A Novel Adduct of TCNQ Dianion with Schiff-Base Cobalt(III) Complex in N-Bonded Coodination Mode in Dmf Solution [TCNQ=7,7,8,8-Tetracyanoquinodimethane]

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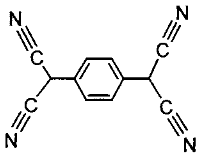
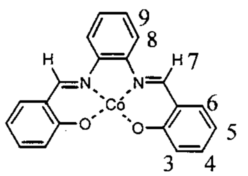
Formation of a stable novel adduct, [Co(III)(saloph)]$_2$ TCNQ(-II), has been confirmed by analysis of the ^{1}H NMR spectra of the N,N-dimethylformamide(dmf)-acetonitrile solution of LiTCNQ and [N,N'-o-phenylenebis(salicylideneaminato)] cobalt (II), denoted as [Co(II)(saloph)]. The time-resolved spectra of the UV-vis absorption of the LiTCNQ-[Co(II)(saloph)] solutions gave information concerning the formation process of the adduct.

The donor-acceptor complexes of TCNQ, one of the conjugated polynitrile, have been widely studied as fascinating materials exhibiting the unique electric and magnetic properties in crystal.[1] The close relation between the properties and the stacking of the TCNQ anions in crystal has been pointed out.[2] The another important factor to support the facile electron transfer between the TCNQ units is the existence of several oxidation states lying with small energy differences.[3,4] The dominant oxidation states reported in crystal were -1/2, -1 and -2. However, in solution TCNQ of the -2 oxidation state, TCNQ(-II), was reported only as an unstable species.[4,5] We considered that by shielding the TCNQ(-II) moiety from contact with solvent molecules, the stable N-bonded TCNQ(-II) adduct may be formed. Our previous work reported that the dmf-solvated bulky complex, [Co(II)(saloph)]·dmf, is a good reductant,[6] so that we examined the reaction between [Co(II)(saloph)] in dmf and TCNQ(-I). In this paper, we give the first report of the generation of a stable TCNQ(-II) adduct in solution.



TCNQ



[Co(saloph)]

[Co(II)(saloph)],[7] [Co(III)(saloph)]I[8] and LiTCNQ-d$_4$[9] were synthesized following literatures. The solvents used were of spectroscopic grade. The ^{1}H NMR spectra were measured at 24 °C in dmf-d$_7$ and acetonitrile-d$_3$ purged by argon gas on JEOL LA300 spectrometer operating at 300.4 MHz at the reactant concentration of 5-10 mM. The measurements of the UV-vis absorption were carried out at 20-60 °C by UV-VIS-NIR scanning spectrophotometer UV-3100PC combined with temperature controller SPR-8. The dmf solutions of [Co(II)(saloph)] and the acetonitrile solutions of LiTCNQ at the reactant concentrations of 0.2-0.8 mM were prepared under nitrogen atmosphere using solvents purged by nitrogen gas.

Through the reaction between [Co(II)(saloph)] in dmf-d$_7$ and LiTCNQ in acetonitrile-d$_3$, [Co(II)(saloph)] was pursued by the ^{1}H NMR measurement of a saloph ligand. Due to the paramagnetic effect of the cobalt(II) ion, the proton signals of [Co(II)(saloph)] were observed to be out of the diamagnetic region.[10] An addition of LiTCNQ in acetonitrile to the [Co(II)(saloph)] dmf solution weakened the signals in the paramagnetic region and the nine signals appeared in the diamagnetic region (Figure 1a). The new spectrum was analogous to that of [Co(III)(saloph)]I in dmf-d$_7$. All the signals derived from the saloph ligand were unambiguously assigned on the basis of the 2D COSY spectrum shown in Figure 2 together with the NOE difference spectrum. Figure 2 depicted that the remaining two doublet signals at 5.95 and 6.72 ppm correlates with each other. In order to assign the signals, we synthesized LiTCNQ-d$_4$. The two doublets disappeared in the solution of [Co(II)(saloph)] and LiTCNQ-d$_4$ (Figure 1b). The integrated intensity of the TCNQ

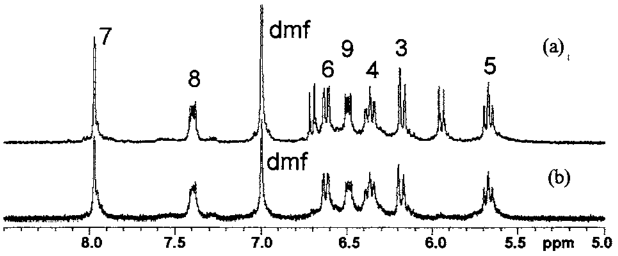


Figure 1. ^{1}H NMR spectra of [Co(II)(saloph)]/dmf-d$_7$ containing a:LiTCNQ-h$_4$/acetonitrile-d$_3$, and b: LiTCNQ-d$_4$/acetonitrile-d$_3$. Numbers indicate saloph protons.

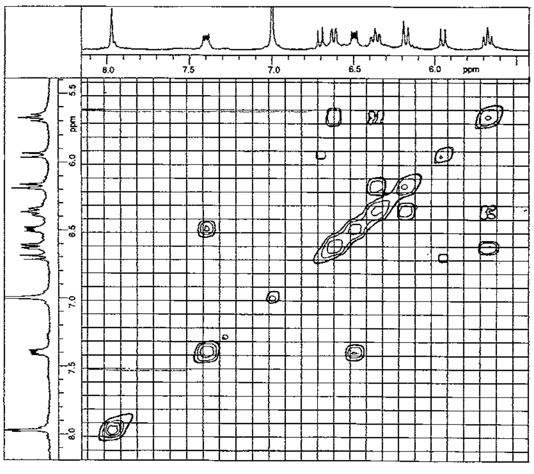


Figure 2. Two dimensional ^{1}H NMR map of correlated spectroscopy for solution of [Co(II)(saloph)] and LiTCNQ-h$_4$.

doublets was equal with each other and was half of the intensity of the saloph signals. Therefore, the nine proton signals are attributed to two $[Co(III)(saloph)]^+$ and one diamagnetic TCNQ, that is, $[Co(II)(saloph)]_2TCNQ(-II)$ **1**. By warming up to 80° C, these proton signals of the adduct **1** scarcely shifted.

