

Materials with electronic transitions in the near-infrared

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Abstract. Concepts have been developed which favor low-energy absorption in the near-infrared (NIR) region. These include metal-metal charge transfer (inter-valence charge transfer) transitions of mixed-valent species, radical ion compounds (anions, cations), and mixtures thereof. Recent examples from ruthenium coordination chemistry are presented in order to illustrate analysis and assignment of such NIR transitions.

Keywords. Charge transfer; mixed valency; near-infrared; radical complexes; Ruthenium compounds.

1. Introduction

Near-infrared radiation was detected as ‘calorific rays’ around 1800 by Friedrich Wilhelm (Sir Frederick William) Herschel (1738–1822); the discoverer of the first non-classical planet, Uranus. Materials with absorptions in the NIR region, between 800 and 2500 nm ($12500\text{--}4000\text{ cm}^{-1}$), were little studied at first, partly because of the rarity and the cost of corresponding spectrometers. However, several recent developments of more facile NIR detection have spurred a growth of corresponding research, related to the following emerging areas of application:

- Telecommunications using glass fiber optics (Nobel Prize in Physics 2009 for C. K. Kao) relies on near-infrared wavelength ranges which ensure minimal attenuation of optical signals.¹
- Bio-imaging and -sensing uses the near-infrared region due to the absorption specifics of tissue. The latter is also employed for thermal and photodynamic therapy.²
- Atmospheric analysis in the near-infrared relies partially on sensitive devices operating in that wavelength region.³
- Analysis of complex mixtures such as food has been greatly boosted by the application of database-supported near-infrared spectroscopy.⁴

Near-infrared absorbing materials, whether organic, organometallic or inorganic, have often been

discovered without support by a systematic approach. In contrast to numerous low-bandgap analyses for solid-state structures (semiconductors, polymers, charge transfer compounds from discrete molecules),⁵ there have been few attempts to classify small molecular compounds with low energy absorbance.^{6–9}

Among the functions resulting in NIR absorption are high-energy vibrational absorption features (overtones), e.g., from O-H groups, low-energy $\pi\text{-}\pi$ type absorptions from radicals or mixed-valent species,⁷ or $f\text{-}f$ transitions. The latter are weak as absorptions but play an important role in NIR emission,¹⁰ as do certain transition metal compounds.¹¹ In the following, the origin of NIR absorption and the interplay between radical ligands and mixed-valent dimetal combinations will be outlined for coordination compounds of ruthenium.

2. Results and Discussion

Radicals and radical ions have long been recognized as chromophores in the low energy region, i.e., in the near-infrared.¹² A straightforward explanation⁷ starts from the typically large HOMO-LUMO gap of stable molecules with a high energy transition between these frontier orbitals. One-electron oxidation may then create an empty site at the HOMO to which a low-energy transition from other filled orbitals can occur. Conversely, the additional electron introduced to the LUMO through one-electron reduction can be excited to other close-lying unoccupied orbitals, resulting also in a low-energy absorption.

Near-infrared absorption caused by such excitation mechanisms can be enhanced electronically and sterically

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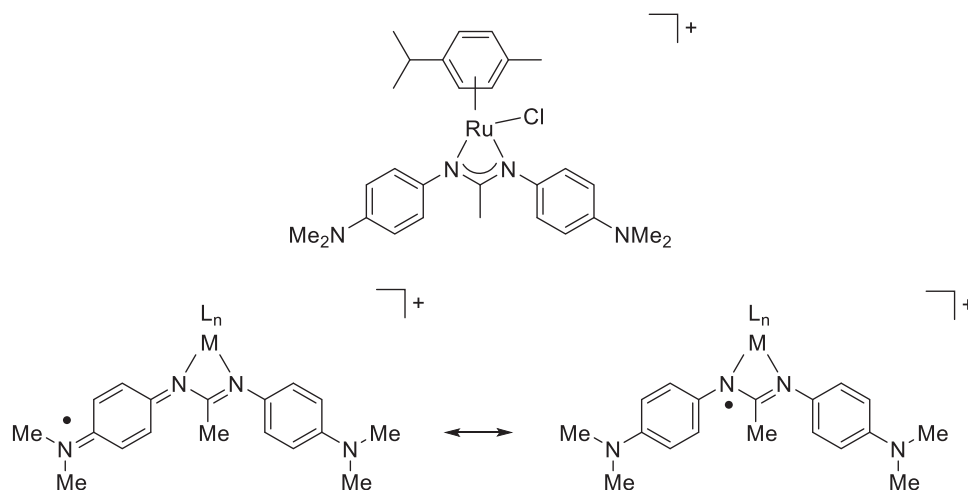
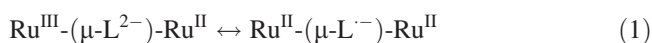


Figure 1. Two resonance formulations within a paramagnetic cationic complex.¹³

through metal coordination even if the main chromophore is the radical ligand. A recent example¹³ uses a new amidinato ligand forming a four-membered chelate ring with ruthenium (Figure 1) and exhibiting the rise of an intense ($\epsilon = 30000 \text{ M}^{-1} \text{ cm}^{-1}$) and relatively narrow absorption at 1230 nm on ligand centered oxidation (Figure 2). The latter is confirmed experimentally by EPR and theoretically through spin density calculations (Figure 3).

