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Ligand Substitution Processes in Aqueous Cobalt(II)-Thiocyanate Solutions. Nuclear Magnetic Resonances of Oxygen-17 and Nitrogen-14¹

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Coordination numbers and ligand substitution equilibrium constants for cobalt(II) species in aqueous solution were determined using oxygen-17 and nitrogen-14 magnetic resonance techniques. Species abundances were determined by analysis of chemical shift data; relaxation parameters and ligand exchange rates were obtained from line broadening over a range of temperatures and solution compositions. Use of both oxygen-17 and nitrogen-14 chemical shift data permitted unique assignment of coordination numbers of NCS⁻ and H₂O in all species involved in the stepwise equilibria and provided verification of the assumption that essentially constant ligand chemical shifts are observed for each nuclear species in complexes of given symmetry at constant temperature. Complex species found to be present in significant amounts over the NaNCS concentration range 0–7.98 *m* are Co(H₂O)₆²⁺, Co(NCS)(H₂O)₅⁺, Co(NCS)₂(H₂O)₄, Co(NCS)₃(H₂O)₃⁻, and Co(NCS)₄²⁻. Those assignments are consistent with observations in other, similar sequences, where the change from six- to four-coordination occurs at the neutral point in going from cationic to anionic species. Ligand hyperfine coupling constants were found to be as follows: tetrahedral, nitrogen-14, 1.13 × 10⁷ Hz; tetrahedral, oxygen-17, 3.34 × 10⁷ Hz; octahedral, oxygen-17, 1.26 × 10⁷ Hz.

Introduction

Addition of thiocyanate ions to aqueous solutions of cobalt(II) perchlorate results in the formation of a series of complexes in which NCS⁻ replaces ligand water molecules in Co(H₂O)₆²⁺, the dominant species in the original solutions. At low NCS⁻ concentrations solutions are characteristically pink, changing to deep blue at higher concentrations. Evidence has been presented, based on spectroscopic and diffraction data, that NCS⁻ in cobalt(II) complexes is bonded to the metal ion through the nitrogen atom in octahedral and tetrahedral species^{3,4} and that the linear NCS⁻ groups are coaxial with the Co–N bond. Both classes exhibit spectra characteristic of the essential symmetry of the complex,^{5,6} octahedral complexes appearing pink and tetrahedral, blue.

Stability constants for the several species of cobalt(II) in aqueous thiocyanate solutions have been listed⁷ from a variety of sources. Of those the most pertinent for aqueous solutions are the spectrophotometric and solvent extraction results of Tribalat and Zeller⁶ and those of Senise and Perrier.⁸ In all reported results coordination numbers were specified for NCS⁻ only and the number of water molecules in each complex species was not given. Nuclear magnetic resonance techniques have been used to investigate kinetics of ligand exchange in nickel(II)-thiocyanate solutions

by Jordan, Dodgen, and Hunt⁹ and proton resonance shifts in cobalt(II)-thiocyanate solutions were studied by Horrocks and Hutchinson.¹⁰ There it was concluded that the isotropic ligand–electron coupling constants depend upon degree of substitution, as well as essential symmetry of the complex. However, it has been pointed out¹¹ that such an assumption is unnecessary if the transition from octahedral to tetrahedral symmetry with increasing NCS⁻ substitution is properly accounted for. An analysis of chemical shift measurements on ¹⁷O and ³⁵Cl in terms of species distribution in aqueous hydrochloric acid solutions was done in that work.¹¹ Here we present additional evidence that a single coupling constant for a particular ligand nucleus in a complex of given symmetry is sufficient to correlate the observed chemical shift data in a complex system. However, linkage isomerization equilibrium in a complex species would be expected to change the coupling constant materially. In this instance, isomerization of NCS⁻ ligands to form S bonds to cobalt(II) could possibly lead to such an effect.

Experimental Section

Reagent grade cobalt(II) perchlorate (G. Frederick Smith Chemical Co.) was recrystallized twice from perchloric acid solution. This contained adhering HClO₄ which caused acid concentrations in the solutions to be comparable to cobalt(II) concentrations. The measurements were independent of acidity in the range studied (0.1–10⁻⁴ *m*). Sodium thiocyanate reagent was used without further purification. Analyses were made of cobalt perchlorate stock solution for total cation by absorption on cation-exchange resin and for cobalt(II) by titration with ethylenediaminetetraacetic acid.

Solutions for nuclear measurements were prepared by mixing weighed amounts of stock solutions which had been made up to ionic strength 1.5 by adding recrystallized sodium perchlorate

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TABLE I
 OXYGEN-17 LINE SHIFTS IN AQUEOUS NaNCS SOLUTIONS AT $27 \pm 1^\circ$

Molality		a_{\pm}	a_1	a_0	α_1	α_2	α_3	α_4	Molality of free NCS ⁻	$10^4(\Delta\omega'/\omega)_{Co(17O)}/\omega_{17O}$	
NaNCS	Co(ClO ₄) ₂									Calcd	Exptl
0.000	0.078	0.0000	0.998	1.000	0.000	863	849
0.090	0.075	0.0408	0.996	0.591	0.367	0.041	0.057	829	823
0.141	0.073	0.0674	0.994	0.450	0.463	0.086	0.001	...	0.095	815	807
0.219	0.081	0.106	0.990	0.321	0.521	0.154	0.004	...	0.150	800	797
0.227	0.088	0.106	0.986	0.320	0.521	0.155	0.004	...	0.151	786	815
0.309	0.084	0.156	0.986	0.223	0.534	0.235	0.009	...	0.222	786	804
0.311	0.088	0.154	0.986	0.225	0.534	0.233	0.009	...	0.220	787	808
0.384	0.071	0.210	0.982	0.159	0.515	0.310	0.016	...	0.299	775	776
0.573	0.076	0.325	0.975	0.089	0.449	0.428	0.034	0.001	0.465	756	757
0.655	0.101	0.350	0.970	0.079	0.432	0.450	0.038	0.001	0.507	752	758
0.798	0.080	0.465	0.965	0.051	0.370	0.519	0.059	0.001	0.668	737	721
0.937	0.076	0.561	0.957	0.036	0.323	0.561	0.078	0.002	0.806	726	708
1.31	0.077	0.804	0.940	0.018	0.235	0.617	0.124	0.005	1.16	699	686
2.88	0.131	2.11	0.880	0.002	0.068	0.570	0.322	0.039	2.57	592	517
3.98	0.189	3.22	0.836	0.001	0.031	0.465	0.422	0.082	3.48	522	500
7.98	0.144	11.32	0.642	...	0.001	0.113	0.470	0.416	7.50	257	267

