J. Am. Chem. Soc. **1980**, *102*, 7247–7252

Annelides. 3. Complexation of Dioxygen in Organized Cobaltous Complex Assemblies. A New Approach to Kinetic Studies in Micellar Phases

J. Simon,* J. Le Moigne, D. Markovitsi, and J. Dayantis

Contribution from the Centre de Recherches sur les Macromolécules (CNRS), 67083 Strasbourg, Cedex, France. *Received May 21, 1980*

Abstract: Amphiphilic ligands belonging to the Annelide class are synthesized and shown to form complexes with transition-metal cations. By aggregation, these complexes can be organized into supermolecular structures. For the first time, it is shown that the formation of micellar phases of cobaltous complexes can lead to a dramatic enhancement of the dioxygen stability constant. Kinetic measurements have been performed to elucidate the mechanism of complexation and, in particular, the respective contributions of the local concentrations, the dimensionality of the reaction, and the orientation of the reactants upon the micellar effect. A new theoretical approach is presented to rationalize the chemical reactions in micellar phases by using the Prigogine–Flory model.

Introduction

The Annelides represent a new type of surfactants which are characterized by a polar head able to bind selectively a metallic ion and by a hydrophobic moiety, usually a paraffinic chain, to ensure an amphiphilic character to the ligand and allow the formation of ordered aggregates.[1-3] Alkali and alkaline earth cation complexation into micellar phases has been previously studied.[1,3] We are concerned in this publication with transition-metal assemblies and particularly in showing what original properties preorganized transition-metal assemblies might bring. As a matter of fact, it is generally thought that polynuclear species should open an immense field in various domains such as the activation of small molecules[4-8] or the design of photosynthetic models.[9] Polymetallic assemblies might favor, for example, polyelectronic transfer ($2H^+ + O_2 \xrightarrow{2e^-} H_2O_2$, $6H^+ + N_2 \xrightarrow{6e^-} 2NH_3$) and thus catalyze reactions where monoelectronic transfer is energetically unfavorable. The most common method of obtaining a cooperativity between metallic cations is to hold them close to each other using a ligand with several binding sites.[10-18] The main disadvantage of this approach is the generally lengthy synthesis of the ligands. This difficulty is largely avoided with the Annelides (Figure 1). In a first step, a chelating moiety is chosen to complex a single metallic ion belonging to a certain class. The crown ether type will be taken to bind an alkali or an alkaline earth cation, whereas a cyclam structure will be convenient for class VIII transition metals (Figure 1a). Owing to the amphiphilic character of the ligand, aggregates may be formed by segregation of the polar and hydrophobic parts (Figure 1b). This leads to polymetallic assemblies whose structural parameters (i.e., the intermetallic distance) are determined by the nature of the aggregates formed, from the less organized, the micelles, to the highly structured lamellar systems. Before our initial report on Annelides,[1] a few amphiphilic ligands with an analogous structure had been described[19,20] but their lipophilic character was only used to selectively extract metallic ions into an organic phase. Since then several other amphiphilic ligands have been reported[21-23] and some original properties of silver complexes in micellar phases have been demonstrated.[24,25]

Table I. Critical Micellar Concentrations (cmc) for the Annelides Ia and IIa and Their Metal Complexes

	pH	cmc
Ia + $2.5H^+$	6.8^a	5×10^{-4}
+ $4H^+$	1.56^b	1.4×10^{-3}
+ $Co^{III}(H_2O)_2$	6.8^a	6×10^{-4}
IIa + $2.5H^+$	6.65^a	5×10^{-4}
+ $4H^+$	1.85^b	2×10^{-3}
+ $Co^{III}(OH)_2$	9.9^a	5×10^{-4}
+ $Ni(NO_3)_2$	$6.8^{a,c}$	7×10^{-4}

[a] [Triethanolamine/HNO_3] = 0.02 M, [KNO_3] = 0.1 M.
[b] [HNO_3] = 0.02 M, [KNO_3] = 0.1 M. Temperature = 25 °C.
[c] 39 °C.

This paper describes the synthesis of Annelides which allow the binding of most of the transition metals. The cobaltous complexation is studied in micellar systems, and the original properties of the polycobaltous assemblies toward dioxygen complexation are observed. Part of this work has been presented at a meeting and subsequently published.[2]

Results

Synthesis of the Ligands. It is apparent from the literature that the triethylenetetramine (trien) and *N,N'*-bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet) subunits are among the most suitable Annelide polar heads since they are known to complex most of the common transition metals (Figure 2). A polar head having a macrocyclic structure had to be used for binding the

---

(1) Le Moigne, J.; Gramain, Ph.; Simon, J. *J. Colloid. Interface Sci.* **1977**, *60*, 565.

(2) Simon, J.; Le Moigne, J. "First International Symposium on Oxygen Activation", May 21–23, 1979, Bendor, France. *J. Mol. Catal.* **1980**, *7*, 137.

(3) Le Moigne, J.; Simon, J. *J. Phys. Chem.* **1980**, *84*, 170.

(4) Fallab, S. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 496.

(5) Valentine, J. S. *Chem. Rev.* **1973**, *73*, 235.

(6) Murray, C. R.; Smith, D. C. *Coord. Chem. Rev.* **1968**, *11*, 429.

(7) Chatt, J.; Leigh, G. J. *Chem. Soc. Rev.* **1972**, *1*, 121.

(8) Borod'Ko, Yu. G.; Shilov, A. E. *Russ. Chem. Rev.* (*Engl. Transl.*) **1969**, *38*, 355.

(9) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Gleria, M. *Science* **1975**, (*Washington, D.C.*) *189*, 852 and references therein.

(10) Robson, R. *Aust. J. Chem.* **1970**, *23*, 2217.

(11) Caselatto, V.; Vigato, P. A.; Fenton, D. E. *Chem. Soc. Rev.* **1979**, *8*, 199 and references therein.

(12) Cheney, J.; Lehn, J. M.; Sauvage, J. P.; Stubbs, M. E. *J. Chem. Soc., Chem. Commun.* **1972**, 1100.

(13) Lehn, J. M.; Simon, J.; Wagner, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 578; *Nouv. J. Chim.* **1977**, *1*, 77; *Helv. Chim. Acta* **1977**, *60*, 141.

(14) Alberts, A. H.; Annunziata, R.; Lehn, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 8502.

