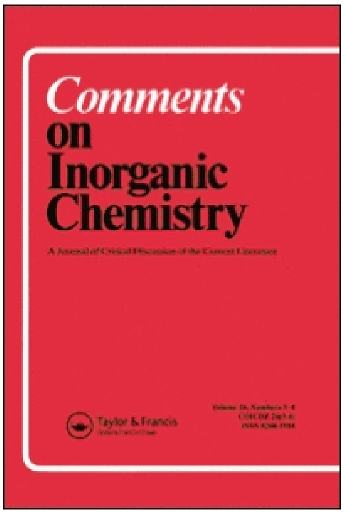


Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Metal and Ligand Oxidation States in Dioxolene Complexes: Meaning, Assignment and Control

Antonín Vlček Jr.[a]
[a] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic

To cite this Article Vlček Jr., Antonín(1994) 'Metal and Ligand Oxidation States in Dioxolene Complexes: Meaning, Assignment and Control', Comments on Inorganic Chemistry, 16: 4, 207 — 228

To link to this Article: DOI: 10.1080/02603599408035860

URL: http://dx.doi.org/10.1080/02603599408035860

Metal and Ligand Oxidation States in Dioxolene Complexes: Meaning, Assignment and Control

ANTONÍN VLČEK, JR.
J. Heyrovský Institute of Physical Chemistry,
Academy of Sciences of the Czech Republic,
Dolejškova 3,
182 23 Prague, Czech Republic

Received March 14, 1994

Many features of the structural, magnetochemical, spectral, electrochemical, and chemical behavior of transition metal complexes with redox-active dioxolene ligands indicate that most of them are valence-localized species with well defined and experimentally distinguishable metal- and dioxolene-oxidation states. The valence localization results mainly from large structural differences between individual oxidation states of the dioxolene ligands. It is shown that dioxolene complexes may be treated like weakly coupled mixed-valence compounds, and a qualitative "localized-valence" model is developed in order to interpret physical and chemical properties of dioxolene complexes, including their bistability, in a unifying way.

Key Words: *dioxolenes, quinones, semiquinones, catecholates, electronic structure, oxidation states, valence localization, bistability, molecular structures, magnetochemistry, electrochemistry, electronic spectroscopy*

Abbreviations Used: The term "dioxolene" (Diox) is used for ligands derived from 1,2-di-oxo-benzene, irrespective of their oxidation state, i.e., for catecholate dianion (Cat), ortho-semiquinone radical-anion (SQ) or ortho-quinone (Q), without specifying the substituents on the benzene ring. The individual oxidation states of the 3,5-di-tert.butyl-1,2-dioxo-benzene (DBDiox) are denoted DBCat, DBSQ and DBQ. CDiox, CQ, CSQ, CCat denote 3,4,5,6-tetrachloro-1,2-dioxo-benzene.

Comments Inorg. Chem.
1994, Vol. 16, No. 4, pp. 207–228
Reprints available directly from the publisher
Photocopying permitted by license only

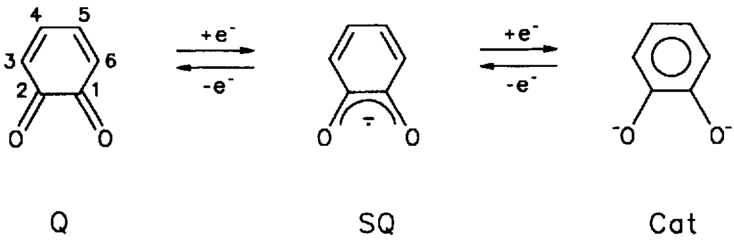
Analogously, PDiox, PCat, PSQ, and PQ stand for 9,10-phenanthrenedioxolen and its particular oxidation states.

INTRODUCTION

The great variety of structural, physical and chemical properties exhibited by metal dioxolene complexes[1,2] makes them the subject of a vigorously growing and truly fascinating research field. Distinct structural types, which are often interconvertible by small variations in the solvent, temperature or co-ligand nature, bistability, extensive redox series whose members have profoundly different properties, unusually intense absorption bands in the visible and near-infrared spectral regions, solvatochromism and thermochromism, intramolecular antiferro- and ferromagnetic spin–spin couplings, and activation of small molecules like O_2 and N_2, represent some of the frequently encountered features. Many unusual aspects of the chemistry of dioxolene complexes appear to be related to the redox activity of the dioxolene ligand that may exist in three different oxidation states, i.e., quinone, Q, semiquinone radical anion, SQ (i.e., $Q^{-\cdot}$), and catecholate dianion, Cat (i.e., Q^{2-}), which are related by one-electron transfers (see Scheme I). Apparently, elucidation of the electron distribution in dioxolene complexes, that is, the assignment of the metal- and dioxolene-oxidation states together with the assessment of the extent of electron (de)localization, would provide the key to the understanding of this unique class of coordination compounds. Surprisingly, with only few exceptions,[3-5] dioxolene complexes escape the attention of theoretical chemists and many aspects of their behavior are still not satisfactorily interpreted. It is the aim of this Comment to indicate how the diverse properties of dioxolene complexes could be, at least qualitatively, approached and interpreted using a single concept of valence localization.

LOCALIZED OR DELOCALIZED VALENCE?

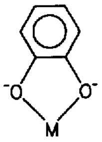
Redox activity of dioxolenes, Scheme I, is retained upon their coordination and, importantly, the dioxolene oxidations and



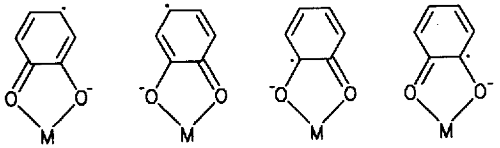
SCHEME I Dioxolene ligands and their redox couples. (The quinone formula on the left shows the numbering of ring carbon atoms.)

reductions occur in the same potential range where metal-localized redox couples may be expected. Hence,[6] a complex molecule containing a dioxolene ligand coordinated to a redox active metal atom may, in principle, exist either in one of the three possible valence-localized structures of similar energy: $\{M^{(n+2)+}(Cat)\}$; **I** $\{M^{(n+1)+}(SQ)\}$; **II**, and $\{M^{n+}(Q)\}$; **III**, or it may occur as a delocalized $\{M(Diox)\}^{n+}$ species. Principal valence-bond, VB, structures of the valence-localized forms are shown in Fig. 1. The delocalized structure may be, in VB terms, viewed as a "mixture" of at least two valence-localized forms. Even more complicated situations arise when two or three dioxolene ligands are coordinated to the same metal atom. The problem of valence localization between the metal and individual dioxolene ligands is then compounded by the possibility of an electronic interaction between dioxolene ligands themselves. If all inter-dioxolene and metal-dioxolene interactions are weak the ligand-localization of valences may give rise to two different situations: (i) all the dioxolene ligands are in the same oxidation state, like in $[Co^{II}(bpy)(DBSQ)_2]$ or $[Cr^{III}(DBSQ)_3]$, (ii) two dioxolene ligands in different, experimentally clearly distinguishable, oxidation states are coordinated to the same metal atom like in $[Co^{III}(bpy)(DBCat)(DBSQ)]$. Such complexes are typical examples of "ligand based mixed valence", LBMV, species.[7]

