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Synthesis of a Trinuclear Ruthenium Cluster Containing Pyridine and 4-Acetylpyridine Ligands and its Immobilization on Functionalized Silica

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Summary. The trinuclear cluster $[Ru_3O(Ac)_6(py)_2(acpy)]PF_6$ (*py*: pyridine; *acpy*: 4-acetylpyridine) has been synthesized and anchored on functionalized silica. Five successive redox couples exhibiting $E^\circ = -1.4, -0.98, 0.21, 1.23$, and 2.2 V *vs.* SHE have been characterized in acetonitrile solutions based on cyclic voltammetry and spectroelectrochemical measurements. The redox and spectroscopic properties are maintained in the immobilized species, allowing its use in optodes and in electron transfer processes.

Keywords. Ruthenium acetate cluster; Spectroelectrochemistry; Functionalized silica.

Synthese eines dreikernigen Rutheniumclusters mit Pyridin- und 4-Acetylpyridinliganden sowie seine Fixierung auf funktionalisiertem Kieselgel

Zusammenfassung. Der dreikernige Cluster $[Ru_3O(Ac)_6(py)_2(acpy)]PF_6$(*py*: Pyridin; *acpy*: 4-Acetylpyridin) wurde hergestellt und an funktionalisiertem Kieselgel verankert. Mit Hilfe cyclischer Voltammetrie und spektroelektrochemischer Messungen konnten fünf aufeinanderfolgende Redoxpaare beobachtet werden ($E^0 = -1.4, -0.98, 0.21, 1.23$ und 2.2 V bezüglich SHE). Die elektrochemischen und spektroskopischen Eigenschaften bleiben in den fixierten Clustern erhalten und erlauben deren Verwendung in Optoden und bei Elektronenübertragungsprozessen.

Introduction

Ruthenium clusters of the general formula $[Ru_3O(Ac)_6L_3]^n$ have been a matter of great interest due to the wide variety of their redox properties in the potential range of −2.0 to 2.5 V, as well as to their potential use as building blocks in supramolecular assemblies [1–6]. The immobilization of this type of ruthenium acetate clusters at the surface of electrodes, based upon its confinement into cyanometallate films or on the formation of functionalized polypyrrole films, has also been described in the literature [7, 8]

Herein we report the synthesis as well as the spectroscopic and electrochemical properties of a new mixed species containing one 4-acetylpyridine and two pyridine ligands (Fig. 1A) and its immobilization onto aminopropyl functionalized

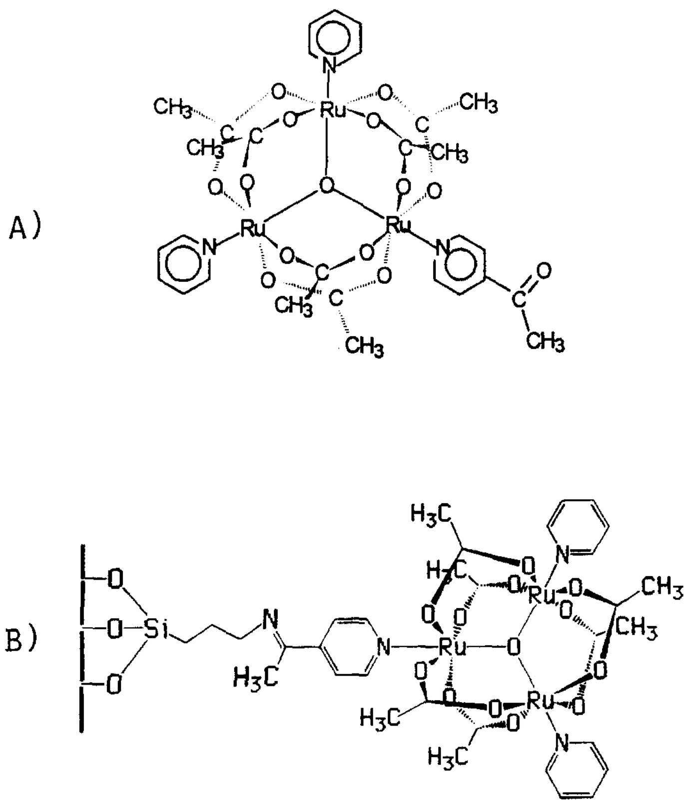

Fig. 1. (A) Structural representation of $[Ru_3O(Ac)_6(\textit{py})_2(\textit{acpy})]PF_6$; (B) its immobilized form on functionalized silica

