Atomic scattering factors from Cromer & Waber (1974) and anomalous-dispersion factors from Cromer (1974) were used for both structure solutions.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry for compounds (1) and (2) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71341 (55 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1033]

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# Structure of the Heteronuclear Cluster $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH{=}CHPPh_2)(CO)_{12}]$


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## Abstract

The X-ray structure analysis shows that the digold tetraruthenium cluster [$\mu$-bis(diphenylphosphino)-ethene-5$\kappa P$:6$\kappa P'$]-dodecacarbonyl-1$\kappa^3 C$,2$\kappa^2 C$,3$\kappa^3 C$,-4$\kappa^3 C$-$\mu_3$-hydrido-1:2:3$\kappa^3 H$-$\mu$-hydrido-1:4$\kappa^2 H$-digoldtetraruthenium (6 *Ru—Ru*)(4 *Ru—Au*)(*Au—Au*), $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH{=}CHPPh_2)(CO)_{12}]$ (1), adopts a capped square-based pyramid geometry. The metal core consists of a square-based pyramid defined by two Au atoms and two Ru atoms in the basal plane with an Ru atom at the apex. The $Ru_3$ face of this $Au_2Ru_3$ unit is capped by another Ru atom [Au—Au 2.861 (2), Au—Ru 2.707 (2)–2.827(2), Ru—Ru 2.796 (3)–3.017 (3) Å]. The bis(diphenylphosphino)ethene ligand, *cis*-$Ph_2PCH{=}CHPPh_2$, bridges the two Au atoms. One of the two hydrido ligands caps an $Ru_3$ face and the other bridges an Ru—Ru edge of an adjacent $Ru_3$ face of the metal polyhedron. Each Ru atom is bonded to three terminal carbonyl groups.


## Comment

A particular class of cluster compounds which are attracting a great deal of current investigation are those in which two or more $MPR_3$ ($M$ = Cu, Ag, Au; $R$ = alkyl or aryl) units form part of the overall metal polyhedron (Freeman, Orpen & Salter, 1987; Brown, Salter & Toupet, 1988; Adatia, McPartlin & Salter, 1988; Bates *et al.*, 1989; Blaxill, Brown, Frankland, Salter & Sïk, 1989). From the numerous studies that have been reported, the most interesting feature of these heteronuclear clusters is the degree of flexibility their metal skeletons exhibit in solution when the nature of the attached phosphine ligand is varied. Variable temperature $^1H$ and $^{31}P$-{$^1H$} NMR studies show that the metal frameworks of these compounds are stereochemically non-rigid, fluctuating between capped trigonal bipyramidal and capped square-based pyramidal geometries (Freeman *et al.*, 1987; Bates *et al.*, 1989). X-ray studies confirm that the type of metal-core geometry adopted by these clusters in the solid state is critically governed by the nature of the attached phosphine ligand (Freeman *et al.*, 1987; Bates *et al.*, 1989).

The X-ray structure analysis confirms that the heteronuclear cluster $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH{=}CHPPh_2)(CO)_{12}]$ (1) adopts a capped square-based pyramidal geometry (Fig. 1), as previously proposed from IR and NMR spectroscopic studies (Blaxill *et al.*, 1989).

The metal-core geometry established for (1) resembles the metal frameworks previously characterized for the monoclinic and orthorhombic crystalline forms of the cluster $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}]$ (2) and for the compound $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2CH_2PPh_2)(CO)_{12}]$ (3) (Bates *et al.*, 1989). For a comparative study, the bond lengths associated with the capped square-based pyramidal metal frameworks in (1), (2) and (3) are displayed in Fig. 2. The range of $M$—$M$ distances around the metal framework in (1) are similar to those observed in clusters (2) and (3) (Fig. 2).

