Synthesis and Reactivity of the Tl^{I} salts of $[TCNE]^{\bullet-}$ and $[TCNE]^{2-}$: The Structural Determination of $Tl^{I}[TCNE]$ and $[TDAE][TCNE]_2$ and Evidence for a Chelated $[TCNE]^{\bullet-}$

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Abstract: Synthons $Tl^{I}[TCNE]^{\bullet-}$ (**1**) and $Tl^{I}_2[TCNE]^{2-}$ (**2**), for $[TCNE]^{\bullet-}$ and $[TCNE]^{2-}$, respectively, in metathesis reactions have been quantitatively prepared and characterized. The structure of **1** was solved and refined in a monoclinic unit cell at 27 °C [*C*2/*c*, $a = 12.6966$ (12) Å, $b = 7.7599$ (7) Å, $c = 15.5041$ (15) Å, $\beta = 96.610$ (5)°, $V = 1517.4$ (2) Å^3, $D_{calcd} = 2.911$ g cm^{-3}, $Z = 8$, $R_1 = 0.0575$, $wR2 = 0.0701$] and exhibits ν_{CN} absorptions at 2191 (s) and 2162 (s) cm^{-1} consistent with metal-bound $[TCNE]^{\bullet-}$. The structure of **1** consists of a distorted square antiprismatic octacoordinate Tl^{I} bound to six monodentate $[TCNE]^{\bullet-}$s with TlN separations ranging from 2.901 to 3.171 Å averaging 3.020 Å, and one bidentate $[TCNE]^{\bullet-}$ with TlN separations averaging 3.279 Å. The TlN bonding is attributed to electrostatic bonding. The $[TCNE]^{\bullet-}$s form dimerized zigzag chains with intra- and interdimer separations of 2.87 and 3.29 Å, respectively. The tight π-$[TCNE]_2^{2-}$ dimer is diamagnetic and has the shortest intradimer $[TCNE]^{\bullet-}$ distance reported. These synthons for $[TCNE]^{\bullet-}$ and $[TCNE]^{2-}$ in metathesis reactions lead to the precipitation of, for example, $Tl^{I}X$ (X = Cl, Br, OAc). Reaction of **1** with Mn^{III}(porphyrin)X (X = Cl, OAc) forms the molecule-based magnets of $[Mn^{III}$(porphyrin)$]$-$[TCNE]$ composition, while the reaction of $[Cr^{I}(C_6H_6)_2]Br$ and $(Me_2N)_2CC(NMe_2)_2Cl_2$, $[TDAE]Cl_2$, with **1** forms $[Cr^{I}(C_6H_6)_2][TCNE]$ and $[TDAE][TCNE]_2$, respectively. The structure of $[TDAE][TCNE]_2 \cdot MeCN$ was solved and refined in an orthorhombic unit cell at 21 °C [*I*222, $a = 10.2332(15)$, $b = 13.341(6)$, $c = 19.907(8)$ Å, $V = 2717.7$ Å^3, $Z = 4$; $D_{calcd} = 1.216$ g cm^{-3}, $R = 0.083$, $Rw = 0.104$] and exhibits ν_{CN} absorptions at 2193 (m), 2174 (s), and 2163 (s) cm^{-1} consistent with isolated $[TCNE]_2^{2-}$, in contrast to the aforementioned Tl^{I} bound $[TCNE]_2^{2-}$. The reaction of **2** with $[TDAE]Cl_2$ forms $[TDAE]^{2+}[TCNE]^{2-}$.

Keywords: crystal structure · electron transfer · magnetic ordering · thallium

Introduction

Tetracyanoethylene, TCNE, is an extremely versatile organic molecule that continues to be the focus of contemporary chemistry.[1–4] In addition to organic transformations, electron transfer salts of TCNE[5] have led to the development of new materials exhibiting bulk magnetic properties, for example ferromagnetism.[6, 7] Electron transfer salts have been prepared by direct electron transfer, acid–base reaction[8] with the strong acid H_2TCNE (pK_a 3.6),[9] or anion exchange. However, drawbacks exist for each of these methods, for example redox-inactive robust substituents are needed for the direct reaction with TCNE or difficulty in removal of a weaker acid (acetic acid) that may lead to unwanted reactions or impure products. The third method of anion exchange may result in contaminated products. Our continuing interest in synthesizing $[TCNE]^{\bullet-}$-based molecule-based magnets,[7] prompted us to develop a method to quantitatively exchange a halide with $[TCNE]^{\bullet-}$. Herein we report the preparation, chemical reactivity of $Tl^{I}[TCNE]$ and $Tl^{I}_2[TCNE]$ as well as the structures of $Tl^{I}[TCNE]$ and $[TDAE][TCNE]_2 \cdot MeCN$ [$TDAE = (Me_2N)_2CC(NMe_2)_2$].

