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Spectroscopic and Magnetic Studies of the 3d Metallocenes

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Received April 17, 1977

The electronic spectra of the metallocenes, MCp_2, and 1,1′-dimethylmetallocenes, $M(MeCp)_2$, of the first transition series (M = V, Cr, Mn, Fe, Co, Ni) have been measured between 10 and 50 $cm^{-1} \times 10^3$ in isooctane solution. Assignments are proposed for the d–d and charge-transfer transitions observed, these being based in the latter case largely on the band shifts produced by methyl substitution. For the V, Cr, Mn, and Fe compounds the charge-transfer bands appear to correspond only to ligand → metal excitations ($e_{2u} \rightarrow e_{2g}, a_{1g}, e_{1g}$) but for the Co compounds (and possibly also for Ni) evidence is also found for metal → ligand ($e_{1g} \rightarrow e_{2u}$) transitions. For the V, Cr, Co, and Ni compounds the paramagnetic susceptibilities have been determined in toluene solution by NMR in the temperature range 183–298 K and for the parent compounds also by the Gouy method using solid samples between 83 and 298 K. The V, Cr, and Ni compounds were found to obey the Curie–Weiss law over the ranges studied, but although the V and Ni complexes yielded the spin-only values for the magnetic moment, a substantial orbital contribution was observed for $CrCp_2$ and $Cr(MeCp)_2$. For $Co(MeCp)_2$ the Curie–Weiss law was obeyed over the limited range accessible, although a moment slightly greater than the spin-only value was obtained, and the parent $CoCp_2$ gave a similar moment but deviated markedly from Curie–Weiss behavior.

Introduction

The ligand field model has been shown in recent years to be of great value in the interpretation of the magnetic properties of the d^x configurations of transition-metal sandwich complexes,[1,2] and its utility also extends to the treatment of the d–d and charge-transfer spectra of such systems.[3-6] Nevertheless, although adequate spectroscopic data have previously been reported[7-10] for the d–d bands of VCp_2, $FeCp_2$, and $NiCp_2$, the other neutral metallocene systems of the 3d series have been little studied in this respect, and no systematic attention has been directed toward understanding the nature of the charge-transfer excitations. We therefore now report the results of a study of the solution spectra in isooctane of all neutral 3d metallocenes, together with their 1,1′-dimethyl derivatives, in which both d–d and charge-transfer transitions may be identified; for the latter excitations, of course, it may be deduced whether the bands observed correspond to ligand → metal or metal → ligand transitions, depending upon whether shifts to lower or to higher energies are observed on methyl substitution.

Moreover, numerous magnetic susceptibility measurements have been made on metallocene systems (see ref 6 for a survey), but the data available for $CrCp_2$ and $CoCp_2$, for which orbital contributions to the moment would be expected, are somewhat fragmentary and relate only to a few temperatures, while very few data at all have been reported for the $M(MeCp)_2$ systems. We have therefore measured the susceptibilities down to liquid-nitrogen temperatures of the parent metallocene systems (M = V, Cr, Co, Ni) by the Gouy technique and have made measurements in toluene solution by the NMR method in the upper part of the temperature range. For the very low-melting dimethyl compounds, however, only the latter method proved feasible, thereby restricting the temperature range to 183–298 K. We have not, however, remeasured the susceptibilities of $MnCp_2$ and $Mn(MeCp)_2$ since these compounds have already been extensively investigated,[11,12] and the brown, low-temperature, form of manganocene is in any case now known[13] not to possess a sandwich structure.

Experimental Section

Metallocenes and 1,1′-Dimethylmetallocenes. These were prepared essentially as described by Evans et al.[14] and had properties agreeing with those there reported. All were purified by repeated vacuum sublimation or distillation and gave satisfactory analyses for carbon, hydrogen, and metal. For the chromium compounds the use of anhydrous chromous chloride, rather than chromic chloride, was found to give greatly improved yields; moreover, if $CrCl_3$ is employed, the water-insoluble[15a] rather than the water-soluble[15b] form should be used since the latter affords only negligible yields of the metallocene.

Isooctane (2,2,4-Trimethylpentane). BDH spectroscopic grade isooctane was passed three times through a silica gel column, activated at 300 °C, and distilled onto and from lithium aluminum hydride. It was then vacuum degassed and distilled under pure nitrogen immediately prior to use.

Toluene. Reagent grade material was shaken with concentrated sulfuric acid, care being taken to keep the temperature below 30 °C. The acid layer was then removed and the process repeated until darkening was negligible. The product was then removed by decantation, distilled under pure nitrogen, and finally vacuum degassed and distilled when required.

Spectroscopic Measurements. These were made in a vacuum apparatus containing a silica glass cell, the solvent being manipulated by vacuum distillation and the substrates by vacuum sublimation or distillation. Concentrations were determined by atomic absorption analysis (verified by colorimetric determinations), and Beer's law was established over the range of concentrations used. The optical densities were measured using a Cary 17 spectrophotometer, and diffuse-reflectance measurements were also made on solid samples, using a Beckman DK2A spectroreflectometer with a magnesium oxide reference.

Magnetic Measurements. For solid samples the susceptibilities were measured on a Newport Instruments variable-temperature Gouy balance, and for toluene solutions a modification[16] of the Evans[17] NMR method was adopted, using a Varian 90-MHz instrument. The appropriate corrections for the temperature dependence of the density of toluene were made.

Theory

Spectra. The theoretical basis for the interpretation of the d–d spectra of all d^x configurations in pseudoaxial ($C_{\infty v}$) symmetry has already been described[3-5] and summarized in a recent review.[6] A framework for the understanding of the

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Table I. Allowed Charge-Transfer Transitions and Polarizations for Various d^x Ground States of Metallocenes

d^5, ${}^6A_{1g}$ ($e_{2g}{}^2a_{1g}e_{1g}{}^2$)

One-electron excitation	Excited states[a]	One-electron excitation	Excited states[a]
$e_{1u} \rightarrow e_{2g}$ (L → M)	${}^6E_{1u}(x, y)$ + (${}^6E_{2u}$)	$e_{1u} \rightarrow e_{1g}$ (L → M)	(${}^6A_{1u}$) + ${}^6A_{2u}(z)$ + (${}^6E_{2u}$)
$e_{1u} \rightarrow a_{1g}$ (L → M)	${}^6E_{1u}(x, y)$	$e_{1g} \rightarrow e_{2u}$ (M → L)	${}^6E_{1u}(x, y)$ + (${}^6E_{2u}$)

d^x (x = 3–8) Ground States

Ground state	Excited states	Ground state	Excited states
d^3, ${}^4A_{2g}$	${}^4E_{1u}(x,y)$; ${}^4A_{1u}(z)$	d^6, ${}^1A_{1g}$	${}^1E_{1u}(x,y)$; ${}^1A_{2u}(z)$
d^4, ${}^3E_{2g}$	${}^3E_{1u}(x,y)$; ${}^3E_{2u}(x,y;z)$	d^7, ${}^2E_{1g}$	${}^2E_{2u}(x,y)$; ${}^2E_{1u}(z)$
d^5, ${}^2E_{2g}$	${}^2E_{1u}(x,y)$; ${}^2E_{2u}(x,y;z)$	d^8, ${}^3A_{2g}$	${}^3E_{1u}(x,y)$; ${}^3A_{1u}(z)$

[a] Upper levels of forbidden transitions shown in parentheses.

allowed charge-transfer transitions was also proposed[6] in which it was assumed that such bands as were observed were most likely to be due to transitions from mainly ligand orbitals of odd symmetry, derived from the π orbitals of the Cp rings, to predominantly metal 3d levels of even symmetry (see Figure 1). This restriction of attention to the interaction between the metal orbitals and the ligand π levels was also adopted by Sohn, Hendrickson, and Gray,[9] in treating the spectra of $FeCp_2$ and $[FeCp_2]^+$, and may be at least partially justified on the grounds that most of the highest occupied and lowest unoccupied molecular orbitals will arise in this way, even though the σ–π separability assumption rests on less secure ground here than for conjugated carbocyclic systems.

