Table 3. *Structural comparisons with oxo-peroxocyanomolybdates*(VI)

	Mo distances (Å) to				
Compound	Equatorial plane	Oxygen oxo	Ligand *trans*/oxo	Carbon *trans*/peroxo	Carbon *cis*
(2)	0·270 (1)	1·694 (3)	2·197 (4)	2·167 (5)	2·175 (4)–2·291 (4)
(3)	0·268 (6)	1·629 (7)	2·19 (1)	2·26 (1)	2·21 (1)–2·31 (1)
(5)	0·213 (4)	1·638 (7)	2·162 (6)*	2·082 (8)	2·191 (1)–2·173 (9)

* O atom linked to hmpa ligand.

compound (5): $[Mo(O)(O_2)(CN)_3hmpa]$ $[PPh_3CH_2Ph]$ (Arzoumanian *et al.*, 1988).

In all cases the Mo atom is out of the equatorial plane (see Table 3). However, the scattering of the Mo—C_{cis} distances does not allow us to distinguish any *trans* effect on the Mo—*L* distances due to the oxygen 'oxo' atom.

Crystals of the title compound are composed of individual entities: one $[Mo(CN)_4(O)(ONPhCH_3)]^{2-}$ anion for two $[PPh_4]^+$ cations which are packed without any remarkable features. Bond distances and angles found in the $[PPh_4]^+$ cations are given in the deposited material.

The general character of the reaction given in the scheme as well as the use of these compounds, considered as metaloxoaziridines, in the synthesis of allylic amines or organic aziridines is presently under investigation.

References

Arzoumanian, H., Petrignani, J. F., Pierrot, M., Ridouane, F. & Sanchez, J. (1988). *Inorg. Chem.* **27**, 3377–3381.

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

Hughes, M. N. (1981). *The Inorganic Chemistry of Biological Processes*, 2nd ed. New York: John Wiley.

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

Liebeskind, L. S., Sharpless K. B., Wilson, R. D. & Ibers, J. A. (1978). *J. Am. Chem. Soc.* **100**, 7061–7063.

Muccigrosso, D. A., Jacobson, S. E., Apgar, P. A. & Mares, F. (1978). *J. Am. Chem. Soc.* **100**, 7063–1965.

Murphy, W. R., Takenchi, K., Barley, M. H. & Meyer, T. H. (1986). *Inorg. Chem.* **25**, 1041–1053.

Sellmann, D., Seubert, B., Moll, M. & Knoch, F. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 1164–1165.

Ullmann's Encyklopädie der Technischen Chemie (1981). Vol. 6, 4th ed., p.172. Weinheim: Verlag Chemie.

Wieghardt, K. (1984). *Adv. Inorg. Bioinorg. Mech.* **3**, 213–239, and references therein.

Wieghardt, K. & Holzbach, W. (1979). *Angew. Chem. Int. Ed. Engl.* **18**, 549–549.

Wieghardt, K. & Quilitzsch, U. (1981). *Z. Naturforsch.* **36**, 683–686.

Acta Cryst. (1990). C**46**, 1410–1414

μ-(η^5:η^5-Pentamethylcyclopentadienyl)-bis[(η^5-pentamethylcyclopentadienyl-ruthenium(II)] Hexafluorophosphate (1) and [2(η^5)-Cyclopentadienyl]-μ-[1(η^5):2(η^5)-pentamethylcyclopentadienyl]-[1(η^5)-pentamethylcyclopentadienyl]-osmium(II)ruthenium(II) Hexafluorophosphate (2)

By Paavo O. Lumme* and Urho Turpeinen

Department of Inorganic Chemistry, University of Helsinki, Vuorik. 20, *SF*-00100 *Helsinki, Finland*

and A. R. Kudinov and M. I. Rybinskaya

A. N. Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences, Vavilov St 28,
117813 *Moscow, USSR*

(*Received* 4 *July* 1988; *accepted* 21 *November* 1989)

