

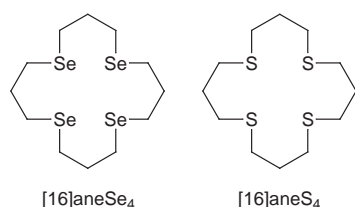
Macrocyclic selenoether complexes of nickel(II). Synthesis and properties of $[\text{NiX}_2([\text{16}] \text{aneSe}_4)]$ ($[\text{16}] \text{aneSe}_4 = 1,5,9,13\text{-tetra-selenacyclohexadecane}$, $\text{X} = \text{Cl}$, Br or I) and $[\text{NiX}_2(\text{MeSeCH}_2\text{CH}_2\text{-SeMe})_2]$ *

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Reaction of NiX_2 ($\text{X} = \text{Cl}$, Br or I) with $[\text{16}] \text{aneSe}_4$ (1,5,9,13-tetraselenacyclohexadecane) under anhydrous conditions in *n*-butanol yielded *trans*- $[\text{NiX}_2([\text{16}] \text{aneSe}_4)]$. Similar reactions using $\text{MeSeCH}_2\text{CH}_2\text{SeMe}$ produced *trans*- $[\text{NiX}_2(\text{MeSeCH}_2\text{CH}_2\text{SeMe})_2]$. The complexes have been characterised by IR and UV/VIS spectroscopy and magnetic measurements. The crystal structure of $[\text{NiCl}_2(\text{MeSeCH}_2\text{CH}_2\text{SeMe})_2]$ showed an octahedral nickel centre co-ordinated to *trans* chlorines [2.370(2)–2.376(2) Å] with the diselenoethers present as chelating ligands in the DL conformation [2.522(1)–2.5623(8) Å]. Structural data on the very poorly soluble $[\text{16}] \text{aneSe}_4$ complexes were obtained *via* nickel K-edge EXAFS (extended X-ray absorption fine structure), and the results compared with related complexes. A ligand field analysis of the UV/VIS spectra of $[\text{NiX}_2([\text{16}] \text{aneSe}_4)]$ and of the tetrathioether analogues $[\text{NiX}_2([\text{16}] \text{aneS}_4)]$ ($[\text{16}] \text{aneS}_4 = 1,5,9,13\text{-tetrathiacyclohexadecane}$) showed that the ligand fields produced by 16-membered ring macrocycles $[Dq(xy)]$ lie in the order $\text{N}_4 > \text{S}_4 > \text{Se}_4$, with $\text{MeSeCH}_2\text{CH}_2\text{SeMe}$ affording a stronger field than $[\text{16}] \text{aneSe}_4$ due to the smaller chelate ring size.

Acyclic thio- or seleno-ether ligands are usually classed as soft donors which typically form complexes with metal carbonyls or with soft metals such as the platinum group halides, but which have little affinity for harder 3d metals in normal oxidation states.^{1,2} In contrast, macrocyclic thioethers are able to form stable complexes with most transition metals.³ The synthesis⁴ of macrocyclic selenoethers including $[\text{16}] \text{aneSe}_4$ opens up the possibility of similarly enhanced M–Se binding, and we have reported complexes with a variety of platinum metal centres, viz. $[\text{M}([\text{16}] \text{aneSe}_4)]^{2+}$ ($\text{M} = \text{Pd}$ or Pt),⁵ $[\text{PtX}_2([\text{16}] \text{aneSe}_4)]^{2+}$ ($\text{X} = \text{Cl}$ or Br),⁶ $[\text{MX}_2([\text{16}] \text{aneSe}_4)]^+$ ($\text{M} = \text{Rh}$ or Ir),⁷ $[\text{RuX}_2([\text{16}] \text{aneSe}_4)]^{n+}$ ($n = 0$ or 1), and $[\text{MX}(\text{PPh}_3)([\text{16}] \text{aneSe}_4)]^+$ ($\text{M} = \text{Ru}$ or Os).⁸ Complexes of Cu^{I} and Cu^{II} have been obtained,⁹ but other 3d examples are limited to $[\text{CoX}_2([\text{16}] \text{aneSe}_4)]^{+7}$ and $[\text{CrX}_2([\text{16}] \text{aneSe}_4)]^{+10}$ both of which benefit from the kinetically inert metal centres. Here we report the first examples of complexes of $[\text{16}] \text{aneSe}_4$ with the hard labile 3d ion nickel(II), along with attempts to prepare acyclic diselenoether analogues.



