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An Investigation of the Reactivity of [(diimine)(dithiolato)M] Complexes Using the Fukui Functions Concept

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Fukui functions are widely used when investigating the reactivity of organic molecules, but rarely with metal complexes. Here, we investigate the reactivity of [(diimine)(dithiolato)M] complexes with different types of reagents and upon oxidation employing this concept. Mixed-ligand complexes of this type have a peculiar electronic description due to the mixed-metal-ligand-to-ligand charge-transfer band, which is why they are considered as very promising candidates for non-linear optical (NLO) materials and molecular photochemical devices (MPD). As a result, their reactivity is of crucial importance for their potential applications. The obtained results of f^+ and f^- for the neutral [(diimine)(dithiolato)M] complexes (M = Pd, Ni and Pt) not only predict that the sulfur atom is the preferable active site for electrophilic attack but also reveal the different tunability of these complexes when they are subjected to an oxidation process, in agreement with experimental results. Under the framework of the Fukui indices we also provide an alternative explanation for crystal packing that could find widespread application.

1. Introduction

The concept of reactivity is a milestone in the investigation of chemical phenomena. Electron density plays a fundamental role in understanding chemical reactivity as it explains the attack of reagent on the basis of electrostatic interactions. However, it seems that things are not as simple as that as electron density by itself does not provide an answer to every question that arises. The reason for this is the influence of the approaching reagent. Small changes in the electron-density distribution and how susceptible this is to these changes are also of importance. In recent years, much attention has been paid to the insights that density functional theory (DFT) can give into chemical reactivity. Global reactivity parameters such as electronegativity (χ), hardness (η) and the electrophilicity index (ω), accompanied by local indices like the local softness and the Fukui function [$f(\mathbf{r})$], have been introduced in the chemical literature[1–3] and have eventually obtained legitimacy within DFT.[4] The latter was proposed by Parr and Yang[5–8] and represents one of the most effective tools of conceptual DFT for the investigation of molecular reaction sites. This model is frequently employed for the interpretation of factors and trends that influence the tunability of organic molecules, but is more rarely used in the case of transition-metal complexes.[9] Here it is the main tool in our effort to gain insight into the reactivity of [(diimine)(dithiolato)M]-type complexes.

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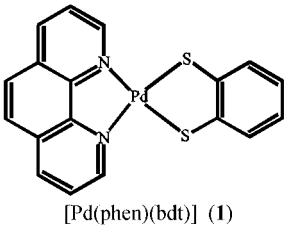
Over the last three decades [(diimine)(dithiolato)M] complexes of group VIII metals have attracted the attention of numerous researchers because of their unique properties, which include solution luminescence, solvatochromism, large molecular hyperpolarizabilities, and large excited-state oxidation potentials.[10–29] Due to these properties, they are considered as very promising candidates for non-linear optical (NLO) materials and molecular photochemical devices (MPD), especially in view of their peculiar electronic structure. This specific structure is dominated by the presence of two different unsaturated chelating ligands in the same molecule, one of which is a good π*-donor (the dithiolato ligand) and the other a good π*-acceptor (the diimine). Moreover, the intense solvatochromic band in the low-energy region of their electronic spectra is considered to involve the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the former of which is a mixture of metal and dithiolato orbitals and the latter is a π*-orbital of the diimine. This transition has been assigned as a "mixed-metal-ligand-to-ligand charge-transfer" (MMLL′CT) transition on the basis of both experimental[15] and theoretical[28,29] work. The square-planar geometry of these complexes permits one to tailor their properties for potential applications as photosensitizers or photocatalysts by designing both the diimine and dithiolato ligands appropriately.

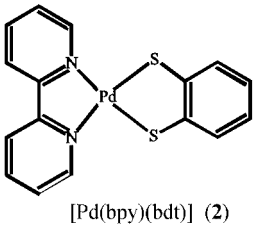
On the other hand, [(diimine)(dithiolato)M] complexes are known to be susceptible to oxidation, either photochemically or chemically induced. The first contributions to this field were provided by Vogler,[19] Srivastava,[20–22] and Schanze.[23] In 1997, Connick and Gray reported the com-

plete structural and spectroscopic characterization of the photooxidation products of [Pt(bpy)(bdt)] (bpy = 2,2′-bipyridine, bdt = 1,2-benzenedithiolate); they identified both a monosulfinate and a disulfinate complex depending on the oxidation conditions.[24] Later, Cocker and Bachman reported that the related Pd complex has a similar tunability, while the reactivity of the nickel analogue is substantially different. In the latter case they managed to isolate an octahedral disulfonate complex and a dimetallic one, suggesting that the mechanistic pathway for their production is not simply the result of differences in the electronic structure of Ni compounds. They attributed it to the ability of nickel to adopt an octahedral coordination and to the relative stability of metal–oxygen bonds for first-row transition metals.[25,26] Matsubashi and co-workers,[27] in order to increase the electrical conductivity of these compounds, have performed halogen doping experiments and proposed that partial oxidation occurred on the sulfur ligand, a suggestion that is also supported by Tang.[17] Other compounds of the same class with ligands such as bme-daco [*N*,*N*′-bis(2-sulfanylethyl)-1,5-diazacyclooctane] are known to be easily thermally or photochemically oxidized.[30] Furthermore, these complexes also undergo electrophilic substitution reactions, as recently demonstrated by Chen.[18]

