Magnetic Properties of Diisothiocyanatobis(thiourea)nickel(II) and Related Complexes

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The magnetic susceptibilities of diisothiocyanatobis(thiourea)nickel(II), diisothiocyanatobis(*N,N'*-dimethylthiourea)nickel(II), diisothiocyanatobis(2-thioimidazolidinone)nickel(II), diisothiocyanatobis(2-thiopyrrolidone)nickel(II), and diisothiocyanatobis(thioacetamide)nickel(II) were observed between the liquid-helium temperature and room temperature. Except for the second complex, antiferromagnetic interaction operates between one-dimensional nickel chains, within each of which ferromagnetic spin coupling exists. The exchange integrals, J within a chain and J' between chains, were evaluated on the basis of the coupled-double-chain model and the molecular-field model. The absence of interaction between chains in the crystals of the second complex can be accounted for by the presence of bulky *N,N'*-dimethylthiourea molecules between chains. The antiferromagnetic interactions between chains in the crystals of other complexes are attributable to the presence of bridging arrangements between chains, as is indicated by X-ray analysis.

The X-ray crystal analysis of diisothiocyanatobis(thiourea)nickel(II), $Ni(tu)_2(NCS)_2$, was carried out by Nardelli *et al.*,[1,2] who found that nickel ions are bridged by sulfur atoms belonging to thiourea to form linear chains in the crystal, as is shown in Fig. 1. Belova *et al.*[3] determined the magnetic susceptibility of this compound in a range between the liquid-nitrogen temperature and room temperature and suggested the presence of ferromagnetic spin interaction between nickel ions. The compound attracted attention as a model compound for one-dimesional ferromagnets. Flint and Goodgame[4] performed similar studies on a series of compounds with the general formula of $M(tu)_2(NCS)_2$ (M=Mn, Fe, Co, Ni), which had been confirmed by Nardelli *et al.*[5] to be isomorphous with the nickel complex. With decreasing temperature, the observed susceptibilities were found to deviate from the Curie-Weiss law, the deviations being inexplicable by an Ising model with spins $S=1$. However, because of the lack of low-temperature data, no further conclusions could be drawn. On the other hand, the X-ray crystal analyses[6,7] and infrared absorptions[8,9] of $Ni(tim)_2(NCS)_2$ (tim=2-thioimida-

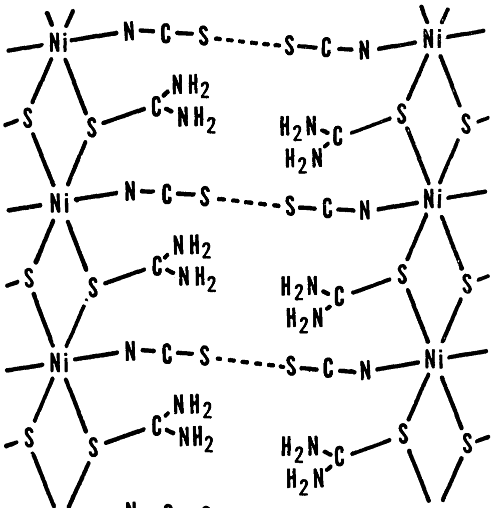

Fig. 1. Structure of $Ni(tu)_2(NCS)_2$.

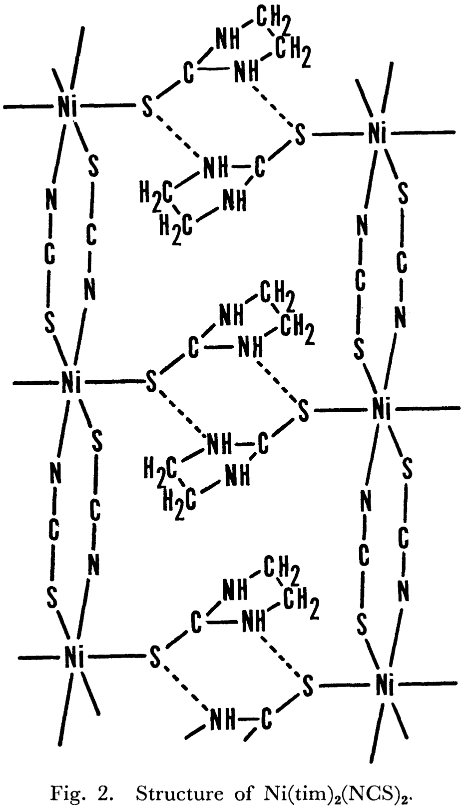

Fig. 2. Structure of $Ni(tim)_2(NCS)_2$.

