Reversible Quintet–Singlet Transition in Dithiocyanatobis(2,2′-dipyridyl)iron(II)

E. König,[1,2] K. Madeja,[3] and K. J. Watson[2]

Contribution from Chemical Laboratory IV, H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark, and Institut für Anorganische Chemie, Universität Greifswald, Greifswald, Germany. *Received June 29, 1967*

Abstract: Magnetic susceptibilities of three polymorphs (I, II, and III) of $[Fe(dip)_2(NCS)_2]$ have been measured as a function of temperature between 300 and 77°K. The magnetic moments, which are $\sim$5.20 BM at 293°K for I, II, and III, decrease at a critical temperature $T_c \sim 215$°K and approach 0.94 BM for I, 1.39 BM for II, and 1.61 BM for III at 77°K. Mössbauer-effect investigations show large isomer shifts, $\delta = 1.06$ mm/sec, at 293°K and small values of δ (0.36 mm/sec) at 77°K. Quadrupole splittings are $\Delta E_Q \sim 2.15$ mm/sec at 293°K and 0.49 mm/sec at 77°K. It is concluded from these results that all three polymorphs of the compound exist above T_c in a $^5T_2$ ground state, whereas below T_c the predominant ground state is $^1A_1$. The transition proceeds almost completely to $^1A_1$ in I but is incomplete in II and III in that a small fraction of molecules remains in the $^5T_2$ state below T_c. The values of the spectral parameters $\Delta = 11{,}200$ cm^{-1} and $B \sim 605$ cm^{-1} for the $^5T_2$ state were estimated from the d–d transitions in the electronic spectra. Paramagnetic resonance has been observed in III only. Infrared studies indicate that the NCS group is N-bonded both in the $^5T_2$ and $^1A_1$ states of I, II, and III. The transition is associated with considerable changes in metal–ligand bonding.

Transition metal complexes having the electronic configuration d^6 may exist in either one of the two different electronic ground states, $^5T_2$ (high-spin $t_2{}^4e^2$) and $^1A_1$ (low-spin $t_2{}^6$).[4] Under special circumstances, the energy difference between these two states at a certain temperature may become comparable to the thermal energy kT. This may occur in dilute solution as well as in the solid state. In solution, the result may be a temperature-dependent equilibrium between the two ground states of different multiplicity. In the solid state, complications may arise, since the transfer of electrons between e and t_2 orbitals alters the ionic radius by a significant amount. A change in metal–ligand distance affects the properties of the crystal lattice through its influence on the molecular dimensions in general. In this case, the change in electronic ground state may occur by way of a cooperative ordering and thus a rather sharp transition in, for example, the magnetic moment might be expected.

We have shown previously[5,6] that the compounds $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$, where phen = 1,10-phenanthroline, undergo, in the solid, a reversible quintet–singlet transition at temperatures T_c of 174 and 232°K, respectively. The transition occurs between the same electronic ground states which would be involved in pure thermal ("spin-state") equilibria. The transition does affect the molecular structure to some extent,[7] although a crystallographic phase change has not been observed. In this paper, we are presenting results which demonstrate that a similar transition occurs in the compound $[Fe(dip)_2(NCS)_2]$, where dip = 2,2′-dipyridyl. However, there are differences in the magnetic behavior of three polymorphs of the substance, particularly at low temperatures, which are discussed in detail.

Experimental Section

(a) **Preparation.** Dithiocyanatobis(2,2′-dipyridyl)iron(II) was obtained by heating $[Fe(dip)_3](NCS)_2$ in dry acetone under nitrogen. Slight variations of the experimental conditions result in the formation of three polymorphs of the substance.

Polymorph I. Anhydrous $[Fe(dip)_3](NCS)_2$ was extracted on a fritted disk with dry acetone using a slight overpressure of nitrogen (20–30 mm, reaction temperature $\sim$57°). A mixture of (presumably) the red starting material and of a dark violet substance crystallized in the receiver. The procedure was repeated, yielding dark violet crystals, which formed as rhombic prisms, as the undissolved residue.[8]

Anal. Calcd for $Fe(C_{22}H_{16}N_6S_2)$: C, 54.55; H, 3.33; N, 17.35; S, 13.24; Fe, 11.53. Found: C, 54.66; H, 3.70; N, 17.30; S, 12.94; Fe, 11.60.

When viewed in polarized light incident perpendicular to the prism faces, the crystals appeared red and almost black when the electric vector was parallel and perpendicular, respectively, to a set of slightly elongated edges. Under crossed Nicols, there was sharp extinction in these directions.

Polymorph II. Anhydrous $[Fe(dip)_3](NCS)_2$ was extracted on a fritted disk with dry acetone using an overpressure of nitrogen (100–200 mm, reaction temperature $\sim$60°). As soon as the passing acetone appeared red-violet (after 1 hr), the extraction was interrupted. The receiver was interchanged and the extraction continued with new acetone. The dark violet product crystallized in the receiver.

Anal. Found: C, 54.53; H, 3.21; N, 17.44; S, 11.61; Fe, 11.02.

The crystals form as diamond-shaped thick plates. In polarized light incident on the plate faces, they appeared red and violet, when the electric vector was approximately parallel to the diagonals of the diamond. Under crossed Nicol prisms there was sharp extinction in these directions.

Polymorph III. The same procedure as in preparation II was followed, except that the product was left in the mother liquor overnight, during which time a color change to brown-red had occurred. After boiling for several hours, the crystals were separated.

Anal. Found: C, 54.26; H, 3.22; N, 17.28; S, 12.60; Fe, 11.23.

The substance forms very small, nearly hexagonal prisms. When examined under polarized light incident on the prism faces, they exhibit similar optical properties to polymorph I.

---

(1) (a) NATO Research Fellow, 1966; (b) to whom inquiries should be addressed: Institut für Physikalische Chemie, Universität Erlangen-Nürnberg, Erlangen, Germany.

(2) H. C. Ørsted Institute.

(3) Universität Greifswald.

(4) For convenience, the notation of octahedral symmetry will be used.

(5) E. König and K. Madeja, *Chem. Commun.*, 61 (1966).

(6) E. König and K. Madeja, *Inorg. Chem.*, 6, 48 (1967).

(7) E. König and K. Madeja, *Spectrochim. Acta*, **23A**, 45 (1967).

(8) In repeated runs, however, we were unable to obtain polymorph I in every case. The accurate conditions under which polymorph I is formed are under investigation.

