The coordination of O atoms to the U atom is hexagonal bipyramidal. The U—O distance in the $UO_2$ group is 1·777 (16) Å, typical for $UO_2$ groups in many uranyl complexes. The six equatorial O atoms belonging to the salicylic ions are at a mean distance U—O 2·46 (2) Å. The hydroxyl groups are unbonded (see Fig. 1). The U—$O_6$ array is a slightly deformed planar hexagon with O—U—O angles of 52·4 (7)° (O atoms of the same salicylate) and O—U—O of 67·6 (8)° (O atoms of adjacent salicylates). The observed bond lengths listed in Table 1 are in fair agreement with those found in other uranyl complexes containing organic-acid molecules.

Although the title compound was prepared from sodium salicylate, we found no evidence for $Na^+$ ions during the structure determination; the same material can also be prepared with the exclusion of any sodium-containing compounds. We therefore conclude that the single cation per uranyl group necessary for charge balance must be a proton. The compound therefore does not correspond to potassium trisalicylate (reported by Weinland & Hager, 1927). We were unable to locate this proton. However, the symmetrical bonding of the salicylate groups makes it unlikely that the proton is attached to one of these anions. The unit cell therefore probably contains two protonated water molecules, distributed at random, in positions 6(h) and 12(i).

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# Structures of Tetracarbonyl(2-3-η-maleic acid)iron, cis-[Fe(C₄H₄O₄)(CO)₄] (1) and Tetracarbonyl(2-3-η-fumaric acid)iron, trans-[Fe(C₄H₄O₄)(CO)₄] (2)

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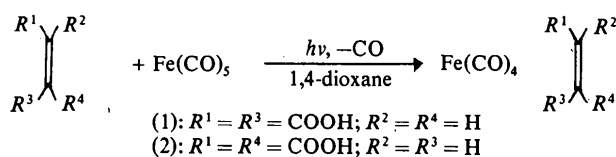*Institute of Chemistry, Academia Sinica, Nankung, Taiwan*

**Abstract.** (1) cis-[Fe(C₄H₄O₄)(CO)₄], $M_r = 284$, monoclinic, $P2_1/c$, $a = 12·897$ (2), $b = 10·799$ (2), $c = 15·416$ (2) Å, $\beta = 104·78$ (1)°, $V = 2076$ (6) Å³, $Z = 8$, $D_x = 1·817$, $D_m = 1·80$ (5) g cm⁻³, $\lambda(Mo\ K\alpha) = 0·7107$ Å, $\mu = 1·48$ cm⁻¹, $F(000) = 1136$, $T = 298$ K, final $R = 0·031$ for 1941 observed reflections. (2) trans-[Fe(C₄H₄O₄)(CO)₄], $M_r = 284$, orthorhombic, Pccn, $a = 6·048$ (2), $b = 13·443$ (3), $c = 12·703$ (3) Å, $V = 1032·7$ (5) Å³, $Z = 4$, $D_x = 1·826$, $D_m = 1·80$ (5) g cm⁻³, $\lambda(Mo\ K\alpha) = 0·7107$ Å, $\mu = 1·49$ cm⁻¹, $F(000) = 568$, $T = 298$ K, final $R = 0·039$ for 908 observed reflections. Compound (1) contains two molecules in the asymmetric unit. Compound (2) contains only half a molecule in the asymmetric unit, with the molecular symmetry, $C_2$, relating to the crystallographic twofold rotation axis. The corresponding bond lengths and angles in the two isomers agree well. The coordination polyhedron around the iron atom in both structures is a trigonal bipyramid with the ethylenic double bond of the maleic and fumaric acid groups in the equatorial plane. Both compounds have rows of hydrogen bonds, directed along the a and the b axes, respectively. The planes containing the Fe atom and the ethylenic double bonds of the acids are rotated from the equatorial plane [Fe(CO)₂] by 3·9 (3) and 5·8 (4)° in compound (1), and 11·2 (3)° in compound (2).

