$A_z^c(\mathrm{Cu}^{2+}) = 40 \times 10^{-4}\ \mathrm{cm}^{-1}$; for "$S$" = $^3/_2$, $g_x^c = 2.345$, $g_y^c = 2.307$, $g_z^c = 2.205$, $A_z^c(\mathrm{Cu}^{2+}) = 44 \times 10^{-4}\ \mathrm{cm}^{-1}$. Kokoszka et al.[18] report the **g** and **A** tensor parameters for this complex doped with diamagnetic Zn^{2+}. This gives the EPR parameters for the isolated Cu^{+2} in the same environment as in the coupled system: $g_{2x} = 2.056$, $g_{2y} = 2.083$, $g_{2z} = 2.306$, and $A_{2z} = 139 \times 10^{-4}\ \mathrm{cm}^{-1}$. This allows for the calculation of the $\mathbf{g}_1$ tensor and the J/D ratio. Inspection of Table I shows that the average of $\mathbf{g}$("S" = $^3/_2$, $M_s = \pm^1/_2$) and $\mathbf{g}$("S" = $^1/_2$, $M_s = \pm^1/_2$) gives $\mathbf{g}_1$ (this is truly independent of the size of λ). The data result in $g_{1x} = 2.492$, $g_{1y} = 2.379$, and $g_{1z} = 2.166$. Further, since the sign of the hyperfine coupling constant cannot be determined from the EPR spectrum, A_2^c("S" = $^3/_2$, $M_s = \pm^1/_2$) = A_2^c("S" = $^1/_2$, $M_s = \pm^1/_2$), which, within experimental error, is as observed. From the values for $\mathbf{g}_1$, $\mathbf{g}_2$, $\mathbf{g}^c$, A_{2z}, and A_{2z}^c, five independent measures of the quantity $f_1(\theta)$ are found. The average of these five values is $f_1(\theta) = 0.88$. This gives $\lambda = +45$ or $\lambda = +3.2$. The correct choice for λ cannot be ascertained from this data, but J and D must have the same sign. The ground state is (primarily) $|^1/_2\ \pm^1/_2\rangle$, implying $J > 0$, so that $D > 0$ is also true. The important conclusion is that even when $|\lambda|$ is quite large (in this case it is possible that $J = 45D$) the EPR data is sensitive enough to observe the perturbations caused by the intermanifold coupling.

This example illustrates the need to consider coupling between spin manifolds when the EPR of spin-coupled systems is interpreted. Buluggiu[3] attributed the small deviation between the observed $\mathbf{A}_2^c$ and the predicted $\mathbf{A}_2^c$ to supertransferred spin density between the nickel and copper ions; the calculations presented here show that the interaction between spin manifolds does equally well in accounting for $\mathbf{A}_2^c$. In addition, the **g** tensor values are also consistently predicted. The sensitivity of the g values to the off-diagonal interaction is large: in the example presented here, if $\lambda = +45$, the ground state would be primarily $|^1/_2\ \pm^1/_2\rangle$ with only 2% admixture of $|^3/_2\ \pm^1/_2\rangle$, yet a significant and easily observable effect on the **g** tensor is noted. In general, unless $|J| > 50|D|$, perturbations in the **g** tensor due to the coupling of spin manifolds will be observed.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corp. for partial support of this research.

Appendix

Consider the system with basis set $|1\rangle$ and $|2\rangle$. The matrix elements of the Hamiltonian H are

$$\langle 1|H|1\rangle = H_{11}$$

$$\langle 2|H|2\rangle = H_{22}$$

$$\langle 1|H|2\rangle = \langle 2|H|1\rangle = V$$

This system diagonalizes to give energies

$$E_a = H_{11} + V \tan\theta$$

$$E_b = H_{22} - V \tan\theta$$

with wave functions

$$|a\rangle = (\cos\theta)|1\rangle + (\sin\theta)|2\rangle$$

$$|b\rangle = -(\sin\theta)|1\rangle + (\cos\theta)|2\rangle$$

where the rotation angle θ is defined by

$$\tan 2\theta = \frac{2V}{H_{11} - H_{22}}$$

Some useful relationships are

$$E_a - E_b = \frac{2V}{\sin 2\theta}$$

$$\cos 2\theta = (H_{11} - H_{22})[(H_{11} - H_{22})^2 + 4V^2]^{-1/2}$$

$$\sin 2\theta = 2V[(H_{11} - H_{22})^2 + 4V^2]^{-1/2}$$

$$\cos\theta = \pm[(1/2)[H_{11} - H_{22}][(H_{11} - H_{22})^2 + 4V^2]^{-1/2} + 1/2]^{1/2}$$

$$\sin\theta = \pm[(1/2)[H_{22} - H_{11}][(H_{11} - H_{22})^2 + 4V^2]^{-1/2} + 1/2]^{1/2}$$

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Electronic Ground States and Spectra of Square-Planar Nickel(II) Complexes with Aromatic Dithiocarboxylato Ligands

