Magnetic and Mössbauer Studies of Some Halogeno(quinolin-8-olato)-iron(III) Complexes

By **D. Cunningham, M. J. Frazer, A. H. Qureshi** and **F. B. Taylor,*** Department of Chemistry, The Polytechnic of North London, Holloway Road, London N7 8DB
B. W. Dale, Materials Physics Division, A.E.R.E., Harwell

Mössbauer and variable-temperature magnetic studies of the complexes $FeX(ox)_2$ and $FeX_2(ox)$ (X = Cl or Br; oxH = quinolin-8-ol) suggest that they exist as magnetically isolated dimeric units in the solid state.

CONSIDERABLE interest has recently centred on the magnetic and Mössbauer properties of dimeric iron(III) complexes, particular attention being paid to distinguishing the spin state of the metal [1] and to determining the molecularity of the complexes. It has been claimed that magnetic susceptibility measurements are not entirely satisfactory for establishing the molecularity of complexes because of the sensitivity of the method to small amounts of impurity and that a Mössbauer study, which does not suffer from this drawback, should give a more accurate description.[2] In particular the deduction, from susceptibility results, that [Fe(salen)Cl]MeCN [salen = *NN'*-ethylenebis(salicylideneiminato)] is dimeric [3] has been questioned.[2]

Recently we have reported the preparation of a series of complexes of iron(III) halides with quinolin-8-ol.[4] In this paper magnetic susceptibility and Mössbauer studies have been used to determine the molecularity of some of these complexes; $FeX(ox)_2$ and $FeX_2(ox)$ (X = Cl or Br; oxH = quinolin-8-ol). The compounds, with the exception of $FeBr_2(ox)$, are insoluble in the usual solvents so that determination of molecular weight by solution methods was not feasible. $FeBr_2(ox)$ is monomeric in tetrahydrofuran and has a normal moment in this solvent.[4] Susceptibility measurements suggest that the chlorides are dimeric. Mössbauer results are consistent with this conclusion, and indicate, further, that the co-ordination numbers of the metal in the $FeX(ox)_2$ and $FeX_2(ox)$ compounds are six and five, respectively.

RESULTS AND DISCUSSION

The magnetic susceptibilities of the complexes were measured over the temperature range 370—90 K and detailed results are given in Table 1. The room-temperature moments, with the exception of $FeBr(ox)_2$ which has a value close to the ' spin-only ' value, are below that expected for a high-spin d^5 system and they decrease markedly with temperature. All complexes have a large negative Weiss constant $[\chi \propto C/(T - \theta)]$ (Table 2) and the graphs of χ^{-1} against T are non-linear. In one case, $FeCl_2(ox)$, a maximum is observed in the χ against T curve (Table 2). These observations are consistent with the presence of antiferromagnetic interactions.

The susceptibilities have been compared with those calculated using a dipolar-coupling model [5,6] involving high-spin iron(III) which includes in the Hamiltonian the term $-2JS_1S_2$ where J is the exchange interaction between two ions and S_1 and S_2 are the spin vectors for the ions. The calculated values, which most closely agree

---

[1] W. M. Reiff, W. A. Baker, and N. E. Erickson, *J. Amer. Chem. Soc.*, 1968, **90**, 4974; W. M. Reiff, G. J. Long, and W. A. Baker, *ibid.*, p. 6347.

[2] G. M. Bancroft, A. G. Maddock, and R. P. Randl, *J. Chem. Soc.* (*A*), 1968, 2939.

[3] J. Lewis, F. E. Mabbs, and A. Richards, *Nature*, 1965, **207**, 855; M. Gerloch, J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc.* (*A*), 1968, 112.

[4] M. J. Frazer, A. H. Qureshi, and F. B. Taylor, *J. Chem. Soc.* (*A*), 1971, 1712.

[5] J. H. Van Vleck, ' Electric and Magnetic Susceptibilities,' Oxford University Press, 1932.

