ESR Studies of Cobalt(II) in $[TMPD^+]_2[Ni(mnt)_2]$ and $[TMPD^+]_2[Pt(mnt)_2]$ (TMPD$^+$: *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine Cation, mnt: 1,2-Dicyano-1,2-ethylenedithiolato)

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The Co(II) and triplet exciton ESR spectra of Co(II)-doped $[TMPD^+]_2[Ni(mnt)_2]$ and $[TMPD^+]_2[Pt(mnt)_2]$ were observed at different temperatures. The triplet exciton signals of the solid solutions yielded practically the same ESR parameters as those of the pure Ni(II) and Pt(II) complexes. The Co(II) spectra showed a well-resolved hyperfine structure, each component line of which became broad with increasing temperature. This can be interpreted in terms of exciton transfer from TMPD$^+$ lattices to the metal ions.

The compound $[TMPD^+]_2[Ni(mnt)_2]$ consisting of planar organic radical cations and also planar metal-chelate anions has recently attracted considerable attention because of its novel crystal structure[1] schematically shown in Fig. 1. In this structure, TMPD$^+$ radicals form alternating chains whereas $[Ni(mnt)_2]^{2-}$ ions are stacked equidistantly to construct regular chains. The intradimer spin interaction of TMPD$^+$ radicals ($2J_1=-0.23$ eV) is strong enough, as compared with the interdimer one in a TMPD$^+$ chain ($|J_2/J_1|\approx 0.1$), to generate triplet excitons which migrate throughout in the chain.[1,2]

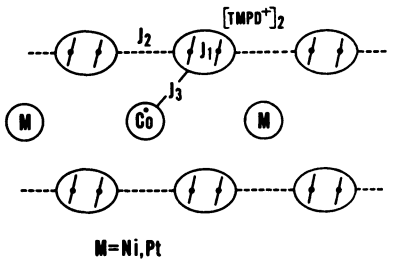

Fig. 1. Structure of $[TMPD^+]_2[M(mnt)_2]$ (M=Ni or Pt) depicted schematically.

Previously, we studied the ESR of the solid solution $[TMPD^+]_2[Cu_xNi_{1-x}(mnt)_2]$ and found the existence of magnetic interaction between Cu(II) ions and TMPD$^+$ dimers. This can be interpreted in terms of the partial migration of triplet excitons onto neighboring metal chelate chains.[2,3] It is known that Co(II) ions usually have an electron-spin relaxation time shorter than that of Cu(II) ions. Therefore, we can expect to obtain further information about the exciton-metal interaction by use of Co(II) ions as a probe to detect it. The present ESR investigation has been undertaken on Co(II) ions and triplet excitons in Co(II)-doped $[TMPD^+]_2[Ni(mnt)_2]$ and $[TMPD^+]_2[Pt(mnt)_2]$, both pure complexes of which are known to be isostructural to each other from our previous ESR study.[3]

Experimental

A boiling ethanol solution of $(Et_4N)_2[Co(mnt)_2]$ and $(Et_4N)_2[Ni(mnt)_2]$ mixed in an appropriate ratio was added all together to a boiling ethanol solution of $[TMPD^+]ClO_4$.[2] On cooling, the resulting solution separated black needle crystals having the crystal form identical with that of the pure Ni(II) complex. The crystals were identified as $[TMPD^+]_2[Co_xNi_{1-x}(mnt)_2]$. The solid solution of $[TMPD^+]_2[Co_xPt_{1-x}(mnt)_2]$ was synthesized in a similar manner from $(Et_4N)_2[Pt(mnt)_2]$, $(Et_4N)_2[Co(mnt)_2]$, and $[TMPD^+]ClO_4$.[2,3] Black needle crystals were obtained. All preparative experiments were carried out under a dry-nitrogen atmosphere.

The ESR spectra of the crystalline powders prepared were recorded by means of a JEOL ES-SCXA X-band spectrometer in a temperature range of 80—300 K. Mn^{2+}/MgO was employed as a marker. The sample temperature was controlled by use of a cold-gas flow system. Two copper *vs.* constantan thermocouples were mounted near either side of the sample tube along the stream of cold nitrogen gas for the determination of sample temperatures. The observed temperature was estimated to be accurate within ± 2 K.

