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 $\{[Co(bpy)_2CN_2][(NC)_2C–CO_2CH_3]\} \cdot 2H_2O$ (**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 $Z = 2$.
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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** $\{[Co(bpy)_2CN_2][(NC)_2C–CO_2CH_3] \cdot 2H_2O$ 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$_2$O forms its anion, [TCNE]$^-$ (**A**). In the presence of H$_2$O, [TCNE]$^-$ lost two CN$^-$ groups, which were transferred to the Co center and gave an active intermediate **B**. Furthermore, **B** reacts with CH$_3$OH at mild condition to provide a dicyanomethylacetate molecule [(NC)$_2$C–CO$_2$CH$_3$]. Meanwhile, the reaction of CoCl$_2 \cdot$ 6H$_2$O, CN– from TCNE, and bpy provided a complex [Co(CN)$_2$(bpy)$_2$].

The infrared spectrum of **1** shows two ν(C≡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)$_2$C–CO$_2$CH$_3$]).

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).
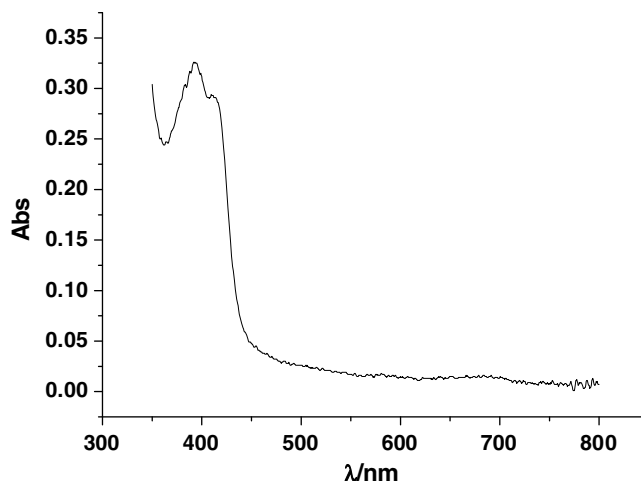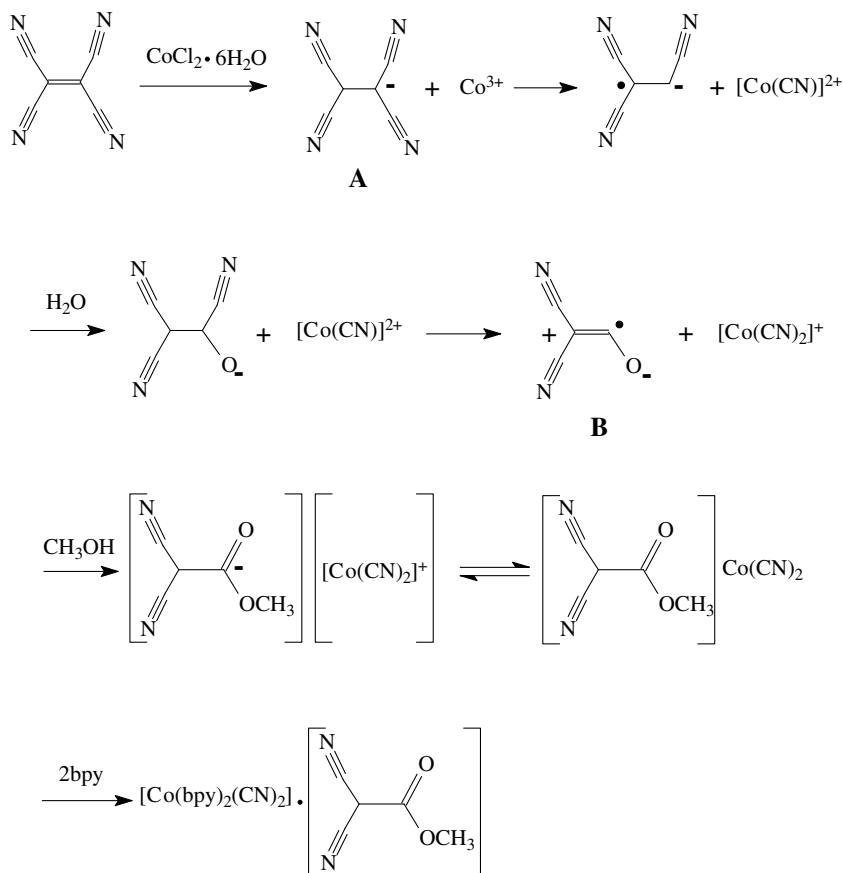

Fig. 1. Absorption spectrum of **1** in CH$_3$CN.

2.2. Structure of compound **1**

The compound **1** crystallizes in space group $P2(1)/n$, 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$_2$O molecules.

Scheme 1.

