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Some Transition Metal Complexes with the Selenocyanate Ion

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The preparations are described of compounds containing the complex anions $M(\text{NCSe})_6^{4-}$ and $M(\text{NCSe})_4^{2-}$, where $M = \text{Mn}$, Fe , Co , and Ni , and of $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Zn}(\text{NCSe})_4$. The results of studies of their electronic and infrared spectra, magnetic properties, and X-ray powder photographs are reported. The anions $M(\text{NCSe})_4^{2-}$, where $M = \text{Mn}$, Fe , Co , and Zn , are tetrahedral, but the nickel ion in $(\text{cat}^{2+})\text{Ni}(\text{NCSe})_4$ is in a six-coordinate, tetragonal ligand field achieved by anion association, with bridging NCSe groups. The low-energy infrared spectra of the complexes have bands assignable as essentially metal-ligand stretching vibrations at 233–261 cm^{-1} for $M(\text{NCSe})_4^{2-}$ and at 195–237 cm^{-1} for $M(\text{NCSe})_6^{4-}$. The complex $[(\text{CH}_3)_4\text{N}]_2\text{Pd}(\text{SeCN})_4$ has been prepared and its infrared spectrum (2500–200 cm^{-1}) is reported.

Introduction

We recently described the preparation and some properties of several complexes of first series transition metals with cyanate² and thiocyanate ions.^{3,4}

Since, apart from the cobalt(II) compounds,⁵ the analogous complexes with NCSe^- appear to have been little studied, we thought it worthwhile to extend our investigations to include this ligand. We report here the results of this work.

Experimental

Preparation of Compounds. $(\text{cat}^{2+})(\text{NCSe})_2 \cdot (\text{CH}_3)_4\text{N}(\text{NCSe})_4$ and $(\text{C}_2\text{H}_5)_4\text{N}(\text{NCSe})_4$.—These were prepared metathetically from the corresponding chlorides and KNCSe in ethanol.

Metal Complexes.—These were prepared by the methods outlined below. The colors, yields, and analyses are listed in Table I.

$(\text{cat}^{2+})\text{M}(\text{NCSe})_4$, $M = \text{Mn}$, Fe , Co , Ni .—A solution of the metal(II) selenocyanate in acetone was prepared from the corresponding hydrated chloride and KNCSe , and this was filtered into a warm solution of the calculated quantity of $(\text{cat}^{2+})(\text{NCSe})_2$ in nitromethane, to give the desired complex. The cobalt complex was recrystallized from nitromethane (0.5 g. in 80 ml.). In the preparation of the nickel compound an excess (~25%) of KNCSe was found to be necessary to stabilize the nickel selenocyanate solution.

$[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{M}(\text{NCSe})_4$, $M = \text{Co}$, Zn .—Potassium selenocyanate was shaken with the respective $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{MBr}_4$ complex in acetone for about 10 min. The precipitated KBr was filtered off and diethyl ether added to the filtrate. The complexes were purified by dissolving them in a small volume of nitromethane, filtering the solution, and then adding diethyl ether.

$[(\text{CH}_3)_4\text{N}]_4\text{M}(\text{NCSe})_6$, $M = \text{Mn}$, Fe , Co , Ni .—A solution of the hydrated metal chloride in ethanol was mixed with an excess over the calculated amount of $(\text{CH}_3)_4\text{N}(\text{NCSe})_4$ also in ethanol. In the preparation of the cobalt complex a blue precipitate formed on addition of the cobalt chloride solution to the tetramethylammonium selenocyanate solution. However, this redissolved on addition of hot methanol, and, on cooling the resulting solution to room temperature, pink crystals of the hexakis complex were obtained. The manganese(II) and iron(II) compounds were recrystallized from methanol (containing a small amount of $(\text{CH}_3)_4\text{N}(\text{NCSe})_4$ in the latter case).

$[(\text{C}_2\text{H}_5)_4\text{N}]_4\text{Ni}(\text{NCSe})_6$.—On mixing the calculated quantities of

nickel selenocyanate and $(\text{C}_2\text{H}_5)_4\text{N}(\text{NCSe})_4$ in ethanol crystals of the desired complex slowly separated. These were recrystallized from ethanol and dried *in vacuo*.

$[(\text{CH}_3)_4\text{N}]_2\text{Pd}(\text{SeCN})_4$.—Potassium selenocyanate (1.6 g.) was shaken with $[(\text{CH}_3)_4\text{N}]_2\text{PdCl}_4$ (1 g.) in acetone (15 ml.) for 30 min. The solution was filtered and diethyl ether added to the filtrate. The complex was twice recrystallized from ethanol; m.p. 120°.

