ONE-DIMENSIONAL POLYMERIZATION OF \( M_2(\text{OAc})_4 \) (\( M = \text{Cu, Rh} \)) UNITS USING 2-(AMINOMETHYL)PYRIDINE: PREPARATION AND CHARACTERIZATION OF \( [\text{Rh}_2(\text{OAc})_4(\text{amp})]_n \) AND \( [\text{Cu}_2(\text{OAc})_4(\text{amp})]_n \)

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Abstract—Synthetic procedures are described for the preparation of polymeric complexes of the general formula \( [M_2(\text{OAc})_4(\text{amp})]_n \) (\( M = \text{Rh, Cu} \); amp = 2-(aminomethyl)pyridine). Reaction of \( \text{Rh}_3(\text{OAc})_4(\text{MeOH})_2 \) (1) with one equivalent of amp in MeCN produces \( [\text{Rh}_2(\text{OAc})_4(\text{amp})]_n \cdot n/2\text{MeCN} \) in good yield (73%). The dinuclear Rh\( ^{II} \) carboxylate core remains intact and has a metal–metal distance of 2.410(1) Å. The coordination sphere of Rh(1) is completed by a pyridine nitrogen atom of one amp ligand while the coordination sphere of Rh(2) is completed by the amine nitrogen atom of a second amp ligand. These amp groups then bridge to adjacent Rh\( ^{II} \) units to give a one-dimensional polymer \( [\text{Rh}_2(\text{OAc})_4(\text{amp})]_n \). Hydrogen bonding is evident between the amp amine groups and the carboxylate oxygen atoms \( [\text{N}(25) \cdot \cdot \cdot \text{O}(3) = 2.964 \text{ Å}] \). The peak with the highest \( m/z \) value in the FAB mass spectrum of 2 from a chloroform/p-nitrobenzylalcohol matrix corresponds to the fragment \( [\text{Rh}_2(\text{OAc})_3(\text{amp})]_2 \). Reaction of \( \text{Cu}_2(\text{OAc})_4(\text{H}_2\text{O})_2 \) (3) with one equivalent of amp in MeCN, followed by recrystallization from EtOH/\( \text{Et}_2\text{O} \), produces crystals of \( [\text{Cu}_2(\text{OAc})_4(\text{amp})]_n \) (4). The structure of 4 consists of well-separated, one-dimensional polymeric chains composed of alternating \( [\text{Cu}_2(\text{OAc})_4]_n \) and \( [\text{Cu}_2(\text{OAc})_4(\text{amp})]_2^{2+} \) units which are linked by syn, anti bridging acetates. The \( [\text{Cu}_2(\text{OAc})_4]_n \) units closely resemble the starting material, with the two copper centres bridged by four \( \eta^1: \eta^1: \mu \text{AcO} \) ligands over a metal–metal separation of 3.282(1) Å. The axial coordination sites are occupied by an oxygen atom of the syn, anti bridging acetates. The \( [\text{Cu}_2(\text{OAc})_4(\text{amp})]_2^{2+} \) units contain two monoatomically bridging acetate groups, with the coordination sphere of the metals completed by a chelating amp ligand and the second oxygen atom of the syn, anti bridging acetates. Hydrogen bonding between the amine group of the amp ligands and the mono-atomic bridging acetate groups is evident \( [\text{N}(22) \cdot \cdot \cdot \text{O}(25) = 2.877 \text{ Å}] \).

The coordination chemistry of the dinuclear tetra-carboxylates of the transition metals are a focus of extensive interest owing to their wide application in fields ranging from materials science and catalysis to biological activity. Our own interest and recent efforts have been concentrated in dinuclear Rh and Mo carboxylates. In recent reports, we have described initial results concerning the reaction of \( \text{Rh}_3(\text{O}_2\text{CR})_4\text{L}_3 \) and \( \text{Mo}_2(\text{O}_2\text{CR})_4 \) species with 2,2′-bipyridine(bpy). These studies were initiated for biological modelling reasons, although many of the results have been of interest in a more general context. For example, treatment of \( \text{Rh}_3(\text{OAc})_4(\text{MeOII})_2 \) with one equivalent of bpy yields, as the initial product, the most unusual adduct \( \text{Rh}_3(\text{OAc})_4(\text{bpy})_3 \), whereas treatment of \( \text{Mo}_2 \)
(O$_2$CCF$_3$)$_2$ with two equivalents of bpy leads to the isomeric compounds [M$_2$(O$_2$CCF$_3$)$_2$(bpy)$_2$] (O$_2$CCF$_3$)$_2$ or M$_2$(O$_2$CCF$_3$)$_2$(bpy)$_2$, depending on the reaction conditions.

