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Structural Investigations of the Dipyrromethene Complexes of Calcium(II), Nickel(II) and Copper(II)

ERIC T. CLARKE, PHILIP J. SQUATTRITO, PHILIP R. RUDOLF, RAMUNAS J. MOTEKAITIS, ARTHUR E. MARTELL* and ABRAHAM CLEARFIELD

Department of Chemistry, Texas A&M University, College Station, TX 77843-3255 (U.S.A.)

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Abstract

Structures of complexes formed between calcium(II), nickel(II) and copper(II) and the ligand, 3,3′,4,4′-tetrachloro-5,5′-dicarbethoxy-2,2′-dipyrromethene, have been determined. The Ni(II) and Cu(II) ions are six-coordinate, with a distorted octahedral configuration consisting of the four pyrrole nitrogen atoms and two oxygen atoms of the ligand. The Ca(II) ion is eight-coordinate with a distorted dodecahedral geometry involving four pyrrole nitrogen atoms and the four carbonyl oxygen atoms of the carbethoxy groups. For each metal complex, oxygen coordination results in distortion away from the tetrahedral conformation of the ligand nitrogen donors. The Ca(II) chelate is monoclinic, space group $P2_1/n$, $Z = 4$, $a = 11.381(2)$, $b = 24.916(4)$, $c = 13.410(2)$ Å, $\beta = 94.31(1)°$, $V = 3792(1)$ Å^3. The Ni(II) and Cu(II) complexes are isostructural, triclinic, space group $P\bar{1}$, $Z = 2$. For the Ni(II) chelate, $a = 12.574(4)$, $b = 14.608(3)$, $c = 10.634(2)$ Å, $\alpha = 96.42(2)$, $\beta = 100.05(2)$, $\gamma = 108.89(2)°$, $V = 1789.6(8)$ Å^3. For the Cu(II) chelate, $a = 12.522(5)$, $b = 14.493(6)$, $c = 10.704(6)$ Å, $\alpha = 96.50(5)$, $\beta = 100.86(2)$, $\gamma = 108.44(1)°$, $V = 1778.41(6)$ Å^3. The structures were solved by direct methods and refined by least-squares techniques to $R = 0.043$ (2531 independent reflections) for the Ca(II) chelate; $R = 0.044$ (3149 independent reflections) for the Ni(II) chelate; and $R = 0.067$ (2468 independent reflections) for the Cu(II) chelate.

Introduction

Structural investigations of bivalent metal chelates of substituted dipyrromethenes are of interest since they provide information about the influence of the bulkiness of the substituent groups and the coordination requirements of the metal ion on the stereochemistry of the complexes formed. In addition, dipyrromethene chelates are important model compounds for studying the conformational preferences and bonding characteristics of the metalloporphyrins in heme and chlorophyll.

Most early work in this area relied on spectroscopic data to obtain structural information in these systems. For example, Motekaitis and Martell [1] have provided infrared spectrophotometric evidence for conformations in which the dipyrromethene ring systems are distorted from planarity in the Ni(II) and Cu(II) complexes of 3,3′,4,4′-tetrachloro-5,5′-dicarbethoxy-2,2′-dipyrromethene. This evidence is in contrast to earlier electronic spectroscopy work [2] which suggested that Co(II), Ni(II) and Cu(II) complexes of 5- and 5′-substituted dipyrromethenes are square-planar, irrespective of the presence of bulky substituent groups which would be expected to force the ligands away from a co-planar configuration. They were also the first to provide detailed infrared evidence [1] for the tetrahedral arrangement of the nitrogen donors (i.e. mutually perpendicular ligand planes) in a Ca(II) dipyrromethene complex based on observations of carbonyl stretching frequencies. Other structural studies [3] suggested on the basis of molecular models, electronic spectroscopy and X-ray powder photographs [4, 5] that the conformations of substituted dipyrromethene ligands in complexes of Co(II), Ni(II) and Cu(II) constitute either a tetrahedral or distorted tetrahedral arrangement of the N donors around the central metal ions.

Murakami *et al.* [6] have studied Co(II), Ni(II), and Cu(II) chelates of 5- and 5′-methyl substituted dipyrromethenes by electronic and vibrational spectroscopy. Their results indicated that the N donors in the Cu(II) complex assume a distorted tetrahedral configuration, whereas the Ni(II) and Co(II) complexes are more regular. In addition, in ligands where the 5-methyl group is absent from the Cu(II) complex, the lack of bulky substituent groups appears to allow twisting toward coplanarity in chloroform as indicated by the direction of the infrared shifts assigned to the pyrrole rings. Murakami

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*Author to whom correspondence should be addressed.

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et al. also investigated the ESR and infrared spectra of bivalent metal complexes of tetrachloro-5,5′-dicarbethoxy dipyrromethenes [7]. They observed two carbonyl stretching bands in the infrared spectrum and concluded that one of the two carbonyl oxygen atoms of each ligand group was coordinated to the central metal ion together with the four planar nitrogen atoms. On this basis, as well as on the basis of anomalous d–d absorption band shifts, they postulated N_4O_2 metal coordination with a distorted octahedral configuration but they did not conclusively show that their calculated *g* tensors explained the observed values.

Clearly, single crystal X-ray diffraction studies of the metal chelates were needed to establish structural conformation. The structure of bis-(diethyl-3,3′,5,5′-tetramethyldipyrromethene-4,4′-dicarboxylate)-copper(II) was found by Elder and Penfold [8] to contain two approximately planar dipyrromethene ligands inclined at an angle of 66°. A dihedral angle of 90° between the ligand planes would yield the smallest contact interaction between the bulky substituents. Cotton *et al.* [9] reported the dihedral angle between the least-squares planes of bis-(3,3′,5,5′-tetramethyldipyrromethanato)nickel(II) as 76.3° which gives Ni(II) a distorted tetrahedral coordination geometry with approximate D_2 symmetry. The bond lengths of the ring atoms indicate that π-delocalization occurs over the two pyrrole rings in each ligand group by conjugation through the bridging carbon atom.

The present structural study was initiated to determine the influences of bulky substituents and metal coordination behavior on the conformations of the Ca(II), Ni(II) and Cu(II) chelates of the ligand 3,3′,4,4′-tetrachloro-5,5′-dicarbethoxy-2,2′-dipyrromethene.

Experimental

Synthesis

The metal chelate compounds used in this crystallographic study were prepared as previously reported [1]. The crystals exhibit green/red dichroism especially with the edge surfaces of the calcium chelate. The analytical data [1] for these compounds are as follows.

