Table I. Structural Comparison of the CuN_2S Units in **2**, **3**, and Blue Copper Proteins

	$Cu(SC_6F_5)L$ (**2**)	$Cu(SCPh_3)L$ (**3**)	Az (*A. denitricans*)	Pc (*popula*)	Pc (*E. prolifera*)	PAz	CBP
Cu–N1 (Å)	1.930 (9)	1.97 (5)	2.08	1.91	1.89	2.16	1.90
Cu–N2 (Å)	2.037 (9)	2.03 (4)	2.00	2.06	2.17	2.13	2.13
Cu–S (Å)	2.176 (4)	2.12 (2)	2.15	2.07	2.12	2.16	1.99
S–Cu–N1 (deg)	134.6 (3)	135 (1)	135	132	125	136	139
S–Cu–N2 (deg)	122.7 (3)	124 (2)	119	123	120	112	110
N1–Cu–N2 (deg)	93.9 (4)	98 (2)	105	97	104	100	99
Cu/N1N2S plane (Å)	0.34	0.20	0.12	0.36[a]	0.37[a]	0.43	0.39[a]
Cu–S* (Å)	2.119 (8)[b]	2.05 (5)[b]	3.11	2.82	2.92	2.76	2.62
EPR	axial	axial	axial	axial	axial	rhombic	rhombic
ref	this work	this work	14	15	16	17	18

[a] The data were provided by H. C. Freeman. [b] The distance between the copper and the apical nitrogen atom.

Table I). Although the refinement is very poor, the X-ray analysis of **3** indicates that its coordination structure is essentially similar to that of **2**.[9]

Blue copper proteins may be classified into three groups on the basis of their spectroscopic properties: (I) proteins that give an axial symmetric EPR spectrum; (II) proteins exhibiting a rhombic EPR spectrum; and (III) nitrous reductase[10] and Cu_A in cytochrome *c* oxidase[11] which exhibit distinctive features in absorption and EPR spectra. Whereas the structure of class III blue copper proteins remains to be solved, the crystal structures of class I and II blue copper proteins are available. The coordination structures of both types of the proteins are generally referred as distorted tetrahedral with a N_2SS^* (S^* denotes methionine sulfur) ligand donor set. The relevant structural parameters of **2**, **3**, and the blue copper proteins are compared in Table I. The CuN_2S unit of **2** (or **3**) is geometrically close to those of Az and Pc. These coordination structures can be described as trigonal, since the separations between the copper and the N_2S basal plane are short (<0.4 Å). On the other hand, the Cu⋯(N_2S) distances in pseudoazurin (PAz) and cucumber basic blue copper protein (CBP) are more separated (~0.4 Å). It should be noteworthy that **2** (or **3**) gives an axial EPR spectrum as Az and Pc, whereas PAz and CBP exhibit a rhombic EPR signal. Hence, the distinct features in EPR may correlate with the Cu⋯(N_2S) separations.[12] Alternatively, the apical ligand seems not to affect the spectroscopic properties of blue copper proteins significantly when the copper positions closely to the N_2S plane. In **2**, the apical nitrogen ligand is apparently more tightly bound to the copper than the methionine sulfur in Az or Pc. Nevertheless, both exhibit an axial EPR spectrum, which is associated with a $d_{x^2-y^2}$ ground state of the unpaired d-electron.[13] Conversely, PAz and CBP give a rhombic EPR spectrum, although the copper ions are surrounded by N_2SS^* ligand donors as in Az and Pc.

In order to prove the hypothesis, more extensive structural characterization of blue copper model complexes is under continued investigation.

Acknowledgment. We thank Prof. H. C. Freeman (University of Sydney) for his courtesy to inform us of the structural parameters of Pcs and CBP used in Table I. This research was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas from the Japanese Ministry of Education, Science, and Culture (04225107).

