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The Interaction of a Planar Co(II) Complex with Dioxygen

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Abstract

The paramagnetic Co(II) complex of 5,14-dihydro-dibenzo[b,i][5,9,14,18]tetraaza[14]annulen-(L) binds dioxygen in solutions containing equimolar concentrations of imidazole and other nitrogen bases. In excess base the paramagnetic Co(II)–dioxygen complex is converted to a diamagnetic Co(III) complex as shown by ESR, NMR, visible spectroscopy and X-ray crystallography.

Introduction

The species formed by the interaction in solution of planar cobalt complexes with organic bases and dioxygen have been the subject of intensive research [1]. Spectroscopic methods, in particular ESR, have established the fast formation of a paramagnetic mononuclear dioxygen complex the rate of formation of which depends on the nature of the base. In the presence of excess of certain bases, the ESR spectrum of the mononuclear complex is either undetectable or decreases with time at a rate dependent on the nature of both the complex and the base. Two types of explanation have been advanced to explain this phenomena. The most common supposition [2] is that a diamagnetic binuclear peroxo-complex is formed; however, in some systems the decrease in the intensity of the signal due to the mononuclear dioxygen complex is accompanied by the growth of a signal due to a paramagnetic species, which is identical with that of the cobalt complex in the absence of oxygen. In this case it is presumed that oxygen is displaced by base [3]. In this report we present evidence for a third reaction, the formation of a diamagnetic mononuclear cobalt(III) complex. A number of workers have reported ESR studies on oxygenated planar cobalt complexes in the presence of bases, but very few single crystal studies have been reported. Most measurements have been made on frozen solutions and the interpretation of the spectra has generally relied on visual inspection, which has drawbacks in the case of molecules in which the principal axes of the g-tensor and the cobalt hyperfine tensor are not colinear. In the present work computer simulation is used to derive magnetic parameters for the base-coordinated oxygenated cobalt complexes (CoL).

Experimental

Propargyl aldehyde was prepared by the method of Sauer [4]. The ligand L was prepared by the method of Hiller *et al.* [5]. The cobalt complex was prepared by reacting the ligand with $Co(OAc)_2 \cdot 4H_2O$ followed by vacuum sublimation at 290 °C. The complex forms violet needles.

ESR measurements were made on a Bruker X-band E-200 spectrometer using a flow system to attain low temperatures. An iron-constantan thermocouple was used to measure temperature. Solutions of cobalt complexes ($<10^{-3}$ M) were made up in toluene, pyridine, or DMF. Magnetic susceptibility in solution at room temperature was measured by the Evan's method using a Bruker NMR spectrometer operating at 250 MHz.

Visible spectra were recorded on a Perkin-Elmer model 554 UV–Vis spectrophotometer.

Computer Simulation

The computer simulation of the ESR spectra of mononuclear paramagnetic cobalt complexes requires the following input: (a) The principal values of the cobalt hyperfine tensor A_{XX}^{Co}, A_{YY}^{Co}, A_{ZZ}^{Co}; (b) the principal values of the mononuclear g-tensor, g_{xx}, g_{yy}, g_{zz}; (c) the relative orientations of the principal values of the A and g tensors; (d) the linewidths of the various lines in the spectrum; (e) the variation of transition probability with the orientation of the g-tensor with respect to the external field.

In practice the starting values taken for the A and g tensors were chosen to fall within the range of approximate values found for similar complexes. The linewidths were taken to obey the expression:

$$\sigma^2 = (g_x^2 l_x^2 W_x^2 + g_y^2 l_y^2 W_y^2 + g_z^2 l_z^2 W_z^2)^{1/2}/g \qquad (1)$$

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W_X, W_Y and W_Z, the linewidths for the external field along the principal axes of the g-tensor, were varied so as to give the best fit between experimental and simulated spectra. The transition probabilities include an orientation dependent factor given by the expression:

$$g_1{}^2 = [g_x{}^2 g_y{}^2 \sin^2\theta + g_y{}^2 g_z (\sin^2\phi + \cos^2\theta \cos^2\phi) + g_x{}^2 g_z{}^2 \times (\cos^2\phi + \cos^2\theta \sin^2\phi)]/(2g^2) \qquad (2)$$

