{Glyoxal bis[(2*S*)-pyrrolidin-2-ylmethylimine]}metal Tetrachlorometallate Complexes. The Detection of Polynuclear Complex Formation in Solution by Circular Dichroism[†]

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The Cu^{II}, Ni^{II}, Pd^{II}, and Co^{II} complexes of the tetradentate chiral ligand, glyoxal bis[(2*S*)-pyrrolidin-2-ylmethylimine] (gpmi) have been prepared. Circular dichroism spectra show strong peaks in the absorption range of the free $[M'Cl_4]^{2-}$ (M' = Cu, Ni, or Co) ions which indicate the polynuclear structures achieved by chloro-bridging between M and M' (M = Cu, Ni, and Co) persist in solution at concentrations >3 mmol dm^{-3}.

The importance of α-di-imine chelate complexes in a variety of analytical, organic, and bioinorganic reactions, and in catalysis, has been widely recognized.[1,2] The introduction of chiral carbon atoms into the di-imine chelate rings is expected to cause asymmetric reactions and asymmetric catalysis. For example, the (2*S*)-pyrrolidin-2-yl group has recently been utilized as an asymmetric centre in organic[3] and organometallic[4] enantioselective reactions. The presence of a disubstituted chiral nitrogen in the pyrrolidinyl moiety seems to be required to achieve effective enantioselection.

In this paper, we report the preparation of Cu^{II}, Ni^{II}, Pd^{II}, and Co^{II} complexes of glyoxal bis[(2*S*)-pyrrolidin-2-ylmethylimine] (gpmi), which is a chiral tetradentate di-imine chelate ligand. The circular dichroism (c.d.) study of the complexes in polar solvents has revealed polynuclear complex formation between the chelate cation $[M(gpmi)]^{2+}$ and the tetrachlorometallate anion. This appears to be an interesting example of the study of metal complexes with polynuclear M–Cl–M–Cl–M chains utilizing c.d. spectroscopy.

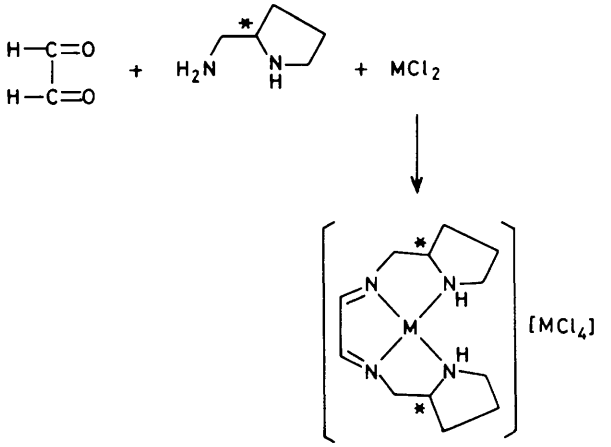
Results and Discussion

The gpmi complexes were all prepared by the template condensation of glyoxal with (2*S*)-pyrrolidin-2-ylmethylamine (pma) in the presence of the appropriate metal chloride in ethanol [equation (1)]. In the absence of the metal salts, the condensation gave a red-brown liquid from which colourless crystals of the mono-condensation product could be isolated.

A similar template condensation between diacetyl or benzil and pma was unsuccessful perhaps for steric reasons. The presence of three five-membered rings as in the gpmi complexes would be envisaged to create some steric strain.

Mononuclear chloride complexes, $[M(gpmi)_2]Cl_2$, were not isolated even in the presence of excess gpmi, but in one instance we have isolated a bromide complex, $[Co(gpmi)_2]Br_2$.

Analytical and spectroscopic data for the $[M(gpmi)][MCl_4]$ complexes prepared in this study are listed in Tables 1 and 2. Since some of the complexes are hygroscopic and the condensation reaction was not always complete, satisfactory analytical data could not be always obtained. The complexes dissolve in water, methanol, *NN*-dimethylformamide (dmf), and dimethyl sulphoxide (dmso). In the case of M = Ni, the extreme solubility and hygroscopic nature of the complex prevented its isolation. The Co^{II} complexes however were stable in air, thus facilitating their characterization.



(1)

The addition of different metal chlorides to the reaction mixtures gave the heterometal complexes, $[M(gpmi)][M'Cl_4]$. The spectral characterization of these indicated a preference of the metal ions for the formation of either the tetrachlorometallate anion or for the gpmi cationic complex $[M(gpmi)]^{2+}$.

