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OBSERVATION AND EVALUATION OF THE SYNCHRONOUS LIGAND ATOM PYRAMIDAL INVERSIONS IN BINUCLEAR RHENIUM CARBONYL HALIDE COMPLEXES OF DISULPHIDES AND DISELENIDES: AN X-RAY CRYSTAL STRUCTURE OF $[Re_2Br_2(CO)_6(C_6H_5CH_2SeSeCH_2C_6H_5)]$

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Summary

The dinuclear complexes $[Re_2X_2(CO)_6(RCH_2EECH_2R)]$ ($X = Cl$ or Br, $R = Ph$ or Me_3Si, $E = S$ or Se) have been prepared and characterized. A variable temperature ^1H NMR study on these complexes demonstrated the pyramidal atomic inversion process at the coordinated sulphur and selenium atoms. Total band-shape fittings were used to yield activation parameters for the rate process, in which the two sulphur or selenium atoms undergo synchronous or correlated inversion.

Introduction

There is now a growing body of knowledge regarding the phenomenon of pyramidal atomic inversion about sulphur and selenium atoms coordinated to metals [1–14]. Most attention has been given to mononuclear metal complexes, but more recently we have observed and evaluated such inversions in dinuclear complexes of platinum [12,13]. In recent years Calderazzo and his co-workers [15–17] have characterized the novel disulphide and diselenide complexes of rhenium, $[Re_2X_2(CO)_6(REER)]$ ($X = Cl$, Br, I; $E = S$ or Se; $R = Me$ or Ph). These are isostructural and isoelectronic with our analogous compounds $[Pt_2X_2Me_6(REER)]$ [12], in which we have observed ligand atom inversions.

In order to study inversions about the chiral ligand atoms in the complexes $[Re_2X_2(CO)_6(REER)]$ it was necessary to have prochiral methylene groups attached directly to the ligand atoms. Hence our specific syntheses of benzyl and trimethylsilylmethyl derivatives.

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Experimental

All solvents were dried and purified by conventional methods. Infrared spectra in the metal carbonyl region were recorded on a Perkin–Elmer Model 257 instrument. ^1H NMR spectra were recorded at 100 MHz on a JEOL MH-100 spectrometer operating under conditions of internal field-frequency lock. A standard JES-VT-3 unit was used to control the probe temperature. Measurements of temperature were made immediately before and after recording spectra, and were considered accurate to $\pm 0.5°C$.

All reactions were carried out routinely under an atmosphere of dry nitrogen. Dibenzyl disulphide was used as supplied, and dibenzyl diselenide and bis(trimethylsilylmethyl) disulphide, b.p. 118–120°C/10 mmHg, n_D^{24} 1.4910, (lit. [18] b.p. 82°C/1 mmHg, n_D^{25} 1.4874), $\delta(CH_2)$ 2.22 ppm, $\delta(Me_3Si)$ 0.15 ppm, were prepared by literature methods.

Preparation of bis(trimethylsilylmethyl) diselenide

Me_3SiCH_2MgBr was prepared from Me_3SiCH_2Br (59.0 g, 0.35 mol) and magnesium (8.6 g, 0.36 mol) in dry ether (125 cm^3), and treated with selenium powder (29 g, 0.36 mol). The reaction was exothermic, and when addition was completed, the mixture was heated under reflux for ca. 45 minutes. After hydrolysis with dilute hydrochloric acid the upper layer was removed, dried and fractionally distilled to yield two major fractions. The first was the yellow liquid characterized as bis(trimethylsilylmethyl)selenide (14 g, 32%), b.p. 90–92°C/6–7 mmHg.

100 MHz ^1H NMR: $\delta(CH_2)$ 1.77, $^2J(^{77}Se\text{–}H)$ 5.0 Hz; $\delta(Me_3Si)$ 0.09 $^2J(^{29}Si\text{–}H)$ 6.6 Hz. The second fraction was the required product, a red-orange liquid (13 g, 22%) b.p. 130–131°C/6–7 mmHg.

