

Synthesis, Properties, and ^{77}Se Nuclear Magnetic Resonance Studies of Platinum Metal Complexes of Two Isomeric Tris(selenoethers), $\text{MeC}(\text{CH}_2\text{SeMe})_3$ and $\text{Se}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SeMe})_2$ †

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The synthesis and properties of platinum metal complexes of $\text{MeC}(\text{CH}_2\text{SeMe})_3$ (tmse) and $(\text{MeSeCH}_2\text{CH}_2\text{CH}_2)_2\text{Se}$ (bmsp), including diamagnetic $[\text{M}(\text{tmse})\text{Cl}_2]$ ($\text{M} = \text{Pd}$ or Pt), $[\text{M}'(\text{tmse})\text{Cl}_3]$ ($\text{M}' = \text{Rh}$ or Ir), $[\text{Pd}(\text{bmsp})\text{Cl}_2]$, $[\text{Pt}(\text{bmsp})\text{Cl}]\text{PF}_6$, and $[\text{M}'(\text{bmsp})\text{Cl}_3]$ are described. Paramagnetic $[\text{RuLCl}_3]$, $[\text{OsLCl}_4]$, and $[\text{OsLCl}_3]$ ($\text{L} = \text{tmse}$ or bmsp) are also reported. The complexes were characterised by i.r., electronic, and ^1H n.m.r. spectroscopy or magnetic measurements as appropriate. For the diamagnetic complexes, ^{77}Se and ^{195}Pt n.m.r. spectroscopy have been used to identify the major invertomers present. Complexes of the trithioether analogues are briefly described.

We have recently reported the synthesis and ^{77}Se n.m.r. spectra of platinum(II), palladium(II), and rhodium(III) complexes of a variety of diselenoethers.¹ Both the ^{77}Se chemical shifts [$\delta(^{77}\text{Se})$] and the coupling constants [$^1J(^{195}\text{Pt}-^{77}\text{Se})$, $^1J(^{103}\text{Rh}-^{77}\text{Se})$] were found to be sensitive parameters, responding in predictable ways to changes in the metal, the substituents at Se, chelate ring size, and the *trans* ligands, and clearly distinguishing the invertomers present. Here we extend these studies to more complicated systems, platinum metal complexes of the isomeric tris(selenoethers)² 1,1,1-tris(methylselenomethyl)ethane $\text{MeC}(\text{CH}_2\text{SeMe})_3$ (tmse) and bis(3-methylselenopropyl) selenide $(\text{MeSeCH}_2\text{CH}_2\text{CH}_2)_2\text{Se}$ (bmsp). The only reported complexes of a polyselenoether are $[\text{Pd}_2\text{X}_4\{(\text{MeSeCH}_2\text{CH}_2\text{SeCH}_2)_2\text{CH}_2\}]$.³

Results and Discussion

The reactions of the two ligands tmse and bmsp with $[\text{Pd}(\text{MeCN})_2\text{Cl}_2]$, PtCl_4^{2-} , $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$, and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ in 1:1 mol ratios produced the expected MLCl_n complexes (Table 1), except for the bmsp-PtCl_4^{2-} reaction which gave an intractable oil. However, reaction of PtCl_4^{2-} , bmsp, and NaPF_6 in water-ethanol gave $[\text{Pt}(\text{bmsp})\text{Cl}]\text{PF}_6$. From the reactions of the ligands with $\text{Na}_2[\text{OsX}_6]$ ($\text{X} = \text{Cl}$ or Br) both osmium(III), $[\text{OsLX}_3]$, and osmium(IV), $[\text{OsLX}_4]$, complexes were produced. With the exception of $[\text{Pt}(\text{bmsp})\text{Cl}]\text{PF}_6$ which is a 1:1 electrolyte, and $[\text{OsLX}_4]$ which were insoluble in common solvents, the complexes (Table 1) were non-electrolytes. This is consistent with the usual behaviour of platinum metal complexes of neutral Group 6B ligands, which co-ordinate halides to neutralise the charge on the metal, and fill any remaining co-ordination sites with the neutral donors.⁴ This effect and the steric constraints of the ligand account for the formation of $[\text{Cl}_2\text{Pd}\{(\text{MeSeCH}_2)_2\text{C}(\text{CH}_2\text{SeMe})_2\}\text{PdCl}_2]$ by the spirocyclic $\text{C}(\text{CH}_2\text{SeMe})_4$. It is convenient to discuss the diamagnetic complexes of the two ligands separately.

Complexes of $\text{MeC}(\text{CH}_2\text{SeMe})_3$ (tmse) with Pd, Pt, Rh, and Ir.—The tripodal tmse ligand is sterically constrained such that

