

## Transition Metal Derivatives of the Tetracyanoquinodimethandiide Ion, $\text{TCNQ}^{2-}$

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*Oxidation of some simple organometallic compounds with tetracyanoquinodimethan (TCNQ) in acetonitrile gave metal derivatives of  $\text{TCNQ}^{2-}$  which were characterized by infrared and X-ray photoelectron spectroscopy and magnetic susceptibility. Strong, low frequency  $\nu\text{C}\equiv\text{N}$  bands around 2180 and 2105  $\text{cm}^{-1}$  are characteristic of  $\text{TCNQ}^{2-}$ . New compounds prepared were  $\text{V}(\text{TCNQ})_2$ ,  $\text{Cr}(\text{TCNQ})_2(\text{CH}_3\text{CH})_2$ ,  $\text{Mo}(\text{TCNQ})(\text{CO})_2(\text{CH}_3\text{CN})_2$ ,  $\text{W}(\text{TCNQ})_2(\text{CH}_3\text{CN})$ ,  $\text{Co}(\text{TCNQ})(\text{CH}_3\text{CN})_2$  and  $\text{Ni}(\text{TCNQ})_2$ .*

### Introduction

In recent years, there has been an increased, interdisciplinary interest in materials which display anisotropic optical and transport properties in the solid state [1–6]. Such properties arise from one- or pseudo-one-dimensional structures and define an extensive class of compounds referred to as low dimensional [7]. Charge transfer salts, of which TTF–TCNQ is exemplary, comprise an important and intensively studied subset of low dimensional materials. We have, accordingly, been interested in the reaction chemistry of the important acceptor molecule tetracyanoquinodimethane (TCNQ), **1**.

This paper describes the oxidation of some simple organometallic compounds with TCNQ and the characterization of the resulting metal tetracyanoquinomethane products [8] and complements our earlier studies of metallotetrathiaethylenes [9–11]. These reactions lead, in contrast to the previously reported chemistry of **1**, to derivatives of the singlet dianion of TCNQ.

### Results and Discussion

The reactions of TCNQ with organometallics proceed slowly in acetonitrile; the rates are presumably

limited by the low solubility of **1** at room temperature. The products are, with the exception of  $\text{Ni}(\text{TCNQ})_2$ , green or purple but the color is so intense that they often appear black. They are at least partly ionic, and, like many TCNQ salts, have virtually no solubility in non-reactive solvents. Because of the low solubility, the microcrystalline metal  $\text{TCNQ}^{2-}$  derivatives cannot be recrystallized. These compounds are also very air sensitive. The reactivity is attributable to the TCNQ dianion and VanDuyne has demonstrated a rapid reaction with molecular oxygen to yield  $\alpha,\alpha$ -dicyano-*p*-toluoyl cyanide by cleavage of one of the cyano groups [12]. Because both TCNQ and transition metals undergo multiple electron transfer reactions, elucidation of the oxidation state(s) of the metal and cyanocarbon is critical to the characterization of metal–TCNQ systems and, indeed, in some cases mixed valence compounds have been obtained [13]. Techniques employed in this work were infrared and X-ray photoelectron spectroscopy (ESCA) and magnetic susceptibility. The solvated lithium salt of  $\text{TCNQ}^{2-}$ ,  $[\text{Li}_2(\text{THF})]\text{TCNQ}$  [14], served as a useful model compound. It exhibited  $\nu\text{CN}$  in a Nujol mull at 2180 and 2105  $\text{cm}^{-1}$ . Similar absorptions (2151 and 2102  $\text{cm}^{-1}$ ) were observed in the first  $\text{TCNQ}^{2-}$  complex,  $[\text{Co}(\text{N}, \text{N}'\text{-ethylene bis(acetylacetonimine)})(\text{C}_5\text{H}_5\text{N})_2]_2\text{TCNQ}$  [15].

The presence of these strong, low frequency  $\text{C}\equiv\text{N}$  stretching bands, far more intense than the corresponding bands in either **1** or  $\text{LiTCNQ}$ , appears to be diagnostic for the TCNQ dianion. This information is applied in the following discussion of individual transition metal–TCNQ derivatives.

