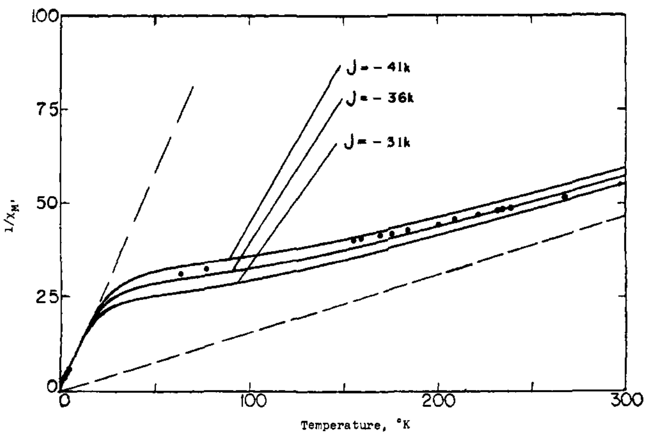

Figure 2. For $K_7[(H_2O)Fe^{3+}O_5Co^{2+}O_4W_{11}O_{30}]\cdot 14H_2O$. Points represent experimental susceptibilities, corrected for Co's TIP and for diamagnetism on basis of adjustment of experimental diamagnetism[10] of $K_4[SiO_4W_{12}O_{36}]\cdot 11H_2O$. Solid lines are susceptibility behaviors predicted by the theory, using S and g values in the last paragraph of the text, for three values of J/k (in °K). Dashed lines are the theoretical asymptotically approached limiting Curie laws for low and for high T's.

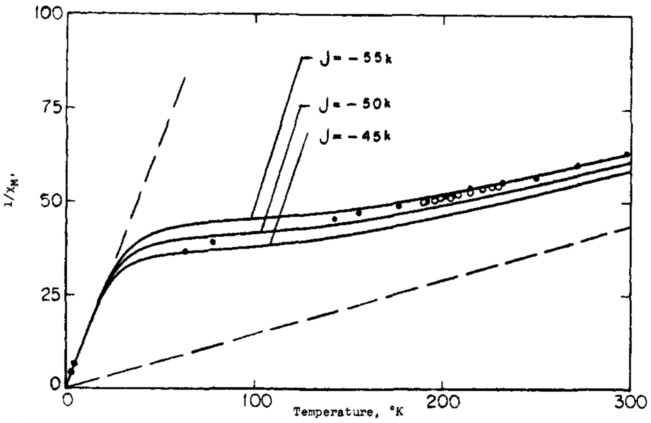

Figure 3. For $K_7[(H_2O)Co^{2+}O_5Fe^{3+}O_4W_{11}O_{30}]\cdot 13H_2O$. Points represent corrected (for Co's TIP and for diamagnetism) experimental susceptibilities. Filled dots taken in order of decreasing T, open dots in order of increasing T. Solid lines are susceptibility behaviors predicted by the theory, using S and g values in the last paragraph of the text, for three values of J/k (in °K). Dashed lines are the theoretical asymptotically approached limiting Curie laws for low and for high T's.

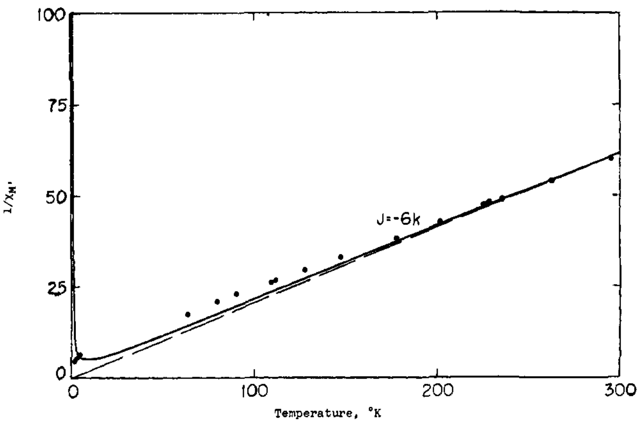

Figure 4. The shape when $S_1 = S_2$. For $(NH_4)_8[(H_2O)Co^{2+}O_5Co^{2+}O_4W_{11}O_{30}]\cdot 13H_2O$. Points represent experimental susceptibilities, corrected for Co's TIP's and for diamagnetism. Solid line is behavior predicted by the theory for $S_1 = S_2 = {}^3/_2$ and unequal g values in the last paragraph of the text. Dashed line is predicted limiting Curie law for rising T. Theory predicts that $1/\chi_{M'}$ should go through a minimum at very low T. The predicted rise in $1/\chi_{M'}$ with decreasing T at very low T was not observed down to 2°K. A small amount of paramagnetic impurity could account for that.

