

Study on spin configuration in photoresponsive iron mixed-valence complexes by Mössbauer spectroscopy

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Abstract We have investigated magnetic properties in a series of photoresponsive dithiooxalato (dto)-bridged iron mixed-valence complexes, (SP-R)[Fe^{II}Fe^{III}(dto)₃] (SP-R = R-substituted pyridospiropyran cation; R = Me, Et, and Pr; abbreviated as **1**^{Me}, **1**^{Et}, and **1**^{Pr}, respectively). As for our previous reports, **1**^{Me} and **1**^{Et} show two-step succeeding ferromagnetic transitions at $T_C = 25$ & 8 K and 22 & 5 K, respectively. However, **1**^{Et} has no hysteresis in the magnetic susceptibility, while **1**^{Me} undergoes the charge transfer phase transition with thermal hysteresis around 75 K. To elucidate the two-step transitions of them, we measured ⁵⁷Fe Mössbauer spectra of **1**^{Et}. The spectra of Fe^{II} ($S = 2$) and Fe^{III} ($S = 1/2$) in the HTP were observed in the magnetically ordered state as well as the paramagnetic state, and revealed that only HTP exists in a temperature range up to 5 K. The result is consistent with that of **1**^{Pr}, where one ferromagnetic phase transition occurs at $T_C = 10$ K. ⁵⁷Fe Mössbauer spectroscopy is useful to clarify the origin of the succeeding magnetic transition for these systems.

Keywords Mixed-valence complex · Dithiooxalate · Photoisomerization · Mössbauer spectroscopy

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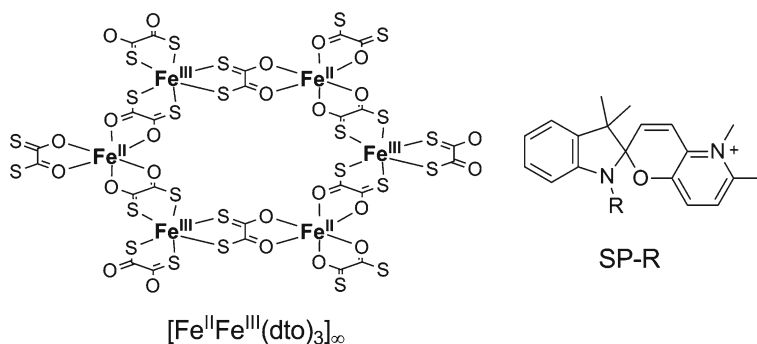


Fig. 1 Schematic representation of a partial structure of two-dimensional honeycomb network layer, $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]_{\infty}$, and structural formula of cationic pyridospiropyran, SP-R

1 Introduction

Multifunctionality coupled with transport, optical or magnetic property has attracted much attention from the viewpoint of developing of exotic materials: e.g., photoinduced magnetism in spin-crossover complexes [1], transition-metal cyanides [2], and organic–inorganic hybrid systems [3]. Intercalation magnetic compounds such as honeycomb-layered bimetallic coordination compounds, $A[\text{M}_1^{\text{II}}\text{M}_2^{\text{III}}(\text{L})_3]$ (A = cations; M_1, M_2 = transition-metal ions; L = oxalate (C_2O_4) and thiooxalates), have an excellent opportunity to control their magnetic properties by the substitution with a photoresponsive counterion [4].

Recently, we have developed a photoresponsive organic–inorganic hybrid material, $(\text{SP-Me})[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$ (abbreviated as $\mathbf{1}^{\text{Me}}$; SP-Me = cationic pyridospiropyran shown in Fig. 1), and demonstrated the control of ferromagnetism and a charge transfer phase transition (CTPT) which is a spin-entropy-driven first-order phase transition with the reversible change of the spin configuration between Fe^{II} ($S = 2$)– Fe^{III} ($S = 1/2$) in the high-temperature phase (HTP) and Fe^{II} ($S = 0$)– Fe^{III} ($S = 5/2$) in the low-temperature one (LTP) [5]. $\mathbf{1}^{\text{Me}}$ undergoes the CTPT with thermal hysteresis around 75 K and two ferromagnetic phase transitions at the Curie temperatures (T_C) of 5 and 22 K corresponding to the LTP and HTP, respectively. By UV irradiation of $\mathbf{1}^{\text{Me}}$, the CTPT is suppressed and the T_C of the LTP is enhanced from 5 K to 22 K.

