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A new tricarbonylrhenium(I) compound incorporating the tridentate ligand *N*,*N*-bispicolyl-2-ethanolamine

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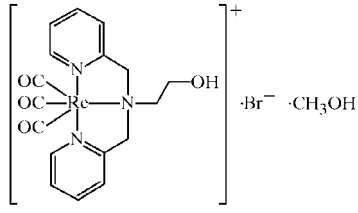
The title compound, {[*N*,*N*-bis(2-pyridylmethyl)amino]ethanol-κ^3N,N',N''}tricarbonylrhenium(I) bromide methanol solvate, $[Re(C_{14}H_{17}N_3O)(CO)_3]Br\cdot CH_4O$, has been prepared in almost quantitative yield by reacting $(NEt_4)_2[Re(CO)_3Br_3]$ with the ligand *N*,*N*-bispicolyl-2-ethanolamine in refluxing methanol. The X-ray structure revealed that the $Re(CO)_3N_3$ coordination sphere is highly distorted from octahedral geometry and that the $Re(CO)_3$ core is facial. The coordinated ligand forms two five-membered rings, with the pyridine rings in a butterfly formation. The OH group is not involved in metal coordination. The packing of the molecule shows a network of classical O···H—O and Br···H—O, and non-classical Br···H—C and O···H—C hydrogen bonds between the methanol solvate molecules, the metal complex cations and the bromide anions.

Comment

The pendant design of novel ^{99m}Tc-based radiopharmaceuticals requires the development of suitable bifunctional ligands, which serve two purposes, *viz*. to hold the radionucleotide securely without leakage *in vivo* and to provide a side arm for linkage to a bioactive molecule while maintaining maximal integrity of the biomolecule (Liu & Edwards, 1999). We have recently reported the synthesis of a series of M^{I} binding ligands (M = Tc and Re) based on a lysine-derived bispicolylamine, referred to as a single amino acid chelate (SAAC), which forms inert complexes with the chemically robust $[M(CO)_3]^+$ core (M = ^{99m}Tc and Re) and which can be incorporated into peptides as if it were a natural amino acid (Banerjee *et al.*, 2002; Levadala *et al.*, 2004; Stephenson *et al.*, 2004).



(I)

As part of continuing efforts to prepare new bifunctional ligands, we have recently investigated the maleimide functionalities for the conjugation of sulfhydryl-containing biomolecules (Banerjee *et al.*, 2004). Recent studies have shown that the maleimide derivatives can be conveniently prepared in good yield from the alcohol precursor under Mitsunobu conditions (King *et al.*, 2002). We report here the synthesis and structural characterization of a novel tricarbonylrhenium(I) compound, (I), incorporating the tridentate ligand bispicolyl-2-ethanolamine (L1) with a free OH functionality, which is potentially useful as a precursor for the maleimide-containing bifunctional linkers. Compound (I) was prepared

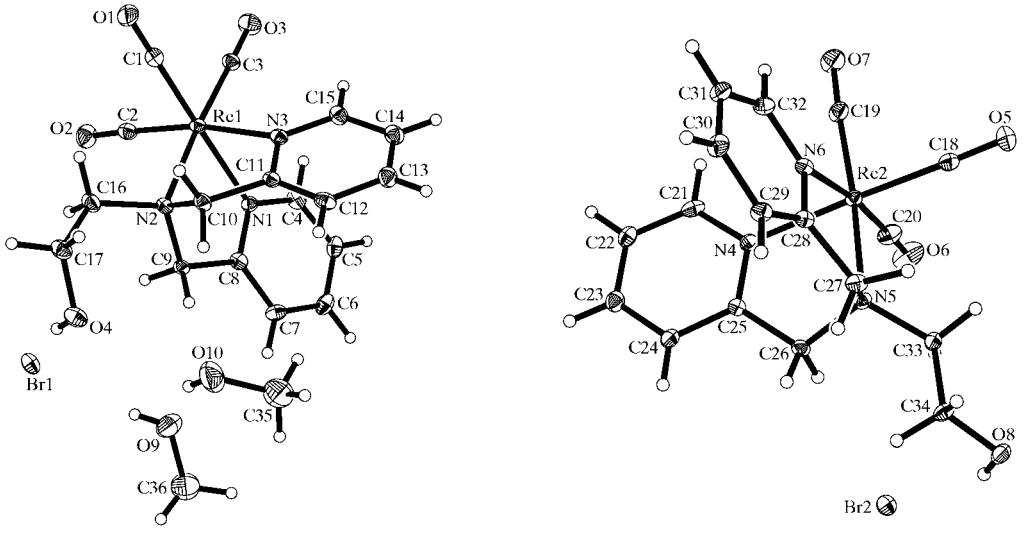


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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quantitatively by the reaction of the rhenium precursor $(NEt_4)_2[Re(CO)_3Br_3]$ with the ligand under refluxing methanol conditions. A perspective view of (I) is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. There are two independent solvated salts in the asymmetric unit. The bond distances and angles of the two molecules are found to be slightly different. The hydrogen-bonded methanol molecules are relatively closer to the Re1 molecule than to the Re2 molecule. These two solvent molecules are responsible for destroying the symmetry of the unit cell and the doubling of the asymmetric unit.

