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On the Electronic Structure and Spectroscopic Properties of d^8-Metal Mixed-ligand Complexes with S/O-donor and N-acceptor Ligands

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Abstract

The structural and spectroscopic properties of d^8-metal mixed-ligand complexes with sulphur- or oxygen-containing donor ligands (dithiolates and catecholates) and nitrogen acceptor ligands of the α-diimine type are studied by qualitative MO considerations. Whereas the HOMO is located mainly on the sulphur ligands with only small metal contributions, the LUMO is located exclusively on the diimines. As the characteristic property of the complexes under discussion an interligand charge-transfer from the donor to the acceptor site has been found. The dependence of the interligand charge-transfer band on the energies of the acceptor and the donor niveau is investigated, resulting in a maximum spectral shift of $\Delta\bar{\nu} = 6480$ cm^{-1} for [Ni(mnt)*N*,*N*] mixed-ligand complexes, where mnt = maleonitriledithiolate and *N*,*N* = aliphatic or aromatic diimines.

Introduction

Besides the well-known charge-transfer processes between a ligand and a transition-metal centre (MLCT or LMCT), interligand charge-transfer transitions between a donor ligand MO and an energetically low-lying acceptor ligand MO (LL′CT) in a mixed-ligand system are of increasing interest [1–8]. This type of transition was first described by Miller and Dance who investigated nickel complexes containing both dithiolate and α-diimine ligands [1]. In the electronic spectra of these mixed-ligand complexes an intense broad absorption band in the visible can be observed which is absent in the spectral pattern of the parent bisdithiolates $[\mathrm{Ni}(S,S)_2]^{2-}$ and the bis-diimine complexes $[\mathrm{Ni}(N,N)_2]^{2+}$. This low-energy absorption is markedly medium dependent and can also be influenced by substituents on the diimine as well as on the dithiolate ligand.

Continuing our investigations concerning the π acceptor ability of α-diimines [9, 10], we systematically studied various nitrogen acceptor ligands in [Ni(mnt)*N*,*N*], where mnt = maleonitriledithiolate and *N*,*N* = aliphatic or aromatic diimine, and obtained a maximum bathochromic shift of $\Delta\bar{\nu} = 6480$ cm^{-1} (*N*,*N* = diacetyldihydrazone: $\bar{\nu}_{\mathrm{CT}} = 21\,230$ cm^{-1}; *N*,*N* = phenanthrenequinone diimine: $\bar{\nu}_{\mathrm{CT}} = 14\,750$ cm^{-1} [8]). The substitution of mnt by aromatic dithiolates leads, as a consequence of an energy destabilization of the donor MO located on the sulphur ligand, to a further bathochromic shift of the LL′CT band.

As discussed in previous work, low-energy charge-transfer bands are of general importance concerning the spectral sensitization of photocatalytic systems with light-sensitive coordination compounds [11, 12]. Ligand combinations which improve the light-gathering characteristics of a complex enhance its potential for solar energy conversion and other applications. The purpose of the present work is a detailed study of the electronic structure and the spectroscopic properties of d^8-metal complexes with dithiolate/catecholate and α-diimine ligands.

Calculational and Experimental Details

The extended Hückel method has been used in its standard version, with charge iteration on the central atom [13, 14]. The values of the valence orbital ionization potentials (VOIP) are taken from ref. 15. Single Slater-type orbitals were used for the main group elements and for the s and p functions of the metals, while the d wave functions were taken as a contracted linear combination of two Slater-type functions. The various orbital exponents have been published by Richardson *et al.* [16] and Summerville and Hoffmann [17].

The bond lengths and angles of the complexes were taken from X-ray crystallographic data [18–26]. The internal coordinates used for the α-diimines are given in ref. 9.

