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Electron Spin Resonance Study of X-Irradiated Single Crystals of Silver(I) Nitrate-Butanedinitrile(1/1)

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ESR spectra of single crystals of silver(I) nitrate–butanedinitrile(1/1) were measured at 77 K. Two paramagnetic centers, –CN···Ag^{2+}···NC– and NO_3^{2-}···Ag^+, appeared simultaneously on X-irradiation at 77 K. The principal values of the g value (g) and the hyperfine coupling constants (A in the units of 10^{-4} cm^{-1}) were $g_1=2.050$, $g_2=2.053$, and $g_3=2.302$, $A(Ag)_1=21.8$, $A(Ag)_2=22.0$, $A(Ag)_3=34.9$, $A(N)_1=15.3$, $A(N)_2=15.9$, and $A(N)_3=14.0$ for the first center, and $g_{//}=2.001$, $g_\perp=2.006$, $A(Ag)_{//}=20.3$, $A(Ag)_\perp=17.4$, $A(N)_{//}=59.4$, and $A(N)_\perp=32.8$ for the second center. When the crystals X-irradiated at 77 K were exposed to visible light, the two centers disappeared simultaneously and the NO_2 radicals increased. When the crystals X-irradiated at 77 K were warmed to room temperature, the first center changed to a new paramagnetic center, in which the unpaired electron coupled with a silver nucleus, two equivalent nitrogen nuclei, and a proton.

Silver(I) ion, Ag^+, can act as an electron donor or electron acceptor. Many studies have shown that Ag^0, Ag^{2+}, Ag_2^+, and Ag_2^{3+} are easily formed from Ag^+ ions in irradiated crystals and frozen solutions at low temperatures.[1–4] Mosley and Moulton have shown that, when silver nitrate crystals are X-irradiated at 77 K, the Ag^+ ions are converted to Ag^{2+} ions and NO_3^- ions to NO_3^{2-} ions, indicating that electrons delivered from Ag^+ ions are trapped on NO_3^- ions.[3]

This paper describes the results of ESR studies on X-irradiated single crystals of silver (I)nitrate–butanedinitrile(1/1), $AgNO_3\cdot NCCH_2CH_2CN$. In the crystals, Ag^{2+} and NO_3^{2-} were primarily produced by X-irradiation at 77 K. The structures and spin densities in these two paramagnetic species were estimated. Electron transfers from Ag^+ to NO_3^- by X-ray excitation and from NO_3^{2-} to Ag^{2+} by visible light excitation were established.

Experimental

Single crystals of silver(I) nitrate–butanedinitrile(1/1) were prepared. Dry silver nitrate (about 10 g) dissolved in butanedinitrile (about 24 g) at 70 °C. After the solution was cooled slowly to room temperature in the dark, single crystals with dimensions of about 4×3×1 mm^3 were obtained (mp 76 °C).[5] Calcd for $AgNO_3\cdot NCCH_2CH_2CN$: C, 19.2; H, 1.6; N, 16.8%. Found: C, 19.6; H, 1.6; N, 17.0%. Figure 1 shows the crystal form. An orthogonal set of axes a′, b′, and c′ were chosen for analysis of the ESR spectra. The crystal has a cleavage plane parallel to the a′b′ plane.

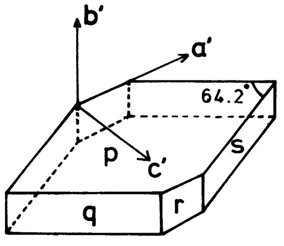

Fig. 1. The crystal form of $AgNO_3\cdot NCCH_2CH_2CN$. Interfacial angles ∠pq, ∠pr, and ∠ps are 90°.