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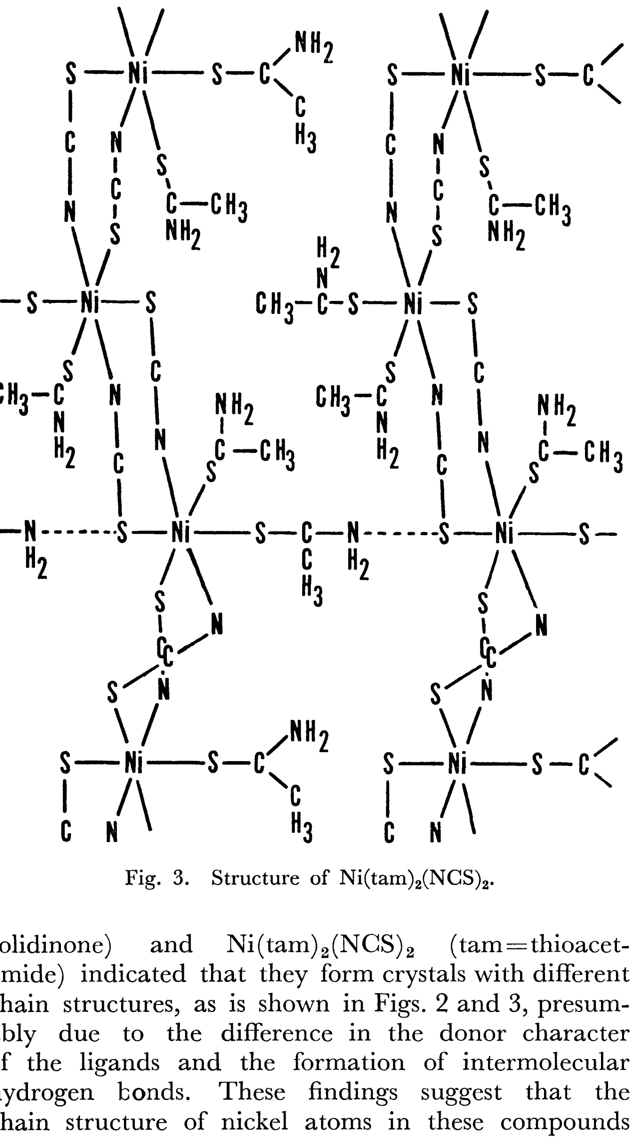

Fig. 3. Structure of Ni(tam)$_2$(NCS)$_2$.

zolidinone) and Ni(tam)$_2$(NCS)$_2$ (tam=thioacetamide) indicated that they form crystals with different chain structures, as is shown in Figs. 2 and 3, presumably due to the difference in the donor character of the ligands and the formation of intermolecular hydrogen bonds. These findings suggest that the chain structure of nickel atoms in these compounds do not represent simple one-dimensional ferromagnets, but involve magnetic interactions between chains. The present investigation has been undertaken in order to discuss magnetic interaction within a chain and between chains in these nickel complexes on the basis of the magnetic susceptibilities observed between the liquid-helium temperature and room temperature.