Anion exchange reactions with ClO_4^- or BPh_4^- have not been successful. In the case of $[PdCl_4]^{2-}$, uncharacterized yellow-brown and brown precipitates were obtained from $[Ni(gpmi)][CoCl_4]$ and $[Co(gpmi)][CoCl_4]$ in methanol, respectively.

Busch *et al.*[5] have prepared [diacetyl bis(3-aminopropylimine)]nickel(II) tetrachlorozincate, $[Ni(dapi)][ZnCl_4]$, and related complexes, and proposed polynuclear solid-state structures with Ni–Cl–Zn–Cl chains. Hatano and co-workers[6] also prepared nickel(II) complexes of *NN'*-bis[(2*S*)-pyrrolidin-2-ylmethyl]ethylene-1,2-diamine (pmen) and 1,2-bis[(2*S*)-2-(aminomethyl)pyrrolidin-1-yl]ethane (ampe), but these do not contain such chains. The α-di-imine ligand thus appears to favour polymeric metal–chloride interaction. In this connection it is interesting to point out that the nickel(II) complex of 2,12-dimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene forms a five-co-ordinate complex with a chloride ion in nitromethane solution.[7]

The i.r. spectra (Table 2) of the gmpi complexes indicate the presence of the co-ordinated imine group (band at 1 600—1 645 cm^{-1}) and tetrachlorometallate anion (bands at 290—304 cm^{-1} and at 110—140 cm^{-1}). The low-frequency absorptions are metal–chlorine stretching and deformation

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[†] *Non-S.I. unit employed:* 1 B.M. = 0.927×10^{-23} A m^2.

Table 1. Analytical data of [M(gpmi)][$M'X_4$] type complexes

	Calc. (%)				Found (%)			
Complex	C	H	N	Metal *	C	H	N	Metal *
(1) [Cu(gpmi)][$CuCl_4$]	29.35	4.50	11.40	25.85 (Cu)	29.85	5.00	10.30	25.3 (Cu)
(2) [Cu(gpmi)][$ZnCl_4$]	29.25	4.50	11.35	12.90 (Cu), 13.25 (Zn)	29.15	4.95	10.70	12.5 (Cu), 12.8 (Zn)
(3) [Cu(gpmi)][$CuBr_4$]	21.55	3.30	8.35		22.35	3.35	8.25	
(4) [Ni(gpmi)][$ZnCl_4$]	29.50	4.55	11.50		33.70	5.45	11.90	
(5) [Ni(gpmi)][$CoCl_4$]	29.90	4.60	11.65	12.20 (Ni), 12.10 (Co)	30.95	5.55	11.65	12.0 (Ni), 12.6 (Co)
(6) [Co(gpmi)][$CoCl_4$]	29.90	4.60	11.60	24.45 (Co)	28.90	5.00	10.05	25.1 (Co)
(7) [Co(gpmi)][$ZnCl_4$]	29.50	4.55	11.45		30.60	5.70	10.10	
(8) [Co(gpmi)][$NiCl_4$]	29.90	4.60	11.65	12.10 (Co), 12.20 (Ni)	31.85	5.40	10.95	12.5 (Co), 11.8 (Ni)
(9) [Co(gpmi)]Br_2	32.70	5.05	12.70		31.90	5.00	11.20	
(10) [Pd(gpmi)][$PdCl_4$]	25.00	3.85	9.70	36.90 (Pd)	25.45	4.30	9.10	36.6 (Pd)

* Analyses of metals were carried out using a Jarrel Ash model AA-8500 atomic absorption spectrometer.

Table 2. Infrared spectral data (cm^{-1}) for the complexes [M(gpmi)][$M'X_4$]

Complex	ν(NH),(NH_2)	ν(C=N)	ν(M–N)	ν(M′–Cl)	δ(Cl–M′–Cl)
(1) [Cu(gpmi)][$CuCl_4$]	3 430, 3 200	1 640, 1 620	465, 440	290	140, 126
(2) [Cu(gpmi)][$ZnCl_4$]	3 450, 3 210	1 645, 1 625	485	290	130
(3) [Cu(gpmi)][$CuBr_4$]	3 400, 3 170, 3 100	1 640, 1 615	—	300	110
(4) [Ni(gpmi)][$ZnCl_4$]	3 400, 3 210	1 640	—	294	130
(5) [Ni(gpmi)][$CoCl_4$]	3 400, 3 220	1 645, 1 612	—	304	130
(6) [Co(gpmi)][$CoCl_4$]	3 430, 3 160, 3 110	1 605br	300br *		130
(7) [Co(gpmi)][$ZnCl_4$]	3 440, 3 200	1 600br	295br *		130
(8) [Co(gpmi)][$NiCl_4$]	3 400, 3 240	1 640, 1 615br	306br *		140
(9) [Co(gpmi)]Br_2	3 400, 3 170, 3 070	1 600br	565,* 518,* 234,* 92 *		
(10) [Pd(gpmi)][$PdCl_4$]	3 420, 3 180, 3 120	1 615br			

