Crystal and Molecular Structures of Di-μ-acetato-*OO'*-bis[acetato-*OO'*)-methylrhenium(III)] (*4Re–Re*) and Di-μ-acetato-*OO'*-bis[chloro(methyl)-rhenium(III)] (*4Re–Re*)–Dimethyl Sulphoxide (1/1)

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The crystal structures of the title compounds, denoted (A) and (B) respectively, have been determined by single-crystal *X*-ray analysis. Compound (A) is monoclinic, space group $C2/c$ with a = 17.102, b = 6.567, c = 14.724 Å, β = 105.56°, and Z = 4. The structure has been refined to an R value of 0.039 using 1 681 observed [$I > 1.5\sigma(I)$] intensities measured on an automatic diffractometer. The centrosymmetric molecule contains two bridging and two chelating acetate groups. One oxygen atom from each chelating acetate group lies along the Re–Re axis at a distance of 2.462 Å. In spite of the two axially co-ordinated ligands, the Re≣Re distance [2.177(1) Å] is equal to the shortest Re–Re distance yet recorded. Compound (B) is triclinic, space group $P\bar{1}$, with a = 7.382, b = 11.259, c = 10.891 Å, α = 94.69, β = 109.87, γ = 73.56°, and Z = 2. The structure has been refined to an R value of 0.035 using 3 936 observed intensities. This molecule also contains two bridging acetate groups in a mutually *trans* arrangement, but the axial–equatorial chelating acetates have now been replaced by equatorially bonded chloride ligands with just one of the rhenium atoms carrying an axial ligand, a dimethyl sulphoxide molecule co-ordinated *via* its oxygen atom (Re–O 2.302 Å). The Re–Re distance in this molecule is longer than in (A), but at 2.184 Å it is still very short.

THE binuclear compound $[Re_2Me_2(O_2CMe)_4]$ (A) was obtained from the interaction of dilithium octamethyl-dirhenate(III) with acetic acid,[1] and the determination of its structure by *X*-ray crystallography was undertaken as an aid to its complete characterisation. Subsequent synthetic work led to the preparation of a series of new compounds containing the $Re_2Me_2(O_2CMe)_2$ unit [1] and the structure of one of these, $[Re_2Me_2(O_2CMe)_2Cl_2(dmso)]$ (B), has also been determined by *X*-ray methods. The two structures show a number of interesting features, particularly with regard to the structural chemistry of quadruply bonded M≣M systems, and in view of the current interest in this topic we considered it worthwhile to present and discuss our results in some detail.

EXPERIMENTAL

Crystals used for *X*-ray work were sealed under nitrogen in Lindemann capillaries although both compounds are fairly stable in air. Unit-cell parameters were initially determined from oscillation and Weissenberg photographs and later refined using setting angles for 15 high-angle reflections automatically centred on a CAD4 diffractometer. The crystal data and details of the data collection and structure refinement are summarised in Table 1.

Intensity data were recorded on the CAD4 diffractometer using graphite monochromated Mo-K_α radiation and an ω—2θ scan method, in the manner described previously.[2] During data collection, the diffracting power of crystal (A) gradually decreased by *ca.* 9%, whilst that of (B) remained constant. Both sets of data were corrected for Lorentz and polarisation effects and for absorption, and that for (A) was corrected for the small amount of decay.

The structure of compound (A) was solved *via* Patterson and difference electron-density synthesis and of (B) *via* application of the automatic centrosymmetric direct-methods routine in the SHELX program,[3] followed by difference electron-density syntheses. Refinement by full-matrix least squares, using first isotropic and then anisotropic thermal parameters for all the heavy atoms, gave final R values of 0.039 for (A) and 0.035 for (B). The weighting scheme $w = 1/[\sigma^2(F) + gF^2]$ was used, with the parameter g chosen to give flat agreement analyses.

Fractional atomic co-ordinates are given in Tables 2 [for (A)] and 3 [for (B). Anisotropic thermal parameters and lists of observed and calculated structure factors have been deposited in Supplementary Publication No. SUP 22394 (32 pp.).†

Neutral-atom scattering factors were taken from ref. 4. (Re) and ref. 5 (Cl, S, O, and C), and corrected for anomalous dispersion using $\Delta f'$ and $\Delta f''$ values from ref. 6. All the calculations were performed on the Queen Mary College ICL 1904S and the University of London CDC 7600 computers using SHELX [3] (Fourier syntheses, refinement, and bond lengths and angles), XANADU [7] (least-squares planes), and PLUTO [8] (diagrams).

