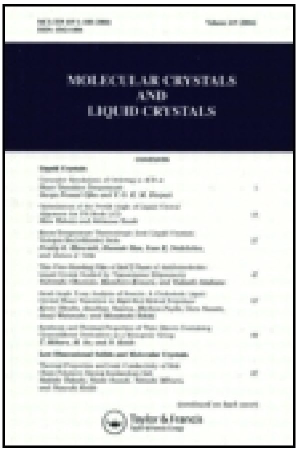

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# Paramagnetic Transition Metal Complexes With [sgrave]-Bonded Tetracyanoethylene (TCNE)

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# PARAMAGNETIC TRANSITION METAL COMPLEXES WITH σ-BONDED TETRACYANOETHYLENE (TCNE)

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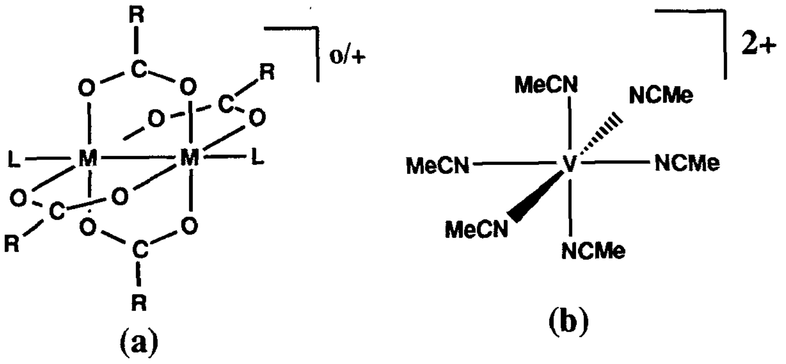
Abstract Mono- and dimetallic building blocks are being studied in charge-transfer reactions with organic π-acceptors such as TCNE to form zero-, one-, and two-dimensional hybrid donor/acceptor compounds. In particular, tetracarboxylate-bridged dinuclear and solvated 3d mononuclear complexes with σ-bonded TCNE ligands are being investigated with regards to their variable temperature magnetic behavior. Results of experiments with dimolybdenum, diruthenium and vanadium complexes are discussed.

## INTRODUCTION

Metal-metal bonded complexes are a rich class of compounds that have been known for over 30 years.[1] Many of these complexes are well characterized both structurally and electronically and exhibit multiple accessible redox states, all of which make them excellent candidates for charge transfer chemistry. In addition, the presence of σ, π, and δ components to the metal-metal bonding opens up the attractive possibility of conjugation with organic π systems. The metal coordination of multidentate ligands such as TCNE with its four nitrile nitrogen atoms has been observed to lead to the formation of one-dimensional[2-5] and two-dimensional compounds[6] with dinuclear as well as mononuclear metal complexes. Work in our laboratories has recently focused on the use of open-shell metal-metal bonded dimetal units such as carboxylate-bridged complexes of $Ru_2^{5+}$ ($S = 3/2$), $Mo_2^{5+}$ ($S = 1/2$), and $Re_2^{5+}$ ($S = 1/2$) (FIGURE 1 a) in reactions with organic acceptors such as TCNE and TCNQ. Other studies involve precursors such as the solvated mononuclear 3d metal cation $[V(MeCN)_6]^{2+}$ (Figure 1b) in the construction of molecule-based magnetic materials.