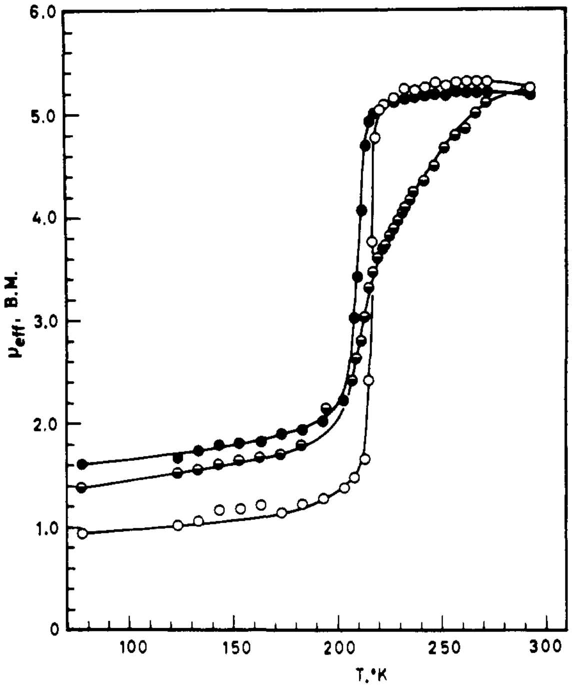

Figure 1. Variation of the magnetic moment μ_{eff} of [Fe(dip)$_2$(NCS)$_2$] with temperature: ○, polymorph I; ⊖, polymorph II; ●, polymorph III.

(b) Microanalyses. Analyses of C, H, N, S, and Fe were carried out both at the Institute of Inorganic Chemistry, University of Greifswald, and by Dr. F. Pascher, Microanalytical Laboratory, Bonn, Germany.

(c) Magnetic Measurements. Magnetic susceptibilities on polycrystalline samples were measured by the Gouy method. Temperatures between 77 and 273°K were achieved by using precooled isopentane as cooling agent and allowing it to warm up slowly. The measured temperature dependence was checked at several points using constant-temperature baths. Good over-all reproducibility was found on repetitive runs. All measurements were made at three different field strengths, and no field dependence of the magnetic susceptibility was observed except where stated The molar susceptibilities were corrected for diamagnetism, using the following corrections: Fe^{2+}, −13; dip, −105; NCS, −35 (in units of 10^{-6} cgs/mole). The effective magnetic moment, μ_{eff}, was obtained from the relation $\mu_{eff} = 2.84\sqrt{\chi_m'T}$, χ_m' being the fully corrected molar susceptibility and T the temperature in °K.

(d) Mössbauer Effect Measurements. Mössbauer ^{57}Fe effect measurements were made, as described elsewhere,[9] with a spectrometer of conventional design. ^{57}Co diffused into stainless steel was used as source. The isomer shifts δ are measured relative to the midpoint of the spectrum of an iron foil absorber at 293°K. Following convention, δ is taken as positive when the source is moved toward the absorber.

(e) X-Ray Diffraction. X-Ray diffraction data for unit cell determinations were recorded photographically with a precession camera. A Philips PW 1010 generator and Cu Kα radiation were used.

(f) Paramagnetic Resonance. Paramagnetic resonance was studied on polycrystalline samples over the temperature range 77–300°K at 9 Gc using a Varian V-4502 spectrometer and] a 100-kc modulation frequency.

(g) Infrared Spectra. Infrared spectra of solid samples were recorded in Nujol mulls on a Perkin-Elmer 125 grating spectrophotometer over the range 4000–400 cm^{-1}. Those regions which were obscured by Nujol bands were remeasured in hexachlorobutadiene mulls. The mulls were supported between potassium bromide plates. Measurements at temperatures below the transition point T_c were performed using a cold cell of standard design and liquid nitrogen as coolant. The spectral changes were followed during the cooling process until a constant spectrum resulted. In a representative run, temperatures down to ~105°K were obtained.

(h) Electronic Spectra. Reflectance spectra were measured on a Beckman DK-2A spectrophotometer. Spectra at 77°K were obtained using a low-temperature reflectance cell of standard design and liquid nitrogen as coolant.

All measurements employing methods c–h were carried out, as far as possible, in dry nitrogen.

Results and Discussion

Magnetic Data. The results of magnetic susceptibility measurements on polymorphs I, II, and III of [Fe(dip)$_2$(NCS)$_2$] between 77 and 293°K are plotted in Figure 1, and the numerical values of the molar magnetic susceptibility χ_m and of the magnetic moment μ_{eff} are listed in Table I. At 293°K, the moment is 5.20 ± 0.05 BM for all three modifications. A slight field dependence of the moment has been detected for polymorph II. Table II lists the susceptibilities χ_g for three different field strengths H and the values of χ_g^∞ resulting from extrapolation to infinite field strength. A limiting value of 5.09 ± 0.10 BM is obtained for the magnetic moment at 293°K.

Table I. Magnetic Data for [Fe(dip)$_2$(NCS)$_2$], Polymorphs I, II, and III[a]

Polymorph I

293, 11,290, 5.23; 273, 12,310, 5.26; 268, 13,003, 5.30;
263, 12,980, 5.30; 258, 13,220, 5.29; 253, 13,300, 5.26;
248, 13,640, 5.29; 243, 13,860, 5.25; 238, 13,900, 5.22;
233, 14,250, 5.23; 228, 14,210, 5.15; 223, 14,100, 5.09;
221, 13,900, 5.03; 219, 12,570, 4.76; 217, 7770, 3.76;
215, 3055, 2.41; 213, 1292, 1.65; 208, 1000, 1.47;
203, 788, 1.33; 193, 746, 1.27; 183, 697, 1.21;
173, 618, 1.13; 163, 716, 1.20; 153, 791, 1.16;
143, 872, 1.16; 133, 731, 1.05; 123, 744, 1.01;
77, 1125, 0.94

Polymorph II

293, 11,240, 5.21; 273, 11,550, 5.10; 268, 11,300, 5.00;
263, 10,900, 4.85; 258, 10,700, 4.79; 253, 10,400, 4.67;
248, 9960, 4.50; 243, 9420, 4.36; 238, 9130, 4.25;
236, 8860, 4.17; 234, 8640, 4.10; 232, 8400, 4.04;
230, 8190, 3.97; 228, 7950, 3.89; 226, 7740, 3.82;
224, 7430, 3.73; 222, 7300, 3.69; 220, 6990, 3.60;
218, 6590, 3.48; 216, 6030, 3.32; 214, 5050, 3.04;
212, 4315, 2.80; 210, 3805, 2.63; 208, 3190, 2.42;
203, 2770, 2.24; 193, 2318, 2.02; 183, 2120, 1.89;
173, 2060, 1.70; 163, 1835, 1.67; 153, 1870, 1.64;
143, 1960, 1.61; 133, 1977, 1.56; 123, 2060, 1.52;
77, 2825, 1.39

Polymorph III

293, 11,060, 5.17; 273, 12,250, 5.25; 268, 12,260, 5.20;
263, 12,570, 5.21; 258, 12,810, 5.22; 253, 12,780, 5.17;
248, 13,190, 5.19; 243, 13,400, 5.17; 238, 13,570, 5.15;
233, 13,740, 5.14; 228, 13,960, 5.11; 223, 14,060, 5.08;
218, 13,940, 5.00; 216, 13,610, 4.92; 214, 12,390, 4.69;
212, 9460, 4.07; 210, 6610, 3.42; 208, 5160, 3.02;
203, 2690, 2.21; 193, 2350, 2.02; 183, 2235, 1.93;
173, 2265, 1.89; 163, 2220, 1.82; 153, 2325, 1.80;
143, 2490, 1.79; 133, 2503, 1.73; 123, 2490, 1.66;
77, 3900, 1.61

[a] Each set of three numbers gives T (°K), χ_m (10^{-6} emu/mole), and μ_{eff}(BM).

