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Review

Mixed valency in ruthenium complexes—Coordinative aspects

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Contents

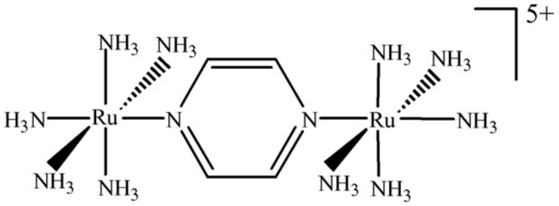
Abstract

The metal–metal interaction in ligand-bridged diruthenium(II,III) complex intermediates is commonly characterized by using the redox potential difference, usually converted to the comproportionation constant K_c, and by analyzing intervalence charge transfer (IVCT) absorption features and deriving electronic coupling parameters. Although these two kinds of information may yield very different estimates of the extent of metal–metal interaction in any given system, the absolute values have often been used interchangeably to quantify the strength of electronic "coupling". Using examples from the literature with substantially different coordination arrangements in terms of denticity and donor/acceptor character of the π conjugated bridging ligand we can show that close correlations between electrochemically and spectroscopically determined coupling are only valid within structurally related classes of compounds with qualitatively similar interaction at the metal–ligand interface. Most strikingly, situations with high K_c values but weak, low energy IVCT absorptions have been identified for complexes with bis- and tris-bidentate acceptor bridges whereas intermediates with small comproportionation constants but intense, narrow IVCT bands are typical with bridging bis-tridentate acceptors.

Keywords: Absorption spectroscopy; Bridging ligands; Comproportionation; Mixed valency; Ruthenium

1. Introduction

Ever since the first report of the Creutz–Taube ion $[(H_3N)_5Ru(\mu\text{-pyrazine})Ru(NH_3)_5]^{5+}$, **1** [1] as a small and simple, yet surprisingly stable ligand-bridged $Ru^{II}Ru^{III}$ coordination compound, there have been numerous experimental and theoretical attempts to understand the stability and physical properties of related symmetrical diruthenium mixed-valent complexes [2,3]. The main focus has been on electronic spectroscopy, with the intervalence charge transfer (IVCT) transitions (1) and corresponding absorption bands being among the most conspicuous and theoretically challenging features of mixed-valent compounds [4,5].



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$$\mathrm{Ru}^{n}(\mu\text{-L})\mathrm{Ru}^{n+1} \xrightarrow[\mathrm{IVCT}]{h\nu} [\mathrm{Ru}^{n+1}(\mu\text{-L})\mathrm{Ru}^{n+}]^{*} \tag{1}$$

The IVCT designation has also been used for convenience in those symmetrical cases (2) where there is clear valence-averaging, i.e. when both the ground and excited states are electronically delocalized over both metal centers [2,5] on any reasonable spectroscopic time scale [6] (Class III according to Robin and Day [4]):

$$\mathrm{Ru}^{n+0.5}(\mu\text{-L})\mathrm{Ru}^{n+0.5} \xrightarrow[\mathrm{IVCT}]{h\nu} [\mathrm{Ru}^{n+0.5}(\mu\text{-L})\mathrm{Ru}^{n+0.5}]^{*} \tag{2}$$

For a valence-localized situation ("Class II" [4a]) the classical Hush perturbation treatment [5a,c] led to a simple expression for the electronic interaction parameter which involves as essential factors the electron-transfer distance (geometrical or "spectroscopically effective" metal–metal distance) and the oscillator strength of the IVCT band. The latter is rarely reported, however; usually the molar extinction coefficients ε and bandwidths $\Delta\nu_{1/2}$ are provided for approximately Gaussian-shaped bands unless very special band shapes are encountered. In an extension of the original Hush approach, Creutz, Newton and Sutin have included formulations from the superexchange concept [18a] to assess the electronic interaction between bridged metals in mixed-valent compounds by using the often easier to determine metal-to-ligand or ligand-to-metal charge transfer spectral data ("CNS model") [5d].

Just like the electrochemical parameters (cf. below), the absorption data are often significantly dependent on the environment (general and specific solvent–solute interactions, ion-pairing for the often highly charged species). Considering dipole moment changes it is evident that centrosymmetric valence-delocalized systems should exhibit smaller solvatochromism of the IVCT band than localized analogues with their built-in polarity, an argument which has even been taken as valid criterion for the Class II/Class III distinction [2a]. However, specific substrate–solvent interactions like hydrogen bonding may still lead to substantial solvent dependence of IVCT bands of clearly valence-averaged species [7], and the situation with faster thermal electron-transfer than the solvent reorganization has given rise to a new "Class II/III borderline" category [2d].

Another physical property immediately connected to the *stability* of mixed-valent intermediates [2b] is the comproportionation constant K_c according to (3)–(5) [2c,8].

$$\underset{\textit{Red}}{\mathrm{Ru^{n}(\mu\text{-}L)Ru^{n}}} \underset{+e^-}{\overset{E_1 \atop -e^-}{\rightleftharpoons}} \underset{\textit{Int}}{\mathrm{Ru^{n}(\mu\text{-}L)Ru^{n+1}} \atop {\text{or} \atop \mathrm{Ru^{n+0.5}(\mu\text{-}L)Ru^{n+0.5}}}} \underset{+e^-}{\overset{E_2 \atop -e^-}{\rightleftharpoons}} \underset{\textit{Ox}}{\mathrm{Ru^{n+1}(\mu\text{-}L)Ru^{n+1}}} \tag{3}$$

$$K_c = \frac{[\mathrm{Int}]^2}{[\mathrm{Red}][\mathrm{Ox}]} = 10^{\Delta E/59\,\mathrm{mV}} \quad \text{at } 298\,\mathrm{K}; \qquad \Delta E = E_2 - E_1 \tag{4}$$

$$RT \ln K_c = nF(\Delta E) \tag{5}$$

Although the free energy of comproportionation is not only determined by the resonance exchange as delocalization parameter but also by contributions from electrostatic forces, ion-pairing, antiferromagnetic exchange, inductive effects and entropy ("statistical factor") [2b,c,8,18a], the ΔE or K_c values have been "widely used", often in an unreflected way, to describe "the extent of inter-metal communication between the metal centres" [9]. The variable ("sometimes unpredictable" [9]) dependence of redox potentials and their differences (and hence of K_c) on the solvent and on the counter-ions has been pointed out by D'Alessandro and Keene [9], following the ground-breaking work by LeSuer and Geiger [10]. Not surprisingly, higher charges lead to more pronounced effects from the medium. The case for standard conditions [9] in reporting E and K_c values is thus strongly advised in order to allow for reasonable comparison and to avoid the "danger of over-interpretation" [9]. For synthetic chemists, the positioning of a new compound relative to known systems is often more important than absolute numbers from rigorous theoretical treatment.

