METAL COMPOUNDS OF THE TCNX REDOX SYSTEMS – FROM ELECTRON TRANSFER TO SPIN DISTRIBUTION AND MAGNETISM

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Dedicated to the memory of Jaime Returet, Dr rer. nat. graduate from the Universitaet Stuttgart in 1972

ABSTRACT

The TCNX ligands, TCNE, TCNQ, and TCNB (Scheme 1) to bridge up to four metal centers in discrete molecular complexes or coordination polymers. In addition, the highly non-innocent TCNX ligands may exist in neutral π acceptor form, as stable monoanionic radicals, or as diatomic, which has generated a unique coordination chemistry (Scheme 2) which has found potential applications in molecular magnetism 25, organic conductor research 4, and in concepts for molecular computing 7.

Keywords: Electron transfer, Non-innocent ligands, Spin distribution, TCNQ, Tetracyanoethene

The ability of the π conjugated tetranuclear ligands TCNE, TCNQ and TCNB (Scheme 1) to bridge up to four metal centers (Scheme 2) and to exist in the neutral π acceptor form, as stable monoanionic radicals, or as diatomic (Scheme 3) has generated a unique coordination chemistry (Scheme 2) which has found potential applications in molecular magnetism 25, organic conductor research 4, and in concepts for molecular computing 7.

Scheme 1

\[
\text{Tetracyanoethene (TCNE)} \\
\text{7,7,8,8-Tetracyano-quinodimethane (TCNQ)} \\
\text{1,2,4,5-Tetracyanobenzene (TCNB)}
\]

Scheme 2

\[
\begin{align*}
\text{(μ₄-TCNQ)(ML₄)} & \quad \text{π complex, side-on, C≡C} \quad \text{M} \\
\text{TCNE + ML₄} & \quad \text{TCNE + ML₄} \\
\text{(μ₄-TCNQ)(ML₄)} & \quad \text{σ complex, end-on, C≡N=M} \\
\text{ML₄} & \quad \text{ML₄} \\
\text{[μ₄-TCNQ(ML₄)]} & \quad \text{discrete 1,1-, cis-1,2-, or trans-1,2-dimers (n = 1)} \\
\text{[μ₄-TCNQ][(CO)₅]} & \quad \text{ML₄} \\
\text{[μ₄-TCNQ][(CO)₅]} & \quad \text{[μ₄-TCNQ][(CO)₅]} \\
\text{[μ₄-TCNQ][(CO)₅]} & \quad \text{[μ₄-TCNQ][(CO)₅]}
\end{align*}
\]

Scheme 3

\[
\begin{align*}
\text{(TCNQ)(ML₄)} & \quad \text{(TCNQ)(ML₄)} \\
\text{(TCNQ)(ML₄)} & \quad \text{(TCNQ)(ML₄)} \\
\text{(TCNQ)(ML₄)} & \quad \text{(TCNQ)(ML₄)}
\end{align*}
\]

Whereas only mono- and dinuclear discrete compounds could be obtained with organometallic complex fragments of Ti 5, V 6, Cr 4 and Co 1 it has been possible to establish the full coordination saturation in tetranuclear complexes of manganese (TCNE, TCNQ) 21,22 rhodium (TCNE, TCNQ, TCNB) 23 and copper (TCNE, TCNQ, TCNB) 24. For iron there has been a report by Diaz and Arancibia describing the complex \(\{\mu₄-TCNQ[Fe(dppe)(C,H₅)_2]\} 4+\), dppe = 1,2-bis(diphenylphosphino)ethane 25 while we could recently describe \(\{\mu₄-TCNQ[Fe(CO)₅](C,H₅)_2]\} 4+ 13. Except for the latter and for \(\{\mu₄-TCNQ[Re(CO)₅(bpy)]\} 4+\) all these compounds showed strong evidence from spectroscopy and electrochemistry for considerable metal-toligand electron transfer δ in the ground state unit (μ₄-TCNQ)(M₄-δL₄) (Scheme 4).

Scheme 4

\[
\begin{align*}
\text{(μ₄-TCNQ)(ML₄)} & \quad \text{↔ (μ₄-TCNQ)(ML₄)}\quad \text{↔ (μ₄-TCNQ)(ML₄)} \\
\text{(μ₄-TCNQ)(ML₄)} & \quad \text{(μ₄-TCNQ)(ML₄)}\quad \text{(μ₄-TCNQ)(ML₄)}
\end{align*}
\]

In addition to the discrete tetranuclear complexes mentioned above, several coordination polymers were reported with μ₄-TCNE 26 or μ₄-TCNQ 27 of which some exhibit structural evidence for intramolecular metal-to-ligand electron transfer.