The distorted octahedral coordination environment of Re is defined by the three facially bound CO groups and the secondary amine and pyridine N-atom donors of the ligand. The mirror plane, which contains the OH group, the ethylene backbone, and the Re1/N2/C3/O3 and Re2/N5/C19/O7 groups for the two independent molecules, divides the two pyridine–methylene units symmetrically. The structure of (I) provides an opportunity to observe the effect of rhenium oxidation states on the metal–ligand bond lengths *via* comparison with $[Re^{V}O(OCH_2CH_2O)(L1)][ReO_4]$ [Cambridge Structural Database (CSD; Allen, 2002) refcode NOMCEX (Botha *et al.*, 1998)], where L1 serves as an *N*,*N*′,*N*″-tridentate ligand with a pendant OH group as in compound (I), with $[Re^{V}OCl(L1)]PF_6$ (CSD refcode NOMCAT; Botha *et al.*, 1998), where L1 acts as an anionic *N*,*N*,*N*,*O*-tetradentate ligand, and with $[Re^{V}OCl_2(L1)]$ (CSD refcode NOMBOG; Botha *et al.*, 1998), where L1 is an anionic *N*,*N*,*O*-tridentate ligand with a pendant pyridine (py) ring (Botha *et al.*, 1998). The $Re^{I}-N_{py}$ bond lengths [average 2.171 (6) Å] in (I) lie at the longer end of the range of $Re^{V}-N_{py}$ bond lengths (2.11–2.17 Å), possibly revealing the contraction of the metal radius upon increase in oxidation state from I to V. However, the $Re-N_{amine}$ bond distance in $[Re^{V}O(OCH_2CH_2O)(L1)][ReO_4]$ is longer than all the other $Re^{V}-N_{amine}$ bonds, including that in (I), by *ca* 0.1 Å, probably as a result of the strong *trans* influence of the Re=O bond.

The *N*,*N*′,*N*″-chelating ligand forms two five-membered rings, with the two pyridine rings in a butterfly formation. The observed $N-Re^{I}-N$ bite angles in (I) are comparable to the related bite angles in the previously discussed structures containing L1 (Botha *et al.*, 1998). The packing of the molecules shows antiparallel stacks, with the ligand (L1) moieties and the bromide ions from adjacent stacks in a face-to-face orientation. The interplanar distance between two pyridine rings of approximately 3.5 Å is of the same order as the π-stacking distances in aromatic and charge-transfer compounds (Batchelor *et al.*, 2000; Glusker *et al.*, 1994). The antiparallel arrangement of the ligand moieties facilitates the formation of intermolecular non-classical hydrogen bonding between carbonyl O atoms and pyridine H atoms. Classical intramolecular O—H···O hydrogen bonds were observed between the two methanol molecules and between the methanol molecules and the complexes. Classical intramolecular hydrogen bonds (*e.g.* O4—H4···Br1, O8—H8···Br2 and O9—H9···Br1) and non-classical intramolecular hydrogen bonding (*e.g.* C17—H17···Br2, C26—H26*B*···Br1, C26—H26*A*···Br2, C27—H27*B*···Br1, *etc.*) are also present (Table 2). In addition, side-to-side intermolecular hydrogen bonding is observed between adjacent pyridine rings and bromide ions (*e.g.* C22—H22···Br1).

Experimental

For the synthesis of the ligand *N*,*N*-bispicolyl-2-ethanolamine (L1), pyridine-2-carbaldehyde (7.36 g, 0.069 mol) was added to a solution of 2-aminoethanol (2 g, 0.033 mol) in dichloroethane (20 ml) and the solution was stirred for 30 min under an argon atmosphere. The reaction mixture was cooled to 273 K, sodium triacetoxyborohydride (16.08 g, 0.076 mol) was added in small portions and the solution was stirred for another hour at room temperature. Thin-layer chromatography indicated the completion of the reaction at this time. The reaction mixture was quenched with 2% sodium bicarbonate solution (30 ml) and extracted with dichloromethane (20 ml). The organic layer containing the product was dried over sodium sulfate, concentrated to a 3 ml volume and purified *via* routine chromatographic techniques using a silica-gel column. The product was eluted with $MeOH/CH_2Cl_2$ (5:95) and dried under reduced pressure to give the ligand as a colorless oil (yield 6.10 g, 76.76%). Analysis found: C 69.30, H 7.08, N 17.30%; $C_{14}H_{17}N_3O$ requires: C 69.11, H 7.04, N 17.27%. For the preparation of (I), L1 (0.030 g, 0.13 mmol) was added to a solution of $(NEt_4)_2[Re(CO)_3Br_3]$ (0.1 g, 0.13 mmol) in methanol (15 ml) and the resulting solution was refluxed for 2 h. The colorless reaction mixture was evaporated to dryness and the solid residue thus obtained was dissolved in dichloromethane (10 ml) and extracted with water (3 × 20 ml) to remove all the tetraethylammonium bromide obtained as the main side product. The organic layer was concentrated to 2 ml and subjected to chromatographic separation using a silica-gel column. The product was eluted with $MeOH/CH_2Cl_2$ (10:90) and evaporated under vacuum to give a colorless solid product (yield 67 mg, 87%). Analysis found: C 34.95, H 2.91, N 7.10%; $C_{17}H_{17}BrN_3O_4Re$ requires: C 34.41, H 2.89, N 7.08%. Crystals suitable for single-crystal X-ray diffraction were grown by slow diffusion of a solution of (I) in CH_2Cl_2 into a hexane solution at room temperature.