The most likely ligand → metal (L → M) transitions are derived (using the D_{5d} symmetry labels) from the one-electron excitations $e_{1u} \rightarrow e_{2g}$, $e_{1u} \rightarrow a_{1g}$, and $e_{1u} \rightarrow e_g$, depending upon the d-orbital occupations, but there also arises the possibility of metal → ligand (M → L) transitions, especially for the d^7 and d^8 systems, where these would correspond to the excitation $e_{1g} \rightarrow e_{2u}$. The excited states thus arising, together with the allowed or forbidden character of transitions thereto, have been tabulated[6] for most d^x (x = 3–8) ground states, and the results for the d^5, ${}^6A_{1g}$ ($e_{2g}{}^2a_{1g}e_{1g}{}^2$) ground level, not previously given, are included in Table I.

Magnetic Properties. The magnetic properties of d^x ground states in $C_{\infty v}$ symmetry (which is more convenient for use in this context than D_{5d} symmetry) have already been treated in detail,[1] including the effects of C_{2v} distortion, and calculations have also been made[2] of the second-order Zeeman contributions to the susceptibility and of the consequences of second-order spin–orbit effects in systems with nonorbitally degenerate ground states. However, no estimates have as yet been made of the effects of spin–orbit mixing of excited states with the ground level for orbitally degenerate systems, and for completeness we now report the results for $C_{\infty v}$ systems with d^1 (d^5), ${}^2\Delta$ (${}^2E_{2g}$), d^2 (d^4), ${}^3\Delta$ (${}^3E_{2g}$), and d^7 (d^9), ${}^2\Pi$ (${}^2E_{1g}$) ground states.

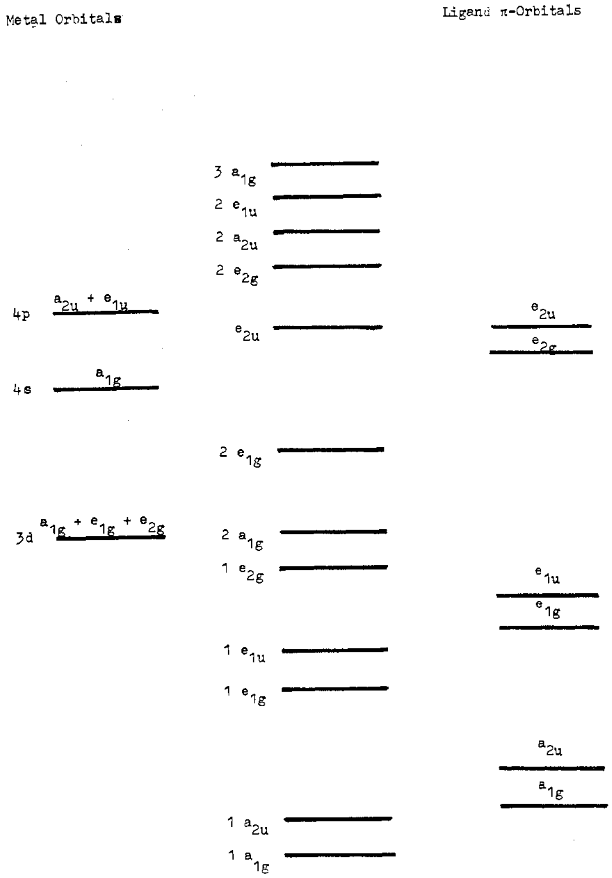

Figure 1. Molecular orbital scheme for metallocenes.

Using the full space–spin symmetry adapted ground- and excited-state wave functions, obtained as previously described,[3] the spin–orbit admixed ground manifold wave functions were obtained by second-order perturbation theory. It is not necessary here to consider exited states differing in spin multiplicity from the ground state since there are no nonvanishing Zeeman-operator matrix elements between them, and there are, moreover, no nonzero contributions for any excited states, due to the $\hat{S}$ operators or to $\hat{L}_z$. In $C_{\infty v}$ symmetry, therefore, the expressions for $\mu_{\parallel}$ are unchanged, but the nonzero $\hat{L}_x$ and $\hat{L}_y$ terms lead to modified expressions for $\mu_{\perp}$. For the d^1 (d^5) and d^2 (d^4) cases the extra terms correspond only to second-order interactions, and all of the matrix elements are changed by a constant factor, but for the d^7 (d^9) system the $\hat{L}_x$ and $\hat{L}_y$ operators now connect the two components of the Π^* ($\pm{}^1/_2$) Kramers doublet, thus leading to a first-order contribution as well and a more complex result. Thus one finds

$$d^1\,(d^5),\ {}^2\Delta:\ \mu_{\perp} = 3^{1/2}(1 - \xi/\Delta E)[(\tanh x)/x]^{1/2}$$

$$d^2\,(d^4),\ {}^3\Delta:\ \mu_{\perp} = 2(3^{1/2})(1 - 2\xi/\Delta E)[(e^x - e^{-x})/x(1 + e^x + e^{-x})]^{1/2}$$

$$d^7\,(d^9),\ {}^2\Pi:\ \mu_{\perp} = 3^{1/2}\left[\frac{9\xi^2}{(\Delta E)^2(1 + e^{-x})} + \frac{2(1 + 5\xi/2\Delta E)^2 \tanh (x/2)}{x}\right]^{1/2}$$

where ξ is the effective spin–orbit coupling constant, ΔE is the average energy of the interacting states above the ground level, and $x = \xi/kT$. For the d^1 (d^5) and d^2 (d^4) cases the results are independent of the sign of x, but for the d^7 (d^9) cases x is positive for d^7 and negative for d^9, with ξ positive in both instances.

For the d^4 and d^5 cases, typified by $CrCp_2$ and $[FeCp_2]^+$, the inclusion of the spin–orbit terms produces only very small effects: thus the interacting states are usually at least some 15–20 $cm^{-1} \times 10^3$ above the ground level, so that with free-ion ξ values[18] for Cr(II) and Fe(III) of 230 and 460 cm^{-1} the μ values will be reduced only by factors of about 0.975, which would scarcely be significant for the moments actually observed. For $CoCp_2$, on the other hand, the free-ion ξ value will be rather greater [ξ(Co(II)) = 515 cm^{-1}] and the spin–orbit contributions are in any case larger and especially significant for a doublet ground state. In fact calculations show that an increase of the order of 0.10 μ_β may be expected from this source, and expressions for the excited-state contributions in the presence of a C_{2v} distortion may similarly be quite readily derived.[19] We have not, however, attempted to fit our

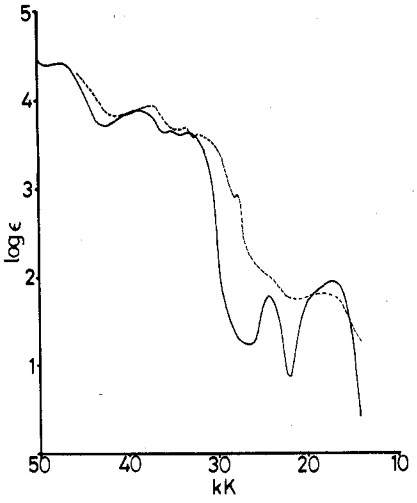

Figure 2. Electronic spectra of VCp_2 (—) and $V(MeCp)_2$ (---) in isooctane solution.

