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Structure of Iron Dirhenium Tetradecacarbonyl, [$Re(CO)_5Fe(CO)_4Re(CO)_5$]

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Abstract. Tetracarbonylbis(pentacarbonylrhenio)-iron, [$FeRe_2(CO)_{14}$], $M_r = 820{\cdot}4$, monoclinic, $C2/m$, $a = 12{\cdot}062\,(1)$, $b = 14{\cdot}679\,(1)$, $c = 11{\cdot}816\,(1)$ Å, $\beta = 97{\cdot}31\,(1)^\circ$, $V = 2075{\cdot}1$ Å^3, $Z = 4$, $D_x = 2{\cdot}626$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 129$ cm^{-1}, $F(000) = 1488$, $T = 295$ K, $R(F^2) = 0{\cdot}049$ for 1580 reflections having $F^2 > \sigma(F^2)$, $wR(F^2) = 0{\cdot}03$. The asymmetric unit contains two crystallographically distinct molecules with symmetry $2/m$, similar to those found in $FeMn_2(CO)_{14}$. Both molecules have linear arrangements of metal atoms without bridging carbonyl linkages, but differ in disposition of symmetry elements. The principal observations discussed are a shortening of the Re—Fe bond [0·027 (2) Å] and a torsional distortion of the $Re(CO)_5$ and $Fe(CO)_4$ groups from an idealized staggered configuration [45→40·2 (5)°] in one of the two independent molecules. These differences between the two molecules are attributed to differences in crystalline environment. Interatomic distances have also been reported but without discussion by Crocker, Mattson, Heinekey & Schulte [*Inorg. Chem.* (1988), **27**, 3722–3729].

Introduction. Molecules with dinuclear and linear trinuclear metal cores octahedrally coordinated with nonbridging carbonyl ligands are of widespread structural interest [$Mn_2(CO)_{10}$ (Dahl & Rundle, 1963); $Tc_2(CO)_{10}$ (Bailey & Dahl, 1965); $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (Churchill, Amoh & Wasserman, 1981); $Mn_2(CO)_{10}$ (Martin, Rees & Mitschler, 1982)]. Both the $M_2(CO)_{10}$ and $FeM_2(CO)_{14}$ molecules show similar deviations from octahedral coordination, namely a bend of the equatorial carbonyl ligands about the metal–metal axis and a shorter axial M—C distance than the equatorial M—C link. Using a well determined set of X-ray and neutron data of transition-metal carbonyl complexes, Braga & Koetzle (1987, 1988) have analyzed the differences in the mean-square-amplitude displacements of the M, C and O atoms of terminally bound carbonyl ligands. The principal observation, that the thermal motion of the C atom along the M—C—O vector is greater than that of the O atom, is confirmed in this study. Martin *et al.* (1982), in a low-temperature X-ray diffraction study of the bonding in $Mn_2(CO)_{10}$, suggest that the bend of the equatorial ligands and the distortion of the torsion angle by 5° from ideal D_{4d} symmetry for the $Mn(CO)_5$—$Mn(CO)_5$ moieties are probably due to crystal environmental effects.

The X-ray structural determination of the trinuclear metal carbonyl $FeMn_2(CO)_{14}$ (Agron, Ellison & Levy, 1967) showed this molecule to be symmetric having a linear arrangement of metal atoms without bridging carbonyl groups. The two crystallographically nonequivalent molecules of $2/m$ symmetry in that structure are closely similar except for an apparent difference in the Mn—Fe bond length of 0·027 (2) Å. The isomorphous rhenium compound has been under investigation to assess the significance of the bond-length variations and angular conformations in this structure (Agron, Ellison & Levy, 1988). An analysis of the thermal motion parameters of molecules 1 and 2, using several assumed models for the correlation function of displacements, failed to produce an explanation for the discrepancy in the M—Fe bond lengths (Agron, Ellison & Levy, 1968). The sample, furnished by Professor R. K. Sheline, was prepared by UV photolysis of an equimolar solution of $Fe(CO)_5$ and $Re_2(CO)_{10}$ in *n*-hexane (Evans & Sheline, 1971).

Our X-ray results show good agreement with the atomic parameters of $FeRe_2(CO)_{14}$ reported by Crocker, Mattson, Heinekey & Schulte (1988) without a discussion of the structure. Our intent is to discuss the differences between the two nonequivalent molecules in terms of their different crystalline environments. The significant difference in the M—Fe bond lengths (Agron *et al.*, 1967) of the two chemically similar but crystallographically nonequivalent molecules has been especially puzzling (Agron *et al.*, 1968). In the following discussion the notation 1C and 2C designates molecules describing the atomic parameters given by Crocker *et al.* which correspond to molecules 1 and 2 respectively of this study.

