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Radiolytic synthesis and characterization of [$Ru^{II}(acac)_2(CO)L$] ($L = MeOH$, $EtOH$ or Pr^iOH)

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Abstract

The radiolysis of alcoholic solutions of [$Ru^{III}(acac)_3$] under CO leads selectively to the formation of a new complex [$Ru^{II}(acac)_2(CO)L$] (L = MeOH, EtOH or Pr^iOH). [$Ru^{II}(acac)_2(CO)MeOH$] **1** has been characterized by microanalysis, UV-visible, IR, ^{13}C-NMR and ^1H-NMR spectroscopies. The X-ray structural study of the complex **1** is also reported.

Keywords: Ruthenium; Radiolysis; Acetylacetonate; Synthesis; X-ray structure

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In our continuing studies on transition metal complexes [1–5], we have recently synthesized a new ruthenium complex by γ radiolysis.

Several ruthenium clusters and complexes such as [$Ru_3(CO)_{12}$], [$Ru_6(CO)_{18}H_2$] and [{$Ru(CO)_3Cl_2$}$_2$] have been already obtained by radiolysis of alcoholic solutions of $RuCl_3$ under CO [5]. The primary products of radiolysis of primary or secondary alcohols (methanol, ethanol, 2-propanol) are solvated electrons (e^-_s), $H^·$ radicals and alcohol radicals R_1R_2-$C^·OH$ as short-lived species, and solvated protons ($R_1R_2CHOH_2^+$ or H_s^+) and H_2 as stable products [6,7]. These species can react with metal complexes or ions in solution. When CO or other ligands are present in solution, competition occurs between reduction, ligation and aggregation processes so that molecular complexes or metal clusters are obtained.

Starting with [$Ru^{III}(acac)_3$] brings in an additional ligand effect since acetylacetonate (acac) is itself an efficient ligand, known to chelate or bridge owing to the delocalization of the negative charge over five atoms (anionic keto form).

Here we report a new ruthenium complex [$Ru^{II}(acac)_2(CO)L$] (L = MeOH, EtOH or Pr^iOH). Alcoholic solutions of [$Ru^{III}(acac)_3$] (concentration 1×10^{-3} mol l^{-1}) were saturated by bubbling CO (1 atm), then exposed to γ source (^{60}Co. Dose rate 0.5 Mrad h^{-1} or 5 kGy h^{-1}) for 2 h. (Pure grade reagents were purchased from Aldrich ([$Ru(acac)_3$]); Merck (methanol, hexane), Prolabo (ethanol, isopropanol, dichloromethane), Air liquid (CO).)

The synthesis of [$Ru^{II}(acac)_2(CO)L$] is:

$$Ru(acac)_3 \xrightarrow[\substack{L=Solvent \\ L=MeOH,EtOH,Pr^iOH}]{CO,1atm,\gamma\text{-}Ray} Ru(acac)_2(CO)L$$

The $Ru(acac)_3$ alcoholic solutions are initially red-brown, with a UV-visible spectrum displaying maxima at 501, 346 and 271 nm. Under irradiation, the spectrum changes slightly and the solution progressively turns to yellow (maximum wavelengths at 259 and 340sh nm) corresponding to the spectrum of [$Ru^{II}(acac)_2(CO)L$] (L = solvent). The synthesis is highly selective.

After irradiation the solvent was removed under vacuum and the product was recrystallized at low temperature from methanol/pentane (50/50 v/v) as yellow crystals with a yield of 95% (**1**, Found: C 39.80, H 4.80, Ru 26.70%. $RuC_{12}H_{18}O_6$ requires: C 40.11, H 5.01, Ru 28.13). The IR spectrum of **1** in dichloromethane displays some bands characteristic of carbonyl groups at 2056s-2027m-2005w-1988-w-1940vs cm^{-1} [8].