RESULTS AND DISCUSSION

The molecular structure found for (A) is shown in Figure 1, which also gives the atom-numbering scheme used. Important bond lengths and angles are given in Table 4 with selected least-squares-plane data in Table 5. The centrosymmetric molecule consists of two rhenium atoms separated by a distance of 2.177(1) Å bridged by two acetate groups arranged in a mutually *trans* configuration. The remaining two acetate groups form an unsymmetrical chelate system on each metal with a short Re–O bond (2.115 Å) in an equatorial site and a longer bond (2.462 Å) approximately collinear with the Re–Re axis. The fourth equatorial site is occupied by a methyl group. The shortness of the Re–Re bond and the eclipsed arrangement of the two sets of equatorial ligands are consistent with the presence of a quadruple metal–metal bond. The tendency of these Re_2 systems to accept axially bonded ligands is quite common,[9-15] but the presence of an axial–equatorial chelating carboxylate is unusual for the whole class of carboxylate-containing M≣M systems.

Following the determination of this structure, it was considered to be of interest to investigate the possible preparation of derivative structures with, for example the equatorial–axial chelating acetate group replaced by a

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

unidentate uninegative ligand in the equatorial site. Replacement by the chloride ion was achieved, but the product was a generally insoluble, probably polymeric, species. However, its solution in dimethyl sulphoxide was possible and from this mixture a crystalline product of stoicheiometry $[Re_2Me_2(O_2CMe)_2Cl_2(dmso)]$ (B) was obtained.[1] We have studied this product by *X*-ray crystallography also and the molecular structure found is shown in Figure 2. Bond lengths and angles are given in Table 6, and least-squares-plane data in Table 7. In this molecule the $Re_2Me_2(O_2CMe)_2$ unit is retained; the equatorial sites formerly occupied by the strongly bound acetate oxygens are occupied by chlorine atoms and now only one Re atom carries an axially bonded ligand, the dmso molecule, co-ordinating *via* its oxygen atom.

TABLE 1

Crystal data and details of the structure analyses

Crystal data	Compound (A)	Compound (B)
Formula	$[Re_2Me_2(O_2CMe)_4]$	$[Re_2Me_2(O_2CMe)_2Cl_2$-(dmso)$]$
M	638.65	669.60
Crystal system	Monoclinic	Triclinic
a/Å	17.102(3) *	7.382(1)
b/Å	6.567(1)	11.259(1)
c/Å	14.724(3)	10.891(2)
α/°	90	94.69(3)
β/°	105.56(2)	109.87(3)
γ/°	90	73.56(2)
U/Å^3	1 592.96	816.38
Space group	$C2/c$	$P\bar{1}$
Z	4	2
D_c/g cm^{-3}	2.66	2.72
$F(000)$	1 16 8	612
Linear absorption coefficient (cm^{-1})	153.9	154.3
Crystal size (mm)	0.20 × 0.08 × 0.04	0.18 × 0.15 × 0.11
Data collection		
$\theta_{min.}$, $\theta_{max.}$/°	1.5, 30	1.5, 30
ω Scan width parameters A,B in width = A + B tan θ	0.8, 0.2	0.8, 0.2
Horizontal aperture parameters, A,B in APT = A + B tan θ	3.0, 0.5	3.0, 0.5
Total data	2 619	4 958
Total unique data	2 321	4 766
Observed data $[(F_o > 3\sigma(F_o)]$	1 681	3 936
Refinement		
No. of parameters	91	163
Weighting scheme coefficient g in $w = 1/[\sigma^2(F_o) + gF_o^2]$	0.001 95	0.000 6
Final $R = \Sigma\Delta F/\Sigma(F_o)$	0.039	0.035
$R' = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.053	0.054

* Estimated standard deviations are given in parentheses, in this and other Tables throughout this paper.

