Huber, 1985) et l'acide aminooxolinique (Czugler, Argay, Franck, Mészáros, Kutschabsky & Reck, 1976).

Comme dans ces composés, la présence du cycle *B* se manifeste dans le cycle *A* par une dissymétrie entre les liaisons des contours N(1)—C(2)—C(3)—C(4) et N(1)—C(8a)—C(4a)—C(4). N(1)—C(2), N(1)—C(8a) et C(7)—N(16) sont comparables aux liaisons N—C présentes dans les cycles pyridiniques. Toutes les autres liaisons N—C sont des liaisons simples; leurs longueurs sont comprises entre 1,463 (8) et 1,502 (9) Å. Dans le cation, seule C(4)—O(14) [1,261 (8) Å] possède une longueur inhabituelle. Celle-ci paraît en relation avec l'existence de la liaison hydrogène O(13)—H(13)···O(14) et avec la conjugaison des électrons π de C(4)—O(14) avec ceux de C(2)—C(3) d'une part et avec ceux du cycle *B* d'autre part.

Deux liaisons hydrogène O—H···O et deux liaisons N—H···Cl participent à la cohésion de la structure. Les deux premières s'établissent entre O*w* et O*w*$^{\rm i}$ d'une part [(i): $-x$, $1-y$, $1-z$], O*w* et O(14) d'autre part. Leurs longueurs respectives sont de 2,73 (2) et de 2,92 (1) Å. Les deux autres sont N(19)—H(19)···Cl(1$^{\rm ii}$) [3,173 (6) Å, 141°] et N(19)—H(19)···Cl(2$^{\rm ii}$) [3,308 (6) Å, 132°] [(ii): $1-x$, $-y$, $-z$].

Références

BAENZIGER, N. C., FOX, C. L. JR & MODAK, S. L. (1986). *Acta Cryst.* C**42**, 1505–1509.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Rapport ORNL-TM306. Oak Ridge National Laboratory, Tennessee, E.-U.

COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.

CYGLER, M. & HUBER, C. P. (1985). *Acta Cryst.* C**41**, 1052–1055.

CZUGLER, M., ARGAY, G., FRANCK, J., MÉSZÁROS, Z., KUTSCHABSKY, L. & RECK, G. (1976). *Acta Cryst.* B**32**, 3124–3126.

FRENZ, B. A. (1982). *Structure Determination Package*. College Station, Texas, E.-U., et Enraf–Nonius, Delft, Pays-Bas.

GOODRICH PURNELL, L. & HODGSON, D. J. (1976). *J. Am. Chem. Soc.* **98**, 4759–4763.

HUBER, C. P., SAKE GOWDA, D. S. & ACHARYA, K. R. (1980). *Acta Cryst.* B**36**, 497–499.

International Tables for X-ray Crystallography (1974). Tome IV, pp. 99 et 149. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)

ITO, T. & SUGAWARA, Y. (1983). *BEST-PLANE PROGRAM*, 3^{e} version (*BP7C*). Institute of Physical and Chemical Research, Wako-Shi, Saitama 351, Japon.

JOHNSON, C. K. (1976). *ORTEP*II. Rapport ORNL-5138. Oak Ridge National Laboratory, Tennessee, E.-U.

OHBA, S., SATO, S., SAITO, Y., OHSHIMA, K. & HARADA, J. (1983). *Acta Cryst.* B**39**, 49–53.

TOFFOLI, P., RODIER, N., CEOLIN, R. & BLAIN, Y. (1987). *Acta Cryst.* C**43**, 1745–1748.