Anal. Calc. for $CaC_{30}H_{22}N_4Cl_8O_8$: C, 40.27; H, 2.49; N, 6.29; Cl, 31.86; Ca, 4.50. Found: C, 40.37; H, 2.83; N, 6.07; Cl, 31.69; Ca, 4.65%.

Calc. for $NiC_{30}H_{22}N_4Cl_8O_8$: C, 39.64; H, 2.44; N, 6.16; Cl, 31.21; Ni, 6.46. Found: C, 39.61; H, 2.61; N, 6.34; Cl, 31.06; Ni, 6.29%.

Calc. for $CuC_{30}H_{22}N_4Cl_8O_8$: C, 39.43; H, 2.43; N, 6.13; Cl, 31.04; Cu, 6.95. Found: C, 38.92; H, 2.45; N, 6.16; Cl, 30.59; Cu, 6.33%.

Crystallographic Study

Needles (Ni(II), Cu(II)) or platelets (Ca(II)) of the dipyrromethene chelates were mounted on glass fibers and diffraction data were obtained with graphite-monochromatic Mo Kα radiation ($\lambda_{K\alpha}$ = 0.71069) on a Rigaku AFC5R rotating anode diffractometer. Data were collected at a temperature of 23 ± 1 °C using the $2\theta-\omega$ scan technique to 50.1° 2θ. Scans were measured at 16.0°/min (in ω). Cell parameters together with final refinement parameters are summarized in Table 1.

Equivalent reflections were averaged and the intensities of three standard reflections were measured periodically to ensure that no loss of intensity from electronic instability or crystal decay occurred during the data collection.

Intensity was measured as $[C - 1/2(t_c/t_b)(b_1 + b_2)]$ where C = total number of counts, t_c = time spent counting peak intensity, t_b = time spent counting one side of background, b_1 = high-angle background counts, b_2 = low-angle background counts. The intensity error, $\sigma(F^2)$, is given by $[C + 1/4(t_c/t_b)^2(b_1 + b_2) + (p \times I)^2]^{1/2}$ where I is the intensity and p is the correction factor that down-weights intense reflections and has the value of 0.05 for each of the data sets.

The linear absorption coefficients (Table 1) are small for Mo Kα radiation but in all cases an empirical absorption correction [10], based on azimuthal scans of three reflections was applied. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods [11, 12]. Non-hydrogen atoms were refined anisotropically. For the Ca(II) complex the hydrogen atoms were refined isotropically, but for the Ni(II) and Cu(II) complexes they were calculated and included as a fixed contribution. The final cycles of full-matrix least-squares refinement converged to weighted and unweighted residuals as reported in Table 1. (Least-squares function minimized: $\Sigma w(F_o - F_c)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/(Lp)^2$; S = scan rate; C = total integrated peak count; R = ratio of scan time to background counting time; B = total background count; Lp = Lorentz–polarization factor; and p = p factor.)

Neutral atom scattering factors were taken from Cromer and Waber [13]. Anomalous dispersion effects were included [14]; the values for $\Delta f'$ and $\Delta f''$ were taken from Cromer [15]. All calculations were performed on a DEC MicroVAX II computer with the TEXSAN [16] single crystal package.

In the course of structure refinement of the Ni(II) and Cu(II) chelates, one of the carbethoxy groups of each complex could not be refined by standard methods. The isotropic thermal parameters for the ethoxy groups were large and the carbonyl oxygen atoms and ether oxygen atoms appeared to have equivalent bond lengths. Removal of the ethoxy

TABLE 1. Collected single crystal data and analysis parameters

Empirical formula	$CaC_{30}H_{22}N_4Cl_8O_8$	$NiC_{30}H_{22}N_4Cl_8O_8$	$CuC_{30}H_{22}N_4Cl_8O_8$
Formula weight	890.23	908.85	913.70
Morphology	platelet	needle	needle
Crystal dimensions (mm)	0.35 × 0.05 × 0.15	0.40 × 0.08 × 0.08	0.20 × 0.03 × 0.08
Crystal system	monoclinic	triclinic	triclinic
Lattice parameters	a = 11.381(2) Å	a = 12.574(4) Å	a = 12.522(5) Å
	b = 24.916(4) Å	b = 14.608(3) Å	b = 14.493(6) Å
	c = 13.410(2) Å	c = 10.634(2) Å	c = 10.704(6) Å
		α = 96.42(2)°	α = 96.50(5)°
	β = 94.31(1)°	β = 100.05(2)°	β = 100.86(2)°
		γ = 108.89(2)°	γ = 108.44(1)°
	V = 3792(1) Å^3	V = 1789.6(8) Å^3	V = 1778.41(6) Å^3
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z value	4	2	2
D_{calc}	1.59 g/cm^3	1.69 g/cm^3	1.74 g/cm^3
F(000)	1880	916	958
μ (MoKα)	7.75 cm^{-1}	11.91 cm^{-1}	12.94 cm^{-1}
Transmission factors	0.891–1.000	0.945–1.000	0.921–1.000
2θ (max) for data	50.1°	50.1°	50.1°
No. observations	2531	3149	2468
No. variables	548	478	478
Residuals: R; R_w	0.043; 0.051	0.044; 0.052	0.067; 0.087
Goodness of fit	1.23	1.23	1.90
Max. shift/error final cycle	2.08	0.94	0.88
Largest peak in final difference map	0.24 e/Å^3	0.40 e/Å^3	0.52 e/Å^3
2θ for high angle cell	30.27–37.89	35.95–46.20	25.83–34.67
A (scan width)	0.924	1.313	1.050
Standards/h, k, l	−2, −7, −1	1, −3, −3	−5, 1, 0
	1, −8, 1	3, 3, −2	−4, −2, −1
	2, 0, −4	2, −4, −2	−4, 3, −2

group followed by a difference Fourier synthesis yielded a disordered arrangement. The orientations were fixed at equal weight. Accordingly, the alternate configurations C25–O5–C26–C27 and C25–O6–C26′–C27′ were assigned equal population in the refinement of the Ni(II) structure. Similarly, the alternate configurations C23–O4–C24–C25 and C23–O3–C24′–C25′ were refined with equal population in the Cu(II) structure.

Results

An unanticipated result of the solution of the Ca(II) dipyrromethene chelate structure is the discovery of eight-coordination of the Ca(II) by the four carbonyl oxygen atoms together with the four pyrrole nitrogen atoms. The resulting geometry of the Ca(II) N_4O_4 coordination is a distorted dodecahedron (Fig. 1). A stereo packing diagram showing the contents of the unit cell of the Ca(II) chelate is given in Fig. 2. The final positional and equivalent isotropic thermal parameters for all three of the dipyrromethene chelates are presented in Table 2. Selected intramolecular bond distances for the Ca(II), Ni(II) and Cu(II) structures are consolidated and presented in Table 3. Table 4 gives selected intramolecular bond angles for each of the chelates. See also ‘Supplementary Material’.

