Journal of Organometallic Chemistry, 187 (1980) 61—71

MAGNETISM BETWEEN 1.02 AND 312 K AND THE ANTIFERROMAGNETIC INTERACTION IN VANADOCENE

E. KÖNIG *, V.P. DESAI

Institut für Physikalische und Theoretische Chemie, Universität Erlangen-Nürnberg, D-8520 Erlangen, Egerlandstr. 3 (West Germany)

B. KANELLAKOPULOS and E. DORNBERGER

Institut für Heisse Chemie, Kernforschungszentrum Karlsruhe, D-7500 Karlsruhe (West Germany)

(Received August 23rd, 1979)

Summary

The magnetism of vanadocene, $V(C_5H_5)_2$, was studied between 1.02 and 312 K. Above ~15 K, the Curie-Weiss law is obeyed (θ —9.0 K, μ_{eff} 3.78 BM at 297.3 K). A transition to long-range (antiferromagnetic) order is observed at $T_N = 8.3$ K. The results are rationalized in terms of a linear chain Ising model (J/k —1.3 K, $g = 2.0$) with added interchain interaction (J'/k —0.05 K, $z = 4$). A reasonable fit is also achieved on the basis of the pair model (J/k —2.3 K, $g = 2.0$). The conclusions are supported by the finding of a heat capacity anomaly at 7.5 K.

Introduction

The magnetism of vanadocene, $V(cp)_2$ where cp = $C_5H_5^-$, was studied in an early investigation by Leipfinger [1]. In that study, the inverse magnetic susceptibility per mole, $1/\chi_m$, was found to show Curie-Weiss behaviour between 14.3 and 400 K, and may be characterized by the effective magnetic moment μ_{eff} (3.78 ± 0.19) BM and the Weiss constant θ —6.5 K. Below 5 K an anomalous increase of $1/\chi_m$ was found, although the region between 5 and 14.3 K was not explored. The anomaly was tentatively attributed to antiferromagnetism, the expected susceptibility maximum being interpolated to ~13.3 K. More recently, the optical absorption spectrum of $V(cp)_2$ was measured [2,3], and from the band assignments two sets of ligand field parameters were deduced. Thus, from the spectrum in 2-methyltetrahydrofuran, Prins and Van Voorst [2] obtained $Ds = 3543$, $Dt = 2074$, $B = 444$ cm^{-1} and $\beta = 0.59$, whereas Pavlik et al. [3] determined, from the spectrum in n-pentane, Ds 3756, Dt 2018, B 418 cm^{-1}, β = 0.557 and B' 563 cm^{-1}, $\beta' = 0.75$, the latter two values from the spin-forbidden transitions. The results clearly establish a ${}^4A_2(a_1e_2^2)$ ground state in D_{5d} symmetry (or a ${}^4\Sigma^-(\sigma\delta^2)$ if $C_{\infty v}$ representation symbols are employed). The above ligand field parameters are useful since they permit detailed calculation of the magnetic susceptibility.

The EPR spectrum of V(cp)$_2$ was studied in methyl-THF glasses [4], in methylcyclohexane glasses, and in a solid solution in Fe(cp)$_2$ [2], all at 77 K. The derived spin Hamiltonian parameters are $g_\parallel = 2.002$, $g_\perp = 1.990$, $|A_\parallel^{51}|$ 36.7×10^{-4} cm^{-1}, $|A_\perp^{51}|$ 21.5×10^{-4} cm^{-1} and the zero-field splitting constant was determined as $|D|$ 2.7 cm^{-1}. Additional EPR results were recently reported by Ammeter [5]. The magnetic susceptibility may be readily calculated within the spin Hamiltonian formalism. On this basis and employing the values for $g_\parallel$, $g_\perp$ and D given by Prins and Van Voorst [2], Warren was able to demonstrate [6] that the observed zero-field splitting cannot be responsible for the magnetic anomaly between 5 and 14.3 K [1]. In fact, the results of Prins and Van Voorst [2] do not suggest any significant deviation from spin-only behaviour even at 4.2 K.

Thus a reinvestigation of the magnetism of V(cp)$_2$ seemed desirable and so we made detailed measurements of the magnetism over the temperature region 1.02 to 312 K and were able to offer a satisfactory interpretation of the results. This report is a continuation of our studies into the magnetism of sandwich molecules of the transition metals [7,8].

