Contribution from the Department of Inorganic and
Analytical Chemistry, The Hebrew University of Jerusalem, Israel

Cobalt(II) Thiocyanate Species Sorbed on Ion Exchangers

C. Heitner-Wirguin and N. Ben-Zwi

Received June 11, 1971

The electronic and infrared spectra of cobalt species sorbed on Dower 1X8 NCS$^-$ and Dowex 50WX8 Li$^+$ from aqueous and nonaqueous media containing various concentrations of thiocyanate ions were measured and interpreted by comparison with those obtained for cobalt-thiocyanate solids and solutions. The oscillator strengths and the B and 10Dq parameters were evaluated. Assignments as to the type of bonding were made by use of the infrared spectra.

Introduction

Two problems arise when studying the cobalt-thiocyanate complexes; the first one is the structure of the complex and its symmetry, and the other is the type of bonding in the complex.

The problem of the composition and the structure of thiocyanate complexes was investigated in most cases by examining the electronic spectra of various systems. A change of colour from red to blue occurs in cobalt-thiocyanate systems when an excess of thiocyanate ions is added. The studies of the colour changes deal mostly with the Co(NCS)$_4^{2-}$ species[1-6] or with mixtures of several thiocyanate species.[7-9]

Katzin[1] used the continuous variation method for a spectroscopic study of nonaqueous media, while other authors determined the reflectance spectra[2] or combined spectrophotometric and potentiometric methods with conductivity measurements for the examination of the cobalt-thiocyanate systems. Other studies[10-13] deal with the determination of the stability constant of Co(NCS)$^+$.

From X-ray studies[14] it is known that the first row transition elements form M–N bonds. Forster[15] combined X-ray structural studies with infrared spectra measurements (in the 450-200 cm^{-1} region) in order to prove the tetrahedral nature of the nitrogen bonded Co(NCS)$_4^{2-}$. Fronaeous[16] observed a peak at 2112 cm^{-1}, which he assigned to the formation of a Co^{2+}–SCN$^-$ complex. Turco *et al.*[17] established the tetrahedrality of an N-bonded cobalt-thiocyanate complex by use of conductivity and infrared spectra measurements. In another work Turco[18] defined the ν_3 (2066 cm^{-1}) and the ν_1 (800 cm^{-1}) bands as characteristic of a Co–N coordination.

In this study an attempt was made to define the cobalt-thiocyanate species sorbed on various ion exchangers from various equilibrating solutions. The sorption on the exchangers was followed by the measurement of the electronic and infrared spectra. The assignment of the spectral bands as well as the spectral parameters (Dq, B) evaluated were compared to those of various solids and solvated Co-thiocyanate systems.

Experimental Section

The methods used for the measurements of the electronic spectra are the same as previously described.[19-20]

Infrared spectra were recorded on the Perkin Elmer Recording Infrared Spectrophotometer Models 21 and 33 from KBr pellets or nujol mulls of the appropriate exchangers.

The oscillator strength was determined from the relation $f = 4.6\times10^{-9}\ \varepsilon_{max}\ \nu_{1/2}$ where ε_{max} is the molar extinction coefficient of the band and $\nu_{1/2}$ is the band width at half height.

The values of Racah's B parameter and 10Dq for an octahedral symmetry were evaluated by use of the suggestion of Abu Eittah and Arafa[21] for the solution of Tanabe and Sugano[22] matrix. The values of B and 10Dq for a tetrahedral symmetry were calculated according to Stahl-Brada and Low[23] and Drago.[24]

Results and Discussion

Electronic Spectra. (a) Species existing in solutions. The results obtained from the measurements