Physical Measurements.—These were carried out as described in previous papers.^{2,4,6}

Results and Discussion

The coordination behavior of NCSe^- in forming $M(\text{NCSe})_x^{n-}$ anions with the first row transition metal ions Mn^{II} to Zn^{II} is generally rather similar to that of NCS^- .^{2–5} One difference is the absence of a complex selenocyanate anion of copper(II). Because of the reducing power of NCSe^- , all attempts to prepare such a compound have so far been unsuccessful.

The compounds we have prepared are listed in Table I. X-Ray powder photographs show that isomorphism exists in the following groups: $(\text{cat}^{2+})\text{M}(\text{NCSe})_4$, where $M = \text{Mn}$, Fe , and Co ; $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{M}(\text{NCSe})_4$, where $M = \text{Co}$ and Zn ; and $[(\text{CH}_3)_4\text{N}]_4\text{M}(\text{NCSe})_6$, where $M = \text{Mn}$, Fe , Co , and Ni .

The electronic spectrum of $(\text{cat}^{2+})\text{Co}(\text{NCSe})_4$ is quite similar to those of several other $\text{Co}(\text{NCSe})_4^{2-}$ salts which have been studied previously,⁵ in which the NCSe groups are bonded tetrahedrally to the metal through nitrogen. From the isomorphism mentioned above it can be concluded that $(\text{cat}^{2+})\text{M}(\text{NCSe})_4$, $M = \text{Mn}$ and Fe , and $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Zn}(\text{NCSe})_4$ also contain tetrahedral isoselenocyanato anions.

Electronic Spectra and Magnetic Properties.—These will be discussed on the basis of the nature of the metal ion.

Manganese(II) Complexes.—The electronic spectrum of $(\text{cat}^{2+})\text{Mn}(\text{NCSe})_4$ (see Table II) closely resembles that of the tetrahedral $\text{Mn}(\text{NCS})_4^{2-}$ ion³ and the bands can be assigned as for the latter complex. From the band energies it appears that the values of the interelectronic repulsion parameters, B and C , are virtually the same for the two complexes, whereas the ligand field in $\text{Mn}(\text{NCSe})_4^{2-}$ is slightly stronger than in its NCS analog.

(1) $\text{cat}^{2+} = [p\text{-xylylenebis(triphenylphosphonium)}]^{2+}$.(2) D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 2790 (1964).(3) D. Forster and D. M. L. Goodgame, *ibid.*, 268 (1965).(4) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, 4, 823 (1965).(5) (a) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *ibid.*, 1, 565 (1962); (b) A. Turco, C. Pecile, and M. Nicolini, *J. Chem. Soc.*, 3008 (1962).(6) D. Forster and D. M. L. Goodgame, *ibid.*, 262 (1965).

TABLE I
 FORMULAS, COLORS, YIELDS, AND ANALYTICAL DATA FOR THE COMPLEXES

Compound	Color	Yield, %	C, %		H, %		N, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
(cat ²⁺)Mn(NCSe) ₄	Pale green	40	52.24	52.61	3.47	3.49	5.08	5.26
(cat ²⁺)Fe(NCSe) ₄	Pale brown	85	52.20	52.49	3.47	3.49	5.07	5.24
(cat ²⁺)Co(NCSe) ₄	Blue	54	52.05	52.41	3.46	3.46	5.06	4.83
(cat ²⁺)Ni(NCSe) ₄	Yellow	80	52.06	51.48	3.46	3.49	5.06	5.66
[(C ₂ H ₅) ₄ N] ₂ Co(NCSe) ₄	Dark green	60	32.49	32.05	5.45	5.65	11.37	11.52
[(C ₂ H ₅) ₄ N] ₂ Zn(NCSe) ₄	White	65	32.21	32.07	5.41	5.32	11.27	11.25
[(CH ₃) ₄ N] ₄ Mn(NCSe) ₆	Pink	25	26.92	27.23	4.93	5.37	14.27	13.63
[(CH ₃) ₄ N] ₄ Fe(NCSe) ₆	Pale brown	32	26.90	26.71	4.93	5.00	14.26	13.92
[(CH ₃) ₄ N] ₄ Co(NCSe) ₆	Pink	20	26.81	27.05	4.91	5.17	14.22	14.06
[(CH ₃) ₄ N] ₄ Ni(NCSe) ₆	Pale blue	35	26.82	26.85	4.91	4.67	14.22	13.94
[(C ₂ H ₅) ₄ N] ₄ Ni(NCSe) ₆	Pale blue	20	37.73	37.31	6.67	6.55	11.58	11.48
[(CH ₃) ₄ N] ₂ Pd(SeCN) ₄	Brown	75	21.36	21.53	3.59	3.65	12.46	12.60