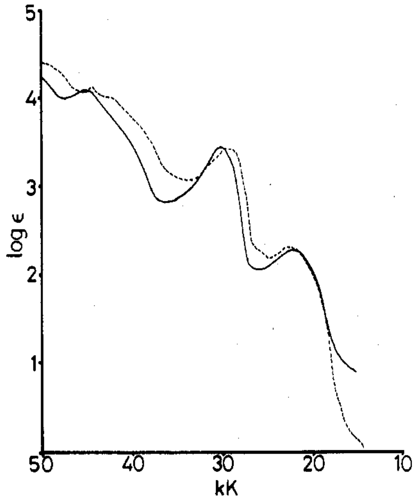

Figure 3. Electronic spectra of $CrCp_2$ (—) and $Cr(MeCp)_2$ (---) in isooctane solution.

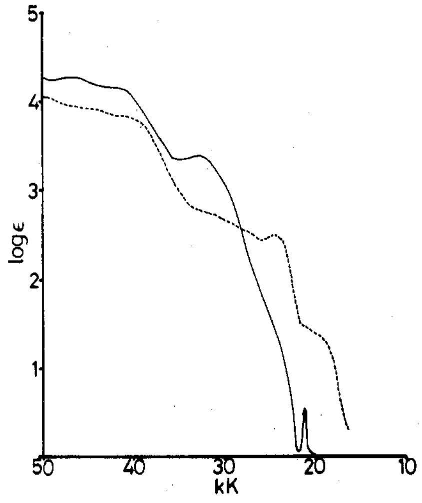

Figure 4. Electronic spectra of $MnCp_2$ (—) and $Mn(Cp)_2$ (---) in isooctane solution.

data to such equations since the measured average moment is not strongly temperature dependent and since the necessary anisotropic susceptibility data are lacking.

Results and Discussion

The electronic spectra in isooctane solution of the MCp_2 and $M(MeCp)_2$ complexes of V, Cr, Mn, Fe, Co, and Ni are shown, respectively, in Figures 2–7, and for the MCp_2 systems the principal features and their assignments are listed in Table II. We deal first with the d–d bands, which for VCp_2, $FeCp_2$, and $NiCp_2$ have already been studied in some detail.[7-10] For these compounds our results are in essential agreement with the earlier data, although the present spectra seem slightly less

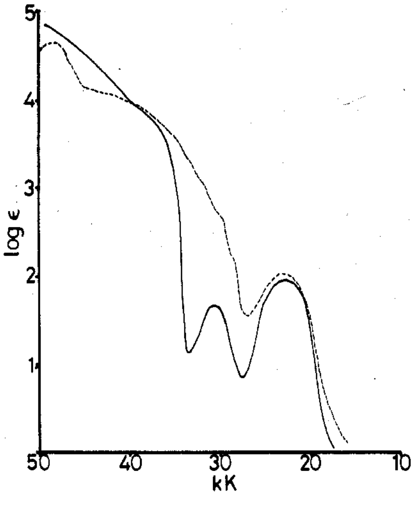

Figure 5. Electronic spectra of $FeCp_2$ (—) and $Fe(MeCp)_2$ (---) in isooctane solution.

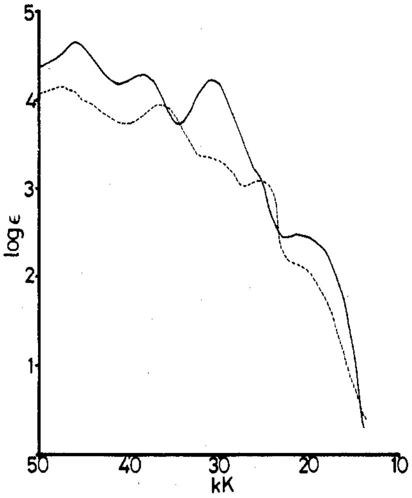

Figure 6. Electronic spectra of $CoCp_2$ (—) and $Co(MeCp)_2$ (---) in isooctane solution.

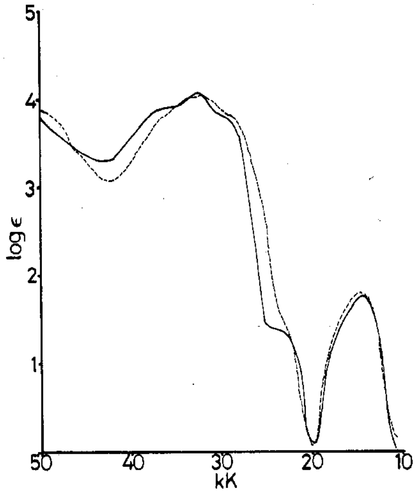

Figure 7. Electronic spectra of $NiCp_2$ (—) and $Ni(MeCp)_2$ (---) in isooctane solution.