100 MHz ^1H NMR: $\delta(CH_2)$ 2.40, $^2J(^{77}Se\text{–}H)$ 5.4 Hz; $\delta(Me_3Si)$ 0.11, $^2J(^{29}Si\text{–}H)$ 6.6 Hz.

Both mono and diselenides gave molecular ions and an appropriate cracking pattern in their mass spectra.

$[Re_2Br_2(CO)_6(THF)_2]$ and $[Re_2X_2(CO)_8]$ (X = Cl or Br) were prepared by literature methods [19,20].

The preparations of all disulphide and diselenide complexes were very similar. One example is presented below.

Preparation of $[Re_2Br_2(CO)_6(PhCH_2SeSeCH_2Ph)]$

To a suspension of $[Re_2Br_2(CO)_6(THF)_2]$ (0.25 g, 0.3 mol) in toluene (10 cm^3) was added with stirring an excess of the ligand (0.14 g, 0.57 mol). After 10 minutes a clear yellow solution was obtained. After standing for a further 12 h the metal carbonyl region of the infrared spectrum exhibited four peaks and the spectrum for the starting material was no longer observed. The volume was reduced to 2 cm^3 and dry heptane (3 cm^3) was added. The slow cooling of this solution to $-20°C$ yielded pale yellow crystals which were washed with light petroleum (b.p. 40–60°C) and dried under vacuum for 3 h. The same complex could be obtained directly from $Re_2(CO)_8Br_2$ and the ligand after reflux in toluene for ca. 5 days. Characterization of this and other complexes prepared are summarized in Table 1.

TABLE 1

DINUCLEAR RHENIUM COMPLEXES $[Re_2X_2(CO)_6(RCH_2EECH_2R)]$ (X = Cl or Br, R = C_6H_5 or $(CH_3)_3Si$, E = S or Se)

Complex	Colour	M.p. (°C)	Analysis (Found (calcd.) (%))		ν(CO) (cm^{-1})
			C	H	
$[Re_2Cl_2(CO)_6(C_6H_5CH_2SSCH_2C_6H_5)]$	Yellow	175–177	27.9	1.58	2067m, 2046s, 1954m, 1926s [a]
		(dec.)	(28.0)	(1.64)	2060m, 2046s, 1966s, 1961(sh), 1934s [b]
$[Re_2Br_2(CO)_6(C_6H_5CH_2SSCH_2C_6H_5)]$	Yellow	172–173	24.9	1.34	2058, 2044, 1954, 1926 [a]
		(dec.)	(25.3)	(1.49)	2058, 2046, 1968, 1962(sh), 1938 [b]
$[Re_2Br_2(CO)_6(C_6H_5CH_2SeSeCH_2C_6H_5)]$	Dark yellow	158–159	23.1	1.35	2054, 2038, 1950, 1926 [a]
		(dec.)	(23.1)	(1.35)	2058, 2042, 1966, 1962(sh), 1934 [b]
$[Re_2Br_2(CO)_6(Me_3SiCH_2SSCH_2SiMe_3)]$	Yellow	178–180	17.8	2.26	2046, 2029, 1957, 1925 [c]
		(dec.)	(17.9)	(2.30)	2056, 2042, 1967, 1952(sh), 1932 [b]
$[Re_2Br_2(CO)_6(Me_3SiCH_2SeSeCH_2SiMe_3)]$	Red-orange	181–182	16.2	2.07	2040, 2027, 1956, 1925 [c]
		(dec.)	(16.3)	(2.13)	2052, 2037, 1963, 1952(sh), 1928 [b]

[a] Solution in toluene. [b] Solution in heptane. [c] Solution in chloroform.

Results and discussion

All five compounds exhibited only four bands in the metal carbonyl stretching region of the infrared spectrum in toluene or chloroform, but five bands in the better resolved spectra in heptane solutions. These five modes $(2A_1 + 2B_1 + B_2)$ are in accord with the local symmetry of the $Re_2(CO)_6$ unit of each molecule.

