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# What is the origin of color on metal complex dyes? Theoretical analysis of a Ni-coordinate azo dye

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**Abstract**

To analyze the ultraviolet and visible (UV/VIS) absorption spectrum on metal complex dyes, we have theoretically elucidated a Ni-coordinate azo dye, bis(1-(2-thiazolylazo)-2-nathptholate)nickel(II) (Ni-$TAN_2$), by using semi-empirical molecular orbital methods. The molecular structure was determined by the MSINDO method; then, the electronic transition properties were calculated by the INDO/S method. The MSINDO optimization well reproduces the X-ray structure, especially the Ni octahedral coordinate moiety. The INDO/S calculated result clearly shows that the intense visible band originates from the intraligand, TAN azo chromophore, transitions accompanied with the Ni coordinate perturbation. Although many Ni d-orbitals originated transitions lie in the lower energy region, these bands should not be observed by their negligible intensities.


*Keywords:* Metal complex dye; UV/VIS absorption spectrum; Molecular structure; Electronic transition; MSINDO method; INDO/S method

## 1. Introduction

Metal complex dyes comprise an important class of chromophores. These dyes have been deeply investigated since antiquity [1] and have been widely used in many practical applications; textile dyeings, coloring polyamide fibers, are typical traditional uses [2,3]. Some kinds of chromophoric ligands have been applied as chelate indicators to detect metal ions, applying their color change by the complex formation [4–7]. Recently, metal complex dyes have been introduced into many high-technological frontier applications as key functional materials, for example, in high-density memory storages (CD-R and DVD-R) [8–10], nonlinear optical elements [11], printing systems [12,13], and so on.

Generally, the metal complex formation on chromophoric ligands causes UV/VIS absorption spectrum shift [4–7,11,13,14] accompanied enhancing the dye fastness [13,15]. Some of their properties, for example, coordination structures, chelate

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formation constants, and stability, have been reported [14,16–23]. In spite of the practical importance of metal complex dyes, the basic physicochemical understanding is still on an insufficient level; analysis of the electronic transition properties still remains an important problem to be resolved. The origin of color and the role of metal coordination have been reported in few papers [24]; but the point of issue, metal is either directly contributing to the transition or acting as the perturbation, has not been clearly elucidated. Theoretical analysis of metal complex dyes is limited [25] due to their large molecule sizes and comprehensive electronic structures. To synthesize the highly enhanced metal complex dyes, we must establish the guiding principle of their molecular design.

1-(2-Thiazolylazo)-2-nathptholate (TAN) is widely used as a chelate reagent for the metal ion detection [26–36], and the three-dimensional structures, both as a ligand and its complexes with a variety of metals, have been already solved by X-ray single crystal analyses [37–49]. In this study, we have chosen bis-TAN nickel(II) (Ni-$TAN_2$) as a typical model system of practically used dyes, since Ni or Cu coordinate heterocyclic azo dyes have been used in many frontier applications [8–13]; moreover, Ni, Cu, and Fe atoms have been recently focused on environmentally friendly chelating metals, alternatives to traditional Cr [2,3].

We have theoretically elucidated the Ni-$TAN_2$ by using molecular orbital calculations and analyzed its UV/VIS absorption spectrum. In the first step, we optimized the molecular structure by using the semi-empirical MSINDO method [50–54] and compared it with the X-ray determined structure [41]. Then, we calculated the electronic transition properties by adopting the semi-empirical INDO/S method [55–59] to study the origin of its color, that is main visible band, and other electronic transitions.

## 2. Calculation method

### 2.1. Molecular structure determination

Ni-$TAN_2$ molecular structure was determined by using the MSINDO method [50–54]. In the optimization process, the X-ray structure [41] was set as the initial guess. The X-ray analysis clearly shows that TAN is a tridentate ligand and Ni-$TAN_2$ is an octahedral coordinate complex; therefore, the electronic structure of the ground state was set as a triplet system. The SCF calculations were performed by the restricted open-shell Hartree–Fock (ROHF) scheme. In the optimization process, none of the constraints was assumed, for example, symmetry, planarity, and coordination structure.

### 2.2. Electronic transitions calculation

The equilibrium structure was then employed in the second step to calculate the electronic transition properties by the ZINDO–INDO/S method [55–59]. In this method, which is a modified INDO version for the UV/VIS absorption spectrum calculation, the integrals were evaluated with the Nishimoto–Mataga formula [60,61] and the SCF calculations were executed by the ROHF scheme. The configuration interaction (CI) calculations were performed including single excited configurations from the triplet ground state, consisting of 30 occupied orbital and 30 virtual orbital configurations.