 TABLE II
 REFLECTANCE SPECTRA FOR SOME
 ISOSELENOCYANATO COMPLEXES

Compound	Absorption max., cm. ⁻¹
(cat ²⁺)Mn(NCSe) ₄	~26,900 sh, ~25,400 sh, 22,700, 21,600, ~19,400, 16,000 ^a
(cat ²⁺)Fe(NCSe) ₄	6050, 4750
(cat ²⁺)Co(NCSe) ₄	16,300, ~8730 sh, 7700
(cat ²⁺)Ni(NCSe) ₄	25,000, ~18,800 sh, 13,800, 6300
[(CH ₃) ₄ N] ₄ Fe(NCSe) ₆	11,150, ~9760 sh
[(CH ₃) ₄ N] ₄ Co(NCSe) ₆	~20,000 br, 9100
[(CH ₃) ₄ N] ₄ Ni(NCSe) ₆	26,400, ~22,300 w sh, 16,600, ~13,800, w sh, 10,000

^a Probably due to trace quantities of Co(NCSe)₄²⁻ (see text).

The band at 16,000 cm.⁻¹ is probably due to the ⁴A₂ → ⁴T₁(P) transition⁵ of trace quantities of Co(NCSe)₄²⁻ from cobalt(II) impurity present in the commercial manganese(II) chloride starting material (the intensities of these bands are ~1000 times greater than those of their manganese(II) analogs).

Unlike the tetrahalomanganate(II) ions⁷ but in common with the other pseudo-halide complexes of manganese(II),^{2,3} (cat²⁺)Mn(NCSe)₄ does not fluoresce in ultraviolet radiation.

The magnetic susceptibility of (cat²⁺)Mn(NCSe)₄ obeys the Curie law over the range 118–298°K., with $\mu_{\text{eff}} = 6.07 \pm 0.05$ B.M. This value is higher than the expected spin-only value, but moments of 6.0–6.05 B.M. have been found for some other tetrahedral complexes of manganese(II).⁸

We could not obtain a reliable reflectance spectrum of [(CH₃)₄N]₄Mn(NCSe)₆ due to the very low intensities of the d-d bands, as is commonly found for octahedral manganese(II) complexes.

Iron(II) Complexes.—The reflectance spectrum of (cat²⁺)Fe(NCSe)₄ shows strong absorption in the near-infrared region, with maxima at 6050 and 4750 cm.⁻¹ (Figure 1). This may be assigned as the ⁵E → ⁵T₂ transition of a tetrahedral iron(II) complex.⁹ The band energy is slightly greater than that observed³ for the corresponding isothiocyanato complex, and this, in agreement with the results mentioned above for the

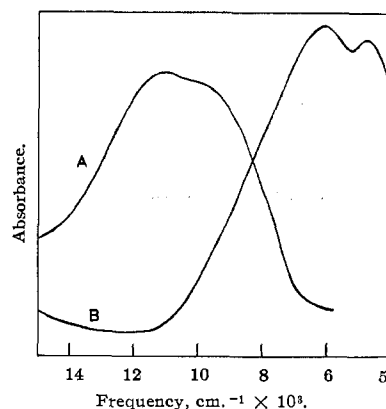


Figure 1.—Reflectance spectra of: A, [(CH₃)₄N]₄Fe(NCSe)₆; B, (cat²⁺)Fe(NCSe)₄.

manganese(II) compounds and the data for cobalt(II),^{5,10} suggests that -NCSe produces a somewhat stronger ligand field than does -NCS (the Δ values for the iron(II) complexes are ~5400 and ~5200 cm.⁻¹, respectively).

The splitting of ~1300 cm.⁻¹ observed for the ⁵E → ⁵T₂ transition of Fe(NCSe)₄²⁻ is larger than that expected simply from the effects of spin-orbit coupling. A similar splitting was found³ for Fe(NCS)₄²⁻. As in the latter case, without X-ray structural data, one cannot decide whether this splitting arises from a permanent, ground-state distortion of the Fe-N₄ tetrahedron or from a dynamic Jahn-Teller effect.