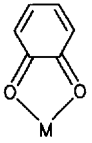
The above discussion indicates that the first question to be answered when interpreting the chemistry of dioxolene complexes is whether we are dealing with valence-localized molecules, for which the oxidation-state concept is applicable, or with electronically delocalized species. From this point, we can proceed further and



$\{M^{(n+2)+}(Cat)\}$, I



$\{M^{(n+1)+}(SQ)\}$, II



$\{M^{n+}(Q)\}$, III

FIGURE 1 Principal valence-bond structures contributing to the valence forms of dioxolene complexes.

investigate the relations between oxidation states of dioxolene ligands and properties of their complexes.

From an experimental point of view, a complex molecule may be looked upon as valence-localized as long as it exhibits properties characteristic for its components, i.e., for the metal atom and dioxolene ligand(s) in their particular oxidation states.[6,8,9] On the other hand, extensive delocalization would lead to a behavior that could be attributed to the whole complex molecule only, bearing no resemblance to that of the components.[6,8,9] Most dioxolene complexes exhibit[1,2,10] a clear correspondence between the metal and dioxolene formal oxidation states on one side and experimentally observable behavior, especially intradioxolene bond lengths and vibrational frequencies, magnetic properties, nature of electronic transitions, electrochemistry and chemical reactivity, on the other. Dioxolene complexes may thus clearly be grouped according to the dioxolene ligand oxidation states into distinct classes whose members show rather similar patterns of behavior. Hence, it may be concluded that most dioxolene complexes are valence-localized species where the formal oxidation states of the metal and dioxolene ligand(s) may be defined and experimentally determined.

PHYSICAL MEANING OF VALENCE LOCALIZATION

Using a simple one-electron MO approach, an assignment of formal oxidation states requires[6,8,9] us to find a scheme of dividing valence electrons between the metal atom and dioxolene ligand(s), which are thus associated with well-defined electron configurations. As the σ-bonding between the metal atom and chelating dioxolenes is the same in all valence forms considered, the orbitals whose occupancy determines the oxidations states are the dioxolene frontier orbital, $3b_1$, and the uppermost metal d orbitals. The $3b_1$ orbital is empty in *o*-quinones, singly occupied in semiquinone radical anions and doubly occupied in catecholate dianions. It is π-antibonding with respect to C–O, C_3–C_4, and C_5–C_6 bonds and π-bonding toward C_1–C_2, C_2–C_3, C_4–C_5, and C_6–C_1 bonds[3–5,10,11] (see Fig. 2). Although the $3b_1$ orbital has the right symmetry to mix with a corresponding d_π metal orbital, their interaction has to

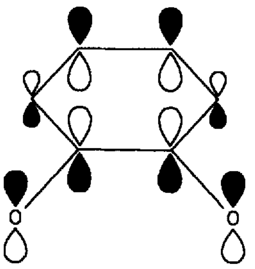


FIGURE 2 The $3b_1$ frontier orbital of a dioxolene ligand.

be rather weak in order to keep both the dioxolene ligand and the metal atom in localized, distinguishable oxidation states. The weakness of the $3b_1$–d_π interaction is usually explained by an energy gap between these orbitals.[1,2,12] The $3b_1$ orbital is simply assumed to lie energetically above the frontier d orbitals in quinone and semiquinone complexes and below them in catecholates. Near-equal $3b_1$ and d_π orbital energies are assumed in several Ru and Os complexes that are believed to have delocalized structures.[12] The MO approach implicitly assumes[13] that the Coulombic and exchange interactions as well as the energies and wavefunctions of all molecular orbitals are identical in different valence forms, i.e., independent of the metal and dioxolene oxidation state. Consideration that different valence forms have profoundly different molecular structures and often also different total spins indicates that the qualitative one-electron MO approach is grossly oversimplified. Despite that, it has been quite successful in explaining some features of the dioxolene chemistry. On the other hand, it is difficult to understand on the MO basis why small changes in $3b_1$ and d_π orbital energies, caused by minor variations in the co-ligand nature, often result in a net switch from one localized valence form to another,[1,2] instead of subtle electron density shifts via the M-Diox π-bonding. The latter behavior is very common for ligands like α-diimines, carbonyls, isocyanides, or phosphines. This difference in the extent of π-bonding is even more striking if we consider that, compared with the $3b_1$ dioxolene π-orbital, the π-orbitals of the latter ligands lie energetically much more above the d_π-metal orbital. The simple MO picture also fails to explain satisfactorily the existence of LBMV dioxolene complexes[1,2] and switching between different valence forms on changing the temperature.[14–18] The electronic spectra of quinone complexes[19–24] also cannot be explained using a simple MO approach.

A clue to the development of a more general model of dioxolene complexes is provided by a realization that they exhibit[1,2,10] all the essential magnetochemical, spectroscopic and electrochemical features typical for class II *mixed valence* compounds[25] with weakly coupled but localized "centers of different valence". However, the centers responsible for the "mixed valence behavior" are completely different species, i.e., the metal atom and the dioxolene ligand(s). Terminologically, it is thus not correct to talk about mixed valence species. Instead, we may use the terms "valence-localized", which is preferred in this Comment, or "valence-trapped".

Contrary to typical mixed valence complexes, where the metal atoms in different oxidation states are separated by a bridging ligand, the dioxolene ligands are covalently σ-bonded to the metal atoms bringing the "centers of different valence" into close proximity. Despite that, the valence localization occurs as a consequence of gross structural differences between the valence forms, as was firmly established by solid-state structural data[1,2,26] and by bond stretching frequencies that might be obtained[19–21,24,27–30] by resonance Raman spectra even in fluid solutions. Comparisons[1,2] and statistical evaluation[26] of intradioxolene bond lengths in many complexes have shown that a characteristic set of intradioxolene bond lengths corresponds to each dioxolene oxidation state, i.e., to each valence form **I–III** (see Table I). This set of structural parameters changes to another, profoundly different, set when a dioxolene oxidation state is changed. Complexes with intermediate values of bond lengths are very rare. As long as their oxidation state is unchanged, dioxolene ligands exhibit only small scatter of structural parameters when bound to different metal atoms or in different coordination environments. These observations point to the following conclusions: (i) A change between any two of the valence forms **I**, **II**, **III** is associated with a large change of the lengths of all bonds of the metal-dioxolene chelate ring and within the dioxolene ligand. (ii) The energy of a given valence form sharply

TABLE I

Intradioxolene C–O and C_1–C_2 bond distances and vibrational frequencies characteristic for different oxidation states of coordinated dioxolene ligands.

