

Nickel(II) Complexes with Oxygen and Sulfur Donors

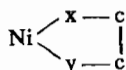
J. T. Morrison and W. A. Baker, Jr.

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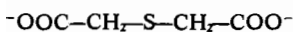
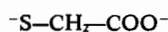
Nickel(II) complexes of dithiooxalate, thioglycolate, oxalate, and thiodiglycolate ions have been prepared, and their magnetic properties and electronic spectra studied. The complexes found are octahedral so long as there are at least four oxygens in the coordination sphere. Complexes containing three sulfur atoms are planar if the sulfurs have a negative charge. One octahedral complex containing three oxygens and three sulfur atoms was prepared, but data suggest that two of the sulfur atoms are protonated.

Introduction

The Ni^{II} ion forms many different complexes with ligands bonding through oxygen or sulfur. Those complexes where oxygen is the bonding atom are generally six coordinate, octahedral and paramagnetic. Complexes having nickel-sulfur bonds are usually four coordinate, square planar and diamagnetic. It would be interesting to know what properties would be exhibited by complexes containing ligands bonding through both oxygen and sulfur. We have investigated a series of complexes in which the coordination sphere of the nickel ion is changed from all oxygen atoms to all sulfur atoms in a regular fashion. The ligand system chosen for this study involves the formation of the chelate ring where



x and y are sulfur and/or oxygen. The four ligands used were the acid anions: oxalate, C₂O₄²⁻, dithiooxalate, C₂O₂S₂²⁻, thiodiglycolate, (C₂H₂O₂)₂S²⁻, **1**, and thioglycolate, C₂H₂O₂S²⁻, **2**.

**1****2**

Some previous work on the nickel(II) complexes of these ligands has been published. A hydrated bis(oxalato)nickelate(II) has been known for some time,¹ as has the bis(dithiooxalato)nickelate(II) complex.² A solution spectrum and a molecular orbital scheme for the latter complex have been reported by Latham, *et al.*³ Only formation constant data are avail-

able for the complexes of nickel and the thiodiglycolate ion.⁴ A number of investigators have reported on aspects of the thioglycolate-nickel system^{5,6} but the most complete work has been done by D. L. Leussing and coworkers.⁷⁻¹⁰ The latest conclusions are that an extensive series of species forms in a basic thioglycolate solution when nickel(II) ion is added, Ni(SCH₂CO₂)₂²⁻ and Ni₄(SCH₂CO₂)₆⁴⁻ being the most stable species.

The bis(thioglycolate) and dithiooxalate complexes of nickel(II) are reported to be diamagnetic in solution.⁵ Little or no characterization has been done on the solid form of these complexes, with the exception of K₂[Ni(C₂O₂S₂)₂] which was shown to be square planar by X-ray studies.¹¹

Experimental Section

Materials. All chemicals used were reagent grade and were used without further purification. Thioglycolic acid was supplied by Evans Chimetics, potassium dithiooxalate by Eastman and thiodiglycolic acid by K and K laboratories.

Potassium bis(oxalato)diaquonickelate(II) tetrahydrate. Nickel oxalate (0.1 moles) was added in small increments to a boiling solution of 0.1 moles potassium oxalate in 200 ml of water. After each addition, stirring and heating were continued until all solid had disappeared before a new portion of solid was added. The final deep green solution was vacuum evaporated until the first crystals appeared. The crystals were recovered by filtration and ground in a mortar under a solution of concentrated HCl in ethanol. This was done to remove any excess oxalate as the acid, H₂C₂O₄, which is very soluble in ethanol. After several such treatments the solid was filtered, water washed and vacuum dried at 50°C. *Anal.* Calcd. for K₂[Ni(C₂O₄)₂(H₂O)₂] · 4H₂O: Ni, 13.93; C₂O₄²⁻, 41.7. Found: Ni, 13.97; C₂O₄²⁻, 41.4.