## 3. Results and discussion

### 3.1. Molecular structure

Although the molecular structure of Ni-$TAN_2$ was already determined by the X-ray crystal structure analysis [41], its structural refinement was insufficient ($R = 0.16$); and also, the molecule in the crystal is largely affected by the intermolecular interactions and should be distorted. Analysis of the UV/VIS absorption spectrum as a dye molecule is a target of this study; the single molecular state, corresponding to the calculation, is the preferable model rather than that in the solid crystal phase. We have already shown that the MSINDO method well reproduces the three-dimensional structures of metal complexes [54]. On the other hand, the ZINDO method provides poor molecular geometries, since it is specialized for the electronic excited state calculation, and highly accurate ab initio and/or DFT methods demand much more computer resources on large molecule

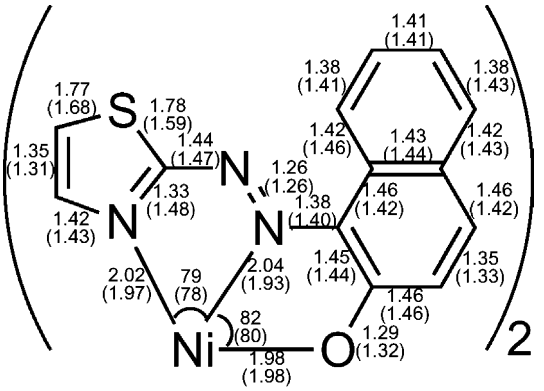


Fig. 1. Molecular structure of Ni-$TAN_2$, optimized by MSINDO method and determined by X-ray analysis [41] (in parentheses).

calculations such as Ni-$TAN_2$. Therefore, we adopted the MSINDO method to theoretically determine the Ni-$TAN_2$ molecular structure.

The MSINDO optimization roughly reproduces the X-ray determined structure [41] (see Fig. 1). Although we did not apply any constraints on the optimization process, the MSINDO calculation well provides the complex framework structure, both the octahedral Ni coordinate moiety and the two perpendicularly conformed planar azo chromophoric ligand parts. Especially, the coordination bond lengths, which are one of the most important points in the metal complex structure, were well reproduced; the calculated Ni–N and Ni–O bond lengths (~2.0 Å) are consistent with the typical lengths in the octahedral coordinate Ni(II) complexes[1] [25,41,62–68]. Despite such rough correspondence between the MSINDO and the X-ray structures, the discrepancy of the thiazole bond lengths is remarkable: differences of the (azo)-C–S and (azo)-C=N are 0.19 Å and 0.15 Å, respectively (Fig. 1). The corresponding thiazole bond lengths on the ligand and other metal complexes are (azo)-C–S, 1.65–1.76 (average 1.71) Å and (azo)-C=N, 1.29–1.32 (average 1.31) Å [39,40,42–48]: these lengths are near the calculated values rather than the X-ray structure [41]. In Fig. 1, the averaged values of both ligands are depicted; the maximum difference in each of the correspondents on both ligands is not over 0.002 Å on the MSINDO optimized structure. On the other hand, the maximum difference is over 0.1 Å on the X-ray structure by its insufficient refinement ($R = 0.16$) and/or the large intermolecular interaction by the crystal packing. Therefore, we consider that the MSINDO optimized structure should be close to that of the actual one as the dye.

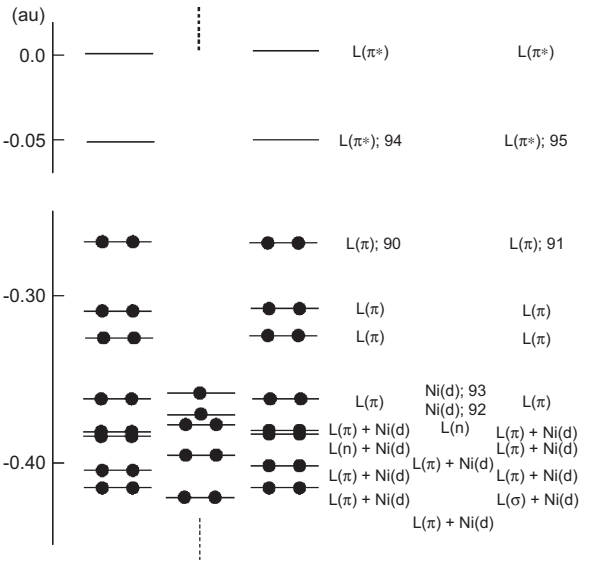


Fig. 2. Molecular orbital energy diagram of Ni-$TAN_2$ by INDO/S method.