Experimental

Preparations of bis(cyclopentadienyl)vanadium(II).

In order to synthesize V(cp)$_2$, anhydrous VCl$_3$ was treated with KC$_5$H$_5$ in benzene with continuous agitation under reflux. The reaction took about 3 d and proceeded according to

$$VCl_3 + 2\ KC_5H_5 \rightarrow V(C_5H_5)_2Cl + 2\ KCl$$

The residue obtained by evaporation of the solvent was dissolved in THF, and the V(C$_5$H$_5$)$_2$Cl was reduced with a stoichiometric amount of sodium,

$$V(C_5H_5)_2Cl + Na \xrightarrow[130\,h]{THF} V(C_5H_5)_2 + NaCl$$

The dry product was extracted for 6 d with benzene in order to remove any unreacted material. All operations were performed with strict exclusion of oxygen.

Another batch of V(cp)$_2$, from which the sample of 23.056 mg was drawn, was obtained by the reduction of anhydrous VCl$_3$ with magnesium metal using THF as the solvent. The mixture was treated for 5 d under reflux, although the colour was observed to change from dark brown to grey after 1 d. The stoichiometric amount of KC$_5$H$_5$ was then added and the mixture was refluxed for a further 5 d. Extraction of the dry product with n-pentane gave 83.1% of vanadocene of high purity. Again, all operations were performed with strict exclusion of oxygen. The resulting V(cp)$_2$ gave satisfactory analyses for C, H and V.

Instrumentation

Magnetic susceptibilities were measured over the range 1.02—212 K by the Faraday method. The equipment employs a 10 in electromagnet (Bruker-

Physik) with Henry-type pole caps, an electrical microbalance (Sartorius type 4102), and the required cryogenic equipment. Temperature below 4.2 K were achieved by pumping on the helium reservoir with a Roots pump (Leybold-Heraeus type WS-250, suction power 324 m^3/h), 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 in the position of the sample. More details may be found elsewhere [9]. 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 diamagnetic correction applied to χ_m is -101×10^{-6} cgs mol^{-1}, and the effective magnetic moment was obtained according to $\mu_{eff} = 2.828\sqrt{\chi_m^{corr}\, T}$ where χ_m^{corr} is the corrected molar magnetic susceptibility and T the temperature.

Numerical treatment of the data

Magnetic measurements were performed with two different samples of V(cp)$_2$, viz. 23.056 mg and 5.287 mg, these weights being particularly well suited for the higher and the lower temperature range, respectively. The data for the V(cp)$_2$ sample of 5.287 mg extend up to 77.64 K (set 1), whereas for the sample of 23.056 mg data between 4.20 and 312.2 K were collected (set 2). The values of μ_{eff} from set 1 were generally slightly lower than values from set 2 at the same temperature. Since the sample employed for the measurements of set 2 is of higher purity, it is assumed that the lower values of set 1 are caused by a small amount of an unidentified impurity. In order to generate a consistent set of experimental data for the complete range of temperature, the best second degree parabolic fit for the data of set 1 was produced, viz.

$$\chi_m = 0.000957\, T^2 - 0.007480\, T + 0.883 \qquad (1)$$

for the temperature range 4.00 to 8.28 K and

$$\chi_m = -4.506\, T^{-2} + 1.277\, T^{-1} + 0.003216 \qquad (2)$$

for the temperature range 8.28 to 77.64 K. In the range where the data of set 1 and set 2 overlap, the differences to set 2 were computed and fitted to two second degree polynomials in T. These polynomials were employed to correct the data of set 1 for all temperatures between 1.02 and 77.64 K.

Results of magnetic measurements

A representative selection of the magnetic data is presented in Table 1. Between 1.02 and 3.32 K, the data obtained for six different field strengths (H 3.50—13.10 kG) are listed individually. Above 3.32 K, the average values for the six fields are given. The results up to and inclusive of 4.17 K are part of data set 1, whereas the data above 4.17 K are from set 2. The complete data are shown only in Fig. 2, whereas in Table 1 and in Fig. 1 the overlapping range (4.20 to 77.7 K) is represented by the data of set 2 only. For the temperature range 1.02 to 4.17 K, the average data corrected as outlined in the Experimental Section are incorporated into Table 1 and, in the Figures, the corrected data are used exclusively for set 1.