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Results and Discussion

An ideal reagent to quantitatively exchange halide with $[TCNE]^{\bullet-}$ would be $Ag^{+}[TCNE]^{\bullet-}$. However, $Ag^{+}[TCNE]^{\bullet-}$

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cannot be prepared as the reaction of Ag^+ and $[TCNE]^{\bullet-}$ forms Ag^0 and $TCNE^0$.[5] Thallium(I) salts react like their corresponding silver(I) salts,[10] but are less redox active ($Tl^+ \rightarrow Tl^0 + e^- = -0.336$ V; $Ag^+ \rightarrow Ag^0 + e^- = 0.799$ V vs. SCE)[11] and $Tl^+[TCNE]^{\bullet-}$ (**1**) and $[Tl^+]_2[TCNE]^{2-}$ (**2**) were targeted for study.

$Tl^+[TCNE]^{\bullet}$ (**1**) is prepared from the 1:1 reaction of $Tl^I[PF_6]$ and $[nBu_4N]^+[TCNE]^{\bullet-}$[4, 12] under nitrogen leading to the quantitative formation of **1** as a microcrystalline purple precipitate. Complex **1** is quite stable as neither the reactivity nor the IR of microcystalline **1** changes upon exposure to ambient light or air; however, oxygen and water must be excluded when **1** is in solution due to the reactivity of the anion.[5] The presence of $[TCNE]^{\bullet-}$ is confirmed from the broad ν_{CN} absorptions [2191 (s) and 2162 (s) cm^{-1}] consistent with metal-bound $[TCNE]^{\bullet-}$, and neither TCNE [$>2200\ cm^{-1}$] nor $[TCNE]^{2-}$ [with bands $<2100\ cm^{-1}$].[13] The presence of $S = \frac{1}{2}$ $[TCNE]^{\bullet-}$ suggests magnetic behavior; however, **1** is diamagnetic at room temperature and an ESR signal is not observed. Diamagnetic $[TCNE]^{\bullet-}$ can arise from either σ-[14] or π-$[TCNE]^{\bullet-}$ dimerization;[15] however, the observed ν_{CN} absorptions for **1** are inconsistent with these formulations. Nonetheless, the purple color is indicative of a π dimer, although it lacks the typical three ν_{CN} absorptions.

The X-ray crystal structure of **1** has been determined at room temperature (Table 1). In spite of the very small specimen size, and a rotational twinning problem, a satisfactory structure was obtained. Tl is eight coordinate with a distorted square antiprismatic geometry (Figures 1a and b), and is bonded to seven $[TCNE]^{\bullet-}$s (six monodentate and one unprecedented chelating ligand). Hence, each $[TCNE]^{\bullet-}$ nitrogen bonds to seven thallium atoms, with the TlN distances in the range of 2.901 to 3.171 Å and an average of 3.020 Å for monodentate $[TCNE]^{\bullet-}$s and a range of 3.265 and 3.293 with an average of 3.279 Å for the bidentate $[TCNE]^{\bullet-}$ (Figure 1c). These distances exceed the sum of the ionic radii of Tl^I (1.49 Å[10]) and covalent radii for N (0.74 Å[16]); this suggests that the TlN bond is electrostatic in character.

Table 1. Summary of the crystallographic data for $Tl^I[TCNE]$ (**1**) and $[TDAE][TCNE]_2 \cdot MeCN$ (**3**).

	$Tl^I[TCNE]$ (**1**)	$[TDAE][TCNE]_2 \cdot MeCN$ (**3**)
formula	C_6N_4Tl	$C_{24}H_{27}N_{13}$
formula weight	332.47	497.572
space group	*C*2/*c*	*I*222
a	12.6966 (12)	10.2332 (15)
b	7.7599 (7)	13.341 (6)
c	15.5041 (15)	19.907 (8)
β	96.610 (5)	90
Z	8	4
V	1517.4 (2)	2717.7
ρ_{calcd}	2.911 g cm^{-3}	1.216 g cm^{-3}
$R(F_o)$ $(I > 1.96\sigma(I)$		0.083
$R_w(F_o)$ $(I > 1.96\sigma(I)$		0.104
R_1 (F_o^2) $(I > 2\sigma(I)$	0.0575	
$wR2$ (F_o^2) $(I > 2\sigma(I)$	0.0701	
T (K)	300	294
λ	0.71073 Å	1.54178 Å

The chemically equivalent $[TCNE]^{\bullet-}$ bond distance and angles are presented in Table 2 and are typical of $[TCNE]^{\bullet-}$.

