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Redox Properties of a Series of Iron(III) Trinuclear Carboxylates, $[Fe_3(\mu_3\text{-}O)(\mu\text{-}RCO_2)_6(L)_3]^{n+}$

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Seventeen trinuclear iron(III) carboxylate complexes, $[Fe_3(\mu_3\text{-}O)(\mu\text{-}RCO_2)_6(L)_3]^{n+}$ (n = 1 or 7; RCO_2 = simple carboxylate, pyridine carboxylic acid, or amino acid; L = H_2O, pyridine, or imidazole) gave two reduction peaks in cyclic voltammogram in CH_3CN. The first reversible redox potential ($E_{1/2}$ = +0.23 to -0.60 V vs. Ag/Ag^+ electrode) has a good linear correlation with pK_a (1.5-4.8) of the bridging carboxylate ligand.

Polynuclear iron(III) complexes with O^{2-}, OH^-, and carboxylate bridges have been extensively studied. Bi-, tetra-, hexa-, octa-, and undeca-nuclear complexes have been prepared and their various properties including magnetic susceptibilities, electronic absorption spectra, and redox properties have been studied with reference to their possible relevance to the certain bi- and polynuclear iron enzymes.1) Trinuclear complexes with a μ_3-oxo center, $[Fe_3(\mu_3\text{-}O)(\mu\text{-}RCO_2)_6(L)_3]^{n+}$ (Fig. 1), have been known from the beginning of this century, and complexes with a wide variety of ligands, RCO_2^- and L, have been already reported.2-5) Yet, their studies have been concentrated to magnetic properties, and the redox properties in solution appear to be even less well understood than their new analogs of other nuclearity.1)

We have carried out systematic studies on the redox properties of a series of trinuclear iron(III) complexes. Table 1 lists complexes studied here including six new ones.

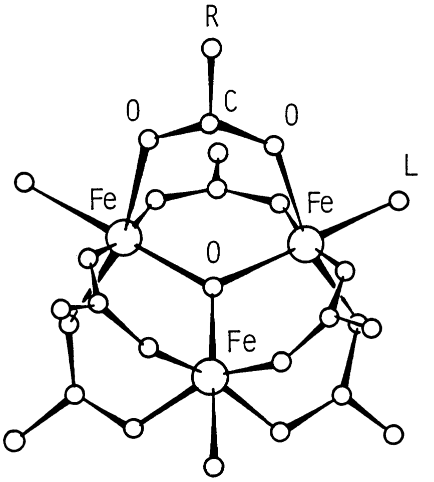

Fig.1. Structure of $[Fe_3(\mu_3\text{-}O)(\mu\text{-}RCO_2)_6(L)_3]^{n+}$.

Known complexes, $[Fe_3(\mu_3\text{-}O)(\mu\text{-}RCO_2)_6(H_2O)_3](ClO_4)_n$ (n = 1 for R = CH_3, C_6H_5, CH_2Cl, and $CHCl_2$; n = 7 for RCO_2 = glycine (glyH), L-alanine, L-phenylalanine, L-proline, L-threonine, and L-valine), were prepared by the methods previously described.2-5) The substitution of pyridine (py) or imidazole (im) for the terminal aqua ligands were carried out in ethanol. New complexes with pyridine carboxylates, including isonicotinic acid (*i*-nicH), nicotinic acid, and pipecolinic acid as μ-*O,O'*-bridging ligands were prepared by a similar method to those of the analogs: a carboxylic acid (0.0042 mol) was added to an aqueous solution of $Fe(ClO_4)_3$ (0.0021 mol in 5 cm^3) under stirring. The solution was filtered and concentrated slowly over P_4O_{10} at room temperature to give dark red crystals after several days. Samples were identified by elemental analyses and IR spectra (especially in the 1400-1700 cm^{-1} region). Preliminary analysis of the X-ray crystallographic data on one of the new complexes, $[Fe_3(\mu_3\text{-}O)(\mu\text{-}i\text{-nicH})_6(H_2O)_3](ClO_4)_7\cdot(i\text{-nicH})\cdot 2HClO_4\cdot 9H_2O$, indicates that the complex cation has a trinuclear skeletal structure similar to the analogs.[6,7] Bond lengths and angles resemble those of other trinuclear iron(III) complexes.[8]

In dry organic solvents, e.g. C_2H_5OH, CH_3CN, and CH_3NO_2, the present complexes are stable, and show distinctive absorption peaks or shoulders.[9,10] The absorption and CD peaks[9] in the visible region disappear in aqueous solution (pH 1.0, $HClO_4$), suggesting that the complexes decompose rapidly in H_2O.

