

M.O. data spin density magnitudes which decrease in the order $4 > 2 > 3$.

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Donor Properties of Methyl Thiocyanate and Methyl Isothiocyanate

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The recent interest in the donor properties of the sulfur and nitrogen ends of the thiocyanate ion¹⁻⁴ toward metal ions prompts us to report the thermodynamics of 1:1 adduct formation of CH_3NCS and CH_3SCN with the acids iodine and phenol. This investigation was undertaken to determine the inherent donor properties of the sulfur and nitrogen ends of the thiocyanate group in a neutral environment. The neutral bases methyl thiocyanate and methyl isothiocyanate were studied, for they, respectively, have only the nitrogen or sulfur end of thiocyanate available for complex formation.

The thermodynamic properties of 1:1 adduct formation of these bases with I_2 have been determined by a spectrophotometric method. The shift in the phenol O-H stretching frequency upon complex formation has been used as a measure of the donor properties toward the hydrogen-bonding acid phenol.

Experimental Section

Reagents and Solutions.—Reagent grade iodine was sublimed before use. Reagent grade phenol was distilled and sublimed once. The bases were obtained in reagent grade from Fisher. They were further purified by vacuum distillation. Fisher Spectroanalyzed carbon tetrachloride was used without further purification. All solutions were prepared and used within a 1-hr. period. No change in the electronic spectra of the solutions was observed over a 24-hr. period.

Apparatus.—Spectroscopic measurements were made with a Beckman DB spectrophotometer with a fluid-thermostated cell compartment. The temperature was measured by inserting a thermocouple directly into the cell. The temperature was maintained constant within $\pm 0.1^\circ$. The solution concentrations were corrected for volume changes due to changing the temperature.

The phenol O-H frequency shifts were measured on a Perkin-Elmer 521 infrared spectrometer.

C_B, M	$10^2 C_A, M$	$A - A^0$	$\epsilon_C - \epsilon_A$	K, M^{-1}
$\text{CH}_3\text{SCN-I}_2$				
0.142	0.407	0.201		
0.177	0.407	0.250	1824	0.17 ± 0.02
0.710	0.407	0.920		
0.145	0.486	0.220		
0.181	0.486	0.270	1806	0.18 ± 0.02
0.361	0.486	0.526		
0.722	0.486	0.990		
$\text{CH}_3\text{NCS-I}_2$				
0.074	0.314	0.166		
0.148	0.314	0.318		
0.185	0.314	0.387	1066	0.71 ± 0.01
0.371	0.314	0.690		
0.742	0.314	1.14		
0.075	0.354	0.185		
0.149	0.354	0.353		
0.186	0.354	0.430	1044	0.71 ± 0.01
0.373	0.354	0.770		
0.746	0.354	1.270		

C_B, M	$10^2 C_A, M$	$A - A^0$	$\epsilon_C - \epsilon_A$	K, M^{-1}
$\text{CH}_3\text{SCN-I}_2 (T = 41.7^\circ)$				
0.144	0.486	0.176		
0.181	0.486	0.218	1820	0.14 ± 0.01
0.361	0.486	0.426		
0.722	0.486	0.810		
$\text{CH}_3\text{NCS-I}_2 (T = 39.5^\circ)$				
0.074	0.314	0.127	1050	0.54 ± 0.01
0.148	0.314	0.243		
0.185	0.314	0.304		
0.371	0.314	0.551		
0.742	0.314	0.952		

Procedure.—The equilibrium constants at 25.0° (Table I) were obtained by a least-squares fit of the absorbance data to a modified Ketelaar^{5,6} equation

$$\frac{C_A}{A - A^0} = \frac{1}{K(\epsilon_C - \epsilon_A)} \frac{1}{C_B} + \frac{1}{\epsilon_C - \epsilon_A} \quad (1)$$

where C_A is the initial acid concentration, C_B is the initial base concentration, $A - A^0$ is the difference in the absorbance of a solution of acid at concentration C_A and a solution of acid and base at concentrations C_A and C_B , and $\epsilon_C - \epsilon_A$ is the difference in molar absorptivity between the complex (C) and acid (A). The intercept and slope of the least-squares straight line were utilized, respectively, in the evaluation of $\epsilon_C - \epsilon_A$ and K . The error limits are reported at the 95% confidence level. The additional measurement of the equilibrium constants at an elevated temperature (Table II) was used to demonstrate that $\epsilon_C - \epsilon_A$ at $450 \text{ m}\mu$ was temperature independent over the range of temperatures studied.

