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

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# Abstract

The title compound, (4-aminophenylimido)trichloro[2-(4-chlorophenyliminomethyl)pyridine]rhenium(V), [Re- $(NC_6H_4NH_2)Cl_3(ClA)$ , where ClA is N-(p-chlorophenyl)pyridine-2-aldimine  $(p-ClC_6H_4N=CHC_5H_4N)$ , was synthesized by reacting the corresponding oxo complex, [ReOCl<sub>3</sub>(ClA)], or the corresponding phosphine oxide complex, [Re(OPPh<sub>3</sub>)Cl<sub>3</sub>(ClA)], with p-phenylenediamine in toluene. The structure determination revealed that the  $ReCl_3N_3$  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-aldimine-chelated  $Re^{V}O$  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>VI</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  $[Re(NC_6H_4-NH_2)Cl_3(ClA)]$ , (1), where ClA is N-(*p*-chlorophenyl)-pyridine-2-aldimine (*p*-ClC<sub>6</sub>H<sub>4</sub>N=CHC<sub>5</sub>H<sub>4</sub>N). This was



synthesized from the oxo complex [ReOCl<sub>3</sub>(ClA)], (2), or from the phosphine oxide complex [Re(OPPh<sub>3</sub>)Cl<sub>3</sub>-(ClA)], (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/Cl2/N2 plane. Additionally, the metal atom is displaced from the N2/Cl1/Cl2/Cl3 mean plane by 0.29 Å towards N3. 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  $\text{Re}^{V}NX$  (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



Fig. 1. A molecular view of (1) showing the atom-numbering scheme. Non-H atoms are represented by 30% displacement ellipsoids. H atoms have been omited for clarity.

Re—N length is known to span the range 1.67-1.74 Å, and the Re—NX moiety is more or less linear (Re— N—C angles are in the range  $167-180^{\circ}$ ), in most cases. This also applies to the present complexes. These values may be compared with those for [Re(NPh)Cl<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>] [1.726 (6) Å and 172.6 (6)°; Forsellini *et al.*, 1984]. Bending of the Re—N—C angle below  $160^{\circ}$  (semibent) is rare (Lahiri *et al.*, 1987; Goeden & Haymore, 1983). The idealized Re—N, Re—N and Re=N bond lengths in Re<sup>V</sup>NX are 2.14, 1.84 and 1.69 Å, respectively (Goeden & Haymore, 1983; Nugent & Haymore, 1980). The distance in the present complex is consistent with a triple bond in the Re–imide fragment.

The Re—N1 bond is longer than Re—N2 by  $\sim 0.15$  Å due to the strong trans influence of the imide N atom. The pyridine N atom is trans to the imide N atom and this is consistent with the qualitative bonding picture having a synergistic aldimine  $\leftarrow$  Re  $\leftarrow$  N<sub>imide</sub>  $\pi$ interaction (Dirghangi, Menon, Banerjee & Chakravorty, 1997; Lahiri et al., 1987). This type of bonding also explains the diamagnetic nature of the complex  $(5d_{n^2})$ . Upon interchanging the positions of the pyridine and aldimine N atoms (i.e. placing the latter trans to the imide N atom), the aldimine  $\pi^*$  orbital fails to interact with the metal  $d_{xy}$  orbitals (participating orbitals for aldimine  $\leftarrow$  Re back-bonding) and the advantage of such bonding is lost. This is also true for the hypothetical facial geometry. Thus, the pyridine N atom is *trans* to the imide N atom as in the observed structure.

## Experimental

 $ReOCl_3(ClA)$ , (2), and  $Re(OPPh_3)Cl_3(ClA)$ , (3), were prepared according to literature methods (Dirghangi, Menon, Pramanik & Chakravorty, 1997) from ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> (Chatt & Rowe, 1962) and their structures confirmed by IR and UVvis spectral analysis, as well as by CHN microanalysis. To a warm solution of (2) or (3) (0.1 mmol) in toluene (10 ml), an excess of p-phenylenediamine (0.5 mmol) was added. The mixture was allowed to reflux for 1 h. The resulting violet solution on chromatographic work-up [silica gel,  $20 \times 1$  cm, 60-120 mesh, BDH; benzene-acetonitrile (5:1) mixture as eluant] gives the desired complex (1) in 80% yield by slow evaporation of the pink-violet eluate. Analysis calculated for C<sub>18</sub>H<sub>15</sub>Cl<sub>4</sub>N<sub>4</sub>Re: C 35.12, H 2.44, N 9.11%; found: C 35.28, H 2.50, N 9.00%. UV-vis data  $[\lambda_{max}, nm (\varepsilon, M^{-1} cm^{-1})]$ : 740 (1460), 540 (7180), 325 (13 285); IR (cm<sup>-1</sup>): 320 and 335 (Re-Cl), 1585 (C=N). Single crystals of (1) suitable for X-ray studies were grown by slow diffusion of hexane into a dichloromethane solution of the complex.

