Inorganica Chimica Acta, 147 (1988) 5–7

EPR Spectra of a Spin-crossover Iron(III) Dithiocarbamate

KRISHNA B. PANDEYA*

Department of Chemistry, A.P.S. University Rewa - 486003, M.P. India

and RAJENDRA SINGH

Department of Chemistry, University of Delhi, Delhi - 110007, India

(Received September 11, 1987)

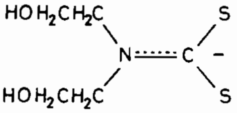
Abstract

Variable temperature (298–4.2 K) EPR spectra of a tris(dithiocarbamato)iron(III) complex involving $^6A_{1g} \rightleftharpoons {}^2T_{2g}$ spin-crossover have been described. Results favour a solid solution model for the spin-crossover.

Introduction

The first row transition metal complexes of d^4–d^7 electron configuration exhibit spin-crossover phenomenon, wherever the ligand field splitting energy and the spin-pairing energy are of the same order of magnitude [1]. Iron(III) dithiocarbamates were the first reported examples [2] of spin-crossover and have been studied in great detail during the last two decades [3], using a variety of physicochemical techniques, *viz.* magnetic susceptibility measurements, UV–Vis, IR, NMR, and Mössbauer spectroscopy, X-ray crystal structure studies and the laser-Raman T-jump method.

The EPR spectroscopic method has the advantage of a larger inverse time scale ($\sim 10^{10}$ s^{-1}), compared to the spin-crossover rate and provides a strong tool for studying the microscopic environment about the ferric ion during the spin-crossover transformation [4]. There are fewer reports [5–7], however, on the EPR spectra of iron(III) dithiocarbamates. In fact, the EPR spectra of iron(III) dithiocarbamates have been difficult both to observe and to interpret, probably because of fast spin-lattice relaxations. This paper reports EPR spectra of spin-crossover iron(III) complex [8], $Fe(dhe{-}dtc)_3 \cdot 3H_2O$, obtained from a new dithiocarbamato ligand, *viz.* di(hydroxyethyl) dithiocarbamate (dhe–dtc), (I)



I, dhe-dtc

Experimental

The complex was prepared [8] by simple mixing of aqueous solutions of $dhe\text{-}dtc \cdot NH_4$ and $Fe(ClO_4)_3 \cdot 6H_2O$ in a stoichiometric ratio, when a black coloured complex precipitated out. The complex is insoluble in water as well as in common organic solvents (only partially soluble in acetone). *Anal.* Found: C, 27.78; H, 5.50; N, 6.40; Fe, 8.60, Calc. for $Fe(dhe\text{-}dtc)_3 \cdot 3H_2O$: C, 27.69; H, 5.55; N, 6.46; Fe, 8.59%.

Variable temperature magnetic susceptibility measurements on the complex were made in the temperature range 15–298 K on a Faraday balance at the Tata Institute of Fundamental Research, Bombay. The results reveal that the complex is a case of $^6A_{1g} \rightleftharpoons {}^2T_{2g}$ equilibrium with almost 100% $^2T_{2g}$ population at and below 20 K (Table I) [8].

Room temperature and near liquid helium temperature X-band EPR spectra (Fig. 1) of the complex were recorded at King's College London and those in the temperature range 298–123 K (Fig. 2) at I.I.T. Bombay.

TABLE I. Magnetic Susceptibility Data for $Fe(dhe\text{-}dtc)_3 \cdot 3H_2O$ Complex at Different Temperatures

Temperature (K)	μ_{eff} (BM)	High-spin (%)	Low-spin (%)
15.3	2.13	0	100
16.1	2.06	0	100
17.7	2.05	0	100
21.4	2.09	0	100
25.6	2.16	2	98
29.2	2.18	2.5	97.5
45.0	2.52	8.0	92
64.0	3.25	21.0	79
86.5	4.03	40.0	60
108.0	4.50	53.0	47
131.0	4.84	63.0	37
298.0	5.60	88.0	12

---

*Author to whom correspondence should be addressed.

