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Contribution from the Laboratorio di Chimica Inorganica e Nucleare and Centro di Strutturistica Diffrattometrica,
Dipartimento di Chimica, Università di Ferrara, 44100 Ferrara, Italy, Dipartimento di Chimica Fisica ed Inorganica,
Università di Bologna, 40136 Bologna, Italy, and Biomedical Chemistry Research Center,
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

Reactivity of 2-(2-Hydroxyphenyl)benzothiazoline with the Oxotetrahalometalate(V) Complexes $[MOX_4]^-$ (M = Tc, Re; X = Cl, Br). Synthesis and Characterization of New Oxo-M(V) Complexes Containing 2-(2-Hydroxyphenyl)benzothiazole. Crystal Structure of Tetraphenylarsonium Oxotrichloro[2-(2-hydroxyphenyl)benzothiazolato]technetate(V)

Adriano Duatti,[*,1] Andrea Marchi,[2] Roberto Rossi,[2] Luciano Magon,[2] Edward Deutsch,[3]
Valerio Bertolasi,[4] and Fabrizio Bellucci[4]

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2-(2-Hydroxyphenyl)benzothiazoline (hbtH) is converted into its oxidized form, 2-(2-hydroxyphenyl)benzothiazole (hbt), by interaction with the five-coordinate tetrahalooxometalate(V) complexes $[MOX_4]^-$ (M = Tc, Re; X = Cl, Br). The reaction proceeds very rapidly at room temperature, and only a small amount of metal complex is necessary to obtain conversion of a large excess of hbtH to hbt. When this conversion is conducted in acetone, the formation of isopropyl alcohol is detected within a few minutes after mixing the reagents. When M = Re, an intermediate in the reaction sequence can be isolated; this intermediate contains one ligand comprised of the hbt product and one ligand comprised of the Schiff base tautomeric form of the hbtH starting material [i.e., *N*-(2-mercaptophenyl)salicylideneamine, S-phsalH_2] and is formulated as the six-coordinate Re(V) complex [ReO(S-phsal)(hbt)]. A general scheme accounting for these and other results is given. The hbt ligand also reacts directly with $[MOX_4]^-$ to yield $[MOX_3(hbt)]^-$ anions and $[MOX(hbt)_2]$ complexes, which have been characterized by elemental analyses and IR, ^1H NMR, and mass spectral analyses. The $[TcOCl_3(hbt)]^-$ anion is characterized by single-crystal X-ray structural analysis refined to a conventional *R* factor of 0.045 for 3041 observed reflections with $I > 2\sigma(I)$. Red-orange crystals of the tetraphenylarsonium salt crystallize in the orthorhombic space group $P2_12_12_1$ with $a = 12.104$ (2) Å, $b = 13.772$ (3) Å, $c = 20.539$ (4) Å, and $V = 3424$ (1) Å^3 with $Z = 4$. The Tc(V) center is in a distorted-octahedral configuration with the three chlorine atoms and the neutral nitrogen atom of the hbt ligand in the plane normal to the Tc═O linkage and the anionic phenolate oxygen atom of the hbt ligand situated trans to the Tc═O linkage.

Introduction

The Schiff base ligand generated by condensing 2-aminothiophenol with salicylaldehyde exhibits a remarkably diverse chemistry. Most importantly, the Schiff base itself, *N*-(2-mercaptophenyl)salicylideneamine (S-phsalH_2), is not the stable form of this noncoordinated molecule.[5] At room temperature this Schiff base thermally converts to 2-(2-hydroxyphenyl)benzothiazoline (hbtH) (Figure 1). However, the dianionic form of the Schiff base may be stabilized by coordination to metal ion centers;[6] this is schematically illustrated in Figure 1. Finally, the S-phsalH_2/hbtH ligand system may function as a reductant; irradiation of hbtH with UV light yields molecular hydrogen and the oxidized species 2-(2-hydroxyphenyl)benzothiazole (hbt)[7] (Figure 1).

In previous studies we have described square-pyramidal Tc(V) complexes of S-phsalH_2 that were, generally, prepared by substitution of the isomeric hbtH ligand onto $[TcOCl_4]^-$.[8] Octahedral Tc(V) complexes have been prepared by reduction of $[TcO_4]^-$ with $Na_2S_2O_4$, in alkaline solution, in the presence of hbtH.[9] Moreover, a series of square-pyramidal and distorted-pseudooctahedral Re(V) complexes have been obtained by mixing equimolar amounts of hbtH and $[ReOCl_4]^-$ in solutions of different alcohols.[10] In these complexes the Schiff base functions as a tridentate ligand that is coordinated to the metal in a plane perpendicular to the M═O or *trans*-O═M═O linkages (M = Tc, Re). Complexes of Tc(V) and Re(V) that contain both tridentate and bidentate Schiff base ligands have also been described.[10] More recently we have prepared Re(I) and Tc(I) complexes containing the coordinated hbt ligand.[11,12]

This paper extends our investigations into the possible reactions and interactions between the S-phsalH_2/hbtH/hbt ligand system and oxo-M(V) centers (M = Tc, Re). The $[MOX_4]^-$-promoted oxidation of hbtH to hbt, the synthesis of new hbt-M(V) complexes, and the crystal structure of the new octahedral complex $[TcOCl_3(hbt)]^-$ are described.

