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# The ESR Spectra of Diamminecopper(II) Tetracyanometallate(II) Aromatic Clathrates*

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*The ESR spectra of Hofmann-type clathrates,* $Cu(NH_3)_2M'(CN)_4.2G$, *where* $M'=Ni$, *Pd, or Pt and where* $G=C_6H_6$, $C_4H_4S$, *or* $C_6H_5NH_2$, *and* $(Cd,Cu)(NH_3)_2Ni(CN)_4.2C_6H_6$ *were studied. From the observed magnetic parameters, it has been concluded that the ligand atoms around the copper(II) ion have a compressed tetragonal configuration in the benzene and the thiophene clathrates, while in the aniline clathrates the symmetry of the configuration must be lower than* $D_{4h}$. *The stabilization of the compressed tetragonal configuration, which has rarely been observed in common copper(II) complexes, may be caused by the clathration of the guest molecules. The structural information obtained from X-ray diffractometry supports the compressed structure fully.*

## Introduction

In this laboratory a series of clathrate compounds with the general formula $M(NH_3)_2M'(CN)_4.2G$ have been prepared and named «Hofmann-type» clathrates.[1-5]

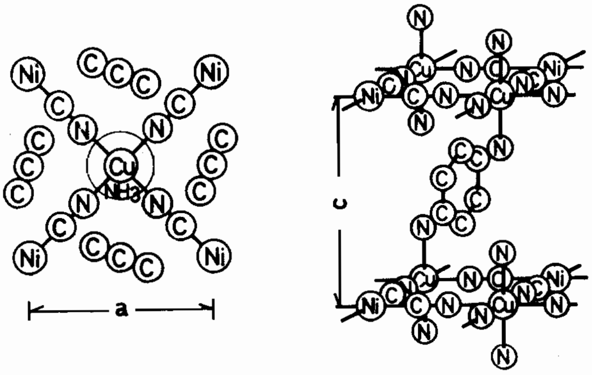

Figure 1. The structure of Hofmann-type clathrate $Cu(NH_3)_2Ni(CN)_4 . 2C_6H_6$.

In a sub-series of Hofmann-type clathrates, $Cu(NH_3)_2M'(CN)_4.2G$, the divalent copper ion is coordinated with four nitrogen atoms of cyanide anions in plane and with two nitrogen atoms of ammonia molecules at *trans* positions, as may be seen in Figure 1. This structure of the Hofmann-type clathrates is based on the crystal structure of Hofmann's clathrate, $Ni(NH_3)_2Ni(CN)_4.2C_6H_6$,[6] reported by Rayner and Powell;[7] it has been confirmed in the case of $Cd(NH_3)_2Ni(CN)_4.2C_6H_6$ by recent X-ray diffraction data on the single crystal.[8] The ESR spectra may give much information about the configuration of the ligands around paramagnetic cations in the clathrates and about the coordination bonding between them. The only ESR data available for this group of compounds, however, have been those on $Ni(NH_3)_2Ni(CN)_4.2G$ with several guest molecules reported by Fujiwara and Bhatnagar.[9]

The present paper will deal with the ESR spectra of the Hofmann-type clathrates $M(NH_3)_2M'(CN)_4.2G$ (abbrev. M–M'–G), where $M^{II}$ is copper or copper diluted with cadmium, where $M'^{II}$ is nickel, palladium, or platinum, and where G is benzene, aniline, or thiophene. A residual host lattice, $Cu(NH_3)_2M'(CN)_4$, left after the escape of the guest molecules from the corresponding clathrate, Cu–M'–G, was also examined.

As a result, six ligand atoms around a copper ion in all the benzene and the thiophene clathrates were found to be arranged in a compressed tetragonal symmetry, a symmetry which has seldom been found in copper complexes, while the configuration of the ligands in the aniline clathrates seems to have a lower symmetry than tetragonal.

## Experimental Section

*Samples.* The clathrates and their residual host lattices were prepared by the methods previously reported.[1-4] A magnetically-dilute sample, $(Cd,Cu)(NH_3)_2Ni(CN)_4.2C_6H_6$ (abbrev. (Cd, Cu)–Ni–Bz), was prepared from carefully-purified reagents in order to

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(*) The Metal Ammine Cyanide Aromatics Clathrates. VI.