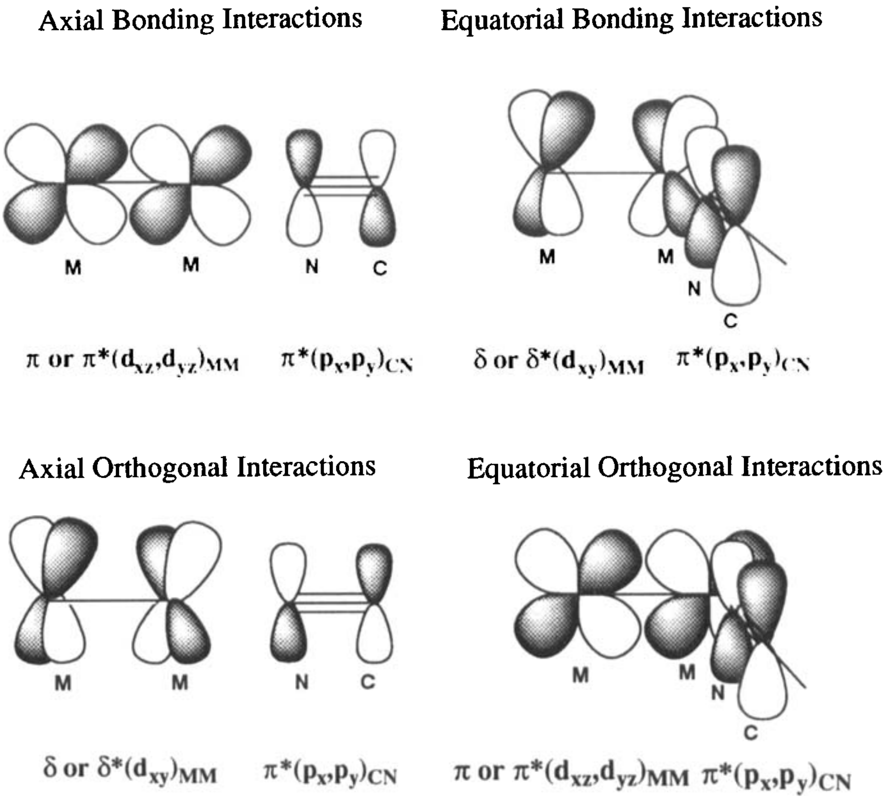


(a)

(b)

FIGURE 1. Structures of inorganic precursors used in this study.

In contemplating the possibilities for bonding between dimetal complexes and TCNE, one must consider the approach of the ligand (axial or equatorial) as well as the orbital symmetry of the dimetal ground state as shown in FIGURE 2 below.


Axial Bonding Interactions

Equatorial Bonding Interactions

Axial Orthogonal Interactions

Equatorial Orthogonal Interactions

FIGURE 2. Possible orbital overlap patterns for dimetal units and TCNE.

## EXPERIMENTAL

### 1. Dimetal Carboxylate Reactions with TCNE

Dinuclear metal carboxylate complexes of TCNE were prepared by one of two methods: (a) by anion metathesis reactions between cationic metal complexes and the TCNE anion radical or (b) by charge-transfer reactions between neutral TCNE and neutral dimetal complexes. Tetracarboxylatodiruthenium (II,III)TCNE complexes are readily prepared via method 1 whereas tetrakiscarboxylatodimolybdenum (II,III) TCNE are usually prepared via method 2.

**$Ru_2(O_2CR)_4$TCNE (R=Et, Pr, $Bu^t$).** A sample of $Ru_2(O_2CR)_4Cl$ dissolved in 15 ml THF was treated with 1 equivalent of LiTCNE and stirred for 48 hours. A black powder was collected and dried.

**$Mo_2(O_2CCF_3)_4$.** A quantity of $Mo_2(O_2CCF_3)_4$ was reacted with TCNE in a mixture of diethyl ether/THF (v/v=1/1) and refluxed under nitrogen for 5 hours to give a dark green solution. The solvent was reduced to 2 mL and filtered to collect the resulting precipitate, after which time diethyl ether was used to wash the dark green solid.

**$Mo_2(O_2CCMe_3)_4$TCNE.** A sample of $Mo_2(O_2CCMe_3)_4$ was dissolved in dichloromethane, treated with TCNE and stirred under nitrogen for 12 h at room temperature and 4 additional days at -20 °C; a red microcrystalline product was collected and stored at low temperature. Single crystals are obtained from cooling a concentrated solution for several weeks at -15 °C.

**$Mo_2(O_2CMe)_4$TCNE** $Mo_2(O_2CMe)_4$ was dissolved in 30 ml 1,2-dichloroethane, reacted with TCNE and refluxed for 5 hours.to give a brown precipitate.

### 2. Solvated Mononuclear Metal Cation Reactions with TCNE

Solvated mononuclear 3d metal cations are excellent candidates for reactions with TCNE. Reactions of the paramagnetic V(II) cation were explored for the purpose of isolating soluble compounds with N-coordinated TCNE.

**$V(MeCN)_6(BPh_4)_2$ with TCNE** $V(MeCN)_6(BPh_4)_2$ was reacted with TCNE in MeCN in a 1:1 ratio to produce a yellow-green solution. A yellow-brown solid was obtained after concentration of the reaction solution.