All of these complexes gave similar ^{1}H NMR spectra for the methylene region of the ligands. The sulphur compounds showed line shape changes in the -55 to $+20$°C range, whilst the corresponding selenium changes were exhibited at somewhat higher temperatures. A typical set of line shape changes is illustrated for $[Re_2Br_2(CO)_6(C_6H_5CH_2SSCH_2C_6H_5)]$ in Fig. 1 along with the corresponding computer simulations.

In all the complexes $[Re_2X_2(CO)_6(RCH_2EECH_2R)$ (X = Cl, Br; R = Ph, Me_3Se; E = S, Se), each E atom represents a chiral centre. Attached to these centres are prochiral benzyl or trimethylsilylmethyl groups, in which pairs of methylene hydrogens are diastereotopic and hence anisochronous in the absence of any interconversion process. As the pairs of benzyl or trimethylsilylmethyl groups attached to

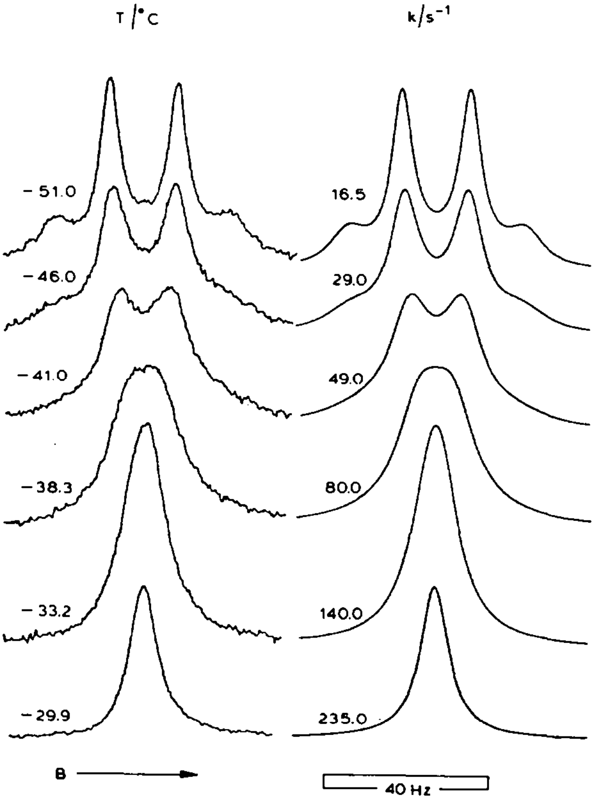

Fig. 1. Experimental and computer simulated 100 MHz ^{1}H spectra of the methylene protons in $[Re_2Br_2(CO)_6(C_6H_5CH_2SSCH_2C_6H_5)]$, showing the effects of synchronous or correlated double site atomic inversions at the sulphur atoms.

different E atoms are enantiomerically related, the corresponding pairs of methylene groups are enantiotopic. In this way the methylene hydrogen spin system for these molecules may be regarded as $[AB]_2$ type. However, as there is no long range spin–spin interaction detected between the different CH_2 groups, the spin system may be regarded as simply AB, as evidenced by the simple quartet at low temperature (Fig. 1).

Increase in temperature causes an exchange process between methylene hydrogens which caused band coalescence at ca. −38°C, and led to a sharp singlet at higher temperature. These dynamic and reversible band shape changes are explained on the basis of inversion at the ligand E atoms. Free rotations about Re–E and E–C bonds alone cannot produce such hydrogen atom interchanges, but are nevertheless assumed to be fast on the NMR time scale. The presence of a sharp methylene resonance due to the added free ligand (throughout the above process), ruled out a dissociation–recombination process.

We have completed an X-ray structural determination of $[Re_2Br_2(CO)_6(C_6H_5CH_2SeSeCH_2C_6H_5)]$ and like other analogues reported [15–17] there is a *trans* relationship between the two organic substituent groups of the ligand. Due to the considerable steric crowding of the corresponding *cis* form, it is likely that the *trans* isomer is also the preferred solution structure.

