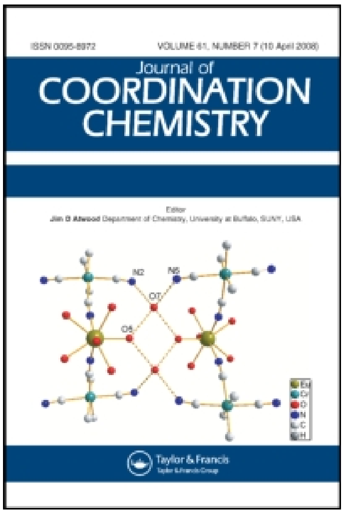

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Akin Baysal[a]; Joseph A. Connor[a]; John D. Wallis[a]
[a] Department of Chemistry, School of Physical Sciences, University of Kent, Canterbury, Kent, United Kingdom

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COMPLEXES OF 4,5-DIAZAFLUORENE AND 9,9′-BIS(4,5-DIAZAFLUORENYL) WITH NICKEL(II), COPPER(II) AND ZINC(II)

AKIN BAYSAL, JOSEPH A. CONNOR* and JOHN D. WALLIS

Department of Chemistry, School of Physical Sciences, University of Kent, Canterbury, Kent CT2 7NJ, United Kingdom

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Complexes having the compositions [$LMCl_2$], [L_2MCl_2], [L_2Cu][PF_6], [$L'MCl_2$] and [$L'(MCl_2)_2$] of 4,5-diazafluorene, L, and 9,9′-bis(4,5-diazafluorenyl), L′, have been prepared from MCl_2 ($M = Ni$, Cu, Zn) and characterised. Steric strain or the bite angle of the pro-ligand has no recognisable effect on its coordination chemistry with smaller 3d-metals.

Keywords: Copper; Nickel; Zinc; Heterocycle; Diazafluorenes

INTRODUCTION

Recent interest in the consequences of steric strain in 3,3′-annelated-2,2′-bipyridine ligands represented by 4,5-diazafluorene [1] has been based on the premise that increase in the bite angle will lead to reduced overlap between metal and ligand orbitals [2]. This is expected to lead to enhanced dissociation of one of the donor nitrogen atoms, and the implied enhancement of opportunity for the formation of labile binuclear complexes which could be catalytically active.

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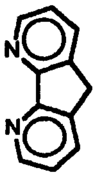
*Corresponding author.



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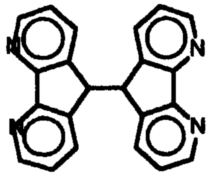

L′

We have investigated certain aspects of the coordination chemistry of 4,5-diazafluorene [3], **L**, with the divalent metal ions copper(II) [4], nickel(II) and zinc(II) and also copper(I). We have prepared complexes of these metals with the closely related bis-didentate proligand 9,9′-bis(4,5-diazafluorenyl) [5], **L**′.

RESULTS AND DISCUSSION

The complexes were made simply by adding an ethanolic solution of the proligand to an equimolar solution of the metal chloride at ambient temperature, or in the case of copper(I), by adding the acetonitrile complex salt $[Cu(NCMe)_4][PF_6]$ [6] to the proligand in ethanol. Complexes of the types $[LMCl_2]$ and $[L_2MCl_2]$ (L = 4,5-diazafluorene) and $[L'MCl_2]$ and $[L'(MCl_2)_2]$ (L′ = 9,9′-bis(4,5-diazafluorenyl)) (M = Cu, Ni, Zn) have been prepared in satisfactory yield (better than 70%). These complexes are non-electrolytes in acetonitrile solution. $[CuL_2][PF_6]$ has also been prepared; this was shown to be a 1 : 1 electrolyte in acetonitrile solution.

