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Nitrosodisulfonates and Hydroxylamine-*N,N*-disulfonates. III. Magnetic Properties of the Triclinic Modification of Potassium Nitrosodisulfonate

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A thermally populated triplet excited state of the triclinic form of potassium nitrosodisulfonate, $[(\text{KSO}_3)_2\text{NO}]_2$, has been detected by EPR and static susceptibility methods. The EPR spectrum of the "molecules" in the triplet state is described by the spin Hamiltonian $\mathcal{H} = \beta_0 \vec{S} \cdot \vec{g} \cdot \vec{B} + D[S_z^2 - (\vec{S} \cdot \vec{S})/3] + E(S_x^2 - S_y^2)$, with $|D|/hc = 0.0686 \pm 0.0005 \text{ cm}^{-1}$ and $|E|/hc = 0.0037 \pm 0.0002 \text{ cm}^{-1}$ at 234 K; \vec{g} was taken to be isotropic and equal to 2.0023. The singlet-triplet energy gap is shown to have a nonlinear dependence on temperature. It is suggested that the triplet excitations are free to propagate as triplet excitons.

I. Introduction

In a recent publication¹ it was shown that the monoclinic modification of potassium nitrosodisulfonate, Fremy's salt, has a thermally accessible triplet ($S = 1$) excited state. The temperature dependence of the magnetic susceptibility was measured by both static and dynamic methods; values for the electronic quadrupole splitting tensor and the singlet-triplet energy gap were reported. In this paper, electron paramagnetic resonance (EPR) and static magnetic susceptibility data are given for the triclinic modification of potassium nitrosodisulfonate, $[(\text{KSO}_3)_2\text{NO}]_2$, hereinafter called I.

Moser and Howie² were the first to point out the dimorphism of potassium nitrosodisulfonate. The room-temperature crystal structure of I was determined by Howie, Glasser, and Moser³ to be triclinic with space group $P\bar{1}$, with lattice parameters $a = 745 \pm 2 \text{ pm}$ ($\text{pm} \equiv \text{picometers}$), $b = 714 \pm 2 \text{ pm}$, $c = 716 \pm 2 \text{ pm}$, $\alpha = 105.0 \pm 0.5^\circ$, $\beta = 82.0 \pm 0.5^\circ$, and $\gamma = 113.0 \pm 0.5^\circ$, and with one "molecule" of I per unit cell. It was found that the arrangement of the nuclei of the nitroso group atoms of the nearest-neighbor nitrosodisulfonate ions is planar and close to rectangular, as shown in Figure 1.

Moser and Howie² reported a room-temperature static magnetic susceptibility for I, corrected for diamagnetism, of $(444 \pm 20) \times 10^{-6} \text{ cgsu/mol}$ of $[(\text{KSO}_3)_2\text{NO}]_2$, corresponding to 1.57 BM (spin-only calculation)/molecule of $[(\text{KSO}_3)_2\text{NO}]_2$. A broad EPR absorption line near $g = 2$ was also observed. It was suggested that these results are due to the presence of "weak covalent bonds" between the nitroso groups of nearest-neighbor monomeric nitrosodisulfonate radical anions (see Figure 1).

II. Experimental Section

I was prepared according to the method of Moser and Howie.² All EPR measurements were made with a Varian Associates V-4502 X-band EPR spectrometer, operating at ca. 9.3 GHz and equipped with a TE₁₀₄ dual rectangular cavity and with 100-kHz and 400-Hz phase-sensitive detectors. Studies of the dependence of both the signal intensity and the shape of the EPR spectrum of I on temperature were carried out in the range 85–339 K with a conventional variable-temperature apparatus using cold nitrogen gas. Temperatures were measured to an accuracy of $\pm 2 \text{ K}$ by a copper-constantan thermocouple placed directly below the sample in the nitrogen stream. Resonance field measurements were made with a Varian Associates Mark II Fieldial unit, which was checked for scan accuracy with a dilute aqueous solution of nitrosodisulfonate radical anions ($a_N = 13.0 \text{ G}$) and with a plasticine sample containing Mn^{2+} ions ($a_{\text{Mn}} = 86.3 \text{ G}$). Microwave frequencies and resonance fields were determined with a sample of I placed in half of the cavity (field modulated at 100 kHz) and simultaneously an aqueous solution of Fremy's salt ($g = 2.0054$) placed in the other half of the cavity (field modulated at 400 Hz).

