Synthesis of an Electron Pooling Ligand Based on Triruthenium Clusters and Electrochemical Reduction of CO_2 by Its Zinc(II) Complex

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An electron pooling complexed ligand (PL) was prepared by linking μ_3-oxo Ru_3 clusters with 1,4,7-tris(4-pyridylmethyl)-1,4,7-triazacyclononane (pic_3tacn). The cyclic voltammogram of the pooling ligand appeared similar to the Ru_3 cluster monomers. Each wave corresponded to three simultaneous $1e^-$ processes. In the presence of Zn(II) ions, CO_2 was reduced, indicating cooperation between the Ru_3 cluster centers. IR spectroelectrochemistry (IRSEC) indicated that the products of reduction were carbonate and formate and CO.

Metalloenzymes need a source of electrons in order to perform multielectron redox reactions, such as CO_2 reduction or N_2 reduction.[1] For example, ferredoxins use Fe–S clusters as an electron source. While extensive research has centered on multielectron redox reactions, these are still difficult to reproduce efficiently in the laboratory.

Furthering our study of μ_3-oxo triruthenium clusters,[2–8] we have prepared an electron pooling complexed ligand $\{[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6L_2](4\text{-py})CH_2\}_3$tacn (L = pyridine (py), **PL1**, and *N*,*N*′-dimethylaminopyridine (dmap), **PL2**; tacn = 1,4,7-triazacyclononane) where three μ_3-oxo Ru_3 clusters are linked by 1,4,7-tris(4-pyridylmethyl)-1,4,7-triazacyclonane (pic_3tacn) (Figure 1).[9,10] Previous work by our research group on dimers of Ru_3 clusters and oligomers of Ru_3 clusters showed that when the μ_3-oxo Ru_3 clusters are linked by bridging ligands, multiple electrons, depending on the number of clusters linked, can be added or removed within a narrow potential range.[4]

The tacn derivative was chosen as a linker because the N atoms of the tacn, itself, are able to coordinate to the metal ions, but not to the Ru_3 clusters owing to steric reasons. Additionally, macrocyclic ligands like 1,4,8,11-tetraazacyclotetradecane (cyclam) have been used as supporting ligands for Ni complexes, which can electrochemically reduce CO_2.[11,12] We report here the synthesis, characterization and electrochemistry of the complexed ligands and the electrochemical reduction of CO_2.

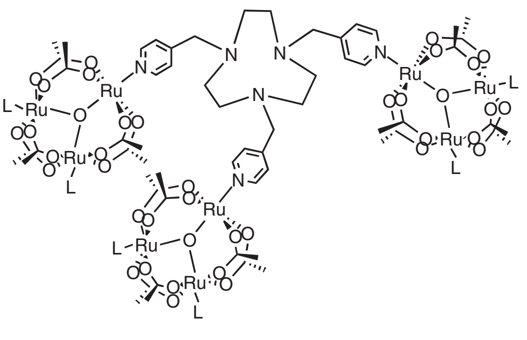

Figure 1. Diagram of the pooling ligand $\{[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6L_2](4\text{-py})CH_2\}_3$tacn (L = py (**PL1**) or dmap (**PL2**)).

The ligands were prepared by mixing $[Ru(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6L_2(Solv)](PF_6)$ [L = pyridine (py) and dimethylaminopyridine (dmap); Solv = coordinated solvent molecule] and pic_3tacn in CH_2Cl_2 for 1 h and were purified by gel chromatography (Biobeads SX-1) with CH_2Cl_2 as the eluent. The yield of **PL2** was 25.4%, which was typical for the ligands. Electrospray mass spectra (ESI–MS) of **PL1** and **PL2** were consistent with three Ru_3 clusters coordinated to one pic_3tacn (m/z $[M]^{3+}$ = 1052 and 1060, respectively). The mass spectral data and the broadened ^1H NMR spectra of **PL1** and **PL2** showed that the Ru ions in each cluster in **PL1** and **PL2** existed in a formal oxidation state of $(Ru^{III})_3$.

The cyclic voltammograms of **PL1** and **PL2** were similar to those of the starting clusters $[Ru(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6L_2(Solv)]^+$. Each wave corresponded to three $1e^-$ redox processes (Figure 2). Like the cluster monomer, three reversible redox waves were observed, and each wave corresponds to three $1e^-$ simultaneous processes. The redox potentials are affected by the ancillary ligand L on the Ru_3 clusters.[13]

Since the ligands **PL1** and **PL2** alone did not reduce CO_2, they were coordinated to Zn(II) via the tacn ring by mixing **PL1** or **PL2** with Zn(II) acetate in CH_3CN for 5 h at room temperature. The cyclic voltammograms of each Zn complex remained similar to the respective PL. When cyclic voltammetry was performed under CO_2, the wave corresponding to the $(III,III,II)_3/(III,II,II)_3$ reduction process showed an enhancement of current, indicating that an electrochemical reduction of CO_2 occurred (Figure 3). Zn(II)–**PL1** also showed a current enhance-

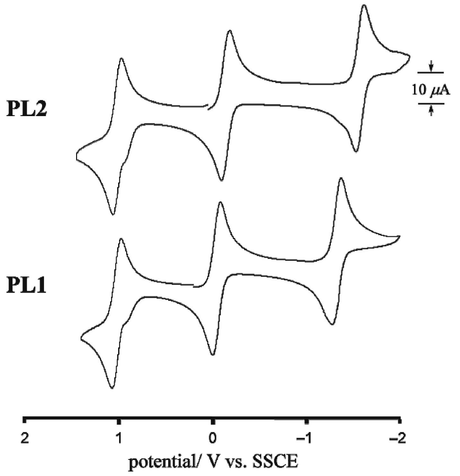

Figure 2. Cyclic voltammograms of **PL1** (lower) and **PL2** (upper) vs SSCE in 0.1 M TBAH/CH_3CN, using a glassy carbon working electrode and a platinum counter electrode and concentration of 1 mM.

