Alkyne-containing chelating ligands: synthesis, properties and metal coordination of 1,2-di(quinolin-8-yl)ethyne[†]

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Received 20th March 2006, Accepted 29th March 2006 First published as an Advance Article on the web 6th April 2006 DOI: 10.1039/b603983a

A new alkyne-containing chelating ligand, 1,2-di(quinolin-8yl)ethyne, is shown to form a mononuclear 1 : 1 complex with silver(I) and chelate the metal ion through both nitrogens and the ethyne moiety as seen by UV and NMR spectroscopy as well as X-ray crystallography.

The coordination of alkynes with soft metal ions, particularly Ag(1) and Cu(1), has attracted considerable interest over the years.^{1,2} Early explorations aimed at evaluating the potential role of such coordination complexes in metal-catalyzed organic transformations. As Ag(1) and Cu(1) ions tend to form oligomeric species, ligands have been developed to facilitate the formation of mononuclear complexes.¹ Several successful ligand systems have been reported to preferentially form monomeric η^2 -coordinated alkynes, including bis(alkynyl)titanocenes³ and other organometallic acetylides,^{1,2,4} as well as cyclic,¹ macrocyclic⁵ and caged alkynes.⁶ Surprisingly, simple alkyne-containing chelators are scarce. Here we report the synthesis, properties and coordination of a chelating alkyne-containing ligand, 1,2-di(quinolin-8-yl)ethyne **3**, capable of forming a stable mononuclear Ag(1) complex **6**.

In designing an alkyne-containing chelating ligand we took advantage of the favorable coordination features of 8-substituted quinolines noting that placing an alkyne moiety at the 8-position can, in principle, facilitate the formation of a stable chelate. To favor intramolecular complexation and secure favorable chelation, a symmetrical bis-quinoline **3** was then contemplated. Simple geometrical considerations of the N–N distance in the alkynebridged bisquinoline (approximately 4.1 Å) and comparison to typical distances found in the Cambridge Data Base for Ag(1)– N bond lengths (*ca.* 2.1–2.5 Å)^{7–10} and Ag(1)–alkyne distances (2.16–2.91 Å)¹¹ suggest that ligand **3** can supply three out of four coordination sites for a distorted square planar cavity accommodating a Ag(1) ion.

The synthesis of 1,2-di(quinolin-8-yl)ethyne **3** is shown in Scheme 1. 8-Hydroxyquinoline **1** is converted in quantitative yields to the corresponding triflate **2**. A one-pot symmetric Sonogashira cross-coupling reaction¹² between **2** and trimethylsilylacetylene produces the desired ligand **3** in 43% yield. Alternatively, a stepwise pathway¹³ can be employed where **2** is first coupled to trimethylsilylacetylene in 52% yield. Quantitative deprotection of the trimethylsilyl protecting group and a standard Sonogashira cross coupling reaction with 8-bromoquinoline generates **3** in 25%



Scheme 1 Reagents and conditions: i) trifluoromethanesulfonyl anhydride, pyridine 99%; ii) **2**, trimethylsilylacetylene, CuI, (PPh₃)₄Pd, DBU, deionized water, acetonitrile 43%; iii) trimethylsilyl acetylene, (PPh₃)₄Pd, CuI, piperidine 52%; iv) sodium hydroxide, methanol 99%; v) **2**, (PPh₃)₄Pd, CuI, piperidine 25%; vi) **3**, silver perchlorate, chloroform/acetonitrile, 99%.

yield. These straightforward synthetic approaches facilitate the rapid preparation of large quantities of $3.\dagger$

The absorption spectrum of ligand 3 in THF shows an intense transition around 240 nm, in addition to weaker fine-structured absorption bands above 300 nm (Fig. 1a). The ligand is highly emissive ($\phi = 0.85$ in THF), with intense emission bands at 375 and 392 nm.† Examination of the photophysical properties in various solvent shows the ground state absorption spectra of 3 are unaffected by changes in solvent polarity while the emission spectra are greatly affected by the microenvironment (Fig. 2). While in nonpolar aprotic solvents (e.g., dichloromethane, ethyl acetate and tetrahydrofuran), the emission of 3 is intense and shows defined structure, in polar protic environments (water and methanol), the emission spectra of **3** are red shifted and partially quenched ($\phi =$ 0.23 in water).[†] This behavior typically occurs in chromophores that possess enlarged dipoles and charge-transfer character in their excited states. It is worth noting that these photophysical features greatly facilitate the examination of the binding characteristics of the ligand in solution, as illustrated below.

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dures, 2D NMR spectra, NMR metal titration spectra, absorption and fluorescence spectra, quantum yield and crystal lattice plots. See DOI: 10.1039/b603983a



Fig. 1 UV-Vis Titration of **3** (20 μ M in THF) with increasing equivalents of AgClO₄; a) 0.0 (black), 0.2 (red), 0.4 (green), 0.6 (dark blue), 0.8 (light blue), 1.0 (orange), 1.2 (purple), 1.4 (yellow); b) 224 nm (black circle), 240 nm (blue square), 275 nm (green diamond), 346 nm (red triangle), 364 nm (light blue triangle).

