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Low Temperature Magnetism of Low-Spin Iron(II) Cation High-Spin Iron(III) Anion Complexes. Supporting Evidence for the True Nature of So-called 'Spin-Triplet Iron(II)' Compounds

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The magnetism of a number of compounds previously believed to contain spin triplet iron(II) ground states has been investigated between 0.96 and 300 K. ^{57}Fe Mössbauer effect including magnetic hyperfine interaction shows that the compounds involve both low-spin iron(II) as well as high-spin iron(III) ions. In combination with additional chemical studies, a double salt formulation has thus been proposed. It is demonstrated that the magnetic behaviour of the compounds is consistent with their formulation as $[Fe^{II}(diimine)_3]_2[Fe^{III}(dianion)_3](^1/_2dianion)\cdot xH_2O$ *where diimine = 2,2′-bipyridyl, 1,10-phenanthroline or 4,7-dimethyl-1,10-phenanthroline and dianion = oxalate or malonate.*

Introduction

Recently, we have reported the first preparation of a number of low-spin iron(II) cation high-spin iron(III) anion complexes of the type $[Fe^{II}(diimine)_3]_m[Fe^{III}(dianion)_3]_n$ (m:n = 1:1, 3:2 or 2:1) where diimine = 1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline or 2,2′-bipyridyl and dianion = oxalate or malonate [1]. The ^{57}Fe Mössbauer spectra of these compounds display a single doublet characterized, *e.g.* for $[Fe(phen)_3]_3[Fe(ox)_3]_2\cdot 15\ H_2O$, by the quadrupole splitting $\Delta E_Q = 0.25 \pm 0.01$ mm s^{-1} and the isomer shift $\delta^{IS} = +0.33 \pm 0.02$ mm s^{-1} (at 308 K) almost independent of temperature. However, the application of an external magnetic field of, say, 50 kG at 4.2 K resolves the spectrum into two individual patterns, thus demonstrating that the $H = 0$ spectrum is, in fact, the result of a superposition of two spectra with almost identical values for ΔE_Q and δ^{IS}. In the magnetic field, a central Collins-type spectrum [2] characteristic for low-spin iron(II) and a six-line hyperfine spectrum typical for high-spin iron(III) are usually obtained. The results have been of some consequence for the clarification of the nature of several red diimine iron compounds which were previously believed to contain a 'spin-triplet iron(II)' [3, 4]. Based on the practical identity of the ^{57}Fe Mössbauer spectra of these compounds with those of the low-spin iron(II) cation high-spin iron(III) anion complexes refered to above, and taking into account the results of additional physical measurements and chemical studies, the 'spin-triplet iron(II)' compounds have been reformulated as the double salts $[Fe^{II}(diimine)_3]_2[Fe^{III}(dianion)_3](^1/_2dianion)\cdot xH_2O$ [1].

In order to provide additional support for the true nature of the so-called 'spin-triplet iron(II)' compounds, we report, in this paper, on the measurements of magnetism between 0.96 and 300 K for the complexes where the diimine is 2,2′-bipyridyl or 4,7-dimethyl-1,10-phenanthroline and the dianion is oxalate or malonate. In addition, the previously published [4] magnetic data down to 1.00 K for $[Fe(phen)_3]_2[Fe(ox)_3](^1/_2ox)\cdot 14\ H_2O$ and $[Fe(phen)_3]_2[Fe(mal)_3](^1/_2mal)\cdot 20\ H_2O$ have been converted to the new stoichiometry. The obtained magnetic data are compared with results of other physical measurements such as ^{57}Fe Mössbauer spectra and discussed with respect to the nature of the red low-spin iron(II) cation high-spin iron(III) anion complexes.

Experimental

The compounds of the type $[Fe^{II}(diimine)_3]_2[Fe^{III}(dianion)_3](^1/_2dianion)\cdot xH_2O$ where diimine = bipy, 4,7-$(CH_3)_2$-phen and dianion = ox^{2-}, mal^{2-}, were prepared following procedures published separately [3, 4]. The correct stoichiometry was determined in the course of a recent study [1].

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Magnetic susceptibilities were measured over the range 0.96 to 303.5 K by the Faraday method. The equipment employs a 10 inch. electromagnet (Bruker-Physik) with Henry-type pole caps, an electrical microbalance (Sartorius type 4102), and the required cryogenic equipment. Temperatures below 4.2 K were achieved by pumping on the helium reservoir with a Roots pump (Leybold-Heraeus type WS-250), all connecting pipes and flanges being of 65 mm diameter or larger. Temperatures in the cryogenic range were measured using a gold/iron *vs.* chromel thermocouple and checked by noting the vapor pressure of helium. The thermocouple was calibrated against a Pt or Ge resistor placed at the position of the sample. All measurements were performed at six different field strengths, *viz.* 3.50, 5.55, 8.60, 10.90, 12.00 and 13.10 kG. The diamegnetic corrections applied to χ_{m_2} are: Fe, -13; bipy, -105; 4,7-$(CH_3)_2$-phen, -152; ox^{2-}, -25; mal^{2-}, -34; H_2O, -13×10^{-6} cgs mol^{-1}. The effective magnetic moment was obtained according to $\mu_{eff} = 2.828\sqrt{\chi_m^{corr}T}$ where χ_m^{corr} is the molar magnetic susceptibility corrected for the diamagnetism of all constituents and T the temperature in K.

