ESR spectra of γ-irradiated samples of iron(III) binuclear complexes

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γ-Irradiation of μ-oxo-bridged binuclear iron complexes $Fe^{III}{}_2OL_n$ in a glycerol or dimethylformamide matrix at 77 K affords unstable mixed-valence $Fe^{II}F^{III}$ forms resulting from the transfer of a mobile electron generated by the ionizing radiation. These nonequilibrium forms retain the ligand environment of the original complexes, and their ESR spectra at 77—200 K are characterized by an asymmetric signal with an axially anisotropic *g*-factor, which is in agreement with the spectra of the $Fe^{II}Fe^{III}$ forms obtained by chemical reduction.

Key words: binuclear iron(III) complexes; γ-irradiation; ESR.

Synthesis and study of binuclear μ-oxo complexes of iron are of interest, because these complexes are incorporated in the active centers of a number of important iron-containing nonheme proteins, such as hemerythrine (Hr), ribonucleotide-reductase (RNR), and methanemonooxygenase (MMO).[1] Our interest in these complexes is due to the modeling of the structure and the function of MMO, the enzyme performing selective oxidation of methane to methanol at normal temperature and pressure,[2] and also due to the search for the possibilities of characterizing these complexes by ESR.[3]

Binuclear iron μ-oxo complexes can exist in three forms: the oxidized $Fe^{III}Fe^{III}$ form, the reduced $Fe^{II}Fe^{II}$ form, and the mixed $Fe^{II}Fe^{III}$ form. Whereas the oxidized form is diamagnetic in the ground state (due to the strong antiferromagnetic bonding of the two paramagnetic iron(III) ions), the other forms are ESR-active.[2] Of particular interest is the mixed-valence form exhibiting a characteristic ESR signal with an average *g*-factor below 2, which could be used for the identification of binuclear iron complexes. However, this form of most of the known binuclear iron complexes is unstable at room temperature and is formed upon the chemical reduction only in specific cases.[4,5] In addition, the ESR signal of the mixed-valence forms obtained by the chemical reduction can be observed only at temperatures below 35 K. Recently it has been shown[6–8] that the mixed-valence forms of the binuclear centers of Hr, RNR, and MMO can be synthesized in a frozen matrix at 77 K by generation of electrons by ionizing radiation, and, furthermore, their ESR spectra can be observed at the temperature of liquid nitrogen and at higher temperatures.[7] We believe that this method may be especially valuable for the preparation and investigation of the extremely unstable $Fe^{II}Fe^{III}$ forms of model binuclear iron complexes.

Experimental

Binuclear iron μ-oxo complexes **1**—**8** (Table 1) used in the present work were synthesized as described previously.[3,9] The samples for the irradiation and for the ESR studies were

Table 1. ESR spectra (77 K) of $Fe^{II}Fe^{III}$ forms of binuclear iron complexes, prepared by transfer of the electron generated by γ-irradiation at 77 K in a matrix of glycerol or dimethylformamide

Complex	Matrix material			
	Glycerol		Dimethylformamide	
	$g_\perp$	$g_\parallel$	$g_\perp$	$g_\parallel$
$Fe_2O(bpy)_4Cl_4$ (**1**)	1.965	1.920	1.969	1.927
$Fe_2O(salen)_2$ (**2**)			—	1.907
$Fe_2O(EDTA)_2$ (**3**)			1.940	1.887
$Fe_2O(bpy)_2(SO_4)_2$ (**4**)	1.953	1.914	1.938	1.875
$[Fe_2O(bpy)_4(OBz)](ClO_4)_3$ (**5**)	1.937	1.914	1.943	1.922
$[Fe_2O(bpy)_2(OBz)_2(MeOH)_2](ClO_4)_2$ (**6**)	1.952	1.924		
$[Fe_2O(bpy)_2(OAc)_2(H_2O)_2](NO_3)_2$ (**7**)			1.955	1.920
$[Fe_2O(bpy)_4(H_2O)_2](ClO_4)_4$ (**8**)			1.968	1.918

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prepared by dissolving these complexes in glycerol or DMF and slow freezing in liquid nitrogen to give glasses.

The radiolysis of the samples was carried out in tubes made of SK-4B glass that gives no signals at 77 K on a "Gammatok" unit (with a ^{60}Co source) with doses of 3.5—4.5 Mrad (the dose power was 0.5 Mrad h^{-1}). Heating the samples to temperatures above 77 K was carried out in liquid nitrogen vapors, the irradiated sample being kept for 5—7 min at a particular temperature.

The ESR spectra were recorded on a "EPR-21" radiospectrometer operating in the 3-cm range at a power of the ultrahigh-frequency field of 10^{-4} W and at a temperature of 77 K.

