Acyclic mononuclear and macrocyclic dinuclear silver(I) complexes of Schiff base ligands derived from *N,N*-bis(2-aminoalkyl)-2-phenylethylamines

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Abstract

The synthesis and characterisation of acyclic mononuclear and macrocyclic dinuclear silver(I) complexes of ligands derived from the Schiff base condensation of *N,N*-bis(2-aminoalkyl)-2-phenylethylamines with 2,6-diacetylpyridine are reported and discussed. It is noted that changing the 2-aminoalkyl groups of the alkylamines from ethyl to n-propyl provides a change from an acyclic mononuclear silver(I) compound to a macrocyclic dinuclear silver(I) compound.

Introduction

Tetraimine Schiff base macrocycles are readily synthesised by the metal templated cyclocondensation of heterocyclic, or phenolic, dicarbonyl derivatives and 1,*n*-diaminoalkanes [1, 2]. If N-functionalised triamines, in which the central nitrogen atom bears a functionalised pendant arm, are used in the cyclocondensation reactions then N,N'-bibracchial macrocyclic complexes of the templating cation are prepared [3]. In these reactions it has been found that mononuclear complexes result from using barium as a template whereas dinuclear complexes are derived from the use of silver(I) as the template. Structural studies have shown that the macrocycles fold to present molecular clefts into which the metal ions coordinate. In this paper we report the contrast in reactivity arising from the use of *N,N*-bis (2-aminoalkyl)-2-phenylethylamines in Schiff base condensation reactions with 2,6-diacetylpyridine.

Experimental

IR spectra were recorded as KBr discs or liquid films between NaCl plates, using a Perkin–Elmer 297 IR spectrophotometer (4000–600 cm^{-1}) or a Perkin–Elmer 1710 IR Fourier transform spectrophotometer (4000–400 cm^{-1}). ^1H NMR spectra were recorded using Perkin–Elmer R34 (220 MHz) or Bruker AM-250 (250 MHz) spectrometers; ^{13}C NMR spectra were obtained on a Bruker AM-250 (62.9 MHz) instrument. Electron impact (EI) and chemical impact (CI, ammonia) mass spectra were recorded with a Kratos MS25 spectrometer; positive ion fast atom bombardment (FAB) mass spectra were recorded, using 3-nitrobenzylalcohol as the matrix solvent, on a Kratos MS80 spectrometer.

N-(p-Tolylsulfonyl)aziridine

This was prepared either from 2-aminoethanol by the procedures of Hope and Horncastle [4] and Bulkowski and co-workers [5], or from 2-chloroethylamine hydrochloride using the procedures described by Wagnon and Jackels [6].

N,N-Bis(N'-(p-tolylsulfonyl)-2-aminoethyl)-2-phenylethylamine

A solution of 2-phenylethylamine (0.5 mol) in acetonitrile (40 cm^3) was added dropwise to a solution of *N*-(*p*-tolylsulfonyl)aziridine (1 mol) in acetonitrile (100 cm^3). This was stirred at room temperature for three days. Cooling to 0 °C resulted in the precipitation of the analytically pure product as a white crystalline solid in 91% yield; m.p. 68 °C. IR (KBr disc): ν(NH) 3282, 3248 cm^{-1}, $\nu(SO_2)$ 1320, 1165 cm^{-1}. MS (EI): 516 a.m.u. (M^+). *Anal.* Found: C, 60.54; H, 6.57; N, 8.10; S, 12.42. Calc. for $C_{26}H_{33}N_3O_4S_2$: C, 60.56; H, 6.45; N, 8.15; S, 12.43%. ^1H NMR ($CDCl_3$) δ_H: 7.75 (4H, d), 7.27 (4H, d), 7.24 (3H, m), 7.01 (2H, d), 5.32 (2H, b), 2.85 (4H, m), 2.48 (8H, m), 2.37 (6H, s). ^{13}C NMR ($CDCl_3$) δ_C: 143.2, 139.9, 136.8, 129.6, 128.6, 128.4, 127.1, 126.1, 55.0, 53.0, 40.5, 32.9, 21.0.

