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Heteroleptic Zinc Dipyrromethene Complexes

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Abstract

^{1}H NMR spectroscopy has been used to study the complexation of a per-alkyl dipyrromethene with zinc acetate. An intermediate, assigned to be the heteroleptic Zn(dipyrromethene)(acetate) complex, is observed under titration conditions although only zinc(dipyrromethene)$_2$ is obtained after simple work-up. This indicates that disproportionation occurs during work-up and that dipyrromethene complexation does not occur under self-assembled control.

Introduction

Dipyrromethenes (dipyrrins) generate fully conjugated, flat monoanionic ligands that coordinate to metal ions to form stable mononuclear complexes[1-7] with a variety of interesting architectures including discrete helicates[8-15] and coordination polymers.[16-20] Bis(dipyrromethene)s, consisting of two dipyrromethene units joined through a linker, form either dinuclear double-helicates or mononuclear helicates, depending upon the length and conformational preferences of the linker and the coordination geometry preferences of the metal ion.[11] As part of our ongoing studies,[21] we needed a method with which to easily assess the coordination efficiencies of dipyrromethenes and bis(dipyrromethene)s. Ideally, we required a method that would be facile, and quick, to conduct on a range of dipyrromethene-containing ligands with various substituents on the pyrrolic sub-units. After considering some literature work that used absorption spectroscopy to assess dipyrromethene complexation, and conducting similar work ourselves, we began to use ^{1}H NMR spectroscopy to investigate the zinc(II) complexation reactions of hydrobromide salts of dipyrromethenes and herein report our observations in this area.

Results and Discussion

For dipyrromethene free-bases to be isolable, and stable, *meso*-substitution with aryl groups is often required. In our work, the *meso*-position of dipyrromethenes is usually unsubstituted and so the ligands are isolated as salts, e.g. 4,4'-diethyl-3,3′,5,5′-tetramethyldipyrromethene hydrobromide (**1**), whereby they are indefinitely stable.[22] From the hydrobromide salt, formation of the homoleptic dipyrromethene complex (**4**) formally involves the *in-situ* formation of the corresponding free-base (**2**), followed by deprotonation and complexation (Scheme 1). Each dipyrromethene unit is bidentate and presumably a number of intermediate mono-coordinated species in various protonation states[23] are incurred along the course of the reaction pathway, including the heteroleptic complex (**3**). The complexity of the reaction mixture is undoubtedly exacerbated for reactions involving bis(dipyrromethene)s where each ligand presents four coordinating sites.

Scheme 1. Formation of a dipyrromethene complex with M(OAc)$_2$.
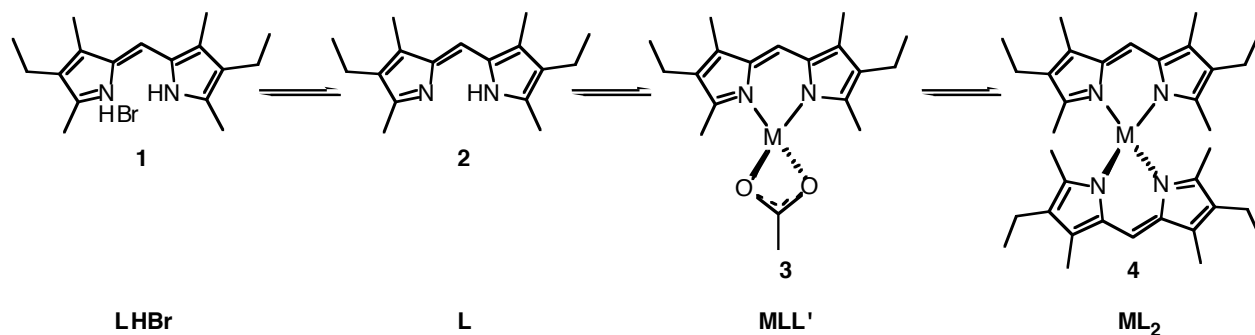
The stability of dipyrromethene-containing heteroleptic complexes[24] is dependent upon the nature of the ancillary ligand, the strength of the metal-nitrogen bond and the nature of the dipyrromethene *meso*-substituent.[16, 19] For example, Cohen has recently reported that heteroleptic complexes incorporating dipyrromethene ligands *meso*-substituted with aryl groups can be formed when sub-stoichiometric quantities of copper(II) hexafluoroacetylacetonate (hfacac) and acetylacetonate (acac) salts are used in the complexation reaction.[16, 19] The heteroleptic copper dipyrromethene/hfacac complexes are stable but the corresponding acac

complexes decompose, giving the homoleptic dipyrromethene complexes, when exposed to basic alumina.