---

(1) Katzin L.I. and Gebert E., *J. Amer. Chem. Soc.*, *72*, 5659 (1950).
(2) Cotton F.A., Goodgame D.M.L., Goodgame M., and Sacco A., *J. Amer. Chem. Soc.*, *83*, 4157 (1961).
(3) Gutmann V. and Bohunovsky O., *Mh. Chem.*, *99*, 368 (1968).
(4) Howell O.R. and Jackson A., *J. Chem. Soc.*, 621 (1937).
(5) Proll P.J. and Sutcliffe L.J. *Phys Chem.*. 1993 (1951).
(6) Gutmann V. and Scherhaufer A., *Inorg. Chim. Acta*, *2*, 325 (1968).
(7) Bobtelsky M. and Spiegler K.S., *J. Chem. Soc.*, 143 (1949).
(8) Donoghue J.T. and Drago R.S., *Inorg. Chem.*, *2*, 572 (1963).
(9) Gutmann V. and Bohunovsky O., *Mh. Chem.*, *99*, 751 (1961).
(10) Senise P. and Perrier M., *J. Amer Chem. Soc.*, *80*, 4194 (1958).
(11) Lehne M., *Bull Soc. Chim. France*, 76 (1951).
(12) Babko A.K. and Drako O.F., *J. Gen. Chem. USSR*, *19*, 1809 (1949).
(13) Smithson J.M., Williams J.P., *J. Chem. Soc.*, 457 (1958).
(14) Nakamoto K., « Infrared Spectra of Inorganic and Coordination Compounds », J. Wiley, N.Y., 1963, p. 173.
(15) Forster D. and Goodgame D.M.L., *Inorg. Chem.*, *4*, 715 (1965).
(16) Fronaeus S. and Larsson K., *Acta Chem. Scand.*, *16*, 1447 (1962).
(17) Turco A., Pecile C., and Nicolini N., *J. Chem. Soc.* (London), 3008 (1962).
(18) Turco A. and Pecile C., *Nature*, *191*, 66 (1961).
(19) Heitner-Wirguin C and Ben-Zwi N., *Inorg. Chim. Acta*, *4*, 517 (1970).
(20) Heitner-Wirguin C. and Ben-Zwi N., *Inorg. Chim. Acta*, *4*, 554 (1970).
(21) Abu Eittah R. and Arafa G., *J. Inorg. Nucl. Chem.*, *32*, 2721 (1970).
(22) Tanabe Y. and Sugano S., *J. Phys. Soc. Japan*, *9*, 766 (1954).
(23) Stahl-Brada R. and Low W., *Phys. Rev.*, *113*, 775 (1959).
(24) Drago R.S., « Physical Methods in Inorganic Chemistry », Reinhold, N.Y., 1965, p. 411.

Table I. Absorption bands of cobalt-thiocyanate ions in aqueous and nonaqueous media (in cm^{-1}). (Molar extinction coefficients are given in parentheses)

Solution	Near Infrared (1)	Visible (2)
water+$Co(NO_3)_2$0.01*M*+KCNS6*M*	5720 sh 6850 (144) 7140 (126) 8070 sh	16330 (800) 17240 sh 18860 sh
water+$Co(NO_3)_2$0.01*M*+KCNS10*M*	7875 (150)	16330 (1240) 17290 sh 18570 sh
ethanol+$Co(NO_3)_2$0.01*M*+KCNS1.5*M*	7940 (186)	16220 (1500) 20000 sh
acetone+$Co(NO_3)_2$0.01*M*+KCNS2*M*	7690 (210)	16120 (400) 17060 sh 20000 sh
acetonitrile+$Co(NO_3)_2$0.01*M*, KCNS1*M*	7140 sh 7750 (240)	16170 (380) 19080 sh 20000 sh

Table II. Absorption bands of cobalt-thiocyanate species sorbed on ion exchangers (in cm^{-1}) (Molar extinction coefficients are given in parentheses).

