Synthesis and Crystal Structure Determination of [H_2-cryptand 222](Br_3)$_2$: A Unique Tribromide Catalyst for the Catalytic Chemoselective *N*-Boc Protection of Amines

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The organic tribromide, [H_2-cryptand 222](Br_3)$_2$ was synthesized and characterized by X-ray crystallography, and was utilized as an active catalyst for the *N*-boc protection of amines. The method is general for the preparation of *N*-boc derivatives of aliphatic (acyclic and cyclic), aromatic, primary and secondary amines. We also applied our new reaction protocols for the *N*-boc protection of some new amines and spectral and physical data for the obtained products are reported.

Keywords: [H_2-cryptand 222](Br_3)$_2$; *diboc*; *N*-Boc protection; Amine; Tribromide; Chemoselective.

INTRODUCTION

Crown ethers have attracted significant attention from various fields of science. Crown ether moieties are popular host compounds in host-guest chemistry and these ligands have shown a remarkable ability to form strong complexes with organic and inorganic cations[1-3] or anions,[4,5] selectively. Among the crown ethers, cryptand 222, a macrobicyclic compound, has been used in a variety of applications including the formation of a conductometric mercury [II] sensor based on poly aniline,[6] the encapsulation of alkali metals, especially K^+,[7-9] use as an acceptor ligand for the formation of complexes containing 7,7,8,8-tetracyanoquinodimethane (*TCNQ*),[10] extraction of uranium(VI),[11] exchanging the cations of micas[12] and extraction of copper(II) with erythrosine B.[13]

Organic tribromide reagents (*OTBs*) are preferable as oxidants to molecular bromine, owing to the hazards associated with elemental bromine. Several tribromides have been reported i.e., tetramethylammonium tribromide,[14,15] phenyltrimethylammonium tribromide,[16] cetyltrimethylammonium tribromide, tetrabutylammonium tribromide,[17] 1,8-diazabicyclo[5,4,0]-tetrabutylammonium tribromide,[18] pyridine hydrobromide perbromide,[19] hexamethylenetetramine-bromine[20] and DABCO-bromine.[21] Recently some ionic liquid tribromides (IL-Br_3^-) for the preparation of bromoesters from aromatic aldehydes[22] and bromination of aromatic substrates[23] were reported. Very recently, we reported {[K.18-crown-6]Br_3}$_n$, a unique tribromide with a columnar nanotube-like structure.[24]

Given the usefulness of such compounds, the development of further synthetic protocols for their synthesis is an area of interest.[25,26]

Due to its great stability under the conditions used in various base-catalyzed nucleophilic substitutions and catalytic hydrogenation reactions, the *tert*-butoxycarbonyl (*boc*) group is perhaps one of the most important protecting groups, especially for amines and amine derivatives.[27,28] The stability of *N*-boc to catalytic hydrogenation and its resistance towards basic and nucleophilic attack make carbamates and benzyl esters ideal orthogonal partners for the protection of amines during the synthesis of multifunctional targets.[29,30] Various reagents and methods have been developed for *N*-*tert*-butoxycarbonylation of amines.[31,32] Commercially available *di*-*tert*-butyl dicarbonate (*diboc*)

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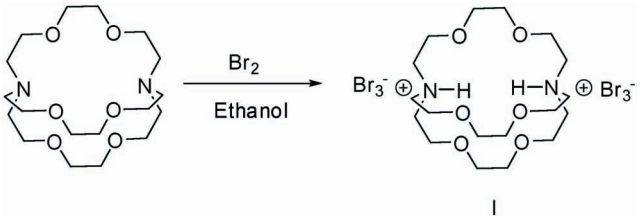
is an efficient reagent for clean and rapid introduction of the boc-protecting group.[33-35]

In this paper, we report the synthesis and structural characterization of [H_2-cryptand 222](Br_3)$_2$ and show that it is as an excellent catalyst for the selective *tert*-butoxycarbonylation of various amines using diboc.

RESULTS AND DISCUSSION

In continuation of our studies on the host-guest chemistry of crown ethers,[36-38] the synthesis and application of tribromide reagents[24,39] and the protection of organic functional groups,[40-44] we found that addition of Br_2 to cryptand 222 in ethanol as solvent gave the unique tribromide reagent [H_2-cryptand 222](Br_3)$_2$ (**I**) which was isolated as red crystals following recrystallization from acetonitrile, (Scheme I).