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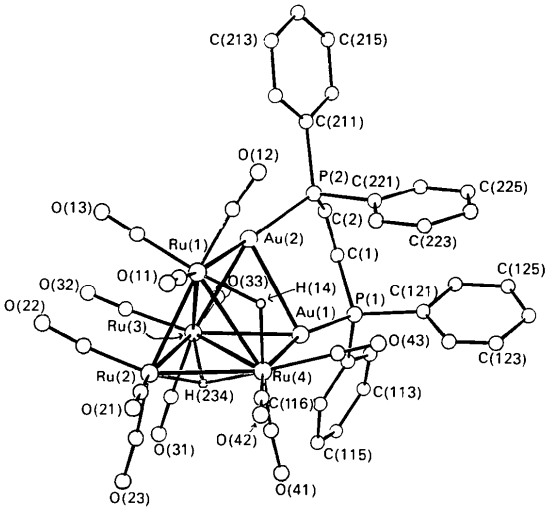


Fig. 1. The molecular structure of the heteronuclear cluster $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH{=}CHPPh_2)(CO)_{12}]$ (1) showing the crystallographic numbering. The C atoms of the carbonyl groups have the same numbering as the O atoms to which they are bonded.

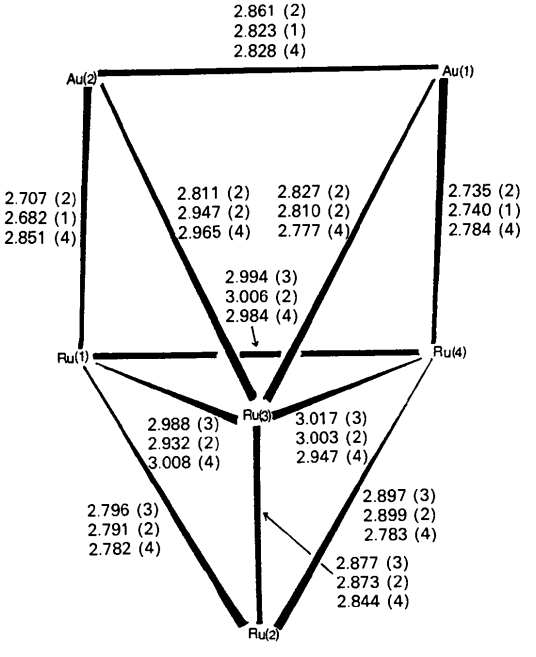


Fig. 2. A comparison of the *M*—*M* bond lengths in the metal-core structures of the title cluster (1), $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}]$ (2) (monoclinic form) and $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2CH_2PPh_2)(CO)_{12}]$ (3). Distances are given in descending order, (1), (2) and (3).

Interestingly, the mean Au—Ru bond length in (1) [2.770 (2) Å] is 0.025 Å shorter than the mean bond length calculated for (2) and 0.074 Å shorter than the corresponding distance in (3). The magnitude of such differences reflects the relative 'softness' of the *M*—*M* bonds which allow the modest forces of crystal packing to cause such variations in bond lengths (Blaxill *et al.*, 1989).

In this series of clusters, a structural feature which forms an interesting topic for discussion is the intramolecular distances present in the basal plane between atoms Au(1)···Ru(1) and Au(2)···Ru(4). There appears to be marked asymmetry between the two sets of contact distances with a difference between the pair of 0.330 Å present in (1) and 0.340 Å in (2). In marked contrast, the analogous separations in (3) display a difference of 0.790 Å. This feature is also apparent in the geometry around the two Au—P vectors in (1) and (3). The two Au—P vectors in (1) appear to be nearer parallel in orientation than the respective vectors in (3); Au(1)—P(1) 2.307 (9), Au(2)—P(2) 2.311 (8) Å, C(1)—P(1)—Au(1) 114 (9), C(2)—P(2)—Au(2) 114.6 (9)° for (1); Au(1)—P(1) 2.286 (4), Au(2)—P(2) 2.276 (4) Å, C(1)—P(1)—Au(1) 109.4 (4), C(2)—P(2)—Au(2) 113.7 (4)° for (3).

In the hexanuclear cluster (1), each Ru atom is bonded to three essentially linear carbonyl groups [Ru—C—O 158–177 (3)°]. The greatest deviation from linearity is exhibited by CO(33). The same carbonyl ligand is found to make a short contact to Au(2) [Au(2)···C(33) 2.63 (4) Å], whereas an even shorter contact exists between C(12) and Au(2) [Au(2)···C(12) 2.59 (4) Å]. Similar short contacts of carbonyl ligands to Group IB Au atoms have been a structural feature of several reported gold–ruthenium heteronuclear cluster compounds (Farrugia *et al.*, 1983; Bateman *et al.*, 1983; Ansell, Modrick & Bradley, 1984).

