

for providing facilities and for helpful discussions. Decoupling and variable-temperature nmr studies done by Varian Associates are gratefully acknowledged.

The author also wishes to acknowledge the support of the Washington University computing facilities through NSF Grant G-22296.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF DELAWARE, NEWARK, DELAWARE 19711

Coordination Complexes of the Selenocyanate Ion¹

By JOHN L. BURMEISTER AND LLOYD E. WILLIAMS

Received February 4, 1966

A series of new selenocyanate complexes of transition metal ions has been prepared. The basic preparative technique involves the reaction of the appropriate metal salt with potassium selenocyanate and $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{SeCN}$ in absolute ethanol. The complexes were characterized by elemental analyses, conductivity measurements in nitrobenzene solution, and infrared spectra of Nujol mulls and acetone solutions. Examples of both bonding modes of the selenocyanate were found: $[\text{M}(\text{NCSe})_4]^{2-}$ ($\text{M} = \text{Fe}(\text{II}), \text{Zn}(\text{II})$), $[\text{M}(\text{NCSe})_6]^{n-}$ ($\text{M} = \text{Mn}(\text{II}), \text{Fe}(\text{III}), \text{Ni}(\text{II}), \text{Y}(\text{III})$), $[\text{Rh}(\text{SeCN})_6]^{3-}$, and $[\text{M}(\text{SeCN})_4]^{2-}$ ($\text{M} = \text{Pd}(\text{II}), \text{Pt}(\text{II})$). The $\text{Cd}(\text{II})$ complex prepared is unique in its constitution, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Cd}_2(\text{NCSe})_6]$. Its infrared spectrum supports a structure involving $\text{Cd}\text{-NCSe}\text{-Cd}$ bridges and terminal $\text{Cd}\text{-NCSe}$ groups. The ranges of integrated absorption intensities of the C-N stretching bands for Se- and N-bonded complexes were found to be, respectively, $0.5\text{-}1 \times 10^4$ and $5\text{-}10 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$. The visible spectrum of the $\text{Pd}(\text{II})$ complex indicates that the ligand field strength of -SeCN is less than that of -SCN , the former being slightly below -Br in the spectrochemical series.

Introduction

The coordination chemistry of the selenocyanate ion was, until this decade, an area almost completely devoid of research. Recent studies²⁻⁶ have emphasized the analogous coordination behavior of the selenocyanate and thiocyanate ions. However, at the inception of this study, complexes containing selenocyanates as the only ligands had been prepared for only five different transition metal ions: $[\text{Co}(\text{NCSe})_4]^{2-}$,^{2,4} $[\text{Cr}(\text{NCSe})_6]^{3-}$,⁵ $[\text{Pt}(\text{SeCN})_6]^{2-}$,² $[\text{Hg}(\text{SeCN})_4]^{2-}$,² and AgSeCN (bridged).² In an effort to obtain a more complete picture, we have synthesized a number of hitherto unknown selenocyanate complexes. As this paper was being written, Forster and Goodgame⁷ published the results of a study involving selenocyanate complexes of several transition metal ions which we had included in our work. However, no two of the compounds prepared from ions common to both studies are identical and the results are, on the whole, complementary.

Experimental Section

Preparation of Compounds. $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{SeCN}$.—This salt was prepared metathetically from the corresponding bromide and KSeCN in ethanol. After the potassium bromide which pre-

cipitated was removed by filtration, the desired product was precipitated from solution by the addition of ethyl ether.