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N,N-Bis(2-aminoethyl)-2-phenylethylamine (1)

This complex was prepared by detosylation of *N,N*-bis[*N'*-(*p*-tolylsulfonyl)-2-aminoethyl]-2-phenylethylamine using an adaptation of the general procedure of Ji *et al.* [7]. Yield = 43%; b.p. 106–148 °C (0.1 mm Hg). IR (NaCl plates): $\nu(NH_2)$ 3367, 3287 cm^{-1}. MS (CI): 208 a.m.u. (M^+). ^1H NMR ($CDCl_3$) δ_H: 7.18 (5H, m), 2.70 (4H, s), 2.68 (4H, t), 2.51 (4H, t), 1.30 (4H, b). ^{13}C NMR ($CDCl_3$) δ_C: 140.5, 128.5, 128.1, 57.1, 56.0, 39.7, 33.6.

N,N-Bis(2-cyanoethyl)-2-phenylethylamine

This was prepared from 2-phenylethylamine according to the method of Whitmore *et al.* [8] as modified in ref. 3. Yield = 66%; b.p. 198–214 °C (0.4 mm Hg). IR (NaCl plates): $\nu(CN)$ 2248 cm^{-1}. MS (CI): 228 a.m.u. (M^+). *Anal.* Found: C, 73.79; H, 7.59; N, 18.46. Calc. for $C_{14}H_{17}N_3$: C, 73.97; H, 7.54; N, 18.48%. ^1H NMR ($CDCl_3$) δ_H: 7.29 (5H, m), 2.88 (4H, t), 2.71 (4H, b), 2.32 (4H, t).

N,N-Bis(3-aminopropyl)-2-phenylethylamine (2)

This complex was prepared from *N,N*-bis(2-cyanoethyl)-2-phenylethylamine according to the method of Alcock *et al.* [9]. Yield = 30%; b.p. 148–162 °C (0.6 mm Hg). IR (NaCl plates): $\nu(NH_2)$ 3366, 3289 cm^{-1}. MS (CI): 236 a.m.u. (M^+). ^1H NMR ($CDCl_3$) δ_H: 7.26 (5H, m), 2.64 (8H, m), 2.48 (4H, t), 1.53 (4H, quin), 1.09 (4H, b).

Reaction of 1 with 2,6-diacetylpyridine in the presence of silver(I) ions

The experimental procedure followed was that described in ref. 3 for silver(I)-templated cyclisation reactions. Ag(**1**)ClO_4 (**4**) was recovered in 26% yield. IR (KBr disc): $\nu(NH_2)$ 3353, 3304 cm^{-1}, $\nu(C{=}O)$ 1700 cm^{-1}, $\nu(C{=}N)$ 1641 cm^{-1}. MS (+FAB): 459 a.m.u. $[Ag(\mathbf{1})]^+$. *Anal.* Found: C, 45.16; H, 5.09; N, 9.88; Cl, 6.28. Calc. for $AgC_{21}H_{28}N_4ClO_5$: C, 45.05; H, 5.04; N, 10.01; Cl, 6.33%. ^1H NMR (CD_3CN) δ_H: 8.24 (1H, d), 8.18 (1H, t), 8.05 (1H, d), 7.19 (2H, m), 6.83 (2H, m), 6.37 (1H, m), 3.44 (2H, m), 2.93 (2H, t), 2.75 (3H, s), 2.72 (8H, b), 2.32 (2H, t), 2.18 (2H, b). ^{13}C NMR (CD_3CN) δ_C: 197.9, 166.2, 152.8, 151.7, 141.9, 141.2, 129.3, 128.4, 127.5, 127.4, 126.4, 56.0, 54.1, 53.8, 48.3, 40.4, 34.1, 27.7, 16.8.

Silver(I)-templated [2+2] cyclisation reaction of 2 with 2,6-diacetylpyridine

This was carried out using the procedure described in ref. 3. $Ag_2(\mathbf{2})(ClO_4)_2 \cdot H_2O$ (**3**) was obtained in 16% yield. IR (KBr disc): $\nu(C{=}N)$ 1636 cm^{-1}. MS (+FAB): 1039 a.m.u. $[Ag_2(\mathbf{2})(ClO_4)]^+$. *Anal.* Found: C, 47.38; H, 5.31; N, 9.52; Cl, 6.06. Calc. for $Ag_2C_{46}H_{68}N_8Cl_2O_9$: C, 47.72; H, 5.40; N, 9.68; Cl, 6.12%. ^{13}C NMR (CD_3CN) δ_C: 155.5, 141.3, 139.8, 129.5, 129.4, 125.8, 125.7, 60.2, 56.9, 54.8, 37.0, 31.5, 17.7.