With decreasing temperature, *i.e.*, down to about 260°K, the moments of polymorphs I and III slightly increase. These variations may be compared with values calculated on the basis of the theory of paramagnetism for axially distorted cubic $^5T_2$ terms.[10]

---

(9) E. König, S. Hüfner, E. Steichele, and K. Madeja, *Z. Naturforsch.*, **22a**, 1543 (1967).

(10) E. König, A. S. Chakravarty, and K. Madeja, *Theoret. Chim. Acta*, **9**, 171 (1967).

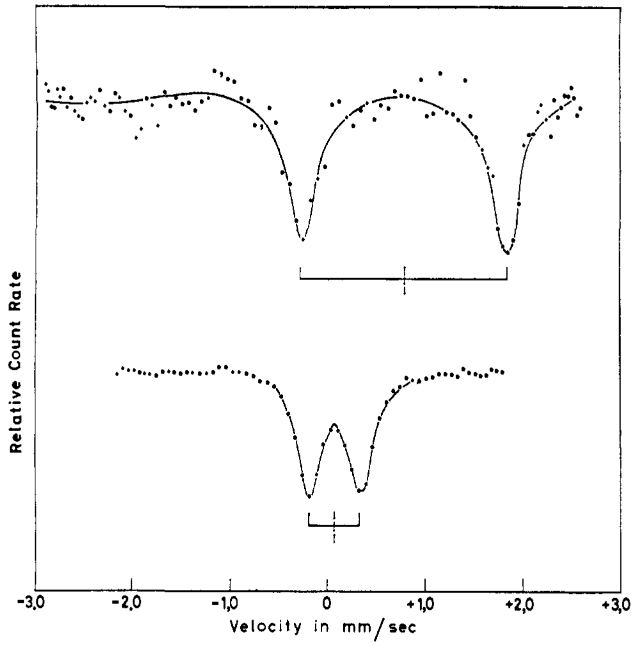

Figure 2. Mössbauer spectrum of $[Fe(dip)_2(NCS)_2]$, polymorph I: upper spectrum at 293°K, lower spectrum at 77°K.

The slopes of the experimental μ_{eff} *vs.* T curves indicate negative values for the axial field splitting parameter Δ_{axial} (which equals $-\delta$, *vide infra*). This means that, very likely, the nondegenerate level ($^5B_2$ or $^5A_1$ in axial fields of tetragonal or trigonal symmetry, respectively) is lowest in energy. Reliable estimates of Δ_{axial} could be obtained if the measurements of μ_{eff} were extended to higher temperatures.

Table II. Field Dependence of the Magnetic Susceptibility χ_g for $[Fe(dip)_2(NCS)_2]$, Polymorph II, and Extrapolation to $H = \infty$[a]

Temp, °K	H, amp	χ_g, 10^{-6} emu/g	χ_g^∞, 10^{-6} emu/g	χ_m^∞, 10^{-6} emu/mole	μ_{eff}^{cor}, BM
293	1.6	23.75			
	2.4	23.20	22.04	10,680	5.09
	3.1	22.90			
273	1.6	24.40			
	2.4	23.82	22.70	10,980	4.99
	3.1	23.60			
195	1.6	5.85			
	2.4	5.39	4.36	2,115	1.94
	3.1	5.08			
77	1.6	6.59			
	2.4	5.83	4.23	2,045	1.20
	3.1	5.39			

[a] The magnetic field strengths corresponding to the electric currents of 1.6, 2.4, and 3.1 amp are approximately 4900, 7350, and 9400 gauss, respectively.

At a transition temperature T_c of 216°K, the moment of polymorph I suddenly decreases, whereas for polymorph III one finds $T_c = 210$°K. The decrease is from 5.03 to 1.65 BM within ~8°K for I, and from 4.92 to 2.21 BM within ~13°K for III. Finally, the moment approaches 0.94 ± 0.01 BM at 77°K for I and 1.61 ± 0.01 BM at 77°K for III.

The magnetic behavior of modification II as a function of temperature is more complicated.[11] Between 293 and 220°K, the moment decreases rather slowly, *i.e.*, from 5.21 to 3.60 BM. At 220°K, there is a pronounced discontinuity of the μ_{eff} *vs.* T. curve. Below this temperature, the moment drops first to 2.42 BM within ~12°K and assumes a value of 1.39 ± 0.01 BM at 77°K. For all three polymorphs, the transitions follow the same curves both with raising and with lowering of temperature, and no hysteresis effects were observed.

The sharp decrease of the magnetic moment of $[Fe(dip)_2(NCS)_2]$ has been noticed previously by Baker and Bobonich.[12] The reported magnetic moments vary between 5.15 BM at 297°K and 1.36 BM at 112°K, and $T_c = 211$°K. The preparative method employed by Baker and Bobonich differs from the procedure used by us in both the solvent (methylcyclohexane) and the reaction temperature (100.4°). Since the resulting polymorph of $[Fe(dip)_2(NCS)_2]$ depends on slight changes in experimental conditions (*cf.* Experimental Section of this paper), the polymorph used by Baker and Bobonich is uncertain. The decrease of the magnetic moment was explained by the assumption of exchange interaction within pairs of Fe^{2+} ions.[12] However, as shown previously,[6] such an assumption would be in disagreement with the experimental evidence.