The magnetic susceptibility of (cat²⁺)Fe(NCSe)₄ was determined over the range 98–300°K. The value of μ_{eff} at 290°K. is 5.30 ± 0.05 B.M. The susceptibility, corrected for the temperature-independent term (estimated to be 200×10^{-6} c.g.s. unit), obeys the Curie-Weiss law with $\theta = -7 \pm 1^\circ\text{K}$. This departure from the Curie law probably arises from small distortions of the ligand field from T_d symmetry.¹¹

The reflectance spectrum of [(CH₃)₄N]₄Fe(NCSe)₆ in the range 4000–20,000 cm.⁻¹ shows a band assignable as the ⁵T_{2g} → ⁵E_g transition at ~11,000 cm.⁻¹ (Figure 1). The fact that the band occurs at higher energy than in the Fe(H₂O)₆²⁺ ion¹² supports the formulation

(7) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 53 (1957); A. Sacco and L. Naldini, *Gazz. chim. ital.*, **89**, 2258 (1960).

(8) D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 3735 (1961).

(9) C. Furlani, E. Cervone, and V. Valenti, *J. Inorg. Nucl. Chem.*, **25**, 159 (1963); D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 454 (1965).

(10) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).

(11) B. N. Figgis, *Trans. Faraday Soc.*, **56**, 1553 (1960).

(12) F. A. Cotton and M. D. Meyers, *J. Am. Chem. Soc.*, **82**, 5023 (1960).

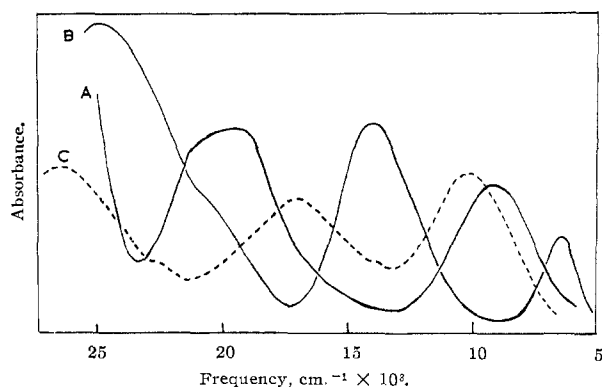


Figure 2.—Reflectance spectra of: A, $[(\text{CH}_3)_4\text{N}]_4\text{Co}(\text{NCSe})_6$; B, $(\text{cat}^{2+})\text{Ni}(\text{NCSe})_4$; C, $[(\text{CH}_3)_4\text{N}]_4\text{Ni}(\text{NCSe})_6$.

of this compound as an isoselenocyanato complex. A similar conclusion may be drawn from the spectra of the complex anions $\text{M}(\text{NCSe})_6^{4-}$ where $\text{M} = \text{Co}$ or Ni (see below).

As may be seen from Figure 1, the band at $\sim 11,000$ cm^{-1} is quite broad and is asymmetric, with a pronounced shoulder on the low-energy side of the band maximum. The band due to ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ for $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ is also broad and can be resolved by Gaussian analysis into two overlapping bands.¹² This splitting for $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ was attributed¹² to a dynamic Jahn-Teller distortion of the excited state, ${}^5\text{E}_g$. However, as in the case of the $\text{Fe}(\text{NCSe})_4^{2-}$ ion discussed above, we cannot decide whether this is also true for $\text{Fe}(\text{NCSe})_6^{4-}$, since permanent, solid-state distortion of the $\text{Fe}-\text{N}_6$ octahedron would cause a similar band splitting.

Cobalt(II) Complexes.—The electronic spectra and magnetic properties of several salts of the $\text{Co}(\text{NCSe})_4^{2-}$ ion have been reported,⁵ but compounds containing the $\text{Co}(\text{NCSe})_6^{4-}$ ion do not appear to have been described previously. Moreover, to our knowledge, NCS^- does not form a discrete hexakis complex anion with cobalt(II), although octahedral $\text{Co}(\text{NCS})_6$ groupings are present in $\text{Co}(\text{NCS})_6\text{Hg}_2 \cdot \text{C}_6\text{H}_6$.¹³

