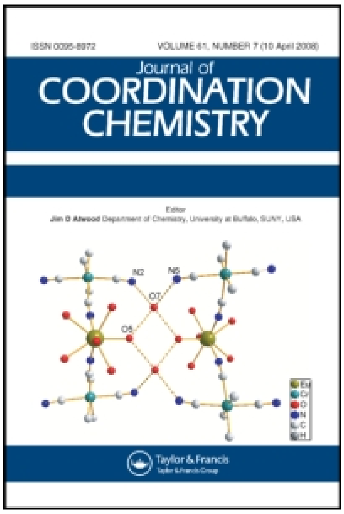

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Khalaji, Aliakbar Dehno , Aoki, Katsuyuki and Amirnasr, Mehdi(2007) 'Silver(I) perchlorate complexes of *N,N*'-bis(*trans*-cinnamaldehyde)ethylenediimine (ca_2en)', Journal of Coordination Chemistry, 60: 2, 201 — 206
To link to this Article: DOI: 10.1080/00958970600763250
URL: http://dx.doi.org/10.1080/00958970600763250

Journal of Coordination Chemistry
Vol. 60, No. 2, 20 January 2007, 201–206

Silver(I) perchlorate complexes of *N*,*N*′-bis(*trans*-cinnamaldehyde)ethylenediimine (ca$_2$en)

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(*Received in final form 20 February 2006*)

Three silver(I) complexes, [Ag(ca$_2$en)(PPh$_3$)]ClO$_4$ (**1**), [Ag(ca$_2$en)(PPh$_3$)$_2$]ClO$_4$ (**2**) and [Ag(ca$_2$en)$_2$]ClO$_4$ (**3**), where ca$_2$en = *N*,*N*′-bis(*trans*-cinnamaldehyde)ethylenediimine, have been synthesized and characterized spectroscopically. The crystal structure of (**1**) was determined by X-ray diffraction methods. Crystal data for **1**: C$_{38}$H$_{35}$AgClN$_2$O$_4$P, triclinic, $P\bar{1}$, $a = 12.086(2)$, $b = 18.204(2)$, $c = 8.550(2)$ Å, $\alpha = 102.69(1)$, $\beta = 105.85(1)$, $\gamma = 91.47(1)°$, $V = 1758.0(5)$ Å^3, $Z = 2$, $R(F) = 0.070$, $wR\ (F) = 0.064$, $T = 296$ K. The coordination geometry of the Ag atom is distorted trigonal involving two N atoms of ca$_2$en and one P atom of triphenylphosphine (PPh$_3$).

Keywords: Schiff base; *N*,*N*′-bis(*trans*-cinnamaldehyde)ethylenediimine; Silver(I); Crystal structure; Spectroscopy

1. Introduction

The chemistry of Ag(I) complexes has been investigated extensively in recent years [1–6] owing to their application in double-helical molecular architectures [1], supramolecular design of structurally well-defined assemblies [2], and organic and inorganic synthesis [3]. Several pseudotetrahedral monomeric Ag(I) complexes with diimine ligands such as bipyridine have been reported [7]. In addition, the structures and spectroscopic properties of many adducts of Ag(I) with triphenylarsine, triphenylstibine and triphenylphosphine have been elegantly studied by White and coworkers [8]. The stabilization of 5s orbitals as a consequence of relativistic effects favours ds or sp hybridization responsible for the significant tendency of heavy metals with d^{10} configuration to form linear two-coordinate complexes; gold(I) is the most representative example [9]. In the case of silver(I), the relativistic effect is less pronounced than

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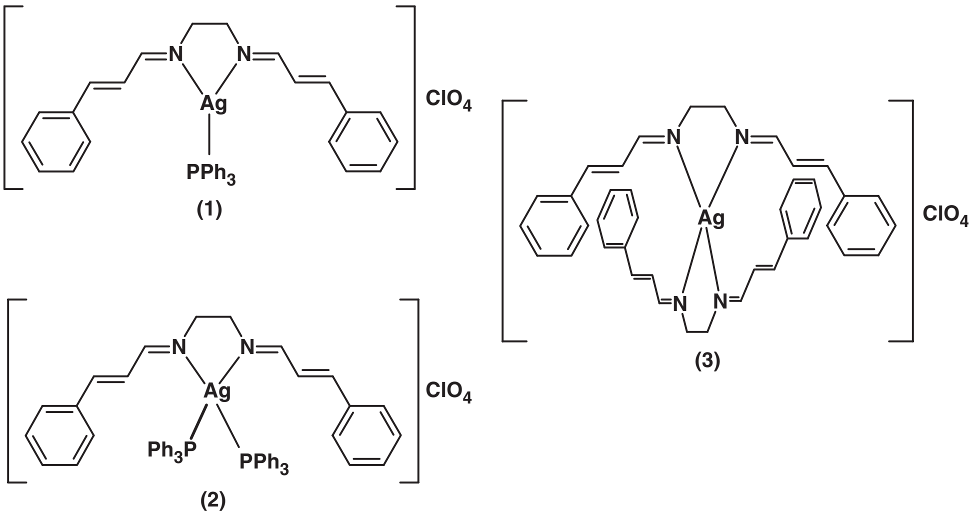
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970600763250



