

Unusual Coordination of Tetraphenylborate to Silver(I): Synthesis and X-ray Crystal Structure of the Complex *N,N'*-bis[3-(2-nitrophenyl)allylidene]ethane-1,2-diamine(tetraphenylborato)silver(I)

Saeed Dehghanpour,^{*,a} Ali Mahmoudi^b and Ramin Hadjikhani^b

^aDepartment of Chemistry, Alzahra University, 1993891176 Tehran, Iran

^bFaculty of Science, Islamic Azad University, Karaj Branch, Karaj, Iran

O complexo *N,N'*-bis[3-(2-nitrofenil)alilideno]etano-1,2-diamino(tetrafenilborato)prata(I), [Ag(nca₂en)(BPh₄)], foi sintetizado e caracterizado por análise elementar e por espectroscopias de RMN de ¹H, de absorção no infravermelho e UV-vis. Sua estrutura cristalina e molecular foi determinada por difratometria de raios X (monocristal). O centro de prata(I) no complexo está em um ambiente tetraédrico distorcido e faz ligações covalentes com os dois átomos de nitrogênio da base de Schiff e com dois átomos de carbono do tetrafenilborato. No complexo, o tetrafenilborato apresenta um comportamento não-usual, agindo como um ligante bidentado.

The complex *N,N'*-bis[3-(2-nitrophenyl)allylidene]ethane-1,2-diamine(tetraphenylborato)silver(I), [Ag(nca₂en)(BPh₄)], has been synthesized and characterized by CHN analyses and ¹H-NMR, IR and UV-vis spectroscopies. Its crystal and molecular structure was determined by X-ray diffractometry from single-crystal data. The coordination geometry about silver(I) is best described as a distorted tetrahedron. The Ag center is covalently bonded to two N atoms of the Schiff base and two C atoms of tetraphenylborate. In the complex, tetraphenylborate shows an unusual behavior and acts as a bidentate ligand.

Keywords: silver(I) complex, diimine ligand, nitrocinnamaldehyde, tetraphenylborate, crystal structure

Introduction

Many notable recent advances in the chemistry of silver(I) complexes have been achieved through the use of diimine ligands. These complexes have drawn special attention because of their applications as reagents in organic and inorganic synthesis,¹ in photography or electrochemical silver plating,² and as free radical scavengers in industrial processes.³⁻⁶ Cation- π interactions between metal ions and polycyclic aromatic hydrocarbons have also received considerable attention in the synthesis of coordination compounds, mainly due to the possibility of introducing a variety of useful electric and electrochemical properties and of giving rise to novel molecular architectures.

Cinnamaldehyde and its substituted derivatives react with ethylenediamine to give a range of diimine compounds;

a small number of such bis(cinnamaldehyde)ethylene-diimine ligands have been used to give complexes with transition metals.⁷⁻⁹ Although reports on [Ag^I(NN)₂]⁺ (NN is a diimine obtained from cinnamaldehyde derivatives and ethylenediamine) and [Ag^I- π -Ar]⁺ complexes are numerous, limited work on silver(I) complexes with mixed ligands, [Ag(NN)(π -Ar)]⁺, has been reported.¹⁰⁻¹⁹ In the present work, we report the synthesis and characterization of the new complex [Ag(nca₂en)(BPh₄)] (**1**), as well as its molecular structure determined from single crystal X-ray diffraction analysis.

Experimental

All chemicals were reagent grade and used as received. Solvents were purified by literature methods.²⁰ *N,N'*-bis[3-(2-nitrophenyl)allylidene]ethane-1,2-diamine, nca₂en, was prepared according to literature procedures.²¹ Elemental

*e-mail: dehghanpour_farasha@yahoo.com

analyses were performed by using a Heraeus CHN-O-RAPID elemental analyzer. Infrared spectra were recorded on a Bruker Tensor 27 instrument. Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer. NMR spectra were obtained on a BRUKER AVANCE DRX500 (500 MHz, 11.75 T) spectrometer. Hydrogen chemical shifts are reported in parts per million (ppm) relative to Me₄Si as internal standard.

