X-Ray Molecular Structures of $[Zn(C_3Se_5)_2]^{2-}$ and $[Zn(CSe_4)_2]^{2-}$ Anion Complexes†

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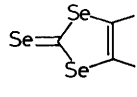
The salts $[PPh_4]_2[Zn(C_3Se_5)_2]$ (**1**) and $[PPh_4]_2[Zn(CSe_4)_2]$ (**2**) were isolated from a solution of carbon diselenide with sodium metal in the presence of zinc(II) chloride and $[PPh_4]Br$ in dimethyl sulphoxide or in $MeOCH_2CH_2OCH_2CH_2OMe$. Single-crystal *X*-ray structure analyses were performed for these complexes: (**1**)·MeCN, triclinic, space group $P\bar{1}$, $a = 17.402(3)$, $b = 19.353(4)$, $c = 9.774(4)$ Å, $\alpha = 99.59(3)$, $\beta = 98.37(3)$, $\gamma = 65.51(2)°$, and $Z = 2$; (**2**) monoclinic, space group $P2_1/n$, $a = 21.586(2)$, $b = 24.136(2)$, $c = 10.208\,4(7)$ Å, $\beta = 104.87(7)°$, and $Z = 4$. The structure refinements converged to $R = 0.060$ and 0.072 for (**1**) and (**2**), respectively. Both complexes assume a tetrahedral geometry around the metal atom, the ligands being almost planar. Electronic absorption and ^{77}Se n.m.r. spectra of the complexes were measured.

In recent years, planar metal (Ni, Pd, and Pt) complexes with the 4,5-dimercapto-1,3-dithiole-2-thionate ligand $(C_3S_5^{2-})$ have attracted much interest since they exhibit high electrical conductivities owing to molecular interactions through sulphur–sulphur contacts.[1] Of these complexes, $[ttf][Ni(C_3S_5)_2]_2$ [ttf = tetrathiafulvalene, 2-(1′,3′-dithiol-2′-ylidene)-1,3-dithiole],[2] $[NMe_4][Ni(C_3S_5)_2]_2$,[3] and $[ttf][Pd(C_3S_5)_2]_2$[4] were reported to be superconductors. Since selenium has more diffuse and spatially extended *p* and *d* orbitals than sulphur, ligands having many selenium atoms should enable more effective molecular interactions with a multidimensional character. Thus, metal complexes with the selenium analogue of the $C_3S_5^{2-}$ ligand are reasonably expected to show extended electrical conducting properties.

Previously Engler *et al.*[5] reported that carbon diselenide is reduced electrochemically to give $C_3Se_5^{2-}$, which was characterized only as the dimethyl derivative, $C_3Se_5Me_2$. Using the 4,5-di(hydroseleno)-1,3-diselenole-2-selonate ligand (**A**) prepared by the electrochemical reduction of carbon diselenide, some metal complexes were isolated.[6] Only a few syntheses of 1,2-diselenolate ligands by methods other than the electrochemical one have been reported.[7]



(**A**)

This paper reports preparations of $[PPh_4]_2[Zn(C_3Se_5)_2]$ and $[PPh_4]_2[Zn(CSe_4)_2]$ by a reaction of carbon diselenide with sodium metal in organic solvents. The former is a starting compound for various electrically conducting metal complexes. The crystal structures of $[PPh_4]_2[Zn(C_3Se_5)_2]$·MeCN and $[PPh_4]_2[Zn(CSe_4)_2]$ are described, together with electronic absorption and ^{77}Se n.m.r. spectra.

Experimental

Preparation of $[PPh_4]_2[Zn(C_3Se_5)_2]$ (**1**).—Carbon diselenide[8] (7.9 g, 46 mmol) was added to a $MeOCH_2CH_2OCH_2CH_2OMe$ (70 cm^3) suspension of sodium metal (1.5 g, 66 mmol) under a nitrogen atmosphere at room temperature. The solution gradually turned red and was stirred for 24 h, followed by addition of methanol (100 cm^3). The unreacted sodium metal was dissolved, the solution turning blue. Solvents were removed under reduced pressure at 65 °C. To the residue was added a concentrated aqueous ammonia solution (60 cm^3) containing zinc chloride (4.6 g, 34 mmol), followed by addition of tetraphenylphosphonium bromide (4.5 g, 11 mmol) in ethanol (30 cm^3). On addition of ethanol–water (1:1 v/v, 45 cm^3) blue-purple microcrystals precipitated, which were collected by filtration and washed with ethanol. Recrystallization from acetone–isopropyl alcohol afforded purple cubic crystals of $[PPh_4]_2[Zn(C_3Se_5)_2]$ (**1**) (15% yield) (Found: C, 40.65; H, 2.8. Calc. for $C_{54}H_{40}P_2Se_{10}Zn$: C, 40.4; H, 2.5%). For the *X*-ray analysis of this complex, recrystallization from acetonitrile gave purple plates of $[PPh_4]_2[Zn(C_3Se_5)_2]$·MeCN (Found: C, 40.7; H, 2.7; N, 0.8. Calc. for $C_{56}H_{43}NP_2Se_{10}Zn$: C, 40.85; H, 2.65; N, 0.85%).

