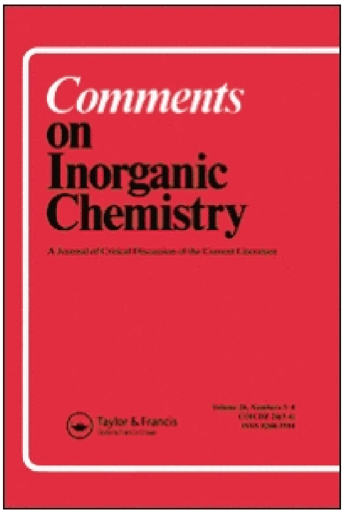

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Bridging the Fields of Organometallic and Classical Coordination Chemistry: Localized and Delocalized Bonding in Polynuclear Complexes of $(C_5R_5)(CO)_2$ Mn

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Bridging the Fields of Organometallic and Classical Coordination Chemistry: Localized and Delocalized Bonding in Polynuclear Complexes of $(C_5R_5)(CO)_2Mn$

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The capability of the title fragment to undergo efficient π back bonding, to exist in two kinetically stable neighboring oxidation states, and to exhibit a relatively small ligand field splitting have allowed the formation of unusual coordination compounds. Several mono- and polynuclear examples with an odd or even electron count and different degrees and direction of electron delocalization between ligand and metal fragment(s) will be discussed.

Key Words: *electronic structure, charge transfer, organo-manganese complexes, UV/vis spectroscopy*

INTRODUCTION

One of the main differences between the areas of organometallic and classical coordination chemistry results from different views

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of bonding between ligand(s) and metal(s): In contrast to most classical complexes with comparatively weak ligand fields and considerably ionic character of the metal/ligand bond, many organometallic systems display rather "covalent" bonds, resulting from the very strong ligand field exerted by ligands such as CO, CNR, CR_n, or η-carbocycles.[1] Although this dichotomy of metal complexes may generally be useful, there exists an intermediate region with complexes exhibiting their own distinctive chemistry.

Arriving from the classical coordination chemistry of metal ions in aqueous solution, the necessary *increase* in covalent metal/ligand interaction, kinetic stability, and ligand field strength has been discovered and exploited in complexes of rather low-valent (+II, +III) ruthenium and osmium, particularly by H. Taube and co-workers.[2] The fascinating chemistry highlighted, e.g., by the first complex of N_2,[3] the first discrete mixed valence dimer (the Creutz–Taube ion),[4] a compound of η^4-benzene[5] and numerous other reactions involving charge and electron transfer[6] could evolve because of

- —strong metal/ligand interaction due to efficient π back bonding,
- —accessibility of at least two neighboring oxidation states in a chemically useful, intermediate potential region, and
- —the kinetic stability of the metal/ligand bond in these different oxidation states of the metal.

The latter and, for the preparative chemistry, most essential requirement obviously favors the use of second and third row transition metals in the case of weak, "inorganic" ligands.

Yet, there is no reason why the aforementioned requirements should not be met by organometallic species, even if there are only few well characterized configurations established. The higher ligand field exerted by typical organic ligands leaves mainly metals from the first transition element row for a single electron transfer active system; choosing the transition metal with the lowest intrinsic ligand field splitting, namely manganese,[7] and employing the low-spin d^6 and d^5 configurations of the successfully used $Ru^{II,III}$ systems, one arrives at the $Mn^{I,II}$ situation for which a well-reputed example, the $(C_5R_5)(CO)_2Mn$ fragment already exists.[8] This kinetically very stable fragment was found to yield many complexes with "unusual" ligands,[8] including those (such as N_2)[9] which have been found to coordinate to ruthenium[3] and osmium ammine species. Incidentally, $Ru^{II,III}$ and $Mn^{I,II}$ are connected via a diagonal relationship in the periodic table.

