

Figure 1.—The temperature dependence of the nmr spectra of $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\pi\text{-C}_3\text{H}_5)$, (a) in CDCl_3 and (b) in C_6H_6 . The high-temperature spectra were obtained using sealed tubes on a Varian A-60 spectrometer equipped with a variable-temperature probe.

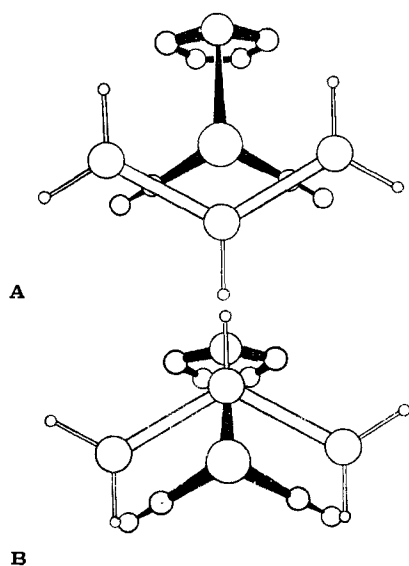


Figure 2.—Probable configurations of $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\pi\text{-C}_3\text{H}_5)$. The cyclopentadienyl protons have been omitted for simplicity.

involves an equilibrium between different configurations, which is rapid compared to the nmr time scale. At low temperatures two isomers exist in unequal amounts (*ca.* 1:7). While we cannot specify the exact

mechanism for the interconversion (*i.e.*, rotation about an axis through the C-C-C plane or an equivalent operation which does not interconvert the *syn* and *anti* protons), we feel that the two most likely structures for the species are those shown in Figure 2, with 2A most probably being the more stable.⁹

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On the Electronic Structure of the Tris(2,2'-bipyridyl)chromium(II) Ion

Sir:

In an earlier paper¹ we reported the magnetic susceptibility at several temperatures for the low-spin d^4 complex, tris(2,2'-bipyridyl)chromium(II) bromide tetra-

(1) A. Earnshaw, L. F. Larkworthy, K. C. Patel, K. S. Patel, R. L. Carlin and E. G. Terezakis, *J. Chem. Soc., Sect. A*, 511 (1966).

hydrate. Our results do not fit the variation predicted by Kotani²

$$\mu_{\text{eff}}^2 = \frac{144[\exp(3x/2)] + (3x - 54)[\exp(x)] + 15x - 90}{2x[(\exp(3x/2)) + 3(\exp(x)) + 5]} \quad (1)$$

Here, $x = \lambda/kT$, where λ is the spin-orbit coupling constant. The magnetic moment is derived as a function of T and λ with the assumptions of perfect octahedral symmetry and no d-electron delocalization. In this note we compare our results to calculations by Kamimura³ that allow for a trigonal or tetragonal distortion of the complex. The expression for μ_{eff}^2 for t_{2g}^4 systems, too lengthy to reproduce here, is in terms of $x = \bar{r}^2A/7kT$ and $y = \lambda/2kT$, where \bar{r}^2A pertains to the noncubic part of the ligand-field Hamiltonian.

Figure 1 shows the experimental moments compared to plots of eq 1 calculated for three values of λ/k . These were the free-ion value (326°K), an estimate of the probable complexed ion value (250°K), and an unrealistically low value (150°K). To see whether inclusion of the effects of the trigonal field could bring the theory closer to experiment, magnetic moments were calculated from Kamimura's equation on an IBM 7044 computer. The parameter λ/k was changed in 10° increments. For each λ/k , several \bar{r}^2A/k values were inserted for the 12 experimental temperatures. Nothing was known in advance about the sign of \bar{r}^2A/k so both negative and positive values were used. It is not necessary to reproduce the results here in detail. As in the case of Kotani's equation, changing λ/k did not significantly improve the fit of the equation. The same was true for the parameter \bar{r}^2/k (\bar{r}^2A/k could not exceed $+7\lambda/k$ without creating a negative square root in one of the terms, but negative values of any magnitude were possible). The maximum in the μ_{eff} vs. T plot could not be shifted above room temperature to fit the shape of the experimental curve nor could the values of the moments be reduced by the 12% needed to make them fall near the experimental curve.

