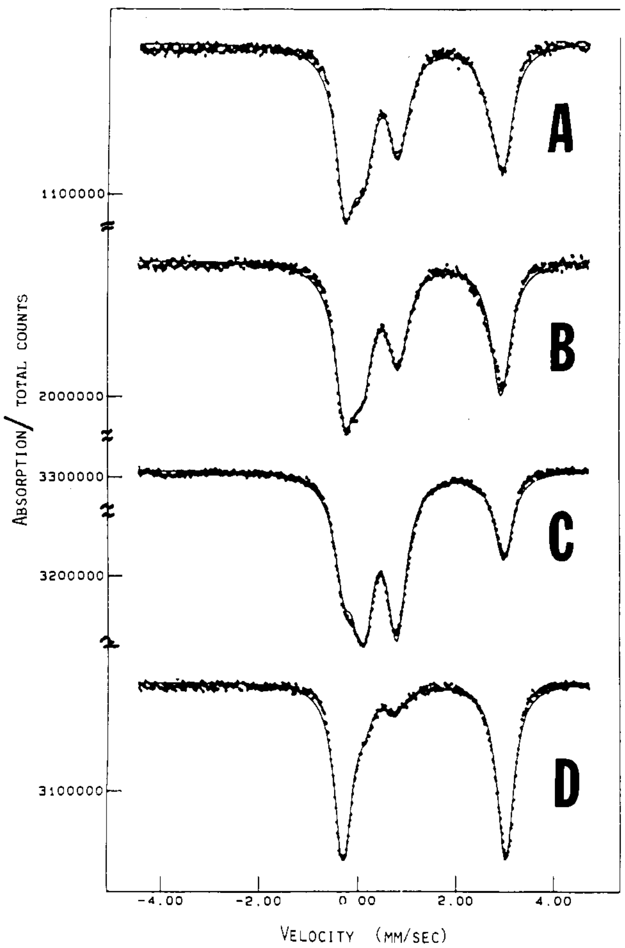

Figure 1. Mössbauer spectra of ^{57}Fe(II) mixed with protein coats from spleen ferritin. Spectra were obtained at 80 K as previously described: (A–C) protein after mixing with Fe(II) for 0.75, 2, or 12 h (see Experimental Section); (D) Fe(III) sample added to deaerated water, transferred to a sample vial, and frozen immediately after addition of ^{57}Fe(II) to the protein sample was completed.

occurred, the surface iron(III) oxide hydroxide might render the remaining Fe(II) inaccessible to *o*-phenanthroline. Such a model also explains the increased availability of Fe(II) in ferritin to chelators when Fe(II) is added in the absence of dioxygen.[9,13,16] An apparently analogous phenomenon occurs when Fe(II) is added to the buffer: ferro/ferri oxide hydroxides (blue-green) precipitate that oxidize (rust) first at the surface; when the protein is present, the iron complexes are maintained in solution.

Two possible ramifications of the sequestration of Fe(II) by protein coats of ferritin when large amounts of iron are added concern the bioenergetics of storing Fe in ferritin and the role of ferritin in evolution. The energetics of cellular iron storage in ferritin predicts a large electron flux for oxidation of iron during ferritin formation and reduction of iron during ferritin core dissolution. The flux may be less than predicted for large amounts of iron when iron turnover is rapid, in macrophages for example, if some of the iron remains as Fe(II) during short recycling times.[5] The possible evolutionary age of ferritin has been related to he appearance of dioxygen in the atmosphere, which produced the need for a variety of proteins to control or detoxify the results of iron/dioxygen interactions in living cells. However, even the metabolic role of Fe(II) is complex.[17-19] Thus, the ability of the protein coats of ferritin to sequester Fe(II) when it is available in large amounts and the high concentrations of Fe(II) used by bacteria thought to represent features of primitive life in the absence of dioxygen, e.g. sulfate-reducing bacteria, suggest that ferritin or ferritin-like proteins may be among the oldest of proteins.

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(16) Watt, G. D.; Jacobs, D.; Frankel, R. B. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 7457–7461.
(17) Postgate, J. R. *The Sulfate-reducing Bacteria*, 2nd ed.; Cambridge University Press: Cambridge, England, 1984; pp 98, 99, 103–105.
(18) Bagg, A.; Neilands, J. B. *Biochemistry* **1987**, *26*, 5471–5477.
(19) Williams, R. J. P. *FEBS Lett.* **1982**, *140*, 3–10.

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Temperature and Pressure Effects on the EPR Zero-Field Splitting of $Cu_2Cl_6^{2-}$ Dimers in $[(C_6H_5)_4Sb]_2Cu_2Cl_6$ Crystals

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The zero-field-splitting parameter *D* of EPR spectra is commonly dependent on temperature and pressure for multielectron paramagnetic ions with $S > {}^1/_2$. It is related to changes in the crystal field gradient at an ion site as a result of a rearrangement of the effective ligand charges due to thermal lattice contraction and/or changes in the amplitude of atomic vibrations.