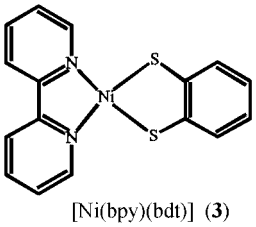
Here we have employed density functional techniques[4] in order to obtain insight into the oxidation of [(diimine)(dithiolato)M] complexes and to address the reactivity factors of these compounds through the local hard–soft acid–base principle (HSAB) and the Fukui functions.[1–8] For this purpose, the complexes [Pd(phen)(bdt)] (**1**), [Pd(bpy)(bdt)] (**2**), [Ni(bpy)(bdt)] (**3**), [Pt(bpy)(bdt)] (**4**), [Pt(bpy)(edt)] (**5**), and [Pt(bpy)(mnt)] (**6**) have been taken under consideration.



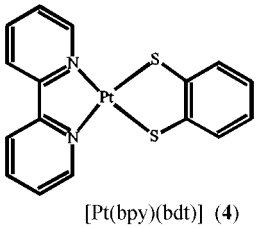
[Pd(phen)(bdt)] (**1**)



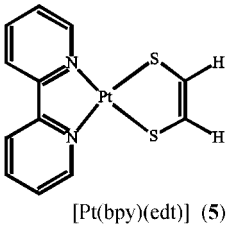
[Pd(bpy)(bdt)] (**2**)



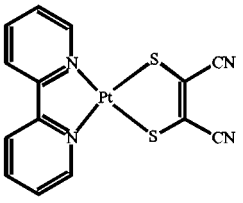
[Ni(bpy)(bdt)] (**3**)



[Pt(bpy)(bdt)] (**4**)



[Pt(bpy)(edt)] (**5**)



[Pt(bpy)(mnt)] (**6**)

The main part of this report is organized as follows: a brief description of the background theory is given in Section 2. The theoretical results are critically analyzed and compared with experimental ones in Section 3. This section is subdivided into three subsections. In Section 3.1 both theoretical and experimental structural data are compared in order to test the correctness of our calculations. The local softness parameters f^+ and f^- are compared to locate the preferable electrophilic and nucleophilic sites, respectively, in these complexes in Section 3.2. Moreover, differences in the local softness descriptors induced by changing both the central metal and the ligands are discussed and compared to experimental results. They are also used to evaluate intermolecular reactivity sequences. The importance of local softness parameters for explaining the molecular stacking in the crystal lattice is shown for the first time in Section 3.3.

2. Theoretical Background

By definition, the Fukui function is given by the functional derivative of the chemical potential with respect to a change in the external potential. Alternatively, because of the Maxwell relations, it is identical to the change in electron density upon a change in the number of electrons and can be written as

$$f(\vec{r}) = \left(\frac{\delta \mu}{\delta v(\vec{r})}\right)_N = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{v(\vec{r})} \quad (1)$$

where μ is the chemical potential, $v(\mathbf{r})$ is the external potential, and the derivative must be taken at a constant number of electrons. An important feature of the Fukui function is that it integrates to unity.

The physical meaning of $f(\mathbf{r})$ is implied directly by its definition as $[\delta\mu/\delta v(\mathbf{r})]_N$: it measures how sensitive a system's chemical potential is to an external perturbation at a particular point. Moreover, local softness is given by[31]

$$S(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial \mu}\right)_{v(\vec{r})} = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{v(\vec{r})}\left(\frac{\partial N}{\partial \mu}\right)_{v(\vec{r})} = f(\vec{r})S \quad (2)$$

From the above equation it is obvious that the Fukui function provides the same information for the system under study as the local softness, and can be used instead of it in deriving the relative site reactivity in a molecule. This implies that the regions of a molecule where the Fukui function is large are chemically softer than those with a small value of the function, and by invoking the HSAB principle in a local sense one may establish the tunability of different sites with respect to different reagents.[32]

Application of a *finite difference* approximation to Equation (1) leads to the following working equations, known as condensed Fukui functions according to Yang and Mortier[8]

$$f_i^+ = -[q_i(N+1) - q_i(N)], \text{ for nucleophilic attack} \quad (3a)$$

$$f_i^- = -[q_i(N) - q_i(N-1)], \text{ for electrophilic attack} \quad (3b)$$

$f_i^0 = -\{\frac{1}{2}[q_i(N+1) - q_i(N-1)]\}$, for radical attack (3c)

where q_i is the partial charge of atom i, extracted from a Mulliken gross population analysis,[33] in a compound with $N-1$, N, and $N+1$ electrons, calculated in the ground-state geometry of the N-electron system, while the negative sign obeys the convention of negative electron charge.

