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Chiral bis(amino alcohol) silver complex derived from (+)-camphor

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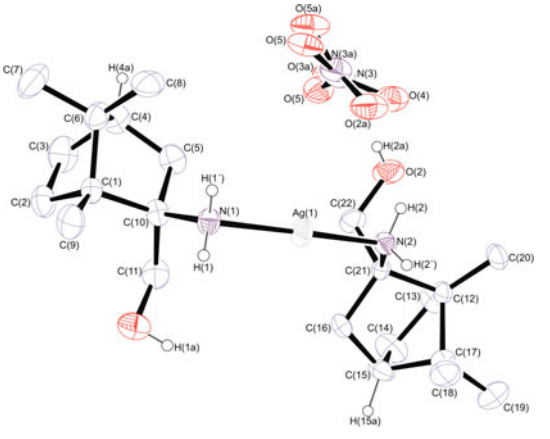

A chiral silver(I) complex was synthesized from the reaction of a chiral amino alcohol derived from (+)-camphor and silver nitrate, with the structure unambiguously disclosed by X-ray analysis and 2-D-NMR experiments. In this complex, the amino alcohol molecule is a monodentate ligand through the amino nitrogen, requiring two amino alcohol units which are coordinated to the silver and located orthogonally through the NH–Ag–NH axis.

Keywords: Silver complex; Amino alcohol; (+)-Camphor

1. Introduction

Interest in amino alcohol metal complexes has increased as these compounds have diverse applications as catalysts [1], inhibitors [2], ion exchangers [3], and dyes [4] as well as other interesting applications. Some research groups have explored metals to modulate some chemical properties in this class of complexes [5–10]. In spite of these examples, the number of reports about the coordination of amino alcohols to metals is limited. In the case

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of silver, a few reports describe only formation and stability constants, while other physical properties or crystallographic studies have not been reported for this kind of compounds [11–14].

In connection with other projects, we initiated studies about the synthesis of chiral amino alcohol metal complexes and applications in asymmetric catalysis. Several works about chiral silver complexes have been described in the literature [15–20], but there are no reports about chiral silver amino alcohol complexes. Herein, is described the preparation of the first chiral silver complex using amino alcohols as ligands.

2. Experimental

2.1. *General remarks*

The starting materials were purchased from Aldrich Chemical Co. and used without purification. Solvents were distilled before use. Silica plates of 0.20 mm thickness were used for thin layer chromatography. Melting points were determined with a Fisher–Johns melting point apparatus and they are uncorrected.

2.2. *Physical measurements*

^{1}H and ^{13}C NMR spectra were recorded using a Varian 500; the chemical shifts (δ) are given in ppm relative to TMS as internal standard (0.00). For analytical purposes mass spectra were recorded on a Shimadzu GCMS-QP2010 Plus and on a JEOL JMS-5X 10217 in the EI mode, 70 eV, 200 °C via direct inlet probe. Only the molecular and parent ions (*m/z*) are reported. IR spectra were recorded on a Bruker TENSOR 27 FT instrument.

Suitable crystals of **2** ($C_{22}H_{42}AgN_3O_5$) were obtained from slow evaporation of a dilute EtOH solution over several days. Single crystals were mounted on a Bruker APEX DUO diffractometer equipped with an Apex II CCD detector, Mo-Kα radiation ($\lambda = 0.71075$ Å) at 293 K. Frames were collected using omega scans and integrated with SAINT [21]. Multi-scan absorption correction (SADABS) [21] was applied. The structures were solved by direct methods (SHELXS) [22] and refined using full-matrix least-squares on F^2 with SHELXL-97 [22] using SHELXLE GUI [23]. Weighted *R* factors, *Rw*, and all goodness-of-fit indicators are based on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogens of the C–H bonds were placed in idealized positions, whereas hydrogens of OH groups were localized from the difference electron density map and their position was refined with U_{iso} tied to the parent atom with distance restraints. The NO_3^- was disordered over two positions in the structure (56.21/43.79%). Refining was carried out using geometry (SADI, SAME) and U_{ij} restraints were (SIMU, DELU) implemented in SHELXL-97. The OH distances in **2** were restrained using DFIX. Three standard reflections for every 97 reflections were used to monitor the crystal stability.