The crystals were irradiated with X-rays at 77 K to an extent of about 0.2 Mrad. The ESR spectra of the crystals were recorded at 10° intervals in the a′b′, b′c′, and c′a′ planes at 77 K with a Varian model V-4501 X-band spectrometer. ESR measurements were also carried out on crystals that had been irradiated with X-rays at 77 K and subsequently illuminated with light from a 40 W tungsten filament lamp at 77 K, and on crystals that had been X-irradiated and successively warmed to room temperature for a minute and then cooled again to 77 K.

Figure 2 shows a typical ESR spectrum of the single crystal X-irradiated at 77 K. A group of lines at the lower magnetic field side will be attributed to the magnetic species –CN···Ag^{2+}···NC–, which we refer to as Ag^{2+} (α) center. A sextet at the high field side will be assigned to NO_3^{2-}···Ag^+, which we refer to as NO_3^{2-}–Ag^+ center, and a sharp triplet (designated as p, p′, and p″) to NO_2.

Results and Discussion

Ag^{2+}(α) Center. The absorption lines at the lower field side consist of two quintets. The intensity ratio of the lines of the quintet is 1 : 2 : 3 : 2 : 1. These

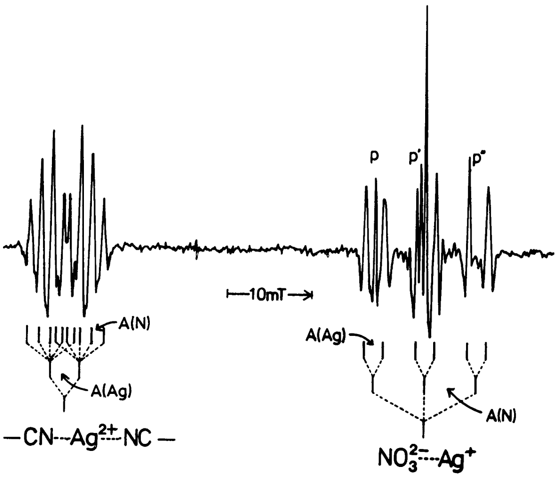

Fig. 2. Second derivative ESR spectrum of the X-irradiated single crystal of $AgNO_3\cdot NCCH_2CH_2CN$ with the magnetic field parallel to the c′ axis. The irradiation and ESR measurements were carried out at 77 K. The strongest line is due to DPPH.

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TABLE 1. PRINCIPAL VALUES OF THE TENSORS, g, A(Ag) AND A(N) FOR THE Ag^{2+} (α) CENTER

Principal values[a)]			Principal axis
g	$A/10^{-4}$ cm^{-1}		
$g_1=2.050$	$A(Ag)_1=21.8$	$A(N)_1=15.3$	$\|\|a'$
$g_2=2.053$	$A(Ag)_2=22.0$	$A(N)_2=15.9$	$\|\|b'$
$g_3=2.302$	$A(Ag)_3=34.9$	$A(N)_3=14.0$	$\|\|c'$

a) Estimated errors are 0.0005 for g and 0.5×10^{-4} cm^{-1} for A(Ag) and A(N).

lines are explained in terms of an unpaired electron interacting with a silver nucleus ($I=1/2$) as well as two equivalent nitrogen nuclei ($I=1$). Analysis of angular dependence of the spectra determined the principal elements of the tensor of the g value and the hyperfine coupling constants for the silver nucleus, A(Ag), and for the nitrogen nuclei, A(N). The results are given in Table 1. A splitting of lines due to the presence of the two abundant isotopes of silver (^{107}Ag and ^{109}Ag) could not be detected. Therefore A(Ag) in the table is the value averaged for the two isotopes. All the tensors are axially symmetric within experimental error about the c′ axis. We refer to the symmetric axis as the z axis and the axes perpendicular to it as the x and y axes.