^{57}Fe Mössbauer effect measurement were performed using a spectrometer of the constant acceleration type (Nuclear Data ND 2400, modulation of the pulse-height achieved by the driving wave form) operating in the multiscaler mode. A superconducting magnet capable of producing 55 kG was used in the magnetic hyperfine studies. For more details we refer to a previous publication [1].

Results of Magnetic Measurements

For the compounds $[Fe(phen)_3]_2[Fe(ox)_3](^1/_2ox)\cdot 14\,H_2O$ and $[Fe(phen)_3]_2[Fe(mal)_3](^1/_2mal)\cdot 20\,H_2O$, the previously obtained magnetic susceptibilities [4] have been converted to the new molecular weights. Results for a number of specific temperatures are collected in Table I. For the compounds $[Fe(bipy)_3]_2[Fe(ox)_3](^1/_2ox)\cdot 8\,H_2O$, $[Fe(bipy)_3]_2[Fe(mal)_3](^1/_2mal)\cdot 8\,H_2O$, $[Fe(4,7\text{-}(CH_3)_2\text{-}phen)_3]_2[Fe(ox)_3](^1/_2ox)\cdot 14\,H_2O$ and $[Fe(4,7\text{-}(CH_3)_2\text{-}phen)_3]_2[Fe(mal)_3](^1/_2mal)\cdot 20\,H_2O$, magnetic measurements were performed on samples of weight between 2.115 and 12.961 mg over a temperature range of typically 0.96 to 303.5 K, the results being listed in Tables II–V. For temperatures between 0.96 and 4.20 K, data obtained for six different field strengths (H = 3.50 to 13.10 kG) are listed individually, whereas above 4.20 K, the average values for the six fields are given. In addition, the temperature dependence of the effective magnetic moment μ_{eff} is illustrated, for the four new compounds, in Fig. 1 and 2. The Figures also contain, as an example, plots of the inverse molar magnetic susceptibility, $1/\chi_m^{corr}$, *versus* temperature, for two of the compounds.

From the Figures and the data of Tables II–V it is evident that, for the four low-spin iron(II) cation high-spin iron(III) anion complexes containing 2,2′-bipyridyl and 4,7-dimethyl-1,10-phenanthroline as diimine ligands, μ_{eff} is practically independent of temperature between 300 and about 10 K. Below 10 K, the effective magnetic moment assumes a continu-

TABLE I. Recalculated Magnetic Susceptibility χ_m^{corr}[a] and Effective Magnetic Moment μ_{eff}[b] for $[Fe(phen)_3]_2[Fe(ox)_3](^1/_2ox)\cdot 14\,H_2O$ (A)[c] and $[Fe(phen)_3]_2[Fe(mal)_3](^1/_2mal)\cdot 20\,H_2O$ (B)[d].

A			B		
T (K)	$10^6\chi_m^{corr}$ (cgs mol^{-1})	μ_{eff} (BM)	T (K)	$10^6\chi_m^{corr}$ (cgs mol^{-1})	μ_{eff} (BM)
1.00	891 249	2.67	0.97	913 639	2.66
1.80	683 210	3.14	1.95	692 111	3.29
2.31	580 637	3.28	2.31	620 672	3.39
3.31	447 311	3.44	3.05	508 591	3.52
4.20	368 858	3.52	4.20	395 798	3.65
8.80	193 803	3.69	7.10	263 212	3.87
13.60	130 246	3.76	11.10	170 405	3.89
77.3	22 240	3.71	77.3	24 271	3.87
147.1	11 910	3.74			
174.6	9 890.0	3.72			

[a] Per Fe atom. Total molecular weight $M = 1809.04$ a.u. for (A) and $M = 1966.23$ a.u. for (B). Diamagnetic correction $\chi_m^{dia} = -1077 \times 10^{-6}$ cgs/mol for (A) and $\chi_m^{dia} = -1186 \times 10^{-6}$ cgs/mol for (B). Experimental uncertainty between 0.2 and 0.9%, dependent on temperature. [b] Per Fe atom. $\mu_{eff} = 2.828(\chi_m^{corr}T)^{1/2}$, experimental uncertainty approximately ±0.005 BM. [c] Previous formulation as $Fe(phen)_2ox\cdot 5\,H_2O$. [d] Previous formulation as $Fe(phen)_2mal\cdot 7\,H_2O$.

TABLE II. Magnetic Susceptibilities χ_g and $\chi_m^{corr\,a}$ and Effective Magnetic Moment $\mu_{eff}{}^b$ for $[Fe(bipy)_3]_2[Fe(ox)_3](^1/_2\text{-}ox)\cdot 8\,H_2O^{c,d}$.

