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N-oxide functionality. This stabilization is reflected in the low *m* value indicating a low sensitivity of the stabilized nitrenium ion to the reaction medium.[20] Finally it has been established that both in vivo and in vitro the carcinogen 4-nitroquinoline 1-oxide **4** gives products with DNA by reaction of a nucleic base at the C-3 position of the quinoline.[9,21] This study proves the susceptibility to nucleophilic attack of metabolites of **4** and in suggesting a nitrenium ion pathway provides a focus for further study of the interaction of carcinogens with DNA.

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(20) A referee has suggested that the formation of **7** might not involve much separation of charge in the transition state but rather occur via intramolecular acetate migration or by an S_N2 process. Our conclusion that reaction is via ionization is based on the clear evidence from the Grunwald–Winstein plot of charge separation in the transition state. Our observed low *m* value we attribute to the stabilization of the *N*-oxide functionality. The comments of the referee highlight the need for further Grunwald–Winstein plots for reactions proceeding via nitrenium ion intermediates.

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EPR Study of a Cubane-Type Mixed Cluster in a Single Crystal: $CoFe_3S_4$ in $[NBu_4]_2[Fe_4S_4(SPh)_4]$

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Mixed-metal cubane-type clusters MFe_3S_4 are of great interest because they may be good models for the active site of some metalloproteins and also for comparison of their electronic structure with that of the Fe_4S_4 parent clusters. Synthesis of compounds containing such species is a great challenge for inorganic chemistry but, up to now, only two mixed clusters have been obtained: $MoFe_3S_4$ and WFe_3S_4.[1,2] An alternative way for creating these clusters is to obtain Fe_4S_4 model compounds slightly doped with the required metal. If the mixed cluster has an odd number of electrons, it will necessarily be paramagnetic and we can hope to see an EPR spectrum associated with it if the matrix itself is diamagnetic. We report the result of such an attempt to the case of the cobalt-doped model compound $[NBu_4]_2[Fe_4S_4(SPh)_4]$. An EPR spectrum clearly associated with cobalt is observed which we attribute to the heteronuclear $(CoFe_3S_4)^{2+}$ core. This study, made on single crystals, provides the first orientational information about the EPR parameters of a mixed-metal cubane-type cluster.[12]

The model compound was prepared as previously described.[3,4] Doping with cobalt was achieved by adding 0.2% of $CoCl_2$ to $FeCl_3$. Single crystals were grown from acetonitrile solution by a transport method. The pure compound crystallizes at room temperature in the monoclinic system.[5] Around 240 K a phase transition occurs, the cell becoming orthorhombic below this temperature. To prevent occurrence of the phase transition the sample was quenched. At about 77 K, the quenched cobalt-doped samples do not exhibit any EPR lines but, as the temperature is decreased, composite spectra appear near $g = 2$ (see Figure 1a).

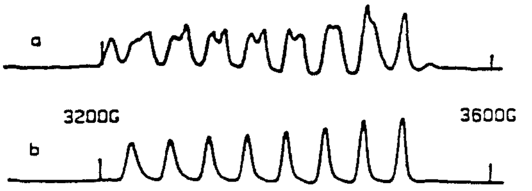

Figure 1. Second-derivative absorption EPR spectra for $\vec{H}\parallel\vec{c}^*$. Microwave frequency, 9.253 GHz; microwave power, 10 mW; 100-kHz field modulation, 2 G. (a) Two predominant $I = {}^7/_2$ centers, including the one studied, are observed at $T \sim 10$ K. (b) Only the center studied in this work remains at $T = 4.2$ K.

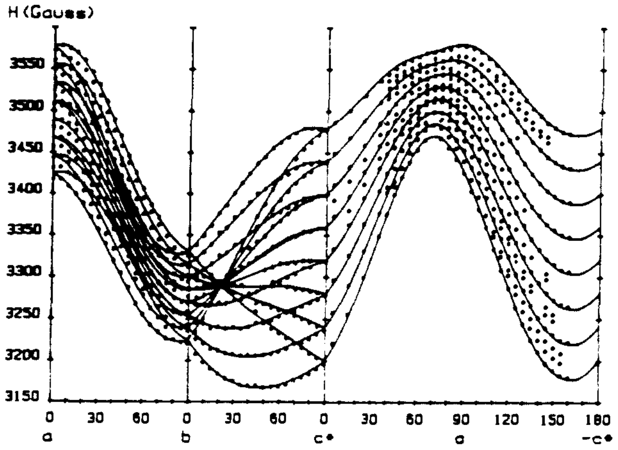

Figure 2. Experimental points and calculated angular dependences in the *ab*, *bc**, and *c*a* planes. Mean microwave frequency, 9.165 GHz. Extra points correspond to "forbidden" lines.