Alternatively, employing a Mulliken population based approach to the *frozen core* approximation[2,5] we derive

$$f_i^- \approx \sum_{a\in i}^{AO} |c_{aHOMO}|^2 + \sum_{b\neq a}^{AO} |c_{bHOMO} \times c_{aHOMO}| S_{ab} \quad \text{for electrophilic attack} \quad (4a)$$

$$f_i^+ \approx \sum_{a\in i}^{AO} |c_{aLUMO}|^2 + \sum_{b\neq a}^{AO} |c_{bLUMO} \times c_{aLUMO}| S_{ab} \quad \text{for nucleophilic attack} \quad (4b)$$

$f_i^0 \approx \frac{1}{2}[f_i^+ + f_i^-]$, for radical attack (4c)

where HOMO and LUMO are the frontier orbitals. Apart from Mulliken population analysis (MPA), there are also other partitioning schemes for the electronic density, such as natural bond orbital analysis and Hirshfield analysis. In fact, Roy et al.[34–38] have shown that the latter is more reliable than MPA for calculating local reactivity descriptors and also produces nonnegative condensed Fukui function values. A lot of other work on nonnegative Fukui functions has been reported,[39–41] and it can be concluded that the Fukui function itself can be negative, although condensed Fukui functions cannot be negative, except in certain cases.

Equations (4a–4c) indicate the relationship between Fukui indicators and molecular orbitals.[7] In a sense, a nucleophilic reaction could be considered as involving the HOMO of the nucleophile and the LUMO of the electrophile. One of the major benefits of using the Fukui functions instead of the frontier orbitals − Equations (3a–3c) instead of Equations (4a–4c) − is that Fukui functions include the effects of orbital relaxation, which is very important.[42–44]

3. Results and Discussion

3.1. Molecular Structure

The six complexes under study have a square-planar geometry with almost C_{2v} molecular symmetry. They were selected as suitable candidates for investigation of the influence induced by the different contributing fragments to the molecule's reactivity. Compounds **1** and **2** were selected, because 1,10-phenanthroline and 2,2′-bipyridine, along with their substituted derivatives, are the most widely used diimines in synthesis. Complexes **4**, **5**, and **6** were used to study the role of the dithiolate by choosing substituents with different π*-accepting ability. More precisely, CN is a better π*-accepting group than H, while benzenedithiolate is a widely used aromatic ligand. Finally, the series **2**–**4** was employed in order to incorporate the role of the metal in our analysis. For this purpose two ligands with medium π*-accepting and π*-donating ability, namely bpy and bdt^{2-}, respectively, were selected.

Their structures were fully optimized at the B3LYP/SDD/6-311+G* level of theory. A comparison between the theoretically derived bond lengths and angles and the crystallographically extracted ones is presented in Table 1, where it can be seen that, apart from the calculated M–X bonds, which are systematically overestimated by 0.04 Å, something that is anticipated,[46] all the other structural parameters are in good agreement with the crystallographic data. Based on these facts the overall agreement between theory and experiment is judged as satisfactory. It is noteworthy that the M–N bonds are longer than those observed in bis(diimine) compounds, while the M–S distances are shorter than those of the related bis(dithiolenes). This trend is a direct consequence of a significant *trans* influence, with d_{C-S} and d_{C-N} being in the area of C–S(sp^2) and N–C(sp^2), respectively. An extensive analysis of the compounds' electronic structure has been presented elsewhere[28,47] and will not be discussed further here.

3.2. Searching Reactivity Sites

We begin our analysis with the palladium complexes **1** and **2** by investigating the diimine's role. Employing the condensed Fukui functions formalism under the *finite difference* approximation we derived the values for f_i^+, f_i^-, and f_i^0. These values are presented in Figures 1 and 2 along with the numbering of the corresponding atoms. Inspection of the two figures shows that the most reactive sites of the molecules upon electrophilic attack are the sulfur atoms in both cases.

Table 1. Comparison of selected calculated bond lengths [Å] and angles [°] for **1**–**6** with experimental values from X-ray analysis.

	M	M–N[a]	M–S[a]	C–S[a]	C=N[a]	C=C$^{dithiol\cdot}$	C=C$^{diim\cdot}$	$\varphi_{diim.}$	$\varphi_{dithiol.}$
1[28]	Exp.	2.096(8)	2.261(3)	1.787(10)	1.368(12)	1.376(13)	1.437(13)	80.2(3)	89.17(10)
	Calcd.	2.128	2.283	1.775	1.364	1.401	1.434	78.69	88.49
2[25]	Exp.	2.071(2)	2.245(1)	1.762(2)	1.353(3)	1.396(3)	1.474(3)	79.41(6)	88.67(2)
	Calcd.	2.120	2.286	1.774	1.358	1.401	1.476	77.85	88.16
3[25]	Exp.	1.937(2)	2.144(3)	1.755(3)	1.358(3)	1.395(3)	1.472(3)	83.31(8)	90.18(3)
	Calcd.	1.970	2.178	1.765	1.358	1.401	1.467	82.26	90.18
4[24]	Exp.	2.050(5)	2.248(2)	1.761(6)	1.367(8)	1.373(8)	1.464(8)	80.1(2)	89.0(1)
	Calcd.	2.095	2.299	1.771	1.363	1.402	1.466	78.00	88.26
5[45]	Exp.	2.049(4)	2.250(1)	1.743(7)	1.362(7)	1.346(14)	1.469(10)	79.26(16)	88.67(6)
	Calcd.	2.092	2.302	1.754	1.365	1.341	1.462	78.10	88.05
6	Calcd.	2.099	2.296	1.759	1.362	1.365	1.469	78.04	88.44

[a] Average of two distances.

