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The Electronic Structure and Photoelectron Spectra of Ni^{II}, Cu^{II} and Pd^{II} Complexes with N.N'-ethylene-bis(acetylacetoneiminato) Dianion

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The He I photoelectron spectra of Ni^{II}, Cu^{II} and Pd^{II} complexes with N,N'-ethylene-bis(acetylacetoneiminato) dianion have ben measured and discussed. The electronic structures have been investigated on the basis of a CNDO method.

Introduction

There has recently been new interest in metal complexes with polydentate Schiff bases which represent very promising tools for the study of relationships between electronic structure and function in biological systems.

In the present approuch N,N'-ethylene-bis(acetylacetoneiminato) dianion (Bae) has been chosen as ligand for d^8 and d^9 transition metals, because the structures of the involved complexes are relatively simple and the corresponding metal chelate compounds are relatively volatile. Moreover a nearly planar arrangement of the ligand chromophore N_2O_2 allows a theoretical insight of the *d* metal orbital partecipation in the molecular orbitals of the higher symmetry square planar complexes.

Experimental

H_2Bae, NiBae, CuBae and PdBae were prepared according to the methods described in literature[1] and purified by recrystallization from ethanol followed by vacuum sublimation.

Photoelectron spectra, with the He I resonance line at 21.21 eV, were recorded on a Perkin-Elmer PS-18 spectrometer using a heated inlet probe. The spectra were calibrated by the simultaneous admission of Xe and Ar gases mixture into the target chamber.

Calculations on the electronic structures of such complexes were restricted to the nickel(II) complex. Unfortunately, the system contains too many atoms for self consistent field calculation to be readily carried out and the system, in which methyl groups are replaced by hydrogens, was studied.

NiBae has been shown to be diamagnetic in the solid state with a planar structure. Bond distances and angles were taken from the X-ray determination of the copper(II) Bae structure[2] and a C-H bond lenght of 1.08 Å was assumed.

SCF-MO calculation has been carried out in the CNDO scheme according to a method which has given satisfactory results dealing with other transition metal compounds[3]. Such method uses one-center quantities evaluated from atomic spectroscopic data of atoms, assuming that each valence orbital is angular independent. Therefore, average energies of electronic configurations of atom for three adiacent oxidation states were fitted with the $U_{\mu\mu}$ core integrals and with the two-electron integrals $\gamma_{\mu\nu}$ which depend only from the radial wave function. More exacly to every valence orbital of the considered atom a single Slater exponent for the s-like radial function was associated in order to reproduce the one-center coulomb integrals.

All the one— and two-center coulomb integrals were calculated to be purely theoretical s-type. For that concerns the out diagonal elements of the core matrix[4], the value of β° was identified with the average ionization energy of the orbital in the neutral atom.

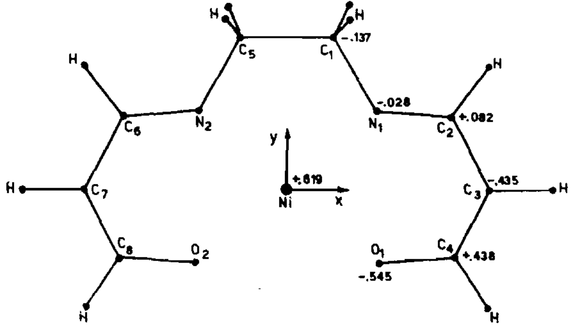

Figure 1. Atom numbering and atomic charges.

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(1) G.T. Morgan and J.D.M. Smith, *J. Chem. Soc.*, 2030 (1925), 912 (1926).

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(3) E. Tondello, to be published.

(4) J.A. Pople and G.A. Segal, *J. Chem. Phys.*, *44*, 3289 (1966).

(5) J.W. Richardson, W.C. Nieuwpoort, R.R. Powel and W.F. Edgell, *J. Chem. Phys.*, 36, 1057 (1962).

(a) J.W. Richardson, R.R. Powell and W.C. Nieuwpoort, *J. Chem. Phys.*, 38, 796 (1963).

(6) E .Clementi, *IBM Research Paper RJ* 256, (1963).