In the crystalline state, TCNQ bridges the cation moieties in several types. Regarding to the bulky complexes of the transition-metal, TCNQ(-I) coordinates at one nitrile-site. Exceptional cases involving TCNQ(-I) bridging were reported for $[\{Re_2Cl_4(dppm)_2\}_2](TCNQ)$[2,11] and $[Ru(PPh_3)_2(TCNQ)]$[2,12] as 1,2-trans-nitrile form (1 and 2 denote the nitrile-groups at opposite side of phenyl). The bridge of TCNQ(-II) was proposed only for $[Ni(III)_2(bdpa)_2TCNQ](ClO_4)_2$ and $[Ni(III)(bdpa)(TCNQ)]ClO_4$ as 1,2-cis-nitrile form based on the vibrational analysis.[13] In the reaction of [Co(II)(acacen)] (Schiff-base complex analogous to [Co(II)(saloph)]) and TCNE (tetracyanoethylene), TCNE(-II) bridges two $[Co(II)(acacen)(py)]^+$ in the forms of 1,1-nitriles and 1,2-trans-nitriles.[14] The two geometric isomers were stable in different solvent. The above results indicate that the three isomers involving TCNQ(-II) bridge can be formed depending on the experimental conditions. With regard to the 1,2-cis- and 1,2-trans-isomers of the adduct **1**, the free rotation around the C-C bond between $C(CN)_2$ and phenyl-group gives one signal for the four TCNQ-protons, contradictory to the observation at 80 °C. The infrared analysis reported that double-bond character of the above C-C bond decreases with increase of electron density on TCNQ.[13] However, coordination of TCNQ(-II) to the Co(III) ions makes the electron density on TCNQ(-II) smaller. It is difficult to estimate the contribution of the two opposite factors from our results.

Figure 3 depicts the time-resolved UV-vis absorption spectrum measured by 2.2 min intervals in the dmf/acetonitrile(1/1) solution of [Co(II)(saloph)]/dmf (0.6 mM) added by LiTCNQ/acetonitrile (0.3 mM) at 20 and 60 °C. Initial and Final in Figure 3 denote the superimposed spectra of the reactants and the spectra after 2 days, respectively. The TCNQ(-I) concentration can be monitored by the absorbance of the strong band at 600-900 nm. At 60 °C, the clear isosbestic points indicate that the formation process of the final product (the adduct **1**) has one rate-determining path. The decay rate of the TCNQ(-I) absorbance was determined as 1×10^{-3} s^{-1}. At 20 °C, the change of TCNQ(-I) exhibited a complicated behavior. The rapid decrease of TCNQ(-I) was accompanied by the increase of the intermediate species with 350nm peak. After the fast decay of the 350nm peak, TCNQ(-I) continued to decrease slowly with the rate of 4×10^{-4} s^{-1}. The final product was the same as that at 60 °C. We reported previously the monomer-dimer equilibrium for [Co(II)(saloph)] in dmf,[6] and in the dmf-acetonitrile solutions the same equilibrium was confirmed to occur. At 60 °C, the dominant species of [Co(II)(saloph)] is a monomer. Then, we propose as a tentative reaction scheme that the dimer, $[Co(II)(saloph)]_2$, easily forms the intermediate species involving the TCNQ(-II) bridge, and that the monomer, [Co(II)(saloph)], slowly forms the stable TCNQ(-II) adduct. The following two reports closely correlate with our scheme; (1) $[Ni(III)_2(bdpa)_2(TCNQ)]$ containing the TCNQ(-II) bridge was synthesized from the dimeric $[Ni(II)_2(bdpa)_3(H_2O)](ClO_4)_2$,[13] and (2) the two geometric isomers were formed for $[Co(acacen)(py)]_2TCNE(-II)$.[14]

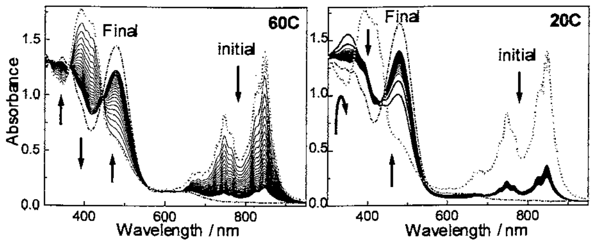


Figure 3. Time-resolved absorption spectra at 20 ℃ and 60 ℃ of [Co(saloph)] (0.6 mM) and LiTCNQ (0.3 mM) in dmf-acetonitrile(1/1) in 1 mm quartz cell, by 2.2 min intervals. Initial and Final denote the spectra of reactants and 2 days after, respectively. Arrows indicate change with time.

Previous work[4] reported that the electrogenerated TCNQ(-II) decomposed to DCTC(-I), α,α-dicyano-p-toluoyl- cyanide, by trace of oxygen in solvent. In our experiment, the adduct **1** of TCNQ(-II) was not so sensitive to oxygen in solvent. In conclusion, the stability of the adduct **1** originates in good balance between the oxidation potential of [Co(II)(saloph)] and the reduction potential of TCNQ(-I) in dmf-acetonitrile solution, and in effective shielding of the bridging TCNQ(-II) from the solvent molecules by the two bulky cation complexes.

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