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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 $(\mathrm{V})$, [Re$\left.\left(\mathrm{NC}_{6} \mathrm{H}_{4} \mathrm{NH}_{2}\right) \mathrm{Cl}_{3}(\mathrm{ClA})\right]$, where ClA is $N$ - $p$-chloro-phenyl)pyridine-2-aldimine ( $p-\mathrm{ClC}_{6} \mathrm{H}_{4} \mathrm{~N}=\mathrm{CHC}_{5} \mathrm{H}_{4} \mathrm{~N}$ ), was synthesized by reacting the corresponding oxo complex, $\left[\mathrm{ReOCl}_{3}(\mathrm{ClA})\right]$, or the corresponding phosphine oxide complex, $\left[\mathrm{Re}\left(\mathrm{OPPh}_{3}\right) \mathrm{Cl}_{3}(\mathrm{ClA})\right]$, with $p$-phenylenediamine in toluene. The structure determination revealed that the $\mathrm{ReCl}_{3} \mathrm{~N}_{3}$ coordination sphere is severely distorted from octahedral geometry and that it has a meridional $\mathrm{ReCl}_{3}$ fragment. The $\mathrm{Re}-\mathrm{N}-\mathrm{C}$ angle in the imide part is nearly linear and the $\mathrm{Re}-\mathrm{N}_{\text {imide }}$ bond can be considered to be triple bond in character. The Re atom is distorted towards the imide N atom by $0.29 \AA$ from the equatorial $\mathrm{Cl}_{3} \mathrm{~N}_{\text {imine }}$ plane. The $\mathrm{Re}-\mathrm{N}_{\text {pyridine }}$ bond is longer by $0.15 \AA$ than the $\mathrm{Re}-\mathrm{N}_{\text {imine }}$ 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 $\mathrm{Re}^{\vee} \mathrm{O}$ species, (2), which undergoes O-atom transfer to
$\mathrm{PPh}_{3}$, affording an $\mathrm{Re}^{\mathrm{III}} \mathrm{OPPh}_{3}$ species, (3) (Dirghangi, Menon, Pramanik \& Chakravorty, 1997). Both (2) and (3) were found to react with $\mathrm{ArNH}_{2}$, furnishing $\mathrm{Re}^{\vee} \mathrm{NAr}$ species which undergo inward O -atom transfer from water followed by metal oxidation to give rare $\mathrm{Re}^{\mathrm{Vl}} \mathrm{NAr}$ 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 $\mathrm{Re}^{V} \mathrm{NAr}$ compounds.

The species of concern to us here is $\left[\operatorname{Re}\left(\mathrm{NC}_{6} \mathrm{H}_{4}-\right.\right.$ $\left.\left.\mathrm{NH}_{2}\right) \mathrm{Cl}_{3}(\mathrm{ClA})\right]$, (1), where ClA is $N$-( $p$-chlorophenyl)-pyridine-2-aldimine ( $p-\mathrm{ClC}_{6} \mathrm{H}_{4} \mathrm{~N}=\mathrm{CHC}_{5} \mathrm{H}_{4} \mathrm{~N}$ ). This was

(1)
synthesized from the oxo complex $\left[\mathrm{ReOCl}_{3}(\mathrm{ClA})\right]$, (2), or from the phosphine oxide complex $\left[\operatorname{Re}\left(\mathrm{OPPh}_{3}\right) \mathrm{Cl}_{3}-\right.$ (CIA)], (3), with $p$-phenylenediamine in toluene. A view of the molecular structure of (1) is shown in Fig. 1. The $\mathrm{ReCl}_{3} \mathrm{~N}_{3}$ coordination sphere is severely distorted from octahedral geometry. The $\mathrm{ReCl}_{3}$ fragment is meridionally disposed. The chelate ring [bite angle $\left.73.8(2)^{\circ}\right]$ along with the pyridine ring constitute a good plane (mean deviation $0.05 \AA$ ) with which the chlorophenyl group makes a dihedral angle of $61.6(3)^{\circ}$. The aryl group of the imide fragment makes a dihedral angle of $39.5(4)^{\circ}$ with the chlorophenyl group.
An interesting feature of the structure is that the pyridine and imide N atoms ( N 1 and N 3 , respectively) bend towards each other in the direction of the $\mathrm{Re} / \mathrm{C} 12 / \mathrm{N} 2$ plane. Additionally, the metal atom is displaced from the $\mathrm{N} 2 / \mathrm{Cl} 1 / \mathrm{Cl} 2 / \mathrm{Cl} 3$ mean plane by $0.29 \AA$ towards N3. This distortion and bending is necessarily reflected in deviations of the trans angles from $180^{\circ}$ [range $162.8(1)-165.2(2)^{\circ}$ ] and in deviations of the cis angles with respect to N 1 and N 3 from $90^{\circ}$ to the lower and higher side, respectively. Other cis angles are very close to $90^{\circ}$. 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 $\operatorname{Re}^{\mathrm{v}} \mathrm{N} X$ ( $X$ 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.
$\mathrm{Re}-\mathrm{N}$ length is known to span the range $1.67-1.74 \AA$, and the $\mathrm{Re}-\mathrm{N} X$ moiety is more or less linear (Re-$\mathrm{N}-\mathrm{C}$ 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 $\left[\mathrm{Re}\left(\mathrm{NPh}^{2} \mathrm{Cl}_{3}\left(\mathrm{PPh}_{3}\right)_{3}\right]\right.$ [1.726 (6) $\AA$ and $172.6(6)^{\circ}$; Forsellini et al., 1984]. Bending of the $\mathrm{Re}-\mathrm{N}-\mathrm{C}$ angle below $160^{\circ}$ (semibent) is rare (Lahiri et al., 1987; Goeden \& Haymore, 1983). The idealized $\mathrm{Re}-\mathrm{N}, \mathrm{Re}=\mathrm{N}$ and $\mathrm{Re} \equiv \mathrm{N}$ bond lengths in $\mathrm{Re}^{\vee} \mathrm{N} X$ are 2.14, 1.84 and $1.69 \AA$, 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 $\mathrm{Re}-\mathrm{N} 1$ bond is longer than $\mathrm{Re}-\mathrm{N} 2$ by $\sim 0.15 \AA$ 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 $\leftarrow \operatorname{Re} \leftarrow \mathrm{N}_{\text {imide }} \pi$ interaction (Dirghangi, Menon, Banerjee \& Chakravorty, 1997; Lahiri et al., 1987). This type of bonding also explains the diamagnetic nature of the complex ( $5 d_{x_{2}}$ ). 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 $d_{x y}$ 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