Ox. State	d(C–O), Å	d(C_1–C_2), Å	Vibr. Frequencies, cm^{-1}	
M(Cat)	1.34–1.47	1.37–1.41	1480(s)	ring breathing
	1.35[a]		1250–1275(s)	C–O stretch
M(SQ)	1.27–1.31	1.43–1.45	1400–1500(s)	C–O stretch
	1.29[a]		1250(w)	
M(Q)	1.23	1.53	1630–1640	C=O stretch
			500–600[b]	

[a] Most frequent value.

[b] Group of skeletal vibrations which dominates resonance Raman spectra.

increases when the bond lengths are distorted from the narrow range typical for the pertinent dioxolene oxidation state. These two interrelated effects suggest that individual valence forms possible for a given dioxolene complex are separated by rather high energy barriers. This is schematically shown in Fig. 3, where the Gibbs free energy of the valence forms possible for several types

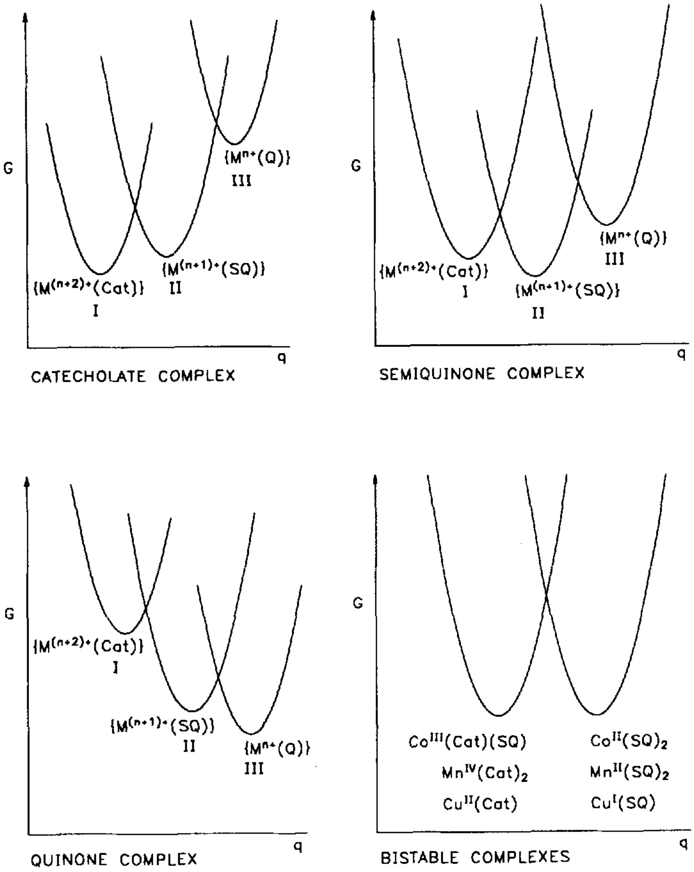


FIGURE 3 Localized-valence model of dioxolene complexes. Gibbs free energies of individual valence forms are plotted against a coordinate q that comprises all structural coordinates which depend on the dioxolene and metal oxidation states. (Electronic interaction between the valence forms manifested by energy separation between corresponding curves at the crossing points is not shown.)

of dioxolene complexes are plotted against a generalized "global" coordinate q that is a function[30,31] of all inner (bond lengths, angles) and outer (solvation or lattice) coordinates which change with the dioxolene oxidation state. According to this *localized-valence model*, structures of dioxolene complex molecules are trapped in narrow, deep energetic minima, each of which corresponds to a definite electron distribution between the metal and dioxolene ligand(s), i.e., to their definite oxidation states, or, in other words, to definite valence forms **I**, **II**, and **III**. The "mixed-valence-like" behavior of many dioxolene complexes is a result of the availability of two such "energy wells" which have similar zero-point energies but which correspond to valence forms with completely different electron distributions.

This model clearly shows that the presence and the height of the energy barriers separating the valence forms of dioxolene complexes are responsible for their valence localization, whereas equilibrium energies of individual valence forms determine in which oxidation states the dioxolene ligand(s) and the metal atom occur (see Fig. 3). Conditions necessary for the presence of high barriers and, thus, for a prominent valence localization are (i) large structural differences, Δq, between individual valence forms, (ii) narrowness of corresponding energy wells, and, importantly, (iii) rather weak interaction between the wavefunctions of the valence forms. The MO requirement of a weak $3b_1-d_\pi$ orbital interaction is implicitly included in the above-mentioned condition of the weak interaction. However, large structural differences between the valence forms also imply significant differences in orbital energies and wavefunctions (i.e., radial distribution and contributions of atomic orbitals) not only of $3b_1$ and d_π, but of all molecular orbitals involved. Hence, the interaction term $H_{i,j} = \langle\Psi_i|H|\Psi_j\rangle$, where $i \neq j$ denotes two non-equivalent valence forms, thus cannot be approximated by a simple $\langle 3b_1|H|d_\pi\rangle$ term pertinent to the simplified MO approach. In conclusion, the localized-valence model allows for some, albeit limited, $3b_1-d_\pi$ interaction to occur *within* each valence form of a dioxolene complex. The $3b_1-d_\pi$ energy gap does not have the paramount importance assumed by the simple MO model. The electronic interaction between the valence forms is weak mainly because of large differences between corresponding wavefunctions Ψ_i, Ψ_j.