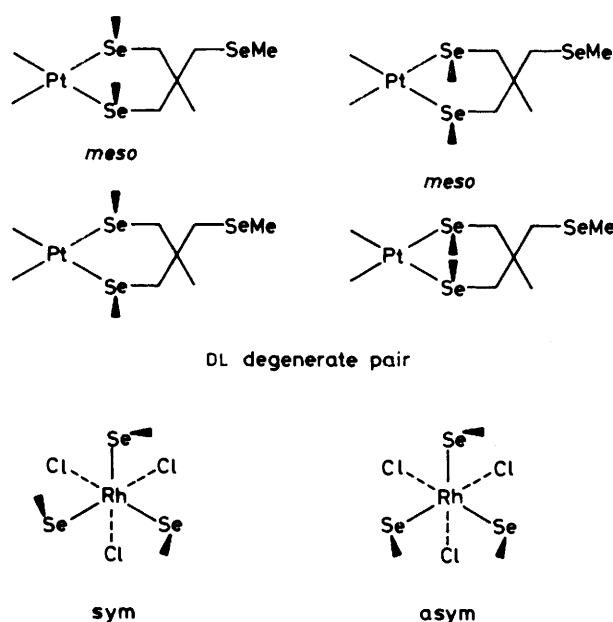


Figure 1. Possible invertomers of $[\text{Pt}(\text{tmse})\text{Cl}_2]$ and $[\text{Rh}(\text{tmse})\text{Cl}_3]$ (▼ = lone pair, methyl groups omitted for clarity)

it can only co-ordinate in a *cis*-bidentate manner to planar four-co-ordinate metal centres, and in a *cis*-bidentate or *fac*-tridentate manner to octahedral metal centres. The assignment of the predicted *cis*-planar geometry (Se_2Cl_2 donor set) to $[\text{M}(\text{tmse})\text{Cl}_2]$ ($\text{M} = \text{Pt}$ or Pd) is confirmed by the similarity of their far-i.r. and electronic spectra to those of corresponding $[\text{M}(\text{diselenoether})\text{Cl}_2]$.¹ However the identification of the invertomers present is less straightforward. For $[\text{Pt}(\text{tmse})\text{Cl}_2]$ the complex ^1H n.m.r. spectrum indicates that pyramidal inversion⁵ is slow on the n.m.r. time-scale at ambient temperatures, but the very small chemical shift differences between the MeC and MeSe resonances of the various isomers make invertomer identification uncertain, a problem exacerbated by the relatively poor solubility. Fortunately the ^{77}Se and

† 1,1,1-Tris(methylselenomethyl)ethane and bis(3-methylselenopropyl) selenide.

Table 1. Selected spectroscopic and physical data

Compound	Colour	$\tilde{\nu}(\text{MX})/\text{cm}^{-1}$	$10^{-3} E_{\text{max}}/\text{cm}^{-1}$	$\mu_{\text{eff.}}^b/\text{B.M.}$	$^1\text{H N.m.r. (CH}_3 \text{ groups only)}$
[Pd(tmse)Cl ₂]	Yellow	314s, 304 (sh)	25.3 (1 700)		^c 1.30, 1.34 (MeC), 2.1, 2.62, 2.64, 2.65, 2.67 (MeSe) ^d
[Pt(tmse)Cl ₂]	Yellow	321s, 308 (sh)	27.0 (500)		^c 1.13, 1.16 (MeC), 1.98, 2.68, 2.70, 2.79, 2.82 (MeSe)
[Rh(tmse)Cl ₃]	Yellow	337s, 307m	21.6 (110), 32.8 (1 920)		^c 1.21, 1.24 (MeC), 2.01, 2.04, 2.06 (MeSe)
[Ir(tmse)Cl ₃]	Buff	309s, 294 (sh)	25.3 (184), 31.6 (360)		^c 1.27, 1.30 (MeC), 2.00, 2.02, 2.04 (MeSe)
[Ru(tmse)Cl ₃]	Brown	308s, 296m	16.1 (1 300), 19.2 (1 540), 23.2 (2 830), 27.4 (3 330)	1.78	
[Os(tmse)Cl ₄]	Black	317 (sh), 308s, 284m	16.3, 17.4, 22.2, 25.4 (dr) ^e	1.37	
[Os(tmse)Cl ₃]	Brown	304s, 291m	23.8 (1 510), 26.2 (4 300), 29.8 (5 230)	2.18	
[Pd(bmsp)Cl ₂]	Yellow	312br	26.6 (2 060), 31.2 (16 000)		^c 2.00, 2.40, 2.46 ^f
[Pt(bmsp)Cl]PF ₆ ^g	Yellow	320m	24.3 (350), 28.0 (2 400)		^h 2.42, 2.52, 2.56, 2.58; ³ J(Pt-H) (av.) ca. 38 Hz
[Rh(bmsp)Cl ₃]	Yellow	336s, 307s	21.7 (230), 26.5 (8 500)		^h 2.34, 2.35, 2.37
[Ir(bmsp)Cl ₃]	Buff	314s, 295 (sh)	26.0 (180), 31.4 (330)		^h 2.24, 2.26, 2.28
[Os(bmsp)Cl ₄]	Black	318s, 312s, 300 (sh)	17.0, 21.0, 28.0, 30.0 (dr)	1.41	
[Os(bmsp)Cl ₃]	Olive-green	308s, 283m	23.3 (1 680), 26.5 (3 130), 30.1 (5 700)	1.98	
[Ru(bmsp)Cl ₃]	Dark brown	327m, 308m, 300 (sh)	18.8 (1 420), 24.2 (1 770)		
[Os(bmsp)Br ₄]	Black		17.0, 19.6, 25.0 (dr)	1.32	
[Os(bmsp)Br ₃]	Brown	220s, br	23.8 (3 950), 26.2 (3 150), 28.9 (3 650)	1.88	
[Pd ₂ {C(CH ₂ SeMe) ₄ }Cl ₄]	Yellow	314s, 305s	21.3, 24.9, 31.5 (dr)		
[Pd(bmtp)Cl ₂]	Yellow	296m, 318m	27.7 (1 980)		^c 2.18, 2.60, 2.70
[Pt(bmtp)Cl]PF ₆	Pale yellow	320s	28.9 (360)		^h 2.55, 2.59, 2.64; ³ J(Pt-H) (av.) 40 Hz
[Rh(bmtp)Cl ₃]	Orange-brown	351s, 311m	22.1 (148), 27.2 (740)		^c 2.34, 2.36, 2.37
[Ir(bmtp)Cl ₃]	Buff	307s, 291s	27.4 (142), 32.5 (275)		^c 2.21, 2.24, 2.28
[Ir(tmte)Cl ₃]	Buff	309s, 281 (sh)	27.2 (230), 32.5 (410)		^c 1.0, 1.1 (MeC), 2.07, 2.15, 2.22 (MeS)

