Table 4. *Bond lengths* (Å) *in the two complexes compared with those in the free acid and in the formate ion*

	Cr[a]	Mo[a]	Free acid[b]	Formate ion[c]
C–O–	1·278 (1)	1·272 (2)	1·309 (2)	1·2561 (4)
C–O*t*	1·228 (1)	1·227 (1)	1·222 (2)	1·2561 (4)

References: (*a*) this work; (*b*) Nahringbauer (1978); (*c*) Fuess & Bats (1982).

identical. C—H distances range from 0·93 (2) to 1·09 (2) Å in the Cr complex and from 1·01 (4) to 1·02 (4) Å in the Mo complex.

In the hexaformato complexes, the *M*—O—C—O geometry can be characterized by (*a*) the planarity of *M*—O—C—O*t*, (*b*) its rotation about the *M*—O bond, (*c*) an in-plane deformation of the *M*—O—C angle and (*d*) whether *M*—O—C—O*t* is *sp* or *ap*. The *M*—O—C—O torsion angles are close to zero or 180°, *i.e.* the atoms are almost coplanar. The torsion angles τ = C—O—*M*—O might be expected to be 0 or 180°, *i.e.* the formate group to lie close to an O—*M*—O plane or to be about 45°, *i.e.* the plane of the formate group bisecting two O—*M*—O planes. For the Cr complex, all formates are 'bisecting', for the Mo complex two are 'bisecting' and four are 'in-plane'. In $Sr[Cu(CHO_2)_6].8H_2O$ (Baggio, de Perazzo & Polla, 1985) four are 'bisecting'. The in-plane deformation is greatest for the *sp* formate groups with *M*—O—C being 5–10° larger than for the *ap* formates.

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Structure of *trans*-Dioxo(oxoacetato)dipyridineosmium(VI)–Methanol (2:1)

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Abstract. $[OsO_2(C_2H_2O_3)(C_5H_5N)_2]_2.CH_3OH$, M_r = 940·92, monoclinic, $P2_1/n$, a = 11·014 (2), b = 16·938 (4), c = 15·343 (4) Å, β = 92·68 (2)°, V = 2859 (1) Å^3, Z = 4, D_x = 2·19 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 89·58 cm^{-1}, $F(000)$ = 1784, T = 295 K, R = 0·037, 2994 unique observed reflections. The compound was prepared by combining dipotassium tetramethylosmate(VI) with glycolic acid and

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an excess of pyridine in methanol solvent. The molecule contains a chelated oxoacetato group and two pyridine ligands bound to an osmyl group, OsO_2^{2+}. The asymmetric unit of the crystal contains two molecules of the osmium complex with a molecule of methanol hydrogen-bonded to one of them. Pyridine-ring-to-central-plane dihedral angles can be correlated with the bend angles of the osmyl groups.

Introduction. The compound was prepared as part of a larger synthetic study in which osmyl complexes are used as precursors of molecules containing osmium in reduced oxidation states. A structural issue in the study of these compounds is the extent to which the osmyl group is bent (Hinckley, Kibala & Robinson, 1987, and references quoted therein). While asymmetric coordination around the Os atom always leads to nonlinear osmyls, no correlations between the osmyl bend angles and other structural features of the complexes have been identified. This compound has provided initial indications of a relationship between osmyl bend angles and pyridine-ring orientations.