Stirring a mixture of  $(\text{C}_5\text{H}_5)_2\text{V}$  and **1** in acetonitrile resulted in slow dissolution of the reactants and the formation of deep green  $\text{V}(\text{TCNQ})_2$ , **2**, whose elemental analysis is shown in Table I. The infrared spectrum, Table II, disclosed three strong bands at 2100, 2140, and 2190  $\text{cm}^{-1}$ , indicating the presence of  $\text{TCNQ}^{2-}$  with a symmetry reduced by interaction with a strongly polarizing, positive metal ion. Plausible formulations for **2** include  $\text{V}^{+2}(\text{TCNQ}^{2-})_2$ .

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TABLE I. Analytical Data and Yields.

Compound	Yield, %	%C, calc. (found)	%H, calc. (found)	% Metal, calc. (found)	%N, calc. (found)
2	100	62.75 (62.84)	1.74 (1.83)	V, 11.11 (11.53)	24.40 22.69
3	86	61.99 (61.56)	2.58 (2.37)	Cr, 9.59 (9.16)	25.83 (22.02)
4 <sup>a</sup>	77	49.32 (49.58)	2.28 (2.55)	Mo, 21.92 (21.24)	19.18 (19.94)
5	82	49.85 (50.05)	2.07 (2.18)	W, 27.30 (26.80)	20.77 (18.04)
6	81	55.65 (55.38)	2.90 (3.08)	Co, 17.10 (16.82)	24.34 23.82
7	90	61.67 (61.44)	1.71 (1.61)	Ni, 12.63 (12.83)	23.98 22.15

<sup>a</sup>O calc., 7.30; found, 8.03.

TABLE II. Infrared Spectral Data.

Compound	Absorption Maxima, cm <sup>-1</sup>
2	3120(w), 2190(s), 2140(s), 2100(s), 1600(w), 1500(s), 1320(m), 1285(w), 1240(m), 1130(w), 1075(w), 1030(m), 845(s), 835(s), 560(m), 505(m)
3	3115(w), 2205(s), 2100(s), 1600(w), 1505(m), 1320(m), 1260(w), 1180(m), 1050(w), 1005(w), 835(s), 820(s), 745(m), 760(m), 565(m), 485(m), 400(m)
4	3120(w), 2190(s), 2090(s), 1590(m), 1510(sh), 1505(m), 1310(m), 1250(w), 1135(m), 1040(w), 1000(w), 825(m), 720(w)
5	3115(w), 2190(s), 2080(s), 1590(m), 1510(sh), 1500(m), 1335(w), 1185(w), 1005(w), 970(w), 920(w), 835(m), 815(m), 720(w), 560(w), 470(w)
6	3110(w), 2200(s), 2135(s), 2065(s), 1600(w), 1575(m), 1500(m), 1380(w), 1245(m), 1285(m), 1160(m), 985(m), 820(m), 810(sh), 480(w)
7	3120(w), 2205(s), 2135(s), 2060(s), 1600(m), 1505(m), 1305(w), 1255(w), 1180(w), 825(m), 815(m), 485(w)

NQ<sup>+</sup>)<sub>2</sub>, **2a**, V<sup>3+</sup>(TCNQ<sup>+</sup>)(TCNQ<sup>2-</sup>), **2b**, and V<sup>4+</sup>-(TCNQ<sup>2-</sup>)<sub>2</sub>, **2c**. The infrared data exclude **2a**. The magnetic susceptibility of 1.73 B.M. at room temperature, Table III, indicates that **2** contains one unpaired electron. This is inconsistent with the presence of 3d<sup>2</sup> V<sup>3+</sup> but agrees well with the value expected for 3d<sup>1</sup>V<sup>4+</sup> in V(TCNQ<sup>2-</sup>)<sub>2</sub>.

