Contribution from the Department of Chemistry,
University College, Cardiff, Wales, United Kingdom

Ligand Field Theory of Metal Sandwich Complexes. Magnetic Properties of d^x Configurations

KEITH D. WARREN

Received October 5, 1973

AIC30728N

The magnetic behavior of transition metal sandwich complexes—especially metallocenes and bis-arene derivatives—is discussed in terms of the ligand field model, and the possible ground states for each d^x configuration are considered, assuming a field of effectively axial ($C_{\infty v}$) symmetry. The spin-orbit splittings and the matrix elements of the Zeeman operators within the various ground-state manifolds have been evaluated, and the temperature dependence and anisotropy of the magnetic moments calculated for d^1, d^2, d^4, d^5, d^7, and d^9 systems—for d^3 and d^8 configurations the spin-only values are expected and d^6 complexes are diamagnetic. Calculations have also been made to determine the effects of variation of the orbital reduction factor and of distortions from pseudoaxial symmetry, and the available experimental data are analyzed in the light of these results.

Introduction

In recent years the ligand field model has been shown to be of considerable value in the interpretation of d-d spectra of transition metal sandwich complexes, such as metallocenes and bis(arene)metal derivatives.[1] It was shown by Scott and Matsen[2] that such species could be treated as possessing effective axial ($C_{\infty v}$) symmetry, and complete strong-field energy matrices, including spin-orbit coupling, have been reported[3] for d^1, d^2, and d^3 systems and their complementary configurations. In addition, the full strong-field repulsion matrices have been given[4] for d^4 (d^6) systems, and a partial treatment has been presented for d^5 configurations.[5]

Nevertheless, despite the amount of work carried out on the electronic spectra (see ref 1-5 and papers cited therein), relatively little attention has latterly been devoted to the study of the magnetic susceptibilities of these compounds, while many of the early studies covered only a limited temperature range and were in any case primarily directed toward deducing ground-state orbital occupations. Consequently these measurements can yield only a restricted amount of information, and the object of the present work is to stimulate further experimental interest by calculating the magnetic susceptibilities of all the d^x configurations, with particular reference to the temperature dependence and anisotropy of the magnetic moments of those systems for which an orbital contribution is possible. Furthermore, the effects of covalency on the magnetic moment are investigated by varying the orbital reduction factor, k', and the results of C_{2v} distortion from pseudoaxial symmetry—possibly of Jahn-Teller origin—are also elucidated.

Theory and Calculations

When only d^x configurations are considered, all systems of C_n, C_{nh}, C_{nv}, D_{nd}, and D_{nh} symmetry may be treated in terms of a purely axial ($C_{\infty v}$) ligand field,[2] as long as $n \geqslant 5$. This therefore includes all the metallocenes and the bis(arene)-metal compounds, and the mixed-ligand sandwich complexes may also be considered to possess pseudoaxial symmetry. In such a field the d orbitals are split into three sets—$\sigma(\mathrm{d}_{z^2})$, $\pi(\mathrm{d}_{xz}, \mathrm{d}_{yz})$, and $\delta(\mathrm{d}_{x^2-y^2}, \mathrm{d}_{xy})$—with one-electron energies[6] $E(\sigma) = 2Ds - 6Dt$, $E(\pi) = Ds + 4Dt$, and $E(\delta) = -2Ds - Dt$. For the metallocenes[3,4] these core energies follow the order $\delta < \sigma << \pi$, with Dt/Ds lying within the range 0.5-0.6 and the ratio of Dt to the Racah parameter, B, usually between 4 and 6. For the metallocenes the $E(\sigma) - E(\delta)$ and $E(\pi) - E(\sigma)$ values are normally between 4 and 7 kK and between 15 and 22 kK, respectively, but despite many molecular orbital calculations being available for the metallocenes,[7,8] there is unfortunately a shortage of both experimental and theoretical data relating to the d-orbital splittings in the bis-arene complexes. A naive ligand field approach would, though, suggest that the overall energy separation may be somewhat smaller than that for the metallocenes.

On the basis of the data for the metallocenes the probable ground states for the various d^x configurations have been deduced, using the appropriate coulombic repulsion matrices[3-5] and assuming $Dt = 0.55Ds$ and a value of 4.0 for the ratio of the Racah parameters C/B. These conclusions are presented in Table I, and the circumstances under which other states may lie lowest are also indicated. In addition Table I shows whether or not an orbital contribution to the magnetic moment is anticipated; for those ground states which are orbital singlets the magnetic moments will be isotropic and will correspond to the spin-only values within the limits of the approximations adopted. Attention has therefore been directed toward those ground states for which an orbital contribution to the moment is possible, *viz.*, d^1 and d^5, $^2\Delta$; d^2 and d^4, $^3\Delta$; and d^7 and d^9, $^2\Pi$, and for which the moment may be anisotropic.

For a ligand field of effectively axial ($C_{\infty v}$) symmetry the appropriate perturbation Hamiltonian, H', is[3] in the absence of a magnetic field

$$H' = \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_i \xi(r_i)\vec{l}_i \cdot \vec{s}_i + \sum_i V_{\mathrm{LF}}(r_i)$$

where the first term represents the interelectronic coulombic repulsions, the second the spin-orbit interactions, and the last the axial ligand field. Calculations in the strong-field scheme, using the appropriate repulsion + axial field matrices,[3-5] show that for the metallocenes, within the designated parameter ranges, the listed ground states always show a purity of 98% or greater, and the inclusion of spin-orbit coupling does not invalidate this conclusion. Thus for the configurations under discussion, the lowest lying excited states correspond either to differing orbital occupations of the

---

[1] C. J. Ballhausen and H. B. Gray, "Coordination Chemistry," Vol. 1, ACS Monograph No. 168, American Chemical Society Publications, Washington, D. C., 1971.

[2] D. R. Scott and F. A. Matsen, *J. Phys. Chem.*, 72, 16 (1968).

[3] K. D. Warren, *J. Phys. Chem.*, 77, 1681 (1973).

[4] K. D. Warren, *Inorg. Chem.*, 13, 1243 (1974).

[5] Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, 93, 3603 (1971).

[6] T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, 33, 1208 (1960).

[7] M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, 91, 3432 (1969).

[8] J. H. Schachtschneider, R. Prins, and P. Ros, *Inorg. Chim. Acta*, 1, 462 (1967).

Table I. Ground States for d^x Metallocenes

Confign	Ground state	Magnetic moment (orbital contribn)	Remarks
d^1	$^2\Delta(\delta)$	Yes	
d^2	$^3\Delta(\sigma\delta)$	Yes	$^3\Sigma^-(\delta^2)$ ground state at high (>5) Dt/B values
d^3	$^4\Sigma^-(\sigma\delta^2)$	No	
d^4	$^3\Delta(\sigma\delta^3)$	Yes	$^3\Sigma^-(\sigma^2\delta^2)$ ground state possible for very small Dt/B range
d^5	$^2\Delta(\sigma^2\delta^3)$	Yes	$^2\Sigma^+(\sigma\delta^4)$ ground state at very high (>8) Dt/B values; $^6\Sigma^+(\sigma\delta^2\pi^2)$ ground state at very low (<3) Dt/B values
d^6	$^1\Sigma^+(\sigma^2\delta^4)$	Diamag	
d^7	$^2\Pi(\sigma^2\delta^4\pi)$	Yes	
d^8	$^3\Sigma^-(\sigma^2\delta^4\pi^2)$	No	
d^9	$^2\Pi(\sigma^2\delta^4\pi^3)$	Yes	

closely juxtaposed σ and δ levels or to transitions to the much higher π level. In the latter case the spin-orbit mixing will be very small, and in the former all matrix elements of the form $\langle\sigma|l\cdot s|\delta\rangle$ are zero in any case.