Static susceptibility measurements were made using the Faraday method. The Faraday magnetic susceptibility balance used was an

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adaptation of the basic design of Hatfield et al.⁴ and utilized a Varian V-4007 electromagnet, fitted with 6-in. Faraday pole caps. The cryostat was built following the design of Figgis and Nyholm⁵ as adapted by Clark and O'Brien.⁶ The temperature control unit, which employs the Wheatstone bridge principle, gives a thermal stability of 0.05 K in the operating range 85–400 K. Force measurements were made with a Cahn RG electrobalance.

III. Results and Discussion

A. Electronic Quadrupole Splitting. We find that I is orange-brown at room temperature and orange-yellow at 77 K; this color change is reversible. At 85 K, powdered samples of I exhibit a weak complex EPR spectrum with an extent of ca. 54 G between the outermost absorptions and a g value at the center of the spectrum of 2.005. This spectrum, which at low temperatures (85–180 K) decreases in intensity with increasing temperature, is ascribed to monomeric nitrosodisulfonate radical ions, with spin $S = 1/2$, located at crystal dislocations and at impurity sites.¹ As the temperature is increased from 175 K, additional absorptions centered about $g = \text{ca. } 2$ with a spacing between the outermost lines of $1.49 \times 10^3 \text{ G}$ (as well as another absorption at $g = \text{ca. } 4$) appear and grow in intensity. As the temperature is increased, the separation between the absorption lines of the spectrum centered about $g = \text{ca. } 2$ gradually decreases until at 335 K it has collapsed to a single line, near $g = 2$, with a first-derivative peak width of 30 G.

A representative EPR spectrum of a polycrystalline sample of I is shown in Figure 2 and was recorded at 234 K with the microwave magnetic field perpendicular to the static magnetic field \vec{B}_0 . This spectrum, with the three pairs of absorptions labeled X, Y, and Z centered about $g = \text{ca. } 2$, is characteristic of a polycrystalline sample of a spin $S = 1$ species with three unequal principal values of the electronic quadrupole tensor, \vec{D} . The three pairs of absorptions are ascribed to "dimeric" nitrosodisulfonate ions, oriented with the three principal axes of \vec{D} lying, respectively, along \vec{B}_0 .⁷ No hyperfine structure due to interaction of the unpaired electrons with any N_{14} nucleus was observed. Therefore, we use the spin Hamiltonian

$$\mathcal{H} = \beta_0 \vec{S} \cdot \vec{g} \cdot \vec{B} + D[S_z^2 - (\vec{S} \cdot \vec{S})/3] + E(S_x^2 - S_y^2) \quad (1)$$

which is diagonal with respect to the electronic quadrupole interaction; we assume \vec{g} to be isotropic with $g = g_0 = 2.0023$. The magnitude of D (divided by $g_0\beta_0$) in eq 1 equals half the distance, in magnetic field units, between the absorptions labeled Z in Figure 2. We calculate $|D|/hc = 0.0686 \pm 0.0005 \text{ cm}^{-1}$ and $|E|/hc = 0.0037 \pm 0.0002 \text{ cm}^{-1}$ for the spectrum shown in Figure 2. The absorption at $g = \text{ca. } 4$ with resonance field B_{min} (see Figure 2) is also ascribed to dimeric nitrosodisulfonate ions with spin $S = 1$. B_{min} is related to the electronic quadrupole splitting parameters D and E by the expression⁷

$$B_{\text{min}} = (2g_0\beta_0)^{-1} \{ (h\nu)^2 - 4[(D^2/3) + E^2] \}^{1/2} \quad (2)$$

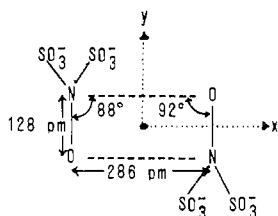


Figure 1. Arrangement of nearest neighbor nitroso groups in I, showing the principal axis system used in the calculation of D and E .

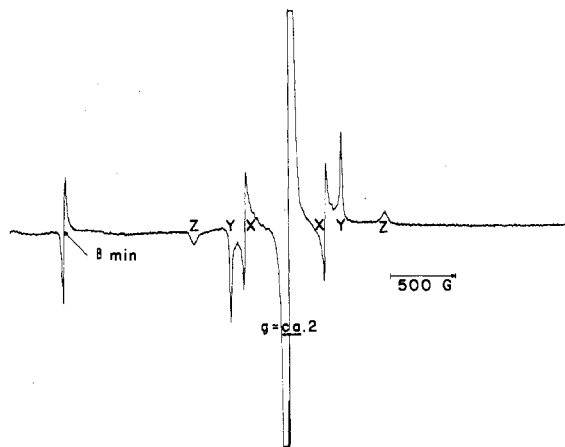


Figure 2. First-derivative X-band EPR spectrum of a powdered sample of I at 234 K.