H (kG)	T (K)	$10^6\chi_g$ (cgs/g)	$10^6\chi_m^{corr}$ (cgs/mol)	μ_{eff} (BM)
3.50	0.96	2658.3	1 379 767	3.255
5.55		2382.9	1 236 852	3.082
8.60		1950.1	1 012 259	2.788
10.90		1771.9	919 784	2.657
12.00		1699.5	882 214	2.603
13.10		1561.8	810 757	2.495
3.50	1.17	2312.7	1 200 423	3.352
5.55	1.35	1917.7	995 134	3.278
8.60	1.46	1605.2	833 278	3.119
10.90	1.58	1388.6	720 878	3.018
12.00	1.68	1293.9	671 734	3.004
13.10	1.77	1306.6	678 325	3.099
3.50	2.64	1254.3	651 185	3.708
5.55	2.69	1188.3	616 935	3.643
10.90	2.82	1034.3	537 019	3.480
12.00	2.91	976.8	507 181	3.436
13.10	3.00	927.3	481 493	3.399
3.50	3.21	1030.8	535 203	3.707
5.55	3.38	977.0	507 285	3.703
10.90	3.56	875.1	454 405	3.597
12.00	3.65	838.5	435 412	3.565
13.10	3.75	799.9	415 382	3.529
	4.20	732.87	380 597	3.575
	4.56	681.70	354 044	3.593
	5.58	574.80	298 570	3.650
	7.50	446.20	231 834	3.729
	9.10	370.45	192 525	3.743
	12.85	268.59	139 667	3.789
	15.95	217.58	113 197	3.800
	20.37	171.26	89 160	3.811
	24.65	140.73	73 316	3.802
	33.33	104.18	54 350	3.806
	48.88	70.525	36 885	3.797
	61.55	56.627	29 673	3.822
	77.42	44.948	23 612	3.824
	97.75	35.743	18 836	3.837
	119.2	29.255	15 468	3.840
	141.2	24.865	13 190	3.859
	177.8	19.605	10 462	3.857
	251.6	13.841	7 469.9	3.877
	278.6	12.296	6 667.5	3.854
	292.0	11.735	6 376.7	3.859
	303.5	11.409	6 207.8	3.882

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[a] Per Fe atom. Total molecular weight $M = 1556.83$ a.u. Diamagnetic correction $\chi_m^{dia} = -861 \times 10^{-6}$ cgs/mol. Experimental uncertainty between 0.2 and 0.9%, dependent on temperature. Sample weight 12.961 mg. [b] Per Fe atom. $\mu_{eff} = 2.828(\chi_m^{corr}\,T)^{1/2}$, experimental uncertainty approximately ±0.005 BM. [c] Previous formulation as $Fe(bipy)_2\text{-}ox\cdot 3\,H_2O$. [d] Between 0.96 and 3.75 K, the values listed apply to the field strengths H = 3.50 to 13.10 kG individually. At and above 4.20 K, the average values for the six fields are given.

TABLE III. Magnetic Susceptibilities χ_g and $\chi_m^{corr\,a}$ and Effective Magnetic Moment $\mu_{eff}{}^b$ for $[Fe(bipy)_3]_2[Fe(mal)^3]\text{-}(^1/_2mal)\cdot 8\,H_2O^{c,d}$.

H (kG)	T (K)	$10^6\chi_g$ (cgs/g)	$10^6\chi_m^{corr}$ (cgs/mol)	μ_{eff} (BM)
3.50	0.96	2360.7	1 263 996	3.115
5.55		2131.6	1 141 357	2.960
8.60		1787.8	957 388	2.711
10.90		1552.1	831 146	2.526
12.00		1407.1	753 527	2.405
13.10		1320.4	707 117	2.330
3.50	1.27	2024.5	1 084 025	3.318
5.55	1.44	1701.5	911 121	3.239
8.60	1.68	1427.9	764 662	3.205
10.90	1.78	1263.8	676 818	3.104
12.00	1.87	1166.5	624 733	3.057
13.10	1.93	1090.9	584 264	3.003
3.50	2.01	1458.0	780 730	3.543
5.55	2.08	1363.9	730 402	3.486
8.60	2.10	1256.7	673 017	3.362
10.90	2.18	1148.1	614 883	3.274
12.00	2.26	1069.8	572 968	3.218
13.10	2.44	988.6	529 502	3.214
3.50	2.55	1202.6	644 057	3.624
5.55	2.63	1138.7	609 851	3.582
8.60	2.70	1064.4	570 078	3.509
10.90	2.99	943.6	505 412	3.476
12.00	3.09	880.7	471 742	3.414
13.10	3.23	841.2	450 597	3.412
3.50	3.35	950.79	509 264	3.694
5.55	3.41	913.09	489 080	3.652
8.60	3.48	871.40	466 764	3.604
10.90	3.54	829.10	444 120	3.546
12.00	3.65	789.10	422 410	3.512
13.10	3.71	761.70	408 040	3.480
	4.20	709.68	380 194	3.574
	4.80	619.33	331 829	3.569
	5.18	579.01	310 245	3.585
	5.85	553.86	296 777	3.726
	6.00	505.48	270 884	3.605
	7.05	449.04	240 671	3.684
	7.93	417.95	224 029	3.770
	10.33	326.10	174 861	3.801
	12.09	272.43	146 131	3.759
	15.31	219.59	117 845	3.799
	19.68	169.45	91 005	3.785
	25.50	134.20	72 135	3.836
	29.82	114.50	61 590	3.833
	40.92	83.510	45 000	3.838
	47.38	70.964	38 284	3.809
	57.85	59.845	32 333	3.868
	68.46	51.198	27 704	3.895
	77.36	44.638	24 193	3.869
	109.2	31.744	17 290	3.886
	151.3	22.989	12 649	3.912
	200.0	17.280	9 547.5	3.908
	293.6	11.649	6 533.6	3.917

