New Near-Infrared Spectrophotometry for d^8 Metal Ions, Ni^{II} and Pt^{II}, with 2,2'-Dithiobis(1-aminonaphthalene) in Aqueous Micellar Solutions

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1-Amino-2-naphthalenethiolate ion ($C_{10}H_6NH_2S^-$), produced from 2,2'-dithiobis(1-aminonaphthalene) (DTAN), forms 1:2 chelates with d^8 metal ions (Ni^{II} and Pt^{II}) in aqueous PONPE 20 micellar solutions, and then subsequent oxidation of the chelates with O_2 yield new NIR-absorbing chelates $[M^{II}(C_{10}H_6NHS\cdot)_2]^0$. The remarkable NIR absorption properties are as follows: for Pt^{II} (794 nm) $\varepsilon = 5.03 \times 10^4$ M^{-1} cm^{-1}; for Ni^{II} (884 nm) $\varepsilon = 4.73 \times 10^4$ M^{-1} cm^{-1}.

Recently, highly sensitive, selective and simple determinations have been demanded in the field of inorganic trace analysis for various biological and environmental samples. Near-infrared spectrophotometry at spectral region over 700—1250 nm is most likely to satisfy these demands. The NIR region has been inherently free from influence of the matrix absorption and emission, since it lies between electronic and vibrational transitions in molecular spectroscopy. However, the present status of the applications of NIR region is limited to the determinations of compounds having hydroxyl groups by the use of vibrational overtone absorption. In recent years, considerable efforts have been devoted to search for substances,[1] which absorb this low-energy light, because they might have great advantages in immunoassay,[2] optical data storage, photochemotherapy, photography,[3] etc. Nowadays, cost effective and high performance semiconductors can be obtained as NIR light sources and its detectors.[4]

We have been studying to develop NIR spectrophotometry for trace metal ions based on a strong electronic transition, having high signal-to-noise ratio and selectivity.[1] The NIR chromogenic reagents we studied, π-electron conjugated 1,2-dithiols and 1,2-diamines, were demonstrated to form intensely NIR-absorbing chelates with d^8 metal ions. However, they were difficult to apply for practical use because the reagents in aqueous solutions are unstable.

In this communication, 2,2'-dithiobis(1-aminonaphthalene) (DTAN, shown in Figure 1), which is used as a fluorometric derivatizing agent for aromatic aldehydes,[5] has been found that it has excellent properties as a new NIR chromogenic reagent for Ni^{II} and Pt^{II} ions. That is, 1-amino-2-naphthalenethiolate ion ($C_{10}H_6NH_2S^-$) in Figure 1, having S and N donor atoms, acts as a chelating ligand, to form 1:2 planar chelates with d^8 metal ions. Subsequent oxidation of the chelates with dissolved dioxygen yield the strongly NIR-active species. Their chelates formation characteristics including an unusual electronic structure have been reported in PONPE 20 micellar solutions as follows. Moreover, DTAN is the disulfide form of the ligand, therefore, it has great advantage in view of degradation resistance against air and light.

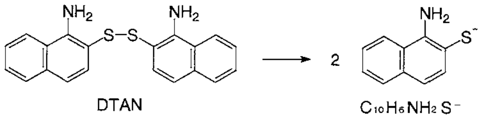

Figure 1. Structures of DTAN and 1-amino-2-naphthalenethiolate ion.

The reagent, DTAN (purity: 99.8%) was used as received from DOJINDO Lab. (Kumamoto, Japan) and its aqueous micellar solution of 2×10^{-3} M was prepared by dissolving it in hot water containing 5 wt% of a nonionic surfactant, polyoxyethylene-4-nonylphenoxyether with 20 oxyethylene units (PONPE 20, Tokyo Kasei, Tokyo, Japan). The DTAN stock solution is stable over two months in an amber bottle in a refrigerator. This surfactant was also useful for solubilization of the chelates in aqueous solutions. Electronic spectra were recorded on a Hitachi Model U-2000 spectrophotometer with a Si photodiode detector (up to 1100 nm).