The temperature dependence of the magnetic data of V(cp)$_2$ is displayed in

TABLE 1

MAGNETIC SUSCEPTIBILITIES χ_g AND χ_m^{corr} [a] AND EFFECTIVE MAGNETIC MOMENT μ_{eff} [b] FOR $V(cp)_2$ [c]

T (K)	H (kG)	$10^6\ \chi_g$ (cgs/g)	$10^6 \chi_m^{corr}$ (cgs/mol)	μ_{eff} (BM)
1.02	3.50	475.95	86315	0.839
	5.55	468.53	84970	0.833
	8.60	456.90	82864	0.822
	10.90	448.90	81415	0.815
	12.00	441.65	80101	0.808
	13.10	436.42	79154	0.804
	av	454.73	82470	0.820
	corr	458.30	83099	0.823
1.04	3.50	477.84	86657	0.849
	5.55	470.79	85380	0.843
	8.60	457.85	83036	0.831
	10.90	448.83	81402	0.823
	12.00	442.78	80306	0.817
	13.10	437.15	79286	0.812
	av	455.87	82678	0.829
	corr	459.55	83326	0.833
1.54	3.50	446.14	80915	0.998
1.60	5.55	439.21	79659	1.010
1.66	8.60	431.61	78283	1.019
1.83	10.90	426.07	77279	1.063
1.87	12.00	422.10	76560	1.070
1.91	13.10	419.26	76046	1.078
1.74	av	430.73	78124	1.043
	corr	438.58	79528	1.052
2.36	3.50	417.17	75667	1.195
2.41	5.55	416.41	75530	1.206
2.47	8.60	414.98	75270	1.219
2.53	10.90	413.16	74941	1.231
2.59	12.00	412.64	74847	1.245
2.64	13.10	410.27	74417	1.253
2.50	av	414.11	75112	1.225
	corr	427.61	77541	1.245
3.02	3.50	406.46	73727	1.334
3.04	5.55	407.80	73970	1.341
3.06	8.60	407.67	73946	1.345
3.07	10.90	408.18	74039	1.348
3.05	av	407.75	73960	1.343
	corr	425.75	77204	1.339
3.24	3.50	404.99	73461	1.380
3.26	5.55	406.49	73733	1.386
3.27	8.60	406.17	73675	1.388
3.29	10.90	407.48	73912	1.395
3.30	12.00	407.45	73906	1.397
3.32	13.10	404.76	73419	1.396
3.28	av	406.22	73684	1.390
	corr	426.59	77357	1.424
3.50		406.34	73705	1.436
	corr	428.60	77720	1.475
3.66		405.64	73579	1.468
	corr	429.26	77840	1.509
3.84		405.63	73576	1.503
	corr	431.62	78268	1.550
4.00		406.16	73673	1.535
	corr	433.82	78666	1.586
4.17		406.92	73811	1.569
	corr	436.45	79142	1.625
4.20		433.70	78661	1.625

TABLE 1 (Continued)

T (K)	H (kG)	$10^6\chi_g$ (cgs/g)	$10^6\chi_m^{corr}$ (cgs/mol)	μ_{eff} (BM)
5.11		457.61	82992	1.842
5.52		468.81	85021	1.937
6.49		498.89	90470	2.167
6.88		517.50	93841	2.272
7.74		560.79	101683	2.509
8.04		587.06	106441	2.616
8.52		582.34	105586	2.682
9.21		573.14	103920	2.767
9.47		568.43	103066	2.794
10.58		540.25	97962	2.879
12.30		506.60	91867	3.006
14.91		451.97	81971	3.126
16.31		427.26	77495	3.179
18.69		391.10	70945	3.256
28.18		286.02	51911	3.420
40.15		211.88	38481	3.515
52.40		169.34	30775	3.591
64.5		141.07	25654	3.638
77.7		120.71	21966	3.695
97.1		98.122	17875	3.726
116.9		82.197	14990	3.744
139.0		69.980	12777	3.769
171.7		56.916	10411	3.781
203.8		48.164	8825.4	3.793
238.5		41.236	7570.5	3.800
268.0		36.693	6747.6	3.803
294.3		33.451	6160.3	3.808
297.3		32.669	6018.7	3.783
312.2		31.568	5819.2	3.812

