

# The coordination chemistry of *N,N'*-ethylenebis(2-acetylpyridine imine) and *N,N'*-ethylenebis(2-benzoylpyridine imine); two potentially tetradentate ligands containing four nitrogen atoms

Sotiris Gourbatsis, Spiros P. Perlepes, and Nick Hadjiliadis\*

Laboratory of Inorganic and General Chemistry, Department of Chemistry, University of Ioannina, 451 10, Ioannina, Greece

George Kalkanis

Department of Chemistry, Physics and Material Technology, Technological Institution of Athens, Egaleo, Athens, Greece

## Summary

New complexes of the general formulae  $[ML_A(H_2O)_2]Cl_2$  ( $M = Ni$  or  $Cu$ ),  $[ML_A X_2]$  ( $M = Co$  or  $Cu$ ;  $X = Cl$  or  $Br$ ),  $[NiL_A Br_2] \cdot H_2O$ ,  $[ML_A][MCl_4]$  ( $M = Pd$  or  $Pt$ ),  $[NiL_B(H_2O)_2]Cl_2 \cdot 2H_2O$ ,  $[ML_B Cl_2]$  ( $M = Co, Ni, Cu, Pd$  or  $Pt$ ;  $X = Cl$  or  $Br$ ) and  $[ML_B][MCl_4]$  ( $M = Pd$  or  $Pt$ ), where  $L_A = N,N'$ -ethylenebis(2-acetylpyridine imine) and  $L_B = N,N'$ -ethylenebis(2-benzoylpyridine imine), have been isolated. The complexes were characterized by elemental analyses, conductivity measurements, t.g./d.t.g. methods, magnetic susceptibilities and spectroscopic (i.r., far-i.r., ligand field,  $^1H$  n.m.r.) studies. Monomeric pseudo-octahedral stereochemistries for the  $Co^{II}$ ,  $Ni^{II}$  and  $Cu^{II}$  complexes and *cis* square planar structures for the compounds  $[ML_B X_2]$  ( $M = Pd$  or  $Pt$ ;  $X = Cl$  or  $Br$ ) are assigned in the solid state. The molecules  $L_A$  and  $L_B$  behave as tetradentate chelate ligands in the  $Co^{II}$ ,  $Ni^{II}$ ,  $Cu^{II}$  and Magnus-type  $Pd^{II}$  and  $Pt^{II}$  complexes, bonding through both the pyridine and methine nitrogen atoms. A bidentate *N*-methine coordination of the Schiff base  $L_B$  is assigned in the  $[ML_B X_2]$  complexes ( $M = Pd$  or  $Pt$ ;  $X = Cl$  or  $Br$ ). The anomalous magnetic moment values of the  $Co^{II}$  complexes are discussed.

## Introduction

Schiff base ligands have played a key role in our understanding of the coordination chemistry of transition metal ions. Transition metal complexes of tetradentate Schiff base ligands are always of interest<sup>(1–5)</sup> since they exhibit a marked tendency to oligomerize, thus leading to novel structural types, and display a wide variety of magnetic properties, act as complex ligands for alkali-metal ions and other metallic elements. They may also serve as models for biologically important species, provide stabilization of various oxidation states, of  $M-C$  bonds and access to bifunctional systems, find applications in analysis and catalysis, form polymers with interesting electrical and thermal properties and also they are relevant to the macrocyclic effect.

Although transition metal complexes of the "classical" tetradentate Schiff base ligands *N,N'*-ethylenebis(acetylacetone imine) and *N,N'*-ethylenebis(salicylaldehyde imine) and their analogues have been known for many years, the coordination chemistry of Schiff base ligands

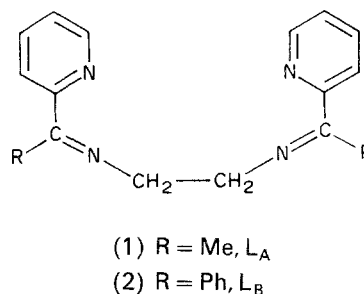


Figure 1. The formulae of the ligands used are as shown.

derived from 2-pyridyl ketones has received only scant attention. We report here the preparation and study of cobalt(II), nickel(II), copper(II), palladium(II) and platinum(II) complexes of the new ligands *N,N'*-ethylenebis(2-acetylpyridine imine) (1) and *N,N'*-ethylenebis(2-benzoylpyridine imine) (2), abbreviated as  $L_A$  and  $L_B$ , respectively.

## Experimental

Elemental analyses, physicochemical measurements and spectroscopic techniques have been carried out by published methods<sup>(6,7)</sup>.

### *N,N'*-ethylenebis(2-acetylpyridine imine) (1)

To a solution of 2-acetylpyridine (0.25 g, 2.01 mmol) in *i*-PrOH (10 cm<sup>3</sup>) was added a solution of ethylenediamine (0.06 g, 1.0 mmol) in *i*-PrOH (10 cm<sup>3</sup>). After stirring at room temperature for 24 h, the solution was allowed to stand at  $-10^\circ C$  overnight. A solid product was precipitated, which was filtered off and washed with ether. The crude ligand was recrystallized from petroleum ether to give white needles which were dried *in vacuo* over silica gel. Yield: 60%. M.p.  $103^\circ C$ . (Found: C, 71.4; H, 6.8; N, 21.8.  $C_{16}H_{18}N_4$ . Calcd.: C, 72.05; H, 6.75; N, 21.0%.)

### *N,N'*-ethylenebis(2-benzoylpyridine imine) (2)

To a solution of 2-benzoylpyridine (0.37 g, 2.1 mmol) in absolute EtOH (10 cm<sup>3</sup>) was added a solution of ethylenediamine (0.06 g, 1.0 mmol) in absolute EtOH (10 cm<sup>3</sup>). The reaction mixture was stirred at room temperature for 48 h during which the solution turned red. The EtOH was then removed by distillation *in vacuo* at room temperature, leaving a red waxy mass. Petroleum ether (100 cm<sup>3</sup>) was added and the residue macerated.

\* Author to whom all correspondence should be directed.

After decantation of the petroleum ether used, this procedure was repeated two or three times to yield a pale brown solid. The mixture was filtered and the insoluble product washed with *i*-PrOH. For further purification the solid product was stirred in *i*-PrOH at room temperature overnight, washed as above and dried *in vacuo* over silica gel. The purified solid was white. Yield: 46%. M.p. 121–123°C. (Found: C, 80.2; H, 5.5; N, 14.5. C<sub>26</sub>H<sub>22</sub>N<sub>4</sub>. Calcd.: C, 80.0; H, 5.7; N, 14.5%).

The two ligands were also characterized by i.r. and <sup>1</sup>H n.m.r. spectroscopy (see below).

#### Preparation of the metal complexes

All the metal complexes in this work were prepared using a 1:1 metal salt:ligand molar ratio. Eight procedures for preparation of complexes were used, varying in the solvents used and the preparative conditions employed (see Table 1).

