

Chapter 2

The Systems of This Project

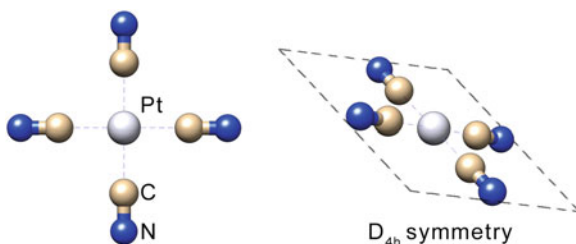
There are two overall groups of complexes in this study: Members of the d^8 -metal complexes, known for the debated nature of the ' d^8 – d^8 -interactions' [1], that can cause oligomerisation [2, 3]. This entails having two (or more) electron-rich elements close to each other, but weaker bound than in the covalent case, such that large changes in molecular geometry are very likely to occur if the system is perturbed; an opportune model system for dynamics measurable with the XDS-pump-probe method.

The other general category also involves transition metals, but in this case they appear in complexes exhibiting octahedral symmetry, where the metal atom is centered between 6 nitrogen atoms of the ligands. The complexes are of interest both due to an intricate relationship between their spin-configurations and the resulting geometries, and furthermore due to the effect this relationship on their excited-state lifetimes.

2.1 Tetracyanoplatinate, $[\text{Pt}(\text{CN})_4]^{2-}$

The origin of the interest in d^8 -metal compounds has been reviewed by Harvey [4], focusing on the origin of—and motivation for—the ligands. Gliemann and Yersin [3] provides an in-depth overview of a single member of the square planar complexes: Tetracyanoplatinate (II), $[\text{Pt}(\text{CN})_4]^{2-}$ (see Fig. 2.1). According to Harvey, the interest in these compounds originated from the work done by Gray et al. from 1977–1981 [5–8], realising that the $[\text{Rh}(\text{CNR})_4]^+$ complex oligomerizes, and that the oligomer structure is concentration dependent. This oligomerization was also found to take place for $[\text{Pt}(\text{CN})_4]^{2-}$ ions in solution [2]. Apart from the fact that the metal-metal distance is concentration (-and pressure [9]) dependent, the metal-metal distance can also be varied by changing the counter ion used in the crystallization. Actually, the Pt–Pt distances in the crystals vary with up to 0.7 Å, depending on the counter ion [3].

Fig. 2.1 Illustration of the Tetracyanoplatinate complex $[\text{Pt}(\text{CN})_4]^{2-}$. The Pt atom is centered between the 4 cyano groups in D_{4h} symmetry, so the complex is *square planar*



The compound can be modeled as a quasi one-dimensional metal-metal bonded chain, exhibiting extremely anisotropic conductivity [10], making it interesting for transport studies and molecular electronics.

This kind of solvated species constitutes a complex system, with oligomers of different numbers of units, and different structures present in the solution at once. Thus, the host of dependencies diminishes the level of attainable control desired for detailed dynamics studies, or later applicability in energy conversion. However, the square planar symmetry of $[\text{Pt}(\text{CN})_4]^{2-}$ makes it feasible for full, 4-component relativistic QM geometry relaxations, as the symmetry-induced degeneracy can be used to reduce the number of needed computations.

2.2 $\text{M}_2(\text{dimen})_4^{2+}$

The need for better control of the binuclear complex structure motivated the search for bridging ligands that could provide this. The most widely employed bridging ligands are shown in Fig. 2.2.

The dimen molecules (see Fig. 2.2, center) have intermediate flexibility when used as ligands in the complex, since they are longer than the ‘bridge’ (Fig. 2.2, left), but are stabilized by the ring, compared to ‘TMB’ (Fig. 2.2, right). This makes them the best candidates for obtaining a useful combination of control and flexibility, to mitigate the difficulties in the experimental detection of structural change upon

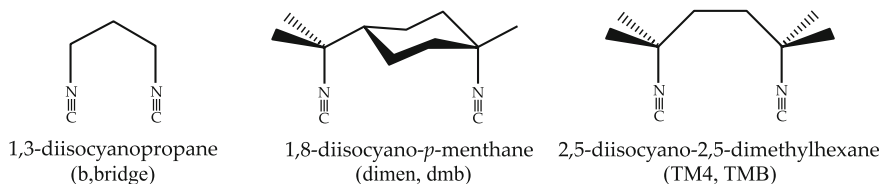


Fig. 2.2 Ligands for the binuclear systems. The complete complexes are made from 2 metal ions, attached at the triple bonded carbon to four opposing ligand units (see Fig. 2.3). Here, the ligands are displayed with increasing flexibility from *left to right*

