Synthesis, Structure and Optical Refractive Effect of Dibutyltin(IV) Complex of $[Ph_2P(S)NP(S)Ph_2]^-$

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Reaction of n-Bu_2SnCl_2 with $K[Ph_2P(S)NP(S)Ph_2]$ in CH_3CN gives the spirobimetallocyclic complex bis(tetraphenyldithioimidodiphosphinato)dibutyltin (IV), $\{n\text{-}Bu_2Sn[Ph_2P(S)NP(S)Ph_2]_2\}$ in which π–π stacking interactions by the phenyl rings of the ligands exist. The nonlinear optical (NLO) properties were studied with an 8 ns-pulsed laser at 532 nm. Its optical responses to the incident light exhibit strong refractive effect with $n_2 = 5.4 \times 10^{-18}$ m^2 W^{-1} in a 1.2×10^{-4} mol dm^{-3} DMF solution.

The ligands bis(dialkylchalcogenidophosphoryl)amide, $[N(QPR_2)_2]^-$ (Q = S or Se; R = Ph or Bu), have recently been the focus of many studies because of the structural diversity of their metal complexes.[1–5] They exhibit a range of binding geometries that can be fine-tuned by Q and R and diverse metallocycles have been created by their coordination. Since electronic flexibility of these ligands deviated from the P–Q π bonds makes both chalcogen atoms become strong donors, we reasoned that the combination of an organometallic fragment with these donor ligands might lead to molecules with unique properties and potentially enhanced NLO coefficients. As part of our program to prepare nonlinear optical materials with different chelate rings and to explore the relationship between structure and functions,[6–7] we synthesized the title product, the first example of this type that contains n-Bu_2Sn^{2+} organometallic moiety, and its non-linear optical properties are also studied.

The complex was synthesized by the reaction of n-Bu_2SnCl_2 with $K[Ph_2P(S)NP(S)Ph_2]$ in CH_3CN and a little water. Slow evaporation of the solution for several days gives satisfactory crystals for X-ray analysis (0.94g, yield 83 %).[8]

The crystal contains discrete, highly symmetric $\{n\text{-}Bu_2Sn[Ph_2P(S)NP(S)Ph_2]_2\}$ molecules [9] (Figure 1). The tin was coordinated by two tetraphenylimidodiphosphino ligands and two butyl groups in a slightly distorted octahedron geometry. Two $[Ph_2P(S)NP(S)Ph_2]^-$ anions in a molecule unit are coordinated to the central tin(IV) atom acting as isobidentate ligands, forming two symmetrical SnS_2P_2N spirometallocycles. The SnS_4 unit forms an equatorial plane [Σ(S–Sn–S) = 360°] with opposite sulfur atoms from different ligand co-linear [S1–Sn–S1A = 180° and S2–Sn–S2A = 180°]. Although the closely related $\{n\text{-}Bu_2Sn[Ph_2P(O)NP(O)Ph_2]_2\}$ possesses the similar octahedral coordination,[10] a distinct difference can be found: compared with the exometallocyclic angles [for example S1–Sn–S2A = 88.92°], the endocyclic bite angle [for example S1–Sn–S2 = 91.08 °] in the chelate ring is greater, as is expected due to the presence of the more sterically demanding two sulfur atoms. Within the crystal the molecule pack exhibits face-to-face π–π interactions by the phenyl rings of the ligands (Figure 2), a similar behavior was observed for mix-ligand complex $\{Pd\text{-}[Ph_2PNP(Se)Ph_2]\text{-}[N(SePPh_2)_2]\}$.[11]