The Ni(II) and Cu(II) chelates are isostructural. In both cases, the four nitrogen atoms and two non-apical carbonyl oxygen atoms are coordinated to the metal centers in a distorted octahedral geometry (Fig. 3). Carbonyl groups containing atoms O1 and O3 are perpendicular to each other and are directed toward the Ni(II) center. The Ni–O1 bond length of 2.326(4) Å and the Ni–O3 distance of 2.285(4) Å can be considered weak bonding interactions since they approach the sum of the ionic radii [17]. The packing diagram for Ni(II), Fig. 4, shows how the geometries of the Ni(II) and Cu(II) complexes differ markedly from that of the Ca(II) complex in that fewer carbethoxy oxygen atoms are swung into the coordination planes of the metal cations. The influence of the coordinated oxygen atoms in the Ni(II) and Cu(II) complexes is to distort the conformation away from one in which the pyrrole planes are mutually perpendicular. This effect is heightened in the Ca(II) complex where four oxygen atoms are coordinated together with the nitrogen atoms to result in distorted dodecahedral N_4O_4 geometry.

For the least-squares planes and dihedral angles of the Ca(II), Ni(II) and Cu(II) complexes see ‘Supple-

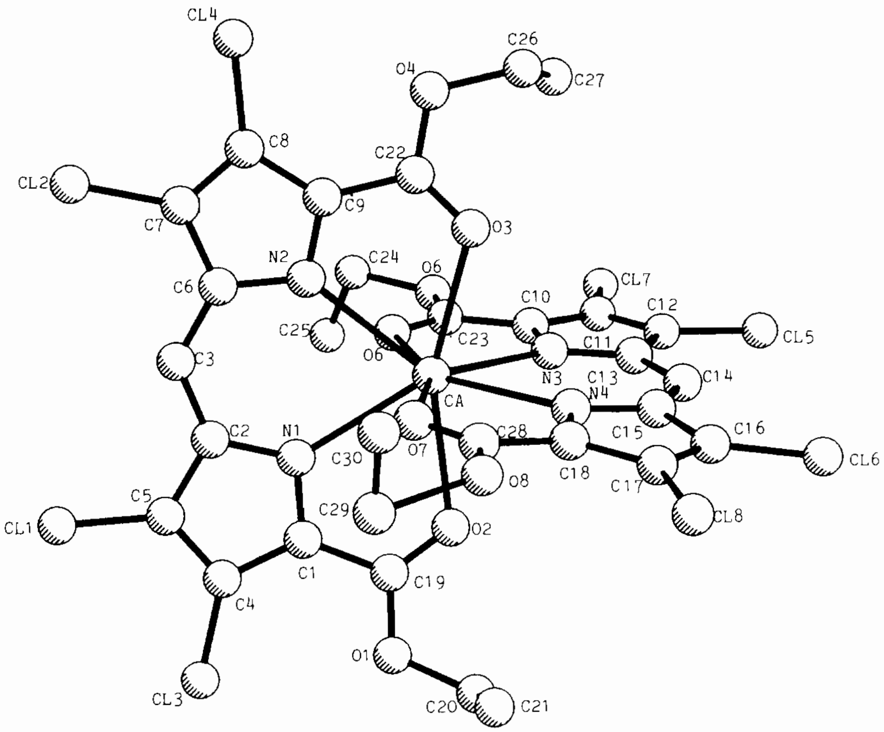

Fig. 1. Molecular representation of the Ca(II) dipyrromethene complex in side view showing the near-perpendicularity of the two ligands. (The dihedral angles between the least-squares planes are available, see 'Supplementary Material'.)

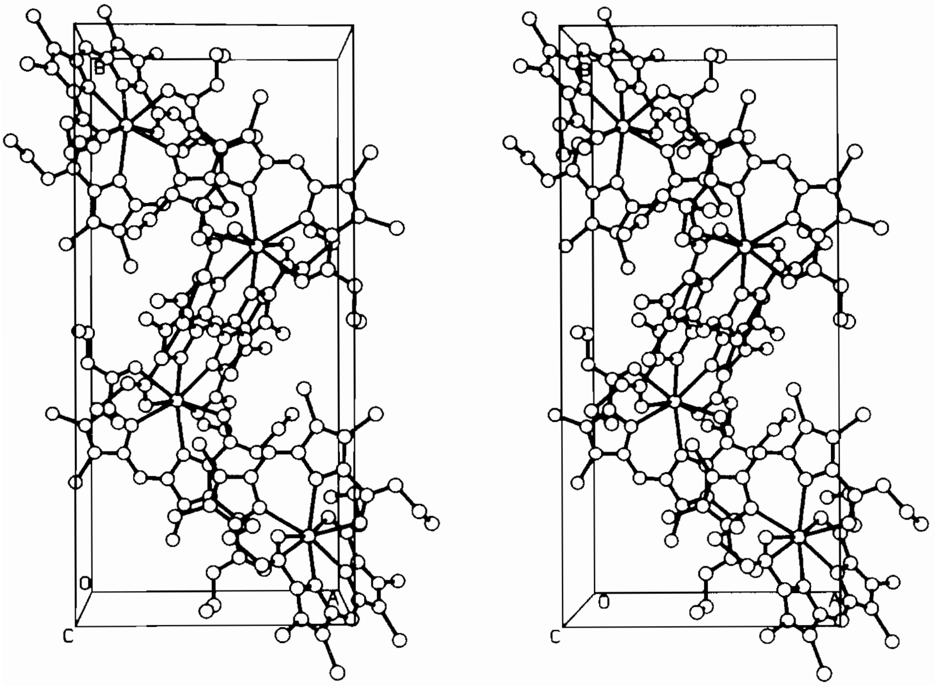

Fig. 2. Stereoview of the Ca(II) complex of dipyrromethene.

mentary Material'. The distortion of the ligand planes away from the ideal dihedral angle of 90° in the Ca(II) complex is evidenced by the observed mean angle of 101.1(2)°, which is greater than the average interplanar angles for the Ni(II) (87.7(2)°) and Cu(II) (88.0(4)°) complexes. The distortion from

TABLE 2. Positional parameters and equivalent isotropic thermal parameters for the Ca(II), Ni(II) and Cu(II) chelates of dipyrromethene