Observations such as the above have prompted us to broaden the scope of our work. For a number of reasons, including biological, we have employed 2-(aminomethyl)pyridine (amp) in reactions with Rh$_2$(OAc)$_4$(MeOH)$_2$ (1). The bidentate nature of amp, its dual aromatic plus aliphatic amine functionalities and its relationship to the DNA base adenine have made it of some interest to us to identify the product of this reaction. We have found that the latter is a one-dimensional polymer, and this represents the subject of this report. Further, to allow potentially useful comparisons with and contrasts to the Rh$_2$ system, we have carried out parallel reactions with Cu$_2$(OAc)$_4$(H$_2$O)$_2$, which contains no metal–metal bond. Finally, we show how FAB mass spectrometry has proven a useful means to aid in characterization of the Rh$_2$/amp polymer.

**EXPERIMENTAL**

**Syntheses**

All manipulations were performed under aerobic conditions unless otherwise noted. RhCl$_3$·3H$_2$O (Sigma), Cu$_2$(OAc)$_4$(H$_2$O)$_2$ (3) (Baker) and solvents were used as received. 2-(Aminomethyl)pyridine (Aldrich) was purified by fractional distillation under a nitrogen atmosphere prior to use. Rh$_2$(OAc)$_4$(MeOH)$_2$ (1) was prepared by literature procedures.

[Rh$_2$(OAc)$_4$(amp)$_2$]$_n$·n/4MeCN (2·n/4MeCN). A violet solution of 1 (0.15 g, 0.30 mmol) in MeCN (15 cm$^3$) was treated with a solution of amp (31 µl, 0.30 mmol) in MeCN (0.5 cm$^3$). A pink solid precipitated from the reaction mixture within 20 min. The solid was isolated by filtration, washed copiously with acetonitrile (3×15 cm$^3$) and dried in vacuo; the yield was 73%. Crystals of 2 suitable for single-crystal analysis were obtained by slow diffusion of an MeCN solution of 1 into an MeCN solution of amp, resulting in deep red crystals of 2 within 3 days. The X-ray structural analysis indicated a formulation 2·n/2MeCN; a vacuum-dried solid analysed as 2·n/4MeCN. Found: C, 31.0; H, 3.7; N, 5.4. Calc. for C$_{14}$H$_{30}$N$_5$O$_{10}$S$_2$Rh$_2$: C, 31.1; H, 3.7; N, 5.6%. Selected IR data (KBr pellet, cm$^{-1}$): 3333 (m), 3272 (m), 1588 (s), 1482 (w), 1435 (s), 1412 (s), 1348 (m), 986 (m), 777 (m), 696 (s), 629 (w). Electronic spectrum in CHCl$_3$: $\lambda_{max}$/nm (e$_m$/mol$^{-1}$ cm$^{-1}$): 236 (13055), 272 (16550), 324 (2520), 450 (165), 536 (285).

[Co$_2$(OAc)$_4$(amp)$_2$]$_n$·n/4CHCl$_3$ (2·n/4CHCl$_3$). Complex 2 (0.050 g, 0.088 mmol) was dissolved in CHCl$_3$ (10 cm$^3$) to produce a deep red–violet solution. Upon prolonged standing, a pink precipitate resulted which was isolated by filtration and dried in vacuo; the yield was 86%. Found: C, 30.6; H, 3.6; N, 5.0. Calc. for C$_{14}$H$_{30}$N$_5$O$_{10}$S$_2$Rh$_2$: C, 31.0; H, 3.7; N, 5.1%.

