

Isolation of bis(1,4-diphenyl-1,4-bis(2-pyridyl)-2,3-diaza-1,3-butadiene)disilver with bridging (N-N) dinucleating subunits: formation of a 6-membered chelate ring

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A novel Ag(I) dinuclear complex $\{[(C_6H_5)(C_5H_4N)-C=N-N=C-(C_5H_4N)(C_6H_5)]Ag\}_2 \cdot ClO_4 (ClO_4)$ ($1/2CH_3CN$) (**1**) that was derived under mild conditions, during the course of combination of $AgClO_4$ with a polymorphic azine ligand, 1,4-diphenyl-1,4-bis(2-pyridyl)-2,3-diaza-1,3-butadiene (L) (condensed product of phenyl 2-pyridyl ketone and hydrazine monohydrate) is reported. The aforementioned complex is based on a central rotationally flexible diazine subunit (N-N). The azine ligand, L, having the N_2 dinucleating fragment, provides a coordination focus for pairs of metal centres and ultimately leads to the formation of a 6-membered chelate ring in **1**.

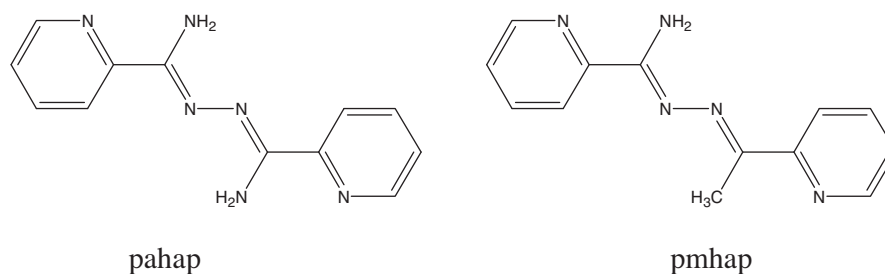
Introduction

Self-assembly reactions are a key strategic tool for the synthesis of specific ligand design strategies, based on the concept of positioned coordination pockets.¹ The use of a single ligand with a repeating array of coordination pockets arranged in a linear fashion has the potential to create a grid-like arrangement of metal centres, and some success has been achieved with linear polytopic ligands of this sort based on pyridazine and pyrimidine as a bridging subunit.^{2,3}

In this regard, N_2 diazine bridging ligands, e.g., pyrazoles, triazoles, pyradazines, and phthalazines, bring 2 metal centres into close proximity.^{4–10} The N-N group has varying degrees of double bond character in these ligands, which is reflected in the extent of exchange coupling, but is rigidly fixed within the 5- or 6-membered diazine ring. The ligands PAHAP (picolinamide azine)¹¹ and PMHAP¹² (Scheme 1), which are derived from

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hydrazine and contain a single N-N bond, present several possible mononucleating and dinucleating coordination modes and also the potential for free rotation about the N-N bond.



Scheme 1

Compared with the diazine moiety in heterocyclic ring systems the N_2 diazine linkages in open-chain systems with N-N single bonds are much more flexible.^{13–15} In combination with other donors, previous studies^{12,16} showed that a series of novel open-chain diazine ligands coordinated to 2 metal centres as N_4 or N_5 donors with a variety of geometrical arrangements, which depends on co-ligands and reaction conditions. These flexible geometrical arrangements result from the ability of the systems to rotate freely about the single N-N bond of the diazine fragment. A planar $Cu(II)_4$ cluster with a tetradentate diazine (N_2) ligand¹⁷ and tetrahedral $Cu(II)_4$ clusters with tetradentate triazolate¹⁸ and pyrazolate¹⁹ ligands with (N_2) bridges are also formed by self-assembly processes. The conditions for the synthesis, which are generally simple, and the possibility to obtain symmetrical or asymmetrical azines, derived from the condensation of an aldehyde or ketone with hydrazine, by using 2 identical or different carbonyl compounds, make them useful in different applied fields. Some examples of macrocyclic bis(azines)²⁰ and ferroelectric liquid crystals containing *ortho*-palladated azines²¹ were also reported. Moreover, the coordination chemistry of azines has produced many different monometallic^{22,23} and homo-²⁴ or hetero-bimetallic²⁵ complexes. In this connection, perusing their studies on the reactivity of hydrazones²⁶ and azines,²⁷ Amadei et al. reported 2 polymorphic forms of phenyl 2-pyridyl ketone azine.²⁸ The behaviour of this ligand was investigated on zinc and copper salts.

