SHORT PAPER

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Self-assembly of a supramolecular cyclic polymer containing pyrazine bridged trinuclear μ-oxo-ruthenium-acetate clusters[†]

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The self-assembly of a novel supramolecular cyclic polymer species of general formula $[Ru_3O(CH_3COO)_6(CO)(pz)]_6$ has been achieved, by starting from μ-oxoruthenium cluster units in the presence of bridging pyrazine (pz) ligands.

Trinuclear ruthenium clusters of general formula $[Ru_3O(CH_3COO)_6(L)_3]^n$ have been extensively studied because of their interesting chemical, electrochemical and catalytic properties.[1–6] The build up of supramolecular assemblies has also been pursued in recent years, exploiting different precursors and synthetic routes.[7–13] Typical examples of supramolecular structures involve four cluster units,[10,11] as well as modified porphyrins containing four trinuclear cluster centres.[12,13] The carbonyl clusters are particularly suitable for assembling supramolecular structures. In general, the central $[Ru_3O]$ core is able to bind only one CO molecule, leaving two Ru sites to interact with appropriate ligands. In this work, we report the self-assembly of a novel supramolecular species, containing six $[Ru_3O(CH_3COO)_6(CO)]$ units held together by pyrazine bridges, as illustrated in Fig. 1.

Although suitable crystals for X-ray analysis have not been obtained up to the present time, strong evidence for the proposed cyclic structure has been provided by NMR, FTIR and resonance Raman spectroscopy.

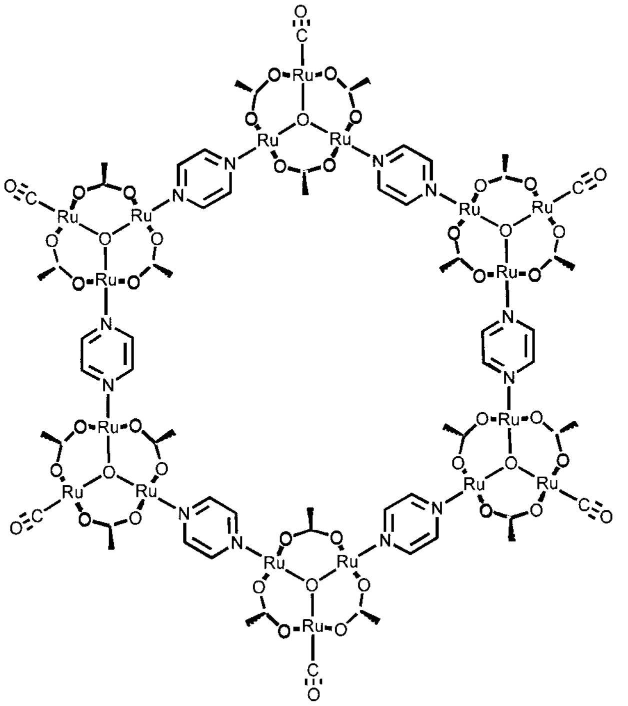

Fig. 1 Schematic MM⁺ structure of the heximer $[Ru_3O(CH_3COO)_6(CO)(pz)]_6$ (the acetate ligands coincide in the projection and the H atoms are hidden).

For linear or non cyclic structures, one would expect two ^1H NMR signals for each non bridging pyrazine ligand, and several signals for the acetate ligands *vicinal* or in *trans*-position with respect to the CO ligands.[14,15] However, a rather simple ^1H NMR spectrum has been observed, exhibiting a single pyrazine peak at 8.81 (24H) ppm, and only two acetate signals at 2.29 (72 H) and 2.13 (36 H) ppm. The single pyrazine peak indicates unequivocally that all the pyrazine protons are equivalent, as in the case of the cyclic polymer, where the pyrazine ligand acts as a bridge between the cluster units and can undergo facile rotation about the N–N axes. In addition, the observation of only two acetate protons with 1:2 intensity ratio, indicates that all the trinuclear cluster moieties are equivalent, exhibiting axial microsymmetry. Therefore, the occurrence of linear or non cyclic structures can be definitely ruled out.