Potassium oxalatothioglycolatodiaquonickelate(II).(4) R. M. Tichane and W. E. Bennet, *J. Am. Chem. Soc.*, **79**, 1243 (1957).(5) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).(6) D. D. Perrin and I. C. Sayce, *J. Chem. Soc. (A)*, **82** (1967).(7) I. M. Kolthoff and D. L. Leussing, *J. Am. Chem. Soc.*, **75**, 3904 (1953).(8) D. L. Leussing, *Ibid.*, **80**, 4180 (1958).(9) D. L. Leussing, R. E. Laramy, and G. S. Alberts, *Ibid.*, **82**, 4826 (1960).(10) D. L. Leussing and G. S. Alberts, *Ibid.*, **82**, 4458 (1960).(11) E. S. Cox, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 1475 (1935).(1) K. V. Krishnamurty and G. M. Harris, *Chem. Rev.*, **61**, 213 (1961).(2) H. O. Jones and H. S. Tasker, *J. Chem. Soc.*, 1909 (1904).(3) A. R. Latham, V. C. Hascal, and H. B. Gray, *Inorg. Chem.*, **4**, 788 (1965).

Thioglycolic acid (0.01 moles) was neutralized with potassium t-butoxide in methanol under nitrogen. Small portions of a slurry of nickel oxalate (0.01 moles) were added over a period of several hours. Stirring under nitrogen at reflux was continued until all solid had dissolved. A light green solid was collected, washed and vacuum dried. *Anal.* Calcd. for $K_2[Ni(C_2O_4)(C_2H_2O_2S)(H_2O)_2]$: C, 13.68; H, 1.72; S, 9.13. Found: C, 13.78; H, 1.79; S, 9.73.

Potassium bis(thioglycolato)nickelate(II) tetrahydrate. Nickel chloride (0.02 moles), thioglycolic acid (0.04 moles) and potassium hydroxide (0.1 moles) were stirred in water under a stream of nitrogen for several hours. The resulting green solution was vacuum evaporated to a small volume, cooled to crystallization and filtered. The green crystals were vacuum dried. *Anal.* Calcd. for $K_2\{Ni[(C_2H_2O_2)_2S]\} \cdot 4H_2O$: Ni, 11.62; C, 19.02; H, 3.19; S, 12.69. Found: Ni, 11.63; C, 19.32; H, 2.70; S, 12.85.

Potassium Dithiooxalatothioglycolatonickelate(II) monohydrate. Nickel hydroxide (0.05 moles), thioglycolic acid (0.06 moles) and potassium dithiooxalate (0.05 moles) were stirred together under nitrogen for an hour in a mixture of methanol and 2,2-dimethoxy propane. The reaction mixture was filtered and the red filtrate vacuum evaporated to one third its original volume and then cooled to produce a red solid. *Anal.* Calcd. for $K_2[Ni(C_2O_2S_2)(C_2H_2O_2S)]H_2O$: Ni, 16.2; C, 13.15; H, 1.0; S, 26.3. Found: Ni, 16.1; C, 13.23; H, 0.72; S, 25.8.

Potassium bis(dithiooxalato)nickelate(II). Nickel sulfate (0.02 moles) was dissolved in a minimum of water and slowly added from a dropping funnel to a very concentrated solution of potassium dithiooxalate (0.04 moles) in water. After thirty minutes stirring under nitrogen, the reaction mixture was filtered to give deep red crystals which were vacuum dried. *Anal.* Calcd. for $K_2[Ni(C_2O_2S_2)_2]$: Ni, 15.56; C, 12.73; S, 34.01. Found: Ni, 15.87; C, 13.08; S, 33.69.

Compounds in the thioglycolate system. The first product in this system, a tris(thioglycolato)-nickelate(II) complex, was discovered in the attempt to prepare a polynuclear species $Ni_2(SCH_2CO_2)_3$. The reaction was carried out in water with no attempt at pH control. Nickel thioglycolate, prepared by mixing nickel sulfate and sodium thioglycolate, was slowly added to an aqueous solution of sodium thioglycolate. A dark green-brown solid precipitated immediately. The analysis of this product is shown below. There are a number of formulations that agree reasonably well with the analytical results such as $Na_4[Ni(SCH_2CO_2)_3]$ and $Na_3[Na_3[Ni(SCH_2CO_2)_2(HSCH_2CO_2)]] \cdot H_2O$. Conductance measurements, however, clearly indicate that the material forms a 2:1 electrolyte in solution. We therefore feel that the compound is best represented as $Na_2[Ni(HSCH_2CO_2)_2(SCH_2CO_2)] \cdot 2H_2O$. *Anal.* Calcd. for $Na_2[Ni(C_2H_2O_2SH)_2(C_2H_2O_2S)] \cdot 2H_2O$: Ni, 14.3; C, 17.4; H, 2.9; S, 23.2. Found: Ni, 13.9; C, 17.2; H, 2.6; S, 23.3.

