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Silver(I) complexes of the naphthyl-azoimine function: single crystal X-ray structure of bis-[1-ethyl-2-(naphthyl-α-azo)imidazole]silver(I) perchlorate

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Abstract

Reaction of AgNO₃ and 1-alkyl-2-(naphthyl-(α/β)-azo)imidazole (α -/ β -NaiR) in MeOH followed by the addition of NaClO₄ has isolated [Ag(α -/ β -NaiR)₂](ClO₄) (**3**/4). The complexes are characterized by microanalytical and spectral data. Single crystal X-ray diffraction study of bis-[1-ethyl-2-(naphthyl- α -azo)imidazole]silver(I) perchlorate confirms the structure of the complex. Argento-philicity of imidazole-N and steric crowding by naphthyl groups have forced a {2+2} distorted linear geometry. The structure shows intramolecular and intermolecular H-bonding in a 1D helical framework along with face-to-face π - π interactions. © 2003 Elsevier Ltd. All rights reserved.

Keywords: Naphthylazoimidazole; Silver(I) complexes; Helical structure; EHMO

1. Introduction

Imidazole is ubiquitous in chemistry and biology [1]. In this respect, the chemical modification of imidazole to synthesize polydentate ligands is of current interest [2–4]. We are also engaged to synthesize imidazole containing ligands, arylazoimidazoles by anchoring an arylazo (Ar–N=N⁺) group to the imidazole backbone. As a part of our continuing program of research in the field of azohetereocyclic molecules we have designed arylazoheterocycles of pyridine, pyrimidine and imidazole [5–7]. They differ in their π -acidity in the order of imidazole < pyridine < pyrimidine [8]. Arylazoheterocycles bear the functional group azoimine, -N=N-C=N-, which is an efficient group to stabilize the low valent metal redox state [9–12].

Imidazole, being a five-membered heterocycle, is less π -acidic and a better π -donor than six-membered pyri-

dine/pyrimidine rings. The electronic property of the molecule may be finely adjusted by changing substituents in the aryl group or complete replacement of the aryl group by an α - and/or β -naphthyl group [9–12]. The α - and β -naphthyl moieties also exhibit different thermodynamic stability [13] which may indirectly perturb the electronic levels of the metal complexes.

We have recently reported the coordination chemistry of platinum(II) [9], ruthenium(II) [10], osmium(II) [11] and palladium(II) [12] naphthylazoimidazoles. In recent years the coordination chemistry of coinage metals came into the field for their (i) biological and medicinal importance [14-16], (ii) metal-metal interaction between closed shell (d¹⁰-d¹⁰) cations or the aurophilic interaction [17-20] and (iii) supramolecular assemblies with particular reference to helicity in silver(I) complexes [21-25]. Several single and double stranded helical polymers of silver(I) and their photophysical and spectrochemical properties are topics of developing interest. Because of the flexibility in coordination number in Ag(I) [26, 27], covalent interaction may lead to the synthesis of coordination polymers [28]. The assembly of coordination networks through H-bonding and π - π stacking

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interactions has been of great interest in recent years [29,30]. Presence of suitable oxo counter ions (e.g. NO_3^- , CIO_4^- , $CF_3SO_3^-$, etc) in the complexes may result in secondary interactions, $C-H\cdots O$ and act as a determining factor for crystal packing and helicity [31].

Ag(I)-azoimidazole complexes have been reported by a different researcher [32–36]. In this work, we have selected closely related ligands, 2-(naphthyl-(α/β)azo)imidazole (α/β -NaiR) (Scheme 1) which provide larger steric crowding and better electron donating ability than a conventional aryl group. In this work we have explored the coordination chemistry of Ag(I)naphthylazoimidazoles. Synthesis, spectral, electrochemical studies have been carried out and a single crystal X-ray structure of Ag(I)-naphthylazoimidazoles are described.

2. Experimental

2.1. Materials

1-Alkyl-2-(naphthyl- (α/β) -azo)imidazoles (α -NaiR (1), β -NaiR (2)) were synthesized by a reported procedure [10,12]. AgNO₃ and α -/ β -naphthylamines were obtained from E. Merck, Germany and NaClO₄ was obtained from Fluka, USA. Purification of solvents was performed as in the reported procedure [12]. All other solvents and chemicals were of reagent grade and were used without further purification.