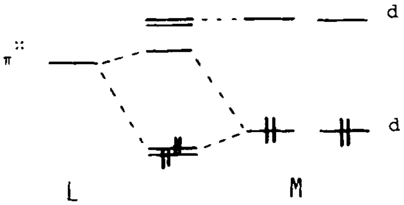
Despite the extended use[8] of the fragments $(C_5R_5)(CO)_2Mn$, R = H, CH_3, in the stabilization of "unusual" molecules, there have not been many examples for coordination compounds with more "ordinary" ligands. Our work in the past few years has shown that quite remarkable results can be obtained in reactions of this fragment with rather inconspicuous ligands; the complexes obtained often display unusual composition, electronic structure and reactivity. One advantage in working with a hydrophobic, neutral organometallic systems is that a variety of non-polar, aprotic solvents can be used, thus eliminating the problems associated with purely ionic (Coulombic) interactions and with hydrogen bonding like, e.g., in $[Ru(NH_3)_5]^{n+}$ chemistry.[6] Another advantage is that the generally monodentate metal fragment η^1-$(C_5R_5)(CO)_2Mn$ does not impose severe geometrical constraints on the metal/ligand bonding so that in the absence of potentially perturbing chelate effects, the system can freely adopt (and exhibit!) the electronically optimal conformation.

This aspect is important because efficient π back bonding must involve considerable π overlap, as in purely organic π systems; thus it should also be possible to treat such coordination compounds using the Hückel MO approach,[10] accounting for the different electronegativity of the metal center by a Coulomb integral perturbation parameter. The following examples, distinguished by the oxidation state and number of participating metal fragments (1) and ligands, demonstrate that such an approach can indeed be successful for the understanding of remarkable new coordination compounds.

$$\begin{array}{lcl} & \underset{\mathbf{1}}{(\eta^5\text{-}C_5R_5)(CO)_2Mn} & Mn^{I}\ (d^6) \\ R = H, CH_3 & \underset{\mathbf{2}}{[(\eta^5\text{-}C_5R_5)(CO)_2Mn]^+} & Mn^{II}\ (d^5) \end{array} \tag{1}$$

SITUATION 1

Coordination of an organometallic fragment, the metal typically being in a low oxidation state, to a π acidic ligand often results in a situation (2), i.e., a small degree of frontier orbital mixing occurs yet the HOMO is still a metal-centered (d-) orbital while the LUMO is mainly a ligand centered π* orbital.



(2)

Evidence for such an interpretation, for instance in complexes of **1** with aromatic nitriles (**3**),[11] acceptor-substituted pyridines (**4**)[11] or pyrazine (**5**),[12] comes from

—the rather slow formation of complexes from solvated precursors via non-catalyzed[13,14] substitution reactions,[12]
—the metal-to-ligand charge transfer (MLCT) absorption (3)

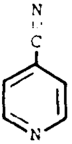
$$(L)(M) \xrightarrow{h\nu} {}^*[(L^{\overline{\cdot}})(M^+)] \qquad (3)$$

which shifts bathochromically after increasing the electron density at the metal through introduction of methyl groups at the cyclopentadienide rings (destabilization of the HOMO, (2)),[12,15]
—irreversible (dissociative) metal-centered oxidation,[11,12]
—reversible, ligand-centered one electron reduction (4) to

$$(L)(M) + e^- \rightarrow (L^{\overline{\cdot}})(M) \qquad (4)$$

—stable anion radical complexes whose electron spin resonance (ESR) analysis clearly shows the predominant localization of the added unpaired electron on the π acceptor ligand (4, 6).[11,12,16,17]

3



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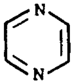

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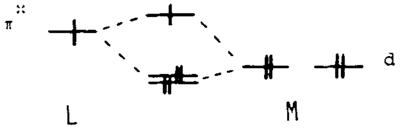
(5)

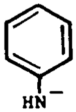


(6)

