Nonlinear Optical Properties of $[C_6H_5N\text{-}R][Ni(mnt)_2]$ (R= *p*-nitrobenzyl)

Xuhui Zhu, Xiaozeng You,* Xiaoming Ren, Weilian Tan,† Wei Ji,*† S. S. Sundara Raj,†† and Hoongkun Fun††
Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China
†Department of Physics, National University of Singapore, Lower Kent Ridge Road, Singapore 119260, Republic of Singapore
††X-Ray Crystallography, School of Physics, Universiti Sains, Malaysia

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Investigation of third-order optical nonlinearity of complex **1,** $[C_6H_5N\text{-}R][Ni(mnt)_2]$ where R= *p*-nitrobenzyl, mnt = maleonitrile-1,2-dithiolate, with 7 ns laser pulses at 532 nm shows that it exhibits negligible nonlinear absorption, but considerable nonlinear refraction. In terms of two calculated figures of merit *W* and *B* resulting from one-photon and two-photon absorptions, complex **1** may be used for all-optical signal processing.

Third-order nonlinear optical materials with low nonlinear absorption but large nonlinear refraction have attracted considerable attention because of their potential uses in all-optical signal processing devices.[1] Metal dithiolenes are of interest based on a number of reasons:[2-4] (i) excellent photostability under laser irradiation; (ii) in the presence of molecular stacking, near-IR and IR absorption occurs, which is essential for a number of electro-optic applications. Salts of metal dithiolene anions offer more structural tunability than the neutral metal dithiolenes with easy incorporation of a variety of cations including NLO chromophores as counter ions.[5-7] Recently we have initiated a program to study the coordination complexes in third-order optical nonlinear applications.[8-10] Herein we report the crystal structure and third-order optical nonlinearity of complex **1**, *N*-*p*-nitrobenzylpyridinium bis(maleonitrile-1,2-dithiolato) Ni(III), i.e. $[C_6H_5N\text{-}R]$ $[Ni(mnt)_2]$.

Complex **1** was synthesized by refluxing $Na[Ni(mnt)_2]$[11] with *N*-*p*-nitrobenzylpyridinium bromide in good yield in ethanol. Anal. Found: C, 43.2; H, 2.4; N, 15.3%. Calcd. for $C_{20}H_{11}N_6NiO_2S_4$: C, 43.3; H, 2.0; N, 15.1%. Single crystals suitable for X-ray analysis was obtained by evaporation of a CH_3CN solution. The structural diagram of complex **1** was shown in Figure 1.[12] The mean bond length of 2.1473 Å of S-Ni bonds is comparable with those reported for other $[Ni(mnt)_2]^-$ salts.[13-15] The monoanions $[Ni(mnt)_2]^-$ are weakly associated with each other and give rise to a typical column structure, separated by the stacking cations which are arranged in a centrosymmetric way as shown in Figure 2; in the column the

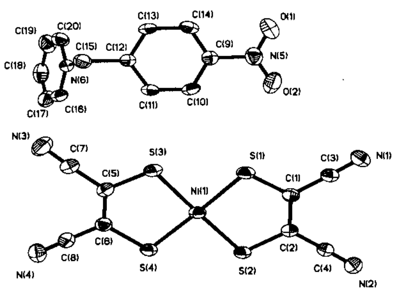


Figure 1. ORTEP of complex **1** with atomic numbering scheme showing 30% probability displacement ellipsoids.

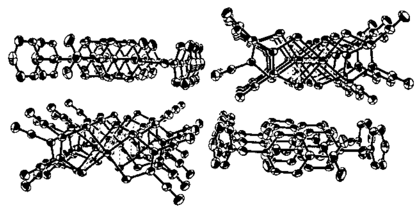


Figure 2. The molecular packing of the monoanions and cations down *a* axis showing the stacking of the cations and anions.

neighboring monoanions form a diad with the closest interplanar distances of Ni· · ·Ni of 3.825 Å and S· · ·Ni of 3.607 Å and S· · ·S of 3.889 Å , a bit longer than the corresponding sums of van der Waals radii of 3.26 Å, 3.48 Å and 3.7 Å, respectively.[14]

The electronic spectrum of complex **1** in Figure 3 shows that it exhibits diagnostic absorption of monoanion $[Ni(mnt)_2]^-$ with maximum at 872 nm (absorption coefficient 5600 dm^2 mol^{-1}).

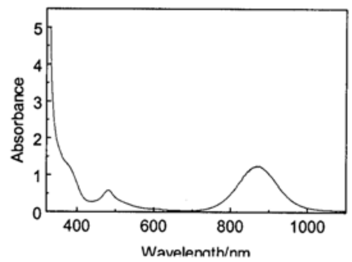
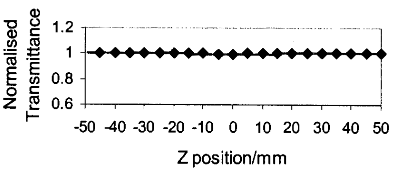


Figure 3. The electronic spectrum of complex **1** in DMF solution (2.27×10^{-4} mol dm^{-3}, 1cm optical path).