An alternative for dinuclear or oligonuclear complexes is the occurrence of metal-to-metal or inter-valence charge transfer transitions (MMCT, IVCT) between formally reduced and oxidized centers.^{14–17} Asymmetrical bonding such as in Prussian Blue with its (*l.s.*) $\text{Fe}^{\text{II}}\text{-C}\equiv\text{N-Fe}^{\text{III}}$ (*h.s.*) arrangement is the prime example for such a mixed-valent situation with low-energy transitions, even if this particular absorption is mostly visible, giving rise to the intense blue color. In contrast to such typical ‘Class II’ mixed-valent species¹⁸ there are compounds clearly identified as symmetrical ‘Class III’ mixed-valent species, e.g., Mössbauer-identified $\text{Fe}^{2.5}\text{-(}\mu\text{-L)-Fe}^{2.5}$ compounds (Figure 4)¹⁹ or the long debated^{14,20} Creutz-Taube ion with a $\text{Ru}^{2.5}\text{-(}\mu\text{-L')-Ru}^{2.5}$ borderline situation (Figure 4).²⁰ In these strongly coupled cases, the near-infrared transition occurs between the bonding and the antibonding combination of metal orbitals.

Those cases (1) where a potentially mixed-valent dimetal pair is bridged by a potentially radical-forming ‘non-innocent’²¹ ligand require further information from calculations or experiment (e.g., IR, Raman, EPR) in order to identify the site of low-energy electronic transition. While spin densities can normally be reliably calculated at the DFT level, the calculations of near-infrared transitions may be less straightforward.



The value of EPR data lies in the effect of metal participation at the spin distribution through its large spin-orbit

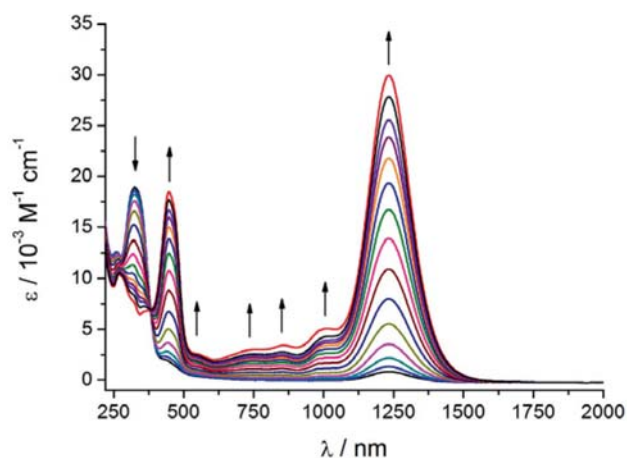


Figure 2. UV-vis-NIR spectroelectrochemical response on oxidation of the neutral to the cationic complex from Figure 1 in $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$.

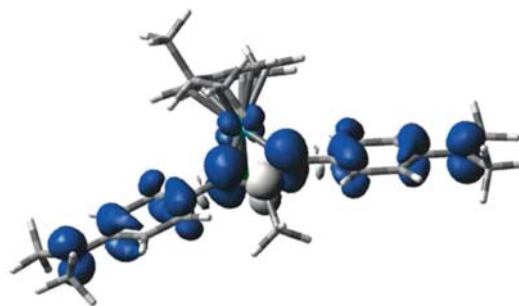


Figure 3. DFT calculated spin densities for the cation from Figure 1.

coupling. The result of strong metal participation is a significant deviation of the g factor from 2.0023 for the free electron,^{22–24} in itself a consequence of relativistic effects.²⁵ Both the isotropic g value and the anisotropy of g in immobilized form correlate with the amount of metal

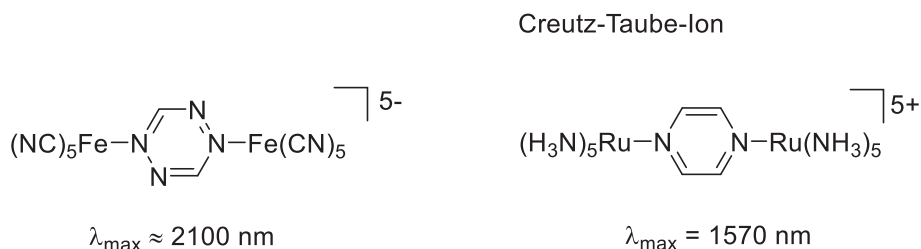


Figure 4. Two NIR absorbing mixed valent ions.^{19,20}

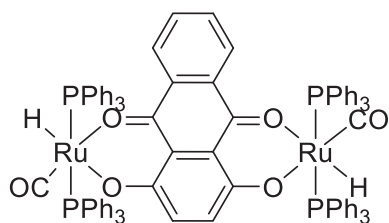


Figure 5. 1,4-Dioxido-9,10-anthraquinone precursor complex.