* Unassignable.

vibrations and are in the range reported for tetramethylammonium tetrachlorometallates, $[NMe_4]_2[MCl_4]$ (M = Co, Ni, Cu, and Zn).[8]

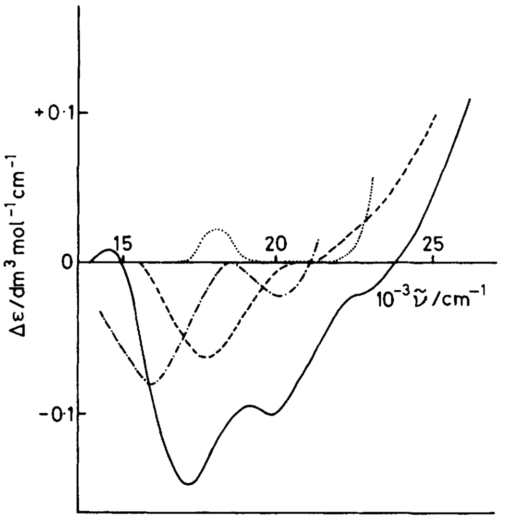

Figure 1. Concentration dependence of the c.d. spectra of [Ni(gpmi)][$CoCl_4$] (5) and [Co(gpmi)][$NiCl_4$] (8) in dmf. [Ni(gpmi)][$CoCl_4$]: 3.4 mmol dm^{-3} (——); 1.0 mmol dm^{-3} (— — —). [Co(gpmi)][$NiCl_4$]: 3.0 mmol dm^{-3} (— · — · —), 0.8 mmol dm^{-3} (· · · ·)

The visible spectra of [Cu(gpmi)][$ZnCl_4$] (2) and [Cu(gpmi)][$CuCl_4$] (1) in methanol show maxima at 15 500 and 15 400 cm^{-1} respectively, indicating a similar ligand field strength of the gpmi ligand as compared with the ligand in α-ethylenebis(3-aminopropylimine)copper(II) ($\lambda_{max.}$ 16 700 cm^{-1}). The presence of the α-di-imine moiety shifts the maximum toward longer wavelengths when comparison is made with the corresponding diamine or tetra-amine ligands such as pmen or ampe. The visible spectrum of [Ni(gpmi)][$ZnCl_4$] (4) shows maxima at 9 750 and 20 600 cm^{-1} in methanol. These bands can be assigned with reference to the spectrum of the [diacetyl bis(3-aminopropylimine)]nickel(II)[5] complex, and the ligand field parameters calculated (Dq_{xy} = 1 260 cm^{-1} and Dq_z = 690 cm^{-1}). The Dq_{xy} and Dq_z values are similar to those obtained for $[Ni(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) and for $[Ni(H_2O)_6]^{2+}$ respectively. The spectrum of [Co(gpmi)][$CoCl_4$] (6) exhibits remarkable solvent and concentration effects. Sharp maxima are observed in dmf at 14 700 and 16 600 cm^{-1} indicating the presence of free $[CoCl_4]^{2-}$ but no such maxima were discernible in methanol. Circular dichroism spectra were measured in dmf at two different concentrations and the extremum at 17 200 cm^{-1} was found to disappear at the lower concentration as shown in Figure 1. If association between the cation and the anion through chloro-ligands is considered to occur as observed for [Ni(dapi)][$ZnCl_4$],[5] the c.d. extremum at 17 200 cm^{-1} may be assigned to a *d–d* transition within the $[CoCl_4]^{2-}$ moiety co-ordinated to the cation $[Co(gpmi)]^{2+}$ containing the optically active chelate ligand. The association of the anion and cation occurs at concentrations higher than 3 mmol dm^{-3}. The c.d. spectrum observed at 1 mmol dm^{-3} is due to the dissociated cation $[(Co(gpmi)(MeOH)_2]^{2+}$, or $[Co(gpmi)(dmf)_2]^{2+}$. At higher concentrations the positive peak at 17 800 cm^{-1} (Δε +0.02 dm^3 mol^{-1} cm^{-1}) for this species is masked by the strong c.d. extremum due to the co-ordinated $[CoCl_4]^{2-}$ moiety. The c.d. peak due to the free $[Ni(gpmi)]^{2+}$ was found to be at 19 700