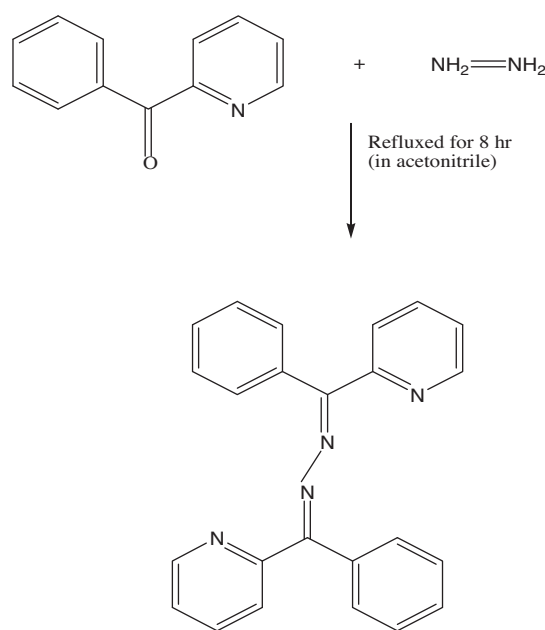
In the current contribution, we report a novel $Ag(I)$ dinuclear complex $\{[(C_6H_5)(C_5H_4N)-C=N-N=C-(C_5H_4N)(C_6H_5)]Ag\}_2 \cdot ClO_4(ClO_4)(1/2CH_3CN)$ (**1**) using the polymorphic ligand 1,4-diphenyl-1,4-bis(2-pyridyl)-2,3-diaza-1,3-butadiene $[(C_6H_5)(C_5H_4N)-C=N-N=C-(C_5H_4N)(C_6H_5)]$ (L) (condensed product of phenyl 2-pyridyl ketone and hydrazine monohydrate) (Scheme 2) with the combination of $AgClO_4$. The above aforementioned complex participates in an excellent metal-organic framework, based on a rotationally flexible N-N bridging unit.

Experimental

Materials

Phenyl 2-pyridyl ketone, hydrazine monohydrate (Across), and silver perchlorate (Janssen) were of reagent grade and used without further purification.

Caution! Although no problems were encountered in this work, perchlorate salts are potentially explosive. They should be prepared in small quantities and handled with care.



Scheme 2

Physical techniques

Infrared spectra were recorded on a PerkinElmer 883 infrared spectrophotometer from 4000 to 200 cm^{-1} as KBr discs. C, H, and N analyses were carried out on a PerkinElmer 2400 II elemental analyser.

X-ray crystallography

A shiny yellow crystal of **1** ($0.20 \times 0.08 \times 0.08 \text{ mm}^3$) was selected for the structural analysis. The intensity data of **1** were collected on a Kappa CCD diffractometer at 150(2). A total of 30,930 reflections of **1** were measured $-21 \leq h \leq 21$, $-9 \leq k \leq 20$, $-24 \leq l \leq 26$, yielding 11347 independent reflections. All data were collected with the ω scan technique using graphite monochromated *Mo-K α* radiation ($\lambda = 0.71073 \text{ \AA}$). All the structures are solved by direct methods using the SHELX-97²⁹ computer program and refined by full-matrix least-squares methods on F^2 using SHELXL-93³⁰. Neutral scattering factors were taken from Cromer and Mann³¹ and for the hydrogen atoms from Stewart et al.³² The non-hydrogen atoms were considered with a riding model under the restriction of ideal symmetry at the corresponding carbon atoms. The unit cell parameters, along with data collection and refinement details, are tabulated in Table 1.

Preparation of the ligand L (1,4-diphenyl-1,4-bis(2-pyridyl)-2,3-diaza-1,3-butadiene)

Phenyl 2-pyridyl ketone (0.366 g, 2 mmol) was added to a 40 mL acetonitrile solution of hydrazine monohydrate (0.050 g, 1 mmol) and refluxed for 10 h. A yellow solid formed, which was separated through evaporation, washed with acetone, and dried under vacuum. Yield: 70%. *Anal. Calc.* for $\text{C}_{24}\text{H}_{18}\text{N}_4$: C, 79.55; H, 5.01; N, 15.46. Found: C, 79.71; H, 5.13; N, 15.30%.