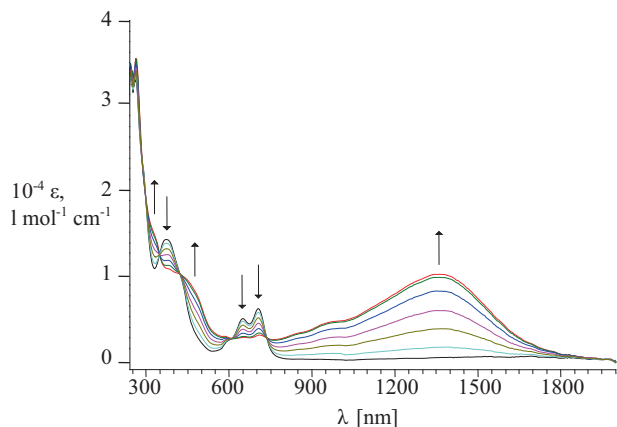


Figure 6. UV-vis-NIR spectroelectrochemical response on oxidation of the neutral to the cationic complex from Figure 5 in $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$.

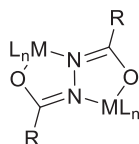
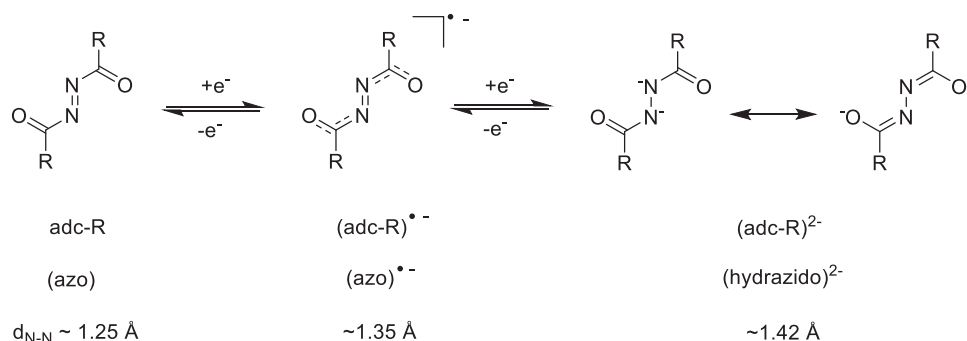


Figure 7. Two-step redox system based on adc-R ligands (top) and dinuclear metal complexes of $(\text{adc-R})^{2-}$ ligands (bottom).

participation at the spin distribution and thus with the character of the corresponding electronic transition.

Quinonoid bridging ligands have been used with diruthenium complexes, often exhibiting intense near-infrared transitions.²⁶ The example in Figures 5, 6 with strong absorption at $\lambda_{\text{max}} = 1370 \text{ nm}$ after oxidation to the (1+) form may suggest the formation of a mixed-valent species such as the Creutz-Taube ion (Figure 4). However, both the EPR and IR results from corresponding spectroelectrochemical experiments^{28,29} reveal very little metal contribution to the singly occupied MO, attributing the near IR transition to the π system of the anthraquinone bridge.

9,10-Anthraquinones are known as useful dyes even in the non-radical state, and the formation of metal-containing radical intermediates with NIR absorption thus creates a further attractive pathway to remarkable chromophores.²⁷

Another class of potentially metal-binding dye functions includes modified azo compounds. These can be designed to bridge two metal ions,³⁰ introducing again the alternative of metal-metal mixed valency or radical formation to cause near-infrared absorption.^{7,26,31} Azodicarbonyl systems (hydrazido(2-) species in the two-electron reduced form, Figure 7) have been shown to bind ruthenium centers in bis-bidentate fashion (Figure 7), with variable spin distribution³¹ and useful electrochromical optical switching behavior in ranges of interest for telecommunication applications.³²⁻³⁹

