

Zalkin, Hopkins & Templeton, 1967). The distances in the methoxycarbonylmethyl moiety are in good agreement with those in $\text{CH}_3\text{COOCH}_3$ (Barrow, Scradock, Ebsworth & Rankin, 1981). The packing of the molecules within the unit cell is shown in Fig. 2.

We thank Dr Z. Janoušek for kindly supplying the crystals.

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Acta Cryst. (1986). **C42**, 665–667

Octacarbonyl-bis{ μ -[pentacarbonylrhenio(–I)]gallio(III)}-dirhenium(–II)(Re–Re)

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(Received 3 April 1985; accepted 3 January 1986)

Abstract. $[\text{Re}_2(\text{CO})_8\{\text{Ga}[\text{Re}(\text{CO})_5]_2\}]$, $M_r = 1388.4$, tetragonal, $I4_1/a$, $a = 13.894$ (4), $c = 28.836$ (9) Å, $U = 5566.6$ Å³, $Z = 8$, $D_x = 3.312$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 185.7$ cm⁻¹, $F(000) = 4912$, $T = 294$ (1) K, final $R = 0.058$ for 1420 unique reflections. The central fragment of the molecule consists of a planar Ga_2Re_2 rhombus with an Re–Re bond [$r(\text{Re}–\text{Re}) = 3.139$ (2) Å]. The Re atoms of the two $\text{Re}(\text{CO})_5$ ligands have a *trans* configuration with respect to the plane of the Ga_2Re_2 ring. The mean value of the Ga–Re bond length is 2.589 (5) Å.

Introduction. In the course of our investigations on the influence of packing forces on the geometry of molecules we have prepared the compound $\text{Re}_2(\text{CO})_8[\mu\text{-GaRe}(\text{CO})_5]_2$ and determined its crystal structure. The title substance shows a thermal cluster condensation process at 573 K $\{2\text{Re}_2(\text{CO})_8[\mu\text{-GaRe}(\text{CO})_5]_2(s) \rightarrow \text{Re}_4(\text{CO})_{12}[\mu_3\text{-GaRe}(\text{CO})_5]_4(s) + 2(\text{CO})(g)\}$ (Haupt & Balsaa, 1985). Such a condensation of preformed clusters offers interesting synthetic possibilities to obtain a polyhedral heteronuclear metal-atom cluster with main-group metals and transition-metal carbonyls.

The analogous compound $\text{Re}_2(\text{CO})_8[\mu\text{-InRe}(\text{CO})_5]_2$ (Preut & Haupt, 1975) does not show this expected cluster condensation. Perhaps a complete set of structural information can allow us to explain the different reaction behaviour.

Experimental. The yellow crystals were prepared by a reaction of GaI_3 with $\text{Re}_2(\text{CO})_{10}$ in the presence of gallium metal and xylene at 413 K for 4 d (Haupt & Balsaa, 1985). Crystal size 0.20 × 0.25 × 0.25 mm; Nonius CAD-4 diffractometer; $\omega/2\theta$ scan, scan speed 0.74–3.33° min⁻¹ in θ ; graphite-monochromated Mo $K\alpha$; lattice parameters from least-squares fit with 25 reflections in the range $8.0 \leq \theta \leq 17.0^\circ$; three standard reflections, recorded every 4 h: only random deviations measured; 2735 reflexions measured, $1 \leq \theta \leq 25^\circ$, $0 \leq h \leq 16$, $0 \leq k \leq 16$, $0 \leq l \leq 34$; after merging ($R_{\text{int}} = 0.026$) 2068 unique reflections; 648 reflections considered unobserved $I < 2\sigma(I)$; Lorentz-polarization correction, absorption correction *via* ψ scans, min./max. correction factor 0.76/1.00; systematic absences: hkl $h + k + l = 2n + 1$, $hk0$ $h = 2n + 1$ and $00l$ $l = 4n + 1$; space group $I4_1/a$; structure solution with Patterson and Fourier methods

(*SHELX76*) and full-matrix least-squares refinements with anisotropic temperature factors for heavy atoms and isotropic temperature factors for C and O; least-squares refinement based on F^2 and 97 refined parameters; $R = 0.058$, unit weights, $(\Delta/\sigma)_{\text{max}} = 0.01$, min./max. height in final ΔF synthesis + 1.1, $-0.8 \text{ e } \text{Å}^{-3}$ near heavy-atom position; complex neutral-atom scattering factors from Cromer & Mann (1968) and Cromer & Liberman (1970); programs (Prime 750 computer): *SHELX76* (Sheldrick, 1976) and *PLUTO* (Motherwell, 1978).

Discussion. The structure of the title compound is shown in Fig. 1 (*PLUTO*). Atomic parameters are given in Table 1,* bond lengths and angles in Table 2.