(15) Wong, K. W.; Bourgouin, M.; Smid, J. *J. Chem. Soc., Chem. Commun.* **1974**, 715.

(16) Chang, C. K. *J. Am. Chem. Soc.* **1977**, *99*, 2819.

(17) Kagan, N. E.; Mauzerall, D.; Merrifield, R. B. *J. Am. Chem. Soc.* **1977**, *99*, 5484.

(18) Collman, J. P.; Elliott, C. M.; Halbert, T. R.; Tavrog, B. S. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 18.

(19) Cinquini, M.; Montanari, F.; Tundo, P. *J. Chem. Soc., Chem. Commun.* **1975**, 393.

(20) Clément, D.; Damm, F.; Lehn, J. M. *Heterocycles* **1976**, *5*, 477.

(21) Tabushi, I.; Taniguchi, Y.; Kato, H. *Tetrahedron Lett.* **1977**, 1049.

(22) Tabushi, I.; Fujiyoshi, M. *Heterocycles* **1977**, *7*, 851.

(23) Lerner, D. A.; Ricchiero, F.; Giannotti, C. *J. Colloid. Interface Sci.* **1979**, *68*, 596.

(24) Moroi, Y.; Pramauro, E.; Grätzel, M.; Pelizzetti, E.; Tundo, P. *J. Colloid. Interface Sci.* **1979**, *69*, 341.

(25) Humphry-Baker, R.; Grätzel, M.; Tundo, P.; Pelizzetti, E. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 630.

0002-7863/80/1502-7247$01.00/0

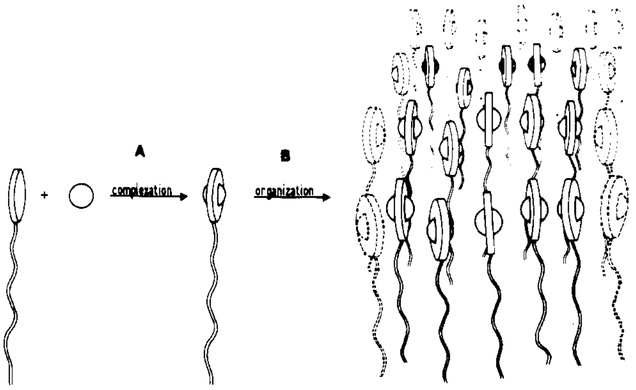

Figure 1. Formation of supermolecular polymetallic assemblies with Annelide type ligands: (A) complexation of a metallic cation by the Annelide polar head; (B) formation of the supermolecular assembly by aggregation.

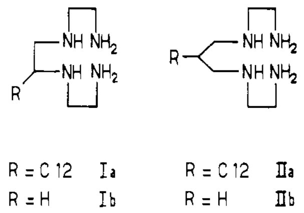

Figure 2. Synthesized and reference ligands.

nonpolarizable alkaline earth cations.[1,3] The transition metals usually form very stable complexes with linear polydentate ligands, thus, macrocyclic binding sites are not required. The reference compounds Ib and IIb are commercially available; the ligand Ia has been synthesized by a method already described.[26] A new reaction pathway has been used for IIa. The paraffinic chain is introduced at the very first stage by using the malonic ester synthesis. The diester derivative is then reacted with a large excess of ethylenediamine to form the diamide. Its reduction with a solution of diborane in THF[27] furnishes the corresponding tetraamine. The overall yield is 22% from the starting material. This pathway is quite general for synthesizing unsymmetrical ligands having different substituents on each nitrogen of the ethylenediamine subunit. Several metal complexes have been isolated and crystallized: Ia, $CoCl_3$ (decomposes above 200 °C); IIa, $Ni(NO_3)_2$ (mp 169 °C); IIa, $Cu(NO_3)_2$ (mp 190 °C); IIa, $CoCl_3$ (mp 246 °C). In all cases a one to one stoichiometry is observed. The trien and the 2,3,2-tet subunits differ by the geometry of the complexes obtained, the former forming preferably α or β cis complexes and the latter trans octahedral ones.[28-30] The absorption spectra are highly sensitive to the geometry around the cation and to the nature of the counterion. Only very small differences have been noticed between the amphiphilic complexes and their nonsubstituted homologues (Ia, $Co(OH)_2NO_3$ in water, $\epsilon_{510} = 82$, $\epsilon_{362} = 218$; Ib, $Co(OH)_2NO_3$, $\epsilon_{515} = 106$, $\epsilon_{367} = 102$; IIa, $Co(OH)_2NO_3$, $\epsilon_{526} = 47$, $\epsilon_{372} = 74$; Ib, $Co(OH)_2NO_3$, $\epsilon_{526} = 52$, $\epsilon_{380} = 61$). In consequence, it does not seem that the micellization influences the structure of the polar head very much. On the other hand, the nature of the isomer used, the cis or the trans complex, will be seen to be of the utmost importance regarding dioxygen complexation. More generally, this leads to a way of obtaining two types of organized polymetallic assemblies differing by the respective positions of the two vacant sites on the metal ion.

Characterization of the Micellar State. Table I shows the critical micellar concentration (cmc) for the Annelides Ia and IIa, either fully (4 H^+) or partially protonated (2.5 H^+). As expected, there is a large increase in the cmc when the number of charges born by the polar head is increased. On the other hand, neither the geometry around the metal ion nor the nature of the complexed cation seem to influence the cmc's to any great extent. The intermetallic distance at the micellar subsurface can be estimated from the molecular weight of the aggregates determined by light scattering (see ref 3 for the calculation in the case of alkaline earth Annelides). The surface available for each polar head depends slightly on the aggregation number for a given shape of the micelles.[54] For usual micellar weight, an interparaffinic distance of 8 Å at the interphase can be taken with some confidence.[3,54] The mean intermetallic distance is thus approximately 10 Å, but owing to the highly unsymmetrical nature of the polar heads there is a big difference between their closest approach (3.3–3.5 Å) and their furthest distance (16.5–16.7 Å). It must be pointed out that those numbers represent approximate values, since the geometry of the micelle probably varies greatly with time.

Table II. Protonation Constants for the Annelides Ia and IIa Compared to the Reference Compounds

ligand	pK_1	pK_2	pK_3	pK_4
Ia	10.04	8.82	6.67	2.40
Ib	10.25	9.32	6.59	2.81
	9.95[a]	9.31[a]	6.86[a]	3.66[a]
IIa	9.83	8.76	6.58	5.09
IIb	10.83	9.42	7.20	5.73
	10.25[a]	9.50[a]	7.28[a]	6.02[a]

[a] From ref 33. All titrations in 0.1 M [KNO_3] at 25 °C ([L_0] = 0.005 M).

