Co-ordination Complexes containing Multidentate Ligands. Part IX.[1] The Synthesis and Donor Properties of the Open-chain Tetraselenoether, 1,3-Bis(methylselenoethylseleno)propane

By **William Levason, Charles A. McAuliffe,*** and **Stephen G. Murray,** Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

The quadridentate selenoether, 1,3-bis(methylselenoethylseleno)propane, (bsep), has been synthesised from the newly prepared propane-1,3-diselenol, 2-chloroethyl methyl selenide, and sodium methoxide. The ligand forms only insoluble $[Pd_2(Se_4)X_4]$ (X = Cl, Br, or I) complexes on reaction with sodium tetrahalogenopalladates(II) and with nickel(II) iodide forms the polymeric octahedral $[Ni_2(Se_4)I_4]$. The behaviour of bsep is compared with that of the analogous tetrathioethers. Polymeric $[NiL']_n$ and $[PdL']_n$ are formed by reaction of propane-1,3-diselenol (L'H_2) and nickel(II) and palladium(II) salts.

THERE is increasing interest in the organic chemistry and biochemical function of selenium,[2,3] and much effort is being devoted to the preparation of organoselenium compounds and to make a comparison with their sulphur analogues. However, due to the difficulty of the organic preparations of selenium donor ligands the co-ordination chemical aspects have not been well investigated. A few complexes of the bidentate $RSe(CH_2)_nSeR$ (R = Me,[4] Pr^i [5,6]) and two multidentate phosphorus–selenium ligands $(o\text{-}MeSeC_6H_4)_2PPh$ [7] and $(o\text{-}MeSeC_6H_4)_3P$ [7] have been prepared. The bidentate chelates formed six-co-ordinate $[NiL_2X_2]$ (X = Cl, Br, or I) and planar MLX_2 (M = Pd or Pt; X = Cl or Br) complexes, and the multidentate ligands formed five-co-ordinate nickel(II) complexes.

As part of a general investigation of open-chain quadridentate ligands we have recently prepared a series of linear tetrathioethers, bis(o-methylthiophenylthio)-alkanes [1] and bis(methylthioalkylthio)alkanes,[8] which form six-co-ordinate nickel(II) complexes, $trans\text{-}[NiLX_2]$, and dimeric planar palladium(II) and platinum(II) complexes, $[M_2LX_4]$. Here we report the preparation of the first quadridentate selenoether ligand, 1,3-bis(2-methylselenoethylseleno)propane, $MeSe(CH_2)_2Se(CH_2)_3\text{-}Se(CH_2)_2SeMe$ (bsep), and its complexing properties towards d^8 metal ions.

EXPERIMENTAL

2-Hydroxyethyl Methyl Selenide.—Dimethyl diselenide was prepared by a method similar to that by Günther.[9] Liquid ammonia (400 cm³) was condensed in a 1-l three-necked flask fitted with gas inlet, mechanical stirrer, and condenser, and held at −78 °C. Then, under a nitrogen atmosphere, sodium (6.15 g, 0.27 g-atom) was added in small pieces with stirring; the blue solution was then stirred for 30 min. Dimethyl diselenide (25.0 g, 0.13 mol) was then added to the mixture which was stirred for 1 h and then allowed to warm to −33 °C; the ammonia was then boiled off. Dry and deaerated tetrahydrofuran (350 cm³) was added to the mixture which was then allowed to reach room temperature. 2-Chloroethanol (21.3 g, 0.27 mol) was added to the mixture which was heated under reflux for 2 h; after cooling it was hydrolysed with a deaerated ammonium chloride solution. The organic layer was dried (Na_2SO_4) and then, after removal of the solvent, distilled to produce a pale yellow oil, b.p. 54 °C/1.5 Torr; yield 21.7 g (57%) (Found: C, 25.9; H, 5.6. Calc. for C_3H_8SeO: C, 25.9; H, 5.8%).