The first (Method A) involved the direct reaction of a solution of the anhydrous metal chloride or bromide in THF with a solution of the required amount of L<sub>A</sub> or L<sub>B</sub> in a small vol of THF. The reaction mixtures were stirred at room temperature and the precipitates were collected by filtration and washed with THF and Et<sub>2</sub>O. In Method B the complexes were prepared by adding a solution of the required hydrated metal chloride in absolute EtOH to a vigorously stirred solution of the ligand in absolute EtOH; the precipitates so obtained were washed with absolute EtOH and Et<sub>2</sub>O. In Method C the complexes were prepared by mixing a solution of the ligand in THF with an equimolar solution of the appropriate hydrated Ni<sup>II</sup> halide in MeOH and stirring for 24 h. The precipitates formed were removed by filtration and washed with THF and Et<sub>2</sub>O. The fourth method (Method D) involved the direct reaction of a solution of CoCl<sub>2</sub> or NiCl<sub>2</sub>·6H<sub>2</sub>O in *i*-PrOH with a solution of the ligand in the same solvent. The reaction mixtures were stirred overnight and the obtained precipitates were collected by filtration and washed with Et<sub>2</sub>O; the complex [CoL<sub>A</sub>Cl<sub>2</sub>] was purified by recrystallization from absolute EtOH. The Magnus-type Pd<sup>II</sup> complexes were prepared (Method E) by dissolving PdCl<sub>2</sub> in 0.1M HCl and adding an aqueous standard 0.1M NaOH solution till the pH was 5.5; to the clear solution obtained was added a solution of L<sub>A</sub> or L<sub>B</sub> in THF. The reaction mixtures were stirred at room temperature for 24 h and the isolated precipitates were washed with THF and acetone. The Magnus-type Pt<sup>II</sup> complexes were obtained (Method F) by mixing an aqueous solution of K<sub>2</sub>[PtCl<sub>4</sub>] with an equimolar quantity of L<sub>A</sub> or L<sub>B</sub> in the minimum required volume of THF, stirring for 24 h and washing the solids collected after filtration, with *i*-PrOH and Me<sub>2</sub>CO. The complexes [PdL<sub>B</sub>X<sub>2</sub>] (X = Cl or Br) were prepared (Method G) by dissolving PdX<sub>2</sub> in 0.1N HX, adjusting the pH to 5.4 using 0.1M NaOH, adding a solution of L<sub>B</sub> in water–acetic acid (1:3.5) and stirring at room temperature for 20 min. During this time yellow crystals separated from the solution, which were filtered off and washed with small quantities of water, EtOH and THF. For the preparation of the compounds [PtL<sub>B</sub>X<sub>2</sub>] (X = Cl or Br) (Method H) the salt K<sub>2</sub>[PtX<sub>4</sub>] was dissolved in water and L<sub>B</sub> in 0.1N HX; the pH of both solutions was adjusted to 2.5. The two solutions were mixed and stirred at room temperature for 24 h. The obtained precipitates were

filtered off and washed with small portions of water, EtOH and THF.

Working with routes A–E and G, solid product formation was usually rapid (5–10 min). The complexes [CuL<sub>A</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub> and [CuL<sub>B</sub>Cl<sub>2</sub>] did not crystallize from EtOH; the reaction mixtures were refrigerated overnight and precipitation was achieved by the addition of small quantities of Et<sub>2</sub>O. The precipitation of the Pt<sup>II</sup> complexes, prepared by routes F and H, occurred slowly over 7–8 h, but satisfactory yields were achieved after stirring the reaction mixtures for 24 h.

All precipitates were dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. Yields were in the 65–85% range.

## Results and discussion

### Characterization of the ligands

The ligands L<sub>A</sub> and L<sub>B</sub> are formed readily *via* Schiff base condensation of ethylenediamine with the required 2-pyridyl ketone in a 1:2 molar ratio. The pure products are soluble in THF, acetone and alcohols, moderately soluble in chloroform and sparingly soluble in ether and saturated hydrocarbons. They exhibit medium thermal stability.

Both i.r. and <sup>1</sup>H n.m.r. spectral techniques were used to characterize the ligands. The i.r. spectra of the two new ligands exhibit several absorptions in common, due to the pyridine rings and the —CH<sub>2</sub>—CH<sub>2</sub>— bridge. The spectra are characterized by one or two medium to strong bands at 1648–1628 cm<sup>-1</sup> assigned to the C=N stretching vibration of the Schiff's base linkages<sup>(8)</sup>, a medium to strong band at 622 (L<sub>A</sub>) and 623 (L<sub>B</sub>) cm<sup>-1</sup> due to an in-plane pyridine ring deformation<sup>(9)</sup>, and a weak to medium band in the region 412–406 cm<sup>-1</sup> which is attributed to an out-of-plane pyridine ring deformation<sup>(9)</sup>. When the methyl group is replaced by a phenyl group in the Schiff's base linkage, there is a decrease in the C=N frequency. This trend has been attributed to conjugation effect<sup>(8)</sup>.

The <sup>1</sup>H n.m.r. spectrum of L<sub>A</sub> in DMSO-d<sub>6</sub> exhibits a sharp singlet at δ (downfield from TMS) 2.47 ppm assigned to methyl protons, two singlets at δ 3.49 and 4.01 ppm due to the methylene protons and four multiplet signals at δ 7.53, 7.93, 8.14 and 8.70 ppm assigned to H(5), H(4), H(3) and H(6), respectively<sup>(10–12)</sup>; the integration of the signals is consistent with the assignments. The appearance of two unequal resonances for the methylene protons and the multiplicity for the ring protons may be interpreted<sup>(12)</sup> as arising from an unequal population of two isomers in solution. Both ligands can, in principle, take up the E(syn), E(syn), the E(syn), Z(anti) or the Z(anti), Z(anti) conformations, considering the orientation of the >C=N— groups with respect to the —CH<sub>2</sub>—CH<sub>2</sub>— bridge<sup>(13,14)</sup>. In both E,E and Z,Z isomeric forms, the four protons of the —CH<sub>2</sub>—CH<sub>2</sub>— group are equivalent and a single signal for them might be expected; in the E,Z isomeric form the —CH<sub>2</sub>— groups are clearly non-equivalent and a coupling <sup>1</sup>H n.m.r. pattern should be observed. The appearance of two singlet signals for the methylene protons in the spectrum of the free ligand L<sub>A</sub> indicates the presence of the E,E and Z,Z isomeric forms in solution. Integration of the proton singlets at 3.49 and 4.01 ppm gives an approximate ratio 1:2 for the two isomeric forms. The fact that the methyl resonances consist of a single peak,

instead of the expected two for the two isomeric forms, may be due to the coincidence of chemical shifts<sup>(15)</sup>.

The <sup>1</sup>H n.m.r. spectrum of L<sub>B</sub> in methanol-d<sub>4</sub> exhibits a triplet at δ 3.81 ppm and a quartet at δ 3.92 ppm, both assigned to the methylene protons, and nine groups of multiplet peaks between δ 7.23 and 8.78 ppm assigned to the ring's protons. The appearance of two multiplet peaks for the methylene protons and the multiplicity of all signals assigned to the rings' protons indicates an equilibrium of the E,E, Z,Z and E,Z forms of L<sub>B</sub> in solution.

#### Physical properties of the complexes

Methods of preparation, analytical data, colours and molar conductivity values for the complexes are given in Table 1. The complexes are microcrystalline or powder-

like, stable in atmospheric conditions [except (6), (7), (15) and (16)] and insoluble in benzene, ether, chloroform, acetone, alcohols and nitromethane. The complexes (1)–(7) and (10)–(16) are soluble in water, frequently with colour changes. Most of the compounds are also soluble in DMF and DMSO. Because of the insolubility of the prepared complexes in suitable organic solvents, we could not obtain samples for single-crystal x-ray structural studies.