Experimental

Preparation of Materials. The crystals of Ni(tu)$_2$(NCS)$_2$, Ni(tim)$_2$(NCS)$_2$, and Ni(tam)$_2$(NCS)$_2$ were prepared by methods proposed by Nardelli *et al.*[1,10,11] Commercial preparations of thiourea and 2-thioimidazolidinone were allowed to react with nickel(II) thiocyanate. The resulting complexes were recrystallized from water and a 1 : 1 mixture of ethanol and water, respectively. In preparing Ni(tam)$_2$(NCS)$_2$ in a similar manner, nickel(II) sulfide precipitated during recrystallization. Therefore, a commercial preparation of thioacetamide was purified in advance by recrystallization from benzene, and then allowed to react with nickel(II) thiocyanate. The X-ray powder patterns of these compounds agreed with the data reported in the literature.[1,2,6,7] Found: Ni, 17.84%. Calcd for Ni(tu)$_2$(NCS)$_2$: Ni, 17.95%. Found: Ni, 15.42%. Calcd for Ni(tim)$_2$(NCS)$_2$: Ni, 15.48%. Found: Ni, 17.94%. Calcd for Ni(tam)$_2$(NCS)$_2$: Ni, 18.05%. The crystals of Ni(dmt)$_2$(NCS)$_2$ (dmt=*N,N'*-dimethylthiourea) were obtained in the same manner as for Ni(tu)$_2$(NCS)$_2$, using *N,N'*-dimethylthiourea in place of thiourea. Found: Ni, 15.11; C, 25.27; N, 21.77; H, 4.41%. Calcd for Ni(dmt)$_2$(NCS)$_2$: Ni, 15.32; C, 25.07; N, 21.93; H, 4.22%. For the preparation of Ni(tpl)$_2$(NCS)$_2$ (tpl=2-thiopyrrolidone), thiopyrrolidone was synthesized by a method reported by Mecke and Mecke[12] and was recrystallized from xylene (fractionated isomeric mixture). A calculated quantity of this starting material was added to a solution of nickel(II) thiocyanate in a 1 : 1 mixture of ethanol and water. The system was heated to dissolve the solid and then filtered. The filtrate was evaporated until crystals separated. Found: Ni, 15.60; C, 32.15; N,14.67 ; H, 3.73%. Calcd for Ni(tpl)$_2$(NCS)$_2$: Ni, 15.56; C, 31.84; N, 14.86; H, 3.75%.

Magnetic Measurements. Above the liquid-nitrogen temperature, the magnetic susceptibility was determined[13] by the Gouy method, using an Ainsworth recording semi-microbalance, the magnetic field strength amounting to about 3000 Oe. The temperature was determined by means of a copper-constantan thermocouple. In a temperature range of 4.2—80°K, the Faraday method was employed by the use of a torsion balance. The accuracy was estimated to be about ±1.5%. The temperature was measured within an accuracy of ±0.1°K by using an Allen-Bradley carbon thermometer below about 10°K and an Au/Co-Pt thermocouple between 10 and 80°K.

The observed molar susceptibilities have been corrected for diamagnetic contributions from ligands (in 10^{-6} emu/mol): nickel ions, -12;[14] thiocyanate ions, -35;[14] thiourea, -42;[15] *N,N'*-dimethylthiourea, -65;[15] 2-thioimidazolidinone, -61;[14] thiopyrrolidone, -61;[14] and thioacetamide, -42.[16] The temperature-independent paramagnetism was assumed to be equal to 193×10^{-6} emu/mol.[17]

Results

The observed magnetic susceptibilities corrected for diamagnetic contributions and the temperature-independent paramagnetism obey the Curie-Weiss law at high temperatures. The reciprocal susceptibility, $1/\chi$, is plotted in Figs. 4—8 against the temperature, emphasis being laid on data in the low-temperature region, where deviations from the Curie-Weiss law are rather marked. The Weiss constants and

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11) M. Nardelli and I. Chierici, *ibid.*, **88**, 359(1958).

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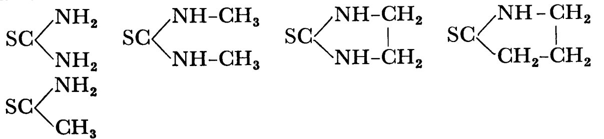
TABLE 1. THE EFFECTIVE MAGNETIC MOMENT μ_{eff} AT ROOM TEMPERATURE (20°C), THE WEISS CONSTANT θ, THE g-VALUE EVALUATED FROM THE CURIE CONSTANTS C, AND THE TEMPERATURE T_m OF THE MAXIMUM SUSCEPTIBILITY OF $NiL_2(NCS)_2$

	μ_{eff} (B.M.)	θ (°K)	g	T_m (°K)
$Ni(tu)_2(NCS)_2$[a]	3.36	41.8[f]	2.18	11.0
$Ni(dmt)_2(NCS)_2$[b]	3.31	53.8	2.12	—[g]
$Ni(tim)_2(NCS)_2$[c]	3.11	11.2	2.16	8.3
$Ni(tpl)_2(NCS)_2$[d]	3.10	10.3	2.17	8.4
$Ni(tam)_2(NCS)_2$[e]	3.13	16.2	2.18	—[g]

a) tu: Thiourea. b) dmt: *N,N'*-Dimethylthiourea. c) tim: Thioimidazolidinone. d) tpl: 2-Thiopyrrolidone. e) tam: Thioacetamide.



f) The value agrees with 40°K reported by Flint and Goodgame.[4] g) T_m was not observed.

the g-values evaluated from the Curie constants are listed in Table 1. The Weiss constants are positive, indicating that ferromagnetic interaction is predominant.