From the position of B_{\min} at $\nu = 9.312$ GHz (i.e., 1603.0 G), the electronic quadrupole splitting parameter $|(D^2 + 3E^2)^{1/2}|/hc$ was calculated to be 0.0700 ± 0.0005 cm^{-1} at 234 K.

Assuming that the spin $S = 1$ of the "dimeric" species arises from the interaction of two unpaired electrons, each of which is localized on one $[\text{ON}(\text{SO}_3)_2]^{2-}$ ion of the nearest neighbor nitrosodisulfonate ions (see Figure 1), we have made a theoretical calculation of the electronic quadrupole splitting parameters, D and E . In this calculation the spin density, ρ , on each atom of these ions is assumed to give rise to a point magnetic dipole, of magnitude $(\mu_B \rho)^{1/2} = 3^{1/2} g \beta_0 \rho / 2$, located at the nucleus of that atom. The point dipoles on one $[\text{ON}(\text{SO}_3)_2]^{2-}$ ion are assumed to interact with only the point dipoles on the other $[\text{ON}(\text{SO}_3)_2]^{2-}$ ion of the "dimer". The elements of \bar{D} arising from these dipole interactions are of the form^{8,9}

$$D_{pq} = \frac{3g^2\beta_0^2}{8} \sum_{ij} \rho_i \rho_j (r_{ij}^{-2} \delta_{pq} - 3p_{ij} q_{ij}) r_{ij}^{-5} \quad (3)$$

where ρ_i and ρ_j are spin densities on the i th atom of one $[\text{ON}(\text{SO}_3)_2]^{2-}$ ion and the j th atom of the nearest neighbor $[\text{ON}(\text{SO}_3)_2]^{2-}$ ion, respectively, r_{ij} is the internuclear distance between atoms i and j and $p, q, = x, y, \text{ or } z$. Here $x, y,$ and z are the axes of a Cartesian coordinate system relative to which the positions of the nuclei of the atoms of the nearest-neighbor nitrosodisulfonate ions are defined. Therefore p_{ij} and q_{ij} are the components of the vector distance between the nuclei of atoms i and j . Last, $\delta = 1$ for $p = q$ and 0 for $p \neq q$.

The magnitude of the spin density in the nitrogen 2p orbital of the nitrosodisulfonate radical ion has been estimated to be 0.41^{10} and is here taken to be positive. The spin density in the s orbitals on the nitrogen atom, which is also taken to be positive, is estimated to be $0.02^{10,11}$. Therefore ρ_N is taken to be 0.43. The remainder of the spin density, which is taken to be only positive,¹² is assigned to the nitroso oxygen atom (i.e., $\rho_O = 0.57$). Thus, we are concerned only with the ar-

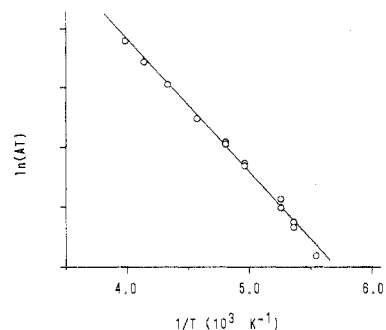


Figure 3. Temperature dependence of the absorption area, A , of the half-field transition of a powdered sample of I.

Table I. The Temperature Dependence of the Molar Magnetic Susceptibility of a Powdered Sample of I

T , K	$10^4 \chi_M^{\text{cor}}$, cgsu	T , K	$10^4 \chi_M^{\text{cor}}$, cgsu
340.9	7.63	249.0	0.50
334.9	6.96	237.9	0.35
331.6	6.50	238.3	0.32
323.6	5.43	225.7	0.24
314.9	4.38	210.0	0.13
304.0	3.21	188.6	0.08
294.6	2.37	172.4	0.00
294.7	2.42	172.3	0.04
284.7	1.71	151.6	-0.06
272.7	1.51	137.7	-0.03
261.3	0.78	118.6	-0.08
258.8	0.68	105.9	-0.07