A polynuclear species of different stoichiometry from that sought above was prepared. To 0.05 moles

$Ni(NO_3)_2$ dissolved in an ethanol-water mixture was added 0.075 moles of sodium thioglycolate in the same solvent which had been raised to pH 11 by addition of sodium hydroxide. Several hours stirring produced a green solid. *Anal.* Calcd. for $Na_4[Ni_4(C_2H_2O_2S)_6] \cdot 15H_2O$: Ni, 20.73; C, 12.72; H, 3.74; S, 16.98. Found: Ni, 19.46; C, 12.74; H, 3.49; S, 16.66.

A bis(thioglycolato)nickelate(II) complex was prepared by adding 0.05 moles nickel chloride dissolved in hot water dropwise to a stirred aqueous solution consisting of 0.1 moles thioglycolic acid raised to a pH of approximately 11 with sodium hydroxide. The addition was complete in two hours, but stirring under nitrogen was continued for twenty hours. In the course of the nickel addition the color of the solution was observed to progress from a clear violet to a dull green. A dull green solid was filtered, washed with water then acetone and vacuum dried. *Anal.* Calcd. for $Na_2[Ni(C_2H_2O_2S)_2(H_2O)_2] \cdot 2H_2O$: Ni, 16.45; C, 13.46; H, 3.39; S, 17.97. Found: Ni, 16.48; C, 13.67; H, 3.40; S, 17.95.

The violet colored solution mentioned above has been well described.⁸⁻¹⁰ We were not able in many different attempts to isolate a violet solid from this solution. The only solid that formed in these systems was green and usually proved to be the bis(thioglycolato)complex.

Spectra. Infrared spectra were obtained with a Perkin-Elmer Model 521 Spectrophotometer. All substances were examined in KBr pellets. Electronic spectra were obtained using a Cary model 14 spectrophotometer or a Perkin-Elmer model 4000-A Spectrophotometer. Solution spectra were obtained using matched 1 cm path length quartz cells. Solvents used were Reagent Grade ethanol, methanol or doubly distilled water. Reflectance spectra were taken on the Cary 14 using the Diffuse Reflectance attachment with finely powdered $MgCO_3$ as the reference solid.

Magnetic Data. Magnetic measurements were obtained with a Gouy balance calibrated with $Hg[Co(NCS)_4]$. Measurements were made at three different field strengths for each temperature and no field dependence was observed. Corrections were made for diamagnetic constituents using the appropriate Pascal constants.

Analytical Data. Microanalyses were performed by: Schwartzkopf Microanalytical Laboratories, New York, Galbraith Laboratories Inc., Knoxville, Tennessee and Alfred Bernhardt Mikroanalytisches Laboratorium, Max Planck Institute, Mulheim (Ruhr), West Germany. Nickel was determined by the dimethylglyoxime method and oxalate was determined by the volumetric permanganate method, both in our laboratory.

Results and Discussion

Complete vibrational studies have been done for dithiooxalate¹² and oxalate¹³ ion metal complexes, but

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(13) J. Fumita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, 36, 324 (1962).

only sketchy information is available for the infrared spectra of the other two ligands. We found considerable differences in band positions and shapes between the uncomplexed and complexed ligand in the case of the thiodiglycolate and thioglycolate ions. Our dithiooxalate infrared spectra agreed with published data. Infrared data for the bis(oxalato) complex of nickel are lacking but that published for the bis(oxalato) complex of platinum agrees well with our finding. We conclude that the ligands are bonding as expected, the oxalate, dithiooxalate, and thioglycolate as bidentate chelates and thiodiglycolate as a tridentate chelate.

As indicated in the experimental section, we have formulated certain of the complexes as containing coordinated water molecules. Unfortunately, we have found no way to prove this contention. The infrared spectra are too complex to use as support. On the basis of the observed magnetic and spectral results, we feel that the formulas proposed are most logical.