The axial symmetry in the tensors g and A(Ag) can be accounted for by the existence of a tetragonal crystalline field at the Ag^{2+} ion,[9,10)] which has been confirmed in many stable Ag^{2+} complexes. The observed relation, $g_3(g_z)>g_2\simeq g_1\simeq 2$, suggests that the unpaired electron is primarily in the $4d_{x^2-y^2}$ orbital of the silver ion. The tetragonal field probably arises from the surrounding four ligands on the corners of a square plane perpendicular to the symmetry axis (the z axis). The most probable model for the $Ag^{2+}(\alpha)$ center is as follows. The Ag^{2+} ion is surrounded by two nitrogen atoms of CN groups on the x axis and by two oxygen atoms of nitrate ions on the y axis. Additional two oxygen atoms must be situated at a greater distance on the z axis. This model is consistent with the crystal structure of $2AgNO_3\cdot NCCH_2CH_2CN$, where the Ag^+ ion is linked to a CN group and surrounded by four oxygen atoms.[6)]

Since superhyperfine structure due to two nitrogen atoms was observed, the unpaired electron must be delocalized on these atoms. The ground state molecular orbital for the unpaired electron is expressed by

$$\psi = \alpha\psi_0 - \sqrt{1-\alpha^2}\,\psi', \tag{1}$$

where ψ_0 is the $4d_{x^2-y^2}$ atomic orbital of Ag^{2+} and ψ' is the appropriate normalized wavefunction of the ligands. Here the overlap integral between ψ_0 and ψ' has been neglected. The silver hyperfine coupling constants are given by[7)]

$$A_{/\!/} = K + \left(\Delta g_{/\!/} + \frac{3}{7}\Delta g_{\perp} - \frac{4}{7}\alpha^2\right)P, \tag{2}$$

$$A_{\perp} = K + \left(\frac{11}{14}\Delta g_{\perp} + \frac{2}{7}\alpha^2\right)P, \tag{3}$$

where $\Delta g_{/\!/}$ and $\Delta g_{\perp}$ are the g shift from 2.0023 due to admixture of excited states, P is the hyperfine interaction parameter

$$P = g_e\mu_B g_{Ag}\mu_n < \psi_0|r^{-3}|\psi_0 >, \tag{4}$$

and K is a constant term mainly due to the core polarization which depends strongly on the spin density in ψ_0 and ψ'.[8)] Using the value of -68.76×10^{-4} cm^{-1} for P,[9)] and the observed values of $|A_{/\!/}|=A(Ag)_3$, $|A_{\perp}|=|A(Ag)_1+A(Ag)_2|/2$, $g_{/\!/}=g_3$, and $g_{\perp}=(g_1+g_2)/2$, one obtains 0.549 for α^2 and 35.4×10^{-4} cm^{-1} for K.

The wavefunction, belonging to two nitrogen atoms, in the molecular orbital ψ can be written as

$$\sqrt{1-\alpha^2}\,\psi' = \cdots C_s[\phi_{2s}(N_1)+\phi_{2s}(N_2)] + C_p[-\phi_{2p}(N_1)+\phi_{2p}(N_2)]+\cdots, \tag{5}$$

where $\phi_{2s}(N_1)$, $\phi_{2p}(N_1)$, $\phi_{2s}(N_2)$, and $\phi_{2p}(N_2)$ are the 2s and 2p atomic orbitals of the nitrogen atoms 1 and 2. The nitrogen hyperfine coupling constants are given by

$$A_{xx}(N_1) = A_{xx}(N_2) = C_s^2A_{2s}(N) + 2C_p^2B_{2p}(N), \tag{6}$$

$$A_{yy}(N_1) = A_{zz}(N_1) = A_{yy}(N_2) = A_{zz}(N_2) = C_s^2A_{2s}(N) - C_p^2B_{2p}(N), \tag{7}$$

where $A_{2s}(N)=519\times10^{-4}$ cm^{-1} and $B_{2p}(N)=15.5\times10^{-4}$ cm^{-1}.[9)] The coupling tensor is axial symmetric about the x axis and $A_{/\!/}$ is larger than $A_{\perp}$. On the contrary the observed nitrogen coupling tensor is axial symmetric about the z(c′) axis and $A_{/\!/}$ is smaller than $A_{\perp}$ (Table 1).

