amalgam and may be reoxidized by air. The visible spectra of the reduced and oxidized forms are quite similar with the 425-nm band of the oxidized form being replaced by a band at 438 nm, ϵ 501 cm^{-1} M^{-1} (mol of dimer)$^{-1}$ (the near-infrared spectra were not examined).

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Registry No. $Rh_2(OAc)_4$, 15956-28-2; $Rh_2(OAc)_3^+$, 55590-55-1; Rh_2^{4+}, 55569-94-3; $Rh_2(OAc)_2^{2+}$, 55590-54-0; $Rh_2(OAc)_4Cl$, 55569-93-2; $Ru_2(OAc)_4Cl$, 24729-38-2.

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Ligand Field Theory of Metal Sandwich Complexes. Ground States and Spectroscopic Properties of d^5 Configurations

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Recently the ligand field model has proved to be of considerable utility for the interpretation of the low energy d–d transitions of metal sandwich complexes[1,2] and for understanding the magnetic susceptibility and magnetic resonance phenomena shown by such species.[3,4] Thus far the familiar strong-field approach has proved to be the most satisfactory, and for d^2, d^3, and d^4 systems and their complementary counterparts full interaction matrices have been given,[2,5] assuming the effectively axial ($C_{\infty v}$) symmetry which obtains[6] for these complexes. For d^4, d^5, d^6, and d^7 systems, as for the analogous O_h compounds, either high-spin or low-spin ground states are in principle possible within the usual range of ligand field parameters, but for both metallocenes and bis(arene) compounds the d^6 and d^7 configurations show exclusively low-spin $^1\Sigma^+$ ($\sigma^2\delta^4$) and $^2\Pi$ ($\sigma^2\delta^4\pi$) ground states, while for the d^4 complex chromocene the low-spin $^3\Delta$ ($\sigma\delta^3$) ground state is well established.[3,5,7]

For d^5 systems however the evidence is confused and at times conflicting. Although it is now clear that the ferricenium cation, $FeCp_2^+$, shows a low-spin $^2\Delta$ ($\sigma^2\delta^3$) ground level and the bis(arenes) a similarly low-spin $^2\Sigma^+$ ($\sigma\delta^4$) ground state, it is still not altogether clear whether the ground state of manganocene, $MnCp_2$, corresponds to the high-spin $^6\Sigma^+$ ($\sigma\pi^2\delta^2$) or to the low-spin $^2\Delta$ ($\sigma^2\delta^3$) situation. The purpose of the present note is therefore to set out the results of a complete ligand field calculation for d^5, $C_{\infty v}$, systems and to correlate these with the known ground state and spectroscopic properties of d^5 metal sandwich complexes.

The complete strong-field electrostatic repulsion matrices have thus been evaluated using the methods described before,[2,5] and the results are given in the Appendix[8] and illustrated diagramatically in Figure 1. The diagonal one-electron core terms are as given earlier, and the ratios $Dt/Ds = 0.55$ (equivalent to $E(\delta) < E(\sigma) << E(\pi)$) and $C/B = 4.0$ are again assumed. With these parameters the high-spin to low-spin crossover is seen to occur at about $Dt/B = 2.8$ for the d^5 configuration as compared with the values of 2.9, 2.55, and 2.7 for the d^4, d^6, and d^7 systems, respectively. Consequently there is no a priori reason to expect $MnCp_2$ to be high spin while $CrCp_2$ remains low spin.

Nevertheless, until a short time ago it was widely accepted that the ground state of manganocene was in fact the high-spin $^6\Sigma^+$ ($\sigma\pi^2\delta^2$) level. This was based largely on the spin-only magnetic behavior found[9] for $MnCp_2$ in solution in benzene and ether and in solid solution in $MgCp_2$. For the pure solid the spin-only moment of 5.92 BM was found above the phase transition temperature of 158°, but below that point the moment was substantially smaller, decreasing markedly with decrease in temperature, this being attributed to antiferromagnetic interactions. Moreover, ESR experiments[10] at 270 and 100°K on pure $MnCp_2$ gave an almost isotropic g value of 2.0, the signal losing intensity on cooling, again consistent with a high-spin ground state.