0020-1693/88/$3.50

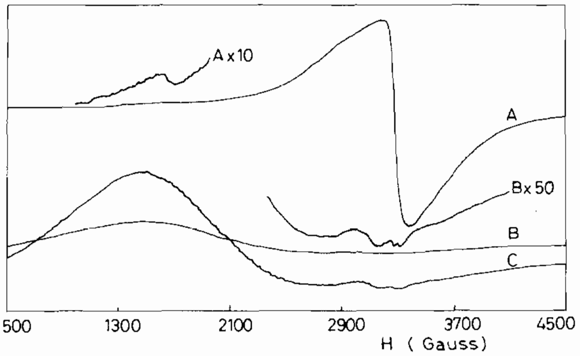


Fig. 1. X-band EPR spectra of the $Fe(dhe\text{-}dtc)_3 \cdot 3H_2O$ complex (polycrystalline) at room temperature and liquid helium temperature, $\nu = 9.19$ GHz.

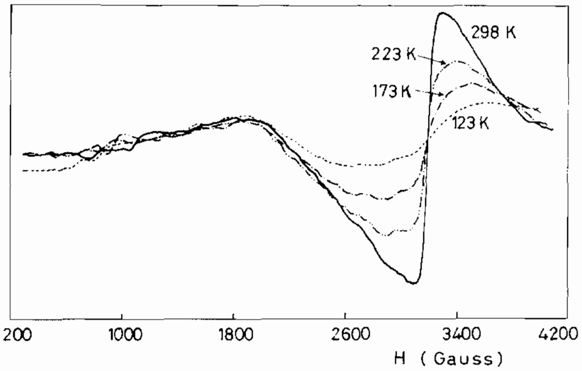


Fig. 2. X-band EPR spectra of the $Fe(dhe\text{-}dtc)_3 \cdot 3H_2O$ complex (polycrystalline) in the temperature range 298–123 K, $\nu = 9.5$ GHz.

Results and Discussion

Temperature dependence of the intensity of a particular EPR signal has to be viewed from at least two angles:

(i) the temperature dependence of the population of the spin state, to which the signal belongs, and

(ii) the temperature dependence of the EPR signals of the individual spin states.

In the following discussion we have isolated the temperature ranges where only one spin state contributes to the EPR spectrum, either because it is exclusively populated or because the other spin state, even if present, is EPR silent due to fast spin-lattice relaxation.

Low-spin State

The complex under discussion is exclusively in the low-spin state at and below 20 K. Near liquid helium temperature 4.2 K and 9 K, therefore, the spectra of the complex correspond to the $^2T_{2g}$ state. The spectrum at 4.2 K (Fig. 1C) shows a very broad signal (peak to peak width 1500 G), showing g-tensor values of $g_\parallel \simeq 2$ and $g_\perp \simeq 3.2$. A comparison of the 9 K spectrum with the 4.2 K (Fig. 1B and C) spectrum shows a rapid loss in intensity of the signal with increase in temperature. Although the very local environment of the iron in $Fe(dhe\text{-}dtc)_3 \cdot 3H_2O$ may be approximated as more or less octahedral, the symmetry of such complexes are typically close to D_3 due to the chelates groups [9, 10]. Splitting of the $^2T_{2g}$ ground state under the combined action of spin orbit coupling and low field components was first worked out by Stevens [11] and Bleany and O'Brien [12]. The theory tells that for the $^2T_{2g}$ state only large trigonal distortions which increase the energy separation between the ground state and nearby excited state and thus increase the electronic relaxation time and hence decrease the line-width, can make possible the appearance of the EPR signal at room temperature. Otherwise, the EPR signal for such a system can be seen only at low temperatures. Present observations suggest that trigonal distortion in $Fe(dhe\text{-}dtc)_3 \cdot 3H_2O$ is not very large.

