to oxygen is much less than that of $[Fe(SR)_4]^{2-}$. Probably the CH_3S^- complexes are the least stable examples in both oxidation states, and this may be why $[Fe_2S_2(SCH_3)_4]^{2-}$ has not previously been reported. Being the simplest member of the series, this complex is of interest for spectroscopic studies[15] and for comparison with theoretical calculations.[16]

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Registry No. $(Et_4N)_2[Fe_2S_2(SCH_3)_4]$, 102261-05-2; $Et_4N[Fe(SCH_3)_4]$, 102261-06-3; $(Pr_4N)_2[Fe_2S_2(SEt)_4]$, 102261-07-4; S, 7704-34-9; $Pr_4N[Fe(SEt)_4]$, 86689-79-4; $(Et_4N)_2[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]$, 56083-11-5; $Et_4N[Fe(S_2\text{-}o\text{-}xyl)_2]$, 57456-65-2.

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Stereoselectivity Induced by an Optically Active Cationic Cobalt(III) Complex Ion on the Outer-Sphere Redox Reaction between Racemic Binuclear Molybdenum(V) Anions and Hexachloroiridate(IV) in Water

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We have reported the existence of stereoselectivity on outer-sphere redox reaction 1.[2–4] The selectivity was in favor of the

$$[Mo^V{}_2O_4(R,S\text{-pdta})]^{2-} + 2\Delta\Delta\text{-}[(en)_2Co(\mu\text{-}NH_2,O_2{}^{(-)})Co(en)_2]^{4+} \rightarrow 2\text{“}Mo^{VI}(pdta)\text{”} + 2\Delta\Delta\text{-}[(en)_2Co(\mu\text{-}NH_2,O_2{}^{(2-)})Co(en)_2]^{3+} \quad (1)$$

S-pdta and the *R*-pdta complex at lower and higher ionic strengths, respectively. Kinetic analysis[5,6] of the observed rate data suggested that the selectivity at the precursor formation (equilibrium constant K_{IP}) and the net electron-transfer step (rate constant k_e) operate in reversed directions, the ratio $K_{IP}(R)/K_{IP}(S)$ being >1.09 at I = 0.5 M.[2]

In order to elucidate the mechanism of selectivity at the precursor formation step, we have used nonchiral hexachloroiridate(IV) as oxidant and examined the influence of optically active cations on the oxidation of the racemic $[Mo^V{}_2O_4(R,S\text{-pdta})]^{2-}$ complex.

Experimental Section

Preparations of the Complexes. $Na_2[Mo_2O_2(\mu\text{-}O)_2(R,S\text{-pdta})]\cdot 3H_2O$,[7] Δ-$[Co(en)_3]Cl_3$,[8] and Δ- and Λ-$[Co(gly)(en)_2]Cl_2$[9] were prepared by the known methods. Δ-$[Co(etaH)(R\text{-chxn})_2](ClO_4)_3\cdot 5H_2O$ and Δ-$[Co(S\text{-praH})(R\text{-pdta})_2](ClO_4)_3$ were supplied by Dr. T. Nishide.[10] Optical purity of the cobalt(III) complexes was checked by the intensity of circular dichroism (CD) spectra to be almost 100%. Commercial $Na_2[IrCl_6]\cdot 6H_2O$ was recrystallized once from water.

Table I. Ratio of Rates of Oxidation of $[Mo^V{}_2O_4(R\text{-pdta})]^{2-}$ and $[Mo^V{}_2O_4(S\text{-pdta})]^{2-}$ with $[IrCl_6]^{2-}$ in the Presence of Optically Active Cobalt(III) Ions[a]

Co^{III} complex	enantiomeric excess (% ee) of unreacted Mo(V) dimer (isomer in excess)	ratio of oxidn rates (easily oxidized isomer)
Λ-$[Co(en)_3]^{3+}$	0.14 (*R*-pdta)	1.003 (*S*-pdta)[b]
	0.51 (*R*-pdta)	1.010 (*S*-pdta)[c]
Δ-$[Co(S\text{-praH})(R\text{-chxn})_2]^{3+}$	0.55 (*S*-pdta)	1.011 (*R*-pdta)[b]
	1.99 (*S*-pdta)	1.04 (*R*-pdta)[c]
Δ-$[Co(etaH)(R\text{-chxn})_2]^{3+}$	0.15 (*S*-pdta)	1.003 (*R*-pdta)[c]
Δ-$[Co(gly)(en)_2]^{2+}$	~0.07 (*S*-pdta)	~1.001 (*R*-pdta)[c]
Λ-$[Co(gly)(en)_2]^{2+}$	~0.04 (*R*-pdta)	~1.001 (*S*-pdta)[c]

[a] Reaction conditions: $[Mo^V{}_2] = [Ir^{IV}] = 1.0 \times 10^{-4}$ M; $[Co^{III}] = 1.0 \times 10^{-3}$ M; 60 °C. [b] I = 0.2 M ($NaClO_4$); pH 3.7 (acetate buffer). [c] pH ca. 5.5; $NaClO_4$ was not added.

