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The Ambiguity of Spectroscopic Techniques in Determining the Nature of the Quinone Adduct of a Nickel(II)–Catecholate Complex

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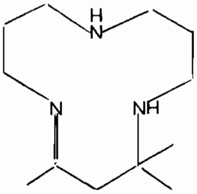
Complexes formed by transition metal ions and ligands having frontier orbitals close in energy to 3d orbitals are often difficult to characterize electronically [1]. Thus, for example, when a dioxolene coordinates to a metal ion such as nickel(II) three isoelectronic formalisms for describing the adduct are available: nickel(II)–catecholate, nickel(I)–semiquinone or (least likely) nickel(0)–quinone.

We have been interested in the specific problem of dioxolene coordination to transition metal ions. Recently we reported that the high-spin five-coordinate nickel(II) complex NiL(TCCat) (L = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene (I); TCCat = tetrachlorocatecholate) reacts with tetrachloro-1,2-benzoquinone (TCQ) yielding a compound of formula 'NiL(TCCat)(TCQ)' [2]. The X-ray crystal structure of the latter compound indicates that the formation of the adduct involves monodentate coordination of the TCQ molecule to the metal ion with the simultaneous formation of a π charge-transfer complex with the coordinated dioxolene. Analysis of the structural parameters suggests that this derivative is best described as containing a semiquinone and quinone coordinated to the nickel ion and, therefore, this leads to the conclusion that the adduct should be formulated as a formally nickel(I) complex, i.e. Ni^{I}L(TCSQ)(TCQ) (TCSQ = tetrachlorosemiquinone). This formulation is consistent with the observed magnetic properties of this derivative. Indeed the experimental value of the effective magnetic moment (2.97 μ_B) is more consistent with a nickel(I)–semiquinone strongly ferromagnetically coupled rather than a nickel(II) pseudo-octahedral derivative.



In order to understand the properties of this and similar chemically related systems, more detailed information about the electronic properties of this molecule is highly desirable. Accordingly we have used three other spectroscopic techniques – optical spectroscopy, ESR and ^{1}H NMR – in order to ascertain whether there is other supporting evidence for the nickel(I) oxidation state in 'NiL(TCCat)(TCQ)' and the strong ferromagnetic coupling with semiquinone.

The electronic spectra of acetonitrile solutions of (A) TCQ, (B) NiL(TCCat) and (C) NiL(TCSQ)TCQ are reported in Fig. 1, but the analysis of their spectral parameters provides equivocal results. The charge-transfer band appearing at 12 700 cm^{-1} in the spectrum of the adduct (C) falls in the spectral region where the n–π^* transitions characterizing the semiquinone derivatives are expected [3]. Moreover, it cannot be established if this intense low-energy charge-transfer band involves only a π–π^* transition between the stacked TCSQ and TCQ ligands or also includes a Ni–TCQ d–π^* transition. Unfortunately, there are no simple complexes containing coordinated TCQ which can be used for comparison.

Both ESR and ^{1}H NMR spectra should, in principle, be able to distinguish between the aforementioned extreme electronic formalisms. If 'NiL(TCCat)(TCQ)' were indeed nickel(I) (d^9) coordinated to free radical semiquinone without any magnetic coupling, a well-defined ESR spectrum would be expected at low temperature[†]. The ^{1}H NMR spectrum should have very broad, perhaps even unobservable, signals due to the long electronic relaxation times of the d^9 ion and free radical. The isotropic shifts of the L protons, influenced predominantly by nickel(I), should be mainly contact and, since $(\Delta H/H)_{\text{contact}}$ is proportional to $S(S + 1)$, they should be 0.375 times as large as in a pseudo-octahedral nickel(II). On the other hand, if the complex has an $S = 1$ ground state from high-spin nickel(II), then entirely different ESR and NMR spectra should be obtained, since the electronic relaxation properties will be that of a triplet state. Indeed there will be no observable ESR spectrum even at 4 K and the NMR spectrum will be broad but observable and strongly shifted [4].

The presence of strong ferromagnetic coupling, however, can cause a blurring of the distinction between the two formalism, at least regarding magnetic

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[†] The ESR spectrum at 77 K should contain separate signals for $S = 1/2$, d^9 nickel(I), and $S = 1/2$, semiquinone radical.

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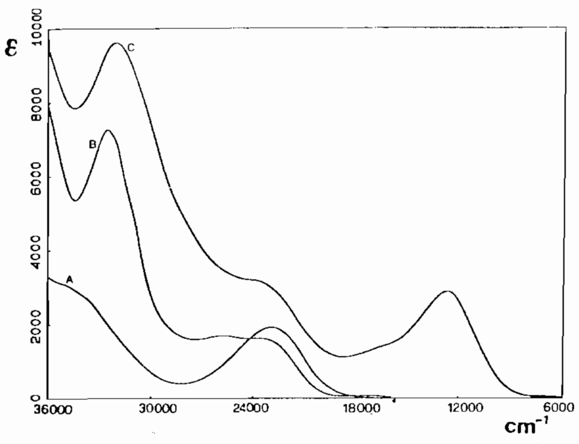