Results and Discussion

Nickel(II) complexes

The reaction of anhydrous nickel(II) halides with $[\text{16}] \text{aneSe}_4$ in dry *n*-butanol gave pale green ($\text{X} = \text{Cl}$ or Br) or brown ($\text{X} = \text{I}$) paramagnetic (μ ca. 3 μ_{B}) complexes $[\text{NiX}_2([\text{16}] \text{aneSe}_4)]$. The complexes are insoluble in chlorocarbons or MeNO_2 , very poorly soluble in MeCN and decomposed by dmsO . They dissolve slightly in strong mineral acids (below). Dry samples

can be handled briefly in air, although hydrolysis occurs on prolonged exposure to moisture. The corresponding $[\text{NiX}_2([\text{16}] \text{aneS}_4)]$ ($[\text{16}] \text{aneS}_4 = 1,5,9,13\text{-tetrathiacyclohexadecane}$) were made similarly for comparison. The $[\text{NiCl}_2([\text{16}] \text{aneS}_4)]$ complex has been made previously by Schröder and co-workers¹¹ who converted it into $[\text{Ni}_2(\mu\text{-Cl})_2([\text{16}] \text{aneS}_4)_2][\text{BF}_4]_2$ by reaction with NaBF_4 in MeNO_2 , but did not characterise the monomer. Attempts to prepare nickel(II) complexes with acyclic diselenoethers had limited success. Under anhydrous conditions, 2,5-diselenahexane ($\text{MeSeCH}_2\text{CH}_2\text{SeMe}$) afforded green $[\text{NiX}_2(\text{MeSeCH}_2\text{CH}_2\text{SeMe})_2]$ ($\text{X} = \text{Cl}$ or Br) or orange $[\text{Ni}_2(\text{MeSeCH}_2\text{CH}_2\text{SeMe})_2]$.¹² In contrast, attempts to isolate complexes with $\text{MeSe}(\text{CH}_2)_3\text{SeMe}$, $\text{C}_6\text{H}_4(\text{SeMe})_2\text{-}o$ or $\text{PhSeCH}_2\text{CH}_2\text{SePh}$ failed, showing that the additional stability conferred by alkyl substituents at Se and five-membered chelate rings are needed to permit isolation of the nickel(II) complexes. The $[\text{NiX}_2(\text{MeSeCH}_2\text{CH}_2\text{SeMe})_2]$ complexes are hydrolysed rapidly in air and decomposed by donor solvents. The assignment of *trans* octahedral geometries to $[\text{NiX}_2([\text{16}] \text{aneS}_4)]$, $[\text{NiX}_2([\text{16}] \text{aneSe}_4)]$ and $[\text{NiX}_2(\text{MeSeCH}_2\text{CH}_2\text{SeMe})_2]$ follows from their paramagnetism (μ ca. 3 μ_{B}) and their UV/VIS spectra (Table 1), and this was confirmed for $[\text{NiCl}_2(\text{MeSeCH}_2\text{CH}_2\text{SeMe})_2]$ by a single-crystal X-ray study (below).

The UV/VIS spectrum of a high spin d^8 ion in O_h symmetry is expected to show three bands in order of increasing energy, ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}(\text{P})$. In tetragonal symmetry (D_{4h}) the ground state becomes ${}^3\text{B}_{1g}$, and the excited states split (${}^3\text{T}_{2g} \longrightarrow {}^3\text{E}_g$, ${}^3\text{B}_{2g}$; ${}^3\text{T}_{1g} \longrightarrow {}^3\text{A}_{2g}$, ${}^3\text{E}_g$).¹⁵ Weak spin-forbidden transitions to singlet states are sometimes seen to low energy of the first spin-allowed band. For our complexes only the first spin-allowed transition is clearly split (Table 1), but the information is sufficient to allow the normal ligand field analysis^{13,15} to obtain the in-plane $[Dq(xy)]$ and out-of-plane $[Dq(z)]$ ligand fields and the tetragonality parameter (Dt). The individual numerical values from such an analysis are not of high precision, but the trends are usually reliable. Comparison of the $Dq(xy)$ values in Table 1 with those of the analogous tetraazamacrocyclic $[\text{16}] \text{aneN}_4$ (1,5,9,13-tetraazacyclohexadecane),¹³ shows that the ligand field strength increases in the order $[\text{16}] \text{aneSe}_4 < [\text{16}] \text{aneS}_4 < [\text{16}] \text{aneN}_4$ for

* Non-SI units employed: $\mu_{\text{B}} \approx 9.27 \times 10^{-24} \text{ J T}^{-1}$, $\text{eV} \approx 1.60 \times 10^{-19} \text{ J}$.