Selenocyanate Complexes.—The preparative technique employed was essentially the same for all of the complexes, with the exception of those of $\text{Y}(\text{III})$ and $\text{Rh}(\text{III})$. To a solution of the hydrated metal nitrate ($\text{Fe}(\text{III}), \text{Ni}(\text{II}), \text{Zn}(\text{II}), \text{Cd}(\text{II})$), sulfate ($\text{Fe}(\text{II})$), chloride ($\text{Mn}(\text{II})$), or complex chloride ($\text{Pd}(\text{II}), \text{Pt}(\text{II})$) in absolute ethanol was added an ethanolic solution of a stoichiometric amount (with respect to metathesis) of KSeCN . The resulting mixture was filtered into an ethanolic solution of the calculated amount of $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{SeCN}$, and the solution thus obtained was stored at -20° until the complex crystallized. The crystals were isolated by filtration, washed with absolute ethanol and anhydrous ethyl ether, dried *in vacuo*, and recrystallized from absolute ethanol. Water was added initially to dissolve the $\text{Fe}(\text{II}), \text{Pd}(\text{II}),$ and $\text{Pt}(\text{II})$ salts completely. The $\text{Ni}(\text{II})$ complex was first precipitated by the addition of anhydrous ethyl ether. The initial $\text{Pt}(\text{II})$ reaction mixture was warmed gently on a steam bath in order to complete the substitution reaction.

The $\text{Y}(\text{III})$ and $\text{Rh}(\text{III})$ complexes were prepared by the direct reaction in ethanol of, respectively, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{K}_3[\text{RhCl}_6] \cdot \text{H}_2\text{O}$ with excess $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{SeCN}$. Water was added to complete the dissolution of the $\text{Rh}(\text{III})$ salt. The reaction mixtures were warmed on a steam bath to complete the reactions, then cooled in an ice bath and treated as above.

Infrared Spectra.—Infrared spectra, in the $4000\text{-}400 \text{ cm}^{-1}$ range, of complexes held in Nujol suspension between KBr plates were measured on a Perkin-Elmer Model 421 recording spectrophotometer. The same instrument was used to record high-resolution spectra of Spectro Grade acetone solutions of the complexes in the selenocyanate C-N stretching range ($2200\text{-}2000 \text{ cm}^{-1}$). Matched 0.1-mm NaCl cells were employed.

The integrated absorption intensities, A ($\text{M}^{-1} \text{ cm}^{-2}$), of the C-N stretching bands were determined by Ramsay's method of direct integration.⁸ Beer's law plots were made for all of the solutions.

Visible and Ultraviolet Spectra.—Visible and ultraviolet absorption spectra of ethanolic solutions of complexes were measured

(1) Presented in part at the Symposium on Coordination Compounds, sponsored by the University of Padova, Bressanone, Italy, July 26-29, 1965, and at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 22-31, 1966.

(2) A. Turco, C. Pecile, and M. Nicolini, *Proc. Chem. Soc.*, 213 (1961); *J. Chem. Soc.*, 3008 (1962).

(3) S. M. Nelson, *Proc. Chem. Soc.*, 372 (1961).

(4) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, 1, 565 (1962).

(5) K. Michelson, *Acta Chem. Scand.*, 17, 1811 (1963).

(6) M. E. Farago and J. M. James, *Inorg. Chem.*, 4, 1706 (1965).

(7) D. Forster and D. M. L. Goodgame, *ibid.*, 4, 1712 (1965).

(8) D. A. Ramsay, *J. Am. Chem. Soc.*, 74, 72 (1952).

TABLE I
 FORMULAS, COLORS, YIELDS, MELTING POINTS, MOLAR CONDUCTANCES, AND ANALYTICAL DATA

Compound ^a	Color	Yield, %	Mp, °C ^b	Λ_m^c , ohm ⁻¹ cm ⁻² mole ⁻¹	Analyses, %					
					Theory			Found		
					C	H	N	C	H	N
R ₄ [Mn(NCSe) ₆]	White	22	85	90	50.81	8.77	8.46	50.62	8.50	8.67
R ₂ [Fe(NCSe) ₄]	Light tan	64	80	49	45.01	7.55	8.75	45.19	7.62	8.96
R ₃ [Fe(NCSe) ₆]	Reddish brown	46	78	66	45.90	7.70	8.92	45.75	7.65	8.73
R ₄ [Ni(NCSe) ₆]	Dark green	49	121 ^d	98	50.69	8.75	8.49	49.98	8.44	8.63
R ₂ [Zn(NCSe) ₄]	White	44	60	51	44.56	7.48	8.66	44.79	7.57	8.67
R ₃ [Y(NCSe) ₆]	White	59	159	68	44.85	7.53	8.72	44.95	7.70	8.90
R ₃ [Rh(SeCN) ₆] ^f	Dark red	52	<i>e</i>	70	44.42	7.45	8.63	44.20	7.35	8.48
R ₂ [Pd(SeCN) ₄]	Reddish brown	92	<i>e</i>	52	42.76	7.18	8.31	42.98	7.21	8.35
R ₂ [Cd ₂ (NCSe) ₆] ^g	White	70	119 ^d	42	34.07	5.42	8.37	34.11	5.45	8.48
R ₂ [Pt(SeCN) ₄] ^h	Reddish brown	55	132	52	39.31	6.60	7.64	39.10	6.46	7.64