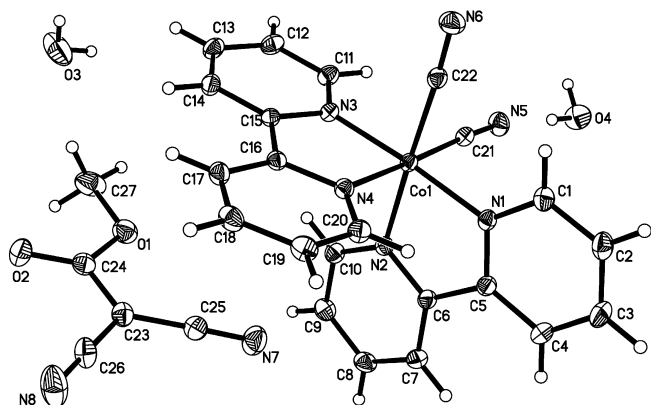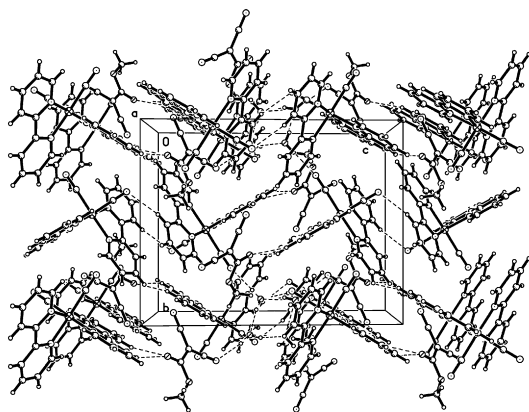Fig. 2. The ORTEP view of **1** {[Co(bpy)$_2$CN$_2$][(NC)$_2$C–CO$_2$CH$_3$]} · 2H$_2$O.

Fig. 3. Crystal packing diagram of compound **1**.

The C≡N distances do not show any significant changes, which range from 1.146(2) to 1.154(3) Å. The average C–CN distance of 1.403(3) Å is 0.032 Å shorter than that observed for the free TCNE (1.435 Å). Dicyanomethylacetate has the NC–C–CN bond angle of 117.74(18)°, which is similar to the observed NC–C–CN angles of the free TCNE (116.5(12)°) in accord with its sp^2 central carbon atom [2b].

For Co complex unit, the cobalt atom is surrounded nearly octahedral by four nitrogen atoms from the bpy ligands and two carbon atoms of the cyano groups, which are in *cis* positions.

2.3. Electrochemical properties

The free TCNE molecule undergoes two reversible one-electron reductions at −0.95 and 0.22 V vs. the saturated calomel electrode (SCE) in CH$_3$CN [1], which is in accord with reversible two-step reductions. The title compound **1** exhibits a reversible one-electron redox process at 0.04 V, which is assigned to that of Co^{3+}/Co^{2+} redox couple and two irreversible oxidation processes at 0.26 and 0.61 V, assigning to that of bpy and dicyanomethylacetate (Fig. 4).

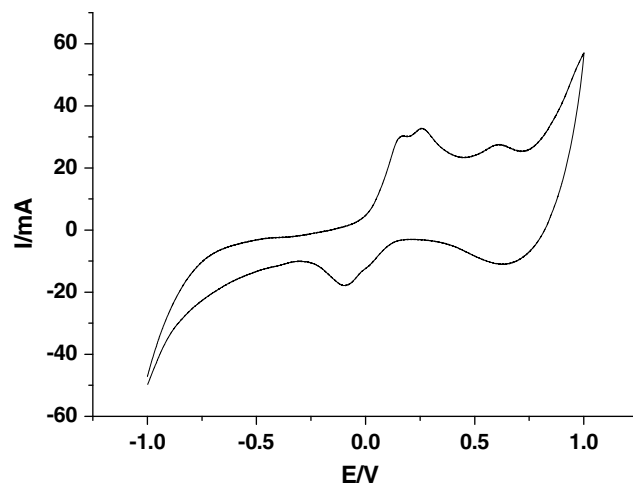Fig. 4. Cyclic voltammogram of **1** in CH$_3$CN/0.1 M Bu$_4$ClO$_4$ at 100 mV s^{-1} scan rate.

3. Experimental

CoCl$_2$ · 6H$_2$O, bpy and TCNE were purchased from commercial sources and used as received.

3.1. Physical measurements

Infrared spectrum was recorded (in the 4000–400 cm^{-1}) as KBr disks on a Bruker 1600 FTIR spectrometer. Electronic spectra were recorded on a Hitachi U-3010 (UV–Vis) spectrophotometer for the solution in CH$_3$CN. Electrochemical experiments were carried out with an Auto Lab Instrument with a Platinum wire working electrode, a platinum plate counter electrode, and a standard calomel electrode (SCE) as the reference electrode. For the experiments performed in CH$_3$CN as solvent (ca. 1.2 × 10^{-4} mol L^{-1}) containing in 0.1 mol L^{-1} tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte, the potentials were referenced to an SCE electrode.

