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Synthesis and Spectroscopic Characterization of Trinuclear $[Ru_3O(O_2CCH_3)_6(pyrazine)_3]^{0,+}$ Clusters

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Summary. $[Ru_3O(O_2CCH_3)_6(pyrazine)_3]^{0,+}$ clusters have been synthesized and characterized based on electronic, infrared and resonance Raman spectra. Selective enhancement of the pyrazine and $Ru_3O(O_2CCH_3)_6$ vibrational modes has been observed in the case of the reduced cluster using excitation wavelengths close to the metal-to-pyrazine and metal-metal charge transfer band in the visible region.

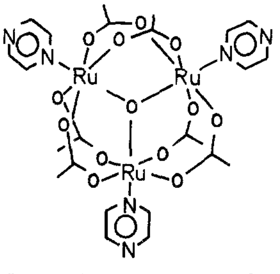
Keywords. Resonance Raman; Ruthenium cluster.

Synthese und spektroskopische Charakterisierung von dreikernigen $[Ru_3O(O_2CCH_3)_6(Pyrazin)_3]^{0,+}$-Clustern

Zusammenfassung. Es wurden $[Ru_3O(O_2CCH_3)_6(Pyrazin)_3]^{0,+}$-Cluster dargestellt und mittels Elektronen-, Infrarot- und Resonanz-Raman-Spektren charakterisiert. Im Fall der reduzierten Cluster wurde bei Anregungswellenlängen nahe den Metall-Pyrazin- und Metall-Metall-Charge-Transfer-Banden im sichtbaren Bereich eine selektive Anhebung der Pyrazin- und $Ru_3O(O_2CCH_3)_6$-Vibrationen beobachtet.

Introduction

Ruthenium clusters of general formula $[Ru_3O(OOCCH_3)_6L_3]$ are of special interest because of their extensive, mixed-valence chemistry [1–6]. These complexes exhibit a triangular structure strongly held by acetate bridges and a central μ-oxo-bridge [1–3], as well as by extended metal-metal bonds. In this work, we report the synthesis and characterization of the $[Ru_3O(OOCCH_3)_6(pz)_3]^{0,+}$ cluster, (*pz* = pyrazine), based on electronic, infrared and resonance Raman spectra. To our knowledge, this cluster has never been investigated before.



$[Ru_3O(OOCCH_3)_6(pz)_3]$

Experimental

The $[Ru_3O(OOCCH_3)_6(pz)_3]PF_6$ and $[Ru_3O(OOCCH_3)_6(pz)_3]$ clusters were synthesized by heating at reflux, for 5 minutes, 25 ml of a methanol solution containing 1 mmol of $[Ru_3O(OOCCH_3)_6(CH_3OH)_3](OOCCH_3)$ [4] and 3.0 g (38 mmol) of pyrazine (Aldrich). In order to isolate the $[Ru_3O(OOCCH_3)_6(pz)_3]PF_6$ product, 0.5 g (3 mmol) of NH_4PF_6 was added, and the resulting mixture was cooled to room temperature. The black crystalline solid was collected on a filter, washed with water and 3 ml of ethanol. Anal. calcd. for $Ru_3C_{24}H_{30}N_6O_{13}PF_6$: C 27.21, H 2.83, N 7.94; found: C 26.5, H 2.9, N 7.8. The $[Ru_3O(OOCCH_3)_6(pz)_3]$ cluster was obtained after the reflux step, by cooling the solution to 0°C and adding a few drops of aqueous hydrazine (10%). The brown solution was concentrated using a rotary evaporator. The resulting solid was collected on a filter and washed with small amounts of ethanol. Calcd. for $Ru_3C_{24}H_{30}N_6O_{13}$: C 31.53, H 3.28, N 9.20; found: C 30.7, H 3.4, N 9.1.

The electronic spectra of the complexes were recorded on a Cary 17, or a Hewlett-Packard model HP 8451-A diode-array spectrophotometer. The infrared spectra of the solids dispersed in KBr pellets (or in Nujol/Fluorolube) were recorded on a Perkin-Elmer model 783 spectrophotometer. Resonance Raman spectra were recorded on a Jarrell-Ash instrument, using Spectra-Physics argon and krypton ion lasers. The measurements were carried out with the solids dispersed in compressed pellets with a supporting medium of sodium sulphate (1 : 100), and placed in a spinning cell to avoid the decomposition of the complexes. The intensities were measured as peak heights relative to the sulphate Raman band at 994 cm^{-1}.