For organic–inorganic hybrid systems, it is easy to perform chemical modification or change the metal ion. To a further development, we have investigated the magnetic properties and photoresponsivities of $(\text{SP-R})[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$ ($\text{R} = \text{Et}$ ($\mathbf{1}^{\text{Et}}$) and Pr ($\mathbf{1}^{\text{Pr}}$)) [6], where the intercalated spirocyclic cations are modified by the substitution with different alkyl side chains, as summarized in Table 1. The HTP and LTP coexist at low temperatures in $\mathbf{1}^{\text{Me}}$ in the result of the CTPT, and then each phase is magnetically ordered. $\mathbf{1}^{\text{Pr}}$ undergoes no CTPT and shows unique ferromagnetic phase transition derived from the HTP. However, $\mathbf{1}^{\text{Et}}$ undergoes two-step ferromagnetic ordering despite no appearance of the CTPT, that is absence of the LTP. To clarify this issue, it is essential to investigate directly the spin configurations of $\mathbf{1}^{\text{Et}}$. We report the spin configurations and the hyperfine parameters at the iron

Table 1 Summary of magnetic properties for $\mathbf{1}^{\text{Me}}$, $\mathbf{1}^{\text{Et}}$, and $\mathbf{1}^{\text{Pr}}$

Compound	T_C^{a}/K	CTPT ^b	Photomagnetism ^c	Mössbauer data
$\mathbf{1}^{\text{Me}}$	5 & 22 ^d	Occur; around 75 K ^d	Change; $T_C = 22 \text{ K}^{\text{d}}$	Ref. [7]
$\mathbf{1}^{\text{Et}}$	8 & 25 ^e	Not occur ^e	No change ^e	This work
$\mathbf{1}^{\text{Pr}}$	10 ^e	Not occur ^e	No change ^e	This work

^aCurie temperature^bCharge transfer phase transition^cPhotoresponse to magnetic ordering after UV irradiation^dSee Ref. [5]^eSee Ref. [6]

sites for $\mathbf{1}^{\text{Et}}$ and $\mathbf{1}^{\text{Pr}}$ by means of ^{57}Fe Mössbauer spectroscopy as compared with the previous results of $\mathbf{1}^{\text{Me}}$ [7].

2 Experimental

The complexes, $\mathbf{1}^{\text{Et}}$ and $\mathbf{1}^{\text{Pr}}$, were prepared according to the previous report [5]. For ^{57}Fe Mössbauer measurement, ^{57}Co in Rh was used as a Mössbauer source. The spectra were calibrated by the six lines of $\alpha\text{-Fe}$, the center of which was taken as zero isomer shift. Mössbauer spectra in paramagnetic states have been fitted with a MossWinn 3.0 program [8], including the following parameters: the isomer shift δ , the quadrupole splitting ΔE_Q , and the line width Γ . For magnetically ordered states, the model was calculated by solving the exact Hamiltonian for mixed magnetic and quadrupole interaction with arbitrary relative orientation, where the following parameters are included; δ , Γ , the internal magnetic field H_n , the angle θ between the principal axis of the electric field gradient (EFG) and the magnetization direction, and the component V_{zz} of the EFG along the principal axis. The asymmetry parameter η of the EFG is herein zero due to the expected three-fold axis of symmetry in the iron coordination geometries of these complexes.