Resin	Equilibrating medium	near infrared (1)	visible (2)
Dowex 50	water+$Co(NO_3)_2$0.01*M*+KCNS0.1*M*	5980 (18.4) 7750 (16.4) 8810 sh	19420 (21.2) 25000 34450
Dowex 50	water+$Co(NO_3)_2$0.01*M*+KCNS0.5*M*	5910 (18) 6410 sh 7820 (16.4) 8810 sh	16130 (45.6) 17100 sh 18870 sh 28190
Dowex 50	water+$Co(NO_3)_2$0.01*M*+KCNS2.0*M*	5940 (16.5) 6460 (17.2) 7690 (32.6) 8870 sh	16050 (167) 27050 (224)
Dowex 50	ethanol+$Co(NO_3)_2$0.01*M*+KCNS1.5*M*	7297(4.8)	19230 (19)
Dowex 50	acetone+$Co(NO_3)_2$0.01*M*+KCNS2*M*	5810 (3.7)	18850 (16)
Dowex 1	water+$Co(NO_3)_2$0.01*M*+KCNS4*M*	6670 sh 7690 (190) 8130 (181)	15550 (1535) 16950 (1530) 20000 sh 21470 sh
Dowex 1	water+$Co(NO_3)_2$0.01*M*+KCNS10*M*	7580 (129) 8340 sh	16000 (1680) 17000 sh 19660 sh 27650 (810)
Dowex 1	acetonitrile+$Co(NO_3)_2$0.01*M*+KCNS1*M*	6625 (180) 8270 (195)	15950 (880) 16950 sh 27400 (930)

of the electronic spectra are summarized in Table I. There is good agreement between the results obtained in the present study and literature results obtained by other methods.[1,4,6,8] A comparison of the results known from the literature with the results listed in Table I indicate that the solutions contain more than one species, and are essentially mixtures of species. The spectra obtained are due to the absorption of several species, most of them tetrahedral. The tetrahedrality of most of the species becomes clear from the values of ε and the ratio between these coefficients in the visible and in the near infrared regions. These ratios (8: 1) are usual for tetrahedral systems.[2] The fact that only mixtures of species exist in various solutions suggests the possibility of separation of the different species by sorption on cation and anion exchangers.

(b) Species sorbed on a cation exchanger. Table II and Figures 1 and 2 summarize the spectral data obtained for species sorbed on a cation exchanger from various media. Three different spectra of the sorbed cation exchanger were obtained when the thiocyanate concentration was changed in the equilibrating solutions.

The spectrum of cobalt species sorbed from solutions containing no thiocyanate ions was identical with those of species sorbed from solutions with a thiocyanate concentration up to $[NCS^-] : [Co^{II}] = 10:1$; apparently this spectrum may be assigned to the octahedral species $Co(H_2O)_6^{2+}$. [19]

When the concentration of thiocyanate was increased up to $[NCS^-] : [Co^{II}] = 50:1$, the bands show a slight shift to lower energies with an increase in the intensity. The existence of a bonded thiocyanate group in the complex is shown by the clear band observed in the ultraviolet at 34,450 cm^{-1}. This band is typical of $Co(NCS)^+$.[25] The presence of a bonded thiocyanate group is recognized from infrared data (as shown below) and there is no evi-

(25) Williams T., *J. Inorg. Nucl. Chem.*, 1215 (1962).

dence (from microscopic examination) for physical sorption on the exchanger. All these results demonstrate the presence of the sorbed cationic species $Co(NCS)(H_2O)_5^+$.

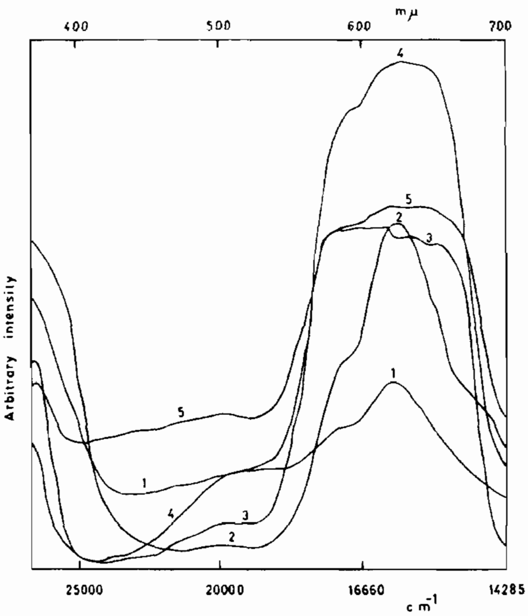

Figure 1. Visible absorption spectra of cobalt(II) species sorbed on ion exchangers

