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Divalent metal complexes of polydentate Schiff base ligands derived from aminothioetherimidazoles and 2,6-diacetyl- or 2,6-diformylpyridine

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Abstract

Four Schiff base ligands containing N_5S_2 donor systems and showing potential binucleating behaviour are reported. Neutral mononuclear complexes $[ML]\cdot nH_2O$ were obtained using an electrochemical procedure by deprotonation of the corresponding ligand and oxidation of a 'sacrificial electrode'. Mononuclear and binuclear complexes with protonated ligands were prepared by chemical reaction between the ligand and $CuCl_2$.

Introduction

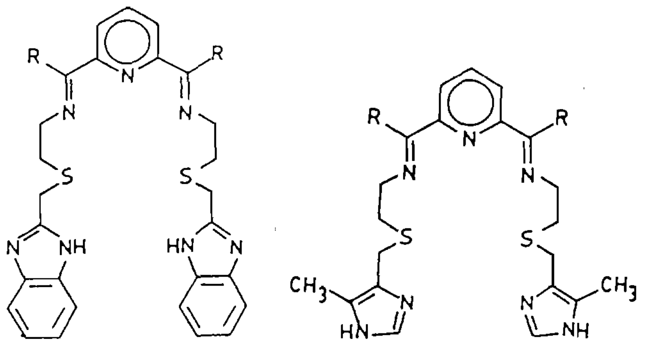
In previous papers [1–3] we have reported the synthesis and structural characterization of neutral copper, zinc, cadmium and nickel complexes involving N_2SO and N_2S_2 tetradentate ligands containing thioether and benzimidazole or imidazole groups. Some of these complexes may be considered as models for active sites of metalloproteins.

Herein we describe the synthesis of new N_5S_2 polydentate ligands containing both thioether and benzimidazole or imidazole groups similar to the N_2SO and N_2S_2 tetradentate ligands, together with their mononuclear and binuclear complexes. This type of ligand, depicted in Fig. 1, gives an opportunity to prepare either complexes which contain two metal ions coordinated to the ligand through the N_5S_2 donor set or binuclear and trinuclear complexes which contain benzimidazolate or imidazolate bridges.

Experimental

Reagents

All reagents were of the highest grade commercially available and were used as received without further purification.



bR-pyratbH2
($R=H, CH_3$)

bR-pyratmiH2
($R=H, CH_3$)

Fig. 1. Schiff base ligands.

Synthesis of Schiff bases

2-[(2-Aminoethyl)thiomethyl]benzimidazole dihydrobromide and 4-[(2-aminoethyl)thiomethyl]-5-methylimidazole dihydrochloride were prepared by the method of Durant *et al.* [4] and treated with methanolic NaOH as described in ref. 1 prior to condensation with the carbonyl compound.

Addition of the 2,6-diformylpyridine or 2,6-diacetylpyridine with stirring to an ethanolic solution of the

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aminothioetherimidazole or aminothioetherbenzimidazole gave orange, or red, solutions which were gently refluxed with magnetic stirring for 1 day. The quantities of reagents, yields and other characteristics are given in Table 1. Evaporation of the solution *in vacuo* gave oils which were stirred with *n*-hexane for *c.* 2 days giving a powder solid. The ligands were dried *in vacuo* and characterized by proton NMR (Tables 2 and 3) and IR spectroscopy (Table 4) prior to use in complexation reactions.

Metal complexes by electrochemical procedure

The electrochemical method used in the synthesis of the complexes [ML] is similar to that described by Habeeb *et al.* [5]. The cell was a 100 ml tall-form beaker fitted with a rubber bung through which the electrical leads entered the cell. The anode, in foil form, was suspended on a platinum wire; the cathode was also a platinum wire. The ligands were dissolved in acetonitrile or absolute ethanol and tetramethylammonium perchlorate (*c.* 10 mg) was added to the solution as the supporting electrolyte. In all cases, the electrolysis was carried out under ambient conditions with magnetic stirring and the insoluble compounds were visible within a few minutes. At the completion of the reaction, the powdery compounds were collected, washed with the solvent of the synthesis and dried *in vacuo*.

The cell can be summarized as: Pt(−)/solvent+H_2L/M(+).