Detailed assignments of the infrared spectrum of 2,2′-bipyridyl have been made [7]. Consequently, it is possible to assign many of the principal absorptions in the infrared and Raman spectra of these ligands by analogy. The infrared spectra of the complexes are dominated by the absorptions of the ligands, as expected. In the simpler spectra of 4,5-diazafluorene and its complexes, the principal proligand absorptions show slight (10 to 20 cm^{-1}) shifts on coordination. The spectra in the region 1430 – 1400 cm^{-1}, assigned [7] to C=C and C=N ring stretch and C—H bending vibrations, contain two medium intensity absorptions for $[L_2MCl_2]$ complexes, whereas there is only one medium-strong absorption in the spectra of the corresponding $[LMCl_2]$ complex in the same region. Similar observations are made for the intense absorption at 742 cm^{-1}, assigned to the ring out-of-plane bending vibration of the proligand, which appears as two strong absorptions (at ca 790, 720 cm^{-1}) in $[LMCl_2]$, and as three medium-strong absorptions (at ca

800, 770 and 725 cm^{-1}) in [L_2MCl_2]. The complexity of both the infrared and Raman spectra of the 9,9′-bis(4,5-diazafluorenyl), L′, proligand in the 4000–200 cm^{-1} region permit no simple assignment at this stage. This problem is only accentuated in the infrared spectra of the complexes [$L'MCl_2$] and [$L'(MCl_2)_2$] so that we have been unable to derive useful structural information from them.

The assignment of the absorptions in the region below 400 cm^{-1} can be made on the basis of comparison with the bipy analogues [8], as shown in Table I. Results support a tetrahedral structure for the four-coordinate metal ion in [$LMCl_2$]. The low-frequency infrared spectra of the six-coordinate [L_2MCl_2] complexes indicate that the two chloride ligands are *cis* (ν(Ni-Cl) 276 m, 227 m cm^{-1}).

The electronic absorption spectra of the free proligands L and L′ are almost indistinguishable in the region 220–600 nm. The molar absorption coefficients, ε/m^{2}mol^{-1}, of L′ are approximately twice those of L, as shown in Table II. Formation of the complexes [$LMCl_2$], [$L'MCl_2$], [L_2MCl_2] and [$L'(MCl_2)_2$] does not produce any significant alteration in the characteristic electronic spectra of the proligands beyond small ($<$ 10 nm) bathochromic shifts accompanied by changes in the absorption intensities. The hyperchromic effect in [L_2MCl_2] (M = Cu, Zn) is most marked. Weak absorptions in the visible region have been assigned to ligand field (d-d) transitions. The intensity of these absorptions are consistent with tetrahedral structures for [$LMCl_2$] (M = Ni, Cu).

FAB mass spectra of the complexes [$LMCl_2$], [L_2MCl_2], [$L'MCl_2$] and [$L'(MCl_2)_2$] (M = Ni, Cu, Zn) do not include a molecular ion. Instead, the loss of chloride occurs and the ions [$LMCl$]$^+$, [L_2MCl]$^+$, [$L'MCl$]$^+$ are formed. In the case of [L_2CuCl_2] a chloride ion and a chlorine atom are lost and reduction to the copper(I) species [L_2Cu]$^+$ is favoured. The FAB-MS of

TABLE I Selected IR data for L_AMCl_2 L_A = 2,2′-bipy (Ref. [7]), 4,5-diazafluorene (daf)

	ν(M-Cl)		*ν(M-N)*	
	Bipy	*Daf*	*Bipy*	*Daf*
Ni	254	276	307	300
Cu	304	302	292	290
Zn	339	326	243	280

TABLE II Ultraviolet absorption data $\lambda_{max}(\log\varepsilon)$ for 4,5-diazafluorene, L, and 9,9′-bis(4,5-diazafluorenyl), L′, in chloroform solution

L	244(3.531)	297(4.255)	304(4.286)	310(4.387)
L′	229(4.832)	300(4.832)	307(4.632)	313(4.757)

[$LNiCl_2$] shows the formation of [$L_2Ni_2Cl_3$]$^+$ (*m*/*z* 560.908); the FAB-MS of [L_2NiCl_2] shows the formation of [$L_2Ni_3Cl_6$] (*m*/*z* 723.749). The greater bite angle of L [9] (126.3°) compared with 2,2-bipyridine [10] (116°), most probably facilitates bridging between two metal ions in these species. It is also possible that chloride bridges exist between monomers in solution but we have not found any convincing evidence for this. The FAB-MS of both [$L'NiCl_2$] and [$L'(NiCl_2)_2$] include the ion [L'_2NiCl]$^+$(*m*/*z* 761). It appears that redistribution (scrambling) reactions of the both the ligand (L, L′) and of nickel-containing fragments occurs easily in these systems.

