

the Co(III) analogs is now possible, since Sargeson¹⁶ recently has isolated these Co complexes as the sulfates and obtained their visible absorption spectra. As shown in Table IV, the two *cis* spectra are very similar, as are the two *trans* spectra.

For complexes of type [MA₂B₂] the total area under the bands (a measure of absorption intensity) of the *cis* isomer, which has no center of symmetry, is substantially greater than for the *trans* isomer, which has a center of symmetry; for [MA₄BC]-type complexes, in which neither geo-

metrical isomer has a center of symmetry, crystal-field theory predicts that the *cis* and *trans* isomers will have approximately the same area under the absorption bands.¹⁷ Examination of Fig. 1¹⁸ shows that this is the case for *trans*- and *cis*-[Cr(en)₂Cl₂]⁺ (curves A and B) but only approximately so for *trans*- and *cis*-[Cr(en)₂(OH₂)Cl]⁺² (curves C and D), the *cis/trans* area-ratios being ~2.1 and ~1.5, respectively. The ratios for these respective cobalt(III) analogs are ~2.0 and ~1.1, respectively.

(17) F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

(18) The plots of σ_M vs. λ can be used in place of the proper plot of σ_M vs. wave number since the extrapolated spectra being compared cover essentially the same wave lengths.

(16) Private communication from Dr. A. M. Sargeson, The John Curtin School of Medical Research, Australian National University, Canberra.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

Magnetic Studies of High-spin Cobaltous Compounds. VII. Some Thiocyanate Complexes

By F. A. COTTON,¹ D. M. L. GOODGAME, M. GOODGAME AND A. SACCO²

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The compound [Co{(C₆H₅)₃P}₂(SCN)₂] has been carefully studied magnetically and spectroscopically. The data lead to these conclusions: (1) the compound is tetrahedral, (2) the SCN groups are bound to Co *via* the sulfur atoms, (3) the position of S-bonded thiocyanate ions in the spectrochemical series is between Cl⁻ and Br⁻ as previously shown by Schäffer. Several salts of the [Co(NCS)₄]²⁻ anion have been studied magnetically and spectroscopically. A number of important parameters pertaining to the electronic structure and ligand field have been evaluated and the effect of bonding the S atom to Hg(II) in moving the -NCS⁻ ion to a stronger position in the spectrochemical series, as observed by Schäffer, has been confirmed. The compound [Co(Ph₃PO)₂(NCS)₂] has been prepared. Comparison of spectral and magnetic data for this compound with similar data for its chloride and bromide analogs shows that in this case the thiocyanate ions are coordinated through the nitrogen atoms.

Introduction

Ligands which occur in tetrahedral cobalt(II) complexes may be placed in the spectrochemical series using the spectral data, in a manner analogous to the use of spectral data for Cr(III) and Co(III) complexes,³ and also using magnetic data as indicated in earlier papers in this series.⁴⁻⁶ In this paper we report the results of studies by both spectral and magnetic methods of the position of S- and N-coordinated thiocyanate ions in the spectrochemical series, as well as a fairly complete analysis of the spectral and magnetic data for the [Co(NCS)₄]²⁻ ion to furnish numerical estimates of certain parameters of the electron configuration of the Co(II) ion in this complex.

Experimental

Preparations. Dithiocyanatobis-triphenylphosphine-cobalt(II).—A solution of triphenylphosphine (12.0 g., 0.046 mole) in acetone (25 ml.) was added to a solution of cobaltous thiocyanate (3.0 g., 0.018 mole) also in acetone (25 ml.). From the blue solution so obtained, a green crystalline com-

ound began to precipitate. The precipitation was completed by careful addition of petroleum ether (~20 ml.) and the compound filtered off. It was recrystallized by solution in methylene chloride and addition of petroleum ether. The yield was practically quantitative, m.p. 140°.

Anal. Calcd. for C₃₈H₃₀CoN₂P₂S₂: C, 65.22; H, 4.32; N, 4.00; P, 8.86. Found: C, 65.10; H, 4.33; N, 4.06; P, 8.61.

The compound was soluble in acetone, giving a blue solution, while green solutions were readily obtained with methylene chloride, chloroform or nitrobenzene. The complex was decomposed by methanol and ethanol.

Tetramethylammonium Tetrathiocyanatocobaltate(II).—A blue solid was immediately precipitated on addition of a solution of cobaltous thiocyanate (1.54 g., 0.0093 mole) in hot absolute ethanol (42 ml.) to one of tetramethylammonium thiocyanate (2.46 g., 0.0185 mole) also in hot absolute ethanol (58 ml.). The blue compound was filtered off while the mixture was still hot, washed with absolute ethanol and dried *in vacuo* over sulfuric acid. The yield was 3.50 g. (86%), m.p. 197°.

