Table I. Preparative-Scale Electrolysis at 1 V of Benzyl Alcohol (0.2 mmol) on Different Modified Electrodes

entry	modified carbon-felt electrode	amt of electroactive species, 10^7 mol	Q, C[e]	amt of benzaldehyde produced, 10^3 mol
1	C/poly$[Ru(L)_3]^{2+}$–RuO_2	$[Ru(L)_3]^{2+}$, 6.6[a] RuO_2, 6.0[b]	29.3	0.131
2	C/poly$[Ru(L)_3]^{2+}$–Pd(0)	$[Ru(L)_3]^{2+}$, 8.3[a] Pd, 9.5[c]	1.5	0.006
3	C/poly(v^{2+})–RuO_2	v^{2+}, 6.6[d] RuO_2, 7[b]	16.9	0.072

[a] Estimated from the charge under the anodic peak (Ru(II) → Ru(III)). [b] Estimated from the charge obtained for the reduction ($RuO_4^{2-} \rightarrow RuO_2$). [c] Estimated from the charge obtained for the reduction ($Pd^{2+} \rightarrow$ Pd(0)). [d] Estimated from the charge under the first reduction peak ($v^{2+} \rightarrow v^{\bullet+}$). [e] Total number of coulombs passed after 340 min.

electrode two successive quasi-reversible redox couples emerge at 1.41 and 1.65 V (Figure 1C), corresponding probably to the two successive one-electron transfers $RuO_4^{2-} \rightleftarrows RuO_4^- \rightleftarrows RuO_4$.[9] These observations seem to indicate that potentiostating the Pt/poly$[Ru(L)_3]^{2+}$–RuO_2 electrode to 1.1–1.2 V produces in the film RuO_4^{2-} from RuO_2. The addition of benzyl alcohol (8 mM) induces a marked increase in the anodic current of the Pt/poly-$[Ru(L)_3]^{2+}$–RuO_2 electrode above 1.1 V (Figure 1A, curve c). It should be noted that the same experiment conducted with Pt/poly$[Ru(L)_3]^{2+}$ without RuO_2 exhibits only the regular direct oxidation of the alcohol on Pt at 2 V,[10] indicating a good diffusion of the substrate through the film. A preparative-scale electrolysis of a solution containing 0.2 mmol of benzyl alcohol and 0.7 mmol of Na_2CO_3 as a basic agent was carried out at 1.16 V on a carbon-felt electrode (20 × 9 × 4 mm, 47 mg of carbon), coated by 6.3×10^{-7} mol of poly$[Ru(L)_3]^{2+}$ and 6.4×10^{-7} mol of RuO_2. The electrooxidation was stopped when the initial amount of electricity needed to oxidize all the alcohol was reached. The oxidation produced benzaldehyde with 76% current efficiency. No benzoic acid was detected.[11]

In order to specify the respective roles of $[Ru(L)_3]^{3+}$ and RuO_4^{2-} in this oxidative process, we have carried out preparative-scale electrolysis at a less positive potential (1 V) close to the redox potential of the $[Ru(L_3)]^{3+/2+}$ couple, on carbon-felt electrodes modified by three kinds of films: (1) poly$[Ru(L)_3]^{2+}$–RuO_2, (2) poly$[Ru(L)_3]^{2+}$–Pd(0),[12] and (3) poly(v^{2+})–RuO_2, where the polypyrrole film is bonded to a viologen group which is nonelectroactive in the anodic region.[13] Electrolysis of 0.2 mmol of benzyl alcohol in the presence of 0.7 mmol of Na_2CO_3 was stopped after 340 min. At this point the catalytic currents dropped to less than 20% of their initial values. Results are summarized in Table I. It appears that, for the C/poly$[Ru(L)_3]^{2+}$–RuO_2 electrode, the oxidation occurs with a rate markedly slower than that observed at 1.16 V. The comparison between entries 1 and 2 demonstrates that RuO_2 is needed to obtain a significant catalysis at 1 V. This indicates that, in contrast with the case for Pd(0), RuO_2 does not act only as an electronic conductor. The difference between entries 1 and 3 of Table I shows that the use of v^{2+} instead of $[Ru(L)_3]^{2+}$ as the pendant substituent group of the polypyrrole decreases appreciably the efficiency of the electrocatalysis. Since polypyrrole films are known to lose their conductivity and adherence at too high an overpotential (1–1.2 V),[14] the presence of the electroactive $[Ru(L)_3]^{2+}$ group makes the film more conductive and stable at 1 V than the v^{2+} film. The $[Ru(L)_3]^{3+}$ species probably acts as an electron relay for the oxidation of RuO_2.