Although (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr and **1** have been reported to form both 1:1 and 1:2 complexes [16-18], the reactivity of (toluene)chromiumtriacarbonyl was distinctive in that oxidation of the chromium with expulsion of toluene and three equivalents of carbon monoxide occurred. The presence of TCNQ<sup>2-</sup> in the product, deep purple Cr(TCNQ)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>, **3**, was revealed by the strong infrared absorptions at 2100 and 2205 cm<sup>-1</sup>; a weak band at 2290 cm<sup>-1</sup> was assigned to the C≡N group of the coordinated acetonitrile. The magnetic susceptibility at room temperature was 4.08 B.M., corresponding to three unpaired electrons on chromium(III) with a small contribution from the TCNQ anion radical [19, 20] in Cr<sup>III</sup>-(TCNQ<sup>+</sup>)(TCNQ<sup>2-</sup>)(CH<sub>3</sub>CN)<sub>2</sub>.

Oxidation of bicyclo[2.2.1]heptadienemolybdenumtetracarbonyl with TCNQ in acetonitrile produced dark purple Mo(CO)<sub>2</sub>(TCNQ)(CH<sub>3</sub>CN)<sub>2</sub>, **4**, bicycloheptadiene, and two equivalents of carbon monoxide. This compound is a TCNQ<sup>2-</sup> derivative as indicated by the two strong infrared bands at 2090 and 2190 cm<sup>-1</sup>. It was diamagnetic with an effective magnetic moment of 0.03 B.M. at room temperature. These data suggest that **3** is an acetonitrile solvate of Mo<sup>II</sup>(CO)<sub>2</sub>(TCNQ<sup>2-</sup>). The Mo 3d<sub>3/2</sub> and 3d<sub>5/2</sub> binding energies were 233.0 and 230.7 eV respectively. Comparison of these ESCA data with those

TABLE III. Physical Properties of Transition Metal-TCN Salts.

Compound	$\mu_{\text{eff}}$ at 298 K, B.M.	$\sigma$ , $\text{ohm}^{-1} \text{cm}^{-1} \times 10^{-4}$	$\lambda_{\text{max}}$ , $\text{cm}^{-1}$
2	1.73	2.6	28,990, 23,260, 12,500(sh), 9175
3	4.08	2.2	34,480, 31,750, 24,100, 11,900
4	0.03	2.3	30,800, 24,400
5	0.00	2.6	
6	3.56	13.0	32,780, 26,320, 12,100
7	3.23	1.7	30,300, 22,220, 13,300, 11,900

obtained for a variety of other molybdenum compounds [21, 22] also indicates the presence of formal Mo(II) in 3. No infrared bands were seen in the usual region for terminal carbonyl group. However, oxidation of the molybdenum is expected to shift  $\nu\text{CO}$  to higher frequencies [23, 24], and the electron density in the cyano group  $\pi^*$  orbitals of  $\text{TCNQ}^{2-}$  shifts  $\nu\text{CN}$  to lower frequencies so that these two bands overlap. The carbonyl content of 4, however, is fully substantiated by measurement of the carbon monoxide evolved during the reaction and by direct oxygen analysis, Table I.

Mesitylenetungsten tricarbonyl displayed a reactivity similar to that of the chromium analogue and afforded with TCNQ, black  $\text{W}(\text{TCNQ})_2(\text{CH}_3\text{CN})_2$ , 5, mesitylene, and three equivalents of carbon monoxide. The infrared spectrum displayed strong bands due to  $\text{TCNQ}^{2-}$  but, unlike 2, the compound was diamagnetic at both 30 and  $-178^\circ\text{C}$ . This suggests that 5 contains strongly coupled W(III) and  $\text{TCNQ}^{2-}$  or, more probably in view of the tendency of TCNQ to produce metal derivatives in which the metal is in a high oxidation state, that it is  $\text{W}(\text{IV})$ .  $(\text{TCNQ}^{2-})_2(\text{CH}_3\text{CN})$ . This formulation is also consistent with the well-known greater stability of the higher oxidation states of third row elements.

