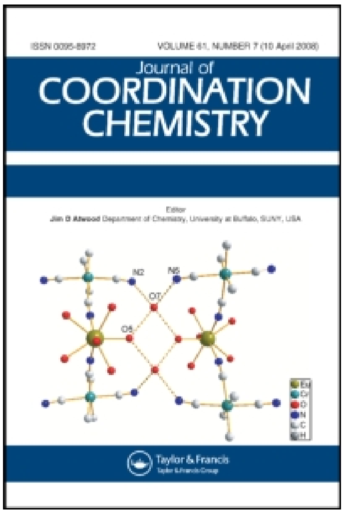

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses and Structures of *Tris*-(1,2-Benzosemiquinone DIimine) Complexes of Rhenium(IV)

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To cite this Article Gerber, T. I. A. , Luzipo, D. , Mayer, P. , Van Brecht, B. J. A. M. and Preez, J. G. H. Du(2003) 'Syntheses and Structures of *Tris*-(1,2-Benzosemiquinone DIimine) Complexes of Rhenium(IV)', Journal of Coordination Chemistry, 56: 12, 1049 — 1061

To link to this Article: DOI: 10.1080/00958970310001596764

URL: http://dx.doi.org/10.1080/00958970310001596764

J. Coord. Chem., Vol. 56, No. 12, 15 August 2003, pp. 1049–1061

SYNTHESES AND STRUCTURES OF *TRIS*-(1,2-BENZOSEMIQUINONE DIIMINE) COMPLEXES OF RHENIUM(IV)

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(Received 24 February 2003; In final form 06 May 2003)

Reactions of *trans*-[$ReO_2(py)_4Cl$] and *cis*-[$ReO_2I(PPh_3)_2$] with 2,3-diaminophenol (H_2dab-OH) and 1,2-diaminobenzene (H_2dab), respectively, in ethanol under aerobic conditions led to the corresponding isolation of [Re(sbqdi-OH)$_3$]Cl (**1**) and [Re(sbqdi)$_3$]I (**2**). Crystallographic data show that the ligand sbqdi represents the monoanionic N,N-coordinated π-radical form of the 1,2-benzosemiquinone diimine of H_2dab. The ligands in Complex **1** clearly show semiquinoid character; e.g., the two C–N and two Re–N bondlengths differ considerably. In **2**, the phenyl rings display typical quinoid distortions with two localized double bonds, and the C–N bondlengths are short, approaching double bonds. Rhenium is formally in the +IV oxidation state.

Keywords: Crystal structure; Rhenium(IV); Semiquinone diimine; π-Radical

INTRODUCTION

Current widespread interest in the coordination chemistry of rhenium is mainly due to the potential application of the radioisotopes ^{186}Re and ^{188}Re in radiotherapy [1]. Our interest is focussed on the synthesis of rhenium(V) complexes containing the molecule 1,2-diaminobenzene (H_2dab) and its derivatives. In fact, increasing attention has lately been devoted to metal complexes derived from H_2dab, mainly because of their unusual redox, magnetic and structural properties [2, 3]. In these compounds, H_2dab can be present as the 1,2-diamine dianion (dab), the 1,2-benzosemiquinone diimine π-radical mono-anion (sbqdi), or the neutral 1,2-benzoquinone diimine

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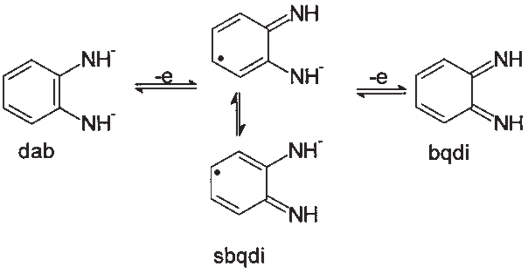
ISSN 0095-8972 print: ISSN 1029-0389 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/00958970310001596764

(bqdi). These three forms are related by two one-electron oxidation–reduction steps, and there are several unusual examples in which the metal and/or the ligands are reduced or oxidized [4]. Crystallographic studies of metal complexes derived from the non-innocent redox ligand H_2dab have been instrumental in assigning oxidation states both to the metal and to the ligands. This is well illustrated by the case of the *o*-quinone complexes, in which the redox series "*o*-quinone, *o*-semiquinone and catechol" is easily monitored by X-ray studies [2, 5]. The dab form has been found in $[TcO(dab)_2]^-$ [6], the sbqdi form exists in diamagnetic square-planar complexes of d^8 metal ions [7], while bqdi forms *tris*-α-diimine complexes with d^6 metal ions [8].



We have found that H_2dab and its derivatives are versatile ligands for rhenium(V). The imido form dab $[(N)(NH_2)C_6H_4]$ was discovered in the complex $[Re^V(dab)Cl_3(PPh_3)_2]$ [9], and the diamide form in the oxo-free complex $[Re^V(dab)_2Cl(PPh_3)]$ [10]. The *cis*-dioxo complex $[Re^VO_2(Hdab)(py)_2]$ contains the terminally reduced monoanionic monoamide form [11]. The simple substitution reaction of $[ReOCl_4]^-$ with H_2dab leads to the formation of $[Re^VO(dab)_2]^-$ [12].

We have now managed to prepare and structurally characterize the rhenium(IV) *tris*-complexes $[Re(sbqdi\text{-}OH)_3]Cl$ (**1**) and $[Re(sbqdi)_3]I$ (**2**). These were formed by the reactions of *trans*-$[ReO_2(py)_4]Cl$ and *cis*-$[ReO_2I(PPh_3)_2]$ with 2,3-diaminophenol (H_2dab-OH) and 1,2-diaminobenzene (H_2dab) in the presence of oxygen in ethanol, respectively.

