## 1Pa071 Particular Structural and Spectroscopic Properties in Distorted Coordination Compounds

F. Cimpoesu,<sup>a</sup> Marilena Ferbinteanu,<sup>b</sup> Y. Fukuda,<sup>b</sup> Y. Mitsutsuka<sup>c</sup> and K. Hirao<sup>a</sup>

<sup>a</sup> Department of Applied Chemistry, School of Engineering,

University of Tokyo, Tokyo, 113-8656

- <sup>b</sup> Ochanomizu University, Faculty of Science, Department of Chemistry, 2-1-1 Otsuka, Bunkyo-ku 112-8610, Tokyo
- <sup>c</sup> Meisei University, Department of Chemistry, 2-1-1 Hodokubo, Hino 191-8506, Tokyo

The mixed ligand complexes with diamine and diketonato ligands and various peripheral substituents have interesting stereochemistries and may display chromotropic phenomena. The present study represents a continuation of our interest for structural features of such systems. Newly synthesized nickel complexes having different chelate ligand types (saturate diamine or aromatic di-imine-AA,  $\beta$ -diketonato-dike, nitrite) are interesting study cases for geometries strongly deviated from regular octahedron pattern (fig.1). The [Ni(AA)(dike)(NO<sub>2</sub>)] complexes are also structural prototypes with respect of peculiar coordination features of nitrite anion. In spite of its small bite angle the Natural Bond Orbital analysis(NBO) based on DFT-b3lyp calculations revealed, rather surprisingly, only a moderate misdirected lone-pair character.



**Fig. 1.** Molecular structures of  $[Ni(tmen)(dbm)(NO_2)]$  (left) and  $[Ni(bipy)(dbm)(NO_2)]$  (right). Ortep view. In center, summary of crystallographic data for the three chelates in  $[Ni(tmen)(dbm)(NO_2)]$ 

In turn, the diketonato coordinating lone pairs are bent with  $\sim 10^{\circ}$  inward of the ring, while a significant coordinative role of outer lone pairs is detected, as shown in table 1(where  $\lambda_1$  and denotes the coordinating respectively the secondary lone pairs). An examination of principles of NBO donor-acceptor analysis suggests a closer similarity to the perturbational Ligand Field Models of Angular Overlap type (AOM). Observing then the utility of NBO concepts in the spectroscopy of transition metal complexes, one may conclude from this point of view the validity of rather disputed AOM increments dealing with misdirected lone pair parameterization. The NBO analysis of lone pairs showed nonstandard composition with respect of hybridization

scheme suggested by chemical intuition. The Natural Resonance Theory (NRT) applied to diketonato ligands revealed that in the complex the aromaticity increases, the weight of the two keto-enolato resonances being close to 40%, as compared to free ionized ligand where these retain only 22%, in favor of diketo-carbanion resonance having almost 30%. The resonance structure approach may be regarded as a new kind of proof for the relevance in diketonato-chelates of the non-aditive Ligand Field ingredient known as Phase Coupling effect.

	$\Delta E_2(D-A)(cm^{-1})$	s%(D1)	p%(D1)	s%(D2)	p%(D2)
λ N (tmen)	147.59	18.64	81.36	18.24	81.76
λ <sub>1</sub> Ο (NO <sub>2</sub> <sup>-</sup> )	194.47	9.93	90.07	9.5	90.5
λ <sub>2</sub> Ο (NO <sub>2</sub> <sup>-</sup> )	61.09	66.81	33.19	67.97	32.03
λ <sub>1</sub> O (dbm <sup>-</sup> )	219.49	13.28	86.72	14.42	85.58
λ <sub>2</sub> O (dbm <sup>-</sup> )	68.75	45.73	54.27	45.41	54.59

 Table 1. The NBO Donor-Acceptor perturbation energy analysis (kcal/mol) and NHO composition of donors (D1 and D2) for each chelate DD in the discussed complex.

The Ligand Field (or AOM) approach of the electronic spectra of asymmetric complexes is difficult due to the over-parameterization problems to the impossibility to predict in advance the order of spectral terms (after splitting of the T, E degenerate states). At this point, the calculations (CASSCF, NBO) are helpful to decide orbital types, shapes and ordering.



Fig. 2. Electronic spectrum of [Ni(tmen)(dbm)(NO<sub>2</sub>)] (a) and orbital assignment for the first transition (b)

The computed spectra reproduce well a ligand field regime, eventough there are differences about 1000-2100 cm<sup>-1</sup> with respect of experimental bands. The electron population on each excited states offer a meaningful understanding of their nature. Thus, the lowest transition in spectrum(fig.2a) is practically an electron jump between the orbitals with  $t_2$  and e formal origin, oriented as shown in fig.2b. The polarized spectra on various different crystal faces were recorded and rationalized in the key of significant asymmetry of the complex. The variation of the absorption with respect of crystal orientation is directly visible in slight changes of the color.