Structural comparison of cluster (1) with related compounds has again shown that the nature of the attached organophosphine group not only governs the geometry of the metal polyhedron in the solid state, but slight changes in the environment of the ligand create structural differences which are very distinct.

## Experimental

*Crystal data*

$[Au_2Ru_4H_2(C_{26}H_{24}P_2)(CO)_{12}]$
$M_r$ = 1532.8
Monoclinic
*I*2/*c*
$a$ = 33.673 (4) Å
$b$ = 12.275 (2) Å
$c$ = 23.057 (3) Å
$\beta$ = 97.828 (2)°
$V$ = 9441.5 Å$^3$
$Z$ = 8
$D_x$ = 2.16 Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda$ = 0.71069 Å
Cell parameters from 25 reflections
$\theta_{max} \simeq 10°$
$\mu$ = 7.23 mm$^{-1}$
$T$ = 298 K
Prism
0.25 × 0.22 × 0.15 mm
Red

*Data collection*

Philips PW1100 diffractometer
$\omega$–$2\theta$ scans
Absorption correction: none
5965 measured reflections
5560 independent reflections
3396 observed reflections [$I > 3\sigma(I)$]
$R_{int}$ = 0.016
$\theta_{max}$ = 30°
$h = -41 \rightarrow 41$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 28$
3 standard reflections
frequency: 360 min
intensity variation: <5%