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**Introduction.** This structural investigation of the two isomers, tetracarbonyl(2-3-η-maleic acid)iron and tetracarbonyl(2-3-η-fumaric acid)iron, was undertaken to study the differences in their molecular structure as well as their solid molecular packing. The comparisons of their Fe-atom coordination spheres and $\pi,\pi^*$ ligand-to-metal, metal-to-ligand interactions are also of interest. The crystal structure of (2) was previously studied with photographic data (Pedone & Sirigu, 1967). The redetermination of the structure of compound (2) was performed for the comparison between the two isomeric structures.

**Experimental.** Compounds (1) and (2) were prepared by photolysis of $Fe(CO)_5$ in the presence of excess olefinic acid, under $N_2$ in 1,4-dioxane.

$$R^1 \diagdown R^2 \quad \diagup \quad \diagdown R^3 \diagup R^4 + Fe(CO)_5 \xrightarrow[1,4\text{-dioxane}]{h\nu, -CO} Fe(CO)_4 \quad R^1 \diagdown R^2 \diagup \diagdown R^3 \diagup R^4$$

(1): $R^1 = R^3 = COOH$; $R^2 = R^4 = H$
(2): $R^1 = R^4 = COOH$; $R^2 = R^3 = H$

Suitable single crystals were obtained by evaporation from acetone–hydrochloric acid. (1) Crystal $0.2 \times 0.2 \times 0.3$ mm. CAD-4 diffractometer. Unit cell from 25 reflections, $2\theta$ range $15.1$ to $29.3°$. $D_m$ by flotation $(CCl_4/CHBr_3)$. $2\theta_{max} = 50°$. Ranges of $h, k, l$: 0 to 15, 0 to 12, $-18$ to 18. $2\theta$ scan range $(1.3 + 0.7\tan\theta)°$. Three reflections monitored; variation $< 2\%$. 3642 unique reflections, 1941 observed with $I > 2\sigma(I)$. $R(F) = 0.031$, $wR(F) = 0.025$, $S = 1.3$. $(\Delta/\sigma)_{max} = 0.001$. Peaks in final map $< \pm 0.25$ e Å$^{-3}$. (2) Crystal $0.2 \times 0.3 \times 0.5$ mm. CAD-4 diffractometer. Unit cell from 25 reflections, $2\theta$ range $20.5$ to $30.6°$. $D_m$ by flotation $(CCl_4/CHBr_3)$. $2\theta_{max} = 50°$. Ranges of $h, k, l$: 0 to 7, 0 to 15, 0 to 15. Three reflections monitored; variation $< 2\%$. 908 unique reflections, 531 observed with $I > 2\sigma(I)$. $R(F) = 0.039$, $wR(F) = 0.028$, $S = 1.95$. $(\Delta/\sigma)_{max} = 0.03$. Peaks in final map $< \pm 0.60$ e Å$^{-3}$. For both crystals: weighting scheme from counting statistics, structure solved by heavy-atom method using the NRCC program package (Gabe, Le Page, White & Lee, 1987) and H atoms found from difference Fourier map after isotropic refinement and then refined. Atomic scattering factors from International Tables for X-ray Crystallography (1974).

**Discussion.** There are two independent molecules in the asymmetric unit of compound (1). However, there is no significant difference between the two independent molecules (see Table 2), and the structure of only one of the molecules is shown in Fig. 1(a). The molecular symmetry of compound (2) is $C_2$, with the twofold rotation axis passing through the Fe atom and the midpoint of the olefinic C=C double bond of the

Table 1. *Atomic fractional coordinates and isotropic thermal parameters with their e.s.d.'s*