SOME EXPERIMENTAL MANIFESTATIONS OF VALENCE LOCALIZATION

Structural investigations[1,2,26] afford the most definite evidence for valence localization in dioxolene complexes, the C–O and C_1–C_2 bond distances providing the most direct criteria for the assignment of a dioxolene oxidation state (see Table I). Dependence of the bond distances on the dioxolene oxidation state may be easily explained using the limiting valence forms of Fig. 1 or, better, by a successive filling of the $3b_1$ orbital when going from Q to SQ and to Cat according to the bonding and antibonding character of the $3b_1$ orbital with respect to individual intradioxolene bonds (see Fig. 2). Thus, the C–O, C_3–C_4, and C_5–C_6 bonds are elongated, whereas the C_1–C_2, C_2–C_3, C_4–C_5, and C_6–C_1 bond lengths decrease when changing the dioxolene oxidation state in the Q → SQ → Cat order. Consequently, the dioxolene carbon ring is diene-like (i.e., C_2–C_3, C_4–C_5, and C_6–C_1 bonds longer than C_3–C_4 and C_5–C_6) for Q and SQ ligands and aromatic (i.e., all C–C bonds nearly equal) for Cat. The relation between molecular structures and valence localization has been nicely demonstrated[26] by a statistical treatment of bond lengths within 146 independent dioxolene ligands in 75 different complexes. Most of the known structures are closely grouped around structurally defined[26] oxidation states -1 (SQ) and -2 (Cat). Obviously, changes in the metal atom or co-ligands either do not influence the intradioxolene bond distances appreciably or change them in major steps due to switching between the valence forms. In contrast, delocalized complexes, like, e.g., metal 1,2-benzodiimines, do not occur in structurally distinct classes, but exhibit broad ranges of intra-ligand bond lengths, the particular values depending gradually on the coordination environment.[33]

Magnetic properties of semiquinone complexes provide excellent evidence for a strict valence localization. EPR spectra of complexes with a single SQ ligand coordinated to a metal atom, whose uppermost d orbital is either empty or doubly occupied, originate from SQ-localized radicals perturbed by a weak interaction with the metal atom. g-factors are close to those of free SQ ligands and metal hyperfine splitting constants are much smaller than those of metal localized radicals.[34,35] On the other hand, EPR signals of paramagnetic catecholate complexes like $[Cu^{II}(bpy)(DBCat)]$ [35] and $[Mn(CO)_3(DBCat)]^{2-}$ [36] clearly correspond to metal-localized d^9 and d^7 configurations, respectively. Well-developed and sharp EPR signals of SQ radical ligands found for LBMV complexes $[V^V(O)(DBSQ)(\mu\text{-}DBCat)]_2$ [37] and $[Co^{III}(bpy)(DBCat)(DBSQ)]$ [14] indicate that the Cat ↔ SQ electron hopping is slow on the EPR timescale, apparently because of high energy barriers between the Cat and SQ structures.

Complexes with a $(d_\pi)^1(3b_1)^1$ electron configuration have spin-paired ground states but they very often possess low-lying thermally accessible high-spin excited state(s). This shows that the interaction between the $3b_1$ and d_π magnetic orbitals is rather weak and may be better described as an antiferromagnetic coupling than a covalent π-bond. The same is true for SQ–SQ interaction in many bis- or tris-SQ complexes. M–SQ and SQ–SQ antiferromagnetic couplings are often experimentally manifested by temperature dependent magnetic moments[38-40] or paramagnetically induced shifts of NMR signals.[41] High-field Mössbauer spectra obtained on antiferromagnetically coupled Fe^{III}–SQ complexes,[42] $[Fe(salen)(DBSQ)]$, $[Fe(bpy)(PSQ)(PCat)]$, $[Fe(DBSQ)_3]$, and $[Fe(PSQ)_3]$, have shown that the residual unpaired electrons, that are not antiferromagnetically coupled with the SQ-electrons, are indeed Fe-localized. This is in accord with the localized Fe^{III} formal oxidation state.

If the metal magnetic orbital is d_σ, i.e., orthogonal to the $3b_1$ dioxolene magnetic orbital, a strong M–SQ ferromagnetic coupling will occur, giving rise to high-spin ground states.[10] This is the case of a $Cu^{II}(SQ)^+$ complex[43] $[Cu(di\text{-}2\text{-}pyridylamine)(DBSQ)]^+$ and of octahedral $Ni^{II}(SQ)^+$ complexes[39,44] $[Ni(py)_2(PSQ)_2]$ and $[Ni(n_4)(DBSQ)]^+$, n_4 = cyclic tetraza-ligand. Interestingly, the analogous 5-coordinated trigonally bipyramidal $[Ni(n_3)(DBSQ)]^+$ complex exhibits an antiferromagnetic Ni^{II}–SQ coupling[45] because of the loss of orthogonality between the magnetic orbitals. Evidently, the magnetic properties might be controlled stereochemically.

Peculiar magnetic properties of dioxolene complexes are clear consequences of their valence localization. Should these species be electronically delocalized, a strong covalent interaction would replace the antiferromagnetic coupling and high-spin states would lie unaccessibly high in energy. On the other hand, if there were no energy barriers between the valence forms, an intramolecular M → SQ electron transfer from higher d_σ to lower $3b_1$ orbital would produce $M^{III}Cat^+$ complexes instead of ferromagnetically coupled $M^{II}SQ^+$ species; M = Cu, Ni.

Electronic absorption spectra. The localized-valence model (Fig. 3) suggests that electronic transitions in dioxolene complexes may occur either within the lowest-energy valence form or between two different valence forms. Transitions which do not change the valence form are best observable for complexes that contain only one dioxolene ligand. They show absorption bands characteristic for the metal atom and/or the dioxolene ligand in their particular oxidation states. For example,[5] [Co(triphos)(DBCat)] exhibits dd transitions typical for trigonal-bipyramidal Co^{II}, whereas $[Co(trien)(DBCat)]^+$ shows two low-intensity absorption bands[46a] that are characteristic for octahedrally coordinated Co^{III}. The observation of low-intensity NIR absorption bands for $[Os(bpy)_2(DBCat)]^+$ was used[46b] to assign the Os oxidation state as III. Many DBSQ complexes may be easily characterized[19] by a sharp intense intraligand band around 310 nm and by a weaker broad band[19,47] between 600 and 700 nm. The intensities and energies of the SQ ligand-localized absorption bands are very similar to those observed for free, uncoordinated SQ radical-anions.[48] The occurrence of weakly perturbed metal- and dioxolene-localized electronic transitions indicates that the metal atom and the dioxolene ligand essentially behave as isolated, weakly interacting chromophores in accord with the localized-valence model.

Spectra of most dioxolene complexes in the visible and NIR spectral regions are dominated by intense absorption bands which belong to transitions between the valence forms. These transitions, if identified, have been described[1,2,10,19,20,23,28] as MLCT for Q and SQ complexes and as LMCT for Cat complexes. However, as follows from Fig. 3, the energies of optical, i.e., vertical, transitions between valence forms are determined mainly by the reorganizational energy[49-52] that might be more important than the differences between the energies of the optical orbitals or between the zero-point energies of the valence forms in question. Hence, the localized-valence model indicates that some of the intense visible and NIR absorption bands exhibited by dioxolene complexes could be treated as intervalence charge transfer bands, i.e., within the framework of the Marcus–Hush theory.[49–52] This hypothesis, however, still remains to be tested experimentally.