Furthermore, the negative solvatochromism of the charge transfer absorption band system as well as the distinct high field NMR shift of the protons from the acceptor ligand in non-polar solvents[11,12] support the presence of a low-lying excited state as described by (3). A good chemical indication for sizable charge transfer to the acceptor ligand is the tendency of bifunctional ligands such as (5) to achieve full coordinative saturation,[11] an effect that becomes even stronger after complete intramolecular electron transfer[14] (cf. Situation 6) or external reduction, i.e., in complexes of the much more basic anion radicals (4, 6).[17] On the other hand, the relatively small ligand field splitting in these complexes results in small *g* values of the anion radical complexes and in a pronounced light sensitivity of the neutral molecules due to photodissociative d → d transitions.[12,18]

SITUATION 2

Since the fragment (1) can exist in two oxidation states **1** and **2**, the reverse of Situation 1 should involve a π donor ligand and the monopositive form **2** of the fragment. Electrochemical studies[13,16] have shown that complexes of **2** are formed at widely varying ($\Delta E > 2$ V) oxidation potentials; numerous such paramagnetic compounds have now been described, some of which were stable enough to be isolated.[16,19–22] The remarkable dependence of the redox potential between **1** and **2** on the coordinated ligand has a parallel in classical coordination chemistry where approximately 1.7 V difference lies between the $Co^{3+/2+}$(aq) and $[Co(CN)_6]^{3-/4-}$ couples. The electronic structure of the compounds $(C_5R_5)(CO)_2Mn^{II}(L)$ is such that diamagnetic σ *and* π donating anions like R_2N^- or RX^-, X = O, S, Se, are necessary to form the coordinative σ bond as well as to provide for some compensation in the singly occupied d_π orbital at the metal. The nitrogen ligands include σ and π electron rich anilide (**6**),[16,19,23] imidazolate (**7**),[21,22] purinate (**8**)[21] or malonodinitrile anions[21,22] (7). Formation of these odd-electron compounds occurs via synergistic oxidative deprotonation of Mn^I precursors (8), e.g., by O_2 from air.



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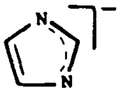

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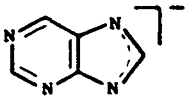

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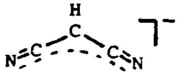
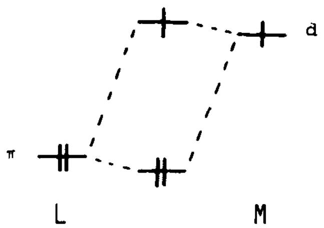


9

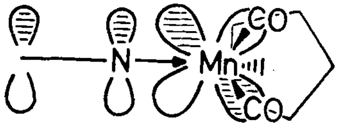
$$(L-H)Mn^{I}Cp(CO)_2 \; - \; e^-, \; -H^+ \rightarrow (L^-)Mn^{II}Cp(CO)_2 \qquad (8)$$

There are several arguments for a molecular orbital situation as depicted in (9):



(9)

—Efficient π-type metal/ligand overlap requires a very special conformation in which the ligand π plane coincides with the mirror plane of the metal fragment (10).[8,21,23–25]



(10)

Some electronically suitable ligands such as diphenylamide cannot form complexes in such a conformation because of steric hindrance; accordingly, not even traces of such complexes have been observed.[21]

—Good overlap and identical symmetry of doubly and singly occupied orbital (10) result in an allowed electronic transition, a ligand-to-metal charge transfer (LMCT) excitation (11).

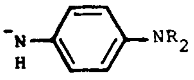
$$(\mathrm{L}^-)(\mathrm{M}^+) \xrightarrow{h\nu} {}^*[(\mathrm{L}^\cdot)(\mathrm{M})] \qquad (11)$$

For most of the ligands (7), this transition lies in the near UV or visible region[21]; there is even a good correlation between this transition energy and the ionization potential of the (protonated) ligand (L–H), because both physical measurements involve the removal of one electron from the HOMO of the ligand π system.[23]

—ESR studies show that the unpaired electron resides in a predominantly metal–based (d–) orbital,[16,21] justifying the designation of the compounds as low–spin Mn(II) systems and not as complexes with "radical" ligands.[16] However, there is some minor ligand (π) participation as suggested by the scheme (9); ^{55}Mn coupling constants and g factors show a distinct decrease with stronger donating ligands, i.e., with ligands with more destabilized π levels.[21]

SITUATION 3

These slight quantitative variations turn into a major qualitative change when extremely electron rich anions such as deprotonated p-phenylenediamines (**10**)[23] and hydrazines (**11**)[21,26] are employed.



