in III. That is $(\tau_{21})^{-1} \gg (T_{22})^{-1}$, $(\tau_{23})^{-1}$ and $(\tau_{32})^{-1} \gg (\tau_{31})^{-1}$.[27,28] If it is also assumed that all $\Delta\omega_i$ terms are small, then

$$(T_{2p})^{-1} = \frac{\tau_{21}}{\tau_{21}}\left\{\frac{1}{T_{22}} + \frac{\tau_{32}}{\tau_{23}(T_{23} + \tau_{32})}\right\} \tag{2A}$$

If $T_{23} \ll \tau_{32}$ because of the hyperfine interaction, then

$$(T_{2p})^{-1} = \frac{\tau_{21}}{\tau_{12}}\left(\frac{1}{T_{22}} + \frac{1}{\tau_{23}}\right) = P_m(\tau_{23})^{-1} \tag{3A}$$

where $P_m = [VO(acac)_2CH_3OH]/[CH_3OH]$. The initial condition that $(T_{22})^{-1}$ is small has been applied to the center expression of (3A).

It is also possible in the present system that only $\Delta\omega_2$ and $(T_{22})^{-1}$ are small relative to the other values in (1A), but that $\Delta\omega_3$ cannot be ignored. This would be more consistent with the condition that T_{23} is short due to a hyperfine interaction since this interaction requires a finite electron–nuclear coupling constant and therefore some finite value for $\Delta\omega_3$. If terms in $\Delta\omega_2$ and $(T_{22})^{-1}$ are dropped and noting that $\lambda_3(\tau_{21})^{-1} + (\tau_{23})^{-1}((T_{23})^{-1} + (\tau_{31})^{-1}) \approx \lambda_3((\tau_{21})^{-1} + (\tau_{23})^{-1})$ since $\lambda_3((\tau_{21})^{-1} + (\tau_{23})^{-1}) \gg (\tau_{32}\tau_{23})^{-1}$, then

$$(T_{2p})^{-1} = \frac{\left\{\frac{1}{\tau_{12}\tau_{23}} + \frac{1}{\tau_{13}}\left(\frac{1}{\tau_{21}} + \frac{1}{\tau_{23}}\right)\right\}\left(\frac{\lambda_3}{T_{23}} + \Delta\omega_3{}^2\right)}{\left(\frac{1}{\tau_{21}} + \frac{1}{\tau_{23}}\right)(\lambda_3{}^2 + \Delta\omega_3{}^2)} \tag{4A}$$

The right-hand terms of the numerator and denominator will cancel under either of the probable conditions $(T_{23})^{-1} \gg (\tau_{32})^{-1}$, $(\tau_{31})^{-1}$ or $\Delta\omega_3{}^2 > \lambda_3{}^2$. If it is also assumed[28] that $(\tau_{21})^{-1} > (\tau_{23})^{-1} > (\tau_{13})^{-1}$, then

$$(T_{2p})^{-1} = \frac{\tau_{21}}{\tau_{12}}\left(\frac{1}{\tau_{23}}\right) = P_m(\tau_{23})^{-1} \tag{5A}$$

The various limiting conditions which have been discussed correspond to easily recognized situations. If $(T_{23})^{-1}$ is short, then nuclear relaxation in site III is very fast and the rate-limiting step for the relaxation in site I is the exchange into III. This might be either I–III or II–III exchange, and under the present circumstances it seems most likely that II–III exchange is faster. Then, as long as I–II exchange is faster than II–III exchange, the nuclear relaxation in site I is controlled by the II–III exchange. Similar considerations apply when $\Delta\omega_3$ is large but then the relaxation occurs through the change in precessional frequency or dephasing of nuclei from site I.

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[27] Values for the exchange lifetimes may be estimated from ref 3, 4, and 28 and the present results on $VO(CH_3OH)_5{}^{2+}$ in methanol.