TABLE 2

Fractional co-ordinates (Re $\times 10^5$; others $\times 10^4$) for (A)

Atom	x	y	z
Re	5 650(2)	1 906(5)	5 495(2)
O(1)	1 161(4)	−1 539(9)	−191(4)
O(2)	8(4)	−2 000(8)	−1 282(4)
O(3)	1 223(4)	2 758(9)	298(4)
O(4)	1 883(4)	1 255(12)	1 589(4)
C(1)	759(5)	−2 339(11)	−967(5)
C(2)	1 192(7)	−3 697(16)	−1 502(7)
C(3)	1 838(5)	2 702(1)3	1 027(5)
C(4)	2 461(7)	4 316(18)	1 151(7)
C(5)	470(7)	−2 360(16)	1 377(7)

TABLE 3

Fractional co-ordinates (Re $\times 10^5$; others $\times 10^4$) for (B)

Atom	x	y	z
Re(1)	51 338(4)	30 449(2)	39 960(2)
Re(2)	28 481(3)	23 925(2)	24 590(3)
Cl(1)	5 603)4)	2 548(2)	6 166(2)
Cl(2)	2 860(3)	3 073(2)	400(2)
S(3)	−1 003(3)	1 995(2)	−345(2)
O(1)	3 075(8)	4 676(4)	4 060(5)
O(2)	780(8)	4 017(5)	2 513(5)
O(3)	7 207(7)	1 441(5)	3 925(5)
O(4)	4 914(7)	801(5)	2 360(6)
O(5)	203(8)	1 701(6)	1 110(6)
C(1)	1 315(11)	4 844(7)	3 278(7)
C(2)	−176(14)	6 039(8)	3 325(10)
C(3)	6 737(11)	631(7)	3 110(8)
C(4)	8 211(13)	−522(7)	3 030(9)
C(5)	6 352(11)	3 945(8)	2 962(8)
C(6)	2 076(13)	1 472(8)	3 766(10)
C(7)	−2 467(14)	3 566(7)	−442(9)
C(8)	−2 911(13)	1 198(9)	−604(10)

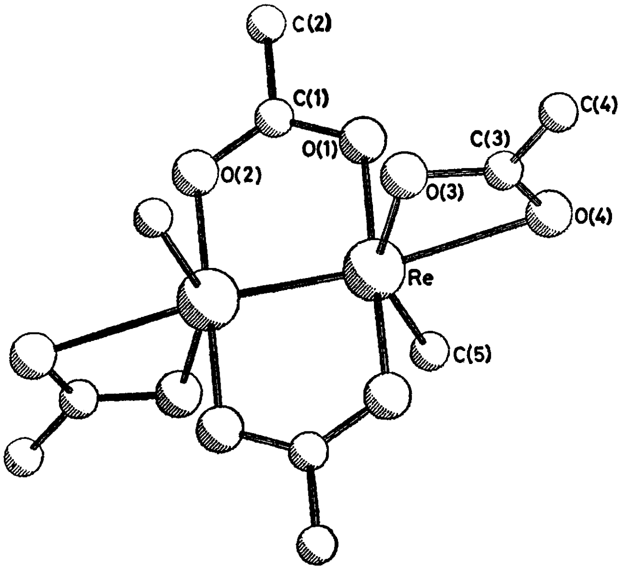

FIGURE 1 Molecular structure of $[Re_2Me_2(O_2CMe)_4]$ (A) and the atom-numbering system of the asymmetric unit

It is interesting to consider the molecular geometries of these two species in relation to each other, and also to the wide variety of similar M≡M species and the many discussions on the factors affecting their geometries, particularly the length of the M≡M bond.[12,13,16] Of all the features discussed in this context the most relevant here is the effect on the metal–metal bond length of axially co-ordinated ligands. Their presence is generally assumed to have a weakening influence, although Cotton *et al.*[16] have recently shown that the effect varies greatly depending on the metal. However, in all cases so far reported where any structure containing axial ligands (on one or both metal atoms) can be directly compared with a parent, non-axially co-ordinated, structure,[12,13] the metal–metal bond is found to be longer in the former. In cases where no such direct comparisons can be made axial co-ordination always seems to produce species in which the metal–metal bond is at the long end of the relevant range. We were therefore rather surprised to find that in structure (A), where both metal atoms carry axial ligands, the Re–Re bond length [2.177(1) Å] is equal to the shortest such