Preparation of $[PPh_4]_2[Zn(CSe_4)_2]$ (**2**).—To a dimethyl sulphoxide (20 cm^3) suspension of sodium metal (0.90 g, 40 mmol) was added carbon diselenide (5.2 g, 30 mmol) under a nitrogen atmosphere at room temperature, and the solution was stirred for 8 h. Methanol (30 cm^3) was added to the solution to dissolve unreacted sodium metal, and the solvents were removed under reduced pressure at 65 °C. To the residue was added a concentrated aqueous ammonia solution (60 cm^3) containing zinc chloride (3.0 g, 22 mmol), followed by addition of tetraphenylphosphonium bromide (4.5 g, 11 mmol). On addition of ethanol–water (1:1 v/v, 50 cm^3) red microcrystals precipitated, which were collected by filtration and washed with ethanol. Recrystallization from acetone–isopropyl alcohol afforded red plates of $[PPh_4]_2[Zn(CSe_4)_2]$ (**2**) (13% yield) (Found: C, 42.3; H, 2.85. Calc. for $C_{50}H_{40}P_2Se_8Zn$: C, 42.9; H, 2.9%).

Complex (**1**) was also obtained by the reaction in dimethyl sulphoxide although in a poor yield (2%). Furthermore, a very

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† Bis(tetraphenylphosphonium) bis[4,5-di(hydroseleno)-1,3-diselenole-2-selenonato-*Se*^{4}*Se*^{5}]zincate and bis(triselenoperoxocarbonato-*SeSe*)-zincate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Experimental data and structure refinement details[a]

Complex	(1)	(2)
Formula	$C_{56}H_{43}NP_2Se_{10}Zn$	$C_{50}H_{40}P_2Se_8Zn$
M	1 646.9	1 400.2
Crystal size/mm	0.12 × 0.37 × 0.56	0.03 × 0.09 × 0.31
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	17.402(3)	21.586(2)
b/Å	19.353(4)	24.136(2)
c/Å	9.774(4)	10.2084(7)
α/°	99.59(3)	90
β/°	98.37(3)	104.87(7)
γ/°	65.51(2)	90
U/Å^3	2 943(1)	5 140.6(7)
Z	2	4
D_c/g cm^{-3}	1.859(1)	1.809(1)
F(000)	1 572.0	2 688.0
μ(Cu-K_α)/cm^{-1}	94.7	88.6
Scan interval/° min^{-1}	1.0 + 0.15 tan θ	0.7 + 0.15 tan θ
Prescan speed/° min^{-1}	8	8
Collected octants	$\pm h, \pm k, l$	$-h, k, \pm l$
No. of data collected at room temperature	9 512	8 448
No. of independent data with $\lvert F_o \rvert > 3\sigma(F)$	6 767	5 166
Absorption correction range[b]	1.00—0.38	1.00—0.53
R	0.060	0.072
R'[c]	0.075	0.080

[a] Radiation Cu-K_α (λ = 1.5418 Å); Rigaku AFC-5 diffractometer; scan range $2.5 < \theta < 62.5°$ [b] A. C. T. North, D. C. Phillips, and F. C. Matheus, *Acta Crystallogr., Sect. A*, 1968, **24**, 351. [c] $[\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/\Sigma w \lvert F_o \rvert^2]^{\frac{1}{2}}$, where $1/w = \sigma^2(F_o) + 0.0005\,(F_o)^2$.

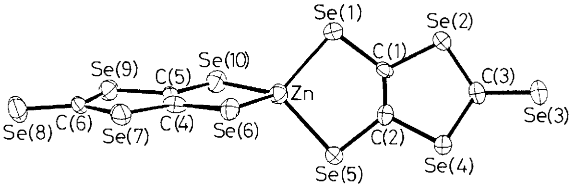


Figure 1. The molecular structure of the anion of $[PPh_4]_2[Zn(C_3Se_5)_2]\cdot$MeCN (**1**) with the atom-labelling scheme

small amount of the $HCSe_3^-$ species was also afforded and isolated as $[PPh_4][HCSe_3]$, as confirmed from the observation of ν(Se–H) at 2 050 cm^{-1} in the i.r. spectrum and the *X*-ray crystal structure determination.[9]

X-*Ray Crystal Structure Determination of* $[PPh_4]_2[Zn(C_3Se_5)_2]\cdot$MeCN (**1**) *and* $[PPh_4]_2[Zn(CSe_4)_2]$ (**2**).—Crystal data and details of the measurements are listed in Table 1. The unit-cell parameters were determined from 25 independent reflections having $35 < 2\theta < 66°$ and $34 < 2\theta < 51°$ for (**1**) and (**2**), respectively.