Subsequently, although the first photoelectron spectrum reported[11] for $MnCp_2$ was surprisingly interpreted in terms of a $^2\Sigma^+$ ground level, it was later shown[5] that the ligand field treatment of the data was more consistent with a high-spin $^6\Sigma^+$ ground level, and this was confirmed by experimental reinvestigation of the spectrum by Orchard et al.,[7] who concluded that $MnCp_2$ was essentially high spin in the vapor phase, although the methyl-substituted analog, $Mn(MeCp)_2$, existed as a mixture of high- and low-spin forms. Finally, INDO type MO calculations by Clack[12] also supported a high-spin ground state for $MnCp_2$ although $E(^2\Delta) - E(^6\Sigma^+)$ was estimated at only 800 cm^{-1}.

However, two very recent studies have shed much additional light on the situation. Thus ESR measurements by Ammeter, Bucher, and Oswald[13] have now shown that both $MnCp_2$ and $Mn(MeCp)_2$ can exist in either high-spin, $^6\Sigma^+$, or low-spin, $^2\Delta$, forms, depending upon the molecular environment: when diluted in $MgCp_2$ manganocene shows typical high-spin behavior at 4.2°K whereas in the isostructural $FeCp_2$ or in $RuCp_2$ the ESR spectrum is characteristic of a low-spin $^2\Delta$ ($\sigma^2\delta^3$) ground state and closely resembles that found for the isoelectronic ferricenium cation. Consequently the anomalous magnetic properties of undiluted $MnCp_2$ were explained in terms of a thermal equilibrium between the high- and low-spin forms, the observed magnetic moment being reproducible by assuming $E(^6\Sigma^+) - E(^2\Delta) \approx 175$ cm^{-1}. Furthermore, the broad ESR signal of pure $MnCp_2$ at $g = 2.0$ disappeared at 4.2°K and was therefore attributed to thermal population of the higher lying $^6\Sigma^+$ state. Here it is pertinent to note that $Mn(MeCp)_2$ would be expected to donate more strongly toward the metal than $MnCp_2$ and thus to lie further over on the low-spin side of the crossover point. This expectation is borne out both by the observation of Ammeter et al.[13] that $Mn(MeCp)_2$ is low spin in $Fe(MeCp)_2$ and in $Mg(MeCp)_2$ and by the fact that the magnetic moments observed[14] for pure $Mn(MeCp)_2$ below the transition temperature are appreciably