Effects of the Micellar State on the Complexation Constants. Acid–base titrations can accurately furnish ligand–cation stability constants when there is competition between complexation and protonation for the same site on the ligand.[31,32] The case of the micellar phases has been treated previously.[3] It was shown that any "filling effect" on protonation or cation stability constants can be neglected; i.e. the overall degree of ionization of the micelle does not influence to a large extent the various complexation constants. However, the presence of an organized structure does play a role in the absolute value of these constants, but it has been shown[3] that this effect almost entirely stems from the perturbation of the local electrostatic properties at the micellar interface. It can be seen from Table II that the aggregation of the trien and 2,3,2-tet units into micellar phases does not lead to a large change in the various characteristic constants of protonation. All the titrations were run at a concentration exceeding by a factor of 2 the highest cmc found. The cobalt complexation does not lead either to large differences (log K_{ass} for Ia = 11.2, Ib = 10.8, IIa = 11.6, IIb = 12.5). Care was taken to avoid any dioxygen contamination of the solutions (see Experimental Section) since the potentiometric curves are highly dependent on dioxygen complexation with the cobaltous complexes (vide infra).

Dioxygen Stability Constants. After the papers of Fremy[35] and Werner[36] many studies have been devoted to dioxygen complexation by ammine complexes of cobaltous ions.[37-39] For tetradentate ligands equilibra 1–3 have to be considered.

$$LCo^{II} + O_2 \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} LCo^{II}(O_2) \qquad (1)$$

$$K_1 = [LCo^{II}O_2]/[LCo^{II}][O_2]$$

---

(26) Melhado, L. L.; Gutsche, C. D. *J. Am. Chem. Soc.* **1978**, *100*, 1850.

(27) Brown, H. C.; Heim, P. *J. Am. Chem. Soc.* **1964**, *86*, 3566.

(28) Bosnich, B.; Gillard, R. D.; McKenzie, Webb, G. A. *J. Chem. Soc. A* **1966**, 1331.

(29) Halliday, R. W.; Court, R. H. *Can. J. Chem.* **1974**, *52*, 3469.

(30) Hamilton, H. G., Jr.; Alexander, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 5065.

(31) Bjerrum, J. "Metal Ammine Formation in Aqueous Solutions"; Hase and Son: Copenhagen, 1941.

(32) Schwarzenbach, G. *Helv. Chim. Acta* **1950**, *33*, 947, 974.

(33) Weatherburn, D. C.; Billo, E. J.; Jones, J. P.; Margerum, D. W. *Inorg. Chem.* **1970**, *9*, 1557.

(34) Sillen, L. G.; Martell, A. E. *Spec. Publ. Chem. Soc.* **1964**, *No. 17*; **1972**, *No. 25*.

(35) Fremy, D. *Ann. Chim. Phys.* **1852**, *35*, 271.

(36) Werner, A. *Justus Liebigs Ann. Chem.* **1910**, *375*, 1.

(37) McLendon, G.; Martell, A. E. *Coord. Chem. Rev.* **1976**, *19*, 1.

(38) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.

(39) Vogt, L. H. J.; Faigenbaum, H. M.; Weberley, S. E. *Chem. Rev.* **1963**, *63*, 269.

$$LCo^{II}O_2 + LCo^{II} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} LCo^{II}(O_2)Co^{II}L \qquad (2)$$

$$K_2 = [LCo^{II}(O_2)Co^{II}L]/[LCo^{II}(O_2)][LCo^{II}]$$

$$H_2O + LCo^{II}(O_2)Co^{II}L \underset{k_3}{\overset{k_{-3}}{\rightleftharpoons}} LCo^{II}\left(\begin{smallmatrix}O_2\\OH\end{smallmatrix}\right)Co^{II}L + H^+ \qquad (3)$$

$$K_3 = [LCo^{II}\left(\begin{smallmatrix}O_2\\OH\end{smallmatrix}\right)Co^{II}L][H^+]/[LCo^{II}(O_2)Co^{II}L]$$

The species $LCo^{II}(O_2)$ is not usually observed and the dioxygen stability constants calculated are

$$K_{O_2}{}^{mono} = \frac{[LCo^{II}(O_2)Co^{II}L]}{[LCo^{II}]^2[O_2]} = K_1K_2 \qquad (4)$$

$$K_{O_2}{}^{di} = \frac{[LCo^{II}\left(\begin{smallmatrix}O_2\\OH\end{smallmatrix}\right)Co^{II}L][H^+]}{[LCo^{II}]^2[O_2]} = K_1K_2K_3 \qquad (5)$$

It is possible by potentiometry to determine K_{O_2} by using the method previously described for the determination of the cobalt association constants while working under a pure atmosphere of dioxygen. The cobaltous complex of 2,3,2-tet does not have the two cis vacant sites which are necessary for the formation of the dibridged species, and the rate of step 3 should be limited by the slow isomerization *trans*-2,3,2-tet to *cis*-2,3,2-tet (Figure 3). In contrast, it is well-known[40-42] that the trien unit leads very rapidly to the dibridged species. Indeed, this has been observed by UV spectrometry (Table III) on considering the charge-transfer band $O_2^{2-} \rightarrow Co^{III}(\pi^* \rightarrow d_\sigma^*)$ which is highly dependent on the geometry of the O–O bond.[43,44] The dioxygen complexes may be written either as $LCo^{II}(O_2)Co^{II}L$ or as $LCo^{III}(O_2^{2-})Co^{III}L$. This latter representation is by far the closest to reality considering both the various X-ray structural determinations[37] and the fact that the complexes can be obtained either by reaction of LCo^{II} and dioxygen or by $LCo^{III}(H_2O)$ plus H_2O_2 (Figure 4).

$$2LCo^{II} + O_2 \rightarrow LCo^{II}(O_2)Co^{II}L \leftrightarrow LCo^{III}(O_2^{2-})Co^{III}L \leftarrow 2LCo^{III} + H_2O_2 \qquad (6)$$