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[a] Per Fe atom. Total molecular weight $M = 1605.92$ a.u. Diamagnetic correction $\chi_m^{dia} = -892 \times 10^{-6}$ cgs/mol. Exper-

(continued overleaf)

TABLE III. *(Continued)*

imental uncertainty between 0.2 and 0.9%, dependent on temperature. Sample weight 7.522 mg. [b]Per Fe atom. $\mu_{eff} = 2.828(\chi_m^{corr}T)^{1/2}$, experimental uncertainty approximately ±0.005 BM. [c]Previous formulation as Fe(bipy)$_2$-mal·3 H_2O. [d]Between 0.96 and 3.71 K, the values listed apply to the field strengths H = 3.50 to 13.10 kG individually. At and above 4.20 K, the average values for the six fields are given.

TABLE IV. Magnetic Susceptibilities χ_g and χ_m^{corr}[a] and Effective Magnetic Moment μ_{eff}[b] for [Fe(4,7-CH_3)$_2$-phen)$_3$]$_2$-[Fe(ox)$_3$] ($^1/_2$ox)·14 H_2O[c,d].

H (kG)	T (K)	10^6 χ_g (cgs/g)	10^6 χ_m^{corr} (cgs/mol)	μ_{eff} (BM)
3.50	0.96	1980.4	1 305 728	3.166
5.55		1747.8	1 152 417	2.975
8.60		1439.8	949 408	2.700
10.90		1234.7	814 222	2.500
12.00		1140.5	752 133	2.403
13.10		1048.9	691 758	2.305
3.50	1.19	1658.1	1 093 294	3.226
5.55	1.34	1443.3	951 715	3.194
8.60	1.46	1191.5	785 748	3.029
10.90	1.60	1038.5	684 903	2.960
12.00	1.67	955.9	630 460	2.902
3.50	1.75	1270.4	837 753	3.424
5.55	1.83	1177.1	776 257	3.371
8.60	1.92	1043.0	687 869	3.250
10.90	1.97	947.5	624 923	3.138
12.00	2.03	882.3	581 949	3.074
13.10	2.08	835.3	550 970	3.027
3.50	2.13	1106.1	729 460	3.525
5.55	2.18	1034.4	682 201	3.449
8.60	2.26	938.2	618 793	3.344
10.90	2.35	859.4	566 855	3.264
12.00	2.50	797.2	525 857	3.243
13.10	2.59	746.5	492 440	3.194
	4.20	549.4	362 528	3.490
	5.10	465.4	307 161	3.540
	5.72	414.5	273 612	3.538
	7.94	315.7	208 491	3.639
	8.67	286.7	189 377	3.624
	13.10	199.6	131 967	3.718
	14.60	177.4	117 335	3.701
	24.00	108.47	71 902	3.715
	38.94	66.64	44 331	3.716
	52.72	49.41	32 974	3.729
	61.72	42.848	28 649.0	3.761
	66.26	40.300	26 969.5	3.780
	77.30	33.652	22 587.7	3.737
	99.05	26.170	17 656.2	3.740
	109.10	24.274	16 406.5	3.784
	154.55	17.405	11 879.0	3.832
	194.50	14.335	9 855.5	3.915
	228.30	12.610	8 718.5	3.990
	270.15	10.835	7 548.6	4.038
	273.9	10.800	7 525.5	4.060
	293.0	10.054	7 033.8	4.060

[a]Per Fe atom. Total molecular weight $M = 1977.36$ a.u. Diamagnetic correction $\chi_m^{dia} = -1221 \times 10^{-6}$ cgs/mol. Experimental uncertainty between 0.2 and 0.9%, dependent on temperature. Sample weight 2.115 mg. [b]Per Fe atom. $\mu_{eff} = 2.828(\chi_m^{corr}T)^{1/2}$, experimental uncertainty approximately ±0.005 BM. [c]Previous formulation as Fe(4,7-(CH_3)$_2$-phen)$_2$ox·4 H_2O. [d]Between 0.96 and 2.59 K, the values listed apply to the field strengths H = 3.50 to 13.10 kG individually. At and above 4.2 K, the average values for the six fields are given.

