rounded by a polarizable continuum are in progress. For more details, see [4].

6. Modelling the Coordination Sphere of Lanthanides

Hydrated lanthanides(III) ions Ln$^{3+}$(H$_2$O)$_x$ (x = 8, 9) with Ln$^{3+}$ = Gd$^{3+}$, Sm$^{3+}$ and Dy$^{3+}$ are currently studied using DFT and the results are in agreement with similar Hartree-Fock results [10]. The calculations are related to experimental results in order to elucidate the hydration behavior of lanthanide(III) ions. It has been established that the coordination number of the lanthanides changes in the middle of the serie: Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$ [11].

The energies between different structures (i.e., cube, square antiprism, and dodecahedron) of the first solvation sphere are compared. The bond energy as a function of ion-water distance obtained in the local density approximation (LDA) is presented in Fig. 3. It is seen that the square antiprism has energetically the most favorable coordination geometry. This result is in good agreement with MD simulations of NMR data obtained by Foglia, Helm, Kowall and Merbach in Lausanne [12].

The charge polarization of the coordinated water molecules at different geometries is also being studied in order to design better interaction potentials to be used in molecular dynamics (MD) simulations of such systems. More results will be presented at the fall session 1994 of the New Swiss Chemical Society.

This work is part of project 20-34067.92 of the Swiss National Science Foundation.

Received: July 6, 1994

1] G. Vignale, M. Rasolt, Phys. Rev. Lett. 1987, 59, 2365; Phys. Rev. B 1988, 37, 10685.
2] C. Daul, Int. J. Quant. Chem. 1994, 49.
3] E. Deiss, O. Haas, C. Daul. J. Electroanal. Chem. 1992, 337, 299.
4] C. Daul, A. Goursot, P.-Y. Morgantini, J. Weber, Int. J. Quant. Chem. 1990, 28, 623; Horizons Nr. 12. October 1991 p. 4, published by the Swiss National Sciences Foundation.
5] Density Functional Methods in Chemistry, Eds. Jan K. Lohbanowski and Jan Andzelm, Springer Verlag, New York, 1990: Density Functional Theory of Atoms and Molecules, Eds. R.G. Parr and W. Yung, Oxford University Press, New York, 1989.
6] C. Daul, H. Gideln, J. Weber. J. Chem. Phys. 1993, 98, 4023; C. Daul, E.J. Baerends, P. Vernoijs, Inorg. Chem. 1994, in press; K. Bellaflrouh, C. Daul, F. Gilardon, J. Weber, Theor. Chim. Acta, in press.
7] W.J. Albery, A. R. Hillman, R. Soc. Chem. Ann. Rep. C 1981, 78, 377.
8] C.P. Andreieux, J.M. Saveant, J. Electroanal. Chem. 1982, 142, 1.
9] C. Daul, O. Haas, Electrochem. Sens. Anal. 1986, 25, 277.
10] S. Hengrasmee, M. M. Probst, Z. Naturforsch., A 1991, 46, 117.
11] D.H. Powell, A.E. Merbach, submitted for publication.
12] Lothar Helm, private communication.

Molecular Devices Based on Bridged Transition-Metal Complexes

Peter Belser*

Abstract. The article from A. von Zelewsky, in this issue gives a broad survey about some scientific activities at the Institute of Inorganic Chemistry of the University of Fribourg. The present contribution will be rather focused on a detailed study of the photophysical and photochemical behavior of a molecular device that is capable to undergo energy- and/or electron-transfer processes.

1. Introduction

The scientific field of supramolecular chemistry [1-3] means that such complicated systems have the potential to achieve much more capabilities than simple molecules. A simple molecule has only the possibility to participate in chemical reactions. Supramolecular systems can perform functions and have, therefore, the potential to behave as molecular devices. Photochemical molecular devices are those that use light to achieve their functions.

The development of photochemical molecular devices for different applications (e.g., artificial photosynthesis and information processing) [4] is based on the design of molecular species in which photoinduced energy- or electron-transfer processes can take place over a long distance with high efficiency.