Experimental Section

Materials. Unless otherwise noted, all chemicals were of reagent grade and were used without purification. Aqueous $NH_4[^{99}TcO_4]$ was obtained from Radiochemical Centre Ltd., Amersham, England. *Caution*! ^{99}Tc is weak β-emitter (0.292 keV, $t_{1/2} = 2.12 \times 10^5$ years). All manipulations were carried out in a laboratory approved for low-level radioactivity with monitored hoods and gloveboxes. Rhenium, as the metallic powder, was purchased from Fluka AG, Switzerland. $KReO_4$ was prepared by oxidation of metallic rhenium with H_2O_2, in water, at 70 °C, followed by addition of an equivalent amount of KCl. The complexes $As(C_6H_5)_4$-$[MOX_4]$ (M = Tc, Re; X = Cl, Br), were prepared as described in the literature.[13]

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(1) Università di Bologna.
(2) Laboratorio di Chimica Inorganica e Nucleare, Università di Ferrara.
(3) University of Cincinnati.
(4) Centro di Strutturistica Diffrattometrica, Università di Ferrara.
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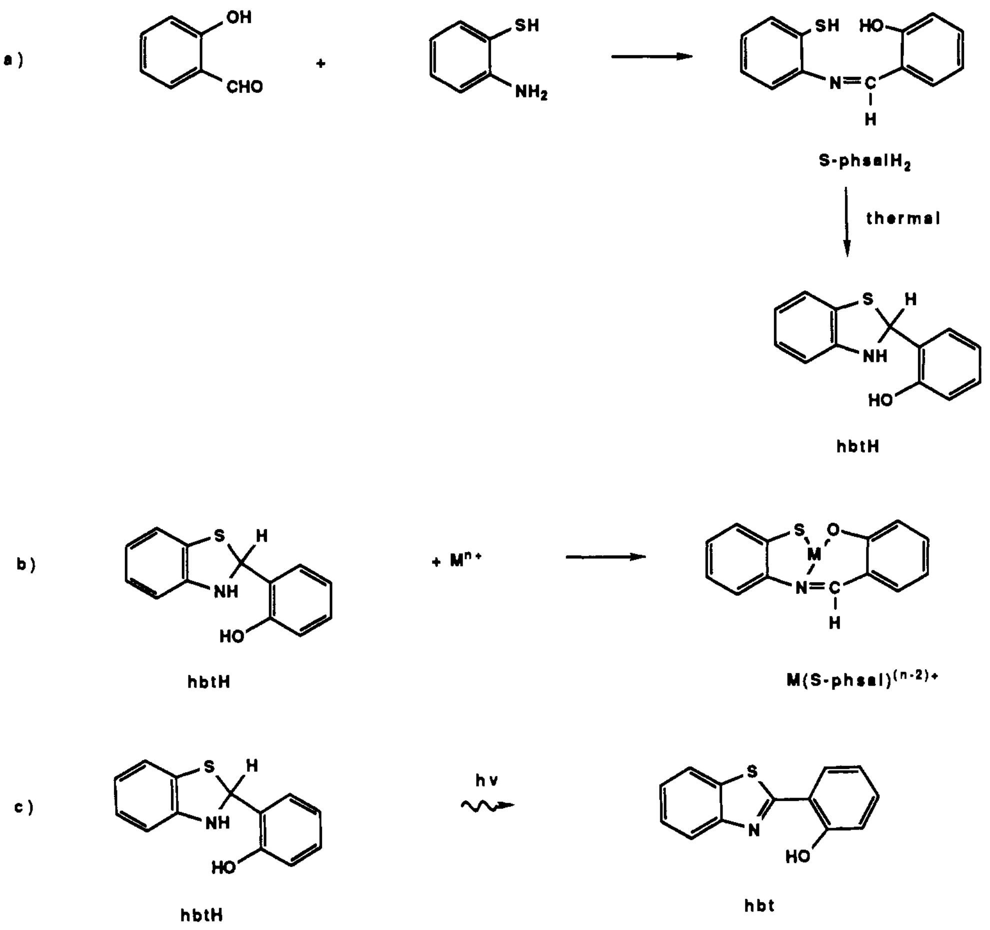

Figure 1. Properties of 2-(2-hydroxyphenyl)benzothiazoline: (a) synthesis; (b) interaction with metals; (c) interaction with light.

Table I. Elemental Analyses of hbt Complexes[a]

complex[b]	% C	% H	% N	% O	% S	% Tc
$As(C_6H_5)_4[TcOCl_3(hbt)]$	53.6	3.6	1.6		3.2	12.4
	(53.5)	(3.4)	(1.7)		(3.9)	(12.0)
$As(C_6H_5)_4[ReOCl_3(hbt)]$	48.8	3.4	1.6		2.9	
	(48.4)	(3.1)	(1.5)		(3.5)	
$As(C_6H_5)_4[TcOBr_3(hbt)]$	46.9	3.3	1.5		2.8	9.7
	(46.1)	(3.0)	(1.5)		(3.3)	(10.3)
$As(C_6H_5)_4[ReOBr_3(hbt)]$	41.7	2.8	1.5		2.4	
	(42.3)	(2.7)	(1.3)		(3.0)	
$TcOCl(hbt)_2$	52.2	2.8	4.5		9.8	15.8
	(51.8)	(2.7)	(4.6)		(10.6)	(16.4)
$ReOCl(hbt)_2$	45.4	2.5	4.3		8.8	
	(45.2)	(2.3)	(4.1)		(9.3)	
$TcOBr(hbt)_2$	47.9	2.7	4.8		8.1	14.7
	(48.2)	(2.5)	(4.3)		(9.9)	(15.3)
$ReOBr(hbt)_2$	43.2	2.4	4.1		8.2	
	(42.5)	(2.2)	(3.8)		(8.7)	
ReO(S-phsal)(hbt)	47.5	2.4	4.2	7.6	9.1	
	(47.6)	(2.6)	(4.3)	(7.3)	(9.8)	

[a] Calculated values are in parentheses. [b] Ligand abbreviations are defined in the text.

