Spectroscopic and Theoretical Investigations of Schiff Base Metal Complexes with Intraligand Charge-transfer Behavior

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Abstract

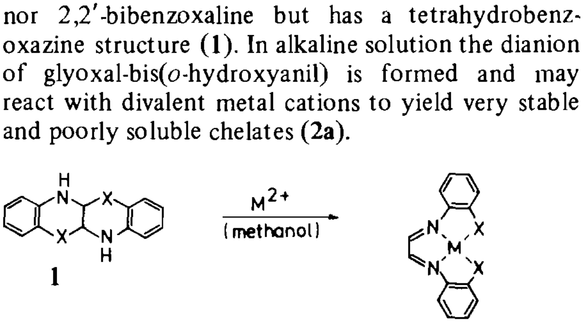
Nickel and zinc complexes of hydroxy or mercapto substituted glyoxaldianiles exhibit unusual long-wavelength absorptions. The electronic structure and spectroscopic properties of the compounds are investigated by means of electron spectroscopic studies and qualitative MO considerations. The deep color of the complexes is caused by intraligand charge-transfer transitions from the oxygen or sulphur-containing donor part to the diimine substructure of the ligand. The transition energies depend sensitively on the nature of the donor part of the ligand, and on the solvent polarity. The close structural relationship between these complexes and the d^8 mixed-ligand complexes with S/O-donor and N-acceptor ligands is discussed.

Introduction

Mixed-ligand complexes with a more readily oxidizable donor ligand and an acceptor ligand with energetically low-lying empty orbitals exhibiting an interligand charge-transfer transition (LL′CT) are of increasing interest. Miller and Dance, who investigated nickel compounds with dithiolate and α-diimine ligands [1], were the first to describe this type of spectroscopic transitions. Thereafter, further examples of complexes with S,S-, S,O-, and O,O-donor ligands and nitrogen-containing acceptors and d^8 metals with typical LL′CT spectra were published [2–8]. As a typical feature of these compounds an intense broad absorption band in the visible region of the electronic spectrum can be observed which is markedly dependent on the solvent polarity. The position of the absorption band depends in a sensitive manner on the coordinated sulphur-containing donor and the diimine acceptor, as well as on substituents within the donor and acceptor site. On the other hand, the energy of the LL′CT band is nearly independent of the choice of d^8 metal. The main function of the metal ion consists in bringing the interacting π-electron systems into the appropriate spatial neighbourhood [4].

Of particular interest are ligands with both a donor and an acceptor unit within the same molecule as this is known from numerous organic chromogens [9, 10]. Recently, Vogler and Kunkely reported the electronic spectrum of biacetyl-bis-(mercaptoethylimine)-nickel(II) (NiBBMEI) with an intense absorption in the visible spectral region ($\lambda > 500$ nm) [11]. The authors suggested that the origin of this long-wavelength absorption band was a new type of electronic transition, an intraligand charge-transfer (ILCT) mediated by the central metal. It was emphasized that the electronic structure of this nickel compound is related to that of M(II)diimine 1,2-dithiolate mixed-ligand complexes with M = Ni [1] and Pt [3].

In 1957 Bayer published the synthesis of metal complexes with Schiff bases prepared from *o*-aminophenol and α-dicarbonyl compounds (biacetyl, glyoxal) [12, 13]. The formed metal complexes have a deep color resulting from intense absorption in the range of 500 to 600 nm which is absent in the spectra of both the free ligands and their alkaline metal salts. Tauer *et al.* [14] have shown recently that the condensation product of *o*-aminophenol and glyoxal is neither the chelating Schiff base (**2**) nor 2,2′-bibenzoxaline but has a tetrahydrobenzoxazine structure (**1**). In alkaline solution the dianion of glyoxal-bis(*o*-hydroxyanil) is formed and may react with divalent metal cations to yield very stable and poorly soluble chelates (**2a**).



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a: X = O
b: X = S
M = Ni, Zn, Cu, Cd

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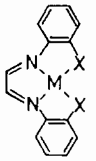
The metal ion induced rearrangement reactions of bibenzthiazoline (**1b**) to Schiff base chelates (**2b**) was described by Jadamus *et al.* [15]. The bibenzthiazolines react similarly to **1a** with various metal ions already in neutral methanolic solution to give the corresponding metal chelates. No explanation has been given regarding the nature of the intense absorptions in the visible region of these deeply colored metal complexes. The purpose of the present paper is a theoretical analysis of the electronic structure and the absorption spectra of donor–acceptor ligand systems and their metal complexes exhibiting intraligand charge-transfer properties.