Oxidation of cyclopentadienylcobalt cyclooctadiene with 1 yielded deep purple  $\text{Co}(\text{TCNQ})(\text{CH}_3\text{CN})_2$ , 6. The infrared spectrum contained strong bands at 2065, 2135, and  $2200 \text{ cm}^{-1}$  due to  $\text{TCNQ}^{2-}$  and was quite distinct from  $[(\text{C}_5\text{H}_5)_2\text{Co}]\text{TCNQ}$  prepared by metathesis of  $[(\text{C}_5\text{H}_5)_2\text{Co}]\text{PF}_6$  and LiTCNQ. The room temperature magnetic susceptibility was 3.56 B.M. consistent with the presence of high spin  $3d^7$  cobalt(II). These data indicate that 5 is  $\text{Co}^{\text{II}}(\text{TCNQ}^{2-})(\text{CH}_3\text{CN})_2$ .

Dicyclopentadienylnickel reacted with two mol of TCNQ to produce  $\text{Ni}(\text{TCNQ})_2$ , 7, as a dark brown powder in 90% yield. The infrared spectrum revealed three strong cyano bands at 2060, 2135, and  $2205 \text{ cm}^{-1}$ , indicative of a reduced symmetry TCN dianion as was observed in the unsolvated  $\text{V}(\text{TCNQ})_2$ . Plausible formal representations of 6 are  $\text{Ni}^{2+}(\text{TCNQ}^-)_2$ , 7a,  $\text{Ni}^{3+}(\text{TCNQ}^-)(\text{TCNQ}^{2-})$ , 7b, and  $\text{Ni}^{4+}(\text{TCNQ}^{2-})_2$ , 7c. The infrared data show that 7a is not a realistic possibility. The room temperature

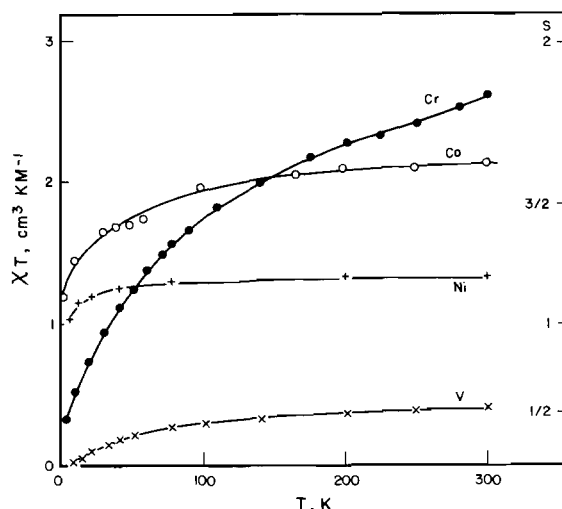
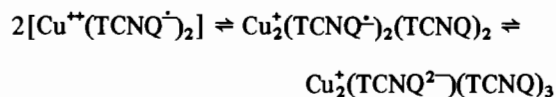


Fig. 1. Magnetic susceptibility of 2(V), 3(Cr), 6(Co) and 7(Ni) as a function of temperature.

magnetic susceptibility was 3.28 B.M. This value, which agrees poorly with that expected for a  $3d^7$  Ni(III) derivative, remained constant down to about 25 K, Fig. 1. Our previous results, which indicate that transition metal derivatives of TCNQ tend to contain the metal in a high oxidation state, suggest that 6 may contain high spin ( $S = 2$ ) Ni(IV).

Support for this idea was obtained from X-ray photoelectron spectroscopic (ESCA) measurements. The nickel  $2p_{1/2}$  and  $2p_{3/2}$  binding energies, 858.1 and 875.9 eV respectively, are among the highest value reported [25, 26], and may be compared, in the absence of charging effects which should be less important in semiconducting 6 than in other nickel compounds studied, with the  $2p_{3/2}$  energy of 857.2 eV in the Ni(IV) dicarbollide complex  $(1,2\text{-B}_9\text{C}_2\text{-H}_{11})_2\text{Ni}$  [27]. The nickel peaks, however, also exhibit shoulders at 855.7 eV and 873.6. These lower binding energy peaks account for about 15% of the total nickel photoelectron counts and are indicative of Ni(III), providing a reasonable explanation for the deviation of the magnetic susceptibility from the value expected for a  $S = 2$  ion. A somewhat similar phenomena was observed by Melby and co-workers who synthesized a series of transition metal salts of

