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## A rhenium(V)–arylimide species incorporating pyridine-2-alimine chelation

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### Abstract

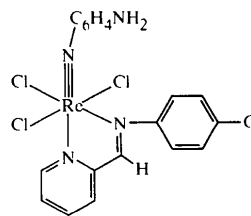
The title compound, (4-aminophenylimido)trichloro[2-(4-chlorophenyliminomethyl)pyridine]rhenium(V), [Re(NC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)Cl<sub>3</sub>(CIA)], where CIA is *N*-(*p*-chlorophenyl)pyridine-2-alimine (*p*-ClC<sub>6</sub>H<sub>4</sub>N=CHC<sub>5</sub>H<sub>4</sub>N), was synthesized by reacting the corresponding oxo complex, [ReOCl<sub>3</sub>(CIA)], or the corresponding phosphine oxide complex, [Re(OPPh<sub>3</sub>)Cl<sub>3</sub>(CIA)], with *p*-phenylenediamine in toluene. The structure determination revealed that the ReCl<sub>3</sub>N<sub>3</sub> coordination sphere is severely distorted from octahedral geometry and that it has a meridional ReCl<sub>3</sub> fragment. The Re—N—C angle in the imide part is nearly linear and the Re—N<sub>imide</sub> bond can be considered to be triple bond in character. The Re atom is distorted towards the imide N atom by 0.29 Å from the equatorial Cl<sub>3</sub>N<sub>imine</sub> plane. The Re—N<sub>pyridine</sub> bond is longer by 0.15 Å than the Re—N<sub>imine</sub> bond due to the *trans* influence of the imide fragment.

### Comment

High-valent rhenium complexes with metal–ligand multiple bonds, *e.g.* imido or oxo complexes, have been of increasing interest in inorganic chemistry (Wang *et al.*, 1993; Nugent & Mayer, 1988). In the course of our search for new and reactive oxorhenium(V) species, we isolated a pyridine-2-alimine-chelated Re<sup>V</sup>O species, (2), which undergoes O-atom transfer to

PPh<sub>3</sub>, affording an Re<sup>III</sup>OPPh<sub>3</sub> species, (3) (Dirghangi, Menon, Pramanik & Chakravorty, 1997). Both (2) and (3) were found to react with ArNH<sub>2</sub>, furnishing Re<sup>V</sup>NAr species which undergo inward O-atom transfer from water followed by metal oxidation to give rare Re<sup>V</sup>NAr species incorporating 2-picolinamide chelation (Dirghangi, Menon, Banerjee & Chakravorty, 1997; Banerjee *et al.*, 1997). This work forms part of a program on the synthesis and characterization of new Re<sup>V</sup>NAr compounds.

The species of concern to us here is [Re(NC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)Cl<sub>3</sub>(CIA)], (1), where CIA is *N*-(*p*-chlorophenyl)pyridine-2-alimine (*p*-ClC<sub>6</sub>H<sub>4</sub>N=CHC<sub>5</sub>H<sub>4</sub>N). This was



(1)

synthesized from the oxo complex [ReOCl<sub>3</sub>(CIA)], (2), or from the phosphine oxide complex [Re(OPPh<sub>3</sub>)Cl<sub>3</sub>(CIA)], (3), with *p*-phenylenediamine in toluene. A view of the molecular structure of (1) is shown in Fig. 1. The ReCl<sub>3</sub>N<sub>3</sub> coordination sphere is severely distorted from octahedral geometry. The ReCl<sub>3</sub> fragment is meridionally disposed. The chelate ring [bite angle 73.8 (2)°] along with the pyridine ring constitute a good plane (mean deviation 0.05 Å) with which the chlorophenyl group makes a dihedral angle of 61.6 (3)°. The aryl group of the imide fragment makes a dihedral angle of 39.5 (4)° with the chlorophenyl group.