IR $n_{CN}$(cm$^{-1}$) =2209 (m, br),

**$V(THF)_3Cl_3$ with $NaBEt_3H/LiTCNE$.** $V(THF)_3Cl_3$ was reacted with 1 equivalent of LiTCNE in acetonitrile for 5 hours. A $NaBEt_3H$/toluene solution was then added to the reaction and the entire mixture was stirred for an additional 5 hours. The resulting NaCl was removed by filtration, the filtrate was concentrated and a dark green precipitate was collected.

IR $n_{CN}(cm^{-1})$ =2216 (s, br)

**$V(THF)_3Cl_3$ with $NaBPh_4/LiTCNE$.** $V(THF)_3Cl_3$ was combined with 3 equivalents of $NaBPh_4$ in MeCN for 4 hours, after which time NaCl was removed and LiTCNE was added with stirring for 8 hours. A blue green product was collected and dried.

IR $n_{CN}(cm^{-1})$ =2216 (s)

**$V(THF)_3Cl_3$ with $NaBEt_3H$/dppe /TCNE.** A solution of $V(THF)_3Cl_3$ in THF and 2 equivalents of dppe was treated with 3 equivalents of $NaBEt_3H$/toluene and stirred for 6 hours at 0 °C. The solution was then added to a toluene solution of 1 equivalent of TCNE for 4 hours at 0 °C which resulted in the deposition of a yellow powder.

IR $n_{CN}(cm^{-1})$ =2208(s), 2186(m), 2139 (w)

## RESULTS AND DISCUSSION

### 1. Syntheses and characterization

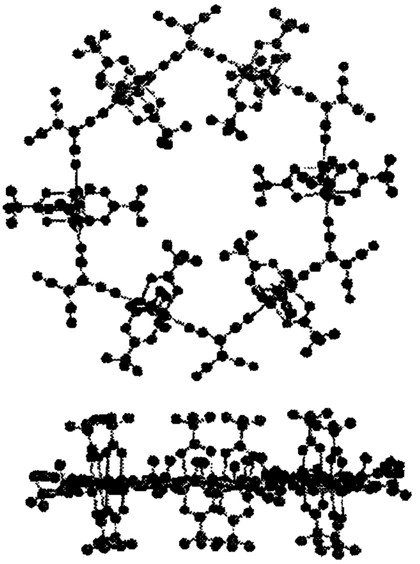
Tetracarboxylate complexes of $Ru_2^{5+}$, $Mo_2^{5+}$, and $Re_2^{5+}$ form low-dimensional arrays with TCNE as the bridging ligand. The R group on the starting materials can be used to tune the system electronically and also to improve crystallinity; for example if the R group is *t*-butylacetate, the $Mo_2(O_2CCMe_3)_4(TCNE)$ product readily crystallizes from dichloromethane whereas the trifluoroacetate does not form crystals. No single crystals were obtained from the *t*-butylacetatodiruthenium(II,III) reaction with lithium(I)tetracyanoethenide(-1), but infrared data in the ν(CN) region support coördinated $\mu^2$-TCNE (although it is not possible to assign an absolute structure as being *trans*-$\mu^2$ or *cis*-$\mu^2$). Selected cyanide stretching frequencies for different R substituents on the carboxylate ligands of $Mo_2^{4+}$ and $Ru_2^{5+}$ complexes are given in Table I.

The cyanide stretching frequencies of diruthenium TCNE products are assigned to coordinated (at lower energy) and dangling, uncoordinated cyanide groups (at higher energies). The lower frequencies of the stretches attributed to coordinated cyanides signifies charge transfer from the tetracarboxylatodiruthenium(II,III) $\pi^*$ orbitals to the $\pi^*$ orbitals in the $TCNE^{\bullet-}$.

| Dimetal TCNE complexes | $\nu_{CN}(cm^{-1})$ |
|---|---|
| $Mo_2(O_2CMe)_4TCNE$ | 2208(m) |
| $Mo_2(O_2CCMe_3)_4TCNE$ | 2201(s) |
| $Mo_2(O_2CCF_3)_4TCNE$ | 2206(m) |
| $Ru_2(O_2CCMe_3)_4TCNE$ | 2222(s), 2135(m) |
| $Ru_2(O_2CPr)_4TCNE$ | 2228(s), 2106(m) |
| $Ru_2(O_2CEt)_4TCNE$ | 2230(s), 2118(m) |
| $V(TCNE)_x$ via $NaBEt_3H$ | 2216(s) |
| $V(TCNE)_x$ via $NaBPh_4$ | 2216(s) |
| $V(dppe)_2TCNE$ | 2208(s),2186(m),2139 |