[Cu$_2$(OAc)$_4$(amp)$_2$]$_n$ (4). An aqua-blue solution of 3 (1.00 g, 5.00 mmol) in acetonitrile (200 cm$^3$) was treated dropwise with one molar equivalent of amp (258 µl, 2.50 mmol) to give an immediate deep blue precipitate. The solid was isolated by filtration, washed with MeCN, and dried in vacuo for 18 h; the yield was 80%. Found: C, 35.8; H, 4.3; N, 6.0. Calc. for C$_{14}$H$_{30}$N$_5$O$_{10}$Cu$_2$: C, 35.7; H, 4.3; N, 5.9%. Selected IR data (KBr pellet, cm$^{-1}$): 3287 (m), 1626 (s), 1605 (s), 1557 (s), 1426 (s), 1379 (s), 1318 (m), 1090 (m), 1044 (m), 768 (m), 681 (m). Electronic spectrum in ethanol: $\lambda_{max}$/nm (e$_m$/mol$^{-1}$ cm$^{-1}$): 228 (5750), 240 (6050), 252 (6660), 264 (6480), 692 (480). Vapour diffusion of Et$_2$O into an ethanol solution of 4 leads to the slow formation within 2 days of deep blue crystals suitable for single-crystal X-ray analysis.

**X-ray crystallography**

Data were collected using a Picker four-circle diffractometer; details of the diffractometry, low-temperature facilities and computational procedures employed by the Molecular Structure Center are available elsewhere. The structure of complexes 2·n/2MeCN and 4 were determined using a combination of direct methods (MULTAN) and Fourier techniques, and refined by full-matrix least-squares cycles.

For complex 2·n/2MeCN, a systematic search of a limited hemisphere of reciprocal space revealed intensities with Laue symmetry and systematic absences consistent with a C-centred monoclinic cell. Following complete intensity data collection, the additional condition $h = 2n$ and $l = 2n$ for h0l data was observed. Space group C2/c was chosen and was later confirmed by the successful solution of the structure. An absorption correction was performed. The positions of the Rh atoms were determined from an initial E-map, with the positions of non-hydrogen atoms obtained from subsequent iterations of least-squares refinement and difference Fourier map calculations. The structure also contains a disordered MeCN molecule with one of its carbon atoms located at a centre of symmetry. Fixed, calculated hydrogen atoms were included on all carbon atoms except the disordered solvent molecule. Hydrogen thermal parameters were fixed.
at one plus the isotropic thermal parameter of the atom to which they were bonded. The hydrogen on N(25) was not located and not included. In the final refinement cycles, the Rh atoms were refined with anisotropic thermal parameters, and all other non-hydrogen atoms were refined with isotropic thermal parameters. The final difference map was essentially featureless, the largest peak being 1.6 e Å\(^{-3}\). Final R and R\(_w\) values are included in Table 1.

For complex 4, a systematic search of a limited hemisphere of reciprocal space failed to locate any symmetry or systematic absences, indicating a triclinic space group. Subsequent solution and refinement confirmed the centrosymmetric choice, P\(_T\). All non-hydrogen atoms were readily located. All hydrogen atoms were clearly visible in a subsequent difference Fourier map phased on the non-hydrogen atoms. In the final cycles of the refinement, hydrogen atoms were allowed to vary isotropically and all other atoms anisotropically. The final difference Fourier map was essentially featureless, the largest peak being 0.49 e Å\(^{-3}\). Final R and R\(_w\) values are included in Table 1.

**Other measurements**

IR (KBr pellet) and electronic spectra were recorded on Nicolet 510P and Hewlett-Packard 8452A spectrophotometers, respectively. FAB mass spectra were recorded on a Kratos MS80 spectrometer. Elemental microanalyses were performed by Atlantic Microlab, Inc.