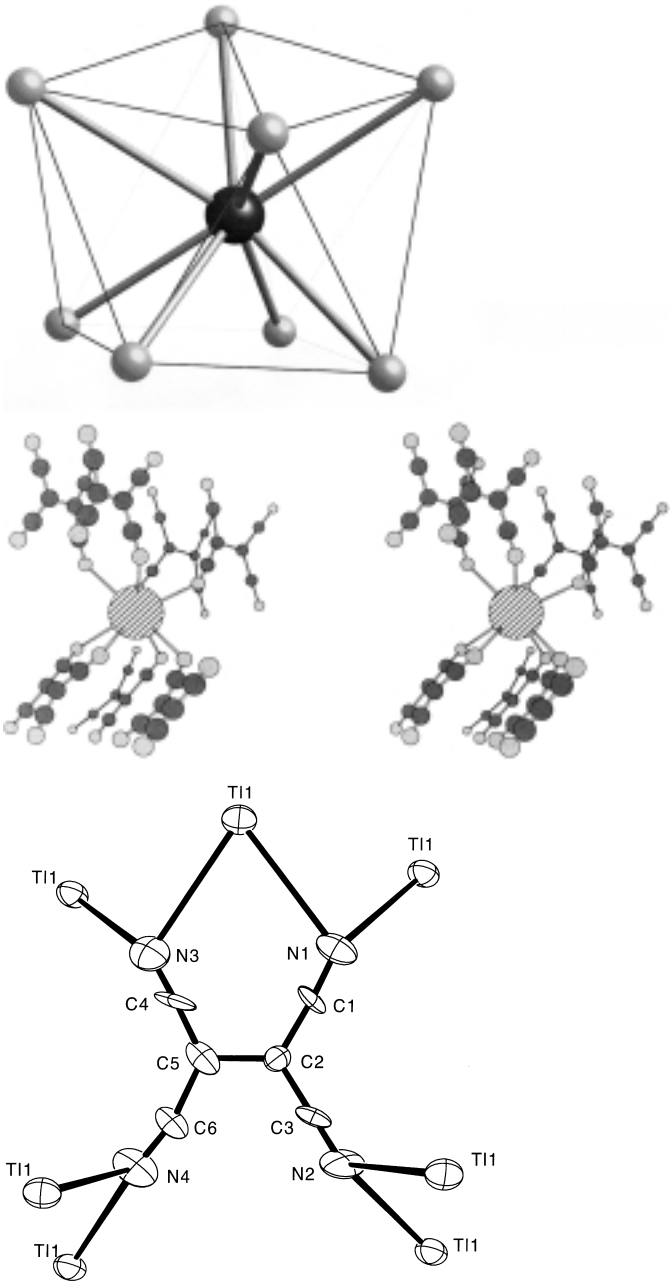

Figure 1. ORTEP (50% probability) atom labeling diagram showing the bonding about Tl^I and $[TCNE]^{\bullet-}$ in **1**. Distorted square antiprism Tl^I coordination sphere a), stereoview of Tl^I coordination sphere depicting the seven bound $[TCNE]^{\bullet-}$s b), and Tl^I bonding to a $[TCNE]^{\bullet-}$ c). Distances (Å): N1–C1 1.142(17), C1–C2 1.39(2), C2–C3 1.42(2), C2–C5 1.51(2), C3–N2 1.134(19), N3–C4 1.112(19), C4–C5 1.29(2), C5–C6 1.47(2), C6–N4 1.160(18), Tl1-4–N2 3.170(10), Tl1-1–N2 2.988(16), Tl1-2–N4 2.901(14), Tl1-3–N4 3.041(12), Tl1-4–N2 3.171(15), Tl1-5–N3 2.970(17), Tl1-7–N1 3.052(13), Tl1-8–N1 3.293(14), Tl1-8–N3 3.265(16). Angles (°): N1-C1-C2 174.3(19); C1-C2-C3 118.3(15), C1-C2-C5 118.8(15), C3-C2-C5 122.7(15), N2-C3-C2 177.0(18), N3-C4-C5 178(2), C4-C5-C6 129.5(17), C4-C5-C2 116.9(16), C6-C5-C2 112.2(16), N4-C6-C5 167(2).

The central C–C bond of 1.51 (2) Å corresponds to a substantially reduced double bond as expected for the 1.5 bond order and bonding to the Tl^Is. The $[TCNE]^{\bullet-}$s dimerize as $[TCNE]_2^{2-}$ and stack as zigzag 1-D chains, with 2.87 intra- and interdimer separations of 3.29 Å, respectively, Figure 2.

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Table 2. Average $[TCNE]^{\bullet-}$ bond distance (Å) and angles (°) for $Tl^{I}[TCNE]$ (**1**) and $[TDAE][TCNE]_2 \cdot MeCN$ (**3**).

Compound	$Tl^{I}[TCNE]$ (**1**)	$[TDAE][TCNE]_2 \cdot MeCN$ (**3**)
C≡N	1.137	1.145
C–CN	1.392	1.411
C–C	1.51	1.406
C-C≡N	174	179.5
C-C-CN	118	120
C-C-$C(CN)_2$[a]	6	3.8
intradimer separation	2.874	2.922

[a] Deviation from planarity.

