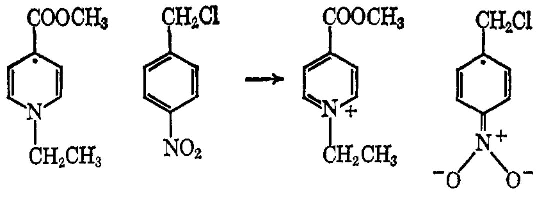

collision or weak complex transition state will resemble ion pair (3)

We have established that solvent effects are strong criteria in reaching decisions about the mechanisms of radical reactions. For systems in which specific solvation is not dominant (as it is in oxy radicals), a small solvent effect implies an atom-transfer reaction and a large solvent effect suggests an electron-transfer reaction. The high solvent sensitivity of electron-transfer reactions should provide a useful test for their occurrence.

Acknowledgment. The authors are grateful to the Research Laboratories, Edgewood, Md., for support through Contract DA 18-035-AMC-138(A).

(4) N. Kornblum, *et al.*, *J. Am. Chem. Soc.*, **88**, 5660, 5662 (1966); 87, 4520 (1965).

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Organometallic Sulfur Complexes. XIII. Synthesis, Structure, and Bonding of a New Metal–Sulfur Cluster System, $S_2Ni_3(C_5H_5)_3$. The Influence of Valence Electrons on Molecular Geometry[1]

Sir:

In the course of our systematic structural investigations of organometallic chalcogen complexes, the synthesis of $SNi_3(C_5H_5)_3$, an electronic equivalent of the previously reported $SCo_3(CO)_9$,[2,3] was attempted. The reaction in organic solvents of $[C_5H_5NiCO]_2$ with sulfur in varying ratios led, however, to the formation in low yield of the new paramagnetic compound tris(cyclopentadienylnickel) disulfide, $S_2Ni_3(C_5H_5)_3$. The constitution of $S_2Ni_3(C_5H_5)_3$ was determined by full elemental analysis, infrared spectrum, and magnetic measurement which gave a μ_{eff} of 1.7 BM corresponding to one unpaired electron.

$S_2Ni_3(C_5H_5)_3$ crystallizes in the hexagonal system with $a = 9.595 \pm 0.006$ Å, $c = 9.923 \pm 0.006$ Å; $\rho_{\text{obsd}} = 1.89$ (flotation method) *vs.* 1.83 g cm^{-3} based on two formula species per cell. All crystals examined by X-ray photographs invariably showed D_{6h}-6/m2/m2/m Laue symmetry. Systematic absences of l odd for $\{000l\}$ indicate a 6_3 axis in the c direction. Three-dimensional intensity data were collected with Mo Kα radiation on a General Electric four-angle automatic diffractometer. Attempts to interpret a computed three-dimensional Patterson function on the basis of the apparent space group $P6_322$ (D_{6h}^6, No. 182),[4] uniquely defined by the above symmetry requirements, were unsuccessful. Instead this interatomic vector map can be explained only in terms of an incoherent twinning mechanism involving an individual hexagonal single-crystal component of symmetry $P6_3/m$ (C_{6h}^2, No. 176).[4] The twinning of the reciprocal lattice of this individual crystal of C_{6h}-6/m point group symmetry by an operation such as reflection across a (100) mirror plane would give rise to a twin composite with the same apparent hexagonal unit cell but of the observed D_{6h} symmetry. The determination of the cyclopentadienyl rings in this twinned crystal by Fourier syntheses was done by the Wei procedure[5] which enabled a breakdown of the observed $F(hkl)^2$ data for the twin composite into the appropriate $F(hkl)$ coefficients for the single-crystal component. The incoherent twinning model was verified by a successful full-matrix, least-squares rigid-body refinement[6] which yielded an $R_1(F^2)$ of 10.2%. In this refinement the cyclopentadienyl parameters were constrained to a regular pentagonal ring geometry; anisotropic thermal parameters were utilized for the nickel atom and isotropic ones for the sulfur and individual carbon atoms.