[a] Molecular weight $M = 181.1$, diamagnetic correction -101×10^{-6} cgs/mol, experimental uncertainty between 0.2 and 0.9%, dependent on temperature. [b] $\mu_{eff} = 2.828\,(\chi_m^{corr}\,T)^{1/2}$, experimental uncertainty approximately ± 0.005 BM. [c] Between 1.02 and 3.32 K, values for six different field strengths (H 3.50—13.10 kG) are listed individually (sample weight 5.287 mg). Above 3.32 K, the average values for the six fields are given (sample weight 23.056 mg).

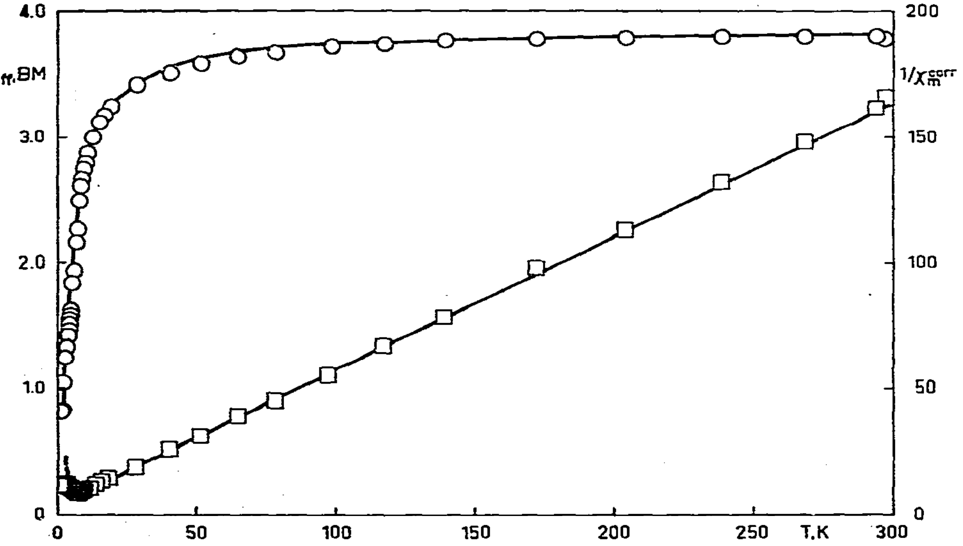

Fig. 1. Temperature dependence of the effective magnetic moment, μ_{eff}, and the inverse molar magnetic susceptibility, $1/\chi_m^{corr}$, for $V(cp)_2$ between 1.02 and 300 K. The curves are calculated on the basis of the Ising model with interchain interaction (J/k −1.3 K, J'/k −0.05 K, $g = 2.0$, $z = 4$).

