Density Functional Derived Structures and Molecular Properties of Nickel Dithiolenes and Related Complexes

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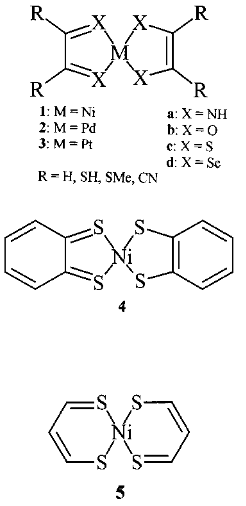
Keywords: Metal dichalcogenolene / Density functional calculations / Cyclic π-electron delocalization / Nickel

The molecular and electronic structure of the planar nickel dithiolene (**1c**, R = H) and of related complexes derived from nickel dithiolene by replacement of Ni by Pd (palladium dithiolene, **2c**, R = H) or by Pt (platinum dithiolene, **3c**, R = H), or by replacement of S by NH (nickel diiminolene, **1a**, R = H), O (nickel dioxylene, **1b**, R = H) or Se (nickel diselenolene, **1d**, R = H), were studied by density functional theory using the B3LYP functional and the valence triple-zeta basis set 6-311+G* for all atoms except Pd and Pt. For the latter atoms the quasirelativistic effective core potentials of the Stuttgart group were employed. The molecular structure of nickel dithiolene (**1c**, R = H) is satisfactorily reproduced by DFT calculations. The geometry of the corresponding platinum complexes **3a**–**3d** is more sensitive to relativistic effects, resulting in the contraction of the X–Pt bonds. As shown with the metal dithiolenes, the two ligands are structurally related to mononegative ions of open shell structure. The C–C bond lengths of the complexes are close to those of aromatic and chain-type polymethine structures (about 1.4 Å). The nickel dithiolene (**1c**, R = H) and related complexes have D_{2h} symmetry and are 14 π-electron systems with 10 π-electrons at the ligands and 4 π-electrons at the metal center. The natural population analysis has confirmed that metal M^{++} does accept electrons from the ligands but to a lesser extent than expected. The empty d-orbitals of M^{++} are only partly occupied in the molecular ground state. The positive charge of the metal decreases in the order Ni > Pd > Pt. The ^{1}H chemical shifts and the nucleus-independent chemical shifts (NICSs) of the ring moieties calculated by GIAO-DFT display a pronounced electron delocalization. In agreement with the calculated C–C bond lengths the ^{1}H chemical shifts and the NICS values show a marked bond delocalization. The NICS values show a change of the aromatic delocalization in the order Ni > Pd < Pt and NH > O < S < Se. The wave numbers of the IR spectra of the complexes calculated by DFT are grouped in separate frequency regions. The very intense absorption of **1c** (R = H) in the visible region of the spectrum is surprisingly well reproduced by ab initio single-only configuration interaction calculations. While the color band of the palladium complex is predicted to be red-shifted relative to the nickel complex, a blue shift is calculated on passing from the palladium to the platinum complex. The blue shift is, in part, due to the relativistic contraction of bond lengths in the Pt complexes.

Introduction

The complexes **1**−**4** (henceforth called metal diheterolenes) are 16-electron metal complexes. In the formal oxidation state of +2 they have a square-planar coordination and two planar bidentate ligand systems. In contrast to porphyrin-based complexes with a metal ion within the cyclic ligand and metallocene-type complexes with a metal ion intercalated between two planar ligands, diheterolenes 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.

Nickel dithiolenes were first synthesized in the 1960s and the results of the subsequent extensive research were reviewed by Schrauzer,[1][2] Eisenberg,[3] Hoyer,[4][5] Burns[6] and Mueller-Westerhoff[7] and co-workers. Early semiempirical quantum chemical studies revealed the ground-state configuration of the parent nickel dithiolene with the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) of π-type character.[1][2] The lowest unoccupied molecular orbital is mainly located at the ligand. Nickel dithiolene (**1c**, R = H) is a 14 π-electron system with five π-electrons at each ligand and four π-electrons at the nickel center.[8] This complex is clearly distinguished from the bis(3-thioxopropene-1-thiolato)nickel complex **5**, which is a 16-π system with six π-electrons at each ligand.



Scheme 1

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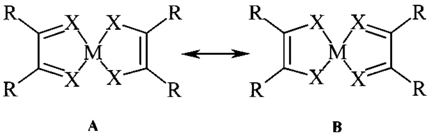
Viewed in terms of building units of appropriate oxidation states, the dithiolene complexes are derived from M^{2+} and two dimethine radical anions that are terminated by sulfur atoms. These components constitute the neutral complex. Such a ligand system is a member of a series of vinylogous $[N + 1]\pi$ polymethines (polymethine violenes) with $N = 4$.[9] In the composite complex the spins of the radical fragments are paired. This composition of the complex may suggest some biradical character and therefore a nonclassical fragment structure. In fact, to avoid nonsymmetrical formulae, nickel dithiolenes were first represented as resonance hybrids of two Lewis−Kekulé-type structures[1][2] **A** and **B**.



Scheme 2

Complexes related to nickel dithiolene (**1c**, R = H) contain metal atoms M, such as Pd (**2**) and Pt (**3**) in place of Ni (**1**), and hetero atoms X such as NH (**a**), O (**b**) or Se (**d**) in place of S (**c**). Nickel complexes are the most extensively studied so far in this field,[1−8,10] and knowledge about the Pd[11−13] and Pt complexes[14−17] is mainly restricted to compounds with more complex ligands or to metal−metal-bonded dimers.[18][19] The nickel complexes are unique in their electronic, optical and photophysical properties. The facile and reversible electron transfer of **1c**-type complexes has been taken as a model in the study of the function of nickel-containing enzymes.[4,5,20] Nickel dithiolenes may also serve as catalysts.[4][5] These compounds form stacks in the solid state or segregated stacks with donor molecules such as tetrathiofulvalene (TTF) and TTF-type compounds and are electric semiconductors or conductors ("1D metals").[21−27] Complexes with 2-thioxo-1,3-dithiole-4,5-dithiolate and related ligands have attracted particular attention. On the other hand, nickel dithiolenes are chromophores that exhibit intense long-wavelength absorptions in the visible or in the near infrared region of the spectrum[10,12,28−32] up to wavelengths of 1400 nm and with absorption coefficients as large as 80000 $cm^2 \cdot mmol^{-1}$. Given their ability to inhibit photofading of organic dyes they were studied in optical data storage systems[12] and, more recently, as near infrared laser dyes.[10][28] Nickel dithiolenes are versatile building blocks for the design of functional supramolecular arrays and polymer systems[33] and in the search for materials for the emerging optoelectronic technology. Conducting nickel dithiolenes and crown ethers form ion channels in the solid that are potential switches.[34] Efficient second-order NLO chromophores have been recently inserted in a layer of a nickel dithiolene derivative.[27]

