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CONTRIBUTION FROM MELLON INSTITUTE, PITTSBURGH, PENNSYLVANIA 15213,
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$^5T_2$–$^1A_1$ Equilibria in Some Iron(II)–Bis(1,10-phenanthroline) Complexes[1]

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Magnetic susceptibilities of the compounds [Fe(phen)$_2$(NCS)$_2$] (I) and [Fe(phen)$_2$(NCSe)$_2$] (II) have been measured as a function of temperature between 440 and 77°K. The magnetic moments, which are ~5.20 BM at 440°K for both I and II, exhibit a pronounced decrease at a critical temperature T_c of 174°K for I and of 232°K for II and approach 0.65 BM for I and 0.84 BM for II at 77.4°K. The results agree qualitatively with predictions made on the basis of the Van Vleck equation for a $^1A_1$ ground state slightly separated from a higher lying $^5T_2$ state. Mössbauer effect investigations show at 293°K large quadrupole splittings ΔE_Q of 2.67 mm/sec for I and 2.52 mm/sec for II, as expected for a $^5T_2$ state and, at 77°K, small values of 0.34 mm/sec for I and 0.18 mm/sec for II, indicating a $^1A_1$ state. Correspondingly, the isomer shifts δ are about 1.00 mm/sec at 293°K and 0.36 mm/sec at 77°K for both I and II. It is concluded that the two compounds exist above T_c in a $^5T_2$ state and below T_c in a $^1A_1$ state. This inference is supported by the temperature dependence of the electronic and vibrational infrared spectra. The values of the spectral parameters $\Delta = 11{,}900$ cm^{-1} and $B \sim 640$ cm^{-1} for the $^5T_2$ state as well as $\Delta \sim 16{,}300$ cm^{-1} and $B \sim 580$ cm^{-1} for the $^1A_1$ state of both I and II were estimated from the d–d transitions. The thermal equilibrium between the $^5T_2$ and $^1A_1$ ground states is associated with significant changes in the molecular dimensions.

Introduction

Depending upon the strength of the ligand field, octahedral transition metal complexes with configurations d^4, d^5, d^6, and d^7 exist in two different electronic ground states, referred to as high-spin and low-spin configurations.[3] According to ligand field theory, the transition between these states should occur discontinuously at a certain value of the field strength Δ, often called the mean spin-pairing energy π. This situation may be illustrated best by the crossing over of ground-state terms in the Tanabe–Sugano diagrams.[4]

If, at a field strength Δ close to π, the separation of the two states of different multiplicity attains values within the thermally accessible range, equilibria between these states are expected to occur. Although considerable effort has been spent in seeking new compounds displaying this sort of behavior, few examples have been established definitely. These include compounds of the configurations d^5 and d^7 in octahedral symmetry and compounds of the configurations d^5 and d^8 in lower symmetry.[5]

The series of iron(II)–bis(1,10-phenanthroline) complexes [Fe(phen)$_2$X$_2$] seems to be a particularly suitable place to look for spin-state equilibria within compounds of configuration d^6. This series includes both high-spin and low-spin compounds, the multiplicity of the ground state being dependent on the position of the ligand X in the spectrochemical series. If X = Cl, Br, I, N$_3$, OCN, HCOO, CH$_3$COO, high-spin compounds are formed.[6,7] At room temperature, they show magnetic moments of 5.0–5.3 BM, *i.e.*, slightly higher moment values than predicted from the spin-only formula.[8] If X = CN, CNO, NO$_2$, diamagnetic low-spin compounds are obtained.[9–11]

For [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$], Baker and Bobonich[12] reported the observation of an unusual change of the magnetic moment with temperature. In this paper, we are presenting results which clearly demonstrate that the observed magnetic behavior is caused by the presence of spin-state equilibria between $^5T_2$ and $^1A_1$ ground states.[13] This investigation has

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(1) This paper has been presented at the 9th International Conference on Coordination Chemistry, St. Moritz-Bad, Switzerland, 1966.

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(3) This statement holds exactly for perfect octahedral symmetry only, though it is valid for most six-coordinated, quasi-octahedral complexes as well. Additional high-spin and low-spin configurations may occur on application of lower symmetries (*viz.*, d^8 nickel(II)–bis(salicylaldimine) complexes and others).

(4) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753, 766 (1954).

(5) See references collected in R. C. Stoufer, D. H. Busch, and W. B. Hadley, *J. Am. Chem. Soc.*, **83**, 3732 (1961).

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(8) A detailed discussion of the temperature dependence of the magnetic moments in high-spin [Fe(phen)$_2$X$_2$] compounds will soon become available; *cf.* E. König, A. S. Chakravarty, and K. Madeja, *Theor. Chim. Acta*, in preparation.

(9) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

(10) W. Beck and E. Schuierer, *Chem. Ber.*, **95**, 3048 (1962).

(11) K. Madeja, *Chem. Zvesti*, **19**, 186 (1965).

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

(13) For convenience, the designation of over-all octahedral symmetry is used throughout, although the actual symmetry of the coordination polyhedron is lower than that.

been started independently.[6,11] A preliminary account of the results has been communicated elsewhere.[14]

Experimental Section

Preparations.—[Fe(phen)$_2$(NCS)$_2$] has been prepared according to two different methods: (a) by placing [Fe(phen)$_3$](NCS)$_2$ on a fritted disk and extracting it with dry acetone under nitrogen;[15] (b) by dropping, under nitrogen, a solution of anhydrous 1,10-phenanthroline (0.02 mole) into a hot solution of [Fe(py)$_4$(NCS)$_2$] (0.01 mole), both in dry pyridine. *Anal.* Calcd for Fe($C_{26}H_{16}N_6S_2$): C, 58.65; H, 3.03; N, 15.79; S, 12.04; Fe, 10.49. Found (a): C, 59.59; H, 3.49; N, 15.31; S, 11.53; Fe, 10.19. Found (b): C, 58.82; H, 2.94; N, 15.46; S, 12.03; Fe, 10.42.