Noteworthy, dioxolene complexes exhibit other unique spectral features that are direct consequences of the valence localization. Low-energy NIR bands were found[2,17] for several LBMV complexes like $[\mathrm{Co^{III}(bpy)(DBCat)(DBSQ)}]$. An intense band at 2300 nm may be assigned either as a DBCat → $\mathrm{Co^{III}}$ LMCT (in accord with a low-energy difference from the $[\mathrm{Co^{II}(bpy)(DBSQ)_2}]$ valence form) or as a Cat → SQ LLCT. In another example, weak coupling between SQ- and M-localized unpaired electrons is responsible for high intensities ($\epsilon \cong 5000\ \mathrm{M^{-1}cm^{-1}}$) of spin-forbidden metal localized transitions in[10,53] $[\mathrm{Cr(n_4)(DBSQ)}]^{2+}$ and, presumably, also in[54] $[\mathrm{Cr(SQ)_3}]$. Some bis- and tris-semiquinone complexes may be looked upon as composed of weakly interacting localized M(SQ) chromophores. This conclusion is supported, e.g., by comparisons of the spectra of $[\mathrm{Co^{II}(bpy)(DBSQ)_2}]$ with $[\mathrm{Co^{II}_4(DBSQ)_8}]$ and of the members of[55] $[\mathrm{Cr^{III}(DBDiox)_2}]^m$ and[56] $[\mathrm{Cr^{III}(bpy)(DBDiox)_2}]^n$ redox series.

The electrochemical behavior of dioxolene complexes exhibits, in accord with the localized-valence model, a series of dioxolene-localized redox couples which might be flanked with metal-localized couples. **Spectroelectrochemical** characterization of individual members of the redox series provides a powerful way to solve the question of the metal- vs. dioxolene-localization of the redox changes and, thus, to assign the oxidation states electrochemically.[19,20,36] For example, detailed UV-VIS, IR, resonance Raman, and EPR spectroelectrochemical studies of Re and Mn carbonyl-dioxolene complexes has afforded a comprehensive view on the dioxolene-metal interaction as a function of a dioxolene oxidation state.[19,20] Redox series based on bis- and tris-dioxolene complexes usually show two groups of redox couples separated by a larger potential gap.[1,2] In analogy with the $[\mathrm{Ru(bpy)_3}]^n$ redox series, this behavior may be explained by one-electron steps that are successively localized on single dioxolene ligands.[57]

Unusually, there are cases in which a one-electron oxidation or reduction of a dioxolene complex leads to a simultaneous change of both metal and dioxolene oxidation states. Thus, oxidation of $[\mathrm{Ru^{III}(NH_3)_4(Cat)}]^+$ produces[58] $[\mathrm{Ru^{II}(NH_3)_4(Q)}]^{2+}$, i.e., it is accompanied by a metal reduction. Similarly, reduction of $[V^{III}(SQ)_3]$ leads[59] to $[V^V(Cat)_3]^-$.

The overall pattern of electrochemical behavior of dioxolene complexes, characterized by well-defined localization of the redox changes either on the metal or dioxolene ligand, supports the localized-valence model. However, this model implies (*vide supra*) that the redox steps are accompanied by energy changes which result from the necessary readjustment of all dioxolene and metal orbitals to the new structures of the redox products. Hence, the redox potentials are not simply proportional to the energies of the redox orbitals, $3b_1$ and d_π for the dioxolene- and metal-localized redox steps, respectively. The relaxation energies[13] might present a very important contribution and must be taken into account when interpreting structural correlations of redox potentials of dioxolene complexes. Indeed, these correlations often exhibit unusual and yet not fully understood features, sometimes inconsistent with spectroelectrochemically assigned localization of the redox steps.

Activation of small molecules such as dioxygen is the most prominent aspect of **chemical reactivity**[1,2,60] of catecholate complexes of Fe^{III}, Co^{II}, Rh^{III}, Ir^{III}, and Cu^{II}. The mechanism is based on a simultaneous O_2 binding to the metal atom and to the C_1-atom of the Cat ligand. Such bicentric substrate activation is made possible by the valence localization of the catecholate complexes which simultaneously provides an electrophilic (M) and nucleophilic (Cat) coordination sites. The Cat ligand also behaves as an electron reservoir able to reduce the metal-coordinated substrate by one or two electrons. Noteworthy, the ability to coordinate O_2 by $[M(triphos)(Cat)]^+$ complexes increases[60] in the order Co < Rh < Ir, i.e., following the spectroscopically and electrochemically established[24] order of increasing valence localization. Such chemical behavior is profoundly different from highly delocalized 1,2-dithiolene complexes which lack definite coordinative and redox sites and are thus much less reactive[61,62] toward substrate (oxidative) additions.

CONTROL OF OXIDATION STATES AND BISTABILITY

The ground-state electron distribution in a dioxolene complex is determined by that valence form which has the lowest Gibbs free energy, G (see Fig. 3). If two different valence forms of a dioxolene complex have similar zero-point energies (Fig. 3—lower right), their relative position may be changed by internal (structural) or external (temperature, medium, etc.) perturbations. Such a dioxolene complex molecule is *bistable*, i.e., it may exist in two different states of very different electron distribution and, hence, properties. Controllable switching between such two states is possible as long as the valence forms are separated by a large energy barrier that prevents their rapid interconversions by electron hopping. The two states in question differ only in the metal and dioxolene oxidation states. Hence, they may be termed *redox isomers* or *valence isomers*.

Co-ligand control of oxidation states in dioxolene complexes is most common for 4-coordinated Cu complexes,[35,63] which exist in the Cu^{I}(SQ) valence form for "soft" (phosphines, arsines, CO, olefins, acetylenes) co-ligands and in the Cu^{II}(Cat) form with a "harder" co-ligand bpy. Apparently, a stronger "hard" donor destabilizes copper d-orbitals. However, this destabilization is compensated by the reorganization energy between the SQ and Cat structures and the valence forms are switched. Noteworthy, the Cu^{I}–SQ π-back bonding is too weak to compensate for the increased electron density on the Cu atom in the latter complexes by a gradual increase in delocalization. The valence-form switching is made possible by the total energy change, not by small shifts in orbital energies (d_{σ} and $3b_1$ in this case).