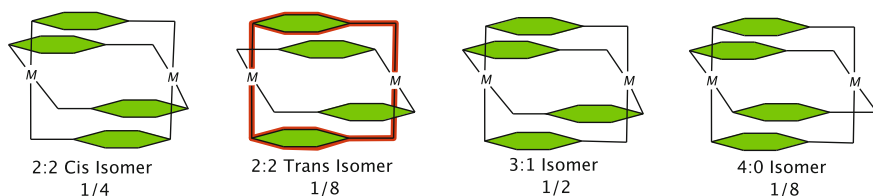


Fig. 2.3 Schematic of the dimen orientation in the four $M_2(\text{dimen})_4^{2+}$ isomers. The *highlighted* part of the 2:2 Trans isomer is represented in the schematic in Fig. 2.4. The statistical distribution in solution [11] is displayed below each isomer. Adapted from [12]

outside action. The cyclohexane ring breaks the ligand symmetry such that the final complex exists in four isomeric structures, as shown in Fig. 2.3.

The Ground State (GS) crystal structure of complexes from this group with the dimen ligand was first determined with $M=\text{Rh}$ by Mann [13]. They were dubbed ‘windmill’-like in their arrangement (see Figs. 2.3 and 2.4). The suggestion that the structure was similar for all complexes in the group was later confirmed for $\text{Rh}_2(\text{dimen})_4^{2+}$ [14] and $[\text{Ir}_2(\text{dimen})_4]^{2+}$ as well [11]. Figure 2.4 shows the structure of the $[\text{Ir}_2(\text{dimen})_4]^{2+}$ complex, without hydrogens, for clarity. While our group has been experimentally investigating both $[\text{Rh}_2(\text{dimen})_4]^{2+}$ [16, 17] and $[\text{Ir}_2(\text{dimen})_4]^{2+}$ [18], the Ir variant was chosen for both the further theoretical modelling, and for experimental investigation at an XFEL. This choice is based upon the following reasons:

- The scattering signal from the Ir-containing complex is larger, due to the larger amount of electrons in Ir.
- The excitation fraction of $[\text{Ir}_2(\text{dimen})_4]^{2+}$ is higher for the employed experimental setup [17].

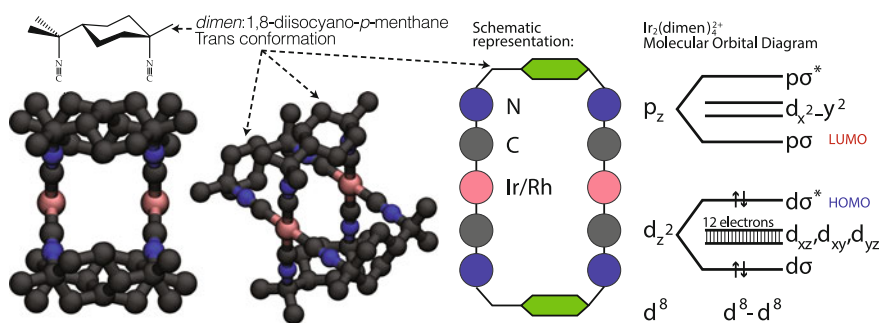


Fig. 2.4 Left The ‘windmill-like’ structure of the $[M_2(\text{dimen})_4]^{2+}$ complex, here shown without hydrogens for clarity. Center Schematic representation which only needs to depict half of the complex, due to its symmetry (see Fig. 2.3). The schematic emphasises the atoms of the ‘ligand legs’ connected to the metals. This representation will be used in the explanation of the simulated dynamics in Chap. 6. Right Molecular orbital diagram, reconstructed from [15], featuring the metal-centered, bonding LUMO and the antibonding HOMO

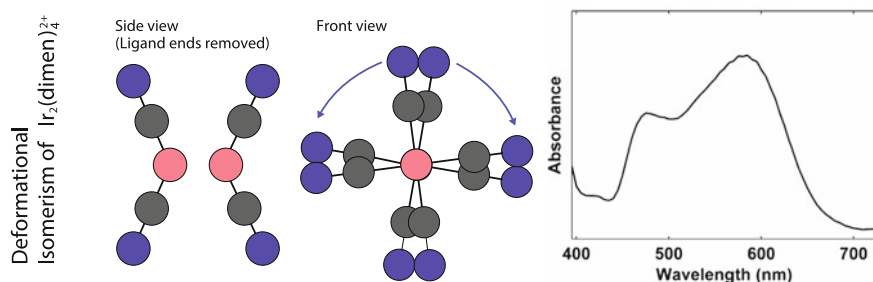


Fig. 2.5 *Left* Deformational isomerism in $[\text{Ir}_2(\text{dimen})_4]^{2+}$. The ‘Short and Twisted’ conformer can only be theoretically described by mapping energy surfaces of the Ir–Ir distance and the twisting angle between the metal ligand planes, while allowing the rest of the structure to relax at each point. *Right* Absorption spectrum of $[\text{Ir}_2(\text{dimen})_4]^{2+}$ in acetonitrile: Pumping the molecule at 475 or 585 nm selectively excites the long and eclipsed, or the short and twisted conformer, respectively [19]