The experimental conditions for the reactions are detailed in Table 5. Melting points: [Cu(bH-pyratb)]·$4H_2O$: 210 °C; [Ni(bH-pyratb)]·$4.5H_2O$: 245 °C; [Zn(bMe-pyratb)]·$6H_2O$: 270 °C; [Zn(bH-pyratmi)]·$5H_2O$·EtOH: 270 °C; [Zn(bMe-pyratmi)]·$2.5H_2O$: 245 °C.

Metal complexes with protonated ligands

[Cu(bMe-pyratbH$_2$)Cl$_2$]·2H$_2$O

The ligand bMe-pyratbH$_2$ (0.2014 g) was dissolved in acetonitrile (15 ml). The golden solution was gently refluxed with magnetic stirring for 15 min. The green solution of $CuCl_2$ (0.0451 g) in acetonitrile (10 ml) was added dropwise to the former. After some minutes, a dark green precipitate appeared and the mixture was gently refluxed for *c.* 4 h. Finally, the complex was collected, washed with acetonitrile and dried *in vacuo*. Melting point: 176 °C.

[Cu$_2$(bMe-pyratbH$_2$)Cl$_4$]·2.5H$_2$O

The ligand bMe-pyratbH$_2$ (0.1859 g) was dissolved in acetonitrile (15 ml). The golden solution was gently refluxed with magnetic stirring for 15 min. The green solution of $CuCl_2$ (0.0924 g) in acetonitrile (12 ml) was added dropwise to the former, giving a bright green precipitate which was collected, washed with acetonitrile and dried *in vacuo*. Melting point: 183 °C.

Analysis

Elemental analyses (C, Cl, H, N) were carried out in a Perkin-Elmer 240B microanalyser, and those for the complexes are given in Table 6.

Physical measurements

IR spectra were recorded, as nujol mulls or KBr discs, using a Perkin-Elmer 180 spectrometer. Diffuse reflectance spectra of solids were obtained using a Pye Unicam SP 700 spectrometer. Proton NMR spectra were run on a Bruker W.H. 250 FT spectrometer and MS were recorded on a Kratos MS50TC. The ESR spectra were recorded on a Bruker ER 200D spectrometer.

Melting points were measured in a Büchi apparatus, magnetic moments were performed on a SQUID MPMS Quantum Design and conductivity measurements were carried out in 10^{-3} mol dm^{-3} dimethylformamide solutions at 20 °C using a WTW conductivimeter LF3.

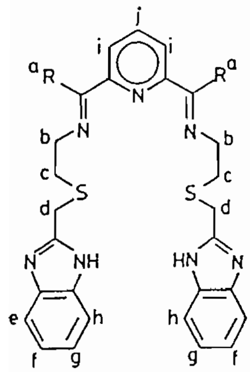
Results and discussion

The four Schiff base ligands (bR-pyratbH$_2$ (R = H, Me); bR-pyratmiH$_2$ (R = H, Me)) were synthesized by condensation of 2-[(2-aminoethyl)thiomethyl]-benzimidazole or 4-[(2-aminoethyl)thiomethyl]-5-methylimidazole with 2,6-diacetylpyridine and 2,6-diformylpyridine. The pyridine 'head' unit and two lateral 'arms' containing the benzimidazole (or imidazole) and a thioether groups (Fig. 1) provide an N_5S_2 donor system, and give the ligands a potential binucleating character.

TABLE 1. Synthesis of Schiff bases

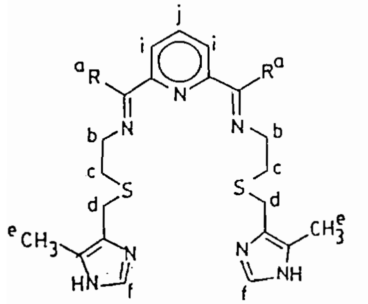
Ligand	Amine (g/mmol)	Aldehyde (g/mmol)	Obtained (g/mmol)	Yield (%)	Colour	m.p. (°C)
bH-pyratmiH$_2$	1.21/3.46	0.23/1.70	0.62/1.40	83	garnet	
bH-pyratbH$_2$	1.83/4.74	0.32/2.37	1.13/2.20	93	light brown	
bMe-pyratmiH$_2$	4.10/12.3	0.96/5.86	2.49/5.31	90	yellow	98
bMe-pyratbH$_2$	5.39/13.9	1.07/6.58	3.48/6.43	97	green–yellow	74