This discrepancy leads us to assume that there are at least two Ag^{2+} centers having the z axes parallel to each other but the x axes perpendicular to each other. Then the hyperfine coupling constants for N_1 and N_2 will be different. If the line widths are large, the observed nitrogen coupling constant must be the average value for N_1 and N_2, *i.e.*,

$$A_{\perp}(N) = \sqrt{[A_{xx}(N)^2+A_{yy}(N)^2]/2}, \tag{8}$$

and

$$A_{/\!/}(N) = A_{zz}(N). \tag{9}$$

Using the values of $A_{/\!/}(N)=14.0\times10^{-4}$ cm^{-1} and $A_{\perp}(N)=15.6\times10^{-4}$ cm^{-1}, one obtains $A_{xx}(N)=17.1\times10^{-4}$ cm^{-1}, $C_s^2=0.029$ and $C_p^2=0.067$. Therefore the spin density is 0.192 on the N_1 and N_2 atoms and 0.549 on the Ag atom, and the rest of 0.259 probably on the two oxygen atoms on the y axis.

If one neglects the in-plane and out-of-plane π-bonding between the Ag atom and ligand atoms, the principal values of the g tensors are given by

$$g_{/\!/} = g_z = 2.0023 - 8\lambda\alpha^2/E_1, \tag{10}$$

$$g_{\perp} = g_x = g_y = 2.0023 - 2\lambda\alpha^2/E_2, \tag{11}$$

where λ is the spin-orbit coupling constant for an Ag^{2+} ion (-1844 cm^{-1}), and E_1 and E_2 are the energy separation of the d_{xy} and $d_{xz}(d_{yz})$ levels from the $d_{x^2-y^2}$ level, respectively.[7,9,11)] Substituting the values of 2.302 and 2.0515 for $g_{/\!/}$ and $g_{\perp}$, respectively, in Eqs. 10 and 11, one finds that E_1 and E_2 are 2.70×10^{-4} cm^{-1} (370 nm) and 4.11×10^{-4} cm^{-1} (243 nm), respectively. Unfortunately, the optical absorption data for the $Ag^{2+}(\alpha)$ center are not available. The spin densities on the silver atoms and nitrogen atoms of typical Ag^{2+} complexes are summarized in Table 2.[8,11–13)] The spin density on the nitrogen atoms indicates that the σ-bonding between the Ag^{2+} ion and the nitrogen atom of cyano groups is weaker than that between the Ag^{2+} ion and aromatic nitrogen atoms.

NO_3^{2-}–Ag^+ Center. The ESR spectra of the

TABLE 2. SPIN DENSITY ON THE SILVER AND NITROGEN ATOMS IN TYPICAL Ag^{2+} COMPLEXES

Complex	Spin density Ag	 N	Ref.
$AgNO_3$, sc., ir.	0.604		8
$AgNO_3$ in HNO_3, fr., ir.	0.711		8
$AgNO_3$ in HNO_3–pyridine, fr., ir.	0.545		8
[Ag bpy_2]S_2O_8 in HNO_3, fr.	0.542	0.197	8, 10
[(Ag, Cd)py_4]S_2O_8, pd. and sc.	0.397	0.208	8, 11, 12
$AgNO_3 \cdot NCCH_2CH_2CN$, sc., ir.	0.549	0.096	This paper

ir.: X- or γ-irradiation, sc.: single crystal, fr.: frozen solution, pd.: powder

TABLE 3. PRINCIPAL ELEMENTS OF THE g, A(Ag), A(N), AND A(H) TENSORS FOR THE NO_3^{2-}–Ag^+ CENTER (a) AND THE Ag^{2+} (β) CENTER (b)

	g	$A/10^{-4}$ cm^{-1}		
(a)	$g_{//}=2.001$	$A(Ag)_{//}=20.3$	$A(N)_{//}=59.4$	
	$g_{\perp}=2.006$	$A(Ag)_{\perp}=17.4$	$A(N)_{\perp}=32.8$	