Abstract. (1) $[Ru_2(C_{10}H_{15})_3]PF_6$, $M_r = 752\cdot80$, monoclinic, Cm, $a = 18\cdot855$ (4), $b = 8\cdot792$ (3), $c = 10\cdot494$ (3) Å, $\beta = 113\cdot64$ (2)°, $V = 1593\cdot7$ (8) Å^3, $Z = 2$, $D_m = 1\cdot567$, $D_x = 1\cdot569$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10\cdot33$ cm^{-1}, $F(000) = 764$, $T = 295$ (1) K, $R = 0\cdot062$ for 1442 unique reflections with

---

* To whom all correspondence should be addressed.

0108-2701/90/081410-05$03.00

$I > 3\sigma(I)$; (2) $[\mathrm{OsRu(C_5H_5)(C_{10}H_{15})_2}]\mathrm{PF_6}$, M_r = 771·79, orthorhombic, $Pnma$, a = 21·384 (4), b = 14·901 (4), c = 8·573 (3) Å, V = 2732 (1) Å^3, Z = 4, D_m = 1·875, D_x = 1·876 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 55·77 cm^{-1}, F(000) = 1496, T = 295 (1) K, R = 0·066 for 2227 unique reflections with $I > 3\sigma(I)$. Both compounds contain a univalent triple-decker-sandwich cation and a hexafluorophosphate anion. In (1) the distances Ru(1)—C(1,2,3), Ru(1)—C(7,8,9), Ru(2)—C(7,8,9) and Ru(2)—C(13,14,15) are 2·15 (1)–2·20 (1), 2·18 (1)–2·20 (1), 2·20 (1)–2·23 (1) and 2·09 (2)–2·21 (2) Å, respectively. In (2) the distances Ru—C(13,14,15), Ru—C(1,2,3), Os—C(1,2,3) and Os—C(7,8,9) are 2·12 (1)–2·21 (2), 2·16 (1)–2·20 (1), 2·15 (1)–2·18 (1) and 2·17 (1)–2·19 (1) Å, respectively. Therefore the triple-decker-sandwich structures of the complexes are in general equally compact. In (1) the third pentamethylcyclopentadienyl ligand is perfectly staggered with respect to the other two. In both structures the cations and anions form discrete units and there exists some hydrogen bonding but the structures are held together mainly through van der Waals forces.

Introduction. The first so-called 34 electron triple-decker-sandwich complex, tris(η-cyclopentadienyl)-dinickel tetrafluoroborate was prepared in 1972 (Werner & Salzer, 1972; Salzer & Werner, 1972) and its crystal structure determined later (Dubler, Textor, Oswald & Salzer, 1974; Dubler, Textor, Oswald & Jameson, 1983). Later quantum-chemical considerations indicated that 30 electron triple-decker-sandwich complexes would also be stable and possible to synthesize (Lauher, Elian, Summerville & Hoffmann, 1976). Recently the first complex of this type for the chromium group metals, μ-(η^6:η^6-mesitylene)-bis(η^6-mesitylene)-dichromium, was synthesized by the co-condensation method (Lamanna, 1986) and its X-ray structure determined (Lamanna & Gleason, 1987). At the same time also the first 30 electron triple-decker-sandwich complexes of the iron group metals were synthesized (Kudinov, Rybinskaya, Struchkov, Yanovskii & Petrovskii, 1987). The X-ray structures of two of these complexes (the title compounds) have now been determined and are described below.