Experimental. Crystals suitable for X-ray study prepared by dissolving dipotassium tetramethylosmate(VI), obtained from 1·0 g of OsO_4, in 800 ml methanol together with 1·0 g glycolic acid and 40 ml pyridine. The dilute solution was placed in a freezer (253 K), crystals obtained after one week. Preparation details and spectroscopic characterization of the compound reported previously (Hinckley & Kibala, 1986). Crystal used for data collection 0·35 × 0·30 × 0·27 mm, reddish-brown, equant. Compound unstable in air, crystal encased in epoxy within a glass capillary. Rigaku AFC-5S diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scans, scan speed 12° min^{-1}, maximum of three scan repetitions to obtain $\sigma F/F < 0{\cdot}10$. Lattice parameters from least-squares fit of 25 strong reflections in 2θ range 30–38°. 5435 reflections measured (h −13 to 13, k 0 to 20, l 0 to 18), 399 redundant and/or systematically extinct reflections deleted, data set comprised 5036 unique reflections. 2994 reflections were considered observed ($I > 3\sigma I$), $R_{\rm int} = 1{\cdot}2\%$ for 204 equivalent reflections, $[(\sin\theta)/\lambda]_{\rm max} = 0{\cdot}60$ Å^{-1}. Three standard reflections ($2\bar{1}\bar{2}$, $0\bar{1}\bar{2}$, $10\bar{3}$) varied by −1·4, −1·1 and −2·1%, respectively; no decay correction applied. Data corrected for Lorentz, polarization and absorption (empirical ψ-scan method, six reflections, transmission range 0·67–1·0). Direct methods provided the locations of the two central OsO_4N_2 groupings. The remaining non-H atoms were found by least-squares/Fourier methods. Full-matrix least-squares refinement of F magnitudes performed on 379 variables including all non-H positional and anisotropic thermal parameters and one scale factor. Pyridine-ring, methylene, and methyl H atoms placed in geometrically correct positions (C—H = 0·95 Å) but not refined; one methyl H atom, found by difference Fourier synthesis, was used to fix the orientation of the CH_3 group. The fact that the O(1) atom of the CH_3OH molecule is 2·79 (2) Å from the O(4)A atom of one of the osmyl complexes led to the assumption that the hydroxyl H atom should be placed along the O(1)—O(4)A vector; the O(1)—H(28) distance was fixed at 0·96 Å (Schuster, Zundel & Sandorfy, 1976) leading to an H(28)—O(4)A distance of 1·83 Å and an O(1)—H(28)—O(4)A angle of 180°. H-atom B's fixed at $1{\cdot}2 \times B_{\rm eq}$ of associated C or O atom. Convergence yielded $R = 0{\cdot}037$, $wR = 0{\cdot}045$ $\{w = 1/\sigma^2(|F_o|)$ and $\sigma^2 = [S^2(C + R^2B) + (pF_o^2)^2]/{\rm Lp}$ where S = scan rate in ° min^{-1}, C = total integrated peak count, R = ratio of peak to background measuring time, B = total background count, and $p = 0{\cdot}05\}$, $S = 1{\cdot}05$, $(\Delta/\sigma)_{\rm max} = 0{\cdot}02$, no correlation coefficients $>0{\cdot}5$. A final difference Fourier synthesis showed $\Delta\rho_{\rm max} = 0{\cdot}82$ and $\Delta\rho_{\rm min} = -1{\cdot}16$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections from Cromer & Waber (1974). All computer programs from the *TEXSAN* crystal-structure-analysis package (Molecular Structure Corporation, 1985).

Discussion. This crystal provides the opportunity of comparing two essentially identical molecules in different crystallographic environments within the same unit cell. The asymmetric cell contains two chemically identical osmyl complexes plus a single molecule of methanol which is hydrogen-bonded to one of the hydroxo O atoms. Positional and equivalent isotropic thermal parameters are presented in Table 1 while Table 2 lists selected interatomic distances and angles.* Fig. 1 depicts one of the osmyl complexes (molecule A) and the methanol molecule to which it is hydrogen-bonded. The second osmyl complex, not shown in this illustration, will be referred to as molecule B in the subsequent discussion. Fig. 2 is a packing diagram of the unit-cell contents showing the spatial relationships among molecule A, molecule B, and the alcohol molecule. The molecular packing is relatively dense (one non-H atom/17·0 Å^3 of cell volume) when compared to the value of one non-H atom/~20 Å^3 of cell volume that we have observed in several other Os complexes. The result is a relatively large number of short intermolecular contacts. The connectivity of the osmyl complexes is as expected for members of this class of compounds (Hinckley & Kibala, 1986). The Os atom is six-coordinate, bound to two O atoms forming

