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# Synthesis and Characterization of the Nickel(II)–Rubeanic Acid Complex on Interlamellar Surfaces of Molybdenum Trioxide

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A stable nickel(II)–rubeanic acid coordination polymer was first prepared in the interlayer space of $MoO_3$ by soaking hydrated nickel molybdenum trioxide in an acetone solution of rubeanic acid. The basal spacing of the rubeanic acid–Ni–$MoO_3$ complex was found to be 9.5 Å by powder X-ray diffraction. Both chemical analysis and thermogravimetry indicated that the molar ratio of nickel ion to rubeanic acid is 1:1. The most probable molecular structure of the intercalated nickel(II)–rubeanic acid complex is suggested from the infrared spectrum and magnetic susceptibility of the material.

## Introduction

The study of coordination polymers has been widely carried out and undoubtedly will be continued in the future, because many of them exhibit interesting physical properties, as evidenced from studies of their semiconductivity, magnetic susceptibility, catalytic activity, and heat resistance. However, neither the molecular weight nor the molecular structure is easily determined because of their low solubilities and, in many cases, their low degree of crystallinity. Among the coordination polymers whose structures are still uncertain at present, there is one class composed of rubeanic acid (dithiooxamide) and transition metals.[2-4] The structural irregularity of the rubeanic acid (RA) complex has prevented a theoretical interpretation of the physicochemical properties of the compound. In order to resolve this ambiguity, a stereospecific synthesis was carried out by utilizing the two-dimensional interlayer spaces of clay mineral.[5] In that case, however, only the monomeric complex was formed, because the interatomic distance between the Cu(II) ions in the interlayer of montmorillonite was too large to bridge the distance between Cu(II) ions with rubeanic acid molecules. In order to solve this problem, it is necessary to find another suitable layered compound as a host material in which the amounts of exchangeable cation could be easily controlled. Fortunately, it was reported that $MoO_3$ can take up hydrated sodium ions and those ions are easily exchanged by various kinds of cations.[6] This behavior of hydrated sodium molybdenum trioxide is quite similar to that of clay minerals. $MoO_3$ is known to crystallize in a layer lattice in which two-dimensional metal oxide sheets are separated by a van der Waals gap.[7] In the present investigation, synthesis of nickel(II)–rubeanic acid coordination polymer in the interlayer space of $MoO_3$ was carried out and the structure of the complex was investigated by chemical analysis, X-ray diffraction, thermogravimetric analysis, infrared spectra, and magnetic susceptibility.

## Experimental Section

**Materials and Preparations.** Rubeanic acid (dithiooxamide) $NH_2C(S)C(S)NH_2$ was obtained from Mallinckrodt Chemical Works, and it was recrystallized from ethanol. Nickel chloride and molybdenum trioxide (Special Grade Reagent, Nakarai Chemicals, Ltd.) were used without further purification. Single crystals of $MoO_3$ were prepared by vapor-phase transport with $I_2$. $MoO_3$ can easily take up hydrated sodium cations between the interlayer space according to the procedure given below. Powders or single crystals of $MoO_3$ were suspended in aqueous solutions of 1 M $Na_2S_2O_4$ at room temperature for a few hours. The chemical formula of the material prepared in this way was determined to be $Na_{0.5}(H_2O)_nMoO_3$ by atomic absorption analysis. The intercalated sodium ions are easily replaced by Ni(II) ions by treating with 1 M aqueous solutions of nickel chloride at 100 °C for 1 day. The product was washed several times with acetone until a negative chloride ion test with $AgNO_3$ was obtained, and then it was dried in air. It was determined by conventional wet methods that this compound had a chemical formula of $Ni_{0.25}(H_2O)_nMoO_3$. The product was soaked in an acetone solution saturated with rubeanic acid at 60 °C for a few days, washed several times with acetone to remove free ligand molecules, and dried in vacuo. This product is denoted RA–Ni–$MoO_3$ in this paper.

**Measurements.** The X-ray diffraction patterns of $Na_{0.5}(H_2O)_nMoO_3$, $Ni_{0.25}(H_2O)_nMoO_3$, and its rubeanic acid complex RA–Ni–$MoO_3$ were obtained using a Rigaku-Denki diffractometer with Ni-filtered Cu Kα radiation.

Differential thermogravimetric analysis was made up to 700 °C using a Rigaku-Denki unit programmed for a heating rate of 10 °C/min.

The infrared spectra in the region 4000–700 $cm^{-1}$ were obtained on a Hitachi Perkin-Elmer spectrophotometer fitted with a sodium chloride prism. Samples were dispersed in potassium bromide disks. Calibration of the spectrophotometer was made using polystyrene bands.