2-(2-Hydroxyphenyl)benzothiazoline (hbtH) was obtained by adding at room temperature an excess of salicylaldehyde to an ethanolic solution of 2-aminothiophenol. After a few minutes of stirring, a white precipitate formed, which was collected by filtration and washed with ethanol and hexane.

2-(2-Hydroxyphenyl)benzothiazole (hbt) was prepared (i) by dissolving 2-(2-hydroxyphenyl)benzothiazoline (hbtH) in methanol, at room temperature, and exposing the resulting solution to sunlight for 60 h, (ii) through the metal-induced oxidation of hbtH discussed in the following sections, the thiazole being recovered by simple evaporation of the reaction solution and recrystallized from CH_2Cl_2, and (iii) by the method of Charles and Freiser.[5]

Synthesis of [ReO(S-phsal)(hbt)]. $As(C_6H_5)_4[ReOX_4]$ (X = Cl, Br) (0.41 mmol) and a 2-fold molar excess of hbtH were mixed in methanol (40 mL), at room temperature. The solution immediately became red-brown, and the resulting mixture was heated under reflux for 5 min. After the reaction solution was cooled and evaporated, a red-brown powder was obtained, which was washed with methanol, diethyl ether, and pentane (yield 40%). The same complex was obtained by reacting, in methanol, the square-pyramidal complex ReOX(S-phsal)[10] with a stoichiometric amount of hbtH under the same conditions as above. Every attempt to obtain good crystals of this material produced only an amorphous solid and some decomposition products. This complex is soluble in acetone, CH_2Cl_2, and $CHCl_3$, slightly soluble in methanol, ethanol, and diethyl ether, and insoluble in pentane and CCl_4. Elemental analyses and characterization data are given in Tables I and II, respectively.

Synthesis of $As(C_6H_5)_4[MOX_3(hbt)]$ (M = Tc, Re; X = Cl, Br). A 2-fold molar excess of hbt was mixed with a solution of $As(C_6H_5)_4[MOX_4]$ (0.41 mmol) in isopropyl alcohol (40 mL), at room temperature. The precipitate that formed immediately (red-orange for Tc, green for Re) was collected by filtration and washed with isopropyl alcohol and

Table II. IR, ^{1}H NMR, Mass Spectral, and Magnetic Susceptibility Data[a] for hbt Complexes[b]

complex[c]	ν(M=O)	ν(C=N)	ν(M—X)	δ(CH=N)	m/e
$As(C_6H_5)_4[TcOCl_3(hbt)]$	945	1585	310		830 (830.97)
$As(C_6H_5)_4[ReOCl_3(hbt)]$	960	1590	308		917 (918.18)
$As(C_6H_5)_4[TcOBr_3(hbt)]$	940	1587			963 (964.33)
$As(C_6H_5)_4[ReOBr_3(hbt)]$	960	1590			1050 (1051.53)
$TcOCl(hbt)_2$	942	1600	260		602 (603.00)
$ReOCl(hbt)_2$	960	1600	250		690 (690.20)
$TcOBr(hbt)_2$	940	1600			645 (647.45)
$ReOBr(hbt)_2$	960	1600			733 (734.65)
ReO(S-phsal)(hbt)	945	1600		8.7	655 (655.76)

[a] All of the complexes in the table are diamagnetic. [b] IR frequencies in cm^{-1}; ^{1}H NMR shifts relative to $Si(CH_3)_4$; theoretical m/e values given in parentheses. [c] Ligand abbreviations are defined in the text.

diethyl ether. Recrystallization was carried out from CH_2Cl_2 and ethanol (yield 90%). This complex is soluble in CH_2Cl_2, $CHCl_3$, and acetone and insoluble in methanol, ethanol, diethyl ether, CCl_4, and pentane. Elemental analyses and characterization data are given in Tables I and II, respectively.

Synthesis of $MOX(hbt)_2$ (M = Tc, Re; X = Cl, Br). To an ethanolic solution (50 mL) of $As(C_6H_5)_4[MOX_4]$ (0.41 mmol) was added a 4-fold molar excess of hbt, and the resulting solution was refluxed for 1 h. After it was cooled, the reaction solution was evaporated under reduced pressure and a solid was recovered (red for Tc, green for Re), which was washed with ethanol and diethyl ether. Recrystallization was carried out from CH_2Cl_2 and ethanol (yield 60%). This complex is soluble in acetone, CH_2Cl_2, and $CHCl_3$ and is insoluble in methanol, ethanol, diethyl ether, CCl_4, and pentane. Elemental analyses and characterization data are given in Tables I and II, respectively.

Reactivity of $As(C_6H_5)_4[MOX_4]$ toward hbtH. When a molar excess ($\geq$2-fold) of hbtH is mixed with a solution of $As(C_6H_5)_4[MOX_4]$, it is rapidly converted into the oxidized form, hbt, with the formal loss of two hydrogen atoms. In a typical experiment, a >50-fold molar excess of solid hbtH was added to a methanolic solution (40 mL) of the starting complex (0.20 mmol), at room temperature. The solution immediately became red-brown and, after 5 min, changed to dark green. In order to avoid interference with light-induced dehydrogenation,[6] the reaction solution was kept in the dark for 1 h. Evaporation of the solution under reduced pressure to one-third of its volume caused the precipitation of the white thiazole (hbt), which was collected by filtration and washed with ethanol and pentane. Increasing the temperature to 60 °C shortened the reaction time to 5 min. When the reaction was carried out in acetone, the formation of isopropyl alcohol was detected by injecting the bulk reaction solution into a gas chromatographic apparatus 5 min after the mixing of the reagents and observing the appearance of a peak corresponding to the alcohol. The same reduction was observed by using the complexes MOCl(S-phsal) and ReO(S-phsal)(hbt) as starting materials [yield calculated on the amount of hbtH converted to hbt in the reaction with $As(C_6H_5)_4[MOX_4]$ 100%].