Anal. Calcd. for C₁₂H₂₄CoN₈S₄: C, 32.79; H, 5.50; N, 19.12. Found: C, 32.62; H, 5.52; N, 19.05.

The compound readily forms blue solutions in acetone, nitrobenzene or nitromethane.

Dithiocyanatobis-triphenylphosphine oxide-cobalt(II).—A solution of 5.60 g. of triphenylphosphine oxide in 25 ml. of anhydrous ethanol was added to 1.80 g. of Co(NCS)₂ dissolved in 25 ml. of the same solvent. After a few minutes, a blue, crystalline compound began to precipitate. After several hours, the precipitate was filtered off, washed with ethanol and dried under vacuum; m.p., 230°. It is soluble in chloroform, dichloromethane, slightly soluble in oxygenated organic solvents and insoluble in non-polar solvents.

Anal. Calcd. for C₃₈H₃₀CoO₂P₂N₂S₂: C, 62.38; H, 4.13; N, 3.83. Found: C, 62.45; H, 4.27; N, 4.00.

(1) Alfred P. Sloan Fellow.

(2) On leave from the Istituto di Chimica Generale dell' Università di Milano.

(3) For a summary of results and references see T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Editors, Interscience Publishers, Inc., New York, N. Y., 1960.

(4) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, (a) **31**, 788 (1959); (b) **32**, 1158 (1960).

(5) F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 1777 (1961).

(6) F. A. Cotton, O. D. Faut, D. M. L. Goodgame and R. H. Holm, *ibid.*, **83**, 1780 (1961).

TABLE I
 MAGNETIC DATA

Compound	Temp., °K.	$\chi_{\text{mol}}^{\text{cor.}} \times 10^6$ c.g.s.u.	Diamagnetic corr. $\times 10^3$, c.g.s.u.	TIP corr. $\times 10^6$, c.g.s.u.	μ , B.M.	θ (°K.)
[Co((C ₆ H ₅) ₃ P) ₂ (SCN) ₂]	297.5 (4) ^a	8,066 ± 44 ^b				
	195.1 (5)	12,226 ± 53	416	500	4.46	-7
	74.3 (4)	30,245 ± 390				
[(CH ₃) ₄ N] ₂ [Co(NCS) ₄]	297.9 (3)	7,860 ± 109				
	194.6 (3)	11,890 ± 136	256	459	4.40	-7
	73.4 (3)	29,812 ± 552				
[Co((C ₆ H ₅) ₃ PO) ₂ (NCS) ₂]	296.3 (2)	8,300 ± 26				
	194.1 (1)	12,720	436	500	4.46	-1
	74.1 (1)	32,550				

^a Figures in parentheses show number of measurements used to calculate mean values. ^b Average deviation from mean.

Tetrathiocyanatocobalt(II)mercury(II).—HgCo(NCS)₄, was prepared by the method of Figgis and Nyholm.^{7a}

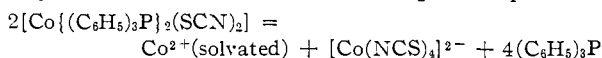
Anal. Calcd. for C₄CoHgN₄S₄: C, 9.77; H, 0; N, 11.39. Found: C, 9.83; H, 0; N, 11.66.

Potassium Tetrathiocyanatocobaltate(II).—The preparation of this compound has been described previously.^{4b}

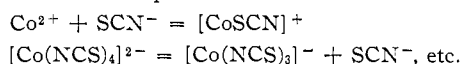
Measurement of Electrolytic Conductances.—Electrolytic conductance measurements were carried out using a Serfass bridge and a conventional cell, previously calibrated with an aqueous solution of potassium chloride

Compound	Molar conductance 10 ⁻³ M in C ₆ H ₅ NO ₂	Temp., °C.
[Co((C ₆ H ₅) ₃ P) ₂ (SCN) ₂]	14.7 ohm ⁻¹	29.0
[(CH ₃) ₄ N] ₂ [Co(NCS) ₄]	62.6	26.5
K ₂ [Co(NCS) ₄]	63.0	24.8
HgCo(NCS) ₄	Insol.	..
[Co((C ₆ H ₅) ₃ PO) ₂ (NCS) ₂]	4.5	29.0