Table 1 Selected UV/VIS spectroscopic data^a

Complex	${}^3B_{1g} \longrightarrow {}^1E_g$	${}^3B_{1g} \longrightarrow {}^3E_g$	${}^3B_{1g} \longrightarrow {}^3B_{2g}$	${}^3B_{1g} \longrightarrow {}^3A_{2g}, {}^3E_g$	${}^3B_{1g} \longrightarrow {}^3A_{2g}, {}^3E_g$	$Dq(xy)$	$Dq(z)$	Dt
[NiCl ₂ ([16]aneSe ₄)]	7267	8405	9390	14 710	26 300	940	740	113
[NiBr ₂ ([16]aneSe ₄)]	7240	8240	9010	14 620	25 000 (sh)	900	745	88
[NiI ₂ ([16]aneSe ₄)]	7235	7700	8065	14 900	22 420	807	735	42
[NiCl ₂ ([16]aneS ₄)]	7290	8530	7930	15 340	25 000 (sh)	973	733	176
[NiBr ₂ ([16]aneS ₄)]	7270	8330	9345	15 450	—	935	713	150
[NiI ₂ ([16]aneS ₄)]	7210	7875	8620 (sh)	12 800 (sh), 15 500	21 300 (br)	862	710	120
[NiCl ₂ (MeSeCH ₂ CH ₂ SeMe) ₂]	7260	8690	9590	14 710	23 530	960	780	102
[NiBr ₂ (MeSeCH ₂ CH ₂ SeMe) ₂]	7250	8450	9400	14 245	25 000 (sh)	940	750	108
[NiI ₂ (MeSeCH ₂ CH ₂ SeMe) ₂]	7230	7900	8710	14 300	ca. 24 000	870	710	23
[NiCl ₂ ([16]aneN ₄)] ^b						1116	440	496
[NiBr ₂ ([16]aneN ₄)] ^b						1128	335	582
[NiCl ₂ ([14]aneS ₄)] ^c						1110	723	285
[NiBr ₂ ([14]aneS ₄)] ^c						1099	687	302

^a Diffuse reflectance spectra (cm⁻¹), samples diluted with BaSO₄, assignments based upon tetragonally distorted nickel geometry (*D*_{4h} symmetry).

^b Data from ref. 13 using mull spectra. ^c Calculated from the diffuse reflectance spectral data in ref. 14.

the 16-membered ring macrocycles, whilst the *Dq(xy)* is slightly greater for 2,5-diselenahexane compared to [16]aneSe₄, reflecting the effects of chelate ring size. Previous studies of 14-membered ring aza- and thia-macrocycles and of open-chain tetrathioethers show similar trends in *Dq(xy)* with chelate ring size.^{13,14,16} Thus we conclude that selenium ligands exert a smaller ligand field than the sulfur analogues towards hard 3d metal ions.

The poor solubility of [NiX₂([16]aneSe₄)] in organic solvents hindered attempts to study their redox chemistry. The complexes dissolve with difficulty in concentrated acids (HClO₄, H₂SO₄ or HNO₃) with the formation of unstable pink or purple solutions which decompose quite rapidly (a few minutes in HNO₃ solution, several hours in 70% HClO₄). The possibility that these solutions contained d⁷ nickel(III) was eliminated when they were found to be ESR silent. Oxidation would be expected to lead to low-spin d⁷, since for Ni^{III} the high spin → low spin crossover occurs with weak ligand fields—even [NiF₆]³⁻ is low spin,¹⁷ and thus in six-co-ordination the moderate field generated in [NiX₂([16]aneSe₄)]⁺ should cause spin pairing. Similar unstable pink solutions were formed in anhydrous trifluoroacetic acid (tfa), which is more suited as a solvent to both UV/VIS spectroscopy and electrochemical studies than the other mineral acids. In fact cyclic voltammetry of these solutions showed only completely irreversible oxidations at highly positive potentials, and it is unclear whether these reflect metal based oxidations or oxidation of displaced halide ions. The UV/VIS spectra of the iodo complexes are ill defined, but in tfa solution [NiX₂([16]aneSe₄)] (X = Cl or Br) have *E*_{max} ca. 17 800 and ca. 20 400 cm⁻¹, inconsistent with *O*_h or square-planar d⁸ centres, but not unreasonable for a high-spin five-co-ordinate (Se₄X) species.^{15,18} The complexes [NiX₂(MeSeCH₂CH₂SeMe)₂] (X = Cl or Br) also gave pink solutions in tfa, but [NiX₂([16]aneS₄)] (X = Cl or Br) gave green solutions with very weak d-d bands (ca. 10 000 and 16 000 cm⁻¹) suggesting the *O*_h geometry is retained in solution, whilst [NiI₂([16]aneS₄)] decomposed immediately in tfa. The instability of these pink solutions has prevented a more definite characterisation, but it seems clear that nickel(III) complexes are not formed, contrasting with the generation of tetragonal low-spin d⁷ in [Ni([9]aneS₃)₂]³⁺¹⁹ and [NiX₂(diphosphine)₂]⁺.²⁰ Unstable low-spin [NiX₂{C₆H₄(EMe₂)(SeMe)-*o*}₂]⁺ (E = P or As) are known,²¹ but here the Group 15 donors will produce much greater ligand fields stabilising the low-spin d⁷ state. The [NiX₂([16]aneSe₄)] did not react with TIPF₆ or NaBF₄ under reflux in MeNO₂ suspension probably reflecting their very poor solubility in this medium [contrast [NiX₂([16]aneS₄)] which gave blue [Ni₂(μ-Cl)₂([16]aneS₄)₂]²⁺].¹¹