[6] A. Earnshaw, B. N. Figgis, and J. Lewis, *J. Chem. Soc.* (*A*), 1966, 1656.

TABLE 1

Experimental and calculated magnetic data *

$FeCl(ox)_2$

T/K	373·2	343·2	303·2	274·2	234·8	196·1	156·9	118·3	88·4
$10^6\chi_A$ obs	10,218	10,853	11,853	12,644	13,970	15,459	16,963	18,427	19,033
$10^6\chi_A$ calc	10,146	10,801	11,802	12,633	13,927	15,389	17,019	18,558	19,344
μ_{eff}/B.M.	5·52	5·46	5·37	5·27	5·13	4·93	4·62	4·18	3·67

$FeBr(ox)_2$

T/K	373·2	343·2	303·2	274·2	234·8	196·1	156·9	118·3	88·4
$10^6\chi_A$ obs	13,001	13,631	14,851	15,405	16,639	18,091	19,646	21,171	22,008
$10^6\chi_A$ calc	12,391	13,156	14,313	15,260	16,705	18,288	19,961	21,388	21,950
μ_{eff}/B.M.	6·23	6·12	6·00	5·82	5·59	5·13	4·97	4·48	3·95

$FeCl_2(ox)$

T/K	373·2	343·2	303·2	274·2	234·8	196·1	176·3	156·9	137·5	118·3	109·1	88·4
$10^6\chi_A$ obs	8242	8655	9187	9563	10,120	10,626	10,795	10,899	10,956	10,936	10,882	10,743
$10^6\chi_A$ calc	8351	8725	9249	9637	10,149	10,588	10,762	10,882	10,939	10,918	10,879	10,708
μ_{eff}/B.M.	4·96	4·88	4·72	4·58	4·36	4·08	3·90	3·70	3·48	3·22	3·08	2·76

$FeBr_2(ox)$

T/K	373·2	343·2	303·2	274·2	234·8	196·1	156·9	118·3	88·4
$10^6\chi_A$ obs	6297	6742	7401	7882	8815	10,055	11,738	14,301	17,714
μ_{eff}/B.M.	4·35	4·30	4·24	4·16	4·07	3·98	3·84	3·68	3·54

* Susceptibilities in c.g.s.u.; $\mu_{eff} = 2{\cdot}83\ (\chi_{A obs}\ T)^{\frac{1}{2}}$.

with the experimental ones are given in Table 1 and the magnetic parameters resulting from the calculation in Table 2. The susceptibilities of both chloro-complexes agree satisfactorily with those calculated from the model. Better agreement was obtained for $FeCl(ox)_2$ if the temperature-independent contribution to the susceptibility (TIP) was increased from zero to 250 × 10^{-6} ($g = 2{\cdot}06$, $J = -9$ cm^{-1}, and $10^2R = 0{\cdot}53$). It was not possible to obtain satisfactory agreement for $FeBr_2(ox)$ and the results for $FeBr(ox)_2$ are only just satisfactory. The lack of agreement probably arises from the presence of a small amount of impurity in these compounds.

TABLE 2

Magnetic parameters

	$-\theta$/K	g	$-J$/cm^{-1}	10^2R [a]
$FeCl(ox)_2$	152	2·08 [b] 2·10 [c]	9	0·83
$FeBr(ox)_2$	272	2·33 [b] 2·35 [c]	10	2·01
$FeCl_2(ox)$	300	2·08 [b] 2·03 [c]	16	0·50
$FeBr_2(ox)$	100	2·36 [c]		

[a] $R^2 = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi^2_{obs}]$. [b] From computer fitting. [c] From e.s.r. [d] Neél temperature = 140 K. *N.B.* TIP taken as zero.

Attempts to fit the susceptibility of $FeBr_2(ox)$ to that calculated for a system of two interacting ions with $S = \frac{3}{2}$ were no more successful.