Dipyrromethene ligands and their complexes are multifaceted chromophoric systems[25] with broad absorption profiles.[22, 23] As such, absorption spectroscopy is generally cumbersome for the study of dipyrromethene complexation reactions since the spectra of reaction mixtures are complicated, and there are many overlapping signals. Additionally, the absorption spectra of dipyrromethenes are highly dependant upon the pH of the solution, tentatively attributed by others to protonation-deprotonation equilibria and resultant conformational changes.[25, 26] Titrations involving the addition of metal salts or complexes to dipyrromethene ligands inevitably result in such pH changes, further complicating the visible spectra.

Using a combination of spectroscopic and calorimetric methods Guseva *et al*. have recently reported on the thermodynamics of dipyrromethene deprotonation and complexation as part of their work towards understanding the metal-template effect in the synthesis of porphyrins.[25, 27-29] The data that Guseva uses to calculate equilibrium constants for dipyrromethene complexation with Zn(II), Ni(II), Co(II), Cu(II) and Hg(II) is extracted from the absorption maxima attributed solely to ligand and homoleptic complexes in titrations and does not take into account any intermediates, e.g. heteroleptic complexes, that may be incurred along the reaction pathway. Heteroleptic complexes possess features of both the uncoordinated and coordinated dipyrromethene chromophore and so exhibit absorption characteristics that overlap with those of ligand and homoleptic complex. Consequently, the presence of these intermediates would interfere with data extracted for ligand and homoleptic complexes at their distinct absorption maxima.

Our titration of **1** with zinc acetate, using absorption spectroscopy to monitor the process, is shown in Figure 1(a). The titration involved the addition of 10 μL aliquots of 5.92×10^{-4} M

zinc acetate dihydrate in methanol to 2 mL of 2.96×10^{-5} M solution of **1** in 1:1 MeOH:CHCl$_3$ with each addition representing 0.1 equivalents of the metal salt with respect to the ligand. Addition of metal ions resulted in a decrease in the λ_{max} at 484 nm for the ligand and a general increase in λ_{max} at 503 nm, as expected, with no isosbectic point. The addition of zinc acetate solution was continued until no further change in absorbance was observed (2.2 eq. of zinc acetate added) and further additions only served to reduce the absorbance at 503 nm as a result of dilution. Figure 1(b) shows plots of pure ligand **1**, pure complex **4** and the final titration point at 2.2 eq. zinc acetate all plotted at 0.026 mM in dipyrromethene chromophore. Species other than the pure complex is/are present in the titration experiment and it is essential that these be accounted for in any thermodynamic rationale.

Figure 1. (a) Absorption spectra for titration of dipyrromethene 1 with zinc acetate (each plot is recorded after the addition of 0.1 eq. of metal salt, and the inset reveals the absence of a isosbectic point); (b) Absorption spectra for ligand 1, complex 4 and a single plot from the titration experiment (2.2 eq. $Zn(OAc)_2$), all at 0.026 mM in dipyrromethene chromophore.

