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Inner- and outer-sphere magnetic moments in the cobalt–quinone valence tautomeric system

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We report valence tautomerism in the spin-labeled complex, Co(nnbpy)(3,5-DTBSQ)$_2$, where nnbpy is a bipyridine substituted nitronyl nitroxide radical, 4-methyl-4′-(4,4,5,5-tetramethyl-1-oxido-3-ylooxy-4,5-dihydro-3*H*-imidazol-2′-yl)-2,2′-bipyridine, and 3,5-DTBSQ is 3,5-di-*tert*-butylbenzosemiquinone. The temperature dependence of the magnetic susceptibility indicates a tautomeric conversion, Co^{3+}(nnbpy)(3,5-DTBSQ$^{-\bullet}$)(3,5-DTBSQ^{2-}) → Co^{2+}(nnbpy)(3,5-DTBSQ$^{-\bullet}$)$_2$, above 250 K with the thermodynamic parameters of $\Delta H = 34$ kJ mol^{-1} and $\Delta S = 98$ J K^{-1} mol^{-1}. The ligand radical, nnbpy, behaves as a Curie spin over the whole temperature region. The EPR spectra in the temperature range 150–380 K consist of a single absorption at $g = 2.004$ that gradually fades away above 300 K with a characteristic increase in linewidth.

The cobalt complexes of semiquinonate and catecholate ligands have attracted much interest, because they undergo a thermally-induced valence tautomeric conversion between the high-spin [Co^{2+}(N–N)(sq)$_2$] and the low-spin [Co^{3+}(N–N)(sq)(cat)] form, where N–N, sq and cat are diimine, *o*-semiquinonate and catecholate, respectively.[1–7] This type of bistability has potential for use as sensors and switches in molecular electronic and magneto-optical devices.[8] The relevance of these compounds to biological systems, such as catechol dioxygenase, bacterial photosynthetic protein, is also interesting.[9,10] In addition, the metal–semiquinonate complexes are good examples for fundamental studies of the direct exchange interactions between metal ions and organic radical ligands.[11]

Nitronyl nitroxide‡ radicals have been extensively studied as building blocks for pure organic ferromagnets[12–15] and as bidentate ligands for various transition and rare-earth metal ions.[16] In this work, we prepared 4-methyl-4′-(4,4,5,5-tetramethyl-1-oxido-3-ylooxy-4,5-dihydro-3*H*-imidazol-2′-yl)-2,2′-bipyridine (abbreviated as nnbpy), consisting of a nitronyl nitroxide moiety and a bipyridyl bidentate ligand, and used it as a spin probe for the valence tautomerism in the cobalt–semiquinonate system. We describe the magnetic properties of Co(nnbpy)(3,5-DTBSQ)$_2$, where 3,5-DTBSQ is 3,5-di-*tert*-butylbenzosemiquinone, in comparison with the reference sample, Co(bpy)(3,5-DTBSQ)$_2$·0.5(C$_6$H$_5$CH$_3$),[1] where bpy is non-magnetic 2,2′-bipyridine.

Experimental

Materials

The radical ligand, nnbpy, was prepared by the reported procedure:[17] 4-methyl-2,2′-bipyridine-4′-carbaldehyde[18] was condensed with 2,3-bis(hydroxyamino)-2,3-dimethylbutane, and the obtained bis(hydroxylamine) was oxidized with lead dioxide. The single crystals were obtained by recrystallization from diethyl ether solution. Co(nnbpy)(3,5-DTBSQ)$_2$ was obtained by the reaction of stoichiometric amounts of Co(3,5-DTBSQ)$_2$[19] and nnbpy: to a solution of nnbpy in diethyl ether, Co(3,5-DTBSQ)$_2$ was added at 0 °C. After stirring for 3 hours, the precipitate (green powder) was filtered off and dried. The elemental analysis gave C, 66.10; H, 7.18; N, 6.73 (calcd. for C$_{46}$H$_{61}$N$_4$O$_6$Co: C, 66.98; H, 7.45; N, 6.73%). Growth of single crystals was unsuccessful. We also prepared the reference material, Co(bpy)(3,5-DTBSQ)$_2$·0.5(C$_6$H$_5$CH$_3$), by the literature method[1] for the control experiments.