2.2. Physical measurements

Microanalytical (C, H, N) data were collected using a Perkin–Elmer 2400 elemental analyzer. UV–Vis spectra were recorded by a JASCO V-570 UV/Vis/NIR spectrophotometer. IR data were collected from a JASCO-420 FTIR (KBr disk, 4000–200 cm⁻¹). ¹H NMR spectra were collected in CDCl₃ using a 500 MHz FT-NMR spectrometer. Electrical conductivity was measured using a Systronics 305 digital conductivity meter with a solution concentration of ~10⁻³ M cm⁻³. Silver was analyzed gravimetrically [37]. Electrochemical measurements were carried out under dinitrogen conditions with the help of an EG&G PARC 270 computer controlled Versastat using a Pt-disk milli working electrode. All results were collected at 298 K with the saturated calomel electrode (SCE) as reference. Reported potentials are uncorrected for junction effects.

Caution! Perchlorate salts of metal complexes are explosive in nature and should be handled carefully.

2.3. Preparation of bis-[1-ethyl-2-(naphthyl- α -azo)imidazole]silver(I) perchlorate, $[Ag(\alpha$ -NaiEt)_2](ClO₄) (**3b**)

The ligand α -NaiEt (0.50 g, 2 mmol) in dry MeOH (20 ml) was added to a methanolic solution of AgNO₃ (0.17 g, 1 mmol). The red-brown solution was stirred for 4 h in a dark environment and covered with carbon paper. The solution volume was reduced to half of its original volume by bubbling nitrogen gas. The compound was collected as the perchlorate salt by adding NaClO₄(1 g in 2 ml aqueous solution). The brown-red mass was recrystalized from diffusion of a CH₂Cl₂ solution of the complex into hexane. Yield was 0.60 gm (90%). *Anal.* Calc. for C₃₀H₂₈N₈ClO₄Ag (**3b**): C, 50.78; H, 3.87; N, 15.90; Ag, 15.03. Found: C, 50.89; H, 3.96; N, 15.83; Ag, 15.24%. IR (KBr, cm⁻¹): 1384 (N=N), 1582 (C=N).

All other complexes were prepared following an identical procedure and yields were 75-90%. Anal. Calc. for C₂₈H₂₄N₈ClO₄ Ag (**3a**): C, 49.35; H, 3.91; N, 15.78; Ag, 16.15. Found: C, 49.46; H, 3.59; N, 16.49; Ag, 15.87%. IR (KBr, cm^{-1}): 1386 (N=N), 1585 (C=N). Anal. Calc. For C40H32N8ClO4Ag (3c): C, 57.60; H, 3.78; N, 13.39; Ag, 13.11. Found: C, 57.74; H, 3.85; N, 13.47; Ag, 13.25%. IR (KBr, cm⁻¹): 1381 (N=N), 1590 (C=N). Anal. Calc. For $C_{28}H_{24}N_8ClO_4$ Ag (4a): C, 49.39; H, 3.51; N, 16.43; Ag, 15.69. Found: C, 49.46; H, 3.59; N, 16.49; Ag, 15.87%. IR (KBr, cm⁻¹): 1382 (N=N), 1587 (C=N). Anal. Calc. for C₃₀H₂₈N₈ClO₄Ag (4b): C, 50.80; H, 3.90; N, 15.73; Ag, 15.84. Found: C, 50.89; H, 3.96; N, 15.83; Ag, 15.24%. IR (KBr, cm⁻¹): (N=N), 1582 (C=N). Anal. Calc. for 1384 C₄₀H₃₂N₈ClO₄Ag (**4c**): C, 57.69; H, 3.80; N, 13.43; Ag, 13.02. Found: C, 57.74; H, 3.85; N, 13.47; Ag, 13.25%. IR (KBr, cm⁻¹): 1381 (N=N), 1585 (C=N).

2.4. Crystallographic data collection and refinement

A crystal suitable for X-ray diffraction study was obtained after several trials by slow diffusion of a CH₂Cl₂ solution of the complex into a hexane layer. A suitable single crystal of complex $[Ag(\alpha-NaiEt)_2](ClO_4)$ (**3b**) was mounted on a Siemens CCD diffractometer equipped with graphite monochromated Mo K α ($\lambda =$ 0.71073 Å) radiation. The intensity data were corrected for Lorentz and polarization effects. Details of data collection and structure solution are given in Table 1. The structure was solved by Patterson syntheses and

Table 1 Summarized crystallography data for $[Ag(\alpha-NaiEt)_2][CIO_4]$ (3b)