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

| | x | y | z | $B_{eq}(\text{Å}^2)$ |
|---|---|---|---|---|
| Compound (1) | | | | |
| Fe(1) | 0.42994 (7) | 0.18344 (8) | 0.63002 (5) | 2.86 (4) |
| Fe(2) | −0.06162 (7) | 0.26587 (9) | 0.67085 (5) | 3.53 (4) |
| O(1) | 0.5118 (4) | 0.5080 (4) | 0.6311 (3) | 3.7 (2) |
| O(2) | 0.3465 (3) | 0.5153 (4) | 0.6375 (3) | 3.9 (2) |
| O(3) | 0.6280 (3) | 0.3701 (4) | 0.5616 (2) | 3.4 (2) |
| O(4) | 0.6009 (4) | 0.2112 (5) | 0.4665 (3) | 4.4 (2) |
| O(5) | 0.3089 (4) | 0.2062 (5) | 0.7666 (3) | 6.2 (3) |
| O(6) | 0.2446 (4) | 0.0606 (4) | 0.5082 (3) | 5.7 (3) |
| O(7) | 0.5534 (4) | −0.0475 (4) | 0.6547 (3) | 5.9 (3) |
| O(8) | 0.6175 (3) | 0.2911 (4) | 0.7585 (3) | 4.9 (2) |
| O(11) | −0.0449 (3) | 0.2314 (4) | 0.4384 (3) | 4.1 (2) |
| O(12) | −0.2145 (3) | 0.2188 (4) | 0.4331 (3) | 4.0 (2) |
| O(13) | 0.1214 (3) | 0.3357 (4) | 0.5383 (3) | 3.9 (2) |
| O(14) | 0.1513 (3) | 0.4842 (4) | 0.6410 (3) | 4.1 (2) |
| O(15) | −0.2305 (4) | 0.0831 (5) | 0.6697 (4) | 7.3 (3) |
| O(16) | −0.1910 (4) | 0.4460 (5) | 0.7421 (3) | 6.7 (3) |
| O(17) | 0.1139 (4) | 0.2704 (7) | 0.8351 (3) | 8.9 (4) |
| O(18) | 0.0581 (4) | 0.0720 (5) | 0.6043 (4) | 7.3 (3) |
| C(1) | 0.3903 (4) | 0.3458 (5) | 0.5574 (4) | 2.8 (3) |
| C(2) | 0.4549 (4) | 0.2720 (6) | 0.5171 (4) | 3.0 (3) |
| C(3) | 0.5692 (4) | 0.2906 (5) | 0.5182 (3) | 2.9 (3) |
| C(4) | 0.4154 (5) | 0.4613 (5) | 0.6109 (4) | 2.9 (3) |
| C(5) | 0.3566 (5) | 0.1966 (6) | 0.7149 (4) | 3.8 (3) |
| C(6) | 0.3155 (5) | 0.1069 (6) | 0.5555 (4) | 3.7 (3) |
| C(7) | 0.5039 (5) | 0.0391 (6) | 0.6447 (4) | 4.1 (3) |
| C(8) | 0.5460 (4) | 0.2522 (6) | 0.7073 (4) | 3.3 (3) |
| C(11) | −0.1140 (4) | 0.3483 (5) | 0.5464 (4) | 2.9 (3) |
| C(12) | −0.0219 (6) | 0.4109 (6) | 0.5966 (4) | 3.3 (3) |
| C(13) | 0.0892 (5) | 0.4055 (6) | 0.5887 (4) | 3.3 (3) |
| C(14) | −0.1283 (4) | 0.2621 (5) | 0.4688 (3) | 3.0 (3) |
| C(15) | −0.1629 (6) | 0.1505 (7) | 0.6724 (4) | 4.7 (4) |
| C(16) | −0.1407 (5) | 0.3769 (7) | 0.7167 (4) | 4.5 (3) |
| C(17) | 0.0433 (5) | 0.2683 (8) | 0.7735 (4) | 5.5 (4) |
| C(18) | 0.0133 (5) | 0.1491 (6) | 0.6278 (4) | 4.3 (3) |
| Compound (2) | | | | |
| Fe | 0.2500 | 0.7500 | 0.22432 (7) | 2.56 (4) |
| C(1) | 0.3914 (7) | 0.8685 (3) | 0.2292 (4) | 3.7 (2) |
| C(2) | 0.0352 (7) | 0.8049 (3) | 0.3028 (3) | 3.6 (3) |
| C(3) | 0.1407 (7) | 0.7663 (3) | 0.0711 (4) | 2.7 (2) |
| C(4) | 0.0850 (8) | 0.8705 (3) | 0.0424 (4) | 2.9 (2) |
| O(1) | 0.4809 (5) | 0.9417 (2) | 0.2374 (3) | 5.8 (2) |
| O(2) | −0.1038 (5) | 0.8415 (2) | 0.3496 (2) | 5.8 (2) |
| O(3) | 0.2200 (5) | 0.9323 (2) | 0.0212 (2) | 4.3 (2) |
| O(4) | −0.1278 (6) | 0.8858 (2) | 0.0427 (4) | 4.5 (2) |