TABLE I. Cyanide stretching frequencies for TCNE complexes (KBr pellet)

To better understand the bonding between carboxylate dimetal complexes and TCNE, we have sought to obtain single crystals of both the ruthenium and the molybdenum complexes. Ruthenium/TCNE products formed only finely divided powder products while the (tetra-butylacetato)dimolybdenum product formed lustrous hexagonal-shaped red crystals from 1,2-dichloroethane at low temperature. Unfortunately, due to facile loss of interstitial solvent molecules and disorder of the *t*-butyl groups, we were unable to refine a data set collected on a Siemens P3/V Mo sealed tube anode instrument. Nevertheless, a hexagonal ring model structure (FIGURE 3) was built based on a DIRDIF solution without refinement in space group 6/mcc (192). A second data set was collected on a rotating anode set-up at -160°C on a similar crystal, but in this case a smaller unit cell was obtained and the data were not able to be solved. A comparison of the two unit cells, one at -100°C: $a = b = 27.1011$Å, $c = 22.8614$Å, $\alpha = \beta = 90°$, $\gamma = 120°$ and one at - 160 8C: $a = b = 26.9673$ Å, $c = 17.0840$Å $\alpha = \beta = 90°$ , $\gamma = 120°$ points to a phase transition that involves a reduction in space between the layers of hexagonal rings stacked along the c axis; this phenomenon is under further investigation.



**1.** a=27.10(1) Å α=β=90°
b=27.10(1) Å γ=120°
c=22.86(2) Å V=14,541Å$^3$
at -100°C Laue group 6/mmm

**2.** a=26.9673(0) Å α=β=90°
b=26.9673(0) Å γ=120°
c=17.0840(0) Å V=10760 Å$^3$
at -160°C

FIGURE 3. Model structure and unit cells for the $Mo_2(O_2CCMe_3)_4$/TCNE product.

## 2.Magnetic Properties

Samples of $Ru_2(O_2CCMe_3)_4TCNE$ and $Mo_2(O_2CCMe_3)_4TCNE$ were subjected to DC susceptibility studies from 5 K to 300 K (FIGURES 4 and 5). The magnetic properties of the diruthenium species are quite interesting, as the ground state is $\sigma^2\pi^4\delta^{*2}(\delta\pi)^3$, *viz*, three unpaired electrons. In polymeric chains formed by the use of bidentate ligands bound to the axial sites of two independent dimers, the diruthenium complexes exhibit one-dimensional antiferromagnetic properties when the bridges are closed shell organic ligands[7], or simple anions such as $Cl^-$ [8]. We have found that if an organic π-acceptor radical is employed, the system instead behaves like a *ferri*magnet with a Neel temperature ($T_N$) of 100 K for $Ru_2(O_2CCMe_3)_4$/TCNE.

In contrast to the diruthenium system, tetracarboxylate complexes of $Mo_2^{4+}$ undergo a charge-transfer reaction with TCNE to give antiferromagnetically coupled (S= 1/2) inorganic and organic (S = 1/2) spins, although we did not observe a definite maximum in the susceptibility curve.

The EPR spectra of $Mo_2(O_2CCMe_3)_4$/TCNE indicate that charge transfer between the dimolybdenum core and TCNE leads to formal oxidation of the quadruply-bonded $Mo_2^{4+}$ unit to a $Mo_2^{5+}$ species. Two g values were observed both in solution and in the solid-state (-157 °C in the solid-state: $g_1 = 2.00$; $g_2 = 1.89$ and -140 °C in frozen $CH_2Cl_2$: $g_1 = 1.99$; $g_2 = 1.92$).