- Transient optical spectroscopy has shown coherent oscillations post excitation of this complex [19] (see Fig. 2.7 and accompanying text).

The electronic configuration of this complex features a σ -antibonding¹ Occupied Molecular Orbital (HOMO), while the Molecular Orbital (LUMO) is σ -bonding [15, 20]. Thus, when photoexcited, the complex effectively forms a chemical bond between the two metals. This, in combination with the previously discussed flexibility of the dimen ligand, causes the complex to undergo large structural changes. We have previously reported a 1.3 Å contraction along the Ir–Ir axis for $[\text{Ir}_2(\text{dimen})_4]^{2+}$ in solution [18], using pulsed synchrotron radiation. While this contraction is far from unique to the Ir-variant (a solid-phase Rh–Rh contraction of 0.86 Å has also previously been reported [21]), it is, to our knowledge, the largest.

Hartscock et al. [19] have carried out transient spectroscopy measurements on the $[\text{Ir}_2(\text{dimen})_4]^{2+}$ complex, and report a deformational isomerism which effectively splits the GS population in two main structures: a ‘short and twisted’ (Ir–Ir distance of ~ 3.6 Å, 17° twist, see Fig. 2.5), and a ‘long–eclipsed’ (Ir–Ir distance of ~ 4.4 Å, 0° twist). This isomerism has previously been observed [22], and is supported computationally by constrained mappings of the energy landscapes, made in-house by van Driel [17] (see Fig. 2.6) and elsewhere [23], and is reflected in the double-peak in the absorption spectrum of the complex (Fig. 2.5, right).

The transient spectroscopy carried out by Harlang [12] and in [19] clearly shows signs of coherent vibrations. The results are reproduced in Fig. 2.7. The choice of which GS deformational isomer structure is excited influences the ES dynamics: When pumping the short and twisted structure (the 585 nm peak), two dynamic modes are observed, with frequencies of 80 and 119 cm^{-1} , and assigned to a pinch along the Ir–Ir axis and a dihedral twist, respectively. When pumping the long–

¹A term originating from orbital- and hybridisation theory, where the overlap of atomic s orbitals makes a molecular σ orbital.

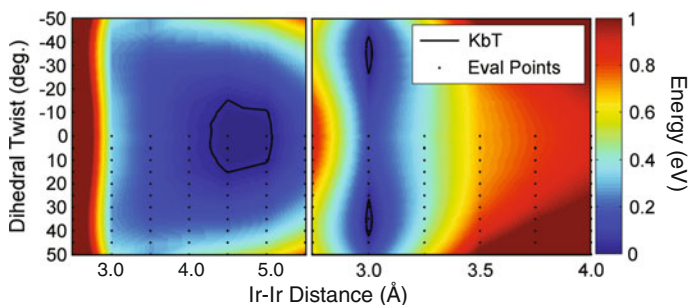


Fig. 2.6 Ground- and excited-state energies (*left* and *right*, respectively) of the 3 : 1 isomer of $[\text{Ir}_2(\text{dimen})_4]^{2+}$, evaluated in vacuum as a function of Ir-Ir distance and dihedral angle of the opposing ligands. While the GS potential is very shallow, there is an indication of a minimum around 3 Å and 35°. Reproduced with permission from van Driel and Nielsen [17]