Table 1. Crystallographic data for **1**.

Empirical formula	C ₄₉ H _{37.50} N _{8.50} Cl ₂ O ₈ Ag ₂
Formula weight	1160.02
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>
<i>Z</i>	4
<i>T</i> (K)	150 (2)
<i>a</i> (Å)	16.8867(14)
<i>b</i> (Å)	15.4146(13)
<i>c</i> (Å)	20.5339(17)
α (°)	90
β (°)	110.879(2)
γ (°)	90
<i>V</i> (Å ³)	4994.0(7)
<i>D</i> _{calc} (Mg/m ³)	1.543
No. of reflections collected	30930
No. of independent reflections	11347
<i>R</i> _{int}	0.0584
Absorption coefficient (mm ⁻¹)	0.952
θ for data collection (°)	1.29-27.51
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1185, 0.1832
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0543, 0.1624
Largest diff. peak and hole (e.Å ⁻³)	1.752 and -0.456

Synthesis of $\{[(C_6H_5)(C_5H_4N)-C=N-N=C-(C_5H_4N)(C_6H_5)]Ag\}_2 \cdot ClO_4 (ClO_4) (1/2CH_3CN)$ (1**)**

To the ligand (**L**) (0.362 g, 1 mmol), a 10 mL aqueous solution of silver perchlorate (0.207 g, 1 mmol) was added slowly and the mixture was heated with constant stirring for 30 min. forming a yellow solution. Then it was filtered and kept at room temperature without disturbing the solvent. After 1 week, shiny yellow crystals of **1** suitable for X-ray crystallography were obtained from the slow evaporation of the solvent (Yield: 65%). *Anal.* Calc. for C₄₉H_{37.50}N_{8.50}Cl₂O₈Ag₂: C, 50.68; H, 3.25; N, 10.25. Found: C, 50.81; H, 3.28; N, 10.07%.

Results and discussion**Crystal structure**

Shiny yellow crystals of **1** suitable for X-ray analysis were obtained from a deep yellowish powder, being left to stand in acetonitrile solution. The Figure shows a perspective view of **1** and the relevant interatomic distances and angles are summarised in Table 2. A single crystal X-ray diffraction study shows that the ligand undergoes *E/Z* conformation with the rotation regarding the N-N bond. Although the ligand is conjugated, it

is not planar. Both the Ag(1) and Ag(2) atom are surrounded by 1 pyridinyl N and 1 azine N atom from each unit of the 1,4-diphenyl-1,4-bis(2-pyridyl)-2,3-diaza-1,3-butadiene ligand (L) on the top and bottom face. Thus participation of 2 azine ligands, each having the N₂ dinucleating fragment, provide a coordination focus for pairs on 4-coordinate metal centres in axial positions, in a ‘chair’ fashion and ultimately lead to the formation of a central 6-membered chelate ring. Again, 2 pairs of structurally symmetrical 5-membered chelate rings formed including Ag(1) and Ag(2) atoms with both pyridinyl ring and azine C, N atoms, causing an overall distortion to the molecule. From another point of view, considering the bond distances of the Ag(1) atom with pyridinyl-N atoms [Ag(1)-N(1) and Ag(1)-N(5), 2.206(5), and 2.195(5) Å, respectively], the Ag1-N (azine) bond distances are much longer [Ag(1)-N(2) and Ag(1)-N(6), 2.428(5), and 2.535(5) Å, respectively], making some possible strain associated with the twisted arrangement. A very similar strain is also observed comparing the bond distances of Ag2-N (pyridinyl) [Ag(2)-N(4) and Ag(2)-N(8), 2.258(5), and 2.245(5) Å, respectively] and Ag2-N (azine) [Ag(2)-N(3) and Ag(2)-N(7), 2.488(5), and 2.545(5) Å, respectively], closely related with the former. This may be also illustrated by a long Ag(1)-Ag(2) distance of 4.898 Å, and quite large torsional angles Ag(1)-N(6)-N(7)-Ag(2) 71.10°, Ag(1)-N(6)-N(7)-Ag(2) 84.17°, around the N-N bridges. There is a stacking interaction, consisting of the torsions of 74.9 and 62.43r, between the 2 pyridinyl planes each of the same ligand. The torsional angles of 2 diazine (N-N) subunits are 150.73 and 155.93°, respectively; considering the top and bottom face ligand. The geometry of the nitrogen donor atoms can be described as distorted square planar. Both Ag(1) and Ag(2) atoms are highly above the least-squares planes through their coordinating nitrogen atoms.

