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Synthesis, characterization and crystal structure of cationic bis(pyridinylimine)cobalt(II) complexes

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ABSTRACT

Ligands 2,6-dimethyl-N-(pyridin-2-ylmethylene)aniline $C_{14}H_{14}N_2$ (**L1**), 2,6-dimethyl-N-(1-(pyridin-2-yl)ethylidene)aniline $C_{15}H_{16}N_2$ (**L2**) and 2,6-diisopropyl-N-(1-(pyridin-2-yl)ethylidene)aniline $C_{19}H_{24}N_2$ (**L3**) were obtained by condensation reactions. The reactions of $CoCl_2 \cdot 6H_2O$ with the corresponding ligands **L1**–**L3** in the presence of the new salt methoxytris(dimethylamino)phosphonium hexafluorophosphate $[CH_3OP(NMe_2)_3]^+PF_6^-$ afford in good yields, the complexes bis[2,6-dimethyl-N-(pyridin-2-ylmethylene)aniline]chloro cobalt(II) hexafluorophosphate $C_{28}H_{28}ClCoF_6N_4P$ (**C1**), bis[2,6-dimethyl-N-(1-(pyridin-2-yl)ethylidene)aniline]chlorocobalt(II) hexafluorophosphate $C_{30}H_{32}ClCoF_6N_4P$ (**C2**) and bis-[2,6-diisopropyl-N-(1-(pyridin-2-yl)ethylidene)aniline]chlorocobalt(II) hexafluorophosphate $C_{38}H_{48}ClCoF_6N_4P$ (**C3**). All new complexes **C1**–**C3** have been characterized by CHN analyses, ^1H, ^{13}C, ^{31}P NMR and IR spectroscopy. Solid state and electronic structures of complex **C1** have been determined.

1. Introduction

In recent years, there has been increasing interest in developing late transition metal complexes containing ligands with an imine moiety as a result of their catalytic behavior. Those ligands include Schiff bases such as α- and β-diimines [1–6], 2,6-bis(imino)pyridines [7–13], pyridyl-imines and N-substituted 2-iminoalkylpyridines [14–28]. Initially, Brookhart discovered that Pd(II) and Ni(II) diimine catalysts were capable of polymerizing ethylene and α-olefins to high-molecular weight polymers [4–6]. Subsequently, Brookhart [7–9] and Gibson [11–12] both reported that tridentate iron and cobalt-based complexes bearing pyridine bisimine ligands with bulky aryl groups were also capable of converting ethylene to high-molecular weight polymers. Several structural variations in the diimines have been reported, and their steric and electronic properties vary because of the polydentate characteristics of these ligands. These variations include the presence of abundant pyridinylimines and analogues in the transition metal complexes. Other groups [29–33] have recently further studied asymmetrical bidentate aryl substituted pyridinylimine-type catalysts and found that oligomerization of ethylene was possible with Ni(II) catalysts. This unsymmetrical bidentate pyridinylimine ligand combines specific features from the bipyridine-type alkene oligomerization catalyst and the sterically hindered α-diimine-based polymerization system [5–6]. In our knowledge, no cationic cobalt(II) complexes with pyridinylimine ligands have been described. Thus, we report herein the synthesis of novel cationic cobalt(II) complexes bearing two pyridinylimine ligands containing a bulky arylimino substituent on one side of the ligand and a relatively unhindered heterocyclic donor on the other. We describe also the structure of a cobalt(II) complex as determined in the solid state by X-ray crystallography. A DFT optimized structure has been also discussed.

2. Results and discussion

2.1. Synthesis and characterization of compounds

The reaction of primary aromatic amine with either 2-pyridinecarboxaldehyde or 2-acetylpyridine to afford the corresponding pyridinylimine ligands (**L1**–**L3**) is a well-known route to obtain bidentate nitrogen ligands (Scheme 1) [29,33].