Crystal structure of [NiCl₂(MeSeCH₂CH₂SeMe)₂]

Pale green crystals were obtained from the reaction mixture.

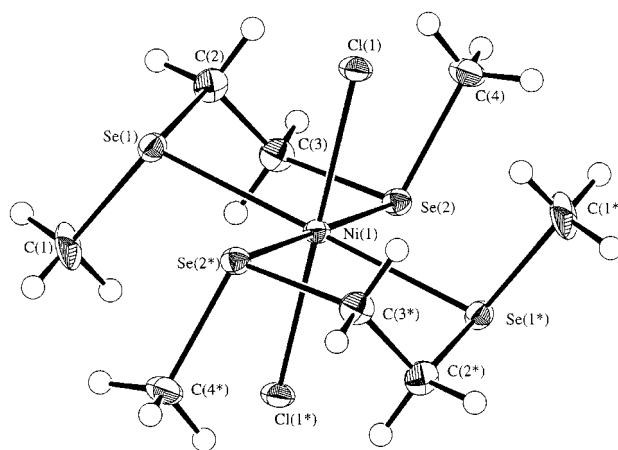


Fig. 1 View of the structure of one of the molecules of *trans*-[NiCl₂(MeSeCH₂CH₂SeMe)₂] with the numbering scheme adopted. Ellipsoids are drawn at the 40% probability level and atoms marked * are related by a crystallographic centre of symmetry. The other molecule is essentially indistinguishable

The structure solution revealed two independent centrosymmetric molecules (Fig. 1) with no chemically significant differences in their dimensions. Selected bond lengths and angles are given in Table 2. The nickel is in a tetragonal six-co-ordinate environment composed of two chelating diselenoethers and two mutually *trans* chlorides, with the selenoether ligands in the *DL* form. The Ni-Cl distances 2.370(2)–2.376(2) Å are typical of high-spin Ni^{II}-Cl bonds and may be compared with those in dichlorobis(1,5-dithiacyclooctane)nickel [2.358(2) Å]²² or [NiCl₂([16]aneN₄)] [2.428(1), 2.535(1) Å].²³ The Ni-Se distances of 2.522(1)–2.5623(8) Å are typically 0.05–0.1 Å longer than the Ni-S bonds in nickel(II) thioethers,^{3,11,18,19} consistent with the differences in radii of Se vs. S.

EXAFS Studies

The insolubility of [NiX₂([16]aneSe₄)] in most solvents precluded growth of crystals suitable for an X-ray study, so we used the combination of UV/VIS spectroscopy to define the metal centre symmetry, and metal K-edge EXAFS (extended X-ray absorption fine structure) data to obtain first co-ordination sphere bond lengths. A similar approach has been used successfully to study nickel(-II), (III) and (-IV) diphosphine and diarsine complexes,²⁴ and platinum(-II) and (-IV) tetrathioether macrocycles,²⁵ and the general methodology follows that used previously (summarised in the Experimental section). Data were also collected on [NiX₂(MeSeCH₂CH₂SeMe)₂], and since we have the single-crystal X-ray data on the chloride (above) this complex provides an excellent model upon which to check the EXAFS data quality and treatment. As can be seen