Discussion

The crystal structure of diisothiocyanatobis(thiourea)nickel(II), $Ni(tu)_2(NCS)_2$, shown in Fig. 1 suggests that the predominant ferromagnetic interaction arises from magnetic interaction through Ni–S–Ni bonds within a one-dimensional nickel chain.

Suzuki *et al.*[18] calculated the parallel susceptibility, χ, of a one-dimensional lattice consisting of Ising spins of $S=1$.

$$\frac{kT\chi}{Ng^2\beta^2}=\frac{1}{2a^2(a+2)}\left[1+\frac{4a^3+5a^2-a+1}{a[(a+a^{-1}-1)^2+8]^{1/2}}\right] \tag{1}$$

where $a=\exp(-2J/kT)$, J is the exchange integral between the nearest neighboring spins in the one-dimensional lattice, T is the absolute temperature, g is the g-value, and β is the Bohr magneton.

Using $g=2.18$, as evaluated from the Curie constant, and assuming $J/k=17$°K, the parallel susceptibility was calculated to be as is shown by a broken curve in Fig. 4. Although the curve well reproduces the experimental data above about 70°K, agreement is poor below this temperature. In addition, the curve of the observed susceptibility shows a maximum at 11.0°K. Accordingly, it is concluded that a weak lateral antiferromagnetic interaction operates between linear chains.

For one-dimensional lattices consisting of spins $S=1/2$, the magnetic susceptibility has been calculated with the Heisenberg model.[19] However, because of the mathematical difficulties involved, rigorous calculations have not been performed for spins greater than 1/2. The series expansion method developed by Rushbrooke and Wood[20] gives a rather poor agreement with the experimental data, because the series converges slowly except at temperatures well above the Néel temperature. Therefore, the following analysis is developed on the basis of the Ising model.

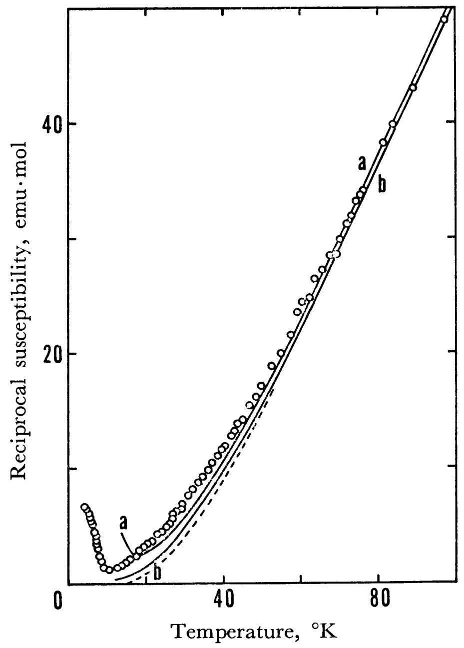


Fig. 4. Reciprocal susceptibility of $Ni(tu)_2(NCS)_2$ as a function of temperature.
Broken curve: Ising model (Eqs. (1) and (2)). Solid curve a: Coupled-double-chain model (Eq. (11)). Solid curve b: Molecular-field model (Eq. (14)).

