into account the increase in the photocurrent while stirring the solution, we conclude that the back-transport is the rate-limiting step. In order to calculate a system like the one briefly described above, it may be possible to combine the unified model of the adiabatic reactions of electron transfer at metal electrodes from Kuznetsov,[24] based on the DKV model[29] with conventional equations for photoelectrodes.[9]

In all cases in which it is possible to form stable bridge type complexes at the semiconductor interface, we have in principle the chance to move the transition from electronic to ionic conduction (which is linked with the risk of recombination and corrosion) from the solid-state interface into the solution, which can in addition imply better conditions for catalysis of energy conversion processes. This provides access to a wide range of interesting surface chemistry with a corresponding variety of kinetic mechanisms. Many examples in the literature are already known of modified semiconductor interfaces. Most of them are also based on strong chemical interactions,[30-33] but mainly those between the reacting species and the surface-modifying chemical species. They do not however emphasize the exchange of electronic charges with the semiconductor electrode. In these cases, only part of the electron or hole path is supported by strong chemical interaction. High photocurrent densities (e.g. 30 mA cm^{-2}) in combination with high stability (Figure 5), as in our experiment, have not yet been obtained.[34] It appears to be advantageous to provide charge carriers for interfacial photoelectrochemical reactions via unbroken chemical bonds instead of attempting to transfer charge carriers from broken chemical bonds to transition-metal complexes attached to the surface.[34] Moreover, a door is opened to a large variety of modifications involving different chemical reactions with the bridges themselves.

We think that related transition-metal compounds can be modified chemically in an analogous way and that such strong interfacial electron-transfer mechanisms promise interesting opportunities for photoelectrochemical energy conversion. Pyrite with its interfacial coordination chemistry and its d-band structure is a good example of a compound displaying strong interfacial interaction, whereas GaAs in contact with acetonitrile is a good example of one exhibiting weak interaction and tunneling processes. Many other systems lie between these, and electron transfer is dependent on the special nature of the chemistry involved. The behavior of such systems can only be described by combination of the two extreme models.

Better theoretical knowledge of electron-transfer processes with strong chemical interaction at the semiconductor/electrolyte interface would be very helpful in developing ideas to chemically modify each individual system in the most effective way.

Acknowledgment. We thank Dr. A. Kuznetsov for valuable discussions with B.S., Mr. M. Wilhelm for making the SEM pictures, and Mr. N. Mgoduka und Mr. K. Büker for experimental support and discussions. A fellowship from the Fonds der Chemischen Industrie for B.S. and financial support from a BMFT grant (03E-8375-A) are gratefully acknowledged.

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(29) Dogonadze, R. R.; Kuznetsov, A. M.; Vorotyntsev, M. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1970**, *25*, 17.

(30) (a) Dominey, R. N.; Lewis, N. S.; Bruce, J. A.; Bookbinder, D. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 467. (b) Stalder, C. J.; Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 3673. Wrighton, M. S. *J. Vac. Sci. Technol., A.* **1984**, *2*, 795.

(31) Ogura, K.; Takagi, M. *Sol. Energy* **1986**, *37*, 41.

(32) (a) Beley, M.; Collins, J. P.; Ruppert, R.; Sauvage, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 7461. (b) Beley, M.; Collins, J. P.; Sauvage, J. P.; Petit, J. P.; Chartier, P. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *206*, 333.

(33) Abruña, H. D.; Bard, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 6898. Krishnan, M.; White, Jr.; Fox, M. A.; Bard, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 7002.

(34) Lewis, N. S.; Wrighton, M. S. In *Photoeffects at Semiconductor-Electrolyte Interfaces*; Nozik, A. J., Ed.; ACS Symposium Series 146; American Chemical Society: Washington, DC, 1981; p 37.

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Electron Delocalization in Molecule-Bridged Polymetallic Systems. Unique Neutral Complexes of TCNE or TCNQ and up to Four Organometallic Fragments $(C_5R_5)(CO)_2Mn$

Renate Gross-Lannert, Wolfgang Kaim,* and Barbara Olbrich-Deussner

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Electron transfer between the π-accepting TCNE or TCNQ (TCNX) ligands and π-electron-rich organometallic species $(C_5R_5)(CO)_2Mn(THF)$ (R = H, CH_3) results in the formation of polynuclear complexes $[(C_5R_5)(CO)_2Mn]_n(\eta^n\text{-TCNX})$ until full coordinative saturation is achieved at the nitrile groups ($n = 4$). Infrared spectroscopy points to the net transfer of one π electron to the TCNX acceptor ligand and indicates a highly symmetrical and strongly coupled situation for the tetranuclear complexes. The polynuclear complexes have intense ($\log \epsilon > 4.3$) absorption bands in the near-infrared region (0.8-1.5 μm), and the corresponding transitions may be formulated either as metal-to-metal ($Mn^I \rightarrow Mn^{II}$) charge transfer in a localized, mixed-valence formulation or as $\pi \rightarrow \pi^*$ transitions of polymetal-containing π systems in a delocalized description. The polynuclear systems may serve as models for the MLCT excited states of symmetrical dimers and tetramers. Results from Hückel molecular orbital calculations involving $d(\pi)$-$p(\pi)$ bonding correlate with the changes in absorption energies on successive polynucleation. The small energy differences between frontier orbitals are confirmed by results from cyclic voltammetry. As an additional complication, the complexes contain metal centers that possess an easily attainable intermediate-spin state ($S = 1$) despite their 18-valence-electron configuration.

Coordination compounds with considerable metal/ligand delocalization have been known e.g. in the form of the dithiolene chelate complexes;[1] several special features make such compounds very interesting also for practical purposes: (i) Intense charge-transfer absorption bands in the visible and in the near-infrared region can make such systems useful as dyes for information storage using fiber optics and 1.0-1.6 μm diode lasers,[2] (ii) the communication between metal-connected ligands and/or ligand-connected metals has received attention in the area of low-dimensional polymers with electron-propagating capabilities and

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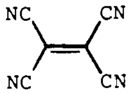
(1) (a) Chandramouli, G. V. R.; Manoharan, P. T. *Inorg. Chem.* **1986**, *25*, 4680. (b) Persaud, L.; Langford, C. H. *Inorg. Chem.* **1986**, *25*, 3438. (c) Best, S. P.; Clark, R. J. H.; McQueen, R. C. S.; Walton, J. R. *Inorg. Chem.* **1988**, *27*, 884. (d) Burns, R. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1978**, *22*, 303.

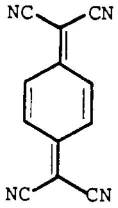
(2) Fabian, J.; Zahradnik, R. *Angew. Chem.* **1989**, *101*, 693; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 677.

within the concept of "molecular electronics",[3] and (iii) the existence of several close-lying and easily accessible redox transitions renders these compounds suitable as "electron reservoirs",[4] especially if small structural changes during the redox transitions of extensively delocalized systems favor rapid electron transfer because of small reorganization barriers.

We report here on the deliberate synthesis[5,6] yet unexpected and highly unusual electronic structures of the title compounds (1).