Fig. 1. Electronic spectra of acetonitrile solutions of (A) TCQ; (B) NiLTCCat; and (C) NiL(TCSQ)(TCQ).

resonance. Current theory [5, 6] – developed for magnetic coupling between two paramagnetic metal ions – points that the NMR contact shifts can be decomposed into two components, reflecting the additive contribution of the two metal ions summed over the occupied Boltzmann levels. For two $S = 1/2$ spins

$$(\Delta H/H) = (h\gamma_I B_0)^{-1}\Sigma_i(A_{c,1} + A_{c,2})\langle S_z\rangle_i/2$$

where $A_{c,1}$ and $A_{c,2}$ are the Fermi coupling constant with metal (1) and (2), respectively, and $\langle S_z'\rangle_i$ is the expectation value of S_z for each Boltzmann level. We can attempt to use this, at least qualitatively, to predict the contact shift of the L protons for the putative ferromagnetically coupled NiL(TCSQ)(TCQ) in which the $S = 1/2$ ground state is fully populated, as indicated by magnetic susceptibility results. For the L protons, the above equation reduces to

$$(\Delta H/H) = -g_e^2\mu_B^2A_{c,Ni}S'(S' + 1)/2(h\gamma_N 3kT)^{-1}$$

where $S' = 1$ and $A_{c,TCSQ} \ll A_{c,Ni}$. The observed contact shifts in Ni^IL(TCSQ)(TCQ) should be approximately half of those found in comparable nickel(II) pseudo-octahedral complexes because the Fermi contact coupling constant is reduced by a factor of 2.

The theory of nuclear relaxation is not as well developed but again an additive approach is suggested [6]. Very broad, perhaps unobservable, resonances are predicted for the L protons because of the very slow electronic relaxation rate expected for nickel(I). Then, in principle, it is possible to identify strongly coupled ferromagnetic Ni^IL(TCSQ)(TCQ) using NMR spectroscopy.

ESR spectroscopy of strong ferromagnetically coupled molecules is, unfortunately, uninformative. Known copper(II)–semiquinone systems do not exhibit any ESR spectrum [7–9] and the 'NiL(TCCat)(TCQ)' is ESR silent even at 4 K. Thus ESR cannot discriminate between pseudo-octahedral nickel(II) and ferromagnetically coupled nickel(I)–semiquinone.

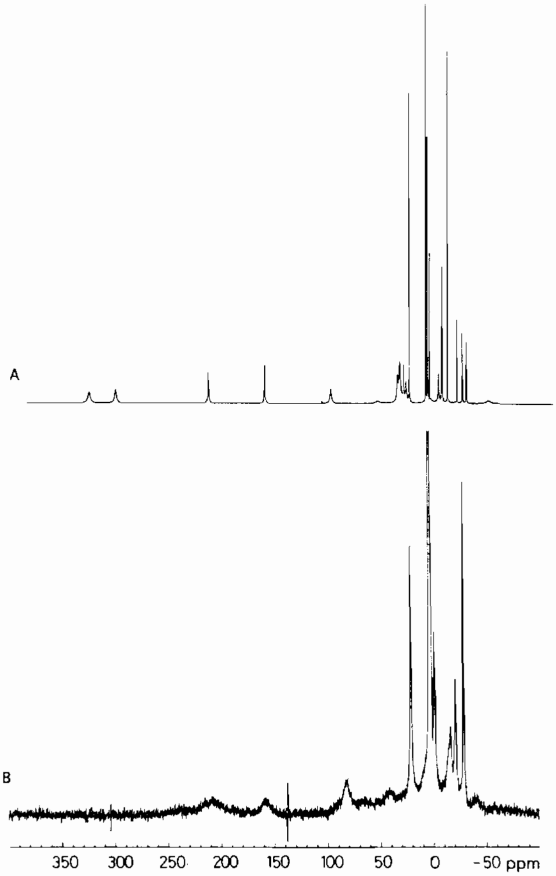

Fig. 2. ^{1}H NMR spectra of d_6-acetone solutions of (A) NiL(TCCat); and (B) NiL(TCSQ)(TCQ).

The ^{1}H NMR spectra of the five-coordinate NiL(TCCat) and its TCQ adduct in d_6-acetone are shown in Fig. 2. The observed resonance signals can be reasonably assigned on the basis of the considerations used in our previous studies on the conformational isomers of nickel(II) macrocyclic complexes [10, 11]. The α-methylene protons are expected to experience downfield shifts, whereas the β-methylene protons are expected to shift upfield because of a dominant spin polarization mechanism. Furthermore, axial protons are expected to experience smaller contact shifts than equatorial protons because of the angular dependence of the hyperfine coupling constant [12].