Acta Cryst. (1988). C**44**, 472–474

Nonacarbonylbis{μ_3-[(pentacarbonylrhenio)germanio(IV)]-*Ge*}-*triangulo*-triiron(*Fe–Fe*)

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Abstract. *closo*-[$Fe_3(CO)_9\{\mu_3$-Ge[Re(CO)$_5$]$\}_2$], $M_r = 1217{\cdot}3$, triclinic, $P\bar{1}$, $a = 9{\cdot}096$ (2), $b = 9{\cdot}991$ (2), $c = 16{\cdot}870$ (4) Å, $\alpha = 99{\cdot}16$ (2), $\beta = 97{\cdot}55$ (2), $\gamma = 98{\cdot}38$ (2)°, $U = 1478{\cdot}5$ (6) Å^3, $Z = 2$, $D_x = 2{\cdot}733$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 117·3 cm^{-1}, $F(000) = 1116$, $T = 298$ (1) K, $R = 0{\cdot}076$ for 3578 unique reflections. The diamagnetic title compound shows an iron–iron bonded triangular $Fe_3(CO)_9$ framework capped by two μ_3-GeRe(CO)$_5$ groups forming a trigonal bipyramidal metal-atom polyhedron. Each iron atom has a facial-CO ligand arrangement. The mean values of the metal–metal bond lengths are Ge—Fe = 2·379 (4), Ge—Re = 2·542 (3) and Fe—Fe = 2·719 (4) Å.

Introduction. In the course of our investigations on bonding capabilities between transition-metal carbonyl fragments and main-group metals in cluster compounds (Haupt, Flörke & Preut, 1986) the title compound was synthesized and its crystal structure determined. The polyhedral heteronuclear metal–metal framework was previously unknown for Ge$^{\rm IV}$ atoms, and the related bond parameters are valid with respect to the continuation of an earlier characterization of heteronuclear metal–metal bonds by Mössbauer spectroscopic measurements (Barbieri, Alonzo, Haupt & Preut, 1977).

Experimental. The dark red crystals were prepared by reaction of MnRe(CO)$_{10}$, GeCl$_2$ and Fe(CO)$_5$ in a sealed glass tube at 493 K (Haupt, Götze & Flörke, 1987). Crystal size 0·25 × 0·40 × 0·65 mm, Nicolet *R*3*m*/V diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, lattice parameters

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refined from 25 reflections, $6 \leq 2\theta \leq 25°$, 4425 reflections recorded, $3 \leq 2\theta \leq 46°$, $0 \leq h \leq 10$, $-10 \leq k \leq 10$, $-18 \leq l \leq 18$, three standards recorded every 400 reflections, only random deviations, Lp correction, empirical absorption correction *via* ψ scans, min./max. transmission factors 0·004/0·023, after merging ($R_{\rm int} = 0{\cdot}031$) 4121 unique reflections of which 543 were considered unobserved [$I < 4\sigma(I)$]; structure solved by direct methods (*SHELXTL-PLUS*), full-matrix least-squares refinement based on F and 216 parameters, Re, Ge and Fe refined anisotropically, max. $(\Delta/\sigma) = 0{\cdot}0005$, max. height in final ΔF syntheses 1·9 e Å^{-3} near heavy-atom position, refinement converged to $R = 0{\cdot}076$. A better value could not be achieved because of rather poor crystal quality, as was indicated by reflection spots on single-crystal photographs. Complex neutral-atom scattering factors corrected for anomalous dispersion (*International Tables for X-ray Crystallography,* 1974), all calculations with *SHELXTL-PLUS* (Nicolet XRD Corporation, 1986); figure drawn by *PLUTO* (Motherwell & Clegg, 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 molecular structure shows a triangular iron–iron bonded $Fe_3(CO)_9$ group as central fragment capped by two μ_3-GeRe(CO)$_5$ groups. The Ge–Fe polyhedron thus formed has a distorted trigonal-bipyramidal shape. Regarding these metal atoms, each of the Fe atoms attains with the neighbouring metal atoms (two Fe and two Ge) and three facially arranged terminal CO ligands the coordination number (c.n.) 7, and each of the bridging Ge$^{\rm IV}$ atoms attains with three neighbouring Fe atoms and the Re atom of the terminal Re(CO)$_5$ group c.n. 7. The tetrahedral ligand geometry of c.n. 4 and the pentagonal bipyramid of c.n. 7 are significantly distorted. The last-named c.n. of the diamagnetic title compound means that for the Fe atoms the EAN rule is fulfilled.