Figgis and co-workers⁴ have calculated magnetic moments for the $(t_{2g}^4) {}^3T_1$ state for various combinations of the parameters describing spin-orbit coupling, trigonal distortion of the octahedral field, d-electron delocalization onto the ligand atoms, and mixing of the 3P and 3F free-ion states. We have used this theory successfully elsewhere⁵ to examine some vanadium complexes whose d^2 configuration also gives rise to 3T_1 . Using Figgis' theory we fit the experimental results for $\text{Cr}(\text{bipy})_3^{2+}$ well with one set of physically reasonable parameters. The ratio of the reduced spin-orbit coupling constant to the free-ion value, λ'/λ , is 0.74; the orbital delocalization factor, k , is 0.6; the trigonal splitting, Δ , between the 3E and 3A states is $+640 \text{ cm}^{-1}$ with the orbital singlet lower in energy; A , the 3F - 3P state mixing coefficient, is 1.3,

(2) M. Kotani, *J. Phys. Soc. Japan*, **4**, 293 (1949).

(3) H. Kamimura, *ibid.*, **11**, 1171 (1956).

(4) B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc., Sect. A*, 1411 (1966).

(5) R. L. Carlin and E. G. Terezakis, *J. Chem. Phys.*, in press; E. G. Terezakis, Ph.D. Thesis, Brown University, June 1967.

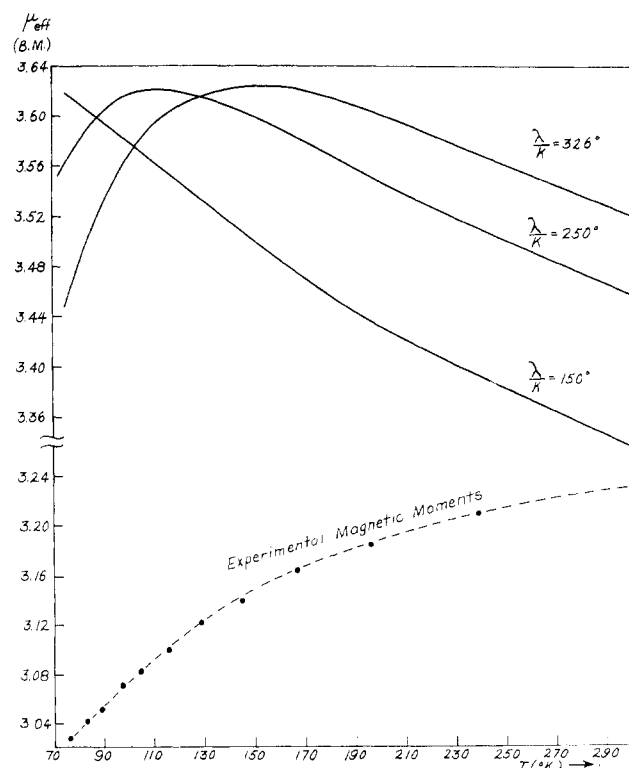


Figure 1.—Magnetic behavior of t_{2g}^4 predicted by Kotani's theory, eq 1, and experimental magnetic moments for $[\text{Cr}(\text{bipy})_3] \cdot 4\text{H}_2\text{O}$.

The exact value of the spin-orbit coupling constant is not very significant⁶ nor is the value of A as long as it indicates partial mixing of the 3F and 3P states. The determination of k is accurate and significant, however, and the low value of 0.6 is expected for the highly π -bonding bipyridyl ligands. This is more reasonable than the $k = 1$ required⁶ to fit the temperature dependence of magnetic susceptibility of the tris(2,2'-bipyridyl)iron(III) ion. The Δ value may be compared with the ferric compound (600 cm^{-1}) where a comparable distortion is expected but the hexaquo-vanadium(III) ion, on the other hand, requires⁵ a Δ of about 800 cm^{-1} . A larger distortion was expected with bidentate ligands. Figgis, Lewis, Mabbs, and Webb⁴ found that the Δ values for a series of nickel(II) compounds were not closely related to the geometric distortions. The main factor causing a reduction in magnetic moments was found by Figgis, *et al.*,⁴ to be a decrease in the value of the electron delocalization parameter, k , and we find the same requirements for the theories of Kotani and Kamimura for t_{2g}^4 . On the other hand, the values of parameters found by Figgis' procedure must be considered only approximate.

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(6) B. N. Figgis, *Trans. Faraday Soc.*, **57**, 204 (1961).

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