Experimental. Yellow crystals of (1) and orange-red crystals of (2) were stable in air. Crystals of size 0·1 × 0·15 × 0·15 (1) (plate like) and 0·1 × 0·2 × 0·2 (2) mm (needle like) were used for collecting intensities on a Nicolet $P3F$ automatic diffractometer with graphite-monochromated radiation, using the ω–2θ technique with the 2θ scan rate varying from 2·0 to 29·3° min^{-1}, depending on the number of counts measured in a fast preliminary scan through the peak. The unit-cell parameters were determined by least-squares treatment of the adjusted angular setting of 18 (2θ = 6·07–21·98°) (1) and 17 (2θ = 6·66–22·96°) (2) reflections. Sets of 1861 (1) and 3077 (2) unique reflections were obtained from the 1907 (1) and 3374 (2) reflections measured within $4 \leq 2\theta \leq 54°$, respectively [h 0, 25; k 0, 12; l −14, 14 for (1) and h 0, 28; k 0, 20; l 0, 11 for (2)]. 1442 (1) and 2227 (2) reflections with $I > 3\sigma(I)$ were considered as observed and used in the refinement. Two [020, 40$\bar{2}$ for (1) and 022, 152 for (2)] strong reflections monitored periodically after 98 reflections exhibited no significant variation of the intensity. The intensities were corrected for Lorentz and polarization effects and for absorption (through the φ-scan technique) with maximum transmission factors 1·000 for both and minimum 0·789 (1) and 0·650 (2), but corrections for extinction were considered unnecessary.

The structures of (1) and (2) were solved for the metal atoms by the Patterson method and developed through successive Fourier syntheses. The refinements were based on F values. With anisotropic temperature factors for the metal atoms, a difference map calculated after full-matrix refinement revealed the positions of the other heavy atoms. Full-matrix least-squares refinement with metal, P and F atoms anisotropic and all C atoms isotropic and the cyclopentadienyl rings as fixed groups led after 5 cycles to R = 0·062 for (1) and 0·066 for (2), and wR = 0·057 for (1) and 0·063 for (2), where $w = 1{\cdot}6132/\sigma^2(F)$ for (1) and $0{\cdot}9750/\sigma^2(F)$ for (2). After the last cycle $(\Delta/\sigma)_{\min}$ = −0·505 for (1) and −0·588 for (2), and $(\Delta/\sigma)_{\max}$ = 0·463 for (1) and 0·202 for (2), respectively. Maximum and minimum heights in final difference Fourier syntheses were 1·78 and −0·75 for (1) and 3·07 (near Os) and −3·01 e Å^{-3} for (2), respectively.

Scattering factors were from Cromer & Mann (1968) and the anomalous-dispersion correction was applied (*International Tables for X-ray Crystallography*, 1974). All calculations were performed on a VAX 8650 computer with *SHELX*76 (Sheldrick, 1976), *SHELXS*86 (Sheldrick, 1986), *XTAL*83 crystallographic programs (Stewart & Hall, 1983) and *MPLN* (Truter & Vickery, 1973). Densities of the crystals were determined by the flotation method in $\mathrm{CHCl_3}$–$\mathrm{CCl_4}$ (1) and $\mathrm{CH_3I}$–$\mathrm{CCl_4}$ (2) mixtures, respectively. The final atomic parameters are given in Table 1.*

