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A Polymeric Oxalate (2,2′-bipyridine)iron Compound with Interesting Magnetic Behaviour

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As a result of an intramolecular redox reaction, both thermolysis and photolysis of iron(III) mixed ligand complexes with oxalate (ox) and the aromatic α-diimines 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) lead to intensive coloured iron(II) α-diimine species of various stoichiometries [1, 2].

During the thermal decomposition of Hbipy[Fe(ox)$_2$(H$_2$O)$_2$] a red-violet insoluble product of the general composition [Fe(bipy)ox] is obtained. The photolysis of the considered iron(III) compound in aqueous–methanolic solution also gives an iron(II) product of analogous structure, not forming the expected $[Fe(bipy)_3]^{2+}$ ion. Using elemental analysis, IR and UV/VIS spectra as well as magnetic measurements, a polymeric octahedral structure with bidentate 2,2′-bipyridine and tetradentate oxalate ligands is suggested for the isolated Fe(II) complex. The remission spectra display the typical diimine band at 522 nm. The value of the magnetic moment μ_{eff} = 4.2 B.M. (295 K) for the solid iron(II) compound is lower than that of high-spin octahedral iron(II) complexes (μ_{eff} ~ 5.2 B.M.) [3].

Commonly, a reduced magnetic moment is due to either a temperature dependent $^5T_2$–$^1A_1$ spin equilibrium (the mean spin pairing energy and ligand field splitting energy are nearly equal) or to the existence of a constant, temperature independent ratio of molecules with different spin ground-states [4–6]. The magnetic moments of the complex $[Fe(bipy)ox]_n$ were found to be practically constant in the range 77–373 K (Fig. 1). That means that the existence of a temperature dependent spin transition can be ruled out.

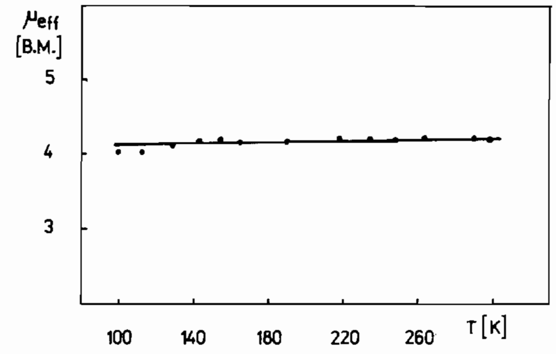

Fig. 1. Temperature dependence of the effective magnetic moment, μ_{eff}, for $[Fe(bipy)ox_{1.1}]_n$.

Recent investigations on similar iron(II) systems with unusual magnetic properties have shown the presence of a well defined iron(III) component in the complex unit [7, 8]. Of course, this component influences the magnetic behaviour of the compound. In this connection, as a result of a careful reexamination of the representatives of the so-called spin triplet ground-state complexes [Fe(phen)$_2$ox]·5H$_2$O and [Fe(phen)$_2$mal]·7H$_2$O with mal = malonate, the analytical data were consistent with formulations containing low-spin iron(II) cations and high-spin iron(III) anions $[Fe^{II}L_3]_2[Fe^{III}(anion)_3](anion)_{1/2}\cdot xH_2O$ [7, 8].

For the compound under consideration extensive investigations have been performed in order to prove the presence of a constant iron(II):iron(III) ratio in the polymeric structure. Attempts at the separate determination of iron(III) using conventional analytical methods were not successful. However, after irradiation of the product of both photolysis and thermolysis in 0.1 *N* HCl a further redox decomposition of the iron(III) constituent occurs and the iron(II) ions formed can be determined spectrophotometrically as $[Fe(N,N)_3]^{2+}$ with N,N = 2,2′-bipyridine [9]. An iron(II):iron(III) ratio of 85%:15% was found which could be reproduced in a large series of experiments. This ratio is exactly reflected in the new empirical formula $[Fe(bipy)ox_{1.1}]_n$.

Although magnetic data provide a convenient means for detecting a spin ground-state or a spin cross-over, the information obtained always represents an average of the magnetism for all the states involved. The observation of properties characteristic of separate spin states and valences is possible by means of Mössbauer spectroscopy. The Mössbauer parameters of low-spin iron(II) and high-spin iron(III) in an octahedral environment are very similar. Therefore, a classification was relatively complicated [4, 7, 10].