EXPERIMENTAL

Reagents

trans-$[ReO_2(py)_4]Cl$ and *cis*-$[ReO_2I(PPh_3)_2]$ were synthesized by literature methods [13]. 2,3-Diaminophenol and 1,2-diaminobenzene were obtained commercially (Aldrich), and their purities were checked by ^{1}H NMR spectroscopy and melting point. Solvents were of reagent grade, and were purified and dried before use. All other chemicals were obtained commercially.

Synthesis of $[Re(sbqdi\text{-}OH)_3]Cl$ (1)

A mixture of 100 mg (174 μmol) of *trans*-$[ReO_2(py)_4]Cl$ and 65 mg (524 μmol) of 2,3-diaminophenol (H_2dab-OH) in 30 mL of ethanol was stirred at room temperature for 18 h in the presence of air. The original red-orange solution gradually turned to a jade-green color, and after the reaction period the reaction solution was filtered and left to evaporate slowly at room temperature. After three days, dark, green-black crystals, suitable for X-ray analysis, with the formulation **1** · H_2O, were collected. They were washed with dichloromethane and diethyl ether, and dried under vacuum. Yield= 54%, m.p. > 300°C. Anal. Calcd. for $C_{18}H_{20}N_6O_4ClRe$ (%): C, 35.67; H, 3.33; N, 13.87. Found: C, 35.83; H, 3.59; N, 13.63. IR(KBr): ν(NH) 3252, 3380; ν(Re–N) 507, 478sh; ν(C–N) 1255; ν(C=C) 1585; ν(C=N) 1601 cm^{-1}. ^1H NMR (295 K) ppm: 13.48 (s, 3H, *NH*), 13.68 (s, 3H, *NH*), 10.75 (br s, 3H, *OH*), 6.39 (d, 3H, *H*(4), $J = 7.3$ Hz), 6.83 (t, 3H, *H*(5), $J = 7.9$ Hz), 6.92 (d, 3H, *H*(6), $J = 7.9$ Hz). Electronic spectrum (CH_3CN): $\lambda_{max}(\varepsilon,\ M^{-1}\,cm^{-1})$: 674 (24 100), 405 (17 000), 383 (18 600). Conductivity (DMF, 10^{-3} M): 63 $ohm^{-1}\,cm^2\,mol^{-1}$.

Synthesis of [Re(sbqdi)$_3$]I (2)

cis-[$ReO_2I(PPh_3)_2$] (100 mg, 115 µmol) in 20 mL of ethanol was mixed with 50 mg (463 µmol) of 1,2-diaminobenzene. The mixture was stirred for 15 h, and heated under reflux for 30 min in the presence of air. After cooling to room temperature, a purple precipitate was obtained from the very dark green solution. The precipitate was filtered off, washed with toluene and diethyl ether and dried under vacuum. Recrystallization was from a 1 : 1 mixture of methanol/acetonitrile. Slower evaporation of the recrystallization mother liquor gave crystals suitable for X-ray diffraction studies. Yield = 67%, m.p. 238°C. Anal. Calcd. for $C_{18}H_{18}N_6IRe$ (%): C, 34.24; H, 2.87; N, 13.31. Found: C, 34.36; H, 2.93; N, 13.11. IR(KBr): ν(NH) 3314, ν(Re–N) 573; ν(C$\cdots$N)1375; ν(C=C) 1551 cm^{-1}. ^1H NMR (295 K) ppm: 13.69 (s, 6H, *NH*), 7.42 (m, 6 H, H(3), H(6)), 7.00 (m, 6 H, *H*(4), *H*(5), $J_{AB} = 3.35$ Hz). Electronic spectrum (CH_3CN): $\lambda_{max}(\varepsilon,\ M^{-1}\,cm^{-1})$: 675 (18 400), 408 (15 400), 390 (16 000). Conductivity (CH_3CN, 10^{-3} M): 36 $ohm^{-1}\,cm^2\,mol^{-1}$.

Physical Measurements

The instrumentation used in this study is the same as reported earlier [6]. IR spectra were obtained in KBr discs and ^1H NMR spectra were run in d_6-DMSO.

X-ray Data Collection, Structure Solution and Refinement

Intensity data for **1** · H_2O were collected on a Bruker SMART 1 K CCD area detector diffractometer with graphite-monochromated Mo Kα radiation. The collection method involved ω-scans of width 0.3°. Data reduction was carried out using the program *SAINT+* [14a] and absorption corrections were made using the program *SADABS* [14b]. Structure determinations were performed using WinGX [14c]. The structure was solved by direct methods using *SHELXTS* [15a]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculation based on F^2 using *SHELXTL* [15a]. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication material were generated using SHELXTS and ORTEP-III [15b].

A water molecule is present in the lattice of **1** with site occupation factor of less than one. This was not refined anisotropically. However, the water molecule did not interfere with the coordination sphere of the complex and is therefore not discussed here.

For Complex **1**, the most important details of the crystallographic work are reported in Table I, and the atomic coordinates and equivalent displacement parameters are given in Table II. Selected bondlengths and angles are listed in Table III.