The prototypical Creutz–Taube ion **1**, for example, has $K_c \approx 10^7$ in various solvents and a major [2c,d], somewhat asymmetrical IVCT absorption band at about $\lambda_{\max} \approx 1560\,\mathrm{nm}$ with $\varepsilon \approx 5000\,\mathrm{M^{-1}\,cm^{-1}}$ [1,2,11] (see Table 1). There are other, very weak IVCT transitions at still lower energies [2c,d]. Studies using additional spectroscopic methods pertaining to different time scales [6] such as EPR, Mössbauer, XPS, Stark or vibrational spectroscopy have also been used successfully to assess intramolecular electron exchange rates, the valence (de)localization, and the degree of electronic coupling for the Creutz–Taube ion [2,12] and for mixed-valent compounds in general [2,4b,6,13].

The inertness and general chemical stability of ruthenium in both the +II ($4d^6$) and the +III ($4d^5$) configurations [14] have largely contributed to the focus on these two states in mixed-valency research [2]. Following several reviews on diruthenium(II,III) chemistry with many listed examples, mostly containing bis-monodentate bridges [2], and an account [3] of efforts to expand the chemistry of the Creutz–Taube ion we intend to focus on the *role of the coordination mode of the bridging ligand* and the apparent contradictions between electrochemical and spectroscopic results for the metal–metal "interaction". Several previous reviews [2c,i] and articles have suggested that certain ranges for K_c values or IVCT band intensities or widths are associated with Class II or Class III category. It is one purpose of this article to show that such generalizations are unwarranted and that correlations can only be drawn within specific kinds of coordinatively related molecular systems.

2. Results and discussion

2.1. Atom-bridged complexes

Although the focus of this survey lies on *molecule-bridged* mixed-valent diruthenium compounds there are many such com-

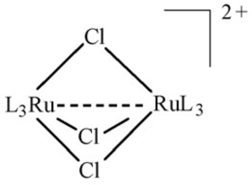
Table 1
Characteristics of mixed-valent compounds $[(L_n)Ru(BL)Ru(L_n)]^k$

BL	L_n	k	K_c	$\tilde{\nu}_{max}(cm^{-1})$	ε (M^{-1} cm^{-1})	References	Medium
Bis-monodentate π acceptor							
pz	$(NH_3)_5$	5+	$\approx 10^7$	≈6400[a]	≈5000	[1,2a,b,11]	Various
pz	$(CN)_5$	5−	$10^{4.7}$	5680	2600	[21]	CH_2Cl_2/0.1 M Bu_4NPF_6
pz	$(bpy)_2Cl$	3+	$10^{2.0}$	7690	455	[23]	CH_3CN/0.1 M Bu_4NPF_6
Bis-monodentate π donor							
$dicyd^{2-}$	$(NH_3)_5$	3+	10	8190	2590	[18]	$H_2O/NaClO_4$
			$10^{4.8}$	6900	19400	[18]	CH_3CN/0.1 M Bu_4NPF_6
Bis-bidentate π acceptor							
bpym	$(NH_3)_4$	5+	$10^{5.1}$	3125	[b]	[24]	CH_3CN/0.1 M Bu_4NPF_6
bpym	$(bpy)_2$	5+	$10^{2.7}$	5000	[c]	[25,80]	CH_3CN/0.1 M Bu_4NPF_6
bptz	$(NH_3)_4$	5+	10^{15}	6880	500	[30]	CH_3CN/0.1 M Bu_4NPF_6
bptz	$(bpy)_2$	5+	$10^{8.5}$	6955	2800	[25,81]	CH_3CN/0.1 M Bu_4NClO_4
bptz	$(acac)_2$	+	10^{13}	8215	20	[53]	CH_2Cl_2/0.1 M Bu_4NPF_6
Bis-bidentate π donor							
$bibzim^{2-}$	$(bpy)_2$	3+	$10^{4.9}$	5130	3300	[37]	CH_3CN/0.1 M Bu_4NPF_6
adc-Ph^{2-}	$(bpy)_2$	3+	$10^{9.7}$	6240	11750	[17]	CH_3CN/0.1 M Bu_4NPF_6
Tris-bidentate π acceptor							
HAT	$(bpy)_2$	5+	$10^{3.8}$	5290, *rac*	4460	[68]	CH_3CN/0.1 M Bu_4NPF_6
			$10^{3.8}$	5300, *meso*	4250		
Bis-tridentate π acceptor							
tppz	$(NH_3)_3$	5+	$10^{8.5}$	[d]	[d]	[71]	DMF/0.1 M Bu_4NPF_6
tppz	(dpk)Cl[e]	3+	$10^{4.4}$	5550	1500	[73]	CH_3CN/0.1 M Bu_4NPF_6
Bis-tridentate π donor							
adc-py^{2-}	terpy	3+	$10^{9.0}$	10000	3800	[76]	CH_3CN/0.1 M Bu_4NPF_6
$tpbp^{2-}$	tterpy	3+	$10^{2.8}$	5495	27000	[75]	CH_3CN/0.1 M Bu_4NPF_6

[a] Asymmetric band.
[b] Overlap with N–H stretching bands, ε not reported.
[c] Not reported.
[d] No IVCT band detected till 7700 cm^{-1}.
[e] dpk = 2,2′-dipyridylketone.

plexes, which have the metals bridged by atomic ions and/or connected through metal–metal bonds [15,16].