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2-Chloroethyl Methyl Selenide.—Thionyl chloride (17.0 g, 0.143 mol) in dry chloroform (20 g) was added during 30 min to 2-hydroxyethyl methyl selenide (20.0 g, 0.144 mol) in dry chloroform (30 g) under nitrogen with vigorous stirring. The reaction mixture was heated as necessary to keep the solvent refluxing but heating after addition of the thionyl chloride was disadvantageous. The mixture was stirred for a further 2 h after which the solvent was distilled off; the remaining oil was distilled *in vacuo*, b.p. 95—96 °C/1.5 Torr; yield 5.9 g (27%) (Found: C, 22.6; H, 4.5; Cl, 22.8. Calc. for C_3H_7ClSe: C, 22.8; H, 4.4; Cl, 22.5%).

Propane-1,3-diselenol.—In absolute ethanol (300 cm³), finely powdered selenium (12.0 g, 0.152 g-atom) was treated with sodium tetrahydroborate (6.4 g, 0.168 mol) in small portions under nitrogen. The reaction was extremely vigorous with rapid evolution of hydrogen. The sodium hydrogenselenide thus formed was treated with 1,3-dibromopropane (15.3 g, 0.076 mol) and the mixture then hydrolysed with deaerated water (400 cm³) and sufficient dilute hydrochloric acid to lower the pH to 5—6. Any H_2Se present was removed by bubbling nitrogen through the mixture for 30 min and then the product was extracted into chloroform (200 cm³). Removal of the solvent from the dried chloroform solution yielded a red oil (8.6 g) which decomposed on attempted distillation.

Tetraselenoether. In absolute ethanol under nitrogen, propane-1,3-diselenol (3.23 g, 0.016 mol) was treated with sodium methoxide (1.73 g, 0.032 mol) and the mixture was then stirred for 30 min. To this was added 2-chloroethyl methyl selenide (5.0 g, 0.032 mol) and the mixture was refluxed for 30 min. The mixture was then cooled to ambient temperature, hydrolysed with a deaerated solution of ammonium chloride, and the product extracted into chloroform. The chloroform solution was separated, dried, and the solvent removed *in vacuo* leaving a red oil which did not distil; yield 5.8 g (82%).
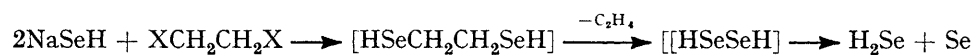
Complexes.—The ligand was dissolved in dichloromethane and aliquot portions were used in the complex preparations.

[Pd₂LCl₄]. Sodium tetrachloropalladate (0.59 g, 2.0 mmol) was dissolved in ethanol (10 cm³) and the ligand (1.0 mmol) was added with stirring. A yellow–orange solid precipitated immediately and after a further 30 min of stirring was isolated and washed with dichloromethane, aqueous ethanol, ethanol, and ether and was then dried *in vacuo*; yield 0.52 g (65%).

[Pd₂LX₄] (X = Br or I). The above procedure was used to prepare these complexes, the $[PdX_4]^{2-}$ (X = Br or I) ions being prepared *in situ* by reaction of the sodium chloropalladate with an excess of sodium halide before addition of the ligand; bromo-complex, yield 0.6 g (62%); iodo-complex yield 0.8 g (69%).
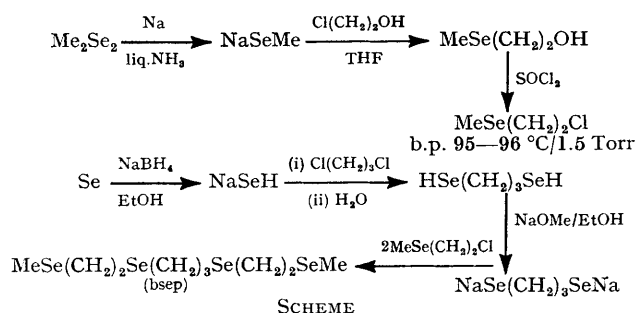
[Ni₂LI₄]. Hydrated nickel iodide (0.75 g, *ca.* 2.0 mmol) was dissolved in the minimum amount of hot n-butanol. The solution was then cooled, filtered, and the ligand (2.0 mmol) was added with stirring. After being stirred for 1 h the solution was filtered to remove a small amount of insoluble material after which it was poured into an excess of light petroleum (250 cm³), to precipitate the complex as a brown solid. The solid was filtered off, washed with a small amount of n-butanol and then with ether, and was then dried *in vacuo*; yield 0.55 g (51%).