The zero-order ground-state spin-orbit wave functions, obtained as previously described,[3] have therefore been used as the basis functions for the present calculations of the magnetic susceptibilities *via* the familiar Van Vleck equation

$$\chi_\alpha = \frac{N\sum_i\left[\frac{(E^{\mathrm{I}}{}_i)^2}{kT} - 2E^{\mathrm{II}}{}_i\right]e^{-E^0{}_i/kT}}{\sum_i e^{-E^0{}_i/kT}}$$

where $E^{\mathrm{I}}{}_i = \langle\psi_i|k'L_\alpha + 2S_\alpha|\psi_i\rangle\beta$, $E^{\mathrm{II}}{}_i = \Sigma_j(\langle\psi_i|k'L_\alpha + 2S_\alpha|\cdot\psi_j\rangle\beta)^2/(E^0{}_i - E^0{}_j)$, with $i \neq j$ and $\alpha = z$ or x, y. The effective magnetic moment is then obtained from the susceptibility *via* the Curie formula $\chi = N\mu_{\mathrm{eff}}{}^2/3kT$ and the average from the z and the x, y components using $\langle\mu\rangle = [{}^1/_3(\mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2)]^{1/2}$. In the above Zeeman operators the factor k' is the orbital reduction parameter which is introduced to enable allowance to be made for the delocalization of electrons out of the metal d orbitals onto the ligand atoms. The spin-orbit splitting of the various ground states, and the effects produced by a magnetic field applied in the z ($H_\parallel$) or x, y ($H_\perp$) direction are shown in Figures 1–3, and the matrix elements of the Zeeman operators are listed, in units of β, in Tables II–IV. The calculations may be appreciably shortened by use of the hole-equivalence relationship since the results for d^5, $^2\Delta(\sigma^2\delta^3)$, d^4, $^3\Delta(\sigma\delta^3)$, and for d^9, $^2\Pi(\sigma^2\delta^4\pi^3)$ may be derived at once from those for d^1, $^2\Delta(\delta)$, d^2, $^3\Delta(\sigma\delta)$, and d^7, $^2\Pi(\sigma^2\delta^4\pi)$, respectively, by reversing the sign of ξ throughout. Note that the orbital reduction factor, k', occurs only for the matrix elements of $H_\parallel$ and that consequently $\mu_{x,y}$, arising from the spin-only terms, is independent of the sign of ξ. In addition the matrix elements of the Zeeman operators are entirely diagonal for $H_\parallel$ and off-diagonal for $H_\perp$: in the latter case therefore the eigenvalues of $k'L_x + 2S_x$ are obtained by second-order perturbation theory and the susceptibilities calculated following the procedure described by Ballhausen.[9] Expressions for the magnetic moments thereby derived are listed in Tables II–IV and the numerical values obtained for a range of k' and kT/ξ values are tabulated in the Appendix.[10] The corresponding limiting values of $\mu_\parallel$, $\mu_\perp$, and $\langle\mu\rangle$, as $kT/\xi \to 0$ and $kT/\xi \to \infty$, are given in Table V, together with the results at $kT/\xi = 1$, for the case of $k' = 1$.

Table II. Zeeman Matrix Elements and Magnetic Moments for d^1 (d^5) $C_{\infty v}$ Systems[a] (Ground State $^2\Delta$)

Representation[b]	Spin-orbit energy	$k'L_z + 2S_z$	$k'L_x + 2S_x$
Δ^*	$-\xi$	$\pm(2k' - 1)$	1
Φ^*	$+\xi$	$\pm(2k' + 1)$	

$$\mu_\parallel = \sqrt{3}\{4k'[k' - \tanh(x)] + 1\}^{1/2}$$

$$\mu_\perp = \sqrt{3}[x^{-1}\tanh(x)]^{1/2}$$

With C_{2v} distortion

$$\mu_\parallel = \sqrt{3}\{[(1 + 4k'ab)^2e^{-\alpha/2} + (1 - 4k'ab)^2e^{\alpha/2}][e^{\alpha/2} + e^{-\alpha/2}]^{-1} + 8k'^2(a^2 - b^2)^2[\tanh(\alpha/2)]\alpha^{-1}\}^{1/2}$$

$$\mu_\perp = \sqrt{3}\{(a^2 - b^2)^2 + 8a^2b^2[\tanh(\alpha/2)]\alpha^{-1}\}^{1/2}$$

[a] For d^5 results reverse sign of ξ; here and hereafter $x = \xi/kT$. $\delta = \Delta/\xi$, $\alpha = x(4 + \delta^2)^{1/2}$, $a = {}^1/_2[\delta + (4 + \delta^2)^{1/2}]\{{}^1/_4[\delta + (4 + \delta^2)^{1/2}]^2 + 1\}^{-1/2}$ and $b = \{{}^1/_4[\delta + (4 + \delta^2)^{1/2}]^2 + 1\}^{-1/2}$. [b] For nomenclature of $C_{\infty v}$ and $C_\infty{}^*$ groups see ref 3.

Table III. Zeeman Matrix Elements and Magnetic Moments for d^2 (d^4) $C_{\infty v}$ Systems[a] (Ground State $^3\Delta$)

Representation	Spin-orbit energy	$k'L_z + 2S_z$	$k'L_x + 2S_x$
Π	$-\xi$	$\pm 2(k' - 1)$	$2^{1/2}$
Δ	0	$\pm 2k'$	$2^{1/2}$
Φ	$+\xi$	$\pm 2(k' + 1)$	

$$\mu_\parallel = 2\sqrt{3}\{(1 + k'^2) - [2k'(e^x - e^{-x}) + 1](1 + e^x + e^{-x})^{-1}\}^{1/2}$$

$$\mu_\perp = 2\sqrt{3}[(e^x - e^{-x})x^{-1}(1 + e^x + e^{-x})^{-1}]^{1/2}$$

With C_{2v} distortion

$$\mu_\parallel = \sqrt{3}\{8[(1 + 2k'ab)^2e^{-\alpha/2} + (1 - 2k'ab)^2e^{\alpha/2} + k'^2(2(a^2 - b^2)^2(e^{\alpha/2} - e^{-\alpha/2})\alpha^{-1} + (e^{\delta x/2} - e^{-\delta x/2})(\delta x)^{-1})] \times [2(e^{\alpha/2} + e^{-\alpha/2}) + (e^{\delta x/2} + e^{-\delta x/2})]^{-1}\}^{1/2}$$

$$\mu_\perp = 4\sqrt{3}\{[a^2(e^{\alpha/2} - e^{-\alpha/2} - e^{\delta x/2} + e^{-\delta x/2})(\alpha - \delta x)^{-1} + b^2(e^{\alpha/2} - e^{-\alpha/2} + e^{\delta x/2} - e^{-\delta x/2})(\alpha + \delta x)^{-1}] \times [2(e^{\alpha/2} + e^{-\alpha/2}) + (e^{\delta x/2} + e^{-\delta x/2})]^{-1}\}^{1/2}$$

[a] For d^4 results reverse sign of ξ; δ, α, a, and b as defined in Table II.