^a For solutions in dimethyl sulphoxide except where stated otherwise; $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ given in parentheses. ^b Obtained by Gouy method; ± 0.05 B.M. (B.M. = $9.274 \times 10^{-24} \text{ J T}^{-1}$) ^c In $(\text{CD}_3)_2\text{SO}$ solutions; relative to SiMe_4 at 298 K unless otherwise indicated. ^d At 193 K. ^e dr = Diffuse reflectance. ^f At 183 K. ^g $\Lambda_M (10^{-3} \text{ mol dm}^{-3}, \text{Me}_2\text{CO}) = 111 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; 1:1 electrolytes have $\Lambda_M = \text{ca. } 120 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (W. J. Geary, *Coord. Chem. Rev.*, 1971, 7, 81). ^h In CD_2Cl_2 at 298 K unless indicated otherwise.

¹⁹⁵Pt n.m.r. spectra are clearer [despite the much poorer receptivities, $Dp(\text{Se}) \text{ ca. } 5.3 \times 10^{-4}$, $Dp(\text{Pt}) \text{ ca. } 3.4 \times 10^{-3}$]⁶ due to the smaller number of magnetically active nuclei and the wider chemical shift ranges. The ¹⁹⁵Pt n.m.r. spectrum shows that three invertomers are present (Figure 1), two 'meso' and one degenerate 'DL' pair,* the latter being identified by the presence of two pairs of selenium satellites (Table 2) since the two co-ordinated seleniums are not equivalent in this invertomer. Correspondingly the ⁷⁷Se spectrum shows four resonances with ¹⁹⁵Pt satellites which can be correlated via the ¹J(¹⁹⁵Pt-⁷⁷Se) coupling constants with the invertomers identified in the ¹⁹⁵Pt spectrum. The ⁷⁷Se spectrum also shows a signal at 24.1 p.p.m. due to the unco-ordinated MeSe groups, little shifted from that in the free ligand (δ 23 p.p.m.). The ⁷⁷Se spectrum of [Pd(tmse)Cl₂] at 298 K is surprisingly simple showing two resonances at 187.4 and 24.9 p.p.m. due to co-ordinated and unco-ordinated MeSe groups respectively, demonstrating that exchange between them does not occur. The simple spectrum is due to rapid pyramidal inversion (*cf.* [Pd{MeSe(CH₂)₃SeMe}Cl₂]¹ but at 223 K four resonances of

co-ordinated MeSe groups are present in addition to the free MeSe signal, analogous to the room-temperature spectrum of the platinum complex. The shift (*ca.* 3 p.p.m.) in the 'free' MeSe resonance between 298 and 223 K is due both to the variation in ⁷⁷Se shift with temperature and a solvent shift produced by adding CD_2Cl_2 to the $(\text{CD}_3)_2\text{SO}$ solution to allow the low temperature to be reached. The co-ordination shifts ($\delta_{\text{complex}} - \delta_{\text{free ligand}}$) in these complexes correlate well with those found in [M{MeSe(CH₂)₃SeMe}Cl₂]¹ which also contain six-membered chelate rings, further support for the presence of a characteristic ring contribution to $\delta(^{77}\text{Se})$.

From the geometry of the ligand [M(tmse)Cl₃] (M = Rh or Ir) are expected to be facial isomers, and this was confirmed by the presence of two i.r.-active $\nu(\text{MCl})$ modes (theory $a_1 + e$) in the far-i.r. spectra (Table 1). Molecular models suggest that only two invertomers are possible (Figure 1) with the MeSe groups symmetrically arranged, or with one 'reversed' (asym in Figure 1). Both complexes are poorly soluble even in dimethyl sulphoxide, and this necessitated very long accumulations to obtain ⁷⁷Se spectra. There are three doublets in the ⁷⁷Se spectrum of [Rh(tmse)Cl₃] and three singlets in that of [Ir(tmse)Cl₃], in agreement with the three environments predicted for the two invertomers. The very poor solubility

* We use 'meso' to describe the forms with *syn* terminal methyl groups and 'DL' those with *anti* groups.