 TABLE II
 NITROGEN-14 LINE SHIFTS IN AQUEOUS NaNCS SOLUTIONS AT $27 \pm 1^\circ$

Molality		a_{\pm}	a_1	a_0	α_1	α_2	α_3	α_4	Molality of free NCS ⁻	$10^4(\Delta\omega'/\omega)_{Co(14N)}/\omega_{14N}$	
NaNCS	Co(ClO ₄) ₂									Calcd	Exptl
0.085	0.0006	0.0611	0.996	0.487	0.435	0.077	0.001	...	0.085	12.7	12.7
0.130	0.0005	0.0931	0.994	0.365	0.497	0.135	0.003	...	0.129	21.7	16.6
0.179	0.0005	0.129	0.991	0.276	0.521	0.198	0.006	...	0.179	37.7	31.5
0.217	0.0005	0.156	0.989	0.227	0.522	0.242	0.009	...	0.217	53.8	51.6
0.238	0.0007	0.171	0.988	0.207	0.520	0.263	0.011	...	0.237	63.1	66.1
0.246	0.0005	0.177	0.988	0.199	0.518	0.272	0.011	...	0.245	67.3	77.1
0.259	0.0006	0.186	0.987	0.187	0.515	0.286	0.013	...	0.259	73.8	87.1
0.280	0.0012	0.201	0.986	0.172	0.509	0.305	0.014	...	0.279	84	101
0.321	0.0005	0.231	0.984	0.145	0.494	0.343	0.019	...	0.320	105	111
0.365	0.0007	0.262	0.982	0.123	0.476	0.377	0.023	...	0.364	128	131
0.373	0.0005	0.268	0.982	0.119	0.473	0.384	0.024	...	0.372	132	134
0.444	0.0008	0.319	0.979	0.093	0.443	0.431	0.033	0.001	0.443	167	166
0.534	0.0010	0.384	0.973	0.070	0.416	0.470	0.044	0.001	0.532	216	212
0.721	0.0021	0.518	0.964	0.043	0.346	0.542	0.069	0.002	0.718	279	266
0.967	0.0037	0.692	0.953	0.025	0.275	0.595	0.102	0.004	0.960	337	343
1.33	0.0037	0.953	0.936	0.013	0.200	0.629	0.151	0.008	1.32	397	390
1.56	0.0058	1.11	0.926	0.009	0.167	0.634	0.179	0.011	1.54	424	421
2.45	0.1170	1.71	0.898	0.003	0.095	0.605	0.272	0.026	2.18	493	484
4.82	0.0964	4.63	0.789	0.002	0.014	0.353	0.489	0.144	4.55	639	638
7.98	0.1436	11.32	0.642	...	0.001	0.113	0.470	0.416	7.50	767	780

dissolved in stock solutions. A few concentrated ($>1.5 M$) solutions of NaNCS were prepared by adding weighed amounts of crystals. In those cases the ionic strength was greater than 1.5.

Nuclear measurements of naturally occurring ¹⁴N were made at 4.000 MHz and of enriched ¹⁷O at 8.000 MHz. Solutions were enriched to 2-4% in ¹⁷O. Details of other experimental techniques and measurements have been given previously.¹¹ As in previous work, shift measurements at 300°K were done with samples in spherical bulbs to minimize the bulk susceptibility correction, which in any event is negligibly small compared to the observed contact shifts for nuclei such as oxygen-17 and nitrogen-14 in cobalt(II) solutions.

Results

Paramagnetic line shifts were measured in aqueous NaNCS solutions containing Co(II) at a variety of temperatures and NCS⁻ concentrations for both ¹⁴N and ¹⁷O. Results are given in Tables I and II and in Figures 1 and 2. Observed fractional line shifts $\Delta\omega'/\omega$ were normalized by the factor p' , the mole ratio of Co-

(II) to total H₂O or to total NCS⁻. Thus, change reflects not only the behavior of $\Delta\omega'/\omega$ but of the quantity $n_i\alpha_i$ as well (n_i is the number of complexed ligands of interest in species i , and α_i is the fraction of total Co(II) in species i). In each measurement, shifts were determined relative to NCS⁻ in equivalent solutions not containing paramagnetic species.

Line broadenings for similar solutions and conditions are given in Figures 3-6. Line widths for relatively broad lines were obtained from peak-to-peak distances of the derivative of absorption. Modulation amplitude and frequency were kept sufficiently low that broadening from those sources was less than 3% of the measured width. In some instances narrow lines were modulation side-banded and their widths were determined at half-maximum amplitude of the side-band peak. In both modes radiofrequency power broadening was minimized by maintaining the power level within the region of linear response.

