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An ESR study on dioxygen adducts of tridentate Schiff base cobalt complexes

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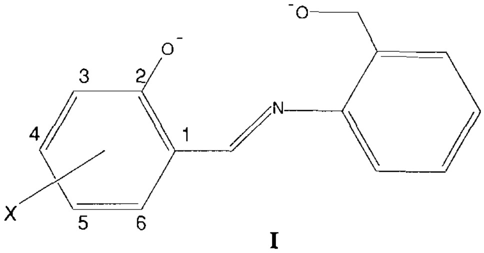
Abstract

ESR spectroscopy has been used to study the dioxygen adducts of the cobalt complexes with tridentate Schiff base *N*-salicydene(*ortho*-hydroxymethylene)aniline derivatives (X-SHMA). Spin Hamiltonian parameters for both terminally bound and bridging dioxygen complexes have been reported. The ligands' influence on these parameters has been discussed in terms of structural aspects of the dioxygen adducts formed with respect to the dimeric structure of the starting Co(II) complex.

Introduction

Co(II) complexes with various ligands are well known as effective dioxygen carriers [1, 2] and activators [3, 4]. Some of these complexes form monomeric, paramagnetic adducts with dioxygen molecule. ESR spectra of such complexes have been used to answer the question of the electronic structure of the metal–dioxygen system. Two alternative models have been proposed: the superoxo [Co(III)O_2^-] model [5] and spin-pairing [Co(II)O_2] model [6]. The ESR technique was also applied to the study of the hydrogen bond formation between the ligand and coordinated dioxygen [7].

In the previous paper [8] formation of the complexes of the *N*-salicydene(*o*-hydroxymethylene)aniline (SHMA) with various metal ions was described and it was concluded that SHMA acts as a tridentate ligand, regardless either of the kind of metal ion or the preparative method. The SHMA ligands of general formula **I** form dimeric or polymeric complexes with all 1st row transition metal ions from iron to zinc. It was also pointed out that the SHMA cobalt(II) complex can bind dioxygen reversibly in the presence of nitrogenous bases.



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In the present paper the results of the ESR study on dioxygen adducts of Co–X-SHMA complexes are reported. The distinguishing feature of this system is the dimeric structure of the parent Co(II) complex which may affect, in some cases, the magnetic properties of the dioxygen adduct.

Experimental

Synthesis

Co(II) complexes with ligands of general formula **I** were synthesized as described previously [8].

The substituted ligands (X = 5-CH_3, 5-Cl, 5-Br, 5-NO_2, 5,6-benzo) were obtained by the condensation of *o*-aminobenzyl alcohol (Fluka) with the appropriate salicylaldehyde derivative. 5-Cl- and 5-Me-salicylaldehydes were obtained by the Duff reaction [9]. 5-NO_2- and 5,6-benzo-salicylaldehydes, as well as unsubstituted salicylaldehyde were purchased from Fluka. 5-Br-salicylaldehyde was purchased from Merck and recrystallized twice from methanol.

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Solvents (toluene, dichloromethane) were purified by standard methods and distilled prior to use.

Physical measurements

ESR spectra were recorded on Jeol Jes-Me 3X and SE/X-3 Radiopan spectrometers using 20 mW X-band microwave radiation ($\nu \sim 9.11$ GHz). Modulation frequency and amplitude were 100 kHz and 5 G, respectively. Manganese standard (0.5% of MnO in MgO) was applied for calibration of the magnetic field and determination of g factors. Samples (0.1 M) were prepared in 4 mm quartz tubes by dissolution of about 0.005 g of the complex in 80 μl of toluene/dichloromethane mixture (1:0.1 vol./vol.).

Spectra in oriented nematic liquid crystal were obtained according to the method described by Fackler *et al.* [10]. The MBBA liquid crystal (MBBA = *N*-(4-methoxybenzylidene)-4′-butylaniline) was used as nematic mesophase. Samples were heated to obtain isotropic phase and oriented in the spectrometer's cavity by applying a magnetic field of 8000 G while cooling to the nematic temperature range. The temperature was then lowered quickly to that of liquid nitrogen. Samples were rotated together with the quartz dewar around the axis perpendicular to the magnetic field direction to obtain the angular dependence of the spectral lines intensities.