The proton NMR spectra of the diamagnetic copper(I) and zinc(II) complexes of L and L′ show that the signal of H3/6, adjacent to the donor nitrogen atoms, shifts very slightly (0.06{L}, 0.03{L′} ppm) to higher field on coordination, whereas the signals of both H1/8 and H2/7 and of the methylene (L)/methine (L′) protons appear ca 0.18 ppm to lower field in these complexes. The same behaviour was noticed for zinc(II) complexes of 9,9′-bis(4,5-diazafluorenylidene) [9]. The ligand proton resonances in [CuL_2][PF_6] are all to lower field of their values in the proligand, H3/6 being the least shifted (0.14 ppm), and the signals are broad, presumably because of the presence of copper(II).

We must conclude that, based on the evidence available for the coordination compounds reported here, the greater bite angle in the proligands L and L′ compared to that in 2,2′-bipyridine does not have a marked influence on the physical properties of these compounds. This may attest more to the small size of the metal ions involved than to the conformation of the proligands themselves.

EXPERIMENTAL

Solvents and materials were used as received, unless stated otherwise. 1,10-Phenanthroline was purchased from Avocado. The compounds L and L′ were prepared by published methods [3, 4]. FAB mass spectra were recorded at the EPSRC mass spectrometry service centre at the University of Wales, Swansea. Proton NMR spectra were measured by Dr D. O. Smith on $CDCl_3$ solutions at room temperature (unless otherwise indicated) using a JEOL GX270 FT spectrometer. Microanalyses were made by Mr. A. J. Fassam on a Carlo Erba instrument. Infrared spectra of compounds prepared as Nujol™ mulls were recorded on a Mattson Instruments Alpha Centauri FT IR spectrometer interfaced with an AT&T UNIX PC. Raman spectra were recorded using a Coderg PHO spectrometer with a krypton ion laser (output 647.1 nm). Electronic absorption spectra were recorded on a Philips PU

8740 spectrophotometer using solutions of known concentration in quartz cells.

Preparation of Dichloro(4,5-diazafluorene) Metal Complexes

A solution of the metal dichloride (0.3 mmol) in ethanol (5 cm^3) was added to a solution of 4,5-diazafluorene (0.3 mmol) in ethanol (5 cm^3) and the mixture was stirred at room temperature (0.5 h). Evaporation of the solvent left a solid product that was washed with dichloromethane and cold ethanol and then dried in vacuum.

Nickel(II)

Yellow-green solid (75% yield as monohydrate). Calc. for $C_{11}H_{10}Cl_2N_2NiO$ (%): C, 41.8; H, 3.2; N, 8.9. Found: C, 41.4; H, 3.0; N, 8.7. FAB-MS: *m/z* (I,%): 559(43), 429(65), 394(25), 261(100). λ_{max}/nm(log ε) (EtOH): 240(3.90), 307(4.21), 312(4.29), 319(4.27), 408(2.11). IR ν/cm^{-1}: 1590 m, 1414 m, 1296 m, 1180 m 1160 s, 1122 m, 896 m, 878 m, 788 s, 718 s, 444 m, 300 m, 276 m.

Copper(II)

Light green solid (84% yield). Calc. for $C_{11}H_8Cl_2CuN_2$(%): C, 43.7; H, 2.7; N, 9.3. Found: C, 43.8; H, 2.6; N, 9.5. λ_{max}/nm(log ε) (EtOH): 242(4.30), 298(4.22), 304(4.30), 311(4.36), 394(2.10). IRν/cm^{-1}: 1590 m, 1414 ms, 1296 m, 1182 w, 1160 m, 1124 w, 900 w, 880 w, 788 m, 778 sh, 718 m, 440 w, 302 m, 274 m.