The Λ<sub>M</sub> values of (1)–(7) and (10)–(16) in water are in accord with them being formulated as 1:2 electrolytes<sup>(16)</sup>. However, the fact that for most of the Co<sup>II</sup>, Ni<sup>II</sup> and Cu<sup>II</sup> complexes the solid state far-i.r. spectra indicate axial halide coordination (see below) and the fact that aqueous solution and solid state d-d spectra differ can be attributed to the strong donor capacity of water, which frequently leads to displacement

**Table 1.** Method of preparation, colours, analytical data and molar conductivity values for the complexes

Nr.	Compound	Method of prepn. <sup>a</sup>	Colour	Found M	(Calcd.)% X	C	H	N	H <sub>2</sub> O <sup>c</sup>	Λ <sub>M</sub> <sup>d</sup> (S cm <sup>2</sup> mol <sup>-1</sup> )
(1)	[CoL <sub>A</sub> Cl <sub>2</sub> ]	A, D	brown-pink	14.9 (14.9)	17.7 (17.9)	b b	b b	b b		235 <sup>e</sup>
(2)	[CoL <sub>A</sub> Br <sub>2</sub> ]	A	brown	12.1 (12.1)	32.7 (32.9)	b	b	b		220 <sup>e</sup>
(3)	[NiL <sub>A</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	B	green	13.2 (13.6)	16.3 (16.4)	43.5 (44.5)	5.0 (5.1)	12.1 (13.0)	8.0 (8.3)	219 <sup>e</sup>
(4)	[NiL <sub>A</sub> Br <sub>2</sub> ]·H <sub>2</sub> O	C	green-brown	11.8 (11.7)	31.3 (31.8)	b	b	b	3.8 (3.6)	230 <sup>e</sup>
(5)	[CuL <sub>A</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub>	B	blue-green	14.3 (14.5)	16.2 (16.2)	42.9 (44.0)	4.9 (5.1)	12.2 (12.8)	8.2 (8.2)	238 <sup>e</sup>
(6)	[CuL <sub>A</sub> Cl <sub>2</sub> ]	A	olive green	16.1 (15.9)	18.1 (17.7)	b	b	b		225 <sup>e</sup>
(7)	[CuL <sub>A</sub> Br <sub>2</sub> ]	A	green	12.6 (13.0)	32.6 (32.6)	b	b	b		210 <sup>e</sup>
(8)	[PdL <sub>A</sub> ][PdCl <sub>4</sub> ]	E	pink-yellow	34.0 (34.3)	22.4 (22.8)	b	b	b		i
(9)	[PtL <sub>A</sub> ][PtCl <sub>4</sub> ]	F	pink-orange	49.1 (48.9)	17.5 (17.8)	24.9 (24.1)	2.6 (2.3)	7.0 (7.0)		59 <sup>f</sup>
(10)	[CoL <sub>B</sub> Cl <sub>2</sub> ]	A	brown	11.3 (11.3)	13.2 (13.6)	b	b	b		240 <sup>e</sup>
(11)	[CoL <sub>B</sub> Br <sub>2</sub> ]	A	green-brown	9.5 (9.7)	26.0 (26.2)	b	b	b		235 <sup>e</sup>
(12)	[NiL <sub>B</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub> ·2H <sub>2</sub> O	D	yellow-green	9.4 (9.9)	11.3 (12.0)	51.7 (52.7)	4.7 (5.1)	9.5 (9.5)	12.0 (12.2)	240 <sup>e</sup>
(13)	[NiL <sub>B</sub> Cl <sub>2</sub> ]	C	brown-green	11.0 (11.3)	13.3 (13.6)	b	b	b		265 <sup>e</sup>
(14)	[NiL <sub>B</sub> Br <sub>2</sub> ]	C	brown-green	9.4 (9.6)	26.1 (26.2)	b	b	b		223 <sup>e</sup>
(15)	[CuL <sub>B</sub> Cl <sub>2</sub> ]	B	blue-green	12.0 (12.1)	13.1 (13.5)	58.2 (59.5)	4.7 (4.2)	10.8 (10.7)		260 <sup>e</sup>
(16)	[CuL <sub>B</sub> Br <sub>2</sub> ]	A	olive green	10.2 (10.3)	26.1 (26.0)	b	b	b		257 <sup>e</sup>
(17)	[PdL <sub>B</sub> Cl <sub>2</sub> ]	G	yellow	18.6 (18.7)	12.0 (12.5)	b	b	b		7 <sup>f</sup>
(18)	[PdL <sub>B</sub> Br <sub>2</sub> ]	G	pale yellow	16.5 (16.2)	24.2 (24.3)	b	b	b		33 <sup>f</sup>
(19)	[PdL <sub>B</sub> ][PdCl <sub>4</sub> ]	E	yellow-pink	28.2 (28.6)	19.3 (19.0)	b	b	b		i
(20)	[PtL <sub>B</sub> Cl <sub>2</sub> ]	H	pale yellow	29.9 (29.7)	10.7 (10.8)	b	b	b		4 <sup>f</sup>
(21)	[PtL <sub>B</sub> Br <sub>2</sub> ]	H	pale yellow	26.3 (26.2)	21.1 (21.4)	b	b	b		20 <sup>f</sup>
(22)	[PtL <sub>B</sub> ][PtCl <sub>4</sub> ]	F	green	42.0 (42.3)	15.3 (15.4)	b	b	b		i

<sup>a</sup>See text; <sup>b</sup>no data available; <sup>c</sup>determined from the t.g. pattern; <sup>d</sup>values of molar conductivity for ca. 10<sup>-3</sup> M solutions at 25°C; <sup>e</sup>in water; <sup>f</sup>in DMF; M = metal; X = Cl, Br; i = insoluble.

of anionic ligands in solution and change of electrolyte type. The  $\Lambda_M$  value of (9) in DMF indicates a 1:2 electrolyte<sup>(17)</sup>, while (17) and (20) appear to be non-electrolyte in DMF<sup>(17)</sup>. The  $\Lambda_M$  values of 18 and 21 indicate partial ionization<sup>(17)</sup>.

The thermal decomposition of the complexes was studied using t.g./d.t.g. techniques. We first comment on the dehydration processes. The t.g. curve of (4) shows a first mass-loss between 50 and 115°C, which corresponds very well to the release of the water content; the relatively low temperature of water loss shows that this is lattice held. The t.g. curves (3) and (5) show a two-step (as revealed from the appearance of two d.t.g. maxima) first mass-loss in the 65–200 and 60–175°C regions, respectively, which corresponds to the release of all the water content. The relatively high temperature of water loss may indicate that the two water molecules are coordinated to the metal ions. The complex (12) releases water in two steps from 40 to 205°C. The absence of t.g. plateaus between 40 and 205°C indicates that stable hydrated intermediates cannot be formed. A clear t.g. plateau after complete dehydration is reached only for complex (4), up to 160°C. In the case of (3), (5) and (12) the decomposition of the anhydrous species starts almost immediately after dehydration. Hence square planar complexes of the types  $[ML_A]Cl_2$  (M = Ni, Cu) and  $[NiL_B]Cl_2$  cannot be prepared from the corresponding octahedral aquo complexes by thermal dehydration.

The (1), (2), (6)–(11) and (13)–(22) complexes decompose with rather complex degradation mechanisms, as revealed by the appearance of a large number of d.t.g. peaks, and without the formation of stoichiometric intermediates, as no stoichiometric compounds can be assigned to the curves' inflections.

### I.r. spectra

Table 2 gives diagnostic i.r. and far-i.r. bands. In the  $\nu(O-H)_{\text{water}}$  region, the spectra of (3), (5) and (12) show respectively two, one and two strong, sharp bands between 3460 and 3300  $\text{cm}^{-1}$  attributed to the presence of coordinated water<sup>(18)</sup>. In the spectrum of (4), a strong and broad absorption (ca. 3500–3100  $\text{cm}^{-1}$ ) indicates that lattice water is present<sup>(18)</sup>. The spectrum of (12) exhibits, in addition to the bands of coordinated water, a broad continuous absorption at 3550–3100  $\text{cm}^{-1}$ ; this is apparently due to the presence of both coordinated and crystal water in this compound.

