found on comparing the two complexes, are small but sufficient to justify the increase of the Cu···Cu separation from 3·51 Å in the previous complex to 3·566 (2) Å in the present one. This separation is the greatest found in Cu^{II} complexes with 3,6-di(2-pyridyl)-pyridazine.

The coordinating water molecule forms an intramolecular hydrogen bond with the apical Cl atom [O(1)–H(1w)···Cl(3) 3·152 (8), H(1w)···Cl(3) 2·28 (7) Å, O(1)–H(1w)···Cl(3) 148 (6)°] and an intermolecular one with the apical Cl atom of a second dinuclear complex [O(1)–H(2w)···Cl(3)(2 − x, $\bar{y}$, 1 − z) 3·115 (8), H(2w)···Cl(3) 2·15 (8) Å, O(1)–H(2w)···Cl(3) 153 (6)°]. There are also two contacts relevant for packing, the geometries of which satisfy the requirements for hydrogen bonds (Berkovitch-Yellin & Leiserowitz, 1984): C(4)–H(4)···O(1)(x, y − 1, z) 3·30 (1), H(4)···O(1) 2·3 (1) Å, C(4)–H(4)···O(1) 146 (9)°, and C(8)–H(8)···Cl(1)(x, $\bar{y} − \frac{1}{2}$, z − $\frac{1}{2}$) 3·50 (1), H(8)···Cl(1) 2·4 (1) Å, C(8)–H(8)···Cl(1) 165 (9)°.

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μ-Oxo-1,1,1,2,2,2-hexaoxo-1,1,2-tris(pyridine)dirhenium(VII), [Re₂O₇(C₅H₅N)₃]: Variability of the Coordination Number of Re^VII

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Abstract. $M_r = 721·7$, monoclinic, $P2_1/c$, $a = 9·068$ (1), $b = 12·280$ (2), $c = 17·494$ (4) Å, $\beta = 95·02$ (1)°, $Z = 4$, $D_x = 2·47$ g cm⁻³, D_m not measured, graphite-monochromatized Mo Kα radiation, $\lambda = 0·71073$ Å, $\mu = 126·8$ cm⁻¹, $F(000) = 1320$, $T = 293$ (2) K. Final $R = 0·026$ for 1764 independent observed reflections. [Re₂O₇py₃] molecules contain two inequivalent rhenium atoms bridged by a single oxygen atom, Re(1)–O = 1·806 (7), Re(2)–O = 2·056 (7) Å. Re(1) is five-coordinate in a trigonal bipyramidal geometry with three oxo ligands [Re(1)–O = 1·695–1·706 (9) Å], the bridging oxygen atom, and a pyridine nitrogen atom in its coordination sphere. Re(2) is six-coordinate in a distorted octahedral geometry with a fac-trioxo group [Re(2)–O = 1·710–1·724 (9) Å], the bridging oxygen atom, and two pyridine nitrogen atoms.

Introduction. The chemistry of oxo complexes of Re⁷⁺ is dominated by tetrahedral [ReO₄]⁻. A few examples of octahedral [ReO₃X₃] units are known in Re₂O₇ (Krebs, Müller & Beyer, 1968, 1969), Re₂O₇.2H₂O (Beyer, Glemser & Krebs, 1968; Beyer, Glemser, Krebs & Wagner, 1970), [Re₂O₆(OH)₂(1,4-dioxane)₃] (Fischer & Krebs, 1982), [ReO₃Cl(2,2'-bipyridine)] (Sergienko, Khodashova, Porai-Koshits & Butman, 1977), H₂phen[ReO₃Cl₂(H₂O)]Cl (Lis, 1979) and Cs₂[ReO₃Cl₃] (Lis, 1983).

Five-coordinate Re⁷⁺ compounds are known. [ReO₂F₃] has been shown by matrix-isolation vibrational spectroscopy to have a trigonal bipyramidal (C_{2v}) structure with equatorial oxygen atoms (Beattie,

Crocombe & Ogden, 1977). ReO_2Me_3 also has been prepared, but not structurally characterized. A trigonal bipyramidal structure (C_s) was proposed on the basis of the NMR and IR spectra (Mertis & Wilkinson, 1976). We recently isolated a pyridine adduct of Re_2O_7 (Johnson, Brody, Ansell & Zentz, 1984). Its structure, reported herein, is composed of $[Re_2O_7py_3]$ molecules in which two inequivalent Re atoms exhibit the coordination numbers five and six.

