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Silver(I) poly(1,2,3-benzotriazolyl)borate complexes containing mono- and bidentate phosphine coligands

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Abstract

New silver(I) derivatives $[Ag\{H_nB(btz)_{4-n}\}(PR_3)_x]$ ($n = 1$ or 2, x ranging from 1 to 3), containing monodentate tertiary phosphines and anionic poly(benzotriazol-1-yl)borates, have been prepared from the reaction of $AgNO_3$ with PR_3 (R = Ph, *o*-tolyl, *m*-tolyl, *p*-tolyl, Bn) and $K[H_2B(btz)_2]$, or $K[HB(btz)_3]$ (Hbtz = 1,2,3-benzotriazole). When the reaction between $K[H_2B(btz)_2]$ and $AgNO_3$ was carried out in the presence of dppe (1,2-bis(diphenylphosphino)ethane), or dppf (1,1′-bis(diphenylphosphino)ferrocene), compounds $[Ag\{H_2B(btz)_2\}]_2(L)$ (L = dppe or dppf) formed, the diphosphine acting as a bidentate bridging P_2-donor. Solid state and solution properties of all complexes have been investigated through analytical and spectroscopic measurements (IR, ^1H, ^{31}P NMR), the ^1H and ^{31}P NMR spectra being interpreted in terms of equilibria that involve mono- and di-nuclear complexes. Adducts $[Ag\{HB(btz)_3\}(PPh_3)_3]\cdot(1/2H_2O)$ and $[Ag\{H_2B(btz)_2\}]_2$ (dppf) have been characterised by single crystal X-ray studies. In the former, the $HB(btz)_3$ is unidentate in an $NAgP_3$ coordination environment; the latter is a dimer, the dppf bridging the two silver atoms, while the $H_2B(btz)_2$ ligand, which chelates one silver, bridges to the second also, the array having 2-symmetry.

Keywords: Benzotriazole; X-ray; Scorpionates; Silver; Phosphines; Spectroscopy

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1. Introduction

Since the pioneering work of Trofimenko [1], a number of papers have been reported on the synthesis and characterisation of poly(pyrazolyl)borate metal complexes [2]. By contrast, only a few poly(azolyl)borate complexes with azolyl groups other than pyrazole have been investigated, although it has been shown that the chemistry of poly(azolyl)borate complexes may be critically dependent upon the pattern of ring substitution [3], motivating several researchers to investigate the behaviour of metal complexes of analogous ligand systems with modified steric and/or electronic properties, for example: poly(1,2,3-triazolyl)borates and poly(1,2,3,4-tetrazolyl)borates [4], poly(2-sulfanyl-1-methylimidazolyl)borate [5] and poly(imidazolyl)-type ligands [6].

In extension of our studies concerning the structural and spectroscopic properties of mixed phosphine/N-donor derivatives of silver(I), we have investigated a variety of complexes incorporating poly(azolyl)borate and phosphine ligands with different steric and electronic profiles [5a,7–12]. The different coordination characteristics of poly(triazolyl)borate species offer the prospect of new and interesting chemistry, paralleling that of pyrazolyl and imidazolyl arrays [10,11,13]. In our research concerning modifications of the poly(pyrazolyl)borate ligands in which the pyrazolyl rings are replaced by 1,2,3-triazolyl or imidazolyl rings, some interesting

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single-stranded silver(I) coordination polymers containing bridging poly(1-imidazolyl) borates have been reported [10].

We report here the synthesis, characterisation and reactivity of some new complexes obtained from the interaction of the dihydrobis(1,2,3-benzotriazolyl)-borate $[H_2B(btz)_2]^-$, and tris(1,2,3-benzotriazolyl)borate $[HB(btz)_3]^-$ ligands (Fig. 1), with $AgNO_3$ and mono- or di-phosphines, together with the crystal and molecular structures of some novel arrays defined by X-ray diffraction studies.

2. Experimental

2.1. General procedures

All syntheses and handling were carried out under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques or a glove box. All solvents were dried, degassed and distilled prior to use. All chemicals were purchased from Aldrich and used without further purification. Potassium salts of the donors hydrotris(1,2,3-benzotriazolyl)borate, $[HB(btz)_3]^-$, and dihydrobis(1,2,3-benzotriazolyl)borate, $[H_2B(btz)_2]^-$, were prepared in accordance with the procedure first reported by Trofimenko [1]. KBH_4, $AgNO_3$, PR_3 (R = Ph, *o*-tolyl, *m*-tolyl, *p*-tolyl, Bn), dppe, dppf and 1,2,3-benzotriazole were purchased from Aldrich and used without further purification. Elemental analyses (C,H,N,S) were performed in house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer System 2000 FT-IR instrument. ${}^{1}H$, and ${}^{31}P$ NMR spectra were recorded on a VXR-300 Varian spectrometer (300 MHz for ${}^{1}H$, and 121.4 MHz for ${}^{31}P$). The electrical resistance of acetone, DMSO and CH_2Cl_2 solutions was measured with a Crison CDTM 522 conductimeter at room temperature.