[Fe(phen)$_2$(NCSe)$_2$] has been prepared according to two different methods: (a) by placing [Fe(phen)$_3$](NCSe)$_2$ on a fritted disk and extracting it with dry pyridine under nitrogen;[15] (b) by dropping, under nitrogen, a solution of anhydrous 1,10-phenanthroline (0.02 mole) into a hot solution of [Fe(py)$_4$(NCSe)$_2$] (0.01 mole), both in dry pyridine. *Anal.* Calcd for Fe($C_{26}H_{16}N_6Se_2$): C, 49.86; H, 2.58; N, 13.42; Se, 25.22; Fe, 8.92. Found (a): C, 50.55; H, 2.68; N, 13.22; Se, 25.06; Fe, 8.83. Found (b): C, 50.95; H, 2.51; N, 13.32; Se, 24.28; Fe, 8.37.

Microanalyses.—Analyses of C, H, N, S, Se, and Fe were performed both at the Institute of Inorganic Chemistry, University of Greifswald, and by Dr. F. Pascher, Microanalytical Laboratory, Bonn, Germany.

Magnetic Measurements.—Magnetic susceptibilities on polycrystalline samples were measured with a novel type magnetobalance[16] by the Faraday method. The equipment consists of a Varian 4-in. electromagnet utilizing Henry-type pole pieces, the associated current regulator and power supply, and a recording vacuum microbalance with a load capacity of 200 g. A cryostat of a similar design as that employed by Soling[17] was used for measurements below room temperature. All measurements were made at three different field strengths and no field dependence of the magnetic susceptibility was observed. The molar susceptibilities obtained were corrected for diamagnetism, using the following corrections: Fe^{2+}, −13; phen, −128; NCS^-, −35; $NCSe^-$, −40; in units of 10^{-6} c.g.s. 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.

Visible and Ultraviolet Spectra.—Visible and ultraviolet spectra of the powdered samples were measured in reflectance using a Zeiss PMQ II spectrophotometer equipped with the reflection attachment RA 2. A PbS cell and an RCA 1P28 photomultiplier served as detectors. Lithium fluoride was used both as reflection standard and as diluent. The particle size of the samples was less than 5 μ. Low-temperature reflectance spectra were obtained using a brass block cooled by liquid nitrogen. The sample was contained in a circular recess of the block, 3 mm in depth, covered by a plate of quartz glass Ultrasil, and the complete reflection unit was kept in an atmosphere of dry nitrogen to prevent condensation and subsequent decomposition of the sample by moisture.

Infrared Spectra.—Infrared spectra of solid samples were recorded in Nujol mulls on a Beckman IR-9 grating spectrophotometer over the range 4000–600 cm^{-1}, and on a Beckman IR-4 instrument equipped with a CsBr prism in the range 860–300 cm^{-1}. Measurements at ~105°K were performed using a cold cell of standard design and liquid nitrogen as coolant.

Mössbauer Spectra.—Mössbauer spectra were obtained with a spectrometer of conventional design. ^{57}Co diffused into stainless steel was used as the source. Motion of the source with sinusoidal velocity relative to the stationary absorber was effected by a feedback-regulated electromechanical drive system. The transmitted 14.4-kev γ rays were measured by an argon–methane proportional counter. The pulses of the single channel analyzer were stored as a function of the source velocity in an R.I.D.L. 400-channel analyzer operated in the multiscaler mode. 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 to be positive when the source is moved toward the absorber.

X-Ray Diffraction.—X-Ray diffraction data were recorded photographically on powdered samples at room temperature and at ~77°K. A Philips diffraction unit and Cu Kα radiation were used.

Results and Discussion

Magnetic Data.—The results of magnetic measurements on [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$] in the temperature range between 77 and 440°K are plotted in Figure 1 and the numerical values are listed in Table I. The high-temperature limit for the moment of [Fe(phen)$_2$(NCS)$_2$] is 5.20 ± 0.05 BM at 430°K. With decreasing temperature, *i.e.*, down to 293°K, the moment closely follows the theory of paramagnetism for axially distorted cubic $^5T_2$ terms.[8] Taking the spin–orbit coupling constant λ as -80 cm^{-1}, the fitting of the experimental results to the calculated curves yields for the axial field splitting Δ_{axial} and for the covalency parameter[18] κ the values listed in Table II.[19] Moreover, it follows from a plot of $1/\chi_m'$ *vs.* T that marked deviations from Curie–Weiss law $\chi_m' = C_m/(T - \Theta)$ do not occur down to ~190°K. The Weiss constant Θ is included in Table II. Similar results are deduced from the magnetic data on [Fe(phen)$_2$(NCSe)$_2$] and are listed in Table II. The high-temperature limit for the moment is 5.10 ± 0.05 BM at 440°K.

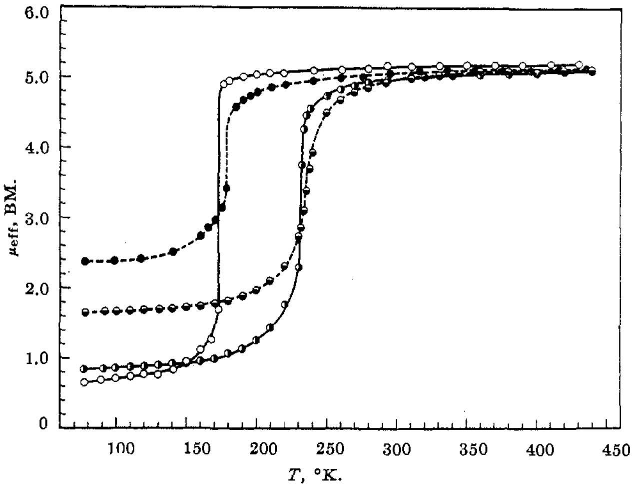

Figure 1.—Variation of the magnetic moments μ_{eff} with temperature for [Fe(phen)$_2$(NCS)$_2$] (○, preparation (a); ●, preparation (b)) and for [Fe(phen)$_2$(NCSe)$_2$] (◑, preparation (a); ◒, preparation (b)).

At 174°K, the magnetic moment of [Fe(phen)$_2$(NCS)$_2$] suddenly decreases. For samples prepared

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

(15) K. Madeja, W. Wilke, and S. Schmidt, *Z. Anorg. Allgem. Chem.*, **346**, 306 (1966).

(16) L. Vaska, unpublished.

(17) H. Soling, *Acta Chem. Scand.*, **12**, 1005 (1958).