To elucidate the role played by various factors in determining the occurrence of photoinuced energy- and electron-transfer processes, we have designed and synthesized different bridged polynuclear metal complexes [5][6]. The requirements for the construction of such a molecular device for charge separation are (Fig. 1):

---

*Correspondence: Prof. Dr. P. Belser
Institute of Inorganic Chemistry
University of Fribourg, Pérolles
CH-1700 Fribourg
rounded by a polarizable continuum are in progress. For more details, see [4].

6. Modelling the Coordination Sphere of Lanthanides

Hydrated lanthanides(III) ions LN³⁺(H₂O)₆ (x = 8, 9) with Ln= Gd³⁺, Sm³⁺ and Dy³⁺ are currently studied using DFT and the results are in agreement with similar Hartree-Fock results [10]. The calculations are related to experimental results in order to elucidate the hydration behavior of lanthanide(III) ions. It has been established that the coordination number of the lanthanides changes in the middle of the serie: Nd³⁺, Sm³⁺, Eu³⁺ [11].

The energies between different structures (i.e., cube, square antiprism, and dodecahedron) of the first solvation sphere are compared. The bond energy as a function of ion-water distance obtained in the local density approximation (LDA) is presented in Fig. 3. It is seen that the square antiprism has energetically the most favorable coordination geometry. This result is in good agreement with MD simulations of NMR data obtained by Foglia, Helm, Kowall and Merbach in Lausanne [12].

The charge polarization of the coordinated water molecules at different geometries is also being studied in order to design better interaction potentials to be used in molecular dynamics (MD) simulations of such systems. More results will be presented at the fall session 1994 of the New Swiss Chemical Society.

This work is part of project 20-3406792 of the Swiss National Science Foundation.

Received: July 6, 1994

[1] G. Vignale, M. Rasolt, Phys. Rev. Lett. 1987, 59, 2360; Phys. Rev. B 1988, 37, 10685.
[2] C. Daul, Int. J. Quant. Chem. 1994, 49.
[3] E. Deiss, O. Haas, C. Daul, J. Electroanal. Chem. 1992, 337, 299.
[4] C. Daul, A. Goursot, P.-Y. Morgantini, J. Weber, Int. J. Quant. Chem. 1990, 28, 623; Horizons, Nr. 12, October 1991, p. 4, published by the Swiss National Science Foundation.
[5] Density Functional Methods in Chemistry, Eds. Jan K. LeBabowski and Jan Andzelm, Springer Verlag, New York, 1990: 'Density Functional Theory of Atoms and Molecules', Eds. R.G. Parr and W. Yang. Oxfords University Press, New York, 1989.
[6] C. Daul, H. Giedel, J. Weber, J. Chem. Phys. 1993, 98, 4023; C. Daul, E.J. Baerends, P. Vermeij, Inorg. Chem. 1994, in press; K. Bellafrouth, C. Daul, F. Gilardoni, J. Weber, Theor. Chim. Acta, in press.
[7] W.J. Albery, A. R. Hillman, R. Soc. Chem. Annu. Rep. C 1981, 78, 377.
[8] C.P. Andreieus, J.M. Saveane, J. Electroanal. Chem. 1982, 142, 1.
[9] C. Daul, O. Haas, Electrochem. Sens. Anal. 1986, 25, 277.
[10] S. Hencrasme, M. M. Probst, Z. Naturforsch., A 1991, 4., 117.
[11] D. H. Powell, A. E. Merbach, submitted for publication.
[12] Lothar Helm, private communication.

Molecular Devices Based on Bridged Transition-Metal Complexes

Peter Belser*

Abstract. The article from A. von Zelewsky, in this issue gives a broad survey about some scientific activities at the Institute of Inorganic Chemistry of the University of Fribourg. The present contribution will be rather focused on a detailed study of the photophysical and photochemical behavior of a molecular device that is capable to undergo energy- and/or electron-transfer processes.

1. Introduction

The scientific field of supramolecular chemistry [1–3] means that such complicated systems have the potential to achieve much more capabilities than simple molecules. A simple molecule has only the possibility to participate in chemical reactions. Supramolecular systems can perform functions and have, therefore, the potential to behave as molecular devices. Photochemical molecular devices are those that use light to achieve their functions.