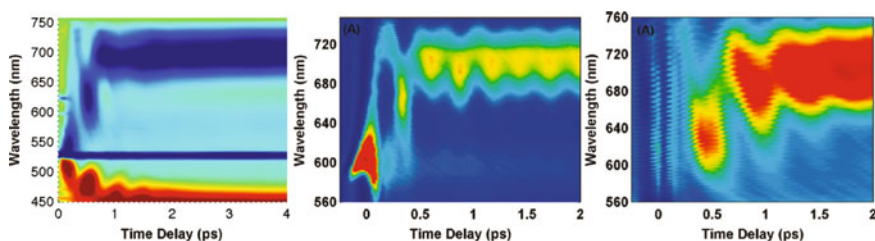


Fig. 2.7 Ultrafast Time-resolved Spectroscopy studies of $[\text{Ir}_2(\text{dimen})_4]^{2+}$ in acetonitrile solution. *Left* Transient absorption, pumped at 527 nm [12]. *Middle* Stimulated Emission from pumping at 590 (short and twisted) [19]. *Right* Stimulated Emission pumped at 477 nm (long-eclipsed). Restating the article, the electronic decay of the signal was fitted to a multiexponential decay. The residual between this decay and the signal was Fourier transformed for time delays after $t \geq 0.5$ ps to get a vibrational frequency of 75 cm^{-1}

eclipsed structure (the 475 nm peak), only one mode is observed, with a frequency of 75 cm^{-1} , assigned to the Ir-Ir pinch.

These assignments of the normal mode vibrations can be significantly expanded upon, and more information of the underlying structural dynamics can be revealed through simulations of this system, when anchored in the experimental results. Furthermore, the experiments must of course be carried out in solution, but it is difficult to experimentally distinguish between solvation-induced effects and features purely from internally in the molecule. Simulations can help establish the role of the solvent, and the interplay between the complex and its environment. All this information can then again be used in the interpretation of data gathered at the Linac Coherent Light Source (LCLS) XFEL, where we have attempted to directly probe these coherent motions.

To our knowledge, no attempts (including our own) to freely relax the geometry of the molecule into the short conformer has proved successful, when using DFT methods. This is why we in Chap. 6 focus on simulating the long-eclipsed isomer.

2.3 $[\text{Fe}(\text{bpy})_3]^{2+}$

The $[\text{Fe}(\text{bpy})_3]^{2+}$ - and related- complexes has a long history of interest and controversy regarding the spin dynamics expressed in them [25–32]. As an example, previous work [30] has mapped the excitation-relaxation cascade devoid of transitions to a triplet intermediate, but recent work by collaborators [25] found the relaxation spin dynamics cascade shown in Fig. 2.8, right. Since the relevant occupied orbitals of the states labeled ^3T and $^5\text{T}_2$ are antibonding [28], the excitation is accompanied by a Fe–N bond elongation. These dynamics are relevant due to the structure-spin-state interplay, and their effect on the lifetimes of each state. Understanding this interplay, and obtaining control of the lifetimes is important since Fe-complexes like $[\text{Fe}(\text{bpy})_3]^{2+}$ could hopefully be able to replace their efficient Ru-counterparts in Dye-Sensitized Solar Cell (DSSC)-technologies (see Fig. 2.9 for a schematic of how a DSSC functions). $[\text{Ru}(\text{bpy})_3]^{2+}$, described in more detail in the next section, is known for its efficiency within photoconversion [33–36], but Ru is a low-abundance metal, so replacing it with Fe while retaining the efficiency could make a significant impact for light-harvesting applications. However, the lifetime of the Metal-to-Ligand Charge Transfer (MLCT) state is greatly reduced for the Fe counterparts [31, 32]. This is problematic, because the longer lived this state is, the more likely it will be for the charge to enter in an electrical circuit. Nevertheless, studies on Ru-complexes with only slightly changed geometries can affect the lifetime by orders of magnitude [37], and similar Fe-based complexes have shown 100-fold increase in the lifetime, compared to $[\text{Fe}(\text{bpy})_3]^{2+}$ [38].

$[\text{Fe}(\text{bpy})_3]^{2+}$ has simultaneously obtained the role of a *photophysical factotum* for benchmarking novel tools, techniques, methods, and machinery [25, 31, 32], [VII, I]. This is also the role it will play in this work. The consequences of electronically

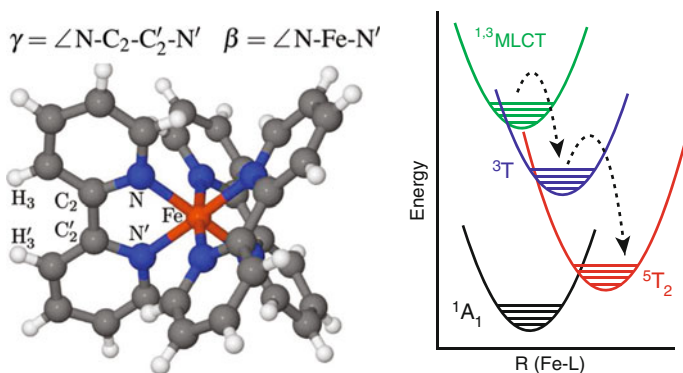


Fig. 2.8 *Left* A Ball-and-stick model of the $[\text{Fe}(\text{bpy})_3]^{2+}$ complex, taken from Daku et al., using their definitions of angles important for the overall structure of the complex [24]. *Right* Schematic drawing of the states believed to take part in the spin crossover dynamics, as represented in [25], where changes in spin induces changes in Fe-ligand bond length