We are aware of only a few high-level quantum chemical calculations on metal diheterolenes. These calculations were performed on particular complexes. The parent nickel dithiolene (**1c**, R = H) was calculated by Hartree−Fock,[35−37] by post-Hartree−Fock second-order perturbation theory[38] and by density functional theory.[12] The spin densities of a substituted nickel dithiolene[20] (**1c**, R = CN) were also studied by the latter method. The INDO-type semiempirical CIS approach was used in a basic study of structure and electronic excitation of nickel dithiolene.[8] Nickel dithiolene was first studied by extended Hückel[37] and Pariser−Parr−Pople calculations.[39]

The availability today of low-cost methods for density functional theory (DFT) and of well-defined quasirelativistic effective core potentials of transition metals enables more extended series of compounds to be studied. The purpose of this study is to calculate structure and structure-property relationships of the parent complexes **1**−**3** and of compounds derived from these by substitution of R (R = SH, SMe, CN) by density functional theory (DFT). For the sake of comparison, compounds **4** and **5** were also calculated. The question has been asked as to what extent electron excitation energies are satisfactorily predicted by ab initio calculations based on DFT optimum geometries.

Computational

DFT quantum chemical calculations were carried out using the 1994 release of the GAUSSIAN suite of programs.[40] The functional used throughout this study consists of a nonlocal hybrid HF/DF exchange functional as defined by Becke's three-parameter-equation[41] in conjunction with the nonlocal Lee−Yang−Parr correlation functional[42] (B3LYP for short). In numerous recent calculations DFT provided results that are comparable with those of post-Hartree−Fock ab initio quantum chemistry. For the sake of comparison, MP2 calculations were also performed with the inner electrons kept frozen. Open-shell structures were calculated by the unrestricted Kohn−Sham method. The eigenvalues of the S^2 operator, calculated as 0.76 and 2.03 at maximum, differ only slightly from the exact values (0.75 and 2.0, respectively) thus indicating low-spin contamination. The ground-state geometries were obtained by full geometry optimization. The optimum structures were confirmed by the Hessians. The second derivatives provided the harmonic vibrational frequencies, which were not corrected in this paper for anharmonicity and additional correlation effect by scaling. The calculations were performed by the valence triple-zeta basis set 6-311G augmented by a set of polarization and a set of diffuse functions at the nonhydrogen atoms. The basis set 6-311+G* was used throughout this study. Effective core potentials (ECP) were employed for complexes with Pd and Pt but not for the majority of calculations of complexes with Ni. Central to the concept of effective core potentials is the idea that electrons of the atomic inner shells are chemically inactive and can be substituted by an effective core potential instead being treated explicitly.[43][44] Furthermore, relativistic effects can be incorporated in full-relativistic or quasi-relativistic ECPs .[43−45] Calculations of Pt- and Pd-containing complexes were performed using the beyond Hartree−

Fock quasirelativistic effective core potentials ECP28MWB and ECP60MWB, respectively, which were developed by Stoll and Preuß.[46] The valence basis set is (8s7p6d)/[6s5p3d] in these cases[46] with an additional p-type polarization function for each of the two metals.[47] Since well-known relativistic effects may play an essential role in describing structure and properties of higher row transition-metal compounds,[43–45] the nonrelativistic effective core potential ECP60MHF[48] of Pt was also used for the sake of comparison. The calculations of ^{1}H chemical shifts and of the nucleus-independent chemical shifts (NICSs) were performed by the gauge-including atomic orbital procedure, designated by GIAO-DFT. Because of computational problems in calculating NICSs of complexes containing transition metals by hybrid HF/DF functionals using GAUSSIAN 94, δ(^{1}H) chemical shifts and NICS values were calculated by the BLYP functional.[49] NICS values are probes for the extent of "aromatic" electron delocalization in cyclic conjugated systems. These values were defined by von Ragué-Schleyer et al.[50] as the negative values of the isotropic magnetic shieldings in ppm calculated at the center of the rings. NICS1 values refer to the location 1 Å above the center. In the NICS1 values local contributions of the σ-bonds are reduced in favor of the π-effects.[51]

Electronic transition energies were calculated at DFT optimum geometries by full single configuration interactions (CIS) at the ab initio level of theory[52] using the 6-311+G* basis set. Atomic charges were derived by Weinhold's natural population analysis (NPA) using the natural orbital (NBO) partitioning scheme.[53][54] Along these lines the electron population of the π-type orbitals was evaluated in terms of the p_π and d_π contributions of the nonhydrogen atoms.

Results and Discussion

Structure

Selected structural data of the compounds 1–5, optimized by DFT, are collected in Table 1 along with the available experimental data. Experimental parameters were determined by X-ray structure analyses. The experimental data of the Pd complex refer to a substituted Pd dithiolene with monomeric subunits. Experimental M–X bond lengths were found to be shorter in the crystal than those of gas-phase structures.[55] In addition, DFT bond lengths of second and higher row main-group elements are systematically too large.[56] C–S bond lengths, for instance, are overestimated by about 0.03 Å. Given these limitations the agreement between theory and experiment is satisfactory.

