A Zirconoxy Carbene from Monocarbonylbis(η-cyclopentadienyl)tungsten and Permethylzirconocene Dihydride: (η^5-C$_5$H$_5$)$_2$W=C(H)OZr(H)(η^5-C$_5$Me$_5$)$_2^*$

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Abstract. C$_{31}$H$_{42}$OWZr, $M_r = 705.75$, monoclinic, $P2_1/n$, $a = 10.178$ (3), $b = 35.611$ (14), $c = 8.293$ (2) Å, $\beta = 109.93$ (2)°, $V = 2825$ (2) Å^3, $Z = 4$, $D_x = 1.66$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 45$ cm^{-1}, $T \approx 290$ K, $F(000) = 1400$; $R = 0.054$ for the 4584 reflections with $F_o^2 > 0$ and 0.033 for the 3377 reflections with $F_o^2 > 3\sigma_{F^2}$. The short W–C bond length of 2.008 (7) Å, moderately long C=O bond length of 1.350 (8) Å, and relatively short Zr–O bond length of 1.970 (4) Å suggest a strong W=C bond, a strong Zr–O bond, and a reduced C–O π interaction, reflecting π backbonding from the electron-rich Cp$_2$W moiety and π donation to the electron-poor (η^5-C$_5$Me$_5$)$_2$Zr group. The Zr–H bond length is 1.93 (4) Å.

Introduction. Permethylzirconocene dihydride, (η^5-C$_5$Me$_5$)$_2$ZrH$_2$, reduces CO stoichiometrically under mild conditions. Likewise, metal monocarbonyls react with the dihydride to generate *zirconoxy* carbenes. Here, we report the single-crystal X-ray structure of (η^5-C$_5$H$_5$)$_2$W=C(H)OZr(H)(η^5-C$_5$Me$_5$)$_2$, the product from the reaction of Cp$_2$W(CO) (Cp: η^5-C$_5$H$_5$), and (C$_5$Me$_5$)$_2$ZrH$_2$. The synthesis (Wolczanski, 1981) and a preliminary report of the X-ray structure have been published (Wolczanski, Threlkel & Bercaw, 1979).

Experimental. Maroon crystals, air-sensitive. Specimen, $0.3 \times 0.3 \times 0.5$ mm, sealed in glass capillary under N$_2$. Space group by oscillation and Weissenberg photographs, $P2_1/n$ (systematic absences: $h0l$ for $h+l$ odd, $0k0$ for k odd). Locally modified Syntex $P2_1$ diffractometer, graphite monochromator. Cell parameters and orientation matrix by least-squares refinement using fifteen reflections, $15 \leq 2\theta \leq 30°$. Intensity data: 10 562, $2\theta \leq 50°$ ($+h$, $+k$, $\pm l$ and $-h$, $-k$, $\pm l$); ω scans, $1.0°$min^{-1}, fixed scan width 1°, 30s background counts at the start and finish of each scan,

four check reflections, every 100 reflections, no unusual variation. No absorption correction, scaling of F_o by Wilson (1942) plot. Structure derivation: Patterson and density maps. Refinement: full-matrix least squares on F^2, *all* reflections, weights $w, w^{-1} = [s + r^2 b + (0.02s)^2]k^4/(Lp)^2$ (s = scan counts, b = background counts, r = scan-to-background time ratio, k = scale factor), anisotropic Gaussian amplitudes, atomic form factors from Stewart, Davidson & Simpson (1965) for H, and *International Tables for X-ray Crystallography* (1962) for other atoms. The coordinates of C$_5$Me$_5$ H atoms were determined from difference maps, and the coordinates of the Cp H atoms were calculated by assuming planar, trigonal geometry at C: C–H = 0.95 Å, and isotropic B=8Å^2; these H atoms were not refined. The carbene H atom and the hydride atom on Zr were located from a difference map and refined with the non-hydrogen atoms. *CRYRM* program library (Duchamp, 1964); final $S = 1.33$ (4871 total, averaged reflections, 415 parameters), $R = 0.054$ and $R_w = 0.066$ (the R's based only on the 4584 reflections with $F_o^2 > 0$), maximum peak 0.7 e Å^{-3} near W in final ΔF map, mean and maximum ratio of shift/error in final cycle: 0.03 and 0.1.