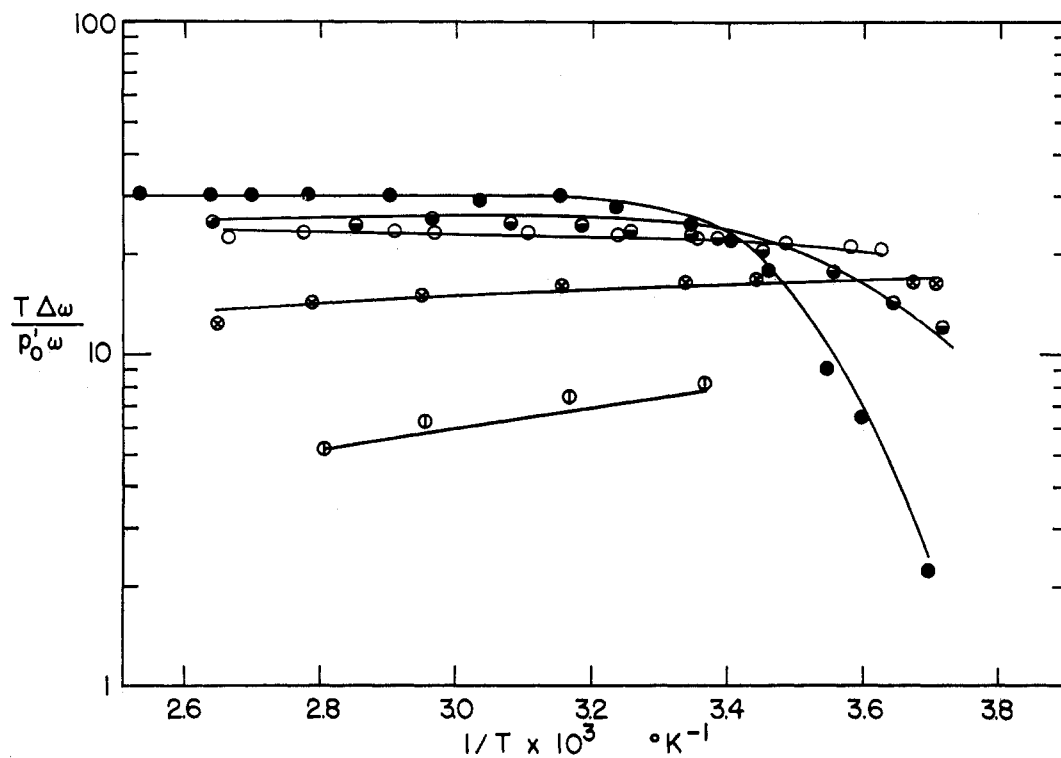


Figure 1.—Temperature dependence of ^{17}O shifts in cobalt thiocyanate solutions: ●, 0.113 *m* $\text{Co}(\text{ClO}_4)_2$; ●, 0.081 *m* $\text{Co}(\text{ClO}_4)_2$, 0.219 *m* NaNCS ; ○, 0.129 *m* $\text{Co}(\text{ClO}_4)_2$, 1.09 *m* NaNCS ; ⊗, 0.125 *m* $\text{Co}(\text{ClO}_4)_2$, 3.60 *m* NaNCS ; ⊕, 0.144 *m* $\text{Co}(\text{ClO}_4)_2$, 7.98 *m* NaNCS .

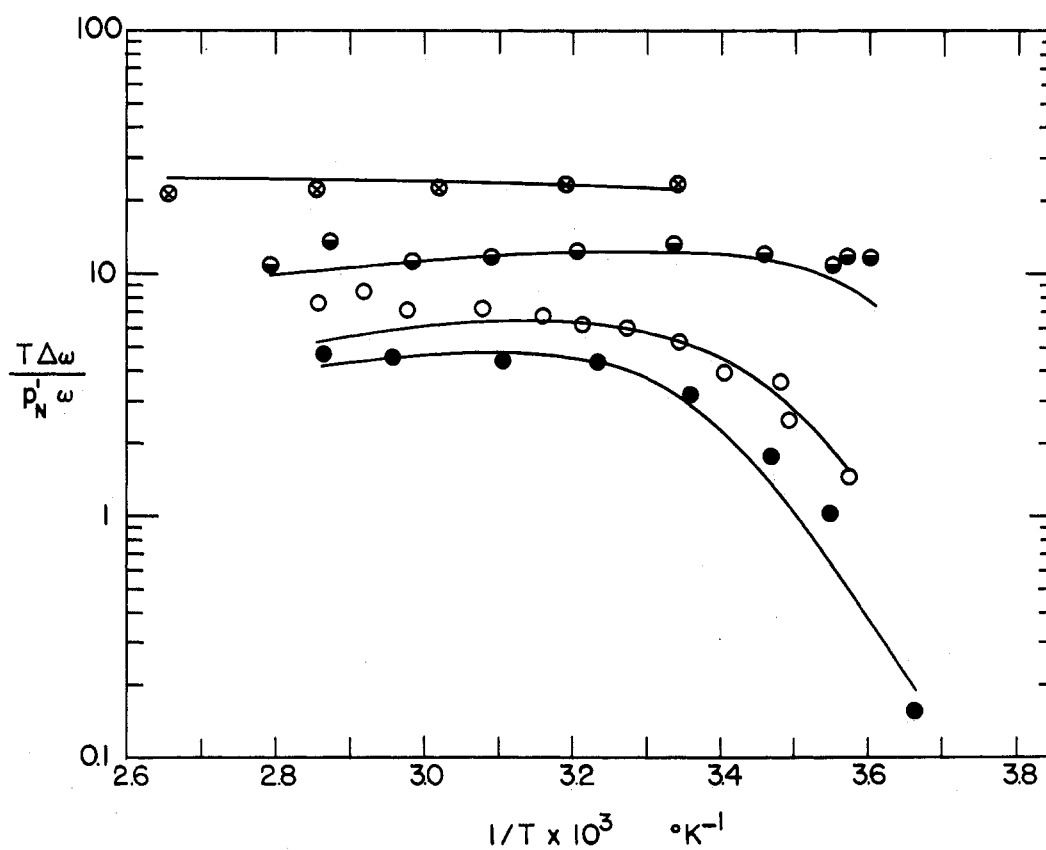


Figure 2.—Temperature dependence of ^{14}N shifts in cobalt thiocyanate solutions: ●, 0.000555 *m* $\text{Co}(\text{ClO}_4)_2$, 0.321 *m* NaNCS ; ○, 0.000551 *m* $\text{Co}(\text{ClO}_4)_2$, 0.502 *m* NaNCS ; ●, 0.00646 *m* $\text{Co}(\text{ClO}_4)_2$, 1.540 *m* NaNCS ; ⊗, 0.1436 *m* $\text{Co}(\text{ClO}_4)_2$, 7.98 *m* NaNCS .

