

Large negative cubic hyperpolarizability for the spin-crossover compound *cis*-bis(thiocyanato)bis[*N*-(2-pyridylmethylene)aminobiphenyl]iron(II)

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The first example of a spin-crossover iron(II) compound with a large negative third-order polarizability, associated with an instantaneous electronic response, is reported; magnetic measurements show that this compound, *cis*-bis(thiocyanato)bis[*N*-(2-pyridylmethylene)aminobiphenyl]iron(II), characterized by X-ray structural data is in the high-spin form at room temperature.

As future generations of optoelectronic devices for telecommunications and information storage, optical switching and signal processing will rely upon the development of materials with large non-linear optical (NLO) responses,¹ many studies have been carried out in this field over the last two decades.^{1–9} Organic derivatives received much attention in view of their efficiency and fast NLO response times and their tailorability towards the chemical structure for a given NLO process.^{1–5} Nevertheless, in the last years, investigations of metallo-organic compounds brought in many new variables and gave a new dimension to the area.^{2,6–9} For instance, compared to organic molecules, metal complexes offer a larger variety of structures, such as diversity of metals, oxidation states and various arrangements of the ligands around the metal. Furthermore, some of these complexes may behave as molecular bistables between low-spin (LS) and high-spin (HS) states.^{11–13} The vast majority of studies involving coordination compounds have been dedicated to quadratic optical non-linearities, while third-order responses have scarcely been investigated.^{6–9} Here, we present the first example of an iron(II) derivative presenting a large negative third-order polarizability together with a crossover between LS and HS states. Negative third-order non-linearities are uncommon, and have the property to induce a self-defocusing effect, which can be applied to eliminate the non-linear optical auto-optical annihilation of a potential all-optical device.³ Additionally, the few negative third-order polarizabilities that have been measured^{3,7–9} are relatively large in absolute magnitude compared to molecules with positive γ .^{4,5} We report here a new iron(II) spin-crossover compound with a large negative polarizability at room temperature, where it is in its high-spin state.

cis-Bis(thiocyanato)bis[*N*-(2-pyridylmethylene)aminobiphenyl]iron(II), [FeL₂(NCS)₂],[†] was prepared in anhydrous methanol by mixing *N*-(2-pyridylmethylene)aminobiphenyl[‡] and Fe(NCS)₂. The ligand was synthesized from 2-pyridine-carbaldehyde and 4-aminobiphenyl. Single crystals of [FeL₂(NCS)₂] were obtained by slow diffusion in methanol, using a H double-tube glass.

Fig. 1 shows the magnetic susceptibility measurements, performed first from 280 K by decreasing and then by increasing temperatures. The $\chi_M T$ (χ_M = molar magnetic susceptibility, T = temperature) product decreases slightly from 3.68 cm³ K mol⁻¹ at 280 K to 2.89 at 222 K, then drops suddenly around T_c ca. 202 K down to 0.46 at 177 K, and

reaches the lower limit of 0.02 in the vicinity of 120 K. The curve $\chi_M T$ vs. T , obtained in the warming up mode, is similar, with a thermal hysteresis of ca. 4 K. The magnetic measurements demonstrate that the iron compound exhibits a complete spin transition between high-spin ($S = 2$) and low-spin ($S = 0$) states.

The molecular structure[§] of this compound in the high-spin state is shown in Fig. 2. The iron atom is located on a twofold axis and the two NCS groups have a *cis* conformation. The Fe–N(CS⁻) distances [Fe–N(2) 2.041(8) Å] are shorter than the Fe–

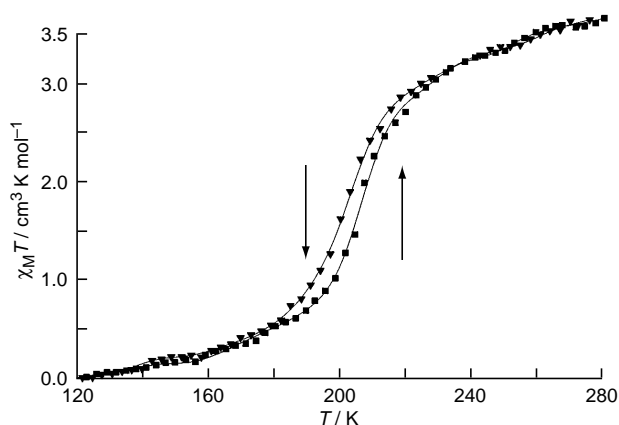


Fig. 1 Magnetic properties of [FeL₂(NCS)₂] at decreasing (▼▼▼) and increasing (■■) temperatures