A Nonius Kappa CCD with Mo Kα radiation was employed for the data collection of Complex **2**. The structure was solved by direct methods and was refined by full-matrix least-squares procedures using SHELXL97 [15a]. All non-hydrogen atoms were refined anisotropically. Crystal data and details of the structure determination are given in Table I, and final atomic coordinates and equivalent isotropic displacement parameters are shown in Table IV. Selected bond distances and angles are given in Table V.

TABLE I Crystal data and structure refinement for $[Re(sbqdi\text{-}OH)_3]Cl \cdot H_2O$ (**1**) and $[Re(sbqdi)_3]I$ (**2**)

Property	(*1*)	(*2*)
Formula	$C_{18}H_{20}ClN_6O_4Re$	$C_{18}H_{18}IN_6Re$
M	606.08	631.49
Temperature (K)	293(2)	200
Wavelength (Å)	0.71073	0.71073
Crystal system	Hexagonal	Monoclinic
Space group	$P6$	$P2_1/n$
Cell dimensions		
a (Å)	13.5348(17)	11.0305(1)
b (Å)	13.5348(17)	13.0623(2)
c (Å)	8.3940(15)	13.4675(2)
α (°)	90	90
β (°)	90	95.4407(7)
γ (°)	120	90
V (Å^3)	1331.7(3)	1931.71(4)
Z	2	4
D_{calcd}(Mg m^{-3})	1.641	2.171
μ (mm^{-1})	4.708	7.903
$F(000)$	632	1184
θ range (°)	1.74 – 28.31	3.4 – 27.5
Index ranges	$-18 \leq h \leq 15$	$-14 \leq h \leq 14$
	$-15 \leq k \leq 18$	$-16 \leq k \leq 16$
	$-11 \leq l \leq 10$	$-17 \leq l \leq 17$
Reflections collected/unique	9221/2194 $[R_{(int)} = 0.0659]$	42570/4426 $[R_{(int} = 0.061]$
Goodness-of-fit	1.096	1.10
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0566$	$R1 = 0.0260$
	$wR2 = 0.1206$	$wR2 = 0.0565$

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for Complex **1**

	x/a	*y/b*	*z/c*	*U*(eq)
Re(1)	3333	6667	1997(4)	57(1)
O(1)	6178(9)	6514(10)	−1300(20)	99(4)
N(1)	4382(8)	6438(10)	3530(20)	63(5)
N(2)	4309(13)	6470(12)	591(19)	81(5)
C(1)	5272(12)	6456(12)	2960(20)	40(4)
C(2)	5367(17)	6521(15)	1330(40)	82(10)
C(3)	6180(20)	6478(18)	310(40)	90(10)
C(4)	7136(12)	6579(14)	1260(30)	80(9)
C(5)	7030(20)	6490(20)	2960(40)	96(8)
C(6)	6250(16)	6530(15)	3740(30)	72(8)
Cl(1)	3333	6667	6960(40)	86(1)

TABLE III Selected bond lengths (Å) and angles (°) for Complex **1**

Re–N(2)	1.887(18)	C(1)–C(6)	1.44(2)
Re–N(1)	2.049(10)	C(2)–C(3)	1.42(3)
O(1)–C(3)	1.35(3)	C(3)–C(4)	1.47(4)
N(1)–C(1)	1.29(2)	C(4)–C(5)	1.43(2)
N(2)–C(2)	1.53(2)	C(5)–C(6)	1.26(4)
C(1)–C(2)	1.37(2)		
N(2)^a–Re–N(2)	85.0(6)	C(2)–N(2)–Re	116.3(15)
N(2)^b–Re–N(1)^b	77.5(3)	N(1)–C(1)–C(2)	115.5(19)
N(2)^b–Re–N(1)	134.6(7)	N(1)–C(1)–C(6)	130.6(19)
N(2)^b–Re–N(1)^a	133.6(7)	C(1)–C(2)–N(2)	110(2)
N(2)^a–Re–N(1)^a	77.5(3)	C(3)–C(2)–N(2)	119(3)
N(2)^a–Re–N(1)	133.6(7)	O(1)–C(3)–C(2)	126(2)
N(2)–Re–N(1)	77.5(3)	O(1)–C(3)–C(4)	124(2)
N(1)^b–Re–N(1)	84.9(7)	C(5)–C(4)–C(3)	119(2)
C(1)–N(1)–Re	118.5(14)	C(5)–C(6)–C(1)	121(3)

TABLE IV Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^4$) for Complex **2**

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)^a
I	2840(1)	770(1)	9848(1)	364(1)
Re	2251(1)	1848(1)	6846(1)	236(1)
N(1)	2153(3)	320(3)	6813(3)	303(11)
N(2)	1865(3)	1495(3)	5401(3)	291(10)
N(3)	1047(3)	2991(3)	6646(3)	282(10)
N(4)	1351(3)	1815(3)	8065(3)	304(11)
N(5)	3449(3)	2860(3)	6425(3)	289(10)
N(6)	3746(3)	1613(3)	7777(5)	275(10)
C(1)	1798(3)	−165(3)	5949(3)	277(11)
C(2)	1619(3)	520(3)	5129(3)	279(11)
C(3)	1281(4)	132(4)	4166(4)	344(14)
C(4)	1167(4)	−891(4)	4033(4)	410(16)
C(5)	1357(4)	−1574(4)	4852(4)	418(16)
C(6)	1662(4)	−1228(3)	5790(3)	326(14)
C(7)	498(3)	3321(3)	7444(3)	254(11)
C(8)	685(3)	2642(4)	8268(3)	272(11)
C(9)	201(4)	2886(4)	9170(3)	371(14)
C(10)	−419(4)	3778(4)	9236(4)	417(16)
C(11)	−618(4)	4450(4)	8420(3)	385(16)
C(12)	−180(3)	4225(3)	7530(3)	321(11)
C(13)	4632(3)	2806(3)	6813(3)	269(11)
C(14)	4806(3)	2073(3)	7580(3)	268(11)
C(15)	5979(4)	1900(3)	8071(4)	344(12)
C(16)	6933(4)	2461(4)	7767(3)	387(14)
C(17)	6758(4)	3199(4)	7006(3)	394(16)
C(18)	5620(1)	3389(1)	6538(3)	349(14)

$^a U(\text{eq}) = 1/3$ of the trace of the orthogonalized U_{ij} tensor.