Discussion. The coordinates and U's are given in Table 1.‡ The C$_5$Me$_5$ ring centroids (R_1 and R_2), the O atom, and the hydride H are arranged pseudo-tetrahedrally around the Zr atom with an R_1–Zr–R_2 angle of 138.5° and O–Zr–H angle equal to 98 (1)° (Fig. 1). The R_1–Zr–R_2 angle is normal, *cf.* 139.2° in (C$_5$Me$_5$)$_2$Zr(pyridine)(C,O-η^2-H$_2$C=CO) (Moore, Straus, Armantrout, Santarsiero, Grubbs & Bercaw, 1983) and 139.2° in (C$_5$Me$_5$)$_2$Zr(μ-η^1-η^2-CO)(μ-CO)CoCp (Barger & Bercaw, 1980), and is greater than the reported Cp–Zr–Cp angles, *e.g.* 126.6° for

Cp$_2$ZrCl$_2$ (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974), 131·1° for Cp$_2$ZrF$_2$ (Bush & Sim, 1971), 130·5° for Cp$_2$ZrCl(SiPh$_3$) (Muir, 1971), and 128·2° for Cp$_2$Zr(CHPh$_2$)$_2$ (Atwood, Barker, Holton, Hunter, Lappert & Pierce, 1977). The average Zr—C(C$_5$Me$_5$) bond length is 2·5472[6] Å* (Table 2), cf., e.g., 2·54 Å in [(C$_5$Me$_5$)$_2$ZrN$_2$]$_2\mu$-N$_2$ (Sanner, Manriquez, Marsh & Bercaw, 1976) and 2·54 Å in (C$_5$Me$_5$)$_2$Zr(μ-η^1-η^2-CO)(μ-CO)CoCp (Barger & Bercaw, 1980).

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*The expression for the standard deviation quoted in square brackets is given in Table 2, footnote (b).

Table 1. Atom coordinates and U_{eq} values

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

	$x(\times 10^4)$	$y(\times 10^5)$	$z(\times 10^4)$	U_{eq} (Å$^2 \times 10^4$)
W	−2181·0 (3)	5720 (1)	8275·4 (4)	297 (1)
Zr	1280·0 (6)	15168 (2)	7616·8 (8)	248 (1)
O	−105 (4)	11226 (12)	7516 (6)	374 (9)
C(11)	2753 (7)	9242 (17)	7982 (9)	351 (13)
C(12)	3495 (6)	11628 (19)	9333 (8)	342 (13)
C(13)	3943 (6)	14785 (19)	8609 (9)	377 (14)
C(14)	3498 (6)	14313 (18)	6836 (8)	300 (12)
C(15)	2692 (6)	10959 (17)	6423 (8)	301 (11)
C(21)	366 (7)	19550 (18)	5052 (8)	365 (14)
C(22)	1161 (7)	21856 (18)	6438 (9)	371 (13)
C(23)	474 (7)	21974 (18)	7649 (8)	358 (13)
C(24)	−744 (7)	19729 (17)	7042 (8)	323 (12)
C(25)	−815 (7)	18287 (17)	5432 (8)	343 (13)
C(M11)	2221 (8)	5335 (20)	8154 (11)	565 (18)
C(M12)	3887 (8)	10787 (24)	11200 (10)	590 (20)
C(M13)	4909 (8)	17882 (24)	9645 (10)	584 (19)
C(M14)	4068 (7)	16401 (21)	5603 (21)	472 (15)
C(M15)	2054 (8)	9275 (21)	4659 (10)	509 (17)
C(M21)	553 (9)	19096 (24)	3348 (9)	584 (19)
C(M22)	2378 (8)	24332 (19)	6509 (11)	543 (17)
C(M23)	877 (9)	24420 (19)	9236 (10)	519 (18)
C(M24)	−1842 (7)	19230 (21)	7883 (10)	506 (16)
C(M25)	−1982 (8)	15894 (21)	4270 (10)	553 (19)
C(31)	−1280 (9)	10316 (20)	10288 (10)	504 (17)
C(32)	−2512 (9)	8939 (22)	10479 (11)	596 (18)
C(33)	−2268 (9)	5076 (21)	10981 (10)	525 (17)
C(34)	−902 (8)	4033 (20)	11021 (9)	482 (17)
C(35)	−306 (8)	7338 (22)	10627 (9)	463 (17)
C(41)	−3696 (9)	5081 (23)	5518 (11)	668 (23)
C(42)	−4453 (8)	4713 (26)	6623 (14)	781 (31)
C(43)	−3951 (8)	1445 (22)	7612 (12)	614 (21)
C(44)	−2855 (8)	−88 (19)	7197 (11)	520 (18)
C(45)	−2720 (8)	2085 (22)	5843 (10)	561 (19)
C	−1111 (7)	8572 (18)	7038 (9)	350 (13)
H(Zr)	1698 (44)	16607 (116)	9988 (56)	1·5 (10)†
H(C)	−1309 (51)	8232 (136)	5801 (67)	2·6 (13)†

† Atom refined with isotropic $B(=8\pi^2 U^2)$, B given here.