Measurements of Stereoselectivity. An aqueous solution (9 cm^3) of 2.0×10^{-3} M $Na_2[IrCl_6]\cdot 6H_2O$ (1 M = 1 mol dm^{-3}) was added to a solution (171 cm^3) containing 1.05×10^{-4} M $Na_2[Mo_2O_4(R,S\text{-pdta})]\cdot 3H_2O$, 1.05×10^{-3} M optically active cobalt(III) complex, and appropriate amounts of $NaClO_4$ and buffer component at 60 °C. The mixture was kept at 60 °C for 1 h until the characteristic strong absorption bands of $[IrCl_6]^{2-}$ in the visible region[11] disappeared. The solution was diluted with water and treated with a cation-exchange column (SP Sephadex C-25 in Na^+ form) to remove the cationic cobalt(III) complex. The eluate was concentrated to less than 10 cm^3 and made up to 10 cm^3 with water for measuring the absorption and CD spectra in the region 340–440 nm. Since the stoichiometry of the redox reaction $[Mo_2]$ vs. [Ir] is 1 to 2,[12,13] half the molybdenum(V) dimer remains unreacted. The observed CD band around 385 nm should be due to the unreacted molybdenum(V) dimer, since neither $[Ir^{III}Cl_6]^{3-}$ nor the molybdenum(VI) complex has a CD band in this region.[2] From the $\Delta\epsilon$ value (−5.5 at 387 nm) of pure $[Mo_2O_4(R\text{-pdta})]^{2-}$[14] was estimated the enantiomeric excess of the unreacted molybdenum(V) dimer.

The absorption and CD spectra were recorded with a Hitachi 330 spectrophotometer and a JASCO J-40A automatic recording spectropolarimeter, respectively. The pH of solution was measured by a Metrohm Herisau E300B pH meter.

Results and Discussion

The overall reaction is written as (2). Equimolar amounts of the reactants were used so that half of the molybdenum(V) dimer remained unchanged, which should give optical activity if the reaction proceeded stereoselectively. Thirteen optically active

$$[Mo_2O_4(R,S\text{-pdta})]^{2-} + 2[IrCl_6]^{2-} \rightarrow 2\text{“}Mo^{VI}(pdta)\text{”} + 2[IrCl_6]^{3-} \quad (2)$$

cobalt(III) complex cations were used, but most of them gave precipitation with $[IrCl_6]^{2-}$ even in the presence of Na_2H_2edta.[2,5] The data were obtained only for a limited number of systems, but significant selectivity was observed in the presence of optically active complex cations, which remained unchanged throughout the progress of the redox reaction (Table I).

Table I clearly indicates that the absolute configuration of the cobalt(III) ion rules the preference with which either the *R*-pdta or the *S*-pdta complex of $Mo^V{}_2O_4{}^{2+}$ is more rapidly oxidized: i.e. a Δ-cation favors more rapid oxidation of the *R*-pdta complex, and a Λ-cation favors that of the *S*-pdta complex. It is less likely that the rate of net electron transfer between nonchiral iridate(IV)

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(4) Abbreviations used in this paper: *R*-$pdta^{4-}$ = (*R*)-propylenediaminetetraacetate(4−); en = ethylenediamine; *S*-praH = (*S*)-2-aminopropanol; *R*-chxn = (*R*)-1,2-cyclohexanediamine; etaH = 1-aminoethanol; $edta^{4-}$ = ethylenediaminetetraacetate(4−); gly^- = glycinate(1−).