*Refinement*

Refinement on $F$
Final $R$ = 0.0603
$wR$ = 0.0605
$S$ = 1.723
3377 reflections
234 parameters
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max}$ = 0.02
$\Delta\rho_{max}$ = 0.38 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.51 e Å$^{-3}$
Atomic scattering factors inlaid (*SHELX76*; Sheldrick, 1976) except for Au and Ru (Cromer & Mann, 1968)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å$^2$)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Au(1) | −0.15949 (4) | 0.25084 (11) | −0.14608 (5) | 0.0425 (8) |
| Au(2) | −0.08529 (4) | 0.26026 (11) | −0.06934 (5) | 0.0389 (8) |
| Ru(1) | −0.0815 (1) | 0.0455 (2) | −0.0424 (1) | 0.043 (2) |
| Ru(2) | −0.1512 (1) | −0.0559 (2) | −0.0161 (1) | 0.054 (2) |
| Ru(3) | −0.1544 (1) | 0.1771 (2) | −0.0291 (1) | 0.042 (2) |
| Ru(4) | −0.1537 (1) | 0.0296 (2) | −0.1336 (1) | 0.044 (2) |
| P(1) | −0.1673 (3) | 0.4216 (7) | −0.1879 (4) | 0.044 (5) |
| P(2) | −0.0650 (2) | 0.4081 (7) | −0.1200 (4) | 0.038 (5) |
| C(11) | −0.0641 (10) | −0.097 (3) | −0.0428 (14) | 0.051 (9) |
| O(11) | −0.0520 (8) | −0.186 (2) | −0.0411 (11) | 0.083 (8) |
| C(12) | −0.0349 (12) | 0.101 (3) | −0.0677 (17) | 0.071 (11) |
| O(12) | −0.0046 (8) | 0.116 (2) | −0.0873 (11) | 0.079 (8) |
| C(13) | −0.0574 (12) | 0.073 (3) | 0.033 (2) | 0.087 (13) |
| O(13) | −0.0462 (9) | 0.088 (3) | 0.0814 (14) | 0.103 (10) |
| C(21) | −0.1411 (11) | −0.203 (3) | −0.0315 (17) | 0.070 (12) |
| O(21) | −0.1371 (9) | −0.296 (3) | −0.0348 (13) | 0.107 (10) |
| C(22) | −0.1310 (11) | −0.067 (3) | 0.0630 (17) | 0.067 (11) |
| O(22) | −0.1172 (9) | −0.072 (2) | 0.1115 (14) | 0.105 (10) |
| C(23) | −0.2062 (14) | −0.081 (3) | −0.0115 (19) | 0.090 (14) |
| O(23) | −0.2386 (12) | −0.082 (3) | −0.0026 (17) | 0.095 (14) |
| C(31) | −0.2083 (12) | 0.175 (3) | −0.0240 (15) | 0.062 (10) |
| O(31) | −0.2430 (10) | 0.181 (3) | −0.0272 (14) | 0.082 (11) |
| C(32) | −0.1410 (12) | 0.171 (3) | 0.052 (2) | 0.082 (13) |
| O(32) | −0.1322 (8) | 0.182 (2) | 0.1025 (14) | 0.101 (9) |
| C(33) | −0.1515 (11) | 0.333 (3) | −0.0339 (16) | 0.067 (11) |
| O(33) | −0.1598 (7) | 0.422 (2) | −0.0260 (11) | 0.073 (8) |
| C(41) | −0.2058 (13) | 0.032 (3) | −0.1545 (18) | 0.085 (13) |
| O(41) | −0.2414 (10) | 0.035 (3) | −0.1713 (14) | 0.090 (11) |
| C(42) | −0.1504 (11) | −0.116 (3) | −0.1480 (17) | 0.071 (12) |
| O(42) | −0.1494 (9) | −0.207 (3) | −0.1668 (14) | 0.098 (11) |
| C(43) | −0.1418 (11) | 0.074 (3) | −0.2073 (16) | 0.062 (10) |
| O(43) | −0.1320 (8) | 0.088 (2) | −0.2537 (13) | 0.095 (9) |
| C(1) | −0.1364 (8) | 0.528 (2) | −0.1471 (12) | 0.038 (8) |
| C(2) | −0.0982 (8) | 0.523 (2) | −0.1240 (12) | 0.034 (7) |
| C(111) | −0.2186 (5) | 0.478 (2) | −0.1851 (10) | 0.040 (8) |
| C(112) | −0.2287 (5) | 0.586 (2) | −0.1985 (10) | 0.099 (15) |
| C(113) | −0.2671 (5) | 0.614 (2) | −0.1934 (10) | 0.109 (16) |
| C(114) | −0.2954 (5) | 0.554 (2) | −0.1747 (10) | 0.080 (12) |
| C(115) | −0.2854 (5) | 0.446 (2) | −0.1613 (10) | 0.088 (16) |
| C(116) | −0.2470 (5) | 0.408 (2) | −0.1664 (10) | 0.078 (12) |
| C(121) | −0.1602 (6) | 0.435 (2) | −0.2652 (8) | 0.043 (8) |
| C(122) | −0.1679 (6) | 0.345 (2) | −0.3020 (8) | 0.059 (10) |
| C(123) | −0.1674 (6) | 0.356 (2) | −0.3611 (8) | 0.102 (15) |
| C(124) | −0.1593 (6) | 0.458 (2) | −0.3854 (8) | 0.082 (16) |
| C(125) | −0.1516 (6) | 0.547 (2) | −0.3485 (8) | 0.082 (16) |
| C(126) | −0.1521 (6) | 0.536 (2) | −0.2884 (8) | 0.089 (13) |
| C(211) | −0.0154 (5) | 0.4680 (15) | −0.0910 (8) | 0.044 (8) |
| C(212) | −0.0071 (5) | 0.5757 (15) | −0.1045 (8) | 0.048 (9) |
| C(213) | 0.0307 (5) | 0.6197 (15) | −0.0859 (8) | 0.055 (10) |
| C(214) | 0.0602 (5) | 0.5561 (15) | −0.0538 (8) | 0.065 (11) |
| C(215) | 0.0519 (5) | 0.4484 (15) | −0.0402 (8) | 0.061 (10) |
| C(216) | 0.0141 (5) | 0.4043 (15) | −0.0589 (8) | 0.048 (9) |
| C(221) | −0.0602 (6) | 0.3714 (18) | −0.1944 (8) | 0.044 (9) |
| C(222) | −0.0598 (6) | 0.2621 (18) | −0.2110 (8) | 0.073 (11) |
| C(223) | −0.0561 (6) | 0.2345 (18) | −0.2687 (8) | 0.071 (11) |
| C(224) | −0.0528 (6) | 0.3161 (18) | −0.3099 (8) | 0.096 (14) |
| C(225) | −0.0533 (6) | 0.4254 (18) | −0.2933 (8) | 0.068 (11) |
| C(226) | −0.0570 (6) | 0.4530 (18) | −0.2356 (8) | 0.073 (11) |