The electronic spectrum of $[(\text{CH}_3)_4\text{N}]_4\text{Co}(\text{NCSe})_6$ in the solid state (Figure 2, Table II) is typical of that of high-spin octahedral cobalt(II) and may be satisfactorily assigned using Liehr's energy-level diagram¹⁴ with $\Delta = 9700$ cm^{-1} . The band at 9100 cm^{-1} is due to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}$. The broad, asymmetric band at $\sim 20,000$ cm^{-1} most probably arises from both the two remaining spin-allowed transitions, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$, since the upper levels of these lie very close together in this region of the energy level diagram.¹⁴

A solution spectrum of $[(\text{CH}_3)_4\text{N}]_4\text{Co}(\text{NCSe})_6$ could not be obtained because the process of solution was accompanied either by complete decomposition of the complex (in strongly coordinating solvents) or by very extensive, if not complete, formation of the blue $\text{Co}(\text{NCSe})_4^{2-}$ ion.

Since the Δ value for the selenocyanate ion in tetrahedral $\text{Co}(\text{NCSe})_4^{2-}$ is known,⁵ we may compare the

values for this ligand in the two geometries, tetrahedral and octahedral. The ratio $\Delta_{\text{tet}}:\Delta_{\text{oct}} = 0.49$, which agrees well with those found for $\text{Ni}(\text{NCS})_4^{2-}$ and $\text{Ni}(\text{NCS})_6^{4-}$ (0.51),⁴ and nickel(II) in ZnO and MgO (0.50),¹⁵ but is a little higher than that (0.42) reported for cobalt(II) in ZnO and MgO .¹⁶

Nickel(II) Complexes.—The electronic spectrum of $[(\text{CH}_3)_4\text{N}]_4\text{Ni}(\text{NCSe})_6$ (Table II and Figure 2) is that expected for an octahedral nickel(II) complex, and the bands may be assigned as follows: ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ at $10,000$ cm^{-1} , ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g(\text{D})$ at $\sim 13,800$ cm^{-1} , ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ at $16,600$ cm^{-1} , ${}^3\text{A}_{2g} \rightarrow {}^1\text{T}_{2g}(\text{D})$ at $\sim 22,300$ cm^{-1} , and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ at $26,400$ cm^{-1} . Except for the ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g(\text{D})$ transition these values agree well with those predicted from the Liehr and Ballhausen energy level diagram for octahedral nickel(II)¹⁷ with $\Delta = 10,000$ cm^{-1} . The ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g(\text{D})$ transition would be expected to lie at $\sim 12,500$ cm^{-1} . This transition was also found to be ~ 1200 cm^{-1} above the calculated¹⁷ value for the $\text{Ni}(\text{NCS})_6^{4-}$ ion.⁴ As in the case of the tetrahedral $\text{M}(\text{NCS})_4^{2-}$ ions, the value of Δ found for $\text{Ni}(\text{NCSe})_6^{4-}$ is greater than that (9600 cm^{-1}) observed⁴ for the isothiocyanato analog.

It was found previously⁴ that two types of compound of composition $(\text{cation})_2\text{Ni}(\text{NCS})_4$ may be prepared. In one class there are discrete, tetrahedral $\text{Ni}(\text{NCS})_4^{2-}$ anions, while in the other, anion association occurs in the solid state so that the nickel atoms are surrounded by a tetragonally distorted octahedral ligand field, composed of four nitrogen and two sulfur atoms. The formation of the tetrahedral complexes appeared to be favored by the use of very large cations such as cat^{2+} and $(\text{C}_6\text{H}_5)_4\text{As}^+$.

Attempts to prepare compounds containing tetrahedral $\text{Ni}(\text{NCSe})_4^{2-}$ ions have so far been unsuccessful even with cat^{2+} as cation. The magnetic moment of the yellow compound $(\text{cat}^{2+})\text{Ni}(\text{NCSe})_4$ (3.17 B.M. at 290°K .) is that expected for a six-coordinate, tetragonal nickel complex, and the electronic spectrum (Table II and Figure 2) also suggests this type of environment for the metal atom. The infrared spectrum of the compound is in agreement with this (see below).

However, in the case of the nickel thiocyanate compounds only the six-coordinate complexes were obtained at room temperature or a little above, higher temperatures being required for the preparation of the tetrahedral forms (e.g., $\sim 155^\circ$ for tetrahedral $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{Ni}(\text{NCS})_4$). Unfortunately the nickel selenocyanate complexes decompose fairly readily on heating, either in solution or in the solid state.