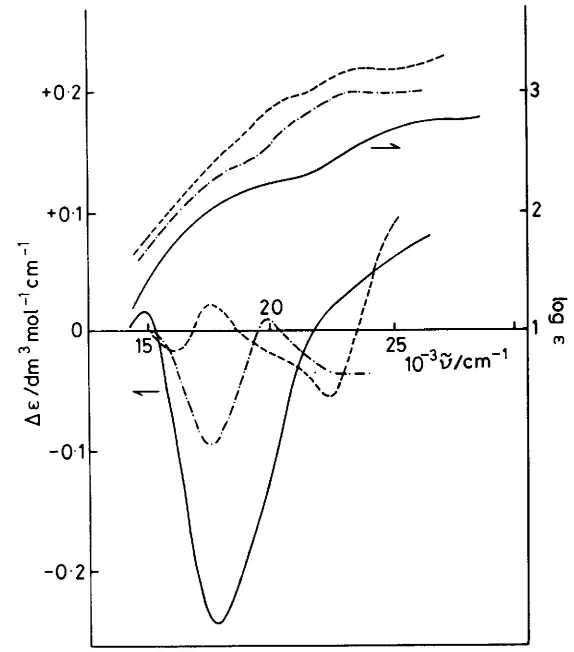

Figure 2. Absorption and c.d. spectra of [Ni(gpmi)][$CoCl_4$] (5) (——), [Co(gpmi)][$NiCl_4$] (8) (— — —), and [Co(gpmi)][$CoCl_4$] (6) (— · — · —) in methanol. Concentration at 3.0 mmol dm^{-3}

cm^{-1} (Δε −0.03 dm^3 mol^{-1} cm^{-1}) from its [$ZnCl_4$]$^{2-}$ salt in methanol or from its [$CoCl_4$]$^{2-}$ salt in dmf (low concentration, Figure 1). Since most Ni^{II} and Co^{II} complexes are labile, there is possibility of a rearrangement of [Ni(gpmi)][$CoCl_4$] (5) or [Co(gpmi)][$NiCl_4$] (8) in solution. The former complex was prepared by the addition of $NiCl_2$ to gpmi followed by the addition of $CoCl_2$ and the latter by the reversed order of addition of these metal chlorides. The visible spectra of both complexes are featureless, but the c.d. spectra in methanol are different (see Figures 1 and 2). The negative c.d. peak of (6) at 16 900 cm^{-1} can be considered to be due to the overlap of positive {due to [Co(gpmi)]$^{2+}$} and negative (due to co-ordinated [$CoCl_4$]$^{2-}$) c.d. peaks. The observed high c.d. intensity of (5) at 16 900 cm^{-1} is then a result of the overlap of two negative c.d. peaks {due to [Ni(gpmi)]$^{2+}$ and co-ordinated [$CoCl_4$]$^{2-}$}. The co-ordinated [$NiCl_4$]$^{2-}$ in (8) may be giving a negative c.d. intensity at a broad range, 16 000—22 000 cm^{-1}, but some hydrolysis products may have caused contamination in this case.

The c.d. spectrum of [Ni(gpmi)][$ZnCl_4$] (4) in methanol exhibits a weak (+) signal at 15 300, a (−) signal at 19 700, and a strong (+) at 24 500 cm^{-1}. The Ni^{II} complex of the saturated analogue of the gpmi ligand, pmen, has been reported[6] to have a (−) peak at 16 900 cm^{-1} and a (+) at 22 500 cm^{-1}. A shift to higher energy is apparent, implying a higher ligand field of gpmi as compared with pmen. Complex (2) showed a (−) peak at 14 800 and a (+) at 19 500 cm^{-1} in methanol, the shape being very similar to that of (4). The complex [Cu(gpmi)][$CuCl_4$] (1) also showed a similar c.d. pattern. Kida and Nishida[9] reported a similarity of square planar Ni^{II} and Cu^{II} chiral tetra-amine chelates in their c.d. patterns where the ligands were the same.

