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interaction potentials,[2] it seems that simple electrical polarization, which may be determined while neglecting intermolecular quantum effects, is the primary electronic structure change of a constituent participating in a weak assembly of atoms and molecules.[4,5] This requires that in addition to energetics, the analysis of the MMC scheme should properly yield induced moments. Is this the case? In molecular beam electric resonance studies of many complexes, Klemperer and co-workers have reported unsatisfactory results from using electrical analysis to compute induced dipoles that they had measured (for instance, ref 41). However, we find the situation to be quite different, with the electrical analysis working nicely in predicting induced moments. Results given in Table VIII for a few systems confirm that induced dipoles arise from simple polarization. The differences between calculated, equilibrium, total dipole moments, and the vibrationally averaged values measured experimentally are small. The Klemperer group reached an opposite conclusion, probably by relying on dipole polarizabilities alone to give the polarization. Finally, reliability in computing a dipole moment, and presumably a dipole moment surface, means that this approach provides the information to obtain vibrational transition moments.[6]

That a molecular mechanics capability for weakly interacting systems should be based on electrical interaction is clear from a number of recent studies.[2,23,49–55] Buckingham and Fowler[49] have used permanent moment interactions with atom–atom infinitely hard walls to locate minima on potential surfaces of binary complexes. Stone has shown that distribution of moment centers is an effective means of representing the charge fields of large molecules.[52,53] Spackman has developed a sophisticated, yet simple-to-use scheme for generating weak interaction potentials and has examined a number of binary complexes.[54,55] A partitioning based on charge densities is used to obtain repulsive and electrostatic contributions that relate to the constituent atoms of the interacting species. Polarization or any perturbation of the constituent species is neglected in Spackman's model. The inclusion of polarization in the present model, though, is the feature that fits so many more of the puzzle pieces together. Often, it is a small energetic effect, but it brings in cooperative elements, accounts for induced moments, and makes refinements in energetics that are important for barrier heights, shapes of potential wells, and sometimes relative stabilities of different conformations.[3–6]

The evaluation of the model's interaction potentials is computationally fast relative to electronic structure calculations. And, of course, the computational expense is roughly independent of the size and form of the constituents, and it grows only quadratically with the number of constituents in a cluster. Thus, it is feasible to study a cluster with tens of constituents on a Macintosh II, for example. The evaluation of the interaction, though, is more cumbersome and slower than conventional molecular mechanics because it involves solving the electrical interaction equations with moderate-sized expansions. The cost of evaluating the Lennard-Jones terms is negligible relative to the electrical part. While it is not yet a technology that ought to be merged with conventional molecular mechanics, it seems likely that simplified representations which match the speeds of conventional molecular mechanics can be worked out without too much sacrifice in accuracy. Thus, in addition to the stand-alone usefulness of this approach, its development could lead to better weak interaction potentials for existing programs.

Acknowledgment. I thank Mr. J. D. Augspurger for carrying out the ab initio calculations on the $(H_2)_2$ potential surface. This work was supported, in part, by a grant from the Physical Chemistry Program of the National Science Foundation (Grant CHE-8721467). Also, acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (Grant 19786-AC).

Registry No. H_2, 1333-74-0; HF, 7664-39-3; HCN, 74-90-8; CO_2, 124-38-9; He, 7440-59-7; Ne, 7440-01-9; Ar, 7440-37-1.

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Evidence for the Existence of the Metastable Manganate(V) Ester Intermediate in the Permanganate Oxidation of *endo*-Dicyclopentadiene

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Contribution from the Department of Chemistry, Faculty of Education, Niigata University, Niigata 950-21, Japan. *Received September 12, 1988*

Abstract: It has been demonstrated that the manganese species observed during the permanganate oxidation of *endo*-dicyclopentadiene in dichloromethane by use of quaternary ammonium salts is a manganate(V) ester intermediate. Although the apparent oxidation state of manganese in the intermediate calculated from the results of iodometric titration was +4, the true oxidation state was found to be +5 because the analyses of the organic products obtained after the titration disclosed that a rapid oxidative decomposition path, which cannot be quenched by iodide, exists during the iodometry. Kinetic studies disclosed a first-order dependence of the decay of the intermediate on the concentration of the alkene. The results of the titration (apparent oxidation state and product ratio) changed with time in accordance with the decay of the intermediate. These results can be explained by a mechanism in which the detectable intermediate is a cyclic manganate(V) diester ion, which is reduced gradually to Mn(IV) via abstraction of a hydrogen atom from the alkene.

