Oligomer Antiferromagnetism. II.
Unusual Exchange Interactions in the Neutral Dimer of Bis(*cis*-1,2-bis(trifluoromethyl)-1,2-dithiolene)iron

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Isotropic magnetic susceptibility data are reported for crystalline $[FeS_4C_4(CF_3)_4]_2$, a centrosymmetrical antiferromagnetic dimer, in the temperature interval 80–300°K. The total molecular magnetic susceptibility ($10^6 x_M$, cgs units) is 3563 at 80°K, maximizes to 3603 at 92°K, then decreases steadily to 1798 at 300°K. The customary form $\mathcal{H}_{ex} = -2JS \cdot S$ of the Dirac–Heisenberg–Van Vleck (DHVV) Hamiltonian cannot account for these observations. In order to reproduce the data it is sufficient to take specific account of all interelectronic interactions between four delocalized, singly occupied valence orbitals, using Heitler–London wave functions and the full DHVV exchange Hamiltonian, eq 1, where $n = 4$. Possible sets of two-electron parameters J_{ij} are derived and examined in terms of the bonding and the nephelauxetic effects. All six exchange interactions are less than 0.17 eV.

Introduction

Dimeric complexes of iron and cobalt with dithiolene ligands[2] have been generally characterized.[3] Crystal structure determinations for three of these compounds reveal that dimerization occurs by sulfur bridging as shown in **1**, with the

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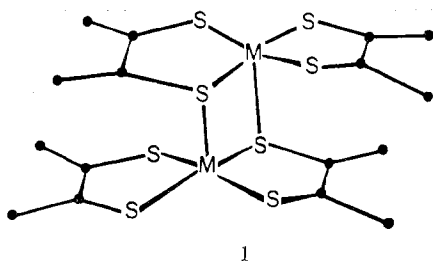
bridging M–S distance 0.22 Å longer than the intrachelate M–S distance,[4] and this familiar structure is assumed for the remainder of the compounds. Mass spectral data indicate that the neutral complexes[5] $[M(S-S,CF_3)_2]_2$ (**1**, R = CF₃; z = 0), M = Fe, Co, exist as dimeric molecules in the gas phase,[3] and there is no evidence that any of the neutral dimers dissociate in solvents with which they do not react.

The electronic structures of these complexes have been little studied. Although the characteristic valence electron delocalization over the whole chelate structure is well substantiated for four-coordinate square-planar dithiolene complexes,[2,6-8] only a simplified valence bond description has been tendered[9] for the iron and cobalt dimers.

In the crystalline state the cobalt compounds $[Co(S-S,-R)_2]_2{}^0$ and $[Co(S-S,R)_2]_2{}^{2-}$ are diamagnetic, consistent with their even total number of electrons, and the magnetic moment of $[Co(S-S,R)_2]_2{}^-$ corresponds to the $S = {}^1/_2$ ground state for an odd number of electrons.[3] In contrast, iron complexes $[Fe(S-S,R)_2]_2{}^z$, z = 0, -1, -2, manifest magnetic

moments which decrease with temperature reduction; they are phenomenologically antiferromagnetic. The purpose of this paper is to describe the magnetic properties of $[Fe(S-S,-CF_3)_2]_2{}^0$, to point out how they *cannot* be accommodated by conventional theoretical models for oligomeric transition metal complexes, and to propose an interpretation based upon weak exchange interactions between individual valence electrons. The conceptual framework and theoretical bases for the model have been described in detail in previous papers.[10,11]

$[Fe(S-S,CF_3)_2]_2$ is a crystal isomorph of its cobalt analog, for which X-ray structure determination has demonstrated the existence of discrete, tight, centrosymmetrical dimers.[12] Each cobalt atom is displaced 0.37 Å from the plane of the four chelated sulfur atoms in the direction of the bridging sulfur atom: Co–S(chelate) = 2.16 Å; Co–S(bridging) = 2.38 Å; Co–Co = 2.78 Å. There are no abnormally short interdimer contacts.

Experimental Section

The compound was prepared as previously described[3] and purified by at least two recrystallizations from carbon tetrachloride: mp 190-191°. Several recrystallizations of all samples permitted completely reproducible and consistent susceptibility measurements over the 80-300°K range, which fact is taken as warrant of magnetic purity.

Magnetic susceptibility measurements were made on finely powdered samples by the Gouy method. A cryostat of modified Figgis-Nyholm[13] design was employed in the temperature range 80-300°K. HgCo(NCS)₄ was employed as calibrant, and the absence of a field dependence of susceptibility was demonstrated for all samples. The 50 observations x_M (referring to the dimeric molecule) employed in the calculations were obtained from three samples. The maximum data spread at any temperature is 3%, and the average deviation from the mean for all temperatures is less than 1%. The susceptibility data are presented in Table I. Nonlinear least-squares calculations were performed with the library program GAUSHAUS of the University of Wisconsin Computing Center.

