Versatility of Bidentate Aniline Derivatives as Ligands for Rhenium(V) and Technetium(V)

T. I. A. Gerber^{*,a} and P. Mayer^b

^aChemistry Department, Nelson Mandela Metropolitan University, Port Elizabeth 6031, South Africa

^bChemistry Department, Ludwig-Maximilians University, D-81377 München, Germany

Received: July 31, 2005; In Final Form: September 30, 2005

The versatility of aniline derivatives as ligands for Re(V) and Tc(V) has been investigated. The reaction of (*n*-Bu₄N)[MOCl₄] (M=Re, Tc) with 1,2-diaminobenzene (H₂dab) and 2,3-diaminopyridine (H₂dap) gave the products (Bu₄N)[MO(dab)₂] (**1**) and [MO(dapH)₂]Cl (**2**) respectively. Both chelates in **1** and **2** are coordinated as diamides; however, in **2** the pyridine nitrogens of dapH are protonated. With *trans*-[ReOCl₃(PPh₃)₂] as a starting complex, a number of products were isolated, depending on the reaction conditions. For example, with 3-hydroxy-1,2-diaminobenzene (H₂dab-OH) under N₂, [Re(dab-OH)Cl₃(PPh₃)₂] (**3**) was produced, in which dab-OH substituted the oxo group and is coordinated as a monodentate imide. With 3-nitro-1,2-diaminobenzene (H₂dab-NO₂), the oxo-free complex [ReCl(PPh₃)₂(dab-NO₂)₂] (**4**) was obtained, with bidentate diamido coordination of each chelate. Using *trans*-[ReO₂(py)₄]Cl as a starting complex, complexes of the type [Re(sbqdi-OH)₃]Cl (**5**) and *cis*-[ReO₂(Hdab)(py)₂] (**6**) were isolated, where sbqdi-OH coordinates as the monoanionic semibenzoquinonediimine and Hdab as a bidentate monoamide. The crystal structures of these complexes are discussed in this account.

1. Introduction

The current widespread interest in the coordination chemistry of rhenium and technetium is mainly due to the potential application of the radioisotopes ¹⁸⁶Re and ¹⁸⁸Re in radiotherapy and the utilization of ^{99m}Tc in diagnostic nuclear medicine.¹ Our interest is focused on the synthesis of Re(V) and Tc(V) complexes containing 1,2-diaminobenzene (H₂dab) and its derivatives. In fact, increasing attention has lately been devoted to metal complexes derived from H₂dab, mainly because of their unusual structural, magnetic and redox properties.^{2,3} In these complexes it was found that the diamine can be present as the 1,2-diamide dianion (dab²⁻), the 1,2-benzosemiquinone diimine (sbqdi) or the neutral 1,2-benzoquinone diimine (bqdi).

In addition to dab and sbqdi, this account also reports on unusual Re(V)/Tc(V) complexes containing the following forms of H₂dab derivatives:

2. Experimental

Materials. *trans*-[ReOCl₃(PPh₃)₂], (*n*-Bu₄N)[MOCl₄] (M=Tc/Re) and *trans*-[ReO₂(py)₄]Cl were synthesized by literature methods.⁴⁻⁷ H₂dab and its derivatives were obtained commercially (Aldrich), and their purities were checked by NMR spectroscopy and melting points. Solvents were of reagent grade and were purified and dried before use. All other chemicals were obtained commercially.

*Corresponding author. E-mail: thomas.gerber@nmmu.ac.za. FAX: +27-41-5044236.

Synthesis of complexes

(*n*-Bu₄N)[MO(dab)₂] (M = Tc(**1a**), Re(**1b**)). A mixture of 150 μmol of (*n*-Bu₄N)[MOCl₄] and 450 μmol of H₂dab in 30 mL of ethanol was stirred at room temperature for 18 h (for Tc) or heated under reflux for 90 min (for Re) in air. After the reaction periods orange precipitates were collected, washed with ethanol and diethyl ether, and dried. Recrystallisation from acetone/ethanol gave crystals suitable for X-ray analysis. IR: **1a**: ν(Tc=O) 891, ν(Tc-N) 432; **1b**: ν(Re=O) 936, ν(Re-N) 452 cm⁻¹.

