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ESR of Hot Ions: Ni(I) Complex Ions Produced in Ni(II) Complexes by γ-Irradiation

Chikara AMANO, Tokuko WATANABE, and Shizuo FUJIWARA

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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X- or γ-Irradiation has been shown to produce in solids metal ions with uncommon valence and geometrical configuration.[1-4] In this paper a report is given on the ESR spectra of monovalent nickel complex ions with the $3d^9$ electron configuration and a discussion on the electronic state of the Ni(I) complex ions in terms of observed g-values.

Forty-six Ni(II) complexes were synthesized by standard methods (Table 1).[5] Nickel(II) chloride hexahydrate, the starting material, was purified by an anion exchange method to remove a trace of cobaltous and cupric ions. The polycrystalline complexes ($\sim$100 mg) were γ-irradiated at room temperature with a γ-ray dosage of 1×10^7 R with dose rate of 5×10^5 R/h, and at 77 K with a γ-ray dosage of 1×10^6 R with dose rate of 5×10^4 R/h. ESR spectra were recorded at 77 K on a JEOL 3BSX spectrometer.

Of the forty-six complexes examined, nine gave strong signals upon γ-irradiation (Table 2). Other complexes gave only weak absorptions at $g\sim2$ probably due to radicals produced from ligand molecules.

γ-Irradiated $[Ni(en)(H_2O)_4]SO_4\cdot H_2O$, $[Ni(en)_2(H_2O)_2](ClO_4)_2$, $[Ni(l\text{-ala})_2(H_2O)_2]2H_2O$, and $[Ni(succinimde)_2(H_2O)_4]4H_2O$ give broad ESR absorptions (line width$\sim$100 G) of an approximately axial pattern. The other complexes in Table 2 shows several narrower absorptions. It is to be noted that in both these cases relatively large g-shifts ($\Delta g=0.2$—0.3) are observed, suggesting that the paramagnetic centers produced upon γ-irradiation are due to nickel ions. In the case of irradiated $[Ni(en)(H_2O)_4]SO_4\cdot H_2O$, $[Ni(en)_2(H_2O)_2](ClO_4)_2$ and $[Ni(l\text{-ala})_2(H_2O)_2]\text{-}2H_2O$, it is observed that $g_\parallel>g_\perp>2$, which is expected for a d^9 electron configuration with tetragonally elongated octahedral symmetry (ground state $^2B_{1g}$). According to ligand field theory a d^7 electron configuration in the ground state $^2B_{1g}$ is also consistent with this observation. However, as far as we know, complex ions

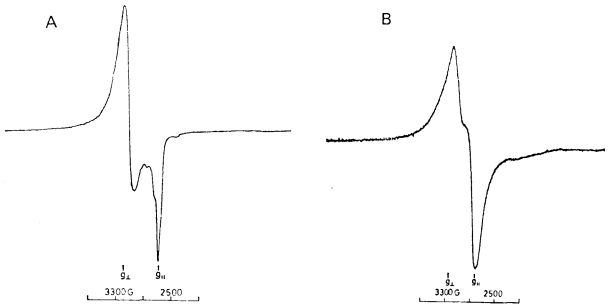

Fig. 1. A. ESR spectrum of $[Ni(en)(H_2O)_4]^+$ produced in γ-irradiated polycrystalline $[Ni(en)(H_2O)_4]SO_4\cdot H_2O$.
B. ESR spectrum of $[Ni(l\text{-ala})_2(H_2O)_2]^-$ produced in γ-irradiated polycrystalline $[Ni(l\text{-ala})_2(H_2O)_2]2H_2O$.

1) D. A. Morton-Blake, *J. Phys. Chem.*, **74**, 1508 (1970).
2) S. Fujiwara, T. Watanabe, and H. Tadano, *J. Coord. Chem.*, **1**, 196 (1971).
3) T. Krigas and M. T. Rogers, *J. Chem. Phys.*, **54**, 4796 (1971).
4) J. Isoya and S. Fujiwara, This Bulletin, **45**, 2182 (1972).
5) Gmelins Handbuch der Anorganischen Chemie, System-Nummer (1969) p. 57.

