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Supramolecular assemblies of organotellurium(IV) dithiocarbamates and third order nonlinear optical susceptibility ($\chi^{(3)}$) of $C_4H_7(CH_3)Te[S_2CN(C_2H_5)_2]_2$

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ABSTRACT

Synthesis of supramolecular assemblies of organotellurium(IV) dithiocarbamates, formed through intramolecular Te···S secondary bonds, intermolecular Te···X (X = I, S) secondary bonds and C–H···O hydrogen bonds are described. The supramolecular assemblies containing diethyldithiocarbamate group may serve as possible "rescue agents". The third order nonlinear optical susceptibility of the organotellurium(IV) diethyldithiocarbamate $C_4H_7(CH_3)Te[S_2CN(C_2H_5)_2]_2$ (**1**) has been studied by degenerate four wave mixing technique using a picosecond laser. It is found to exhibit efficient third-order nonlinear optical susceptibility ($\chi^{(3)}$) of 7.21×10^{-14} esu and second order hyperpolarizability (γ) of 4.88×10^{-32} esu.

1. Introduction

Thiocarbamates/metal thiocarbamates have impressive applications for example in (a) coordination chemistry [1–3], (b) supramolecular chemistry [4–7], and (c) constructing sensors for guest substrates [8–10]. Among dithiocarbamate ions, diethyldithiocarbamate ion $[(Et_2NCS_2)^-]$ containing soft sulfur atoms occupies special place in view of its use as competitive "rescue agent" in place of (*cis*-platin) *cis*-diamminedichloroplatinum (II) $[Pt(NH_3)_2Cl_2]$ and related drugs for the protection of thiols. The chemotherapeutic use of *cis*-platin and related drugs consists of some negative side effects including nephrotoxicity which are thought to be primarily because of the inactivation of enzymes by coordination of Pt (II) to thiol groups [11] while it is believed that $[Et_2NCS_2]^-$ does not exhibit nephrotoxic effect [12–14]. Further in recent years, there have been very rapid developments in the field of nuclear medicine [15,16] and now a days, the coordination compounds of Tc^{99m} are extensively used as diagnostic agents (imaging agents) for the diagnosis of the ailments of almost all the organs of human body [17,18].

On the other hand, tellurium-organic compounds have the tendency to get deposited in myocardium [19,20]. A combination of the two, i.e. organo(heterocyclic) tellurium diethyl dithiocarbamates will supposedly be (a) potential candidates to mimic the above discussed characteristics shown by Tc^{99m} – organic compounds useful as imaging agents in nuclear medicine as well as (b) the suitable candidates for balancing the thiol level as "rescue agents".

In view of the probable potential applications of organotellurium diethyldithiocarbamates as "rescue agents", we in the present investigation have synthesized and X-ray characterized organo(heterocyclic) tellurium diethyldithiocarbamates and a comparative account of X-ray structures and their supramolecular associations is presented.

Further, the design of materials with good third order nonlinear optical (NLO) properties and fast response time have found applications such as power limiting for sensor protection, optically addressed optical switches for photonics switching, all optical signal processing and optical computing [21–30]. A promising approach to developing such materials with improved third order NLO properties is to incorporate transition element centers into organic materials (organotransition metals). In contrast, in the present investigation, we have introduced semimetal (Te) into organic group yielding organosemimetal (tellurium) and derivatised it as organotellurium(IV) diethyldithiocarbamate $C_4H_7(CH_3)Te[S_2CN(C_2H_5)_2]_2$ (**1**) and probed its NLO properties using a short laser pulse 30 ps at 532 nm and a repetition rate of 10 Hz through standard degenerate four wave mixing technique (DFWM) in the boxcar geometry.

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[1] P.C.S. dedicates this work to esteemed Prof. Dr. H.W. Roesky.

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2. Experimental

2.1. Reagents, general procedures and Instrumentation

$C_4H_8TeI_2$ [31], $C_4H_7(CH_3)TeI_2$ [32], and $C_8H_8TeI_2$ [33,34] were prepared according to the literature methods. Aniline, morpholine, piperidine and carbon disulfide (Aldrich) were distilled before use. Sodium/ammonium salts of dithiocarbamates were freshly prepared. Sodium diethyl dithiocarbamates was bought from Aldrich. The solvents and other general reagents used in the present investigation were purified according to the standard procedure and freshly distilled before use. Tellurium content was determined in the laboratory [35]. Elemental analyses for C, H and N were carried out on an Elemental Analyser Heraeus Carlo Erba 1108. IR spectra were recorded with a sample in KBr disc, using Shimadzu 8210 PC FTIR spectrophotometer in the frequency range 4000–400 cm^{-1}. Solution ^1H NMR spectra were recorded at 300.13 MHz in $CDCl_3$ on Varian DRX 300 NMR spectrometer.

