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Rapid Unidentate-Chelate Equilibrium of Acetate Ligands on the Ruthenium-Analog of the Hemerythrin Active Center and the Crystal Structure of $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2\text{-}(CH_3COO)_2(H_2O)(CH_3OH)(P(C_6H_5)_3)_2]\cdot H_2O$ Having Unidentate Acetates

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$[Ru_2(O)(CH_3COO)_4(H_2O)(CH_3OH)(PPh_3)_2]$, has an $Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$ core and unidentate acetates with H_2O and CH_3OH coordinated to the trans positions to the oxide bridge as determined by the X-ray structural analysis. This is in contrast to the recent report of the chelating acetate on the similarly prepared complex. ^1H NMR spectra in $CDCl_3$ revealed that the complex undergoes rapid unidentate-chelate equilibrium of acetates between the bis(chelate) and mono(chelate)mono(unidentate) forms.

Dinuclear complexes bridged by one oxide (or hydroxide) and two carboxylate ions are of increasing interest,1) because of their relevance to some metalloenzymes represented by hemerythrin.2,3) Ruthenium complexes with such dimeric structure were first reported by Wilkinson and coworkers in 1973 as "$[Ru_2(\mu\text{-}O)(\mu\text{-}RCOO)_2(RCOO)_2(PPh_3)_2]\cdot CH_3OH$" ($PPh_3 = P(C_6H_5)_3$) for the product of the reaction mixture containing $RuCl_3 \cdot 3H_2O$, PPh_3 and RCOONa (R = CH_3, C_6H_5, etc.) in methanol.4) The X-ray structural determination of the *p*-methoxybenzoate 5) and acetate derivatives6) disclosed the existence of two chelating carboxylate. Purple crystals of the acetate complex were obtained from the toluene solution.6) We have also carried out the structural determination of the purple acetate derivative recrystallized from methanol, and found unidentate rather than chelating acetates. Further experiments have disclosed that whether non-bridging acetate ligands take unidentate or chelating forms depends on the kind of solvents and that the relevant species exist in rapid equilibrium under certain conditions. This is quite unusual for the substitution inert ruthenium(III) complexes, and manifests an unusual reactivity related to the hemerythrin-like dimeric structure.

Figure 1 shows an ORTEP drawing of the structure of the complex, $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2\text{-}(CH_3COO)_2(H_2O)(CH_3OH)(PPh_3)_2]\cdot H_2O$ (**1**),7) which contains two unidentate acetate ions. The two positions trans to the oxide bridge are occupied by one water and one methanol. Other structural characteristics are very similar to those of previously reported complexes with similar core structure, $\{Ru^{III}{}_2(\mu\text{-}O)(\mu\text{-}XOO)_2\}^{n+}$ (X = CH_3C, *p*-$MeOC_6H_4C$, PO(OH)).5,6,8-10) The Ru-Ru distance (3.170(3) Å) of the present complex is the shortest among those complexes.

In solution, **1** shows complicated behavior which is summarized by Scheme 1. In CD_3OD, two methyl signals of similar integrated intensity (1.66 and 1.57 ppm vs. TMS; assignable to bridging and non-bridging acetates) are observed at 24 °C, which belong to **A**, a di(methanol) analog of the structurally determined species.

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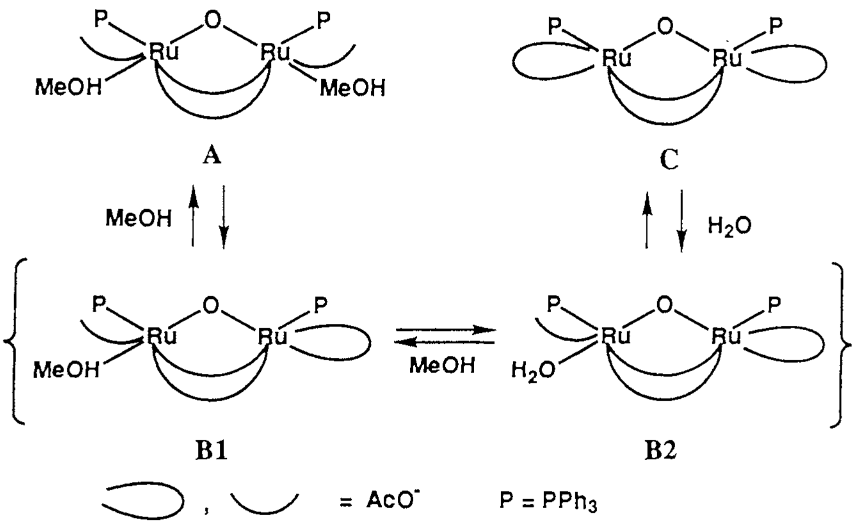

Scheme 1.