The aliphatic diimine ligands [27, 28], disodium maleonitriledithiolate $\mathrm{Na_2mnt}$ [29] and *o*-xylol-4,5-dithiolate [30] were synthesized by published procedures. Other chemicals used were of analytical reagent grade. The nickel mixed-ligand complexes

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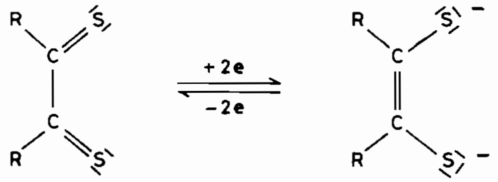
were prepared by the following procedure [8]: to a solution of 1 mmol Na$_2$mnt in 30 ml methanol 1 mmol diimine in 20 ml chloroform was added with stirring. After dropwise addition of 1 mmol NiCl$_2\cdot$6H$_2$O in methanol the reaction mixture was stirred and the formed precipitate was filtered off, washed with acetone and dried under vacuum. In some cases heating under reflux is required to get complete precipitation.

Electronic absorption spectra were recorded on a Specord M 40 of VEB Carl-Zeiss-Jena. Spectrograde solvents were used for all spectroscopic measurements.

Results and Discussion

Square-planar complexes with conjugated sulphur-containing ligands are interesting examples of compounds with highly delocalized covalent bonding. A number of MO calculations on metal dithiolenes have been reported [31–36]. However, the MO order in the valence region varies from one calculation to another. Therefore, a short discussion of the coordinative properties of the dithiolate ligand and the orbital characteristics of the bis(dithiolate)-nickel(II) anion as parent compound of the mixed-ligand system under study will be given.

Dithiolenes can be considered as neutral (**I**) or dianionic (**II**) ligands, differing in the number of π electrons: the neutral dithioglyoxal (dtg) has four π electrons, whereas the dianionic dithiolate has six.



I **II**

Figure 1 shows the MO diagrams of both forms. Representations are given for all ligand orbitals that contribute significantly to the valence MOs of the metal complexes. Hydrogen atoms have been omitted for the sake of clarity. The symmetry labels are taken from the C_{2v} point group. The 5a$_1$ and 4b$_2$ orbitals of dtg interact with the $d_{x^2-y^2}$ and d_{xy} orbitals of the metal in a σ fashion, respectively. They are primarily localized on sulphur. The 1a$_2$ and 2b$_1$ dtg orbitals interact with the metal d orbitals in a π fashion. The 1a$_2$ orbital is a doubly occupied carbon–sulphur π-bonding level and the 2b$_1$ orbital of dithioglyoxal a carbon–sulphur π^*-antibonding orbital. This χ_3-type π MO of the underlying butadienoid system is doubly occupied for the dithiolate. Therefore, assuming the presence of a dithiolate structure (**II**) in the d^8-metal bis-dithiolene anion, π back donation effects are negligible. Otherwise, the bisdithiolates have energetically high-lying donor orbitals enabling these compounds to form charge-transfer complexes with organic acceptors [37–40].

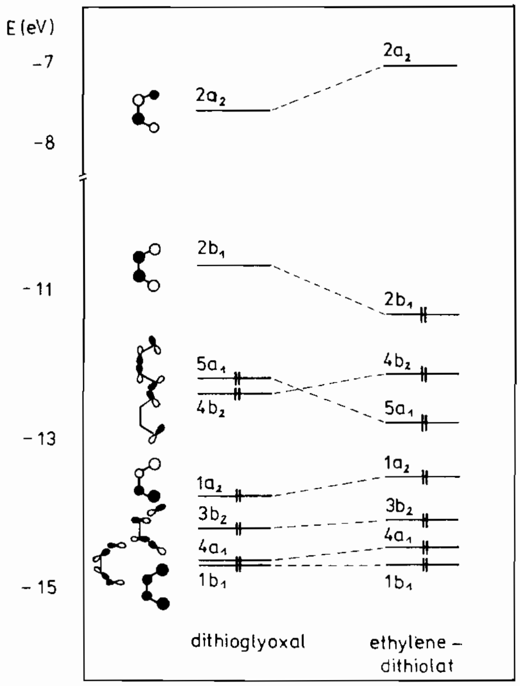


Fig. 1. Molecular orbital diagrams of dithioglyoxal and ethylenedithiolate; the symmetry labels are taken from C_{2v} point group.