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* Lists of structure factors, anisotropic thermal parameters, distances and angles involving the pyridine rings, H-atom coordinates, intermolecular distances, and selected least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44888 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the osmyl group (O=Os=O), to the hydroxo and one of the carboxylato O atoms of the chelated glycolate ligand, and to two pyridine N atoms. The Os—O distances within the osmyl groups of the *A* and *B* molecules and the related osmyl oxobenzoato complex (Hinckley *et al.,* 1987) are the same within standard deviations. Corresponding Os—O and Os—N bond distances in the central plane are essentially the same for molecules *A* and *B*, and are also similar to the analogous bond distances previously reported for the related osmyl oxobenzoato complex (Hinckley *et al.,* 1987). Bond distances and angles involved in the glycolate ligands are also similar for molecules *A* and *B*.

A comparison of Os-centered bond angles in the central plane (defined as the plane normal to the osmyl group) shows some interesting differences, most notably O(3)—Os—N(1) [94·6 (4)° for *A*, and 92·8 (4)° for *B*], N(1)—Os—N(2) [89·3 (4)° for *A*, and 94·2 (4)° for *B*], and N(2)—Os—O(4) [91·7 (4)° for *A*, and 88·4 (4)° for *B*]. In addition, least-squares-plane calculations show significant differences in the pyridine-ring-to-central-plane dihedral angles [70·5° for ring N(1) and 87·0° for ring N(2), molecule *A*; 65·5° for ring N(1) and 95·5° for ring N(2), molecule *B*]. In both molecules the N(2)-pyridine-ring-to-central-plane dihedral angle approaches 90° while the N(1)-pyridine-ring-to-central-

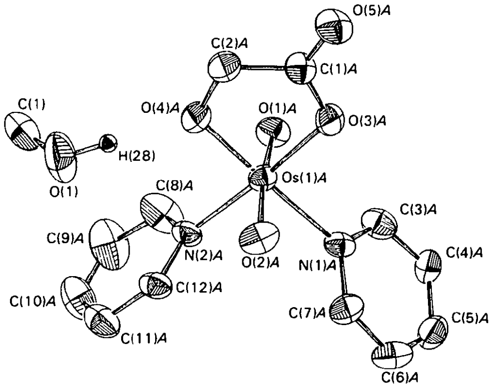

Fig. 1. Molecular structure and numbering scheme for molecule *A* and the methanol molecule; thermal ellipsoids at the 50% probability level.

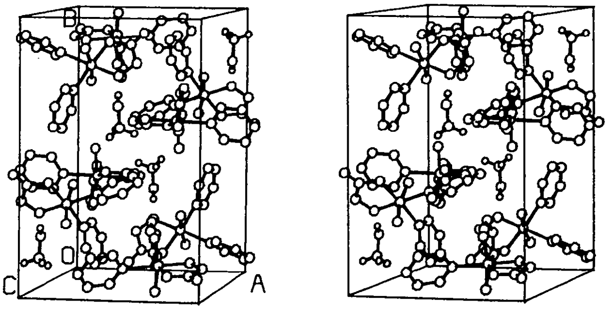

Fig. 2. Stereoscopic view of the molecular packing.

Table 1. *Positional and equivalent isotropic thermal parameters for the non-*H *atoms and their e.s.d.'s*