(18) K. W. H. Stevens, *Proc. Roy. Soc.* (London), **A219**, 542 (1953).

(19) Due to *cis* configuration of the compounds, there should be a small rhombic field component present which would cause a splitting of the ^5E term. The values of Δ_{axial} deduced from the magnetic moments provide only a first estimate of the deviation from O_h symmetry.

TABLE I

MAGNETIC DATA FOR $[Fe(phen)_2(NCS)_2]$ AND $[Fe(phen)_2(NCSe)_2]$[a]

$[Fe(phen)_2(NCS)_2]$, Preparation (a)

430.1, 7449, 5.20; 410.2, 7828, 5.20; 389.6, 8229, 5.19;
369.9, 8667, 5.18; 350.2, 9178, 5.18; 330.3, 9695, 5.17;
310.4, 10314, 5.16; 293.2, 10948, 5.17; 279.4, 11326, 5.13;
260.5, 12097, 5.11; 240.4, 13081, 5.10; 219.1, 14148, 5.06;
209.0, 14827, 5.06; 199.4, 15451, 5.04; 190.2, 16043, 5.01;
179.8, 16556, 4.95; 175.8, 16667, 4.91; 172.6, 1726, 1.70;
167.6, 859, 1.27; 159.8, 640, 1.12; 149.4, 405, 0.95;
140.4, 281, 0.84; 129.6, 220, 0.76; 119.4, 272, 0.77;
109.9, 279, 0.74; 99.7, 296, 0.71; 89.0, 323, 0.69;
77.4, 346, 0.65

$[Fe(phen)_2(NCS)_2]$, Preparation (b)

435.8, 7135, 5.13; 416.0, 7474, 5.12; 395.9, 7851, 5.11;
375.8, 8245, 5.10; 355.9, 8740, 5.11; 336.2, 9288, 5.11;
316.3, 9848, 5.10; 294.9, 10456. 5.07; 275.5, 10982, 5.02;
259.6, 11596, 5.00; 239.8, 12400, 4.96; 220.4, 13234, 4.91;
210.2, 13647, 4.87; 199.9, 13930, 4.80; 195.1, 14023, 4.75;
189.7, 14026, 4.69; 184.9, 13777, 4.59; 178.0, 7849, 3.43;
175.3, 6718, 3.16; 170.5, 6098, 2.98; 164.8, 5841, 2.87;
160.0, 5503, 2.75; 140.0, 5291, 2.52; 117.1, 5869, 2.42;
97.8, 6926, 2.39; 77.4, 8697, 2.38

$[Fe(phen)_2(NCSe)_2]$, Preparation (a)

439.8, 6983, 5.10; 419.9, 7304, 5.09; 400.3, 7634, 5.08;
380.2, 7984, 5.06; 359.6, 8450, 5.05; 339.9, 8921, 5.04;
330.6, 9161, 5.04; 319.8, 9440, 5.02; 310.2, 9689, 5.01;
293.7, 10120, 4.98; 279.7, 10461, 4.94; 269.7, 10648, 4.89;
259.7, 10824, 4.84; 250.3, 10788, 4.74; 238.3, 10463, 4.56;
235.6, 10151, 4.47; 233.6, 9337, 4.27; 231.8, 7222, 3.76;
229.9, 2512, 2.30; 220.2, 1418, 1.77; 210.0, 882, 1.44;
200.0, 641, 1.26; 189.9, 500, 1.14; 180.3, 432, 1.07;
169.9, 386, 1.00; 160.0, 369, 0.96; 149.7, 372, 0.93;
140.2, 393, 0.92; 130.2, 417, 0.90; 120.4, 455, 0.88;
110.3, 499, 0.87; 99.4, 576, 0.86; 91.2, 633, 0.85;
77.2, 783, 0.84

$[Fe(phen)_2(NCSe)_2]$, Preparation (b)

440.2, 7014, 5.11; 420.0, 7354, 5.11; 400.5, 7666, 5.09;
380.0, 8135, 5.10; 360.1, 8534, 5.10; 340.2, 9003, 5.07;
330.4, 9209, 5.05; 320.0, 9406, 5.02; 310.4, 9621, 5.00;
292.4, 10018, 4.94; 279.4, 10157, 4.87; 269.7, 10230, 4.80;
259.7, 10157, 4.69; 250.0, 9739, 4.51; 239.6, 7686, 3.94;
237.7, 6824, 3.71; 235.5, 5739, 3.40; 233.7, 4815, 3.12;
231.6, 4062, 2.87; 230.0, 3735, 2.75; 219.9, 2721, 2.33;
209.6, 2283, 2.11; 199.4, 2097, 1.98; 189.9, 1997, 1.90;
179.6, 1968, 1.83; 170.1, 1987, 1.79; 160.2, 2033, 1.75;
149.6, 2132, 1.73; 139.8, 2241, 1.71; 130.5, 2383, 1.70;
119.4, 2621, 1.69; 109.6, 2856, 1.68; 99.9, 3130, 1.67;
91.8, 3395, 1.67; 77.4, 4029, 1.65

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

TABLE II

MOLECULAR AND PHENOMENOLOGICAL PARAMETERS FROM HIGH-TEMPERATURE MAGNETIC BEHAVIOR

Compound	T range, °K	Δ_{axial},[a] cm^{-1}	κ	T range, °K	Θ, °K
$[Fe(phen)_2(NCS)_2]$	430–293	−880	0.8	430–190	−25
$[Fe(phen)_2(NCSe)_2]$	440–330	−1400	0.8	440–300	−42

[a] Negative values of Δ_{axial} indicate that the nondegenerate level ($^5B_2$ or $^5A_1$ as sublevel of $^5T_2$) is lower in energy than the ^5E level.

according to method (a), the decrease is from 4.91 to 1.70 BM within 3.2° and the moment finally approaches 0.65 ± 0.01 BM at 77.4°K. For $[Fe(phen)_2(NCSe)_2]$, the analogous reduction of the moment occurs at 232°K. The decrease is less sudden, the most pronounced drop being from 4.27 to 2.30 BM within 3.7° for samples of type (a). At the lowest temperature investigated, *i.e.*, 77.2°K, the moment approaches 0.84 ± 0.01 BM. The transition takes place both with raising and with lowering of temperature and no hysteresis effects were observed.