Although Eq. (1) is rigorous for an isolated one-dimensional lattice, it is difficult to incorporate the effect of interaction between chains into the equation. Therefore, the following alternative method was used. Flint and Goodgame[4] analyzed the susceptibility of $Ni(tu)_2(NCS)_2$ by extending the theoretical equation for the linear Ising model with $S=1/2$ to $S\geq 1$.

$$\chi=\frac{Ng^2\beta^2S(S+1)}{3kT}\exp(j/kT) \tag{2}$$

This equation is based on "reduced" spin magnetic moments capable of orienting only in parallel and antiparallel directions defined as

$$\mu=\frac{1}{2}\left[\frac{S(S+1)}{3/4}\right]^{1/2}g\beta \tag{3}$$

The parameter, j, is related to the exchange integral, J, by[21]

$$j=\frac{S(S+1)}{3/4}J \tag{4}$$

As was pointed out by Flint and Goodgame,[4] Eq. (2) well reproduces the observed susceptibility of

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[20] G. S. Rushbrooke and P. J. Wood, *Mol. Phys.*, **1**, 257(1958).

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Table 2. Exchange integrals, J within a chain and J' between chains, in the crystals of some nickel(II) complexes evaluated by the Ising model (Eq. (1)), the coupled-double-chain model (Eq. (11)), and the molecular-field model (Eq. (14))

	Ising model	Coupled-double-chain model		Molecular-field model	
	$J/\boldsymbol{k}$ (°K)	$J/\boldsymbol{k}$ (°K)	$-J'/J$	$J/\boldsymbol{k}$ (°K)	$-J'/J$
$Ni(tu)_2(NCS)_2$	17	19	0.02_0	19	0.002
$Ni(dmt)_2(NCS)_2$	20	21	0	21	0
$Ni(tim)_2(NCS)_2$	3.0	3.6	0.2_0	3.6	0.27
$Ni(tpl)_2(NCS)_2$	3.0	3.6	0.2_0	3.6	0.28
$Ni(tam)_2(NCS)_2$	4.5	4.6	0.03_3	4.6	—[a]

[a] Because T_m was not observed, J' cannot be estimated.

$Ni(tu)_2(NCS)_2$ at high temperatures, but gives poor agreement with it at low temperatures because of the presence of interaction between chains.

For mutually interacting one-dimensional lattices of spins $S=1/2$, theoretical equations have been derived on the basis of a coupled-double-chain model[22,23] as well as a molecular-field model.[24] In the former model, a pair of interacting chains is considered to obtain the magnetic susceptibility given by[23]

$$\frac{\boldsymbol{k}T\chi}{Ng^2\beta^2}=\frac{e^{2K}(e^{K'}R-\sinh^2 K)}{4(R-e^{K'}\sinh 2K)(\cosh^2 K'\cosh^2 2K-\sinh^2 2K)^{1/2}} \tag{5}$$

In this expression,

$$R=\cosh K'\cosh 2K+(\cosh^2 K'\cosh^2 2K-\sinh^2 2K)^{1/2} \tag{6}$$

$$K=j/2\boldsymbol{k}T \tag{7}$$

$$K'=zj'/2\boldsymbol{k}T \tag{8}$$

where j is the exchange integral within a chain, j' is that between chains, and z is the number of nearest chains. In the latter model, antiferromagnetic interaction between Ising chains lying in a plane in parallel to one another is approximated by a molecular field to yield the parallel susceptibility given by[24]

$$\frac{\boldsymbol{k}\chi}{Ng^2\beta^2}=\frac{1}{4}e^{j/\boldsymbol{k}T}\left\{T+T_c\exp\left[\frac{j}{\boldsymbol{k}}\left(\frac{1}{T}-\frac{1}{T_c}\right)\right]\right\}^{-1} \tag{9}$$

where the parameter, T_c, expressing the interaction between chains is equal to the temperature, T_m, of the maximum susceptibility and is related to the exchange integral, j', between chains by

$$j'=-T_c\exp(-j/\boldsymbol{k}T_c) \tag{10}$$

where the first minus sign on the right-hand side takes into account the antiferromagnetic interaction between chains ($j'<0$). Needless to say, Eq. (5) and Eq. (9) lead to Eq. (2) when $K'=0$ and $T_c=0$, respectively.