The binding of silver ions to **3** was initially monitored in tetrahydrofuran solution by absorption spectroscopy. As seen in Fig. 1a, addition of silver perchlorate to a 20 μ M solution of **3** results in a bathochromic shift of all major absorption bands. Concomitant hyper- and hypochromic effects result in the appearance of three major isosbestic points. Plotting the changes for all absorption maxima between 220–400 nm as function of Ag⁺ concentration (Fig. 1b) reveals saturation of **3** at one equivalent of the metal ion. ¹H NMR titration of **3** with silver perchlorate reveals similar behavior (Fig. 3). The well-resolved and fully assigned proton signals of **3** undergo a downfield shift upon addition of Ag⁺. Saturation occurs at approximately 1 equivalent of Ag(1)



Fig. 2 Relationship between emission energy and microenvironment polarity ($E_{\rm T}(30)$): water (circle), methanol (square), dichloromethane (diamond), ethyl acetate (up triangle) and tetrahydrofuran (down triangle).



Fig. 3 NMR Titration of 3 (3 mM) with AgClO₄ (400 MHz, CD₃CN).

suggesting the formation of a $3-Ag^+$ complex (Scheme 1). Note that at the onset of the NMR titration (up to *ca.* 0.5 eq. Ag⁺), protons 2 and 3 experience a minor upfield shift, but end up with

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lower field signals at the end point. We suggest that a 2 : 1 complex 3_2 -Ag⁺ is initially formed at the higher ligand concentrations used for the NMR experiment. As additional Ag⁺ is added, this complex dissociates into the 1 : 1 3-Ag⁺ complex 6 observed at low overall concentrations using absorption spectroscopy.

Addition of 1 equivalent of silver perchlorate in acetonitrile to a solution of **3** in chloroform results in the formation of a white precipitate (Scheme 1). ¹H NMR spectra of the free ligand and the isolated complex in both acetonitrile and DMSO[†] reveal comparable patterns and chemical shifts changes to the ones observed in the titration experiments described above, supporting the coordination of a single Ag⁺ ion to ligand **3**. ¹³C NMR spectroscopy shows a small upfield shift of the alkyne carbons upon metal coordination ($\Delta \delta = 1.5$ ppm), in agreement with previous observations of Ag⁺-coordinated alkynes.¹⁴⁻¹⁶

Large single crystals of the complex 6, suitable for X-ray crystallography, were obtained by slowly diffusing isopropyl ether into a solution of the complex in acetonitrile. As seen in the solved structure (Fig. 4),‡ the metal ion is coordinated in a distorted square planar fashion to the alkyne, the quinolyl nitrogens and a single acetonitrile molecule. The coplanarity of the two coordinating rings is evident by the small dihedral angle (1°) between the aromatic moieties. Of interest is the distance between the silver(I) ion and the alkyne moiety (2.73 Å Ag–C11/C10). While somewhat long, this distance falls within the range seen in related Ag-ethyne interactions (2.16-2.91 Å).¹¹ To accommodate the silver cation, the cavity of 3 opens up slightly as evident by the difference in distances between the two bridging aromatic carbons (4.06 Å C12-C9) and the coordinating nitrogen atoms (4.46 Å N1–N2), as well as by the cavity side angles (94.18° N2–C12–C9 and 95.26° N1-C9-C12). The opening of 3 pushes N1 and N2 away from the silver cation and brings the alkyne closer to the coordinated ion.17,18



Fig. 4 Thermal ellipsoid plot (50% probability) of $[Ag(3)(CH_3CN)]$ -(ClO₄). Perchlorate anions and hydrogen atoms were removed for clarity.

Ligand 3 represents a prototypical structure of a family of accessible alkyne-containing chelating ligands. The favorable

photophysical properties of such conjugated heterocycles and the effective coordination observed for this ligand are likely to inspire the preparation and study of related systems.

We thank the National Institutes of Health (GM 069773) and National Science Foundation (CHE 0213323) for support.

Notes and references

[‡] *Crystallographic data.* **3**: C₂₀H₁₂N₂ (280.32), monoclinic, space group C2/*c*, *a* = 15.582(5) Å, *b* = 8.095(3) Å, *c* = 12.481(4) Å, *a* = 90°, *β* = 117.326(4)°, *γ* = 90°, *V* = 1398.2(8) Å³, *Z* = 4, *μ* = 0.079 mm⁻¹, *D* = 1.332 g cm⁻³, *T* = 208(2) K, *F*(000) = 584. 4647 reflections (1639 independent), *R*(int) = 0.0295, final *R* indices [*I* > 2*σ*(*I*)] are *R*1 = 0.0449, *wR*2 = 0.1236, *R* indices (all data) *R*1 = 0.0551, *wR*2 = 0.1321. **6**: C₂₂H₁₅AgClN₃O₄ (528.69), monoclinic, space group *P*2(1)/*c*, *a* = 6.8416(17) Å, *b* = 23.779(6) Å, *c* = 12.724(4) Å, *a* = 90°, *β* = 105.290(4)°, *γ* = 90°, *V* = 1996.7(9) Å³, *Z* = 4, *μ* = 1.180 mm⁻¹, *D* = 1.759 g cm⁻³, *T* = 213(2) K, *F*(000) = 1056. 12985 reflections (3925 independent), *R*(int) = 0.0394, final *R* indices [*I* > 2*σ*(*I*)] are *R*1 = 0.0606, *wR*2 = 0.1441, *R* indices (all data) *R*1 = 0.0725, *wR*2 = 0.1492. CCDC reference numbers 600754 and 600755. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603983a

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- 17 The packing of each complex in the crystal lattice shows an intriguing pattern, governed by π stacking between the aromatic ligands (see ESI[†]).
- 18 The external angle created by C9–C10–C11 and C12–C11–C10 decreases from 179.2° in the free ligand 3, to 176.9° in the silver complex 6, pushing the alkyne toward the coordinated ion.