Results and discussion

Ligand synthesis

N,N-Bis(2-aminoethyl)-2-phenylethylamine (**1**) was prepared by reductive detosylation of *N,N*-bis(*N'*-tosyl-2-aminoethyl)-2-phenylethylamine with sodium naphthalenide in tetrahydrofuran [7]. The triamine was isolated, in moderate yield (*c.* 40%), as a viscous, hygroscopic oil which was purified by vacuum distillation in an inert atmosphere. The precursor *N,N*-bis(*N'*-tosyl-2-aminoethyl)-2-phenylethylamine was synthesised by stirring two equivalents of *N*-tosyl-aziridine with one equivalent of benzylamine in acetonitrile at room temperature. The product was isolated from the reaction mixture as a white crystalline solid in excellent yield (*c.* 90%).

A versatile procedure for the preparation of *N,N*-bis(3-aminopropyl)alkylamines is via the synthesis and subsequent reduction of *N,N*-bis(2-cyanoethyl)-alkylamines. *N,N*-Bis(2-cyanoethyl)-2-phenylethylamine was readily prepared by the acetic acid catalysed addition of two equivalents of acrylonitrile to benzylamine according to the method of Alcock *et al.* [9]. *N,N*-Bis(2-cyanoethyl)-2-phenylethylamine was then reduced in a straightforward and generally high yield procedure employing sodium metal dissolved in ethanol

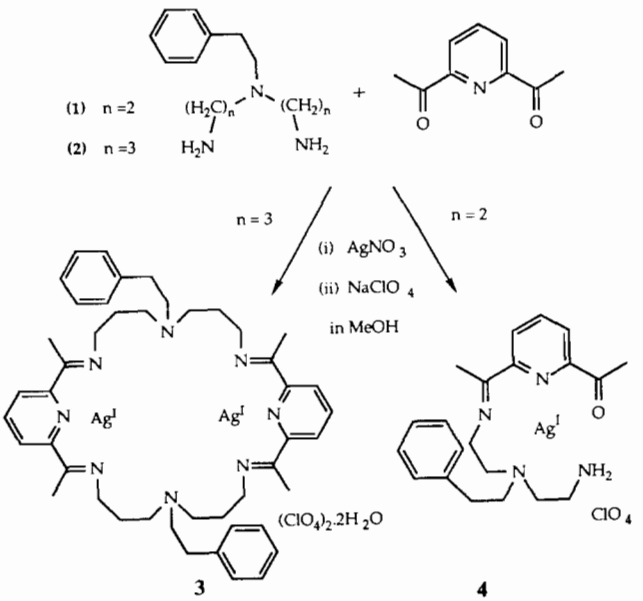
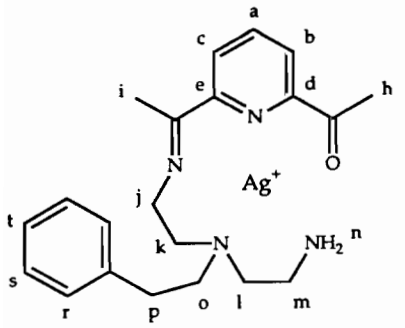


Fig. 1. The contrasting reactivities of *N,N*-bis(2-aminoethyl)-2-phenylethylamine (**1**) and *N,N*-bis(3-aminopropyl)-2-phenylethylamine (**2**) with 2,6-diacetylpyridine in the presence of silver(I) ions.