Atom	x	y	z	B_{eq}
Ca dipyrromethene				
Ca	0.8461(1)	0.13607(4)	0.7156(1)	4.76(6)
Cl1	0.4377(2)	0.29163(7)	0.5363(2)	7.5(1)
Cl2	0.8302(2)	0.39201(6)	0.7202(2)	8.0(1)
Cl3	0.3446(1)	0.16363(7)	0.5162(1)	7.0(1)
Cl4	1.0888(2)	0.34977(7)	0.8379(1)	7.4(1)
Cl5	1.1952(2)	−0.05396(7)	0.6196(2)	8.8(1)
Cl6	0.9405(2)	−0.08464(7)	0.9464(2)	9.3(1)
Cl7	1.2041(2)	0.04155(8)	0.4411(2)	8.0(1)
Cl8	0.2617(2)	0.0130(1)	0.9379(2)	10.9(1)
O1	0.4908(3)	0.0679(2)	0.6065(3)	6.2(2)
O2	0.6817(4)	0.0761(1)	0.6576(3)	5.8(2)
O3	1.0325(4)	0.1632(2)	0.8061(3)	6.5(2)
O4	1.1600(4)	0.2285(2)	0.8525(3)	6.8(2)
O5	1.0567(4)	0.1442(2)	0.4409(4)	7.6(3)
O6	0.9283(4)	0.1621(2)	0.5550(3)	6.4(2)
O7	0.7282(4)	0.1425(2)	0.8654(4)	7.3(3)
O8	0.6660(6)	0.1013(3)	0.9988(5)	12.2(4)
N1	0.6652(4)	0.1833(2)	0.6407(3)	4.6(2)
N2	0.8734(4)	0.2359(2)	0.7340(4)	4.8(2)
N3	0.9893(4)	0.0704(2)	0.6512(4)	4.9(2)
N4	0.8648(4)	0.0571(2)	0.8310(4)	5.2(3)
C1	0.5745(5)	0.1532(2)	0.6085(4)	4.9(3)
C2	0.6333(5)	0.2359(2)	0.6228(4)	4.5(3)
C3	0.7000(6)	0.2795(2)	0.6532(5)	5.4(3)
C4	0.4782(5)	0.1847(2)	0.5677(4)	5.1(3)
C5	0.5157(5)	0.2356(2)	0.5757(4)	5.1(3)
C6	0.8097(5)	0.2807(2)	0.7048(4)	4.8(3)
C7	0.8759(5)	0.3267(2)	0.7385(5)	5.2(3)
C8	0.9774(5)	0.3100(2)	0.7854(5)	5.4(3)
C9	0.9737(5)	0.2531(2)	0.7805(4)	4.8(3)
C10	1.0401(5)	0.0828(2)	0.5687(5)	5.0(3)
C11	1.1209(5)	0.0434(3)	0.5415(5)	5.7(3)
C12	1.1176(5)	0.0054(2)	0.6140(6)	6.0(4)
C13	1.0357(5)	0.0218(2)	0.6828(5)	5.3(3)
C14	1.0043(6)	−0.0062(3)	0.7651(6)	6.2(4)
C15	0.9258(6)	0.0088(2)	0.8315(6)	6.0(4)
C16	0.8885(6)	−0.0221(3)	0.9141(6)	6.8(4)
C17	0.8087(7)	0.0068(3)	0.9597(5)	7.2(4)
C18	0.7968(6)	0.0561(3)	0.9069(5)	6.0(4)
C19	0.5889(5)	0.0953(2)	0.6260(5)	5.0(3)
C20	0.4929(7)	0.0119(3)	0.6390(7)	7.1(4)
C21	0.465(1)	0.0082(3)	0.7439(8)	9.0(6)
C22	1.0571(5)	0.2104(3)	0.8146(5)	5.6(4)
C23	1.0018(6)	0.1336(3)	0.5215(5)	5.8(4)
C24	1.038(1)	0.1979(6)	0.3924(9)	12.8(8)
C25	0.951(2)	0.1895(6)	0.325(1)	17(1)
C26	1.2448(7)	0.1852(3)	0.8835(7)	8.6(5)
C27	1.301(1)	0.1606(5)	0.7936(9)	11.4(7)
C28	0.7277(7)	0.1052(3)	0.9204(6)	7.2(5)
C29	0.550(1)	0.1473(6)	0.008(1)	14(1)
C30	0.632(1)	0.169(1)	0.055(1)	28(2)
Ni dipyrromethene				
Ni	0.24843(2)	0.25421(5)	0.50695(7)	2.92(2)
Cl1	0.0835(2)	0.2220(1)	0.9942(2)	5.69(6)
Cl2	0.2431(2)	−0.0673(1)	0.1474(2)	5.28(6)
Cl3	0.0870(1)	0.5646(1)	0.3992(2)	4.85(6)
Cl4	0.7019(1)	0.5324(1)	0.7972(1)	4.35(5)
Cl5	0.3601(1)	0.6775(1)	0.5830(1)	4.16(5)
Cl6	0.0488(2)	−0.0104(1)	0.8501(2)	5.27(6)
Cl7	0.7089(1)	0.2986(1)	0.7996(2)	5.16(6)
Cl8	0.1352(1)	−0.1692(1)	0.3920(2)	5.01(6)
O1	0.3150(3)	0.2646(3)	0.3164(3)	3.7(1)
O2	0.3395(4)	0.1629(3)	0.1590(4)	4.7(2)
O3	0.0691(3)	0.2358(3)	0.3921(4)	4.1(1)
O4	−0.0285(3)	0.3304(3)	0.3171(4)	4.8(2)
O5	0.1164(5)	0.3918(4)	0.7905(8)	13.1(4)
O6	0.2952(4)	0.4084(3)	0.8404(5)	6.8(2)
O7	0.4752(4)	0.1259(3)	0.5066(4)	5.0(2)
O8	0.4439(3)	0.1078(2)	0.7036(4)	4.2(1)
N1	0.1787(4)	0.2026(3)	0.6628(4)	3.2(2)
N2	0.4198(4)	0.3114(3)	0.6092(4)	2.7(1)
N3	0.2483(4)	0.3895(3)	0.5166(4)	2.8(1)
N4	0.2242(4)	0.1164(3)	0.4324(4)	3.0(2)
C1	0.1132(5)	0.1867(4)	0.8488(5)	3.8(2)
C2	0.0997(5)	0.0958(4)	0.7909(5)	3.7(2)
C3	0.1396(4)	0.1034(4)	0.6747(5)	3.0(2)
C4	0.1625(5)	0.2510(4)	0.7656(5)	3.4(2)
C5	0.2260(5)	−0.0052(4)	0.2844(5)	3.4(2)
C6	0.1794(5)	−0.0474(4)	0.3809(5)	3.4(2)
C7	0.1787(5)	0.0301(4)	0.4737(5)	3.2(2)
C8	0.2528(4)	0.0970(4)	0.3205(5)	3.1(2)
C9	0.1772(5)	0.5077(4)	0.4661(5)	3.5(2)
C10	0.2864(5)	0.5524(4)	0.5391(5)	3.3(2)
C11	0.3327(4)	0.4791(3)	0.5676(5)	2.6(2)
C12	0.1567(5)	0.4059(4)	0.4538(5)	3.1(2)
C13	0.5984(5)	0.3331(4)	0.7285(5)	3.2(2)
C14	0.4902(4)	0.2662(3)	0.6524(5)	2.7(2)
C15	0.4820(4)	0.4127(3)	0.6552(5)	2.7(2)
C16	0.5934(5)	0.4231(4)	0.7259(5)	3.3(2)
C17	0.4423(5)	0.4874(3)	0.6337(5)	2.9(2)
C18	0.1409(5)	0.0264(4)	0.5882(6)	3.4(2)
C19	0.3051(5)	0.1825(4)	0.2651(5)	3.5(2)
C20	0.3951(6)	0.2471(5)	0.1007(6)	5.7(3)
C21	0.4255(8)	0.2054(6)	−0.0152(7)	8.7(4)
C22	0.0611(5)	0.3166(4)	0.3850(5)	3.5(2)
C23	−0.1250(6)	0.2437(5)	0.2468(8)	6.7(3)
C24	−0.1928(8)	0.2681(6)	0.1425(8)	8.5(4)
C25	0.1929(6)	0.3595(4)	0.7964(6)	4.3(2)
C26	0.131(1)	0.4868(9)	0.874(2)	6.2(6)
C27	0.043(1)	0.486(1)	0.946(2)	8.1(8)
C28	0.4674(5)	0.1579(4)	0.6101(6)	3.3(2)
C29	0.4365(6)	0.0050(4)	0.6751(7)	5.6(3)
C30	0.4178(8)	−0.0379(5)	0.7899(8)	8.3(4)
C26′	0.334(2)	0.508(1)	0.905(1)	8.4(7)
C27′	0.456(2)	0.537(1)	0.984(2)	10.6(9)
Cu dipyrromethene				
Cu	0.2493(1)	0.2592(1)	0.5085(1)	3.40(6)
Cl1	0.3617(3)	0.6798(2)	0.5824(3)	4.4(1)
Cl2	0.0865(3)	0.5686(2)	0.4000(4)	5.1(1)
Cl3	0.0828(4)	0.2203(3)	0.9999(4)	5.8(2)
Cl4	0.7062(3)	0.5356(2)	0.7998(3)	4.1(1)