^a R = [(n - C₄H₉)₄N]⁺. ^b Uncorrected. ^c Phillips and Tyree [D. J. Phillips and S. Y. Tyree Jr., *J. Am. Chem. Soc.*, **83**, 1806 (1961)] give the following ranges for molar conductances in nitrobenzene (25°, 10⁻³ M): 1:1, 20-30; 2:1, 40-60; 3:1 (extrapolated), 60-90; 4:1 (extrapolated), 80-120. ^d Melts with decomposition. ^e Softening, tacky range with transition to melt. ^f This complex has recently been prepared by Schmidtke [H.-H. Schmidtke, private communication]. ^g Calcd: Se, 35.37. Found: Se, 35.00. ^h Calcd: Pt, 17.73. Found: Pt, 17.89.

 TABLE II
 INFRARED DATA FOR THE COMPLEXES

Compound ^a	C-Se str., $\nu_1(\text{SeCN})$, cm ⁻¹	SeCN bend, $\nu_2(\text{SeCN})$, cm ⁻¹	C-N stretch			
			$\nu_3(\text{SeCN})$, cm ⁻¹	$\Delta\nu_{1/2}^b$, cm ⁻¹	ϵ_{max}^c , M ⁻¹ cm ⁻¹	10 ⁻⁴ A, ^c M ⁻¹ cm ⁻²
R ₄ [Mn(NCSe) ₆]	(M) 640 vw, 617 w (S)	424 m	2097 sh, 2082 s, br, 2070 s, br 2064 s, br	26	920	8.7
R ₂ [Fe(NCSe) ₄]	(M) 673 sh, 666 w (S)	432 m	2067 s, br, 2055 sh 2064 s, br	27	1080	11
R ₃ [Fe(NCSe) ₆]	(M) 673 sh, 666 w (S)	431 m	2067 s, br, 2055 sh 2064 s, br	27	1050	10
R ₄ [Ni(NCSe) ₆]	(M) 625 w (S)	430 m	2118 sh, 2102 s, br 2100 s, br 2070 m, br	30 20	364 210	4.0 1.5
R ₂ [Zn(NCSe) ₄]	(M) 661 m (S)	429 m	2087 s, br	25	1050	9.5
R ₃ [Y(NCSe) ₆]	(M) 634 m (S)	429 m	2067 s, br, 2030 sh 2068 s, br	27	514	5.0
R ₃ [Rh(SeCN) ₆]	(M) 515 w (S)	<i>d</i>	2104 s, sp, 2071 m, sp 2107 s, sp	15	176	0.96
R ₂ [Pd(SeCN) ₄]	(M) 519 w (S)	<i>d</i>	2107 s, sp, 2060 w 2113 s, sp	10	170	0.62
R ₂ [Cd ₂ (NCSe) ₆]	(M) 589 sh, 582 m (S)	417 w, 408 m	2125 sh, 2109 s, br 2120 s, sp ^g 2076 s, br ^f	16 24	557 300	3.2 2.6
R ₂ [Pt(SeCN) ₄]	(M) 516 w (S)	<i>d</i>	2105 s, sp, 2060 w 2117 s, sp	13	124	0.59
KSeCN	(S)		2068 s, sp	16	307	1.8
[(n-C ₄ H ₉) ₄ N]SeCN	(S)		2067 s, sp	16	356	2.1

