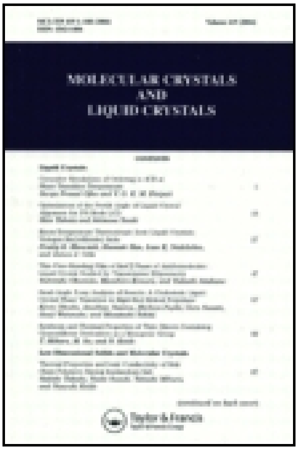

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“Organic Metals” - Charge Transfer Complexes and Radical-Ion Salts, from 4,4′-Biselenopyranylidenes

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"ORGANIC METALS" - CHARGE TRANSFER COMPLEXES AND RADICAL-ION SALTS, FROM 4,4'-BISELENOPYRANYLIDENES

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The synthesis and electrochemical data of new donors -4,4' biselenopyranylidenes- are described. The optical and electrical properties of complexes with TCNQ and DDQ are mentioned.

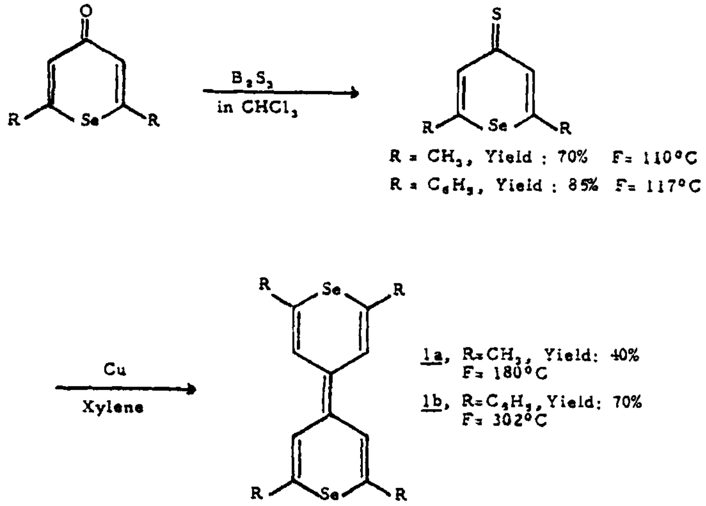
INTRODUCTION

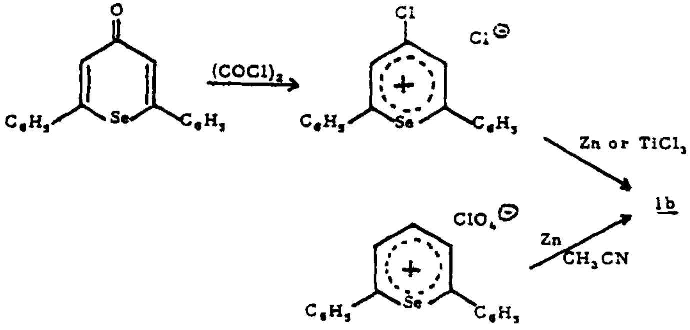
Charge transfer complexes which possess high conductivity include generally electron π donors whose aromaticity is increased by electron transfer [1]. Most of the organic metals actually known are obtained from heterocyclic sulfur compounds such as TTF. The substitution of sulfur atoms by selenium often leads to a higher conductivity [2] and recently superconductivity phenomenon has been found in such compounds [3].

The 4,4'-bithiopyranylidenes (BTP), are isoelectronic with TTF and some complexes with TCNQ have been isolated and possess a high conductivity [4-6]. We have studied now some new seleno-donors : the 4,4'-biselenopyranylidenes (BSeP).

SYNTHESIS OF BSeP

The synthesis[7] of BSeP has been achieved from selenopyranethiones [7,8] or selenopyrylium ions [9] following scheme :


O
R
Se
R
B_2S_3
in $CHCl_3$
S
R
Se
R
R = CH_3, Yield : 70% F= 110°C
R = C_6H_5, Yield : 85% F= 117°C
Cu
Xylene
R
Se
R
R
Se
R
1a, R=CH_3, Yield: 40% F= 180°C
1b, R=C_6H_5, Yield: 70% F= 302°C


O
C_6H_5
Se
C_6H_5
$(COCl)_2$
Cl
$Cl^{\ominus}$
+
C_6H_5
Se
C_6H_5
Zn or $TiCl_3$
1b
$ClO_4^{\ominus}$
+
C_6H_5
Se
C_6H_5
Zn
CH_3CN

IR spectra of selenopyranones exhibit $\nu c{=}o$ vibrations in KBr at 1625 cm^{-1} ($R{=}CH_3$) and 1585cm^{-1} ($R{=}C_6H_5$). These absorptions do not exist in the corresponding sulfur compounds which show absorptions at 1070cm^{-1}($R{=}CH_3$) and 1075cm^{-1}($R{=}C_6H_5$) ($\nu c{=}s$).