[MO(dapH)₂]Cl·2H₂O (M=Tc(**2a**), Re(**2b**)). (*n*-Bu₄N)[MOCl₄] (150 μmol) and 300 μmol of H₂dap were dissolved in 20 mL of a 10:1 benzene/ethanol solvent mixture, and heated under reflux for 60 min. After cooling to room temperature, the solutions were filtered and left to evaporate slowly at room temperature. After two days crystals, suitable for X-ray studies, were collected. IR: **2a**: ν(Tc=O) 931, ν(Tc-N) 454; **2b**: ν(Re=O) 956, ν(Re-N) 469 cm⁻¹.

[Re(dab-OH)Cl₃(PPh₃)₂] (**3**). To a quantity of 180 μmol of *trans*-[ReOCl₃(PPh₃)₂] in 20 mL of ethanol were added 200 μmol of H₂dap-OH, and the mixture was heated under reflux under a N₂ atmosphere for 90 min. After cooling to room temperature, a precipitate was filtered off, washed with ethanol and diethyl ether, and dried. Further slow evaporation of the filtrate gave crystals suitable for X-ray crystallography. IR: ν(Re=N-) 1092; ν(Re-Cl) 313, 295 cm⁻¹.

[ReCl(PPh₃)₂(dab-NO₂)₂] (**4**). A mixture of 130 μmol of *trans*-[ReOCl₃(PPh₃)₂] and 260 μmol of H₂dab-NO₂ in 30 mL of ethanol was heated under reflux for 3 h. After cooling a red-brown solid was removed by filtration, washed with EtOH and Et₂O and dried under vacuum. Recrystallization was from acetone. IR: ν(Re-Cl) 301 cm⁻¹.

[Re^{IV}(sbqdi-OH)₃]Cl (**5**). A mixture of 170 μmol of *trans*-[ReO₂(py)₄]Cl and 520 μmol of H₂dab-OH in 30 mL of ethanol was stirred at room temperature for 18 h in air. After the reaction period the solution was filtered and left to evaporate slowly at room temperature. After 3 days green-black crystals, suitable for X-ray analysis, were collected. IR: ν(Re-N) 507 cm⁻¹.

cis-[ReO₂(Hdab)(py)₂] (**6**). A mixture of 150 μmol of *trans*-[ReO₂(py)₄]Cl and 305 μmol of H₂dab in 15 mL of ethanol was stirred at room temperature for 30 h. After the reaction period

TABLE 1: Crystal and Structure Refinement Data

Crystal system Space group	1 Orthorhombic $P2_12_12_1$	2b Triclinic $P\bar{1}$	3 Monoclinic $P2_1/n$	4 Monoclinic $P2_1/c$	5 Hexagonal $P6$	6 Triclinic $P\bar{1}$
$a(\text{\AA})$	11.644(3)	7.1477(2)	12.127(1)	14.937(11)	13.535(2)	9.570(2)
$b(\text{\AA})$	15.303(4)	9.2464(4)	14.385(1)	15.017(8)	13.535(2)	12.493(3)
$c(\text{\AA})$	16.950(5)	12.1316(5)	21.711(1)	15.394(12)	8.394(2)	12.851(3)
$\alpha(^{\circ})$	90	73.838(1)	90	90	90	61.60(3)
$\beta(^{\circ})$	90	78.658(2)	99.09(1)	112.12(6)	90	70.56(3)
$\gamma(^{\circ})$	90	73.786(1)	90	90	120	78.68(4)
$V(\text{\AA}^3)$	3020.3(2)	733.29(5)	3740.0(6)	3199(4)	1331.7(3)	1273.1(4)
Z	4	2	4	4	2	2
Reflections obs.	1568 ¹	3004 ²	4702 ²	1739 ²	2194 ²	3519 ²
R	0.058	0.0299	0.061	0.0807	0.0566	0.048
GOF	1.29	1.08	1.07	1.07	1.10	1.06

¹for $|F_o| > 3\sigma(F_o)$; ²for $|F_o| > 2\sigma(F_o)$

a purple precipitate was collected. The slow evaporation of the mother liquor over a period of 3 days at room temperature gave crystals suitable for X-ray crystallography. IR: $\nu_s(\text{ReO}_2)$ 905, $\nu_a(\text{ReO}_2)$ 876 cm^{-1} .