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52803 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3) (*Hamilton,* 1959) *for non*-H *atoms with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}*
Compound (1)				
Ru(1)	0	0	0	28 (3)
Ru(2)	−1861 (1)	0	−3047 (2)	25 (3)
C(1)	1207 (8)	806	849 (15)	30 (4)
C(2)	815 (8)	1307	1683 (15)	33 (4)
C(3)	602 (8)	0	2243 (15)	33 (4)
C(4)	1550 (12)	2110 (25)	338 (21)	53 (5)
C(5)	750 (12)	3071 (28)	1845 (23)	60 (6)
C(6)	202 (15)	0	3336 (28)	48 (7)
C(7)	−1194 (6)	806	−916 (11)	30 (2)
C(8)	−809 (6)	1307	−1761 (11)	31 (2)
C(9)	−575 (6)	0	−2288 (11)	17 (2)
C(10)	−1521 (18)	2074 (39)	−176 (33)	117 (10)
C(11)	−642 (20)	3020 (44)	−2024 (36)	137 (12)
C(12)	−125 (24)	0	−3231 (45)	100 (13)
C(13)	−2995 (10)	806	−4004 (19)	56 (6)
C(14)	−2625 (10)	1307	−4888 (19)	60 (6)
C(15)	−2300 (10)	0	−5244 (19)	56 (6)
C(16)	−3474 (12)	1533 (26)	−3122 (22)	55 (6)
C(17)	−2446 (10)	2851 (21)	−5237 (18)	37 (4)
C(18)	−1811 (10)	0	−6118 (19)	92 (6)
P	4081 (18)	0	3500 (32)	62 (4)
F(1)	5042 (20)	0	4298 (33)	124 (26)
F(2)	3242 (16)	0	3169 (32)	90 (20)
F(3)	4043 (15)	0	1941 (24)	73 (16)
F(4)	4027 (37)	0	4919 (57)	249 (60)
F(5)	3922 (20)	1741 (15)	3272 (42)	148 (20)
Compound (2)				
Ru	484 (1)	2500	114 (3)	47 (1)
Os	2172	2500	466 (1)	35 (1)
C(1)	1372 (4)	2023	−876 (12)	47 (3)
C(2)	1310 (4)	1729	692 (12)	48 (3)
C(3)	1288 (4)	2500	1664 (12)	49 (3)
C(4)	1400 (11)	3589 (15)	−2376 (29)	92 (7)
C(5)	1294 (10)	706 (15)	1362 (28)	92 (7)
C(6)	1211 (14)	2500	3459 (37)	77 (9)
C(7)	3063 (5)	2023	−481 (17)	58 (3)
C(8)	3005 (5)	1729	1088 (17)	87 (3)
C(9)	2962 (5)	2500	2055 (17)	92 (3)
C(10)	3178 (11)	1415 (16)	−1897 (28)	99 (8)
C(11)	3049 (15)	806 (23)	1840 (41)	156 (13)
C(12)	2891 (5)	2500	3842 (17)	109 (3)
C(13)	−316 (6)	2500	−1527 (22)	110 (5)
C(14)	−349 (6)	3271	−557 (22)	94 (5)
C(15)	−377 (6)	2976	1017 (22)	109 (5)
P	0	0	5000	64 (5)
F(1)	700 (7)	212 (16)	4787 (21)	171 (16)
F(2)	97 (9)	−18 (13)	6822 (16)	166 (15)
F(3)	124 (13)	−1021 (11)	4950 (28)	212 (21)

* For all C atoms of (1) and (2) $U_{eq} = U_{iso}$.