Table 1. γ-Irradiated Ni(II) complexes

A. $[Ni(NH_3)_6]Cl_2$, $[Ni(NH_3)_6](ClO_4)_2$, $[Ni(en)_3]Cl_2\cdot 2H_2O$, $[Ni(en)_3]SO_4$, $[Ni(en)_3](ClO_4)_2\cdot 1/2\,H_2O$, $Ni(N_2H_4)_3SO_4$, $Ni(N_2H_4)_3Cl_2$, $Ni(N_2H_4)_3(NO_3)_2$

B. $[Ni(NH_3)_4(NCS)_2]$, $[Ni(en)_2(H_2O)_2](NO_3)_2$, $[Ni(en)_2(H_2O)_2](ClO_4)_2$, $[Ni(en)(H_2O)_4](NO_3)_2$, $[Ni(en)(H_2O)_4]SO_4\cdot H_2O$, $Ni(N_2H_4)_2Cl_2$, $Ni(N_2H_4)_2SO_4\cdot 3H_2O$, $Ni(py)_2Cl_2$, $Ni(py)_4Cl_2$, $Ni(py)_2(H_2O)_2(NO_2)_2$, $Ni(py)_2(H_2O)_2SO_4$, $[Ni(dipy)(H_2O)_4]SO_4\cdot 2H_2O$, $[Ni(gly)_2(H_2O)_2]$, $[Ni(l\text{-}ala)_2(H_2O)_2]2H_2O$, $[Ni(C_7H_5O_2)_2(H_2O)_2]$, $[Ni(C_5H_7O_2)_2(H_2O)_2]$, $[Ni(C_9H_6NO)_2(H_2O)_2]$, $[Ni(C_{10}H_8NO)_2(H_2O)_2]$, $[Ni(C_9H_4NOBr_2)_2(H_2O)_2]$, $Ni(C_9H_7N)_2Cl_2$, $Ni(iso\text{-}C_9H_7N)_4Cl_2$, $[Ni(C_{10}H_9O_2)_2(H_2O)_2]$, $Ni(C_3H_5NO_2)_2\cdot 8H_2O$, $[Ni(C_7H_7NO_2)_2(H_2O)_2]$

C. $K_2[Ni(CN)_4]H_2O$, $Na_2[Ni(CN)_4]\cdot 3H_2O$, $[Ni(C_4H_7N_2O_2)_2]$, $[Ni(C_7H_6NO_2)_2]$, $[Ni(C_7H_6NO)_2]$, $[Ni(C_8H_8NO)_2]$, $[Ni(C_9H_{10}NO)_2]$, $[Ni(C_{10}H_{12}NO)_2]$, $[Ni(C_2H_3OS_2)_2]$, $[Ni(C_3H_5OS_2)_2]$, $[Ni(C_3H_6NS_2)_2]$, $[Ni(C_6H_6N_2O)_2]$

D. $[Ni(C_7H_5O_2)_2]$, $[Ni(C_9H_6NO)_2]$

en = ethylenediamine, N_2H_4 = hydrazine, py = pyridine, dipy = α,α'-dipyridyl, gly$^-$ = glycinate, l-ala$^-$ = l-alaninate, $C_7H_5O_2^-$ = salicylaldehyde anion, $C_5H_7O_2^-$ = acetylacetonate, $C_9H_6NO^-$ = 8-hydroxyquinolinate, $C_{10}H_8NO^-$ = 2-methyl-8-hydroxyquinolinate, $C_9H_4NOBr_2^-$ = 5,7-dibromo-8-hydroxyquinolinate, $C_9H_7N^-$ = quinolinate, *iso*-$C_9H_7N^-$ = isoquinolinate, $C_{10}H_9O_2^-$ = benzoylacetonate, $C_3H_5NO_2^-$ = succinimide anion, $C_7H_7NO_2^-$ = *o*-aminobenzoate, $C_4H_7N_2O_2^-$ = dimethylglyoximate, $C_7H_6NO_2^-$ = salicylaldoxime anion, $C_7H_6NO^-$ = salicylaldimine anion, $C_8H_8NO^-$ = *N*-methylsalicylaldimine anion, $C_9H_{10}NO^-$ = *N*-ethylsalicylaldimine anion, $C_{10}H_{12}NO^-$ = *N*-propylsalicylaldimine anion, $C_2H_3OS_2^-$ = methylxanthogenate, $C_3H_5OS_2^-$ = ethylxanthogenate, $C_3H_6NS_2^-$ = dimethyldithiocarbamate, $C_6H_6N_2O^-$ = picolinamide anion