In the last decade, there has been considerable discussion concerning the nature of the "detectable intermediates" observed during the permanganate oxidation of carbon–carbon double bonds in aqueous[2–6] and nonaqueous solution.[1,7–10] Although it was

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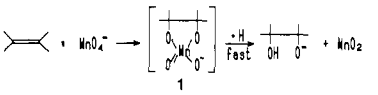
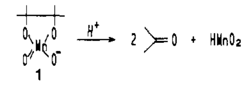
initially thought that these intermediates were the previously proposed cyclic manganate(V) diesters,[11] recent reports[12-18] have concluded that the observed species are soluble (colloidal) manganese dioxide formed via rapid decomposition of the undetectable cyclic manganate(V) diesters **1** by abstraction of a hydrogen atom from the solvent (eq 1).



(1)[16-18]

These conclusions were largely based on the fact that the oxidation state calculated for manganese in the intermediates from the results of iodometric titration was +3.5–+4.0. Since iodometric titration of manganese is necessarily conducted under acidic conditions where the manganese intermediates may also undergo oxidative decomposition to give bond cleavage products, as in eq 2,[7] the results of the titration should be assessed together with



(2)

product analysis performed after the titration. However, there have been no investigations undertaken from this point of view.

We wish to report the experimental results, which clearly demonstrate that the manganese species observed during the permanganate oxidation of *endo*-dicyclopentadiene (DCPD) in dichloromethane by use of quaternary ammonium salts is a manganate(V) diester intermediate and not manganese dioxide as other authors claimed.

Experimental Section

Materials. The solvent (dichloromethane) used in all of the experiments was purified by refluxing with potassium permanganate and benzyltriethylammonium chloride followed by distillation from the solution. *endo*-Dicyclopentadiene (DCPD) was purified by distillation using a 20-cm Vigreux column. The quaternary ammonium halides were obtained from Tokyo Kasei Kogyo Co. and used without purification.

Solutions of permanganate were prepared in the following manner. Powdered potassium permanganate (1 mmol) and a quaternary ammonium halide (1 or 2 mmol) were dissolved in dichloromethane (10 mL), and the solution was allowed to stand overnight in a refrigerator. The concentration of permanganate ion was adjusted by dilution and determined accurately by iodometric titration or spectrophotometric method immediately before use.

General Procedure. A solution of $KMnO_4$ (2×10^{-4} M) prepared by the above method and a solution of excess DCPD [$(3-10) \times 10^{-3}$ M] in dichloromethane were thermostated at 25.0 °C for 30 min. Aliquots (2.0 mL) of each solution were mixed together in a flask and the mixture was quickly transferred to a 10-mm thermostated cuvette for spectral measurements or kinetic experiments.

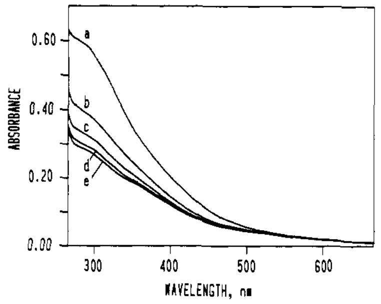


Figure 1. Repetitive scan of absorbance for the intermediate obtained from the reaction of permanganate ion with DCPD in CH_2Cl_2 by use of $n\text{-}Bu_4N^+Br^-$ at 25 °C: (a) 1 min; (b) 10 min; (c) 20 min; (d) 30 min; (e) 40 min. $[DCPD]_0 = 5.05 \times 10^{-3}$ M, $[KMnO_4]_0 = 0.98 \times 10^{-4}$ M, $[n\text{-}Bu_4N^+Br^-] = 2.05 \times 10^{-4}$ M.

