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]

Acknowledgments.—The authors wish to acknowledge support from the Advanced Research Projects Agency for work done at the University of Pennsylvania under Contract No. SD-69 and support by the National Science Foundation Undergraduate summer research program.

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(16) J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85**, 2517 (1963).

(17) J. L. Burmeister and M. Y. Al-Janabi, *Inorg. Chem.*, **4**, 962 (1965).

CONTRIBUTION FROM THE CHEMICAL LABORATORY
AT NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS

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

BY A. A. VLČEK[1] AND F. BASOLO

Received August 3, 1965

In the course of our studies on the oxidation–reduction properties and the coordination ability of $Co(CN)_5^{3-}$, 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 $Co(CN)_5^{3-}$ (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. Analysis[2] 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 $Co(CN)_5$ groups connected with a bridge containing one sulfur atom. This is supported by the potentiometric titration of a $Co(CN)_5^{3-}$ solution with a solution of $KHSO_3$, which shows that 2 moles of $Co(CN)_5^{3-}$ 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.

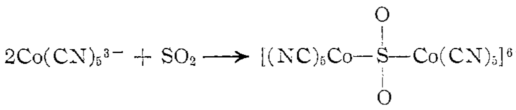
TABLE I
INFRARED SPECTRA (CM.$^{-1}$) OF SOME SO_2 COMPOUNDS

Compd.	$\nu_{\text{S-O}}$ (asym.)	$\nu_{\text{S-O}}$ (sym.)	$\nu_{\text{O-S-O}}$ (bend)
$K_6[(CN)_5Co\cdot SO_2\cdot Co(CN)_5]$	1078 s, 1072 s[a]	984 s	533 m, 525 m
$[Ru^{II}(NH_3)_5SO_2]Br_2$[b]	1327 s, 1301 s	1117 s	551 m
$SO_2(s)$[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). [c] R. N. Wiener and E. R. Nixon, *J. Chem. Phys.*, **25**, 1751 (1956).

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 $Co(CN)_5^{3-}$ with SO_2 or $KHSO_3$ can be formulated as $K_6[Co(CN)_5\cdot SO_2\cdot Co(CN)_5]\cdot 4H_2O$ (I), and the over-all reaction can be represented by cq. 1. Compound I is identical with that obtained by Cambi and Paglia[4] by treating a solution of $Co(C_2H_3O_2)_2$ and K_2SO_3 with gaseous HCN. However, these authors claim that the reaction of "$Co(CN)_6^{4-}$ with K_2SO_3 results in the formation of $Co(CN)_6^{3-}$ and $S_2O_4^{2-}$." Perhaps this is due to a higher pH and to a higher cyanide ion concentration than was used in our experiments.



$$2Co(CN)_5^{3-} + SO_2 \longrightarrow [(NC)_5Co-\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle O}{|}}{S}}-Co(CN)_5]^{6-} \qquad (1)$$

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 Å. (ε 50,000; value obtained after extrapolation to zero time) and at 2500 Å. (ε

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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.

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

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

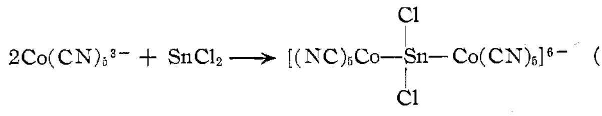
(4) L. Cambi and D. Paglia, *Gazz. chim. ital.*, **88**, 691 (1958).

5000). The band at 4450 Å. decreases very rapidly with time, and a new band is formed at 3080 Å. ($\epsilon \sim 13{,}000$). The band at 3080 Å., which increases with time to a maximum and then slowly disappears, is thus due to an intermediate product which decomposes much more slowly than I. After complete decomposition, a band is observed at 3800 Å., with ϵ 800. This band is identical with that of $Co(CN)_5OH^{3-}$ which has ϵ 380,[5] *i.e.*, half of the extinction observed in the decomposed solutions, thus proving the presence of two $Co(CN)_5$ groups in I. The rate constant of the first step is 4×10^{-3} sec.$^{-1}$ at 25°; that of the second step is about 5×10^{-5} sec.$^{-1}$.

This behavior, which is similar to that observed for other $Co(CN)_5$ bridge complexes,[6] can be interpreted as a rapid dissociation of one $Co(CN)_5$ group from the binuclear complex in the first step which is then followed by much slower separation of the sulfur ligand from the monomeric intermediate.