silica surface. The *acpy* ligand was introduced as an anchoring group, linking the cluster moiety covalently to the aminopropyl residues *via Schiff* base formation as illustrated in Fig. 1B.

Results and Discussion

Infrared spectra

The infrared spectra of the cluster in free and anchored form are presented in Fig. 2. The peak at 1700 cm^{-1} (Fig. 2A) for the free cluster, corresponding to the carbonyl stretching mode ($\nu_{C=O}$) of the coordinated 4-acetylpyridine ligand, disappears when the complex is anchored (Fig. 2B), thus confirming the formation of a *Schiff* base. The peaks at 1608 and 1487 cm^{-1} are associated with stretching vibrations of the aromatic ligands ($\nu_{C=C}$) and appear superimposed to the broad vibrational peak of adsorbed water molecules in the modified silica. The vibrational peaks characteristic of the CO_2^- groups are located at 1551, 1426, and 680–690 cm^{-1} whereas the peaks in the range of 1353–1050 cm^{-1}, corresponding to the C–H deformation modes in the free species, are masked by the broad Si–O vibrational band around 1100 cm^{-1} in the modified silica.

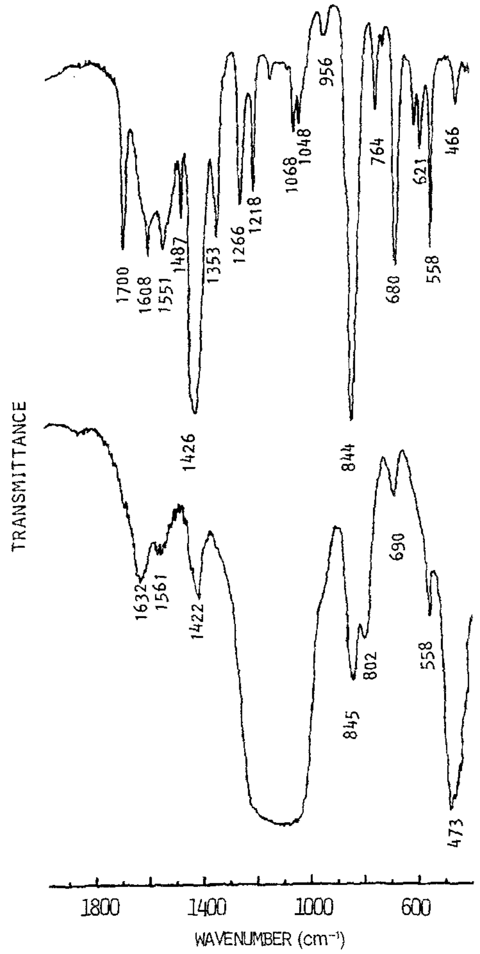

Fig. 2. (A) FTIR spectra of $[Ru_3O(Ac)_6(py)_2(acpy)]PF_6$; and (B) its immobilized form (KBr pellets)

The bands associated with the counterions are well defined and can be used to probe the redox states of the anchored cluster. In the case of +1 state, the FTIR spectra show two strong bands ascribed to the active modes of PF_6^- ($\delta_{F-P-F} = 558cm^{-1}, \nu_{P-F} = 844\ cm^{-1}$). When the cluster is oxidized to the +2 state with Ce(IV) sulfate, the stretching vibration of the SO_4^{2-} counterion can be detected in the spectra at 1080 cm^{-1}, whereas the PF_6^- vibrational peaks disappear. When the chromophore is reduced with borohydride, neither the PF_6^- nor the SO_4^{2-} bands can be detected in the vibrational spectra.