3 Results and discussion

The Mössbauer spectra in the paramagnetic states for $\mathbf{1}^{\text{Et}}$ and $\mathbf{1}^{\text{Pr}}$ are shown in Fig. 2, and the fitting parameters are listed in Table 2 in addition to those of $\mathbf{1}^{\text{Me}}$. For all the compounds, two doublets were observed at 200 or 250 K and the line profiles are quite similar to those of $(n\text{-C}_n\text{H}_{2n+1})_4\text{N}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$ ($n = 3\text{--}6$) at 200 K [9]. The spectra can be assigned to the paramagnetic states of the HTP containing Fe^{II} ($S = 2$) and Fe^{III} ($S = 1/2$), the parameters of which are $\delta = 1.18\text{--}1.24 \text{ mm/s}$, $\Delta E_Q = 1.60\text{--}1.72 \text{ mm/s}$ and $\delta = 0.30\text{--}0.38 \text{ mm/s}$, $\Delta E_Q = 0.54\text{--}0.71 \text{ mm/s}$, respectively. The spectral profiles of $\mathbf{1}^{\text{Et}}$ and $\mathbf{1}^{\text{Pr}}$ remain almost unchanged down to 20 K. The result is in marked contrast with the line profile of $\mathbf{1}^{\text{Me}}$ which drastically changes at 70 K because of the CTPT [7]. The increase of the isomer shifts on $\mathbf{1}^{\text{Et}}$ and $\mathbf{1}^{\text{Pr}}$ was observed with decreasing temperature, resulting from the second-order Doppler-shift contribution.

On further cooling, the Mössbauer spectrum of $\mathbf{1}^{\text{Et}}$ broadened and reached from ca. -4 to $+4 \text{ mm/s}$ at 5 K because of magnetic ordering. A similar behavior was

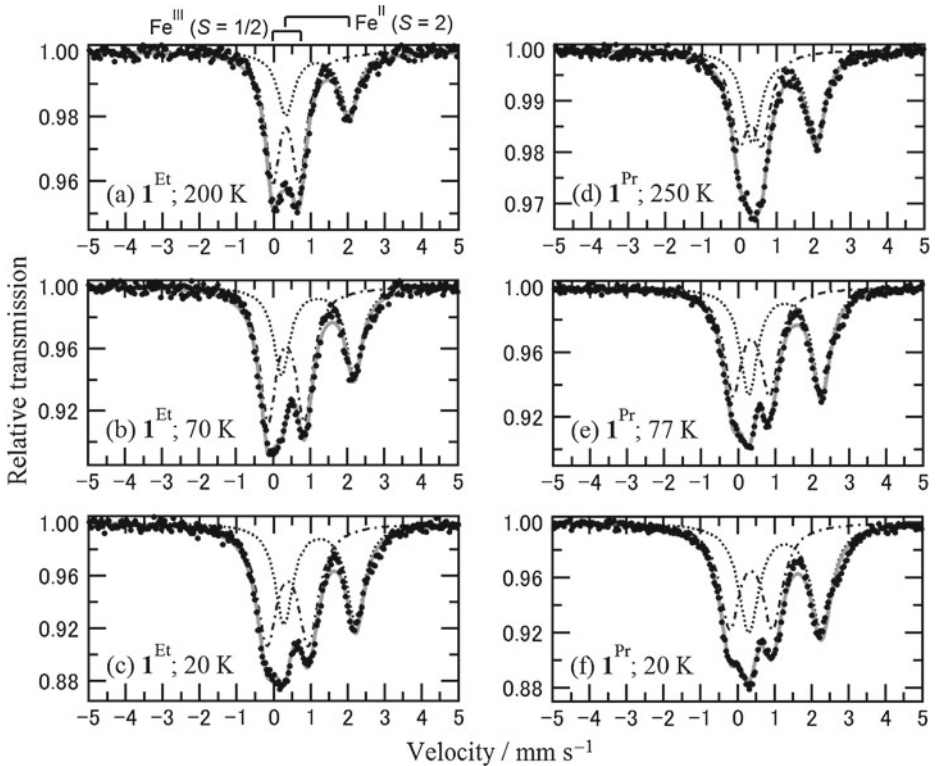
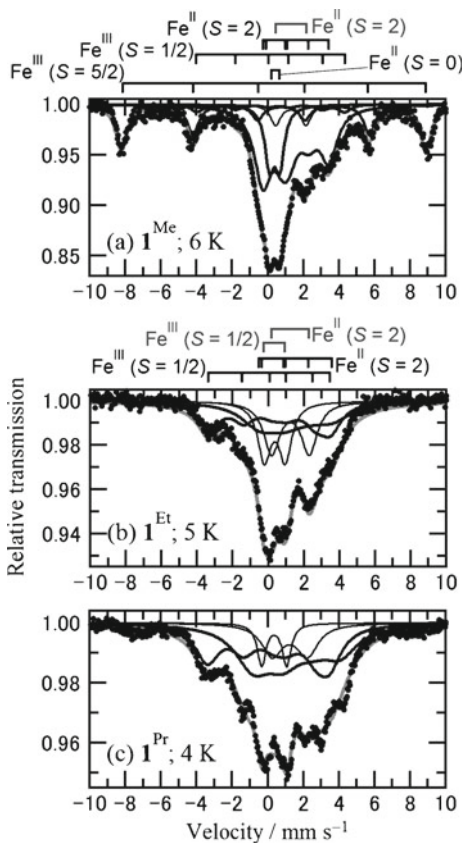