### 3.2. Electronic transition properties

Since the theoretically determined structure is preferable to evaluate the molecular properties as a dye, we have calculated the electronic transitions of Ni-$TAN_2$ by using the INDO/S method at the MSINDO optimized structure and discuss the characteristics based on this calculated result.[2]

[1] In contrast, on the low spin square planar coordinate Ni(II) complex, the corresponding bond lengths are shorter, typically 1.8–1.9 Å; Alcock NW, Spencer RC, Prince RH, Kennard O. J Chem Soc A 1968; 2383–8. And on the high spin pyramidal coordinate Ni(II) complex, the correspondents are slightly shorter, ~1.95 Å; Nivorozhkin AL, Toftlund H, Nivorozhkin LE, Kamenetskaya IA, Antsishkina AS, Porai-Koshits MA. Transition Met Chem 1994;19:319–24.

[2] We also adopted the X-ray structure [41] for the electronic transitions' evaluation; but by its poor geometry, the calculated properties were inconsistent with the octahedral coordinate Ni(II) complex, for example, one of the singly occupied molecular orbitals (SOMOs) corresponded to the ligand LUMO.

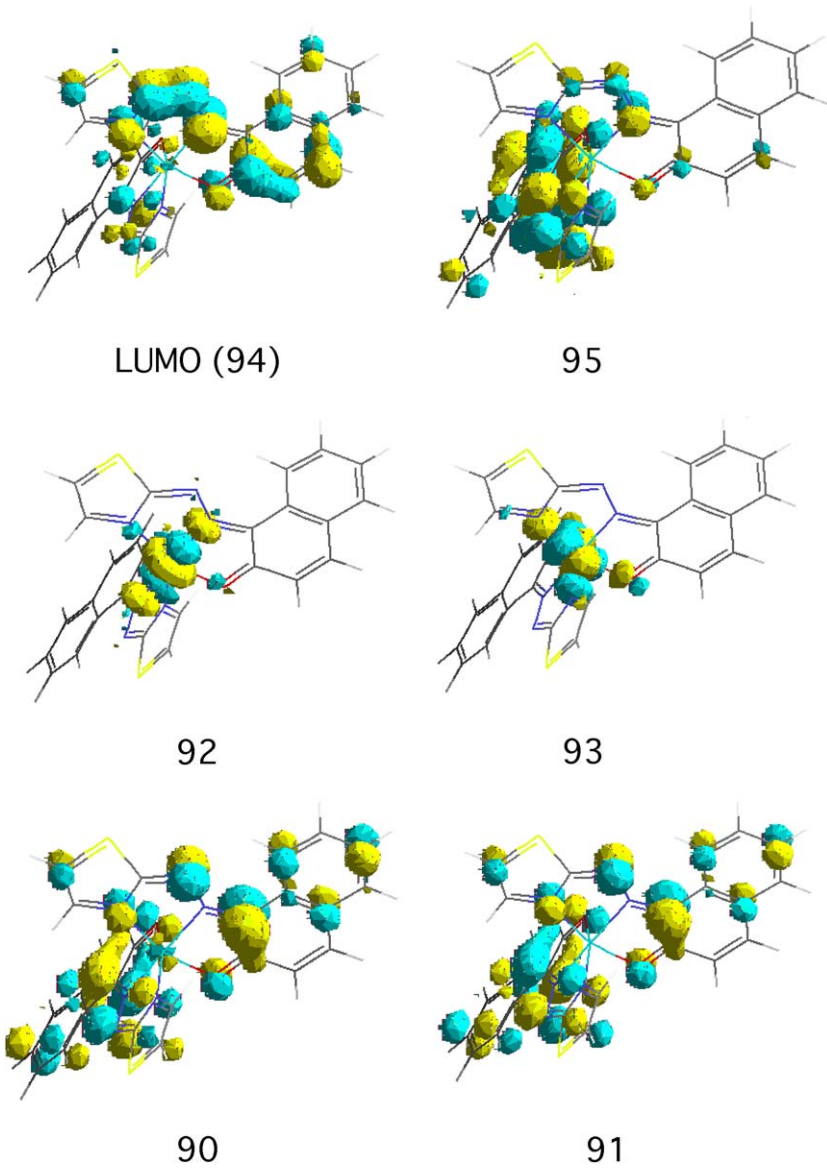


Fig. 3. Frontier molecular orbitals of Ni-$TAN_2$ by INDO/S method.

