

676, 650, 600, 590, 355, 341, 327, and 315 cm^{-1} are absent from our spectra.

However, the Indian authors have also carried out a normal coordinate analysis of nickel *N,N*-dimethyldiselenocarbamate, but here the model used has been unsatisfactory. In fact, the spectrum of this compound (which was not available to the authors) shows none of the calculated frequencies, except the band near 1550 cm^{-1} . Especially, there is no absorption between 1040 and 900 cm^{-1} so the calculated frequency for $\nu(\text{C}=\text{Se})$ as 946 cm^{-1} cannot be correct.

Our empirical assignments have been corroborated by a normal coordinate analysis,⁹ carried out in this laboratory, of nickel dimethyldithiocarbamate.

Experimental. The dimethyldithiocarbamates were prepared by known methods;¹⁰ the nickel complex was recrystallized from dimethylformamide and the cobalt complex from chloroform-ethanol.

The dimethyldiselenocarbamates were prepared in a similar manner as the diethyldiselenocarbamates.¹ The nickel complex (yellow) could be recrystallized from dimethylformamide but was much less soluble than the corresponding dithiocarbamate. (Found: C 14.72; H 2.47; N 5.78. Calc. for $\text{C}_6\text{H}_{12}\text{N}_2\text{NiSe}_2$: C 14.81; H 2.49; N 5.76). The cobalt complex (brown) was recrystallized from chloroform-ethanol. (Found: C 15.40; H 2.53; N 5.64. Calc. for $\text{C}_9\text{H}_{18}\text{CoN}_3\text{Se}_2$: C 15.42; H 2.59; N 6.00).

Infrared spectra. $\{[(\text{CH}_3)_2\text{NCS}_2]_2\text{Ni}\}$: 1550vs, 1445m, 1379vs, 1232m, 1142vs, 1050m, 890m, 870vw, 375w, 325m. $\{[(\text{CH}_3)_2\text{NCS}_2]_2\text{Co}\}$: 1528vs, 1448m, 1390vs, 1235m, 1138vs, 1048m, 900m, 875w, 754w, 746w, 375w, 330w.

$\{[(\text{CH}_3)_2\text{NCS}_2]_2\text{Ni}\}$: 1550vs, 1445m, 1400vs, 1245s, 1150vs, 1052m, 1015w, 975s, 894vw, 572vw, 550vw, 442m, 414m, 387s, 375s, 300m. $\{[(\text{CH}_3)_2\text{CS}_2]_2\text{Co}\}$: 1528vs, 1450m, 1390vs, 1255s, 1145vs, 1050w, 1025vw, 975s, 895vw, 580w, 442m, 360s, 324w.

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Organic Selenium Compounds

X. Coordination Compounds of 1,1-Diselenolates

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Lately much interest has centered around coordination compounds of 1,1-dithiols and 1,2-dithiols (*cf.* the reviews by Gray¹ and Jørgensen²) but, so far, the only selenium analogue investigated has been 1,2-bis(trifluoromethyl)-1,2-diselenol, of which some metal compounds have recently been described.³ In connection with investigations, in this laboratory, of the reactions of carbon diselenide with active methylene compounds, alkali metal salts of 2,2-dicyanoethylene-1,1-diselenol, $(\text{NC})_2\text{C}=\text{C}(\text{SeH})_2$, and cyanimidodiselenocarbonic acid, $\text{NC}-\text{N}=\text{C}(\text{SeH})$, have been prepared,⁴ from which some transition metal complexes have been obtained.

When a heavy metal salt is added to an aqueous solution of a 1,1-diselenolate an intensely coloured, brown or red-brown, solution is obtained, containing the anions I or II. The corresponding alkali metal salts are very soluble but, as in the case of the corresponding dithiolates, certain onium salts are only slightly soluble. Usually the anions I and II were isolated as tetraphenylphosphonium salts. When strong acid is added to solutions of the

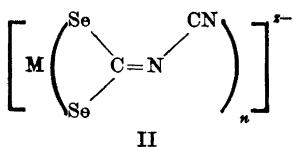
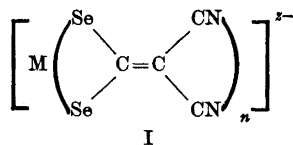
Table I. Diselenolato complexes.