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exclude possible paramagnetic impurities such as $Mn^{II}$ ions. The purification procedures were as follows. The potassium cyanide was purified by an ion-exchange method in which its aqueous solution was passed through a column of strongly acidic cation-exchange resins (Diaion SK 1B K-form) and strongly basic anion-exchange resins (Diaion SA No. 100 CN-form) successively. The nickel chloride and copper sulfate were purified by the method described previously.[1] The impurities in cadmium nitrate were eliminated from its aqueous solution by coprecipitation with aluminum hydroxide.

By the use of these purified reagents (Cd, Cu)–Ni–Bz was obtained as fine crystals by shaking benzene with a mixed ammoniacal solution of pH 10 containing cadmium nitrate and copper sulfate in a 8: 1 ratio and potassium tetracyanoniccolate. The pH value is appropriate for the formation of Cd–Ni–Bz, but too high for the precipitation of Cu–Ni–Bz. The content of a trace of copper ions in the precipitated clathrate was not determined, but the color of the clathrate was exactly the same as that of Cd–Ni–Bz.

*ESR Measurements.* The ESR spectra were recorded with a JEOL JES-118 spectrometer with an X-band frequency (9 kMc) and a field modulation of 100 kc. The magnetic field was calibrated with an NMR probe and subesequently with DPPH and $Mn^{II}$ in MgO. The ESR spectra of the benzene and the aniline clathrates were measured at room temperature and at the temperature of liquid nitrogen. No meaningful difference in the magnetic parameters caused by the temperature change was detected. The ESR spectra of the thiophene clathrate could not be measured at room temperature because the compound was so unstable that it could not be dried without a partial escape of the guest thiophene. Therefore, the ESR measurement was carried out with a wet precipitates at the temperature of liquid nitrogen. When the sample was partially decomposed, the observed ESR spectrum could be interpreted as an overlapping of the spectrum of the clathrate and that of the residual host lattice, as is illustrated in Figure 2.

The spectra of these polycrystalline samples were analyzed by the usual method.[10,11]

*Diffuse Reflection Spectra.* The spectra in the ultraviolet and visible regions were measured with a Hitachi EPO-2A spectrophotometer equipped with a reflection attachment (Hitachi R-3). The reflectance were calculated by means of Kubelka-Munk's equation.[12]

## Results and Discussion

The ESR spectra and the diffuse reflection spectra are shown in Figures 2, 3, and 4. The observed values of the magnetic parameters and the wave numbers of the optical absorption maxima are given in Table I, together with the lattice constants cited from previous papers.[1-3,5] As may clearly be seen in the table, the $g_{\parallel}$ and $g_{\perp}$ values of Cu–M′–Bz (M′ = Ni, Pd or Pt) and Cu–Ni–Thp did not shift with the change in the species of the guest molecules and the diamagnetic metal ions, M′. This constancy of the *g* values seems to indicate that the strength of the crystal field around a copper ion is almost always the same in these clathrates, even though their lattice constants vary considerably in size. According to their crystal structures, the symmetry of the crystal field around a copper ion in Cu–M′–Bz and Cu–Ni–Thp may be tetragonal. The *g* values of a copper ion in a tetragonal field are given from the crystal field theory as follows:[13]

$$g_{\parallel} = g_e - (4 \pm 4)\lambda/(E_{B2g} - E_0) \qquad (1)$$

$$g_{\perp} = g_e - (4 \mp 2)\lambda/(E_{Eg} - E_0) \qquad (2)$$

where $E_0$ is the energy of the ground state, which is $B_{1g}$ in the elongated tetragonal field along the symmetry axis and $A_{1g}$ in the compressed tetragonal field.