X-Ray structure determination§

X-Ray diffraction data for nnbpy were collected on a RIGAKU AFC-5 automatic four-circle diffractometer with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were obtained by a least-squares refinement using 25 reflections with $20° < 2\theta < 25°$. Three standard reflections were measured as a check on crystal stability and revealed no fluctuation in intensities. The crystal structure was solved by direct methods (SHELXS-86). With anisotropic thermal parameters for all non-hydrogen atoms, block-diagonal least-squares refinement was employed (UNICS III).[20] The positions of hydrogen atoms were found by differential Fourier methods, and were refined with isotropic thermal parameters. Crystal data are as follows: C$_{18}$H$_{21}$N$_4$O$_2$, $M = 325.39$, monoclinic, space group $P2_1/c$, $a = 14.107(2)$ Å, $b = 9.904(2)$ Å, $c = 12.226(2)$ Å, $\beta = 96.26(1)°$, $V = 1697.9(4)$ Å^3, $Z = 4$, $D_c = 1.27$, $R = 0.056$ and $R_w = 0.055$ for 2462 independent reflections, with $|F_o| \geqslant 3\sigma(|F_o|)$ and 302 parameters.

Magnetic measurements

Magnetic susceptibility measurements in the temperature range 3–300 K were performed under a magnetic field of 1 T, using a Faraday susceptometer with an Oxford superconducting magnet.[21] The data for Co(nnbpy)(3,5-DTBSQ)$_2$ and Co(bpy)(3,5-DTBSQ)$_2$·0.5(C$_6$H$_5$CH$_3$) above 300 K, were recorded on a SQUID magnetometer (Quantum Design MPMS) and on a Faraday susceptometer with an electrical magnet. The measurements for Co(bpy)(3,5-DTBSQ)$_2$·0.5(C$_6$H$_5$CH$_3$) were

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‡The IUPAC name for nitronyl nitroxide is nitronylaminoxyl.

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limited below 350 K, because of evaporation of the crystal solvent at this temperature. Diamagnetic corrections were carried out, compensating the diamagnetic susceptibilities estimated by assuming that the paramagnetic component followed the Curie law in the temperature range 100–200 K. X-Band EPR spectra were recorded on a JEOL JES-RE2X spectrometer with an N_2 flow cryostat in the temperature range 150–400 K.

Results and discussion

The crystal structure and the magnetic properties of the ligand radical, nnbpy, have been examined. The obtained molecular structure is depicted in Fig. 1. The bipyridine unit is nearly coplanar; the dihedral angle between the two pyridyl rings is 1.38(7)°. The nitrogen atoms on the pyridine rings are in an s-*trans* orientation. The nitronyl nitroxide group makes a dihedral angle of 32.90(6)° with the neighboring pyridyl ring, which is a typical value for the nitronyl nitroxide radical family. In this crystal, there is no significant intermolecular contact between the NO groups of nnbpy, on which the unpaired electrons are nearly localized. The temperature dependence of the magnetic susceptibility follows the Curie–Weiss law with a negative Weiss constant of −0.54 K (not shown), indicating a very weak antiferromagnetic intermolecular interaction.

The temperature dependence of the magnetic susceptibility for the reference sample, Co(bpy)(3,5-DTBSQ)$_2$·0.5($C_6H_5CH_3$), was examined, in order to compare it with that for Co(nnbpy)(3,5-DTBSQ)$_2$. The obtained paramagnetic susceptibilities χ_p are shown in Fig. 2 (triangles), where the product χ_pT is plotted as a function of temperature. The values of χ_pT are nearly constant below 260 K. This value can be explained by the formula, Co^{3+}(bpy)(3,5-DTBSQ$^{-\bullet}$)(3,5-DTBSQ^{2-})·0.5($C_6H_5CH_3$), in which Co^{3+} takes a low-spin ($S = 0$) configuration and 3,5-DTBSQ$^{-\bullet}$ is $S = 1/2$. Above 260 K χ_pT shows a significant increase, indicating generation of the Co^{2+} form, namely Co^{2+}(bpy)(3,5-DTBSQ$^{\bullet}$)$_2$·0.5($C_6H_5CH_3$) in which Co^{2+} takes a high-spin ($S = 3/2$) configuration. The temperature dependence of this tautomeric conversion is well explained by the equilibrium model with the following equation;[5]

$$\chi_pT = (\chi_p^{\mathrm{Co(III)}}\,T)(1-n) + (\chi_p^{\mathrm{Co(II)}}\,T)n \qquad (1)$$