TABLE 1. ^{1}H NMR and ^{13}C NMR spectral assignments for **4** recorded at 250 MHz in CD_3CN



Hydrogen atom	δ_H	Coupling constants (Hz)	Carbon atom	δ_C	Carbon atom	δ_C
H_a	8.18, t, 1H		C_a	141.9	C_p	34.1
H_b	8.24, dd, 1H	^4J H_b–H_c = 1.5	C_d	152.8	C_q	141.3
H_c	8.05, dd, 1H		C_e	151.7	C_r	129.4
H_h	2.75, s, 3H		C_f	197.8	C_s	128.4
H_i	2.32, t, 2H	^5J H_i–H_j = 1.25	C_g	166.2	C_t	127.6
H_j	3.44, td, 2H	^4J H_j–H_k = 5.5	C_h	27.7	C_b	127.4
$H_{k,l,o,p}$	2.72, m, 8H		C_i	16.8	C_c	126.4
H_m	2.93, t, 2H	^3J H_m–H_l = 5	C_j	56.0		
H_n	2.18, b, 2H		C_k	54.1		
H_r	7.19, dd, 2H	^4J H_r–H_t = 1	C_l	53.8		
H_s	6.83, t, 2H	^3J H_r–H_s = 8.5	C_o	48.3		
H_t	6.37, tt, 1H	^3J H_s–H_t = 7.5	C_m	40.4		

to yield *N,N*-bis(3-aminopropyl)-2-phenylethylamine (**2**) as a viscous hygroscopic oil.

The nature of the ligands and their precursors was confirmed by MS, IR and NMR spectroscopies.

Silver(I)-templated [2+2] condensation reactions of 2,6-diacetylpyridine with the triamines 1 and 2

The synthesis of a number of dinuclear silver(I) complexes of [2+2] tetraimine Schiff base macrocycles has been achieved through the silver(I)-templated cyclocondensation of 2,6-diacetylpyridine with the appropriate functionally substituted triamine [3]. The macrocyclic complex $Ag_2(2)(ClO_4)_2$ (**3**) was prepared by application of this technique using the triamine **2**. The failure of reactions attempting to use lead(II), barium(II) or lanthanide(III) cations as templating agents demonstrated that the [2+2] cyclocondensation of the precursors is apparently specific to the use of silver(I). The IR spectrum of **3** showed no bands indicative of the presence of carbonyl or primary amine groups; instead a strong absorption was observed at 1635 cm^{-1} assigned to the stretching frequency of the imino C=N bond. Confirmation of the dinuclear [2+2] nature of the product was provided by positive ion FAB mass spectrometry which showed a substantial peak corresponding to the generation of $[Ag_2(2)(ClO_4)]^+$.

The ambient temperature ^1H NMR spectra of complex **3** run in CD_3CN at ambient temperature show the protons of the pyridine diimine head unit as a triplet and a doublet at δ_H 8.10 and 7.99, respectively, with the imino methyl resonance at δ_H 2.17. The phenyl protons from the pendant arms groups give well resolved peaks at 6.95 (4H, m) and 7.12 (6H, m) but the remaining aliphatic regions of the spectra consist of a series of broad unresolved signals, suggesting that the complex exhibits fluxional behaviour in solution. A reduction in the temperature to 233 K resulted in only a limited improvement in the resolution of the ^1H NMR spectra which was insufficient to allow unambiguous assignments to be made. The applicability of low temperature ^1H NMR studies was restricted however by the poor solubility of the complex in solvents other than acetonitrile. The fluxional behaviour of the complexes in solution is also reflected in the ^{13}C NMR spectrum.

The attempted cyclocondensation of **1** with 2,6-diacetylpyridine in the presence of silver(I) ions results in the isolation of the yellow crystalline species **4**. A comparison of the IR spectra of the two reaction products **3** and **4** revealed significant differences in the nature of the products. In addition to an absorption at the imino C=N stretching frequency of 1641 cm^{-1} the spectrum of **4** contained three intense peaks at 3353, 3304 and 1700 cm^{-1}. These are characteristic of