Table IV. Zeeman Matrix Elements and Magnetic Moments for d^7 (d^9) $C_{\infty v}$ Systems[a] (Ground State $^2\Pi$)

Representation	Spin-orbit energy	$k'L_z + 2S_z$	$k'L_x + 2S_x$
Π^*	$-{}^1/_2\xi$	$\pm(k' - 1)$	1
Δ^*	$+{}^1/_2\xi$	$\pm(k' + 1)$	

$$\mu_\parallel = \sqrt{3}\{k'[k' - 2\tanh(x/2)] + 1\}^{1/2}$$

$$\mu_\perp = [6x^{-1}\tanh(x/2)]^{1/2}$$

With C_{2v} distortion

$$\mu_\parallel = \sqrt{3}\{[(1 + 2k'ab)^2e^{-\gamma/2} + (1 - 2k'ab)^2e^{\gamma/2}](e^{\gamma/2} + e^{-\gamma/2})^{-1} + 2k'^2(a^2 - b^2)^2[\tanh(\gamma/2)]\gamma^{-1}\}^{1/2}$$

$$\mu_\perp = \sqrt{3}\{(a^2 - b^2)^2 + 8a^2b^2[\tanh(\gamma/2)]\gamma^{-1}\}^{1/2}$$

[a] For d^9 results reverse sign of ξ. $\delta = \Delta/\xi$, $\gamma = x(1 + \delta^2)^{1/2}$, $a = [\delta + (1 + \delta^2)^{1/2}]\{1 + [\delta + (1 + \delta^2)^{1/2}]^2\}^{-1/2}$, and $b = \{1 + [\delta + (1 + \delta^2)^{1/2}]^2\}^{-1/2}$.

In principle it should be possible to determine the anisot-

---

[9] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962.

[10] See paragraph at end of paper regarding supplementary material.

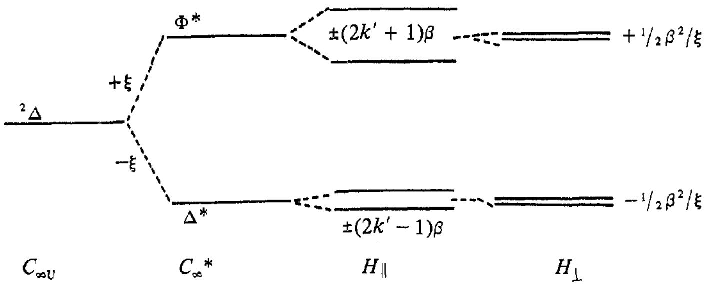

Figure 1. Energy level diagram for d^1 (d^5) systems in $C_{\infty v}$ symmetry. (In Figures 1–3 and 4–6 reverse sign of ξ to obtain results for hole-equivalent configurations.)

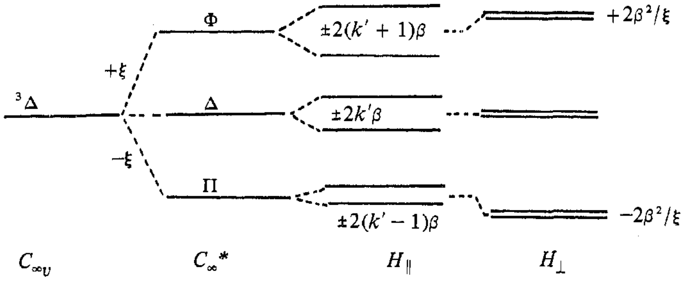

Figure 2. Energy level diagram for d^2 (d^4) systems in $C_{\infty v}$ symmetry.

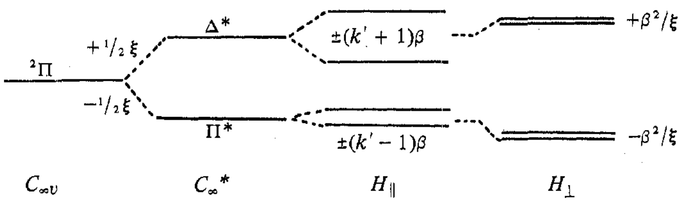

Figure 3. Energy level diagram for d^7 (d^9) systems in $C_{\infty v}$ symmetry.

Table V. Limiting Values of Magnetic Moments for d^x $C_{\infty v}$ Systems ($k' = 1$)

	$kT/\xi \to 0$			$kT/\xi = 1$			$kT/\xi \to \infty$		
Confign	$\mu_\parallel$	$\mu_\perp$	$\langle\mu\rangle$	$\mu_\parallel$	$\mu_\perp$	$\langle\mu\rangle$	$\mu_\parallel$	$\mu_\perp$	$\langle\mu\rangle$
d^1, $^2\Delta$	$\sqrt{3}$	0	1	2.42	1.51	1.86	$\sqrt{15}$	$\sqrt{3}$	$\sqrt{7}$
d^2, $^3\Delta$	0	0	0	2.69	2.63	2.65	$2\sqrt{5}$	$2\sqrt{2}$	$2\sqrt{3}$
d^4, $^3\Delta$	$4\sqrt{3}$	0	4	5.90	2.63	4.03	$2\sqrt{5}$	$2\sqrt{2}$	$2\sqrt{3}$
d^5, $^2\Delta$	$3\sqrt{3}$	0	3	4.91	1.51	3.09	$\sqrt{15}$	$\sqrt{3}$	$\sqrt{7}$
d^7, $^2\Pi$	0	0	0	1.80	1.67	1.71	$\sqrt{6}$	$\sqrt{3}$	2
d^9, $^2\Pi$	$2\sqrt{3}$	0	2	2.96	1.67	2.18	$\sqrt{6}$	$\sqrt{3}$	2

ropy of the paramagnetic susceptibility for some systems of pseudoaxial symmetry, but there are no experimental data available for metal sandwich complexes. The metallocenes and mixed sandwich compounds are found to crystallize in either a monoclinic (*e.g.*, Fe(Cp)$_2$)[11] or orthorhombic (*e.g.*, Ru(Cp)$_2$, (Co)V(C$_7$H$_7$))[12,13] system, which should exhibit magnetic anisotropy, but of the bis-arene complexes Cr(C$_6$H$_6$)$_2$ is found[14] to belong to a cubic system for which only the average moment can be determined.

A number of circumstances may however lead to varying degrees of distortion from the effective axial symmetry. For those systems which may show an orbital contribution to the magnetic moment a ground-state orbital degeneracy is of course found. Systems of pseudoaxial symmetry such as D_{5d}, D_{5h}, or D_{6h} may therefore suffer distortion from their regular geometries by the operation of the Jahn-Teller effect, thereby lowering the symmetry to C_{2h}, C_{2v}, or D_{2h}, respectively, and resolving the degeneracies of the π and δ levels. Calculations similar to those above have therefore been carried out to determine the influence of such distortions on the magnetic moment and its temperature dependence; for convenience the symbolism of the C_{2v} point group is adopted throughout. The distortions are everywhere assumed to be static since, although dynamic Jahn-Teller effects may well be operative, the treatment of their influence on magnetic properties requires a more sophisticated approach than that presented here.

The basis functions are taken as the strong-field orbital functions which are assumed to be diagonal in the distortion parameter, the two components of the appropriate π or δ level being separated by an energy, Δ. The energy splitting of the ground-state components is then calculated in terms of Δ and ξ, the eigenfunctions are derived, and the Zeeman matrices of $k'L_z + 2S_z$ and $k'L_x + 2S_x$ are constructed—within the limits of the present treatment the same moments are derived for the x and y directions, and the result is independent of which of the two formerly degenerate components lies lower. The effects thus produced by the successive application of C_{2v} distortion, spin-orbit coupling, and $H_\parallel$ or $H_\perp$ magnetic fields are shown in Figures 4–6; the eigenvalues of the Zeeman matrices are then found using perturbation theory and the susceptibilities determined as before, expressions for the appropriate moments for d^1 (d^5), d^2 (d^4), and d^7 (d^9) systems also being given in Tables II–IV, respectively. Finally, in Figures 7–9 are shown the effects of variations of the distortion parameters, δ ($=\Delta/\xi$), on the average magnetic moment, assuming an orbital reduction factor 0.7 (*vide infra*).

As indicated above the calculations have throughout been performed using the zero-order functions and restricting at-

---

(11) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, **9**, 373 (1956).

(12) G. L. Hardgrove and D. H. Templeton, *Acta Crystallogr.*, **12**, 28 (1959).