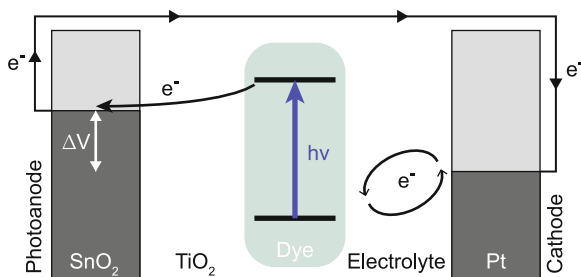


Fig. 2.9 The basic principle of a Dye-Sensitized Solar Cell (DSSC). The semiconductor material is photosensitized by a dye adsorbed to the surface, which, when photoexcited, injects an electron into it, into the anode. This oxidizes the dye, which then in turn oxidizes the electrolyte mediator, which is then reduced by the cathode

exciting $[\text{Fe}(\text{bpy})_3]^{2+}$ has already been simulated in the inspiring work by Daku and Hauser [24], where the authors use *ab initio* MD, an electronic structure-dynamics method akin to Direct Dynamics used in the main part of this project, to show that the Fe–N bond expansion results in further structural deformations. The changes in both electronic and geometric structure causes a change in solvent orientation, and ultimately leads to an expulsion of two water molecules from the first solvation shell. As such, the system of solvated $[\text{Fe}(\text{bpy})_3]^{2+}$ exhibits both non-specific, and specific solvation dynamics.

Chapter 4 deals with how solvent-contributions to the scattering signal are simulated, and presents a ‘first approximation’-model, based on sampling solvent configurations of fixed-structure solutes using classical MD, and calculating the scattering. This is computationally less demanding than the QM/MM MD, but also has limitations with regards to the level of intricacy of the systems and processes it can describe.

2.4 $[(\text{bpy})_2\text{Ru}^{\text{II}}(\text{tpphz})\text{Co}^{\text{III}}(\text{bpy})_2]^{5+}$: Ru=Co

The $[(\text{bpy})_2\text{Ru}^{\text{II}}(\text{tpphz})\text{Co}^{\text{III}}(\text{bpy})_2]^{5+}$ (Ru=Co, for brevity) system is a member of a larger group of heteronuclear, charge-transfer model complexes. The system can be thought of as a $[\text{Ru}(\text{bpy})_3]^{2+}$ complex,² linked to a $[\text{Co}(\text{bpy})_3]^{3+}$ complex by an aromatic bridge (Fig. 2.10). The $[\text{Ru}(\text{bpy})_3]^{2+}$ end is very well-studied [40, 41], in part due to its photo-sensitizing/-conversion abilities [33–36], related to its MLCT-state following electronic excitation [40, 42–48]. The singlet $^1\text{MLCT}$ undergoes efficient ISC to a triplet $^3\text{MLCT}$ [44, 46], with a lifetime of 600 ns [45].

It has been known for a long time that the metal-ligand bond lengths of Co are changed by 10–45 pm upon ET [49]. Like with $[\text{Fe}(\text{bpy})_3]^{2+}$, population of the

²Structurally similar to the Fe variant from the last section.

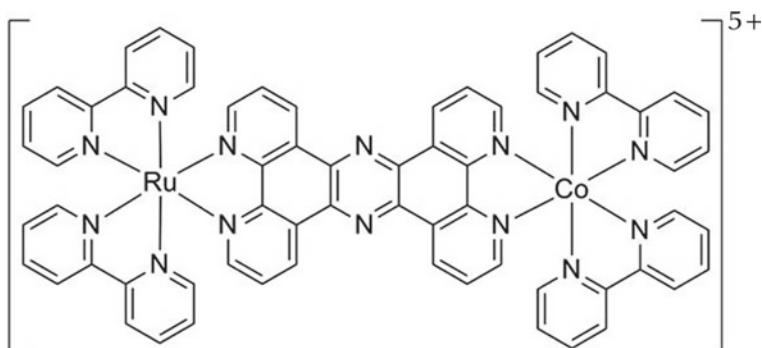


Fig. 2.10 The $[(bpy)_2Ru^{II}(tpphz)Co^{III}(bpy)_2]^{5+}$ complex, where (tpphz) = tetrapyrido (3,2-a:2'3'-c:3'',2''-h::2''',3''' - j) phenazine [39]. For brevity, the molecule is called Ru=Co throughout this work

