

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 formulae 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

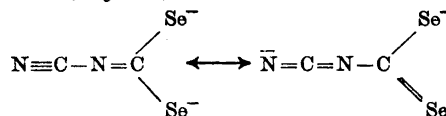
Table 1. Infrared and electronic spectra of diselenolates (wavenumbers in cm^{-1} ; $\log \epsilon$ in parenthesis).

Compound	Assignments						
	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{CSe}_2)$	$\delta(\text{CSe}_2)$	$\text{L}\rightarrow\text{L}^*$	$\text{M}\rightarrow\text{L}^*$	$d\rightarrow d$
$\text{L: (NC)}_2\text{C}=\text{C}(\text{Se}^-)_2$							
K_2L	2210vs 2195vs	1355vs	845s 830m	467m	27000 (4.1)		
$(\text{Ph}_4\text{P})_2[\text{NiL}_2]$	2200vs	1395vs	845m	440w	27200 (4.5)	21400 (3.8)	19600 (4.3)
$(\text{Ph}_4\text{P})_2[\text{CuL}_2]$	2190vs	1395vs	850m	440w	27400 (4.6)	23000 (3.8)	19200 (4.0)
$(\text{Ph}_4\text{P})[\text{AuL}_2]$	2200vs	1460vs	845m	445w	28000 (5.0)	21000 (3.0)	
$(\text{Ph}_4\text{P})_2[\text{ZnL}_2]$	2200vs	1400vs	838m	445w	28000 (4.7)		
$(\text{Ph}_4\text{P})_2[\text{CdL}_2]$	2200vs	1400vs	835m	448w	28000 (4.7)		
$(\text{Ph}_4\text{P})_2[\text{PtL}_2]$	2200vs	1395vs	847m	435w	27000 (4.1)	22600 (4.6)	20800sh (4.0)
$(\text{Ph}_4\text{P})_3[\text{CrL}_2]$	2200vs	1365vs	840m	435w	26200 (4.6)		
$(\text{Ph}_4\text{P})_3[\text{CoL}_2]$	2200vs	1370vs	848m	435w	27200 (4.5)	22100 (3.8)	14700sh (3.0)
$(\text{Ph}_4\text{P})_3[\text{RhL}_2]$	2195vs	1370vs	848m	435w	26200 (4.2)		
$(\text{Ph}_3\text{P})_2\text{NiL}$	2200vs	1400vs	845m	435vw	27000 (4.2)		19900 (3.3)
$\text{NC}-\text{N}=\text{C}(\text{SeK})_2$	2165vs	$\nu(\text{C}=\text{N})$ 1340vs	870s	435w			
$(\text{Ph}_4\text{P})_2[(\text{NC}-\text{N}=\text{CSe}_2)_2\text{Ni}]$	2160vs	1430vs	870m		27400 (4.1)	21700 (4.4)	20400sh (2.8)

case of the diselenocarbamates,¹ no difference in the frequency of this band was noted between the tetrahedral and planar tetracoordinated complexes with a divalent metal. For the gold complex the shift was as much as 105 cm^{-1} . The shift of the corresponding band in the series, alkali metal dithiolates < heavy metal dithiolates < *S*-alkyl derivatives, has been pointed out earlier by Jensen and Henriksen.² Fackler and Coucouvanis³ failed to recognize this shift in the case of 1,1-dithiolate complexes, because a strong band at 1320 cm^{-1} due to $(\text{NC})_2\text{C}=\text{C}(\text{SK})_2$, which moves to 1380 cm^{-1} in the spectrum of $[(\text{NC})_2\text{C}=\text{CS}_2]_2\text{Ni}[\text{K}]_2$, was omitted from their spectra.

In the cyanimidodiselenocarbonates and cyanimidodithiocarbonates the double bond frequency is increased by *ca.* 100 cm^{-1} on complex formation (or alkylation).

The unusually low double-bond frequency of the alkali metal diselenolates may be rationalized by formulating the anion as a resonance hybrid of a 1,1-diselenolate and a diselenocarboxylate anion, *e.g.*:



(and analogously for the dithiolates). The increase in the double-bond frequency on complex formation can then be said to be caused by a diminished contribution from the diselenocarboxylate structure, *cf.* the discussion of the infrared spectra of diselenocarbamate complexes¹ and alkyl derivatives of 1,1-diselenols⁴ and 1,1-

dithiols.³ The very large shift in the case of the gold complex, as compared to the complexes of divalent metals, is explained by the higher positive charge of the central atom, which will cause an increased drift of electrons towards the selenium atoms.

The position of the =CSe₂ stretching band of the ligand, near 850 cm⁻¹, appears to be almost unchanged in the spectra of the complexes. A ligand infrared band, at 467 cm⁻¹, is shifted towards lower frequencies in the spectra of the complexes, and is assigned to a deformation mode of the =CSe₂ group. The ligand further exhibits infrared bands near 1200 cm⁻¹ and 600 cm⁻¹. These bands, which are only weak in the spectra of the complexes, will be discussed elsewhere in another connection.⁴

Electronic spectra. The ligand (as the potassium or tetraphenylphosphonium salt) has an absorption maximum at 370 nm and the same maximum is found, with only small variations, in the spectra of the metal complexes. Whilst the zinc and cadmium complexes exhibit only this band, most of the transition metal complexes exhibit an additional band (Table 1) which, like the corresponding band of the 1,1-dithiolate complexes,⁵ is assigned to an M→L* intramolecular charge transfer. Finally, the lowest bands of the Ni(II), Pt(II), Cu(II), Co(III) complexes are assigned to spin-allowed *d-d* transitions.

Experimental. The infrared spectra (KBr discs) were recorded on a Perkin-Elmer model 337 grating spectrophotometer and the electronic spectra (acetone solutions) on a Perkin-Elmer model 137 ultraviolet-visible spectrophotometer.

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Phosphinodithioformates

III. *P,P*-Disubstituted Thiophosphinoylthioformamides

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During an investigation of some derivatives of phosphinodithioformic acid, R₂PCSSH, the aminolysis of esters of thiophosphinoylthioformic acid, R¹₂P(S)CSSR² (I), to give thiophosphinoylthioformamides, R¹₂P(S)CSNR³R⁴ (II), has been studied. Previously, such amides have been prepared from secondary phosphine sulfides and thiocyanic acid or isothiocyanates,¹ and by the reaction of secondary phosphines with isothiocyanates, followed by treatment with sulfur.² Both methods are limited to the preparation of unsubstituted or *N*-monosubstituted amides, in contrast to the method described here.

Esters of the type (I), R¹ = ethyl or phenyl, R² = methyl, ethyl or benzyl,³ reacted readily with ammonia and moderately sterically hindered primary aliphatic amines; for example, isopropylamine reacted readily in ether solution, whereas *tert*-butylamine reacted very slowly. No amides could be obtained from (I) and aromatic amines. In the case of secondary