Infrared Spectra.—The infrared spectra of the complexes have been examined, as Nujol mulls, in the region 2500 – 200 cm^{-1} . The compounds $[(\text{CH}_3)_4\text{N}]_4\text{M}(\text{NCSe})_6$, where $\text{M} = \text{Mn}$, Fe , and Co , have also been studied down to 170 cm^{-1} . The results and suggested

(13) R. Grønbaek and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 1889 (1964).

(14) A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

(15) R. Pappalardo, D. L. Wood, and R. C. Linares, *J. Chem. Phys.*, **35**, 1460 (1961).

(16) R. Pappalardo, D. L. Wood, and R. C. Linares, *ibid.*, **35**, 2041 (1961).

(17) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **6**, 134 (1959).

TABLE III

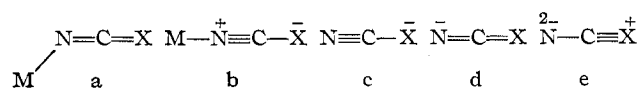
INFRARED DATA (CM. ⁻¹) FOR THE COMPLEXES				
Compound	$\nu(\text{C-N})$	$\nu(\text{C-Se})$	$\delta(\text{N-C-Se})$	$\nu(\text{M-N})$
(cat ²⁺)Mn(NCSe) ₄	2058 vs 2049 vs	649 vw 636 vw	429 w ^b	243 s
(cat ²⁺)Fe(NCSe) ₄	2062 vs 2049 vs	662 vvw 646 vvw	428 w ^b	249 s
(cat ²⁺)Co(NCSe) ₄	2073 vs 2062 vs	654 vvw	430 m ^b	261 s
(cat ²⁺)Ni(NCSe) ₄	2145 m 2092 vs 2075 s	653 vw	429 w ^b	237 s
[(C ₂ H ₅) ₄ N] ₂ Co(NCSe) ₄	2053 s ^a	666 w	433 m ^a 417 m ^a 432 m	260 s
[(C ₂ H ₅) ₄ N] ₂ Zn(NCSe) ₄	2066 vs	660 w	415 w	233 s
[(CH ₃) ₄ N] ₄ Mn(NCSe) ₆	2072 s	623 w	420 m	195 s
[(CH ₃) ₄ N] ₄ Fe(NCSe) ₆	2083 s	606 w	422 m	205 s
[(CH ₃) ₄ N] ₄ Co(NCSe) ₆	2087 s	623 w 606 w	426 m	214 s
[(CH ₃) ₄ N] ₄ Ni(NCSe) ₆	2096 s	606 w	423 m	237 s
[(C ₂ H ₅) ₄ N] ₄ Ni(NCSe) ₆	422 m	233 s
[(CH ₃) ₄ N] ₂ Pd(SeCN) ₄	2114 s 2105 s	521 w	410 w 374 m	240 m ^c

^a From ref. 5b. ^b Assignment uncertain due to cation absorption in this region. ^c $\nu(\text{Pd-Se})$.

assignments are listed in Table III (bands due to the cations have been omitted).

The high values observed for the C-N stretch in (cat²⁺)Ni(NCSe)₄ are in accord with the presence of bridging NCSe groups in this compound.⁵ Thus the infrared results agree with the magnetic and electronic spectral data in indicating the occurrence of anion association.

The octahedral M(NCSe)₆⁴⁻ ions have higher values of $\nu(\text{C-N})$ and lower values of $\nu(\text{C-Se})$ than do the corresponding tetrahedral M(NCSe)₄²⁻ ions. Now for covalent metal-nitrogen bonding in M-NCX the main canonical forms contributing to the electronic structure will be a and b, while for the free NCX⁻ ion forms

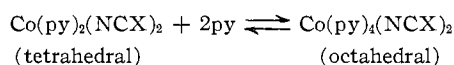


c, d, and e may be considered (Jones has calculated¹⁸ that form c predominates (71%) in the case of NCS⁻). In the complex anions M(NCX)_n^{m-} discussed here the metal-nitrogen bonding is unlikely to be purely covalent and therefore in any consideration of bond orders in the NCX groups all forms a-e can be taken into account to varying degrees. In order to avoid the buildup of excessive negative charge on the metal ion in M(NCX)₆⁴⁻ it is probable that the contribution of form c will increase as compared with that in the M(NCX)₄²⁻ ions, thus raising $\nu(\text{C-N})$ and lowering $\nu(\text{C-X})$.