The decrease of the magnetic moment has been noticed previously by Baker and Bobonich.[12] To explain qualitatively the observed magnetic behavior, these authors suggested an antiferromagnetic type of interaction between pairs of Fe^{2+} ions and assumed the formation of binuclear bridged complexes. If the spins of the two Fe^{2+} ions are denoted by S_1 and S_2, and the exchange coupling coefficient by J, the Hamiltonian of this system under an external magnetic field H is

$$\mathcal{H} = -2JS_1S_2 + g\beta H(S_1 + S_2) \qquad (1)$$

The susceptibility per gram-atom for two interacting centers each with spin $S = 2$ has been derived from eq 1 and is given by

$$\chi_A = \frac{Ng^2\beta^2}{kT} \times \left\{\frac{\exp(18z) + 5\exp(14z) + 14\exp(8z) + 30}{\exp(20z) + 3\exp(18z) + 5\exp(14z) + 7\exp(8z) + 9}\right\} + N\alpha \qquad (2)$$

In eq 2, $z = -J/kT$, k is the Boltzmann constant, N the Avogadro number, β the Bohr magneton, g the spectroscopic splitting factor, and $N\alpha$ the temperature-independent paramagnetism. Assuming $N\alpha = 0$, no reasonable fit of the curves for χ_A could be obtained for any value of the exchange coefficient J. The results of the calculation reproduced neither the sharp decrease of the moment nor the temperature of the decrease. Thus the assumption[12] of exchange-coupled pairs of Fe^{2+} ions does not seem to be reasonable. Since Earnshaw, *et al.*, have shown[20] that in exchange-coupled linear chains of ions the decrease is less pronounced, the more ions are considered, the assumption of exchange-coupled chains of ions seems to be even more unlikely.

Persuing an alternative explanation, we investigated the temperature dependence of the magnetic susceptibility for a $^1A_1$ state separated by ΔE from a higher lying $^5T_2$ state (*cf.* Figure 2). The susceptibility expression for this system is readily derived by application of Van Vleck's equation[21]

$$\chi_A = N\frac{\sum_{n,m}\left\{\frac{(E_{nm}^{(1)})^2}{kT} - 2E_{nm}^{(2)}\right\}\exp(-E_n^{(0)}/kT)}{\sum_n g_n \exp(-E_n^{(0)}/kT)} \qquad (3)$$

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(20) A. Earnshaw, B. N. Figgis, and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

(21) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, 1932.

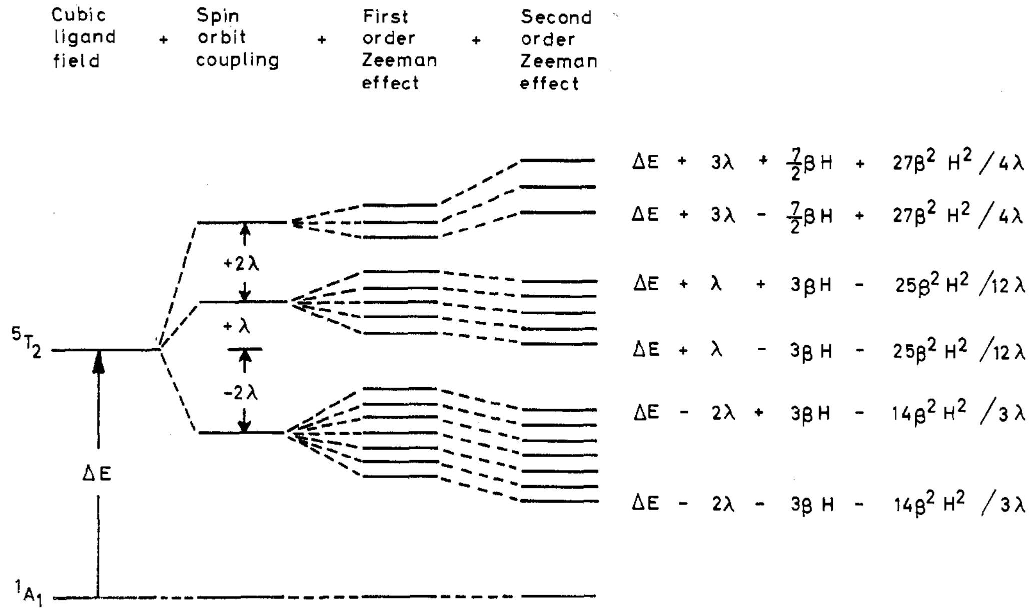

Figure 2.—Energy levels of the d^6 configuration in the crossover region (not to scale).

to the energy expressions of Figure 2. In eq 3, $E_n^{(0)}$, $E_{nm}^{(1)}$, and $E_{nm}^{(2)}$ are the zero-, first-, and second-order terms in H, respectively, and g_n is a degeneracy number. The resulting susceptibility is given by eq 4,

$$\chi_A = \frac{N\beta^2}{kT}\left\{\frac{(28x + 9.333)\exp[-(\Delta E/\lambda - 2)x] + (22.5x + 4.167) \times \exp[-(\Delta E/\lambda + 1)x] + (24.5x - 13.5)\exp[-(\Delta E/\lambda + 3)x]}{\{x1 + 7\exp[-(\Delta E/\lambda - 2)x] + 5\exp[-(\Delta E/\lambda + 1)x] + 3\exp[-(\Delta E/\lambda + 3)x]\}}\right\} + N\alpha \qquad (4)$$

where $x = \lambda/kT$. In terms of the magnetic moment μ_{eff}, a set of curves similar to those computed by Ewald, *et al.*,[22] for thermal equilibria in the configuration d^5 (*cf.* Figure 4 of the reference) is obtained for varying values of ΔE. Large values of ΔE result in diamagnetic behavior. For intermediate values of ΔE, the curves approach zero magnetic moment at low temperatures and moments of about 4.0–5.0 BM in the limit of high temperatures. For very small values of ΔE, *i.e.*, for $\Delta E + 3\lambda < 0$, moments of about 5.0 BM are obtained even at the lowest temperatures, since, in this case, the ground state is a sublevel of the paramagnetic $^5T_2$ state rather than the diamagnetic $^1A_1$ state.