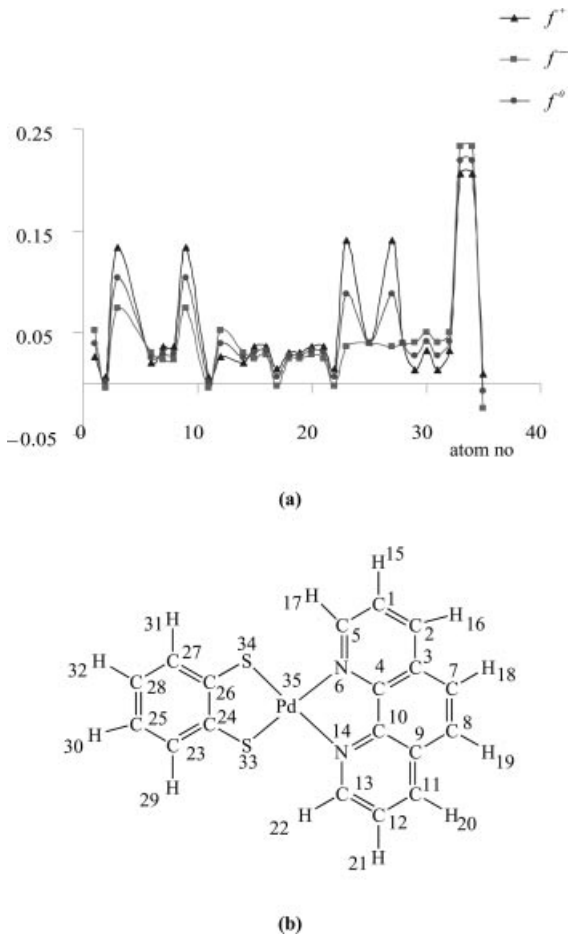


Figure 1. Condensed Fukui indices for **1** as derived from the *finite difference* approximation (a) and the atom numbering system (b).

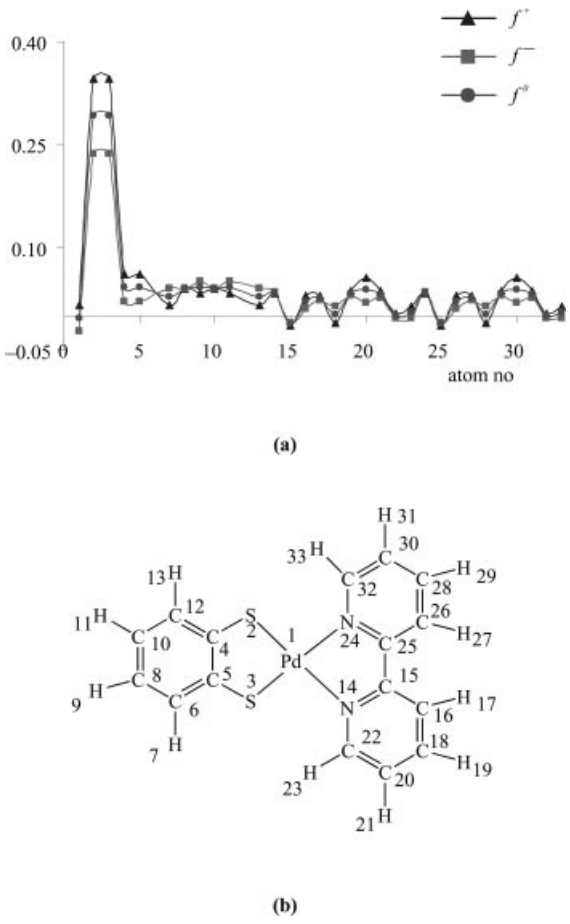
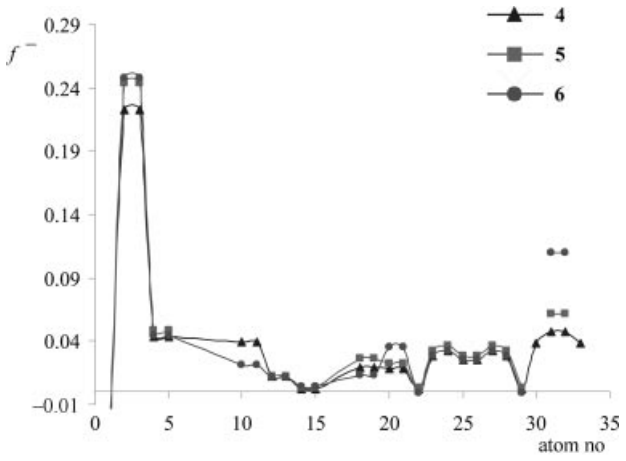


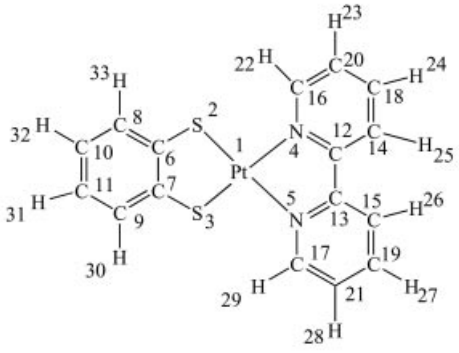
Figure 2. Condensed Fukui indices for **2** as derived from the *finite difference* approximation (a) and the atom numbering system (b).