Magnetic Properties. Magnetic data were obtained over the range 79-300° K. The results, in terms of the molar susceptibilities ($\times 10^6$ cgsu) after corrections for diamagnetism, with the temperature of the measurement are: $K_2[Ni(C_2O_4)_2(H_2O)_2] \cdot 4H_2O$; 2570(290), 3050(237), 4170(162), 5540(111), 7330(79). $K_2[Ni(C_2O_4)(SCH_2CO_2)(H_2O)_2]$; 2370(294), 2850(251), 3720(178), 5740(110). $Na_2[Ni(SCH_2CO_2)_2(H_2O)_2] \cdot 2H_2O$; 3170(293), 3860(245), 5600(174), 9240(110), 13640(79). $Na_4[Ni_4(SCH_2CO_2)_6] \cdot 15H_2O$; 2740(294), 3690(218), 5100(158), 7900(102). $K_2[Ni(O_2CCH_2)_2S]_2 \cdot 4H_2O$; 2870(295), 3620(229), 4710(178), 7480(108). $Na_2[(HSCH_2CO_2)_2(SCH_2CO_2)] \cdot 2H_2O$; 1400(294), 1670(232), 2470(134), 3620(79), 8680(1.63). $K_2[Ni(C_2O_4S_2)(SCH_2CO_2)] \cdot H_2O$; diamagnetic. $K_2[Ni(C_2O_4S_2)_2]$; diamagnetic. $Ni(SCH_2CO_2)_2^{2-}$ (in aqueous solution); diamagnetic. It can be seen that the complexes are paramagnetic (and octahedral as shown by the spectra) when there are more oxygens than sulfurs coordinated. All of the paramagnetic compounds except $Na_2[(HSCH_2CO_2)_2(SCH_2CO_2)] \cdot 2H_2O$ follow the Curie-Weiss law. The values of μ_{eff} and Θ obtained from a plot of $1/X_M'$ vs T are shown in Table I. In three of the compounds there are rather large Weiss Constants but no field dependence of the moment was observed. Thus although magnetic dilution may not be complete, no clearly ferromagnetic or antiferromagnetic behavior was observed.

Table I. Magnetic Data for Ni(II) Complexes

Compound	μ_{eff} (BM)	Θ (°K)
$K_2[Ni(C_2O_4)_2(H_2O)_2] \cdot 4H_2O$	3.25	-40
$K_2[Ni(C_2O_4)_2(SCH_2CO_2)(H_2O)_2]$	3.05	-20
$K_2[Ni(O_2CCH_2)_2S]_2 \cdot 4H_2O$	3.25	0
$Na_2[Ni(SCH_2CO_2)_2(H_2O)_2] \cdot 2H_2O$	3.30	17
$Na_4[Ni_4(SCH_2CO_2)_6] \cdot 15H_2O$	3.17	0

The « tris(thioglycolate) » complex, $Na_2[Ni(HSCH_2CO_2)(SCH_2CO_2)] \cdot 2H_2O$, does not follow the Curie-Weiss law and exhibits a temperature dependent mo-

ment that is appreciably below the value expected for paramagnetic Ni^{II} (see Table II). The possibility that this compound represents a system with a singlet ground state and a thermally accessible triplet state is immediately suggested. Treatment of the magnetic data in the standard way¹⁴ by evaluating the equilibrium constant at each temperature and plotting $\ln K$ vs. $1/T$ yielded a plot with significant curvature. Curvature itself is not unusual but in this case the data indicate that the triplet state is being stabilized (that is, the separation between the singlet and triplet state decreases) as the temperature decreases. This is the opposite of what is usually found,^{14,15} although Goodgame *et al.*, have reported a similar case.¹⁶ It is worth noting that the bis(thioglycolato)nickelate(II) complex is paramagnetic and octahedral in the solid but diamagnetic in aqueous solution.

Table II. Magnetic Data for $Na_2[Ni(HSCH_2CO_2)_2(SCH_2CO_2)] \cdot 2H_2O$

Temperature (°K)	μ_{eff} (BM) ^a	Keq ^c
293.5	2.27	0.96
231.6	2.20	0.82
133.7	2.03	0.63
79.0	1.89	0.50
16.3	1.33 ^b	0.18

^a Calculated from the expression $\mu_{eff} = 2.83[X_M T]^{1/2}$; ^b Obtained using a Faraday balance as described in reference 15; ^c Defined as the triplet: singlet ratio. A value of 3.2 B.M. was used for the triplet and 0.5 B.M. for the singlet.

Electronic Spectra

On the basis of their electronic spectra, the compounds fall into two clear groups, one having an octahedral and the other a square planar geometry.

Octahedral Complexes. The complexes having more oxygen atoms than sulfur atoms bonded to the nickel(II) gave typically octahedral spectra. Three ligand field bands were observed for each, in the near infrared around 9500 and in the visible region around 15,000 and 25,000 cm^{-1} . For those compounds having a negatively charged sulfur bonded to the metal, the high energy band appears as a shoulder on a charge transfer band. The band positions and extinction coefficients where they could be determined are given in Table III.