The Reaction with Tin(II) Chloride

The addition of a methanol solution of $SnCl_2$ to an aqueous solution of $CoCl_2$ and KCN in the molar ratio 1:5 results in an immediate change of the original green color into a dark brown color. From the resulting solution, a brown solid can be precipitated upon the addition of deaerated methanol. However, as spectrophotometric studies and analyses of the products obtained show, the reaction is not straightforward, and the composition of the products depends strongly upon the rate of mixing of the solutions and upon the concentration of $SnCl_2$ present. With slow and very efficient mixing, potentiometric as well as spectrophotometric studies show a consumption of 1 mole of $SnCl_2$ per 2 moles of $Co(CN)_5^{3-}$. This again strongly suggests the formation of a binuclear compound with $SnCl_2$ as a bridging group and the reaction designated by eq. 2. This bridged complex is isoelectronic with the


$$2Co(CN)_5^{3-} + SnCl_2 \longrightarrow [(NC)_5Co{-}\underset{\substack{| \\ Cl}}{\overset{\substack{Cl \\ |}}{Sn}}{-}Co(CN)_5]^{6-} \qquad (2)$$

known compound $Cl_2Sn[Mn(CO)_5]_2$.[7] This formulation of the cyano complex is supported by the analyses of the products which, even though variable from sample to sample, show the approximate molar ratio of C to N to Cl to be 5:5:1.

The solutions, containing more than 2 moles of $Co(CN)_5^{3-}$ per mole of $SnCl_2$ and prepared with vigorous mixing under nitrogen, show a strong absorption band at 4050 Å. ($\epsilon \sim 10{,}000$) which decreases very rapidly with time, and a band is formed at 3450 Å. ($\epsilon \sim 16{,}000$). The band at 3450 Å. decreases very slowly with time, an absorption band of $Co(CN)_5OH^{3-}$ being formed.

Solutions containing 2 or less than 2 moles of $Co(CN)_5^{3-}$ per mole of $SnCl_2$ show two more absorption bands, at 5800 and 4850 Å. The ratio of these bands to that at 4050 Å. depends upon the excess of $SnCl_2$ present, being larger the greater the excess of $SnCl_2$. The bands at 5800 and 4850 Å. develop also upon addition of $SnCl_2$ to a solution showing originally the 4050-Å. band.

The species giving the 4050-Å. band, which is probably $[Co(CN)_5 \cdot SnCl_2 \cdot Co(CN)_5]^{6-}$, decomposes very rapidly in solution ($k > 10^{-4}$ sec.$^{-1}$). The species giving the band at 3450 Å. (which seems to be a monomeric species, according to preliminary results with isolation) is relatively stable. The species with the bands at 4050 and 5800 Å. is very sensitive to air oxidation (unless a large excess of $SnCl_2$ is present) but decomposes slowly in deaerated solutions.

The reaction of $Co(CN)_5^{3-}$ with $SnCl_2$ shows, in spite of several complicating factors, the same general pattern as the reaction with SO_2 and with some other compounds. Thus, a binuclear complex is most probably formed as the primary product of the reaction which then decomposes rapidly giving a monomeric compound. The monomer is, in contrast to other intermediates studied, relatively stable and loses the tin(II) ligand very slowly.

Both of the reactions described differ somewhat from the reactions of $Co(CN)_5^{3-}$ with most other reagents studied thus far.[8] The reactions with halogens or hydrogen result in the addition of the oxidizing group to the complex with the formation of a monomer of the type $Co(CN)_5X^{3-}$. The reactions with oxygen[9] or quinone[6] result in the formation of a dimer, the extra electrons from Co(II) being accommodated in π^*-antibonding orbitals of the bridging group or in molecular orbitals formed by these π orbitals. In the case of SO_2 and $SnCl_2$, which both contain only one electron pair in their ground states, the reaction results in the formation of a new σ pair during the process of coordination. The electron density on the bridging group is thus increased considerably, but the electrons are still shared with the cobalt atoms. This raises the interesting question of the proper assignment of the oxidation state of the donor atom of the bridging group. As the infrared spectrum of I shows, the stretching frequencies of the bridging SO_2 group are much less than those of sulfur dioxide itself or of the ruthenium–sulfur dioxide complex (Table I). This indicates an increase of the electron density on the bridging SO_2 group as compared with the free SO_2 or with SO_2 bonded with one σ bond only, as in the ruthenium complex. A study of the oxidation–reduction properties of the bridging groups is now in progress in an attempt to elucidate the charge distribution in the complexes described.