The *trans* form has *d* and *l* diastereomers, and it is the intramolecular interconversion of these by inversion at both E ligand atoms that causes the variable temperature ^1H NMR spectra that we report. It is likely that the change takes place by a synchronous double-site atomic inversion of both ligand atoms as illustrated in Fig. 2. We cannot, however, rule out the possibility of a correlated inversion involving rapid sequential single site inversions. Such a mechanism would involve the presence of a distinctive *meso* isomer, which was not detected. Non-detection may be due to its presence in undetectably small quantities, or (more likely) its non-requirement for the synchronous mechanism. The situation is analogous to that of the complexes $[Pt_2X_2Me_6(MeEEMe)]$, where both E inversion mechanisms were considered possible [12].

Total band shape fitting methods have been applied to all spectra. Static parameters for computer simulation are summarized in Table 2. For all the benzyl complexes, the transverse relaxation time T_2^* was taken as 0.106 s and was found to be temperature independent for each complex. For $[Re_2Br_2(CO)_6(Me_3SiCH_2SeSeCH_2SiMe_3)]$ chemical shifts were too small to allow a computer simulation of the spectra.

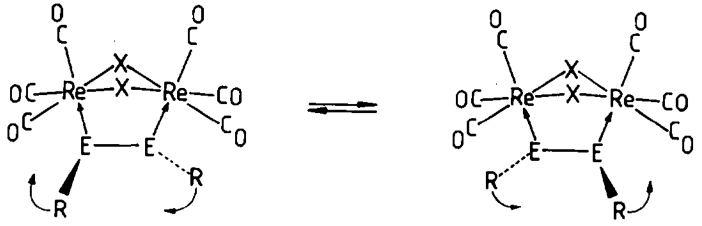

Fig. 2. Inversion of the diastereoisomers of compounds $Re_2X_2(CO)_6[(RCH_2EECH_2R)]$ by synchronous double site atomic inversions at the ligand (E) atoms.

TABLE 2

STATIC ^{1}H NMR PARAMETERS FOR THE DINUCLEAR COMPLEXES $[Re_2X_2(CO)_6RCH_2EECH_2R)]$

Complex	Solvent	Temperature (°C)	$\nu(H_A)$ (Hz)[a]	$\nu(H_B)$ (Hz)[a]	J_{AB} (Hz)	T_2^*(s)	Other couplings (Hz)
$[Re_2Cl_2(CO)_6(C_6H_5CH_2SSCH_2C_6H_5)]$	$CDCl_3$	−63.5	428.0	456.2	12.9	0.106	
$[Re_2Br_2(CO)_6(C_6H_5CH_2SSCH_2C_6H_5)]$	$CDCl_3$	−68.8	432.8	459.6	13.1	0.106	
	$C_6D_5CD_3$[b]	−110.0					
$[Re_2Br_2(CO)_6(C_6H_5CH_2SeSeCH_2C_6H_5)]$	$CDCl_3$	−23.7	450.7	469.3	11.9	0.106	
	$C_6D_5CD_3$	−24.5	358.7	387.3	11.2	–	
$[Re_2Br_2(CO)_6(Me_3SiCH_2SSCH_2SiMe_3)]$	$CDCl_3$	−69.5	320.2	329.3	13.7	0.125[c]	$^2J(^{29}Si–H)$ 5.6[d]
$[Re_2Br_2(CO)_6(Me_3SiCH_2SeSeCH_2SiMe)]$	$CDCl_3$	−38.1	314.8	321.7	13.2	–	$^2J(^{29}Si–H)$ 6.8[d] $^2J(^{77}Se–H)$ 4.4[d]

[a] All chemical shifts relative to internal reference TMS. [b] No observable resolution of H_A and H_B at this temperature. [c] Temperature dependent. [d] Values obtained from high temperature spectra.