The spectrum is basically the same at -60 °C with small changes in chemical shifts. The NMR spectrum of **1** in $CDCl_3$ is temperature dependent (Fig. 2). At -60 °C, six methyl singlets are observed, which are assigned to the species **C** (two peaks for bridging and chelating acetates) and **B2** (all the four acetates are non-equivalent).[11] On raising the temperature, the two peaks of **C** seem to increase their relative integrated intensity,[12] and simultaneously each three peaks assignable to bridging and non-bridging (terminal) acetates, respectively,[13] start to coalesce to give two signals eventually.[14] At -60 °C, the equilibrium between **C** and **B2** is frozen, while rapid interconversion takes place at 24 °C,[15] with the shift of the equilibrium to **C** at higher temperature. Successive addition of a few drops of methanol drastically changes the spectrum at -60 °C. With the first drop, all the species in the scheme are seen (12 CH_3 singlets). On further addition, only two signals correspond to the species **A** remain finally and all other signals disappear successively (in the order of **C**, **B2**, and **B1**).

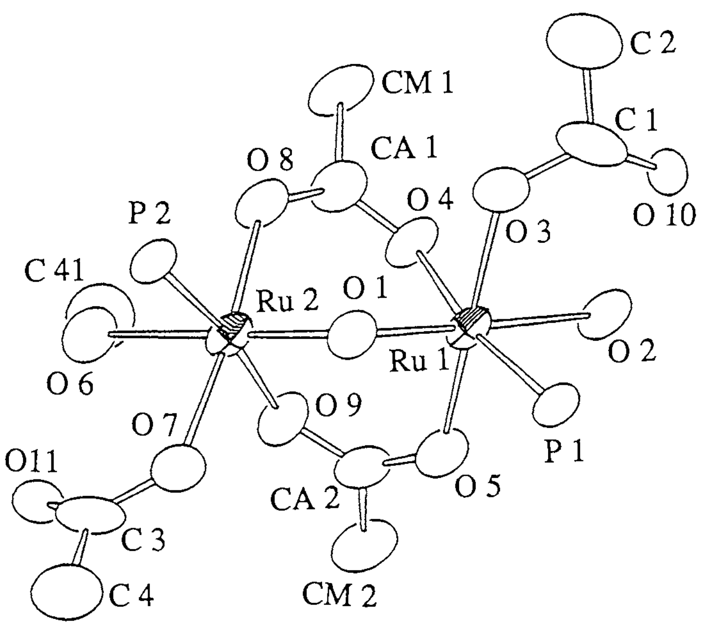

Fig. 1. Structure of $Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(CH_3COO)_2(H_2O)(CH_3OH)(P(C_6H_5)_3)_2$ showing the 40% probability thermal ellipsoids and atomic labeling scheme. Aromatic rings of $P(C_6H_5)_3$ are omitted to show the core structure clearly. Selected interatomic distances (Å) and angles (deg) are as follows: Ru1-Ru2 = 3.170(3), Ru1-O1 = 1.860(8), Ru2-O1 = 1.884(9), Ru1-P1 = 2.273(4), Ru2-P2 = 2.295(4), Ru1-O2 = 2.150(9), Ru2-O6 = 2.181(10), Ru1-O3 = 2.06(1), Ru2-O7 = 2.09(1), Ru1-O4 = 2.160(9), Ru1-O5 = 2.01(1), Ru2-O8 = 2.05(1), Ru2-O9 = 2.16(1), Ru1-O1-Ru2 = 115.7(4).

Visible absorption spectrum of **1** depends significantly on the kind of solvent. In $CHCl_3$ it shows absorption maximum in the visible region at 560 nm with ε = 5600 $M^{-1}cm^{-1}$ (M = mol dm^{-3}) as reported.4) The spectrum shows remarkable temperature dependence; absorption intensity of the peak at 560 nm increases with decrease in temperature (at -60 °C the intensity was ca. 1.5 times) with three isosbestic points. The change should correspond to the shift of the equilibrium between **C** and **B1**. **1** in CH_3OH shows absorption maximum at 543 nm with ε = 11100 $M^{-1}cm^{-1}$, which should represent the species **A**.

The unusual lability for generally substitution inert ruthenium(III) center16) should be related to the strong trans effect of the oxide bridge. We have recently found that the pyridine (py) trans to oxide bridge in $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(py)_6]^{2+}$ in CH_2Cl_2 exchanges with bulk pyridine at least 10 times more rapidly than the one at cis to the oxide bridge.17) The Ru-N distance in the hexapyridine complex8,17) as well as the Ru-O(*p*-methoxybenzoate and acetate) distance in the chelating carboxylate complexes 5,6) trans to the oxide bridge are appreciably longer than those at cis positions.