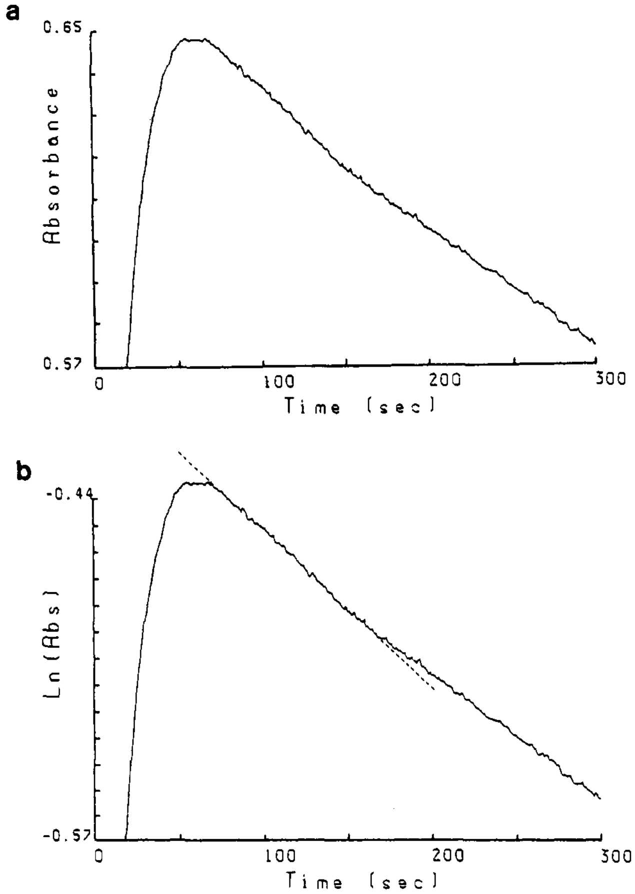


Figure 2. Plot showing changes in absorbance at 280 nm (a) and corresponding plot for ln (absorbance) (b) recorded as the intermediate forms and subsequently decomposes at 25 °C. $[DCPD]_0 = 2.50 \times 10^{-3}$ M, $[MnO_4^-]_0 = 0.95 \times 10^{-4}$ M, $[Et_4N^+Br^-] = 3.22 \times 10^{-4}$ M.

The kinetics were determined by following absorbance at 280 nm on a Hitachi Model 200-10 spectrophotometer, which was connected to a Sharp MZ-80B personal computer, and the plots of ln (absorbance) against time, as well as the plots of absorbance against time, were recorded on a X-Y plotter.

The ultraviolet-visible spectra were obtained by periodic scanning on a Union Giken MCPD-350PC spectrophotometer.

Iodometric Titration and Product Analysis. A solution of potassium permanganate (0.012 M) in dichloromethane prepared by using tetraethylammonium bromide or benzyltriethylammonium chloride was allowed to react by mixing with an equal volume of a solution of DCPD (0.24 M) in dichloromethane. To an aliquot (2 mL) of the resulting intermediate solution, 5 mL of an aqueous acidic solution ($[H_2SO_4]$ = 0.5 M) of excess NaI was added and the mixture was vigorously stirred for 10 min. The amount of liberated iodine was then titrated with a standard sodium thiosulfate solution.

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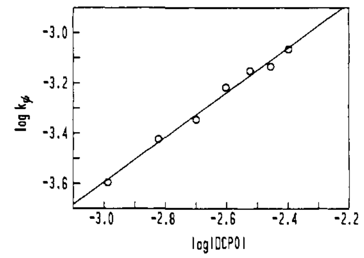


Figure 3. Dependence of the pseudo-first-order rate constants (k_ψ) for the decay of the intermediate on DCPD concentration in CH_2Cl_2 at 25 °C. $[MnO_4^-]_0 = 1.0 \times 10^{-4}$ M, $[Et_4N^+Br^-] = (2.7\text{–}3.9) \times 10^{-4}$ M. Slope = 0.89, correlation coefficient = 0.995.