Table I. One-center quantities for atoms used in the calculation.[a]

	U_{ss}	U_{pp}	U_{dd}	$\beta_s°$	$\beta_p°$	$\beta_d°$	ζ_s	ζ_p	ζ_d
Ni	−93.70	−73.48	−145.50	7.50	3.90	10.60	1.45	1.18	2·25
O	−100·84	−76.62		32.39	15·57		1.56	1.18	
N	−74.04	−58.93		25.57	13.18		1.29	1.13	
C	−53.74	−42.59		19.65	10.27		1.19	1.03	
H	−13.60			13.60			.756		

[a] $U_{\mu\mu}$ and $\beta_\mu°$ are in eV; ζ_μ refer to Slater exponents.

Table II. Molecular orbital scheme for NiBae.

Symmetry	Eigenvalue (eV)	Composition[a]
$5a_2$	−8.09	Ligand π system
$15a_1$	−8.35	
$5b_2$	−8.61	Ligand π system
$12b_1$	−8.93	Ligand σ system
$11b_1$	−9.89	
$14a_1$	−10.22	
$10b_1$	−10.29	
$13a_1$	−10.36	
$4a_2$	−11.24	Ligand π system
$4b_2$	−11.79	" "
$12a_1$	−12·11	
$9b_1$	−12.56	
$8b_1$	−13.00	
$11a_1$	−13.96	36% d_{z^2}
$10a_1$	−14.11	17% d_{z^2}, 63% $d_{x^2-y^2}$
$3a_2$	−14.11	91% d_{zx}
$3b_2$	−14.29	93% d_{zy}
$9a_1$	−14.32	39% d_{z^2}, 25% $d_{x^2-y^2}$
……	……	……
$10a_1$	−53.06	

[a] Composition is given in per cent for *d* metal orbital.

All the one-center quantities used in the calculation are reported in Table I.

Overlap integrals were computed from the Richardson et al.[5] papers for nickel and from Clementi[6] for other elements. Orbital basis set consists of 3d, 4s and 4p for nickel, 2s and 2p for carbon, nitrogen and oxygen and 1s for hydrogen. Numbering of atoms and the coordinate axes system, with the z axis perpendicular to the molecular plane, are shown in Fig. 1. In such figure atom charges, as output of the calculation, are also reported.

Results and Discussion

In the past it was commonly assumed that the highest filled molecular orbitals of d^n, with n greater than zero, metal complexes were those largely localized on the metal *d* orbitals. If various experimental data accords with such assumption, photoelectron spectra demonstrated that in many cases ligand ionizaion energies may be lower than metal ionization energy, as in pentacarbonylmanganese halides[7] or in $Fe(hfa)_3$[8] for example.

The present writers accord to Jørgensen[9] in considering that photoelectron spectra cannot be fulfilled by a secular determinant of one-electron energies, mainly because the role of interelectronic repulsion integrals cannot be neglected. Therefore the adopted method of calculation seems suitable to overcame such peculiarity, even if CNDO eigenvalues are expected to be lower than −I energies. Nevertheless m.o. composition can be usefull to investigate photoelectron spectra.

The upper filled m.o. are reported in Table II and characterized according to C_{2v} point group symmetry for NiBae; on examining these, one can note that the upper filled m.o. $5a_2$ is essentially located on the ligand π system and it is followed by many other m.o., until $8b_1$, largely localized on the ligand. The set of largely 3d metal orbitals, $11a_2$ to $9a_1$, is about 6 eV lower than the outer $5a_2$ level. Such state of affairs is also encountered in the ab-initio calculation[10] on $Ni(CN)_4^{2-}$ as well as in various semi-empirical approuches[11] to the electronic structures of metal complexes with Schiff bases and its analogous.

Because of the molecular complexity of the examined compounds, investigations of PE spectra will be based on theoretical results of NiBae as well as on theoretical and experimental deductions.

It has been concluded from infrared, dipole moment and proton resonance data that Bae-H_2 ligand is largely present in enolic form in the solid state and in solution[12]. Moreover it was outlined that there is freedom of rotation about the CH_2-CH_2 bond of he bridge and that the probable configuration has a large deviation from coplanarity of the two chelate rings[13]. With such assumption the total electronic distribution may be separated in two non ineracting rings with equivalent electronic distribution as long as the outer m.o. are concerned. Therefore PE spectrum of Bae-H_2 will closely resembles that of acetylacetone taking into account a substitution of an oxygen with a nitrogen containing group.