TABLE 3

ARRHENIUS AND ACTIVATION PARAMETERS FOR PYRAMIDAL INVERSION IN $[Re_2X_2(CO)_6(RCH_2EECH_2R)]$[a]

Complex	E_a (kJ mol^{-1})	$\log_{10} A$	$\Delta G^{\neq}$ (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})
$[Re_2Cl_2(CO)_6(C_6H_5CH_2SSCH_2C_6H_5)]$	49.5 ± 2.3	12.8 ± 0.5	49.1 ± 0.6	47.5 ± 2.3	−5.0 ± 9.8
$[Re_2Br_2(CO)_6(C_6H_5CH_2SSCH_2C_6H_5)]$	56.3 ± 2.5	14.4 ± 0.5	46.9 ± 2.4	54.3 ± 2.4	25.0 ± 10.7
$[Re_2Br_2(CO)_6(C_6H_5CH_2SeSeCH_2C_6H_5)]$	71.9 ± 2.2	14.5 ± 0.4	61.9 ± 2.2	69.5 ± 2.2	25.3 ± 7.8
$[Re_2Br_2(CO)_6(Me_3SiCH_2SSCH_2SiMe)]$	51.6 ± 1.1	13.3 ± 0.2	48.4 ± 0.3	49.7 ± 1.1	4.2 ± 4.9
$[Re_2Br_2(CO)_6(Me_3SiCH_2SeSeCH_2SiMe_3)]$	[b]				

[a] At 298.15 K. [b] Insufficient separation of $\nu(H_A)$ and $\nu(H_B)$ for an accurate simulation.

Internal chemical shifts were found to be quite solvent dependent. Thus for example $[Re_2Br_2(CO)_6(C_6H_5CH_2SSCH_2C_6H_5)]$ exhibited only one broad signal for CH_2 protons even at −110°C in perdeutero-toluene, whereas in deutero-chloroform a sharply defined AB quartet was observed at −68.8°C. In contrast, the corresponding selenium complex gave a better resolved quartet in toluene-d_8 than in chloroform-d_1.

The Arrhenius and Eyring parameters for these complexes are given in Table 3. The by now predictably higher values of ΔG^* for selenium complexes over their sulphur analogues are confirmed here to exist to the extent of 12–15 kJ mol^{-1}.

X-ray crystal structure of $[Re_2Br_2(CO)_6(PhCH_2SeSeCH_2Ph)]$

Crystal data: $[Re_2Br_2(CO)_6(PhCH_2SeSeCH_2Ph)]$, $M = 1038.3$, monoclinic, a 14.087(5), b 12.578(3), c 14.561(3) Å. β 89.94(2)°, U 2580.0 Å^3, D_c 2.67 g cm^{-3}. $F(000) = 18803$, space group $P2_1/c$. $Z = 4$, $\lambda(\text{Mo-}K_\alpha)$ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 153.8 cm^{-1}). The crystals used were recrystallized from toluene, and found to be monoclinic on the basis of oscillation and Weissenberg photographs using Cu-K_α radiation. The space group was uniquely confirmed as $P2_1/c$. Accurate lattice parameters were obtained from a least squares refinement of the setting angles of 25 reflections automatically centred on the CAD-4 diffractometer.

The intensity of 4528 reflections in the range $1.5° \leqslant \theta \leqslant 25.0°$ were measured on the same instrument using Mo-K_α radiation in conjunction with a graphite monochromator. After Lorentz, polarization and absorption corrections, the averaging of equivalent reflections gave 2737 unique reflections with $F_0 \geqslant 4\sigma(F_0)$. The crystal used in the intensity data collection was $0.30 \times 0.21 \times 0.15$ mm. and was bounded by six faces (001), $(00\bar{1})$, (110), $(\bar{1}\bar{1}0)$, $(1\bar{1}0)$ and $(\bar{1}10)$. The structure was solved by conventional heavy atom methods and refined by full-matrix least-squares procedures using the programme SHELX 76. In the final stages of the refinement all C–C bond lengths in the phenyl rings were fixed at 1.40 Å. The refinement was converged at $R\ [=\Sigma\Delta F/\Sigma|F_0|] = 0.065$ and $R_w\ [=\Sigma w\Delta F^2/\Sigma w|F_0|^2]^{1/2} = 0.068$. The weighting scheme applied was $w = 1/[\sigma^2|F_0| + 0.005|F_0|^2]$, and this gave a satisfactory analysis of variance with $\sin\theta$ and (F_0/F_{max}). Neutral atom scattering factors were taken for non-hydrogen atoms from ref. 21, and were corrected for anomalous dispersion $(\Delta f', \Delta f'')$.