Formula (L: (CN) ₂ C=C(Se ⁻) ₂)		Colour	M.p., °C	Analyses (C, H, N)
(Ph ₄ P) ₂ [NiL ₂]	C ₃₆ H ₄₀ N ₄ NiP ₂ Se ₄	dark red	226–227	Found: 55.5; 3.42; 4.63 Calc.: 55.8; 3.34; 4.65
(Ph ₄ P) ₂ [ZnL ₂]	C ₃₆ H ₄₀ N ₄ P ₂ Se ₄ Zn	light yellow	227–228	Found: 55.2; 3.37; 4.56 Calc.: 55.5; 3.33; 4.62
(Ph ₄ P) ₂ [CdL ₂]	C ₃₆ H ₄₀ CdN ₄ P ₂ Se ₄	yellow	240–241	Found: 53.3; 3.33; 4.52 Calc.: 53.4; 3.20; 4.46
(Ph ₄ P) ₂ [PtL ₂]	C ₃₆ H ₄₀ N ₄ P ₂ PtSe ₄	red	248–250	Found: 49.5; 2.95; 4.15 Calc.: 50.1; 3.01; 4.17
(Ph ₄ P) ₂ [CuL ₂]	C ₃₆ H ₄₀ CuN ₄ P ₂ Se ₄	dark brown	205–206	Found: ^a 53.7; 3.32; 4.56 Calc.: 55.6; 3.33; 4.63
(Ph ₄ P)[AuL ₂]	C ₃₂ H ₃₀ AuN ₄ PSe ₄	red	214–215	Found: 38.2; 2.11; 5.50 Calc.: 38.3; 2.01; 5.58
(Ph ₄ P) ₃ [CrL ₃]	C ₈₄ H ₈₀ CrN ₆ P ₃ Se ₆	bronzy		Found: ^b 54.4; 3.33; 4.54 Calc.: 56.9; 3.42; 4.74
(Ph ₄ P) ₃ [CoL ₃]	C ₈₄ H ₈₀ CoN ₆ P ₃ Se ₆	dark brown		Found: ^b 54.7; 3.35; 4.80 Calc.: 56.7; 3.40; 4.73
(Ph ₄ P) ₃ [RhL ₃]	C ₈₄ H ₈₀ N ₆ P ₃ RhSe ₆	red		Found: ^b 55.8; 3.72; 4.84 Calc.: 55.6; 3.33; 4.64
[(Ph ₃ P) ₂ NiL]	C ₄₀ H ₃₀ N ₂ NiP ₂ Se ₂	reddish-brown	165–166	Found: 58.7; 3.87; 3.59 Calc.: 58.8; 3.78; 3.43
(Ph ₄ P) ₂ [NC–N=C(Se ₂) ₂ Ni]	C ₅₂ H ₄₀ N ₄ NiP ₂ Se ₂	red-brown	decomp.	Found: 52.9; 3.15; 4.90 Calc.: 53.9; 3.46; 4.84

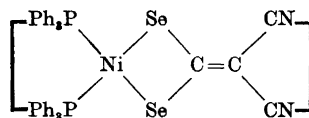
^a The compound contained excess selenium (ca. 28 % instead of 26 %) which could not be removed by recrystallization.

^b Crude products, which could not be recrystallized.

alkali metal salts of I or II, almost insoluble precipitates are formed. From analytical data it was concluded⁶ that the nickel compound might be a neutral complex derived from the monovalent anion of the diselenol. However, further studies of the insoluble products, by analyses and infrared spectra, have established that, in all cases, the addition of strong acid provokes complete decomposition of the diselenolates.