The title compound crystallizes in the tetragonal system; the molecule resides on a twofold axis and the two central Re atoms are at the special position 8(e) of space group $I4_1/a$. The analogous In compound (Preut & Haupt, 1975) crystallizes in the monoclinic crystal system with space group $P2_1/n$ and the molecule resides on a centre of symmetry. In the central four-membered ring of the Ga compound the acute angle Re–Ga–Re is $3.2(1)^\circ$ larger than the corresponding Re–In–Re angle [$71.07(3)^\circ$] in the In compound. The two compounds $M_2\text{Mn}_4(\text{CO})_{18}$ ($M = \text{Ga}, \text{In}$) (Preut & Haupt, 1974) crystallize in the same crystal structure as the title compound. In these compounds the difference between the two acute ring angles Mn–Ga–Mn $76.86(2)^\circ$ and Mn–In–Mn $76.36(2)^\circ$ is only $0.50(2)^\circ$. Furthermore, the two M –Re bonds in the asymmetric part of the central four-membered rings do not differ in the case of $M = \text{Ga}$ and exhibit a significant difference of $0.053(1) \text{ Å}$ in the monoclinic In compound. Going from Ga to In in the case of the Mn compounds results in an increase of the molecular volume (U/Z) of 27.7 Å^3 whereas for the two Re compounds, which crystallize in different packings, this step causes no significant change in the molecular volume. This means that $\text{In}_2\text{Re}_4(\text{CO})_{18}$ with the lower monoclinic symmetry has a higher packing density than $\text{Ga}_2\text{Re}_4(\text{CO})_{18}$ in the tetragonal system. This is in accordance with the rule given by Kitaigorodskii (1979). Packing-energy calculations with the program *PCK6* (Williams, 1972) based on the non-bonding intermolecular interactions between C and O atoms with $\text{C}\cdots\text{C}$, $\text{C}\cdots\text{O}$ and $\text{O}\cdots\text{O}$ potential curves given by Mirsky (1978) and a summation limit of 6.0 Å result in a lower energy for $\text{In}_2\text{Re}_4(\text{CO})_{18}$ ($-142.74 \text{ kJ mol}^{-1}$) than for $\text{Ga}_2\text{Re}_4(\text{CO})_{18}$ ($-136.18 \text{ kJ mol}^{-1}$). Obviously, the molecular dimensions of $\text{Ga}_2\text{Re}_4(\text{CO})_{18}$ and

$\text{In}_2\text{Re}_4(\text{CO})_{18}$ are differently deformed by the different intermolecular non-bonding forces in the crystalline state.

The terminal Ga–Re bond length is significantly shorter than the Ga–Re bond lengths in the central four-membered ring. Intermolecular distances do not indicate any interactions exceeding van der Waals forces.

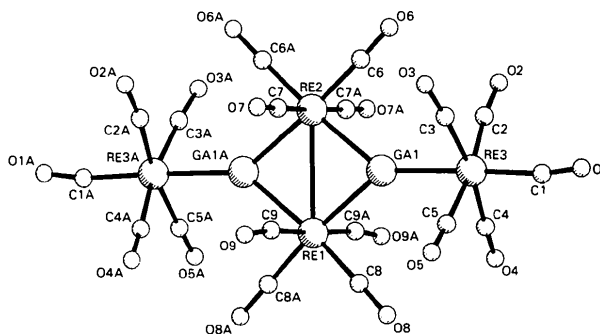


Fig. 1. General view of the molecule $\text{Re}_2(\text{CO})_8[\mu\text{-Ga}[\text{Re}(\text{CO})_5]_2$.

Table 1. Fractional atomic coordinates and isotropic thermal parameters ($\text{Å}^2 \times 10^3$) with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
Re(1)	0	0.25	0.2232 (1)	20 (1)*
Re(2)	0	0.25	0.3322 (1)	21 (1)*
Re(3)	-0.1042 (1)	-0.0669 (1)	0.2769 (1)	20 (1)*
Ga	0.0531 (3)	0.3892 (2)	0.2779 (1)	24 (2)*
C(1)	0.134 (3)	0.705 (3)	0.271 (1)	38 (9)
C(2)	0.007 (3)	0.576 (3)	0.324 (1)	39 (9)
C(3)	0.196 (2)	0.534 (2)	0.325 (1)	16 (7)
C(4)	0.009 (2)	0.578 (2)	0.227 (1)	26 (8)
C(5)	0.203 (3)	0.534 (3)	0.229 (2)	42 (9)
C(6)	0.030 (2)	0.348 (2)	0.376 (1)	21 (7)
C(7)	0.139 (2)	0.204 (2)	0.332 (1)	11 (7)
C(8)	0.042 (2)	0.341 (2)	0.177 (1)	24 (8)
C(9)	0.124 (2)	0.190 (2)	0.226 (1)	27 (8)
O(1)	0.157 (2)	0.783 (2)	0.276 (1)	53 (8)
O(2)	-0.047 (3)	0.593 (3)	0.355 (1)	73 (9)
O(3)	0.257 (3)	0.504 (3)	0.353 (1)	73 (9)
O(4)	-0.052 (2)	0.588 (2)	0.201 (1)	58 (9)
O(5)	0.260 (2)	0.513 (2)	0.203 (1)	57 (9)
O(6)	-0.048 (2)	0.096 (2)	0.405 (1)	50 (9)
O(7)	0.215 (2)	0.179 (2)	0.333 (1)	41 (7)
O(8)	-0.076 (2)	0.100 (2)	0.150 (1)	54 (9)
O(9)	0.202 (2)	0.153 (2)	0.220 (1)	45 (8)

* Anisotropically refined.