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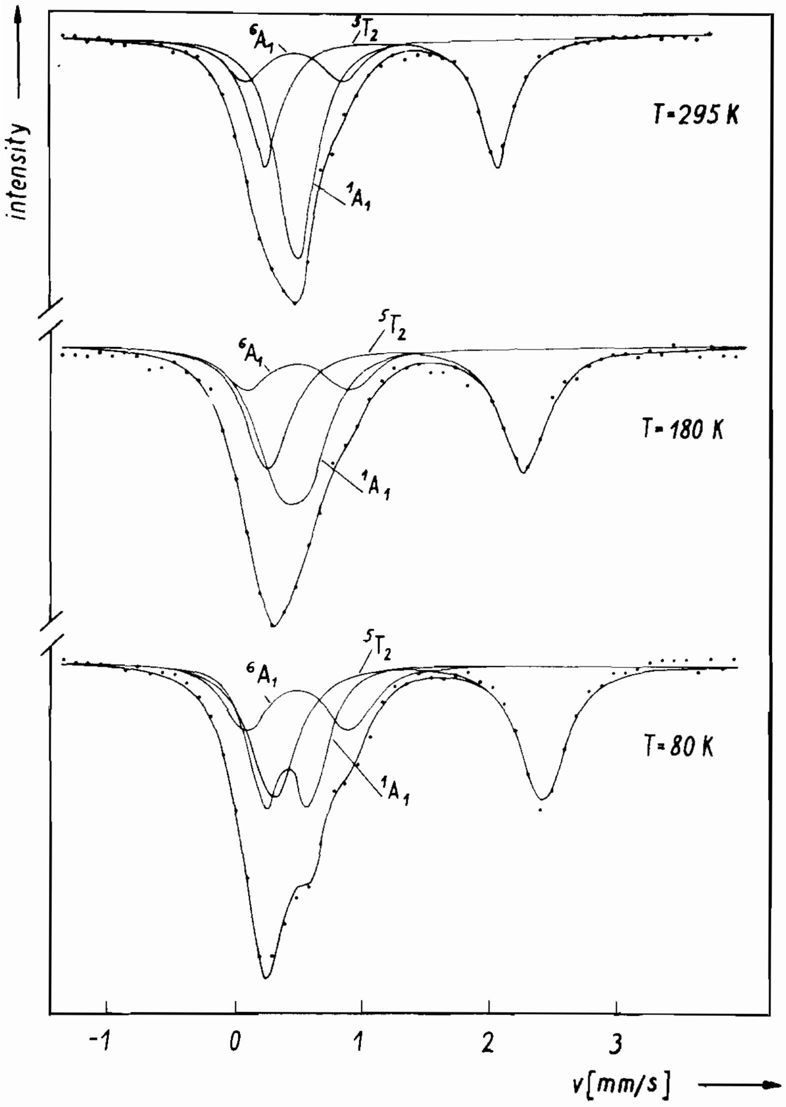

Fig. 2. ^{57}Fe Mössbauer effect spectra for [Fe(bipy)ox$_{1.1}$]$_n$ at 80 K, 180 K and 295 K (●–●–●); full curves represented fitted spectra.

TABLE 1. ^{57}Fe Mössbauer Effect Parameters for Polymeric [Fe(bipy)ox$_{1.1}$]$_n$.

T (K)	Spin state	IS^a (mm/s)	QS^b (mm/s)	I_{rel}^{c}
295	Fe(II) $^5T_2$	1.14	1.82	0.43
	Fe(II) $^1A_1$	0.47	0.10	0.42
	Fe(III) $^6A_1$	0.45	0.76	0.15
180	Fe(II) $^5T_2$	1.26	2.01	0.46
	Fe(II) $^1A_1$	0.44	0.24	0.38
	Fe(III) $^6A_1$	0.48	0.81	0.16
80	Fe(II) $^5T_2$	1.35	2.11	0.47
	Fe(II) $^1A_1$	0.40	0.36	0.31
	Fe(III) $^6A_1$	0.48	0.81	0.22

[a] Isomer shift relative to Fe atom, experimental uncertainty ± 0.02 mm/s. [b] Quadrupole splitting, experimental uncertainty ± 0.02 mm/s. [c] Relative intensity ratio, uncertainty ± 0.05.

The Mössbauer spectra of the complex [Fe(bipy)ox$_{1.1}$]$_n$ were observed at 80, 180 and 295 K with a constant acceleration type spectrometer

(SM-6, Swierk/poland) using 10 mCi ^{57}Co in Pd as source (Fig. 2). The parameters resulting after fitting the spectra with 3 doublets are given in Table I.

The Mössbauer spectrum recorded at 4.2 K shows a magnetic hyperfine splitting with internal magnetic fields of H_{eff} = 5.8 T (Fe(II) $^5T_2$) and H_{eff} = 30.6 T (Fe(III) $^6A_1$), respectively, for the subspectra. This behaviour may be interpreted as a consequence of antiferromagnetic interactions between oxalate bridged iron ions in a quasi one-dimensional chain [11, 12]. On the basis of the measurements at 4.2 K the assignment of the subspectra to Fe(II) $^5T_2$, Fe(II) $^1A_1$ and Fe(III) $^6A_1$ could be achieved for higher temperatures as well. The total ratio Fe(II): Fe(III) determined by the analytical method described above and the value of the magnetic moment μ = 4.2 B.M. (295 K) are in agreement with the relative intensity ratio of the Mössbauer subspectra at room temperature assuming the following Debye–Waller factors for the iron atoms in different states: $f_{Fe(III)}$ $^6A_1$ = 1.00; $f_{Fe(II)}$ $^5T_2$ = 0.70; $f_{Fe(II)}$ $^1A_1$ = 1.75. The given values are related to $f_{Fe(III)}$ = 1.0 at room temperature. Consequently, the complex $[Fe(bipy)ox_{1.1}]_n$ provides an example of a compound with a nearly temperature independent ratio of spin ground-states Fe(II) S = 2, Fe(II) S = 0 and Fe(III) S = 5/2 and with remarkable magnetic interactions at low temperatures.

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