Equations (5) and (9), which are valid for $S=1/2$, were extended to $S=1$ using the reduced spin model. The former equation leads to

$$\frac{\boldsymbol{k}T\chi}{Ng^2\beta^2}=\frac{2e^{2K}(e^{K'}R-\sinh 2K)}{3(R-e^{K'}\sinh 2K)(\cosh^2 K'\cosh^2 2K-\sinh^2 2K)^{1/2}} \tag{11}$$

where, in accordance with Eqs. (4), (7), and (8), K and K' are given by

$$K=4J/3\boldsymbol{k}T \tag{12}$$

$$K'=4zJ'/3\boldsymbol{k}T \tag{13}$$

On the other hand, Eq. (9) is extended to

$$\frac{\boldsymbol{k}\chi}{Ng^2\beta^2}=\frac{2}{3}e^{8J/3\boldsymbol{k}T}\left\{T+T_c\exp\left[\frac{8J}{3\boldsymbol{k}}\left(\frac{1}{T}-\frac{1}{T_c}\right)\right]\right\}^{-1} \tag{14}$$

where T_c is related to the exchange integral, J', between chains by (see Eqs. 4 and 10)

$$J'=-\frac{3}{8}T_c\exp(-8J/3\boldsymbol{k}T_c) \tag{15}$$

As is shown in Fig. 4, the susceptibility of $Ni(tu)_2(NCS)_2$ can be expressed by Eq. (2) above about 70°K with the parameter, $j/\boldsymbol{k}$, equal to 51°K. This, along with Eq. (4), yields the exchange integral within a chain given by $J/\boldsymbol{k}=19$°K. Using this value for J, and assuming that $J'/J=-0.02$ (Table 2), theoretical calculation was performed on the basis of the coupled-double-chain model (Eq. (11), $z=2$). The result is shown by a solid curve in Fig. 4. The agreement with the experimental data is excellent except for the region near the temperature of the maximum susceptibility.

The susceptibility was calculated theoretically by means of the molecular-field model also (Eq. (14)). As has been mentioned above, the parameter, J, can be evaluated from the data in the high-temperature region as $J/\boldsymbol{k}=19$°K. From this, along with the observed temperature of the maximum susceptibility, T_m ($=T_c=11$°K), J' can be calculated by means of Eq. (15) as $J'/\boldsymbol{k}=0.04$°K. The solid curve b in Fig. 4 shows the results of calculation by means of Eq. (14) using these parameters. The agreement of the theoretical curve with the experimental data is satisfactory. Thus, the ratio, $-J'/J$, of the exchange integral between chains to that within a chain is estimated to be of the order of 0.002—0.02.

The observed positive value for J implies that ferromagnetic interaction exists within a chain. This is anticipated because two orthogonal sp^2 orbitals of a sulfur atom are involved in magnetic interaction through a Ni–S–Ni linkage.

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On the other hand, the negative value for J' indicates that antiferromagnetic interaction predominates between chains through Ni–NCS···SCN–Ni linkages. In fact, the distance between the nearest sulfur atoms belonging to neighboring chains amounts to 3.45 Å, which is smaller than the sum (3.70 Å) of van der Waals radii.[1,2]

The observed susceptibility of diisothiocyanatobis-(N,N'-dimethylthiourea)nickel(II), $\mathrm{Ni(dmt)_2(NCS)_2}$, shows no maximum in the temperature range investigated (see Fig. 5) and can be reproduced by Eq. (1) with $g=2.12$, as evaluated from the Curie constant and $J/k=20$°K. The exchange integral is not much different from that of $\mathrm{Ni(tu)_2(NCS)_2}$ (see Table 2). In addition, the X-ray powder patterns bear a close resemblance to those of $\mathrm{Ni(tu)_2(NCS)_2}$, the crystal of which belongs to the triclinic system and yields a very complicated powder spectrum. Accordingly, it is concluded that this compound has one-dimensional nickel chains similar to those in $\mathrm{Ni(tu)_2(NCS)_2}$. However, the substitution of thiourea with bulky N,N'-dimethylthiourea molecules leads to an increase in the distance between chains leading to a decrease in lateral magnetic interaction, and hence to the absence of any maximum in the susceptibility *versus* temperature curve.