Results

The submolecule model, with the attendant use of the Dirac–Heisenberg–Van Vleck spin exchange Hamiltonian (eq 1), forms the conceptual basis[10,11] of the following ap-

(1) Department of Chemistry, University of Wisconsin.
(2) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).
(3) A. L. Balch, I. G. Dance, and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 1139 (1968).
(4) R. Eisenberg, *Progr. Inorg. Chem.*, **12**, 295 (1970).
(5) The abbreviation (S-S,R) is used for the dithiolene ligand R-C(S)--C(S)-R.
(6) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964).
(7) R. D. Schmitt and A. H. Maki, *J. Amer. Chem. Soc.*, **90**, 2288 (1968).
(8) D. C. Olson, V. P. Mayweg, and G. N. Schrauzer, *J. Amer. Chem. Soc.*, **88**, 4876 (1966).
(9) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *J. Amer. Chem. Soc.*, **88**, 4604 (1966).

$$\mathcal{H}_{DHVV} = -2 \sum_{i>j}^{n} \sum_{j}^{n} J_{ij} s_i \cdot s_j \qquad (1)$$

(10) I. G. Dance, *Inorg. Chem.*, **12**, 2743 (1973).
(11) I. G. Dance, unpublished results.
(12) J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).
(13) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 331 (1959).

Table I. Susceptibility Data for $[Fe(S-S,CF_3)_2]_2$

T, °K	$10^6 \chi_M$, cgs	T, °K	$10^6 \chi_M$, cgs
81.3	3544, 3564	175.5	2704
83.7	3556, 3601	184.5	2616, 2659
87.2	3594, 3604	197.8	2517
91.6	3610	202.2	2440, 2457
95.9	3586, 3603	211.3	2347, 2409
100.4	3590	220.3	2301
104.9	3533, 3567	229.4	2267, 2239
109.4	3521	238.5	2139
113.8	3485, 3469	247.5	2123
122.6	3370, 3364	256.5	2037
131.5	3250, 3275	265.3	1972, 2021, 1992
140.1	3167, 3156	274.0	1960, 1935
148.6	3023, 3064	283.1	1849
157.5	2937, 2891	296.1	1803
166.4	2810	299.3	1796
170.9	2803	301.0	1750

Table II

	10^6 Corr, cgs units	$\bar{g}$	J, cm^{-1}	R_1,[a] %	$10^6 R_2$,[b] cgs units
i	−3570	2.00[c]	−38.4	3.1	199.7
ii	−540	1.30	−27.8	0.85	28.6

[a] $R_1 = \Sigma |\chi(obsd) - \chi(calcd)|/\Sigma\chi(obsd)$. [b] $R_2 = \Sigma |\chi(obsd) - \chi(calcd)|/$(number of observations). [c] $\bar{g}$ held constant.

$$\chi_M = \frac{N\beta^2}{3kT}(\bar{g})^2 \frac{\Sigma_{S'} S'(S'+1)(2S'+1)\exp[-E(S')/kT]}{\Sigma_{S'}(2S'+1)\exp[-E(S')/kT]} + X + D \quad (5)$$

unknown temperature independent susceptibility from the second-order Zeeman effect, and D is the diamagnetism of all doubly occupied orbitals. As no independent experimental data on the magnitudes of X and D are available, they are combined into one adjustable parameter, Corr. The model is then eq 6.

$$\chi_M = \frac{N\beta^2}{3kT}(\bar{g})^2 \frac{6\exp(2J/kT) + 30\exp(6J/kT)}{1 + 3\exp(2J/kT) + 5\exp(6J/kT)} + Corr \quad (6)$$

For no reasonable parameters will this model reproduce the observations. This is demonstrated graphically in Figure 1, where χ_M data and eq 6 are plotted for a range of J and assumed $\bar{g} = 2.00$, Corr = 0. As D may be estimated at -360×10^{-6} cgs unit from Pascal's constants, Corr is expected to be of order $-(0-400) \times 10^{-6}$ cgs unit and cannot therefore account for the large discrepancies in Figure 1. Analytical expression of this conclusion is given by the parameters of Table II, which were derived from nonlinear least-squares fitting of eq 6 to the 50 χ_M-T observations. Two calculations were performed: (i) with $\bar{g}$ held at 2.00, and (ii) with $\bar{g}$ allowed free variation. For case i the derived value of Corr implies a very large negative temperature independent term X, which is entirely unreasonable. The discrepancy residual R_1 is outside the probable limits of experimental error. In ii, where $\bar{g}$ is unrestricted, there are sufficient parameters to allow close correspondence with the observations, but the derived $\bar{g}$ value of 1.3 is completely implausible.