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Spectral and Magnetic Studies on Thiourea Complexes of Some Metal Thiocyanates

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Infrared and electronic spectra and magnetic measurements are reported for the compounds $M(tu)_2(NCS)_2$ (M = Mn, Fe, Co, Ni, Cd; tu = thiourea). Mössbauer results for the iron compound are also presented. The electronic spectrum of the iron compound is interpreted in terms of a strongly tetragonal ligand field, but for the other compounds too few bands were observed to permit a satisfactory analysis. The manganese compound shows negative and the nickel one positive magnetic interactions but the temperature dependence of the susceptibilities cannot be accounted for by the one-dimensional Ising model. The origin of the magnetic interactions is discussed in terms of the electron configuration of the ions.

Introduction

In the isomorphous[2] series of compounds $M(tu)_2(NCS)_2$ (M = Mn, Fe, Co, Ni, Cd), the coordination polyhedron of the metal ion approximates to D_{4h} symmetry, with infinite chains of bridging sulfur atoms from the thiourea in the plane and nitrogen-bonded thiocyanate groups in the axial positions.[3] The nickel–thiocyanate bond distance (1.99 Å) is one of the shortest known, whereas the nickel–sulfur distances (2.56 and 2.53 Å) are appreciably longer than in $Ni(tu)_4Cl_2$ (2.46 Å).[4] As a part of a study of the spectral and magnetic properties of the complexes of sulfur-donor ligands, we now report the electronic and infrared spectra and the magnetic properties of this interesting series of compounds.

Experimental Section

Preparation of Compounds.—The following general method was used except as stated below. The calculated quantity of thiourea was added to a solution of the metal thiocyanate in water, heated to dissolve the solid, filtered, and cooled (for cobalt and cadmium) or evaporated until crystallization commenced (for nickel and manganese). After filtration the complexes were dried at 50° *in vacuo*. For manganese, only about

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one-third of the calculated quantity of thiourea was used. For the ferrous complex, a solution of ferrous thiocyanate was shaken with finely divided iron until it became green and was then filtered under nitrogen into a deoxygenated solution of thiourea in water. The solution was concentrated *in vacuo*, and the yellow crystalline complex was filtered off under nitrogen and dried *in vacuo*. *Anal.* Calcd for $\mathrm{Mn(tu)_2(NCS)_2}$: C, 14.9; H, 2.5; N, 26.0; Mn, 17.0. Found: C, 15.0; H, 2.1; N, 25.9; Mn, 17.3. Calcd for $\mathrm{Fe(tu)_2(NCS)_2}$: C, 14.8; H, 2.5; N, 25.9; Fe, 17.3. Found: C, 14.9; H, 2.5; N, 25.7; Fe, 17.3. Calcd for $\mathrm{Co(tu)_2(NCS)_2}$: C, 14.7; H, 2.5; N, 25.7; Co, 18.0. Found: C, 15.1; H, 2.3; N, 25.1; Co, 18.1. Calcd for $\mathrm{Ni(tu)_2(NCS)_2}$: C, 14.7; H, 2.5; N, 25.7; Ni, 18.0. Found: C, 15.1; H, 2.5; N, 25.8; Ni, 18.0. Calcd for $\mathrm{Cd(tu)_2(NCS)_2}$: C, 12.6; H, 2.1; N, 22.1; Cd, 29.5. Found: C, 12.9; H, 1.8; N, 22.4; Cd, 29.5.

Physical Measurements.—Infrared spectra were obtained using Grubb–Parsons Spectromaster, DM4, and GM3 spectrometers, and electronic spectra were obtained using a Beckman DK2a spectrometer with a reflectance accessory. Magnetic measurements, using a Gouy balance of conventional design, were made on at least two samples of each compound. Measurements at several different fields were made at each temperature, but no field dependence was observed.

Results

Infrared Spectra.—The internal modes of the thiocyanate ion are in the range normally found for N-bonded thiocyanate groups. Those vibrational modes of the thiourea which involve appreciable C–S stretching character are shifted slightly to lower energy relative to nonbridging, coordinated thiourea. At lower energy than the internal modes of the ligands, these compounds show bands due to the skeletal vibrations of the complexes (Table I).