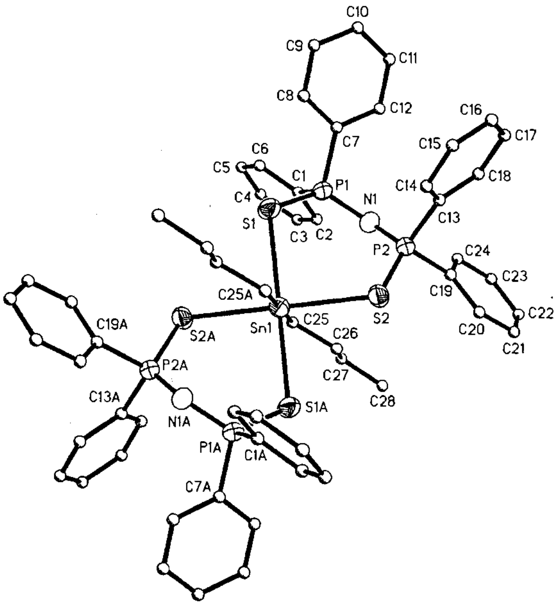

Figure 1. A perspective view of $\{n\text{-}Bu_2Sn[Ph_2P(S)NP(S)Ph_2]_2\}$ with the ellipsoids drawn at 30% probability level. Main bond distances (Å) and angles (°): Sn1–C25, 2.156 (3); Sn1–C25A, 2.156 (3); Sn1–S1, 2.7201 (9); Sn1–S1A, 2.7201 (9); Sn1–S2, 2.7320 (8); Sn1–S2A, 2.7320 (8); S1–Sn1–S1A, 180.00 (4); S1–Sn1–S2, 91.08 (2); S1–Sn1–S2A, 88.92 (2); S1A–Sn1–S2, 88.92 (2); S1A–Sn1–S2A, 91.08 (2); S2–Sn1–S2A, 180.000 (13).

A DMF solution of the complex was placed in a 5-mm quartz cuvette for NLO measurements. Their NLO properties were measured with an 8 ns pulse at 532 nm generated from a Q-switched frequency-doubled Nd:YAG laser. The spatial profiles of the optical pulses were nearly Gaussian after passing through a filter. The pulsed laser was focused onto the sample cell with a 15 cm focal length mirror. The spot radius of the laser beam was measured to be 55 μm. Incident and transmitted pulsed energies were measured simultaneously by two energy detectors (RJP-735 Energy probes, laser precision). The NLO properties of the sample were determined by performing *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. An aperture of 0.5 mm radius was placed in front of the transmission detector. The transmittance recorded as a function of the sample position on the *Z*-axis (closed-aperture *Z*-scan). For measuring the NLO absorption, the *Z*-dependent sample transmittance was taken without the aperture (open-aperture *Z*-scan). *Z*-scan experiment shows that its NLO properties are

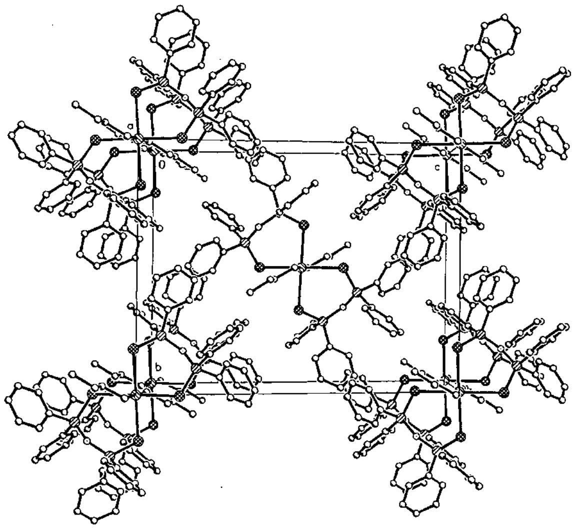

Figure 2. View down the *a* direction in the crystal showing the aromatic π–π stacking.