The dioxygen stability constants have been determined in micellar (ligands Ia and IIa) and nonmicellar phases (Ib and IIb) (log $K_{O_2}{}^{mono}$ for IIa = 11.2, IIb = 10.4, log $K_{O_2}{}^{di}$ for Ia = 8.8, Ib = 6.7). The comparison between the ligands of type I and II is hard to make since the species involved are not the same. It has been stated[37] that the formation of the second bridge "locks-in" the dioxygen complex. Such an effect is not apparent from the association constants found. On the other hand, the presence of micellar phases drastically influences the strength of the association. In the trien case the dioxygen complex is as much as 125 times more stable when the cobaltous complexes are organized at the micellar subsurface. The 2,3,2-tet ligands lead only to a sixfold increase in K_{O_2} in favor of the micellar phase. The change of dioxygen solubility when micelles are formed cannot account for such a large difference.[45] Figure 5 represents the various dioxygen complexes when Annelide type ligands are used. It is worth noting that although the mean intermetallic distance is too large to really offer the proper site of complexation of the dioxygen molecule,[37,56] one of the micellar conformations does furnish the correct cobalt–cobalt distance (3.3–3.5 Å) without perturbing the interparaffinic spacing. The cobaltous ions are thus partly preorganized prior to the complexation of the dioxygen molecule. It must be now checked out that this factor is really the cause of the micellar effect found. For that the various kinetic constants for the formation of the dioxygen complexes have been determined to elucidate (i) the mechanism of the complexation and (ii) the nature of the micellar effect.

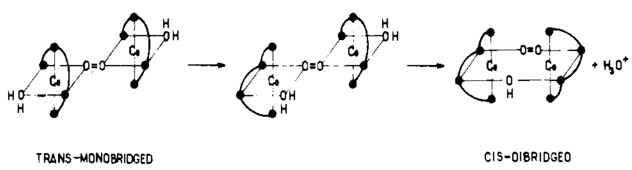

Figure 3. Schematic representation of the isomerization between the trans-monobridged to the cis-dibridged dioxygen complex.

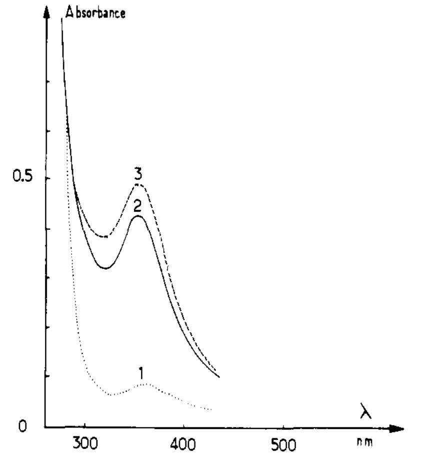

Figure 4. UV spectra of the trien–dioxygen complex obtained from $LCo^{II} + O_2$ (2) or $LCo^{III} + H_2O_2$ (3): (1) $[LCo^{II}] = 0.00776$ M (pH 5.20, L = trien); (2) pure O_2 bubbled into (1); (3) 3 mequiv of $AgNO_3$ (0.1 M) added to 3 mL of an acidic solution of $LCo^{III}Cl_3$. After filtration, 0.5 mL of H_2O_2 (30%) is added (final pH 5.20), and the solution is left at room temperature 3 days.

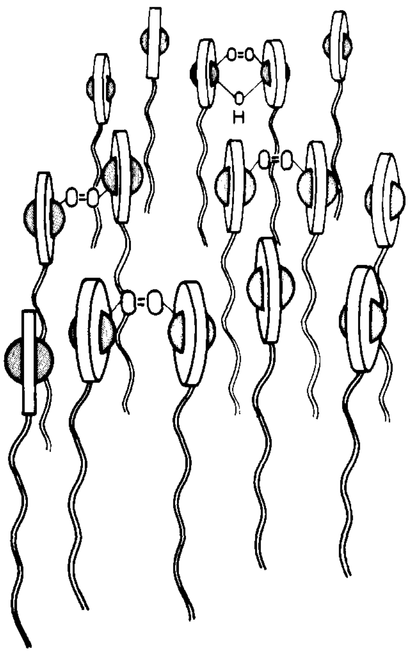

Figure 5. Schematic picture of the various dioxygen complexes formed at the micellar subsurface of Annelide type ligand.

Table III. Maximum Absorption Wavelengths (λ_{max}) and Absorption Coefficients (log ϵ) for Mono- and Dibridged Dioxygen Complexes of Ia and IIa

ligand	λ_{max}, nm	log ϵ, M^{-1} cm^{-1}
μ-peroxo monobridged[a]	300 ± 5	3.8 ± 0.2
μ-peroxo dibridged[a]	352 ± 5	3.7 ± 0.1
C(12)-trien (Ia)[d]	365	3.89
trien (Ib)[b]	355	4.00
C(12)-2,3,2-tet (IIa)[c]	297	3.57
2,3,2-tet (IIb)[b]	290	4.02

[a] General abosrption spectral data from ref 43. [b] pH 5.9, phosphate buffer (0.1 M). [c] pH 5.4 adjusted with HNO_3, KNO_3 (0.1 M). [d] pH 6.8, triethanolamine buffer.

---

(40) Fallab, S. *Chimia* **1967**, *21*, 538.

(41) Nakon, R.; Martell, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 3026.

(42) Zehnder, M.; Fallab, S. *Helv. Chim. Acta* **1975**, *58*, 13.

(43) Barraclough, C. G.; Lawrance, G. A.; Lay, P. A. *Inorg. Chem.* **1978**, *17*, 3317.

(44) Lever, A. B. P.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 348.

(45) Matheson, I. B. C.; King, A. D., Jr. *J. Colloid. Interface Sci.* **1978**, *6*, 464.

Table IV. Rate Constants for the Formation of the Dioxygen Monobridged Binuclear Complexes in Micellar and Nonmicellar Phases

	k_1, M^{-1} s^{-1}			
pH[a]	Ia	Ib	IIa	IIb
6.8	6.5×10^3	8.1×10^3	$>2.5 \times 10^5$	$>2.5 \times 10^5$
7.8	8.3×10^3	1×10^4 (1.9×10^4)[b]		
8.8	1.2×10^4	1.4×10^4 (2.3×10^4)[b]		

[a] Buffer = triethanolamine/HNO_3 (0.02 M), KNO_3 (0.1 M). [b] From ref 46.

