10742 *J. Am. Chem. Soc.* **2001,** *123,* 10742−10743

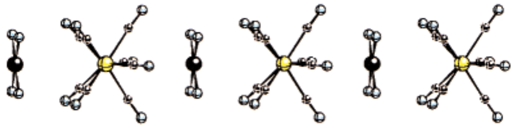
Electron Transfer in the $[Pt(NH_3)_4]^{2+}$ $[W(CN)_8]^{3-}$ Donor−Acceptor System. The Environment Effect: A Time-Dependent Density Functional Study

Vincenzo Barone,[†] Fabrizia Fabrizi de Biani,*[‡,||]
Eliseo Ruiz,*[‡] and Barbara Sieklucka[§]

Dipartimento di Chimica, Università di Napoli
Complesso Universitario Monte S.Angelo
80126 Napoli, Italy
Departament de Química Inorgànica
Universitat de Barcelona, Diagonal, 647
08028 Barcelona, Spain
Faculty of Chemistry, Jagiellonian University
Ingardena 3, 30-060 Krakow, Poland

Received February 20, 2001
Revised Manuscript Received May 24, 2001

The ability of polycyanometalate complexes to undergo charge-transfer processes is a mirror of their redox ability: indeed, they are often stable in more than one oxidation state and can easily afford donor−acceptor systems even as ion pairs.[1] This is the case for the $\{[Pt^{II}(NH_3)_4]^{2+};[W^{V}(CN)_8]^{3-}\}$ ion pair in the double salt $[Pt^{II}(NH_3)_4]_2[W^{V}(CN)_8][NO_3]\cdot 2H_2O$ (**1**).[1] In this compound chains of $\{Pt^{II}-W^{V}\}$ pairs can be identified. In the chain, the square planar $[Pt(NH_3)_4]^{2+}$ cations face the square antiprismatic $[W(CN)_8]^{3-}$ anion, alternating staggered and eclipsed conformations.



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By mixing the colorless solutions of $[W(CN)_8]^{3-}$ and $[Pt(NH_3)_4]^{2+}$ an intense orange color appears, which disappears again on dilution. The spectra of the concentrated mixture in solution and of the solid salt show a broad absorbance with two overlapping bands at 430 and 485 nm. In a previous work the band at 430 nm was ascribed to $[W^{IV}(CN)_8]^{4-}$ impureness, while the band at 485 nm was interpreted as the sign of the electron-transfer transition $\{Pt^{II}; W^{V}\} \rightarrow \{Pt^{III}; W^{IV}\}$.[1]

To elucidate the mechanism of the observed electron transfer we undertook a series of quantum mechanical calculations on the system. The computational method was based on the use of the B3LYP hybrid functional[2] and the TDDFT algorithm implemented in the Gaussian98 package.[3] Solvent shifts of excitation bands were evaluated by a recent nonequilibrium implementation[4,5] of the polarizable continuum model (in its conductor version, CPCM),[6] using a version of Gaussian98 modified by one of us. Most of the computations were carried out using Dunning/Huzinaga valence double-ζ basis set[7] for C, N, and H and Hay−Wadt effective core potentials (ECP) for W and Pt.[8] Some tests were also done employing the Stoll−Preuss ECP's[9] for these latter atoms.

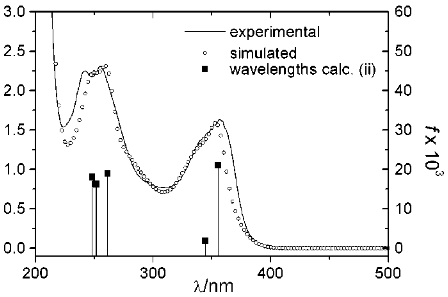

Figure 1. Experimental spectrum in water and calculated transitions of $[W^{V}(CN)_8]^{3-}$ (case ii).

As a first step, we performed the calculations on the two separate moieties: $[Pt(NH_3)_4]^{2+}$ and $[W(CN)_8]^{3-}$. For these two models we performed TDDFT calculations for (i) the experimental coordinates, (ii) a symmetric model with averaged experimental bond lengths, (iii) the geometry optimized in vacuo, (iv) the structure issuing from full geometry optimization in aqueous solution using the PCM. Only for the calculation (i) both Stoll−Preuss and Hay−Wadt ECP's have been used. We found a linear relationship (with slope ≈ 1) between both the wavelengths and the oscillator strengths (*f*) calculated with the different basis sets.