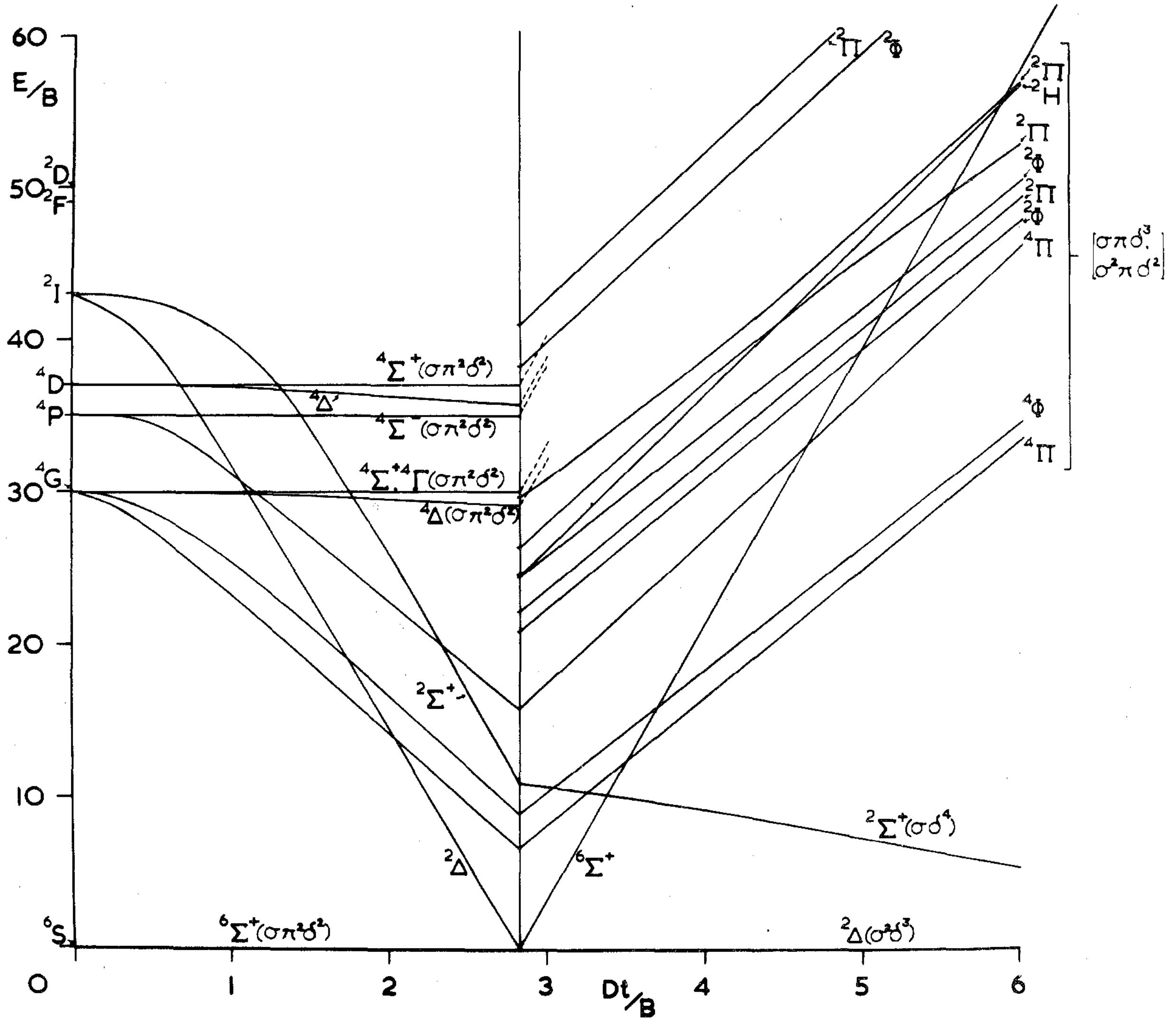

Figure 1. Energy level diagram for d^5 systems in $C_{\infty v}$ symmetry; $Dt = 0.55Ds$ and $C = 4B$ (with these parameters the ground state becomes $^2\Sigma^+$ at $Dt/B \approx 8.8$).

smaller than the corresponding values for pure MnCp2, in accordance with the expectation that $E(^6\Sigma^+) - E(^2\Delta)$ should be greater than for MnCp2.

These conclusions powerfully reinforce the results of an extensive study of the magnetic susceptibilities and the ESR and spectroscopic properties of MnCp2 and Mn(MeCp)2 due to Rettig et al.[15] Again the ESR data showed MnCp2 in MgCp2 at 4.2°K to exist in the high-spin, $^6\Sigma^+$, form, but although MnCp2 in hydrocarbon glasses showed only a single resonance at $g = 2.0$, Mn(MeCp)2 in similar media gave g values typical of a low-spin, $^2\Delta$, ground level. Furthermore, although regular high-spin moments had been observed[14] for Mn(MeCp)2 in the strong donor tetrahydrofuran, a thermal equilibrium was now found[15] for hydrocarbon solvents with $^2\Delta$ lying some 630 cm^{-1} lower, thereby supporting the view that $E(^6\Sigma^+) - E(^2\Delta)$ is greater for the methyl-substituted compound than for MnCp2 itself.

The above arguments have however important consequences as regards the spectroscopic characteristics expected for MnCp2 and Mn(MeCp)2. Experiment shows the former to be high-spin in hydrocarbon solvents and the latter to exist as an equilibrium mixture, but the undiluted solids should show predominantly low-spin properties. Thus the electronic spectrum of MnCp2 in solution should be that corresponding to a $^6\Sigma^+$ ground level, for which no moderately strong d–d bands would be anticipated since all such transitions must necessarily be spin-forbidden excitations to low-lying quartet levels. The diffuse reflectance spectrum of the solid should, though, be dominated by that corresponding to a $^2\Delta$ ground state, leading to spin-allowed doublet–doublet bands which would probably overwhelm any sextet–quartet absorptions arising from thermal population of the $^6\Sigma^+$ level. For Mn(MeCp)2 the spectrum of the solid should again be that of a $^2\Delta$ ground state while for solutions the spin-allowed absorptions of the low-spin $^2\Delta$ form should prevail over the spin-forbidden bands arising from the high-spin $^6\Sigma^+$ form.