Simulation of ESR spectra

ESR spectra of complexes with terminally bound dioxygen were simulated according to the model proposed by Smith and Pilbrow [2]. The g and A tensors were assumed to be non-coincident. In such a model the coordinate system of A is rotated around the z axis, which is common for both g and A coordinate systems, by an angle of α (Fig. 1). In the simulation procedure ten parameters were taken into account: g_x, g_y, g_z, A_x, A_y, A_z, linewidths σ_x, σ_y, σ_z and α. Spectra were calculated for 30 values of θ angle (θ varies from 0 to $\pi/2$) and 60 values of ϕ angle (variation from 0 to π). The orientation dependent transition probability was calculated according to Aäsa and Vängård [11]. Spectra were fitted by means of the Marquardt method [12] in 150 field points using difference between experimental and simulated spectrum in the first derivative of intensity as an optimized function. Simulations were carried out on an IBM PC/AT microcomputer fitted with an arithmetical coprocessor. The program used for the simulation was written in Pascal by one of the authors (P.C.).

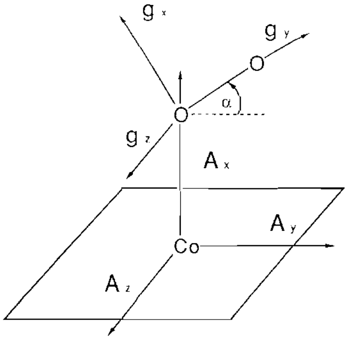

Fig. 1. Coordinate systems of the magnetic tensors applied for the simulation of the ESR spectra.

Results and discussion

No ESR signal was observed for the parent complex [Co(SHMA)(H_2O)$_2$]$_2$ or for its anhydrous analogue [Co(SHMA)]$_n$ [8] or any of its X-substituted derivatives, in solid or in toluene/dichloromethane solution. These complexes are ESR-silent both at room and liquid nitrogen temperature because of the high-spin state of cobalt(II) ions [8]. Under anaerobic conditions addition of a monodentate ligand (organic N-base) does not cause the appearance of an ESR signal, thus the high-spin state is retained. The signal appears after bubbling of O_2 through the complex solution in a toluene/dichloromethane mixture with the amine aliquot, but it can be observed only for frozen solution. The spectra are typical for cobalt–dioxygen adducts with a terminally bounded O_2 molecule (Fig. 2). Spin Hamiltonian parameters obtained by computer simulation are collected in Table 1.

Analysis of the data from Table 1 leads to the conclusion that ESR parameters for the complexes

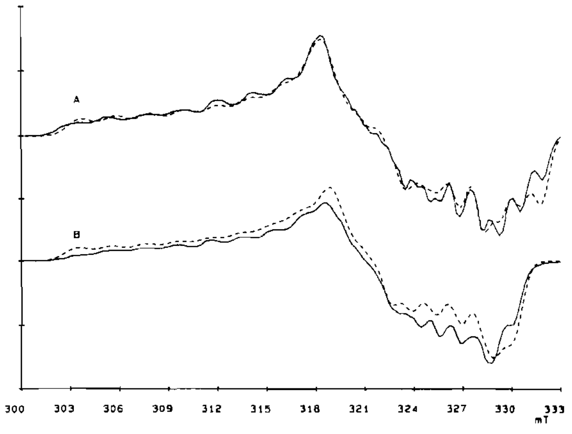

Fig. 2. ESR spectra of the Co(5-Me-SHMA)-pyridine-O_2 system at 0.05 (A) and 1 (B) M pyridine concentration in frozen toluene/dichloromethane solution at 77 K. Microwave frequency $\nu = 9.108$ GHz. Solid lines = experimental spectra, dashed lines = simulated spectra.