(1)

(2)

(3)

Scheme 1. Silver (I) complexes $[Ag(ca_2en)(PPh_3)]C10_4$(**1**), $[Ag(ca_2en)(PPh_3)_2]$ $C10_4$(**2**), $[Ag(ca_2en)_2]$ $C10_4$(**3**).

with gold(I). Therefore, silver shows greater variety in its coordination chemistry, and can serve to link bridging ligands to form polymeric compounds with novel coordination patterns [10]. Structural and solution equilibria as well as dynamic studies of silver(I) compounds containing phosphine ligands are also of importance owing to their application as potent anti-tumor agents [11], as free radical scavengers in industrial processes [12], or as models for photophysical studies [13]. In the present work, we report the synthesis and characterization of three Ag(I) complexes $[Ag(ca_2en)(PPh_3)]ClO_4$ (**1**), $[Ag(ca_2en)(PPh_3)_2]ClO_4$ (**2**) and $[Ag(ca_2en)_2]ClO_4$ (**3**) (scheme 1).

2. Experimental

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

2.1. *Materials and physical measurements*

All chemicals were purchased from commercial sources and used as received. Elemental analyses were performed using a Heraeus CHN–O–RAPID system. IR spectra were recorded on a FT-IR JASCO 680 instrument. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. ^{1}H NMR spectra were measured with a Bruker AVANCE DR × 500 spectrometer (500 MHz). Proton chemical shifts are reported in ppm relative to internal standard Me_4Si. The ca_2en ligand *N,N′*-bis(*trans*-cinnamaldehyde)ethylenediimine, was prepared as reported elsewhere [14].

2.2. *Preparation of $[Ag(ca_2en)(PPh_3)]ClO_4$ (1)*

To a solution of 0.207 g of $AgClO_4$ (0.1 mmol) in 2 cm^3 of acetonitrile was added dropwise a solution of 0.262 g of PPh_3 (0.1 mmol) in 5 cm^3 of acetonitrile at room temperature, and the mixture stirred for 15 min. The volume of the solution was reduced under vacuum to about 3 cm^3 and a solution of 0.288 g of ca$_2$en (0.1 mmol) in 3 cm^3 of methanol added and the reaction mixture was stirred for an additional 20 min. Colourless crystals of [Ag(ca$_2$en)(PPh$_3$)]ClO$_4$ (**1**) were obtained by diffusion of diethylether vapour into the solution at 0°C. The crystals were collected by filtration and dried under vacuum. Yield: 0.629 g (83%). Anal. Calcd. for $C_{38}H_{35}N_2AgClO_4P$ (%): C, 60.21; H, 4.65; N, 3.69. Found: C, 60.30; H, 4.60; N, 3.75. IR (KBr, cm^{-1}) 1627 (C=N), 1093 (ClO$_4$). ^{1}H NMR (CDCl$_3$) 3.87 (s, 4H, NC**H**$_2$C**H**$_2$N); 6.87, (dd, 2H, 2 –C=C**H**–C); 6.98 (d, 2H, 2 –C**H**=C–); 7.26–7.49 (m, 25H, Ar**H**); 8.14 (d, 2H, 2 –C**H**=N).