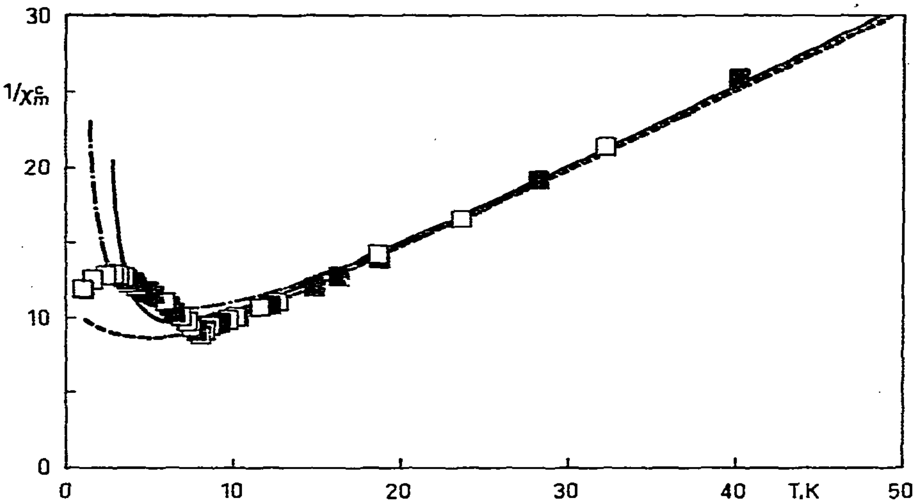

Fig. 2. Inverse molar magnetic susceptibility for $V(cp)_2$ as function of temperature between 1.02 and 50 K. Experimental data indicated by open squares are part of set 1, full squares derive from set 2. The curves are calculated. Solid curve: Ising model with interchain interaction (Eq. 12; $J/k = -1.3$ K, $J'/k = -0.05$ K, $g = 2.0$, $z = 4$). Dashed curve: Heisenberg linear chain (Eq. 15; $J/k = -1.3$ K). Dot-dash curve: pair model (Eq. 20; $J/k = -2.3$ K, $g = 2.0$).

Fig. 1, both in terms of the effective magnetic moment, μ_{eff}, and the inverse molar magnetic susceptibility, $1/\chi_m^{corr}$. In addition, the data relating to the important region below 50 K are shown, in terms of $1/\chi_m^{corr}$, in Fig. 2.

From Fig. 1 it is evident that $1/\chi_m^{corr}$ for $V(cp)_2$ follows the Curie-Weiss law, $\chi_m = C_m/(T - \theta)$, above ~15 K ($\theta$ —9.0 K). At 8.3 K, a sharp minimum appears in the $1/\chi_m^{corr}$ vs. T curve (cf. Fig. 2) which is attributed to an antiferromagnetic interaction between the magnetic ions (T_N 8.3 K). This minimum is followed at lower temperatures by a broad maximum at ~3.0 K. A slight field dependence of the magnetic data below 3.28 K is evident from the values of Table 1. This field effect is not very pronounced (at most, $\Delta\mu_{eff}$ 0.040 BM), and will not be considered further.

Theoretical interpretation

Ligand Field approach.

Employing the ligand field parameters of Prins and Van Voorst [2] and Pavlik et al [3] in conjunction with the spin-orbit coupling parameter $\zeta = \zeta_0 =$ 170 cm^{-1}, the effective magnetic moment was calculated as function of temperature. Details of the method have been described elsewhere [10,11]. The orbital reduction factor, κ, was varied over the range 0.3 to 1.0, and proper allowance for the reduction of ζ_0 was taken. The result is largely similar to that of Warren [6] which was based on the spin Hamiltonian formalism. Briefly, one obtains μ_{eff} ~ 3.8 BM almost independent of temperature down to ~10 K, where a gradual decrease of μ_{eff} sets in. The agrement with the experimental results is not very pleasing, particularly below ~20 K. A variation of the values of Ds, Dt, B around the values quoted above [2,3] does not yield a significant improvement. Obviously, ligand field theory cannot account for the reduction of μ_{eff} from the spin-only value of a $^4A_2$ ground state. In view of the low-temperature behaviour, we will introduce an antiferromagnetic coupling between the magnetic ions which will be discussed in more detail in the next Section. This interaction does lower the magnetic moment even at higher temperatures.

Treatment of the magnetic interaction

The crystal structure of the dark-brown modification of manganocene, Mn(cp)$_2$, (for more details, see to the Discussion and ref. 12) suggests by analogy that the predominant antiferromagnetic interaction in V(cp)$_2$ arises from the spin exchange through V—C$_5$H$_5$—V bonds within a one-dimensional vanadium chain. The existence of a rather sharp maximum in the susceptibility curve at 8.3 K indicates that an additional antiferromagnetic interaction is operative between the chains.

In the Heisenberg model of one-dimensional lattices, the nearest-neighbour exchange interaction is assumed to be isotropic,

$$\mathcal{H} = -2J \sum_{i} S_i \cdot S_{i+1} \tag{3}$$

where, for the antiferromagnetic case, $J < 0$. A rigorous solution to the Hamiltonian of Eq. 3 is available for $S = 1/2$ [13] although, because of the mathematical difficulties involved, not for $S > 1/2$. Since in the present case of V(cp)$_2$, $S = 3/2$, the following analysis has been based mainly on the Ising model.