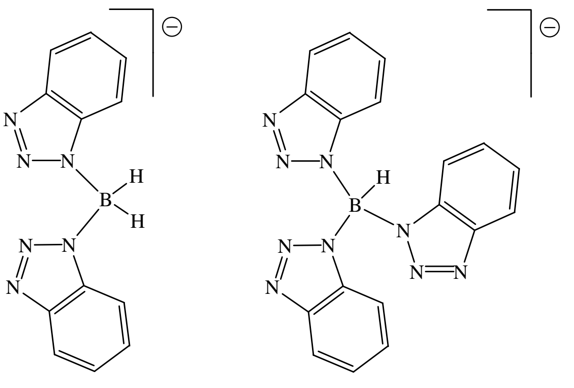

Fig. 1. Structure of the ligands employed in this work.

2.2. Syntheses

2.2.1. Synthesis of $[Ag\{H_2B(btz)_2\}(PPh_3)_2]$ (1)

$K[H_2B(btz)_2]$ (0.288 g, 1.0 mmol) was added at room temperature to a methanol solution (50 ml) of $AgNO_3$ (0.170 g, 1.0 mmol) and Ph_3P (0.525 g, 2 mmol). After the addition, the solution was stirred for 3 h. The colourless precipitate obtained was filtered off and washed with methanol. Re-crystallisation from chloroform/methanol (1:3) gave complex **1** as a micro-crystalline solid in 72% yield; m.p. 167–169 °C. ${}^{1}H$ NMR ($CDCl_3$, 293 K): δ 7.19–7.28 (m, 30H, C*H*), 7.66 (d, 4H, C*H*), 7.90 (d, 4H, C*H*). ${}^{31}P\ \{{}^{1}H\}$ NMR ($CDCl_3$, 293 K): δ +7.91 (s); ${}^{31}P\ \{{}^{1}H\}$ NMR ($CDCl_3$, 223 K): δ +7.40 (dd, ${}^{1}J({}^{31}P, {}^{107}Ag) = 300$ Hz, ${}^{1}J({}^{31}P, {}^{109}Ag) = 332$ Hz). IR (nujol, cm^{-1}): 3059 w (CH), 2431 m, 2405 m (BH), 1586 m (C=C + C=N), 514 s, 502 sbr (Ar_3P), 440 m, 442 m, 416 w, 347 w, 320 w, 309 w. *Anal.* Calc. for $C_{48}H_{40}AgBN_6P_2$: C, 65.60; H; 4.67; N, 9.53. Found: C, 65.85; H, 4.84; N, 9.31%.

2.2.2. Synthesis of $[Ag\{H_2B(btz)_2\}(P\text{-}o\text{-}tolyl_3)]$ (2)

Compound **2** was prepared similarly to compound **1**, by using $AgNO_3$ (0.170 g, 1.0 mmol), P(*o*-tolyl)$_3$ (0.304 g, 1.0 mmol) and $K[H_2B(btz)_2]$ (0.288 g, 1.0 mmol) in methanol solution (50 ml). Re-crystallisation from methanol gave complex **2** as a micro-crystalline solid in 42% yield; m.p. 187–191 °C. ${}^{1}H$ NMR (DMSO, 293 K): δ 2.41 (s, 9H, C*H$_3$*), 6.78 (m, 4H, C*H*), 7.10–7.48 (m, 12H, C*H*), 7.79 (m, 4H, C*H*). ${}^{31}P\ \{{}^{1}H\}$ NMR (DMSO, 293 K): δ −16.08 (d, ${}^{1}J({}^{31}P, Ag) = 601$ Hz). IR (nujol, cm^{-1}): 3052 w (CH), 2450 m, 2313 m (BH), 1589 w (C=C + C=N), 565 s, 533 w, 521 m, 463 s, 440 m (Ar_3P), 411 w, 272 w, 264 w. *Anal.* Calc. for $C_{33}H_{31}AgBN_6P$: C, 59.94; H; 4.72; N, 12.71. Found: C, 59.76; H, 4.52; N, 12.41%.

2.2.3. Synthesis of $[Ag\{H_2B(btz)_2\}(P\text{-}m\text{-}tolyl_3)]$ (3)

$K[H_2B(btz)_2]$ (0.288 g, 1.0 mmol) was added at room temperature to a methanol solution (50 ml) of $AgNO_3$ (0.170 g, 1.0 mmol) and P(*m*-tolyl)$_3$ (0.304 g, 1.0 mmol). After the addition, the solution was stirred for 2 h and the solvent subsequently removed with a rotary evaporator. Chloroform (50 ml) was added. The suspension was filtered and the organic layer was dried on Na_2SO_4, filtered and concentrated under reduced pressure. A precipitate was formed, which was filtered off and washed with diethyl ether. Re-crystallisation from methanol/acetone (1:2) gave complex **3** as a micro-crystalline solid in 70% yield; m.p. 98–100 °C. ${}^{1}H$ NMR (acetone, 293 K): δ 2.12 (s, 9H, C*H$_3$*), 7.20–7.49 (mc, 12H, C*H*), 7.89 (br, 4H, C*H*), 8.06 (d, 4H, C*H*). ${}^{31}P\ \{{}^{1}H\}$ NMR (acetone, 293 K): δ 12.81 (d, ${}^{1}J({}^{31}P, Ag) = 545$ Hz); ${}^{31}P\ \{{}^{1}H\}$ NMR (acetone, 218 K): δ 9.79 (dd, ${}^{1}J({}^{31}P, {}^{107}Ag) = 426$ Hz, ${}^{1}J({}^{31}P, {}^{109}Ag) = 500$ Hz); 11.79 (dd, ${}^{1}J({}^{31}P, {}^{107}Ag) = 584$ Hz, ${}^{1}J({}^{31}P, {}^{109}Ag) = 674$ Hz). IR