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

| | | | |
|---|---|---|---|
| Au(1)—Au(2) | 2.861 (2) | Au(1)—Ru(3) | 2.827 (2) |
| Au(1)—Ru(4) | 2.735 (2) | Au(1)—P(1) | 2.307 (9) |
| Au(2)—Ru(1) | 2.707 (2) | Au(2)—Ru(3) | 2.811 (2) |
| Au(2)—P(2) | 2.311 (8) | Ru(1)—Ru(2) | 2.796 (3) |
| Ru(1)—Ru(3) | 2.988 (3) | Ru(1)—Ru(4) | 2.994 (3) |
| Ru(2)—Ru(3) | 2.877 (3) | Ru(2)—Ru(4) | 2.897 (3) |
| Ru(3)—Ru(4) | 3.017 (3) | Ru—CO | 1.76–1.92 (4) |
| Ru(3)—Au(1)—Au(2) | 59.2 (1) | Ru(4)—Au(1)—Au(2) | 86.0 (1) |
| Ru(4)—Au(1)—Ru(3) | 65.7 (1) | Ru(1)—Au(2)—Au(1) | 96.4 (1) |
| Ru(3)—Au(2)—Au(1) | 59.8 (1) | Ru(3)—Au(2)—Ru(1) | 65.5 (1) |
| Ru(2)—Ru(1)—Au(2) | 118.0 (1) | Ru(3)—Ru(1)—Au(2) | 58.9 (1) |
| Ru(3)—Ru(1)—Ru(2) | 59.5 (1) | Ru(4)—Ru(1)—Au(2) | 83.9 (1) |
| Ru(4)—Ru(1)—Ru(2) | 59.9 (1) | Ru(4)—Ru(1)—Ru(3) | 60.6 (1) |
| Ru(3)—Ru(2)—Ru(1) | 63.5 (1) | Ru(4)—Ru(2)—Ru(1) | 63.5 (1) |
| Ru(4)—Ru(2)—Ru(3) | 63.0 (1) | Au(2)—Ru(3)—Au(1) | 61.0 (1) |
| Ru(1)—Ru(3)—Au(1) | 91.1 (1) | Ru(1)—Ru(3)—Au(2) | 55.5 (1) |
| Ru(2)—Ru(3)—Au(1) | 114.5 (1) | Ru(2)—Ru(3)—Au(2) | 112.0 (1) |
| Ru(2)—Ru(3)—Ru(1) | 56.9 (1) | Ru(4)—Ru(3)—Au(1) | 55.7 (1) |
| Ru(4)—Ru(3)—Au(2) | 81.8 (1) | Ru(4)—Ru(3)—Ru(1) | 59.8 (1) |
| Ru(4)—Ru(3)—Ru(2) | 58.8 (1) | Ru(1)—Ru(4)—Au(1) | 92.8 (1) |
| Ru(2)—Ru(4)—Au(1) | 116.8 (1) | Ru(2)—Ru(4)—Ru(1) | 56.6 (1) |
| Ru(3)—Ru(4)—Au(1) | 58.6 (1) | Ru(3)—Ru(4)—Ru(1) | 59.6 (1) |
| Ru(3)—Ru(4)—Ru(2) | 58.2 (1) | Ru—C—O | 158–177 (3) |

The synthesis and NMR spectroscopic studies of [$Au_2Ru_4$-($\mu_3$-H)($\mu$-H)($\mu$-$Ph_2PCH{=}CHPPh_2$)$(CO)_{12}$] (1) have been reported elsewhere (Blaxill *et al.*, 1989). The methods of data collection and data processing used for cluster (1) were similar to those described previously (Adams *et al.*, 1980).

