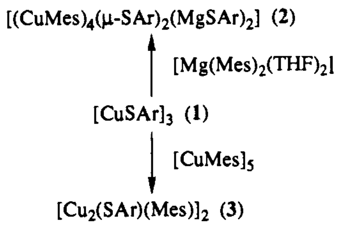
Scheme I[a]



[a] SAr = $SC_6H_4(CH(Me)NMe_2)$-2. Mes = $C_6H_2Me_3$-2,4,6.

are typical for three-center two-electron carbon-bridged copper atoms. The shortest Cu···Cu distance of 2.700 (1) Å across the Cu_4 array in **2** (Cu1–Cu1′) is 0.1 Å longer than the comparable feature in the structure of $[Cu_4(Mes)_4(THT)_2]$. The central mesitylcopper unit in **2** contains two two-coordinate copper atoms (C1–C1–C30′ = 142.8 (3)°) and two planar three-coordinate copper atoms (C1–Cu2–C30 = 168.1 (3)°, S1–Cu2–C1 = 90.0 (2)°, S1–Cu2–C30 = 101.4 (2)°).

For the sulfur atom S1 bridging between Cu2 and magnesium, there are two extreme bonding descriptions possible that necessarily affect our view of the nature of complex **2**. In one description (Figure 2a) there is a tetranuclear organocopper unit, $[CuMes]_4$, to which two $Mg(SAr)_2$ units are connected through thiolate S → Cu donative coordination. This situation is analogous to the coordination of the THT molecule in the organocopper complex $[Cu_4(Mes)_4(THT)_2]$. The second description (Figure 2b) of **2** is based on an ionic structure containing a $[Cu_4Mes_4(SAr)_2]^{2-}$ anion with two $[MgSAr]^+$ cations, each of which is bonded to a thiolato sulfur atom of the cuprate by a S → Mg bond. The X-ray data do not allow us to readily discriminate between these two descriptions.

There are no experimental geometries available for $MgSR^+$ or $Mg(SR_2)^{2+}$ units in which a sulfur atom is bound to a magnesium ion. The Mg–S bond lengths in **2** are 2.375 (4) Å for S2 of the chelate and 2.427 (4) Å for S1 of the bridge, and the bond angles Mg–S–Ar are 89.5 (3)° and 89.7 (3)°, respectively. These values give support to ab initio calculations carried out by Pappas on $Mg(SH)^+$ and $Mg(SH)_2$ that gave Mg–S bond distances of 2.264 and 2.324 Å, respectively,[12] and a Mg–S–H bond angle of 95.2°.

In the bridging thiophenolate group of **2** the Cu2–S1–C10 bond angle is 120.1 (3)° and the Mg–S1–C10 bond angle is approximately 90°. These bond angles lead us to the conclusion that the sulfur atom is most likely sp^2 hybridized. The magnesium ion is bound through a sulfur p_z orbital, while the copper atom (Cu2) and the carbon atom (C10) are bound through two sp^2 orbitals of sulfur. The use of the sulfur p_z orbital to form the Mg–S bond is logical since this orbital is anticipated to have higher electron density than the sp^2 orbital and it is therefore a harder Lewis base.[13] Compared to Mg^{2+}, the Cu^+ cation is a softer Lewis acid and prefers binding to the softer Lewis base sp^2 hybrid orbital of the sulfur atom. We think that the bonding of the sulfur atom S2 of the chelating thiophenolate also occurs through its p_z orbital (Mg1–S2–C20 ≅ 90°).

For the bridging sulfur atom S1 the Cu2–S1–Mg bond angle of 136.4 (1)° is much larger than the 90° that might be expected when copper is bound through an sp^2 orbital and magnesium is bound through a p_z orbital. There are several possible explanations for this discrepancy. One reason could be the presence of Coulombic repulsion between the Cu^+ and Mg^{2+} cations. A second explanation is that the sulfur atom S1 is bridging between copper and magnesium ion by means of a four-electron three-center bond without any direct metal–metal interaction. Consequently, the copper–magnesium distance of 4.472 (3) Å is much longer than that in the cuprate $[Cu_4MgPh_6{\cdot}OEt_2]$ (2.754 Å) where the same metal ions are bridged by a carbon atom with a two-electron three-center bond which assists the metal–metal interaction.[4b] Steric reasons for the large Cu–S–Mg angle cannot be excluded, either.