Experimental. Clear crystals of $[Re_2O_7(C_5H_5N)_3]$ were wedged into quartz capillary tubes containing a small amount of mother liquor. The tubes were sealed before removal from the dry box. $0·2 \times 0·2 \times 0·2$ mm parallelepiped crystal, Enraf–Nonius CAD-4 diffractometer. Cell dimensions determined by centering 25 diffraction maxima $14·9 < 2\theta < 21·4°$. Three check reflections measured 68 times during data collection, data corrected for 7·2% overall decay. Data corrected for absorption using ψ- scan data with transmission factors varying between 0·66 and 0·99. 5917 unique reflections measured up to $2\theta = 50°$, range of $hkl = 0\rightarrow10$, $0\rightarrow14$, $-20\rightarrow20$, 1764 judged observed with $I > 3\sigma(I)$ where $I = S(C\text{-}RB)$ and $\sigma(I) = [S^2(C+R^2B) + (kI)^2]^{1/2}$, where $C =$ total counts recorded during scan, $R = 2·0$, $B =$ ratio of scanning time to total background, $S =$ scan rate (varied between 4 and $20°$ min^{-1}) and $k = 0·05$, a factor introduced to reflect instrumental stability. From these data the structure factors and their e.s.d.'s were computed using $|F_o| = (I/\text{Lp})^{1/2}$ and $\sigma(F_o) = \sigma(I)/2 \, |F_o| \, \text{Lp}$, where Lp is the Lorentz – polarization correction. Structure solved using Patterson and Fourier techniques. Hydrogen atoms placed in calculated positions $[d(\text{C–H}) = 1·05 \text{ Å}]$. Full-matrix least-squares refinement of non-hydrogen atoms with anisotropic temperature factors led to $R = 0·026$, $R_w = 0·031$. Final cycle of least-squares refinement contained 1764 observations and 244 variables. $(\Delta/\sigma)_{\max} = 0·2$. A final difference Fourier map showed no feature $> 0·73$ e Å^{-3}. Solution and refinement performed using Enraf–Nonius (1980) *SDP*.* Quantity minimized in least-squares analysis $w(|F_o| - |F_c|)^2$ where $w = \sigma(F_o)^{-2}$ with $\sigma(F_o)$ defined above.

Discussion. The final positional and thermal parameters are listed in Table 1, bond lengths and angles of the Re coordination spheres in Table 2.†

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* The *SDP* package of programs provided by Enraf–Nonius was used for all calculations (scattering-factor tables, Cromer & Waber, 1974). Anomalous-scattering-factor corrections were included in least-squares calculations.

† Lists of bond lengths and angles in the pyridine rings, structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39663 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The crystal structure is composed of isolated $[Re_2O_7py_3]$ molecules located on general positions. The molecules, shown in Fig. 1, contain two inequivalent rhenium atoms bridged by a single oxygen atom. Each rhenium atom is bonded to three additional oxygen atoms at distances ranging from 1·695 (8) to 1·724 (9) Å. Re(1) is bound to the nitrogen atom of a single pyridine ligand at a distance of 2·44 (1) Å, while

Table 1. *Positional and isotropic thermal parameters for* $[Re_2O_7(C_5H_5N)_3]$

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos \gamma) B(1,2) + ac(\cos \beta) B(1,3) + bc(\cos \alpha) B(2,3)]$.