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The electronic structure and related properties of five nickel(II) complexes of chelating aromatic dithiocarboxylato ligands have been investigated by means of EHMO–SCCC calculations. Overlap populations, two-center energy terms, and computed atomic charges were found to provide adequate information on the mechanism of the π-back-bonding effect. The role of sulfur 3d AO's was revealed to be unimportant in determining the bonding mode. The trimeric nature of the complexes in the solid state in a "skewed-sandwich" form and their ability to form adducts with Lewis bases as well as their sulfur addition reactions affording perthio complexes by chelate ring expansion are explained in view of the energies and characters of the frontier MO's. Correlation of the electronic spectral data with calculated electronic transitions facilitated the characterization of all the observed bands for the square-planar $\mathrm{NiS_4}$ chromophores. The Δ_1 values related to ligand field strength were calculated from the energies of the ligand field states, taking into account configuration interaction with reasonable values for the interelectronic repulsion parameters. These values were found to be in excellent agreement with the positions of the 1,1-dithio ligands in the spectrochemical series.

Introduction

The electronic structure of square-planar complexes of Ni(II) with sulfur-containing conjugated ligands has attracted considerable interest.[1-6] Particular emphasis has been placed upon the interpretation of the observed electronic properties of these compounds with respect to their highly delocalized covalent bonding. Simple molecular orbital methods of the extended-Hückel[7-10] LCAO–MO–SCF type[11] as well as more sophisticated molecular calculations of the INDO–SCF–CI[12] and ab initio type[13] have

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been used to probe the electronic structure and related properties in the case of square-planar NiS_4 chromophores containing five- or six-membered chelating rings with a high degree of cyclic electron delocalization. However, analogous theoretical studies on the other very interesting class of square-planar NiS_4 chromophores containing four-membered chelating rings are very few. To our knowledge only LCAO-MO-SCF calculations on the bis(difluorodithiophosphato)nickel ($Ni(S_2PF_2)_2$), bis(dithiocarbamato)nickel ($Ni(S_2CNH_2)_2$), and bis(dithiobenzoato)nickel ($Ni(S_2CC_6H_5)_2$) complexes are available to date.[11] These approximate parameter-free molecular calculations involved an extensive use of the Mulliken-type approximation and some point charge approximation. In addition the sulfur 3d orbitals were not included in the basis sets used, and for the bis(dithiobenzoato)nickel complex the σ skeleton of the benzene ring was embodied in the core. However, due to the approximations used in these calculations, especially in the case of the bis(dithiobenzoato)nickel complex, some ambiguities still exist in the understanding of the chemical bonding within the complex. These ambiguities are mostly related to the contribution of the sulfur 3d AO's on the bonding effects of the ligands and the possible cyclic electron delocalization in the four-membered chelating rings of the NiS_4 chromophores as well.

In the study reported herein we have utilized the EHMO-SCCC method, including as well configuration interaction (CI) on the ligand field states, to investigate the electronic structure and related properties of some new square-planar Ni(II) complexes with hydroxy-substituted dithiobenzoato ligands.[14] In order to find out if the presence and the position of the OH groups in the phenyl ring have any significant effect on the electronic structure, reactivity, and spectra of the NiS_4 chromophore, the parent bis(dithiobenzoato)nickel complex has been also included in our calculations. Within this framework attempts have been made to interpret the electronic spectral data and some other very interesting properties of the compounds, such as their trimeric nature in the solid state in a "skewed sandwich" fashion, their ability to form adducts with Lewis bases, and their sulfur addition reactions affording perthio complexes by chelate ring expansion.

Computational Details

All calculations were performed in the framework of the extended-Hückel LCAO-MO method with self-consistent charge and configuration (EHMO-SCCC)[15,16] by using option 3 of the FORTICON-8 computer program.[17] In these iterative calculations the so-called "weighted H_{ij} formula" for the off-diagonal matrix elements (H_{ij}), which is a modified Wolfsberg-Helmholz formula, was used in order for the intriguing phenomenon of counterintuitive orbital mixing (COM) common in calculations on transition-metal complexes to be reduced.[18] Furthermore, a Madelung energy correction[17,19] was applied to the diagonal matrix elements H_{ii}. The value of 1.65 was used for the parameter K, as this value was found, by a series of calculations, to give the best agreement between the experimental and theoretical frequencies of the first ligand field transition $^1B_{1g} \leftarrow {}^1A_g$ of the complexes.

Orbital exponents for sulfur, carbon, oxygen, and hydrogen were those previously used.[20] The basis set of valence AO's for Ni consisted of 3d, 4s, and 4p with the last two being single Slater-type functions,[21] whereas the 3d functions were considered as contracted linear combinations of two Slater-type functions.[22] The exponents of the two d AO's were taken as 5.75 and 2.20 with corresponding relative weights of 0.5817 and 0.5890. The 4s and 4p exponents for Ni were taken as 1.925 and 1.250, respectively.

Due to the lack of literature data for the valence state ionization energies (VSIE) of the sulfur 3d AO's, their values were calculated by Hartree-Fock SCF calculations on the sulfur atom at different oxidation states. The VSIE obtained 56×10^3, 135×10^3, and 213×10^3 cm^{-1} for the 0, 1, and 2 oxidation states, respectively, and were fitted by least squares to the expresion $VSIE(q) = Aq^2 + Bq + C$, which describes the charge dependency of the VSIE, with $A = 0$, $B = 78$ and $C = 59 \times 10^3$ cm^{-1}.