On the other hand, we found that addition of water up to a percentage of about 4% to the anolyte induced a strong increase of the catalytic current, while a pseudoplateau was reached for higher percentages and improved the stability of the electrode. An electrolysis of a large amount of alcohol (10 mmol), in a 9/1 CH_3CN–H_2O mixture, carried out to the total loss of electroactivity of the C/poly$[Ru(L)_3]^{2+}$–RuO_2 electrode, leads to 4.47 mmol of aldehyde after 490 min with a current efficiency of 96%. No benzoic acid was detected. The turnover (moles of benzaldehyde formed divided by the moles of RuO_2 in the film) was close to 5000. The strong increase of the rate of the catalysis could be due to an easier formation of RuO_4^{2-} in the water–CH_3CN mixture since the potential of the RuO_4^{2-}–RuO_2 system depends on the basicity[3b] of the medium.

In summary this preliminary study demonstrates that a modified electrode based on $[Ru(L)_3]^{2+}$ as an electron relay associated with RuO_2 as an oxidizing agent is useful to the electrooxidation of benzyl alcohol to benzaldehyde. Further investigations are currently being made, in order to improve the lifetime of this type of electrode and to extend its utilization to activate less oxidizable organic compounds.

Acknowledgment. We are grateful to Professor G. Cauquis for his interest in this work and PIRSEM (ARC "Electrodes modifiées") for partial financial support.

Registry No. RuO_2, 12036-10-1; RuO_4^{2-}, 14333-22-3; Pt, 7440-06-4; Pd, 7440-05-3; poly($V^{2+}\cdot 2BF_4^-$), 100779-25-7; benzyl alcohol, 100-51-6; benzaldehyde, 100-52-7.

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(8) The preparation of this electrode was similar to that of poly[Ru-$(L)_3]^{2+}$–RuO_2 except that the incorporated RuO_4^{2-} was not reduced. The electrode was washed several times with CH_3CN and dried under vacuum before its use in dry CH_3CN in a controlled-atmosphere glovebox.

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(11) Product analysis was performed by HPLC vs authentic samples.

(12) The impregnation of the film with Pd(0) was accomplished by incorporation of $PdCl_4^{2-}$ followed by reduction to Pd(0) at −0.1 V vs SCE in aqueous medium. The impregnation procedure was repeated twice to obtain ~1 mol of Pd/mol of $[Ru(L)_3]^{2+}$ units.

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Crystal and Molecular Structure, Magnetic Properties, and EPR Spectra of a Trinuclear Copper(II) Complex with Bridging Nitronyl Nitroxides

Sir:

Transition-metal ions and stable organic radicals, such as the nitroxides, can form clusters containing variable numbers of spins.[1] For instance finite clusters containing from 2 to 12 spins have been reported, as well as infinite arrays.[2] The nitronyl nitroxides are

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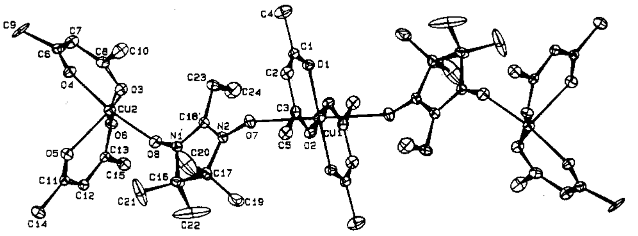

Figure 1. ORTEP view of $[Cu(hfac)_2]_3(NITEt)_2$. The fluorine atoms were omitted for the sake of clarity.

Table I. Selected Bond Lengths (Å) and Angles (deg)

Cu1–O1	1.921 (4)	Cu1–O2	1.925 (5)	Cu1–O7	2.452 (4)
Cu2–O3	1.911 (5)	Cu2–O4	1.956 (5)	Cu2–O5	2.180 (5)
Cu2–O6	1.935 (4)	Cu2–O8	1.944 (5)	O7–N2	1.261 (8)
O1–Cu1–O2	87.2 (2)	O1–Cu1–O7	82.4 (1)	O2–Cu1–O7	84.7 (1)
Cu1–O7–N2	145.4 (2)	O3–Cu2–O4	92.0 (2)	O3–Cu2–O5	107.5 (2)
O3–Cu2–O6	163.6 (2)	O3–Cu2–O8	90.8 (2)	O4–Cu2–O5	91.0 (2)
O4–Cu2–O6	91.5 (2)	O4–Cu2–O8	168.2 (2)	O5–Cu2–O6	88.5 (1)
O5–Cu2–O8	99.1 (2)	O6–Cu2–O8	82.7 (1)	Cu2–O8–N1	125.2 (3)

particularly versatile in giving different arrangements of spins, because they can bind to metal ions in many different ways, i.e. as monodentate ligands to one or two different ions and as bidentate ligands to two different ions.[2-8]