with

$$\ln((1-n)/n) = \Delta H/RT - \Delta S/R$$

where $\chi_p^{\mathrm{Co(III)}}T$ and $\chi_p^{\mathrm{Co(II)}}T$ are the χ_pT values for the Co^{3+} and the Co^{2+} form, respectively, n is the fraction of the Co^{2+} form, ΔH and ΔS are the enthalpy and the entropy gain at the conversion, respectively, and R is the gas constant. The solid curve going through the plots for Co(bpy)(3,5-DTBSQ)$_2$·0.5($C_6H_5CH_3$) is the theoretical best fit, obtained with the fitting parameters; $\chi_p^{\mathrm{Co(III)}}T = 0.41$ emu K mol^{-1} (1.81 μ_B), $\chi_p^{\mathrm{Co(II)}}T = 2.51$ emu K mol^{-1} (4.47 μ_B), $\Delta H = 38$ kJ mol^{-1} and $\Delta S = 104$ J K^{-1} mol^{-1}. These values are in agreement with the reported values for the non-solvated form of Co(bpy)(3,5-DTBSQ)$_2$.[6]

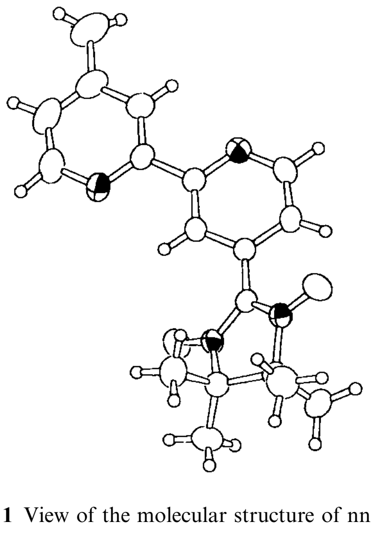


Fig. 1 View of the molecular structure of nnbpy.

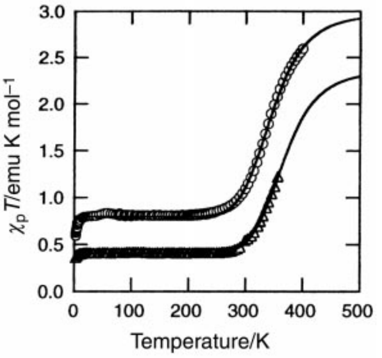
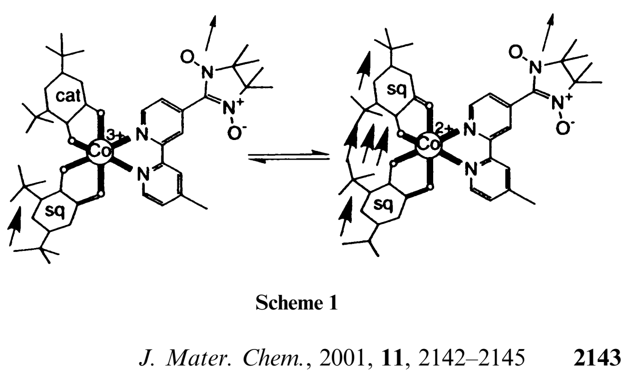


Fig. 2 Temperature dependence of the paramagnetic susceptibility χ_p for Co(nnbpy)(3,5-DTBSQ)$_2$ (○) and Co(bpy)(3,5-DTBSQ)$_2$·0.5($C_6H_5CH_3$) (△). The products χ_pT are plotted as a function of temperature. The solid curves are the theoretical best fits of eqn. (1) calculated with the parameters reported in the text.

The circles in Fig. 2 show the results for Co(nnbpy)(3,5-DTBSQ)$_2$. In the range 30–250 K, the value of χ_pT (0.79 emu K mol^{-1}) is temperature-independent. As the temperature increases from 250 K, χ_pT increases to a value more than 2.5 emu K mol^{-1} at 400 K. It is concluded that the spin-labeled complex, Co(nnbpy)(3,5-DTBSQ)$_2$, exhibits valence tautomeric conversion above 250 K, as well as Co(bpy)(3,5-DTBSQ)$_2$·0.5($C_6H_5CH_3$). The expected change at the conversion is depicted in Scheme 1. At low temperatures, Co(nnbpy)(3,5-DTBSQ)$_2$ has two doublet spins; one is on nnbpy and the other is on 3,5-DTBSQ$^{-\bullet}$. The temperature-independent χ_pT values indicate that the magnetic interaction between the two spin species is weaker than the thermal energy in this temperature range. This is analogous to the weak magnetic interactions between metal ions and *p*- or *o*-pyridyl nitronyl nitroxide through the pyridyl rings.[22,23] Below 20 K χ_pT shows a significant decrease that could be caused by a weak antiferromagnetic coupling between 3,5-DTBSQ$^{-\bullet}$ and nnbpy. The magnetic data for Co(nnbpy)(3,5-DTBSQ)$_2$ above 30 K were fitted to eqn. (1). The theoretical best fit was obtained with $\chi_p^{\mathrm{Co(III)}}T = 0.79$ emu K mol^{-1} ($\mu_{\mathrm{eff}} = 2.51$ μ_B), $\chi_p^{\mathrm{Co(II)}}T = 2.98$ emu K mol^{-1} (4.87 μ_B), $\Delta H = 34$ kJ mol^{-1} and $\Delta S = 98$ J mol^{-1} K^{-1}. The values of ΔH and ΔS for Co(nnbpy)(3,5-DTBSQ)$_2$ are close to the corresponding ones for Co(bpy)(3,5-DTBSQ)$_2$·0.5($C_6H_5CH_3$), respectively, although it is known that the equilibrium is strongly dependent on the donor strength of the nitrogen coligands.[3,24]

