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Structure of Tris-μ-[bis(8-quinolinolato)hydrogen(I)-*N*,*O*]-dinickel(II) Triiodide

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Abstract. $[Ni_2\{H(C_9H_6NO)_2\}_3]I_3$, $M_r = 1366{\cdot}04$, monoclinic, $P2_1/c$, $a = 21{\cdot}151$ (10), $b = 15{\cdot}231$ (3), $c = 15{\cdot}993$ (6) Å, $\beta = 98{\cdot}75$ (2)°, $V = 5092$ (3) Å^3, $Z = 4$, $D_m = 1{\cdot}76$ (1), $D_x = 1{\cdot}78$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}60$ mm^{-1}, $F(000) = 2672$, $T = 298$ K, $R = 0{\cdot}096$ for 3029 observed reflections. Each Ni$^{\rm II}$ atom is surrounded by three bidentate 8-quinolinol ligands with facial conformation in a distorted octahedral coordination. Two such facial isomers form a dinuclear cation of $[Ni_2\{H(C_9H_6NO)_2\}_3]^+$ joined face to face by three strong O···H···O hydrogen bonds with an average distance of 2·45 (3) Å. Counteranions exist as I_3^- with I(1)—I(2) 2·921 (3) Å and I(2)—I(3) 2·897 (3) Å, and I(1)—I(2)—I(3) 176·9 (1)°.

Introduction. 8-Quinolinol is a useful analytical reagent, which forms neutral bidentate chelates with many metal ions. Recently, nickel 8-quinolinol complexes containing anions such as iodide, perchlorate or thiocyanate were obtained from ethanol solution (Sekido & Fukuyori, 1984, unpublished), but their chemical compositions have been ambiguous from the chemical and spectroscopic analyses. In this study the crystal structure of the nickel 8-quinolinol complex with iodide anions was determined by means of X-ray diffraction in order to make clear its stoichiometry and structural details.

Experimental. Nickel(II) chloride hexahydrate (10 mmol in 20 ml of ethanol) and 8-quinolinol (60 mmol in 100 ml of ethanol) were added dropwise into a sodium iodide solution (20 mmol in 30 ml ethanol). The mixture was stirred and filtered. The filtrate was allowed to stand in air to evaporate for several days, during which time the color of the solution changed from yellow to brown and then dark-brown crystals were obtained. Density measured by flotation (*m*-xylene–1,2-dibromoethylene mixture); crystal 0·2 × 0·15 × 0·15 mm; Rigaku AFC-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, 40 kV–200 mA; unit-cell parameters determined from least squares of setting angles of 30 reflections in 2θ range 20–24°; 7334 reflections measured, 7020 unique reflections, $R_{\rm int} = 0{\cdot}052$, ω–2θ scan technique, ω scan width $(0{\cdot}8 + 0{\cdot}35\tan\theta)$°, $2\theta_{\max} = 50°$ (h −25→25, k 0→18, l 0→19), 3029 (43%) with $|F_o| > 3\sigma(F_o)$; standard reflections 040, 815 and 400, intensity variation <2·2%; corrections for Lorentz–polarization and absorption (North, Phillips & Mathews, 1968) (min. = 1·006, max. = 1·138); structure solved by heavy-atom method and refined by block-diagonal least squares on F with anisotropic thermal parameters for I, Ni, O and N atoms and isotropic thermal parameters for C atoms; H atoms included in fixed theoretical positions (C—H = 1·0 Å and O—H = 1·0 Å) with an isotropic temperature factor of 5·0 Å^2; $\sum w(|F_o| - |F_c|)^2$ minimized for 371 parameters. Final $R = 0{\cdot}096$, $wR = 0{\cdot}061$, $S = 1{\cdot}38$; $w = 1/\sigma^2(F_o)$, which was the best weighting scheme among various ones tested such as $w = 1{\cdot}0$, $w = [\sigma^2(F_o) + 0{\cdot}05|F_o|]^{-1}$ and $w = [\sigma^2(F_o) + 4{\cdot}626|F_o| - 0{\cdot}0304|F_o|^2]^{-1}$ derived from an analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$; $(\Delta/\sigma)_{\max} = 0{\cdot}47$, $(\Delta/\sigma)_{\rm av} = 0{\cdot}03$. The ensuing refinement with anisotropic thermal parameters of all non-H atoms was unsuccessful in that anisotropic thermal parameters of five C atoms became unreasonable.