Configuration interaction (CI) calculations were constrained only on the ligand field states resulting from the EHMO-SCCC calculations. The calculation of the two-electron molecular integrals J_{ij} and K_{ij} was done by means of the well-established expressions[23] for these matrix elements in terms of the Condon-Shortley F_2 and F_4 parameters. For all complexes the F_2 and F_4 parameters were taken as 55% of the free ion values, e.g. 950 and 76 cm^{-1}, respectively. These values are in accordance with those ($F_2 = 10F_4 = 800$ cm^{-1}) suggested by Gray et al.[9] for Ni(II) chelates of dithio ligands.

Geometries and Their Optimization

The geometry of the parent $Ni(dtb)_2$ complex was taken from a crystal structure determination[24] and regularized to give D_{2h} symmetry. This regularization needs only small changes of NiS bond lengths on the order of 0.01 Å, which, however have no significant consequences on the energies of the MO's, the changes observed being only on the order of 0.001 eV. The same geometry was also employed for the hydroxy-substituted (dithiobenzoato)nickel(II) complexes, but was optimized in each case with respect to the Ni-S and C-O bond lengths and the SNiS bond angle. The optimized values of Ni-S, C-O, ∠SNiS were found to be 2.187 Å, 1.35 Å, and 78.25°, respectively, for all complexes despite of the position of the hydroxyl group. These values are very close to those of the parent $Ni(dtb)_2$ complex (Ni-S = 2.197 Å and ∠SNiS = 77.80°), as well as those of other square-planar Ni(II) chelates of dithio ligands.[1b,24] Furthermore, for the 2-hydroxy- and 2,4-dihydroxydithiobenzoate ligands the linear conformation of the existing intramolecular hydrogen bond S···H-O was predicted by a series of calculations to be the most stable one. The same conformation was also adopted for the corresponding nickel(II) complexes as well. The coordinate system adopted was in accordance with the symmetry rules.

Results and Discussion

Electronic Structure of Complexes. The calculated eigenvalues and character of the molecular orbitals of main interest for the parent $Ni(dtb)_2$ complex in its diamagnetic singlet ground state are listed in Table I, whereas those of the hydroxy-substituted derivatives are summarized in Tables II and III.[25] For the parent $Ni(dtb)_2$ complex (Table I) the eigenvalues are also compared with those calculated by neglecting the sulfur 3d AO's from the basis set functions. It should be noted that only those MO's which are highly mixed with substantial metal and ligand character are given in the tables. A more complete listing of the MO's of main interest is given in the correlation diagram shown in Figure 1.

At first sight, one discovers from Figure 1 a large similarity between the energy-level schemes of all five molecules except for that part including the antibonding predominantly 3d orbitals localized mainly on the central atom. The sequence of the eigenvalues of these antibonding MO's is found to be $3d_{xy} > 3d_{z^2} > 3d_{x^2-y^2} > 3d_{xz} > 3d_{yz}$, with the obvious inversion of the $3d_{x^2-y^2}$ and $3d_{xz}$ orbitals in $Ni[(2\text{-}OH)dtb]_2$ and $Ni[(2,4\text{-}(OH)_2)dtb]_2$ complexes.

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Table I. Eigenvalues and Character of the Valence MO's of Main Interest for the Ni(dtb)$_2$ Complex

MO	eigenvalues,[a] 10^{-3} cm^{-1}	charge distribution, %			basis functions		%S: |3d⟩
		Ni	4S	Ph	Ni	S	
$6b_{1u}$	−60.1	4	90	6	z	z, xz, yz	89
$6b_{2g}$	−63.0 (−57.5)	0	15	85		z, xz, yz	14
$8b_{2u}$	−63.1	0	90	10		s, $x, y, x^2 - y^2, z^2, xy$	81
$5b_{1u}$	−63.4 (−52.2)	0	17	83		z, xz, yz	17
$11b_{3u}$	−65.5	2	91	7	x	s, $x, y, z^2, x^2 - y^2, xy$	68
$3a_u$	−69.0 (−68.9)	0	0	100			
$4b_{3g}$	−69.0 (−68.9)	0	1	99		z	
$13a_g$	−70.6 (−68.3)	6	88	6	s, $x^2 - y^2, z^2$	s, $x, y, z^2, x^2 - y^2, xy$	64
$9b_{1g}$	−75.6 (−67.5)	44	55	1	xy	s, $x, y, z^2, x^2 - y^2, xy$	26
$5b_{2g}$	−79.9 (−74.9)	2	61	37	xz	z, xz, yz	20
$4b_{1u}$	−83.2 (−77.2)	14	53	33	4p$_z$	z, xz, yz	23
$8b_{2u}$	−90.6 (−88.8)	0	95	5		$s, x, y, z^2, x^2 - y^2, xy$	9
$3b_{3g}$	−90.8 (−90.0)	34	66	0	yz	z, xz, yz	4
$10b_{3u}$	−91.4 (−91.3)	2	80	18	x	$x, y, x^2 - y^2$	
$2a_u$	−93.2 (−92.8)	0	100	0		z, yz	2
$12a_g$	−94.3 (−94.0)	78	20	2	z^2	s, x, y	
$11a_g$	−94.7 (−94.3)	80	5	15	$x^2 - y^2$	s, x, y, z^2, xy	2
$4b_{2g}$	−95.1 (−94.4)	68	8	24	xz	z, xz	4
$8b_{1g}$	−98.1 (−97.5)	18	63	19	xy	s, $x, y, xy, x^2 - y^2$	3
$2b_{3g}$	−98.8 (−98.8)	2	1	93	yz	z	
$1a_u$	−98.9 (−98.9)	0	1	99		z	
$1b_{3g}$	−99.9 (−99.6)	62	37	1	yz	z, xz	2
$3b_{1u}$	−100.2 (−99.9)	1	21	78	z	z	3
$10a_g$	−100.5 (−100.2)	3	53	44	$x^2 - y^2, z^2$	s, $x, y, z^2, x^2 - y^2$	1
$3b_{2g}$	−101.5 (−100.8)	19	13	68	xz	z, xz, yz	

