Reaction of 3,5-di-t-butyl-*o*-benzoquinone on Co(II)M(III) (M = Y, La) heterodinuclear centres: the formation and ESR spectra of Co(III)M(III)–semiquinone adducts

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Abstract

The reactions of 3,5-di-t-butyl-*o*-benzoquinone (DBQ) with the Co(II)M(III) (M = Y, La) complexes of *N,N'*-bis(3-carboxysalicylidene)ethylenediamine have been studied in dmf solutions by means of ESR spectroscopy. The ESR spectral study has shown that DBQ oxidizes the Co(II) ion of the Co(II)M(III) complexes to afford a Co(III)M(III)–DBSQ species (DBSQ = semiquinone form of DBQ) but the DBSQ is bound to the M(III) ion but not to the Co(III). The reaction of the mononuclear cobalt(II) complex [Co(H_2L)] with DBQ afforded [Co(H_2L)(DBSQ)] where DBSQ coordinates to the cobalt(III) ion as a bidentate chelate.

Introduction

Heterodinuclear complexes consisting of a d-transition metal ion and a lanthanoid ion have attracted much attention recently because such a combination of dissimilar metal ions gives rise to unique physicochemical properties and functions effected by metal–metal interactions of cooperative effects [1–4]. Previously [1–3] we have studied the Cu(II)Ln(III) or Co(II)Ln(III) complexes (Ln = lanthanoid) of a heterodinucleating ligand *N,N'*-bis(3-carboxysalicylidene)ethylenediamine (Fig. 1, abbreviated as H_4L hereafter) and found that they show unique 'selective solvation' depending upon the nature of the solvent. That is, in nitrogen-containing solvents like pyridine the solvation occurs preferentially at the copper or cobalt center, whereas in oxygen-containing solvents like dimethylformamide or dimethyl sulfoxide the solvation occurs at the lanthanoid center. Such a selective solvation has been extended to the specific binding of substrates possessing a nitrogen and an oxygen donor atom on the heteronuclear center.

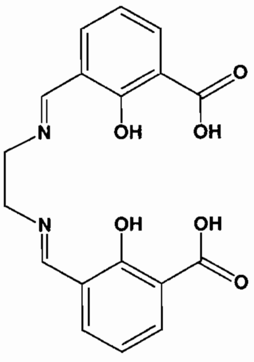

Fig. 1. Chemical structure of H_4L.

In this study we have examined the reaction of 3,5-di-t-butyl-*o*-benzoquinone (DBQ) with the Co(II)Y(III) and Co(II)-La(III) heterodinuclear complexes of H_4L by means of ESR spectroscopy. For comparison the reaction of DBQ with the mononuclear cobalt(II) complex of H_4L, [Co(H_2L)], was also examined.

Experimental

Materials and preparations

3-Formylsalicylic acid [5] was obtained by the modified Duff reaction and *N,N'*-bis(3-carboxysalicylidene)ethylenediamine (H_4L) was prepared by the literature method [6]. 3,5-Di-t-butyl-*o*-benzoquinone (DBQ) was purchased from Aldrich Chemical Co. *N,N'*-Dimethylformamide (dmf) as the solvent was dehydrated over BaO and degassed prior to use.

Syntheses of the complexes were carried out under argon or nitrogen using a Schlenk apparatus or a

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VAC inert atmosphere & vacuum deposition equipment model HE-43-2. [$Co(H_2L)(H_2O)_2$] and [$Co(H_2L)$] were synthesized by the method of Zarembowitch *et al.* [7]. The synthesis of [$CoLa(L)(NO_3)(CH_3OH)$] was described in our previous paper [3].

[$CoY(L)(NO_3)(H_2O)$]

A methanolic solution (10 cm^3) of [$Co(L)(H_2O)_2$] (500 mg) and $LiOH \cdot H_2O$ (100 mg) was refluxed for 2 h. To this was added a methanolic solution (15 cm^3) of yttrium(II) nitrate hexahydrate (450 mg) and the mixture was refluxed for 1 h to give reddish orange microcrystals. They were recrystallized from a large amount of methanol and dried *in vacuo*. Yield 78%.

Anal. Found: C, 37.58; H, 2.35; N, 7.35; Co, 9.9% $\mu_{eff} = 2.27$ μ_B at 300 K. Calc. for $C_{18}H_{14}CoN_3O_{10}Y$: C, 37.27; H, 2.43; N, 7.24; Co, 10.2%.

Physical measurements

Elemental analyses for C, H, and N were obtained at The Service Center of Elemental Analysis, Kyushu University. Analyses of Co were made on a Shimadzu Atomic Absorption/Flame Emission Spectrophotometer Model A-680. Infrared spectra (IR) were measured on a JASCO IR-810 spectrometer on KBr disks or Nujol mulls. Magnetic moments were measured on a Faraday balance at room temperature. Electronic absorption spectra were recorded on a Shimadzu MPS-2000 spectrometer at room temperature. X-band ESR spectra were recorded on a JES-FE3X spectrometer at room temperature.