The magnetic susceptibility of the gpmi complexes in the solid state (shown in Table 3) indicates some antiferromagnetic coupling for (1), (5), (6), and (8). The values for these complexes are lower than expected for the sum of the individual moments of the complex ions. The values for (4) (2.3 B.M.) and (7) (3.0 B.M.) are lower than the typical values for normal octahedral Ni^{II} and Co^{II} complexes (2.9—3.3 and 4.3—5.2 B.M., respectively). The values in methanol solutions (concentration, *ca.* 50 mmol dm^{-3}) are lower than those in the solid state. This trend is consistent with polynuclear complex formation in solution as described above. By contrast, the values in dmso are higher than those in the solid state. The association between the cation and anion is thus weaker in dmso.

Table 3. Magnetic properties of the [M(gpmi)][$M'Cl_4$] type complexes

Complexes	$\mu_{eff.}$(B.M.) Solid state[a]	$\mu_{eff.}$(B.M.) In solution[b]
(1) [Cu(gpmi)][$CuCl_4$]	2.5	2.9[c]
(2) [Cu(gpmi)][$ZnCl_4$]	—	1.7[c]
(4) [Ni(gpmi)][$ZnCl_4$]	2.3	2.5[c]
(5) [Ni(gpmi)][$CoCl_4$]	4.7	4.0[d]
(6) [Co(gpmi)][$CoCl_4$]	5.7	5.5[d]
(7) [Co(gpmi)][$ZnCl_4$]	3.0	3.7[c]
(8) [Co(gpmi)][$NiCl_4$]	5.4	4.7[d]

[a] At 292.5 K. [b] Determined by ^{1}H n.m.r. at 313 K. [c] In methanol. [d] In dimethyl sulphoxide (dmso).

The conductivity of some gpmi complexes indicates a considerable association in dmf at concentration higher than 1 mmol dm^{-3}. The values observed [*e.g.* 8 Ω^{-1} cm^2 mol^{-1} for (6) in dmf are lower than that of [NEt_4]$_2$[$CoCl_4$] (20 Ω^{-1} cm^2 mol^{-1}) at a similar concentration. In methanol the conductivity was higher than the value expected for a 2 : 2 electrolyte due to partial hydrolysis in the case of (8), because the tetrachlorometallate anion of Ni or Co is kinetically unstable to a small amount of water.

The Pd^{II} complex [Pd(gpmi)][$PdCl_4$] (10) was prepared in aqueous ethanol and isolated as diamagnetic brown powder, soluble in water. The n.m.r. spectrum of (10) indicates its diamagnetism but the peaks were not well resolved owing to its limited solubility in $CDCl_3$. The solubility in water suggests the complex is not associated. The strong preference of Pd^{II} for square planar co-ordination means association with a tetrachlorometallate anion is not favoured.

The evidence for halogen bridging for the Ni^{II} and Co^{II} complexes cited in this paper is not convincing in view of the complex effect of the solvents, bridging halide, and preference for stacking. However, we think chiral electronic perturbation on the achiral anion as revealed by the c.d. spectra to be noteworthy.

Experimental

Materials.—All chemicals and solvents were of reagent grade and used without further purification or purified by the usual methods if necessary.

Physical Measurements.—The i.r. spectra and far-i.r. spectra were determined by KBr pellet or Nujol mull techniques with JASCO model DS-402G and Hitachi model FIS-3 spectrophotometers, respectively. The near-i.r. spectra were measured in dmf and methanol with a Hitachi model EPI-2 spectrophotometer. The ^{1}H n.m.r. spectra were measured with Varian T-60, Varian A-60, and Varian XL-100 machines. The electronic spectra and c.d. spectra were measured by a JASCO UVIDEC-5A spectrometer and a JASCO J-40 spectropolarimeter, respectively. Magnetic susceptibility data for the solids were obtained at room temperature by the Faraday method using Mohr's salt as the calibrant in Professor M. Koizumi's Laboratory, Osaka University. Magnetic susceptibility data in methanol and dmso were obtained at 40 °C by a Varian A-60 ^1H n.m.r. spectrometer using copper(*II*) nitrate as the calibrant.

Preparation of (S)-*Pyrrolidin*-2-*ylmethylamine* (*pma*).—L-Proline methyl ester was prepared according to the procedure of Hillman.[10] L-Prolinamide was prepared according to the procedure of Putochin [11] with a slight modification.