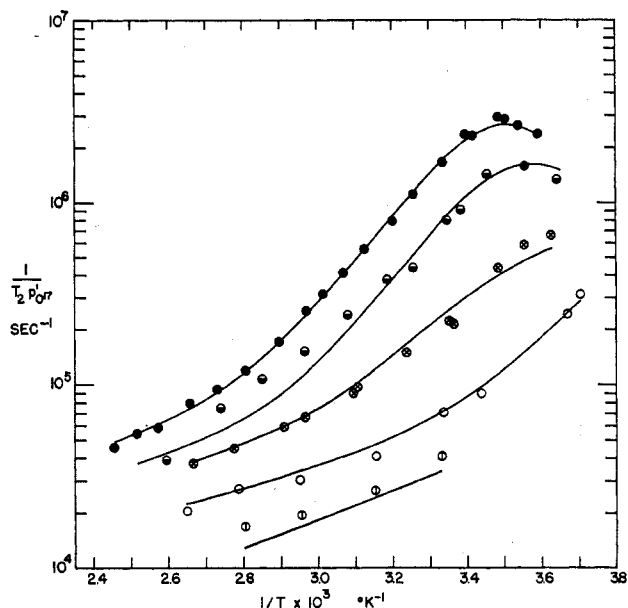
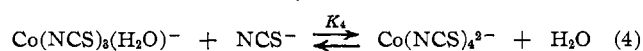
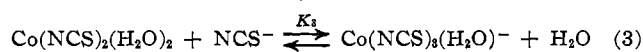
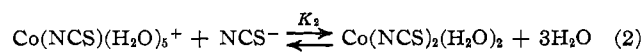
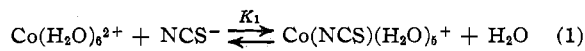


Figure 3.—Temperature dependence of ^{17}O line broadening in solutions of cobalt thiocyanate: ●, 0.100 *m* $\text{Co}(\text{ClO}_4)_2$; ◐, 0.081 *m* $\text{Co}(\text{ClO}_4)_2$, 0.219 *m* NaNCS ; ⊗, 0.129 *m* $\text{Co}(\text{ClO}_4)_2$, 1.09 *m* NaNCS ; ○, 0.125 *m* $\text{Co}(\text{ClO}_4)_2$, 3.60 *m* NaNCS ; ◑, 0.144 *m* $\text{Co}(\text{ClO}_4)_2$, 7.98 *m* NaNCS .

In derivative of absorption measurements, the reciprocal of nuclear transverse relaxation time is $T_2^{-1} = \pi\sqrt{3}\Delta\nu_{p-p}$, and for side-banded signals, $T_2^{-1} = \pi\Delta\nu_{1/2}$ ($\Delta\nu$ in hertz for each). Line broadenings were found by subtracting the natural width for ^{14}N or ^{17}O in corresponding solutions not containing paramagnetic ions. That implies the absence of second-shell broadening effects, which in the past has proved to be a reasonable assumption where coordination sphere relaxation is large. Again, observed line broadenings were normalized with the factor p' .

Treatment of Data

Published data^{6,8} on the cobalt(II) thiocyanates indicate the formation of four complexes. Those results refer to degree of thiocyanate coordination and are not concerned with extent of aquation and total coordination number. The latter may be obtained by utilization of oxygen-17 shifts and in this work both six- and four-coordinate complexes were considered. Quantitative treatment of the data was based on the following four equilibria among the several complexes



A number of alternate reaction schemes wherein change from six- to four-coordination occurs at a different step were inconsistent with the use of a constant shift parameter for each ligand in a given coordination symmetry. Designating cobalt species by the fractional abundances α_i , with i specifying the number of co-

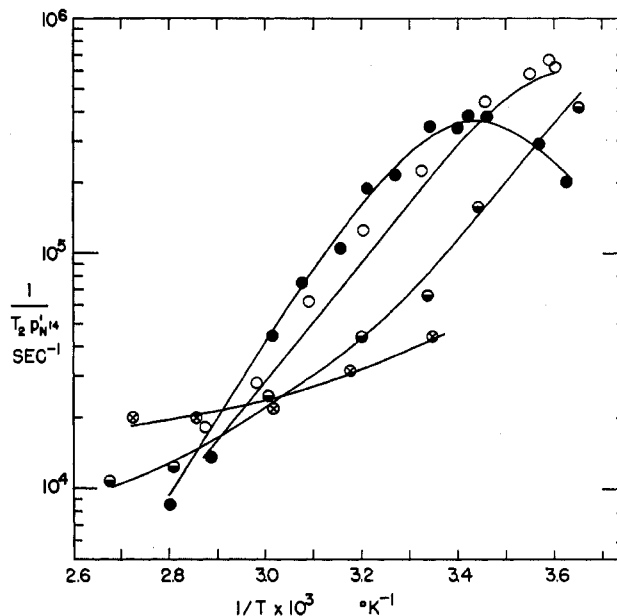


Figure 4.—Temperature dependence of ^{14}N line broadening in solutions of cobalt thiocyanate: ●, 0.000551 *m* $\text{Co}(\text{ClO}_4)_2$, 0.502 *m* NaNCS ; ○, 0.00646 *m* $\text{Co}(\text{ClO}_4)_2$, 1.540 *m* NaNCS ; ◐, 0.0482 *m* $\text{Co}(\text{ClO}_4)_2$, 3.77 *m* NaNCS ; ⊗, 0.1436 *m* $\text{Co}(\text{ClO}_4)_2$, 7.98 *m* NaNCS .