Cyclic voltammogram of all the present complexes in CH_3CN shows two reduction waves, i.e. reversible or quasi-reversible one, W1, (irreversible for $[Fe_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(H_2O)_3]^+$) at $E_{1/2}$ = +0.23 to -0.60 V vs. Ag/Ag^+ electrode, and irreversible one, W2, at E_{pc} = -0.29 to -1.5 V (Table 1). These two waves correspond to Fe_3(III,III,III)/Fe_3(II,III,III),[11] and to further reduction, respectively. The redox potential, $E_{1/2}$(W1), of the complex with terminal aqua ligands increases with a decrease in pK_a of the carboxylate moiety of the bridging ligands. The plot between them gave a good straight line regardless of the total charge number (+1 or +7) of the complex cation, and expressed with the equation:[12]

$$E_{1/2}(\text{W1}) = (-0.17 \pm 0.01)\ pK_a + (0.48 \pm 0.03)$$

E_{pc}(W2) also shows a similar trend. These results suggest that the redox potential of the Fe_3 core is affected significantly by the extent of the electron donation through the σ bonds from the bridging ligands.[13] With an increase in basicity of the terminal ligands, $E_{1/2}$(W1) and E_{pc}(W2) also shift toward nagative potential, although the number of ligands (H_2O, py or im) are limited.

The $E_{1/2}$ value is clearly independent of the overall charge number of the complex. For several other redox systems, $E_{1/2}$ is found to be affected by the overall charge of the complex,[14] which may be the result of different extent of the solvation around the species. In the present system, however, influence of the ligand may be sufficiently large compared with that of the overall charge. The redox center, the Fe_3O core, is hidden by the bulky carboxylate moieties from the solvent, and is distant from protonating nitrogens in the case of complexes with +7 charge numbers.

Only few relevant cyclic voltammetric studies were reported. Straughan et al.[15] have studied electrochemistry on $[Fe_nCr_{3-n}(\mu_3\text{-}O)(\mu\text{-glyH})_6(H_2O)_3](NO_3)_7$ (n = 0-3) in C_2H_5OH, and $[Fe_3(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(H_2O)_3](CH_3CO_2)$ in CH_3CN, and reported that the former (n = 3) gave a reversible redox peak at +0.05 V vs. SCE, while the latter an irreversible reduction wave at -0.25 V vs. SCE, which is consistent with our observation. Finally, it should be emphasized that the redox potential of the Fe_3O core spans in fairly wide range as much as 1 V, and

Table 1. Redox potentials of iron(III) trinucler carboxylates, $[Fe_3(\mu_3\text{-}O)\text{-}(\mu\text{-}RCO_2)_6(L)_3](ClO_4)_n$, in CH_3CN containing *n*-Bu_4NClO_4 (0.2 M) at 21 ± 3 °C[a)]

	Complex[b)]			W1			W2[c)]	pK_a[d)]
				$E_{1/2}$[e)] V	$E_{pa}-E_{pc}$[f)] mV	i_c / i_a[g)]	E_{pc}[e,f)] V	
n = 1;	RCO_2^-	L						
	CH_3CO_2	H_2O	(**1**)	(-0.30)[h,i)]	-	-	-1.15	4.8
		py	(**2**)	-0.41	70	0.50	-1.20	
		im	(**3**)	-0.60	70	0.31	-1.13	
	$C_6H_5CO_2$	H_2O	(**4**)	-0.26	60	0.49	-0.93	4.2
		py	(**5**)	-0.34	60	0.80	-0.94	
		im	(**6**)	-0.53	70	0.73	-1.01	
	CH_2ClCO_2	H_2O	(**7**)	-0.03	80	0.69	-1.10	2.85
	$CHCl_2CO_2$	H_2O	(**8**)	+0.23	80	0.51	-0.51	1.48
n = 7;	RCO_2(zwitter ion);	L = H_2O						
	glycine		(**9**)	+0.06[i)]	60	0.88	-0.48	2.35
	L-alanine		(**10**)	+0.07	70	0.85	-0.53	2.35
	L-phenylalanine		(**11**)	+0.13	70	0.86	-0.53	2.16
	L-proline		(**12**)	+0.12	60	0.83	-0.50	1.95
	L-threonine		(**13**)	+0.13	80	0.95	-0.48	2.09
	L-valine		(**14**)	+0.16	70	0.89	-0.56	2.29
	isonicotinic acid		(**15**)	+0.16	60	0.51	-0.29	1.79
	nicotinic acid		(**16**)	+0.18	70	0.79	-0.34	2.05
	pipecolinic acid		(**17**)	+0.12	70	0.96	-0.59	2.29