Table 2. Important ring distances (Å)

	Zr—C(ij)		W—C(ij)		$\Delta(a)$	
j	$i=1$	$i=2$	$i=3$	$i=4$	$i=1$	$i=2$
1	2·546 (7)	2·545 (7)	2·294 (8)	2·292 (9)	0·19	0·21
2	2·551 (7)	2·562 (7)	2·278 (9)	2·279 (9)	0·12	0·21
3	2·554 (7)	2·562 (7)	2·287 (8)	2·278 (9)	0·10	0·15
4	2·570 (6)	2·538 (6)	2·285 (8)	2·265 (8)	0·41	0·07
5	2·502 (6)	2·535 (7)	2·289 (8)	2·300 (8)	0·05	0·07
Average (b)	2·547 [6]		2·285 [3]		0·16	

(a) Displacements of the methyl C atoms, C(Mij), from the least-squares plane of the five ring atoms.

(b) Averages, with e.s.d.'s, over chemically equivalent distances. The standard deviation of the average is estimated as $[\sum_{k=1}^n (d_k - d)^2 / n(n-1)]^{1/2}$.

The Cp ring centroids (R_3 and R_4) and the carbene C atom form a planar, distorted-trigonal arrangement around W with R_3—W—R_4 = 145·6°. The average W—C(Cp) bond length is 2·285[3] Å (Table 2), in the range 2·21 to 2·49 Å (average 2·33 Å), determined by the 62 structures with a WCp fragment reported in the Cambridge Crystallographic Database.*

The C$_5$Me$_5$ rings are staggered, but the Cp rings are eclipsed (see Fig. 2). The Cp rings can vary, from an eclipsed to staggered orientation, depending on the crystal packing (Prout et al., 1974); in contrast, the C$_5$Me$_5$ rings are always staggered. The C$_5$Me$_5$ methyl

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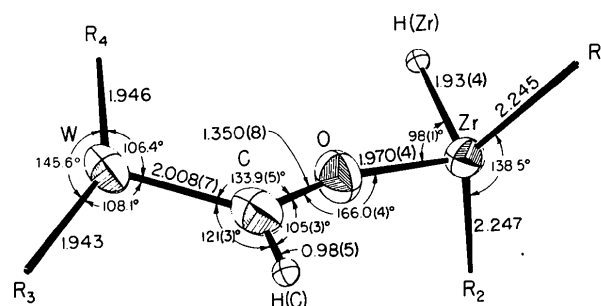* Data file current to May, 1982; see Allen et al. (1979).

Fig. 1. Skeletal view of $(\eta^5$-C$_5$H$_5)_2$W=C(H)OZr(H)(η^5-C$_5$Me$_5)_2$ with important distances (Å) and angles.
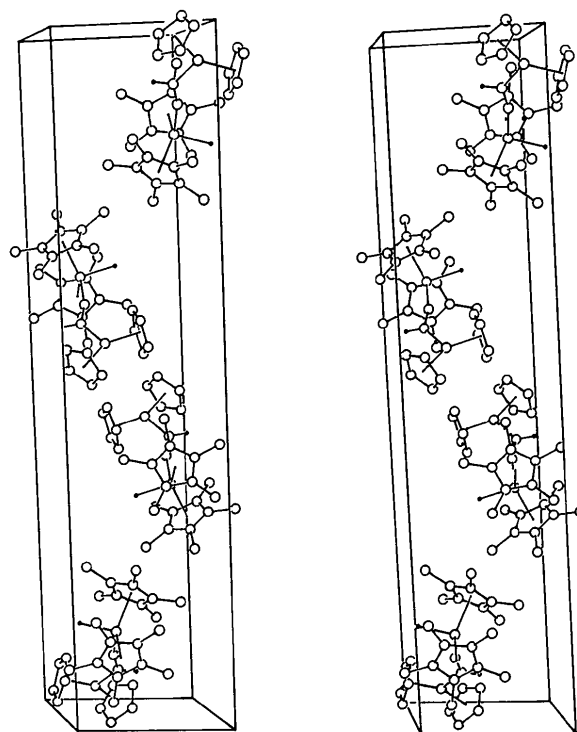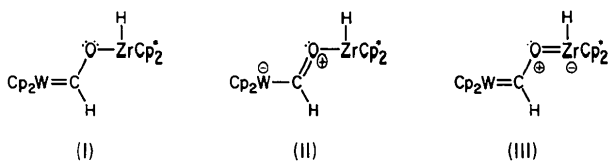