^a R = [(n - C₄H₉)₄N]⁺. ^b Apparent half-band width. ^c Calculated per mole of coordinated selenocyanate. Concentration of all solutions used was 5 × 10⁻² M (with respect to coordinated selenocyanate). ^d No band found down to the scanning limit (400 cm⁻¹). ^e Assigned to bridging selenocyanates. ^f Assigned to terminal selenocyanates (see text). Abbreviations: (M), complex held in Nujol suspension; (S), acetone solution; s, strong; m, medium; w, weak; br, broad; sp, sharp; sh, shoulder.

on a Perkin-Elmer Model 202 recording spectrophotometer using matched 1.0-cm quartz cells.

Conductance Measurements.—Molar conductances, at 25°, of 10⁻³ M solutions of the complexes in Fisher Certified Reagent grade nitrobenzene were measured with an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge and a cell with platinized electrodes.

Analyses.—Carbon, hydrogen, and nitrogen microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Mülheim, Germany. Selenium was determined gravimetrically after precipitation with hydrochloric acid and hydroxylammonium chloride.⁹ Platinum was determined gravimetrically by igniting a weighed sample of the compound in a porcelain crucible over a Meker burner.

(9) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," 3rd ed, Longmans, London, 1961, p 509.

The formulas, colors, yields, melting points, molar conductances, and analyses for the complexes are shown in Table I.

Results and Discussion

Representative infrared spectra are shown in Figures 1 and 2; the infrared data for all of the complexes are given in Table II. The ultraviolet and visible absorption maxima for the selenocyanato and thio-cyanato¹⁰ complexes of rhodium(III), palladium(II), and platinum(II) are given in Table III.

The complexes were formulated with respect to the bonding mode of the selenocyanate ion on the basis of

(10) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, pp 196, 287, 288, 295.

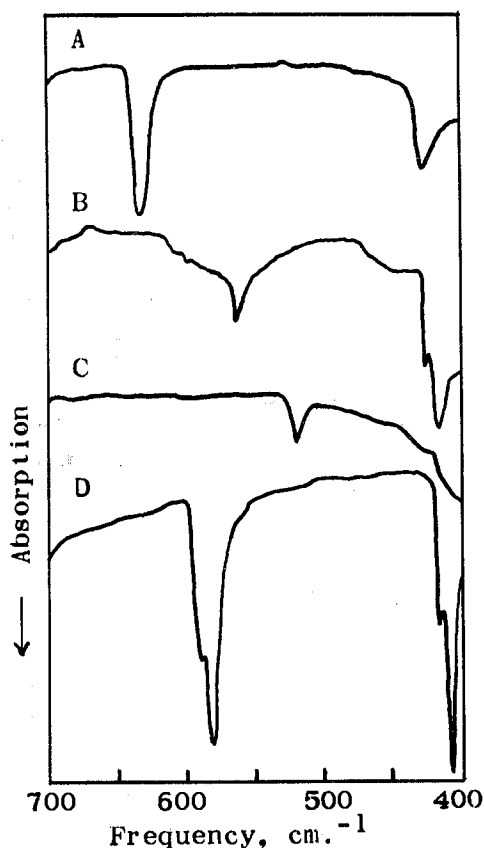


Figure 1.—Infrared spectra (Nujol mulls) of: A, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{[Y(NCSe)}_6]$; B, $[(n\text{-C}_4\text{H}_9)_4\text{N]SeCN}$; C, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Pd}(\text{SeCN})_4]$; D, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Cd}_2(\text{NCSe})_6]$.