TCNE



TCNQ

$(C_5Me_5)(CO)_2Mn(TCNE)$ 1

$[(C_5Me_5)(CO)_2Mn]_2(TCNE)$ 2

$[(C_5Me_5)(CO)_2Mn]_3(TCNE)$ 3

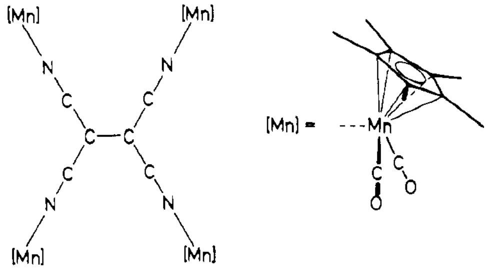
$[(C_5Me_5)(CO)_2Mn]_4(TCNE)$ 4

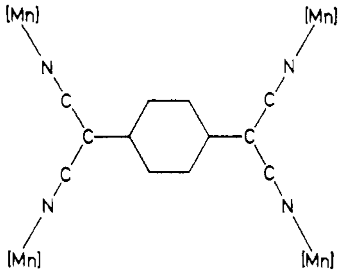
$[(C_5H_4Me)(CO)_2Mn]_4(TCNE)$ 5

$[(C_5Me_5)(CO)_2Mn]_4(TCNQ)$ 6

I

While several di- and polynuclear complexes[3,7-14] with extensive π delocalization including the metal centers have been reported, the unique complexes I of the standard π-acceptor ligands TCNE[15] and TCNQ[16] require *four* well-separated metal centers (>800 pm according to scale drawings based on established[15,16] geometries, II) for full coordinative saturation at the nitrile nitrogen atoms.





II

Non-reduced TCNE and TCNQ are rather poor ligands for metal centers; however, on electron uptake by back-donation or by full reduction with one or two electrons, they can bind metal fragments via the C=C π system or via the nitrile nitrogen centers.[17] Dinuclear C≡N (σ-) coordinated complexes have been described[18] with Co, Ir, Os, and Re fragments, as has one tricationic trinuclear Re(I) complex of TCNQ[18d] and one polycationic (8+ to 12+) ruthenium(II) tetramer of μ_4-bridging TCNE.[19] All compounds presented here are neutral and thus soluble, e.g. in toluene; their formation involves an electron-transfer step in the extremely rapid initial formation of mononuclear complexes,[17] which leads to an increase in basicity at the conjugatively connected free coordination sites (electron-transfer-assisted polynucleation[6]).

Experimental Section

General Procedures. All manipulations were carried out under argon atmosphere by using Schlenk techniques. IR spectra were obtained on a Jasco A100 spectrometer. Electronic absorption spectra were recorded on a Shimadzu UV 160 or a Perkin-Elmer Lambda 9 instrument. Cyclic voltammetry was performed on a system containing a PAR Model 363 potentiostat and a Bank Model VSG 72 ramp generator. A three-electrode configuration (glassy-carbon working electrode, saturated calomel as reference) was employed with 100 mV/s scan rate; a 0.1 M solution of tetrabutylammonium perchlorate in rigorously dried ($CuSO_4$) and vacuum-distilled *N,N*-dimethylformamide served as electrolyte. Hückel MO calculations were performed on AT computers using the standard program.[20] Parameters employed for calculation of complexes $(TCNX)(metal)_n$ were the Coulomb integral values $h_C = h_{metal} = 0.0$ and $h_N = 1.0$; all resonance integral parameters were maintained at $k = 1.0$.

Photolyses of the starting materials were carried out in a thermostated falling-film photoreactor from Normag (Hofheim, West Germany), equipped with a mercury high-pressure lamp, TQ 150/Z1, from Quarzlampen GmbH (Hanau, West Germany).

Complexes were purified by preparative column (40 cm × 1.5 cm) chromatography at low temperatures under argon atmosphere. Dried Florisil (100–200 mesh) was used as the stationary phase; the eluents used according to increasing polarity were hexane, toluene, diethyl ether, and THF.

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(3) (a) Hünig, S.; Aumüller, A.; Erk, P.; Meixner, H.; von Schütz, J. U.; Gross, H.-J.; Langohr, U.; Werner, H.-P.; Wolf, H. C.; Burschka, C.; Klebe, G.; Peters, K.; von Schnering, H. G. *Synth. Met.* **1988**, *27*, B181. (b) Kato, R.; Kobayashi, H.; Kobayashi, A. *J. Am. Chem. Soc.* **1989**, *111*, 5224. (c) Maata, E. A.; Kim, C. *Inorg. Chem.* **1989**, *28*, 623. (d) Kuhlmann, T.; Roth, S.; Roziere, J.; Siebert, W.; Zenneck, U. *Synth. Met.* **1987**, *19*, 757. (e) Cayton, R. H.; Chisholm, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 8921.

(4) (a) Astruc, D. *Acc. Chem. Res.* **1986**, *12*, 377. (b) Desbois, M.-H.; Astruc, D.; Guillin, J.; Varret, F.; Trautwein, A. X.; Villeneuve, G. *J. Am. Chem. Soc.* **1989**, *111*, 5800.

(5) Gross, R.; Kaim, W. *Angew. Chem.* **1987**, *99*, 257; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 251.

(6) Kaim, W.; Olbrich-Deussner, B.; Gross, R.; Ernst, S.; Kohlmann, S.; Bessenbacher, C. In *Importance of Paramagnetic Organometallic Species in Activation, Selectivity and Catalysis*; Chanon, M., Ed.; Kluwer Academic Publishers: Dordrecht, Holland, 1989; p 283.

(7) Lippard, S. J. *Science* **1982**, *218*, 1075.

(8) Sakai, K.; Matsumoto, K. *J. Am. Chem. Soc.* **1989**, *111*, 3074.

(9) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer: Berlin, 1983.

(10) Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 7627.

(11) Huttner, G.; Evertz, K. *Acc. Chem. Res.* **1986**, *19*, 406.

(12) Elschenbroich, C.; Heikenfeld, G.; Wünsch, M.; Massa, W.; Baum, G. *Angew. Chem.* **1988**, *100*, 397; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 414.

(13) Bunel, E. E.; Valle, L.; Jones, N. L.; Carroll, P. J.; Barra, C.; Gonzalez, M.; Munoz, N.; Visconti, G.; Aizman, A.; Manriquez, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 6596.

(14) Sellmann, D.; Barth, I. *Inorg. Chim. Acta* **1989**, *164*, 171.

(15) (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; Chapters 15 and 16. (b) Fatiadi, A. J. *Synthesis* **1986**, 249; **1987**, 959. (c) Dixon, D. A.; Miller, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 3656.

(16) (a) Endres, H. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1983; Vol. 3. (b) Humphrey, D. G.; Fallon, G. D.; Murray, K. S. *J. Chem. Soc., Chem. Commun.* **1988**, 1356.

(17) (a) Olbrich-Deussner, B.; Gross, R.; Kaim, W. *J. Organomet. Chem.* **1989**, *366*, 155. (b) Olbrich-Deussner, B.; Kaim, W.; Gross-Lannert, R. *Inorg. Chem.* **1989**, *28*, 3113. (c) Schwederski, B.; Olbrich-Deussner, B.; Kaim, W. To be submitted for publication.

(18) (a) Crumbliss, A. L.; Basolo, F. *Inorg. Chem.* **1971**, *10*, 1676. (b) Beck, W.; Schlodder, R.; Lechler, K. H. *J. Organomet. Chem.* **1973**, *54*, 303. (c) Moers, F. G.; Langford, J. P. *J. Inorg. Nucl. Chem.* **1977**, *39*, 591. (d) Sacher, W.; Nagel, U.; Beck, W. *Chem. Ber.* **1987**, *120*, 895.

(19) Amer, S. L.; Dasgupta, T. P.; Henry, P. M. *Inorg. Chem.* **1983**, *22*, 1970.

(20) Heilbronner, E.; Bock, H. *The HMO-Model and its Applications*; Wiley: London, 1976.