Table 2. ESR parameters of Ni(I) complex ions

Complex ions	Matrices	$g_\parallel$	$g_\perp$	Ref.
$[Ni(en)(H_2O)_4]^+$	$[Ni(en)(H_2O)_4]SO_4\cdot H_2O$	2.434±0.005	2.080±0.005	
$[Ni(en)_2(H_2O)_2]^+$	$[Ni(en)_2(H_2O)_2](ClO_4)_2$	2.275±0.005	2.039±0.005	
$[Ni(l\text{-}ala)_2(H_2O)_2]^-$	$[Ni(l\text{-}ala)_2(H_2O)_2]2H_2O$	2.309±0.005	2.037±0.005	
$[Ni(C_3H_5NO_2)_2(H_2O)_4]^-$	$[Ni(C_3H_5NO_2)_2(H_2O)_4]4H_2O$	2.012±0.005	2.364±0.005	
$[Ni(CN)_4]^{3-}$	$K_2[Ni(CN)_4]H_2O$	2.298±0.002[b]		
$[Ni(CN)_4]^{3-}$	$Na_2[Ni(CN)_4]3H_2O$	2.271±0.002[b]		
$[Ni(C_2H_3OS_2)_2]^-$	$[Ni(C_2H_3OS_2)_2]$	2.300±0.003[b]		
$[Ni(C_3H_5OS_2)_2]^-$	$[Ni(C_3H_5OS_2)_2]$	2.278±0.003[b]		
$[Ni(C_3H_6NS_2)]^-$	$[Ni(C_3H_6NS_2)_2]$			
$[Ni(en)(H_2O)_4]^+$	EG–H_2O[a]	2.359±0.002	2.072±0.002	10)
$[Ni(en)_2(H_2O)_2]^+$	EG–H_2O	2.282±0.002	2.068±0.002	10)
$[Ni(CN)_4]^{3-}$	EG–H_2O	2.131±0.002	2.030±0.002	10)
$[Ni(C_2H_3OS_2)_2]^-$	Xylene	2.282±0.002	2.076±0.002	10)
$[Ni(C_3H_5OS_2)_2]^-$	Xylene	2.280±0.002	2.074±0.002	10)

a) Ethyleneglycol: water = 2 : 1 v/v. b) g-value for the most intense line.

with the d^7 electron configuration always give the relation $g_\perp > g_\parallel \sim 2$.[6-9] Therefore it may be concluded that in the above complexes, monovalent nickel complex ions are produced through reduction of Ni(II) complexes by γ-irradiation. On the other hand, in irradiated $[Ni(succinimide)_2(H_2O)_4]4H_2O$ we find $g_\perp > g_\parallel \sim 2$, which is expected for d^9 ions with tetragonally compressed octahedral symmetry (ground state $^2A_{1g}$).

Each of the remaining five complexes in Table 2 gives several absorptions which are most likely due to Ni(I) complex ions from their relatively large g-shifts, such shifts being due to heavy atoms, *i.e.* nickel ions in the present case. A preliminary investigation on a single crystal of $Na_2[Ni(CN)_4]3H_2O$ shows that the number of paramagnetic species is greater than that of inequivalent sites in the host crystal. In X-irradiated nickel(II) acetate tetrahydrate, Morton-Blake observed seven monovalent nickel complex ions with different g-values.[1]

It should be noted that for $[Ni(en)(H_2O)_4]^+$ and $[Ni(CN)_4]^{3-}$ g-values observed in the lattice of the host complexes are considerably larger than in rigid solutions (Table 2). This suggests that the structure of the Ni(I) complex ions is different in these two matrices. The yield of the Ni(I) species produced by γ-irradiation is strongly dependent on the counter ions and crystal structure of the complexes. ESR spectra of Ni(I) can be observed in irradiated $[Ni(en)(H_2O)_4]SO_4\cdot H_2O$ and $[Ni(en)_2(H_2O)_2](ClO_4)_2$, but not in $[Ni(en)(H_2O)_4](NO_3)_2$ and $[Ni(en)_2(H_2O)_2](NO_3)_2$. In the latter two complexes the yield of paramagnetic species, if exist at all, should be lower at least by two orders of magnitude.

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6) S. Geschwind and J. P. Rameika, *J. Appl. Phys.*, **33**, 721 (1961).
7) U. Höchli and K. A. Müller, *Phys. Rev. Lett.*, **12**, 730 (1964).
8) R. Lacroix, U. Höchli and K. A. Müller, *Helv. Phys. Acta*, **37**, 627 (1964).
9) U. Höchli, K. A. Müller, and P. Wysling, *Phys. Lett.*, **15**, 5 (1965).
10) C. Amano and S. Fujiwara, This Bulletin, **46**, 1379 (1973).