As an example, structural, electrochemical and spectroscopic investigations (EPR, UV–vis–NIR) for the valence-averaged $Ru^{II}Ru^{III}$ species **2** as well as theoretical approaches [15] confirm a σ^* MO involving the metal $d_z{}^2$ orbitals as the site of the unpaired electron. The broad IVCT bands at about 1600 nm are rather weak ($\varepsilon \approx 300\ M^{-1}\ cm^{-1}$). While the formal metal–metal bond order is only 0.5 ($d_{Ru–Ru}$ = 2.75–2.90 Å) there are three halide bridges as π donors, allowing a hole transfer [3,17,18] valence exchange mechanism (see (8)); the K_c values are very large at about 10^{20} [15], reflecting the vicinity of valence exchanging metals.



2

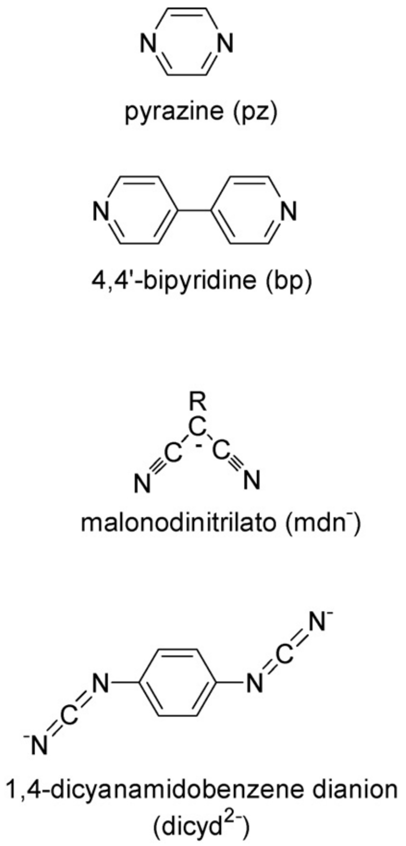
L_3 = 3 NH_3, TACN or Me_3TACN
TACN = 1,4,7-triazacyclononane

2.2. Complexes with bis-monodentate bridging ligands

Diruthenium(II,III) complexes with symmetrically *bis-monodentate* ($\mu,\eta^1:\eta^1$) molecular bridges such as π *accepting* pyrazine (pz) [1] or 4,4′-bipyridine (bp) [2] and π *donating* malonodinitrilato anions (mdn^-) [19] or 1,4-dicyanamidobenzene dianions ($dicyd^{2-}$) [18] have been extensively studied [2] as typically “strongly coupled” bis(pentaammineruthenium) compounds with frequently high K_c values and intense IVCT bands (Table 1; Scheme 1).

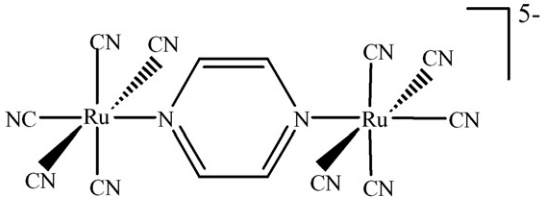
In fact, following the Creutz–Taube ion **1** as a model, π acceptor-bridged bis(pentaammineruthenium) complexes have been the most studied type of diruthenium mixed-valence systems [2], the bridges ranging from N_2 to long-chain α,ω-bis(4-pyridyl)polyenes and -polyaryls [20], discussed as potential molecular wires and switches [2f,20]. The overwhelming focus [2] on these bis-monodentate ligand-bridged complexes has inevitably made them the basis for standard theoretical treatments [5].

It has also been possible to obtain the bis(pentacyanoruthenium) analogue $[(NC)_5Ru(\mu\text{-pz})Ru(CN)_5]^{5-}$ **3** of the Creutz–Taube ion **1** and to study its revealingly different



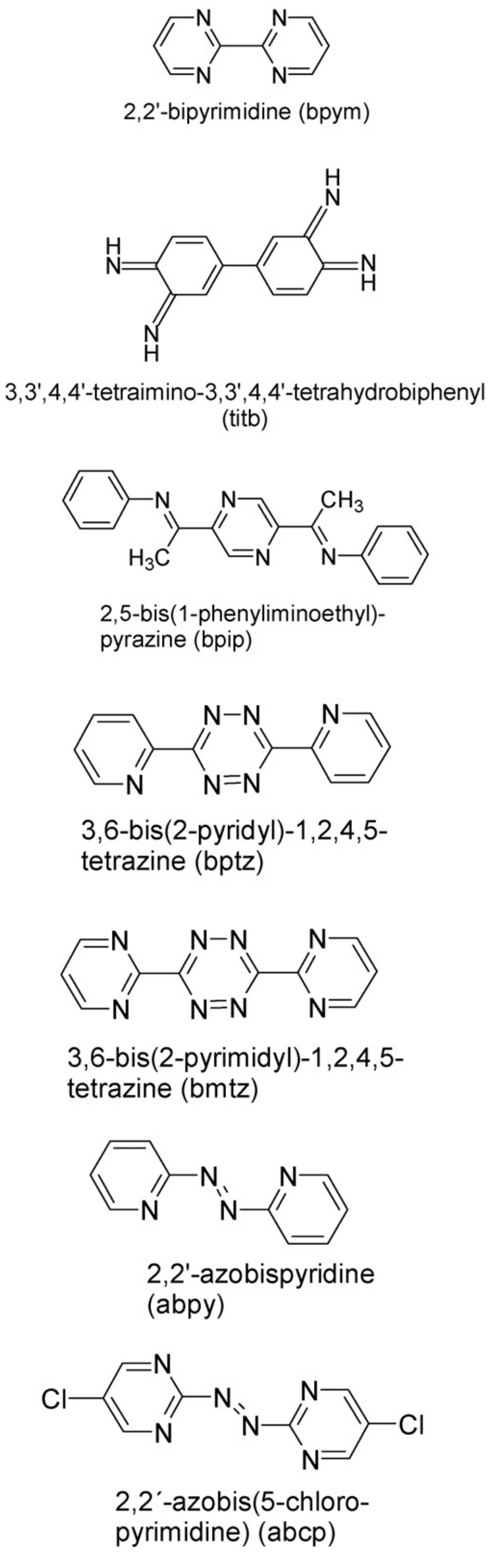
Scheme 1.

physical and electrochemical properties [21]. Similarly to the diiron(II,III) [22a] and diosmium(II,III) [22b] homologues, the electrogenerated ion **3** is distinguished by a rather small K_c value of only $10^{4.7}$ (in CH_3CN) and a very broad IVCT band ($\Delta\nu = 4200\,cm^{-1}$) in the near-infrared region ($\lambda_{max} = 1760\,nm$, $\varepsilon = 2600\,M^{-1}\,cm^{-1}$). Taken together with the EPR silence down to 4 K this suggests a distinctly weaker metal–metal interaction than in **1** due to the multiple competitions from the π accepting cyano co-ligands with the pyrazine bridge [21].