(continued)

TABLE 2. *(continued)*

Atom	x	y	z	B_{eq}
Cl5	0.2428(3)	−0.0652(2)	0.1562(3)	5.3(1)
Cl6	0.1361(3)	−0.1629(2)	0.3987(4)	5.2(1)
Cl7	0.7142(3)	0.3008(2)	0.8001(4)	5.1(1)
Cl8	0.0497(3)	−0.0115(2)	0.8488(4)	5.4(1)
O1	0.3424(8)	0.1597(6)	0.1642(8)	4.9(4)
O2	0.3224(8)	0.2688(6)	0.3080(8)	4.9(4)
O3	0.289(1)	0.4117(8)	0.834(1)	10.4(6)
O4	0.116(1)	0.3939(9)	0.817(2)	14.6(8)
O5	0.0637(8)	0.2385(6)	0.3888(8)	4.6(3)
O6	−0.0305(7)	0.3360(6)	0.3182(9)	4.9(4)
O7	0.4798(8)	0.1266(6)	0.5081(9)	5.1(4)
O8	0.4471(7)	0.1096(6)	0.7045(8)	4.1(3)
N1	0.2505(8)	0.3918(7)	0.5194(8)	2.8(4)
N2	0.4233(8)	0.3136(6)	0.6070(8)	2.8(3)
N3	0.1760(9)	0.2064(7)	0.667(1)	3.5(4)
N4	0.2285(8)	0.1234(6)	0.433(1)	2.9(4)
C1	0.333(1)	0.4811(8)	0.567(1)	2.5(4)
C2	0.286(1)	0.5562(8)	0.539(1)	2.8(4)
C3	0.174(1)	0.509(1)	0.465(1)	3.5(5)
C4	0.155(1)	0.4065(8)	0.456(1)	3.6(5)
C5	0.488(1)	0.4165(8)	0.654(1)	2.4(4)
C6	0.599(1)	0.4263(9)	0.727(1)	3.0(4)
C7	0.605(1)	0.3363(9)	0.730(1)	3.6(5)
C8	0.494(1)	0.2681(8)	0.652(1)	3.3(5)
C9	0.445(1)	0.4910(9)	0.632(1)	3.0(4)
C10	0.256(1)	0.1011(8)	0.324(1)	2.7(4)
C11	0.225(1)	−0.0022(8)	0.291(1)	3.3(5)
C12	0.182(1)	−0.0412(8)	0.386(1)	3.5(5)
C13	0.179(1)	0.0384(8)	0.480(1)	3.2(5)
C14	0.139(1)	0.0304(8)	0.593(1)	3.7(5)
C15	0.138(1)	0.1059(9)	0.679(1)	3.4(5)
C16	0.098(1)	0.097(1)	0.795(1)	4.2(5)
C17	0.111(1)	0.186(1)	0.856(1)	4.1(5)
C18	0.159(1)	0.2537(8)	0.772(1)	3.8(5)
C19	0.438(1)	0.007(1)	0.672(1)	5.4(6)
C20	0.314(1)	0.186(1)	0.266(1)	3.8(5)
C21	0.399(2)	0.239(1)	0.099(1)	6.4(7)
C22	0.426(2)	0.197(1)	−0.011(2)	10(1)
C23	0.188(1)	0.362(1)	0.802(1)	4.3(6)
C24	0.122(3)	0.488(2)	0.894(3)	5(1)
C25	0.036(4)	0.494(3)	0.955(4)	10(2)
C26	0.059(1)	0.322(1)	0.380(1)	3.5(5)
C27	−0.127(1)	0.251(1)	0.249(2)	6.5(7)
C28	−0.190(2)	0.271(2)	0.145(2)	12(1)
C29	0.469(1)	0.1599(9)	0.608(1)	3.6(5)
C30	0.418(2)	−0.037(1)	0.785(2)	8.5(8)
C24′	0.339(4)	0.512(2)	0.905(2)	8(1)
C25′	0.467(3)	0.529(2)	0.989(4)	9(2)

mutual perpendicularity of the ligands can be viewed readily for the Ca(II) and Ni(II) complexes in Figs. 1 and 3, respectively.