A preliminary investigation indicated that reasonable agreement between the calculated and the measured temperature dependence of μ_{eff} could be achieved, and approximate values of ΔE were derived.[14] However, as soon as a complete set of theoretical curves became available, it was realized that a detailed fitting of the experimental results would be unsuccessful. Although the calculated moments vary, for intermediate ΔE values, between the expected limits, they do not reproduce the pronounced decrease of μ_{eff} at the temperatures of 174 and 232°K as observed experimentally. It is thus impracticable to derive ΔE values with any reliable accuracy, though the theoretical plots indicate that values of several hundreds of cm^{-1} should have the right magnitude.

The axial fields, which were deduced, *e.g.*, from the magnetic moments (*cf.* Table II), cause additional splittings of the levels and were not included in the calculations resulting in eq 4. However, such axial fields only slightly influence the magnetic susceptibility of a d^6 configuration.[8] It is therefore not very likely that they would modify eq 4 to such an extent as to account for the observed sharp decrease in μ_{eff}.

In some iron(III) compounds, the experimental moments are well-reproduced by the theory for thermal equilibria between $^6A_1$ and $^2T_2$ ground states, if the changes of metal–ligand vibration frequencies with respect to the two states are taken into account.[22] These changes influence the population of the zero-field levels and consequently affect the magnetic susceptibility. In the iron(II)–bis(1,10-phenanthroline) compounds studied at present, the vibration frequencies are expected to change accordingly, since the ground states $^5T_2$ and $^1A_1$ have to be characterized by different values of the ligand field strength Δ (see below), and thus will possess different metal–ligand distances r. However, a modification of eq 4 of the type as applied to iron(III) compounds[22] does not improve the agreement between theory and experiment.

In addition, the results are complicated by the fact that the low-temperature values of the magnetic moments depend to some extent on the preparative method employed. For [Fe(phen)$_2$(NCSe)$_2$], *e.g.*, a sample obtained by thermal decomposition of [Fe(phen)$_3$](NCSe)$_2$ *in vacuo* gave, according to Baker and Bobonich,[12] a moment of 1.46 BM at 110°K. Our preparative methods (a) and (b) yield samples having, at

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[22] A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc.* (London), **A280**, 235 (1964).

77.4°K, moment values of 0.84 and 1.65 BM, respectively. Mössbauer effect measurements, infrared spectra, electronic spectra, and X-ray powder patterns did not indicate any apparent differences for samples obtained by the methods (a) and (b). Thus, except for the magnetic susceptibility, all properties studied on these samples give practically identical results.

Mössbauer Spectra.—The ^{57}Fe Mössbauer spectra of [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$] were measured both at 293 and at ~77°K. Values of the isomer shift δ and the quadrupole splitting ΔE_Q as derived from these spectra are listed in Table III. The values reported recently by Collins, Pettit, and Baker,[23] which were derived from measurements at 77°K, are in error. On careful reinvestigation, these authors were able to confirm our present results.[24]

Table III

Results of ^{57}Fe Mössbauer Spectroscopy

Compound	T, °K	δ,[a] mm/sec	ΔE_Q, mm/sec
[Fe(phen)$_2$(NCS)$_2$]	293	0.98	2.67
	77	0.37	0.34
[Fe(phen)$_2$(NCSe)$_2$]	293	1.03	2.52
	77	0.35	0.18

[a] The isomer shifts δ are measured relative to the midpoint of the spectrum of a natural iron absorber.

The observed isomer shift measures the total s-electron density at the nucleus and is given by[25]

$$\delta = \frac{2}{5}\pi Z e^2[R_{ex}^2 - R_{gr}^2]\{|\psi_s(0)|_a^2 - |\psi_s(0)|_s^2\} \qquad (5)$$

where the quantities have their usual meaning. In iron(II) compounds, δ is in general larger for $^5T_2$ than for $^1A_1$ ground states.[26] This fact has been interpreted in terms of increased covalency of the metal–ligand bond in the $^1A_1$ state, since a larger d-electron delocalization decreases the shielding of core s electrons. In the systems studied at present, this assumption is well-supported by results of the electronic and vibrational spectra.

The quadrupole splitting ΔE_Q arises from the interaction of the ^{57}Fe nuclear quadrupole moment Q with an electric field gradient eq in the region of the nucleus

$$\Delta E_Q = \frac{1}{2}e^2qQ\left(1 + \frac{1}{3}\eta^2\right)^{1/2} \qquad (6)$$

where η is the asymmetry parameter.[27] From a spherical ground state like $A_1(t_2^6)$, a very small electric field gradient and thus a small quadrupole splitting will be expected. On the other hand, substantial values of ΔE_Q are obtained from T_2 terms in the absence of octahedral symmetry.

These expectations are supported by the available experimental data. For the low-spin [Fe(phen)$_3$]$^{2+}$ ion,[28] for example, $\delta = 0.45$ mm/sec, $\Delta E_Q \sim 0.30$ mm/sec was obtained, and similar values were reported for iron(II) complexes having 2,2′-dipyridyl, tripyridyl, and various substituted 1,10-phenanthroline ligands.[28] On the other hand, numerous high-spin iron(II) compounds yield values of δ between 0.8 and 1.4 mm/sec and values of ΔE_Q between 1.7 and 3.1 mm/sec.[26]

From the series [Fe(phen)$_2$X$_2$], the high-spin compound [Fe(phen)$_2$Cl$_2$] and the low-spin compound [Fe(phen)$_2$(NO$_2$)$_2$] were studied for comparison. At 293°K, they gave $\delta = 0.96$, $\Delta E_Q = 3.00$ mm/sec and $\delta = 0.28$, $\Delta E_Q = 0.38$ mm/sec, respectively. Almost unchanged values were measured at 77°K. The data of Table III in conjunction with the results of magnetic measurements thus clearly demonstrate that, at 293°K, the ground state of [Fe(phen)$_2$(NCS)$_2$] and of [Fe(phen)$_2$(NCSe)$_2$] is $^5T_2$, whereas, at 77°K, the ground state is $^1A_1$.

Infrared Spectra.—The infrared spectra of [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$] were studied between 4000 and 300 cm^{-1}, both at 298 and ~105°K. The 298°K spectrum is considered as being representative for the $^5T_2$ ground state, the 105°K spectrum as representative for the $^1A_1$ state. This assumption is supported by the finding[29] that the intensity of the C–N stretching mode shows practically the same dependence on temperature as the magnetic moment.