	x	y	z	$B(\text{Å}^2)$
Re(1)	0·14094 (6)	0·18538 (4)	0·46611 (2)	3·450 (9)
Re(2)	0·20638 (5)	0·28972 (3)	0·65739 (2)	3·028 (8)
O(1)	0·020 (1)	0·0984 (6)	0·4175 (4)	4·8 (2)
O(2)	0·308 (1)	0·1231 (8)	0·4620 (5)	5·7 (2)
O(3)	0·161 (1)	0·3052 (6)	0·4200 (5)	5·3 (2)
O(4)	0·0900 (9)	0·3924 (6)	0·6246 (4)	4·3 (2)
O(5)	0·3682 (9)	0·3136 (6)	0·6152 (5)	4·7 (2)
O(6)	0·2511 (9)	0·3235 (5)	0·7514 (4)	4·2 (2)
O(7)	0·1328 (8)	0·1879 (5)	0·5688 (4)	3·0 (1)
N(1)	−0·097 (1)	0·2712 (6)	0·4824 (5)	3·6 (2)
N(2)	0·0049 (9)	0·2090 (6)	0·7022 (5)	2·6 (2)
N(3)	0·304 (1)	0·1234 (7)	0·6969 (5)	3·5 (2)
C(1)	−0·213 (2)	0·2073 (9)	0·5019 (8)	5·3 (3)
C(2)	−0·356 (1)	0·248 (1)	0·5079 (8)	5·9 (3)
C(3)	−0·383 (2)	0·355 (1)	0·4932 (9)	6·6 (4)
C(4)	−0·265 (2)	0·420 (1)	0·4761 (8)	5·8 (4)
C(5)	−0·124 (1)	0·3763 (9)	0·4708 (6)	4·2 (3)
C(6)	−0·052 (1)	0·1116 (8)	0·6790 (6)	3·3 (2)
C(7)	−0·175 (1)	0·0665 (9)	0·7085 (7)	4·4 (3)
C(8)	−0·241 (1)	0·124 (1)	0·7633 (6)	4·3 (3)
C(9)	−0·186 (1)	0·224 (1)	0·7856 (7)	4·5 (3)
C(10)	−0·062 (1)	0·2656 (8)	0·7559 (6)	3·2 (2)
C(11)	0·373 (1)	0·0606 (8)	0·6490 (6)	3·7 (3)
C(12)	0·441 (1)	−0·036 (1)	0·6727 (8)	4·6 (3)
C(13)	0·430 (2)	−0·0711 (9)	0·7456 (8)	5·4 (3)
C(14)	0·356 (1)	−0·009 (1)	0·7950 (7)	4·8 (3)
C(15)	0·297 (1)	0·0887 (9)	0·7677 (7)	3·9 (3)

Table 2. *Bond distances (Å) and angles (°) in the Re coordination spheres*

Re(1)–O(1)	1·705 (9)	Re(2)–O(4)	1·711 (8)
Re(1)–O(2)	1·706 (9)	Re(2)–O(5)	1·724 (9)
Re(1)–O(3)	1·695 (8)	Re(2)–O(6)	1·710 (8)
Re(1)–O(7)	1·806 (7)	Re(2)–O(7)	2·056 (7)
Re(1)–N(1)	2·440 (10)	Re(2)–N(2)	2·278 (9)
		Re(2)–N(3)	2·307 (10)
O(2)–Re(1)–O(1)	103·6 (5)	O(4)–Re(2)–O(5)	104·7 (4)
O(2)–Re(1)–O(3)	103·7 (5)	O(4)–Re(2)–O(6)	103·3 (4)
O(2)–Re(1)–O(7)	99·4 (4)	O(5)–Re(2)–O(6)	103·4 (4)
O(1)–Re(1)–O(3)	113·4 (5)	O(4)–Re(2)–O(7)	92·6 (4)
O(1)–Re(1)–O(7)	115·3 (4)	O(5)–Re(2)–O(7)	90·8 (4)
O(3)–Re(1)–O(7)	118·3 (4)	O(4)–Re(2)–N(2)	86·9 (4)
N(1)–Re(1)–O(1)	77·9 (4)	O(5)–Re(2)–N(3)	87·8 (4)
N(1)–Re(1)–O(3)	79·2 (4)	O(6)–Re(2)–N(2)	84·5 (4)
N(1)–Re(1)–O(7)	76·3 (3)	O(6)–Re(2)–N(3)	82·8 (4)
N(1)–Re(1)–O(2)	175·6 (4)	O(7)–Re(2)–N(2)	77·2 (3)
Re(1)–O(7)–Re(2)	136·2 (4)	O(7)–Re(2)–N(3)	77·1 (3)
		N(2)–Re(2)–N(3)	79·0 (3)
		O(7)–Re(2)–O(6)	155·0 (3)
		N(2)–Re(2)–O(5)	163·7 (3)
		N(3)–Re(2)–O(4)	164·1 (4)