The final positional parameters for non-hydrogen atoms are presented in Table 4, and bond lengths and interbond angles in Tables 5 and 6, respectively.

Diagrams of the structure are given in Fig. 3 and 4. Observed and calculated structure factors and thermal parameters are available from the authors on request.

Calculations were performed upon the Queen Mary College ICL 2980 and University of London CDC 6600 and 7600 computers.

A detailed discussion regarding the essential structure of this type of complex has already been made [15], and although the structure of $[Re_2Br_2(CO)_6(C_6H_5\text{-}CH_2SeSeCH_2C_6H_5)]$ does not possess any crystallographic 2-fold symmetry, the overall geometry is substantially the same as reported for the diphenyl analogue [17]. The absence, in this case, of the molecular symmetry may be attributed to the differing conformation of the dibenzyl ligand, as discussed below.

The Re–Re and mean Re–Br distances are 3.899 and 3.883 Å, and 2.656 and 2.644 Å, respectively, for the diphenyl [17] and our dibenzyl complexes, whilst the folding angle about the Br- - -Br vector in the dibenzyl complex is 25.4°.

(Continued on p. 382)

TABLE 4

REFINED FRACTIONAL COORDINATES FOR NON-HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	X	*Y*	*Z*
Re(1)	0.2053(1)	0.1266(1)	-0.0024(1)
Re(2)	0.4076(1)	0.1316(1)	-0.1837(1)
Br(1)	0.3933(2)	0.1239(3)	-0.0020(2)
Br(2)	0.2322(2)	0.2006(3)	-0.1700(2)
Se(1)	0.2097(2)	-0.0588(2)	-0.0785(2)
Se(2)	0.3448(2)	-0.0625(3)	-0.1762(2)
O(1)	0.1810(21)	0.3480(18)	0.0841(18)
O(2)	-0.0101(18)	0.1238(22)	-0.0228(16)
O(3)	0.1870(18)	0.0375(24)	0.1932(17)
O(4)	0.6108(18)	0.0543(23)	-0.1922(17)
O(5)	0.4851(23)	0.3577(23)	-0.1834(23)
O(6)	0.4048(19)	0.1319(26)	-0.3944(16)
C(1)	0.1905(20)	0.2652(25)	0.0511(21)
C(2)	0.0728(22)	0.1244(24)	-0.0192(19)
C(3)	0.1980(39)	0.0643(29)	0.1186(30)
C(4)	0.5330(24)	0.0793(28)	-0.1900(20)
C(5)	0.4575(22)	0.2731(35)	-0.1865(29)
C(6)	0.3949(27)	0.1330(34)	-0.3113(27)
C(7)	0.2634(23)	-0.1561(27)	0.0182(22)
C(8)	0.2656(18)	-0.2710(21)	-0.0180(18)
C(9)	0.1828(23)	-0.3320(21)	-0.0247(24)
C(10)	0.1951(30)	-0.4372(23)	-0.0540(26)
C(11)	0.2848(28)	-0.4801(31)	-0.0724(28)
C(12)	0.3658(33)	-0.4168(25)	-0.0619(28)
C(13)	0.3569(20)	-0.3107(24)	-0.0342(25)
C(14)	0.2739(32)	-0.0813(27)	-0.2974(23)
C(15)	0.1849(23)	-0.1442(26)	-0.2832(22)
C(16)	0.1832(25)	-0.2527(26)	-0.2617(23)
C(17)	0.0964(28)	-0.3052(35)	-0.2503(26)
C(18)	0.0130(27)	-0.2470(26)	-0.2645(24)
C(19)	0.0158(26)	-0.1393(24)	-0.2886(23)
C(20)	0.1021(23)	-0.0854(30)	-0.2990(24)