Direction cosines of the parallel axis in the a′b′c′ system are (0.00, ±0.47, 0.88).

	g	$A/10^{-4}$ cm^{-1}		
(b)	$g_{//}=2.170$	$A(Ag)_{//}=37.5$	$A(N)_{//}=6.1$	$A(H)_{//}=2.0$
	$g_{\perp}=2.015$	$A(Ag)_{\perp}=28.0$	$A(N)_{\perp}=6.9$	$A(H)_{\perp}=2.4$

Direction cosines of the parallel axis in the a′b′c′ system are (0.00, ±0.14, 0.99).

NO_3^{2-}–Ag^+ center have two sets of sextets when the magnetic field is in general directions. They merge into a single sextet when the magnetic field is in the a′b′ or a′c′ plane. Similar spectra have been observed in irradiated silver nitrate crystals and assigned to NO_3^{2-}–Ag^+, referred to as an $AgNO_3^-$ center.[3] The sextet, which consists of six lines with equal intensity (Fig. 2), arises from a hyperfine interaction with a nitrogen nucleus and a silver nucleus. The angular dependence of the g value and the coupling constants for the nitrogen and silver nuclei, A(N) and A(Ag), were analyzed to give their principal elements listed in Table 3. The principal values are similar to those of $AgNO_3^-$ trapped in silver nitrate crystals.[3] Furthermore, the principal values of A(N) are in good agreement with those of the nitrogen nucleus in NO_3^{2-} trapped in KNO_3 and other compounds.[14]

We discuss below the electronic structure of the NO_3^{2-}–Ag^+ center. The fact that A(Ag) is nearly isotropic indicates that the Ag atomic orbital in which the unpaired electron partly spends its time contains s character. If the unpaired electron localizes only on the 5s orbital, the average hyperfine interaction for $^{107}Ag^0$ and $^{109}Ag^0$ is 424×10^{-4} cm^{-1}.[9] The spin density on the 5s orbital of Ag in the NO_3^{2-}–Ag^+ center is 18.8/424, or 0.04.

The ion radical NO_3^{2-} has a pyramidal form with the nitrogen atom on the vertex. The unpaired electron occupies an sp^n hybrid orbital,

$$\psi = C_s\phi_{2s}(N) + C_p\phi_{2p}(N), \qquad (12)$$

which extends along the C_3 symmetry axis (x axis). Here $\phi_{2s}(N)$ and $\phi_{2p}(N)$ are the 2s and 2p$_x$ atomic orbitals of the nitrogen atom. Then the principal values of the A(N) are given by Eqs. 6 and 7. From the observed values in Table 2, the spin densities on the 2s and 2p orbitals are calculated to be 0.077 and 0.52, respectively. The remaining spin density of 0.37 would be distributed mainly on the three oxygen atoms. The bond angle ∠ONO for the pyramidal NO_3^{2-} ion is given by

$$\theta = \cos^{-1}\left(\frac{1.5}{2\xi^2+3} - \frac{1}{2}\right), \qquad (13)$$

where $\xi^2 = C_p^2/C_s^2$.[14] The observed value of 6.69 for ξ^2 predicts that θ is 114°.

