Identification of Three Different Iron Sites in a Polymeric Oxalate (2,2'-Bipyridine) Iron Compound

M. KRAUSE*, C. MICHALK, B. LIPPOLD

Sektion Physik, Karl-Marx-Universität, Linnéstrasse 5, Leipzig, DDR-7010, G.D.R.

M. BENEDIX

Sektion Chemie, Karl-Marx-Universität, Leipzig, DDR-7010, G.D.R.

and J. SUWALSKI

Institute of Nuclear Research, Swierk, Poland

(Received July 21, 1986)

Abstract

The compound $[Fe(bipy)_{1.03}(ox)_{1.1}]$ forms chains with iron bridged by tetradentate oxalate ligands. From this empirical formula the ratio of the several spin states was calculated. In the Mössbauer spectra three subspectra can be separated; the detected spin and valence states are as assumed for the several surroundings of the iron. Susceptibility measurement provides a mean magnetic moment as expected for such a coexistence of spin states.

Introduction

In recent papers the complex polymer $[Fe(bipy)_{1.03}(ox)_{1.1}]$ was described and characterized [1, 2]. The polymer contains tetradentate oxalate as bridging ligand; the iron has three possible surroundings in the chain [2], but until now no assignment was given between the Mössbauer subspectra and the iron sites.

In this paper we report on the calculation of the ratio of the three iron sites using the empirical formula. The results are compared with the Mössbauer spectrum at 4.2 K, where the subspectra are separable, and with the susceptibility measurement. From the Mössbauer spectrum informations about the electronic zero field splitting parameter D are obtained.

Experimental

The compound $[Fe(bipy)_{1.03}(ox)_{1.1}]$ was prepared by the procedure described earlier [3, 4].

---

*Author to whom correspondence should be addressed.

From a typical analysis Fe 14.88; N 7.68; oxalate 25.76%; the empirical formula $[Fe(bipy)_{1.03}(ox)_{1.1}] \cdot 3H_2O$ can be calculated.

^{57}Fe Mössbauer measurements were performed using a constant acceleration spectrometer SM-3 (Swierk, Poland) with a 100 mCi $^{57}Co/Cr$ source. The spectra were obtained in transmission geometry and fitted by least squares fits. The isomer shifts are given relative to iron.

Magnetic susceptibilities were measured with a self-made SQUID-magnetometer (for the principle see for example ref. 5). The magnetic field of the superconducting solenoid was 3 mT. The total diamagnetic correction is -0.0023×10^{-6} m³/mol [6], the experimental error was $\pm 0.02 \times 10^{-6}$ m³/mol. The magnetic moment was obtained from $\mu_{eff} = 797.8 \sqrt{C}$, C being the Curie constant of the Curie–Weiss law.

Results and Discussion

From the empirical formula $[Fe(bipy)_{1.03}(ox)_{1.1}] \cdot 3H_2O$ the ratio of the several possible iron sites can be calculated. In order to solve the problem it has to be assumed that a part of the oxalate is bidentate. Iron in the tris-bipyridine coordination can be excluded for chemical reasons, e.g. the extreme unsolubility in polar and nonpolar solvents. We obtained the following composition: 20% of the iron is coordinated with three oxalate ligands, 57% with one bipyridine and two oxalate ligands and 23% with two bipyridine and one oxalate ligand. 20% of the oxalate is bidentate, for that reason there is no evidence that the iron in the tris-oxalato coordination forms branching points.

Mössbauer Spectroscopy

The Mössbauer spectrum at 4.2 K is shown in Fig. 1; the parameters are given in Table 1. Three subspectra can be separated:

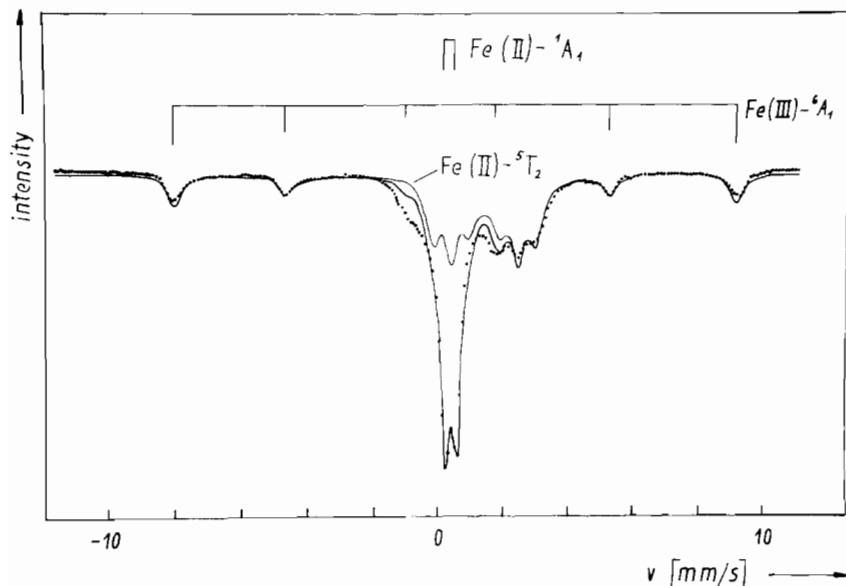Fig. 1. ^{57}Fe Mössbauer spectrum for [Fe(bipy)$_{1.03}$(ox)$_{1.1}$] at 4.2 K (·······); full curves represent fitted spectra.

