

Synthesis and Characterization of a Dodecanuclear Ruthenium Pyrazine Cluster

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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 $[\text{Ru}_3\text{O}(\text{Ac})_6\{(\text{pz})\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2\}_3]^{4+}$ (Ac = íon acetato, pz = pirazina, py = piridina), formada por quatro unidades do tipo $[\text{Ru}_3\text{O}(\text{Ac})_6\text{L}_3]^+$ unidas por pontes de pirazina, em simetria D_{3h} . Nesse tetrâmero, 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 unities *via* bridging ligands, is reported in this work. The prototype species consists of a new dodecanuclear complex of the general formula $[\text{Ru}_3\text{O}(\text{Ac})_6\{(\text{pz})\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2\}_3]^{4+}$ (Ac = acetate ion, pz = pyrazine, py = pyridine), exhibiting four $[\text{Ru}_3\text{O}(\text{Ac})_6\text{L}_3]^+$ unities bridged by pyrazine ligands, according to a D_{3h} symmetry. The electronic interaction between the various unities 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 $[\text{Ru}_3\text{O}(\text{Ac})_6\text{L}_3]^n$ 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 chemistry¹⁻¹³, reactivity¹⁴⁻¹⁵ and catalytic properties¹⁶⁻¹⁷. The central unity employed, $[\text{Ru}_3\text{O}(\text{Ac})_6(\text{pz})_3]^n$, and its ability to bind transition metal complexes have been previously studied in this laboratory¹⁸⁻²¹. Here, we have extended the previous work¹⁸⁻²⁰ to a novel dodecanuclear species containing four triangular ruthenium acetate unities 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 ¹H 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 complexes¹⁻¹³. The synthesis of the dodecanuclear cluster²¹, $[\text{Ru}_3\text{O}(\text{Ac})_6\{(\text{pz})\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2\}_3][\text{PF}_6]_4$ 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 NH_4PF_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 $\text{C}_{90}\text{H}_{108}\text{N}_{12}\text{O}_{52}\text{P}_4\text{F}_{24}\text{Ru}_{12}$: C, 27.1; N, 4.2, H, 2.8. Found: C, 26.6; N, 3.8; H, 2.8.

¹H NMR spectra were recorded on a Bruker AC 200 spectrometer, in CD_3CN . The electronic spectra were re-

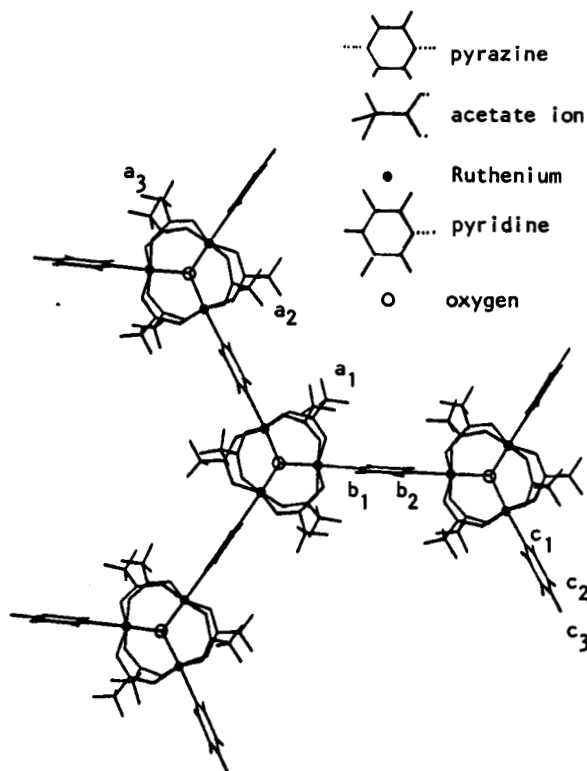


Figure 1. Structural representation of the $[\text{Ru}_3\text{O}(\text{Ac})_6(\text{pz})\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2]^{4+}$ cluster, with a theoretical, energy minimized configuration based on molecular mechanic (MM^+) calculations.