Elemental analyses were performed by Mikroanalytisches Laboratorium Malissa & Reuter, Gummersbach, FRG (**1**, **5**), and by the Institut für Organische Chemie, Universität Frankfurt (all others); the latter gave invariably too small C values. The synthesis of complex **1** was described previously.[17]

$[(C_5Me_5)(CO)_2Mn]_2(\mu,\eta^2\text{-TCNE})$ (2). A 1.64-g (6-mmol) sample of $(C_5Me_5)(CO)_3Mn$ was converted to the red THF solvate complex $(C_5Me_5)(CO)_2Mn(THF)$ by irradiation for 3 h at −40 °C. The warmed solution was treated with 0.38 g (3 mmol) of solid TCNE. After 3 h at room temperature, the solvent was removed from the green solution and the residue chromatographed on a column: Florisil as stationary phase, initial solvent hexane, −30 °C working temperature. While small amounts of the mononuclear complex were eluted with toluene, the dinuclear system could be obtained with toluene/ether (1:1, v/v). After removal of the solvent, the compound was recrystallized from toluene/hexane (1:2, v/v) in 30% yield (0.56 g). Anal. Calcd for $C_{30}H_{30}Mn_2N_4O_4$ (M_r = 620.47): C, 58.07; H, 4.87; N, 9.03. Found: C, 52.96; H, 4.81; N, 8.87.

$[(C_5Me_5)(CO)_2Mn]_3(\mu,\eta^3\text{-TCNE})$ (3) and $[(C_5Me_5)(CO)_2Mn]_4(\mu,\eta^4\text{-TCNE})$ (4). A solution containing approximately 6 mmol of the THF complex as described above was treated with 0.19 g (1.5 mmol) of solid TCNE. After 1 h at room temperature, the solvent was removed and the residue chromatographed at −20 °C. A brighter green zone of **3** was eluted with toluene/ether (2:1, v/v), and a dark green zone of **4** with THF. After removal of the solvent, the trinuclear complex was recrystallized from toluene/hexane (1:2, v/v) in 16% yield (0.21 g); the tetranuclear complex was crystallized from THF/hexane (1:2, v/v) in 24% yield (0.40 g). Anal. Calcd for **3** ($C_{42}H_{45}Mn_3N_4O_6$) (M_r = 866.65): C, 58.21; H, 5.23; N, 6.46. Found: C, 52.79; H, 5.28; N, 6.04. Calcd for **4** ($C_{54}H_{60}Mn_4N_4O_8$) (M_r = 1112.84): C, 58.28; H, 5.43; N, 5.03. Found: C, 56.16; H, 5.69; N, 4.74.

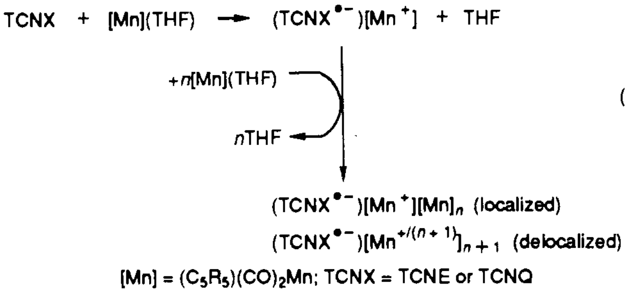
$[(C_5H_4Me)(CO)_2Mn]_4(\mu,\eta^4\text{-TCNE})$ (5). The THF solvent complex was prepared from 4.36 g (20 mmol) of $(C_5H_4Me)(CO)_3Mn$ as described above. After reaction with 0.64 g (5 mmol) of solid TCNE at room temperature, the solvent was removed and the residue chromatographed at −20 °C. Yellow tricarbonyl was eluted with hexane, small amounts of mono- and dinuclear complex were eluted with toluene, and the dark green tetranuclear complex was eluted with THF. Removal of that solvent and crystallization from THF/hexane (1:1, v/v) at −28 °C gave 20% (0.87 g) of the product. Anal. Calcd for $C_{38}H_{28}Mn_4N_4O_8$ (M_r = 888.41): C, 51.37; H, 3.18; N, 6.31; Mn, 24.73. Found: C, 50.96; H, 3.24; N, 6.73; Mn, 24.90.

$[(C_5Me_5)(CO)_2Mn]_4(\mu,\eta^4\text{-TCNQ})$ (6). A solution containing about 4 mmol of $(C_5Me_5)(CO)_2Mn(THF)$ was prepared as described above. A 0.20-g (1-mmol) amount of solid TCNQ was added, and the mixture was stirred at room temperature overnight. Removal of the solvent and column chromatography at −30 °C gave a major greenish zone as eluted with toluene/diethyl ether (3:1, v/v). The solvent was removed and the remainder crystallized as rhombic platelets from toluene/hexane (1:2, v/v) at −28 °C. Yield: 0.35 g (30%). MS (FD): *m/z* 1188 (M^+). Anal. Calcd for $C_{60}H_{64}Mn_4N_4O_8$ (M_r = 1188.95): C, 60.62; H, 5.43; N, 4.71. Found: C, 58.53; H, 5.32; N, 4.76.

Attempts to synthesize dinuclear complexes $[(C_5H_4CH_3)(CO)_2Mn]_2(TCNE)$ and $[(C_5Me_5)(CO)_2Mn]_2(TCNQ)$ yielded product mixtures of different nuclearities, which could not be separated well enough by column chromatography.

Results

In contrast to the very rapid electron-transfer autocatalytic formation of the mononuclear systems,[17] the subsequent coordination (eq 1) of metal fragments via substitution of $(C_5R_5)(CO)_2Mn(THF)$ proceeds at a distinctly slower rate. Reaction times of hours were needed to achieve completion in case of the tetranuclear $(C_5Me_5)(CO)_2Mn$ complexes, despite the absence of significant steric hindrance (II). The lability of the manganese–nitrogen bond, promoted by coordinating solvents and visible light,[21,22] has made it necessary to separate the usually encountered mixtures of oligomers by low-temperature column chromatography; it was especially difficult to isolate the di- and trinuclear complexes in the middle of the series. TCNQ complexes are more labile than their TCNE analogues;[17] cyclopentadienyl or methylcyclopentadienyl complexes proved to be less inert than their pentamethylcyclopentadienyl counterparts.[22a] In the solid state, however, the compounds could be stored for several months at −28 °C in the dark; all polynuclear complexes had a dull greenish appearance as solids, in contrast to the mononuclear TCNE complexes with their possibly structurally based (TCNE dimerization[23]) metallic luster.



(1)

Table I. IR Vibrational Frequencies $\tilde{\nu}$ (cm^{-1}) for Complexes **1**–**6** in THF Solution

complex	$\tilde{\nu}_{CN}$	$\tilde{\nu}_{CO}$	$\tilde{\nu}_{CC(TCNX)}$[a]
1	2230 (vw) 2205 (s) 2125 (m)	1985 (vs) 1950 (s)	1380 (m) 1365 (m) 1420 (s)[b]
2	2205 (vw) 2160 (vw) 2125 (m)	1960 (m) 1895 (vs)	n.o.
3	2150 (m) 2105 (s)	1950 (w) 1890 (vs)	1370 (w) 1420 (w)[b]
4	2160 (m) 2110 (s)	1950 (w) 1890 (vs)	n.o.
5	2175 (m) 2130 (s)	1970 (w) 1915 (vs)	n.o.
6	2170 (w) 2105 (s)	1950 (m) 1915 (vs) 1885 (s) 1860 (vs)	n.o.