Variable temperature X-band EPR was examined on the powder samples of Co(nnbpy)(3,5-DTBSQ)$_2$ and Co(bpy)(3,5-DTBSQ)$_2$·0.5($C_6H_5CH_3$) in the range 150–400 K. The EPR



Scheme 1

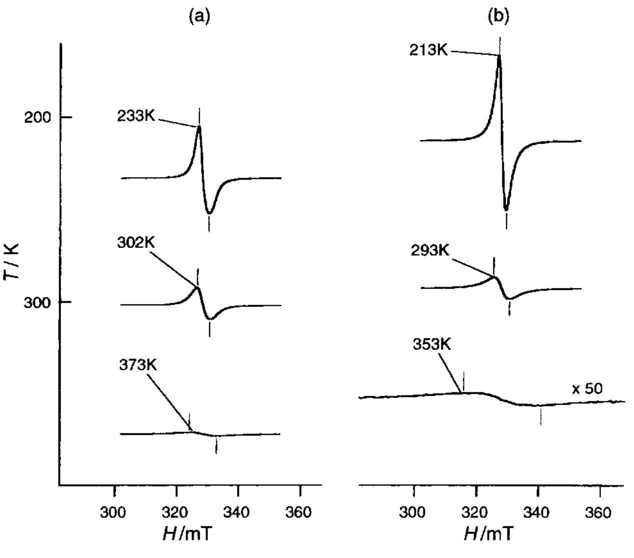


Fig. 3 X-Band EPR spectra for Co(bpy)(3,5-DTBSQ)$_2$·0.5(C$_6$H$_5$CH$_3$) (a) and Co(nnbpy)(3,5-DTBSQ)$_2$ (b) at representative temperatures.

spectra at representative temperatures for the two complexes are compared in Fig. 3. The reference sample, Co(bpy)(3,5-DTBSQ)$_2$·0.5(C$_6$H$_5$CH$_3$), exhibits a single absorption at $g = 2.001$, which quickly decreases in intensity above 250 K. This signal is assigned to the absorption of 3,5-DTBSQ$^{-\bullet}$. The spectra for the radical complex, Co(nnbpy)(3,5-DTBSQ)$_2$, consists of a single EPR absorption at $g = 2.004$. While this lineshape is slightly asymmetric, the integrated ones are rather close to Lorentzian. Interestingly, this signal also fades away quickly in the conversion process, although this material involves nnbpy in addition to 3,5-DTBSQ$^{-\bullet}$.

Fig. 4(a) and (b) depict the temperature dependence of the g-factor and the peak-to-peak linewidth ΔH_{pp}, respectively, for the two complexes. Their g-factors are nearly the same and depend little on temperature in the whole range 150–400 K. In contrast there is a crucial difference between the temperature dependence of ΔH_{pp} for the two: ΔH_{pp} of Co(nnbpy)(3,5-DTBSQ)$_2$ shows a rapid increase above 280 K, while the broadening of the Co(bpy)(3,5-DTBSQ)$_2$·0.5(C$_6$H$_5$CH$_3$) signal is much less significant. The EPR absorption of Co(nnbpy)(3,5-DTBSQ)$_2$ involves the contributions of 3,5-DTBSQ$^{-\bullet}$ and nnbpy, while that of Co(bpy)(3,5-DTBSQ)$_2$·0.5(C$_6$H$_5$CH$_3$) is caused only by 3,5-DTBSQ$^{-\bullet}$. Therefore it is considered that the linewidth broadening for Co(nnbpy)(3,5-DTBSQ)$_2$ occurs on the absorption of nnbpy. In the other words, the high-spin Co^{2+} ion has significantly different interactions with nnbpy and 3,5-DTBSQ$^{-\bullet}$.