The enthalpy measurements were made from the temperature dependence of the equilibrium constants. A single solution technique that utilizes the Rose-Drago equation was used in the enthalpy calculations.⁶

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$$K^{-1} = \frac{C_A C_B}{A - A^0} (\epsilon_C - \epsilon_A) - C_A - C_B + \frac{A - A^0}{\epsilon_C - \epsilon_A} \quad (2)$$

Each enthalpy measurement was made on a single solution of iodine and base at concentrations C_A and C_B . Experimentally, the change in absorbance ($A - A^0$) was determined as a function of temperature. The equilibrium constant (K) at different temperatures was then calculated from eq. 2 by use of the previously determined values of $\epsilon_C - \epsilon_A$ (Tables I and II). The reported enthalpies are calculated from a least-squares fit of the data to the equation $\log K = \Delta H/2.30RT + C$. The results are reported at the 95% confidence level.

The ΔH values determined by the single-solution technique are insensitive to small errors in K and $\epsilon_C - \epsilon_A$. The value of ΔH is, however, very sensitive to the temperature dependence of $\epsilon_C - \epsilon_A$.^{6,7} The absorptivity difference ($\epsilon_C - \epsilon_A$) was found to be temperature independent in the range 25–40° for the systems studied (Tables I and II).

The phenol frequency shift measurements were made on CCl_4 solutions containing 0.15 M phenol with several base concentrations. Two well-resolved O–H frequencies are observed for these solutions. The frequency shift $\Delta\nu_{\text{OH}}$ is the difference in the O–H stretching frequency for free and complexed phenol.

Results

The data obtained in the equilibrium constant determinations are summarized in Table I.

Representative data used in the calculations of the enthalpies of formation of the iodine adducts are given in Table III.

TABLE III
HEATS OF FORMATION FOR 1:1 IODINE-BASE ADDUCTS

C_B, M	$10^2 C_A, M$	$A - A^0$	$T, ^\circ\text{C.}$	K, M^{-1}	$-\Delta H, \text{kcal. mole}^{-1}$
$\text{CH}_3\text{SCN}-\text{I}_2$ (λ 450 $m\mu$, $\epsilon_C - \epsilon_A = 1815$)					
0.361	0.486	0.526	25.0	0.176	
0.360	0.483	0.499	29.0	0.168	
0.357	0.480	0.474	32.7	0.161	2.2 ± 0.2
0.355	0.478	0.447	37.0	0.153	
0.353	0.475	0.418	41.7	0.144	
$\text{CH}_3\text{NCS}-\text{I}_2$ (λ 450 $m\mu$, $\epsilon_C - \epsilon_A = 1055$)					
0.372	0.314	0.690	25.0	0.709	
0.371	0.312	0.652	28.7	0.667	
0.369	0.311	0.610	32.2	0.620	3.3 ± 0.3
0.367	0.309	0.571	36.2	0.580	
0.365	0.308	0.539	39.5	0.546	

The shifts in the phenol O–H stretching frequency due to complex formation with CH_3NCS and CH_3SCN are given in Table IV. The enthalpies of adduct formation are estimated from the reported linear correlation between the phenol O–H frequency shift and the enthalpy of adduct formation.⁷

TABLE IV
PHENOL O–H STRETCHING FREQUENCY SHIFTS FOR PHENOL-BASE ADDUCTS

Base	$\Delta\nu_{\text{O-H}}, \text{cm.}^{-1}$	$-\Delta H, \text{kcal. mole}^{-1}$
CH_3SCN	168 ± 5	3.3 ± 0.4
CH_3NCS	117 ± 5	2.5 ± 0.4