Table 2. Selected bond distances (Å) and bond angles (°) for **1**.

Ag(1)-N(1)	2.206(5)	Ag(1)-N(5)	2.195(5)	Ag(1)-N(2)	2.428(5)
Ag1-N6	2.535(5)	Ag2-N4	2.258(5)	Ag2-N8	2.245(5)
Ag2-N3	2.488(5)	Ag2-N7	2.545(5)		
N1-Ag1-N5	164.78(18)	N1-Ag1-N2	70.42(17)	N5-Ag1-N6	69.43(17)
N4-Ag2-N8	166.74(18)	N4-Ag2-N3	68.89(18)	N8-Ag2-N7	69.20(17)
N2-Ag1-N6	82.86(16)	N7-Ag2-N3	84.64(16)	Ag1-N2-N3	124.8(4)
Ag1-N6-N7	125.8(4)	Ag2-N7-N6	122.6(4)	Ag2-N3-N2	120.0(4)

IR spectrum

The IR spectrum of complex **1** is consistent with the structural data represented in this paper. The absorption bands at 1635 cm⁻¹ for **1** arise due to the [ν (C=N)] stretching frequency.³³ The pyridine ring breathing mode is observed at 1019 and 1015 cm⁻¹. The characteristic bands at 794, 763, and 693 cm⁻¹ for **1** is attributed to the ring motions. The bands at 1080 and 625 cm⁻¹ are assigned to ν (ClO₄).

Supplementary data

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with deposition number 289959. Copies of the information may be obtained free of charge from The Director, CCDC,

12 Union Road, Cambridge, CB2 1EZ, UK. (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

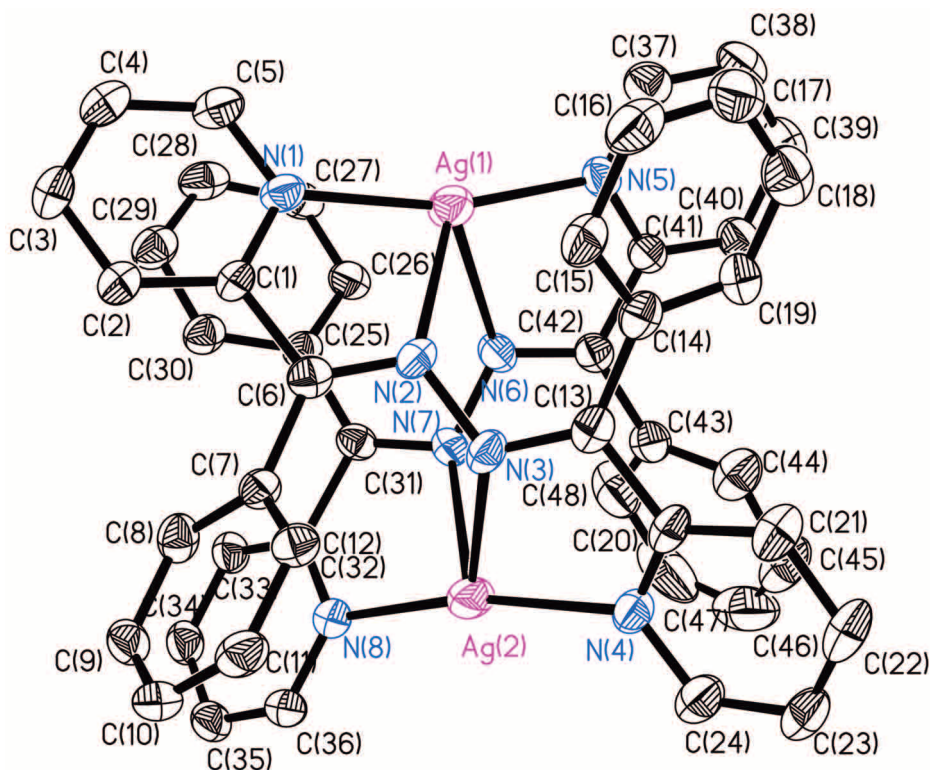


Figure. ORTEP diagram of the unit cell of complex **1** with atom numbering scheme (thermal ellipsoids are drawn at 40% probability level). The H atoms are omitted for clarity.

Acknowledgements

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