

Solution Structures of the Tetrakis(1,2-ethanedithiolato)diiron(III) Ion

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(Received April 11, 1988)

Abstract

Coordination structures of tetrakis(1,2-ethanedithiolato)diiron(III) ion, $[\text{Fe}_2(\text{S}_2\text{-C}_2\text{H}_4)_2]^{2-}$, in solution have been examined with magnetic circular dichroism and magnetic moment measurements using acetonitrile, acetone, dimethylformamide (DMF), dimethylsulfoxide (DMSO) and pyridine as solvents. The spectral and magnetic moments data indicated that $[\text{Fe}_2(\text{S}_2\text{-C}_2\text{H}_4)_2]^{2-}$ exists as a dimer in acetonitrile, but that it was dissociated into a monomer in pyridine. In acetone $[\text{Fe}_2(\text{S}_2\text{-C}_2\text{H}_4)_2]^{2-}$ was present as an equilibrium mixture of a dimer and a monomer. The equilibrium between a dimer and monomers was also observed in DMF and DMSO, but the monomers had two different forms in equilibrium in these solvents.

Introduction

In the solid state a tetrakis(1,2-ethanedithiolato)diiron(III) ($[\text{Fe}_2(\text{edt})_4]^{2-}$)** ion has a dimeric structure with two antiferromagnetically coupled Fe(III) ions [1]. The respective Fe(III) ion center possesses a distorted trigonal bipyramidal or a square pyramidal coordination geometry [2, 3]. When $[\text{Fe}_2(\text{edt})_4]^{2-}$ was dissolved in solution, it showed a magnetic moment expected for a spin quartet state different from that in the solid state [4]. Hence the complex was believed to be dissociated to a monomeric complex in a coordinating solvent. Magnetic properties for some dithiolato complexes in solution have been characterized [5–12]. A solvent coordinated dithiolato complex, $[(\text{n-C}_4\text{H}_9)_4\text{N}]^+[\text{Fe}(\text{tdt})_2(\text{py})]^-$,

has been synthesized and shown to have the magnetic moment of the parent dimeric complex $[\text{Fe}_2(\text{tdt})_4]^{2-}$ ion in pyridine solution [5]. Similar phenomena have been disclosed for $[\text{Fe}_2\{\text{S}_2\text{C}_2(\text{COOCH}_3)\}_4]^{2-}$ ion [13]. A dimeric $[\text{Fe}_2\{\text{S}_2\text{C}_2(\text{COOCH}_3)\}_4]^{2-}$ ion was dissociated to a monomeric five-coordinated complex in coordinating solvents, but remains as the dimer in non-coordinating solvents such as methylene chloride [13].

Here we report a detailed study of the solution behavior of $[\text{Fe}_2(\text{edt})_4]^{2-}$ with magnetic circular dichroism (MCD) and nuclear magnetic resonance spectroscopy using acetonitrile, acetone, dimethylformamide (DMF), dimethylsulfoxide (DMSO) and pyridine as solvents. The MCD spectra contain valuable information about optical transitions as well as magnetic properties of both the ground and excited states, and the NMR measurement gives a magnetic moment of a complex in solution [14–26]. Physicochemical properties obtained for $[\text{Fe}_2(\text{edt})_4]^{2-}$ in solution with MCD and NMR disclosed the solution structures of the complex.

Experimental

All experiments and manipulations were performed under purified Ar atmosphere, and all solvents were used after complete evacuation. The bis(tetra-n-butylammonium) salt of the tetrakis(1,2-ethanedithiolato)diiron(III) ion, $[(\text{C}_4\text{H}_9)_4\text{N}]_2[\text{Fe}_2(\text{edt})_4]$, was synthesized according to the procedure of Herskovitz *et al.* [1]. The complex used for the spectral and magnetic moment measurements was recrystallized three times from acetonitrile solution under Ar atmosphere. All solvents were guaranteed grade, and were purified carefully by the usual methods, and dried with molecular sieves 3 Å.

Magnetic moments of the complex in the solutions were determined by the Evans method using an NMR technique [20]. ^1H NMR spectra were measured at

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** Abbreviations used: edt, ethanedithiolato ion; tdt, toluedithiolato ion; py, pyridine; DMF, dimethylformamide; DMSO, dimethylsulfoxide; MCD, magnetic circular dichroism, NMR, nuclear magnetic resonance.