The significant change in the ligands' bands upon complexing is the increase in  $\nu(C=N)_{\text{Schiff}}$ . This shift to higher frequencies in the spectra of the complexes suggests coordination through both nitrogens of the methine groups<sup>(8, 19)</sup>. Recent studies<sup>(8)</sup> have shown that the s character of the nitrogen lone pair in the C=N bond increases upon coordination; this change in hybridization produces the shorter C=N bond length and greater C=N stretching force constant, relative to the free neutral Schiff base. The variable magnitude of the shift reflects the variable Lewis acidity of the metal ions in the complexes under study.

In the spectra of (1)–(16), (19) and (22) the characteristic in-plane and out-of-plane deformation bands of the pyridine rings shift to higher wavenumbers to indicate coordination of the ring N-atoms<sup>(20)</sup>. The absence of shifts of  $\delta(\text{Py})$  and  $\gamma(\text{Py})$  bands in the spectra of (17), (18), (20) and (21), compared with the frequencies of these modes in the spectrum of  $L_B$ , implies that there is no interaction between ring N-atoms and palladium(II) or platinum(II).

The far-i.r. data of the complexes give an insight into

**Table 2.** Diagnostic i.r. and far-i.r.<sup>a</sup> bands ( $\text{cm}^{-1}$ ) of the ligands  $L_A$  and  $L_B$  and their transition metal complexes.

Compounds	$\nu(C=N)_{\text{Schiff}}^b$	$\delta(\text{P}_y)^b$	$\gamma(\text{P}_y)^b$	$\nu(M-O_{\text{water}})^c$	$\nu(M-N_{\text{Schiff}})^c$	$\nu(M-N_{\text{ring}})^c$	$\nu(M-X)_t^c$
$L_A$	1648m, 1636s	622s	406w				
(1)	1653w	633m	422w		306m	288m, 252m	231s
(2)	1650m, 1639m	633w	422m		359m, 330w	301m, 252m	152s
(3)	1669s	639m	422w	375m	360m	288m	
(4)	1681s	640m	419w		328m	292m	143m
(5)	1660s	640w	420w	402m	378w	283m	
(6)	1661s	642w	420m		378m	284s	314vs
(7)	1661s	646m	429m		396m	293m	252vs
(8) <sup>e</sup>	1646m	653w	411w		475m, 450m	322m, 292m	336vs
(9) <sup>e</sup>	1661s	639w	410w		456w, 443m	279m, 260m	319vs
$L_B$	1628s	623m	412w <sup>d</sup>				
(10)	1630m	640m	424m		355w, 303mb	255w, 238w	232m
(11)	1631m	652m	433w		347s, 298s	251m, 242m	168m
(12)	1652s	641m	426w	378w	312m	242s	
(13)	1652s	642m	421m		312m	252m	217vs
(14)	1650s	641m	427m		312s	251s	152s
(15)	1648m	642m	418m		343m	242m	300s
(16)	1649s	644m	426m		396m	268w	249vs
(17)	1672s	616w	404w		468s, 462w		350s, 321m <sup>f</sup>
(18)	1670s	622w	405w		466m, 449w		247s, 236s
(19) <sup>e</sup>	1633m	635w	421m		466wb	257m, 251w	320vsb
(20)	1675s, 1666s	n.o.	404w		456w, 442m		341s, 334s
(21)	1674s	620vw	405vw		456w, 442m		233s, 219sh
(22) <sup>e</sup>	1630w	622m	425m		473m, 452w	262wb	308vsb

<sup>a</sup>Fourier-transform far-i.r. spectra; <sup>b</sup>assignments of these bands have been given by (i) studying literature<sup>(8, 9)</sup> and (ii) comparing the spectra of the organic ligands with those of their corresponding complexes; <sup>c</sup>assignments of these far-i.r. bands have been made by noting (i) the frequencies of the internal modes of  $L_A$  and  $L_B$ , (ii) bands principally dependent on X, (iii) the variation in band position with changing metal ion, (iv) the appearance of new bands in the far-i.r. spectra of the complexes containing coordinated water, and (v) extensive literature reports<sup>(20, 25)</sup>; <sup>d</sup> $\nu(\text{P}_y)$  +  $\gamma(\text{Q})$ , where Q = phenyl ring; <sup>e</sup>a characteristic<sup>(24)</sup> deformation mode of the  $(MCl_2)^{2-}$  (M = Pd, Pt) ion appears at 155(8), 150(9), 146(19) and 145(22)  $\text{cm}^{-1}$  as a medium to strong band; <sup>f</sup> $\nu(\text{Pd}-\text{Cl})_t$  + ligand vibration. b = broad;  $\gamma$  = out-of-plane deformation;  $\delta$  = in-plane deformation; m = medium, M = metal; = stretching;  $\nu(M-X)_t$  = the stretching vibration of the terminal M—X bond; n.o. = not observed;  $\text{P}_y$  = pyridine ring; X = Cl, Br.

the structure and bonding in the solid state. A medium to very strong metal- and X-sensitive band at a frequency lower than  $314\text{ cm}^{-1}$  in the spectra of (1), (2), (4), (6), (7), (10), (11) and (13)–(16) arises from the  $\nu(\text{M}-\text{X})_t$  vibration in a monomeric *trans* octahedral structure<sup>(20,21)</sup>. The absence of  $\nu(\text{M}-\text{X})_t$  bands in the appropriate region and the appearance of a new weak to medium band at  $402\text{--}375\text{ cm}^{-1}$ , assigned to  $\nu(\text{M}-\text{O}_{\text{water}})^{(21)}$ , in the spectra of (3), (5) and (12) precludes an axial halide coordination and is consistent with these complexes containing apical aquo ligands. The  $\nu(\text{M}-\text{Cl})_t$  ( $\text{M} = \text{Pd}$  or  $\text{Pt}$ ) modes are assigned to strong intensity bands in the region  $350\text{--}321\text{ cm}^{-1}$  for the complexes (17) and (20). They shift to the  $247\text{--}219\text{ cm}^{-1}$  region in the bromo-analogues (18) and (21). The appearance of these bands is consistent with the formulation  $[\text{ML}_B\text{X}_2]$ . The presence of two  $\nu(\text{M}-\text{X})_t$  vibrations in each far-i.r. spectrum confirms the *cis* structures of the square planar complexes (17), (18), (20) and (21)<sup>(20–22)</sup>. The spectra of (8), (9), (19) and (22) show a very strong band at  $336\text{--}308\text{ cm}^{-1}$ , assigned to the  $\text{M}-\text{Cl}$  ( $\text{M} = \text{Pd}$  or  $\text{Pt}$ )  $E_u$  stretching vibration of the square planar  $[\text{MCl}_4]^{2-}$  ions (point group  $D_{4h}$ )<sup>(21,23,24)</sup>. The existence of these anions in (8), (9), (19) and (29) is further proved by the appearance of a characteristic i.r.-active deformation mode between  $155$  and  $145\text{ cm}^{-1}$ <sup>(24)</sup>.