The inapposite feature of this one energy-parameter model is the low energy of the second excited state ($S' = 2$) relative the first ($S' = 1$). The susceptibility contributions from excited states of energy $E(S') = -JS'(S'+1)$ are shown in Figure 2 for states up to $S' = 3$, as a function of temperature (plots of reduced susceptibility, $J\chi$, vs. reduced temperature, kT/J, are preferable for such general characterizations of exchange models). This is to be compared with Figure 3, on which are plotted the observations and the calculated susceptibility arising only from *one* $S' = 1$ excited state at 102 cm^{-1} above the ground diamagnetic state. It is clearly apparent that only at temperatures above 200°K should susceptibility contributions from higher excited states become appreciable, a conclusion at variance with the model for Figure 2. In fact, if the $S' = 2$ state occurs at *ca.* 1000 cm^{-1}, the observations are readily reproduced. There is no uncertainty about the spin of the molecular ground state, even though data for temperatures well below the Neel point are unavailable; the observed susceptibility, 80–300°K, is too small by a factor of *ca.* 3 to support a triplet ground state.

The assumption of the preceding model is that intrasubmolecule exchange energies are at least an order of magnitude larger than the investigated intersubmolecule exchange energies.[10] Although this is valid for classical coordination complexes, it would be expected to be less appropriate for

proach. The J_{ij} parameterize the energy difference between the spin-singlet and spin-triplet states for the pair of electrons in submolecular orbitals ψ_i and ψ_j, according to the Lowdin[14] definition (eq 2).

$$J_{ij} = {}^1/_2(E_{singlet} - E_{triplet}) \quad (2)$$

Assignment of submolecules is straightforward and obvious, by separation of the dimer through the two bridging Fe–S bonds into two equivalent monomeric $[Fe(S-S,CF_3)_2]$ chelate units. Each of these submolecules contains an even number of electrons. The oligomer bonding is provided by the two Fe–S bridge bonds. Assuming that this oligomer bonding utilizes a sulfur lone pair of electrons and an empty orbital at iron, the number of electrons in each submolecule is even, and therefore the number of singly occupied orbitals must be even.[15] Neither monomeric $[Fe(S-S,CF_3)_2]$ nor any dithiolene complex isoelectronic with the submolecule is independently observable, and so submolecule spin states must be postulated, as $S = 1, 2, \ldots$.

The customary exchange Hamiltonian $\mathcal{H}_{ex}$ (eq 3) was investigated first. $\mathcal{H}_{ex}$ derives from $\mathcal{H}_{DHVV}$ when the exchange energies between singly occupied orbitals *within* the submolecule are sufficiently large to ensure that the submolecule spin states S_a and S_b are strongly stabilized with respect to alternative submolecule spin states.[10] The spin states arising from eq 3 have total spin[16] $S' = (S_a + S_b)$, $(S_a + S_b - 1), (S_a + S_b - 2), \ldots, 0$ or $^1/_2$, each occurring once in a dimer, with relative energies $E(S')$ (eq 4). The

$$\mathcal{H}_{ex} = -2J_{ab}\mathbf{S}_a \cdot \mathbf{S}_b \quad (3)$$

$$E(S') = -J_{ab}S'(S'+1) \quad (4)$$

energies of the $S' = 0$, 1, and 2 molecular states are independent of whether $S = 1, 2, \ldots$, and as it rapidly becomes apparent that these three S' states alone can be responsible for the paramagnetism below 300°K, it is sufficient to consider $S = S_a = S_b = 1$ (that is, four singly occupied orbitals in the dimer). Thus the one-parameter model is ($J \equiv J_{ab}$): $S' = 2, E(2) = -6J; S' = 1, E(1) = -2J; S' = 0, E(0) = 0$. The molar susceptibility χ_M for the total molecule is given by eq 5, in which $\bar{g}$ is the mean g factor, X represents the

(14) P. O. Lowdin, *Rev. Mod. Phys.*, **34**, 80 (1962).

(15) Note that if the oligomer bonding is due to molecular orbital formation between a filled (or empty) sulfur orbital and a singly occupied orbital at iron, there would still be an even number of singly occupied orbitals per submolecule.

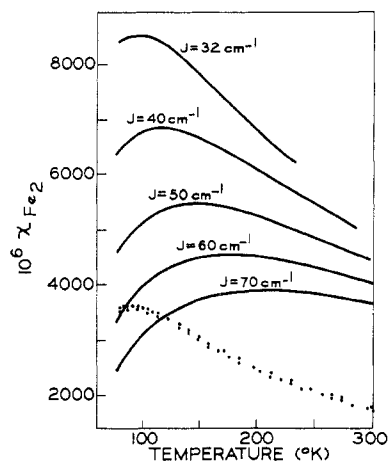(16) Primed spin quantum numbers refer to the total molecule and unprimed symbols to the submolecules.

