

Controlling second coordination sphere effects in luminescent ruthenium complexes by external pressure

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Abstract: Two luminescent heteroleptic Ru(II) complexes with a 2,2'-biimidazole (biimH₂) ligand form doubly hydrogen-bonded salt bridges to 4-sulfobenzoate anions in single crystals. The structure of one of these cation-anion adducts shows that the biimH₂ ligand is deprotonated. Its ³MLCT luminescence bands does not shift significantly under the influence of an external hydrostatic pressure, a behavior typical for these electronic transitions. In contrast, hydrostatic pressure on the other crystalline cation-anion adduct induces a shift of proton density from the peripheral N-H groups of biimH₂ towards benzoate, leading to a pronounced red-shift of the ³MLCT luminescence band. Such a significant and pressure-tuneable influence from an interaction in the second coordination sphere is unprecedented in artificial small molecule-based systems.

Atoms or groups that are not directly bonded to a metal center, but to the outer periphery of the ligands, can have a crucial influence on the properties of a complex. Such second coordination sphere effects play an important role in many proteins, but in artificial systems they are usually difficult to emulate. For instance, in blue copper enzymes certain amino acid point mutations in the second coordination sphere of the active site have a remarkable influence on its redox potential, but in small synthetic complexes this cannot be modeled easily.^[1] The importance of controlling the second coordination sphere in small metal complexes has been widely recognized in recent years, as it has been found that the performance of certain artificial catalysts for H₂ generation and CO₂ reduction crucially depends on the presence of proton relay stations.^[2] In artificial metalloenzymes, second coordination sphere effects have been exploited to influence the enantio- or diastereo-selectivity of chemical reactions.^[3]

Our approach for controlling the three-dimensional structure beyond the first coordination sphere is to employ hydrogen-bonding motifs in single crystals of luminescent ruthenium complexes. These noncovalent interactions give access to highly ordered and precise arrangements of individual molecular components and we decided to use the 1:1 adducts that can be formed between complexes bearing a biimH₂ ligand and a carboxylate counterion.^[4] Such hydrogen bonded adducts are readily accessible in apolar solution, but in the following we focus on the solid state, where hydrogen bonds depend on the three-dimensional packing and on the charge balance of the compounds.^[5] With the dicationic Ru(II) complexes from Figure 1a/b such 1:1 adducts can be obtained when crystallizing them with the dianionic 4-sulfobenzoate. These heteroleptic Ru(II) complexes with biimH₂ and bpy ligands commonly exhibit photoluminescence from the lowest ³MLCT excited states which is sensitive to the interactions of the biimH₂ ligand with Brønsted bases in the second coordination sphere.^[6] By applying external pressure on the crystalline 1:1 adducts we varied the biimH₂ – benzoate distance and followed changes of the protonation state by luminescence spectroscopy.

Increasing pressure leads to a continuous variation of proton delocalization across the salt bridge and a continuous shift of the luminescence maximum in one of the two adducts. To the best of our knowledge, there exist no prior studies that demonstrate such direct and continuous control of a second coordination sphere effect.

Ru(II) biimH₂ complexes with either ^tBu or CF₃ substituents on the bpy spectator ligands were synthesized and crystallized as 4-sulfobenzoate salts (Figure 1, synthesis and crystallization in the SI on pages S4 – S7), hereafter referred to as Ru(^tBu) and Ru(CF₃). The single crystal X-ray structures of both compounds at 300 K are presented in Figure 1c-d. Ru(^tBu) crystallized in the monoclinic space group *P* 2₁/c with one cation-anion pair in the asymmetric unit, and Ru(CF₃) crystallized in the triclinic space group *P* 1 with two isomers per unit cell, one of which is shown in Figure 1d and the second one is shown in Figure S6 of the SI. The hydrogen bonding distances between the two peripheral biimH₂ N-atoms and the two O-atoms of the carboxylate group are in the typical range for such hydrogen bonds (2.58(2) – 2.674(3) Å).^[6d, e, 7] The biimH₂ ligand and the carboxylate plane are at an angle of 12.4° in Ru(^tBu) and at 34.7° and 26.1° in Ru(CF₃), with the overall arrangement clearly indicative of twofold N...H...O hydrogen bonding in both structures, in line with prior studies of related systems.^[5] The most important difference between the two compounds is the protonation state of the biimH₂ ligand in the crystal structure. In the case of Ru(^tBu), the biimH₂ ligand is fully protonated (solid lines marking the N-H bonds in Fig. 1a) whereas for the Ru(CF₃) structure only one N-H bond