The relatively high conductance of [Co((C₆H₅)₃P)₂(SCN)₂] may be attributed to dissociation according to the equation



with of course other equilibria such as



also being established. It has been found that addition of a little excess triphenylphosphine causes a marked reduction in the molar conductances as illustrated by the following data for the molar conductances of 10⁻³ M solutions in C₆H₅NO₂ containing the molar concentration of triphenylphosphine given in parentheses: 14.7 (0), 13.9 (2.2 × 10⁻³), 12.0 (5.8 × 10⁻³), 9.3 (1.3 × 10⁻²), 7.0 (3.0 × 10⁻²), 5.6 (7.9 × 10⁻²). [Co{(C₆H₅)₃P}₂]₂I₂ shows very similar behavior as the data indicate: 8.3 (0), 4 (7.20 × 10⁻³), 2.9 (9 × 10⁻³). [Co{(C₆H₅)₃P}₂Br]₂ shows only a slight effect: 3.4 (0), 3.1 (5 × 10⁻³), 2.7 (1.4 × 10⁻²).

Magnetic Measurements.—Determinations of magnetic susceptibility were made at various temperatures and field strengths, using the Gouy method as previously described.⁴⁻⁶ No dependence of susceptibility on field strength was observed in any case. The Gouy tubes were calibrated with HgCo(NCS)₄, using the data of Figgis and Nyholm,^{7a} and the calibrations were checked with copper sulfate pentahydrate. The measured values of the mass susceptibility for copper sulfate pentahydrate were in excellent agreement with the most reliable values in the literature, namely, those of Figgis and Nyholm^{7c} and Gorter and de Haas.⁸ Determinations at room, acetone/solid CO₂ and liquid nitrogen temperatures were made by two workers in the case of tetramethylammonium tetrathiocyanatocobaltate(II) and by three workers in the case of dithiocyanatobis-(triphenylphosphine)cobalt(II). The average results are given in Table I. The diamagnetic corrections were calculated using the experimental values for triphenylphosphine and tetra-

methyllumonium ion given by Foex⁹ and the values for cobalt(II) and thiocyanate ions listed by Selwood.¹⁰

We have noticed that there is a discrepancy in the susceptibility data for HgCo(NCS)₄ between ref. 7a and 7b. Taking the μ_{eff} values in 7b and calculating corrected molar susceptibility values of 24,068 × 10⁻⁶ and 7,748 × 10⁻⁶ at 90° and 300°K. respectively, we find that they are consistent with the θ value of 10°K. as given in both references. However, we calculate from the corrected molar susceptibility of 7,748 × 10⁻⁶ at 300°K., using $\theta = 10^\circ$, $\chi_{\text{mol}}^{\text{corr.}} = 7927$ at 293°K. Adding to this the diamagnetic susceptibility of -137 × 10⁻⁶ and dividing the result by the molecular weight (491.9), we obtain 15.83 × 10⁻⁶ as the observed gram susceptibility at 293° whereas ref. 7a reports 16.44 × 10⁻⁶. This discrepancy is sufficient to make a difference of 0.08 B.M. in the magnetic moments calculated from the two sets of data. Since an uncertainty of this magnitude would completely vitiate our comparison of the moments for [N(CH₃)₄]₂[Co(NCS)₄], we have ignored the data on HgCo(NCS)₄ in ref. 7b and calculated the moment for cobalt(II) in HgCo(NCS)₄ from the data given in ref. 7a. Since all the susceptibility data for the other compounds have been obtained using HgCo(NCS)₄ to calibrate the Gouy tubes and taking for its susceptibility the value in ref. 7a, all of our moments are at least internally consistent, and, particularly, our comparison of the moments of [N(CH₃)₄]₂[Co(NCS)₄] and HgCo(NCS)₄ is meaningful.

All magnetic moments reported and discussed in this paper have been obtained by correcting measured susceptibility values for diamagnetism and temperature independent paramagnetism (either calculated accurately from spectra data or, if not otherwise indicated, assuming a value of 500 × 10⁻⁶ c.g.s.u.), plotting the reciprocals of these $\chi_{\text{mol}}^{\text{corr.}}$ values against temperature to give by graphical evaluation the Weiss constant, and inserting the $\chi_{\text{mol}}^{\text{corr.}}$ and θ values so obtained into the Curie-Weiss equation, *viz.*, $\mu = 2.84 \sqrt{\frac{\chi_{\text{mol}}^{\text{corr.}}}{\chi_{\text{mol}}^{\text{corr.}} (T - \theta)}}$.

