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ESR Investigation of Tetracyanoethylene Anion Radical with Magnesium as Counterion

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The tetracyanoethylene anion radical formed by the reaction of metallic magnesium or anhydrous magnesium halides with TCNE in tetrahydrofuran shows an esr spectrum whose features differ from the spectrum of $TCNE^{\dot{-}}$ *obtained by other methods; the hyperfine splitting pattern indicates a weak interaction of TCNE radical with the metal through a nitrogen end of the molecule.*

Introduction

It is well known that TCNE anion radicals can be readily generated in electron donating solvents by a variety of methods: reaction of TCNE with alkali metals or their salts [1–4], organometallic compounds [5], metallocenes and other transition metal compounds [6–8]. In all cases, the anion radical produced can be readily detected by esr spectroscopy; it exhibits a characteristic spectrum consisting of nine sharp hyperfine lines (a = 1.56 gauss; g = 2.0026) [1] due to coupling of the unpaired electron with four equivalent nitrogen nuclei ($I_N = 1$) and two weak outer lines due to hyperfine coupling with isotopic ^{13}C.

Although early reports [1] mentioned also the formation of this anion radical by the reaction of metallic Mg, Al, Cu, or Pb with TCNE in solution, no detailed studies have to our knowledge been heretofore devoted to these systems probably due to the belief that the species produced will have an overall behavior identical to those obtained by other methods.

In this study we report on the preparation of the magnesium salt of TCNE and on the esr spectrum obtained when metallic magnesium or its anhydrous salts are allowed to react with TCNE in THF as solvent.

Results and Discussion

When metallic magnesium is stirred with a 0.3 *M* solution of TCNE in THF, a yellowish color develops within a few minutes. The esr spectrum of the solution consists of nine lines characteristic of the TCNE anion radical. If the reaction is allowed to proceed further, a solution is obtained whose spectrum at room temperature shows a more complex hyperfine splitting pattern, the components of which vary in relative intensity as the reaction progresses, until a situation is reached where the 21-line spectrum shown in Figure 1 is obtained.

The spectrum is temperature-dependent; cooling down to –60 °C gives the usual nine hyperfine lines (a = 1.65 gauss; g = 2.0041) while raising back to room temperature yields again the spectrum shown in Figure 1, indicating a reversible process. The same reaction performed in deuterated THF leads to identical results, which precludes the interference of the solvent protons.

In order to gain more insight into the phenomenon involved, the magnesium salt of TCNE was isolated from the reaction mixture (*vide infra*) and its spectra measured in the solid phase and in solution. The powder gives a broad signal with several shoulders while the THF solution exhibits the regular features of a TCNE radical (nine lines). However, the 21-line pattern begins to appear when excess TCNE is added to the solution.

This observation is consistent with the fact that the same 21-line pattern appears at the early stages of the reaction when neutral TCNE is in excess. On the other hand, if the reaction is conducted in acetonitrile, the esr signal consists of nine lines at all stages of the reaction.

The above results demonstrate that the species formed by the reaction of magnesium with TCNE in

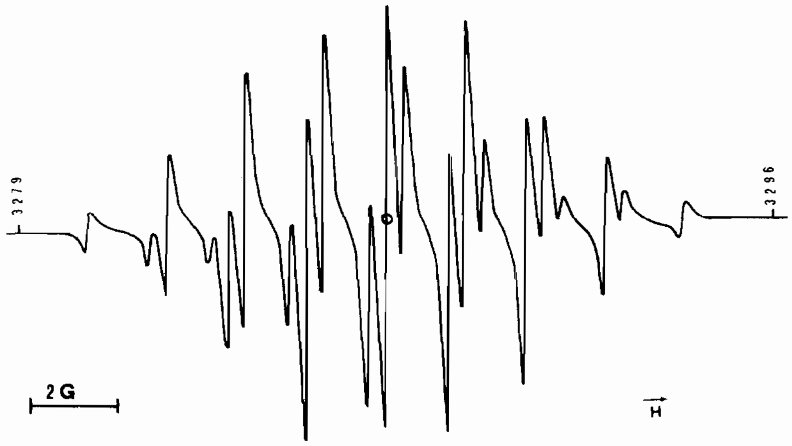
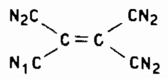


Figure 1. Esr spectrum at room temperature of TCNE anion radical prepared from Mg and TCNE in THF. Field markers in gauss.

THF differ remarkably from the TCNE anion radical generated by other known methods.

The 21-line spectrum shown in figure 1, centered around g = 2.0041, can be interpreted as being due to the non-equivalent hyperfine interaction of the unpaired electron of the TCNE radical with the four nitrogen atoms, and can be analyzed in terms of a seven-line spectrum due to coupling with three equivalent nitrogens (a_{N_2} = 1.65 gauss), each line being split into a triplet due to a weaker interaction with the fourth nitrogen (a_{N_1} = 1.36 gauss).

