COMMENT ON THE ANOMALOUS PARAMAGNETISM OF $[Fe(NCS)_2 phen_2]$*

By A. T. Casey† and F. Isaac‡

Recently[1,2] anomalous variations of magnetic susceptibility with temperature have been reported for $[Fe(NCS)_2 phen_2]$ and $[Fe(NCSe)_2 phen_2]$. At a temperature of about 174°K for the former compound and about 232°K for the latter, there is a large change in the magnetic susceptibility which at higher temperatures follows a Curie–Weiss type of variation. This behaviour is explained qualitatively in terms

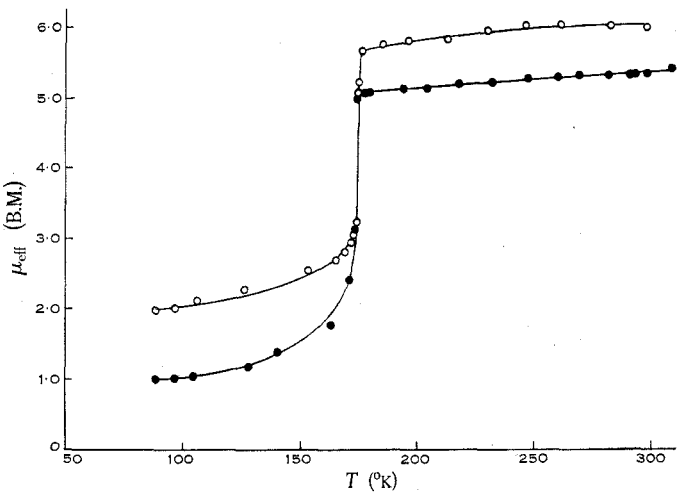

Fig. 1.—Variation of magnetic moment of $[Fe(NCS)_2 phen_2]$ with temperature. Each sample was prepared by the same method.

of an equilibrium between a $^1A_1$ ground state for the iron atom and a low-lying $^5T_2$ state. In particular, X-ray powder patterns are used to suggest there is no phase change. We believe that such patterns, even of the similarity of those reproduced,[1] do not represent unequivocal evidence for the absence of a phase change. For example, the powder patterns for the bis(*N*,*N*-diethyldithiocarbamato) complexes of copper(II) and zinc(II) are remarkably similar, but a full analysis[3] shows the structures are different. We here report measurements which indicate that something other than an electronic equilibrium occurs.

* Manuscript received June 5, 1967.

† Department of Inorganic Chemistry, University of Melbourne, Vic. 3052.

‡ Coroner's Court Laboratory, Melbourne, Vic. 3000.

[1] Baker, W. A. Jr., and Bobonich, H. M., *Inorg. Chem.*, 1964, **3**, 1184.

[2] König, E., and Madeja, K., *Inorg. Chem.*, 1967, **5**, 48.

[3] Bonamico, M., Dessy, G., Mazzone, G., Mugnoli, A., Vaciago, A., and Zambonelli, K., *Atti Accad. naz. Lincei Rc.*, 1963, **35**, 338.

We confirm the observations of König and Madeja[2] that different methods of preparation, and even different samples prepared by the same method, give a variety of values for the effective magnetic moment, but the qualitative behaviour is identical. Typical results are shown in Figure 1. The "critical temperature" for the sharp change in magnetic moment varied over a range of 2° (171–173°K) for the samples studied, but each sample had a definite temperature at which the rate of change of magnetic moment is very slow. When the cryostat was set at this temperature, a

TABLE 1

VARIATION OF $10^6\chi'_M$ FOR $[Fe(NCS)_2 phen_2]$ AT 173°K

Time (min)	$10^6\chi'_M$	Time (min)	$10^6\chi'_M$	Time (min)	$10^6\chi'_M$	Time (min)	$10^6\chi'_M$
0	18073	13	12936	27	8148	50	6281
5	16742	16	11739	29	7960	55	6182
7	16009	19	10363	31	7692	60	6174
9	15223	22	9515	34	7335	85	5780
10	14571	24	8934	37	7031		
11	14142	26	8452	45	6611		

period of up to 2 hr was required to complete the transition. A typical set of readings is listed in Table 1. Other samples gave similar results. The values, except for the first and the last, fit a first-order rate law quite well, with a rate constant of 0·060 min^{-1}. The fact that nearly 2 hr is required to pass from one state to the other implies an appreciable energy barrier and a significant rearrangement of the environment of the iron atom. The possibility of a crystallographic phase change cannot be ruled out without a detailed structural analysis.

Experimental

$[Fe(NCS)_2 phen_2]$ was prepared by heating freshly prepared $[Fe phen_3](NCS)_2$ with chloroform containing 1% water, replenishing the water from time to time. The residue was taken up with 200 ml of a 1 : 1-mixture of chloroform and ethanol, filtered, and washed with the same mixture (Found: C, 58·1; H, 3·0; Fe, 10·25; N, 17·1; S, 11·7. Calc. for $C_{26}H_{16}FeN_6S_2$: C, 58·65; H, 3·0; Fe, 10·5; N, 15·8; S, 12·0%).

The magnetic susceptibility was measured on a conventional Gouy balance using freshly prepared $HgCo(CNS)_4$ as calibrant.