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The Relationship Between Aromaticity and Charge-Transfer Transitions: A Combined Study of Square-Planar Metal Complexes Based on DFT, NMR and Nucleus-Independent Chemical Shifts

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Dedicated to the memory of Professor Dimitris F. Katakis

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The aromaticity of square-planar metal complexes, in this case mixed diiminodithiolate complexes of group VIII metals, has been investigated by ^{1}H and ^{1}H-^{15}N NMR spectroscopy, both experimentally and theoretically, as well as NICS indices. The electron-donating/-attracting ability of the substituent group and the metal ion interact with each other and control the aromaticity of the chelated rings and, as a consequence, the extent of the delocalization in the molecular plane. Evolution of the nucleus-independent chemical shift (NICS) of the ligands upon complexation is consistent with the change in their electron distribution. At the same time, and in analogy with the EMF in closed circuits, a positive difference of the NICS value (Δ_{NICS}) between two points (where HOMO and LUMO are located) can be envisioned as the driving force for charge-transfer transitions.

Introduction

Despite the lack of a unique and precise definition, the concept of aromaticity is one of the most frequently used in organic chemistry[1] and nowadays in inorganic and organometallic chemistry as well.[2] Aromaticity is associated with the widely understood concept of electron delocalization, but until recently was mainly related to cyclic π-systems. Today, the Hückel $(4n+2)$ π-electron rule is known to be just an ideal case and aromaticity is no longer limited to fully conjugated organic rings or even nonmetals. The terms σ-aromaticity, δ-aromaticity, and even σ/δ-antiaromaticity that are currently in use imply the contribution of highly or not delocalized σ-, π-, and δ-type (referring to the symmetry) molecular orbitals.[3] Moreover, the concept of multiple (π- *and* δ-) aromaticity has been introduced for metal heterocyclic compounds, such as planar bis- and tris(dithiolene) complexes,[4,5] while a 3D aromaticity of relevant complexes has also been proved.[6] The former not only explains the peculiar properties of this class of compounds but also the "non-innocent" character of the dithiolene ligand. The latter has a significant role over a wide range of chemistry since complexes with ligands of this class are widely applicable in bioinorganic chemistry[4c] and catalysis,[4d] and as magnetic and non-linear optics materials.[4e] Here, one should stress that aromaticity/antiaromaticity in all the aforementioned systems will not manifest itself exactly the same way as in organic chemistry. Many specific deviations are expected. Nevertheless, it is believed that the overall chemical bonding picture and most of the molecular properties of these compounds should be explainable using the concepts of aromaticity and antiaromaticity.

With all this in mind, we tried to "measure" the aromaticity, or more accurately, the existence or not of significant diatropic ring currents, of a different class of compounds that bear dithiolate ligands, namely the mixed α-diiminodithiolate complexes. The latter have attracted researchers' attention since their first introduction by Miller and Dance[7] due to their interesting chemistry and their potential applications as new materials and photosensitizers.[8–11] The combination of a good π*-donor (the dithiolate ligand) and a good π*-acceptor (the diimine) leads to systems that possess intriguing properties, namely photoluminescence in solution, electrical conductivity in the solid state, large molecular hyperpolarizabilities, and large excited oxidation potentials. These properties are the result of the existence of a mixed metal-ligand-to-ligand charge transfer (MMLL′CT) band in the low-energy region of the UV/Vis/NIR spectrum, as has been indicated both experimentally[8] and theoretically.[11d]

As aromaticity is not defined exactly, since it is not a directly measurable quantity, we had to use one of the in-

