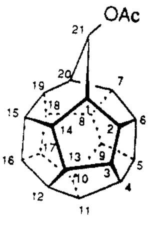
Table I. Deuterium Labeling Results Based on ^{2}H NMR Analysis of **8**



$\underset{\sim}{d}_1$

	chemical shift, δ	rel intensity, %	assignment[a]
		First Acetolysis	
	5.29	16	C21
	3.60–3.20	9	others
	3.03	9	C1, C20
	2.84	31	C14, C15, C19
d$_1$	2.59	35	C2, C6, C7
		Second Acetolysis	
	5.29	11	C21
	3.60–3.20	17	others
	3.03	13	C1, C20
	2.84	30	C14, C15, C19
	2.59	29	C2, C6, C7

[a] The capability of the acetoxy group for influencing the chemical shift of nearby protons by its magnetic anisotropy effect plays a key role in these assignments. For example, deuterons located at C2, C6, or C7, which find themselves syn to OAc are positioned approximately 0.25 ppm upfield from the 14, 15, 19 triad.

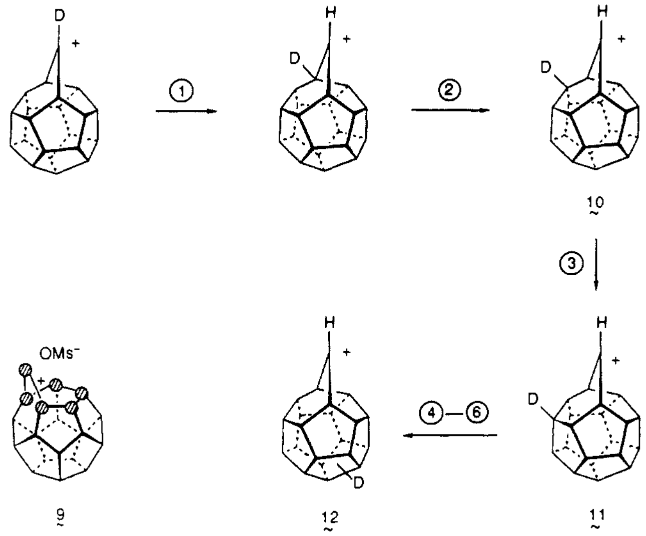
acetic acid for 3 h provided **6c** in 83% isolated yield. Thus, ready ionizability to the 21-homododecahedryl cation with retention of the intact carbon framework was demonstrated. Rate constants for the acetolysis of **6b** and 2-Ad-OMs were determined conductometrically[14] at 110.0 °C. Good first-order kinetics to 2 half-lives was observed in both instances. The respective k_1 values are 2.18×10^{-4} and 2.81×10^{-4} s^{-1}, in line with the Foote–Schleyer correlation based on internal dihedral angle considerations.[12,13]

In order to assess the level of C–H peregrination in **3**, monodeuteriated mesylate **7b** was prepared and acetolyzed as before. Analysis of recovered acetate **8** by ^{1}H and ^{2}H NMR showed that a reasonable level of deuterium migration had indeed occurred under these short-lived conditions (Table I). Since complete degeneracy had clearly not been achieved, the d_1-scrambled acetate was saponified, reconverted to mesylate, and acetolyzed again. More extensive interchange of framework methine units resulted (Table I).

Two mechanistic possibilities for deuterium scrambling require consideration. In the first, localized carbonium mesylate ion pairs are produced, for which backside 1,2-migratory stereospecificity would be enforced. A process having this restriction would, in effect, simply allow but one six-membered ring (viz., C1, C2, C6, C7, C20, and C21) to "rotate" above a [5]peristylane base while precluding migration of deuterium into the larger lower sector of the cation. Exchange would thereby be relegated exclusively to those sites explicitly depicted as shaded circles in **9**. The actual results do not conform to this option.

Rather, the findings are in agreement with predominant adoption of the nonstereospecific process which is limited, however, by covalent capture of acetic acid after relatively few rearrangement steps have transpired. Relevantly, more than three Wagner–Meerwein shifts are necessary before the deuterium label finds it possible to exit the six-membered ring (Scheme II). On the other hand, formation of the *freely solvated* carbocation allows for passage of **10** and **11** to stereoisomeric pairs of acetates (as indeed observed) and for the ultimate production of **8** (from **12**).

