Separation of a Nickel(II)–Rubeanic Acid Complex prepared on Interlamellar Surfaces of Molybdenum Trioxide

By **S. Son, N. Kinomura, F. Kanamaru,** and **M. Koizumi,*** The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan

A stable Ni^{II}–rubeanic acid co-ordination polymer prepared in the interlayer space of MoO_3 has been separated by dissolving the MoO_3 layers. The molecular structure of the separated complex has been examined by chemical analysis, thermogravimetry, i.r. spectroscopy, and magnetic measurements, and the structure and properties compared with those of a Ni^{II}–rubeanic acid co-ordination polymer prepared by the usual precipitation method. It is concluded that the two methods of preparation result in different forms of the nickel complex.

PREVIOUS studies of the i.r. spectra [1,2] of the polymeric 1 : 1 complexes of Ni^{II}, Cu^{II}, and Co^{II} with rubeanic acid [dithio-oxamide, $H_2NC(S)(S)CNH_2$] have shown that the metal ion is co-ordinated to sulphur and nitrogen and it was concluded that the nickel(II) complex was a simple linear-chain polymer with a square-planar configuration about the nickel atoms. However, magnetic studies have shown that the nickel complex with its anomalous magnetic moment may be basically regarded as containing planar units with a proportion of octahedral sites which may arise from the interaction between the nickel and S or N atoms of adjacent groups.[3,4] This ambiguity in structure is still unresolved and restricts further discussions of the various physical properties. Therefore, the synthesis of a stereospecific co-ordination polymer is now essential.

The first reported attempt to control the stereoregularity of the co-ordination compound was Kanda and co-workers [5] who synthesized the polymer by a so-called monolayer method in which monolayer films of the ligand were spread on the surface of an aqueous solution containing transition-metal ions. However, it is very difficult in practice to prepare the monomolecular film using this method. Another disadvantage is that the yield of sample is very small (*ca.* 1 mg per m^2 water surface). We first attempted to prepare the nickel(II)–rubeanic acid co-ordination polymer by utilizing the two-dimensional interlayer space of MoO_3, the stereoregularity of which enables one to control the bonding between the transition-metal ions and the ligands.[6] Only one type of stereospecific co-ordination polymer with a coplanar configuration about the nickel atoms could be easily prepared. In order to investigate the intrinsic properties of this co-ordination polymer it is necessary to remove it from the host material.

The present paper reports this separation, and describes the structure and properties of the complex as found by chemical analysis, thermogravimetry, i.r. spectroscopy, and magnetic susceptibility measurements.

EXPERIMENTAL

Preparations.—Large flakes and powders of $Ni_{0.25}MoO_3$ were prepared by the method described previously.[6] Rubeanic acid (Nakarai Chemicals Ltd.) was purified by recrystallization from ethanol.

The synthesis of the Ni^{II}–rubeanic acid (H_2ra) co-ordination polymer in the interlayer region of MoO_3 was conducted as follows. Host $Ni_{0.25}MoO_3$ material was soaked in an acetone solution saturated with rubeanic acid, and kept at 60 °C for a few days. In order to remove the free ligand, the product was washed several times with acetone and dried *in vacuo*. The final product is denoted as ra–Ni–MoO_3.

The separation of the Ni^{II}–ra complex from MoO_3 was performed as follows. About 1 g of ra–Ni–MoO_3 was immersed in boiling $[NH_4]Cl$ solution (1 mol dm^{-3}, 200 cm^3) for *ca.* 1 h, and the residual fine black precipitates that could not be filtered off were separated from the mother-liquor by centrifugation. For washing, the colloidal precipitates were suspended in water and centrifuged. The complex was dried *in vacuo*.

Measurements.—The elemental analysis (C, H, N, and S) for all the complexes was made by using standard techniques. Quantitative analysis for Ni and Mo was conducted by a conventional wet method and by atomic absorption. Differential thermogravimetric analysis was carried out up to 700 °C by using a Rigaku-Denki unit programmed for a heating rate of 10 °C min^{-1}.

Infrared spectra in the region 700—4 000 cm^{-1} were obtained on a Hitachi–Perkin-Elmer spectrophotometer equipped with a sodium chloride prism. Samples were dispersed in potassium bromide disks, and the spectrophotometer was calibrated by using the bands of polystyrene.

Magnetic susceptibilities were determined by the Faraday method, using a magnetic field of *ca.* 10 000 G.† The measurements were conducted between 80 and 300 K. The equipment was calibrated by measuring the magnetic susceptibility of $[NH_4]_2Fe[SO_4]_2\cdot 6H_2O$.

RESULTS AND DISCUSSION

The chemical analysis data for the Ni–ra co-ordination polymer [denoted Ni–ra(bulk) hereafter], which was prepared by the usual precipitation method, and the Ni–ra complex, completely separated from ra–Ni–MoO_3 [denoted Ni–ra(layer)], are listed in Table 1. The calculated values for each element assumed that the molecular structure of the Ni–ra complex is composed of an infinite linkage of nickel and ligand with a 1 : 1 mol ratio. The results indicate that the Ni–ra(layer) complex was removed from the MoO_3 layers of ra–Ni–MoO_3 with the maintenance of this 1 : 1 mol ratio. The poor agreement between the observed and cal-

---

† Throughout this paper: 1 G = 10^{-4} T.