Supplementary Material Available: Summary of X-ray analysis and tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles for $2\cdot0.5(C_8H_{18})$ (6 pages); table of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Synthesis of Novel Solid-State Compounds in Supercritical Solvents: Preparation and Structure of $K_2Ag_{12}Se_7$ in Supercritical Ethylenediamine

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Received July 16, 1992

One important aspect of the recent surge of interest in solid-state chemistry[1] has been the preparation of kinetically stabilized solids. These are prepared at relatively low temperatures and thus are not the thermodynamically stable products appearing on high-temperature phase diagrams. The synthetic challenge is to develop techniques whereby there is intimate contact between the (mostly solid) starting materials and sufficient thermal energy for them to react. A desirable side benefit would be the ability to grow single crystals of the product. A common technique is the use of fluxes or molten salts to dissolve reactants at a relatively low temperature. These are often low-melting metals, oxides, halides,[2] or sulfides[3] and are usually chemically inert under the reaction conditions. A recent novel modification is the use of low-melting alkali metal polychalcogenides as both reactant and molten salt

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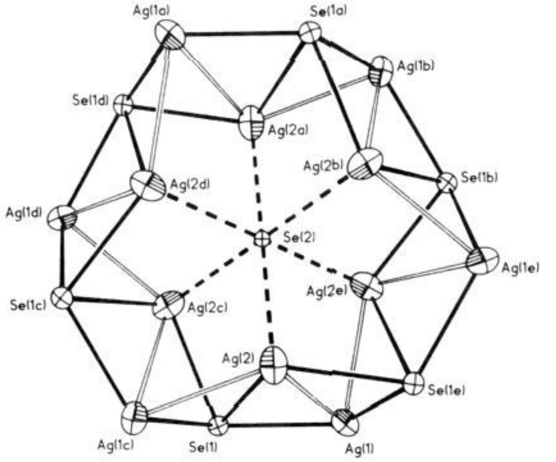

Figure 1. ORTEP view (50% probability) of the ring repeat unit in $K_2Ag_{12}Se_7$. Symmetry operators: (a) $-x, -y, 1 - z$; (b) $-y, x - y, z$; (c) $y, -x + y, 1 - z$; (d) $-x + y, -x, z$; (e) $x - y, x, 1 - z$. The rings stack in an infinite chain, forming tubes. Selected bond distances in angstroms: Ag(1)–Ag(2), 3.071 (2); Ag(1)–Se(1), 2.733 (4); Ag(1)–Se(1e), 2.747 (2); Ag(2)–Se(2), 2.701 (2).

medium.[4] These react with metals to form an enormous variety of interesting compounds.[5]

A somewhat less explored route is the use of superheated solvents as reaction media. It is known that water often shows enhanced solubilizing properties when heated above its boiling point under pressure. This hydrothermal technique has resulted in the synthesis of some spectacular new solid-state materials.[6] If the temperature, pressure, and density are sufficient, the solvents reach the supercritical phase, and the resultant dramatic change in solvation power allows for the growth of enormous crystals of quartz, emerald, and other normally intractable species.[6a,7] This technique has been extended to solvents other than water as well.[8,9] Our interest in the chemistry of Zintl ions and their well-known solubility and stability in amine solvents[10] has led us to explore the use of supercritical amines as a reaction medium for the conversion of Zintl ions to novel kinetically stabilized solids. We have recently used techniques developed by Rabenau[6a] to show that supercritical ethylenediamine (en) is an excellent solvent for the synthesis of new Zintl phases.[11] In this communication we extend this methodology to incorporate transition metals and report the synthesis and structural characterization of the unusual new ternary solid-state compound $K_2Ag_{12}Se_7$ prepared from potassium polyselenide and silver powder in supercritical ethylenediamine.

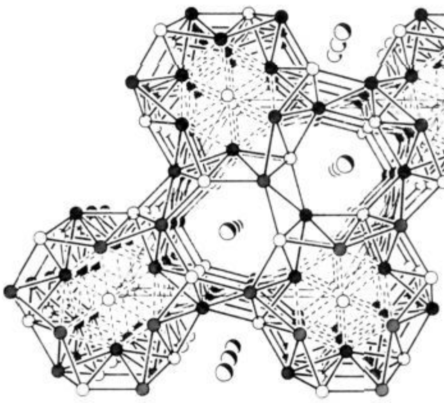

Figure 2. Extended view of $K_2Ag_{12}Se_7$ down the c-axis emphasizing its columnar structure. The bridging Ag–Se distance between columns is 2.774 (3) Å, with K–Se(1) 3.350 (1) Å.