a) $[Fe_3] = 1.0 \times 10^{-3}$ M (M = mol dm^{-3}); scanning rate, 100 mV s^{-1}. A Yanaco P-1000 potentiometric analyzer was used with glassy carbon working-, Pt counter-, and Ag/Ag^+ (ClO_4^-, 0.10 M in CH_3CN) reference electrodes. CH_3CN was distilled twice over P_4O_{10}, and then over CaH_2. *b*) Compounds **3**, **5**, **6**, **15**, **16**, and **17** are new. *c*) Irreversible. *d*) pK_a at the carboxylate moiety of the bridging ligand: E. P. Serjeant and B. Dempsey, "*Ionisation Constants of Organic Acids in Aqueous Solution*," Pergamon Press, London (1979); R. M. C. Dawson, D. C. Elliot, W. H. Elliot, and K. M. Jones, "*Data for Biochemical Research*," Oxford University Press, Oxford (1969); L. G. Sillén and A. E. Martell, "*Stability Constants of Metal-Ion Complexes*," The Chemical Society, London (1964), and the Supplemental publications. *e*) vs. $Ag/AgClO_4$ (0.10 M in CH_3CN). *f*) E_{pa}: anodic peak potential. E_{pc}: cathodic peak potential. *g*) Ratio of cathodic and anodic current. *h*) E_{pc} value, since the wave is irreversible. *i*) Corresponding data are available in Ref. 15 (see text).

can be controlled by changing bridging and terminal ligands.

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6) The space group ($P6_3/m$) was the same as that of $[Cr_3(\mu_3\text{-}O)(nicH)_6(H_2O)_3](ClO_4)_7 \cdot NaClO_4 \cdot (nicH) \cdot 6H_2O$ (described in Ref. 7). Some interatomic distances (Å): Fe-Fe = 3.302(3); Fe-(μ_3-O) = 2.08(1); Fe-O(carboxyl) = 1.98(1), 1.906(2). Detailes will be reported elsewhere.

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9) The peak or shoulder wavelength and the molar extinction coefficient per Fe_3 in CH_3CN ($[Fe_3] = 1 \times 10^{-3}$ M): 335-354 nm (3380-8400 $M^{-1}cm^{-1}$); 400-410 (sh.) (790-1720); 440-465 (sh.) (170-640). Some of them are in agreement with those reported in Refs. 3, 4, and 10. Complexes with bridging L-amino acids exhibited circular dichroism (CD) spectra in the UV-visible region in CH_3CN ($[Fe_3] = 1 \times 10^{-3}$ M), which was very similar to those in solid in KBr disk. The peak wavelength and the relative CD intensity vs. UV, $|\Delta\varepsilon / \varepsilon| \times 10^4$, per Fe_3: 278-289 nm (0.59-6.7); 326-358 (0.49-1.6); 358-518 (0.8-6.8).

10) R. N. Puri, R. O. Asplund, and W. F. Tucker, *Inorg. Chim. Acta*, 66, 7 (1982)

11) DC polarographic analyses on W1 of the systems **1** and **4** gave reasonable slopes of the E vs. $\log[i/(i_d - i)]$ plot, ca.60 mV, and diffusion constants, (0.6-1.0) x 10^{-5} cm^2s^{-1} at ca. 22°C in CH_3CN, for one-electron transfer.

12) System **1** was omitted since W1 is irreversible.

13) Correlation between the electron donor abilities of a series of ligands and the redox potentials of the complexes are often observed: see for example, M. L. Bento and E. Tfouni, *Inorg. Chem.*, 27, 3410 (1988).

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Note added in proof. After the submission of this letter, similar relationships between $E_{1/2}$ and pK_a were reported for tri- and dinuclear ruthenium(III) carboxylates: H. E. Toma, C. J. Cunha, and C. Cipriano, *Inorg. Chim. Acta*, 154, 63 (1988); P. Neubold, K. Wieghardt, B. Nuber, and J. Weiss, *Inorg. Chem.*, 29, 459 (1989).

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