Table 1. *Atomic coordinates* (×10^4) *and isotropic or equivalent isotropic displacement parameters* (Å^2×10^3) *with e.s.d.'s in parentheses*

Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
Re(1)	342 (1)	8161 (1)	6300 (1)	50 (1)*
Re(2)	−4122 (2)	1853 (1)	8548 (1)	58 (1)*
Ge(1)	−967 (3)	6388 (2)	7025 (1)	28 (1)*
Ge(2)	−2870 (3)	3821 (2)	7958 (1)	28 (1)*
Fe(1)	−422 (3)	4587 (3)	7717 (2)	27 (2)*
Fe(2)	−2317 (3)	6295 (3)	8150 (2)	28 (2)*
Fe(3)	−3084 (3)	4585 (3)	6700 (2)	28 (2)*
C(1)	1358 (27)	5653 (24)	7788 (14)	37 (6)
O(1)	2557 (20)	6260 (18)	7910 (11)	49 (4)
C(2)	8 (26)	3135 (24)	7154 (14)	36 (5)
O(2)	293 (23)	2134 (21)	6808 (13)	66 (6)
C(3)	−68 (26)	4180 (24)	8700 (14)	35 (5)
O(3)	241 (20)	3832 (18)	9319 (11)	52 (5)
C(4)	−3344 (28)	6017 (25)	8951 (15)	41 (6)
O(4)	−4022 (24)	5952 (22)	9469 (13)	67 (6)
C(5)	−803 (28)	7452 (26)	8781 (15)	41 (6)
O(5)	177 (23)	8211 (21)	9198 (12)	63 (5)
C(6)	−3422 (27)	7387 (25)	7751 (15)	39 (6)
O(6)	−4192 (21)	8098 (19)	7515 (11)	54 (5)
C(7)	−3483 (26)	5636 (24)	6008 (14)	35 (5)
O(7)	−3907 (22)	6285 (20)	5503 (12)	57 (5)
C(8)	−4995 (29)	4039 (26)	6738 (15)	43 (6)
O(8)	−6260 (22)	3669 (20)	6751 (12)	61 (5)
C(9)	−2791 (28)	3192 (26)	6000 (16)	43 (6)
O(9)	−2676 (25)	2283 (23)	5514 (14)	73 (6)
C(10)	−551 (29)	6869 (26)	5260 (16)	43 (6)
O(10)	−995 (22)	6207 (21)	4678 (12)	61 (5)
C(11)	−1453 (28)	9003 (25)	6321 (15)	39 (6)
O(11)	−2466 (22)	9533 (20)	6335 (12)	59 (5)
C(12)	1234 (28)	9216 (26)	7380 (16)	42 (6)
O(12)	1718 (23)	9878 (21)	7967 (13)	63 (5)
C(13)	2082 (27)	7170 (24)	6267 (14)	35 (5)
O(13)	3031 (22)	6653 (20)	6206 (12)	58 (5)
C(14)	1279 (26)	9531 (24)	5775 (14)	37 (6)
O(14)	1783 (20)	10382 (19)	5456 (11)	53 (5)
C(15)	−3216 (32)	2925 (29)	9655 (18)	52 (7)
O(15)	−2711 (22)	3504 (20)	10254 (12)	60 (5)
C(16)	−2295 (30)	1098 (27)	8454 (16)	46 (6)
O(16)	−1271 (25)	650 (22)	8378 (13)	71 (6)
C(17)	−4967 (29)	958 (27)	7381 (17)	46 (6)
O(17)	−5395 (21)	524 (20)	6771 (12)	56 (5)
C(18)	−5846 (30)	2826 (27)	8617 (16)	46 (6)
O(18)	−6846 (24)	3363 (22)	8581 (13)	67 (6)
C(19)	−5048 (33)	341 (31)	8926 (18)	58 (8)
O(19)	−5578 (28)	−683 (26)	9122 (15)	83 (7)

* Anisotropically refined.