bilities from 2 to 300°K were obtained for I–V using a single set of S's and g's obtained independently from spectra and/or magnetic behaviors of isomorphous complexes containing only one paramagnetic atom apiece.[10,11]

For Fe^{3+}(oct or tet), $S = {}^5/_2, g = 2.0$. For Co^{2+}(tet), $S = {}^3/_2$, $g = 2.2$. For Co^{2+}(oct), $S = {}^3/_2$, $g = 2.4$. For Co^{3+}(tet), $S = 2$, $g = 2.07$.[24] Figures 2–4, for I, II, and V, show typical results. For III, $J/k = -36 \pm 5$°K. For IV (partial data published[1]), $J/k = -72 \pm 5$°K. $K_5[Fe^{3+}O_4W_{12}O_{36}]\cdot 15H_2O$ and VI each follow simple Curie law to 2°K for spin-only $S = {}^5/_2$, since Co^{3+}(oct) is diamagnetic.

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(24) The X-ray structure[25,26] of hexagonal $K_5[Co^{3+}O_4W_{12}O_{36}]\cdot 20H_2O$ shows the $Co^{3+}O_4$ tetrahedron has Jahn–Teller elongation, whereas the $Si^{4+}O_4$ in isomorphous[12] $K_4[Si^{4+}O_4W_{12}O_{36}]\cdot 18H_2O$ is regular.[27] Thus the $Co^{3+}O_4$ elongation is not caused by crystal packing forces. These *complexes* are isomorphous with the biheteroatom 11-heteropoly species ($M^{m+} = W^{6+}$ and $Y^{y-} = O^{2-}$). $K_5[Co^{3+}O_4W_{12}O_{36}]\cdot 20H_2O$ follows very precisely a Curie–Weiss law ($\theta = -1.1 \pm 0.5$) with $g = 2.07$. The increase of g above 2.00 and the negative θ coincide with elongation of the $Co^{3+}O_4$ in accordance with theory.[10] Isomorphous $K_5H[Co^{2+}O_4W_{12}O_{36}]\cdot 15H_2O$, containing a regular $Co^{2+}O_4$ tetrahedron,[28] precisely follows a Curie law with $g = 2.20$.

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Interpretation of Photoelectron Spectra of Hydrocarbons by Use of a Semiempirical Calculation

Sir:

The interpretation of photoelectron spectra of organic molecules has appeared to be more difficult than expected as the present nonempirical and semiempirical theories give orbital energies that usually differ very much from the observed ionization potentials. In the comparison of experiment and theory it has therefore appeared to be necessary to introduce empirical corrections of different kinds.

To avoid this we have tried to parametrize the semiempirical procedure, INDO, to get agreement with photoelectron-spectroscopic ionization potentials.

The new procedure, SPINDO (spectroscopic potentials adjusted INDO),[1] can briefly be described as MINDO[2,3] with the following changes for a hydro-

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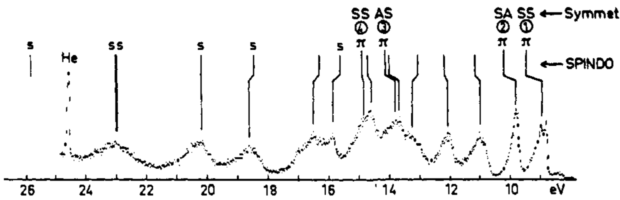