TABLE I

FAR-INFRARED SPECTRA (400–130 CM^{-1})

Compound	M–NCS str	Other bands
$\mathrm{Ni(tu)_2(NCS)_2}$	303 ms	230 s, 206 m, 170 m
$\mathrm{Co(tu)_2(NCS)_2}$	297 ms	208 s, 194 m, 162 m, 146 m
$\mathrm{Fe(tu)_2(NCS)_2}$	293 ms	198 s, 173 m, 148 m
$\mathrm{Ms(tu)_2(NCS)_2}$	286 b, ms	189 s, 181 s, 166 m, 140 m
$\mathrm{Cd(tu)_2(NCS)_2}$	226 b	181 s

$\mathrm{Fe(tu)_2(NCS)_2}$.—In a crystal field of D_{4h} symmetry, the ^5D term of the Fe(II) ion splits into the levels ^5E_g, $^5B_{2g}$, $^5B_{1g}$, and $^5A_{1g}$, but the value of the magnetic moment (Table II) suggests that the separation between the ^5E_g and the $^5B_{2g}$ levels is small. The Mössbauer spectrum shows an isomer shift of 1.01 ± 0.04 mm/sec (relative to Pd/^{57}Co), with a quadrupole splitting of 2.08 ± 0.04 mm/sec. This quadrupole splitting in itself suggests that the $^5B_{2g}$ level lies lowest and, together with the magnetic moment, it fits the calculated curve[5] for a $^5B_{2g}$ ground state. The ^5E_g–$^5B_{2g}$ separation is then found, using the expressions of Burbridge, *et al.*,[6] to be either *ca.* 300 or *ca.* 4000 cm^{-1}. The latter value is excluded by the high magnetic moment.

The electronic reflectance spectrum (Table III) shows the expected large separation of the $^5B_{1g}$ ($d_{x^2-y^2}$) and $^5A_{1g}$(d_{z^2}) levels, and we assign the 10,800-cm^{-1} band as the $^5B_{2g} \rightarrow {}^5A_{1g}$ transition and the 5420-cm^{-1} band as $^5B_{2g} \rightarrow {}^5B_{1g}$. The following values of the tetragonal parameters[7,8] may then be calculated: $Dq = 810$ cm^{-1}, $Ds = -810$ cm^{-1}, $Dt = -430$ cm^{-1}, $\delta\sigma = 2000$ cm^{-1}, and $\delta\pi = 150$ cm^{-1}. The in-plane field is about 5500 cm^{-1}, compared with an octahedral field of about 8600 cm^{-1} for nonbridging thiourea in $\mathrm{Ni(tu)_6X_2}$.[9] It is clear that, as expected from crystal field theory, the tetragonal component of the field has a much greater influence on the $d_{x^2-y^2}$–d_{z^2} separation than it has on the $d_{x^2-y^2}$–d_{xy} separation. This effect has been observed in other iron(II) compounds.[5]

TABLE II

MAGNETIC PROPERTIES

Compound	Temp range of Curie–Weiss law, °K	μ_{eff},[a] BM	Θ, deg
$\mathrm{Fe(tu)_2(NCS)_2}$	80–360	5.51	−4
$\mathrm{Ni(tu)_2(NCS)_2}$	170–370	3.27	+40
$\mathrm{Co(tu)_2(NCS)_2}$	80–360	4.99	−7
$\mathrm{Mn(tu)_2(NCS)_2}$	170–370	5.81	−1

[a] Calculated from $\mu = 2.83\sqrt{\chi(T - \Theta)}$ where χ is corrected for diamagnetism.

TABLE III

ELECTRONIC SPECTRA OF THE COMPLEXES

Compound	Absorption maxima, cm^{-1}
$\mathrm{Mn(tu)_2(NCS)_2}$	26,800, 22,500, 18,600
$\mathrm{Fe(tu)_2(NCS)_2}$	10,800, 5420
$\mathrm{Co(tu)_2(NCS)_2}$	~19,200 sh, 18,500, 15,000, 9430, 6250
$\mathrm{Ni(tu)_2(NCS)_2}$[a]	14,800, 8400, ~6200 sh

[a] Higher energy bands obscured by charge-transfer absorption.