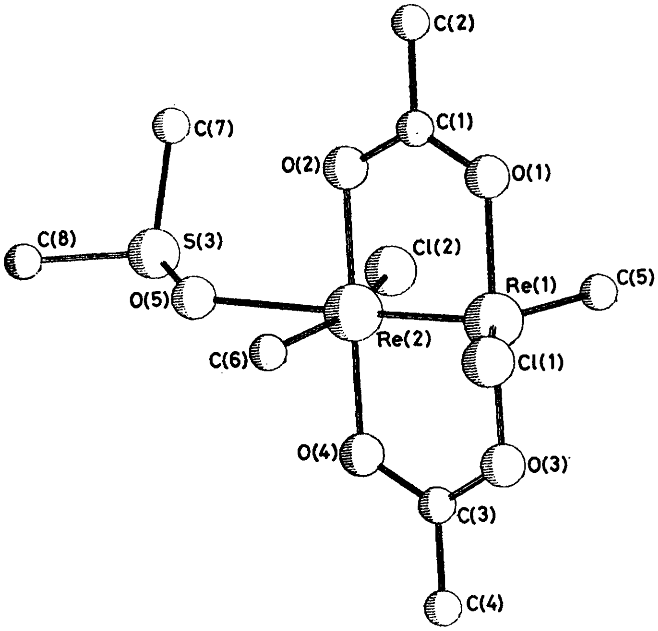

FIGURE 2 Molecular structure of $[Re_2Me_2(O_2CMe)_2Cl_2(dmso)]$ (B) and the atom-numbering system

TABLE 4

Intramolecular interatomic distances and interbond angles for (A)

(*a*) Bond lengths (Å)

Re–Re′	2.177(1) *	O(1)–C(1)	1.278(9)
Re–O(1)	2.029(6)	O(2)–C(1)	1.262(10)
Re–O(2′)	2.025(6)	O(3)–C(3)	1.287(10)
Re–O(3)	2.115(6)	O(4)–C(3)	1.249(10)
Re–O(4)	2.462(6)	C(1)–C(2)	1.510(12)
Re–C(5)	2.099(10)	C(3)–C(4)	1.479(12)

(*b*) Bond angles (°)

Re′–Re–O(1)	90.6(1)	Re–O(1)–C(1)	118.8(6)
Re′–Re–O(2′)	90.2(1)	Re′–O(2)–C(1)	119.8(6)
Re′–Re–O(3)	111.7(1)	O(1)–C(1)–O(2)	120.4(8)
Re′–Re–O(4)	167.7(1)	O(1)–C(1)–C(2)	119.1(8)
Re′–Re–C(5)	98.5(1)	O(2)–C(1)–C(2)	120.4(8)
O(1)–Re–O(2′)	178.1(1)		
O(1)–Re–O(3)	89.1(2)	Re–O(3)–C(3)	100.7(5)
O(1)–Re–O(4)	89.1(3)	Re–O(4)–C(3)	85.5(5)
O(1)–Re–C(5)	89.5(3)	O(3)–C(3)–O(4)	117.8(7)
O(2)–Re–O(3)	89.0(2)	O(3)–C(3)–C(4)	118.9(8)
O(2)–Re–O(4)	89.7(2)	O(4)–C(3)–C(4)	123.3(8)
O(2)–Re–C(5)	92.0(3)		
O(3)–Re–O(4)	56.0(2)		
O(3)–Re–C(5)	149.8(3)		
O(4)–Re–C(5)	93.8(3)		

* The primed atoms are generated by symmetry $-x$, $-y$, $-z$ and belong to one and the same molecule.

TABLE 5

Least-squares planes for (A) in the form $Ax + By + Cz = D$, where x,y,z are fractional co-ordinates, and deviations (Å) of the relevant atoms in square brackets

Plane (1):

Re, Re′, O(1), O(2), C(1); $5.869x + 5.303y - 8.159z = 0.001$

[Re −0.017, Re′ 0.015, O(1) 0.020, O(1′) −0.022, O(2) −0.011, O(2′) 0.009, C(1) −0.007, C(1′) 0.005, C(2) −0.036, C(2′) 0.034, O(4) 0.473, O(4′) −0.475]

Plane (2):

Re, O(3), O(4), C(3); $-10.944x + 3.707y + 9.923z = -0.008$

[Re 0.006, Re′ 0.011, O(3) −0.012, O(3′) 0.028, O(4) −0.011 O(4′) 0.027, C(3) 0.017, C(3′) −0.001, C(4) 0.057, C(4′) −0.041, C(5) −0.015, C(5′) 0.031]