Cyclic voltammetry

A typical cyclic voltammogram of the cluster in acetonitrile solution is presented in Fig. 3.

Five waves can be detected in the voltammograms three of which are essentially reversible (−0.98, 0.21, and 1.23 V), whereas the other two appear less reversibly because of their proximity to the limiting potentials (−1.4 and 2.2 V; increasing background currents).

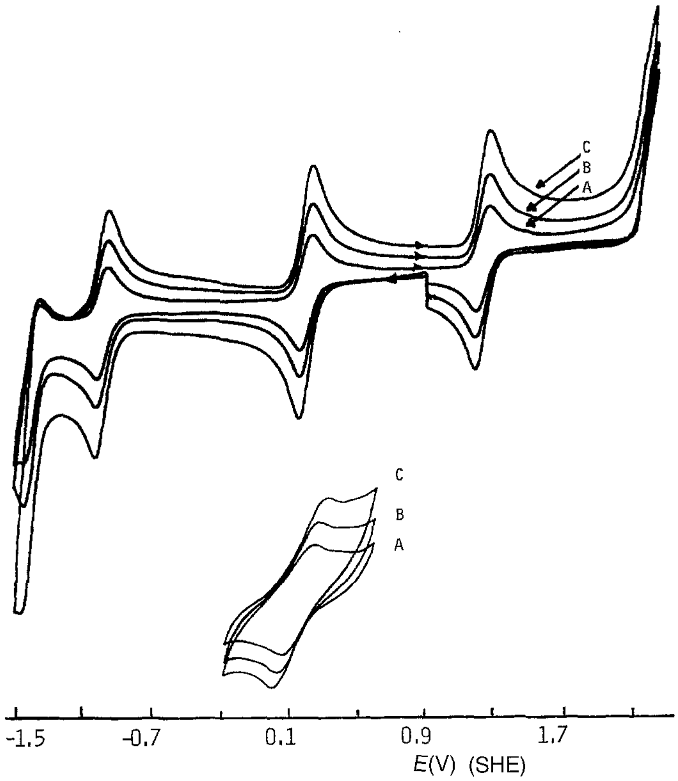

Fig. 3. Cyclic voltammograms of $[Ru_3O(Ac)_6(py)_2(acpy)]^+$ (5.0×10^{-3} mol · dm^{-3} in acetonitrile, 0.10 mol · dm^{-3} tetraethylammonium perchlorate) and of its immobilized form (insert) dispersed into carbon paste in the presence of 0.5 mol·dm^{-3} KCl at (A) 50, (B) 100, and (C) 200 mV·s^{-1}

The oxidation states of the ruthenium ions in $[Ru_3O(Ac)_6(py)_2(acpy)]PF_6$ correspond formally to $Ru^{III}Ru^{III}Ru^{III}$. The five redox waves, in order of decreasing E^0, can be ascribed to the successive redox couples $Ru^{IV}Ru^{IV}Ru^{III}$/ $Ru^{IV}Ru^{III}Ru^{III}$ / $Ru^{III}Ru^{III}Ru^{III}$/$Ru^{III}Ru^{III}Ru^{II}$/$Ru^{III}Ru^{II}Ru^{II}$/$Ru^{II}Ru^{II}Ru^{II}$ by comparison with related clusters reported in the literature [1, 2].

As can be seen in Fig. 3 (inset), the cluster maintains its reversible electrochemical behavior when immobilized onto silica. In aqueous solution, however, the electrochemistry is restricted by the solvent working limits to the $Ru^{III}Ru^{III}Ru^{III}$ / $Ru^{III}Ru^{III}Ru^{II}$ oxidation states with $E^0 = 0.20 \pm 0.01$V. The restriction is eliminated in non aqueous solution; however, the use of carbon paste electrodes would be precluded in this case.

Spectroelectrochemical measurements

The electronic spectra of the free cluster, obtained at several applied potentials, are shown in Fig. 4.