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Highest residual in final difference Fourier synthesis of 1·26 e Å^{-3}. No extinction effect was noticed for intense and low-angle reflections. The accuracy of refinements was lowered owing to the relatively weak intensities, particularly in high-angle reflections [of 2898 in the range $38° < 2\theta < 50°$ only 776 (26%) with $|F_o| > 3\sigma(F_o)$], arising from the small size of the crystal and also the large thermal parameters of the I atoms. Scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974); computations using the programs of *The Universal Crystallographic Computing System–Osaka* (1979) and their modifications on an ACOS 1000 computer at the Information Processing Center of Kobe University.

Discussion. Final positional and thermal parameters are listed in Table 1* and selected interatomic distances and angles in Table 2. The complex cation with the atom-numbering scheme and the crystal structure viewed along the *b* axis are shown in Figs. 1 and 2, respectively.

The structure determination confirmed the stoichiometry of this complex to be $[Ni_2\{H(C_9H_6NO)_2\}_3]I_3$. Two crystallographically independent Ni^{II} atoms are chelated in the same manner by three bidentate 8-quinolinols in a distorted octahedral coordination environment. The intraligand angles [av. 79·3 (2)°] of N(1)—Ni—O(8) in the five-membered chelate rings are considerably smaller than the ideal value of 90°. The average Ni—O and Ni—N distances are 2·07 (4) and 2·06 (3) Å, respectively, and can be compared to the analogous distances found in $Na_2[Ni(Gly)_3]ClO_4.D_2O$ (Campana, Shepard & Litchman, 1981) and $[Ni(N_2H_3COOC_2H_5)_3]$ (Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1976). Each 8-quinolinol ligand labeled as *A,B,C,D,E* or *F* lies in a plane with deviations less than 3σ, except for atoms O(8*A*) and O(8*D*) [0·18 (2) and 0·20 (2) Å, respectively]. The dihedral angles between the chelate planes range from 71·6 (4) to 88·2 (4)°. The three ligands are arranged in such a way that their O atoms are mutually *cis*, to yield the facial isomer.

These two tris chelates combine to form a dimer joined face to face by three strong hydrogen bonds with O···O distances of 2·41 (2), 2·47 (2) and 2·47 (2) Å. The positions of the H atoms were not located from the difference Fourier map. However, for every pair of hydrogen-bonded 8-quinolinol ligands, *A–D*, *B–F*, and *C–E*, the corresponding Ni—O and also C—O bonds do not show any significant difference in length within the experimental errors. This finding together with the very short O···O distances suggests that the O···H···O bonds are virtually symmetrical, although the average structure with $\frac{1}{2}$ H at 1·0 Å from each O atom along the

Table 1. *Final atomic coordinates and isotropic thermal parameters* (Å^2) *for non*-H *atoms*