Average bond distances and estimated standard deviations (e.s.d.) (sigma average = $\Sigma|(\text{ave.} - \text{obs.})^2|/N(N-1)$) were computed for equivalent atoms in the four rings for both the Ca(II) and Ni(II) chelates. The average N–Ca(II) bond length is 2.510(3) Å while the average O–Ca(II) bond length is 2.484(11) Å. The average N–Ni(II) and N–Cu(II) bond distances are 2.03(3) and 2.03(6) Å, respectively. Average nitrogen to transition metal bond distances are shorter than the N–Ca(II) bond distances and reflect the smaller transition metal covalent radii: Ni(II), 0.70 Å; Cu(II), 0.87 Å versus Ca(II) 1.26 Å [18].

Discussion

The observed coordination of the Ca(II) ion to the nitrogen atoms of the dipyrromethene complex is unusual in that it represents a 'hard–soft' metal donor interaction but the N–Ca(II) bond distance compares well with other examples of Ca(II) complexes with aromatic nitrogen ligands [19, 20]. The observed N–Ni(II) and N–Cu(II) bond distances for the dipyrromethene complexes are also in agreement with the literature values of several complexes of these metal ions [21–26].

Crystal packing influences do not appear to affect the geometries of the dipyrromethene chelates. There are no intermolecular contacts between non-hydrogen atoms of less than 3.0 Å in any of the complexes.

Coplanarity of the pyrrole rings in the individual dipyrromethene ligands is almost completely maintained, as the interplanar angles for the Ca(II) complex are 5.2 and 6.1°, and those of the Ni(II) and Cu(II) complexes are about 2.0°. Electron delocalization across the two pyrrole planes of each ligand can also be determined by the bond lengths of the atoms in the pyrrole planes which are connected by the methene bridges. The difference in C–N bond lengths on opposite sides of the ring is about 0.06 Å (significant compared to e.s.d.s in the third decimal place for the Ca(II) and Ni(II) complexes). The shorter C–N bond occurs on the side of the pyrrole ring that is opposite the methene bridge and can be explained by the greater electron density imparted by resonance conjugation through the methene carbon atoms. Similar differences in C–N bond lengths in pyrrole rings were reported by Cotton *et al.* [9] and also by March *et al.* [27].

The planarity of the ring system in the dipyrromethene ligand of metal chelates is explained by the stabilizing influences observed in the free ligands. In the single crystal X-ray structure of 5,5′-dicarbethoxy-3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrromethene [28] it was found that the 5- and 5′-substituted ligand has an almost planar *syn-Z* conformation which is stabilized by intramolecular N–H...N hydrogen bonding. The ligand is bent at the methene bridge to give approximate C_{2v} symmetry with an interplanar angle between the pyrrole rings of 0.6°. Furthermore, the hydrobromide of the same ligand was determined [29] to possess an almost

TABLE 3. Intramolecular bond distances for the Ca(II), Ni(II) and Cu(II) chelates of dipyrromethene

Atom	Atom	Distance	Atom	Atom	Distance	Atom	Atom	Distance
Ca dipyrromethene								
Ca	O3	2.458(4)	O5	C23	1.314(7)	C6	C7	1.426(7)
Ca	O2	2.474(4)	O5	C24	1.50(1)	C7	C8	1.339(8)
Ca	O6	2.498(5)	O6	C23	1.210(7)	C8	C9	1.419(8)
Ca	N4	2.502(5)	O7	C28	1.187(8)	C9	C22	1.475(8)
Ca	O7	2.504(5)	O8	C28	1.311(8)	C10	C11	1.413(8)
Ca	N3	2.507(5)	O8	C29	1.76(1)	C10	C23	1.466(8)
Ca	N1	2.515(5)	N1	C1	1.312(6)	C11	C12	1.358(9)
Ca	N2	2.516(5)	N1	C2	1.377(6)	C12	C13	1.420(9)
Cl 1	C5	1.716(6)	N2	C9	1.330(7)	C13	C14	1.38(1)
Cl 2	C7	1.721(6)	N2	C6	1.372(7)	C14	C15	1.36(1)
Cl 3	C4	1.705(6)	N3	C10	1.323(7)	C15	C16	1.440(9)
Cl 4	C8	1.719(6)	N3	C13	1.376(7)	C16	C17	1.34(1)
Cl 5	C12	1.722(6)	N4	C18	1.324(7)	C17	C18	1.419(9)
Cl 6	C16	1.710(7)	N4	C15	1.389(7)	C18	C28	1.47(1)
Cl 7	C11	1.704(7)	C1	C4	1.424(8)	C20	C21	1.47(1)
Cl 8	C17	1.714(8)	C1	C19	1.469(8)	C24	C25	1.31(2)
O1	C19	1.317(6)	C2	C3	1.369(8)	C26	C27	1.53(1)
O1	C20	1.462(8)	C2	C5	1.436(7)	C29	C30	1.21(2)
O2	C19	1.206(6)	C3	C6	1.382(8)			
O3	C22	1.213(7)	C4	C5	1.339(7)			
O4	C26	1.485(8)						
Ni dipyrromethene								
Ni	N3	1.968(4)	O6	C25	1.226(7)	C8	C19	1.451(7)
Ni	N4	1.983(4)	O6	C26′	1.42(1)	C9	C10	1.360(7)
Ni	N2	2.082(4)	O7	C28	1.180(6)	C9	C12	1.412(7)
Ni	N1	2.107(4)	O8	C28	1.318(6)	C10	C11	1.411(7)
Ni	O3	2.285(4)	O8	C29	1.468(7)	C11	C17	1.393(7)
Ni	O1	2.326(4)	N1	C4	1.318(7)	C12	C22	1.465(7)
Cl 1	C1	1.715(6)	N1	C3	1.400(6)	C13	C16	1.339(7)
Cl 2	C5	1.712(5)	N2	C14	1.317(6)	C13	C14	1.428(7)
Cl 3	C9	1.716(6)	N2	C15	1.413(6)	C14	C28	1.513(7)
Cl 4	C16	1.715(5)	N3	C12	1.333(7)	C15	C17	1.366(7)
Cl 5	C10	1.726(5)	N3	C11	1.369(6)	C15	C16	1.421(7)
Cl 6	C2	1.711(5)	N4	C8	1.329(6)	C20	C21	1.48(1)
Cl 7	C13	1.712(6)	N4	C7	1.363(6)	C23	C24	1.43(1)
Cl 8	C6	1.708(5)	C1	C2	1.345(7)	C26	C27	1.45(2)
O1	C19	1.219(6)	C1	C4	1.432(8)	C29	C30	1.45(1)
O2	C19	1.311(6)	C2	C3	1.415(7)	C26′	C27′	1.51(3)
O2	C20	1.467(7)	C3	C18	1.377(7)			
O3	C22	1.226(6)	C4	C25	1.488(8)			
O4	C22	1.314(6)	C5	C6	1.376(8)			
O4	C23	1.453(7)	C5	C8	1.411(7)			
O5	C25	1.196(8)	C6	C7	1.419(7)			
O5	C26	1.50(1)	C7	C18	1.382(7)			
Cu dipyrromethene								
Cu	N1	1.91(1)	O6	C26	1.28(1)	C8	C29	1.50(2)
Cu	N4	1.96(1)	O6	C27	1.43(2)	C10	C11	1.41(1)
Cu	N2	2.08(1)	O7	C29	1.17(1)	C10	C20	1.48(2)
Cu	N3	2.18(1)	O8	C29	1.35(1)	C11	C12	1.34(2)
Cu	O5	2.34(1)	O8	C19	1.46(1)	C12	C13	1.45(2)
Cu	O2	2.49(1)	N1	C1	1.34(1)	C13	C14	1.40(2)
Cl 1	C2	1.70(1)	N1	C4	1.35(2)	C14	C15	1.35(2)
Cl 2	C3	1.70(1)	N2	C8	1.31(1)	C15	C26	1.43(2)
Cl 3	C17	1.69(1)	N2	C5	1.43(1)	C16	C17	1.33(2)

