tained only at ligand concentrations of 2.5×10^{-3} *F* or less and, therefore, only these current–voltage curves were used in calculating log β_1 from the Cu(I)–Cu(0) data. Over this rather limited concentration range the shift of $(E_{1/2})_c - (E_{1/2})_s$ *vs.* log [cyc] is −0.060 giving again a value of 1 for *p*. The combined behavior of the Cu(II)–Cu(I) and Cu(I)–Cu(0) couples indicates that Cu(II) is not complexed by the olefin in acetone. The value of log β_1 calculated from the Cu(I)–Cu(0) data is 4.6.

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Magnetic Studies with Copper(II) Salts. VIII. Vibrational Effects in the Singlet–Triplet Equilibrium of Copper(II) Acetate

BY R. L. MARTIN

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The application of Van Vleck's equation[1] in the calculation of the temperature variation of the magnetic susceptibility of systems involving spin equilibria tacitly assumes that there is no difference between vibrational frequencies of the different spin states. The effect of neglecting this correction emerged in a recent investigation of the magnetic properties of iron(III) dithiocarbamates which lie at the $^6A_1$–$^2T_2$ crossover.[2] Although the temperature dependence of the magnetism did not conform exactly with the predictions of the Van Vleck equation, it was considered to be tractable when molecular vibrational partition functions were introduced into this equation.

The present note explores the consequences of introducing vibrational partition functions into the susceptibility equation for the copper(II) acetate dimer which involves singlet and triplet states in thermal equilibrium.[3] A noteworthy difference between this compound and the mononuclear iron(III) dithiocarbamates is that the singlet and triplet spin states originate in a metal-to-metal interaction rather than in changes of metal–ligand internuclear separation with electron configuration. Accordingly, the correction is likely to be significant only if the Cu–Cu vibration frequency differs appreciably between the singlet and triplet states.

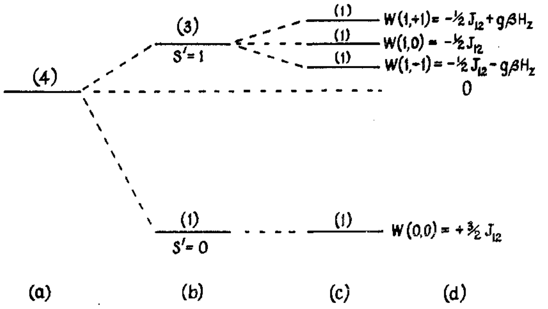

Figure 1.—(a) Lowest energy level of a system of two interacting Cu^{2+}–Cu^{2+} ions. (b) Splitting into a singlet ($S' = 0$) and a triplet ($S' = 1$) level due to spin–spin interaction, $V_{12} = -2J_{12}\hat{S}_1 \cdot \hat{S}_2$. (c) Further splitting of the triplet in a magnetic field, *H*. (d) Energy levels, $W(S',M_{S'})$.

The anomalous temperature dependence of the magnetic susceptibility of the dimer is most simply described by assuming that the spin–spin interaction V_{12} between two copper atoms, 1 and 2, takes the form[1]

$$V_{12} = -2J_{12}\hat{S}_1 \cdot \hat{S}_2 \qquad (1)$$

where in magnetism theory J_{12} is an isotropic exchange interaction and $\hat{S}_1$ and $\hat{S}_2$ are spin operators for the two copper atoms. Ambiguities of interpretation have occasionally arisen because some authors[3-6] have preferred to write the exchange interaction in the form $V_{12} = +J_{12}\hat{S}_1 \cdot \hat{S}_2$. The interaction expressed by eq 1 implies that if a pair of contiguous copper atoms have their electron spins parallel, there is an interaction energy of $-J_{12}$; if their spins are antiparallel, the interaction energy is $+J_{12}$. For copper(II) acetate, the trend of $\chi_M(T)$ data[3] confirms that J_{12} is negative so that the singlet state of the dimer lies lowest (Figure 1).