Experimental. The structure determination was carried out on a specimen of dimensions 0·055 × 0·092 × 0·29 mm enclosed in a thin-walled capillary. The

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lattice parameters were determined by least-squares refinement of 12 centered reflections measured in the 2θ range 39–49° (Mo $K\alpha_1$, $\lambda = 0{\cdot}70926$ Å). Diffraction data range to $(\sin\theta/\lambda)_{\max} = 0{\cdot}595$ Å^{-1}, $-14 \le h \le 14$, $0 \le k \le 17$, $0 \le l \le 14$. X-ray intensity measurements were made on 1932 independent reflections (Mo $K\alpha$, 0·71073 Å, Zr filtered) with the Oak Ridge computer-controlled diffractometer (Busing, Ellison, King, Levy & Roseberry, 1968). The θ–2θ and ω scans were collected in the ranges 3–50 and 3–22°, respectively (see note in deposited material). No significant variation of standard reflections was observed. Absorption corrections ($\mu = 129$ cm^{-1}) were computed analytically with the program *ORABS* (Busing & Levy, 1957). The range of transmission was 33 to 49%. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962, Vol. III). An anomalous-dispersion correction was applied to the Re atom ($f'' = 8{\cdot}30$). Examination of the Patterson function showed the structure to be closely similar to that of the manganese analog. The 160 structural parameters, including the components of the anisotropic temperature factors, were refined on F^2 by the method of least squares with weights $w = [\sigma_c^2 + (0{\cdot}03F^2)^2]^{-1}$; the values of the usual measures of agreement* are $R(F) = 0{\cdot}0658$, $R(F^2) = 0{\cdot}0523$, GOF = 1·10 for all 1932 reflections, and $R(F) = 0{\cdot}0470$, $R(F^2) = 0{\cdot}0488$, $wR(F^2) = 0{\cdot}03$, GOF = 1·18 for the 1580 reflections with integrated intensity greater than σ. $|\Delta/\sigma|_{\max} = 3{\cdot}93$; maximum and minimum heights in the final difference Fourier map were 1·59 and $-1{\cdot}30$ e Å^{-3}. The fractional coordinates and the equivalent isotropic thermal displacement factors (Hamilton, 1959) of each of the atoms are shown in Table 1. For identification of the atoms see Fig. 1 and Table 2.

Discussion. As in the Mn structure, the asymmetric unit of $FeRe_2(CO)_{14}$ contains two nonequivalent molecules having linear metal cores without bridging carbonyl groups. One molecule of each type is shown in Fig. 1, with the positions of the symmetry elements indicated. Table 2(*a*) lists the bond distances and bond angles along with the values reported by Crocker *et al.* (1988). The cell parameters for the two crystal structure determinations differ slightly, but the geometry of the equivalent molecules is similar. It should be noted that the Re—Fe bond length is distinctly shorter in one of the nonequivalent molecules: the differences are 0·026 (2)

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic atomic displacement factors* (Å$^2 \times 10^3$) *for* $FeRe_2(CO)_{14}$

	x	y	z	U_{eq}†
Fe(1)	0	0	0	51 (2)
Re(1)	2221·6 (5)	0	−640·4 (4)	44 (3)
C(11)	549 (13)	0	1446 (15)	68 (11)
C(12)	0	1215 (13)	0	72 (12)
C(13)	1703 (8)	954 (7)	−1772 (9)	57 (7)
C(14)	3680 (14)	0	−1032 (12)	65 (10)
C(15)	2584 (9)	974 (8)	517 (8)	63 (7)
O(11)	904 (11)	0	2393 (10)	107 (10)
O(12)	0	2003 (9)	0	117 (12)
O(13)	1417 (7)	1506 (6)	−2427 (7)	91 (6)
O(14)	4593 (10)	0	−1291 (10)	96 (10)
O(15)	2815 (8)	1567 (6)	1141 (7)	98 (6)
Fe(2)	0	5000	5000	33 (1)
Re(2)	0	3058 (4)	5000	43 (3)
C(21)	1216 (13)	5000	4358 (12)	60 (9)
C(22)	817 (12)	5000	6353 (12)	53 (9)
C(23)	0	1742 (11)	5000	86 (13)
C(24)	2491 (6)	3158 (7)	5674 (9)	61 (7)
C(25)	460 (8)	3080 (6)	3440 (8)	55 (6)
O(21)	2075 (9)	5000	3915 (10)	84 (8)
O(22)	1392 (8)	5000	7229 (8)	71 (7)
O(23)	0	969 (7)	5000	124 (11)
O(24)	2491 (6)	3227 (6)	6092 (7)	89 (6)
O(25)	719 (7)	3100 (6)	2529 (6)	86 (6)

† U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensors, where U_{ij} are the components of the root-mean-square thermal displacement, and $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*)$.