The spectrum of $[Pt(NH_3)_4]^{2+}$ in water has a dominant, very strong, absorption at 197 nm.[10] This has been ascribed to a d → p transition.[10] Our calculations provided 20 closely grouped transitions in the range 160−300 nm, most of them having a vanishing *f* value, but for the strongest absorption reported in Table 1 for models (i−iv). The best agreement between experimental and calculated absorption is found for the solvated model (iv). This can be understood by looking at the nature of the transitions: in all cases the dominating absorption corresponds to $d_{z^2} \rightarrow p_z$ transition. To our calculations, p_z is nonbonding, and so can be considered d_{z^2}, which shows just little signs of antibonding interactions. Reasonably, the energy of these orbitals is almost unaffected by changes in the bond distances, while they are highly exposed to interaction with the solvent. Indeed, the energy of both is raised by the interaction with the solvent, but d_{z^2} is more destabilized than p_z, causing the calculated red-shift. Significantly, this is the same effect observed upon the interaction of $[Pt(NH_3)_4]^{2+}$ with $[W(CN)_8]^{3-}$ in the ionic pair. In conclusion, due to the square planar coordination, the UV−vis spectrum of $[Pt(NH_3)_4]^{2+}$ ion is strongly influenced by the presence of the solvent.

The spectrum of $[W(CN)_8]^{3-}$ in solution exhibits as dominant features three intense absorptions at 242, 255, and 357 nm.[11] A

[†] Università di Napoli.

[‡] Universitat de Barcelona.

[§] Jagiellonian University.

[||] Present address: Dipartimento di Chimica dell'Università di Siena, Via A. Moro, 53100, Italy.

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10.1021/ja015695y CCC: $20.00

Table 1. Calculated and Experimental Wavelengths (in nm) for $[Pt(NH_3)_4]^{2+}$ and $[W(CN)_8]^{3-}$ [a]

(i) Hay-Wadt	(i) Stoll-Preuss	(ii)	(iii)	(iv)	exptl
$[Pt(NH_3)_4]^{2+}$					
165	169	165	169	193	197vs
$[W(CN)_8]^{3-}$					
353	348	355	384, 379	384, 382	357s
349, 346, 333	344, 341, 332	344		371	340w
263, 262	260, 259	261, 251	293, 270	291, 290	255s
252, 251	249, 248	248	268	271, 268	242s

[a] (i) experimental coordinates; (ii) symmetric model; optimized geometry without (iii) and with (iv) solvent effect.

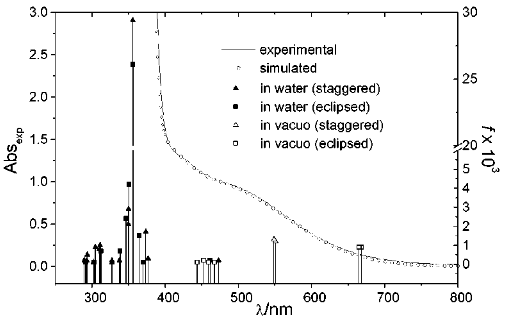

Figure 2. Experimental spectrum of the double salt **1** in water, and TDDFT calculated transitions for the $Pt^{II}-W^{V}$ ionic pair.

fourth, much weaker, band at ~340 nm is also visible as a shoulder. All of them have been attributed to MLCT processes.[11] As result of our calculations we found 20 transitions grouped in a short range (240−385 nm) and *f* vanishing for most of them. All of the calculated transitions are indeed LMCT, involving the hopping of a β electron from the filled π orbitals of the ligands to the empty tungsten d_{z^2} β orbital, which is the β LUMO. The calculated wavelengths (with $f \neq 0$) closer to the experimental ones are obtained with model (ii) and (i) (see Table 1), while in Figure 1 we show the comparison with the experimental spectrum. Noticeably, this time the agreement between calculated and experimental absorptions strongly depends on bond lengths, while solvent shifts are negligible. This behavior is not unexpected: in fact in the present case all of the absorptions involve transitions from *bonding* CN orbitals to a *nonbonding* W orbital. The minor influence of the solvent on the wavelength is due to the fact that all of the orbitals are rigidly shifted by interaction with it.

Confident on the reliability of the method, we undertook TDDFT calculations on the $Pt^{II}-W^{V}$ ionic pair for both the staggered and the eclipsed conformations, using the experimental coordinates, (i) without solvent effect, (ii) in the presence of water (see Figure 2). We calculated that in water the staggered conformation is only 1 kcal/mol more stable than the eclipsed one. We then assumed that both the conformations are present in solutions and contribute to the spectrum. Due to their poor reliability, wavelengths calculated in vacuo are not shown in Table 2, where instead the first four absorptions obtained in water are indicated. Higher energy absorptions are not reported, since there are not experimental data to compare: indeed, the strong absorption below 350 nm in the spectrum does not allow assigning the bands.

