Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006

To cite this article: Erik J. Brandon, Ken-Ichi Sugiura, Atta M. Arif, Louise Liable-sands, Arnold L. Rheingold & Joel S. Miller (1997): The Structure of Several meso Tetraarylporphinato-Manganese(III) Tetracyanoethenide Complexes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 305:1, 269-278

To link to this article: http://dx.doi.org/10.1080/10587259708045064

Mol. Cryst. Liq. Cryst., 1997, Vol. 305, pp. 269–278
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THE STRUCTURE OF SEVERAL *meso* TETRAARYLPORPHINATO-MANGANESE(III) TETRACYANOETHENIDE COMPLEXES

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Abstract The structures of several uniform ···D$^+$A$^{\cdot-}$D$^+$A$^{\cdot-}$D$^+$A$^{\cdot-}$··· (D: S = 2 Mporphryin; A: S = 1/2 TCNE) chain compounds with the [TCNE]$^{\cdot-}$ *trans*-μ_2 bonded to two Mn(III)'s exhibiting cooperative magnetic properties have been studied by single crystal x-ray diffraction. Herein we summarize the structures obtained for these compounds and their νCN infrared absorptions.

INTRODUCTION

The study of molecule-based magnetic materials based upon organic radicals spins is an area of increasing interdisciplinary research worldwide.[1,2] Ferro- or ferrimagnetic ordering has been observed for several classes of materials possessing the [TCNE]$^{\cdot-}$ (TCNE = tetracyanoethylene) radical anion. For example, [FeCp*$_2$]$^{\cdot+}$[TCNE]$^{\cdot-}$ (Cp* = pentamethylcyclopentadienide) is a ferromagnet with a Curie (critical or ordering) temperature, T_c, of 4.8 K,[3] while V(TCNE)$_x$·y(solvent) (T_c ~ 400 K)[4] and [MnTPP]$^+$[TCNE]$^{\cdot-}$·2PhMe (TPP = *meso*-tetraphenylporphinato),[5] (T_c = 14 K) are ferrimagnets. Current research focuses toward establishment of relationships between structure and magnetic phenomena, particularly in the correlation of dimensionality, connectivity and the critical temperature of the material.[1,2] The clathrate nature of this class of materials[6] enables the introduction of different solvents into the structure to alter the inter- and intrachain couplings and subsequently the ordering temperatures. We have prepared [MnTPP][TCNE]·xS [S = PhR (R = H, Me, Et, Cl, F, Br, NO_2, CN), $C_6H_4R_2$ (R = Me, Cl), and $C_6H_3R_3$ (R = Me, Cl)] and have obtained crystals structure for [MnTPP][TCNE]·xS{S = 1,2-dimethylbenzene [x = 1, **A**),[6] 1,2-dichlorobenzene (x = 4, **B**[6]), 1,2,4-trichlorobenzene, **C**] in addition to that reported for S = PhMe, x = 2, **D**.[5] Additionally, the [TCNE]$^{\cdot-}$ salts of 4-phenyl-substituted

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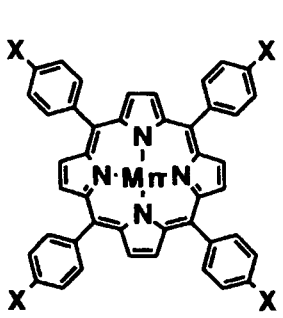
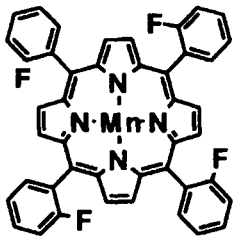
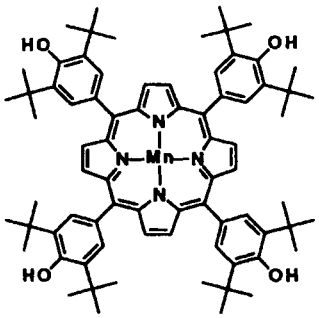
[MnTPP]$^+$'s, *i. e.*, **1** (**E** - **H**), 2-fluorophenyl substituted [MnTPP]$^+$, *i. e.*, **I**, and *meso*-tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)porphinatomanganese(III), MnTP'P,[7] **J**, have been studied by single crystal x-ray and herein we report the structures of **A-J**.



