Synthesis and Characterization of a Dodecanuclear Ruthenium Pyrazine Cluster

Henrique E. Toma and Anamaria D.P. Alexiou

Instituto de Química, Universidade de São Paulo,
C.P. 26077, 05599-970 São Paulo - SP, Brazil

Received: October 29, 1994; December 1, 1994

O acoplamento de complexos triangulares de acetato de rutênio por meio de ligantes de ponte foi utilizado neste trabalho para ilustrar a obtenção de estruturas supramoleculares. O protótipo investigado corresponde a uma nova espécie dodecanuclear, de fórmula geral \([\text{Ru}_3\text{O}(\text{Ac})_6((\text{pz})\text{Ru}_2\text{O}(\text{Ac})_6(\text{py})_2)_3]^{4+}\) (Ac = íon acetato, pz = pirazina, py = piridina), formada por quatro unidades do tipo \([\text{Ru}_2\text{O}(\text{Ac})_6\text{L}_3]^{3+}\) unidas por pontes de pirazina, em simetria \(D_{3h}\). Nesse tetramero, a interação interunidades torna-se mais intensa quando se reduz o estado formal de oxidação, observando-se maior participação da interação retrodoadora rutênio-pirazina na estabilização dos centros metálicos.

The assembly of supramolecular structures, based on the binding of triangular ruthenium-acetate cluster units via bridging ligands, is reported in this work. The prototype species consists of a new dodecanuclear complex of the general formula \([\text{Ru}_3\text{O}(\text{Ac})_6((\text{pz})\text{Ru}_2\text{O}(\text{Ac})_6(\text{py})_2)_3]^{4+}\) (Ac = acetate ion, pz = pyrazine, py = pyridine), exhibiting four \([\text{Ru}_2\text{O}(\text{Ac})_6\text{L}_3]^{3+}\) units bridged by pyrazine ligands, according to a \(D_{3h}\) symmetry. The electronic interaction between the various units in the tetrameric species increases as the oxidation states decrease, while the backbonding interactions through the ruthenium-pyrazine bonds become very important for the stabilization of the metallic centers.

Keywords: supramolecular cluster, ruthenium-acetate tetramer, bridged complex

Introduction

The use of triangular ruthenium acetate clusters of the general formula \([\text{Ru}_3\text{O}(\text{Ac})_6\text{L}_3]^{3+}\) to design supramolecular structures involving bridging ligands, is reported in this paper. This type of cluster is highly symmetric (\(D_{3h}\)) and exhibits rich mixed-valence chemistry\(^1\)\text{--}^{13}\), reactivity\(^{14}\)\text{--}^{15}\) and catalytic properties\(^1\)\text{--}^{17}\). The central unity employed, \([\text{Ru}_3\text{O}(\text{Ac})_6(\text{pz})_3]^{3+}\), and its ability to bind transition metal complexes have been previously studied in this laboratory\(^{18}\)\text{--}^{21}. Here, we have extended the previous work\(^{18}\)\text{--}^{20}\) to a novel dodecanuclear species containing four triangular ruthenium acetate units bridged via pyrazine ligands, as illustrated in Fig. 1. Unfortunately, suitable single crystals for X-ray studies have not been obtained up to the present time. For this reason, a detailed characterization of the extended cluster will be provided based on \(^1\)H NMR and cyclic voltammetry techniques.

Experimental

The \([\text{Ru}_3\text{O}(\text{Ac})_6(\text{MeOH})_3]\text{Ac}\) and \([\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2((\text{pz})]\text{PF}_6\) clusters were synthesized and characterized as previously reported for related complexes\(^1\)\text{--}^{13}\). The synthesis of the dodecanuclear cluster\(^\text{21}\), \([\text{Ru}_3\text{O}(\text{Ac})_6((\text{pz})\text{Ru}_2\text{O}(\text{Ac})_6(\text{py})_2)_3]\text{PF}_6\) was carried out by reacting 0.03 mmol of \([\text{Ru}_3\text{O}(\text{Ac})_6(\text{MeOH})_3]\text{Ac}\) in 3.5 mL of methanol with 0.09 mmol of \([\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2((\text{pz})]\text{PF}_6\) dissolved in 15 mL of dichloromethane containing 0.04 mol of \(\text{NH}_3\)\text{PF}_6. After 45 h under stirring at room temperature, the slightly turbid solution was filtered and mixed with 40 mL of diethyl ether in order to precipitate the dodecanuclear product. The precipitate was collected on a filter, washed with diethyl ether and dried under vacuum. Yield: 38% Anal. Calcd. for \(\text{C}_{50}\text{H}_{108}\text{N}_{12}\text{O}_{32}\text{P}_{42}\text{Ru}_{12}\): C, 27.1; N, 4.2, H, 2.8. Found: C, 26.6; N, 3.8; H, 2.8.