The present results of magnetic measurements agree well with the assumption of a transition between $^5T_2(t_2^4e^2)$ and $^1A_1(t_2^6)$ ground states. An analogous transition has been described recently in some iron(II)–bis(1,10-phenanthroline) complexes.[6] The rather sharp decrease of μ_{eff} indicates that the expected thermal equilibrium between the $^5T_2$ and $^1A_1$ ground states is associated with significant changes of the molecular dimensions.[6,7]

The moderate change of μ_{eff} between 293 and 220°K in polymorph II of $[Fe(dip)_2(NCS)_2]$ suggests that a somewhat different mechanism is operative. In this range of temperature, the slope of the experimental μ_{eff} *vs.* T curve approaches much closer to the magnetic behavior expected for a pure thermal $^5T_2$–$^1A_1$ equilibrium, which is described by eq 1. However, the remaining deviation inhibits a reliable determination of ΔE and λ.

$$\mu_{eff}^2 = \frac{\left(28x + \frac{28}{3}\right)e^{2x-y} + \left(\frac{45}{2}x + \frac{25}{6}\right)e^{-x-y} + \left(\frac{49}{2}x - \frac{27}{2}\right)e^{-3x-y}}{(x/3)(1 + 7e^{2x-y} + 5e^{-x-y} + 3e^{-3x-y})} + 3kT\alpha/\beta^2 \quad (1)$$

In (1), $x = \lambda/kT$, $y = \Delta E/kT$; λ is the spin–orbit coupling parameter, ΔE the separation of the $^5T_2$ from the $^1A_1$ state, β the Bohr magneton, and $N\alpha$ the temperature-independent paramagnetism.

Mössbauer Spectra. The ^{57}Fe Mössbauer spectra of polymorphs I, II, and III of $[Fe(dip)_2(NCS)_2]$ were measured at 293 and 77°K. The spectrum of polymorph I at these two temperatures is displayed in Figure 2. Values of the isomer shift δ and of the quadrupole splitting ΔE_Q are listed in Table III. The values re-

---

(11) For convenience, the uncorrected μ_{eff} values of Table I are used in the discussion. To compare with moments extrapolated to fields $H = \infty$, Table II should be consulted.

(12) W. A. Baker, Jr., and H. M. Bobonich, *Inorg. Chem.*, **3**, 1184 (1964).

Table III. Isomer Shifts, δ, and Quadrupole Splittings, ΔE_Q, from ^{57}Fe Mössbauer Spectra of $[Fe(dip)_2(NCS)_2]$

Polymorph of $[Fe(dip)_2(NCS)_2]$	Temp, °K	δ,[a] mm/sec	ΔE_Q, mm/sec
I	293	1.06 ± 0.04	2.18 ± 0.03
	77	0.36 ± 0.04	0.50 ± 0.03
II	293	1.06 ± 0.05	2.31 ± 0.03[b]
	77	0.36 ± 0.04	0.47 ± 0.02
III	293	1.06 ± 0.04	2.13 ± 0.03
	77	0.34 ± 0.04	0.50 ± 0.03

[a] Isomer shifts δ are measured relative to the center of the spectrum of a natural iron absorber. [b] Presence of a small percentage of the 77°K spectrum is indicated by a weak shoulder.

cently reported by Collins, Pettit, and Baker[13] for the Mössbauer spectrum of $[Fe(dip)_2(NCS)_2]$ at 77°K, *viz.* $\delta = 1.077$, $\Delta E_Q = 2.40$ mm/sec, were shown to be in error.[9] On careful reinvestigation, Collins, *et al.*, were able to confirm our present results.[14]

The observed isomer shift δ is determined by[15]

$$\delta = (2\pi/3)Ze^2[|\psi(0)|_a^2 - |\psi(0)|_s^2]\delta\langle r^2\rangle \qquad (2)$$

with

$$\delta\langle r^2\rangle = \langle r^2\rangle_e - \langle r^2\rangle_g \qquad (3)$$

where the quantities have their usual meaning. Application of the method of Walker, *et al.*,[15] to eq 2 of $[Fe(dip)_2(NCS)_2]$ yields 21% 4s character for the $^5T_2$ ground state if recent results of SCF calculations on d^5 and d^6 complex ions[16] are used for the calibration of $|\psi(0)|^2$. This interpretation neglects any contribution from 3d bonding, which approximation cannot be used for low-spin ions.[17] In this case, much smaller values of δ are found than in $^5T_2$ ground states.[18,19]

The quadrupole splitting ΔE_Q of the ^{57}Fe nucleus has been given as[20]

$$\Delta E_Q = \frac{1}{2}e^2qQ\left[1 + \frac{1}{3}\eta^2\right]^{1/2} \qquad (4)$$

where $eq = V_{zz}$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$, V being the electric potential. Since, in general, the largest contribution to the electric field gradient, eq, comes from incompletely filled d electron shells, rather small values of ΔE_Q will be expected for $^1A_1(t_2^6)$ terms and substantial values for $^5T_2$ in absence of octahedral symmetry. For the high-spin compound $[Fe(dip)_2Cl_2]$ at 293°K, for example, we determined $\delta = 1.01 \pm 0.05$ and $\Delta E_Q = 3.04 \pm 0.03$ mm/sec, whereas for the low-spin compound $[Fe(dip)_3(ClO)_4]_2$, $\delta = 0.300 \pm 0.008$ and $\Delta E_Q \sim 0.30$ mm/sec have been obtained.[21] Values of δ and ΔE_Q measured at 77°K differ only by the normal temperature shift.

The data of Table III thus clearly demonstrate that, at 293°K, the ground state of $[Fe(dip)_2(NCS)_2]$ is $^5T_2$, whereas, at 77°K, the ground state is $^1A_1$. This statement holds for all three polymorphs I, II, and III. The weak shoulder observed in the 293°K spectrum of II, which is characteristic for the $^1A_1$ state, indicates that the transition is not complete at this temperature.

Crystal Data. Single-crystal precession X-ray photographs of polymorphs I and II of $[Fe(dip)_2(NCS)_2]$ were used to determine lattice parameters at room temperature. Space groups were deduced from systematically absent spectra on the zeroth and upper layer photographs.

The resulting data for polymorph I are orthorhombic, $a = 16.04 \pm 0.05$ Å, $b = 16.98 \pm 0.05$ Å, $c = 15.94 \pm 0.05$ Å, $D_m = 1.475 \pm 0.010$ g cm^{-3} (by flotation); with $Z = 8$ molecules per unit cell, $D_c = 1.482 \pm 0.010$ g cm^{-3}; space group, Pbca ($=D_{2h}^{15}$). The developed prism faces are {101} and {010}. The red direction, in polarized light on {101} is parallel to the b axis.

For polymorph II, the data are: orthorhombic, $a = 13.17 \pm 0.05$ Å, $b = 16.50 \pm 0.05$ Å, $c = 10.08 \pm 0.04$ Å; $D_m = 1.459 \pm 0.010$ g cm^{-3} (by flotation); with $Z = 4$ molecules per unit cell, $D_c = 1.469 \pm 0.010$ g cm^{-3}; space group, Pcnb ($=D_{2h}^{14}$). The developed plate faces are {010} and the plate edges are defined by {101} faces. The red diagonal direction in polarized light on {010} is parallel to the a axis, and the violet direction is parallel to the b axis.

Because of the very small size of the crystals, we were unable to determine the analogous data for polymorph III. However, in polarized light the colors, although similar to those of form I, were significantly different therefrom, being much less intense and browner, and there is little doubt that the crystal structure of this modification is unique.