2.3. *Preparation of [Ag(ca$_2$en)(PPh$_3$)$_2$]ClO$_4$ (2)*

To a solution of 0.207 g of AgClO$_4$ (0.1 mmol) in 2 cm^3 of acetonitrile was added dropwise a solution of 0.524 g of PPh$_3$ (0.2 mmol) in 5 cm^3 of acetonitrile at room temperature, and the mixture stirred for 15 min. The volume of the solution was reduced under vacuum to about 3 cm^3 and a solution of 0.288 g of ca$_2$en (0.1 mmol) in 3 cm^3 of methanol added; and the reaction mixture was stirred for an additional 20 min. Colourless crystals of [Ag(ca$_2$en)(PPh$_3$)$_2$]ClO$_4$ (**2**) were obtained as above. The crystals were collected by filtration and dried under vacuum. Yield: 0.908 g (89%). Anal. Calcd. for $C_{56}H_{50}N_2AgClO_4P_2$ (%): C, 65.93; H, 4.93; N, 2.75. Found: C, 65.88; H, 4.89; N, 2.71. IR (KBr, cm^{-1}) 1624 (C=N), 1095 (ClO$_4$). ^{1}H NMR (CDCl$_3$) 3.80 (s, 4H, NC**H**$_2$C**H**$_2$N); 6.56, (dd, 2H, 2 –C=C**H**–C); 6.89 (d, 2H, –C**H**=C); 7.14–7.40 (m, 40H, Ar**H**); 8.40 (d, 2H, 2 –C**H**=N).

2.4. *Preparation of [Ag(ca$_2$en)$_2$]ClO$_4$ (3)*

To a solution of 0.207 g of AgClO$_4$ (0.1 mmol) in 3 cm^3 of acetonitrile was added dropwise a solution of 0.576 g of ca$_2$en (0.2 mmol) in 3 cm^3 of methanol and the reaction mixture stirred for 20 min. Colourless crystals of [Ag(ca$_2$en)$_2$]ClO$_4$ (**3**) were obtained as above. The crystals were collected by filtration and dried under vacuum.Yield: 0.612 g (78%). Anal. Calcd. for $C_{40}H_{40}N_4AgClO_4$ (%): C, 61.27; H, 5.14; N, 7.14. Found: C, 61.30; H, 5.11; N, 7.15. IR (KBr, cm^{-1}) 1631 (C=N), 1091 (ClO$_4$). ^{1}H NMR (CDCl$_3$) 3.99 (s, 4H, NC**H**$_2$C**H**$_2$N); 6.67, (dd, 2H, –C=C**H**–C); 7.08 (d, 2H, 2 –C**H**=C); 7.25–7.35 (m, 20H, Ar**H**); 8.35 (d, 2H, 2 –C**H**=N).

2.5. *X-ray crystallography*

Determination of unit cell parameters and data collection were performed with Mo-Kα radiation ($\lambda = 0.7107$ Å) at 296 K on a Rigaku AFC7R diffractometer. The structure was solved by the heavy atom method, expanded using Fourier techniques, and refined by full-matrix least-squares methods on F with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were added at calculated positions and fixed in the refinement. All calculations were carried out using the teXsan crystallographic software package [15]. Crystal and experimental data are given in table 1. Selected bond distances and angles are given in table 2.

Table 1. Crystallographic and refinment data for [Ag(ca$_2$en)(PPh$_3$)]ClO$_4$ (**1**).

Empirical formula	$C_{38}H_{35}O_4N_2ClPAg$
Formula weight	758.00
Temperature (K)	296
Crystal size (mm^3)	$0.30 \times 0.40 \times 0.50$
Wavelength (Å)	0.71069
Crystal system and space group	Triclinic, $P\bar{1}$
a (Å)	12.086(2)
b (Å)	18.204(2)
c (Å)	8.550(2)
α (°)	102.69(1)
β (°)	105.85(1)
γ (°)	91.47(1)
V (Å^3)	1758.0(5)
Z	2
D (Calcd) (g cm^{-3})	1.432
μ (mm^{-1})	7.35
F (000)	776.00
Index ranges	$0 \le h \le 15$, $-23 \le k \le 23$, $-10 \le l \le 9$
Scan type	$\omega - 2\theta$
$2\theta_{\max}$ (°)	55.0
No. of reflections measured	Total: 8506
	Unique: 8081 ($R_{\text{int}} = 0.118$)
No. observations ($I > 3.00\sigma(I)$)	6096
Reflection/parameter ratio	14.38
Residuals: R; R_w	0.070; 0.064
Goodness-of-fit	2.85
Maximum peak in final diff. Map (e Å^{-1})	0.97
Minimum peak in final diff. Map (e Å^{-1})	−0.82

Table 2. Selected bond distances (Å) and angles (°) for [Ag(ca$_2$en)(PPh$_3$)]ClO$_4$ (**1**).