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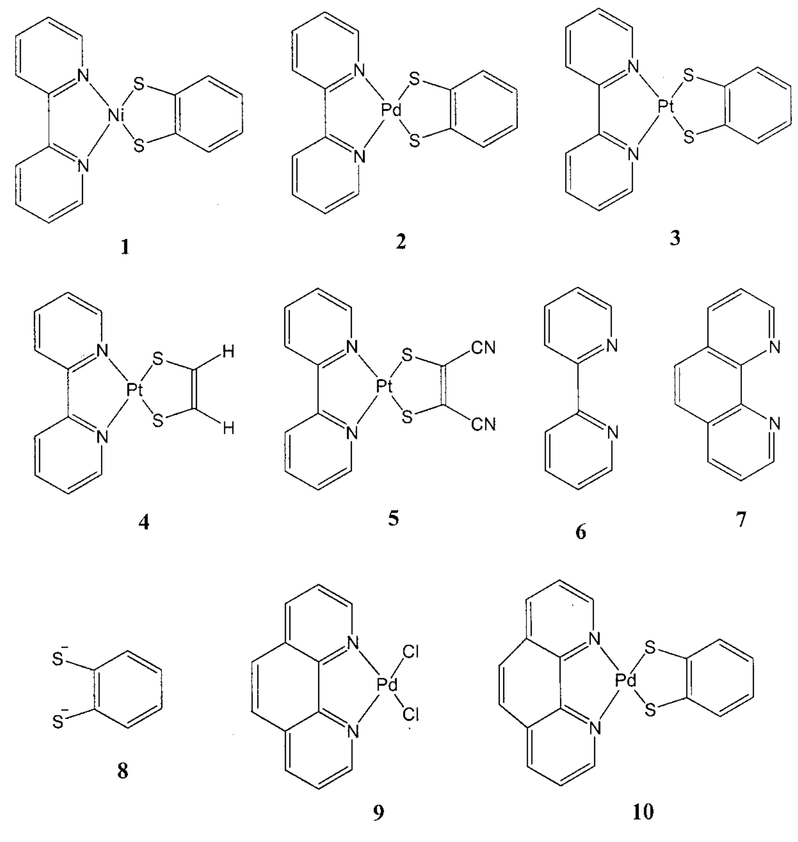
dices available in the literature. Some of the main criteria on which aromatic behavior are based are the geometrical indices, ^{1}H NMR chemical shifts, ASE (aromatic stabilization energy) on the basis of homodesmotic reactions, the exaltation of magnetic susceptibility (Λ), and HOMA (harmonic oscillator model of aromaticity),[12] none of which, however, has proved to be generally applicable.[13] On the contrary, the NICS (nucleus-independent chemical shift), which is a magnetism-based index,[14] is not only widely used to characterize the aromaticity and antiaromaticity of organic rings[15] but it is also well accepted as one of the most efficient tools for the understanding and interpretation of ring currents[16] of organic compounds, boranes and fullerenes,[17] and inorganic[18] and organometallic[2] complexes. NICS values have been defined by Schleyer et al.[14] based on the absolute magnetic shieldings computed at the ring center at the ab initio, density functional, and semi-empirical (MNDO) levels; the signs are reversed to conform to the NMR chemical shift convention (negative upfield and positive downfield). Significantly negative NICS values in the interior positions of rings or cages indicate aromaticity or diatropic ring currents, whereas positive values denote antiaromaticity or paratropic ring currents.[14] Moreover, the σ-contribution can be separated from the π-contribution by using NICS(1) instead of NICS(0) values.[16a] NICS(1) refers to the location 1 Å above the center of the ring plane, where local contributions of σ-bonds are reduced in favor of the π-effects.

The above examples of the application of NICS encouraged us to undertake a systematic study, firstly to find out if mixed diiminodithiolate complexes have an aromatic character and, as a consequence, gain some hints about their electronic structure, and secondly to reveal the role of the metal atom or the substituents on the chelating ligands in the extent of delocalization of the electron current. To the best of our knowledge, although there are a few papers[2b,2c] dealing with NICS in coordination compounds, this is the first attempt at a systematic use of NICS as a probe of the change of "aromatic" delocalization in mixed-ligand metal complexes by changing the metal ion or the substituents on the conjugated rings.

Results and Discussion

The compounds employed for this study are displayed in Scheme 1. The selection of these ten compounds was done as follows. First of all, in the formal oxidation state +2 the mixed diiminodithiolate complexes have a square-planar coordination and two planar didentate ligand systems. In other words, compounds **1**–**5** and **10** contain the metal ion as a link between two planar ligands, forming a coplanar compound with five-membered conjugated rings. The metal ion is part of a delocalized π-electron system. This delocalized system is mainly composed of the metal d_{xz} orbitals, the sulfur $3p_z$, the nitrogen $2p_z$, and the carbon p_z orbitals.



Scheme 1.

Complexes **1**–**3** consist of an aromatic α-diimine and an aromatic dithiolate ligand coordinated to a formally d^8 metal atom. Both ligands are characterized by their medium-strength π*-donating/-accepting ability and are suitable for the investigation of the metal's role. Thus, changes in the diatropic ring currents of the chelated ligands induced by tuning the metal ion will be discussed.

The next series of compounds, **3**–**5**, were employed in order to determine the substituents' effect on the dithiolate chelate ring. The dithiolate ligand in these complexes acts as a strong σ-donor, whereas its π*-donating role is reduced along the series edt^{2-} > bdt^{2-} > mnt^{2-}.[8,11d] The influence of the substituents' π*-accepting ability on the MMLL′CT band and the complexes' electron properties is very well established.[7–11] Finally, based on compounds **7**–**10** we will try to reveal the way that ring currents arise upon complexation.

Selected structural data for compounds **1**–**10**, optimized by DFT, are collected in Table 1 along with the available experimental data. From a close inspection of the data we can see that the DFT M–X bond lengths systematically exceed the corresponding X-ray values by about 0.04 Å, which is generally anticipated. All other parameters are in accordance with the experimental ones, thus revealing the overall agreement between theory and experiment.