Techniques and Instrumentation. The IR spectra of solid samples in KBr or as Nujol mulls between CsI disks were recorded on a Perkin-Elmer 580B spectrophotometer in the range 4000–200 cm^{-1}. ^{1}H NMR spectra of $CDCl_3$ solutions with $SiMe_4$ as internal reference were collected on a Bruker WP 80-MHz instrument. Magnetic suceptibility measurements were performed in solution by the Evans method[14] using a Varian FT80 spectrometer and in the solid state with an Oxford Instruments spectrometer. Mass spectrometric measurements were carried out on a WG ZAB2F instrument operating in the electron-impact mode (70 eV = 1.12×10^{-17} J; 200 A). Gas chromatographic analyses were accomplished by using an OV-101 10% FFAP on 80/100 Supelcoport (80–100 mesh) glass column (2 m × 2 mm i.d.). The temperature conditions were as follows: injections 200 °C, isotherm 60 °C, detector 250 °C. The flow rate of the helium carrier gas was 20 mL/min. Elemental analyses were performed on a Carlo Erba Model 1106 elemental analyzer. The elemental analyses for the radioactive technetium were carried out on a Packard Model TRI-CARB 300 C liquid-scintillation instrument, with Insta-gel as scintillator, after dissolution of the samples in hydrogen peroxide/nitric acid solutions.

Collection of the X-ray Data. Crystal data and other crystallographic parameters are given in Table III. A red prismatic crystal was used for data collection on an Enraf-Nonius CAD-4 diffractometer with monochromated Mo Kα radiation. After alignment of the crystal, 25 reflections in the range $9 < \theta < 12°$ were found and indexed by using the automatic searching, centering, and indexing routines of the instruments. Cell parameters were obtained by a least-squares procedure on the diffractometer positions of these reflections. Data were collected at room temperature with use of a $\omega/2\theta$ scan ($0 < h < 15$, $0 < k < 17$), $0 < l < 26$). Intensities were corrected for Lorentz, polarization, and absorption (minimum transmission factor 0.93). Scattering factors and anomalous scattering corrections were taken from ref 15.

Table III. Crystallographic Data for $As(C_6H_5)_4[TcOCl_3(hbt)]$

$[TcCl_3O_2SNC_{13}H_8]^-[As(C_6H_5)_4]^+$
$a = 12.104$ (2) Å
$b = 13.772$ (3) Å
$c = 20.539$ (4) Å
$V = 3424$ Å^3
$Z = 4$
$M_r = 830.98$
space group: $P2_12_12_1$ (No. 19)

$T = 22$ °C
$\gamma = 0.71069$ Å
$\rho_{obsd} = 1.56$ g cm^{-3}
$\rho_{calcd} = 1.61$ g cm^{-3}
$\mu = 16.96$ cm^{-1}
transmission coeff: 0.93–1.0
$R(F_o) = 0.045$
$R_w(F_o^2) = 0.053$

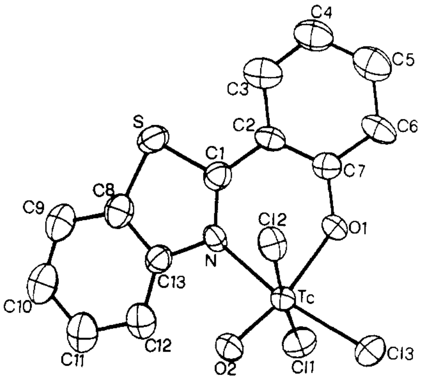

Figure 2. Perspective view of the $[TcOCl_3(hbt)]^-$ anion. Thermal ellipsoids are at 40% probability; hydrogen atoms have been omitted for clarity.

Solution and Refinement of the Structure. The positions of Tc and As atoms were located from a Patterson synthesis. All non-H atoms were located in the subsequent Fourier maps. After a few cycles of isotropic refinement ($R = 0.18$) the structure was refined by full-matrix least squares using anisotropic temperature factors for the non-H atoms except for the carbon atoms of the $[As(C_6H_5)_4]^+$ cation. H atoms were given calculated positions with C–H bond distances of 0.95 Å and fixed isotropic B's of 5.0 Å^2. Weights were applied according to the scheme given in Table III. All calculations were performed with the CAD4-SDP system of programs[16] and PARST.[17]

Results

Properties of hbt Complexes. Table I lists the results of elemental analyses conducted on the hbt complexes prepared in this study. Table II lists pertinent IR, ^{1}H NMR, mass spectral, and magnetic susceptibility data for these same complexes. All of the complexes exhibit elemental analyses and MS parent ion m/e peaks that are consistent with their formulations. The observed

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Table IV. Positional (×10^4) and Thermal Parameters (Å^2) for $As(C_6H_5)_4[TcOCl_3(hbt)]$[a]