Physical measurements were obtained as previously described.[10]

RESULTS AND DISCUSSION

The Ligand.—Dimethyl diselenide was used as the precursor of sodium methyl selenide because the obvious source, methaneselenol, has a boiling point of 25.5 °C at atmospheric pressure and is extremely malodorous. Aynsley *et al.*[4] obtained their bidentate selenoethers 1,2-bis(methylseleno)ethane and 1,3-bis-(methylseleno)propane by treating sodium methyl selenide with the appropriate αω-dihalogenoalkane in liquid ammonia. Their whole reaction sequence took 2 days. By replacing liquid ammonia with dry tetrahydrofuran (THF) after cleavage of the dimethyl diselenide the total reaction sequence takes only a few hours (see Scheme) to produce 2-hydroxyethyl methyl selenide. The ¹H n.m.r. of this compound shows two triplets, CH_2Se (3.80 p.p.m.) and CH_2OH (2.70 p.p.m.), and two singlets, O*H* (2.61 p.p.m.) and CH_3Se (4.48 p.p.m.) (all referenced high field of external benzene). The hydroxy-compound is readily chlorinated with thionyl chloride to give 2-chloroethyl methyl selenide, the ¹H n.m.r. spectrum of which shows two triplets, CH_2Se (3.55 p.p.m.) and CH_2Cl (2.72 p.p.m.), and a singlet, CH_3Se (4.42 p.p.m.).

Attempts to prepare the diselenol with the $-CH_2CH_2-$ linkage by reaction of NaSeH with 1,2-dihalogenoethanes produced a deep red colouration and vigorous evolution of a gas which gave a black precipitate (PbSe) when bubbled through lead acetate solution. The reasons for this apparently inherent instability of ethane-1,2-diselenol are unclear. The reaction probably proceeds thus:

$$2NaSeH + XCH_2CH_2X \longrightarrow [HSeCH_2CH_2SeH] \xrightarrow{-C_2H_4} [[HSeSeH] \longrightarrow H_2Se + Se$$

However, when a 1,3-dihalogenopropane was used the resulting diselenol is quite stable, although distillation causes decomposition. The ¹H n.m.r. of this compound shows a singlet, Se*H* (−0.5 p.p.m.), a multiplet $CH_2CH_2CH_2$ (2.25 p.p.m.), and a triplet $SeCH_2$ (2.8 p.p.m.). (The diselenol reacts with nickel(II) halides and sodium tetrahalogenopalladates to produce dark brown polymeric $[M(SeCH_2CH_2CH_2Se)]_n$ (M = Ni or Pd) complexes.)

Preparation of the tetraselenoether, 1,3-bis(methylselenoethylseleno)propane, (bsep), is readily accomplished by deprotonation of the diselenol with sodium methoxide and subsequent reaction with 2-chloroethyl methyl selenide (see Scheme). The oily product could not be distilled or crystallised and so was heated under vacuum to remove impurities. The bsep ligand exhibits a complex ¹H n.m.r. pattern, a singlet at 7.9 p.p.m. (CH_3Se) and complex multiplets at 7.30 and 7.0 p.p.m. due to trimethylene and dimethylene groups.

¹⁰ L. Baracco and C. A. McAuliffe, *J.C.S. Dalton*, 1972, 948.