Fig. 2. Stereoscopic view of the unit cell with **c** horizontal and **b** vertical.

groups are not coplanar with the rings, but are bent back away from Zr, on the average, by 0·16 Å (Table 2). The greatest deviations are by C(M14) on one ring and C(M21) and C(M22) on the other ring [the shortest $CH_3 \cdots CH_3$ contacts are, in fact, C(M14)$\cdots$C(M22) 3·52 and C(M14)$\cdots$C(M21) 3·56 Å]. The vector normals to the planes of our four (C_5H_5, C_5Me_5) rings are nearly coincident with their $M{-}R_i$ vectors, forming angles of 0·5 and 0·7° (Cp around W) and 1·2 and 0·9° (C_5Me_5 around Zr); the maximum tilt of the rings in WCp complexes (Cambridge Database) is almost 6°. The rings are each coplanar to within ±0·02 Å, and coordinate to the metals in the conventional pentahapto manner. The metal—carbon and ring bond lengths are normal (average inner-ring C—C bond lengths in the C_5H_5 and C_5Me_5 rings are equal, 1·411 [5] and 1·412 [3] Å; average C—CH_3 bond lengths in C_5Me_5 rings 1·512 [4] Å).

The skeletal view (Fig. 1) and stereoview of the unit cell (Fig. 2) reveal a remarkable feature of the structure: the two Cp ring centroids (R_3 and R_4), W, Zr, O, C, H(C), and H(Zr) atoms are nearly coplanar, the maximum deviation being 0·12 Å by R_4 and H(Zr). This configuration presumably reflects minimization of non-bonding contacts between the permethylcyclopentadienyl methyl groups and the Cp rings on W [closest approach C(M15)$\cdots$C(35) 3·46, C(M24)$\cdots$ C(31) 3·69, C(M15)$\cdots$C(42) 3·74 Å]; in an analogous manner, $C_5Me_5(Zr_1)\cdots C_5Me_5(Zr_2)$ interactions in $[(C_5Me_5)_2ZrN_2]_2\mu\text{-}N_2$ (Sanner *et al.*, 1976) result in a similar molecular configuration, with $R{-}Zr_1{-}Zr_2{-}R$ dihedral angles of 70–90° (we observe $R{-}W{-}Zr{-}R$ dihedral angles of 71·9, 73·8, 86·7, and 88·6°). Furthermore, the observed molecular configuration and bond lengths can be rationalized on electronic grounds: the π interaction of the carbene p orbital with the filled b_2 orbital in the equatorial plane of the Cp_2W moiety [see Lauher & Hoffmann (1976) for MO scheme of bent metallocenes], and a Zr—O π interaction perpendicular to the W—C π bond, leading to $R{-}W{-}Zr{-}R$ dihedral angles $\approx 90°$. As to the valence-bond description, there are three major Lewis structures: (I) and (III), the formal tungsten carbenes; and (II), the Fischer-type carbene.

(I)   (II)   (III)

These bonding schemes are consistent with the short W—C bond, 2·008 (7) Å, *cf.* $(CO)_5W{=}CPh_2$, 2·14 (2) Å (Casey, Burkhardt, Bunnell & Calabrese, 1977), the relatively long C=O bond, 1·350 (8) Å (as found in alkoxy-substituted carbenes, 1·32–1·36 Å; Cardin, Cetinkaya & Lappert, 1972), and the short

Zr—O bond, 1·970 (4) Å, *cf.* $Zr(acac)_4$ (2·20 Å; Clearfield, 1964) and $(C_5Me_5)_2 ZrOC[Zr(I)Cp_2]C(H)O$ (2·01 and 2·09 Å; Barger, Santarsiero & Bercaw, 1982).