ELECTROCHEMISTRY

Electrochemical measurements have been performed in dimethylformamide (DMF) (10^{-4}M) with platinum electrodes p-toluene tetraethylammonium sulfonate is used as electrolyte (0.1M).

The 4,4'-bi(2,6-diphenylselenopyranylidene) 1b shows, on rotating electrode, only one oxydation wave ($E_{1/2}$= 0.35V vs SCE). The limit current i_l is proportional to the concentration C and to the square root of the electrode rotation rate ω, showing that the oxydation process is fast and simple. With the same stationary electrode and for a potential situated on the level of the polarographic wave (E=0.55V), the variation of the current is linear in inverse ratio to the square root of the time (t). The slopes of the curves : $i_l = f(\sqrt{\omega})$ and $i = f(1/\sqrt{t})$ show that the chemical process is equivalent to two electrons in only one step. We observe only one polarographic wave, only one a.c. polarographic peak ($E_{1/2}$= 0.34V vs SCE) and one oxydation wave (0.42V) and one reduction wave (0.27V) in cyclic voltametry. Logarithmic analysis of the polarographic wave is in agreement with the study of I. Ruzic [10] for two closely spaced processes :

$$D \rightleftharpoons D^{+\cdot} + e^- \qquad E_1^0$$
$$D^{\cdot +} \rightleftharpoons D^{2+} + e^- \qquad E_2^0$$

If the diffusion of the three species are equivalent :

$$\frac{i_l - i}{i} = \frac{2 + f_1}{f_1(1+2f_2)} \qquad f_1 = \exp\,(E - E_1^0)\frac{F}{RT}$$

$$f_2 = \exp\,(E - E_2^0)\frac{F}{RT}$$

The half-wave potential ($E_{1/2}$= 0.344V) and the curve slope graphic determinations at this point [Log $i_l - i/i = f(E)$] give the values of the standard potential of each step :

E_1^0= 0.306V $\qquad$ E_2^0 = 0.382V

The difference $\Delta E^0 = E_2^0 - E_1^0$ = 0.076V is too small to separate the adjacent steps. The observed value (0.34V) corresponds to the potentials half-sum E_1^0 and E_2^0, for instance to the potential of :

$$2D \rightleftharpoons D^{2+} + 2e^-$$

There is an equilibrium between the different species :

$$D + D^{2+} \rightleftharpoons 2D^+$$

The disproportionation constant is in relation with the potentials E_1^0 and E_2^0

$$E_1^0 - E_2^0 = \frac{RT}{F} \text{ Log } K \qquad K = 16.6$$

This value is much smaller than the value of other donors $BSPPh_4$: $K = 3.8 \times 10^2$ - TTF : $K = 5.8 \times 10^5$.

However, it appears that a small value of ΔE must be a positive datum to lead to an "organic metal" [11].

CHARGE TRANSFERT COMPLEXES

The biselenopyranylidenes 1 give with TCNQ and DDQ (2,3-dichloro-5,6-dicyano p-benzoquinone), in 1,2,4-trichlorobenzene, complexes of 1:1 stoicheoimetry.

$BSePPh_4$ + TCNQ ⟶ $BSePPh_4$ - TCNQ 2b
F=270°C Yield: 70%

$BSePMe_4$ + DDQ ⟶ $BSePMe_4$ - DDQ 3a
F=350°C Yield: 50%

$BSePPh_4$ + DDQ ⟶ $BSePPh_4$ - DDQ 3b
F=152°C Yield: 65%

The complexes are obtained by slow precipitation of a warm solution of trichlorobenzene as microcrystalline black powder. The conductivities are determined on compacted powder ($P \simeq 4T/cm^2$).

2b $\sigma = 0,5\ \Omega^{-1}cm^{-1}$
3a $\sigma = 4,3 \times 10^{-8}\ \Omega^{-1}cm^{-1}$
3b $\sigma = 8 \times 10^{-3}\ \Omega^{-1}cm^{-1}$

RADICAL-ION SALTS

Oxydation of $BSePPh_4$ 1b by iodine leads to a non-stoicheiometric salt :

4 $BSePPh_4$ - 3.14 I F=208°C $\sigma = 3.6 \times 10^{-2}\ \Omega^{-1} cm^{-1}$

This salt 4 is isolated as shiny black crystals by slow cooling of a trichlorobenzene solution from 100°C with a concentration ratio $BSePPh_4/I_2 = 0.7$. With a ratio of 0.2 a salt $BSePPh_4$-$3I_2$ is isolated with a smaller conductivity.