for this complex by comparing the data in Tables 2 and 3, the agreement in $d(\text{Ni}-\text{Cl})$ and $d(\text{Ni}-\text{Se})$ is satisfactory within the usual precision of EXAFS determined first shell distances ($\pm 0.02-0.03$ Å). For the chloro- and iodo-complexes the EXAFS data were modelled to two shells of four Se and two halides, and refined straightforwardly to the parameters in Table 3. For the bromo-complexes, in view of the similar back-scattering of Br and Se, the data were fitted to models comprising 4Se + 2Br, 6Se, and then 6Br. The two-shell fits were statistically better, resulting in significant²⁶ reductions in R factors and fit indices, and with no unacceptably large correlations. Thus we conclude that the two-shell fit is appropriate in this case also, consistent with the conclusions from UV/VIS spectroscopy. A typical example of the background-subtracted EXAFS data and the resulting Fourier transform are shown in Fig. 2. Comparison of the bond lengths in Table 3 show that $d(\text{Ni}-\text{X})$ is marginally greater in the complexes of [16]aneSe₄ than in those of MeSeCH₂CH₂SeMe, but the variations in $d(\text{Ni}-\text{Se})$ are irregular. X-Ray crystallographic studies²³ on a range of azamacrocyclic complexes of Ni^{II} have identified an inverse correlation between $d(\text{Ni}-\text{X})$ and $d(\text{Ni}-\text{N})$, although changes in bond lengths between complexes are small. In the present case of the selenium ligands the small number of examples available makes more detailed discussion impossible. Nonetheless the structural data confirm the pseudo-octahedral geometries inferred spectroscopically.

Experimental

Infrared spectra were measured as CsI discs or as Nujol mulls between CsI plates using a Perkin-Elmer 983 spectrometer over the range 200–4000 cm⁻¹, UV/VIS spectra by diffuse reflectance

using samples diluted with BaSO₄ using a Perkin-Elmer Lambda 19 spectrophotometer. Magnetic measurements used a Johnson Matthey balance. The EXAFS measurements were made at the Daresbury Synchrotron Radiation Source, operating at 2.0 GeV with typical currents of 200 mA. Nickel K-edge data were collected on station 7.1 using a silicon(111) order-sorting monochromator, with harmonic rejection achieved by stepping off the peak of the rocking curve by 50% of full height level. Data were collected in transmission mode from either neat samples, or samples diluted with boron nitride as appropriate, and mounted between Sellotape in 1 mm aluminium holders.

The compounds [16]aneSe₄ and MeSeCH₂CH₂SeMe were prepared by the literature procedures.^{2,27}

Synthesis

The products were assumed to be air and moisture sensitive and prepared using Schlenk equipment. Samples were manipulated in a glove-box (<10 ppm water) using standard air sensitive

Table 2 Selected bond lengths (Å) and angles for *trans*-[NiCl₂(MeSeCH₂CH₂SeMe)₂]

Se(1)–Ni(1)	2.5581(9)	Se(1)–C(1)	1.941(9)
Se(1)–C(2)	1.949(9)	Se(2)–Ni(1)	2.5536(9)
Se(2)–C(3)	1.951(9)	Se(2)–C(4)	1.944(9)
Se(3)–Ni(2)	2.522(1)	Se(3)–C(5)	1.946(9)
Se(3)–C(6)	1.933(9)	Se(4)–Ni(2)	2.5623(8)
Se(4)–C(7)	1.942(9)	Se(4)–C(8)	1.966(9)
Ni(1)–Cl(1)	2.370(2)	Ni(1)–Cl(1)	2.370(2)
Ni(2)–Cl(2)	2.376(2)	Ni(2)–Cl(2)	2.376(2)
C(2)–C(3)	1.50(1)	C(6)–C(7)	1.51(1)
Ni(1)–Se(1)–C(1)	110.0(3)	Ni(1)–Se(1)–C(2)	96.9(3)
C(1)–Se(1)–C(2)	96.9(4)	Ni(1)–Se(2)–C(3)	98.4(3)
Ni(1)–Se(2)–C(4)	107.2(3)	C(3)–Se(2)–C(4)	97.5(4)
Ni(2)–Se(3)–C(5)	111.2(3)	Ni(2)–Se(3)–C(6)	97.2(3)
C(5)–Se(3)–C(6)	97.4(4)	Ni(2)–Se(4)–C(7)	97.5(3)
Ni(2)–Se(4)–C(8)	110.0(3)	C(7)–Se(4)–C(8)	97.8(4)
Se(1)–Ni(1)–Cl(1*)	95.34(5)	Se(1)–Ni(1)–Se(2)	89.55(3)
Se(2)–Ni(1)–Cl(1*)	84.35(6)	Se(1)–Ni(1)–Cl(1)	84.66(5)
Se(3)–Ni(2)–Se(4)	90.15(3)	Se(1)–Ni(1)–Se(2*)	90.45(3)
Se(3)–Ni(2)–Cl(2)	96.73(5)	Se(4)–Ni(2)–Cl(2)	84.69(6)
Se(1)–C(2)–C(3)	114.1(6)	Se(2)–C(3)–C(2)	113.5(6)
Se(3)–C(6)–C(7)	114.7(6)	Se(4)–C(7)–C(6)	113.5(6)