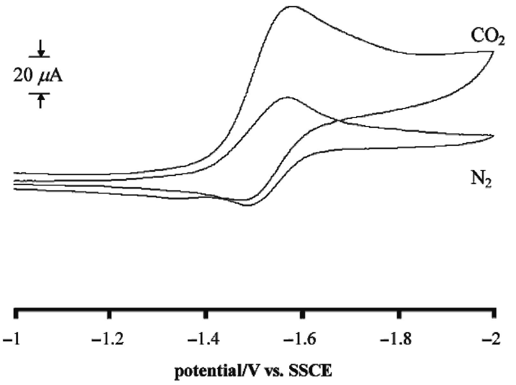

Figure 3. Cyclic Voltammograms of Zn–**PL2** under N_2 (lower) and CO_2 (upper) vs SSCE in 0.1 M TBAH/CH_3CN using a glassy carbon working electrode and platinum counter electrode and a concentration of 1 mM.

ment, but it was less pronounced than that observed for **PL2**. The differences in catalytic activities can be understood in the following way. The electron donating ability of dmap ($pK_a = 9.71$) is higher than py ($pK_a = 5.17$), and therefore, the Ru_3 cluster cores are more electron rich. Thus, the $(III,II,II)_3$ state of **PL2** has more reducing power than that of **PL1**.

In order to identify the reduction products, infrared spectroelectrochemistry (IRSEC) was employed. The IRSEC cell[14] was charged with a CO_2-saturated solution of the Zn–**PL2** complex and the potential was stepped to cathodic potentials until no further changes in the IR spectra were observed.[15]

As the potential became more cathodic, new peaks were observed at 1922, 1685, 1646, 1608, and 1307 cm^{-1} in the IR spectrum (Figure 4). The peaks at 1685, 1646, and 1307 cm^{-1} and at 1608 cm^{-1} are in agreement with those observed for fresh samples of tetrabutylammonium bicarbonate and formate salts, respectively.[16] The peak at 1922 cm^{-1} is similar in frequency to an Ir formato complex (1917 cm^{-1}) reported by Mann and coworkers,[16] which suggests the possibility that a Zn formato complex forms during the reduction process. Another possibility is the formation of a Ru_3–CO cluster. No peak was observed for free CO, but the peak at 1922 cm^{-1} is consistent with a singly reduced Ru_3–CO cluster.[3,5,7] Neither **PL2** nor Zinc acetate alone reduced CO_2.

Both intermolecular and intramolecular electron transfer pathways are possible for this system. The electrochemical data obtained showed that the Ru clusters are reduced prior to electron transfer. It is reasonable to suggest that the Zn(II) ions interact and consequently activate CO_2 towards reduction. However, the structure of the active species $\{Zn–CO_2\}$ is not clear. In the absence of water, CO_2 has been reported to undergo disproportionation to produce CO and CO_3^{2-}.[16] However, bicarbonate may form as a result of $CO_2^{\bullet-}$ reacting with residual H_2O.[13] Formate has also been reported to form upon the $2e^-$ reduction of CO_2,[16] and since the pooling ligands have the ability to provide $3e^-$ at each potential, the formation of formate is possible.

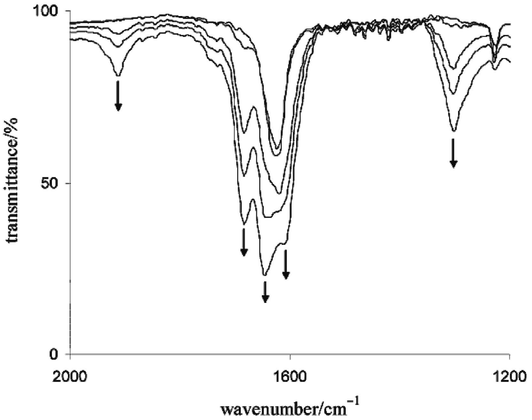

Figure 4. IR spectra from the IRSEC experiment under CO_2.

In summary, an electron pooling complexed ligand was prepared that can coordinate to different metal ions via the N atoms of the tacn macrocyclic ligand. The complexed ligands **PL1** and **PL2** were shown to display similar electrochemical properties to the uncomplexed μ_3-oxo Ru_3 clusters. Both ligands have the ability to either add or remove multiple electrons within a narrow potential range. As a result, **PL1** and **PL2** in cooperation with Zn(II) ions were shown to reduce CO_2. Further studies are underway to determine the products and mechanism of this reduction process.

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References and Notes

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