Fig. 2 ^{57}Fe Mössbauer spectra in paramagnetic states for 1^{Et} at **a** 200, **b** 70, and **c** 20 K and 1^{Pr} at **d** 250, **e** 77, and **f** 20 K

Table 2 Selected ^{57}Fe Mössbauer parameters in paramagnetic states for 1^{Mc} , 1^{Et} , and 1^{Pr}

	$T[\text{K}]$	Assignment	Area [%]	δ [mm/s]	ΔE_Q [mm/s]	Γ [mm/s]	Ref.
1^{Mc}	200	$\text{Fe}^{\text{II}} (S = 2)$	62.6	1.24	1.60	0.83	[7]
		$\text{Fe}^{\text{III}} (S = 1/2)$	37.4	0.38	0.54	0.83	[7]
	70	$\text{Fe}^{\text{II}} (S = 2)$	31.7	1.24	1.71	0.54	[7]
		$\text{Fe}^{\text{III}} (S = 1/2)$	18.4	0.38	0.73	0.58	[7]
		$\text{Fe}^{\text{II}} (S = 0)$	19.8	0.39	0.54	0.50	[7]
1^{Et}	200	$\text{Fe}^{\text{II}} (S = 2)$	37.1	1.178(7)	1.705(13)	0.544(19)	This work
		$\text{Fe}^{\text{III}} (S = 1/2)$	62.9	0.328(3)	0.707(7)	0.480(9)	This work
	70	$\text{Fe}^{\text{II}} (S = 2)$	40.4	1.208(4)	1.955(8)	0.537(12)	This work
		$\text{Fe}^{\text{III}} (S = 1/2)$	59.6	0.351(3)	0.981(5)	0.543(7)	This work
	20	$\text{Fe}^{\text{II}} (S = 2)$	43.6	1.244(3)	1.935(6)	0.578(10)	This work
1^{Pr}	250	$\text{Fe}^{\text{II}} (S = 2)$	53.8	1.200(4)	1.723(8)	0.592(13)	This work
		$\text{Fe}^{\text{III}} (S = 1/2)$	46.2	0.300(4)	0.613(9)	0.553(13)	This work
	77	$\text{Fe}^{\text{II}} (S = 2)$	50.4	1.262(2)	1.955(4)	0.564(7)	This work
		$\text{Fe}^{\text{III}} (S = 1/2)$	49.6	0.348(3)	0.994(4)	0.579(6)	This work
	20	$\text{Fe}^{\text{II}} (S = 2)$	52.1	1.278(2)	1.961(4)	0.665(7)	This work
	$\text{Fe}^{\text{III}} (S = 1/2)$	47.9	0.360(2)	1.159(4)	0.656(7)	This work	