$$B_{eq} = \tfrac{8}{3}\pi^2(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	B_{eq}(Å^2)
Os(1)*A*	0·69169 (5)	0·18295 (3)	0·27586 (4)	2·40 (2)
O(1)*A*	0·7186 (9)	0·2454 (6)	0·3647 (6)	3·2 (4)
O(2)*A*	0·6992 (9)	0·1201 (6)	0·1872 (7)	3·6 (5)
O(3)*A*	0·6104 (9)	0·1022 (6)	0·3496 (6)	3·3 (5)
O(4)*A*	0·5278 (8)	0·2191 (6)	0·2485 (6)	3·5 (5)
O(5)*A*	0·428 (1)	0·0705 (6)	0·3937 (7)	4·2 (5)
N(1)*A*	0·877 (1)	0·1408 (7)	0·3090 (7)	2·5 (5)
N(2)*A*	0·765 (1)	0·2726 (7)	0·1983 (7)	2·9 (5)
C(1)*A*	0·489 (1)	0·1111 (9)	0·349 (1)	3·0 (6)
C(2)*A*	0·439 (1)	0·175 (1)	0·290 (1)	3·6 (7)
C(3)*A*	0·929 (1)	0·154 (1)	0·387 (1)	3·6 (7)
C(4)*A*	1·048 (1)	0·128 (1)	0·408 (1)	3·5 (7)
C(5)*A*	1·113 (1)	0·093 (1)	0·346 (1)	3·9 (8)
C(6)*A*	1·060 (1)	0·079 (1)	0·266 (1)	3·7 (8)
C(7)*A*	0·942 (1)	0·1034 (9)	0·249 (1)	3·2 (7)
C(8)*A*	0·786 (2)	0·346 (1)	0·230 (1)	4·7 (9)
C(9)*A*	0·824 (2)	0·408 (1)	0·180 (1)	6 (1)
C(10)*A*	0·842 (2)	0·396 (1)	0·094 (1)	4·4 (9)
C(11)*A*	0·823 (1)	0·323 (1)	0·059 (1)	3·9 (8)
C(12)*A*	0·782 (1)	0·263 (1)	0·1139 (8)	3·0 (7)
Os(1)*B*	0·73682 (5)	0·11339 (3)	0·86625 (4)	2·35 (2)
O(1)*B*	0·7115 (8)	0·0160 (6)	0·8355 (6)	3·0 (4)
O(2)*B*	0·7218 (8)	0·2127 (5)	0·8928 (6)	2·9 (4)
O(3)*B*	0·8184 (8)	0·0878 (6)	0·9834 (6)	3·1 (5)
O(4)*B*	0·9002 (8)	0·1214 (6)	0·8277 (6)	3·3 (5)
O(5)*B*	1·003 (1)	0·0870 (7)	1·0482 (6)	4·0 (5)
N(1)*B*	0·553 (1)	0·1042 (6)	0·9168 (7)	2·5 (5)
N(2)*B*	0·673 (1)	0·1457 (7)	0·7377 (7)	2·7 (5)
C(1)*B*	0·939 (1)	0·092 (1)	0·984 (1)	3·3 (7)
C(2)*B*	0·989 (1)	0·109 (1)	0·894 (1)	3·4 (7)
C(3)*B*	0·476 (1)	0·0459 (8)	0·8932 (9)	2·8 (6)
C(4)*B*	0·361 (1)	0·0363 (9)	0·9284 (8)	2·6 (6)
C(5)*B*	0·327 (1)	0·0883 (9)	0·9894 (9)	2·8 (6)
C(6)*B*	0·405 (1)	0·149 (1)	1·014 (1)	3·6 (7)
C(7)*B*	0·516 (1)	0·1567 (9)	0·976 (1)	3·0 (7)
C(8)*B*	0·669 (1)	0·092 (1)	0·673 (1)	3·8 (8)
C(9)*B*	0·649 (2)	0·115 (1)	0·586 (1)	4·2 (8)
C(10)*B*	0·634 (2)	0·194 (1)	0·566 (1)	4·5 (9)
C(11)*B*	0·631 (1)	0·247 (1)	0·632 (1)	4·4 (9)
C(12)*B*	0·650 (1)	0·221 (1)	0·717 (1)	3·7 (8)
C(1)	0·484 (2)	0·399 (1)	0·127 (1)	5 (1)
O(1)	0·487 (1)	0·3195 (8)	0·1060 (8)	6·2 (7)