The IR spectrum shown in Fig. 2 exhibits the peaks of the ruthenium cluster core[16,17] at 1568 cm^{-1}, $\nu_{as}(COO)$; 1423 cm^{-1}, $\nu_a(COO)$; 1348 cm^{-1}, δ (CH_3) and 623 cm^{-1}, $\pi(COO)$; and of the pyrazine vibrations at 1604 cm^{-1}, ν(CC); 1043, 943, 814 cm^{-1}, ν(CH ring); and 687 cm^{-1}, δ(ring). Most important, a single νCO peak is observed at 1951 cm^{-1}, in complete agreement with the symmetric structure proposed for the cyclic species (Fig. 1). The resonance Raman spectra exhibit the pyrazine vibrational peaks at 1603 cm^{-1}, ν(CC); 1226 ν(CH ring), 1036 ν(ring), 779 π(CH ring) in addition to the cluster peaks at 667 cm^{-1} π(COO); 447 ν(Ru–OCO); and 301 cm^{-1} $\delta(Ru_3O)$. In this type of system, it has been shown that the most strongly enhanced vibrations in resonance Raman spectra correspond to totally symmetric modes.[16,17] Since the infrared active modes are anti-symmetric, the lack of coincidence between the FTIR and the resonance Raman spectrum, confirms that the molecule under investigation has a centre of symmetry.

Therefore we conclude that the most probable structure for this molecule is a cyclic and symmetric one. It is known[19] that the $[Ru_3O]$ core has an equilateral triangle geometry. When there is a CO molecule coordinated to the core, this geometry is slightly distorted into an isosceles triangle. In spite of the distortion, the angles between each Ru and the central O ions remain very close to 120°. This fact strongly favours the build up of a hexagonal structure for the oligomer, in which each vertex of the heximer is occupied by one $[Ru_3O(CH_3COO)_6(CO)]$ unit. This expectation has been confirmed by molecular mechanics simulations carried out for the system (Fig. 1), which indicated a preferential stabilization of the cyclic heximer structure over all other possible spatial arrangements. This special stability would also explain the self-assembly of the cyclic heximer structure observed in this work.

The electronic spectrum of the heximer (Fig. 3) shows two bands at 462nm and 611nm, respectively ascribed to cluster-to-pyrazine charge transfer (CLCT) and intra-cluster (IC)

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

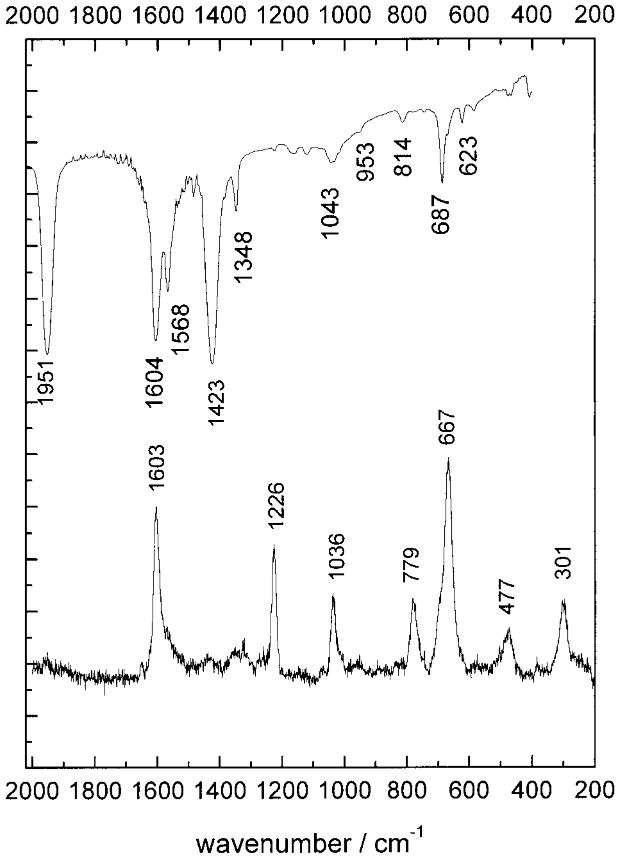

Fig. 2 Infrared (top) and resonance Raman (bottom) spectra of $[Ru_3O(CH_3COO)_6(CO)(pz)]_6$, obtained in KBr pellet and solid sample, respectively.