	x	y	z	B_{eq}[b]/B
Tc	2697.6 (5)	−798.7 (4)	3680.2 (3)	2.79 (1)
Cl(1)	4618 (2)	−682 (2)	3986 (1)	3.70 (4)
Cl(2)	813 (2)	−716 (2)	3372 (1)	4.39 (5)
Cl(3)	3219 (2)	−1158 (2)	2598 (1)	4.58 (5)
O(1)	2892 (4)	574 (3)	3482 (2)	2.9 (1)
O(2)	2699 (5)	−1904 (4)	3990 (3)	3.8 (1)
N	2247 (5)	−197 (4)	4611 (3)	2.6 (1)
S	2223 (2)	889 (2)	5641 (1)	3.93 (4)
C(1)	2624 (7)	641 (6)	4847 (3)	3.2 (2)
C(2)	3270 (6)	1355 (5)	4487 (4)	2.9 (2)
C(3)	3752 (7)	2136 (6)	4832 (5)	4.1 (2)
C(4)	4314 (8)	2871 (6)	4493 (5)	4.9 (2)
C(5)	4403 (8)	2813 (6)	3800 (5)	5.0 (2)
C(6)	3915 (8)	2026 (5)	3458 (5)	4.0 (2)
C(7)	3358 (6)	1306 (5)	3817 (4)	3.0 (2)
C(8)	1521 (7)	−204 (7)	5678 (4)	3.8 (2)
C(9)	942 (7)	−584 (7)	6206 (4)	4.4 (2)
C(10)	445 (8)	−1466 (8)	6123 (4)	4.8 (2)
C(11)	511 (8)	−1954 (7)	5527 (4)	4.7 (2)
C(12)	1065 (8)	−1559 (6)	4994 (4)	3.9 (2)
C(13)	1584 (6)	−681 (6)	5080 (4)	3.0 (2)

[a] Esd's are given in parentheses. This form is used throughout. [b] $B_{eq} = {}^4/_3\sum_i\sum_j a_i a_j \beta_{ij}$.

Table V. Selected Bond Distances (Å) for the $[TcOCl_3(hbt)]^-$ Anion

Tc–Cl(1)	2.413 (2)	C(2)–C(3)	1.414 (11)
Tc–Cl(2)	2.370 (2)	C(2)–C(7)	1.382 (12)
Tc–Cl(3)	2.363 (2)	C(3)–C(4)	1.404 (13)
Tc–O(1)	1.948 (4)	C(4)–C(5)	1.430 (14)
Tc–O(2)	1.650 (6)	C(5)–C(6)	1.420 (12)
Tc–N	2.153 (6)	C(6)–C(7)	1.408 (11)
O(1)–C(7)	1.345 (8)	C(8)–C(9)	1.393 (12)
N–C(1)	1.332 (10)	C(8)–C(13)	1.395 (12)
N–C(13)	1.420 (10)	C(9)–C(10)	1.366 (14)
S–C(1)	1.735 (7)	C(10)–C(11)	1.399 (12)
S–C(8)	1.730 (10)	C(11)–C(12)	1.394 (12)
C(1)–C(2)	1.458 (11)	C(12)–C(13)	1.374 (12)

Table VI. Selected Bond Angles (deg) for the $[TcOCl_3(hbt)]^-$ Anion

Cl(1)–Tc–Cl(2)	173.4 (1)	S–C(1)–C(2)	119.6 (5)
Cl(1)–Tc–Cl(3)	90.1 (1)	C(1)–C(2)–C(3)	118.7 (7)
Cl(1)–Tc–O(1)	82.7 (1)	C(1)–C(2)–C(7)	120.9 (6)
Cl(1)–Tc–O(2)	87.7 (2)	C(3)–C(2)–C(7)	120.3 (7)
Cl(1)–Tc–N	89.3 (2)	C(2)–C(3)–C(4)	120.0 (9)
Cl(2)–Tc–Cl(3)	90.9 (1)	C(3)–C(4)–C(5)	119.3 (8)
Cl(2)–Tc–O(1)	90.8 (1)	C(4)–C(5)–C(6)	120.2 (8)
Cl(2)–Tc–O(2)	98.5 (2)	C(5)–C(6)–C(7)	118.5 (8)
Cl(2)–Tc–N	88.6 (2)	O(1)–C(7)–C(2)	120.9 (6)
Cl(3)–Tc–O(1)	88.5 (1)	O(1)–C(7)–C(6)	117.4 (7)
Cl(3)–Tc–O(2)	99.7 (2)	C(2)–C(7)–C(6)	121.6 (7)
Cl(3)–Tc–N	169.5 (2)	S–C(8)–C(9)	127.4 (7)
O(1)–Tc–O(2)	167.4 (2)	S–C(8)–C(13)	110.1 (6)
O(1)–Tc–N	80.9 (2)	C(9)–C(8)–C(13)	122.4 (8)
O(2)–Tc–N	90.7 (3)	C(8)–C(9)–C(10)	117.3 (8)
Tc–O(1)–C(7)	132.2 (4)	C(9)–C(10)–C(11)	120.7 (9)
Tc–N–C(1)	124.7 (5)	C(10)–C(11)–C(12)	121.8 (8)
Tc–N–C(13)	124.4 (5)	C(11)–C(12)–C(13)	117.5 (8)
C(1)–N–C(13)	110.7 (6)	N–C(13)–C(8)	114.0 (7)
C(1)–S–C(8)	90.4 (4)	N–C(13)–C(12)	128.7 (7)
N–C(1)–S	114.6 (6)	C(8)–C(13)–C(12)	120.2 (8)
N–C(1)–C(2)	125.7 (6)		

M═O and M—X IR stretching frequencies are concordant with those reported for similar M(V) Schiff base complexes.[19] All of the complexes are diamagnetic, consistent with their expected spin-paired d^2 electronic configuration. The $[TcOCl_3(hbt)]^-$ anion is characterized by the single-crystal X-ray structure determination described below.

Crystal Structure. Figure 2 shows a perspective view of the $[TcOCl_3(hbt)]^-$ anion and defines the atom-numbering scheme. Final positional and equivalent isotropic vibrational parameters are given in Table IV, while selected bond distances and angles are presented in Tables V and VI. Listings of observed and calculated structure factors, anisotropic thermal parameters and hydrogen positional parameters, positional and thermal parameters, and least-squares planes and deviations therefrom and an ORTEP[18] view of the tetraphenylarsonium cation have been deposited as supplementary material.