	x	*y*	*z*	B_{eq}/B_{iso}
I(1)	0·14314 (9)	0·03501 (13)	0·24983 (11)	6·60 (7)*
I(2)	0·27846 (9)	0·01726 (12)	0·23490 (9)	6·28 (6)*
I(3)	0·41284 (9)	0·00986 (15)	0·21814 (11)	7·57 (7)*
Ni(1)	0·2859 (1)	0·4856 (2)	0·3786 (1)	2·3 (1)*
Ni(2)	0·2074 (1)	0·4900 (2)	0·0873 (1)	2·5 (1)*
N(1*A*)	0·3708 (7)	0·4224 (11)	0·4162 (9)	2·6 (5)*
N(1*B*)	0·2263 (7)	0·4281 (9)	0·4505 (9)	2·7 (5)*
N(1*C*)	0·3067 (7)	0·5986 (11)	0·4532 (9)	2·9 (5)*
N(1*D*)	0·1190 (7)	0·4368 (10)	0·0366 (9)	2·9 (5)*
N(1*E*)	0·2624 (7)	0·4206 (10)	0·0168 (9)	2·8 (5)*
N(1*F*)	0·1966 (7)	0·6036 (11)	0·0155 (9)	2·9 (5)*
O(8*A*)	0·2790 (6)	0·3864 (8)	0·2954 (8)	2·7 (4)*
O(8*B*)	0·1960 (5)	0·5359 (8)	0·3203 (7)	2·8 (4)*
O(8*C*)	0·3274 (6)	0·5641 (8)	0·2968 (7)	2·8 (4)*
O(8*D*)	0·2010 (5)	0·3915 (8)	0·1692 (7)	2·5 (4)*
O(8*E*)	0·2994 (5)	0·5283 (8)	0·1451 (7)	2·5 (4)*
O(8*F*)	0·1695 (5)	0·5742 (8)	0·1692 (7)	2·1 (4)*
C(2*A*)	0·4139 (9)	0·4354 (14)	0·4865 (12)	3·9 (5)
C(3*A*)	0·4750 (10)	0·3934 (16)	0·4950 (15)	5·4 (6)
C(4*A*)	0·4926 (11)	0·3445 (16)	0·4324 (14)	5·4 (6)
C(5*A*)	0·4593 (10)	0·2791 (16)	0·2914 (14)	5·1 (6)
C(6*A*)	0·4143 (10)	0·2663 (17)	0·2253 (14)	5·6 (6)
C(7*A*)	0·3509 (9)	0·3011 (13)	0·2208 (12)	3·1 (5)
C(8*A*)	0·3370 (8)	0·3528 (12)	0·2891 (11)	2·2 (4)
C(9*A*)	0·3886 (9)	0·3698 (14)	0·3554 (12)	3·5 (5)
C(10*A*)	0·4505 (10)	0·3323 (14)	0·3578 (13)	4·1 (5)
C(2*B*)	0·2445 (9)	0·3701 (13)	0·5133 (12)	3·4 (5)
C(3*B*)	0·1964 (9)	0·3315 (14)	0·5569 (12)	3·8 (5)
C(4*B*)	0·1351 (10)	0·3479 (14)	0·5317 (13)	4·0 (5)
C(5*B*)	0·0482 (11)	0·4268 (16)	0·4337 (15)	5·6 (6)
C(6*B*)	0·0376 (10)	0·4850 (17)	0·3670 (13)	5·4 (6)
C(7*B*)	0·0856 (9)	0·5186 (15)	0·3267 (12)	4·4 (5)
C(8*B*)	0·1488 (8)	0·5014 (13)	0·3579 (10)	2·8 (4)
C(9*B*)	0·1631 (8)	0·4426 (12)	0·4268 (11)	2·5 (4)
C(10*B*)	0·1120 (10)	0·4052 (14)	0·4665 (12)	3·8 (5)