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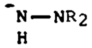

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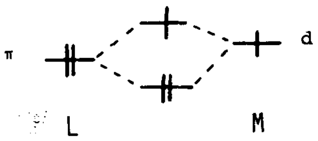
(12)

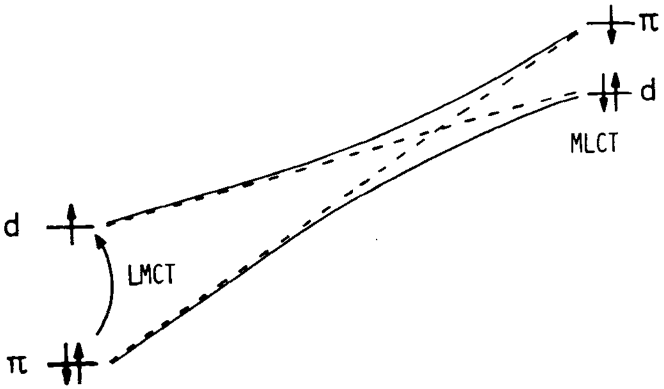


(13)

A situation (13) in which the interacting metal and ligand orbitals are roughly equivalent in energy has several special consequences:

—ESR shows that the unpaired electron now resides in an orbital of considerably mixed metal/ligand character; metal hyperfine coupling, *g* factor and *g* anisotropy are markedly reduced while appreciable superhyperfine splitting from nuclei of the ligand emerges. This change in spin distribution could be successfully reproduced by a Hückel MO calculation incorporating the Mn π center with the same Coulomb integral parameter as carbon.[23]

—The "covalent" character of the metal/ligand bond is also evident from electronic spectroscopy; as a result of the mixed metal/ligand character of the ground state as well as of the very low-lying excited state (absorption in the near IR), one notices virtual insensitivity of the transition energy towards change of solvent or modification at the cyclopentadienide rings.[23] According to perturbation scheme (14), there is a point where the differentiation between MLCT and LMCT becomes meaningless because of delocalization and covalent bonding.

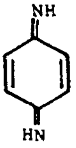


(14)

SITUATION 4

In complexes with additional acidic hydrogen atoms at the same or other potential coordination centers, the enormous electron excess provided by some ligands can result in a second oxidative deprotonation/metal coordination sequence, yielding even-electron dinuclear complexes of the (2*e*,2H) "oxidized" forms of those ligands.[19,21,23,26]

While ESR studies of paramagnetic compounds provide a good way to establish the character of a singly occupied MO,[16,17] the situation is more difficult to analyze for even-electron systems with appreciable delocalization. Dinuclear complexes of ligands such as **12** or **13**[19,23] may thus be viewed as consisting either of dianionic bridging ligands and oxidized metal fragments or of neutral, in the free form unstable ligands (e.g., p-quinonediimines, nitrenes, diazenes) which are stabilized by coordination of low valent Mn^I fragments.[8]



12

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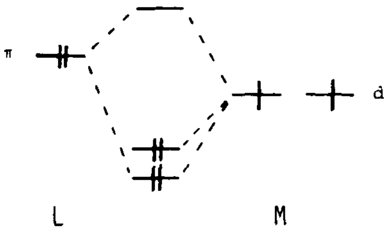
(15)

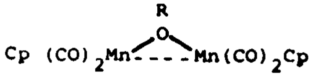


(16)

Instability of reduced or oxidized paramagnetic forms and an only weak response of the absorption spectra on exchange of C_5H_5 by $C_5(CH_3)_5$ have so far prevented an unambiguous assignment[26]; the apparently high degree of delocalized bonding (16) as established for the corresponding mononuclear precursors[23] (Situation 3) is one typical requirement for the stabilization or activation of "unusual" (cf. N_2) or "unstable" ligands (cf. R_2N_2[27] or cyclo-C_4R_4[28]) by complex formation.

