Table 3. *A comparison of the average dimensions* (Å, °) *of the* $[Cu_2(COO)_4]$ *cage and* $-2J$ *values* (cm^{-1})

	(I) $[Cu_2(2\text{-Cl-PhCOO})_4(H_2O)_2]$	(II) $[Cu_2(2\text{-Cl-PhCOO})_4(\text{pyridine})_2].2CCl_4$
Cu···Cu	2.599 (1)	2.679 (1)
Cu—O	1.966 (2)	1.974 (5)
Cu—*L*	2.138 (2)	2.149 (6)
C—O	1.253 (4)	1.26 (1)
Cu—O—C	123.0 (2)	123.2 (5)
O—C—O	124.5 (2)	126.2 (7)
φ_{rot}*	2.6 (3), 24.0 (2)	84.5 (3), 48.8 (3), 88.7 (3), 55.1 (3)
φ_{bend}†	2.2 (1), 12.5 (1)	2.1 (2), 2.8 (2), 2.6 (2), 2.5 (2)
$-2J$	262	351‡

* The dihedral angle between the Ph ring and carboxyl moiety in the bridging benzoate ions.

† The dihedral angle between the Cu—O···O—Cu plane and carboxyl moiety in the bridge.

‡ The $-2J$ value of (II) was measured after the removal of CCl_4 from crystals under reduced pressure.

molecular hydrogen bonds in the aqua adduct, the O···O distance being 2.847 (4) Å with φ_{bend} less than 2° (Furukawa, Nakashima, Tokii & Muto, 1992). These results suggest that the $-2J$ value is more sensitive to the φ_{bend} than the intermolecular hydrogen bonds. One more example supports this speculation. The aqua adduct of copper(II) 2-methoxybenzoate shows the small $-2J$ value, 284 cm^{-1} (Adelsköld, Eriksson, Werner, Westdahl, Lučanska, Krätsmár-Šmogrovič & Valent, 1989) in accordance with the large φ_{bend} angles of 8.1 (6)–12.7 (6)°, the O···O distances of intermolecular hydrogen bonds ranging from 2.92 (2) to 3.11 (2) Å.

Rotation angles of the phenyl group to the carboxyl moiety, φ_{rot}, are 2.6 (3) and 24.0 (2)° in (I), and from 48.8 (3) to 88.7 (3)° in (II). However, the φ_{rot} angle does not correlate with the $-2J$ value (Kawata *et al.*, 1992).

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Acta Cryst. (1992). **C48**, 1594–1597

Structure of the Clathrate Compound Tris(2,4-pentanedionato)iron(III)–*trans*-1,2-Dichloroethene (1/1)

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(*Received* 25 *November* 1991; *accepted* 28 *January* 1992)

Abstract. $[Fe(C_5H_7O_2)_3].C_2H_2Cl_2$, $M_r = 450.12$, orthorhombic, $P2_1ca$, $a = 7.8439$ (23), $b = 10.2444$ (19), $c = 26.550$ (5) Å, $V = 2133.5$ (8) Å^3, $Z = 4$, D_m(flotation in KI/H_2O) = 1.37, $D_x = 1.40$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.70930 Å, $\mu = 0.98$ mm^{-1}, $F(000) = 931.89$, $T = 295$ K, final $R = 0.056$ and $wR = 0.054$ for 1008 reflections with $I > 2.5\sigma(I)$. The molecular structure of the $Fe(acac)_3$ in the $Fe(acac)_3.C_2H_2Cl_2$ (II) clathrate phase is not significantly different from that in the non-clathrated phase (I) or in the clathrate phase of $Fe(acac)_3.CCl_4$ (IV). The *trans*-CHCl═CHCl guest molecule is located at an ordered general position in the clathrate phase.

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Introduction. Tris(acetylacetonato)iron(III), Fe(acac)$_3$, was observed to form 1/2 addition compounds with chloroform molecules over 30 years ago (Steinbach & Bruns, 1958). This chelate complex was recently shown to form clathrate compounds with

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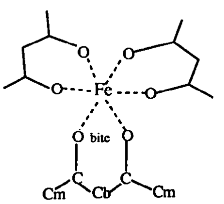
different small solvent molecules, such as CH_2Cl_2, $CHCl_3$, CCl_4, *trans*-CHCl=CHCl and 1,2-CH_2Cl-CH_2Cl (Pang, 1989). The $Fe(acac)_3$ complex (I) crystallizes from benzene to give the non-clathrated phase in the space group *Pbca* (Iball & Morgan, 1967). However, an X-ray analysis of $Fe(acac)_3$.-CCl_4 revealed that the compound has the space group *R*3 and the host $Fe(acac)_3$ molecule utilizes crystallographic C_3 symmetry in construction of the cage, generating trigonal cavities to accommodate the CCl_4 guest molecule (Pang, Lucken & Bernardinelli, 1990). We report here a crystallographic study of the $Fe(acac)_3.C_2H_2Cl_2$ clathrate (II) whose structure has not previously been described.