TABLE III
ULTRAVIOLET AND VISIBLE SPECTRA OF
SELENOCYANATO AND THIOCYANATO COMPLEXES

Complex	Absorption maxima, kK	
	X = Se	X = S ^a
$[\text{Rh}(\text{XCN})_6]^{3-}$	38.2, ^b 32.8 ^b	34.5, ^c 19.4 sh
$[\text{Pd}(\text{XCN})_4]^{2-}$	31.0, ^b 23.2 sh, 18.9 sh	32.5, ^c 24.5 sh, 20.0 sh
$[\text{Pt}(\text{XCN})_4]^{2-}$	39.4, ^b 22.2 sh	37.4, ^c 27.0 sh, 23.8 sh

^a Values taken from ref 10. ^b Selenocyanate internal transition. ^c Thiocyanate internal transition.

the known behavior of the ion's infrared absorption bands resulting from N or Se coordination. The low-frequency stretching mode (approximating a C-Se stretch) is shifted² to a higher frequency upon N coordination and to a lower frequency upon Se coordination, both relative to that of ionic selenocyanate, as in KSeCN (558 cm^{-1}).¹¹ The C-Se stretching frequencies of bridging selenocyanates lie intermediate between the N-bonded and ionic values.² The high-frequency stretching mode (approximating a C-N stretch) increases in the order $-\text{NCSe} < -\text{SeCN} < \text{M}-\text{NCSe}-\text{M}$.² The SeCN bending frequencies of N-bonded selenocyanates occur at higher wavenumbers (above 400 cm^{-1})² than those of Se-bonded selenocyanates (main band $<400\text{ cm}^{-1}$).^{2,12} The tetra-*n*-butylammonium ion does not absorb in any of these regions (see curve B in Figure 1).

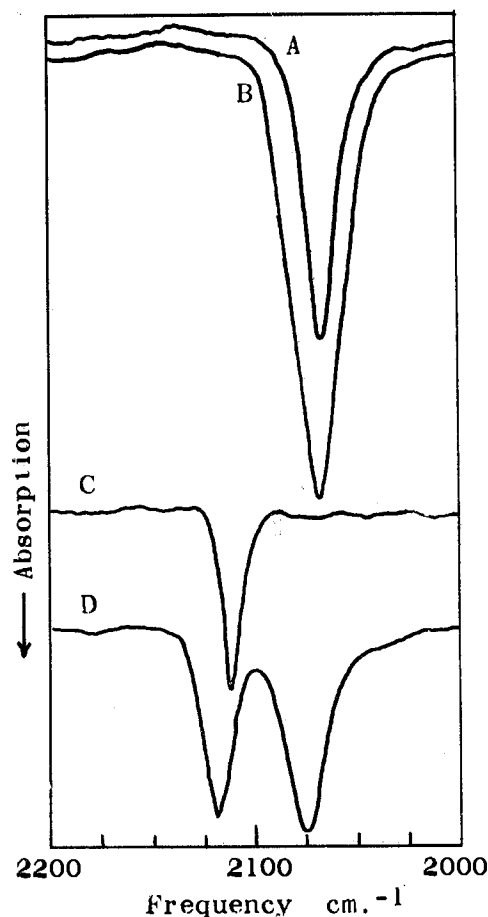


Figure 2.—Infrared spectra (acetone solutions, 0.05 *M* in coordinated SeCN^-) of: A, $[(n\text{-C}_4\text{H}_9)_4\text{N]SeCN}$; B, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{[Y(NCSe)}_6]$; C, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Pd}(\text{SeCN})_4]$; D, $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Cd}_2(\text{NCSe})_6]$.

Very recently, Pecile¹³ has found that, for solutions of thiocyanates in inert solvents, the value of the integrated absorption intensity of the C-N stretching band is diagnostic of the bond type, those of S-bonded thiocyanates occurring in the range $0.8\text{--}2.3 \times 10^4\text{ M}^{-1}\text{ cm}^{-2}$, whereas those of N-bonded thiocyanates are up to an order of magnitude larger, $9\text{--}12 \times 10^4\text{ M}^{-1}\text{ cm}^{-2}$. He predicted that a similar correlation would hold for selenocyanate complexes, although his measurements were limited to only three such complexes. That this is indeed the case is shown by the data in Table II. The ranges of integrated absorption intensities for Se- and N-bonded complexes were found to be, respectively, $0.5\text{--}1 \times 10^4$ and $5\text{--}10 \times 10^4\text{ M}^{-1}\text{ cm}^{-2}$. The value for the nickel(II) complex is not included because it was the only complex whose Beer's law plot did not go through the origin, and the band at 2070 cm^{-1} is undoubtedly due to free selenocyanate resulting from the dissociation of the complex. The cadmium(II) complex represents a special case which will be discussed later.