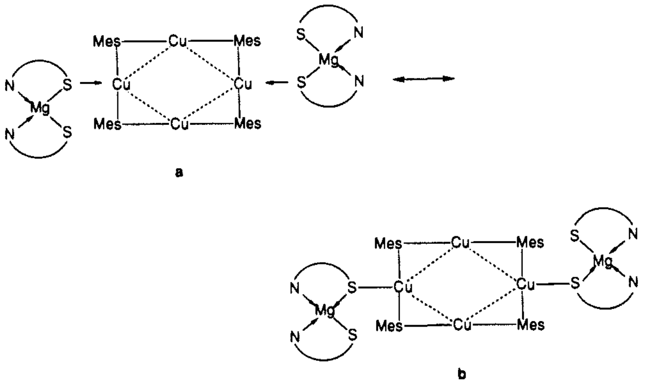


Figure 2. Schematic structure of $[(CuMes)_4(\mu\text{-}SAr)_2(MgSAr)_2]$ (**2**) with donative coordination of the bridging sulfur (μ-SAr) (a) to a copper atom or (b) to a magnesium atom.

Currently the structure in solution of $[(CuMes)_4(\mu\text{-}SAr)_2(MgSAr)_2]$ (**2**) is being studied by ^1H NMR spectroscopy (toluene-d_8). Preliminary results indicate that dissolved **2** breaks up into various species. By comparison with the ^1H NMR shifts of authentic samples, some of the species could be identified as **3**, $[CuMes]_4$, and $[Mg(SAr)_2]$. Further studies are needed to substantiate that the interaction found between $[CuMes]_4$ and $[Mg(SAr)_2]$ in the solid state is also present in solution. The use of **2** and **3** in 1,4-conjugated addition reactions to α,β-unsaturated ketones is under investigation.

Acknowledgment. This work was supported in part (A.L.S. and W.J.J.S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supplementary Material Available: Tables of fractional coordinates of all atoms, bond distances and angles, and anisotropic thermal parameters for **2** (8 pages); listing of observed and calculated structure factor amplitudes for **2** (38 pages). Ordering information is given on any current masthead page.

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(12) Pappas, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 6023.

(13) (a) Coppens, P.; Yang, Y. W.; Blessing, R. H.; Cooper, W. F.; Larsen, F. K. *J. Am. Chem. Soc.* **1977**, *99*, 760. (b) Guru Row, T. N.; Parthasarathy, R. *Ibid.* **1981**, *103*, 477.

Nuclear Overhauser Effect in Solids

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In 1953, Carver and Slichter[1] confirmed the predictions of Overhauser[2] concerning polarization transfer from the conduction electrons of metals to nuclear spins upon saturation of the electron resonance. The nuclear Overhauser effect (NOE), as it has come to be known, has been exploited primarily in solution NMR for sensitivity enhancement, spectral assignment, and conformational analysis.[3,4] Curiously, with the popularization of solid-state NMR techniques through line-narrowing methods such as magic-angle spinning (MAS), the potential for exploitation of the NOE in solids has not been fully explored. This neglect is likely due to the widely

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(1) (a) Carver, T. R.; Slichter, C. P. *Phys. Rev.* **1953**, *92*, 212. (b) Carver, T. R.; Slichter, C. P. *Phys. Rev.* **1956**, *102*, 975.

(2) Overhauser, A. W. *Phys. Rev.* **1953**, *92*, 411.

(3) Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH Publishers: New York, 1989.

(4) Noggle, J. H.; Schirmer, R. E. *The Nuclear Overhauser Effect*; Academic Press: New York, 1971.