**RESULTS**

**Syntheses**

The initial reaction explored was that between Rh\(_2\)(OAc)\(_4\)(MeOH)\(_2\) (1) and one equivalent of amp in acetonitrile. Upon addition of amp, an immediate colour change from violet to deep red occurs, followed by precipitation of a pink solid, [Rh\(_2\)(OAc)\(_4\)(amp)]\(_n\) (2), whose identity was determined by single-crystal X-ray analysis. The formation of 2 is summarized in eq. (1).

\[ n \text{Rh}_2\text{OAc}_4\text{(MeOH)}_2 + n\text{amp} \rightarrow \text{[Rh}_2\text{OAc}_4\text{(amp)}]_n + 2n\text{MeOH} \]  
(1)

In fact, the initial indication that the product might be polymeric was the very low solubility in solvents with which it did not react, except CHCl\(_3\) in which it is moderately soluble but then re-precipitates within an hour as the CHCl\(_3\) solvate. FAB mass spectral results on the latter, together with its visual

**Table 1. Crystallographic data for complex 2\(\cdot n\)2MeCN and 4**

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<thead>
<tr>
<th></th>
<th>2(\cdot n)2MeCN</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula(^a)</td>
<td>C(<em>{12})H(</em>{24})N(_2)O(_8)Rh(_2)</td>
<td>C(<em>{19})H(</em>{20})N(_2)O(_2)Cu2</td>
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<tr>
<td>Formula wt (g mol(^{-1}))</td>
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<td>471.41</td>
</tr>
<tr>
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<td>C2/c</td>
<td>P(_T)</td>
</tr>
<tr>
<td>(a) (Å)</td>
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<td>8.522(1)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>14.218(2)</td>
<td>13.066(2)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>18.680(2)</td>
<td>7.942(1)</td>
</tr>
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<td>(\alpha) (°)</td>
<td>90</td>
<td>99.22(1)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>113.35(1)</td>
<td>90.73(1)</td>
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<tr>
<td>(\gamma) (°)</td>
<td>90</td>
<td>97.66(1)</td>
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<tr>
<td>(V) (Å(^3))</td>
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<td>864.6</td>
</tr>
<tr>
<td>(Z)</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>(T) (°C)</td>
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<td>-169</td>
</tr>
<tr>
<td>Radiation (Å(^\text{b}))</td>
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<td>0.71069</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}) (g cm(^{-3}))</td>
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<td>1.81</td>
</tr>
<tr>
<td>(\mu) (cm(^{-1}))</td>
<td>16.252</td>
<td>25.110</td>
</tr>
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<td>Octants</td>
<td>+h, +k, ±l</td>
<td>+h, ±k, ±l</td>
</tr>
<tr>
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<td>2386</td>
</tr>
<tr>
<td>Unique data</td>
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<td>2261</td>
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<tr>
<td>(R_{\text{merge}})</td>
<td>0.042</td>
<td>0.009</td>
</tr>
<tr>
<td>Obsd. data ((F &gt; 3\sigma(F)))</td>
<td>2199</td>
<td>1931</td>
</tr>
<tr>
<td>(R(F_o)(%^{a\text{dd}}))</td>
<td>6.67 (6.47)</td>
<td>2.75 (2.93)</td>
</tr>
</tbody>
</table>

\(^a\)Including solvate molecules.
\(^b\)Graphite monochromator.

\(R = \Sigma ||F_o|| - |F_c|| \Sigma |F_c||/|F_o||, \)

\(R_w = [\Sigma w(|F_o|^2 - |F_c||^2)^2]^{1/2} \Sigma w|F_o|^2]^{1/2} \) where \(w = 1/\sigma^2(|F_o|).\)
appearance, elemental analysis, and solid-state IR spectrum, indicate that no change has occurred to the complex, which is thus formulated as \([\text{Rh}_2(\text{OAc})_4(\text{amp})]_n \cdot n/4\text{CHCl}_3\). On dissolution in the good donor solvents DMF or DMSO, however, the polymer is broken up and the products are \(\text{Rh}_2(\text{OAc})_4(\text{sol})_2\) and free amp, as deduced from \(^1\text{H}\) NMR spectroscopy. These results are not surprising in view of the fact that the amp ligands occupy the labile axial sites of the \([\text{Rh}_2(\text{OAc})_4]\) unit (vide infra).