(13) G. Engebretson and R. E. Rundle, *J. Amer. Chem. Soc.*, **85**, 481 (1963).

(14) J. A. Ibers, *J. Chem. Phys.*, **40**, 3129 (1946).

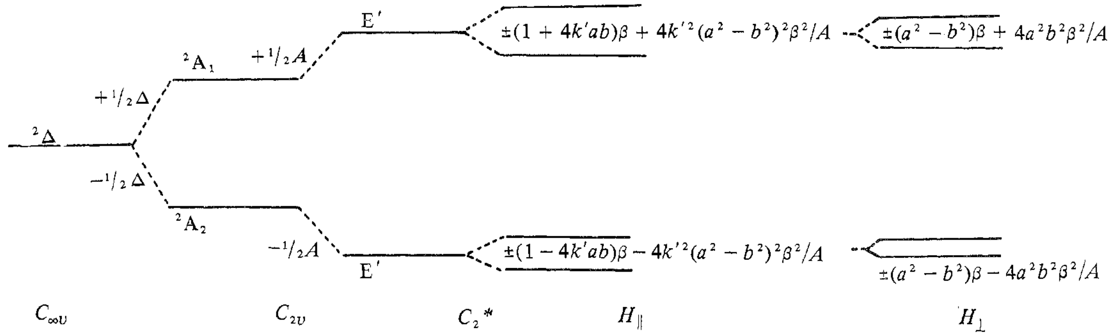

Figure 4. Energy level diagram for d^1 (d^5) $C_{\infty v}$ systems with C_{2v} distortion ($A = (4\xi^2 + \Delta^2)^{1/2}$).

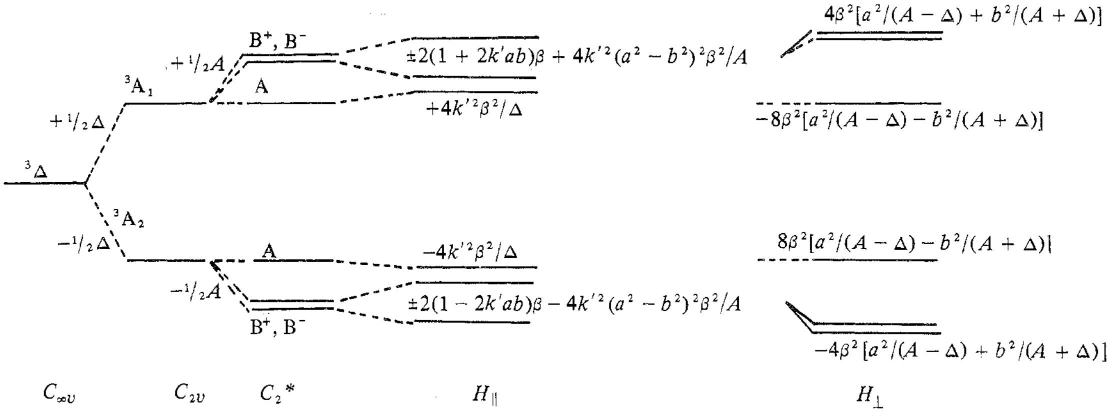

Figure 5. Energy level diagram for d^2 (d^4) $C_{\infty v}$ systems with C_{2v} distortion ($A = (4\xi^2 + \Delta^2)^{1/2}$).

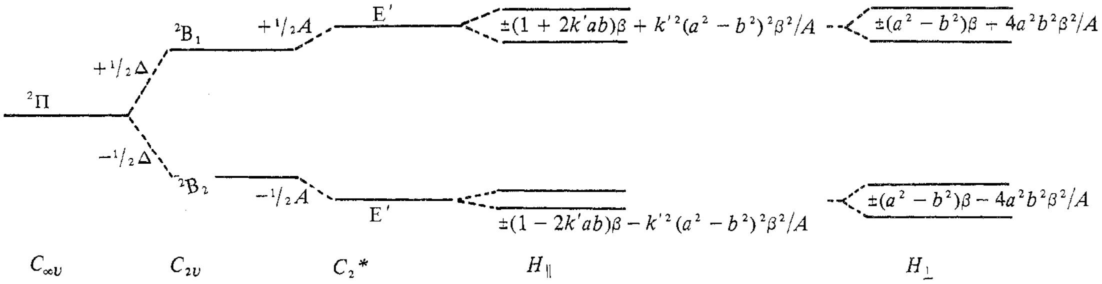

Figure 6. Energy level diagram for d^7 (d^9) $C_{\infty v}$ systems with C_{2v} distortion ($A = (\xi^2 + \Delta^2)^{1/2}$).

tention to the ground-state manifold. For systems in which the effective spin-orbit coupling constant is fairly small and the π level lies well above the σ and δ levels, this constitutes a reasonable approximation but would prove less satisfactory in the second and third transition series, especially if the ligand field splitting were rather smaller as seems possible for some bis-arene complexes. However, the bulk of the existing experimental results relate to compounds of the 3d series and may therefore be satisfactorily interpreted in terms of the present approach.

Discussion

The results summarized in Table V (see also Appendix) show that for all the configurations studied the magnetic moments are substantially anisotropic, this being most marked for the d^4 and d^5 systems. The degree of temperature dependence of the calculated average moment however varies quite appreciably from one configuration to another; thus the dependence is most evident for d^1, d^2, and d^7 systems, while the $\langle\mu\rangle$ values for d^4, d^5, and d^9 species are much less sensitive to temperature over the range normally examined. In the latter case though this result is largely due to the contrary temperature dependence exhibited by the $\mu_\parallel$ and $\mu_\perp$ components.

However, these results relate to an idealized situation in which pseudoaxial symmetry is strictly maintained and no cognizance is taken of the possible delocalization of electron density onto the ligands. It is therefore necessary to consider the effects of metal-ligand mixing, as reflected in the orbital reduction factor, k', and the results of C_{2v} distortions—possibly due to Jahn-Teller instabilities—as comprehended by the distortion parameter, Δ. As for octahedral systems[15] the most frequent effect of the reduction of k' below unity is to lead to average moments which become progressively closer to the spin-only values, although here also there are exceptions. Thus for d^1 systems although a decrease in k' below unity ultimately affords μ values closer to the spin-only result, the moment may in fact initially be further reduced below that figure at the lower kT/ξ values and only approach the spin-only result more closely as $kT/\xi \rightarrow \infty$. Increase of the distortion parameter, δ ($=\Delta/\xi$), tends throughout to produce average moments nearer to the spin-only value. (See Figures 7-9.)

For many of the metallocenes a nephelauxetic ratio, β, of about 0.5 has been deduced from the electronic spectra.[3] If it is assumed[16] that this parameter shows a fourth-power

(15) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).
(16) C. K. Jorgensen, *Struct. Bonding (Berlin)*, **1**, 3 (1966).

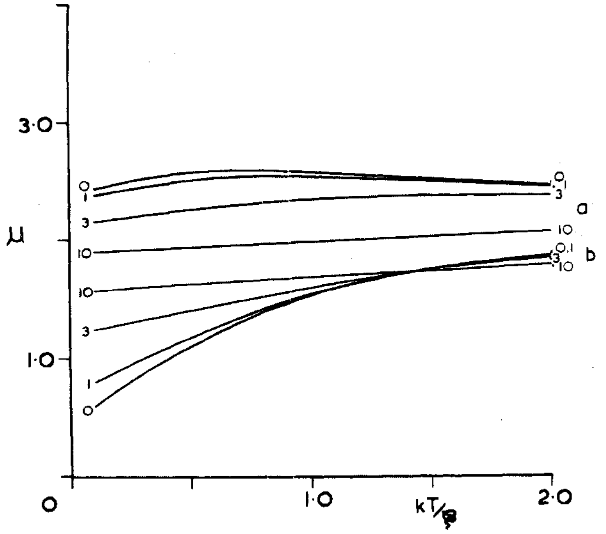

Figure 7. Variation of $\langle\mu\rangle$ with C_{2v} distortion for d^1 (d^5) systems ($k' = 0.7$): a, d^5; b, d^1. δ values are as shown.