The concentrations of paramagnetic centers (PMC) of the complex were calculated from the area of the asymmetrical spectrum with $g < 2$ by comparing it with the area of the spectrum of the reference sample of stable NO$^{\bullet}$ radical. Along with integration, the area of the spectrum was also determined from the coefficient of form and the height of the high-field component of the asymmetrical singlet. (The coefficient of form was determined by integration of the asymmetrical singlet isolated on heating of irradiated solutions of the complex in DMF at 140—150 K, when the signal with $g < 2$ least overlaps with the signal at $g = 2$.) The convergence of the results of the determination of the spectrum area by the two methods (by integration and by using the coefficient of form) was within the error of the determination of the areas of ESR spectra (±15 %).

Results and Discussion

Before γ-irradiation, the complexes under study in a glycerol or DMF matrix exhibit absolutely no paramagnetic absorption in the g = 2.0 to 1.7 region. After γ-irradiation at 77 K in air, along with the intense signal at $g = 2$ caused by hydrocarbon radicals and the doublet due to atomic hydrogen with the splitting ΔH = 503 G, intense asymmetrical lines with an axially anisotropic g-factor are observed in the high-field region at $g < 2$ (Fig. 1, spectra *1* and *2*). The values of the g-factor and the form of the signal make it possible to assign it to a mixed-valence form of the binuclear iron complex having the $S = 1/2$ spin.

Spectra *1* and *2* in Fig. 1 differ in the degree of overlap with the spectrum of the radical at $g = 2$. The asymmetrical line in glycerol is more open, because the signal at $g = 2$ is narrower. However, when the temperature is increased to 140—150 K, when the spectrum of the complex in DMF becomes almost entirely open (see Fig. 1, spectra *3* and *4*), the signals in glycerol and DMF differ in the form of the component corresponding to $g_{\parallel}$. A comparison with the theoretical spectra has shown[10] that this is due to the difference in the form of an individual component, which conforms to the Gaussian form for spectrum *1* and to the Lorentzian form for spectrum *2*. The almost complete isolation of the asymmetrical singlet of PMC in DMF on increasing the temperature to 140—150 K made it possible to determine the coefficient of form and to evaluate the concentration of PMC from its area. In addition, the coefficient of form was used to determine the relationship between the concentration of PMC and the concentration of the initial complex (Fig. 2). It can be seen that when the concentration of complex **1** in DMF is ~37 mmol L^{-1}, the curve flattens out. The efficiency of the capture of radiolytic electrons of the matrix by iron complexes estimated from the initial slope of the curve was ~60 %.

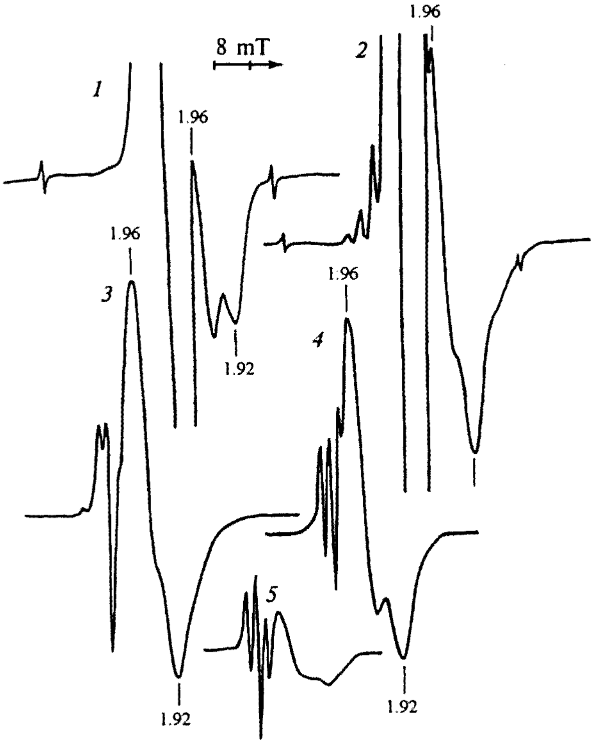

Fig. 1. ESR spectra in the $g < 2$ region of samples of complex **1** γ-irradiated with a dose of 4 Mrad at 77 K in glycerol (*1*) and DMF (*2*) matrices and of sample **2** heated after radiolysis to 140 (*3*), 150 (*4*), and 170 K (*5*). The spectra were recorded at 77 K.

