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Assembly of a 1D Coordination Polymer through in Situ Formation of a New Ligand by Double C−C Coupling on $CHCl_3$ under Solvothermal Conditions

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A rare in situ metal/ligand reaction has been observed during the assembly of a maganese-coordination polymer under solvothermal conditions, which leads to double C−C coupling on $CHCl_3$ involving cleavage of three C−Cl bonds and the formation of two new C−C bonds at the same carbon center.

Solvothermal synthesis has evolved as a widely used method in the fields of nanostructures, crystal engineering, coordination polymers, and so forth. Besides the advantage of being easily accessible to the hardly soluble metal−organic frameworks, solvothermal conditions often facilitate in situ metal/ligand reactions, which, in contrast to conventional organic syntheses, are featured in either a simple one-pot reaction or the in situ formation of organic ligands.[1] A variety of in situ metal/ligand reactions, such as the hydroxylation of aromatic rings, decarboxylation of arene carboxylates, cycloaddition of organic nitriles with azide or ammonia, cleavage of C−C, C−N, C−O, and S−S bonds, etc., have already been reported in solvothermal syntheses of coordination compounds.[2] In addition, the metal redox behaviors have often been observed under solvothermal conditions, which may play important roles in activating the precursors or catalyzing a specific organic reaction.[1]

The C−C bond formation under solvothermal conditions has also long been known. Since the observation of oxidative coupling on CH_3OH to form oxalic acid in the preparation of zinc($^{2+}$) oxalate 1D chains, several examples of in situ dehydrogenative C−C coupling have been reported in solvothermal syntheses of coordination polymers,[3] although the detailed C−C coupling mechanism was not completely understood because of unusual conditions generated by the black-box-like solvothermal reactions, which are hard to monitor.[1] Herein, we report the assembly of a 1D Mn^{3+}-coordination polymer under solvothermal conditions through a series of unusual in situ metal/ligand reactions with a pyridyl-substituted naphthalenediimide **1**, where mono- and di-N-methylated compounds (**2** and **3**) and a new ligand **4** were generated (Scheme 1). The ligand **4** is formed by double C−C coupling on $CHCl_3$, leading to cleavage of three C−Cl bonds and the formation of two new C−C bonds at the same carbon center. Such a transformation, to the best of our knowledge, represents an unprecedented double alkyl−alkyl coupling on poly(chloroalkane).[4]

The original ligand, *N*,*N*′-bis(4-pyridylmethyl)naphthalenediimide (**1**), was prepared from the reaction of 1,4,5,8-naphthalenedianhydride with 4-(aminomethyl)pyridine (see the Supporting Information). The molecular structure of **1** has been identified by single-crystal X-ray analysis[5] and ^1H NMR measurement (Figure S1 in the Supporting Information) of its cocrystal $\mathbf{1}\cdot CH_3OH$. The reaction of **1** with $Mn(CF_3CO_2)\cdot 2H_2O$ and NaSCN in a $CH_3OH-CHCl_3$ mixture (1:13, v/v) under solvothermal conditions afforded red crystals along with massive yellow solids. The red crystal was characterized by single-crystal diffraction[6] as a 1D

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(5) Crystal data for $\mathbf{1}\cdot CH_3OH$: $C_{27}H_{20}N_4O5$, M_r = 480.47, monoclinic, space group $C2/c$, a = 21.2761(4) Å, b = 4.8975(2) Å, c = 21.3259(5) Å, β = 97.045(2)°, V = 2205.38(11) $Å^3$, Z = 4, D_{calcd} = 1.447 g/cm^3, μ = 0.844 mm^{-1}, T = 150(2) K, 1502 unique reflections out of 3065 with $I > 2\sigma(I)$ (R_{int} = 0.0159), 172 parameters, final R1 = 0.0374, wR2 = 0.0967. CCDC 725179.

(6) Crystal data for $\{[Mn(NCS)_4\cdot(\mathbf{4})]\cdot 2.5H_2O\}_n$: $C_{118}H_{80}Mn_2N_{24}O_{21}S_8$, M_r = 2536.42, monoclinic, space group $C2/c$, a = 27.2244(4) Å, b = 13.8402(3) Å, c = 15.5301(3) Å, β = 91.498(2)°, V = 5849.60(19) $Å^3$, Z = 2, D_{calcd} = 1.440 g/cm^3, μ = 3.766 mm^{-1}, T = 150(2) K, 4254 unique reflections out of 8952 with $I > 2\sigma(I)$ (R_{int} = 0.0223), 408 parameters, final R1 = 0.0846, wR2 = 0.2008. CCDC 725181.