Considering one sp^2 lone pair on nitrogen and two on oxygen of the same half anionic ligand, intra-ligand interactions suggest that the three resulting m.o., bonding h_+, non bonding h_o and antibonding h_- in the N-O region, will have the energetic order $h_- > h_o > h_+$. Moreover, while h_o is essentially one lone pair on oxygen and h_- has no bonding properties, protonation of the anionic ligand will lower ulteriorly the h_+ level. In addition to these in plane m.o. it

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(7) S. Evans, J.C. Green, M.L.H. Green, A.F. Orchard and D.W. Turner, *Disc. Faraday Soc.*, *47*, 112 (1969).

(8) S. Evans, A. Hammett, A.F. Orchard and D.R Lloyd, *Disc. Faraday Div.*, Sussex, Sept. 1972.

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(13) P.J. McCarthy and A.E. Martell, *J. Am. Chem. Soc.*, *78*, 264, 2106 (1956).

has to be considered the π system, which in a simple Hückel scheme is not influenced by proton binding and consists of the filled $\pi_3 > \pi_2 > \pi_1$.

Looking at the experimental PE spectrum of Fig. 2 the order $\pi_3 \sim h_- > h_o > h_+ \sim \pi_2$ seems reasonable. In fact the first band at 7.71 eV with a marked shoulder at 7.9 eV well accounts for π_3 and h_- assignment in spite of their relative order, the second band at 8.78 eV is sharp and may be assigned to the non bonding h_o electrons while the third band may be ascribed to h_+ electrons ionization and for its broadness also to other contributions due, for instance, to π_2 level. The diffuse structure of the spectrum above 11 eV originates from too many overlapping bands and is hardly allottable.

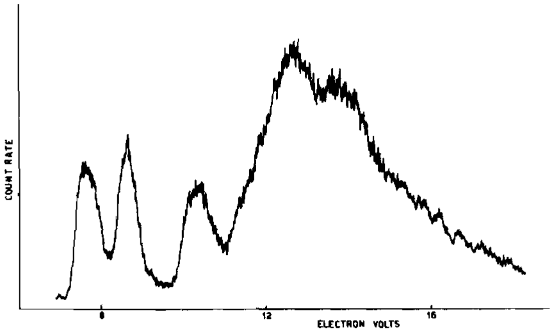

Figure 2. The He I PE spectrum of Bae-H_2.

Therefore this process makes the Bae-H_2 spectrum very similar to those of other β-diketones but with a shift of bands towards lower energies so to allow the appearance of a third band[8].

The role of the mainly ligand orbitals in PE spectra of NiBae, CuBae and PdBae, reported in Fig. 3, 4, 5 and in Table III, can be derived in a rough manner by examining firstly the interactions between atoms in the N_2O_2 chromofore and secondly the interactions between central atom and the chromophore itself.

Table III. Ionization Energy Data (eV) up to 13 eV.

Bae-H_2		NiBae	PdBae	CuBae
7.71	A	6·80	6.88	7.00
			(7.13)	
(7.90)	B	7.60	7.54	7.57
		(7.70)	(7.65)	
		7.90	7.85	
8.78	C	8.40	8·25	8.65
			8.46	
			8.81	
	D	9.30	9.18	
		9.68	9.68	9.73
10.47		(9.9)	(10.0)	(10.1)
(11.7)		10.60		
(12.2)		(11.6)	(11·0)	11.5
12.9		(12.3)	(12.4)	

The out of plane π orbitals of a ring of Bae anion give origin to a_2 and b_2 symmetry orbitals in C_{2v} point group. Simple intraligand overlap considerations and with metal orbitals d_{zx} and d_{zy} leads to conclude that $a_2(\pi_3)$ orbital is greater in energy than $b_2(\pi_3)$. All the other in plane orbitals (h) transform as a_1 and b_1 represenations and thus a large interaction between m.o. of the same symmetry arises. Nevertheless to a first approuch it may be assumed that the following order halds:

$$a_2(\pi_3) > b_2(\pi_3) > a_1(h_-) > b_1(h_-) > a_1(h_o) \sim b_1(h_o) > b_1(h_+) > a_1(h_+)$$