Table V. Kinetic Parameters for the Formation of the Dibridged Binuclear Complexes in Micellar and Nonmicellar Phases

	k_3,[c] s^{-1}		
pH[a]	Ia	Ib	IIb
6.8	0.17	1.1	3.9×10^{-5}
7.8	0.18	1.3 (1.6)[b]	1.9×10^{-5}
8.8	0.13	1.3 (2.0)[b]	2.1×10^{-5}

[a] Buffer = triethanolamine/HNO_3 (0.02 M), KNO_3 (0.1 M). [b] From ref 46. [c] k_3 for IIa was not found.

Kinetic Determinations for the Dioxygen Complexation and the Dibridge Formation. Miller and Wilkins have already studied the kinetics of dioxygen complexation in the trien case.[46] It was found that the formation of the mononuclear dioxygen complex (eq 1) is the rate-limiting step, thus

$$\frac{d[LCo^{II}(O_2)Co^{II}L]}{dt} = k_1[LCo^{II}][O_2] \tag{7}$$

The experiments are generally run under pseudo-first-order conditions so that

$$k_1[LCo^{II}] \approx \text{constant} = k'_1$$

The second stage of the reaction is the dibridge closure

$$\frac{d[LCo^{II}(^{O_2}_{OH})Co^{II}L]}{dt} = k_3[LCo^{II}(O_2)Co^{II}L] \tag{8}$$

With use of stopped-flow techniques, both the k_1 and k_3 constants can be measured in presence and in absence of micelles (Tables IV and V). It is apparent that the nature of the polar head (cis or trans geometry) greatly influences both the rate of appearance of the mononuclear complex and the rate of formation of the second bridge. This latter observation can be rationalized by our previous considerations on the geometrical preferences of the trien and 2,3,2-tet subunits. Clearly, the reduction in rate stems from the slow cis-trans isomerization of the 2,3,2-tet complex which is necessary for the ring closure. Regarding the rate of dioxygen complexation, it has been postulated[46] that the exchange rate of the water molecules coordinated to the cobalt is the limiting step for the dioxygen complex formation. A trans ammine effect decreasing this exchange rate in the trien case is possible although such an effect is not expected. Moreover, the rates of water displacement are generally faster ($k = 5 \times 10^5$) than the values found.[47,48] An ^{17}O NMR study is under way to elucidate this point. No detectable micellar effect on the rate of formation of the dioxygen complex (k_1) is observed. This shows that (i) there is no change in the local concentration of O_2 at the micelle subsurface and (ii) the kinetics of complexation is identical in the isolated subunit and in the micellar phase (or that these two effects exactly compensate each other). This important point will be considered more thoroughly in the discussion (vide infra).

On the other hand, the presence of an organized assembly decreases the rate of the dibridge formation by a factor of 6.5. This is readily explained by realizing that this closure requires a rotation around the O-O bond in such a way that the paraffinic chain may no longer stay inside the hydrophobic part of the micelle (see Figure 5). This effect destabilizes the dioxygen complex as compared to the homogeneous solution. In consequence, all other things being equal, the micellar effect should thus be close to 800 (125 × 6.5) in the case of the trien and its amphiphilic analogue.

Discussion

The micellar effect previously observed may arise from two main contributions: (i) an effect of dimensionality change from ^3D in an homogeneous medium to ^2D at the micellar surface; (ii) an effect of local concentration in which we will neglect any orientational or anisotropic effect which will be included into the previous contribution. The dimensionality effect is very difficult to estimate by using the classical kinetic theories. We thus decided to use a Prigogine-Flory model (for a review see ref 49). A unit volume of solution is divided into N cells of volume v, the solvent molecules (or a cluster of water molecules) and the reactants occupying one cell each and having Z closest neighbors. It is postulated that each molecule vibrates inside the cell formed by its closest neighbors and that a proportion α of the total collisions leads to the products (reactive collisions). Within these assumptions it can be readily demonstrated that[49,55]

$$N_c = \frac{\alpha\mu N}{l}\varphi_A\varphi_B \tag{9}$$

where φ_A and φ_B are the proportion of the cells occupied by A or B molecules, N_c is the total number of reactive A-B collisions per unit of time, l is the mean free path of the molecule inside the cell, and μ is the vibration rate of the molecule inside the cell. The dimensionality effect N_c^{III}/N_c^{II} will then be given by eq 10

$$\frac{N_c^{III}}{N_c^{II}} = \frac{\alpha_{III}}{\alpha_{II}} \tag{10}$$

with the reasonable assumption that $\mu_{III}/l_{III} = \mu_{II}/l_{II}$, the number of collisions per second inside the cell, is the same whatever the dimensionality.[50] It is thus seen that a large dimensionality effect can only come from a large change in the proportion of reactive collisions at two or three dimensions, namely, the directionality of the reaction must be quite high. Negligible isotropic contributions to dimensionality effect are predicted.

Previously, the effect of local concentrations has been estimated by introducing partition coefficients between the bulk solvent and the micellar phase.[51,52] This approach is not possible in our case since we have, first, reaction between a molecule belonging to a micelle and a molecule dissolved in the bulk solvent and, second, a reaction between two amphiphilic molecules at the micellar surface. Since all the experiments were run at a concentration far higher than the cmc, the concentration of amphiphilic molecules which are not aggregated can be neglected. The only straightforward way to estimate the concentration effect is to compare the mean distance between the reactant molecules in the two cases. Considering the case of a bimolecular reaction

$$A + B \xrightarrow{k} C \tag{11}$$

the classical rate equation

$$v = \frac{d[C]}{dt} = k[A][B] \quad [A] \text{ and } [B] \text{ in M} \tag{12}$$

means there is a proportionality between the reaction rate and the probability of collision between A and B. The definition of

---

(46) Miller, F.; Wilkins, R. G. *J. Am. Chem. Soc.* **1970**, *92*, 2687.

(47) Eigen, M. *Pure Appl. Chem.* **1963**, *6*, 97.

(48) Glaeser, H. H.; Dodgen, H.; Hunt, J. P. *Inorg. Chem.* **1965**, *4*, 1061.

(49) Prigogine, I.; Bellemans, A.; Mathot, V. "The Molecular Theory of Solutions"; North Holland Publishing Co.: Amsterdam, 1957.

(50) In fact $\mu_{III}/\mu_{II} = (3/2kT)^{1/2}/(kT)^{1/2} = (3/2)^{1/2}$ and $(l_{III}/l_{II})[(a(3^{1/2})/2)/(a(2^{1/2})/2)] = (3/2)^{1/2}$, a being the length of the cube or of the corresponding square and thus $\mu_{III}/l_{III} = \mu_{II}/l_{II}$

(51) Menger, F. M.; Portnoy, C. E. *J. Am. Chem. Soc.* **1967**, *89*, 4698.