Crystal parameters	
Empirical formula	$C_{30}H_{28}N_8ClO_4Ag$
Formula weight	707.9
Crystal system	tetragonal
Space group	<i>P</i> -4 <i>n</i> 2
$a(\mathbf{A})$	16.376(4)
b (Å)	16.376(4)
<i>c</i> (Å)	22.971(8)
α (°)	90
β (°)	90
γ (°)	90
$V(Å^3)$	6160(3)
λ (Å)	0.71073
$ ho_{ m calc}~({ m Mg}~{ m m}^{-3})$	1.52
Ζ	8
<i>T</i> (K)	293(2)
μ (Mo K α) (mm ⁻¹)	0.791
Total data	37,885
Unique data	7091
Observed data $(I > 2\sigma(I))$	2938
Refined parameters	397
R	0.0394
wR_2	0.0920
Goodnees-of-fit	1.00
	2 2 2 2 2 2 1 /2

 $\frac{R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. wR_{2} = [\sum w(|F_{o}|^{2} - |F_{c}|^{2})^{2} / \sum w(|F_{o}|^{2})^{2}]^{1/2},}{w = 1 / [\sigma^{2}(F_{o}^{2}) + (0.0299P)^{2}], P = (F_{o}^{2} + 2F_{c}^{2}) / 3. \text{ Goodness-of-fit (GOF)}}$ is defined as $[w(F_{o} - F_{c}) / (n_{0} - n_{v})]^{1/2}$ where n_{0} and n_{v} denote the number of data and variables, respectively.

followed by successive Fourier and difference Fourier syntheses. Full-matrix least-squares refinements on F^2 were carried out using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon atoms with an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of their parent atom. Since the complex was crystallized in a non-centrosymmetric space group, the absolute configuration was determined (Flack × parameter = -0.00(3)) [38]. Complex neutral atom scattering factors were used throughout this program. All calculations were carried out using SHELXS 86 [39] SHELXL 97 [40], PLATON 99 and ORTEP-3 [41,42] programs.

3. Results and discussion

3.1. Synthesis

The two classes of ligands used in the present study belong to the azoimine (-N=N-C=N-) family. 1-Alkyl-2-(naphthyl- α -azo)imidazoles are abbreviated as α -NaiMe (1a), α -NaiEt (1b), α -NaiBz (1c); 1-alkyl-2-(naphthyl- β -azo)imidazoles are abbreviated as β -NaiMe (2a), β -NaiEt (2b) and β -NaiBz (2c). They are synthesized by the reported procedure [10–12]. The ligands are an unsymmetric bidentate N,N' chelating type.

These ligands in MeOH–CHCl₃ mixture react with AgNO₃in MeOH and the complexes have been isolated as their perchlorate salts. They were purified by crystallization by diffusion of CH₂Cl₂ solution of the complex into hexane. The complexes are highly photosensitive and decomposed with separation of black metallic silver from solution upon exposure to light. The complexes are characterized by elemental analyses, IR, UV–Vis (Table 2), ¹H NMR (Table 3) data and support the formulation $[Ag(\alpha-/\beta-NaiR)_2][ClO_4]$ (3, 4). The complexes are diamagnetic and 1:1 electrolytes in nitromethane. The structural configuration has been determined by a single crystal X-ray diffraction study of $[Ag (\alpha-NaiEt)_2][ClO_4]$ (3b).

3.2. Spectral properties

The complexes $[Ag(NaiR)_2]^+$ exhibit characteristic IR transmissions for v(N=N) and v(C=N) at around 1382 and 1485 cm⁻¹. The free ligand values are 1410 and 1600 cm⁻¹, respectively. The observation is interesting. The v (C=N) is red-shifted by >100 cm⁻¹. This supports very strong interaction of Ag⁺ with imidazolic-N compared to azo-N. This is also confirmed by bond length data (Table 4). The perchlorate (ClO₄⁻) exhibits bands at 1147, 1108 and 1090 cm⁻¹ along with a weak band at 620–625 cm⁻¹. The splitting of $v(ClO_4^-)$ supports reduction in symmetry, which may be due to some hydrogen bonding interaction. This is observed, indeed (vide infra).

Solution electronic spectra of the complexes were recorded in dichloromethane in the range of 600-200 nm. Bathochromic shift relative to the free ligand indicates interaction between Ag⁺ and the ligand (Table 2). The silver(I) complexes exhibit the absorption at ca. 400 nm and are assigned to intraligand charge transitions.