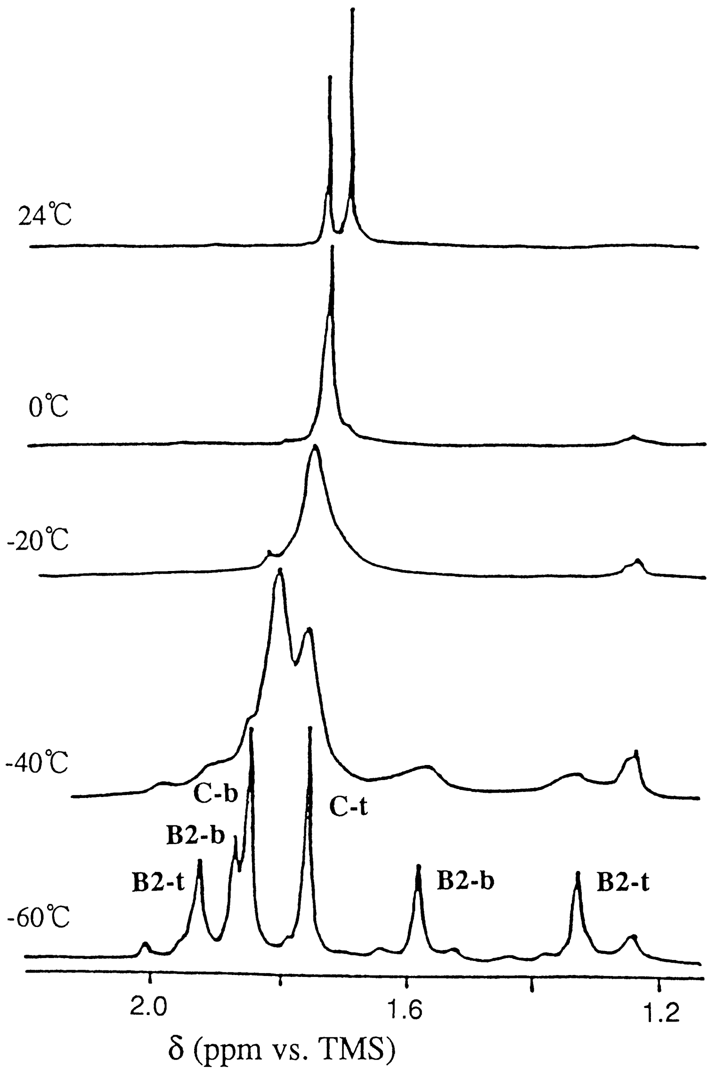

Fig. 2. Temperature dependence of ^1H NMR spectra of **1** in $CDCl_3$: **B2** and **C** represent the species given in Scheme 1, and **b** and **t** indicate bridging and non-bridging (terminal) acetates.

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7) $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(CH_3COO)_2(H_2O)(CH_3OH)(PPh_3)_2]\cdot H_2O$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.883(3)$ Å, $b = 19.696(2)$ Å, $c = 22.157(2)$ Å, $\beta = 96.32(1)°$, $V = 4720(1)$ Å^3, and $Z = 4$. Using 5245 unique reflections ($F_o > 3\sigma(F_o)$) collected at room temperature with Cu Kα ($\lambda = 1.5406$ Å) radiation $3° \leq 2\theta \leq 128°$ on a Rigaku AFC-5R diffractometer, the structure was solved by the heavy-atom method and refined by block-diagonal least-squares techniques with anisotropic temperature factors for non-hydrogen atoms except for C of CH_3OH and O of lattice water. Hydrogen atoms were located at the calculated positions. The current R value is 0.079. Tables of crystallographic data, atomic positional and thermal parameters, intramolecular atomic distances and bond angles, and observed and calculated structure factors are available on request to the authors.

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11) Water involved in the equilibrium comes from the complexes and solvent $CDCl_3$ (ca. 10^{-3} M).

12) Temperature dependence of the ^1H NMR in CD_3COCD_3 more clearly showed the similar equilibrium shift between **C** and **B2** with temperature, since the coalescence occurs at higher temperature. Furthermore, on successive addition of drops of water to the acetone solution, the equilibrium is observed more clearly than in the $CDCl_3$ solution among the three species including **C**, **B2** and the di(aqua) species (corresponds to **A**).

13) Signals were unambiguously assigned with the aid of the spectral change on addition of CD_3COOD to the $CDCl_3$ solution, which causes the exchange of only the non-bridging acetates (this change takes place within a few minutes at room temperature). In the -60 °C spectrum, the three disappearing signals are assigned to the non-bridging acetates.

14) The signal positions appear to be subject to temperature dependence. At 0 °C, two signals are accidentally overlapped.

15) Similar experiments on the benzoate derivative showed that the chelated species **C** is much more stable, which is consistent with the isolation of bis(chelate) form in the case of *p*-methoxybenzoate derivative.5)

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