In the Ising Hamiltonian for a linear chain, the exchange interaction is assumed to be perfectly anisotropic,

$$\mathcal{H} = -2J \sum_{i} S_{z,i} \cdot S_{z,i+1} \tag{4}$$

For V(cp)$_2$, magnetic anisotropy may be introduced by the appreciable zero-field splitting of $2|D| = 5.4\ \text{cm}^{-1}$. Based on Eq. 4, a closed expression for the susceptibility of $S = 1/2$ spins has been derived as

$$\chi_{\text{m}} = \frac{Ng^2\mu_{\text{B}}^2}{4kT} \exp(J/kT) \tag{5}$$

whereas numerical solutions have been obtained for $S = 1$ and $S = 3/2$ [14]. In Eq. 5, all quantities have the usual meaning. For mutually interacting linear chains of $S = 1/2$ spins, theoretical expressions have been derived on the basis of the coupled-double-chain model [15]. The magnetic susceptibility for this type of system is given by

$$\chi_{\text{m}} = \frac{Ng^2\mu_{\text{B}}^2}{4kT} \frac{P}{Q} \tag{6}$$

In Eq. 6,

$$P = e^{2K}(e^{K'}R - \sinh 2K)$$

$$Q = (R - e^{K'} \sinh 2K)(\cosh^2 K' \cosh^2 2K - \sinh^2 2K)^{1/2} \tag{7}$$

$$R = \cosh K' \cosh 2K + (\cosh^2 K' \cosh^2 2K - \sinh^2 2K)^{1/2}$$

$$K = J/2kT \tag{8}$$

$$K' = zJ'/2kT \tag{9}$$

where J is the exchange parameter within a chain, J' is that between chains, and z is the number of nearest chains. In order to adopt this model to the present situation, we have made use of the "reduced spin" formalism [16]. The reduced effective magnetic moment is defined by

$$\mu_{\text{eff}} = \frac{1}{2}\left(\frac{S(S+1)}{3/4}\right)^{1/2} g\mu_{\text{B}} \tag{10}$$

whereas the reduced exchange parameter is given by

$$J' = \frac{S(S+1)}{3/4} J \tag{11}$$

With these definitions, Eq. 6 of Inoue and Kubo [15] may be reformulated for $S = 3/2$ as

$$\chi_{\text{m}} = \frac{Ng^2\mu_{\text{eff}}^2}{kT} \frac{3}{4} \frac{P}{Q} \tag{12}$$

Here,

$$K = 5J/2kT \tag{13}$$

$$K' = 5zJ'/2kT \tag{14}$$

and the quantities P, Q and R are determined by Eq. 7.

In Fig. 2, the susceptibility calculated by Eq. 12 is compared with the experimental low temperature data for V(cp)_2. In the calculation, $J/k = -1.3$ K, $J'/k = -0.05$ K, $g = 2.0$ and $z = 4$ was used, the latter value being based on the structure of Mn(cp)_2 [12]. Included in the Figure is the solution of Fisher [17] to the Heisenberg linear chain in the classical limit (i.e. for $S \to \infty$), scaled to $S = 3/2$,

$$(\chi_0 |J|)^{-1} = y \frac{[1 + u(y)]}{[1 - u(y)]} \tag{15}$$

where

$$u(y) = \coth(\tfrac{3}{2} y^{-1}) - \tfrac{2}{3} y \tag{16}$$

and

$$y = \frac{3kT}{4|J|S(S+1)} \tag{17}$$

In Eq. 15, χ_0 is the susceptibility per spin which is related to the actual molar magnetic susceptibility by

$$\chi_{\text{m}} = N\mu_{\text{B}}^2 \chi_0 \tag{18}$$

Also shown in the Figure is $1/\chi_{\text{m}}$ for exchange coupled pairs of spins with $S = 3/2$. According to Lines and Eibschütz [18], the susceptibility per spin χ_0

is given in the isolated pair model by

$$\chi_0 = \frac{\Sigma \frac{2}{3} S'(S'+1)(2S'+1)\exp[JS'(S'+1)/kT]}{kT\Sigma(2S'+1)\exp[JS'(S'+1)/kT]} \tag{19}$$

where the summation runs over $S' = 0, 1, 2, ..., 2S$. For the case of $S = 3/2$ one derives readily

$$\chi_m = \frac{N\mu_B^2 g^2}{kT}\,\frac{e^{-2x} + 5e^{-6x} + 14e^{-12x}}{1 + 3e^{-2x} + 5e^{-6x} + 7e^{-12x}} \tag{20}$$

where $x = |J|/kT$. In the calculation, $J/k = -2.3$ K and $g = 2.0$ was used.