TABLE V. Magnetic Susceptibilities χ_g and χ_m^{corr}[a] and Effective Magnetic Moment μ_{eff}[b] for [Fe(4,7-(CH_3)$_2$-phen)$_3$]$_2$-[Fe(mal)$_3$]($^1/_2$mal)·20 H_2O[c,d].

H (kG)	T (K)	10^6 χ_g (cgs/g)	10^6 χ_m^{corr} (cgs/mol)	μ_{eff} (BM)
3.50	0.94	1917.5	1 364 770	3.203
5.55		1683.8	1 198 489	3.002
8.60		1390.5	989 803	2.728
10.90		1201.3	855 184	2.536
12.00		1086.8	773 716	2.412
13.10		1016.2	723 483	2.332
3.50	1.14	1661.7	1 182 765	3.284
5.55	1.27	1415.5	1 007 590	3.199
8.60	1.41	1181.4	841 025	3.080
10.90	1.52	1029.3	732 804	2.985
12.00	1.63	871.3	620 385	2.844
3.50	1.75	1261.8	898 231	3.546
5.55	1.86	1145.5	815 482	3.483
8.60	1.91	1021.8	727 468	3.334
10.90	1.99	928.4	661 012	3.243
12.00	2.18	846.9	603 024	3.242
13.10	2.24	804.0	572 500	3.203
3.50	2.33	1018.2	724 906	3.675
5.55	2.42	944.2	672 254	3.607
8.60	2.58	844.4	601 245	3.522
10.90	2.71	776.4	552 862	3.462
12.00	2.88	723.3	515 081	3.444
13.10	2.94	690.4	491 672	3.400
3.50	3.14	787.3	560 618	3.752
5.55	3.20	750.6	534 505	3.699
8.60	3.28	708.7	504 693	3.639
10.90	3.38	668.6	476 161	3.588
12.00	3.60	621.5	442 649	3.570
13.10	3.62	615.3	438 237	3.562
3.50	3.67	678.6	483 276	3.766
5.55	3.70	657.9	468 548	3.724
8.60	3.79	628.7	447 772	3.684
10.90	3.89	597.3	425 430	3.638
12.00	3.95	576.5	410 631	3.602
	4.20	554.82	395 205	3.643
	8.34	301.05	214 644	3.784
	16.37	157.97	112 841	3.844
	27.72	93.40	66 899	3.851
	40.35	64.550	46 372	3.868
	52.55	49.730	35 827	3.880
	65.02	40.653	29 368.5	3.908
	77.43	33.388	24 199.3	3.871
	102.25	25.234	18 397.7	3.879

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TABLE V. *(Continued)*

H (kG)	T (K)	$10^6\ \chi_g$ (cgs/g)	$10^6\ \chi_m^{corr}$ (cgs/mol)	μ_{eff} (BM)
	147.95	17.733	13 060.6	3.931
	204.20	12.780	9 536.47	3.946
	253.00	10.360	7 814.61	3.976
	303.20	8.788	6 696.11	4.030

[a] Per Fe atom. Total molecular weight M = 2134.54 a.u. Diamagnetic correction $\chi_m^{dia} = -1330 \times 10^{-6}$ cgs/mol. Experimental uncertainty between 0.2 and 0.9%, dependent on temperature. Sample weight 2.827 mg. [b] Per Fe atom. $\mu_{eff} = 2.828(\chi_m^{corr}\ T)^{1/2}$, experimental uncertainty approximately ±0.005 BM. [c] Previous formulation as Fe(4,7-$(CH_3)_2$-phen)$_2$mal·7 H_2O. [d] Between 0.94 and 3.95 K, the values listed apply to the field strengths H = 3.50 to 13.10 kG individually. At and above 4.2 K, the average values for the six fields are given.

ously decreasing character. Thus, at 0.96 K, the values of μ_{eff} obtained are (for a field strength H = 13.10 kG) 2.495, 2.330, 2.305 and 2.332 BM for the 2,2′-bipyridyl oxalato, 2,2′-bipyridyl malonato, 4,7-dimethyl-1,10-phenanthroline oxalato and 4,7-dimethyl-1,10-phenanthroline malonato complex, serially. This is very similar to the magnetic behaviour of the corresponding 1,10-phenanthroline complexes, *viz.* $[Fe(phen)_3]_2[Fe(ox)_3](^1/_2ox)\cdot14\ H_2O$ and $[Fe(phen)_3]_2[Fe(mal)_3](^1/_2mal)\cdot20\ H_2O$, which assume at about 1.00 K μ_{eff}-values of 2.67 and 2.66 BM, respectively (*cf.* Table I).