Table 2. *Bond distances* (Å), *bond angles* (°) *and interatomic distances* (Å) *in iron dirhenium tetradecacarbonyl*

(*a*) Bond distances and selected bond angles; the bond distances are not corrected for thermal motion; for atom designations, see Figs. 1 and 2

	This work, mol. 1	Crocker *et al.* (1988) mol. 1*C*		This work, mol. 2	Crocker *et al.* (1988) mol. 2*C*
Fe(1)Re(1)	2·876 (1)	2·881 (1)	Fe(2)Re(2)	2·849 (1)	2·855 (1)
Fe(1)C(11)	1·75 (2)	1·85 (2)	Fe(2)C(21)	1·74 (2)	1·78 (1)
Fe(1)C(12)	1·78 (2)	1·81 (2)	Fe(2)C(22)	1·77 (1)	1·75 (1)
Re(1)C(13)	1·98 (1)	2·02 (1)	Re(2)C(24)	1·99 (1)	2·00 (1)
Re(1)C(14)	1·88 (2)	1·93 (2)	Re(2)C(23)	1·93 (2)	1·93 (1)
Re(1)C(15)	1·99 (1)	2·01 (1)	Re(2)C(25)	1·99 (1)	2·01 (1)
C(11)O(11)	1·15 (2)	1·07 (2)	C(21)O(21)	1·22 (2)	1·17 (2)
C(12)O(12)	1·16 (2)	1·16 (2)	C(22)O(22)	1·17 (1)	1·21 (2)
C(13)O(13)	1·14 (1)	1·07 (1)	C(24)O(24)	1·14 (1)	1·15 (1)
*C(14)O(14)	1·18 (2)	1·15 (2)	*C(23)O(23)	1·14 (2)	1·10 (2)
C(15)O(15)	1·15 (1)	1·11 (2)	C(25)O(25)	1·16 (1)	1·13 (1)
C(11)Fe(1)Re(1)	90·4 (5)	89·3 (5)	C(21)Fe(2)C(22)	89·4 (6)	89·9 (6)
Fe(1)Re(1)C(14)	179·1 (4)	179·0 (4)	Fe(2)Re(2)C(23)	180	180
Fe(1)Re(1)C(13)	87·8 (3)	87·3 (3)	Fe(2)Re(2)C(24)	85·8 (3)	85·7 (3)
Fe(1)Re(1)C(15)	87·1 (3)	86·9 (3)	Fe(2)Re(2)C(25)	89·1 (3)	88·7 (3)
C(13)Re(1)C(15)	88·8 (4)	87·9 (5)	C(24)Re(2)C(25)′	90·1 (4)	90·4 (4)
C(13)Re(1)C(13)′	89·9 (6)	91·2 (6)	C(24)Re(2)C(25)′	89·8 (4)	89·4 (4)
C(15)Re(1)C(15)′	92·0 (6)	92·5 (7)	C(24)Re(2)C(24)′	171·5 (6)	171·4 (5)
C(13)Re(1)C(15)′	174·3 (4)	174·6 (4)	C(25)Re(2)C(25)′	178·2 (5)	177·5 (5)
Re(1)C(13)O(13)	179·1 (18)	178·5 (11)	Fe(2)(C22)(O22)	177·6 (12)	178·5 (13)
Re(1)(C15)O(15)	176·2 (10)	175·6 (11)	Re(2)(C24)(O24)	177·8 (11)	179·6 (6)
			Re(2)(C25)(O25)	179·3 (9)	179·5 (10)

(*b*) Significant environmental interatomic distances for molecules 1 and 2

Molecule 1		Molecule 2	
O(14)···O(22)(54405)	2·96	O(23)···O(23)(55503)	2·85 (2·95)†
O(15)···O(22)(54606)	3·07	O(22)···O(14)(45605)	2·96
O(14)···O(14)(65502)	3·08	O(15)(55506)	3·07
O(25)(54506)	3·15	C(15)(55608)	3·07
O(25)(55508)	3·15	C(15)(55606)	3·13
C(14)(65502)	3·23	C(15)(55608)	3·13
O(11)···O(22)(54606)	3·23	O(11)(55606)	3·23