Ag(1)–N(1)	2.302(4)	N(1)–Ag(1)–N(2)	77.2(2)
Ag(1)–N(2)	2.252(4)	N(1)–Ag(1)–P(1)	133.6(1)
Ag(1)–P(1)	2.346(1)	N(2)–Ag(1)–P(1)	149.0(1)
N(1)–C(9)	1.257(7)	Ag(1)–N(1)–C(9)	127.9(4)
N(2)–C(12)	1.256(7)	Ag(1)–N(1)–C(10)	109.2(4)
C(10)–C(11)	1.492(9)	Ag(1)–N(2)–C(12)	131.5(4)
P(1)–C(21)	1.814(4)	Ag(1)–N(2)–C(11)	109.7(3)
P(1)–C(27)	1.822(4)	Ag(1)–P(1)–C(21)	114.8(1)
P(1)–C(33)	1.816(4)	Ag(1)–P(1)–C(27)	113.5(1)
		Ag(1)–P(1)–C(33)	112.6(1)

3. Results and discussion

3.1. *Synthesis*

The colourless complexes are stable in air in the solid state for 7–8 weeks. Stability in solution depends on the solvent. These complexes are stable in acetonitrile solution at room temperature for 20 days; they remain unchanged for 5 days in methanol and for two days in dicholoromethane at 0°C.

3.2. *Spectroscopic studies*

The IR spectrum of the free ligand exhibits the characteristic band of an imine at 1634 cm^{-1} [14]. This band is shifted to lower frequencies in the IR spectra of the complexes, due to the coordination of the imine nitrogen. It is well known that silver(I) compounds are diamagnetic and colourless. Since no d–d transitions are expected, electronic absorption bands are either of CT or intraligand character. The first MLCT is clearly observed at 345 nm only for $[Ag(ca_2en)_2]ClO_4$ (**3**), but this transition may be obscured by intraligand transitions in $[Ag(ca_2en)(PPh_3)]ClO_4$ (**1**) and $[Ag(ca_2en)(PPh_3)_2]ClO_4$ (**2**). An absorption band at about 280 nm can be assigned to the π–π^* transition of the coordinated ligand in the three complexes. ^1H NMR data and peak assignments are presented in the experimental section. Peaks are assigned based on splitting and spin coupling constants in the literature, and clearly conform to the X-ray molecular structure in **1**. The down field shift of the iminic protons in the spectra of the complexes relative to that of the free ligand can be attributed to deshielding resulting from the coordination of the ligand. In principle there is the possibility of having geometrical isomers with respect to the imine. However, the appearance of a unique signal for each of proton in $CDCl_3$ solution indicates that the symmetry of the molecules is retained in solution and only one isomer is present.

3.3. *Crystal structure of [Ag(ca$_2$en)(PPh$_3$)]ClO$_4$ (1)*

The molecular structure of $[Ag(ca_2en)(PPh_3)]ClO_4$ (**1**) with the atom-numbering scheme is presented in figure 1 and consists of a $[Ag(ca_2en)(PPh_3)]^+$

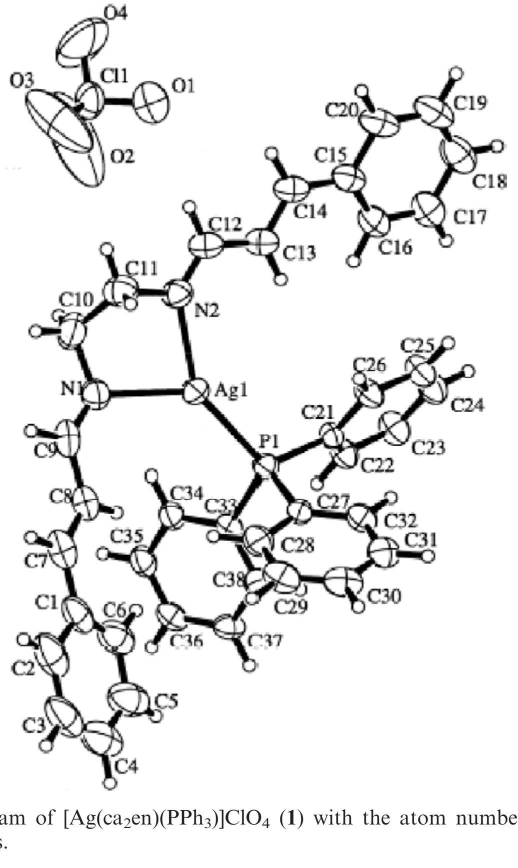


Figure 1. ORTEP diagram of $[Ag(ca_2en)(PPh_3)]ClO_4$ (**1**) with the atom numbering scheme, drawn with 30% probability ellipsoids.