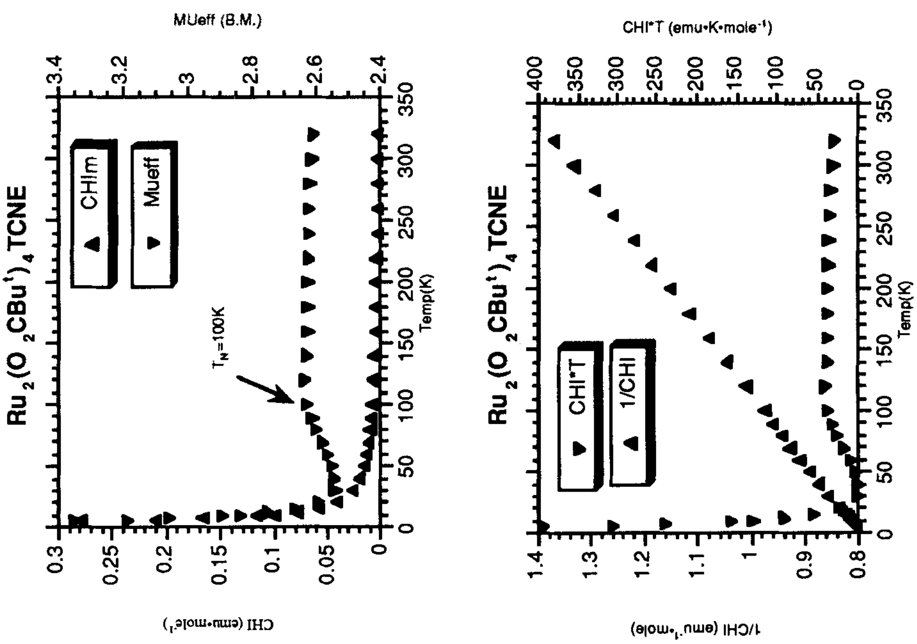


FIGURE 4. Magnetic properties of Ru$_2$(O$_2$CCMe$_3$)$_4$TCNE.

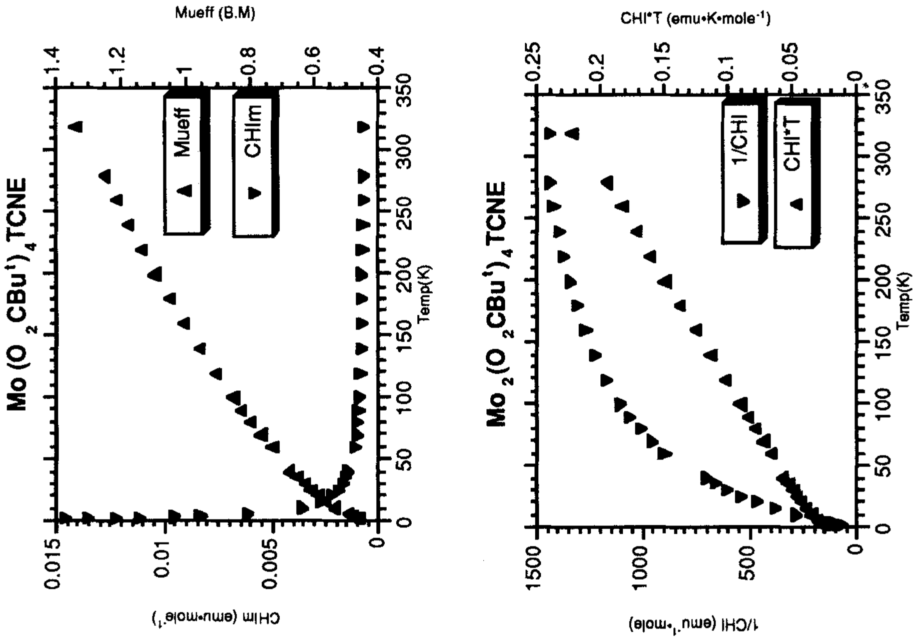


FIGURE 5. Magnetic properties of Mo$_2$(O$_2$CCMe$_3$)$_4$TCNE.

## SUMMARY

The following conclusions can be drawn regarding the aforementioned studies:

- Metal-metal bonded complexes readily react with TCNE to form σ-bonded complexes.
- The magnetic behavior of $Ru_2((O_2CCMe_3)_4/TCNE$ is characteristic of a 1-D ferrimagnet, whereas $Mo_2(O_2CCMe_3)_4/TCNE$ exhibits antiferromagnetic coupling.
- $TCNE^{\bullet-}$ also reacts with solvated as well as phosphine-containing mononuclear vanadium complexes to form σ-bonded complexes.

Future work will focus on other metal-metal bonded building blocks that will interact more strongly with TCNE (e.g.. $Re_2^{5+}$, $Os_2^{5+}$) and on the exploration of the interaction between TCNE and the equatorial bonding sites of the metal-metal units.

## ACKNOWLEDGEMENT

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