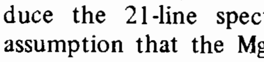


Computer-simulation on the basis of the above parameters gives a spectrum identical to the experimental one, which lends support to the above interpretation.

The non-equivalence of the four nitrogens is believed to result from a weak interaction of one nitrogen (through electron pair donation for example) with the positive magnesium center; this will result in an increased charge density on this nitrogen nucleus which may lead to an enhanced screening, and consequently a weaker interaction with the electron in the TCNE antibonding molecular orbital, compared to the other three nitrogens. It would be expected that out of these three nitrogens, two should be equivalent while the third one, adjacent to the coordinated nitrogen atom, should exhibit a different hyperfine constant; it is believed, however, that the difference is too small compared to the linewidth of the individual components of the signal (0.15 gauss) to produce a distinguishable splitting.

It should be noticed that the coupling constant $a_{N_{1,2,3}}$ = 1.65 gauss) is identical to that of the nine-line spectrum of an electron interacting with four equivalent nitrogens in the solution of the Mg–TCNE salt in the absence of excess neutral TCNE.

A similar situation, although with different consequences on the hyperfine splitting parameters has been detected in the reaction products of TCNE with binuclear transition metal carbonyls [8]. Cleavage of the metal–metal bond in $[(CO)_5Mn]_2$ by addition of TCNE results in bond formation between the transition metal and the nitrogen end of an iminocyanoallyl radical



The hyperfine constant a_{N_3} (2.530 gauss) is higher than either of the other two ($a_{N_{1,1}}$ = 1.734, a_{N_2} = 1.201 gauss) due to the strong metal to nitrogen *sigma* bond enhanced by hyperconjugation with the allyl molecular orbital system.

The ncesssity of adding neutral TCNE to solutions of the magnesium salt in THF in order to produce the 21-line spectrum (fig. 1) leads to the assumption that the Mg–TCNE ion pairs are of the contact type with dynamic site exchange between the metal and the nitrogen centers. If the site exchange rate is fast enough, the four nitrogens should be indistinguishable on the esr time-scale and the spectrum of the pure Mg–TCNE salt solution will exhibit a hyperfine splitting similar to that of the free TCNE anion radical. In presence of excess neutral TCNE, two phenomena will occur simultaneously: electron exchange between TCNE and $\mathrm{TCNE}^{\cdot-}$

$$\mathrm{TCNE} + \mathrm{TCNE}^{\cdot-} \rightleftharpoons \mathrm{TCNE}^{\cdot-} + \mathrm{TCNE}$$

on the one hand, and an enhanced probability of a nitrogen end of the molecule to encounter a magnesium ion center on the other. This will create an instantaneous structure with two distinct sites: coordinated and free nitrogen centers, a situation which will give rise to the 21-line spectrum observed.

The observation of equivalent hyperfine splitting (9-line spectrum) both at low temperatures and in solvents such as acetonitrile, dioxane, *etc.*, are both consequences of an increase of the dielectric constant of the solvent, which favors the separation of the ion pairs.

Although the true nature of the phenomenon involved in the Mg/TCNE/THF system is not very clear at this stage, its study by esr reveals a type of ion pair interaction which apparently has not been hitherto encountered in the TCNE radical ion chemistry. The nature of the metal and the solvent are clearly the main responsible factors.

Experimental

Esr spectra were recorded on a JEOL ME 3X X-band spectrometer, with a proton resonance probe for field calibration. Klystron frequency was measured with a tunable cavity.

All manipulations were conducted under inert atmosphere. THF was distilled over sodium naphthalenide and then on $AlLiH_4$ prior to use. Acetonitrile was dried over molecular sieves. TCNE (Aldrich-Europe) was used without further purification since the resublimed product gave identical results.

Preparation of the Magnesium Salt of TCNE

In a typical run, 105 mg of magnesium turnings are introduced into a reaction flask with 500 mg of TCNE in 20 ml of THF. Trace amounts of iodine are needed to insure a rapid initiation of the reaction. A gray gelatinous precipitate forms shortly after a few minutes' stirring. The reaction is allowed to continue overnight when a voluminous precipitate is obtained. Filtration under Argon yields a gray powder, the composition of which is consistent with the formula Mg–2TCNE,2THF. *Anal.* Found: C, 54.73; H, 3.87; N, 26.53; Mg, 5.99. Calc: C, 56.56; H, 3.79; N, 26.38; Mg, 5.72%. The compound is very sensitive to air and moisture and turns violet very rapidly after exposure to air.

An alternative method for obtaining the product is to introduce stoichiometric amounts of TCNE and anhydrous MgI_2 (prepared for example from iodine and metallic magnesium in ether) in THF. The precipitate is then filtered and dried under Argon.

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