Inspection of the data collected in Table 1 shows that the bond lengths are sensitive to the nature of the metal, M, as well as to the hetero atoms, X. As one would expect, the M–S bond lengths in the series of metal dithiolenes increase on passing from Ni–S (2.178 Å) to Pd–S (2.310 Å) and Pt–S (2.314 Å). Thus, the bonds of Pd–S and Pt–S are nearly equal in length. The Pt–S bond length is overestimated if relativistic effects are neglected (ECP60MHF of Pt). The Pt–S bond is contracted by 0.09 Å on replacing the nonrelativistic by the quasirelativistic effective core po-

Table 1. DFT-calculated bond lengths [Å] and angles [°] for complexes **1–5** and experimental data available (in italics)

	R	C–X	X–M	C–C	C–R	CXM	CCX	XMX	XMX′
1a	H	1.340	1.849	1.396	1.085	115.0	113.3	83.3	96.7
1b	H	1.295	1.839	1.396	1.088	111.3	115.6	86.2	93.8
1c	H	1.705	2.178	1.374	1.08	102.9	121.1	92.1	87.9
		1.687[a]	*2.100*	*1.357*	*0.950*	*107.8*	*117.9*	*88.5*	
		1.71[b]	*2.15*		*1.08*	*103*		*88*	*92*
1c	SH	1.715	2.177	1.396	1.775	104.2	120.1	91.4	88.6
1c	SMe	1.718	2.177	1.404	1.770	104.5	119.9	91.3	88.7
		1.70[c]	*2.13*	*1.40*	*1.74*	*105*	*119*	*92*	*88*
1c	CN	1.711	2.171	1.399	1.422	103.7	120.3	92.1	87.9
		1.72[b]	*2.15*		*1.37*	*107*		*91*	*89*
1d	H	1.854	2.296	1.363	1.086	101.4	122.1	93.0	87.0
2a	H	1.342	1.995	1.394	1.084	115.3	115.2	78.9	101.1
2b	H	1.296	2.002	1.396	1.086	111.6	117.8	81.2	98.8
2c	H	1.707	2.310	1.373	1.086	102.6	122.9	88.7	91.3
2c[d]		*1.690*	*2.295*	*1.397*		*99.2*	*124.6*	*92.5*	*87.5*
2d	H	1.855	2.423	1.363	1.086	101.0	123.9	90.2	89.8
3a	H	1.341	2.084	1.395	1.086	115.3	116.3	76.7	103.3
3a[e]	H	1.347	1.997	1.389	1.084	116.6	114.6	77.8	102.2
3b	H	1.294	2.098	1.398	1.089	111.5	119.2	78.7	101.3
3b[e]	H	1.304	2.005	1.387	1.086	112.9	117.1	79.9	100.1
3c	H	1.707	2.406	1.374	1.087	102.4	124.3	86.6	93.4
3c[e]	H	1.709	2.314	1.369	1.086	103.2	122.8	88.1	91.9
3d	H	1.857	2.515	1.364	1.087	100.7	125.1	88.2	91.8
3d[e]	H	1.859	2.429	1.359	1.086	101.5	123.7	89.6	90.4
4		1.728	2.173	1.424		104.3	119.6	92.2	87.8
5	H	1.681	2.226	1.388	1.088	116.6	131.6	97.1	82.9

[a] Ref.[8] – [b] Ref.[3] – [c] Ref.[37] – [d] Experimental data from averaged bond lengths of a substituted palladium dithiolene, see ref.[12] – [e] ECP60MWB of Pt instead of the ECP60MHF.

tential. The C−C bond lengths of the Pt complexes are only slightly shortened and the C−X bonds slightly lengthened. In the series **1c**−**3c** (R = H) the C−S bond lengths are nearly constant (1.71 Å). The lengths of these bonds are practically unaffected by the choice of the effective core potentials. According to the DFT calculations, substitution of the hydrogen atoms of nickel dithiolene by CN (**1c**, R = CN) results in a slight increase in the C−S and C−C bond lengths, whereas the Ni−S bond lengths are slightly shortened. The extension of the C−S bond length is confirmed by the X-ray data. However, the extension in the bond length of the C−C bond with donor and acceptor substitution is noticeable. The bond lengths increase from 1.374 Å (H) to 1.399 Å (CN) and 1.404 Å (SMe).

The C−C bond lengths of the complexes should be an indicator of the cyclic electron delocalization. The calculated C−C bond lengths are mostly affected by the hetero atom X and are in the range between 1.36 Å (X = Se) and 1.40 Å (X = NH). The latter value corresponds to the bond lengths of benzene. According to the C−C bond lengths the degree of bond delocalization decreases in the order NH = O > S > Se. The conjugated electronic system of the complexes appears more or less delocalized. As would be expected, the C−C bond lengths of the dithiolene **4** are more benzenoid if the C−C bonds are simultaneously part of an annulated benzenoid ring. These compounds seem to be only known as anions,[57] a situation that is in contrast to the analogous nitrogen-containing hetero compounds.[58]

In the case of nickel dithiolene (**1c**, R = H) the geometrical parameters were calculated both by DFT and ab initio MP2 with the same basis set 6-311+G* for all main atoms. The most interesting bond lengths are compared in Figure 1.

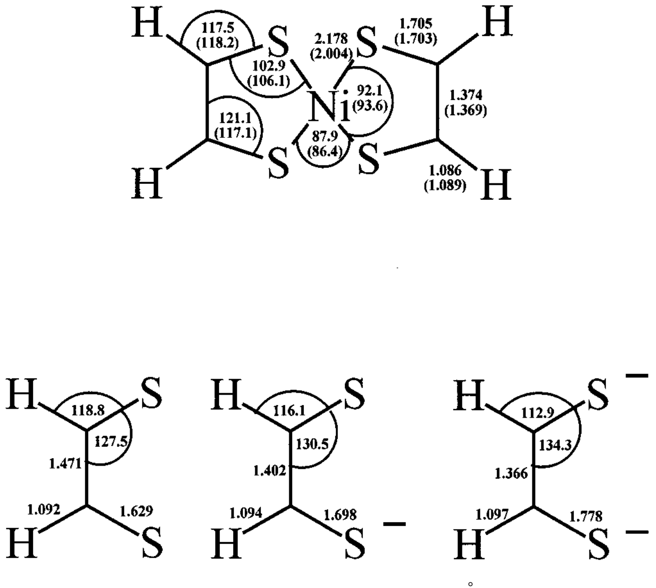


Figure 1. Comparison of selected bond lengths [Å] and bond angles [°] of nickel dithiolene (**1c**, R = H) calculated by DFT (B3LYP/6-311+G*) and by ab initio MP2/6-311+G* calculations (MP2 in parentheses) and the neutral, mononegative and dinegative ligand molecules