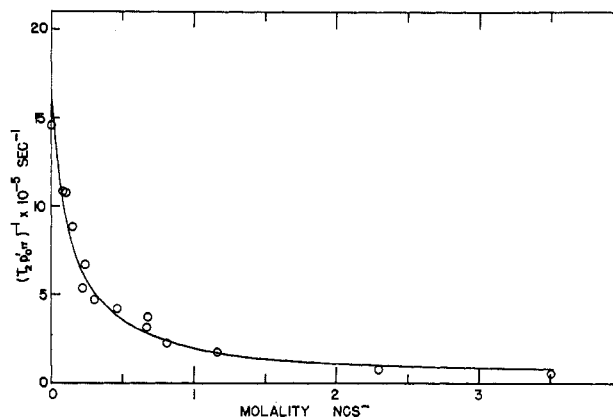


Figure 5.—Oxygen-17 line broadening at 27° as a function of thiocyanate concentration.

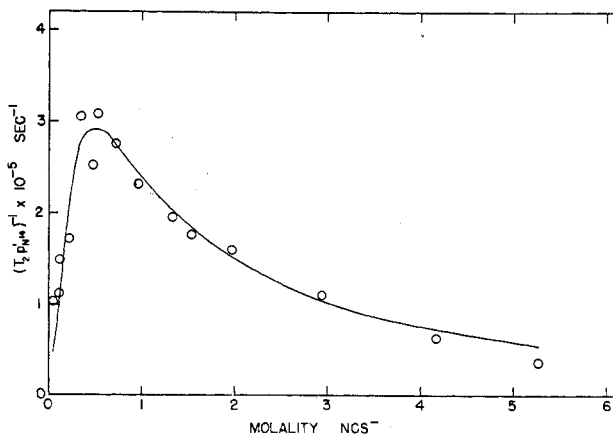


Figure 6.—Nitrogen-14 line broadening at 27° as a function of thiocyanate concentration.

ordinated thiocyanate ions, the successive equilibrium constants are, with a_1 for water activity and a_{\pm} for mean ion activity of NaNCS, as follows

$$K_1 = (\alpha_1/\alpha_0)(a_1/a_{\pm}) \quad (5)$$

$$K_2 = (\alpha_2/\alpha_1)(a_1^2/a_{\pm}) \quad (6)$$

$$K_3 = (\alpha_3/\alpha_2)(a_1/a_{\pm}) \quad (7)$$

$$K_4 = (\alpha_4/\alpha_3)(a_1/a_{\pm}) \quad (8)$$

in which it is assumed that the ratio of activity coefficients for the cobalt(II) complexes is constant.

In principle, one should observe a separate resonance absorption line for a given nucleus in each chemical environment occupied by the nucleus. However, if one environment predominates, nuclei in that state are those principally observed, and if chemical exchange is relatively rapid, the effects of mixing nuclei between bound sites and bulk solution species are observed in the behavior of the bulk solution resonance. Both line widths and positions are affected. In the following, attention is focused on the predominant solution species for oxygen-17 (H_2O) and nitrogen-14 (NCS^-). Water and thiocyanate ions bound in the several complex species are assumed to exchange primarily with the bulk species and intercomplex exchange is neglected. Experimental results may then be correlated with line positions expected for nuclei in bound ligands relative to those in the bulk species H_2O or NCS^- . The difference is the ligand shift parameter, which may arise through the averaged dipole-dipole nuclear (pseudocontact) interaction or through the isotropic hyperfine or Fermi contact interaction as described in detail below. Calculations done in connection with previous work¹¹ indicate that pseudocontact interactions contribute essentially nothing to the observed shifts, which are taken to be the result of isotropic contact interactions alone. Assuming contact ligand shift values to depend upon coordination number and configuration only, there are four shift parameters to be considered in the treatment of experimental data: $\Delta\omega_1$, $\Delta\omega_2$, $\Delta\omega_3$, and $\Delta\omega_4$, corresponding to octahedral $^{14}\text{NCS}^-$, tetrahedral $^{14}\text{NCS}^-$, octahedral H_2^{17}O , and tetrahedral H_2^{17}O , respectively. The observed shift values in the solutions corrected for slow exchange are then given by¹²

$$\Delta\omega(^{14}\text{N}) = p'[\alpha_1\Delta\omega_1(1 + \tau_{1\text{N}}^2\Delta\omega_1^2)^{-1} + 2\alpha_2\Delta\omega_2(1 + \tau_{2\text{N}}^2\Delta\omega_2^2)^{-1} + 3\alpha_3\Delta\omega_3(1 + \tau_{3\text{N}}^2\Delta\omega_3^2)^{-1} + 4\alpha_4\Delta\omega_4(1 + \tau_{4\text{N}}^2\Delta\omega_4^2)^{-1}] \quad (9a)$$

and

$$\Delta\omega(^{17}\text{O}) = p'[6\alpha_0\Delta\omega_3(1 + \tau_{0\text{O}}^2\Delta\omega_3^2)^{-1} + 5\alpha_1\Delta\omega_3(1 + \tau_{1\text{O}}^2\Delta\omega_3^2)^{-1} + 2\alpha_2\Delta\omega_4(1 + \tau_{2\text{O}}^2\Delta\omega_4^2)^{-1} + \alpha_3\Delta\omega_4(1 + \tau_{3\text{O}}^2\Delta\omega_4^2)^{-1}] \quad (9b)$$

The $\tau_{i\text{N}}$ and $\tau_{i\text{O}}$ are ligand residence times for NCS^- and H_2O , respectively, and are related to ligand-exchange rate constants by

$$\tau_{i\text{N}}^{-1} = k'_{i\text{N}}a_{\pm} = (k_{i\text{N}}/n_i)a_{\pm} \quad (10)$$

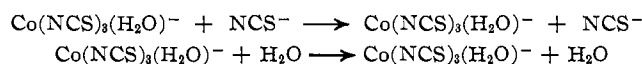
(12) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962); *Erratum*, *ibid.*, **41**, 2553 (1964).

