proposed orientation of intercalated dimeric ruthenium arene complexes (a) and their ligands: benzene (b), 1,4-methylisopropylbenzene (c) and 1,2,4,5-tetramethylbenzene (d)



**Fig. 5** TG curve of the MoS<sub>2</sub> intercalation compound **3** (argon atmosphere, heating rate 5 °C min<sup>-1</sup>)

roughly corresponds to the total removal of organic ligands (calculated content 13.6%). However, the curve does not show a precise end to the removal of organic ligands: no plateau can be detected and at higher temperature the mass continues to decrease slowly. A powder diffraction study shows that thermal decomposition under TG conditions results in the formation of disordered layered compounds; their interlayer distance is *ca.* 11 Å after heating at 500 °C, and it decreases after higher temperature treatment (*ca.* 10 Å for 700 °C) [Fig. 1(c)]. In contrast to the (phenanthroline)<sub>x</sub>MoS<sub>2</sub> intercalates,<sup>19</sup> complete deintercalation and the formation of an

MoS<sub>2</sub>-like structure are not observed, and it can therefore be assumed that decomposition of [(arene)Ru(μ-OH)<sub>3</sub>Ru(arene)]<sup>+</sup> cations is accompanied by the formation of RuO<sub>x</sub> clusters in the interlayer space of MoS<sub>2</sub>. The progressive decomposition of these clusters at high temperature (for instance to Ru and O<sub>2</sub>, as is known to occur for crystalline RuO<sub>2</sub><sup>20</sup>) may explain the progressive evolution of the interlayer spacing and of the mass loss.

## Conclusions

The single-layer dispersion technique is already known to allow the room-temperature intercalation of organic (alkylammonium, phenanthroline) or transition- and rare-earth-metal cations between MoS<sub>2</sub> layers. The present work shows that, under the same mild conditions, a MoS<sub>2</sub> single-layer dispersion can also be used as a precursor for the intercalation of ruthenium arene cationic complexes to be achieved. This synthetic approach is expected to be suitable for other water-soluble cationic complexes.

Depending upon the reaction conditions, the ruthenium-arene complexes can be introduced into the host structure as either monomeric or dimeric species. This allows one to monitor the structural arrangement of the intercalated layer. Moreover, the arene ligand can be chosen on the basis of its geometry in order to control the interlayer spacing and the content of the intercalant, which may be of interest for possible catalytic applications.

The authors are grateful to Paul J. Schilling, Roland C. Tittsworth and the director of CAMD Volker Saile (Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rouge, USA) for EXAFS facilities, Stéphane Grolleau (Institut des Matériaux de Nantes, France) for help in the TG experiments. At the Institute of Organoelement Compounds this work was supported by the Russian Foundation for Basic Research.

#### References

- 1 E. Furimsky, *Catal. Rev.*, 1980, **22**, 371.
- 2 A. Meister, G. Meister and G. Süß-Fink, *J. Mol. Catal.*, 1994, **92**, L123.
- 3 P. Joensen, R. F. Frindt and S. Morrison, *Mater. Res. Bull.*, 1986, **21**, 457.
- 4 M. G. Kanatzidis, R. Bissessur, D. C. DeGroot, J. L. Schindler and C. R. Kannewurf, *Chem. Mater.*, 1993, **5**, 595.
- 5 A. S. Golub, G. A. Protzenko, L. V. Gumileva, A. G. Buyanovskaya and Yu. N. Novikov, *Russ. Chem. Bull.*, 1993, **42**, 632.
- 6 M. Danot, J. L. Mansot, A. S. Golub, G. A. Protzenko, Yu. N. Novikov, P. B. Fabritchnyi and J. Rouxel, *Mater. Res. Bull.*, 1994, **29**, 833.
- 7 A. S. Golub, G. A. Protzenko, I. M. Yanovskaya, O. L. Lependina and Yu. N. Novikov, *Mendeleev Commun.*, 1993, 199.
- 8 E. F. Valeev, Ya. V. Zubavichus, Yu. L. Slovokhotov, A. S. Golub, G. A. Protzenko and Yu. N. Novikov, *Physica B*, 1995, **208–209**, 569.
- 9 M. Stebler-Röthlisberger, W. Hummel, P. A. Pittet, H. B. Bürgi, A. Ludi and A. E. Merbach, *Inorg. Chem.*, 1988, **27**, 1358.
- 10 M. Stebler-Röthlisberger and A. Ludi, *Polyhedron*, 1986, **5**, 1217.
- 11 T. Arthur, D. R. Robertson and D. A. Stephenson, *J. Organomet. Chem.*, 1981, **208**, 389.
- 12 R. O. Gould, C. L. Jones, T. A. Stephenson and D. A. Tocher, *J. Organomet. Chem.*, 1984, **264**, 365.
- 13 R. O. Gould, C. L. Jones, D. R. Robertson, D. A. Tocher and T. A. Stephenson, *J. Organomet. Chem.*, 1982, **226**, 199.
- 14 E. A. Stern, M. Newville, B. Ravel, Y. Yacoby and D. Haskel, *Physica B*, 1995, **208–209**, 117.
- 15 J. J. Rehr, J. Mustre de Leon, C. I. Zabinsky and R. C. Alberts, *J. Am. Chem. Soc.*, 1991, **113**, 5135.
- 16 M. S. Eisen, A. Haskel, H. Chen, M. M. Olmsted, D. P. Smith, M. F. Maestre and R. Fish, *Organometallics*, 1995, **14**, 2806.
- 17 T. D. Kim, T. J. McNeese and A. L. Rheingold, *Inorg. Chem.*, 1988, **27**, 2554.
- 18 D. Yang, S. Jiménez Sandoval, W. M. R. Divigalpitiya, J. C. Irvin and R. F. Frindt, *Phys. Rev. B*, 1991, **14**, 12053.
- 19 A. S. Golub, I. B. Shumilova, Yu. N. Novikov, J. L. Mansot and M. Danot, *Solid State Ionics*, submitted.
- 20 R. Kötzt, H. J. Lewerenz and S. Stucki, *J. Electrochem. Soc.*, 1983, **130**, 825.