A preliminary low-temperature study using Weissenberg techniques has shown that there is no marked crystallographic change at the transition temperature T_c[22] in polymorph II.

Paramagnetic Resonance. Between 293 and 77°K, polycrystalline samples of polymorphs I and II give only an extremely weak spurious signal at $g \sim 1.97$, showing a partly resolved hyperfine structure with a splitting constant $a \sim 90$ gauss. Polymorph III yields at 293°K an intense resonance at $g = 2.24$ having $\Delta H_{1/2} \sim 900$ gauss, which is superposed on the same weak signal which occurs in polymorphs I and II. The signal intensity is almost unaffected by cooling to 77°K whereas, normally, the intensity varies as $1/T$. This observation is apparently due to the fact that the expected intensity increase (to 3.8 times the value observed at 293°K) is counterbalanced by the decrease in the number of paramagnetic Fe^{2+} ions, as exemplified by the lowering of the magnetic moment from 5.17 BM at 293°K to 1.61 BM at 77°K.

Assuming in polymorph III a ligand field of trigonal microsymmetry as suggested by the macroscopic hexagonal crystal symmetry, the cubic $^5T_2$ term is split into a lower $^5A_1$ and a higher ^5E term of separation δ, if the condition $\delta > \lambda$ holds. Spin-orbit interaction partly removes the degeneracy of the $^5A_1$ producing a

---

(13) R. L. Collins, R. Pettit, and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, **28**, 1001 (1966).

(14) W. A. Baker, private communication.

(15) L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters*, **6**, 98 (1961).

(16) H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, **44**, 10 (1966).

(17) J. Danon, *ibid.*, **41**, 3378 (1964).

(18) V. I. Goldanskii, "The Mössbauer Effect and its Applications in Chemistry," Consultants Bureau, New York, N. Y., 1964.

(19) P. R. Brady, J. F. Duncan, and J. F. Mok, *Proc. Roy. Soc.* (London), **A287**, 343 (1965).

(20) O. C. Kistner and A. W. Sunyar, *Phys. Rev. Letters*, **4**, 412 (1960).

(21) L. M. Epstein, *J. Chem. Phys.*, **40**, 435 (1964).

(22) Full crystal structure analyses both above and below the transition temperature (293 and ~100°K) are in progress.

Table IV. Infrared Frequencies of the NCS Group in [Fe(dip)$_2$(NCS)$_2$] (in cm^{-1})

I		II		III		
293°K	~105°K	293°K	~105°K	293°K	~105°K	Assignment
	2126 (m, sh)				2128 (w, sh)	ν_1(SCN), CN stretch ($^1A_1$)
	2118 (vs)		2118 (m, sh)		2118 (m)	
	2109 (vs)	2110 (w)	2109 (vs)		2109 (vs)	
2100 (vw)		2100 (vw)	2100 (vs)	2101 (vw)	2100 (vs, sh)	
			2080 (vw)	2091 (vw, sh)	2079 (m)	ν_1(SC^{13}N), C^{13}N stretch ($^1A_1$)
			2073 (vw)			
2065 (vs)		2065 (vs)	2066 (vw, sh)	2066 (vs)	2062 (w, sh)	ν_1(SCN), CN stretch ($^5T_2$)
2055 (vs)		2055 (vs)	2056 (vw)	2056 (vs)	2053 (m)	
2020 (vw, sh)		2020 (vw, sh)		2020 (vw)		ν_1(SC^{13}N), C^{13}N stretch ($^5T_2$)
2010 (vw, sh)		2010 (vw, sh)		2010 (vw)		
	804 (vs)		806 (vs)		802 (vs)	ν_3(SCN), CS stretch
802 (m)		802 (s)		800 (m)		
	798 (s)		797 (s)		795 (s)	
477 (m)	475 (m)	477 (s)	481 (m)	476 (s)	473 (m)	ν_2(SCN), S–C–N bend
473 (w, sh)	470 (m)	472 (m)	477 (w)	472 (m)	469 (m)	
			470 (w)			

singlet ground state and two doublets at $D \sim \lambda^2/\delta$ and at $4D$, respectively. The g value for this system is determined by[23]

$$g \sim 2 - 4\lambda/3\delta + \lambda^2/\delta^2 \qquad (5)$$

The observed value of g thus suggests δ values between 400 and 500 cm^{-1}, if λ is taken between -80 and -100 cm^{-1}.

If, in polymorphs I and II, a rhombic microsymmetry is assumed, the first doublet is likely to be so far above the lowest singlet level that resonance might not be observed.

Infrared Spectra. The infrared spectra of [Fe(dip)$_2$(NCS)$_2$] were studied between 4000 and 400 cm^{-1}, both above and below T_c. It has been shown previously for the specific case of the C–N stretching mode[24] that the plot of infrared absorption intensity *vs.* T shows practically the same functional relationship as the plot of μ_{eff} *vs.* T. The 293°K spectrum and the constant spectrum obtained on cooling to sufficiently low temperatures beneath T_c are thus considered as representative for the $^5T_2$ and $^1A_1$ ground states, respectively. The infrared frequencies due to the NCS and dipyridyl ligands will be discussed separately.

(a) NCS Group. The thiocyanate group is known to act as a difunctional ligand, both SCN and NCS linkages being possible. It has been shown[25–27] that the positions of the three fundamental frequencies, *viz.* ν_1 (C–N stretch), ν_2 (N–C–S bend), and ν_3 (C–S stretch), depend on the mode of attachment of the group to the metal ion. Table IV lists the observed frequencies and the assignments which were arrived at by comparison with the infrared spectrum of [Fe(dip)$_2$Cl$_2$]. The data suggest that, in the $^5T_2$ state of [Fe(dip)$_2$(NCS)$_2$], the thiocyanate group is N bonded. This is in agreement with the A-type character of iron(II) according to the Ahrland–Chatt–Davies classification[28] as well as with the π-bonding properties of the 2,2′-dipyridyl ligand. In the $^1A_1$ ground state, the C–N stretching mode is shifted to 2109 cm^{-1} (strongest peak). Although this frequency falls into the range characteristic for S-bonded thiocyanate, a change in linkage from SCN to NCS is extremely unlikely for similar reasons to those for the analogous 1,10-phenanthroline compounds:[6] (a) ν_2 and ν_3 are not shifted out of the region characteristic for N bonding; (b) the different steric arrangements would require a crystallographic phase change,[29] which X-ray diffraction experiments show does not take place. Rather, the frequency shift $\Delta\nu_1 \sim +50$ cm^{-1} is taken as indication of decreased Fe–NCS bond strength due to lower availability of t$_2$ electrons in the $^1A_1$ state of the central iron(II) ion.[6] This is in agreement with the larger overlap of filled metal t$_2$ and empty π^* orbitals of the 2,2′-dipyridyl ligands in the low-spin t$_2{}^6$ configuration.