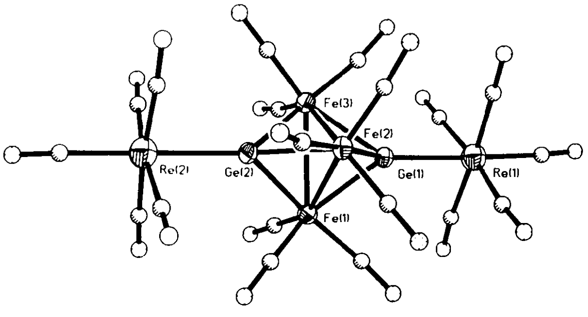

Fig. 1. General view of a molecule of the title compound.

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Re(1)–Ge(1)	2·551 (3)	Fe(1)–Ge(1)–Re(1)	139·8 (1)
Re(2)–Ge(2)	2·533 (3)	Fe(2)–Ge(1)–Re(1)	139·6 (1)
Ge(1)–Fe(1)	2·372 (4)	Fe(3)–Ge(1)–Re(1)	136·8 (1)
Ge(1)–Fe(2)	2·398 (4)	Fe(1)–Ge(2)–Re(2)	135·8 (1)
Ge(1)–Fe(3)	2·377 (4)	Fe(2)–Ge(2)–Re(2)	142·8 (1)
Ge(2)–Fe(1)	2·356 (4)	Fe(3)–Ge(2)–Re(2)	137·3 (1)
Ge(2)–Fe(2)	2·410 (4)	Fe(2)–Ge(1)–Fe(1)	68·5 (1)
Ge(2)–Fe(3)	2·361 (4)	Fe(3)–Ge(1)–Fe(1)	71·6 (1)
Fe(1)–Fe(2)	2·684 (4)	Fe(2)–Ge(1)–Fe(3)	68·7 (1)
Fe(1)–Fe(3)	2·777 (4)	Fe(2)–Ge(2)–Fe(1)	68·6 (1)
Fe(2)–Fe(3)	2·694 (4)	Fe(3)–Ge(2)–Fe(1)	72·2 (1)
		Fe(2)–Ge(2)–Fe(3)	68·8 (1)
Mean values		Fe(3)–Fe(2)–Fe(1)	62·2 (1)
Re–C	1·960 (31)	Fe(3)–Fe(1)–Fe(2)	59·1 (1)
Fe–C	1·756 (26)	Fe(2)–Fe(3)–Fe(1)	58·7 (1)
O–C	1·131 (34)		

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* Lists of structure factors, anisotropic temperature factors and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44570 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The metal framework is surrounded by a crowded and compact ligand sphere of 19 carbonyl groups. A minimization of their intra- and intermolecular repulsive forces in the packing to the present equilibrium C···O, C···C and O···O contact lengths is a suitable explanation of the differences obtained in the values of analogous Fe—Fe—Fe and Fe—Ge—Fe bond angles and of metal–metal bond lengths. The mean values of such bond lengths along the edges of the polyhedron are Fe—Fe = 2·719 (4) and Ge—Fe = 2·379 (4) Å. By comparison with the average Fe—Fe covalent single-bond length of 2·673 (7) Å – resulting from the two unbridged Fe—Fe bonds in $Fe_3(\mu\text{-}CO)_2(CO)_{10}$ (Wei & Dahl, 1969) – and the average Ge—Fe single-bond distance of 2·412 (1) Å in $\{(\mu_4\text{-}Ge)[\eta^5\text{-}C_5H_4CH_3\text{-}Mn(CO)_2][Fe(CO)_4]_3\}$ (Forster, Mackay & Nicholson, 1985), it can be assumed that the corresponding bond lengths of the title compound are also single bonds. Finally, the same bond type is realized in the remaining Ge—Re bond [ave. 2·542 (3) Å] because of the univalent chemical property of the related $Re(CO)_5$ group.