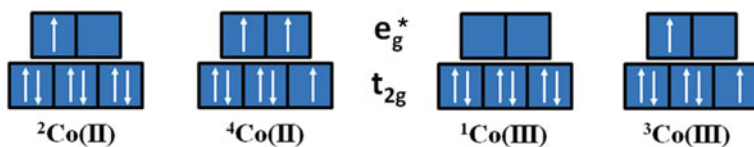


Fig. 2.11 The various electronic valence configurations of Co-systems for their common multiplicities and oxidation states

antibonding e_g^* orbitals (see Fig. 2.11), affects the bond length. We recently experimentally observed that photoexcitation of Ru=Co induced ET from the Ru centre to the Co site, This was accompanied by a spin-flip of 2Co to 4Co , and an on average 0.2 Å elongation of the Co-N bonds in Ru=Co [V]. The spin state of the entire complex when the Co-centre is a doublet, or quartet, is denominated Low Spin (LS), or High Spin (HS), respectively.

The bond-elongation is effectively a relocation of the nitrogen atoms in the Co-centre. Therefore, the reorganization energy—both from solvent- and the intramolecular—will play a large role in the final ET rates of these compounds. These ET rates (both from Ru to Co and the return ET) have been studied for similar complexes [39, 50], where the later article introduces an ISC step to a $^4Co(II)$ state in the ET mechanism, and shows that the return ET in the Ru(III) $\rightarrow$ Ru(II) recovery in the complexes is faster for $^2Co(II)$ ions than for $^4Co(II)$, due to a suspected smaller intramolecular reorganization for the doublet pathway [39].

Recently, Co(II)/Co(III) have been proposed as an alternative to the more volatile I_3^-/I^- redox mediators [51, 52] for DSSC. Unfortunately, the same studies have shown that the efficiency drops dramatically. In a combined computational/experimental study, Mosconi et al. [53] argued that the cause of the reduced efficiency was the possible formation of a flexible complex between the cobalt electrolyte and the dye, which brings the cobalt molecule too close to the semiconductor surface.

This allows the cobalt molecule to intercept the semiconductor-injected charges, effectively ‘short-circuiting’ the DSSC.

In any case, the relevance of these systems are not limited to solar energy conversion; another application perspective is the known (photo-)catalytic activity of cobalt containing complexes in water-splitting processes [54–56].

Apart from the already published results [V] that confirms the Co-N elongation of the final excited state: [²Ru^{III}=⁴Co^{II}], the first round of results we obtained at the Japanese XFEL SACLA further suggests an intermediate spin-state in the electronic relaxation cascade, before the final state is reached: [²Ru^{III}=²Co^{II}], [III]. The next step in the ongoing investigation, also encompassing experimental data from LCLS, will require simulations of the structural dynamics, and solvent interplay of all these three electronic configurations: the GS, the low spin ES, and the high spin ES. Therefore, Chap. 7 is dedicated to these simulations, where we attempt to achieve a clearer picture of the average solvated structures, their distributions, and how the solvent responds to the charge transfer.

2.5 Summarising the Systems

The systems studied here are interesting in their own right, some as model systems for processes with application-potential within the fields of green technologies and catalysis, others maybe as direct candidates for application in technology. However, it is through the study of the processes themselves—*exemplified* through these systems—where basic knowledge about natural phenomena—and nature itself—can be obtained. Therefore, in this work, the described complexes has been used to concretise the questions posed in the introduction further, in the following ways:

[Pt(CN)₄]^{2−}: *What are the options for treating relativistic effects in a satisfactory manner, while ending up with a computationally feasible description for the later studies?*

[Fe(bpy)₃]²⁺: *How far can we get with purely classical methods and steady-state approximations? Furthermore, how does one calculate the experimental signal from simulations?*

[Ir₂(dimen)₄]²⁺: *What dynamic modes channels the dissipation of excess excitation energy? For how long is the process coherent, and what is the cause for decoherence? What is the role of the solvent in this case?*

[(bpy)₂Ru^{II}(tpphz)Co^{III}(bpy)₂]⁵⁺: *How does the solvent affect the structure and the ISC-induced structural changes? Are the solvation effects purely non-specific, or does this complex exhibit specific solvation dynamics?*

The next part of the thesis will attempt to answer the first two set of questions, to build the foundation for using Direct Dynamics in tackling the final sets of challenges.