- I. $n = 2, z = 1$; M = Au(III)
 $n = z = 2$; M = Ni(II), Cu(II), Zn(II),
 Cd(II), Pt(II),
 $n = z = 3$; M = Cr(III), Co(III),
 Rh(III)
 II. $n = z = 2$; M = Ni(II)



III

Conductance measurements in dry acetone show that the gold complex is a 1:1 electrolyte, the complexes with divalent metals are 1:2 electrolytes, and the chromium, cobalt, and rhodium complexes 1:3 electrolytes, in agreement with the assigned formulae.

A neutral complex III was obtained from [NiCl₂(Ph₃P)₂] and (NC)₂C=C(SeK)₂.

Experimental. The conductivities of acetone solutions of the complexes were measured with a type CDM 2d conductivity meter from Radiometer, Copenhagen.

Dipotassium 2,2-dicyanoethylene-1,1-diselenolate and dipotassium cyanimidodiselenocarbonate were prepared by the method described by Jensen and Henriksen.⁴

The tetraphenylphosphonium salts of bis(2,2-dicyanoethylene-1,1-diselenolato) metallates were prepared in the following manner: A solution of 1 mmol of the appropriate metal salt ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, K_2PtCl_4 , NaAuCl_4 , etc.), in 10 ml of water, was added to a solution of the equivalent amount (2 or 3 mmol) of $(\text{NC})_2\text{C}=\text{C}(\text{SeK})_2$, also in 10 ml of water, and the mixture was heated to 50°C for a few minutes. The resulting dark solutions were filtered and a solution of the equivalent amount (2 or 3 mmol) of tetraphenylphosphonium chloride, in 10 ml of warm water, was added to the filtrate. A precipitate separated immediately; in all cases precipitation was quantitative (the filtrates were colourless). An almost black precipitate, which turned dark-brown on aeration, was formed from the solution of the cobalt complex prepared from cobalt(II) chloride. The precipitates were filtered off and washed with water.

The complexes of all the divalent metals and the gold complex could be recrystallized from acetone-water or acetone-methanol. They showed sharp melting points and (with the exception of the copper compound) gave satisfactory analyses (Table 1). The presumably octahedral complexes of chromium(III), cobalt(III), and rhodium(III), on the other hand, could not be purified by recrystallization; they had a tendency to separate as semi-solid masses and on repeated treatment with various solvents the products gave analyses which departed more and more from the theoretical values (lower carbon content and higher selenium content). At the same time the UV ligand band at 370 nm moved to higher wavelengths, possibly because of the formation of diselenides. However, according to their infrared and electronic spectra the crude products contained the unchanged ligand, so that the assigned formulæ seem quite plausible.

Tetraphenylphosphonium bis(cyanimidodiselenocarbonato)-nickelate(II) was prepared from potassium cyanimidodiselenocarbonate in the same manner as the 2,2-dicyanoethylene-1,1-diselenolates.

(2,2-Dicyanoethylene-1,1-diselenolato) bis-(triphenylphosphine)-nickel(II), $[\text{Ni}\{(\text{NC})_2\text{C}=\text{CSe}_2\}(\text{Ph}_3\text{P})_2]$. Dipotassium 2,2-dicyanoethylene-1,1-diselenolate (0.32 g) was added, with shaking, to a solution of $[(\text{Ph}_3\text{P})_2\text{NiBr}_2]$

(0.74 g) in dry acetone until the green colour of the latter had changed to red-brown. The solution was filtered and sufficient water added, slowly, to initiate precipitation; on cooling a reddish-brown crystalline precipitate was obtained.

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Organic Selenium Compounds

XI. Infrared and Electronic Spectra of Diselenolato Complexes

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The following is a discussion of the infrared and electronic spectra of the diselenolato complexes described in the preceding paper.

Infrared spectra. The prominent infrared bands of the ligands are those assigned to the CN group, the CSe_2 group, and the double bond (see Table 1). Only the last frequency is affected significantly by complex formation; in the case of the 2,2-dicyanoethylene-1,1-diselenolates this band is shifted by ca. 40 cm^{-1} towards higher frequencies for the nickel, copper, zinc, cadmium, and platinum complexes, and by 15 cm^{-1} for the chromium, cobalt, and rhodium complexes, reflecting the different coordination numbers. Contrary to the