The  $\nu(\text{M}-\text{N}_{\text{Schiff}})$  and  $\nu(\text{M}-\text{N}_{\text{ring}})$  assignments are in agreement with literature data<sup>(20,21,23–25)</sup>. It is well known<sup>(25)</sup> that metal–nitrogen stretching vibrations are often coupled with other normal modes of vibration of the same symmetry, especially ring vibrations; so, the proposed assignments in Table 2 must be regarded as approximate descriptions of the vibrations. The number of  $\nu(\text{M}-\text{N})$  bands to be expected in the cobalt(II), nickel(II) and copper(II) complexes is uncertain. The actual symmetry of the complexes would be very low and all four possible metal–nitrogen stretching modes would theoretically be observable. However, the effective symmetry may be higher and in this case a smaller number of  $\nu(\text{M}-\text{N})$  bands should be active in the i.r. spectrum. This is true for the nickel(II) and copper(II) complexes, in the spectra of which one  $\nu(\text{M}-\text{N}_{\text{Schiff}})$  and one  $\nu(\text{M}-\text{N}_{\text{ring}})$  band each are observed. A possible explanation for the appearance of two  $\nu(\text{Co}-\text{N}_{\text{ring}})$  and two  $\nu(\text{Co}-\text{N}_{\text{Schiff}})$  bands in (1), (2), (10) and (11) is given in the concluding remarks. The presence of two  $\nu(\text{M}-\text{N}_{\text{Schiff}})$  vibrations in the spectra of (17), (18), (20) and (21) confirms their *cis* structures<sup>(20,21)</sup>.

It is evident from Table 2 that for a given metal salt of cobalt(II), nickel(II) or copper(II) both  $\nu(\text{M}-\text{N}_{\text{Schiff}})$  and  $\nu(\text{M}-\text{N}_{\text{ring}})$  modes shift to higher frequencies as the organic ligand is changed, in the order  $L_B < L_A$ . This suggests that the strength of the metal–nitrogen equatorial bonds increases in the above order of ligands; this is in accord with the expected lower basicities of the ring- and methine-nitrogen atoms when phenyl groups are bonded to the adjacent carbon atoms, as compared to methyl groups with their large inductive (electron releasing) effect<sup>(26)</sup>.

#### Magnetochemical and ligand field spectral studies

Table 3 gives the room temperature effective magnetic moments and details of the solid state electronic spectra of the complexes.

The  $\mu_{\text{eff}}$  values of the nickel(II) complexes (3), (4), (13) and (14) show a small orbital contribution, in accord with octahedral stereochemistry<sup>(5)</sup>, while the moment of (2) is found towards the high end of the “octahedral” region for this metal ion. The solid state d–d spectra of the nickel(II) complexes contain a large number of bands. From the presence of splitting in the  $20400\text{--}14400\text{ cm}^{-1}$  spectral region it is concluded that tetragonal distortion arising from the different nature of the organic ligands  $L_A$  or  $L_B$ , and water or halo ligands, is significant<sup>(27)</sup>. Accordingly, we have assumed a  $D_{4h}$  symmetry with *trans*  $-\text{NiN}_4\text{O}_2$  or  $\text{NiN}_4\text{X}_2$  chromophores<sup>(28)</sup>. If the equatorial and axial ligands differ sufficiently in  $\sigma$  or  $\pi$  bonding properties, the orbital triplets (in  $O_h$ ) show partial or complete resolution into their single and doubly degenerate components; under ideal conditions, six spin-allowed transitions may be observed to arise from the orbital singlet ground term  $^3B_{1g}$ . Another strong piece of evidence for the presence of a tetragonal distortion is the appearance of a well-defined band at  $13610\text{--}12270\text{ cm}^{-1}$ . If this band were assigned as the  $^3A_{2g} \rightarrow ^3T_{2g}$  transition in  $O_h$  symmetry, this would lead to a  $10Dq$  value between  $13610$  and  $12270\text{ cm}^{-1}$ ; such a  $10Dq$  value is very high and has never been calculated in octahedral nickel(II) complexes with  $\text{NiN}_4\text{X}_2$  or  $\text{NiN}_4\text{O}_2$  chromophores<sup>(28)</sup>. In the six-coordinate tetragonally distorted high-spin nickel(II) complexes ( $D_{4h}$ ) the energy of the  $^3B_{1g} \rightarrow ^3B_{2g}$  transition is equal to the  $10Dq^{xy}$  value of the equatorial ligand field<sup>(29)</sup>. The values of  $Dq^{xy}$  indicate that nickel(II) interacts more strongly with  $L_A$  than with  $L_B$ , a conclusion also obtained from the far-i.r.  $\nu(\text{NiN})$  frequencies.

The room temperature  $\mu_{\text{eff}}$  values indicate that the copper(II) complexes prepared are magnetically dilute. Their solid state d–d spectra are fairly typical of distorted six-coordinate copper(II) complexes<sup>(28)</sup>. For a given axial ligand, the slight blue shift of the main d–d maximum in the case of the complexes of  $L_A$  indicates that this molecule is a slightly stronger in-plane ligand compared with  $L_B$ <sup>(25)</sup>. There is a correlation between the electronic and vibrational data, such that as the in-plane bond strength increases both the in-plane metal–ligand stretching frequencies  $\nu(\text{Cu}-\text{N})$  and the electronic transition frequency increase. The existence of this correlation is itself an indication of the reliability of the far-i.r. assignments which have been made<sup>(25)</sup>.

The magnetic moments and ligand field spectra of the cobalt(II) complexes are interesting. At room temperature these compounds show effective magnetic moments between the two extreme values of  $\mu_{\text{eff}}$  ca. 2.0 B.M. for a pure octahedral doublet ground state  $^2E_g$  and  $\mu_{\text{eff}}$  ca. 4.7 B.M. for a pure octahedral quartet ground state  $^4T_{1g}$ . This is explained by the occurrence of a thermal equilibrium between the two spin states<sup>(5,6,30–33)</sup>. Assuming such a thermal equilibrium, about 70–80% and 20–30% of the high-spin states should be occupied with electrons at room temperature in the chloride and bromide complexes, respectively<sup>(31)</sup>. The proposed equilibrium between the two spin states is also supported by the study of the solid state ligand field spectra of (1), (2), (10) and (11) (Table 3, see also footnotes to this table), which exhibit bands characteristic of a  $d^7$  high-spin octahedral structural unit and also maxima due to the doublet–doublet transitions arising from the  $d^7$  low-spin octahedral cobalt(II) site<sup>(28,30)</sup>.

**Table 3.** Solid state magnetic moments and electronic spectral data (29400–11200 cm<sup>-1</sup>) for the Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Pd<sup>II</sup> and Pt<sup>II</sup> complexes of L<sub>A</sub> and L<sub>B</sub>.