Electronic Spectra.—The reflectance spectra of the solid compounds were measured using a Beckman DU spectrophotometer with the standard Beckman reflectance accessory and magnesium carbonate as the reference sample. All other spectra were obtained with a Cary Model 14 recording spectrophotometer. The bands at about 1200 and 1300 m μ in the spectra of HgCo(NCS)₄ and [(CH₃)₄N]₂[Co(NCS)₄], respectively, were obtained with the solid compounds suspended in Nujol mulls. Filter paper soaked in Nujol was used as scattering agent in both reference and sample beams of the spectrophotometer. The degree of resolution of the absorption bands and their intensities with respect to the base-line depend upon the extent of grinding of the solid, the homogeneity of the mull and the extent to which the mull covers the light beam. However, by suitable variation of these factors excellent results have been obtained for these and other compounds. The numerical results are available.¹¹

(9) G. Foex, "Constantes Selectionées Diamagnetisme et Paramagnetisme," Masson et Cie, Paris, 1957.

(10) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, page 78.

(11) Persons interested in the exact numerical data relating to the spectra may obtain a table by writing to F.A.C. if this is done within the next two years. For greater permanence, a copy of the table has been deposited as Document Number 6735 with the AD1 Auxiliary

(7) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, (a) 4190 (1958); (b) 338 (1959); (c) 331 (1959).

(8) C. J. Gorter and W. J. de Haas, *Comm. Kammerlingh Onnes Lab., Leiden No. 210 d*, p. 39 (1930).

It was found that the solution spectrum of $[\text{Co}(\text{Ph}_3\text{P})_2(\text{SCN})_2]$ altered on addition of some triphenylphosphine to the solution and the spectra reported here were taken in solvent containing about 0.05 mole/l. of phosphine. This observation is related to the anomalies in the electrolytic conductance data, *q.v.*

Discussion

$[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{SCN})_2]$.—The electronic spectrum, magnetic moment and infrared spectrum of the bright green $[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{SCN})_2]$ point consistently to the following conclusions: (1) the compound is tetrahedral; (2) the thiocyanate ions are coordinated *via* sulfur; (3) the position in the spectrochemical series of S-coordinated thiocyanate ion is between Cl^- and Br^- . Figure 1 shows the visible spectra of bis-(triphenylphosphine)-cobalt (II) chloride, bromide and thiocyanate. It can be seen that these data demonstrate that all three compounds contain tetrahedrally coordinated^{5,6,12} Co(II) and that the average ligand field strength in the thiocyanate complex is probably intermediate between those for the chloride and bromide complexes.^{12b} The magnetic moment of the thiocyanate complex, when compared (see Table II) with the moments of other $\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{X}_2$ and $[\text{CoX}_4]^{2-}$ complexes, leaves virtually no doubt that the three conclusions stated above are correct. The moments of the $\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{X}_2$ species run about 0.2 B.M. below those of the corresponding $[\text{CoX}_4]^{2-}$ species for $\text{X} = \text{Cl}, \text{Br}$ and I , whereas for $\text{X} = \text{SCN}$, the moment of the bisphosphine complex is actually higher than that of the $[\text{Co}(\text{NCS})_4]^{2-}$ ion, and 0.2 to 0.3 B.M. higher than would be expected if the thiocyanate ion were coordinated in the same way in both $[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{SCN})_2]$, $[\text{Co}(\text{NCS})_4]^{2-}$. Since N-coordination is definitely established for the latter, it must be concluded that in the phosphine complex coordination is through sulfur and that S-coordinated thiocyanate provides a significantly weaker contribution to the ligand field than does N-coordinated thiocyanate. Moreover, comparison of the moments of the four $[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{X}_2]$ compounds listed in Table III shows that the position of the S-coordinated thiocyanate ion in the spectrochemical series is between Cl^- and Br^- . This is in agreement with the conclusions reached by Schaffer¹³ in his work on octahedral Cr(III) and Co(III) complexes.

The infrared spectrum of $[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{SCN})_2]$ has been studied as part of a broader program of study of infrared spectra of thiocyanate complexes

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(12) (a) L. I. Katzin, *J. Am. Chem. Soc.*, **76**, 3089 (1954). (b) We say probably because the position of ν_3 is determined⁵ by both the ligand field strength (*i.e.*, the position of the ligands in the spectrochemical series) and by the effective value of the Racah parameter, B (*i.e.*, by the position of the ligands in the nephthaluxetic series); thus, the position of ν_3 alone does not unambiguously indicate the relative position of the ligands in the spectrochemical series. Because the pronounced splitting of the ν_3 bands in these compounds shows that the C_{2v} components of the ligand fields are quite large, we have not deemed it worthwhile to measure the ν_2 bands and attempt a calculation of the Δ values. A decision of what to assume for the mean frequencies of the severely split bands would be required and this would have to be quite arbitrary and subject to great uncertainty.