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In $CDCl_3$, the ^1H-NMR spectrum [5] of **1** shows four signals (12:3:2:1) owing to methyl, methoxy, methine and hydroxy protons, respectively at $\delta = 2$, 3.49, 5.35 and 5.74 ppm. The ^{13}C-NMR spectrum in $CDCl_3$ was recorded at room temperature, $\delta = 27.29$ (s, 4 CH_3); 30.63 (s, OCH_3), 101.01 (s, 2 CH), 209.00 (s, 4 C-O(acac)), 230.00 (s, C=O) ppm, consistent with the formulation $[Ru(acac)_2(CO)(CH_3OH)]$.

The molecular structure of **1** has been also determined by single crystal X-ray diffraction study [9] and is shown in Fig. 1.

When irradiation of $[Ru^{III}(acac)_3]$ is carried out in ethanol or isopropanol under CO, the radiolysis products are $[Ru^{II}(acac)_2(CO)(EtOH)]$ **2** and $[Ru^{II}(acac)_2(CO)(Pr^iOH)$ **3**, respectively. ^1H-NMR spectrum in $CDCl_3$ of **2**: $\delta = 1.20$ (m, CH_3), 2.00 (s, $4CH_3$), 3.70 (m, CH_2), 5.35 (s, $2CH$), 5.80 (s, OH) ppm with intensity ratios (3:12:2:2:1); for compound **3** $\delta = 1.06$ (d, $2CH_3$); 1.84 (s, $4CH_3$); 3.91 (m, CH); 5.32 (m, $2CH$), 5.55 (s, OH) ppm with intensity ratios (6:12:1:2:1). Prolonged exposure of **2** and **3** to methanol results in $[Ru^{II}(acac)_2(CO)(MeOH)]$. Such alcohol molecules are usually readily displaced by stronger donors. $[Ru^{II}(acac)_2(CO)L]$ may be good precursors for a wide range of Ru^{II} compounds containing *O*, *N* or *S* donor ligands.

Radiolysis has proved to be very successful in the synthesis of metal aggregates, clusters and complexes which are often difficult to synthesize by conventional means. In this paper we have shown that it can also be used to synthesize new products and that it can be highly selective.

Computations were performed using the program crystals [11] adapted to a PC. Atomic scattering factors for neutral Ru, O, C and H atoms were taken from Ref. [12]. Anomalous dispersion was applied. The structure was solved by direct methods using the SHELX86 program [13]. Hydrogen atoms attached to carbon atoms were located by difference Fourier syntheses, but the H coordinates were introduced in the refinement as fixed contributors in calculated positions. (The H atom attached to the oxygen atom could not be located, but the geometry around oxygen atom is consistent with the presence of a MeOH ligand.) Their atomic coordinates were recalculated each cycle. They were assigned isotropic thermal parameters 20% higher than those of the carbon to which they were attached. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Full-matrix least-squares refinements were carried out by minimizing the function $\Sigma_w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = w'(1 - \Delta F/(6\sigma(F_o))^2)^2$ where $w' = 1/\Sigma_1^r A_r T_r(x)$ with three coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$ where x was $F_c/F_c(\max)$ [14].