The MO diagram of [Ni(edt)$_2$]$^{2-}$ (edt = ethylenedithiolate) shows the usual pattern for square-planar transition-metal complexes (Fig. 2). The characteristic feature of this complex type consists in a significant mixing between metal and ligand orbitals. The d_{xz} function strongly interacts with the 2b$_1(\pi)$ orbital of the sulphur ligand, whereas the two d orbitals of a$_g$ symmetry (d_{z^2} and $d_{x^2-y^2}$) combine with ligand σ orbitals of appropriate symmetry. In accordance with other semiempirical calculations by Schrauzer and Mayweg [31], Shupack *et al.* [32] and with the results of X$_\alpha$-calculations given by Sano *et al.* [33], there are four orbitals with predominant d population as the highest occupied ones. Below the d block (−9.8 to −10.4 eV) two χ_3-type π orbitals are present, followed by four lone pair orbitals which are mainly located on sulphur. The two χ_2-bonding MOs of the butadienoid structure are positioned at lower energy. The corresponding χ_1 MOs are not shown in Fig. 2.

The combination of a dithiolate and a nitrogen-containing acceptor ligand in a nickel(II) mixed-ligand complex is shown in Fig. 3. The delocalization of electronic density within the metal–edt unit is markedly decreased, and the HOMO of [Ni(edt)dim], where dim = glyoxaldiimine, is almost

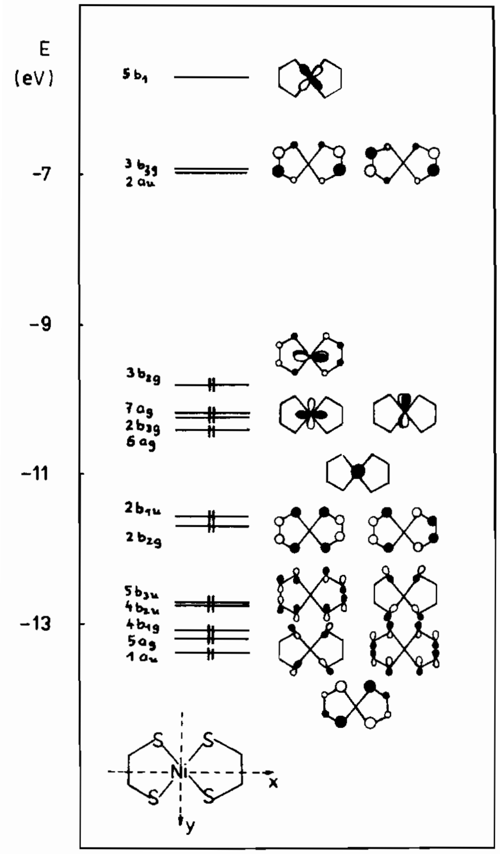


Fig. 2. Molecular orbital diagram of $[Ni(edt)_2]^{2-}$; the symmetry lavels are taken from D_{2h} point group.