\(^1\)H NMR spectra were recorded on a Bruker AC 200 spectrometer, in CD$_3$CN. The electronic spectra were re-
corded on a Hewlett Packard model 8452-A diode-array spectrophotometer. Spectral deconvolution was carried out using a modified version of the SPECSOLV program. Molecular mechanic calculations using MM* force fields were carried out only for the purposes of illustration (Fig. 1). Cyclic voltammetry was carried out with a Princeton Applied Research instrument, consisting of a model 173 potentiosstat and a model 175 universal programmer. A platinum disk electrode was employed for the measurements, using the conventional Luggin capillary arrangement with an Ag/AgNO₃ (0.010 M) reference electrode (E° = 0.503 V vs. SHE) in acetonitrile containing 0.10 M tetraethylammonium perchlorate (TEAP). A platinum wire was used as the auxiliary electrode.

Results and Discussion

The dodecanuclear compound exhibits four [Ru₃O(Ac₆)₃L₃]⁺ groups consisting of three ruthenium ions formally in +II oxidation state, i.e., Ru²⁺Ru³⁺Ru³⁺. These species exhibit composite bands at 716 nm (log ε = 4.1), 616 nm (sh = shoulder), and 514 nm (sh), ascribed to metal-metal transitions within the triangular units, in addition to a cluster-to-pyrazine charge-transfer band at 420 nm, and a cluster-to-pyridine charge-transfer band around 310 nm, as shown in Fig. 2. The electronic spectrum of the [Ru₃O(Ac₆)(py)₂(pz)]⁺ isolated species (Fig. 2), exhibits the corresponding metal-metal bands at 706 nm (log ε = 3.8), 616 (sh), 502 (sh), and the cluster-to-pyrazine and cluster-to-pyridine charge transfer bands at 370 nm and 310 nm, respectively.

The most important difference in the spectra of the tetrameric and monomeric species is observed in the region of the cluster-to-pyrazine charge-transfer bands. In fact, the binding of the cluster unites via the pyrazine bridging ligands is accompanied by a bathochromic shift in the corresponding charge transfer bands from 370 nm to 420 nm, reflecting a significant backbonding interaction through the cluster-pyrazine bond. Unfortunately, except for this difference, the remaining bands are rather similar, and the electronic spectra do not provide a good indication of the complex composition.

The best evidence for the formation of the tetrameric complex can be obtained from the ¹H NMR spectra of the pure species, in comparison with those of the isolated fragments. The complete data can be seen in Table 1. It should be noted that the reported chemical shifts are not usual, since all the complexes in the Table are paramagnetic due to the presence of three low spin ⁴d⁵ Ru³⁺ ions in each triangular cluster unity.

The ¹H NMR peaks observed for the dodecanuclear cluster at 4.83, 5.14 and 5.64 ppm, can be ascribed to the a₂, a₃ and a₁ acetate protons illustrated in Fig. 1. The a₂ peak at 4.83 ppm involves 36 protons and its strong intensity allows for a reliable assignment in this case. Because pyrazine is a good electron acceptor, as compared with pyridine, the central cluster unity is under the influence of
Table 1. $^1$H NMR chemical shift data (ppm) for the (A) [Ru$_3$O(Ac)$_6$(py)$_2$]$^+$, (B) [Ru$_3$O(Ac)$_6$(py)$_2$(pz)$_2$]$^+$ and (C) [Ru$_3$O(Ac)$_6$(pz)$_2$Ru$_3$O(Ac)$_6$(py)$_2$]$^{3+}$ clusters.

<table>
<thead>
<tr>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
<th>Assignments$^b$</th>
</tr>
</thead>
</table>
| CD$_2$Cl$_2$ | CD$_2$Cl$_2$ | CD$_3$CN | CD$_3$CN | Ac ($\delta_2$) protons  \
| 4.83 (18) | 4.34 (12) | 5.14 (12) | 4.83 (36) | Ac ($\delta_1$) protons  \
| 4.82 (6)  | 5.48 (6)  | 5.14 (18) | 5.64 (18) | Ac ($\delta_1$) protons  \
| 0.45 (6)  | 0.50 (4)  | 0.20 (4)  | 0.22 (12) | py ($\delta_1$) protons  \
| 5.76 (6)  | 4.83 (4)  | 5.67 (4)  | 5.35 (12) | py ($\delta_2$) protons  \
| 6.51 (3)  | 5.81 (2)  | 6.68 (2)  | 6.52 (6)  | py ($\delta_3$) protons  \
| 0.70 (2)  | 0.74 (2)  | 0.31 (6)  | 0.34 (6)  | pz ($\delta_1$) protons  \
| 5.92 (6)  | 6.05 (2)  |           |           |                      \

$^a$ Relative intensities in parenthesis. $^b$ See Figure 1.

electron withdrawing groups, and a de-shielding effect can be expected for the corresponding acetate ligands, supporting the assignment of the peak at 5.64 ppm as the $\delta_1$ protons.

As the aromatic protons become closer to the metal cluster they are increasingly influenced by paramagnetic anisotropy effects, as well as by inductive effects from the ruthenium ions$^{23}$. As a consequence, upfield shifts are expected for their resonance peaks. On the other hand, paramagnetic anisotropy effects decay very rapidly with the distance, and become less effective for the more remote protons. These arguments were employed in the assignment of the $^1$H aromatic protons shown in Table 1.