1 X = Cl, MnTClPP, **E**
1 X = Me, MnTtolP, **F**
1 X = OMe, MnTOMePP, **G**
1 X = Bu^t, MnTBu^{t}PP, **H**



I



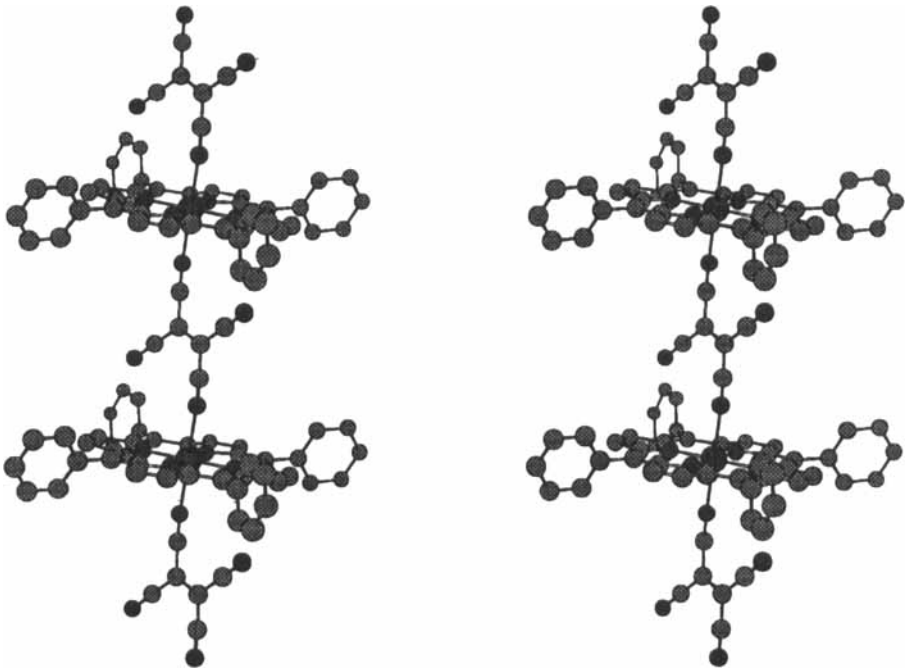
J

Each of these [Mpor]$^+$[TCNE]$^{\cdot-}$ salts possess an uniform $\cdots D^+A^{\cdot-}D^+A^{\cdot-}D^+A^{\cdot-}\cdots$ (D: S = 2 Mpor; A: S = 1/2 TCNE) chain with the [TCNE]$^{\cdot-}$ *trans*-μ_2 bonded to two Mn(III)'s, Stereoviews 1 - 10. **A** - **J** belong to the $P\bar{1}$ (Z = 1) space group with an unit cell axis being the chain direction the its length being the intrachain Mn···Mn separation. The unit cell parameters are listed in Table 1. Table 2 lists the Mn-NC and intrachain Mn···Mn distances, the Mn-N-C and Mn-Mn-N angles as well as the dihedral angle formed by the MnN_4 and TCNE planes. Each of these bonding modes have characteristic υCN infrared absorptions, Figure 12. The magnetic properties of **A**,[6] **B**,[6] **D**,[5,8] and **J**[7] have been reported while in addition to more detailed studies the determination of the magnetic properties of the other salts are in progress.

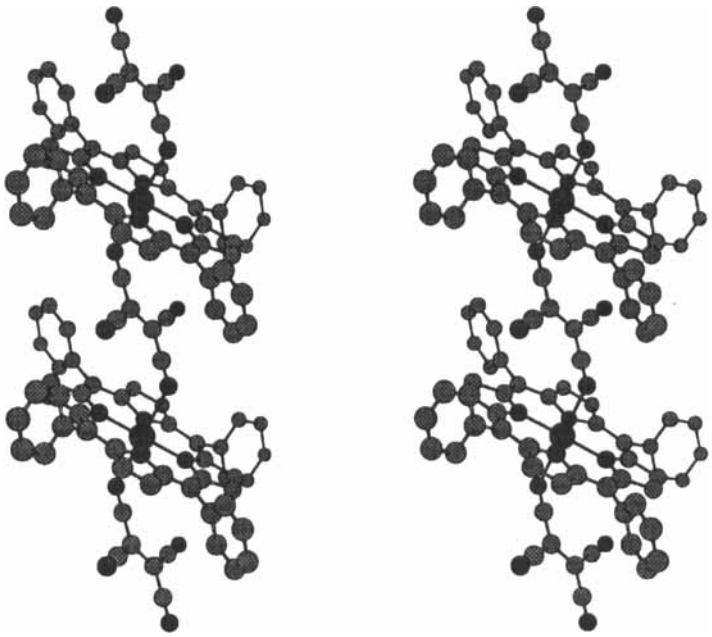
TABLE 1 Unit Cell Parameters[a] for **A** - **J**.