Discussion

In order to demonstrate the nature of the low-spin iron(II) cation high-spin iron(III) anion complexes discussed in this paper, Fig. 3 shows, as an example, the ^{57}Fe Mössbauer effect spectrum of $[Fe(bipy)_3]_2[Fe(ox)_3](^1/_2ox)\cdot8\ H_2O$. Evidently, at H = 0 and 4.2 K, the compound shows a single closely spaced doublet with a quadrupole splitting $\Delta E_Q = 0.33 \pm 0.01$ mm s^{-1} and an isomer shift $\delta^{IS} = +0.24 \pm 0.02$ mm s^{-1}. The values for ΔE_Q and δ^{IS} at higher temperatures, *e.g.* at 300 K, are practically identical to the values at 4.2 K. The observed doublet is formed by a superposition of the Mössbauer spectra of the low-spin iron(II) cation and the high-spin iron(III) anion. Indeed, $\Delta E_Q = 0.39$ mm s^{-1}, $\delta^{IS} = +0.32$ mm s^{-1} have been reported for the $[Fe(bipy)_3]^{2+}$ cation [5], whereas the anion $[Fe(ox)_3]^{3-}$ is known to produce the parameter values $\Delta E_Q = 0.32$ mm s^{-1}, $\delta^{IS} = +0.25$ mm s^{-1} [6]. An experimental separation of the two spectra would thus not be expected. A resolution may be achieved, however, if the effect of an external magnetic field of, say, 55 kG, on the ^{57}Fe Mössbauer resonance absorption is investigated, cf.

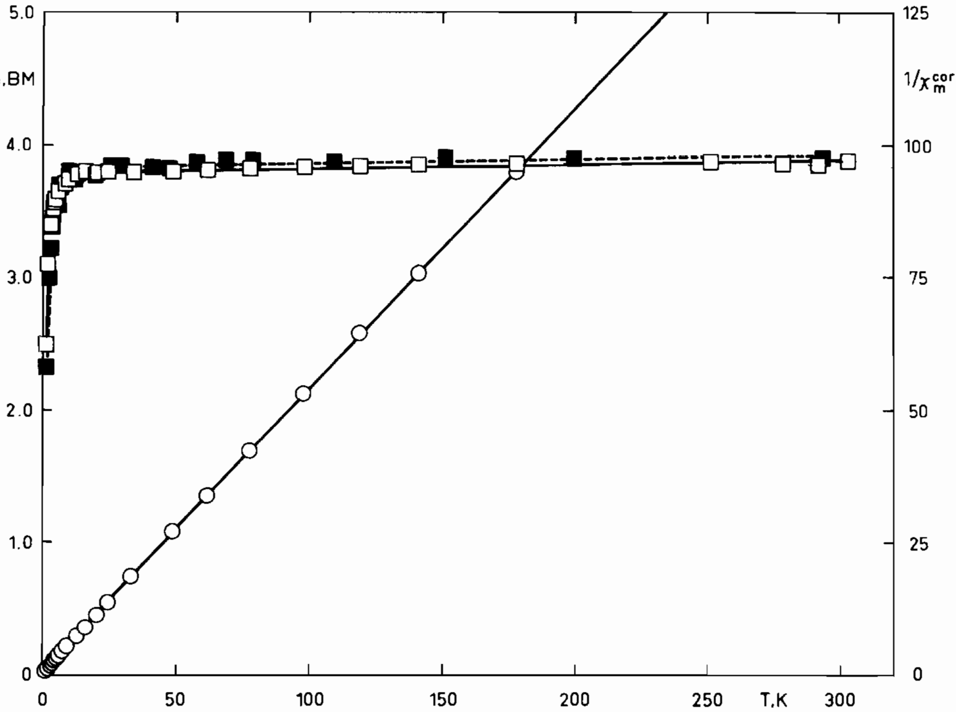

Fig. 1. Temperature dependence of the effective magnetic moment, μ_{eff}, for $[Fe(bipy)_3]_2[Fe(ox)_3](^1/_2ox)\cdot8\ H_2O$ (□) and $[Fe(bipy)_3]_2[Fe(mal)_3](^1/_2mal)\cdot8\ H_2O$ (■) between 0.96 and 303.5 K (left ordinate). For $[Fe(bipy)_3]_2[Fe(ox)_3](^1/_2ox)\cdot8\ H_2O$ the inverse molar magnetic susceptibility, $1/\chi_m^{corr}$, is also shown (○; right ordinate).