Mössbauer spectra have been recorded both in zero field and in applied fields of 3 T (30,000 G). Parameters are in Table 3. In all cases peaks are broad in the zero-field room-temperature spectra but become narrower on cooling to 80 K. Least-squares fits of spectra, of all four compounds, recorded at 4·2 K in an applied field were good (see the Figure); normal line-widths (*ca.* 0·24 mm s^{-1}) were obtained and it is concluded, therefore, that each of the complexes contains only one iron environment. This eliminates the possibility of chain polymeric structures containing more than one iron site. The line broadening in the zero-field spectra at 80 K and room temperature is discussed later.

TABLE 3

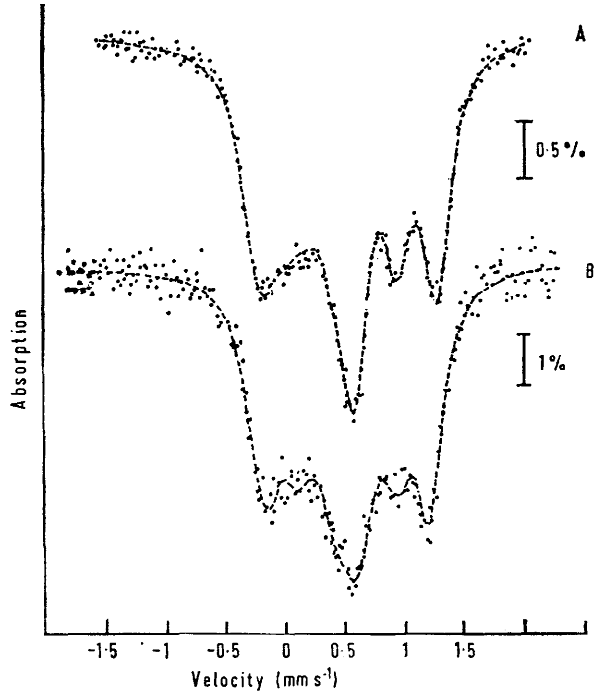
Mössbauer parameters

	T/K	δ */mm s^{-1}	Δ */mm s^{-1}	Γ_1/mm s^{-1}	Γ_2/mm s^{-1}	H_1/H_2	η
$FeCl(ox)_2$	290	0·41	0·80	0·282	0·270	1·129	0·4
	80	0·49	0·77	0·186	0·204	1·041	
$FeBr(ox)_2$	290	0·41	0·81	0·241	0·306	1·435	0·9
	80	0·51	0·79	0·197	0·256	1·245	
	4·2	0·56	0·74	0·125	0·130	1·00	
$FeCl_2(ox)$	290	0·29	0·40	0·140	0·182	1·061	0·4
	80	0·41	0·46	0·145	0·150	1·003	
$FeBr_2(ox)$	290	0·31	0·46	0·185	0·319	1·097	*ca.* 1·0
	80	0·43	0·48	0·164	0·165	1·033	

* Relative to iron.

Γ_1 = Half-width at half height of lower energy peak. Γ_2 = Half-width at half height of higher energy peak. H_1 = Height of low-energy peak. H_2 = Height of high-energy peak. η = Asymmetry parameter (obtained from spectra in magnetic field of 3 T at 1·7 K)

Chemical shifts and quadrupole splittings are in the range normally associated with a sextet ground state.[7] We now have chemical-shift data for the series $Fe(ox)_3$ (0·46 mm s^{-1}),[8] $FeCl(ox)_2$ (0·49 mm s^{-1}), $FeCl_2(ox)$ (0·41 mm s^{-1}), and $FeCl_3$ (0·53 mm s^{-1}).[9] The first and last members of the series have six-co-ordinate iron and similar co-ordination for $FeCl(ox)_2$ is reasonable. On the other hand, the lower value for $FeCl_2(ox)$ may indicate five-co-ordinate iron. Furthermore, the value for $FeCl_2(ox)$ lies between that of $Fe(ox)_3$ and $FeCl_4^-$ (0·29 mm s^{-1}).[10] These co-ordination numbers support dimeric formulations for $FeCl_2(ox)$ and $FeCl(ox)_2$.