The reactions of $CoCl_2 \cdot 6H_2O$ with two equivalents of the ligands **L1**–**L3** in dichloromethane at room temperature in the presence of the methoxyphosphonium salt afford, in good yields, the [bis(iminopyridine)CoCl]$^+$[PF$_6$]$^-$ complexes **C1**–**C3**. The new salt methoxytris(dimethylamino)phosphonium hexafluorophosphate has the advantage to contain a good leaving group as hexamethylphosphoramide (HMPA) and the methylium cation generated is able to

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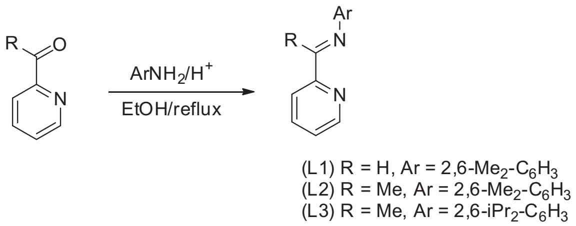
abstract a chloride from the metal center giving rise to the cationic complexes with PF_6^- as counteranions (Scheme 2).

Those new cationic complexes of cobalt(II) (**C1**–**C3**) were isolated as a yellow pale solids soluble in dichloromethane but sparingly soluble in diethyl ether and in n-hexane. ^{1}H, ^{13}C, ^{31}P NMR, IR spectroscopy and elemental analyses were consistent with the cobalt(II) complex formulation. The ^{1}H NMR spectra of complexes **C1**–**C3**, in CD_2Cl_2 at room temperature, show similar trends especially in the aromatic region. There is a distinct shift of the signals of the aromatic groups of the imine system including the pyridine ring on complexing of the ligand to the metal center. A significant downfield shift in the ^{1}H NMR is observed for the imine sp^2 proton upon coordination of the ligand to the metal center. For instance, the singlet at 8.34 ppm for the free ligand **L1** shifts to 8.54 ppm in complex **C1**. Analysis of the cobalt complexes **C2** and **C3** by ^{1}H NMR reveals certain changes in chemical shifts. First of all, the sharp singlet and doublet signals from the ortho-methyl and ortho-isopropyl methyl groups of the free ligands **L2** and **L3** at 1.90 and 1.08 ppm, respectively, have been split into two smaller singlets at 2.24 and 2.31 ppm for **C2** and into two smaller doublets at 1.03 and 1.30 ppm for **C3**. This may be explained by the blocking effect caused by the presence of two bulky pyridinylimine ligands attached to the cobalt center. While in the free ligands the aryl group can rotate around the carbon–nitrogen bond.

Furthermore, the two triplets, which occur at 7.09 and 7.50 ppm for **L2** and at 7.29 and 7.72 ppm for **L3** move significantly downfield to 7.18 and 8.03 and to 7.93 and 8.32 ppm, respectively, during complexation. In ^{13}C NMR spectroscopy, the imine functions are shifted to low field by approximately 4 ppm when compared to free ligands and appear at 167.31, 172.98 and 171.63 ppm for **C1**, **C2** and **C3**, respectively. In addition, these cobalt complexes were characterized by FT-IR spectra, which revealed that the $\nu_{C=N}$ stretching frequencies shifted to lower values with weaker intensity on comparison with those of the corresponding free ligands. All IR spectra present the characteristic band of the PF_6^- counterion at around 832 cm^{-1}. The magnetic moments of complexes **C1**–**C3** were determined by the Evans NMR method [34–37]. The cobalt(II) complexes afford magnetic moments between 1.3 and 1.4 μ_B, consistent with one unpaired electron and a doublet ground state for the Co(II) centres.

