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Communication

Chemistry of tetracyanoethylene (TCNE): From TCNE to dicyanomethylacetate

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Abstract

In the presence of $CoCl_2 \cdot 6H_2O$, the reaction of TCNE (tetracyanoethylene) with CH_3OH forms a dicyanomethylacetate molecule, which has been obtained as one solvent molecule in one new compound $\{[Co(bpy)_2CN_2][(NC)_2C\text{–}CO_2CH_3]\} \cdot 2H_2O$ (**1**). It was characterized by IR spectra, UV–Vis spectra, and cyclic voltammogram. Its structure was determined by X-ray crystallography: **1** crystallizes in $P2(1)/n$ with $a = 13.3368(17)$, $b = 12.5299(16)$, $c = 16.074(2)$ Å, $\alpha = 90$, $\beta = 94.6320(10)$, $\gamma = 90°$, and $Z = 2$.

Keywords: N-ligand; Crystal structure; Co complex; Dicyanomethylacetate

1. Introduction

Tetracyanoethylene (TCNE) molecule is one of the most versatile organic compounds as it is used in many different reactions [1], due to its very low-lying π^* orbital. TCNE reacts with water in neutral solution to form tricyanoethanolate anion, $[C_2(CN)_3O]^-$ [2]. In the presence of a metal ion, 2,3,3-tricyanocrylamidate, $[(NC)_2C{=}C(CN)(CONH)]^-$, can be formed from TCNE [3]. On the other hand, the ability to accept one or two electrons to form simple anions in conjunction with its ability to bond to as many as four metal ions, leads to the formation of mixed-valence complexes; the reaction of radicals TCNE in conjunction with paramagnetic transition metal ions has produced some of the most remarkable molecular magnetic materials [4,5], such as ferromagnetic $(TCNE^{\cdot -})[Fe(C_5Me_5)_2]$ [6], or $(TCNE^{\cdot -})_2V$, an organometallic ferrimagnet active beyond room temperature (T_c ca. 400 K) [7]. Recently, one new organic-based magnet $[Fe(TCNE)_2] \cdot zCH_2Cl_2$ ($T_c = 100$ K) was prepared by the reaction of TCNE and FeI_2 [8], which has the NC–C–CN bond angle of 121(1)° in accord with its sp^2 central carbon atom. Our interest focus on the reactivity of TCNE and electron-rich metal complexes to form discrete as well as polymeric charge-transfer compounds in which the donors and acceptors are coordinated through nitrile positions. With this mind, we have tried the reaction of TCNE, $CoCl_2 \cdot 6H_2O$, and bpy (2,2-bipyridine) with a molar ratio set of 1:1:2 in methanol, surprisingly, an novel product **1** $\{[Co(bpy)_2CN_2][(NC)_2C\text{–}CO_2CH_3]\} \cdot 2H_2O$ is obtained. In this work, we describe an unusual reaction of TCNE, and CH_3OH, as well as the structure, and properties of compound **1**.

2. Results and discussions

2.1. Synthesis and general properties

Considering the typically similar reactivity of the TCNE molecule with paramagnetic transition metal centers, the reaction of TCNE ligand, $CoCl_2 \cdot 6H_2O$ and bpy in methanol provided an unexpectedly different result. In the presence of H_2O, TCNE reacts with $CoCl_2 \cdot 6H_2O$ and bpy in CH_3OH solvent to give a novel compound **1** containing

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one $[Co(CN)_2(bpy)_2]$ unit, one dicyanomethylacetate molecule, and two water molecules. To our knowledge, this is the first example of the synthesis of dicyanomethylacetate from TCNE.

The possible mechanism of the formation of dicyanomethylacetate is illustrated by Scheme 1. The reduction of TCNE by $CoCl_2 \cdot 6H_2O$ forms its anion, $[TCNE]^-$ (**A**). In the presence of H_2O, $[TCNE]^-$ lost two CN^- groups, which were transferred to the Co center and gave an active intermediate **B**. Furthermore, **B** reacts with CH_3OH at mild condition to provide a dicyanomethylacetate molecule $[(NC)_2C–CO_2CH_3]$. Meanwhile, the reaction of $CoCl_2 \cdot 6H_2O$, CN– from TCNE, and bpy provided a complex $[Co(CN)_2(bpy)_2]$.