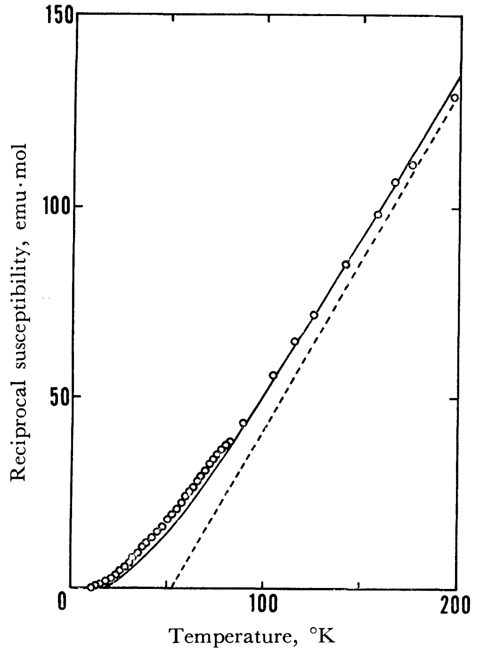

Fig. 5. Reciprocal susceptibility of $\mathrm{Ni(dmt)_2(NCS)_2}$ as a function of temperature.
Broken curve: The Curie-Weiss law. Solid curve: Ising model.

The theoretical equation (2) ($j=8J/3, J/k=21$°K) based on reduced moments also fits experimental data, as is shown by the solid curve in Fig. 5, which is indistinguishable from the curve of Eq. (1). This indicates that both Eq. (1) and Eq. (2) are good approximations to the susceptibility of linear Ising ferromagnets free from lateral interactions.

Diisothiocyanatobis(2-thioimidazolidinone)nickel(II), $\mathrm{Ni(tim)_2(NCS)_2}$, forms one-dimensional lattices of nickel atoms through bridging by thiocyanate ions, as is shown in Fig. 2.[6] Although the Weiss constant is positive (Table 1), the susceptibility assumes a maximum value at 8.3°K, below which antiferromagnetic behavior appears. Theoretical calculations (Eq. (1) with $J/k=3.0$°K and Eq. 2 with $J/k=3.6$°K) for isolated Ising chains give broken curves in agreement with each other (*cf.* Fig. 6), but in poor agreement with the experimental data. This indicates that, in addition to ferromagnetic interaction within a chain, antiferromagnetic interaction exists between chains and gives rise to deviations from theoretical calculations for the Ising model, especially at low temperatures. The only conceivable interaction within a chain is superexchange interaction through Ni–N–C–S–Ni linkages, whereas that between chains is an antiferromagnetic superexchange interaction through Ni–S–C–NH···S–Ni linkages lying on a $(0\bar{1}1)$ plane. This is because NH···S hydrogen bonds exist in the crystals,[6] no other paths being conceivable. From this structure, it can be concluded that $z=2$ in Eq. (15). Theoretical calculations were carried out with Eqs. (11) and (14). Curves calculated with the J'/J ratios listed in Table 2 are shown in Fig. 6. The agreement with the experimental data is excellent.

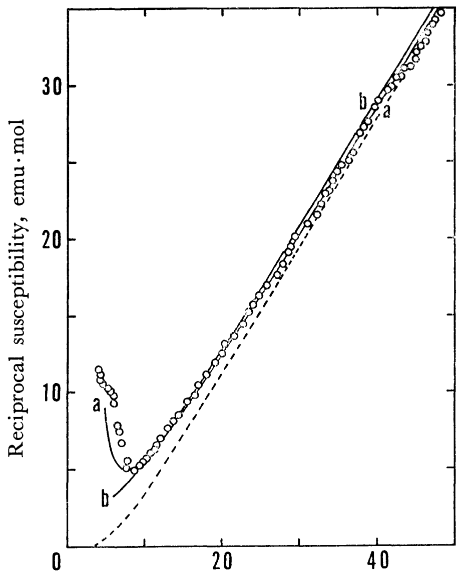

Fig. 6. Reciprocal susceptibility of $\mathrm{Ni(tim)_2(NCS)_2}$ as a function of temperature.
Broken curve: Ising model. Solid curve a: Coupled-double-chain model. Solid curve b: Molecular-field model.