A comparison of the mull and solution spectra shows the usual effects of solid-state splitting. The effect of the cation on the number and frequency of the bands

(11) H. W. Morgan, *J. Inorg. Nucl. Chem.*, **16**, 387 (1961).

(12) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).

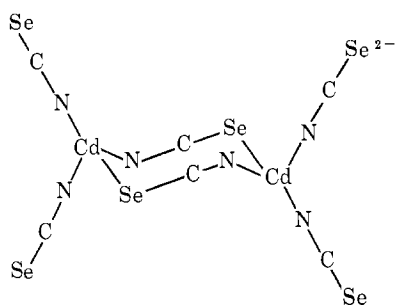
(13) C. Pecile, *ibid.*, **5**, 210 (1966).

is vividly demonstrated by a comparison of the data in Table II with those of Forster and Goodgame.⁷

Over-all, the bonding pattern exhibited by the selenocyanate ion in these complexes is identical (with the exception of the cadmium(II) complex) with that exhibited by the thiocyanate ion. For both, the change from class a to class b behavior¹⁴ apparently occurs at rhodium(III). Seen in this light, the dissimilarity in behavior exhibited by these ligands when other ligands are introduced into the coordination sphere,¹⁵ either by means of activated-bridge electron-transfer reactions or substitution reactions, becomes all the more surprising.

Jørgensen¹⁶ has suggested that elements with varying oxidation number, z , may exhibit maximum class a tendencies at an intermediate value of z , and postulated that iron(II) might form an N-bonded thiocyanate complex, whereas that of iron(III) might be S-bonded. This has not proved to be the case with either the thiocyanate¹⁷ or selenocyanate complexes, all being N-bonded. The fact that yttrium(III) readily forms a complex with selenocyanate raises the intriguing possibility that the lanthanide tripositive ions, all similar in size to yttrium(III), might do likewise. We are currently investigating this possibility.

The cadmium(II) complex, which crystallizes as well-formed cubic crystals, is unique in two respects. It is the only one, of those prepared in this study, wherein it is necessary to postulate the formation of bridging selenocyanate groups, and it is the sole case where the bonds formed by the selenocyanates are not analogous to those formed by thiocyanates. The results of repetitive elemental analyses and conductivity measurements of different samples support its formulation as $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Cd}_2(\text{NCSe})_6]$. Its solution infrared spectrum is compatible with the bridged structure



wherein one selenium and three nitrogen atoms are tetrahedrally disposed about each cadmium, the nitrogen and selenium atoms in the bridging groups being sp^2 hybridized and the carbon atoms sp hybridized. The construction (to scale) of a Prentice-Hall Framework molecular model shows that an eight-membered ring is readily formed in this manner, with no evident steric strain. The chair form shown requires that the

unhybridized p orbitals of the selenium atoms in the bridging groups be tilted somewhat with respect to the corresponding carbon p orbitals. The carbon atoms in the bridging groups are left with only three formal bonds if the ring is constructed in the boat form. The bridge is formulated as being symmetrical, owing to the large steric strain encountered in closing the ring when the relatively large selenium atoms of the bridging groups are bonded to the same cadmium. A comparison of the solution and solid-state infrared spectra of the complex shows that the lower frequency C-N stretch (assigned to the terminal -NCSe groups) is shifted to a higher wavenumber in the latter spectrum. This rather high value (2109 cm^{-1}), plus the relatively low SeCN bending frequencies, would seem to indicate that the terminal selenocyanates are Se-bonded in the solid state. However, the broadness and relatively large intensity of the C-N stretching band and the position of the C-Se stretching band (the most reliable infrared criterion for the solid state) argue in favor of the terminal Cd-NCSe linkages in the solid state as well. There is thus a very smooth change from class a to class b behavior in the selenocyanate complexes of group IIB. The corresponding cadmium(II) thiocyanate complex is formulated as $\text{K}_2[\text{Cd}(\text{SCN})_4] \cdot 2\text{H}_2\text{O}$ and contains two terminal -SCN and two bridging -SCN- groups,¹⁸ albeit not as a discrete $[\text{Cd}_2(\text{SCN})_6]^{2-}$ unit.