The development of photochemical molecular devices for different applications (e.g., artificial photosynthesis and information processing) [4] is based on the design of molecular species in which photoinduced energy- or electron-transfer processes can take place over a long distance with high efficiency.

To elucidate the role played by various factors in determining the occurrence of photoinduced energy- and electron-transfer processes, we have designed and synthesized different bridged polynuclear metal complexes [5][6]. The requirements for the construction of such a molecular device for charge separation are (Fig. 1):

![Fig. 1. Block diagram of a molecular device that is capable for an energy-transfer process](image-url)
A molecular component that can act as an interface toward light (M₁). This component can be easily transferred to the excited state and has fully reversible redox behavior. Further requirements in practical systems are: a) stability towards thermal and photochemical decomposition reactions; b) suitable ground- and excited-state redox potentials; c) high efficiency of population of the reactive excited state; d) sufficiently long lifetime of the reactive excited state, and e) appropriate kinetic factors for ground- and excited-state electron-transfer reactions. An excellent candidate for such a molecular component is \([\text{Os}(\text{bpy})_2]^2+\) (bpy = 2,2'-bipyridine) [7].

- The second molecular component (M₂) is a species capable of undergoing a one-electron reversible redox reaction. Other requirements are: a) suitable redox potentials; b) thermal and photochemical stability in both of the oxidation states; c) good quenching ability for electron transfer (or energy transfer), and d) suitable kinetic factors for electron-transfer reactions. In our study, we have used \([\text{Os}(\text{bpy})_2]^2+\)-type metal complexes as the acceptor part of the molecular device.

- We need also a connecting component (rigid bridge), which can be used to link together the two above mentioned active components in the desired spatial arrangement. In the present article, some of such spacers, used in our laboratories, are depicted.

As mentioned before an important requirement for the usefulness of such supramolecular devices is their degree of spatial organization. Species in which the active components are linked by non-rigid spacers are of little practical interest, because practical devices require vectorial energy or electron transfer over long distances.

\(\text{Ru}^\text{II}\) and \(\text{Os}^\text{II}\) polypyridine-type complexes exhibit suitable excited-state and redox properties to play the role of building blocks for the construction of photoactive supramolecular systems [8]. For synthetic reasons, it is difficult to assemble these metal-containing building blocks with the appropriate bridges to build up extended and rigid structures.

We have now synthesized a series of dinuclear metal complexes that are connected by the novel bridging ligand 1,4-bis\{[2,2'-bipyridine-5-yl]ethyl|\)bicyclo[2.2.2]octane (bpy-S-bpy and the corresponding metal complexes \(\text{M}_1\)-S-\(\text{M}_2\); see Fig. 2). The ligand synthesis is depicted in the Scheme.

The two bpy units are separated by a 1.0 nm long spacer (S) which contains a rigid bicyclooctane component and two linear acetylene-type units. In the dinuclear species, the distance between the two metal centers (ca. 1.7 nm; Fig. 3) changes only slightly on rotation around the single bonds connecting the bridge to the bpy units. These rod-like, nanoscale supramolecular metal complexes exhibit interesting excited-state and redox properties.

The novel ligand bpy-S-bpy has been synthesized [5][6] through the corresponding bis-alkene 3. The phosphonate 1 was obtained by an Arbusov rearrangement from 3-(bromomethyl)-2,2'-bipyridine [9]. Bicyclo[2.2.2]octane-1,4-dicarboxaldehyde (2) [10] and 1 were coupled by a Wadsworth-Emmons reaction to give the \((E,E)\)-diene 3. Bromination at room temperature gave 4 and subsequent dehydrobromination by refluxing with excess KOH yielded the diyne bpy-S-bpy 5, which was isolated as a colorless, crystalline solid. An X-ray structure of the bridging ligand bpy-S-bpy shows clearly the rod-like structure (Fig. 4).