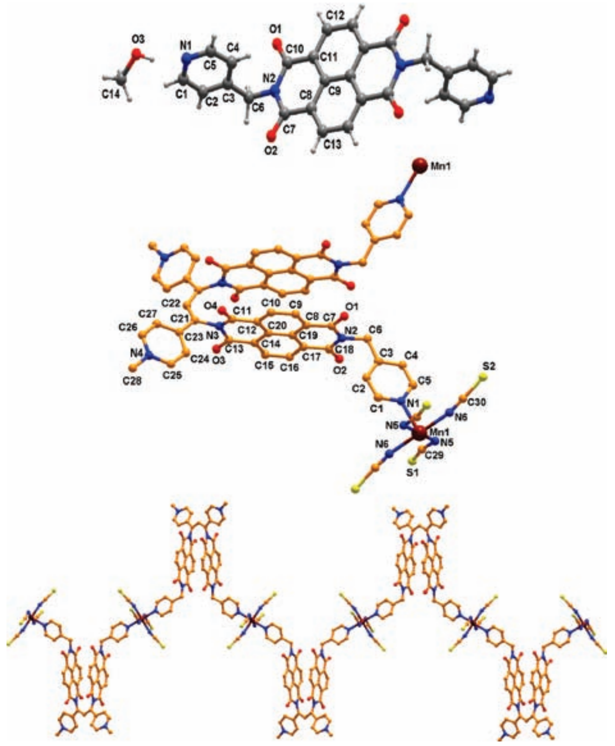
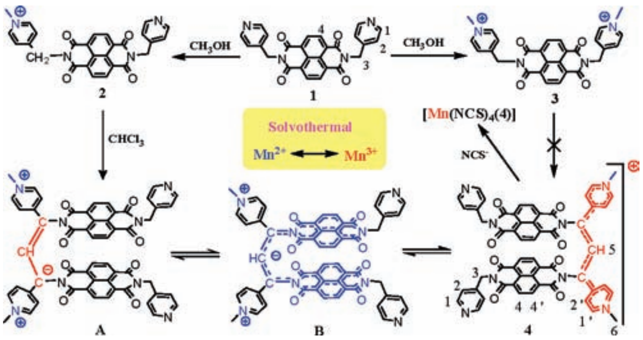


Figure 1. Structures of the $\mathbf{1}\cdot CH_3OH$ adduct (upper), the [Mn(NCS)$_4$(**4**)] motif (middle), and a 1D chain in complex $[Mn(NCS)_4(\mathbf{4})]\cdot 2.5H_2O$. The asymmetric units are labeled with the atomic scheme.

Scheme 1. Procedures for the Formation of Compounds **2** and **3** and Complex [Mn(NSC)$_4$(**4**)] from **1** by Solvothermal in Situ Metal/Ligand Reactions



coordination polymer, namely, $\{[Mn(NCS)_4(\mathbf{4})]\cdot 2.5H_2O\}_n$, in which the new ligand **4** was formed apparently via a metal/ligand in situ reaction and further characterized by electron spray ionization mass spectroscopy (ESI-MS) and ^1H NMR (Figures S1−S3 in the Supporting Information). Moreover, the yellow solid byproducts were verified by ESI-MS to contain **1** and its di-N-methylated **3** (Figure S3c in the Supporting Information), while the mother liquid contains **1** and the monomethylated **2** (Figure S3b in the Supporting Information).

Single-crystal structural analysis of the $\mathbf{1}\cdot CH_3OH$ adduct discloses a centrosymmetric molecule of **1** as shown in Figure 1. Two pyridyl (Py) groups take on a trans conformation on the two sides of the planar naphthalenediimide ring, imposing an inversion center in the middle of naphthalene ring, in accordance with the ^1H NMR results.