The recommended procedure is as follows: To a 1 ml aliquot of acidic solution containing up to 20 µg of Pt^{II} ion, 100 µl of 1 M acetate buffer solution (pH 4.7), and 2.5 ml of the 2×10^{-3} M DTAN solution were added. The mixture was diluted to 10 ml with water and transferred in an amber capped tube, and heated for 30 min on a boiling water bath. After cooling to room temperature, the absorption spectra in NIR region were measured. For Ni^{II} ion were added 1 ml of 0.1 M N-cyclohexyl-3-aminopropanesulfonic acid (CAPS) — NaOH solution at pH 11 as a pH buffer and 1 ml 0.05 M L-ascorbic acid solution before heating for 5 min.

The reaction and spectral properties of Pd^{II} were also investigated. For Pd^{II} ion, CAPS beffer at pH 11 was added.

The NIR absorption spectra of Ni, Pd, and Pt-DTAN systems are shown in Figure 2. The ligand, DTAN, and chelates of other metal ions have no absorption in this region at all; their absorption bands locate only shorter wavelengths than 500 nm, therefore, these facts guarantee lower background absorption

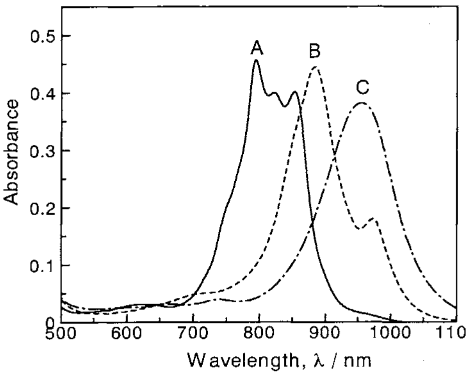

Figure 2. Absorption spectra of Pt(A), Ni(B), and Pd(C)-DTAN systems with reference to water.
$[Ni^{II}] = [Pt^{II}] = 1 \times 10^{-5}$ M; $[Pd^{II}] = 2.5 \times 10^{-5}$ M; $[DTAN] = 5 \times 10^{-4}$ M; [pH buffer] = 0.01 M: Pt, pH 4.7; Pd, pH 11; Ni, pH 11; [L-ascorbic acid (for Ni)] = 5 mM; Heating time: Pt, 30 min; Pd, 60 min; Ni, 5 min.

and unique selectivity. The absorption spectra of the solutions obtained by the recommended procedure were identified to the chelate having a stoichiometry of 1:2 by elemental analysis and mass spectral data of the synthesized chelates, prepared by the method similar to that of $[Ni(C_6H_4NHS)_2]$.[6] The electronic spectra of the chelates in DMF solution were in good agreement with that of the *in situ* prepared one in PONPE 20 micellar solutions. The coordination mode of the ligands in the chelate was sure to be imido-thiolato form by mass spectral data including parent peaks at *m/e* 404 and 541 for Ni and Pt, respectively. A cyclic voltammetric study of Pt chelate (1 mM, scan rate 5 mV/sec) in anhydrous DMF with 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte at room temperature displayed three redox processes at –1.54 V (irreversible), –0.80 V (reversible, formation of NIR-active species), and +0.25 V (irreversible) *versus* the Ag/Ag^+ reference pair. It corresponds to ligand-centered one-electron redox series of the chelate. According to NMR studies of the Pt and Ni chelates indicating paramagnetic feature, the possible electronic structure of the NIR-active compound would be an unusual biradical form, $[M^{II}(C_{10}H_6NHS\bullet)_2]^0$. Moreover, on the basis of the ESR spectrum of $[Ni(C_6H_4NHS\bullet)_2]^-$ reported by Stiefel,[7] these low energy transitions are assigned as M^{II}-radical ligand structure with both spin-singlet and spin-triplet ground state as possibilities in a molecular orbital system for planar geometry.

The optimal conditions for NIR-absorbing chelate formation of d^8 metal ions in aqueous PONPE 20 micellar solutions are listed in Table 1. Even though the stoichiometry of the chelate is 1:2 at the 10^{-5} M of d^8 metal ions, an excess of the ligand is necessary to saturate the NIR color development: DTAN concentration were 1×10^{-4} M and 5×10^{-4} M for Ni and Pt ions, respectively. This fact suggests that DTAN and the ligand redox pair may play an important role in the chelation and the oxidation process of the chelate. The optimal solution pH conditions for d^8 metal ions shown in Table 1 were remarkably different from each other, which seem to be caused by pH influences on the chelate oxidation by dissolved dioxygen coupled with the deprotonation of coordinating amido groups.