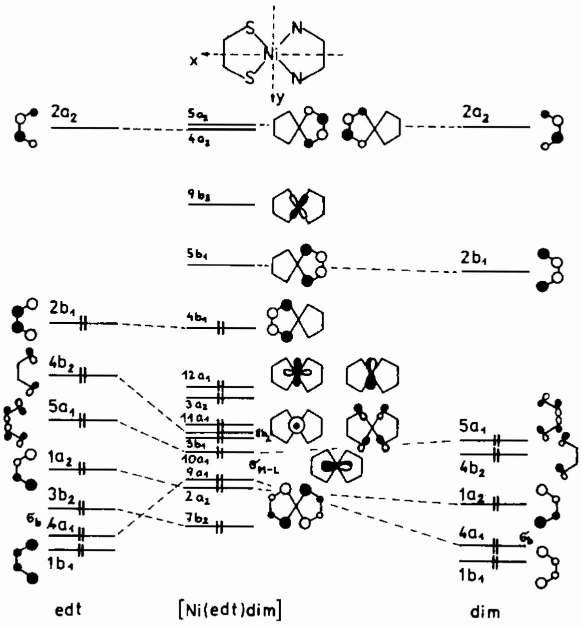


Fig. 3. Orbital interaction diagram of [Ni(edt)dim].

completely located on the sulphur ligand. The energies and components of the valence orbitals of [Ni(mnt)gmi] (gmi = glyoxal-bis(methylimine)) are given in Table I. As the highest occupied MO of all [Ni(mnt)N,N] complexes under discussion a π b_1 MO is obtained which primarily consists of S 3p and C_{mnt} 2p orbitals with a small d_{xz} contribution.

TABLE I. Valence-shell MOs of [Ni(mnt)gmi]

Symmetry	Orbital energy (eV)	Orbital population (%)					
		Ni	mnt			gmi	
			S	C	N	N	C
$8b_1$	−6.85			75^{π}	24^{π}		
$7a_2$	−6.95					18^{π}	81^{π}
$15b_2$	−7.24			68^{σ}	27^{σ}		
$18a_1$	−7.75			66^{σ}	30^{σ}		
$14b_2$	−8.26	$46(xy)$	24^{σ}			22^{σ}	
$6a_2$	−9.40		10^{π}	64^{π}	25^{π}		
$7b_1$	−10.34					45^{π}	46^{π}
$6b_1$[a]	−11.66		36^{π}	35^{π}	9^{π}		
$17a_1$	−12.37	$52(x^2-y^2)$	21^{σ}	16^{σ}			
$5a_2$	−12.40	$57(yz)$	23^{π}				
$16a_1$	−12.71	$29(x^2-y^2)$	10^{σ}			25^{σ}	10^{σ}
$15a_1$	−12.92	$72(z^2)$					
$5b_1$	−13.00	$67(xz)$		17^{π}			
$13b_2$	−13.02		59^{σ}			25^{σ}	
$12b_2$	−13.36		22^{σ}	31^{σ}	40^{σ}		
$4a_2$	−13.55		25^{π}			48^{π}	15^{π}

[a] The highest occupied MO.

However, it should be noted that because of the neglect of interelectronic repulsion inherent in the extended Hückel method, the final VOIP values of nickel are predicted probably at too low energies, and the metal contribution to the HOMO could be somewhat larger.

There is some disagreement in the literature concerning the nature of the HOMO of this mixed-ligand complex type. Miller and Dance concluded from electrochemical investigations an 'oxidation orbital' with mainly metal (d_{yz}) character and a small diimine contribution. Vogler *et al.* [4] suggest a dithiolate-based orbital as highest occupied molecular orbital for the d^8-metal mixed-ligand compounds under consideration with the possible exception of [Ni(mnt)dad] (dad = diacetyldianile). Generally, the oxidation potential depends very much on the nature of the dithiolate ligand. As a result of our calculations for both mnt and benzenedithiolate (bdt) nickel(II) complexes with various diimines, a mainly on the sulphur ligand centered MO has been obtained where the metal contribution in the former case is higher (12%) than for the aromatic dithiolate (5%). The occupied MOs with a metal d orbital as main component are in order of decreasing energy $17a_1$ ($d_{x^2-y^2}$), $5a_2$ (d_{yz}), $15a_1$ (d_{z^2}) and $5b_1$ (d_{xz}). Therefore, the nickel atom is considered to have d^8 configuration. The relative order in a crystal field sense corresponds to a square-planar arrangement of the ligands. As a consequence of the planar arrangement of two bidentate ligands, the e_g level splits up giving nondegenerated d_{xz} and d_{yz} functions.