Table 3 The nickel K-edge EXAFS data^a for nickel(II) selenoether compounds

Complex	$d(\text{Ni}-\text{Se})^b/\text{Å}$	$2\sigma^2/\text{Å}^2$	$d(\text{Ni}-\text{X})^b/\text{Å}$	$2\sigma^2/\text{Å}^2$	R^d	Fit index ^e
[NiCl ₂ ([16]aneSe ₄)]	2.600(3)	0.0187(5)	2.393(4)	0.0085(6)	17.2	2.3
[NiBr ₂ ([16]aneSe ₄)]	2.584(6)	0.0206(10)	2.507(3)	0.0094(4)	21.8	3.0
[NiI ₂ ([16]aneSe ₄)]	2.506(2)	0.0129(2)	2.781(5)	0.0175(07)	25.2	4.1
[NiCl ₂ (MeSeCH ₂ CH ₂ SeMe) ₂]	2.531(4)	0.0169(6)	2.349(5)	0.0074(7)	26.0	4.6
[NiBr ₂ (MeSeCH ₂ CH ₂ SeMe) ₂]	2.574(5)	0.0097(6)	2.446(6)	0.0072(8)	17.6	3.5
[NiI ₂ (MeSeCH ₂ CH ₂ SeMe) ₂]	2.541(3)	0.0164(5)	2.739(7)	0.0182(13)	26.9	7.2

^a Data were recorded in transmission mode on station 7.1, using powdered samples diluted with BN where appropriate. AFAC = 0.80 for all refinements. ^b Standard deviations in parentheses. Note that the systematic errors in bond distances arising from data collection and analysis procedures are $\pm 0.02-0.03$ Å for well defined co-ordination shells. ^c Debye–Waller factor. ^d Defined as $[(\chi^T - \chi^E)k^3 dk / \chi^E k^3 dk] \times 100\%$. ^e Defined as $\sum [(\chi^T - \chi^E)k_i^3]^2$.

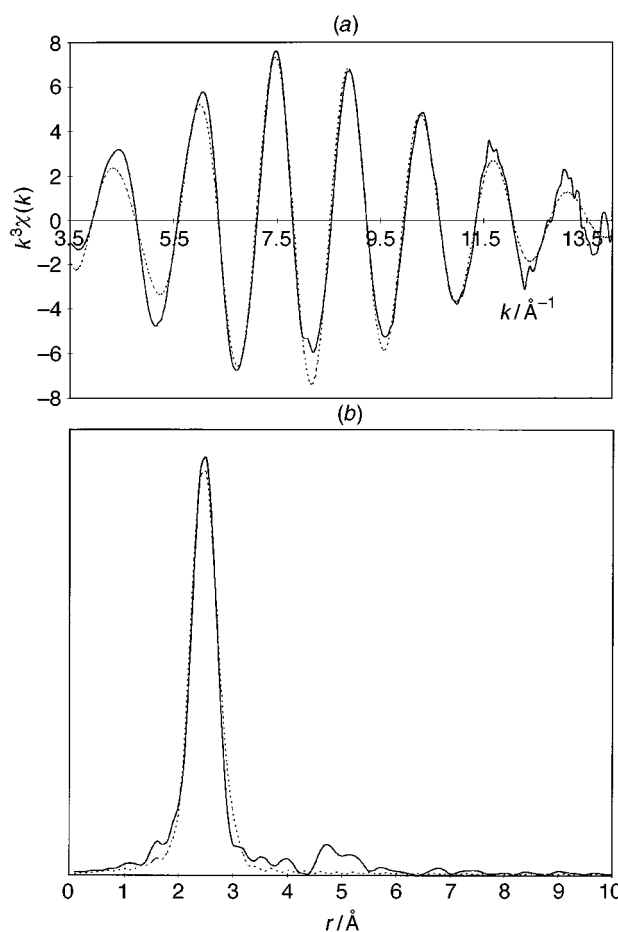


Fig. 2 The background subtracted nickel K-edge EXAFS data (a) and the corresponding Fourier transform (b) for *trans*-[NiCl₂([16]aneSe₄)] (solid line, experimental; dashed line, calculated data)

techniques. Solvents were dried using conventional methods and distilled under dinitrogen. Nickel(II) iodide was prepared *in situ* by the reaction of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 2 equivalents of KI in *n*-butanol or nitromethane, the precipitated KNO_3 being removed by filtration.