[a] n.o. = not observed. [b] Cyclopentadienyl ring.

Table II. Electrochemical Data for TCNX Ligands and Their Complexes[a]

compd	E_{ox}^{pa} [b]	E_{red1}	E_{red2}^{pc} [c]
TCNE		+0.18	−0.82[d]
1	+0.81	−0.20	−1.01
2	+0.28	−0.31	−0.90
4	+0.25	−0.41	−0.85
5	+0.35	−0.26	−0.75
TCNQ		+0.15	−0.43[d]
6	+0.29	−0.05	−0.58

[a] From cyclic voltammetry at 100 mV/s scan rate in DMF/0.1 M tetrabutylammonium perchlorate. Potentials in V vs aqueous SCE (corrected for junction potentials). [b] Anodic peak potentials for completely irreversible oxidation. [c] Cathodic peak potentials for second reduction (peak-to-peak separations > 100 mV). [d] Reversible process.

Representative infrared vibrational spectra as taken in THF solution are shown in Figures 1 and 2. The most intense bands are due to the informative C≡N, C≡O, and C=C stretching modes; the data are summarized in Table I.

Due to the lability of the complexes, the cyclic voltammetric experiments had to be carried out rapidly in the absence of light.[22a] Figure 3 shows one cyclic voltammogram, illustrating the closeness of reduction and oxidation processes. DMF was chosen because it stabilizes anions particularly well; the potentials for the completely irreversible oxidation, the reversible reduction, and the less reversible (ΔE_{pp} > 100 mV) second reduction are listed in Table II.

Intense electronic absorption bands were observed for the polynuclear complexes in the visible and near-infrared regions

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(21) (a) Giordano, P. J.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 160. (b) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61. (c) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771.

(22) (a) Gross, R.; Kaim, W. *Inorg. Chem.* **1986**, *25*, 498. (b) Kaim, W.; Gross, R. *Comments Inorg. Chem.* **1988**, *7*, 269. (c) Kaim, W.; Gross-Lannert, R.; Olbrich-Deussner, B.; Roth, T.; Jordanov, J.; Roth, E. Manuscript in preparation.

(23) Braunwarth, H.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1989**, *372*, C23.

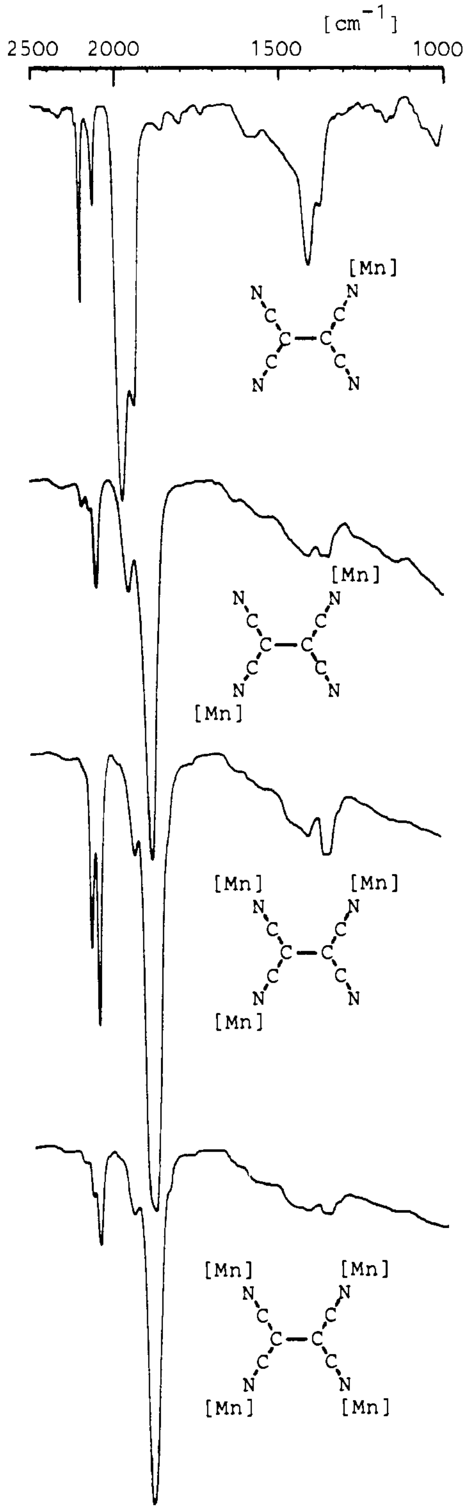

Figure 1. Infrared vibrational spectra of mono-, di-, tri-, and tetranuclear TCNE complexes **1**–**4** in THF solution.

(Figures 4 and 5). Table III summarizes the absorption maxima, some extinction coefficients, and band half-widths.

Results from Hückel MO calculations for the system TCNE-(metal)$_n$, n = 1–4, allowing for p(π)–d(π) overlap between the metal atoms and the coordinating nitrogen centers are depicted in Figure 6. Calculations for TCNQ systems are qualitatively similar with somewhat smaller HOMO–LUMO separations. A correlation between calculated HOMO–LUMO separations and the energies of long-wavelength absorption maxima of complexes **1**–**4** is shown in Figure 7.

Magnetic resonance investigations of complexes **1**–**6**[5,24] have been hampered by their easy dissociation in solution and by the presence of small yet disturbing amounts of high-spin Mn(II)

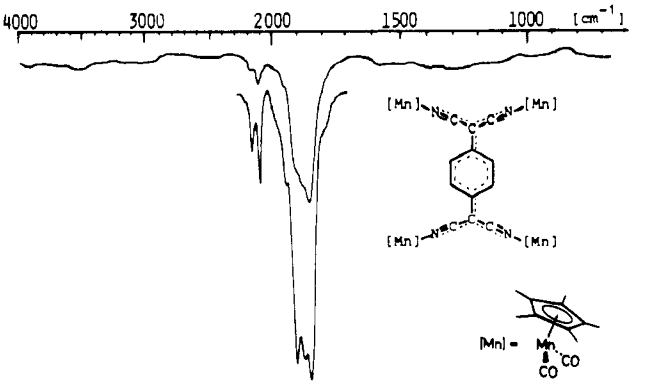

Figure 2. Infrared vibrational spectrum of the tetranuclear TCNQ complex **6** in THF solution.

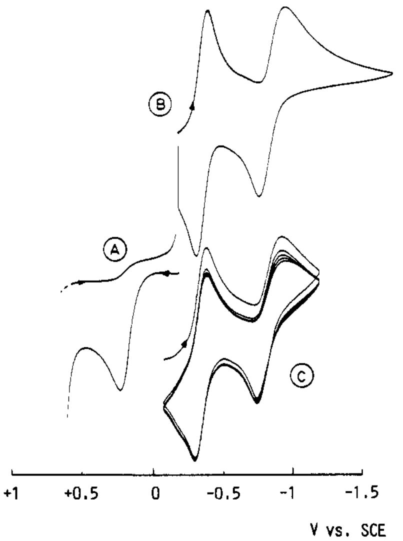

Figure 3. Cyclic voltammograms of complex **2** in DMF/0.1 M tetrabutylammonium perchlorate: (A) oxidation scan; (B) reduction scan; (C) reduction scan, some cycling at 100 mV/s.