As it is shown in Figure 2, in this case the solvent effect has been found to be dramatic. Indeed, as a result of the introduction of the solvent in the calculation we obtain much more than a simple shift of the wavelengths, the main result being, in effect, the complete change of the nature of the transitions. Indeed, according to the results of the calculations which do not include solvent, *all* of the transitions are intermolecular electron transfer *from* $[W^{V}(CN)_8]^{3-}$ *to* $[Pt^{II}(NH_3)_4]^{2+}$, which would give rise formally to $[W^{VI}(CN)_8]^{2-}$ and $[Pt^{I}(NH_3)_4]^{+}$ excited states. Also, in this case, the energy of Pt d_{z^2} orbital is extremely low with respect to W d_{z^2}; therefore, the Pt d_{z^2} → W d_{z^2} transition would have a wavelength lower by far than 485 nm. A very low-energy transition from W $d_{z^2}$to Pt $d_{x^2-y^2}$ was calculated with both the basis sets (>1700 nm for the eclipsed conformation and >1100 nm for the staggered one). This latter transition, as well as all of the higher-energy ones, involves the hopping of α electrons. Inclusion of solvent effects in the TDDFT computations has a dramatic effect, leading to a spectrum in remarkable agreement with the experimental one. This is evidenced by the very good quality of the simulated spectrum in Figure 2. The nature of the transitions also agrees with the hypothesized one. Indeed, for both the staggered and eclipsed conformation, we calculated a first absorption at 477 and 462 nm, respectively, which corresponds to the foreseen Pt d_{z^2} → W d_{z^2} transition. The following absorption at 430 (*388*) nm, which was previously ascribed[1] to $[W^{IV}(CN)_8]$,$^{4-}$ also involves Pt d → W d_{z^2}. Finally, a very strong absorption is calculated at 356 nm for the eclipsed conformation and at 357 nm for the staggered one; this corresponds to the same LMCT found for $[W(CN)_8]^{3-}$ and then is not affected by the conformation of ionic pair. As a further difference with case (i) all of the transitions now involves hopping of β electrons.

Table 2. Calculated and Experimental Wavelengths (in nm) for $Pt^{II}-W^{V}$ Ionic Pair, Including Solvent Effect

staggered	eclipsed	exptl[a]
477	462	485[b]*452*[c]
383, 379	370, 365	430[b]*388*[c]
357	356	*d 383*[c]

[a] The wavelengths obtained by fitting the experimental spectrum with three Gaussian curves are indicated in italics. [b] Experimental peak value. [c] Centre of the Gaussian curve used in the fitting of the experimental spectrum. [d] Not clearly identifiable in the experimental spectrum, very strong absorption.

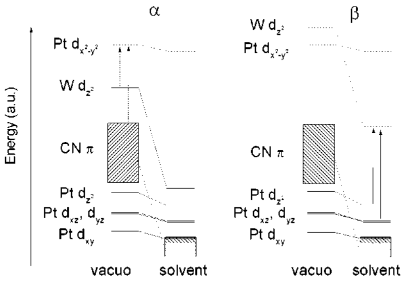

Figure 3. Solvent effect on the energies of α and β frontier orbitals of $[W(CN)_8]^{3-}$ and $[Pt(NH_3)_4]^{2+}$ in **1**. The arrows indicate the electron-transfer transitions in vacuo (dotted) and with solvent (solid).

The effect of the solvent on the orbitals is resumed in Figure 3. The W d_{z^2} and CN π orbitals of $[W^{V}(CN)_8]^{3-}$ are stabilized, while there is only a minor effect on the d orbitals of $[Pt^{II}(NH_3)_4]^{2+}$. Actually, both solvent and interaction with $[W^{V}(CN)_8]^{3-}$ destabilize Pt d orbitals, but it seems that the presence of $[W^{V}(CN)_8]^{3-}$ protect Pt from the solvent interaction. These results support the reliability of including solvent effects in TDFFT calculations, as it would be confidently confirmed by further related works.

Acknowledgment. F.F.deB. thanks the *Access to Research Infrastructure Action of the Improving Human Potential Programme* of the EC, for a grant to visit CESCA−CEPBA. Our work was supported by DGES (PB98-1166-C02-01) and CIRIT (SGR99-0046).

JA015695Y

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