RESULTS AND DISCUSSION

Synthesis

The reaction of *trans*-[$ReO_2(py)_4$]Cl with 2,3-diaminophenol (H_2dab-OH) at room temperature for 18 h in ethanol under aerobic conditions gave the product

TABLE V Selected bond lengths (Å) and angles (deg) for Complex **2**

Re–N(1)	2.000(4)	Re–N(2)	2.006(4)
Re–N(3)	1.999(4)	Re–N(4)	1.998(4)
Re–N(5)	1.989(4)	Re–N(6)	1.997(4)
N(1)–C(1)	1.350(6)	N(2)–C(2)	1.346(6)
N(3)–C(7)	1.353(5)	N(4)–C(8)	1.349(5)
N(5)–C(13)	1.361(5)	N(6)–C(14)	1.362(5)
C(1)–C(6)	1.411(6)	C(7)–C(12)	1.408(5)
C(1)–C(2)	1.420(6)	C(7)–C(8)	1.420(6)
C(2)–C(3)	1.409(7)	C(8)–C(9)	1.409(6)
C(3)–C(4)	1.352(7)	C(9)–C(10)	1.358(7)
C(4)–C(5)	1.419(8)	C(10)–C(11)	1.407(7)
C(5)–C(6)	1.354(7)	C(11)–C(12)	1.366(6)
C(13)–C(18)	1.408(6)	C(15)–C(16)	1.376(6)
C(13)–C(14)	1.408(6)	C(16)–C(17)	1.407(7)
C(14)–C(15)	1.414(6)	C(17)–C(18)	1.373(6)
N(1)–Re–N(2)	75.1(2)	N(1)–Re–N(3)	135.1(1)
N(1)–Re–N(4)	88.1(2)	N(1)–Re–N(5)	133.9(2)
N(1)–Re–N(6)	84.3(2)	N(3)–Re–N(4)	75.6(2)
N(5)–Re–N(6)	75.5(2)	Re–N(1)–C(1)	119.9(3)
Re–N(3)–C(7)	118.2(3)	Re–N(2)–C(2)	120.0(3)
Re–N(4)–C(8)	118.1(3)	Re–N(5)–C(13)	119.7(3)
C(2)–C(1)–C(6)	119.8(4)	Re–N(6)–C(14)	119.0(3)
N(1)–C(1)–C(6)	127.6(4)	N(3)–C(7)–C(8)	112.3(3)
N(2)–C(2)–C(3)	128.3(4)	N(4)–C(8)–C(9)	127.9(4)
C(1)–C(2)–C(3)	119.6(4)	C(7)–C(8)–C(9)	119.6(4)
C(3)–C(4)–C(5)	120.9(5)	C(9)–C(10)–C(11)	121.7(5)
C(1)–C(6)–C(5)	118.9(4)	C(7)–C(12)–C(11)	119.2(4)
C(8)–C(7)–C(12)	119.9(4)	N(5)–C(13)–C(14)	112.1(3)

[Re(sbqdi-OH)$_3$]Cl (**1**). The best yield was obtained with a 1 : 3 metal–ligand molar ratio, and slow evaporation of the mother liquor of the synthetic solution led to the crystallization of a compound with the formulation **1** · H_2O. In our hands, the corresponding complex with 1,2-diaminobenzene, [Re(sbqdi)$_3$]Cl could not be isolated using this method. However, reaction of H$_2$dab with the *cis*-dioxo complex [$ReO_2I(PPh_3)_2$] in ethanol under aerobic conditions did lead to the formation and isolation of [Re(sbqdi)$_3$]I (**2**) in good yield. The best yield was obtained with a fourfold molar excess of ligand. Both Complexes **1** and **2** are air-stable and 1 : 1 electrolytes in DMF. They dissolve in the polar solvents acetone, acetonitrile, tetrahydrofuran, DMF, DMSO and chloroform to give jade-green solutions that are stable for days. They are insoluble in non-polar solvents such as ether, dichloromethane, hexane, carbon tetrachloride and benzene.

Description of the Structure of 1 · H_2O

Structural investigations have proven essential to the characterization of benzoquinone diimine complexes. The metal–nitrogen bondlengths are often characteristic of a particular oxidation state of the metal, with the quinone carbon–nitrogen lengths sensitive to the charge of the ligand. These parameters, coupled with supplementary spectroscopic and magnetic evidence, make it possible to classify ligands in most complexes as either dab, sbqdi, or bqdi. In some complexes evidence was present to suggest mixed valency for these diimine-type ligands within a single complex molecule.