### Crystal data

[Re(C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>)Cl<sub>3</sub>(C<sub>12</sub>H<sub>9</sub>-ClN<sub>2</sub>)]  $M_r = 615.34$ Triclinic  $P\overline{1}$ a = 8.533 (8) Åb = 10.643 (8) Åc = 12.287 (12) Å $\alpha = 110.23 (7)^{\circ}$  $\beta = 92.65 (7)^{\circ}$  $\gamma = 103.34 (7)^{\circ}$  $V = 1009.0 (16) Å^{3}$ Z = 2 $D_x = 2.025 \text{ Mg m}^{-3}$  $D_m$  not measured

## Data collection

Siemens R3m/V diffractom-<br/>eter3307eterI > $\omega$  scans $R_{int} =$ Absorption correction:<br/> $\psi$  scan (North *et al.*,<br/>1968)h = 0 $T_{min} = 0.096$ ,  $T_{max} = 0.194$ I = -3924 measured reflections<br/>3586 independent reflections2 stan

#### Refinement

Refinement on  $F^2$   $R[F^2 > 2\sigma(F^2)] = 0.026$   $wR(F^2) = 0.061$  S = 1.086 3582 reflections 244 parameters H atoms constrained  $w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.4494P]$  $where P = (F_o^2 + 2F_c^2)/3$ 

3307 reflections with  $I > 2\sigma(I)$  $R_{int} = 0.020$ 

Mo  $K\alpha$  radiation  $\lambda = 0.71073$  Å

 $\mu = 6.562 \text{ mm}^{-1}$ 

T = 293 (2) K

Parallelepiped

Dark violet

 $\theta = 7 - 14^{\circ}$ 

Cell parameters from 30 reflections

 $0.40 \times 0.30 \times 0.25$  mm

 $R_{int} = 0.020$   $\theta_{max} = 25.05^{\circ}$   $h = 0 \rightarrow 10$   $k = -12 \rightarrow 12$   $l = -14 \rightarrow 14$ 2 standard reflections every 198 reflections intensity decay: none

 $(\Delta/\sigma)_{max} = 0.001$   $\Delta\rho_{max} = 1.04 \text{ e } \text{\AA}^{-3}$   $\Delta\rho_{min} = -1.50 \text{ e } \text{\AA}^{-3}$ Extinction correction: none Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Re—N3 Re—N2 Re—N1 Re—C11 Re—C13 Re—C12	1.723 (4) 2.052 (4) 2.204 (4) 2.372 (2) 2.382 (3) 2.414 (3)	N1—C5 N1—C1 N2—C6 N2—C7 N3—C13 C1—C6	1.342 (6) 1.357 (6) 1.296 (6) 1.452 (6) 1.375 (6) 1.443 (7)
N3—Rc—N2 N3—Re—N1 N2—Re—C11 N2—Re—C11 N1—Re—C13 N2—Re—C13 N1—Re—C13 N1—Re—C13 C11—Re—C13	95.0 (2) 165.2 (2) 73.8 (2) 102.00 (15) 162.76 (11) 89.93 (12) 102.07 (15) 86.14 (13) 86.97 (13) 87.38 (9)	N3-Re-Cl2 N2-Re-Cl2 N1-Re-Cl2 Cl3-Re-Cl2 Cl3-Re-Cl2 Cl-N1-Re C6-N2-Re Cl3-N3-Re N1C1-C6	90.97 (15) 94.86 (13) 80.70 (13) 87.90 (10) 166.80 (5) 115.3 (3) 120.8 (3) 171.6 (3) 112.7 (4)

The highest electron-density peak (1.04 e  ${\rm \AA}^{-3})$  lies near the Cl4 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[ $\mu$ -2-hydroxy-2-methylpropanoato(2–)]- $O^1$ , $O^2$ : $O^2$ ; $O^2$ : $O^1$ , $O^2$ -bis-[dioxovanadate(V)] heptahydrate

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### Abstract

The title complex,  $Na_2[V_2O_4(C_4H_6O_3)_2]\cdot7H_2O$ , contains the { $[V{OC(CH_3)_2COO}(O_2)]_2$ <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( $\mu$ -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-