fumaric acid moiety. The molecular structure of compound (2) is shown in Fig. 1(b). The fractional atomic coordinates and equivalent thermal parameters are given in Table 1.* Selected bond distances and angles are listed in Table 2. As expected, a trigonal bipyramidal coordination around the iron atom is found in both structures. The olefinic C=C double bonds are in the equatorial position. There are no significant differences in interatomic distances and angles between the two compounds. In addition, the Fe—CO and CH=CH bond lengths are essentially the same as those in the literature (Krüger, Barnett & Brauer, 1978).

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## Table 2. *Selected bond distances* (Å) *and angles* (°)

**Compound (1)**

| | | | |
|---|---|---|---|
| Fe(1)–C(1) | 2·073 (6) | Fe(2)–C(11) | 2·067 (6) |
| Fe(1)–C(2) | 2·082 (6) | Fe(2)–C(12) | 2·079 (6) |
| Fe(1)–C(5) | 1·805 (6) | Fe(2)–C(15) | 1·809 (7) |
| Fe(1)–C(6) | 1·821 (6) | Fe(2)–C(16) | 1·830 (7) |
| Fe(1)–C(7) | 1·811 (7) | Fe(2)–C(17) | 1·800 (6) |
| Fe(1)–C(8) | 1·817 (6) | Fe(2)–C(18) | 1·814 (7) |
| | | | |
| C(1)–Fe(1)–C(2) | 39·6 (2) | C(11)–Fe(2)–C(12) | 39·9 (2) |
| C(1)–Fe(1)–C(5) | 102·8 (3) | C(11)–Fe(2)–C(15) | 104·0 (3) |
| C(1)–Fe(1)–C(6) | 89·7 (3) | C(11)–Fe(2)–C(16) | 89·7 (3) |
| C(1)–Fe(1)–C(8) | 93·3 (2) | C(11)–Fe(2)–C(18) | 92·2 (3) |
| C(2)–Fe(1)–C(6) | 87·4 (2) | C(12)–Fe(2)–C(16) | 87·7 (3) |
| C(2)–Fe(1)–C(7) | 108·1 (3) | C(12)–Fe(2)–C(17) | 103·7 (3) |
| C(2)–Fe(1)–C(8) | 94·8 (2) | C(12)–Fe(2)–C(18) | 95·4 (3) |
| C(5)–Fe(1)–C(6) | 90·1 (3) | C(15)–Fe(2)–C(16) | 88·3 (3) |
| C(5)–Fe(1)–C(7) | 109·5 (3) | C(15)–Fe(2)–C(17) | 112·4 (3) |
| C(5)–Fe(1)–C(8) | 89·4 (3) | C(15)–Fe(2)–C(18) | 88·8 (3) |
| C(6)–Fe(1)–C(7) | 90·2 (3) | C(16)–Fe(2)–C(17) | 91·1 (3) |
| C(6)–Fe(1)–C(8) | 177·0 (3) | C(16)–Fe(2)–C(18) | 176·9 (3) |
| C(7)–Fe(1)–C(8) | 87·2 (3) | C(17)–Fe(2)–C(18) | 88·9 (3) |