(13) C. Schaffer, Abstracts of Conference on Coordination Chemistry, London, 1959, and private communications.

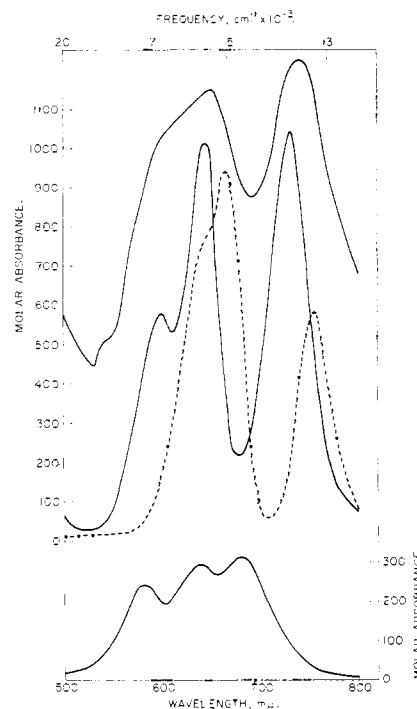


Fig. 1.—The visible spectra of several $\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{X}_2$ compounds. Lower curve (—): $\text{X} = \text{Cl}$, molar absorbance scale at right; middle curves: $\text{X} = \text{Br}$ (-----), $\text{X} = \text{SCN}$ (.....), molar absorbance scale at left; upper curve (—): reflectance spectrum of $\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{SCN})_2$, molar absorbance scale arbitrary.

and will not be discussed in detail here. It may be noted, however, that a band which we believe to be a C-S stretching band is found at 760 cm^{-1} .

TABLE II
MAGNETIC MOMENTS (B.M.) OF $\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2(\text{SCN})_2$ AND SOME RELATED COMPLEXES^a

X	$\text{Co}\{(\text{C}_6\text{H}_5)_3\text{P}\}_2\text{X}_2$	$[\text{CoX}_4]^{2-}$
I^-	4.62	4.88
Br^-	4.52	4.72
Cl^-	4.41	4.60
CNS^-	4.46	4.40

^a All data for the complexes containing halide ions are taken from ref. 6. The moments for both thiocyanate-containing complexes are from the present work.

In view of the fact that the C-N stretching absorption is a doublet (presumably symmetric and anti-symmetric modes) a second C-S band might be expected, but due to the triphenylphosphine absorptions between 675 and 750 cm^{-1} it has not been observed. There was no detectable absorption from 760 to 1000 cm^{-1} . There is evidence¹⁴⁻¹⁶ that the C-S stretching frequencies of N-coordinated thiocyanate ions generally lie in the range 780 ¹⁷

(14) M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1959).

(15) J. Lewis, R. S. Nyholm and P. W. Smith, private communication.

(16) F. A. Cotton, D. M. L. Goodgame, A. Sacco, unpublished observations.

(17) More recently M. E. Baldwin, *J. Chem. Soc.*, 471 (1961), has presented evidence that some of the bands at about 785 cm^{-1} assigned by Bailar and Chamberlain¹⁴ to S-C stretching frequencies may actually be due to vibrations in the ethylenediamine ligands, and she

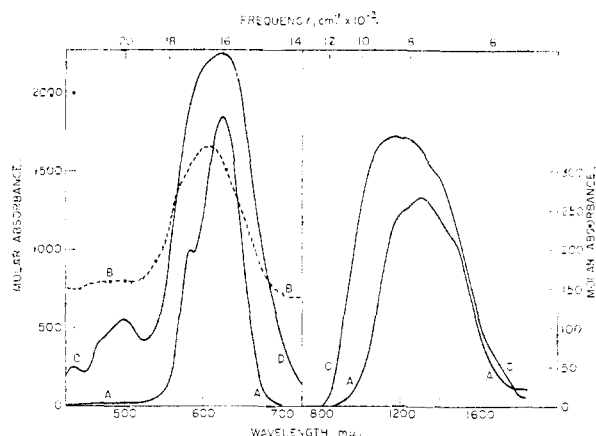


Fig. 2.—Spectra of $[(\text{Co}(\text{NCS})_4)]^{2-}$ salts: A, $[(\text{CH}_3)_4\text{N}]_2[\text{Co}(\text{NCS})_4]$ in acetone solution; B, $\text{HgCo}(\text{NCS})_4$ by reflectance, molar absorbance scale arbitrary; C, $\text{HgCo}(\text{NCS})_4$ measured using a Nujol mull, molar absorbance scale arbitrary; D, $[(\text{CH}_3)_4\text{N}]_2[\text{Co}(\text{NCS})_4]$ by reflectance, molar absorbance scale arbitrary.