The rather rapid NIR color formation was advantageous especially for Pt ion because of 'soft base' nature of the ligand. It takes 30 min and 5 min for the quantitative coloration of Pt and Ni at 10^{-6} M levels under the heating conditions, respectively. Only in the case of Pd ion, as heating time passed from 1 to 60 min, the absorption band gradually shifted to longer wavelength from 898 to 974 nm.

The dissolved dioxygen was one of the most suitable oxidant for the Pt and Pd-DTAN systems. With more strong oxidants such as $KBrO_3$ or KIO_3, the Pt chelate was overoxidized to an NIR-inactive chelate, assumed to be cationic. On the other hand, in the case of Ni-DTAN system, it is interesting that the addition of L-ascorbic acid at 5×10^{-3} M greatly enhanced the NIR color development; beside, it should be added only before heating. Cutting the disulfide bond of DTAN to derive the working ligand with L-ascorbic acid before the chelate formation favored the overall NIR color formation.

The calibration curve for Pt^{II} was linear over a wide concentration range of $1 \times 10^{-7} - 1 \times 10^{-5}$ M (r = 0.9990), and the 3σ detection limit depending only on the inherent noise of the spectrophotometer was 9×10^{-8} M. The reproducibility was as good as 1.4% in terms of relative standard deviation at 1×10^{-6} M of Pt ion for 5 determinations. In the case of Ni^{II}, the chelate was derived quantitatively in spite of the competitive hydrolysis reaction at pH 9 – 11, therefore calibration curve had a good linearity in $5 \times 10^{-7} - 3 \times 10^{-5}$ M (r = 0.9994). The NIR color of the chelates was stable for at least 3 days in an amber capped tube at room temperature. There were no spectral influences on Pt-DTAN system at 1×10^{-5} M from Fe^{III}, Cu^{II}, and Zn^{II} ions at the normal human serum level, 2×10^{-5}, 3×10^{-5}, and 5×10^{-5} M, respectively.

Table 1. Spectral properties and optimal conditions for NIR color development in aqueous micellar solutions.

	Conditions	λ_{max}/ nm (ε_{max} / 10^4 M^{-1} cm^{-1})
Ni^b	5 min^a pH 9 – 11	884 nm (4.72)
Pd	1 – 60 min^a pH > 11	898 – 974 nm (0.5 – 1.6)
Pt	30 min^a pH 4 – 6	794 nm (5.03)

^{a}All reactions were carried out on a boiling water bath. ^{b}The solution was containing 5 mM L-ascorbic acid.

Consequently, the NIR-absorbing chelate formation reaction for Ni^{II} ion in aqueous micelles is most likely composed of the following three reaction steps:

$$\mathrm{DTAN} \rightarrow 2\,C_{10}H_6NH_2S^- \tag{1}$$

$$M^{II} + 2\,C_{10}H_6NH_2S^- \rightarrow [M^{II}(C_{10}H_6NH_2S^-)_2]^0 \tag{2}$$

$$[M^{II}(C_{10}H_6NH_2S^-)_2]^0 + 1/2O_2 \rightarrow \underset{\text{NIR-active form}}{[M^{II}(C_{10}H_6NHS\bullet)_2]^0} + H_2O \tag{3}$$

The NIR-inactive chelate, derived from Ni^{II} ion and the ligand (Eq. 2), is oxidized with O_2; furthermore, concomitantly deprotonation of amido groups is carried out (Eq. 3). Only the uncharged biradical chelate is NIR-active. For Pt^{II} ion, it reacts directly with DTAN to give the NIR-active species.

In conclusion, NIR spectrophotometry for d^8 metal ions with DTAN has an outstanding potential for biological samples because of reagent's stability, high sensitivity, selectivity, and the spectral transparency for the matrix.

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