Moreover, the sulfur atoms tend to react similarly during a radical attack, according to the f^0 values. In the phenanthroline compound **1** the reactive sites could also be the diimine's C1/C12 and C3/C9 atoms, although to a considerably lower degree. On the other hand, things change when discussion comes to f^+. The most reactive atoms are bdt's C23/C27 and phenanthroline's C3/C9 atoms in **1**. Of course, based on the relative nucleophilicity (s_k^-/s_k^+) and electrophilicity (s_k^+/s_k^-) introduced by Roy et al.,[48] we could accurately locate the preferable site for electrophilic and nucleophilic attack, respectively, and distinguish these carbon atoms. The reactive sites in **2** would also be dithiolate's C4/C5 and bpy's C20/C30. In other words, selection of the diimine as a bipyridine or phenanthroline derivative would not affect the complexes' reactivity towards an electrophile, but would certainly do so in the case of nucleophiles. The reason for this different reactivity is due to the nature of these attacks. In the case of the f_i^+ index, for example, one more electron is added to the system and the latter has to partition the excess of charge. Complex **1** can easily accommodate an extra electron through extended resonance of the phen's three condensed aromatic rings. Complex **2** can also accommodate an extra electron because of the presence of the two aromatic rings (bpy), but this is less effective than with phen rings. On the contrary, an electron subtraction from an almost identical HOMO (if the situation warranted, for example when an electrophile approaches S atoms), is expected to have a similar effect in both cases. In other words, although the HOMO has the same nature in both complexes, the LUMO is different since it is mainly present on diimine rings (phen vs. bpy).

Complex **2** would also be more reactive than **1** in the case of radical attack. Taking all these results into account, we conclude that, despite the similarity of the frontier orbitals of **1** and **2**, as was shown previously by us,[28] the two complexes are not expected to show an identical reactivity. Since most experimental results in this field have their origin in an electrophilic attack type of reaction or oxidation, in the next section we will try to shed light on their thermodynamics. Proceeding in a similar manner, we examine the dithiolate's role during electrophilic attack (Figure 3). In Figure 3(b) the numbering scheme concerns **4** but is also the same for **5** and **6** along with the following additions. Contributions from the dithiolate protons in **5** are represented by positions 31 and 32, while the nitrile carbon and nitrogen atoms in **6** are labeled as sites 10 and 11, and 31 and 32, respectively.



(a)



(b)

Figure 3. Condensed Fukui indices f_i^- for **4**, **5**, and **6** as derived from the *finite difference* approximation (a), along with the atom numbering system (b).

Figure 3 shows that electron-accepting groups on the dithiolate moiety increase the sulfur atom's softness towards electrophilic reagents in keeping with the observed softness of the sulfur atoms in the series **6** > **5** > **4** (or mnt > edt > bdt). Moreover, in the case of **6**, the nitrogen atoms of the CN groups seem to be an additional reactive site on the molecule. As a result, 1,2-dithiolates with strong electron-accepting groups as substituents are considered to be more reactive towards soft electrophiles or photochemically/chemically induced oxidation than those having donor groups, while the presence of a π*-delocalized system on the S ligand reduces its reactivity.

Complexes **2**–**4** provide a great opportunity for demonstrating the role of the metal from the Fukui functions (Figure 4). We prefer to elaborate the Fukui function in this series in terms of the *frozen core* instead of the *finite difference* approximation due to the fact that metal atoms in the case of the latter give a value slightly below zero as a result of the following partitioning scheme (MPA). Thus, $q_i(N-1)$ is found to have a higher value than $q_i(N)$ and when these are replaced in Equation (3b) a negative f_i^- value is obtained.

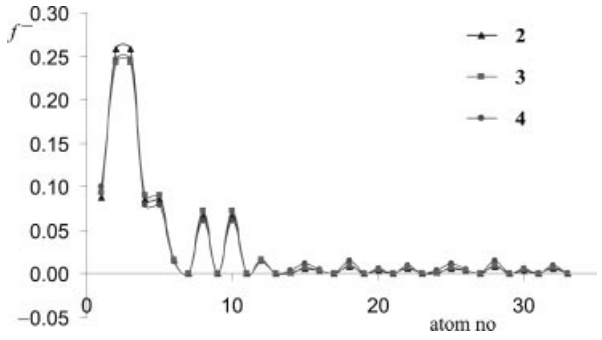


Figure 4. Condensed Fukui indices for **2**–**4** as derived from the *frozen core* approximation. The numbering system is the same as in Figure 2(b).