2.3. *Synthesis of (1R, 2R, 4R-2-amino-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl)methanol (1)*

According to a modification of the procedure described by Hoyer [24] and Maki [25], a mixture of (+)-camphor (9.78 g, 64.24 mM), KCN (16.87 g, 259.10 mM), and $(NH_4)_2CO_3$ (30.0 g, 312.10 mM) in MeOH (50 mL) was poured into a Parr-type reactor. The reaction

mixture was stirred at 50–60 °C for 24 h with a pressure of 220 psi of CO_2 gas, and then allowed to reach 120–130 °C and stirred for 10 h. The reaction mixture was cooled to room temperature. Addition of a 1 : 1 ethanol–water mixture (200 mL) was kept at 0 °C until precipitation of white solid which was filtered and crystallized from methanol to afford the camphor-2-spirohydantoin in 50% yield. The camphor-2-spirohydantoin (8.95 mM) was added to a mixture of NaOH (3.224 g, 80.61 mM) in H_2O (9 mL). The reaction mixture was heated to 150 °C for 10 h in a tubular autoclave. The mixture flowed from the autoclave through a valved outlet to a condenser, where it was cooled below 90 °C. As the mixture flowed from the reaction system, it was treated with activated carbon, filtered through Celite, and the filtrate was neutralized with acetic acid to precipitate the product. The product was removed by filtration, washed with water, and dried to give 2-amino-camphor-2-carboxylic acid in 75% yield. Using a modification of the method by Würtz and co-workers [26], 2-amino-camphor-2-carboxylic acid (10.0 g, 50.43 mM) was added to a vigorously stirred dispersion of $NaBH_4$ (6.20 g, 163.89 mM) in dry THF (180 mL) and the reaction mixture was cooled to 0 °C. A solution of iodine (14.08 g, 55.47 mM) in THF (70 mL) was added dropwise to the reaction mixture at 0 °C. Vigorous evolution of hydrogen occurred and the mixture was stirred at reflux for 18 h. The mixture was cooled to room temperature and MeOH was added slowly until gas evolution ceased. Solvent was removed *in vacuo*, the residue was dissolved in aqueous 20% KOH solution (180 mL), and was stirred at reflux temperature for 3 h. The mixture was cooled to room temperature and extracted with CH_2Cl_2 (4 × 150 mL). The combined organic layers were joined and dried over Na_2SO_4 and the solvent was removed *in vacuo* to afford **1** as white solid (87% yield), which was used without further purification. M.p. 108–110 °C; $[\alpha]_D^{20} = -35.5$ (c 0.0012 in DMSO). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.38 (q, $J = 5.9$ Hz, 2H), 1.90 (s, broad, 3H), 1.73 (d, $J = 2.5$ Hz (apparent), 2H), 1.68 (t, $J = 3.5$ Hz (apparent), 2H), 1.45 (d, $J = 6.4$ Hz (apparent), 2H), 1.36 (d, $J = 12.8$ Hz (apparent), 1H), 1.07 (s, 3H), 0.88 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ. 69.0 (CH_2), 61.5 (C), 50.9 (C), 49.9 (C), 44.9 (CH_2), 44.6 (CH), 30.6 (CH_2), 27.2 (CH_2), 21.9 (CH_3), 21.0 (CH_3), 12.0 (CH_3). IR (KBr) ν_{max} 3400, 3124, 2991, 2938, 1700, 1592 cm^{-1}. MS [EI+] *m/z* (%): 183 [M]+ (73). Anal. Calcd for $C_{11}H_{21}NO$ (%): C, 72.08; H, 11.55; N, 7.64. Found: C, 72.05; H, 11.50; N, 7.67.

2.4. *Synthesis of bis(1R, 2R, 4R-2-amino-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl)methanol silver complex (2)*