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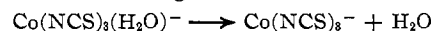
$$\tau_{i\text{O}}^{-1} = k'_{i\text{O}}a_1 = (k_{i\text{O}}/n_i)a_1 \quad (11)$$

$\Delta\omega$ varies with temperature as indicated in eq 12, below, while equilibrium constants, K , and exchange rate constants, k or k' , are exponential functions of temperature. Note that if τ is sufficiently long in a given term, that term becomes very small and makes no contribution to the observed shift in the bulk species. Equations 10 and 11 are given as single-term expressions. Other terms could be significant, giving a more complicated dependence on temperatures and solution composition. However, no improvement was noted in the analysis of data when such terms were introduced. One might expect an H_2O -dependent term in eq 10 or an NCS^- -dependent term in eq 11, but they are apparently not necessary for satisfactory interpretation of the results and have been omitted.

Rate-determining exchange reactions of $\text{Co}(\text{NCS})_3(\text{H}_2\text{O})^-$ may then be represented by



and similarly for other complex species. Necessity for inclusion of water activity, a_1 , in eq 11 is not firmly established in these experiments although the subsequent analysis of broadening data gives best results with that factor present. The alternative dissociation process for H_2O exchange



must also be considered as a possibility. In any event, with a_1 referenced to unity at infinite dilution the rate constants $k_{i\text{O}}$ are of first-order form.

All chemical shift data reported in Tables I and II and shown in Figures 1 and 2 were used in obtaining the necessary parameters for all pertinent relations by a nonlinear least-squares program for the CDC-6600 computer.¹³ The solid curves drawn in Figures 1 through 7 were computed using the equilibrium and shift parameters listed in Tables III and IV and line-

TABLE III
EQUILIBRIUM PARAMETERS FOR COBALT(II) SPECIES
IN AQUEOUS NaNCS SOLUTIONS

Equil const (300°K)	Value	ΔH_i° kcal/mol
K_1	15 ± 7	4.1 ± 1.4
K_2	2.8 ± 0.2	-5.7 ± 1.8
K_3	0.24 ± 0.03	1.8 ± 1.1
K_4	0.050 ± 0.006	1.6 ± 1.2

^a The constants K_n are semithermodynamic and do not contain the ratios of cobalt(II) complex species activity coefficients.

TABLE IV
SHIFTS AND COUPLING CONSTANTS FOR OXYGEN-17 AND
NITROGEN-14 IN COBALT(II)-ISOTHIOCYANATE COMPLEXES
(300°K)

Nucleus	Symmetry	$10^4(\Delta\omega_{\text{Co}}/\omega)$	$10^{-7}(A/h)$, Hz
^{14}N	Tetrahedral	233 ± 3	1.13
^{17}O	Octahedral	158 ± 2	1.26
^{17}O	Tetrahedral	368 ± 7	3.34

(13) This program is based on work by R. H. Moore and R. K. Zeigler, Report LA-2367, Los Alamos Scientific Laboratory, Los Alamos, N. M., Oct 1959. It is available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Va.

TABLE V
 LINE-BROADENING PARAMETERS FOR OXYGEN-17 AND NITROGEN-14 IN AQUEOUS NaNCS SOLUTIONS OF COBALT(II)

		$k'(300^\circ\text{K}),^a$ sec ⁻¹	$E_a,$ kcal/mol	$T_{2i}^{-1}(300^\circ\text{K}),$ sec ⁻¹	$E_{T_{2i}},$ kcal/mol
¹⁷ O	Co(H ₂ O) ₆ ²⁺	$(2.45 \pm 0.10) \times 10^8$	11.5 ± 0.4	$(1.40 \pm 0.20) \times 10^4$	-1.5 ± 0.3^b
	Co(NCS)(H ₂ O) ₅ ⁺	$(9.46 \pm 0.95) \times 10^8$	10.7 ± 1.1	$(1.25 \pm 0.28) \times 10^4$	-1.5 ± 0.3
	Co(NCS) ₂ (H ₂ O) ₂	$2-4 \times 10^8$	11-14	$(2.0 \pm 1.0) \times 10^4$	-2.2 ± 1.0^c
	Co(NCS) ₃ (H ₂ O) ⁻	$>5 \times 10^8$		$(5.6 \pm 1.8) \times 10^4$	-2.2 ± 1.0
		$k'(300^\circ\text{K}), M^{-1} \text{sec}^{-1} d$			
¹⁴ N	Co(NCS)(H ₂ O) ₅ ⁺	$1.8 \times 10^8 e$	14 ^e	$2.5 \times 10^3 e$	-1.5^e
	Co(NCS) ₂ (H ₂ O) ₂	$(3.0 \pm 0.2) \times 10^8$	12.6 ± 0.6	$(1.5 \pm 1.0) \times 10^3$	-2.2 ± 0.3^c
	Co(NCS) ₃ (H ₂ O) ⁻	$(4.7 \pm 0.1) \times 10^8$	10.2 ± 1.7	$(7.5 \pm 2.5) \times 10^3$	-2.2 ± 0.3
	Co(NCS) ₄ ²⁻	$>1.0 \times 10^7$		$(1.1 \pm 0.2) \times 10^4$	-2.2 ± 0.3

^a For a given ligand: $k' = k/n$. Overall exchange rate is given by: $R = k[\text{Co}(\text{NCS})_x(\text{H}_2\text{O})_{n+2-x}]_{\text{aq}}$. ^b Assumed to be the same for all octahedral species. ^c Assumed to be the same for all tetrahedral species. ^d $k' = k/n$. $R = k[\text{Co}(\text{NCS})_n(\text{H}_2\text{O})_{y+2-n}]_{\text{aq}}/[\text{NaNCS}]$. ^e Values were inferred from low-concentration behavior but are essentially indeterminate within the experimental error limits. In this case the constant is pseudomolecular with units of sec⁻¹.