Such coordination polymers have found particular attention because the first room-temperature molecule-based magnet, V₂(TCNE)₆, X solvent, is assumed to consist of a three-dimensional coordination polymeric network involving the bridging TCNE anion radical 28,29. Unfortunately, the absence of detailed structural information beyond XANES/EXAFS data 30 predicted a better understanding of this fascinating amorphous material. Infrared spectroscopy has also been extensively used in analyzing the coordination mode and/or oxidation state of TCNE 21 in non-crystalline materials. It should be added that another (TCNE)-containing compound, [Fe₃(C₆H₅)₅]TCNE, had been presented by Miller et al. as a ferromagnetic material (\(T_c = 4.2\) K) 31, however, the anion radical and the decamethylferrocenium cation are not directly coordinated in this ion-pair compound.

The importance to establish and identify “physical oxidation states” 32 in complexes involving non-innocent 33 ligands is thus obvious, especially when dealing with oligomeric compounds of redox-active molecular bridges. Using group 8 metals we have focussed on tetranuclear complexes of TCNE (TCNE, TCNQ, TCNB) with two classical, widely used d⁸ metal complex fragments, the readily oxidizable [Ru(NH₃)₅Cl]⁺ (Scheme 5, cf. the mixed-valent Creutz-Taube ion 34), and the organometallic prototype [Fe(CO)₅(C₆H₅)]⁺ (Scheme 6).

Scheme 5

\[
\begin{align*}
\text{[H₃N]₅Ru₂(NC)₂} & \quad \text{C≡C} \quad \text{[CRu₂(NC)₂(NH₃)]₅} \\
\text{[H₃N]₅Ru₂(NC)₂} & \quad \text{[CRu₂(NC)₂(NH₃)]₅} \\
\text{[H₃N]₅Ru₂(NC)₂} & \quad \text{[CRu₂(NC)₂(NH₃)]₅}
\end{align*}
\]

Experimental evidence including electrochemical potentials, magnetic behavior 35, charge transfer absorption spectra and infrared vibrational spectroscopy has suggested negligible metal-to-ligand electron transfer in the ground states of \(\{\mu₄-TCNQ[Fe(CO)₅](C₆H₅)_2]\} 4+ whereas extensive such interaction according to formation \(\{\mu₄-TCNQ[Fe(CO)₅](C₆H₅)_2]\} 4+ was proposed for the pentaammineruthenium systems with TCNE and TCNQ 36. In the absence of experimental structures e.g. from single crystal X-ray diffraction, DFT methodology was recently applied to confirm and clarify the situation in such discrete model complexes for coordination polymeric
As with the crystallographically confirmed tetraruthenium complex \((\mu_4^2\text{TCNQ})\text{[Re(bpy)(CO)\text{C}]_{2}}\) the similar tetraruthenium species \((\mu_4^2\text{TCNX})\text{[Fe(CO)\text{C}]_{2}}\), \(\text{TCNX} = \text{TCNE}, \text{TCNQ}\), were calculated with \(\text{TCNX}\) ligand parameters which suggest only small metal-to-ligand electron transfer in the ground state. Most conspicuously, the \(\text{TCNX}\) ligands remain virtually coplanar, and the bond distances correspond to the bond orders as indicated in Scheme 1. Slight differences in relation to the free ligands arise from multiple metal coordination. In contrast, significantly reduced TCNE and TCNQ exhibit a twisted framework with considerably decreased CC double bonds. Effects of multiple metal coordination can be studied separately for the complexes of much less acceptor TCNB which is more difficult to reduce (by more than 1 V) than TCNE or TCNB and which is unable to twist into a non-planar state.

DFT calculations of the complexes \((\mu_4^2\text{TCNX})\text{[Ru(NH\text{C})\text{C}]_{2}}\), \(\text{TCNX} = \text{TCNE}, \text{TCNQ} \), yield very different results. The lowest energy structures correspond to triplet states with considerably twisted moieties \(\text{RNCCCNRu}\) and \(\text{C}_2\text{H}_4\) (TCNQ). The twist angle is close to 90° for the complex with TCNQ. Accordingly, the original CC double bonds are lengthened to 1.544 Å (TCNE complex) and 1.508 Å (TCNQ complex, exocyclic CC). The compounds are thus best described by the limiting case 1,1° coupled (Ru–Ru)–o coupled (Ru–Ru) which is unable to twist into a non-planar state.

Using DFT calculations for the remarkable tetraruthenium complex ions \((\mu_4^2\text{TCNX})\text{[Ru(NH\text{C})\text{C}]_{2}}\), \(\text{TCNX} = \text{TCNE}, \text{TCNQ} \), TCNQ and TCNE can thus provide consistent computational evidence for the model invoking weakly interacting pairs of strongly (NCCCN)–o coupled (RuRu) containing dimers. The near orthogonality in the triplet ground state configurations and the computed C–C bond distances point to extensive intramolecular metal-to-ligand electron transfer in contrast to the (TCNQ) and (TCNE) complexes. The twist angle is close to 90° for the complex with TCNQ. Accordingly, the original CC double bonds are lengthened to 1.544 Å (TCNE complex) and 1.508 Å (TCNQ complex, exocyclic CC). The compounds are thus best described by the limiting case 1,1° coupled (Ru–Ru)–o coupled (Ru–Ru) which is unable to twist into a non-planar state.

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