2.2. Crystal structure of complex C1

The molecular structure for **C1** has been determined by a single crystal X-ray diffraction study at 296 K and is shown in Fig. 1. Crystallographic details are provided in Table 1, and relevant geometrical parameters are listed in Table 2. In our case, complex **C1** was successfully crystallized from a mixture of CH_2Cl_2/n-hexane solution at room temperature. The single-crystal X-ray diffraction study of complex **C1** reveals a structure consisting of loosely associated $[Co(L1)_2Cl]^+$ cations and octahedral PF_6^- counteranions without direct interactions as appears from the large distance between the metal and the nearest fluorine atom (Co…F1 = 5.25 Å). Another aspect of the relatively weak cation–anion attraction is the presence of C–H…F hydrogen bonding with ranging distances between 2.450 and 2.924 Å. The nitrogen–cobalt bonds of 2.104(5), 2.130(4) Å (pyridine) and 2.180(4), 2.201(5) Å (imine) are similar to those reported in other imine cobalt(II) systems [38–41]. The imine C1–N1 and C15–N3 distances of 1.269(7) and 1.272(7) Å are in the range of reported carbon–nitrogen double bonds [38–41]. In the structure of **C1**, the iminyl nitrogens are trans to one another and the N-imine aryl rings lie perpendicular to the pyridine plane as indicated by the torsion angles C1–N1–C7–C12 and C15–N3–C21–C26 of 92.53(5) and 93.01(5)°, respectively, likely because of steric repulsion between the two bulky dimethylphenyl groups. In the penta-coordinate complex **C1**, a pseudo C_2 axis coincides perfectly with the Co–Cl vector, so that the two iminopyridines are approximately equivalent within the crystal, as is consistent with its ^{1}H and ^{13}C NMR spectra. To describe the coordination geometry of five-coordinated species, it is convenient to use the combination of the angles around the central metal ion. The distortions of the coordination polyhedron from square pyramidal to trigonal bipyramidal is expressed as τ, an index of the degree of trigonality. The tau parameter (τ) is defined as the difference between the two largest such angles divided by 60°. The τ value calculated for the complex **C1** is 0.59 which suggests a distorted trigonal–bipyramidal geometry, wherein the pyridyl nitrogens are nearly axial as indicated by the N2–Co–N4 angle of 156.86(16)°. The two iminyl nitrogen atoms and the chlorine lie in the equatorial plane as indicated by the torsion angle N1–Co–N3–Cl of 179.58(17)°: the sum of N1–Co–N3 (120.45(17)°), N1–Co–Cl (121.28(13)°), and N3–Co–Cl (118.26(13)°) angles is 359.99(17)°.



Scheme 1. Synthetic route to pyridinylimine ligands **L1**–**L3**.

2.3. Density functional theory (DFT) calculations

Geometry optimization reported in this article was done with the GAUSSIAN 09 [42] program package supported by GaussView 5.0.8. The DFT [43–44] calculations have been performed with the Long-range corrected hybrid density meta-GGA functional wB97XD [45–47] with dispersion corrections. In this study, we chose the double-zeta Pople-type basis set 6-31+G(d,p) [48] for all atoms except the cobalt and the chlorine atoms, which were described by the widely used double zeta Los Alamos National Laboratory 2 basis set LANL2DZ [49–51] along with the corresponding effective core potentials (ECPs). This mixed basis set was created through the use of the GEN keyword in GAUSSIAN 09. Both of these basis sets have been widely used along with density functional methods for studies of TM-containing systems, and mixed basis sets of this type have been very popular in computational chemistry studies in recent years. The initial geometry has been taken from crystal structure. The geometry of **C1** in the gas phase has been optimized using tight convergent SCF procedure ignoring symmetry and using both $S = 1/2$ and $S = 3/2$ spin state. Optimized structure obtained from unrestricted UwB97XD method was confirmed to be local minima by performing analytical vibrational frequency analysis at the same level of theory (no imaginary frequency observed). The cation $[Co(L1)_2Cl]^+$ attained a distorted trigonal bipyramid arrangement around the Co atom as shown in Fig. 2. Experimental and theoretical geometric parameters are summarized in Tables 2 and 3. It can be seen that the X-ray solid state and the electronic structures are similar. The experimental bond distances may be underestimated by the effect of anisotropic vibrations, especially as the X-ray diffraction data were measured at room temperature. The theoretical bond distances are slightly overestimated. This can be explained by the use of moderate basis function. The use of more extended basis functions may lead to distances and angles closer to experimental values. The formal charge of cobalt is +2 in the complex **C1**. The calculated charge on the cobalt atom, obtained from natural population analysis, is 0.578.