Results

Figure 2 shows the ESR spectra of $[TMPD^+]_2[Co_xNi_{1-x}(mnt)_2]$ ($x\approx 0.02$) recorded at different tem-

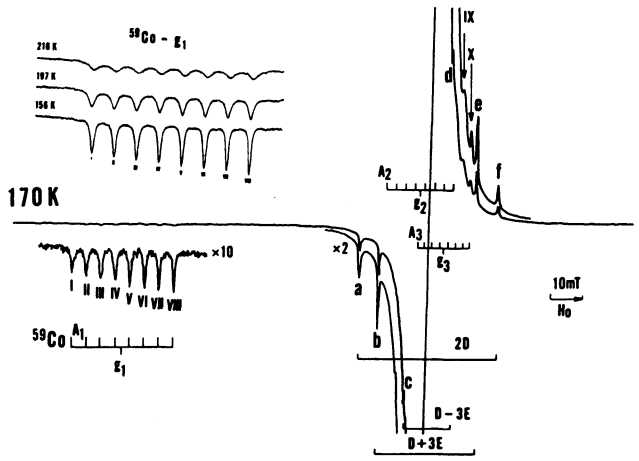

Fig. 2. ESR spectrum of $[TMPD^+]_2[Co_xNi_{1-x}(mnt)_2]$ ($x\approx 0.02$) recorded at 170 K. The hyperfine peaks I—VIII due to ^{59}Co are shown for the temperatures 156, 197, and 216 K. g_2 and A_2 determined for the Bu_4N^+ salt are shown for reference.

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peratures. In the temperature range 160—200 K, signals assignable to Co(II) (indicated by Roman numerals) were observed well separately from triplet exciton signals (indicated by the alphabet) arising from $TMPD^+$ dimers. With decreasing temperature, the $TMPD^+$ signals became weak whereas the Co(II) signals increased their intensity in conformity with the Curie law. Below 160 K, only the latter signals were observed. The ESR spectra of $[TMPD^+]_2[Co_xPt_{1-x}(mnt)_2]$ are given in Fig. 3. These spectra closely resemble those of the Co(II)-doped Ni(II) analogue.

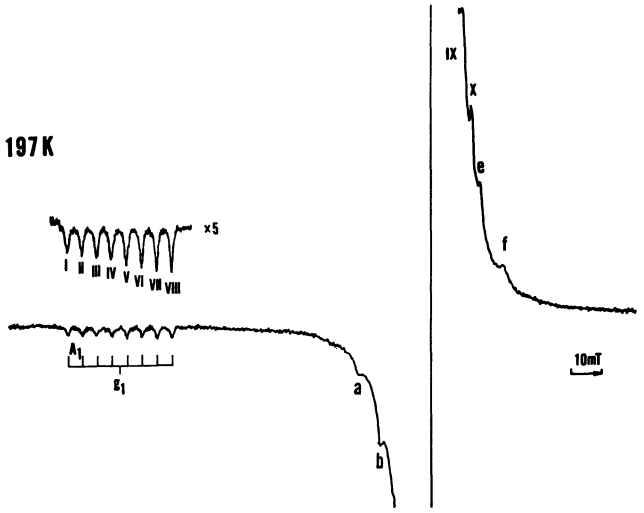

Fig. 3. ESR spectrum of $[TMPD^+]_2[Co_xPt_{1-x}(mnt)_2]$ ($x\approx0.01$) recorded at 197 K.

The triplet exciton signals are interpreted in terms of a fine structure represented by

$$\mathcal{H}_{fs} = D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2). \quad (1)$$

The zero splitting parameters (D and E) obtained from the spectra of the Ni(II) and Pt(II) solid solutions agree well with those of the pure Ni(II) and Pt(II) complexes, respectively, as given in Table 1. The well resolved hyperfine structure due to ^{59}Co nuclei yields the g_1 value and the corresponding hyperfine coupling constant A_1 as indicated in Table 2. The peaks IX and X can be assigned to the component lines of the g_3 signal by comparing them to the ESR spectrum of Co(II) ions diluted in $(Bu_4N)_2[Ni(mnt)_2]$.[4] The separation between the two peaks is nearly equal to the A_3 value of Co(II) in the butylammonium salt. If the equal separation is assumed for the eight component lines, the g_3 value can be evaluated as given in Table 2 in agreement with the value of Co(II) in the butylammonium salt. In each spectrum of the Ni(II) and Pt(II) solid solutions, an extra strong signal attributable to $TMPD^+$ monomers unavoidably involved as an impurity appeared at $g=2.006$, where the g_2 signals of Co(II) should be observed. Therefore, we could not determine the g_2 and A_2 values of the present compounds. The values of g_2 and A_2 in Fig. 2 show the data reported for Co(II) diluted in $(Bu_4N)_2[Ni(mnt)_2]$.[4] These g_2 and A_2 values are thought not to be much different from the respective inherent values of the $TMPD^+$ complex. All of the ESR parameters thus determined were independent of the concentration of Co(II) ions.