broadening parameters listed in Table V. Nitrogen-14 shifts attributable to Co(NCS)(H₂O)₅⁺ made little contribution to the overall observed values except at very low NCS⁻ concentrations, where measurements are quite difficult to make with accuracy. The least-squares program failed to find a significant value for $\Delta\omega_1$. On the basis of ratios for octahedral and tetrahedral parameters observed¹¹ for ¹⁷O and ³⁵Cl and on preliminary values for $\Delta\omega_2$ obtained at high NCS⁻ concentrations, the octahedral value was fixed at 1.0×10^{-2} in the final analysis of data. Other choices in the range 0.7×10^{-2} – 1.3×10^{-2} did not significantly change results obtained for the remaining parameters.

Values of K obtained in this analysis are in reasonable agreement with stability constants previously obtained^{8,9} after correction for water and mean ion activities in ammonium thiocyanate and sodium thiocyanate solutions, respectively. The distribution of species at 300°K is shown in Figure 7.

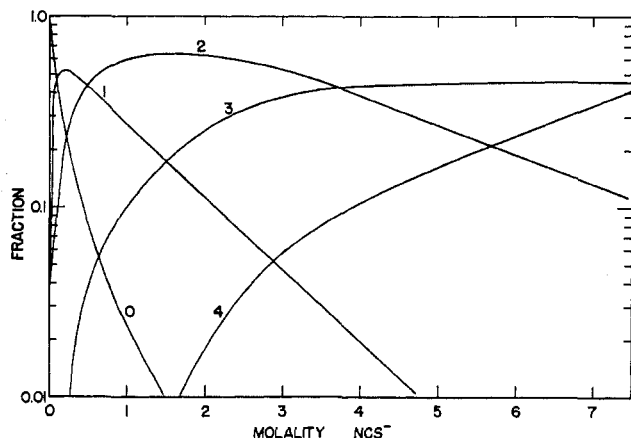


Figure 7.—Fraction of Co(II) species as a function of free thiocyanate concentration: 0, Co(H₂O)₆²⁺; 1, Co(NCS)(H₂O)₅⁺; 2, Co(NCS)₂(H₂O)₂; 3, Co(NCS)₃(H₂O)⁻; 4, Co(NCS)₄²⁻.

Activity data used for the calculations were obtained from Miller and Sheridan¹⁴ and Robinson.¹⁵ The data were fitted with an extended Debye-Hückel equation.¹⁶

(14) M. L. Miller and C. L. Sheridan, *J. Phys. Chem.*, **60**, 184 (1956).

(15) R. A. Robinson, *J. Amer. Chem. Soc.*, **62**, 3131 (1940).

(16) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," 3rd ed, Reinhold, New York, N. Y., 1958, p 520.

The parameters found by least-squares error program were $A' = 1.584$, $B = 0.04095$, and $D' = 0.005120$.

Temperature-dependent data for the activity of sodium thiocyanate solutions were unavailable. Those were approximated by assuming the same temperature dependence as the corresponding NaCl solutions (see p 726 of ref 16). The activity of water in each instance was obtained by integration of the Gibbs-Duhem equation over the appropriate range of molality. Free thiocyanate ion concentrations and ionic strengths were corrected for complexed thiocyanate ion by successive approximations. Mean ion activities have been used throughout since single-ion activities are not known. Values of the equilibrium constants and their temperature dependences are given in Table III. Shift values used and the corresponding coupling constants are listed in Table IV. The latter were calculated using¹⁷

$$\Delta\omega/\omega = S(S+1)(A_N/3kT)(g_{\text{eff}}\beta/\hbar\gamma_N) \quad (12)$$

The value of g_{eff} for tetrahedral species was chosen to be consistent with $\mu_{\text{eff}} = 4.40 \text{ BM}^2$ and for octahedral species, 5.00 BM^2 .¹⁸ The γ_N for ¹⁴N and ¹⁷O are 1.9328×10^8 and -3.6267×10^8 radians sec⁻¹ G⁻¹.

Analysis of line shift data required estimation of exchange-rate parameters to account for some degree of nonaveraging between ligand and bulk solution species. That effect is apparent in Figures 1 and 2 where variations of $T\Delta\omega$ at low temperature are attributable to slow exchange as well as to species changes.

First estimates of the k_i were made on the basis of temperature dependence of the line shifts. However, better values were obtained from line broadening, which were then used to reevaluate the shift data. Only final values are given in the tables.

Broadening results were treated using the relation¹²

$$(T_{2p}^{-1})_i = \left[\frac{p'\alpha_i n_i}{\tau_i} \right] \left[\frac{T_{2i}^{-1}(T_{2i}^{-1} + \tau_i^{-1}) + \Delta\omega_j^2}{(T_{2i}^{-1} + \tau_i^{-1})^2 + \Delta\omega_j^2} \right] \quad (13)$$

and summation over i . The T_{2i} are transverse relaxation times for nuclei in the complex species i and $(T_{2p}^{-1})_i$ is the contribution of the species to overall broadening.

(17) N. Bloembergen, *J. Chem. Phys.*, **27**, 595 (1957).

(18) R. L. Carlin, *Transition Metal Chem.*, **1**, 22 (1965).