Compound	*a*, Å	*b*, Å	*c*, Å	α, deg	β deg	γ deg	*V*, Å^3
A	9.261	*10.218*	13.294	98.880	94.630	110.640	1151
B	*9.489*	12.865	12.890	92.660	106.190	105.470	1444
C	*9.588*	10.885	14.475	106.912	99.137	107.511	1327
D	*10.116*	11.008	12.498	108.150	98.040	67.920	1224
E	10.171	*10.189*	14.522	107.510	85.580	111.510	1334
F	10.082	14.515	*10.280*	105.870	111.110	84.810	1350
G	9.896	*10.256*	14.447	82.640	92.400	109.070	1374
H	*10.189*	15.822	16.195	83.410	108.140	100.570	2435
I	*10.185*	11.081	12.378	107.550	82.880	111.090	1243
J	*8.597*	14.756	17.573	101.160	100.560	96.370	2125

[a] The intrachain Mn···Mn separation is italicized



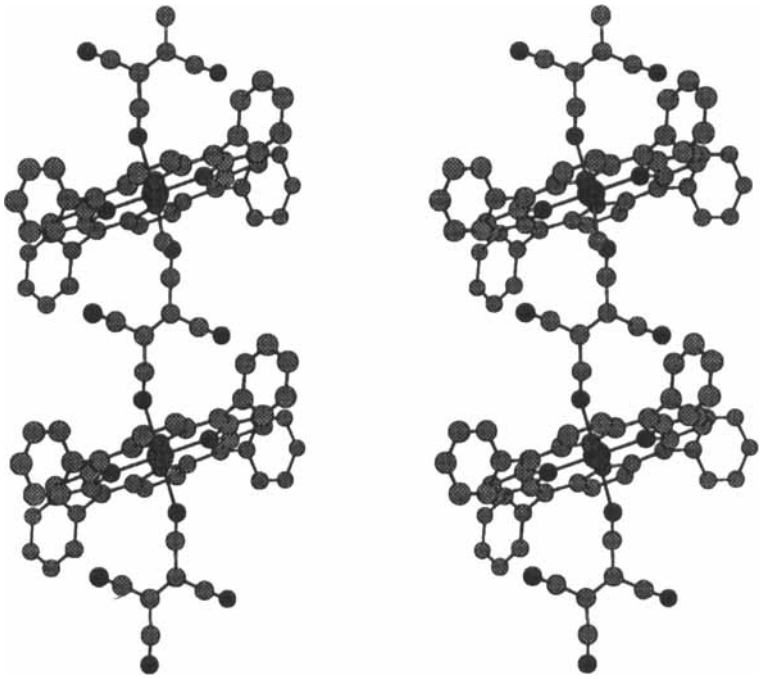
STEREOVIEW 1. **A**, [MnTPP][TCNE]·1,2-$C_6H_4Me_2$ (the solvents and Hs are omitted for clarity).