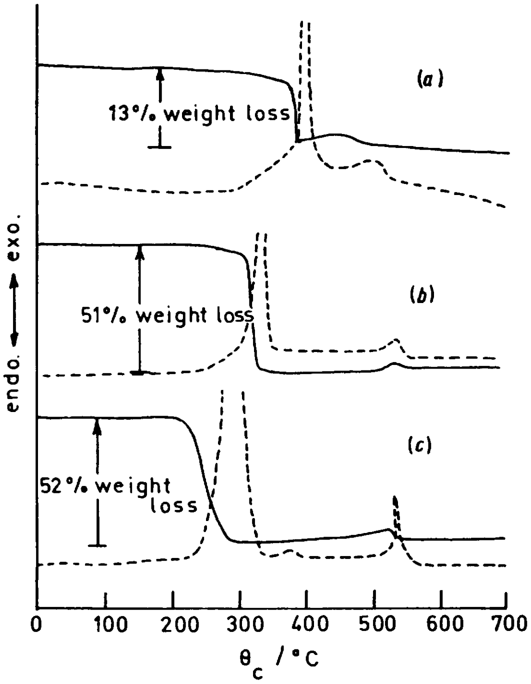
culated data is probably due to a small amount of partially decomposed ligand and of host material introduced during the separation process. At the present stage we have not been able to develop a more effective method of removing the Ni–ra complex from the MoO_3 host material.

TABLE 1

Chemical analysis data (%) of Ni–ra(bulk) and Ni–ra(layer)

	C	H	N	S	Ni	Mo
Calc. for $(C_2H_2N_2S_2)Ni$	13.6	1.15	15.85	36.3	33.2	
Ni–ra(bulk) $(C_2H_2N_2S_2)_{1.06}Ni$	13.85	1.20	16.0	37.25	32.05	
Ni–ra(layer) $(C_{2.2}H_2N_2S_2)_{1.03}Ni$	13.85	1.05	14.5	33.25	29.85	4.60

Thermal analysis data for ra–Ni–MoO_3, Ni–ra(layer), and Ni–ra(bulk) are illustrated in the Figure. In the case of Ni–ra(layer), the weight loss began at 220 °C and ended at *ca.* 330 °C accompanied by a strong exothermic peak which appeared 110 °C lower than for ra–Ni–MoO_3. These strong exothermic peaks correspond to the decomposition of rubeanic acid. The thermal analysis of Ni–ra(layer) resembles that of Ni–ra(bulk) as is shown in Figure (*c*), indicating that the two co-ordination polymers are similar. From the thermal study of Ni–ra(bulk), it was found that the decomposition temperature varied between 280 and 330 °C and was not reproducible. Even duplicate preparations by the same method at the same time resulted in different decomposition temperatures. This variation was also found in the magnetic behaviour.



Thermal analysis data of (*a*) ra–Ni–MoO_3, (*b*) Ni–ra(layer), and (*c*) Ni–ra(bulk). Solid and broken lines indicate t.g. and d.t.a. curves, respectively

The i.r. bands of rubeanic acid, Ni–ra(bulk), and Ni–ra(layer) and their assignments, taken from refs. 2 and 7—9, are listed in Table 2. The spectra of both Ni–ra(bulk) and Ni–ra(layer) differ from that of ra because of the complex formation between rubeanic acid and Ni^{2+} according to equation (1). The spectra of Ni–

$$nNi^{2+} + nH_2NCSSCNH_2 \longrightarrow [\{Ni(HNCSSCNH)\}_n] + 2nH^+ \quad (1)$$

ra(bulk) and Ni–ra(layer) between 3 500 and 1 000 cm^{-1} are very similar. However, in the region of 700—900 cm^{-1} there is an obvious difference. Thus, in the case of Ni–ra(bulk) there are two narrow bands at 872 and 835 cm^{-1} and a broad band at 774 cm^{-1}, whereas for Ni–ra(layer) there is one narrow band at 870 cm^{-1} and one broad band at 770 cm^{-1}. We conclude from ref. 10 that the band near 770 cm^{-1} could be attributed to the displacement of the N–H deformation band of rubeanic acid (at 695 cm^{-1}) on complex formation. The bands in the region of 900 to 800 cm^{-1} were assigned to the C–S stretching vibration. In the spectrum of Ni–ra(bulk), the two stretching vibrations of the C–S group were observed at 872 and 835 cm^{-1}, indicating two different configurations around the Ni atoms. The spectra of Ni–ra(layer) and ra–Ni–MoO_3 [6] show only one band around 870 cm^{-1}. The band near 835 cm^{-1} was absent for these two complexes. From the previous study on ra–Ni–MoO_3 and the magnetic properties of Ni–ra(layer), the band around 870 cm^{-1} was attributed to the C–S stretching vibration in a planar configuration and the band around 835 cm^{-1} to an octahedral configuration.