A polymeric compound is also formed in the reaction of \(\text{Cu}_2(\text{OAc})_4(\text{H}_2\text{O})_2\) with amp. Treatment of a solution of \(\text{Cu}_2(\text{OAc})_4(\text{H}_2\text{O})_2\) (3) in MeCN with one equivalent of amp results in an immediate colour change from aqua-blue to deep blue, followed by precipitation of \([\text{Cu}_4(\text{OAc})_6(\text{amp})_2]\)_n (4) (eq. (2)).

\[
2n\text{Cu}_2(\text{OAc})_4(\text{H}_2\text{O})_2 + 2n\text{amp} \rightarrow [\text{Cu}_4(\text{OAc})_6(\text{amp})_2]_n + 4n\text{H}_2\text{O}
\] (2)

X-Ray quality crystals of 4 were obtained by recrystallization from EtOH/Et\(_2\)O. The X-ray structure revealed that the compound consists of linear polymeric chains with an overall stoichiometry of 1:1 \(\text{Cu}^{2+} : \text{amp}\), as was found in 2, but with two different types of repeating \(\text{Cu}_2\) units (vide infra).

**Description of structures**

ORTEP projections of the repeating units of 2 and 4 are shown in Figs 1 and 3, and stereoviews of the polymeric chains are shown in Figs 2 and 4. Selected metric parameters for 2 and 4 are collected in Tables 2 and 3, respectively.

Compound 2 \(\cdot n/2\text{MeCN}\) crystallizes in monoclinic space group \(C2/c\) with no crystallographically-imposed symmetry on the \(\text{Rh}_2(\text{OAc})_4\) (amp) repeating unit. The two Rh atoms are bridged by four \(\eta^1 : \eta^1\) acetate ligands over a metal–metal distance of 2.410(1) Å. Pseudo-octahedral coordination at \(\text{Rh}(1)\) is completed by pyridine nitrogen \([(\text{N}19)]\) of one amp ligand and the second Rh atom, \(\text{Rh}(2)\). Coordination at \(\text{Rh}(2)\) is completed by \(\text{Rh}(1)\) and the amine nitrogen atom of a second amp ligand. Thus, the amp ligands act as bridges between the dinuclear rhodium units to give a one-dimensional polymeric structure, as shown in Fig. 2. Although the amine protons were not located, hydrogen bonding is nevertheless evident in the solid state between the amine group of the amp ligand and the carboxylate oxygen atoms of the \(\text{Rh}_2(\text{OAc})_4\) core \([\text{N}(25') : \cdot \cdot \cdot \text{O}(3) = 2.964\ \text{Å}\].\)

The polymer chains are not linear but instead form a “zig-zag” pattern with alternating \(\text{Rh}_2\) units at an angle of 88.4° to each other. There is only a slight difference between the \(\text{Rh}—\text{N}(\text{pyridine})\) and \(\text{Rh}—\text{N}(\text{amine})\) distances [2.250(11) and 2.311(11) Å, respectively].

Complex 2 is not the first example of a chain polymer of \([\text{Rh}_3]\) units. Previous examples are \([\text{Rh}_2(\text{O}_2\text{CEt})_4(\text{phz})]\) (phz = phenazine),\(^4\) \([\text{Rh}_2(\text{O}_2\text{CEt})_4(\text{dda})]\) (dda = durenediamine),\(^8\) \([\text{Rh}_2(\text{OAc})_4(\text{aamp})]\) (aamp = 4-amino-5-(aminomethyl)-2-
Fig. 2. Stereoview of complex 2 demonstrating the polymeric nature of the compound.

Fig. 3. ORTEP diagram at the 50% probability level of the repeating unit found in complex 4. Hydrogen atoms have been omitted for clarity.
methylpyrimidine), [Rh\textsubscript{2}(O\textsubscript{2}CC\textsubscript{3})\textsubscript{4}(NITMe)] (NITMe = a nitronyl nitroxide radical group)\textsuperscript{9} and Rh\textsubscript{2}(O\textsubscript{2}CCF\textsubscript{3})\textsubscript{4}(IMMe) (IMMe = an imino nitroxide radical group).\textsuperscript{10} In each case, the inter-Rh\textsubscript{2} bridging groups are bound at the axial positions of the [Rh\textsubscript{2}(O\textsubscript{2}CR)\textsubscript{4}] unit.