Applicability of the equation requires $p'\alpha_i n_i \ll 1$ and that no direct exchange occur between complex species. For H_2O exchange in $\text{Co}(\text{NCS})_3(\text{H}_2\text{O})^-$ and NCS^- exchange in $\text{Co}(\text{NCS})_4^{2-}$ the limiting equation

$$(T_{2p})_i^{-1} = p'\alpha_i n_i (T_{2i})^{-1} \quad (14)$$

may be used. With species concentrations suggested by the analysis of shift data we obtained the parameters given in Table V. As the T_{2i} are determined predominantly by isotropic spin exchange

$$T_{2i}^{-1} = \frac{1}{3}S(S+1)(A_N/\hbar)^2[\tau_e + \tau_e(1 - \omega_s^2\tau_e^2)^{-1}] \quad (15)$$

and if $T_{1e} = T_{2e}$

$$\tau_e^{-1} = T_{1e}^{-1} + \tau_i^{-1} \quad (16)$$

it might be expected that T_{2i} would vary as τ_e^{-1} with species. The longitudinal electronic relaxation time, T_{1e} , for cobalt(II) species is of the order of 10^{-13} – 10^{-12} sec so that $\tau_e = T_{1e}$ and $\omega_s^2\tau_e^2 \ll 1$. Using the observed coupling constants and relaxation parameters we find the values for τ_e given in Table VI.

TABLE VI
ESTIMATED ELECTRONIC RELAXATION TIMES FOR COBALT(II)

	$10^{13}\tau_e$, sec				
	Octahedral		Tetrahedral		
	$\text{Co}(\text{H}_2\text{O})_6^{2+}$	$\text{Co}(\text{NCS})_2(\text{H}_2\text{O})_4^+$	$\text{Co}(\text{NCS})_2(\text{H}_2\text{O})_2$	$\text{Co}(\text{NCS})_3(\text{H}_2\text{O})^-$	$\text{Co}(\text{NCS})_4^{2-}$
^{17}O data	8.9	8.0	1.9	5.1	
^{14}N data			1.2	6.0	8.8

Discussion

The exchange rate for H_2O in $\text{Co}(\text{NCS})(\text{H}_2\text{O})_5^+$ is 3.9 times larger than that in $\text{Co}(\text{H}_2\text{O})_6^{2+}$, which is probably attributable to decreased overall ionic charge. In a previous paper¹¹ values for H_2O exchange in $\text{Co}(\text{H}_2\text{O})_6^{2+}$ and $\text{CoCl}(\text{H}_2\text{O})_5^+$ were reported to be 2.6×10^6 and 1.7×10^7 sec⁻¹, respectively. The small deviation in the first value from that given in this work is attributable to differences in media (aqueous HCl solutions for the aquochloro complex). The increase of the H_2O exchange rate in that instance, upon substitution of Cl^- for H_2O , was larger (a factor of 6.5) but not significantly so.

Exchange of NCS^- between $\text{Co}(\text{NCS})_2(\text{H}_2\text{O})_2$ or $\text{Co}(\text{NCS})_3(\text{H}_2\text{O})^-$ and bulk solution is measurably slow and required an NCS^- -dependent bimolecular term in the analysis of data. For $\text{Co}(\text{NCS})_4^{2-}$, NCS^- exchange is too rapid to obtain a meaningful rate constant and the same is true for all tetrahedral species with respect to H_2O exchange. The principal reason for rapid NCS^- exchange in $\text{Co}(\text{NCS})_4^{2-}$ is apparently the high NCS^- concentration required for observation of the species. A similar restriction applied to all tetrahedral aquochlorocobalt(II) complexes in HCl solutions and direct comparisons of rates cannot be made.

For nitrogen-14 in neutral nitrogen atoms, A_{2s}/h

$= 1.545 \times 10^9$ Hz,¹⁹ so that in tetrahedral species the fractional s character in the ligand NCS^- nitrogen atoms is²⁰

$$f_s = 2SA_N/A_{2s} = 0.0220 \quad (17)$$

A value $f_s = 0.023$ was observed for nitrogen in bis-(ethylenediamine)copper(II)²¹ where ligand hyperfine interaction is restricted to the four planar nitrogens. It might be expected that s character of the Co–N bond in the thiocyanate is greater than that of the Cu–N bond in the ethylenediamine complex ion and that the corresponding f_s would be somewhat larger. That it is actually slightly smaller suggests that π bonding to the cobalt(II) contributes a negative factor or that possibly a portion of the NCS^- is bonded through S. The slight decrease in observed ^{14}N shift values in 7.98 *m* NaNCS solution at high temperatures may also be attributable to equilibrium between S-bonded and N-bonded ligands. However, deviations from calculated values are not sufficiently large to draw any positive conclusions on that score.

The assumption of constant isotropic coupling constants for ligands in a given symmetry leads to reasonable and self-consistent equilibrium constants, K_i . The dual requirement to fit both ^{14}N and ^{17}O shift data reduces the ambiguity of interpretation in terms of solute species. If the complexes are restricted to six- and four-coordination, consistency of the interpretation suggests strongly that the hyperfine interaction does not vary with substitution in a complex of given symmetry.

The calculated fractional shifts, $\Delta\omega/\omega$, for ^{17}O in octahedral and tetrahedral aquoisothiocyanato complexes are 1.58×10^{-2} and 3.68×10^{-2} . Those values may be compared with 1.70×10^{-2} and 3.54×10^{-2} obtained for the corresponding aquochloro complexes in aqueous HCl solutions.¹¹ In these cases, neighboring groups have little influence on hyperfine coupling to a given ligand nucleus.

It would have been desirable to take more data in the region in which the lower complexes dominate the distribution, in order to get good kinetic parameters for $\text{Co}(\text{NCS})(\text{H}_2\text{O})_5^+$. However, the gross NCS^- concentration in that range is very small and measurements are difficult, if not impossible, with available techniques. Several experiments were tried with highly enriched nitrogen-15, with no better results.

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(20) F. Keffler, T. Oguchi, W. O. Sullivan, and J. Yamashita, *Phys. Rev.*, **115**, 1553 (1959).

(21) W. B. Lewis, M. Alei, Jr., and L. O. Morgan, *J. Chem. Phys.*, **45**, 4003 (1966).