TABLE 2

Infrared bands (cm^{-1}) of ra, Ni–ra(bulk), and Ni–ra(layer)

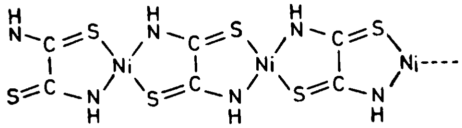
Rubeanic acid	Assignments [2,8–11]	Ni–ra (bulk)	Ni–ra (layer)	Assignment
3 275m				
3 190m	$\nu(NH_2)$	3 248s, br	3 248m	$\nu(NH)$
3 144m				
		1 600m	1 600m	
1 585vs, br	$\delta(NH_2)$			
1 428s, br	$\nu(CN)$	1 480s, br	1 480s, br	$\nu(CN)$
1 201m	$\rho(NH_2)$	1 102m	1 108m	$\delta(NH)$
		1 020m	1 020w	
		872m	870m	$\nu(CS)$
832s	$\nu(CS)$	835m		
695m	$\omega(NH_2)$	774m	770m	$\omega(NH)$

The Ni–ra(layer) complex separated from ra–Ni–MoO_3 was found to be diamagnetic. The diamagnetism of both ra–Ni–MoO_3 and Ni–ra(layer) indicates a square-planar N_2S_2 co-ordination geometry about the nickel ion. For Ni–ra(bulk), paramagnetic behaviour was observed. Menabue *et al.*[3] reported the presence of 70—80% octahedral co-ordination in Ni–ra(bulk), whereas Kanekar and Casey[4] estimated that this complex contained 80% planar units and 20% octahedral units. It should be noted that the Ni–ra(bulk) co-ordination polymer in this investigation[4] lacked reproducibility in its structure.

The basis for the separation of Ni–ra(layer) from ra–Ni–MoO_3 can be explained as follows. As discussed previously,[6] the O–H bonding between the O atoms of the MoO_3 layers and the H^+ ions released from rubeanic acid was recognized after the reaction of $Ni_{0.25}MoO_3$ with rubeanic acid. This O–H bond formation in the MoO_3 layers seems to have changed the host layers of molybdenum bronze to molybdenum blue. Usually, molybdenum blue is obtained by mild reduction of an acidified solution of molybdates or of aqueous suspensions of MoO_3. This molybdenum blue actually contains both the oxide and hydroxide, and is stable to NH_3 and alkali, but is soluble in acidic solutions.

Conclusions.—In this study, a stable Ni–ra co-ordination polymer prepared in the interlayer space of MoO_3 was first separated by dissolving the MoO_3 layers. The molecular structure was estimated from the results of d.t.a., t.g., i.r., and chemical analysis and the magnetic susceptibility. From the C, H, N, S, and Ni elemental analysis together with the weight loss, the mol ratio of rubeanic acid to nickel ion was determined to be 1 : 1. This ratio, the high decomposition temperature, and the low solubility indicate that the complex is a co-ordination polymer. Both i.r. spectra and diamagnetic susceptibility data of Ni–ra(layer) clearly indicate that the rubeanic acid is linked to Ni^{2+} so as to form a square-planar configuration, as shown below.

Thus, the possibility of preparing a stereospecific co-ordination polymer by using a two-dimensional interlayer space and of separating it from the host material has been established.



The authors thank Professor S. Kanda of Tokushima University for his helpful discussion, and Mr. T. Fujino for C, H, and N analyses.

[9/1004 *Received, 27th June*, 1979]

REFERENCES

[1] J. Barceló, *Spectrochim. Acta*, 1958, **10**, 245.

[2] R. N. Hurd, G. De La Mater, G. C. McElheny, and J. P. McDermott, 'Advances in the Chemistry of Coordination Compounds,' McMillan, 1961, p. 350.

[3] L. Menabue, C. C. Pellicani, and G. Peyronel, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 187.

[4] C. R. Kanekar and A. T. Casey, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3105.

[5] A. Suzuki, K. Ohkawa, S. Kanda, M. Emoto, and S. Watari, *Bull. Chem. Soc. Japan*, 1975, **48**, 2643.

[6] S. Son, F. Kanamaru, and M. Koizumi, *Inorg. Chem.*, 1979, **18**, 400.

[7] T. A. Scott and E. L. Wagner, *J. Chem. Phys.*, 1959, **30**, 465.

[8] B. Milligan, E. Spinner, and J. M. Swan, *J. Chem. Soc.*, 1961, 1920.

[9] H. O. Desseyn and W. A. Herman, *Spectrochim. Acta*, 1969, **A25**, 1685.

[10] S. Kanda, A. Suzuki, and K. Ohkawa, *Ind. and Eng. Chem. (Product Res. and Development)*, 1973, **12**, 88.