Synthesis of N,N'-bis[3-(2-nitrophenyl)allylidene]ethane-1,2-diamine(tetraphenylborato)silver(I), 1

To a stirring solution of *N,N'*-bis[3-(2-nitrophenyl)allylidene]ethane-1,2-diamine (nca₂en, 378 mg, 1 mmol) in 5 mL acetonitrile, silver nitrate (169 mg, 1 mmol in 5 mL acetonitrile) and sodium tetraphenylborate (342 mg, 1 mmol in 5 mL acetonitrile) were added. After stirring for 10 min, the volume of the solvent was reduced under vacuum to about 4 mL. The diffusion of diethyl ether vapor into the concentrated solution gave light yellow crystals, which were filtered off, washed with a mixture of diethyl ether-acetonitrile (9:1 v/v) and dried under vacuum. Anal. calcd. for C₄₄H₃₈AgBN₄O₄: C, 65.61; H, 4.76; N, 6.96 %. Found: C, 65.63; H, 4.75; N, 6.98 %. IR (KBr pellets, v/cm⁻¹): 1610 (C=N). ¹H-NMR (500MHz, CDCl₃): δ 4.02 (s, NCH₂CH₂N), 7.38-7.75 (m, 2PhCH-CH, 28 Ar-H), 8.35 (d, ³J(H-H) 9 Hz, 2 CHCH=N).

X-ray crystallography

Diffraction data for **1** were collected on a STOE-IPDSII diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data were collected and integrated using the Stoe X-Area software package.²² A numerical absorption correction was applied using X-RED and X-SHAPE softwares.²³ The structure was solved by direct methods (SHELXS-97).³³ The structure refinement was performed by a full-matrix least-squares method against *F*² (SHELXL-97).²⁴ All non-H atoms were refined anisotropically and all H atoms were inserted in calculated positions.

Results and Discussion

The IR spectrum of the proligand exhibits the characteristic band of the imine group, which appears at 1605 cm⁻¹. This band is shifted to lower frequencies in the IR spectra of the corresponding complexes due to the coordination of the imine nitrogen.²⁵

Since no d-d transitions are expected for a d¹⁰ complex, the UV-Vis bands are assigned to metal to ligand charge transfer (MLCT) or ligand-centered π→π* transitions.²⁶ The

absorption spectrum of [Ag(nca₂en)(BPh₄)] (**1**) in chloroform features a clear shoulder at 320 nm (log ε = 3.73). Additional absorption bands are also observed in the spectra of **1** in chloroform in the UV region [λ_{max} = 280 nm (log ε = 4.61)]. The intensity of these bands is consistent with ligand-centered π→π* and/or charge-transfer transitions.

¹H NMR peak assignments, based on the splitting of resonance signals, spin coupling constants, and the literature, are presented in the experimental section. These assignments are in accordance with the molecular structure determined by X-ray crystal structure analysis. The ¹H resonances of the coordinated nca₂en are clearly observed in complex **1**; however, the aromatic H atoms of the coordinated Ph₄B overlap to some extent with those of the phenyl H atoms of nca₂en. Aside from the aromatic-H atoms, which appear at 7.38-7.45 ppm, the two imine hydrogens appear as a doublet at ca. 8.35 ppm in **1**. The shift of the iminic hydrogens to high frequency relative to the proligand can be attributed to the deshielding effect resulting from coordination. The singlet at 4.02 ppm in **1** is assigned to the H atoms of the CH₂CH₂ group. In principle, geometrical isomers are possible with respect to the C=N bond. However, the appearance of only one signal for each type of proton in CDCl₃ solution indicates that the symmetry of the molecule is retained in solution, and only one isomer is present.

A view of complex **1**, including the atom numbering scheme, is illustrated in Figure 1. Crystallographic data are summarized in Table 1 and selected bond distances and angles are listed in Table 2. Compound **1** crystallizes with two molecules per asymmetric unit, probably due to some small conformational differences (1A, 1B). The coordination environment around the metal ion in this complex is pseudotetrahedral, with a large angular distortion arising from the low intraligand N—Ag—N chelate angle [75.64(13)° in 1A and 76.44(13)° in 1B] and the intraligand C—Ag—C chelate angle [99.71(16)° in 1A and 98.86(15)° in 1B]. The other angles around the Ag center are larger than those of a non-distorted tetrahedral complex. The Ag—N bond distances [2.322(4) and 2.293(4) Å in 1A and 2.331(4) and 2.324(4) Å in 1B] are similar to those found in other Ag pseudotetrahedral complexes.²⁷⁻²⁹ In the complex, the average Ag—C bond distance is 2.48 Å, which is comparable to those reported for Ag—C bond distances for coordinated polyenes.³⁰⁻³³ The coordination environment around the boron atom is approximately tetrahedral, since the average of six angles involving B is 109.5°, although the angles C21—B1—C27 in 1A and C65—B1—C71 in 1B have values of 103.5(3)° and 103.9(3)° respectively. The Ag center is approximately perpendicular to the coordinated phenyl rings of tetraphenylborate (for example, the angles

Table 1. Crystal data and single crystal X-ray diffraction refinement details for compound **1**