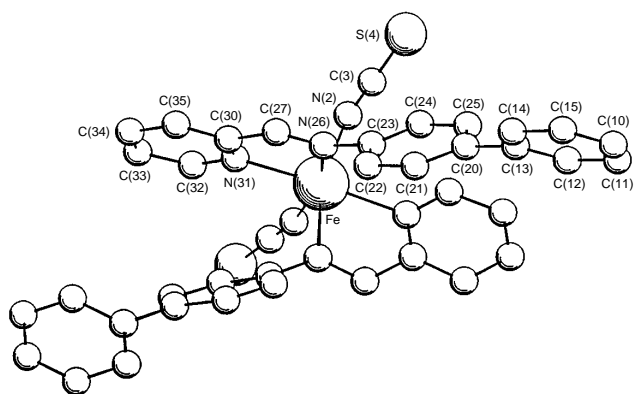


Fig. 2 Perspective view of [FeL₂(NCS)₂] including the numbering of non-hydrogen atoms. Hydrogen atoms were omitted for clarity. Fe–N bond lengths are consistent with high-spin Fe^{II} and close to those reported for [Fe(phen)₂(NCS)₂].¹¹ It can also be noticed that the NCS⁻ groups are linear [N(2)–C(3)–S(4) 179.7°], whereas the Fe–N(CS) linkages are bent (167.0°), as previously reported for [Fe(phen)₂(NCS)₂] (179.4, 167.0°).¹¹

N (organic ligand) distances [Fe–N(26) 2.250(8) Å, Fe–N(31) 2.228(8) Å], which leads to a pronounced distortion of the FeN₆ octahedron. This is also illustrated by the N–Fe–N angles: N(26)–Fe–N(31) 74.4(3)°, N(31)–Fe–N(2) 90.3(3)° and N(26)–Fe–N(2) 96.0°.

The third-order non-linear optical susceptibility (γ) recorded by optical Kerr effect[¶] at room temperature for [FeL₂(NCS)₂] dissolved in acetonitrile is presented in Fig. 3 and compared to the response for pure acetonitrile. From this figure we can clearly conclude that (i) the γ susceptibility of [FeL₂(NCS)₂] is negative. This has been also observed for (cyclopentadienyl)-bis(phosphine)ruthenium σ -nitroarylacetylides ($\gamma = -210$ to 450×10^{-36} esu),⁷ metallotriazolohemiporphyrines (with Fe²⁺, $\gamma = -3100 \times 10^{-36}$ esu)⁸ and metallophthalocyanines (with Co²⁺, $\gamma = -32\,800 \times 10^{-36}$ esu);⁹ (ii) the magnitude of the signal, recorded for the weak concentration of molecules largely overcomes the Kerr signal due to the acetonitrile solvent. Taking into account the molecular concentration, we obtain $\gamma = -130\,000 \times 10^{-36}$ esu (vs. 1×10^{-36} esu for acetonitrile); (iii) the time response allows us to assign the Kerr signal to the electronic contribution exclusively. It is important to notice that no slower processes, such as reorientation mechanisms (picosecond timescale), are observed for [FeL₂(NCS)₂], where the γ signal at longer times is mainly due to acetonitrile. It can be also noticed that the comparison between the signal recorded for [FeL₂(NCS)₂] ($\gamma = -130\,000 \times 10^{-36}$ esu) and the ligand (L, $\gamma = 1500 \times 10^{-36}$ esu) in acetonitrile shows clearly that the negative magnitude is induced by the metal ion.

We noticed a very weak absorption of the sample around 800 nm, which may bring about a resonant contribution to the γ susceptibility. In order to address this problem, we have recorded γ as a function of the laser wavelengths. The data

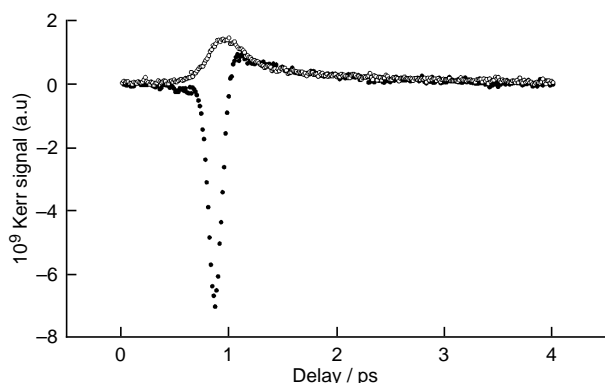


Fig. 3 Third-order molecular optical non-linearities for acetonitrile (○ ○ ○) and [FeL₂(NCS)₂] (● ● ●) in the HS state dissolved in acetonitrile ($c = 7.85 \times 10^{-4}$ mol dm⁻³)