Figure 1. ($\cdots$) observed magnetic susceptibility for [Fe(S–S,-CF$_3$)$_2$]$_2$; (———) susceptibility calculated from eq 6 with J as shown.
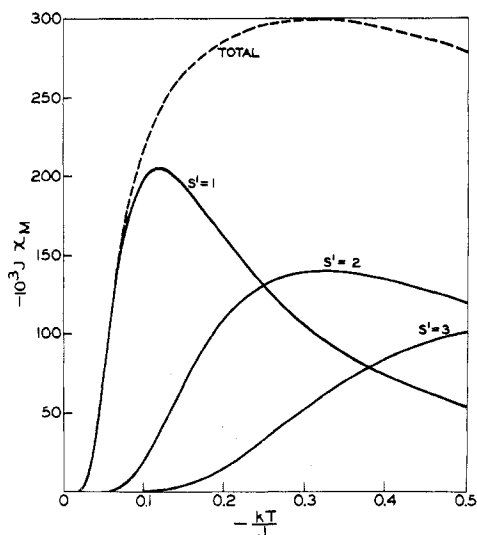

Figure 2. Reduced susceptibility contributions, $J\chi_M$, plotted vs. reduced temperature, kT/J, for $S' = 1$, $S' = 2$, and $S' = 3$ excited states of exchange model $\mathcal{H}_{ex}$.
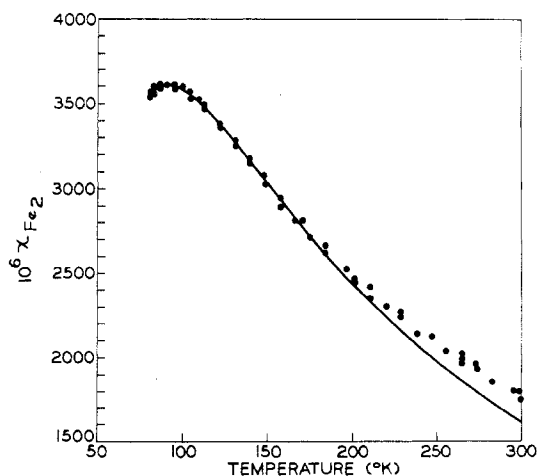

Figure 3. ($\cdots$) observed magnetic susceptibility for [Fe(S–S,-CF$_3$)$_2$]$_2$; (———) calculated susceptibility for one $S' = 1$ excited state at 102 cm^{-1}, $\bar{g} = 2.00$, and Corr = 0.

dithiolene complexes, which have properties indicative of extensive delocalization of valence electrons,[2,6-8] and therefore of reduced interelectronic repulsion energies. This restriction on the relative magnitude of the intrasubmolecule exchange energies is now removed, and all exchange inter-
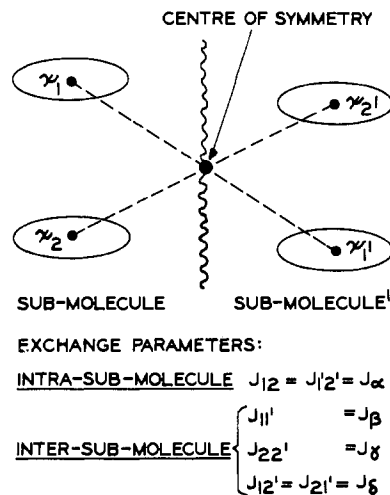

Figure 4. The submolecular symmetry relationships of the four valence orbitals ψ_1, ψ_2, ψ_1', ψ_2' for [Fe(S–S,CF$_3$)$_2$]$_2$ and the four independent exchange parameters between them.

actions for the four electrons are explicitly included, using eq 1.

Inclusion of All Electron-Pair Exchange Interactions.
The simplest complete exchange model involves two singly occupied orbitals at each submolecule. The four orbitals, ψ_1, ψ_2, ψ_1', ψ_2', and the four independent Lowdin exchange parameters between them are shown diagrammatically in Figure 4, which defines all symbolism. There are 16 spin product functions $s(1)s(2)s(1')s(2')$, and six molecular spin states, one $S' = 2$, three $S' = 1$, and two $S' = 0$, the energies of which are obtained[10,17] in terms of the exchange parameters J_α, J_β, J_γ, and J_δ.

$$E(S') = \zeta(J_\alpha, J_\beta, J_\gamma, J_\delta)$$

Interpretation for [Fe(S–S,CF$_3$)$_2$]$_2$ then requires identification of the combinations of the four energy parameters which can reproduce the χ_M-T data. This exploration was made by the device explained in the Appendix, with the aid of an initial simplifying assumption that one of the three intersubmolecular parameters was *relatively* negligible, which is not unreasonable in view of the known bridging geometry. Two variants of this assumption occur, depending whether the degenerate (J_δ) or nondegenerate (J_β or J_γ) parameter is neglected initially: simplified model A, $J_\delta \equiv J_{12}' = J_{21}' = 0$; simplified model B, $J_\gamma \equiv J_{22}' = 0$. There are three satisfactory solutions in model A and one in model B. Each of these four sets of parameters was refined, together with parameters $\bar{g}$ and Corr, by fitting the calculated susceptibility to the observations with an iterative least-squares procedure. Although certain restrictions were necessary to control convergence in the early cycles, all J parameters were eventually allowed free optimization, partly removing the simplifying restrictions of models A and B. In each of the four cases two refinements were made: (i) with $\bar{g}$ held at 2.00; and (ii) with $\bar{g}$ unrestricted. The results[18] are given in Table III together with the values of the discrepancy residuals R_1 and R_2 (the latter provides a more legitimate test).