(52) Yatsimviski, A. K.; Martinek, K.; Berezin, I. V. *Tetrahedron* **1971**, *27*, 2855.

concentration is not straightforward when, for example, there is reaction between a molecule belonging to a micelle and another molecule dissolved in the bulk. Does one have to take overall concentrations or local concentrations? Every time there are several phases (or pseudophases) present, we propose to express the reaction as a function of the mean distance between A and the closest molecule B

$$v = k'(\bar{d}_{AB})^{-n}N_{AB} \tag{13}$$

where n is the dimensionality of the reaction medium and N_{AB} is the number of couples A–B per unit of volume. The expression of $\bar{d}_{AB}$ is in general rather tedious to derive. In the very common case where [A] >> [B], $\bar{d}_{AB}$ can be approximated by $\bar{d}_{AA}$ and N_{AB} by N_B. Since

$$\bar{d}_{AA}{}^3 = \frac{1.66 \times 10^3}{[A]} \quad d \text{ in Å, [A] in M} \tag{14}$$

in the case of a centered cubic lattice, it is apparent that eq 13 is equivalent to the usual definition under these conditions. It is now straightforward to compare any couple of chemical reactions even though they have different dimensionalities or are conducted in nonisotropic media (we will further use only the case [A] >> [B]). For example, one may calculate the concentration effect expected when two molecules of amphiphiles react at a micelle surface as compared to the homogeneous case

$$\left(\frac{v_{\text{micelle}}}{v_{\text{bulk}}}\right)_{t=0} = \frac{k'_{\text{mic}}}{k'_{\text{bulk}}}\left(\frac{(\bar{d}_{AB})_{\text{mic}}}{(\bar{d}_{AB})_{\text{bulk}}}\right)_{t=0}^{-n} \tag{15}$$

$$(N_{AB})_{t=0}{}^{\text{mic}} = (N_{AB})_{t=0}{}^{\text{bulk}}$$

$(\bar{d}_{AB})_{\text{mic}}$ is approximately the mean distance between the polar heads at the micelle surface (~10 Å) and $(\bar{d}_{AB})_{\text{bulk}}$ is readily estimated from eq 14. In our case, [LCo^{II}] = 0.001 M, $(\bar{d}_{AB})_{\text{bulk}}$ = 118 Å. Thus a micellar effect of 1600 is predicted which can be compared with the experimental value (800) previously estimated. It may thus be concluded that most of the micellar effect arises from an isotropic effect of local concentration and that the orientational effects are small, if present at all. It is also worth noting that this effect of local concentrations is almost entirely due to an inappropriate use of overall concentrations to determine the kinetic constants. As a matter of fact, the micellar effect thus found should be concentration dependent.

Conclusion

Several members of a new type of amphiphilic ligand, the Annelides, have been synthesized. They allow the formation of organized assemblies of transition metals. The cobaltous complexes have been extensively studied in terms of their ability to complex dioxygen. It has been shown, for the first time, that the formation of micellar phases of cobaltous complexes can bring a very important stabilization of the dioxygen complex. A new approach to rationalize these results has been proposed, allowing the estimation of the respective contributions of the orientational and local concentration effects. It appears that the magnitude of this latter is sufficient to explain the micellar effect previously found.

A very large range of transition metals could not be studied, due to solubility problems. New ligands are being synthesized to avoid this difficulty. The fundamental property of the supermolecular assemblies, i.e., the local concentration effect, could be predicted and was indeed observed. However, the system used is as far as we know the only one allowing a detailed study of the reaction kinetics of an amphiphile with a micromolecule and of two amphiphiles both belonging to an organized phase. The cooperativity between the metal sites is still low, mainly because of the large distance between them. Work is in progress to increase this cooperativity by using bridging ligands or by diminishing the intersite distance by using more concentrated and structured media (liquid crystals and mesomorphic phases).

At the same time, the activation of the dioxygen molecule complexed at the micellar subsurface is under study. Irradiation of the complexes at 300–350 nm should give rise to either the triplet or the singlet state of O_2 depending on the geometry of the complex (mono- or dibridged species).

Experimental Section

Syntheses of the Ligands. The ligand Ia was prepared by the method of Melhado and Gutsche;[26] it was purified just before use by vacuum distillation.

2-Dodecylmalonic Acid Diethyl Ester (3). A 826-mmol sample of sodium is reacted with 200 mL of absolute ethanol under nitrogen. The reaction is completed at 80 °C overnight. At room temperature 1.02 mol of diethyl malonate is added. The mixture is heated to 70 °C until complete dissolution and then cooled down to room temperature. A 1.03-mol sample of dodecyl bromide is added, and the mixture is slowly heated to 60 °C. The reaction may start very suddenly, and the temperature can rise very rapidly, in which case it is necessary to slow it down by cooling. The mixture is stirred under nitrogen at 80 °C for 12 h and evaporated to dryness. The oily residue is distilled under vacuum (155 °C (1mmHg)) to give pure **3** in 51% yield.

Anal. Calcd for $C_{19}H_{36}O_4$ (328.48): C, 69.47; H, 11.05. Found: C, 69.39; H, 10.90.

6-Dodecyl-5,7-dioxo-1,4,8,11-tetraazaundecane (4). Under nitrogen, 152 mmol of **3** is dissolved in 250 mL of freshly distilled ethylenediamine. After 20 h under reflux, the mixture is evaporated to dryness. At 80 °C, 300 mL of toluene is added. The mixture is left overnight at room temperature, and the white precipitate is filtered off under nitrogen to give pure **4** in 87% yield (mp 110 °C).

Anal. Calcd for $C_{19}H_{40}O_2N_4$ (356.53): C, 64.00; H, 11.31; O, 8.97; N, 15.71. Found: C, 63.98; H, 11.46; O, 9.26; N, 15.49 (total 100.19%).