Finally, calculations were also performed within the pair model employing the Hamiltonian

$$\mathcal{H} = -2JS_1 \cdot S_2 + D(S_{1z}^2 + S_{2z}^2) + g_\parallel S_z H_z + g_\perp(S_x H_x + S_y H_y) \tag{21}$$

thus taking account of the observed zero-field splitting as well as of the anisotropy in the g factor. Here, the values of D, $g_\parallel$ and $g_\perp$ determined on the basis of EPR [2,4] were employed. No significant improvement over the results shown in the Figure has been achieved.

Discussion

The results, especially those shown in Fig. 2, reveal that the magnetic suceptibility of $V(cp)_2$ shows a sharp inflection at the temperature $T_N = 8.3$ K. Evidently, this change has to be attributed to the onset of long-range order, i.e. to a phase transition to an antiferromagnetically ordered state. This finding is supported by the observation of a λ-type anomaly in the heat capacity of $V(cp)_2$ at T_c 7.5 K [19]. Because of short-range order effects, T_N is about 10% higher in temperature than T_c, as expected [20]. The enthalpy and entropy of the transition were determined as ΔH 46 Jmol^{-1} and ΔS 6.3 JK^{-1} mol^{-1}, respectively. The entropy change associated with spin ordering is always R ln$(2S + 1) \sim$ 11.53 JK^{-1} mol^{-1} for $S = 3/2$ and thus is considerably larger than the reported value [19]. The difference may be tentatively attributed to the difficulty of estimating the lattice contribution to ΔS.

The detailed structure of vanadocene has not been determined, although it has been shown [21] that $V(cp)_2$ is isomorphous with ferrocene which is known to consist of discrete sandwich molecules in the staggered, D_{5d}, configuration [22]. Of particular interest here is the comparison with manganocene, $Mn(cp)_2$, which forms a dark-brown (rhombic) modification stable up to 432 K and a pink (monoclinic) form stable above 432 K. Whereas the behaviour of $Mn(cp)_2$ in solvents and various matrices is rather complex [5], undiluted solid $Mn(cp)_2$ in the brown form shows antiferromagnetic behaviour with a broad susceptibility maximum at 134K [23]. Recently, Bünder and Weiss [12] demonstrated that the brown modification forms a polymeric chain structure with a zigzag arrangement of C_5H_5—Mn units and bridging C_5H_5 rings. An X-ray powder diffraction study of the pink form of $Mn(cp)_2$ indicates [24] that the structure of this modification is similar to that of ferrocene, and thus contains discrete

$Mn(cp)_2$ molecules. The structural transformation

$$\underset{\text{brown}}{Mn(cp)_2} \xrightarrow{432\,K} \underset{\text{pink}}{Mn(cp)_2}$$

may then be easily envisaged as the result of a rotation of one C_5H_5 ring around the *b* axis by ~45° coupled with a slight translation. It is not unreasonable to assume that the transformation of $V(cp)_2$ at $T_N = 8.3$ K is of a similar nature.

It should be noted that there is no transition to long-range order in the linear-chain models of both the Ising and Heisenberg types [20,25]. This situation is not improved by the inclusion of an interchain interaction as was done above for the Ising model. It is clear, therefore, that the employed models are basically incapable of reproducing the observed discontinuity of magnetic properties. Nevertheless, at temperatures above the discontinuity, good agreement between the susceptibility calculated by the Ising model with added lateral interaction and the experimental data has been obtained. Since Eq. 12 represents only the parallel susceptibility, the agreement is particularly impressive at higher temperatures where the contribution of the perpendicular component is very small.