Table II. Electronic Spectra of d^x (x = 3-8) Metallocenes

Band energy, cm^{-1}, × 10^3	Type	Assignment	log ϵ	Methyl shift, cm^{-1} × 10^3
		VCp_2, d^3, $^4A_{2g}$		
17.24	d-d	$^4A_{2g} \rightarrow {}^4E_{1g}$	1.96	
19.23	d-d	$^4A_{2g} \rightarrow {}^4E_{2g}$	1.84	
24.27	d-d	$^4A_{2g} \rightarrow {}^4E_{1g}$	1.79	
33.33	L → M	$e_{1u} \rightarrow e_{2g}$, $^4A_{2g} \rightarrow {}^4E_{1u}$	3.65	−1.08
38.92	L → M	$e_{1u} \rightarrow a_{1g}$, $^4A_{2g} \rightarrow {}^4E_{1u}$	3.91	−1.18
47.39	L → M	$e_{1u} \rightarrow e_{1g}$, $^4A_{2g} \rightarrow {}^4A_{1u}$	4.42	Negative
		$CrCp_2$, d^4, $^3E_{2g}$		
21.97	d-d	$^3E_{2g} \rightarrow 3\,{}^3E_{1g}$, $^3E_{2g}$, $^3A_{1g}$, $^3A_{2g}$	2.27	
29.59	L → M	$e_{1u} \rightarrow e_{2g}$, $^3E_{2g} \rightarrow {}^3E_{1u}$	3.43	−0.77
40.00	L → M	$e_{1u} \rightarrow a_{1g}$, $^3E_{2g} \rightarrow {}^3E_{1u} + {}^3E_{2u}$	3.55	−1.54
44.64	L → M		4.08	−0.78
>50	L → M	$e_{1u} \rightarrow e_{1g}$, $^3E_{2g} \rightarrow {}^3E_{1u} + 2\,{}^3E_{2u}$	4.25	Negative
		$MnCp_2$, d^5, $^6A_{1g}$		
19.61	d-d	$^6A_{1g} \rightarrow {}^4A_{1g}$, $^4E_{1g}$, $^4E_{2g}$	0.55	
24.69	?[a]	$^6A_{1g} \rightarrow {}^4A_{1g}$, $^4A_{2g}$ or $^6A_{1g} \rightarrow {}^6E_{1u}$	1.79	
33.00	L → M	$e_{1u} \rightarrow a_{1g}$, $^6A_{1g} \rightarrow {}^6E_{1u}$	3.34	
42.37	L → M	$e_{1u} \rightarrow e_{1g}$, $^6A_{1g} \rightarrow {}^6A_{2u}$	4.13	
46.95	L → M		4.25	
		$Mn(MeCp)_2$, d^5, $^2E_{2g}$		
19.53	d-d	$^2E_{2g} \rightarrow 3\,{}^2E_{1g}$, $2\,{}^2E_{2g}$, $^2A_{1g}$, $^2A_{2g}$	1.34	
24.39	L → M	$e_{1u} \rightarrow e_{2g}$, $^2E_{2g} \rightarrow {}^2E_{1u}$	2.49	
31.25 sh	L → M		2.72	
39.22	L → M	$e_{1u} \rightarrow e_{1g}$, $^2E_{2g} \rightarrow {}^2E_{1u} + 2\,{}^2E_{2u}$	3.75	
42.92	L → M		3.88	
50	L → M		4.05	
		$FeCp_2$, d^6, $^1A_{1g}$		
22.73	d-d	$^1A_{1g} \rightarrow {}^1E_{1g}$, $^1E_{2g}$	1.94	
30.77	d-d	$^1A_{1g} \rightarrow {}^1E_{1g}$	1.65	
38.17 sh	L → M	Forbidden $e_{1u} \rightarrow e_{1g}$ transitions (?)	3.85	?
41.67 sh	L → M		4.13	−0.42
50	L → M	$e_{1u} \rightarrow e_{1g}$, $^1A_{1g} \rightarrow {}^1A_{2u}$	4.75	−1.22
		$CoCp_2$, d^7, $^2E_{1g}$		
15.15	d-d	$^2E_{1g} \rightarrow {}^2A_{2g}$, $2\,{}^2E_{2g}$, $^2A_{1g}$, $^2E_{1g}$	1.23	
16.39	d-d		1.86	
17.86	d-d		2.21	
21.19	d-d		2.48	
27.03	L → M	$e_{1u} \rightarrow e_{1g}$, $^2E_{1g} \rightarrow 3\,{}^2E_{1u}$	3.46	−1.39
30.77	L → M		4.24	Negative
38.46	L → M		4.28	−2.23
46.08	M → L	$e_{1g} \rightarrow e_{2u}$, $^2E_{1g} \rightarrow {}^2E_{2u}$	4.66	+1.10
		$NiCp_2$, d^8, $^3A_{2g}$		
11.74	d-d	$^3A_{2g} \rightarrow {}^1A_{1g}$	0.60	
14.49	d-d	$^3A_{2g} \rightarrow {}^3E_{1g}$	1.75	
16.95	d-d	$^3A_{2g} \rightarrow {}^3E_{2g}$	1.40	
23.04	d-d	$^3A_{2g} \rightarrow {}^3E_{1g}$	1.35	
29.50	L → M	$e_{1u} \rightarrow e_{1g}$, $^3A_{2g} \rightarrow {}^3A_{1u}$ + forbidden transitions	3.79	−1.23
32.63	L → M		4.05	−0.63
36.10	L → M		3.89	−2.20
>50	M → L	$e_{1g} \rightarrow e_{2u}$, $^3A_{2g} \rightarrow {}^3E_{1u}$ (?)	3.90	?

[a] Either d-d or $e_{1u} \rightarrow e_{2g}$, or possibly both.

well resolved, and the same assignments and parameters as previously suggested[6] may be deduced. For the $CrCp_2$ and $CoCp_2$ complexes, however, only fragmentary spectroscopic data have hitherto been reported,[6,20] while for $MnCp_2$ the solution spectrum has not been presented diagramatically.[21]

The ligand field splitting pattern of the d-orbital set in pseudoaxial, $C_{\infty v}$, symmetry has already been discussed,[1,3-6] and for metallocene systems the one-electron ordering $\delta < \sigma \ll \pi$ is found. The splitting may be represented in terms of the parameters Ds and Dt (or ϵ_1 and ϵ_2) and the interelectronic repulsions via the familiar Racah parameters, B and C. For the MCp_2 systems the ratio $Dt/Ds = 0.55$ was found[6] to be the most generally appropriate, together with the simple assumption $C = 4B$, and Tanabe-Sugano type diagrams have been given for all d^x configurations.[4-6]

For the d^4 complex, $CrCp_2$ magnetic moment and PES measurements[14,22,23] have clearly established the $^3\Delta$ ($\sigma\delta^3$) ground state (also vide infra), and the first spin-allowed transitions are found[4,6] (neglecting the very low-lying $^3\Sigma$ ($\sigma^2\delta^2$) level) to be a closely juxtaposed group of levels, $2\,{}^3\Pi$, $^3\Phi$, ^3H ($\sigma\pi\delta^2$), and $^3\Pi$ ($\pi\delta^3$). Consequently, the rather broad band system with a peak at 21.97 cm^{-1} × 10^3 (ϵ_{max} 186) may reasonably be thus assigned (cf. Krieger and Voitlander[24] who quoted an unpubished source reporting a broad band near 22 cm^{-1} × 10^3). With essentially only one d-d band observable it is clearly not possible to derive a unique value for B, but if a value for Dt/B of ca. 4.80 is assumed (based on results for VCp_2), one obtains $B \approx 560$ cm^{-1} or, taking[25] B_{gas} (Cr^{2+}) as 808 cm^{-1}, a nephelauxetic ratio β of 0.69, which is slightly larger than found[6] for other neutral metallocenes. In the spectrum, however, there is a suggestion of a weak inflection at ca. 15–16 cm^{-1} × 10^3, more noticeable in Cr(MeCp)$_2$, which might reasonably be attributed to a spin-forbidden transition, possibly $^3\Delta$ ($\sigma\delta^3$) → $^1\Sigma^+$ (δ^4), and on this basis a B value of ca. 430 cm^{-1} would result (β = 0.53), which is quite comparable to other B values for the series.[6] Thus, although it is not possible to define B accurately for CrCp$_2$, the above estimates for β probably represent a reasonable range of values.

For the d^7 CoCp$_2$ system, with a $^2\Pi$ ($\sigma^2\delta^4\pi$) ground state, a large number of spin-allowed transitions are again expected to occur within a narrow compass.[6] Thus the lowest energy bands should represent transitions to the $^2\Sigma^-$, $^2\Delta$ ($\sigma\pi^2\delta^4$) and $^2\Sigma^+$, $^2\Gamma$, $^2\Delta$, $^2\Sigma$ ($\sigma^2\pi^2\delta^3$) levels, clearly corresponding to the broad band observed with a maximum at 21.19 cm^{-1} × 10^3 (ϵ 302). This absorption does, however, show weaker shoulders at 15.15, 16.39, and 17.86 cm^{-1} × 10^3, and these four features do in fact correspond rather well to the four groups of levels predicted in the Tanabe–Sugano diagram,[6] viz.: $^2\Sigma^-$ ($\sigma\pi^2\delta^4$); $^2\Delta$ ($\sigma\pi^2\delta^4$) and $^2\Sigma^+$ ($\sigma^2\pi^2\delta^3$); $^2\Gamma$ and $^2\Delta$ ($\sigma^2\pi^2\delta^3$); and $^2\Sigma^-$ ($\sigma^2\pi^2\delta^3$). The relative positions of these groups of levels are, however, rather insensitive to the Dt/B value, although interpolation[6] from the Ds, Dt, and B values for FeCp$_2$ and NiCp$_2$ does yield a reasonable fit, with $B \approx$ 490 cm^{-1} ($\beta \approx$ 0.5). A previous investigation of the spectrum of crystalline CoCp$_2$, due to Ammeter and Swalen,[20] also found only one broad d–d band, extending from 15 to 20 cm^{-1} × 10^3 with maxima at 17.0 and 18.3 cm^{-1} × 10^3, which is paralleled closely by our own reflectance measurements. In both cases, however, as in the solution spectrum, the absorption shows a sharp rise above about 22.5 cm^{-1} × 10^3.