Scheme I



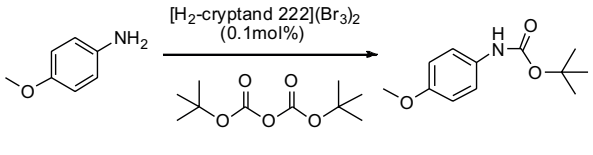
I

Crystallographic analysis at 89 K confirmed the formulation of these crystals as [H_2-cryptand 222](Br_3)$_2$. The structure comprises a doubly protonated cryptand cation and two tribromide anions. Diprotonated cryptands have three possible conformers, namely *exo-exo*, *endo-endo* and *exo-endo*.[45] Like all but five of the 55 examples of diprotonated cryptans 222 in the Cambridge Crystallographic Database, [H_2-cryptand 222](Br_3)$_2$ displays an *endo-endo* conformation (Fig. 1) in which the two *N*-protons point into the cavity of the cryptand.[46]

As the first application of these new structure, we studied the conversion of 4-methoxyaniline (1 mmol) to its corresponding *N*-boc protected derivative using the [H_2-cryptand 222](Br_3)$_2$ catalyst (0.001 mmol) and diboc (1 mmol) in a variety of solvents at room temperature (Table 1). The results show that acetonitrile is the best solvent in terms of time and product yield.

We then prepared a range of *tert*-butoxycarbonylated amines under the following reaction conditions: amine compound (1 mmol), diboc (1-2 mmol), [H_2-cryptand 222](Br_3)$_2$ (0.0015-0.003 mmol) and acetonitrile (4 mL)

Table 1. Comparative performances of various solvents in the *N*-boc protection of 4-methoxyaniline with diboc at room temperature



Entry	Solvent	Time (h)	Yield (%)
1	CH_3CN	5	80
2	$CHCl_3$	12	70
3	CH_2Cl_2	10	60
4	1,4-dioxane	10	65
5	*n*-Hexane	10	30
6	Acetone	2	--
7	EtOAc	15	50
8	Ethanol	15	60

(Scheme II and Table 2).

A wide range of various amines undergo *N*-boc protection using this procedure to provide the corresponding *tert*-butoxycarbonylated products in good to excellent yields. Aliphatic amines generally react more rapidly than aromatic. We also applied our reaction protocols to the *N*-boc protection of some new amines (Table 2, entries 11, 14, 17, 19, 20, 21, 23, 25 and 26). Spectral and physical data for the obtained products are consistent with their proposed structures.

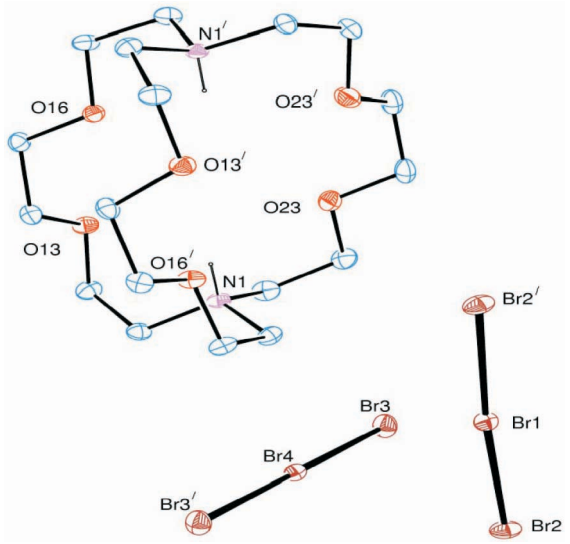
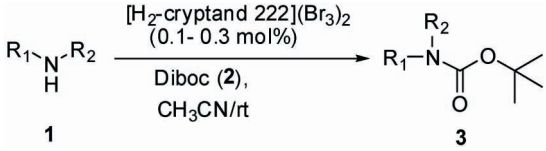


Fig. 1. ORTEP diagram of [H_2-cryptand 222](Br_3)$_2$. H atoms have been omitted for clarity.

Scheme II



Chemoselectivity

Organic tribromide reagents are well known as brominating agents for aromatic species.[22-24] Our results for the protection of aromatic amines further shows the chemoselectivity of the [H_2-cryptand 222](Br_3)$_2$/diboc combination, as the *N*-boc protected amine is the only product observed in all cases. This system thus appears superior to other reported methods[22-24] in that bromination of the aromatic ring in aromatic amines does not occur (Table 2, Scheme III).

Spectroscopic data for unreported products

[H_2-cryptand 222](Br_3)$_2$: Red crystals, yield 0.95%; Mp: 145 °C, IR (KBr): 3320 (w), 2985 (w), 1450 (w), 1345 (m), 1125 (s). ^{1}H NMR (90 MHz, $CDCl_3$): δ = 4.1 (s, 36H), 6.67 (br, 2H, NH).

Entry 11: Yellow solid, yield 65%; Mp: 188 °C; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.4 (s, 18H), 3.8 (s, 2H), 6.4 (br, 2H, NH), 7.2 (m, 8H); IR (KBr): 3356, 2980, 1690, 1550 cm^{-1}.