1. Dowex 50+$Co(NO_3)_2$0.01M+KCNS0.5M in mater
2. Dowex 50+$Co(NO_3)_2$0.01M+KCNS2M in water
3. Dowex 1+$Co(NO_3)_2$0.01M+KNCS4M in water
4. Dowex 1+$Co(NO_3)_2$0.01M+KCNS10M in water
5. *Dowex* 1+$Co(NO_3)_2$0.01M+KCNS1M in acetonitrile

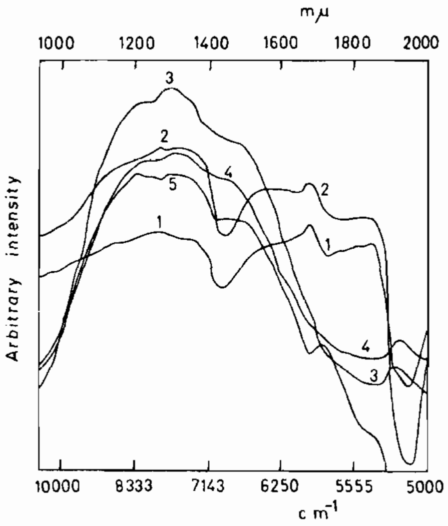

Figure 2. Near infrared absorption spectra of cobalt(II) species sorbed on ion exchangers

1. Dowex 50+$Co(NO_3)_2$0.01M+KCNS0.5M in water
2. Dowex 50+$Co(NO_3)_2$0.01M+KCNS2M in water
3. Dowex 1+$Co(NO_3)_2$0.01M+KNCS4M in water
4. Dowex 1+$Co(NO_3)_2$0.01M+KCNS10M in water
5. *Dowex* 1+$Co(NO_3)_2$0.01M+KCNS1M in acetonitrile

A further increase in the thiocyanate concentration up to $[NCS^-] : [Co^{II}] = 200:1$ brings about a remarkable change in the spectrum. The visible and the near infrared bands are shifted very sharply towards lower energies, changing the intensities ratio up to 10: 1. As the spectral examinations deal with a cation exchanger, and as no physical sorption could be discovered microscopically, the species sorbed under these working conditions could only be $Co(NCS)_2(H_2O)_2$. (No anionic species can be sorbed.[26]) Larger thiocyanate concentrations in solution cause the formation of tetrahedral negative species $Co(NCS)_4^{2-}$ and $Co(NCS)_3(H_2O)^-$ in solution; consequently the concentration of the available cobalt cationic species decreases; the sorption by the cation exchanger decreases markedly, showing at the same time a high physical sorption.

Sorption from nonaqueous solutions such as ethanol or acetone on the cation exchanger shows only the spectra of CoL_6^{2+} (L = solvent molecule),[20] even when the solutions are saturated with thiocyanate ions. It may be assumed that the high thiocyanate concentration brings about the formation of the tetrahedral $[Co(NCS)_4]^{2-}$ species in the solution; but this species cannot be sorbed on the cation exchanger and therefore the only species sorbed is the remaining uncomplexed $[CoL_6]^{2+}$.

(c) Species sorbed on an anion exchanger. Table II and Figures 1 and 2 summarize the spectral data for species sorbed on an anion exchanger from various media. Cobalt species were sorbed from aqueous and nonaqueous solutions highly concentrated with respect to thiocyanate. The spectra of the sorbed species on the exchanger were similar to the spectra obtained by Katzin,[1] Gutmann[3,6] and Howell[4] in solutions and Cotton *et al.*[2] in the solid complexes. There is a marked resemblance between the present spectral data of the anion exchanger sorbed from acetonitrile solution and the literature data for $Co(NCS)_4^{2-}$. Even a decrease in the thiocyanate ion concentration in nonaqueous solutions does not affect the complex species. When, on the other hand, a 4-molar aqueous thiocyanate solution is used, a different spectrum is obtained for the anion exchanger. The visible and the near infrared bands are slightly shifted to higher energies without changing the general pattern of the tetrahedral thiocyanate bands. This shift is accompanied by a marked increase in the molar extinction coefficients (the ratios of the intensities in both regions remaining as in the more concentrated solutions). It may be inferred from these spectra that the species sorbed on an anion exchanger from solutions containing lower thiocyanate concentrations is $Co(NCS)_3(H_2O)^-$.[27]