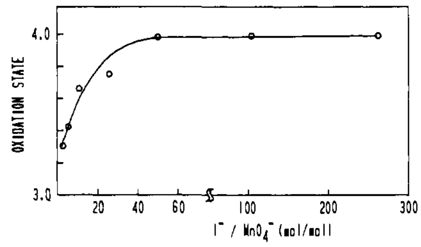


Figure 4. Apparent oxidation state of manganese determined immediately after the intermediate formed by iodometric titration using varying amounts of sodium iodide. $[DCPD]_0 = 0.31$ M, $[MnO_4^-]_0 = 0.64 \times 10^{-2}$ M, $[Et_3(PhCH_2)N^+Cl^-] = 1.2 \times 10^{-2}$ M.

The organic products were extracted with dichloromethane from the titration mixture and allowed to react with acetone in the presence of anhydrous $CuSO_4$ until the diol **2** in the mixture was completely converted into the acetone acetal. GLC analysis was then performed on a Hitachi 263-30 gas chromatograph (5% DEGS/Uniport B) with a calibration curve prepared beforehand.

Results

UV-Visible Spectra. Figure 1 shows the spectral change of the intermediate recorded at regular time intervals following its formation.[19] On losing the absorption maximum at 280 nm, the initially formed intermediate was transformed into a more stable species in ~40 min (a → e). No precipitation was observed during this process. Since flocculation of a colloid would cause an increase in the absorbance due to light scattering,[20] the spectral change cannot be ascribed to that of colloidal manganese dioxide.

Kinetic Data. Figure 2 shows a plot indicating the changes in absorbance at 280 nm (a) and the corresponding plot for ln (absorbance) (b) recorded as the intermediate forms and subsequently decomposes. The latter plot gives a straight line with negative slope at the early stage of the decomposition (until ca. 5% conversion), and a first-order rate constant (k_ψ) could be obtained directly from the slope. Furthermore, the decay of the intermediate shows a first-order dependence on the concentration of the alkene as shown in Figure 3.

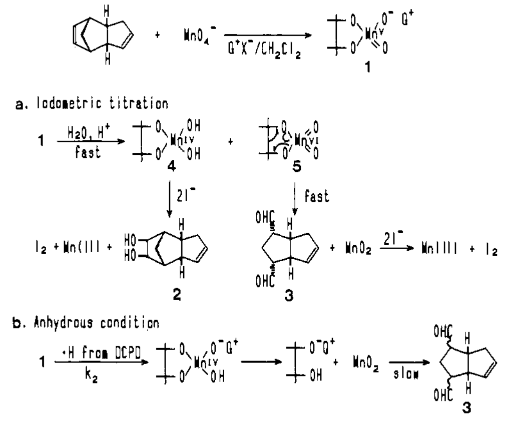
Oxidation State of Manganese in the Intermediate. A definite value of the apparent oxidation state, +3.99 ± 0.01, was obtained for manganese in the intermediate from iodometry carried out immediately after it had formed by use of acidic solutions of a large excess of NaI. The value is in accord with those reported by Perez-Benito and Lee[17] for the manganese species obtained in the oxidation of 26 alkenes by methyltributylammonium permanganate. The value of the oxidation state converges to +4.0 when NaI is used more than 50 times the molar quantity of permanganate initially used, while smaller values of the oxidation state were obtained when the amount of NaI was not sufficient (Figure 4). Apparently, oxidative decomposition of the intermediate plays an important part in the latter case.

Table I. Apparent Oxidation State for Manganese in the Intermediate and Product Ratio After the Iodometric Titration[a]

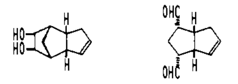
time elapsed, min	oxidation state[b]	**3**/**2**[b]
1[c]	3.99	1.05
10	3.96	0.37
30	3.79	0.25
120	3.59	0.31
1440	3.38	1.08

[a] $Et_4N^+Br^-$ was used as the catalyst. [b] Average of three experiments. [c] The reaction between permanganate and DCPD was completed at this time.