The thiocyanate and selenocyanate groups exhibit three fundamental frequencies, *i.e.*, ν_1 (C–N stretch), ν_2 (N–C–S or N–C–Se bend), and ν_3 (C–S or C–Se stretch). Since both thiocyanate and selenocyanate are difunctional ligands, the positions of ν_1, ν_2, and ν_3 depend on whether these groups are attached to the metal ion through N or through S or Se, respectively. For N-bonded thiocyanate, the following absorption ranges are proposed:[30–32] ν_1, 2040–2080; ν_2, 465–480; ν_3, 780–860 cm^{-1}, whereas for S-bonded thiocyanate the ranges are: ν_1, 2080–2120; ν_2, 410–470; ν_3, 690–720 cm^{-1}. For the selenocyanate group, a similar relationship seems to exist.[33–36] In addition, Cotton, *et al.*, have shown[32] that analogous isothiocyanato (M–NCS) and isoselenocyanato (M–NCSe) complexes exhibit C–N stretching frequencies within 10 cm^{-1} of each other. Inspection of Table IV demonstrates that in the $^5T_2$ state both thiocyanate and selenocyanate are N-bonded. In [Fe(phen)$_2$(NCSe)$_2$], ν_2 and ν_3, which are known to appear in KNCSe at 424/416 and 558 cm^{-1}, respectively,[37] were not observed. It is assumed that they coincide with some of the numerous bands of the phenanthroline ligand or that

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TABLE IV

INFRARED FREQUENCIES OF THE NCS AND NCSe GROUPS IN IRON(II)–BIS(1,10-PHENANTHROLINE) COMPLEXES

[Fe(phen)$_2$(NCS)$_2$] $^5T_2$ (298°K)	[Fe(phen)$_2$(NCS)$_2$] $^1A_1$ (105°K)	[Fe(phen)$_2$(NCSe)$_2$] $^5T_2$ (298°K)	[Fe(phen)$_2$(NCSe)$_2$] $^1A_1$ (105°K)	Assignments
2075 vs	2116 vs	2075 vs	2112 vs	ν_1, C–N str
2063 vs	2108 vs	2065 vs	2106 vs	
809 w	809 vs			ν_3, C–S str
	807 vs			
483 s	476 s			ν_2, N–C–S bend
473 s				

they are weak in intensity as noticed for some selenocyanate complexes.[38]

In the $^1A_1$ state, the C–N stretching mode is shifted to 2116/2108 cm^{-1} for [Fe(phen)$_2$(NCS)$_2$] and to 2112/2106 cm^{-1} for [Fe(phen)$_2$(NCSe)$_2$]. Although the position of the C–N stretch in the $^1A_1$ state is within the range for S-bonded thiocyanate and Se-bonded selenocyanate groups, the assumption of a change in linkage from N- to S-bonded (or Se-bonded) groups can easily be ruled out. First of all, such an assumption could hardly be reconciled with the fact that no phase change was detected by X-ray techniques. Since the steric requirements of M–SCN bonding are greater than for M–NCS groups,[39] it is unlikely that such change could take place within the same lattice. In addition, such an assumption would be in disagreement with the behavior of ν_2 and ν_3 with temperature.

The shift of ν_1 by 40 cm^{-1} to higher frequencies on transition from the $^5T_2$ to the $^1A_1$ ground state rather indicates a considerable strengthening of the C–N bond. Turco and Pecile observed[40] that in mixed complexes the electron density on the thiocyanate ion depends on the additional ligands present. Thus in Pt(II) and Pd(II) complexes, the acceptor properties of π-bonding ligands favor M–NCS linkage over M–SCN bonds. Since 1,10-phenanthroline is a good π-bonding ligand, and since iron has to be considered as an A-type metal according to the Ahrland–Chatt–Davies classification,[41] the observed M–NCS linkage is expected. On transition to the low-spin t_2^6 configuration, the tendency of 1,10-phenanthroline to reduce the electron density on the metal will be enhanced by the larger overlap of metal t_2 and antibonding π^* orbitals of phenanthroline. It may be anticipated that due to the lower availability of t_2 electrons on the metal, the back donation into π^* orbitals of the NCS or NCSe ligands will be reduced, thus decreasing the strength of the Fe–NCS or Fe–NCSe bond.[42] This mechanism provides the explanation for the observed shift of the C–N stretching frequency, since the increased ionic character of the Fe–NCS (or Fe–NCSe) bond is implied by the strengthening of the C–N bond.[43]

The observed splitting of the C–N stretching mode both in [Fe(phen)$_2$(NCS)$_2$] and in [Fe(phen)$_2$(NCSe)$_2$] into two bands separated by 12 and 10 cm^{-1}, respectively, is taken as an indication of *cis* configuration. For comparison, the compound [Fe(dmph)$_2$(NCS)$_2$] (dmph = 2,9-dimethylphenanthroline) was studied. This complex should have a *cis* configuration for stereochemical reasons and exhibits a splitting of the C–N stretching band of 11 cm^{-1}. A *cis* configuration has also been reported[44] for [Fe(phen)$_2$(CN)$_2$], where the C–N stretch is showing two peaks at 2075 and 2062 cm^{-1}, as well as for [Fe(phen)$_2$(CNO)$_2$].[10] Finally, infrared data indicate *cis* configuration for [Fe(phen)$_2$(OCN)$_2$] and for [Fe(phen)$_2$(NO$_2$)$_2$] as well.[45] This preference for *cis* arrangement is evident on the basis of molecular models, since two phenanthroline molecules cannot be accommodated in the same plane without nonbonded H–H interactions in the 2,9 position.[46]

Electronic Spectra.—The spectrum of [Fe(phen)$_2$(NCS)$_2$] between 7000 and 45,000 cm^{-1} measured both at 298 and at ~77°K is shown in Figure 3. The positions of absorption maxima and band assignments for [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$] are listed in Table V.