There are also several examples of one-dimensional chains involving metal–metal bonded [M\textsubscript{2}(O\textsubscript{2}CR)\textsubscript{4}] units containing other transition metals. These include [Mo\textsubscript{2}(O\textsubscript{2}CR)\textsubscript{4}L] (L = pyrazine (pz), \textsuperscript{11} 4,4'-bipyridine (4,4'-bpy), \textsuperscript{11} 1,4-diazabicyclo[2.2.2]octane, \textsuperscript{11} bis(dimethylphosphino) ethane (dmpe)\textsuperscript{12} and tetramethylethylenediamine (tmed)\textsuperscript{12}), [Ru\textsubscript{2}(O\textsubscript{2}CR)\textsubscript{3}Cl]\textsuperscript{13} [Re\textsubscript{2}(O\textsubscript{2}CR)\textsubscript{2}Cl\textsubscript{2}]\textsuperscript{14} [M\textsubscript{2}(OAc)\textsubscript{4}(pz)] (M = Cr, \textsuperscript{15} Cu\textsuperscript{16}) and [Ru\textsubscript{2}(O\textsubscript{2} CR)\textsubscript{4}L] (L = pyz, phz, quinoxaline and 4,4'-bpy).\textsuperscript{17} Many of these have been structurally characterized.
Polymerization of $M_2(OAc)_4$ ($M = Cu, Rh$)

Table 2. Bond distances and angles for complex $2 \cdot n/2$MeCN

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<tr>
<th>Bond Distances (Å)</th>
<th>Rh(1)−Rh(2)</th>
<th>Rh(1)−O(3)</th>
<th>Rh(1)−O(7)</th>
<th>Rh(1)−O(13)</th>
<th>Rh(1)−O(17)</th>
<th>Rh(1)−N(19)</th>
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<td></td>
<td>2.410(1)</td>
<td>2.040(9)</td>
<td>2.039(9)</td>
<td>2.050(9)</td>
<td>2.031(9)</td>
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<table>
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<tr>
<th>Bond Angles (°)</th>
<th>O(3)−Rh(1)−O(7)</th>
<th>O(3)−Rh(1)−O(13)</th>
<th>O(3)−Rh(1)−O(17)</th>
<th>O(7)−Rh(1)−N(19)</th>
<th>O(7)−Rh(1)−O(17)</th>
<th>O(13)−Rh(1)−O(17)</th>
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<td></td>
<td>91.7(3)</td>
<td>174.6(4)</td>
<td>93.0(4)</td>
<td>89.7(3)</td>
<td>175.6(4)</td>
<td>91.2(4)</td>
<td>93.2(4)</td>
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The structure of 4 is composed of well-separated, one-dimensional polymeric chains that contain two distinct types of $Cu^2+$ units, each lying on a crystallographic centre of symmetry. The chains are formed by alternating $[Cu_2(OAc)_4]$ and $[Cu_2(OAc)_2(amp)]^2+$ units connected by syn, anti bridging acetate groups. The Cu−Cu vectors are not collinear, the Cu(14)−Cu(14′) vector being at an angle of 27.57° to the Cu(1)−Cu(1′) vector. The $[Cu_2(OAc)_4]$ units contain four bridging acetate ligands in the familiar $\eta^1: \eta^1: \mu$ coordination mode, as found in the starting material, 3.

The Cu(1)⋯Cu(1′) distance of 2.636(1) Å is slightly longer than that of the parent compound [2.614(2) Å in 3], and other bond distances and angles in the $[Cu_2(OAc)_4]$ units of 4 are also very similar to those in 3. Square-pyramidal coordination at the Cu centres is completed by an oxygen atom O(10) of the syn, anti bridging acetates, with the Cu atom 0.20 Å above the basal plane [O(2), O(4), O(6), O(8)] towards O(10).

The other part of the repeating unit of 4 is composed of a Cu₂ unit [Cu(14) and Cu(14′)] bridged by two mono-atomically-bridging acetate groups, O(23), with five-coordination and approximately square-pyramidal geometry at each metal centre.