Table III. Long-Wavelength Absorption Maxima $\tilde{\nu}$ (cm^{-1}) for TCNX Complexes in Toluene and Acetonitrile Solution[a]

complex	$\tilde{\nu}_{LMCT}$	$\tilde{\nu}_{MMCT}$
1	12 670 (13 850) log ϵ 4.23 $\Delta\tilde{\nu}_{1/2}$ 3660	
2	13 930 (13 890) log ϵ 4.15 $\Delta\tilde{\nu}_{1/2}$ 3340	8680 (8730) log ϵ 4.40 $\Delta\tilde{\nu}_{1/2}$ 2230
3	16 750 (sh)	10 930 $\Delta\tilde{\nu}_{1/2}$ 2700
4	15 630 (sh)	9060 log ϵ 4.75 $\Delta\tilde{\nu}_{1/2}$ 2285
5	15 650 (sh)	9050 (9580)
6	18 180 (sh)	7050 log ϵ 4.70 $\Delta\tilde{\nu}_{1/2}$ 2460

[a] Values in parentheses: acetonitrile solutions. Molar extinction coefficients ϵ in M^{-1} cm^{-1}. Bandwidths at half-height $\Delta\tilde{\nu}_{1/2}$ in cm^{-1}.

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(24) Heck, J. Unpublished results.

(25) (a) Heim, P.; Dörr, F. *Tetrahedron Lett.* **1964**, *42*, 3095. (b) Hinkel, J. J.; Devlin, J. P. *J. Chem. Phys.* **1973**, *58*, 4750. (c) Khatkale, M. S.; Devlin, J. P. *J. Chem. Phys.* **1979**, *70*, 1851.

(26) (a) For a lucid discussion: Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, *84*, 137. (b) Dei, A.; Wicholas, M. *Inorg. Chim. Acta* **1989**, *166*, 151.

(27) The Creutz–Taube ion was found to be delocalized on the vibrational time scale: Best, S. P.; Clark, R. J. H.; McQueen, R. C. S.; Joss, S. *J. Am. Chem. Soc.* **1989**, *111*, 548.

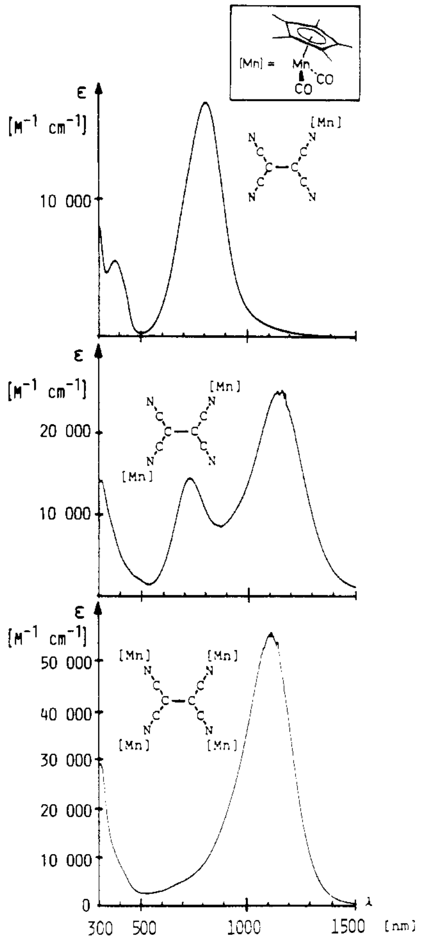
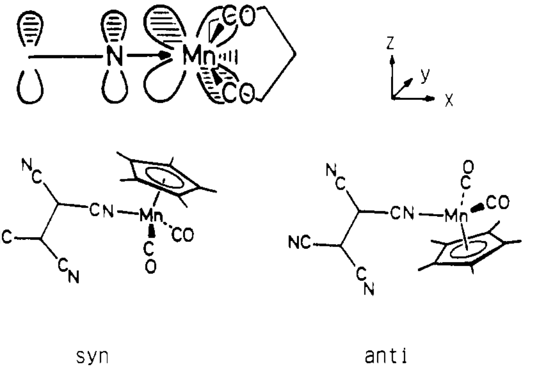


Figure 4. Electronic absorption spectra of TCNE complexes **1**, **2**, and **4** in toluene solution. Absorbance scales are different for each spectrum.

impurities. Furthermore, there is a significantly populated intermediate-spin state ($S = 1$) at each formally 18-valence-electron metal center as determined by solid-state magnetic measurements that will be reported in detail elsewhere.[17,22c] Careful reversible reduction of the complexes to odd-electron-containing anions did not produce any ESR spectra at room temperature; low-temperature (4 K) studies showed only weak featureless signals at $g = 2.0$.

Discussion

Infrared Spectra and Structure. The crystal structure of the monomer $(C_5H_5)(CO)_2Mn(\eta^1\text{-TCNE})$ has been reported recently,[23] confirming the previously postulated[17a,b] nitrile coordination, the metal configuration (III) necessary for p(π)–d(π) overlap,[29c] and the reduced form of the TCNE ligand. A special



III

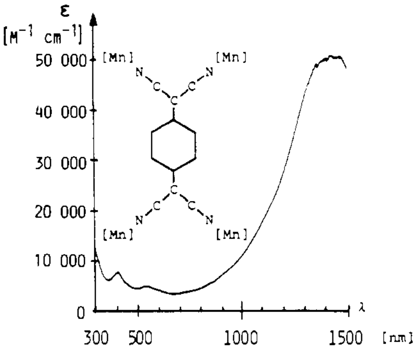


Figure 5. Electronic spectrum of the tetranuclear TCNQ complex **6** in toluene solution (maximum at 386 nm is due to small amounts of $TCNQ^{•-}$).

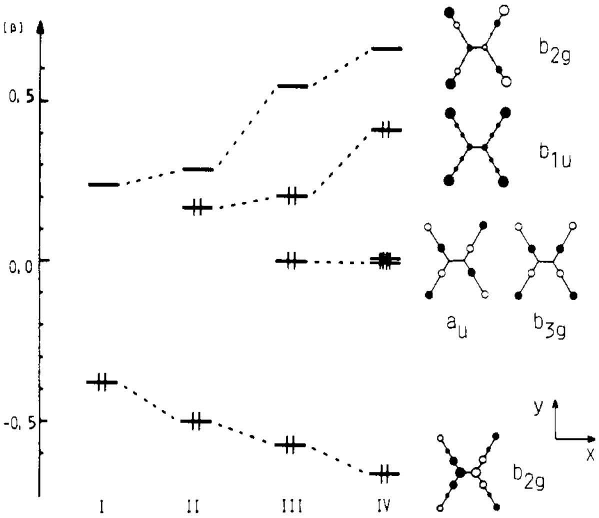


Figure 6. Frontier orbital energy diagram from Hückel MO calculations for mono- (I), di- (II), tri- (III), and tetranuclear complexes (IV) of TCNE ($h_{metal} = h_C = 0.0$, $h_N = 1.0$, all $k = 1.0$). Comparable orbitals are connected, orbital characters and symmetry representations are indicated for the tetranuclear case (effective D_{2h} symmetry).