The reaction of K_2Se_4:Se:Ag in a ratio of 1:2:1 in ethylenediamine at 300 °C[12] results in the formation of dark maroon-red rods with the formula $K_2Ag_{12}Se_7$. The crystals are moderately air and water stable and do not appear to be soluble in any common solvents. The structure[13] contains tubes formed by infinite stacks of folded 18-membered rings (Figure 1). The 18-membered rings actually interpenetrate to form a continuous column. The Ag–Se distances (2.733(4)–2.938 Å) are comparable to other known phases,[14] but somewhat longer than in silver selenides of a more molecular nature.[15] The tubes have a complex structure consisting of an outside layer of nets of Ag-Se 6-membered rings and an inner column made up of 3-membered silver rings stacked in a trigonal antiprismatic fashion (see Supplementary Figure SF1). Passing down the center of each column is a row of selenium atoms disordered over two $\bar{3}$ sites ($^1/_3$ occupancy each) with an Ag–Se distance of 2.701 (2) Å and two $\bar{6}$ sites ($^1/_6$ occupancy each) with an Ag–Se distance of 2.467 (3) Å. The tubes stack like logs, and each one is fused to six other tubes by slightly longer Ag–Se bridges (2.774 (3) Å) (Figure 2). This in turn creates new channels containing the isolated K^+ ions, which interact with six selenides in a trigonal antiprismatic environment (K–Se1 3.350 (1) Å). All of the silver atoms are formally Ag(I), and the Ag–Ag distances are reasonably short at 3.071 (2) Å. However, all of the Ag–Ag vectors are bridged by selenides, so that there is no convincing evidence for real Ag–Ag interactions. It is known that d^{10}–d^{10} interactions are often not straightforward,[16] and these distances may be indicative of some Ag–Ag interactions.

To our knowledge this is an entirely new solid-state structural type. Several alkali metal silver chalcogenide phases have been prepared previously, but none have structures related to that of the title compound. The compound KAgSe has the PbFCl structure,[14a] and the structure of $K_2Ag_4Se_3$ has not been determined but probably has a much more open framework with linear fused 8-membered rings.[14b] Thus we have prepared a new compound having an unusual extended framework construction, which apparently cannot be prepared at higher temperatures. This clearly demonstrates that solid-state synthesis in supercritical ethylenediamine can be used to generate a novel phase at intermediate temperatures. A number of other new ternary metal chalcogenides have subsequently been prepared using this method.[17]

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(12) The new solid was prepared by a variation of the methods of Rabenau.[6a] Thus 73 mg of (0.19 mmol) K_2Se_4, 29 mg (0.37 mmol) of Se, and 20 mg (0.19 mmol) of Ag powder were combined in 0.7 mL of en in a $^1/_4$-in. quartz tube (1.4 mL volume) sealed under vacuum. Since this amount of en exceeds the critical density ($\rho_c = 0.29$ g/mL), heating the tube to a value near its critical temperature (320 °C) will generate a supercritical fluid within the ampule. The tube was placed in a high-pressure autoclave which was counterpressured to 2400 psi with argon, placed in a tube furnace, and heated to 300 °C for 6 days. The products were isolated and washed with several aliquots of dry en and THF under argon and isolated as well-formed dark red-black rods which are air and water stable over several hours. The yields vary from reaction to reaction but can be as high as 80% based on silver.

(13) Crystal data for $K_2Ag_{12}Se_7$ at 294 K: $a = 10.940$ (1) Å, $c = 4.3983$ (5) Å, $V = 455.9$ (1) Å^3, $Z = 1$, $D_{calcd} = 7.013$ g cm^{-3}, space group $P6_3/m$ (No. 176). Of the 2231 reflections collected (Mo Kα, $3.5 < 2\theta < 55°$), 401 were unique ($R_{int} = 0.065$), and the 344 having $F > 6\sigma(F)$ were used in the refinement. All atoms were refined anisotropically except for the minor component of the disordered selenium atom. Final residuals are $R(F) = 0.0575$ and $R_w(F) = 0.0760$.

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J. Am. Chem. Soc. 1992, 114, 9235–9236

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Supplementary Material Available: Supplementary Figure SF1 and caption, crystallographic summary, and tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters (5 pages); table of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

Magnetic Field Effect on Reactions of Radical Pairs Possessing Large Spin–Orbit Coupling Constants

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Received June 25, 1992
Revised Manuscript Received August 21, 1992

In several previous reports, we have described how free radical chain reactions can be initiated by UV laser photolysis in thin solid films at cryogenic temperatures.[1-11] In this communication, we report that application of an external magnetic field during photolysis has a dramatic effect on the measured quantum yield for the solid-state reaction of chlorine with methylcyclopropane.