Discussion

The thiocyanate anion (NCS^-) can utilize either the sulfur or the nitrogen end when bonding with

metal ions.^{1–4} In general, heavy metals ions like Pt(II) and Hg(II) form thiocyanate (M-SCN) complexes,^{4,8,9} while the lighter first transition series metal ions such as Ni(II) and Cu(II) form isothiocyanate (M-NCS) complexes.⁴ Metals that form sulfur-bonded complexes are grouped as class b or soft acids according to the Chatt¹⁰ or Pearson¹¹ classifications, respectively. Metals that prefer the nitrogen-donor end are classified as class a or hard acids. The thermodynamics of 1:1 adduct formation with iodine (I_2) and phenol ($\text{C}_6\text{H}_5\text{OH}$) have been used to gain a semiquantitative understanding of the class b and class a character of bases.¹² Iodine is a soft or class b acid and interacts best with soft bases, while phenol, a class a hydrogen-bonding acid, interacts best with hard bases. The class a and b character of acids and bases is, of course, a relative property, and every acid and base has differing amounts of both a and b character. The recent double-scale correlation for the enthalpies of 1:1 adduct formation is an attempt to place the dual nature of donor-acceptor properties on a quantitative basis.¹²

The thermodynamics of 1:1 adduct formation of CH_3NCS and CH_3SCN with iodine clearly indicate that the sulfur donor CH_3NCS is a somewhat better class b (soft base) than is the nitrogen donor CH_3SCN . The reversed order of donor properties for these bases toward the acid phenol indicates that the nitrogen donor CH_3SCN is a better class a base (hard base) than is CH_3NCS . This result is in agreement with CH_3SCN having a larger dipole moment (3.56 D.) than CH_3NCS (3.18 D.).¹³ The reversal of donor properties toward iodine and phenol for analogous sulfur and oxygen bases has been reported.¹⁴ The reversal of the order of basicity for methyl thiocyanate and methyl isothiocyanate from $\text{CH}_3\text{NCS} > \text{CH}_3\text{SCN}$, with the acid iodine, to $\text{CH}_3\text{SCN} > \text{CH}_3\text{NCS}$, with the acid phenol, is in agreement with the change in thiocyanate coordination from nitrogen to sulfur when the changing from class a to class b metal.

The discussion to this point has emphasized the differences in the donor strengths of the alkyl thiocyanate and isothiocyanate. A closer examination of the data indicates that the donor properties for these bases are not drastically different. The equilibrium constants with iodine differ by only a factor of 4, and the enthalpies of adduct formation with either iodine or phenol differ by only about 30%. Qualitative application of this result to the case of the thiocyanate ion leads to the prediction that *in solution* there should be measurable amounts of both nitrogen- and sulfur-bonded thiocyanate with many metal ions. This effect should be most prevalent for the

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less discriminating electrostatic interactions of class a metal cations with the thiocyanate anion. A mixture of isomers in solution should, of course, occur when the metal ion has properties between those of extreme class a and extreme class b. This behavior has been reported for the second transition series metals Pd(II) and Cd(II).^{3,15} The similar donor abilities of RSCN and RNCS also suggest that, when the thiocyanate anion functions as a bridging group, it will bond through both the sulfur and the nitrogen rather than through just one of the atoms as in the case of bridging carbonyl groups. There is very little definitive structural work on bridging thiocyanates at present. The data available indicate that both sulfur- and nitrogen-donor sites are utilized in bridging thiocyanate.^{16,17}

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The Reaction of Pentacyanocobaltate(II) Ion with Sulfur Dioxide and with Tin(II) Chloride

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In the course of our studies on the oxidation-reduction properties and the coordination ability of $\text{Co}(\text{CN})_5^{3-}$, its reactions with SO_2 and with SnCl_2 have been investigated.

Reaction with Sulfur Dioxide

The introduction of a mixture of SO_2 and N_2 into an aqueous solution of CoCl_2 and KCN , in the molar ratio 1:5, results in an immediate color change from green to orange-red. The same result is obtained when a solution of $\text{Co}(\text{CN})_5^{3-}$ (without excess of cyanide ions) is treated with a solution of KHSO_3 .