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under XXX. It contains a description of equipment and methods, as well as syntheses, product characterization data and crystallographic tables. CCDC 1583830 and CCDC 1583965 (for Ru(^tBu)), and CCDC 1583848 and CCDC 1583964 (for Ru(CF₃)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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could clearly be found in the electron density map (dashed line marking one of the N-H bonds in Fig. 1b). In this crystal structure, the exact position of the second hydrogen

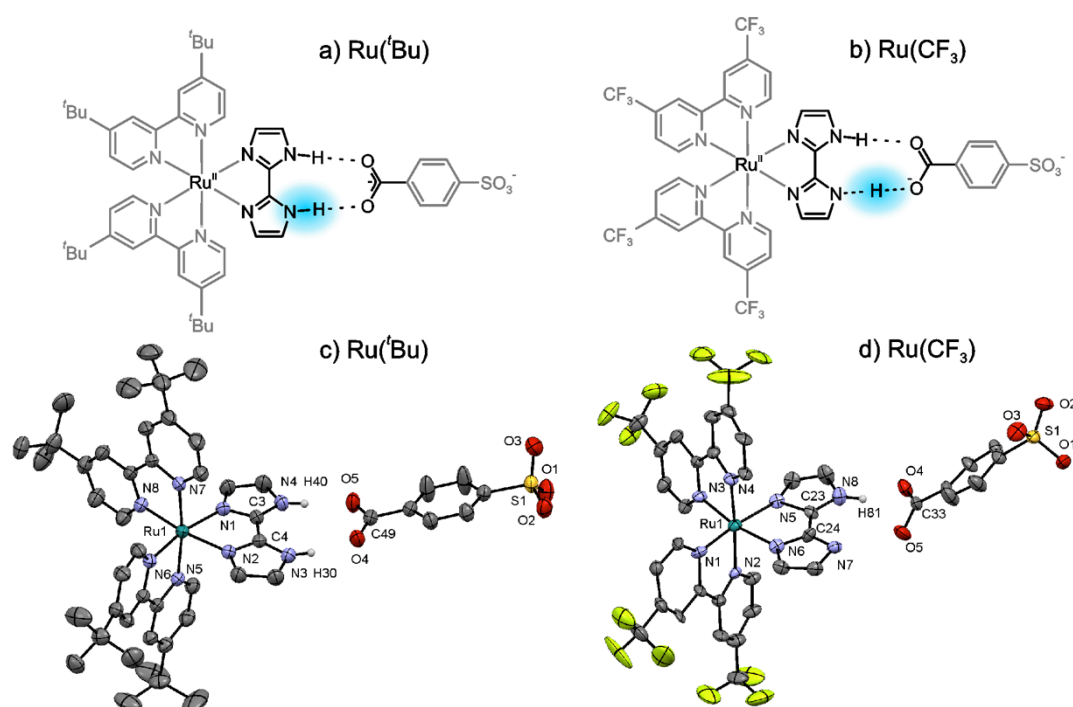


Figure 1. (a) Lewis structures of the 1:1 adducts between $\text{Ru}(\text{R-bpy})_2(\text{biimH}_2)^{2+}$ complexes and 4-sulfobenzoate: (a) $\text{Ru}(\text{tBu})$ and (b) $\text{Ru}(\text{CF}_3)$. Single crystal X-ray structures at 300 K of (c) $\text{Ru}(\text{tBu})$ and (d) $\text{Ru}(\text{CF}_3)$ (isomer 1, isomer 2 is shown in the Figure S6 of the SI). Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms are omitted for clarity, except for hydrogen atoms involved in the N-H...O hydrogen bond that were found in the electron density map.

atom within the N...H...O hydrogen bond in this case is more compatible with delocalization of one proton between biimH₂ and the carboxylate group.

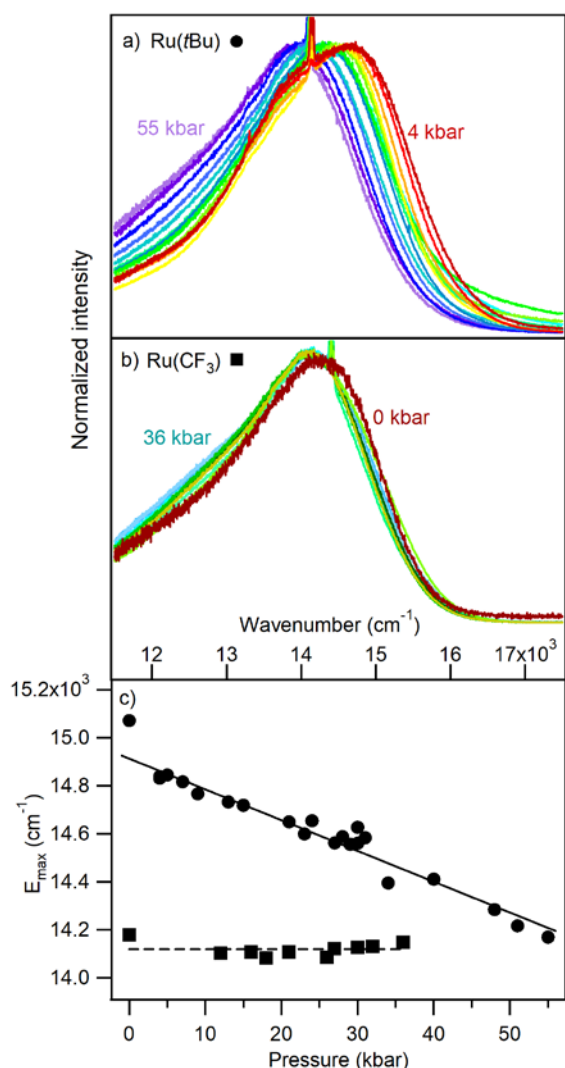
This key finding is compatible with the higher acidity of the biimH₂ ligand for the more electron-deficient $\text{Ru}(\text{CF}_3)$ complex (see SI page S13 for details).