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and the *R*- and *S*-pdta complex of $Mo_2O_4^{2+}$ is different among the enantiomers of the molybdenum(V) dimer. The selectivity should result from the formation step of the precursor, which is likely an ion triplet composed of the nonchiral oxidant, optically active countercation, and one of the enantiomer reductants. The ion-pair formation constant between $[Mo_2O_4(R\text{-pdta})]^{2-}$ and $\Delta\Delta\text{-}[Co_2(\mu\text{-}NH_2,O_2^{(-)})(en)_4]^{4+}$ was larger by a factor of at least 1.09 than that between the *S*-pdta complex and the ΔΔ-cation.[2] A difference of similar nature can be expected for the association constants among the redox pair and the optically active counterion, which should mediate the approach of the anionic reductant to the anionic oxidant.

$$K_{OS}\{[Mo_2O_4(R\text{-pdta})]^{2-},\Delta\text{-}[Co^{III}]^{n+},[Ir^{IV}]^{2-}\} > K_{OS}\{[Mo_2O_4(S\text{-pdta})]^{2-},\Delta\text{-}[Co^{III}]^{n+},[Ir^{IV}]^{2-}\}$$

The enantiomeric excess decreases with decreasing charge of the cations and with increasing ionic strength, and this fact supports the belief that the precursor formation is responsible for the stereoselective reaction.

Interaction of optically active compounds with a racemic mixture of an optically active labile coordination compound in solution is well-known as the Pfeiffer effect.[15] The origin of the effect has been considered to be a stereoselective interaction between an optically active compound and a racemic mixture of a metal complex. Stereoselective ion-pair formation between chiral cations and anions was first pointed out by Ogino in 1967,[16] and more examples have been reported since.[17] Preferential interaction among the *R*-pdta complex of $Mo_2O_4^{2+}$, the Δ-cobalt(III) complex, and the iridate(IV) complex must be brought about by the particular combination of chiral structures of the octahedral Δ-cation and around the twisted $Mo_2O_4^{2+}$ core.[18]

The importance of ion triplet precursor formation constants in determining the overall rate of redox reactions was demonstrated as the influence of cations on the rate of thermal redox reactions between anionic oxidants and reductants, e.g. MnO_4^- vs. MnO_4^{2-}[19] and $[Fe(CN)_6]^{4-}$ vs. $[Fe(CN)_6]^{3-}$ in water,[20] and of photoquenching reactions between $[Mo_6Cl_{14}]^{2-}$ and $[IrCl_6]^{2-}$ in acetonitrile.[21] Our present results indicate that the ease with which the oxidant comes close to the reductant is dependent not only on their electronic charges but also on the charges and the configurations of the added ions.

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Registry No. $[Mo_2O_4(R\text{-pdta})]^{2-}$, 75520-37-5; $[Mo_2O_4(S\text{-pdta})]^{2-}$, 75520-38-6; $[IrCl_6]^{2-}$, 16918-91-5; $\Lambda\text{-}[Co(en)_3]^{3+}$, 27228-84-8; $\Delta\text{-}[Co(S\text{-praH})(R\text{-chxn})_2]^{3+}$, 55669-01-7; $\Delta\text{-}[Co(extaH)(R\text{-chxn})_2]^{3+}$, 55627-47-9; $\Delta\text{-}[Co(gly)(en)_2]^{2+}$, 19657-79-5; $\Lambda\text{-}[Co(gly)(en)_2]^{2+}$, 19657-80-8.

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Additions and Corrections

1981, Volume 20

Akira Katagiri,* Seiji Yoshimura, and Shiro Yoshizawa: Formation Constant of the Tetracyanocuprate(II) Ion and the Mechanism of Its Decomposition.

Pages 4143, 4145, 4146. An error was found in the calculation of the standard electrode potential of the redox couple $Cu^{II}(CN)_4^{2-}/Cu^{I}(CN)_4^{3-}$ and the formation constant of $Cu^{II}(CN)_4^{2-}$. The correct values are as follows:

$$E°(Cu^{II}(CN)_4^{2-}/Cu^{I}(CN)_4^{3-}) = 0.54 \text{ V vs. NHE}$$

$$\beta(Cu^{II}(CN)_4^{2-}) = 10^{24.0}\ M^{-4}$$

According to the above corrections, the stepwise formation constant of $Cu^{II}(CN)_4^{2-}$ (K_4) is recalculated to be $10^{4.8}$–$10^{5.0}$ M^{-1}, which gives the k_a value of $10^{11.9}$–$10^{11.5}$ $M^{-1}\ s^{-1}$.

Page 4147. In Table I the k_r values in the first section (data from ref 8) and the fourth section (data from ref 5) should be multiplied by 10^4, and corresponding changes should be made in Figure 5. Equation 30 should be changed as follows:

$$\log k_r = 6.65 \log [CN^-] + 49.6$$

In the Appendix the estimated values of K_i should be multiplied by $10^{0.5}$. However, these corrections do not alter the conclusion.—Akira Katagiri