To a solution of **1** (0.090 g, 0.535 mM) in methanol (5 mL), $AgNO_3$ was added (0.0417 g, 0.246 mM). The resulting suspension was stirred at room temperature for 1 h. The resulting pale-brown solution was filtered through Celite to remove $AgNO_3$ and any black decomposition product. The filtrate was evaporated *in vacuo*. Purification by crystallization in EtOH afforded **2** as white solid (0.084 g, 72% yield), m.p. 77–82 °C; $[\alpha]_D^{20} = -37.5$ (c 0.0028 in DMSO). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.84 (s, broad 1H, OH), 3.62 (dd, $J = 5.9$ Hz, 2H, assigned to H8, scheme 3), 3.51 (s, broad, 2H, NH_2), 1.83 (dt, $J = 12.8$, 6.5 Hz, 1H, assigned to H3β, scheme 3), 1.74 (m, 3H, assigned to H5 and H4, scheme 3), 1.61 (ddd, $J = 13.5$, 9.2, 2.9 Hz, 1H, assigned to H6α, scheme 3), 1.52 (ddd, $J = 13.7$, 11.4, 3.0 Hz, 1H, assigned to H6β, scheme 3), 1.27 (d, $J = 13.2$ Hz, 1H, assigned to H3α, scheme 3), 1.05 (s, 3H, assigned to H9, scheme 3), 1.03 (s, 3H, assigned to H11, scheme 3), 0.88 (s, 3H, assigned to H10, scheme 3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 66.7 (CH_2), 60.9 (C), 48.8 (C), 47.3 (CH_2), 42.1 (C), 41.7 (CH), 28.8 (CH_2), 24.1 (CH_2), 18.9 (CH_3), 18.0

(CH_3), 9.9 (CH_3). IR (KBr) ν_{max} 3406, 3367, 3248, 29,952, 2874, 1714, 1596 cm^{-1}. HRMS (ESI+): for $C_{22}H_{42}AgN_2O_2$ Calcd 473.2297, found 473.2292. Anal. Calcd for $C_{22}H_{42}AgN_2O_2$ (%): C, 55.69; H, 8.92; N, 6.74. Found: C, 55.71; H, 8.97; N, 6.68.

3. Results and discussion

3.1. *Synthesis of ligand and silver complex*

The first experiments were to prepare the chiral amino alcohol ligand. We considered that commercially available enantiopure (+)-camphor is an ideal starting point for the synthesis of the desired ligand. According to appropriate modifications in previous reports by Hoyer [24], Maki [25], and Würtz *et al.* [26], (+)-camphor was successfully converted to amino alchohol **1** after 3 reaction steps in 33% overall yield from camphor (scheme 1). The straightforward mixing of **1** with silver nitrate using methanol as solvent afforded the chiral silver complex **2** as a moisture-stable solid without adding any base to adjust the pH (scheme 2).

3.2. *Crystal structure*

Suitable crystals of **2** were obtained from ethanol upon slow evaporation over several days. A single-crystal X-ray diffraction analysis was performed on the silver complex confirming the spectroscopic results. An ORTEP and atom labeling diagram for **2** is presented in figure 1. Crystallographic data and structural refinement parameters of **2** are summarized in table 1 and relevant bond length and angle data are collected in supplementary material. From these studies, **2** has a 1-D network and crystallizes in the orthorhombic space group *P 21 21 21*, and the asymmetric unit contains four molecules. Two chiral amino alcohol ligands bind

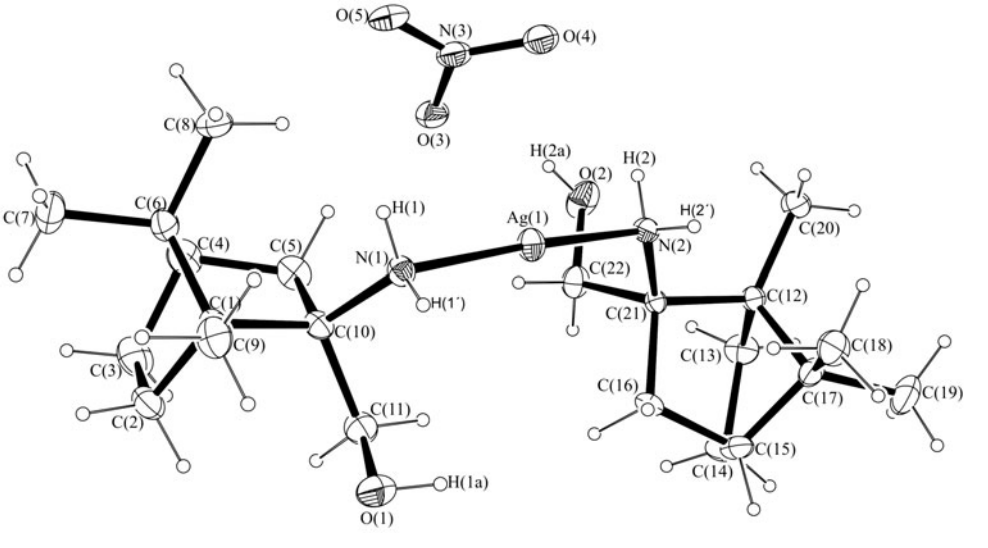


Figure 1. ORTEP diagram and atom labeling system for **2**. The NO_3^- is disordered and occupies two sites. Only one site is depicted (40% probability ellipsoids).