6-Dodecyl-1,4,8,11-tetraazaundecane (IIa). A 450-cm^3 sample of a solution of diborane, 1 M in THF, is added dropwise under nitrogen to 56 mmol of **4** in 100 mL of anhydrous THF. The mixture is kept under reflux 20 h and cooled down to room temperature. The excess of diborane is destroyed by cautious addition of water. The solution is evaporated to dryness, and 250 mL of hydrochloric acid (6 N) is added. The mixture is stirred 1 h at room temperature and 15 h at 110 °C and evaporated to dryness. A 200-mL sample of water is added, and the pH is adjusted to 11 with a concentrated solution of potassium hydroxide. The solution is extracted with 3 × 300 mL of chloroform. The combined organic extracts are dried over Na_2SO_4, filtered, and evaporated. The colorless oily residue is distilled under vacuum (140 °C (0.03mmHg)) to give pure IIa in 49% yield.

Anal. Calcd for $C_{19}H_{44}N_4$ (328.57): C, 69.45; H, 13.50; N, 17.05. Found: C, 69.76; H, 13.38; N, 16.21.

Transition-Metal Complexes of IIa. The nickel and copper complexes are prepared by merely mixing methanolic solutions of IIa and the corresponding nitrate salt. The pure complexes crystallize at −5 °C.

IIa, $Ni(NO_3)_2$ (mp 169 °C). Calcd for $C_{19}H_{44}O_6N_6Ni_1$ (511.29): C, 44.63; H, 8.67; N, 16.44. Found: C, 44.62; H, 8.63; N, 16.55.

IIa, $Cu(NO_3)_2$ (mp 190 °C). Calcd for $C_{19}H_{44}O_6N_6Cu_1$ (516.13): C, 44.21; H, 8.59; N, 16.28. Found: C, 44.47; H, 8.74; N, 16.59.

The cobaltic complex is prepared by adding 6.5 mmol of $CoCl_2 \cdot 6H_2O$ in 20 mL of degassed distilled water into a solution of IIa (6.1 mmol in 30 mL of water). Pure dioxygen is bubbled through the solution for 5 min and then 50 mL methanol is added. After 2 h of dioxygen bubbling another 60 mL of methanol is added. The solution is warmed to 60 °C under a pure dioxygen atmosphere and kept at this temperature for 20 h under vigorous stirring. The mixture is evaporated to dryness, 30 mL of concentrated hydrochloric acid is added and the solution is evaporated. The green residue obtained is recrystallized from 100 mL of methanol (mp 246 °C, yield 26%).

Anal. Calcd for $C_{19}H_{44}N_4Co_1Cl_3 \cdot 1H_2O$ (511.88): C, 44.57; H, 9.06; N, 10.94. Found: C, 44.95; H, 9.42; N, 11.15.

The cobaltic complex of Ia is prepared in a similar way (yield 20%).

Anal. Calcd for $C_{18}H_{42}N_4Co_1Cl_3$ (479.82): C, 45.05; H, 8.82; N, 11.68; Cl, 22.16. Found: C, 45.25; H, 8.91; N, 11.62; Cl, 20.55.

cmc Measurements. The cmc have been determined by interfacial tension measurements as previously described.[3] In a typical experiment a standard solution of the ligand (0.1 M) is adjusted at pH 7.0 ± 0.1 with HNO_3 (1 M) and gradually added to 25 mL of a buffer solution ([triethanolamine] = 0.02 M, [KNO_3] = 0.1 M). Between each addition the interfacial tension is measured until a plateau value is obtained, indicating the presence of micelles. The temperature was kept at 25 °C in all cases. Both solutions must be filtered through a millipore 0.1 μm system in order to obtain reproducible results.

Potentiometric Measurements. The protonation and cation stability constants were determined as previously described.[3] All the solutions were carefully degassed before use and then saturated with the appropriate gas (N_2 or O_2) by bubbling through the solutions. This bubbling was maintained throughout the titration experiments. The dioxygen stability constants were calculated by using a published program.[53]

Stopped-Flow Determinations. A Durrum D 110 stopped-flow apparatus was used for all the kinetic measurements. In a typical experiment 50 mL of a buffer solution ([triethanolammonium nitrate] = 0.02 M, [KNO_3] = 0.1 M) was added to 1 mL of ligand solution (0.1 M) and 0.95 mL of cobalt nitrate solution (0.1 M). All the solutions were carefully degassed under vacuum. This constitutes the cobaltous complex solution ([LCo^{II}] = 0.002 M). A 50-mL sample of the same buffer solution degassed and saturated with dioxygen constitutes the second one. The concentration of dioxygen was measured with an Orion electrode, Model 97.08 ([O_2] = 2.7 10^{-4} M). After the solution was mixed the rate of appearance of the complex was observed at 400 nm which corresponds to the tail of the charge-transfer band.

Acknowledgment. This work was financially supported by the CNRS (Grant ATP No3792). We thank Mrs. E. Simon, Mr. Kraeminger and Dr. Tondre for their valuable assistance and helpful discussions.

---

[53] Kaden, Th.; Zuberbühler, A. *Talanta*, **1971**, *18*, 61.
[54] Tanford, C., *Science* (*Washington, D.C.*) **1978**, *200*, 1012.
[55] A full description of this approach is going to be published.
[56] Vannerburg, N. G. *Acta Crystallogr.* **1965**, *18*, 449.

Solar Energy Storage Reactions. Thermal and Photochemical Redox Reactions of Polynuclear Rhodium Isocyanide Complexes

I. S. Sigal, Kent R. Mann, and Harry B. Gray*

Contribution No. 6170 from the Arthur Amos Noyes Laboratory, California Institute of Technology, Pasadena, California 91125. Received February 1, 1980