Physical measurements. The instrumentation used is the same as reported earlier.⁸ A Nicolet Siemens R3m/V (for **1a**, **3**, **4**) and a Nonius Kappa CCD (for **2b**, **5**, **6**) diffractometer were used. Crystal and structure refinement data are given in Table 1. Structural refinements were made by the full-matrix least-squares method on F^2 using the program SHELXL97.⁹

3. Results and Discussion

Structure of 1a. This complex (Figure 1) shows a square-pyramidal geometry with the oxo group occupying the apical position, with the Tc atom lying above the mean plane defined by the four amido nitrogens by 0.67 $\text{\AA}$. On coordination to the Tc(V) center, the two bidentate ligands both lose two amine

Figure 1. Structure of the $[\text{TcO}(\text{dab})_2]^+$ anion. (Tc-O = 1.668(7), Tc-N(1) = 1.99(1), Tc-N(2) = 1.98(1), C(1)-N(1) = 1.38(2) $\text{\AA}$; O-Tc-N(1) = 109.3(4), O-Tc-N(2) = 110.0(4), N(1)-Tc-N(2) = 78.8(5) $^{\circ}$).

Figure 2. The molecular structure of $[\text{ReO}(\text{dapH})_2]\text{Cl}$. (Re-O(1) = 1.688(4), Re-N(2) = 2.002(4), Re-N(3) = 1.995(4), C(1)-N(1) = 1.346(7) $\text{\AA}$; O(1)-Re-N(2) = 108.7(2), O(1)-Re-N(3) = 110.1(2), Re-N(3)-C(2) = 117.6(3), N(2)-Re-N(6) = 141.4(2) $^{\circ}$).

protons to form an anionic complex. The Tc=O distance of 1.668(7) $\text{\AA}$ is typical, and the Tc-N distance (mean 1.98(1) $\text{\AA}$) is intermediate between Tc=N (1.91 $\text{\AA}$) and Tc-NH₂ (2.08 $\text{\AA}$).¹⁰ The angles around the nitrogens are in the order of 120 $^{\circ}$, consistent with sp^2 -hybridization. The average bite angle of the two dab chelates is 78.9 $^{\circ}$.

Structure of 2b. The complex (Figure 2) has a square-pyramidal geometry with the Re atom lying 0.68 $\text{\AA}$ above the plane defined by the four amido nitrogen atoms. The Re = O distance of 1.688(4) $\text{\AA}$ is typical for monooxorhenium(V) complexes, and the Re-N distances (mean = 1.993(5) $\text{\AA}$) are similar to those found for Re-amide bonds.¹¹ The average bite angle of the two chelates is 77.4 $^{\circ}$. Protonation of the pyridyl nitrogen atoms has a minor effect on the aromaticity of the rings, with a slight deviation from planarity. The packing of the molecules in the crystal is essentially achieved by hydrogen bonds between Cl⁻, NH and H₂O. The Cl⁻ counterion hydrogen-bonds to the protons on the pyridyl N(1) [N(1)-H...Cl = 3.380(5) $\text{\AA}$] and N(2) [N(2)-H...Cl = 3.378(5) $\text{\AA}$]. The proton on the pyridyl N(4) is hydrogen-bonded to O(2) of a water molecule (2.982(7) $\text{\AA}$).