Scheme II



Consequently, the 21-homododecahedryl cation does exhibit the degeneracy anticipated for it.

Acknowledgment. Support of this work by the National Institutes of Health (Grant AI-11490) is gratefully acknowledged.

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Optical Memory in Cu^{+}-Doped β''-Alumina

Gary Hollingsworth,[†] James D. Barrie,[‡] Bruce Dunn,*[,‡] and Jeffrey I. Zink*[,†]

Departments of Chemistry and Biochemistry and Materials Science and Engineering, University of California Los Angeles, California 90024

Received May 9, 1988

The conduction plane of the fast ion conductor, Na β''-alumina, can be doped with a wide variety of metal ions[1] and even small molecules[2] to produce luminescent solids. During the course of studies of the luminescence of single crystals of Cu^{+}-doped β''-alumina, we discovered that the low-temperature luminescence can be deliberately and reversibly changed depending on whether or not the sample was cooled while being irradiated or while in the dark. This dependence on irradiation is a type of optical memory. Regions of the crystals can be *written* by cooling under irradiation, *read* by detecting the new luminescence in the irradiated region, and *erased* by heating. In this communication we describe the conditions required for this memory and the mechanism of the phenomenon.

Single crystals of β''-alumina[3] (5 × 5 × 0.2 mm) were prepared by the flux evaporation technique.[4] The Cu^{+}-doped samples were prepared by standard ion exchange techniques. The crystals were immersed in molten salts containing 75 mol % CuCl and 25 mol % NaCl at 400–600 °C. Typical exchange times were 2 h. A flowing nitrogen atmosphere was used to prevent oxidation of the melt. The resultant crystals were colorless, and no divalent copper could be detected by ESR. X-ray diffraction measurements confirmed retention of the β''-alumina phase. The copper ion

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[†] Department of Chemistry and Biochemistry.

[‡] Department of Materials Science and Engineering.

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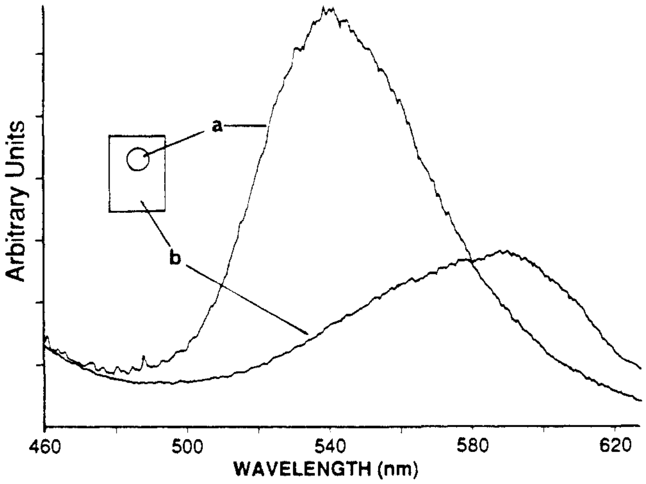

Figure 1. Emission from Cu$^+$-doped β''-alumina at 10 K: (a) dimer emission from the "written" spot and (b) emission from the region cooled in the dark.

concentrations were determined by chemical analysis (ICAP, Coors Laboratories). In a typical sample, the copper concentration was approximately 5×10^{18} ions/cm^3 (copper:sodium $\cong$ 1:1000). Luminescence spectra were obtained, and optical writing was achieved with the 351-nm line from an argon ion laser. The output power was approximately 30 mW for all of the experiments.

The doped crystals show a green luminescence ($\lambda_{max} \sim 540$ nm) at room temperature.[1] If the crystal is cooled to 10 K in the dark, the green emission is reduced in intensity. In addition, a red emission peak ($\lambda_{max} \sim 590$ nm) and two blue emission peaks ($\lambda_{max} \sim 410,440$ nm) are observed. If a spot is irradiated as the crystal is cooled, the intensity of the green emission from the spot increases. The spectrum from the spot is similar to the room temperature spectrum ($\lambda_{max} \sim 540$ nm). This spectral and spatial selectivity at 540 nm (Figure 1) constitutes the basis for the read/write characteristics of Cu$^+$-doped β''-alumina.