range of the nearest neighbor nitroso group nuclei of I, as shown in Figure 1, for the theoretical calculation. For simplicity, it is assumed that this arrangement is rectangular with a nearest-neighbor $\text{N} \cdots \text{O}$ internuclear distance of 286 pm and $\text{N} \cdots \text{N}$ and $\text{O} \cdots \text{O}$ internuclear distances of 313 pm. With this arrangement of nuclei, taking g to be equal to g_0 and substituting the above values of the spin densities into eq 3, we calculate $|D|/hc = 0.069$ cm^{-1} and $|E|/hc = 0.002$ cm^{-1} , where $|D| = 3|D_{ZZ}|/2$ and $|E| = |D_{XX} - D_{YY}|/2$.¹³ The D_{PP} terms ($P = X, Y, Z$) are the principal values of the diagonalized electronic quadrupole tensor, \bar{D} . The principal value opposite in sign to the others was chosen to be D_{ZZ} . The agreement between experimental and calculated values of both $|D|$ and $|E|$ is reasonably good, particularly in view of the simplistic nature of the theoretical derivation.

B. Temperature Dependence of the Magnetic Susceptibility.

The temperature dependence of the absorption area, A , of the half-field ($\Delta m = \pm 2$) transition of I was measured in the range 175–250 K and was found to be proportional to $T^{-1} \exp(T^{-1})$ as shown in Figure 3. The form of the temperature dependence of the magnetic susceptibility, χ , for an ensemble of noninteracting molecules with spin $S = 1$, thermally activated from a singlet ground state, is¹⁴

$$\chi \propto T^{-1} [3 + \exp(E_j/kT)]^{-1} \quad (4)$$

where E_j is the average singlet–triplet energy gap per molecule and k is Boltzmann's constant. Taking $A \propto \chi^{15}$ and $[3 + \exp(E_j/kT)] \approx \exp(E_j/kT)$, for $E_j \gg kT$, the data in Figure 3 give $E_j = 0.191 \pm 0.006$ eV/molecule. However, these data would also yield a straight line if E_j were a linear function of temperature and it is more correct to say that the above value is the singlet–triplet energy gap per molecule extrapolated to 0 K, hereinafter called $E_j(0)$.

The temperature dependence of the magnetic susceptibility of I was also measured by a static (Faraday) method. These data, corrected for diamagnetism (with $\chi_d = -2.03 \times 10^{-4}$ cgsu/mol),¹⁶ are given in Figure 4 and Table I and clearly show the growth in the concentration of the paramagnetic excited state of I with increasing temperature. Attempts to

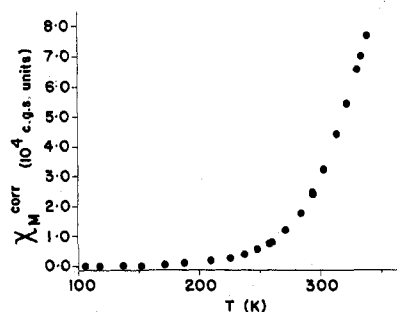


Figure 4. Temperature dependence of the molar magnetic susceptibility of a powdered sample of I.

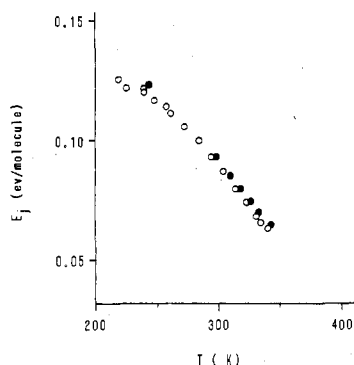


Figure 5. Temperature dependence of the singlet-triplet energy gap, E_j , of two independently prepared samples of I, where $E_j = kT \ln [(2Ng_0^2\beta_0^2/\chi_M^{corr}kT) - 3]$.

fit these data to eq 4¹⁴ demonstrated that E_j has a nonlinear dependence on temperature, as shown in Figure 5. Thus at appreciable concentrations of triplet "molecules" of I, the assumption of the noninteraction of these excited molecules, implicit in eq 4, seems to be invalid. This is in agreement with a report¹⁸ of the temperature-dependent magnetic behavior of some other materials having a thermally accessible triplet state.