Table 2. Selenium-77 and ^{195}Pt n.m.r. data^a

Compound		$^{77}\text{Se}^b$	^{195}Pt	Solvent
[Pt(tmse)Cl ₂]	<i>meso</i>	155.6 (561)	-3 442 -3 444 -3 499	(CD ₃) ₂ SO
	<i>meso</i>	166.9 (486)		
	DL	160.5 (445), 164.1 (509)		
[Pd(tmse)Cl ₂]		187.4, 24.9		(CD ₃) ₂ SO
[Rh(tmse)Cl ₃]	<i>c</i>	190.2, 188.8, 186.7, 181.5, 28.5		
	<i>sym</i>	235.3 (41)		(CD ₃) ₂ SO
[Ir(tmse)Cl ₃]	<i>asym</i>	227.5 (39), 222.2 (38)		
	<i>sym</i>	185.2		(CD ₃) ₂ SO
[Pt(bmsp)Cl] [†]	<i>asym</i>	183.2, 181.7		
	<i>meso</i>	189.5 (360), 162.2 (211)	-3 786	CD ₂ Cl ₂
	<i>meso</i>	185.7 (309), 167.0 (232)	-3 743	
[Rh(bmsp)Cl ₃] ^d	DL	183.5 (308), 124.2 (308), 121.9 (304)	-3 699	
	<i>meso</i>	229.3 (43.5), 170.0 (39)		CD ₂ Cl ₂
	<i>meso</i>	228.3 (52), 169.0 (50)		
[Ir(bmsp)Cl ₃]	DL	220.9 (42), 166.7 (38), 165.5 (37)		
		188.2, 182.8, 145.8, 144.1, 139.1		CD ₂ Cl ₂

^a At 298 K unless indicated otherwise. ^b $^1J(^{195}\text{Pt}-^{77}\text{Se})$ or $^1J(^{103}\text{Rh}-^{77}\text{Se})$ in Hz given in parentheses. ^c At 223 K in (CD₃)₂SO-CD₂Cl₂. ^d Tentative assignments.

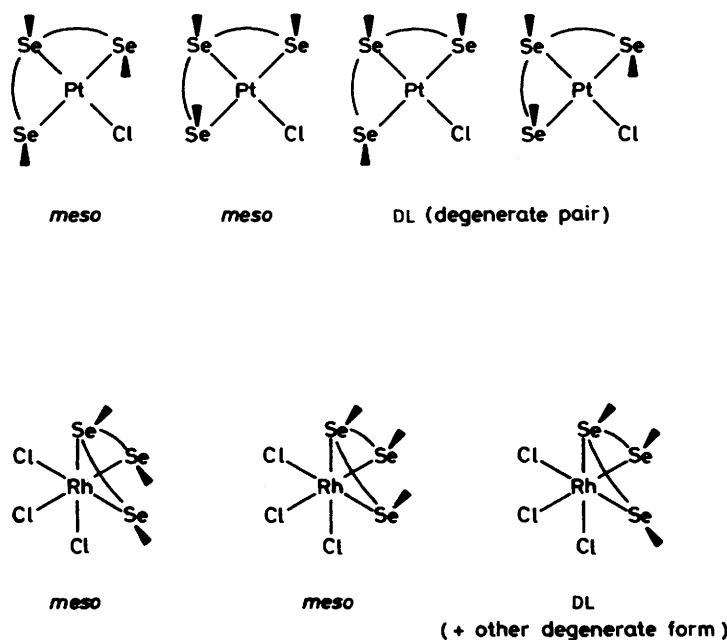


Figure 2. Possible invertomers of [Pt(bmsp)Cl][†] and [Rh(bmsp)Cl₃]; for the latter, three other invertomers have the central lone pair pointing away from the Se₃ face (▼ = lone pair, methyl groups omitted for clarity)

prevented the ^{103}Rh n.m.r. spectrum from being obtained as an independent check.

Complexes of Se(CH₂CH₂CH₂SeMe)₂ with Pd, Pt, Rh, and Ir.—The flexible tris(selenoether) bmsp does not impose steric constraints on the structures of the metal complexes, and in principle could bind in a *cis*-bidentate or tridentate manner to planar four-co-ordinate metal centres, and in a *cis*-bidentate, *mer*- or *fac*-tridentate manner to six-co-ordinate metals. The physical data on [Pt(bmsp)Cl]PF₆ show that it is planar (Se₃Cl donor set), the static ^1H n.m.r. spectrum confirming that both MeSe groups are co-ordinated and that several invertomers are present. Models predict three invertomers, two *meso* forms and an n.m.r.-indistinguishable DL pair (Figure 2). This is consistent with the ^{195}Pt n.m.r. spectrum which shows three resonances with selenium satellites (Table 2, Figure 3). The resonances of

the *meso* forms have two selenium satellites (central Se and equivalent terminals), and the DL should have three (central Se and inequivalent terminals) but only *one* was evident. However the ^{77}Se spectrum shows the expected four MeSe and three CH₂SeCH₂ resonances (Figure 4) and those due to the *meso* invertomers can be correlated *via* the $^1J(^{195}\text{Pt}-^{77}\text{Se})$ couplings with the ^{195}Pt spectrum. The apparent anomaly of 'one' selenium satellite upon the ^{195}Pt resonance of the DL invertomer arises since the three $^1J(^{195}\text{Pt}-^{77}\text{Se})$ couplings are very similar, as measured in the ^{77}Se spectrum, 304, 308, and 308 Hz, and in view of the poor solubility (the spectrum shown in Figure 3 required 90 000 transients) our failure to resolve them is not surprising.