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

(1)			
Ru(1)-Ru(2)	3·679 (7)	C(1)—C(4)	1·52 (3)
Ru(1)—C(1)	2·20 (1)	C(2)—C(5)	1·57 (2)
Ru(1)—C(2)	2·15 (1)	C(3)—C(6)	1·61 (4)
Ru(1)—C(3)	2·17 (1)	C(7)—C(10)	1·62 (4)
Ru(1)—C(7)	2·18 (1)	C(8)—C(11)	1·59 (4)
Ru(1)—C(8)	2·19 (1)	C(9)—C(12)	1·54 (6)
Ru(1)—C(9)	2·20 (1)	C(13)—C(16)	1·66 (3)
Ru(2)—C(7)	2·20 (1)	C(14)—C(17)	1·48 (2)
Ru(2)—C(8)	2·22 (1)	P—F(1)	1·66 (5)
Ru(2)—C(9)	2·23 (1)	P—F(2)	1·48 (5)
Ru(2)—C(13)	2·09 (2)	P—F(3)	1·61 (4)
Ru(2)—C(14)	2·21 (1)	P—F(4)	1·53 (8)
Ru(2)—C(15)	2·11 (2)	P—F(5)	1·56 (1)
(2)			
Ru–Os	3·622 (4)	Os—C(8)	2·19 (1)
Ru—C(15)	2·12 (1)	Os—C(9)	2·17 (1)
Ru—C(14)	2·20 (1)	C(1)—C(4)	1·58 (3)
Ru—C(13)	2·21 (2)	C(2)—C(5)	1·63 (2)
Ru—C(1)	2·20 (1)	C(3)—C(6)	1·55 (3)
Ru—C(2)	2·16 (1)	C(7)—C(10)	1·54 (3)
Ru—C(3)	2·17 (1)	C(8)—C(11)	1·52 (3)
Os—C(1)	2·18 (1)	P—F(1)	1·54 (1)
Os—C(2)	2·18 (1)	P—F(2)	1·58 (1)
Os—C(3)	2·15 (1)	P—F(3)	1·54 (2)
Os—C(7)	2·19 (1)		
(1)			
C(1)—C(2)—C(5)	117 (1)	F(1)—P—F(2)	165 (3)
C(2)—C(1)—C(4)	113 (1)	F(1)—P—F(3)	96 (3)
C(2)—C(3)—C(6)	126 (1)	F(1)—P—F(4)	90 (3)
C(7)—C(8)—C(11)	126 (2)	F(1)—P—F(5)	100 (2)
C(8)—C(7)—C(10)	118 (1)	F(2)—P—F(3)	99 (3)
C(8)—C(9)—C(12)	126 (1)	F(2)—P—F(4)	75 (3)
C(13)—C(14)—C(17)	131 (1)	F(2)—P—F(5)	81 (2)
C(14)—C(13)—C(16)	139 (1)	F(3)—P—F(4)	174 (3)
C(14)—C(15)—C(18)	126 (1)	F(3)—P—F(5)	85 (2)
C(15)—C(14)—C(17)	121 (2)	F(4)—P—F(5)	94 (2)
(2)			
C(1)—C(2^{i})—C(5^{i})	129 (1)	C(8^{i})—C(9)—C(12)	126 (1)
C(2^{i})—C(1)—C(4)	127 (1)	C(9)—C(8^{i})—C(11^{i})	119 (2)
C(2^{i})—C(3)—C(6)	126 (1)	F(1)—P—F(3)	92 (1)
C(7)—C(8)—C(11)	133 (1)	F(1)—P—F(2)	90 (1)
C(8)—C(7)—C(10)	126 (1)	F(2)—P—F(3)	89 (1)

Symmetry code for (2): (i) x, $-y + 0·5$, z.

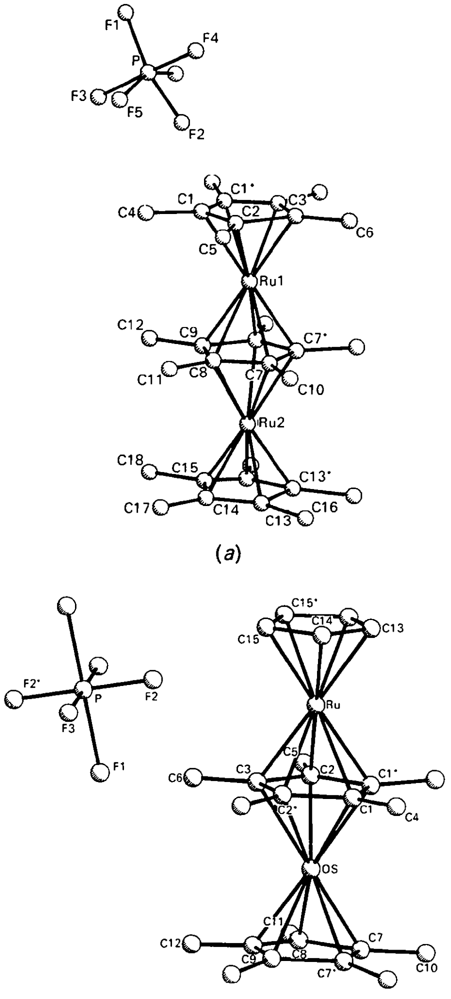
Discussion. Fig. 1 shows the *PLUTO* drawings (Motherwell & Clegg, 1978) of both complexes (1) and (2) with the atom numbering. (1) has two and (2) has four molecules in the unit cell. Selected bond lengths and angles for non-H atoms are listed in Table 2.

