beyond the range of effective coupling with the C–O bending mode, which then appears together with the second C–O mode at *ca.* 676 cm.$^{-1}$. The *uncoupled* Mn–H bending frequency is thus fixed at *ca.* 665 cm.$^{-1}$!

Thus both Mn–H stretching and bending frequencies are established. They are consistent with the *metal–hydrogen bonding limit* of the model of Edgell, Magee and Gallup,[1] and with those of Hieber[5] and Cotton and Wilkinson.[3] While not definitely proven, the above findings imply that the bonding of the hydrogen in $HCo(CO)_4$ and $H_2Fe(CO)_4$ is similar to that in $HMn(CO)_5$ with greater hydrogen–CO coupling.

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W. F. EDGELL
CHEMISTRY DEPARTMENT G. ASATO
PURDUE UNIVERSITY W. WILSON
LAFAYETTE, INDIANA C. ANGELL

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$D_{\infty h}$ LIGAND FIELDS AND "SANDWICH" COMPLEXES[1]

Sir:

Numerous molecular orbital treatments of ferrocene and its analogs have been published.[2–7] There is presented here a strong-field, ligand-field model for sandwich-type complexes with the general formula $M^{\mu}(R^{\nu})_2$. Here M^{μ} is a transition metal atom in its μth valence state and R^{ν} is a planar ring carrying a charge ν. The field on M^{μ} from rings R^{ν} is due to the formal charges on the ring and/or virtual charges arising from mutual polarization of M and R. It is assumed that the actual field is adequately reproduced by one of $D_{\infty h}$ symmetry and that the field uncouples the d electrons on the transition metal atom.[8] Since the field is axially symmetric, m remains a good quantum number, the d functions of different $|m|$ are not mixed, and the five d orbitals have at most three different energies. Let $a = r \sin \theta$ be the coördinate perpendicular, and $z = r \cos \theta$ the coördinate parallel to the symmetry axis. The perturbing field contains no odd powers in z because of the symmetry plane through M^{μ}. The field is assumed to be continuous at the origin so that it contains no first power in a. To the second power

$$\begin{aligned} V &= V_0 + V_a a^2 + V_z z^2 \\ &= \{V_0 + V_a(a^2 + z^2)\} - (V_a - V_z)z^2 \end{aligned}$$

The portion of the perturbation in braces is spherically symmetric, produces no d splitting, and is neglected. With hydrogenic orbitals of effective charge Z, $E(e_{2g}) = -3Dd$, $E(e_{1g}) = -9Dd$, and $E(a_{1g}) = -11Dd$, where $Dd = 6(V_a - V_z)(Z/a_0)^2$ is the $D_{\infty h}$ ligand field strength. In Table I are listed the $D_{\infty h}$ electron configurations of some ferrocene analogs assuming $V_a > V_z$ and a formal charge of -1 on each ring. Also listed are the observed paramagnetic moments expressed as number of unpaired electrons.

TABLE I

Species[a]	Assignment ($D_{\infty h}$ field)	Unpaired electrons (obs.)[b]
$(Cy)_2Ti$	$(a_{1g})^2$	0
$[(Cy)_2Mo]^{+2}$	$(a_{1g})^2$	0
$(Cy)_2V$	$(a_{1g})^2(e_{1g})^1$	3
$[(Cy)_2Cr]^+$	$(a_{1g})^2(e_{1g})^1$	3
$(Cy)_2Cr$	$(a_{1g})^2(e_{1g})^2$	2
$[(Cy)_2Fe]^+$	$(a_{1g})^2(e_{1g})^3$	1
$(Cy)_2Mn$	$(a_{1g})^2(e_{1g})^3$	5
$(Cy)_2Fe$	$(a_{1g})^2(e_{1g})^4$	0
$[(Cy)_2Co]^+$	$(a_{1g})^2(e_{1g})^4$	0
$[(Cy)_2Rh]^+$	$(a_{1g})^2(e_{1g})^4$	0
$[(Cy)_2Ir]^+$	$(a_{1g})^2(e_{1g})^4$	0
$(Cy)_2Ru$	$(a_{1g})^2(e_{1g})^4$	0
$(Cy)_2Co$	$(a_{1g})^2(e_{1g})^4(e_{2g})^1$	1
$(Cy)_2Ni$	$(a_{1g})^2(e_{1g})^4(e_{2g})^2$	2

[a] Cy = C_5H_5. [b] Bibliography is given in reference 7.

The predictions agree with experiment except for $(Cy)_2V$, $(Cy)_2Cr^+$, and $(Cy)_2Mn$ which suggest that a weak field treatment may be required. The considerations given here should apply also to the benzene metal complexes. The author is indebted to Professor G. W. Watt for the suggestion of a field theory approach to the problem and for a preliminary correlation of the data.

DEPARTMENTS OF CHEMISTRY AND PHYSICS
THE UNIVERSITY OF TEXAS F. A. MATSEN
AUSTIN 12, TEXAS

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SYNTHETIC STUDIES ON SPHINGOLIPIDS. V. THE SYNTHESIS OF DIHYDROCEREBROSIDES

Sir:

The structure of the cerebrosides has been established by Carter and co-workers[1–3] as Va, in which R is a long-chain fatty acid residue. We wish to report the synthesis of palmitoyl- and stearoyl-dihydrocerebrosides (Vb and Vc).

As key intermediate we employed the substituted *cis*-oxazoline I ($R^1 = CH_3(CH_2)_{14}$).[4] Hydrolysis with diluted hydrochloric acid gave *erythro*-3-O-benzoyldihydrosphinogosine (II), which was not isolated, but was acylated directly in the presence of sodium acetate to give the *erythro* form of the amidoester III. (IIIb: m.p. 74–75.5°; found: C, 76.8; H, 11.8; N, 2.2; IIIc: m.p. 73–75°; found: C, 76.9; H, 11.35; N, 2.0.)

When a benzene solution of III was shaken with tetraacetyl-α-D-galactosyl bromide[5] in the presence of freshly-prepared silver carbonate,[6] a 60% yield of IV was obtained. (IVb: m.p. 43–45°; found: C, 67.9; H, 9.7; N, 1.8; IVc: m.p. 43–45°; found: C, 67.9; H, 9.3; N, 1.6). Saponification

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