SITUATION 5

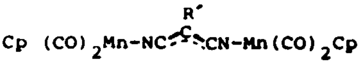
Starting from Situations 2 or 3, there is an alternative for the formation of dinuclear complexes. If a bridging anionic ligand is sufficiently basic, it may coordinate a neutral metal fragment **1** in addition to the positively charged one (**2**), thereby creating the possibility to obtain paramagnetic, molecule-bridged mixed-valent dimers. With very strong bridging bases such as certain alkoxides, imidazolate (**7**) or malonodinitrile anions (**9**), such dimers (17) were obtained as rather labile species, sometimes only in the presence of the mononuclear Mn^{II} systems.[22]



14

15

(17)

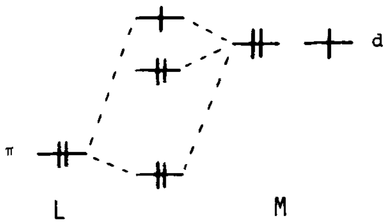


16

Nevertheless, the appearance of characteristic intervalence transfer (IT) absorptions (18) in the near infrared region

$$(M^+)(L)(M) \xrightarrow{h\nu} {}^*[(M)(L)(M^+)] \qquad (18)$$

and, most notably, the equivalence of the two metal centers on the ESR time scale provided clear evidence for a delocalized mixed-valence system (19) even in those instances where the metal centers must be separated by more than 800 pm (cf. **16**).



(19)

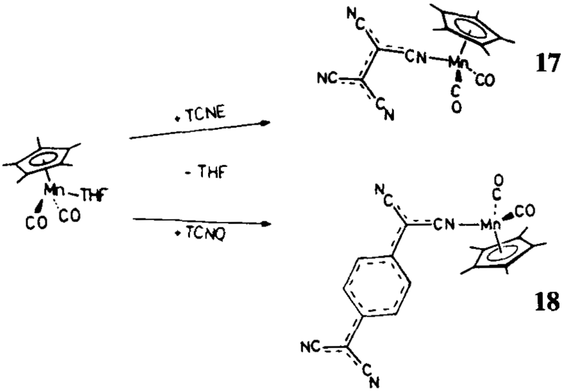
Two results merit special mentioning: While the imidazolate-bridged dimer **15** shows ESR features compatible with a simple sharing of spin with one more metal center, the alkoxide bridged dimers **14** exhibit more unusual changes relative to the mononuclear counterparts. Apparently, the bridging by just the small oxygen atom can bring about some direct metal/metal interaction,[22] as may be anticipated also from structural studies of a thiolate bridged analogue.[29]

On the other hand, the tert.-butylmalonodinitrile-bridged dimer **16** reveals some typical features of a more ligand-centered unpaired electron such as narrow ESR lines, small *g* and small ^{55}Mn hyperfine splitting; in addition, the IT and LMCT absorption bands are rather close in energy (19).[22] The same Hückel MO calculation approach that proved successful[23,26] in rationalizing the spin distribution in compounds listed under Situations 2 and 3 suggests that the imidazolate-bridged dimer **15** should indeed have little ligand participation in the singly occupied MO while the malonodinitrile complex **16** should have a sizable amount of spin delocalized onto the carbon centers of these ligands.[30] The preferential binding and strong interaction of the fragments (1) with nitriles such as **3**, **4** or **9** ("cyanophilicity")[11,21,22] has then prompted us to study their coordination to the well-known acceptors TCNE and TCNQ in more detail.