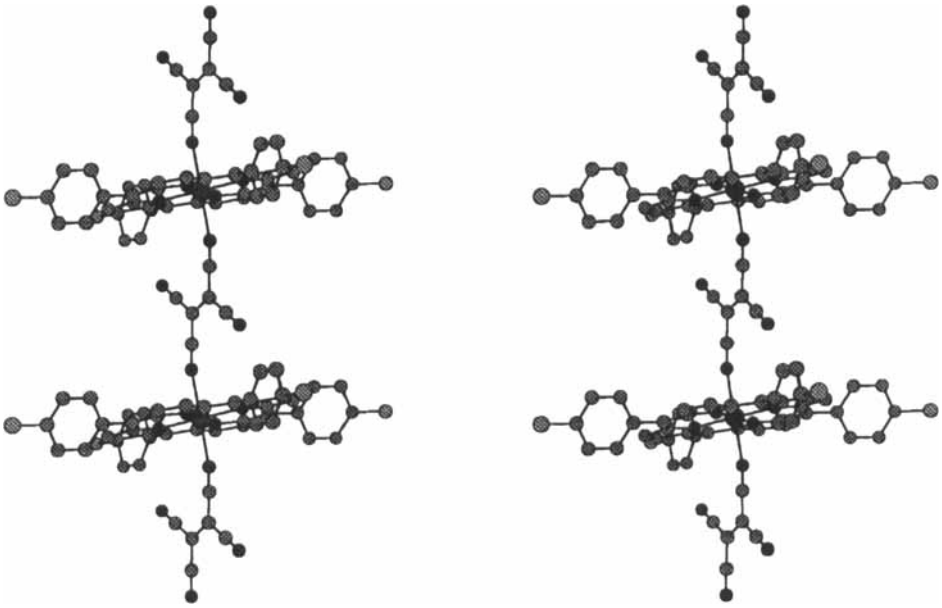
STEREOVIEW 2. **B**, [MnTPP][TCNE]·2(1,2-$C_6H_4Cl_2$) (the solvents and Hs are omitted for clarity).

TABLE 2 Mn-NC, Intrachain Mn···Mn Distances, Mn-N-C and Mn-Mn-N angles, and the Dihedral Angle Formed by the MnN_4 and TCNE planes for **A** - **J**.

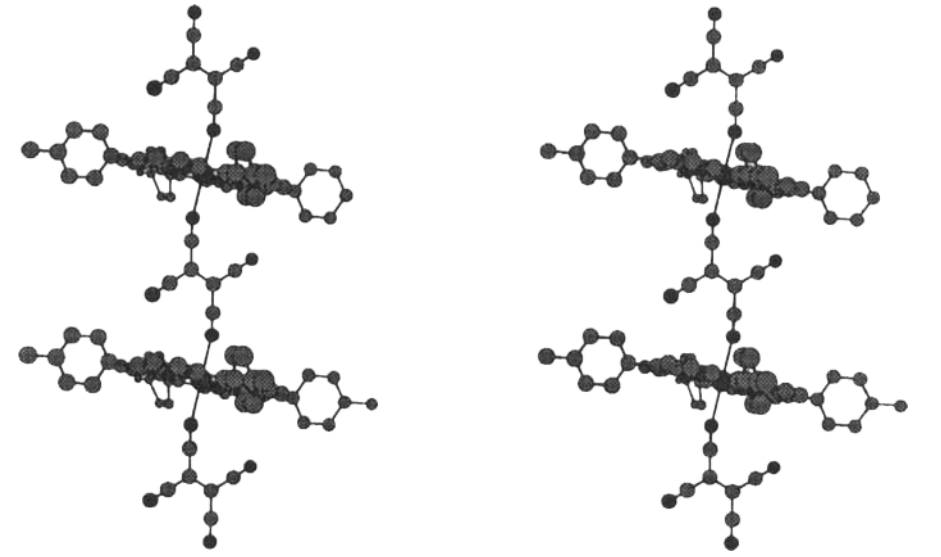
Compound	Mn-NC, Å	Mn-N-C, deg	Dihedral Angle, deg	Mn···Mn, Å	Mn-Mn-N, deg
A	2.288	167.0	93.99	10.218	14.8
B	2.356	125.1	29.50	9.489	31.2
C	2.334	130.2	36.80	9.588	29.0
D	2.305	148.1	69.51	10.116	19.3
E	2.267	167.2	86.78	10.189	14.6
F	2.294	168.4	90.47	10.280	14.0
G	2.290	165.3	83.69	10.256	14.3
H	2.254	169.6	100.10	10.189	13.8
I	2.316	148.4	74.17	10.185	18.3
J	2.299	129.0	30.40	8.587	29.4