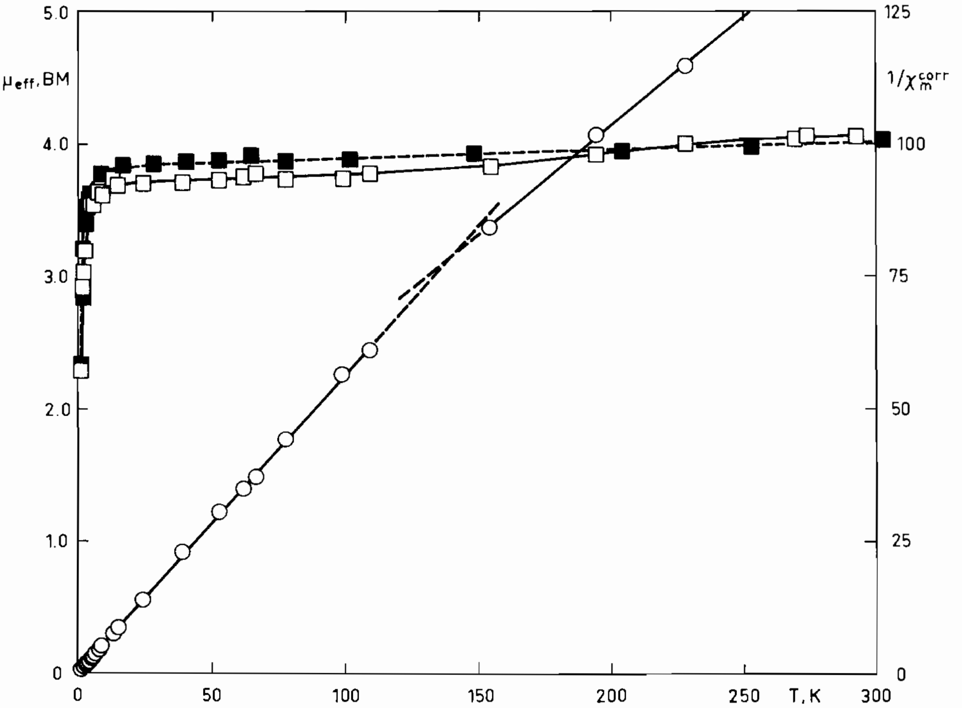

Fig. 2. Temperature dependence of the effective magnetic moment, μ_{eff}, for $[Fe(4,7\text{-}CH_3)_2\text{-phen})_3]_2[Fe(ox)_3](^1/_2ox)\cdot 14\ H_2O$ (□) and $[Fe(4,7\text{-}(CH_3)_2\text{-phen})_3]_2[Fe(mal)_3](^1/_2mal)\cdot 20\ H_2O$ (■) between 0.94 and 303.2 K (left ordinate). For $[Fe(4,7\text{-}CH_3)_2\text{-phen})_3]_2[Fe(ox)_3](^1/_2ox)\cdot 14\ H_2O$ the inverse molar magnetic susceptibility, $1/\chi_m^{corr}$, is also shown (○; right ordinate).

Fig. 3. As a consequence of the magnetic hyperfine interaction, the doublet originating in the low-spin iron(II) cation is transformed into a Collins-type spectrum [2] at the center; the additional six-line spectrum which may be characterized by the effective field $H_{eff} = 509$ kG is typical for iron(III) and is therefore attributed to the high-spin iron(III) anion. The remaining complexes dealt with in this study show a behaviour which is closely similar to that of $[Fe(bipy)_3]_2[Fe(ox)_3](^1/_2ox)\cdot 8\ H_2O$, some of the obtained Mössbauer effect data being shown in Table VI.

The measured values of the magnetic susceptibility χ_m are the average values of the susceptibilities for the low-spin iron(II) cations and the high-spin iron(III) anion contained in the complex under consideration. The $[Fe(ox)_3]^{3-}$ ion, *e.g.*, is known to show at 297.5 K an effective magnetic moment $\mu_{eff} =$ 5.92 BM [7]. If the value of $\mu_{eff} = 3.859$ BM for the compound $[Fe(bipy)_3]_2[Fe(ox)_3](^1/_2ox)\cdot 8\ H_2O$ at 292.0 K is employed (*cf.* Table II), the effective magnetic moment $\mu_{eff} = 2.19$ BM may be easily estimated for the $[Fe(bipy)_3]^{2+}$ cation within the compound. This value is considerably higher than the moment value $\mu_{eff} = 0.82$ BM which was reported for $[Fe(bipy)_3](ClO_4)_2\cdot 3\ H_2O$ at 297.6 K [8]. It should be noted, however, that siginificantly higher magnetic moments have also been found for various tris diimine iron(II) complexes, the increased values having been generally attributed to temperature-independent paramagnetism [8]. The ion $[Fe(mal)_3]^{3-}$ shows, at 297.5 K, a magnetic moment $\mu_{eff} = 5.87$ BM [7] and thus a closely similar result is obtained for the $[Fe(bipy)_3]^{2+}$ ion if the magnetic data for $[Fe(bipy)_3]_2[Fe(mal)_3](^1/_2mal)\cdot 8\ H_2O$ are used. Finally, even somewhat higher values of μ_{eff}, *viz.* 2.68 BM and 2.67 BM, are found for the $[Fe(4,7\text{-}(CH_3)_2\text{-phen})_3]^{2+}$ cation within the compounds $[Fe(4,7\text{-}(CH_3)_2\text{-phen})_3]_2[Fe(ox)_3](^1/_2ox)\cdot 14\ H_2O$ and $[Fe(4,7\text{-}(CH_3)_2\text{-phen})_3]_2[Fe(mal)_3](^1/_2mal)\cdot 20\ H_2O$, respectively. A contribution to the magnetism of a low-spin $3d^6$ ion, by the second-order Zeeman effect, as high as that observed in the present study is certainly unusual. Increased values of the magnetic moment may be due to a significant admixutre of states of higher spin multiplicity which will be particularly notable if the complex ion considered is close to the $^1A_1/^5T_2$ cross-over point. Indeed, this situation has been often discussed for tris diimine iron(II) ions such as those considered here [8]. However, some chemical effects such as differences in hydration of the samples cannot be ruled out. In view of the high molecular weight and the specific properties of these complexes, conditions such as the amount of hydration are difficult to control. For more details we refer to a previous publication [1].