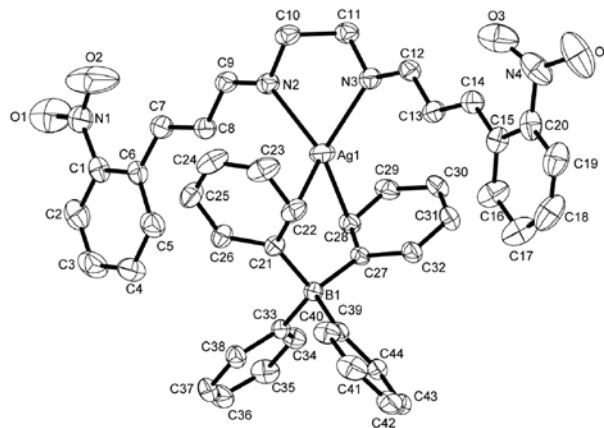
Formula	$C_{44}H_{38}AgBN_4O_4$
Formula weight	804.96
Crystal system	Triclinic
Space group	P-1
<i>a</i> (Å)	12.698(3)
<i>b</i> (Å)	13.610(3)
<i>c</i> (Å)	22.491(5)
α (°)	89.68(3)
β (°)	87.82(3)
γ (°)	88.88(3)
<i>V</i> (Å ³)	3883.3(13)
<i>Z</i>	4
Density (g cm ⁻³)	1.378
μ (Mo-K α) (mm ⁻¹)	0.57
<i>F</i> (000)	1656
Data collection	
Temperature (K)	293(2)
θ min - max	1.50-27.12
Dataset [h, k, l]	-16/15, -17/17, -28/28
Tot., Uniq. Data, R(int)	29700, 15388, 0.0430
Observed data	>2 σ (I)
Refinement	
No. reflections, No. parameters	15388, 973
R1, R2	0.0699, 0.0951
wR1, wR2	0.1635, 0.1779
Goodness-of-fit	1.114
Max. and Av. Shift/Error	0.006, 0.000
Min, Max. Resd. Dens. (e/Å ³)	0.88, -0.85

Table 2. Selected bond lengths [Å] and bond angles [°] for **1**

	1A	1B	
Ag1—N2	2.322 (4)	Ag2—N7	2.331 (4)
Ag 1—N3	2.293 (4)	Ag2—N6	2.324 (4)
Ag 1—C22	2.503(5)	Ag2—C66	2.497 (5)
Ag 1—C28	2.479 (5)	Ag2—C72	2.443(4)
N2—Ag1—N3	75.64 (13)	N6—Ag2—N7	76.44 (14)
C22—Ag1—C28	99.71 (16)	C66—Ag2—C72	98.86 (15)
N2—Ag1—C22	119.22 (16)	N6—Ag2—C66	117.10 (15)
N2—Ag1—C28	120.94 (14)	N6—Ag2—C72	125.38 (15)
N3—Ag1—C22	125.73 (14)	N7—Ag2—C66	118.82 (16)
N3—Ag1—C28	125.73 (14)	N7—Ag2—C72	121.47 (14)
Ag1—C22—C23	91.9 (4)	Ag2—C72—C73	90.0 (3)
Ag1—C28—C29	91.1 (3)	Ag2—C66—C67	90.6 (4)
Ag1—N2—C9	132.0 (3)	Ag2—N7—C55	107.7(3)
Ag1—N2—C10	108.2 (3)	Ag2—N7—C56	132.1(3)
C9—N2—C10	119.7 (4)	C55—N7—C56	120.1 (4)
C21—B1—C27	103.5 (3)	C65—B2—C71	103.9 (3)
C39—B1—C27	110.3 (3)	C77—B2—C71	114.2 (3)
C39—B1—C33	106.4 (3)	C77—B2—C83	106.2 (3)

Ag1—C22—C23 in **1A** and Ag2—C72—C73 in **1B** have values of 91.9(4)° and 90.0(3)°, respectively).

Despite the fact that the *N*-donor atoms are sp²-hybridized, the chelate ring is significantly puckered in this complex, and some strain in the chelate ring is suggested by deviation from the 120° angle about the *N*-atom, as for C9—N2—C10 [119.7(4)°], Ag1—N2—C9 [132.0(3)°], and Ag1—N2—C10 [108.2(3)°] in **1A**, and C55—N7—C56 [120.1(4)°], Ag2—N7—C55 [107.7(3)°] and Ag2—N7—C56 [132.1(3)°] in **1B**.

**Figure 1.** ORTEP view of the crystal structure of [Ag(*nca*,*en*)(BPh₄)] (**1A**), with the atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Conclusions

A novel silver(I) complex has been synthesized, containing *N,N'*-bis[3-(2-nitrophenyl)allylidene]ethane-

1,2-diamine and tetraphenylborate ligands. The structure determination of the complex shows a discrete molecular structure and a distorted tetrahedral geometry around the silver atom. A major finding of the present work is that the tetraphenylborate shows an unusual behavior and acts as a bidentate ligand.