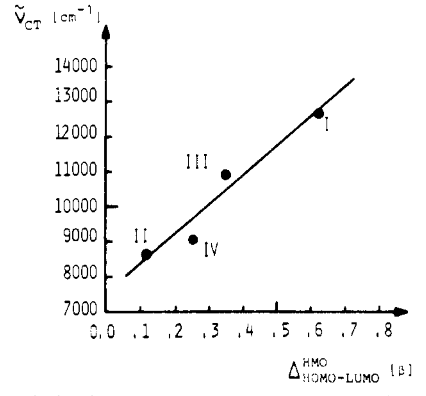


Figure 7. Correlation between long-wavelength absorption maxima $\tilde{\nu}_{CT}$ of TCNE complexes **1**–**4** (I–IV) in toluene and HOMO–LUMO differences Δ as obtained from the Hückel MO model (Figure 6); correlation coefficient $r = 0.970$.

feature of mononuclear complexes formulated as $(ML_n^+)(TCNE^{•-})$ ($ML_n = (C_5R_5)(CO)_2Mn$, $(C_6R_6)(CO)_2Cr$, and $(C_5H_5)_2(Hal)V$) is the metallic luster, which may be related to intermolecular association (face-to-face dimerization of TCNE ligands, IV[23]). Close association (≈335 pm[23]) of TCNE ligands is not possible for the polynuclear systems because of interference

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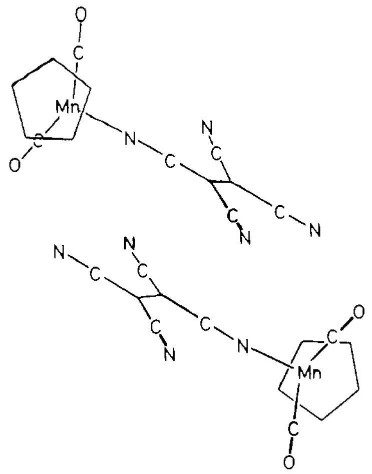
[28] Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

[29] (a) Gross, R.; Kaim, W. *Angew. Chem.* **1985**, *97*, 869; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 856. (b) Gross, R.; Kaim, W. *Inorg. Chem.* **1987**, *26*, 3596. (c) Gross, R.; Kaim, W. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 3549.



IV

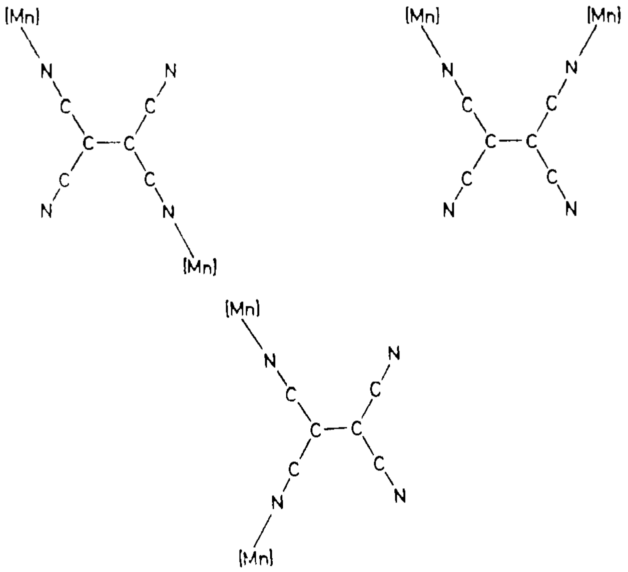
between the bulky organometallic fragments.

Suitable single crystals of the polynuclear complexes could not be obtained despite repeated attempts, possibly because of isomerism resulting from differently arranged metal fragments: p(π)–d(π) overlap is possible in syn and anti conformations (III), which leads to several possible combinations, e.g. for tetranuclear complexes. While the syn conformation had been established in a single crystal of dimeric $(C_5H_5)(CO)_2Mn(TCNE)$,[23] infrared vibrational studies indicated the presence of both isomers for "free" $(C_5Me_5)(CO)_2Mn(TCNE)$ in KBr pellets or THF solution.[17a] Fortunately, the infrared spectra of the polynuclear complexes (Figures 1 and 2) also provide valuable information (Table I) on the molecular and electronic structure.

The IR absorption bands due to CN stretching modes are quite intense and shifted to lower wavenumbers when compared to those of the free, nonreduced ligands.[17,25] This already indicates nitrile N coordination and sizable back-donation of π-electron density from the metal fragments to the TCNX ligand.[17,18] The wavenumbers $\tilde{\nu}_{CN}$ of the complexes lie between those of the free anion radicals and the values found for the dianions,[17a,25] indicating some ambiguity of oxidation-state assignment.[26] The polynuclear complexes are distinguished from mononuclear systems[17a] and the free ligands,[25] as the highest intensity is displayed by the low-energy band.

The number and the pattern of bands observed by IR absorption spectroscopy depend on the symmetry; effectively D_{2h}- and C_{2h}-symmetric systems should show two, and C_s- or C_{2v}-symmetric complexes should exhibit four, bands. While the tetranuclear species **4**–**6** display two bands, in agreement with a slightly perturbed D_{2h} symmetry and thus quite effective electronic delocalization on the vibrational time scale,[27] the situation is more complicated for the other complexes. Mono- (**1**) and trinuclear complexes (**3**) reveal only three and two bands, respectively, presumably because of overlapping. The observation of two small bands in addition to one large feature for dimer **2** could be attributed to the presence of isomers (V: 1,2-trans, 1,2-cis, or 1,1′ arrangement), although the absence of C=C stretching bands from the cyclopentadienyl groups or the TCNE ligand in the IR spectrum points to the predominance of the C_{2h}-symmetric 1,2-trans isomer.

The intensities of the bands due to TCNE and cyclopentadienyl C=C stretching modes[17a] are as expected from symmetry considerations for strongly coupled systems: High intensity is observed for the mononuclear system **1**,[17a] while the formally equally unsymmetrical trinuclear complex **3** displays much weaker features due to a smaller change of the dipole moment in the course of the vibration. C=C stretching bands are absent for di- and tetranuclear complexes (Figure 1). The shifts observed for complexes **1** and **3** suggest an approximately 1e-reduced state of the TCNE ligand[17a] with an effective bond order of ca. 1.5 for the central C=C bond (cf. below).



V

The third kind of multiple bonds that provide information about molecular and electronic structures via their IR absorption bands is represented by the carbonyl groups of the metal fragments, which could yield direct evidence for metal/metal (de)localization. Two bands are expected for the individual $(C_5R_5)(CO)_2Mn$ fragments;[17,21,22a] however, unusually small interaction constants k_i[17a,b,28] and the symmetry-dependent pattern in the case of TCNX-mediated strong vibrational coupling between the metal fragments can reduce the number of observable bands due to severe overlap. Such a situation seems to determine the appearance of IR spectra of TCNE complexes **1**–**4** (Figure 1), whereas the tetranuclear TCNQ complex **6** still shows all four CO stretching bands of comparable intensity that are allowed under D_{2h} selection rules (two pairs, each separated by a "normal"[21,22a] $\Delta\tilde{\nu}_{CO} = 60$ cm^{-1}, Figure 2).

Typical for the TCNE complexes **1**–**4** is that the balance between low-energy and high-energy bands of the two observed features changes very distinctly on polynucleation **1** → **4** (Figure 1). If the initial high-energy shift of both bands is attributed to an oxidation of the metal fragment with concomitant reduction in CO → Mn back-donation,[17a,b,29] the addition of further, nonreducing organomanganese fragments (eq 1) should result in an increase of bands at lower energies. Following this argument, one might interpret the bands of e.g. **4** in the CO stretching region as consisting of one low-intensity feature at high energy (one Mn^{II} fragment) and one broad high-intensity band at low energy (three Mn^{I} fragments). Such an interpretation based on a localized description (eq 1) stands in contrast to the explanation given for the spectrum of the TCNQ analogue, which is rather compatible with a delocalized formulation. Unfortunately, the lack of resolution for the TCNE systems (Figure 1) does not permit a final unambiguous distinction between both interpretations at this point.