Except for the S−Ni bond the differences in the bond lengths calculated by the two theoretical models are remarkably small and confirm the good performance of DFT with respect to ab initio calculations. Because experimental geometries of **1c** (R = H)[3] do not refer to free molecules, the S−Ni bond length does not allow more detailed evaluation of the two methods. It should be mentioned that replacement of the all-electron treatment of Ni by the full-relativistic effective core potential ECP10MDF gives essentially the same bond lengths. The MP2 S−Ni bond length of nickel dithiolene (**1c**, R = H) reported in the literature[38] is between those found in this paper by the different theoretical models. This calculation was performed with a minimal basis set and the LANL1DZ effective core potential of Ni and S atoms.

The C−C bond lengths of the ligands in the complex differ greatly from those of the dithial and ethene-1,2-dithiolate ligand systems, which are the precursor compounds in the synthesis of the complex using reductive and oxidative conditions, respectively. However, the most closely related ligand is the sulfur-terminated dimethine radical. The C−C and C−S bond lengths of this radical are 1.402 and 1.698 Å, respectively, compared with 1.374 and 1.705 Å in the nickel dithiolene complex (see Figure 1).

Electron Distribution and Bonding

The total atomic charges and the population of π-type orbitals are determined by NBO analysis and are listed in Tables 2 and 3, respectively.

Table 2. Total atomic charges of the complexes **1**−**5** calculated by natural orbital population analysis (NPA)

	R	X	M	H_X	C	R
1a	H	−0.753	0.977	0.369	−0.035	0.184
1b	H	−0.624	1.167	−	0.159	0.173
1c	H	0.046	0.463	−	−0.384	0.221
1c	SH	0.030	0.489	−	−0.414	0.261
1c	CN	0.149	0.465	−	−0.284	0.019
1d	H	0.133	0.351	−	−0.443	0.222
2a	H	−0.727	0.837	0.369	−0.037	0.186
2b	H	−0.589	1.009	−	0.163	0.173
2c	H	0.079	0.334	−	−0.384	0.221
2d	H	0.163	0.239	−	−0.444	0.221
3a	H	−0.728	0.849	0.365	−0.034	0.184
3a[a]	H	−0.726	0.848	0.369	−0.045	0.188
3b	H	−0.592	1.015	−	0.167	0.171
3b[a]	H	−0.587	1.026	−	0.151	0.179
3c	H	0.074	0.351	−	−0.382	0.221
3c[a]	H	0.096	0.278	−	−0.389	0.224
3d	H	0.156	0.257	−	−0.442	0.221
3d[a]	H	0.181	0.172	−	−0.447	0.223
4		0.045	0.492	−	−0.211	0.085
5	H	0.006	0.466	−	−0.343[b]/ −0.273	0.216[b]/ 0.213

[a] ECP60MWB of Pt instead of the ECP60MHF. − [b] Non-adjacent to sulfur.

All parts of the molecules, viz. the metal M, the hetero atom X and the substituents R, affect the electron population markedly. M^{++} is an acceptor of electrons. The posi-

Table 3. Selected natural atomic orbital occupancies of π-type orbitals of the complexes **1−5** calculated by natural orbital population analysis (NPA)

	R	p_π(X)	p_π(M)	d_{yz}(M)	d_{xz}(M)	π_{total}(M)	p_π(C)	π_{total}[a]
1a	H	1.518	0.019	1.979	1.824	3.822	1.027	14
1b	H	1.601	0.022	1.984	1.838	3.844	0.938	14
1c	H	1.500	0.027	1.981	1.810	3.818	1.045	14
1c	SH	1.571	0.022	1.982	1.859	3.863	1.119	14.6
1c	CN	1.464	0.026	1.975	1.801	3.802	1.081	14
1d	H	1.498	0.024	1.987	1.798	3.809	1.049	14
2a	H	1.518	0.021	1.979	1.811	3.811	1.028	14
2b	H	1.601	0.018	1.987	1.847	3.852	0.936	14
2c	H	1.497	0.023	1.981	1.816	3.820	1.048	14
2d	H	1.493	0.020	1.985	1.814	3.819	1.052	14
3a	H	1.517	0.021	1.981	1.829	3.831	1.019	14
3a[b]	H	1.531	0.025	1.871	1.808	3.704	1.043	14
3b	H	1.599	0.016	1.989	1.871	3.876	0.932	14
3b[b]	H	1.612	0.021	1.979	1.739	3.739	0.953	14
3c	H	1.496	0.021	1.983	1.835	3.839	1.044	14
3c[b]	H	1.505	0.029	1.972	1.742	3.743	1.058	14
3d	H	1.492	0.018	1.986	1.834	3.838	1.049	14
3d[b]	H	1.503	0.025	1.979	1.743	3.747	1.060	14
4		1.531	0.024	1.984	1.773	3.781	1.041	14.1
5	H	1.525	0.014	1.913	1.989	3.916	0.946[c]/1.099	16

[a] Total population of π-type orbitals at the parent complexes. − [b] ECP60MWB of Pt instead of the ECP60MHF. − [c] Non-adjacent to sulfur.

tive charges alter in the order: Ni > Pd < Pt. The atomic charge of Ni in nickel dithiolene is +0.46. In other words, 1.54 electrons are transferred from the two ligands to Ni^{++}. The charge at the Ni increases to a maximum value of about +1 when S is replaced by N or O. Thus, the charge of the Ni is less than expected given the oxidation number of Ni^{II}. The negative charge at the hetero atoms, X, decrease in the order NH > O and becomes positive with S and Se. The carbon atoms adjacent to the chalcogen atoms are also negatively charged. As expected, substituents R may act as donors (SMe) or as acceptors (CN) relative to hydrogen. The effect of the CN acceptor group is characterized by the considerably reduced electron population at the hetero atoms X.