Experimental and Calculational Details

Metal complexes of the type **2a** and **2b** with glyoxal-bis(*o*-hydroxyanil) (GBHA) and glyoxal-bis-(*o*-mercaptoanil) (GBMA) as ligands, and with M = Ni and Zn were prepared by procedures described in the literature [12, 15]. All the other chemicals used were of analytical reagent grade. Electronic absorption spectra were recorded on a Specord M 40, VEB Carl-Zeiss-Jena. Spectro-grade solvents were used for the spectroscopic measurements.



2a: X = O
2b: X = S
M = Ni, Zn

For the quantum chemical calculations the standard version of the EHT (Extended-Hückel-Theory) method [16, 17] and the PPP-CA (Pariser-Parr-Pople procedure with Configuration Analysis) method [18] were used.

The valence state ionization potentials of main group elements were taken from ref. 19, those of the transition metals were obtained by an iterative procedure on a model system. Single Slater-type functions have been taken into account for main group elements and also for the s and p functions of metal atoms. For the d orbitals the 'double ζ-functions' of Richardson *et al.* [20] were used.

The following parameters were used for the PPP-CA calculations of the ligand molecules:

$I_C = 11.66$ eV, $E_A(C) = 0.58$ eV,
$\beta_{CC} = 2.318$ eV [21];
$I_N = 17.89$ eV, $E_A(N) = 1.95$ eV,
$\beta_{CN} = \beta_{CC}$*;
$I_O = 27.6$ eV, $E_A(O) = 9.6$ eV,
$\beta_{CO} = 0.95\ \beta_{CC}$ [22].

The configuration interaction procedure included 36 singly excited singlet electronic configurations and the ground state configuration.

Unfortunately, X-ray crystallographic data of the ligands and the metal complexes are not available. Therefore, we used molecular geometries based on experimental bond lengths and bond angles in related compounds [8, 14, 23]. The bond alternation within the diimine structure element was taken into account roughly using a variable β-technique.

Results and Discussion

The absorption spectra of NiGBHA and NiGBMA are shown in Fig. 1. The spectra are characterized by two absorption bands. The long-wavelength absorption of the complexes with GBHA is centered at about 585 nm with $\epsilon_{max} \sim 10^4$, for complexes with GBMA at about 630 nm. The second absorption band occurs at about 350–400 nm and is somewhat less intensive ($\epsilon_{max} \sim 6\text{–}8 \times 10^3$).

In Fig. 2 the electronic spectra of NiGBHA in various solvents of different polarity are given. It can be seen that both the absorption bands are hypsochromically shifted with the increase of solvent polarity. A more quantitative study of the solvatochromic behavior could not be carried out due to the poor solubility of both the zinc and the nickel chelates.

In this case, the maximum absorption in the visible region is again almost independent of the central metal, analogously to the above mentioned mixed-ligand systems. Since the zinc(II) complex (closed shell d^{10} configuration) is also intensely colored, the ligand field transitions can be excluded as a reason for the absorptions.

Bayer [13] discussed the appearance of the absorption in the visible region as a typical feature

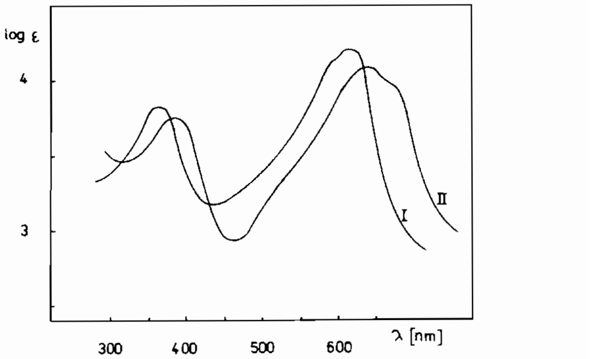


Fig. 1. Absorption spectra of the complexes NiGBHA (I) and NiGBMA (II) in pyridine (293 K).

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*Optimized parameters to reproduce the experimental spectrum.