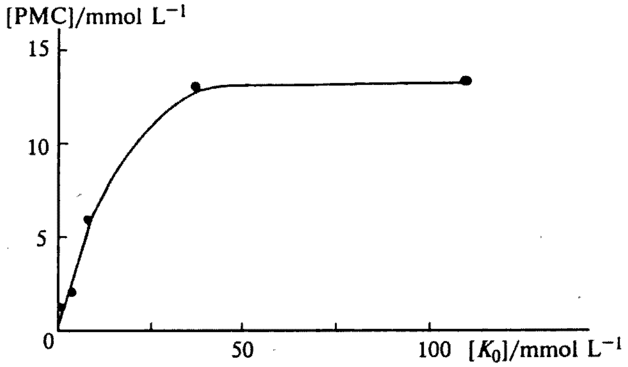

Fig. 2. Dependence of the concentration of the PMC of complex **1** on its concentration [K_0] in DMF after irradiation with 4 Mrad at 77 K.

The thermal stability of the diamagnetic species in glycerol is higher than in DMF, these species disappearing completely only at ~200 K (Fig. 3).

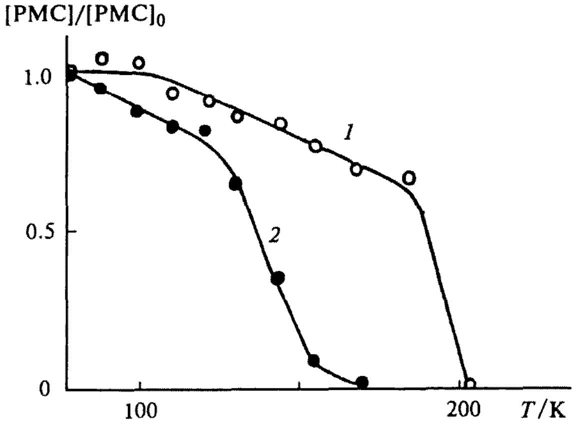

Fig. 3. Variation of the concentration of PMC with increase in temperature for solutions of complex **1** in glycerol (*1*) and DMF (*2*) γ-irradiared with 4 Mrad.

The $g_\perp$ and $g_\parallel$ factors in the ESR spectra of the $Fe^{II}Fe^{III}$ forms have typical values; they depend on the matrix used and lie within a narrow range: $g_\perp$ is 1.94—1.97 and $g_\parallel$ is 1.91—1.92 in the case of glycerol and 1.87—1.93 in the case of DMF (see Table 1). They are identical to the values found for the products of the chemical reduction of complex $Fe_2O(O_2CH)_4(BIPhMe)_2$:[4] $g_\perp$ = 1.94 and $g_\parallel$ = 1.84, and of complex $Fe_2O(O_2CMe)_2(Me_3TACN)$:[5] $g_\perp$ = 1.95 and $g_\parallel$ = 1.89, and are comparable to the ESR parameters of the $Fe^{II}Fe^{III}$ forms of Hr and RNR synthesized by a similar procedure:[7] $g_\perp$ = 1.936 and $g_\parallel$ = 1.82 for RNR and $g_\perp$ = 1.954 and $g_\parallel$ = 1.85 for Hr. It was also noted[7] that analogous ESR signals of $Fe^{II}Fe^{III}$ forms of some iron(III) binuclear complexes can be observed on irradiation; however, these data were not reported.

It is known[11] that during the transfer of an electron generated by radiolysis in a frozen matrix to a metal ion, the geometry of the ligand environment of the latter (interatomic distances and bond angles) is retained, while the oxidation state simultaneously changes. Thus, the resulting reduced metal ion exists in a nonequilibrium, kinetically stabilized conformation that corresponds to the oxidized ion. Therefore, the ESR characteristics obtained by us could be regarded at the same time as characteristics of the $Fe^{III}Fe^{III}$ forms. However, our attempts to establish the correlations between these characteristics and the parameter J of the antiferromagnetic interaction of the iron atoms ($H = -J \cdot S_1 \cdot S_2$) failed, possibly, due to the fact that, as has been shown previously,[12] the g-factors of $Fe^{II}Fe^{III}$ forms are not only sensitive to the constant of antiferromagnetic interaction, but also depend on the parameter D of the zero-field splitting for the Fe^{II} ion. Nevertheless, we believe that the ESR parameters of nonequilibrium mixed-valence iron complexes may be useful for the identification of model binuclear iron complexes.

Thus, γ-irradiation in a glycerol or DMF matrix at 77 K is a convenient way of preparing mixed-valence $Fe^{II}Fe^{III}$ forms, which are difficult to obtain in the case of ordinary complexes. The high stability of these species in a glycerol matrix almost up to 200 K enables the use of other spectral methods for their investigation. Unlike the relaxed $Fe^{II}Fe^{III}$ forms synthesized by the chemical reduction,[4,5] the nonequilibrium mixed-valence forms exhibit an ESR signal at the temperature of liquid nitrogen and at higher temperatures.

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