Abstract: The binuclear Rh^I complex $Rh_2(bridge)_4^{2+}$ (or Rh_2^{2+}) (bridge = 1,3-diisocyanopropane) reacts with 12 M HCl to form H_2 and $(Rh_2(bridge)_4)_2Cl_2^{4+}$ (or $Rh_4Cl_2^{4+}$). Air oxidation of 1 N H_2SO_4 solutions of Rh_2^{2+} produces $(Rh_2(bridge)_4)_2^{6+}$ (or Rh_4^{6+}). Irradiation ($\lambda > 520$ nm) of this tetranuclear species in 12 M HCl solutions at 25 °C produces H_2 and $Rh_2(bridge)_4Cl_2^{2+}$ (or $Rh_2Cl_2^{2+}$). Product analyses and redox titrations ($Rh_2Cl_2^{2+}$ with Cr^{2+}; Rh_4^{6+} with Ce^{4+}) have confirmed the following reaction scheme: $Rh_2^{2+} + HCl \xrightarrow{\Delta} {}^1/_2Rh_4Cl_2^{4+} + {}^1/_2H_2$; ${}^1/_2Rh_4Cl_2^{4+} + HCl \xrightarrow[550\ nm]{h\nu} Rh_2Cl_2^{2+} + {}^1/_2H_2$. Rh_4^{6+} reacts photochemically (500–600 nm irradiation) with Fe^{3+} to give $Rh_2^{4+} + Fe^{2+}$ ($Rh_4^{6+} + 2Fe^{3+} \xrightarrow{h\nu} 2Rh_2^{4+} + 2Fe^{2+}$). Controlled reduction of Rh_4^{6+} in 10 M H_2SO_4 produces a hexanuclear cation, $(Rh_2(bridge)_4)_3^{8+}$ (or Rh_6^{8+}) ($\lambda_{max} = 780$ nm), and an octanuclear cation, $(Rh_2(bridge)_4)_4^{10+}$ (or Rh_8^{10+}) (λ_{max} : 960 nm); Rh_6^{8+} reacts with Ce^{4+} to form Rh_4^{6+} ($Rh_6^{8+} + Ce^{4+} \rightarrow {}^3/_2Rh_4^{6+} + Ce^{3+}$). Dimerization of Rh_6^{8+} occurs to give Rh_{12}^{16+} ($\lambda_{max} > 1300$ nm). The following interpretation of the photoreactions of $Rh_4Cl_2^{4+}$ in HCl solutions is proposed. In 12 M HCl, Rh_2^{2+} produced by irradiation reacts with HCl to give H_2. In 6 M HCl, however, photogenerated Rh_2^{2+} is trapped by Rh_4^{6+} to give Rh_6^{8+}.

An attractive means of solar energy storage involves the photocatalytic conversion of water to hydrogen and oxygen.[1-10] Much progress has been made recently in running the reductive half of this cycle, that is, the step in which protons from water are reduced to hydrogen.[5-10] Particularly promising from a mechanistic point of view are the systems in which $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) is utilized as the photoreceptor and hydrogen production is facilitated by homogeneous[9a] or heterogeneous[5-8,9b] catalysts.

Our interest in this area began in 1977, when we discovered that $Rh_2(bridge)_4^{2+}$ (bridge = 1,3-diisocyanopropane)[11] (or Rh_2^{2+}) dissolved in 12 M HCl produces H_2 and $Rh_2(bridge)_4Cl_2^{2+}$ (or $Rh_2Cl_2^{2+}$) upon irradiation at 550 nm.[10] This system is very attractive for mechanistic study in the sense that additional catalysts are not necessary for H_2 evolution. From early observations it was known that the photoactive species ($\epsilon_{572} = 56\,500$ M^{-1} cm^{-1}) most likely was produced in a thermal reaction of Rh_2^{2+} with 12 M HCl.[10,12,13] Subsequently, flash photolysis experiments strongly suggested that the photoactive species was $(Rh_2(bridge)_4Cl)_2^{4+}$ (or $Rh_4Cl_2^{4+}$).[14,15] The tetranuclear nature of this species has recently been confirmed by a crystal structure determination.[16] Although the measured bond lengths (2.93 Å for the two outer Rh–Rh bonds and 2.78 Å for the inner one) are consistent with a $Rh^IRh^{II}Rh^{II}Rh^I$ unit, the presence of hydronium

---

[1] Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolleta, F.; Gleria, M. *Science* (*Washington, D.C.*) **1975**, *189*, 852.
[2] Fong, F. K.; Galloway, L. *J. Am. Chem. Soc.* **1978**, *100*, 3594.
[3] Wrighton, M. S.; Ellis, A. B.; Wolczanski, P. J.; Morse, D. L.; Abrahamson, H. B.; Ginley, D. S. *J. Am. Chem. Soc.* **1976**, *98*, 2772.
[4] Kuznicki, S. M.; Eyring, E. M. *J. Am. Chem. Soc.* **1978**, *100*, 6790.
[5] Kiwi, J.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7214.
[6] Lehn, J. M.; Sauvage, J. P. *Nouv. J. Chim.* **1977**, *1*, 449.
[7] Moradpour, A.; Amouyal, E.; Keller, P.; Kagan, H. *Nouv. J. Chim.* **1978**, *2*, 547.
[8] Delaive, P. J.; Sullivan, B. P.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 4007.
[9] (a) Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298. (b) Brown, G. M.; Chan, S.-F.; Creutz, C.; Schwarz, H. A.; Sutin, N. *Ibid.* **1979**, *101*, 7638.
[10] Mann, K. R.; Lewis, N. S.; Miskowski, V. M.; Erwin, D. K.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 5525.
[11] Lewis, N. S.; Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7461.
[12] Gray, H. B.; Mann, K. R.; Lewis, N. S.; Thich, J. A.; Richman, R. M. *Adv. Chem. Ser.* **1978**, *No. 168*, 44.
[13] Mann, K. R.; Gray, H. B. *Adv. Chem. Ser.* **1979**, *No. 173*, 225.
[14] Miskowski, V. M.; Sigal, I. S.; Mann, K. R.; Gray, H. B.; Milder, S. J.; Hammond, G. S.; Ryason, P. R. *J. Am. Chem. Soc.* **1979**, *101*, 4383.
[15] Gray, H. B.; Miskowski, V. M.; Milder, S. J.; Smith, T. P.; Maverick, A. W.; Buhr, J. D.; Gladfelter, W. L.; Sigal, I. S.; Mann, K. R. *Fundam. Res. Homogeneous Catal.* **1979**, *3*, 819.
[16] The structure determination was performed on $H_3[Rh_4(bridge)_8Cl][CoCl_4]_4{\cdot}xH_2O$. These crystals contain Rh_4Cl^{n+} units with n = 5 for the assumed proton stoichiometry (Mann, K. R.; Dipierro, M. J.; Gill, T. P. *J. Am. Chem. Soc.* **1980**, *102*, 3965). The Cl^-/Rh_4^{6+} stoichiometry is not known in HCl solutions with [Cl^-] > 0.01 M (at lower chloride concentrations, the principal chloro complex is Rh_4Cl^{5+}). On the basis of the flash photolysis results in 0.1 M HCl,[15] we shall assume that the principal species present with [Cl^-] ≥ 0.1 M is $Rh_4Cl_2^{4+}$.

0002-7863/80/1502-7252$01.00/0