TABLE 5

SELECTED BOND LENGTHS (Å) FOR THE NON-HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Re(1)-Br(1)	2.649(3)	Re(2)-Br(1)	2.655(3)
Re(1)-Br(2)	2.639(3)	Re(2)-Br(2)	2.625(3)
Re(1)-Se(1)	2.583(3)	Re(2)-Se(2)	2.599(3)
Re(1)-C(1)	1.92(3)	Re(2)-C(4)	1.89(3)
Re(1)-C(2)	1.88(3)	Re(2)-C(5)	1.91(4)
Re(1)-C(3)	1.93(4)	Re(2)-C(6)	1.87(5)
C(1)-O(1)	1.15(4)	C(4)-O(4)	1.14(4)
C(2)-O(2)	1.17(3)	C(5)-O(5)	1.14(5)
C(3)-O(3)	1.15(4)	C(6)-O(6)	1.22(6)
	Se(1)-Se(2) 2.375(4)		
Se(1)-C(7)	2.01(3)	Se(2)-C(14)	2.04(2)
C(7)-C(8)	1.54(4)	C(14)-C(15)	1.50(5)

TABLE 6

BOND ANGLES (°) FOR THE NON-HYDROGEN ATOMS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Br(1)-Re(1)-Br(2)	82.2(1)	Br(1)-Re(2)-Br(2)	82.3(1)
Br(1)-Re(1)-Se(1)	88.0(1)	Br(1)-Re(2)-Se(2)	84.1(1)
Br(1)-Re(1)-C(1)	96.8(9)	Br(1)-Re(2)-C(4)	96.0(9)
Br(1)-Re(1)-C(2)	172.5(8)	Br(1)-Re(2)-C(5)	95(1)
Br(1)-Re(1)-C(3)	93(1)	Br(1)-Re(2)-C(6)	170(2)
Br(2)-Re(1)-Se(1)	85.3(1)	Br(2)-Re(2)-Se(2)	89.3(1)
Br(2)-Re(1)-C(1)	94.0(8)	Br(2)-Re(2)-C(4)	178.1(8)
Br(2)-Re(1)-C(2)	91.5(9)	Br(2)-Re(2)-C(5)	92(1)
Br(2)-Re(1)-C(3)	174(1)	Br(2)-Re(2)-C(6)	89(2)
Se(1)-Re(1)-C(1)	175.0(9)	Se(2)-Re(2)-C(4)	89(1)
Se(1)-Re(1)-C(2)	87.3(9)	Se(2)-Re(2)-C(5)	178(1)
Se(1)-Re(1)-C(3)	92(1)	Se(2)-Re(2)-C(6)	91(2)
C(1)-Re(1)-C(2)	88(1)	C(4)-Re(2)-C(5)	89(1)
C(1)-Re(1)-C(3)	90(1)	C(4)-Re(2)-C(6)	93(2)
C(2)-Re(1)-C(3)	94(2)	C(5)-Re(2)-C(6)	90(2)
Re(1)-Br(1)-Re(2)	94.1(1)	Re(1)-Br(2)-Re(2)	95.1(1)
Re(1)-Se(1)-Se(2)	107.0(1)	Re(2)-Se(2)-Se(1)	106.2(1)
Re(1)-Se(1)-C(7)	105(1)	Re(2)-Se(2)-C(14)	104(2)
Se(2)-Se(1)-C(7)	96(1)	Se(1)-Se(2)-C(14)	97(1)
Se(1)-C(7)-C(8)	110(2)	Se(2)-C(14)-C(15)	111(2)
Re(1)-C(1)-O(1)	179(2)	Re(2)-C(4)-O(4)	176(3)
Re(1)-C(2)-O(2)	175(3)	Re(2)-C(5)-O(5)	176(4)
Re(1)-C(3)-O(3)	172(4)	Re(2)-C(6)-O(6)	168(5)