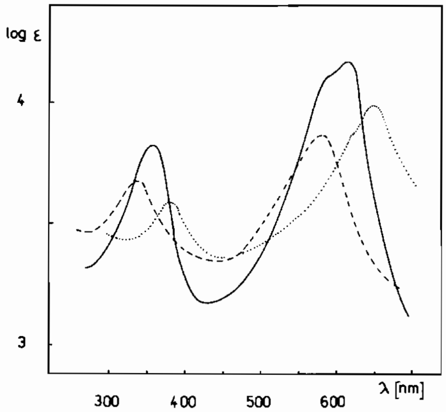

Fig. 2. Absorption spectra of NiGBHA in different solvents: — pyridine, --- DMSO, ······· piperidine; 293 K.

of quasi-aromatic metal diimine 5-membered ring chelates formed by complexation of these ligands with metal ions. This assumption is founded on the absence of a long-wavelength absorption band in the case of a saturated acceptor site (e.g. ethylenediamine). However, this interpretation does not consider the influence of the electron-donating part of the ligand. The pecularity of the ligand molecules under study consists in the presence of a readily oxidizable donor part and a reducible acceptor substructure in the same molecule. Furthermore, a charge-transfer transition from nickel(II) to the diimine ligand should be markedly higher in energy [24].

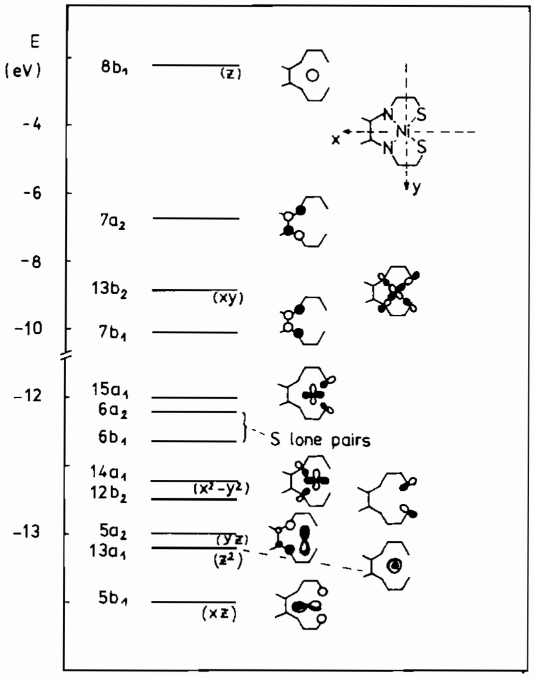

Fig. 3. MO diagram of biacetyl-bis(mercaptoethylimine)-nickel(II).

To characterize the electronic spectra and the types of electronic transitions we have calculated the molecular orbital schemes of the different complex types. Firstly, we studied the electronic structure of biacetyl-bis(mercaptoethylimine)-nickel(II) to compare our results with those of Vogler and Kunkely [11]. Based on spectroscopic investigations Vogler and Kunkely assigned the long-wavelength absorption at 530 nm ($\epsilon_{max} \sim 1500$ in acetonitrile) to an intraligand charge-transfer from sulphur to the diimine acceptor unit. The MO diagram of NiBBMEI calculated by the EHT method is shown in Fig. 3. Hydrogen atoms have been omitted in the orbital representations for the sake of clarity. The symmetry labels are taken from the C_{2v} point group. The highest occupied MO ($15a_1$) with a relatively large sulphur contribution interacts with the $d_{x^2-y^2}$ orbital of the metal in a σ fashion. Below the HOMO two sulphur lone-pair orbitals ($6a_2$, $6b_1$) are situated. The lowest unoccupied MO is almost completely localized within the α-diimine substructure ($7b_1$) and is of π symmetry. That means that the $6a_2 \rightarrow 7b_1$ (y-polarized) and $6b_1 \rightarrow 7b_1$ (x-polarized) transitions are responsible for the long-wavelength absorptions of NiBBMEI. They are of intraligand CT type characterized by an electron transfer from sulphur to the diimine acceptor site. Unlike the mixed-ligand systems [1, 7] with a charge-transfer from a π MO mainly localized on the sulphur ligand to the anti-bonding π MO of the diimine, the considered electronic transitions of NiBBMEI indicate a n-π^* character. The MO diagram of NiGBHA is shown in Fig. 4. The two highest occupied molecular orbitals obtained by the calculation are localized primarily on the phenolate parts. For the $6b_1$ π MO an especially large oxygen $2p_z$ contribution is obtained. Below a CC π bonding MO of the benzene units ($5a_2$) follows the d block with the d functions in order of decreasing energy $x^2-y^2 > z^2 > yz > xz$. The LUMO ($7b_1$) can be described as a nearly pure π orbital of the diimine structure of GBHA with the typical symmetry properties of the butadienoid χ_3 orbital. At higher energies the d_{xy} metal orbital and CC antibonding π MOs of the ligand are arranged. Based on this MO scheme the longest-wavelength absorption can be assigned to an allowed y-polarized $6a_2 \rightarrow 7b_1$ transition. The absorption maximum in the region between 350 and 400 nm is caused by a $6b_1 \rightarrow 7b_1$ transition (x-polarized). Both electronic transitions are of ILCT type characterized by electron transfer from the phenolate donor parts to the α-diimine substructure. The ordering of the molecular orbitals does not depend materially on the ligand geometry. Using experimental bond distances and bond angles of related compounds a relatively large Ni–O distance of about 2.4 to 2.5 Å is obtained for NiGBHA compared