A [Pd(bmsp)Cl₂] complex in which bmsp acts in a bidentate manner was isolated. The presence of a Se₂Cl₂ donor set was shown by the small conductance [Λ_{M} (10⁻³ mol dm⁻³,

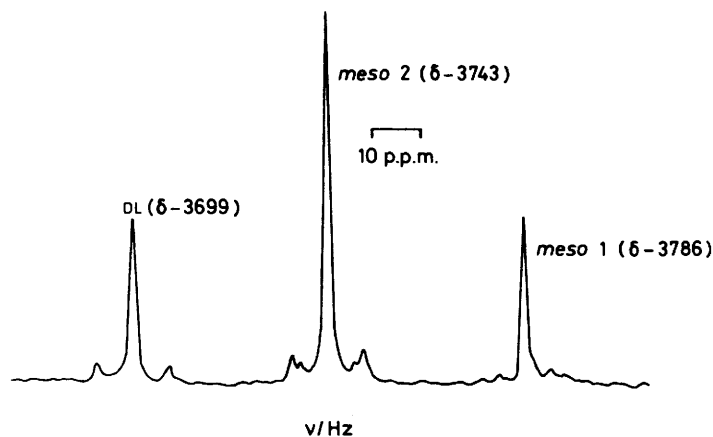


Figure 3. 19.16-MHz ^{195}Pt n.m.r. spectrum of $[\text{Pt}(\text{bmsp})\text{Cl}]\text{PF}_6$ (90 000 transients)

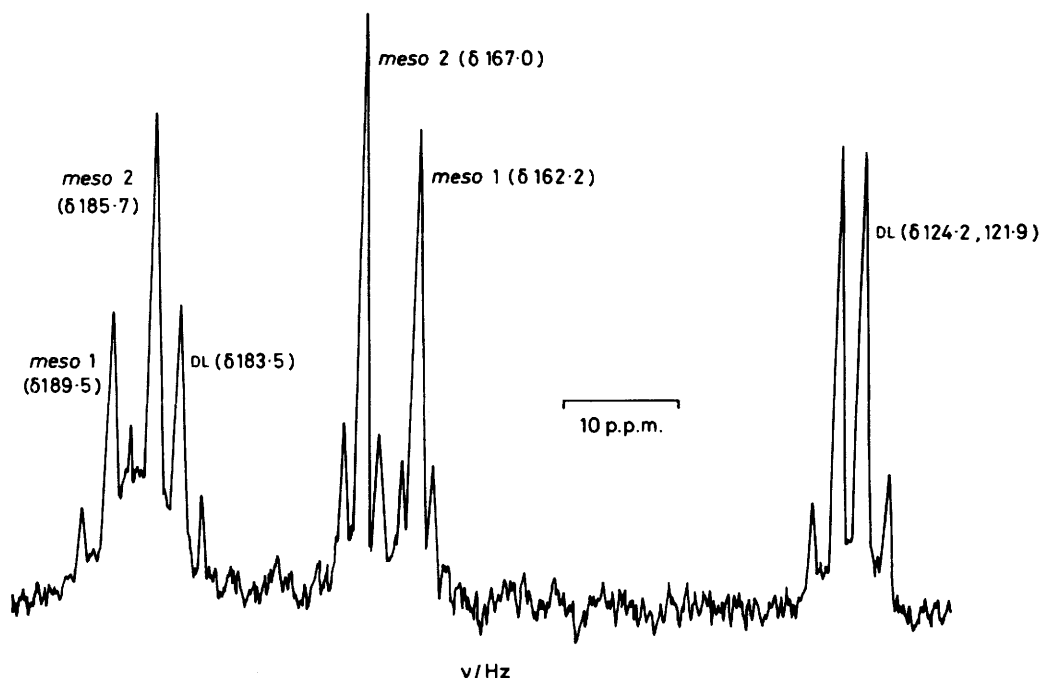


Figure 4. 68.68-MHz ^{77}Se n.m.r. spectrum of $[\text{Pt}(\text{bmsp})\text{Cl}]\text{PF}_6$ (34 000 transients)

$\text{Me}_2\text{CO}) = 29 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$],* and the electronic spectrum which rules out a five-co-ordinate palladium centre.⁷ However both the ^1H and ^{77}Se n.m.r. spectra at 298 K contain broad ill defined resonances, and neither showed the expected resonance due to the 'unco-ordinated' MeSe group, indicating fast exchange between the bound and free MeSe groups. On cooling a CD_2Cl_2 solution of the complex the ^1H n.m.r. spectrum sharpens and at 193 K both exchange and pyramidal inversion have ceased. The solubility of $[\text{Pd}(\text{bmsp})\text{Cl}_2]$ at this temperature is poor and the assignment should be viewed in this light, but we propose that the unco-ordinated MeSe group has $\delta(\text{Me}) = 2.00$ p.p.m., and the two Me signals at $\delta = 2.40$ and 2.46 p.p.m. are due to invertomers produced by bidentate co-ordinated bmsp. The ^{77}Se n.m.r. spectrum at 298 K shows a single very broad resonance at $\delta = 237$ p.p.m. which is probably due to $\text{Se}(\text{CH}_2)_2$, but no SeMe resonances were observed; presumably they are too broad due to exchange. A ^{77}Se spectrum at low

temperature (< 213 K) could not be obtained due to solubility problems.

The complexes $[\text{M}(\text{bmsp})\text{Cl}_3]$ ($\text{M} = \text{Rh}$ or Ir) have very similar patterns of $\nu(\text{MCl})$ stretches in the i.r. spectra to those of *fac*- $[\text{M}(\text{tmse})\text{Cl}_3]$, and the electronic spectra are also analogous, suggesting the bmsp complexes are *fac* isomers. The ^{77}Se n.m.r. spectrum of $[\text{Rh}(\text{bmsp})\text{Cl}_3]$ is shown in Figure 5 and exhibits three doublets due to CH_2SeCH_2 , and four assignable as SeMe.