C(2*C*)	0·2953 (8)	0·6123 (12)	0·5323 (10)	1·9 (4)
C(3*C*)	0·3110 (9)	0·6905 (13)	0·5761 (11)	2·6 (5)
C(4*C*)	0·3391 (9)	0·7544 (14)	0·5369 (12)	3·1 (5)
C(5*C*)	0·3824 (10)	0·8027 (14)	0·4063 (12)	4·1 (5)
C(6*C*)	0·3915 (10)	0·7848 (15)	0·3249 (13)	4·6 (6)
C(7*C*)	0·3746 (9)	0·7034 (13)	0·2857 (11)	2·8 (5)
C(8*C*)	0·3473 (9)	0·6420 (13)	0·3301 (11)	2·6 (4)
C(9*C*)	0·3358 (8)	0·6615 (12)	0·4125 (11)	2·1 (4)
C(10*C*)	0·3534 (9)	0·7423 (14)	0·4543 (11)	2·9 (5)
C(2*D*)	0·0835 (9)	0·4560 (14)	−0·0351 (12)	3·7 (5)
C(3*D*)	0·0224 (10)	0·4187 (15)	−0·0588 (13)	4·4 (6)
C(4*D*)	0·0013 (13)	0·3625 (14)	0·0048 (17)	4·6 (5)
C(5*D*)	0·0163 (10)	0·2895 (16)	0·1378 (14)	5·5 (7)
C(6*D*)	0·0550 (11)	0·2725 (17)	0·2077 (14)	6·0 (7)
C(7*D*)	0·1175 (10)	0·3043 (15)	0·2230 (13)	4·7 (6)
C(8*D*)	0·1397 (9)	0·3595 (13)	0·1636 (11)	2·9 (5)
C(9*D*)	0·0975 (8)	0·3796 (12)	0·0894 (11)	2·1 (4)
C(10*D*)	0·0338 (10)	0·3422 (14)	0·0738 (13)	4·1 (5)
C(2*E*)	0·2426 (9)	0·3677 (13)	0·0478 (11)	2·8 (5)
C(3*E*)	0·2834 (9)	0·3233 (14)	−0·0928 (12)	3·7 (5)
C(4*E*)	0·3479 (9)	0·3344 (14)	−0·0729 (12)	3·3 (5)
C(5*E*)	0·4369 (10)	0·4102 (15)	0·0226 (13)	4·3 (6)
C(6*E*)	0·4559 (10)	0·4615 (15)	0·0895 (13)	5·3 (6)
C(7*E*)	0·4128 (9)	0·5063 (15)	0·1333 (11)	4·2 (5)
C(8*E*)	0·3471 (8)	0·4915 (14)	0·1102 (10)	2·9 (4)
C(9*E*)	0·3286 (9)	0·4392 (14)	0·0387 (12)	3·3 (5)
C(10*E*)	0·3714 (9)	0·3930 (13)	−0·0059 (11)	2·8 (5)
C(2*F*)	0·2121 (9)	0·6172 (13)	−0·0597 (12)	3·1 (5)
C(3*F*)	0·2001 (9)	0·6962 (14)	0·1052 (12)	3·3 (5)
C(4*F*)	0·1736 (9)	0·7621 (14)	−0·0668 (12)	3·2 (5)
C(5*F*)	0·1325 (9)	0·8157 (14)	0·0644 (12)	3·4 (5)
C(6*F*)	0·1187 (10)	0·8005 (14)	0·1418 (12)	3·7 (5)
C(7*F*)	0·1327 (9)	0·7204 (14)	0·1835 (12)	3·8 (5)
C(8*F*)	0·1564 (9)	0·6546 (13)	0·1394 (11)	2·7 (5)
C(9*F*)	0·1713 (8)	0·6735 (12)	0·0564 (11)	2·1 (4)
C(10*F*)	0·1570 (9)	0·7529 (15)	0·0146 (11)	2·8 (4)