$\mu_{\text{eff}}^{\text{a,b}}$ (B.M.) values and assignments of the diffuse reflectance spectra <sup>b</sup> (10 <sup>3</sup> cm <sup>-1</sup> )	Complexes and their data				
<i>Octahedral Co<sup>II</sup> complexes<sup>c,d</sup></i>	(1)	(2)	(10)	(11)	
$\mu_{\text{eff}}$	4.01 <sup>e</sup>	2.85	4.37	3.11	
C.T.	24.69	24.39	25.00	24.75	
${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{P}), {}^4A_{2g}^f$	20.53, 18.94	18.73sh	20.62	20.75, 19.49	
${}^2E_g \rightarrow {}^2T_{1g}$	17.24	17.18	17.39	16.53	
${}^2E_g \rightarrow {}^2T_{2g}$	15.08sh, 14.43	14.39sh, 13.70	14.99sh, 14.33	13.76	
<i>Octahedral Ni<sup>II</sup> complexes<sup>h,i</sup></i>	(3)	(4)	(12)	(13)	(14)
$\mu_{\text{eff}}^{\text{(BM)}}$	3.08	3.12	3.44	2.98	3.06
${}^3B_{1g} \rightarrow {}^3A_{2g}(\text{P}), {}^3E_g(\text{P})$	27.03	24.51	25.19	24.57, 22.99	22.99, 22.22
${}^3B_{1g} \rightarrow {}^3E_g(\text{F})$	20.40	18.52vb	19.80	18.66	n.o.
${}^3B_{1g} \rightarrow {}^3A_{2g}(\text{F})$	15.87	14.49	n.o.	16.13	16.95
${}^3B_{1g} \rightarrow {}^3B_{2g}$	12.71	13.61	12.27	13.19	13.24
$D_q^{xy}(\text{cm}^{-1})^j$	1271	1361	1227	1319	1324
<i>Octahedral Cu<sup>II</sup> complexes</i>	(5)	(6)	(7)	(15)	(16)
$\mu_{\text{eff}}$	1.78	1.90	1.81	2.02	1.95
I.M.C.T.	24.70	26.18	21.28	27.03	21.14
d-d	14.56	14.39	14.77	13.99, 20.62	14.70
Magnus-type Pd <sup>II</sup> and Pt <sup>II</sup>	(8)	(19)	(9)	(22) <sup>m</sup>	
<i>Square planar complexes<sup>k,1</sup></i>					
$\mu_{\text{eff}}$	dia.	dia.	dia.	dia.	
${}^1A_{1g} \rightarrow {}^3E_g$	13.75w		14.08w		
${}^1A_{1g} \rightarrow {}^3E_g, {}^3A_{2g}$				13.42vs	
${}^1A_{1g} \rightarrow {}^3A_{2g}$			20.66		
${}^1A_{1g} \rightarrow {}^3A_{2g}$ and/or ${}^3B_{1g}$	16.26	15.80			
${}^1A_{1g} \rightarrow {}^3B_{1g}$				22.37	
${}^1A_{1g} \rightarrow {}^1A_{2g}$	19.81	20.53	25.64	25.00	
${}^1A_{1g} \rightarrow {}^1E_g$	22.73	21.74sh	28.57	26.81	
${}^1A_{1g} \rightarrow {}^1B_{1g}$	$\eta$	28.17	$\eta$	$\eta$	
<i>Square planar [ML<sub>B</sub>X<sub>2</sub>]</i>	(17)	(18)	(20)	(21)	
(M = Pd or Pt; X = Cl or Br) complexes <sup>o,p</sup>					
$\mu_{\text{eff}}$	dia.	dia.	dia.	dia.	
${}^1A_{1g} \rightarrow {}^3A_{2g}$ and/or ${}^3B_{1g}$		19.42	22.22	23.81sh	
${}^1A_{1g} \rightarrow {}^1A_{2g}$	25.00	23.36	26.67	27.78	
${}^1A_{1g} \rightarrow {}^1E_g$	28.73	28.98sh	$\eta$	$\eta$	

<sup>a</sup>Per metal ion; <sup>b</sup>measured at room temperature; <sup>c</sup>assignments of the ligand field transitions have been given in  $O_h$  for both the high-spin and low-spin octahedral components of these complexes (see text). However it must be noted that the low-spin component possesses a  $(t_{2g})^6(e_g)^1$  configuration and should be Jahn-Teller distorted. This distortion is clearly reflected by the appearance of two bands in the spectra of (1), (2) and (10) in the 15.08–13.70 kK region which, assuming axially elongated systems with  ${}^2A_{1g}$  as the ground state, can be assigned to the  ${}^2A_{1g} \rightarrow {}^2E_g$  and  ${}^2B_{2g}$  transitions ( ${}^2E_g$  and  ${}^2B_{2g}$  are the split components of  ${}^2T_{2g}(O_h)$ ); <sup>d</sup>the band due to the spin-allowed  ${}^4T_{1g} \rightarrow {}^4T_{2g}$  transition from the high-spin components is expected to appear below the lowest energy limit of the instrument used (28); <sup>e</sup>this is the  $\mu_{\text{eff}}$  value of the product isolated using route D (the  $\mu_{\text{eff}}$  value of the product isolated using route A is 4.12 B.M.); <sup>f</sup>these transitions arise from the high-spin structural component; <sup>g</sup>these transitions arise from the low-spin structural component; <sup>h</sup>assignments of the electronic transitions have been given assuming six-coordinate tetragonally distorted complexes ( $D_{4h}$ ). The spectra fit this model well; <sup>i</sup>the band due to the spin-allowed  ${}^3B_{1g} \rightarrow {}^3E_g$  transition is expected to appear below the lowest frequency limit of the instrument used (28); <sup>j</sup>the value of this parameter is obtained directly from the energy of the  ${}^3B_{1g} \rightarrow {}^3B_{2g}$  transition. The value of the parameter  $D_q^2$  was not calculated because the transition  ${}^3B_{1g} \rightarrow {}^3E_g$  occurs below 11.2 K; <sup>k</sup>the observed bands are due to transitions arising from the  $[\text{MCl}_4]^{2-}$  (M = Pd, Pt) ions. The  $[\text{ML}_A]^{2+}$  and  $[\text{ML}_B]^{2+}$  ions are expected to absorb above the highest energy limit of the instrument used (28); <sup>l</sup>assignments in  $D_{4h}$  with  $d_{x^2-y^2}$  as the least stable orbital; <sup>m</sup>a weak band also appears at 20.32 k K; <sup>n</sup>above the highest frequency limit of the instrument used; <sup>o</sup>assignments in  $D_{4h}$  with  $d_{x^2-y^2}$  as the least stable orbital. However these *cis* planar complexes actually belong to the point group  $C_{2v}$ ; <sup>p</sup>the band due to the third spin-allowed  ${}^1A_{1g} \rightarrow {}^1B_{1g}$  transition is expected to appear above the highest energy limit of the instrument used (28). C.T. = charge transfer, dia = diamagnetic; I.M.C.T. = ligand-to-metal charge transfer; n.o. = not observed.

Square planar structures for the bromo complexes (2) and (11) can be ruled out with certainty. Square planar cobalt(II) complexes have magnetic moments between 2.2 and 2.8 B.M. at room temperature<sup>(5,34)</sup> and exhibit d-d maxima at different energies<sup>(35)</sup>. The  $\mu_{\text{eff}}$  values of the

prepared cobalt(II) complexes can also be interpreted on the basis of mixed structures containing tetrahedral and low-spin octahedral units<sup>(36)</sup>. However, this possibility can also be ruled out because a completely different d-d spectrum would be expected<sup>(28)</sup>.