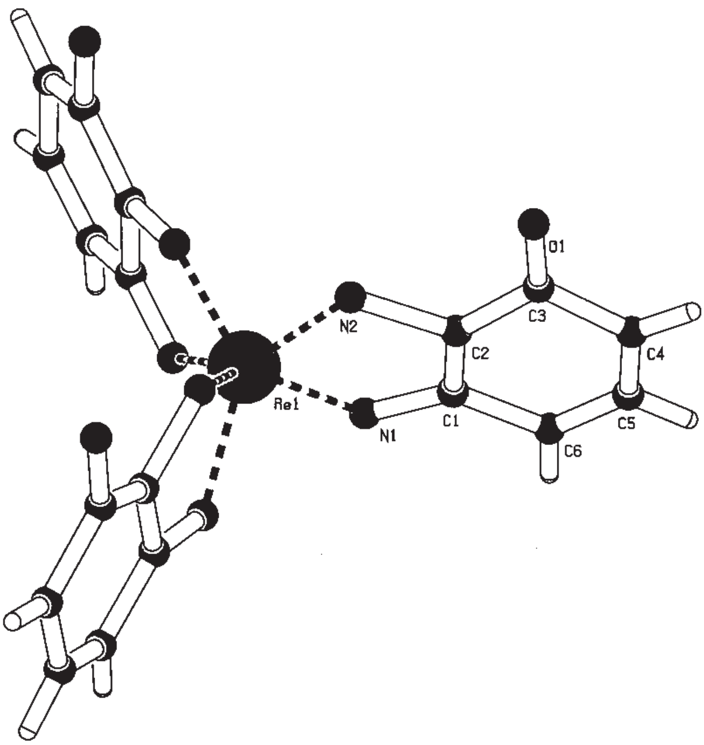
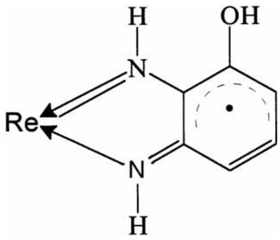


FIGURE 1 Molecular view and atom-labelling scheme for the monocation of **1**, $[Re(sbqdi\text{-}OH)_3]^+$.

Single crystals $\mathbf{1} \cdot H_2O$ of X-ray quality were obtained from the slow evaporation of the ethanolic mother liquor of the synthetic solution. A PLUTON perspective view of the asymmetric unit, along with the atom-numbering scheme, is given in Fig. 1. The complex crystallizes in the highly symmetrical hexagonal *P*6 space group with two molecules per unit cell. The rhenium atom is at the centre of a trigonal-prismatic environment. The solvate molecule H_2O is well separated from the complex.

Selected bond distances and angles are presented in Table III. The two Re–N bondlengths differ considerably. The Re–N(2) bond is short at 1.887(18) Å, and is indicative of bonding of the amide ($-NH^-$) to Re, with additional $p\pi$–$d\pi$ interaction leading to double-bond character. The longer Re–N(1) bond (2.049(10) Å) indicates a single bond with the quinone imine (=NH) nitrogen, with only the lone pair electrons being used for bonding to the metal. This value compares well with Re–N(imine) bonds that vary in the range 2.03(1)–2.15(1) Å in a wide variety of Re(V) Schiff-base complexes [16,17]. Further, the Re–N–C bond angles (118.5° and 116.3°) correspond with what one would expect for sp^2 hybridization of nitrogen donor atoms.

Bonding in the ligand is of particular interest. The C(1)–N(1) bond (1.29(2) Å) is short, consistent with its identification as a localized double bond of the form sbqdi. This value is of the same order as the two C=N bonds in $[Fe(bqdi)(CN)_4]^{2-}$ (average = 1.321 Å) [18]. $[Ru(bipy)_2(bqdi)](PF_6)_2$ (1.303 Å) [8], $[Fe(bqdi)_3]^{2+}$ (1.295 Å) [10], and in the salicylideneiminato rhenium(V) complexes $[ReOCl(Mesal)_2]$ (average = 1.287(8) Å) [17], and $[ReO(Phsal)(PPh_3)]$ (1.29(1) Å). The C(2)–N(2) bond is long (1.53(2) Å) and indicates a localized single bond, reflecting the participation of N(2) in p$\pi \rightarrow$ dπ donation. The six-membered ring of the benzosemiquinone diimine displays typical quinoid distortions, with a statistically significant deviation of the six ring carbons from planarity. The C(5)–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 C(1)=N(1) double bond. The five other C–C bonds have an average length of 1.42(1) Å, which is intermediate between the value for a benzene C=C bond of 1.392 Å, and the C–C bond distance in cyclooctatetraene of 1.462 Å. In typical bqdi complexes the average C=C and C–C bonds have values of 1.35(1) Å and 1.48(1) Å, respectively [18–20], and in sbqdi complexes of some 3d transition metals the average C–C ring bond is 1.41(1) Å [19–21]. A typical average value of 1.44(1) Å for C–C bondlengths for semiquinones is also documented [22]. The crystallographic data thus justify the assignment of an oxidation state of +IV to the rhenium, with the bonding interaction of the sbqdi radical anions with an allyl structure represented as shown below:



Description of Structure of 2

Single crystals of good quality were obtained by the slow evaporation of a 1 : 1 methanol/acetonitrile solution of the recrystallized complex. An ORTEP perspective view of the asymmetric unit, together with the atom-numbering scheme, is given in Fig. 2.

