grated rate law (eq 1), and d[CH_4]/dt and [CH_4]$_t$ were measured experimentally. The rate constant, k_4, could then be evaluated by substituting into eq 9. The value of k_2/[H^+] remained constant while [H^+] and [Cr^{2+}]/[$CrCH_2I^{2+}$] were independently varied and agreed very well with the experimental values (Table III) determined under conditions of excess Cr(II).

The data do not provide substantive information about the means by which $CrCH_2\cdot^{2+}$ is converted to $CrCH_3^{2+}$ (step 6). One two-step sequence which is consistent with the present study and the well-known tendency of aquochromium(II) to undergo inner-sphere electron-transfer reactions[18] is the following.

$$Cr^{2+} + CrCH_2\cdot^{2+} \rightarrow [CrCH_2Cr]^{4+}$$

$$[CrCH_2Cr]^{4+} + H^+ \rightarrow CrCH_3 + Cr^{+3}$$

In this sequence, a bridged dinuclear complex, $[CrCH_2Cr]^{4+}$, is formed. Attempts were made to separate the species present in the reaction solution on an ion-exchange column maintained at low temperatures and under an inert atmosphere. A species of charge 2+ other than $CrCH_2I^{2+}$, CrI^{2+}, or Cr^{2+} was detected, but an adequate separation was not achieved. No species of charge 4+ was detected, so that if a dichromiumalkyl species is formed it must rapidly dissociate. The agreement between values of the rate constant for the production of methane determined under various experimental conditions also supports the view that there is only one long-lived intermediate.

It is of course not necessary to invoke the alkyl-bridged species,[5] but it is analogous to other well-established bridged dichromium species.[21-23] Further work on chromium(II) reactions with other halomethylchromium(III) ions is in progress; we seek evidence pointing to existence of C-bridged dichromium intermediates.

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Registry No. Cr^{2+}, 22541-79-3; $CrCH_2I^{2+}$, 17477-14-4; $CrCH_3^{2+}$, 32108-96-6; CH_4, 74-82-8.

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(21) M. Ardon and R. A. Plane, *J. Amer. Chem. Soc.*, 81, 3197 (1959).

(22) M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962).

(23) D. L. Ball and E. L. King, *J. Amer. Chem. Soc.*, 80, 1091 (1958).

Notes

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Ligand Field Theory of Metal Sandwich Complexes. d^4 Configurations

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The usefulness of the ligand field model for the assignment of low-energy d-d transitions of metal sandwich complexes is now widely realized[1] and this approach is also appropriate for the interpretation of magnetic susceptibilities[2] and magnetic resonance phenomena.[3] Scott and Matsen[4] showed that such species could be treated on the basis of an effective axial ($C_{\infty v}$) symmetry (as long as only d^n configurations were involved and a fivefold or higher rotation axis was present), and a complete strong-field treatment, including spin-orbit coupling, has recently been given for the d^1, d^2, and d^3 systems and their complementary configurations.[5] Partial strong-field treatments (excluding spin-orbit interactions) have also been reported for d^5 and d^6 systems,[6] but the lack of spectroscopic data has so far resulted in the complete neglect of d^4 configurations.

In the course of a full survey of the magnetic susceptibilities of metal sandwich complexes,[7] it became necessary to establish with greater certainty the probable ground state of chromocene ($3d^4$). The complete d^4 strong-field electrostatic repulsion matrices in $C_{\infty v}$ symmetry have been evaluated and are given in the Appendix,[8] in terms of the Racah parameters B and C and the axial field quantities[9] Ds and Dt. In such systems the fivefold degenerate d-orbital set is split into one nondegenerate (σ) and two twofold degenerate (π and δ) levels, the usual energetic order of these one-electron core terms being $\delta < \sigma \ll \pi$, where $E(\sigma) = 2Ds - 6Dt$, $E(\pi) = Ds + 4Dt$, and $E(\delta) = -2Ds - Dt$.