These mechanisms seem to not be effective in binuclear complexes of ions with $S = {}^1/_2$ since the **D** tensor is not "quadrupolar" in origin there and is, rather, determined by dipolar and exchange coupling. Thus, the **D** tensor is an intrinsic property of a dimeric unit and is related to the geometrical structure, which is stable over a large temperature range, as is proved by magnetic susceptibility χ data. In fact, in the vast majority of copper(II) dimers the $\chi(T)$ dependence can be described by the temperature-independent singlet–triplet splitting *J*, which is known to be very sensitive to the dimer geometry.[1] Thus, a **D** tensor for binuclear $S_1 = S_2 = {}^1/_2$ complexes is not expected to be affected by temperature.

We have found, however, that in the chlorocuprates $[(C_6H_5)_4A]_2Cu_2Cl_6$ (A = P, Sb, As) the *D* values increase on cooling.[2] The dipolar contribution to the **D** tensor is overdominated by anisotropic exchange splitting in these crystals; thus the $D(T)$ dependence seems to be related to the temperature dependence of the anisotropic exchange coupling between Cu(II) ions within Cu_2Cl_6 units. Since generally an increase in pressure affects the spectra in the same way as a decrease in temperature, we decided to perform EPR experiments over a large temperature range under hydrostatic pressure up to 400 MPa on powdered samples of $[(C_6H_5)_4Sb]_2Cu_2Cl_6$ with the aim of having a closer insight into the factors determining the behavior of *D*.

The compound was prepared as described in ref 2. X-Band EPR spectra were recorded with a Radiopan SE/X-2542 spectrometer equipped with a hydrostatic pressure apparatus.[3,4] A cylindrical TE_{112} corundum resonator and 80-Hz modulation were used. Powder spectra were recorded as depending on temperature under different pressures and as depending on hydrostatic pressure at different temperatures.

EPR spectra under atmospheric pressure are presented in Figure 1. The following three effects appear with a lowering of temperature as is clearly seen in Figure 1: (a) an increase in the splitting of the principal **D**-tensor components D_i ($i = x, y, z$), as marked by arrows, (b) an increase in the intensity of the

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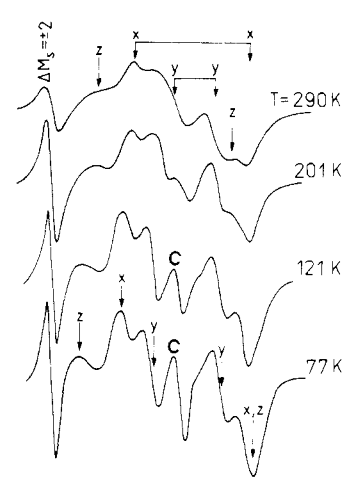

Figure 1. Temperature variations of the powder spectra recorded at 9.42 GHz under atmospheric pressure (p = 0.1 MPa). Line C is a central line from interdimer coupling (see text).

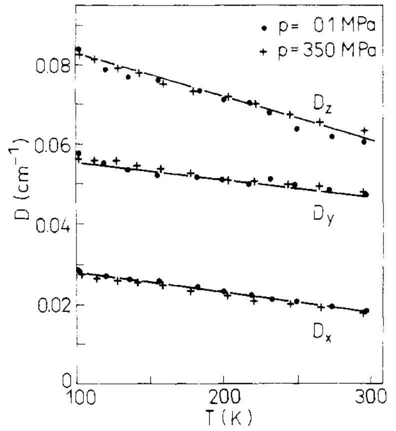

Figure 2. Temperature dependence of zero-field splitting under atmospheric and high hydrostatic pressure.

spin-forbidden half-field transition ($\Delta M_s = \pm 2$), and (c) the appearance of a central line (marked as C) at about 310 mT, which grows in intensity. When hydrostatic pressure is applied, merely effect c appears. Thus, the **D** tensor is pressure independent within experimental error. It is presented in Figure 2, where $D(T)$ data for two pressures are shown.

The $CuCl_4^{2-}$ complexes in our crystal have a pseudotetrahedral geometry with the flattening angle 2γ = Cl-Cu-Cl = 147° in approximately D_{2d} symmetry.[2] Thus, the geometry deviates from a free $CuCl_4^{2-}$ geometry (2γ = 123°) as a result of lattice forces or a strain resulting from dimer formation.