During the course of our systematic attempts to obtain low-dimensional magnetic materials using copper bis(hexafluoroacetylacetonate), $Cu(hfac)_2$, and nitronyl nitroxides,[9] NITR (R = methyl, ethyl, *n*-propyl, isopropyl, and phenyl), we obtained a compound of formula $[Cu(hfac)_2]_3(NITEt)_2$, which contains five spins. We wish to report here the crystal and molecular structure and the magnetic and EPR properties of such a compound.

By reaction of $Cu(hfac)_2$ in *n*-heptane with NITEt[10] in 1:1 molar ratio brown crystals were obtained, which gave satisfactory analysis for $[Cu(hfac)_2]_3(NITEt)_2$.[11] An X-ray analysis[12,13] showed that the structure consists of trinuclear $[Cu(hfac)_2NITEt]_2Cu(hfac)_2$ molecules, shown in Figure 1. One copper atom, Cu1, lies on an inversion center and is octahedrally coordinated to two hfac molecules and to two oxygen atoms of two different NITEt radicals. Each NITEt molecule is bound to two different copper atoms with its two oxygen atoms. The terminal copper atoms are five-coordinated in a distorted-square-pyramidal environment to two hfac molecules and the oxygen atom of NITEt. A similar structure has been previously reported for other copper complexes with asymmetric nitroxide radicals.[14]

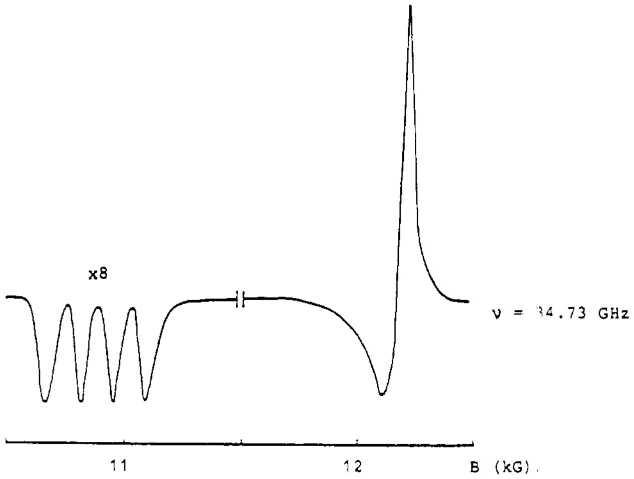

Figure 2. Q-band polycrystalline spectrum of $[Cu(hfac)_2]_3(NITEt)_2$ recorded at room temperature.

The coordination environment around the central copper ion is distorted-octahedral, with the axial bonds to the nitroxides much longer than the equatorial bonds,[15] 2.45 (6) Å vs an average of 1.92 (5) Å. Bond distances and angles in the hfac molecules are normal.

The NITEt molecules are also normal, and the five-membered ring is fairly planar, the maximum deviation from the average being 0.05 Å. The N1–O8 distance, 1.303 (8) Å, is larger than N2–O7, 1.261 (8) Å, indicating a stronger coordination of O8 compared to that of O7, but still in the range expected for a nitroxide. The nitroxide occupies an equatorial position in the square pyramid of Cu2 while the axial position is occupied by an oxygen atom of a hfac molecule. The axial Cu2–O5 bond is larger than the equatorial ones, and the copper atom lies 0.22 Å above the average plane of equatorial oxygen atoms. Selected bond lengths and angles are listed in Table I.