These considerations may also be relevant to the apparent increasing ability to form hexakis complex anions in the sequence NCO⁻ \ll NCS⁻ \approx NCSe⁻ (a similar order has been found by King, *et al.*,¹⁹ for the equilibrium constants for

(18) L. H. Jones, *J. Chem. Phys.*, **25**, 1069 (1956).

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From the electronegativities of O, S, and Se one would expect that the contribution of form c, and hence distribution of electronic charge and the likelihood of forming M(NCX)₆⁴⁻, would be greater for NCO⁻ than for NCS⁻ or NCSe⁻. This, however, does not seem to be the case. The observed trend may possibly be attributed to the greater p_π-p_π bonding expected for the C-O bond, as compared with C-S or C-Se, which would make form c more difficult to attain in the cyanates.

The spectra of M(NCSe)₄²⁻, where M = Mn, Fe, Co, or Zn, in the range 200-400 cm.⁻¹ all have a strong band at 233-261 cm.⁻¹, which may be assigned as ν_{11} , essentially the MN₄ degenerate stretch of an M(NCX)₄ species with T_d symmetry.^{6,20} The frequencies of ν_{11} follow the usual sequence of metal-ligand stretches of tetrahedral complexes.^{6,21} They are 40-50 cm.⁻¹ lower than those of the analogous M(NCS)₄²⁻ ions²² and 75-85 cm.⁻¹ less than ν_{11} for the corresponding isocyanate complexes⁶ (*e.g.*, Co(NCO)₄²⁻ (345 cm.⁻¹), Co(NCS)₄²⁻ (~340 cm.⁻¹), and Co(NCSe)₄²⁻ (260 cm.⁻¹)).

The compound (cat²⁺)Ni(NCSe)₄ also shows one band in this region, at 237 cm.⁻¹, but in view of the more complicated structure, an unambiguous assignment of this band cannot be given. It is likely, however, that the mode responsible for this absorption is predominantly Ni-N stretching in character, since the Ni-Se frequencies would probably lie below 200 cm.⁻¹.

The infrared spectra of all the M(NCSe)₆⁴⁻ ions show a strong band in the region 190-240 cm.⁻¹. This may be assigned as ν_{14} , the MN₆ degenerate stretch of an M(NCX)₆ species with O_h symmetry.²³ The values of ν_{14} vary, on changing M, in the sequence Mn < Fe < Co < Ni, which is the order of increasing crystal field stabilization energy. However, the values of ν_{14} for Ni(NCSe)₆⁴⁻ are rather higher than might have been expected. Whereas ν_{14} for Mn(NCSe)₆⁴⁻ is ~27 cm.⁻¹ lower than for Mn(NCS)₆⁴⁻ (~222 cm.⁻¹),²² in the case of the nickel complexes the difference is only ~7 cm.⁻¹.

The C-N and C-Se stretching frequencies of [(CH₃)₄N]₂Pd(SeCN)₄ support the formulation with Pd-Se bonds.^{5b} Two bands are observed in the N-C-Se bending region. Since the Pd-Se₄ grouping is most probably planar both in-plane and out-of-plane, N-C-Se bends would be expected. However, splitting of $\delta(\text{NCSe})$ could arise from solid-state effects, as has been observed for KNCSe, for example.^{5b} Both $\delta(\text{NCSe})$ bands are at lower energy than in the isoselenocyanato complexes. A similar difference has been observed in $\delta(\text{NCS})$ for N- and S-bonded thio-cyanate complexes.²⁴ The band at 240 cm.⁻¹ is tentatively assigned as the Pd-Se stretch.

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Transition Metal Complexes with Ligands Derived from 2-Sulfenamido-pyridine

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A variety of complexes have been synthesized with ligands derived from the Schiff base reaction of 2-pyridinaldehyde and 2-acetylpyridine with 2-sulfenamido-pyridine, 2-sulfenamido-4-methylpyridine, and 2-sulfenamido-pyridine 1-oxide. The resultant ligands all chelate in a tridentate manner. Magnetic moments, molar conductances, and spectral data have been applied to the characterization of the complexes. The properties of the cobalt(II) and nickel(II) species are typical of spin-free octahedral structures in all cases. In contrast, the iron(II) complexes show significant changes in properties coinciding with alterations in the structures of the ligands. All the Schiff base ligands derived from 2-sulfenamido-pyridine and 2-sulfenamido-4-methylpyridine result in iron(II) complexes which are diamagnetic, a behavior which is typical for imines of this type. In contrast is the behavior of bis((N-(2-thiopyridine 1-oxide)2-pyridinalimine)iron(II) perchlorate, which is paramagnetic with a moment of 5.16 B.M. Finally, a study of the visible spectra of the nickel complexes of the various ligands suggests that the electron pair on the sulfur atom of the sulfenamide moiety is not appreciably delocalized.