The ligands and complexes show highly resolved ¹H NMR spectra in CDCl₃ at 298 K. 1-Alkyl-2-(naphthylazo)imidazoles (NaiR) have been characterized previously [10,12] and serve as guides to determine the structure of the silver(I) complexes. The spectral data are collected in Table 3. The 1-alkyl groups in $[Ag(NaiR)_2]^+$ show significant shifting downfield by 0.1-0.2 ppm from that of the free ligand values [10-12]. A significant difference is observed in the resonance signal of imidazole protons 4- and 5-H from that of naphthyl protons. Imidazole protons 4- and 5-H appear upfield (6.9–7.2 ppm) and naphthyl protons (8-H–15-H) resonate downfield, 7.5–8.0 ppm. In $[Ag(NaiR)_2]^+$ the signal pattern shows that imidazole protons are shifted to the downfield side by 0.4–0.5 ppm and naphthyl protons are shifted to upfield side except 9-H in α-NaiR and 8, 10-H in β -NaiR compared to the free ligand values.

Compound	UV–Vis spectral data	Redox data	Ligand reductions ^c	
	$\lambda_{\rm max}$, nm (10 ⁻³ ϵ , M ⁻¹ cm ⁻¹)	$E_0^{\rm d}$ (V)	$E_{\rm s}^{\rm e}$ (V)	azo/azo [_]
3a	480 (1555) ^f , 434 (2011), 418 (9305), 384 (10,043)	-0.087	0.503	-0.551
3b	472 (1240) ^f , 436 (1665), 354 (7450)	-0.093	0.495	-0.569
3c	484 (1465) ^f , 436 (1911), 354 (8940)	-0.088	0.505	-0.578
4a	414 (1675) ^f , 400 (2430), 378 (9450)	-0.081	0.462	-0.679
4b	416 (2248) ^f , 400 (3260), 384 (10,936)	-0.085	0.449	-0.761
4c	414 (1765) ^f , 402 (2050), 384 (9467), 378 (9840)	-0.091	0.476	-0.881

Table 2 Electronic spectroscopic a and cyclic voltammetric b,c data

^a Solvent CH₂Cl₂.

^b Solvent MeCN, working electrode Pt-disk, reference SCE, supporting electrolyte [*n*Bu₄N][ClO₄] (0.1 M), solute concentration ~10⁻³ M, scan rate 50 mV, potential is expressed in V, E_{pa} stands for anodic peak potential.

^c $E_{\rm pc}$ cathodic peak potential in V and $i_{\rm pa}/i_{\rm pc}$ lies between 0.5 and 0.6.

^d Threshold potential to reduction of $Ag(I) \rightarrow Ag(0)$ on the electrode surface.

^eAnodic stripping potential for $Ag(0) \rightarrow Ag(I)$.

^fShoulder.

Table 3						
¹ H NMR	data	recorded	in	CDCl ₃	at	298K

Compound	δ (ppm (J, Hz))										
	4-H ^a	5-H ^a	8-H ^a	9-H ^b	10-H °	11-H ^c	12-H ^d	13-H ^d	14-H ^c	15-H ^b	N-R
(3a)	7.58	7.52		8.44 (7.10)	7.77 (7.0)	7.46 (7.0)	7.08	7.08	7.19 (7.2)	7.04 (7.5)	4.13 ^e
(3b)	7.61	7.59		8.44 (8.1)	7.80 (7.5)	7.44 (7.2)	7.04	7.04	7.15 (7.2)	6.91 (7.5)	4.44 ^f (12.0)
(3c)	7.65	7.63		8.45 (8.4)	7.82 (7.5)	7.46 (7.2)	7.12	7.12	7.23 (7.5)	7.06 (7.8)	5.67 ^g
(4 a)	7.55	7.45	8.03		7.78 (8.1)	7.67 (7.5)	7.50	7.42	7.42 (7.5)	7.62 (7.5)	4.11 ^e
(4b)	7.58	7.50	8.04		7.75 (8.1)	7.65 (7.5)	7.49	7.41	7.41 (7.2)	7.60 (7.8)	4.35 ^f (12.0)
(4c)	7.63	7.55	8.08		7.83 (8.4)	7.71 (8.1)	7.5	7.47	7.47 (8.1)	7.69 (7.8)	5.74 ^g
a Cinglat head	^a Singlet broad										

^a Singlet broad.