The Zr—H bond length, 1·93 (4) Å, is consistent with related $(C_5Me_5)_2MH$ (M = Zr or Hf) cases: $(C_5Me_5)_2Zr(H)CH_2PMe_2CH_2$ [1·89 (4) Å; Santarsiero, Moore & Bercaw, 1982], $(C_5Me_5)_2Zr(H)(C,O\text{-}\eta^2\text{-}PMe_3CH{=}CO)$ [1·90 (2) Å; Santarsiero, Moore & Bercaw, 1982], and $(C_5Me_5)_2Hf(H)(C_3H_5)$ [1·86 (7) Å; Roddick, Santarsiero & Bercaw, 1982]. Only a few hydride structures have been reported with early transition metals (see Teller & Bau, 1981; Toogood & Wallbridge, 1982). Two structures having Zr and a terminal hydride ligand have been reported: $HZr(C_8H_{11})(dmpe)_2$ (Fischer *et al.*, 1980) with a Zr—H bond length of 1·67 Å (the coordinates of the H atom were taken from a Fourier difference map and not refined), and $[(C_5H_4Me)_2ZrH(\mu\text{-}H)]_2$ (Jones & Peterson, 1981) with a Zr—H(terminal) bond length of 1·78 (2) Å. Finally, it should be noted that the hydride ligand occupies a stereochemically active position in the *equatorial wedge* of the $(C_5Me_5)_2Zr$ fragment, and the O—Zr—H angle of 98 (1)° can be reasonably compared to the $L{-}Zr{-}L$ angle in other zirconocene complexes, *e.g.* $Cp_2Zr(CH_2SiMe_3)_2$, 97·8 (1)° (Jeffrey, Lappert, Luong-Thi, Webb, Atwood & Hunter, 1981) and $Cp_2Zr(CHPh_2)_2$, 95·5 (4)° (Atwood *et al.*, 1977).

References

ALLEN, F. H., BELLARD, S., BRICE, M. D., CARTWRIGHT, B. A., DOUBLEDAY, A., HIGGS, H., HUMMELINK, T., HUMMELLINK-PETERS, B. G., KENNARD, O., MOTHERWELL, W. D. S., RODGERS, J. R. & WATSON, D. G. (1979). *Acta Cryst.* B35, 2331–2339.

ATWOOD, J. L., BARKER, G. K., HOLTON, J., HUNTER, W. E., LAPPERT, M. F. & PIERCE, R. (1977). *J. Am. Chem. Soc.* 99, 6645–6652.

BARGER, P. T. & BERCAW, J. E. (1980). *J. Organomet. Chem.* 201, C39–C44.

BARGER, P. T., SANTARSIERO, B. D. & BERCAW, J. E. (1982). Unpublished results.

BUSH, M. A. & SIM, G. A. (1971). *J. Chem. Soc. A*, pp. 2225–2229.

CARDIN, D. J., CETINKAYA, T. J. & LAPPERT, M. F. (1972). *Chem. Rev.* 72, 545–574.

CASEY, C. P., BURKHARDT, T. J., BUNNELL, C. A. & CALABRESE, J. C. (1977). *J. Am. Chem. Soc.* 99, 2127–2133.

CLEARFIELD, A. (1964). *Rev. Pure Appl. Chem.* 14, 91–108.

DUCHAMP, D. J. (1964). *CRYRM Computing System*. California Institute of Technology.

FISCHER, M. B., JAMES, E. J., McNEESE, T. J., NYBURG, S. C., POSIN, B., WONG-NG, W. & WREFORD, S. S. (1980). *J. Am. Chem. Soc.* 102, 4941–4947.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 209 ff. Birmingham: Kynoch Press.

JEFFREY, J., LAPPERT, M. F., LUONG-THI, N. T., WEBB, M., ATWOOD, J. L. & HUNTER, W. E. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1593–1605.

JONES, S. B. & PETERSON, J. L. (1981). *Inorg. Chem.* **20**, 2889–2894.

LAUHER, J. W. & HOFFMANN, R. (1976). *J. Am. Chem. Soc.* **98**, 1729–1742.

MOORE, E. J., STRAUS, D. A., ARMANTROUT, J., SANTARSIERO, B. D., GRUBBS, R. H. & BERCAW, J. E. (1983). *J. Am. Chem. Soc.* **105**, 2068–2070.