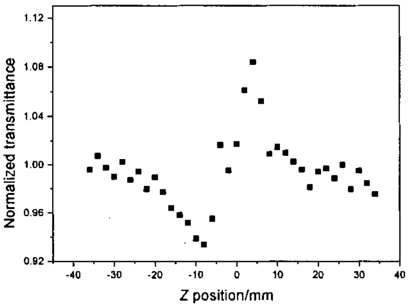

Figure 3. *Z*-scan measurement of complex in 1.2×10^{-4} M DMF solution: The data were obtained by dividing the normalized *Z*–scan measured under a closed aperture configuration by the normalized *Z*-scan data of open aperture configuration.

dominated by non-linear refraction, and the data are given in Figure 3. The filled boxes are the experimental data measured under a closed aperture and it is observed that compound shows positive sign for n_2. This indicates that the laser beam propagating in compound undergoes a self-focusing process.

The nonlinear refractive component of the complex was assessed by dividing the normalized *Z*-scan data obtained under open aperture configuration. An effective third-order nonlinear refractive index n_2 can be derived from the difference between normalized transmittance values at valley and peak positions ($\Delta T_{V\text{–}P}$) by using equation (1).[12]

$$n_2^{eff} = \frac{\lambda\alpha_0}{0.812\pi I\left(1-e^{-\alpha_0 L}\right)}\Delta T_{V-P} \qquad (1)$$

The effective NLO refractivity n_2 value of the complex was estimated to be 5.4×10^{-18} m^2 W^{-1}. Therefore it exhibits strong NLO refractive properties. Although this value of the measured n_2 was obtained with a 1.2×10^{-4} mol dm^{-3} solution of the title compound, this is comparable with many best known third-order NLO materials in neat solid form, such as SiO_2 (2×10^{-20} m^2 W^{-1}) and CdS (2.5×10^{-18} m^2 W^{-1}),[13] $SrLaGa_3O_7$ (11.1×10^{-20} m^2 W^{-1}) and $Ca_2Ga_2SiO_7$ (6.5×10^{-20} m^2 W^{-1}).[14] The n_2 value of this mononuclear complex is also comparable to that of the polynuclear heterothiometallate complex of $[Ph_2P(S)NP(S)Ph_2]^-$ in DMF solution.[4] A much larger n_2 value may be expected with more concentrated solutions. So this work may open up broad prospects of producing NLO materials through rational molecule design approach. It should be noted that although the *Z*-scan measurements reported here could not reveal the origin of the measured n_2 values for title compound, because of the similarity of electronic flexibility in the metallocycles of this complex with that of the 'electron-deficient' heterometal clusters from σ-donor ligands,[6] we can deduce that the good NLO effect may comes from two origins: (a) the resonance and thermal-effect; (b) the third-order bound-electronic effect, excited-state effect, two-photon absorption, and nonlinear scattering.[15] To gain insight into the mechanisms leading to the observed phenomena, further works on a nanosecond or picosecond time-resolved pump-probe experiments are underway.[16]

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8 Found: C, 59.46; H, 5.17; N, 2.48%. Calcd. for $C_{56} H_{58} N_2 P_4 S_4Sn$: C, 59.53; H, 5.17; N, 2.48%. IR (KBr pellet, cm^{-1}): $\nu(P_2\text{–}N)$, 1176(s) and 784(s); ν(P–S), 565(vs); $\nu(P\text{–}C_2)$, 715(m) and 690(s).

9 Crystal data for complex $C_{56} H_{58} N_2 P_4 S_4$ Sn, MW = 1129.85, monoclinic, space group $P2_1/n$, a = 9.2692(13), b = 15.142(2), c =19.5265(18) Å, β = 98.7473(18)°, V = 2708.7(6) Å^3, Z = 2, D_c = 1.385 g/cm^3, $F(000)$ = 1164, μ = 0.782 mm^{-1}. Crystal dimensions: $0.29 \times 0.27 \times 0.18$ mm^3. R = 0.0357, R_w = 0.0949. All measurements were on a Siemens Smart 1-K CCD area-detector diffractometer by using a ω-scan technique at 293(2) K. Mo Kα radiation, λ = 0.71073 Å.

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