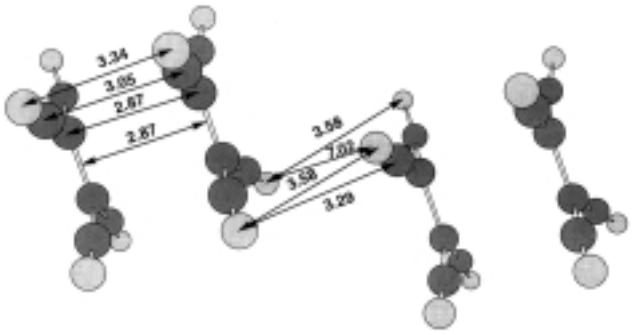

Figure 2. Intra- and interdimer $[TCNE]_2^{2-}$ interactions in $Tl^{I}[TCNE]^{\bullet-}$ (**1**).

Each $[TCNE]^{\bullet-}$ is twisted by 3.12°. The $[TCNE]^{\bullet-}$ is not planar as the CNs lie 5.5[16] and 7.3° (averaging 6.4°) outside the expected TCNE plane. This deviation from nonplanarity has been previously observed for $[Fe^{III}(C_5H_4)_2C_3H_6]_2[TCNE]_2$ (5.4°),[15b] $[Cr^{I}(C_6H_6)_2]_2[TCNE]_2$ (5.2°),[15a] $[Cr^{I}(C_6H_3Me_3)_2]_2$-$[TCNE]_2$ (6.0°),[15a] $K_2[TCNE]_2(glyme)_2$ (3.2°),[15c] α-$[TTF]_2$-$[TCNE]_2$ (2.5°),[15e] β-$[TTF]_2[TCNE]_2$ (4.0°),[15e] and $[TDAE]$-$[TCNE]_2$ (3.8°) (vide infra). The nonplanarity is attributed to greater sp^3 character on the central carbon atoms, and corresponds to a b_{3u} out-of-plane distortion.[15b]. The short intradimer separation suggests strong π bonding, greater sp^3 character of the central carbon atoms, and a diamagnetic $S_{tot} = 0$ ground state as observed. $Tl^{I}[TCNE]$ has the shortest intradimer separation reported for $[TCNE]_2^{2-}$ dimers.[15] The nonplanarity leads to intradimer 3.35 Å N···N interactions, which is 0.61 Å greater than the intradimer C···C separation.

An unique structural feature is the unprecedented chelating $[TCNE]^{\bullet-}$ forming a distorted planar pentagonal seven-membered ring. This ring has nearly linear CCN angles that average 173.9°, and N-Tl-N, Tl-N-C and NC-C-C angles of 70.6, 132.6, and 117.7° (Figure 1b). Note that the TlN distances for the chelate ring, which average 3.28 Å, are somewhat longer than those observed for the terminally bound $[TCNE]^{\bullet-}$s which average 3.085 Å.

Due to the good solubility of **1** and poor solubility of $Tl^{I}X$ (X = Cl, Br, OAc) in coordinating solvents such as acetonitrile, glyme, pyridine, and tetrahydrofuran, metathesis reactions can be executed at room temperature. Typically the reaction is carried out in glyme, for example a solution of **1** is added dropwise to a rapidly stirring solution of the halide. The reaction is stirred to completion, which can be monitored by IR spectroscopy. However, the exchange reaction is usually complete within minutes of addition, assuming both reagents are completely dissolved. The TlX precipitate is removed by filtration through diatomaceous earth and subsequent evaporation of the solvent from the filtrate affords the crude $[TCNE]^{\bullet-}$ products, which are recrystallized. This is most readily accomplished by dissolving the product in a less coordinating solvent and filtering again to remove any excess **1** and TlX, and precipitation yields the pure compounds. This reaction has been carried out with several organic and organometallic salts to illustrate the generality and utility of this reagent. The $[TCNE]^{\bullet-}$ ν_{CN} IR data of the products are summarized in Table 3. The reactions of $Mn^{III}TPPCl$ [$Mn^{II}TPP$ = *meso*-tetraphenylporphyrinatomanganese(II)] and $Mn^{III}TPPOAc$ to form [MnTPP][TCNE][18] demonstrates that both chlorides and acetates react with **1** to yield pure products. The reaction of $Mn^{III}TP'PCl$ [$Mn^{II}TP'P$ = *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphinatomanganese(II)] demonstrates that the redox sensitive phenoxy groups are not affected by this synthetic methodology which thwarted the preparation of [MnTP'P][TCNE] in the past.[8] The reactions of **1** with $[Cr^{I}(C_6H_6)_2]Br$ to form $[Cr^{I}(C_6H_6)_2]$-[TCNE][15a] and $[TDAE]Cl_2$ (2:1) to form $[TDAE]^{2+}$-$[TCNE]_2^{2-} \cdot MeCN$,[15d] (**3**) demonstrates the generality of synthon **1**. Furthermore, the structure of **3** was determined, Table 1.