TABLE 2. Proton NMR data for the ligands bR-pyratbH$_2$ in $(CD_3)_2SO$ with $SiMe_4$ as internal reference



R	a	b	c	d	H^i; H^j	H^e---H^h	NH
H	8.36(s)	3.84(t)	2.90(t)	3.96(s)	7.96(m); 7.86(m)	7.49(m); 7.13(m)	12.42(b)
CH_3	2.30(s)	3.68(t)	2.95(t)	4.01(s)	8.02(m); 7.81(m)	7.49(m); 7.14(m)	12.38(b)

TABLE 3. Proton NMR data for the ligands bR-pyratmiH$_2$ in $(CD_3)_2SO$ with $SiMe_4$ as internal reference



R	a	b	c	d	e	f	H^i; H^j	NH
H	8.37(s)	3.81(t)	2.77(t)	3.66(s)	2.09(s)	7.40(s)	7.98(m)	
CH_3	2.35(s)	3.67(t)	2.82(t)	3.71(s)	2.10(s)	7.39(s)	8.02(m); 7.81(m)	11.68(b)

The four ligands were characterized by proton NMR (Tables 2 and 3) and IR spectroscopy (Table 4). IR spectra show a strong band in the region 1635–1645 cm^{-1} ascribable to the imine stretch. Bands between 1620 and 1500 cm^{-1} are assignable to ν(C=N) of benzimidazole or imidazole and pyridine groups as well as to ν(C=C) of aromatic rings. In particular, a strong band at 1580–1585 cm^{-1} and a weak one at 620 cm^{-1} can be assigned to the pyridine fragment of the bases.

Complexes with bianionic ligands

Neutral mononuclear complexes $[ML]\cdot nH_2O$ were obtained using an electrochemical procedure involving deprotonation of the corresponding polydentate ligand and oxidation of a sacrificial electrode as described in 'Experimental'. The reaction involved in the preparation of the complexes can be represented by eqn. (1)

$$M + H_2L \longrightarrow ML + H_2 \qquad (1)$$

The electrochemical efficiency (E_f), defined as the quantity of metal dissolved per Faraday of charge, takes a value close to 0.5 mol F^{-1} for nickel(II) and zinc(II) complexes and close to 1 mol F^{-1} for the copper(II) compound. Therefore, the process involved in the synthesis of the Ni(II) and Zn(II) complexes can be represented by reactions (2) and (3)

$$\text{Cathode: } H_2L + 2e^- \longrightarrow L^{2-} + H_2 \qquad (2)$$

$$\text{Anode: } L^{2-} + M \longrightarrow ML + 2e^- \qquad (3)$$

while the synthesis of Cu(II) complex involves the processes (4) and (5) followed by the oxidation reaction (6)

TABLE 4. IR data for the Schiff bases[a]

Ligand	IR bands (cm^{-1})[b]
bH-pyratbH_2[c]	1645(s), 1620(w), 1585(s), 1530(m) 1440(vs), 1275(vs), 1220(m), 1150(m) 1105(m), 1020(m), 840(w), 805(w) 740(vs), 630(w), 620(w)
bMe-pyratbH_2[c]	1640(s), 1580(sh), 1570(m), 1530(m) 1440(vs), 1275(vs), 1220(m), 1145(w) 1120(w), 1020(m), 840(vw), 805(m) 740(vs), 630(w)
bH-pyratmiH_2	1645(s), 1600(sh), 1585(m), 1570(m) 1280(w), 1230(w, b), 1080(m), 1030(m) 950(s), 800(s), 740(s), 630(m), 610(sh)
bMe-pyratmiH_2[c]	1635(s), 1605(w), 1580(sh), 1570(m) 1360(m), 1280(w), 1230(s), 1070(w) 960(s), 810(s), 750(m), 670(m), 625(m)

[a]Abbreviations: (b) broad; (m) medium; (s) strong; (sh) shoulder; (vs) very strong; (vw) very weak; (w) weak. [b]Spectra recorded as nujol mulls. [c]Spectra recorded as KBr discs.

$$\text{Cathode: } H_2L + e^- \longrightarrow HL^- + 1/2H_2 \quad (4)$$

$$\text{Anode: } HL^- + Cu \longrightarrow Cu(HL) + e^- \quad (5)$$

$$Cu(HL) \longrightarrow CuL + 1/2H_2 \quad (6)$$

The complexes obtained were recovered as powders and characterized by elemental analysis (Table 6), IR (Table 7), mass, visible and ESR spectroscopy. The great insolubility of these compounds limits opportunity for their study in solution. Attempts to obtain pure compounds of copper and nickel with bR-pyratmiH_2 and bMe-pyratbH_2, as well as the pure [Zn(bH-pyratb)] complex, by the electrochemical method failed.