The crystal structure consists of pairs of $[TcOCl_3(hbt)]^-$ anions and $[As(C_6H_5)_4]^+$ cations, with no significant interactions between them. The coordination geometry around the Tc atom is nearly octahedral; the two oxygen atoms, O(2) of the Tc═O linkage and O(1) of the hbt ligand, occupy apical positions while the three chlorine atoms along with the N(1) nitrogen atom of the hbt ligand occupy equatorial positions (Figure 2). The maximum distortion from octahedral symmetry is caused by repulsion between the sterically demanding Tc═O(2) linkage and the coordinated chloride ligands Cl(2) and Cl(3). The O(2)–Tc–Cl(2) and O(2)–Tc–Cl(3) angles are 98.5 (2) and 99.7 (2)°, respectively; the Tc atom is concomitantly displaced 0.154 (1) Å toward O(2) from the mean equatorial plane [N(1), Cl(1), Cl(2), Cl(3)].

Reactivity. Interaction of excess 2-(2-hydroxyphenyl)benzothiazoline (hbtH) with $[MOX_4]^-$ anions (M = Tc, Re; X = Cl, Br) in methanol leads to efficient formation of the oxidized species 2-(2-hydroxyphenyl)benzothiazole (hbt). The noncoordinated hbt product is readily recovered by evaporation of the reaction solution. Only a small amount of metal complex is required for conversion of a large excess of hbtH to hbt. When the reaction is conducted in acetone, the solvent undergoes net reduction and isopropyl alcohol is formed.

Discussion

Synthesis and Properties of hbt Complexes. The reactions of the thiazole ligand hbt (Figure 1) with the metal(V) complexes $[MOX_4]^-$ (M = Tc, Re; X = Cl, Br) parallel those observed for related bidentate Schiff base ligands.[19] Reaction under mild conditions (room temperature, 2-fold excess of hbt) leads to the monosubstituted $[MOX_3(hbt)]^-$ product, while reaction under more stringent conditions (refluxing ethanol, 4-fold excess of hbt) leads to the disubstituted product $[MOX(hbt)_2]$:

$$[MOX_4]^- + hbt \rightarrow [MOX_3(hbt)]^- + HX$$

$$[MOX_3(hbt)]^- + hbt \rightarrow [MOX(hbt)_2] + HX + X^-$$

In these complexes hbt is deprotonated at the phenol moiety and thus functions as a monoanionic, bidentate ligand. Elemental analyses and mass spectral data establish the composition of these complexes, while IR and magnetic susceptibility measurements confirm that the spin-paired d^2 metal(V) center is present as the $[M{=}O]^{3+}$ core. Analogous monoanionic, bidentate Schiff base complexes invariably contain an anionic oxygen atom situated trans to the M═O double bond,[19,20] and thus this stable *trans*-O═M—O$^-$ configuration is presumed to be present in these hbt complexes. This presumption is confirmed for $[TcOCl_3(hbt)]^-$ by single-crystal X-ray structural analysis (Figure 2). The IR and ^1H NMR data, as well as the synthetic routes used to prepare these complexes, are consistent with the coordinated ligand being present in the thiazole (hbt) form but are not consistent with it

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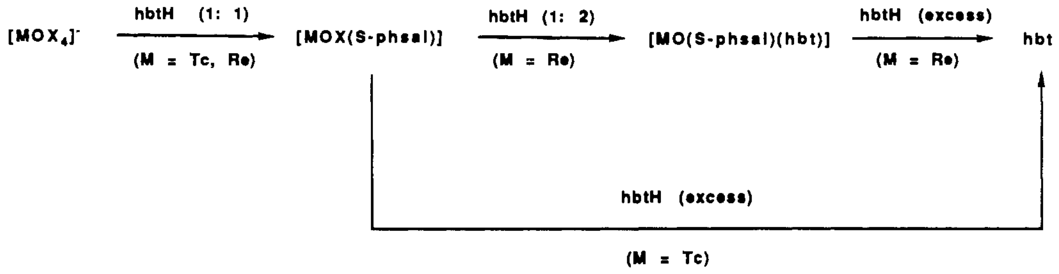

Figure 3. Reaction diagram.

being present in the thiazoline (hbtH) or Schiff base (S-phsal^{2-}) forms (Figure 1). Specifically, the C═N stretch is observed at 1600 cm^{-1}, and no resonance for the CH═N linkage is observed in the ^{1}H NMR spectrum.

Very recently, we reported the crystal structure determination of the bisubstituted complex [TcOCl(hbt)$_2$].[21] In that study, such a compound was obtained through a method apparently different from that described here, as it was isolated from a dichloromethane/heptane solution of the complex [TcOCl(S-phsal)] after slow evaporation of the solvent. This result was attributed to the same kind of intramolecular ring closure of the S-phsalH$_2$ ligand to give the oxidized hbt discussed here, but it was not understood whether the hbt moiety was an impurity in the original preparation of the S-phsalH$_2$ ligand or if it formed during the reaction of this ligand with the technetium starting complex. In view of the results presented in this study, and in particular considering that (i) the first interaction between the complex [TcOCl$_4$]$^-$ and hbtH appears to favor the ring opening of the ligand (see below), (ii) the [TcOCl(hbt)$_2$] complex was a minor product in the original preparation of the parent complex [TcOCl(S-phsal)],[21] and (iii) no formation of the bisubstituted hbt complex was observed by mixing [TcOCl(S-phsal)] with hbtH, we conclude that it was, probably, the presence of hbt as an impurity in the original preparation of [TcOCl(S-phsal)] to cause the formation of the complex [TcOCl(hbt)$_2$].

