Preparation of a New π-Conjugated Polymer Chelating Ligand, Poly(2,2'-bipyridimidine-5,5'-diyl), and Its Metal Complexes

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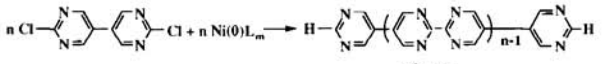
A New π-conjugated chelating polymer ligand, poly(2,2'-bipyrimidine-5,5'-diyl), with a molecular weight higher than 1800 has been prepared. The polymeric ligand forms complexes with $Ru(bpy)_2^{2+}$ and $Os(bpy)_2^{2+}$.

Recently many examples of metal complexes with diazine ligands such as 2,2'-bipyrimidine,[1] pyrimidine,[2] and phenazines[3] have been reported.[4] Especially 2,2'-bipyrimidine has attracted growing attention of coordination chemists and its complexes have interesting chemical properties including recenltly reported catalytic effect for oxidation of methane.[1d] On the other hand, π-conjugated chelating ligands like poly(2,2'-bipyridine-5,5'-diyl) and their metal complexes are the subject of recent interest.[5] Herein we report preparation of a new π-conjugated chelating polymer ligand constituted of 2,2'-bipyrimidine unit in the main chain and formation of its metal complexes with $M(bpy)_2^{2+}$ (M = Ru, Os).

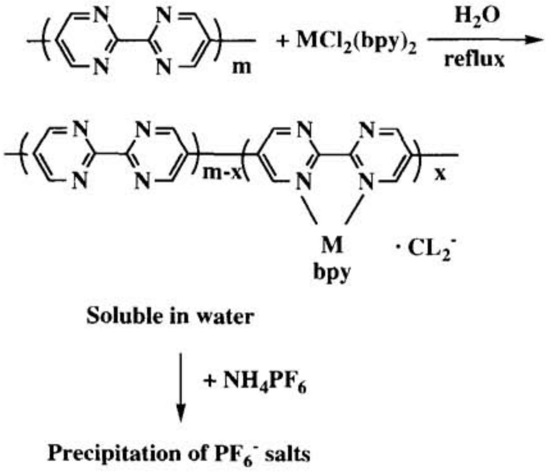
The polymeric chelating ligand was prepared by the following organometallic dehalogenation polymerization[5a] from the corresponding monomer.[6]



(1)

$Ni(0)L_m$: zerovalent nickel complex (a mixture of bis(1,5-cyclooctadiene)nickel(0), $Ni(cod)_2$, and 2,2'-bipyridyl, bpy, or triphenylphosphine, PPh_3)

Use of bpy as the neutral ligand in eqn 1 at 60 °C for 48 in DMF gave the polymer, PBpym,[7] with a high molecular weight in 93% yield, whereas use of PPh_3 at 20 °C for about 1 h gave the polymer with a weight average molecular weight of 1800,[7] corresponding to the degree of polymerization of about 12. It has been reported that use of PPh_3 gives poly(2,2'-bipyridine-5,5'-diyl) with a lower molecular weight, compared with use of bpy as the added ligand.[5a] The polymer with the lower molecular weight is fully soluble in concentrated H_2SO_4, however, the polymer with the higher molecular weight was only partly soluble in conc. H_2SO_4. Both the polymers were partially soluble in HCOOH and CF_3COOH. They gave essentially the same IR and solid ^{13}C-NMR data, and showed a π-π* absorption band at 325 nm in HCOOH, which is shifted to a longer wavelength from that of the monomer at 262 nm in HCOOH. The position of the π-π* absorption band is at somewhat shorter wavelength than that (373 nm in HCOOH[5a]) of poly(2,2'-bipyridine-5,5'-diyl).



PBpym with the lower molecular weight had higher reactivity toward metal compounds, and its reactions with $MCl_2(bpy)_2$ (M = Ru, Os)[8] gave the corresponding metal complexes.[9] According to the complex formation, PBpym became soluble in water and the polymer complexes were precipitated by addition of NH_4PF_6. 2,2'-Bipyrimidine, bpym, is known to form 1 : 1 and 1 : 2 complexes ($[Ru(bpy)_2(bpym)]^{2+}$ and ($[(bpy)_2Ru(\mu\text{-}bpym)Ru(bpy)_2]^{4+}$) with $Ru(bpy)_2^{2+}$.[10]

The Ru complex with the PF_6^- counter anion is soluble in CH_3CN, and the solid line in Figure 1 exhibits the UV-visible spectrum of the Ru complex. For the comparison, positions of