2.2. Synthesis

2.2.1. Synthesis of $C_4H_7(CH_3)Te[S_2CN(C_2H_5)_2]_2$ (**1**)

To the clear solution of 2-methyl-1,1-diiodo-1-telluracyclopentane $[C_4H_7(CH_3)TeI_2]$ (1.00 g, 2.21 mmol) in ~25 ml dichloromethane was added sodium diethyl dithiocarbamate (0.99 g, 4.42 mmol) in 1:2 M ratio and stirred for 4 h at room temperature. The reaction mixture was filtered to eliminate the unidentified material. The filtrate was concentrated to ~15 ml and a layer of pet-ether (40–60°) was laid on it. Pale yellow crystals of 2-methyl bis(diethyl dithiocarbamato)-1-telluracyclopentane (**1**) were obtained; yield: 0.42 g (38%), m.p. 94 °C. *Anal.* Calc. for $C_{15}H_{30}N_2S_4Te$: C, 36.47; H, 6.08; N, 5.67; Te, 25.85. Found: C, 36.45; H, 6.07; N, 5.64; Te, 25.84%. FT-IR (KBr, cm^{-1}): 1485 s, 1422 s (νCN), 983 m, 918 m (νCS), 560 w ($\nu TeCH_2$). ^1H NMR ($CDCl_3$) δ ppm: 3.9 (m, 3H, 2, 5-H), 3.60 (q, 8H, NCH_2), 3.0 (m, 4H, 3, 4-H), 1.95 (d, 3H, C_2–Me), 1.26 (t, 12H, $NCCH_3$).

Similarly 2-metyl-1-iodo-1-morpholine dithiocarbamato-1-telluracyclopentane $C_4H_7(CH_3)TeI[S_2CNC_4H_8O]$ (**2**) and 2-metyl-1-iodo-1-piperidine dithiocarbamato-1-telluracyclopentane $C_4H_7(CH_3)TeI[S_2CNC_5H_{10}]$ (**3**) were prepared by the reactions of $C_4H_7(CH_3)TeI_2$ with freshly prepared ammonium salts of morpholine- and piperidene dithiocarbamates in 1:1 M ratio respectively. Complex (**2**) yield: 0.12 g (11%), m.p. 145 °C. *Anal.* Calc. for $C_{10}H_{18}NS_2OTeI$: C, 24.66; H, 3.70; N, 2.88; Te, 26.22. Found: C, 24.63; H, 3.67; N, 2.87; Te, 26.20%. FT-IR (KBr, cm^{-1}): 1458 s, 1424 vs (νCN), 1024 m, 988 s (νCS), 542 s ($\nu TeCH_2$). ^1H NMR ($CDCl_3$) δ ppm: 4.12 (t, 2H, NCH_2), 4.0 (t, 4H, CH_2O), 3.79 (m, 3H, TeCH and $TeCH_2^{++}$), 2.97 (m, 4H, $TeCCH_2$), 1.96 (d, 3H, $TeCCH_3$). Complex (**3**) yield: 0.20 g (19%), m.p. 90 °C. *Anal.* Calc. for $C_{11}H_{20}NS_2TeI$: C, 27.24; H, 4.13; N, 2.89; Te, 26.33. Found: C, 27.22; H, 4.10; N, 2.88; Te, 26.31%. FT-IR (KBr, cm^{-1}): 1435 s, 1400 s (νCN), 1020 m, 960 w (νCS), 468 w ($\nu TeCH_2$). ^1H NMR ($CDCl_3$) δ ppm: 4.38 (t, 8H, NCH_2), 3.9 (m, 3H, TeCH and $TeCH_2$), 2.8 (m, 4H, $TeCCH_2$), 1.93 (d, 3H, $TeCCH_3$), 1.73 (s, 4H, $NCCH_2$), 1.55 (d, 4H, $NCCCH_2$).

2.2.2. Synthesis of 1-iodo-1-morpholine dithiocarbamato-1-telluracyclopentane $C_4H_8TeI[S_2CNC_4H_8O]$ (**4**) and 1-iodo-1-piperidine dithiocarbamato-1-telluracyclo-pentane $C_4H_8TeI(S_2CNC_5H_{10})$ (**5**)