A moderately stable rhenium(V) complex that contains both oxidized and reduced forms of the ligand, ReO(S-phsal)(hbt), can be prepared by utilizing hbtH as reactant:

$$2\text{hbtH} + [\text{ReOX}_4]^- \rightarrow \text{ReO(S-phsal)(hbt)}$$

$$\text{hbtH} + \text{ReOX(S-phsal)} \rightarrow \text{ReO(S-phsal)(hbt)}$$

The equivalent technetium(V) complex cannot be isolated. Moderate yields (ca. 40%) of ReO(S-phsal)(hbt) are obtained when the above reactions are conducted with stoichiometric amounts of reagents; the chemical fate of the reducing power released in these reactions has not been determined. Elemental analyses and mass spectral data establish the composition of ReO(S-phsal)(hbt), while IR and magnetic susceptibility measurements confirm the presence of the spin-paired d^2 [M═O]$^{3+}$ core. Moreover, IR and ^{1}H NMR data are consistent with the reduced form of the ligand being coordinated as the Schiff base (S-phsal^{2-}) but are not consistent with it being coordinated as the thiazole (hbtH) (Figure 1). Specifically, no NH signal is observed in either the ^{1}H NMR or the IR spectra, and no IR signal due to the C–S–C linkage is observed in the 970–910-cm^{-1} region; these signals have been observed in hbtH complexes of molybdenum.[6] Rhenium(V) complexes of Schiff base ligands derived from salicylaldehyde invariably contain the *trans*-O═Re—O$^-$ configuration, in which the anionic phenolate oxygen atom is coordinated trans to the Re═O linkage.[19,20,22] Thus, a reasonable structure for ReO(S-phsal)(hbt) consists of a dianionic, tridentate S-phsal^{2-} ligand coordinated in the plane normal to the Re═O linkage and a monoanionic, bidentate hbt ligand coordinated to the remaining two positions of the octahedron, with the charged phenolate oxygen atom situated trans to the Re═O linkage.

Crystal Structure. Structural parameters within the Tc(V) coordination polyhedron are quite normal and do not differ significantly from those reported for similar complexes containing the [Tc═O]$^{3+}$ core.[20,23] The short Tc═O distance of 1.650 (6) Å is characteristic for this multiple bond,[20,23] and the relative Tc–N(1) and Tc–O(1) distances can be understood within a previously presented[22] interpretation based on Pearson's hard–shoft acid–base theory.[24] The hbt ligand is remarkably planar; the angles between the mean planes of the rings P1 [C(8)–C(13); $(\Delta/\sigma)^2 = 4.8$], P2 [S, C(1), N(1), C(13), C(8); $(\Delta/\sigma)^2 = 17.2$], and P3 [C(2)–C(7); $(\Delta/\sigma)^2 = 0.5$] are P1–P2 = 2.1 (3)° and P1–P3 = 12.6 (3)°. This planarity, as well as the values of the bond distances and angles within the benzothiazole moiety, indicate complete delocalization of the π system; such delocalization has been observed in other thiazole and benzothiazole rings.[25]

π delocalization can also account for the fact that the hbt ligand is N,O-bonded rather than S,O-bonded: ring delocalization of the p$_z$ electron pair (the z axis being chosen normal to the ring plane) of the sp^2-hybridized sulfur atom imparts to it a partial positive charge, which makes its coordination to the metal atom through the sp^2 electron pair less favored than for the nitrogen atom.

Reactivity. The oxidation of 2-(2-hydroxyphenyl)benzothiazoline (hbtH) to 2-(2-hydroxyphenyl)benzothiazole (hbt) is driven by the attendant gain in aromatic stabilization energy (Figure 1). This oxidation readily occurs upon irradiation with UV light, leading to the production of molecular hydrogen by a radical mechanism.[7] Oxidation of hbtH also readily occurs upon its interaction with [MOX$_4$]$^-$ complexes (M = Tc, Re; X = Cl, Br). The several observations made in this study are all consistent with this oxidation occurring by the following sequence of steps (Figure 3).

(1) Initial coordination of hbtH to the metal center forces the ring to open, and the coordinated ligand assumes the Schiff base form (S-phsal^{2-}). This Schiff base form functions as a dianionic, tridentate ligand coordinated to the metal center through the charged phenolic oxygen atom, the neutral imine nitrogen atom, and the charged sulfur atom. The resulting neutral, square-pyramidal complexes [MOX(S-phsal)] have been previously described for X = Cl[8,10] and under our experimental conditions are readily obtained by using a hbtH/metal ratio of unity. Under these conditions no oxidation of hbtH is observed; the reduced ligand is stabilized by coordination in the Schiff base form (Figure 1).

(2) The addition of a second molar equivalent of hbtH leads to its oxidation to hbt. When M = Re, the resulting hbt moiety is retained in the coordination sphere and [ReO(S-phsal)(hbt)] can be isolated in moderate yields. Formation of this six-coordinate complex from the five-coordinate [ReOX(S-phsal)] formally involves displacement of the equatorial halide ligand by the neutral nitrogen atom of hbt and completion of the coordination sphere by the charged phenolate oxygen atom of hbt (the originally vacant site is situated trans to the Re═O linkage). When M = Tc, the

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analogous complex cannot be isolated; this may be due to the tendency of monooxo–Tc(V) complexes to prefer (relative to the Re(V) analogues) five-coordinate geometry over six-coordinate geometry.[17,22]

(3) The addition of further equivalents of hbtH leads rapidly to the formation of hbt, without any requirement for additional metal complex. The efficient conversion of large excesses of hbtH to hbt is accomplished by all the $[MOX_4]^-$, [MOX(S-phsal)], and [ReO(S-phsal)(hbt)] complexes, and thus all of these species can be readily incorporated into the reaction cycle. Presumably, the hbt product is lost from [MO(S-phsal)(hbt)] to generate a five-coordinate solvated species that can then accept another 1 mol of hbtH and continue the cycle.