There are several features of the spectra that merit some discussion. The first band, which can be assigned to the ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition, is in all cases broad and asymmetric. In some cases, a shoulder is clearly discernible. These features of the band could be due primarily either to spin-orbit coupling splitting¹⁷ of the ${}^3T_{2g}$ state or the splitting due to low symmetry fields.¹⁸ Considering the fact that the com-

(14) S. L. Holt, Jr., R. J. Bouchard, and R. L. Carlin, *J. Am. Chem. Soc.*, **86**, 519 (1964).

(15) J. S. Judge and W. A. Baker, Jr., *Inorg. Chim. Acta*, **1**, 68 (1967).

(16) D. M. L. Goodgame, and M. T. Weeks, *J. Chem. Soc. (A)*, 1125 (1967).

(17) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **6**, 134 (1959).

(18) David A. Rowley and Russel S. Drago, *Inorg. Chem.*, **6**, 1092 (1967).

Table III. Electronic Spectra ^a

Compound	Absorption Spectra, cm ⁻¹					State
K ₂ [Ni(C ₂ O ₄) ₂ (H ₂ O) ₂] · 4H ₂ O ^b	8,300 (sh)	9,060 (7)	13,400 (sh)	15,260 (8)	26,160 (17)	solution
K ₂ [Ni(C ₂ O ₄)(SCH ₂ CO ₂)(H ₂ O) ₂]	9,160	9,900 (sh)		15,400	27,000	reflectance
K ₂ [Ni[(O ₂ CCH ₂) ₂ S] ₂] · 2H ₂ O ^b	9,520 (13)		12,300 (2)	16,120 (9)	25,550 (15)	solution
Na ₂ [Ni(SCH ₂ CO ₂) ₂ (H ₂ O) ₂] · 2H ₂ O	9,500		12,900	15,950	25,300	reflectance
Na ₂ [Ni(HSCH ₂ CO ₂) ₂ (SCH ₂ CO ₂)] · 2H ₂ O	9,500		11,000	16,500	24,350	reflectance
Na ₄ [Ni ₄ (SCH ₂ CO ₂) ₆] · 15H ₂ O	8,760	9,300 (sh)	13,000 (sh)	16,140	25,000	reflectance
K ₂ [Ni(C ₂ O ₂ S ₂) ₂]	17,700 (sh)	19,900 (4,660)				solution
K ₂ [Ni(C ₂ O ₂ S ₂)(SCH ₂ CO ₂)]	17,700 (sh)	19,800 (2,980)				solution
Na ₂ [Ni(SCH ₂ CO ₂) ₂ (H ₂ O) ₂] · 2H ₂ O	15,500 (sh)	19,650 (104)				solution

^a Molar extinction coefficients are given in parentheses for solution spectra. All solution spectra are in aqueous solution. ^b Reflectance spectra are in good agreement with the solution spectra reported here.

Table IV. Ligand Field Parameters

Compound	Chromophore	10 Dq(cm ⁻¹)	B(cm ⁻¹)
K ₂ [Ni(C ₂ O ₄) ₂ (H ₂ O) ₂] · 4H ₂ O	NiO ₆	8,800	1,000
K ₂ [Ni(C ₂ O ₄)(SCH ₂ CO ₂)(H ₂ O) ₂]	NiO ₅ S	9,300	965
K ₂ [Ni[(O ₂ CCH ₂) ₂ S] ₂] · 2H ₂ O	NiO ₄ S ₂	9,520	882
Na ₂ [Ni(SCH ₂ CO ₂) ₂ (H ₂ O) ₂] · 2H ₂ O	NiO ₄ S ₂	9,500	850
Na ₂ [Ni(HSCH ₂ CO ₂) ₂ (SCH ₂ CO ₂)] · 2H ₂ O	NiO ₄ S ₂	9,500	823
Na ₄ [Ni ₄ (SCH ₂ CO ₂) ₆] · 15H ₂ O	?	9,100	922

compound which shows this effect most clearly is the bis(oxalato) complex, it seems reasonable to conclude that spin-orbit coupling is probably the more important factor since this compound would be expected to have one of the more nearly octahedral ligand fields due to the similarity of ligand field strengths of water and oxalate.¹⁹ Certainly it can be said that there is no evidence for band splitting due to lowered symmetry.