TABLE 1. ESR parameters[a] of the superoxo complexes formed in the Co(5-Me-SHMA)–B–O_2 system

B	g_x	g_y	g_z	A_x	A_y	A_z	α	$\langle g \rangle$	$\langle A \rangle$
py[b]	2.016	2.093	1.986	6.4	22.4	11.4	29	2.032	13.4
py[c]	2.014	2.094	1.993	4.5	22.0	10.0	30	2.034	12.2
n-BuNH_2[b]	2.016	2.094	1.986	6.5	24.0	10.5	28	2.032	13.6
n-BuNH_2[c]	2.014	2.092	1.991	7.5	24.0	11.0	27	2.032	14.2
i-BuNH_2[b]	2.017	2.094	1.986	7.0	24.0	10.5	28	2.032	13.8
i-BuNH_2[c]	2.015	2.092	1.991	7.5	24.0	11.0	27	2.033	14.2
s-BuNH_2[d]	2.011	2.096	1.987	8.0	26.6	12.7	30	2.031	15.7
t-BuNH_2[d]	2.010	2.097	1.987	8.4	26.6	12.7	30	2.031	15.9
pip[d]	2.012	2.100	1.987	8.0	27.6	13.0	30	2.033	16.2

[a] Parameters were obtained by computer simulation, according to the coordinate scheme shown in Fig. 1. Absolute values of hyperfine constants A in 10^{-4} cm^{-1}, α in degree; error limits: $g \pm 0.001$, $A \pm 0.2 \times 10^{-4}$ cm^{-1}, $\alpha \pm 1°$. Solvent used was toluene/dichloromethane mixture (90/10), temperature 77 K. py = pyridine, pip = piperidine. [b] Base (B) concentration 0.2 M. [c] Base (B) concentration 1 M. [d] Parameters do not depend on base concentration.

with terminally bound dioxygen depend on steric factors present in the amine ligand. The mean values of the hyperfine constants $\langle A \rangle$ are significantly greater for systems containing amine with bulky substituents near the nitrogen donor (piperidine, sec-and tert-butylamine) than for other systems. It could be explained as an effect of the greater distance between the cobalt ion and nitrogen donor which is caused by steric hindrance. A more detailed discussion, however, is difficult, because the striking feature of the system under study is that spin Hamiltonian parameters depend not only on the kind of amine ligand, but also, in some cases, on the concentration of the amine. The latter dependence occurs for the systems with pyridine, n- and iso-butylamine but not for those with piperidine, sec- and tert-butylamine. For the first group of bases two limiting kinds of spectra were observed: one at a lower amine concentration (0.01–0.2 M) and another using excess base, from about 1 M (Fig. 2). At intermediate base concentrations the sum of both spectra were recorded. For the latter group of amines only one kind of spectrum was observed, regardless of amine concentration.

It is evident that the difference between the two groups of systems arises from steric factors. That fact is well documented by butylamine groups, for which amine basicity is almost constant, but steric hindrance grows markedly with substituent appearance on the α-carbon of the amine (sec- and tert-butylamine). On the other hand, the behavior of the system with pyridine is the same as for those with n- and iso-butylamine, despite the low basicity of pyridine in comparison with the butylamines ($pK_a \cong 10.5$ for butylamines and 6.0 for pyridine). On this basis we conclude that the concentration dependence of the spectra in the case of systems which contain bases without great steric hindrance is due to coordination of two amine molecules to the cobalt ion. Regarding the dimeric structure of the starting complex [8], it must be accompanied with bridge breaking and placing of both amine molecules in the *cis* position. Such location is unfavorable if there are bulky substituents in the vicinity of the donor atom.

In the case when the original dimeric structure of the complex is retained it is possible that only one of the cobalt ions is in the oxy form. This is likely when amine (B) concentration does not exceed concentration of the complex, thus it is not sufficient to saturate base binding equilibria to both cobalt ions of the dimer.

After thawing and re-freezing of the solution, the resulting spectra showed diminished intensity and disappeared after approximately 1 h of storage at room temperature. However, after bubbling with inert gas and consecutive O_2 passage through the solution, one can observe the return of the ESR spectrum, with an intensity which is very close to that obtained originally.