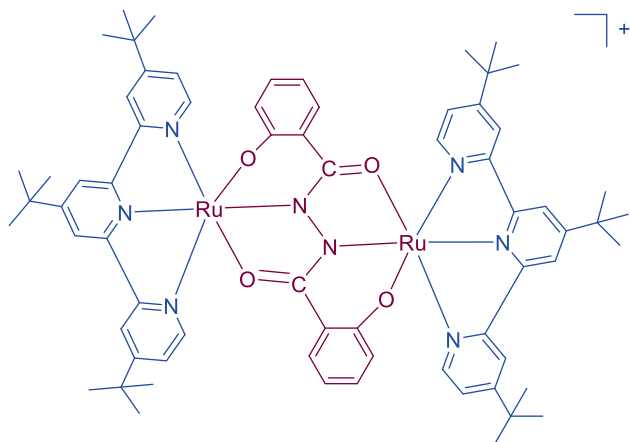


Figure 8. Bis(tridentate) chelating of the bridge in a paramagnetic diruthenium complex ion.

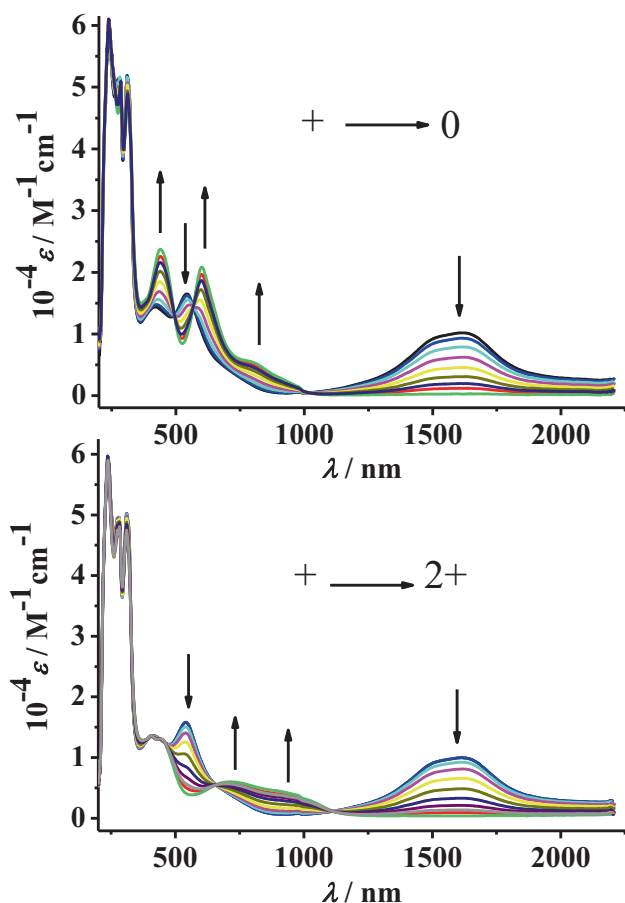


Figure 9. UV-vis-NIR spectroelectrochemical reduction and oxidation of the cation from Figure 8 in $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$ at 298 K.

A recent extension to a bis-tridentate bridging azo ligand has produced a complex redox system of which the paramagnetic cation absorbs at 1660 nm and 1530 nm (Figures 8, 9).³⁴

EPR and DFT spin density calculations point again to a dimetal/bridge mixed spin situation in the singly occupied

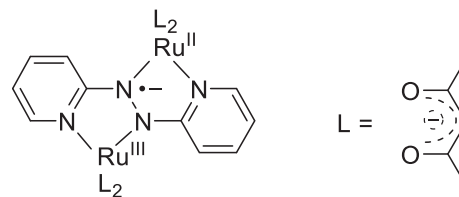
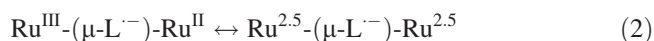


Figure 10. Radical anion-bridged mixed-valent compounds.⁴⁰

MO (SOMO), i.e., a resonance situation between a mixed valent and a radical formulation (1).

Such a resonance description (1) is related to formulation (2)



which was evidenced by structural and computational studies for the diamagnetic compounds from Figure 10 (two diastereoisomers possible).⁴⁰

Antiparallel spin-spin coupling accounts for the diamagnetism, and the intense near IR absorption occurs at 840 nm, i.e., at relatively high energy.⁴⁰

3. Conclusions

The increasing interest in near-infrared absorbing materials has prompted the need to develop concepts for stable molecular compounds with small frontier orbital gaps. Beyond empirically discovered examples, there are representative advanced classes of materials that can provide the necessary physical and chemical requirements, mostly due to a combination of electron delocalization and intramolecular charge transfer activity.

Making use of persistent odd-electron systems (radicals, mixed-valent arrangements), this article describes an ingenious way to achieve NIR absorption in attractive spectral regions that is provided by dinuclear (or oligonuclear)^{41,42} metal complexes with non-innocent bridging ligands, where mixed-valency and (2)/or (1) radical formation can lead to small frontier orbital differences and corresponding intense low energy transitions.

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