3

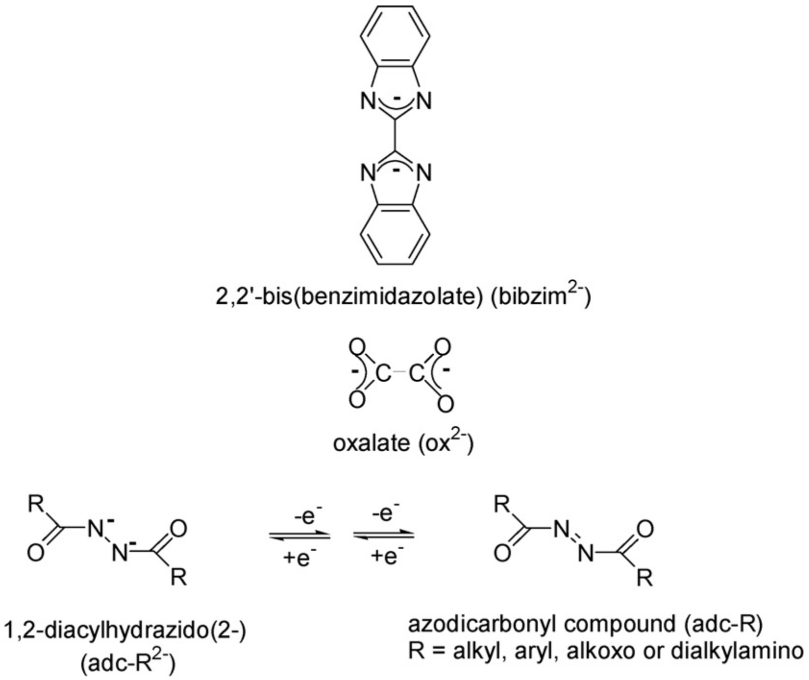
Even more pronounced ancillary (or peripheral [2h]) ligand effects attenuating the metal-bridge interaction have been established for $[Cl(bpy)_2Ru(\mu\text{-pz})Ru(bpy)_2Cl]^{3+}$ [23] with π accepting 2,2′-bipyridine (bpy; Table 1). In all three cases, **1**, **3** and $[Cl(bpy)_2Ru(\mu\text{-pz})Ru(bpy)_2Cl]^{3+}$, the electrochemical ($K_c$) and IVCT band intensity values (ε) decrease uniformly (Table 1), suggesting a correlation between those two kinds of parameters. However, changing the coordination mode results in a distinctly different relation of mixed-valence characteristics.



Scheme 2.

2.3. Complexes with bis-bidentate bridging ligands

Systems with symmetrically *bis-bidentate* bridges have raised our own interest because the chelate effect can provide improved stability and conformational rigidity. There is no more



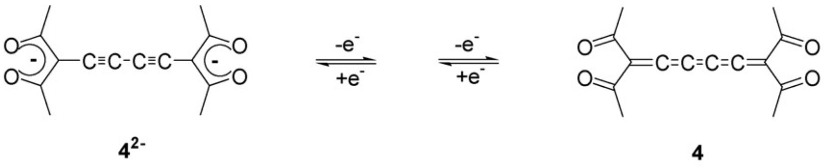
Scheme 3.

rotation possible around the essential Ru–N "interface" bonds as in pentaammineruthenium species. Among the $\mu,\eta^2:\eta^2$ bridging ligands used were π accepting 2,2′-bipyrimidine (bpym) [9,24–26], 3,3′,4,4′-tetraimino-3,3′,4,4′-tetrahydrobiphenyl (titb) [27,28], 2,5-bis(1-phenyliminoethyl)pyrazine (bpip) [29], 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) [25,30,31], 3,6-bis(2-pyrimidyl)-1,2,4,5-tetrazine (bmtz) [31–33], 2,2′-azobispyridine (abpy) [25,34,35] and 2,2′-azobis(5-chloropyrimidine) (abcp; Scheme 2) [34,36]. Typical $\mu,\eta^2:\eta^2$ bridging π donor ligands are 2,2′-bis(benzimidazolate) (bibzim^{2-}) [37] or the O-containing bridges oxalate (ox^{2-}) [38] and 1,2-diacylhydrazido(2-) (adc-R^{2-}; Scheme 3) [17]. The latter can be derived by reduction from azodicarbonyl species (adc-R), which points already to the possible "non-innocence" [39–41] of such bridges according to (6). A further unusual $\mu,\eta^2:\eta^2$ bridging π donor ligand is $\mathbf{4}^{2-}$ (Scheme 4) in which there is an apparent separation between the inorganic coordinating functions ("acac") and the central $(C_4)^n$ valence-mediating unit [42].