Temperature switching of valence forms was best studied for $[Co^{III}(\alpha\text{-diimine})(DBCat)(DBSQ)]$ / $[Co^{II}(\alpha\text{-diimine})(DBSQ)_2]$ valence isomers.[14–17] A temperature-dependent equilibrium between these two distinct valence isomers exists in solutions, whereas sudden switching was found in the solid state, the switching temperature being dependent on the α-diimine co-ligand. Other examples of temperature-dependent equilibria between dioxolene valence isomers comprise,[2,18,64] e.g., $[Mn^{II}(py)_2(DBSQ)_2]$/$[Mn^{IV}(py)_2(DBCat)_2]$, $[(BuOCS_2)Ni^{II}(SQ)]$/$[(BuOCS_2)Ni^{III}(Cat)]$, and $[Rh^{I}(cod)(AsEt_3)(SQ)]$/$[Rh^{II}(cod)(AsEt_3)(DBCat)]$ complexes. Switching from the $\{M^{(n+2)+}(Cat)\}$ to the $\{M^{(n+1)+}(SQ)\}$ valence form with rising temperature appears to be caused[2,16] by higher entropy of the latter that results from higher degeneracy (orbital and, namely, spin) and from "looser" M-Diox vibrations.

Temperature control of valence forms is often accompanied by a **medium control**. Solid state switching between $[Co^{III}(\alpha\text{-diimine})(DBCat)(DBSQ)]$ and $[Co^{II}(\alpha\text{-diimine})(DBSQ)_2]$ valence isomers is strongly dependent on the presence of a solvent molecule in the crystal lattice.[16] The $[Mn^{II}(py)_2(DBSQ)_2]/[Mn^{IV}(py)_2(DBCat)_2]$,[18] $[(BuOCS_2)Ni^{II}(SQ)]/[(BuOCS_2)Ni^{III}(Cat)]$,[2] and $[Rh^{I}(cod)(AsEt_3)(SQ)]/[Rh^{II}(cod)(AsEt_3)(DBCat)]$ [64] equilibria are solvent-dependent, more polar solvents favoring the $\{M^{(n+2)+}(Cat)\}$ forms.

DO DELOCALIZED DIOXOLENE COMPLEXES EXIST?

Delocalization in dioxolene complexes might occur if the energy barrier between the valence forms was strongly diminished by their electronic interaction, $H_{i,j}$ (see Fig. 4—left). There is virtually no experimental evidence available that would indicate a delocalization within the {M(SQ)} valence form. SQ ligands behave as very weak π-acceptors, the amount of electron density transferred being rather limited.[34] The possibility of tuning the extent of M → SQ π-back donation by changing the co-ligands was recently demon-

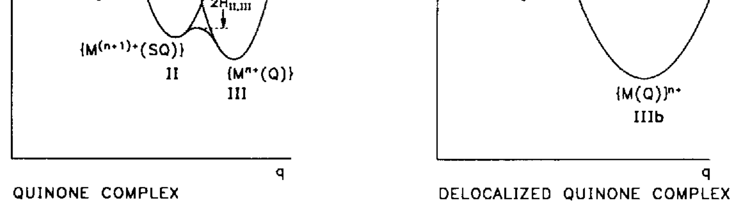


FIGURE 4 Delocalization in quinone complexes. Left: electronic interaction $H_{II,III}$ causes separation of the energy curves. Right: strong interaction leads to a completely delocalized complex. Curves $\{M(Q)\}^{n+}$ and $^*\{M(Q)\}^{n+}$ correspond to the delocalized structure **IIIb** and its electronic excited state, respectively.

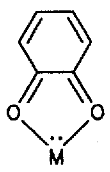
strated[24] by the EPR, resonance Raman and electrochemical study of $[Re^{I}(CO)_{4-n}(PPh_3)_n(DBSQ)]$ complexes; $n = 0, 1, 2$. Although the Re–SQ π-interaction increases with increasing n, the oxidation states remain well defined.

Catecholate complexes usually possess well-localized oxidation states. However, some (but not all!) of the catecholate complexes of electron-deficient metal atoms exhibit structures distorted toward those of SQ complexes. The structural oxidation states[26] then have values between -1 and -2. $[V^{V}(phen)(DBCat)_2]^+$,[65] $[V^{IV}(bpy)(CCat)_2]$,[66] and $[Tc^{VI}(DBCat)_3]$ [26,67] are some examples. Apparently, the catecholate ligand may behave as a π-donor, transferring some electron density toward the metal. This effect is especially apparent in the structure[5] of $[Co^{III}(triphos)(DBCat)]^+$ whose structural oxidation state is[26] -1.3. The presence of an extensive $Co^{II} \leftarrow$ Cat π-interaction is also indicated by a strong dependence of the potential of the Co^{III}/Co^{II} couple on the substituents on the dioxolene ligand.[60] However, spectral and spectroelectrochemical results[5] still support the valence-localized view of $[Co^{III}(triphos)(DBCat)]^+$.

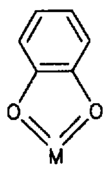
Structures intermediate between those of SQ and Cat were found for Ru and Os complexes $[Ru(DBDiox)_3]$,[12] $[Os(DBDiox)_3]$,[12] $[Os(PPh_3)_2(DBDiox)Cl_2]$,[68] $[Ru(4\text{-}Bu^t\text{-}pyridine)_2(DBDiox)_2]$ [69] and $[Ru(bpy)(DBDiox)_2]$.[70] Although these structures were originally regarded as evidence for extensively delocalized electronic structures, it cannot be excluded[2] that they actually belong to a structurally disordered mixture of valence-localized Cat and SQ species. Moreover, the solution spectral and electrochemical properties of these complexes resemble[2] those of their valence-localized congeners like $[M(bpy)_2(Diox)]^{n+}$, M = Ru, Os. The problem of Ru–Diox and Os–Diox delocalization remains open for further investigations. Nevertheless, there appears to be good evidence for an SQ–SQ delocalization in $[Ru(PPh_3)_2(SQ)_2]$ complexes as the potentials of the oxidation and reduction of $[Ru(PPh_3)_2(DBSQ)(CSQ)]$ are intermediate[71] between those of $[Ru(PPh_3)_2(DBSQ)_2]$ and $[Ru(PPh_3)_2(CSQ)_2]$ and the DBSQ- and CSQ-localized redox steps cannot be distinguished in the mixed-ligand compound.[71]

Quinone complexes are the least understood members of dioxolene family. The only example characterized crystallographically, $[MoO_2Cl_2(PQ)]$,[72] shows very short C–O bonds and long C_1–C_2