Experimental Section

To a deaerated aqueous solution (*ca.* 40 ml.) containing 1.19 g. of $CoCl_2 \cdot 6H_2O$ and 1.7 g. of KCN a solution (*ca.* 10 ml.) containing 1 g. of $KHSO_3$ was added under nitrogen at 0° followed by the addition of 15 ml. of ice-cold, deaerated methanol with

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[5] N. K. King and M. E. Winfield, *J. Am. Chem. Soc.*, **83**, 3366 (1961).

[6] A. A. Vlček and F. Basolo, to be published.

[7] R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962).

[8] See review with references to original papers: J. Kwiatek, I. L. Mador, and J. K. Seyler, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p. 201.

[9] A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).

strong mixing. The crystals that separated were collected on a filter under nitrogen, washed with a 1:1 water–methanol mixture, and then with methanol. The solid material was redissolved in a small amount of ice-cold, deaerated water, and the solution was filtered rapidly and treated with methanol (*ca.* 30 vol. %). The crystals were collected on a filter, washed with a 1:1 methanol–water mixture, then with methanol and subsequently with ether, and dried for 8 hr. *in vacuo* over P_2O_5 at 100°.

Anal. Calcd. for $K_6[(CN)_5Co\cdot SO_2\cdot Co(CN)_5]\cdot 4H_2O$: C, 16.10; H, 1.07; S, 4.28; N, 18.7. Found: C, 16.3; H, 1.25; S, 4.15; N, 18.65.

To 70 ml. of an aqueous deaerated solution of 1.19 g. of $CoCl_2\cdot 6H_2O$ and 1.7 g. of KCN was slowly added 30 ml. of methanol containing 0.57 g. of $SnCl_2\cdot 2H_2O$ with vigorous mixing and in an N_2 atmosphere at 0°. The color changed from green to pale brown and then to dark brown. Finally, a dark brown solid started to separate. Its separation was completed by the addition of about 30 ml. of deaerated methanol. The crystalline product was collected on a filter and washed with a 1:1 methanol–water mixture and then with methanol. The dark brown solid was dissolved in a small amount of ice-cold, deaerated water and precipitated very rapidly with methanol. After filtration and washing with a methanol–water mixture followed by methanol, the solid was dried over P_2O_5 *in vacuo.*

Anal. Calcd. for $K_6[(CN)_5Co\cdot SnCl_2\cdot Co(CN)_5]$: C, 14.83; N, 17.46; Cl, 8.88. Found: Sample 1: C, 14.2; N, 16.8; Cl, 9.05. Sample 2: C, 13.4; N, 15.4; Cl, 10.3.

Spectra.—A Cary Model 14 spectrophotometer was used. The solutions were prepared in an N_2 atmosphere and transferred to the cell under nitrogen (the details will be described later[6]). Infrared spectra were taken on a Perkin-Elmer grating infrared Model 337 spectrophotometer in Nujol mull. An ordinary Beckman Model 9 potentiometer was used for potentiometric titrations with a bright platinum electrode combined with a commercial saturated calomel electrode.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Reaction of Boron Trifluoride with Sodium Nitrate and Sodium Nitrite

BY ROBERT N. SCOTT AND D. F. SHRIVER

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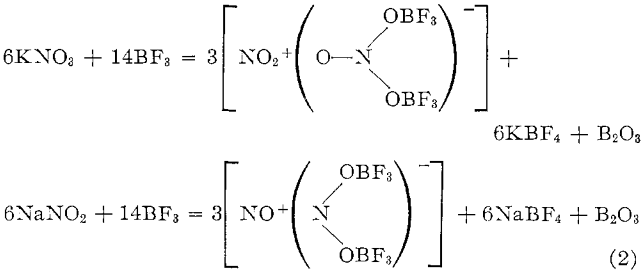
The interaction of nitrate[1,2] and nitrite[2] salts with boron trifluoride has been studied previously. Baumgarten proposed reaction 1 for potassium nitrate and boron trifluoride at 400–500°.