(17) H. M. McConnell, A. D. McLean, and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).
(18) Standard least-squares estimates of the variance of the derived parameters are often unreliable due to high correlation between some parameters and are quoted in Table III only when examination of the correlation matrix supported their legitimacy. More reliable semiquantitative estimates of the variance of each J parameter may be obtained by plotting appropriate line sections in the spherical representations (see Appendix).

Table III. Refined Parameters for the General Models[a]

Parameter	A1 i[b]	A1 ii[b]	B1 i	B1 ii	A2 i	A2 ii	A3 i	A3 ii
10^6 Corr, cgs unit	-502 ± 20	-377	-502 ± 27	-376	-462 ± 71	-324	-428	-177
$\bar{g}$	2.00	1.96	2.00	1.96	2.00	1.94	2.00	1.90
J_{intra} J_α, cm^{-1}	$+488 \pm 2$	$+544$	$+1379$	$+1303$	-323 ± 18	-309	-356	-351
J_{inter} $\{$ J_β, cm^{-1}	-592 ± 24	-652	-1109	-1133	-429	-407	-897	-893
J_γ, cm^{-1}	$+2.4$	$+11$	-2.5	-2.5	$+323$	$+316$	$+47.5$	$+47.4$
J_δ, cm^{-1}	$+16.3$	$+16$	$+379$	$+371$	0	0	-49.2	-49.1
R_1,[c] %	0.51	0.52	0.51	0.52	0.68	0.54	0.96	0.61
$10^6 R_2$[d] cgs units	16.9	16.6	16.9	16.6	22.4	17.0	31.2	18.4

[a] Computed standard deviations are listed only where reliable. See text. [b] Refinement i with $\bar{g}$ maintained at 2.00 and ii with $\bar{g}$ unrestricted. [c] $R_1 = \Sigma |\chi(\text{obsd}) - \chi(\text{calcd})|/\Sigma |\chi(\text{obsd})|$. [d] $R_2 = \Sigma |\chi(\text{obsd}) - \chi(\text{calcd})|/(\text{number of observations})$.

Plots of observed and calculated susceptibility are given in Figure 5, and the excited state energy level diagrams for the four models are shown in Figure 6. The general $\mathcal{H}_{DHVV}$ model is demonstrably able to account for low-lying paramagnetic states of $[Fe(S-S,CF_3)_2]_2$. However, with the data at hand, a fourfold ambiguity occurs in the details of the model. For temperatures below 300°K the susceptibilities calculated for the four models reproduce the data within the 1% experimental uncertainty, and the differences between the residuals R_2 are hardly significant. Susceptibility differences between the models (except between A1 and B1) develop at temperatures *above* 300°K (see Figure 7).

The correctness of each of the models might be assessed in terms of the parameters $\bar{g}$ and Corr. Expectation $\bar{g}$ values are in the range of 2.00 ± 0.03; comparable results are $\bar{g} = 1.98$-2.01 for complexes $[M(S-S,R)_3]^{z}$;[2,19] $\bar{g} = 2.009$ for $[(NO)Fe(S-S,Ph)_2]$;[20] and $\bar{g} = 2.02$-2.03 for complexes $[(R_3P)Co(S-S,CF_3)_2]$.[21] Compounds of the latter two classes bear strong resemblances to $[Fe(S-S,CF_3)_2]_2$ in electronic- and five-coordinate geometrical structure. The calculated ligand diamagnetic correction for $[Fe(S-S,CF_3)_2]_2$ is -360×10^{-6} cgs unit by Pascal's constants; inclusion of any additional susceptibility arising from quasiaromaticity of the dithiolene chelate system would make this value more negative. Therefore, derived Corr values ranging $-(360$-$500) \times 10^{-6}$ cgs unit are not unreasonable on the assumption of zero temperature independent paramagnetism, X, whereas the reduced Corr value of -177×10^{-6} cgs unit for model A3 could be explained by the inclusion of a small positive X. With cognisance that $\bar{g}$ and Corr are strongly correlated in the susceptibility equation, it is concluded that all models are equally valid on the basis of Corr parameters, while the $\bar{g}$ values of models A1 and B1 are slightly more acceptable than those of A2 and A3.

Discussion

$[Fe(S-S,CF_3)_2]_2$ is the first example of an oligomeric transition metal complex in which the customary treatment in terms of eq 3 has been found inadequate to account for magnetic susceptibility data. Explicit parameterization of all pairwise interelectronic exchange energies in the general DHVV Hamiltonian, eq 1, is, however, sufficient for that purpose. The model involves four singly occupied orbitals for the most energetic electrons in the molecule. The interactions between these electrons are all small, less than 1400 cm^{-1}, or 0.17 eV, which is but a small fraction of ex-
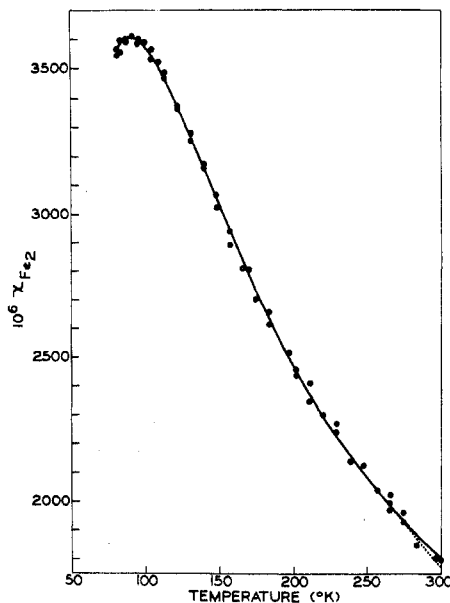
(19) (a) G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **88**, 3235 (1966); (b) E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, **88**, 2956 (1966).