Both complex cations have a triple-decker-sandwich structure in which one of the pentamethylcyclopentadienyl ligands is bridging between the metal atoms. In (2) the cyclopentadienyl ligand bonds to the Ru atom (Fig. 1). In (1) the distances of the Ru(1) and Ru(2) atoms from the mean planes of the outer and bridging ligand rings are 1·803 (5) and 1·826 (4), and 1·769 (7) and 1·853 (5) Å, respectively. In (2) the distances of the Ru and Os atoms from the mean planes of the outer and bridging ligand rings are 1·799 (6) and 1·812 (4), and 1·821 (5) and 1·810 (4) Å, respectively. Therefore the cations are practically equally compact. The Ru–Ru distance is 3·679 (7) Å in (1) and the Ru–Os distance is 3·622 (4) Å in (2). Therefore, there is probably no or very weak interaction between the metal atoms in the cations.

In both compounds the hexafluorophosphate ion is structurally normal, the P—F distances varying between 1·48 (5) and 1·66 (5) Å and the F—P—F angles between 75 (3) and 100 (2)° (Table 2). The anions form columns in the **b** directions in both structures (Fig. 2). The crystal structures are shown in Fig. 2. There are several contacts C(—H)···F less than or near the sum (3·35 Å) of the van der Waals radii (Taylor & Kennard, 1982) in both crystal structures. In (1) the relevant distances are: C(17^{i})···F(2) = 3·13 (4), C(10^{i})···F(3) = 3·28 (4), C(16)···F(1) = 3·30 (3), C(17^{i})···F(4) = 3·31 (6) and C(18^{i})···F(5) = 3·35 (3) Å [symmetry code: (i) $x + 0·5$, $y + 0·5$, z]. In (2) they are: C(5)···F(1) = 3·28 (3) and C(4^{i})···F(1) = 3·37 (3) Å [symmetry code: (i) x, $-y + 0·5$, z]. Thus both complexes have one intramolecular hydrogen bond and four (1) or one (2) intermolecular hydrogen bonds. Therefore the hydrogen-bond formation partly stabilizes the crystal structures along with van der Waals forces.

There is interesting similarity between the structures of the two compounds. In (1), the third pentamethylcyclopentadienyl ring is perfectly staggered with respect to the two others due to the crystallographic mirror plane. In (2) the cyclopentadienyl ring is staggered on the Ru-atom side. Therefore the methyl substitution in the cyclopentadienyl ring does not change the orientation.

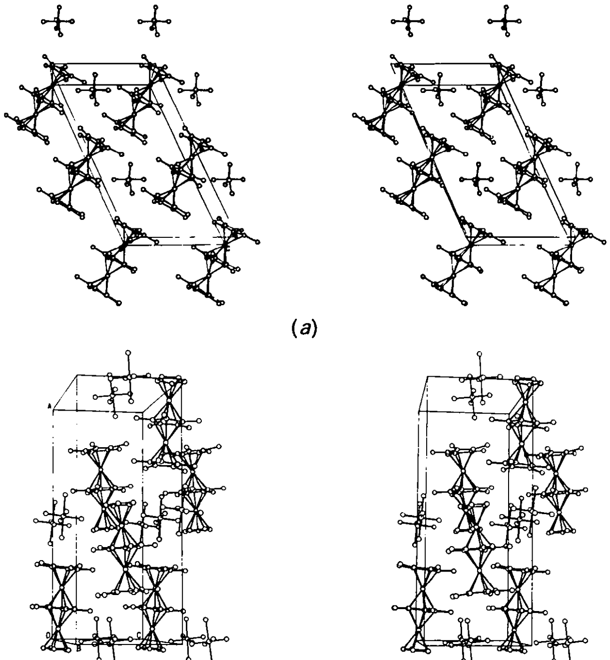
The second interesting feature is that in (1) the P atom and four of the F atoms lie in the mirror plane, whereas in (2) the P atom lies on a symmetry centre. In both structures the metal atoms lie in the mirror plane.