In all the metallocene systems for which ligand field fittings have been made ($V(Cp)_2$, $Cr(Cp)_2^+$, $Fe(Cp)_2^+$, $Fe(Cp)_2$, $Co(Cp)_2^+$, $Ni(Cp)_2$)[3,5,6,10] the Dt/Ds ratio lies between about 0.5 and 0.6, and the Tanabe-Sugano type d^4 diagram shown in Figure 1 was therefore calculated using the mean value $Dt/Ds = 0.55$, assuming $C/B = 4.0$. For the metallocenes listed above a range of Dt/B values have been derived, but none of these gives Dt/B as less than 3.5 and mostly they lie within the range 4.5-6.5. The results therefore show that at all normal field strengths the $^3\Delta$ ($\sigma\delta^3$) level will constitute the ground state. Increase of the C/B ratio to 4.4 (the Cr^{2+} free-ion value) has the effect of eliminating the small region in which $^3\Sigma^-$ ($\sigma^2\delta^2$) lies lowest and slightly raising the high-spin-low-spin crossover point to about $Dt/B = 3.2$. However, the $^1\Sigma^+$ (δ^4) level always lies substantially above $^3\Delta$ ($\sigma\delta^3$) and cannot be the ground state for any feasible field strength—it lies lowest only for $Dt/B > ca.$ 20.

For chromocene, molecular orbital calculations[11,12] also predict a $^3\Delta$ ($\sigma\delta^3$) ground state, and for this an orbital contribution to the magnetic moment is predicted. Thus one

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

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

(3) R. Prins and J. D. W. van Voorst, *J. Chem. Phys.*, 49, 4665 (1968).

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

(5) K. D. Warren, *J. Phys. Chem.*, 77, 1681 (1973).

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

(7) K. D. Warren, *Inorg. Chem.*, in press.

(8) See paragraph at end of paper regarding supplementary material.

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

(10) E. O. Fischer and K. Ulm, *Chem. Ber.*, 95, 692 (1962).

(11) E. M. Shustorovich and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, 131, 113 (1960).

(12) D. W. Clack, unpublished calculations (private communication).