If an external homogeneous magnetic field *H* is applied along the *Z* axis, the Hamiltonian operator for the dimer is

$$\mathcal{H}_{12} = -2J_{12}\sum\hat{S}_1 \cdot \hat{S}_2 - g\beta S'_Z H_Z \qquad (2)$$

where $\hat{S}'_Z$ is the operator for the *Z* component of total spin. The eigenvalues of $\mathcal{H}_{12}$ are

$$W(S',M_{S'}) = -J_{12}[S'(S + 1) - 2S(S + 1)] - g\beta M_{S'}H_Z \qquad (3)$$

For the molecule $[Cu_2(CH_3CO_2)_4(H_2O)_2]$, $S = {}^1/_2$, $S' = 0$ or 1, and $M_{S'} = S', S' - 1$, or $-S'$, giving the manifold of spin levels shown in Figure 1; the energy difference between singlet and triplet states is $-2J_{12}$.

The variation with temperature of the magnetic susceptibility per mole of dimer is given simply by Van Vleck's formula[1]

$$\chi_M = \frac{2N \sum\limits_{S',M_{S'}} \dfrac{(W_{S'}{}^{(1)}{}_{,M_{S'}})^2}{kT} \exp(-W_{S'}{}^{(0)}/kT)}{\sum\limits_{S',M_{S'}} \exp(-W_{S'}{}^{(0)}/kT)} \qquad (4)$$

where the superscripts refer to the order of the Zeeman displacements and each member of a degenerate set is counted individually. The summation (4) gives

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(6) J. T. Schriempf and S. A. Friedberg, *J. Chem. Phys.*, **40**, 296 (1964).

$$\chi_M = \frac{N\beta^2}{3kT}2g^2[1 + {}^1/_3 \exp(-2J_{12}/kT)]^{-1} \qquad (5)$$

Equation 5 is identical with eq 2 of Figgis and Martin[3] provided that the singlet–triplet interval $+J$ is substituted for the isotropic magnetic exchange interaction $-2J_{12}$.

The Inclusion of a Vibrational Correction

In order to assess the relevance, or otherwise, of a vibrational correction for copper(II) acetate, the procedure developed[2] for interpreting the magnetism of the iron(III) dithiocarbamates is followed. Equation 5 expresses χ_M as a weighted mean of the individual χ_M values of the singlet and triplet levels, the populations of which are in the ratio

$$1:3 \exp(-J/kT)$$

The energy J is interpreted here as a change in internal energy at 0°K, ΔE_0, but should strictly be replaced by the free energy change (with due allowance for the degeneracy factor) at the temperature of measurement, T, *viz.*

$$\Delta G°_T = \Delta H°_T - T\Delta S°_T \qquad (6)$$

where the superscript degree signifies a standard-state change, namely, that involved in transferring 1 mole of pure crystalline singlet species to 1 mole of pure crystalline triplet species. This distinction is of no great consequence if the frequencies of molecular and lattice vibrations are unchanged upon excitation to the triplet level, since

$$\Delta G°_T = J - RT \ln \frac{Q_T}{Q_S} \qquad (7)$$

where Q_T and Q_S are complete partition functions referred to the zero-point energies of the triplet and singlet species, respectively. We assume here that the difference in molar volume between the singlet and triplet states represents an insignificant correction in the context of constant pressure measurements and that the quotient Q_T/Q_S is separable into a simple product of vibrational and electronic partition functions. In the case of iron(III) dithiocarbamates, substantial differences in the frequencies associated with the vibrational modes of the FeS_6 core between the $^6A_1$ and $^2T_2$ states do occur and the equality of $\Delta G°_T$ and ($J - RT \ln 3$), which is so often tacitly assumed in applying the Van Vleck equation, is thereby destroyed.[2]