(*a*)

(*b*)

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawings with atomic numbering. (*a*) Compound (1); (*b*) compound (2).



(*a*)

(*b*)

Fig. 2. Stereoscopic views of the crystal structures down **b**. (*a*) Compound (1); (*b*) compound (2).

Table 3. *Stereochemistry of some iron group metal sandwich complexes; mean distances* (Å) *with e.s.d.'s in parentheses*

	Space group	*M*—(ring plane)	*M*—C	C—C (ring)	Reference
$[\mathrm{Fe^{II}}(\eta^5\text{-}\mathrm{C_5H_5})_2]$	$P2_1/a$	1·648	2·046 (3)	1·426 (3)	(*a*)
$[\mathrm{Ru^{II}}(\eta^5\text{-}\mathrm{C_5H_5})_2]$	*Pnma*	–	2·191	1·441	(*b*)
$[\mathrm{Ru^{II}}(\eta^5\text{-}\mathrm{C_5Me_5})_2]$	$P2_1/m$	1·80 (1)	2·17 (1)	1·43 (1)	(*c*)
$[\mathrm{Os^{II}}(\eta^5\text{-}\mathrm{C_5Me_5})_2]$	$P2_1/m$	1·81 (1)	2·18 (1)	1·43 (1)	(*c*)
$[\mathrm{Ru^{II}}_2(\eta^5\text{-}\mathrm{C_5Me_5})_2\text{-}(\mu\text{-}\eta^5{:}\eta^5\text{-}\mathrm{C_5Me_5})]^+$	*Cm*	1·813 (5)	2·18 (1)	1·42	(*d*)
$[\mathrm{Ru^{II}}(\eta^5\text{-}\mathrm{C_5H_5})(\mu\text{-}\eta^5{:}\text{-}\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Os^{II}}(\eta^5\text{-}\mathrm{C_5Me_5})]^+$	*Pnma*	1·806 (5)(Ru) 1·817 (5)(Os)	2·18 (1) 2·18 (1)	1·42 1·42	(*d*) (*d*)

References: (*a*) Seiler & Dunitz (1979*a*,*b*); (*b*) Seiler & Dunitz (1980); (*c*) Albers *et al.* (1986); (*d*) present work.

Comparison of the stereochemistry of the present triple-decker complexes and known ferrocene, ruthenocene, decamethylruthenocene and decamethylosmocene sandwich complexes in Table 3 shows that the bond distances in ferrocene differ from those of the Ru, Os complexes which are comparable. The difference must lie in the metal-ion size and complex stability.

References

Albers, M. O., Liles, D. C., Robinson, D. J., Shaver, A., Singleton, E., Wiege, M. B., Boeyens, J. C. A. & Leoendis, D. C. (1986). *Organometallics*, **5**, 2321–2327.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
Dubler, E., Textor, M., Oswald, H. R. & Jameson, G. B. (1983). *Acta Cryst.* **B39**, 607–612.
Dubler, E., Textor, M., Oswald, H. R. & Salzer, A. (1974). *Angew. Chem.* **86**, 125.
Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Kudinov, A. R., Rybinskaya, M. I., Struchkov, Yu. T., Yanovskii, A. I. & Petrovskii, P. V. (1987). *J. Organomet. Chem.* **336**, 187–197.
Lamanna, W. M. (1986). *J. Am. Chem. Soc.* **108**, 2096–2097.
Lamanna, W. M. & Gleason, W. B. (1987). *Organometallics*, **6**, 1583–1584.
Lauher, J. W., Elian, M., Summerville, R. H. & Hoffmann, R. (1976). *J. Am. Chem. Soc.* **98**, 3219–3224.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
Salzer, A. & Werner, H. (1972). *Angew. Chem. Int. Ed. Engl.* **11**, 930–931.
Seiler, P. & Dunitz, J. D. (1979*a*). *Acta Cryst.* **B35**, 1068–1074.
Seiler, P. & Dunitz, J. D. (1979*b*). *Acta Cryst.* **B35**, 2020–2032.
Seiler, P. & Dunitz, J. D. (1980). *Acta Cryst.* **B36**, 2946–2950.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Sheldrick, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.
Stewart, J. M. & Hall, S. R. (1983). Editors. *The XTAL System of Crystallographic Programs*. Tech. Rep. TR-1364. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
Truter, M. R. & Vickery, B. L. (1973). *J. Appl. Cryst.* **6**, 323; Program No. 124.
Werner, H. & Salzer, A. (1972). *Synth. Inorg. Met. Org. Chem.* **2**, 239–248.