(a)
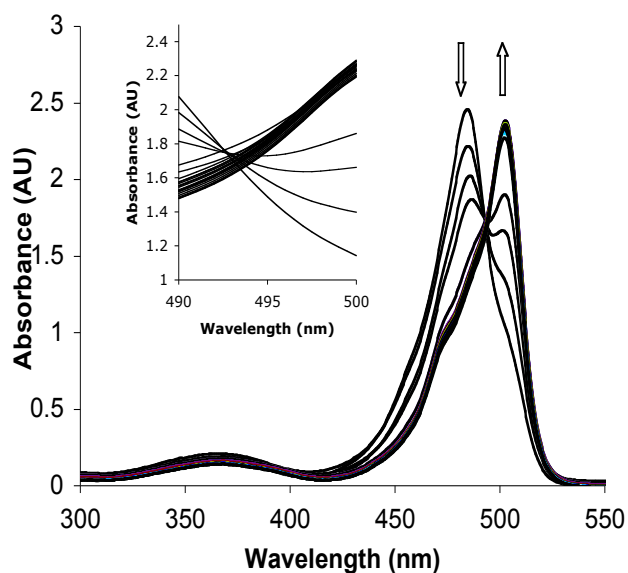
(b)
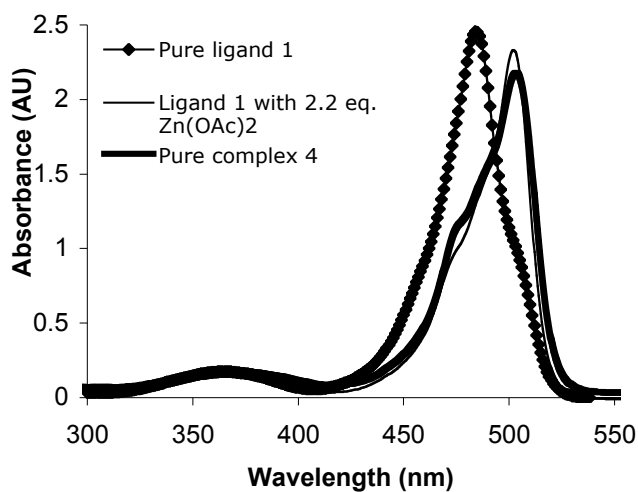
We then performed another titration experiment with dipyrromethene hydrobromide **1** and zinc acetate dihydrate, this time using ^{1}H NMR spectroscopy to monitor the process. The ^{1}H NMR C*H* signal at the *meso*-position of the dipyrromethene was used to follow the progress of the complexation. In the hydrobromide salt **1**, the signal corresponding to this C*H* has a chemical shift of 7.25 ppm, compared to 6.99 ppm in the homoleptic complex **4**. To an NMR tube containing 800 μL of 5.0×10^{-3} M **1** in 1:1 $CD_3OD:CDCl_3$ were added 8 μL aliquots of 0.106 M $Zn(OAc)_2.2H_2O$ in CD_3OD, with each addition representing approximately 0.2 equivalents of the metal salt with respect to the ligand. The samples were shaken and then immediately analyzed using ^{1}H NMR spectroscopy. In our initial experiments, spectra recorded after 24 hours were identical to those obtained immediately following the addition of zinc acetate and shaking.

With increasing presence of zinc acetate the signal due to the hydrobromide salt **1** decreased and that due to the complex **4** increased (Figure 2). Concurrently a previously unobserved signal at 6.89 ppm, attributable to neither **1** nor **4**, was also observed upon the addition of zinc acetate. The spectra maintained a 1:4 ratio of ML_2:MLL' after the addition of 1.2 equivalents of the metal salt, suggesting an equilibrium between these species that is unaffected by the presence of excess metal salt. The addition of pyridine to a $CDCl_3$ solution of **1** resulted in no change to the spectral signals corresponding to **1**, indicating that the newly-observed signal did not correspond to dipyrromethene free-base. We tentatively assigned the new signal to the heteroleptic complex **3**. This is supported by electrospray mass spectrometry, whereby a peak at *m/z* 378.2, corresponding to the molecular mass of **3** (^{64}Zn), was observed in the reaction mixture along with the appropriate isotope pattern. Even after the addition of eight equivalents of metal, we were unable to convert all of the ligand to **4**, as seen by NMR spectroscopy and confirmed by TLC.