The complex *fac*- $[\text{Rh}(\text{bmsp})\text{Cl}_3]$ has potentially six invertomers (four *meso* and two degenerate DL pairs). The observed spectrum (Figure 5, Table 2) is assigned as follows: the rhodium-split doublets at $\delta = 165.5$ and 166.7 p.p.m. to MeSe groups of a DL form, that at 170.0 p.p.m. to a *meso* invertomer, and the associated CH_2SeCH_2 doublets at 220.9 and 229.3 p.p.m. A weak doublet at 169.0 p.p.m. is tentatively assigned to a small amount of a further *meso* form, with the associated $\text{Se}(\text{CH}_2)_2$ resonance (228.3 p.p.m.) just evident above the noise. Abel *et al.*⁸ have shown that in *fac*- $[\text{PtMe}_3\text{X}\{\text{MeE}(\text{CH}_2)_n\text{EMe}\}]$ ($n = 2$ or

* 1:1 Electrolytes have Λ_m ca. $120 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

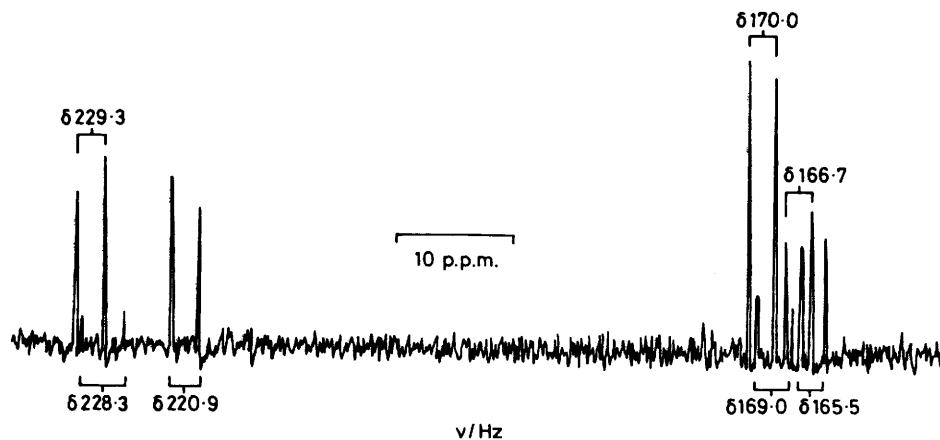


Figure 5. 17.06-MHz ^{77}Se n.m.r. spectrum of $[\text{Rh}(\text{bmsp})\text{Cl}_3]$ (35 000 transients)

3, E = Se or S) the invertomer populations are very sensitive to steric effects, and that some invertomers may have vanishingly small populations. In the case of *fac*- $[\text{Rh}(\text{bmsp})\text{Cl}_3]$, the poorer solubility and greater complexity of the system complicates the interpretation, but attempts to estimate the strain and steric hindrance in the conceivable invertomers *via* molecular models indicate that, of the six invertomers, three with one orientation at the central selenium are highly strained. Of the remaining three (two *meso* and one DL), the orientations of the methyl groups in one *meso* form produce greater steric interactions, and would make this form relatively unfavourable (*cf.* ref. 8). The ^{77}Se n.m.r. spectrum of the corresponding $[\text{Ir}(\text{bmsp})\text{Cl}_3]$ consists of five lines corresponding to the major (one *meso* and one DL) invertomers expected by analogy with $[\text{Rh}(\text{bmsp})\text{Cl}_3]$ and can be assigned in the same manner.

Complexes of Ru and Os.—The reaction of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ with tmse and bmsp in ethanol gave brown $[\text{RuLCl}_3]$, paramagnetic ($\mu_{\text{eff.}}$ ca. 1.8) non-electrolytes. A comparison of the i.r. spectra with those of ruthenium(III) polythioethers^{9,10} leads to tentative assignments of *fac* geometry to the tmse complex and *mer* to the bmsp. The first reported osmium(IV) selenoethers have been prepared from $\text{Na}_2[\text{OsCl}_6]$ in refluxing 2-methoxyethanol. Black (dark green-black when finely powdered) $[\text{OsLCl}_4]$ (L = tmse or bmsp) precipitate on cooling, and dark brown $[\text{OsLCl}_3]$ can be isolated from the filtrates. The electronic spectra of the two types are characteristic of the respective metal oxidation states,^{10,11} but do not distinguish the geometry. In fact $[\text{OsLCl}_4]$ are probably *cis*-octahedral (Se_2Cl_4) like the thioether analogues,¹⁰ but the isomers present in $[\text{OsLCl}_3]$ are unclear.

Polythioether Complexes.—Analogues of the selenoether complexes described above with two thioethers 1,1,1-tris(methylthiomethyl)ethane $\text{MeC}(\text{CH}_2\text{SMe})_3$ (tmte), and bis(3-methylthiopropyl) sulphide $(\text{MeSCH}_2\text{CH}_2\text{CH}_2)_2\text{S}$ (bmtp) have been obtained (Table 1). The complexes of Ru^{III} , Os^{III} , and Os^{IV} have been described elsewhere.¹⁰ In the case of tmte only one further complex, *fac*- $[\text{Ir}(\text{tmte})\text{Cl}_3]$, was isolated; reactions with rhodium, palladium, or platinum chlorides gave intractable oils. For bmtp, complexes of similar formulae to the bmsp analogues were prepared and appear to be of similar geometry, although the lack of a suitable sulphur isotope for n.m.r. studies prevented an investigation of the invertomers.