298 K using a Bruker CXP-300 FT-NMR spectrometer at 300.066 MHz. Diamagnetic corrections for the ligands and ferric ion in the complex were obtained by using Pascal's constants [20]. Effective magnetic moments were shown in the unit of Bohr magneton per iron atom. Absorption spectra were recorded on a Jasco UVIDEK 510 spectrophotometer and magnetic circular dichroism (MCD) spectra were measured with a Jasco J-500 circular dichroism spectrometer equipped with a Jasco electromagnet of 1.53 T at a sample. The values of molar extinction coefficient ϵ in absorption spectra and magnetic molar ellipticity $[\theta]_M$ in MCD spectra were expressed in the units of $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ and $\text{degree dm}^3 \text{mol}^{-1} \text{Gauss}^{-1}$, respectively, where mol dm^{-3} is the molar concentration in iron atom.

Results and Discussion

Coordination Structures in Solutions

Figures 1a–e show the absorption and MCD spectra of the $[\text{Fe}_2(\text{edt})_4]^{2-}$ ion in acetonitrile, acetone, DMF, DMSO and pyridine at various temperatures. Tables I and II give the summary of the results of magnetic and spectral measurements for the $[\text{Fe}_2(\text{edt})_4]^{2-}$ ion in five different solvents.

In acetonitrile the $[\text{Fe}_2(\text{edt})_4]^{2-}$ ion has a magnetic moment of 2.43 BM like that in a solid state (2.58 BM) [1], which indicates that it is present as a dimer similar to that in a solid state. The lower magnetic moment in the solid state is due to the anti-ferromagnetic exchange interaction between Fe(III) ions. In pyridine solution the effective magnetic