The addition of 25–30 vol. % of methanol to the resulting deep orange-red solution precipitates an orange crystalline material, extremely soluble in water, highly hygroscopic, and insoluble in methanol and other common organic solvents. The compound can be purified by a rapid reprecipitation with added alcohol from an

ice-cold aqueous solution. Upon drying *in vacuo* over phosphorus pentoxide the compound turns deep orange-red; upon exposure to the air, it turns orange-yellow, the change of color being reversible. The solid material is stable in air but decomposes very rapidly in aqueous solution, the decomposition not being influenced by the presence of oxygen. Analysis² of the dry material shows the molar ratio of C to N to S to be 10:10:1. The solid compound is diamagnetic.

On the basis of its composition, the compound can be formulated as containing two $\text{Co}(\text{CN})_5$ groups connected with a bridge containing one sulfur atom. This is supported by the potentiometric titration of a $\text{Co}(\text{CN})_5^{3-}$ solution with a solution of KHSO_3 , which shows that 2 moles of $\text{Co}(\text{CN})_5^{3-}$ react with 1 mole of KHSO_3 .³ Further support of the SO_2 -bridged structure is provided by the infrared spectrum of the compound. This shows three bands, which, according to their position, can be assigned to an SO_2 group rather than to an SO_3^{2-} group. Table I summarizes the infrared bands attributable to the SO_2 group, together with the values observed for other analogous compounds.

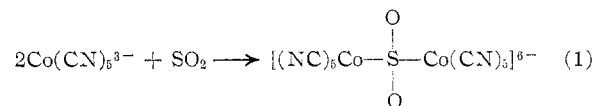
TABLE I
INFRARED SPECTRA (CM^{-1}) OF SOME SO_2 COMPOUNDS

Compd.	$\nu_{\text{S-O}}$ (asym.)	$\nu_{\text{S-O}}$ (sym.)	$\nu_{\text{O-S-O}}$ (bend)
$\text{K}_6[(\text{CN})_5\text{Co} \cdot \text{SO}_2 \cdot \text{Co}(\text{CN})_5]_2$	1078 s, 1072 s ^a	984 s	533 m, 525 m
$[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{SO}_2]\text{Br}_2^b$	1327 s, 1301 s	1117 s	551 m
$\text{SO}_2(\text{s})^c$	1330 s, 1308 s	1147 s	521 m

^a The band has a weak shoulder at 1120 cm^{-1} . ^b L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).
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The CN^- groups show infrared bands at 2132 cm^{-1} (m) and 2098 cm^{-1} (s) with a shoulder at 2106 cm^{-1} .

On the basis of these results, the product of the reaction of $\text{Co}(\text{CN})_5^{3-}$ with SO_2 or KHSO_3 can be formulated as $\text{K}_6[\text{Co}(\text{CN})_5 \cdot \text{SO}_2 \cdot \text{Co}(\text{CN})_5] \cdot 4\text{H}_2\text{O}$ (I), and the over-all reaction can be represented by eq. 1. Com-



pound I is identical with that obtained by Cambi and Paglia⁴ by treating a solution of $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$ and K_2SO_3 with gaseous HCN . However, these authors claim that the reaction of " $\text{Co}(\text{CN})_6^{4-}$ with K_2SO_3 results in the formation of $\text{Co}(\text{CN})_6^{3-}$ and $\text{S}_2\text{O}_4^{2-}$." Perhaps this is due to a higher pH and to a higher cyanide ion concentration than was used in our experiments.

Fresh solutions of I are deep orange-red, but the color fades very rapidly to yellow and on longer standing to very pale yellow. The rate of this color change is strongly pH dependent, decreasing with increasing pH. A spectrophotometric study of the compound in 0.2 M NaOH solution shows in fresh solutions a very strong absorption band at 4450 \AA . (ϵ 50,000; value obtained after extrapolation to zero time) and at 2500 \AA . (ϵ

(2) The analysis was performed by Micro-Tech, Skokie, Ill.

(3) The accuracy of the titration is $\pm 15\%$ owing to the instability of the reaction product as well as the KHSO_3 solutions.

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(1) On leave of absence from the J. Heyrovsky Polarographic Institute, Czechoslovakia Academy of Sciences, Prague, Czechoslovakia. Senior Foreign Scientist National Science Foundation Fellowship, 1964–1965.