

the S_T states with the corresponding quantum number. The energy levels were determined by diagonalizing the H_{ij} matrix ($H_{ij} = \langle \Psi_i | \mathcal{H} | \Psi_j \rangle$). The diagonalization was simplified by block-factoring the matrix into M_{ST} submatrices, where $M_{ST} = m_{S1} + m_{S2} + m_{S3}$. The magnetic susceptibilities of the trimer were calculated from the spin-coupled wave functions by using a simplified form of the Van Vleck equation¹⁶

$$\chi = N \frac{\sum_{i=1,n} \frac{|\langle \Psi_i | \hat{\mu} | \Psi_i \rangle|^2}{kT} e^{-E_i/kT}}{\sum_{i=1,n} e^{-E_i/kT}} \quad (3)$$

where E_i is the energy of the energy level with wave function Ψ_i and $\hat{\mu}$ is the moment operator ($\hat{\mu} = g\mu_B \hat{S}_z$).

The results of a least-squares fit of the magnetic data are illustrated in Figures 1 and 2 as plots of the effective magnetic moment ($\mu_{\text{eff}} = (8\chi T)^{1/2}$) for the selenide and telluride complexes, respectively. The smooth curves drawn through the points represent the best fit of the trimer model using the fitted parameters listed in Table I.

It is concluded that the nearest-neighbor chromium centers are antiferromagnetically coupled following the symmetric linear trimer model with a quartet ground state for both complexes. The magnetic coupling is sufficiently strong that the highest energy

levels are not fully populated in the accessible temperature range and the high-temperature moment is less than the normal value associated with chromium(III). The lowest temperature data however are consistent with the coupled total spin of $S = 3/2$ for the trimer as a whole. The selenide complex has a significantly stronger antiferromagnetic exchange when compared with the tellurium analogue, but this could be attributed to the closer bonding proximity of the chromium(III) ions in the selenide complex (Cr1–Cr2 distance of 3.207 Å for the selenide and 3.41 Å for the telluride). Attempts to fit the magnetic data to a model that neglected the J' coupling term (i.e., coupling between the two outer Cr^{III} ions) gave inferior results. Other authors have often used a biquadratic term to analyze chromium(III) dimer systems.¹⁷ This term was not needed for our analysis, since we obtained acceptable fits with the unmodified spin Hamiltonian given (eq 2). Any improvement of the fit that would occur upon the addition of more terms to the spin Hamiltonian could be attributed to overparameterization.

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(16) Van Vleck, J. H. *The Theory of Electric and Magnetic Susceptibilities*; Oxford University Press: London, 1932.

(17) Hodgson, D. J. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, The Netherlands, 1983; p 497.

Additions and Corrections

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Robert L. Blackburn and Joseph T. Hupp*: Electron-Transfer Reactions in Mixed Solvents. An Electrochemical Probe of Unsymmetrical Selective Solvation.

Page 3788. The caption to Figure 3 is incorrect. The correct caption is as follows: E_f vs solvent composition ($\text{CH}_3\text{CN} + \text{DMSO}$ mixtures) for reduction of (a) $\text{Ru}(\text{bpy})_3^{3+}$, (b) $(\text{NH}_3)_2\text{Ru}(\text{bpy})_2^{3+}$, (c) $(\text{NH}_3)_4\text{Ru}(\text{bpy})^{3+}$, (d) $(\text{NH}_3)_5\text{Ru}(\text{py})^{3+}$, and (e) $\text{Ru}(\text{NH}_3)_6^{3+}$.—Joseph T. Hupp