Figure 2. Stacked ^{1}H NMR spectra for titration of dipyrromethene 1 with zinc acetate.
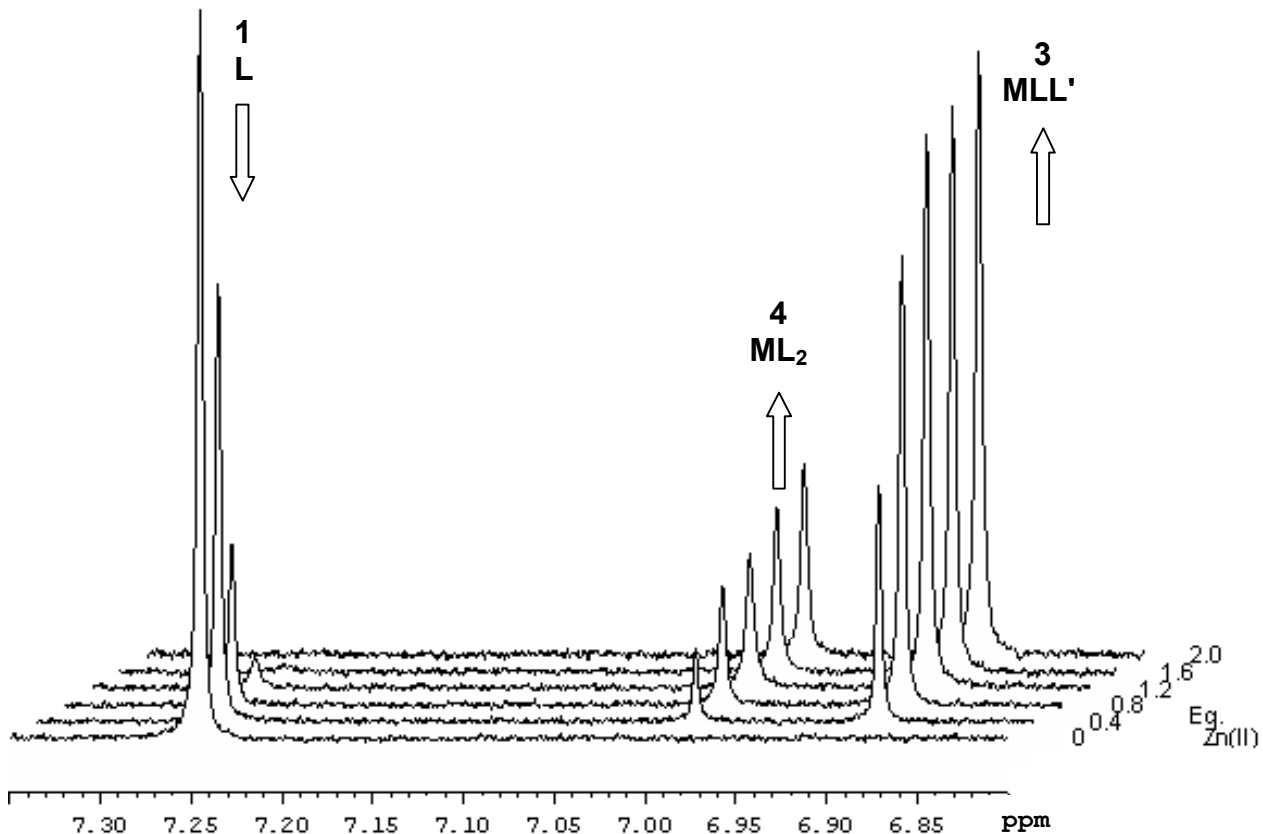
Although the two titrations monitored by absorbance spectroscopy and NMR spectroscopy were necessarily conducted at different concentrations and so exact parallels between the two cannot be drawn, the two experiments gave very similar results: complexation of **1** with zinc acetate gives a persistent intermediate species under equilibrium conditions and the addition of more zinc(II) does not effect complete complexation. It is therefore essential that the intermediate species, assigned to be the heteroleptic complex (**3**), is accounted for when using absorbance to report on the complexation as there is significant overlap in the absorption profiles of **1**, **3** and **4**.