TABLE I. Mössbauer Parameters for [Fe(bipy)$_{1.03}$(ox)$_{1.1}$] at 4.2 K

	Spin state		
	Fe^{2+} (^{1}A$_1$)	Fe^{2+} (^{5}T$_2$)	Fe^{3+} (^{6}A$_1$)
I_R	0.32 ± 0.02	0.50 ± 0.05	0.18 ± 0.03
δ (mm s^{-1})	0.38 ± 0.03	1.4 ± 0.1	0.48 ± 0.04
ΔE_Q (mm s^{-1})	0.36 ± 0.02	2.0 ± 0.2	0.27 ± 0.03
B (T)	–	5.3 ± 1.5	53.1 ± 0.4
θ (°)	–	54.7 ± 15.0	–
Γ (mm s^{-1})	0.28 ± 0.01	0.30 ± 0.04	0.50 ± 0.05

I_R, relative intensity ratio; δ, isomer shift; ΔE_Q, quadrupole splitting; B, internal magnetic field; θ, angle between $\vec{B}$ and V_{zz}; Γ line width.

(i) A narrow doublet is due to low spin Fe^{2+} (^{1}A$_1$). The low spin state is caused by coordination of the iron with two strong field ligands (bipyridine) and only one weak field ligand (oxalate). The relative intensity of 32% agrees with the calculated 23% of the iron on the [Fe(bipy)ox$_2$]-site within the error limits. Debye–Waller factors of the iron on the different sites are unknown.

(ii) The sextet can clearly be assigned to high spin Fe^{3+} (^{6}A$_1$) because of the internal magnetic field of 53.1 T. The field is caused by a Fermi contact term of 5 unpaired spins of the Kramers doublet |±5/2⟩ with a spin expectation value near 5/2. In all known compounds the iron in the tris-oxalato coordination is trivalent [7], so we assume that the high spin Fe^{3+} is coordinated with three oxalate ligands. The relative Mössbauer intensity of 18% agrees well with the

calculated (20%) and measured (15% [1]) Fe^{3+} content. The isomer shift of 0.48 mm s^{-1} is in a good agreement with the values for Fe^{3+} in Sr$_3$[Fe ox$_3$]$_2$·2H$_2$O, 0.45 mm s^{-1}, and in Ba$_3$[Fe ox$_3$]$_2$·8H$_2$O, 0.46 mm s^{-1} [8].

(iii) The shape of the third subspectrum is caused by high spin Fe^{2+} (^{5}T$_2$) (indicated by the isomer shift [9]) with a slowly relaxing electronic spin in a non-Kramers ground state doublet |±2⟩ [10]. The iron is coordinated with two oxalate ligands and one bipyridine ligand. The angle θ between $\vec{B}$ and V_{zz} seems to be close to the magic value (54.7°) causing a nearly symmetric subspectrum. Similar spectra are produced by high spin Fe^{2+} in similar surroundings in the linear chain compounds [Fe(phen)Cl$_2$]$_n$ and [Fe(bipy)-Cl$_2$]$_n$ [11, 12]. The relative intensity of 50% agrees with the calculated chain site population of 57%.

The intensity ratio of the line pairs of the Fe^{3+} sextet indicates that the zero field splitting parameter D of the electronic Hamiltonian

$$\mathcal{H} = D[S_z^2 - \tfrac{1}{3}S(S+1)]$$

is negative for the high spin Fe^{3+}, *i.e.* the Kramers doublet |±5/2⟩ forms the ground state. The intensity ratio of the line pairs 1–6 and 2–5 is not 3:2 but 3.00:2.84. The reason for this behaviour is the lines 1 and 6 of the Mössbauer sextet produced by the Kramers doublet |±3/2⟩ have nearly the same position as the lines 2 and 5 of the sextet produced by |±5/2⟩. From the intensity ratio the population ratio of the doublets |±5/2⟩ and |±3/2⟩ was determined to be 3.6, the D-parameter is approximately –1.4 K.