Table 1. Crystal data and structure refinement for **2**, Ag $[C_{20}H_{32}(CH_2)_2(OH)_2(NH_2)_2]NO_3$.

Crystal data	**2**
Identification code	Complex **2**
Empirical formula	$C_{22}H_{42}AgN_3O_5$
Formula weight	536.46
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*P2(1)2(1)2(1)*
Unit cell dimensions	a = 7.3336(10) Å, $\alpha = 90°$ b = 12.1467(16) Å, $\beta = 90°$ c = 28.836(4) Å, $\gamma = 90°$
Volume	2568.7(6) Å^3
Z	4
Density (calculated)	1.387 mg m^{-3}
Absorption coefficient	0.819 mm^{-1}
F (0 0 0)	1128
Crystal size	0.36 × 0.25 × 0.15 mm^3
Theta range for data collection	1.82°–25.11°
Index ranges	$-8 \le h \le 8$, $-14 \le k \le 14$, $-34 \le l \le 34$
Reflections collected	36,189
Independent reflections	4583 [R(int) = 0.0787]
Completeness to theta = 25.11°	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8870 and 0.7592
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4583/149/340
Goodness-of-fit on F^2	1.033
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0357[a], wR_2 = 0.0812[b]
R indices (all data)	R_1 = 0.0405[a], wR_2 = 0.0840[b]
Absolute structure parameter	0.06(3)
Largest diff. peak and hole	0.509 and −0.701 (e Å^{-3})

[a] $= R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b] $= wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$.

with one Ag(I) in the common linear N–Ag–N coordination (angle 173.83°) described by other groups [17, 27–30] with weak interactions with the nitrate. Both Ag–N2 and Ag–N1 distances (2.130 and 2.136 Å) in **2** are standard in N–Ag coordination complexes with similar interactions (within experimental error) [31–35]. For example, Fromm and Sagué observed Ag–N distances of 2.136 and 2.143 Å for a polymer with N–Ag–N coordination [36]. The two organic ligands lie opposite each other at both sides of the plane bisecting the Ag center. In contrast, oxygens in amino alcohol ligands are not coordinated to silver; therefore, the ligands and the metal center in **2** do not achieve metallocycles and only the linear coordination is observed. As a consequence, the structure of **2** in solid state does not contain a crystallographically imposed C_2-symmetry axis, keeping only natural C_1-symmetry axis in this chiral complex. In addition, no structural differences between the coordinated and the free ligand were found. Oxygens of the NO_3^- interact with both OH and NH_2 groups of ligand through hydrogen bridges, while the other oxygen interacts with the metal center (O(4)–Ag(1) 2.93 Å), stabilizing **2** through a network of weak H-bond interactions.

The nitrate interacts through two oxygens, one establishes a hydrogen bridge with a NH, while the other binds to the metal center, forming a six-membered metallacycle with bond distances O(5)–H(2′) = 2.367 Å and O(4)–Ag(1) = 2.93 Å (table 2 and figure 2). A similar O–H bond distance (2.25 Å) was identified by Kim and co-workers [39]. The metallacycle

Table 2. Hydrogen bonds for **2** (Å, °).[a]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(1)–H(1A)···O(3)^{i}	0.82	2.10	2.89(2)	163.8
O(1)–H(1A)···O(3A)^{i}	0.82	2.02	2.83(2)	174.8
O(2)–H(2A)···O(3)	0.83(1)	2.21(4)	2.81(2)	140(5)
O(2)–H(2A)···O(3A)	0.83(1)	2.12(4)	2.76(2)	134(4)
N(1)–H(1)···O(5A)^{i}	0.83(2)	2.50(3)	3.30(2)	162(4)
N(1)–H(1)···O(5)^{i}	0.83(2)	2.17(3)	2.95(2)	157(4)
N(2)–H(2′)···O(5A)^{ii}	0.83(2)	2.44(3)	3.12(2)	139(3)
N(2)–H(2′)···O(5)^{ii}	0.83(2)	2.37(3)	2.98(2)	131(3)
N(2)–H(2)···O(4)	0.82(2)	2.44(3)	3.07(1)	134(3)
N(2)–H(2)···O(4A)	0.82(2)	2.43(3)	3.16(2)	148(4)

[a]D = donor; A = acceptor.
Symmetry codes: (i) $x+1, y, z$; (ii) $x+1/2, -y+1/2, -z$.