cation and a ClO_4^- anion. Ca_2en acts as a bidentate ligand coordinating *via* two N atoms to silver(I). The coordination geometry around silver is distorted trigonal. The intra-chelate N(1)–Ag(1)–N(2) bond angle [77.20(2)°] is similar to the corresponding bond angle in related complexes [4–6], as are the intra-ligand N(1)–Ag(1)–P(1) and N(2)–Ag(1)–P(1) bond angles [133.6(1) and 149.0(1)°] [4]. The bond lengths Ag(1)–N [2.252(4), 2.302(4) Å] and Ag(1)–P(1) [2.346(1) Å] are in good agreement results found for similar species [4–6]. Despite the fact that the donor nitrogen atoms are sp^2 hybridized, the chelate ring is significantly puckered in the complex and some strain in the chelate ring is suggested by bond angles about nitrogen [C(10)–N(1)–Ag(1) 109.2(4), C(11)–N(2)–Ag(1) 109.7(3), C(10)–N(1)–C(9) 120.8(5), C(12)–N(2)–C(11) 118.8(5)°]. The phenyl rings are perfectly planar (largest deviation 0.02 Å) and the chain connecting the ring to the coordinated nitrogen atom is quite planar ($N(1) \rightarrow C(6)$ 0.092 Å, $N(2) \rightarrow C(16)$ 0.060 Å). This degree of coplanarity, which allows for increased π conjugation in the ligand, is consistent with the observed C–C single bond distances in the coordinated ligand; C(8)–C(9), 1.432(8) Å < C(1)–C(7), 1.466(9) Å < C(10)–C(11), 1.492(9) Å. This demonstrates that π delocalization is diagnostic of an *endo* configuration with respect to the metal centre in complexes of this type (*trans–trans* conformation) [16–19].

Supplementary material

Crystallographic data for **1** (CCDC number 286157) can be obtained free of charge from the Cambridge Crystallographic Data Centre, 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).

References

[1] M.J. Hannon, C.L. Painting, N.W. Alock. *Chem. Commun.*, 2023 (1999).
[2] M. Schmittel, A. Ganz, D. Fenske, M. Herderich. *J. Chem. Soc., Chem. Commun.*, 353 (2000).
[3] R. Mehrotra, R. Bohra. *Metal Carboxylates*, Academic Press, London (1983).
[4] M. Amirnasr, R. Welter, A.D. Khalaji. *Acta. Cryst.*, **E61**, m1452 (2005).
[5] A.D. Khalaji, M. Amirnasr, R. Welter. *Anal. Sci.*, **22**, x49 (2006).
[6] L. Zhang, C. Chen, Q. Zhang, H. Zhang, B. Kang. *Acta. Cryst.*, **E59**, m536 (2003).
[7] T.G. Richmond, E.P. Kelson, A.M. Arif. *J. Am. Chem. Soc.*, **110**, 2334 (1988).
[8] J.D. Effendy, A.H. Kildea. *Aust. J. Chem.*, **50**, 671 (1997).
[9] M. Gimeno, A. Laguna. *Chem. Rev.*, **97**, 511 (1997).
[10] S.-P. Yang, X.-M. Chen, L.-N. Ji. *J. Chem. Soc., Chem. Commun.*, 2337 (1999).
[11] S.G. Berners-Price, R.K. Johnson, C.K. Mirabelli, L.F. Faucette, F.L. McCabe, P.J. Sadler. *Inorg. Chem.*, **26**, 3383 (1987).
[12] H. Cohen, D. Meyerstein. *Inorg. Chem.*, **25**, 1505 (1986).
[13] G. Zhang, G. Yang, J.S. Ma. *Inorg. Chem. Commun.*, **7**, 994 (2004).
[14] M. Amirnasr, K.J. Schenk, M. Salavati, A. Gorji, S. Dehghanpour, A. Taeb, A. Tajarrodi. *J. Coord. Chem.*, **56**, 231 (2003).
[15] *teXsan*, *Crystal Structure Analysis Package*, Molecular Structure Coorporation (1992).
[16] G. Kickelbick, M. Amirnasr, A.D. Khalaji, S. Dehghanpour. *Aust. J. Chem.*, **56**, 323 (2003).
[17] G. Kickelbick, M. Amirnasr, A.D. Khalaji, S. Dehghanpour. *Acta Cryst.*, **E58**, m381 (2002).
[18] S. Meghdadi, M. Amirnasr, K.J. Schenk, S. Dehghanpour. *Helv. Chim. Acta*, **85**, 2807 (2002).
[19] M. Amirnasr, A.D. Khalaji, L.R. Falvello, T. Soler. *Anal. Sci.*, **22**, x47 (2006).