Crystalline $S_2Ni_3(C_5H_5)_3$ consists of discrete molecules with the configuration shown in Figure 1. The nickel and sulfur atoms form a regular trigonal bipyramid with the cyclopentadienyl rings stereochemically disposed about the nickel atoms such that lines passing from the center of the equilateral nickel triangle through the nickel atoms intersect the centroids of the cyclopentadienyl rings. With the assumption of *cylindrical* symmetry for each cyclopentadienyl ring, the molecular configuration of $S_2Ni_3(C_5H_5)_3$ approximately possesses D_{3h}-$\bar{6}$2m symmetry; the local crystallographically demanded site symmetry for each molecule based on a twofold orientational disorder of each cyclopentadienyl ring is C_{3h}-$\bar{6}$. The important bond lengths (with individual esd's of the last significant figures given in parentheses) are Ni–Ni = 2.801 (5) Å, Ni–S = 2.172 (6) Å, Ni–C (av) = 2.13 Å; the Ni–S–Ni and S–Ni–S angles are 80.3 (3) and 83.8° (4), respectively. This unusually long Ni–Ni distance is approximately 0.4 Å greater than that observed in other polynuclear organometallic complexes containing nickel triangles,[7,8] whereas the Ni–S bond length is in the range normally observed for triply bridging substituent-free sulfur atoms.[1,2,9] Both the relatively small intramolecular S···S distance of 2.90 (2) Å and the rather acute S–Ni–S angle can be attributed to a compression of the trigonal bipyramidal S_2Ni_3 fragment due to the long Ni–Ni distances.

A consideration of bonding schemes to rationalize these molecular features is informative. As in other

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[1] Previous paper in this series: C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, in press.

[2] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **6**, 1229 (1967).

[3] S. A. Khattab, L. Markó, G. Bor, and B. Markó, *J. Organometal. Chem.* (Amsterdam), **1**, 373 (1964), and references therein.

[4] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952.

[5] C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 4792 (1967); C. H. Wei, Abstracts of Papers, National Meeting of the American Crystallographic Association, University of Minnesota, Minneapolis, Minn., Aug 20–25, 1967, p 83.

[6] The function minimized was $\Sigma w[|F(hkl)_o|^2 - s^2|F(hkl)_c|^2]^2$, where s is the one adjusted scale factor; $R_1(F^2) = \{[\Sigma||F(hkl)_o|^2 - s^2|F(hkl)_c|^2|]/\Sigma|F(hkl)_o|^2\} \times 100$.

[7] A. Hock and O. S. Mills, "Advances in the Chemistry of Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p 640.

[8] S. Otsuka, A. Nakamura, and T. Yoshida, *Inorg. Chem.*, **7**, 261 (1968).

[9] D. L. Stevenson, V. R. Magnuson, and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 3727 (1967); C. H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *Inorg. Chem.*, **5**, 900 (1966); R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *ibid.*, **5**, 892 (1966).

molecular complexes containing similar triply bridging metal-coordinated sulfur atoms,[1,2,9] a tetrahedral-like valency can be assumed for each apical sulfur atom with one of its orbitals interacting with a σ-like orbital from each nickel atom to give an electron-pair Ni–S bond; the fourth localized sulfur orbital located on the threefold principal axis thereby contains an unshared electron pair. From a valence-bond formalism the assumption of no nickel–nickel bonding results in the entire molecule being one electron short of a closed-shell electronic configuration for each nickel atom; this conceptual representation, if correct, immediately suggests the probable addition of an electron to give the $[S_2Ni_3(C_5H_5)_3]^-$ anion. An alternative explanation of the molecular parameters, which in this case gives rise to different predictions, is obtained from the application of qualitative MO symmetry arguments. This LCAO–MO treatment[10] presumes that each nickel atom primarily utilizes five of its nine valence orbitals in localized coordination with a cyclopentadienyl group and the two sulfur atoms; it also assumes that the perfect-pairing approximation allows separation of the metal–cyclopentadienyl and nickel–sulfur interactions from the metal–metal interactions. Within the framework of this MO scheme, the remaining *four* valence orbitals (or hybrids) per nickel atom are combined under D_{3h} symmetry to give *six* bonding and *six* antibonding metal symmetry orbitals. A reasonable orbital-ordering pattern can be obtained from overlap considerations. The 23 electrons available for nickel–nickel interactions occupy all of the bonding and antibonding levels with one unpaired electron in the highest energy antibonding level. Since the corresponding occupied bonding and antibonding levels are assumed to practically cancel one another's bonding, the nickel–nickel interactions are effectively due to the *net* difference of only one electron in a strongly bonding metal symmetry orbital. Hence, it is expected that the nickel–nickel interactions are weak in agreement with the long nickel–nickel distances. The obvious implication is that electrons can be selectively removed to give cationic species with considerably shorter nickel–nickel bonds.