The structures of both complexes were solved according to the direct (MULTAN) method.[10] Subsequent Fourier maps showed the positions of all the non-hydrogen atoms, which were refined anisotropically by the block-diagonal least-squares procedure. Atomic scattering factors used in the refinement were taken from ref. 11. Atomic positional parameters are shown in Tables 2 and 3.

Crystallographic calculations were performed using the programs of Professor K. Nakatsu, Kwansei Gakuin University, on an ACOS 900S computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Spectral Measurements.—Selenium-77 n.m.r. spectra of the complexes were recorded on a JEOL JNM-GSX-450 spectrometer at 76.10 MHz in $[^2H_6]$ dimethyl sulphoxide. The chemical shifts were measured relative to dimethyl selenide in $[^2H_1]$chloroform as an external standard. The conditions were as follows: pulse 45°, relaxation delay 2 s, digital resolution 6 Hz, and 600—26 000 scans accumulated for a 4.0% (w/w) solution.

Electronic absorption spectra were recorded as described elsewhere.[12]

Results and Discussion

Description of the Structure of $[PPh_4]_2[Zn(C_3Se_5)_2]\cdot$MeCN (**1**).—The molecular structure of the $[Zn(C_3Se_5)_2]^{2-}$ anion is shown in Figure 1, together with the atom-labelling scheme. Bond distances and angles of the anion are summarized in Table 4. There are no unusual intermolecular atom–atom contacts in the crystal phase. Four selenium atoms are co-ordinated to the zinc atom forming a tetrahedral geometry. Since this is the first structure determination of a bis(1,2-diselenolato)zinc(II) complex no comparative Zn–Se bond distances and angles are available. The Zn–Se distances (2.436—2.456 Å) are close to those [2.435(4) and 2.446(4) Å] of bis(*N,N*-diethylselenocarbamato)zinc(II) although this is a neutral complex with unidentate Se_2 ligands and contains somewhat longer Zn–Se bonds [2.568(4) and 3.033(4) Å].[13] The Zn–Se distances are longer than those of bis(1,2-dithiolato)zinc(II) anions and the Se–Zn–Se bite angle [96.5(1)°] is slightly larger than those of the dithiolato-complexes: $[AsPh_4]_2[Zn(mnt)_2]$ [mnt = 1,2-dicyanoethylene-1,2-dithiolate(2−)] (Zn–S 2.320—2.340 Å, S–Zn–S, 93.2 and 94.2°)[14] and the corresponding 1,1′-dimethyl-4,4′-bipyridinium salt (2.319 and 2.358 Å, 93.4—94.6°).[15] This difference comes from a larger atomic covalent radius of selenium (1.17 Å) than sulphur (1.04 Å).[16] The average Zn–Se (1,5,6, and 10) and Se–C [Se(1)–C(1), Se(5)–C(2), Se(6)–C(4), and Se(10)–C(5)] distances of the present complex are 2.443 and 1.890 Å, respectively, while the average Zn–S and S–C distances in the above dithiolatozinc(II) complexes are 2.333 and 1.737 Å, respectively. The difference (0.110 Å) between the average Zn–Se and Zn–S distances is smaller than that (0.153 Å) between the average Se–C and S–C distances, indicating that the Zn–Se bonds are of somewhat higher order than the Zn–S.

All the atoms of the $C_3Se_5^{2-}$ ligands are almost planar (±0.039 and ±0.007 Å), the metal atom deviating by 0.150 and 0.073 Å from the C_3Se_5 planes constructed from Se(1)–Se(5) and C(1)–C(3) and from Se(6)–Se(10) and C(4)–C(6), respectively. Such a deviation was also observed for $C_3S_5^{2-}$ complexes, such as $[C_5H_5NEt]_2[Cu(C_3S_5)_2]$[17] and the bis(*N*-methylphenazinium)salt of $[V(C_3S_5)_3]^{2-}$.[18] The C(1)–C(2) [1.299(11) Å] and C(4)–C(5) distances [1.335(16) Å] are close to the corresponding C–C distances of the $C_3S_5^{2-}$ ligand observed for the above two complexes [1.357(14)[17] and 1.335(7), 1.354(7), and 1.347(7) Å[18]].