The infrared spectrum of **1** shows two $\nu(C{\equiv}N)$ stretches at 2192 and 2160 cm^{-1} at lower energies than free TCNE (2255, and 2216 cm^{-1}), assigning to two different cyanide modes of **1**. It is also noteworthy that two sharp features that appear at 1654, 1606 and 1111 cm^{-1} are assigned to the stretching of the hydrolyzed TCNE molecule $([(NC)_2C–CO_2CH_3])$.

The absorption spectrum of compound **1** is shown in Fig. 1, the two longwavelength absorption bands (393 and 414 nm) can be attributed to an intra-ligand transition of dicyanomethylacetate, which are similar to that of TCNE (see supporting information).

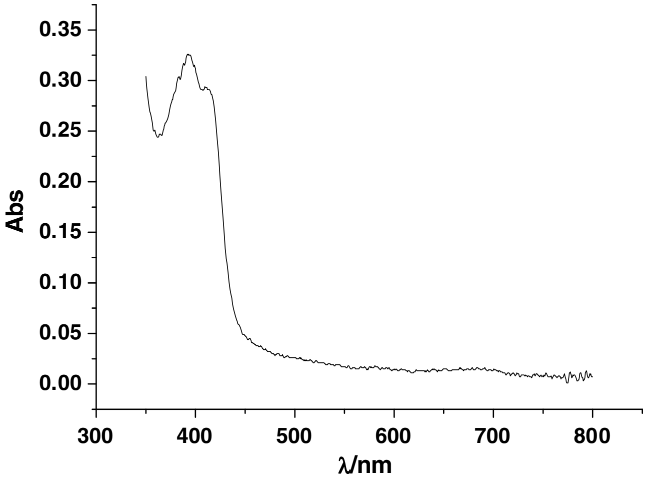
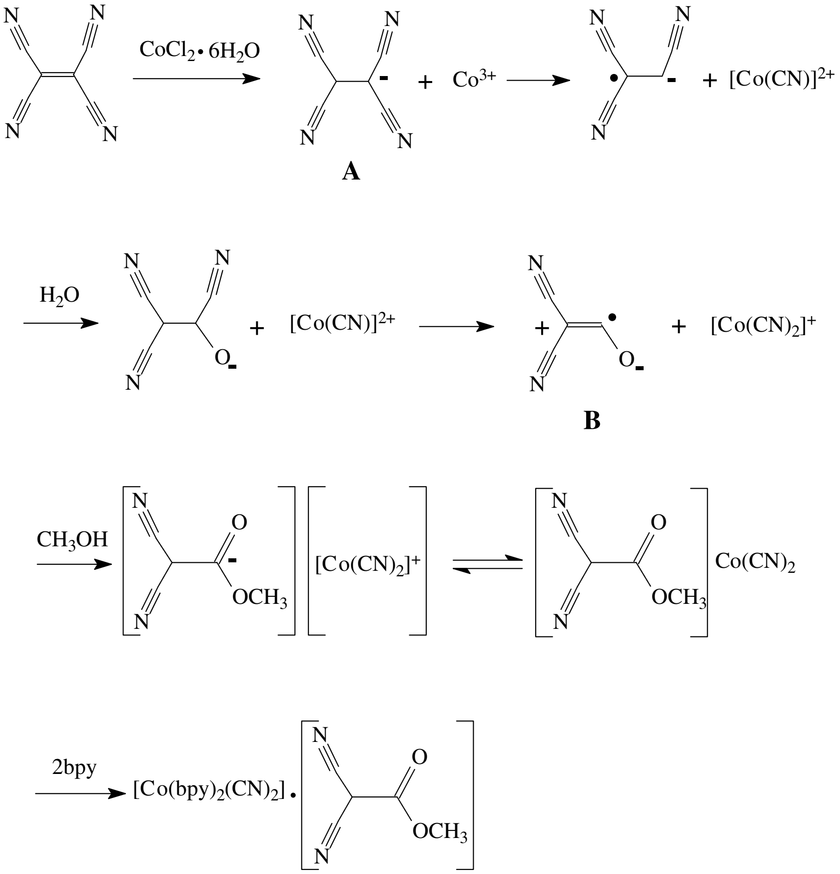


Fig. 1. Absorption spectrum of **1** in CH_3CN.

2.2. Structure of compound 1

The compound **1** crystallizes in space group *P*2(1)/*n*, with two formula units present per unit cell. As shown in Figs. 2 and 3, compound **1** consists of one $[Co(CN)_2(bpy)_2]$ unit, one dicyanomethylacetate molecule, and two H_2O molecules.



Scheme 1.