Cyclic Voltammetry. Despite severe problems due to the lability of the complexes in DMF solution, it has been possible to determine half-wave potentials for reversible reduction and anodic peak potentials for irreversible oxidation of the complexes. Electrochemical data for the free ligands (Table II) and for the metal fragments and their DMF solvates[22a] are available so as to rule out any mistakes.

Not only the mononuclear system **1** but also all polynuclear complexes **2**–**6** are reduced at *more negative* potentials than the TCNX ligands (Table II). We have pointed out[5,6,17,30] that this is a consequence of metal-to-ligand electron transfer in the ground state which, in a localized view, leaves either the singly reduced ligand or the oxidized metal fragment available for reduction at relatively negative potentials.[17b] However, the reduction potentials of the complexes never fall below the *second* reduction potentials of the TCNX ligands (Table II), thereby confirming the transfer

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(30) Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187.

Table IV. Comparison of Electrochemical Potential Differences (V) and Energies E_{op} (eV) of Long-Wavelength Absorption Maxima

complex	$E_{ox}^{pa} - E_{red1}$	E_{op}	diff ξ
1	1.01	1.57	0.56
2	0.59	1.08	0.49
4	0.66	1.12	0.46
5	0.61	1.12	0.51
6	0.34	0.87	0.53

of less than 2 electron equiv from the metal(s) to the ligands.

Assuming anion-radical ligands $TCNX^{•-}$, the observed shifts of reduction potentials to *higher* values on metal coordination can be considered as normal (electrostatic effect[30]). These shifts are larger for the metal fragment with the less electron-donating methylcyclopentadienyl group (**5** vs **4**); on the other hand, the shifts also decrease with an increasing number of (charge delocalizing) metal fragments bonded to the $TCNE^{•-}$ ligand (**1** → **4**). This latter observation is more compatible with a metal-based reduction than with a second reduction of $TCNX^{•-}$ to $TCNX^{2-}$; in fact, the absence of ESR signals after electrochemical reduction at room temperature supports a strong contribution from intermediate-spin[22c] metals to the LUMO (fast relaxation[31]). Results from MO calculations (Figure 6) are also in agreement with this interpretation. The TCNQ complex **6** is more easily reduced than its TCNE analogue **4** because $TCNQ^{•-}$ is a weaker base than $TCNE^{•-}$;[17a,b] $TCNQ^{•-}$ is also easier reduced to the dianion (Table II).

Oxidation of the complexes is always irreversible (Figure 3); it may thus be safely assumed[21] that these are also metal-based processes. Peak potentials around +0.4 V vs SCE for complexes $(C_5R_5)(CO)_2Mn(L)$ with neutral nitrogen ligands L were observed previously;[21b,c] it is revealing that the mononuclear complex **1**, which contains only one *oxidized* metal fragment, has a distinctly higher oxidation peak potential than the polynuclear systems which formally (eq 1) contain *nonoxidized* metal fragments (Table II).

Electronic Absorption Spectroscopy. The small differences of less than 1 V between oxidation and reduction potentials suggest that a small HOMO–LUMO gap may also be manifest in the electronic absorption spectra. As a matter of fact, the differences between the long-wavelength transition energies at the absorption maximum (in eV) and the electrochemical potential differences $E_{ox}^{pa} - E_{red1}$ (in V) are quite similar for all studied systems: $\xi = 0.51 \pm 0.05$ (e)V (Table IV). We have previously analyzed the situation in the monomer **1** and described the intense low-energy transition as ligand-to-metal charge transfer (LMCT): $\pi^*(TCNE^{•-}) \rightarrow d(Mn^{II})$,[17b] albeit with considerable mixing. Coordination of a second, nonoxidized metal fragment (Mn^I) should—in a localized description (eq 1)—leave the LMCT little changed (slight high-energy shift because of lowered HOMO); however, there is now a possibility for TCNE-mediated metal-to-metal charge transfer (MMCT) $d(Mn^I) \rightarrow d(Mn^{II})$,[32] resulting in an intervalence transition (IT). In fact, Figure 4 illustrates just this expectation for dimer **2**, showing the rise of a new, even more intense band at the low-energy side of the LMCT band in the near-infrared region. Both bands show hardly any solvatochromism in going from nonpolar toluene to polar acetonitrile (Table III). The transition probability for the MMCT should increase on further organomanganese coordination, as is indeed observed (Figure 4, Table III); the intensity of the LMCT band decreases so that it appears only as a very weak shoulder in the tetranuclear complexes (cf. below).

For the dimer, a simple potential diagram (Figure 8) illustrates the two vertical transitions from the ground state to an MMCT *and* a close-lying LMCT excited state. Incidentally, the ground states of dimers such as **2** may be viewed as models for MLCT excited states of many symmetrical dinuclear metal carbonyl complexes (eq 2) where the question of (de)localization also

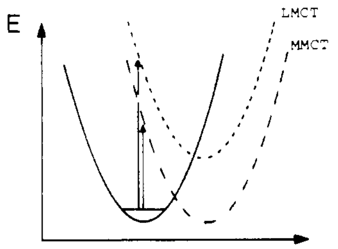
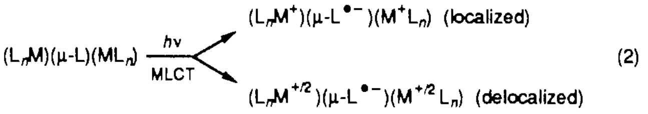


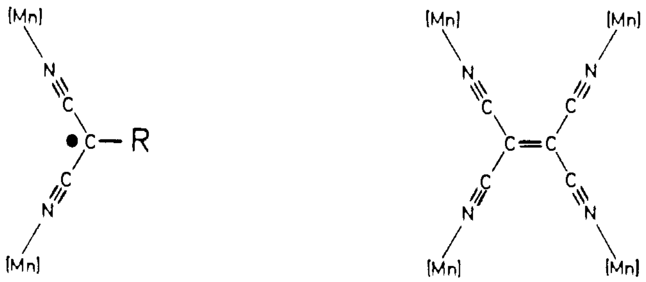
Figure 8. Simplified potential diagram for the electronic structure of complex **2**, indicating vertical MMCT *and* LMCT transitions.



$$(L_nM)(\mu\text{-}L)(ML_n) \xrightarrow[\text{MLCT}]{h\nu} \begin{cases} (L_nM^+)(\mu\text{-}L^{•-})(M^+L_n) & \text{(localized)} \\ (L_nM^{+/2})(\mu\text{-}L^{•-})(M^{+/2}L_n) & \text{(delocalized)} \end{cases} \qquad (2)$$

pertains, e.g. with regard to the significant solvatochromism of such centrosymmetric species.[33,34]

Some of the results summarized in Table III are quite readily interpreted. The virtually unchanged spectra of tetranuclear complexes **4** (strongly donating metal fragment) and **5** (weaker donating metal fragment) as well as the negligible solvatochromism reveal[17b] that the metal centers are about equally contributing to the HOMO and LUMO. The widths of the MMCT bands (≈ 2250 cm^{-1} at half-height, Table III) are similar to those observed for odd-electron mixed-valent complexes $[(C_5H_4Me)(CO)_2Mn]_2(L^-)$, L = malodinitriles;[32] actually, the tetranuclear TCNE complexes may be regarded as dimers of these latter systems (VI).