In a previous paper,[28] based on spectroscopic and mainly on DFT and TDDFT results, we clarified that the main, highly solvatochromic band in these complexes' visible spectra arises from a mixed-metal-ligand-to-ligand charge transfer despite the relatively low metal contribution in the frontier orbitals. Moreover, we have suggested that the metal atom is not just the right connector between the two conductors but its role is essential for the reactivity of this class of compounds. In order to test the validity of this suggestion, we examined the reactivity of **2**–**4** towards a common reagent (O_2) in combination with Fukui indices. Before we proceed to the analysis of experimental results, however, the bonding picture of these compounds should be given. First of all, recalling results from Table 5 in ref.[28] we can see that the HOMO is mainly localized on the dithiolato ligand (85.4% for **2**, 84.2% for **3**, and 81.1% for **4**), whereas the metal contribution is 8.8%, 9.3%, and 10.0% for **2**, **3**, and **4**, respectively.

The HOMO is the orbital where any oxidation process or electrophilic attack should take place. A closer inspection reveals that it originates from the antibonding combination of the metal's d_{xz} orbital with the dithiolate's $4b_1$ out-of-plane HOMO localized mainly on sulfur's $3p_z$ (51.7% for **2**, 48.6% for **3**, and 49.1% for **4**), whereas the diimine's contribution arises from the $4b_1$ LUMO of bipyridine. Hence, the dithiolate, which is a strong π-donor, interacts in an antibonding way with the metal's t_{2g} (under a pure O_h geometry) orbital. This interaction is valid since both orbitals lie relatively close in energy, and the stronger the interaction the higher the HOMO lies. On the other hand, the metal back-donates electron density to the diimine, which is a good π-acceptor. As the metal–dithiolate interaction increases, back-donation becomes more effective. Taking the whole picture into consideration, it is clear that the metal's involvement in the HOMO increases as a direct consequence of a more effective interaction with the bdt^{2-} moiety, the nucleophilicity of whose sulfur atoms also rises (the HOMO in all cases is largely a sulfur-based orbital). Grapperhaus et al. have referred to a relative bonding situation using the term π-repulsion.[47] Moreover, since the above description of the HOMO is, by definition, consistent with the characteristics of the Fukui function f^-, according to the *frozen core* approximation, it is clear that the driving

force of the reaction with an electrophilic reagent is maximized in **4** (thermodynamic criterion), according to the series **4** > **3** > **2** (Pt > Ni > Pd). On the other hand, as the sulfur contribution to the HOMO is lower for Ni compounds (48.6% vs. 51.7% for Pd), an electrophilic attack on it could elongate the Ni–S bond and break it. Thus, the sulfur atom is not favorable for electrophilic attack (Figure 4).

On the basis of the points mentioned above, and in order to test our results, we elaborated Bachman and Gray's excellent oxidation experiments.[24–26] Our analysis showed that the sulfur atoms in platinum complex **4** are more nucleophilic and thus more reactive, while the metal's larger contribution to the HOMO raises its energy and makes it more easily oxidized with more stable oxidation products (vide supra). Comparing the reported oxidation potentials for **2** (25 mV)[24] and **4** (165 mV),[25] we conclude that the first two results are correct. Moreover, the similarity of the f^- index (Figure 4) for both **2** and **4** indicates that both complexes yield the same product upon oxidation. Indeed, oxidation takes place for both Pd and Pt complexes (Scheme 1).[25]

The reactivity of the nickel analogue **3** is substantially different, according to the f^- function (based on finite difference approximation). Indeed, the sulfur atoms do not appear to be the unique active sites in this complex as the Ni atom and the C atoms of the bdt and bpy moieties also take part in the oxidation. In addition to these results, we must take into consideration that Ni^{II} can also form complexes with octahedral or trigonal-bipyramidal structures, whereas Pd^{II} and Pt^{II} cannot. The observed photochemical oxidation of **3** to give a mixture of octahedral disulfonate complex **8** and a dimetallic complex **9** is in agreement with this (Scheme 2).[25]

We have shown that the most reactive sites in [(diimine)-(dithiolato)M] complexes from an electronic point of view are the sulfur atoms, although the site preferences for each type of attack differ. Thus, an electrophilic attack should occur from the upper (or lower) side of the molecule while a nucleophilic substitution should occur from the side (Figures 5 and 6). Based on these diagrams we can select the appropriate ligands in order to proceed stereochemically or

