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LETTER

The preparation of $[Cu^{2+}(TCNE^{2-})]_n$ and its ligand-induced intramolecular electron transfers

Antal Rockenbauer
Central Research Institute for Chemistry of the Hungarian Academy of Sciences, 1335 Budapest (Hungary)

Gábor Speier*
Department of Organic Chemistry, University of Veszprém, 8201 Veszprém (Hungary)

and Lajos Szabó
Research Group for Petrochemistry of the Hungarian Academy of Sciences, 8201 Veszprém (Hungary)

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Abstract

The study of coordination compounds of tetracyanoethylene (TCNE) and related redox-active molecules has been the subject of much interest recently in relation to the development of materials with unusual electronic and magnetic properties [1–5]. The chemistry of copper tetracyanoethylene compounds is rather poor and only very limited data are available in the literature. The reaction of TCNE with copper powder was claimed to give $[Cu^+(TCNE^-)]$ in good yield [6]. We have found that in the reaction of Cu^0 with TCNE in pyridine C–CN bond rupture occurs and $[CuCN(py)_2]_n$ could be isolated and characterized by X-ray analysis along with a polymeric organic material [7]. In the course of our studies of metallic copper with TCNE we reinvestigated the reaction of Cu^0 with TCNE, also in the presence of different ligands.

Experimental

Preparation of $[Cu^{2+}(TCNE^{2-})]_n$ *(1)*

Tetracyanoethylene (0.526 g, 4.1 mmol) and copper turnings (4.1 g) were stirred in acetonitrile (15 ml) under argon at room temperature for 8 h. The precipitated black-colored powder was filtered off and the remaining copper turnings separated manually, washed two times with ether (3 ml) and dried in vacuum to give $[Cu^{2+}(TCNE^{2-})]_n$ (**1**) (0.658 g, 84%). IR (Nujol): ν(CN) 2210 and 2162 cm^{-1}. $\mu_{eff}=1.59$ BM. *Anal.* Found: C, 38.0; N, 28.9; Cu, 35.3. Calc. for C_6N_4Cu: C, 37.6; N, 29.2; Cu, 33.2%.

ESR measurements

ESR measurements were carried out with a JEOL JES-ME/3X spectrometer at room temperature. **1** was reacted with the corresponding ligands (ligand to copper ratio 2:1) in toluene and then sealed under argon in glass capillaries.

Results and discussion

In order to study the solvent dependence of the electron transfer reaction from Cu^0 to tetracyanoethylene (TCNE) and the ability of C–CN bond cleavage by metallic copper, as a continuation of our investigations of TCNE coordination chemistry, we changed the solvent from pyridine to acetonitrile. The reaction of Cu^0 with TCNE in acetonitrile proceeded well with the smooth precipitation of a black deposit (**1**). Elemental analysis and IR data showed **1** to be identical with that found by Webster *et al.* formulated as $[Cu^+(TCNE^-)]$ [6]. The magnetic properties of **1** show a magnetic moment somewhat below the spin only value of one unpaired electron signalizing intramolecular magnetic coupling, and the low solubility in acetonitrile suggests a possible polymeric structure.

The solid state ESR spectrum of **1** (Fig. 1) consists of an intensive broad singlet (linewidth 720 G, $g=2.006$) and a weak narrow singlet (linewidth 10 G, $g=2.003$). The broad singlet can be assigned to exchange coupled Cu(II) ions, while the narrow singlet shows the presence of a trace amount of radical anion. That means that under the conditions $TCNE^{2-}$ is readily formed via a two-electron transfer from Cu^0 to TCNE. The favorable coordination environment of **1** stabilizes the Cu(II) oxidation state and the high insolubility of **1** might contribute an additional driving force for the second, uneasy reduction step. Upon dissolution of **1** in acetonitrile the well resolved pattern of the $TCNE^-$ radical anion appears ($g=2.0026$, $a_{4N}=1.59$ G) [8]. Clearly in that case the TCNE radical anion is not coordinated to the copper. The EPR feature of **1** in pyridine was identical. Moreover, toluene solutions of **1** in the presence of ligands such as tetramethylethylenediamine, 2,2′-bipyridine or bis(diphenylphosphino)ethane showed the characteristic 9-line spectrum of uncoordinated $TCNE^-$ [8]. The toluene solution of **1**, if a large surplus of triphenylphosphine is also present, gives a multi-line EPR spectrum ($g=2.0026$, $a_{Cu}=1.6$ G, $a_{2P}=3.2$ G, $a_N=2.8$ G, $a_N=1.2$ G, $a_{2N'}=1.6$ G) (Fig.