According to the NBO analysis, the occupation of the p_π orbitals of the metal center is negligibly small while the two d_π orbitals are occupied by about 3.8 electrons (see Table 3). The d_π orbital population of the carbon and the hetero atoms is less than 0.005 and, therefore, not listed in Table 3. The populations of the p_π orbitals of nickel dithiolene (**1c**, R = H) at the sulfur and carbon atoms (1.500 and 1.045, respectively) are reminiscent of those in the dimethine ligand system with values of 1.437 and 1.058, respectively. The highly delocalized π-system of the dimethine radical is essentially retained in the complex. The electron populations of the hetero atoms X shows that their donor strength in the π-system is in the order (NH, O) < (S, Se). Clearly, the more polarizable atoms are more strongly involved in the delocalization. Inspection of the electron occupation shows that the 4s and 4p orbitals of the metal center are hardly occupied. This clearly conflicts with the dsp^2-hybridisation model. According to the NBO analysis the d^8 element Ni is occupied by 9.54 electrons ($3d^{9.01}$ $4s^{0.45}$ $4p^{0.07}$) in the nickel dithiolene parent complex. The occupation of the metal 4p orbital is very low. There is an increasing doubt[59] as to whether NBO analysis provides an adequate occupation of (*n* + 1)p orbitals of transition metals. The occupation is considerably larger if p orbitals are enclosed in the valence shell.[60]

In agreement with Zerner et al.[8] the complex **1c** (R = H) is a 14π-electron system. According to the DFT calculations this conclusion holds for the whole series **1−3**. As expected, the metal complex **5** is a 16π-electron system. The electron structure of **5** differs slightly from **1c** (R = H) in the population of π-type orbitals of metal and hetero atoms and in the total amount of electrons that occupy π-type orbitals due to the presence of two more π-type orbitals at the two additional carbon atoms (see Table 3).

Spectral Properties

Because of their intense long-wavelength light absorption, nickel dithiolene and related compounds are well characterized by UV/Vis spectroscopy. For the whole series of compounds considered, one intense low energy electron transition appears in the visible or near infrared region. The calculated absorption wavelength of 623 nm (vertical transition) of nickel dithiolene (**1c**, R = H) has to be compared with the value of 719 nm measured in hexane.[8] Thus, the calculated absorption is about 100 nm in error, a deviation that corresponds to 0.27 eV in units of energy. In general, the error of CIS transition energies is larger.[61] According to CIS calculations of **1−3**, the color-determining π→π* ($A_g - B_{3u}$) transition is allowed and of large intensity. This finding is in agreement with previous semiempirical calculations on nickel dithiolenes.[1,2,8] The electronic transition is essentially determined by the HOMO−LUMO one-electron transition. The HOMO (b_{1u}) and LUMO (b_{2g}) are essentially localized over the two ligands (intra-ligand tran-

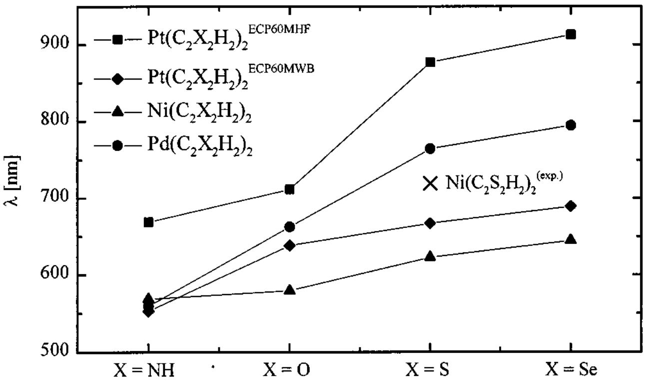


Figure 2. Absorption wavelengths [λ] of the complexes **1**−**3** (R = H) of the first intense electronic transition $\pi \rightarrow \pi^*$ in the visible region of the spectrum (experimental value λ_{max} in hexane see ref.[6])

sition). A $3d_\pi$-type orbital of the metal ion contributes to the LUMO to a minor extent only. Due to the HF-based single-only approximation the calculated oscillator strengths are too large. In accordance with the predominant localized nature of the frontier orbitals, the ligand-to-metal CT character of the color-determining transition is small and amounts only to 0.01 electrons. As long as the nonrelativistic effective core potential of Pt was used (ECP60MHF) for the CIS calculations the absorption wavelengths of the color band λ_{max} are predicted to increase in the order Ni < Pd < Pt and NH < O < S < Se for nickel dithiolene complexes (see Figure 2 and Table 4). However, the calculated absorption wavelength of the platinum complex is lower than that of the palladium complex if the quasirelativistic ECP60MWB for Pt is taken into account (see Figure 2 and Table 4). The spectral shift is clearly due to the relativistic Pt−S bond contraction that naturally results in an increased energy gap as well as the relativistic destabilization of the LUMO, which includes $5d_\pi$-type orbitals.[45] This conclusion was supported by additional calculations: The CIS absorption wavelengths were calculated by using both nonrelativistic and quasirelativistic ECPs for **3c**, whose geometry was optimized without consideration of any relativistic effects. The quasirelativistically calculated absorption wavelength is nearly 100 nm blue-shifted in comparison with that calculated nonrelativistically. If the absorption energy of **3c** is calculated with quasirelativistic ECPs and with the molecular geometry optimized in the same quasirelativistic approximation, then the absorption wavelength is nearly 200 nm blue-shifted.

Thus, the absorption wavelength is predicted to increase on passing from the Ni to the Pd complexes and to decrease from the Pd to the Pt complexes.