---

**Fig. 2.** Schematic representation of the bridging ligand bpy-S-bpy and of its mononuclear and dinuclear complexes

**Fig. 3.** Conformational arrangement of the dinuclear metal complexes

The average value is 1.7 nm
Using this bridging ligand, we have synthesized the mononuclear metal complexes [(bpy)$_2$Ru(bpy-S-bpy)]$^{2+}$ (Ru-S); [(bpy)$_2$Os(bpy-S-bpy)]$^{2+}$ (Os-S) and the dinuclear complexes [(bpy)$_2$Ru(bpy-S-bpy)Ru(bpy)$_2$]$^{2+}$ (Ru-S-Ru); [(bpy)$_2$Os(bpy-S-bpy)Os(bpy)$_2$]$^{2+}$ (Os-S-Os), and [(bpy)$_2$Ru(bpy-S-bpy)Os(bpy)$_2$]$^{2+}$ (Ru-S-Os) as PF$_6$-salts [8]. We have characterized the compounds by elemental analysis, FAB mass spectrometry, $^1$H-NMR, UV/VIS spectroscopy and determined their spectroscopic, luminescence, and electrochemical properties. We have also investigated the quenching of the luminescence of the Ru-based unit by the Os-based unit in the heterometallic species [(bpy)$_2$Ru(bpy-S-bpy)Os(bpy)$_2$]$^{2+}$. The rate constant for the photoinduced energy-transfer process was measured and compared with the current theories.

2. Discussion and Results

The absorption spectra in the visible region and the luminescence spectra of the binuclear compounds are displayed in Fig 5. Two isosbestic points are present at 416 and 466 nm. Excitation at one of these wavelengths on the Ru-S-Os compound (as was the case for the luminescence experiments), each metal-based unit absorbs 50% of the incident light. In oligonuclear complexes electronic interaction between the mononuclear components may range from very strong to very weak (with almost equal properties for separated and bridged units) depending on the nature of the bridge. In the case of the novel bridge bpy-S-bpy, we can notice (Table) that the first oxidation potential, the first reduction potential, the absorption maxima, and all the luminescence properties are almost identical for Ru-S, Os-S, Ru-S-Ru, and Os-S-Os. This suggests little or a very weak electronic interaction between the metal-containing units in the dinuclear compounds.

In the dinuclear heterometallic species Ru-S-Os, the quantum yield of the Ru-based luminescence is ca. ten times smaller than those of the reference compounds Ru-S and Ru-S-Ru, whereas the quantum yield of the Os-based luminescence is about the same as that observed for the reference compounds Os-S and Os-S-Os.

The Ru-based luminescence intensity of a 1:1 mixture of Ru-S-Ru and Os-S-Os in MeCN solutions is 50% of an isoabsorptive (at the 466 nm isosbestic point) Ru-S-Ru solution, indicating that intermolecular quenching does not occur under the experimental conditions used. Therefore, the results demonstrate that in Ru-S-Os an intramolecular energy-transfer process takes place, which quenches the luminescent excited state of the Ru-based unit and sensitizes the luminescent excited state of the Os-based unite one. This is confirmed by the decrease in the excited state lifetime of the Ru-based unit (from 231 ns in Ru-S-Ru to 22 ns in Ru-S-Os) and by the rise time (21 ns) observed for the development of the luminescence of the Os-based unit.
Table. Spectroscopic and Electrochemical Data of the Ru and Os Complexes. The data are measured in acetonitrile solutions. For comparison purposes the 'parent' [Ru(bpy)$_3$]$^{2+}$ and [Os(bpy)$_3$]$^{2+}$ are also shown. Further informations about the experimental conditions are given in [3].