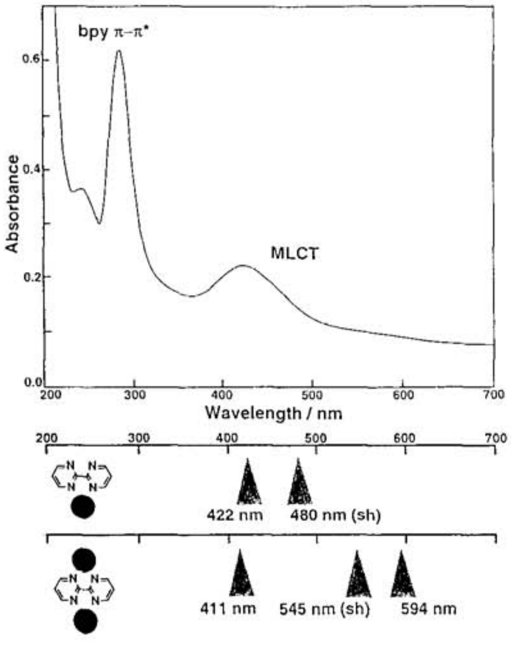


Figure 1. UV-visible spectrum of the PBpym-Ru(bpy)$_2$ complex (–) in CH_3CN. Peak positions of $[Ru(bpy)_2(bpym)]^{2+}$ and $[(bpy)_2Ru(\mu\text{-}bpym)\text{-}Ru(bpy)_2]^{4+}$ are shown below the spectrum (cf. the text).

MLCT bands[10] of ($[Ru(bpy)_2(bpym)]^{2+}$ and ($[(bpy)_2Ru(\mu\text{-}bpym)Ru(bpy)_2]^{4+}$ are shown below the UV-visible spectrum. As shown in Figure 1, the PBpym-$Ru(bpy)_2$ gives rise to a MLCT band at 423 nm characteric of the ($[Ru(bpy)_2(bpym)]^{2+}$ type complex; an additional weak and broadened absorption band is also observed at 590 nm and may be assigned to partly formed 1 : 2 complex. The π-π^* absorption band of PBpym observed at 325 nm is not observed after the complex formation, indicating a large change in the electronic state of PBpym possibly due to occurrence of a strong M → PBpym back-donation owing to strong electron-acccpting properties of the pyrimidine ring.[11] The PBpym-$Os(bpy)_2$ complex also show analogous UV-visible spectrum with peaks at 435 and 490 nm assigned to the MLCT peaks.

As described above, a new π-conjugated chelating polymer ligand constituted with 2,2'-bipyrimidine unit has been prepared and it forms metal complexes.

References and Notes

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6 The monomer was prepared by chlorination of 5,5'-bipyrimidine-2,2'-(1*H*, 1*H*')-dione by a mixture of $POCl_3$ and PCl_5. Anal. Found: C, 42.3; H, 1.7; N, 24.7; Cl, 30.8%. Calcd. C, 42.3; H, 1.8; N, 24.7; Cl, 31.2%. ^1H-NMR ($CDCl_3$, ppm): 8.83 (s). IR(cm^{-1}): 3034, 1571, 1528, 1389, 1344. Tetragonal. Space group: P4, 2, (#92). a = 7.055 Å, c = 18.922 Å, Z = 4. $D_{calc} = 1.601\ gcm^{-3}$. R = 0.0445. $R_w = 0.040$. Torsion angle between the two rings = 35 °.

7 Analytical data for PBpym with the higher molecular weight: Found: C, 55.8; H, 3.9; N, 30.7; Cl, 0%. Calcd for $(C_8H_4N_4{\cdot}H_2O)_n$: Analytical data for PBpym with the lower molecular weight: Found: C, 58.3; H, 3.2; N, 33.8%. Calcd for $(C_8H_4N_4{\cdot}0.5H_2O)_n$: C, 58.2; H, 2.8; N, 33.9%. C, 55.2; H, 3.5; N, 32.2%. IR(cm^{-1}): 1576, 1522, 1409. The light scattering method in concentrated H_2SO_4 gave a very large molecular weight of 96 x 10^4 for the polymer obtained by using bpy, and partial aggregation of this polymer in conc. H_2SO_4 is suggested. CP-MAS solid ^{13}C-NMR spectrum: δ: 155.3 (2,4,6-c), 125.6 (5-c).

8 $RuCl_2(bpy)_2$ was used as purchased. $OsCl_2(bpy)_2$ was prepared according to the literature: *Inorg. Chem.*, **27**, 4587 (1998). An equimolar amount of $MCl_2(bpy)$ per the monomeric unit was added.

9 Anal. Found: C, 37.3; H, 2.5; N, 11.2%. Calcd for 1 : 1.3 complex with $Ru(bpy)_2{\cdot}2PF_6$, $(C_{34}H_{24.8}F_{15.6}N_{9.2}\text{-}P_{2.6}Ru_{1.3}{\cdot}2H_2O)_n$: C, 36.9; H, 2.6; N, 11.6%. Yield = 82% for the Ru complex. Anal. Found: C, 35.4; H, 2.7; N, 10.0%. Calcd for a 1 : 1.1 complex with $Os(bpy)_2{\cdot}2PF_6$, $(C_{30}H_{21.6}F_{13.2}N_{8.4}Os_{1.1}P_{2.2}{\cdot}3H_2O)$: C, 33.3; H, 2.6; N, 10.9%. Yield = 64% for the Os complex.

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