HOMO−LUMO energy gaps calculated by RHF ab initio methods are, in general, not used to estimate electron-excitation energies and the calculated energies are much to high. This is not the case with the corresponding Kohn−-Sham orbital gap (see Table 4). Encouraged by a recent study,[62] DFT energy gaps were also calculated. The results are listed in Table 4. As can be seen, both the energy differences of the Kohn−Sham frontier orbitals and the CIS excitation energies are nearly of the same order of magnitude and in the correct order: Ni < Pd ≥ Pt (see ref.[21]). Finer details, however, are not reproduced. Whereas the effect of the different metal ion is correctly calculated, the effect of the hetero atoms is at variance with the results of the CIS calculations.

It should be mentioned that the recently tested and very promising time-dependent density functional theory (TD-DFT) methods[63] predict the color band in the visible region at nearly the same absorption wavelength (656 nm) as CIS (623 nm) for nickel dithiolene (**1c**, R = H) based on

Table 4. Comparison of the energy differences of the Kohn−Sham frontier orbitals and CIS excitation energies

	R	ε_{HOMO}[a] [a.u.]	ε_{LUMO}[a] [a.u.]	$\Delta\varepsilon$[a] [a.u.]	ΔE [eV]	[nm]	ΔE_{CIS}[b] [eV]	[nm]
1a	H	−0.15037	−0.08315	0.06722	1.829	678	2.182	568
1b	H	−0.20313	−0.15266	0.05047	1.373	903	2.141	579
1c	H	−0.22805	−0.15912	0.06893	1.876	661	1.991	623
1c	SH	−0.20737	−0.15672	0.05065	1.378	900	1.619	766
1c	SMe	−0.18519	−0.13753	0.04766	1.297	956	1.546	802
1c	CN	−0.28825	−0.22461	0.06364	1.732	716	1.829	678
1d	H	−0.22971	−0.15967	0.07004	1.906	651	1.924	645
2a	H	−0.15019	−0.08835	0.06184	1.683	737	2.217	559
2b	H	−0.20223	−0.15734	0.04489	1.222	1015	1.872	662
2c	H	−0.22391	−0.16302	0.06089	1.657	748	1.623	764
2d	H	−0.22477	−0.16310	0.06167	1.678	739	1.561	794
3a	H	−0.14576	−0.08928	0.05648	1.537	807	1.854	669
3a[c]	H	−0.15440	−0.08106	0.07334	1.996	621	2.243	553
3b	H	−0.19993	−0.15966	0.04027	1.096	1131	1.743	711
3b[c]	H	−0.20899	−0.15573	0.05326	1.449	856	1.943	638
3c	H	−0.22022	−0.16608	0.05414	1.473	842	1.414	877
3c[c]	H	−0.22653	−0.15795	0.06858	1.866	664	1.858	667
3d	H	−0.22104	−0.16602	0.05502	1.497	828	1.358	913
3d[c]	H	−0.22664	−0.15812	0.06852	1.865	665	1.797	689
4		−0.22888	−0.16522	0.06366	1.732	716	1.734	715
5	H	−0.21786	−0.11090	0.10696	2.910	426	[d]	[d]

[a] HOMO and LUMO energies obtained by DFT. − [b] CIS excitation energies based on DFT optimum geometries. − [c] ECP60MWB of Pt instead of the ECP60MHF. − [d] More than one intense absorption between 200 and 300 nm (3.5 and 6 eV).

the DFT optimum geometry using the 6-311+G* basis. The TD-DFT calculation with the smaller basis set (6−31+G*) provides nearly the same absorption wavelength (655 nm) and is more economical.

Biradicaloid chromophoric ylides may have exceptional behavior in that the visible absorption features are well predicted.[64][65] Therefore, the question has been asked as to whether the complexes **1a−1d** may be biradicaloid as well. The biradicaloid character should be indicated by the S_0/T_1 splitting energy. The adiabatic S_0/T_1 energy gaps were therefore calculated by an energy-difference method by (U)DFT after optimization of the singlet and triplet molecules (see Figure 3). U in (U)DFT stands for unrestricted Kohn−Sham used in the calculation of the triplet molecule.

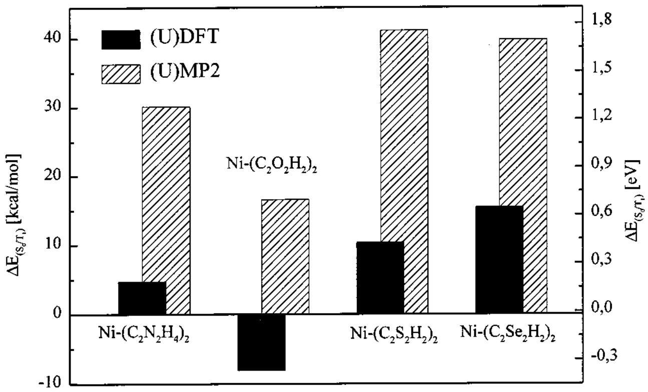


Figure 3. The adiabatic singlet/triplet (S_0/T_1) splitting energies of the complexes **1a−1d** (R = H) calculated by (U)DFT (B3LYP/6-311+G*) and (U)MP2 (B3LYP/6-311+G*)

Except for the oxygen-containing complex **1b** (R = H) all molecules are calculated with singlet multiplicity in the ground state. The adiabatic S_0/T_1 energy gap of nickel dithiolene (**1c**, R = H) calculated by (U)DFT is low (10.4 kcal/mol). Because (U)DFT seems to underestimate the singlet-triplet gap, the calculations were repeated on the (U)MP2 level of theory. In this approximation the energy gap amounts to 41.2 kcal/mol for nickel dithiolene. This splitting energy is clearly outside of the range of typical singlet biradicaloid organic compounds (about 25 kcal/mol[66]). In contrast to the (U)DFT calculations, (U)MP2 predicts the oxygen-containing complex **1b** (R = H) as a biradicaloid singlet molecule with an S_0/T_1 splitting energy of about 16 kcal/mol (see Figure 3).

The vibrational spectra of the parent structures **1a** (R = H), **2a** (R = H) and **3a** (R = H) have 45 normal modes, and all the other parent structures of the series **1−3** have 33 modes. Because of the D_{2h} symmetry the vibration belongs to 8 representations. Only vibrations due to the representations B_{1u} (out of plane), B_{2u} and B_{3u} (in plane) are allowed in the infrared spectrum and are considered in the following discussion. The calculated wave numbers are hardly dependent on the metal. The line spectra presented in relative intensity in Figure 4 are well grouped in few frequency regions.