Optical and Thermal Conversion of $Ag^{2+}(\alpha)$ and NO_3^{2-}–Ag^+ Centers. When the crystals of $AgNO_3 \cdot NCCH_2CH_2CN$ X-irradiated at 77 K were exposed to light from a tungsten filament lamp at the same temperature, ESR signals of the $Ag^{2+}(\alpha)$ and NO_3^{2-}–Ag^+ centers disappeared in half an hour. During the exposure the intensity of a triplet (p, p′, p″ in Fig. 2) increased. The magnetic species responsible for the triplet are reasonably identified as NO_2 because the observed g value (1.994—2.006) and hyperfine splitting of nitrogen ((41—60) × 10^{-4} cm^{-1}) are similar to those reported for NO_2 trapped in other compounds.[14]

These two paramagnetic centers, $Ag^{2+}(\alpha)$ and NO_3^{2-}–Ag^+, simultaneously appeared on X-ray irradiation and disappeared on visible light irradiation; this is explained as follows : At 77 K an electron is liberated from an Ag^+ ion through excitation by X-rays, it migrates in the lattice, and is trapped by an NO_3^- ion. This process gives rise to these two centers. The trapped electron in NO_3^{2-}–Ag^+ center is released by optical excitation and recombines with the hole on the $Ag^{2+}(\alpha)$ center. Some of the NO_3^{2-}–Ag^+ centers may be degraded into NO_2 during the irradiation.

When the crystals X-irradiated at 77 K were warmed to room temperature for a minute, the $Ag^{2+}(\alpha)$ center changes into a new Ag^{2+} center, which is designated as $Ag^{2+}(\beta)$ center. Figure 3 illustrates the ESR spectrum of the $Ag^{2+}(\beta)$ center, which is explained by an unpaired electron delocalized over an Ag^{2+} ion, two equivalent

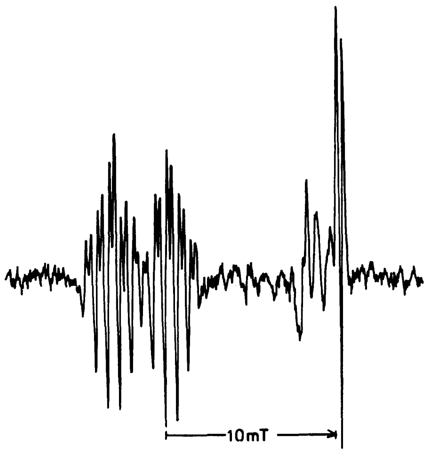

Fig. 3. Typical second derivative spectrum of the $Ag^{2+}(\beta)$ center. The magnetic field was applied in the a′c′ plane, making an angle of 45° with the a′ axis.

nitrogen atoms and a proton. The principal elements of the *g* tensor and hyperfine coupling tensors are tabulated in Table 3. The $Ag^{2+}(\beta)$ center has spin Hamiltonian parameters different from those for the $Ag^{2+}(\alpha)$ center. This fact suggests that the configuration of the ligands in the $Ag^{2+}(\alpha)$ center is altered irreversibly through thermal reorientation, giving rise to the $Ag^{2+}(\beta)$ center.

Crystal Structure and Orientation of Radicals. Two sets of ESR spectra were generally observed for the NO_3^{2-}–Ag^+ and $Ag^{2+}(\beta)$ centers. The angular dependence of these spectra are inherent in radicals trapped in a monoclinic crystal. The unique axis of the crystal must be parallel to the b′ or c′ axis. The observed interfacial angles ∠ps, ∠pq, and ∠pr are 90°, strongly suggesting that the b′ axis is the unique axis. Only one set of ESR spectra was observed for the $Ag^{2+}(\alpha)$ center. It indicates that the Ag^{2+} ion is on the symmetry axis of the unit cell. For the $Ag^{2+}(\alpha)$ center, the direction along N–Ag–N is perpendicular to the c′ axis. The C_3 symmetry axis of NO_3^{2-} in NO_3^{2-}–Ag^+ center lies on the b′c′ plane and makes an angle of 62° with the b′ axis. The infrared study of $AgNO_3\cdot NCCH_2CH_2CN$ showed that butanedinitrile molecule assumes the *trans* rotomeric conformation and forms a bridge between two silver atoms.[5)] These facts give some structural information for the parent (undamaged) complex, the structure of which is not known.

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