Entry 14: White solid, yield 70%; Mp: 150 °C; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.4 (s, 18H), 2.2 (s, 3H), 6.5 (br, 1H, NH), 6.7-7.2 (m, 4H, NH, CH); ^{13}C NMR (22.5 MHz, $CDCl_3$): 20.9, 28.3, 80.5, 124.1, 124.2, 125.6, 127.1, 130.7, 135.4, 153.8; IR (KBr): 3278, 2978, 1700, 1541 cm^{-1}.

Entry 17: Colorless oil, yield 95%; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.3-1.7 (m, 17H), 3.2 (br, 4H, CH_2); IR (KBr): 2978, 1690 cm^{-1}.

Entry 19: White solid yield 90%; Mp: 163 °C; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.3 (m, 22H), 1.9 (br, 4H), 3.2 (br, 2H), 4.8 (br, 2H, NH); IR (KBr): 3363, 2974, 1684 cm^{-1}.

Entry 20: Colorless oil yield 85%; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.2 (s, 9H), 2.2-2.4 (m, 6H), 3.3-3.5 (m, 7H, CH); IR (KBr): 3450, 2976, 1680 cm^{-1}.

Entry 21: Yellow oil yield 95%; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1 (d, *J* = 7 Hz, 3H), 1.2-1.3 (m, 15H), 2.5 (m, 1H), 3.6 (m, 1H), 4.1 (m, 1H); IR (Nujol): 2974, 1670 cm^{-1}.

Entry 23: Pink oil yield 85%; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.48 (s, 9H), 3.1 (t, *J* = 17 Hz, 4H), 3.5 (t, *J* = 17 Hz, 4H), 6.8-7.2 (m, 5H); IR (Nujol): 2978, 1700, 1597 cm^{-1}.

Entry 25: Colorless solid yield 85%; Mp: 80 °C; ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.4 (s, 18H), 3.2-3.7 (m, 24H); ^{13}C NMR (22.5 MHz, $CDCl_3$): 28, 48, 65, 68, 83, 157; IR (KBr): 2978, 1650, 1200 cm^{-1}.

Entry 26: Colorless oil yield 90%; ^{1}H NMR (90 MHz, $CDCl_3$): d = 1.4 (s, 9H), 3.4-3.7 (m, 24H); ^{13}C NMR (22.5 MHz, $CDCl_3$): 25, 55, 67, 70.1, 70.4, 70.7, 159; IR (Nujol): 2930, 1660, 1167 cm^{-1}.

Experimental description of structure

Suitable crystals of [H_2-cryptand 222](Br_3)$_2$ were obtained by slow evaporation of a CH_3CN solution. Crystal data and experimental parameters for the crystal structure are reported in Table 3. The orange crystals (dimensions of 0.29 × 0.25 × 0.18 mm^3) were mounted on a glass fibre and used for data collection. X-ray data were collected at 89 K on a Bruker Kappa APEX-II system using graphite-monochromated Mo Kα radiation with exposures over 0.5°, and were corrected for Lorentz and polarization effects using SAINT.[47] All structures were solved using SIR-97[48] running within the WinGX package[49] and weighted full-matrix refinement on F^2 was carried out using SHELXL-97.[50] Hydrogen atoms attached to carbon and nitrogen, were included in calculated positions, and were refined as riding atoms with individual (or group, where appropriate) isotro-

Scheme III

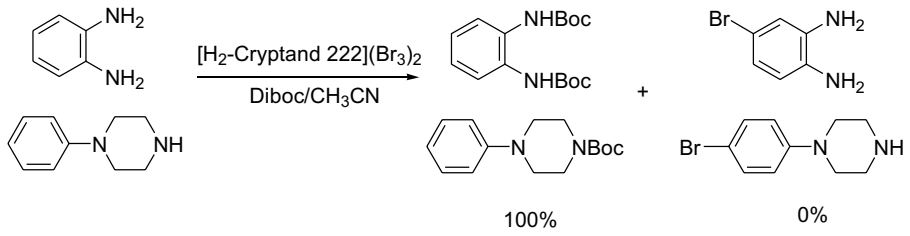
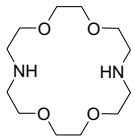
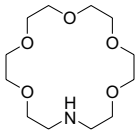


Table 2. Protection of amines (**1**) with diboc (**2**) using [H_2-cryptand 222](Br_3)$_2$ as catalyst in acetonitrile at room temperature