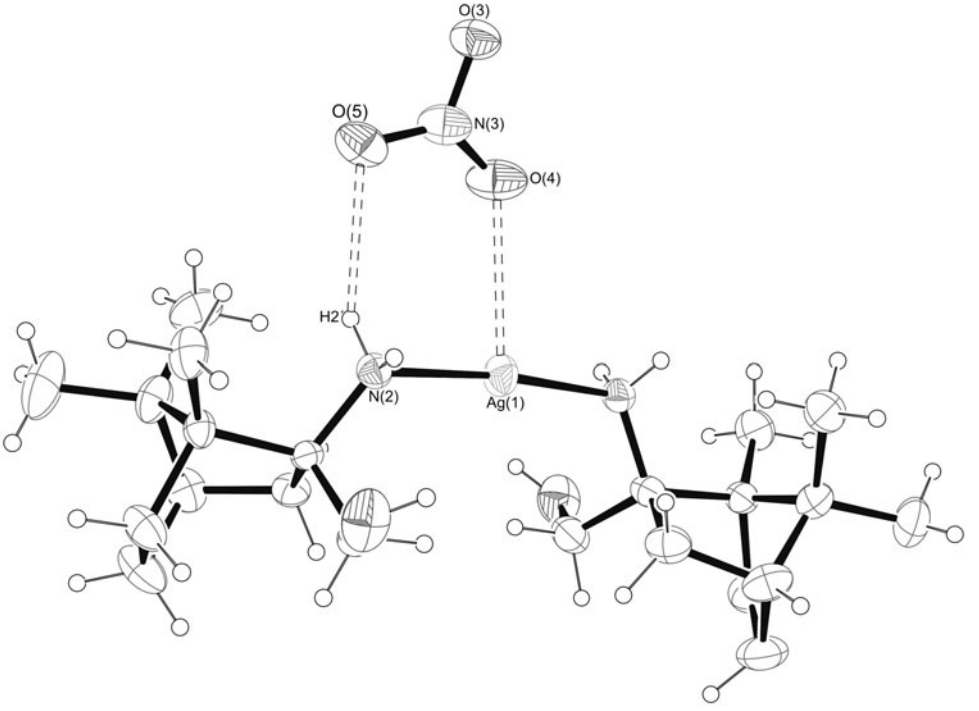


Figure 2. View of six-membered metallacycle in **2**.

stemming from NO_3^- and Ag–NH_2 fragments is well documented in the literature [37–40]. In addition, supramolecular interactions are achieved from these hydrogen bonds which reveal the presence of a 1-D zigzag chain according to figure 3.

3.3. *NMR spectra*

The ^{1}H NMR spectrum for **2** using $CDCl_3$ as solvent is presented in figure 4. At low field in this spectrum, a broad singlet is observed at 3.51 ppm, corresponding to hydrogens from