This is a slight modification of the full expression given by Pilbrow [6], where the angles θ and ϕ are defined. It is certain that the principal axes (X, Y, Z) of the cobalt hyperfine tensor do not coincide with those of the g-tensor (x, y, z). Single crystal studies on oxycobalto–myoglobin [7] have shown that: (1) the principal axes of the g and A^{Co} tensors do not coincide (although those of g and $A^{^{17}\mathrm{O}}$ do); (2) the principal axes associated with the largest principal value of A^{Co} is not perpendicular to the heme plane, as it is in the deoxygenated complex, but parallel to the direction of the largest principal value of the g-tensor, which is almost certainly associated with the direction of the O–O bond in the dioxygen ligand. These findings have been assumed to hold for the complexes reported here since the heme group and the ligand used in this work are coordinated to cobalt via four coplanar nitrogen atoms, and in both systems the fifth position is occupied by a nitrogen base. If one axis, say z, of the g-tensor is coincident with an axis, say z', of the A^{Co} tensor there is only one angle, which we label α, remaining to be determined, namely the angle of rotation about z of the (x, y) axes of the g-tensor with respect to the (x', y') of the cobalt hyperfine tensor. In powder spectra the absolute orientation of the g and A principal axes to the heme group cannot be determined. Only the relative orientation of the g and A tensors can be found.

The resonance field of each hyperfine line for each orientation of the complex was defined by:

$$H = H_\circ - \left(\frac{A}{g\beta}\right) m_I - \frac{\tau_1{}^2 + \tau_2{}^2 + \tau_3{}^2}{4(g\beta)^2 H_\circ} [I(I+1) - m_I{}^2] - \frac{\tau_4{}^2 + \tau_5{}^2}{2(g\beta)^2 H_\circ} m_I{}^2 \qquad (3)$$

where

$$g^2 = g_x{}^2 \mathrm{l}_x{}^2 + g_y{}^2 \mathrm{l}_y{}^2 + g_z{}^2 \mathrm{l}_z{}^2, \qquad (4)$$

and

$$\tau_1 = A_\perp A_{zz}/A \qquad (5)$$

$$\tau_2 = (A_{xx}A_{yy} - A_{xy}A_{yx})/A_\perp \qquad (6)$$

$$\tau_3 = [A_{zz}g_z \cos\theta/A_\perp g_\perp] \{\sin\phi \cos\phi\ [g_x g_y (A_{yy}{}^2 - A_{xx}{}^2 + A_{yx}{}^2 - A_{xy}{}^2) + (g^2{}_x - g_y{}^2) \times (A_{xx}A_{yx} + A_{xy}A_{yy})]\}/(Agg_\perp) \qquad (7)$$

$$\tau_4 = g_z g_\perp (A^2 - A^2{}_{zz}) \sin\theta \cos\theta/Ag^2) \qquad (8)$$

$$\tau_5 = \tau_3 \tan\theta\ A_\perp g_\perp/(A_{zz}g_z) \qquad (9)$$

$$A_\perp{}^2 = \{(A_{xx}g_x \cos\phi + A_{yx}g_y \sin\phi)^2 + (A_{xy}g_x \cos\phi + A_{yy}g_y \sin\phi)^2\}/g_\perp{}^2 \qquad (10)$$

$$g_\perp{}^2 = g_x{}^2 \cos^2\phi + g^2_y \sin^2\phi \qquad (11)$$

The lineshape was taken as

$$\mathrm{f}(H) = -\sigma(H - H'_\circ)/[\sigma^2 + (H - H_\circ{}')^2]^2 \qquad (12)$$

where $H'_\circ$ is the resonance field for the line. The intensity of the line is given by

$$I = \mathrm{f}(H) g_1{}^2 \sin\theta \qquad (13)$$

where $g_1{}^2$ is given by eqn. (2). The spectrum was computed at intervals of 12° for ϕ and 3° for θ for 400 magnetic field positions between 3150 and 3650 gauss. In certain frozen solutions there is a superposition of the spectra of two different complexes. In these cases the spectrum was simulated by computer summation of weighted contributions from the individual spectra, 400 points being taken between 3150 to 3550 gauss. The solution spectra of the complexes consist of eight hyperfine lines differing in width due to motion-induced modulation of the g and A tensor. The m_I dependence of the linewidths was taken as

$$\sigma = A + Bm_I + Cm_I{}^2 \qquad (14)$$

and Lorentzian lineshape assumed. The spectrum was calculated for 250 points from 3200 to 3450 gauss.