Mössbauer spectra of $FeCl(ox)_2$ (A) and $FeBr(ox)_2$ (B) at 4·2 K in a field of 3 T perpendicular to the direction of γ-ray propagation. Broken lines indicate computer-simulated spectra

Mössbauer spectra of the complexes recorded at 4·2 and 1·7 K in an externally applied magnetic field of 3 T show that the internal field is small in all cases. In the absence of exchange, large internal fields are associated with the ^6S state. If, however, there is an interaction of the form $H = -2JS_1S_2$ the eigen states have total-spin quantum numbers $S = 0, 1 \ldots 5$, the eigenvalues being given by $E_{S'} \cong -JS'(S'+1)$. Assuming such exchange takes place in the halide complexes, the energy of the $S' = 1$ state will be equal to $2J$ which, from the experimental values (Table 2) is *ca.* 20 cm^{-1}, with the result that at 4·2 K only the $S' = 0$ state is occupied significantly. This state is non-magnetic to first order and small internal fields are predicted in agreement with our observations.

Further evidence in support of the proposed co-ordination numbers arises from the sign of the largest component of the electric field-gradient tensor. Positive field gradients have been observed for the five-co-ordinate complexes $FeCl(acac)_2$[11] and $Fe(salen)_2O$[2] whereas a negative field gradient was observed for dimeric [Fe(salen)Cl][12] which contains six-co-ordinate iron. The sign for $FeCl_2(ox)$ is positive and for $FeCl(ox)_2$ is negative.

The spectra of the bromo-complexes show pronounced asymmetry in both peak-heights and line-widths at room temperature. This asymmetry largely disappears in $FeBr_2(ox)$ at 80 K and in $FeBr(ox)_2$ at 4·2 K. As spectra of very finely powdered samples are reproducible the asymmetry cannot be attributed to that arising from preferred orientation of crystallites within samples. A temperature-dependent asymmetry may arise from either the Goldanskii–Karyagin effect or from relaxation effects. The Goldanskii–Karyagin effect[13] gives rise to integral asymmetry and thus cannot account for the present asymmetry where the component peaks have approximately equal areas. The theory of relaxation effects in Mössbauer spectroscopy has been discussed by several authors.[12] In the present cases only the non-magnetic $S' = 0$ state is significantly populated at low temperatures. At higher temperatures, states having non-zero magnetic moments become occupied and if relaxation of spin states occurs with frequencies comparable to the Larmor frequency of the ^{57}Fe nucleus line broadening will be observed in the spectra. The fact that the asymmetry parameter is large for both bromides and that preferential line broadening is observed in the room-temperature spectra indicate that the S vector has low symmetry (*i.e.* $S_x \neq S_y$).

The component peak-heights in the room-temperature spectrum of $FeCl(ox)_2$ are not equal but it is possible that in this case the asymmetry is due to the Goldanskii–Karyagin effect. The broad line-widths in the zero-field spectrum of this compound and in that of $FeCl_2(ox)$ may result from relaxation effects as the asymmetry parameter is non-zero in both cases. Room-temperature e.s.r. spectra of the undiluted solids show a broad resonance *ca.* $g = 2$. g-Values close to 2 were observed for the chlorides but the values for the bromides were considerably larger (Table 2). Normally for a high-spin d^5 system a g-value close to 2·0 is expected. However, when an even number of d^5 ions interact the system is no longer of the Kramers type and the possibility of zero-field splittings of the spin multiplets arises which could give rise to apparent g-values different from 2. This effect would be expected to increase with increasing

---

[7] 'Chemical Applications of Mössbauer Spectroscopy,' eds. V. I. Goldanskii and R. H. Herber, Academic Press, 1968.