For all the neutral metallocenes but one, there is no dramatic difference between the spectra of the parent and methyl-substituted systems, although as might be anticipated the M(MeCp)$_2$ compounds generally show broader and less well-resolved bands: for the Mn complexes, however, there is a striking dissimilarity between the two species, which requires further elaboration and a consideration of all available data for these two systems. Thus, recent ESR and magnetic studies[21,26] have shown that MnCp$_2$ lies very close to the high-spin–low-spin crossover point for d^5 systems, while for Mn(MeCp)$_2$ a thermal equilibrium between high- and low-spin species may be encountered. In short, magnetic moment measurements show that MnCp$_2$ displays the high-spin $^6\Sigma^+$ ($\sigma\pi^2\delta^2$) ground state, either as the pure pink form or in solid solution in MgCp$_2$, and a similar result holds for solutions in ether or benzene.[11] For the brown form, however, the magnetic measurements are of doubtful significance since the symmetry is not pseudoaxial and some uncertainly therefore also attaches to the magnetic data for pure Mn(MeCp)$_2$. Nevertheless, ESR measurements on MnCp$_2$ in dilute solid solution show that either a high-spin $^6\Sigma^+$ or a low-spin $^2\Delta$ ($\sigma^2\delta^3$) ground state may occur, depending upon the nature of the host lattice, while for Mn(MeCp)$_2$ the low-spin ground state is generally found.[21,26] However, magnetic susceptibility data for toluene solutions show that for Mn(MeCp)$_2$ a thermal equilibrium results, with the low-spin form only marginally more stable,[26] a conclusion supported by the PES studies of Evans et al.,[14] and finally the electronic spectra of MnCp$_2$ and Mn(MeCp)$_2$ in methylcyclohexane solution were interpreted by Switzer et al.[20] in terms of a high-spin ground state for the former and a low-spin ground level for the latter.

Our own electronic spectra (Figure 4) closely parallel the general outline of the results of Switzer et al.,[21] although there are minor differences in peak positions and extinction coefficients. For a high-spin $^6\Sigma^+$ ground state there will be no spin-allowed d–d transitions, so that the quite well-defined peak (ϵ ~3.6) at 21.05 cm^{-1} × 10^3 is readily assigned as a spin-forbidden excitation, probably[6] $^6\Sigma^+ \rightarrow {}^4\Sigma^+$, $^4\Gamma$, $^4\Delta$, with the rather weak shoulder (ϵ 61) at 24.7 cm^{-1} × 10^3 on the side of the strong charge-transfer band possibly representing the $^6\Sigma^+ \rightarrow {}^4\Sigma^-$, $^4\Sigma^+$ transition. Thus one obtains B = 705 cm^{-1} and β = 0.81, which although appreciably higher than the parameters found for the other neutral metallocenes are in accord with the generally more ionic bonding thought to prevail in MnCp$_2$.

For Mn(MeCp)$_2$, however, the absorption in the 17–22 cm^{-1} × 10^3 region is much stronger than for the parent compound and may clearly be attributed to one or more spin-allowed d–d excitations; reference to the appropriate Tanabe–Sugano type diagram[6] shows a closely bunched group of excited doublet states (3$^2\Pi$, $^2\Phi$, and ^{2}H) so that the band with a maximum at 19.53 cm^{-1} × 10^3 may readily be assigned to transitions to these levels from a $^2\Delta$ ($\sigma^2\delta^3$) ground state. The extinction coefficient (ϵ 22) is rather low for neutral metallocenes, but it must be remembered that a thermal equilibrium may very well exist here and that the probably appreciable sextet population would make only a negligible contribution to the intensities of any d–d bands. As far as the charge-transfer spectra are concerned though, fully allowed transitions may occur for either the $^6\Sigma^+$ or the $^2\Delta$ ground levels, so that the anticipated behavior for Mn(MeCp)$_2$ is rather complex with contributions from both spin states; on the other hand, it seems probable that for MnCp$_2$ itself only the $^6\Sigma^+$ state will make any appreciable contribution to the spectrum, judging by the clearly spin-forbidden nature of the 21.05 cm^{-1} × 10^3 peak.

Turning now to the charge-transfer transitions, we may conveniently consider these in three groups. Thus for the MCp$_2$ complexes of V, Cr, and Fe the more intense fully allowed bands all appear to be shifted to lower energies by methyl substitution and may be treated together, while as indicated above the Mn species are in a sense each unique since it is likely that MnCp$_2$ itself is high spin but that Mn(MeCp)$_2$ is predominantly low spin. Finally, for the compounds of Co and Ni the results suggest that both L → M and M → L excitations may occur, since, for Co at least, methyl substitution produces spectral shifts in both directions.

As shown in Figure 2, for the vanadium complexes there are three clearly defined bands in the charge-transfer region, with a number of subsidiary features. These latter we are inclined to attribute to vibrational structure (which low-temperature measurements might clarify) since the whole spectrum is generally shifted to lower energy by methyl substitution and since theory indicates[6] that there should be three allowed L → M transitions involving excitation of an electron from the predominantly ligand e$_{1u}$ level, namely, $e_{1u} \rightarrow e_{2g}$, $e_{1u} \rightarrow a_{1g}$, and $e_{1u} \rightarrow e_{1g}$, corresponding to the transitions $^4A_{2g} \rightarrow {}^4E_{1u}$, $^4A_{2g} \rightarrow {}^4E_{1u}$, and $^4A_{2g} \rightarrow {}^4A_{1u}$. We therefore propose the assignments listed in Table II, and although we were unable to extend our measurements on V(MeCp)$_2$ beyond about 46 cm^{-1} × 10^3, the attribution of the 47.39 cm^{-1} × 10^3 peak of VCp$_2$ to an L → M excitation seems well founded since this band is significantly more intense than the two lower energy absorptions; this would indeed be expected since the $^4A_{2g} \rightarrow {}^4A_{1u}$ band is predicted to be long-axis (z) polarized, as opposed to the short-axis (x, y) polarization of the two $^4A_{2g} \rightarrow {}^4E_{1u}$ transitions, while what is presumably the lowest energy M → L excitation, $a_{1g} \rightarrow e_{2u}$, leads only to the forbidden transition, $^4A_{2g} \rightarrow {}^4E_{2u}$. As noted before the V(MeCp)$_2$ spectrum is a good deal less well resolved than that for the parent complex, but the spectrum is otherwise unremarkable except for the sharp feature at 27.79 cm^{-1} × 10^3, for which no convincing explanation presents itself.