TCNQ<sup>-</sup> [28]. The diamagnetism and low resistivity of Cu(TCNQ)<sub>2</sub>, prepared from CuSO<sub>4</sub> and LiTCNQ in water was attributed to a possible solid state equilibrium



The mechanistic details of reactions between TCNQ and organometallic materials are not known. It is probable that the first step is complex formation. Charge transfer complexes have been obtained from 1 and *trans*-bis(trialkylphosphine)dialkynylplatinum(II) compounds [29] and from tetracyanoethylene (TCNE) and ferrocene [30]. Collapse of such an intermediate complex by electron transfer to yield a salt of the cyanocarbon anion radical is a reasonable subsequent step. Electron transfer from organometallics such as *t*-butylmagnesium bromide [34] to TCNE have been reported [35]. Tetracyanoethylene is also known to oxidize organometallic compounds which contain metal-metal bonds, *e.g.*, Mn<sub>2</sub>(CO)<sub>10</sub> and [(C<sub>5</sub>H<sub>5</sub>)Cr(CO)<sub>3</sub>]<sub>2</sub> to form iminotricyanoalkyl radicals [36, 37]. In accord with this suggestion, we found that dilute acetonitrile solutions of 1 and the organometallics studied in this report exhibited the characteristic electronic spectrum of the TCNQ anion radical during the initial stages of the reactions reported here. We believe that TCNQ reacts with organometallic compounds by mechanistic pathways analogous to those established for TCNE. However, since TCNQ is a stronger oxidizing agent than TCNE [3], additional electron transfer steps leading to TCNQ<sup>2-</sup> ensue. Oxidation of the transition metal center reduces the π donor capacity of the metal. Bonding to π acceptors such as arenes, olefins, cyclopentadienide and carbon monoxide is therefore weakened and these ligands are lost. Another illustrative example, drawn from cyanocarbon chemistry, is found in the reaction of Ni(CO)<sub>4</sub> with TCNE to produce Ni<sup>(II)</sup>-(TCNE)<sub>2</sub> [38].

A distinctive feature of TCNQ relative to other cyanocarbons is its propensity to yield derivatives containing the cyanocarbon dianion and a transition metal in a high oxidation state. The metal-TCNQ compounds prepared in this work are evidently at least partly ionic in view of the similarities of the cyano group stretching frequencies with the solvated lithium salt, [Li<sub>2</sub>(THF)]TCNQ. However, interaction between the metal ion and TCNQ<sup>2-</sup> is indicated in some cases, namely, the unsolvated M(TCNQ)<sub>2</sub> (M = V, Ni) and Co(TCNQ)(CH<sub>3</sub>CN)<sub>2</sub>. In uncomplexed TCNQ<sup>2-</sup>, only two νCN bands are expected and found. The occurrence of three νCN bands in the vanadium, cobalt, and nickel compounds is attributed to a reduction in symmetry

of the TCNQ<sup>2-</sup> caused by an interaction between the highly polarizing metal center and the cyano groups. Such an interaction has been observed in (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>VBr TCNE [39] and, moreover, short Ag-N contacts have been found in the silver cyanocarbon derivatives, AgC(CN)<sub>2</sub>NO and AgC(CN)<sub>2</sub>NO<sub>2</sub> [40, 41].

Optical absorption spectra of the new metal tetracyanoquinodimethandiides were measured in Nujol mulls. The data, shown in Table III, are in qualitative accord with literature spectra of TCNQ<sup>2-</sup> and TCNQ<sup>-</sup>. High energy bands in the 34,500–29,000 cm<sup>-1</sup> range are attributable to transitions in TCNQ<sup>2-</sup> since the solution ultraviolet spectrum of this ion, generated electrochemically, shows a strong absorption at 30,300 cm<sup>-1</sup> [12]. Absorptions appearing as shoulders in the 22,000–26,000 cm<sup>-1</sup> region are likewise probably due to intramolecular transitions of aggregated TCNQ<sup>2-</sup> [42] as they are not observed in the fluid state. Interpretation of the bands in the 9,200–13,000 cm<sup>-1</sup> region is not straightforward but these absorptions may reasonably be attributed to TCNQ<sup>2-</sup> to metal charge transfer processes; their low energies are consistent with the involvement of highly charged centers. It is surprising that no unique bands were observed in the mixed valence compounds 3 and 7 due to intervalence electron transfer between TCNQ<sup>-</sup> and TCNQ<sup>2-</sup>.