The LUMO (b_1 symmetry) of [Ni(mnt)gmi] can be described as a pure π orbital of the α-diimine followed by a virtual $6a_2$ π MO of mnt and the d_{xy} metal orbital. The net charge of 0.21 on nickel is in accordance with other theoretical results for bis-dithiolate nickel(II) and related systems [32–34]. The total d population of the ^1A_g state (8.86) indicates that the system tends to approach rather a d^9 configuration.

The intense low-frequency absorption band is assigned to the allowed x-polarized $6b_1 \rightarrow 7b_1$ transition. As can be seen from the MO diagram of [Ni(mnt)gmi] this low-energy transition is of dithiolate → diimine CT character (LL'CT). Using Burns functions [41] a $6b_1$–$7b_1$ energy separation of 2.06 eV (= 16617 cm^{-1}) is obtained which is in surprisingly good agreement with the absorption band energies of these compounds estimated experimentally. Application of Slater exponents provides a LL'CT transition in the NIR region. A detailed NDDO/CI study of the absorption spectra of these mixed-ligand complexes is in preparation [42].

The π electronic densities of the ground and the lowest CT excited states are shown in Fig. 4. Significant redistribution of electronic density proceeds from the $^-S{-}\underset{|}{C}{=}\underset{|}{C}{-}S^-$ substructure of the sulphur ligand to the diazabutadiene system of the nitrogen acceptor ligand. The π density within the CN groups of mnt and of the metal is nearly unchanged. The resulting brutto transition of 0.81 electrons is accompanied by a partial charge compensation within the mixed-ligand complex unit. Assuming a LL'CT excitation from sulphur donor to the diimine acceptor ligand the transition is in opposite direction to the ground state dipole and therefore a blue shift in more polar solvents is observed.

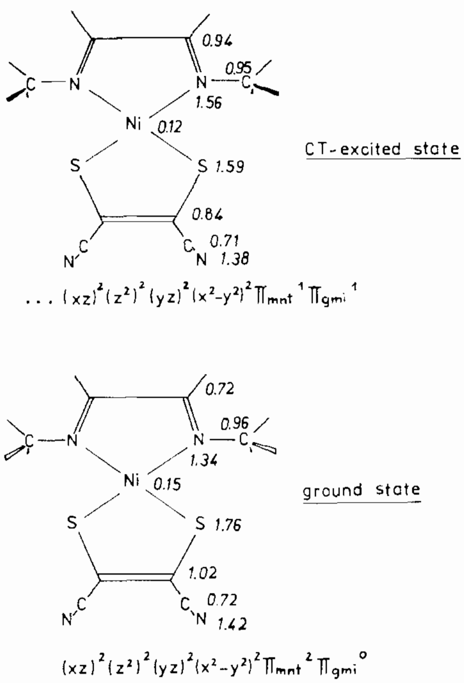


Fig. 4. π electronic density of the ground and the lowest CT-excited state of [Ni(mnt)gmi].

Variation of the α-diimine acceptor ligands of the complexes under investigation leads to a relatively large shift of the LL'CT band to the low-energy spectral region [8]. Both experimental and theoretical investigations on this class of ligands exhibit a higher π acceptor ability for the aliphatic diimines (glyoxal and diacetyl derivatives) compared to the aromatic representatives 2,2'-bipyridine and 1,10-phenanthroline [9]. The preferential position of the NH unsubstituted diimines, *o*-benzoquinone diimine and phenanthrenequinone diimine (phi), is due to particular low-lying acceptor MOs. The higher the π acceptor ability of the nitrogen ligand the larger is the spectroscopic shift of the CT band to lower wave numbers in accordance with the calculated order of LUMO energies. In the result of our EHT calculations of various mixed-ligand complexes [Ni(mnt)*N,N*] a stepwise decreasing of the energy of the LUMO centered on the diimine has been obtained (Fig. 5), whereas the energy of the highest occupied MO located on the sulphur ligand remains