Results and Discussion

The electronic spectra of the $[Ru_3O(OOCCH_3)_6(pz)_3]^{0,+}$ clusters in aqueous solution are shown in Fig. 1. The assignment of the absorption bands can be suggested based on the qualitative molecular orbital scheme proposed by Cotton and Norman [3] and by Baumann et al. [4] for the triangular Ru_3O cluster. The symmetry assumed is D_{3h}. The central oxygen atom is considered to be sp^2 hybridized leaving a single p orbital to interact with the d_{zy} orbitals of the three ruthenium ions, in order to generate two a_2'' levels and one e'' level. Metal-metal bonding involving the combination of the neighboring $Ru(d_{xz})$ orbitals leads to the $e'(1)$ and a_2' levels. The remaining $d_{x^2-y^2}$ orbitals are separated by a considerable distance, but can interact weakly via a through-space interaction, giving rise to the $e'(2)$ and a_1' levels.

The $[Ru_3O(OOCCH_3)_6(pz)_3]^+$ complex can be formally described as $Ru^{III}Ru^{III}Ru^{III}$, exhibiting the electronic configuration $(a_2'')^2(e')^4(a_1')^2(e')^4(e'')^4(a_2')$. There is a second empty a_2'' orbital. The complex displays strong absorption bands

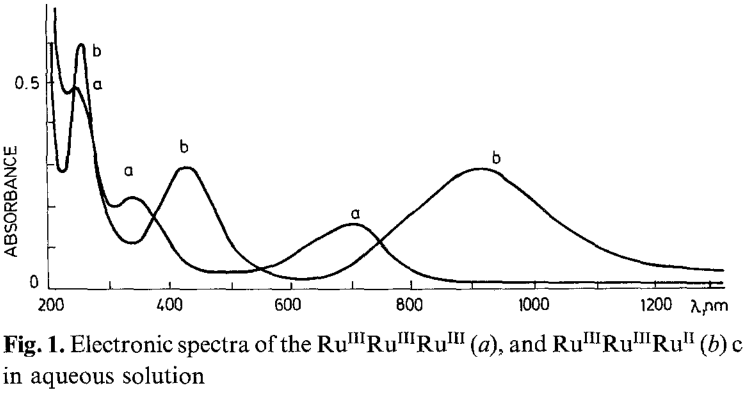


Fig. 1. Electronic spectra of the $Ru^{III}Ru^{III}Ru^{III}$ (*a*), and $Ru^{III}Ru^{III}Ru^{II}$ (*b*) clusters ($1.0 \cdot 10^{-3}$ mol dm^{-3}) in aqueous solution

at 260 nm ($\varepsilon = 20\,600\,dm^3\,mol^{-1}\,cm^{-1}$), 340 nm ($\varepsilon = 9\,600\,dm^3\,mol^{-1}\,cm^{-1}$) and 710 nm ($\varepsilon = 6\,600\,dm^3\,mol^{-1}\,cm^{-1}$). Deconvolution of the absorption band at 710 nm leads to two main components at 705, 603 nm and another weak one at 495 nm, ascribed to the symmetry allowed $e'' \rightarrow a_2''$ and $a_1' \rightarrow a_2''$ transitions, and to the $e'(1) \rightarrow a_2''$ electric dipole forbidden transition, as in the analogous pyridine complex [4]. The pyrazine ligands have π orbitals which can interact with the $Ru(d_\pi)$ orbitals of a_2'' and e'' symmetry, if the plane of the ligand is parallel to the plane of the cluster, or with the a_2' and $e'(1)$ orbitals, in the case of a perpendicular configuration [4]. Since the ligands are rotating freely in solution, all four orbitals can be involved in an average interaction. The absorption band in the region of 300–400 nm in the trinuclear ruthenium(III) clusters has not yet been assigned, but a cluster-to-pyrazine (e.g., $e'' \rightarrow p_\pi{}^*$) charge-transfer transition seems quite probable. The absorption band at 260 nm is also observed in aromatic N-heterocyclic molecules, and can be ascribed to the π-π^* transition in the pyrazine ligand.

In the case of the $Ru^{III}Ru^{III}Ru^{II}$ μ-oxo complex, the absorption band at 260 nm is more intense ($\varepsilon = 28\,000\,dm^3\,mol^{-1}\,cm^{-1}$). The visible and near-infrared bands are shifted, respectively, to 420 nm ($\varepsilon = 12\,800\,dm^3\,mol^{-1}\,cm^{-1}$) and 905 nm ($\varepsilon = 12\,600\,dm^3\,mol^{-1}\,cm^{-1}$), with Gaussian components at 950, 815 and 610 nm.

