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Preliminary communication

THE MAGNETIC SUSCEPTIBILITIES OF COBALTOCENE AND CHROMOCENE

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Summary

The magnetic susceptibilities of cobaltocene and chromocene have been measured between 83 and 293 K; for cobaltocene the results suggest an appreciable orthorhombic splitting of the $^2\Pi(\sigma^2\pi\delta^4)$ ground state, whilst for chromocene the data provide further support for the $^3\Delta(\sigma\delta^3)$ ground state previously deduced.

Early studies of the magnetic susceptibilities of the 3*d* metallocenes were principally concerned with the deduction of ground state orbital occupations, and thus tended to be carried out at only one or a few temperatures. Consequently, although a comprehensive theoretical treatment of the magnetic properties of transition metal sandwich complexes has now been given [1], the existing experimental data are in some cases insufficient for detailed analysis. Thus, measurements on solid samples made by Engelmann [2] related only to 90 K and room temperature, giving for cobaltocene and chromocene respectively the results $\mu = 1.76 \pm 0.07$ and 3.20 ± 0.10 BM, whilst the room temperature solution studies of Fritz and Schwarzhans [3], using the NMR technique, gave corresponding values of 1.69 and 3.10 BM.

However, for a satisfactory study of the temperature dependence of the magnetic moments of these systems more extensive data are desirable, and we now therefore report the results of measurements of the magnetic susceptibilities of cobaltocene and chromocene by the Gouy method at numerous temperatures within the range 83 to 293 K. The metallocenes were prepared by standard methods and purified by several sublimations in vacuo: the sample tubes were then filled in a Vacuum Atmospheres Glove Box and transferred under nitrogen to the magnetic balance. The need for these precautions was underlined by the fact that even for the less unstable cobaltocene

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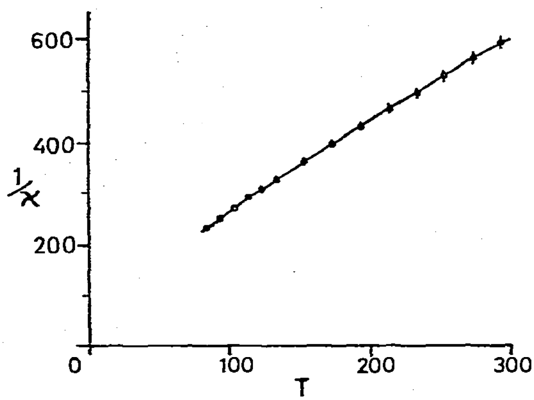
appreciably smaller magnetic moments were obtained for samples handled under less stringent conditions.

The results for cobaltocene and chromocene are shown in Fig. 1 and 2 as plots of $1/\chi$ against T, but the data for the former show a marked curvature, corresponding to an effective magnetic moment falling with decreasing temperature. Part of this curvature may however be due to temperature independent paramagnetism, since for d^7 systems these second order Zeeman terms may add about 220×10^{-6} cgsu to $\chi_\perp$ [4], which is a significant contribution for a doublet ground state system. When due allowance is made for this effect, the temperature dependent susceptibility corresponds to an effective moment of about 1.70—1.90 BM between 83 and 293 K, which is in reasonably good agreement with the literature values.



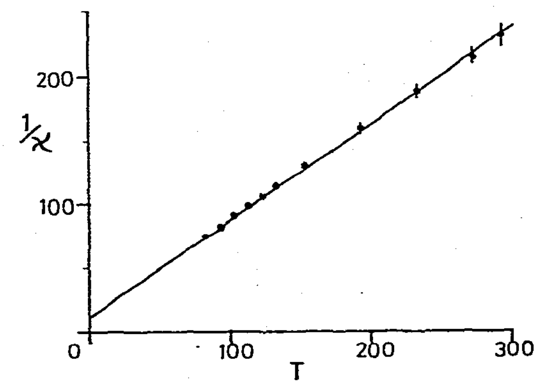


Fig. 1. Temperature dependence of the magnetic susceptibility of cobaltocene. (In both Figures the vertical lines indicate the reproducibility of the results.)

Fig. 2. Temperature dependence of the magnetic susceptibility of chromocene.

Nevertheless, for undistorted d^7 systems theory [1] predicts a substantial temperature dependence for the magnetic moment, and even assuming an effective orbital reduction factor, k', of 0.25 and an orthorhomic distortion of the magnitude indicated by ESR measurements [5] the predicted moments in the lower part of the temperature range are appreciably smaller than the observed values. Thus, to obtain moments which approach the spin-only value (1.73 BM) and are almost temperature independent, a distortion parameter, Δ/ξ, of about 3 is required, where ξ is the effective spin-orbit coupling constant. Thus, taking ξ as 330 cm^{-1} [5] yields an orthorhombic splitting, Δ, of almost 1000 cm^{-1}, or nearly twice the value suggested by any of the ESR studies [5,6]. A full analysis of the data necessitates however the inclusion of terms due to the admixture into the ground state by spin-orbit coupling of higher doublet levels [7], and details of this will be presented separately.

In contrast the Curie—Weiss law is closely followed for chromocene, the plot of $1/\chi$ against T yielding a slope corresponding to μ 3.27 BM, with θ 17°. The results are therefore in good agreement with the older fragmentary data and provide powerful support for a $^3\Delta(\sigma\delta^3)$ ground state. Thus, assuming k' to be about 0.80, as found by ESR studies [8,9] for other systems with a

δ orbital degeneracy, a distortion parameter, Δ/ξ, of about 4 is found [1] to produce a virtually temperature independent moment of the correct magnitude. Taking ξ as ca. 180 cm^{-1} then yields a splitting, Δ, of a little over 700 cm^{-1}, but no definitive parameterisation can be established since k' could well be somewhat less than 0.80, with necessarily smaller orthorhombic splittings.

Significantly however the present results indicate a moment for chromocene well above the spin-only value (2.83 BM), and thus afford clear evidence of an orbital contribution. Consequently the ground level must then be $^3\Delta(\sigma\delta^3)$ and not $^3\Sigma^-(\sigma^2\delta^2)$ as was concluded by Perkins et al. [10] in a recent CNDO based molecular orbital calculation. Moreover, contrary to the suggestions of these authors, the photoelectron studies of chromocene by Orchard et al. [11] clearly indicate a $^3\Delta$ ground state, too many *d*-ionisation bands being observed for a $^3\Sigma^-$ level, and ligand field theory [12] also strongly supports a $^3\Delta$ ground state. Finally, INDO SCF calculations by Clack and Monshi [13], which make full allowance for one-centre exchange terms, also show the ground level to be $^3\Delta$ and correctly reproduce the NMR paramagnetic shift.

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