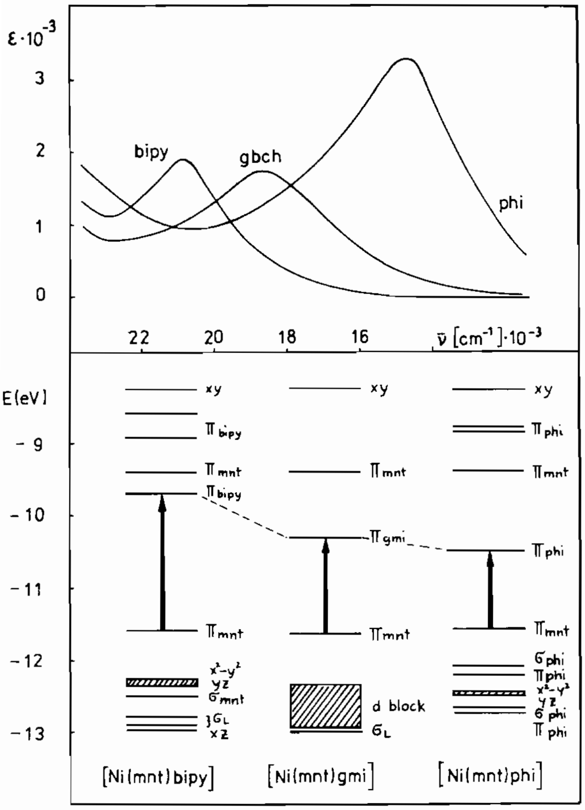


Fig. 5. Absorption spectra and MO scheme of the complex type [Ni(mnt)N,N], where N,N = bipy, gmi and phi (electronic spectra in acetone, 293 K).

nearly constant. Going from N,N = bipy to N,N = phi the calculated energy difference corresponds to the experimental value of $\Delta\tilde{\nu} = 6215$ cm^{-1}.

The position of the interligand absorption band should be dependent on the energy of the donor MO analogously as described for the variation of the acceptor niveau. Instead of maleonitriledithiolate we investigated the influence of *o*-xylol-4,5-dithiolate on the spectroscopic behaviour of the mixed-ligand complexes [8]. It is well known that aromatic dithiolates are essentially easier to oxidize than mnt. This experimental fact can be explained by the ability of the electron-withdrawing CN groups of the mnt anion to stabilize the electron-rich dithiolate form [43, 4]. The higher energy of the HOMO located on the aromatic sulphur ligand should also lead to a bathochromic shift of the LL′CT absorption assuming a constant acceptor niveau in the mixed-ligand unit.

From the MO diagrams of the complexes [Ni(S,S)-gmi], where S,S = mnt or benzenedithiolate (bdt) an energy destabilization of the highest occupied MO π_{bdt} of $\Delta E = 0.21$ eV for [Ni(bdt)gmi] follows compared to the mnt complex. This is reflected in the electronic spectra of the corresponding xdt–diimine nickel(II) compounds by bathochromic shifts of the interligand CT band of about 3000 cm^{-1}.