**Compound (2)**

| | | | |
|---|---|---|---|
| Fe–C(1) | 1·809 (4) | Fe–C(3) | 2·067 (4) |
| Fe–C(2) | 1·796 (4) | | |
| | | | |
| C(1)–Fe–C(2) | 87·8 (2) | C(2)–Fe–C(3) | 104·4 (2) |
| C(1)–Fe–C(3) | 95·2 (2) | C(3)–Fe–C(3a) | 39·4 (2) |
| C(2)–Fe–C(2a) | 112·6 (2) | | |

The olefinic acid moieties of both molecules appear to be nonplanar. The carboxylic acid planes, C(3)–C(2)–C(1)–C(4) in (1) and C(4)–C(3)–C(3a)–C(4a) in (2), are bent away from the axial carbonyl groups C(8)–O(8) in (1) and C(1)–O(1) in (2), making an angle of about 15° from their ideal parallel position; the dihedral angles: C(1), C(2), C(3), C(4) with Fe(1), C(1), C(2); C(11), C(12), C(13), C(14) with Fe(2), C(11), C(12) (Fig. 1); and C(3), C(3a), C(4) with Fe, C(3), C(3a), are 73·6 (6), 74·7 (3) and 73·4 (4)° respectively. This is also consistent with the strong tendency of $d$ back-donation from the Fe atom, which will make the olefinic C atom rehybridize giving a larger proportion of $p$ character than $sp^2$. The lengthening of the C=C double bond relative to that in free acids (Brown, 1966; James & Williams, 1974) and the shortening of the Fe—C bonds are in accordance with such metal-to-olefin $d\pi$–$\pi^*$ back-bonding.

Perspective views of the crystal structures are shown in Fig. 2. Both structures are hydrogen bonded; they
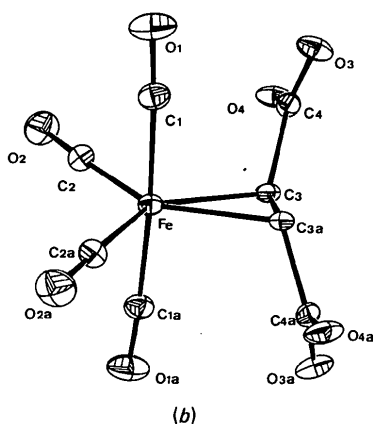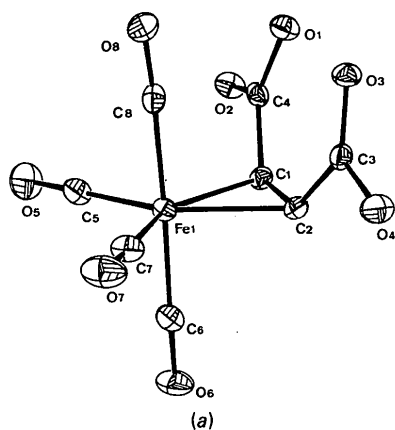


Fig. 1. (a) Molecular geometry of compound (1); the other molecule in the asymmetric unit has the same conformation but is labeled so that Fe(2) corresponds to Fe(1), C(11) to C(1), C(12) to C(2), etc. (b) Molecular geometry of compound (2).
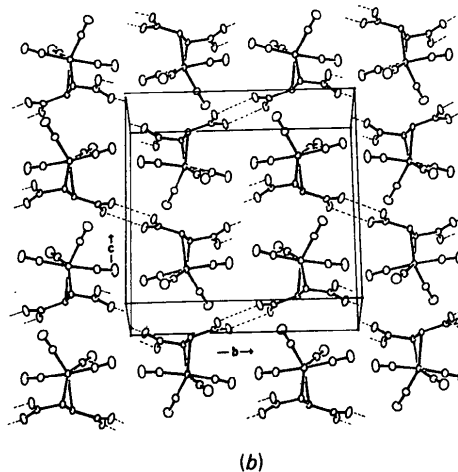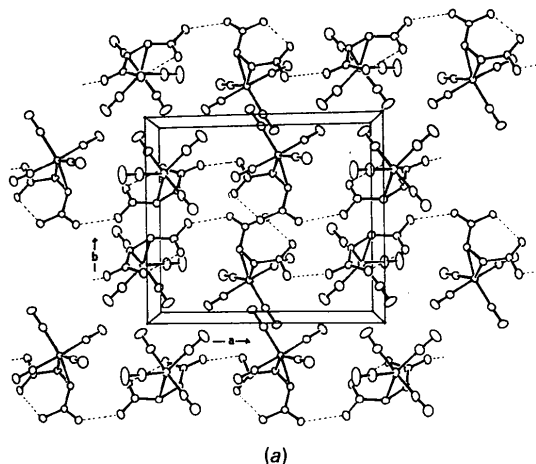