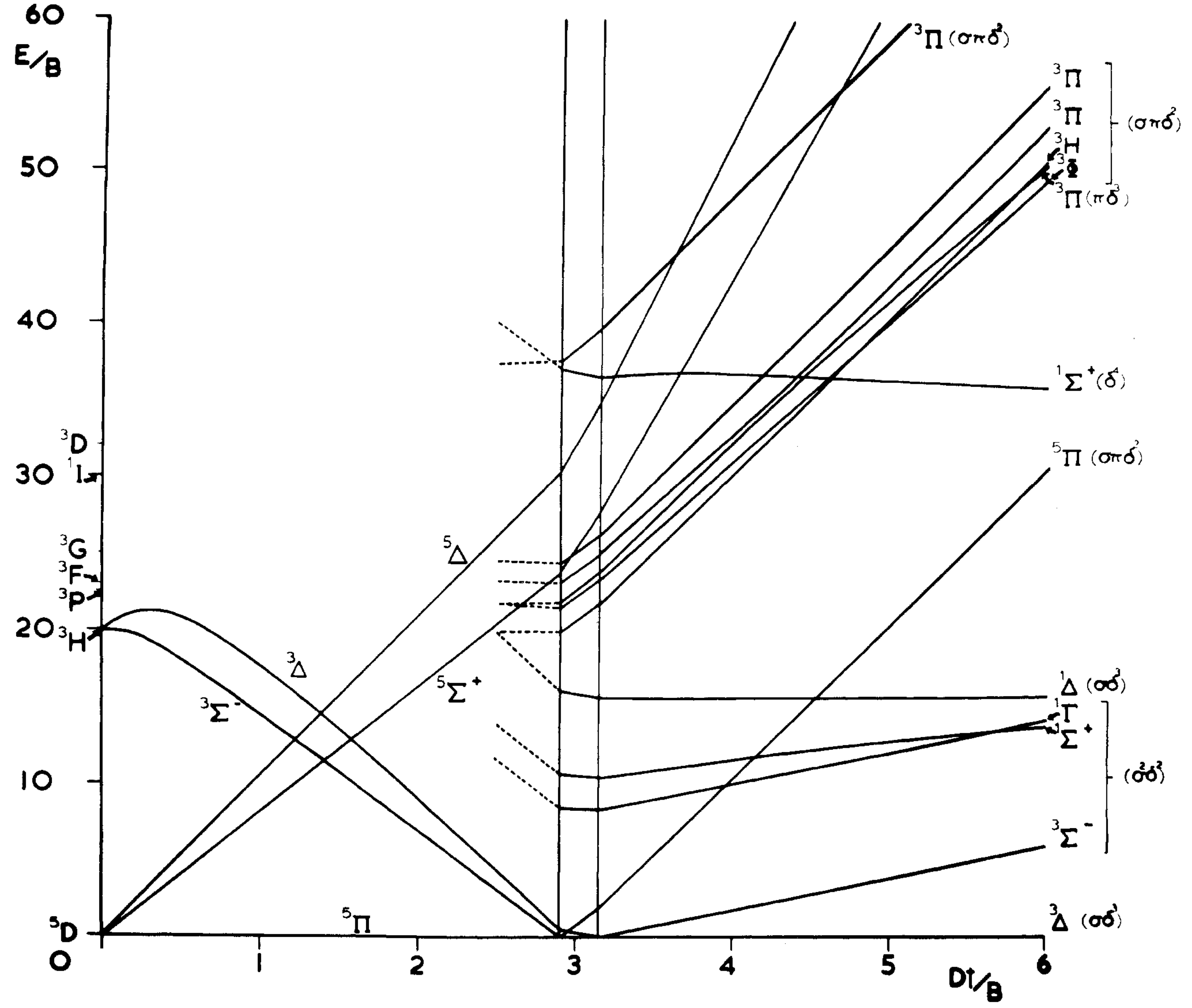

Figure 1. Energy level diagram for d^4 systems in $C_{\infty v}$ symmetry; $Dt = 0.55Ds$ and $C = 4B$.

obtains[7]

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

and

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

where k' is the orbital reduction factor and $x = -\xi/kT$; with $k' = 0.7$ and a small distortion from pseudoaxial symmetry (*ca.* 500-cm^{-1} splitting of the δ level) the observed average moment of 3.20 BM[13] (as against the spin-only value of 2.83 BM) can be reproduced.

From Figure 1 it is seen that the $^3\Sigma^-$ $(\sigma^2\delta^2)$ level lies only slightly above the ground state for much of the Dt/B range; however, this should not further complicate the magnetic behavior since the spin-orbit matrix elements connecting these states are all zero, and the second-order Zeeman contributions also vanish.[7] Only where $E(^3\Sigma^-) - E(^3\Delta) \approx kT$ would the moment tend to be reduced toward the spin-only value.

Information concerning the ground state and the lower energy excited states of d^4 systems in $C_{\infty v}$ symmetry is also of value in interpreting the recently reported[14] He(I) photoelectron spectra of the d^4 and d^5 molecules $Cr(Cp)_2$ and $Mn(Cp)_2$. For $Cr(Cp)_2$ Rabelais, *et al.*,[14] did assume a $^3\Delta$ $(\sigma\delta^3)$ ground state, which on ionization may give rise to states derived from the δ^3 and $\sigma\delta^2$ configurations, but they attributed the successive lower energy bands for the resulting $Cr(Cp)_2^+$ ion to the levels $^2\Delta$ (δ^3), $^4\Sigma^-$ $(\sigma\delta^2)$, $^2\Gamma$ $(\sigma\delta^2)$, and $^2\Sigma^+$, $^2\Sigma^-$ $(\sigma\delta^2)$, in that order (see Table I). However, diagonalization of the complete d^3 $C_{\infty v}$ energy matrices[5] shows (see Figure 2) that the $^2\Delta$ (δ^3) state can only constitute the ground state at improbably high Dt/B values and that the lowest level will always be $^4\Sigma^-$ $(\sigma\delta^2)$. As shown in Figure 2, the predicted order of levels using the ligand field approach is $^4\Sigma^-$ $(\sigma\delta^2)$, $^2\Gamma$ $(\sigma\delta^2)$, $^2\Delta$ (δ^3), and $^2\Sigma^+$, $^2\Sigma^-$ $(\sigma\delta^2)$, and this sequence in fact gives as good a correlation between the observed and calculated intensity ratios as does the original assignment.