The FAB mass spectrum of [Zn(bMe-pyratb)]·$6H_2O$ shows a signal at 604 corresponding to the molecular-ion peak. It is also possible to assign peaks to other fragments; so, a peak at 208 may be due to a fragment containing the zinc ion linked to both imine groups as well as to the pyridine group of the ligand. The other peak at 474 can be attributed to the molecular-ion peak without a benzimidazole group.

The IR spectra of the zinc(II) compounds confirm the presence of the intact ligand in the complexes; bands which the free ligands show in the region 1570–1645 cm^{-1}, ascribed to $\nu(C=N)$ of the imine, pyridine and benzimidazole or imidazole groups, are shifted in the complexes. Coordinated pyridine can be distinguished from free pyridine by the appearance of a weak band at 1235–1250 cm^{-1}, as well as shifts of the strong band from 1580 to 1600 cm^{-1} and of the bands at 601 and 403 cm^{-1} to 625 and 420 cm^{-1}, respectively [6]. In our case, it is very difficult to detect the weak band at 1235–1250 cm^{-1} because of the large number of ligand bands present in this region. However, it is possible to observe shifts in the bands which appear at 1585 and 620–610 cm^{-1} in the free ligands (Tables 4 and 7); this indicates that the nitrogen atom of the pyridine fragment in the polydentate ligand is coordinated to the metal in zinc(II) complexes.

This spectroscopic study of these Zn(II) systems suggests that the metal ion is linked to both imine groups, to the pyridine nitrogen and to both imidazolate or benzimidazolate deprotonated nitrogens giving an N_5-pentacoordinated geometry around the Zn(II). In this situation, both thioether groups of the arms can be regarded as acting as 'elbows' and are far from the metal site. They are uncoordinated while both benzimidazolate and imidazolate, situated above and below the plane which contains the other three nitrogen atoms and the zinc ion, are coordinated through the deprotonated nitrogens (Fig. 2). A similar coordination may be proposed for the nickel compound and bands for the coordinated pyridine fragment are shown in the IR spectrum.

A typical axial ESR spectrum with $g_{\parallel} > g_{\perp}$ for the copper(II) complex, [Cu(bH-pyratb)]·$4H_2O$, is observed. The ESR parameters, $g_{\parallel} = 2.16$, $g_{\perp} = 2.00$ and $A_{\parallel} = 150 \times 10^{-4}$ cm^{-1}, suggest a N_5 square-pyramidal geometry around the metal [7, 8]. A possibility for this coordination could be that in which the metal ion is bonded to both imine nitrogens, to the pyridine nitrogen

TABLE 5. Experimental conditions for the electrochemical synthesis of the complexes [ML]·nH_2O

Complex	Amount of ligand (g)[a]	Intensity (mA)	Time (s)	Metal used (mg)	E_f (mol F^{-1})	Colour
[Cu(bH-pyratb)]·$3H_2O$	0.2030	9	5820	27.0	0.78	violet
[Ni(bH-pyratb)]·$4.5H_2O$	0.2050	10	12600	18.0	0.47	light brown
[Zn(bMe-pyratb)]·$6H_2O$	0.2849	10	8700	21.0	0.36	golden
[Zn(bH-pyratmi)]·$2.5H_2O$	0.2260	9	9300	21.0	0.37	brown
[Zn(bMe-pyratmi)]·$2.5H_2O$	0.3183	9	11400	25.4	0.36	light brown

[a]Plus NMe_4ClO_4 (*c.* 10 mg).