Table 3. Bond distances and angles for complex 4

<table>
<thead>
<tr>
<th>Bond Distances (Å)</th>
<th>Cu(1)−O(2)</th>
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<th>Cu(1)−O(8)</th>
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<th>Bond Angles (°)</th>
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<th>O(2)−Cu(1)−O(10)</th>
<th>O(4)−Cu(1)−O(6)</th>
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<th>O(6)−Cu(1)−O(8)</th>
<th>O(6)−Cu(1)−O(10)</th>
<th>O(8)−Cu(1)−O(10)</th>
<th>O(12)−Cu(14)−O(23)</th>
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<td>96.76(11)</td>
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</tbody>
</table>
completed by a chelating amp ligand and the second oxygen atom, O(12), of the syn, anti bridging acetate group. Oxygen atom O(23) bridges Cu(14) and Cu(14') in an asymmetric manner [Cu(14)—O(23) = 2.277(3) Å, Cu(14')—O(23) = 1.965(3) Å] owing to the fact that it occupies the apical position of the Cu(14) square pyramid and a basal position of the Cu(14') square pyramid. For similar reasons, Cu(1)—O(10) (2.130(3) Å) is significantly longer than Cu(14')—O(12) [1.945(3) Å]. As in complex 2, the amp NH, group is involved in hydrogen-bonding with acetate oxygen atoms, with N(22)···O(10') = 2.877 Å and N(22)···O(10') = 2.851 Å. The polymeric structure results in three distinct Cu···Cu separations within the chain: Cu(1)···Cu(1') = 2.626(1) Å, Cu(1)···Cu(14') = 5.151(1) Å and Cu(14)···Cu(14') = 3.282(1) Å in a repeating ABCBABC... pattern. Other structural features are unexceptional, and, overall, complex 4 is similar to the structure of [Cu₄(OAc)₈(bpy)₂]ₙ, which also contains polymeric chains.¹⁸

**FAB mass spectral data**

As an additional potential means of characterization of the polymers, complexes 2·n(2)MeCN and 4 were examined by low-resolution FAB mass spectrometry. Complex 2 was dissolved in CHCl₃, p-nitrobenzyl-alcohol added, and the CHCl₃ evaporated to deposit a pink solid in the alcohol matrix. The results for both complexes are shown in Fig. 5. For complex 2 in the range 0–2000 amu (estimated precision ±1 amu) the parent fragment with the largest m/z value is at 1540 amu (20% relative intensity) corresponding to [Rh₄(OAc)₁₂(amp)]⁺ (theoretical for M—H, 1541 amu) consisting of a chain of three Rh₃(OAc)₄ units bridged by two amp ligands, namely [Rh₄(OAc)₈(amp)] [Rh₂(OAc)₄(amp)] [Rh₂(OAc)₄(amp)]. Loss of one or two Rh₂(OAc)₄ units (442 amu) from the two ends of this fragment yields the peaks at 1099 (theoretical 1099) and 657 (theoretical 657), respectively. The peak at 1039 (theoretical 1040) corresponds to loss of AcO⁻ (59 amu) from the 1099 peak. The other major peak at 931 amu corresponds to the loss of both an AcO⁻ and an amp ligand from the 1099 amu fragment, namely [Rh₃(OAc)₄(amp)] [Rh₂(OAc)₄] (theoretical 932). The successful observation of fragments containing more than one Rh₃(OAc)₄ was welcome, and additionally supports retention of the polymeric structure after dissolution and recrystallization from CHCl₃.

The high solubility of 4 in good donor solvents (MeCN, EtOH, etc.) suggests that the polymeric structure is destroyed in solution, as would be intuitively expected for Cu²⁺. In support of this, the FAB mass spectrum of solid dissolved in MeCN shows no high mass fragments that could comprise two or more Cu₂ units. The peak at 613.8 amu corresponds to Cu₅(OAc)₉(amp)₂(H₂O)ₘ (theoretical 614), the peak at 518.7 amu to Cu₅(OAc)₉(amp)₂ (theoretical 519) and that at 458.7 amu to Cu₅(OAc)₉(amp)₂ (theoretical 460).

We are unaware of mass spectra having been obtained previously on oligomeric or polymeric [Rh₃] complexes but it is clearly a useful technique for the study of such materials and for related ones with other metals. It is pleasing that, for the present complex, fragments containing more than one [Rh₃] were observed; indeed the identification of the [Rh₃(OAc)]₄(amp)₂ fragment would have been very suggestive of the presence of a [...] [Rh₃(OAc)]₄(amp)[Rh(OAc)]₄(amp) ... repeating sequence and a consequent linear polymeric structure, had crystallographic data not been available. In this particular case, of course, the crystal structure was at hand and the linear polymeric structure was already known, but one can imagine how FAB mass spectra could be used in other cases to obtain indications of or support for the presence of bridges between [Rh₃] units in complexes that could not be structurally characterized or where the loss of a solid-state polymeric structure on dissolution in a particular solvent might be suspected.

