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# A Reinterpretation of the Anisotropy in the Magnetic Susceptibility of $VO(acac)_2$

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Bis(pentan-2,4-dionato)oxovanadium(IV), $VO(acac)_2$, is a relatively stable $d^1$ complex that has attracted extensive spectroscopic [1], magnetic [2–4] and magneto-optical [5] studies. Although assignments of the u.v.–visible spectrum are still not settled [1] there seems to be a consensus favouring the Ballhausen–Gray [6] ordering of the metal ion d states over a clustering of d-levels proposed by Selbin and co-workers [7, 8].

Information concerning the ordering of the d states can, in principle [9], be obtained by analysing the temperature independent (ti) part, $\Delta\chi^{ti}$, of the anisotropy

$$\Delta\chi = \chi_{zz} - 1/2(\chi_{xx} + \chi_{yy})$$

in the magnetic susceptibility. Mitra [10] recently analysed the observed temperature dependences [4] of the magnetic susceptibilities parallel and perpendicular to the vanadyl axis (z) and has found $\Delta\chi^{ti}$ to be negative. He interpreted $\Delta\chi^{ti}$ as the anisotropy, $\Delta\chi^{tip}_{dd}$, in the temperature independent paramagnetism associated with d–d transitions and discussed the ordering of d states on this basis. Here we present theoretical evidence indicating that $\Delta\chi^{tip}_{dd}$ is, in fact, positive and that the negative experimental value of $\Delta\chi^{ti}$ stems mainly from additional contributions not associated with the unpaired electron.

The uv–visible spectrum of the crystal exhibits absorption bands in the vicinity of 15,000, 17,000 and 25,000 $cm^{-1}$ [1]. According to the Ballhausen–Gray assignment [6] these represent d–d transitions from the $C_{4v}$ ground state $b_2(d_{xy})$ to the $e(d_{xz}, d_{yz})$, $b_1(d_{x^2-y^2})$ and $a_1(d_{z^2})$ excited states, respectively. The crystal field parameters Dq, Ds and Dt appropriate to $C_{4v}$ symmetry [11] and to the Ballhausen–Gray assignments have been listed [12] and typical values are given below

$$Dq \simeq 1700\ cm^{-1},\ Ds \simeq -3400\ cm^{-1},\ Dt \simeq 900\ cm^{-1}$$

Selbin's cluster scheme [7, 8] on the other hand, attributes the band at highest frequency to charge-transfer and/or spin-forbidden transitions. It also permits the $b_1(d_{x^2-y^2})$ state to lie below the $e(d_{xz}, d_{yz})$ states which are split by spin–orbit coupling. From assignments of reflectance spectra published by Selbin and coworkers [8] we obtain the crystal field parameters

$$Dq \simeq 1500\ cm^{-1},\ Ds \simeq -2840\ cm^{-1},\ Dt \simeq 1210\ cm^{-1}$$

Symmetry labels and orbital designations adopted here are favoured by inorganic chemists [4, 6, 8, 10] but do not conform with standard spectroscopic practice [1].

Employing these parameters in conjunction with a spin–orbit coupling constant of 150 $cm^{-1}$ [6, 13] we have used crystal field theory [9] to compute magnetic properties of the complex. Calculations were performed using both the $\{l\ s\ m_l\ m_s\}$ and the $\{l\ s\ j\ m_j\}$ basis sets with $l = 2$, $s = 1/2$ and $j = 3/2, 5/2$. Eigenvalues and eigenfunctions of the isolated complex were computed from the matrix of the effective hamiltonian (including both crystal field and spin–orbit terms) of the d electron. Quantum mechanical perturbation theory leads directly to theoretical g-valves and paramagnetic susceptibilities of the complex [9, 14].