The second point is that the weak maximum around 12,000 cm⁻¹ is more compatible with the calculations of Liehr and Ballhausen¹⁷ than the Tanabe-Sugano diagrams. The Liehr and Ballhausen calculation clearly predicts a spin forbidden transition in this region for 10 Dq of the order of 8,000-10,000 cm⁻¹ while the Tanabe-Sugano results place it about 3,000 cm⁻¹ higher.

From the three spin-allowed bands, it is possible to determine both the value of 10 Dq and the Racah parameter B. In the determination of these values, the centers of the rather wide spin-allowed bands were simply estimated visually and these energies used in the calculation. The first band around 9000 cm⁻¹ is 10 Dq. The value of B can then be calculated using the diagonal sum rule.²⁰ Values of 10 Dq and B obtained in this manner are given in Table IV. It can be seen that for the compounds studied, there is a trend toward increasing 10 Dq and decreasing B as the number of coordinated sulfur atoms increases. The trend in B values is in accord with the generally accepted comparison of the nephelauxetic effects of oxygen and sulfur. The difference in B values between the two complexes having the NiO₄S₂ chromophore may be real since in the thioglycolate complex the sulfur bears a negative charge and in the thioglycolate it is a thioether type of sulfur. The trend in

10 Dq values is harder to rationalize so we only observe that sulfur appears to have a significant effect. The order of ligand field strengths for the ligands studied is C₂O₄²⁻ < SCH₂CO₂²⁻ < (O₂CCH₂)₂S²⁻ and all lie between water and ammonia in the spectrochemical series. The values of 10 Dq and B for the polynuclear species would seem to suggest a high degree of oxygen coordination, but it is possible that the structure involves bridging sulfur atoms which might then be expected to have smaller ligand field strength than in simple mononuclear complexes.

Planar Complexes. Of the three planar complexes reported in Table III, only the mixed (C₂O₂S₂)(SCH₂CO₂) complex is new. The dithiooxalate complex has been studied by a number of workers³ as has the bis(thioglycolato) species.^{8-10,21} The spectra we observe are essentially identical to those previously reported except that Jørgensen²¹ reports a shoulder at 417 mμ in the thioglycolate spectrum which does not appear in our spectrum or the spectrum published by Leussing. The purpose of reporting the data is to point out the great similarity between the band energies of the three complexes and the large differences in band intensities. The mixed complex has intensities one half those of the dithiooxalate complex while the thioglycolate has very low intensities compared to the others. Thus the intense charge transfer bands seem to be limited to the dithiooxalate ion. It should be mentioned that there is little doubt about the formulation of the mixed complex. It can be dissolved and reprecipitated without change. This would be unlikely to occur if it were disproportionating in solution to give the bis(dithiooxalato) complex.

The Thioglycolate System. The Ni(II)-thioglycolate system exhibits complicated behavior. The nature of the species present is strongly pH dependent. The

(19) C. K. Jørgensen, « Absorption Spectra and Chemical Bonding in Complexes », Addison-Wesley, Reading, Mass., 1962, p. 110.

(20) *Ibid.*, p. 136.

(21) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, 24, 1571 (1962).

solid isolated from a solution containing a 2:1 ligand:metal ratio appears to be a « tris » complex if the pH of the solution is less than 10. As discussed previously, the best representation of the complex is probably one involving two protonated ligands, probably on the sulfur, and one completely ionized ligand. Using the same 2:1 ratio of ligand:metal but raising the pH above 10, a paramagnetic bis complex is isolated. This is in accord with the suggestion⁸ that the solution species present under these conditions is a 2:1 complex. We have also obtained data that support the assumption⁹ that under certain conditions there exists in solution a polynuclear species containing four nickel ions and six ligands. The isolation of such a species can be accomplished from a solution containing a 3:2 ligand:metal ratio. Again the pH must be above 10. Why both the polynuclear and the bis complex are fully paramagnetic in the solid and diamagnetic in aqueous solution is not explainable

at this time. It would be unusual if it were simply due to coordinated water in the solid since the same possibility is present in aqueous solution where the substances are diamagnetic. It is possible that more complex structures exist in the solid.

The behavior of the « tris(thioglycolate ») complex is in line with the general trends found for all the complexes. With two or less sulfur atoms coordinated, the complex is paramagnetic, but with as many as three the resulting species is generally diamagnetic. In the « tris » complex, however, where two sulfurs are presumably protonated, the system is on the borderline between the two spin states.

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