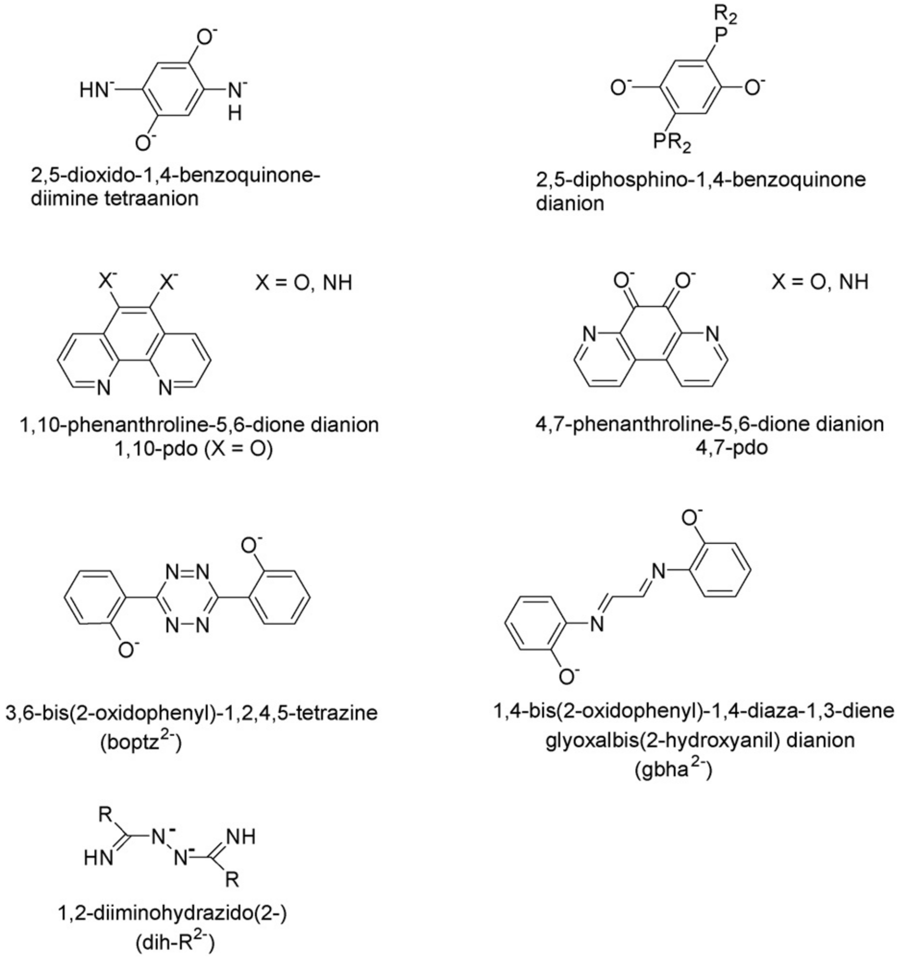
In addition to the differentiation between a valence-trapped or valence-averaged mixed-valent situation (3) and between an acceptor- or donor-mediated valence exchange pathway [(7) and (8)] the ground state of such an intermediate in a two-step redox system may also involve largely or even exclusively the ligand as electron-transfer active component, illustrated by description (6):

$$\mathrm{Ru}^{n+}(\mu\text{-L}^{2-})\mathrm{Ru}^{n+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Ru}^{n+}(\mu\text{-L}^{-\bullet})\mathrm{Ru}^{n+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Ru}^{n+}(\mu\text{-L})\mathrm{Ru}^{n+} \qquad (6)$$

The ambiguity between the formulations (3) and (6) may be assessed using combined spectroelectrochemical approaches (UV–vis–NIR and in particular EPR); typical bridging ligands exhibiting the potential for such behavior are quinonoid systems [41,43,44] with various dinucleating structural arrangements (cf. Formula **5** and Scheme 5) [45–52]. Remarkably, the terminal ligand set can also considerably influence that configuration, e.g. with donating acac$^-$ favoring higher and strongly π accepting 2-phenylazopyridine stabilizing lower metal oxidation states in the $[\mathrm{L}_n\mathrm{Ru}(\mu\text{-boptz})\mathrm{RuL}_n]^x$ series [50]. As ancillary ligands the weaker donor NH_3 and the weaker π acceptor 2,2′-bipyridine exhibit a greater tolerance for *several* neighboring oxidation

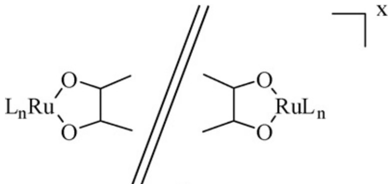


Scheme 4.



Scheme 5.

states of ruthenium.



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The crucial role of the frontier orbital composition at the interface between the bridging ligand and the mixed-valent metals has long been recognized as decisive for the comproportionation constant [25]. The effect of competition from ancillary ligands for the π donor capacity of ruthenium(II) in π acceptor-bridged Ru^{II}Ru^{III} species is strikingly illustrated by dinuclear bpym [24,25] and bptz complexes [25,30,53,54]. With $(H_3N)_4Ru^{2+/3+}$ [24,30] or $(acac)_2Ru^{0/+}$ [53] containing σ donor co-ligands the K_c values are very much larger at 10^{13} to 10^{15} than with $(bpy)_2Ru^{2+/3+}$ or $([9]aneS_3)ClRu^{2+/+}$ ($K_c \approx 10^8$; Table 1) [25,54]. The latter contain the weakly but nonetheless noticably π accepting ancillary ligands bpy = 2,2′-bipyridine or $[3]aneS_3$ = 1,4,7-trithiacyclononane.

The initially most surprising result for the diruthenium(II,III) complexes of π accepting bis-bidentate ligands has been the very low intensity of the IVCT bands. With weakly mediating μ-bpym or μ-titb these bands may be hardly visible or sometimes undetectable [24,28], and even complexes of strongly mediating azo or tetrazine containing ligands often show $\varepsilon < 1000\,M^{-1}\,cm^{-1}$ [30,34,35,37,53–55]. Unfavorable dπ/ligand π*/dπ orbital overlap in the rigid chelate conformation was made responsible for this effect [30] which has similarly been observed for related trinuclear systems [56] and for complexes with other metals [3].