transitions, (*i.e.* involving metal-to-metal excitation within each $[Ru_3O]$ core), by analogy with the literature.[2–4, 10,11]

Both CLCT and IC bands are redshifted when compared to the same transitions for the monomeric cluster[20] $[Ru_3O(CH_3COO)_6(CO)(pz)_2]$, *e.g.* at 406nm and 593nm respectively. The bathochromic shift in the CLCT band is consistent with extended structures in which the pyrazine ligand acts as bridge connecting two ruthenium cluster units[11,20] and reflects the π-electronic interaction through the cluster-pyrazine bond. In addition, the red shift in the IC band, is also consistent with a pronounced electronic delocalization over the heximer species.

Experimental

The precursor complex $[Ru_3O(CH_3COO)_6(CO)(CH_3OH)_2].H_2O$ was obtained from a synthetic route slightly different from that previously reported,[20] by using $NaBH_4$ as the reductant and ethanol as the eluent in cromatography.

The synthesis of $[Ru_3O(CH_3COO)_6(CO)(pz)]_6$ was carried out by adding 4.78 mg (5.98×10^{-5} mol) of pyrazine to 10 cm^3 of a methanol solution of $[Ru_3O(CH_3COO)_6(CO)(CH_3OH)_2].H_2O$ (45.8 mg, 5.98×10^{-5} mol), and allowing the reaction to proceed during 24 hours, in the dark, at room temperature. After evaporating the solvent, the green solid was redissolved in $CHCl_3$. The resulting solution was transferred to a neutral alumina column, and $CHCl_3$ was used as the eluent. Most of the material, presumably containing open chain fragments, remained strongly adsorbed in the column. The main fraction eluted was evaporated to dryness yielding a dark green solid. Yield: 10mg (19.8%). ^1H NMR data in $CDCl_3$ (δ/ppm): 8.81 (24H pyrazine); 2.29 and 2.13 (72H and 36H, respectively, acetate methyl groups). (Found: C, 25.5; H, 3.1; N, 3.3. $C_{102}H_{132}N_{12}O_{84}Ru_{18}$ requires C, 26.1; H, 2.9; N, 3.5).

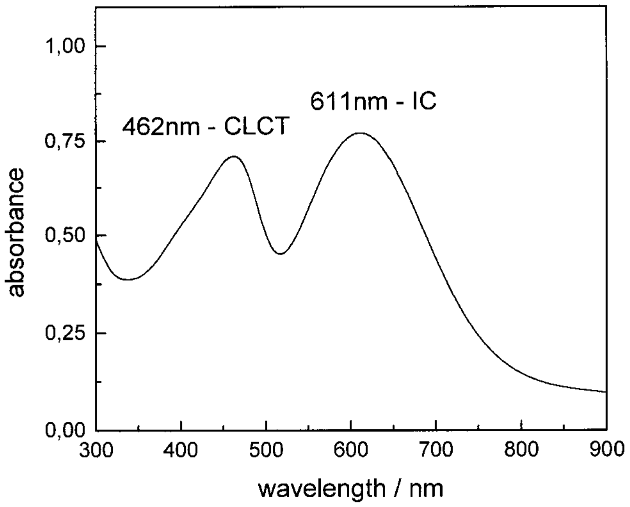

Fig. 3 Electronic spectrum of $[Ru_3O(CH_3COO)_6(CO)(pz)]_6$, obtained from a 2.85×10^{-5} mol/dm CH_3CN solution (IC = intracluster and CLCT = cluster-to-ligand charge transfer transitions).

The NMR spectrum was recorded on a Varian INOVA 1 300MHz spectrophotometer. The electronic spectrum was recorded on a Hewlett Packard model 8453-A diode array spectrophotometer. The infrared spectrum was obtained from KBr pellets on a SHIMADZU FTIR model 8300 spectrophotometer. The resonance Raman spectrum of the solid heximer was recorded on a Renishaw model U3000 instrument, using a spinning cell ($\lambda_{exc.}$=632.8 nm). Molecular simulation was carried out using the MM$^+$ force field[18] from Hyperchem 5.10, and a gradient of 10^{-4} kcal/mol as convergence criterion.

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