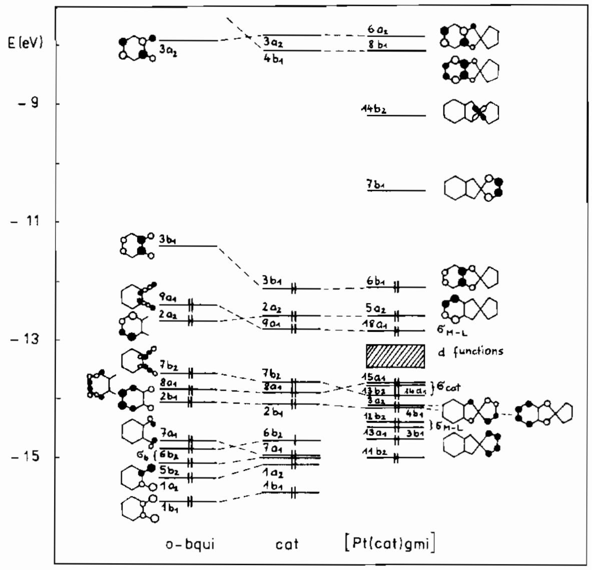


Fig. 6. Molecular orbital diagrams of *o*-benzoquinone (*o*-bqui), catecholate (cat) and [Pt(cat)gmi].

A further group of ligands with an analogous electronic structure possessing energetically favoured donor MOs are oxygen-containing ligands of the catecholate or salicylate type. Again, the occupied χ_3 MO of the underlying 4 π bonding system acts as donor MO and provides an interligand charge-transfer from the O-donor ligand to an appropriate acceptor within the complex unit (Fig. 6). This fact has been confirmed experimentally by Kumar *et al.* [5] who prepared bipy platinum complexes with salicylate, catecholate (cat) and some sulphur-containing ligands. In all cases a new, solvent-dependent absorption band in the range from 23 000 to 16 000 cm^{-1} has been observed which is assigned to a LL′CT transition. In contradiction to the S-ligand complexes considered above the HOMO centered on cat in [Pt(cat)gmi] is decreased by 0.46 eV. This result is in agreement with the easier oxidization of both the free sulphur ligand and the corresponding mixed-ligand complex yielding a hypsochromic shift of the LL′CT band in going from [Pt(tdt)bipy] ($\tilde{\nu}$(LL′CT) = 18 250 cm^{-1}) to [Pt(cat)bipy] ($\tilde{\nu}$(LL′CT) = 20 200 cm^{-1}), where tdt = 3,4-toluenedithiolate.

In a comprehensive electrochemical and spectroscopic study Vogler *et al.* [4] showed that the energy of the LL′CT band is almost independent on the chosen d^8-metal. In Fig. 7 the MO diagrams of the compounds [M(mnt)gmi], where M = Ni, Pd and Pt are shown. As expected, the HOMO–LUMO separation remains nearly constant. The empty d_{xy} orbital is destabilized in the given order connected with hypsochromic shifts of the d–d transitions which

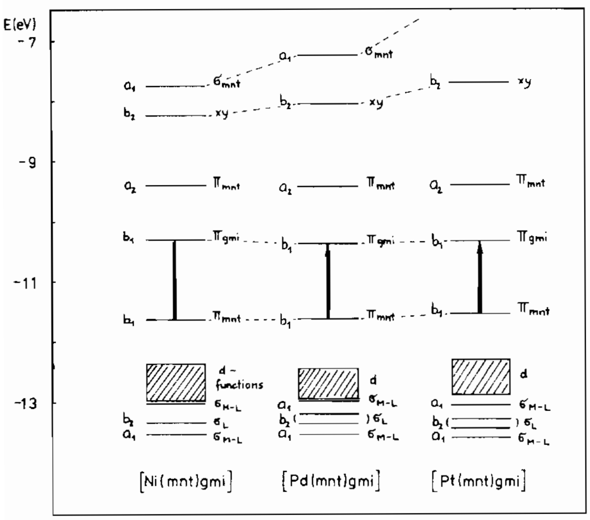


Fig. 7. MO diagrams of [M(mnt)gmi], where M = Ni, Pd and Pt.

is in accordance with ligand-field considerations [44]. The main function of the metal center is to fix the interacting π systems, and to bring them into the appropriate spatial neighbourhood.

It can be summarized that the mixed-ligand complexes described in this paper are attractive examples of transition-metal compounds with frontier orbitals located on different ligands originating an interesting electrochemical, spectroscopic, photochemical [45–47] and solvent behaviour [4, 8].

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