$\mathrm{Ni(tu)_2(NCS)_2}$.—The lowest energy band in the reflectance spectrum of this compound has a shoulder on the low-energy side which is not due to vibrational overtones. If the splitting of the $^3T_{2g}$ (in O_h) level is calculated using the values of Dq and Dt found for the iron(II) complex, but neglecting the $E_g(^3T_{2g})$–$E_g(^3T_{1g})$ interaction, then it is predicted that the $^3B_{2g}$ state will lie at 5500 cm^{-1} and the ^3E_g state at 9300 cm^{-1}. However, inclusion of the most important off-diagonal matrix element ($\langle {}^3E_g, {}^3T_{2g} | V_t | {}^3E_g, {}^3T_{1g} \rangle = -3^{1/2}Ds - {}^5/_4(3^{1/2})Dt = \sim 2300$ cm^{-1}) depresses the energy of ^3E_g ($^3T_{2g}$) some 1000 wave numbers, in agreement with the measured spectrum. The position of the $^3B_{2g}$ state, however, suggests that either Dq is slightly larger or Dt is (numerically) smaller in the nickel than in the iron compound. Since only three of the six spin-allowed transitions are observed in the spectrum, a more detailed interpretation cannot be given.

The magnetic susceptibility of this compound follows a Curie–Weiss law over the temperature range 370–170°K but at lower temperatures an appreciable deviation occurs (Tables II and IV). No field dependence was detected.

$\mathrm{Co(tu)_2(NCS)_2}$.—The electronic reflectance spectrum of this complex has been interpreted[10] as indicating the

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TABLE IV

MAGNETIC SUSCEPTIBILITY OF $M(tu)_2(NCS)_2$ (M = Mn, Ni)

M = Ni			M = Mn		
Temp, °K	10^{-3} χ_M^{a}	u,^{b} BM	Temp, °K	10^{-3} χ_M^{a}	μ,^{b} BM
367	4.08	3.48	362	11.50	5.79
332	4.54	3.51	325	12.79	5.79
298	5.14	3.52	302	13.82	5.80
252.5	6.23	3.56	292	14.27	5.79
226	7.13	3.61	247	16.87	5.79
203.5	8.11	3.65	222	18.69	5.79
182	9.33	3.70	202	20.61	5.79
161.5	10.82	3.76	190	21.88	5.79
147.5	12.12	3.79	184	22.60	5.79
138	13.15	3.82	174	23.80	5.78
127	14.60	3.87	161	25.18	5.72
115	16.38	3.90	148.5	26.45	5.63
102	19.23	3.98	145	26.75	5.59
94	21.28	4.01	127	29.40	5.49
88	23.15	4.05	112	33.10	5.47
77	27.30	4.12	95	38.6	5.44
			83.5	42.2	5.33
			78	45.5	5.34

[a] Corrected for diamagnetism. [b] Calculated from the Curie law.

presence of a tetrahedral species in addition to the octahedral structure. Careful measurements of the reflectance spectrum in the region around 15,000 cm^{-1} did not reveal the fine structure normally associated with the $^4A_2 \rightarrow {}^4T_1(P)$ transition of tetrahedrally coordinated cobalt(II), although this structure is clearly resolved for $Co(ta)_2(NCS)_2$ (ta = thioacetamide).[11] Moreover the electronic spectra of $Co(tu)_2(NCS)_2$ and $Co(NCS)_2 \cdot 0.5H_2O$ are very similar except in the charge-transfer region, and it seems unlikely that both these compounds would contain similar amounts of tetrahedral species giving absorption maxima at similar energies.

The separation of the $^4B_{2g}$ and ^4E_g (from $^4T_{2g}$ in O_h) levels is clearly resolved, with the more intense transition to ^4E_g lying lower, as expected. However, even when off-diagonal elements are included, it is not possible to account quantitatively for the whole spectrum using parameters similar to those found for iron and nickel and it appears that spin–orbit coupling must be included for any full interpretation.