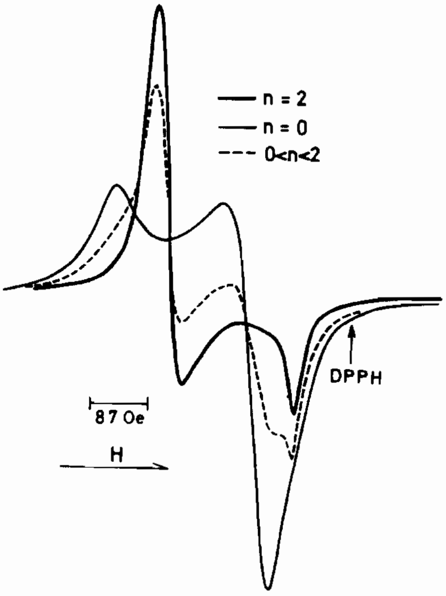

Figure 2. The ESR spectra of $Cu(NH_3)_2Ni(CN)_4 \cdot nC_6H_6$.

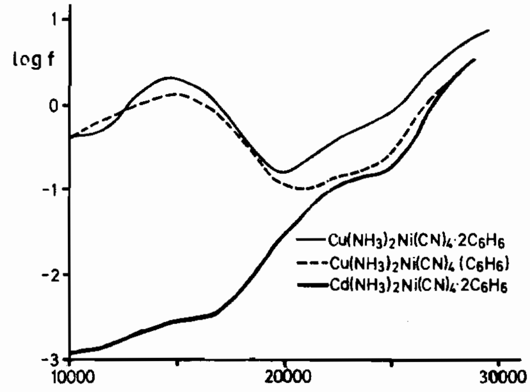

Figure 3. The diffuse reflection spectra.

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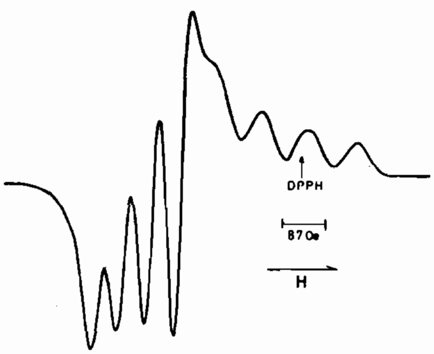

Figure 4. The ESR spectra of (Cd, Cu)$(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$.

The upper sign applies to the former case and the lower sign to the latter case. $g_e$ and $\lambda$ are the symbol of the $g$ value of a free spin, 2.0023, and the spin-orbit coupling constant of a copper ion, $-828$ cm$^{-1}$, respectively.[14] By using the values of the energy differences determined from the diffuse reflection spectra, $E_g-B_{1g}=1.65\times10^4$ cm$^{-1}$, $B_{2g}-B_{1g}=1.50\times10^4$ cm$^{-1}$, and $E_g-A_{1g}=1.48\times10^4$ cm$^{-1}$, the $g$ values may be calculated from Equations (1) and (2) to be $g_{\parallel}=2.00$ and $g_{\perp}=2.34$ for Cu–Ni–Bz and $g_{\parallel}=2.44$ and $g_{\perp}=2.10$ for its residual host lattice.

The calculated $g$ values coincide approximately with the observed values. A better agreement between them can not be expected by the use of this simple crystal field model in which the covalency of the bonding is neglected. Furthermore, the discrepancy in the $g_{\parallel}$ value of Cu–Ni–Bz may result from either contribution of a weak rhombic component of the crystal field[15] or of the $B_{1g}$ state through a dynamical Jahn-Teller effect.[16] In any case, it can be concluded, to a good approximation, that the copper ions in Cu–M′–Bz and Cu–Ni–Thp have a compressed tetragonal field around them, while those in their residual host lattices have an elongated one.* This change in the crystal field around a copper ion, along with the escape of guest molecules, may be explained as follows. In the benzene and the thiophene clathrates, the nitrogen atoms of two ammonia molecules coordinate to the copper ion more closely than do the nitrogens of four cyanide anions, and consequently a compressed octahedron is formed. On the other hand, when the host lattice loses the guest molecules, the distance between the copper ion and the ammonia molecule is lengthened and the distance between the copper ion and the cyanide anion is shortened, thus forming an elongated octahedron.