$\mathrm{ReOCl}_{3}(\mathrm{ClA})$, (2), and $\mathrm{Re}\left(\mathrm{OPPh}_{3}\right) \mathrm{Cl}_{3}(\mathrm{ClA})$, (3), were prepared according to literature methods (Dirghangi, Menon, Pramanik \& Chakravorty, 1997) from $\mathrm{ReOCl}_{3}\left(\mathrm{PPh}_{3}\right)_{2}$ (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, $20 \times 1 \mathrm{~cm}$, 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 $\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{Cl}_{4} \mathrm{~N}_{4} \mathrm{Re}$ : C 35.12, H 2.44 , $\mathrm{N} 9.11 \%$; found: C 35.28, H 2.50 , N $9.00 \%$. UV-vis data $\left[\lambda_{\max }, \mathrm{nm}\left(\varepsilon, M^{-1} \mathrm{~cm}^{-1}\right)\right.$ ]: 740 (1460), 540 ( 7180 ), 325 ( 13285 ); IR ( $\mathrm{cm}^{-1}$ ): 320 and 335 ( $\mathrm{Re}-\mathrm{Cl}$ ), $1585(\mathrm{C}=\mathrm{N})$. 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

$\left[\operatorname{Re}\left(\mathrm{C}_{6} \mathrm{H}_{6} \mathrm{~N}_{2}\right) \mathrm{Cl}_{3}\left(\mathrm{C}_{12} \mathrm{H}_{9}-\right.\right.$ $\mathrm{ClN}_{2}$ )]
$M_{r}=615.34$
Triclinic
$P \overline{1}$
$a=8.533(8) \AA$ 。
$b=10.643(8) \AA$
$c=12.287(12) \AA$
$\alpha=110.23(7)^{\circ}$
$\beta=92.65$ (7) ${ }^{\circ}$
$\gamma=103.34$ (7) ${ }^{\circ}$
$V=1009.0(16) \AA^{3}$
$Z=2$
$D_{x}=2.025 \mathrm{Mg} \mathrm{m}^{-3}$
$D_{m}$ not measured

## Data collection

Siemens $R 3 \mathrm{~m} / V$ diffractometer
$\omega$ scans
Absorption correction:
$\psi$ scan (North et al., 1968)
$T_{\text {min }}=0.096, T_{\text {max }}=0.194$
3924 measured reflections
3586 independent reflections

## Refinement

Refinement on $F^{2}$
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.026$
$w R\left(F^{2}\right)=0.061$
$S=1.086$
3582 reflections
244 parameters
H atoms constrained
$w=1 /\left[\sigma^{2}\left(F_{o}^{2}\right)+(0.0416 P)^{2}\right.$
$+0.4494 P]$
where $P=\left(F_{o}^{2}+2 F_{c}^{2}\right) / 3$

Mo $K \alpha$ radiation
$\lambda=0.71073 \AA$
Cell parameters from 30 reflections
$\theta=7-14^{\circ}$
$\mu=6.562 \mathrm{~mm}^{-1}$
$T=293$ (2) K
Parallelepiped
$0.40 \times 0.30 \times 0.25 \mathrm{~mm}$
Dark violet

3307 reflections with
$I>2 \sigma(I)$
$R_{\mathrm{int}}=0.020$
$\theta_{\text {max }}=25.05^{\circ}$
$h=0 \rightarrow 10$
$k=-12 \rightarrow 12$
$l=-14 \rightarrow 14$
2 standard reflections every 198 reflections intensity decay: none

$$
\begin{aligned}
& (\Delta / \sigma)_{\max }=0.001 \\
& \Delta \rho_{\max }=1.04 \mathrm{e}^{-3} \\
& \Delta \rho_{\min }=-1.50 \mathrm{e}^{-3}
\end{aligned}
$$