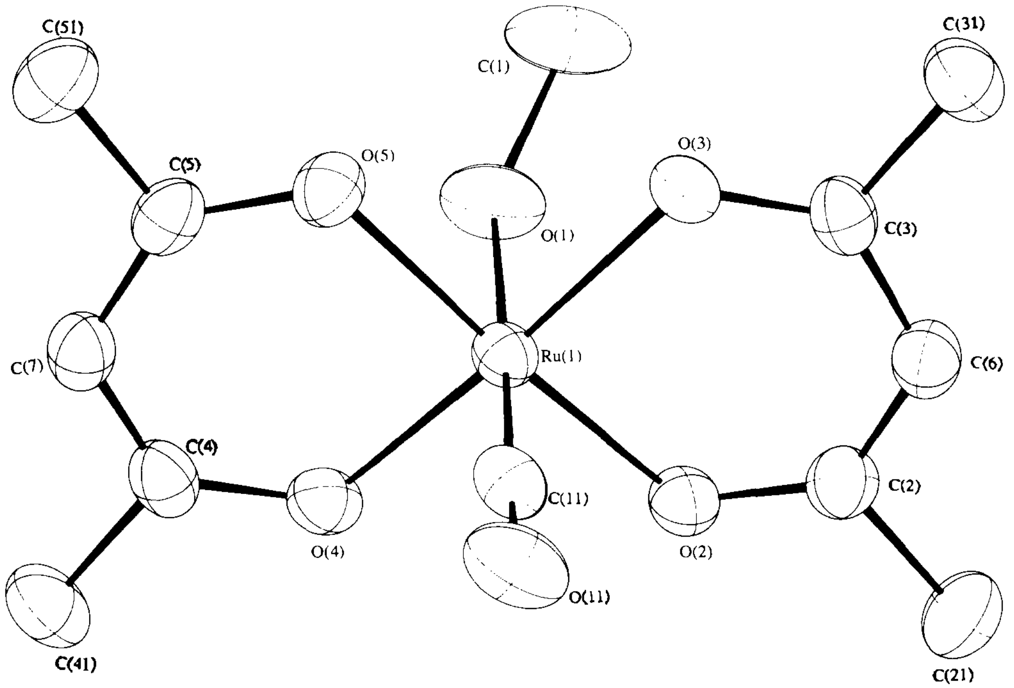

Fig. 1. Molecular structure of $[Ru(acac)_2(CO)(MeOH)]$ **1** without hydrogen atoms. Ellipsoids represent 30% probability. Selected bond lengths (Å) and angles (deg): Ru(1)-O(1), 2.177(4); Ru(1)-C(11), 1.795(6); Ru(1)-O(3), 2.044(4); Ru(1)-O(1)-C(1), 128.0(4); O(1)-Ru(1)-C(11), 177.8(2); O(3)-Ru(1)-O(5), 86.0(2); O(3)-Ru(1)-O(4), 173.6(2).

Models reached convergence with $R = \Sigma w(||Fo| - |Fc||)/\Sigma|Fo|$ and $Rw = (\Sigma w(|Fo| - |Fc|)^2/\Sigma w(Fo)^2)^{1/2}$. Full lists of atomic parameters, etc. have been deposited with the Cambridge Crystallographic Data Centre.

Crystal parameters, $C_{12}H_{18}O_6Ru$ (compound **1**): Fw 358.33, crystal system monoclinic, space group $P21/n$; $a = 7.802$ Å (2) $b = 12.863$ Å (4) $c = 14.880$ Å (4); $B = 96.84°$ (4), $V = 1493$ Å^3 (2), $Z = 4$, ρ(calcd) = 1.605 g cm^{-3}, ϑ(Mo-Kα) = 10.53 cm^{-1}.

Data collection: monochromator (graphite), radiation (Mo-Kα($\lambda = 0.71069$), scan type ($\omega = 2\Theta$), scan rangeΘ, deg(0.8 + 0.345tgΘ), 2Θ range,deg ($1.5 < 2\Theta < 25$); reflections collected (2946), reflectors merged (Rm) 2194 (0.031), reflections used ($1 > 3\sigma(1)$) (1737).

Refinement: $R = 0.0374$, $R_w = 0.0458$, abs. corr. = Difabs, min/max correction 0.9–1.10^{37}, weighting scheme (Chebyshev), coeff. Ar (4.68, 0.464, 3.53), GOF (1.21, 1s parameters 173).

References and notes

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[8] ^{1}H and ^{13}C-NMR spectra were recorded with a Bruker AM250 instrument. The IR spectra were recorded on a type 23 Perkin-Elmer apparatus using cells with CaF_2 windows (optical length 0.2 mm), UV-visible spectra were recorded on a Beckman Acta MIV spectrophotometer.

[9] Crystallographic analysis. A selected crystal was mounted on an automatic CAD4-F diffractometer. Unit cell dimensions with standard deviations were obtained from least-squares refinements of setting angles of 25 well-centred reflections. Two standard reflections were monitored periodically; they showed no change during data collection carried out at room temperature (21°C). Corrections were made for Lorentz and polarization effects. Absorption corrections (Difabs) were applied [10].

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