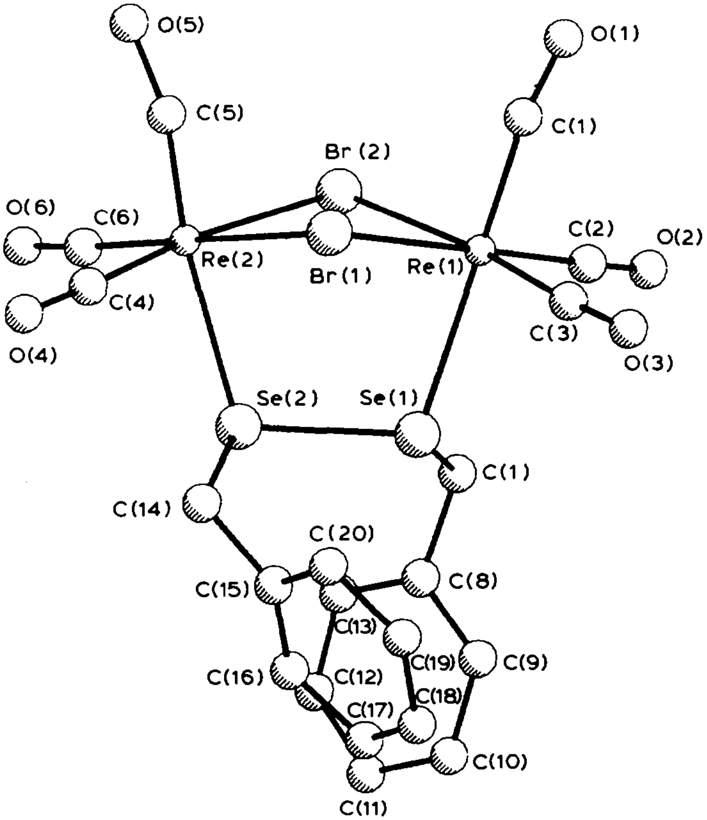

Fig. 3. The molecular structure of $[Re_2Br_2(CO)_6(C_6H_5CH_2SeSeCH_2C_6H_5)]$.

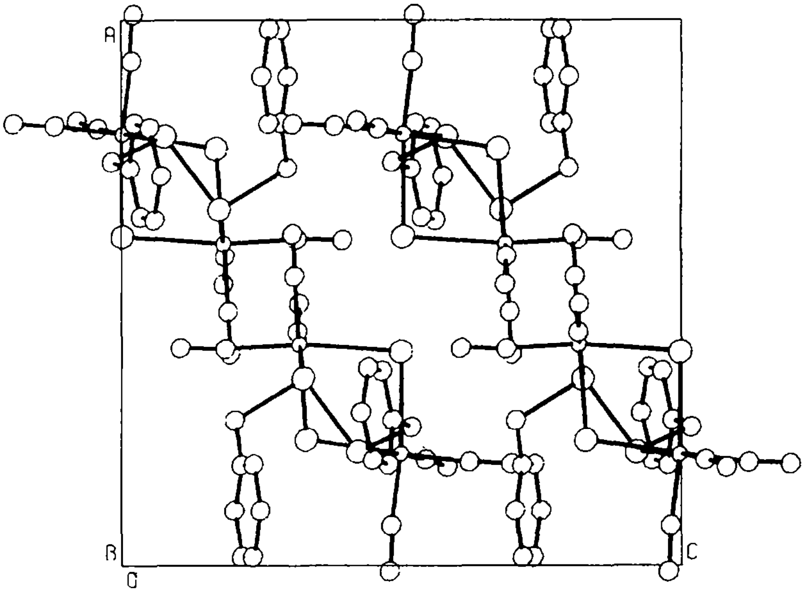

Fig. 4. Unit cell packing in the crystal of $[Re_2Br_2(CO)_6(C_6H_5CH_2SeSeCH_2C_6H_5)]$.

Significantly different is the configuration of the $C_6H_5CH_2SeSeCH_2C_6H_5$ ligand in the complex, as shown by the torsional angle about the Se----Se vector and least-squares planes calculated through relevant groups of atoms. The torsional angle for C–Se–Se–C is 135.6°; and the phenyl rings C(8)----C(13) and C(15)----C(20) make angles of 74.5° and 81.7°, respectively, with the plane containing Se(1), Se(2) and C(7).

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