To our surprise, single-crystal X-ray analysis of the red crystal turned out an infinite 1D zigzag chain structure containing an unexpected new ligand **4**. The asymmetric unit consists of half of a Mn^{3+} ion, half of a **4** molecule, two SCN^- anions, and 1.25 water molecules, leading to a composition of $[Mn(NCS)_4(\mathbf{4})]\cdot 2.5H_2O$. As seen from Figure 1, the Mn^{3+} ion lies on an inversion center, displaying a distorted MnN_6 octahedral geometry binding four thiocyanates and two **4** molecules. The newly formed ligand **4** can be regarded as two monomethylated **2** molecules coupled by a carbon atom (C22) through the formation of two C−C bonds. That is, the original ligand **1** was mono-N-methylated to give molecule **2**, and then two **2** molecules were joined by double C−C coupling on $CHCl_3$ with full cleavage of the C−Cl bonds (vide infra). The C−C coupling took place on the methylene carbon atom, which connects the Py ring with N-methylation, while on the other side, another Py ring remained unmethylated, making **4** a bis-monodentate ligand that linked Mn^{3+} ions alternately to result in the 1D coordination polymer (Figures 1 and S4 in the Supporting Information).

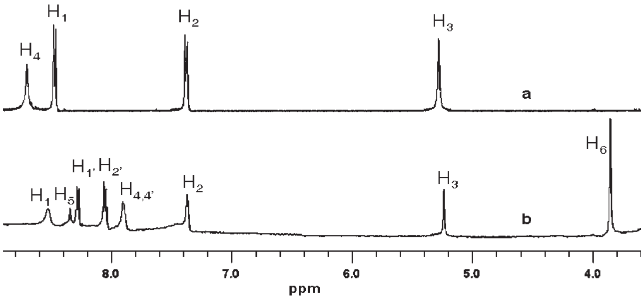


Figure 2. ^1H NMR spectra of (a) **1** and (b) [Mn(NCS)$_4$(**4**)] in DMSO-d_6.

It is noticeable that the C22−C21 bond distance [1.381(6) Å] is between the normal single C−C (1.541 Å) and double C=C (1.331 Å) bond lengths, the C21−C23 [1.432(8) Å] bond is significantly shorter than the corresponding C3−C6 single bond [1.504(8) Å] connecting the unmethylated Py ring, and C21, C22, C23, and N3 atoms are nearly coplanar. This structural information convincingly denotes that the C21 and C22 atoms are sp^2-hybridized, indicative of a conjugated structure. Because a crystallographically imposed C_2 axis passes through the middle C22 atom, the corresponding bond distances of the two coupled parts are averaged, which prevents us from the exact determination of the bond order among the C23−C21−C22−C22i−C23i (symmetry code i: $-x$, y, $^3/_2 - z$) fragment. Furthermore, the molecule **4** takes on a folded conformation with two naphthalenediimide cores aligned face-to-face, forming intramolecular $\pi-\pi$ interactions (3.52 Å).

To further characterize ligand **4**, ESI-MS and ^1H NMR measurements were carried out in dimethyl sulfoxide (DMSO) for complex [Mn(NCS)$_4$(**4**)]. The MS spectra (Figure S2a in the Supporting Information) display a sole peak at m/z 935.3, undoubtedly certifying **4** as an uncharged molecule, which has been verified by simulation of the isotopic distribution. No Mn^{3+}-related species were detected, indicating that the complex dissociates in solution. The NMR spectra disclose that two groups of equivalent H_{Py} signals (H_1, H_2) in **1** become nonequivalent (H_1, H_2 and $H_{1'}$, $H_{2'}$) in **4**, as shown in Figures 2 and S1c in the Supporting Information. The H_1 and H_2 signals on the unmethylated Py ring become broadened with a slight downfield shift of the H_1 signal, denoting manganese−ligand interaction, although the complex falls apart in DMSO. On the contrary, the $H_{1'}$ and

$H_{2'}$ signals on the methylated Py ring are getting closer and well-resolved, suggesting electron delocalization due to conjugation. In addition, proton signals attributable to the bridging carbon C22 (H_5), naphthalene ring (H_4, $H_{4'}$), and methylene (H_3) and methyl (H_6) groups were all detected, and the assignment of all of the proton signals can be well confirmed by the 2D H−H COSY NMR measurement (Figure S2 in the Supporting Information). Even more informative, a large upfield shift was observed for naphthalene protons (H_4, $H_{4'}$, 0.8 ppm), clearly suggesting a folded conformation of **4** to shield protons under the ring current. These results support a conjugating structure of **4** possessing C_2 symmetry, well in agreement with the ESI-MS and X-ray diffraction analyses.