Complex **3** consists of isolated $[TDAE]^{2+}$ cations and isolated $[TCNE]_2^{2-}$ dianions (Figure 3). The $[TDAE]^{2+}$ distances and angles as well as torsion angle of 61.45° are similar to that observed in $[TDAE]X_2 \cdot 2H_2O$ (X = Cl, Br),[19] and 1:1 [TDAE][TCNE][15d] while the TCNE distances and angles are comparable to those reported for **1**, Table 2, and others.[15] The $[TCNE]^{\bullet-}$s dimerize as $[TCNE]_2^{2-}$ and form 1-D chains, with intra- and interdimer centroid-to-centroid separations of 2.922 and 3.558 Å, respectively, Figure 4a. The $[TCNE]^{\bullet-}$s deviate from planarity by 3.8° as has been previously observed for $[Fe^{III}(C_5H_4)_2C_3H_6]_2[TCNE]_2$ (5.4°),[15b] $[Cr^{I}(C_6H_6)_2]_2$-$[TCNE]_2$ (5.2°),[15a] $[Cr^{I}(C_6H_3Me_3)_2]_2[TCNE]_2$ (6.0°),[15a] $K_2[TCNE]_2(glyme)_2$ (3.2°),[15c] α-$[TTF]_2[TCNE]_2$ (2.5°),[15e]

Table 3. Examples of ν_{CN} absorptions of $[TCNE]^{\bullet-}$ salts prepared from $Tl^{I}[TCNE]$ (**1**) and $Tl^{I}_2[TCNE]^{2-}$ (**2**) and those reported in the literature.

Compound	$\tilde{\nu}_{CN}$ (cm^{-1}) Literature values	$\tilde{\nu}_{CN}$ of product synthesized by $Tl^{I}[TCNE]$ (**1**)	$\tilde{\nu}_{CN}$ of product synthesized by $Tl_2[TCNE]$ (**2**)
$[Mn^{III}TPP][TCNE]$[a]	2192 (m), 2147 (s)[19]	2193 (m), 2147 (s)	–
$[Mn^{III}TPP][TCNE]$[b]	2192 (m), 2147 (s)[19]	2192 (s), 2146 (s)	–
$[Mn^{III}TP'P][TCNE]$[a]	2197 (m), 2133 (s)[8]	2197 (m), 2129 (s)	–
$[TDAE][TCNE]_2$[a]	2193 (m), 2174 (s), 2163 (s)[15d]	2195 (m), 2172 (s), 2162 (s)	–
$[Cr(C_6H_6)_2][TCNE]$[c]	2183 (s), 2144 (s)[15a]	2185 (s), 2146 (s)	–
[TDAE][TCNE][c]	2144 (s), 2078 (s)[15d]	–	2144 (s), 2076 (s)

[a] From the chloride. [b] From the acetate. [c] From the bromide.

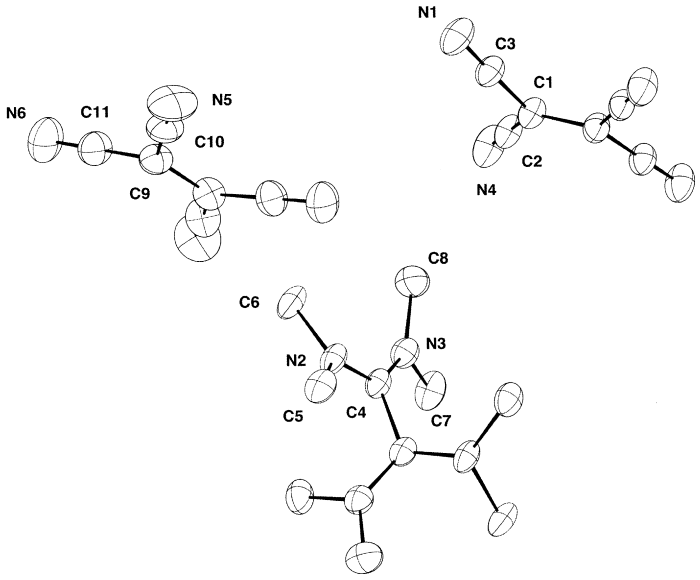

Figure 3. Atom labeling and 35% probability ellipsoids for $[TDAE]^{2+}$ and $[TCNE]^{-}$ in $[TDAE][TCNE]_2 \cdot MeCN$ (**3**). C4–C4′ 1.513(9), C4–N2 1.317(6), C4–N3 1.324(6), C5–N2 1.482(7), C6–N2 1.473(7), C7–N3 1.471(6), C8–N3 1.466(8), C4′-C4-N2 116.4(5), C4′-C4-N3 117.8(5), N2-C4-N3 125.8(4), C4-N2-C5 – 123.0(4), C4-N2-C6 122.8(4), C5-N2-C6 114.2(4), C4-N3-C7 120.1(4), C4-N3-C8 123.9(4), C7-N3-C8 116.0(5).