Table 2. *Selected bond distances* (Å), *bond angles* (°), *and their e.s.d.'s*

Os(1)*A*	O(2)*A*	1·73 (1)	Os(1)*B*	O(2)*B*	1·740 (9)
Os(1)*A*	O(1)*A*	1·739 (9)	Os(1)*B*	O(1)*B*	1·73 (1)
Os(1)*A*	O(4)*A*	1·93 (1)	Os(1)*B*	O(4)*B*	1·92 (1)
Os(1)*A*	O(3)*A*	2·012 (9)	Os(1)*B*	O(3)*B*	2·019 (9)
Os(1)*A*	N(2)*A*	2·12 (1)	Os(1)*B*	N(2)*B*	2·14 (1)
Os(1)*A*	N(1)*A*	2·19 (1)	Os(1)*B*	N(1)*B*	2·21 (1)
O(3)*A*	C(1)*A*	1·34 (2)	O(3)*B*	C(1)*B*	1·32 (2)
O(4)*A*	C(2)*A*	1·40 (2)	O(4)*B*	C(2)*B*	1·40 (2)
O(5)*A*	C(1)*A*	1·20 (2)	O(5)*B*	C(1)*B*	1·19 (2)
C(1)*A*	C(2)*A*	1·51 (2)	C(1)*B*	C(2)*B*	1·54 (2)
C(1)	O(1)	1·38 (2)			

O(2)*A*	Os(1)*A*	O(1)*A*	167·5 (4)	O(2)*B*	Os(1)*B*	O(1)*B*	165·2 (4)
O(2)*A*	Os(1)*A*	O(4)*A*	95·9 (5)	O(2)*B*	Os(1)*B*	O(4)*B*	96·0 (4)
O(2)*A*	Os(1)*A*	O(3)*A*	93·6 (4)	O(2)*B*	Os(1)*B*	O(3)*B*	92·4 (4)
O(2)*A*	Os(1)*A*	N(2)*A*	88·0 (5)	O(2)*B*	Os(1)*B*	N(2)*B*	86·4 (4)
O(2)*A*	Os(1)*A*	N(1)*A*	84·5 (4)	O(2)*B*	Os(1)*B*	N(1)*B*	83·5 (4)
O(1)*A*	Os(1)*A*	O(4)*A*	95·8 (4)	O(1)*B*	Os(1)*B*	O(4)*B*	97·1 (4)
O(1)*A*	Os(1)*A*	O(3)*A*	92·1 (4)	O(1)*B*	Os(1)*B*	O(3)*B*	95·6 (4)
O(1)*A*	Os(1)*A*	N(2)*A*	87·0 (4)	O(1)*B*	Os(1)*B*	N(2)*B*	87·2 (4)
O(1)*A*	Os(1)*A*	N(1)*A*	83·9 (4)	O(1)*B*	Os(1)*B*	N(1)*B*	83·7 (4)
O(4)*A*	Os(1)*A*	O(3)*A*	84·4 (4)	O(4)*B*	Os(1)*B*	O(3)*B*	84·6 (4)
O(4)*A*	Os(1)*A*	N(2)*A*	91·7 (4)	O(4)*B*	Os(1)*B*	N(2)*B*	88·4 (4)
O(4)*A*	Os(1)*A*	N(1)*A*	178·9 (4)	O(4)*B*	Os(1)*B*	N(1)*B*	177·3 (4)
O(3)*A*	Os(1)*A*	N(2)*A*	175·9 (4)	O(3)*B*	Os(1)*B*	N(2)*B*	172·7 (4)
O(3)*A*	Os(1)*A*	N(1)*A*	94·6 (4)	O(3)*B*	Os(1)*B*	N(1)*B*	92·8 (4)
N(2)*A*	Os(1)*A*	N(1)*A*	89·3 (4)	N(2)*B*	Os(1)*B*	N(1)*B*	94·2 (4)
C(1)*A*	O(3)*A*	Os(1)*A*	112·8 (9)	C(1)*B*	O(3)*B*	Os(1)*B*	113·5 (9)
C(2)*A*	O(4)*A*	Os(1)*A*	113·6 (9)	C(2)*B*	O(4)*B*	Os(1)*B*	113·6 (8)
O(5)*A*	C(1)*A*	O(3)*A*	121 (1)	O(5)*B*	C(1)*B*	O(3)*B*	124 (1)
O(5)*A*	C(1)*A*	C(2)*A*	124 (1)	O(5)*B*	C(1)*B*	C(2)*B*	122 (1)
O(3)*A*	C(1)*A*	C(2)*A*	115 (1)	O(3)*B*	C(1)*B*	C(2)*B*	114 (1)
O(4)*A*	C(2)*A*	C(1)*A*	114 (1)	O(4)*B*	C(2)*B*	C(1)*B*	114 (1)