The decrease of the effective magnetic moment below 10 K is due to the depopulation of all paramag-

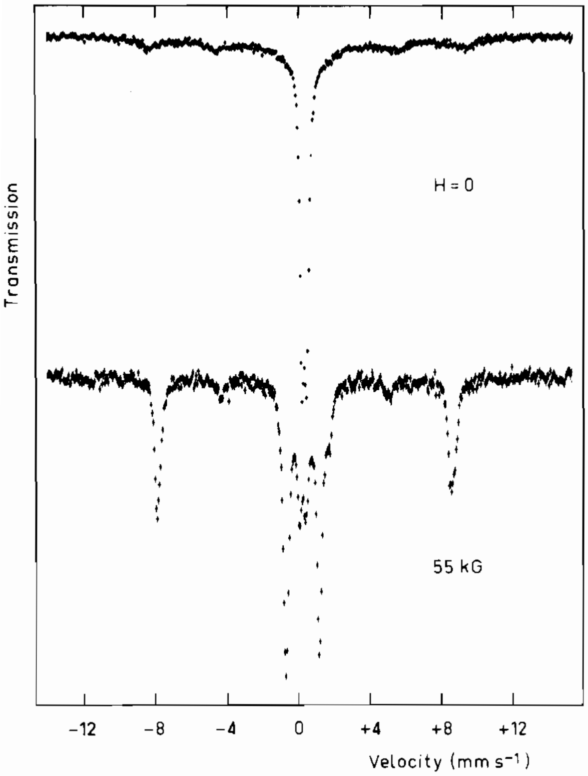

Fig. 3. ^{57}Fe Mössbauer effect spectra for $[Fe(bipy)_3]_2[Fe(ox)_3](^1/_2ox)\cdot 8\ H_2O$ at 4.2 K for magnetic field strength H O and H = 55 kG. The magnetic field is parallel to the direction of the γ-rays.

netic states which are contributing to the overall μ_{eff} values at the higher temperatures. A similar behaviour has been described previously for various other iron(II) complexes [9, 10]. The argument is also supported by the observation that the Curie law is closely followed down to 1.00 K by all the compounds investigated. For $[Fe(4,7\text{-}(CH_3)_2\text{-phen})_3]_2[Fe(ox)_3]\cdot(^1/_2ox)\cdot 14\ H_2O$, the slope of the $1/\chi_m^{corr}$ line changes at about 140 K, a Curie–Weiss law, $\chi_m = C_m/(T - \Theta)$ with $\Theta = -50$ K, rather than the Curie law being followed above that temperature. It is not clear at present whether a change in the crystal lattice or the population of another level from the $^6A_1(t_2^5)$ manifold of the iron(III) ion is the origin of this observation.

In summary, the magnetic behaviour down to below 1.00 K of the compounds previously believed to contain spin-triplet iron(II) ground states is consistent with their new formulation as double salts involving low-spin iron(II) complex cations and a high-spin iron(III) complex anion. The nature of the compounds has been established on the basis of ^{57}Fe Mössbauer effect magnetic hyperfine studies.

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TABLE VI. ^{57}Fe Mössbauer Effect Parameters for Low-Spin Iron(II) Cation High-Spin Iron(III) Anion Complexes.

Compound	T (K)	$\Delta E_Q{}^a$ (mm s^{-1})	$\delta^{IS\ b}$ (mm s^{-1})	H_{eff} (kG)
$[Fe(bipy)_3]_2[Fe(ox)_3](^1/_2ox)\cdot 8\ H_2O$	4.2	0.33	+0.24	509
$[Fe(bipy)_3]_2[Fe(mal)_3](^1/_2mal)\cdot 8\ H_2O$	4.2	0.34	+0.23	521
$[Fe(4,7\text{-}(CH_3)_2\text{-phen})_3]_2[Fe(ox)_3](^1/_2ox)\cdot 14\ H_2O$	4.2	0.27	+0.26	509
$[Fe(4,7\text{-}(CH_3)_2\text{-phen})_3]_2[Fe(mal)_3](^1/_2mal)\cdot 20\ H_2O$	4.2	0.27	+0.26	521

[a] Experimental uncertainty ±0.02 mm s^{-1}. [b] Isomer shifts δ^{IS} are listed relative to natural iron at 298 K. Experimental uncertainty ±0.03 mm s^{-1}.

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