For a $^6\Sigma^+$ ground state only transitions to quartet levels of the same $(\sigma\pi^2\delta^2)$ configuration, which should lead to relatively sharp bands, are likely to be readily observable, these corresponding (see Figure 1) to the band groups $^6\Sigma^+ \rightarrow {}^4\Sigma^+, {}^4\Gamma, {}^4\Delta$ (^{4}G), and $^6\Sigma^+ \rightarrow {}^4\Sigma^-$ (^{4}P), $^4\Sigma^+$ (^{4}D), respectively. Thus the very weak band found[15] at 21,050 cm^{-1} for MnCp2 is most reasonably assigned as $^6\Sigma^+ \rightarrow {}^4\Sigma^+, {}^4\Gamma, {}^4\Delta$ (which is virtually independent of Dt/B) which would give $B = 700$ cm^{-1} and $\beta = 0.81$, the rather high β value being consistent with the more ionic character expected for high-spin manganocene. For Mn(MeCp)2 the stronger band found at 21,300 cm^{-1} is more likely to represent a spin-allowed doublet–doublet transition, but for neither complex is it clear whether the bands reported at higher energies represent any further d–d excitations.

The solid-phase spectra are however predicted to be those arising from $^2\Delta$ ground states and should thus broadly resemble the known spectrum of $FeCp_2^+$, for which a partial treatment has been given by Sohn, Hendrickson, and Gray.[16] These authors appear however to have employed a different set of basis orbitals from that used here since the diagonal energy differences and off-diagonal matrix elements listed do not correspond with the present results (which have been checked by diagonalization in the free-ion limit), and not all the one-electron excitations possible for a $^2\Delta$ $(\sigma^2\delta^3)$ ground state were considered. Thus, as stated by Sohn et al. (using the D_{5d} symbolism) the $\sigma \rightarrow \delta$ and $\delta \rightarrow \pi$ excitations yield respectively the states $^2\Sigma^+$ $(\sigma\delta^4)$ and $2(^2\Pi) + {}^2\Phi + {}^2H$ $(\sigma^2\pi\delta^2)$, but the $\sigma + \pi$ excitation leads to $2(^2\Pi) + 2(^2\Phi)$ $(\sigma\pi\delta^3)$, instead of one state of each symmetry as reported.[16] With the parameters used in Figure 1 the spectrum of the ferricenium cation may be interpreted in terms of three groups of d–d transitions (in addition to the charge-transfer band at 16,200 cm^{-1}), viz., $^2\Delta \rightarrow {}^2\Phi, {}^2\Pi, {}^2\Phi$; $^2\Delta \rightarrow {}^2\Pi, {}^2H, {}^2\Pi$; and $^2\Delta \rightarrow {}^2\Phi, {}^2\Pi$; and the bands recorded[16] at 17,700–19,100 and at 21,400 and 26,300 cm^{-1} may be tolerably well fitted on this basis yielding $Dt/B \approx 4.5$ and $B \approx 500$ cm^{-1}. (The designations $(\sigma^2\pi\delta^2)$ and $(\sigma\pi\delta^3)$ are omitted from the excited states because of the appreciable mixing of these closely juxtaposed levels.) With these parameters the $^2\Sigma^+$ $(\sigma\delta^4)$ level is calculated to lie some 4000 cm^{-1} above the $^2\Delta$ $(\sigma^2\delta^3)$ ground state, and may well not be detectable optically. However, although the NMR studies of Anderson and Rai[17] suggest the separation to be rather smaller with $^2\Sigma^+$ only 400 cm^{-1} above the lower spin–orbit component of $^2\Delta$, the $^2\Sigma^+ - {}^2\Delta$ separation is very sensitive to the value of Dt/Ds and is markedly lowered by reduction of this ratio. Also estimates[18,19] from photoelectron and susceptibility data give $E(^2\Sigma^+) - E(^2\Delta)$ as between 2300 and 3400 cm^{-1}, in much better agreement with the present calculation. It should though also be noted that a decrease of Dt/Ds corresponds to a greater $E(\sigma) - E(\delta)$ separation; consequently for the bis(arene) complexes the more effective metal–ligand interaction for the δ level results in a larger $E(\sigma) - E(\delta)$ separation, thus moving the $^2\Delta$:$^2\Sigma^+$ crossover point to lower Dt/B values and allowing $^2\Delta$ to be superseded by $^2\Sigma^+$ as the ground state for these species.[20,21]