Optical writing was achieved by focussing the laser on small regions of the crystals. Away from the spot at which the laser had been focussed, the observed spectrum was similar to that obtained from samples cooled in the dark. Thus, the sample "remembers" where the laser was focussed. If the excitation is defocussed to cover the entire crystal, there is a spot of bright green emission on a less intense field. The process of irradiating a specific region during cooling and then detecting the irradiated region constitutes a write/read operation. Other experiments have indicated that it is not necessary to irradiated while the sample is cooling. It is sufficient to focus the laser on a sample held at temperatures less than 77 K to produce the changes in the spectrum. However, the best contrast between the written spot and the background is achieved if the sample is irradiated during cooling.

The changes are reversible. If the sample is warmed to room temperature, the green emission is again observed uniformly throughout the crystal. Thus, the memory can be "erased" and "rewritten".

The blue and green emissions are assigned to individual Cu$^+$ ions and to dimers, respectively. The blue emissions seen at low temperature are similar to the emissions of Cu$^+$ in alkali halide hosts.[5] Therefore, we assign these emissions to the $d^9s^1 \rightarrow d^{10}$ transition of the copper ion in the fields of oxide ions in the conduction plane. However, the green emission and its dependence on irradiation cannot be explained solely by emission from isolated copper ions. We assign this emission to copper pairs in the conduction plane. A similar emission was observed from Cu$^+$ in SrCl$_2$ which was attributed to Cu$^+$ pairs.[6]

The stability of d^{10}–d^{10} dimers has been the subject of several investigations.[7] Excitation of the dimer removes an electron from an antibonding orbital and populates a bonding orbital. This gives the dimers increased stability under UV irradiation. The formation of copper and silver dimers under UV irradiation in inert gas matrices has been reported by Ozin and co-workers.[8] Only wavelengths absorbed by the metal atoms were effective in inducing the formation of dimers. We find the same result here. Wavelengths longer than 351 nm do not produce the changes in the spectrum.

The mechanism of copper pair formation is associated with the ion conducting nature of the host lattice. At room temperature, the copper and sodium ions are mobile in the conduction plane. The measured conductivity at room temperature of sodium β''-alumina implies a hopping rate of $\sim 10^9$ s^{-1}. At this rate, the probability of a Cu$^+$ ion encountering another is high even at low doping concentrations. Once a dimer is formed, it may remain for a time before being forced apart (for example, by the action of the mobile Na$^+$ ions). The monomers do not emit at room temperature, and a uniform green emission is observed. As the crystal is cooled without excitation, the ions settle into the most stable sites. Emission is seen from all of the copper-containing species but primarily from the more prevalent Cu$^+$ monomers. If the sample is irradiated while it is cooled, the dimers that form remain together and are trapped as the temperature is lowered. This results in a higher concentration of dimers within the irradiated area and a visible difference in the emissions from the different parts of the crystals.

The novel ion transport properties of β'' alumina provide the opportunity to create materials in which the luminescent species are mobile. The photoaggregation of the Cu$^+$ dimers and the spectroscopic contrast between the monomers and dimers is the basis for the optical write/read characteristics of the material.

Acknowledgment. This work was supported in part by the Office of Naval Research and the National Science Foundation.

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Sequence-Specific Scission of RNA by 1,10-Phenanthroline–Copper Linked to Deoxyoligonucleotides

Chi-hong B. Chen and David S. Sigman*

Department of Biological Chemistry
School of Medicine and Molecular Biology
Institute, University of California
Los Angeles, California 90024

Received March 2, 1988

Site-specific scission of DNA has been achieved by linking carrier ligands such as polynucleotides and protein to the oxidative nuclease activity of 1,10-phenanthroline–copper.[1,2] On the basis of product analysis, the following reaction pathway (see Scheme I) has been proposed for the DNase activity of the oxidative species formed by the DNA-bound 2:1 1,10-phenanthroline–cuprous complex and its coreactant hydrogen peroxide.[3-6]

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