The assignment of the observed electronic transitions can be discussed based on the qualitative molecular orbital scheme previously reported for this type of Ru_3O cluster [1, 4, 9]. It should be noted that in the $[Ru_3O(Ac)_6(py)_2(acpy)]PF_6$

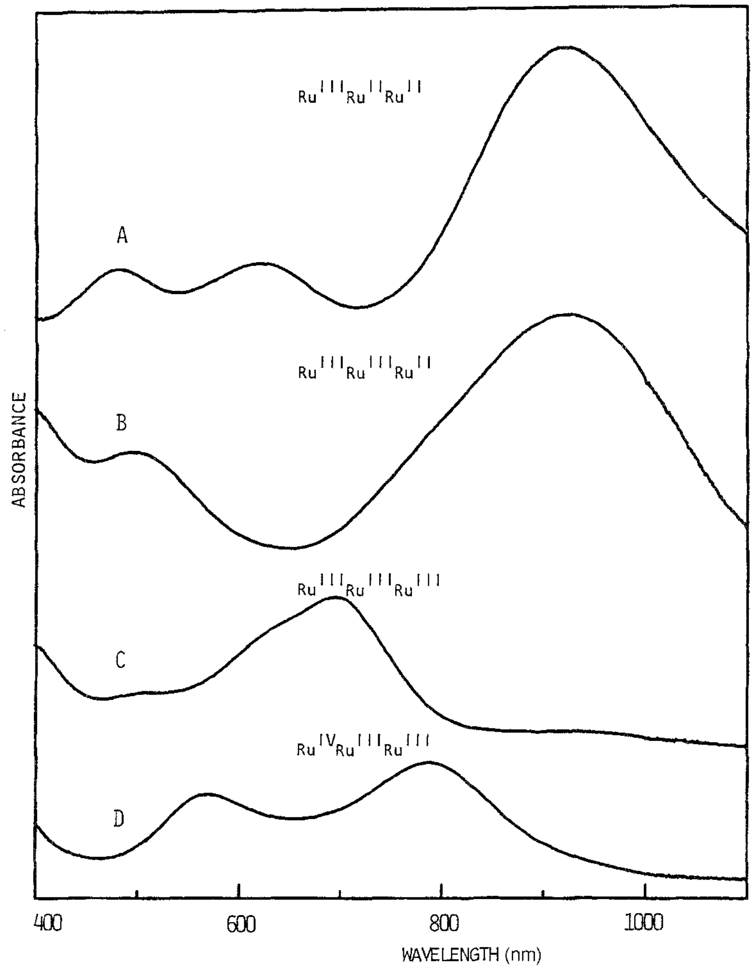

Fig. 4. Fiber optics spectroelectrochemical measurements for $[Ru_3O(Ac)_6(py)_2(acpy)]^+$ (5.0×10^{-3} mol · dm^{-3}) in acetonitrile at (A) – 1.3, (B) – 0.50, (C) 0.50 and (D) 1.4 V *vs.* SHE in the presence of 0.10 mol · dm^{-3} tetraethylammonium perchlorate

complex, both pyridine and 4-acetylpyridine have π^* orbitals of suitable symmetry to interact with the ruthenium d_π orbitals. The electronic spectrum of the starting cluster is very close to that of the $[Ru_3O(Ac)_6(py)_3]PF_6$ analogue [1], consisting of a strong composite band at 695 nm ascribed to the internal transitions of the Ru_3O unit and a less intense band at 395 nm associated with a cluster-to-pyridine (and acetylpyridine) charge transfer transition.

From the spectroelectrochemical results one can see that, as the cluster charge is reduced from +2 to – 1, the electronic bands ascribed to internal transitions in the Ru_3O unit suffer a bathochromic shift from 570 to 922 nm, respectively. It can be figured out that the increase in the number of electrons in the cluster reflects in the energy of the occupied d_π levels, shortening the energy gap associated with the electronic transition. For the cluster with charge +2 ($Ru^{IV}Ru^{III}Ru^{III}$), there are two empty levels available, so that an additional band in 788 nm is observed, arising from a second metal-to-metal transition [4].