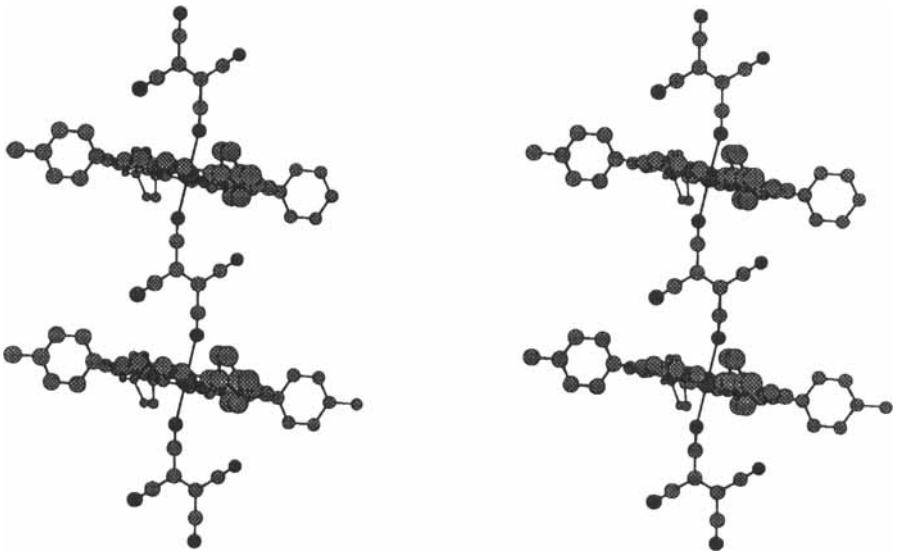
STEREOVIEW 4. **C**, [MnTPP][TCNE]·2(1,2,4-$C_6H_3Cl_3$) (the solvent sand Hs are omitted for clarity).



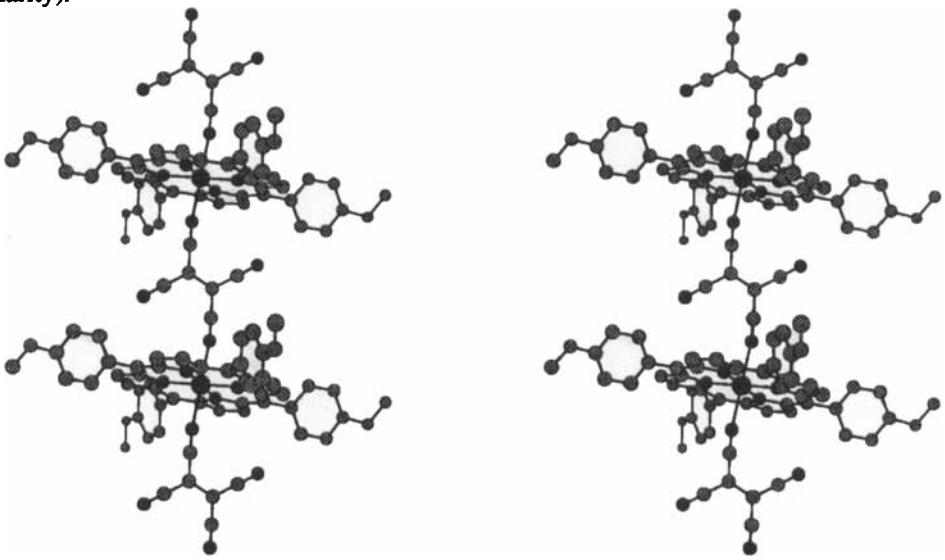
STEREOVIEW 5. **D**, [MnTPP][TCNE]·2PhMe (the solvents and Hs are omitted for clarity).



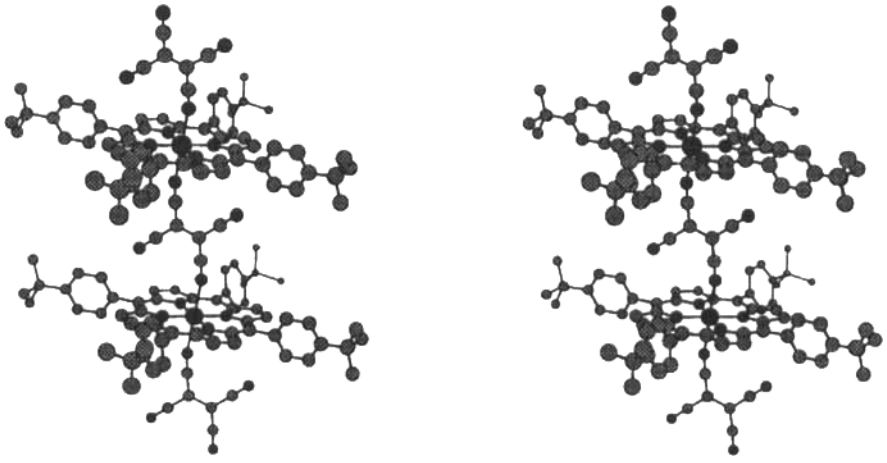
STEREOVIEW 6. **E**, [MnTClPP][TCNE]·2PhMe (the solvents and Hs are omitted for clarity).