[8] D. Cunningham, M. J. Frazer, and F. B. Taylor, unpublished results.

[9] C. W. Kocher, *Phys. Letters*, 1967, **24**, 93.

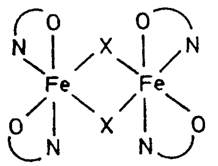
[10] P. R. Edwards and C. E. Johnson, *J. Chem. Phys.*, 1968, **49**, 211.

[11] M. Cox, B. W. Fitzsimmons, A. W. Smith, L. F. Larkworthy, and K. A. Rogers, *Chem. Comm.*, 1969, 183.

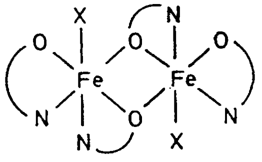
[12] A. N. Buckley, I. R. Herbert, B. D. Rumbold, G. V. H. Wilson, and K. S. Murray, *J. Phys. and Chem. Solids*, 1970, **31**, 1423.

[13] S. V. Karyagin, *Doklady Akad. Nauk S.S.S.R.*, 1963, **148**, 1102.

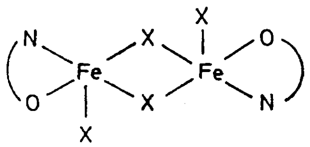
asymmetry in the molecule, therefore the observed high *g*-values for the bromides are consistent with the conclusion, from Mössbauer spectroscopy, of asymmetry of the *S*-vector.



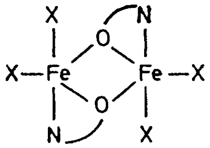
(I)



(III)



(II)



(IV)

O N=quinolin-8-olato

The two most likely structures for dimeric FeX(ox)$_2$ and FeX$_2$(ox) involve either halogen bridges [structures (I) and (II)] or oxygen bridges [structures (III) and (IV)]. Examples of dimeric iron(III) oxygen-bridge systems are numerous but there are very few examples of compounds with halogen bridges, two examples are gaseous ferric chloride [14] and α-Cs$_2$Fe$_2$Cl$_9$.[15] Evidence for bridging oxygen atoms in other dimeric metal quinolin-8-olates is largely circumstantial being claimed to be present in CuX(ox) (X = Cl or Br), Cu(ox)NO$_3$,H$_2$O, and Cu$_2$(ox)$_3$ClO$_4$, 0·5 EtOH [16] because of the similarity between these compounds and the copper(II) complex of acetylacetone-mono-(*o*-hydroxyanil) which does contain two copper atoms bridged by phenolic oxygen.

EXPERIMENTAL

The complexes were prepared as previously described.[4] Magnetic susceptibilities were determined by the Gouy method and were independent of field strength (5440, 6360, and 7050 G). Mössbauer spectra were measured at the P.C.M.U., Harwell. Least-squares fits of the spectra recorded at 4·2 K in an externally applied field of 3 T have been obtained using proven routines to simulate the spectra [17] and to minimise the sum of squares.[18] Details of the complete program will be available shortly.[19] E.s.r. spectra were investigated in the *X*-band under the University of London Intercollegiate Research Service.

We thank the staff at the U.L.I.R.S. for their assistance and L. W. Becker for collecting the Mössbauer data.

[1/2421 *Received, 17th December*, 1971]

---

[14] A. Lallemand, *Ann. Physique*, 1935, **3**, 97.

[15] A. P. Ginsberg and M. B. Robin, *Inorg. Chem.*, 1963, **2**, 817.

[16] C. M. Harris, E. Kokot, and S. L. Lenzer, *Nature*, 1962, **196**, 471.

[17] G. Lang and W. T. Oosterhuis, *J. Chem. Phys.*, 1969, **51**, 3608.

[18] M. J. D. Powell, Theoretical Physics Division, A.E.R.E. Harwell.

[19] G. Lang and B. W. Dale, to be submitted for publication.