^b Doublet.

^c Triplet.

^d Multiplet.

^e1-CH₃

^fQuartet for $-CH_2$ - and $\delta(CH_2)$ - CH_3 : **5b**, 1.51(7.0)^b; **6b**, 1.47(7.0)^b ppm.

^g 1-CH₂(Ph) and δ (Ph): 7.4–7.5 ppm.

Table 4 Selected bond distances (Å) and angles (°) for $[Ag(\alpha-NaiEt)_2](ClO_4)$ (**3b**) along with their esd in parentheses

Bond distances (Å)			Bond angles (°)			
	Ag–N(1)	2.124(5)	N(1)-Ag-N(4)	65.45(2)		
	Ag-N(5)	2.128(5)	N(5)-Ag-N(8)	64.86(2)		
	Ag-N(4)	2.851(5)	N(1)-Ag-N(5)	174.54(2)		
	Ag-N(8)	2.859(5)	N(4)-Ag-N(8)	74.88(1)		
	N(3)–N(4)	1.266(5)	N(3)-N(4)-Ag	106.6(3)		
	N(7)–N(8)	1.265(5)	N(7)-N(8)-Ag	106.6(4)		
	C (3)–N(3)	1.360(7)	C(3)–N(1)–Ag	122.8(4)		
	C (3)–N(1)	1.333(7)	C(18)–N(5)–Ag	123.8(5)		
	C (18)–N(5)	1.310(7)				
	C (18)–N(7)	1.369(7)				

3.3. Molecular structure

A molecular view of the complex $[Ag(\alpha-Na-iEt)_2][ClO_4]$ (**3b**) is shown in Fig. 1 and the bond parameters are given in Table 4. A review of the bond lengths and angles shows that the complex is essentially

linear with a further two weak interactions to azo-N of the azoimine group. The N=N distances are equivalent in the two azoimine chelates (1.266(5), 1.265(5) Å). Free ligand bond parameters are available for 1-ethyl-2-(naphthyl-azo)imidazolium hexafluorophosphate, [α-NaiEtH]⁺[PF $_{6}^{-}$] [43] and the N–N distance is 1.267(3) Å. The N-N distance in 1-methyl-2-(phenylazo)imidazolium perchlorate is 1.250(1) Å [44]. The elongation is likely to be a result of a high steric crowding provided by the naphthyl group relative to the phenyl group. This may be due to better σ -donor character of the ligand compared to the aryl group. The Ag-N distances are as follows: Ag-N (imidazole) [Ag-N(1), 2.124(5); Ag-N(5), 2.128(5) Å]. The distance is shortened by >0.7 Å than that of the proposed Ag-N(azo) distance [Ag-N(4), 2.851(5); Ag-N(8), 2.859(5) A]. This accounts for the argentophilicity [17,18] of imidazole-N compared to azo-N donor centers. On considering the weak interaction of Ag(I) with the azo-N leading to the chelated structure, the proposed chelate angles are: N(1)-Ag-



Fig. 1. X-ray crystal structure of $[Ag(\alpha-NaiEt)_2]$ (ClO₄) (3b).

N(4), 65.45(2)° and N(5)-Ag-N(8), 64.86(2)°. This example bears the lowest chelate bite angles so far reported in the azoimine family [9-12]. This smallest chelate angle may lead to distortion in the tetrahedral geometry. The naphthyl ring is no longer planar with the chelate plane. The plane-1 (Ag-N(1)-C(3)-N(3)-N(4))inclines at an angle of $23.4(2)^{\circ}$ with the α -naphthyl group whereas plane-2 (Ag-N(5)-C(18)-N(7)-N(8))makes an angle of 49.89(2)°. Thus, the two naphthyl groups are skewed by 18.9(2)°. The bulky size of the naphthyl groups may provide high steric interaction and may be responsible for the unusual distortion in geometry. The strain is manifested in stereochemical change from tetrahedral to linear symmetry. This has led us to conclude that the structure may be described as a $\{2+2\}$ distorted linear geometry tending to tetrahedral symmetry. Usually macrocycles are described by [m+n] nomenclature. For brevity we use the $\{2+2\}$ symbol to designate bi-coordinated linear geometry with some distortion towards tetrahedral symmetry.