Since ring currents are very sensitive to geometrical characteristics, a closer inspection of the structural data is necessary. Firstly, in the series **1**–**5** and **10** the M–N bonds are longer than those observed in M–diimine complexes, while the M–S bonds are shorter by 0.02 Å than the M–S bond of M–dithiolene complexes.[2b] This is consistent with the significant *trans* influence in similar compounds.[8d] Secondly, the C–S bond lengths in these complexes are in close agreement with the typical S–C(sp^2) distance (1.751 Å), indicating that the observed delocalization in similar dithiolene complexes (S–C = 1.704 Å) is not seen in the mixed diiminodithiolate ones.

Focusing on the central metal's structural role, a comparison of the M–N and M–S bond lengths in the series **1**–**3** must be made. Inspection of the data collected in Table 1 shows that the above bond lengths are sensitive to the nature of the metal. Thus, the M–N bond lengths increase in the order Ni–N < Pt–N < Pd–N; Ni has a significantly smaller bonding radius than Pd and Pt. According to the contribution of each fragment and the relative energies of the bonding orbitals (Table 2), we can conclude that the better overlap between the metal atom and the dithiolate ligand in Pd complexes reduces the electron density of the M–N bonds. On the other hand, as both Pd^{2+} and Pt^{2+} have almost the same radius (86 and 85 pm, respectively), they can successively overlap with both conjugated ligands, thus providing the series Ni–S > Pd–S ≈ Pt–S on passing from Ni to Pt.

For chelated five-membered rings, the C–C bond should be an indicator of the cyclic electron delocalization. Thus, for a dithiolate ring the C–C bond length changes from 1.341 Å for **4** to 1.365 Å for **5** and 1.402 Å for **3**, which is close to the bond length in benzene [1.40 Å; for comparison, (sp^2)C=C(sp^2) = 1.331 Å]. According to the above bond lengths the degree of bond delocalization decreases in the order **3** > **5** > **4**, thereby indicating that diatropic ring currents are reinforced by the presence of π*-accepting substituents on the dithiolate ring, in accordance with the benzene derivatives. Here, it could be argued that a C–C bond is expected to be the longest in the case of **3** since the benzene ring would try to achieve its aromatic sextet as much as possible by following the Clar rule; although this is generally true, the overall assignment must be considered to be correct as it is completely consistent with the π*-accepting ability of the substituents. The last assertion has also been stated for dithiolene complexes.[2b,2c] In the series **3**–**5**, the C–C bond lengths in the diimine-containing conjugated ring are nearly constant (1.466 Å). Thus, these bonds are practically unaffected by the substituents on the dithiolate

Table 1. Comparison of selected calculated bond lengths [Å] and angles [°] for the compounds under study with experimental values from X-ray analysis.

	M	M–N	M–S	C–S	C=N	C=C$^{\text{dith.}}$	C=C$^{\text{diim.}}$	$\varphi_{\text{diim.}}$	$\varphi_{\text{dith.}}$
1	exp.[20]	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
2	exp.[20]	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	exp.[21]	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
4	exp.[22]	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
5	calcd.	2.099	2.296	1.759	1.362	1.365	1.469	78.04	88.44
6	exp.[23c]	–	–	–	1.35(3)	–	1.50(3)	–	–
	calcd.	–	–	–	1.341	–	1.500	–	–
7	exp.[23a,23b]	–	–	–	1.362(8)	–	1.441(8)	–	–
	calcd.	–	–	–	1.350	–	1.459	–	–
8	calcd.	–	–	1.771	–	1.454	–	–	–
9	calcd.	2.082	–	–	1.363	–	1.430	80.15	–
10	exp.[11d]	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

ligands. However, in the series **1**–**3** the C–C bond lengths in the diimine-containing conjugated ring decrease in the order **2** > **1** ≈ **3**, while the corresponding bond for the dithiolate ring remains practically the same (1.401 Å). This observation reveals the significant role of the metal in determining the extent of delocalization. Complexes **2** and **10** have identical structural characteristics, as anticipated, since bpy and phen have almost the same σ-donating and π*-accepting behavior.

Table 2. Contribution of different fragments to the valence orbitals of the complexes. HOMOs and LUMOs are shown in bold.