TABLE 6. Analytical data for the complexes[a]

Complex	n[b]	C (%)	N (%)	H (%)	Cl (%)
[Cu(bH-pyratb)]	4	50.19(50.11)	14.89(15.15)	9.92(9.89)	
[Ni(bH-pyratb)]	4.5	49.44(49.79)	14.74(15.06)	4.14(5.22)	
[Zn(bMe-pyratb)]	6	48.97(48.85)	13.77(13.76)	5.40(5.75)	
[Zn(bH-pyratmi)]	[c]	42.01(43.10)	15.15(15.30)	6.41(6.40)	
[Zn(bMe-pyratmi)]	2.5	47.52(47.80)	16.44(16.97)	5.39(5.88)	
[Cu(bMe-pyratbH_2)Cl_2]	2	49.16(48.91)	13.46(13.77)	4.59(4.92)	10.26(9.96)
[Cu_2(bMe-pyratbH_2)Cl_4]	2.5	40.80(40.70)	10.85(11.46)	3.82(4.09)	16.45(16.59)

[a]Calculated values in parentheses. [b]Lattice water. [c]$5H_2O\cdot EtOH$.

TABLE 7. IR data for the complexes[a]

Complex	IR bands (cm^{-1})[b]
[Cu(bH-pyratb)]$\cdot 4H_2O$	1640(m), 1600(w), 1275(s) 1220(m), 1150(m), 800(w), 740(vs)
[Ni(bH-pyratb)]$\cdot 4.5H_2O$	1630(m, b), 1600(s), 1530(w), 1270(s) 1220(m), 1030(m), 805(vw), 745(vs) 620(vw), 435(w)
[Zn(bMe-pyratb)]$\cdot 6H_2O$	1600(sh), 1589(b), 1270(s), 1230(w) 1145(w), 1020(w), 860(w), 810(w) 740(s), 640(m)
[Zn(bH-pyratmi)]$\cdot 5H_2O\cdot EtOH$	1645(m), 1590(m, b), 1230(w) 1100(s, b), 810(w), 750(sh) 730(s), 670(m), 620(w)
[Zn(bMe-pyratmi)]$\cdot 2.5H_2O$[c]	1640(s), 1595(s, sh), 1580(s), 1480(s) 1360(m), 1260(w), 1240(m) 1220(m), 1100(vs), 1020(m) 820(vs), 740(s), 670(s), 630(vw)
[Cu(bMe-pyratbH_2)Cl_2]$\cdot 2H_2O$[c]	1620(s), 1590(s), 1580(sh), 1520(m) 1445(vs), 1310(w), 1270(s), 1220(m) 1150(w), 1040(w), 840(w), 810(m) 750(vs), 670(vw), 435(w)
[Cu_2(bMe-pyratbH_2)Cl_4]$\cdot 2.5H_2O$[c]	1620(s), 1595(s), 1580(sh), 1520(m) 1445(vs), 1315(w), 1280(m), 1260(m) 1220(m), 1210(m), 1040(m), 1000(w) 840(w), 810(m), 770(vs), 750(vs) 670(vw), 435(w), 305(vw), 270(w)

[a]Abbreviations: (b) broad; (m) medium; (s) strong; (sh) shoulder; (vs) very strong; (vw) very weak; (w) weak. [b]Spectra recorded as nujol mulls. [c]Spectra recorded as KBr discs.

and to both deprotonated nitrogens of benzimidazolates. The IR spectrum (Table 7) is consistent with this coordination.

Reaction of the neutral complex [Zn(bMe-pyratmi)]$\cdot 2.5H_2O$ with $CuCl_2$ in molar ratio (1:2) gave a trinuclear complex, [Zn(bMe-pyratmi)($CuCl_2$)$_2$]$\cdot$ 0.5EtOH for which the elemental analysis was successful. *Anal.* Found: C, 33.31; Cl, 17.28; H, 4.12; N, 11.56. Calc. for $C_{24}Cl_4Cu_2H_{32}N_7O_{0.5}S_2Zn$: C, 32.96; Cl, 16.94; H, 3.94; N, 11.70%. The presence of both metals was corroborated by X-ray fluorescence. In the light of its spectra, a situation in which both benzimidazolates bridge zinc and copper atoms such as described by Borer and Sinn [9] might be suggested. Further studies are being carried out. The ESR spectrum is isotropic and no conclusions can be deduced from it.