A DMF solution of complex **1** was contained in 1-mm quartz cell. The sample was irradiated by 7-ns (FWHM) laser pulses at a repetition rate of 10 Hz and placed at the focus where the spot radius of the pulses was 32 ± 5 µm for the 532-nm pulses.[8] The NLO property of the sample was determined by performing the Z-scan measurements. The sample was mounted on a translation stage that was controlled by the computer to move along the Z-axis with respect to the focal point. For determining both the sign and magnitude of the nonlinear refraction, a 1.0-mm diameter aperture was placed in front of the transmission detector and the Z-axis (closed-aperture Z-scan). For measuring the nonlinear absorption, the Z-dependent sample transmittance was taken without the aperture (open-aperture Z-scan).

Complex **1** is very stable toward air and under laser irradiation and the NLO property is dominated by nonlinear refrac-

(a)



(b)

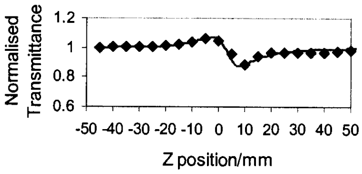


Figure 4. Z-scan data of complex 1 in DMF solution at laser wavelength 532 nm (1.35×10^{-3} mol dm^{-3}, 1mm optical path): (a) collected under the open aperture configuration showing negligible NLO absorption; (b) collected under the closed aperture configuration showing the self-defocusing effect. The solid curves show the theoretical fittings.

tion. The nonlinear absorption is negligible, as illustrated in Figure 4. The valley-peak pattern of the normalized transmittance curve obtained under closed aperture configuration shows characteristic self-defocusing behavior of the propagation light in the sample. Accounting for the input energy of 25 μJ, beam waist of 32 μm, optical path of 1mm and linear absorption coefficient, α_0 of 2.1cm^{-1} at 532 nm and by fitting Figure 4 with the Z-scan theory,[16] we calculated the nonlinear refractive index coefficient, n_2 and two-photon absorption coefficient, β to be -2×10^{-13} cm^2/W and 1.6×10^{-9} cm/W, respectively. Experiments with varied I show that n_2 so measured is indeed independent of I, consistent with the notion that $n=n_0+n_2I$ and the observed NLO phenomenon is third-order in nature where I is the on-axis irradiation; n, n_o is the nonlinear refractive index and linear refractive index, respectively. If we ignore the contribution of the NLO absorption, the third-order NLO susceptibility $\chi^{(3)}$ of complex **1** in DMF solution can be calculated from the n_2 value according to the following equation (n_o=1.429):

$$\left|\chi^{(3)}\right| = \left|\chi_r^{(3)}\right| = \left|\frac{Cn_0^{\ 2}}{80\pi} n_2\right| = 4.88\times10^{-11} esu$$

It should be noted that the nonlinear optical signal observed for the DMF solvent was negligible. Thus, we confirmed that the nonlinear contribution was by complex **1**.

For a material to be used for all-optical signal processing, two figures of merit W and B should satisfy the conditions (1) and (2)[17,18]

$$W = \frac{n_2(\lambda)I_{dam}}{\alpha_0\lambda} > 1 \quad (1), \qquad B = \frac{n_2(\lambda)}{2\beta\lambda} > 1 \qquad (2)$$

In our case the I_{dam} is the sample damage threshold and assumed as 3 GW/cm^2 due to excellent photostability of complex **1**, then the calculated W and B were 5.4 and 1.2, respectively. Therefore the result is interesting for all-optical signal processing though the response time is not on a picosecond scale as complex **1** admits of full potentials for structural modifications and is very stable under laser irradiation. Further work is in progress as to the picosecond optical nonlinearity to be investigated.

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12 Crystal data: $C_{20}H_{11}N_6NiO_2S_4$, M = 554.30, monoclinic, space group $P2_1/c$, a =12.2019(2), b = 26.5443(7), c = 7.2409(2) Å, β = 102.928(1)°, V = 2285.81(9) Å^3, Z = 4, Dc = 1.611 Mg/m^3, μ(Mo-Kα) = 1.246 mm^{-1}. Black crystal 0.48×0.28×0.06 mm. 16240 reflections measured, 5653 unique (R_{int} = 0.0729). $R1$ = 0.0502, $wR2$ = 0.1065 for $I>2\sigma(I)$; $R1$, $wR2$ = 0.0977, 0.1228 (all data), goodness of fit (on F^2) = 0.919. The data were collected on a Siemens Smart CCD diffractometer with monochromated Mo-Kα (λ=0.71073 Å) radiation at 293(2) K and reduced by using the program SAINT. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXTL V5.1). Anisotropic thermal factors were assigned to all the non-hydrogen atoms.
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