plane angle is much more acute. The summations of the absolute deviations of these dihedral angles from 90°, $\sum\Delta$, are 22·5° for molecule *A* and 30·0° for molecule *B*. The rotation of the N(1) pyridines around the Os(1)–N(1) vector is visible in Fig. 2. While electronic effects may be involved, these differences in dihedral angles can be largely attributed to packing forces. There are 28 pyridine···pyridine, pyridine···glycolate, or pyridine···osmyl intermolecular contacts with distances ranging from 3·11 (2) to 3·60 (2) Å.

Variations in the bend of the osmyl groups of the two molecules do not appear to be directly due to crystal packing effects. Both of the osmyl groups have seven intermolecular contacts and the ranges and averages of the contact distances are virtually the same. Yet the O(1)–Os–O(2) angle of 167·5 (4)° for molecule *A* is significantly larger than the 165·2 (4)° value of molecule *B*. This indicates that osmyl angle differences between these molecules may be attributed to electronic effects arising from the variations in pyridine-ring-to-central-plane dihedral angles.

The rationale for such an effect is based upon the ability of the pyridines to act as π acids, and the involvement of osmium d_{xz} and d_{yz} electron orbitals in Os–O bonding in the osmyl group. Rotations of the planes of the pyridine molecules which tend to facilitate overlap between these electron orbitals on the Os atom with the pyridine π-antibonding orbitals, provide the means to distort the π-electron distribution of the osmyl group, leading to the bend. The rationale would go on to say that the larger the $\sum\Delta$ value, the more pronounced will be the osmyl bend angle. Support for this argument may be found in the osmyl oxobenzoato complex reported previously (Hinckley *et al.*, 1987). In this compound the dihedral angles of the two pyridine ligands to the central plane are 77·5 and 90·5° respectively, yielding a $\sum\Delta$ value of 13·0°, and the O(1)–Os–O(2) angle is 169·8 (3)°. In the narrow range of O–Os–O angles spanned by this group of three molecules, the relationship between $\sum\Delta$ and O–Os–O angle is linear within experimental error.

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A (Dithioformato)rhodaselenaborane Complex: [2,2-(η^2-S_2CH)-2-(PPh_3)-1,2-$SeRhB_{10}H_{10}$]

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Abstract. 2-(η-Dithioformato)-2-(triphenylphosphine)-1-selena-2-rhoda-*closo*-dodecaborane(12), $C_{19}H_{26}B_{10}PRhS_2Se$, $M_r = 639{\cdot}5$, monoclinic, $P2_1/n$, $a = 12{\cdot}874$ (2), $b = 13{\cdot}847$ (2), $c = 14{\cdot}612$ (3) Å, $\beta = 94{\cdot}16$ (1)°, $V = 2598$ Å^3, $Z = 4$, $D_x = 1{\cdot}63$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 22{\cdot}6$ cm^{-1}, $F(000) = 1264$, $T = 298$ K, $R = 0{\cdot}023$ for 3555 observed reflections. In the title compound the Rh atom is bonded to a bidentate S_2CH ligand asymmetrically [Rh–S 2·328 (1), 2·406 (1) Å], a PPh_3 ligand [Rh–P 2·385 (1) Å], and an SeB_4 face of an $SeB_{10}H_{10}$ cluster ligand [Rh–Se 2·4395 (4), Rh–B 2·223 (4)–2·293 (4) Å]. The $RhSeB_{10}$ cage is the basis of a 12-atom *closo* structure. The conformation of the η^2-S_2CHRh unit above the SeB_4 face is such that the shorter Rh–S bond is directly *trans* to the Se atom and the S–Rh–S angle is 72·20 (3)°.

Introduction. From a study of the reactions of [2,2-(PPh_3)-2-(H)-1,2-$MM'B_{10}H_{10}$] (M = Se or Te,

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