Table 1. TRIPLET EXCITON ESR PARAMETERS D AND E AND THE EXCHANGE INTEGRAL J_1 OF $[TMPD^+]_2[Co_xNi_{1-x}(mnt)_2]$ ($x\approx0.02$) AND $[TMPD^+]_2[Co_xPt_{1-x}(mnt)_2]$ ($x\approx0.01$)

Compound	D/mT	E/mT	$-2J_1$/eV
$[TMPD^+]_2[Co_xNi_{1-x}(mnt)_2]$	21.6	2.8	0.19
$[TMPD^+]_2[Co_xPt_{1-x}(mnt)_2]$	23.0	2.9	0.23
$[TMPD^+]_2[Ni(mnt)_2]$[a]	21.6	2.9	0.23
$[TMPD^+]_2[Pt(mnt)_2]$[b]	22.9	2.9	0.21

a) Refs. 1 and 2. b) Ref. 3.

With increasing temperature above 160 K, the signals of $TMPD^+$ in the Ni(II) solid solution become gradually strong. The intensity I of the triplet exciton ESR signal should increase in proportion to the triplet density ρ and also to reciprocal temperature. Accordingly, one can obtain the following equation when $2|J_1| \geqq kT$.

$$I \propto \rho/T = 3[\exp(2J_1/kT)]/T. \quad (2)$$

From the temperature dependence of the exciton signal intensity, the exchange integral J_1 of $TMPD^+$ dimers was determined as $2J_1 = -0.19$ eV. Above 200 K, the $TMPD^+$ signals gradually broaden owing to the migration of triplet excitons within $TMPD^+$ chains. It is interesting to note that the Co(II) signals also gradually broaden above 200 K. This indicates that the triplet excitons have some magnetic interaction with the Co(II) ions.

Since the peaks I—VIII are separated well from each other, we can determine the temperature dependence of the half-height width. When the line broadening is assumed to be caused by a thermal activation process with an activation energy ΔE, the linewidth W can be expressed as[2,5]

$$W = W_0 + W_1 \exp(-\Delta E/kT). \quad (3)$$

Here, W_0 denotes the linewidth at the low temperature limit, and can be regarded, in the present problem, as that observed at 78 K. Figure 4 shows the semilogarithmic plot of $(W - W_0)$ against T^{-1} for the Ni(II) solid solution. The experimental results deviate from

Table 2. Co(II) ESR SIGNAL PARAMETERS OF $[TMPD^+]_2[Co_xNi_{1-x}(mnt)_2]$ ($x\approx0.02$) AND $[TMPD^+]_2[Co_xPt_{1-x}(mnt)_2]$ ($x\approx0.01$)

Compound	g_1	g_2	g_3	A_1/mT	A_2/mT	A_3/mT
$[TMPD^+]_2[Co_xNi_{1-x}(mnt)_2]$	2.847	—[b]	1.98_3	4.6	—[b]	2.3
$[TMPD^+]_2[Co_xPt_{1-x}(mnt)_2]$	2.871	—[b]	1.97_6	4.7	—[b]	2.5
$(Bu_4N)_2[Co_xNi_{1-x}(mnt)_2]$[a]	2.798	2.025	1.977	3.8	3.0	2.5

a) Ref. 4. b) Unable to observe the signals because of a strong impurity signal.

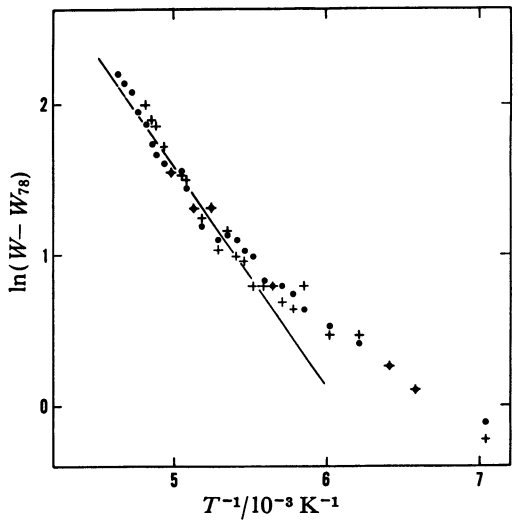

Fig. 4. Temperature dependence of the half-height width of the ^{59}Co hyperfine peaks I (+) and VIII (●) observed for the Co(II)-doped $[TMPD^+]_2[Ni(mnt)_2]$. The straight line shows the best fit of Eq. 3 to the peak VIII above 185 K. W_{78} in the ordinate denotes the linewidth at 78 K.