SITUATION 6

Returning to reactions of even-electron ligands and metal centers, the π acceptor level of the ligand reacting with the electron rich metal fragment may be lowered to such an extent that electron transfer occurs in the ground state[15] (and not only in the excited state as described by Situation 1). Frequently, such single electron transfer (SET) processes (20) are accompanied by rapid follow-up reactions[31,32]; however, TCNE or TCNQ and the Mn^I fragments **1** yield simple addition products.[30,33]

$$(L) + (M) \xrightarrow[\text{SET}]{} [(L^{\cdot -})(M^+)] \tag{20}$$



17

18

(21)

There are several pieces of evidence for the description (20) of **17** and **18** as single electron transfer products[33]:

—The redox potentials of the reactands (21) require an electron exchange reaction.[13,33]

—The rate of formation is several orders of magnitude faster than in a "normal" substitution process,[12] suggesting an electron transfer "autocatalytic" reaction.[14]

—The charge transfer energy of the long-wavelength transition (22) is *increased* upon replacement of C_5H_5 by $C_5(CH_3)_5$, indicating predominantly LMCT character (destabilization of the LUMO).[15]

$$[(L^{\cdot -})(M^+)] \xrightarrow{h\nu} {}^*[(L)(M)]; \tag{22}$$

—The reduction potentials of the complexes are more negative than those of the free ligands, suggesting[17] that the ligand is already reduced and it is mainly the metal fragment that accepts the electron.

—An ESR spectrum of the reduction product could not be observed at room temperature; fast spin-lattice relaxation is typical for transition-metal centered "radicals" with close-lying excited states.[21]

—The IR spectra of compounds **17** in solution not only suggest σ-coordination of the metal fragment to one nitrile group but are also compatible with the formulation of a TCNX anion radical ligand (ν_{CN},ν_{CC}) and an oxidized metal fragment (ν_{CO}).[33]

—Whereas ^{13}C-NMR spectra of the TCNE systems support the σ-coordination, the TCNQ complexes dissociate in coordinating solvents to yield ESR-detectable $TCNQ^{\cdot-}$ and Mn^{II} components[26,33] ("radical-ion pairs"[31,32]).

All those results support the formulation of these compounds as anion radical complexes of an odd-electron metal fragment, yet with some degree of delocalized bonding. The most spectacular consequence of the reduced character of the TCNX ligands is their ability to coordinate up to three more (neutral) fragments **1**, thereby forming the first neutral tetranuclear complexes of TCNE and TCNQ.[33]

SITUATION 7

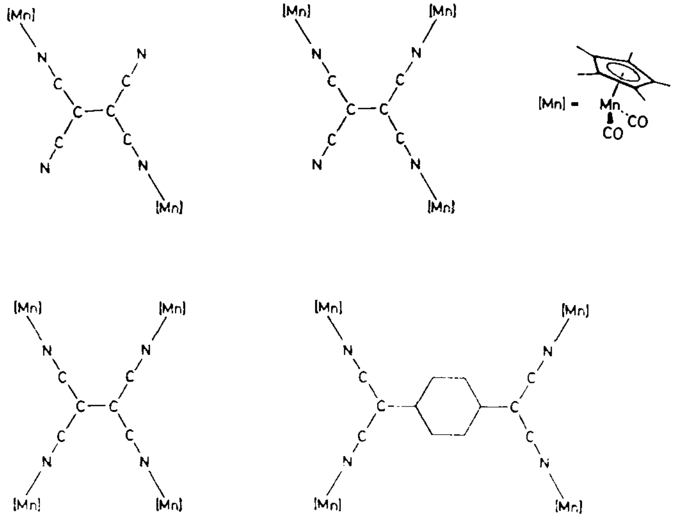
Additional coordination of one or more neutral Mn^I fragments **1** to the $Mn^{II}/TCNX^{\cdot-}$ species **17** or **18** would create a mixed valence polymetal arrangement, bridged by an anion radical ligand (23).

$$(M^+)(L^{\cdot-}) + n(M) \longrightarrow (M^+)(L^{\cdot-})(M)_n \qquad (23)$$

Such a formulation seems quite exotic and should rather represent an electronically excited (charge transfer) state (24) of polynuclear complexes[34] such as mentioned under Situation 1,

$$(L)(M)_{n+1} \xrightarrow{h\nu} {}^*[(M^+)(L^{\cdot-})(M)_n]; \qquad (24)$$

however, spectroscopic data support this formulation at least as a resonance structure for the situation in complexes (25).