[a] Figures in parentheses are the eigenvalues calculated by neglecting sulfur d AO's from the basis set.

Table IV. Atomic Net Charges and Orbital Populations for the Chelate Rings of the Ni(dtb)$_2$ Complex and the (dtb)$_2{}^{2-}$ Moiety

	Ni(dtb)$_2$			(dtb)$_2{}^{2-}$	
	Ni	S	C	S	C
net charge	+0.447 (+0.124)[a]	−0.252 (−0.158)	+0.161 (+0.189)	−0.722	+0.297
orbital pop.					
s	0.002 (0.363)	1.341 (1.656)	0.876 (1.209)	1.710	1.185
x	0.358 (0.002)	1.662 (1.392)	1.225 (0.882)	1.698	0.824
y	0.233 (0.267)	1.438 (1.498)	0.876 (0.879)	1.502	0.856
z	0.039 (0.047)	1.545 (1.612)	0.862 (0.841)	1.557	0.838
$x^2 - y^2$	1.907 (1.999)	0.086		0.083	
z^2	1.961 (1.972)	0.018		0.037	
xy	1.261 (1.274)	0.062		0.072	
xz	1.861 (1.952)	0.045		0.013	
yz	1.931 (2.000)	0.055		0.050	

[a] Figures in parentheses are the values calculated by neglecting sulfur d AO's from the basis set.

The major contribution to the σ-bonding arises from the lower energy MO's with symmetry species A_g and B_{1g} for the parent complex (D_{2h} symmetry) and A_g for its hydroxy-substituted derivatives (C_{2h} symmetry). These orbitals (Tables I–III) exhibit a significant metal 3d (d_{xy}, $d_{x^2-y^2}$, d_{z^2}, or their mixtures allowed by symmetry) character. It should be stressed that there is no participation of the nickel(II) 4s and 4p AO's in the chemical bonding of the complexes. The metal 4p$_z$ AO participates only in the LUMO's of the complexes, its contribution being 14% for all five complexes, and therefore does not essentially participate in the π-bonding of the complexes. This finding is significant in that the participation of the 4p$_z$ AO in the in-plane π-system of nickel(II) complexes with 1,1-dithio ligands was considered as a reason for its unavailability for axial σ bonds in base–adduct formation.[1,26]

The nickel 3d$_{xz}$ and 3d$_{yz}$ AO's contribute significantly to π-bonding through their interaction with the ligand group orbitals (LGO's) of appropriate symmetry. The π MO's with a strong 3d$_{yz}$ character are localized on the chelate rings, while those with a strong 3d$_{xz}$ character have an appreciable localization on the phenyl rings. The character of the MO's strongly suggest a degree of cyclic electron delocalization on the four-membered chelate rings, as a result of the π-back-bonding effect.

The inclusion of the sulfur 3d orbitals in the basis set does not greatly alter the results of the calculations. This is in agreement with the results of INDO–SCF–CI calculations on analogous complexes with NiS$_4$ chromophore containing five- and six-membered chelate rings.[12] The eigenvalues of both the occupied and virtual orbitals (Table I) are generally lowered by inclusion of the sulfur 3d AO's with the latter ones being more affected. This might be expected since most of the occupied orbitals have less than 4% sulfur 3d character, whereas the virtual MO's acquire greater 3d character.

Insights concerning the role of the sulfur 3d functions on the chemical bonding of the complexes under investigation can be further gained through the population analysis and charge distribution. The relevant data for the parent Ni(dtb)$_2$ complex only along with those of the (dtb)$_2{}^{2-}$ moiety are collected in Table IV.