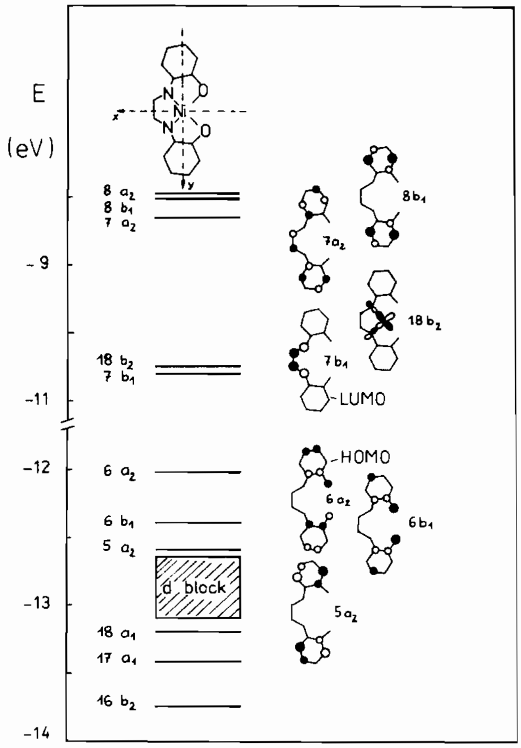

Fig. 4. MO diagram of glyoxal-bis(*o*-hydroxyanil)-nickel(II).

to the 'normal' Ni(II)–O distance of about 2.03 Å within other Ni(II) complexes [25–27]. This means that the stability of the GBHA metal chelates should be conditioned primarily by the metal–diimine interactions [13].

Comparing the electronic spectra of the GBHA complexes with those of GBMA, a bathochromic shift in the low-energy absorption band of about 20 to 40 nm can be observed in the case of sulphur-containing ligand. This is reasonable because of the easier oxidation both of the free sulphur ligand and of the corresponding metal complex.

The MO diagrams (Figs. 4 and 5) show that the orbital characteristics of the two complex types are in qualitative agreement. Figure 5 represents the MO diagram of glyoxal-bis(mercaptoanil)-nickel(II). Again, the highest occupied MOs are of π symmetry ($6a_2$, $6b_1$), mainly centered on the thiophenolate sites. At lower energy two lone-pair orbitals ($20a_1$, $17b_2$) primarily localized on sulphur and a CC π bonding $5a_2$ MO are obtained followed by the d functions (x^2–$y^2 > z^2 > yz > xz$). In relation to NiGBHA the two highest occupied π orbitals ($6a_2$, $6b_1$) are about 0.3 eV destabilized. Additionally, the π MOs contain a remarkably higher contribution of sulphur p_z orbitals compared to the contribution of the oxygen $2p_z$ AOs in the case of NiGBHA. The LUMO has π symmetry and is localized within the diimine part.