Table I. Principal Values of the $\tilde{g}$ and $\tilde{A}$ Tensors and Their Direction Cosines in the $\vec{a}$, $\vec{b}$, $\vec{c}^*$ Frame (A Values in MHz)

	$\vec{a}$	$\vec{b}$	$\vec{c}^*$
$g_1 = 1.860$	0.955	0.019	0.296
$g_2 = 1.998$	0.015	0.994	−0.113
$g_3 = 1.970$	−0.296	0.112	0.949
$\lvert A_1\rvert = 38$	0.939	−0.108	0.328
$\lvert A_2\rvert = 0$	−0.017	0.935	0.355
$\lvert A_3\rvert = 123$	−0.345	−0.339	0.875

By varying the temperature and the microwave power four sets of lines could be distinguished, all clearly associated with cobalt ions. At 4.2 K and 10 mW of microwave power, three sets are saturated and thus only one remains. We will focus only on the latter, for which the complete angular variations could be obtained.

A typical spectrum, recorded at 4.2 K with the magnetic field $\vec{H}$ directed along $\vec{c}^*$, is shown in Figure 1b. Clearly, the eight equally spaced lines are the hyperfine components associated with the cobalt 59 nuclear spin $I = {}^7/_2$. As the temperature is raised, the lines begin to broaden out around 15 K due to a fast spin–lattice relaxation, showing the presence of low-lying excited states. No lines indicative of an $S > {}^1/_2$ state appear in the low-field region: we are dealing with $-{}^1/_2 \rightarrow +{}^1/_2$ transitions of an $S = {}^1/_2$ ground state. The angular variations of the lines when $\vec{H}$ is swept in the *ab*, *bc**, and *c*a* planes are reported in Figure 2. They show the presence of two sites which become equivalent for $\vec{H}$ along the twofold screw axis $\vec{b}$ or in the plane *c*a*, in agreement with the monoclinic symmetry of the lattice. These angular variations are rather well fitted in a first-order perturbation approximation by the spin Hamiltonian $\vec{H}\tilde{g}\vec{S} + \vec{S}\tilde{A}\vec{I}$ with $S = {}^1/_2$ and $I = {}^7/_2$. The small discrepancies that occur between the calculated curves and the experimental points are due to second-order effects, to the nuclear quadrupole coupling neglected in the calculation, and also to some slight misalignments of the sample. The appearance of "forbidden" lines, specially in the *ab* and *c*a* planes near the $\vec{a}$ axis, is due to this quadrupolar interaction. Table I gives the principal values of the $\tilde{g}$ and $\tilde{A}$ tensors and the direction cosines of their principal axes with respect to

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the crystal axes. The differences in the principal directions of the $\bar{g}$ and $\bar{A}$ tensors reflect the low symmetry (triclinic) of the center.

The question that arises now is, where is the cobalt ion located? Owing to the method of preparation of the doped compound, it is very likely that the cobalt enters into the core and substitutes for one of the core iron ions. It is worth noting that Co^{2+} ions pseudotetrahedrally coordinated to sulfur ions have already been observed.[6-8] The most convincing evidence for our assumption is the existence of the three other species since the cobalt ion has on the whole four ways of substituting for an iron ion of the core. We reject the possibility that the cobalt ion is located in an interstitial site of the lattice (in particular no proton superhyperfine structure appears, which might be the case since the cobalt ion would then be placed closer to an organic part of the compound). We are thus dealing with a mixed-cluster $CoFe_3S_4$ which must be in the +2 oxidation state in order to preserve the electrical neutrality of the compound.