(I) $[Fe(C_5H_7O_2)_3]$
(II) $[Fe(C_5H_7O_2)_3].C_2H_2Cl_2$
(III) $[Fe(C_5H_7O_2)_3].C_2H_4Cl_2$
(IV) $[Fe(C_5H_7O_2)_3].CCl_4$
(V) $[Fe(C_5H_7O_2)_3].2CHCl_3$
(VI) $[Fe(C_5H_7O_2)_3].2CH_2Cl_2$

Experimental. The host $Fe(acac)_3$ (Johnson Matthey) was dissolved in the *trans*-CHCl=CHCl solvent, and on recrystallization the red plate single crystals of the clathrate (II) were obtained. The host/guest ratio was determined from a crystal density measurement (flotation in KI/H_2O), $D_m = 1.37$ g cm^{-3}. A crystal of a suitable size ($0.40 \times 0.15 \times 0.05$ mm) was selected and removed from the mother liquor, quickly covered with epoxy to prevent deterioration, and then mounted on the tip of a glass fibre.

Cell parameters and refinement intensities were measured at 295 K on a Rigaku diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Accurate cell parameters were obtained by least-squares analysis of 23 reflections measured in the range $25 < 2\theta < 32°$; $2\theta_{max} = 49.9°$; collection range $0 \le h \le 9$, $0 \le k \le 12$, $0 \le l \le 31$; ω-scan mode, scan rate 16° min^{-1}, scan width 1.5°. A total of 2026 reflections (all unique) were measured. No absorption correction was applied. Standard intensities dropped an average of 0.95% over the collection. The structure was solved by direct methods, and all the non-H atoms were refined anisotropically using the *NRCVAX* system of structure-solving programs (Gabe, Le Page, Charland, Lee & White, 1989). All positions and thermal parameters of the H atoms were calculated. In the final cycle, 234 parameters were refined using 1008 unique reflections with $I > 2.5\sigma(I)$. The structure refinement (based on *F*) converged with $R = 0.056$, $wR = 0.054$ [$w = 1/\sigma^2(F)$] and $S = 1.51$; maximum $\Delta/\sigma = 0.075$; maximum/minimum $\Delta\rho = 0.40/-0.45$ e Å^{-3}. Atomic scattering factors and f',f'' values were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Atomic parameters are reported in Table 1,* Bond distances and bond angles in the clathrate (II) are shown in Table 2 using the numbering scheme in Fig. 1. Table 3 compares various structural parameters of $Fe(acac)_3$ in its non-clathrated phase (I) with those in the two clathrate phases (II) and (IV). The $Fe(acac)_3$ molecule is seen to have similar geometrical structures in the different compounds because the mean bond distances hardly change from one compound to another. Therefore, $Fe(acac)_3$ is a rigid host complex since the presence of the *trans*-CHCl=CHCl or CCl_4 guest molecules has no effect on the host molecular structure. This fact has not been observed in the Werner host complexes (Lipkowski, 1984), which change their usual molecular configuration to reflect the size and the shape of a guest molecule.

Although the presence of the guest molecules *trans*-CHCl=CHCl or CCl_4 does not affect the $Fe(acac)_3$ geometrical structure, the guest molecules do change the crystal structure of clathrates related to each other and to the crystal structure of non-clathrated phases. The *trans*-CHCl=CHCl clathrate (II) crystallizes in the same crystal system as non-clathrated $Fe(acac)_3$ (orthorhombic), but different packing of the $Fe(acac)_3$ in the crystals significantly changes the volume per molecule from 435 Å^3 in the non-clathrated phase to 533 Å^3 in the clathrate (II), generating respectively the space groups *Pbca* and $P2_1ca$. Thus the clathrate forms a 'porosity' type solid lattice which is able to absorb the guest molecule solvent. In the CCl_4 clathrate (IV), the packing of the $Fe(acac)_3$ changes the crystal system completely to give the space group *R*3. Also, the volume per molecule in the crystal changes to 557 Å^3 to reflect a more symmetrical and larger guest molecule of CCl_4.