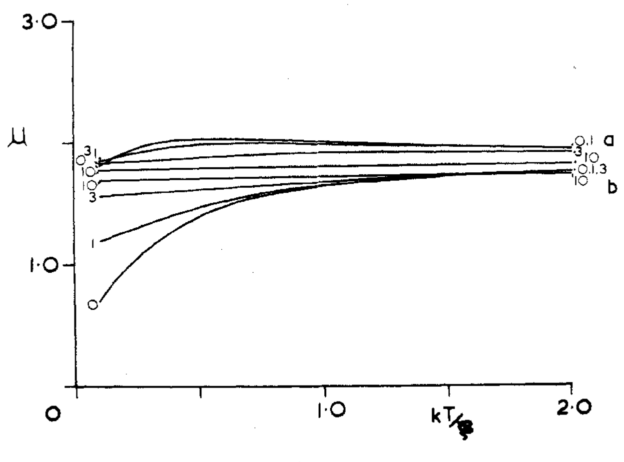

Figure 9. Variation of $\langle\mu\rangle$ with C_{2v} distortion for d^7 (d^9) systems ($k' = 0.7$): a, d^9; b, d^7. δ values are as shown.

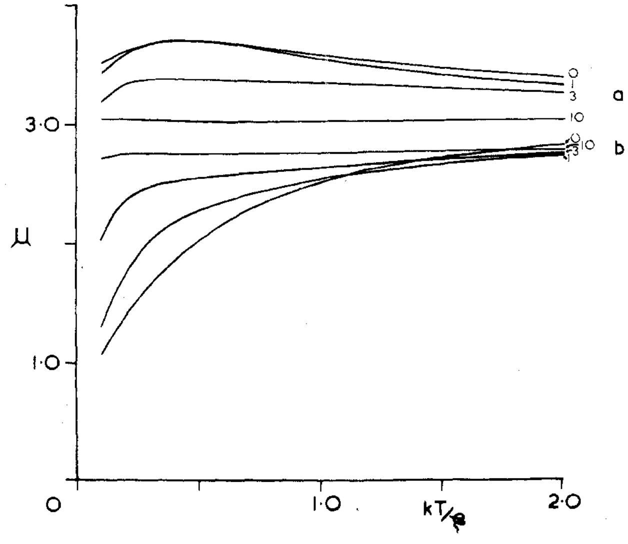

Figure 8. Variation of $\langle\mu\rangle$ with C_{2v} distortion for d^2 (d^4) systems ($k' = 0.7$): a, d^4; b, d^2. δ values are as shown.

dependence on the metal mixing coefficient and the one-electron quantities show a quadratic dependence, a value of k' in the region of 0.7 should be appropriate. Consequently, the effects of increasing the distortion parameter (Figures 7-9) have been evaluated assuming this figure for k'.

In Table VI are summarized the most recent and reliable data for the magnetic moments of the metallocenes and bis-arene derivatives. The d^6 systems, which are all diamagnetic with a $^1\Sigma^+(\sigma^2\delta^4)$ ground state, have been omitted, but the results for the d^3 and d^8 configurations are included. For these systems the spin-only value or thereabouts is found for all the d^3 complexes which have been studied, as is also the case for nickelocene. For other d^8 systems—*e.g.*, the bis-hexamethylbenzene compounds of Fe^0 and Co^I—slightly higher average moments have been reported[17,18] (3.08 and 2.95 BM, respectively) which may well originate in second-order Zeeman contributions from the higher excited states. Thus if the separation between the π and the σ, δ levels were rather smaller for bis-arene compounds than for metallocenes, a rather larger contribution from the temperature-independent paramagnetism would be anticipated. Lacking information regarding the fitting parameters for the bis-arene complexes it is not thought possible to calculate these effects quantitatively.

The results for the d^x configurations treated above remain however to be discussed and are now considered in turn. Only for the d^4 $Cr(Cp)_2$ and the d^5 $Fe(Cp)_2{}^+$ is there clear-cut evidence for an orbital contribution to the average moment, but similar effects seem likely for the d^7 and d^9 configurations. In all these cases it appears probable that some distortion from pseudoaxial symmetry takes place, and estimates have been made for this. Nevertheless, more accurate measurements over a wide temperature range, preferably with anisotropic data, would be required to evaluate such tendencies precisely, and the present results can only be taken as approximations.

d^1 Systems. It is rather doubtful whether Ti(III) and V(IV) systems such as $Ti(Cp)_2Cl$ and $V(Cp)_2Cl_2$ approximate in any way to pseudoaxial symmetry. Thus Langford and Aplington[19] have presented evidence that $Ti(Cp)_2Cl_2$ is roughly tetrahedral, and the work of Doyle and Tobias[20,21] suggests a similar conclusion for the vanadium analog. It also seems probable that in aqueous solution these and similar species such as $Ti(Cp)_2Cl$ undergo hydrolytic reactions to give products of uncertain geometry.

Nevertheless, for $Ti(Cp)_2{}^+$,pic$^-$ and $V(Cp)_2{}^{2+}$,2Cl$^-$ magnetic moments of 2.29 and 1.90 BM, respectively at 298°K have been reported,[22,23] which would apparently be consistent with a $^2\Delta$ ground state and an orbital contribution to the moment. However, esr measurements on the vanadium compound[21] and on a wide range of other formally $Ti(Cp)_2{}^+$ systems[24] yield almost isotropic g values, just below 2, which as previously shown[3] cannot be reconciled with a $^2\Delta$ ground state but are consistent only with a $^2\Sigma^+$ ground level or with a large distortion from pseudoaxial symmetry. Moreover, more recent magnetic results[25] indicate a virtually temperature-independent moment of 1.68 BM for $Ti(Cp)_2$-

---

(17) E. O. Fischer and F. Rohrscheid, *Z. Naturforsch. B*, 17, 483 (1962).

(18) E. O. Fischer and H. H. Lindner, *J. Organometal. Chem.*, 1, 307 (1964).

(19) C. H. Langford and J. P. Aplington, *J. Organometal. Chem.*, 4, 271 (1965).

(20) G. Doyle and R. S. Tobias, *Inorg. Chem.*, 6, 1111 (1967).

(21) G. Doyle and R. S. Tobias, *Inorg. Chem.*, 7, 2479 (1968).

(22) G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, 1, 1 (1959).

(23) G. Wilkinson and J. M. Birmingham, *J. Amer. Chem. Soc.*, 76, 4281 (1954).

(24) R. E. Dessy, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, 88, 5112 (1966).

(25) R. Coutts and P. C. Wailes, *Inorg. Nucl. Chem. Lett.*, 3, 1 (1967).