It is worthwhile to recapitulate our relevant observations: the resonance occurs in an $S = {}^1/_2$ ground state, the spin-lattice relaxation time is short, and the g values are less than 2 with an average g of 1.943. For a $CoFe_3S_4$ heteronuclear system, we cannot expect to see an EPR spectrum similar to that given by a cobalt ion pseudotetrahedrally coordinated to sulfur ions, because the cobalt is in the vicinity of the three iron ions. Indeed, the g values and the saturation behavior of the center are very different from all the previously reported data for cobalt complexes.[9] All the relevant observations we have made are consistent with a polynuclear system $(CoFe_3S_4)^{2+}$ where the metal ions are antiferromagnetically exchange-coupled to yield an $S = {}^1/_2$ ground state as in the $(Fe_4S_4)^+$ parent core.[10] The latter is encountered in reduced 4Fe-4S ferredoxins and their synthetic model compounds and we have succeeded in creating it also in the $[NBu_4]_2[Fe_4S_4(SPh)_4]$ compound itself by γ irradiation.[11] In that case, three high-spin ferrous ions ($3d^6$, $S = 2$) and one high-spin ferric ion ($3d^5$, $S = {}^5/_2$) couple together to give an $S = {}^1/_2$ ground state. For the $(CoFe_3S_4)^{2+}$ core, the $S = {}^1/_2$ ground state plausibly results from one of the two combinations of formal integral oxidation states $Co^{II} + Fe^{II} + 2Fe^{III}$ or $Co^{III} + 2Fe^{II} + Fe^{III}$ where $S = {}^3/_2$ for high-spin Co^{II} ($3d^7$) and $S = 2$ for high-spin Co^{III} ($3d^6$). But as the $(CoFe_3S_4)^{2+}$ core must be, like the $(Fe_4S_4)^+$ core, a mixed-valence system, the distinction between these two configurations is not relevant.

It would have been interesting to find tensorial pseudosymmetries associated with the structure of the Fe_4S_4 cluster to localize the cobalt ion in the core. A comparison of the principal directions of the tensors with atomic directions calculated from the X-ray crystallographic data for the pure compound do not show any clear relation either with one of the four FeS_4 coordination units or with the overall pseudosymmetry of the pure cluster. This is not surprising because the replacement of an iron ion by a cobalt ion introduces some extra distortions of the core. More information about the problem may come from the analysis of the relative orientations of the tensors of the four species. Work is in progress to attempt to extract this information.

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Free-Radical-Induced Elimination of H_2S from Dithiothreitol. A Chain Reaction

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Dithiothreitol (DTT) is used in many biochemical studies because it is a powerful reducing agent, like many thiols, but it can be handeled with some advantage over other thiols, because it is not as readily oxidized by air.[1] In radiation biological and flanking radiation chemical studies it has been used quite often and its free-radical chemistry has found considerable attention.[2-6] It was originally assumed that OH radicals abstract an H atom from one of the thiol groups (cf. reaction 3) but it was reported later that OH radicals cause considerable H_2S formation and it has been concluded that, depending on pH, as much as 25-40% of the OH radicals react by abstracting carbon-bound H atoms thereby forming **4**.[5] In the present paper we show that the H_2S formation is entirely due to a chain reaction and OH attack at carbon is negligible.

In the radiolysis of N_2O-saturated aqueous DTT solutions the solvated electrons (e^-_{aq}) from reaction 1 are converted into OH radicals (reaction 2). Thus the system contains mainly OH

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} {}^\bullet OH,\ e^-_{aq},\ H^\bullet,\ H^+,\ OH^-,\ H_2O_2,\ H_2 \qquad (1)$$

$$e^-_{aq} + N_2O + H_2O \rightarrow {}^\bullet OH + OH^- + N_2 \qquad (2)$$

radicals (90%g, $G(OH) = 5.4$ molecules $(100\ eV)^{-1}$) and only a small amount of H atoms (10%, $G(H) = 0.55$). These primary water radicals react with the substrate (DTT) by H-abstraction. The H atom is also known to undergo displacement reactions thereby forming H_2S (for a review see ref 7). In the present system the latter reaction only contributes about 15%.[8]

It can be seen from Table I that at pH 4 and at a given dose rate $G(H_2S)$ is independent of DTT concentration but that at a given DDT concentration $G(H_2S)$ strongly increases with decreasing dose rate. At low dose rates $G(H_2S)$ exceeds $G(OH + H)$, hence a chain reaction must prevail. If in a chain reaction a propagation process, kinetically of first order in radicals, competes with the bimolecular decay of the radicals, the yield of the chain product must increase linearly with the inverse of the square root of the steady-state concentrations of the radicals (i.e., the dose rate). Such a plot is shown in Figure 1. Extrapolation to infinite dose rate ((dose rate)$^{-1/2} \rightarrow 0$) shows that practically all H_2S originates from the chain reaction. The small intercept ($G(H_2S) = 0.2$) can be accounted for by the reaction of the H atoms. We therefore conclude that OH radicals as such do not cause H_2S formation.

We propose that H_2S formation is due to an intramolecular H-abstraction of the primary thiyl radical **1** (reaction 8) followed by either H_2S elimination (reaction 10) or $HS^\bullet$ elimination (reaction 11). H-Abstraction of carbon-bound H atoms by thiyl radicals is not without precedence[9], and reaction 10 finds its

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