The agreement between the calculated and experimental values of $|D|$ and of $|E|$ and the known crystal structure of I³ strongly suggests that the triplet "excitation" arises on nearest-neighbor nitrosodisulfonate radical ions with the nitroso groups 286 pm apart. The crystal contains one "dimer" per unit cell and the nearest-neighbor "dimer" is at a distance of 714 pm; thus the salt might behave as a strongly alternating linear Heisenberg antiferromagnet.^{17,18} The spin Hamiltonian for such an antiferromagnet is (for an even number, N , of interacting species with spin $S = 1/2$)

$$\mathcal{H} = \sum_{j=1}^{N/2} [J(1 + \Delta)\vec{S}_{2j}\vec{S}_{2j+1} + J(1 - \Delta)\vec{S}_{2j}\vec{S}_{2j-1}] \quad (5)$$

where $-1 \leq \Delta \leq 1$ and Δ is the alternation parameter which relates the intrasite coupling $J(1 + \Delta)$ to the intersite coupling $J(1 - \Delta)$. Both exchange integrals, $J(1 + \Delta)$ and $J(1 - \Delta)$, are positive, corresponding to antiferromagnetic coupling, and include charge-transfer^{19,20} and phonon effects,²¹ as well as the usual electrostatic contributions. For a system exhibiting strongly alternating antiferromagnetic behavior ($0.6 \leq \Delta \leq 1$) the theoretical dependence of the reduced singlet-triplet energy gap, $E_j(T)/E_j(0)$ (where $E_j(T)$ is the singlet-triplet energy gap at temperature T as shown in Figure 5), on the reduced temperature, $kT/E_j(0)$, is shown in Figure 6.¹⁸ The corresponding experimental dependence for I is also shown and does not agree with the theoretical dependence. There are two factors that could explain this disagreement.

(i) Equation 5 does not account for thermal expansion of the crystal lattice. As the crystal expands with increasing

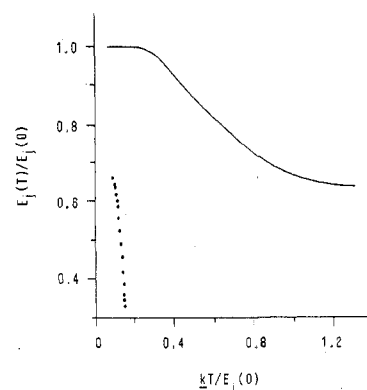


Figure 6. Temperature dependence of the singlet-triplet energy gap for strongly alternating linear Heisenberg antiferromagnets. The theoretical (solid) curve is for $0.6 \leq \Delta \leq 1.0$. The experimental points (dots) are for I.

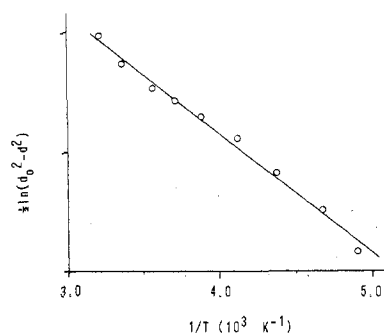


Figure 7. Temperature dependence of the splitting between the absorptions labeled Y in Figure 2.

temperature, $E_j(T)$ decreases due to increasing separation of neighboring nitrosodisulfonate anions.

(ii) Although I does show antiferromagnetic behavior, the assumption that it will behave as a linear Heisenberg antiferromagnet may be incorrect, since the detailed crystal structure shows no preferential direction for intersite coupling.

C. Effect of Temperature on the Exchange Interaction. To determine if the triplet "excitations" of I show exciton behavior, we have measured the temperature dependences of the line width of and the "fine structure" splitting between the absorptions labeled Y in Figure 2. Following the treatment by Anderson²² of spin exchange between paramagnetic species giving rise to two-line spectra, the mean time between spin-exchange events of the triplet excitations, τ , is given by the relations^{9,23}

$$1/\tau \propto (d_0^2 - d^2)^{1/2} \quad (6)$$

and

$$1/\tau \propto (\Delta B - \Delta B_0) \quad (7)$$

where d_0 and d are the fine structure splittings in the absence and in the presence of spin exchange, respectively, and ΔB_0 and ΔB are the line widths at half-height of the absorptions in the absence and in the presence of spin exchange, respectively. Equations 6 and 7 are valid when $d_0 \gg 2\pi/\gamma_e\tau$ (i.e., under conditions of "slow" exchange), where γ_e is the gyromagnetic ratio of the electron. With these relations we find that $\ln(1/\tau) \propto T^{-1}$ for I as shown in Figures 7 and 8, respectively. The slopes of the lines in these figures are $(1.00 \pm 0.03) \times 10^{-3}$ and $(5.3 \pm 0.2) \times 10^{-3} \text{ K}^{-1}$, respectively. The difference between these two values is not fully understood, although dipolar broadening makes an increasing contribution to the line width but not to the "fine structure" splitting as the concentration of triplet excitations increases.