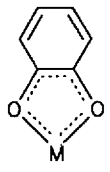
bonds in accord with the expectation based on the localized-valence model. However, most of quinone complexes are chemically very unstable toward dissociation of the Q ligand. The only stable examples known are[21,22] $[Ru(bpy)_2(Q)]^+$ and[19,20,24] $[M(CO)_2(PPh_3)_2(DBQ)]^+$; M = Mn, Re. Contrary to simple MO expectations, the M → Q CT absorption band occurs at an energy higher than for analogous SQ complexes[19-22] and the Ru → CQ transition was found[22,23] at higher energy than Ru → DBQ. Moreover, resonance Raman spectra measured using excitation into the unusually intense "M → Q" absorption band exhibit[19-21] very large enhancement of Raman peaks corresponding to a group of skeletal M–O vibrations that are coupled to the C_1–C_2 and ring deformation vibrations. Also, the potential of the dioxolene-localized SQ/Q redox couple is strongly dependent on the co-ligand nature as was found[19,20] for $[M(CO)^{4-n}(PPh_3)_n(DBQ)]^+/[M(CO)^{4-n}(PPh_3)_n(DBSQ)]$ couples; M = Re^I, Mn^I, $n = 0, 1, 2$. All these observations indicate that the stable "quinone" complexes are the only genuinely delocalized dioxolene complexes for which it is not possible to distinguish the metal and dioxolene oxidation states. In VB terms, the delocalized $\{M(Q)\}^{n+}$ valence form could be expressed by a resonance between structures **III** and **IIIa** that produces a delocalized structure **IIIb**. In a simple one-electron MO model, the {M(Q)} valence form may be characterized by a doubly occupied orbital described as $(d_\pi + 3b_1)$ that results from a (nearly) complete mixing between the metal and dioxolene frontier orbitals. The localized-valence model interprets these "quinone" complexes as a delocalized Robin–Day class III mixed valence species.[25] Delocalization arises from a strong interaction between localized valence forms $\{M^{(n+1)+}(SQ)\}$, **II**, and $\{M^{n+}(Q)\}$, **III**, as shown in Fig. 4. Conditions that would enable such a strong electronic interaction



III



IIIa



IIIb

need to be elucidated by further research. Examples known so far comprise only a few complexes of electron-donating, albeit difficult to oxidize, metal centers of d^6 configuration: Ru^{II}, Re^{I}, and Mn^{I}. The energy gain from a formation of a delocalized π-bonding within the MQ chelate ring might, in these special cases, overcome the energy needed to reorganize the intradioxolene bonds into the delocalized structure.

CONCLUDING REMARKS

The behavior of most dioxolene complexes is, essentially, a behavior of class II, i.e., weakly coupled, mixed valence compounds. Localization of the metal- and dioxolene-oxidation states produces at least two distinct redox, magnetic, chromophoric or reactive centers whose simultaneous presence in the molecule is responsible for all the peculiar properties observed for dioxolene complexes. However, the "right" strength of electronic interaction between the metal and dioxolene centers is a necessary prerequisite for the bistability, intense low-energy electronic transitions, magnetic interactions, localization of successive redox steps on individual ligands and substrate activation by concerted coordination and electron transfer. If the interaction was too low (class I), a simple sum of the behaviors of the isolated dioxolene ligand and metal atom in their particular oxidation states would be observed. On the other hand, too large a delocalization (class III) would level off the distinctiveness of the metal and ligand centers. Delocalized molecules would be much less reactive, certainly not exhibiting any bistability.

The localized-valence model proposed above has many consequences for the interpretations and predictions of the experimental behavior of dioxolene complexes. Although the structural chemistry and magnetochemistry appears to be quite well understood, their electrochemistry and, particularly, electronic spectroscopy and excited state behavior need to be investigated much more deeply. Some aspects of dioxolene chemistry will certainly be further developed aiming at specific applications like molecular switching, optical materials active in the red and NIR spectral regions, photochromism, electrochromism, and (electro)catalytic substrate activation.

Acknowledgment

Financial support from the Granting Agency of the Czech Republic, grant no. 203/93/0250, is gratefully appreciated.

References

1. C. G. Pierpont and R. M. Buchanan, Coord. Chem. Revs. **38**, 45 (1981).
2. C. G. Pierpont and C. W. Lange, Progr. Inorg. Chem. **41**, 331 (1994).
3. D. J. Gordon and R. F. Fenske, Inorg. Chem. **21**, 2907 (1982).
4. D. J. Gordon and R. F. Fenske, Inorg. Chem. **21**, 2916 (1982).
5. C. Bianchini, D. Masi, C. Mealli, A. Meli, G. Martini, F. Laschi and P. Zanello, Inorg. Chem. **26**, 3683 (1987).
6. A. A. Vlček, Rev. Chim. Minerale **5**, 299 (1968).
7. A. Vogler and H. Kunkely, Comments Inorg. Chem. **9**, 201 (1990).
8. J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry* (University Science Books, Mill Valley, California, 1987), pp. 20–37.
9. C. K. Jørgensen, *Oxidation Numbers and Oxidation States* (Springer-Verlag, New York, 1969).
10. A. Dei and D. Gatteschi, Inorg. Chim. Acta **198–200**, 813 (1992).
11. C. Benelli, A. Dei, D. Gatteschi and L. Pardi, Inorg. Chem. **28**, 1476 (1989).
12. S. Bhattacharya, S. R. Boone, G. A. Fox and C. G. Pierpont, J. Am. Chem. Soc. **112**, 1088 (1990).
13. K. Wittel and S. P. McGlynn, Chem. Revs. **77**, 745 (1977).
14. R. M. Buchanan and C. G. Pierpont, J. Am. Chem. Soc. **102**, 4951 (1980).
15. D. M. Adams, A. Dei, A. L. Rheingold and D. N. Hendrickson, Angew. Chem. Int. Ed. Engl. **32**, 880 (1993).
16. D. M. Adams, A. Dei, A. L. Rheingold and D. N. Hendrickson, J. Am. Chem. Soc. **115**, 8221 (1993).
17. O.-S. Jung and C. G. Pierpont, J. Am. Chem. Soc. **116**, 1127 (1994).
18. M. W. Lynch, D. N. Hendrickson, B. J. Fitzgerald and C. G. Pierpont, J. Am. Chem. Soc. **106**, 2041 (1984).
19. F. Hartl, D. J. Stufkens and A. Vlček, Jr., Inorg. Chem. **31**, 1687 (1992).
20. F. Hartl and A. Vlček, Jr., Inorg. Chem. **31**, 2869 (1992).
21. D. J. Stufkens, T. L. Snoeck and A. B. P. Lever, Inorg. Chem. **27**, 953 (1988).
22. M. Haga, E. S. Dodsworth and A. B. P. Lever, Inorg. Chem. **25**, 447 (1986).
23. A. B. P. Lever, H. Masui, R. A. Metcalfe, D. J. Stufkens, E. S. Dodsworth and P. R. Auburn, Coord. Chem. Revs. **125**, 317 (1993).
24. F. Hartl and A. Vlček, Jr., to be published.
25. M. B. Robin and P. Day, Adv. Inorg. Chem. Radiochem. **10**, 247 (1967).
26. O. Carugo, C. B. Castellani, K. Djinovic and M. Rizzi, J. Chem. Soc. Dalton Trans. 837 (1992).