L-Proline methyl ester (20 cm^3) was dissolved in absolute methanol (230 cm^3) and cooled with chilled water. The solution was saturated with dry NH_3 gas and allowed to stand at room temperature for 3 h. The reaction mixture, cooled to 0 °C, was again saturated with dry NH_3 gas. The solution in a 1 cm^3 round-bottomed flask was heated at 65 °C in a water-bath for 15 h. Methanol was distilled off under reduced pressure. The resulting white product was filtered off, washed with ether, and dried *in vacuo*. The product was used in the next reaction without further purification. Yield 40 g (90%). (*S*)-Pyrrolidin-2-ylmethylamine was prepared according to the procedure of Schnell and Karrer,[12] and isolated as (*S*)-pyrrolidin-2-ylmethylamine dihydrochloride (Found: C, 34.30; H, 8.20; N, 15.75. Calc. for $C_5H_{12}N_2\cdot 2HCl$: C, 34.65; H, 8.15; N, 16.20%); α (H_2O, 588nm) = −5.3° (lit.,[12] −1.2° in water).

$[Cu(gpmi)][CuCl_4]$ (1).—The compound $CuCl_2\cdot 2H_2O$ (1.3 mmol) in dry ethanol (8 cm^3) was added to an ethanolic solution in which pma (2.6 mmol) and glyoxal (40% aqueous solution, 0.2 g, 1.3 mmol) were dissolved. The colour of the solution turned from blue to green. The resulting mixture was heated at 65 °C for 12 h. After cooling, the solution was filtered and diethyl ether was added to the filtrate. The resulting green precipitate was collected, recrystallized from methanol–diethyl ether (1 : 1), and dried over P_2O_5 at reduced pressure. Yield was 40% based on $CuCl_2\cdot 2H_2O$.

$[Cu(gpmi)][ZnCl_4]$ (2).—A reaction mixture of $CuCl_2\cdot 2H_2O$, pma, and glyoxal was heated at 65 °C for 12 h in absolute ethanol as described for $[Cu(gpmi)][CuCl_4]$. After cooling, anhydrous zinc chloride (1.3 mmol), dissolved in anhydrous methanol (3 cm^3), was added and the resulting green precipitate was collected and recrystallized from methanol–diethyl ether (1 : 1) in 60% yield.

$[Ni(gpmi)][ZnCl_4]$ (4).—The preparative procedure was similar to that described above except that $NiCl_2\cdot 6H_2O$ was added instead of $CuCl_2\cdot H_2O$ and the reaction mixture was stirred for 24 h at room temperature before addition of a methanol solution of zinc chloride. The dark red precipitate was recrystallized from boiling methanol. Yield 80%.

$[Cu(gpmi)][CuBr_4]$ (3) *and* $[Ni(gpmi)][CoCl_4]$ (5).—These complexes were prepared in the same manner as described above except that $CuBr_2$ was used instead of $CuCl_2\cdot 2H_2O$ for $[Cu(gpmi)][CuBr_4]$ and $CoCl_2\cdot 6H_2O$ was used instead of $ZnCl_2$ for $[Ni(gpmi)][CoCl_4]$.

$[Co(gpmi)][CoCl_4]$ (6) *and* $[Co(gpmi)][ZnCl_4]$ (7).—All operations were performed in a pure argon atmosphere. The synthetic procedures were similar to those described for the corresponding Cu^{II} or Ni^{II} complexes.

$[Pd(gpmi)][PdCl_4]$ (10).—The complex $Na_2[PdCl_4]$ (0.93 mmol) in H_2O (3 cm^3) was added to an ethanol (15 cm^3) solution in which pma (1.86 mmol) and glyoxal (40% aqueous solution, 0.14 g, 0.93 mmol) were dissolved. The resulting mixture was heated at 65 °C for 12 h. The resulting black precipitate (Pd metal) was filtered off and diethyl ether was added to the filtrate to induce precipitation. The brown product was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield was 28% based on $Na_2[PdCl_4]$.

Conductivity Data.—Taken at 30 °C with bright Pt electrodes, the data are shown in the order: complex, solvent, molar conductivity in Ω^{-1} cm^{-2} mol^{-1}, and concentration in mmol dm^{-3}. $[NEt_4]_2[CoCl_4]$, dmf, 20, 8.9; dmf, 14, 42; $[Cu(pma)_2][ZnCl_4]$, dmf, 8, 15; MeOH, 17, 9.3; $[Co(gpmi)][CoCl_4]$, dmf, 8, 4.4; $[Co(gpmi)][NiCl_4]$, MeOH, 30, 4.5; $[Ni(gpmi)][CoCl_4]$, MeOH, 30, 4.4.

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