The $[Ru_3O(OOCCH_3)_6(pz)_3]$ cluster exhibits strong resonance Raman effects, as one can see in Fig. 2, in constrast to the $[Ru_3O(OOCCH_3)_6(pz)_3]PF_6$ complex, which

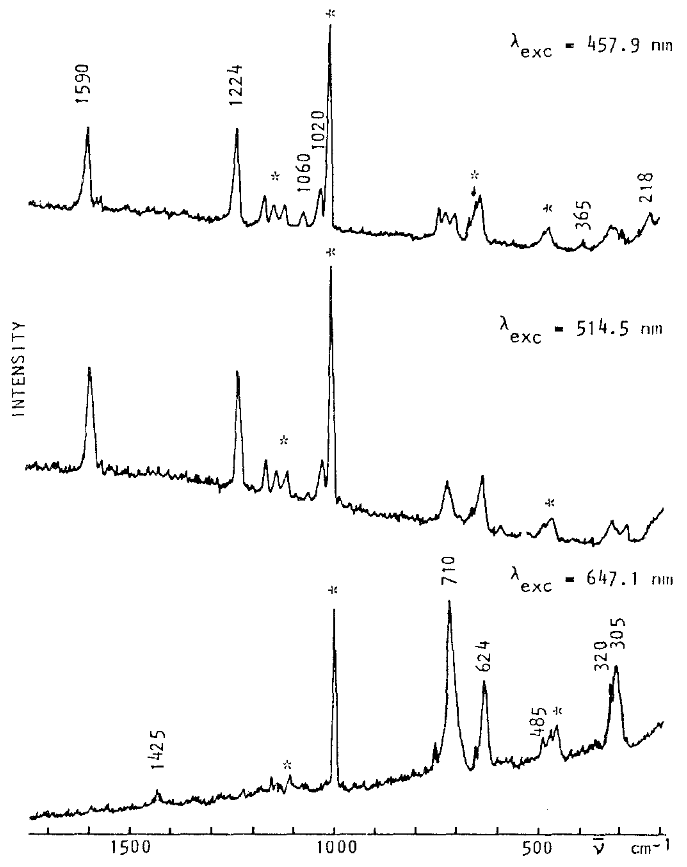


Fig. 2. Resonance Raman spectra of the $[Ru_3O(OOCCH_3)_6(pz)_3]$ cluster at several excitation wavelengths (* = sulphate peak)

shows only a weak enhancement of the 1 610 and 1 430 cm^{-1} vibrational peaks, using the available excitation wavelengths in the 457–647 nm range.

A comparison of the resonance Raman and the infrared spectral data can be seen in Table 1. The assignment of the vibrational spectra was attempted, as shown in the table, based on the data of related clusters [7–10] and pyrazine species [11–13]. In general, the vibrational peaks of the trinuclear clusters correlate with those reported in the literature [7–9], except for the peak at 710 cm^{-1} (Fig. 2), which was ascribed to the $v_{as}(Ru_3O)$ vibrational mode because of its resonance Raman behaviour. This frequency seems a little high with respect to a previous assignment for the $[Ru_3O(OOCCH_3)_6(NC_5H_5)_3]ClO_4$ complex [8]; however, it is very close to those recently assigned to $v_{as}(Fe_3O)$, at 600 and 695 cm^{-1}, for the

Table 1. Infrared and Raman vibrational frequencies for the $[Ru_3O(OOCCH_3)_6(pyrazine)_3]^{0,+}$ clusters[a]

$[Ru_3O(OOCCH_3)_6(pz)_3]PF_6$		$[Ru_3O(OOCCH_3)_6(pz)_3]$		Assignment
IR	Raman[b]	IR	Raman[b]	
1 610 sh	1 610 s	1 585 s	1 590 s	ν(*pz* ring), A_1
1 590 s		1 545 m		$\nu_{as}(COO)$
1 530 s		1 520 sh		ν(*pz* ring), B_1
1 480 m		1 480 m		ν(*pz* ring), A_1
1 420 s	1 430 w[c]	1 425 s	1 425 w[c]	$\nu_s(COO)$
1 350 s		1 346 m		$\delta(CH_3)$
1 225 m	1 230 m	1 218 w	1 224 s	δ(CH ring in plane), A_1
1 160 s		1 155 m		ν(*pz* ring), B_1
1 122 s		1 120 w		δ(CH ring in plane), A_1
1 080 m		1 080 w		ν(*pz* ring breath), A_1
1 058 s	1 060 w	1 040 m	1 060 w	δ(CH ring in plane), B_1
1 025 m	1 025 w	1 030 m	1 020 m	ν(*pz* ring breath), A_1
1 015 m		1 015 s		$\rho(CH_3)$
950 m		955 w		δ(CH ring out of plane), A_2
848 s				$\nu_3(PF_6^-)$, T_{1u}
808 s		808 s		δ(CH ring out of plane), B_2
740 m	710 w	740 w		δ(*pz* ring), B_2
605 w	600 w[c]	695 s	710 s[c]	$\nu_{as}(Ru_3O)$
680 s		685 s		δ(*pz* ring in plane), A_1
645 w				$\delta(OCO)$
620 m	620 s[c]	622 m	624 s[c]	$\pi(COO)$
560 s				$\nu_4(PF_6^-)$, T_{1u}
490 s		485 m	485 w[c]	ν(Ru—OCO)
375 m		365 m		δ(*pz* ring out of plane), B_2
350 m	355 w[c]	320 w	320 m[c]	ν(Ru—OCO)
305 w	292 s[c]	305 w	305 s[c]	$\delta_s(Ru_3O)$