-850 cm.^{-1} (e.g., 836 cm.^{-1} in $[(\text{CH}_3)_4\text{N}]_2[\text{Co}(\text{NCS})_4]$) while those of S-coordinated thiocyanates are generally between 760 and 690 cm.^{-1} . Thus the infrared spectrum of $\text{Co}[(\text{C}_6\text{H}_5)_3\text{P}]_2(\text{SCN})_2$ corroborates the assignment of S-coordination.

TABLE III

SOME PARAMETERS OF THE SPECTRA AND ELECTRONIC STRUCTURE OF $\text{Co}(\text{II})$ IN $[(\text{CH}_3)_4\text{N}]_2[\text{Co}(\text{NCS})_4]$ AND $\text{HgCo}(\text{NCS})_4$

	$[(\text{CH}_3)_4\text{N}]_2[\text{Co}(\text{NCS})_4]$	$\text{HgCo}(\text{NCS})_4$
$\nu_2, \text{cm.}^{-1}$	7,780	8,300
$\nu_3, \text{cm.}^{-1}$	16,250	16,700
$\Delta, \text{cm.}^{-1}$	4,550	4,880
$B', \text{cm.}^{-1}$	691	691
$\beta (= B'/B)^a$	0.715	0.715
TYP, c.g.s. u. $\times 10^6$	459	428
Oscillator strengths		
$f(\nu_2)$	3.44×10^{-3}
$f(\nu_3)$	1.46×10^{-2}
$f(\nu_3)/f(\nu_2)$	4.25
Magnetic moment, B.M.	4.40	4.32^b
$\theta, ^\circ\text{K.}$	-7	-4^b
$\lambda', \text{cm.}^{-1}$	149	135

^a $B(\text{free ion}) = 967 \text{ cm.}^{-1}$. ^b For the reasons explained in the Experimental section these numbers are calculated from the susceptibility data of ref. 7a.

$[\text{Co}(\text{NCS})_4]^{2-}$ Complexes.—It is known from X-ray structure determinations that the thiocyanate ions are coordinated to $\text{Co}(\text{II})$ *via* nitrogen in the compounds¹⁸: $\text{K}_2[\text{Co}(\text{NCS})_4] \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2[\text{Co}(\text{NCS})_4] \cdot 4\text{H}_2\text{O}$, $\text{Na}_2[\text{Co}(\text{NCS})_4] \cdot 8\text{H}_2\text{O}$, $\text{K}_2[\text{Co}(\text{NCS})_4]$ and $\text{HgCo}(\text{NCS})_4$. From the virtual identity of the spectral and magnetic properties of the $[\text{Co}(\text{NCS})_4]^{2-}$ complex ions in $[(\text{CH}_3)_4\text{N}]_2[\text{Co}(\text{NCS})_4]$ with the same properties for this ion in several of the compounds mentioned above, it may safely be assumed that here too it exists as an isothiocyanato-(N-coordinated) complex.

has placed the S-C bands at $825\text{--}840 \text{ cm.}^{-1}$. Thus the range of S-C frequencies for N-bonded SCN may actually have a lower bound of $\sim 800 \text{ cm.}^{-1}$.

(18) See ref. 4b for literature citations.

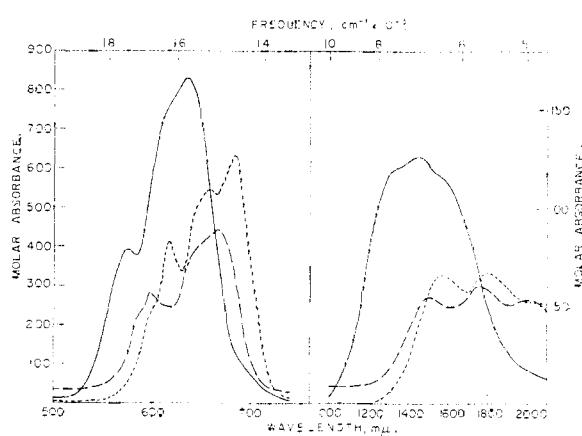


Fig. 3.—Absorption spectra of the three $\text{Co}\{(\text{C}_6\text{H}_5)_3\text{PO}\}_2\text{X}_2$ complexes: (1) $\text{X} = -\text{NCS}^-$, —; (2) $\text{X} = \text{Cl}^-$, ---; (3) $\text{X} = \text{Br}^-$, -.-.-.

