Table V. Positional and Equivalent Isotropic Thermal Parameters for **2**

atom	x	y	z	10^4U,[a] Å^2
Fe(03)	0.1710 (1)	0.0889 (1)	0.0000	320 (6)
C(01)	0.2203 (8)	0.2532 (14)	–0.0999 (6)	437 (25)*
C(02)	0.2011 (8)	0.0476 (14)	–0.1322 (7)	433 (25)*
B(04)	0.1125 (8)	0.3350 (14)	–0.0478 (8)	389 (25)*
B(05)	0.1416 (9)	0.3923 (15)	–0.1614 (8)	448 (29)*
B(06)	0.2014 (9)	0.2105 (16)	–0.2129 (9)	477 (29)*
B(07)	0.0817 (10)	–0.0299 (18)	–0.1014 (8)	454 (34)*
B(08)	0.0216 (8)	0.1572 (13)	–0.0470 (8)	387 (24)*
B(09)	0.0166 (8)	0.3303 (15)	–0.1307 (7)	424 (26)*
B(10)	0.0688 (8)	0.2571 (16)	–0.2317 (8)	454 (28)*
B(11)	0.1101 (8)	0.0315 (15)	–0.2140 (8)	431 (28)*
B(12)	–0.0049 (8)	0.1048 (14)	–0.1624 (7)	403 (25)*
C(31)	0.2669 (7)	–0.1205 (13)	0.0497 (6)	430 (57)
C(32)	0.1634 (7)	–0.1441 (13)	0.0770 (6)	431 (55)
C(33)	0.1097 (8)	–0.0040 (15)	0.1207 (6)	445 (63)
C(34)	0.1613 (8)	0.1618 (15)	0.1371 (6)	457 (59)
C(35)	0.2617 (8)	0.1855 (14)	0.1071 (7)	491 (64)
C(36)	0.3169 (7)	0.0457 (14)	0.0631 (6)	451 (60)
C(37)	0.3237 (7)	–0.2698 (14)	0.0009 (13)	671 (59)
C(38)	0.1024 (10)	0.3104 (16)	0.1834 (8)	741 (86)

[a] $U_{eq} = {}^1/_6\pi^2\sum\sum\beta_{ij}a_ia_j$. Values marked with an asterisk denote atoms refined with isotropic thermal parameter.

of the experiment. Of the 978 unique reflections measured, 848 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects but not for absorption effects.[15]

Solution and Refinement of the Structure of 2. Atoms were located by use of the heavy-atom method. All calculations were performed on the VAX 11/750 crystallographic computer. All carborane hydrogen atoms were kept in located positions and all xylyl hydrogen atoms were included in calculated positions, C–H = 1.0 Å, with assigned B values of 4.0 and 7.0 Å^2 for cage and ring H and for methyl H, respectively. Anisotropic thermal parameters were refined for Fe and for arene non-hydrogen atoms. Scattering factors for H were obtained from Stewart et al.[16] and for other atoms were taken from ref 17. Anomalous dispersion terms were applied to the scattering of Fe. A final difference electron density map was essentially featureless, the maximum and minimum peaks being about 0.6 e/Å^3. Final positional and thermal parameters for non-hydrogen atoms are given in Table V.

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Registry No. **1**, 110045-26-6; **2**, 110045-27-7; **3**, 65465-56-7; K-[*nido*-7,8-$C_2B_9H_{12}$], 12304-72-2; $FeCl_3$, 7705-08-0; Me_3NH[*nido*-7,8-$C_2B_9H_{12}$], 12543-22-5.

Supplementary Material Available: Tables of positional and thermal parameters of hydrogen atoms, anisotropic thermal parameters, and interatomic distances and angles (14 pages); listings of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Molecular
Spectroscopy, Research Institute of Materials,
University of Nijmegen, Toernooiveld,
6525 ED Nijmegen, The Netherlands

Spin–Orbit Contribution to the Zero-Field-Splitting Tensor in Weakly Interacting $S = {}^1/_2$ Dimers

M. C. M. Gribnau and C. P. Keijzers*

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It is the purpose of this note to clarify the role of the spin–orbit coupling in the zero-field-splitting (ZFS) tensor of weakly interacting $S = {}^1/_2$ dimers. Moriya[1,2] was the first to derive an analytical expression for this contribution in infinite crystals. In recent years much experimental work[3,4] has been done in order to establish the magnitude of the spin–orbit contribution (which is also called "pseudodipolar interaction" or "anisotropic exchange") to the ZFS in weakly coupled copper dimers with oxygen-,[5-9] sulfur-,[9,10] fluorine-,[11] chlorine-,[12,13] and nitrogen-based[14-16] bridges. The ZFS consists of two contributions, which cannot be measured independently: the dipole–dipole interaction and the spin–orbit contribution. Therefore, the procedure to obtain the spin–orbit contribution is to subtract the calculated dipole–dipole interaction from the experimental ZFS tensor. In the interpretation of the spin–orbit contribution using the theory of Moriya approximations are necessary which are, however, not always valid. In the course of time, the approximate method of interpretation developed a momentum of its own. We have the impression that authors do not always realize that they are using approximate expressions instead of the original exact one of Moriya. The value of the interpretations may, therefore, be very limited. In the following we will first summarize the theory of Moriya. Subsequently, we will clarify the nature of the approximations on the basis of an alternative derivation.