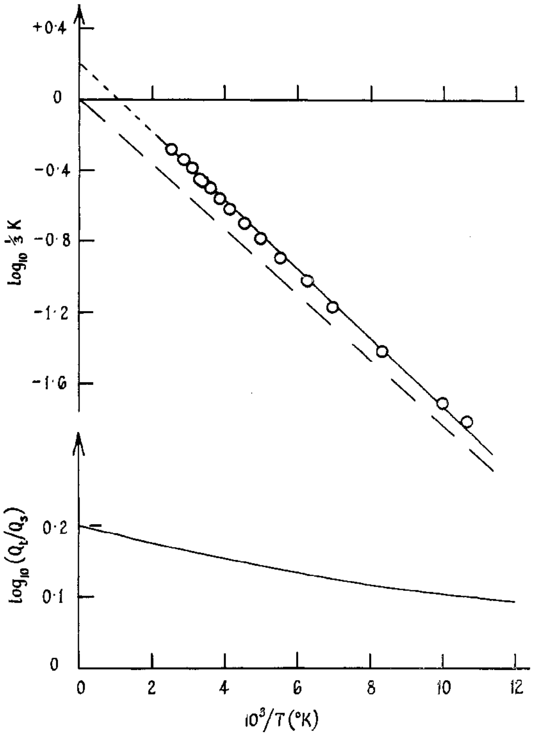

Figure 2.—Upper curves: temperature dependence of the apparent equilibrium constant (K); full line calculated using $\mu_T^2 = 8$ ($S' = 1$), $\mu_S^2 = 0$ ($S' = 0$), and $N\alpha = 60 \times 10^{-6}$ cgs emu; broken line calculated after applying vibrational corrections. Lower curve: illustrative vibrational correction curve calculated assuming $\nu_s = 100$ cm^{-1} and $\nu_t = 63$ cm^{-1}.

For copper acetate, the required elaboration of eq 5 can be written

$$\chi_M = \frac{N\beta^2}{3kT}2g^2\left[1 + \frac{1}{3}\exp\left(\frac{J}{kT}\right)\exp\left(-\frac{\Delta S_{vib}}{R}\right)\right]^{-1} \qquad (8)$$

where an entropy contribution of $\Delta S_{elec} = R \ln 3 - R \ln 1 = 2.2$ eu is already embodied in eq 5 and 8 as the degeneracy factor of $^1/_3$. The vibrational entropy change in passing from the singlet to the triplet levels, ΔS_{vib}, should be dominated by vibrations involving the Cu_2 core of the molecule. The magnitude of this effect can be readily ascertained by replacing the Boltzmann ratios listed above by

$$1:3(Q_t/Q_s) \exp(-J/kT)$$

where Q_t and Q_s are now molecular vibrational partition functions, respectively. Equation 8 can now be conveniently handled by defining an equilibrium constant K as the ratio of the populations in the triplet state to those in the lower singlet state.

$$\ln \frac{1}{3}K = \ln (Q_t/Q_s) - J/kT \qquad (9)$$

If $Q_t = Q_s$, a plot of $\log {}^1/_3K$ *vs.* $1/T$ should be a straight line passing through the origin. However, since Q_t/Q_s will generally depend on T, such plots are likely to be atypical.

The experimental magnetic data for copper(II) acetate monohydrate[3] are replotted in Figure 2 according to eq 9. Log $^1/_3K$ varies linearly with $1/T$ within the experimental limits, the mean slope corresponding to $J = 885$ cal mole^{-1} (*i.e.*, $-2J_{12} = 310$ cm^{-1}). The positive intercept at $1/T = 0$, $\log {}^1/_3K = 0.2$, suggests that molecular vibrational partition functions for the singlet and triplet states do differ and should not be neglected in any thermodynamic treatment of such data. The near linearity of the log $^1/_3K(1/T)$ plot demonstrates that the quotient Q_t/Q_s is not very sensitive to temperature for this compound.

Equation 9 requires that it should be possible to find a vibrational correction curve, which, when subtracted from the plot of log $^1/_3K(1/T)$, yields a straight line which intercepts the origin of the Cartesian axes. If it is assumed that the dominant contribution to Q_t/Q_s comes only from the single Cu–Cu stretching vibration, ν, then

$$Q_t/Q_s = \left\{\frac{1 - \exp(-h\nu_s/kT)}{1 - \exp(-h\nu_t/kT)}\right\} \qquad (10)$$

The Cu–Cu stretching mode, ν_s, appears to be about 1.6 times higher in frequency than ν_t, since as $T \rightarrow \infty$, $\log (Q_t/Q_s) \rightarrow \log (\nu_s/\nu_t) = 0.2$. As an illustrative calculation, we take $\nu_s = 100$ cm^{-1} and $\nu_t = 63$ cm^{-1} to obtain the correction curve given in the lower part of Figure 2. The order of magnitude of the Cu–Cu vibrational correction is, in fact, sufficient to yield the expected intercept for the log $^1/_3K(1/T)$ plot (see dashed line of Figure 2). A necessary consequence of the correction is a slightly diminished value of $J = 840$ cal mole^{-1} (*i.e.*, $-2J_{12} = 294$ cm^{-1}).