and β-$[TTF]_2[TCNE]_2$ (4.0°),[15e] and 6.4° for **1** (vide supra). The intradimer interactions are rotated by 10.8° with the N···N separations of 3.20 and 3.35 Å (Figure 4b). The interdimer TCNEs are rotated about the CC centroid by 59.1° and the distances range from 3.39 to 3.68 Å and have a weak contact at the nitrile carbons. The closest contact of 2.59 Å is between a nitrogen of TCNE to a hydrogen of TDAE, which can be considered as a weak hydrogen-bonding interaction (C6-H62-N1 145°, C6–N1 3.41 Å). The C3-N1···H62 angle is 103°; this

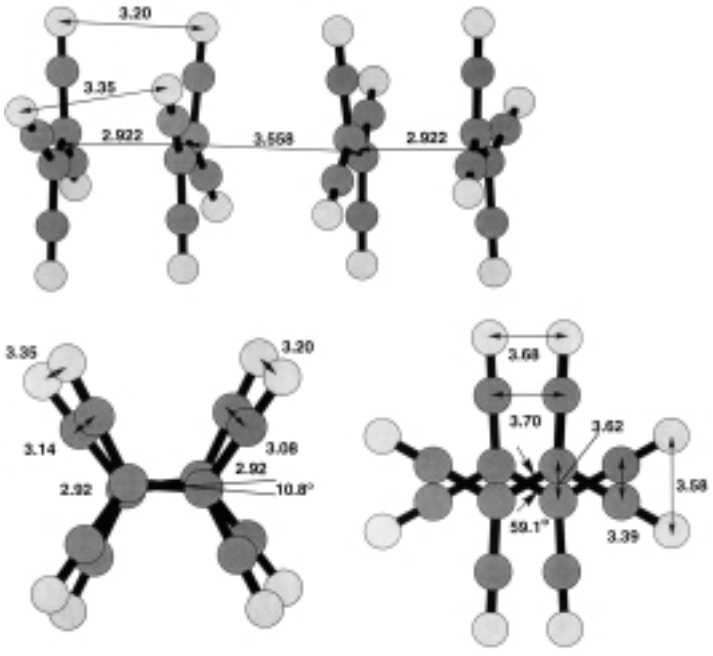

Figure 4. Intra- (a, b) and interdimer (a, c) $[TCNE]_2^{2-}$ interactions in $[TDAE][TCNE]_2 \cdot MeCN$ (**3**).

value is slightly larger than those observed for the hydrogen bonds between $[TDAE]^{2+}$ and the C–N π bonds of the $[TCNE]^{2-}$ in [TDAE][TCNE].[15d]

$[Tl^+]_2[TCNE]^{2-}$ (2) is prepared from the reaction of $Tl^I[PF_6]$ and $[TDAE]^{2+}[TCNE]^{2-}$ (2:1)[15d] in hot acetonitrile in greater than 98% yield. This light pink solid is only sparingly soluble even in strongly coordinating solvents, such as MeCN, pyridine, and glyme, even at reflux. The presence of $[TCNE]^{2-}$ is confirmed from the broad ν_{CN} absorptions at 2219 (w), 2194 (vw), 2139 (m), and 2057 (s) cm^{-1} consistent with metal-bound $[TCNE]^{2-}$ as these values are in good agreement with those observed for $Na_2[TCNE]$ [2251 (w), 2211 (w), 2162 (m), 2145 (w), 2091 (s), 2073 (m), and 2051 (w) cm^{-1}],[13] and differ from the 2143 (m) and 2078 (s) cm^{-1} values reported for isolated $[TCNE]^{2-}$ in [TDAE][TCNE][15d] and $[Co(C_5Me_5)_2]_2[TCNE]$[13]. Single crystals of **2** suitable for X-ray studies could not be isolated. Due to the proclivity of Tl^I for high coordination (see **1** above) and fewer donor atoms to bind to Tl^I due to the 2:1 ratio, a complex electrostatic structure consistent with the poor solubility is expected.

To demonstrate the utility of **2** 1:1 the reaction with $[TDAE]Cl_2$ led to [TDAE][TCNE].[15d] This reaction utilized a Soxhlet apparatus, with **2** being continuously extracted into a solution of the halide in boiling acetonitrile. Complex **2** also has limited solubility in glyme and pyridine and is insoluble in most other common organic solvents.