Moriya[1,2] included spin–orbit coupling into Anderson's theory of superexchange.[17,18] Using a third-order perturbation treatment in which both the spin–orbit and the isotropic exchange act as perturbations, he derived an expression that was reformulated for dimeric systems by Kanamori.[19,20] It contains terms such as

$$\frac{\langle g_1g_2|\vec{L}_1\cdot\vec{S}_1|e_1g_2\rangle\langle e_1g_2|\mathcal{H}_{ex}|e_1g_2\rangle\langle e_1g_2|\vec{L}_1\cdot\vec{S}_1|g_1g_2\rangle}{(E_e - E_g)^2}$$

Here g_1 and g_2 represent the orbital singlet ground states of the monomers with energy E_g and e_1 is an excited state monomer orbital of energy E_e. The approximation mentioned above is that the term in $\mathcal{H}_{ex}$ is replaced by a simple two-electron exchange integral, while, in fact, it represents a singlet–triplet splitting of an excited state. This approximation is analogous to approximating the singlet–triplet splitting of the dimer ground state by a simple exchange integral. However, Anderson[17,18] and, more recently, Kahn and co-workers[21] have shown that the singlet–triplet splitting ($2J_0$ in the effective Heisenberg spin Hamiltonian $-2J_0\vec{S}_1\cdot\vec{S}_2$) in the ground state may, in first order, be calculated according to

$$2J_0 = 4tS + 2(j - kS^2) \qquad (1)$$

where t, S are one-electron integrals and j, k are two-electron integrals. The approximation $2J_0 = 2j$ is correct only if the monomer oribitals are orthogonal. This means that the approx-

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imation mentioned above is valid only if the orbitals e_1 and g_2 are orthogonal, which is highly unlikely for bridged dimers. This orthogonality may be strick as the result of the molecular symmetry, or it may be accidental. Both cases are discussed by Kahn and co-workers.[22,23]

An analytical expression analogous to the one of Moriya may be derived by second-order instead of third-order perturbation theory.[4,10] This is a consequence of the fact that we are no longer dealing with an infinite lattice but instead with two spins each with $S = {}^1/_2$. Therefore, it is possible to start from ground and excited singlet ($|\psi_S{}^n\rangle$) and triplet ($|\psi_T{}^n\rangle$) states in which the exchange interactions have been included to the highest accuracy possible. The resulting singlet–triplet splitting in the state n is defined as $2J_n$, where J_n is the effective exchange constant in the spin Hamiltonian $-2J_n\vec{S}_1\cdot\vec{S}_2$. The spin–orbit perturbation is $\mathcal{H}_{SO} = \zeta_1\vec{l}_1\cdot\vec{s}_1 + \zeta_2\vec{l}_2\cdot\vec{s}_2$ where ζ_i is the one-electron spin–orbit coupling constant. The second-order energy correction to the three triplet ground-state functions may be calculated by diagonalizing the matrix with elements

$$E_{ij}{}^{(2)} = \sum_n\sum_\sigma \frac{\langle\psi_{Ti}{}^0|\mathcal{H}_{SO}|\psi_\sigma{}^n\rangle\langle\psi_\sigma{}^n|\mathcal{H}_{SO}|\psi_{Tj}{}^0\rangle}{E_T{}^0 - E_\sigma{}^n} \qquad (2)$$

where the summation σ runs over all (four) spin states of the excited states n. After some algebra this may be written as

$$E_{ij}{}^{(2)} = 2\sum_n \sum_{\alpha,\beta=x,y,z} \langle\psi_T{}^0|\zeta_1 l_{1\alpha}|\psi_T{}^n\rangle\langle\psi_T{}^n|\zeta_2 l_{2\beta}|\psi_T{}^0\rangle \times \langle T_i|S_{1\alpha}S_{2\beta} + \delta_{\alpha\beta}|T_j\rangle[1/(E_n + 2J_n) - 1/E_n] \qquad (3)$$

By comparison with the matrix elements within the ground state triplet manifold of the spin-Hamiltonian $\vec{S}_1\cdot\bar{\bar{D}}_{SO}\cdot\vec{S}_2$ and after omitting an isotropic contribution, one obtains for the tensor elements

$$D_{SO,\alpha\beta} = 2\sum_n\langle\psi_T{}^0|\zeta_1 l_{1\alpha}|\psi_T{}^n\rangle\langle\psi_T{}^n|\zeta_2 l_{2\beta}|\psi_T{}^0\rangle[1/(E_n + 2J_n) - 1/E_n] \qquad (4)$$