Square-planar $CuCl_4^{2-}$ complexes are known to undergo second-order Jahn-Teller interactions in such a way that the potential surface has the lowest symmetrical minimum in the ground state and two additional minima in the excited state corresponding to two distorted-tetrahedral geometries of b_{2u} vibrations. The relative heights of these minima are reflected in the temperature dependence of electronic spectra and spin Hamiltonian parameters.[5,6] In dinuclear species such as $Cu_2Cl_6^{2-}$ this pattern can be more complicated, for instance making the two excited minima nonequivalent and lowering the symmetry of the ground state, despite the fact that the electronic structure observed by optical absorption spectra for mononuclear $CuCl_4^{2-}$ complexes is not strongly affected by a Cu_2Cl_6 dimer formation.[7] The Jahn-Teller activity, however, should result in the temperature dependence of the electronic parameters. This is indeed what we observed in $[(C_6H_5)_4Sb]_2Cu_2Cl_6$ by EPR spectroscopy.

The EPR parameter that most clearly shows a temperature dependence is D. The g factors also seem to be temperature dependent. They are, however, determined from powder spectra with less accuracy. The D parameter has already been found to be mainly determined by anisotropic exchange;[2] therefore, it seems reasonable to attribute the temperature variation of D to the change in population of the vibronic levels, which must be characterized by different anisotropic exchange integrals. Indeed, for a square-planar geometry the magnetic orbital is xy and $D_{zz} = {}^1/_3(g_z - g_0)^2 J^{an}_{xy,x^2-y^2}$, where J^{an} represent coupling between the ground state of the first ion and the excited $x^2 - y^2$ state of the second ion.[8,9] J^{an}_{xy,x^2-y^2} is expected to be strongly ferromagnetic. When the planar geometry is deformed toward a tetrahedron, we have an admixture of $x^2 - y^2$ and xz in the ground state. This mixing exists in vibronic levels and produces a decrease of the effective J^{an} value since much smaller values are expected for both $J_{x^2-y^2,x^2-y^2}$ and J_{xz,x^2-y^2} couplings. Thus, the maximum anisotropic exchange appears in the planar geometry and decreases with tetrahedral deformation, yielding variations in D. This is what we observe as a linear decrease of D on heating.

A confirmation of this model comes from the observed pressure independence of D, since a hydrostatic pressure lower than gigapascals does not affect molecular vibrations.[10] Thus, our crystal represents a rare case where a physical parameter is affected by temperature but not by pressure.

The interdimer exchange coupling J_1 is very weak in our crystal, as is proved by resolved fine-structure lines. This coupling, however, influences, our EPR spectra. An effect of the interdimer coupling becomes evident as an appearance of the central line in the powder spectrum (Figure 1). This line is due to the merging effect between EPR lines split less than about $0.3J_1$. The J_1 value can be estimated by the method of ref 11 and 12 as equal to J_1 = 0.005 cm^{-1} at room temperature. The central line intensity increases on cooling and under pressure, indicating that the interdimer coupling increases with a shortening of intermolecular distances similarly to that observed in other chloro-bridged Cu(II) dimers.[13]

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(1) Hatfield, W. E. In *Magneto-Structural Correlations in Exchange Coupled System*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, Holland, 1985.
(2) Bencini, A.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1985**, *24*, 704.
(3) Stankowski, J.; Maćkowiak, M.; Krupski, M. *Sci. Instrumentation* **1986**, *1*, 3.
(4) Stankowski, J.; Gałęzewski, A.; Krupski, M.; Waplak, S.; Gierszal, H. *Rev. Sci. Instrum.* **1976**, *47*, 128.
(5) McDonald, R. G.; Riley, M. J.; Hitchman, M. A. *Inorg. Chem.* **1988**, *27*, 3205.
(6) Riley, M. J.; Hitchman, M. A. *Inorg. Chem.* **1987**, *26*, 3205.
(7) Desjardins, S. R.; Wilcox, D. E.; Musselman, R. L.; Solomon, E. I. *Inorg. Chem.* **1987**, *26*, 288.
(8) Banci, L.; Bencini, A.; Gatteschi, D. *J. Am. Chem. Soc.* **1983**, *105*, 701.
(9) Chow, C.; Willett, R. D. *J. Chem. Phys.* **1973**, *59*, 5903.
(10) Drickamer, H. R. *Acc. Chem. Res.* **1986**, *19*, 329.
(11) Hoffmann, S. K. *Chem. Phys. Lett.* **1983**, *98*, 329.
(12) Hilczer, W.; Hoffmann, S. K. *Chem. Phys. Lett.* **1988**, *144*, 199.
(13) Hoffmann, S. K.; Towle, D. K.; Hatfield, W. E.; Chaudhuri, P.; Wieghardt, K. *Inorg. Chem.* **1985**, *24*, 1307.

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Formation of Reactive Cationic Iron Clusters by Halogen Exchange and Abstraction from Nonacarbonylbis(μ_3-fluoromethylidyne)triiron with Lewis Acids

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Nonacarbonylbis(μ_3-alkylidyne)triiron clusters have been of great recent interest.[1-7] In order to study the limits of stability

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