[NiCl₂([16]aneSe₄)]. The compound [16]aneSe₄ (0.100 g, 2.1×10^{-4} mol) was added to a stirring solution of NiCl₂ (0.027 g, 2.1×10^{-4} mol) in *n*-butanol (10 cm³) under an atmosphere of dinitrogen. The resulting mixture was heated at 60 °C for *ca.* 45 min yielding a pale green precipitate. This solid was isolated by filtration, rinsed with diethyl ether and dried *in vacuo*. Yield 0.1 g, 78% (Found: C, 23.5; H, 4.1. Calc. for C₁₂H₂₄Cl₂NiSe₄: C, 23.5; H, 3.9%). $\tilde{\nu}/\text{cm}^{-1}$ (Ni–Cl) 249. μ 3.02 ± 0.01 μ_{B} .

[NiBr₂([16]aneSe₄)]. This was prepared similarly from [16]aneSe₄ (0.100 g, 2.1×10^{-4} mol) and NiBr₂ (0.046 g, 2.1×10^{-4} mol) in *n*-butanol (10 cm³). Yield 0.116 g, 79% (Found: C, 20.2; H, 3.6. Calc. for C₁₂H₂₄Br₂NiSe₄: C, 20.5; H, 3.4%). μ 3.07 μ_{B} .

[NiI₂([16]aneSe₄)]. The compound [16]aneSe₄ (0.100 g, 2.1×10^{-4} mol) was added to a stirring solution of NiI₂ (2.1×10^{-4} mol, prepared as described above) in *n*-butanol (10 cm³) under an atmosphere of dinitrogen. The resulting mixture was heated at 60 °C for *ca.* 45 min yielding an orange-brown precipitate. This solid was isolated by filtration, rinsed with diethyl ether and dried *in vacuo*. Yield 0.122 g, 73% (Found: C, 17.8; H, 2.9. Calc. for C₁₂H₂₄I₂NiSe₄: C, 18.1; H, 3.0%). μ 3.10 μ_{B} .

[NiCl₂(MeSeCH₂CH₂SeMe)₂]. To a solution of NiCl₂ (0.052 g, 4×10^{-4} mol) in *n*-butanol (10 cm³) was added a solution of MeSeCH₂CH₂SeMe (0.17 g, 8×10^{-4} mol) in *n*-butanol (2 cm³) *via* a syringe. The resulting pale green solution was heated at 60 °C for *ca.* 1 h under an atmosphere of dinitrogen, filtered (Celite) and reduced *in vacuo* to *ca.* 6 cm³. This solution was then stored in a freezer (−18 °C) yielding lime green blocks of [NiCl₂(MeSeCH₂CH₂SeMe)₂]. The crystalline product was isolated by filtration, rinsed with diethyl ether and dried *in vacuo*. Yield 0.117 g, 52% (Found: C, 17.3; H, 3.7. Calc. for C₈H₂₀Cl₂NiSe₄: C, 17.1; H, 3.6%). $\tilde{\nu}/\text{cm}^{-1}$ (Ni–Cl) 260.

[NiBr₂(MeSeCH₂CH₂SeMe)₂]. To a solution of NiBr₂ (0.087 g, 4×10^{-4} mol) in *n*-butanol (10 cm³) was added a solution of MeSeCH₂CH₂SeMe (0.17 g, 8×10^{-4} mol) in *n*-butanol (2 cm³) *via* a syringe. Work-up as above yielded a lime green solid. Yield 0.196 g, 75% (Found: C, 14.8; H, 3.1. Calc. for C₁₂H₂₄Br₂NiSe₄: C, 14.8; H, 3.1%).

[NiI₂(MeSeCH₂CH₂SeMe)₂]. Prepared as above from a solution of NiI₂ (4×10^{-4} mol) in *n*-butanol (10 cm³) and a solution of MeSeCH₂CH₂SeMe (0.17 g, 8×10^{-4} mol) in *n*-butanol (2 cm³) as an orange-brown precipitate. Yield 0.217 g, 68% (Found: C, 12.7; H, 2.8. Calc. for C₁₂H₂₄I₂NiSe₄: C, 12.9; H, 2.7%).

[NiCl₂([16]aneS₄)]. To a solution of NiCl₂ (0.026 g, 2.0×10^{-4} mol) in nitromethane (10 cm³) was added a solution of [16]aneS₄ (0.061 g, 2.0×10^{-4} mol) in dichloromethane (3 cm³) *via* a syringe. The reaction mixture was heated at 60 °C for *ca.* 1 h under an atmosphere of dinitrogen yielding a pale turquoise precipitate. This solid was isolated by filtration, rinsed with diethyl ether and dried *in vacuo*. Yield 0.049 g, 58% (Found: C, 34.0; H, 5.4. Calc. for C₁₂H₂₄Cl₂NiS₄: C, 33.8; H, 5.6%). $\tilde{\nu}/\text{cm}^{-1}$ (Ni–Cl) 224. μ 3.0 μ_{B} .