An interesting feature of the structure is that the pyridine and imide N atoms (N1 and N3, respectively) bend towards each other in the direction of the Re/Cl<sub>2</sub>/N<sub>2</sub> plane. Additionally, the metal atom is displaced from the N<sub>2</sub>/Cl<sub>1</sub>/Cl<sub>2</sub>/Cl<sub>3</sub> mean plane by 0.29 Å towards N<sub>3</sub>. This distortion and bending is necessarily reflected in deviations of the *trans* angles from 180° [range 162.8 (1)–165.2 (2)°] and in deviations of the *cis* angles with respect to N1 and N3 from 90° to the lower and higher side, respectively. Other *cis* angles are very close to 90°. This type of metal deviation is common to multiple-bonded metal–ligand complexes (Dirghangi, Menon, Banerjee & Chakravorty, 1997; Shivakumar *et al.*, 1998; Bélanger & Beauchamp, 1999; Banerjee *et al.*, 1997; Lahiri *et al.*, 1987; Bakir & Sullivan, 1995).

Among hexacoordinated Re<sup>V</sup>NX (X is alkyl or aryl) structures (Bakir *et al.*, 1992; Masood *et al.*, 1994; Fung *et al.*, 1995; Wang *et al.*, 1993; Yan *et al.*, 1995; Rossi *et al.*, 1993; Dirghangi, Menon, Banerjee & Chakravorty, 1997; Banerjee *et al.*, 1997; Lahiri *et al.*, 1987), the



Table 1. Selected geometric parameters (Å, °)

Re—N3	1.723 (4)	N1—C5	1.342 (6)
Re—N2	2.052 (4)	N1—C1	1.357 (6)
Re—N1	2.204 (4)	N2—C6	1.296 (6)
Re—C11	2.372 (2)	N2—C7	1.452 (6)
Re—C13	2.382 (3)	N3—C13	1.375 (6)
Re—C12	2.414 (3)	C1—C6	1.443 (7)
N3—Re—N2	95.0 (2)	N3—Re—C12	90.97 (15)
N3—Re—N1	165.2 (2)	N2—Re—C12	94.86 (13)
N2—Re—N1	73.8 (2)	N1—Re—C12	80.70 (13)
N3—Re—C11	102.00 (15)	C11—Re—C12	87.90 (10)
N2—Re—C11	162.76 (11)	C13—Re—C12	166.80 (5)
N1—Re—C11	89.93 (12)	C1—N1—Re	115.3 (3)
N3—Re—C13	102.07 (15)	C6—N2—Re	120.8 (3)
N2—Re—C13	86.14 (13)	C13—N3—Re	171.6 (3)
N1—Re—C13	86.97 (13)	N1—C1—C6	112.7 (4)
C11—Re—C13	87.38 (9)		

The highest electron-density peak (1.04 e Å<sup>-3</sup>) lies near the C14 atom.

Data collection: *SHELXTL-Plus90* (Sheldrick, 1990). Cell refinement: *SHELXTL-Plus90*. Data reduction: *SHELXTL-Plus90*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1115). Services for accessing these data are described at the back of the journal.

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## Disodium bis[μ-2-hydroxy-2-methylpropanoato(2-)]-O<sup>1</sup>,O<sup>2</sup>:O<sup>2</sup>;O<sup>2</sup>:O<sup>1</sup>,O<sup>2</sup>-bis-[dioxovanadate(V)] heptahydrate

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## Abstract

The title complex, Na<sub>2</sub>[V<sub>2</sub>O<sub>4</sub>(C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>)<sub>2</sub>]·7H<sub>2</sub>O, contains the {[V{OC(CH<sub>3</sub>)<sub>2</sub>COO}(O<sub>2</sub>)]<sub>2</sub>}<sup>2-</sup> complex anion in which two five-coordinate inversion-related vanadium centres are doubly bridged by hydroxyl-O atoms and each vanadium centre has distorted trigonal bipyramidal geometry. In the crystals, there are also two Na<sup>+</sup> cations and seven molecules of water of crystallization.

## Comment

Vanadium(V) complexes are of interest because they can act as models for enzyme inhibitors (Crans *et al.*, 1990, 1991). In the structure of ribonuclease A inhibited by vanadate and uridine, reported by Kostrewa *et al.* (1989), the V<sup>V</sup> complex has a trigonal bipyramidal geometry. Hambley *et al.* (1992) prepared the diammonium complex of bis(μ-2-ethyl-2-hydroxybutyrato-O,O,O')dioxovanadium(V), which they reported was stable at room temperature. The title compound, (I), is also very stable and exists as a dimer of two five-coordinate vanadium centres doubly bridged by hydroxyl-O atoms. The V atoms are related by an in-