Whereas valence exchange in the π acceptor (A) bridged species can be described using an electron-transfer formalism with the anion radical of the central ligand bridging two ruthenium(III) centers as conceivable intermediate (7), the systems bridged by π donating dianions (D^{2-}) can also be formulated with a radical bridge structure (8) [7,17,18].

$$Ru^{II}(A)Ru^{III} \leftrightarrow [Ru^{III}(A^{-\bullet})Ru^{III}] \leftrightarrow Ru^{III}(A)Ru^{II} \tag{7}$$

$$Ru^{II}(D^{2-})Ru^{III} \leftrightarrow [Ru^{II}(D^{-\bullet})Ru^{II}] \leftrightarrow Ru^{III}(D^{2-})Ru^{II} \tag{8}$$

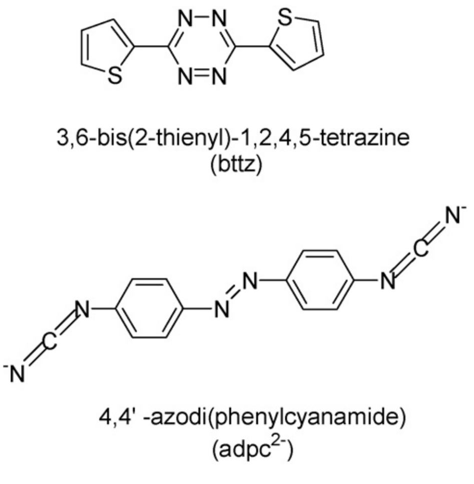
In fact, contributions from a radical structure can be deduced indirectly from ESR spectroscopy through the diminished anisotropy of the *g* factor components in the immobilized state. These effects were most striking for complexes $\{(adc\text{-}R)[Ru(bpy)_2]_2\}^{3+}$, depending strongly on the nature of R (Scheme 3) [17]. Donating groups R such as dialkylamino favor a radical ($D^{-\bullet}$) containing formulation whereas acceptors such as aryl substituents favor the $Ru^{II}Ru^{III}$ alternative with D^{2-} as bridge. Characteristically, there is also an opposite effect on K_c through the replacement of ruthenium by osmium, rationalized by the more electron rich +II state of Os and the less stable +III state for Ru [17]. Otherwise, most bis-bidentate donor bridged systems exhibit moderate-to-large K_c values and rather intense IVCT bands in the near-infrared [17,37,38], quite in contrast to the π acceptor-bridged analogues. Simple MO arguments using a five electron/three center model as opposed to a three electron/three center situation can explain the enhanced ligand contribution in the π donor bridged systems [2e,7].

With exclusive coordination through negatively charged oxygen donor atoms as in dinuclear $(acac)_2Ru$ complexes of dianionic oxalate [38] or $\mathbf{4}^{2-}$ [42] the K_c values and the IVCT band intensities decrease for the diruthenium(II,III) states. However, when oxidation was possible to a formally $Ru^{III}Ru^{IV}$ situation as with the dianionic ligand $\mathbf{4}^{2-}$ the IVCT band intensity showed a huge increase to $\varepsilon = 25000\,M^{-1}\,cm^{-1}$ [42]. Resonance contributions according to (9) may be involved to rationalize this dramatic effect.

$$Ru^{III}(L^{2-})Ru^{IV} \leftrightarrow Ru^{II}(L)Ru^{III} \qquad (9)$$

Mixing π acceptor and π donor functions in one and the same bridging ligand seems to enhance the metal–metal interaction. For instance, the bis-bidentate bttz ligand has both tetrazine π acceptor and thiophene π donor coordination functions in conjugation [57]. This ligand forms a mixed-valent complex with two $(bpy)_2Ru^{n+}$ complex fragments that is distinguished by a strongly enhanced $K_c = 10^{16.6}$ and $\lambda_{max}(IVCT) = 990\,nm$ ($\varepsilon = 1650\,M^{-1}\,cm^{-1}$), corresponding to a comparatively high-energy transition [57] (Scheme 6).

Similar effects were noticed for the bis-monodentate bridge $adpc^{2-}$ where a π accepting azo function connects two π donating cyanamidobenzene groups [58]. Simultaneous electron and hole transfer mechanisms were tentatively made responsible for the enhanced metal–metal interaction ($K_c = 10^{13.1}$, $\lambda_{max} = 1920\,nm$, $\varepsilon = 10^4\,M^{-1}\,cm^{1}$) across 19.5 Å although the unambiguous characterization of the singly occupied MO as metal-based is still lacking.


3,6-bis(2-thienyl)-1,2,4,5-tetrazine
(bttz)

4,4' -azodi(phenylcyanamide)
($adpc^{2-}$)

Scheme 6.

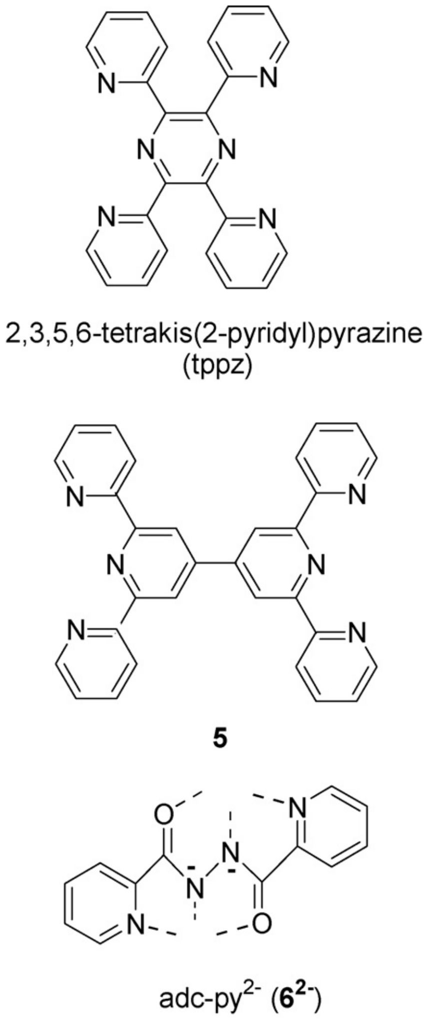
In contrast to the vast number of diruthenium(II,III) mixed-valent compounds [2] and to several diruthenium(III,IV) species [2c,d,42,51,59] there has been a conspicuous absence of molecule-bridged diruthenium mixed-valent intermediates with lower oxidation number combinations such as $Ru^I = 4d^7$ or $Ru^0 = 4d^8$. The d^7/d^8 combination has been observed for ligand-bridged systems involving dirhodium(I,II), diiridium(I,II) and diplatinum(II,III) arrangements [60,61]. The latter three showed only small splittings $\Delta E < 0.15$ V of corresponding redox potentials, translating to comproportionation constants $K_c < 10^{2.5}$ [60,61].