(20) J. A. McCleverty, N. M. Atherton, J. Locke, E. J. Wharton, and C. J. Winscom, *J. Amer. Chem. Soc.*, **89**, 6082 (1967).

(21) (a) A. L. Balch, *Inorg. Chem.*, **6**, 2158 (1967); (b) E. E. Genser, *ibid.*, **7**, 13 (1968).

Figure 5. ($\cdots\cdots$) observed magnetic susceptibility for $[Fe(S-S,CF_3)_2]_2$; (————) calculated susceptibility for models A1 and B1; ($\cdots\cdots$) calculated susceptibility for model A3. The calculated susceptibility for model A2 lies between those of models A1 and A3.

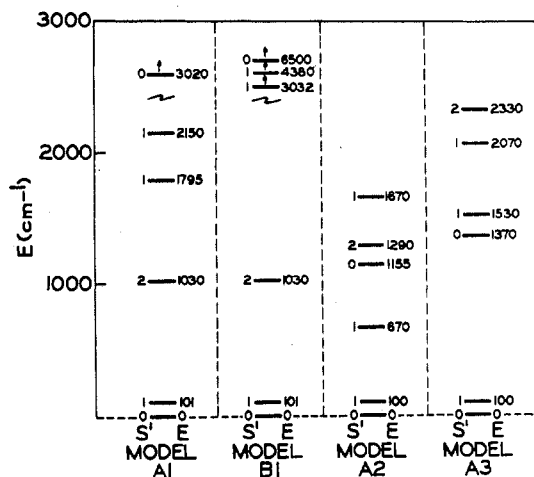**Figure 6.** Excited-state energy level diagrams of the four models for $[Fe(S-S,CF_3)_2]_2$.

change energies for bonding electrons. The electrons which are involved in the observable excited-spin states are essentially nonbonded electrons, their motions are highly correlated, and they are appropriately combined by Heitler-London product wave functions which provide the basis for $\mathcal{H}_{DHVV}$. The model places no restriction on the com-
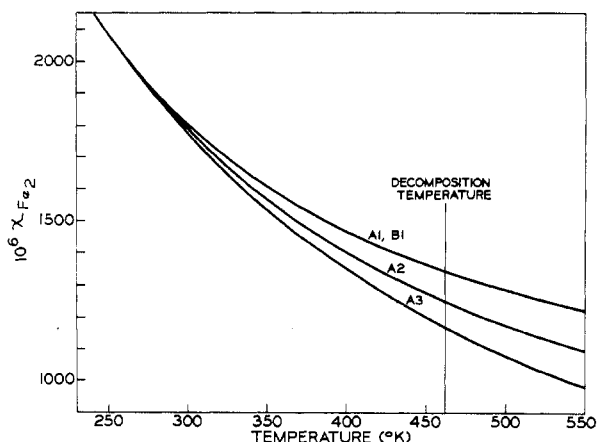
Figure 7. Calculated susceptibilities for the exchange models at high temperatures.

position or the spatial properties of the two independent orbitals ψ_1 and ψ_2 at each submolecule, except that they are very probably confined to the monomer region and not delocalized across the center of symmetry.

An unequivocal determination of the detailed interaction energies between these singly occupied orbitals is not experimentally possible. However, from a theoretical viewpoint two of the models, A2 and A3, can be rejected on the grounds that the negative values for J_α, the intrasubmolecular interaction, are inconsistent with the conventional orthogonality of a set of molecular orbitals within a submolecule.[10] The order of magnitude of J_α in models A1 and B1, when compared with the average exchange energy for appropriate 3d orbitals of a free iron atom, *ca.* 6500 cm^{-1},[22] yields a nephelauxetic ratio of 0.1–0.2,[23] which is entirely consistent with the established notion of extensive valence electron delocalization in dithiolene complexes.[2]

The magnitudes of J_α also indicate that the spin-triplet ground state of hypothetical monomeric [Fe(S–S,CF$_3$)$_2$] is only slightly stabilized with respect to the spin-singlet state. This is consistent with another observation, unsung but suggestive, for dithiolene complexes, namely the variability of spin state for related complexes. Thus, for [Fe(S–S,R)$_2$·L]$^-$, $S = {}^1/_2$ or ${}^3/_2$ depending on L,[24,25] and in [Co(tdt)$_2$]$^-$[26] the ground ($S = 0$) and first excited ($S = 1$) spin states are separated by only 8.5 cm^{-1}.