A suitable approximation to the experimental data has also been achieved on the basis of the pair model, viz. Eq. 20. This result is not surprising when it is appreciated that the arrangement of the individual chains in brown $Mn(cp)_2$ is not strictly linear but zigzag, and a similar situation may be anticipated for $V(cp)_2$ below T_N. In fact, the superiority of the pair model for linear chains with a superposed pair-wise prefered interaction has been previously noted, e.g. for $Cu(NO)_3)_2 \cdot 2\frac{1}{2}\,H_2O$ [26] and for certain methylpyrazine complexes of copper(II) [27].

The behaviour of $1/\chi_m^{corr}$ at very low temperatures, where the curve passes through a maximum (at ~3.0 K) and turns down for the lowest temperatures measured, has been observed for some cluster compounds before [28], and seems to indicate the presence of a small amount of paramagnetic impurity. This assumption nicely accounts for the deviations between the experimental data and the curves calculated on the basis of the Ising and the pair model as shown above (cf. Fig. 2) and moreover may be the reason for the small field dependence observed below 3.0 K.

Acknowledgement

The authors appreciate financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

References

1 H. Leipfinger, Z. Naturforsch., 13B (1958) 53.
2 R. Prins and J.D. Van Voorst, J. Chem. Phys., 49 (1968) 4665.
3 I. Pavlik, V. Černy and E. Maxova, Coll. Czech. Chem. Commun., 37 (1972) 171.
4 R. Prins, P. Biloen and J.D.W. Van Voorst, J. Chem. Phys., 46 (1967) 1216.
5 J.H. Ammeter, J. Magn. Reson., 30 (1978) 299.
6 K.D. Warren, Struct. Bonding (Berlin) 27 (1976) 45.

7 E. König, R. Schnakig, B. Kanellakopulos and R. Klenze, Chem. Phys. Lett., 50 (1977) 439.
8 E. König, R. Schnakig, S. Kremer, B. Kanellakopulos and R. Klenze, Chem. Phys., 27 (1978) 331.
9 C. Aderhold, F. Baumgärtner, E. Dornberger and B. Kanellakopulos, Z. Naturforsch., 33A (1978) 1268.
10 E. König and S. Kremer, Magnetism Diagrams for Transition Metal Ions, Plenum Press, New York, 1979.
11 E. König and S. Kremer in J.C. Donini (Ed.), Recent Advances in Group Theory and their Application to Spectroscopy, Plenum Press, New Yor, 1979.
12 W. Bünder and E. Weiss, Z. Naturforsch., 33B (1978) 1235.
13 J.C. Bonner and M.E. Fisher, Phys. Rev., 135A (1964) 640.
14 M. Suzuki, B. Tsujiyama and S. Katsura, J. Math. Phys. (N.Y.), 8 (1967) 124.
15 M. Inoue and M. Kubo, J. Magn. Reson., 4 (1971) 175.
16 S. Emori, M. Inoue, M. Kishita and M. Kubo, Inorg. Chem., 8 (1969) 1385.
17 M.E. Fisher, Amer. J. Phys., 32 (1964) 343.
18 M.E. Lines and M. Eibschütz, Phys. Rev., 11 (1975) 4583.
19 I.B. Rabinovich, V.P. Nistratov, M.S. Sheiman and G.V. Burchalova, J. Chem. Thermodyn., 10 (1978) 523.
20 R.L. Carlin and A.J. Van Duyneveldt, Magnetic Properties of Transition Metal Compounds, Springer Publ., Berlin, 1977.
21 E. Weiss and E.O. Fischer, Z. Anorg. Allg. Chem., 278 (1955) 219.
22 J.D. Dunitz, L.E. Orgel and A. Rich, Acta Cryst., 9 (1956) 373.
23 G. Wilkinson, F.A. Cotton and J.M. Birmingham, J. Inorg. Nucl. Chem., 2 (1956) 95.
24 W. Bünder, thesis, Hamburg (1974).
25 L.J. de Jongh and R.A. Miedema, Adv. Phys., 23 (1974) 1.
26 S.A. Friedberg and C.A. Raquet, J. Appl. Phys., 39 (1968) 1132.
27 G.W. Inman and W.E. Hatfield, Inorg. Chem., 11 (1972) 3085.
28 M.E. Lines, A.P. Ginsberg, R.L. Martin and R.C. Sherwood, J. Chem. Phys., 57 (1972) 1.