Using the synthetically popular [62] areneruthenium(II) complex fragments [33] we set out to investigate whether similar results could be obtained starting from the diruthenium(II) precursors $\{(\mu\text{-}L)[RuCl(p\text{-}Cym)]_2\}(PF_6)_n$, p-Cym = p-cymene, L = bpip and n = 2, or L = abpy and n = 1 [63]. Stepwise reduction under loss of both chloride ions proceeds with formation of $\{(\mu\text{-}L)[Ru(p\text{-}Cym)]_2\}^+$, which could be identified as ruthenium(I) (d^7) containing mixed-valent species through UV–vis–NIR spectroelectrochemistry (intervalence charge transfer bands around 1500 nm with $\varepsilon \approx 1000\,m^{-1}$) and EPR (distinctly rhombic g tensor anisotropy) [63]. The weak metal–metal coupling of the d_σ electrons from the e_g set is responsible for the small electrochemical coupling with $K_c \leq 10^2$, the much larger K_c values for corresponding acceptor-bridged diruthenium(II,III) species [55] is attributed to the involvement of the dπ orbitals from the t_{2g} subset [2].

2.4. Complexes with tris-bidentate bridging ligands

While atom-bridged triruthenium clusters of mixed valency are well known [64], including molecule-bridged cluster dimers [65] with a remarkable potential for the observation of charge transfer (valence) isomerism [66], there have been only few studies of such compounds with heterocyclic molecular bridges. Reports by Keene and co-workers have described in detail the systems $\{(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-HAT})[RuL_2]_3\}^{n+}$, HAT = 1,4,5,8,9,12-hexaazatriphenylene, L = bpy or phen [67–69], while recent extensions to $\{(\mu_3,\eta^2{:}\eta^2{:}\eta^2\text{-}\mathbf{7})[RuL'_2]_3\}^{n+}$, L′ = acac and **7** = diquinoxaline[2,3-*a*:2′,3′-*c*]phenazine (DQP) or its derivatives, provided further results [56]. In all cases the $Ru^{II}Ru^{II}Ru^{III}$ and $Ru^{II}Ru^{III}Ru^{III}$ mixed-valent states were rather stable with variable K_c values between 10^3 and 10^8, however, IVCT bands were not always detectable in the NIR or IR regions [56,67]. It was assumed that these bands are either too weak [56] or high-energy shifted due to delocalization [67]. The potential trigonal symmetry of such systems with degenerate frontier MOs may yield different effects for electronic transitions (Jahn-Teller situation) and ESR signals than those observed for species without orbital degeneracy.

Ward, Thomas and co-workers have recently described a $Ru^{II}Ru^{II}Ru^{II}/Ru^{II}Ru^{II}Ru^{III}/Ru^{II}Ru^{III}Ru^{III}/Ru^{III}Ru^{III}Ru^{III}$ series with mixed N/S donor ligation at the metal and very different K_c and IVCT features of the two mixed-valent intermediates [70]; clearly, the experimental basis has to become broader in order to allow for more general conclusions (Scheme 8).



2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz)

5

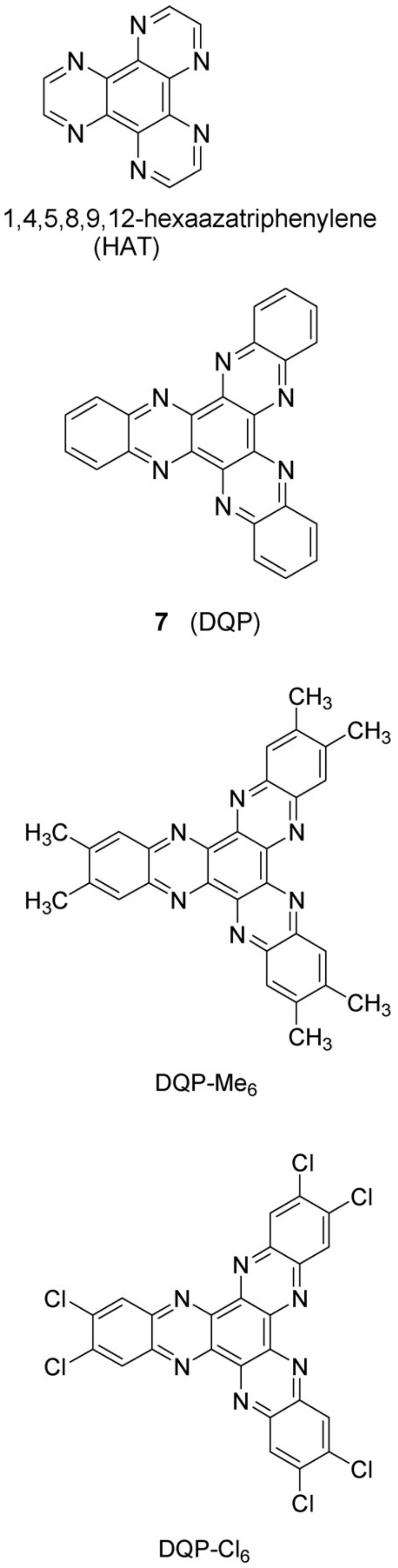
adc-py^{2-} ($\mathbf{6^{2-}}$)

Scheme 7.

2.5. Complexes with bis-tridentate bridging ligands

Bis-tridentate ($\mu,\eta^3:\eta^3$) bridging ligands have been employed in diruthenium(II,III) complexes with π *acceptors* such as 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz) [71–73] or conjugated π systems such as **5** which contain two “terpy-type” binding sites [74] (Scheme 7); the use of cyclometallated analogues [75] or adc-py^{2-} = $\mathbf{6}^{2-}$ as bis-tridentate $\mu,\eta^3:\eta^3$ *donor* bridges for (terpy)Ru^{n+} species has also been probed [76].