From Table IV we notice that the inclusion of the sulfur 3d AO's into the calculation has the result of increasing the positive charge on the central atom and the negative charge on the sulfur atoms, as well. These changes strongly suggest a back-donation of electron density from the central atom to the ligands through the sulfur 3d AO's, which aquire a total electron population of 0.266. Further support of the back-donation effect is gained from a comparison of the net charges and the atomic orbital populations of the complex with those of the (dtb)$_2{}^{2-}$ moiety. Thus, although the negative charge on the sulfur atoms decreases upon complexation of the (dtb)$_2{}^{2-}$ moiety, the electron population of the

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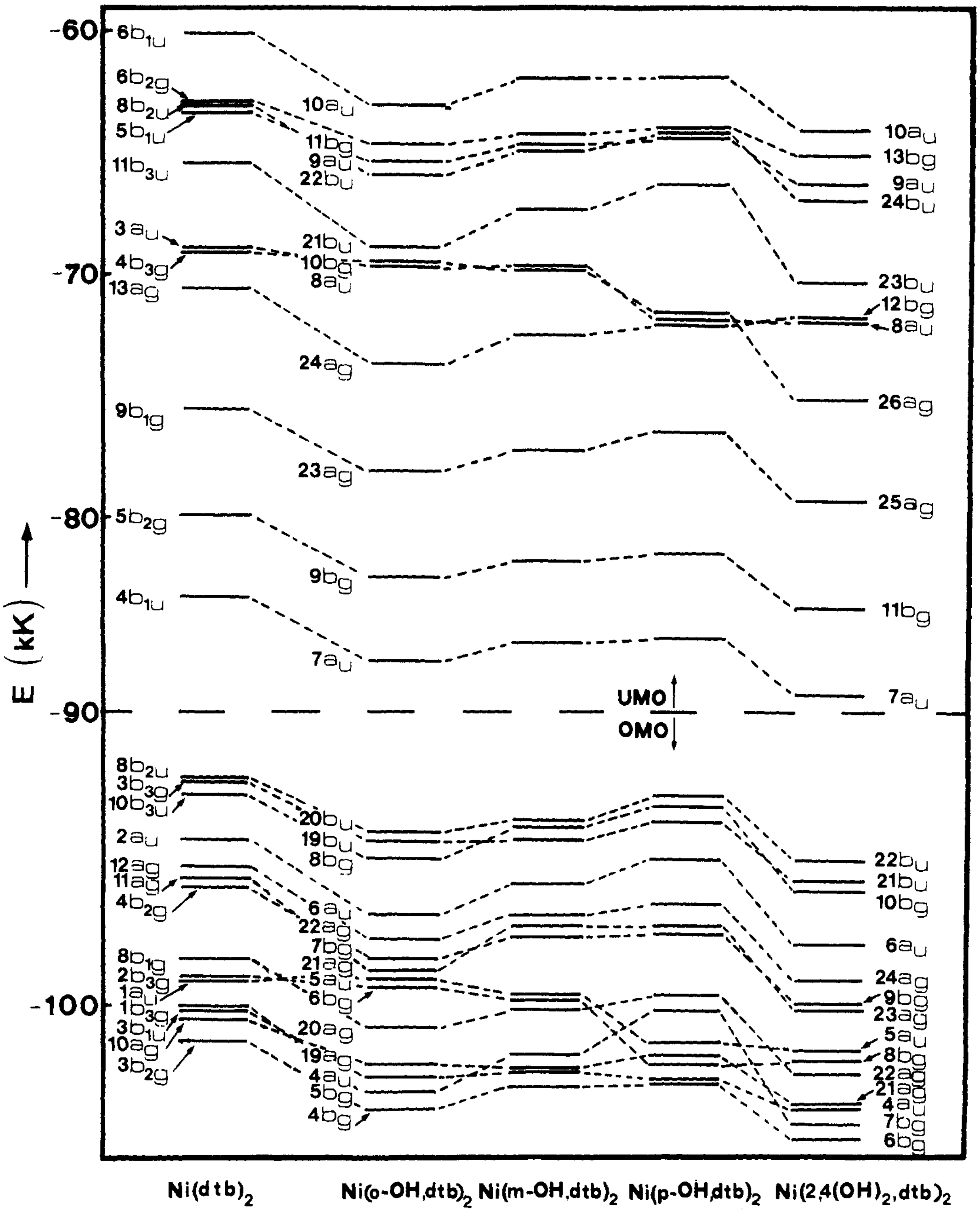

Figure 1. Correlation diagram of the molecular orbitals of main interest for the Ni(II)-dithio complexes.

sulfur $3d_{xz}$ and $3d_{yz}$ AO's increases. Therefore, there seems to be no doubt that the sulfur $3d_{xz}$ and $3d_{yz}$ AO's are indeed responsible for the π-back-bonding effect in the complex. The same is also true for the hydroxy-substituted derivatives whose net charges and atomic orbital and overlap populations are shown in Tables V and VI.[27] A comparison of these results with those of the parent complex clearly show the enhancement of the π-back-bonding effect by the introduction of the hydroxyl groups in the phenyl rings. In fact, the introduction of the hydroxyl groups has the result of increasing ρ(Ni-S). The increase of ρ(C-Ar) accompanied by the decrease of ρ(C-S) in the hydroxy derivatives clearly shows the higher degree of π-electron delocalization in these compounds.

Ground-State Properties. Let us now examine some important ground-state properties of the compounds under investigation in the light of the quantum chemical results.