[a] Solid state, in the presence of KBr (IR) or Na_2SO_4 (Raman)
[b] Excitation wavelength = 457 nm
[c] Excitation wavelength = 647 nm

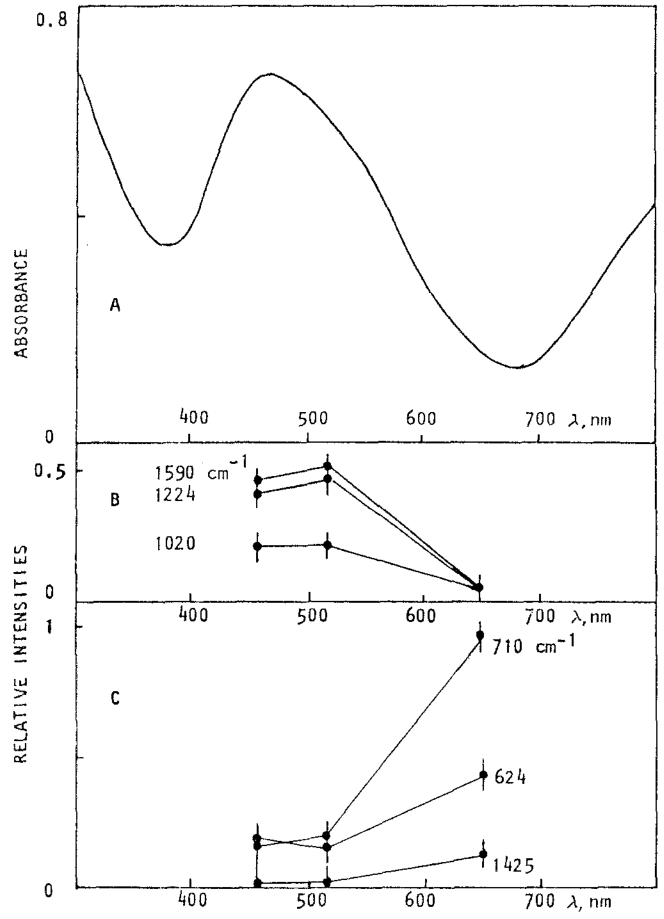


Fig. 3. Electronic spectrum of the $[Ru_3O(OOCCH_3)_6(pz)_3]$ cluster, as a solid suspension in fluorolube (*A*), and resonance Raman excitation profiles for the pyrazine (*B*) and $Ru_3O(OOCCH_3)_6$ (*C*) vibrational peaks

$[Fe_3O(OOCCH_3)_6(NC_5H_5)_3]NO_3$ and $[Fe_3O(OOCCH_3)_6(NC_5D_5)_3]$ clusters, respectively [7].

In the solid state, the $[Ru_3O(OOCCH_3)_6(pz)_3]$ cluster exhibits an electronic spectrum (Fig. 3) with small red shifts with respect to those of the corresponding aqueous solutions. There is also a small splitting of the high energy visible absorption bands, indicating, perhaps, some structural distortion in the solid state.

The vibrational peaks of the complex are enhanced according to two excitation profiles, as one can see in Fig. 3. The optical excitation at 457 nm induces a resonance Raman effect with the electronic transition at 460 nm, leading to selective enhancement of pyrazine vibrational modes. These observations are consistent with the assignment of a cluster-to-pyrazine charge-transfer transition for the visible electronic band. The enhanced vibrations correlate with the totally symmetric modes of pyrazine, a fact which can be explained according to the A term in the theoretical formalisms of the resonance Raman effect [14]. On the other hand, the Ru_3O and COO^- vibrational peaks in the region of 710–300 cm^{-1} are selectively enhanced near the low energy electronic band, being consistent with the involvement of a metal-metal transition.

Acknowledgements

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