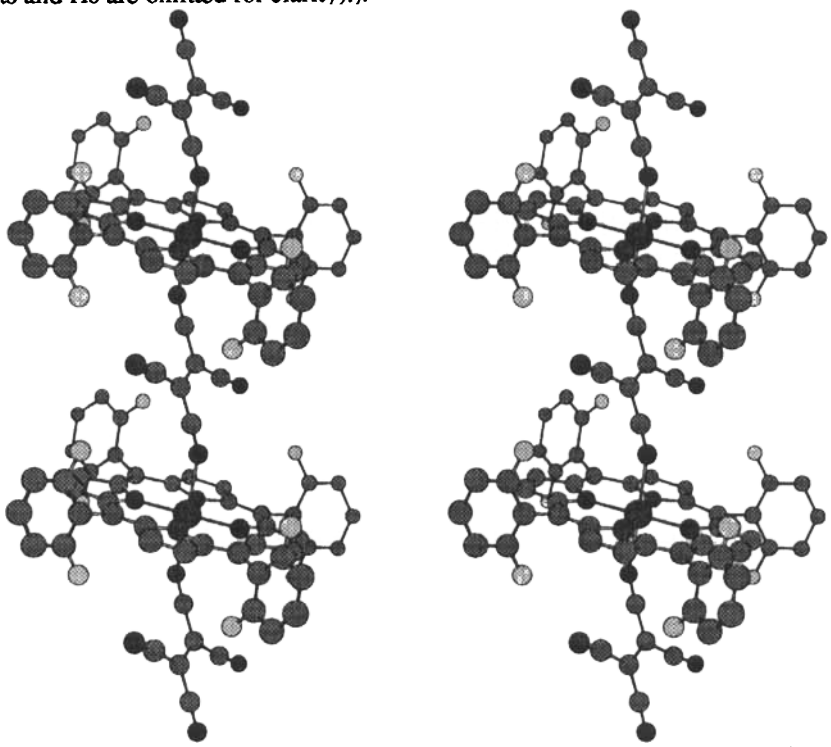
STEREOVIEW 7. **F**, [MnTtolP][TCNE]·2PhMe (the solvents and Hs are omitted for clarity).



STEREOVIEW 8. **G**, [MnTOMePP][TCNE]·2PhMe (the solvents and Hs are omitted for clarity).



STEREOVIEW 9. **H**, [MnTBu^{t}P][TCNE]·6(1,4-$C_6H_4Me_2$) (note the disordered Fs; the solvents and Hs are omitted for clarity).).



STEREOVIEW 10. **I**, [MnTFPP][TCNE]·2PhMe (note the disordered Fs; the solvents and Hs are omitted for clarity).