First of all we consider the tendency of the compounds to increase their coordination number by trapping Lewis bases, affording adducts. It was verified experimentally that all five complexes react easily with pyridine to form 1:2 adducts, which in most cases were isolated and identified.[2,4,14] The capacity of the compounds studied for base-adduct formation can be rationalized in terms of the nature and energy of the frontier MO's. The major contribution to the σ-bond formation between the complex and the base arises from the interaction of the LUMO's of the complexes possessing 14% metal p_z character with the sp^2-hybridized orbital of the nitrogen donor atom of the base bearing the lone pair of electrons. This interaction is depicted schematically in Figure 2a. Moreover, the next LUMO (NLUMO) of the complexes, having energy very close to the energy of the LUMO and possessing 2% metal $3d_{xz}$ character, can also contribute to the axial bonding in the adducts. Thus it can be involved in a π-bond formation by the interaction with a π orbital of the pyridine molecule of appropriate symmetry. This interaction is shown schematically in Figure 2b. It should be noticed that the plane of the pyridine molecules would be expected to be coincident with the yz molecular plane as a result of the π-bond formation. However, this theoretical expectation must wait for an X-ray crystal structure determination in order to be confirmed.

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[27] Supplementary material.

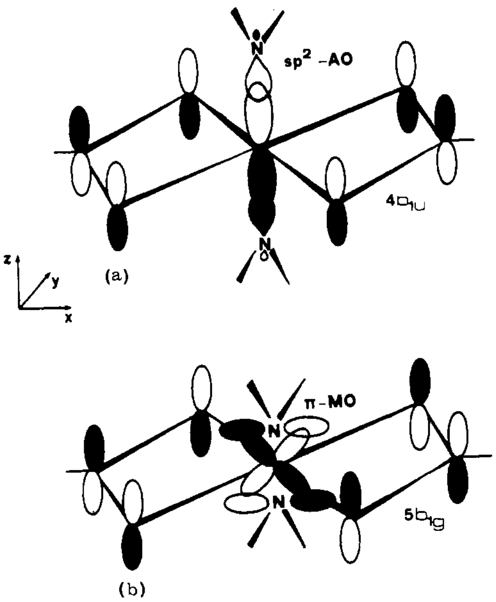

Figure 2. Schematic pictures of the orbital interactions accounting for the formation of pyridine adducts of the Ni(II)–dithio complexes: (a) σ-bond formation, (b) π-bond formation.

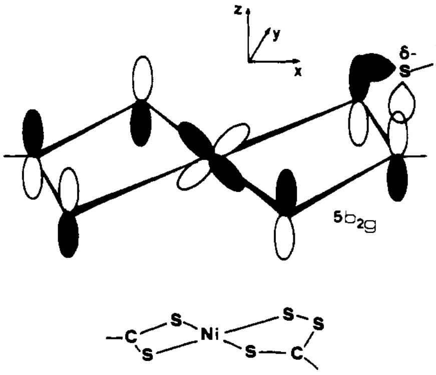

Figure 3. Schematic picture of the orbital interactions accounting for the chelate-ring expansion of the complexes upon reaction with elemental sulfur.

The character and energy of the frontier MO's could also account for the unusual ability of these compounds for chelate-ring expansion upon reaction with elemental sulfur.[28] Among the frontier orbitals, the NLUMO seems to play the most prominent role in the chelate-ring expansion due to its large localization within the CSS moieties. Thus, the first step of the chelate-ring expansion involves the interaction of the NLUMO with the sulfur's frontier MO's of appropriate symmetry bearing lone pairs of electrons. This interaction, depicted schematically in Figure 3, leads to the weakening of the C–S bond and the insertion of a sulfur atom between carbon and sulfur. Furthermore, if we take into consideration the planarity of the five-membered ring established by X-ray structure determinations,[28d] the insertion reaction must be accompanied by the twisting of the CSS* plane (S* is the label for the inserted sulfur atom). The twisting of the CSS* plane, becomes evident from the significant deviation of the phenyl ring plane from the plane of the five-membered ring established also by the X-ray crystal data. Therefore, there seems to be no doubt that the proposed orbital interactions are responsible for these unusual chelate-ring expansion reactions.

Another important property of the compounds under investigation is their trimeric nature in the solid state in a "skewed-sandwich" fashion. This structure, which was previously established by an X-ray crystal structure determination on the parent $Ni(dtb)_2$ complex,[24] could be explained in view of the nature and energies of the frontier MO's. It is obvious that for the NiS_4 chromophore the frontier MO's that will be responsible for the solid-state interactions of the isolated units are only those exhibiting significant metal $3d_{z^2}$ and $4p_z$ character and sulfur $3p_z$ character. For the complexes under investigation these MO's are the NNNNHOMO and LUMO with significant metal character and the NNHOMO with significant sulfur character. We are thus faced with two possible types of orbital interactions, each one leading to a different kind of solid-state interaction of the isolated units. The first type corresponds to the orbital interactions NNNNHOMO–LUMO–NNNNHOMO and LUMO–NNNNHOMO–LUMO and leads to a columnar structure of the trimeric forms with weak intermolecular metal to metal interactions. In contrast, the second type corresponds to the orbital interactions NNHOMO–LUMO–NNHOMO and LUMO–NNHOMO–LUMO and leads to a skewed-sandwich structure with weak intermolecular metal to sulfur interactions. Based on the energy-matching criterion the second type of orbital interaction is the most favorable one for the complexes under investigation. Therefore, all five complexes would be expected to adopt the skewed-sandwich structure in the solid state in agreement with the X-ray structural data of the parent $Ni(dtb)_2$ complex.[24] It is interesting to note that the columnar structure was found in the bis(dithioacetato)palladium(II) complex,[29] whose metal $3d_{z^2}$ AO appears in the HOMO.[30] For this complex the first type of orbital interaction (HOMO–LUMO–HOMO and LUMO–HOMO–LUMO in this case) would be the most favorable one on the basis of the energy matching criterion, explaining thus its columnar structure with weak Pd···Pd interactions.