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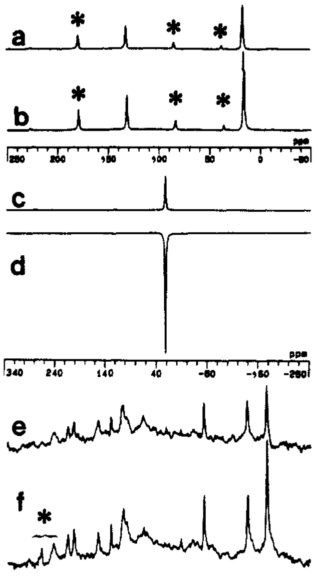

Figure 1. MAS NMR spectra demonstrating the nuclear Overhauser effect in solids: (a) ^{13}C spectrum of hexamethylbenzene, 12 scans, no enhancement; (b) same as in part a but with NOE; (c) ^{15}N spectrum of $^{15}NH_4NO_3$, four scans, no enhancement; (d) same as in part c but with NOE; (e) ^{13}C spectrum of mephobarbital, eight scans, no enhancement; (f) same as in part e but with NOE.

held notion that the motions present in typical solids are characterized by frequencies that are too low for significant cross relaxation, thus precluding enhancement.

The enhancement η observed for a nuclear spin I (following saturation of the S spin reservoir sufficiently long to allow the I spins to reach steady state) is a function of the relative values of the transition probabilities:

$$\eta = (\gamma_S/\gamma_I)(W_2 - W_0)/(2W_1 + W_2 + W_0) \qquad (1)$$

where W_2, W_1, and W_0 are the second-, first-, and zero-quantum transition rates,[5] respectively. From perturbation theory, the transition probabilities are products of time independent spin operator terms and time dependent angular terms, which are modulated in a manner described by a correlation function. Therefore, spectral densities at the Larmor frequency as well as at $(\omega_I + \omega_S)$ and $(\omega_I - \omega_S)$ determine the amount of enhancement observed. These transition probabilities are orientation dependent in solids, as was previously demonstrated by Waugh and coworkers in NOE measurements on solid benzene.[6]

There exist several possibilities for rapid motions in solids. Firstly, the molecules or ions in the solid could in fact be characterized by rotational correlation times approaching the limit of extreme narrowing, such as may exist for (1) plastic crystalline compounds, (2) highly mobile species weakly adsorbed on catalyst surfaces, and (3) polymers at temperatures above their glass transitions. Secondly, even in molecules that do not rotate as a whole, there may exist sources of local motion which serve to modulate dipolar interactions with effective correlation times such that appreciable cross relaxation ($W_2 - W_0$) occurs. Methyl group rotation is such a motion. We have observed useful enhancements for each of the cases listed above.

Parts a and b of Figure 1 are ^{13}C NMR spectra without and with enhancement, respectively, for the plastic crystal hexamethylbenzene.[7,8] When a proton saturation pulse of 10 s and a total pulse delay of 20 s were used, the methyl peak was enhanced by 76% whereas the aromatic peak was enhanced by 54% (η = 0.76 and 0.54, respectively). Although significant, this is less than the theoretical maximum for the extreme narrowing limit of 199%. For adamantane and camphor, which undergo rapid isotropic reorientation in their plastic crystalline phases, the theoretical maximum NOE was obtained for most of the carbon resonances (spectra not shown).

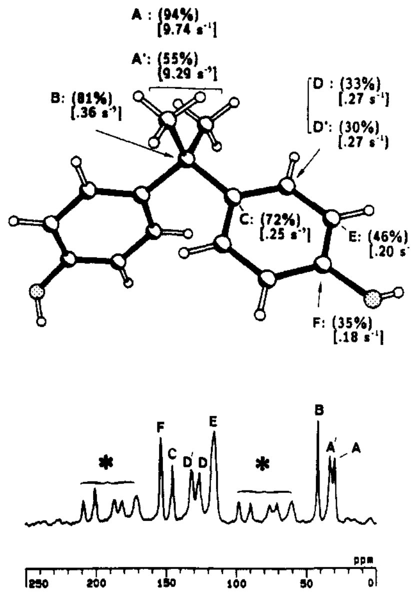

Figure 2. NOE growth rates [square brackets] and maximum enhancements (parentheses) for the ^{13}C signals of 4,4'-isopropylidenediphenol (bisphenol A). One of three similar conformers is depicted. The ^{13}C MAS spectrum without enhancement is shown at the bottom of the figure.