Figure 1. Photoelectron spectrum of 1,4-cyclohexadiene, obtained using the 304-Å helium line with interpretation according to a SPINDO/1 calculation. For the π orbitals the symmetry is indicated.[10,11]

carbon. For the carbon atom $U_{ss} = -48.289$ eV and Slater exponent = 1.925. In the resonance integrals

$$H_{\mu\nu} = S_{\mu\nu}[I_\mu{}^A + I_\nu{}^B]f(R_{AB})$$

the factors f have different values for different types of interaction: for 1s/1s, $f(R) = 0.13647$; for 1s/2s, $f(R) = 0.17832$; for 1s/2pσ, $f(R) = 0.35100$; for 2s/2s, $f(R) = 0.20187 + 0.09500/R^2$; for 2s/2p$\sigma$, $f(R) = 0.27625 + 0.13000/R^2$; for 2p$\sigma$/2p$\sigma$, $f(R) = 0.47000 + 0.24000/R^2 + 100 \exp(-5R)$; for 2p$\pi$/2p$\pi$, $f(R) = 0.40375 + 0.19000/R^2$. The parameters were chosen to give reasonable agreement in the case of benzene (with interpretation according to Jonsson and Lindholm[4]), methane, ethane, ethylene, and acetylene.

To demonstrate the usefulness of the new procedure we will in this communication apply it to two molecules: 1,4-cyclohexadiene and *trans*-1,3-butadiene.

In the SPINDO calculation of cyclohexadiene the "planar" geometry discussed by Oberhammer and Bauer[5] was used (*cf.* ref 6, 7). The SPINDO orbital energies are compared in Figure 1 with the photoelectron spectrum, observed in our photoelectron spectrometer.[8] Its low-energy part agrees well with an earlier study.[9] It can be seen that the distribution of the orbital energies corresponds well to the maxima of the curve. This supports our method and indicates that also the form of the molecular orbitals is obtained approximately correctly from the SPINDO calculation.

The most interesting feature of the molecular orbitals of 1,4-cyclohexadiene is that the σ orbitals are nearly identical with the corresponding orbitals in benzene. Also the orbital energies are nearly the same as in benzene, although, of course, the degenerate benzene orbitals are split. The introduction of two extra hydrogens in cyclohexadiene does not influence the σ-orbital system much.

The π orbitals of 1,4-cyclohexadiene have no similarity with those of benzene. Owing to the two extra hydrogens the cyclohexadiene has four π orbitals. The two highest are in-phase ① and out-of-phase ② combinations of the ethylene π orbitals and the two lowest are similar combinations of the CH_2 orbitals, ③ and ④. That the in-phase combination ① is highest depends upon the destabilizing influence of the two CH_2 orbitals. This result is in good agreement with earlier treatments of interaction through bonds[10-12] in this molecule.

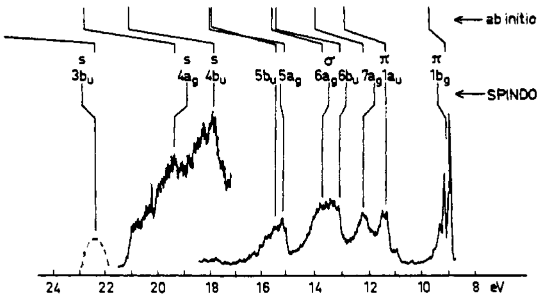

Figure 2. Photoelectron spectrum of butadiene[16] compared with orbital energies from SPINDO/1 and from an *ab initio* calculation.[17] The band at 22.4 eV was observed by Brundle and Robin.[21]

In the SPINDO calculation of butadiene the geometry given by Haugen and Traetteberg[13,14] and Kuchitsu, *et al.*,[15] was used. The SPINDO orbital energies are compared in Figure 2 with the photoelectron spectrum observed by Turner.[16] It can be seen that the orbital energies correspond well to the different maxima of the photoelectron curve, especially when compared to the *ab initio* results[17] at the top of the figure.

Our calculation may contribute to recent discussions whether the second ionization potential in butadiene is σ or π. The *ab initio* calculations[17,18] indicate π, but semiempirical calculations[19,20] indicate σ. Brundle and Robin[21] tried to solve the problem by a study of fluoro-substituted butadienes and found evidence for σ. It follows, however, from Figure 2 that the SPINDO calculation indicates that the second ionization potential is π, in agreement with the *ab initio* calculations.

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Synthesis and Electrochemical Behavior of a New Series of Macrocyclic Complexes of Iron Produced by Oxidative Dehydrogenation and Tautomerization

Sir:

The Fe(II) complexes of the ligands shown in Chart I constitute a distinctive series of compounds containing ligand systems with different degrees and types of