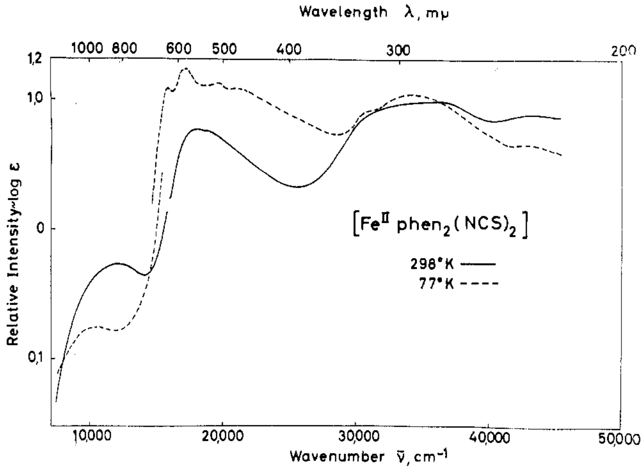

Figure 3.—Electronic spectrum of [Fe(phen)$_2$(NCS)$_2$] at 298°K (full line) and at 80°K (broken line). Left part of the spectrum: undiluted sample; right part of the spectrum: sample diluted with LiF (1:50).

In the region characteristic for d–d transitions, the room-temperature spectrum of [Fe(phen)$_2$(NCS)$_2$] shows a band at 11,900 cm^{-1} corresponding to the $^5T_2 \rightarrow {}^5E$ transition,[47] which determines $\Delta(^5T_2) = 11{,}900$ cm^{-1}. It is required by the analysis of the magnetic data that $\Delta(^5T_2)$ should be almost equal to the spin-pairing energy $\pi = {}^5/_2B + 4C \sim 18.5B$ (assuming the usual relation $C \sim 4B$ between the electron repulsion parameters). Thus taking $\Delta(^5T_2) = \pi$, one obtains $B(^5T_2) \sim 640$ cm^{-1}. Since $B(\text{free Fe}^{II}) =$

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TABLE V

ABSORPTION MAXIMA IN ELECTRONIC SPECTRA OF IRON(II)–BIS(1,10-PHENANTHROLINE) COMPLEXES (CM^{-1})

$[Fe(phen_2)(NCS)_2]$		$[Fe(phen)_2(NCSe)_2]$		
298°K	80°K	298°K	80°K	Assignments
11,900		11,900		$^5T_2 \rightarrow {}^5E$
	10,400		10,400	$^1A_1 \rightarrow {}^3T_1$
18,000	15,900	18,200	16,100	$(core)\pi^2t_2^6 \rightarrow (core)\pi^2t_2^5\pi^*$
19,050	17,200	19,200	17,550	
	18,500		18,700	
	19,700		20,000	
	21,000		22,800	
31,200	30,800	29,400	29,400	$(core)\pi^2t_2^6 \rightarrow (core)\pi t_2^6\pi^*$
33,200	33,900	33,300	33,300	
36,400	36,400	36,500	36,800	
43,500	43,000	43,000	43,500	

1058 cm^{-1}, the nephelauxetic ratio $\beta = B(\text{complex})/B(\text{free ion}) \sim 0.61$.

At 77°K, a new spectrum is observed, showing a band at $\sim$10,400 cm^{-1}. This band is assigned to the $^1A_1 \rightarrow {}^3T_1$ transition in analogy to the spectrum of the diamagnetic $[Fe(phen)_3]^{2+}$ ion.[6,48] The lower intensity of this band is consistent with the fact that the $^1A_1 \rightarrow {}^3T_1$ transition is multiplicity forbidden, whereas $^5T_2 \rightarrow {}^5E$ is multiplicity allowed. To obtain an estimate of the ligand field parameter $\Delta(^1A_1)$, the rule of average environment[50] is applied, according to which

$$\Delta\{Fe(phen)_2(NCS)_2\} = \frac{2}{3}\Delta\{Fe(phen)_3{}^{2+}\} + \frac{1}{3}\Delta\{Fe(NCS)_6{}^{4-}\}$$

Δ for the $[Fe(phen)_3]^{2+}$ ion is practically the same as for $[Fe(dip)_3]^{2+}$ (dip = 2,2′-dipyridyl), which is estimated using eq 130 from Jørgensen's book.[50] To this end, $f(\text{dip}) = 1.44$ has been determined from the values of Δ for $[Ni(dip)_3]^{2+}$ and $[Co(dip)_3]^{2+}$, *viz.*, 12,790 and 12,670 cm^{-1}, respectively.[49] The function f is defined by[50] $\Delta = f(\text{ligand}) \times g(\text{central ion})$. One obtains[51] $\Delta\{Fe(phen)_3{}^{2+}\} \sim 18{,}000$ cm^{-1}. Analogously, the values for $[Cr(NCS)_6]^{3-}$ and $[Mn(NCS)_6]^{4-}$, *viz.*, 17,800 and 8800 cm^{-1}, and the corresponding values for the hexaaquo ions determine $f(NCS) = 1.03$ and $\Delta\{Fe(NCS)_6{}^{4-}\} \sim 12{,}900$ cm^{-1}. Finally, the low-spin ground state of $[Fe(phen)_2(NCS)_2]$ is characterized by $\Delta(^1A_1) \sim 16{,}300$ cm^{-1}.

The energy separation between $^1A_1$ and $^3T_1$ is reasonably well approximated by $\Delta - 3C + 50B^2/\Delta \sim \Delta - 12B + 50B^2/\Delta$. The wavenumber of the observed transition, *i.e.*, 10,400 cm^{-1}, enables one to calculate $B(^1A_1) \sim 580$ cm^{-1} and $\beta \sim 0.55$.

The inequality $\Delta(^5T_2) < \pi < \Delta(^1A_1)$ thus appears to be satisfied. The increase in Δ per electron transferred from an e to a t_2 orbital amounts to 18.5%. The decrease in B from 640 to 580 cm^{-1} and the corresponding decrease in β from 0.61 to 0.55 are consistent with the increase in back π bonding of the Fe–N (phenanthroline) bond inferred on the basis of infrared spectra.[42]

In analogy to the tris(1,10-phenanthroline)iron(II) complex ion, we assign the intense visible absorption band of the $^1A_1$ ground state having the highest maximum at 17,200 cm^{-1} to a charge-transfer transition $(core)\pi^2t_2^6 \rightarrow (core)\pi^2t_2^5\pi^*$. The structure of the band is most likely due to vibrational coupling. The distance between the single components, $\sim$1300 cm^{-1}, is very close to two of the infrared-active vibrational modes of the phenanthroline ligand, *viz.*, 1300 and 1307 cm^{-1}.[42] The intense absorption band at $\sim$18,000 cm^{-1} of the $^5T_2$ ground state originates very likely in the same type of transition. Thus, in the $^1A_1$ state, the main charge-transfer band is shifted by 800 cm^{-1} to lower energy as compared to the $^5T_2$ state. The lower band energy may be considered as an indication of a higher π-bonding contribution.