Several authors^{2,4,5,7} have found that -NCSe is very close to but slightly higher than -NCS in the spectrochemical series. A comparison of the visible spectra of the palladium(II) selenocyanate and thiocyanate complexes, where the observed spectra are completely analogous (Table III), indicates that -SeCN lies lower in the spectrochemical series than -SCN . Support for this conclusion is found in the observation that, in general, for the complexes of both palladium(II) and platinum(II), the position of the first spin-allowed ligand field band follows the accepted spectrochemical series.¹⁹ This is in agreement with the work of Fenske, *et al.*,²⁰ who have presented a complete crystal field treatment of the d^8 problem with electron-electron interactions and spin-orbit coupling. They showed that the energy of this band is equal to $-35F_4 - 10Dq$, where F_4 is one of the two Slater-Condon²¹ parameters. The transition energies calculated by them for nine platinum(II) complexes are in good agreement with the observed spectra. Since the calculations were carried out using the same value of F_4 in each case, it follows that the energy of this band is a measure of Dq . According to Jørgensen,¹⁹ the first spin-allowed bands in the spectra of the palladium(II) and platinum(II) thiocyanate complexes are found at 20.0 and 23.8 kK, respectively. The corresponding bands in the spectra of the selenocyanates are found at 18.9 and

(14) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

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

(16) C. K. Jørgensen, *ibid.*, **3**, 1201 (1964).

(17) D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 268 (1965); *Inorg. Chem.*, **4**, 715 (1965).

(18) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

(19) See ref 10, pp 287, 288, for necessary data.

(20) R. F. Fenske, D. S. Martin, Jr., and K. Ruedenberg, *Inorg. Chem.*, **1**, 441 (1962).

(21) E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge University Press, London, 1959.

22.2 kK. This places $-\text{SeCN}$ below $-\text{Br}$ (19.9 and 24.1 kK)¹⁹ in the spectrochemical series. Although we did not observe a band in the visible region in the spectrum of the rhodium(III) selenocyanate complex, Schmidtke²² has observed a very weak band at 18.2 kK. This is lower than the value of 19.4 kK reported¹⁰ for the

corresponding thiocyanate complex, in agreement with the conclusion stated above.

Acknowledgments.—We wish to thank Dr. C. Pecile for suggesting the integrated absorption intensity measurements and for providing us with a copy of his paper prior to publication. This research was supported by the University of Delaware Research Foundation.

(22) H.-H. Schmidtke, *J. Inorg. Nucl. Chem.*, in press.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
ARIZONA STATE UNIVERSITY, TEMPE, ARIZONA

Reactions of Niobium Tetrahalides with Some Tertiary Amines¹

By T. M. BROWN AND GERALD S. NEWTON²

Received January 28, 1966

The reactions of the niobium tetrahalides with triethylamine have been studied under the conditions described (72 hr at 25 or 50°). Only with niobium tetrachloride was a product obtained free of unreacted tetrahalide. Comparison of its visible reflectance spectrum and diamagnetic character with the spectra and magnetic properties of niobium tetrachloride and other compounds containing the niobium–niobium bond suggests that at least partial retention of the metal–metal bond may have occurred. Similar results were obtained when NbCl_4 was placed in an excess of N,N,N',N' -tetramethylpropylenediamine or N,N' -dimethylpiperazine. The reactions with N,N,N',N' -tetramethylethylenediamine yield the monoadducts, $\text{NbX}_4 \cdot \text{C}_6\text{H}_{16}\text{N}_2$ ($\text{X} = \text{Cl, Br, I}$), as the major reaction products. Partial reduction of the metal also occurred, resulting in the formation of the diamine dihydrohalides and organic oxidation products. The visible and ultraviolet spectra of the $\text{NbX}_4 \cdot \text{C}_6\text{H}_{16}\text{N}_2$ complexes were examined over the range 220 to 670 $\text{m}\mu$. Two low-intensity transitions were observed in the visible region as expected for a tetragonally distorted complex.