The magnetic susceptibilities were determined by the Faraday method using a magnetic field of about 10000 G. The measurement was conducted in the temperature region between 80 and 300 K. The temperature calibration of the equipment was obtained by the measurement of the magnetic susceptibility of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$.

The electrical resistivity measurements were carried out on a pressed body of powdered specimens with a four-probe technique in about $10^{-2}$ Torr at room temperature.

## Results and Discussion

The X-ray diffraction data of $MoO_3$, $Na_{0.5}(H_2O)_nMoO_3$, and $Ni_{0.25}(H_2O)_nMoO_3$ and its rubeanic acid complex are tabulated in Table I. In the Na ion uptake reaction, the basal spacing of $MoO_3$ increased from 6.9 to 11.4 Å at 25 °C and 70% humidity. In the case when the Na ion was exchanged by Ni(II) ion, the value of the basal spacing increased to 14.6

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**Table I.** X-ray Diffraction Data

| $MoO_3$ | | | $Na_{0.5}(H_2O)_nMoO_3$ | | |
|---|---|---|---|---|---|
| *hkl* | I[a] | *d*, Å | *hkl* | I[a] | *d*, Å |
| 100 | s | 6.99 | 100 | vs | 11.5 |
| 200 | vs | 3.50 | 300 | s | 3.83 |
| 300 | s | 2.33 | 400 | vs | 2.88 |
| | | | 500 | m | 2.30 |
| $Ni_{0.25}(H_2O)_nMoO_3$ | | | RA-Ni-$MoO_3$ | | |
| *hkl* | I[a] | *d*, Å | *hkl* | I[a] | *d*, Å |
| 100 | vs | 14.60 | 100 | vs | 9.5 |
| 200 | s | 7.30 | 200 | vw | 4.76 |
| 400 | m | 3.65 | 300 | m | 3.16 |
| 600 | w | 2.43 | 400 | w | 2.36 |
| | | | 500 | vw | 1.90 |

[a] Intensity. Key: s, strong; m, medium, w, weak; v, very.

**Table II.** Basal Spacings at Various Temperatures

| temp, °C | $Ni_{0.25}(H_2O)_n$-$MoO_3$ *d*, Å | RA-Ni-$MoO_3$ *d*, Å |
|---|---|---|
| room temp | 14.6 | 9.5 |
| 200 | 7.24 | 9.5 |

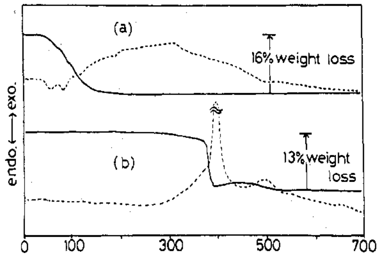

**Figure 1.** Thermal analysis data of (a) $Ni_{0.25}(H_2O)_nMoO_3$ and (b) RA–Ni–$MoO_3$. Solid and broken lines indicate TG and DTA curves, respectively.

Å at room temperature and 70% humidity. This basal spacing changed easily depending on the circumstances of temperature and humidity. On the other hand, in the case of rubeanic acid–Ni–$MoO_3$, only one basal spacing of 9.5 Å was found and it did not depend on humidity at room temperature. In order to examine if the rubeanic acid molecules were really intercalated in the space between the layers of $MoO_3$, both $Ni_{0.25}(H_2O)_nMoO_3$ and RA–Ni–$MoO_3$ were heated to around 200 °C. The relationships between the basal spacings and heating temperatures of $Ni_{0.25}(H_2O)_nMoO_3$ and its rubeanic acid complex are indicated in Table II. When $Ni_{0.25}(H_2O)_nMoO_3$ was heated to 200 °C, the basal spacing decreased to 7.24 Å because of desorption of intercalated water. On the other hand, in the case of RA–Ni–$MoO_3$, no change was found in the basal spacing even if the complex was heated to 200 °C. These facts indicate that the Ni–RA complex was surely formed between the interlayer region of the $MoO_3$ and that it is stable at fairly high temperatures. Further, the difference in the basal spacing between RA–Ni–$MoO_3$ and $MoO_3$ was almost equal to a van der Waals height of ca. 2.6 Å. This value for the height of the space between the $MoO_3$ layers suggests that the Ni–RA complex which was formed in the interlayer space of $MoO_3$ lies flat with its molecular plane parallel to the $MoO_3$ layer surface.