Conclusion

In summary, two versatile synthons have been developed and show great promise to access $[TCNE]^{\bullet-}$ and $[TCNE]^{2-}$ complexes that would otherwise be very difficult to obtain pure. These easily prepared reagents can be stored for long periods of time without degradation and have the advantage over the putative Ag^I salts of greater redox stability. We are currently characterizing other Tl^I salts of common electron acceptors such as 7,7,8,8-tetracyano-*p*-quinodimethane, TCNQ, hexacyanobutadiene, HCBD, and anils to take advantage of what thallium(I) salts offer.

Experimental Section

Synthesis: $Tl^I[PF_6]$ (Strem) was dried in vacuo at 60 °C overnight and used without further purification. The $[nBu_4N][TCNE]$ was prepared by literature methods[12] and was recrystallized before use from hot acetonitrile. Tetrakis(dimethylamino)ethylene, TDAE, (Aldrich) was used as received. The $[TDAE]Cl_2$,[19] [TDAE][TCNE],[15d] and $[TDAE][TCNE]_2$[15d] were prepared by literature methods. $Mn^{III}TPPOAc$,[17] $Mn^{III}TPPCl$,[17] and $Mn^{III}TP'PCl$[8] were prepared by literature methods.[20] $[(Cr^IC_6H_6)_2]Br$ was kindly provided by Prof. T. G. Richmond and was used after recrystallization from THF.

All manipulations were carried out in a vacuum atmospheres DriLab under a purified N_2 atmosphere. All glassware was flame dried before use. All solvents were distilled under N_2 from appropriate drying agents and stored in the DriLab. Dichloromethane and acetonitrile were distilled twice from CaH_2. THF and glyme were distilled from sodium benzophenone ketyl and pyridine was predried over 4 Å molecular sieves and distilled twice from KOH.

Synthesis of $Tl^+[TCNE]^{\bullet-}$ (1): A solution of $[nBu_4N][TCNE]$ (265 mg, 0.715 mmol) in dichloromethane (10 mL) was added dropwise to a rapidly

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stirring solution of $Tl^{I}[PF_6]$ (50 mg, 0.716 mmol) in acetonitrile (5 mL) at room temperature. The immediate dark purple precipitate was collected on a fritted glass disk after stirring for 10 min to yield **1** (0.235 mg, 99%, 0.707 mmol). Crystals were grown by slow diffusion of acetonitrile solutions of $Tl^{I}[PF_6]$ and of $[n\mathrm{Bu}_4\mathrm{N}][\mathrm{TCNE}]$ in an H-tube at room temperature. Elemental analysis: calcd (%) C 21.67, H 0.0, N 16.86; found (%) C 21.72, H 0.0, N 16.73; IR: $\tilde{\nu}_{CN}$ 2191 (s), 2162 (s), $\tilde{\nu}_{CC}$ 1360 (s).

Tetraphenylporphyrinatomanganese(III) tetracyanoethenide, $[Mn^{III}PP][TCNE]$, via $Mn^{III}TPPCl$ as an example of the general procedure for reactions with complex 1: $Tl^{I}[TCNE]$ (**1**, 24 mg, 723 mmol) in THF (10 mL) was added dropwise at room temperature to a rapidly stirring solution of $Mn^{III}TPPCl$ (50 mg, 712 mmol) in THF (15 mL). An immediate precipitate was observed and the mixture was allowed to stir for an additional 10 min. The TlCl precipitate was collected by filtration through diatomaceous earth (Celite) and the solvent was removed under reduced pressure. The $[Mn^{III}TPP][TCNE]$ formed was recrystallized from boiling toluene and the $\tilde{\nu}_{CN}$ matched the literature values, Table 3.

$[Mn^{III}TPP][TCNE]$ via $Mn^{III}TPPOAc$: The above reaction was repeated with $Mn^{III}TPPOAc$. The $\tilde{\nu}_{CN}$ matched the literature values, Table 3.

$[Mn^{III}TP'P][TCNE]$, via $Mn^{III}TP'PCl$: The first reaction was repeated with $Mn^{III}TP'PCl$. The $\tilde{\nu}_{CN}$ matched the literature values, Table 3.

$[Cr^{I}(C_6H_6)_2][TCNE]$: The first reaction was repeated with $[Cr^{I}(C_6H_6)_2]Br$. The $\tilde{\nu}_{CN}$ matched the literature values, Table 3.

$[TDAE][TCNE]_2$ (1:2) (3): The first reaction was repeated with $[TDAE]Cl_2$ and $[n\mathrm{Bu}_4\mathrm{N}][\mathrm{TCNE}]$. The $\tilde{\nu}_{CN}$ matched the literature values, Table 3. Crystals of $[TDAE][TCNE]_2 \cdot MeCN$ (**3**) were obtained from acetonitrile solutions of TDAE which was slowly added to the solution of TCNE in a 1:2 stoichiometric ratio in a 20 mL scintillation vial. This solution was then placed into a $-22\,^{\circ}C$ freezer and allowed to stand for one week. The dark crystals were then collected as thick needles.