Fig. 3 ^{57}Fe Mössbauer spectra in magnetically ordered states for **a** $\mathbf{1}^{\text{Me}}$, **b** $\mathbf{1}^{\text{Et}}$, and **c** $\mathbf{1}^{\text{Pr}}$



observed in $\mathbf{1}^{\text{Pr}}$ as shown in Fig. 3. The Mössbauer spectra in the ferromagnetic states for $\mathbf{1}^{\text{Et}}$ and $\mathbf{1}^{\text{Pr}}$ apparently differ from that for $\mathbf{1}^{\text{Me}}$ [7]. A sextet with a large hyperfine field from -8 to 8 mm/s, which is typical of the magnetically ordered spectrum of Fe^{III} ($S = 5/2$) in the LTP, is absent in the spectra of $\mathbf{1}^{\text{Et}}$ and $\mathbf{1}^{\text{Pr}}$. The result indicates that $\mathbf{1}^{\text{Et}}$ and $\mathbf{1}^{\text{Pr}}$ undergo no CTPT. These magnetically ordered spectra exhibit a superposition of broadened sextets and paramagnetic doublets at 4 or 5 K. The Mössbauer spectra were reasonably fitted with two sextets of the magnetically ordered states and two additional doublets for Fe^{III} ($S = 1/2$) and Fe^{II} ($S = 2$) in the HTP. Here, to avoid overparameterization we use the δ values evaluated for the paramagnetic states at the temperature of 20 K. Moreover, the θ parameters were fixed as 90° according to the measurement on anisotropic magnetization of $(n\text{-C}_3\text{H}_7)_4\text{N}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$ [10]. The hyperfine parameters are listed in Table 3. The sextets of the Fe^{III} ($S = 1/2$) have larger H_n of 210 kOe ($n = 5$) and 213 kOe ($n = 6$). The Fe^{II} ($S = 2$) sites, on the other hand, have relatively small H_n of 108 kOe ($n = 5$) and 140 kOe ($n = 6$). These H_n values are similar to those of the HTP for $\mathbf{1}^{\text{Me}}$ [7] as well as $(n\text{-C}_n\text{H}_{2n+1})_4\text{N}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$ ($n = 3\text{--}6$) [11]. Thus, the given hyperfine parameters are direct and sufficient evidence to elucidate that $\mathbf{1}^{\text{Et}}$ and $\mathbf{1}^{\text{Pr}}$ remains to be the HTP down to 5 K.

Table 3 Selected ^{57}Fe Mössbauer parameters in magnetically ordered states for $\mathbf{1}^{\text{Et}}$, $\mathbf{1}^{\text{Et}}$, and $\mathbf{1}^{\text{Pr}}$

	T [K]	Assignment	δ^{a} [mm/s]	$\Delta E_{\text{Q}}^{\text{b}}$ [mm/s]	Γ^{b} [mm/s]	Area ^b [%]	V_{ZZ}^{c} [10^{21} V/m ²]	H_{n}^{c} [kOe]	Γ^{c} [mm/s]	Area ^c [%]
$\mathbf{1}^{\text{Me d}}$	6	$\text{Fe}^{\text{II}} (S = 2)$	1.29	1.71	0.70	5.6	-10.28	92	1.15	48.2
		$\text{Fe}^{\text{III}} (S = 1/2)$	0.38	0.73	–	–	+4.39	264	0.81	4.8
		$\text{Fe}^{\text{II}} (S = 0)$	0.39	0.57	0.63	14.1	–	–	–	–
		$\text{Fe}^{\text{III}} (S = 5/2)$	0.55	0.86	–	–	+5.19	529	0.77	27.2
$\mathbf{1}^{\text{Et}}$	5	$\text{Fe}^{\text{II}} (S = 2)$	1.28 ^e	2.12	1.07(4)	20.8	-12.75(12)	96(5)	2.30(14)	27.5
		$\text{Fe}^{\text{III}} (S = 1/2)$	0.36 ^e	1.18	0.90(3)	19.9	+7.10(11)	204(2)	1.59(5)	31.7
$\mathbf{1}^{\text{Pr}}$	4	$\text{Fe}^{\text{II}} (S = 2)$	1.24 ^e	1.97	1.43(4)	14.1	-11.85(18)	131(2)	2.37(4)	40.7
		$\text{Fe}^{\text{III}} (S = 1/2)$	0.37 ^e	1.41	0.580(13)	7.7	+8.45(8)	205(8)	1.63(2)	37.5

^aIsomer shift of paramagnetic and magnetically ordered states^bComponent for a residual paramagnetic state^cComponent for a magnetically ordered state^dRef [7]^eParameter constrained to the value estimated at 20 K