Table VI. Magnetic Moments of Transition Metal Sandwich Complexes

Confign	Complex[q]	Magnetic moment, BM	Temp range, °K	Ref	Ground state
d^1	$Ti(Cp)_2^+$	1.68 ± 0.05	120–320	*a*	Geometry uncertain
	$V(Cp)_2^{2+}$	1.90	296	*b*	
d^2	$V(Cp)_2^+$	2.86 ± 0.06	296	*b*	$^3\Sigma^-(\delta^2)$
d^3	$V(Cp)_2$	3.84 ± 0.04	20–423	*c*	$^4\Sigma^-(\sigma\delta^2)$
	$Cr(Cp)_2^+$	3.87	90–296	*d*	$^4\Sigma^-(\sigma\delta^2)$
d^4	$Cr(Cp)_2$	3.20 ± 0.16	90–295	*e*	$^3\Delta(\sigma\delta^3)$
	$V(Mes)_2^+$	2.80 ± 0.17	88–293	*f*	?
d^5	$Mn(Cp)_2$	5.94 ± 0.05	77–438	*g*	$^6\Sigma^+(\sigma\delta^2\pi^2)$
	$Fe(Cp)_2^+$	2.30–2.60	40–300	*h*	$^2\Delta(\sigma^2\delta^3)$
	$V(Bz)_2$	1.68 ± 0.08	88–294	*i*	$^2\Sigma^+(\sigma\delta^4)$
	$Cr(Bz)_2^+$	1.77	90–290	*j*	$^2\Sigma^+(\sigma\delta^4)$
d^7	$Co(Cp)_2$	1.76 ± 0.07	90–295	*e*	$^2\Pi(\sigma^2\delta^4\pi)$
	$Ni(Cp)_2^+$	1.78 ± 0.10	90–room temp	*k*	$^2\Pi(\sigma^2\delta^4\pi)$
	$Fe(HMBz)_2^+$	1.89	Room temp	*l*	$^2\Pi(\sigma^2\delta^2\pi)$
	$Co(HMBz)_2^{2+}$	1.73 ± 0.05	Room temp	*m*	$^2\Pi(\sigma^2\delta^4\pi)$
d^8	$Ni(Cp)_2$	2.89 ± 0.15	70–300	*n*	$^3\Sigma^-(\sigma^2\delta^4\pi^2)$
	$Fe(HMBz)_2$	3.08	Room temp	*l*	$^3\Sigma^-(\sigma^2\delta^4\pi^2)$
	$Co(HMBz)_2^+$	2.95 ± 0.08	90–291	*m*	$^3\Sigma^-(\sigma^2\delta^4\pi^2)$
	$Ni(HMBz)_2^{2+}$	3.00 ± 0.09	294	*o*	$^3\Sigma^-(\sigma^2\delta^4\pi^2)$
d^9	$Co(HMBz)_2$	1.86	83–295	*p*	$^2\Pi(\sigma^2\delta^4\pi^3)$

[a] R. Coutts and P. C. Wailes, *Inorg. Nucl. Chem. Lett.*, **3**, 1 (1967). [b] G. Wilkinson and J. M. Birmingham, *J. Amer. Chem. Soc.*, **76**, 4281 (1954). [c] E. O. Fischer and H. Leipfinger, *Z. Naturforsch. B*, **10**, 354 (1957). [d] E. O. Fischer and H. P. Kogler, *Angew. Chem.*, 68, 462 (1956); E. O. Fischer and K. Ulm, *Chem. Ber.*, 95, 692 (1962). [e] F. Engelmann, *Z. Naturforsch. B*, 8, 775 (1953). [f] E. O. Fischer, G. Joos, and W. Meer, *ibid.*, **13**, 456 (1958). [g] G. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, **2**, 95 (1956). [h] D. N. Hendrickson, Y. S. Sohn, and H. B. Gray, *Inorg. Chem.*, 10, 1559 (1971). Moment is almost temperature independent–magnitude depends on anion. [i] E. O. Fischer, G. Joos, and W. Meer, *Z. Naturforsch. B*, **13**, 456 (1958); E. O. Fischer and H. P. Kogler, *Chem. Ber.*, **90**, 250 (1957). [j] E. O. Fischer and U. Piesbergen, *Z. Naturforsch. B*, **11**, 758 (1956). [k] E. O. Fischer and R. Jira, *ibid.*, 8, 217 (1953). [l] E. O. Fischer and F. Rohrscheid, *ibid.*, **17**, 483 (1962). [m] E. O. Fischer and H. H. Lindner, *J. Organometal. Chem.*, **1**, 307 (1964). [n] R. Prins, J. D. W. van Voorst, and C. J. Schinkel, *Chem. Phys. Lett.*, **1**, 54 (1967). [o] H. H. Lindner and E. O. Fischer, *J. Organometal. Chem.*, **12**, P18 (1968). [p] E. O. Fischer and H. H. Lindner, *ibid.*, **2**, 222 (1964). [q] Cp = π-cyclopentadiene, Bz = π-benzene, HMBz = π-hexamethylbenzene, Mes = π-mesitylene.

(NCO); this is very close to the spin-only value and consistent with the esr results, thus casting some doubt on the earlier data. As shown in Figure 7 though, a substantial C_{2v} distortion could lead to a nearly temperature-independent moment close to the spin-only value.

d^2 Systems. For these systems a $^3\Delta(\sigma\delta)$ ground state is predicted at lower Dt/B values, but for larger ligand fields ($Dt/B > 5$) the $^3\Sigma^-(\delta^2)$ level will lie lowest. The neutral d^2 system, $Ti(Cp)_2$, is however, anomalous, being dimeric and diamagnetic,[26] but a species thought to be the vanadocinium cation, $V(Cp)_2^+$, is reported[23] to have a moment of 2.86 BM at 296°K, close to the spin-only value expected for a $^3\Sigma^-(\delta^2)$ ground state. It is though uncertain whether or not this measurement relates to the same compound, $V(Cp)_2Cl$, as was more recently studied by esr techniques.[24] For this latter system a g value of 1.98 has been recorded, which could be compatible with a $^3\Sigma^-$ ground level. Nevertheless, although it is not clear if these results pertain to systems of pseudoaxial symmetry or not, the observed moment, corresponding to two unpaired spins, would seem to indicate either a doubly degenerate lowest level, or else two lowest lying levels sufficiently close together to produce a triplet ground state. A $^3\Delta(\sigma\delta)$ ground state though appears improbable since, as seen from Figure 8, with $k' = 0.7$, a distortion of 10 times the value of ξ would be required to produce a moment of approaching 2.80 BM. A study of the temperature dependence of the moment for $V(Cp)_2^+$ would however clearly be of value.

d^4 Systems. For this system magnetic data are available for only two complexes–the bis(mesitylene)vanadium(I) cation, $V(Mes)_2^+$, and the metallocene chromocene, $Cr(Cp)_2$. For the former compound a moment of 2.80 ± 0.17 BM is found[27] from measurements at 88, 200, and 293°K, and for the latter[28] a value of 3.20 ± 0.16 BM is found from data at 90 and 295°K. For chromocene the reported moment exceeds the spin-only value (2.83 BM) sufficiently to provide reasonable evidence for an orbital contribution to the moment, and a $^3\Delta(\sigma\delta^3)$ ground state, but for the V(I) complex the moment approximates within experimental error to the spin-only figure. However, although Anderson and Drago[29] interpreted their nmr measurements on the bis(arene)vanadium(I) complex as requiring a $^3\Delta(\sigma\delta^3)$, rather than a $^3\Sigma^-(\sigma^2\delta^2)$, ground state, reference to Figure 8 shows that this is hard to reconcile with the experimental result. Thus, once more even $\delta = 10$ does not constitute a large enough distortion to reduce the moment to around the spin-only figure, a value of some 3.0 BM being predicted. It would therefore seem more likely that the ground state is actually $^3\Sigma^-(\sigma^2\delta^2)$ but it is not clear why this is preferred to $^3\Delta(\sigma\delta^3)$ in this case since a simple ligand field approach[4] gives $E(^3\Sigma^-) - E(^3\Delta) = E(\sigma) - E(\delta) - 8B$. Thus if one takes a nephelauxetic ratio of 0.5 and a free-ion B value[30] for V(I) of 594 cm^{-1}, then $^3\Delta(\sigma\delta^3)$ should lie lowest so long as $E(\sigma) - E(\delta) > 2.4$ kK. Since this is well below the range usually encountered for the metallocenes, the implication of a $^3\Sigma^-$ ground state raises some difficulties, and more detailed magnetic studies would be welcome.