MO	*E* [eV]	Diimine	Dithiolate[a]	Metal
		1		
		unoccupied		
39a$_1$	–0.98	70.1	21.9	8.0
33b$_2$	–1.59	11.0	38.0	51.0
8a$_2$	–1.77	99.1	0.1	0.8
11b$_1$	–2.08	99.0	0.1	1.0
10b$_1$	**–2.93**	**91.4**	**5.3**	**3.3**
		occupied		
9b$_1$	**–4.67**	**6.5**	**84.2**	**9.3**
7a$_2$	–5.14	0.7	89.1	10.3
38a$_1$	–6.25	1.2	14.6	84.2
6a$_2$	–6.67	2.4	60.4	37.2
8b$_1$	–6.71	5.3	33.5	61.2
32b$_2$	–6.81	6.1	65.7	28.2
		2		
		unoccupied		
39a$_1$	–0.67	65.7	–9.4	43.7
33b$_2$	–1.71	9.2	48.2	42.6
8a$_2$	–1.79	99.0	0.2	0.8
11b$_1$	–2.08	99.0	0.3	0.8
10b$_1$	**–2.93**	**92.4**	**4.6**	**3.0**
		occupied		
9b$_1$	**–4.69**	**5.8**	**85.4**	**8.8**
7a$_2$	–5.14	0.8	89.1	10.1
38a$_1$	–6.28	8.6	39.0	52.3
6a$_2$	–6.75	1.8	75.9	22.3
8b$_1$	–6.89	5.0	55.6	39.4
32b$_2$	–7.22	18.1	60.8	21.1
		3		
		unoccupied		
39a$_1$	–0.66	59.9	2.3	37.8
33b$_2$	–1.06	6.5	46.6	46.9
8a$_2$	–1.8	98.2	0.5	1.3
11b$_1$	–2.04	98.1	0.5	1.4
10b$_1$	**–2.92**	**87.4**	**7.2**	**5.4**
		occupied		
9b$_1$	**–4.63**	**10.0**	**79.9**	**10.0**
7a$_2$	–5.13	1.7	83.7	14.6
38a$_1$	–6.4	6.7	24.2	69.1
6a$_2$	–6.73	3.3	70.0	26.7
8b$_1$	–6.82	7.6	51.9	40.5
37a$_1$	–7.27	3.4	53.1	43.5
		4		
		unoccupied		
33a$_1$	–0.58	57.1	4.6	38.4
28b$_2$	–1.01	12.6	44.9	42.4
7a$_2$	–1.69	98.4	0.4	1.3
10b$_1$	–1.92	98.1	0.5	1.4
9b$_1$	**–2.81**	**84.6**	**9.7**	**5.6**
		occupied		
8b$_1$	**–4.50**	**12.7**	**78.0**	**9.3**
6a$_2$	–5.68	3.0	67.4	29.6
32a$_1$	–6.35	7.7	23.9	68.4
7b$_1$	–7.04	11.6	25.8	62.6
31a$_1$	–7.26	4.3	52.9	42.8
27b$_2$	–7.36	17.6	62.2	20.1
		5		
		unoccupied		
9a$_2$	–1.60	3.8	94.4	1.8
33b$_2$	–1.89	10.0	46.1	43.9
8a$_2$	–2.37	96.5	2.5	0.9
11b$_1$	–2.59	98.3	0.4	1.2
10b$_1$	**–3.49**	**90.4**	**5.0**	**4.5**
		occupied		
9b$_1$	**–5.51**	**7.5**	**81.1**	**11.4**
7a$_2$	–6.53	2.8	67.0	30.2
37a$_1$	–7.15	7.8	21.0	71.2
8b$_1$	–7.63	7.9	49.3	42.8
36a$_1$	–8.17	2.0	52.3	45.7
32b$_2$	–8.20	18.4	61.2	20.3
		9		
		unoccupied		
78 (a$_2$)	–1.16	99.5	0.0	0.5
77 (b$_1$)	–1.80	98.9	0.1	1.0
76 (b$_2$)	–2.42	17.6	31.0	51.4
75 (a$_2$)	–2.98	99.3	0.1	0.6
74 (b$_1$)	**–3.18**	**96.6**	**0.7**	**2.7**
		occupied		
73 (a$_2$)	**–6.27**	**2.1**	**72.8**	**25.0**
72 (a$_1$)	–6.51	–4.5	74.2	30.3
71 (b$_1$)	–6.51	6.8	63.7	29.5
70 (b$_2$)	–6.61	–1.0	96.8	4.2
69 (a$_1$)	–6.81	15.7	24.9	59.3
68 (b$_1$)	–7.83	**78.8**	13.8	7.4
		10		
		unoccupied		
9a$_2$	–0.90	99.5	0.0	0.5
12b$_1$	–1.56	99.0	0.3	0.8
35b$_2$	–1.69	11.8	46.6	41.7
8a$_2$	–2.73	99.3	0.2	0.5
11b$_1$	**–2.89**	**92.8**	**4.3**	**2.9**
		occupied		
10b$_1$	**–4.66**	**5.4**	**85.6**	**9.0**
7a$_2$	–5.11	0.9	88.8	10.3
41a$_1$	–6.25	2.8	33.9	63.4
6a$_2$	–6.72	1.7	75.9	22.3
9b$_1$	–6.84	9.1	52.7	38.1
40a$_1$	–7.22	4.7	48.3	47.0

[a] In the case of **9** this denotes the contribution of the two Cl atoms.

Finally, the Pd–N bond of **9** is shorter than that of **10** due to the weaker *trans* influence of the chlorine atoms, whereas the phenanthroline moiety **7** is slightly affected by complexation (changes of ±0.015 Å in bond lengths). On the other hand, the C–C bond lengths of benzedithiolate **8** (1.454 Å) are more benzene-like after complexation (1.401 Å in **10**).