Table VII. Electronic Transitions along with Their Assignments for the $Ni(dtb)_2$ Complex

ν,[a] 10^{-3} cm^{-1}		electronic transition	general classification
exptl	calcd		
13.2 (2.99)	13.2	${}^1B^+{}_{1g} \leftarrow {}^1A_g$	M(d) ← M(d)
15.2 sh (3.32)	15.1	$10b_{3u} \rightarrow 9b_{1g}$	M(d) ← L(π)
	15.9	$8b_{2u} \rightarrow 9b_{1g}$	
	16.6	${}^1B_{3g} \leftarrow {}^1A_g$	M(d) ← M(d)
16.9 (4.03)	16.7	$1b_{3g} \rightarrow 4b_{1u}$	L(π*) ← M(d)
18.2 sh (3.67)	17.7	$2a_u \rightarrow 9b_{1g}$	M(d) ← L(π)
	19.8	${}^1B_{1g} \leftarrow {}^1A_g$(LF)	
	21.3	${}^1B_{2g} \leftarrow {}^1A_g$(LF)	
23.0 sh (3.31)	23.3	$1a_u \rightarrow 9b_{1g}$	M(d) ← L(π)
	25.3	$12a_g \rightarrow 3a_u$	L(π*) ← M(d)
27.0 sh (4.45)	25.7	$11a_g \rightarrow 3a_u$	
	26.1	$4b_{2g} \rightarrow 3a_u$	
	28.8	$12a_g \rightarrow 11b_{3u}$	L(π*) ← M(d)
29.2 (4.90)	29.2	$11a_g \rightarrow 11b_{3u}$	
	29.5	$4b_{2g} \rightarrow 11b_{3u}$	
	29.8	$2b_{3g} \rightarrow 3a_u$	
	32.1	$3b_{2g} \rightarrow 3a_u$	L(π*) ← L(π)
34.2 (4.19)	35.5	$2b_{3g} \rightarrow 5b_{1u}$	

[a] Figures in parentheses are the log ϵ_{mol} values.

Electronic Transitions of Complexes. The electronic excitation energies of the parent $Ni(dtb)_2$ complex, calculated by using the EHMO–SCCC–CI method, are compared with the experimental peak positions of the corresponding absorption spectra in Table VII, whereas those of the hydroxy-substituted derivatives are summarized in Tables VIII and IX.[31] These tables contain all the electronic transitions allowed by symmetry along with their assignments. For a more precise characterization of the spectra we have utilized configuration interaction constrained on the LF states of the complexes. Furthermore, for all complexes we have considered that the NiS_4 chromophore belongs to the D_{2h} point group. The configuration interaction consisted of all single and

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(31) Supplementary material.

double LF excitations symmetry factored for each of the irreducible representations belonging to the point group D_{2h}, by making use of the hole formalism.[32] By solving then the corresponding four CI matrices we obtained the energies of the ligand field states, which have been used for the calculation of the electronic transition energies.

As can be seen from Tables VII–IX the agreement between the calculated and experimentally observed transitions is remarkably good. For all five complexes there are many allowed transitions in the entire region of observed spectral transitions including intraligand $L \rightarrow L^*$ and charge-transfer (CT) $L \rightarrow M^*$ and $M \rightarrow L^*$ transitions. In addition, there are forbidden LF transitions ($d \rightarrow d^*$), most of them being hidden under the more intense CT transitions. The only observable LF transition is that appearing in the region $(12.9\text{–}13.7) \times 10^3$ cm^{-1} of the spectra, which is assigned to the $^1B^+_{1g} \leftarrow {}^1A_g$ electronic transition.

It is interesting to compare for the five complexes the calculated energy difference $E(xy) - E(z^2)$, this quantity representing the ligand field splitting Δ_1 of the metal d orbitals. The values of Δ_1 are 18.7×10^3, 19.07×10^3, 19.39×10^3, 19.48×10^3, and 19.67×10^3 cm^{-1} for the parent complex and its 3-, 4-, 2-hydroxy- and 2,4-dihydroxy-substituted derivatives, respectively. According to these values the following spectrochemical series for the ligands under investigation can be proposed:

$$(2,4\text{-}(OH)_2)dtb^- > (2\text{-}OH)dtb^- > (4\text{-}OH)dtb^- > (3\text{-}OH)dtb^- > dtb^-$$

This series is in agreement with the spectrochemical series of the ligands under investigation established previously[33] from the $10Dq$ values of their octahedral complexes.

Concluding our discussion on the electronic spectra, it is important to note that despite the simplistic approach adopted in the calculations, for example the neglect of spin–orbit coupling, multiplet structure, and many electron effects, they have provided a reasonable basis for the interpretation of the spectra.