The best fit anisotropic and isotropic magnetic parameters of the oxygenated complexes derived from computer simulations (Table I) are similar to those reported for other systems. The value of α, 31°, can be compared with 38° obtained for oxycobaltomyoglobin [7]. The cobalt hyperfine interaction decreases in the order Py > MeIm > Im, which is opposite to the order of base strengths. The isotropic cobalt splitting also decreases in the same order. The bases are not expected to be sterically hindered in their interaction with the complex and electronic effects presumably dominate. However, it would be unjustified to use the results as a basis for discussing differences in the electronic structure of the complexes. The range of bases is too limited and the variation in magnetic parameters, although well outside experimental error, is small. Furthermore, attempts to rationalize the data obtained from a much wider selection of bases have not resulted in a scheme capable of accommodating all the facts [8]. The similarity of the hyperfine and g-tensors for the pyridine and imidazole complexes is an indication that variations in the metal–nitrogen bond are not enough to account for the great disparity in rate between the disappearance of the ESR signal in the

TABLE I. Magnetic Parameters for Co(II) Complex with Dioxygen

Base	Total width of spectra (gauss)	$g_{\parallel}$	$g_{\perp}$	$A_{\perp}$ (gauss)	$A_{\parallel}$ (gauss)	a_{Co} (gauss)
DMF	144					
DMF/pyridine	100	2.088	1.993	19.7	13.7	13.5
DMF/methylimidazole	95	2.088	1.991	19.0	12.3	12.5
DMF/imidazole	94	2.086	2.002	18.6	11.2	11.5

two complexes. It may be that the acidic proton of the imidazole ring accounts for the high rates at which cobalt protoporphyrin complexes react with oxygen to give what are presumed to be peroxo-bridged complexes.

When small amounts of imidazole are added to oxygenated DMF solutions of the complex there are spectral changes. The overall width of the spectrum as measured between the maximum and minimum intensities decreases from 143 to 93 gauss. In a slight excess of imidazole the addition of further imidazole gives no change in the form of the spectrum but the intensity decreases until, at molar concentrations of imidazole slightly over twice that of cobalt, the spectrum is undetectable. It was shown by computer simulation that at all concentrations of imidazole the spectrum could be entirely accounted for in terms of varying weights of the spectrum in pure DMF and that in excess imidazole, with no other paramagnetic species contributing to the spectrum. Furthermore, the decrease in the ESR signal at high imidazole concentrations is exactly paralleled by a drop in magnetic susceptibility of the solution. These observations contrast with the superficially similar results of Walker [3] who found that the ESR signal of the dioxygen adduct of cobalt porphyrin complexes was reduced in intensity by the addition of excess base. Thus trinitrobenzene and picric acid, which both form 2:1 complexes with Co(p-CH_3)TTP cause complete dissociation of the dioxygen complex but the ESR signal of the 2:1 complex is observed. In the present case the destruction of the dioxygen complex leads only to diamagnetic species. No other ESR spectra appears. Imidazole is not unique in this respect; both methylimidazole and pyridine produce the same effect. The cobalt complex dissolved in oxygenated pyridine displays an ESR spectrum which rapidly decreases in intensity and is undetectable after 45 min. In methylpyridine as solvent and base, the process is considerably slower.

Spectrophotometric titration of [CoL] with pyridine or imidazole in air gives rise to several sharp isosbestic points, clearly indicating the formation of only one new species in solution which is believed to be the ESR-active complex [$BCoLO_2$] (B = nitrogenous base). As mentioned above, in the presence of excess base, the ESR signal gradually disappears. The resulting ESR-inactive complex exhibits an electronic absorption spectra which is slightly but significantly different from that of [$BCoLO_2$] but which is identical to the one obtained from Br_2 oxidation of [CoL] under nitrogen in the presence of excess base.

In order to determine the nature of the ESR inactive complex in solution, [CoL] was dissolved in pyridine which upon addition of $NaBF_4$ yields dark blue crystalline material which was shown by X-ray crystallography to have the composition $[CoL(py)_2]BF_4 \cdot 2py$*. As expected, the low-spin d^6 cobalt atom is six-coordinate with a distorted octahedral geometry. The metal atom and the four macrocyclic nitrogen atoms are nearly coplanar. One of the two pyridine ligands has its plane parallel to the short axis of the macrocyclic ligand and the other pyridine has its plane parallel to the lone axis so that there is an angle of approximately 90° between them.

The electronic absorption spectra of the Co(III) complex $[CoL(py)_2]^+$ is identical to that of the ESR-inactive species. Thus we may conclude that in the presence of excess base, the disappearance of the ESR signal of [$pyCoL \cdot O_2$] results from the oxidation of the metal which leads to a stable Co(III) complex. Whether this occurs by direct displacement of an O_2^- molecule or by displacement of a peroxo group from a peroxo-bridged dinuclear complex is not known. It should be mentioned that the oxidation of [$pyCoLO_2$] is also rapid in the presence of water, resulting in a Co(III) complex which on the basis of its electronic absorption spectra may reasonably be formulated as $[pyCoL(H_2O)]^+$.

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