The magnetic properties of $Co(tu)_2(NCS)_2$ are normal (Table II).

$Mn(tu)_2(NCS)_2$.—The reflectance spectrum of $Mn(tu)_2(NCS)_2$ is similar to those of other octahedral manganese(II) complexes. Three d–d bands are detected before the onset of charge-transfer absorption. No splitting of the lowest energy band is observed, and no assignments in tetragonal symmetry can be attempted.

The magnetic susceptibility of this compound follows a Curie–Weiss law over the temperature range 370–170°K (Table II), but below 170°, the susceptibility is lower than would be predicted by this law. The form of the $^1/\chi$ *vs.* T graph suggests that there may be a transition at this temperature to a phase showing negative magnetic interactions.

Discussion of Magnetic Results

These compounds consist of infinite chains of sulfur-bridged metal atoms with relatively large distances between the chains. It therefore seems appropriate to attempt to use the one-dimensional Ising model[12] to fit the experimental results. After correcting for temperature-independent paramagnetism, the susceptibility of a chain of ions of spin S at temperature $t \gg \mu H/k$ is given by this model as

$$\chi' = \frac{N\mu^2}{kt}\left[\exp\left(\frac{-2J}{kt}\right) + \left(\frac{\mu H}{kt}\right)^2\right]^{-1/2}$$

where μ is the magnetic moment per atom, H is the magnetic field strength, and J is the interaction energy. In the compounds studied in this work χ was independent of H, therefore $(\mu H/kt)^2$ is small compared with $\exp(-2J/kt)$. Substituting for μ we have for an ion of spin S

$$\chi' = \frac{N\beta^2 g^2 S(S+1)}{3kt}(\exp(J/kt))$$

Thus a graph of log $[(3k/N\beta^2 S(S+1))\chi' T]$ against $1/T$ should be a straight line.

These expressions neglect the effects of the zero-field splitting of the ground state. This will be small for Mn^{2+} but may have an appreciable effect for d^8 Ni^{2+} in this highly anisotropic environment. However, in the latter case the zero-field splitting cannot be reliably estimated and will be neglected.

In Figures 1 and 2 observed log $[(3k/N\beta^2 S(S+1)) \cdot \chi' T]$ is plotted against $1/T$ for the nickel and manganese compounds. Clearly this model does not adequately account for the magnetic properties of these two compounds. In both cases the susceptibility does not increase as rapidly at low temperatures as is predicted by

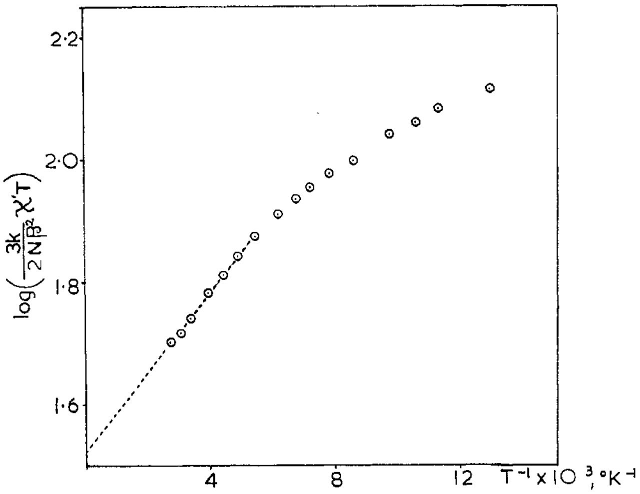

Figure 1.—Plot of log $[(3k/2N\beta^2)\chi' T]$ against $1/T$ for $Ni(tu)_2(NCS)_2$. χ' is corrected for diamagnetism and temperature-independent paramagnetism (χ_{TIP}, taken as 340 × 10^{-6} cgs emu/mol). The broken line corresponds to J/K = 69 and g = 2.14.