Results and discussion

The Co(II)Y(III) complex, [$CoY(L)(NO_3)H_2O$], obtained in this study resembles those of the Co(II)Ln(III) (Ln = Ln, Nd, or Gd) [3] complexes in physicochemical properties. The nitrate ion may function as a bidentate ligand judged from the splitting of the antisymmetric vibration into 1440 and 1380 cm^{-1} [8]. It appears that the Y(III) ion adopts a seven-coordinate surrounding with the O_4-donor atoms of $(L)^{4-}$, the bidentate NO_3^- and the water molecule. The cobalt(II) ion is of low spin (2.27 μ_B at room temperature) and shows a d–d band at 7300 cm^{-1} characteristic of planar cobalt(II) of tetradentate Schiff bases [9].

The reaction of the Co(II)Y(III) or Co(II)La(III) complex with DBQ (1:1 molar ratio) in dmf under anaerobic conditions resulted in the immediate color change of the solution from reddish orange to brown and the reaction mixture showed new absorption bands of significant intensities at 18 500 (ϵ 570), 23 000 (2800) and 27 800 cm^{-1} (7800 dm^{-3} mol^{-1} cm^{-1}). This is presumed to be due to the formation of a Co(III)M(III)–DBSQ adduct (DBSQ = 3,5-di-t-butyl-*o*-semiquinone). Our attempts to isolate the reaction product were in vain. Thus, the resulted solutions were subjected to ESR spectral measurements to characterize the species generated *in situ*. For comparison [$Co(H_2L)$] was reacted with DBQ in the 1:1 molar ratio in dmf and the resulted brown solution (absorption bands at 18 500 (ϵ 610), 23 800 (3160) and 28 500 cm^{-1} (13 400 dm^{-3} mol^{-1} cm^{-1}) was subjected to ESR spectral studies.

The ESR spectra of the $Co(H_2L)$/DBQ, CoY/DBQ and CoLa/DBQ solutions measured at room temperature are given in Figs. 2, 3 and 4, respectively. The spectra differ from those of planar, low-spin cobalt(II) complexes [9] of quadridentate Schiff bases

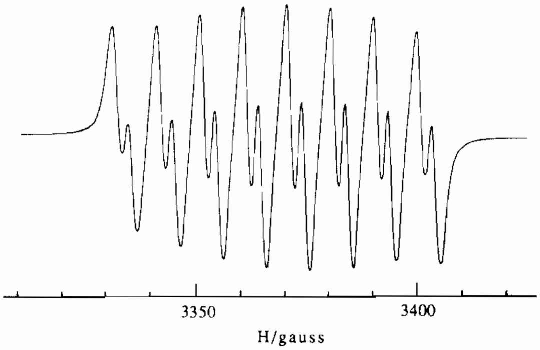

Fig. 2. ESR spectrum of $Co(H_2L)$/DBQ in dmf at room temperature.

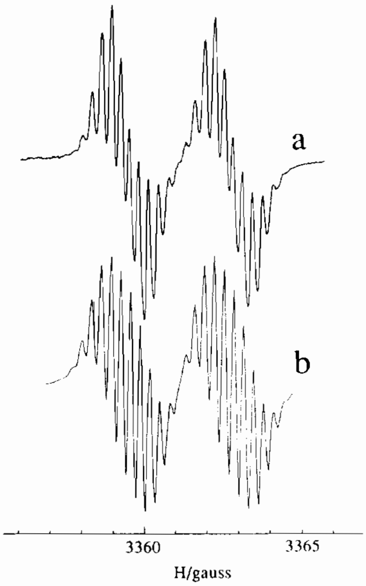

Fig. 3. ESR spectra of CoY/DBQ: (a) measured in dmf at room temperature; (b) simulated based on the Hamiltonian and the parameters given in the text.

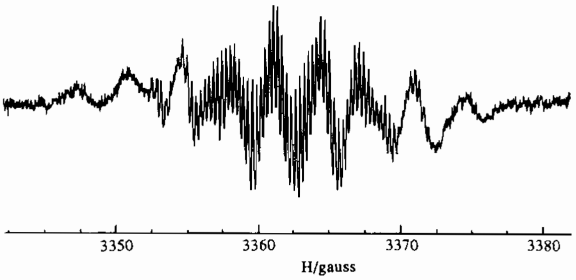

Fig. 4. ESR spectrum of CoLa/DBQ in dmf at room temperature.