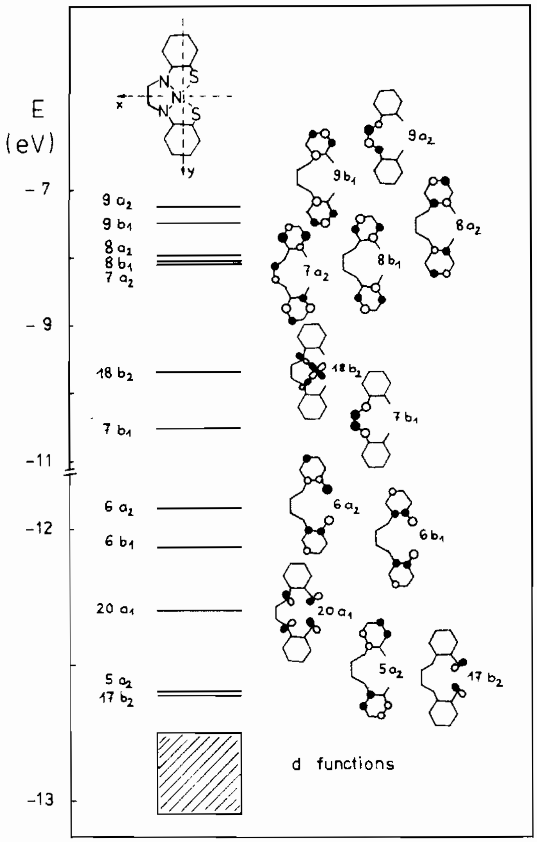

Fig. 5. MO diagram of glyoxal-bis(*o*-mercaptoanil)-nickel(II).

Considering that the spectroscopic properties of the metal complexes under study are primarily due to the ligand molecules and that the metal plays only a mediating role, we gave more attention to the ligand spectra, too.

The free ligand molecules GBHA and GBMA are only stable in alkaline solution [12, 15]. In neutral and acidic medium a rearrangement product is formed which is unable to coordinate. The absorption spectra measured in alkaline solution show similarities to the complex spectra. The spectra consist of two absorption bands hypsochromically shifted in relation to the maxima of the metal chelates. The long-wavelength absorption occurs in the visible region at 490 nm. The intensity of this band is higher than the intensity of the second absorption at 312 nm ($\epsilon = 8.4 \times 10^3$) (Fig. 6).

In order to study the spectroscopic properties of the free ligand molecules theoretically, PPP-CA calculations were carried out. The geometry and the parameters used are described above. In Table I are summarized the calculated and experimental transition energies, intensities, and the calculated polarization direction of the electronic transitions for the s-*cis* and s-*trans* isomers. The agreement between the calculated transition energies and the

TABLE I. Calculated (Transition Energy ΔE, Oscillator Strength f, Polarization Direction) and Experimental (Wavelength λ, Extinction Coefficient ϵ) Spectral Data of GBHA

Configuration	ΔE		f	Polarization direction	Experimental spectrum[c]	
	(nm)	(eV)			λ	ϵ[d]
s-*cis*	453	2.74	0.731	y		
	392	3.17	0.470	x		
	321	3.66	0.568	y		
s-*trans*	470	2.64	0.841	y[a]	490	10^4
	412	3.01	0.189	x[b]		
	323	3.64	0.613	y[a]	312	8.4×10^3

[a]Corresponds to the long molecular axis. [b]Corresponds to the short molecular axis. [c]In alkaline DMSO solution. [d]In l $\text{mol}^{-1}\ \text{cm}^{-1}$.

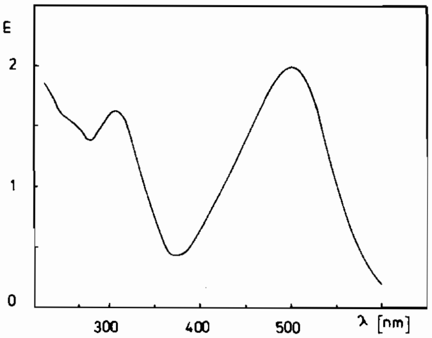

Fig. 6. Absorption spectrum of GBHA in alkaline DMSO solution.

experimental measured absorption maxima is fairly good. The configuration analysis indicates that the ground state S_0 of the ligand molecule is described by a no-bond structure characterized by doubly occupied MOs which are localized at the orbitals of the donor and acceptor fragments. The first excited singlet state S_1 is a charge-transfer state (charge-transfer from the two phenolic molecular parts to the diimine structure element).

Summarizing it can be concluded that the electronic structure of the metal complexes of both GBHA and GBMA is quite similar to the mixed-ligand complexes of the type [M(O,O)N,N] and [M(S,S)N,N] with O,O = catecholate, salicylate; S,S = mnt, aromatic dithiolates, and N,N = aliphatic or heteroaromatic α-diimines. This is reflected in their analogous MO schemes, and in similar spectroscopic behavior as well as in analogous solvatochromic properties of the absorption bands.

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