For the two Cr complexes a similar displacement of the charge-transfer bands to lower energies with methyl substitution is again evident, so that here too the transitions are all of L → M character. For CrCp$_2$, peaks at 29.59 and 44.64

cm^{-1} × 10^3 are observed, with a well-marked shoulder at 40 cm^{-1} × 10^3, and the lowest energy absorption is readily assigned to the $e_{1u} \rightarrow e_{2g}$ excitation which produces a single allowed transition, $^3E_{2g} \rightarrow {}^3E_{1u}$, predicted to be x, y polarized. On the other hand, the $e_{1u} \rightarrow a_{1g}$ excitation leads to two allowed transitions, $^3E_{2g} \rightarrow {}^3E_{1u}$ and $^3E_{2g} \rightarrow {}^3E_{2u}$; since the latter is allowed with either x, y or z polarization, it is reasonable to identify the 44.64 cm^{-1} × 10^3 peak in this way, by virtue of its greater intensity, with the 40 cm^{-1} × 10^3 shoulder corresponding to the second $^3E_{2g} \rightarrow {}^3E_{1u}$ transition. The spectrum also shows evidence of a yet stronger peak above 50 cm^{-1} × 10^3, which also seems to be of L → M type and which may be interpreted as arising from the $e_{1u} \rightarrow e_{1g}$ excitation; this leads to transitions to a $^3E_{1u}$ level and two $^3E_{2u}$ levels, again in agreement with the high intensities observed.

For $FeCp_2$ and $Fe(MeCp)_2$ our results once more reveal a general shift to lower energies on substitution, and the corollary that the charge-transfer bands are all L → M necessitates a reconsideration of the assignments previously suggested.[6,9] Thus the very strong band at about 50 cm^{-1} × 10^3 was attributed to the $^1A_{1g} \rightarrow {}^1A_{2u}$ transition, this being the only allowed transition arising from the $e_{1u} \rightarrow e_{1g}$ L → M excitation, and this assignment appears reasonably secure since the predicted z polarization accords with the high observed intensity and since the shifts in the band position for the $[CoCp_2]^+$ and $RuCp_2$ systems[9] agree well with electronegativity predictions. However, the identification[6,9] of the bands near 41.7 and 28.3 cm^{-1} × 10^3 as M → L transitions cannot be sustained since in $Fe(MeCp)_2$ the whole band system is obviously shifted to lower energies; indeed, the second distinct d–d band of the parent compound is, in $Fe(MeCp)_2$, largely obscured by just this effect. Consequently, an alternative explanation for the absorption in the 40 cm^{-1} × 10^3 region must be sought, and if we discount the possibility of $L(\sigma) \rightarrow M$ excitations, the observed bands may be due either to parity-forbidden (g → g) charge-transfer transitions, vibronically enabled by an odd vibrational mode, or to symmetry-forbidden (but u → g) transitions which become allowed by coexcitation of the appropriate Raman-active (g) vibrational modes. With the information available it is not, however, possible to distinguish between these possibilities.

For the two Co complexes the portions of the spectra above about 22 cm^{-1} × 10^3 may be considered in two regions. Thus the very strong band at 46.08 cm^{-1} × 10^3 in $CoCp_2$ is shifted to higher energies on methyl substitution and is therefore clearly M → L, whereas the peaks at 38.46 and 30.77 cm^{-1} × 10^3 and the shoulder at 27.03 cm^{-1} × 10^3 are all shifted to lower energies and thus represent L → M transitions. For the M → L $e_{1g} \rightarrow e_{2u}$ excitation only the $^2E_{1g} \rightarrow {}^2E_{2u}$ transition is allowed, but the $e_{1u} \rightarrow e_{1g}$ L → M one-electron jump leads to three $^2E_{1u}$ levels and, since all these states are of the same symmetry, an overall splitting of some 11 cm^{-1} × 10^3 is not unreasonable. Furthermore, transitions to these $^2E_{1u}$ levels are allowed with z polarization, so that the peak intensities ($\log \epsilon \approx 4$) may also readily be rationalized.

For $NiCp_2$ and $Ni(MeCp)_2$ the situation is unfortunately less clear since there are obviously absorptions just above 50 cm^{-1} × 10^3 for which it is impossible to be certain of the direction of the shift of the peak position produced by methyl substitution. Thus the single L → M excitation $e_{1u} \rightarrow e_{1g}$ leads only to a single z-polarized transition, $^3A_{2g} \rightarrow {}^3A_{1u}$, which may be identified as the band showing its maximum as the peak at 32.63 cm^{-1} × 10^3, the high observed ϵ value being clearly consistent with long-axis polarization. The weaker shoulders may then be attributed to vibrationally enabled L → M transitions (cf. $FeCp_2$) to $^3A_{2u}$ and $^3E_{2u}$ states,[6] but it is more difficult to assign the band system near 50 cm^{-1} × 10^3. It could, of course, be ascribed to an L → M $a_{2u} \rightarrow e_{1g}$ excitation, which would yield the x, y-polarized $^3A_{2g} \rightarrow {}^3E_{1u}$ transition, but since the $NiCp_2$ absorption is rising slightly more steeply than that of $Ni(MeCp)_2$ at 50 cm^{-1} × 10^3, it is uncertain whether the peak is shifted to lower or to higher energy and therefore whether it is L → M or M → L in origin. In the latter case ($e_{1g} \rightarrow e_{2u}$) one obtains the excited states $^3E_{1u}$ and $^3E_{2u}$, of which the former is allowed with x, y polarization, so that the assignment M → L is also feasible, and by analogy with the Co species such a transition would certainly be expected in this region of the spectrum.

Finally, for $MnCp_2$ and $Mn(MeCp)_2$, the assignment of the charge-transfer spectra presents rather more difficulty. Thus, the d–d spectrum of $MnCp_2$ strongly suggests that it is high spin in isooctane solution, whereas the markedly greater intensity of the same spectral region for $Mn(MeCp)_2$ is indicative at least of the predominance of a low-spin ground level.[21] It did not, unfortunately, prove possible to measure the magnetic moments of $MnCp_2$ and $Mn(MeCp)_2$ in isooctane solution, but on the basis of the available evidence we have assumed $MnCp_2$ to have a $^6A_{1g}$ ground level, whereas for $Mn(MeCp)_2$ we have supposed the system to exist predominantly as the low-spin $^2E_{2g}$ state. We have therefore no clear information, from methyl substitution, about the L → M or M → L nature of the charge-transfer bands in these two systems, but by analogy with the d^3, d^4, and d^6 systems we have once more assumed all the bands to be of L → M character.

For $MnCp_2$ we thus attribute the broad asymmetric band system between 24 and 34 cm^{-1} × 10^3 to the $e_{1u} \rightarrow e_{2g}$ and $e_{1u} \rightarrow a_{1g}$ excitations, these both leading to allowed $^6A_{1g} \rightarrow {}^6E_{1u}$ transitions. For the inflection at 24.4 cm^{-1} × 10^3, however, the intensity is low for an allowed transition, and it is not certain whether or not this feature should be assigned as the lower $^6A_{1g} \rightarrow {}^6E_{1u}$ transition. The stronger band system between 40 and 50 cm^{-1} × 10^3 is nevertheless more readily attributed to the $e_{1u} \rightarrow e_{1g}$ excitation, which is predicted to lead to the long-axis polarized transition $^6A_{1g} \rightarrow {}^6A_{2u}$, the band structure possibly being due to vibrationally enabled but formally forbidden transitions (cf. $FeCp_2$).