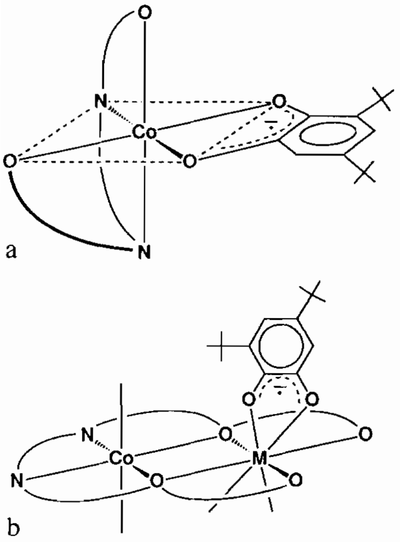

Fig. 5. Schematic representations of DBSQ adducts: (a) Co(III)–DBSQ; (b) Co(III)M(III)–DBSQ (M = Y, La).

and show features characteristic of the DBSQ radical [10], indicating the formation of a Co(III)M(III)–DBSQ adduct in each case.

First the ESR spectrum of the Co(H_2L)/DBQ solution (Fig. 2) is discussed as the reference. The spectrum shows an eight-lined hyperfine structure (9.9 G) due to the cobalt nucleus ($I = 7/2$) at g 2.0 and upon which a doublet structure of a coupling constant 3.5 G is superimposed. The doublet structure can be assigned to the coupling to the proton at the 4-position of DBSQ [10]. The ESR spectral feature is very similar to that of a Co(III)–semiquinone complex [Co(salen)(DBSQ)] [11] (H_2salen = N,N'-disalicylideneethylenediamine) that shows a coupling to the cobalt ($A_{\mathrm{Co}} = 10.2$ G) and a coupling to the proton at the 4-position ($A_{\mathrm{H(4)}} = 3.5$ G). The result indicates that [Co(H_2L)(DBSQ)] is formed in solution where the metal ($\mathrm{Co^{III}}$) adopts a pseudo-octahedral configuration with the *cis*-tetradentate $(H_2L)^{2-}$ and the bidentate DBSQ (Fig. 5(a)). It should be emphasized that the unpaired electron of the DBSQ is delocalized significantly over the cobalt nucleus judged from the large hyperfine coupling constant to the cobalt nucleus.

The ESR spectrum of the CoY/DBQ solution (Fig. 3) shows basically a doublet of a coupling constant 3.3 gauss and on each component is superimposed a multiplet of at least 14 lines (coupling constant *c*. 0.3 G). The doublet structure may be referred to the proton at the 4-position judging from the coupling constant similar to that of [Co(H_2L)(DBSQ)] (3.5 G). Assuming that only one paramagnetic species exists in solution within the time-scale of ESR spectroscopy, the ESR simulations were carried out based on the isotropic spin Hamiltonian,

$$\mathrm{H} = g\beta HS + \sum A_i S I_i,$$

and by taking consideration the ESR spectra of free DBSQ [10] and *o*-benzosemiquinonatoyttrium(III) [12]. As shown in Fig. 3(a) good simulation of the ESR spectrum was attained with the hyperfine coupling constants, $A_{\mathrm{H(4)}} = 3.3$ G, $A_{\mathrm{Y}} = 0.6$ G, $A_{\mathrm{H(6)}} = 0.6$ G and $A_{\mathrm{Bu(5)}} = 0.3$ G, where the subscripts H(4), H(6) and Bu(5) refer to the proton at the 4- and 6-positions of DBSQ and the t-butyl group at the 5-position of DBSQ, respectively. Thus, it is revealed that the cobalt nucleus does not couple with the unpaired electron of the DBSQ.

The ESR spectrum of the CoLa/DBQ solution (Fig. 4) is very complicated probably because of the large nuclear spin ($I = 7/2$) and nuclear magnetic moment of La compared with Y. On the whole it shows a nine-lined hyperfine structure with a coupling constant of *c*. 3 G and on each signal are superimposed smaller structures with a separation of *c*. 0.3 G. It appears that the hyperfine coupling to ^{139}La ($I = 7/2$) and the coupling to the proton at the 4-position of the DBSQ are comparable to afford the main nine structures. Though we have not yet succeeded in the ESR simulation, the spectral feature indicates that the DBSQ is bonded to the La(III) but not to the Co(III), similarly to the case of the Co(III)Y(III)–DBSQ adduct.

Based on the above ESR investigations it is found that DBQ oxidizes the Co(II) center of the Co(II)M(III) (M = Y, La) complexes to form a Co(III)M(III)–DBSQ adduct where the DBSQ is bonded to the M(III) presumably as a bidentate chelate (Fig. 5(b)). It is very plausible that DBQ oxidizes the Co(II) by an inner-sphere mechanism [11] but the resulted DBSQ shifts to the Ln(III) because the axial site of Co(III) surrounded planarly by a salen-like ligand is considerably labile [13] and the neighboring La(III) or Y(III) ion has a high affinity toward oxygenous donor groups [1–3]. In the Co(III)–DBSQ adducts derived from mononuclear cobalt(II) complexes such as [Co(salen)] and [Co(H_2L)], on the other hand, DBSQ coordinates bidentately to Co(III) ion (Fig. 5(a)) as demonstrated by a large hyperfine coupling to the Co nucleus in ESR spectra.

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