(continued)

TABLE 3. *(continued)*

Atom	Atom	Distance	Atom	Atom	Distance	Atom	Atom	Distance
Cl 4	C6	1.70(1)	N3	C18	1.33(2)	C17	C18	1.47(2)
Cl 5	C11	1.71(1)	N3	C15	1.41(1)	C18	C23	1.47(2)
Cl 6	C12	1.70(1)	N4	C10	1.31(1)	C19	C30	1.46(2)
Cl 7	C7	1.69(1)	N4	C13	1.39(1)	C21	C22	1.41(2)
Cl 8	C16	1.70(1)	C1	C9	1.40(2)	C24	C25	1.39(5)
O1	C20	1.27(1)	C1	C2	1.43(2)	C27	C28	1.36(2)
O1	C21	1.47(2)	C2	C3	1.38(2)	C24′	C25′	1.61(5)
O2	C20	1.20(1)	C3	C4	1.42(2)			
O3	C23	1.20(2)	C4	C26	1.44(2)			
O3	C24′	1.44(2)	C5	C9	1.37(2)			
O4	C23	1.17(2)	C5	C6	1.41(2)			
O4	C24	1.48(3)	C6	C7	1.33(2)			
O5	C26	1.24(1)	C7	C8	1.45(2)			

TABLE 4. Selected intramolecular bond angles for the Ca(II), Ni(II) and Cu(II) chelates of dipyrromethene

Atom	Atom	Atom	Angle
Ca dipyrromethene			
O3	Ca	O2	157.8(1)
O3	Ca	O6	89.4(2)
O3	Ca	N4	83.1(1)
O3	Ca	O7	94.6(2)
O3	Ca	N3	77.9(1)
O3	Ca	N1	136.0(1)
O3	Ca	N2	65.4(1)
O2	Ca	O6	102.1(1)
O2	Ca	N4	75.4(1)
O2	Ca	O7	81.5(1)
O2	Ca	N3	89.7(1)
O2	Ca	N1	65.1(1)
O2	Ca	N2	135.4(1)
O6	Ca	N4	135.9(2)
O6	Ca	O7	158.9(2)
O6	Ca	N3	65.0(2)
O6	Ca	N1	83.2(1)
O6	Ca	N2	77.1(1)
N4	Ca	O7	65.2(2)
N4	Ca	N3	70.9(2)
N4	Ca	N1	130.1(2)
N4	Ca	N2	135.4(2)
O7	Ca	N3	136.0(2)
O7	Ca	N1	79.5(2)
O7	Ca	N2	85.8(2)
N3	Ca	N1	134.5(2)
N3	Ca	N2	126.9(2)
N1	Ca	N2	70.6(1)
Ni dipyrromethene			
N3	Ni	N4	159.7(2)
N3	Ni	N2	88.7(2)
N3	Ni	O3	75.8(2)
N3	Ni	N1	105.4(2)
N3	Ni	O1	90.2(2)
N4	Ni	N2	104.5(2)
N4	Ni	O3	89.7(2)
N4	Ni	N1	88.7(2)
N4	Ni	O1	75.3(2)
N2	Ni	N1	96.2(2)
N2	Ni	O3	164.3(2)
N2	Ni	O1	88.0(2)
N1	Ni	O3	90.7(2)
N1	Ni	O1	163.9(2)
O3	Ni	O1	89.2(2)
Cu dipyrromethene			
N1	Cu	N4	159.8(4)
N1	Cu	N2	89.3(4)
N1	Cu	O2	90.9(4)
N1	Cu	N3	104.9(4)
N1	Cu	O5	77.2(4)
N4	Cu	N2	102.1(4)
N4	Cu	O2	73.6(4)
N4	Cu	N3	90.1(4)
N4	Cu	O5	89.6(4)
N2	Cu	N3	98.0(4)
N2	Cu	O2	85.7(4)
N2	Cu	O5	165.7(4)
N3	Cu	O2	163.8(4)
N3	Cu	O5	89.9(4)
O5	Cu	O2	90.0(4)

planar *Z* configuration where the Br^- anion is connected via two hydrogen bonds to the ring nitrogen atoms. In addition, the planarity of the related tripyrromethene was investigated by determination of the crystal structure of 3,3′,3″,5,5″-pentamethyltripyrro-2,2′-methene-5′,2″-ethene hydrochloride hydrate, which was found to contain two ligand groups held together by four N—H..Cl hydrogen bonds and two N—H...H_2O hydrogen bonds [30]. The tripyrro-