This estimation is not contradictory to the structural data obtained by the powder X-ray diffraction method. In the Ni–Ni–Bz clathrate, the paramagnetic nickel ion is coordinated with two ammonia molecules at a distance of 2.08 Å and with four nitrogen atoms of cyanide anions in plane at the distance of 2.15 Å, thus forming a compressed octahedron.[7] As may clearly be seen in Table I, Ni–Ni–Bz has a unit cell with the shortest $a$ and the longest $c$ of all the benzene and the thiophene clathrates except Cu–Pd–Bz, whose $c$ is nearly equal to that of Ni–Ni–Bz. Thus, the unit cells of the copper clathrates are more compressed

**Table I.** The observed magnetic parameters and the wave numbers of the absorption maxima

| Benzene and thiophene Clathrates | $g_{\parallel}$ | $g_{\perp}$ | Lattice constants $a$ | $c$ | $\Delta E$ |
|---|---|---|---|---|---|
| Cu–Ni–Bz | 2.060±0.002 | 2.207±0.003 | 7.39 Å | 8.24 Å | $1.48\times10^4$ cm$^{-1}$ ($A_{1g}\rightarrow E_g$) |
| Cu–Pd–Bz | 2.060±0.003 | 2.207±0.003 | 7.58 Å | 8.29 Å | |
| Cu–Pt–Bz | 2.062±0.002 | 2.211±0.003 | 7.58 Å | 8.25 Å | |
| Cu–Ni–Thp | 2.062±0.003 | 2.210±0.003 | 7.40 Å | 8.09 Å | |
| Ni–Ni–Bz | | | 7.24 Å | 8.28 Å | |
| Residual host lattices | $g_{\parallel}$ | $g_{\perp}$ | | | $\Delta E$ |
| Cu–Ni (Bz) | 2.247±0.005 | 2.080±0.003 | | | $1.50\times10^4$ cm$^{-1}$ ($B_{1g}\rightarrow B_{2g}$)<br>$1.65\times10^4$ cm$^{-1}$ ($B_{1g}\rightarrow E_g$) |
| Cu–Pd (Bz) | 2.253±0.005 | 2.081±0.004 | | | |
| Cu–Pt (Bz) | 2.256±0.005 | 2.081±0.004 | | | |
| Cu–Ni (Thp) | 2.248±0.005 | 2.080±0.003 | | | |
| Magnetically-dilute sample | $g_{\parallel}$ | $g_{\perp}$ | $A_{\parallel}$ | | $A_{\perp}$ |
| (Cd, Cu)–Ni–Bz | 2.027±0.006 | 2.237±0.006 | $(90.1\pm0.5)\times10^{-4}$ cm$^{-1}$ | | $-(60.7\pm0.5)\times10^{-4}$ cm$^{-1}$ |
| Aniline clathrates | $g_1$ | $g_2$ | $g_3$ | | |
| Cu–Ni–An | 2.058±0.002 | 2.088±0.004 | 2.289±0.006 | | |
| Cu–Pd–An | 2.056±0.002 | 2.161±0.004 | 2.227±0.006 | | |

M–M′–G = $M(NH_3)_2M'(CN)_4 \cdot 2G$. G: Bz = benzene, An = aniline, Thp = thiophene. M–M′ (G) = $M(NH_3)_2M'(CN)_4$ obtained from M–M′–G.

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(*) The X-ray spectrum of the residual host lattice could not be assigned to any single phase.[4] Nevertheless, the ESR data suggest the presence of only one cationic species of copper(II) in the residual host lattice.

than that of Ni–Ni–Bz along the symmetry axis (the *c* axis) of the compressed octahedron around the paramagnetic nickel ion. Therefore, it is very likely that the ligands are arranged to form also a compressed octahedron around a copper ion, as the ESR data indicate.

The stereochemistry of copper(II) complexes has been investigated as examples of the Jahn-Teller effect.[17-19] Theoretical calculations by Liehr and Ballhausen[20] have shown that both elongated and compressed deformations from $O_h$ symmetry are possible and that the uncommon deformation is found in copper complexes with an ionic bond between ligands and the central copper ion. Most of the copper complexes so far studied by the X-ray diffraction method are elongated along the tetragonal axis; the only compressed forms have been those of $K_2CuF_4$,[21] $Cu(NH_3)_2Cl_2$, and $Cu(NH_3)_2Br_2$.[22] An ESR study of magnetically-dilute Tutton salts $(Zn, Cu)M_2(SO_4)_2 \cdot 6H_2O$ ($M = NH_4$, K, Rb) has shown that the copper ions are in compressed tetragonal fields at room temperature.[15] The present group of clathrates provides new example of this type of crystal field around the copper ions. The presence of the guest molecules may stabilize this configuration of the ligands.