corded on a Hewlett Packard model 8452-A diode-array spectrophotometer. Spectral deconvolution was carried out using a modified version of the SPECSOLV program²². 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 potentiostat and a model 175 universal programmer. A platinum disk electrode was employed for the measurements, using the conventional Luggin capillary arrangement with an Ag/AgNO_3 (0.010 M) reference electrode ($E^\circ = 0.503$ 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 $[\text{Ru}_3\text{O}(\text{Ac})_6\text{L}_3]^+$ groups consisting of three ruthenium ions formally in +III oxidation state, *i.e.*, $\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$. These species exhibit composite bands at 716 nm ($\log \epsilon = 4.1$), 616 nm (sh = shoulder), and 514 nm (sh), ascribed to metal-metal transitions^{4,8,10} within the triangular unities, in addition to a cluster-to-pyrazine charge-transfer band at 420 nm¹⁰, and a cluster-to-pyridine charge-transfer band around 310 nm⁸, as shown in Fig. 2. The electronic spectrum of the $[\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2(\text{pz})]^+$ isolated species (Fig. 2),

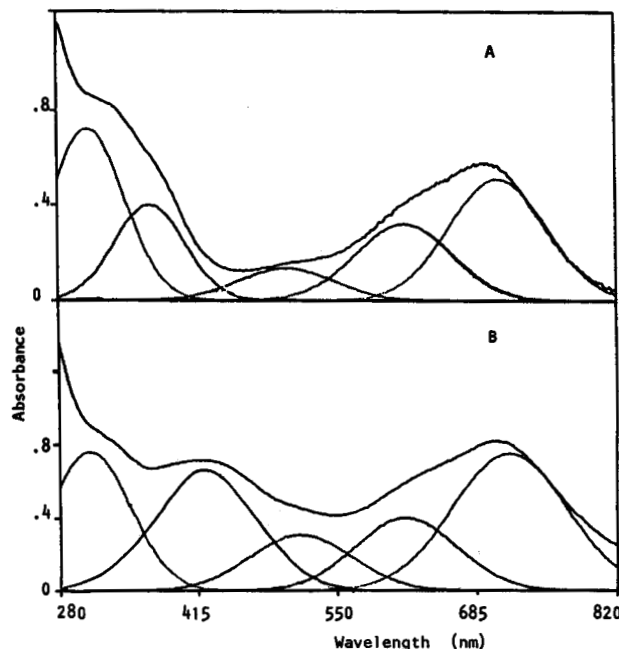


Figure 2. Electronic spectra of the (A) $[\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2(\text{pz})]^+$ and (B) $[\text{Ru}_3\text{O}(\text{Ac})_6\{(\text{pz})\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2\}_3]^{4+}$ clusters in CH_3CN , showing the main Gaussian components.

exhibits the corresponding metal-metal bands at 706 nm ($\log \epsilon = 3.8$), 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 unities *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 $4d^5$ Ru^{III} 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 a_2 , a_3 and a_1 acetate protons illustrated in Fig. 1. The a_2 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. ^1H NMR chemical shift data (ppm)^a for the (A) $[\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_3]^+$, (B) $[\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2(\text{pz})]^+$ and (C) $[\text{Ru}_3\text{O}(\text{Ac})_6\{(\text{pz})\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2\}_3]^{4+}$ clusters.

(A)	(B)	(C)	Assignments ^b	
CD_2Cl_2	CD_2Cl_2	CD_3CN	CD_3CN	
4.83 (18)	4.34 (12)	5.14 (12)	4.83 (36)	Ac (a ₂) protons
	4.82 (6)	5.48 (6)	5.14 (18)	Ac (a ₃) protons
			5.64 (18)	Ac (a ₁) protons
0.45 (6)	-0.50 (4)	0.20 (4)	-0.22 (12)	py (c ₁) protons
5.76 (6)	4.83 (4)	5.67 (4)	5.35 (12)	py (c ₂) protons
6.51 (3)	5.81 (2)	6.68 (2)	6.52 (6)	py (c ₃) protons
	0.70 (2)	0.74 (2)	0.31 (6)	pz (b ₂) protons
	5.52 (2)	6.05 (2)	-0.34 (6)	pz (b ₁) protons

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 a₁ 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 ions²³. 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 ^1H aromatic protons shown in Table 1.