Thermal analyses data of $Ni_{0.25}(H_2O)_nMoO_3$ and its rubeanic acid complex are illustrated in Figure 1. In the case of $Ni_{0.25}(H_2O)_nMoO_3$ equilibrated with air (25 °C, 70% humidity), a weight loss of 16% accompanied by an endothermic peak around 100 °C can be assigned to desorption of hydrated water to nickel ion, indicating that the $Ni_{0.25}(H_2O)_nMoO_3$ contained almost 1 mol of water/mol of $MoO_3$.

**Table III.** Vibration Frequencies (in $cm^{-1}$) of RA and RA-Ni-$MoO_3$

| RA | RA-Ni-$MoO_3$ | assignment[a] |
|---|---|---|
| 3275 m | | |
| 3190 m | 3250 m | $\nu$(NH) |
| 3115 m | | |
| | 1600 m b | |
| 1585 vs b | 1505 s b | $\delta(NH_2)$ |
| 1429 s b | | $\nu$(CN) |
| 1200 m | | $\rho(NH_2)$ |
| | 1106 m | |
| | 1045 vw | |
| | 1020 w | |
| | 935 w | |
| | 870 m | |
| 835 s | 780 m | $\nu$(CS) |
| 700 m | | |

[a] Assignments for RA and RA-Ni-$MoO_3$ were taken from ref 8–11.

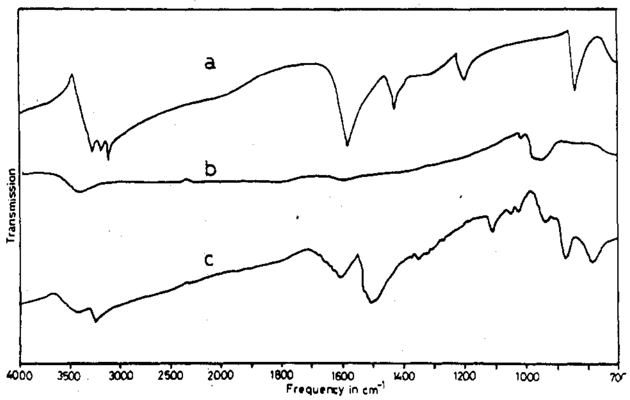

**Figure 2.** Infrared spectra of (a) RA, (b) $Ni_{0.25}(H_2O)_nMoO_3$, and (c) RA–Ni–$MoO_3$.

On the other hand, in the case of RA–Ni–$MoO_3$, the decomposition of the intercalated rubeanic acid occurred in the range 280–380 °C accompanied by a strong exothermic peak. This decomposition is higher by almost 250 °C than the decomposition temperature of rubeanic acid itself.

The weight loss caused by the decomposition of the intercalated rubeanic acid was about 13%. From this weight loss data and CHN chemical analysis data of RA–Ni–$MoO_3$, the amount of intercalated rubeanic acid was evaluated to be 0.25 mol/mol of $MoO_3$, about the same as that of nickel ion which was determined by conventional wet methods. The chemical analysis data of C, H, N and Ni were as follows. Anal. Calcd: C, 3.18; H, 0.53; N, 3.71; Ni, 7.78. Found: C, 2.97; H, 0.67; N, 3.15; Ni, 7.27. From these results the molar ratio of rubeanic acid to nickel ion was determined to be 1:1.

The infrared spectra of rubeanic acid ligand, $Ni_{0.25}(H_2O)_nMoO_3$, and RA–Ni–$MoO_3$ complex are shown in Figure 2, and their band assignments are listed in Table III. The spectra of the rubeanic acid ligand and RA–Ni–$MoO_3$ are illustrated in Figure 2a,c, respectively. In the spectrum of rubeanic acid, in the region of 3000–3500 $cm^{-1}$ there appears three strong bands which can be interpreted by the existence of an $NH_2$ group, whereas in that of the RA–Ni–$MoO_3$ complex those three bands are reduced to one, which appears around 3250 $cm^{-1}$. These results indicate that the nitrogen atoms of rubeanic acid molecule are used for the linking to nickel ion. Interpretation of the spectrum between 2000 and 700 $cm^{-1}$ is more difficult, but there can be seen a great change of the spectrum attributed to some characteristic frequencies such as the deformation and rocking of N–H, C–N, and the S–C–N group. This would seem to be attributed to the presence of a heavy atom bound to the nitrogen and

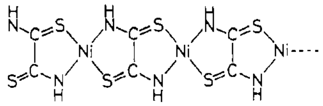

**Figure 3.** Proposed structure of the Ni–RA complex in the interlayer region of $MoO_3$.

sulfur atoms of rubeanic acid molecule. Coordinate bond and coordination forces cause the frequencies of these groups to undergo a considerable displacement.