Copper complexes of the protonated ligand (bMe-pyratbH_2)

Chemical reaction between the ligand bMe-pyratbH_2 and $CuCl_2$ in molar ratios (1:1) and (1:2) yielded the two complexes, [Cu(bMe-pyratbH_2)Cl_2]$\cdot 2H_2O$ and [Cu_2(bMe-pyratbH_2)Cl_4]$\cdot 2.5H_2O$, respectively, in which the ligand remains protonated. IR spectra of these complexes are similar in the region 600–4000 cm^{-1} suggesting that there is a similar coordination for the organic ligand in both cases. Shifts of bands due to the imine stretch and to the pyridine fragment can be

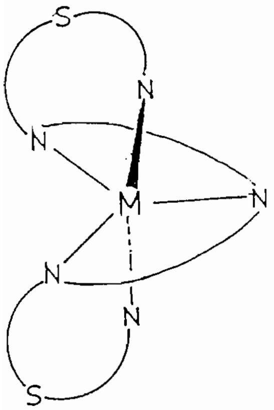


Fig. 2. Proposed structure for the [ML] complexes with bianionic ligands.

detected when the IR spectra of ligand and complexes are compared. The band due to the imine stretch shifts *c.* 30 cm^{-1} to lower wavenumbers, while the bands at 1580 and 630 cm^{-1} in the free ligand are shifted to higher wavenumbers in the complexes (to 1590–1595 and 670 cm^{-1}, respectively). Coordination of both imine nitrogens and pyridine nitrogen to the metal can be suggested.

The FAB mass spectrum of $[Cu(bMe\text{-}pyratbH_2)Cl_2]\cdot 2H_2O$ in nitrobenzylalcohol shows a peak at 604 corresponding to the fragment $[Cu(bMe\text{-}pyratbH_2)]^+$ as well as other peaks derived from the fragmentation of this one. A peak centred at 639 due to $[Cu(bMe\text{-}pyratbH_2)Cl]^+$ is observed. In order to determine if both chlorine atoms were linked to the Cu(II) ion, molar conductivity measurements were carried out in DMF. The value found (22.53 ohm^{-1} cm^2 mol^{-1}) suggests that $[Cu(bMe\text{-}pyratbH_2)Cl_2]$ is a non-electrolyte [10]. The electronic spectrum in the solid state contains a band at 13 800 cm^{-1} typical of pentacoordinate Cu(II). The powder ESR spectrum is axial with $g_{\parallel}=2.24$, $g_{\perp}=2.09$ and $A_{\parallel}\sim 120\times 10^{-4}$ cm^{-1}. These values are well within the range of distorted square-pyramidal copper(II) complexes [7, 8]. A N_3Cl_2 coordination may be proposed with both the imine groups and the pyridine ring in the same plane as well as the copper ion to which they are bonded. The chloride ions lie above and below the plane.

The FAB mass spectrum of the bright green binuclear compound, $[Cu_2(bMe\text{-}pyratbH_2)Cl_4]\cdot 2.5H_2O$, also shows a peak at 604 due to $[Cu(bMe\text{-}pyratbH_2)]^+$. A peak at 668 corresponding to $[Cu_2(bMe\text{-}pyratbH_2)]^+$ suggests that both copper(II) ions are linked to the ligand. Conductivity measurements in dimethylformamide indicate that the compound is a non-electrolyte and the chloride ions must be coordinated. The electronic spectrum for this compound in the solid state shows a band at 13 100 cm^{-1} with a shoulder at 10 200 cm^{-1}. From the similarity of the IR spectra, the presence of a peak at 604 in the mass spectrum and a band at 13 100 cm^{-1} in the electronic spectrum, it can be suggested that one of the copper atoms possesses a similar geometry and coordination to that found in the mononuclear complex. Magnetic measurements give a value of 2.47 BM for the magnetic moment at 300 K and a strong magnetic interaction between both copper(II) ions occurs. The second Cu(II) appears to be coordinated to both benzimidazole groups and two chloride ions in a distorted pseudotetrahedral geometry. The ESR spectrum is uninformative and no conclusion can be deduced from it.

These studies suggest that in some cases the ligands may act as binucleating systems. The thioether sulfur atoms remain uncoordinated, probably because of their poor donor character, as compared with the other donor atoms present in these ligands.

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