In the temperature range below T_c, the characteristic double band at 2066–2056 cm^{-1} corresponding to ν_1 of the $^5T_2$ ground state is present in spectra of polymorph III with considerable intensity, and it is still discernible in polymorph II (*cf.* Table IV); however, in spectra of polymorph I, the band has not been detected. This is an indication that the higher magnetic moments encountered in polymorphs II and III at 77°K are due to a fraction of the molecules which remains in the $^5T_2$ state, although the overwhelming number of molecules has undertaken the transition to the $^1A_1$ state (*cf.* discussion below). On the other hand, the intense double band at 2100–2109 cm^{-1}, ν_1 ($^1A_1$), may still be observed as a very weak band at 293°K, thus indicating that, even at a temperature approximately 80° higher than T_c, the transition $^1A_1 \rightarrow {}^5T_2$ is not complete.

Splitting of the C–N stretching mode into two bands is revealed for the $^5T_2$ ground state of [Fe(dip)$_2$(NCS)$_2$] by a slight indentation of the main peak (separation ~10 cm^{-1}). This could be considered as indicating a *cis* configuration; however, the resolution of the two bands in the supposedly *cis*-coordinated analogous 1,10-phenanthroline compound is considerably better (*cf.* Figure 3 of ref 7). In the $^1A_1$ state, the splitting has been clearly resolved for polymorph II only. The *trans*-octahedral[30] compound [Fe(py)$_4$(NCS)$_2$] has been

---

[23] R. S. Rubins, *Proc. Phys. Soc.* (London), **80**, 244 (1962).

[24] W. A. Baker, Jr., and G. J. Long, *Chem. Commun.*, 368 (1965).

[25] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

[26] J. Lewis, R. S. Nyholm, and P. W. Smith, *ibid.*, 4590 (1961).

[27] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, **1**, 565 (1962).

[28] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

[29] F. Basolo, W. H. Baddley, and J. L. Burmeister, *Inorg. Chem.*, **3**, 1202 (1964).

Table V. Infrared Spectra of the 2,2′-Dipyridyl Ligand in $[Fe(dip)_2(NCS)_2]$ (all frequencies in cm^{-1})

2,2′-Dipyridyl	$[Fe(dip)_2Cl_2]$	$[Fe(dip)_2(NCS)_2]$		Assignments
		293°K	~105°K	
			1605 (w, sh)	8a(A_2), ν(CC)
	1596 (s, sh)	1598 (vs)	1601 (m)	
1582 (vs)	1592 (vs)	1593 (vs)	1593 (w, sh)	
	1569 (vs)	1573 (vs)	1567 (w)	8b(B_2), ν(CC)
1560 (vs)	1558 (vs)	1562 (vs)	1562 (w)	
			1553 (w)	
	1484 (m)	1486 (m)	1482 (w)	19a(A_1), ν(CC,CN)
1456 (vs)	1474 (s)	1468 (s)	1470 (m)	
			1462 (vs)	
			1445 (vs)	19b(B_2), ν(CC,CN)
	1436 (vs)	1437 (vs)	1439 (vs)	
1417 (vs)				
	1424 (s)	1428 (s)	1424 (s)	
	1418 (vs)		1419 (vs)	
989 (s)	1009 (vs)	1012 (vs)	1018 (w)	1(A_1), ring
		1003 (m, sh)	1006 (vw)	
	780 (s, sh)	770 (s, sh)	773 (s)	10b(B_1), γ(CH)
	775 (vs)	764 (vs)	766 (s)	
753 (vs)	772 (vs)			
	766 (s, sh)	756 (s, sh)	758 (vs)	
	746 (w)	740 (m)	745 (m)	
617 (vs)	622 (s)	624 (s)	496 (s)	6b(B_2), α(CCC)

studied and does not show any splitting of the C–N stretch at 2062 cm^{-1}. These facts as well as the observation of several unresolved shoulders suggest a rather low molecular symmetry for $[Fe(dip)_2(NCS)_2]$, although the additional splitting could arise from solid-state effects.

It has been suggested[31,32] that the splitting of the 2,2′-dipyridyl out-of-plane C–H deformation mode in some bis(2,2′-dipyridyl) complexes is characteristic of *cis* configuration. No such splitting is observed in the $^5T_2$ state of the present compound, although in all three polymorphs, the γ(CH) band at 765 cm^{-1} shows two additional shoulders which are resolved in the $^1A_1$ state only. This would support the assumption of a low symmetry distortion; however, the definite establishment of the ligand disposition about the iron(II) ion must await a full structure determination.

(b) 2,2′-Dipyridyl. The infrared spectra of both free and coordinated solid dipyridyl in the 2000–200-cm^{-1} region have been studied previously.[33–36] Considering dipyridyl as two *ortho*-substituted pyridine molecules, one would expect close similarities between vibrational frequencies of dipyridyl and those of pyridine. The approximate magnitude of the shifts in frequency may be obtained by a study of the monosubstituted pyridines.[37] Three C–H modes from each pyridine molecule will be replaced in dipyridyl by six inter-ring fundamentals which are nonpyridine-like (inter-ring stretch, inter-ring torsion, in-plane and out-of-plane scissoring, and shearing modes). The assignments of these modes can be made according to Katritzky[38] by comparison with biphenyl.[39]

Free solid 2,2′-dipyridyl is of *trans* configuration,[40] *i.e.*, C_{2h} symmetry, and assumes *cis* configuration (C_{2v} symmetry) in the process of complex formation. Since the effect of the symmetry change on the vibrational frequencies is rather slight, band assignments of complexed dipyridyl may be obtained, at least for the strong bands, by direct comparison with the *trans* form of dipyridyl. We list in Table V only the frequencies of those bands which undergo considerable changes on transition between the ground states $^5T_2$ and $^1A_1$ of $[Fe(dip)_2(NCS)_2]$. Corresponding frequencies of $[Fe(dip)_2Cl_2]$ and of free 2,2′-dipyridyl are included for comparison. The notation for fundamentals corresponds to that used by Wilmshurst and Bernstein[41] for pyridine apart from an interchange of the B_1 and B_2 species and a few corrections introduced by Green, *et al.*,[37] in order to conform with assignments in 2-, 3-, and 4-substituted pyridines. Approximate normal coordinate calculations for pyridine have indicated[42] significant mixing of C–C stretching and C–H bending modes. It is anticipated that similar mixing is present in free and more so in complexed[43] dipyridyl.

Two intense bands observed at 1582 and 1560 cm^{-1} in free 2,2′-dipyridyl, which correspond to C–C stretch-

---

(30) D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *Inorg. Chem.*, **5**, 635 (1966).