For $Mn(MeCp)_2$ it seems likely that both the peak at 24.39 cm^{-1} × 10^3 and the shoulder at 31.25 cm^{-1} × 10^3 are associated with the $e_{1u} \rightarrow e_{2g}$ excitation. This leads to a single allowed $^2E_{2g} \rightarrow {}^2E_{1u}$ transition, with x, y polarization, but the intensity is rather low even so, and it is possible that this may be due to the ground-state population residing partially as $^6A_{1g}$. The broader more intense band between about 37 and 50 cm^{-1} × 10^3 is however more readily ascribed to the $e_{1u} \rightarrow e_{1g}$ excitation, since this leads to three allowed transitions, $^2E_{2g} \rightarrow {}^2E_{1u} + 2\,{}^2E_{2u}$, of which the latter two are permitted with long-axis polarization.

We have also measured the spectra of all the systems described above, using diffuse-reflectance spectroscopy. However, with only one exception, the spectra thus obtained did not differ significantly from those measured in isooctane, within the region 10–50 cm^{-1} × 10^3. For $NiCp_2$ though, the reflectance spectrum, although still displaying the broad band between about 27 and 40 cm^{-1} × 10^3, no longer exhibited the maximum at 32.65 cm^{-1} × 10^3, which in solution is the dominant feature. Since it has been suggested[27] that this band is actually characteristic of the nickelicenium species, $[NiCp_2]^+$, we examined carefully our solution data for $NiCp_2$: however, although the relative and absolute intensities of all the features of this band are susceptible to the presence of oxygen, repeated measurements, with the most rigorous exclusion of oxygen and other impurities, led reproducibly to the results presented here. Below 10 cm^{-3} × 10^3 our reflectance data were in essential agreement with those reported by Reid et al.[28] with bands in the region of 3–5, 6, and 9 cm^{-1} × 10^3, due to binary and ternary vibrational combinations. For the

Table III

Magnetic Parameters for Metallocenes[a]

Compd	Moment, μ_B	Θ, K	Compd	Moment, μ_B	Θ, K
VCp_2	3.90[b]	16[b]	$CoCp_2$	2.04[c]	38[c]
$V(MeCp)_2$	3.74	1	$Co(MeCp)_2$	1.98	11
$CrCp_2$	3.23	21	$NiCp_2$	2.90	0
$Cr(MeCp)_2$	3.17	17	$Ni(MeCp)_2$	2.95	0

Magnetic Susceptibility of $CoCp_2$ by Gouy Measurements

T, K	χ, 10^{-6} cgsu	T, K	χ, 10^{-6} cgsu
293	1746	153	2836
273	1848	133	3149
253	1960	123	3378
233	2094	113	3571
213	2242	103	3863
193	2409	93	4166
173	2604	83	4494

[a] Data from Curie–Weiss plots. For MCp_2 compounds results are for Gouy measurements on solid samples; for $M(MeCp)_2$ compounds results are for NMR measurements in toluene solutions. [b] In toluene solution $\mu = 3.87\ \mu_B$ and $\Theta = 0$ K; for all other MCp_2 compounds the Gouy and NMR results are virtually identical. [c] For $CoCp_2$ the $1/\chi$ vs. T plot shows substantial curvature and deviates appreciably from the Curie–Weiss law.

V, Fe, and Ni systems the spectra are quite sharp and well defined but for $CrCp_2$ and $CoCp_2$ the bands are broad and featureless, as was also reported by Reid et al.,[28] who attributed this result to the presence of low-lying electronic transitions. However, consideration of the Tanabe–Sugano type diagrams for d^4 and d^7 systems[6] shows that this explanation is improbable; thus for $CrCp_2$ the ${}^3A_{2g}$ (${}^3\Sigma^-$) level is probably too low in energy to correspond to the observed features, while for $CoCp_2$ there should be no doublet levels lying below about $10\ \mathrm{cm^{-1}} \times 10^3$. Consequently, it appears more reasonable to attribute the band broadening in these two cases to the Jahn–Teller activity of the respective ${}^3E_{2g}$ (${}^3\Delta$) and ${}^2E_{1g}$ (${}^2\Pi$) ground states, since those systems displaying the normal vibrational spectrum all possess Jahn–Teller impotent ground levels.

Turning now to the magnetic susceptibility measurements, we consider first those systems with orbital singlet ground states, i.e. $NiCp_2$ and $Ni(MeCp)_2$, ${}^3\Sigma^-$ (${}^3A_{2g}$), and VCp_2 and $V(MeCp)_2$, ${}^4\Sigma^-$ (${}^4A_{2g}$). Of these the parent systems have already been quite extensively investigated (see ref 6 for a survey), and our results are generally in good agreement with the earlier studies, but little previous work has been carried out on the dimethyl derivatives. For orbital singlet ground states the effects on the magnetic behavior of the zero-field splitting due to second-order spin–orbit interactions have recently been surveyed,[2] but even for the d^8 $NiCp_2$, which shows the largest splitting, there should be no significant deviation from the spin-only behavior above 77 K. However, for the d^8 systems the zero-field splitting of the ${}^3\Sigma^-$ ground state leaves the magnetically inactive Σ^+ (0) level lowest,[2] so that these species would be expected to be the least affected by antiferromagnetic interactions and to approach most closely to the ideal spin-only situation. This expectation is in fact strikingly fulfilled (see Table II) since for both $NiCp_2$ and $Ni(MeCp)_2$ essentially spin-only values of the moment were obtained, in each case with $\Theta \approx 0$ K (cf. $\mu = 2.89\ \mu_B$ with $\Theta = 6$ K, found by Prins et al.[29]); moreover, although the observation of a zero Θ value is probably fortuitous, bearing in mind the normal experimental uncertainties, measurements on the parent compound gave the same results both by the Gouy technique using solid samples and by the NMR method in toluene solution.

For VCp_2 however the Gouy and NMR techniques, although both yielding the same essentially spin-only value for the moment, lead to significantly different Θ values (16 K for the solid and 0 K for toluene solution), and the Gouy data also differ somewhat from those of Leipfinger[30] ($\mu = 3.78\ \mu_B$ and $\Theta = 6.5$ K). However, the difference in the Θ values between solid and solution is most probably due to antiferromagnetism in the solid phase, bearing in mind that the lowest lying ground-state component is now the Π^* ($\pm{}^1/_2$) level, which is no longer magnetically inactive. Thus Leipfinger[30] found anomalous, almost temperature-independent paramagnetism at very low temperatures (below 5 K), which was ascribed to antiferromagnetism, and calculations using the simple dipolar interaction model support this conclusion.[2] As might therefore be anticipated, the solution measurements for $V(MeCp)_2$ again yield a virtually spin-only moment, with Θ almost zero.