Final comment concerns some possible but rejected alternative explanations for the unusual magnetic properties of [Fe(S–S,CF$_3$)$_2$]$_2$.

1. Following section IV of the previous paper,[10] if two electrons, one from each submolecule, are relatively strongly interacting (for example, *via* Fe–Fe bonding), then the effective spin states of the submolecules become $S = {}^1/_2$, leading to the ground $S' = 0$ and first excited $S' = 1$ states only for the dimer. This would permit a data fit similar to that

shown in Figure 3, which is inadequate at the higher temperatures. It is clear that a *second* paramagnetic state is required to account for the data.

2. The existence of *intermolecular* exchange between [Fe(S–S, CF$_3$)$_2$]$_2$ dimers in the crystalline state can be discounted on the basis of the structure of the cobalt isomorph.[12] Such intermolecular electron correlation would have to traverse a 3.5-Å Co–F$'$ distance and the σ bonding of the ligand periphery, which is surely prohibitive.

3. Partitioned vibrational energy contributions to the electronic exchange energies and account of excited state geometries would be expected to introduce a temperature dependence into J_{ij},[27] but this effect would be very small (the electrons involved are nonbonding) and appears incapable of accounting for the large discrepancy between eq 4 and the observations.

4. Spin–orbit coupling has been incorporated only *via* $\bar{g}$. However, spin–orbit coupling to the implausible extent of $\bar{g} = 1.3$ is necessary to enable eq 4 to describe the observations, and in view of the low molecular symmetry it is difficult to see how sufficient orbital degeneracy could arise.

Appendix

The exploration for all combinations of the four exchange parameters, $J_\alpha, J_\beta, J_\gamma, J_\delta$, which could reproduce the χ_M-T data was effected as follows. Substitution, $J_m = mJ$, m = α, β, γ, or δ, leads to $E(S') = J\xi(\alpha,\beta,\gamma,\delta)$ with $\alpha^2 + \beta^2 + \gamma^2 + \delta^2 = 1$ and $\xi(\alpha,\beta,\gamma,\delta)$ independent of J. Initially assuming Corr = 0, the molar susceptibility equation

$$\chi_M = \frac{N\beta^2}{3kT}(\bar{g})^2 \frac{\Sigma_{S'}S'(S'+1)(2S'+1)\exp[-\xi(\alpha,\beta,\gamma,\delta)\cdot J/kT]}{\Sigma_{S'}(2S'+1)\exp[-\xi(\alpha,\beta,\gamma,\delta)\cdot J/kT]}$$

may be rewritten to give reduced susceptibility, $J\chi_M$, as a function of the reduced temperature, $kT/J = x_T$.

$$J\chi_M = \frac{N\beta^2}{3}\cdot\frac{1}{x_T}(\bar{g})^2 \frac{\Sigma_{S'}S'(S'+1)(2S'+1)\exp[-\xi(\alpha,\beta,\gamma,\delta)/x_T]}{\Sigma_{S'}(2S'+1)\exp[-\xi(\alpha,\beta,\gamma,\delta)/x_T]}$$

The magnetic moment for the total molecule is

$$\mu_M = \bar{g}\sqrt{\frac{\Sigma_{S'}S'(S'+1)(2S'+1)\exp[-\xi(\alpha,\beta,\gamma,\delta)/kT]}{\Sigma_{S'}(2S'+1)\exp[-\xi(\alpha,\beta,\gamma,\delta)/kT]}}$$

For any set of spin state energy levels determined by J_α, etc., the reduced susceptibility and magnetic moment can be calculated as a function of the reduced temperature in terms only of the *ratios* of the exchange parameters, $\xi(\alpha,\beta,\gamma,\delta)$.

In this procedure each model is completely characterized by the shape of the $J\chi_M$ curve, and the shape and magnitude of μ_M, over any factorial range of x_T. As the observables, χ_M, μ_{eff}, and T are directly proportional to $J\chi_M$, μ_M, and x_T, respectively, any model, dependent upon $\xi(\alpha,\beta,\gamma,\delta)$, may be straightforwardly compared with the experimental data.

After the simplifications of models A or B the three remaining normalized factors, α, β, and γ or δ, possess the same properties as the direction cosines of the radius vector of a sphere, and therefore all possible models, dependent on $\xi(\alpha,\beta,\gamma,$ or $\delta)$, are represented by points on the surface of

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a unit sphere. A plot of a semiquantitative measure of the correlation between model and observation over the surface of a sphere each for models A and B enabled location of all

trial sets of exchange parameters.