From the measurement of the magnetic susceptibility, the RA–Ni–$MoO_3$ complex was found to be nearly diamagnetic, while $Ni_{0.25}(H_2O)_nMoO_3$ showed paramagnetic behavior. This result indicates that the rubeanic acids are linking to Ni(II) ions so as to form a square-planar configuration. In contrast, the Ni–RA complex, prepared by the usual precipitate method, exhibited paramagnetic behavior. From this magnetic property, it was concluded that the Ni–RA complex consists of both coplanar and octahedral configurations about the nickel atoms.[12,13]

The electrical resistivities of $Na_{0.5}(H_2O)_nMoO_3$ and $Ni_{0.25}(H_2O)_nMoO_3$ were found to be about 20–30 Ω cm at room temperature; however, in the case of RA–Ni–$MoO_3$, the electrical resistivity was about $10^6$ Ω cm. This high electrical resistivity could be explained by localization of negative charges on $MoO_3$ layers, which was caused by bond formation between O atoms of $MoO_3$ layers and $H^+$ ions released from N atoms of rubeanic acid by chelation with $Ni^{2+}$ ions. The agreement of H values of RA–Ni–$MoO_3$ between the calculated and found values also indicated the presence of $H^+$ ions in the interlayer region of $MoO_3$ layers. Further, the existence of O–H bonding was recognized by the fact that a broad band around 3380 $cm^{-1}$ assignable to stretching vibration of OH was found in the IR spectrum of RA–Ni–$MoO_3$. From these results, it might be considered that the neutral Ni–RA complex was formed in the interlayer space of $MoO_3$.

The present results are summarized below. In this study Ni(II)–RA coordination polymer was first prepared in the interlayer region of $MoO_3$. The molecular structure was estimated from the results of X-ray, DTA, TG, IR, and chemical analyses of the complex and the magnetic susceptibility. These results suggest a possible structure of the intercalated Ni–RA complex as follows: each Ni(II) ion is coordinated with rubeanic acid molecules maintaining the molar ratio of rubeanic acid and Ni(II) ion to be 1:1, and as a whole the Ni–RA complex forms a linear polymeric configuration as illustrated in Figure 3.

This structure could be supported by the following considerations. The interatomic distance between $Ni^{2+}$ ions of the above mentioned model is in good agreement with that obtained from an approximate calculation, assuming even distribution of $Ni^{2+}$ ions in $Ni_{0.25}MoO_3$. Further, rubeanic acid takes a trans conformation in the solid state,[14] and this chelating ligand has a tendency to coordinate with $Ni^{2+}$ ion to give a chelate complex. In the future the authors will attempt to remove the intercalated Ni–RA complex from $MoO_3$.

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**Registry No.** $MoO_3$, 1313-27-5; $Na_{0.5}(H_2O)_nMoO_3$, 68510-66-7; $Ni_{0.25}(H_2O)_nMoO_3$, 68510-67-8; Ni–RA, 54787-47-2; RA, 79-40-3.

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# On the Role of the Bridging Ligand in Electrochemical Inner-Sphere Electron-Transfer Processes

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The treatment of the relative electron-transfer rates for electrochemical inner- and outer-sphere pathways in terms of "intrinsic" and "thermodynamic" contributions is discussed in order to explore the possible roles of bridging ligands in catalyzing such processes. By combining rate measurements with adsorption data for the appropriate ligand-bridged intermediates, this treatment has been applied to some inner- and outer-sphere reactions involving Cr(III)/Cr(II) and Co(III)/Co(II) couples at the mercury–aqueous interface. For complexes containing azide and thiocyanate bridging ligands, the rate increases that result from the presence of ligand-bridged pathways appear to arise merely from the presence of more favorable thermodynamic work terms, rather than by a decrease in the reorganization energy required for electron transfer. A similar conclusion applies, although with less certainty, to chloride and bromide bridges. The physical relation between the reorganization barriers for heterogeneous and homogeneous inner-sphere processes is also considered, and the extent of catalysis of heterogeneous and homogeneous Cr(III)/Cr(II) exchange reactions by bridging anions is compared. Sizable decreases in the intrinsic reorganization barrier for ligand-bridged vs. outer-sphere pathways are seen for the homogeneous exchange reactions, but negligible or only modest decreases are seen for the corresponding electrochemical processes. The explanation for these differences is sought in terms of electronic coupling effects between the homogeneous reacting centers.

## Introduction

The structure of the electrode–solution interface is both expected and generally found to have a marked influence on the kinetics of heterogeneous electron-transfer reactions. This influence is simplest and best understood for electrode reactions that proceed via outer-sphere pathways, i.e., where both the reactant's and the electrode's coordinated ligands remain intact during electron transfer,[1] since only weak electrostatic in-