For $Cr(Cp)_2^+$ a solution spectrum has been reported,[10] in which peaks at 18 and 22 kK may be assigned as the $^4\Sigma^-$ $(\sigma\delta^2) \rightarrow {}^4\Pi$ $(\pi\delta^2)$ and $^4\Sigma^-$ $(\sigma\delta^2) \rightarrow {}^4\Phi$ $(\sigma\pi\delta)$ excitations, respectively. A broad band with a shoulder at *ca.* 25 kK and a maximum at 27 kK presumably corresponds to the higher energy $^4\Sigma^-$ $(\sigma\delta^2) \rightarrow {}^4\Pi$ $(\sigma\pi\delta)$ transition, and the spectrum is

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(13) F. Engelman, *Z. Naturforsch. B*, 8, 775 (1953).

(14) J. W. Rabelais, L. O. Werme, T. Bergmark, L. Karlssohn, M. Hussain, and K. Siegbahn, *J. Chem. Phys.*, 57, 1185 (1972).

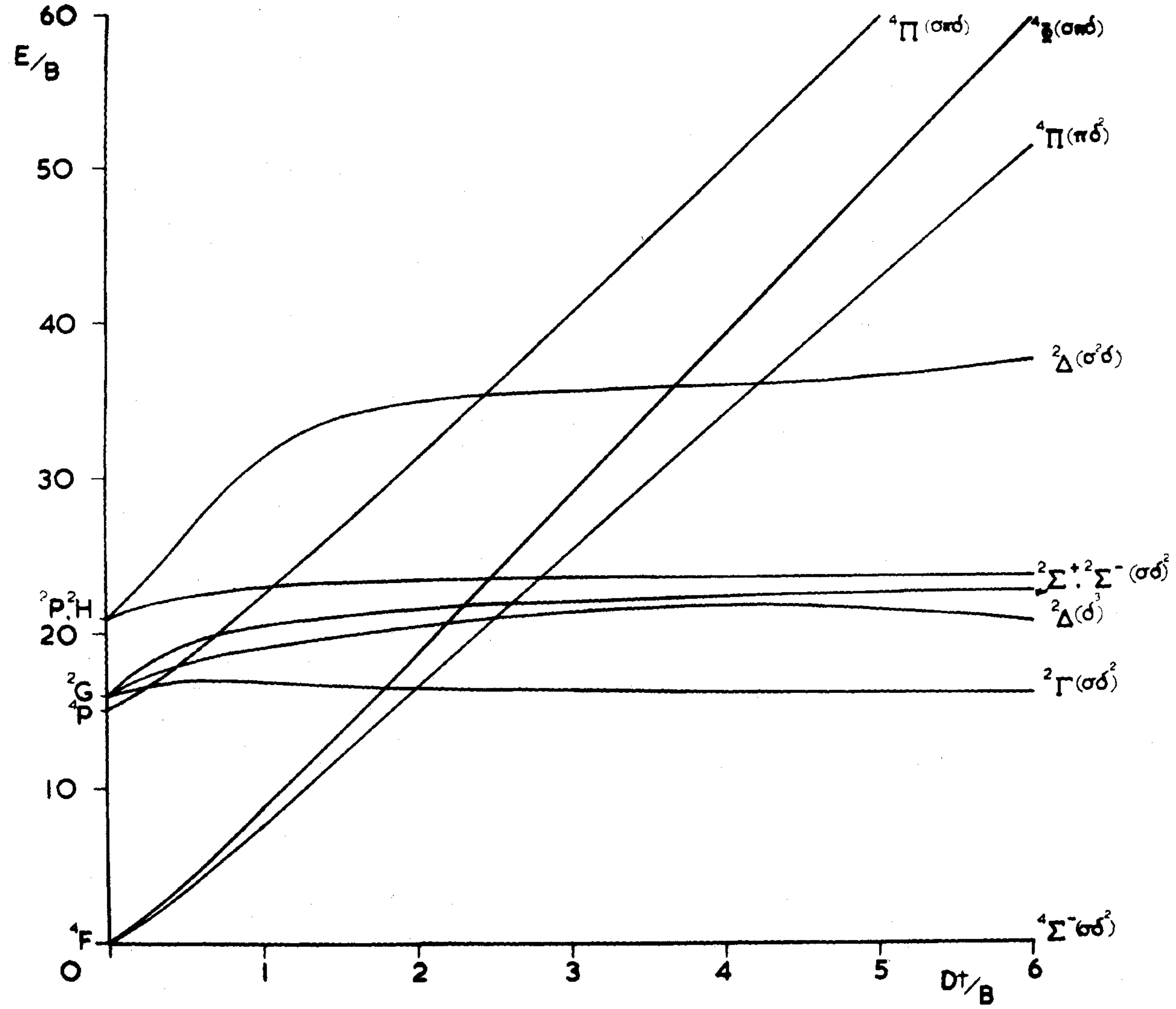

Figure 2. Energy level diagram for d³ systems in $C_{\infty v}$ symmetry; $Dt = 0.55Ds$ and $C = 4B$.

Table I. Observed and Calculated Energy Levels[a]

$Mn(Cp)_2^+$ (d^4)

Obsd[b]		Calcd[d]					
ΔE	Assignment	ΔE^c	Assignment	ΔE^e	Assignment	ΔE^f	Assignment
0.00	$^1\Sigma^+ (\delta^4)$	0.00	$^3\Delta (\sigma\delta^3)$	0.00	$^3\Delta (\sigma\delta^3)$	0.00	$^5\Pi (\sigma\pi\delta^2)$
0.15	$^3\Delta (\sigma\delta^3)$	0.98	$^1\Delta (\sigma\delta^3)$	0.17	$^3\Sigma^- (\sigma^2\delta^2)$	1.52–2.28	$^5\Sigma^+ (\pi^2\delta^2)$
0.40	$^1\Delta (\sigma\delta^3)$	2.27	$^1\Sigma^+ (\delta^4)$	0.69	$^1\Gamma (\sigma^2\delta^2)$	1.94–2.91	$^5\Delta (\sigma\pi^2\delta)$