When the metal(V)-promoted conversion of hbtH to hbt is conducted in methanol, the chemical fate of the released reducing power has not yet been determined. However, when this conversion is conducted in acetone, the formation of isopropyl alcohol can be detected within a few minutes after mixing the reagents. In this situation the small amount of metal(V) complex promotes hbtH reduction of acetone to yield isopropyl alcohol and hbt. Reduction of ketones is effected by the hydride ion but not by the hydrogen radical, and thus it appears as though the metal(V)-promoted conversion of hbtH to hbt proceeds by a 2-equiv mechanism rather than by a free-radical process. This is in contrast to the light-induced oxidation of hbtH, which proceeds with the formation of hydrogen radicals that are unable to reduce ketones.[7]

The studies reported herein are placed into a larger context by consideration of two literature reports on the reactivity of hbtH. First, hbtH reacts with high-valent metals such as Mo(V) and Mo(VI) without undergoing oxidation to hbt.[6] This observation indicates that metal-promoted oxidation of hbtH is not a general reaction and strongly implies that there is some specific aspects of the $[Tc{=}O]^{3+}$ and $[Re{=}O]^{3+}$ cores which promotes conversion of hbtH to hbt. Second, hbtH has been used as an olefin reducing agent,[26] but in this application the carbon–carbon double bond of α,β-unsaturated carbonyl compounds is reduced *without* concomitant reduction of the carbonyl group. This observation implies that in our studies it is not hbtH itself which reduces acetone but rather it is some activated metal center which effects the actual hydride transfer. In sum, it appears as though the five-coordinate, square-pyramidal, monooxo-Tc(V) and -Re(V) centers play an essential role in the conversion of hbtH to hbt, and it is reasonable to suppose that this conversion proceeds by a hydride transfer which invovles the M=O linkage. The details of this process, and the details of the subsequent reaction steps leading to carbonyl reduction, remain to be elucidated.

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Registry No. hbtH, 7361-94-6; hbt, 3411-95-8; ReO(S-phsal)(hbt), 116887-50-4; $As(C_6H_5)_4[ReOCl_4]$, 14853-14-6; $As(C_6H_5)_4[ReOBr_4]$, 14853-12-4; $As(C_6H_5)_4[^{99}TcOCl_3(hbt)]$, 116887-52-6; $As(C_6H_5)_4[ReOCl_3(hbt)]$, 116887-58-2; $As(C_6H_5)_4[^{99}TcOBr_3(hbt)]$, 116887-54-8; $As(C_6H_5)_4[ReOBr_3(hbt)]$, 116887-60-6; $As(C_6H_5)_4[^{99}TcOBr_4]$, 116887-56-0; $As(C_6H_5)_4[^{99}TcOCl_4]$, 97101-52-5; $TcOCl(hbt)_2$, 113754-30-6; $ReOCl(hbt)_2$, 116887-61-7; $TcOBr(hbt)_2$, 116887-55-9; $ReOBr(hbt)_2$, 116887-62-8; salicylaldehyde, 90-02-8; 2-aminothiophenol, 137-07-5.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom positional parameters, positional and thermal parameters, least-squares planes and deviations thereform, and crystal data for the complex $As(C_6H_5)_4[TcOCl_3(hbt)]$ and an ORTEP view of the cation $[As(C_6H_5)_4]^+$ (7 pages); a table of structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Virginia, Charlottesville, Virginia 22901

nido-Carborane Building-Block Reagents. 4.[1] Regiospecific Substitution at Boron in 2,3-$R_2C_2B_4H_6$ Cages. Evidence for Intramolecular C–H- - -H_{bridge} Interactions in 2,3-$R_2C_2B_4H_5$-4-R′ Derivatives

James H. Davis, Jr., and Russell N. Grimes*

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Reactions of *nido*-2,3-$R_2C_2B_4H_5^-$ ions (R = ethyl, benzyl) with organic halides (R′X) generate B(4)-substituted derivatives together with the B(6)-substituted enantiomers. The formation of the $R_2C_2B_4H_5$-4-R′ products (R′ = Me, Et, CH_2Ph, $(CH_2)_3Ph$, $CH_2C_6H_4Me$) is proposed to occur via $R_2C_2B_4H_5$-μ(4,5)-R′ bridged intermediates, which rapidly rearrange to the 4-substituted species. The reaction occurs cleanly, with $\leq 1\%$ contamination by other geometric isomers, and thus furnishes a useful regiospecific synthetic route to B-monosubstituted derivatives. In all cases examined, the products are air-stable liquids of low volatility that can be employed as building-block units in the synthesis of organometallic complexes and oligomers. Proton NMR spectra of several of the 2,3,4-trisubstituted products, supported by NOE experiments, indicate spin coupling between a C–CH_2 methylene proton and a B–H–B bridging hydrogen. The triethyl and tribenzyl derivatives were bridge-deprotonated by NaH, complexed to Fe^{2+}, and oxidatively fused to produce the hexasubstituted $R_6C_4B_8H_6$ carboranes, although the reaction was sluggish compared to those of the parent C,C′-disubstituted carboranes. The fused compounds are nonfluxional in solution, as determined from NMR spectra.

Carbon-substituted $RR'C_2B_4H_6$ *nido*-carboranes are readily obtained via the base-promoted reaction of B_5H_9 and RC≡CR′ under mild conditions.[2] This method has provided a reliable, general synthetic route to a wide variety of alkyl-,[2-4] arylalkyl-,[2] aryl-,[1b] and silylcarboranes[5] as well as bis- and tris(carboranes)[1b] having two or more *nido*-C_2B_4 cages linked by –$(CH_2)_n$– chains;

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