The values of f, 10Dq and B obtained in this work are summarized in Table III. The values of 10 Dq and B for $Co(NCS)_4^{2-}$ are known from the literature[2] and are in good agreement with the present results (4550 and 691 cm^{-1} respectively). Values of 10 Dq for intermediate species were also calculated using «the rule of the average environment»[27] and the calculated values fit the experimental values (e.g., 9180 cm^{-1} for $Co(NCS)(H_2O)_5^+$).

---

(26) Kraus K.A., Michelson D.C., and Nelson F., *J. Amer. Chem. Soc.*, *81*, 3204 (1959).
(27) Schläfer H.L. and Gliemann G., « Basic Principles of Ligand Field Theory », Wiley Interscience (1969).

Table III.

Species	$f_{(1)} \times 10^3$ (near IR)	$f_{(2)} \times 10^3$ (visible)	10Dq (cm^{-1})	B
$Co(NCS)(H_2O)_5^+$	0.30	0.97	9390	854
$Co(NCS)_4^{2-}$	6.72	20.85	4360	688
$Co(NCS)_3(H_2O)^-$	6.47	16.32	4180	771
$Co(NCS)_2(H_2O)_2$	4.34	12.60	3860	740

Table IV. Infrared frequencies of cobalt - thiocyanate species sorbed on ion exchangers from aqueous solutions (in cm^{-1}).

Exchanger	Equilibrating medium	C≡N stretching	C—S stretching
Dowex 50 Li^+	water+KCNS 10 *M*	2070 m	740w
	water+KNCS 0.1*M*, $Co(NO_3)_2$ 0.1*M*	2070w	728m
	water+KNCS 0.5*M*, $Co(NO_3)_2$ 0.1*M*	2070vs	728w
Dowex 1 NCS^-	water+KCNS 10*M*	2070m	
	water+KCNS 4*M*, $Co(NO_3)_2$ 0.01*M*	2150m 2060vs	860m 728m 708w
	water+KCNS 10*M*, $Co(NO_3)_2$ 0.01*M*	2150m 2055vs	860m 728m 710m
	acetonitrile+KCNS 0.5*M*, $Co(NO_3)_2$ 0.01*M*	2150m 2050vs	860m 728m 708w
	acetonitrile+KCNS 0.1*M*, $Co(NO_3)_2$ 0.01*M*	2150m 2060m	860m 728s 710w

Infrared Spectra. Infrared measurements were made in order to ascertain the type of bonding in the complex species sorbed. These results are presented in Table IV.

In most of the studies based on the thiocyanate complexes[17,18,28-30] it is accepted that the thiocyanate is bonded to the cobalt ion through the nitrogen. In the present study, however, the results obtained cannot be interpreted so simply. The complex structure of the bands obtained implies that the thiocyanate group may be linked to the cobalt ion as mentioned by Mitchell and Williams.[31]

As the matrix of the exchanger is very compact, different modes of bonding seem possible. In some cases weak bonds with the thiocyanate through the sulphur may be formed.[31] The tertiary amine group in the anion exchanger should be sufficiently electropositive for coordination with the thiocyanate to take place, thus forming an asymmetrical bridge: $-N-(CH_3)_3-NCS-Co$ or $-N(CH_3)_3-SCN-Co$. This possibility should be taken into account to explain the fact that the infrared spectrum of the exchanger indicates bonding of cobalt both through nitrogen (2060, 860 cm^{-1}) and through sulphur (2150, 728, 710 cm^{-1}) in the same sample.

---

(28) Miller F.A. and Wilkins C.H., *Analyt. Chem.*, *24*, 1253 (1952).
(29) Herzberg G. and Reid C., *Disc. Far. Soc.*, *9*, 92 (1950).
(30) Jones L.H., *J. Chem. Phys.*, *25*, 1069 (1956).
(31) Mitchell P.C.H. and Williams R.J.P., *J. Chem. Soc.*, 1912 (1960).