Fig. 2. Perspective view of the crystal structure (a) of compound (1) and (b) of compound (2).

contain rows of intermolecular hydrogen bonds along the *a* and *b* axes, respectively. In compound (1), each molecule has both intra- and intermolecular hydrogen bonds with O···O distances 2·536 (6), 2·560 (6) and 2·553 (6), 2·562 (6) Å, and corresponding O—H···O angles 164 (6), 164 (6), and 174 (7), 163 (5)°, respectively. However, in compound (2), because of the *trans* conformation, only intermolecular hydrogen bonding is possible. Each molecule has two identical inter-molecular hydrogen bonds with O···O distance 2·637 (4) Å and O—H···O angle 175 (5)°. The two bonds are related by a center of inversion as are those in the common carboxylic acid dimer. The molecules are hydrogen bonded throughout the crystal as depicted in Fig. 2(*b*).

In this series of compounds, the interesting structural features appear not only in the interaction between the olefin group and the metal ion, but also in the coplanarity of the atoms in the equatorial plane. It is apparent that compound (1) has much better co-planarity than compound (2) ($\chi^2$ ratio of 1:10). Such deviation can be seen as a rotation of 11·23° of the fumaric acid molecule around the bond between the Fe atom and the ethylenic double bond; it corresponds to a

rotation of only 3·9 (3) and 5·8 (4)° in compound (1). These rotations could be rationalized by the crystal lattice energy, intermolecular hydrogen bonding or a low-energy rotation barrier around the bond between the Fe atom and the ethylenic double bond. More work has to be performed before any definite conclusions can be drawn.

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# (η-8,9,10-Trinorbornadiene)[1,1,1-tris(diphenylphosphinomethyl)ethane-*P,P',P''*]rhodium Trifluoromethanesulfonate Methanol Solvate

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**Abstract.** [Rh(C₇H₈)(C₄₁H₃₉P₃)]CF₃SO₃.CH₄O, C₄₈-H₄₇P₃Rh⁺CH₄O.CF₃O₃S⁻, $M_r = 1000·8$, monoclinic, $P2_1/c$, $a = 10·404$ (6), $b = 17·239$ (7), $c = 25·349$ (7) Å, $\beta = 90·95$ (6)°, $V = 4546$ (3) Å³, $Z = 4$, $D_x = 1·460$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0·71073$ Å, $\mu = 5·7$ cm⁻¹, $F(000) = 2061$, $T = 293$ K, $R = 0·059$ for 7015 observed reflections. The Rh atom is penta-coordinated in a distorted square-pyramidal arrangement. The midpoints of the diolefinic coordinated double bonds and two P atoms of the tridentate phosphine ligand occupy equatorial sites, while the third P atom lies in the axial position.

**Introduction.** The coordination chemistry of the tripod-like tridentate ligand 1,1,1-tris(diphenylphosphino-

methyl)ethane, triphos, has been widely studied (Sacconi & Mani, 1982). Its geometry is such that it can only occupy three facial sites of a coordination polyhedron. As a consequence of its specific geometry, complexes with a stereochemistry and a reactivity not readily achievable with three unidentate ligands may be realized.

Since the catalytic activity of triphos complexes has not been extensively investigated, a study was undertaken on the synthesis, structure and reactivity of Rhᴵ and Rhᴵᴵᴵ triphos complexes of relevance to homogeneous hydrogenation such as hydrido, alkyl and olefin complexes.

The triphos ligand was found to stabilize penta-coordinated complexes of the type [Rh(diol)(triphos)]