Registry No. Ni(dtb)$_2$, 20002-43-1; Ni(*o*-OH,dtb)$_2$, 20565-59-7; Ni(*m*-OH,dtb)$_2$, 101376-68-5; Ni(*p*-OH,dtb)$_2$, 101401-86-9; Ni(2,4-(OH)$_2$,dtb)$_2$, 54412-76-9.

Supplementary Material Available: Listings of the eigenvalues and character of the valence MO's of main interest for the hydroxy-substituted derivatives (Tables II and III), atomic net charges and orbital populations for the NiS$_4$ chromophore of the hydroxy-substituted dithiobenzoato complexes (Table V), overlap populations and two-center energy terms of the Ni–S bonds for the dithio complexes of Ni(II) (Table VI), and electronic transitions along with their assignments for the hydroxy-substituted (dithiobenzoato)nickel(II) complexes (Tables VIII and IX) (6 pages). Ordering information is given on any current masthead page.

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Octahedral d^3 and d^4 Complexes of Molybdenum with 1,2-Bis(dimethylphosphino)ethane

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Reaction of amorphous molybdenum dichloride with 1,2-bis(dimethylphosphino)ethane (dmpe) affords a convenient route to *trans*-[Mo(dmpe)$_2$Cl$_2$], while reaction of [Mo(CO)$_4$Cl$_2$] with dmpe leads to the formation of the seven-coordinate cation [Mo(dmpe)$_2$(CO)$_2$Cl]$^+$, isolated as the PF$_6^-$ salt and shown by a single-crystal X-ray diffraction study to have a capped-trigonal-prismatic geometry (orthorhombic space group *Pnma*, with $a = 13.483$ (3) Å, $b = 11.065$ (2) Å, $c = 17.796$ (3) Å, $\rho_{calcd} = 1.54$ g cm^{-3}, $\rho_{obsd} = 1.54$ g cm^{-3}, $Z = 4$, and $R_w = 3.83\%$). Cyclic voltammetry has established that the neutral dichloride is reversibly oxidized to *trans*-[Mo(dmpe)$_2$Cl$_2$]$^+$ with $(E_a + E_c)/2 = -0.510$ V vs. SCE. The cation can be obtained as the PF$_6^-$ salt if AgPF$_6$ is the oxidant, or as the SnCl$_3^-$ salt if SnCl$_2$ is the oxidant. The d^4 and d^3 dichlorides have both been characterized by single-crystal X-ray diffraction studies: [Mo(dmpe)$_2$Cl$_2$] crystallizes in the monoclinic space group $P2_1/c$ with $a = 13.218$ (3) Å, $b = 12.640$ (2) Å, $c = 13.327$ (3) Å, $\beta = 93.18$ (2)°, $\rho_{calcd} = 1.40$ g cm^{-3}, $\rho_{obsd} = 1.42$ g cm^{-3}, $Z = 4$, and $R_w = 3.22\%$, while [Mo(dmpe)$_2$Cl$_2$]SnCl$_3$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 14.756$ (4) Å, $b = 10.808$ (2) Å, $c = 18.572$ (5) Å, $\beta = 109.80$ (2)°, $\rho_{calcd} = 1.65$ g cm^{-3}, $\rho_{obsd} = 1.65$ g cm^{-3}, $Z = 4$, and $R_w = 4.01\%$. Both have octahedral geometries with trans dichlorides. [Mo(dmpe)$_2$Cl$_2$] can be reduced by 40% sodium amalgam in the presence of N$_2$ or CO to give [Mo(dmpe)$_2$(N$_2$)$_2$] and [Mo(dmpe)$_2$(CO)$_2$], respectively, both of which are formed as a mixture of the cis and trans isomers.

Introduction

We have recently been examining the chemistry of some of the electron-rich complexes formed by the strongly σ-donating bischelate phosphane (CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$ (dmpe), and a brief report[1] on the existence and paramagnetism of the 16-electron complex [Mo(dmpe)$_2$Cl$_2$], together with our recent observation of unusual hydrogen abstraction reactions from some paramagnetic transition-metal alkyls,[2-4] have led us to attempt to prepare the 16-electron alkyl complex [Mo(dmpe)$_2$(CH$_3$)$_2$]. A recent publication on the preparation of the isologous complex [Cr(dmpe)$_2$(CH$_3$)$_2$][5] has prompted us to report some of our results in this area, including the development of a synthetically convenient route to *trans*-[Mo(dmpe)$_2$Cl$_2$] from "monomeric" MoCl$_2$,[6] one-electron oxidation of this complex to the 15-electron cationic complex [Mo(dmpe)$_2$Cl$_2$]$^+$, and reduction of [Mo(dmpe)$_2$Cl$_2$] under N$_2$ to give the dinitrogen complexes *cis*- and *trans*-[Mo(dmpe)$_2$(N$_2$)$_2$]. The closely related d^4 and d^3 dihalides [Mo(dmpe)$_2$Cl$_2$] and [Mo(dmpe)$_2$Cl$_2$]$^+$ have been structurally characterized, as has the seven-coordinate cation [Mo(dmpe)$_2$(CO)$_2$Cl]$^+$.

Experimental Section

General Data. All manipulations were carried out under a dry, oxygen-free atmosphere of nitrogen. Most solvents were freshly distilled

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