[NiBr₂([16]aneS₄)]. To a solution of NiBr₂ (0.044 g, 2.0×10^{-4} mol) in nitromethane (10 cm³) was added a solution of [16]aneS₄ (0.061 g, 2.0×10^{-4} mol) in dichloromethane (3 cm³)

via a syringe. The reaction mixture was heated at 60 °C for *ca.* 1 h under an atmosphere of dinitrogen yielding a pale green precipitate. This solid was isolated by filtration, rinsed with diethyl ether and dried *in vacuo*. Yield 0.065 g, 63% (Found: C, 27.9; H, 4.4. Calc. for C₁₂H₂₄Br₂NiS₄: C, 28.0; H, 4.7%). μ 2.95 μ_{B} .

[NiI₂([16]aneS₄)]. Prepared as above from a solution of NiI₂ (2.0×10^{-4} mol) in nitromethane (10 cm³) and a solution of [16]aneS₄ (0.061 g, 2.0×10^{-4} mol) in dichloromethane (3 cm³), as a brick-red precipitate. Yield 0.080 g, 66% (Found: C, 23.2; H, 4.1. Calc. for C₁₂H₂₄I₂NiS₄: C, 23.7; H, 3.9%). μ 3.1 μ_{B} .

Crystallography

Lime green blocks of [NiCl₂(MeSeCH₂CH₂SeMe)₂] were obtained from *n*-butanol solution. The selected crystal (0.40 × 0.20 × 0.15 mm) was coated with mineral oil and mounted on a glass fibre under a cold stream of nitrogen gas.

Crystal data. C₈H₂₀Cl₂NiSe₄, *M* = 561.69, monoclinic, space group *P*2₁/*c*, *a* = 14.466(4), *b* = 7.838(2), *c* = 15.641(5) Å, β = 114.86(2)°, *U* = 1607.9(8) Å³ [from 2θ values of 16 reflections measured at ±ω (2θ = 21.7–27.5°, λ = 0.710 73 Å)], *Z* = 4, *D*_c = 2.320 g cm^{−3}, μ = 105.67 cm^{−1}, *F*(000) = 1064.

Data collection and processing. Data collection used a Rigaku AFC7S diffractometer equipped with an Oxford Systems cryostream operating at 150 K, using graphite monochromated Mo-Kα radiation (ω–2θ scan technique). 3198 Data collected (2θ_{max} 50.0°), 3072 unique (*R*_{int} = 0.040 based on *F*²). An absorption correction was applied *via* ψ-scans (maximum transmission factor = 1.000, minimum transmission factor = 0.435). No significant crystal decay or movement was observed.

Structure solution and refinement. The structure was solved by heavy atom methods²⁸ and expanded using Fourier techniques to locate all non-H atoms for the two half molecules in the asymmetric unit, each of which possesses crystallographic *i* symmetry.²⁹ All non-H atoms were refined anisotropically and hydrogen atoms were included in fixed, calculated positions [*d*(C–H) = 0.96 Å] but not refined. The final cycle of full-matrix least-squares refinement (on *F*) was based on 2053 observed reflections [*I* > 2.5σ(*I*)] and 139 variable parameters and converged with *R* = 0.037, *R*_w 0.049 and *S* = 1.48, using the weighting scheme *w*^{−1} = σ²(*F*). The maximum residual peak and minimum residual trough corresponded to +0.81 and −0.96 e Å^{−3}.

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EXAFS data refinement

Typically two or three data sets were collected for each complex and the analyses were carried out on the averaged spectra. The raw data were background-subtracted using the program PAXAS³⁰ by fitting a six- or eight-order split polynomial to the pre-edge subtracted spectrum between *k* = 2 up to 13–15 Å^{−1}. Curve fitting was carried out using the program EXCURV-92.³¹ Ground state potentials of the atoms were calculated using Von Barth theory and phase shifts using Hedin–Lundqvist potentials. Two shells (4 Se and 2 X) were fitted in each case. EXAFS Refinements were also carried out for the bromo-complexes using 6 Se or 6 Br, but here as well the two-shell model was statistically better.²⁶ The distances and Debye–Waller factors were refined for all the shells, as well as the Fermi energy difference. No attempt was made to refine the carbons of the ligand backbones since these occur over a range of distances and are not expected to be well defined. The [NiCl₂(MeSeCH₂CH₂SeMe)₂] complex served as a model to check data collection and refinement.

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