Structure of 3. The complex (Figure 3) exhibits an approximate octahedral geometry with the Re(V) atom displaced from the mean Cl(1)P(1)Cl(3)P(2) plane by 0.08 $\text{\AA}$ towards N(1). The 2,3-diaminophenol ligand acts as a dianionic moiety, and the Re-N(1)-C(1) bond angle (179.5(7) $^{\circ}$) emphasizes the linear coordination mode of the triply bonded phenylimido unit, and

Figure 3. An ORTEP view of $[\text{Re}(\text{dab-OH})\text{Cl}_3(\text{PPh}_3)_2]$. (Re-N(1) = 1.730(9), Re-P(1) = 2.475(3), Re-P(2) = 2.502(3), Re-Cl(1) = 2.421(3), Re-Cl(2) = 2.442(3), Re-Cl(3) = 2.420(2) $\text{\AA}$; N(1)-Re-Cl(2) = 176.7(3), P(1)-Re-P(2) = 177.8(1), N(1)-Re-P(1) = 89.7(3), N(1)-Re-Cl(1) = 93.5(3) $^{\circ}$).

Figure 4. The molecular structure of $[\text{ReCl}(\text{PPh}_3)(\text{dab-NO}_2)_2]$. ($\text{Re-Cl} = 2.393(9)$, $\text{Re-P}(1) = 2.431(9)$, $\text{Re-N}(1) = 1.98(3)$, $\text{Re-N}(2) = 1.96(2)$ Å; $\text{N}(1)\text{-Re-N}(2) = 77(1)$, $\text{Re-N}(1)\text{-C}(1) = 120(2)$, $\text{Cl-Re-N}(1) = 139.1(8)^\circ$).

Figure 5. Molecular view for the monocation $[\text{Re}(\text{sbqdi-OH})_3]^+$. ($\text{Re-N}(1) = 2.049(10)$, $\text{Re-N}(2) = 1.887(19)$, $\text{N}(1)\text{-C}(1) = 1.29(1)$, $\text{N}(2)\text{-C}(2) = 1.53(2)$ Å; $\text{N}(1)\text{-Re-N}(2) = 77.5(3)$, $\text{C}(1)\text{-N}(1)\text{-Re} = 118(1)^\circ$).

the $\text{Re-N}(1)$ distance of $1.730(9)$ Å agrees with the values found in other Re(V) -phenylimido octahedral complexes.¹² The phenylimido moiety is virtually perpendicular to the mean equatorial plane (dihedral angle of $89.2(3)^\circ$), and to minimize steric congestion around the metal atom, the ligand fits between two phenyl rings.

Structure of 4. The crystal structure (Figure 4) shows that **4** exhibits a skew-trapezoidal bipyramidal geometry. The complex contains two dinegative dab- NO_2 ligands symmetrically coordinated to the Re(V) centre. The four Re-NH bond distances have an average of $1.98(2)$ Å, with the Re-P bond ($2.43(1)$ Å) shorter than in other Re(V) complexes.¹³ The Re-Cl bond length ($2.393(9)$ Å) is within the range observed for a large variety of Re(V) oxo complexes.¹⁴ The Re , Cl and $\text{P}(1)$ atoms are above the $\text{N}(1)$, $\text{N}(2)$, $\text{N}(1')$, $\text{N}(2')$ mean plane by 0.72 , 2.51 and 2.57 Å, respectively. The two dab- NO_2 ligands make a dihedral angle of 60.3° .

Structure of 5. The rhenium atom is at the center of a trigonal-prismatic environment (Figure 5). The $\text{Re-N}(2)$ bond is short at $1.89(2)$ Å, and is indicative of bonding of an amide ($-\text{NH}$) to Re . The longer $\text{Re-N}(1)$ bond ($2.05(1)$ Å) indicates a single bond with the quinone imine ($=\text{NH}$) nitrogen. This value compares well with other $\text{Re-N}(\text{imine})$ bonds, which vary in the range $2.03(1)\text{--}2.15(1)$ Å.¹⁵ Bonding in the ligand is of particular

Figure 6. The $\text{cis-}[\text{ReO}_2(\text{Hdab})(\text{py})_2]$ neutral complex. ($\text{Re-O}(1) = 1.723(7)$, $\text{Re-O}(2) = 1.716(6)$, $\text{Re-N}(1) = 2.053(8)$, $\text{Re-N}(2) = 2.042(9)$, $\text{Re-N}(3) = 2.163(9)$, $\text{Re-N}(4) = 2.155(9)$ Å; $\text{O}(1)\text{-Re-O}(2) = 118.2(3)$, $\text{O}(1)\text{-Re-N}(1) = 157.8(3)$, $\text{O}(1)\text{-Re-N}(2) = 85.2(3)$, $\text{N}(3)\text{-Re-N}(4) = 174.3(3)$, $\text{N}(1)\text{-Re-N}(2) = 72.7(3)^\circ$).