Acta Cryst. (1990). **C46**, 1414–1416

Structure of Triaqua[*N*-(5-bromosalicylidene)-L-tryptophanato]nickel(II) Dihydrate

By M. L. Rodríguez, C. Ruiz-Pérez and F. V. Rodríguez-Romero

Centro de Productos Naturales Orgánicos 'Antonio González', Universidad de La Laguna-CSIC, Carretera de La Esperanza 2, 38206 *La Laguna, Tenerife, Spain*

and M. S. Palacios and P. Martín-Zarza

Departamento de Química Inorgánica Universidad de La Laguna, La Laguna, Tenerife, Spain

(*Received* 8 *May* 1989; *accepted* 21 *November* 1989)

Abstract. $[Ni(C_{18}H_{13}BrN_2O_3)(H_2O)_3].2H_2O$, $M_r = 534{\cdot}0$, monoclinic, $P2_1$, $a = 7{\cdot}379\,(1)$, $b = 7{\cdot}636\,(1)$, $c = 19{\cdot}981\,(3)$ Å, $\beta = 99{\cdot}29\,(1)°$, $V = 1111{\cdot}1\,(2)$ Å^3, $D_x = 1{\cdot}59$ g cm^{-3}, $Z = 2$, $F(000) = 544$, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 37{\cdot}7$ cm^{-1}, room temperature. Final $R = 0{\cdot}051$, $wR = 0{\cdot}050$ for 1811 observed reflections. The structure consists of discrete molecules of the complex, with the Ni^{II} ion octahedrally coordinated to one terdentate Schiff-base moiety and three water molecules; there are two additional non-coordinated water molecules in the asymmetric unit. The crystal structure is supported by a network of hydrogen bonds, involving water molecules and the phenolic and carboxylic O atoms.

Introduction. The magnetic properties of complexes of *N*-salicylidene-L-amino acids with transition-metal ions have been extensively investigated by variable-temperature magnetic susceptibility measurements and ESR spectroscopy. These compounds exhibit a wide range of magnetic and spectroscopic properties and have been described as monomers, dimers and polymers. As part of the study initiated to investigate the structural factors which cause such differences, we describe in this paper the preparation and the crystal structure determination of the nickel(II) complex with the Schiff base derived from the condensation of 5-bromosalicylaldehyde and L-tryptophan.

Experimental. All chemicals are reagent grade and were used without further purification. The title compound was prepared by the following method: a solution of the amino acid (0·05 mol) in water (100 ml) was added dropwise and with magnetic stirring to a solution obtained from 5-bromosalicylaldehyde (0·05 mol) and ethanol (400 ml). Nickel(II) acetate tetrahydrate (0·05 mol) was disolved in 200 ml water and slowly added to the Schiff-base solution, and the resulting mixture was refluxed overnight.

A green precipitate was filtered off, washed with ethanol, water and diethyl ether and air dried. The precipitate was redissolved and crystallized as dark

0108-2701/90/081414-03$03.00