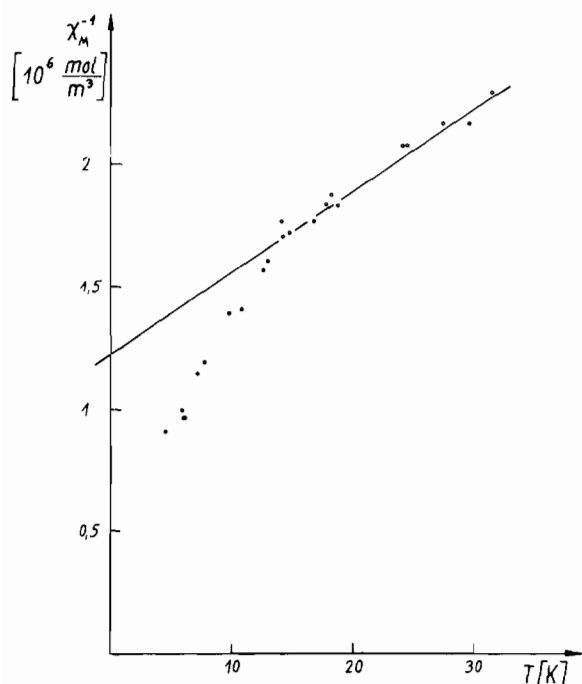The shape of the high spin Fe^{2+} subspectrum is caused by a non-Kramers ground state doublet |±2⟩,

Fig. 2. Temperature dependence of the reciprocal molar magnetic susceptibility for [Fe(bipy)$_{1.03}$(ox)$_{1.1}$].

the contribution of the nonmagnetic state |0⟩ is small. So the *D*-parameter should be negative and have a magnitude greater than 1 K.

Magnetic Susceptibility

The reciprocal low temperature molar magnetic susceptibility is presented in Fig. 2. The straight line represents the Curie–Weiss law obeyed by the susceptibility above 14 K. The Curie temperature Θ amounts to (−36 ± 5) K, the mean magnetic moment per iron ion is (4.3 ± 0.3) BM as in the temperature range 100–300 K [1]. The negative Curie temperature Θ indicates an antiferromagnetic interaction as

in other one-dimensional [13–15] and three-dimensional systems [6] with organic ligands, but the behaviour of the susceptibility below 14 K indicates, that there is no antiferromagnetic order. Assuming a high spin Fe^{3+} content in the range 10–20%, the mean magnetic moment of 4.3 BM requires a high spin Fe^{2+} content of 64–53% and a low spin Fe^{2+} content of 26–27%.

In the complex polymer [Fe(bipy)$_{1.03}$(ox)$_{1.1}$] · 3H$_2$O three chain sites could be identified. The calculated population ratio agrees well with the data obtained from Mössbauer spectroscopy and susceptibility measurement.

References

1 M. Benedix, R. Benedix, C. Michalk and J. Suwalski, *Inorg. Chim. Acta, 96,* L1 (1985).
2 M. Krause, C. Michalk, M. Benedix and J. Suwalski, *Phys. Stat. Sol. A, 90,* 657 (1985).
3 Ph. Thomas, M. Benedix and H. Hennig, *Z. Anorg. Allg. Chem., 468,* 213 (1980).
4 H. Hennig, M. Benedix, R. Benedix and Ph. Thomas, *Z. Anorg. Allg. Chem., 514,* 231 (1984).
5 R. P. Giffard, R. A. Webb and J. C. Wheatley, *J. Low Temp. Phys., 6,* 533 (1972).
6 E. König and K. Madeja, *Inorg. Chem., 7,* 1848 (1968).
7 K. V. Krishnamurthy and G. M. Harris, *Chem. Rev., 61,* 213 (1961) and refs. therein.
8 P. K. Gallagher and C. R. Kurkjian, *Inorg. Chem., 5,* 214 (1966).
9 N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy', Chapman and Hall, London, 1971.
10 M. Krause, C. Michalk, B. Lippold, M. Benedix and J. Suwalski, *Phys. Status. Solidi. A, 97,* 521 (1986).
11 W. M. Reiff and F. Foner, *J. Am. Chem. Soc., 95,* 260 (1973).
12 F. F. Charron Jr., G. A. Eisman, H. Wong and W. M. Reiff, *Inorg. Chim. Acta, 68,* 233 (1983).
13 R. Dingle, M. E. Lines and S. L. Holt, *Phys. Rev., 187,* 643 (1969).
14 J. T. Wrobleski and D. B. Brown, *Inorg. Chem., 18,* 498 and 2738 (1979).
15 J.-Y. Chen, S. Simizu and S. A. Friedberg, *J. Appl. Phys., 57,* 3338 (1985).