$$6KNO_3 + 9BF_3 = 6KBF_4 + (BOF)_3 + 3N_2O_3\,(2NO_2 + {}^1/_2O_2) \qquad (1)$$

Sprague, *et al.*, studied the interaction of boron trifluoride with potassium nitrate and sodium nitrite by passing a stream of boron trifluoride over the salt in a Pyrex tube. The reaction was initiated by flaming the material with a torch. They proposed the reaction shown below.



$$6KNO_3 + 14BF_3 = 3\left[NO_2^+\left(O{-}N\begin{matrix}OBF_3\\ OBF_3\end{matrix}\right)^-\right] + 6KBF_4 + B_2O_3$$

$$6NaNO_2 + 14BF_3 = 3\left[NO^+\left(N\begin{matrix}OBF_3\\ OBF_3\end{matrix}\right)^-\right] + 6NaBF_4 + B_2O_3 \qquad (2)$$

We have recently reinvestigated these reactions at lower temperatures and under more controlled conditions.

Experimental Section

Materials.—Reagent grade sodium nitrite and sodium nitrate were purchased from the Allied Chemical Co.

Purification of Boron Trifluoride.—Matheson 99% pure material was fractionated through a −126° bath. The vapor pressure at −111.6° was 301.4 mm., in good agreement with the value of 301 mm. given by Brown.[3] The infrared spectrum agrees with that of Baily, *et al.*,[4] and Vanderryn.[5]

Reaction of Boron Trifluoride and Sodium Nitrate.—In a typical reaction 0.0395 g. (0.464 mmole) of sodium nitrate and 1.35 mmoles of boron trifluoride were sealed in a Pyrex tube fitted with a break-seal. The lower three-fourths of the tube was placed in a furnace which was maintained at 180° for 48 hr. Gaseous products were then admitted to the vacuum line, condensables were collected at −196°, and noncondensables were collected by means of a Toepler pump. After *PVT* measurement of these fractions, condensables were characterized by an infrared spectrum and noncondensables by a mass spectrum. The reaction vessel was filled with dry nitrogen and transferred to a nitrogen-flushed drybag, where X-ray capillaries were loaded and mulls for infrared spectra were prepared. There was no evidence of etching in any of the reaction tubes.

Raman Spectra.—The Brandmuller technique[6] was employed on samples of the solid which had sublimed to the cold ends of the reaction tubes. The 4358-Å. Hg line was used for excitation, and a Gaertner two-prism spectrograph was employed (*f* 3.5; dispersion, *ca.* 150 cm.$^{-1}$/mm. in the region of interest). Considerable fluorescence was evident in all spectra.

Reaction of Boron Trifluoride and Sodium Nitrite.—The procedures were the same as those for sodium nitrate. In addition, the reaction of BF_3 with a suspension of $NaNO_2$ in *sym*-tetrachloroethane was followed on the vacuum line at −23 and 0°.[7]

Results

Sodium Nitrate.—When sodium nitrate and boron trifluoride were heated in a tube furnace as previously described, a white solid sublimed to the top of the reaction tube, leaving behind a white residue. X-Ray powder diffraction data for $NaBF_4$ and for nitrosyl tetrafluoroborate[8] were compared with products of the reaction, and it was found that the powder pattern of the sublimate matched quite well that of nitrosyl tetrafluoroborate, while the powder pattern of the residue matched the most intense lines of sodium tetrafluoroborate.

The mass spectrum of the noncondensable gas produced in this reaction contained only two sets of peaks

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[1] P. Baumgarten and W. Bruns, *Ber.*, **72**, 1753 (1939).

[2] R. W. Sprague, A. B. Garett, and H. H. Sisler, *J. Am. Chem. Soc.*, **82**, 1059 (1960).

[3] H. C. Brown and R. B. Johannsen, *ibid.*, **72**, 2937 (1950).

[4] C. R. Baily, J. B. Hale, and J. W. Thompson, *Proc. Roy. Soc.* (London), **161**, 107 (1937).

[5] J. Vanderryn, *J. Chem. Phys.*, **30**, 331 (1959).

[6] J. Brandmuller, *Z. angew. Phys.*, **5**, 95 (1953).

[7] This experiment was performed by John J. Rupp. In view of the explosive nature of dinitrogen tetroxide in the presence of chloronated solvents [*Chem. Eng. News*, **42**, No. 47, 53 (1964)] there may be some danger of explosion associated with this reaction.

[8] J. C. Evans, H. W. Rinn, S. J. Kuhn, and G. A. Olah, *Inorg. Chem.*, **3**, 857 (1964).