Crystal data

$[Re(C_{14}H_{17}N_3O)(CO)_3]Br\cdot CH_4O$	D_x = 2.007 Mg m^{-3}
M_r = 625.49	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1200 reflections
a = 14.962 (2) Å	θ = 1.5–31.5°
b = 16.577 (3) Å	μ = 7.83 mm^{-1}
c = 18.117 (3) Å	T = 91 (2) K
β = 112.881 (3)°	Parallelepiped, colorless
V = 4139.9 (11) Å^3	0.22 × 0.14 × 0.09 mm
Z = 8	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	13 759 independent reflections
φ and ω scans	10 981 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)	R_{int} = 0.062
T_{min} = 0.278, T_{max} = 0.508	θ_{max} = 31.5°
52 775 measured reflections	$h = -22 \rightarrow 22$
	$k = -24 \rightarrow 24$
	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0255P)^2 + 54.5922P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.058	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.132	$\Delta\rho_{max}$ = 6.45 e Å^{-3}
S = 1.18	$\Delta\rho_{min}$ = −2.59 e Å^{-3}
13 759 reflections	
511 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Re1—C1	1.922 (9)	Re2—N4	2.171 (6)
Re1—C2	1.927 (9)	Re2—N5	2.233 (6)
Re1—C3	1.932 (8)	Re2—N6	2.171 (6)
Re1—N1	2.174 (6)	O1—C1	1.148 (10)
Re1—N2	2.225 (6)	O2—C2	1.147 (10)
Re1—N3	2.167 (6)	O3—C3	1.160 (9)
Re2—C18	1.925 (8)	O5—C18	1.146 (10)
Re2—C19	1.927 (8)	O6—C20	1.132 (10)
Re2—C20	1.936 (8)	O7—C19	1.150 (10)
C1—Re1—C2	89.8 (4)	C18—Re2—C19	86.4 (3)
C1—Re1—C3	87.3 (4)	C18—Re2—C20	89.2 (4)
C1—Re1—N3	96.7 (3)	C18—Re2—N4	173.3 (3)
C2—Re1—N3	170.3 (3)	C19—Re2—N4	98.5 (3)
C1—Re1—N1	172.4 (3)	C20—Re2—N4	95.7 (3)
C2—Re1—N1	96.2 (3)	C18—Re2—N6	95.5 (3)
C3—Re1—N1	97.6 (3)	C20—Re2—N6	173.5 (3)
N3—Re1—N1	76.9 (2)	N4—Re2—N6	79.3 (2)
C3—Re1—N2	175.9 (3)	C19—Re2—N5	174.7 (3)
N1—Re1—N2	78.9 (2)	N4—Re2—N5	78.3 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···Br1	0.84	2.39	3.213 (7)	167
O8—H8···Br2	0.84	2.51	3.282 (6)	153
O9—H9···Br1	0.84	2.56	3.390 (8)	168
O10—H10···O9	0.84	2.27	3.059 (16)	156
C9—H9*A*···O4	0.99	2.57	2.969 (10)	104
C24—H24···O4^{i}	0.95	2.37	3.299 (8)	167
C30—H30···O7^{ii}	0.95	2.47	3.225 (11)	137
C17—H17*A*···Br2^{iii}	0.99	2.87	3.788 (10)	155
C22—H22···Br1^{iv}	0.95	2.79	3.552 (7)	138
C26—H26*B*···Br1^{i}	0.99	2.82	3.798 (6)	167
C27—H27*A*···Br1^{i}	0.99	2.83	3.798 (8)	166
C34—H34*A*···Br1^{v}	0.99	2.90	3.724 (9)	141

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $x, y-1, z$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (v) $x-1, y+1, z$.

All H atoms were located in difference Fourier maps and refined as riding, with U_{iso}(H) values of $1.2U_{eq}$(C) (CH and CH_2 H atoms) and $1.5U_{eq}$(C) (CH_3 H atoms), and with C—H = 0.95–0.99 Å. A residual peak of electron density was located 0.83 Å from atom Re1. This residual density is mainly due to an inadequate absorption correction.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1108). Services for accessing these data are described at the back of the journal.

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