MUIR, K. M. (1971). *J. Chem. Soc. A*, pp. 2663–2666.

PROUT, K., CAMERON, T. S., FORDER, R. A., CRITCHLEY, S. R., DENTON, B. & REES, G. V. (1974). *Acta Cryst.* **B30**, 2290–2304.

RODDICK, D. M., SANTARSIERO, B. D. & BERCAW, J. E. (1982). Unpublished results.

SANNER, R. D., MANRIQUEZ, J. M., MARSH, R. E. & BERCAW, J. E. (1976). *J. Am. Chem. Soc.* **98**, 8351–8357.

SANTARSIERO, B. D., MOORE, E. J. & BERCAW, J. E. (1982). Unpublished results.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TELLER, R. G. & BAU, R. (1981). *Struct. Bonding (Berlin)*, **44**, 1–82.

TOOGOOD, G. E. & WALLBRIDGE, M. G. H. (1982). *Adv. Inorg. Chem. Radiochem.* **25**, 267–340.

WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.

WOLCZANSKI, P. T. (1981). PhD Thesis, California Institute of Technology.

WOLCZANSKI, P. T., THRELKEL, R. S. & BERCAW, J. E. (1979). *J. Am. Chem. Soc.* **101**, 218–220.

The Structure of *catena*-Di-μ-chloro-iodo(1H⁺-S-methylisothiocarbonohydrazidium-N)cadmium(II), C₂H₉CdCl₂IN₄S

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Abstract. $M_r = 431 \cdot 391$, orthorhombic, *Pnma*, $a = 17 \cdot 702$ (3), $b = 7 \cdot 462$ (2), $c = 8 \cdot 060$ (2) Å, $V = 1064 \cdot 7$ (4) Å^3, $Z = 4$, $T = 295$ K, $D_m = 2 \cdot 68$, $D_x = 2 \cdot 69$ Mg m^{-3}, λ(Mo $K\alpha_1$) = 0·70926 Å, μ(Mo $K\alpha_1$) = 55·652 cm^{-1}, $F(000) = 800$, $R = 0 \cdot 0496$ for 556 reflections. The structure consists of polymeric chains of edge-shared octahedra running parallel to **b** held together by weak N—H⋯Cl and N—H⋯I hydrogen bonds and van der Waals contacts.

Introduction. This study is part of a systematic investigation on the behaviour of a thiocarbonohydrazide derivative (S-methylisothiocarbonohydrazide, S-tcaz) as ligand in metal complexes. To the authors' knowledge this structure has turned out to be the only example of a six-coordinate polymeric mixed-halogen cadmium(II) complex with a protonated ligand so far studied by X-ray analysis. The known CdCl₃⁻ complexes form polymeric chains of face-shared octahedra and the only studied complex of the |CdCl₃LH| type is monomeric and tetrahedral.

Experimental. Colourless prismatic crystals grown by very slow evaporation from aqueous solution of cadmium dichloride and S-methylisothiocarbonohydrazide hydroiodide, D_m by flotation, crystal 0·30 × 0·19 × 0·13 mm, Siemens AED diffractometer, Nb-

filtered Mo $K\alpha_1$, lattice parameters refined by least squares on 18 reflections ($8 < \theta < 15°$), 1125 *hkl* (including 111 systematic absences), $0 \le h \le 21$, $0 \le k \le 8$, $0 \le l \le 9$, $3 < \theta < 25°$ ($\theta/2\theta$ scan), 1014 independent, 556 observed with $I \ge 2\sigma(I)$ (1 standard reflection, checked after every 50, no decomposition of specimen), Lp correction, absorption ignored, atomic scattering factors and anomalous-scattering corrections from *International Tables for X-ray Crystallography* (1974), heavy-atom technique, anisotropic full-matrix least squares (*SHELX*76, Sheldrick, 1976), ΔF synthesis not valuable in locating all H atoms, $\sum w |\Delta F|^2$ minimized, unit weights in the first cycles of refinement then $w = k[\sigma^2(F_o) + g F_o^2]^{-1}$ ($k = 0 \cdot 0421$, $g = 0 \cdot 119638$) in the last cycles, final $R = 0 \cdot 0496$, $R_w = 0 \cdot 056$,* $(\Delta/\sigma)_{max} = 0 \cdot 48$, max. height in final difference Fourier = 1·3 e Å^{-3}, Cyber 76 computer of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna, with the financial support of the University of Parma.