Intermolecular distances do not indicate any interactions exceeding van der Waals forces.

References

Barbieri, R., Alonzo, G., Haupt, H.-J. & Preut, H. (1977). *Inorg. Chim. Acta*, **22**, 253–259.

Forster, S. P., Mackay, K. M. & Nicholson, B. K. (1985). *Inorg. Chem.* **24**, 909–913.

Haupt, H.-J., Flörke, U. & Preut, H. (1986). *Acta Cryst.* C**42**, 665–667.

Haupt, H.-J., Götze, A. & Flörke, U. (1987). *Z. Anorg. Allg. Chem.* In the press.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Nicolet XRD Corporation (1986). *SHELXTL-PLUS*. Program for crystal structure determination. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Wei, Ch. H. & Dahl, L. F. (1969). *J. Am. Chem. Soc.* **91**, 1351–1361.

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Structure of a Cyclic Hydroxo-Bridged Pt^{II} Trimer with Platinum–Silver Bonds

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Abstract. *cyclo*-Tri-μ-hydroxo-(trinitroargentio)tris[(ethylenediamine)platinum(II)] nitrate, $[AgPt_3(C_2H_8N_2)_3(OH)_3(NO_3)_3]NO_3$, M_r = 1172·48, monoclinic, *Pc*, *a* = 8·283 (4), *b* = 8·319 (5), *c* = 17·507 (9) Å, β = 96·37 (4)°, *V* = 1199 (1) Å^3, *Z* = 2, D_x = 3·247 Mg m^{-3}, λ(Mo *K*α) = 0·71069 Å, μ = 18·79 mm^{-1}, *F*(000) = 1068, *T* = 295 K, *R* = 0·046 for 2094 unique observed reflections. The structure consists of a cyclic hydroxo-bridged trimer $[Pt(en)OH]_3^{3+}$ with an Ag atom located at equal distances from the three Pt atoms. The Pt_3O_3 ring assumes a chair conformation with approximate C_{3v} symmetry. The three Pt atoms possess square-planar coordination with minor distortion towards the square-pyramidal arrangement caused by the presence of the Ag atom. The Pt—Ag distances [2·838 (2), 2·890 (2) and 2·893 (2) Å] suggest the presence of metal–metal bonds. The coordination around the Ag atom defines a distorted trigonal antiprism including three nitrate O atoms with Ag—O distances = 2·47 (2), 2·60 (2) and 2·62 (2) Å. The amine and hydroxo ligands are hydrogen bonded to the nitrate groups.

Introduction. Neutral *cis*-dichloro Pt^{II} amine complexes are effective antitumor agents. The neutrality of the drug is believed to be important for its passage through the cell membranes. Within the cells where the chloride concentration is much lower than in the blood plasma, the platinum(II) compound is believed to hydrolyze. Hydrolysis of cisplatin, *cis*-$[Pt(NH_3)_2Cl_2]$, has been studied by several authors. The presence of several hydrated species, which are believed to play an important role in the antitumor activity of the drug, has been reported. At physiological pH, the hydrolyzed products isolated so far, for which X-ray structural data are available, were shown to contain oligomeric species. The crystal structures of hydroxo-bridged dimers (Faggiani, Lippert, Lock & Rosenberg, 1977*a*; Stanko, Hollis, Schreifels & Hoeschele, 1977; Lippert, Lock, Rosenberg & Zvagulis, 1978) and trimers (Faggiani, Lippert, Lock & Rosenberg, 1977*b*, 1978) have been reported. These oligomers are toxic (Rosenberg, 1978) and might be partly responsible for the toxicity of *cis*-$[Pt(NH_3)_2Cl_2]$.

Chelates in which the ammine ligands have been replaced by 1,2-cyclohexanediamine (dach) seem superior to NH_3 complexes as antitumor drugs especially because of their reduced toxicity. Oligomers of dach are much less toxic than those of NH_3 (Gill & Rosenberg, 1982). The crystal structure of a hydroxo-

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