The C(3)–Se(3) [1.823(12) Å] and C(6)–Se(8) distances [1.818(11) Å] are somewhat shorter than those of C(3)–Se(2,4) and C(6)–Se(7,9) (1.833—1.856 Å), indicating some remaining double-bond character in these two terminal C–Se bonds. The sum of the covalent bond radii for selenium and carbon is 1.94 Å for a single bond and 1.74 Å for a double bond.[16] The lengths of the terminal Se–C bonds in the present complex are intermediate between these limits, suggesting delocalization of electrons in the CSe_3 moieties. The terminal Se–C bond distances are close to those of partial Se–C double bonds observed for *N*-benzoyl-*N*′-phenylselenourea [1.82(1) Å][19] and 6,7-dihydro-6,6-dimethyl-5*H*-2,3-dioxa-2aλ^4-selena-1,4-diazacyclopent[*cd*]indene [1.802(11) Å].[20]

Table 2. Fractional atomic co-ordinates for $[PPh_4]_2[Zn(C_3Se_5)_2]{\cdot}MeCN$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	Atom	x	y	z
Zn	0.231 94(8)	0.283 99(7)	0.592 8(1)	C(23)	0.799 0(7)	0.060 5(7)	0.164 7(14)
Se(1)	0.159 91(7)	0.421 52(6)	0.584 8(1)	C(24)	0.718 6(7)	0.082 4(6)	0.222 1(13)
Se(2)	0.231 69(7)	0.547 81(6)	0.717 8(1)	C(25)	0.619 7(6)	0.170 4(5)	0.609 1(8)
Se(3)	0.371 22(8)	0.611 28(7)	0.869 2(1)	C(26)	0.612 8(7)	0.243 3(6)	0.662 0(12)
Se(4)	0.399 96(7)	0.433 47(6)	0.842 4(1)	C(27)	0.629 0(7)	0.259 9(6)	0.806 6(12)
Se(5)	0.356 13(7)	0.287 01(6)	0.745 2(1)	C(28)	0.652 4(7)	0.203 8(7)	0.895 7(11)
Se(6)	0.246 96(7)	0.215 79(6)	0.357 7(1)	C(29)	0.657 9(7)	0.130 4(6)	0.836 9(12)
Se(7)	0.183 20(8)	0.083 93(7)	0.231 5(2)	C(30)	0.641 8(6)	0.113 8(6)	0.695 3(10)
Se(8)	0.100 5(1)	−0.036 79(8)	0.227 4(2)	C(31)	0.135 1(6)	0.544 0(6)	0.160 2(12)
Se(9)	0.116 55(7)	0.078 46(7)	0.503 4(2)	C(32)	0.165 2(7)	0.476 4(6)	0.224 3(14)
Se(10)	0.166 97(7)	0.211 52(6)	0.678 9(1)	C(33)	0.160 3(8)	0.410 3(7)	0.140 6(16)
P(1)	0.608 0(2)	0.147 8(1)	0.423 8(3)	C(34)	0.129 4(9)	0.415 0(8)	0.001 3(16)
P(2)	0.148 8(2)	0.625 9(2)	0.263 2(3)	C(35)	0.099 8(10)	0.482 6(8)	−0.058 4(15)
C(1)	0.250 9(6)	0.442 4(5)	0.691 7(10)	C(36)	0.102 9(8)	0.547 3(7)	0.022 5(12)
C(2)	0.320 4(5)	0.393 9(5)	0.748 7(10)	C(37)	0.110 3(6)	0.705 8(5)	0.161 2(11)
C(3)	0.335 5(6)	0.534 2(5)	0.810 5(8)	C(38)	0.024 4(7)	0.753 3(7)	0.160 6(13)
C(4)	0.195 6(6)	0.152 4(5)	0.383 3(9)	C(39)	−0.008 1(8)	0.813 1(7)	0.078 4(14)
C(5)	0.166 8(5)	0.150 5(5)	0.501 5(13)	C(40)	0.047 7(9)	0.824 7(7)	0.001 5(12)
C(6)	0.130 6(6)	0.039 3(5)	0.318 9(12)	C(41)	0.131 3(7)	0.777 0(7)	0.007 2(14)
C(7)	0.575 1(5)	0.069 7(5)	0.382 1(10)	C(42)	0.163 7(7)	0.716 6(6)	0.083 9(13)
C(8)	0.489 3(6)	0.085 3(5)	0.351 0(10)	C(43)	0.260 0(6)	0.598 1(5)	0.309 9(10)
C(9)	0.465 2(6)	0.023 2(6)	0.320 4(11)	C(44)	0.291 5(7)	0.618 3(6)	0.439 1(10)
C(10)	0.526 1(6)	−0.052 9(6)	0.318 0(10)	C(45)	0.381 1(6)	0.595 4(6)	0.468 4(12)
C(11)	0.610 1(7)	−0.064 6(5)	0.352 6(11)	C(46)	0.434 6(7)	0.553 5(6)	0.365 1(11)
C(12)	0.636 1(6)	−0.004 3(5)	0.382 4(11)	C(47)	0.402 9(7)	0.533 8(6)	0.237 6(14)
C(13)	0.528 7(6)	0.229 5(5)	0.346 3(10)	C(48)	0.315 9(6)	0.554 8(6)	0.206 0(12)
C(14)	0.456 8(7)	0.274 4(6)	0.416 8(12)	C(49)	0.091 3(6)	0.655 4(5)	0.416 5(10)
C(15)	0.390 5(8)	0.332 8(6)	0.352 7(14)	C(50)	0.050 6(6)	0.612 5(6)	0.451 9(10)
C(16)	0.397 2(8)	0.346 6(7)	0.223 1(16)	C(51)	0.006 9(6)	0.639 7(6)	0.574 5(10)
C(17)	0.468 6(8)	0.302 5(7)	0.156 8(14)	C(52)	0.006 2(6)	0.705 7(6)	0.659 0(11)
C(18)	0.535 5(7)	0.242 7(7)	0.218 5(12)	C(53)	0.047 4(7)	0.746 9(6)	0.619 4(12)
C(19)	0.707 9(6)	0.120 4(5)	0.357 6(9)	C(54)	0.090 6(7)	0.721 3(6)	0.497 4(11)
C(20)	0.773 7(6)	0.133 2(6)	0.440 4(14)	N	0.370 4(15)	0.014 6(13)	−0.006 5(18)
C(21)	0.854 1(7)	0.108 5(7)	0.383 7(15)	C(55)	0.358 5(14)	0.086 9(11)	0.005 9(17)
C(22)	0.862 3(7)	0.073 7(7)	0.244 1(16)	C(56)	0.365 2(15)	0.153 5(10)	0.007 7(18)