Considering the data in Table 2, one could suppose that the HOMO–LUMO gap can be used as an index of aromaticity.[19] However, this is quite a complicated task for the complexes under study as both the HOMO and LUMO are located in different parts of the complex (on the dithiolate ring and the diimine ring, respectively). Thus, proceeding with our analysis of the delocalization of the ring currents in M(diimine)(dithiolate) complexes by studying the NMR data and NICS indices, a cage of sampling points was built around every molecule at distances of 0, 0.5, and 1 Å above the ring plane. The grid of points includes the NICS(0) and NICS(1), as calculated by definition. NICS(0) and NICS(1) constants for all compounds under investigation are displayed in Table 3, and the ^{1}H NMR frequencies of selected nuclei are shown in Table 4. The selected sampling points are indicated in Figure 1.

Table 3. NICS(0)/NICS(1) values for the center of the selected rings.[a]

	A	B	C	D	E
1	+0.27/–1.18	–10.32/–5.29	–4.22/–7.71	–	–7.99/–9.31
2	+1.58/–1.21	–7.21/–3.77	–4.93/–7.97	–	–7.79/–9.00
3	–1.14/–3.27	–7.56/–4.61	–4.59/–7.39	–	–7.79/–9.09
4	–1.84/–3.53	–7.41/–4.41	–4.05/–6.87	–	–
5	–0.93/–2.89	–10.31/–5.61	–5.30/–8.09	–	–
6	–	–	–5.43/–9.07	–	–
7	+7.30/ +2.34	–	–7.37/–10.41	–5.81/–8.34	–
8	–	–	–	–	–4.30/–6.31
9	+2.36/ +0.88	–	–7.47/–10.24	–	–
10	+2.52/–0.45	–6.70/–3.20	–6.14/–9.36	–6.21/–8.24	–7.40/–8.70

[a] NICS/NICS(1) of benzene: –7.92/–9.93.

Table 4. ^{1}H NMR chemical shifts in [D$_6$]DMSO.

	H1-H1′	H2-H2′	H3-H3′	H4-H4′
1	8.66	8.25	–	6.72
2	8.67	8.32	–	6.75
3	9.28	8.41	–	6.80
4	9.36	8.08	–	–
5	9.12	8.52	–	–
6	8.69	7.94	–	–
7	9.01	8.93	8.28	–
8	–	–	–	6.55
9	9.27	8.97	8.29	–
10	9.10	8.47	7.98	6.90

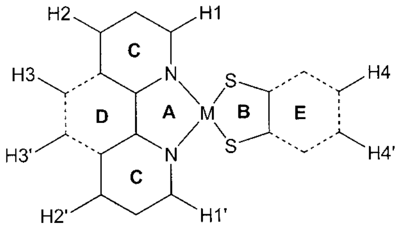


Figure 1. Sampling grid of NICS values and selected nuclei.

Specific proton nuclei were selected as indicators for the electron delocalization for the following reasons. For both bipyridine and phenanthroline complexes, H1-H1′ are close to the chelated ring – they are coupled through two bonds to the nitrogen atom and three to the metal atom – whereas protons H2-H2′ (for bpy), H3-H3′ (for phen), and H4-H4′ (for bdt) lie furthest from the metal atom and, as a result, are the most effective indicators of alterations in the π-electron current.

Based on NICS values in the ring centers (Table 3), the aromaticity of the dithiolate ring (B) is only marginal (maximum of around –5 ppm vs. around –10 ppm for benzene) while the diimine ring (A) is not aromatic (maximum NICS about –3 ppm). The nonaromatic character of the diimine ring (A) can be explained by the large difference in electronegativity between nitrogen (3.04), carbon (2.55), and the metal (2.28 for Pt and 2.20 for Pd), which leads to localization of electron density on the nitrogen atom; on the other hand, delocalization is observed in the dithiolate ring (B) due to the similar electronegativities of carbon (2.55) and sulfur (2.58). Moreover, differences in NICS values are observed with changes of metal or the substituents, thereby providing us with the opportunity to monitor changes of the diatropic current in the complexes. Thus, in the series **3**–**5** the NICS(1) values of the dithiolate ring (B) decrease in the order **5** > **3** > **4**, thereby indicating the enhanced ring diatropicity in the presence of substituents with a relatively high electron-withdrawing ability. The reverse order is found for the diimine ring, as the NICS values for (A) decrease from **4** to **3** and **5**. The electron-withdrawing groups on the dithiolate ring tend to stabilize the HOMO, thus increasing the HOMO–LUMO gap, as has been proved experimentally[8] and further supported by our calculations.[11] This stabilization has its origin in the better overlap of the central metal atom with the dithiolate ligand and causes the shielding of the latter. Moreover, the NICS(1) values of (C) (considering also the free ligand) decrease in the order **6** > **5** > **3** > **4**, in accordance with the HOMO stabilization (Table 2).

