Hydrogen-bonded Charge-Transfer Complex of Ethylenediaminoglyoxime Transition Metal Complex with Tetracyanoquinodimethane

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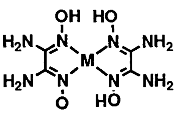
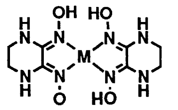
We prepared the hydrogen-bonded charge-transfer complex containing a transition metal, (ethylenediaminoglyoximato)-(ethylenediaminoglyoxime)palladium(II), with TCNQ, which showed a segregated stacking mode of crystal structure and contained H-bonds between the anionic and cationic columns and between the cationic columns. The high electrical conductivity (90 Scm^{-1}) was observed.

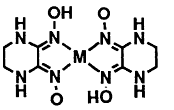
The hydrogen-bonded (H-bonded) charge-transfer (CT) systems (the HBCT systems), which exhibit cooperative interaction between H-bonding and CT, can be a good candidate for new molecular materials having interesting solid state properties.[1, 2] Generally, the solid state properties of the HBCT systems depend on the degree and cooperativity of H-bonding and CT. Endres and his coworkers have reported good examples of HBCT system, that is, CT complexes of (diaminoglyoximato)-(diaminoglyoxime)transition metal complex **1** with tetracyanoquinodimethane, M(Hdag)(H_2dag)·TCNQ (M = Ni or Pt), which showed highly electrical conductivity.[3] In order to accumulate a variety of such examples and to develop our idea,[2,4] we have modified the diaminoglyoxime (Hdag) ligand. We now report the synthesis and crystal structure of a HBCT system having the reduced number of H-bonds, that is, (ethlenediaminoglyoximato)(ethylenediaminoglyoxime)palladium(II) **2b** with TCNQ, Pd(Hedag)(H_2edag)·TCNQ.



1 M(Hdag)(H_2dag)

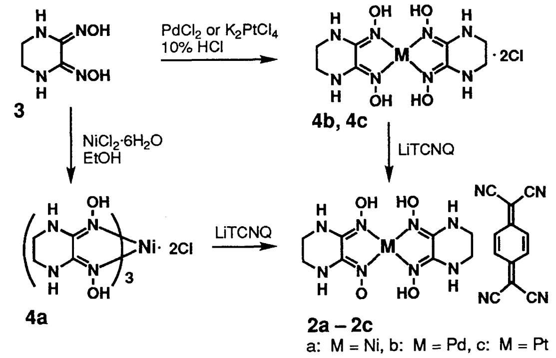


2 M(Hedag)(H_2edag)



5 M(Hedag)$_2$

We have utilized the ethylenediaminoglyoxime ligand, H_2edag **3**, which contains the reduced number of H-bonding donor sites compared with the H_2dag ligand.[5] The CT complexes of the Hedag transition metal complexes **2a**, **2b**, and **2c** with TCNQ, were prepared by adopting similar procedures reported by Endres and his coworkers for the complex **1**·TCNQ (Scheme 1). Thus, the Hedag transition metal complex **4a** (M = Ni) was prepared by reaction of H_2edag with $NiCl_2 \cdot 6H_2O$ in ethanol.[6] The complexes **4b** (M = Pd) and **4c** (M = Pt), were prepared by reaction of H_2edag with $PdCl_2$ and K_2PtCl_4 in 10% HCl solution, respectively.[7] The CT complexes with TCNQ were prepared by mixing an aqueous solution of these transition metal complexes with an ethanol solution of LiTCNQ.[3] The molecular structure was confirmed by the data of the elemental analysis, infrared spectra, and electronic absorption spectra.[8]



Scheme 1.

The components of the transition metal complexes having the diaminoglyoxime type ligand are known to exist as the three formal charge states, neutral, +1, and +2, depending on the number of the protons on the oxime moiety.[9] Among them, extensive investigations have been performed for the crystal structures of the neutral complexes, M(Hdag)$_2$. The crystal structure of neutral complex of ethylenediaminoglyoximato nickel, Ni(Hedag)$_2$ **5a**, has also been reported, though the R value is 0.115.[10] All these results show the inclusion of the additional components, such as solvents, water, or ionic salts

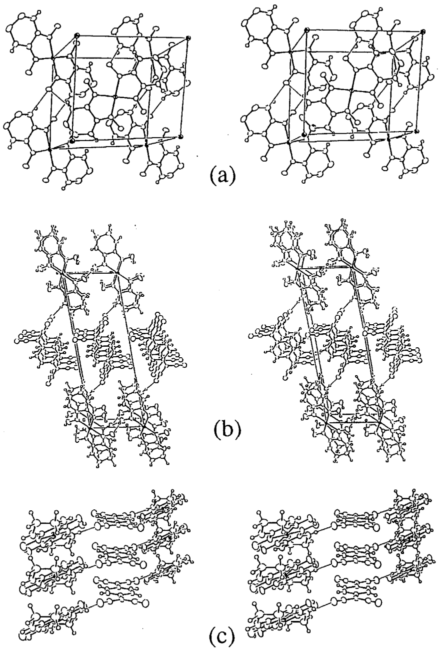


Figure 1. Stereoviews of the crystal packing: (a) for **5a**, and (b) and (c) for **2b**.

forming H-bonds. In sharp contrast, we obtained single crystals of **5a** suitable for X-ray crystal structure analysis by recrystallizing from dimethylsulfoxide-methanol, whose elemental analysis showed no contamination of an additional component.[11] The crystal structure analysis actually shows the direct intermolecular H-bonding interactions between the Hedag ligands[12] (Figure 1). This indicates a positive effect of the ethylene moiety to simplify the H-bonding interactions.