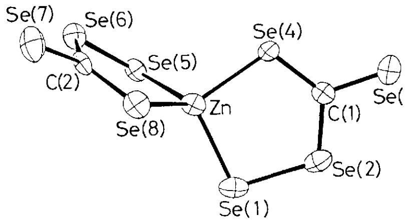
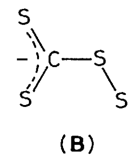


Figure 2. The molecular structure of the anion of $[PPh_4]_2[Zn(CSe_4)_2]$ (**2**) with the atom-labelling scheme

Description of the Structure of $[PPh_4]_2[Zn(CSe_4)_2]$ (**2**).—The molecular structure of the $[Zn(CSe_4)_2]^{2-}$ anion is illustrated in Figure 2, together with the atom-labelling scheme. Bond distances and angles of the anion are listed in Table 5. This complex also has no appreciable intermolecular atom–atom contacts in the crystal phase. The zinc atom is ligated by four selenium atoms forming a tetrahedral geometry, as described for complex (**1**). The average Zn–Se distance [2.445(4) Å] is close to that of complex (**1**). Owing to the five-membered ring including three selenium atoms the Se–Zn–Se bite angles [100.0(1), 100.5(1)°] are larger than that [96.5(1)°] of complex (**1**) having the Zn–Se–C–C–Se ring. The Se–Se distances [2.320(2) and 2.337(3) Å] are very close to those of elemental selenium [average 2.334(5) Å][21] and of other organoselenium compounds such as bis(pentafluorophenyl)diselenide [2.319(4) Å][22] and dimorpholino- and dipiperidino-tetraselane 2.327—2.356 Å.[23] The CSe_4^{2-} anion moieties are essentially planar (±0.045 and ±0.051 Å), the selenium atom deviating from these planes by 0.273 and 0.426 Å, as described for complex (**1**). No metal complexes with the CSe_4^{2-} ligand have been reported. However, the geometry around the metal may be compared with that of bis(trithioperoxybenzoato)zinc(II) which contains a Zn–S–C–S–S five-membered chelate ring.[24,25] In this complex, the chelate ring including the metal atom is almost planar (±0.03 Å), in contrast to the appreciable deviation of the zinc atom from the CSe_4 ligand plane in the present complex. The structure of K_2CS_4[26] may be compared with the geometry of (**2**). The C(1)–Se(3) [1.825(13) Å] and C(2)–Se(7) bonds [1.804(14) Å] are appreciably shorter than the C(1)–Se(2,4) and C(2)–Se(6,8) bonds (1.843—1.863 Å), indicating some double-bond character. In K_2CS_4 the contribution of the electronic structure (**B**) is suggested to be important since two terminal C–S bond distances are quite similar. In this salt, the potassium ions are not located in the regions of the sulphur atoms, and the geometry of the CS_4 moiety is considered essentially to be that of the free CS_4^{2-} anion. Thus, the remarkable difference in the C–Se and C–S bond characters between the selenium and sulphur analogues seems to come from the metal co-ordination.