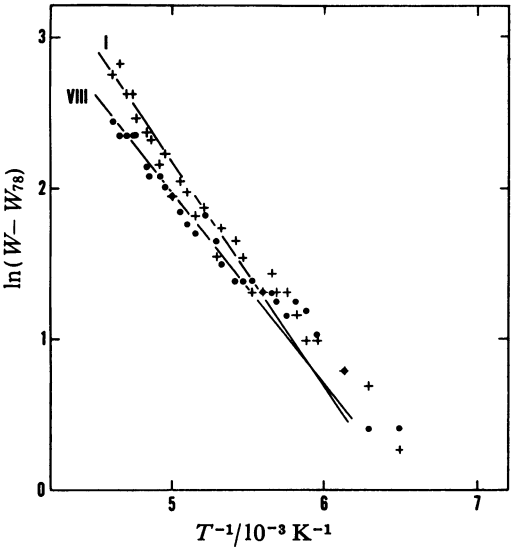

Fig. 5. Temperature dependence of the half-height width of the ^{59}Co hyperfine peaks I (+) and VIII (●) observed for Co(II) in $[TMPD^+]_2[Pt(mnt)_2]$. The straight lines show the best fits of Eq. 3 to the peaks I and VIII. The slopes of the lines give different activation energies, but the difference is smaller than the experimental errors.

Eq. 3 in the low temperature region. However, the linear relation is satisfied above 200 K yielding $\Delta E = 0.15 \pm 0.04$ eV.

The Co(II)-doped platinum salt yielded the ESR parameters very similar to those of the Ni(II) solid solution as given in Tables 1 and 2. The temperature dependence of the Co(II) linewidth in the Pt(II) complex (shown in Fig. 5) gave the ΔE value equal to that of the Ni(II) solid solution.

Discussion

Since the $TMPD^+$ signal parameters D, E, and J_1 of the present solid solutions agree with the corresponding values of the pure Ni(II) or Pt(II) salt, it is thought that the crystal lattices remain almost unchanged even in the solid solutions. Therefore, the ESR results can be discussed on the basis of the structure of the respective pure salts. The Co(II) signals of the solid solutions yield similar ESR parameters to those of Co(II) in $(Bu_4N)_2[Ni(mnt)_2]$. This indicates that magnetic interaction operating between organic radicals and metal chelates is weak enough to permit one its quantitative evaluation with ESR experiments. It is interesting to note that Co(II) ions diluted in $(Et_4N)_2[Ni(mnt)_2]$ yielded Co(II) ESR signals showing no line broadening in the temperature range in which the line broadening was observed for the $TMPD^+$ salt. Therefore, the line broadening of the Co(II) signals observed is ascribable to the triplet excitons.

When magnetic interaction between Co(II) ions and triplet excitons is a main cause for the Co(II) electron spin relaxation, the linewidth W of Co(II) ESR signals can be written as[2,6]

$$W = W_0 + W'\rho = W_0 + 3W' \exp(2J_1/kT). \quad (4)$$

On comparing the functional form of this equation with that of Eq. 3, ΔE is apparently equal to $2|J_1|$. The magnetic interaction of triplet excitons is accompanied by their migration over a barrier into adjacent sites. If this effect is taken into account, the ΔE value should be greater than $2|J_1|$. In the present solid solutions, however, the value of ΔE determined from the data at higher temperatures is certainly smaller than $2|J_1|$. This clearly indicates that the relaxation mechanism of Co(II) ESR given by Eq. 4 is inadequate for the interpretation of the present results. It is known that an electron spin on an isolated Co(II) ion can easily relax through *IS*- and/or *LS*-coupling.[7] In our previous experiments,[2,3] Cu(II) ESR signals in both Et_4N^+ and $TMPD^+$ salts showed a remarkable saturation effect, whereas no such effect was detectable for the Co(II) signals even at the highest power level ($\approx$100 mW) of our microwave oscillator. Accordingly, we have to take into account another relaxation mechanism for the Co(II) ESR of the present compounds such as modulation of *IS*- and/or *LS*-coupling through field fluctuation induced by the motion of $TMPD^+$ triplet excitons.