Conclusions

This study has provided further examples of the sensitivity of ^{77}Se chemical shifts to the selenium environment, and has

demonstrated that even in cases of far from ideal solubilities it is possible to distinguish the major invertomers present more readily from the ^{77}Se than from the ^1H n.m.r. spectroscopic data.

Experimental

Physical measurements were made as described previously.^{1,2} The ^{77}Se n.m.r. spectra were recorded with JEOL FX-90 (at 17.06 MHz) and Bruker AM-360 (at 68.68 MHz) spectrometers using external Me_2Se as zero reference; ^{195}Pt n.m.r. spectra were also recorded with JEOL FX-90 (at 19.16 MHz) and Bruker AM-360 (at 76.64 MHz) spectrometers using external 1 mol dm^{-3} $\text{Na}_2[\text{PtCl}_6]$ in water as zero reference. The high frequency positive convention is employed. The preparations of the ligands have been described elsewhere.^{2,10}

Dichloro[1,1,1-tris(methylselenomethyl)ethane]palladium(II).—Bis(acetonitrile)dichloropalladium(II) (0.26 g, 1 mmol) and the ligand (0.35 g, 1 mmol) were dissolved in dichloromethane (40 cm^3) and stirred for 3 h. The volume of solvent was reduced *in vacuo*, and on addition of diethyl ether a yellow precipitate was formed. Yield 67% (Found: C, 18.3; H, 3.0. Calc. for $\text{C}_8\text{H}_{18}\text{Cl}_2\text{PdSe}_3$: C, 18.2; H, 3.4%).

[Bis(3-methylselenopropyl) selenide]dichloropalladium(II).—Bis(acetonitrile)dichloropalladium(II) (0.26 g, 1 mmol) was dissolved in dichloromethane (50 cm^3) and added dropwise over 1 h to the ligand (0.35 g, 1 mmol) in dichloromethane (100 cm^3) with rapid stirring. The mixture was stirred for a further 3 h, when it was filtered and the filtrate concentrated *in vacuo*. Treatment with diethyl ether gave a yellow solid which was filtered off and dried *in vacuo*. Yield 66% (Found: C, 18.6; H, 3.3. Calc. for $\text{C}_8\text{H}_{18}\text{Cl}_2\text{PdSe}_3$: C, 18.2; H, 3.4%).

[Bis(3-methylthiopropyl) sulphide]dichloropalladium(II) was made in 72% yield by an analogous route (Found: C, 24.8; H, 4.6; Cl, 17.6. Calc. for $\text{C}_8\text{H}_{18}\text{Cl}_2\text{PdS}_3$: C, 24.8; H, 4.6; Cl, 18.3%).

Dichloro[1,1,1-tris(methylselenomethyl)ethane]platinum(II).—To potassium tetrachloroplatinate(II) (0.24 g, 1 mmol) in water (20 cm^3) was added the ligand (0.35 g, 1 mmol) in ethanol (20 cm^3) and the reaction mixture stirred for 3 h. The solvent was removed *in vacuo*, the residue dissolved in hot dichloromethane, filtered, and concentrated *in vacuo*. On treatment with diethyl ether a yellow precipitate was obtained. Yield 55% (Found: C, 15.5; H, 2.9. Calc. for $\text{C}_8\text{H}_{18}\text{Cl}_2\text{PtSe}_3$: C, 15.6; H, 2.9%).

[Bis(3-methylselenopropyl) selenide]chloroplatinum(II) Hexafluorophosphate.—Potassium tetrachloroplatinate(II) (0.42 g,

1 mmol) and sodium hexafluorophosphate (0.6 g, 4 mmol) in water (30 cm³) were added dropwise to a rapidly stirring solution of the ligand (0.35 g, 1 mmol) in ethanol (50 cm³) over 30 min. The solution was stirred for a further 3 h when the solvent was removed *in vacuo*. The residue was dissolved in hot dichloromethane, filtered, and the residue concentrated *in vacuo*. On treatment with methanol at 0 °C overnight and careful removal of the solvent *in vacuo* at low temperatures, a yellow crystalline precipitate was formed. Yield 25% (Found: C, 13.8; H, 2.6. Calc. for C₈H₁₈ClF₆PtSe₃: C, 13.5; H, 2.7%).

[Bis(3-methylthiopropyl) sulphide]chloroplatinum(II) hexafluorophosphate was prepared by an analogous route in 64% yield (Found: C, 16.0; H, 3.2. Calc. for C₈H₁₈ClF₆PPtS₃: C, 16.4; H, 3.1%).

Trichloro[1,1,1-tris(methylselenomethyl)ethane]rhodium(III).

—Rhodium trichloride hydrate (0.26 g, 1 mmol) and the ligand (0.35 g, 1 mmol) were dissolved in ethanol (30 cm³) with stirring. The mixture was heated to reflux and allowed to cool when a yellow precipitate was obtained, filtered off, and washed with ethanol and diethyl ether. Yield 61% (Found: C, 17.2; H, 3.2. Calc. for C₈H₁₈Cl₃RhSe₃: C, 17.1; H, 3.2%).