3.2. Synthesis of compound **1**

All synthetic procedures were performed anaerobically. After addition of TCNE (0.13 g, 1 mmol) in methanol (20 mL) to the solution containing CoCl$_2$ · 6H$_2$O (0.238 g, 1 mmol) and bpy (0.31 g, 2 mmol) in methanol (20 mL), the mixture was stirred at room temperature for 1 h. The solution color turned from red to deep yellow. Single crystals were obtained from the filtrate which was allowed to stand at room temperature for several days, collected by filtration, and dried *in vacuo* (0.212 g, 36.4%). Anal. Calc. for C$_{54}$H$_{42}$Co$_2$N$_{16}$O$_6$: C, 57.4; H, 3.72; N, 19.84. Found: C, 57.85; H, 3.73; N, 19.73%. IR bands (KBr pellets, cm^{-1}): v = 2192 (m), 2160 (s) (v(C≡N)); v = 1654 (s), 1606 (s) (v(–CO$_2^-$)); v = 1111 (s) (v(–C–O–C)); [CH$_3$CN, λ_{max}/nm (ϵ/L mol^{-1} cm^{-1})]: 232 (6.5 × 10^4), 305 (2.5 × 10^4), 393 (460), 414 (409).

3.3. X-ray crystallography

Data were collected with a Bruker SMART CCD area detector using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. All empirical absorption corrections were applied by using the SADABS program [9]. The structures were solved using direct methods and the corresponding non-hydrogen atoms were refined anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system of computer program [10]. Details of the crystal parameters, data collection and refinement for compound **1** are listed in Table 1, and selected bond distances and angles are given in Table 2.

4. Conclusions

In the presence of $CoCl_2 \cdot 6H_2O$, TCNE reacts with CH_3OH to give a dicyanomethylacetate molecule, which is the first example from TCNE. The reactivity of TCNE with other metal centers, for example, nickel and iron complexes are being under further investigation.

Appendix A. Supplementary material

CCDC 662604 contains the supplementary crystallographic data for **1**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.01.044.

Table 1
Crystallographic data for **1**

1	
Empirical formula	$C_{54}H_{46}Co_2N_{16}O_8$
Formula weight	1164.93
λ (Å)	0.71073 Å
Crystal system	Monoclinic
Space group	$P2(1)/n$
a (Å)	13.3368(17)
b (Å)	12.5299(16)
c (Å)	16.074(2)
α (°)	90
β (°)	94.6320(10)
γ (°)	90
V (Å^3)	2677.3(6)
Z	2
D_{calc} (Mg m^{-3})	1.445
$F(000)$	1200
θ Range for data collection (°)	2.51–25.50
Reflections collected/unique	19894/4981
Maximum and minimum transmission	0.7418 and 0.7328
Data/restraints/parameters	4981/0/362
Goodness-of-fit on F^2	1.036
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0270$, $wR_2 = 0.0694$
R indices (all data)	$R_1 = 0.0325$, $wR_2 = 0.0731$

Table 2
Selected bond distances (Å) and angles (°) for complex **1**

Bond distances (Å)			
Co(1)–C(21)	1.8846(17)	Co(1)–C(22)	1.8875(17)
Co(1)–N(1)	1.9352(13)	Co(1)–N(3)	1.9356(13)
Co(1)–N(4)	1.9702(13)	Co(1)–N(2)	1.9745(13)
O(1)–C(24)	1.361(2)	O(1)–C(27)	1.450(3)
O(2)–C(24)	1.213(2)	N(5)–C(21)	1.146(2)
N(6)–C(22)	1.148(2)	N(7)–C(25)	1.149(2)
N(8)–C(26)	1.154(3)	C(23)–C(26)	1.404(3)
C(23)–C(25)	1.406(3)	C(23)–C(24)	1.432(3)

Bond Angles (°)			
C(21)–Co(1)–C(22)	88.16(7)	C(24)–O(1)–C(27)	114.99(18)
N(5)–C(21)–Co(1)	176.76(15)	N(6)–C(22)–Co(1)	176.68(16)
C(26)–C(23)–C(25)	117.74(18)	C(26)–C(23)–C(24)	118.74(17)
C(25)–C(23)–C(24)	123.47(17)	O(2)–C(24)–O(1)	122.27(19)
O(2)–C(24)–C(23)	124.98(19)	O(1)–C(24)–C(23)	112.74(16)
N(7)–C(25)–C(23)	177.7(2)	N(8)–C(26)–C(23)	179.0(2).

Symmetry transformations used to generate equivalent atoms: x, y, z; $-x + 1/2$, $y + 1/2$, $-z + 1/2$; $-x$, $-y$, $-z$; $x - 1/2$, $-y - 1/2$, $z - 1/2$.

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