At this point we should comment on the reverse direction of ^{1}H NMR and NICS(1) values that is observed on moving from free bipyridine ligand to the coordinated one. According to the NICS(1) values of (C), diatropic ring currents on the pyridine moieties diminish as a consequence of σ-donation of electron density to the metal atom through the nitrogen atoms. On the other hand, the ^{1}H NMR chemical shifts (H2-H2′, Table 4) indicate that the protons of complexed bipyridine are more deshielded than those of the free ligand due to the paratropic effect of the metal atom. The asymmetrical charge-distribution in the valence orbitals of the metal atom is responsible to a large extent for the strong diamagnetic shift of the nucleus bound to it.[24] The resulting paramagnetic moment deshields the metal atom, but shields the other nucleus as in a synergic procedure. For the complexes under study, this is clearly demonstrated by the ^{15}N NMR chemical shifts, which upon complexation are shielded from δ = 313.13 ppm for free phenanthroline to δ = 240.45 ppm for **10** (Figure 2). As a result, the rest of the bipyridine molecule is deshielded, with the effect being more apparent for the H1-H1′ nuclei (Table 4); since complexation has taken place, the ^{1}H NMR and NICS(1) values are in total accordance within the series **5** > **3** > **4** provided that relativistic effects for heavy metals (i.e. Pt) are taken into account even for the NICS values. In this class of complexes, the bipyridine also acts as a weak π*-acceptor, with its vacant π-orbitals interacting with filled metal d-orbitals. As H1-H1′ is deshielded in the series **4** > **3** > **5**, we expect the metal atom to be deshield in the same order. Our results are in close agreement with those reported by Bereman and Purrington et al. in their extensive study of various dithiolene complexes.[22]

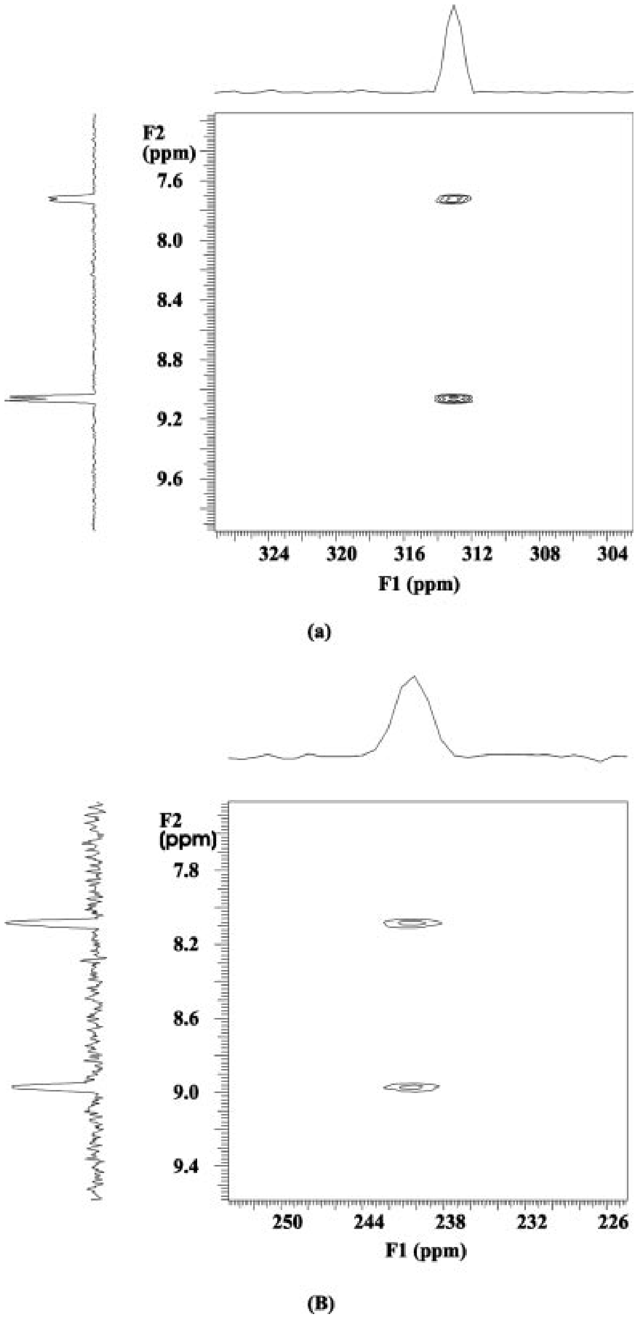


Figure 2. ^{1}H-^{15}N HMBC spectra of 1,10-phenanthroline (a) and Pd(phen)(bdt) (b).