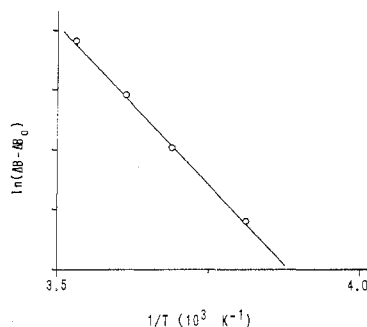


Figure 8. Temperature dependence of the width at half-height of the absorptions labeled Y in Figure 2.

From measurements of the static susceptibility, we estimate that the percentage of "dimers" in the triplet state increases from 0.1 to 0.3% over the temperature range 194–214 K. In this concentration range, spin exchange between "dimers" would be negligible if the triplet "excitations" were localized. However, a measurable decrease of the splitting between the absorptions labeled Y in Figure 2 is observed over this concentration range; this is taken as evidence that the triplet "excitations" of I are excitons.²⁰ Two further experimental observations support this idea.

(i) A small single crystal, large enough to observe EPR spectra, was obtained on one occasion; no splitting of the resonance lines due to hyperfine interaction with the ¹⁴N nuclei (even at temperatures at which the spin exchange interaction was assumed to be negligible) was observed, as is expected in the EPR spectrum of triplet exciton salts.²⁴

(ii) At triplet concentrations of greater than ca. 0.1%, a continuous broadening of the absorption lines and an enhancement of the intensity of the EPR signal ascribed to $S = 1/2$ monomeric $[\text{ON}(\text{SO}_3)_2]^{2-}$ ions was observed. A similar broadening effect has been observed in an X-irradiated single crystal of $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]^+[\text{TCNQ}]_2^-$ and was interpreted as

arising from spin exchange between triplet excitons and free radicals.²⁵

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Registry No. $[(\text{KSO}_3)_2\text{NO}]_2$, 14293-70-0.

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Ternary Hydrides of Calcium with Silver

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A new ternary hydride, CaAg_2H , can be prepared either by hydriding the alloy CaAg_2 or by a solid state reaction of calcium hydride and silver in a hydrogen atmosphere. The hydride is a black, nonvolatile, diamagnetic solid. The X-ray powder pattern can be indexed orthorhombic. No other hydrides could be isolated from the calcium-silver system except the one which was related to the alloy phase. The correlation of alkali and alkaline earth ternary hydrides with model systems such as complex halides and alloy phases is discussed.

Introduction

Previous work at the University of Connecticut has shown the existence of the following alkaline earth-noble metal hydrides: Ca_2IrH_5 ,^{2a} Sr_2IrH_5 ,^{2a} Ca_2RhH_5 ,^{2a} Ca_2RuH_6 ,^{2a} Sr_2RhH_5 ,^{2a} Sr_2RuH_6 ,^{2a} SrPd_2H ,^{2b} Sr_2PdH_4 ,^{2b} and $\text{Ca}_3\text{Pd}_2\text{H}_4$.^{2b} In general, these compounds were prepared by the solid state reaction of the alkaline earth metal hydride and the group 8 metal. One of the compounds, SrPd_2H , was also prepared by hydriding the intermetallic phase SrPd_2 . In order to develop the systematic chemistry of the alkaline earth-transition metal hydrides, we have been interested in exploring the stoichiometries and properties of the hydrides of the neighboring elements of the compounds listed above. In this paper we report the preparation and characterization of a new

ternary hydride in the calcium-silver system, $\text{CaAg}_2\text{H}_{1.0}$.

Experimental Section

Calcium was purified by distillation under vacuum in a steel apparatus. Hydrogen was Matheson extra dry or prepurified grade further purified by passage through a palladium tube in a Bishop hydrogen diffusion cell Model No. A-1-D. Calcium hydride was synthesized by direct combination of the elements at 450–500°. The binary hydride thus produced was checked by X-ray diffraction and by hydrolysis of the hydridic hydrogen. Silver metal was 99.99% purity obtained from Cerac, Inc. and was used without further purification. Argon was Matheson high purity grade.

The ternary hydride was prepared either by the reaction of calcium hydride with silver or by hydrogenation of the intermetallic alloy CaAg_2 . To prepare the alloy, a stoichiometric mixture of 1Ca–2Ag was compressed into a dense pellet with a hydraulic press. The pellet