The complex crystallizes in the monoclinic $P2_1/n$ space group with four molecules per unit cell (Fig. 3). The rhenium atom is at the centre of a trigonal-prismatic coordination environment. Selected bond distances and angles are given in Table V. The six Re–N distances are all equal within experimental error, with an average of 1.998(4) Å, and are not localized, as was observed in Complex **1**. The Re–N distances are shorter than expected single-bond values. For example, the Re–N(amido) bond length in $[Re(NHPh)(N_2)(PMe_3)_4]$ [23], with no π character associated with the bond, equals 2.20 Å. For the formally ReN_6 system in **2**, with filled π orbitals on the nitrogens perpendicular to the ligand plane, N→M π bonding is to be expected. The average bite angle of the chelating diaminobenzene ligand is 75.39(15)°, significantly smaller than that in the rhenium(VII) complex $[Re(dab)_3]^+$, where this angle was 76.9° on average [24]. It was also found earlier in complexes of iron(III) and chromium(III) containing catechol ligands and derivatives, that the ligand bite angle of the semiquinone is typically 2° smaller than that of the catecholate ligand [2]. The compression of these bite angles from 90° causes the octahedron to be trigonally twisted (~ 20°) along the threefold axis. The average Re–N–C bond angle of 119.2(3)° is consistent with sp^2 hybridization of the nitrogen donor atoms.

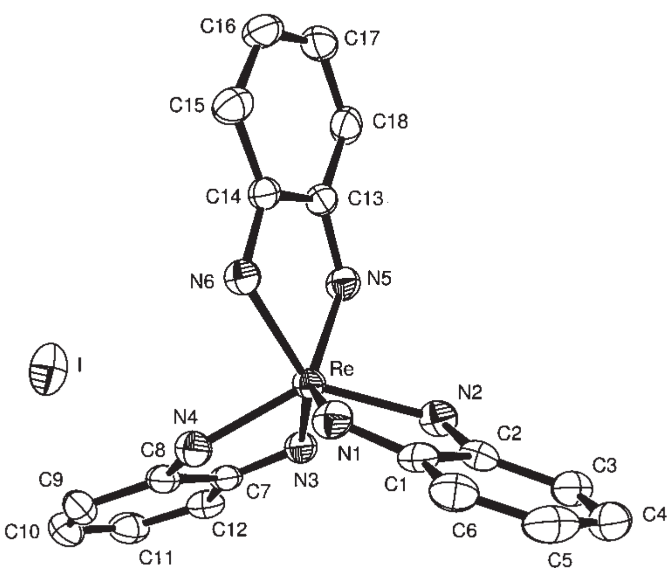


FIGURE 2 An ORTEP view of the asymmetric unit of [Re(sbqdi)$_3$]I (**2**). Hydrogen atoms have been omitted for clarity.

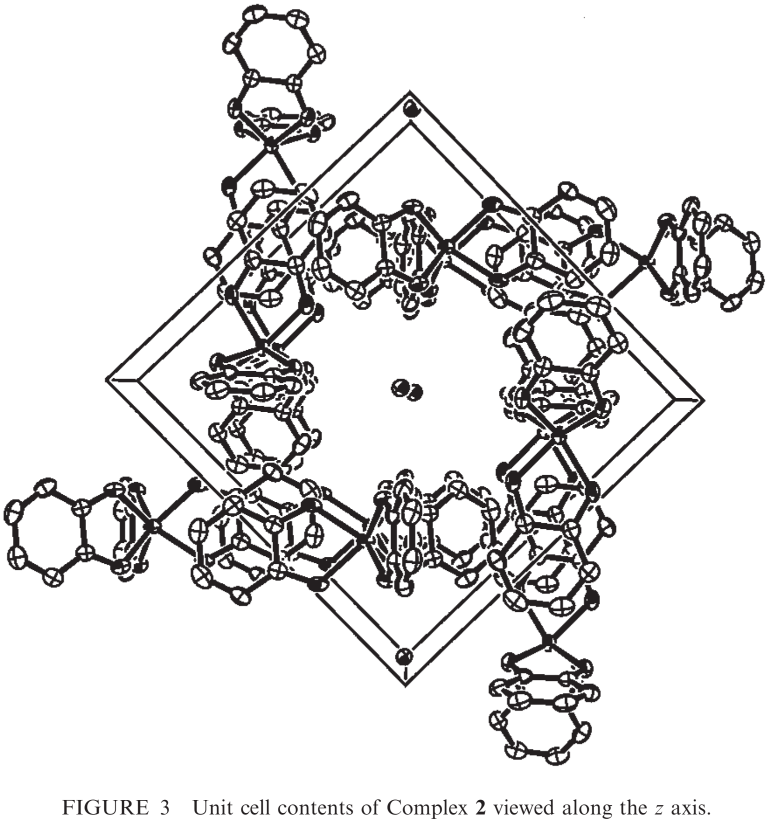
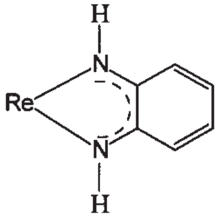


FIGURE 3 Unit cell contents of Complex **2** viewed along the *z* axis.