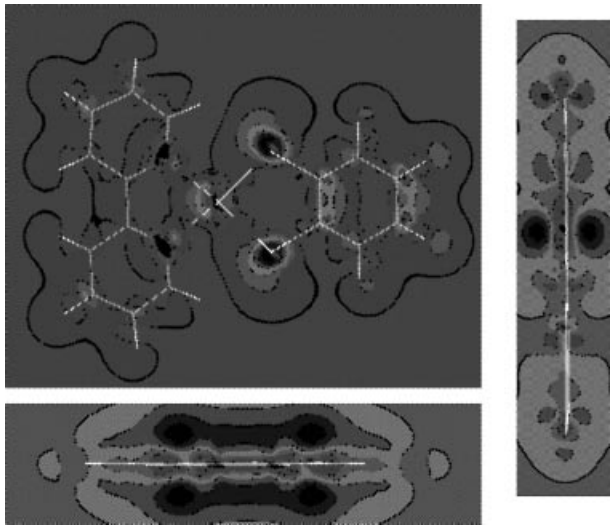
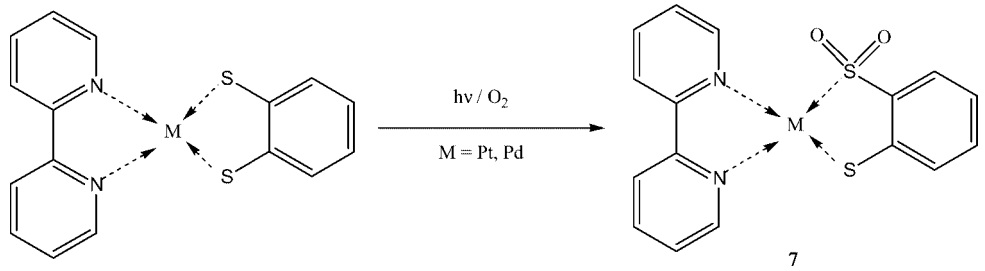
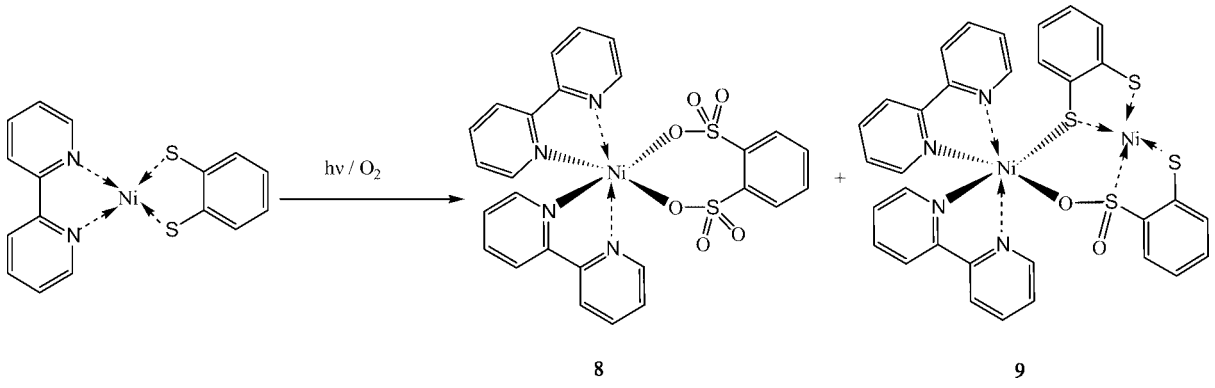


Figure 5. Projections of the difference in electron density between the neutral and the cationic form of **2**.



Scheme 1.



Scheme 2.

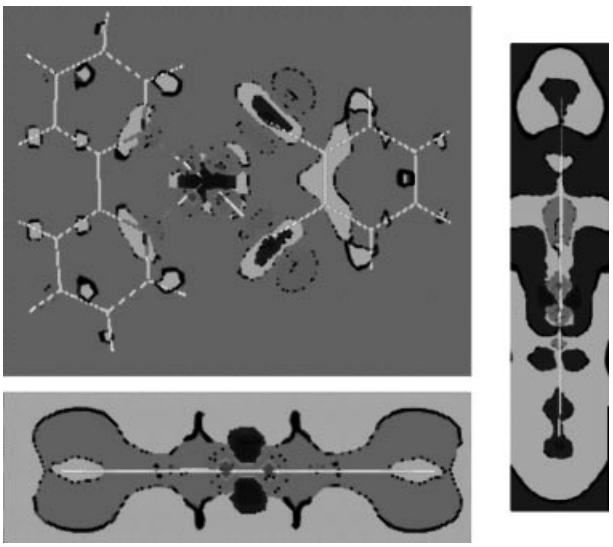
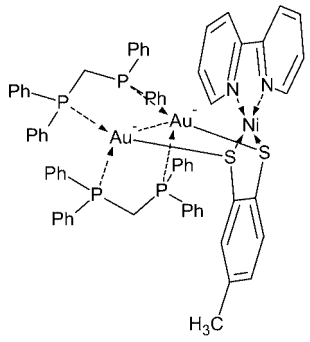


Figure 6. Projections of the difference in electron density between the anionic and the neutral form of **2**.

stop a certain type of substitution reaction. An experimental proof of the above discussion would be the complexes' interaction with electrophiles. Chen et al. in their fine paper[18] have shown that a series of platinum complexes analogous to **4** can act as ligands to unsaturated [bis(diphenylphosphanyl)methane]Ag^{I} and -Au^{I} compounds, yielding heterotrinuclear complexes of the type $Pt^{II}Au^{I}_2$ or $Pt^{II}Ag^{I}_2$. The formation of this class of compounds, and especially their structure, can be understood from the Fukui functions in Figures 3 and 5. Both Au^{I} and Ag^{I} are soft, and their soft–soft interaction with mixed (diimine)(dithiolato) complexes will take place from the upper side of the molecule at the sulfur atom to yield compound **10**.