The solution of 1,1,2,3,4,5-hexahydro-1,1-diiodo telluracyclopentane $[C_4H_8TeI_2]$ (2 g, 4.57 mmol) in dry acetone (~20 ml) was added dropwise to the suspension of freshly prepared ammonium morpholine dithiocarbamate (0.822 g, 4.57 mmol) in the same solvent and stirred for 4 h at room temperature. The reaction mixture was filtered to eliminate the insoluble material. The filtrate was concentrated under reduced pressure to obtain yellow needles of $C_4H_8TeI[S_2CNC_4H_8O]$ (**4**) yield: 0.52 g (24%), m.p. 168 °C. *Anal.* Calc. for $C_9H_{16}INOS_2Te$: C, 22.85; H, 3.39; N, 2.96; Te, 27.00. Found: C, 22.82; H, 3.35; N, 2.93; Te, 26.97%. FT-IR (KBr, cm^{-1}): 1564 vs 1426 vs (νCN); 1099 vs 1036 s (νCS); 583 s ($\nu TeCH_2$). ^1H NMR ($CDCl_3$) δ ppm: 4.12 (t, 4H, NCH_2), 3.93 (t, 4H, CH_2O), 3.75 (m, 4H, $TeCH_2$), 3.14 (m, 4H, $TeCH_2CH_2$). $C_4H_8TeI(S_2CNC_5H_{10})$ (**5**) was synthesized in the same way by the reaction of 1,1,2,3,4,5-hexahydro-1,1-diiodo telluracyclopentane $[C_4H_8TeI_2]$ (2 g, 4.57 mmol) and freshly prepared ammonium piperidine dithiocarbamate (0.813 g, 4.57 mmol) yield: 0.530 g (25%), m.p. 175 °C. *Anal.* Calc. for $C_{10}H_{18}INS_2Te$: C, 25.50; H, 3.82; N, 2.97; Te, 27.11. Found: C, 25.48; H, 3.81; N, 2.96; Te, 27.10%. FT-IR (KBr, cm^{-1}): 1473 vs 1428 vs (νCN); 1006 w, 955 w (νCS); 549 m ($\nu Te–CH_2$). ^1H NMR ($CDCl_3$) δ ppm: 4.04 (s, 4H, NCH_2), 3.57 (m, 4H, $TeCH_2$), 2.83 (m, 4H, $TeCH_2CH_2$), 1.72 (s, 4H, $NCCH_2$), 1.54 (s, 2H, $NCCCH_2$).

2.2.3. Synthesis of $C_8H_8TeI[S_2CN(C_2H_5)_2]$ (**6**)

To the clear solution of 1,3-dihydro-2λ^4-benzotellurole-2,2-diyl diiodide (2.00 g, 4.11 mmol) and sodium diethyldithiocarbamate (0.92 g, 4.11 mmol) were stirred in (~25 ml) dichloromethane. The reaction mixture was filtered to eliminate the insoluble material. The filtrate was concentrated under reduced pressure to obtain yellow orange crystals of $C_8H_8TeI[S_2CN(C_2H_5)_2]$ yield: 0.73 g (35%), m.p. 125 °C. *Anal.* Calc. for $C_{13}H_{18}INS_2Te$: C, 30.79; H, 3.55; N, 2.76; Te, 25.18. Found: C, 30.68; H, 3.42; N, 2.75; Te, 25.12%. FT-IR (KBr, cm^{-1}): 1483 m, 1423 m (νCN), 985 m (νCS) 559 s ($\nu TeCH_2$). ^1H NMR ($CDCl_3$) δ ppm: 7.32 (m, 4H, C_6H_4), 4.84 (s, 4H, $TeCH_2$), 3.72 [q, 4H, $(NCH_2)_2$], 1.24 (t, 6H, $NCCH_3$).

2.2.4. Crystal structure determination and refinement

A summary of the crystal data and refinement parameters for $C_4H_7(CH_3)Te[S_2CN(C_2H_5)_2]_2$ **1**, $C_4H_8TeI[S_2CNC_4H_8O]$ (**4**), $C_4H_8TeI[S_2CNC_5H_{10}]$ (**5**), and $C_8H_8TeI[S_2CN(C_2H_5)_2]$ (**6**) are given in Table 1. The crystals were mounted on a Bruker SMART CCD diffractometer with a CCD area detector using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz polarization and absorption effects. The structures were solved by the routine heavy atom method SHELXS-97 [36] and Fourier methods. nonhydrogen atoms were refined anisotropically by full-matrix least-square using the SHELXL-97 [36] program with hydrogen atoms in idealized positions.

2.2.5. Degenerate four wave mixing technique (DFWM)

Measurement of third order nonlinear susceptibility is carried out through the DFWM technique in the boxcar geometry [37] using a frequency doubled, Q-switched Nd: YAG (EKSPLA-2143A) laser, delivering 30 ps laser pulses at 532 nm and a repetition rate of 10 Hz. In brief, in a boxcar arrangement the fundamental beam is divided into three nearly equal intensity beams in such a way that the three form three corners of a square box and are focused into the nonlinear medium (sample) both spatially and temporally. The resultant DFWM signal that comes along the fourth corner of the box is generated as a result of the phase-matched interaction $k_4 = k_3 - k_2 + k_1$ of the three incident beams. The sample under consideration is taken in the form of solution filled in a 1 mm glass cuvette. Care is taken to reduce the contribution of the cuvette towards the overall DFWM signal by choosing suitable focusing conditions. By maintaining same polarization for the three incident beams we estimated $\chi^{(3)}_{1111}$. By introducing a half-wave plate in the path of beam-2 and beam-4, so that their polarizations are 90^0 with respect to the beam-1 and beam 3, we estimated $\chi^{(3)}_{1212}$. The transient DFWM profiles for the sample are obtained by delaying the beam-3 with respect to the other two incident beams with the help of a retro-reflector. Choice of low input powers allowed us to neglect the contribution of higher order nonlinearities.