Metal Complexes.—The bsep ligand reacts with the appropriate sodium tetrahalogenopalladate(II) in ethanol–dichloromethane to yield only $[Pd_2(bsep)X_4]$ (X = Cl, Br, or I) irrespective of the molar ratios of the reactants;

$$Me_2Se_2 \xrightarrow[\text{liq.NH}_3]{\text{Na}} NaSeMe \xrightarrow[\text{THF}]{Cl(CH_2)_2OH} MeSe(CH_2)_2OH$$

$$\downarrow SOCl_2$$

$$MeSe(CH_2)_2Cl$$
$$\text{b.p. 95—96 °C/1.5 Torr}$$

$$Se \xrightarrow[\text{EtOH}]{NaBH_4} NaSeH \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) Cl(CH}_2)_3\text{Cl}} HSe(CH_2)_3SeH$$

$$\downarrow NaOMe/EtOH$$

$$MeSe(CH_2)_2Se(CH_2)_3Se(CH_2)_2SeMe \xleftarrow{2MeSe(CH_2)_2Cl} NaSe(CH_2)_3SeNa$$
$$\text{(bsep)}$$

SCHEME

no thiocyanate complex could be isolated. The complexes are insoluble in all common solvents although they dissolve slowly in refluxing *NN*-dimethylformamide to

Analytical ^{a} and spectral data of the selenium complexes

Complex	Colour	% C	% H	% Hal	Reflectance spectra ($\times 10^{-3}$ cm^{-1})	ν(Pd−X) cm^{-1}
$[Pd_2(bsep)Cl_4]$	Orange	13.6 (13.6)	2.5 (2.4)	17.8 (17.8)	22.5	312, 308
$[Pd_2(bsep)Br_4]$	Brown	11.1 (11.4)	2.1 (2.2)	32.8 (33.2)	21.5	220
$[Pd_2(bsep)I_4]$	Dark brown	9.3 (9.7)	1.7 (1.9)	43.6 (44.0)	18.5	
$[Ni_2(bsep)I_4]$	Dark brown	10.0 (9.9)	1.8 (2.0)	47.5 (46.8)	26.6, 18.5, 12.9sh, 8.5	
$[NiL]^b$	Black	13.9 (14.1)	2.3 (2.5)	0.0 (0.1)		
$[PdL]^b$	Black	11.9 (12.0)	2.0 (2.3)	0.0 (0.1)		

^{a} Calculated (found). ^{b} L = SeCH$_2$CH$_2$CH$_2$Se.

produce a complex mixture of Se-dealkylated products which could not be separated. The electronic reflectance spectra (Table) are consistent with a planar $PdSe_2X_2$

chromophore,[5] and the chloro- and bromo-complexes exhibit ν(Pd−X) bands consistent with a *cis*-PdX$_2$ set.[11] Thus, it appears that these complexes are structurally analogous to those of the quadridentate thioethers prepared earlier.[1] Comparison of the electronic spectra of analogous $[Pd_2(S_4)X_4]$ [1] and $[Pd_2(Se_4)X_4]$ complexes shows the expected band shift to lower energy S > Se.

The only nickel(II) complex which could be isolated was $[Ni_2(Se_4)I_4]$, which is insoluble in all solvents in which it does not decompose. The nickel(II) halide complexes isolated with the S$_4$ ligands were of stoicheiometry Ni(S$_4$)X$_2$. This interesting difference in complexing behaviour may be steric (the larger Se atoms making it difficult to fit around one nickel atom) or electronic in origin (a symbiosis effect—the softer selenium donors needing more co-ordinated iodides for stabilisation of the Ni−Se bonds).

The magnetic moment of $[Ni_2(Se_4)I_4]$ is 2.98 B.M. and its electronic reflectance spectrum (Table) shows no indication of tetragonal distortion [12] (indicating that Se and I have similar positions in the spectrochemical series), contrasting with the tetragonally distorted *trans*-$[Ni(S_4)X_2]$ species. In order to produce six-co-ordination only one structure is possible for $[Ni_2(Se_4)I_4]$, that of a three-dimensional polymer with all iodines bridging:
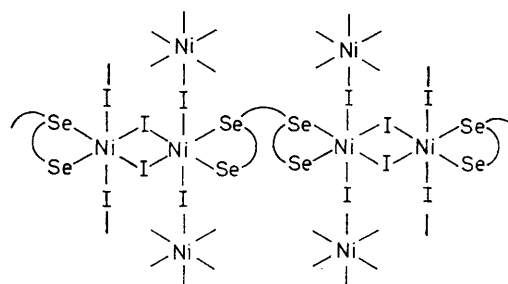
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