The cavity size can be evaluated by subtracting the volume per molecule of the clathrates from that of the non-clathrated phase (I). The cavity volume per guest molecule thus obtained, 98 Å^3, in the clathrate (II), is considered to be large enough to accommodate one *trans*-CHCl=CHCl guest molecule, which occupies 78 Å^3. For the $Fe(acac)_3.CCl_4$ clathrate (IV), the cavity volume increases to 122 Å^3, and can accommodate a slightly larger CCl_4 guest molecule of 83 Å^3.

* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55108 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR0016]

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* ($Å^2$) *with e.s.d.'s in parentheses for* $Fe(acac)_3$.*trans*-CHCl=CHCl

B_{eq} is the mean of the principal axes of the thermal ellipsoid.

	x	*y*	*z*	B_{eq}
Host molecule				
Fe	0.39468*	0.38940 (17)	0.12619 (6)	2.94 (8)
O(1)	0.3003 (13)	0.2523 (8)	0.1719 (3)	3.9 (4)
O(2)	0.4286 (15)	0.5017 (8)	0.1863 (3)	4.4 (5)
O(3)	0.4768 (11)	0.5315 (9)	0.0824 (3)	4.2 (5)
O(4)	0.1590 (12)	0.4584 (8)	0.1139 (4)	4.3 (5)
O(5)	0.3539 (10)	0.2642 (8)	0.0686 (3)	3.4 (4)
O(6)	0.6298 (11)	0.3194 (8)	0.1298 (3)	3.8 (4)
C(1)	0.2598 (18)	0.2659 (14)	0.2192 (5)	4.1 (7)
C(2)	0.1751 (19)	0.1466 (13)	0.2456 (9)	5.2 (9)
C(3)	0.2901 (23)	0.3740 (13)	0.2486 (5)	5.2 (8)
C(4)	0.381 (3)	0.4858 (11)	0.2322 (4)	4.4 (7)
C(5)	0.420 (3)	0.5910 (12)	0.2681 (5)	5.0 (8)
C(6)	0.394 (3)	0.6057 (12)	0.0525 (4)	3.8 (7)
C(7)	0.5027 (22)	0.6970 (15)	0.0197 (5)	5.2 (8)
C(8)	0.2238 (19)	0.6070 (14)	0.0482 (4)	4.0 (7)
C(9)	0.1093 (19)	0.5470 (14)	0.0802 (5)	4.1 (7)
C(10)	0.0810 (20)	0.5620 (14)	0.0780 (5)	4.9 (8)
C(11)	0.4513 (18)	0.1767 (11)	0.0525 (5)	3.6 (7)
C(12)	0.382 (3)	0.0876 (14)	0.0124 (5)	6.4 (10)
C(13)	0.6134 (19)	0.1525 (13)	0.0699 (5)	4.1 (7)
C(14)	0.6962 (18)	0.2270 (13)	0.1068 (5)	3.4 (6)
C(15)	0.885 (3)	0.1939 (12)	0.1213 (5)	4.5 (8)
Guest molecule				
C(16)	0.465 (3)	0.8199 (15)	0.1535 (6)	8.9 (15)
C(17)	0.3487 (25)	0.9095 (16)	0.1484 (6)	7.4 (11)
Cl(1)	0.6669 (8)	0.8663 (5)	0.15812 (24)	9.9 (4)
Cl(2)	0.1285 (9)	0.8664 (6)	0.1462 (3)	12.1 (5)

* Coordinate fixed to define origin of non-centrosymmetric structure.

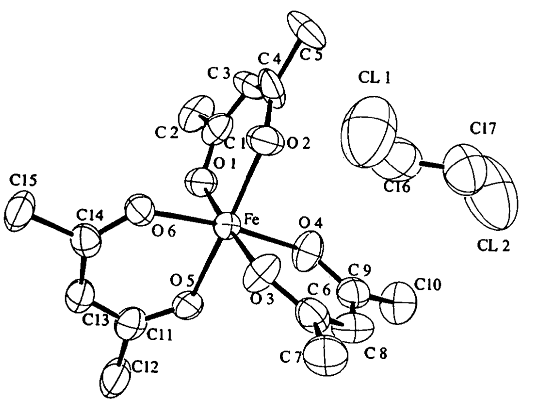


Fig. 1. An *ORTEP* (Johnson, 1976) drawing of $Fe(acac)_3$.*trans*-CHCl=CHCl showing the atomic numbering and thermal ellipsoids at 50% probability. H atoms have been omitted for clarity.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses in* $Fe(acac)_3$.*trans*-CHCl=CHCl