|        | Absorption $\lambda_{\text{max}}$ [nm] | Luminescence $\tau$ [ns] | Electrochemistry $E_{1/2}$ [V] |
|--------|----------------------------------------|--------------------------|-------------------------------|
|        | $\lambda_{\text{max}}$ | $\Phi \times 10^2$ | $\lambda_{\text{max}}$ | $\Phi \times 10^2$ | Ru | Os |
| Ru-S   | 453 | 635 | 226 | 1.5 | 787 | 28 | 0.18 | 0.18 | +1.25(1) | +0.84(1) |
| Os-S   | - | 484 | - | - | 787 | 29 | 0.18 | - | +1.28(2) | +0.84(2) |
| Ru-S-Ru | 452 | 635 | 231 | 1.5 | - | - | - | - | +1.27(1) | +0.84(2) |
| Os-S-Os | 452 | 484 | sh | 638 | 22 | 0.13 | 787 | 29 | 0.18 | +1.26(1) | +0.83(1) |
|[Ru(bpy)$_3$]$^{2+}$ | 452 | - | 615 | 170 | 1.5 | - | - | - | - | - |
|[Os(bpy)$_3$]$^{2+}$ | - | 478 | - | - | 743 | 49 | 0.32 | - | - | - |

Fig. 5. Absorption and (inset) uncorrected luminescence spectra of [{(bpy)}$_2$Ru(bpy-S-bpy)Ru(bpy)}$_2]^+$ (---), [{(bpy)}$_2$Os(bpy-S-bpy)Os(bpy)}$_2]^+$ (--), and [{(bpy)}$_2$Ru(bpy-S-bpy)Os(bpy)}$_2]^+$ (-).

**3. The Rate Constant of the Energy-Transfer Process**

The rate constant for energy transfer of (Ru-S-Os) can be calculated from Eqn. 1,

$$k_{en} = \frac{1}{\tau} - \frac{1}{\tau_0} = 4.1 \times 10^7 \text{s}^{-1}$$

where $\tau$ and $\tau_0$ are the luminescence lifetime of the Ru-based component in Ru-S-Os and in the Ru-S-Ru species, respectively. Energy-transfer processes can take place by Förster-type (dipole-dipole resonance) [11] and/or Dexter-type (electron exchange) [12] mechanisms (Fig. 6).

The expected rate of energy transfer according to the Förster mechanism can be calculated on the basis of spectroscopic quantities by Eqn. 2.

$$k_{en} = 5.9 \times 10^{-25} \left( \frac{\Phi_D}{n^4 \tau_D \Phi_J} \right) \int_0^\infty F_D(\bar{v}) d\bar{v} \bar{v}^4$$

For Ru-S-Os, $\Phi_D = 0.015$, $\tau_D = 226$ ns, $r = 1.7$ nm ($n = \text{refractive index of the used solvent}$, $\bar{v} = \text{wavenumber}$, $e_\lambda = \text{molar extinction coefficient}$), and the value obtained for the overlap integral is $4.7 \times 10^{-14} \text{M}^{-1} \text{cm}^{-1}$. The calculated value obtained for $k_{en}$ (Eqn. 2, $2.4 \times 10^7 \text{s}^{-1}$) is of the same order of magnitude of the experimental value ($4.1 \times 10^7 \text{s}^{-1}$). In view of the approximations involved, it could well be that the Förster mechanism counts for the observed energy-transfer process. The possibility cannot be excluded, however, that a Dexter-type energy-transfer mechanism (Fig. 6) is also involved and plays a major role.

For an exchange energy-transfer mechanism, the rate constant in the nonadiabatic limit can be expressed as in Eqns. 3 [13] and 4 [14]. $v_{en}$ and $\Delta G_f$ can be obtained from Eqns. 4 and 5, respectively. In an absolute rate formalism $v_{en}$ can be expressed with the following factors: $v_{en} \cdot \kappa$, as where $V_n$ is the average nuclear frequency factor, $\kappa$ is the electronic transmission coefficient, and $\Delta G_f$ is the free activation energy. This last term can be expressed by the Marcus quadratic relationship (Eqn. 5), where $\lambda_{en}$ is the intrinsic barrier and $\Delta G_f$ is the standard free-energy change of the energy-transfer process.