Zinc(II)

White solid (78% yield). Calc. for $C_{11}H_8Cl_2N_2Zn$(%): C, 43.4; H, 2.7; N, 9.0. Found: C, 43.5; H, 2.7; N, 9.0. λ_{max}/nm(log ε) (MeOH): 243(4.01), 298(4.34), 304(4.38), 310(4.51). IR ν/cm^{-1}: 1585 m, 1420 m, 1183 m, 1110 w, 915 w, 880 w, 794 m, 775 w, 722 m, 438 w, 326 m, 280 m. ^{1}H NMR (dmso-d_6): δ8.67(ddd, 3-,6-H, J = 4.9, 1.4, 0.6 Hz), 8.10(ddd, 1-,8-H, J = 7.7, 1.4, 0.6 Hz), 7.45(dd, 2-,7-H, J = 4.9, 7.6 Hz), 4.00(CH_2).

Bis(4,5-diazafluorene) Metal Complexes

A solution of the metal dichloride (0.3 mmol) in ethanol (5 cm^3) was added to a solution of 4,5-diazafluorene (0.6 mmol) in ethanol (10 cm^3) and the mixture was stirred at room temperature (0.5 h). Evaporation of the solvent left a solid that was washed and then dried in vacuum.

Nickel(II)

Yellow solid (85% yield). Calc. for $C_{22}H_{16}Cl_2N_4Ni$(%): C, 56.7; H, 3.5; N, 12.0. Found: C, 56.9; H, 3.6; N, 11.8. FAB-MS *m/z* (I,%): 723(8), 688(5), 561(14), 429(100), 394(45), 261(40). λ_{max}/nm(log ε) (H_2O): 242(4.25), 304(4.22), 310(4.31), 621(0.87). IRν/cm^{-1}: 1587 m, 1409 m, 1288 m, 1180 w, 1161 m, 1115 w, 873 w, 801 m, 772 m, 724 ms, 649 w, 332 m, 320 sh, 276 ms, 260 sh, 227 m.

Copper(II)

Dark green solid (86% yield). Calc. for $C_{22}H_{16}Cl_2CuN_4$(%): C, 56.1; H, 3.4; N, 11.9. Found: C, 55.4; H, 3.2; N, 11.5. FAB-MS *m/z* (I,%): 434(3), 399(12), 231(15), 169(100). λ_{max}/nm(log ε) (H_2O): 243(4.33), 301(4.51), 307(4.57), 312(4.64), 756(1.68). IRν/cm^{-1}: 1572 m, 1422 m, 1405 m, 1302 m, 1262 w, 1162 m, 1106 m, 1080 w, 920 w, 870 w, 796 ms, 760 m, 724 m, 652 w, 318 w, 300 wsh, 266 s. 250 sh, 218 m.

Zinc(II)

White solid (79% yield). Calc. for $C_{22}H_{16}Cl_2N_4Zn$(%): C, 55.9; H, 3.4; N, 11.9. Found: C, 55.4; H, 3.3; N, 11.7. FAB-MS *m/z* (I,%): 569(5), 435(37), 267(29). λ_{max}(log ε) (EtOH): 242(4.21), 298(4.55), 304(4.59), 311(4.71). IR ν/cm^{-1}: 1570 m, 1420 m, 1294 m, 1180 w, 1164 m, 1110 w, 870 w, 798 m, 774 m, 726 m, 320 m, 305 sh, 272 m, 260 sh, 220 m. ^{1}H NMR (dmso-d_6): 8.67(ddd, 3-,6-H, J = 4.9, 1.4, 0.5 Hz), 8.10(dd, 1-,8-H, J = 7.7, 1.4 Hz), 7.45(dd, 2-,7-H, J = 7.7, 4.9 Hz), 3.99(CH_2).

Copper(I)

[Cu(NCMe)$_4$][PF$_6$] was prepared [7] and added to a solution of L (0.6 mmol) in ethanol (10 cm^3). The precipitate which formed was isolated by filtration, washed (CH_2Cl_2) and dried in vacuum to give yellow crystals (84% yield). Calc. for $C_{22}H_{16}CuF_6N_4P$(%): C, 48.5; H, 3.0; N, 10.3. Found: C, 48.0; H, 2.8; N, 10.2. FAB-MS *m/z* (I,%): 399(100), 231(50), 169(24). λ_{max}/nm(log ε) (CH_3CN): 244(4.70), 298(4.47), 302(4.50), 310(4.57). ^{1}H NMR (dmso-d_6): 8.87(3-,6-H), 8.28(1-,8-H), 7.69(2-,7-H), 4.10(CH_2).