1.2–2.6	Ligand excitations			0.76	$^1\Sigma^+ (\sigma^2\delta^2)$		
				0.98	$^1\Delta (\sigma\delta^3)$		

$Cr(Cp)_2^+$ (d^3)

Obsd[b]				Calcd[h]			
ΔE	Assignment	ΔE	Assignment	ΔE^g	Assignment	ΔE^g	Assignment
0.00	$^2\Delta (\delta^3)$	1.61	$^2\Gamma (\sigma\delta^2)$	0.00	$^4\Sigma^- (\sigma\delta^2)$	1.41	$^2\Sigma^+ (\sigma\delta^2)$
1.33	$^4\Sigma^- (\sigma\delta^2)$	1.71	$^2\Sigma^+, {}^2\Sigma^- (\sigma\delta^2)$	1.01	$^2\Gamma (\sigma\delta^2)$	1.48	$^2\Sigma^- (\sigma\delta^2)$
				1.36	$^2\Delta (\delta^3)$		

[a] ΔE throughout is expressed in eV relative to the energy of the lowest photoelectron band. For the metallocenes the d^n electronic states are often expressed in terms of the representations of the groups D_{5d} or D_{5h}. The correlations between D_5 and $C_{\infty v}$ are as follows: $C_{\infty v}, D_5$; Σ^+, A_1; Σ^-, A_2; Π, E_1; Δ, E_2; Φ, E_2; Γ, E_1; H, $A_1 + A_2$. [b] Reference 12. [c] $^2\Sigma^+ (\sigma\delta^4)$ d^5 ground state assumed. [d] $Dt/Ds = 0.55$, $C/B = 4.0$, $Dt/B = 4.5$, $B = 500$ cm^{-1}. [e] $^2\Delta (\sigma^2\delta^3)$ d^5 ground state assumed. [f] $^6\Sigma^+ (\sigma\pi^2\delta^2)$ d^5 ground state assumed; Dt/B range 3.0–4.5. [g] $^3\Delta (\sigma\delta^3)$ d^4 ground state assumed. [h] $Dt/Ds = 0.55$, $C/B = 4.0$, $Dt/B = 5.0$, $B = 500$ cm^{-1}.