It is evident, that dioxygen binding is reversible in this system. The decay of the ESR signal of the superoxo-type complex described above is due to formation of a diamagnetic complex most likely containing peroxo bridge between the cobalt(III) ions. In the case of this system ESR delivers no information about the structure of the dioxygen adduct, however indication for the presence of the peroxo-bridged complex was supplied by experiments involving the oxidation of these ESR-silent complexes. After the addition of iodine to the solution (about 0.5 M solution in dichloromethane), another signal with a 15-line hyperfine structure was observed, which is characteristic for a μ-superoxo complex. Both in liquid and in frozen solutions well resolved ESR spectra were obtained. This is especially interesting because, to the best of the authors' knowledge, this is only the second example of μ-superoxo systems for which well-resolved anisotropic spectra have been obtained [13], and the first one which allowed both iso- and anisotropic spectra to be observed.

In Fig. 3(A), the anisotropic spectrum of the complex which contains a μ-superoxo bridge is presented. The spectrum is well resolved and clearly indicates the hyperfine interaction of one electron with two cobalt nuclei. The intensity distribution, however, is not well reproducible by computer simulation when the rhombic symmetry of magnetic tensors and equivalence of both metal centers are assumed, particularly in the central region of the spectrum.

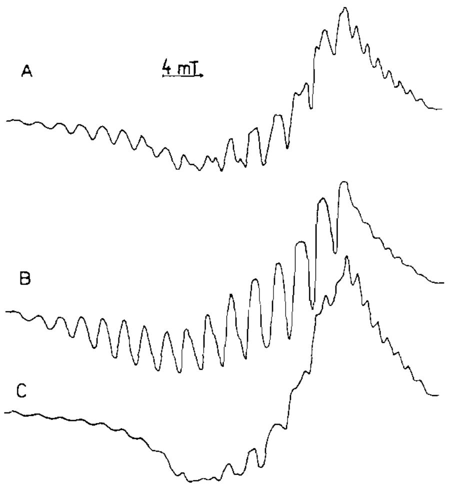

Fig. 3. ESR spectra of the Co(5-Me-SHMA)–pyridine–O_2–I_2 system in frozen toluene/dichloromethane mixture (A) and in frozen oriented nematic liquid crystal (MBBA) at 0° (B) and 90° (C) orientations with respect to the magnetic field. $T=77$ K.

The spectra in oriented nematic liquid crystal (Fig. 3(B) and (C) allow the assignment of the orientation of particular components. At 0° orientation the low-field component is enhanced, thus it can be labelled as the in-plane component [9]. After rotation of the sample by 90° the relative intensity of high-field component increases, so it can be assigned as the out-of-plane (z) component. Unfortunately, the component of intermediate g value is obscured by other components at both sample orientations, as well as in non-oriented samples.

Experimental ESR parameters for μ-superoxo complexes are collected in Table 2, both for anisotropic and isotropic hyperfine parameters. A dependence on the electronic factors imposed by the ligands is observed. This dependence is particularly well documented for the A_{iso} constant. Both for the row of various X substituents on the Schiff base ligand and for that with various pyridine derivatives, the linear dependence of the absolute value of A_{iso} on the Hammett acidity constants σ is observed [14] (Fig. 4). These tendencies have opposite directions. The slope (Hammett reaction constant ρ) is positive for the row of various pyridines but negative for that of the X substituent variation on the salicydene ligand. In another words, the A_{iso} absolute value decreases when electron-donating substituents are placed on pyridine molecule, while the same effect is caused by electron-withdrawing substituents attached to the SHMA ligand. The opposite sign of

TABLE 2. ESR parameters[a] of the μ-superoxo complexes formed in the Co(X-SHMA)–B–O_2–I_2 system