Parts c and d of Figure 1 show ^{15}N NMR spectra of the ionic solid $^{15}NH_4NO_3$, without and with enhancement, respectively. An η of −4.50 was obtained when a 3-min saturation pulse and a total pulse delay of 4 min were used. This approaches the theoretical maximum η of −4.90. The negative enhancement unambiguously demonstrates that the Overhauser effect is the enhancement mechanism.

We have also observed significant enhancements for typical rigid crystalline solids. Figure 1e shows a ^{13}C NMR spectrum of mephobarbital obtained in eight scans using a pulse delay of 120 s. When a 60-s proton saturation pulse was used (Figure 1f), the methyl resonance at 11 ppm was enhanced approximately 100%, while the remaining resonances were enhanced 40–60%.

The possibility of relating observed NOE enhancements to distances from methyl groups was investigated in detail for the model compound 4,4'-isopropylidenediphenol, whose structure is shown in Figure 2.[9] For ^1H saturation times of 30 s, significant fractional enhancements were observed for all of the resonances (listed in parentheses next to the carbon of interest in Figure 2). NOE growth experiments revealed that the initial rates of enhancement (given in square brackets next to the appropriate carbons in Figure 2) generally decrease with increasing distance from the methyl carbons.[10]

Analogous results have been obtained for a variety of methyl-containing compounds as well as proteins and synthetic polymers. Essentially no NOE enhancement was observed for the glassy polymer polystyrene, which has no methyl groups. The

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(5) (a) Abragam, A. *Principles of Nuclear Magnetism*; Oxford University Press: Oxford, 1961. (b) Reference 3, Appendix II.

(6) Gibby, M. G.; Pines, A.; Waugh, J. S. *Chem. Phys. Lett.* **1972**, *16*, 296.

(7) (a) Spectra were obtained by using 90° pulses immediately following a variable-length ^1H saturation pulse. All spectra were acquired on a Chemagnetics CMX-300 spectrometer with magic-angle spinning. (b) ^1H field strengths of 40 kHz were used for the saturation pulse whereas field strengths of 60 kHz were used for decoupling.

(8) Allen, P. S.; Cowking, A. *J. Chem. Phys.* **1967**, *47*, 4286.

(9) The space group for 4,4'-isopropylidenediphenol is $P112/n$, and there are 12 molecules per unit cell. One of three similar conformations is shown in Figure 2. See: Belskii, V. K.; Chernikova, N. Y.; Rotaru, V. K.; Kruchinin, M. M. *Krystallografiya* **1983**, *28*, 685.

(10) The observed rates do not decrease in accordance with an r^{-6} dependence. This suggests that intermolecular NOE effects and/or additional cross-relaxation pathways may be significant for ^{13}C nuclei remote from the methyl groups.

enhancements observed in this study are significant and promise to be applicable to a variety of problems. For example, in mobile systems[11] that do not cross polarize efficiently, single-pulse experiments with NOE enhancement could be a superior alternative. NOE measurements in solids may also be useful for probing high-frequency motions, for studying relaxation mechanisms and pathways, and for spectral assignments.

Acknowledgment. This work was supported by grants for the National Science Foundation (CHE-8918741) and the Office of Naval Research (N00014-88-K-0239). The NMR instrumentation was provided through a grant from the Department of Defense. J.L.W. is a Department of Education Fellow.

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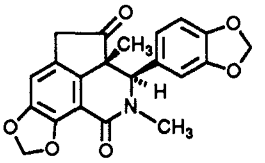
(11) Haw, J. F.; Richardson, B. R.; Oshiro, I. S.; Lazo, N. D.; Speed, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2052.

Additions and Corrections

Total Synthesis of (±)-14-Epicorynoline, (±)-Corynoline, and (±)-6-Oxocorynoline [*J. Am. Chem. Soc.* **1983**, *105*, 2873]. MARK CUSHMAN,* AZIZ ABBASPOUR, and YASH PAL GUPTA

In 1988, the isolation and characterization of 13-epicorynoline was reported (Zeng, W.; Liang, W.; He, C.; Zheng, Q.; Tu, G. *Phytochemistry* **1988**, *27*, 599). The spectroscopic data of this natural product did not match that of our earlier prepared synthetic compound **31**, which had been assigned a structure identical with that of 13-epicorynoline. An X-ray analysis of **31** has indicated that the previously assigned structure is incorrect. Since **31** was prepared by $LiAlH_4$ reduction of **30**, structure **30** as given in the publication is also incorrect. The correct structures of **30** and **31** are shown below. Since these compounds were not on the synthetic pathway to the natural products listed in the title, the synthesis of the title compounds is still valid.