Angle between normals to planes (1) and (2): 90.79°

TABLE 6

Intramolecular interatomic distances and interbond angles for (B)

(*a*) Bond lengths (Å)

Re(1)–Re(2)	2.183 6(5)	O(1)–C(1)	1.259(9)
Re(1)–Cl(1)	2.360(2)	O(2)–C(1)	1.256(9)
Re(2)–Cl(2)	2.432(2)	P(3)–C(3)	1.256(9)
Re(1)–O(1)	2.040(5)	O(4)–C(3)	1.284(9)
Re(1)–O(3)	2.025(5)	C(1)–C(2)	1.487(10)
Re(2)–O(2)	2.035(5)	C(3)–C(4)	1.457(10)
Re(2)–O(4)	2.021(5)		
Re(2)–O(5)	2.302(6)	S(3)–O(5)	1.540(6)
Re(1)–C(5)	2.120(8)	S(3)–C(7)	1.783(8)
Re(2)–C(6)	2.134(9)	S(3)–C(8)	1.808(8)

(*b*) Bond angles (°)

Re(2)–Re(1)–Cl(1)	116.7(1)	Re(1)–Re(2)–Cl(2)	106.4(1)
Re(2)–Re(1)–C(5)	103.9(2)	Re(1)–Re(2)–C(6)	94.8(2)
Re(2)–Re(1)–O(1)	90.4(1)	Re(1)–Re(2)–O(2)	90.0(2)
Re(2)–Re(1)–O(3)	90.1(1)	Re(1)–Re(2)–O(4)	90.2(2)
Cl(1)–Re(1)–O(1)	91.3(2)	Cl(2)–Re(2)–O(2)	88.9(2)
Cl(1)–Re(1)–O(3)	89.3(2)	Cl(2)–Re(2)–O(4)	89.4(2)
Cl(1)–Re(1)–C(5)	139.4(2)	Cl(2)–Re(2)–C(6)	158.7(3)
O(1)–Re(1)–O(3)	179.0(2)	O(2)–Re(2)–O(4)	178.3(2)
O(1)–Re(1)–C(5)	89.9(3)	O(2)–Re(2)–C(6)	93.3(3)
O(3)–Re(1)–C(5)	89.2(3)	O(4)–Re(2)–C(6)	88.4(3)
		Re(1)–Re(2)–O(5)	170.3(2)
Re(2)–O(5)–S(3)	129.7(4)	Cl(2)–Re(2)–O(5)	82.6(2)
O(5)–S(3)–C(7)	106.7(4)	O(2)–Re(2)–O(5)	86.4(2)
O(5)–S(3)–C(8)	101.3(4)	O(4)–Re(2)–O(5)	93.7(2)
C(7)–S(3)–C(8)	100.5(4)	O(5)–Re(2)–C(6)	76.4(3)
Re(1)–O(1)–C(1)	118.5(5)	Re(1)–O(3)–C(3)	120.3(5)
Re(2)–O(2)–C(1)	119.2(5)	Re(2)–O(4)–C(3)	119.7(5)
O(1)–C(1)–O(2)	121.8(7)	O(3)–C(3)–O(4)	119.7(7)
O(1)–C(1)–C(2)	118.2(6)	O(3)–C(3)–C(4)	121.2(7)
O(2)–C(1)–C(2)	119.9(7)	O(4)–C(3)–C(4)	119.1(7)

TABLE 7

Least-squares planes for (B) in the form $Ax + By + Cz = D$, where x,y,z are fractional co-ordinates, and deviations (Å) of the relevant atoms in square brackets

Plane (1):

Re(1), Re(2), O(1), O(2), O(3), O(4), C(1), C(3)

$-4.502x - 6.173y + 9.249z = -0.516$

[Re(1) 0.021, Re(2) 0.031, O(1) −0.000, O(2) 0.009, O(3) 0.012, O(4) −0.008, O(5) 0.401, C(1) −0.035, C(2) −0.058, C(3) −0.030, C(4) −0.056]

Plane (2):

Re(1), Re(2), Cl(1), Cl(2), C(5), C(6)

$-3.867x + 7.518y + 2.532z = 1.295$

[Re(1) 0.021, Re(2) 0.025, Cl(1) 0.015, Cl(2) 0.011, O(5) 0.0187, C(5) −0.035, C(6) −0.037]