Such order is indeed very much alike to that obtained from the CNDO calculation. The experimental spectra of the compounds are very similar and it may be surprising that the spectrum of CuBae is by the far the most simple in spite of the fact that the electronic ground state is $^2B_1$. Moreover, because the spectrum consists of sharp bands untill 9 eV, it is consistent to assume the bands originate from mainly ligand ionizations as the metal-ligand exchange inte-

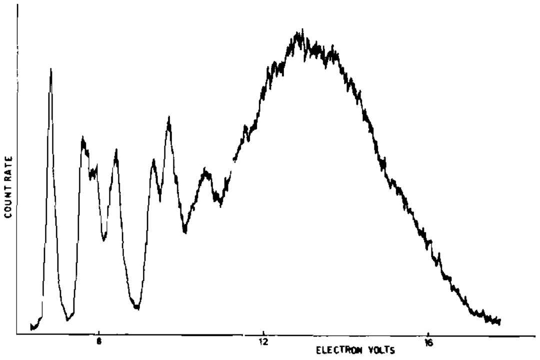

Figure 3. The He I PE spectrum of NiBae.

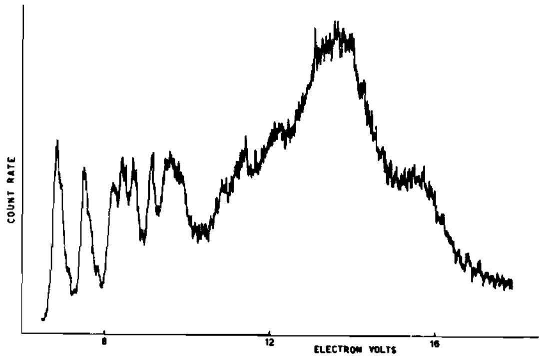

Figure 4. The He I PE spectrum of PdBae.

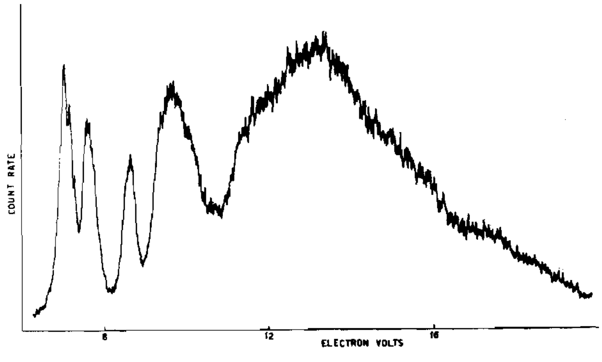

Figure 5. The He I PE spectrum of CuBae.

grals, which determine the singlet triplet separations in the ionic states, are expected be small compared to *d* metal-metal exchanges.

Consequently the first sharp band A, at 6.80 eV for NiBae, 7.00 eV for CuBae and 6.88 eV for PdBae, originates from $a_2(\pi_3)$ ionization and correlates with a pure π ligand combination a_{2g} (or b_{2u}) in a strictly square planar D_{4h} environment. The second band B may be assigned to $b_2(\pi_3)$ ionization as well as to $a_1(h_-)$ and $b_1(h_-)$ while the band C to $a_1(h_o)$ and $b_1(h_o)$. This latter assignment agrees with the constancy of such band in energy and in form on going from Bae-H_2 to the compounds and makes reasonable its origin from essentially non bonding ligand electrons. The band D, which in nickel(II) and palladium(II) compounds is splitted, is assigned to the in plane bonding $a_1(h_+)$ and $b_1(h_+)$.

In such investigation from 6 to 21 eV *d*-metal ionization energies have not been considered and if one would accept electronic structure calculation results such energies would be greater than the first ionization energy of about 6 eV. However, owing to the approximate nature of the calculation with large molecules, this assumption cannot be taken too seriously, and the band broadening on going from closed to open-shell systems, i.e. on comparing NiBae and PdBae with CuBae, in the D band may account for an increase of more ionic states due to exchange effects over *d* ionizations.

In this circumstance the detailed structure between 8 and 9 eV for PdBae and at 8 eV for NiBae might have *d* character.