For the complexes of Cr and Co, in contrast to those of V and Ni, the ground states are orbitally degenerate, and deviations from the spin-only values of the moments are to be expected. For the d^4 $CrCp_2$ a recent remeasurement of the moment[23] has confirmed the early value[22] of ca. 3.20 μ_B and established unequivocably the ${}^3\Delta$ (${}^3E_{2g}$) ground state, in agreement with the results of PES studies.[14] The present results, moreover, yield the same values for μ and for Θ by both the Gouy and the NMR methods, thus encouraging the belief that the appreciable Θ value is not in this case solely due to antiferromagnetism, while the NMR results for $Cr(MeCp)_2$ afford a very similar value for the moment, again with quite a significant Θ value. Theory[1] shows that for a d^4, ${}^3\Delta$ system in pseudoaxial symmetry, the observed μ values would require an orbital reduction parameter k' significantly less than unity, together with some C_{2v} distortion, and the data for both Cr species are quite well fitted with the parameters $k' = 0.7$–0.8 and δ ($=\Delta/\xi$) ≈ 3–4 (cf. ref 23). It is not possible to obtain a unique fit to the experimental results since both k' and δ may be varied independently, but the observed parameter range is nevertheless reasonably consistent[1] with the nephelauxetic ratios (ca. 0.5) found for most metallocenes and the k' values of about 0.8 obtained from ESR measurements[26,31] on systems with δ (e_{2g}) orbital degeneracies. Thus, assuming $\xi_{\mathrm{eff}} = k' \cdot (\xi_{\text{free ion}})$, one finds $\Delta \approx 500$–$700\ \mathrm{cm^{-1}}$, which is closely comparable to the splittings of the δ (e_{2g}) level deduced for $MnCp_2$ and $[FeCp_2]^+$ from the results of ESR investigations.[26,31] If one takes $\xi_{\mathrm{eff}} \approx 180\ \mathrm{cm^{-1}}$, the present measurements correspond to a range of about 0.3–1.15 for the parameter kT/ξ, for which the moment is predicted[1] to be essentially temperature independent and thus to be in accord with the observed Curie–Weiss behavior, while for lower temperatures some fall in the average moment is predicted, which is compatible with the appreciably positive Θ value found. The rather small ξ_{eff} value for $CrCp_2$ indicates, however, that the effects of excited-state mixing with the ground level, due to spin–orbit coupling, will be insignificant as far as the magnetic moment is concerned. Nevertheless, for both $CrCp_2$ and $Cr(MeCp)_2$ the moments are substantially greater than the spin-only value, thus providing unequivocal support for the ${}^3\Delta$ ground state deduced from PES measurements[14] and, as previously argued,[23] ruling out the possibility of a ${}^3\Sigma^-$ ground level.

For the d^7 Co(II) systems in the undistorted $C_{\infty v}$ situation, theory indicates a substantial temperature dependence of the moment, which is predicted to fall from around the spin-only value (1.73 μ_B) at $kT/\xi = 2$ to reach zero as $T \rightarrow 0$ K. When allowance is made for k' being less than unity (ESR data[20] indicate a value as small as 0.25) and for the operation of a moderate C_{2v} distortion, an almost temperature-independent moment, approaching the spin-only value, should result for δ ($=\Delta/\xi$) greater than about 3, so that the previously reported moment values for $CoCp_2$ were interpreted[1,23] as indicating a substantial orthorhombic distortion with $\delta \approx 3$–4. Nevertheless, the present Gouy measurements and the NMR data over the limited range covered both yield $1/\chi$ vs. T plots showing a marked curvature (and thus deviating from Curie–Weiss behavior), the moment values obtained ranging from 2.04 μ_β at 298 K to 1.75 μ_β at 83 K.

In principle it is possible to account for a moment greater than the spin-only value by considering the effects of spin–orbit mixing of excited states with the ground level and the contributions due to temperature-independent paramagnetism (TIP), although the latter is unlikely here to contribute more than 150×10^{-6} cgsu to the susceptibility. However, taking the lowest energy interacting doublet levels to lie at 15 000 cm^{-1} and the free-ion ξ value[18] for Co(II) of 515 cm^{-1}, one calculates a maximum increase in the moment of some 0.1 μ_β in the undistorted situation, due to the spin–orbit mixing, which is clearly significant for a doublet ground state. Nevertheless, calculations including C_{2v} distortions[19] (as well as the spin–orbit and TIP terms) still fail to give a particularly satisfactory fit for $CoCp_2$. Thus, with $\delta \approx 4$, $k' = 0.25$, and TIP = 150×10^{-6} cgsu, the calculated moments were 1.97, 1.88, and 1.80 μ_β at 300, 180, and 80 K, respectively, as against the experimental values of 2.02, 1.90, and 1.73 μ_β.

Significantly the values of the distortion parameter δ, obtained by Ammeter et al.[20,31,32] from ESR studies, are all markedly smaller than the estimate of about 3–4 deduced from the susceptibility data. Thus, for a variety of host lattices the δ values range from as little as 0.12 for $MgCp_2$ to a little under and a little over 2 for $FeCp_2$ and $Fe(MeCp)_2$, and with a value of ξ_{eff} of 330 cm^{-1} then assumed[20] these correspond to Δ values between 40 and some 600–700 cm^{-1}. For metallocene host lattices the Δ parameters obtained by Ammeter et al.[20,31,32] all lie within the range 200–700 cm^{-1} (i.e., δ is between 0.6 and 2.1), and it therefore seems probable that the smaller δ quantities thus deduced are more likely to reflect the extent of the C_{2v} distortion than the larger result obtained from the present data, which are inherently less precise and involve more unknown parameters. Clearly measurements below 77 K, preferably of the anisotropic susceptibilities, are required to give a more accurate indication of the extent of the temperature dependence of the magnetic moment.

For $Co(MeCp)_2$ our solution data over the limited temperature range do appear to follow the Curie–Weiss law and appear to give a much smaller Θ value than for $CoCp_2$ itself. The moment is thus slightly closer to the spin-only result and significantly more nearly temperature independent, so that qualitatively, at least, this would suggest a larger value of δ than for the parent compound. This is in contrast to the two Cr complexes which yield almost identical Curie–Weiss parameters. For $Co(MeCp)_2$, however, the results of ESR studies[32] support the deduction of an appreciably larger C_{2v} splitting for the methyl derivative: thus for a variety of host lattices the δ parameters range from a little under 4 to slightly over 7, supporting the conclusion of Ammeter and Brom[33] that the magnetic parameters for the $d^7\ ^2\Pi$ system are particularly sensitive to external orthorhombic fields.

Finally, magnetic susceptibility results for the bis(hexamethylbenzene) derivatives of Co(I) and Fe(I),[19] $[Fe(HMBz)_2]^+[PF_6]^-$ and $[Co(HMBz)_2]^+[PF_6]^-$, again show abnormal behavior for the latter (d^7) system. Thus for $[Fe(HMBz)_2]^+[PF_6]^-$, between 83 and 298 K, we found μ = 1.98 μ_β with Θ = 30 K, but again with a marked curvature in the $1/\chi$ vs. T plot, similar to that observed for $CoCp_2$. In contrast, the d^8 Co(I) system, $[Co(HMBz)_2]^+[PF_6]^-$, over the same range, gave μ = 2.79 μ_β, almost exactly the spin-only value, with only a small Θ value of 3 K.

Acknowledgment. K.R.G. thanks the Science Research Council for support.

Registry No. VCp_2, 1277-47-0; $CrCp_2$, 1271-24-5; $MnCp_2$, 1271-27-8; $FeCp_2$, 102-54-5; $CoCp_2$, 1277-43-6; $NiCp_2$, 1271-28-9; $V(MeCp)_2$, 12146-93-9; $Cr(MeCp)_2$, 12146-92-8; $Mn(MeCp)_2$, 32985-17-4; $Fe(MeCp)_2$, 1291-47-0; $Co(MeCp)_2$, 12146-91-7; $Ni(MeCp)_2$, 1293-95-4.

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