(**B**)

Table 3. Fractional atomic co-ordinates for $[\mathrm{PPh_4}]_2[\mathrm{Zn(CSe_4)_2}]$ (**2**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zn	0.614 33(8)	0.246 68(8)	0.266 8(2)	C(21)	0.312 2(7)	0.051 3(5)	0.174 4(13)
Se(1)	0.713 52(7)	0.299 80(8)	0.320 1(2)	C(22)	0.372 8(7)	0.027 8(6)	0.218 8(16)
Se(2)	0.672 45(8)	0.384 60(8)	0.226 0(2)	C(23)	0.392 8(9)	−0.011 1(8)	0.133 7(19)
Se(3)	0.547 6(1)	0.449 56(7)	0.118 7(2)	C(24)	0.348 1(8)	−0.026 1(6)	0.011 1(16)
Se(4)	0.535 37(7)	0.321 44(7)	0.193 9(2)	C(25)	0.287 7(8)	−0.000 5(7)	0.034 5(18)
Se(5)	0.599 05(7)	0.169 38(6)	0.107 8(1)	C(26)	0.269 0(7)	0.038 6(6)	0.051 6(15)
Se(6)	0.549 88(8)	0.108 08(7)	0.224 4(2)	C(27)	0.403 1(5)	0.295 6(5)	0.676 3(12)
Se(7)	0.532 2(1)	0.083 21(9)	0.506 3(2)	C(28)	0.412 7(6)	0.260 8(6)	0.572 3(13)
Se(8)	0.600 16(9)	0.198 91(8)	0.468 0(2)	C(29)	0.456 4(7)	0.217 4(6)	0.606 7(14)
P(1)	0.289 1(2)	0.105 9(1)	0.273 9(3)	C(30)	0.490 1(7)	0.208 2(7)	0.742 2(17)
P(2)	0.347 6(2)	0.352 6(1)	0.627 4(3)	C(31)	0.477 7(7)	0.242 6(7)	0.841 4(16)
C(1)	0.583 7(6)	0.383 7(6)	0.185 8(12)	C(32)	0.435 9(6)	0.287 8(6)	0.811 5(14)
C(2)	0.562 3(6)	0.131 8(5)	0.403 1(12)	C(33)	0.382 2(6)	0.405 0(5)	0.542 1(12)
C(3)	0.204 4(6)	0.113 9(5)	0.241 0(12)	C(34)	0.410 7(7)	0.388 2(6)	0.439 1(14)
C(4)	0.169 6(6)	0.137 3(5)	0.120 0(12)	C(35)	0.436 2(8)	0.428 1(6)	0.365 5(14)
C(5)	0.103 6(6)	0.147 7(6)	0.100 7(13)	C(36)	0.429 8(7)	0.482 0(7)	0.393 3(14)
C(6)	0.072 8(7)	0.133 7(7)	0.200 6(15)	C(37)	0.404 0(7)	0.498 7(7)	0.494 4(18)
C(7)	0.106 9(7)	0.109 7(6)	0.320 8(15)	C(38)	0.377 7(7)	0.459 5(6)	0.571 2(14)
C(8)	0.175 2(7)	0.098 3(5)	0.346 8(14)	C(39)	0.327 7(6)	0.380 9(5)	0.773 2(11)
C(9)	0.322 4(6)	0.170 8(6)	0.230 8(12)	C(40)	0.377 6(7)	0.410 3(6)	0.870 2(12)
C(10)	0.287 5(6)	0.220 2(5)	0.215 0(12)	C(41)	0.361 7(8)	0.428 5(6)	0.991 4(15)
C(11)	0.313 4(6)	0.267 5(5)	0.176 0(13)	C(42)	0.301 1(7)	0.421 5(6)	1.009 3(13)
C(12)	0.373 0(7)	0.266 9(6)	0.156 9(15)	C(43)	0.255 0(7)	0.391 7(6)	0.913 1(14)
C(13)	0.409 4(8)	0.218 7(7)	0.173 7(20)	C(44)	0.268 3(6)	0.373 7(6)	0.793 9(13)
C(14)	0.383 6(6)	0.167 9(7)	0.205 6(17)	C(45)	0.276 5(5)	0.326 8(5)	0.512 8(11)
C(15)	0.320 3(6)	0.091 6(5)	0.452 2(13)	C(46)	0.252 9(6)	0.275 4(6)	0.540 6(12)
C(16)	0.326 9(7)	0.136 2(6)	0.538 1(13)	C(47)	0.195 6(6)	0.255 2(6)	0.454 1(13)
C(17)	0.347 1(7)	0.126 6(7)	0.678 1(15)	C(48)	0.163 6(6)	0.286 6(7)	0.341 9(13)
C(18)	0.362 2(8)	0.075 6(8)	0.727 1(15)	C(49)	0.186 3(7)	0.337 9(6)	0.316 6(12)
C(19)	0.354 9(9)	0.027 5(8)	0.642 1(17)	C(50)	0.245 0(6)	0.359 3(6)	0.402 8(12)
C(20)	0.331 2(9)	0.036 8(7)	0.497 4(16)				