**Possible relationship between 2 and [Rh₂(OAc)₄(ade)]ₙ.** The dinuclear Rh³⁺ carboxylates Rh₂(O₂CR)₄L₂ (R = alkyl) were discovered by Bear and co-workers in the 1970s to exhibit anticancer activity against a number of tumours.¹⁹ This stimulated a variety of studies designed to identify the mechanism of action.²⁰ The Rh complexes were shown to significantly inhibit DNA and RNA synthesis in vivo, with DNA synthesis being affected to a much larger degree.¹⁹ In binding studies with poly-G and poly-A, Rh₂(OAc)₄ was found to bind only to the latter (Scheme 1).¹⁹c,d

Since the metal–purine interaction would be expected to form through lone-pair donation by N(7) into the labile axial site of the Rh₂(OAc)₄ unit, the preference for A over G binding was rationalized as arising from the hydrogen-bonding between the exocyclic-NH₂ group in A and an equatorial acetate oxygen atom; this is not possible for G.²¹ Such hydrogen-bonding interactions have been crystallographically confirmed in simple model complexes containing bound A groups (Scheme 2).²²

In an attempt to prepare simple Rh₃(OAc)₄/adenine adducts that might be amenable to detailed characterization, Pneumatikakis and Hadjiliadis
treated \( \text{Rh}_2(\text{OAc})_4 \) with one or more equivalents of 9-methyladenine (9-Me-A) (and related adenine derivatives). The 9-Me-A reactions lead to immediate precipitation of a pink, insoluble solid with a \([\text{Rh}_2] : 9\text{-Me-A} = 1:1\) ratio, even when excess 9-Me-A is present. The identity of this material has been of significant interest to the field but its structure remains unknown to this day. On the basis of the low solubility, the analytical data and spectroscopic measurements, Pneumatikakis
and Hadjiliadis proposed the solid to be polymeric with N(7),N(1)-bound 9-Me-A providing the intermolecular bridging interactions. This would provide a zig-zag polymer, as shown in Fig. 6 (A).

Recognizing that the amp ligand bears structural similarity to A, and since we have been able crystallographically to characterize complex 2, we are able to offer a second means by which an adenine-bridged polymer might form. Shown in Fig. 6 (B) is a representation of the 1:1 polymer that would form if adenine were bridging in the same manner as amp in 2, employing the N(7) and exocyclic amine N atoms, including hydrogen-bonding to the acetate oxygen atoms. Again, a zig-zag polymer would result. We emphasize that amp is not adenine and does not have any other N-atoms that could become involved in metal binding. Also, we are not suggesting that our second possibility is preferable, only that it is feasible and is based on a structurally-characterized 1:1 polymer with amp. However, only a crystal structure of the adenine polymer itself can definitively identify its structure.

CONCLUSIONS

Treatment of Mz(OzCR)4 (M = RhII, CuII) complexes with one equivalent of amp leads to the one-dimensional polymeric products 2 and 4. The Rh—Rh bond in the former case and the inertness of equatorially-bound carboxylate ligands are undoubtedly the reasons the Rh2(OAc)4 unit remains intact, with the amp groups binding only to the labile axial sites. The particular intermolecular bridging mode adopted by amp in 2, facilitated by hydrogen-bonding interactions with equatorial oxygen atoms, suggests that this group could find general application for linking metal—metal bonded dinuclear units possessing carboxylate or other oxygen-based ligation that can hydrogen-bond to NH2 groups.

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Supplementary material available—Tables of atomic coordinates, thermal parameters, bond distances and angles, and full details of the data collection and refinement for 2 and 4 (22 pages). Ordering information is given on any current masthead page.

REFERENCES

Polymerization of $\text{M}_2(\text{OAc})_4$ ($\text{M} = \text{Cu}, \text{Rh}$) 2943