(31) B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nucl. Chem.*, **23**, 207 (1961).

(32) W. R. McWhinnie, *ibid.*, **26**, 15 (1964).

(33) A. A. Schilt and R. C. Taylor, *ibid.*, **9**, 211 (1959).

(34) R. G. Inskeep, *ibid.*, **24**, 763 (1962).

(35) R. J. H. Clark, *J. Chem. Soc.*, 1377 (1963).

(36) R. J. H. Clark and C. S. Williams, *Spectrochim. Acta*, **21**, 1861 (1965).

(37) J. H. S. Green, W. Kynaston, and H. M. Paisley, *ibid.*, **19**, 549 (1963).

(38) A. R. Katritzky, *Quart. Rev.* (London), **13**, 353 (1959).

(39) J. E. Katon and E. R. Lippincott, *Spectrochim. Acta*, **15**, 627 (1959).

(40) L. L. Merritt and E. D. Schroeder, *Acta Cryst.*, **9**, 801 (1956).

(41) J. K. Wilmshurst and H. J. Bernstein, *Can. J. Chem.*, **35**, 1183 (1957).

(42) E. Wachsmann and E. W. Schmidt, *Z. Physik. Chem.* (Frankfurt), **27**, 146 (1961).

(43) Compare the mixing encountered in metal β-diketonates[44] and α-diimines.[45]

(44) K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066, 1272 (1961).

(45) K. Nakamoto, "Advances in the Chemistry of Coordination Compounds," S. Kirschner Ed., The Macmillan Co., New York, N. Y., 1961, p 437.

ing vibrations of the heterocyclic rings (vibrations 8a, 8b), are likewise found in the $^5T_2$ ground state of the complex, where each is split into a doublet. On transition to the $^1A_1$ state, these bands become extremely weak in intensity. This, as well as other effects to be described below, compares well with observations on the analogous bis(1,10-phenanthroline) complexes.[7] We propose therefore that differences in the infrared spectra of $^5T_2$ and $^1A_1$ states of [Fe(dip)$_2$(NCS)$_2$] should be attributed to differences in π-electron distribution on the dipyridyl ligands, which are caused by increased partial double bond character of the Fe–N(dip) bond in the $^1A_1$ state of the complex. For a more detailed argumentation refer to the discussion in ref 7.

Additional changes comprise the intense bands of dipyridyl at 1456 and 1417 cm^{-1} (vibrations 19a, 19b) which are shifted to longer wavelengths and split into doublets in the $^5T_2$ state of the complex. In the $^1A_1$ state, only the highest band is retained, whereas the remaining three are split into doublets again. The strong peak at 989 cm^{-1} has been recognized[46,47] as the pyridyl ring breathing mode (vibration 1). In the $^5T_2$ state of the complex, this band is shifted to 1012 cm^{-1} with an enhanced intensity which is lost again on transition to the $^1A_1$ state. In agreement with the π-bonding hypothesis,[7] the 753-cm^{-1} band, which is ascribed to out-of-plane bending motions of hydrogens in the pyridyl rings[33,34] (vibration 10b), is split in the $^1A_1$ state into four single peaks. The strong dipyridyl band at 617 cm^{-1} is assigned to the planar pyridyl ring vibration 6b. In the $^5T_2$ state of the complex, it is observed at 625 cm^{-1} whereas, in analogy to the corresponding bis(1,10-phenanthroline) complexes,[7] it is shifted to 496 cm^{-1} in the $^1A_1$ state.

It is thus apparent that, in the $^1A_1$ state of the complex, a considerably stronger Fe–N(dip) bond is indicated on the basis of infrared spectra than in the $^5T_2$ state. In addition, multiple splittings of bands, which are observed in the low-temperature spectra, suggest a rather low molecular symmetry for the $^1A_1$ ground state.

As far as the strong bands are concerned, the spectra of polymorphs I, II, and III are practically identical. On close inspection, however, similar differences are encountered as discussed above for the particular case of the CN-stretching vibration. The infrared spectra of the 2,2′-dipyridyl ligand are thus in agreement with the observed magnetic behavior.

Electronic Spectra. The spectrum of [Fe(dip)$_2$(NCS)$_2$], polymorph I, has been measured at 293 and at ~77°K between 10,000 and 50,000 cm^{-1}, and, in general, it was found to be similar to the spectrum of [Fe(phen)$_2$(NCS)$_2$] (*cf.* ref 6). The spectra of polymorphs II and III were briefly studied and are practically identical with that of polymorph I.

The room temperature d–d spectrum is characterized by a flat-topped band at ~11,200 cm^{-1} corresponding to the $^5T_2 \rightarrow {}^5E$ transition. The band envelope contains, according to a Gaussian analysis, two component bands with maxima at ~12,300 and ~10,200 cm^{-1}. The upper ^5E term is therefore split by ~2100 cm^{-1} and thus gives evidence for low-symmetry fields. To compare the spectral parameters with those deduced from [Fe(phen)$_2$(NCS)$_2$], we assume an average field of practically octahedral symmetry and take $\Delta(^5T_2) = 11{,}200$ cm^{-1}. The electron repulsion parameter $B(^5T_2) \sim 605$ cm^{-1} and the nephelauxetic ratio[48] $\beta \sim 0.57$ are estimated as shown previously.[6] Thus the average nephelauxetic effect seems to be slightly larger in [Fe(dip)$_2$(NCS)$_2$] than in [Fe(phen)$_2$(NCS)$_2$]. The intense visible absorption band has the maximum at 18,400 cm^{-1} and is assigned to the charge-transfer transition $(\text{core})\pi^2t_2{}^4e^2 \rightarrow (\text{core})\pi^2t_2{}^3e^2\pi^*$. No vibrational structure of the band was detected. At higher energies, the only bands observed are those due to internal $\pi \rightarrow \pi^*$ transitions of the 2,2′-dipyridyl ligands.

In the 77°K spectrum, resolution of d–d bands is rather poor, probably subject to the action of low-symmetry ligand fields. We are thus unable to quote reliable values of the spectral parameters in the $^1A_1$ ground state. There is no doubt, however, that the spectrum observed originates in singlet–triplet transitions. The characteristic charge-transfer band is shifted to 17,000 cm^{-1}. As in the corresponding 1,10-phenanthroline compound,[6] the red shift of ~1400 cm^{-1} may be considered as indicating a higher amount of π bonding in the $^1A_1$ ground state.