$Tl_2[TCNE]$ (2): A hot acetonitrile solution (70 °C, 10 mL) of $[TDAE]^{2+}[TCNE]^{2-}$[15a] (47 mg, 1.43 mmol) was stirred rapidly in a 50 mL Erlenmeyer flask. A 70 °C acetonitrile solution (2 mL) of $Tl^{I}[PF_6]$ (100 mg, 0.287 mmol) was added dropwise to this solution and a pink precipitate was collected on a fritted glass disk, and washed with room temperature portions (3×5 mL) of acetonitrile. The yield was 99% (76 mg; 0.142 mmol). Elemental analysis: calcd (%): C 13.42, H 0.0, N 10.44; found (%): C 13.67, H 0.22, N 10.43; IR: $\tilde{\nu}_{CN}$ 2219 (w), 2194 (vw), 2139 (m), 2057 (s).

$[TDAE][TCNE]$ (1:1): The above reaction was repeated with $[TDAE]Cl_2$ and 1.0 equiv $[n\mathrm{Bu}_4\mathrm{N}][\mathrm{TCNE}]$. This was recrystallized twice from acetonitrile The $\tilde{\nu}_{CN}$ matched the literature values, Table 3.

X-ray structure determination: Isolation of crystals suitable for X-ray diffraction of **1** was difficult, and only very-small ($0.08 \times 0.08 \times 0.08$ mm) black block crystals were obtained. Data were collected at room temperature on a Bruker SMART 1000/P4 CCD area detector ($Mo_{K\alpha}$ radiation) at 2000 W. A summary of data collection parameters is given in Table 1. The Bruker rotational twinning software package (TWINDX, TWUTIL, and TWROT)[21a] was used to analyze the two-fold twinning law (180° rotational about the 110 direction) and to calculate orientation matrices for integration. The frames were integrated twice (once for each twin component) with the Bruker SAINT program[21b] using a narrow-frame integration algorithm. This process produced a total of 4362 reflections to a maximum 2θ angle of 50.00° (0.84 Å resolution, completeness = 97.2%). The crystal structure was solved by direct methods using SHELXTL[21c] followed by full-matrix least-squares refinement on F_o^2, using the space group $C2/c$, with $Z = 8$ for the formula unit C_6N_4Tl. The Bruker TWHKL[21a] program was then used to merge the data sets into one file suitable for twin refinement with SHELXTL.[21c] The final anisotropic full-matrix least-squares refinement on F^2 for 1300 independent reflections converged at $R1 = 5.57\%$, $wR2 = 7.01\%$ and a goodness-of-fit of 1.061. The twinning parameter converged at 0.46. The largest peak on the final difference map was 1.145 $e^- Å^{-1}$. $F(000)$ is 1160 e^-. The final cell constants are based upon the refinement of the XYZ-centroids of 1658 reflections above $20\sigma(I)$.

Crystals of $[TDAE][TCNE]_2 \cdot MeCN$ (**3**) suitable for X-ray diffraction were obtained as thick black needles by recrystallization from MeCN at $-22\,^{\circ}C$. Data were collected on a Nonius CAD-4U diffractometer ($Cu_{K\alpha}$ radiation). Cell constants and an orientation matrix for the data collection were obtained by least-squares refinement of 25 unique reflections; a summary of data collection parameters is given in Table 1. An empirical absorption correction was applied to the data (transmission factors of 0.96–1.0; $\mu = 0.59\ mm^{-1}$). Systematic absences and subsequent least-squares refinement were used to determine the space group as the noncentrosymmetric $I222$. The crystal structure was solved by direct methods using SIR-92[21d] followed by full-matrix least squares refinement (based on F_o; 1196 data for which $I/\sigma(I) > 1.96$, 169 parameters) of positional and anisotropic displacement parameters for all nonhydrogen atoms (H atoms fixed) using the Oxford CRYSTALS program suite;[21e] $R = 8.27\%$; $Rw = 10.39\%$. The asymmetric unit of the crystal contains one half-cation, two half-anions, and one-half MeCN (disordered); all four species are located on crystallographic two-fold axes. The largest peak on the final difference map was 0.30 $e^- Å^{-3}$.

Physical methods: The elemental analysis was performed by Atlantic Microlab for C, H, and N. The IR spectra were collected on a BIO-RAD FTS-40 with 2 cm^{-1} resolution using the WIN-IR software package as Nujol mulls on NaCl disks. The EPR was collected on a Bruker ES300. The magnetic susceptibility was measured on a Quantum Design SQUID 5XL magnetometer at 300 Kelvin in a 1 T applied magnetic field.

X-ray crystal structure analysis: Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114260 (**3**) and CCDC-114261 (**1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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