DeSimone and Drago [13] analysed the EPR spectra of a number of iron(III) tris-di-imine complexes (FeN_6 chromophore). These complexes showed $g_\perp$ of 2.6–2.7 and $g_\parallel$ of 1.2–1.6. The EPR spectrum of $Fe(dhe\text{-}dtc)_3 \cdot 3H_2O$, however, yields g-tensor values of $g_\perp \simeq 3.2$ and $g_\parallel \simeq 2.0$ which may be typical of low-spin iron(III) with FeS_6 chromophore. These values fitted to the DeSimone and Drago [12] $g_\parallel$ *versus* $g_\perp$ plot as also to the Hall and Hendrickson [5] g *versus* D/ξ plot require the orbital reduction parameter k to have values larger than 1. Such a situation has earlier been obtained [13] for $Fe(bipy)_3(PF_6)_3$ (FeN_6 chromophore) and has been attributed to the configuration interactions and to the contribution of the orbital angular momentum to the t_{2g} electrons from the ligand itself.

High-spin State

Although the magnetic moment data suggest about 88% population of high-spin state at room temperature, the EPR spectrum at this temperature can be taken to be free from low-spin state signals, because the same are observed only near liquid helium temperature and lose intensity rapidly enough to vanish at higher temperatures. The spectrum at room temperature (Fig. 1A) shows a strong signal at $g \simeq 2.0$ with a shoulder at $g \simeq 2.5$ and a weak signal at $g \simeq 4.3$. The present observation is noteworthy in view of the report of Hall and Hendrickson [5] that a number of iron(III) dithiocarbamates do not show an EPR signal at room temperature. Only Flick and Gelerinter [7] have reported room temperature EPR signals for the iron(III)–dicyclohexyldithiocarbamate complex.

The EPR spectrum of the high-spin iron(III) system is described by the following Hamiltonian [14].

$$\mathcal{H} = D[S_{z^2} - (1/3)S(S+1)] + E(S_{x^2} - S_{y^2}) + g\beta HS$$

At the rhombic extreme ($E/D = 1/3$) a signal is expected at $g \simeq 4.3$ and at the axial extreme ($E/D \simeq 0$) signals are expected at $g \simeq 2.0$ and $g \simeq 6.0$. Intermediate rhombicity should lead to mixed patterns. The position and intensity of any signal is, however, highly sensitive to the E/D value. This weak low field signal at $g \simeq 4.3$ is thus the typical high-spin d^5 signal. The temperature dependence of the signal could not be monitored due to its weak nature.

The $g \simeq 2.0$ signal is certainly not due to the low-spin state as no such signal is present in the spectrum at low temperature (9 K, Fig. 1B), where the complex is exclusively in the low-spin state. In earlier cases, this signal has been assigned to copper(II) impurity. In our case, the temperature dependence of the size and the shape of the signal rules out this possibility. We assign the signal to the high-spin state. With a decrease in the temperature from 298 to 123 K, the high-spin state population decreases from *ca.* 88 to 60% as indicated by the magnetic susceptibility data (Table I). Curie–Weiss law, the Boltzman population difference between the Zeeman split levels involved in the resonance will increase by *ca.* 298/123. Thus we expect an increase in EPR intensity of the order of 1.6 on lowering the temperature from 298 to 123 K. The signal does in fact increase as the temperature is lowered. The width at 123 K is *ca.* three times that at 298 K giving an intensity increase of *ca.* 9. The amplitude on the other hand decreases by *ca.* five times. Thus there appears to be an overall intensity increase of *ca.* 1.8 (a considerable error margin must be put on this number from estimation of the relative widths) on going from 298 to 123 K. The predicted increase in the intensity is 1.6 times.

What causes the broadening of the $g \simeq 2.0$ signal with decreasing temperature? It could arise either from a widening range of D (and E?) values or from cross-relaxation with the increasingly populated low-spin state.

Either of these favour the solid solution model [15] over the domain model. In the domain model, the high-spin molecular ions would always be in a totally high-spin domain with only high-spin neighbours (4h, 4i), excluding the possibility of cross-relaxation with the low-spin state.

Acknowledgements

We thank Professor S. Mitra of TIFR, Bombay, who kindly provided the laboratory facilities for carrying out variable temperature magnetic susceptibility measurements, Dr Cammack of King's College, London, for carrying out the EPR spectroscopic measurements, and the University Grants Commission New Delhi, for awarding a research fellowship to R.S.