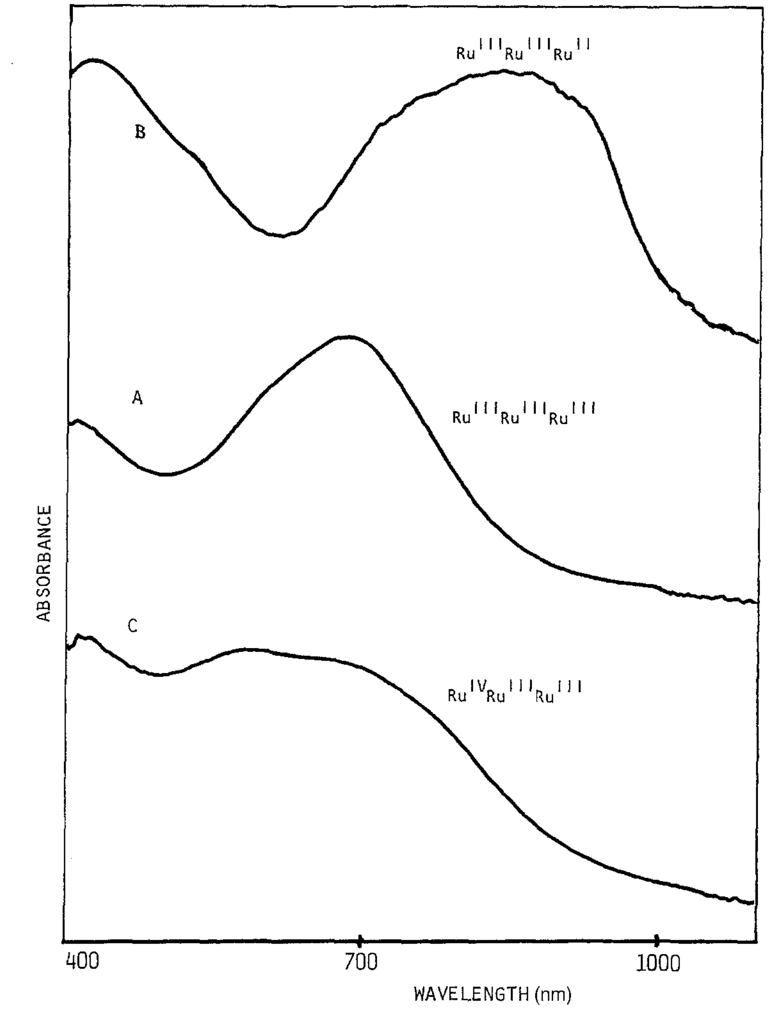

Fig. 5. Spectroelectrochemical behavior of the anchored cluster on functionalized silica (A) in its original redox state (+1), (B) after treatment with sodium borohydride (0), and (C) oxidation with Ce(IV) sulfate (+2)

For the cluster with charge $-1(Ru^{III}Ru^{II}Ru^{II})$, two distinct bands can be observed at 482 and 622 nm, being consistent with the expected metal-to-pyridine and metal-to-4-acetylpyridine charge transfer transitions. In the case of the redox state 0 $(Ru^{III}Ru^{III}Ru^{II})$, these bands are found at 394 and 494 nm. For the $+1(Ru^{III}Ru^{III}Ru^{III})$ and $+2(Ru^{IV}Ru^{III}Ru^{III})$ states, these two bands occur superimposed at 395 and 381 nm, respectively. It should be pointed out that the observed bathocromic shifts accompanying the decrease of the oxidation states are typical of metal-to-ligand charge transfer transitions, reflecting the increase of the electron donor properties of the metal center.

The electronic spectra of the anchored cluster at several oxidation states cannot be obtained in the presence of the carbon paste electrode. However, the several oxidation states can be chemically generated by reacting the anchored species with sodium borohydride of Ce(IV) solutions, and the corresponding spectra recorded using fiber optics reflectance probes are shown in Fig. 5.