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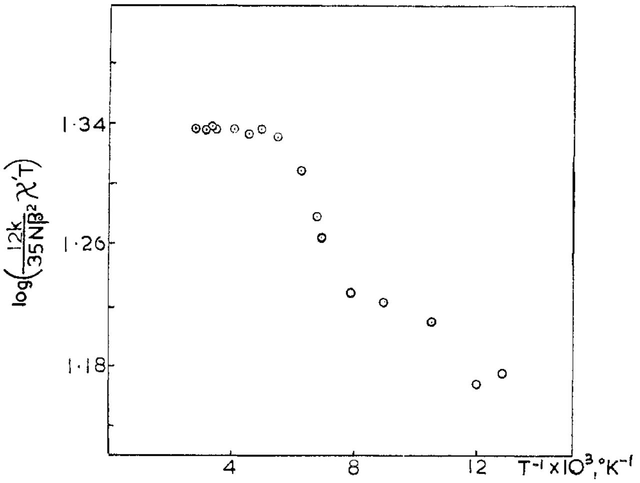

Figure 2.—Plot of log $[(12k/35N\beta^2\chi' T)]$ against $1/T$ for $Mn(tu)_2(NCS)_2$.

the Ising model. This might be attributed to a Curie–Weiss susceptibility term as utilized by Inoue, *et al.*[13] Inclusion of such a term improves the fit somewhat but reasonable agreement between experimental and theoretical curves cannot be obtained for acceptable values of *g*. In view of the approximations of the model and the small temperature range available to us, the inclusion of more than two adjustable parameters cannot be justified.

Since the Ising model does not enable a quantitative account of the magnetic properties of the individual compounds to be made, it seems reasonable to apply the approach of Goodenough[14] to attempt a qualitative description of the mechanisms contributing to magnetic interactions in these systems.

For a complex of this structure, two mechanisms predominate. First a delocalization effect considers the overlap of metal orbitals on different cations. For the t_{2g} orbitals this can occur directly, whereas an intermediary ligand orbital is necessary for t_{2g}–e_g or e_g–e_g exchange, and these last will be weaker. This effect will cause electrons in half-filled overlapping metal orbitals to line up antiparallel, while overlap of filled with half-filled metal orbitals will result in parallel alignment of spins on the two metal ions. This is due to the fact that when an electron is partially transferred from an orbital ϕ_1 to an orbital ϕ_2, already containing an electron with α spin, the second electron in ϕ_1 must also have α spin, and the exchange effect then favors α spin for any other unpaired electron on the same metal ion as ϕ_1.

The second mechanism is an electron correlation effect, which results because if an electron is transferred, through overlap, from a "ligand orbital" to a "metal orbital," it will tend to line up with its spin antiparallel to an unpaired electron already in that orbital or, if the metal orbital is empty, parallel to unpaired electrons in other orbitals on the same center. For these compounds the main interaction will involve transfer of one electron from a σ-bonding hybrid orbital on each of two thiourea sulfur atoms to the metal ion. Additional interactions involving π-overlap between ligand and metal ion are expected to be considerably weaker, since the metal ions are not coplanar with the thiourea.[2]

This approach gives a qualitative explanation of the trend in behavior from manganese to nickel as a consequence of the different number of t_{2g} electrons. Since overlap of two half-filled orbitals gives a negative interaction and overlap of one half-filled and one filled orbital gives a positive interaction, the increasing number of t_{2g} electrons on going from manganese to nickel results in a decreasing negative interaction. With nickel, the predominantly positive effect from other sources becomes the major factor (Table V).

Table V

Summary of Magnetic Interactions

Metal	Delocalization exchange t_{2g}–t_{2g}[a]	t_{2g}–e_g	e_g–e_g	Correlation exchange	Expt
Mn(II)	–[b]	–	–	+	–
Fe(II)	±[c]	±	–	+	0
Co(II)	±	±	–	+	0
Ni(II)	0	+	–	+	+

[a] This interaction is expected to be relatively strong. [b] Minus indicates negative and plus indicates positive magnetic interactions. [c] Plus or minus indicates that the sign of the interaction depends on which t_{2g} orbitals are overlapping. It occurs only when some t_{2g} orbitals are completely and others are partly filled.

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