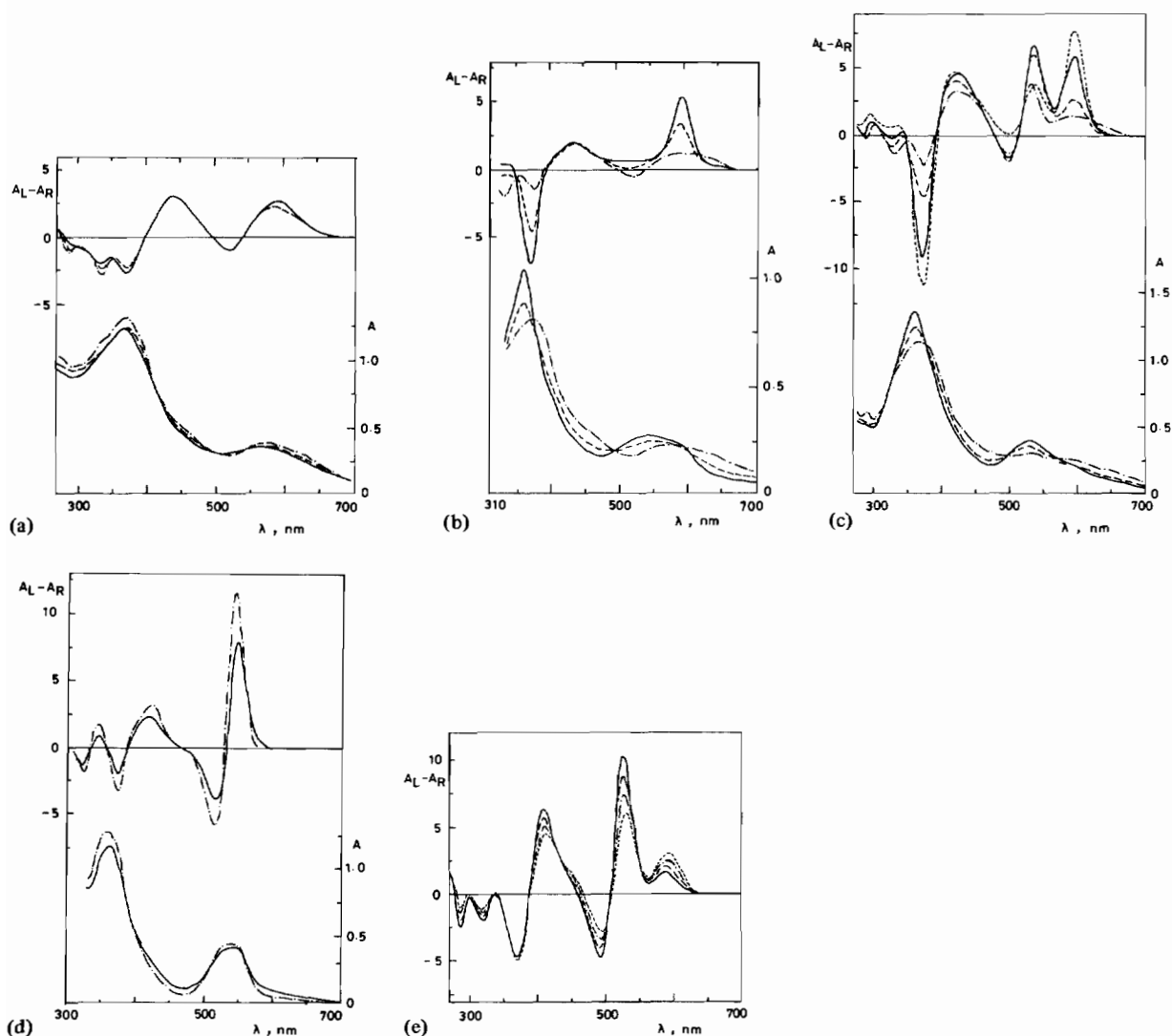


Fig. 1. Temperature dependence of MCD (top) and absorption (bottom) spectra in (a) acetonitrile: 300 K (—), 273 K (---) 213 K (- - -); (b) acetone: 300 K (—), 273 K (---) and 184 K (- - -); (c) DMF: 343 K (- - -), 300 K (—), 273 K (---) 219 K (- - -); (d) pyridine: 300 K (—), 233 K (- - -); (e) DMSO: 342 K (- - -), 323 K (- - -), 308 K (- - -) and 293 K (—).

TABLE I. Optical and Magnetic Data for the $[Fe_2(edt)_4]^{2-}$ Ion in Solution at Room Temperature

Solvent	Absorption			MCD			Magnetic moment μ_{Fe} (BM) ^b			
	$\tilde{\nu}$ (cm^{-1})	λ (nm)	ϵ ($dm^3 mol^{-1} cm^{-1}$)	$\tilde{\nu}$ (cm^{-1})	λ (nm)	$[\theta]_M \times 10$ ($degree dm^3 mol^{-1} cm^{-1} G^{-1}$) ^a				
CH ₃ N	27.2	(367)	18000	30.0	(333)	-3.7	2.43 (3.2 mM)			
				26.8	(373)	-4.7				
				22.3	(447)	5.6				
				19.1	(523)	1.2				
				16.8	(597)	5.1				
Acetone	27.7	(361)	23000	26.8	(373)	-20.9	2.83 (2.9 mM)			
				23.0	(435)	6.4				
				19.0	(525)	2.4				
DMF	18.4	(543)	5490	16.7	(598)	15.9	2.83 (2.9 mM)			
				29.9	(334)	0.4				
				27.5	(363)	23100		26.8	(373)	-13.5
				23.5	(425)	-6.6				
				19.9	(503)	-2.5				
DMSO	19.0	(524)	7260	18.6	(539)	10.0	4.11 (2.7 mM)			
				16.6	(600)	8.8				
				33.6	(298)	-5.0				
				30.9	(324)	-3.8				
				27.4	(365)	23800		26.9	(372)	-9.2
Pyridine	27.6	(362)	31900	24.3	(412)	12.8	4.11 (2.7 mM)			
				20.2	(494)	-9.5				
				18.8	(531)	20.2				
				17.0	(587)	3.2				
				30.8	(325)	-7.5				
Pyridine	18.4	(543)	10800	28.6	(350)	4.9	4.11 (2.7 mM)			
				26.6	(376)	-11.0				
				23.6	(424)	13.9				
				19.3	(518)	-22.0				
				18.1	(553)	46.3				

^aG = Gauss ($10^{-4}T$).^bBM = Bohr magneton.