Following excitation at 488 nm, single crystalline samples of $\text{Ru}(\text{tBu})$ and $\text{Ru}(\text{CF}_3)$ both exhibit ³MLCT luminescence (Figure 2a/b). According to DFT calculations (SI pages S14 – S26), the HOMO is metal-based with some biimH₂ contribution, whereas the LUMO and the LUMO+1 are predominantly bpy-centered in both cases, with the LUMO of $\text{Ru}(\text{tBu})$ showing a more important biimH₂ contribution, as seen in Figure S9 of the SI. The luminescence band maximum in $\text{Ru}(\text{CF}_3)$ is ~800 cm⁻¹ lower in energy than in $\text{Ru}(\text{tBu})$, compatible with a more stabilized LUMO due to the electron-withdrawing CF₃ substituents on bpy and a more destabilized HOMO due to proton delocalization into the hydrogen bond (see below for further details).

When applying hydrostatic pressure in a diamond anvil cell (SI page S2), the two compounds exhibit markedly different changes in luminescence behavior. $\text{Ru}(\text{CF}_3)$ behaves similarly to the $\text{Ru}(\text{bpy})_3^{2+}$ complex showing a very weak variation of the emission band maximum (E_{max}) with pressure (Figure 2b). Between ambient pressure and 36 kbar, E_{max} stays constant within the

experimental error with an average value of 14120 cm⁻¹ (Figure 2c), showing that the luminescence of $\text{Ru}(\text{CF}_3)$ is pressure-independent (squares and dotted line in Figure 2c). For comparison, E_{max} values for $\text{Ru}(\text{bpy})_3^{2+}$ shift in the range of -2 to -8.5 cm⁻¹/kbar depending on pressure regimes and solid state matrix.^[8] The relative pressure insensitivity of the luminescence for both $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{CF}_3)$ is similar and typical for MLCT transitions in octahedral d⁶ metal complexes.^[8a] In marked contrast, $\text{Ru}(\text{tBu})$ shows a constant shift of E_{max} by -13 ± 1 cm⁻¹/kbar between ambient pressure and 55 kbar (spectra in Figure 2a and circles in Figure 2c). Pressure-induced red shifts of comparable magnitude have been reported for square-planar Pd(II) complexes, where a non-coordinated alkyl group interacts with the metal center, also an effect other than straightforward first-sphere metal-ligand bonding.^[9] The strongest pressure-induced shifts occur for stacked square-planar Pt(II) complexes, with values of -115 to -320 cm⁻¹/kbar due to intermolecular metal-metal interactions.^[10] In both literature cases, the red shift is due to a destabilization of the metal-based HOMO. In our case, an interaction directly on the metal is not possible due to the saturated coordination sphere, but the hydrogen bonding influences the electronic structure of the first coordination sphere. Previous studies of biimH₂ complexes show a strong variation of HOMO energies with the protonation state of the ligand.^[6a-d] DFT

calculations for the protonated and deprotonated Ru('Bu) complex have been carried out to model the variations of HOMO, LUMO energies with deprotonation. These variations are expected to go in the same direction as the pressure-induced shifts since pressure reduces intermolecular distances and therefore significantly changes hydrogen bonding. The calculations illustrated in Fig. S10 in the SI clearly show that HOMO has metal "t_{2g}" character. Upon deprotonation, biimH₂ becomes a strong π donor, leading to the destabilization of the metal-based HOMO, documented by the orbital energies in Table S8 in the SI. The calculated LUMO and LUMO+1 of the deprotonated complex are predominantly bpy based, as shown in Fig. S10. This



destabilization leads to a calculated HOMO-LUMO energy gap smaller by 20% for the deprotonated Ru('Bu) complex, predicting a red shift of the MLCT emission with deprotonation. This calculated trend is in agreement with luminescence spectra in acetonitrile solution at 22 °C (Figure S8, SI) showing a red shift of the MLCT emission band maximum by 370 cm⁻¹ upon single deprotonation of biimH₂ to biimH⁻. These comparisons show that it is likely that the pressure-induced red-shift observed for Ru('Bu) in the solid state is caused by a second-sphere effect.

