Refinement

Refinement on F^2
$R(F) = 0.067$
$wR(F^2) = 0.165$
$S = 1.143$
2161 reflections
361 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0951P)^2 + 2.6167P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.798$ e Å^{-3}
$\Delta\rho_{\min} = -0.452$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Fe1—O1	1.897 (5)	Fe1—N2	2.099 (6)
Fe1—O2	1.910 (5)	Fe1—Cl1	2.227 (3)
Fe1—N1	2.065 (6)		
O1—Fe1—O2	93.9 (2)	N1—Fe1—N2	77.4 (2)
O1—Fe1—N1	85.9 (2)	O1—Fe1—Cl1	109.1 (2)
O2—Fe1—N1	148.9 (2)	O2—Fe1—Cl1	107.2 (2)
O1—Fe1—N2	145.1 (2)	N1—Fe1—Cl1	102.2 (2)
O2—Fe1—N2	85.6 (2)	N2—Fe1—Cl1	104.3 (2)

Data collection: *SDP* (Frenz, 1985). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrakis(μ-2-biphenylcarboxylato-*O*:*O*′)bis[chlororhenium(III)] Bis(dichloromethane) Solvate

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Abstract

The title complex, $[Re_2Cl_2(C_{13}H_9O_2)_4].2CH_2Cl_2$, has the well known 'paddle-wheel' structure common in many $M_2(O_2CR)_4$ structures and the Cl ligands occupy the axial positions. The Re atoms are joined by a quadruple bond of length 2.2363 (7) Å and each metal atom is in a pseudo-octahedral environment. The molecule contains an inversion centre and two *ortho*-phenyl groups of the carboxylate ligands extend out over each axial region.

Comment

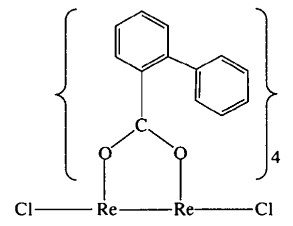
The chemistry of dirhenium(III) carboxylates has occupied a crucial place in the development of the chemistry of the metal-to-metal quadruple bond. Over 20 such compounds have been structurally characterized and their properties and reactivities are well documented (Cotton & Walton, 1993).

The first dimetal tetrakis(2-biphenylcarboxylate) compound reported was that of chromium (Cotton & Thompson, 1981*a*), in which the strategy was to use the pendant phenyl group to block the axial position of the molecule. This would, in principle, keep the molecule from forming infinite chains in which the coordinated O atoms of one molecule interact with the axial position of the next, a mode of interaction common in dichromium tetrakis(carboxylate) compounds. In this case, however, the pendant phenyl groups of all four of the 2-biphenylcarboxylate ligands were oriented towards one end of the molecule, leaving the other end free to associate with a similar molecule.

Tetracarboxylato compounds of Mo_2^{4+} have a much lower propensity for the type of intermolecular association found in the Cr_2^{4+} compounds and therefore the $[Mo_2\{O_2C(2\text{-biphenyl})\}_4]$ compound crystallized without such interaction (Cotton & Thompson, 1981*b*). While the steric bulk of the 2-biphenylcarboxylate ligand is somewhat useful in preventing intermolecular association, it does not adequately shield the axial position from coordination by a sufficiently small moiety, *e.g.* CH_3CN in the rhenium compound (Cotton &

Thompson, 1984) and Cl^- in the homologous compound of osmium (Cotton, Ren & Wagner, 1993).

The title $[Re_2Cl_2\{O_2C(2\text{-biphenyl})\}_4]$ molecule, (I), crystallizes with two of the *ortho*-phenyl groups directed towards each axial region and also has Cl^- ligands coordinated at each axial position. Lines drawn from the axial Cl atom to the centroid of the two nearby phenyl groups are close to being perpendicular to the plane of the group, but as these lines are 4.07 and 4.45 Å long, any meaningful chemical interaction is doubtful.



(I)

The symmetry of the core of the molecule is essentially D_{4h}, with O—Re—Re—O torsion angles of 0.0 (1) and 0.2 (1)°. The metal–metal distance of 2.2363 (7) Å matches the average distance of 2.23 [2] Å for dirhenium(III) carboxylates (Cotton & Walton, 1993).

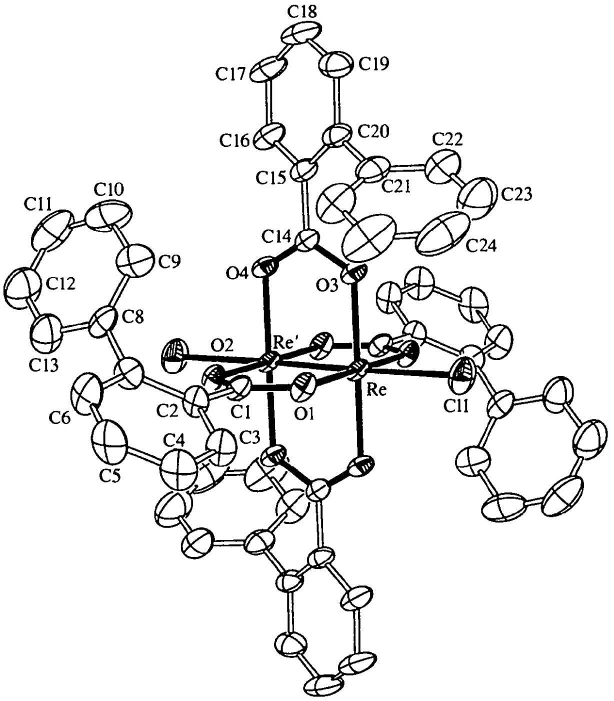


Fig. 1. View of the title molecule with the atom-numbering scheme. Atoms are represented by anisotropic displacement ellipsoids at the 40% level.