Figures 2 and 3 obviously show that the Co(II) signals I—VIII carefully taken at a given temperature for finely powdered samples have different linewidths from each other, whereas the component lines of Co(II) in the Et_4N^+ salt showed practically the same half-height width. The electronic state of the Co(II) ions can be fluctuated by exciton transfer from the $TMPD^+$ lattices to the metal ions. This transfer is accompanied by the so-called partial oxidation of the Co(II) ions in solids. This is considered to take place without difficulty, since the ligand mnt forms stable metal complexes with high oxidation states of the central metals.[8] The fluctuated electronic state of Co atoms induces the fluctuation of the g and A values. Owing to this effect,

the ESR Hamiltonian for the peaks I—VIII is given by the time dependent g and A:

$$\mathcal{H} = g_1(t)\mu_B HS_1 + A_1(t)I_1S_1. \quad (5)$$

The fluctuation in the present complexes is slow enough as compared with the ESR frequency, because the hyperfine lines are well separated. Under this condition, the linewidth W is[7]

$$W \approx \frac{1}{T_2}$$
$$= \frac{1}{2\hbar}\int_{-\infty}^{\infty} \overline{[H_{\alpha\alpha}(t+\tau) - H_{\beta\beta}(t+\tau)][H_{\alpha\alpha}(t) - H_{\beta\beta}(t)]}\mathrm{d}\tau, \quad (6)$$

where $H_{\alpha\alpha}$ and $H_{\beta\beta}$ are the matrix elements of the above Hamiltonian. The values $g_1(t)$ and $A_1(t)$ can be reasonably assumed to be fluctuated with the same time constant τ_c, because the fluctuation comes from the same origin. Under this assumption along with $\omega\tau_c \gg 1$, we obtain

$$\frac{1}{T_2} = \frac{\tau_c}{\hbar^2}(g_1\mu_B H + A_1M_I)^2, \quad (7)$$

where g_1 and A_1 are time independent. The ratio of the linewidths of the peaks $M_I = 7/2$ and $-7/2$ is evaluated as $(225+4.6\times 7/2)^2/(225-4.6\times 7/2)^2 = 1.3$, which agrees well with the observed ratio 1.5 of the half-height widths of the peaks I and VIII. Thus, the difference of linewidth among the peaks I—VIII at an arbitrary temperature can be interpreted in terms of a random modulation of the *IS* coupling by the motion of triplet excitons.

Since the linewidth of each Co(II) peak broadens with increasing temperature, τ_c in Eq. 7 should be temperature dependent. If we assume that the aforementioned triplet-exciton transfer is thermally activated with an energy ε, the correlation time τ_c may be written as,

$$\tau_c \propto \frac{1}{|J_3|}\exp(-\varepsilon/kT), \quad (8)$$

where J_3 denotes the exchange integral between $[TMPD^+]_2$ and Co(II) ions. In this mechanism, the linewidth can be given by the same functional form as Eq. 3. Accordingly, the triplet excitons in the present solid solutions transfer onto the metal lattices with the activation energy of $\Delta E \approx 0.15$ eV and result in the relaxation of the Co(II) electron spin through its *IS*-coupling. The relaxation is correlated only in the indirect process to the triplet excitons activated thermally with $2|J_1|$. The activation energy does not depend on the kind of the host crystals. The interaction between the metal chelates is so weak that an exciton transferred to a Co(II) chelate undergoes no further transfer to the adjacent metal chelates.

References

1) M. J. Hove, B. M. Hoffman, and J. A. Ibers, *J. Chem. Phys.*, **56**, 3490 (1972).
2) M. Inoue, H. Kuramoto, and D. Nakamura, *J. Magn. Reson.*, **33**, 409 (1979).
3) M. Inoue, *J. Magn. Reson.*, **38**, 481 (1980).
4) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).
5) P. L. Nordio, Z. G. Soos, and H. M. McConnell, *Ann. Rev. Phys. Chem.*, **17**, 237 (1966).
6) J. S. Valentine, A. J. Silverstein, and Z. G. Soos, *J. Am. Chem. Soc.*, **96**, 97 (1974).
7) G. E. Pake and T. L. Estle, "The Physical Principles, of Electron Paramagnetic Resonance," W. A. Benjamin, Inc., London (1973).
8) R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, **22**, 303 (1979).