TABLE II. Temperature Dependences of Absorption and MCD Spectra in Five Different Solutions

Solvent	Room temperature				Low temperature			
	$\lambda_{AB}/\lambda_{MCD}$ (nm)	ϵ ($dm^3 mol^{-1} cm^{-1}$)	$([\theta]_M/\epsilon) \times 10^5$ ^a ($degree G^{-1}$)	T (K)	$\lambda_{AB}/\lambda_{MCD}$ (nm)	ϵ ($dm^3 mol^{-1} cm^{-1}$)	$([\theta]_M/\epsilon) \times 10^5$ ^a ($degree G^{-1}$)	T (K)
CH ₃ CN (0.35 mM)	367/373	18000	2.6	300	374/377	19200	2.2	231
	561/597	5070	10		568/588	5300	7.9	
Acetone (0.28 mM)	361/373	23000	9.1	300	375/378	18600	2.5	184
	543/598	5490	29		575/590	4400	8.7	
DMF (0.22 mM)	363/373	23100	5.9	300	370/373	18300	1.9	219
	535/539	6170	16		536/535	4600	13	
DMSO (0.33 mM)	365/372	23800	3.4	293				
	524/531	7260	28					
Pyridine (0.13 mM)	362/376	31900	3.4	300	359/376	35400	5.1	233
	543/553	10800	43		534/548	11200	60	

^a $[\theta]_M/\epsilon = [\theta]_{M peak}/\epsilon_{peak}$.^bG = Gauss ($10^{-4}T$).

moment of the $[\text{Fe}_2(\text{edt})_4]^{2-}$ ion was found to be 4.11 BM, which is much larger than that in the solid state (2.58 BM) [1], or in acetonitrile (2.43 BM). The magnetic moment in pyridine (4.11 BM) corresponds to an $S = 3/2$ ground state of a monomeric Fe(III) unit, which is possible in D_{4h} or lower symmetry field. The magnetic results observed, therefore, indicate that $[\text{Fe}_2(\text{edt})_4]^{2-}$ ion is dissociated to a monomer to form a solvent adduct, $[\text{Fe}(\text{edt})_2(\text{py})]^-$ or a tetragonally distorted $[\text{Fe}(\text{edt})_2(\text{py})_2]^-$. The value of $[\theta]_{\text{Mpeak}}/\epsilon_{\text{peak}}$ in acetonitrile changed little with temperature (see Table II). The small temperature dependence of the intrinsic MCD value ($[\theta]_{\text{Mpeak}}/\epsilon_{\text{peak}}$) indicates a small contribution of Faraday C terms [26]. The absorption and MCD spectra in pyridine increased in magnitude upon lowering the temperature. A large contribution of Faraday C term for a monomeric Fe(III) ion was ascribed to the spin and orbital degeneracies of the ground state. It should be noted that $[\text{Fe}_2(\text{edt})_4]^{2-}$ in acetonitrile has much smaller values of ($[\theta]_{\text{Mpeak}}/\epsilon_{\text{peak}}$) than corresponding values in pyridine. Therefore solution structures of the complex can be estimated from intrinsic MCD magnitudes of the complex in solution. The absorption spectra in acetone and DMF decreased in intensity with lowering temperature, except for the shoulder band in the region from 600–700 nm. The absorption spectra in acetone have an isosbestic point at 490 nm, indicating that there exists an equilibrium between the two species. At 184 K the values of ($[\theta]_{\text{M}378}/\epsilon_{375}$) and ($[\theta]_{\text{M}590}/\epsilon_{575}$) are smaller by 1/3 than those at 300 K and close to the value in acetonitrile at 300 K. Since the magnitudes of MCD are dependent on the structures of complexes as discussed above, the MCD results suggest that in acetone a dimeric species is predominant at lower temperature, but that a monomeric species is predominant at room temperature.

In DMF solution the values of ($[\theta]_{\text{Mpeak}}/\epsilon_{\text{peak}}$) at 219 K are smaller than those at 300 K and are relatively close to those in acetonitrile. The temperature dependent behavior of MCD in DMF, similar to that in acetone, therefore, indicates that in DMF a dimeric species is predominant at lower temperature, and that the amount of monomer increases with increasing temperature. However, species in DMF are considered to be different from those in acetone for the following two reasons. (i) Above 500 nm two peaks are found in the absorption spectra in DMF, while only one is present in acetone. (ii) In DMF the magnitudes of the MCD bands do not vary simply upon decreasing the temperature; the band around 539 nm increased with lowering temperature to 275 K but decreased below 275 K. Significant temperature dependence in the MCD magnitude in the region from 500 to 650 nm was also seen in DMSO solution, but the spectral change in DMSO is monotonous and much simpler than that in DMF within the range of

temperature used (Fig. 1e). The temperature dependent behavior will be discussed in the following section in more detail.