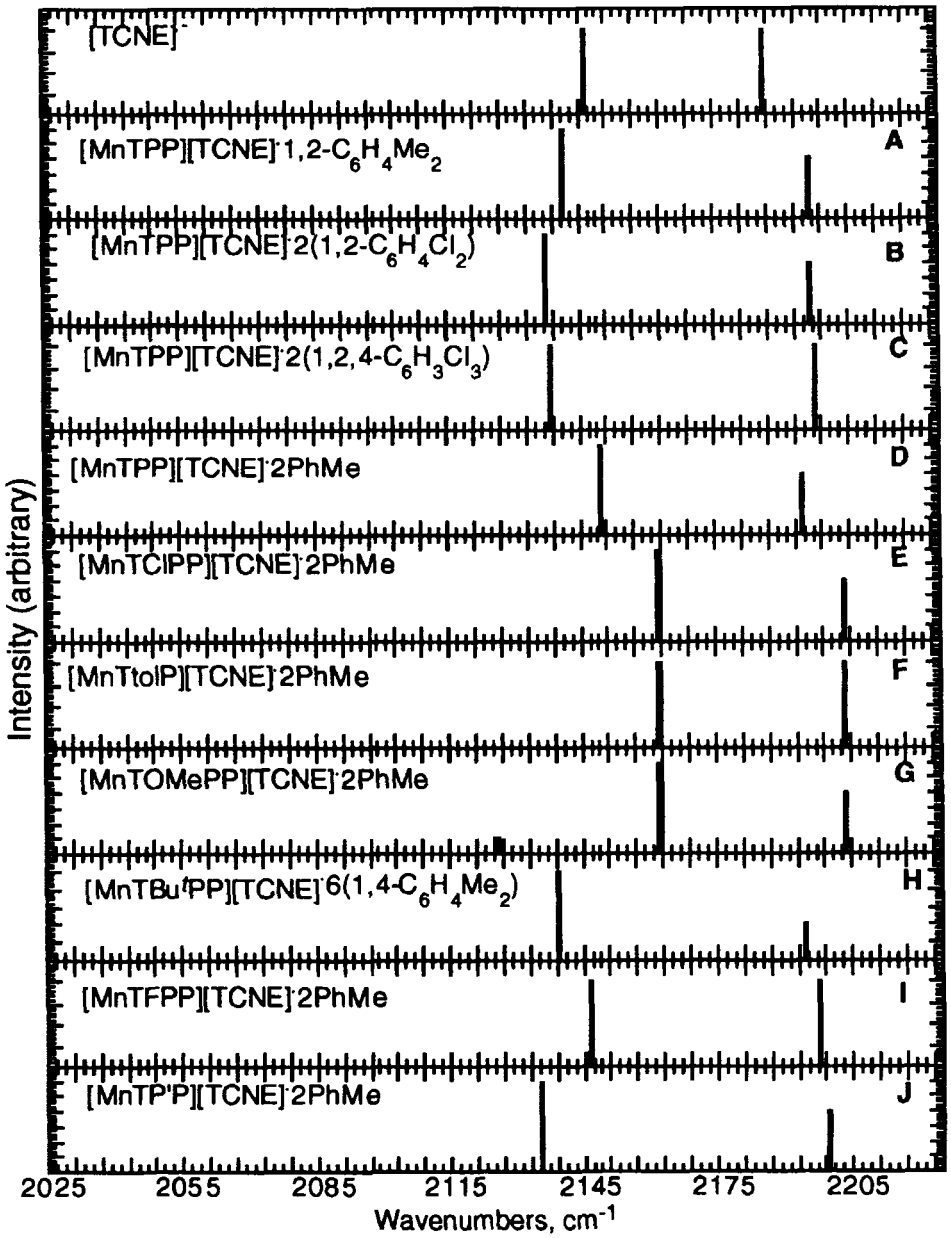
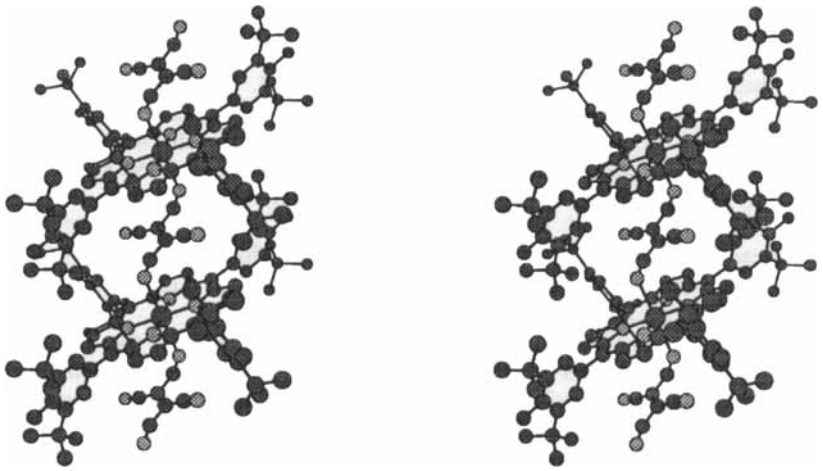


FIGURE 12. Summary of the νCN IR absorptions for isolated $[TCNE]^{\cdot-}$ and **A** - **J**.



STEREOVIEW 11. **J**, [MnTP'P][TCNE]·2PhMe (the solvents and Hs are omitted for clarity).

ACKNOWLEDGMENT

The authors gratefully acknowledge support from the U. S. Department of Energy Division of Materials Science (Grant No. DE-FG03-93ER45504) and the National Science Foundation (Grant No. CHE9320478). We appreciate the discussions of C. M. Wynn, M. Girtu, and A. J. Epstein. K-i. S also acknowledges support by the Monbu-sho fellowship program.

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