Angle between normals to planes (1) and (2): 89.05°

bond yet observed [12] and that the bond [2.183 6(5) Å] in structure (B), where only one metal atom carries an axial ligand, is longer than in (A). The relation between the two Re–Re bond lengths could presumably be explained in terms of the *strength* of the axial ligand-to-metal bond with one strong interaction having more effect than two weaker ones. In the context of the wide range of Re_2^{6+} structures, the two Re–O axial contacts in (A) (2.462 Å) are shorter than many, whilst the dmso interaction in (B) (2.302 Å), must be considered quite strong. Only in the cases of two ' perrhenates ', $[Re_2(O_2CPr)_4]\cdot ReO_4$ [10] and $[Re_2(O_2CPr)_3Cl_2]\cdot ReO_4$,[9] and $Na_2[Re_2(SO_4)_4]\cdot 8H_2O$ [14] are the axial Re–O bond lengths [2.18—2.28(3) Å] shorter than in compound (B). In these compounds the Re–Re distances are 2.251, 2.259, and 2.214 Å respectively. Thus the data for the two structures described in this paper suggest that *either* the parent system ' $Re_2Me_2(O_2CMe)_2X_2$ ' where X is a unidentate monoanionic ligand would, if such a species could be obtained as a discrete molecule, have an Re–Re bond shorter than any other yet recorded, *or* the presence of axially co-ordinated ligands may not necessarily weaken the metal–metal bonding. This would certainly agree with the suggestion of Cotton *et al.*[16] that the Re≡Re bond, like the Mo≡Mo bond, is strong and not easily affected by axial co-ordination, or indeed any other factors.

TABLE 8

Intermolecular short contacts <3.80 Å

Compound (A)		Compound (B)	
$O(1)\cdots C(4^{I})$	3.73	$Re(1)\cdots O(1^{I})$	3.46
$O(1)\cdots C(4^{II})$	3.39	$Cl(1)\cdots S(3^{II})$	3.76
$O(2)\cdots C(2^{III})$	3.54	$Cl(1)\cdots O(1^{I})$	3.58
$O(3)\cdots C(2^{IV})$	3.52	$Cl(1)\cdots C(7^{II})$	3.69
$O(3)\cdots C(4^{II})$	3.75	$Cl(1)\cdots C(8^{II})$	3.63
$O(4)\cdots C(2^{V})$	3.70	$Cl(2)\cdots C(7^{III})$	3.71
$O(4)\cdots C(2^{VI})$	3.73	$Cl(2)\cdots C(8^{IV})$	3.70
$O(4)\cdots C(4^{VII})$	3.46	$O(1)\cdots O(1^{I})$	3.13
$C(1)\cdots C(4^{II})$	3.71	$O(1)\cdots C(5^{I})$	3.42
$C(2)\cdots C(4^{II})$	3.63	$O(2)\cdots C(5^{V})$	3.49
		$O(3)\cdots C(6^{IV})$	3.67
		$O(4)\cdots C(8^{VI})$	3.19
		$O(5)\cdots C(8^{VI})$	3.42
		$C(2)\cdots C(4^{VII})$	3.72

Symmetry code:

	A	B
I	$x, -1+y, z$	$1-x, 1-y, 1-z$
II	$\frac{1}{2}-x, \frac{1}{2}-y, -z$	$1+x, y, 1+z$
III	$-x, y, -\frac{1}{2}-z$	$-x, 1-y, -z$
IV	$x, 1+y, z$	$1+x, y, z$
V	$x, -y, \frac{1}{2}+z$	$-1+x, y, z$
VI	$\frac{1}{2}-x, \frac{1}{2}-y, -z$	$-x, -y, -z$
VII	$\frac{1}{2}-x, -\frac{1}{2}+5, \frac{1}{2}-z$	$-1+x, 1+y, z$