Introduction

Since the turn of the century when Blau¹ first reported on 2,2'-bipyridine, a great deal of interest has centered on ligands containing the α -diimine linkage ($-\text{N}=\text{C}-\text{C}=\text{N}-$). Of particular fascination has been the nature of the metal-nitrogen bond in the metal chelates. The interest has been aroused because of the unusual stability of these complexes as demonstrated by the diamagnetism exhibited by almost all iron(II) complexes containing this array of atoms. This typical behavior has been reported for the iron(II) complexes of pyridinalimines,² α -diketodihydrazones,³ pyridinalhydrazones,⁴ and so forth. An exception is tris(2-pyridinaldimethylhydrazone)iron(II) iodide which has a magnetic moment of 5.45 B.M.⁵ This anomalous behavior is a consequence of steric considerations which results in a forced lengthening of the metal-nitrogen bond.

The research reported herein is concerned with the synthesis of a new group of ligands containing the α -diimine array as well as the preparation and characterization of 28 transition metal derivatives.

Experimental

Materials.—2-Pyridinaldehyde and 2-acetylpyridine were obtained from Aldrich Chemical Co. and purified when necessary. Sodium 2-thiopyridine 1-oxide was obtained from the Olin Mathieson Chemical Corp. All the metal perchlorates were purchased from the G. F. Smith Co. and used without further

purification. The other materials are standard reagent grade chemicals.

Complexes of 2-Sulfenamido-pyridine. 2-Mercaptopyridine.—This compound was synthesized by the method of Thirtle⁶; m.p. 126–128°. *Anal.* Calcd. for $\text{C}_5\text{H}_5\text{NS}$: C, 54.1; H, 4.5; N, 12.6. Found: C, 54.1; H, 4.5; N, 12.5.

2-Sulfenamido-pyridine.—An aqueous chloramine solution was prepared by the slow addition of 90 ml. of an iced 1.84 *M* sodium hypochlorite solution to 278 ml. of a 1.84 *M* ammonium hydroxide solution which had been previously cooled to -5° . To the resulting chloramine solution, an aqueous solution of the sodium salt of 2-mercaptopyridine (16.5 g., 0.15 mole) was added slowly, taking care that the temperature did not exceed 5° . The desired product precipitated immediately and was filtered, vacuum dried to remove excess water, and recrystallized from a petroleum ether-isopropyl alcohol mixture. This resulted in 10.5 g. (55% yield) of a white crystalline product; m.p. 79–80°. *Anal.* Calcd. for $\text{C}_5\text{H}_6\text{N}_2\text{S}$: C, 47.6; H, 4.8; N, 22.2. Found: C, 47.7; H, 5.2; N, 22.1.

Dichlorobis(2-sulfenamido-pyridine)iron(II) 1-Hydrate.—Ferrous chloride 4-hydrate (2.0 g., 0.01 mole) was dissolved in methanol and added dropwise, with stirring, to a methanol solution of 2-sulfenamido-pyridine (3.8 g., 0.03 mole). The mixture was stirred for an additional 30 min. and then placed in a refrigerator overnight. The brown solid that formed was filtered, washed successively with methanol and ether, and air dried; yield 45%. *Anal.* Calcd. for $[\text{Fe}(\text{C}_5\text{H}_6\text{N}_2\text{S})_2\text{Cl}_2] \cdot \text{H}_2\text{O}$: C, 30.2; H, 3.5; N, 14.1; Fe, 14.1. Found: C, 29.8; H, 3.7; N, 14.0; Fe, 14.5.

Dichlorobis(2-sulfenamido-pyridine)cobalt(II).—This compound was isolated as a pink material in a method analogous to that previously described; yield 30%. *Anal.* Calcd. for $[\text{Co}(\text{C}_5\text{H}_6\text{N}_2\text{S})_2\text{Cl}_2]$: C, 31.4; H, 3.1; N, 14.7; Co, 15.4. Found: C, 31.7; H, 3.2; N, 14.7; Co, 15.0.

Tris(2-sulfenamido-pyridine)iron(II) Perchlorate.—Ferrous perchlorate 6-hydrate (1.2 g., 0.0033 mole) was dissolved in methanol and added dropwise, with stirring, to a methanol

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