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High-Pressure (70-kbar) Synthesis of New Crystalline Lead Dichalcogenides

BY MEYER S. SILVERMAN

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By subjecting mixtures of the elements or of lead monochalcogenides with excess sulfur and selenium to temperatures of 600–2400° and pressures of 20–70 kbars, we have synthesized the stable crystalline compositions $PbSe_2$, PbSSe, and two polymorphs of PbS_2, one of the latter appearing to be isomorphous with SnS_2. Until now, only crystalline PbS, PbSe, PbS·PbSe, or amorphous polysulfides and polyselenides had been reported.

Experimental Section

Starting materials consisted of compressed pellets of 99.9+% lead, 99.999+% sulfur, and 99+% selenium prepared at ambient conditions with chalcogenide:lead ratios of at least 3:1. Also pellets composed of mixtures of PbS + S, PbS + PbSe + S + Se, and PbSe + Se in ratios of 1:2, 1:1:2:2, and 1:2 were used in tetrahedral pyrophyllite sample holders with graphite heating elements described previously.[1] Thin-walled boron nitride sleeves were used to insulate the reaction mixture from the heater. A tetrahedral anvil apparatus of National Bureau of Standards design[2] was used for all syntheses. Discussion of temperature and pressure calibrations and experimental procedure have been reported earlier.[3]

Results and Discussion

Duncan and Ott[4] reported the synthesis and isolation of an amorphous lead disulfide which was quite unstable at ambient conditions. We have prepared two crystalline polymorphs of lead disulfide from elemental and PbS + S mixtures. One of these was prepared repeatedly at 20 kbars and 1600–1800°. Each time this synthesis was carried out, an explosion or blowout occurred so that the quantity of gray-black solid remaining in the sample cavity was sufficient only for X-ray characterization. The complete X-ray powder diffraction pattern we obtained for this product, which we shall call α-PbS_2, is shown in Table I. As indicated, the material appears to be isostructural with the CdI_2-type SnS_2 structure. The calculated lattice constants for α-PbS_2 based on hexagonal indexing are $a = 3.89$, $c = 5.91$ A. These constants seem reasonable when compared to the reported values $a = 3.63$ and $c = 5.86$ A for the tin sulfide,[5] which would be expected to occupy a smaller volume than PbS_2 considering the relative sizes of tin and lead radii. When we tried thicker BN capsules, Ni reaction vessels, or substituted pulse heating to maintain the reaction conditions without blowouts, we obtained either PbS or Ni_3PbS_2 as the only products indicated by X-ray analyses.

TABLE I
X-RAY POWDER DIFFRACTION PATTERNS

	SnS_2[a]		α-PbS_2[b]		
			d, A		
hkl	*d*, A	*I*	Obsd	Calcd	I^c
001	5.9	50	6.0	5.9	s
100	3.15	40			
101	2.78	100	2.85	2.83	s
102	2.14	50	2.13	2.18	m
110	1.82	50			
111	1.74	40			
103	1.66	13	1.68	1.67	s
201	1.52	20			
202	1.391	13			
113	1.334	10			
210	1.192	4	1.23	1.22	m
211	1.170	13			
114	1.146	8	1.16	1.16	w

[a] ASTM 1-1010. [b] Cu Kα radiation taken as 1.5418 A. [c] Visually estimated.

The other crystalline products were prepared from Pb–S, Pb–S–Se, and Pb–Se elemental mixtures in atomic ratios of 1:3, 1:1.5:1.5, and 1:4, respectively. Successful syntheses were also carried out with mixtures of the monochalcogenides and excess sulfur and/or selenium. The strongest lines of the X-ray powder diffraction patterns obtained for these are listed in Table II. The patterns could be indexed on the basis of a tetragonal KN_3 structure type with average lattice constants as follows: β-PbS_2, $a = 6.10 \pm 0.10$, $c = 7.48 \pm 0.10$ A; PbSSe, $a = 6.27$ [illegible] 0.01, $c = 7.57 \pm 0.02$ A; and $PbSe_2$, $a = 6.36 \pm 0.08$, $c = 7.63 \pm 0.10$ A. The increasing lattice constants with increasing

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