27. F. Hartl, A. Vlček, Jr. and D. J. Stufkens, Inorg. Chim. Acta **192**, 25 (1992).
28. D. D. Cox, S. J. Benkovic, L. M. Bloom, F. C. Bradley, M. J. Nelson, L. Que, Jr. and D. E. Wallick, J. Am. Chem. Soc. **110**, 2026 (1988).
29. S. Salama, J. D. Stong, J. B. Neilands and T. G. Spiro, Biochemistry **17**, 3781 (1978).
30. B. Vlčková, T. L. Snoeck and D. J. Stufkens, J. Mol. Struct. **218**, 7 (1990).
31. R. A. Marcus, Angew. Chem. Int. Ed. Engl. **32**, 1111 (1993).
32. R. A. Marcus and P. Siddarth, in *Photoprocesses in Transition Metal Complexes, Biosystems and Other Molecules. Experiment and Theory*, ed. E. Kochanski (Kluwer, 1992), p. 49.
33. O. Carugo, K. Djinovic, M. Rizzi and C. B. Castellani, J. Chem. Soc. Dalton Trans. 1551 (1991).
34. T. van der Graaf, D. J. Stufkens, J. Víchová and A. Vlček, Jr., J. Organomet. Chem. **401**, 305 (1991).
35. R. M. Buchanan, C. Wilson-Blumenberg, C. Trapp, S. K. Larsen, D. L. Greene and C. G. Pierpont, Inorg. Chem. **25**, 3070 (1986).
36. (a) F. Hartl and A. Vlček, Jr., Inorg. Chem. **30**, 3048 (1991); (b) F. Hartl, A. Vlček, Jr., L. A. deLearie and C. G. Pierpont, Inorg. Chem. **29**, 1073 (1990).
37. M. E. Cass, D. L. Greene, R. M. Buchanan and C. G. Pierpont, J. Am. Chem. Soc. **105**, 2680 (1983).
38. R. M. Buchanan, S. L. Kessel, H. H. Downs, C. G. Pierpont and D. N. Hendrickson, J. Am. Chem. Soc. **100**, 7894 (1978).
39. M. W. Lynch, R. M. Buchanan, C. G. Pierpont and D. N. Hendrickson, Inorg. Chem. **20**, 1038 (1981).
40. M. W. Lynch, M. Valentine and D. N. Hendrickson, J. Am. Chem. Soc. **104**, 6982 (1982).
41. G. A. Fox and C. G. Pierpont, Inorg. Chem. **31**, 3718 (1992).
42. M. J. Cohn, C.-L. Xie, J.-P. M. Tuchagues, C. G. Pierpont and D. N. Hendrickson, Inorg. Chem. **31**, 5028 (1992).
43. O. Kahn, R. Prins, J. Reedijk and J. S. Thompson, Inorg. Chem. **26**, 3557 (1987).
44. C. Benelli, A. Dei, D. Gatteschi and L. Pardi, Inorg. Chem. **27**, 2831 (1988).
45. C. Benelli, A. Dei, D. Gatteschi and L. Pardi, Inorg. Chem. **29**, 3409 (1990).
46. (a) P. A. Wicklund and D. G. Brown, Inorg. Chem. **15**, 396 (1976); (b) M. Haga, K. Isobe, S. R. Boone and C. G. Pierpont, Inorg. Chem. **29**, 3795 (1990).
47. E. S. Dodsworth and A. B. P. Lever, Chem. Phys. Lett. **172**, 151 (1990).
48. M. D. Stallings, M. M. Morrison and D. T. Sawyer, Inorg. Chem. **20**, 2655 (1981).
49. N. S. Hush, Progr. Inorg. Chem. **8**, 391 (1967).
50. A. B. P. Lever, *Inorganic Electronic Spectroscopy* (Elsevier, Amsterdam, 1984).
51. T. J. Meyer, Acc. Chem. Res. **11**, 94 (1978).
52. C. Creutz, Progr. Inorg. Chem. **30**, 1 (1983).
53. C. Benelli, A. Dei, D. Gatteschi, H. U. Güdel and L. Pardi, Inorg. Chem. **28**, 3089 (1989).
54. M. Daněk and A. Vlček, Jr., to be published.
55. S. R. Sofen, D. C. Ware, S. R. Cooper and K. N. Raymond, Inorg. Chem. **18**, 234 (1979).
56. R. M. Buchanan, J. Claflin and C. G. Pierpont, Inorg. Chem. **22**, 2552 (1983).
57. S. Záliš and V. Drchal, Chem. Phys. **118**, 313 (1987).
58. S. D. Pell, A. Abelleira and M. J. Clarke, Inorg. Chem. **23**, 385 (1984).

59. M. E. Cass, N. R. Gordon and C. G. Pierpont, Inorg. Chem. **25**, 3962 (1986).
60. P. Barbaro, C. Bianchini, K. Linn, C. Mealli, A. Meli, F. Vizza, F. Laschi and P. Zanello, Inorg. Chim. Acta **198–200**, 31 (1992).
61. A. Vlček, Jr., Inorg. Chim. Acta **43**, 35 (1980).
62. A. Vlček, Jr., A. A. Vlček, Inorg. Chim. Acta **41**, 123 (1980).
63. G. A. Razuvaev, V. K. Cherkasov and G. A. Abakumov, J. Organomet. Chem. **160**, 361 (1978).
64. G. A. Abakumov, G. A. Razuvaev, V. I. Nevodchikov and V. K. Cherkasov, J. Organomet. Chem. **341**, 485 (1988).
65. T. A. Kabanos, A. J. P. White, D. J. Williams and J. D. Woollins, J. Chem. Soc. Chem. Commun. 17 (1992).
66. C. L. Simpson and C. G. Pierpont, Inorg. Chem. **31**, 4308 (1992).
67. L. A. deLearie, R. C. Haltiwanger and C. G. Pierpont, J. Am. Chem. Soc. **111**, 4324 (1989).
68. S. Bhattacharya and C. G. Pierpont, Inorg. Chem. **30**, 2906 (1991).
69. S. R. Boone and C. G. Pierpont, Inorg. Chem. **26**, 1769 (1987).
70. S. R. Boone and C. G. Pierpont, Polyhedron **9**, 2267 (1990).
71. S. Bhattacharya and C. G. Pierpont, Inorg. Chem. **30**, 1511 (1991).
72. C. G. Pierpont and H. H. Downs, Inorg. Chem. **16**, 2970 (1977).