The single crystals of the CT complex, (ethlenediaminoglyomimato)(ethylenediaminoglyoxime)palladium(II) **2b** with tetracyanoquinodimethane, Pd(Hedag)(H_2edag)·TCNQ, were obtained by a diffusion method using H-tube containing an aqueous solution of the palladium complex **4b** and an acetonitrile solution of LiTCNQ. The chemical composition of **2b**·TCNQ is determined by the elemental analysis and the crystal structure analysis.[11] Such a composition indicates the +1 ionic charge for the component of the transition metal complex. Therefore, the formal charge of TCNQ is –1 and **2b**·TCNQ is classified into an ionic CT complex.

The complex **2b**·TCNQ crystallizes in the triclinic and the space group $P\bar{1}$.[12] The crystal structure (Figure 2) indicates that the cationic component of the palladium complex and the anionic component of TCNQ are arranged in uniform, segregated stacking mode along *c* axis. The O···O distance of the intramolecular H-bonds in oxime moiety is 2.94(1) Å. The other hydrogen atom on the oxime is in a positional disorder and form intermolecular H-bond (2.61(1) Å) to the adjacent transition metal column. The intermolecular H-bonding interactions between the cationic transition metal and the anionic TCNQ components of **2b**·TCNQ are more simple compared with those of **1a**·TCNQ.[3b] Thus, the cationic and anionic components are linked via one kind of intermolecular H-bonding between NH of the amino group and N of the nitrile group (2.94(1) Å). The cationic stacks are linked to sheet via one kind of intermolecular H-bonding between the oxime oxygen involving the disordered H atom, as mentioned above.

We estimated the degree of CT for **2b**·TCNQ to be 0.70 and 0.67 by using the nitrile stretching frequency and by the bond length ratio procedure[14] of TCNQ skeleton, respectively. The corresponding values for the complex **1a**·TCNQ are 0.61 and 0.78.[13] As mentioned, the formal charge of the TCNQ skeleton for the complex **2b**·TCNQ and **1a**·TCNQ is one. The reason of the discrepancy between the estimated values and the formal charge is not clear at this stage, but the H-bonding interaction between NH of the amino group and N of the nitrile group might reduce the ionicity to a some extent. We observed a broad absorption band around 3300 cm^{-1}, which can be assigned to the intra band CT transition in the TCNQ column with a partial ionicity.[13] The preliminary measurement of the electrical conductivity for a single crystal of the complex **2b**·TCNQ gave 90 Scm^{-1} with metallic behavior around room temperature and semi-conducting behavior below 200 K with the activation energy of 79 meV. Such a highly conducting behavior is consistent with the partial ionicity estimated and the existence of the intra-band CT transition.

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References and Notes

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8 All new compounds described in this report gave satisfactory elemental analyses.
2a: IR (KBr pellet): 3378, 2196, 1654, 1345 cm^{-1}, λ_{max} (KBr pellet): 361, 612, 997 nm. **2b**: IR (KBr pellet): 3364, 2195, 1634, 1346 cm^{-1}, λ_{max} (KBr pellet): 361, 609, 852 nm. **2c**: IR (KBr pellet): 3363, 2197, 1636, 1345 cm^{-1}, λ_{max} (KBr pellet): 359, 606 nm.

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11 **5a**, Anal. Found: C, 28.00; H, 4.10; N, 32.48%. Calcd for $C_8H_{14}N_8O_4Ni$: C, 27.86; H, 4.09; N, 32.48%; **2b**·TCNQ, Anal. Found: C, 41.97; H, 3.20; N, 28.11%. Calcd for $C_{20}H_{19}N_{12}O_4Pd$: C, 40.18; H, 3.21; N, 28.25%

12 Crystal data: for **5a**, $C_8H_{14}N_8O_4Ni$, monoclinic, $P2_1/c$, $a = 7.769(2)$, $b = 9.8642(2)$, $c = 8.597(3)$ Å, $\beta = 110.51(1)$ °, $V = 617.1(3)$ Å^3, $Z = 2$, $R = 0.032$, $Rw = 0.030$, D(calcd) = 1.856 Mg m^3. for **2b**·TCNQ, $C_{20}H_{19}N_{12}O_4Pd$, triclinic, $P\bar{1}$, $a = 7.051(1)$, $b = 20.275(5)$, $c = 3.883(1)$ Å, $\alpha = 94.09(2)$, $\beta = 92.38(2)$, $\gamma = 98.91(2)$ °, $V = 546.3(2)$ Å^3, $Z = 1$, $R = 0.056$, $Rw = 0.093$, D(calcd) = 1.817 Mg m^3.

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