This tetramethylammonium salt has been used for spectral and magnetic studies of $[\text{Co}(\text{NCS})_4]^{2-}$ since it affords reasonable insurance that the outer sulfur atoms of the N-coordinated thiocyanate ions in the $[\text{Co}(\text{NCS})_4]^{2-}$ ion are not significantly coordinated or electrostatically perturbed by the cations necessarily present in any $[\text{Co}(\text{NCS})_4]^{2-}$ salt. The magnetic data for this compound are given in Table III. After correcting the susceptibility values for diamagnetism and temperature independent paramagnetism (estimated from the spectral data), the magnetic moment was found to be $4.40 \pm 0.05 \text{ B.M.}$, with a θ value of $-7 \pm 3^\circ\text{K.}$ This moment is in good agreement with that (4.38 B.M.) which may be calculated from data¹⁸ for $\text{K}_2[\text{Co}(\text{NCS})_4] \cdot 4\text{H}_2\text{O}$. The visible and near infrared spectra of both the potassium and tetramethylammonium salts of $[\text{Co}(\text{NCS})_4]^{2-}$ in several solvents and in the solid state were measured to provide the frequencies and oscillator strengths of the electronic absorption bands ν_2 and ν_3 . The results and some derived quantities are also given in Table IV and several of the spectra are shown in Fig. 2. The data were treated as described previously.⁵ From the combined spectral and magnetic data λ' was calculated.

Schäffer has previously observed that when the free sulfur ends of N-coordinated thiocyanate ions become bound to other ions such as Hg^{2+} the contribution of the N-coordinated thiocyanate to the ligand field around the first ion is enhanced. In effect, $-\text{NCSHg}$ lies further to the strong end of the spectrochemical series than does $-\text{NCS}$. That coordination of the sulfur end of the ligand influences the ligand behavior of the nitrogen end is not too surprising, but the quantitative study of the phenomenon is of interest, and for this reason we have compared the spectral and magnetic properties of the $[\text{Co}(\text{NCS})_4]^{2-}$ ion in its tetramethylammonium salt, where there can be no significant interaction of the sulfur atoms with any other cations, with the properties of $\text{Co}(\text{II})$ in $\text{HgCo}(\text{NCS})_4$ where all sulfur atoms are strongly coordinated to $\text{Hg}(\text{II})$ ions.¹⁹ Our results completely confirm the behavior reported by Schäffer. The mag-

(19) J. W. Jeffery, *Nature*, **159**, 610 (1947).

netic moment of Co(II) in $[(\text{CH}_3)_4\text{N}]_2\text{-}[\text{Co}(\text{NCS})_4]$ was measured in a tube carefully calibrated with $\text{HgCo}(\text{NCS})_4$ using the susceptibility reported by Figgis and Nyholm^{7a,20} for the latter. Thus the difference in the moments of Co(II) in the two compounds is measured with maximal accuracy. It is seen that both the spectral data and the magnetic moments support the conclusion that in these compounds, as in those studied by Schäffer, attachment of the sulfur atoms enhances the ligand field at the ion to which the nitrogen atoms are coordinated.

Finally, we have prepared the complex $\text{Co}[(\text{C}_6\text{H}_5)_3\text{PO}]_2(\text{NCS})_2$, that is, the triphenylphosphine oxide analog of the triphenylphosphine complex discussed above, and studied its spectrum and magnetic moment. We have also measured the spectra and treated the spectral data along with previously reported magnetic data^{4,6} in the manner outlined in ref. 5. All of these data and derived quantities are reported in Table IV. It is evident from the comparisons exhibited there that in the phosphine oxide complex the thiocyanate ion is coordinated

(20) See the Experimental section for more detailed discussion of the accuracy of calibrations and comparisons of moments.

TABLE IV
SOME PARAMETERS OF THE SPECTRA AND ELECTRONIC STRUCTURE OF Co(II) IN $[\text{Co}\{(\text{C}_6\text{H}_5)_3\text{PO}\}_2\text{X}_2]$, X = $-\text{NCS}^-$, Co^- , Br^-

	$-\text{NCS}^-$	Cl^-	Br^-
ν_1 , cm.^{-1}	6900 ± 400	5710 ± 200	5560 ± 400
ν_2 , cm.^{-1}	16,000	15,500	15,300
Δ , cm.^{-1}	4030 ± 300	3270 ± 150	3180 ± 300
B' , cm.^{-1}	725	760	754
β ($= B'/B$) ^a	0.75	0.79	0.78
Magnetic moment, B.M.	4.46 ^b	4.63 ^c	4.69 ^c
λ' , cm.^{-1}	148	156	164

^a B (free ion) = 967 cm.^{-1} . ^b Measured by present authors. ^c Cf. ref. 4b and 6.

through nitrogen since both the spectra and the magnetic moments show that it is here providing a contribution to the ligand field which is far greater than that given by either Cl^- or Br^- rather than one intermediate between those due to these two ions.