Conclusions Regarding the Nature of the Observed Transition

It has been deduced from results of magnetic susceptibility and Mössbauer effect measurements that above a transition temperature T_c of ~215°K, the compound [Fe(dip)$_2$(NCS)$_2$] exists in a $^5T_2$ ground state, whereas below T_c the ground state is $^1A_1$. Since the investigations were carried out, and the compound is stable, in the solid state only, it has to be assumed that the transition is induced by the temperature effect on the molecules of the lattice as a whole rather than by the normal statistical temperature-dependent change in the population of the lowest energy levels of relatively free molecules. There are two electrons being transferred from an e to a t_2 orbital, if T_c is approached from higher temperatures, and thus the transition should be followed by a decrease in the metal ion radius. This difference in radii between high-spin and low-spin iron(II) ions in octahedral compounds may be estimated as 0.06–0.20 Å.[49,50] In fact, infrared spectra indicate a significantly stronger Fe–N(dip) bond in the $^1A_1$ state than in the $^5T_2$ state; however, a weaker Fe–NCS bond is formed simultaneously. It might be argued that the expected decrease of the Fe–N(dip) distance in the $^1A_1$ state could be counterbalanced by an increase in the Fe–NCS bond length. However, the changes in distances introduce distortions of the molecular framework, the amount and the consequences of which are difficult to estimate at present, although the lower symmetry of the $^1A_1$ state is apparent from various splittings of infrared vibrational and electronic bands. In addition, the above assumption seems to be supported by the sudden decrease of the magnetic moment at T_c. Thus the unusually sharp nature of the transition may be caused by the eventual overcoming of the

---

(46) S. P. Sinha, *Spectrochim. Acta*, **20**, 879 (1964).

(47) A. I. Popov, J. C. Marshall, F. B. Stute, and W. B. Person, *J. Am. Chem. Soc.*, **83**, 3588 (1961).

(48) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962.

(49) G. Albrecht, J. Tschirnich, and K. Madeja, *Z. Chem.*, **5**, 312 (1965).

(50) G. Blasse, *J. Inorg. Nucl. Chem.*, **27**, 748 (1965).

lattice packing forces by those which tend to alter the geometries of the individual molecules.

The various low-temperature magnetic susceptibilities indicate that, dependent on the polymorph, a certain percentage of molecules remains in the $^5T_2$ state even below T_c. This inference is well supported by infrared spectral observations as discussed above. Usually, a second-order Zeeman effect accounts for the small paramagnetism encountered in low-spin d^6 ions. This contribution to the susceptibility has been estimated by Ballhausen and Asmussen[51] as $\sim 200 \times 10^{-6}$ cgs/mole or up to about 0.70 BM. Subtracting this temperature-independent paramagnetism from the slightly temperature-dependent moment below T_c, one arrives at the estimate that, in the polymorphs I, II, and III, the moment observed at 77°K is due to one in 20, 8,[52] and 6 molecules, respectively, being in a $^5T_2$ ground state. There are two possibilities for the distribution of the high-spin molecules throughout the lattice. In the case of random distribution, a considerably disordered structure would have to be anticipated. If the molecules assume lattice positions in an ordered way, a superlattice should be formed.

The reason why the transition does not proceed to 100% of the $^1A_1$ state is not obvious. Of course, a sufficiently large number of impurity ions could produce the same effects as observed. However, $\sim 18\%$ of Fe^{3+} ion impurities, for example, would be needed to give the high moment value of 1.61 BM at 77°K in polymorph III and, in any case, the various spectroscopic methods employed would have given evidence for any large amounts of such impurities. In particular, the spurious signals observed in paramagnetic resonance are in the ppm range and thus in a much too small concentration to account for the low-temperature magnetic moments, and no indication of signals due to Fe^{3+} ions (the most likely impurity) has been detected. One possible explanation for the observations is suggested on the basis of infrared spectra. The distortions, which are apparent from these results, could result in larger space requirements of the individual molecules with the possible consequence that the change-over to the low-spin state does not proceed to include all molecules within the lattice. However, a detailed characterization of the observed transition must await at least the results of the structure determinations both above and below T_c.

In the recently investigated compounds[6] $[Fe(phen)_2(NCS)_2]$ and $[Fephen_2(NCSe)_2]$, it has also been found that more than one value of the low-temperature terminal moment (*viz.* at 77°K) results. In this case, the low-temperature infrared spectra in the region of the CN stretch clearly demonstrate that, below T_c, the high moment values originate in some percentage of molecules which are in the $^5T_2$ ground state. Thus it is very likely that, in these compounds, several polymorphs may also be formed, and, in this case, the observed transition would be completely analogous to the transition in $[Fe(dip)_2(NCS)_2]$.

Acknowledgments. One of the authors (E. K.) expresses his gratitude to Professor C. J. Ballhausen for his hospitality at the H. C. Ørsted Institute and acknowledges a NATO fellowship provided by the DAAD. The cooperation of Dr. D. H. Christensen and Dr. E. Lindner in measurements of infrared spectra is gratefully appreciated.

(51) C. J. Ballhausen and R. W. Asmussen, *Acta Chem. Scand.*, **11**, 479 (1957).

(52) If susceptibilities extrapolated to $H = \infty$ are used, the ratio of $^5T_2$ to $^1A_1$ molecules of polymorph II at 77°K is 1:10.

Linkage Isomerism of Cyanide Ion. Kinetics and Mechanisms of Reactions of Chromium(II) and Cyanocobalt(III) Complexes[1]

James P. Birk and James H. Espenson

Contribution from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010. Received October 26, 1967

Abstract: The reaction of Cr^{2+} with $Co(NH_3)_5CN^{2+}$, *trans*-$Co(NH_3)_4(H_2O)CN^{2+}$, and *trans*-$Co(en)_2(H_2O)CN^{2+}$ produces a metastable intermediate common to all three reactions. On the basis of its kinetic, spectral, and Cr-51 tracer behavior, the intermediate is postulated to be the N-bonded isocyano complex $(H_2O)_5CrNC^{2+}$, in rapid equilibrium with the acid form $(H_2O)_5CrNCH^{3+}$. The isomerization reaction forms quantitative yields of $(H_2O)_5CrCN^{2+}$ under all conditions, and the rate equation has two terms, one of which corresponds to Cr(II) catalysis of ligand isomerization. Various properties and reactions of the intermediate have been studied in some detail. Results are discussed in terms of the isomeric model, and other formulations are also considered.

The possible existence of linkage isomers of cyanide ion in coordination compounds has been recognized for some time.[2] This phenomenon finds considerable precedence in organic compounds, and the intramolecular isomerization of isocyanides to the generally more stable nitriles has been studied extensively in solution and in the gas phase.[3] In an earlier communication[4] on

(1) (a) Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Contribution No. 2157. (b) Based on the Ph.D. thesis of J. P. B., Iowa State University, 1967.

(2) N. V. Sidgwick, "Chemical Elements and their Compounds," Vol. I, Clarendon Press, Oxford England, 1950, p 671.

(3) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **84**, 4215 (1962).

(4) J. H. Espenson and J. P. Birk, *ibid.*, 87, 3280 (1965).