Complexes of 9,9'-bis(4,5-diazafluorenyl)

Nickel(II)

Yellow solid (86% yield as dihydrate). Calc. for $C_{22}H_{18}Cl_2N_4NiO_2$(%): C, 52.8; H, 3.6; N, 11.2. Found: C, 52.6; H, 3.6; N, 11.2. FAB-MS *m/z* (I,%): 761(15), 726(16), 559(5), 427(30), 392(43), 260(55), 225(100). λ_{max}/nm(log ε) (H_2O): 246(4.03), 302(4.47), 308(4.48), 314(4.53). IRν/cm^{-1}: 1708 m, 1590 m, 1412 m, 1298 w, 1158 m, 896 w, 860 w, 816 m, 775 m, 752 s, 730 m, 644 w, 401 w, 325 w, 270 w, 245 msh, 220 m.

Green solid (76% yield). Calc. for $C_{22}H_{14}Cl_4N_4Ni_2$(%): C, 44.5; H, 2.4; N, 9.4. Found: C, 44.2; H, 2.5; N, 9.4. FAB-MS *m/z* (I,%): 558(20), 427(20), 392(35). λ_{max}/nm(log ε) (H_2O): 244(4.17), 302(4.56), 308(4.58), 314(4.63). IR ν/cm^{-1}: 1592 m, 1414 ms, 1300 m, 1160 s, 818 m, 770 w, 754 s, 726 m, 401 m, 325 m, 270 m, 230 m.

Copper(II)

Turquoise solid (79% yield). Calc. for $C_{22}H_{14}Cl_2CuN_4$(%): C, 56.4; H, 3.0; N, 12.0. Found; C, 56.0; H, 2.9; N, 11.9. FAB-MS *m/z* (I,%): 432(15), 397(20). λ_{max}/nm(log ε) (H_2O): 262(4.22), 302(4.54), 308(4.53), 314(4.62). IR ν/cm^{-1}: 1708 m, 1572 m, 1408 m, 1298 m, 1192 m, 1162 m, 822 m, 770 m, 760 sh, 748 s, 724 m, 648 m, 430 m, 315 m, 288 sh, 272 m, 235 sh, 220 m.

Copper(II)

Light green solid (76% yield). Calc. for $C_{22}H_{14}C1_4Cu_2N_4$(%): C, 43.8; H, 3.3; N, 9.3. Found: C, 43.6; H, 2.1, N, 9.1. λ_{max}/nm(log ε): 272(4.80), 312(4.53). IRν/cm^{-1}: 1696 w, 1594 ms, 1556 m, 1415 sh, 1300 w, 1236 m, 1158 m, 1100 m, 1024 w, 864 m, 834 m, 806 m, 770 s, 756 s, 715 m, 696 w, 680 w, 648 w, 594 w, 546 m, 514 m, 440 m, 346 m, 276 m, 235 w.

Zinc(II)

White crystals (72% yield). Calc. for $C_{22}H_{14}Cl_2N_4Zn$(%): C, 56.1; H, 3.0; N, 11.9%. Found: C, 55.8; H, 3.0; N, 11.8%. λ_{max}/nm(log ε) (DMF): 266(3.94), 304(4.54), 306(4.54), 312(4.65). IRν/cm^{-1}: 1630 w, 1572 m, 1410 m, 1296 w, 1194 m, 1175 m, 1158 ms, 1122 m, 818 m, 772 s, 768 m, 752 ms, 720 m, 470 mbr, 420 w, 315 sh, 276 m, 235 w, 220 m. ^{1}H NMR: (J/Hz) (dmso-d_6): 8.60(s, br, 3-,6-H), 7.42(s, br, 1-,8-H), 7.28(dd, 2-,7-H, J = 6.6, 4.9 Hz), 5.27(s, CH).

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