VI

It is not surprising that the TCNQ complex **6** shows a low-energy shifted MMCT band (Figure 5) when compared to the TCNE analogue **4**; weaker basicity of $TCNQ^{•-}$ and lower orbital coefficients at the nitrile groups[35] cause a decrease of orbital splitting and hence of the frontier orbital gap.[17a,b]

One result, the seemingly erratic change of the HOMO–LUMO energy difference on going from **1** to **4**, defies a simple explanation. We therefore employed simple Hückel MO calculations,[20] accounting for the metal atoms by treating them like a carbon π center with the Coulomb integral parameter $h_{Mn} = 0.0$, thereby disregarding the syn/anti isomerism (III). The results as depicted in Figure 6 are quite compatible with all experimental observations made: (i) The TCNQ complexes show smaller HOMO–LUMO gaps than the TCNE analogues; (ii) the decreased reducibility on polynucleation (Table II) is reflected by a destabilization of the LUMO; (iii) the divergence between the destabilized LUMO and the stabilized first occupied ligand-based MO (b_{3g} in D_{2h} symmetry) explains the hypsochromic shift of the LMCT band on polynucleation and its low intensity (symmetry-forbidden transition $b_{3g} \rightarrow b_{3g}$) in the tetranuclear systems; (iv) the increased MMCT band intensity of the tetranuclear complexes is probably due to overlapping features from two allowed transitions (a_u, b_{2u}

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(31) (a) Bencini, A.; Gatteschi, D. *Transition Met. Chem.* (*N.Y.*) **1982**, *8*, 1. (b) Lexa, D.; Momenteau, M.; Mispelter, J.; Saveant, J.-M. *Inorg. Chem.* **1989**, *28*, 30. (c) Kaim, W.; Kasack, V.; Binder, H.; Roth, E.; Jordanov, J. *Angew. Chem.* **1988**, *100*, 1229; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1174.

(32) Gross, R.; Kaim, W. *Inorg. Chem.* **1986**, *25*, 4865.

(33) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1987**, *26*, 68.

(34) Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 499.

(35) (a) Rieger, P. H.; Fraenkel, G. K. *J. Chem. Phys.* **1962**, *37*, 2795. (b) Rieger, P. H.; Bernal, I.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1961**, *83*, 3918.

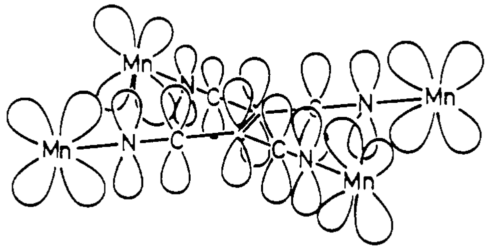
Table V. Comparison of MMCT Band Features for an Odd-Electron Malonodinitrile Complex and the Even-Electron Dimer **2**

	$[(NH_3)_5Ru]_2(NC-C(t\text{-}Bu)-CN)$[32b]	**2**
$\tilde{\nu}_{MMCT}$, cm^{-1}	8550	8680
ϵ, M^{-1} cm^{-1}	16000	25000
$\Delta\tilde{\nu}_{1/2}$, cm^{-1}	2200	2230
d_{M-M},[a] Å	≈9	≈11

[a] Estimated metal–metal distance.

→ b_{3g}); (v) the metal character of the HOMO *and* LUMO of the polynuclear complexes is compatible with the lack of ESR signals for the anion and with the small solvatochromism of the long-wavelength bands.

However, the most striking result is the successful correlation between calculated HOMO–LUMO differences and the energies of the long-wavelength absorption maxima within the series of TCNE complexes **1**–**4** (Figure 7). The otherwise hardly predictable energy sequence **2** < **4** < **3** < **1** is well reproduced, confirming the suitability of such model calculations not only for assessment of spin density[29b,c] but also for reproduction of electrochemical trends and major electronic transitions. Furthermore, the calculated π-bond orders for the central C=C bond in TCNE complexes are 0.400 (**1**), 0.440 (**2**), 0.414 (**3**), and 0.494 (**4**), in agreement with observed C=C stretching frequencies (Table I) and the formulation of the ligand as being reduced a little beyond the monoanionic state. The remaining π-bond orders calculated for the tetranuclear TCNE system are 0.528 (C–CN), 0.580 (C–N), and 0.614 (N–Mn); clearly, this kind of calculation favors extensive delocalization[20] with ($\sigma + \pi$) bond orders between 1 and 2. The successful application of the Hückel MO model thus suggests that the ground state of the polynuclear complexes described here may indeed be regarded as delocalized; instead of formulating mixed-valent polymetallic systems strongly coupled by anion-radical ligands[5,14c] (localized formulation), it seems more appropriate to describe these species as *metalla π systems* with extensive electron delocalization (VII).



VII

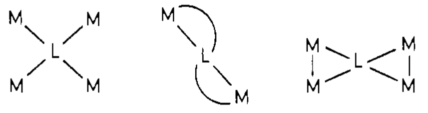
The question of the "true" nature of the TCNX ligands, anion radicals (eq 1), or dianions, becomes less relevant if multiple weak covalent bonding occurs as is implicated in Figure 6. This situation is somewhat reminiscent of the dispute over the $O_2^{\bullet -}$/Fe(III) vs $^1O_2$/Fe(II) formulation in oxyhemoglobin and myoglobin;[26a] additional complications can arise through spin-state equilibria of the metal center itself.[26b]

Another argument for delocalization is drawn from the striking similarity between the MMCT features of the (delocalized[32b]) *tert*-butylmalonodinitrile-bridged dimer of $[Ru(NH_3)_5]^{2+/3+}$ fragments and those of dimer **2** (Table V); similar parameters for the electron delocalization energies should result if the treatments by Hush[36a] or by Piepho, Krausz, and Schatz[36b] are applied. Nevertheless, the use of a localized formulation can be useful in order to rationalize certain experimental results.[37,38b]

The additional complication of an easily attainable intermediate-spin excited state at the manganese centers ($S = 1$)[17,22c] is relevant only insofar as magnetic coupling takes place in polynuclear complexes[22c] and as low-intensity d → d transitions in the low-energy region cause rapid photodissociation in solution.[21,22] The d(π) orbital (d_{xz}, Figure 6; d_{yz} according to the system of Schilling et al.[39a]) is not affected by the excitation of a d_{yz} electron to a d_{z^2} (3a′) orbital.

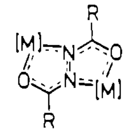
Outlook

With the results presented in this work, the range of compositions of metal/ligand delocalized complexes has been extended beyond the known 1:1 and 2:1 arrangements to (open chain) 3:1 and 4:1 systems (VIII) with more than 10 participating π centers,



VIII

including the molecular bridge. Challenges for future work are structured polymeric derivatives (using polyfunctional metal fragments)[3] and small *cyclically delocalized* metalla π systems (VIII); one such example has recently been found by us in the form of dinuclear azo dicarbonyl complexes (IX) with their pentalene-like atom configuration (edge-sharing five-membered chelate rings).[31c,38]



IX

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(36) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (b) Piepho, S. B.; Krausz, E. R.; Schatz, P. N. *J. Am. Chem. Soc.* **1978**, *100*, 2006.

(37) Ernst, S.; Kasack, V.; Kaim, W. *Inorg. Chem.* **1988**, *27*, 1146.

(38) (a) Kaim, W.; Kohlmann, S.; Jordanov, J.; Fenske, D. *Z. Anorg. Allg. Chem.*, in press. (b) Kaim, W.; Kasack, V. *Inorg. Chem.* **1990**, *29*, 4696.

(39) (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. (b) Marynick, D. S.; Kirkpatrick, C. M. *J. Am. Chem. Soc.* **1985**, *107*, 1993.