The persistent nature of **3** under the titration conditions is somewhat surprising, since work-up (removal of solvent, dissolution in CH_2Cl_2, aqueous wash, drying the organic fraction over $MgSO_4$, and then analysis of a $CDCl_3$ solution by NMR spectroscopy) gives the pure homoleptic complex **4** in quantitative yield. Ribó[30] has commented that the solid- and solution-

state structures of dipyrromethene complexes may vary, and that a heteroleptic complex probably precedes the formation of the homoleptic complex. Our NMR spectroscopic results unequivocally confirm the presence of an intermediate under equilibrium conditions, and the fact that work-up gives only the homoleptic complex confirms that disproportionation takes place, akin to the dipyrromethene Cu(II) acac heteroleptic complexes reported by Cohen.[16, 19]

In order to be able to easily compare the binding ability of different ligands, we decided upon a single protocol that could be used with any dipyrromethene. Thus, equimolar (5×10^{-3} M) concentrations of ligand hydrobromide salt and zinc acetate dihydrate in a 1:1 $CDCl_3$:CD_3OD solution were prepared. Equations 1-7 were used to determine K_1 and K_2 and so the overall equilibrium constant β (i.e. $K_1 \cdot K_2$). Under these conditions, our equilibrium constants for dipyrromethene **1** complexation with zinc acetate dihydrate are: $K_1 = (2.3 \pm 0.1) \times 10^3$ M^{-1}; $K_2 = 68 \pm 3$ M^{-1}; $\beta = (1.6 \pm 0.1) \times 10^5$ M^{-2}. We are planning to use these standardized conditions to analyze the zinc(II) complexation of other dipyrromethenes and bis(dipyrromethene)s.∫ κ ›

Eq. 1 $L \; + \; ML' \; \overset{K_1}{\rightleftharpoons} \; MLL'$

Eq. 2 $L \; + \; MLL' \; \overset{K_2}{\rightleftharpoons} \; ML_2$

Eq. 3 $\kappa = \dfrac{[L]_0}{\Sigma \int {}^1H}$

Eq. 4 $[ML_2] = \dfrac{\kappa \int \langle ML_2({}^1H) \rangle}{2}$

Eq. 5 $[ML] = \kappa \int \langle ML({}^1H) \rangle$

Eq. 6 $[L] = \kappa \int \langle L({}^1H) \rangle$

Eq. 7 $[M] = [M]_0 - [ML_2] - [MLL']$

To conclude, the *in-situ* observation of heteroleptic dipyrromethene zinc(II) complexes is intriguing. We have established defined conditions under which the complexation abilities of dipyrromethenes may be compared by NMR spectroscopy, namely $5x10^{-3}$ M each of ligand hydrobromide salt and zinc acetate hydrate in a 1:1 $CDCl_3$:CD_3OD solution. Only the homoleptic complex is isolated from the complexation reactions, despite heteroleptic species being present prior to work-up. This raises interesting questions, as the isolated products of dipyrromethene complexation reactions with zinc(II) have always been assumed to be the same as those present in the reaction medium;[11] evidently this is not the case here as the isolated products are a result of disproportionation during work-up.

Experimental Section

[1]H nuclear magnetic resonance (NMR) spectra were recorded using a Bruker AV-500 instrument maintained at 300 K *via* thermostat. Chemical shifts are quoted in parts per million (ppm), referenced to the appropriate residual solvent peak. Mass spectra are reported in units of mass over charge (*m/z*) and were recorded in electrospray mode using a Thermo Finnigan LCQ Duo ion trap. Absorption spectra were collected using a Varian (CARY-100 Bio) spectrophotometer with a 10 mm cell. 4,4'-Diethyl-3,3′,5,5′-tetramethyldipyrromethene hydrobromide[31] (**1**) and its zinc complex[32] (**4**) were prepared according to literature procedures.