[Bis(3-methylselenopropyl) selenide]trichlororhodium(III).—Rhodium trichloride hydrate (0.52 g, 2 mmol) and the ligand (0.7 g, 2 mmol) were dissolved in 2-methoxyethanol (100 cm³) and refluxed gently with stirring for 1 h. On cooling, the mixture was filtered and the solvent removed *in vacuo*. The residue was dissolved in dichloromethane and on treatment with diethyl ether an orange precipitate appeared. Yield 75% (Found: C, 17.3; H, 3.1. Calc. for C₈H₁₈Cl₃RhSe₃: C, 17.1; H, 3.2%).

[Bis(3-methylthiopropyl) sulphide]trichlororhodium(III) was made by an analogous route in 62% yield (Found: C, 23.1; H, 4.2; Cl, 26.0. Calc. for C₈H₁₈Cl₃RhS₃: C, 22.9; H, 4.3; Cl, 25.4%).

Trichloro[1,1,1-tris(methylselenomethyl)ethane]iridium(III).

—Iridium trichloride (0.41 g, 1 mmol) and the ligand (0.35 g, 1 mmol) were dissolved in ethanol (50 cm³) with stirring. The mixture was refluxed for 3 h to give a buff precipitate. This was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 35% (Found: C, 15.0; H, 2.9. Calc. for C₈H₁₈Cl₃IrSe₃: C, 14.8; H, 2.8%).

Trichloro[1,1,1-tris(methylthiomethyl)ethane]iridium(III) was made by an analogous route in 46% yield (Found: C, 19.3; H, 3.5; Cl, 19.7. Calc. for C₈H₁₈Cl₃IrS₃: C, 18.9; H, 3.5; Cl, 20.9%).

[Bis(3-methylselenopropyl) selenide]trichloroiridium(III) and [bis(3-methylthiopropyl) sulphide]trichloroiridium(III) were made by routes analogous to those for their rhodium(III) analogues above in 64 and 72% yields respectively (Found: C, 14.9; H, 2.8. Calc. for C₈H₁₈Cl₃IrSe₃: C, 14.8; H, 2.8. Found: C, 18.8; H, 3.6; Cl, 21.8. Calc. for C₈H₁₈Cl₃IrS₃: C, 18.9; H, 3.5; Cl, 20.9%).

Trichloro[1,1,1-tris(methylselenomethyl)ethane]ruthenium(III).—Ruthenium trichloride trihydrate (0.27 g, 1 mmol) and the ligand (0.35 g, 1 mmol) were mixed in 2-methoxyethanol and stirred for 1 h. The brown precipitate formed was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 38% (Found: C, 17.2; H, 3.2; Cl, 18.7. Calc. for C₈H₁₈Cl₃RuSe₃: C, 17.2; H, 3.2; Cl, 19.1%).

[Bis(3-methylselenopropyl) selenide]trichlororuthenium(III).—Ruthenium trichloride trihydrate (0.27 g, 1 mmol) and the ligand (0.35 g, 1 mmol) were refluxed in ethanol for 2 h. The mixture was cooled and the brown precipitate filtered from the solution, washed with diethyl ether, and dried *in vacuo*. Yield 89% (Found: C, 17.0; H, 3.1; Cl, 19.0. Calc. for C₈H₁₈Cl₃RuSe₃: C, 17.2; H, 3.2; Cl, 19.1%).

[Bis(3-methylselenopropyl) selenide]tetrachloroosmium(IV).—Sodium hexachloroosmate (0.45 g, 1 mmol) and the ligand (0.35 g, 1 mmol) were refluxed together in 2-ethoxyethanol for 3 h under nitrogen. The solution was filtered hot, and the very dark green solid washed with diethyl ether and dried *in vacuo*. Yield 38% (Found: C, 13.7; H, 2.4; Cl, 22.0. Calc. for C₈H₁₈Cl₄OsSe₃: C, 14.1; H, 2.6; Cl, 20.8%).

The filtrate was concentrated *in vacuo* to ca. 5 cm³, and treated dropwise with diethyl ether to give a brown powder, [bis(3-methylselenopropyl) selenide]trichloroosmium(III), yield 44% (Found: C, 14.6; H, 3.0; Cl, 15.4. Calc. for C₈H₁₈Cl₃OsSe₃: C, 14.8; H, 2.8; Cl, 16.4%).

A similar route gave [Os{Se(CH₂CH₂CH₂SeMe)₂}Br₄] (16%) and [Os{Se(CH₂CH₂CH₂SeMe)₂}Br₃] (61%) from Na₂[OsBr₆] (Found: C, 11.1; H, 2.1; Br, 35.8. Calc. for C₈H₁₈Br₄OsSe₃: C, 11.1; H, 2.1; Br, 37.2. Found: C, 12.5; H, 2.4; Br, 31.0. Calc. for C₈H₁₈Br₃OsSe₃: C, 12.3; H, 2.3; Br, 30.7%). A similar route also gave [Os{MeC(CH₂SeMe)₃}Cl₄] (25%) and [Os{MeC(CH₂SeMe)₃}Cl₃] (50%) from Na₂[OsCl₆] and ligand (Found: C, 13.8; H, 2.7; Cl, 19.9. Calc. for C₈H₁₈Cl₄OsSe₃: C, 14.1; H, 2.6; Cl, 20.8. Found: C, 14.7; H, 2.9; Cl, 17.0. Calc. for C₈H₁₈Cl₃OsSe₃: C, 14.8; H, 2.8; Cl, 16.4%).

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