reasonably well fitted with $Dt/Ds = 0.55$, $Dt/B \approx 5.0$, and $B \approx 450$ cm^{-1}—if the shoulder at 25 kK is ignored one derives $Dt/B = 6.25$ and $B = 515$ cm^{-1}. It is not unfortunately possible fully to fit the photoelectron data for $Cr(Cp)_2^+$ since only the δ^3 and $\sigma\delta^2$ configurations are involved, and the observed levels lead to unrealistically high values of both B and $E(\sigma) - E(\delta)$. However, the energies of the $^2\Gamma$, $^2\Delta$, and $^2\Sigma^+$, $^2\Sigma^-$ levels above the $^4\Sigma^-$ ground state are virtually independent of the Dt/B

value over quite a wide range, and the positions of these levels were therefore calculated using an approximate value of $B \approx 500\ \mathrm{cm}^{-1}$ (based on the solution data) and the other parameters as shown in Table I. It is seen that the calculated energies are somewhat smaller than the photoelectron results indicate and, although it is not clear why this should be so, the qualitative agreement is not unreasonable, and the proposed assignment is much more consistent with the ligand field treatment than that previously suggested.[14]

For the d^5 system, $\mathrm{Mn(Cp)_2}$, a high-spin $^6\Sigma^+$ ($\sigma\pi^2\delta^2$) ground state is normally assumed on the basis of the magnetic moment of 5.92 BM found for solid samples.[15] Furthermore, esr measurements[16] yield an almost isotropic g value of 1.99-2.01 which is also consistent with a $^6\Sigma^+$ ground state, although the low-spin $^2\Sigma^+$ ($\sigma\delta^4$) cannot be ruled out. Nevertheless, Rabelais, *et al.*,[14] concluded that in the gas phase the ground state is low spin and that it actually is $^2\Sigma^+$ ($\sigma\delta^4$) rather than the $^2\Delta$ ($\sigma^2\delta^3$) ground state found[6] for the isoelectronic $\mathrm{Fe(Cp)_2}^+$. They argued that on ionization to the d^4 ion $\mathrm{Mn(Cp)_2}^+$ a $^2\Sigma^+$ ($\sigma\delta^4$) state gives rise to the δ^4 and $\sigma\delta^3$ configurations corresponding to the states $^1\Sigma^+$ (δ^4), $^3\Delta$ ($\sigma\delta^3$), and $^1\Delta$ ($\sigma\delta^3$), and these levels were equated with the three closely grouped components into which they resolved the first photoelectron band (see Table I). However, as indicated in Figure 1, for any reasonable parameter choice $^1\Sigma^+$ (δ^4) will always lie substantially above $^3\Delta$ ($\sigma\delta^3$), usually to the extent of some 2 eV, so that the proposed assignment cannot be maintained. On the other hand the ligand field calculations of Sohn, Hendrickson, and Gray,[6] indicate that for a low-spin d^5 system, $^2\Delta$ ($\sigma^2\delta^3$) will normally lie lowest and that the $^2\Sigma^+$ ($\sigma\delta^4$) state would only become the ground level at very high Dt/B values. Thus for a $^2\Delta$ ($\sigma^2\delta^3$) ground state the d^4 configurations δ^3 and $\sigma^2\delta^2$ would arise on ionization, leading to the states (in ascending energetic order) $^3\Delta$ ($\sigma\delta^3$), $^3\Sigma^-$ ($\sigma^2\delta^2$), $^1\Gamma$, $^1\Sigma^+$ ($\sigma^2\delta^2$), and $^1\Delta$ ($\sigma\delta^3$), the first three therefore being possible components of the first photoelectron band. Unfortunately, $\mathrm{Mn(Cp)_2}^+$ is not known in solution but interpolated values of Ds, Dt, and B suggest that $^3\Sigma^-$ and $^1\Gamma$, $^1\Sigma^+$ lie respectively about 0.2 and 0.7 eV above $^3\Delta$. Thus the energy separation for the $^3\Sigma^-$ ($\sigma^2\delta^2$) level is of the right order of magnitude to support this assignment, but the calculated energy difference for the $^1\Gamma$, $^1\Sigma^+$ levels is appreciably greater than the observed value. Moreover, a further band about 1 eV above $^3\Delta$ ($\sigma\delta^3$) is also predicted corresponding to the $^1\Delta$ ($\sigma\delta^3$) level, but the photoelectron spectrum shows no evidence of this.