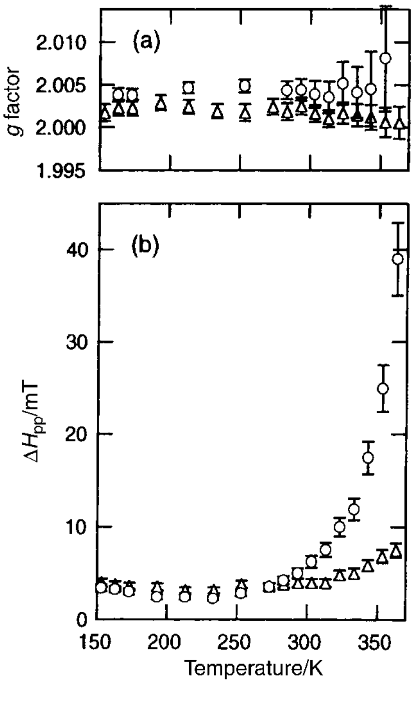


Fig. 4 Temperature dependence of the g-factors (a) and the peak-to-peak linewidths ΔH_{pp} (b) for the EPR signals of Co(nnbpy)(3,5-DTBSQ)$_2$ (○) and Co(bpy)(3,5-DTBSQ)$_2$·0.5(C$_6$H$_5$CH$_3$) (△).

The unpaired electron on semiquinonate has large populations on the oxygen atoms on its skeleton. In the present complexes, such oxygen atoms directly bind to the central cobalt ion. The reference complex, Co(bpy)(3,5-DTBSQ)$_2$·0.5(C$_6$H$_5$CH$_3$), exhibits an EPR signal which gradually disappears above 250 K with nearly constant linewidth. It is reasonable to ascribe this behavior to the exchange interaction between 3,5-DTBSQ$^{-\bullet}$ and the EPR-silent high-spin Co^{2+} ion: the excited spin states rapidly relax, sending the excess energies to the lattice through spin–orbit interactions on Co^{2+}. The EPR signal of Co(nnbpy)(3,5-DTBSQ)$_2$ also fades away above 250 K, but this process is accompanied by abrupt broadening of the linewidth. The unpaired electron on nitronyl nitroxide is localized on the two NO groups and has little population on the substituent at the α-carbon (namely the bipyridine moiety of nnbpy).[25] The Co^{2+} ion should have a much weaker exchange interaction with nnbpy than with 3,5-DTBSQ$^{-\bullet}$, while the disappearance of the EPR signal for Co(nnbpy)(3,5-DTBSQ)$_2$ suggests the presence of an exchange and/or superexchange interaction between nnbpy and Co^{2+}. It would be reasonable to consider that the observed line-broadening is caused by an insufficient exchange-narrowing and/or a dipole interaction of nnbpy with the high-spin Co^{2+} and 3,5-DTBSQ$^{-\bullet}$.

Conclusion

The complexation of the nitronyl nitrooxide-substituted bipyridine with the cobalt semiquinonate complex was performed. The magnetic measurements on the obtained compound, Co(nnbpy)(3,5-DTBSQ)$_2$, revealed the valence tautomeric conversion above 250 K. The valence tautomerism was probed using the nitronyl nitroxide radical by means of EPR. The comparison between the EPR for Co(nnbpy)(3,5-DTBSQ)$_2$ and Co(bpy)(3,5-DTBSQ)$_2$·0.5(C$_6$H$_5$CH$_3$) suggested that the high-spin Co^{2+} ion had significantly different magnetic interactions with 3,5-DTBSQ$^{-\bullet}$ and nnbpy.

The positions of 3,5-DTBSQ$^{-\bullet}$ and nnbpy remind us of the inner- and the outer-sphere mechanism in the redox reactions of the transition metals.[26] The exchange interaction between Co^{2+} and 3,5-DTBSQ$^{-\bullet}$ in the present materials must be relevant to the inner-sphere electron transfer processes with fast kinetic rates. The location of the unpaired electron on nnbpy seems to be close to those of the outer-shell electrons. It is believed that the redox reactions caused by metal–quinone electron transfers play important roles in biological systems, such as mitochondria, bacterial photosynthetic systems, catalytic enzymes, *etc.* There is an interesting example: the iron–catechol complex in dioxygenase enzymes, in which a catechol is oxidized to aliphatic carboxylic acids by dioxygen, contains three kinds of magnetic species; metal ion, semiquinonate and dioxygen. Since they correspond to the three magnetic moments in Co(nnbpy)(3,5-DTBSQ)$_2$, this spin-labeled complex may be a useful model for discussion of the biochemical activity.

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