The pyridine peaks associated with the dodecanuclear species are correlated with those observed for the [Ru$_3$O(Ac)$_6$(py)$_2$]$^+$ and [Ru$_3$O(Ac)$_6$(py)$_2$(pz)$_2$]$^+$ clusters, as shown in Table 1. The resonance peaks for the pyrazine ligand are expected to change drastically, due to its double coordination with the ruthenium ions. In this case, both the $\delta_1$ and $\delta_2$ protons are susceptible to the paramagnetic anisotropy of the metal ions, and their peaks should occur in a high field region (-0.34 and 0.31 ppm, respectively).

Comparative cyclic voltammograms for the [Ru$_3$O(Ac)$_6$(py)$_2$(pz)$_2$]$^{3+}$ and [Ru$_3$O(Ac)$_6$(pz)$_2$Ru$_3$O(Ac)$_6$(py)$_2$]$^{3+}$ clusters can be seen in Fig. 3. The dodecanuclear cluster exhibits a strong, reversible wave at $E_{1/2} = 1.23$ V and a shoulder at 1.35 V involving the three peripheral and the central Ru$^{III}$/Ru$^{IV}$/Ru$^{III}$ clusters, respectively, generating the corresponding Ru$^{IV}$/Ru$^{III}$Ru$^{III}$ species. It should be noted that the $E_{1/2}$ values for the [Ru$_3$O(Ac)$_6$(py)$_2$(pz)$_2$]$^{3+}$ and [Ru$_3$O(Ac)$_6$(pz)$_2$]$^{3+}$ clusters, i.e., 1.22 and 1.32 V$^{10}$, are very close to the ones observed for the tetrameric species. The clusters undergo further oxidation at 2.2 V (Fig. 3) generating the corresponding Ru$^{IV}$/Ru$^{IV}$/Ru$^{III}$ species; however, the process is near the limit of the working potential for acetonitrile, and coupled reactions with the solvent may also be involved.

Figure 3. Cyclic voltammogram of the (A) [Ru$_3$O(Ac)$_6$(py)$_2$(pz)$_2$]$^+$ (4.5 mM) and (B) [Ru$_3$O(Ac)$_6$(pz)$_2$Ru$_3$O(Ac)$_6$(py)$_2$]$^{3+}$ (1.1 mM) clusters in CH$_3$CN, 0.1 M TEAP, 25 °C.
The reduction of the Ru III/Ru III dodecanuclear cluster to the corresponding Ru III/Ru II species proceeds according to two reversible steps, at $E_{1/2} = 0.37$ and 0.22 V, ascribed to the central $[\text{Ru}_3\text{O}(_3\text{Ac})_6(\text{pz})_3]$ and the peripheral $[\text{Ru}_3\text{O}(_3\text{Ac})_6(\text{py})_2(\text{pz})]$ units, respectively. The corresponding $E_{1/2}$ values for the isolated trinuclear clusters, $[\text{Ru}_3\text{O}(_3\text{Ac})_6(\text{pz})_3]^{10+}$ and $[\text{Ru}_3\text{O}(_3\text{Ac})_6(\text{py})_2(\text{pz})]^{10+}$, are 0.32 and 0.21 V, respectively.

The next reduction process, which converts the Ru III/Ru III species to the corresponding Ru III/Ru II oxidation state, occurs in three steps, at $E_{1/2} = -0.71$, -0.99 and -1.16 V. The $E_{1/2}$ values for the isolated $[\text{Ru}_3\text{O}(_3\text{Ac})_6(\text{pz})_3]$ and $[\text{Ru}_3\text{O}(_3\text{Ac})_6(\text{py})_2(\text{pz})]$ clusters are -0.78 and -0.98 V, respectively. The occurrence of three peaks at the $[\text{Ru}_3\text{O}(_3\text{Ac})_6(\text{pz})_3]$ center at -0.71 V has a strong influence on the reduction of the peripheral $[\text{Ru}_3\text{O}(_3\text{Ac})_6(\text{py})_2(\text{pz})]$ groups, splitting their corresponding wave into two peaks, separated by 0.17 V. The splitting of the electrochemical waves for the equivalent units in a polymeric system is indicative of a strong electronic interaction via the pyrazine bridging ligands. The role of the pyrazine ligands is particularly important in this case, as they contribute to the stabilization of the lower oxidation states of the clusters by means of backbonding interactions with the ruthenium ions. When the interaction between the electrochemically active centers is weak, the statistical factor predominates, and a single wave is usually observed at the characteristic redox potential of the isolated species.

In conclusion, the dodecanuclear cluster synthesized in this work exhibits spectroscopic (NMR) and electrochemical behavior consistent with the proposed composition. The complex is the prototype for a series of extended clusters under investigation in this laboratory, employing triangular $[\text{Ru}_3\text{O}(_3\text{Ac})_6\text{L}_3]$ units as the building blocks.

Acknowledgments

We are grateful to FAPESP, CNPq and PADCT for financial support.

References


FAPESP helped in meeting the publication costs of this article.