Magnetic susceptibility was measured in the temperature range 300–5 K by using a SQUID susceptometer at a field strength of 0.5 T. The susceptibility of $[Cu(hfac)_2]_3(NITEt)_2$ follows the Curie law with $C = 0.4639$, corresponding to a spin $S = {}^1/_2$ with $g = 2.225$. These data clearly show that the five spins present in the molecule are strongly coupled in an antiferromagnetic way. This result is expected on the basis of the coordination of the central and terminal copper atoms, and the comparison with other copper nitroxide complexes suggests a strong antiferromagnetic coupling, J_1, between the radical and Cu2 and a relatively weak ferromagnetic coupling, J_2, of Cu1 with the nitroxides:

$$\mathrm{Cu2}\overset{J_1}{\text{---}}\mathrm{R}\overset{J_2}{\text{---}}\mathrm{Cu1}\overset{J_2}{\text{---}}\mathrm{R}\overset{J_1}{\text{---}}\mathrm{Cu2}$$

In fact it has always been found that when the nitroxide occupies an equatorial position in the coordination environment of copper(II) the two spins are strongly coupled[15] in an antiferromagnetic way with $J > 500\ \mathrm{cm}^{-1}$ (the Hamiltonian is used in the form $H = JS_i{\cdot}S_k$), while when it occupies an axial position a weak-to-moderate ferromagnetic coupling is present.[15] Given the larger value expected for J, χT is expected to correspond to one unpaired electron even at room temperature. This is indeed what is experimentally observed. This model requires that the $\bar{g}$ and $\bar{A}$

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(11) One millimole of $Cu(hfac)_2$ was dissolved in 60 mL of hot *n*-heptane, and then 1 mmol of NITEt was added; the solution was cooled down with stirring, filtered, and stored at 4 °C for 1 day. Large elongated brown crystals were collected and gave satisfactory analysis for $[Cu(hfac)_2]_3(NITEt)_2$. Anal. Calcd for $C_{48}Cu_3H_{40}F_{36}N_4O_{16}$: C, 31.95; Cu, 10.57; H, 2.22; N, 3.11. Found: C, 31.96; Cu, 10.50; H, 2.23; N, 3.01.

(12) X-ray data for $[Cu(hfac)_2]_3(NITEt)_2$ were collected on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation. Crystal data: crystal system monoclinic, space group $P2_1/c$, $a = 19.22$ (1) Å, $b = 9.074$ (9) Å, $c = 19.71$ (1) Å, $\beta = 91.60$ (2)°, $V = 7334.3$ Å^3, $Z = 4$, calculated density 1.662 g cm^{-3}, crystal size 0.30 × 0.20 × 0.15 mm, temperature 22 °C, scan mode ω, Bragg angle $1 \le \vartheta \le 27$. Of 7751 reflections 3783 ($F \ge 3\sigma$) were used in structure refinement. The copper positions were determined by means of sharpened Patterson functions; the remeaning non-hydrogen atoms were revealed by successive difference Fourier maps. The final refinement, including all hydrogen atoms in fixed and idealized positions, converged to $R = 0.064$ and $R_w = 0.062$.

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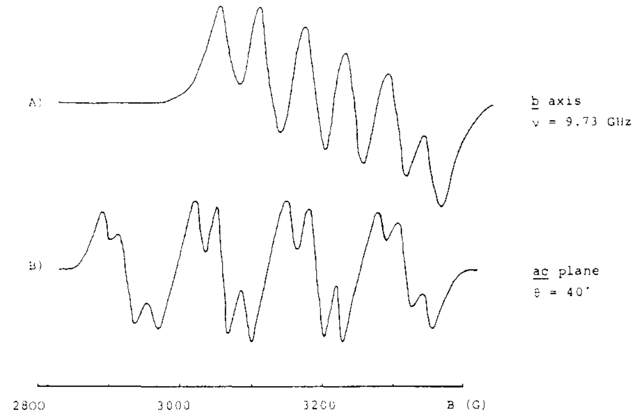

Figure 3. Room-temperature single-crystal X-band spectra of $[Cu(hfac)_2]_3(NITEt)_2$ with the static magnetic field (A) along *b* and (B) on the *ac* plane making an angle of 40° with a^*.

tensors of $[Cu(hfac)_2]_3(NITEt)_2$ correspond to those of the central copper atom. In order to verify this, we recorded both polycrystalline powder and single-crystal EPR spectra.

The polycrystalline powder EPR spectrum recorded at room temperature and Q-band frequency is shown in Figure 2. This is indeed typical of a copper(II) ion[16] with $g_\parallel = 2.29$, $g_\perp = 2.05$, and $A_\parallel = 145$ G. The values compare well with those of elongated-octahedral copper complexes, thus confirming the model.