Table 2. Selected bond lengths (Å) and angles ($^\circ$) with e.s.d.'s in parentheses

Re(1)–Re(2)	3.139 (2)	Re(1)–Ga–Re(2)	74.3 (1)
Ga–Re(1)	2.599 (4)	Re(1)–Ga–Re(3)	142.0 (1)
Ga–Re(2)	2.599 (4)	Ga–Re(1)–Re(2)	52.8 (1)
Ga–Re(3)	2.569 (5)	Ga–Re(1)–Ga	105.6 (1)
Ga–Ga	4.142 (5)	Ga–Re(2)–Ga	105.6 (1)

Mean values

Re(1)–C	1.935 (35)
Re(2)–C	1.956 (33)
Re(3)–C	1.960 (33)
O–C	1.171 (43)

* Lists of structure factors, anisotropic temperature factors and a complete list of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42752 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The higher number of molecules and their arrangement in the tetragonal unit cell for the Ga compound are possibly more advantageous for the above-mentioned thermal cluster condensation for $M = \text{Ga}$ than for $M = \text{In}$ with starting material of the type $M_2\text{Re}_4(\text{CO})_{18}$.

We thank Fonds der Chemie for financial support.

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Acta Cryst. (1986). **C42**, 667–669

Structure of Tetrakis[μ_3 -(2-diethylaminoethanolato-*O*)isocyanatocopper(II)]-Trichloromethane (1/1)

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(Received 22 December 1984; accepted 7 January 1986)

Abstract. $\text{C}_{28}\text{H}_{56}\text{Cu}_4\text{N}_8\text{O}_8 \cdot \text{CHCl}_3$, $M_r = 1006.3$, monoclinic, $P2_1/c$, $a = 12.861$ (3), $b = 14.039$ (3), $c = 24.236$ (5) Å, $\beta = 100.39$ (1)°, $V = 4303.9$ Å³, $Z = 4$, $D_m = 1.54$ (3), $D_x = 1.552$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 21.07$ cm⁻¹, $F(000) = 2200$, $T = 297$ K, final $R = 0.059$, 3828 unique reflections. The asymmetric part of the unit cell contains one tetrameric molecule of the cubane type with a Cu_4O_4 core and one trichloromethane molecule, which occupies two positions with occupancy factors of 0.40 and 0.60 respectively. The coordination around the copper atom is fivefold and may be described as between square pyramidal and trigonal bipyramidal.

Introduction. The crystal structure of the title compound without crystal solvent has been determined as part of our investigations of the magnetostructural properties of tetrameric copper(II) complexes (Merz & Haase, 1980, and references therein). The magnetic behaviour of the title complex has already been published (Schwabe & Haase, 1985*a*). Recently, the magnetic and structural behaviours of some tetrameric copper(II) compounds containing crystal solvent have been described as being completely different (Mergenhenn, Merz, Haase & Allmann, 1976; Mergenhenn, Merz & Haase, 1980) from the solvent-free forms (Haase, 1973; Bertrand & Kelley, 1970). In this

paper we report the molecular structure of a tetrameric copper(II) complex with trichloromethane as crystal solvent. A solvent-free tetragonal modification of the title compound results on synthesis in methanol (Merz & Haase, 1978); recrystallization of this modification in benzene leads to another solvent-free triclinic form (Schwabe & Haase, 1985*b*).

Experimental. The solvent-free title compound was prepared following the procedure of Merz (Merz & Haase, 1978). Recrystallization from trichloromethane led to dark green orthorhombic crystals; D_m by flotation in $\text{CHCl}_3/\text{CCl}_4$; cell constants and e.s.d.'s at 297 K from least-squares refinement of 2θ values of 16 reflections in range 13.4 to 15.8°. Data collected on Stoe Stadi 4 four-circle diffractometer. Dimensions of crystal used from faces to center: $\{101\}$ 0.324, $\{\bar{1}0\bar{1}\}$ 0.324, $\{\bar{1}\bar{1}2\}$ 0.171, $\{11\bar{2}\}$ 0.171, $\{1\bar{3}\bar{3}\}$ 0.438, $\{\bar{1}33\}$ 0.438 mm. 4417 intensities measured; 2θ (max.) = 45°, $0 < h < 13$, $-14 < k < 3$, $-24 < l < 23$; 3 standard reflections (115, $31\bar{2}$, $15\bar{1}$), intensity variation < 3%; 3828 unique reflections, $R_{\text{int}} = 0.0356$; 476 unobserved with $F_o < 4\sigma(F_o)$; 110 and $\bar{1}02$ reflections omitted due to error in data collection; numerical absorption correction, min. and max. transmission factors 0.2684 and 0.5113; direct methods (F refined) (*SHELX76*; Sheldrick, 1976); anisotropic refinement;