The ESR spectra of the aniline clathrates, Cu–Ni–An and Cu–Pd–An, showed anisotropies of the *g* values in three directions. The crystal field around the copper ion, therefore, must have a symmetry lower than $D_{4h}$ in both the compounds. Their powder X-ray diffraction patterns could not be assigned to the tetragonal systems.[1,3,5]

The *g* values of Cu–Ni–An differ considerably from those of Cu–Pd–An even though the *g* values of Cu–Ni–Bz, Cu–Pd–Bz, and Cu–Pt–Bz are all nearly equal. This characteristic differentiates the aniline clathrate from the corresponding benzene clathrate, although the reason for it has not yet been determined. The coordination of the aniline to the copper ion can not account for the difference, because the absence of the coordination bond between the copper ion and the amino-group of aniline has been established by IR spectroscopy.[4] To discuss this problem in detail, more information about the orientation of the aniline molecules in the clathrate will be necessary.

The spectra of the magnetically-dilute copper ion in (Cd, Cu)–Ni–Bz have clear hyperfine structures, as is shown in Figure 4. The extra sharp peaks observed in preliminary experiments were identified with a signal of $Mn^{II}$ ion, present as an impurity. Atfer the purification of all the reagents used in the preparation, the peaks no longer appeared.

The fact that the value of $g_{\parallel}$ is larger than that of $g_{\perp}$ suggests that the copper ion in this chlathrate also has a compressed tetragonal field around it. However, slight differences between the *g* values of the Cu–Ni–Bz and (Cd, Cu)–Ni–Bz were observed. This must result from the fact that the two fields are not exactly the same.

Theoretical formulae giving the relationship between $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, $A_{\perp}$, and a parameter $\varkappa$ are derived as follows:[23]

$$A_{\parallel} = g_e\gamma\beta_e\beta_N\langle r^{-3}\rangle[-\varkappa \mp 4/7 + g_{\parallel} - g_e + \{(1 \pm 2)/7\} \times (g_{\perp} - g_e)] \quad (3)$$

$$A_{\perp} = g_e\gamma\beta_e\beta_N\langle r^{-3}\rangle[-\varkappa \pm 2/7 + g_{\perp} - g_e - \{(1 \pm 2)/14\} \times (g_{\perp} - g_e)] \quad (4)$$

where the upper sign applies to the $B_{1g}$ ground state and the lower sign to the $A_{1g}$ state. By putting the observed values of $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, $A_{\perp}$ and $g_e\gamma\beta_e\beta_N\langle r^{-3}\rangle = 0.036\ cm^{-1}$ [14] into Equations (3) and (4), the value $\varkappa$ was calculated to be 0.31 from Equation (3) and 0.13 from Equation (4). This discrepancy can also be accounted for by assuming some covalent character of the bonding. Although, generally speaking, the ESR spectra of polycrystalline samples give only the absolute values of the hfs constants, in the present case Equations (3) and (4) can account reasonably for the sign of $A_{\parallel}$ and $A_{\perp}$ given in Table I, but can not account for the other sets of the signs. It may be worth noting that this is the first observation of a hyperfine structure with four separate lines of copper(II) ions in a compressed tetragonal configuration except for the extreme case of copper(II) ions in $NH_4Cl$, whose magnetic parameters have been reported to be $g_{\parallel} \sim 2$, $g \sim 2.22$, $|A_{\parallel}| \sim 240 \times 10^{-4}\ cm^{-1}$, and $|A_{\perp}| \sim 70 \times 10^{-4}\ cm^{-1}$.[24]

One of the few copper complexes with compressed configurations, $Cu(NH_3)_2Br_2$, was prepared, and its ESR spectra were measured. The spectra, however, were so broad ($\Delta H_{1/2} \sim 2{,}000$ Oe) that the complex's *g* values could not be determined.

A more detailed study using a single crystal of the diluted (Cd, Cu)–Ni–Bz is in progress and the preliminary data support the results obtained from the polycrystalline samples.

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