Table 4. Selected bond distances (Å) and angles (°) of $[\mathrm{PPh_4}]_2[\mathrm{Zn(C_3Se_5)_2}]\cdot\mathrm{MeCN}$ (**1**)

Zn–Se(1)	2.436(2)	Zn–Se(5)	2.456(2)
Zn–Se(6)	2.443(2)	Zn–Se(10)	2.437(2)
Se(1)–C(1)	1.916(11)	Se(2)–C(1)	1.905(10)
Se(2)–C(3)	1.833(10)	Se(3)–C(3)	1.823(12)
Se(4)–C(2)	1.903(10)	Se(4)–C(3)	1.855(9)
Se(5)–C(2)	1.893(9)	Se(6)–C(4)	1.856(12)
Se(7)–C(4)	1.869(9)	Se(7)–C(6)	1.856(13)
Se(8)–C(6)	1.818(11)	Se(9)–C(5)	1.933(11)
Se(9)–C(6)	1.845(12)	Se(10)–C(5)	1.928(11)
C(1)–C(2)	1.299(11)	C(4)–C(5)	1.335(16)
Se(1)–Zn–Se(5)	96.5(1)	Se(1)–Zn–Se(6)	110.7(1)
Se(1)–Zn–Se(10)	122.1(1)	Se(5)–Zn–Se(6)	121.1(1)
Se(5)–Zn–Se(10)	111.9(1)	Se(6)–Zn–Se(10)	96.5(1)
Zn–Se(1)–C(1)	93.6(3)	C(1)–Se(2)–C(3)	95.5(4)
C(2)–Se(4)–C(3)	96.0(4)	Zn–Se(5)–C(2)	93.4(3)
Zn–Se(6)–C(4)	95.6(3)	C(4)–Se(7)–C(6)	97.6(5)
C(5)–Se(9)–C(6)	94.8(5)	Zn–Se(10)–C(5)	92.8(4)
Se(1)–C(1)–C(2)	127.6(8)	Se(2)–C(1)–C(2)	118.8(8)
Se(4)–C(2)–C(1)	116.6(8)	Se(5)–C(2)–C(1)	128.7(8)
Se(2)–C(3)–Se(3)	123.9(5)	Se(2)–C(3)–Se(4)	112.8(6)
Se(6)–C(4)–C(5)	126.0(8)	Se(7)–C(4)–C(5)	116.3(9)
Se(9)–C(5)–C(4)	118.5(8)	Se(10)–C(5)–C(4)	129.1(9)
Se(7)–C(6)–Se(8)	121.4(6)	Se(7)–C(6)–Se(9)	112.9(6)

Table 5. Selected bond distances (Å) and angles (°) of $[\mathrm{PPh_4}]_2[\mathrm{Zn(CSe_4)_2}]$ (**2**)

Zn–Se(1)	2.434(2)	Zn–Se(4)	2.462(2)
Zn–Se(5)	2.440(2)	Zn–Se(8)	2.442(3)
Se(1)–Se(2)	2.337(3)	Se(2)–C(1)	1.853(13)
Se(3)–C(1)	1.825(13)	Se(4)–C(1)	1.843(14)
Se(5)–Se(6)	2.320(2)	Se(6)–C(2)	1.863(12)
Se(7)–C(2)	1.804(14)	Se(8)–C(2)	1.860(13)
Se(1)–Zn–Se(4)	100.5(1)	Se(1)–Zn–Se(5)	120.8(1)
Se(1)–Zn–Se(8)	110.7(1)	Se(4)–Zn–Se(5)	113.2(1)
Se(4)–Zn–Se(8)	112.0(1)	Se(5)–Zn–Se(8)	100.0(1)
Zn–Se(1)–Se(2)	98.6(1)	Zn–Se(4)–C(1)	104.8(4)
Zn–Se(5)–Se(6)	98.5(1)	Zn–Se(8)–C(2)	104.5(4)
Se(2)–C(1)–Se(3)	113.0(7)	Se(2)–C(1)–Se(4)	124.4(7)
Se(6)–C(2)–Se(7)	113.0(7)	Se(6)–C(2)–Se(8)	123.7(7)