Re(2) is bound to two pyridine molecules at Re—N distances of 2·278 (9) and 2·31 (1) Å. The coordination sphere around Re(1) is very distorted trigonal bipyramidal; the angle O(2)—Re(1)—N(1) is 175·6 (4)°. The structure is actually quite similar to that of $Re_2O_7.2H_2O$ which is composed of molecules containing an octahedral rhenium with two coordinated water molecules and a tetrahedral rhenium without additional ligands (Beyer et al., 1968). The difference in [$Re_2O_7py_3$] is that an additional pyridine ligand is coordinated to a tetrahedral face of the otherwise four-coordinate rhenium. The observed Re—N distance of 2·44 (1) Å is about 0·15 Å longer than the Re—N distances of the octahedral Re(2). This difference in Re—N bond lengths is balanced by the difference in the Re—O bond lengths to the bridging oxygen. Re(1)—O(7) is 1·806 (7) Å while Re(2)—O(7) is 2·056 (7) Å.
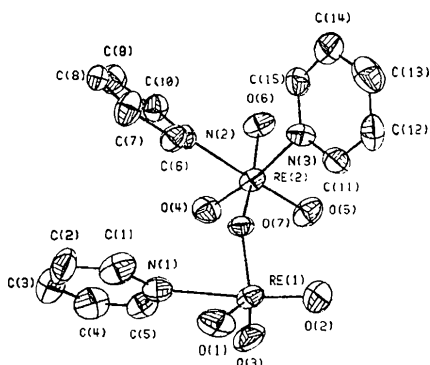
This pattern of bridging-oxygen distances is similar to that in Re_2O_7 and $Re_2O_7.2H_2O$ where the Re(tet)—O(bridging) distance runs from 1·76–1·80 Å and Re(oct)—O(bridging) is 2·05–2·10 Å. The angle at the bridging oxygen in [$Re_2O_7py_3$] is 136·2 (4)°. This reflects the crowding caused by the addition of a pyridine molecule as a fifth ligand on Re(1). The corresponding Re(tet)—O—Re(oct) angle in $Re_2O_7.2H_2O$ is linear (179°) and in Re_2O_7 runs from 146·6 to 152·4° (Beyer et al., 1970; Krebs et al., 1969).

The coordination sphere around Re(2) is similar to that found in other octahedral Re^{7+} compounds containing three oxygens and oxygen, nitrogen, or chlorine as the additional ligands. There are three short (1·71 Å) Re—O bonds that are mutually cis. The remaining ligands (two pyridine nitrogens and the shared oxygen in this case) are at considerably longer distances from the rhenium atom. Some of the octahedral complexes of the d^0 Mo^{6+}, for example [MoO_3(diethylenetriamine)] (Cotton & Elder, 1964), show similar distortions from octahedral symmetry. The most important feature of the coordination sphere, shared by both Re(1) and Re(2), is the presence of a tightly bound fac-ReO_3 unit. The Re—O distances are similar to those found in tetrahedral ReO_4 compounds, 1·64–1·77 Å (Lock & Turner, 1975; Betz & Hoppe, 1983).

The packing arrangement can be seen in Fig. 2.

Fig. 1. A view of the [$Re_2O_7py_3$] molecule showing the atom labeling.
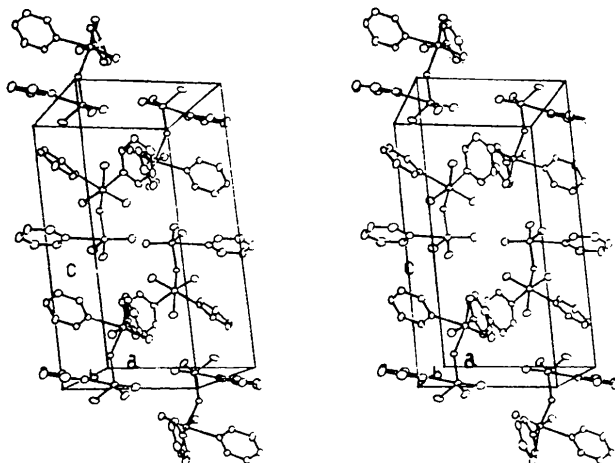
Fig. 2. A stereoscopic view showing the packing arrangement of [$Re_2O_7(C_5H_5N)_3$].

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