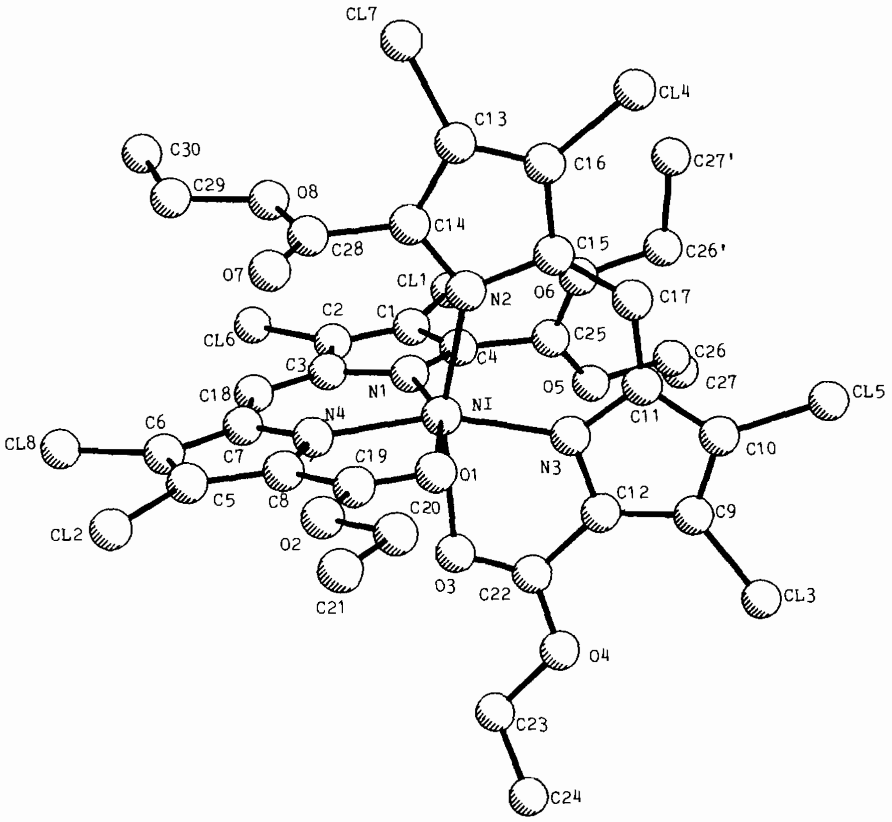

Fig. 3. Molecular representation of the Ni(II) dipyrromethene complex in side view showing the near-perpendicularity of the two ligands.

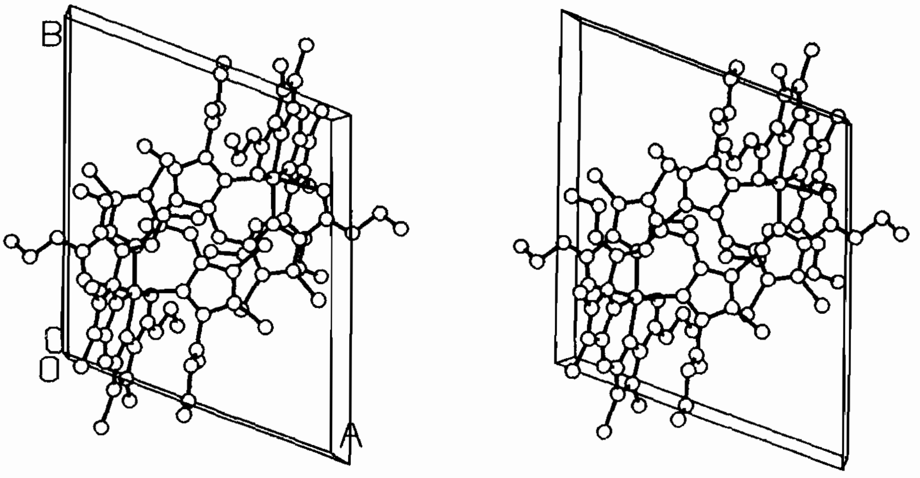

Fig. 4. Stereoview of the Ni(II) complex of dipyrromethene.

methene groups are almost planar and electron delocalization occurs over the whole of the ligand group since conjugation extends across the methene and ethylene bridges between the pyrrole rings.

These arguments do not preclude the possibility that in some instances a bivalent metal ion complex with substituted dipyrromethenes could have a planar coordination environment about the metal ion at the expense of loss of planarity in the ring system of the ligand. In fact, a planar coordination of Pd(II) with four pyrrole nitrogen atoms of the ligand bis-(4,4'-dicarbethoxy-3,3',5,5'-tetramethyldipyrromethene) [31] was determined to form by a folding of the ligands at C–N bonds adjacent to the bridge atoms such that each pyrrole ring was tilted 14.7° to 17.0° with respect to the nitrogen–Pd(II) plane to give the complex a saddle shape. The folded configuration of the ligand groups overcomes short intramolecular contacts between methyl groups, yet the π-delocalization of the ligand was impaired only slightly by the deformation of the rings since folding occurred at the C–N bond of each pyrrole ring rather than at the bridging carbon atoms.

Another example of a square-planar coordination environment about Pd(II) is the solid state chelate of 3,4′-bis-(carbethoxy)-5-chloro-3′,4,5′-trimethyldipyrromethene [27]. One of the nitrogen atoms of a dipyrromethene is displaced from the metal ion, rendering the ligand unidentate. The square coordination plane of Pd(II) thus consists of three planar nitrogen atoms which are supplied by the unidentate ligand, the other unchanged bidentate dipyrromethene ligand and a Cl^- anion. The distortion of the pyrrole planes away from planarity was explained by molecular overcrowding imparted by repulsive forces between the bidentate ligand and the uncoordinated nitrogen atom.

The results of the present single crystal X-ray diffraction studies indicate that the preferred conformation of dipyrromethene ligands in bivalent metal complexes in the solid state is one in which the ligand planes are essentially mutually perpendicular, in agreement with other structural studies [8, 9]. The influence of the coordinated carbonyl oxygen atoms is to distort the least-squares planes away from 90.0°. Thus, for the Ni(II) and Cu(II) chelates, the distorted octahedral N_4O_2 metal configurations [7] are confirmed.

Greater distortions away from a tetrahedral N donor arrangement toward a planar arrangement are possible, but occur as in the Pd(II) complexes at the expense of the coplanarity of the pyrrole rings or by breaking one of the metal to nitrogen coordinate bonds. Interestingly, the coordination of four carbonyl oxygen atoms to the Ca(II) ion in the dipyrromethene complex and the resultant dodecahedral coordination of Ca(II) is accomplished with only a slightly larger disruption of the tetrahedral conformation of the two dipyrromethene ligands than for Cu(II) and Ni(II). Therefore, the order of distortion in this system is $Cu(II) = Ni(II) < Ca(II)$, and is a function primarily of the tendency of the metal ion to coordinate the carbethoxy oxygen atoms.

Supplementary Material

Tables listing structure factors, anisotropic thermal parameters, hydrogen positional parameters, intermolecular non-bonding contact distances, intramolecular bond angles, least-squares planes and dihedral angles are available from the authors.

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