The bond distances in the chelating phenyl-amido ligands provide an indication of their specific form, i.e., dab, sbqdi or bqdi. The six C–N bondlengths are all equal within error, with a value of 1.354(6) Å. There is therefore also no localization in these bonds. This value compares well with that of 1.352(10) Å found in $[RhCl(PPh_3)_2(sbqdi)]$ [22b]. It is longer than the formal C=N bondlengths of 1.324(5) Å (average) of the bqdi ligands [25] in $[Os(bqdi)_3]^{2+}$ and of 1.30 Å in other transition metal complexes containing bdqi ligands [22c]. The chelates in Complex **2** are therefore not of the bdqi form. Chelated dab ligands have an average C–N bond length around 1.372 Å, statistically significantly longer than in **2** [22c]. This means that the bidentate ligands in **2** are not in the dab form either. From a comparison of the C–N bond distances, the only possible conclusion is that Complex **2** contains the sbqdi form of the 1,2-diaminobenzene ligand, i.e., with a delocalized C$\overset{...}{-}$N bond that contains a fair amount of double-bond character as shown below:



The C–C bond distances in the phenyl rings of **2** provide additional evidence of the presence of the sbqdi chelates. In all three rings there are six localized C=C double bonds [C(3)=C(4), C(5)=C(6), C(9)=C(10), C(11)=C(12), C(15)=C(16), C(17)=C(18)] with an average distance of 1.363(6) Å. The other C–C single bonds have an average distance equal to 1.412(6) Å, as expected for the ligands in the sbqdi state. The difference of 0.049 Å between these two average values is larger than the experimental error of ± 0.006 Å. Therefore, the oxidation level of the ligands is considered to be correctly represented by the above resonance structure. An average of 1.415 Å was obtained for these bonds in a number of complexes containing sbqdi ligands [22c], slightly longer than the aromatic value of 1.39(1) Å for 1,2-diaminobenzene in the free state [22a].

A comparison of the torsion angles in the phenyl rings clearly shows deviations from planarity, and hence a decrease in aromaticity of the rings. The N(2)–C(2)–C(3)–C(4) torsion angle deviates from planarity by 5.3(4)°, and that of, for example, C(14)–C(13)–C(18)–C(17) by 2.5(6)°. Figure 4, a paddle-wheel view of Complex **2**, clearly shows a fold in the Re–N–C angles, indicative of a decrease in planarity and aromaticity. For example, the "fold" angle between the least-squares planes ReN(1)N(2) and N(1)N(2)C(1)C(2) is 5.7(2)°, between planes ReN(3)N(4) and N(3)N(4)C(8)C(7) it is 15.0(2)°, and between ReN(5)N(6) and N(5)N(6)C(13)C(14) the angle is 9.6(3)°.

The crystallographic data thus justify the assignment of an oxidation state of +IV to rhenium in the complex $[Re(sbqdi)_3]I$. The evidence for the presence of the three benzosemiquinone diimine(-) radical ligands in **2** can therefore be summarized by the observations that both nitrogens are sp^2 hybridized and not protonated, the six-membered phenyl rings display the typical quinoid distortions, and the C–N bondlengths are short, approaching double bonds.

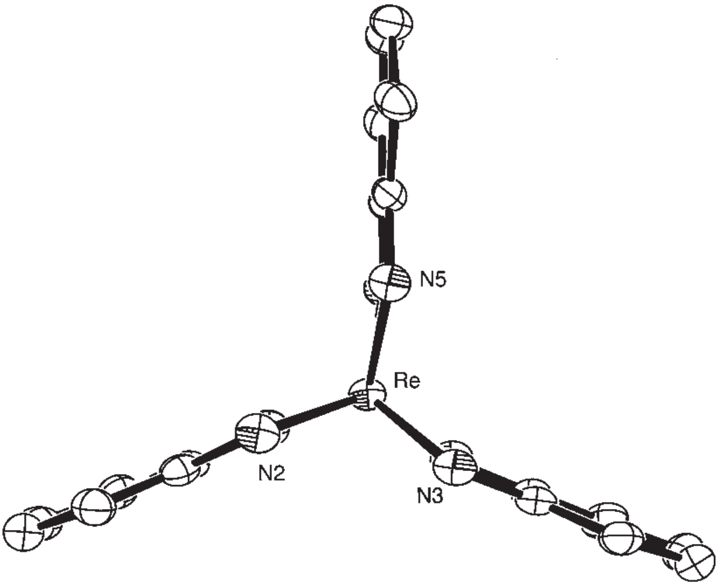


FIGURE 4 A paddle-wheel view of Complex **2**.

Spectroscopic Data

Surprisingly for a d^3 rhenium(IV) complex, **1** and **2** are diamagnetic at room temperature. Examples and data on complexes in which radical ligands are bound to a paramagnetic transition metal ion are scarce in the literature. The few examples that were found display temperature-dependent effective magnetic moments [26, 27].

If Complexes **1** and **2** are formulated as *tris*(semiquinone diimine) complexes of high-spin rhenium(IV), as is indicated by their crystal structures, a strong intramolecular antiferromagnetic exchange interaction between the ligand-based unpaired radical electrons and the three unpaired electrons of the metal would result in a singlet ($S = 0$) ground state. If the exchange interaction is relatively weak, there would be thermally accessible excited states that would lead to μ_{eff} values that are temperature dependent. This is, however, not the case for **1** and **2**. In our opinion, the unpaired electron of each semiquinone diimine ligand is directly involved in the bonding of the sbqdi ligand to the rhenium(IV) ion, in addition to the lone pairs of electrons on each nitrogen that are used in bonding. It is this phenomenon that may be responsible for the short Re–N(2) bond of 1.887(18) Å in **1**, and consequently the intramolecular antiferromagnetic interaction is strong, leading to diamagnetism. Similar behavior has been found for the chromium(III) metal ion (d^3) coupled to the three 3,5-*di*(*tert*-butyl)benzosemiquinone (bsbq) ligands in the complex $Cr(bsbq)_3$, which was found to be diamagnetic at all measured temperatures [28].