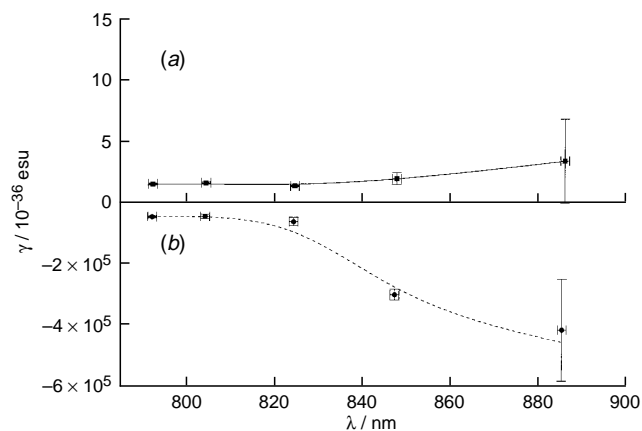


Fig. 4 Third-order molecular optical non-linearities as a function of wavelength for (a) butyronitrile (—) and (b) [FeL₂(NCS)₂] (---) dissolved in butyronitrile ($c = 10^{-4}$ mol dm⁻³)

recorded for [FeL₂(NCS)₂], dissolved in butyronitrile are presented in Fig. 4. The decrease of the negative signal intensity at shorter wavelength can be attributed to an increase of a positive component, due to the resonant contribution. This is further confirmed, if we compare the signal recorded for [FeL₂(NCS)₂] in acetonitrile ($-130\,000 \times 10^{-36}$ esu at $\lambda = 800$ nm) and in butyronitrile ($-49\,000 \times 10^{-36}$ esu at $\lambda = 804$ nm), where the maxima of the UV–VIS spectra is bathochromically shifted; *i.e.* $\lambda(\text{acetonitrile}) = 577$ nm and $\lambda(\text{butyronitrile}) = 620$ nm, respectively.

NLO measurements of this compound, with a low-spin state configuration, are in progress to further probe the role of the metal centre.

Footnotes

† Anal. Calc. for [FeL₂(NCS)₂], C₃₈H₂₈FeN₆S₂: C, 66.28; H, 4.07; N, 12.21; S, 9.30; Fe, 8.14. Found: C, 66.26; H, 4.09; N, 12.03; S, 8.90; Fe, 8.32%. IR (KBr) 3027, 2060, 1594, 1484, 1441, 1008, 850, 773, 700 cm⁻¹. λ/nm (KBr, nm) 400, 620.

‡ ¹H NMR (CDCl₃, 200 MHz) 7.30–7.49 (6 H, m), 7.62–7.66 (4 H, t), 7.83–7.84 (1 H, t), 8.22–8.25 (1 H, d), 8.68 (s, 1 H), 8.71–8.75 (d, 1 H). MS: m/z 258 (M⁺, 100), 231 (31), 152 (36), 79 (20).

§ Crystal data for C₃₈H₂₈FeN₆S₂: $M = 688$, orthorhombic, space group *Pccn* ($Z = 4$), $a = 12.949(7)$, $b = 15.183(2)$, $c = 17.609(5)$ Å; $U = 3462(2)$ Å³; $D_c = 1.33$; $\mu = 4.921$ mm⁻¹. Measurements were made with a Nonius CAD-4 diffractometer; Cu-K α radiation (1.5418 Å); crystal shape: black plate, $0.125 \times 0.35 \times 0.50$ mm; the unit-cell parameters came from 25 reflections; Bragg angle $\theta < 65^\circ$; empirical absorption correction $0.822 < T < 1.000$; scan type ω - θ ; 3331 measured reflections, 1109 observed [$I > 3\sigma(I)$]; structural determination with MITHRIL and structural refinement with SHELX76; 215 parameters; $R = 0.045$; $R_w = 0.035$; $w = 1.985/[\sigma^2(F)]$; $(\Delta/\sigma)_{\text{max}} = 0.2$; $\Delta\rho_{\text{max,min}}: 0.20, -0.15$ e Å⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/374.

¶ Third-order optical non-linearities $\chi^3(-3\omega; \omega, \omega, \omega)$ were performed at 800 nm using a CW mode-locked Ti:sapphire laser working at 76 MHz. The molecular γ (esu unit) has been deduced from $\chi^3(-3\omega; \omega, \omega, \omega)$ by $\gamma = \chi^3/(LN\eta_a)$, where η_a is the Avogadro number, L the local field correction and N is the concentration. All results are referenced to $\chi^3(-3\omega; \omega, \omega, \omega)$ of SF59 (6.5×10^{-21} m² V² = 4.6×10^{-13} esu), which leads to $\gamma_{\text{CS}_2} = 4.32 \times 10^{-34}$ esu.

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