The positions of the two Au and two Ru atoms of the metal framework were deduced from a Patterson synthesis. The remaining non-H atoms were located from subsequent difference Fourier syntheses. In the final stages of structure refinement, anisotropic displacement factors were assigned to the two Au, four Ru and two P atoms. The six C atoms of each phenyl ring were grouped as rigid hexagons (C—C = 1.395 Å; C—C—C = 120°) with the phenyl H atoms geometrically calculated to ride on their respective C atoms at distances of C—H = 1.08 Å with fixed thermal factors of 0.08 Å$^2$. The H atoms on C(1) and C(2) of the bis(diphenylphosphino)ethene ligand were treated in a similar manner. Full-matrix least-squares refinement was carried out on the atomic positions and the thermal parameters of all the non-H atoms ($wR$ = $\Sigma w^{1/2}||F_o| - |F_c||/\Sigma w^{1/2}|F_o|$). Although the two hydrido ligands were not located directly from the data, suitable positions were deduced from potential-energy minimization calculations using *HYDREX* (Orpen, 1980). The atomic positions of these atoms were included in the structure-factor calculations but were not refined. Crystallographic calculations were performed using *SHELX76* (Sheldrick, 1976). Geometrical calculations and plotting of figures were carried out with *NRCVAX* (PC version; Gabe, Lee & Le Page, 1985).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances and angles, and inter- and intramolecular distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71356 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0555]

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*Acta Cryst.* (1993). C**49**, 1929–1932

# Structure of $[Cr_3O(OOCCH_3)_6(OH_2)_3]Cl.3[SC(NH_2)_2].2H_2O$


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## Abstract

The title compound, hexakis($\mu$-acetato-$\kappa O$:$\kappa O'$)-triaqua-1$\kappa O$,2$\kappa O$,3$\kappa O$-$\mu_3$-oxo-trichromium chloride tris(thiourea) dihydrate, has an oxo-centred trinuclear structure with molecular symmetry $m$, the mirror plane relating two of the three Cr atoms, but all three Cr···Cr distances are identical within experimental error [3.289 (1) Å]. The central O atom is within 0.012 Å of the $Cr_3$ plane. The thiourea molecules are not coordinated but are linked to the coordinated water molecules by hydrogen bonds.


## Comment

Oxo-centred trinuclear complexes of the general formula $[M_3O(OOCR)_6L_3]^{n+}$ occur with various trivalent metals, with mixed metals and with mixed valencies, $M^{III}_2M^{II}$. The chemistry and physical properties have been reviewed (Cannon & White, 1988). X-ray and spectroscopic work on compounds of this class has shown that those with three identical metal ions rarely, if ever, show the full $\bar{6}m2$ symmetry of the idealized molecular structure. The prototype salt $[Cr_3O(OOCCH_3)_6(OH_2)_3]Cl.5H_2O$ has the most complicated of all structures, with the trinuclear units on general sites (Figgis & Robertson, 1965; Chang & Jeffrey, 1970), and below a phase-transition temperature of 211 K it has two sets of non-equivalent molecules in each unit cell (Sorai, Tachiki, Suga & Seki, 1971; Schenk & Güdel, 1982; Jayasooriya, Cannon, White & Kearley, 1989). For the interpretation of physical properties it is desirable to find a structure with fewer complications. We report here the structure of a different salt of the same complex cation which has molecular symmetry $m$.

When first reported the title compound was assigned the formula $[Cr_3(OOCCH_3)_6(OH)_2(H_2NCSNH_2)_3]Cl.xH_2O$, with $x = 2$ or 3 (Weinland & Hachenburg, 1923). In view of the later work on complexes of this type, cited above, this could be revised to the oxo-centred form, and by analogy with other known structures the three thiourea molecules could be expected to be bonded to the three Cr atoms, as $[Cr_3(OOCCH_3)_6O(H_2NCSNH_2)_3]Cl.(x+1)H_2O$. However, all our attempts to detect inner-sphere coordination of thiourea were unsuccessful. Visible–UV spectra and kinetic behaviour in solution, and IR and Raman spectra of the solid, suggested the tris(aqua) formulation; this is now confirmed.

The structure is remarkable for the regularity of the central Cr atom triangle. Two Cr atoms are related by the mirror plane of symmetry which passes through the third, and all three Cr···Cr distances are identical within experimental error [3.289 (1) Å]. The three central O—Cr distances differ by only 0.005 Å [1.902 (3) and 1.897 (1) Å] and the central O atom is within 0.012 Å of the $Cr_3$ plane. This is a very small displacement and probably not significant when compared with the probable positional e.s.d. of *ca* 0.004 Å. As shown in Fig. 2, each terminal $H_2O$ molecule is hydrogen bonded

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