Strong evidence can already be cited in favor of the predictive power of this MO formulation. The analogous molecular complex $(C_5H_5)_3Ni_3(CO)_2$,[7] which can be formally derived from $S_2Ni_3(C_5H_5)_3$ by replacement of the two apical sulfur atoms with carbonyl groups, has identical transformation properties of the nickel metal symmetry orbitals but has four fewer electrons available for direct nickel–nickel interactions. The qualitatively pleasing consequence of the removal of these four electrons from the antibonding metal symmetry orbitals is an expected shortening of the nickel–nickel distance in $(C_5H_5)_3Ni_3(CO)_2$ in agreement with its observed value of 2.39 (1) Å compared to 2.801 (5) Å for the Ni–Ni distance in $S_2Ni_3(C_5H_5)_3$.[11–13] Moreover, these MO symmetry arguments predict that the unpaired electron in $(C_5H_5)_3Ni_3(CO)_2$ is also in an *antibonding* rather than a *bonding* metal symmetry orbital as previously reported.[14] In order to test this hypothesis the diamagnetic, isomorphous analog, $(C_5H_5)_3CoNi_2(CO)_2$, has been prepared,[15] and a structural study is currently underway to determine whether the metal–metal bond lengths will further decrease through the formal removal of the unpaired electron in $(C_5H_5)_3Ni(CO)_2$ by substitution of a cobalt for a nickel atom.[16,17]

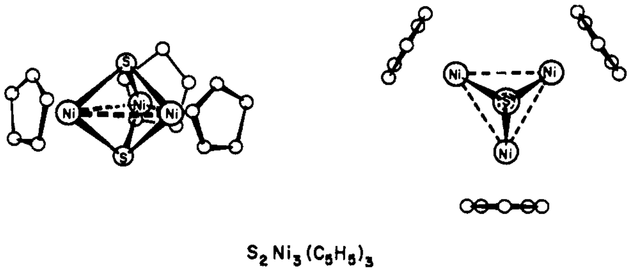

Figure 1. Molecular configuration of $S_2Ni_3(C_5H_5)_3$.

Further synthesis and characterization by single-crystal esr and X-ray measurements of these and similar metal chalcogen complexes are in progress in order to extend these structural and bonding principles.

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(10) For similar MO treatments applied to metal atom cluster systems, see (a) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 3, 10 (1964); (b) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, in press.

(11) The "constraining size effect" stereochemically imposed on the $(C_5H_5)_3Ni_3$ fragment by the formal substitution of the two *smaller* triply bridging carbonyl carbon atoms in place of the two sulfur atoms would be expected to shorten the Ni–Ni distances somewhat (an estimated diminution of 0.1 Å is reasonable) but certainly not by the observed decrease of 0.4 Å. In this connection the average Co–Co bond length of 2.467 Å (individual esd, 0.007 Å) in the tricyclic $Co_3(CO)_9CY$ complex ($Y = CH_3$)[12] is 0.1 Å shorter than the average metal–metal bond length of 2.554 Å (individual esd, 0.007 Å) in the structurally analogous and electronically equivalent molecular complex $SFeCo_2(CO)_9$.[13] In both of these diamagnetic analogs (containing an apical carbon or sulfur atom coordinated to a common basal $Co_3(CO)_9$ fragment), each of the metal atoms attains a closed-shell configuration through single bonds to the other two metal atoms.

(12) P. W. Sutton and L. F. Dahl, *J. Am. Chem. Soc.*, 89, 261 (1967).

(13) D. L. Stevenson, C. H. Wei, and L. F. Dahl, submitted for publication.

(14) H. C. Longuet-Higgins and A. J. Stone, *Mol. Phys.*, 5, 417 (1962).

(15) V. A. Uchtman and L. F. Dahl, submitted for publication.

(16) Direct evidence[17] of the drastic influence of an unpaired electron on the molecular geometry of a metal atom cluster complex was first made apparent from structural studies of the paramagnetic complex $SCo_3(CO)_9$[2] and its isomorphous, diamagnetic analog $SFeCo_2(CO)_9$[13] which revealed that the average metal–metal bond length of 2.554 (7) Å in $SFeCo_2(CO)_9$ is 0.08 Å shorter than the average Co–Co bond length of 2.637 (7) Å in $SCo_3(CO)_9$. These results (which show that a formal removal of the unpaired electron by the substitution of an iron for a cobalt atom gives rise to a shortening and hence strengthening of the metal–metal bonds) thereby indicate that the unpaired electron in $SCo_3(CO)_9$ must be accommodated in an antibonding metal symmetry orbital in agreement with the relative orbital energy diagrams of these complexes.

(17) L. F. Dahl, Abstracts of Proceedings, The 3rd International Symposium on Organometallic Chemistry, München, Germany, Aug 28–Sept 1, 1967, p 92.

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