4 Conclusion

^{57}Fe Mössbauer spectroscopy is useful to the spin configuration of the iron mixed-valence complexes, $\mathbf{1}^{\text{Et}}$ and $\mathbf{1}^{\text{Pr}}$ as well as $\mathbf{1}^{\text{Me}}$. We directly investigated the spin states in $\mathbf{1}^{\text{Et}}$ by means of ^{57}Fe Mössbauer spectroscopy and confirmed the presence of only HTPs containing $\text{Fe}^{\text{III}} (S = 1/2)$ and $\text{Fe}^{\text{II}} (S = 2)$. Therefore, it can be concluded that the succeeding two-step ferromagnetic transition is derived from different HTPs, which is consistent with our previous magnetic results.

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References

- Gütlich, P., Goodwin, H.A.: Spin Crossover in Transition Metal Compounds I–III. Springer-Verlag, Berlin Heidelberg (2004)
- Sato, O., Iyoda, T., Fujishima, A., Hashimoto, K.: Photoinduced magnetization of a cobalt-iron cyanide. *Science* **272**, 704–705 (1996)
- Kojima, N., Okubo, M., Shimizu, H., Enomoto, M.: Control of magnetism by isomerization of intercalated molecules in organic–inorganic hybrid systems. *Coord. Chem. Rev.* **251**, 2665–2673 (2007)
- Aldoshin, S.M.: Heading to photoswitchable magnets. *Russ. Chem. Bull. Int. Ed.* **57**, 718–735 (2008)
- Kida, N., Hikita, M., Kashima, I., Okubo, M., Itoi, M., Enomoto, M., Kato, K., Takata, M., Kojima, N.: Control of charge transfer phase transition and ferromagnetism by photoisomerization of spiropyran for an organic–inorganic hybrid system, (SP)[$\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3$] (SP = spiropyran, $\text{dto} = \text{C}_2\text{O}_2\text{S}_2$). *J. Am. Chem. Soc.* **131**, 212–220 (2009)
- Yoshida, J., Kida, N., Okazawa, A., Kojima, N.: Cation size effect on photomagnetism and charge transfer phase transition of iron mixed-valence complexes with spiropyran. *Polyhedron* (2013). doi:10.1016/j.poly.2013.02.070
- Kida, N., Hikita, M., Kashima, I., Enomoto, M., Itoi, M., Kojima, N.: Mössbauer spectroscopic study of photo-sensitive organic–inorganic hybrid system, (SP)[$\text{Fe}(\text{II})\text{Fe}(\text{III})(\text{dto})_3$] ($\text{dto} = \text{C}_2\text{O}_2\text{S}_2$, SP = spiropyran). *Polyhedron* **28**, 1694–1697 (2009)
- Klencsár, Z., Kuzmann, E., Vértes, A.: User-friendly software for Mössbauer spectrum analysis. *J. Radioanal. Nucl. Chem.* **210**, 105–118 (1996)

9. Kojima, N., Ono, Y., Kobayashi, Y., Seto, M.: Control of charge transfer phase transition in iron mixed-valence system $(n\text{-C}_n\text{H}_{2n+1})_4\text{N}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$ ($n = 3\text{--}6$; $\text{dto} = \text{C}_2\text{O}_2\text{S}_2$). *Hyperfine Interact.* **156/157**, 175–179 (2004)
10. Itoi, M., Enomoto, M., Kojima, N.: Ferromagnetism of iron mixed-valence complex $(n\text{-C}_3\text{H}_7)_4\text{N}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$ (dithiooxalato: $\text{dto} = \text{C}_2\text{O}_2\text{S}_2$). *J. Magn. Magn. Mater.* **272**, 1093–1094 (2004)
11. Ono, Y., Okazawa, A., Enomoto, M., Kojima, N.: Study on the ferromagnetic state in iron mixed-valence complexes, $\text{A}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{dto})_3]$ ($\text{A} = (n\text{-C}_n\text{H}_{2n+1})_4\text{N}$; $\text{dto} = \text{C}_2\text{S}_2\text{O}_2$) by means of Mössbauer spectroscopy. *Hyperfine Interact.* **207**, 139–143 (2012)