References

1 R. L. Martin and A. H. White, *Transition Met. Chem., 4,* 113 (1968).

2 (a) L. Cambi and A. Cagnasso, Atti. *Accad. Naz. Lincei, 13,* 809 (1931); (b) L. Cambi and L. Szego, *Ber. Deut. Chem. Ges., 64,* 2591 (1931).

3 (a) K. Stahl and I. Ymen, *Acta Chem. Scand., Ser. A, 37,* 729 (1983), and refs. therein; (b) A. Terzis, S. Fillippakis, D. Mentzafos, V. Petrovleas and A. Malliaris, *Inorg. Chem., 23,* 334 (1984), and refs. therein.

4 (a) M. S. Haddad, W. D. Federer, M. W. Lynch and D. N. Hendrickson, *J. Am. Chem. Soc., 102,* 1468 (1980); (b) M. S. Haddad, M. W. Lynch, W. D. Federer and D. N. Hendrickson, *Inorg. Chem., 20,* 123 (1981); (c) M. S. Haddad, W. D. Federer, M. W. Lynch and D. N. Hendrickson, *Inorg. Chem., 20,* 131 (1981); (d) Y. Maeda, N. Tsutsumi and Y. Takashima, *Chem. Phys. Lett.,* 88, 248 (1982); (e) Y. Maeda, H. Ohshio and Y. Takashima, *Chem. Lett.,* 943 (1982); (f) H. Ohshio, Y. Maeda and Y. Takashima, *Inorg. Chem., 22,* 2684 (1983); (g) Y. Maeda, N. Tsutsumi and Y. Takashima, *Inorg. Chem., 23,* 2440 (1984); (h) W. D. Federer and D. N. Hendrickson, *Inorg. Chem., 23,* 3861 and 3870 (1984); (i) M. D. Timken, D. N. Hendrickson and E. Sinn, *Inorg. Chem., 24,* 3947 (1985); (j) M. D. Timken, S. R. Wilson and D. N. Hendrickson, *Inorg. Chem., 24,* 3450 (1985); (k) M. D. Timken, C. E. Strouse, S. M. Soltis, S. Daverio, D. N. Hendrickson, A. M. Abdel-Mawgoud and S. R. Wilson, *J. Am. Chem. Soc., 108,* 395 (1986); (l) M. D. Timken, A. M. Abdel-Mawgoud and D. N. Hendrickson, *Inorg. Chem., 25,* 160 (1986).

5 G. R. Hall and D. N. Hendrickson, *Inorg. Chem., 15,* 607 (1976).

6 E. J. Cukauskas, B. S. Deaver Jr. and E. Sinn, *J. Chem. Soc., Chem. Commun.,* 698 (1974).

7 C. Flick and E. Gelerinter, *Chem. Phys. Lett., 23,* 422 (1973).

8 (a) K. B. Pandeya, R. Singh, C. Prakash and J. S. Baijal, *Inorg. Chem., 26,* (1987), in press; (b) K. B. Pandeya and R. Singh, *Solid State Commun.,* 1987, in press.

9 P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.,* 1163 (1972).

10 B. F. Hoskins and B. P. Kelly, *J. Chem. Soc., Chem. Commun.,* 1517 (1968).

11 K. W. H. Stevens, *Proc. Roy. Soc. Ser. A, 219,* 542 (1953).

12 B. Bleany and M. C. M. O'Brien, *Proc. Phys. Soc. London, Sect. B, 69,* 1215 (1956).

13 R. E. DeSimone and R. S. Drago, *J. Am. Chem. Soc., 92,* 2343 (1970).

14 H. H. Wickman, M. P. Klein and D. A. Shirley, *J. Chem. Phys., 42,* 2113 (1965).

15 (a) E. König, G. Ritter, W. Irler and H. A. Goodwin, *J. Am. Chem. Soc., 102,* 4681 (1980); (b) E. König, G. Ritter, S. K. Kulshreshtha and S. M. Nelson, *J. Am. Chem. Soc., 105,* 1924 (1983).