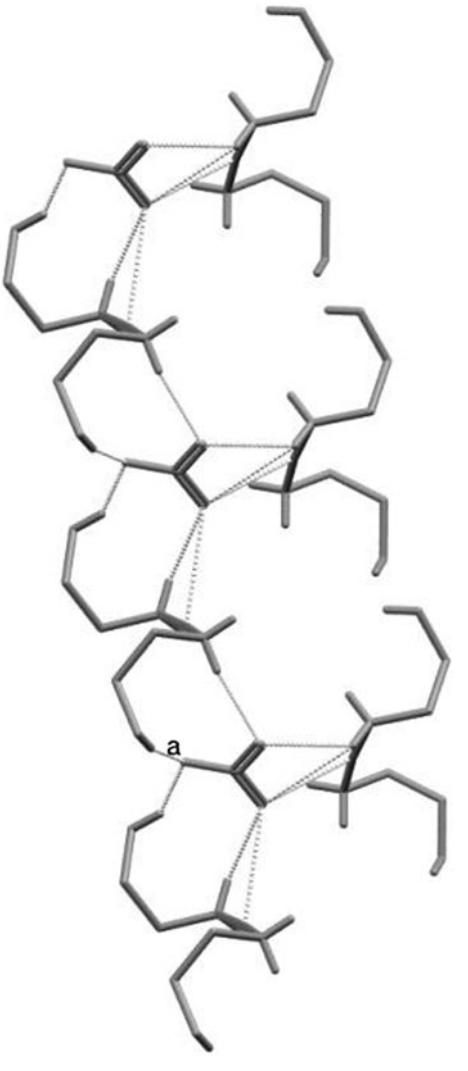


Figure 3. View of 1-D chain in **2**. View of the zigzag interaction.

the nitrogen. Although amine protons tend to appear over a wide range in the NMR spectrum, it was possible to make a comparison between the monomer molecule **1**, whose amine proton signals are assigned at 1.90 ppm, and the corresponding coordination complex **2** showing a change in the amine protons shift, due to nitrogen coordination.

At 3.62 ppm, a doublet of doublets is present for the protons of the hydroxymethyl group, this multiplicity owing to the magnetic and chemical difference between the hydrogens in this methylene, giving a geminal coupling (J = 12 Hz). The methylene hydrogens assigned to C-3 (scheme 3) have different shifts in the spectrum, the proton H-3β is at 1.83 ppm, however, the proton H-3α is at 1.27 ppm. On the other hand, the H-3β is a doublet of doublet of doublets signal, while the H-3α is only a doublet system. The methylene group on C-6 presents two multiplets for their protons in 1.61 and 1.53 ppm. In the region

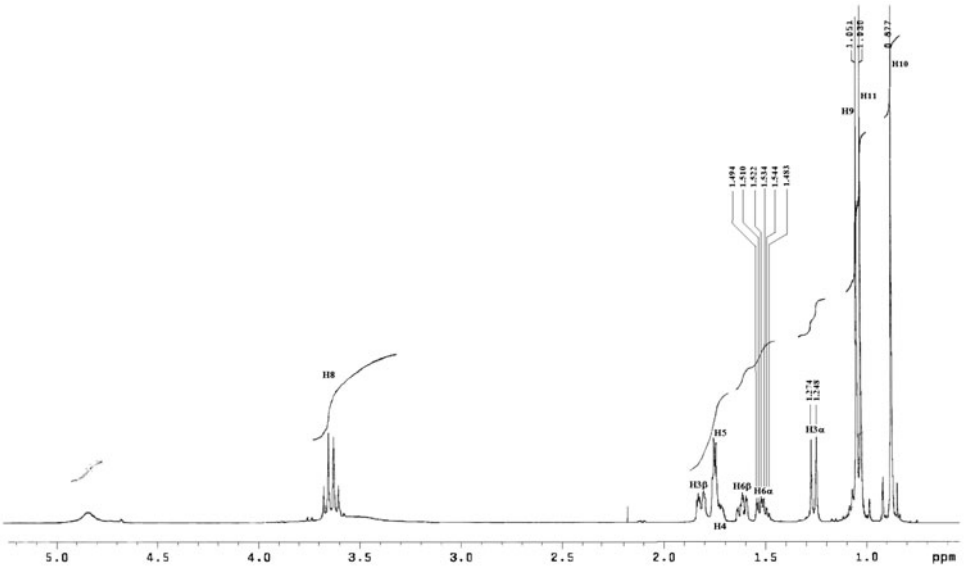


Figure 4. ^{1}H NMR spectrum for **2**.