Host molecule			
Fe—O(1)	1.999 (9)	C(1)—C(2)	1.558 (21)
Fe—O(2)	1.985 (8)	C(1)—C(3)	1.376 (20)
Fe—O(3)	1.971 (9)	C(3)—C(4)	1.420 (21)
Fe—O(4)	2.006 (9)	C(4)—C(5)	1.469 (17)
Fe—O(5)	2.020 (8)	C(6)—C(7)	1.536 (21)
Fe—O(6)	1.981 (9)	C(6)—C(8)	1.34 (3)
O(1)—C(1)	1.302 (16)	C(8)—C(9)	1.381 (20)
O(2)—C(4)	1.283 (15)	C(9)—C(10)	1.502 (22)
O(3)—C(6)	1.277 (17)	C(11)—C(12)	1.503 (19)
O(4)—C(9)	1.332 (17)	C(11)—C(13)	1.375 (20)
O(5)—C(11)	1.253 (15)	C(13)—C(14)	1.403 (19)
O(6)—C(14)	1.240 (15)	C(14)—C(15)	1.564 (24)
Guest molecule			
C(16)—C(17)	1.30 (3)	Cl(2)—C(17)	1.784 (20)
Cl(1)—C(16)	1.659 (22)		
Host molecule			
O(1)—Fe—O(2)	88.2 (4)	O(1)—C(1)—C(2)	117.0 (13)
O(1)—Fe—O(3)	176.6 (4)	O(1)—C(1)—C(3)	126.2 (13)
O(1)—Fe—O(4)	90.3 (4)	C(2)—C(1)—C(3)	116.7 (13)
O(1)—Fe—O(5)	87.4 (3)	C(1)—C(3)—C(4)	124.2 (13)
O(1)—Fe—O(6)	93.5 (4)	O(2)—C(4)—C(3)	122.6 (12)
O(2)—Fe—O(3)	90.1 (4)	O(2)—C(4)—C(5)	117.6 (12)
O(2)—Fe—O(4)	92.9 (4)	C(3)—C(4)—C(5)	119.7 (12)
O(2)—Fe—O(5)	175.6 (4)	O(3)—C(6)—C(7)	115.7 (17)
O(2)—Fe—O(6)	92.7 (4)	O(3)—C(6)—C(8)	124.4 (13)
O(3)—Fe—O(4)	86.9 (4)	C(7)—C(6)—C(8)	119.9 (13)
O(3)—Fe—O(5)	94.3 (4)	C(6)—C(8)—C(9)	126.2 (12)
O(3)—Fe—O(6)	89.5 (4)	O(4)—C(9)—C(8)	121.7 (13)
O(4)—Fe—O(5)	87.4 (4)	O(4)—C(9)—C(10)	112.8 (12)
O(4)—Fe—O(6)	173.4 (4)	C(8)—C(9)—C(10)	125.2 (13)
O(5)—Fe—O(6)	87.3 (3)	O(5)—C(11)—C(12)	117.1 (13)
Fe—O(1)—C(1)	126.9 (8)	O(5)—C(11)—C(13)	125.2 (12)
Fe—O(2)—C(4)	130.6 (9)	C(12)—C(11)—C(13)	117.6 (13)
Fe—O(3)—C(6)	129.8 (11)	C(11)—C(13)—C(14)	124.4 (12)
Fe—O(4)—C(9)	128.2 (9)	O(6)—C(14)—C(13)	124.4 (13)
Fe—O(5)—C(11)	128.1 (8)	O(6)—C(14)—C(15)	116.2 (12)
Fe—O(6)—C(14)	130.1 (9)	C(13)—C(14)—C(15)	119.4 (12)
Guest molecule			
Cl(1)—C(16)—C(17)	118.3 (14)	Cl(2)—C(17)—C(16)	120.5 (14)

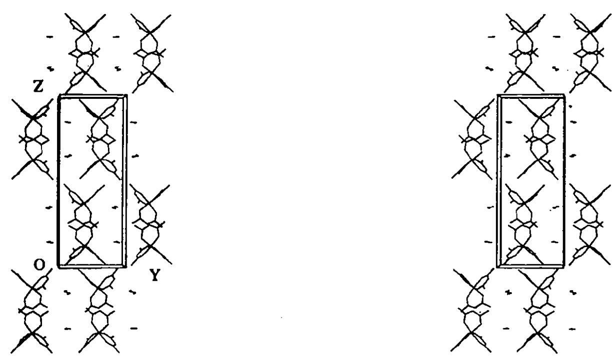


Fig. 2. Stereoscopic view of the unit cell of $Fe(acac)_3$.*trans*-CHCl=CHCl down the *a* axis.