If therefore $\mathrm{Mn(Cp)_2}$ is in fact low-spin, it clearly cannot possess a $^2\Sigma^+$ ($\sigma\delta^4$) ground level according to the above interpretation of the photoelectron spectrum. A $^2\Delta$ ($\sigma^2\delta^3$) ground level is more consistent with the experimental data, but here one band appears at much lower energy than anticipated, and another is missing altogether. On the other hand though, the He(I) spectra appear to exclude the possibility of a high-spin ground level: on ionization the $^6\Sigma^+$ ($\sigma\pi^2\delta^2$) state would give rise to the configurations $\pi^2\delta^2$, $\sigma\pi^2\delta$, and $\sigma\pi\delta^2$, of which the last proves to lead to the lowest energy states for the parameter range considered here. In fact the $^5\Pi$ ($\sigma\pi\delta^2$) state will lie some 1.2 eV below the next lowest $\sigma\pi\delta^2$ levels—four closely juxtaposed states, ^{3}H, $^3\Phi$, $^3\Pi$, and $^3\Pi$—but photoionization to these should not take place from a sextet ground level[17] since the coefficients of fractional parentage which connect them are necessarily zero. The higher lying quintet levels, $^5\Sigma^+$ ($\pi^2\delta^2$) and $^5\Delta$ ($\sigma\pi^2\delta$), to which transitions are possible, will lie at 1.5-2.25 and at 1.9-2.9 eV, respectively, above $^5\Pi$ for the Dt/B range 3.0-4.5, assuming $Dt/Ds = 0.55$, which again is not consistent with the reported photoelectron results.

However, one possible interpretation would be to regard the three reported components of the first photoelectron band as arising from incompletely resolved vibrational structure rather than from separate electronic states. The first band could then be assigned as being due to the $^5\Pi$ ($\sigma\pi\delta^2$) level and the broad band found between 1.2 and 2.6 eV ascribed either to the $^5\Sigma^+$ ($\pi^2\delta^2$) and $^5\Delta$ ($\sigma\pi^2\delta$) states or to excitations involving dominantly ligand orbitals, as suggested by Rabelais, *et al.*,[14] for bands of similar energy found for this and other metallocenes. It is thus a feasible alternative to assign the photoelectron data on the basis of a $^6\Sigma^+$ ground state, and although it is not possible to decide between the two explanations in the absence of further experimental evidence, it is hard to believe that $\mathrm{Mn(Cp)_2}$ is high spin in the solid state and low spin in the gas phase. Moreover, recent INDO-type molecular orbital calculations[12] show the $^6\Sigma^+$ level to be appreciably more stable than either of the doublet configurations.

Finally, the d^4 repulsion matrices are also of value for the treatment of the complementary d^6 systems, of which many examples (*e.g.*, $\mathrm{Fe(Cp)_2}$) are known. However, the partial results including all the singly excited states have already been given,[6] and the inclusion of the higher excited levels has usually only a minor effect on the fitting parameters.

Registry No. $\mathrm{Mn(Cp)_2}^+$, 50803-41-3; $\mathrm{Cr(Cp)_2}^+$, 12793-15-6.

Supplementary Material Available. The Appendix 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-74-1243.

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

[16] J. Voitlander and E. Schimitschek, *Z. Elektrochem.*, **61**, 941 (1957).

[17] P. A. Cox and F. A. Orchard, *Chem. Phys. Lett.*, **7**, 273 (1970).

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Magnetic Properties of Di-μ-chloro-bis[dichloro(guaninium)copper(II)] Dihydrate. A Second Determination[1]

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In 1970 Carrabine and Sundaralingam reported the structure of di-μ-chloro-bis[dichloro(guaninium)copper(II)]

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[1] Subsequent to the submission of a complete paper on the magnetic properties of this compound, an article describing similar measurements appeared.[2] While we basically are in agreement with Villa's conclusions, our more extensive measurements have permitted a more precise determination of the singlet-triplet splitting.

[2] J. F. Villa, *Inorg. Chem.*, **12**, 2054 (1973).