Equilibrium Between Complexes

Figure 2 is a replot of MCD spectra in the region from 16 000 to 19 000 cm^{-1} of $[\text{Fe}_2(\text{edt})_4]^{2-}$ in coordinating solvents at room temperature. The first band in acetone, DMF or DMSO is located around 16 800 cm^{-1} (region I), whereas the first band in pyridine is around 18 000 cm^{-1} (region II) where the second MCD bands of DMF and DMSO solutions appear with a positive sign. The magnitudes of the MCD in region I decrease in the order, acetone > DMF > DMSO, which is in opposite order to the coordination ability of the solvent. In contrast to region I the magnitudes of the positive bands in region II decreased in the order, pyridine > DMSO > DMF. Since the decreasing order in magnitude in region I coincides with the increasing order in magnitude in region II, the MCD bands in the respective regions correspond with those for solvated complexes with specific coordination structures. Only one positive MCD band is observed in acetone, and in pyridine, respectively, in regions I and II, while two positive bands are observed in both regions in DMF and DMSO. Therefore, the MCD in region I represents the formation of a species like that in acetone and the

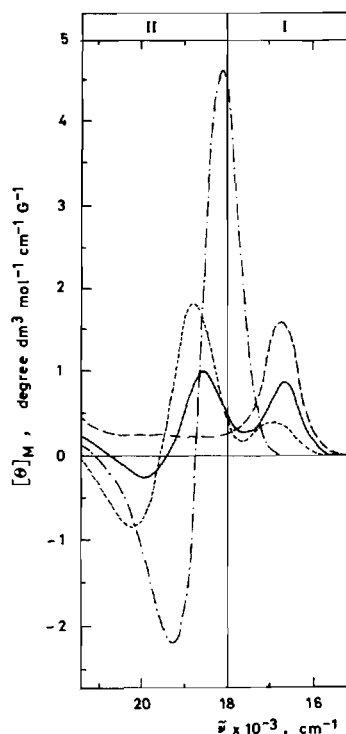


Fig. 2. MCD spectra in the lower energy region in pyridine (---), acetone (-.-.-), DMF (—) and DMSO (- - -) at room temperature.

MCD in region II indicates the formation of a species similar to that in pyridine. The ratio of the MCD magnitudes in region I to that in region II is about 1/1 in DMF, and 1/6 in DMSO at room temperature. These ratios vary with changing temperature. There exists an isosbestic point in the temperature varied MCD spectra at 555 nm in DMSO and at 498 nm in DMF, indicating that a chemical equilibrium between the two species exists in DMSO and DMF solution in this temperature range. As mentioned above, the $[\text{Fe}_2(\text{edt})_4]^{2-}$ ion was dissociated into a solvent coordinated monomeric species in coordinating solvents. We interpreted, therefore, that there exists an interconversion reaction between the two solvent coordinated species in DMSO and DMF solutions. We cannot identify the exact structures of the complexes at present, but a typical complex is either square pyramidal or trigonal bipyramidal geometry with a five coordination.

Although these geometries belong to different symmetries, they easily transform to each other because of the small energy difference [27]. Hence the two geometries, square pyramidal and trigonal bipyramidal, may be possible candidates for the two types of complexes.

Conclusions

Optical spectra of the $[\text{Fe}_2(\text{edt})_4]^{2-}$ ion at various temperatures in five different solvents show characteristic dependence of its structures on solvent and temperature. In particular, positions and magnitudes of the first and second MCD bands in the region from 15 000 to 19 000 cm^{-1} are closely related to the coordination ability of the solvent. Additional evidence from magnetic data leads us to conclude as follows.

(i) In acetonitrile which has an extremely weak coordination ability, the $[\text{Fe}_2(\text{edt})_4]^{2-}$ ion conserves its dimeric structure, although in pyridine, a powerful coordination solvent, the ion is dissociated into a monomeric species.

(ii) In acetone a monomer is predominant at room temperature, but the dimer is predominant at 184 K.

(iii) In DMF and DMSO two monomeric species coexist around room temperature.

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