Unlike the trigonal cage cavity in the $Fe(acac)_3.CCl_4$ clathrate (IV) (Pang, Lucken & Bernardinelli, 1990), the $Fe(acac)_3.C_2H_2Cl_2$ clathrate (II) has channel cavities. The guest molecules are located in an ordered general position in channels which are in the direction of the *a* axis. Fig. 2 shows stereoscopic views of the unit cell down the *a* axis.

The *trans*-CHCl=CHCl and CCl_4 guest molecules have been found to escape easily from their host cavities within 30 min when standing in air, which implies that only weak molecular interactions of the order of van der Waals bonding are present in these clathrate compounds. This result has also been confirmed by a nuclear quadrupole resonance study (Pang, 1989): the resonance frequencies of the *trans*-CHCl=CHCl and CCl_4 guest molecules in the clathrates shift only slightly from that of the pure *trans*-CHCl=CHCl and CCl_4 molecules.

Table 3. *Average values of various structural parameters* (*volumes* Å^3, *distances* Å) *in tris*(*acetylacetonato*)*iron*-(III)

Compound	Space group	Volume per molecule	Volume of cavity	Fe—O	O···O 'bite'	O···O other	C—O	C—C_m	C—C_b	Reference
(I)	*Pbca*	435		1.99	2.74	2.86	1.26	1.53	1.38	Iball & Morgan (1967)
(II)	*P*2$_1$*ca*	533	98	1.99	2.76	2.85	1.28	1.52	1.38	This work
(IV)	*R*3	557	122	2.00	2.75	2.86	1.27	1.51	1.39	Pang, Lucken & Bernardinelli, (1990)

The National Sciences and Engineering Research Council of Canada partially supported this research.

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Acta Cryst. (1992). C**48**, 1597–1599

Structure of a 1:1 Addition Compound of Mercuric Bromide with 3-Methyl-4-nitropyridine 1-Oxide

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(*Received* 19 *February* 1991; *accepted* 27 *January* 1992)

Abstract. Polymeric dibromo(3-methyl-4-nitropyridine 1-oxide)mercury, [$HgBr_2(C_6H_6N_2O_3)$], M_r = 514.53, monoclinic, $P2_1/c$, a = 13.338 (2), b = 11.599 (1), c = 7.096 (2) Å, β = 93.74 (3)°, V = 1095.5 Å^3, Z = 4, D_x = 3.120 g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 212.6 cm^{-1}, F(000) = 920, T = 294 K, R = 0.061 for 1387 observed reflections. The structure is polymeric through six bridging atoms, the Hg coordinating to two O atoms from the pyridine 1-oxide ligand and four Br atoms. The Hg atom has a very distorted octahedral environment. The $HgBr_2$ subunit deviates slightly from linearity [Br—Hg—Br = 172.67 (7)°] with a mean bond length of 2.424 Å. The closest non-bonded Hg···Hg contacts are at 4.119, 4.354 and 4.119 Å, in three directions.

Introduction. In previous research, some relationships were discovered among the frequency-doubling effect (the effect of a light wave at twice the frequency of an incident wave passing through a nonlinear media), molecular electronic structure, and molecular orientation in some organic crystals (Li, Liu, Wu, Shi & Hu, 1987). In order to find crystals with a higher frequency-doubling effect, 15 complexes of some metal halides with the organic ligand 3-methyl-4-nitropyridine 1-oxide (pom) have been synthesized and investigated. Among them the crystal structures of complexes $Cd(pom)_2Br_2$ and $Hg(pom)Br_2$ have been determined. The former belongs to the orthorhombic space group *Fdd*2 with a = 15.733 (3), b = 56.739 (11), c = 3.957 (1) Å, having the expected frequency-doubling effect, for which a structural report is in preparation. However, the latter belongs to the centrosymmetric space group $P2_1/c$ and has no frequency-doubling effect, though Hg belongs to the same group as Cd (group IIB). In this paper the synthesis and crystal structure of $Hg(pom)Br_2$ are reported.

Experimental. Equimolar $HgBr_2$ and pom (3-methyl-4-nitropyridine 1-oxide) were dissolved in water/methyl alcohol under stirring at 323–343 K, then

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