For chromocene, $\xi_{\text{free ion}} = 230$ cm^{-1} for Cr(II), and assuming the same orbital reduction factor the experimental data relate to the kT/ξ region from 0.38 to 1.27; from Figure 8 it is seen that these data may be accommodated by postulating a moderate C_{2v} distortion, in this case with Δ some 3–4 times the spin-orbit coupling constant, *i.e.*, a δ level splitting of about 500–600 cm^{-1}. For chromocene the expectation of a $^3\Delta(\sigma\delta^3)$ ground state is backed up by

---

(26) G. W. Watt, L. J. Baye, and F. O. Drummond, *J. Amer. Chem. Soc.*, **88**, 1138 (1966).

(27) E. O. Fischer, G. Joos, and W. Meer, *Z. Naturforsch. B*, **13**, 456 (1958).

(28) F. Engelmann, *Z. Naturforsch. B*, **8**, 775 (1953).

(29) S. E. Anderson, Jr., and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 4244 (1970).

(30) G. C. Allen and K. D. Warren, *Struct. Bonding (Berlin)*, **9**, 49 (1971).

ligand field calculations based on the known Dt, Ds, and B parameter ranges for the other metallocenes[4] and by the nmr data and molecular orbital calculations of Rettig and Drago,[7,31] but more extensive measurements of the temperature dependence of the magnetic moment of $Cr(Cp)_2$ would also be helpful.

If the moderate distortion deduced from the magnetic data is due to a Jahn–Teller instability, it would seem to suggest that the dominantly metal δ level is neither strongly bonding nor strongly antibonding. This is at least consistent with the molecular orbital calculations of Prins[32] which indicate that the δ level is only slightly bonding, the σ level almost nonbonding, and the π level quite strongly antibonding.

d^5 Systems. For these systems the experimental evidence, especially esr measurements,[33-35] provides a clear indication that both a $^2\Delta(\sigma^2\delta^3)$ and a $^2\Sigma^+(\sigma\delta^4)$ ground state may be found, the former for metallocenes and the latter for the bis-arene complexes. In the former case one expects $g_\parallel = 2(2k' + 1)$ and $g_\perp = 0$, for a strictly axial system, with distortion bringing both g tensors toward 2, and for the latter g should be nearly isotropic and close to 2. The case of manganocene appears to be anomalous since although both magnetic moment data[36] and esr results[37] support a high-spin $^6\Sigma^+(\sigma\delta^2\pi^2)$ ground state, recent He(I) photoelectron spectra[38] were thought to suggest a low-spin $^2\Delta(\sigma^2\delta^3)$ ground level, and this case has not therefore been considered further.

For d^5 configurations the ligand field model shows that the energy separation between the $^2\Sigma^+(\sigma\delta^4)$ and the $^2\Delta(\sigma^2\delta^3)$ levels is given by $E(^2\Sigma^+) - E(^2\Delta) = E(\delta) - E(\sigma) + 20B$, to the first order.[5] If, for example, the complexes $Fe(Cp)_2^+$ and $Cr(Bz)_2^+$ are considered, taking β as 0.5 as before, then with[30] $B_{\text{free ion}}(\text{Fe(III)}) = 1035\ \text{cm}^{-1}$ and $B_{\text{free ion}}(\text{Cr(I)}) = 652\ \text{cm}^{-1}$, the $^2\Delta(\sigma^2\delta^3)$ level will lie lower if $E(\sigma) - E(\delta)$ is less than 6.52 kK (for $Cr(Bz)_2^+$) or less than 10.35 kK (for $Fe(Cp)_2^+$). For the metallocene $Fe(Cp)_2^+$ the separation between the σ and δ levels is most unlikely to approach 10 kK, but for the bis-arene compounds, because of the greater importance of the δ level in back-bonding to the metal, the separation will probably be greater than that for the metallocenes, even though the overall d-orbital splitting might be less. Consequently the ligand field model is quite consistent with the experimental observation of a $^2\Delta$ ground state for the ferrocinium cation and a $^2\Sigma^+$ level for $Cr(Bz)_2^+$.

As expected therefore from the esr data both $Cr(Bz)_2^+$ and $V(Bz)_2$ with orbital singlet ground states show temperature-independent magnetic moments very close to the spin-only value for one unpaired electron.[27,39] On the other hand for the ferrocinium cation an early measurement of the moment[40] gave a value of 2.26 BM, providing good evidence for an orbital contribution, and the recent detailed measurements of Hendrickson, Sohn, and Gray[41] give values lying mostly between 2.4 and 2.6 BM, depending upon the nature of the anion.

However, despite the general consistency of these results with the esr data of Prins and Reinders,[33] which indicated a $^2\Delta$ ground state with a fairly small C_{2v} distortion, the observed moments were found to be virtually temperature independent over the range 50–300°K, whereas the theory required a small but definite (*ca.* 0.15 BM) variation. Although Hendrickson, *et al.*,[41] used the simplified nonexponential form of the Van Vleck equation, which is not strictly justified under the circumstances, the use of the full form in the present work does not materially affect their conclusions. Thus, even with an orbital reduction factor of 0.7 (Figure 7), although it is possible to reproduce the average values of $\langle\mu\rangle$ over the range studied, the predicted temperature dependence significantly exceeds that observed.

It therefore seems likely that one of the two alternative explanations put forward by Hendrickson, *et al.*, is valid—*i.e.*, that either the extent of the C_{2v} distortion is temperature dependent or, more probably, that the results are due to the thermal population of a low-lying $^2\Sigma^+(\sigma\delta^4)$ level. Thus, from the relationship between $E(^2\Delta)$ and $E(^2\Sigma^+)$ given above, it follows, assuming $Dt = 0.55Ds$, that $^2\Delta(\sigma^2\delta^3)$ will lie lower as long as $Dt/B < 8.8$, or for $Dt = 0.50Ds$ if $Dt/B < 6.66$. Since Dt/B values in the region of 6–7 have been observed for some metallocenes, it is therefore quite possible that the $^2\Sigma^+$ level should lie only about 1 kK or less above the $^2\Delta$ ground state, thereby producing an almost temperature-independent moment for the $Fe(Cp)_2^+$ salts. Taking $\xi_{\text{free ion}}(\text{Fe(III)})$ as $450\ \text{cm}^{-1}$ and $k' = 0.7$ (Figure 7), the average values of the moments observed[41] can be reproduced with $\Delta = 200\text{–}400\ \text{cm}^{-1}$ or, taking $k' = 0.8$, with $\Delta = 300\text{–}600\ \text{cm}^{-1}$, in reasonable agreement with the values $k' = 0.8$ and $\Delta = 400\ \text{cm}^{-1}$ deduced from the esr data of Prins and Reinders.[33] The extent of the distortion indicated by the susceptibility measurements is thus fairly small, so that if this arises from a Jahn–Teller instability, its magnitude may be rationalized along the same lines as for the d^4 $^3\Delta(\sigma\delta^3)$ ground state.

d^7 Systems. Magnetic susceptibility data have been reported for four complexes of this configuration. For $Co(Cp)_2$ and $Ni(Cp)_2^+$ moments of 1.76 ± 0.07 and 1.82 ± 0.09 BM, respectively, have been found[28,42] from measurements at 90°K and room temperature, while for $Co(HMBz)_2^{2+}$ a moment of 1.73 ± 0.05 BM was obtained[18] from results at 90, 193, and 290°K. For $Fe(HMBz)_2^+$ a value of 1.89 BM has been reported[17] from a single room-temperature measurement.