On the basis of the above structural and spectroscopic results, the formation procedures of complex [Mn(NCS)$_4$(**4**)] and the molecular structure of the in situ generated ligand **4** may be proposed as shown in Scheme 1. N-Methylation is believed to take place on the Py rings of **1** at first to afford **2** and **3**. This is confirmed by detection of the monomethylated **2** in the mother liquid and the dimethylated **3** in the solid byproducts. Methylation of the Py ring in CH_3OH under solvothermal conditions is also well-known in the literature.[7] Afterward, the partially methylated **2** may be selectively activated in the presence of Mn^{2+}/Mn^{3+} redox under solvothermal conditions, resulting in double C−C coupling on $CHCl_3$ to lead to the formation of **4**. Metal redox conversion represents a common phenomenon in solvothermal in situ metal/ligand reactions,[1] and oxidation of Mn^{2+} is evident by the deep-red color of both the mother liquid and the crystal products. To confirm the origin of the coupling carbon atom, comparison experiments were carried out under similar reaction conditions in CH_3OH, $CHCl_3$, and a $CH_3OH-CH_2Cl_2$ mixture separately. The formation of **4** cannot be detected by ESI-MS in any cases, and monomethylated **2** was the only detectable product in the last case. These results imply that both CH_3OH and $CHCl_3$ are essential for the transformation from **1** to **4**, where N-methylation originated from CH_3OH and $CHCl_3$ is responsible for the C−C coupling.

The molecular structure of **4** is intriguing. Di-N-methylation in **4** should give two *N*-methylpyridinium cations, while ESI-MS is indicative of a positively uncharged molecule. Because the single-crystal structure confirms that the C21 and C22 atoms are sp^2-hybridized, it is reasonable to expect a negative charge locating around the C21−C22−C22i fragment. Such speculation is supported by the literature finding that N-substituted naphthalenediimide can form a stable radical anion and the radical anion can delocalize over the core naphthalene extendable into the hydrocarbon substituents.[8] Therefore, the molecular structure of **4** may be presented in the extreme form A or tautomeric form B with anion delocalization,[8] as shown in Scheme 1. On the other hand, because the structural and spectroscopic analyses indicate a large-scale conjugation along the Py−C23−C21−C22−C22i−C23i−Py fragment, an overall uncharged form **4** may be simply depicted.

We are currently carrying out further investigations on the detailed C−C coupling mechanism and molecular nature of **4**; nevertheless, a radical-based reaction pathway may be expected on the basis of the following facts: (a) $CHCl_3$ has been well-known to be able to produce radical species easily at elevated temperature,[9] (b) Mn^{3+} has been proven to be apt to induce free-radical reactions,[10] (c) N-substituted naphthalenediimide can form a stable radical anion at modest potentials,[8] and (d) many metal-catalyzed coupling reactions of poly(chloroalkane)s have been reported to proceed via the radical pathway.[4,11] In addition, a comparable reaction involving full cleavage of the C−Cl bonds and alkylation of CH_2Cl_2 and $CHCl_3$ catalyzed by a nickel complex has been reported recently,[4a] where a radical process was proposed.

In summary, we have observed an intriguing metal/ligand in situ reaction system where a series of unusual reactions, including C−H activation, C−Cl bond cleavage, C−C bond coupling, and pyridyl N-methylation, occur. The in situ generated ligand has been identified by ESI-MS and NMR spectroscopy, as well as its mangaese-coordination polymer single-crystal structure. A radical reaction pathway has been proposed for the double C−C coupling on $CHCl_3$, which leads to an unprecedented C−C bond formation possibly catalyzed by Mn^{2+}/Mn^{3+} redox. Although solvothermal reactions may lack precise control and prediction, the observation of such a transformation gives a hint to exploring alternative approaches to alkyl−alkyl coupling by using cheap poly(chloroalkane)s.

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Supporting Information Available: Synthesis details, ^1H NMR and ESI-MS spectra, and crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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