The sensitivity of the spin-crossover phenomenon with regard to sample preparation has been reported by several workers<sup>(32,37)</sup>. The spin-crossover transformation is a cooperative phase transition in the solid state. Small homogeneous regions (domains) of minority-spin molecules form in the crystallite of majority-spin molecules. There is kinetic control in the solid state. Before a minority-spin domain can persist and continue to grow, it has to attain a critical size which is generally believed to be temperature dependent. Kinetic control could result by virtue of the fact that the growth of a minority-spin domain involves the incorporation into the minority-spin domain of majority-spin molecules on the boundaries of the domain. If the boundary of the minority-spin domain encounters a defect in the crystal, then the activation energy for further growth of the minority-spin domain is increased. Crystallites are rarely free of defects such as vacancies, crystal dislocations and impurities. The presence of crystal defects not only inhibits the growth of critical-size minority-spin domains, crystal defects are also preferred sites for the initial formation of minority-spin domains. This sensitivity to defects explains why different preparations of a given compound can have different magnetic characteristics. To substantiate the proposal that (1), (2), (10) and (11) are spin-crossover complexes, we prepared complex (1) using two different routes. The two solids thus obtained have different  $\mu_{\text{eff}}$  values. In a series of experiments defects were also introduced into the microcrystalline cobalt(II) complexes by mechanically grinding them<sup>(37)</sup>. One microcrystalline sample of each of the complexes (1), (2), (10) and (11) was divided into three parts. One part was left unperturbed, while another was ground with a mortar and pestle. The third fraction was more thoroughly ground in a ball mill for a period of 20–25 min. Magnetic susceptibilities were determined for the three samples at room temperature. Grinding the sample did indeed affect the  $\mu_{\text{eff}}$  value. As an example we report the values for (10): the unperturbed microcrystalline solid has  $\mu_{\text{eff}} = 4.37$  B.M. at 292 K, the solid ground with mortar and pestle has  $\mu_{\text{eff}} = 4.19$  B.M. at 292 K and the solid ground in a ball mill has  $\mu_{\text{eff}} = 4.07$  B.M. at 292 K. Similar trends were observed for (1), (2) and (11). It is clear that grinding leads to the formation of more low-spin molecules at room temperature, because defects are preferred sites for nucleation of a low-spin domain<sup>(37)</sup>.

In another experiment it was found that the application of pressure<sup>(32,37)</sup> to a microcrystalline sample of (10) also affects the room temperature  $\mu_{\text{eff}}$  value. The sample was loaded into a die used to prepare KBr disks for i.r. spectroscopy. The sample was then subjected to a pressure of 12 kbar for 5 min. Magnetic measurements were carried out on a fragment of the disk so obtained;  $\mu_{\text{eff}}$  was found to be 4.04 B.M. It is evident that this treatment, which considerably multiplies the grain boundaries and crystal defects<sup>(32)</sup>, leads to the same effect that was seen after sample grinding.

All the above results clearly support the coexistence of appreciable quantities of low- and high-spin octahedral  $[\text{CoL}_2\text{X}_2]$  ( $\text{L} = \text{L}_A, \text{L}_B$ ;  $\text{X} = \text{Cl}, \text{Br}$ ) species in (1), (2), (10) and (11).

In these cobalt(II) complexes the order of  $\mu_{\text{eff}}$  for a particular axial ligand is  $\text{L}_B > \text{L}_A$ , which implies that the doublet–quartet state separation is higher in the  $[\text{CoL}_A\text{X}_2]$  than in  $[\text{CoL}_B\text{X}_2]$ <sup>(34)</sup>. This is due to the

weaker equatorial ligand field in the case of  $\text{L}_B$  compared with that of  $\text{L}_A$ , which allows the axial ligand to approach the cobalt(II) atom more closely (this is confirmed by the higher cobalt-halide stretching frequency in the  $\text{L}_B$  compounds, see Table 2) and consequently to lower the quartet-state energy, thus favouring the high-spin configurations<sup>(32,34)</sup>.

In contrast, the fact that for a given equatorial ligand the order of  $\mu_{\text{eff}}$  is  $\text{Cl} > \text{Br}$  cannot be so easily explained. The general condition required for axial ligands to give spin-crossover  $d^7$  compounds seems to be<sup>(32)</sup> that these ligands must complete the cobalt(II) coordination environment so as to form an elongated octahedron; such a structure can be considered as intermediate between an essentially octahedral stereochemistry, which would stabilize the high-spin form, and a planar surrounding in which cobalt(II) is in the low-spin configuration<sup>(5)</sup>. The smaller  $\mu_{\text{eff}}$  value of the bromo complexes may be the result of two opposite effects; (1) the greater polarizability of  $\text{Br}^-$  versus  $\text{Cl}^-$ . Bromide is a weaker field ligand than chloride because the electron cloud of a bromide ion is more readily deformed than that of a chloride ion<sup>(38)</sup>. The weaker ligand field of  $\text{Br}^-$  implies that it is a better  $\pi$ -donor than  $\text{Cl}^-$ <sup>(38)</sup>; the 4p  $\pi$ -orbitals of  $\text{Br}^-$  are larger than the 3p orbitals of  $\text{Cl}^-$  and can overlap better with the 3d orbitals of the cobalt centre. The better  $\pi$ -donor characteristics of bromide relative to chloride, i.e., stronger interaction with the  $t_{2g}$  orbitals, greatly contributes to the increased destabilization of the low-spin state for the dibromo complexes<sup>(38)</sup>; and (2) the steric effect associated with the larger bromide ion hinders a close approach to the equatorial plane. The longer axial bond lengths in the case of the bromide ion favour the low-spin form. The latter effect prevails over the former.

Square planar structures are assigned to the diamagnetic complexes (17), (18), (20) and (21) on the basis of their solid state electronic spectra<sup>(28)</sup>.

The diamagnetic complexes (8), (9), (19) and (22) belong to the class of Magnus-type palladium(II) and platinum(II) compounds<sup>(5,23,24,39–44)</sup>. To our knowledge these are the first examples of Magnus-type complexes in which the ligands in the complex cations are tetradentate. Complex (22) is green, while complexes (8), (9) and (19) have a yellow-pink or pink-orange colour. Both these colours have been observed in Magnus-type complexes. The planar complex ions in the “classical” Magnus’ green salt,  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ , are arranged in columnar stacks in the solid, giving rise to linear chains of platinum atoms with a uniform metal–metal separation of 3.25 Å<sup>(39)</sup>; adjacent cations and anions are staggered by 28°<sup>(41)</sup>. It is believed<sup>(40–44)</sup> that all the green Magnus-type platinum(II) compounds have similar structures. The structures of the pink compounds are not known in detail, except that the metal atoms are separated by more than 5 Å<sup>(39,41)</sup>. The formation of Magnus’ pink salt rather than the green modification is capricious and cannot be controlled<sup>(41)</sup>.

The bands in the solid state d–d spectra of (8), (9), (19) and (22) were assigned according to literature<sup>(40,41,43,44)</sup>. The observed bands are due to ligand field transitions of the anions, perturbed to varying degrees by their closely spaced cation neighbours<sup>(41,43,44)</sup>; the  $[\text{ML}_A]^{2+}$  and  $[\text{ML}_B]^{2+}$  ions are expected to absorb<sup>(28)</sup> above the highest frequency limit of the instrument used. The spectra of the complexes are similar to those of the  $\text{K}_2[\text{MCl}_4]$  salts<sup>(28)</sup>, but all transitions



apparently have been shifted to lower energies relative to those in the free  $[\text{MCl}_4]^{2-}$  ions due to electronic interactions with the  $[\text{ML}_A]^{2+}$  or  $[\text{ML}_B]^{2+}$  ions<sup>(41,43)</sup>. The closer packing of anions and cations in the lattice in the Magnus-type complexes of this work should increase spin-orbit interactions, and hence the intensities of spin-forbidden bands<sup>(28,41)</sup>. Our assignments of rather intense bands to singlet  $\rightarrow$  triplet transitions are therefore reasonable. This is clearly seen in the spectrum of (22), in which the band at  $13420\text{ cm}^{-1}$ , due to the spin-forbidden transition  $^1A_{1g} \rightarrow ^3E_g$ ,  $^3A_{2g}$ , is the most intense band of the spectrum and responsible for the green colour of (22).