Supplementary Information

Crystallographic data (excluding structure factors) for the structure (**1**) reported in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 616197. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). ¹H NMR data of compound **1** are available free of charge at <http://jbcbs.s bq.org.br>, as PDF file.

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Saeed Dehghanpour,^{*,a} *Ali Mahmoudi*^b and *Ramin Hadjikhani*^b

^aDepartment of Chemistry, Alzahra University, 1993891176 Tehran, Iran

^bFaculty of Science, Islamic Azad University, Karaj Branch, Karaj, Iran

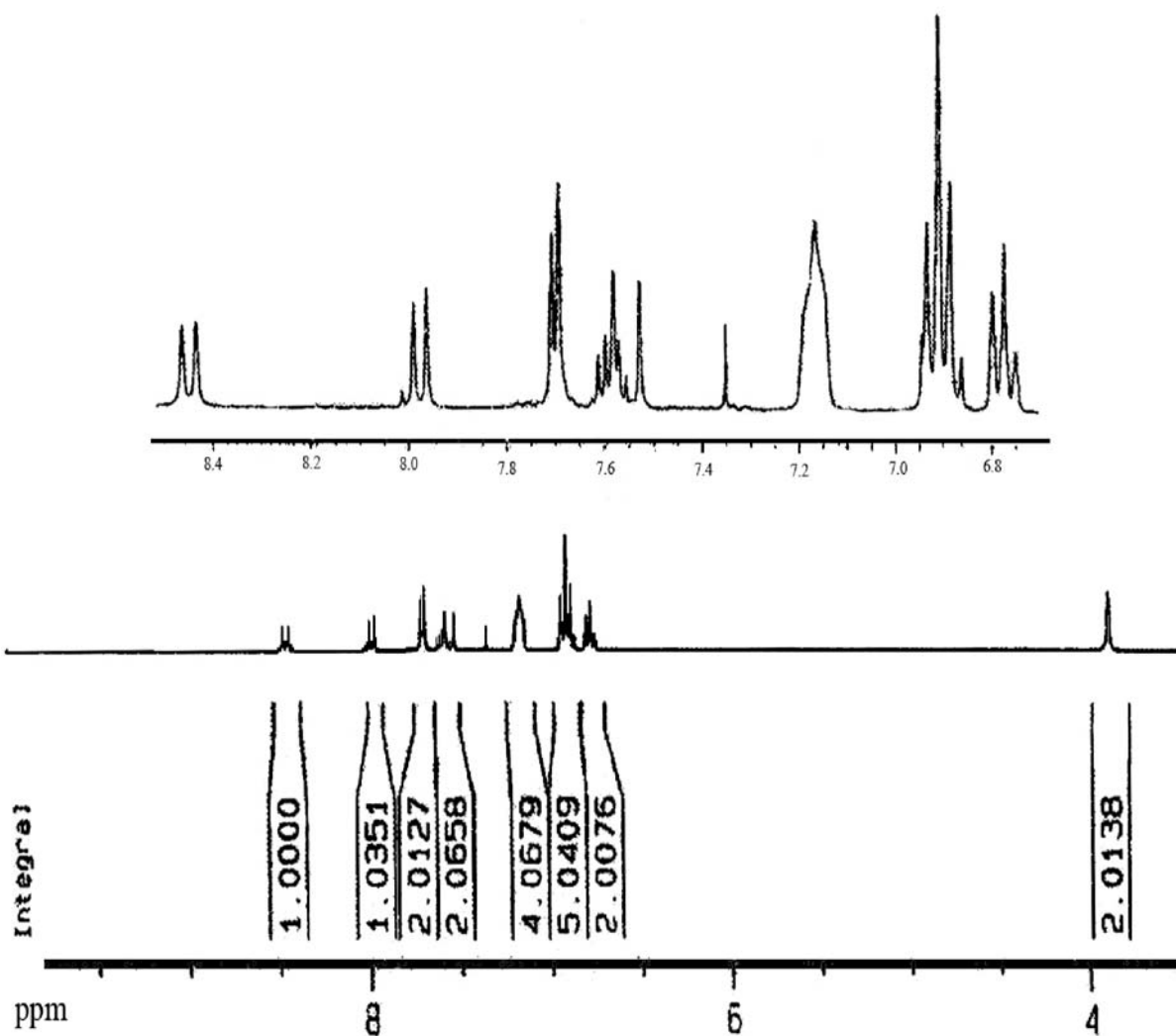


Figure S1. ¹H NMR data for compound 1 in CDCl₃ (500 MHz, 11.75 T).

*e-mail: dehghanpour_farasha@yahoo.com