References

1. S. Grimme, J. Djukic, *Inorg. Chem.* **50**, 2619 (2011)
2. J.W. Schindler, R.C. Fukuda, A.W. Adamson, *J. Am. Chem. Soc.* **104**, 3596 (1982)
3. G. Gliemann, H. Yersin, *Struct. Bond.* **62**, 87 (1985)
4. P.D. Harvey, *Coord. Chem. Rev.* **219**, 17 (2001)
5. H.B. Gray, A.W. Maverick, *Science* **214**, 1201 (1981)
6. I.S. Sigal, K.R. Mann, H.B. Gray, *J. Am. Chem. Soc.* **102**, 7252 (1980)
7. V.M. Miskowski, I.S. Sigal, K.R. Mann, H.B. Gray, S.J. Milder, G.S. Hammond, P.R. Ryason, *J. Am. Chem. Soc.* **101**, 4383 (1979)
8. K.R. Mann, N.S. Lewis, V.M. Miskowski, D.K. Erwin, G.S. Hammond, H.B. Gray, *J. Am. Chem. Soc.* **99**, 5525 (1977)
9. A. Lechner, G. Gliemann, *J. Am. Chem. Soc.* **111**, 7469 (1989)
10. L. Interrante, *ACS Symposium* (American Chemical Society, Washington DC, 1974)
11. A.G. Sykes, K.R. Mann, *J. Am. Chem. Soc.* **112**, 7247 (1990)
12. T. Harlang, N. Harrit, *Spectroscopic and X-ray Structural Investigations of $[Rh_2(\text{dimen})_4]^{2+}$ and $[Ir_2(\text{dimen})_4]^{2+}$ on Pico- and Femtosecond Timescales* (Denmark, Copenhagen, 2010)
13. K.R. Mann, *Cryst. Struct. Commun.* **10**, 451 (1981)
14. M.R. Rhodes, K.R. Mann, *Inorg. Chem.* **23**, 2053 (1984)
15. M.D. Roundhill, H.B. Gray, C. Che, *Acc. Chem. Res.* **22**, 55 (1989)
16. T.B. van Driel, N. Harrit, *Time-Resolved Structural Analysis of $Rh_2(\text{dimen})_4^{2+}$ in Solution* (Denmark, Copenhagen, 2010)
17. T.B. van Driel, M.M. Nielsen, *Time-Resolved X-ray Scattering of Molecules in Solution: Approaching the Molecular Movie* (Lyngby, Denmark, 2014)
18. K. Haldrup, T. Harlang, M. Christensen, A. Dohn, T.B. van Driel, K.S. Kjær, N. Harrit, J. Vibenholt, L. Guerin, M. Wulff et al., *Inorg. Chem.* **50**, 9329 (2011)
19. R.W. Hartsock, W. Zhang, M.G. Hill, B. Sabat, K.J. Gaffney, *J. Phys. Chem. A* **115**, 2920 (2011)
20. K.R. Mann, J.G.I. Gordon, H.B. Gray, *J. Am. Chem. Soc.* **97**, 3553 (1975)
21. P. Coppens, O. Gerlits, I.I. Vorontsov, A. Kovalevsky, Y. Chen, T. Graber, M. Gembicky, I. Novozhilova, *Chem. Commun.* **19**, 2144 (2004)
22. C.L. Exstrom, D. Britton, K.R. Mann, *Inorg. Chem.* **35**, 549 (1996)
23. B.M. Hunter, R.M. Villahermosa, C.L. Exstrom, M.G. Hill, K.R. Mann, H.B. Gray, *Inorg. Chem.* **51**, 6898 (2012)
24. L.M.L. Daku, A. Hauser, *J. Phys. Chem. Lett.* **1**, 1830 (2010)
25. W. Zhang, R. Alonso-Mori, U. Bergmann, C. Bressler, M. Chollet, A. Galler, W. Gawelda, R.G. Hadt, R.W. Hartsock, T. Kroll et al., *Nature* **509**, 345 (2014)
26. C. Creutz, M. Chou, T.L. Netzel, M. Okomura, N. Sutin, *J. Am. Chem. Soc.* **102**, 1309 (1980a)
27. J.K. McCusker, K.N. Walda, R.C. Dunn, J.D. Simon, D. Magde, D.N. Hendrickson, *J. Am. Chem. Soc.* **115**, 298 (1993)
28. P. Gütllich, H.A. Goodwin, *Top. Curr. Chem.* **233**, 1 (2004)
29. W. Gawelda, A. Cannizzo, V.-T. Pham, F. van Mourik, C. Bressler, M. Chergui, *J. Am. Chem. Soc.* **129**, 8199 (2007)
30. C. Bressler, C. Milne, V.-T. Pham, A. El-Nahhas, R.M. van der Veen, W. Gawelda, S. Johnson, P. Beaud, D. Grolimund, M. Kaiser et al., *Science* **323**, 489 (2008)
31. N. Huse, H. Cho, K. Kong, L. Jamula, F.M.F. de Groot, T.K. Kim, J.K. McCusker, R.W. Schoenlein, *J. Phys. Chem. Lett.* **2**, 880 (2011)
32. H.T. Lemke, C. Bressler, L.X. Chen, D.M. Fritz, K.J. Gaffney, A. Galler, W. Gawelda, K. Haldrup, R.W. Hartsock, H. Ihee et al., *J. Phys. Chem. A* **117**, 735 (2013)
33. K. Kalyanasundaram, *Coord. Chem. Rev.* **46**, 159 (1982)
34. K. Kalyanasundaram, M. Grätzel, *Coord. Chem. Rev.* **77**, 347 (1998)
35. B. O'Reagan, M. Grätzel, *Nature* **353**, 737 (1991)
36. C. Creutz, M. Chou, T. L. Netzel, M. Okumura, N. Sutin, *J. Am. Chem. Soc.* **102**, 1309 (1980b)