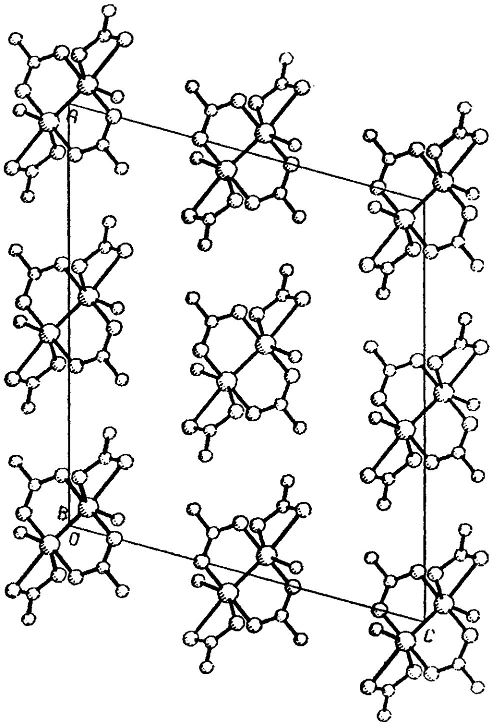

FIGURE 3 Molecular packing of (A)

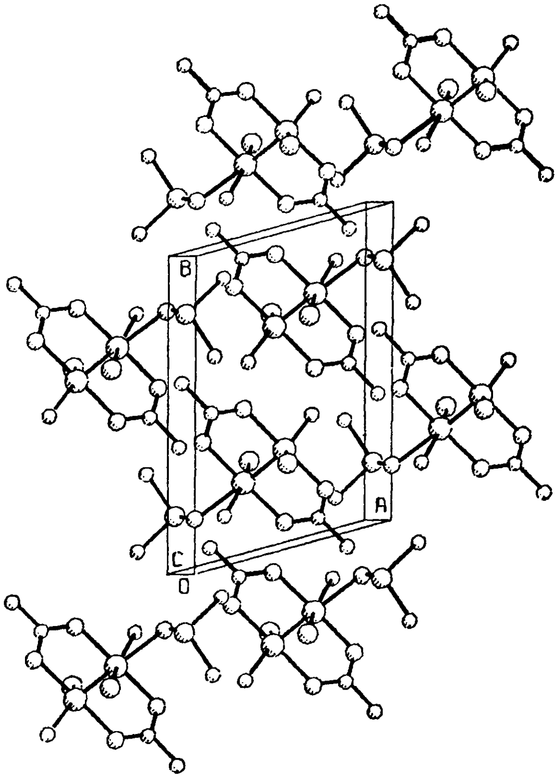

FIGURE 4 Molecular packing of (B)

Other parts of the molecular structures also show some interesting features. Parameters relating to the geometries of the di-μ-acetato-dirhenium portions are almost identical, with, for example, the Re–O distances all equal to within 2σ. The Re–C(Me) distance in both molecules, whilst significantly shorter than in $[Re_2Me_8]^{2-}$,[17] are also equal to within 3σ. In molecule (B), however, the two Re–Cl distances are quite different with the larger value, for Re(2)–Cl(2) (which, incidentally, is greater than any other Re^{III}–Cl distance in these systems), reflecting the higher co-ordination number for Re(2). This difference is also reflected in the angular distribution of the two unidentate ' equatorial ' ligands on each metal atom in molecule (B). Thus for Re(1), which is essentially only five-co-ordinate, the Re–Re–Cl (or Me) angles are some 10° greater than on atom Re(2). A similar difference has been found for the unsymmetrical molecules $[Re_2Cl_4(N_2CPh_3)_2]\cdot C_4H_8O$ [12] and $[Re_2Cl_5\{(Ph_2P)_2CH_2\}_2]$.[15]

In molecule (A) the ' equatorial ' Re–O distance to the chelating acetate group is significantly longer (*ca.* 0.1 Å) than those in the acetate bridging system. This could be an indication that the Re–O bonds in the acetate bridge are shortened, in agreement with the suggestion [18] that the acetate π system might be involved in a delocalisation with the metal–metal bond. Two other important parameters relating to the chelating acetate group in (A) are the C(3)–O(3)–Re angle of 101° and the O(3)–Re–Re angle of 112° (*cf.* Me–Re–Re at 99°) indicating that O(4) *is* being pulled into its position on the Re–Re axis. This suggests that the co-ordination of axial ligands, certainly in the case of Re_2^{6+} species, involves a fairly strong, positive interaction. In this context, the geometry of the dmso ligand in (B) is interesting since the O(5)–S(3)–C(7) angle is 6° wider than the chemically equivalent O(5)–S(3)–C(8) angle. The reason seems to be the short intramolecular C(7) · · · O(2) contact of 3.40 Å.

The packing diagrams for (A) and (B) are presented in Figures 3 and 4 respectively, and the intermolecular short contacts between the non-hydrogen atoms are listed in Table 8.

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