(25)

—Successive $\mathrm{Mn}^{(\mathrm{I})}$ fragment coordination causes a decrease in the reduction potential of the complexes,[33] while an additional oxidation process occurs at a low potential typical for $\mathrm{Mn}^{\mathrm{I}} \rightarrow \mathrm{Mn}^{\mathrm{II}}$.[11–33]

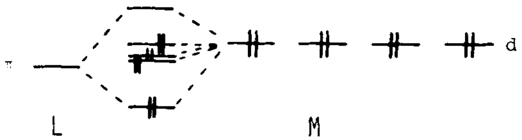
—IR data establish again the reduced character of the bridging TCNX ligand systems, while the average charge on the metal fragments decreases as demonstrated by the low frequency shift of carbonyl stretching bands.[30,33] Just as the NMR data of one tetranuclear complex, the IR results are fully compatible with a delocalized formulation (26).[33]

$$(\mathrm{L}^{\overline{\cdot}})(\mathrm{M}^{1/n+})_n \qquad (26)$$

—In agreement with the very small differences between oxidation and reduction potentials, the polynuclear complexes display electron absorption bands at rather low energies, in the near infrared part of the spectrum.[33] Most intriguingly, there are generally two bands discernible: One band represents the LMCT transition which occurs also in the mononuclear system while a second band grows very much in intensity on additional metal coordination. The latter may be tentatively assigned to an intervalence transfer (IT) transition, e.g.,

$$(M^+)(L^{\cdot-})(M) \xrightarrow{h\nu} {}^*[(M)(L^{\cdot-})(M^+)] \qquad (27)$$

as in Situation 5 and may thus be taken as evidence for a localized description (23) on the time scale of the electronic spectroscopy experiment. However, the π MO calculational procedures described before yield a sequence (28) of *delocalized* orbitals which also reproduces the observed electronic transitions surprisingly well.[26,30] This does not only include the number of allowed transitions in the long wavelength (IT) band and the observed hypsochromic shift of the LMCT transition; HMO calculations also reproduce the unexpected result that the long wavelength absorption energy increases along the series of (trans-1,2-)dinuclear < tetranuclear < trinuclear < mononuclear complexes of TCNE.[26,30]



(28)

Therefore seems that the compounds (25) represent a new class of polynuclear complexes with delocalized bonding and yet unusually small frontier orbital differences. Structural and magnetic studies will have to further elucidate the nature of these remarkable species.

OUTLOOK

The examples shown here do not only cover the whole spectrum from ligand-localized via delocalized to metal-localized bonding in odd- and even-electron cases; they also illustrate that there are various other combinations than a 1:1 ratio between metal and non-innocent ligand[25] possible (cf. the textbook case of 1, 2-dithiolene complexes[35]). A very convincing piece of evidence for delocalized bonding is the remarkable success of Hückel MO calculations in reproducing not only ESR spin populations but also charge transfer absorption energies.

Studies of o-(semi)quinone complexes by Pierpont and co-workers have shown[36] that the relative closeness of metal and ligand levels alone is not sufficient for effective delocalization; an essential requirement according to the second order perturbation equation (29)[10] is a sizable resonance integral H_{AB}.

$$\delta = (H_{AB})^2/\Delta E. \tag{29}$$

As the extraordinary charge transfer band intensities found for compounds in (21) and (25)[33] attest, this latter requirement is apparently fulfilled in coordination compounds of the fragments (1) with nitrogen ligands, especially nitriles. The existence of such compounds stimulates the search for other polynuclear delocalized coordination compounds as hybrids between true π systems and metal clusters with delocalized bonding; particularly attractive with respect to potential applications would be the long attempted[37] construction of low-dimensional coordination polymers with delocalized bonding.

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