* $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

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* Lists of structure factors, anisotropic thermal parameters for I, Ni, O, and N atoms, H-atom parameters, intramolecular bond distances and angles, and calculations of least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42336 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

O···O line was used in the present calculation. Tris(8-quinolinolato)metal complexes have been found so far in the cases of metal(III) such as manganese(III) (Hems & Mackay, 1975) and chromium(III) (Folting, Cox, Moore & Merritt, 1968). These complexes are monomeric and are in the meridional conformation. Consequently, the title compound is the first example of a dimeric chelated complex between 8-quinolinol and metal(II) formed by three strong hydrogen bonds. Similar dinuclear cations with hydrogen-bonding bridges were found in the crystals of $[Co_2(eta)_3(etaH)_3](ClO_4)_3.\frac{1}{2}H_2O$ and $[Ni_2(eta)_2(etaH)_4](ClO_4)_2$ (where etaH represents 2-aminoethanol and eta the anion formed by removing the proton from 2-aminoethanol) (Bertrand, Eller, Fujita, Lively & Van Derveer, 1979).

In the counteranion the two I—I bond distances are 2·921 (3) and 2·897 (3) Å and the I—I—I angle is 176·9 (1)°, indicating the presence of almost symmetrical triiodide ions. Furthermore, the thermal ellipsoid of the central I(2) atom is not significantly different from those of the end I(1) and I(3) atoms in both size and shape. Therefore, the nearly symmetric appearance of the I_3^- ion is unlikely to be due to the disorder of asymmetric units. Thus, the $[Ni_2\{H(C_9H_6NO)_2\}_3]^+$ cations and I_3^- anions are in the alternate arrangement analogous to the NaCl structure. Some intermolecular I···H distances are slightly less than the sum of the van der Waals radii of 3·15 Å (Bondi, 1964), suggesting weak interaction due to C—H···I hydrogen bonds. For example, the minimum distances are 3·05 Å for I(1)···H(6*B*), 3·03 Å for I(2)—H(2*C*) and 2·92 Å for I(3)···H(2*A*). Such an environment may cause the triiodide ions to be almost symmetric without any requirement being imposed by the crystal symmetry.

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Table 2. *Selected interatomic distances* (Å) *and angles* (°)

I(1)–I(2)	2·921 (3)	I(2)–I(3)	2·897 (3)
Ni(1)–N(1A)	2·05 (2)	Ni(1)–N(1B)	2·03 (2)
Ni(1)–N(1C)	2·10 (2)	Ni(1)–O(8A)	2·01 (1)
Ni(1)–O(8B)	2·13 (1)	Ni(1)–O(8C)	2·06 (1)
Ni(2)–N(1D)	2·09 (2)	Ni(2)–N(1E)	2·04 (2)
Ni(2)–N(1F)	2·07 (2)	Ni(2)–O(8D)	2·01 (1)
Ni(2)–O(8E)	2·11 (1)	Ni(2)–O(8F)	2·08 (1)
O(8A)–C(8A)	1·35 (2)	O(8B)–C(8B)	1·35 (2)
O(8C)–C(8C)	1·34 (2)	O(8D)–C(8D)	1·38 (2)
O(8E)–C(8E)	1·35 (2)	O(8F)–C(8F)	1·33 (2)
O(8A)–O(8D)	2·41 (2)	O(8B)–O(8F)	2·47 (2)
O(8C)–O(8E)	2·47 (2)		
I(1)–I(2)–I(3)	176·9 (1)		
N(1A)–Ni(1)–N(1B)	102·9 (6)	N(1A)–Ni(1)–N(1C)	96·9 (6)
N(1A)–Ni(1)–O(8A)	79·2 (5)	N(1A)–Ni(1)–O(8B)	169·6 (5)
N(1A)–Ni(1)–O(8C)	91·2 (5)	N(1B)–Ni(1)–N(1C)	97·3 (6)
N(1B)–N(i(1)–O(8A)	93·5 (5)	N(1B)–Ni(1)–O(8B)	79·2 (5)
N(1B)–Ni(1)–O(8C)	165·8 (5)	N(1C)–Ni(1)–O(8A)	169·1 (5)
N(1C)–Ni(1)–O(8B)	92·9 (5)	N(1C) Ni(1) O(8C)	79·2 (5)
O(8A)–Ni(1)–O(8B)	90·6 (5)	O(8A)–Ni(1)–O(8C)	90·6 (5)
O(8B)–Ni(1)–O(8C)	87·2 (5)	N(1D)–Ni(2)–N(1E)	97·8 (6)
N(1D)–Ni(2)–N(1F)	95·3 (6)	N(1D)–Ni(2)–O(8D)	79·5 (5)
N(1D)–Ni(2)–O(8E)	172·9 (5)	N(1D)–Ni(2)–O(8F)	94·4 (5)
N(1E)–Ni(2)–N(1F)	98·7 (6)	N(1E)–Ni(2)–O(8D)	94·3 (5)
N(1E)–Ni(2)–O(8E)	79·6 (5)	N(1E)–Ni(2)–O(8F)	167·8 (5)
N(1F)–Ni(2)–O(8D)	166·6 (5)	N(1F)–Ni(2)–O(8E)	91·6 (5)
N(1F)–Ni(2)–O(8F)	79·2 (5)	O(8D)–Ni(2)–O(8E)	94·1 (5)
O(8D)–Ni(2)–O(8F)	88·8 (5)	O(8E)–Ni(2)–O(8F)	88·4 (4)
Ni(1)–O(8A)–O(8D)	120·3 (6)	Ni(1)–O(8A)–C(8A)	111·2 (10)
O(8D)–O(8A)–C(8A)	117·8 (11)	Ni(1)–O(8B)–O(8F)	124·7 (6)
Ni(1)–O(8B)–C(8B)	109·7 (10)	O(8F)–O(8B)–C(8B)	117·1 (10)
Ni(1)–O(8C)–O(8E)	115·7 (6)	Ni(1)–O(8C)–C(8C)	113·5 (11)
O(8E)–O(8C)–C(8C)	126·8 (11)	Ni(2)–O(8D)–O(8A)	117·7 (6)
Ni(2)–O(8D)–C(8D)	112·2 (10)	O(8A)–O(8D)–C(8D)	124·2 (11)
Ni(2)–O(8E)–O(8C)	124·0 (6)	Ni(2)–O(8E)–C(8E)	113·8 (10)
O(8C)–O(8E)–C(8E)	114·6 (10)	Ni(2)–O(8F)–O(8B)	114·8 (6)
Ni(2)–O(8F)–C(8F)	114·9 (11)	O(8B)–O(8F)–C(8F)	125·1 (11)