Table I summarizes our calculations of g-values and of the temperature independent component,

TABLE 1. A Comparison of Theoretical with Experimental g-values and Susceptibility Anisotropies.[a]

| Quantity | Estimate from Ballhausen–Gray crystal field[b] | Estimate from Selbin crystal field[b] | Experimental values |
|---|---|---|---|
| $g_{\parallel}$ | 1.93 | 1.90 | 1.93[c], 1.943[d], 1.943[e] |
| $g_{\perp}$ | 1.98 | 1.98 | 1.99[c], 1.982[d], 1.983[e] |
| $10^6\ \Delta\chi^{tip}_{dd}$ | +87 | +146 | |
| $10^6\ \Delta\chi^{p}$ (300 K) | +25 | +44 | |
| $10^6\ \Delta\chi$ (300 K) | −35[f] | −16[f] | −76[c] |

[a] In units of $cm^3\ mol^{-1}$. [b] With a spin–orbit coupling of 150 $cm^{-1}$. [c] Reference [4]. [d] Reference [3]. [e] Reference [2]. [f] Assumes $10^6\ \Delta\chi([VO(acac)_2]^+) \simeq -60$.

$\Delta\chi^{tip}_{dd}$, of the paramagnetic anisotropy, $\Delta\chi^{p}$, associated with the d electron. The anisotropy, $\Delta\chi^{p}$, is the sum [14] of $\Delta\chi^{tip}_{dd}$ and a first order Zeeman term directly proportional to $g_{\|}^2 - g_{\perp}^2$ and inversely proportional to the temperature.

Our calculations show that neither the Ballhausen–Gray nor the Selbin crystal field parameters support Mitra's assumption that $\Delta\chi^{tip}_{dd}$ is negative. The negative sign of the experimental quantity $\Delta\chi^{ti}$ can be reconciled with the positive sign of $\Delta\chi^{tip}_{dd}$ if we suppose that Mitra has neglected contributions from the closed shell skeleton of the complex and that this contribution dominates the temperature independent component of the magnetic anisotropy.

Compilations [15] of magnetic anisotropies of closed shell molecules containing fragments similar to those in $VO(acac)_2$ suggest that the hypothetical complex ion $[VO(acac)_2]^+$, formed by removing the d electron while retaining the equilibrium nuclear geometry of the parent species, has a magnetic anisotropy of about $-60 \times 10^{-6}$ cm$^3$ mol$^{-1}$. If the d-electron diamagnetism [14] and certain charge-transfer terms are neglected we can write the experimental quantity, $\Delta\chi^{ti}$, as

$$\Delta\chi^{ti} = \Delta\chi^{tip}_{dd} + \Delta\chi([VO(acac)_2]^+)$$

Corrections similar to the second term in this equation are commonly applied for ligands such as phthalocyanine [16] with particularly large susceptibility anisotropies but the hazardous consequences of neglecting more moderate skeletal anisotropies in molecules, such as $VO(acac)_2$, with small paramagnetic anisotropies should also be recognised. The value of $\Delta\chi^{ti}$ extracted from data in reference [4] is close to $-25 \times 10^{-6}$ cm$^3$ mol$^{-1}$. This value, in conjunction with a skeletal anisotropy of $-60 \times 10^{-6}$ cm$^3$ mol$^{-1}$, suggests that covalency and vibronic couplings neglected in Van Vleck's crystal field model might substantially reduce the values for $\Delta\chi^{tip}_{dd}$ reported in the table but that their positive signs are still appropriate. Finally, we note the unexpectedly large discrepancy between the directly measured value of $-0.235$ for $g_{\|}^2 - g_{\perp}^2$ reported by Gregson and Mitra [4] and a value close to $-0.081$ for the same quantity extracted from an analysis of the temperature dependence of their susceptibilities.

We conclude that the Ballhausen–Gray crystal field parameters lead to better g-components and susceptibility anisotropies than the corresponding parameters based on Selbin's spectral assignments. The magnitude but not the sign of $\Delta\chi^{tip}_{dd}$ is sensitive to the ordering of the $b_1(d_{x^2-y^2})$ and $e(d_{xz}, d_{yz})$ states for both cases reported in Table I and for several others that we have considered. In the absence of reliable estimates of skeletal anisotropy, susceptibility measurements provide little quantitative information about the d states not already available from g-anisotropy. The contention [4] that the Ballhausen–Gray and Selbin spectral assignments lead to opposite signs for the anisotropy in the magnetic susceptibility is not supported by our analysis.

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