The  $d_{z^2}$  electrons are the ones which should be the most affected by the adjacent members in the stacking chain. If interionic repulsions were the only factor, the  $^1A_{1g} \rightarrow ^1B_{1g}$  ( $d_{z^2} \rightarrow d_{x^2-y^2}$ ) would be expected to have a considerably greater red shift than other d-d transitions<sup>(44)</sup>; unfortunately this transition was not observed below the highest frequency limit of our instrument in (8), (9) and (22). However, comparisons can be made by studying the frequency of the  $^1A_{1g} \rightarrow ^1E_g$  ( $d_{xz}$ ,  $d_{yz} \rightarrow d_{x^2-y^2}$ ) transition, because the  $d_{xz}$ ,  $d_{yz}$  orbitals of  $[\text{MCl}_4]^{2-}$  are perturbed by the  $d_{z^2}$  electrons of the adjacent cations, while the influence of axial neighbours on the transition  $^1A_{1g} \rightarrow ^1A_{2g}$  ( $d_{xy} \rightarrow d_{x^2-y^2}$ ) should be quite small<sup>(41,44)</sup>. Indeed, the  $^1A_{1g} \rightarrow ^1A_{2g}$  transition in the platinum(II) complexes (9) and (22) has shifted toward the red relative to  $\text{K}_2[\text{PtCl}_4]$ <sup>(28)</sup> by only *ca.*  $400\text{ cm}^{-1}$  for (9) and  $1000\text{ cm}^{-1}$  for (22), whereas the  $^1A_{1g} \rightarrow ^1E_g$  transition is shifted by *ca.*  $1000\text{ cm}^{-1}$  for (9) and  $2800\text{ cm}^{-1}$  for (22). The greater shift of the last transition in the case of the green complex (22) reflects the shorter platinum(II)–platinum(II) distance.

#### <sup>1</sup>H n.m.r. spectra

<sup>1</sup>H n.m.r. spectra of the diamagnetic complexes (17), (18) and (20) in DMSO-*d*<sub>6</sub> have been used to confirm the structural identity of these compounds. The insoluble nature of the Magnus-type complexes and (2) in DMSO-*d*<sub>6</sub> or D<sub>2</sub>O prevented comparisons with the n.m.r. spectra of the ligands and (17), (18) and (20).

The spectra of (17), (18) and (20) exhibit a sharp singlet at  $\delta$  (downfield from TMS) at 3.34, 4.31 and 3.33 ppm, respectively, assigned to the methylene protons<sup>(10–12)</sup>. The single resonance observed for the methylene protons is a strong piece of evidence to suggest that the coordinated ligand L<sub>B</sub> takes up either the E, E or the Z, Z conformation in the complexes<sup>(45)</sup>. This is also supported by the appearance of a relatively simple pattern for the rings' protons. The E, Z isomeric form of L<sub>B</sub> in the complexes would give rise to two resonances for the methylene protons and to a complex pattern for the rings' hydrogens<sup>(46)</sup>. The difference in the chemical shift of the methylene protons between (17) and (18) may be explained by the larger deshielding capability of the bromide atom in (18) or to a different ligand conformation in the two complexes, i.e., assuming that L<sub>B</sub> takes up the E, E form in (17), it may have the Z, Z form in (18).

The occurrence of the 6-pyridyl hydrogen signal at almost the same  $\delta$  values in the spectra of (17) (doublet at 8.74 ppm), (18) (doublet at 8.75 ppm), (20) (doublet at 8.73 ppm) and L<sub>B</sub> (multiplet centered at 8.77 ppm) indicates the non-involvement of the ring N-atoms in coordination.

#### Concluding remarks

From the overall study presented it is concluded that in the complexes (1)–(16), (19) and (22) L<sub>A</sub> and L<sub>B</sub> behave as tetradentate chelate ligands, bonding through both the ring and methine nitrogen atoms, while a bidentate chelate *N*-methine coordination of L<sub>B</sub> is proposed for the compounds (17), (18), (20) and (21) in spite of the more basic character of the ring nitrogens. The strong chelating ability of L<sub>A</sub> and L<sub>B</sub>, which contain two  $-\text{N}=\text{C}-\text{C}=\text{N}-$  groupings, is considered to result in part from  $d\pi-p\pi$  bonding from the metal to the ligand; this  $\pi$ -bonding imparts some aromatic character to the chelate rings<sup>(47)</sup>.

Monomeric *trans* pseudo-octahedral stereochemistries are assigned to the cobalt(II), nickel(II) and copper(II) complexes in the solid state. The compounds (8), (9), (19) and (22) are Magnus-type complexes containing a planar  $[\text{ML}_A]^{2+}$  or  $[\text{ML}_B]^{2+}$  cation and a planar  $[\text{MCl}_4]^{2-}$  anion (M = Pd, Pt). The results for (17), (18), (20) and (21) are compatible with a structure consisting of a monomeric, square planar  $[\text{ML}_B\text{X}_2]$  unit, containing a bidentate chelate L<sub>B</sub> ligand and *cis* halo ligands, possibly stacked in the solid as has been found in analogous complexes<sup>(45,48)</sup>. The failure to isolate  $[\text{ML}_A\text{X}_2]$  complexes (M = Pd, Pt; X = Cl, Br) can be tentatively attributed to the presence of the methyl groups in L<sub>A</sub>; their large inductive (electron releasing) effect seems to favour the tetradentate coordination.

A characteristic feature of the compounds of this work is the high-spin character of the nickel(II) complexes and the spin-crossover nature of the cobalt(II) complexes. Analogous complexes of these metal ions with other ligands containing the  $-\text{N}=\text{C}-\text{C}=\text{N}-$  grouping display both high- (or low-spin) behaviour or an equilibrium situation at room temperature, the spin state of the central metal ion being often dependent on minor structural variation in the chelating agent, on the particular metal ion or on the nature of any other ligands present in the complex<sup>(26)</sup>. The chloride and bromide ions used in this work have a medium to strong tendency for apical coordination, favouring an octahedral stereochemistry. This stereochemistry always leads to high-spin complexes in the case of nickel(II) and can give either high- or low-spin complexes in the case of cobalt(II), thus explaining the equilibrium situation between the two spin states found in (1), (2), (10) and (11). We are currently investigating the coordination chemistry of other N<sub>4</sub> Schiff base ligands, which have a phenyl "bridge", instead of the methylene "bridge" present in L<sub>A</sub> and L<sub>B</sub>. With a phenyl "bridge" the equatorial ligand is quite planar and consequently too rigid to enable other ligands to closely approach the apical sites, the resulting axial elongation being expected to favour low-spin forms.

A final point to be discussed is the appearance of two  $\nu(\text{Co}-\text{N}_{\text{ring}})$  and two  $\nu(\text{Co}-\text{N}_{\text{Schiff}})$  bands in the far-i.r. spectra of (1), (2), (10) and (11). For both types of vibration, the higher frequency mode is tentatively assigned to the cobalt(II)–nitrogen stretching vibration in the low-spin molecules and the lower frequency mode to the similar vibration in the high-spin percentage of the complexes, due to the marked strengthening of the coordination bonds in going from the high- to the low-spin species<sup>(21,34,49–51)</sup>. The  $d_{x^2-y^2}$  orbitals have a different occupancy in the high-spin and low-spin states



for the octahedral  $d^7$  complexes, while the  $d_{z^2}$  orbitals are similarly occupied. Consequently, variations in the metal–ligand bond lengths associated with the high-spin–low-spin equilibrium mainly occur in the equatorial plane<sup>(33)</sup>; the appearance in each spectrum of one  $\nu(\text{Co—X})$  vibration, instead of two, is then reasonable.

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