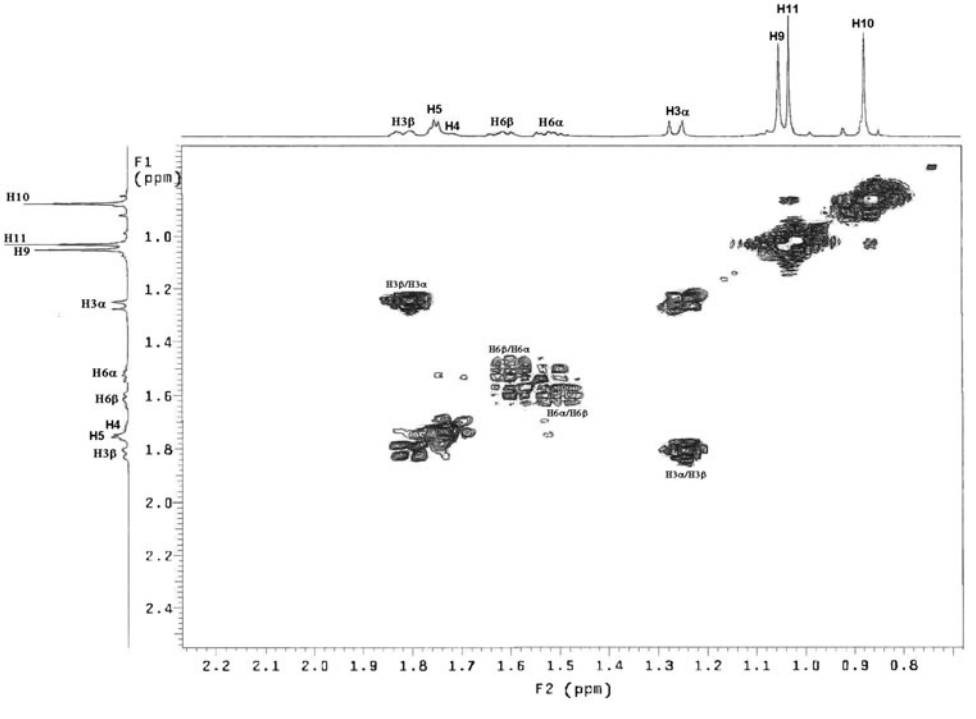


Figure 5. COSY spectrum for **2**.

1.76–1.71 ppm, a multiple signal for three hydrogens assigned to the methylene on C-5 and the methyne on C-4 is presented. Finally, the shifts for the methyl groups were assigned as follows: H-9 at 1.05, H-11 at 1.03, and H-10 at 0.877 ppm.

The correct assignation for the hydrogens was made using 2-D RMN COSY and NOESY experiments. Through the COSY experiment (figure 5), the proton shifts for the three different methylenes were identified through cross-peak correlations; for instance, the C-3 methylene shows two different shifts for their protons, due to the presence of the amine and hydroxymethyl groups which cause a paramagnetic shield on the β-hydrogen (1.81 ppm), whereas the α-hydrogen chemical shift (1.26 ppm) is not affected. For the methylene protons on C-6, two signals at 1.53 and 1.61 ppm are observed and both hydrogens from the methylene on C-5 are present at 1.75 ppm forming a multiplet. The chemical shift assignment of these protons was important to substantiate the (*R*) configuration of the stereogenic center in the molecule.

Analysis of the NOESY spectrum displayed some interesting features. For instance, the C-8 methylene protons at 3.64 ppm present a through-space interaction at 1.03 ppm assigned to the methyl group C-11, another interaction with the doublet at 1.26 ppm corresponding to the α-hydrogen in C-3, and also an interaction with the doublet of doublets system at 1.61 ppm corresponding to the α-hydrogen in C-6 (scheme 3 and figure 6). In addition, the hydrogen on C-4 at 1.74 ppm has an interaction through space with a signal at 1.05 ppm assigned to the methyl C-9 which in turn has a cross-peak with the signal at 0.87 ppm corresponding to the methyl C-10. The hydrogen on C-10 exhibits a through-space interaction with two signals; one of these signals at 1.61 ppm is assigned to