In case $|J_n| \ll E_n$, this can also be written as

$$D_{SO,\alpha\beta} = -4\sum_n\langle\psi_T{}^0|\zeta_1 l_{1\alpha}|\psi_T{}^n\rangle\langle\psi_T{}^n|\zeta_2 l_{2\beta}|\psi_T{}^0\rangle J_n/E_n{}^2 \qquad (5)$$

This expression is equivalent to the one derived by Moriya, and it shows that the spin–orbit coupling contributes to the ZFS provided that the singlet–triplet splitting in the excited states is not zero. Moreover, this alternative derivation clearly shows that J_n in formula 5 is not a simple two-electron exchange integral but instead is the singlet–triplet separation in the excited state. Therefore, we think it dangerous that in recent articles the effective exchange has been treated as a simple exchange integral.

In this context we think it worthwhile to mention another aspect of the analytical expression for J_0 mentioned above: the model upon which this expression is based is a two-electron description. The effects of the doubly occupied orbitals in the dimer are neglected. They play a role only insofar as they influence the energies and delocalization of the unpaired electron functions. Wormer and Van der Avoird[24] tested this approximation on the O_2–O_2 dimer (two spins $S = 1$). They compared the results of an extensive all-electron calculation with a four-electron model and found that the orientational dependencies of J_0 are qualitatively the same but are quantitatively not so! The much more economic four-electron model turns out to be quite inaccurate. This was also found by Charlot et al.[25] on a model system for azido-bridged copper dimers. A full CI calculation including all core levels was needed in order to understand the behavior of the singlet–triplet separation in these systems.

In conclusion, we think it is now clear that the spin–orbit term will contribute to the ZFS if an effective exchange interaction is present in the excited states and that this effective exchange interaction represents a singlet–triplet splitting and is not equal to a simple two-electron exchange integral. Furthermore, extensive all-electron calculations are needed in order to obtain quantitatively correct results for the single–triplet splittings.

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Contribution No. 914 from the Battelle-Kettering
Laboratory, Yellow Springs, Ohio 45387

Synthesis and Characterization of the $[(CO)_4MoS_2MS_2]^{2-}$ and $[(CO)_4MoS_2MS_2Mo(CO)_4]^{2-}$ Ions (M = Mo, W): Species Containing Group VI (6[†]) Metals in Widely Separated Formal Oxidation States

Laurence D. Rosenhein[1a] and John W. McDonald*[1b]

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Although the group VI tetrathiometalates ($[MS_4]^{2-}$; M = Mo, W) were initially prepared over 100 years ago,[2] their ability to function as bidentate ligands to other metals has only been explored extensively in the past 10–15 years.[3]

Much of the interest in this behavior has arisen because of the importance of molybdenum–sulfur moieties in biological systems. For example, an Fe–Mo–S cluster unit is thought to comprise the active site of the nitrogenase enzyme,[4] Mo=S linkages have been implicated in other molybdenum enzymes that contain the "Mo cofactor",[5] and thiomolybdates are thought to be an important factor in the copper–molybdenum antagonism in ruminants.[6] In addition, there is considerable interest in molybdenum–sulfur species as industrial catalysts for hydrodesulfurization.[7] Activity in this area has focused on reactions involving the chelation of relatively *high-valent* metals such as Fe(II/III),[8] Co(II),[9] Ni(II),[10] and Zn(II)[11] by $[MS_4]^{2-}$ ions to form simple $M'S_2MS_2$ units. By contrast, reactions of thiometalates with *low-valent* metals containing π-accepting ligands, such as CO and PR_3, are rare. However, the feasibility of this type of reactivity recently has been demonstrated[12] by studies that showed that $[MS_4]^{2-}$ (M = Mo, W) will readily chelate Rh(I) and Ru(II) fragments to form heterometallic, sulfido-bridged complexes, such as $[(COD)RhS_2MS_2Rh(COD)]$ (COD = cyclooctadiene), where the tetrathiometalate functions as a ligand to an organometallic moiety.

We have recently begun to investigate the chemistry of low-valent Mo and W carbonyl–sulfur species,[13-17] some of which[16,17] were prepared by utilizing the labile $Mo(CO)_4$(norbornadiene) complex as a source of reactive $Mo(CO)_4$ fragments. Herein we report that this type of reactivity can also be exploited with $[MS_4]^{2-}$ (M = Mo, W), resulting in simple dinuclear and trinuclear sulfido-bridged complexes that are unusual in that they contain group VI metals in the same cluster that differ in formal oxidation state by 6 units.

Experimental Section

Materials and Methods. The compounds $Mo(CO)_4(C_7H_8)$ (C_7H_8 = norbornadiene)[18] and $[Et_4N]_2[MS_4]$ (M = Mo, W)[19] were prepared by the literature methods cited. All operations were carried out under an argon atmosphere by using Schlenk tube or glovebox techniques. Reagent grade solvents were used as obtained, except for MeCN, which

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[†] The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)