OPTICAL SPECTRA

Optical spectra have been recorded between 40,000-4,000 cm^{-1} by relative diffuse reflectance (R_{∞}) with compounds in KBr disks. The transformation of the diffuse reflectance by the means of Kubelka fonction [12] gives sample absorbance. In IR range, spectra are directly recorded in absorbance on disks made by pressing a mixture of powdered KBr and the desired compound.

The optical spectrum of 2b is similar to spectra of bi-(2,6-diphenylthiopyranylidene)-TCNQ [6] and TTF-TCNQ [13]. Effectively, one absorption peak situated at 27,000cm^{-1} corresponds to a peak at 26,000cm^{-1} for $BSePPh_4$-TCNQ[6] probably due to an electronic transition in TCNQ. Another absorption situated at 11,000-13,000cm^{-1} similar to absorptions in TTF-TCNQ and $BTPPh_4$-TCNQ, near 11,000cm^{-1}, is attributed to intramolecular transitions in $TCNQ^{\bullet -}$ [6]. One absorption is located near 2,500cm^{-1} and ascribed to intermolecular charge transfer transition from $TCNQ^{\bullet -}$ to $TCNQ^{0}$ and very characteristic of organic conductors [13]. *On the spectrum of* 2b one absorption near 8,000cm^{-1} corresponds approximatively to a plasma frequency.

For $BSePPh_4$-DDQ we note a peak near 14,000cm^{-1} due to DDQ, another band near 19,000cm^{-1} relative to an intramolecular transition of the donor. Peaks at 27,500cm^{-1} and 35,500cm^{-1} correspond to intramolecular transitions of the acceptor (cf. figure 2). About 3,000cm^{-1} no absorption peak is observed because 3b is not an organic metal but rather a semi-conductor.

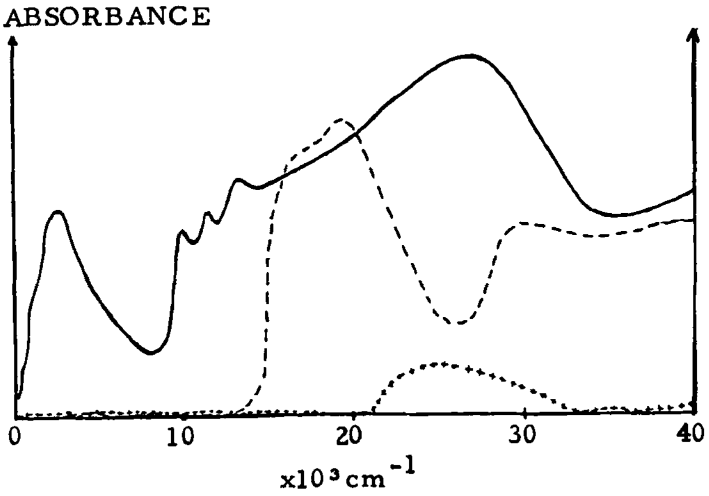


FIGURE 1 Powder absorption spectra of $BSePPh_4$ - TCNQ (—), $BSePPh_4$ (---), TCNQ (+++)

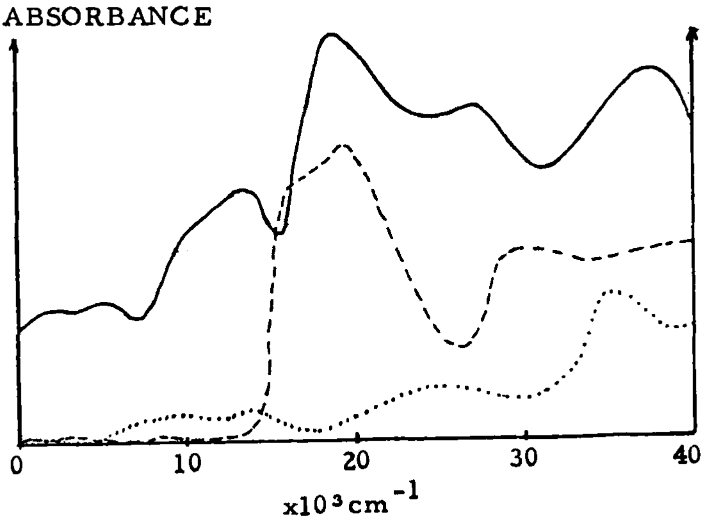


FIGURE 2 Powder absorption spectra of $BSePPh_4$ - DDQ (—), $BSePPh_4$ (---), DDQ (. . .)

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