For the d^5 bis(arene) systems there are no adequate electronic spectra available, but the ligand field model shows that for a $^2\Sigma^+$ $(\sigma\delta^4)$ ground state three one-electron excitations are possible, namely, $\delta \rightarrow \sigma$, $\sigma \rightarrow \pi$, and $\delta \rightarrow \pi$. These in turn correspond to the doublet excited states $^2\Delta$ $(\sigma^2\delta^3)$ and $^2\Pi$ $(\pi\delta^4)$, respectively, together with the doublet states listed above for the $\sigma\pi\delta^3$ configuration.

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Supplementary Material Available. The Appendix, showing electrostatic repulsion matrices for d^5 configurations in $C_{\infty v}$ symmetry, 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 \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC500249-9-75.

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Tin-119 Mössbauer Quadrupole Splittings for Distorted Me_2Sn^{IV} Structures

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Partial quadrupole splittings[1] (in either the point-charge approximation[2] or the molecular orbital approximation[3,4]) have been very useful for distinguishing between *cis*- and *trans*-R_2SnL_4 isomers[5,6] and a number of six-coordinate Fe^{II} geometrical isomers[3,7] in the solid state. For many of the trans–cis Sn^{IV} and Fe^{II} pairs, the theoretically predicted 2:(−)1 trans:cis quadrupole splitting ratio is obeyed rather well. However, recent crystal structure data indicate that some Me_2SnL_4 compounds (where L_2 is a chelating ligand) and associated $Me_2SnL'_2$ compounds have structures which are intermediate between cis and trans. This rather surprising structural situation is represented by the structures of $Me_2Sn(oxin)_2$,[8] $Me_2Sn(S_2CNMe_2)_2$,[9] and $Me_2Sn(Salen)$[10] for which the C–Sn–C bond angles vary from 110 to 136 to 160°, respectively. In these three complexes (and in all the substantially distorted Me_2Sn compounds), the L–Sn–L angles differ substantially from 90° and/or the Sn–L bond lengths differ by a significant amount. Thus in $Me_2Sn(S_2CNMe_2)_2$, the Sn–S distances are 2.50, 2.51, 2.95, and 3.06 Å. The compounds appear to be unambiguously six-coordinate, however. The arrangement of the four S ligands and the Sn atom is planar with the sum of all S–Sn–S angles being close to 360°. In addition, the $J_{^{119}Sn-CH_3}$ coupling constants are normally characteristic of six-coordinate Sn. This bonding situation has been labeled by de Vries and Herber[11] as anisobidentate.

The quadrupole splittings (QS) for the aforementioned compounds $Me_2Sn(oxin)_2$, $Me_2Sn(S_2CNMe_2)_2$, and $Me_2Sn(Salen)$ are 2.02, 3.14, and 3.46 mm sec^{-1}, respectively. On the basis of these quadrupole splittings, the first structure has been labeled cis,[5] while the last two have been labeled trans[5,1,12] or distorted trans structures. From the recent structural data, it is apparent that the labeling of such compounds as cis or trans is no longer appropriate[13] for such structures. However, the additivity treatment, instead of just the 2:1 ratio,[13] is capable of rationalizing these changes in quadrupole splittings. In this paper, we present a simple model which readily accounts for the changes in QS as a function of C–Sn–C angle for 17 of 19 known Me_2Sn^{IV} structures.