37. D.G. Brown, N. Sanguatrakun, B. Schulze, U.S. Schubert, C.P. Berlinguette, *J. Am. Chem. Soc.* **134**, 12354 (2012)
38. L.A. Fredin, M. Pápai, E. Rozsályi, G. Vankó, K. Wärnmark, V. Sundström, P. Persson, *J. Phys. Chem. Lett.* **5**, 2066 (2014)
39. H. Torieda, K. Nozaki, A. Yoshimura, T. Ohno, *J. Phys. Chem. A* **108**, 4819 (2004)
40. A.T. Yeh, C.V. Shank, J.K. McCusker, *Science* **289**, 935 (2000)
41. A. Juris, V. Balzani, *Coord. Chem. Rev.* **84**, 85 (1988)
42. N.H. Damrauer, G. Cerullo, A.V. Yeh, T.R. Boussie, C.V. Shank, J.K. McCusker, *Science* **275**, 54 (1997)
43. K.D. Demadis, C.M. Hartshorn, T.J. Meyer, *Chem. Rev.* **101**, 2655 (2001)
44. A.C. Basikhuttan, M. Suzuki, S. Nakashima, T. Okada, *J. Am. Chem. Soc.* **124**, 8398 (2002)
45. A.N. Tarnovsky, W. Gawelda, M. Johnson, C. Bressler, M. Chergui, *J. Phys. Chem. B* **110**, 26597 (2006)
46. A. Cannizzo, M. Chergui, C. Bressler, W. Gawelda, G. Zgrablic, F. van Mourik, *Angewandte Chemie* **45**, 3174 (2006)
47. M. Benfatto, S.D. Longa, K. Hatada, K. Hayakawa, W. Gawelda, C. Bressler, M. Chergui, *J. Phys. Chem. B* **110**, 14035 (2006)
48. D.A. Hoff, R. Silva, L.G.C. Rego, *J. Phys. Chem. C* **115**, 15617 (2011)
49. K.H. Schmidt, A. Müller, *Inorg. Chem.* **14**, 2183 (1975)
50. H. Torieda, K. Nozaki, A. Yoshimura, T. Ohno, *J. Phys. Chem. A* **106**, 11034 (2002)
51. Y. Liu, J.R. Jennings, Y. Huang, Q. Wang, S.M. Zakeeruddin, M. Grätzel, *J. Phys. Chem. C* **114**, 18847 (2011)
52. H. Nusbaumer, S.M. Zakeeruddin, J.-E. Moser, M. Grätzel, *Chem. Eur. J.* **9**, 3756–3763 (2003)
53. E. Mosconi, J.-H. Yum, F. Kessler, C.J.G. García, C. Zuccaccia, A. Cinti, M.K. Nazeeruddin, M. Grätzel, F.D. Angelis, *J. Am. Chem. Soc.* **134**, 19438 (2012)
54. V. Artero, M. Chavarot-Kerlidou, M. Fontecave, *Angewandte Chemie* **50**, 7238 (2011)
55. D. Shevchenko, M.F. Anderlund, A. Thapper, S. Styring, *Energy Environ. Sci.* **4**, 1284 (2011)
56. D. Hong, J. Jung, J. Park, Y. Yamada, T. Suenobu, Y. Lee, W. Nam, S. Fukuzumi, *Energy Environ. Sci.* **5**, 7606 (2012)

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