In order to check if the principal directions correspond to the central copper atom, we recorded X-band-frequency single-crystal spectra at room temperature and 4.2 K rotating around the a^*, *b*, *c* crystal axes. The high- and low-temperature spectra are substantially similar. The signals of two magnetically nonequivalent sites are resolved in the a^*b and *bc* planes as expected for a monoclinic cell. This fact shows that the $[Cu(hfac)_2]_3(NITEt)_2$ intermolecular exchange interactions are smaller than the smaller hyperfine resolved, i.e. 0.0040 cm^{-1}. This result is not unexpected since the shortest distances between the paramagnetic Cu1 centers are 9.070 Å, and no obvious exchange pathway is present.

Copper hyperfine structure is resolved in many orientations, but also additional splittings are observed in some crystal settings. The presence of the fine splitting of the lines and their broadness makes the analysis of the spectra not straightforward. However, in the a^*c plane an extreme close to that observed in the powder spectra is found parallel to a^*, with $a_1 = 2.29$ and copper hyperfine $A_1 = 145$ G. The other extreme in this rotation corresponds to $g_2 = 2.07$ and $A_2 = 35$ G.

Comparing these data with the crystal structure, we see that the direction g_1 is almost parallel to the Cu1–O7 direction, making an angle of about 18° with it, confirming that we are indeed observing the resonance of the central copper ion.

In Figure 3 we show two typical spectra, recorded with the static magnetic field parallel to the crystal *b* axis and in the *ac* plane at 40° from a^*. The latter spectrum clearly shows a hyperfine quartet, with each line further split by ca. 30 G into triplets with intensity ratios 1:2:1 on each hyperfine line as showed by a simple simulation of the spectrum. The *b* spectrum shows six lines equally split by 60 G. Our interpretation of this splitting is that it is due to the fine interaction of the central copper with two copper ions translated by ±1 along the *b* axis. Similar effects were previously observed in other undiluted copper systems.[17-19] These two ions are 9.07 Å apart from the central one, and the simple point dipolar approximation suggests a splitting of 52 G of the lines in the spectrum along *b* and 26 G for the other spectrum. Therefore, the calculated values immediately allow us to assign the latter spectrum. In the *b* spectrum we suggest that the six lines are due to similar fine and hyperfine splitting of 60 G. The intensity ratio calculated from the assumption of simply additive fine and hyperfine splittings is 1:3:4:4:3:1. The experimental value does not agree with this, but a similar case was previously reported, and it was shown[18] that when fine and hyperfine splitting are comparable, the simple additive model does not work; spectra very similar to ours were simulated by using a more accurate model, which takes into account various combinations of hyperfine states of interacting ions.

Registry No. $Cu(hfac)_2$, 14781-45-4; $[Cu(hfac)_2]_3(NITEt)_2$, 114719-66-3.

Supplementary Material Available: Anisotropic thermal parameters for the non-hydrogen atoms (Table SI), complete listings of bond lengths (Table SIII) and angles (Table SIV), atomic positional parameters (Table SV), and experimental parameters of the X-ray data collection (Table SVI) for $[Cu(hfac)_2]_3(NITEt)_2$ (10 pages); observed and calculated structure factors (Table SII) (18 pages). Ordering information is given on any current masthead page.

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Time Dependence of the Excitation Polarization Ratio of $Ru(bpy)_3^{2+}$ in 4:1 Ethanol/Methanol Glass at 77 K

Sir:

Myrick, Blakley, and DeArmond[1] (MBD) have recently reported the luminescence excitation polarization ratio, *P*, of $Ru(bpy)_3^{2+}$ (RBY) to be time dependent on the 0–300-ns time scale in a number of frozen glasses at 77 K, including the most commonly studied glass-forming mixture, 4:1 ethanol/methanol (EM). These results were used to support the idea of *intrinsic* localization in the excited luminescent state of RBY, i.e. that MLCT luminescence arises from excitation of a single ligand. A maximum value for *P* of 0.5 would be allowed by such a process.

The high values observed at short times (0.30 ± 0.01 at 5–10 ns), compared to the long-time value of *P* (0.22 ± 0.02 at ≥300 ns) were used by MBD to propose a hopping model, where excitation, initially localized, would subsequently diffuse around the ligands, giving rise to a gradually reducing value of *P* until a steady-state level was reached.

In view of the unexpected and potentially important nature of these results, we have carefully repeated those in EM using a different and experimentally advantageous procedure over that used by MBD. We have found no observable time dependence for *P* of the magnitude reported by these workers, with effectively constant in time (but different) values being observed for excitation at a number of wavelengths throughout the MLCT region of 400–500 nm.

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