X	B	A_x[b]	A_y[b]	A_z[b]	g_x	g_y	g_z	A_{iso}[b]	g_{iso}
5-NO_2	py	19.1	10.8	9.4	2.073	2.033	1.984	11.69	2.033
5-Br	py	19.7	11.3	9.5	2.075	2.036	1.985	11.91	2.033
5-Cl	py	19.8	11.6	9.6	2.077	2.034	1.985	11.96	2.032
H	py	19.9	11.4	9.5	2.082	2.032	1.985	12.00	2.033
5,6-Benzo	py	19.9	11.4	9.6	2.082	2.034	1.985	12.00	2.033
5-Me	py	19.9	11.1	9.5	2.081	2.034	1.986	12.15	2.033
5-Me[c]	py	20.0	11.0	9.5	2.082	2.033	1.985		
5-Me	3-CNpy	20.8	12.1	10.2	2.081	2.039	1.984	12.71	2.035
5-Me	4-CNpy	20.5	12.1	10.0	2.081	2.032	1.984	12.56	2.034
5-Me	3-Clpy	20.5	11.9	10.0	2.083	2.033	1.983	12.40	2.033
5-Me	4-CHOpy	20.2	11.7	9.9	2.081	2.033	1.983	12.48	2.033
5-Me	4-Mepy	20.0	11.2	9.7	2.081	2.032	1.986	12.00	2.032
5-Me	3,4-Me_2py	19.9	11.1	9.7	2.081	2.032	1.986	11.95	2.033
5-Me	piperidine	19.6	11.5	9.7	2.081	2.032	1.985	11.66	2.033

[a] Anisotropic spectra were taken at 77 K for toluene/dichloromethane (90/10) mixture, unless otherwise stated. Isotropic spectra were recorded for dichloromethane solution at ambient temperature. Error limits: A_x, A_z $\pm 0.1\times10^{-4}$ cm^{-1}; A_y $\pm 0.3\times10^{-4}$ cm^{-1}; g_x, g_z ± 0.001; g_y ± 0.002; A_{iso} $\pm 0.05\times10^{-4}$ cm^{-1}; g_{iso} ± 0.001. Complex concentration: 0.1 M; base (B) concentration: 0.2 M; $P_{O_2}=1$ atm; iodine concentration: 0.5 M. [b] Absolute values of hyperfine constants in 10^{-4} cm^{-1}. [c] Solution in the frozen MBBA liquid crystal.

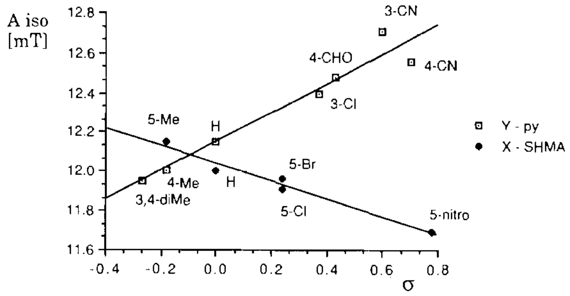

Fig. 4. Dependence of the isotropic hyperfine constant A_{iso} on the Hammett substituent constant σ for the Co(5-Me-SHMA)–Y-py–O_2–I_2 and Co(X-SHMA)–py–O_2–I_2 systems.

Hammett reaction constants for the rows of pyridine and X-SHMA ligands indicates that the amine ligand interacts with a different set of cobalt orbitals than the chelating tridentate Schiff base. It is likely that the amine is bound in *trans* position to the μ-superoxo bridge. It is in agreement with the tendency to diminish the electron density on the cobalt ion (which is reflected by A_{iso} constant decay) by monodentate ligands of greater basicity. Such a tendency is expected for ligands in the *trans* position with respect to the dioxygen moiety if spin density is transfered through the σ-framework [6]. On the other hand the chelating ligand orbitals are overlapping with those of the metal which are not involved in the dioxygen–cobalt(III) bond, thus electron withdrawing substituents simply diminish the electron density on the cobalt and make the core electron spin polarization less effective.

Conclusions

Results suggested that, at least in some conditions, the dioxygen molecule is bound to the CoSHMA complex while still retaining its original dimeric structure. This conclusion, based on the tendencies observed both for complexes with terminally bound O_2 and for those with bridging dioxygen, raises the question concerning the actual Co:O_2 stoichiometry of that type of adduct. The strong tendency for the reversible formation of the diamagnetic peroxo bridged complexes may suggest a permanent presence of another Co(II) ion in the proximity of the oxygenated cobalt. Thus, 2:1 Co:O_2 formulation may be present, even when the observed ESR signal indicates the presence of a terminally bound dioxygen. The neighboring unoccupied cobalt may serve as an active site for an oxidized substrate which opens some new perspectives on studies of catalytic properties of this system. A study on this subject is currently in progress.

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