Introduction

The known chemistry of niobium(IV) may be conveniently divided into two parts: (1) binary compounds, *i.e.*, the oxide and simple halides, and (2) complex compounds in which reaction of the tetrahalides, and in some cases the pentahalides, with donor ligands has occurred. The simplest coordination compounds of niobium(IV) are the highly colored hexahalo complexes, A_2NbX_6 ($\text{A} = \text{K, RB, Cs}$; $\text{X} = \text{Cl, Br, I}$), recently prepared by Torp³ by fusion of the tetrahalides with stoichiometric amounts of alkali metal halides. In addition, the coordination compounds, $\text{NbX}_4 \cdot 2\text{L}$ and $\text{NbX}_4 \cdot \text{B}$ ($\text{X} = \text{Cl, Br, I}$; $\text{L} = \text{pyridine, acetonitrile}$; $\text{B} = 2,2'$ -bipyridine, 1,10-phenanthroline), have been reported.^{3–5} The visible and ultraviolet spectra of these complexes were studied and the behavior of the hexahalo and acetonitrile complexes was found to be in accord with simple ligand field theory.

The visible spectra of the tetrahalides in pyridine solution, however, yielded quite unusual results in that the extinction coefficients were much higher than expected for simple $d-d$ transitions and were comparable

in magnitude to those expected of charge-transfer transitions which are not usually found in the visible region of the spectrum. McCarle and Torp⁴ attributed these absorption bands to charge transfer from filled π orbitals of ligand pyridine to metal atom d orbitals. The fact that the absorptions occur at progressively shorter wavelengths in the order $\text{Cl} > \text{Br} > \text{I}$ indicates a possible reversal of the usual spectrochemical series. The investigators reason that if pyridine is a strong π -bonding ligand in these complexes, the order of π bonding of halogens is $\text{Cl} < \text{Br} < \text{I}$ and is sufficient to offset the normal order of the spectrochemical series.

Carnell and Fowles have studied^{6,7} the action of primary, secondary, and tertiary amines on the niobium(V) chlorides and bromides. With most primary amines, the aminobasic metal halides, $\text{MX}_3(\text{NHR})_2 \cdot \text{NH}_2\text{R}$, resulted. With secondary amines, the analogous products, $\text{MX}_3(\text{NR}_2)_2 \cdot \text{NHR}_2$, resulted. With trimethylamine, highly insoluble products were obtained, possibly mixtures, but giving the over-all composition $\text{MX}_5 \cdot 2\text{N}(\text{CH}_3)_3$. None of these reactions resulted in reduction to the tetravalent state.

In view of the π -bonding ability of the ligands present in compounds of the type $\text{NbX}_4 \cdot 2\text{L}$, it was of interest to study the properties of niobium tetrahalide

(1) This work was supported by the National Science Foundation, Grant No. GP-3810.

(2) NASA Predoctoral Fellow, 1964–1965.

(3) B. A. Torp, Doctoral Dissertation, Iowa State University of Science and Technology, Ames, Iowa, 1964.

(4) R. E. McCarley and B. A. Torp, *Inorg. Chem.*, **2**, 540 (1963).

(5) M. Allbutt, K. Feenan, and G. W. A. Fowles, *J. Less-Common Metals*, **6**, 299 (1964).

(6) P. J. H. Carnell and G. W. A. Fowles, *J. Chem. Soc.*, 4113 (1959).

(7) P. J. H. Carnell and G. W. A. Fowles, *J. Less-Common Metals*, **4**, 40 (1962).