The role of the central metal is revealed by studying the series **1**–**3**. First of all, the diatropic ring current of the dithiolate (bdt) chelate ring (B) decreases in the order **1** > **3** > **2** while the corresponding one for the (bpy) diimine conjugated ring (A) decreases in the order **3** > **2** ≈ **1**, in accordance with the energy of the MMLL′CT of these complexes. The former order was derived by Lauterbach and Fabian for a series of bis(dithiolenes).[2b] As a matter of fact, based on NICS(1) values for the bpy ring (–3.27 ppm) and the bdt ring (–4.61 ppm) complex **3** can be considered as aromatic, as opposed to **1** and **2**, where only the dithiolate ring (–5.29 and –3.77 ppm, respectively) is considered marginally aromatic. The conjugated electronic system of complex **3** appears more delocalized than the corresponding ones of **1** and **2**. The above differences can only be due to the metal atom since both chelating ligands are the same for all three complexes. Ni has not only the smallest bonding radius but also low-lying π-orbitals that could interact with the dithiolate ones; the dithiolate ligand is a π*-donor to the metal atom. Thus, the dithiolate ring in **1** is more aromatic or, more accurately, diatropic (–5.29 ppm) than the other two complexes. Due to Ni's smaller size, the overlap with the diimine orbitals is quite as effective and, as a consequence, the five-membered diimine ring is paratropic (–1.18 ppm). Pt enhances the aromaticity of both rings, as compared to Pd, probably due to the extension of its 5d orbital in spaces, which causes a better overlap with the ligand's valence orbitals, as supported by the extended delocalization of valence orbitals (Table 2).

Based on NICS(1) values for the benzenedithiolate ligand (E) (Table 3), we can conclude that its aromaticity decreases in the order **1** > **3** ≈ **2** due to its proximity to another aromatic ring. The ^{1}H NMR chemical shifts change very slowly in the direction **3** > **2** > **1** due to the paramagnetic influence of the central metal.

Finally, we determined the changes of diatropic and paratropic currents upon complexation by applying a procedure completely analogous to that of the synthesis, namely **7** → **9** → **10** ← **8**. First of all, phenanthroline is a highly aromatic compound, with the diimine rings being more aromatic than the benzenoid one, as is also observed in phenanthrene.[14] Complex **9** also possesses an aromatic phenanthroline ligand, but the benzenoid ring (D) is slightly more aromatic after coordination, whereas the chelated five-membered ring is slightly paratropic (+0.88 ppm). The ^{1}H NMR chemical shifts are, in general, consistent with the above discussion apart from a slight deviation of H1-H1′ due to the paratropic effect of the metal atom.

Complex **10** results from coordination of **8** to **9**, and several changes are induced in the ring currents. First of all, the aromaticity of the whole phenanthroline ligand is reduced, which is also confirmed by the ^{1}H NMR chemical shifts. NICS(1) of the diimine five-membered ring indicates a slight diatropic current (–0.45 ppm) but still the ring is not aromatic. On the other hand, the conjugated dithiolate ring is more diatropic (–3.20 ppm) and its aromaticity is marginal, while the aromaticity of the benzenoid ring (E) is maximized (–6.31 ppm for the free bdt to –8.70 ppm for the coordinated one). This behavior is expected since the interaction of the metal atom with the good σ-donor/π*-donor bdt$^{2–}$ focuses electron density on the dithiolate and benzenedithiolate ring, thereby reducing ring currents in the diimine rings. Moreover, the aforementioned complexation route is in favor of the delocalization of the conjugated electronic system. A graphic representation of selected NICS values is shown in Figure 3.

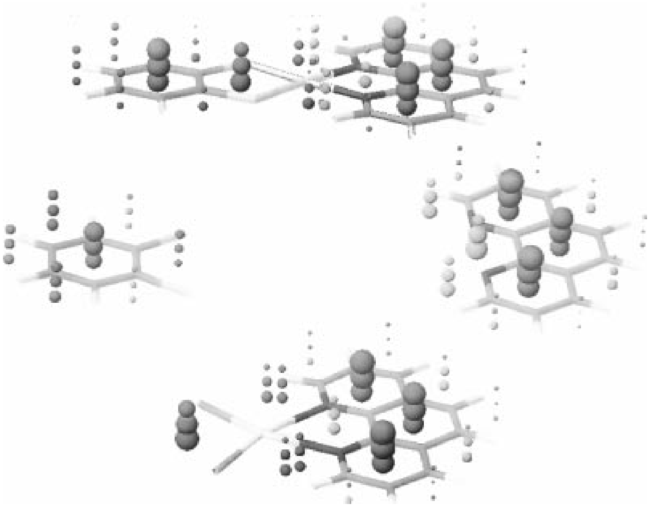


Figure 3. Graphic representation of NICS values for the selected grid for Pd(phen)(bdt), Pd(phen)Cl_2, phen, and bdt^{2-}. Dark grey spheres: diatropicity. Light grey: paratropicity.

Summarizing the effects on **10**, we suggest that a motion of diatropicity from the diimine to the dithiolate ligand is observed in a manner that is opposite to the route the electron cloud follows during the mixed metal-ligand-to-ligand transition. In that sense, the positive difference of the NICS value (Δ_{NICS}) between two points where the orbitals involved in the charge-transfer transition are located can be envisioned as a difference in electron distribution and, in analogy with the EMF (electromotive force), in close circuits, as the driving force for charge-transfer transitions.