The spectroscopic behavior of the anchored cluster resembles that of the free complex in acetonitrile solution, showing the characteristic bands for the $Ru^{IV}Ru^{III}Ru^{III}$, $Ru^{III}Ru^{III}Ru^{III}$ and $Ru^{III}Ru^{III}Ru^{II}$ redox states, the colour changing from light green to red-brown along the series.

In conclusion, the spectroscopic and eletrochemical assays indicated that the cluster maintains its redox and optical properties when immobilized on the modified silica gel surface. Its reversible redox behavior can be exploited for the design of versatile reducing or oxidizing supported catalysts. Immobilization of the cluster onto fiber optic bundle probes makes it possible to use it in redox optodes displaying a wide range of optical responses as a function of the several oxidation states involved.

Experimental

Materials

The starting complex $[Ru_3O(Ac)_6(py)_2(CH_3OH)]PF_6$ was prepared as described elsewhere [1]. The $[Ru_3O(Ac)_6(py)_2(acpy)]PF_6$ complex was synthesized by reacting 0.10 g (0.1 mmol) of $[Ru_3O(Ac)_6(py)_2(CH_3OH)PF_6$ and 0.12 g (1 mmol) of 4-acetylpyridine (Aldrich) in 25 cm^3 of dichloromethane at room temperature. After 20 h, the solid was collected on a filter, washed with diethyl ether, and dried under vacuum.

Yield: 70%; $C_{29}H_{35}N_3O_{13}PF_6Ru_3$; calc.: C 32.2, H 3.3, N 3.9; found: C 31.7, H 3.3, N 3.8.

The functionalization of silica (typically 60 mesh) with 3-aminopropyl trimethoxysilane (Aldrich) was carried out as previously reported [10]. The complex was anchored on the surface by adding 0.20 g (0.2 mmol) of the solid to a suspension of 1.0 g of functionalized silica, containing approximately 0.15 mmol of aminopropyl residues, in 20 cm^3 of methanol. The mixture was allowed to react under stirring at room temperature for 9 h. The solid was filtered, washed with methanol and dichloromethane, and dried under vacuum.

Measurements

Cyclic voltammetry measurements were performed with a Princeton Applied Research instrument, consisting of a model 173 potentiostat and a model 175 universal programmer. In the case of the free cluster species, a platinum disc electrode was employed in the presence of an $Ag/AgNO_3$ (0.01 $mol \cdot dm^{-3}$) reference electrode in acetonitrile containing 0.1 $mol \cdot dm^{-3}$ tetraethylammonium perchlorate (*TEAP*). In the case of the immobilized species, a carbon paste electrode was prepared by mulling 1 g of graphite, 0.1 g of KCl, and 1 cm^3 of nujol together in a mortar until the mixture acquires the consistency of a stiff paste which was packed into the cavity of the electrode. An Ag/AgCl (1 $mol \cdot dm^{-3}$) reference electrode was used. In both cases, a conventional *Luggin* capillary arrangement was utilized with a platinum wire as the auxiliary electrode. All potentials measured in this work were converted to the SHE scale by adding 0.222 V (Ag/AgCl) or 0.503 V ($Ag/AgNO_3$).

The infrared spectra were recorded as KBr pellets on a FTIR spectrophotometer from Midac.

The electronic spectra were obtained on a Hewlett-Packard model 8452-A spectrophotometer or on a Guided Wave model 260 fiber optics spectrophotometer which was also employed for *in situ* spectroelectrochemical assays for the free complex. The electronic spectra of the anchored cluster at several oxidation states were obtained by supporting the solid on a glass frit and then treating it with 1.0 $mol \cdot dm^{-3}$ aqueous sodium borohydride (for reduction) or 0.50 mol dm^{-3} cerium(IV) sulfate (for oxidation) using suction (water jet pump). After drying, the reflectance spectra were recorded using a fiber optics bundle probe connected to the Guided Wave spectrophotometer.

Acknowledgements

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