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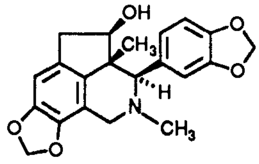

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Book Reviews

Second Quantized Approach to Quantum Chemistry. An Elementary Introduction. By P. R. Surjān (Chinoin Pharmaceutical and Chemical Works Ltd.). Springer-Verlag: New York and Berlin. 1989. xii + 184 pp. $79.50. ISBN 0-387-51137-7.

The purpose of this book is to make the second-quantized approach accessible to chemists. By discussing a number of topics that ordinarily are not encountered in a standard course of quantum chemistry, Surjān helps to bridge the gap between chemists and physicists. However, this is a very thin book that should be a bit thicker.

Surjān assumes that the reader is familiar with basic quantum mechanics and has a good working knowledge of quantum chemistry, including σ–π separation, Hückel theory, spin orbitals, antisymmetrization, Slater determinants, the Slater–Condon rules, Hartree–Fock theory, and projection operators. Chapters 1–5 introduce the particle-number representation, creation and annihilation operators (and their anticommutation relations), particle-number operators, the second-quantized representation of operators, and the evaluation of matrix elements. The particle-hole formalism is introduced, although it is not used in the book. These chapters are rather terse; additional explanation would be very useful in several places. However, most students should be able to work through them and thereby obtain a working grasp of the second-quantized approach.

The remainder of the book purportedly shows the utility of second quantization in treating a number of chemical problems. In most cases the author is content to develop equations, without much explanation of their significance.

Some parts of the book are confusing, probably because of the author's brevity. At the end of Chapter 8, Surjān shows that the use of incomplete basis sets leads to some mathematical inconsistencies. However, the reader is told nothing about their practical consequences, or how to get around them in actual calculations. In Section 10.4, students will be confused by the sudden insertion of extra electron-interaction terms to convert the electronic Hamiltonian into the Fockian. The discussion of quasi-particle transformations in Chapter 16 contains too many gaps to be very useful to inexperienced readers.

The book contains some inconsistencies. In Chapter 7, Surjān employs commutators rather than anticommutators for Fermion creation and annihilation operators. In developing the second-order density matrix, he uses a unitary transformation between basis functions and Hartree–Fock orbitals. This implies that the creation and annihilation operators for the latter anticommute, just like those for the basis functions. However, the desired result cannot be obtained by using that anticommutation. The development of the Brillouin theorem in Chapter 11 is confusing because basis functions and Hartree–Fock eigenfunctions are not differentiated.

Several chapters are quite interesting. Chapter 10 shows that second quantization provides a very neat path to the particle-hole symmetry relations in alternant π-electron systems. Chapter 13 is a concise discussion of the difficulties encountered with non-orthogonal basis sets. The chapters on the Hellmann–Feynmann theorem and intermolecular interactions are really thought-provoking. Unfortunately, not enough space is devoted to any topic. However, the careful reader will gain a modicum of familiarity with second quantization, and may then be able to understand papers where more complete discussions are given.

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Laser Micro Analysis. By L. Moenke-Blankenburg (Martin-Luther-University). Wiley-Interscience: New York and Chichester. 1989. xvi + 288 pp. $69.95. ISBN 0-471-63707-6.

This monograph (Volume 105 in the Chemical Analysis series of monographs) discusses the use of laser-based techniques for analysis of materials, with the term micro implying the emphasis on high-spatial resolution through the use of tightly focused laser beams. The principal methods discussed are optical emission spectroscopy and mass spectrometry. The most sensitive of these methods can provide ppm detection limits while using only picograms of the sample. These analytical methods, coupled with laser excitation, are illustrated through a large number of referenced applications (tabulated references make up one-third of the book). The broad overview of this important topic will be useful to most beginning practitioners, while the detailed lists and tables