The intense bands observed at energies higher than that of the charge-transfer transition are essentially due to $\pi \rightarrow \pi^*$ internal ligand transitions.

The spectrum of $[Fe(phen)_2(NCSe)_2]$ is completely analogous to that of $[Fe(phen)_2(NCS)_2]$, and thus the same band assignments may be applied.

X-Ray Diffraction.—X-Ray data were collected from powder photographs both at 298 and $\sim$77°K. From a comparison of the data, the possibility of a phase change with decreasing temperature has been ruled out. Essentially the same result has been obtained by Baker and Bobonich.[12]

General Discussion of the Observed Transition

It has been demonstrated that above a critical temperature of 174 and 232°K, respectively, the compounds $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$ exist in a $^5T_2$ ground state, whereas below this temperature the ground state is $^1A_1$. Although most of the results agree in a qualitative way with the theoretical expectations for thermal equilibria between $^5T_2$ and $^1A_1$ states, the quantitative agreement for the magnetic moments is considered poor. It is suggested that in part of the $^1A_1 \rightarrow {}^5T_2$ transition, nonequilibrium conditions might be involved. This assumption is supported by the changes in infrared spectra[42] which follow the transition in magnetic behavior. Unlike some iron(III) dialkyldithiocarbamates,[22] where the transition between high-spin and low-spin states seems to be governed solely by the population of the low-lying levels, the transition between ground states of different multiplicity in iron(II)–bis(1,10-phenanthroline) compounds is associated with a significant modification of the

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(48) According to recent single crystal spectra,[49] the perpendicularly-polarized band observed at 11,500 cm^{-1} (ϵ 3.6 in solution) in the $[Fe(dip)_3]^{2+}$ ion and, correspondingly, the band at 12,260 cm^{-1} (ϵ 4.4) in $[Fe(phen)_3]^{2+}$ should be assigned to the $^1A_1 \rightarrow {}^3T_1$ transition. Polarization and intensity may be explained assuming admixture with the perpendicularly-allowed $(core)\pi^2t_2^6 \rightarrow (core)\pi^2t_2^5\pi^*$ charge-transfer band at 18,800 cm^{-1}. Our previously proposed assignment[6] is in error.

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molecular structure, although a crystallographic phase change is not involved. The sharp increase of the magnetic moment with rising temperature thus indicates the transition of a potential barrier between the two molecular configurations,[55] the character of which may only tentatively be described at present.[42] The activation energy of the transition can be estimated at $\Delta E_{\mathrm{A}} = 120\ \mathrm{cm}^{-1}$ (about 350 cal/mole) for [Fe(phen)$_2$(NCS)$_2$] and at 160 cm^{-1} (about 460 cal/mole) for [Fe(phen)$_2$(NCSe)$_2$].

The transition $^1\mathrm{A}_1(\mathrm{t}_2{}^6) \rightarrow {}^5\mathrm{T}_2(\mathrm{t}_2{}^4\mathrm{e}^2)$ involves the transfer of two electrons from a t$_2$ to an e orbital which should be followed by a marked increase in the ionic radius of about 0.2 A.[50,56,57] In addition, the low-spin d^6 configuration involves the filled t$_2$ subshell and is thus particularly stable (ligand field stabilization 2.4Δ as compared to 0.4Δ for the high-spin configuration). Thus it is not unreasonable to assume that spin-state equilibria in compounds of the d^6 configuration are *in general* associated with a change in molecular dimensions. Further investigations on this problem are in progress.

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Raman Study of Glycine Complexes of Zinc(II), Cadmium(II), and Beryllium(II) and the Formation of Mixed Complexes in Aqueous Solution[1]

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Raman spectra are reported for the aqueous systems zinc(II)–glycine, cadmium(II)–glycine, and beryllium(II)–glycine in the pH range 2.0–7.0. At the lower pH range, glycine forms monodentate complexes with the metal ions, through the oxygen atom of the carboxyl group. At the higher pH range, glycine forms, mono, bis, and tris bidentate complexes with Zn(II) and Cd(II) ions. However, at higher pH, glycine does not bind the Be(II) ion, and for this system, glycine does not seem to form a bidentate complex with beryllium. Spectra of the system ZnCl$_2$–glycine at pH 5.0 indicate the presence of at least two mixed complex species involving bidentate glycine and the chloride ion bound to the metal. The system CdCl$_2$–glycine at pH 5.0 also contains a mixed complex species. These systems at low pH contain mixed species containing monodentate glycine and chloride ions bound to the metal ions. Spectra of systems Zn(II)–glycine–SCN$^-$ and Cd(II)–glycine–SCN$^-$ at pH 5.0 indicate the presence of at least two mixed complex species containing bidentate glycine and one and two thiocyanate ions bound to the metal. Finally, the spectra of the systems ZnCl$_2$–glycine–SCN$^-$ and CdCl$_2$–glycine–SCN$^-$ at pH 5.0 seem to indicate the presence of a ternary complex containing bidentate glycine, chloride, and the thiocyanate ions bound to the metals.

The Raman spectra in solution of glycine in its various protonated forms have been the subject of numerous investigations.[2–4] The infrared spectra of glycine in aqueous solutions have been reported by Nakamoto, *et al.*,[5] who have also studied the solution spectra of some metal complexes of amino acids. Detailed vibrational normal coordinate analysis of glycine[6] and its 1:1 metal complex[7] have also been reported in the literature. Infrared spectra in the solid state of a variety of metal–glycino complexes have also been studied by a number of investigators.[8–12] To date, however, Raman spectra of metal–glycino complexes have not been investigated. The present study concerns the Raman spectra in aqueous solution of some zinc(II)–glycine complexes and includes mixed complexes of zinc glycinate with chloride and thiocyanate

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