Scheme I



Products After Titration. At first, the results of the iodometric titration seemed to suggest that, as long as a sufficient amount of iodide is used, the reduction of manganese in the intermediate is brought about only by the reaction with iodide ion, and the oxidative decomposition of the manganate(V) ester intermediate as in eq 2 is not important here even in the acidic medium. To confirm this, we analyzed the organic products after the titration and found unexpectedly a 1:1 mixture of the diol **2** and the dialdehyde **3**. Since treatment of the intermediate with alkaline solution gives **2** exclusively,[7] the formation of **3** must have occurred during the titration through rapid oxidative decomposition of the manganate ester that escaped the reduction by iodide. This implies that the true oxidation state of the manganese intermediate is higher than that determined by the iodometry.



2 **3**

Table I shows the data of the iodometry carried out after the intermediate solution was allowed to stand for 10 min, 30 min, 2 h, and 24 h as well as the data obtained immediately after it formed. In the first 10 min, the apparent oxidation state did not change appreciably. However, in accordance with the spectral change (Figure 1), the **3**/**2** ratio decreased rapidly in this period and then increased gradually until it became ca. 1 again.

Discussion

These experimental results, when considered with our previous study[1] that showed the intermediate has an ionic nature, can be successfully explained with a mechanism depicted in Scheme I where the first-formed metastable intermediate is the cyclic manganate(V) diester ion **1**. Although the intermediate is stable to some extent in the nonaqueous solvent, it undergoes a rapid disproportionation to give a Mn(IV) ester **4** and a Mn(VI) ester **5** upon contact with the acidic solution added for the titration (Scheme Ia). Similar disproportionation of a manganate(V) diester was also proposed by Wolfe and Ingold[21] in the mechanism

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(19) A series of curves with an isosbestic point at 480 nm similar to those reported in ref 6 and 9 has been observed when the progress of the formation of the intermediate was monitored by UV-vis spectroscopy. Kinetic studies for the formation of the intermediate performed by measuring the rate at 420 and 525 nm using a stopped-flow technique also resulted in a set of kinetic parameters ($\Delta H^\ddagger = 3.8$ kcal mol^{-1}, $\Delta S^\ddagger = -39.3$ eu) similar to those in ref 6 and 9: Ogino, T.; Hasegawa, K.; Hoshino, E., unpublished work.

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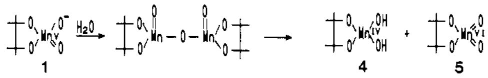
of α-ketol formation in aqueous solution, and it was pointed out that the disproportionation proceeds very rapidly via protonation and dimerization from analogy with inorganic manganate(V), as in eq 3. From this point of view, the stability of the manganate(V)



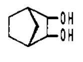
(3)

diester **1** in the nonaqueous solvent can be explained in terms of the tight ion pair formation[1] with quaternary ammonium ion in the solvent cage that obstructs the dimerization.

The Mn(VI) ester **5** thus formed undergoes a rapid oxidative decomposition to give the dialdehyde **3** and MnO_2 but escapes reaction with iodide due to its short lifetime. On the other hand, the Mn(IV) ester **4** has a longer lifetime and reacts with iodide to give Mn(II) and the diol **2**. Consequently, this mechanism well explains the **3**/**2** ratio observed after the titration. Since only Mn(IV) (including MnO_2 formed from **5** by the oxidative decomposition) reacts with iodide, the mechanism is also consistent with the results of the titration.

The rapid decrease in the **3**/**2** ratio and the little change in the apparent oxidation state observed in the first 10 min (Table I), when considered with the kinetic results, indicate that the spectral change (Figure 1) is a result of the subsequent reduction of the manganate(V) ester ion **1** to a manganese(IV) species, probably by abstraction of a hydrogen atom from the excess alkene as shown Scheme Ib. Since the spectrum e (Figure 1) resembles that of a colloid,[22] the initial products of this reaction may be manganese dioxide and the alkoxide ion of **2**.