interest. The $\text{C}(1)\text{-N}(1)$ bond ($1.29(2)$ Å) is short, consistent with a localized double bond of the sbqdi form. The $\text{C}(2)\text{-N}(2)$ bond is long ($1.53(2)$ Å) and indicates a localized single bond. The six-membered ring of the benzosemiquinone diimine displays typical quinoid distortions. The $\text{C}(5)\text{-C}(6)$ length of $1.26(4)$ Å is short and indicative of a localized double bond, as would be expected for the sbqdi form with a $\text{C}(1)\text{-N}(1)$ double bond. The assignment of a $+IV$ oxidation state to Re is thus justified on the basis of the crystallographic data.

Structure of 6. The rhenium atom is at the center of a distorted octahedral environment (Figure 6). The small bite angle (72.7°) of Hdab may be responsible for the *cis* orientation of the two oxo groups, which have an $\text{O}(1)\text{-Re-O}(2)$ angle of 118.2° . The mean planes of the pyridines define angles of 97.1° and 87.5° with the Hdab plane, and the mean planes passing through the pyridines define an angle to each other of only 12.5° . The $\text{N}(3)\text{-Re-N}(4)$ angle deviates from linearity ($174.3(3)^\circ$), and the $\text{Re}=\text{O}$, Re-N_{py} and $\text{Re-N}_{\text{amine}}$ bond lengths fall within the reported limits.¹⁶

4. Conclusions

This report illustrates the versatility of 1,2-diaminobenzene and its derivatives as ligands for Re(V) and Tc(V) . A variety of unusual complexes of these metals, containing different coordination modes of the chelate H_2dab , were prepared by using different starting materials and reaction conditions.

References

- (1) J. R. Dilworth and S. J. Parrott, *Chem. Soc. Rev.* **27**, 43 (1998).
- (2) C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.* **38**, 45 (1981).
- (3) M. J. O'Connor, *Prog. Inorg. Chem.* **14**, 241 (1971).
- (4) N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *Inorg. Synth.* **9**, 145 (1967).
- (5) F. A. Cotton, A. Davison, V.W. Day, L. D. Gage, and H. S.

- Trop, *Inorg. Chem.* **18**, 3024 (1979).
- (6) M. S. Ram and J. T. Hupp, *Inorg. Chem.* **30**, 130 (1991).
- (7) T. Lis and B. Jezowska-Trzebiatowska, *Acta Cryst.* **B33**, 1248 (1977).
- (8) T. I. A. Gerber, D. Luzipo, and P. Mayer, *J. Coord. Chem.* **57**, 1345 (2004).
- (9) G. M. Sheldrick, *SHELX-97, Program for Refinement of Crystal Structures* (University of Göttingen, Germany, 1997).
- (10) P. R. Sharp and D. E. Troutner, *Inorg. Chem.* **26**, 3576 (1987).
- (11) T. I. A. Gerber, D. Luzipo, and P. Mayer, *J. Coord. Chem.* **57**, 1399 (2004).
- (12) M. Bakir, S. Paulson, P. Goodson, and B. P. Sullivan, *Inorg. Chem.* **31**, 1127 (1992).
- (13) T. I. A. Gerber, D. Luzipo, and P. Mayer, *J. Coord. Chem.* **57**, 1419 (2004).
- (14) T. I. A. Gerber, D. Luzipo, and P. Mayer, *J. Coord. Chem.* **57**, 1393 (2004).
- (15) G. Gilli, M. Sacerdoti, V. Bertolasi, and R. Rossi, *Acta Cryst.* **B28**, 100 (1982).
- (16) A. Abrahams, G. Bandoli, S. Gatto, T. I. A. Gerber, and J. G. H. du Preez, *J. Coord. Chem.* **42**, 303 (1997).