Spectroscopic Properties of Complexes (**1**) *and* (**2**).—Figure 3 shows the absorption spectra of complex (**1**) and $[\mathrm{NBu^n_4}]_2[\mathrm{Zn(C_3S_5)_2}]$. The intense absorption band at 550 nm ($\varepsilon = 16\,300~\mathrm{dm^3~mol^{-1}~cm^{-1}}$) for (**1**) is ascribed to the ligand π–π* transition, which corresponds to the band at 504 nm of $[\mathrm{NBu^n_4}]_2[\mathrm{Zn(C_3S_5)_2}]$. Another π–π* band is observed at 370 nm ($\varepsilon = 20\,400~\mathrm{dm^3~mol^{-1}~cm^{-1}}$), which also corresponds to the band at 300 nm observed for the $[\mathrm{Zn(C_3S_5)_2}]^{2-}$ anion. These π–π* transition bands of (**1**) occur at longer wavelengths than those of the $[\mathrm{Zn(C_3S_5)_2}]^{2-}$ anion. This may suggest that the occupied π orbitals of the $\mathrm{C_3Se_5}^{2-}$ ligand are less stabilized than those of the $\mathrm{C_3S_5}^{2-}$ ligand, which is related to the higher order of the Zn–Se than the Zn–S bond as described above. Complex (**2**) also shows a π–π* band in the visible region similar to complex (**1**) [401 ($\varepsilon = 24\,000$) and 490 ($\varepsilon = 14\,000$) with 550 nm ($\varepsilon = 1\,800~\mathrm{dm^3~mol^{-1}~cm^{-1}}$) in acetonitrile]. Although these complexes may exhibit *n*–π* transitions due to the terminal C–Se groups at around 500—600 nm as reported for selenocarbonyl compounds,[27] the intense π–π* absorptions seem to obscure the bands of complexes (**1**) and (**2**).

The ^{77}Se n.m.r. spectra of complexes (**1**) and (**2**) were measured in [^{2}H$_6$] dimethyl sulphoxide. The chemical shifts relative to the external standard of dimethyl selenide for (**1**) are

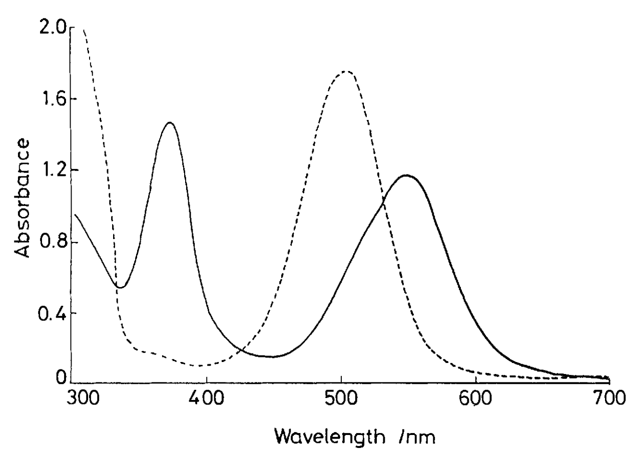


Figure 3. Electronic absorption spectra of complex (**1**) (——) and $[NBu^n_4]_2[Zn(C_3S_5)_2]$ (– – – –) in acetonitrile

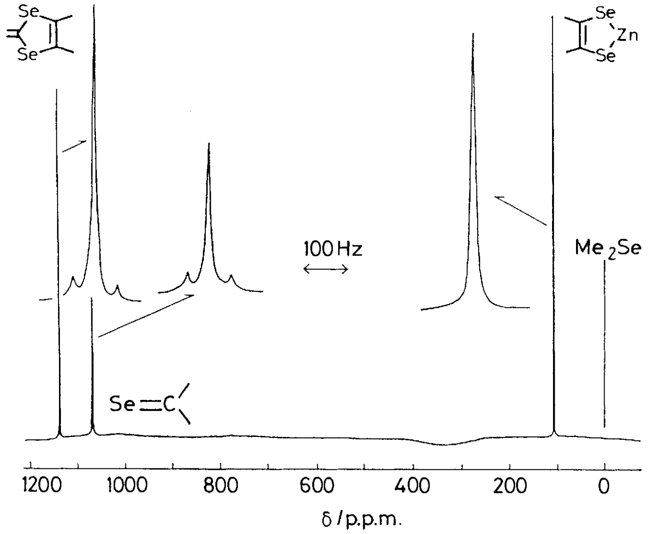


Figure 4. Selenium-77 n.m.r. spectrum of $[PPh_4]_2[ZnC_3Se_5)_2]$ (**1**) in $[^2H_6]$dimethyl sulphoxide

assigned on the basis of the signals of organoselenium compounds[28] having the 1,3-diselenole-2-selone (C_3Se_3) skeleton, as shown in Figure 4. Moreover, both the selenocarbonyl and the C_3Se_3 heteroring signals exhibit satellites due to $^{77}Se-^{77}Se$ coupling [^2J(Se–Se) = 96 Hz], while the other signal at high field shows no satellites. This is reasonable because of the electron delocalization in the CSe_3 moiety as described above. The signal of the Se nucleus ligating the metal atom occurs at significantly high field (104.7 p.p.m.), in contrast to the signal of bis(*N*,*N*-dialkyldiselenocarbamato)zinc(II) (648—669 p.p.m. from Me_2Se).[29] Complex (**2**) also shows ^{77}Se n.m.r. signals at 403.6, 836.2, 881.1, and 1 241.2 p.p.m. with reference to the external standard of dimethyl selenide.

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