1-Ethyl-2-(naphthyl- α -azo)imidazoles (α -NaiEt) and 2-(phenylazo)pyrimidines (papm) [45] have an azoimine, -N=N-C=N-, chelating function with an inbuilt imine (-C=N-) group in a heterocyclic back bone. Imidazole is a five-membered *meta* related two-N heterocycle while pyrimidine is a six-membered two-N heterocycle system. The replacement of a six-membered heterocycle by a five membered one reduces both the σ -donor and π -acceptor character of the system [8] and also introduces angular strain in the chelate ring [2]. This is reflected in the comparison of chelate ring structures of Ag(I)-naphthylazoimidazole and Ag(I)-2-(phenylazo)pyrimidine (Ag(papm) system [28]) molecules (Fig. 2). The elongation of the Ag-N (azo) [Ag-N(4)] distance by ~0.3 Å in Ag(-NaiEt) compared to Ag(papm) is a support of the



Fig. 2. Dimensions of chelate rings of (a) $Ag(\alpha\text{-NaiEt})_2^+$ and (b) $Ag(papm)^+.$

reduction in σ -donation capacity of α -NaiEt with respect to papm. The naphthyl group is a better electron donor, and provides higher steric strain relative to the phenyl ring and that plays a crucial role to monitor the σ -/ π -acidity of the azo function [46]. The π -acidity of naphthyl < phenyl as well as imidazole < pyrimidine [8]. This may support the shortening of the Ag-N(4) bond in Ag-(papm) [28] compared to the present silver(I) complex. The same argument cannot explain the shortening of bond length (by ~0.15 Å) of Ag-N(1) (Ag-N (heterocycle)) in $Ag(\alpha-NaiEt)_2^+$ relative to that of Ag-(papm). The strain that is developed due to replacement of pyrimidine by imidazole has been released by the elongation of the Ag–N(azo) bond length in the Ag(α - $NaiEt)_2^+$ system compared to that of the Ag-(papm) complex. However, the -N=N- bond length is unusually shortened in Ag-papm, which may be due to the helical network and triangular Ag(N)₃ coordination in the complex. The phenomena is more likely to be a result of bond alteration in Ag(papm) vs. a bond delocalization in Ag(α -NaiEt) in C3–N3–N4 bond lengths, probably caused by electronic effects.

The packing view of the crystal structure shows (Fig. 3) that $Ag(\alpha-NaiEt)_2^+$ contains an intramolecular and intermolecular H-bonded 1D helical framework. Intramolecular H-bonding is playing between the azo-N and α -H of the naphthyl group [N(4)...H(12), 2.477(8); N(8)...H(27), 2.531(3) Å]. This enhances the acidity of the C(12)–H(12)/C(27)–H(27) group leading to activation of this bond. This is observed by adding PdCl₄²⁻ to the solution of this complex and the cyclopalladated complex has been synthesized by a transmetallation reaction followed by the C–H activation process [12]. Intermolecular H-bonds operate between the two



Fig. 3. Helical 1D polymer showing intramolecular and intermolecular H-bonding.

	e	e		
D–H···A	D–H (Å)	H···A (Å)	$D \cdots A$ (Å)	$\angle D$ -H···A (°)
C12-H12···N4	0.93	2.478	2.812(9)	101.3
C27–H27···N8	0.93	2.521	2.835(8)	100.1
C15–H15···O1	0.93	2.554	3.461(14)	165.5
C1–H1···O3	0.93	2.440	3.199(13)	138.7
C16–H16· · · O4	0.93	2.568	3.314(12)	137.8
C–H··· π interaction				
$X-H \cdot \cdot \cdot Cg(J)$	H···Cg	H-Perp	$\angle X$ –H···Cg	X···Cg
$C14-H14\cdots Cg(1)$	3.365	3.332	81.97	3.363(13)
$\pi - \pi$ Interaction				
Cg(I)-Cg(J)	Cg–Cg	Dihedral (I,J ring)	Perp. From CgI to J	
Cg(1)-Cg(4)	3.8404(52)	0.71	3.307	
Cg(2)-Cg(6) 3.7900(40)		2.40	3.261	
Cg(3)–Cg(5)	3.9209(44)	19.38	3.842	

Table 5 Hydrogen bonding and weak interaction geometry (Å, °), H-bonding interaction