Extinction correction: none Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters $\left(\AA,{ }^{\circ}\right)$

| $\mathrm{Re}-\mathrm{N} 3$ | $1.723(4)$ | $\mathrm{N} 1-\mathrm{C} 5$ | $1.342(6)$ |
| :--- | :---: | :--- | :---: |
| $\mathrm{Re}-\mathrm{N} 2$ | $2.052(4)$ | $\mathrm{N} 1-\mathrm{Cl}$ | $1.357(6)$ |
| $\mathrm{Re}-\mathrm{N} \mathrm{l}$ | $2.204(4)$ | $\mathrm{N} 2-\mathrm{C} 6$ | $1.296(6)$ |
| $\mathrm{Re}-\mathrm{Cl} 1$ | $2.372(2)$ | $\mathrm{N} 2-\mathrm{C} 7$ | $1.452(6)$ |
| $\mathrm{Re}-\mathrm{Cl} 3$ | $2.382(3)$ | $\mathrm{N} 3-\mathrm{Cl} 3$ | $1.375(6)$ |
| $\mathrm{Re}-\mathrm{Cl} 2$ | $2.414(3)$ | $\mathrm{C} 1-\mathrm{C} 6$ | $1.443(7)$ |
| $\mathrm{N} 3-\mathrm{Re}-\mathrm{N} 2$ | $95.0(2)$ | $\mathrm{N} 3-\mathrm{Re}-\mathrm{Cl} 2$ | $90.97(15)$ |
| $\mathrm{N} 3-\mathrm{Re}-\mathrm{N} 1$ | $165.2(2)$ | $\mathrm{N} 2-\mathrm{Re}-\mathrm{Cl} 2$ | $94.86(13)$ |
| $\mathrm{N} 2-\mathrm{Re}-\mathrm{N} 1$ | $73.8(2)$ | $\mathrm{N} 1-\mathrm{Re}-\mathrm{Cl} 2$ | $80.70(13)$ |
| $\mathrm{N} 3-\mathrm{Re}-\mathrm{Cl} 1$ | $102.00(15)$ | $\mathrm{Cll}-\mathrm{Re}-\mathrm{Cl} 2$ | $87.90(10)$ |
| $\mathrm{N} 2-\mathrm{Re}-\mathrm{Cl} 1$ | $162.76(11)$ | $\mathrm{Cl} 3-\mathrm{Re}-\mathrm{Cl} 2$ | $166.80(5)$ |
| $\mathrm{N} 1-\mathrm{Re}-\mathrm{Cll}$ | $89.93(12)$ | $\mathrm{Cl}-\mathrm{Nl}-\mathrm{Re}$ | $115.3(3)$ |
| $\mathrm{N} 3-\mathrm{Re}-\mathrm{Cl} 3$ | $102.07(15)$ | $\mathrm{C} 6-\mathrm{N} 2-\mathrm{Re}$ | $120.8(3)$ |
| $\mathrm{N} 2-\mathrm{Re}-\mathrm{Cl} 3$ | $86.14(13)$ | $\mathrm{C} 13-\mathrm{N} 3-\mathrm{Re}$ | $171.6(3)$ |
| $\mathrm{N} 1-\mathrm{Re}-\mathrm{Cl} 3$ | $86.97(13)$ | $\mathrm{N} 1-\mathrm{Cl}-\mathrm{C} 6$ | $112.7(4)$ |
| $\mathrm{Cl1}-\mathrm{Re}-\mathrm{Cl} 3$ | $87.38(9)$ |  |  |

The highest electron-density peak ( $1.04 \mathrm{e} \AA^{-3}$ ) lies near the Cl 4 atom.

Data collection: SHELXTL-Plus90 (Sheldrick, 1990). Cell refinement: SHELXTL-Plus90. Data reduction: SHELXTLPlus90. 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, $\mathrm{Na}_{2}\left[\mathrm{~V}_{2} \mathrm{O}_{4}\left(\mathrm{C}_{4} \mathrm{H}_{6} \mathrm{O}_{3}\right)_{2}\right] \cdot 7 \mathrm{H}_{2} \mathrm{O}$, contains the $\left\{\left[\mathrm{V}\left\{\mathrm{OC}\left(\mathrm{CH}_{3}\right)_{2} \mathrm{COO}\right\}\left(\mathrm{O}_{2}\right)\right]_{2}\right\}^{2-}$ 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 $\mathrm{Na}^{+}$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 $\mathrm{V}^{\mathrm{V}}$ complex has a trigonal bipyramidal geometry. Hambley et al. (1992) prepared the diammonium complex of $\operatorname{bis}(\mu$-2-ethyl-2-hy-droxybutyrato- $O, O, O^{\prime}$ )dioxovanadium $(\mathrm{V})$, 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-