On the assumption of a $\sigma^2\delta^4\pi$ orbital occupation a $^2\Pi$ ground state will ensue with a single unpaired spin. However, inspection of the results shown in Table V and in Figure 9 shows that the general expectation will not necessarily be that of a temperature-independent spin-only moment and that this result should follow only for quite significant distortions from pseudoaxial symmetry. The $^2\Pi(\sigma^2\delta^4\pi)$ ground state seems though to be well established, at least for $Co(Cp)_2$, $Co(HMBz)_2^{2+}$, and $Fe(HMBz)_2^+$, by the nmr results of Rettig and Drago[31] and of Anderson and Drago,[29] and for $Co(Cp)_2$ and $Fe(HMBz)_2^+$ esr data provide further support. The latter are also indicative of appreciable deviations from axial geometry since for a $^2\Pi(\sigma^2\delta^4\pi)$ ground state

---

(31) M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, 91, 1361 (1969).

(32) R. Prins, *J. Chem. Phys.*, 50, 4804 (1969).

(33) R. Prins and F. J. Reinders, *J. Amer. Chem. Soc.*, 91, 4929 (1969); R. Prins, *Mol. Phys.*, 19, 603 (1970).

(34) G. Henrici-Olivi and S. Olivi, *Z. Phys. Chem. (Frankfurt am Main)*, 56, 223 (1967).

(35) R. Prins and F. J. Reinders, *Chem. Phys. Lett.*, 3, 45 (1969).

(36) G. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, 2, 95 (1956).

(37) J. Voitlander and E. Schimitschek, *Z. Elektrochem.*, 61, 941 (1957).

(38) J. W. Rabelais, L. O. Werme, T. Bergmark, L. Karlssohn, M. Hussian, and K. Seigbahn, *J. Chem. Phys.*, 57, 1185 (1972).

(39) E. O. Fischer and U. Piesbergen, *Z. Naturforsch. B*, 11, 758 (1956).

(40) G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Amer. Chem. Soc.*, 74, 2125 (1952).

(41) D. N. Hendrickson, Y. S. Sohn, and H. B. Gray, *Inorg. Chem.*, 10, 1559 (1971).

(42) E. O. Fischer and R. Jira, *Z. Naturforsch. B*, 8, 217 (1953).

one calculates to the first order $g_{\parallel} = 2(k' - 1)$ and $g_{\perp} = 0$, which for $k' = 1$ would give both g tensors equal to zero. The observation[43] of two g values of 1.69 and 1.76 for $Co(Cp)_2$ and of a more anisotropic result[44] for $Fe(HMBz)_2^+$ thus provides clear evidence for a distorted axial structure in these systems.

However, neither the above esr results due to Ammeter and Swalen[43] nor the earlier investigation by Nussbaum and Voitlander[45] (which gave g values of 1.67 and 1.74) led to unambiguous conclusions about the nature and extent of the distortion in $Co(Cp)_2$, and it seems probable that the combined effects of spin-orbit coupling, a static distortion, and a dynamic Jahn-Teller instability, all of comparable magnitude, have to be taken into account. Because of this and the limited accuracy of the data available, the experimental magnetic moment values are now interpreted simply on the basis of the $^2\Pi(\sigma^2\delta^4\pi)$ level being split by an amount, Δ, without making any assumptions as to the origin of this distortion.

For $Co(Cp)_2$ $\xi_{\text{free ion}}(\text{Co(II)}) = 530\ \text{cm}^{-1}$, and with $k' = 0.7$-0.8 a distortion, Δ, of about 3-4 times the spin-orbit coupling constant is required to produce an essentially temperature-independent moment approaching the observed value, *i.e.*, a splitting of some 1000-1500 cm^{-1}. Unfortunately, although the temperature dependence of the moment is quite strongly correlated with the extent of the distortion, the absolute value is rather insensitive to this parameter within the range $\delta \approx 3$-10, so that in estimating the extent of the distortion the smallest value required to produce an effectively temperature-independent moment has been taken. For the kT/ξ range involved—*ca.* 0.15-0.55—the calculated value is somewhat less than the experimental, but the discrepancy is relatively small (*ca.* 0.10 BM) and may well be due to the neglect of second-order Zeeman contributions arising from interactions outside the ground-state manifold. For the other d^7 systems discussed the kT/ξ ranges concerned are very similar, and the extent of distortion suggested by the moments is of comparable magnitude.

For the $4d^7$ system $Rh(HMBz)_2^{2+}$, a moment of 1.32 ± 0.08 BM is obtained from measurements at 90, 193, and 291°K. Taking $\xi_{\text{free ion}}(\text{Rh(II)})$ as 1235 cm^{-1} and $k' = 0.7$, the relevant kT/ξ range is from about 0.07 to 0.24, and the observed value can be reasonably well represented with Δ some 1.5 times ξ—*i.e.*, about 1300 cm^{-1}. Thus, for all the d^7 systems considered the extent of the distortions indicated by the magnetic moment data is appreciably greater than that encountered for systems in which the orbital degeneracy involved the δ level. However, if the distortions are in both cases due to Jahn-Teller instabilities, this result is not altogether unexpected since the π level is thought to be appreciably more strongly involved in the bonding scheme and to be markedly antibonding in character. This result would thus parallel that found for O_h systems in which much larger Jahn-Teller effects are found for the σ-bonding e_g level than for the π-bonding t_{2g} level.

d^9 Systems. The only system representing this configuration for which data are available is the bis(hexamethylbenzene)cobalt molecule, $Co(HMBz)_2$, which was shown[46] to have a permanent dipole moment of 1.78 D, thereby providing unequivocal evidence of distortion from axial symmetry. From results at 83 and 295°K a magnetic moment of 1.86 ± 0.08 BM was found.

For $Co(HMBz)_2$ Nicholson and Longuet-Higgins[47] concluded that a pseudo Jahn-Teller effect was responsible for the observed distortion; the normal Jahn-Teller process was thought to be unlikely to be able to account for the experimental results since the d^7 $Co(Cp)_2$ system, also Jahn-Teller unstable, showed no dipole moment,[48] and revealed no indication of significant static distortions under X-ray diffraction studies.[49]

Nevertheless, irrespective of the origin of the distortion, the magnetic data provide further evidence for an appreciable splitting of the π level. Taking $\xi_{\text{free atom}}(\text{Co(0)})$ as 515 cm^{-1} and $k' = 0.7$ as before, the experimental results refer to the kT/ξ range from 0.17 to 0.57; with an orbital reduction factor as low as 0.7 the moment is not strongly temperature dependent even in the absence of distortions but for part of the range is in excess of 2.0 BM, and a distortion of about 3 times the spin-orbit coupling constant is required to produce a moment of around 1.85 BM, which is then virtually independent of temperature. This implies that the splitting, Δ, of the π level is of the order of 1100 cm^{-1} for $Co(HMBz)_2$, of the same order of magnitude as deduced for the π-level splittings of the d^7 configurations.

In this case also esr data would be of value since for strictly axial symmetry one predicts $g_{\parallel} = 2(k' + 1)$ and $g_{\perp} = 0$, and the deviation of the g tensors from these results would provide an additional estimate of the extent of the π-level splitting.

Supplementary Material Available. The Appendix, showing listings of magnetic moments, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1317.

---

(43) J. H. Ammeter and J. D. Swalen, *J. Chem. Phys.*, 57, 678 (1972).

(44) H. Brintzinger, G. Palmer, and R. H. Sands, *J. Amer. Chem. Soc.*, 88, 623 (1966).

(45) M. Nussbaum and J. Voitlander, *Z. Naturforsch. A*, 20, 1417 (1965).

(46) E. O. Fischer and H. H. Lindner, *J. Organometal. Chem.*, 2, 222 (1964).

(47) B. J. Nicholson and H. C. Longuet-Higgins, *Mol. Phys.*, 9, 461 (1965).

(48) E. O. Fischer and S. Schreiner, *Chem. Ber.*, 92, 938 (1959).

(49) W. Pfab and E. O. Fischer, *Z. Anorg. Allg. Chem.*, 274, 317 (1953).