Optical and Magnetic Properties and Geometry of Some d^5 Ruthenium Complexes

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Magnetic and optical properties of two d^5 ruthenium–triphenylarsine complexes have been investigated. The complexes have D_{4h}, C_{2v}, and D_{3h} molecular symmetries. The complex RuCl$_3$[As(C$_6$H$_5$)$_3$]$_2$ has been found to possess C_{2v} symmetry in the solid state and a trigonal-bipyramidal geometry (D_{3h}) in solution. The D_{3h} geometry has been established on the basis of the dipole moment measurement, optical spectra, and epr results. Optical spectra of all complexes have been correlated with the epr g values. One of the L → L charge-transfer transitions involving the $\pi \rightarrow \pi^*$ transitions in the phenyl rings shows fine structures, better resolved than what has been reported for triphenylarsine ligand, and is considerably blue shifted in the trigonal-bipyramidal molecule, indicating a large amount of conjugation between arsenic and benzene through d$_\pi$–p$_\pi$ interactions.

Introduction

Several low-spin d^5 complexes of second- and third-row transition metal ions with arsines and phosphines as ligands have been reported in the literature.[2-7] Ruthenium(III) and osmium(III) form quite a large number of these complexes and seem to possess a wide variation in geometry. Magnetic susceptibility and esr measurements have been used to identify their symmetries and establish the low-spin nature of these compounds. So far, no attempt has been made to interpret the optical spectra in detail, nor have the solution properties been studied. In this report, we have tried to interpret the optical and magnetic properties of two complexes: RuCl$_3$·(CH$_3$OH)(AsPh$_3$)$_2$ (I) with a C_{2v} symmetry and N(C$_2$H$_5$)$_4$·[RuCl$_4$(AsPh$_3$)$_2$] (II) with a D_{4h} symmetry in both solid and solution states. We report the conversion of I into a trigonal-bipyramidal molecule in benzene with interesting magnetic and electronic structures.

Experimental Section

Reagents. Ruthenium trichloride hexahydrate and triphenylarsine were obtained from Alfa Inorganics. Organic solvents are spectral grade. The complexes I and II were prepared according to the methods of Stephenson and Wilkinson[5b] and Stephenson, respectively,[5a] and were recrystallized in proper solvents.

Preparation of RuCl$_3$(AsPh$_3$)$_2$. The green compound, I, was ground in a mortar; the color changed to brown. This was extracted into benzene and filtered from any insoluble residue. The filtrate was evaporated at room temperature to dryness. This was redissolved in benzene; deep brown crystals of RuCl$_3$(AsPh$_3$)$_2$ (III) were obtained by slow crystallization from the solution. *Anal.* Calcd: C, 52.7; H, 3.69. Found: C, 52.9; H, 3.8.

Physical Measurements. The dipole moment of III in benzene at various concentrations was measured by a microwave method.[8]

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The electronic spectra were measured in methanol, benzene, and isooctane, using Cary Model-14 and Carl Zeiss DMR-21 instruments.

The electron paramagnetic resonance (epr) spectra were measured in a Varian E-4 epr instrument with 100-kHz modulation. The spectral g values were calibrated with DPPH standard.

Results

Electron Paramagnetic Resonance. The epr spectra of the polycrystalline samples of green RuCl$_3$(CH$_3$OH)(AsPh$_3$)$_2$ (I) and brown N(C$_2$H$_5$)$_4$[RuCl$_4$(AsPh$_3$)$_2$] (II) were measured at both room and liquid nitrogen temperatures. Both of them exhibit almost similar spectra, characteristic of an axially symmetric complex with a $g_{\parallel}$ around 1.71 and $g_{\perp}$ around 2.46–2.52. The isotropic g value turns out to be 2.20–2.23. Compound II does not exhibit any change in g value pattern when brought into benzene solution. Also, compound I in benzene or methanol solutions exhibits the same g values as in the solid state. However, when I is ground in a mortar, dissolved in benzene, and evaporated to a brown solid, then the epr measurement of this brown solid, identified by analysis as RuCl$_3$(AsPh$_3$)$_2$ (III), shows only a small change in the g values. The g values of III were measured to be $g_{\parallel}$ = 1.73 and $g_{\perp}$ = 2.41, with a g_{av} = 2.18, not too different from those values obtained for I and II. However, when the epr of III in benzene solution was measured, it showed drastic changes. At room temperature, the g_{av} was measured to be 2.30 as opposed to that calculated for compounds I-III (solid) to be in region 2.18–2.23. The same, when cooled to liquid nitrogen temperature, showed a spectrum characteristic of axial symmetry with $g_{\parallel}$ = 2.00 and $g_{\perp}$ = 2.48 resulting in a calculated g_{av} = 2.32. Though the value for $g_{\perp}$ did not show any remarkable change from those of I-III, there was a drastic shift in $g_{\parallel}$ to that of a free-electron value. This is indicative of a gross change in geometry in solution. All the epr results are given in Table I. The epr spectra of all these compounds at liquid nitrogen temperature are shown in Figure 1 for the sake of comparison. None of the spectra revealed any hyperfine interaction due to the nuclei with magnetic moments, *viz.*, Ru, As, and Cl.

Dipole Moment. The dipole moment of the benzene solution of compound III was measured to be nearly zero at various concentrations.

Electronic Spectra. Compounds I and II showed similar spectra with bands at 24,510 (ϵ 1065) and 28,820 cm^{-1} (ϵ