The temperature dependence of the susceptibility of diisothiocyanatobis(2-thiopyrrolidone)nickel(II), $\mathrm{Ni(tpl)_2(NCS)_2}$, bears a striking resemblance to that of $\mathrm{Ni(tim)_2(NCS)_2}$, as is shown in Fig. 7. Theoretical calculations analogous to those employed for the latter compound yield the exchange integrals listed in Table 2. The exchange integrals are also close to the corresponding ones of the latter compound. Accordingly, it is concluded that this compound forms crystals similar to those of $\mathrm{Ni(tim)_2(NCS)_2}$ shown in Fig. 2. The X-ray powder patterns of the two compounds resemble each other in agreement with the

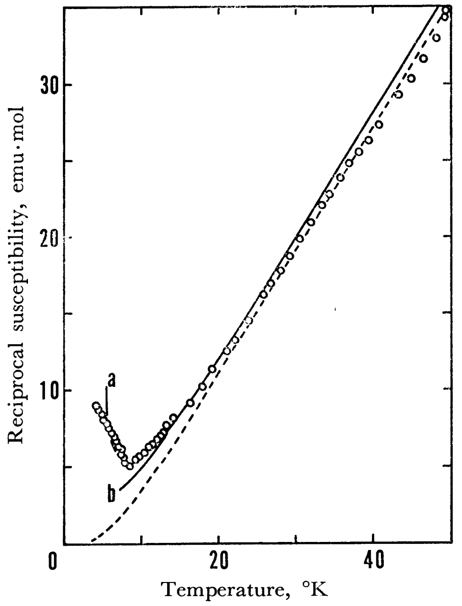

Fig. 7. Reciprocal susceptibility of $Ni(tpl)_2(NCS)_2$ as a function of temperature.
Broken curve: Ising model. Solid curve a: Coupled-double-chain model. Solid curve b: Molecular-field model.

prediction from magnetic measurements.

The crystal structure[7] of diisothiocyanatobis(thioacetamide)nickel(II), $Ni(tam)_2(NCS)_2$, reveals that nickel atoms are bridged by thiocyanate ions to form one-dimensional chains, as is shown in Fig. 3. However, unlike the case with $Ni(tim)_2(NCS)_2$, two thiocarbonyl groups are coordinated on the *cis* positions of the coordination octahedron of a nickel atom. The one-dimensional chain has a threefold screw axis, and the crystal belongs to the rhombohedral system.

At high temperatures, the observed magnetic susceptibility can be explained by both Eq. (1) and Eq. (2), which coincide with each other, as is shown in Fig. 8. Below 40°K, deviations appear from the theoretical curve. However, no maximum susceptibility was observed in the temperature range investigated. Accordingly, calculations are infeasible with the molecular-field model. With the coupled-double-chain model (Eq. (11) with $z=6$), the exchange integrals, J within a chain and J' between chains, were calculated to be as shown in Table 2. The latter amounts to about 3% of the former. If a single chain is replaced by a resultant spin moment, interactions between chains can be represented by those among such resultant moments in two-dimensional triangular lattice. It has been shown theoretically that antiferromagnetic ordering can never be realized in two-dimensional triangular lattices.[25] This seems to be the reason why no transition to an antiferromagnetic state was observed for this compound.

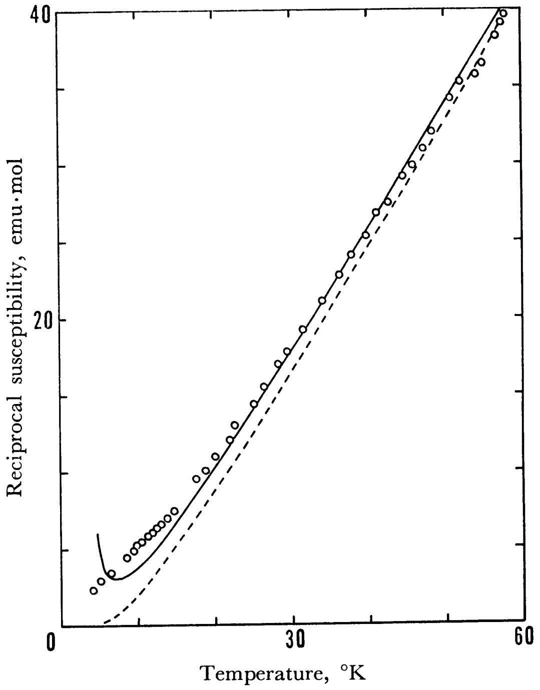

Fig. 8. Reciprocal susceptibility of $Ni(tam)_2(NCS)_2$ as a function of temperature.
Broken curve: Ising model. Solid curve: Coupled-double-chain model.

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