Confirmation of the sbqdi bonding in **1** and **2** is also provided by their infrared spectra. For **1**, a sharp band at $3252\,cm^{-1}$ is assigned to the stretch of the amide NH group, with a broader band at $3380\,cm^{-1}$ being attributed to the imide NH group. In the spectrum of **2** a single peak of weak intensity at $3314\,cm^{-1}$ is assigned to imine NH stretching. There is a band at $507\,cm^{-1}$, and a shoulder at $478\,cm^{-1}$, in the ν(Re–N) region of **1**. The former is ascribed to the Re–N(1) stretch, and the latter to the Re-N(2) bond; ν(Re–N) in **2** occurs at 573 cm^{-1}. Two sharp bands at 1585 and 1601 cm^{-1} are assigned to ν(C=C) and ν(C(1)=N(1)), respectively. In **2** there are no peaks around 1600 cm^{-1} with the corresponding ν(C=C) band at 1551 cm^{-1}. A peak at 1375 cm^{-1} in the spectrum of **2**, which is absent in the spectrum of **1**, is ascribed to ν(C$\overset{...}{-}$N) of the sbqdi ligands. A strong absorption at 1255 cm^{-1}, absent in the spectrum of **2**, is assigned to ν(C(2)–N(2)) in **1**.

Complex **1** shows sharp, well-resolved peaks in its ^{1}H NMR spectrum, whose simplicity establishes the high symmetry of the complex in solution and equivalence of the three sbqdi molecules. There are no detectable paramagnetic shifts or line broadening of the signals. There are two sharp singlets at δ13.48 and 13.68 ppm, both integrating for three protons each, and they are assigned to the six NH protons (the latter signal to the imine proton). The three OH protons appear as a broad singlet at δ10.75 ppm. The above signals all disappear on the addition of D_2O to the sample solution. The doublet at δ6.39 ppm is assigned to H(4), the triplet at δ6.83 ppm to H(5) and the doublet at δ6.92 ppm to H(6); all three signals integrate for three protons each. The position of these relative high-field peaks (δ6.39–6.92 ppm) is indicative of the presence of the benzosemiquinone diimido ligands, suggesting a loss of aromaticity. This effect was observed and explained earlier [23, 24].

The ^{1}H NMR spectrum of **2** has a sharp singlet at δ13.69 ppm assignable to NH, and a well resolved AA′BB′ pattern of two sets of multiplets at δ7.42 and 7.00 ppm ($J_{AB} = 3.35$ Hz) due to the aromatic ring protons. The three signals integrate with a ratio of 1 : 1 : 1. Again the simplicity and well-resolved peaks not only establish the diamagnetic character of **2**, but also the high symmetry and equivalence of the three sbqdi chelates, at least on the NMR timescale. Furthermore, the small ^{1}H–^{1}H coupling constant suggests reduced aromaticity of the phenyl rings, consistent with the semiquinone diimine form. This is in contrast to the diamido form of the ligand, which shows high J_{AB} values and the presence of high aromaticity [24].

In the electronic spectrum of **1**, there are three bands of high intensity at 674 nm (675 nm), a shoulder at 405 nm (408 nm), and at 383 nm (390 nm), the intensity of which is between those of the first two bands. The values in brackets are those of Complex **2**. This pattern agrees well with that observed for $[Re(dab)_3]^+$, $Re(dab)_3$ and $M(S_2C_2Ph_2)_3$ (M = Mo, W, Re) [24, 29, 30], which have all been shown to be trigonal prismatic. This implies that the electronic transitions in these complexes are more ligand related than metal related, and it seems certain that the longest wavelength transition is to a π* orbital of the sbqdi ligands.

Complexes containing the sbqdi form of H_2dab are quite common in the literature, while the bqdi form in metal compounds is extremely rare. Pen *et al.* [31] have prepared and structurally characterized the complexes $[Co^{II}(sbqdi)_2]$, $[Co^{III}Cl(sbqdi)_2]$ and $[Co^{III}(sbqdi)_2(py)]Cl$, with the cobalt in a square-pyramidal geometry in the last complex [32]. The neutral complex $[Ni^{IV}(dab)_2]$ was reported [33], in 1927, but a subsequent X-ray crystal structure determination [21] has revealed that the complex is best described as $[Ni^{II}(sbqdi)_2]$, a diamagnetic square-planar complex containing the two spin-coupled sbqdi radical anions. Similar complexes, $[M^{II}(sbqdi)_2]$ (M=Co, Pd, Pt), have also been prepared [4].

Cobalt(II) salts also catalyze the autooxidation of H_2dab in a slightly alkaline solution. Air oxidation of the $[Co^{II}(H_2dab)_3]^{2+}$ ion gives a low-spin Co(II) complex, which was structurally characterized [7]; the complex has a square-pyramidal arrangement in which two of the aromatic ligands have the benzoquinonediimine form, while the third, which is coordinated by one amino group only, is in the semiquinoid form. The complex can therefore be formulated as $[\mathrm{Co(sbqdi)(bqdi)_2}]^+$. Oxidation of the yellow species $[\mathrm{Fe^{II}[(CN)_4(H_2dab)]}]^{2-}$ with molecular oxygen yields a very intensely purple-coloured product [34]. The X-ray diffraction structure determination indicates that the H_2dab molecule has been oxidized by two electrons, and that the product is the low-spin iron(II) complex [18], $[\mathrm{Fe^{II}(CN)_4(bqdi)}]^{2-}$.

Supplementary Data

Full lists of crystallographic data are available from the author upon request.

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