Entry	Amine	Catalyst (mol %)	Diboc (mmol)	Time (h)	Isolated yields[a] (%)	Ref.
1	Ph-NH_2	0.1	1.1	5	80	34
2	4-Cl-Ph-NH_2	0.15	1.1	4	80	33
3	4-Br-Ph-NH_2	0.2	1.1	8	85	33
4	4-OMe-Ph-NH_2	0.1	1	5	80	34
5	4-OH-Ph-NH_2	0.1	1	5	90	32
6	2-OH-Ph-NH_2	0.1	1	4	85	27
7	2-Me-Ph-NH_2	0.15	1	4	65	33
8	3-Me-Ph-NH_2	0.1	1	7	85	33
9	3-Br-Ph-NH_2	0.2	1	10	75	33
10	$(PhCH_2)_2NH$	0.1	1	0.5	98	27
11	$(4\text{-}NH_2Ph)_2CH_2$	0.2	2	4.5	65	--
12	Ph-CH_2NH_2	0.1	1	2	80	34
13	Benzene-1,2-diamine	0.3	2	10	85	32
14	4-Methylbenzene-1,2-diamine	0.2	2	8	70	--
15	Naphthalen-1-amine	0.15	1	6	80	33
16	Azepane	--	1	0.75	80	--
17	Azepane	0.1	1	0.25	95	--
18	Piperazine	0.1	2	1	70	32
19	Cyclohexane-1,2-diamine	0.15	2	1	90	--
20	2-(Piperazin-1-yl)ethanol	0.1	1	0.25	85	--
21	2-Methylpiperidine	--	1	0.75	95	--
22	2-Methylpiperidine	0.1	1	0.33	95	--
23	1-Phenylpiperazine	0.2	1	0.33	85	--
24	1*H*-imidazole	0.1	1	2	75	28
25		0.1	2	0.33	85	--
26		0.1	1	0.16	83	--
27	3-(Trifluoromethyl)aniline	0.3	1	--	Mixture of products	--
28	Pyridin-2-amine	0.2	1	--	Mixture of products	34
29	4-Nitrobenzene-1,2-diamine	0.2	2	--	Mixture of products	--
30	1*H*-indole	0.15	1	--	--	34
31	1*H*-pyrrole-3-carbaldehyde	0.15	1	--	--	--
32	Melamine	0.1	3	--	--	--

pic displacement parameters.

In conclusions, we have prepared and characterized a novel crystalline tribromide catalyst based on cryptand 222 which has high active bromine content per molecule and which acts as an excellent bromine carrier capable of catalyzing the chemoselective *N*-boc protection of amines. The reaction is carried out under mild conditions and yields of products are good to excellent.

EXPERIMENTAL

General

Chemicals were purchased from Merck. *N*-Boc pro-

Table 3. Refinment and crystal structure data of compound [H_2-cryptand 222]$(Br_3)_2$

Empirical formula	$C_{18}H_{38}Br_6N_2O_6$
Formula weight	857.96
Temperature	89(2) K
Wavelength	0.71073
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	
a (Å)	11.902(3)
b (Å)	15.671(3)
c (Å)	15.660(3)
α	90°
β	95.882(10)°
γ	90°
V(Å) ^{3}	2905.5(10)
Z	4
Dcalc (Mg/m^3)	1.961
Absorption coefficient (mm^{-1})	8.324
F(000)	1672
Crystal size (mm^3)	0.29 × 0.25 × 0.18
θ range for data collection (°)	2.16 to 26.55
Index ranges	-14 ≤ h ≤ 14, -19 ≤ k ≤ 19, -17 ≤ l ≤ 19
Reflections collected	26588
R_{int}	0.0419
Completeness to θ = 26.55°	98.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.646031
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2998 / 0 / 151
Goodness-of-fit on F^2	1.054
Final R indices [I > 2σ(I)]	R1 = 0.0208, wR2 = 0.0439
R indices (all data)	R1 = 0.0264, wR2 = 0.0454
Largest diff. peak and hole (e.Å^{-3})	0.414 and -0.399

tected products were characterized by comparison of their spectral (IR, ^{1}H-NMR and ^{13}C-NMR) and physical data with those of known samples.[27,28,33-35]

Preparation of [H_2-cryptand 222]$(Br_3)_2$

In a round-bottomed flask (100 mL) equipped with a magnetic stirrer, bromine (0.494 g, 3.1 mmol) was added to a solution of cryptand 222 (0.376 g, 1 mmol) in ethanol (30 mL) and the mixture was stirred for 0.5 hour. Filtration through a sintered glass funnel gave a fine yellow powder [0.81 g, 95% yield], which was recrystallized from CH_3CN to give red crystals [Mp: 145 °C].

General procedure for the *N*-boc protection of amines

To a solution of diboc (1-2 mmol) in CH_3CN (4 mL) was added [H_2-cryptand 222]$(Br_3)_2$ (0.001-0.003 mmol). The solution was stirred at room temperature for one minute. The amine (1 mmol) was then added and the solution was stirred at room temperature for the appropriate time (see Table 2). After completion of the reaction, CH_3CN was removed by water-bath distillation. To the residue was added *n*-hexane or ethyl acetate (5 mL) and the mixture was filtered. The solid was washed with *n*-hexane or ethyl acetate (2 × 10 mL) and the combined filtrates were reduced to dryness to yield pure products.

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