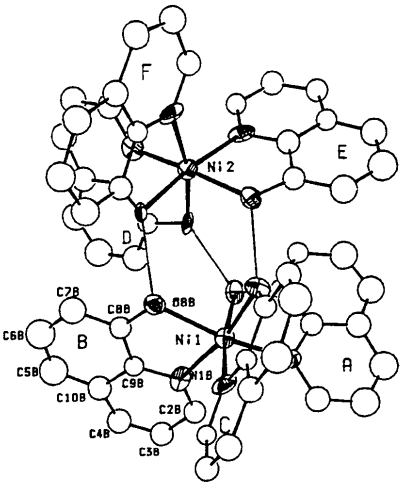

Fig. 1. *ORTEP* drawing (Johnson, 1976) of the $[Ni_2\{H(C_9H_6NO)_2\}_3]^+$ cation. Thermal ellipsoids are shown at the 50% probability level.

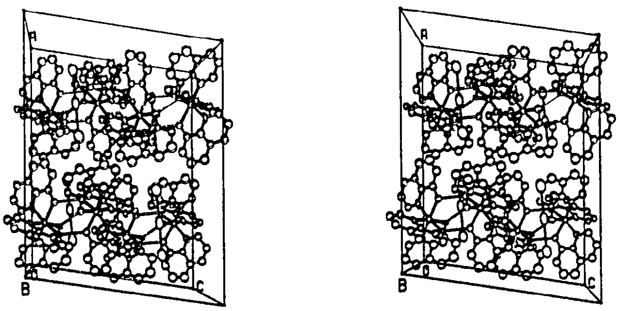

Fig. 2. Stereoscopic drawing of the crystal structure viewed along the *b* axis.

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Structure of $(Ph_3P)_2Pt(\mu_2\text{-}CS_2)W(CO)_5$

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Abstract. Bis(triphenylphosphine)platinum-{μ-[(*C*,*S*-η)-carbon disulfide-*S'*]}-pentacarbonyltungsten, $C_{42}H_{30}O_5P_2PtS_2W$, $M_r = 1119{\cdot}75$, monoclinic, $P2_1/n$, $a = 14{\cdot}572\,(1)$, $b = 15{\cdot}244\,(2)$, $c = 18{\cdot}897\,(2)$ Å, $\beta = 96{\cdot}663\,(7)°$, $V = 4169{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}78$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 6{\cdot}1$ mm^{-1}, $F(000) = 1904$, $T = 296$ K, $R = 0{\cdot}046$ for 2628 unique reflections. The dinuclear complex $(Ph_3P)_2Pt(\mu_2\text{-}CS_2)W(CO)_5$ consists of a distorted square-planar $(Ph_3P)_2Pt(\eta^2\text{-}CS_2)$ fragment in which a CS_2 ligand is π-bonded through a C=S linkage to a Pt atom, with the second, *exo*-S atom σ-bonded to a W atom. The non-bonded Pt—W distance is 5·55 (1) Å. The W coordination sphere is pseudo-octahedral containing a σ-bonded S atom and five CO ligands.