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*Author to whom correspondence should be addressed.

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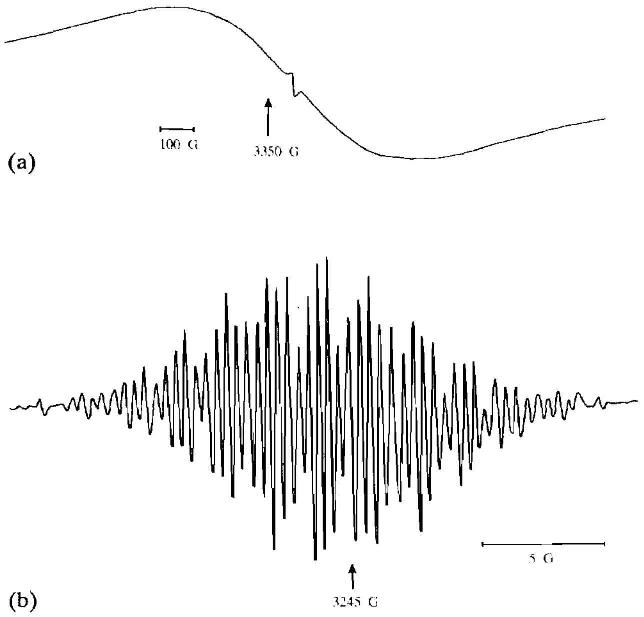
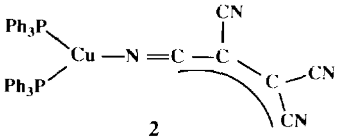


Fig. 1. The solid state EPR spectrum of compound **1** in toluene (a) and in the presence of excess triphenylphosphine at room temperature (b).

1). The nitrogen hfs couplings indicate the formation of the iminotricyanoallyl radical [9] coordinated to Cu(II), where the latter is also coordinated further to two PPh_3 molecules (**2**). If the molar ratio of PPh_3 and **1** is 2:1, the toluene solution gives a superimposed EPR signal. In the center of the spectrum the well resolved peaks of **2** can be seen, but on the wings additional equidistant lines appear. This new signal can be interpreted by assuming one phosphorous coupling ($a_P = 8.0$ G), one copper coupling ($a_{Cu} = 4.8$ G) and four equivalent nitrogen couplings ($a_{4N} = 1.6$ G). The signal can be assigned to the radical **3** where the Cu(II) ion is coordinated to one PPh_3 and one TCNE, but the latter ligand coordinates with two nitrogen donors to the metal. The variation of EPR spectra as a function of PPh_3 concentration reveals the equilibrium as shown in eqn. (1).



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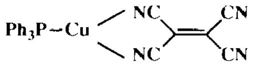

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$$3 + PPh_3 \rightleftarrows 2 \qquad (1)$$

In the reaction of metallic copper with TCNE **1** is probably formed by a stepwise electron transfer from Cu^0 to TCNE according to eqn. (2). When coordinating

$$n\mathrm{Cu}^0 + n\mathrm{TCNE} \overset{m\mathrm{L}}{\rightleftarrows}$$

$$n[\mathrm{Cu}^+(\mathrm{TCNE}^-)\mathrm{L}_m] \overset{-m\mathrm{L}}{\rightleftarrows} [\mathrm{Cu}^{2+}(\mathrm{TCNE}^{2-})]_n \qquad (2)$$

ligands are present $[Cu^{2+}(TCNE^{2-})]_n$ undergoes intramolecular electron transfer from $TCNE^{2-}$ to Cu^{2+} resulting in $[Cu^+(TCNE^-)L_2]$. The ESR spectra from the mixtures with ligands discussed above suggest that they stabilize the oxidation state one of copper and their presence induces a one-electron transfer from $TCNE^{2-}$ to Cu^{2+}. From the ligands used only PPh_3 is bounded strongly enough to copper(I) to show phosphorus hyperfine structure couplings. Studies are underway to isolate and structurally characterize the copper species with $TCNE^-$ and $TCNE^{2-}$ ligands.

Acknowledgement

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