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Electronic Spectra of Some Tetrahedral Nickel(II) Complexes

BY D. M. L. GOODGAME, M. GOODGAME AND F. A. COTTON¹

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The electronic spectra of eight tetrahedral complexes of nickel(II), *viz.*, $[\text{NiCl}_4]^{2-}$, $[\text{NiBr}_4]^{2-}$, $[\text{NiI}_4]^{2-}$, $[\text{Ni}(\text{Ph}_3\text{PO})_2\text{Cl}_2]$, $[\text{Ni}(\text{Ph}_3\text{PO})_2\text{Br}_2]$, $[\text{Ni}(\text{Ph}_3\text{PO})_2\text{I}_2]$, $[\text{Ni}(\text{Ph}_3\text{AsO})_2\text{Cl}_2]$ and $[\text{Ni}(\text{Ph}_3\text{AsO})_2\text{Br}_2]$, have been carefully studied in the region of the two highest energy, spin-allowed bands, ν_3 and ν_2 . It is shown that the tetrahalo ions are very sensitive to solvolysis, even by nitromethane and acetonitrile, and that the spectra of the solvolyzed species, most probably $[\text{NiX}_4\text{solvent}]^-$, especially in the region of ν_2 , are quite different from the true spectra of the $[\text{NiX}_4]^{2-}$ ions. The true spectra can be obtained by measuring solid compounds either by reflectance (ν_3 only) or using mulls. It is then found that if excess X^- , in the form of soluble salts of R_4P^+ or R_4N^+ cations, is added to the solutions the bands of the solvolyzed species can be completely, or almost completely, suppressed and the true $[\text{NiX}_4]^{2-}$ spectra obtained. From these spectra the values of Δ and B have been calculated using Liehr and Ballhausen's complete theory. The order of Δ values is $[\text{NiI}_4]^{2-} \sim [\text{NiBr}_4]^{2-} < [\text{NiCl}_4]^{2-}$. The five mixed ligand complexes are not so readily subject to solvolysis. Their spectra in the ν_3 and ν_2 regions are also reported and analyzed to yield Δ and B values. The oscillator strengths of the bands are reported and discussed. Some remarks on the relatively low magnetic moment of $[\text{NiI}_4]^{2-}$ are also given.

Introduction

It has been established conclusively during the last few years that tetrahedral complexes of nickel(II) do exist. It has been shown by Nyholm and Gill² and others^{3,4,5} that the tetrahedral tetrahalonickel(II) complex anions can exist in crystalline compounds provided the cations are large and also in solvents of only moderate dielectric constant and coordinating power. It is now also known that certain mixed ligand complexes are tetrahedral. The most numerous class of these have the general formula $[\text{NiL}_2\text{X}_2]$; they include three types: (1) those in which L is triphenylphosphine and X is Cl, Br or I^{6,7}; (2) those in which L is triphenylphosphine oxide and X is Cl, Br or

I⁸; and (3) those in which L is triphenylarsine oxide and X is Cl or Br.⁹ The second established class of mixed ligand complexes are those of the stoichiometry $[\text{NiLX}_3]^-$, and the known members of this class include some well-characterized compounds in which L is triphenylphosphine and X is Br or I⁷ as well as, probably, some similar ones which are not so well characterized.⁷

A study of the spectra of the mixed ligand complexes containing triphenylphosphine was published recently. It was shown that the ligands present in these species differ so much in their positions in the spectrochemical series that there are strong low symmetry components in the ligand fields which have quite pronounced effects on the spectra. For the complexes containing triphenylphosphine oxide and triphenylarsine oxide the low symmetry components are evidently rather small since no effects clearly attributable to them were found in the spectra^{8,9} nor did the magnetic moments of the

(1) Alfred P. Sloan Foundation Fellow.
(2) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).
(3) D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959).
(4) F. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960).
(5) F. Cotton and R. Francis, *J. Inorg. Nuclear Chem.*, **17**, 82 (1961).
(6) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).
(7) F. A. Cotton, O. D. Faut and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, 344 (1961).

(8) F. A. Cotton and D. M. L. Goodgame, *ibid.*, **82**, 5771 (1960).

(9) D. M. L. Goodgame and F. A. Cotton, *ibid.*, **82**, 5774 (1960).