The metal-TCNQ compounds were all found to be semiconductors with conductivities in the range of 1.7–2.6 × 10<sup>-4</sup> (ohm cm)<sup>-1</sup>. The conductivity of Co(TCNQ)(CH<sub>3</sub>CN)<sub>2</sub> was 13 × 10<sup>-4</sup> (ohm cm)<sup>-1</sup>, significantly higher than for other derivatives, but the reason for the increased conductivity is not clear.

Measurements of magnetic susceptibilities over the temperature range 5–300 K were made with a SQUID magnetometer. Corrections for diamagnetic susceptibility were made using literature values for neutral TCNQ (-1.21 × 10<sup>-4</sup> cgsu mol<sup>-1</sup>) [43] and acetonitrile (-0.28 × 10<sup>-4</sup> cgsu mol<sup>-1</sup>) [44]. The magnetic behavior of the vanadium, nickel and cobalt TCNQ<sup>2-</sup> derivative is dominated by the transition metal atoms and the room temperature susceptibilities are quite close to the spin-only values. On cooling to below 100 K, antiferromagnetic coupling is observed, as shown in Fig. 1. The interaction appears, for unobvious reasons, to be much stronger in the chromium complex Cr(TCNQ)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>. This coupling is most probably due to bridging of the metal centers by the potentially bidentate TCNQ<sup>2-</sup> ions. Infrared spectroscopic evidence for such an interaction has been cited and this feature is consistent with molecular orbital calculations, which indicate extensive charge delocalization onto the dicyanomethylene groups [45], and with the recently reported antiferromagnetic coupling of manganese ions in Mn(TCNQ)<sub>2</sub>·3H<sub>2</sub>O [46].

## Experimental

Commercial organometallic compounds were purified by vacuum sublimation. TCNQ was recrystallized from pure acetonitrile. Spectro grade acetonitrile was purified by distillation under nitrogen from  $P_2O_5$ , deoxygenated by purging with nitrogen, and stored over 4A molecular sieves. Infrared and electronic spectra were recorded on Nujol mulls prepared in a dry box; replicate spectra were run to ensure the absence of spurious bands due to sample decomposition. Samples for magnetic susceptibility measurements were weighed in a dry box into quartz tubes. These were evacuated on a high vacuum line, back-filled with helium, and sealed with a torch. Electrical conductivities were measured on compressed discs of powdered material by the microwave cavity perturbation technique. The cavity was thoroughly purged with helium before inserting the samples. Elemental analyses were performed by Schwarzkopf Laboratories.

The synthetic procedure used for all the compounds reported consisted of stirring the organometallic starting compound, TCNQ, and acetonitrile. The product was isolated by filtration. Consequently, only one detailed illustrative procedure, that for  $Cr(TCNQ)_2(CH_3CN)_2$ , is given.

Toluenechromiumcarbonyl, 0.228 g (1.0 mmol) and 0.204 g (1.0 mmol) **1** were loaded in a dry box into a flask. Acetonitrile, 25 ml, was added. The flask was quickly transferred to a vacuum line and degassed by three freeze-pump-thaw cycles. After stirring at room temperature for 72 hr, the flask was cooled to  $-45^\circ C$  and opened via a  $-178^\circ C$  trap to Toepler pump. Carbon monoxide, 1.56 mmol, was collected and identified by mass spectrometry.

The reaction mixture was filtered in a dry box to give 0.22 g (81%) of  $Cr(TCNQ)_2(CH_3CN)_2$  as a dark purple solid; some of the product adhered to the stirrer bar and walls of the flask. The filtrate was subjected to trap-to-trap distillation. Analysis of the distillate by gas chromatography revealed that  $0.47 \pm 0.07$  mmol of toluene was present. The residue remaining after the distillation, 0.089 g, was identified as (toluene)chromiumtricarbonyl by infrared analysis.

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