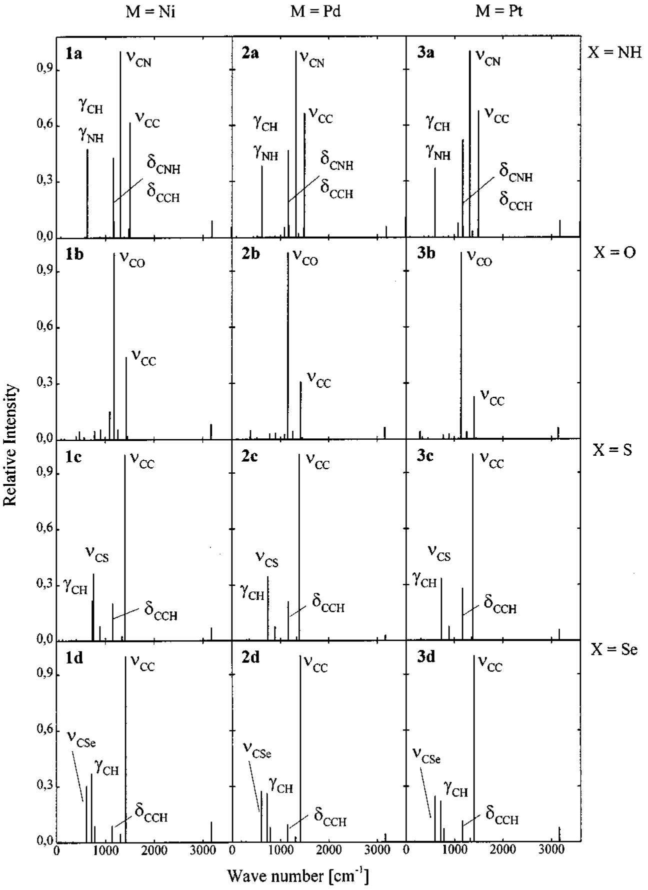


Figure 4. Line spectra of the allowed vibrations of **1−3** and assignments of the most intense transitions (relative intensity with respect to the most intense vibrational transitions)

As already documented in some cases, vibrations including the metal center are of small energy. The frequencies are lower than 500 cm^{-1} and of low intensity. However, the intensity of the whole spectrum seems to be greatly dependent on the hetero atoms X. The most intense IR vibrations are ν_{CN}, ν_{CO} and ν_{CC}.

The allowed vibrational frequencies of nickel dithiolene (**1c**, R = H) are compared with data of three experimental studies[67−69] in Table 5. In order to facilitate comparison of the frequencies they are classified according to the symmetry. This classification was also undertaken in two of the experimental studies.[67][68] As far as possible the assignments were given with the same descriptors. The assignments in refs.[67][68] were based on normal coordinate analyses and, in part,[67] on nickel isotope substitution.

The best agreement between the data predicted by DFT and experimental findings was reported by Schläpfer[67] et al. The assignment of the vibration for the systems reported in this paper is fully confirmed. The most intense calculated frequencies deviate by 40 cm^{-1} at maximum without scaling. Some vibrations, such as C−H, C−S and C=C, appear twice in the experimental spectrum.[67] Higher frequencies are overestimated because of the fact that anhar-

Table 5. Comparison of the allowed, calculated vibrational frequencies of nickel dithiolene (**1c**, R = H) with results of experimental studies (s = strong, vs = very strong)

	Descriptor	$\tilde{\nu}$ [cm^{-1}][a]	$\tilde{\nu}$ [cm^{-1}][b]	$\tilde{\nu}$ [cm^{-1}][c]	$\tilde{\nu}$ [cm^{-1}][d]
B_{2u}					
	δ_{SNiS}	311	237		
	ν_{Ni-S}	417	428	420	422
	ν_{C-S}	760 (s)	798	790	872
	ν_{C-S}				1099 (vs)
	δ_{CCH}	1151 (s)	1098 (s)	1092	
	δ_{CCH}		1110	1104	
	$\nu_{C=C}$, δ_{CCH}	1397 (vs)	1350 (s)	1340	1331 (vs)
	$\nu_{C=C}$, δ_{CCH}		1358		1346 (vs)
	ν_{C-H}				2933
	ν_{C-H}	3176	3018		3012
B_{3u}					
	$\delta_{SNiS'}$	127	76		
					132 (s) in-plane def$_{ring}$
					233 δ_{NiSC}, def$_{ring}$
	ν_{Ni-S}				309 (s)
	ν_{Ni-S}	410	398	420	311 (s)
	δ_{CCS}	637	735 (s)		
	ν_{C-S}, δ_{CCS}	892	865	714	
			878 (s)		
				874 δ_{C-H}, ν_{C-S}	
	δ_{CCH}		1260	1253	1258
	δ_{CCH}	1344	1295	1288	1296
	ν_{C-H}	3158	3030		3027
B_{1u}					
	out-of-plane$_{ring}$	52	131		85
	out-of-plane$_{ring}$	252	307		
	out-of-plane$_{C-H}$	738 (s)	760 (s)	754	718 (s)
					727
					747 (s)
					798

[a]Assigned by animation of the calculated vibrations (program: GAUSSIAN94, GAUSSVIEW). – [b] Ref.[67] – [c] Ref.[68] – [d] Ref.[69], no classification of the representations was given.

monicity has been neglected and insufficient consideration has been given to the electron correlation. The assignment in this study does not correspond with that of ref.[68] in the region between 700 and 800 cm^{-1} (see Table 5). The intense vibrations in the region 50 to 500 cm^{-1} found by Adams[69] et al. are also not confirmed.