The pyridine peaks associated with the dodecanuclear species are correlated with those observed for the $[\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_3]^+$ and $[\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2(\text{pz})]^+$ 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 b₁ and b₂ 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 $[\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2(\text{pz})]^+$ and $[\text{Ru}_3\text{O}(\text{Ac})_6\{(\text{pz})\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2\}_3]^{4+}$ 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 $\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$ clusters, respectively, generating the corresponding $\text{Ru}^{\text{IV}}\text{Ru}^{\text{IV}}\text{Ru}^{\text{III}}$ species. It should be noted that the $E_{1/2}$ values for the $[\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2(\text{pz})]^{2+/+}$ and $[\text{Ru}_3\text{O}(\text{Ac})_6(\text{pz})_3]^{2+/+}$ clusters, *i.e.*, 1.22 and 1.32 V¹⁰, 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 $\text{Ru}^{\text{IV}}\text{Ru}^{\text{IV}}\text{Ru}^{\text{IV}}$ species; however, the process is near the limit of the working potential for acetonitrile, and coupled reactions with the solvent may also be involved.

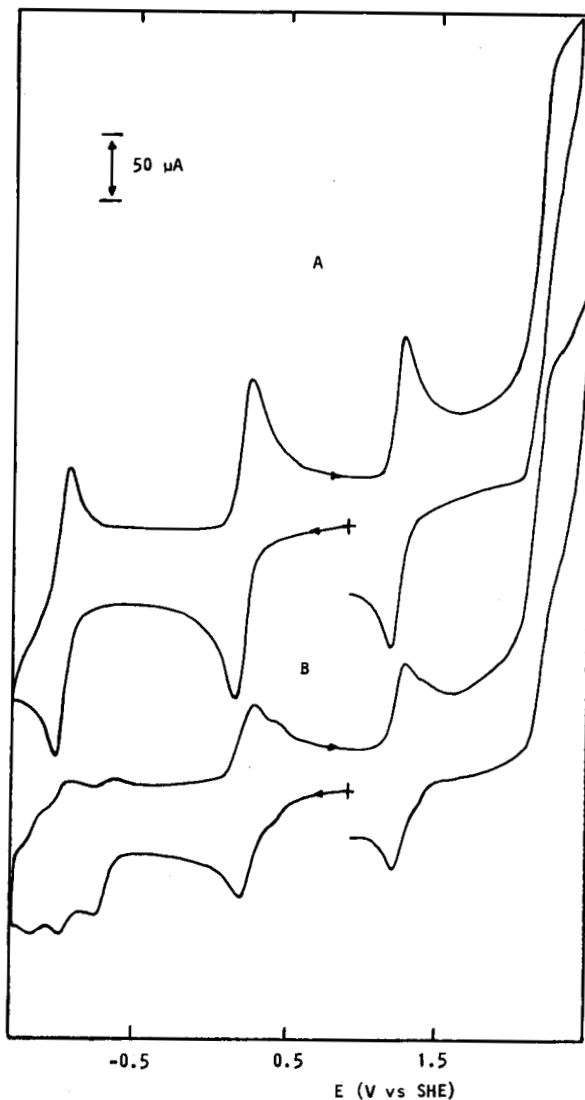


Figure 3. Cyclic voltammogram of the (A) $[\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2(\text{pz})]^+$ (4.5 mM) and (B) $[\text{Ru}_3\text{O}(\text{Ac})_6\{(\text{pz})\text{Ru}_3\text{O}(\text{Ac})_6(\text{py})_2\}_3]^{4+}$ (1.1 mM) clusters in CH_3CN , 0.1 M TEAP, 25 °C.

The reduction of the Ru^{III}Ru^{III}Ru^{III} dodecanuclear cluster to the corresponding Ru^{III}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 [Ru₃O(Ac)₆(pz)₃] and the peripheral [Ru₃O(Ac)₆(py)₂(pz)] unities, respectively. The corresponding $E_{1/2}$ values for the isolated trinuclear clusters, [Ru₃O(Ac)₆(pz)₃]⁺⁰ and [Ru₃O(Ac)₆(py)₂(pz)]⁺⁰, are 0.32^{10} and 0.21 V, respectively.

The next reduction process, which converts the Ru^{III}Ru^{III}Ru^{II} species to the corresponding Ru^{III}Ru^{II}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 [Ru₃O(Ac)₆(pz)₃] and [Ru₃O(Ac)₆(py)₂(pz)] clusters are -0.78 and -0.98 V, respectively. The occurrence of three peaks indicates that the reduction of the [Ru₃O(Ac)₆(pz)₃] center at -0.71 V has a strong influence on the reduction of the peripheral [Ru₃O(Ac)₆(py)₂(pz)] groups, splitting their corresponding wave into two peaks, separated by 0.17 V. The splitting of the electrochemical waves for the equivalent unities 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 observed²⁴ 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 [Ru₃O(Ac)₆L₃] unities as the building blocks.

Acknowledgments

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