Introduction. One approach to building organometallic clusters involves the interacton of a metal fragment with the CS_2 moiety of a metal—CS_2 compound which induces fragmentation of the CS_2 ligand to give S and CS ligands. Only a few examples of this behaviour have been cited in the literature; these include (dppe)Pt(μ_2-S)Pt(CS)(PPh$_3$) (Hawling, Walker & Woitzik, 1983) [dppe = bis(1,2-diphenylphosphino)ethane], $(CoCp)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ (Werner & Leonhard, 1979) and $Fe_4(CO)_{12}(\mu_4\text{-}CS)(\mu_3\text{-}S)$ (Broadhurst, Johnson, Lewis & Raithby, 1980). The complex $Pt_2(\mu_2\text{-}CS_2)(PBu_2Ph)_2$, which contains a bridging CS_2 ligand without a metal—metal bond, is stable towards this type of fragmentation of the CS_2 ligand (Farrar, Gukathasan & Morris, 1984). We have found that the title complex, $(Ph_3P)_2Pt(\mu_2\text{-}CS_2)W(CO)_5$ (1), does not undergo this metal-assisted CS_2 fragmentation which is consistent with our belief that the CS_2 ligand must bridge a metal—metal bond before fragmentation can occur. The complex (1) does not exhibit (Fehlhammer, Mayr & Stolzenberg, 1979; Fehlhammer & Stolzenberg, 1980) all of the characteristic IR frequencies normally associated with the bridging CS_2 ligand (Farrar, Gukathasan & Won, 1984) which led us to confirm the structure by a single-crystal X-ray analysis.

Experimental. (1) was prepared by the reaction of $W(CO)_5(THF)$ and $(Ph_3P)_2Pt(\eta^2\text{-}CS_2)$ following the reported method (Fehlhammer & Stolzenberg, 1980). Yellow crystals were obtained by slow evaporation of an ether/hexane solution. Data collection: crystal $0{\cdot}01 \times 0{\cdot}19 \times 0{\cdot}20$ mm; Enraf–Nonius CAD-4 diffractometer; cell parameters from 24 reflections at $22 < 2\theta < 27°$; 4725 unique reflections with $1 < 2\theta < 45°$ (*hkl* range: *h* 0–15, *k* 0–16, *l* −20–20); three standard reflections checked every 4 h (200, 040, 002), intensity variation 0·02%. Data reduction: Enraf–Nonius structure determination package, *SDP-PLUS* version 4–0; Gaussian absorption correction with crystal bounded by the planes (101), ($\bar{1}01$), ($10\bar{1}$), ($\bar{1}0\bar{1}$), ($0\bar{1}0$) and ($13\bar{1}$), relative transmission factors 0·3926 to 0·9024. Structure solution and refinement: solved by automatic direct methods and difference Fourier syntheses using *SHELX*76 (Sheldrick, 1976); full-matrix refinement on *F*; $w^{-1} = \sigma^2(F) + 0{\cdot}0003F^2$; 2628 unique reflections with $F > 6\sigma(F)$; phenyl groups as rigid hexagons with C—C 1·395, C—H 0·95 Å on external C—C—C angle bisectors; anisotropic thermal parameters for Pt, W, S, P and O atoms; scattering factors from *International Tables for X-ray Crystallography* (1974); 196 parameters, $R = 0{\cdot}046$, $wR = 0{\cdot}042$, $(\Delta/\sigma)_{\max} = 0{\cdot}02$; largest peak in final difference map 0·84 e Å^{-3} [associated with W—C(4)]; no correction for secondary extinction.

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