It is apparent that the observed ^{1}H NMR linewidths are significantly smaller for the five-coordinate NiL(TCCat) complex than for its TCQ adduct. This result can be ascribed to the different electronic relaxation rates of the interacting paramagnetic centers [6]. Indeed five-coordinated high-spin d^8

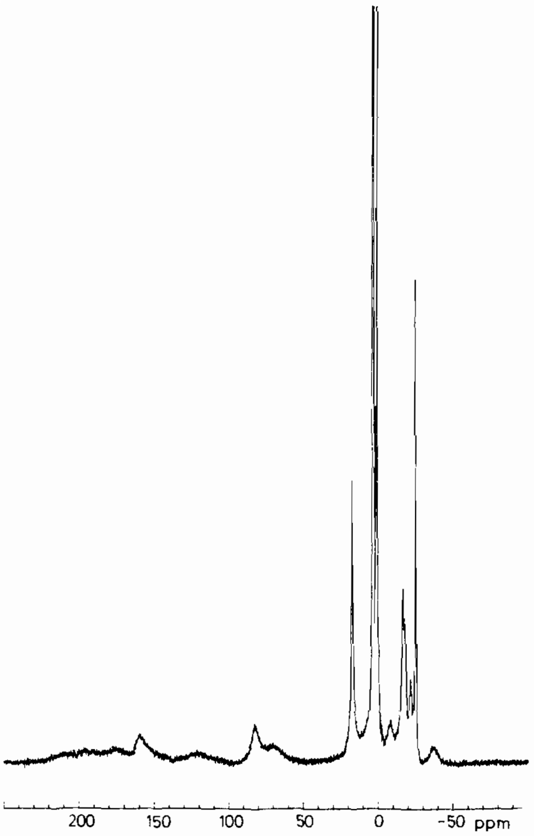

Fig. 3. ^1H NMR spectrum of $[NiL(NO_3)(H_2O)]NO_3$ in d_6-acetone solution.

metal ions, which are characterized by a ^3E electronically degenerate ground state, are expected to possess shorter electronic relaxation times than either ferromagnetically coupled d^9-TCSQ adducts or pseudo-octahedral high spin d^8 metal ions, for which a non-degenerate ^3A ground state is expected*.

The observed pattern of isotropic shifts is also different for the two complexes. Since this may be related to the different orbital ground states of the paramagnetic centers, it is best to compare the two experimental spectra with that of the six-coordinate $[NiL(NO_3)(H_2O)]NO_3$ (Fig. 3), which should be the most appropriate NMR model for pseudo-octahedral 'NiL(TCCat)(TCQ)'. This compound exhibits a quite complicated NMR spectrum, which can be explained by taking into account the presence of two conformers in the same solution. This isomerism has been observed also by Curtis *et al.* [14] in other complexes containing this nickel(II) triazamacrocyclic moiety and has been attributed to the two possible reciprocal chiralities of nitrogen donors. However, the most important aspect of this spectrum is that its general features are remarkably similar to those observed for the NiL(TCSQ)(TCQ) complex. This result leads us to conclude that the ^1H NMR does not provide a definitive answer for the characterization of the electronic ground state. Indeed, the linewidths and the isotropic shifts of the resonating triazamacrocycle protons appear very similar if induced from a ferromagnetically coupled d^9-TCSQ system or an high-spin pseudo-octahedral d^8 metal ion. In this respect, the spectral parameters appear to be dependent only upon the presence of a triplet ground state. Apparently the point-dipole model for the magnetic exchange coupling breaks down when applied to the NMR of strongly coupled ferromagnetic systems. Whether this is due to the presence of a free radical remains to be determined and we are accordingly investigating other systems.

Experimental

Complexes NiL(TCCat), NiL(TCSQ)(TCQ) and $[NiL(NO_3)(H_2O)]NO_3$ were prepared according to literature methods [2, 9, 15]. Whereas the NiL(TCCat) complex is quite stable, freshly prepared solutions containing NiL(TCSQ)(TCQ) change from blue–green to orange slowly with time. The orange–red compound which separates from concentrated solutions has been identified as hexachloro-2,3-oxanthrenequinone, a product of the nucleophilic reaction between the two dioxolene ligands [16, 17]. Electronic spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer. Polycrystalline ESR powder spectra were recorded with a Bruker ER200 spectrometer working at the X-band frequency. ^1H NMR spectra were measured with a Bruker MSW200 spectrometer at 298 K.

^1H NMR shifts data (ppm) and spectral assignments (ax = pseudo-axial, eq = pseudo-equatorial; Me_1 and Me_2 are the geminal methyl groups): NiL(TCCat), α-CH_{eq}: 321, 296, 200, 155; α-CH_{ax}: 93, 29.5, 25.7, 21.3; β-CH_{eq}: −26.9, −32.1, −35.8; β-CH_{ax}: −9.6, −13.0(2); Me_{1eq}: 18.2; Me_{2ax}: 27.3; Me_3: −18.1. NiL(TCSQ)(TCQ): α-CH_{eq}: 230, 207(2), 158; α-CH_{ax}: 91, 70(2), 41.5; β-CH_{eq}: −26; β-CH_{ax}: −21; Me_{1eq}, 21; Me_{2ax}, 0.9; Me_3, −29.

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*In this respect it is worth making comparison with the NMR spectrum of the ferromagnetically coupled copper(II)-tetraphenylporphyrin radical; see ref. 13.

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