Experimental

Dichlorotetrakis(μ-2-biphenylcarboxylato)dirhenium(III) was prepared by heating 0.50 mmol of $[Re_2(OAc)_4Cl_2]$ (Cotton, Oldham & Robinson, 1966) and 8.0 mmol of 2-biphenylcarboxylic acid at 413 K for 6 h under argon. The initially orange molten mixture gradually turned to rosy red as the acetic acid produced refluxed away from the melt. Excess ligand was removed *via* vacuum sublimation. The crude product was recrystallized from CH_2Cl_2 to afford 0.53 g of red needles. Single crystals suitable for X-ray work were obtained by allowing hexane to diffuse slowly into a CH_2Cl_2 solution of the pure product.

Crystal data

$[Re_2Cl_2(C_{13}H_9O_2)_4].2CH_2Cl_2$
$M_r = 1401.96$
Triclinic
$P\bar{1}$
$a = 11.364\ (3)$ Å
$b = 11.372\ (3)$ Å
$c = 11.668\ (4)$ Å
$\alpha = 76.13\ (2)°$
$\beta = 89.66\ (3)°$
$\gamma = 65.21\ (2)°$
$V = 1321.3\ (6)$ Å^3
$Z = 1$
$D_x = 1.762$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 28.5\text{–}31.0°$
$\mu = 12.045$ mm^{-1}
$T = 293\ (2)$ K
Column
0.30 × 0.25 × 0.20 mm
Red

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.77$, $T_{max} = 0.90$
3561 measured reflections
3561 independent reflections

3370 reflections with $I > 2\sigma(I)$
$\theta_{max} = 57°$
$h = -12 \rightarrow 12$
$k = -11 \rightarrow 12$
$l = 0 \rightarrow 12$
3 standard reflections every 250 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0314$
$wR(F^2) = 0.0842$
$S = 1.079$
3561 reflections
316 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 4.3865P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.764$ e Å^{-3}
$\Delta\rho_{min} = -1.881$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Re—Re^i	2.2363 (7)	Re—O4^i	2.017 (4)
Re—Cl1	2.482 (2)	O1—C1	1.294 (7)
Re—O1	2.013 (4)	O2—C1	1.268 (7)
Re—O2^i	2.009 (4)	O3—C14	1.279 (7)
Re—O3	2.019 (4)	O4—C14	1.275 (7)
Re^i—Re—Cl1	178.23 (5)	O2^i—Re—O3	90.7 (2)
O2^i—Re—Re^i	89.39 (11)	O1—Re—O3	89.3 (2)
O1—Re—Re^i	90.17 (11)	O4^i—Re—O3	179.49 (14)
O4^i—Re—Re^i	90.20 (11)	O2^i—Re—Cl1	90.11 (12)
O3—Re—Re^i	89.35 (12)	O1—Re—Cl1	90.33 (12)

O2^i—Re—O1	179.56 (14)	O4^i—Re—Cl1	91.50 (12)
O2^i—Re—O4^i	89.5 (2)	O3—Re—Cl1	88.95 (12)
O1—Re—O4^i	90.4 (2)		

Symmetry code: (i) $-x, 1-y, -z$.

The title structure was solved *via* direct methods and all non-H atoms were refined with anisotropic displacement parameters. A molecule of dichloromethane resides on a general position. H atoms were placed in idealized positions with C—H distances of 0.93 Å. The common orientation of the displacement ellipsoids of the core atoms of the molecule suggests the presence of systematic error, most probably associated with the effects of residual effects of uncorrected absorption. It is therefore to be anticipated that a small systematic error is associated with the atomic positions and necessarily with the bond lengths and angles involving these atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BS1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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6-L-Alanineferrirubin, a Ferrichrome-type Siderophore from the Fungus *Aspergillus ochraceous*

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Abstract

The molecular structure of 6-L-alanineferrirubin tetradecahydrate, [Fe(C$_{41}$H$_{64}$N$_9$O$_{16}$)].14H$_2$O, has been determined in order to confirm its chemical structure. The structural results show that the presence of an alanine in place of a serine or a glycine at position 6 in the cyclic hexapeptide has very little effect on the conformation of the 18-membered ring or on the geometry of the octahedral iron coordination.

Comment

The ferrichrome-type siderophores are a group of iron-chelating cyclic hexapeptides produced by a number of fungal species in response to low iron availability (Neilands, 1981). All the hexapeptides in this family have the general formula cyclo{Orn1–Orn2–Orn3–*A*–*B*–Gly}, where Orn1, Orn2 and Orn3 are *N*-acylated-*N*-hydroxyornithine residues, and *A* and *B* are either glycine or serine, and sometimes alanine, as in ferrichrome C (Tademura & Sato, 1967) and malinochrome (Emery, 1980). The *N*-acyl groups are derivatives of carboxylic acids.

Asperchromes are a group of new siderophores belonging to the ferrichrome family isolated from the fungus *Aspergillus ochraceous*. Most of them are characterized by having heterogeneous *N*-acyl groups, a feature which was not observed previously in ferrichromes. The isolation and description of their chemical structures