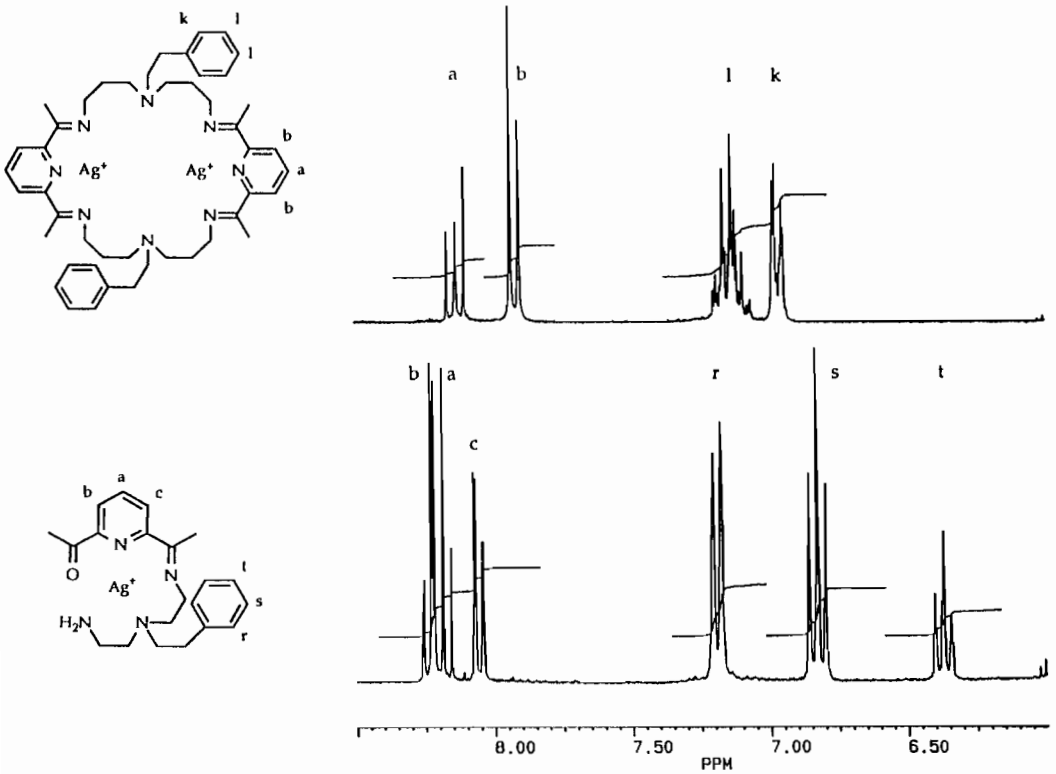


Fig. 2. Comparison of the aromatic regions of the ^{1}H NMR spectra of **3** and **4**.

primary amine and carbonyl groups indicating that in contrast to the above pathway a Schiff base complex had been formed from **1** without full ring closure to form a macrocycle. Positive ion FAB mass spectrometry identified the product **4** as the mononuclear silver(I) complex of the acyclic ligand formed from the condensation of one molecule of **1** and one molecule of 2,6-diacetylpyridine (Fig. 1). The mass spectral peak of 100% intensity at 459 a.m.u. corresponds to the cation generated by the loss of the perchlorate ion from the parent molecule. The reluctance to form a [2+2] macrocycle in this case may be related to the need for a donor atom presence in the pendant arm rather than to the available macrocyclic ring size as in silver(I)-templated reactions involving *N,N*-bis(2-aminoethyl)-2-aminomethylpyridine [3] and tris(2-aminoethyl)amine [10] dinuclear complexes of the corresponding [2+2] macrocycles have been formed.

The proposed characterisation of **4** is supported by elemental analysis, and by the ^{1}H and ^{13}C NMR spectroscopic data (Table 1). It is worthwhile to compare the aromatic regions of the ^{1}H NMR spectra of the mononuclear acyclic complex **4** with the dinuclear macrocyclic counterpart **3** (Fig. 2). The differences in the pyridyl signals are in accordance with those anticipated, reflecting the lower symmetry of the pyridine ring in **4**. The contrast between the phenyl signals of the two complexes is more unexpected. The aromatic pendant arm hydrogen atoms of the macrocyclic complex **3** give rise to a pattern typical of a mono-substituted benzene. The signals of the corresponding protons in the acyclic complex **4** however are dispersed by a range of over 1 ppm and are clearly resolved according to their position on the phenyl ring.

The physical origin of these spectral changes in **4**, as compared to **3**, may arise from the phenyl group interacting with another part of the molecule. Examination of molecular models appears to disfavour the possibility that stacking is occurring with the conjugated pyridine system. An alternative proposal is that the phenyl ring is participating in a π-interaction with the silver(I) ion; the general occurrence of this interaction is well documented [11], however a ^{1}H NMR nuclear Overhauser enhancement experiment directed at identifying proximal hydrogen atoms was inconclusive. The complex was frustratingly reluctant to form crystals suitable for X-ray studies and so any suggestion concerning the exact structure of **4** must remain speculative.

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