Figure 2. Luminescence spectra of (a) Ru('Bu) and (b) Ru(CF₃) as a function of hydrostatic pressure at room temperature. Excitation occurred at 488 nm. (c) Energy of the MLCT luminescence band maxima (E_{max}) from (a) in circles and (b) in squares as a function of pressure. Least-squares fits show values of -13 ± 1 cm⁻¹/kbar for Ru('Bu) (solid line) and 0 cm⁻¹/kbar for Ru(CF₃) (dotted line) with an average E_{max} value of 14120 cm⁻¹. E_{max} at 0 kbar for Ru('Bu) was calculated from an extrapolation of the E_{max} values at variable temperature (see SI on pages S27 and S28). E_{max} at 0 kbar for Ru(CF₃) was obtained from the spectrum at ambient temperature measured outside the pressure cell.

In the electron density map of the X-ray crystal structure of Ru('Bu) at ambient pressure, the biimH₂ ligand is fully protonated. Pressure is expected to shorten the two N-H...O hydrogen bonds, making proton delocalization between the cationic Ru(II) complex and the counter-anion more readily possible, in analogy to what is observed for Ru(CF₃) already at ambient pressure (Figure 1b/d). In a previous study with a deuterated N...H...O hydrogen bond, N...O distance decrease was accompanied by a net proton migration from O to N as observed crystallographically using averages over time.^[11] Delocalization was observed for hydrogen bonded benzoic acid at high pressure^[12] and is generally enhanced upon distance shortening. This is a result of the decrease distances between hydrogen bond donor and acceptor, which decreases the potential wells of the two discrete protonation states and increases proton transfer and tunneling rates.

Compression of single crystals of Ru('Bu) and Ru(CF₃) induces similar shrinking of the respective unit cells by approximately 0.7 Vol-%/kbar and 0.8 Vol-%/kbar, as seen in Tables S1 and S2 of the SI. Therefore, the change in the biimH₂ – carboxylate distance is expected to be similar in Ru(CF₃) and in Ru('Bu) with increasing pressure. The transition from localized proton density to more delocalization in Ru('Bu) seems to be the most important structural change. This effect is more important in Ru('Bu) compared to Ru(CF₃) because in the latter structure the proton delocalization is already present (in both crystallographic isomers) from the beginning. Raman spectra at variable pressure (Figures S15 and S16 of the SI) show the expected minor frequency increases with pressure, indicating that the crystalline structures and phases remain stable at high pressures.

The control of second coordination sphere effects in artificial small complexes commonly requires substantial synthetic efforts, and in several cases remarkable results have been obtained.^[2, 13] Our herein demonstrated approach is fundamentally different in that we use doubly hydrogen-bonded salt bridges as a motif to precisely place an anion in the second coordination sphere of two Ru(II) complexes in the solid state. Through external pressure, we are then able to continuously vary the hydrogen-bonding interaction. This concept should be readily applicable to a range of supramolecular structures with transition metal complexes and opens the possibility to explore and control second coordination sphere effects on luminescence and other electronic properties.

Acknowledgements

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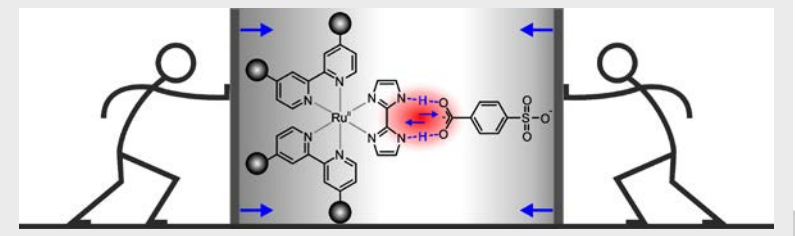
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Layout 2:

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<p>Cation-anion adducts are squeezed together by hydrostatic pressure, leading to delocalization of protons in the hydrogen bonds between these cation-anion adducts and changes in the luminescence of Ru(II) complexes.</p> 	<p><i>Andrea Pannwitz, Stéphanie Poirier, Nicolas Bélanger-Desmarais, Alessandro Prescimone, Oliver S. Wenger,* Christian Reber*</i></p> <p>Page No. – Page No.</p> <p>Controlling second coordination sphere effects in luminescent ruthenium complexes by external pressure</p>