The subsequent slow increase in the **3**/**2** ratio and slow decrease in the apparent oxidation state are due to oxidation of **2** to **3** by resulting MnO_2, because separately added *exo-cis*-bicyclo[2.2.1]heptane-2,3-diol (**6**) was also converted slowly to a corresponding dialdehyde **7** in the colloidal solution obtained by the reaction of permanganate with DCPD. In these experiments the dialdehydes **3** and **7** were obtained as a mixture of isomers due to the presence of the alkoxide ion of **2**.



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(22) The plot of log (absorbance) vs log λ for this spectrum shows a linear relationship with a slope of –4.3 as expected by Raileigh's law (absorbance = C/λ^4) for colloidal solution where the energy loss is due to light scattering.[20]

Chemistry, Structure, and Bonding in Diruthenium(II) Tetracarboxylates

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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Contribution No. 7896 from the Arthur Amos Noyes Laboratory, California Institute of Technology, Pasadena, California 91109. *Received January 4, 1989*

Abstract: $Ru_2(O_2CCH_3)_4Cl$ reacts with L-mandelic acid (Hmand) to convert 50% of the ruthenium to $Ru_2(mand)_4(H_2O)_2$ (**2**) and 50% to the accompanying disproportionation product, $[Ru_3O(mand)_6(H_2O)_3]^+$. The Ru_2(II,II) mandelate has been isolated and structurally characterized as $Ru_2(mand)_4 \cdot 2H_2O$, which crystallizes in space group $P2_1$ with the following unit cell parameters: a = 7.610 (2) Å, b = 32.181 (7) Å, c = 13.587 (4) Å, β = 90.28 (2)°, V = 3328 (3) Å^3, Z = 4. Two independent but essentially identical molecules having mandelate ions of the correct absolute chirality were found. The Ru–Ru distances are 2.266 (1) and 2.256 (1) Å; the water molecules are axially coordinated with a mean Ru–O distance of 2.35 Å. This is the first time a Ru_2(II,II) compound has been obtained directly, on a preparative scale from a Ru_2(II,III) compound. Compound **2** can be used to prepare other Ru_2(II,II) compounds, e.g., $Ru_2(O_2CC_6H_5)_4$ (**4**) and $Ru_2(O_2CCPh_3)_4$ (**5**) in good yield. Preliminary spectroscopic results on **2** are also reported. The magnetic susceptibilities of **4** and $Ru_2(O_2CCH_3)_4$ (**6**) have been measured in the temperature range 6–298 K. The derived magnetic moments drop from ca. 3.0 μ_B at room temperature to an extrapolated value of 0 μ_B at 0 K, and the shape of the curve can be fitted by an equation derived by postulating that a $^3A_{2g}$ state, derived from a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ configuration, undergoes a second-order splitting to give a nonmagnetic ground state (S_z = 0) lying 215 (25) or 244 (10) cm^{-1} for **4** and **6**, respectively, below a state with $S_z = \pm 1$, while all other spin singlet states arising from the same configuration lie ca. 3000 cm^{-1} higher. This evidence for a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ configuration is fully supported by structural relationships between the $Ru_2(O_2CR)_4^+$, $Ru_2(O_2CR)_4$, and $Ru_2(RNNNR)_4$ compounds.

Of all of the multiply bonded dimetal compounds[2] those of ruthenium have shown perhaps the most interesting variety of electronic structures. The major factor giving rise to this variety is the sensitivity of the relative energies of the two types of M–M antibonding orbitals, δ^* and π^*, which are—or can be—occupied in the Ru_2^{n+} units. The first authentic[3] diruthenium compounds reported (1966) were of the type $Ru_2(O_2CR)_4Cl$,[4,5] although their true nature was not recognized[6] until several years after the report[4] of their preparation (1969). It was then 6 more years until detailed experimental data on their electronic structures was obtained,[7] and it was not until 1979 that a full and rigorous theoretical study was published.[8] Subsequently, there have been extensive spec-

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(1) Texas A&M University. (b) California Institute of Technology.

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(3) In ref 4 the possibility that other types of $Ru_2(O_2CR)_2^{x+}$ compounds had been made was also tentatively advanced, but all of these others have either been shown to be something else (e.g., $[Ru_3O(O_2CR)_6(H_2O)]_6^+$ in some cases[5]) or have remained ill-defined.

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