Symmetry code: 01: x, y, z; 02: $-x, y, -z$; 03: $x, -y, z$; 04: $-x, -y, -z$; 05: $\frac{1}{2}+x, \frac{1}{2}+y, z$; 06: $\frac{1}{2}-x, \frac{1}{2}+y, -z$; 07: $\frac{1}{2}+x, \frac{1}{2}-y, z$; 08: $\frac{1}{2}-x, \frac{1}{2}-y, -z$.

* Axial ligands.

† This value was corrected for thermal motion (Busing & Levy, 1964).

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* Lists of structure factors, anisotropic thermal parameters and crystal data, and views of the molecules have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53637 (46 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Crocker *et al.*, 1988) or 0·027 (2) Å (present work, Table 2); a similar difference was observed in the Mn compound.

The disposition of the $FeRe_2(CO)_{14}$ molecules* in this structure is analogous to that indicated previously for the Mn compound (Agron *et al.*, 1967, Fig. 5). As in the $FeMn_2(CO)_{14}$ structure, the linear triatomic groups have two distinct orientations; one lying in the mirror plane of symmetry across twofold rotation axes and the other along a twofold rotation axis across a mirror plane. The coordination of each metal atom is nearly octahedral; however, the equatorial C—O groups around each Re atom are appreciably displaced toward the center of the molecule, resulting in an average Fe—Re—CO bond angle of 87° (Table 2). Projections down the metal axes of molecules 1 and 2 show the conformation of the ligands (Fig. 1).

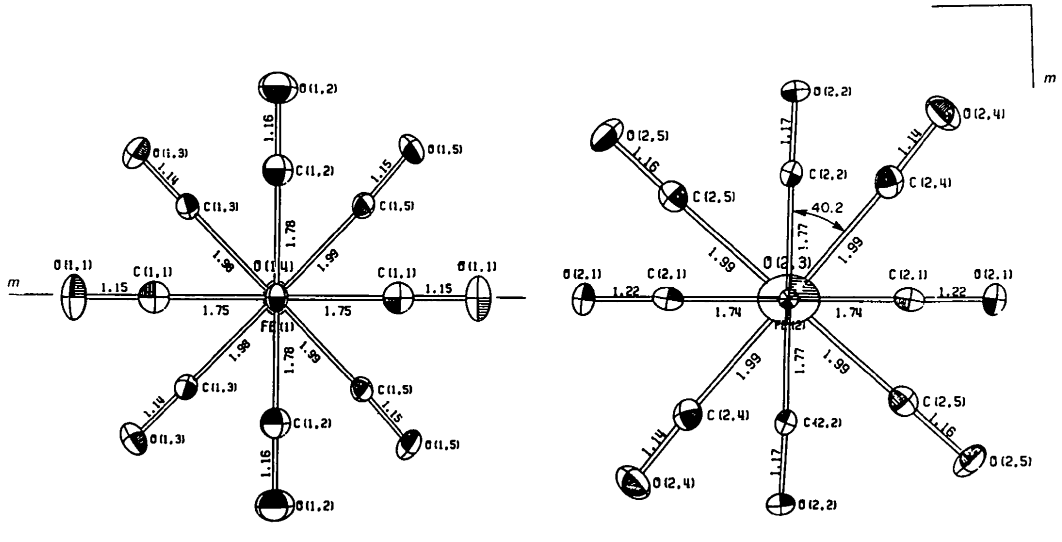
Although molecules 1 and 2 are chemically alike, they are crystallographically distinct, and their crystal environments differ. A view of molecules 1 and 2 along the *b* axis (Fig. 2) shows the significant intermolecular van der Waals distances, which are listed in Table 2(*b*).