A typical experiment of this type begins with deposition of a mixture of gaseous chlorine and a simple hydrocarbon from the vapor onto a CsI window at 77 K in a high-vacuum Dewar vessel. The thin solid film is then irradiated with a pulsed nitrogen laser (337 nm) to dissociate a small fraction of the chlorine molecules to atoms. This begins a sequence of free radical chain propagation reactions forming HCl and a chlorinated hydrocarbon; e.g., for photochlorination of methylcyclopropane,[12]

$$Cl_2 + h\nu \leftrightarrow 2Cl^\bullet \tag{1}$$

$$Cl^\bullet + cyclo\text{-}C_3H_5CH_3 \rightarrow HCl + cyclo\text{-}C_3H_5CH_2^\bullet \tag{2}$$

$$cyclo\text{-}C_3H_5CH_2^\bullet + Cl_2 \rightarrow cyclo\text{-}C_3H_5CH_2Cl + Cl^\bullet \tag{3}$$

The concentrations of reactants and products are monitored by FTIR spectroscopy as a function of incident cumulative laser fluence. In this way, we are able to determine the photochemical quantum yield or number of product molecules formed per UV laser photon absorbed by the sample. The details of this procedure are described elsewhere.[12]

As illustrated in Figure 1, application of a magnetic field causes the quantum yield to drop sharply from 180 ± 20 (the zero-field value) to a minimum of 70 ± 10 at about 300 G. Thereafter, the yields increase with applied field, reaching a plateau of 120 ± 10 above 1000 G. No experiments were conducted above 3000 G.

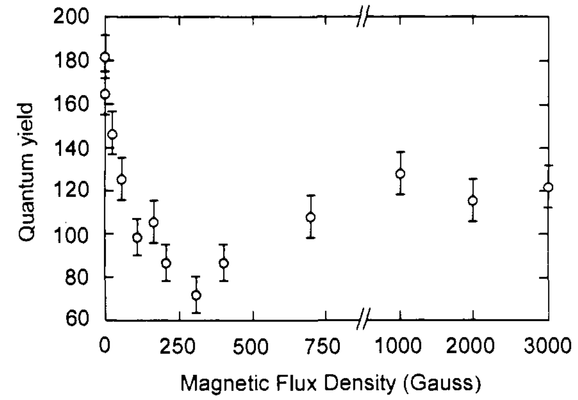

Figure 1. Photochemical quantum yield for solid-state photochlorination of methylcyclopropane versus magnetic flux density.

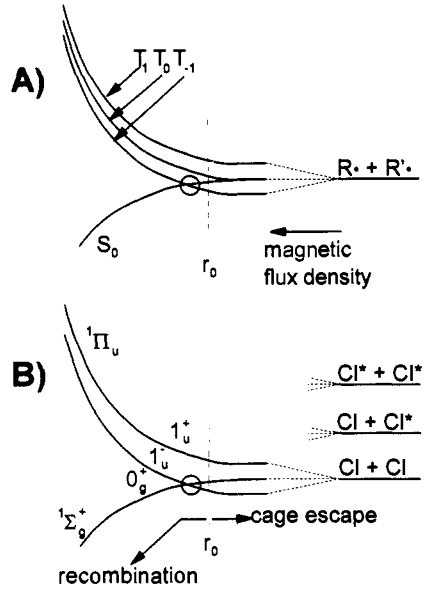

Figure 2. Schematic diagram of potential energy surfaces responsible for magnetic field effects in (A) molecular radicals with small spin–orbit coupling constants (or heavy-atom radicals with ill-defined orbital angular momenta) and (B) molecular chlorine surfaces relevant to this study. The magnetic components of the 1_u spin–orbit state are labeled + or − according to the value of M_J (+1 or −1, respectively), whereas the + on the 0_u^+ term symbol denotes positive reflection symmetry. A complete correlation diagram for the chlorine radical pair states is presented in ref 31.

It is now well established that magnetic fields can affect chemical reactions in solids[13] and in solution[14-19] by altering the rate of radical recombination, the reverse of reaction 1, relative to cage escape and reaction. An external magnetic field can shift the potential energy surfaces of the radical pair, causing crossings between repulsive and attractive surfaces in the asymptotic region. A typical scheme for this is pictured in Figure 2A, where the crossing of interest is circled. The position of the crossing can be less than, greater than, or equal to the radical pair contact distance (indicated schematically in Figure 2 by r_0), depending on the applied magnetic flux density. At the crossing, the two states can be coupled by the nuclear hyperfine interaction, which provides a mechanism for transferring the system from a repulsive

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