The C=C frequency of the experimental and theoretical studies is remarkably low. For comparison, the IR spectrum of 2*H*-1,3-dithiole **7** was calculated. The metal of the five-membered ring is now replaced by CH_2. Whereas the C=C vibration of **7** was calculated at 1598 cm^{-1}, the C=C frequency of nickel dithiolene (**1c**, R = H) appears at 1397 cm^{-1}. The assignment of this vibration is more complicated, with the CCH bending also being involved in the vibration.

6 **7**

Scheme 3

The NMR chemical shifts may provide information regarding the electronic structure of the complexes. The paramagnetic ^1H chemical shift is a probe for cyclic electronic delocalization.[70] The results of the calculations are gathered in Table 6. The calculated ^1H chemical shifts are compared with experimental data of ref.[7] in the cases of **1c**, **2c**, **3c** and **5**. The theoretical ^1H chemical shifts of these compounds are slightly underestimated by our calculations compared to the experimental values.

For the sake of comparison the corresponding ^1H chemical shifts of 1,3-dithiolylium (δ = 8.95) (**6**) and 2*H*-1,3-dithiol (δ = 5.58) (**7**) were also calculated. Compound **6** is a prototype for a delocalized 6π-electron system with two sulfur atoms, while the bond system is fully localized in **7**. The proton shifts of the complexes **1**–**5** are strongly low-field shifted with respect to the shift in **7** and approach that of the cationic system **6**. Thus, all calculated compounds **1**–**3** seem to have a cyclic electron delocalization, which is in the order NH < O < S < Se and Ni ≈ Pd ≈ Pt.

Finally, Schleyer's nucleus-independent chemical shifts (NICSs)[50] are considered as a probe of "aromatic" delocalization (see Table 6). NICS values of less than about $\delta = -3$ indicate aromatic delocalization in organic compounds.[71] For nickel dithiolene the calculated NICS values are lower than $\delta = -8$ and indicate aromatic delocalization. According to NICSs the complex **5**, with two six-membered rings, appears to be less delocalized. Electron delocalization is also supported in the five-membered rings of the annulated aromatic rings of **4**. The NICS values of the benzene rings of **4** are about $\delta = -6.6$. The NICS values decrease in the order Ni > Pd > Pt if the Pt complexes were calcu-

Table 6. ^{1}H-NMR chemical shifts and nucleus-independent chemical shifts (NICS) [ppm] calculated by GIAO BLYP/6-311+G*, based on the B3LYP/6-311+G* optimum geometries

		X = NH	X = O	X = S[a]	X = Se
δ (^{1}H)	**1**	6.80	7.81	8.83 (9.14)	9.53
	2	6.92	7.72	8.80 (9.01)	9.72
	3	7.47	7.65	8.33 (8.77)	9.06
	3[b]	6.70	7.91	8.50 (8.77)	9.18
	5			8.49 (8.73) 6.98[c] (7.40)	
NICS/NICS1[d]	**1**	−9.73/−6.69	−8.78/−6.12	−8.09/−8.54	−9.09/−9.28
	2	−5.21/−5.03	−2.29/−4.05	−4.62/−5.76	−5.79/−6.30
	3	−4.12/−4.74	−0.09/−2.77	−2.89/−4.34	−4.09/−4.97
	3[b]	−6.28/−5.50	−4.53/−5.01	−5.76/−6.26	−6.90/−6.94
	4			−7.98/−8.54[e] −6.64/−8.51[f]	
	5			−1.37/−1.54	

[a] Experimental value from ref.[7] in parenthesis, measured in $CDCl_3$. – [b] ECP60MWB of Pt instead of ECP60MHF. – [c] The larger value of the ^{1}H-chemical shift belongs to the carbon atom adjacent to the sulfur atom. – [d] NICS/NICS1 of benzene: −7.7/−9.9, calculated by GIAO BLYP/6-311+G*; NICS/NICS1 of benzene: −9.7/−11.5, calculated by HF/6−31+G* (Schleyer et al.[50]). – [e] NICS/NICS1 of the five-membered ring. – [f] NICS/NICS1 of the annelated aromatic ring.

lated with the nonrelativistic effective core potential ECP60MHF. Thus, the aromatic delocalization of Pt-containing complexes appears low in this classification scheme. If relativistic effects for platinum are taken into account, the NICS values alter in the order Ni > Pd < Pt, and the Pt complexes seem to be more aromatic. NICS1 values confirm these conclusions. Less is known of specific effects of the metal on NICS values.

Conclusions

A series of iso-π-electronic metal complexes of the same topology was considered and calculated by the Hohenberg−Kohn−Sham density functional theory. Valence triple-zeta basis sets augmented by two sets of polarization functions and quasirelativistic effective core potentials for transition metals were used. As shown with nickel dithiolene, experimental bond lengths and bond angles are satisfactorily reproduced by DFT calculations. A remarkable relativistic M−X bond length contraction is calculated for platinum complexes. The calculated C−C bond lengths of all Ni, Pd and Pt complexes are in the range between 1.36 Å and 1.40 Å. The strong bond delocalization is supported by the proton chemical shift calculated by GIAO. The chemical shifts are low-field shifted with respect to protons at the double bond in a nonconjugated system. The aromatic delocalization is also supported by Schleyer′s nucleus-independent chemical shift. Ab initio CIS calculations predict satisfactorily an intense absorption in the visible region. The transition is essentially a $\pi \rightarrow \pi^*$ transition between HOMO and LUMO and is mainly located at the ligand. According to CIS calculations the wavelengths of the color band λ_{max} increases in the order NH < O < S < Se and Ni < Pd > Pt. The singlet/triplet (S_0/T_1) splitting energies of the complexes **1a**−**1d** (R = H) calculated by the energy difference method by (U)DFT is relatively small. The larger values obtained by (U)MP2 are more reliable. The biradicaloid character of nickel diheterolenes suggested by the formula representation with 5 π-electrons at each ligand is therefore not supported in general, except for the oxygen-containing complex. The electrons clearly interact strongly through the metal center

Acknowledgments

The study was supported by the "Deutsche Forschungsgemeinschaft" (Graduiertenkolleg: Struktur-Eigenschafts-Beziehungen bei Heterocyclen) and by the "Fonds der Chemischen Industrie".

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Received March 4, 1999
[I99085]