The O(23)···O(23) distance between adjacent apical atoms along the *b* axis is the shortest contact (2·85 Å); it lies along the twofold axis between neighboring molecules. Although the separation is not unacceptably short, the large thermal displacement of O(23), which is nearly isotropic in the *ac* plane (Fig. 2), suggests that the two neighboring O(23) atoms are in repulsion, and that their displacements are to some extent anticorrelated. On this assumption, the corrected mean separation (Busing & Levy, 1964) may be as great as 2·95 Å. The next closest O distance for molecule 2 is O(22) to O(14) at 2·96 Å (uncorrected) (Fig. 2). This short distance appears to have caused the $Fe(CO)_4$ group of molecule 2 to be displaced from its expected 45° configuration (Fig. 1): the magnitude of the conformational angle C(24)—Re(2)—Fe(2)—C(22) is 40·2 (5)°, distinctly smaller than the expected 45° for an isolated molecule. [If this rotation had not occurred, we estimate that the O(22)···O(14) separation would have an improbably short value of 2·71 Å.] The corresponding conformation angles are 40° for molecule 2*C* and 41° for molecule 2 of $FeMn_2(CO)_{14}$. The conformation angles are normal at 45 (1)° for molecule 1 in both the Re and Mn structures.

In both molecules 1 and 2, the axial Re—CO length is distinctly shorter than the equatorial Re—CO link. This shortening is in accord with the concept that $Md_\pi \rightarrow CO\pi^*$ backbonding is greater for the axial links (Cotton & Daniels, 1983). Differences in the extent of backbonding may also be invoked to account for the striking difference of 0·027 (2) Å in the Re—Fe bond length of the chemically equivalent molecules. Differences in axial bond lengths between molecules 1 and 2 show a consistent alternation in sign:

$$\text{——Fe}\,\frac{2{\cdot}876\,(1)}{2{\cdot}849\,(1)}\,\text{Re}\,\frac{1{\cdot}88\,(2)}{1{\cdot}93\,(2)}\,\text{C}\,\frac{1{\cdot}18\,(2)}{1{\cdot}14\,(2)}\,\text{O}\quad\begin{array}{l}\text{Molecule 1}\\ \text{Molecule 2}\end{array}$$

This pattern of differences must result from the different molecular environments, and suggests that



Molecule 1 Molecule 2

Fig. 1. The two molecules viewed along the metal–metal axis showing the conformation of the equatorial carbonyl groups about the metal atoms. Distances are given in Å.

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* See deposited material, Fig. 3.

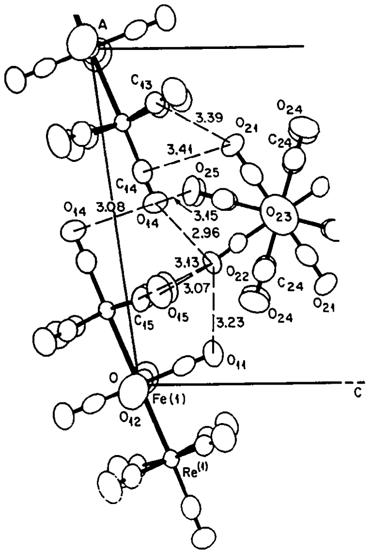

Fig. 2. A perspective drawing along the *b* axis of molecules 1 and 2 showing significant interatomic distances (Å).

the extent of backbonding is influenced by the van der Waals distances, perhaps dominated by the short O(23)···O(23) approach.

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Refinement of the Structure of Liroconite, a Heteropolyhedral Framework Oxysalt Mineral

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Abstract. Aluminium dicopper arsenate tetrahydroxide tetrahydrate, $Cu_2Al(AsO_4)(OH)_4.4H_2O$, $M_r = 433$, monoclinic, $I2/a$, $a = 12{\cdot}664\ (2)$, $b = 7{\cdot}563\ (2)$, $c = 9{\cdot}914\ (3)$ Å, $\beta = 91{\cdot}32\ (2)^\circ$, $V = 949{\cdot}4\ (3)$ Å^3, $Z = 4$, $D_x = 3{\cdot}04$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 84{\cdot}9$ cm^{-1}, $F(000) = 848$, $T = 297$ K, $R = 0{\cdot}027$ for 1215 observed reflections. The structure is a heteropolyhedral framework of $[AsO_4]$ tetrahedra, $[CuO_2(OH)_2(H_2O)_2]$ octahedra and $[AlO_2(OH)_4]$ octahedra.

Introduction. We have a systematic study of the stereochemistry of Cu^{2+} oxysalt minerals currently under way (Eby & Hawthorne, 1989*a*,*b*; Hawthorne & Eby, 1985; Hawthorne & Groat, 1985, 1986; Hawthorne, 1985*a*,*b*, 1986*a*,*b*; Groat & Hawthorne, 1987; Hawthorne, Groat & Eby, 1989) focused primarily on the heteropolyhedral connectivity of these structures and the interaction between local Jahn–Teller distortion, polyhedral connectivity and structural periodicity. As part of this work a refinement and reconsideration of the structure of clinoclase was initiated.

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