The aforementioned conclusions suggest that NICS values are not only probes for the extent of aromatic electron delocalization in cyclic conjugated systems[3a] but also in square-planar bis(chelated) metal complexes. Moreover, the evolution of the NICS during complexation is consistent with the evolution of the diatropicity of the rings and implies, at the same time, the direction of the charge-transfer transition.

Conclusions

In the present report, structural aspects, ^1H- and ^1H-^{15}N NMR data, as well as NICS constants are employed in order to determine the aromaticity of the mixed-ligand complexes of the type M(diimine)(dithiolate). The following are the principal results and conclusions of this investigation:

1) All complexes and ligands were fully optimized in the gas phase, giving structures in accordance with those anticipated or crystallographically determined.
2) The aromaticity of the dithiolate chelate ring is marginal, whereas the relative diimine chelate ring can be generally characterized as nonaromatic.
3) The aromatic diimine ligands lose some of their diatropicity upon complexation, an effect which is not immediately obvious from the ^1H NMR chemical shifts due to the presence of the metal atom but is revealed by NICS(1) values.
4) Aromatic substituents on dithiolate ligands enhance their aromaticity upon complexation as a direct consequence of the complexes' electronic properties and the Clar rules.
5) Electron-withdrawing groups as substituents on the coordinated dithiolate ring tend to enhance its diatropicity and have the opposite effect on the chelated diimine ring.
6) The role of the central metal is significant in determining the aromaticity of the complexes as it is part of the delocalized π-electron system.

The most important conclusion is:

7) In light of the diatropicity changes induced by complexation and the MMLL′CT transition which characterize these complexes, the difference in NICS values between the chelated rings (where the valence orbitals are located) can be regarded as an electronic analogue of the EMF and is the driving force of the transition. This conclusion can be applied in every case, and Δ_{NICS} for charge-transfer transitions could be analogous to $\Delta E°$ for oxidative processes.

Experimental Section

General: All reactions and manipulations were conducted under argon using standard Schlenk techniques. Solvents were purified by standard procedures prior to use.[25] The chemicals 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy), 1,2-benzenedithiol (H_2bdt), disodium maleonitriledithiolate ($Na_2mnt\cdot 2H_2O$), [PdCl_2(phen)], [PtCl_2(bpy)], were purchased from Aldrich and used as received. The complexes [Pt(bpy)(bdt)],[20,21] [Pt(bpy)(mnt)],[8d] [Pt(bpy)(edt)],[22] [Pd(bpy)(bdt)],[20] [Ni(bpy)(bdt)],[20] and [Pd(phen)(bdt)][11a,11d] were prepared according to literature procedures. Their physical properties are consistent with those reported. ^1H NMR and ^1H-^{15}N HMBC spectra were recorded with Varian UNITYplus spectrometers operating at 300 and 600 MHz, respectively. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS), using the solvent peaks as an internal reference.

Computational Methods: DFT[26] quantum chemical calculations were carried out using the 1998 release of the GAUSSIAN suite of programs.[27] The functional used throughout this study is B3LYP (BLYP was also tested and does not influence our results in a qualitative way), which consists of a hybrid exchange functional as defined by Becke's three-parameter equation[28] and the Lee–Yang–Parr correlation functional.[29] The ground-state geometries were obtained in the gas phase by full geometry optimization, starting from structural data,[20–22,24] and were 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 minima on the potential energy surfaces were verified by the absence of imaginary frequencies. No imaginary frequencies were found apart from two cases. 2,2′-bipyridine at the C_{2v} symmetry is a first-order saddle point that corresponds to the transition state that links the two energy minima at the potential energy surface through rotation of the C1–C1′ bond. We preferred to use this structure because it is the one which the compound has during the complexes' formation. Every attempt to optimize

[PdCl$_2$(phen)] in the C_{2v} point group by employing basis sets with a quality superior to double-ζ was unsuccessful, giving a second-order saddle point. Optimization of the same complex with the selected basis sets under no symmetry constraint yielded a structure that is essentially equivalent (based on geometrical and NICS criteria) to that derived previously. Therefore, in our analysis we will use the first structure for uniformity reasons. The derived wavefunctions were found to be free from internal instabilities. The basis set used for all non-metal atoms was the well-known valence triple-zeta 6-311+G*.[30] The quasi-relativistic Stuttgardt–Dresden effective core potential of the type ECP28MWB and ECP60MWB was used when the central metal was Pd and Pt, respectively.[31] In the case of the Ni complex, a small core potential of the type ECP10MDF was used.[31] The core potentials were complemented by the respective valence basis sets. For all other calculations related to the investigation an additional diffuse and a polarization function was added to the hydrogen atoms. Preliminary calculations showed that the addition of a p-type polarization function to the metals' valence basis sets[2b] gave practically the same results and its addition was not selected in order to avoid further computational cost. NICS constants were calculated with the gauge-independent atomic orbital method (GIAO).[32] Finally, Mulliken population analysis was performed with the AOMix program.[33]

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