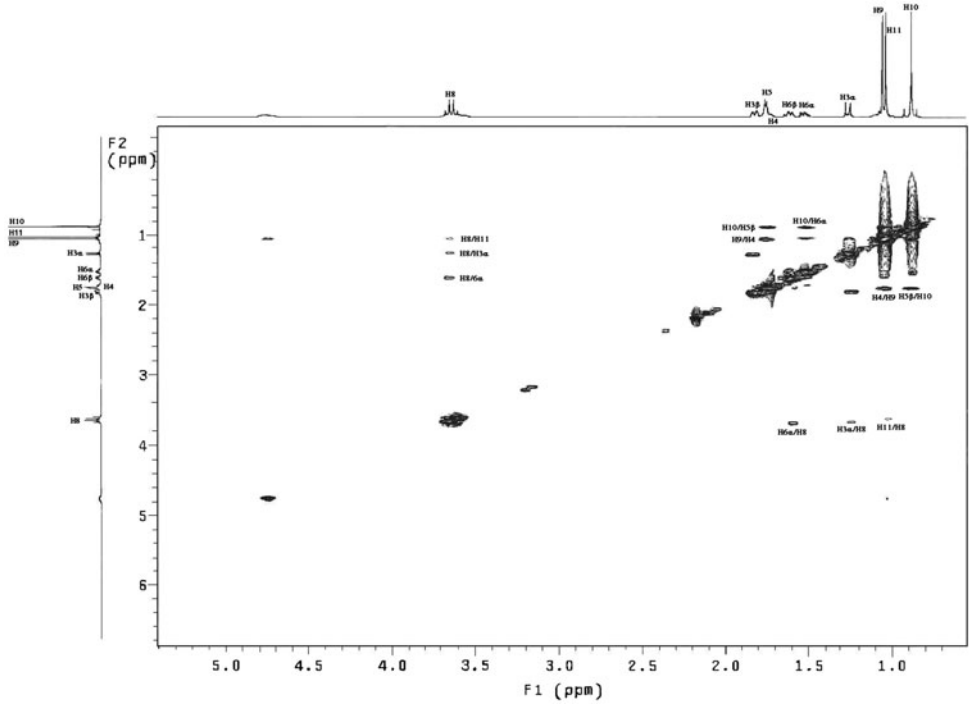
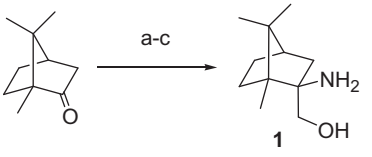
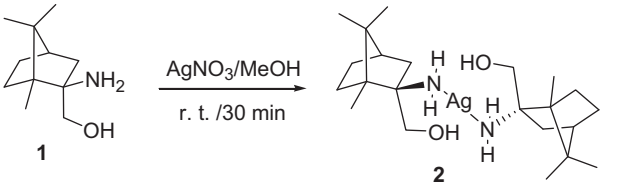


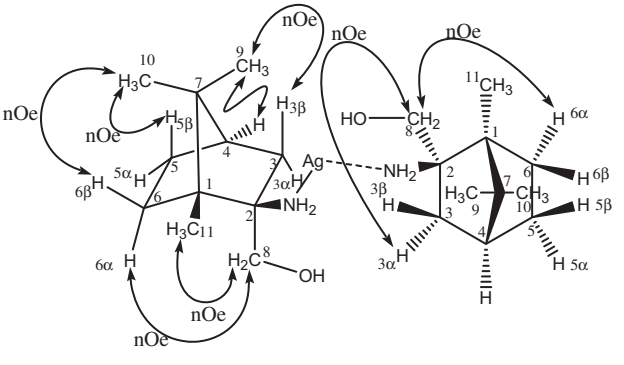
Figure 6. NOESY spectrum for **2**.



Scheme 1. Reagents and conditions: (a) KCN, $(NH_4)_2CO_3$, MeOH, 220 psi, 120–130 °C, and 10 h. (b) NaOH, 150 °C, and 10 h. (c) $NaBH_4$, I_2, THF, reflux, and 18 h.



Scheme 2. Preparation of **2** from amino alcohol (**1**).



Scheme 3. nOe interactions for **2**.

the β-hydrogen on C-6, and other interaction with the β-hydrogen on C-5 at 1.75 ppm. All these nOe interactions are displayed in scheme 3 and the spectrum is presented in figure 6.

4. Conclusion

A chiral silver complex was prepared from silver nitrate and an amino alcohol derived from (+)-camphor through a mild and efficient method with a simple workup affording excellent yields. This is the first report about the use of chiral amino alcohols for the synthesis chiral silver complexes. Selectivity of NH_2 and silver ion was observed. This coordination of amino alcohol **1** indicates a versatile ligand which will be investigated in future research. The simplicity of the method suggests that amino alcohol **1** and silver complex **2** will enjoy widespread applications.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 911160). Copies of available materials can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Facsimile: +(44) 01223 336033; E-mail: deposit@ccdc.ac.uk).

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Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2015.1012071].

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