$$v_{en} = \frac{2(H_m)^2}{h} \left( \frac{r^2}{\lambda_{en}RT} \right)^{1/2}$$

Using the reasonable assumptions [15][16] that $i)$ the free energy change can be understood as the difference between the zero-zero spectroscopic energies of the donor and acceptor excited state ($-0.33 \text{ eV}$), and $ii)$ the reorganizational
energy $\lambda_{\text{ex}}$ is equal to the spectroscopic Stokes shift [15][16] (i.e., ca. 0.2 eV) between absorption and emission of donor, the process falls in the Marcus inverted region with a value of 0.4 for the exponential term of Eqn. 3 at room temperature. Assuming $\gamma_N = 1 \times 10^{-10}$ s$^{-1}$, the experimental value $\kappa_{\text{ex}} = 4.1 \times 10^7$ s$^{-1}$ yields (Eqn. 1) a value of ca. $1 \times 10^{-5}$ for the electronic factor $\kappa$. This shows that the process is strongly nonadiabatic. From Eqn. 4, a value of 0.4 cm$^{-1}$ can thus be obtained for the through-bond electronic interaction energy $\mathcal{H}_{\text{eb}}$ between the two metal-containing units, under the assumption that the observed energy-transfer process takes place only by an exchange mechanism.

5. Conclusion and Further Developments

In conclusion, we have synthesized a rigid bist(bipyridine) bridging ligand, bpy-S-bpy, which has been used to construct rod-like dinuclear metal complexes on nanometric dimension. In spite of the long metal-metal distance (1.7 nm), in the dinuclear, heterometallic Ru-S-Os compound light excitation of the Ru-based unit is followed by a very efficient (>90%) energy-transfer process ($\kappa_{\text{ex}} = 4.1 \times 10^7$ s$^{-1}$), which causes the sensitized emission of the Os-based unit.

The new ligand might be used to build up more complicated molecular devices, which contains donor and acceptor ligands. Such types of supramolecules are capable to hold the charged separated state for a long time and open the field for chemical applications. An interesting question is the dependence of the length of the bridge on the effectiveness of the energy-electron-transfer process. To answer this question, we are preparing new bridging systems with different length of the spacer unit (Fig. 7).

Received: July 6, 1994

[1] V. Balzani, L. Moggi, F. Scandola, ‘Supramolecular Photochemistry’, Ed. V. Balzani, NATO ASI Ser. C 1987, 214, 1.
[2] J. Lehn, Angew. Chem. Int. Ed. 1990, 29, 1304.
[3] V. Balzani, F. Scandola, ‘Supramolecular Photochemistry’, Horwood, Chichester, 1991.
[4] R.A. Bissel, A.P. de Silva, H.Q.N. Gunaratne, P.L.M. Lynch, G.E.M. Maguire, K.R.A.S. Sandanayake, Chem. Soc. Rev. 1992, 27, 187.
[5] F. Vögtle, M. Frank, M. Nierer, P. Belser, A. von Zelewsky, V. Balzani, L. De Cola, L. Flamigni, Angew. Chem. Int. Ed. 1993, 32, 1643.
[6] L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, P. Belser, A. von Zelewsky, M. Frank, F. Vögtle, Inorg. Chem. 1993, 32, 5228.
[7] A. Juris, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, Coord. Chem. Rev. 1988, 84, 85.
[8] P. Belser, A. von Zelewsky, M. Frank, C. Seel, F. Vögtle, L. De Cola, F. Barigelletti, V. Balzani, J. Am. Chem. Soc. 1993, 115, 4076.
[9] J.G. Eaves, H.S. Munro, D. Parker, J. Chem. Soc., Chem. Commun. 1985, 684.
[10] K. Kumar, S.S. Wang, C.N. Sukenik, J. Org. Chem. 1984, 49, 665.
[11] T.H. Förster, Discuss. Faraday Soc. 1959, 27, 7.
[12] D.L. Dexter, J. Phys. Chem. 1953, 21, 836.
[13] V. Balzani, F. Bolletta, F. Scandola, J. Am. Chem. Soc. 1980, 102, 2552.
[14] V. Balzani, F. Scandola, J. Chem. Soc. 1983, 60, 814.
[15] C.K. Ryu, R.H. Schmehl, J. Phys. Chem. 1989, 93, 7961.
[16] N. Sutin, Acc. Chem. Res. 1982, 15, 275.