The π acceptor-bridged compounds exhibit K_c values of 10^6 or less and moderately intense IVCT bands in the near-infrared [72–74]. The compound $\{(\text{adc-py})[\text{Ru(terpy)}]_2\}^{3+}$ with a rather short metal–metal distance of about 5 Å has $K_c = 10^9$ and an intervalence band at 1000 nm ($\varepsilon = 3800\ \text{M}^{-1}\ \text{cm}^{-1}$) [76] whereas cyclometallation involving the bridging ligand yields intense near-infrared bands but small K_c values [75]. The particular bis-meridional configuration at the ruthenium centers in such complexes seems to favor the overlap of the orbitals relevant for the IVCT transition, even if the K_c value becomes smaller because of large Ru–Ru distances. The tppz ligand cannot adopt a coplanar conformation due to CH/CH bond repulsion between



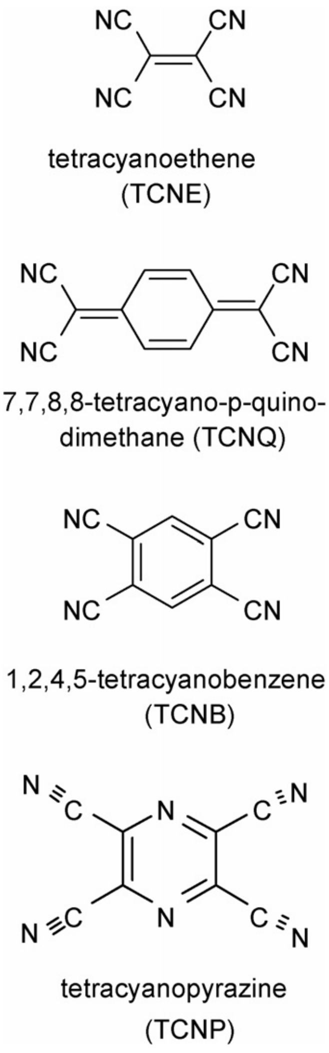
1,4,5,8,9,12-hexaazatriphenylene (HAT)

7 (DQP)

DQP-Me$_6$

DQP-Cl$_6$

Scheme 8.



Scheme 9.

neighboring pyridyl rings; the comparatively weak IVCT bands may thus be rationalized [72,73].

2.6. Complexes with tetrakis-monodentate bridging ligands

Tetraruthenium mixed-valent complexes have been described for compounds $\{(\mu_4,\eta^1:\eta^1:\eta^1:\eta^1\text{-TCNX})[\mathrm{Ru(NH_3)_5}]_4\}^{n+}$, TCNX = TCNE, TCNQ, TCNB, TCNP; n = 6,7,8,10 [77,78] (Scheme 9).

For the very strong π acceptors TCNE and TCNQ a double mixed-valent situation $\mathrm{Ru^{II}Ru^{III}(TCNX^{2-})Ru^{II}Ru^{III}}$ has been invoked [77] as the main contributing form to explain the spectral similarity, e.g. with analogous systems $\mathrm{Ru^{II}(mdn^{-})Ru^{III}}$ [19]. The long wavelength bands lie below 950 nm with very high intensities ($\varepsilon \approx 50{,}000\,\mathrm{M^{-1}\,cm^{-1}}$). The formal K_c for the oxidizable and reducible states $\mathrm{Ru^{II}Ru^{III}(TCNX^{2-})Ru^{II}Ru^{III}}$ ranges from 10^{12} to 10^{19}. DFT calculations [78b] have confirmed the “dimer of mixed-valent dimers” model [77] for the TCNE and TCNQ complexes, yielding triplet ground states [78a] with orthogonal molecular halves containing malonodinitrilato-bridged $(\mathrm{Ru^{2.5}})_2$ centers.

Table 2
General response of $\mathrm{Ru^{II}Ru^{III}}$ complexes to different coordination characteristics of the bridging ligand

Ligand characteristics	Example	K_c	$\varepsilon_{\mathrm{IVCT}}$
$\mu,\eta^1:\eta^1$ π acceptor	pz, bp	Medium	High
$\mu,\eta^1:\eta^1$ π donor	$\mathrm{mdn^{-}}$, $\mathrm{dicyd^{2-}}$	High	High
$\mu,\eta^2:\eta^2$ π acceptor	bpym, bptz	High	Low
$\mu,\eta^2:\eta^2$ π donor	$\mathrm{bibzim^{2-}}$, $\mathrm{adc\text{-}R^{2-}}$	Medium	High
$\mu,\eta^3:\eta^3$ π acceptor	tppz, 5	Medium	Medium
$\mu,\eta^3:\eta^3$ π donor	$\mathrm{adc\text{-}py^{2-}}$	Medium	High

Other, spectroelectrochemically obtainable states include one-electron-reduced $\mathrm{Ru^{II}Ru^{II}(TCNX^{-\bullet})Ru^{II}Ru^{II}}$, two-electron-reduced $\mathrm{Ru^{II}Ru^{II}(TCNX^{2-})Ru^{II}Ru^{II}}$, and two-electron oxidized $\mathrm{Ru^{III}Ru^{III}(TCNX^{2-})Ru^{III}Ru^{III}}$ as homovalent but less stable forms [77].

2.7. Overview

This short review of some recent results in ruthenium mixed-valent chemistry shows that qualitatively different coordination patterns may lead to very different quantitative responses in terms of electrochemical stabilities and electronic spectra. Table 2 illustrates this in a very general way for the type of $\mathrm{Ru^{II}Ru^{III}}$ examples described here.

Of course, the general guidelines given in Table 2 have to be modified in each individual case considering, e.g. ancillary ligand effects and the influence of the interface situation between the metal and the bridging ligand [25]. However, it should be obvious and understandable that there cannot be a simple correlation between K_c values and IVCT band intensities (ε) because electrochemical potential differences and orbital overlap phenomena are determined by different sets of geometrical and electronic parameters. Although the “electrochemically derived values of K_c have been interpreted as a means of assessing the coupling between metal centres” [9] the IVCT transitions are not simply “better indicator(s)” [9], they are describing a *different* phenomenon. The use of certain experimental parameters from electrochemistry or spectroscopy as direct criteria for Class II or Class III assignment is thus discouraged as long as appropriate references for each concrete coordination situation are not yet established. The apparent success in the case of the predominantly researched bis-monodentate bridged complexes may have contributed to a false sense of security in applying simple approaches to the question of valence delocalization. Ingenious use of spectroscopy can provide much more elucidating results [66]. After recognition of the coordinative effects future research will have to quantitatively elucidate these factors and to further explore higher nuclearities, different oxidation state combinations, and unconventional ligand configurations [79], employing increasingly reliable computational methods.

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