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References and Notes

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1.   Y. Murakami, Y. Matsuda, K. Sakata, and A. E. Martell *J. Chem. Soc., Dalton Trans.* **17**, 1729 (1973).
2.   R. J. Motekaitis and A. E. Martell, *Inorg. Chem.* **9**,1832 (1970).
3.   C. Brückner, Y. Zhang, S. J. Rettig, and D. Dolphin, *Inorg. Chim. Acta* **263(1-2)**, 279 (1997).
4.   J. E. Fergusson and C. A. Ramsay, *J. Chem. Soc.* 5222 (1965).
5.   M. W. Roomi, *Tetrahedron Lett.* **13**, 1131 (1974).
6.   F. C. March, D. A. Couch, K. Emerson, J. E. Fergusson, and W. T. Robinson, *J. Chem. Soc., A* 440 (1971).
7.   A. T. T. Hsieh, C. A. Rogers, and B. O. West, *Austr. J. Chem.* **29**, 49 (1976).
8.   D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, and I. T. Kay, *J. Chem. Soc. (C)* 30 (1966).
9.   W. S. Sheldrick and J. Engel, J. Chem. Soc., *Chem. Commun.* 5 (1980).
10.   G. Struckmeier, U. Thewalt, and J.-H. Fuhrhop, *J. Am. Chem. Soc.* **98**, 278 (1976).
11.   A. Thompson and D. Dolphin, *J. Org. Chem.* **65**, 7870 (2000).
12.   A. Thompson, S. J. Rettig, and D. Dolphin, *Chem. Commun.* 631 (1999).
13.   Y. Zhang and J. S. Ma, *Org. Prep. Proced. Int.* **33**, 81 (2001).
14.   Y. Zhang, A. Thompson, S. J. Rettig, and D. Dolphin, *J. Am. Chem. Soc.* **120**, 13537 (1998).
15.   Y. Zhang, Z. Wang, C. Yan, G. Li, and J. Ma, *Tetrahedron Lett.* **41**, 7717 (2000).
16.   L. Do, S. R. Halper, and S. M. Cohen, *Chem. Commun.* 2662 (2004).
17.   S. R. Halper and S. M. Cohen, *Chem. Eur. J.* **9**, 4661 (2003).
18.   S. R. Halper and S. M. Cohen, *Angew. Chem. Int. Ed.* **43**, 2385 (2004).
19.   S. R. Halper, M. R. Malachowski, H. M. Delaney, and S. M. Cohen, *Inorg. Chem.* **43**, 1242 (2004).
20.   J. M. Sutton, E. Rogerson, C. J. Wilson, A. E. Sparke, S. J. Archibald, and R. W. Boyle, *Chem. Commun.* 1328 (2004).
21.   T. E. Wood, N. D. Dalgleish, E. D. Power, A. Thompson, X. Chen, and Y. Okamoto, *J. Am. Chem. Soc.* **127**, 5740 (2005).
22.   A. Gossauer and J. Engel in *The Porphyrins*, Academic Press, 1978.
23.   J. Subramanian and J.-H. Fuhrhop in *The Porphyrins*, Academic Pres, 1978.
24.   C. R. Porter, *J. Chem. Soc. Abstracts* 368 (1938).
25.   G. B. Guseva, E. V. Antina, M. B. Berezin, A. S. Semeikin, and A. I. V'yugin, *Russ. J. Gen. Chem.* **72**, 126 (2002).
26.   J.-H. Fuhrhop, A. Salek, J. Subramanian, C. Mengersen, and S. Besecke, *Justus Liebigs Ann. Chem.* **1975**, 1131 (1975).
27.   G. B. Guseva, E. V. Antina, and M. B. Berezin, Russ. *J. Coord. Chem.* **29**, 690 (2003).
28.   G. B. Guseva, E. V. Antina, M. B. Berezin, and A. I. V'yugin, *Russ. J. Gen. Chem.* **74**, 1282 (2004).
29.   G. B. Guseva, E. V. Antina, M. B. Berezin, and A. I. V'yugin, *Russ. J. Gen. Chem.* **30**, 30 (2004).
30.   A. Jaumà, J.-A. Farrera, and J. M. Ribó, *Monatsh. Chem.* **127**, 927 (1996).
31.   A. W. Johnson, I. T. Kay, E. Markham, R. Price, and K. B. Shaw, *J. Chem. Soc. Abstracts* 3416 (1959).

32.   H. Falk, O. Hofer, and H. Lehner, *Monatsh. Chem.* **105**, 169 (1974).