The INDO/S calculated orbital diagram is shown in Fig. 2 and some frontier orbitals are drawn in Fig. 3. These arrangements and shapes are consistent with the typical orbital pattern of octahedral coordinate Ni(II) complexes. Two SOMOs (92 and 93) originate from the Ni-d orbitals, and almost degenerated two highest occupied orbitals (90 and 91) and two lowest unoccupied orbitals (94 and 95) roughly correspond to HOMO and LUMO of the TAN ligand. Generally in inorganic metal complexes, SOMOs lie on the frontier energy level [69]; but the

Ni-$TAN_2$ SOMOs do not appear the highest occupied level (Fig. 2), since the large π-conjugation causes elevation of the ligand HOMO level.

Because Ni-$TAN_2$ is constructed from two tridentate π-conjugated ligands (TAN) with one transition metal (Ni), many kinds of electronic transitions should appear; these can be classified into metal to ligand charge transfer (MLCT), ligand to metal CT (LMCT), intrametal d–d* orbitals, intraligand, and interligand transitions. The calculated transitions have been assigned to these classes (Table 1) by the generated configurations (CI components) analysis based on the orbitals characteristics (Figs. 2 and 3). The main absorption band in the visible region, which is observed at 595 nm [30], corresponds to two intense π–π* transitions (17th and 18th rows in Table 1). These transitions are intraligand characteristics, excitations from the TANs' HOMO (90 and 91) to LUMO (94 and 95), and the combinations of these generated configurations clearly show the intraligand transitions rather than the interligand characteristics. Two TAN ligands locate each other's perpendicular conformation (Fig. 3); therefore, nearly degenerate two intense transitions, indicating the perpendicularly directed transition moments, appear.

Many electronic transitions lie in lower energy region (1st to 16th rows in Table 1). But these are originally weak intensity, such as d–d* in Ni atom, LMCT, MLCT, and interligand characteristics; therefore, we should not observe these bands in the UV/VIS absorption spectrum. That is to say, the main absorption band of Ni-$TAN_2$ originates from the HOMO→LUMO excitations of the ligands and the Ni coordination serves as the perturbation for the azo chromophoric system.

Table 1
Calculated transition properties of Ni-$TAN_2$ (INDO/S)

| Transition energy ($cm^{-1}$) | $f$[a] | Transition property |
|---|---|---|
| 9910 | 0.000 | Interligand (π–π*) |
| 9930 | 0.000 | Interligand (π–π*) |
| 11 380 | 0.000 | MLCT |
| 11 450 | 0.000 | MLCT |
| 11 900 | 0.000 | LMCT + Ni(d–d) |
| 12 050 | 0.000 | LMCT + Ni(d–d) |
| 13 020 | 0.000 | LMCT + Ni(d–d) |
| 16 660 | 0.000 | Interligand (π–π*) |
| 16 700 | 0.000 | Interligand (π–π*) |
| 17 250 | 0.001 | MLCT |
| 17 490 | 0.001 | MLCT |
| 17 990 | 0.000 | Interligand (π–π*) |
| 18 030 | 0.000 | Interligand (π–π*) |
| 21 040 | 0.008 | LMCT + Ni(d–d) |
| 21 410 | 0.030 | Interligand (π–π*) |
| 21 420 | 0.025 | Interligand (π–π*) |
| 21 790 | 0.612 | Intraligand (π–π*) |
| 21 840 | 0.574 | Intraligand (π–π*) |
| 22 460 | 0.096 | LMCT + Ni(d–d) |
| 22 520 | 0.052 | LMCT + Ni(d–d) |

[a] Oscillator strength.

## 4. Conclusion

To analyze the molecular structure and the electronic transition properties of metal complex dyes, we have theoretically elucidated the Ni-coordinate azo dye, Ni-$TAN_2$, by using the semi-empirical molecular orbital methods. The molecular structure, both of the transition metal coordination and the chromophoric π-conjugated ligand, is well reproduced by the MSINDO method. The INDO/S calculation clearly shows that the visible main band of Ni-$TAN_2$ originates from the intraligand transitions, which roughly correspond to the HOMO→LUMO excitation of the azo chromophoric ligand, and the transition metal coordination can be regarded as the perturbation for the azo ligand moieties.

We are currently investigating the mechanism of the absorption spectrum shift by the metal coordination, adopting further accurate methodologies; these results will appear in due course.

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