 $\begin{array}{l} Cg(I) \rightarrow centroid \ of \ ring \ I. \ Ring(1) \rightarrow N1-C1-C2-N2-C3; \ Ring(2) \rightarrow N5-C16-C17-N6-C18; \ Ring(3) \rightarrow C6-C7-C8-C9-C10-C11; \ Ring(4) \rightarrow C10-C11-C12-C13-C14-C15; \ Ring(5) \rightarrow C21-C22-C23-C24-C25-C26; \ Ring(6) \rightarrow C25-C26-C27-C28-C29-C30. \end{array}$

fragments around the azo group. The C–H group of the imidazole moiety *ortho* to metal coordinated-N (imidazole) [C(1)-H(1)/C(16)-H(16)] develops an electrostatic interaction with perchlorate-O(1)/O(4) while naphthyl C(15)–H(15) gives a H-bonding interaction with the second perchlorate ion. In addition to these, the complex experiences C–H–O as well as face-to-face π – π interactions (Table 5).



Fig. 4. HOMO, LUMO, HOMO-1 and LUMO+1 of $Ag(\alpha$ -NaiEt)₂⁺.

Table 6 Relative percent atomic contribution to MOs of the complex $Ag[\alpha$ -NaiEt]₂⁺

МО	Energy (eV)	Ag	N(imidazole)	Azo(N=N)	Naphthyl ring
Percentage of contribution					
92 (HOMO-1)	-11.575	5.5	6.6	78.9	6.6
91 (HOMO)	-11.491	2	3.3	77	7.7
90 (LUMO)	-10.806	0	21.4	52.5	25.5
89 (LUMO+1)	-10.783	0	24.5	55.31	20.2

3.4. Redox studies

The electrochemical properties of the complexes were examined by cyclic voltammetry in MeCN using $[nBu_4N][ClO_4]$ as supporting electrolyte at the scan rate 50 mV s⁻¹. The complexes of silver exhibit an irreversible oxidation-reduction response with the Pt-disk working electrode and saturated calomel electrode (SCE) as reference electrode. The complexes undergo reduction processes, which, given the redox non-innocence of the azoimine group [10], are assigned to ligandcentred-processes. The quasireversibility of the reductive process is observed from the peak separation ($\Delta E > 130$ mV) and the reduction is referred to the accommodation of an electron to the azo function dominated orbital of the bound ligand. Such processes, coupled to chemical complications for the reduction of Ag(I) on the electrode surface, result in that the current ratio i_{pa}/i_{pc} is always less than unity (i_{pa}/i_{pc}) lies between 0.5 and 0.6). In this connection, the presence of anodic stripping peaks in the backscan ($E_{pa} \sim +0.5$ V, Table 2) looks likely to testify for reoxidation of electro-deposed silver metal. This means that the reduction processes more than likely trigger release of silver ion with its consequent reduction to silver metal [47]. The reoxidation of $Ag(0) \rightarrow Ag(I)$ is associated with very high anodic current at positive to SCE (stripping potential \sim +0.5 V) which on repeat scan progressively increases the current. Besides, the approach to more negative potential followed by backscan increases the peak current height. The increase in potential gradient enhances the reaction rate which may cause deposition of larger amounts of Ag on the surface.

3.5. EHMO calculation and correlation with spectral and electrochemical properties

In order to highlight the electronic properties of silver(I)-naphthylazoimidazoles, an MO calculation has been performed in the framework of extended Huckel formalism. Crystallographic data of **3b** are used for the EHMO calculation. The MO pictures are shown in Fig. 4 and the percentage contribution of participating fragment/atomic functions to the MOs are given in Table 6. The HOMO(91) is contributed from 2% silver and 88% [77% azo (N=N), 7.7% naphthyl group and 3.3% N(imidazole)] ligand orbital. The LUMO has no metal

contribution, it is mainly ligand orbital, 99.4% [52.5% azo (N=N), 25.5% naphthyl group and 21.4% N(imidazole)]. Other low-lying orbitals (HOMO-1, HOMO-2) show a greater metal contribution but other higher energy orbitals (UMOs) show no metal contribution. It can be concluded that there should be no $M \rightarrow$ Ligand charge transfer and this happens indeed. The complexes show only the interligand (between imidazole and naphthyl group) charge transition in the lower wavelength region. Because of the weak M–L interaction, Ag⁺ is quickly separated from the ligands claw under the electrode field potential and has been deposited on the electrode surface. However, Cu(I)-complexes show somewhat different results because of the higher contribution of copper(I) to the HOMO and other occupied MOs [48].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 172833 for bis-[1-ethyl-2-(naphthyl-α-azo)imidazole]silver(I) perchlorate. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit @ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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