10

3.3. Crystal Packing Under the Prism of Soft–Soft Interactions

Until now crystal packing has been explained mainly in terms of π–π interactions, hydrogen bonding, and intermolecular metal–ligand interactions. We report here an alternative explanation of stacking in terms of the Fukui functions (vide supra). Our working hypothesis starts from the assumption that in a molecule with distinct electrophilic and nucleophilic atoms or areas it is very likely that these atoms/areas interact and play a major role in the formation of the complexes' lattice. Complex **1** crystallizes in the $P2_1/c$ space group,[28] and slight intermolecular interactions seem to be present in the crystal (Figure 7).

If packing is examined in terms of Fukui function indices for **1**, as computed under the *finite difference* approximation (vide supra), S33/S34–C3/C9 and C3/C9–C23/C29 interactions of the electrophile–nucleophile type are expected. The latter provides a reasonable explanation for the relative position of each molecule in the crystal lattice and simultaneously implies that soft–soft interactions define the molecules' stacking. In a forthcoming paper the validity of this working hypothesis will be tested both experimentally and theoretically for a series of analogous Ni, Pd, and Pt complexes.[49]

4. Conclusions

In this study we have tested the usefulness of condensed Fukui functions in locating the preferred sites (atoms) for nucleophilic and electrophilic attack in a metal complex and predicting/explaining the products (even the minor ones) obtained during a reaction. The studied cases are referred especially to the addition of oxygen and other electrophiles such as unsaturated complexes of Ag^{I} or Au^{I} to mixed (diimine)(dithiolato) complexes.

For this purpose, the condensed Fukui indices were determined to characterize the nucleophile (and electrophile) sites in [(diimine)(dithiolato)M] complexes (M = Ni, Pd, and Pt). The former were calculated by two approximations well established in the literature, namely *frozen core* and *finite difference*. In general, we have found a good agreement between the results obtained for the condensed Fukui indices of [(diimine)(dithiolato)M] complexes and the experimental results of electrophilic attack and oxidation. In every case, except Ni complexes, the electrophilic attack occurs at a unique atomic site – the sulfur atom. Different reactive sites upon changing the central metal are reflected

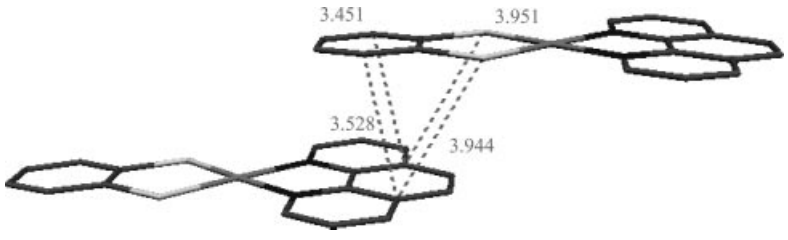


Figure 7. Packing of two molecules in molecular crystals of **1**.

in the differences products obtained, in accordance with experimental results. Moreover, the nucleophilicity of the sulfur atoms has been shown to increase in the series phen ≈ bpy, mnt > edt > bdt and Pt > Ni > Pd. There is total agreement between the condensed Fukui function indices and the existence of different products obtained upon oxidative addition to mixed (diimine)(dithiolato) complexes. Moreover, the Fukui indicators provide the correct intermolecular reactivity sequence of these complexes, which is not always attainable when comparing only the frontier orbitals. Last but not least, a different approach from π-stacking theory for crystal packing of these complexes is proposed based on Fukui indices and soft–soft interactions. This idea could be applied generally and could be the main reason for the different ways of molecular stacking in a crystal lattice, even within the same class of compounds, although the validity of this hypothesis has yet to be verified.

5. Experimental Section

5.1. Computational Details

Ground-state electronic structure calculations of all compounds under study were performed using density functional theory (DFT) [4] methods employing the GAUSSIAN 98/03 software package.[50] The functional used throughout this study is the B3LYP, which consists of a nonlocal hybrid exchange functional as defined by Becke's three-parameter equation[51] and the nonlocal Lee–Yang–Parr correlation functional.[52] The ground-state geometries were obtained in the gas phase by full geometry optimization, starting from structural data, regularized in order to satisfy the C_{2v} symmetry. The VeryTight option was used in all cases, which demands tighter convergence criteria than the default ones, while numerical integration was performed using the UltraFine option, which requests a pruned (99,590) grid. The optimum structures located as stationary points on the potential-energy surfaces were verified by the absence of imaginary frequencies. The derived wavefunctions were found to be free of internal instabilities.

The basis set used for all nonmetal atoms was the well-known valence triple-ζ 6-311+G*.[53,54] The quasi-relativistic Stuttgardt–Dresden effective core potential of the type ECP10MDF, ECP28MWB, and ECP60MWB was used for Ni, Pd, and Pt, respectively.[55] The core potentials were complemented by the relative valence basis sets.[55] For all other calculations related to the properties' investigation an additional diffuse and polarization function was added to the hydrogen atoms. Percentage compositions of molecular orbitals from the three contributing fragments (metal, dithiolate, diimine) and condensed Fukui functions according to the *frozen core* approximation were calculated using the AOMix program.[56,57] The graphics presented here were drawn with the aid of GaussView[58] and Molekel.[59]

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