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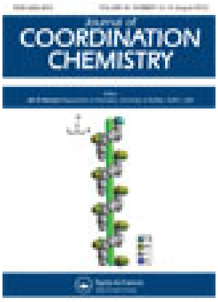

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Effects of metal ions and ligands on transesterification: synthesis, structures, and catalytic activities of a series of cation-anionic complexes with dipyridylamine ligands

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Accepted author version posted online: 20 Jun 2012.Published online: 04 Jul 2012.

To cite this article: Yuan Deng , Ying Bai , Long-Guan Zhu , Jian-Xiong Jiang & Guo-Qiao Lai (2012) Effects of metal ions and ligands on transesterification: synthesis, structures, and catalytic activities of a series of cation-anionic complexes with dipyridylamine ligands, Journal of Coordination Chemistry, 65:16, 2793-2803, DOI: 10.1080/00958972.2012.704996

To link to this article: http://dx.doi.org/10.1080/00958972.2012.704996

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Journal of Coordination Chemistry
Vol. 65, No. 16, 20 August 2012, 2793–2803

Effects of metal ions and ligands on transesterification: synthesis, structures, and catalytic activities of a series of cation–anionic complexes with dipyridylamine ligands

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(*Received 28 February 2012; in final form 8 May 2012*)

A series of cation–anion complexes derived by 2,2′-dipyridylamine (Hdpa) and carboxylate ligands with formulas $[Ni(Hdpa)_2(CH_3COO)]Cl(CH_3OH)$ (**1**), $[Co(Hdpa)_2(CH_3COO)]Cl(CH_3OH)$ (**2**), $[Ni(Hdpa)_2(CH_3CH_2CH_2COO)]Cl$ (**3**), $[Co(Hdpa)_2(CH_3CH_2CH_2COO)]Cl$ (**4**), $[Ni(Hdpa)_2(C_6H_5COO)]Cl$ (**5**), and $[Co(Hdpa)_2(C_6H_5COO)]Cl$ (**6**), were synthesized and characterized by IR, elemental analysis, MS(ESI), TG analysis, UV-Vis, and fluorescence spectra. X-ray single crystal structural analysis showed that the coordination geometries of metal ions in these complexes are similar and they are cation–anion species. The hydrogen-bonding structures are 1-D chains through the N–H···Cl bonds. There are weak stacking interactions between pyridine rings in **1**–**4**, while there are no stacking interactions in **5** and **6**. We have investigated the transesterification of phenyl acetate with methanol catalyzed by **1**–**6** under mild conditions; **1**–**4** are homogeneous catalysts while **5** and **6** are heterogeneous catalysts due to their poor solubility in methanol. Cobalt complexes exhibit higher catalytic activities than corresponding nickel complexes. Complex **4** is the best catalyst of these six complexes.

Keywords: 2,2′-Dipyridylamine; Catalytic activity; Transesterification

1. Introduction

Supramolecular structures based on non-covalent weak intermolecular interactions, such as hydrogen bonds, π–π and C–H···π interactions have attracted attention due to their potential applications as functional materials [1–6]. Transesterification is a classic reaction in synthesizing carboxylic esters [7, 8], catalyzed by a variety of protic and Lewis acids, organic and inorganic bases, enzymes, complexes, and antibodies [9]. Moreover, the ester-to-ester transformation is particularly useful in laboratory and industrial applications [10].

Although many efforts have been made to design transesterification catalysts based on metal ions with 2,2′-dipyridylamine (Hdpa), these complexes focus on Zn and other

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.704996

metals have not been mentioned [11–13]. The effect of different carboxylates on transesterification has not been reported. To find efficient catalysts to catalyze transesterification reactions under mild conditions, we have chosen chelating Hdpa with nickel and cobalt salts containing different carboxylates to investigate their catalytic activity. Herein, we report the syntheses, structures, and catalytic activities of [Ni(Hdpa)$_2$(CH$_3$COO)]Cl(CH$_3$OH) (**1**), [Co(Hdpa)$_2$(CH$_3$COO)]Cl(CH$_3$OH) (**2**), [Ni(Hdpa)$_2$(CH$_3$CH$_2$CH$_2$COO)]Cl (**3**), [Co(Hdpa)$_2$(CH$_3$CH$_2$CH$_2$COO)]Cl (**4**), [Ni(Hdpa)$_2$(C$_6$H$_5$COO)]Cl (**5**), and [Co(Hdpa)$_2$(C$_6$H$_5$COO)]Cl (**6**).

2. Experimental

2.1. *General procedures*

Chemicals (except 2,2′-dipyridylamine) and solvents were of analytical grade purchased from commercial sources and used as obtained without purification. 2,2′-Dipyridylamine was prepared according to the literature [14]. Elemental analyses (C, H, and N) were performed on a Elementar Vario Elemental Analyzer. The infrared spectrum (KBr pellet) was recorded on a Bruker VERTEX 70 spectrophotometer from 400–4000 cm^{-1}. Thermal analysis was performed on a NETZSCH 409 F3 thermal analyzer at a heating rate of 10°C min^{-1} in flowing nitrogen from 30–800°C using Al$_2$O$_3$ crucibles. MS (ESI) was determined by a Thermo LCQ Advantage MAX. The UV-Vis spectra were recorded in methanol at room temperature with a Thermo Evolution 300 spectrophotometer. The fluorescence spectroscopic studies were carried out in methanol at room temperature with a Hitachi F-2700 FL spectrometer. Analysis of catalytic transesterification product was performed with a Trace 2000 GC-DSQ MS instrument (Thermo Electron, USA). Mass spectra were acquired by electron-impact ionization under normal conditions. Catalytic reaction conversion was monitored by an Agilent 7890A gas chromatograph with SE-30 capillary column.

2.2. *Synthesis*

2.2.1. Preparation of [Ni(Hdpa)$_2$(CH$_3$COO)]Cl(CH$_3$OH) (1). A mixture of NiCl$_2$ · 6H$_2$O (0.238 g, 1.0 mmol), anhydrous sodium acetate (0.082 g, 1.0 mmol), and 2,2′-dipyridylamine (0.342 g, 2.0 mmol) was dissolved in methanol (20 mL), stirring at room temperature for 12 h and mother liquor carefully layered with ether. After one week, suitable purple crystals for X-ray crystal structure analysis were obtained. Calcd for C$_{23}$H$_{25}$N$_6$O$_3$ClNi (%): C, 52.42; H, 4.75; N, 15.95. Found (%): C, 52.24; H, 4.85; N, 15.79. MS (ESI, *m*/*z*): 459 ([Ni(Hdpa)$_2$(CH$_3$COO)]$^+$), 399 ([Ni(Hdpa)(dpa)]$^+$), 288([Ni(Hdpa)(CH$_3$COO)]$^+$). IR (KBr, cm^{-1}): 3437s, 3283m, 3238w, 3179m, 3131m, 2970s, 1639s, 1584s, 1536s, 1477s, 1364s, 1270m, 1240s, 1160s, 1058w, 1013s, 938m, 907m, 844w, 791s, 770s, 741w, 676m, 647w, 626w, 537m, 432m.

2.2.2. Preparations of 2, 3, 4, and 6. The synthetic procedures of **2**, **3**, **4**, and **6** are very similar to the synthesis of **1**. Crystals of **2** are orange. Calcd for C$_{23}$H$_{25}$N$_6$O$_3$ClCo (%): C, 52.32; H, 4.74; N, 15.92. Found (%): C, 52.40; H, 4.87; N, 15.82. MS (ESI, *m*/*z*):

460 ($[Co(Hdpa)_2(CH_3COO)]^+$), 400 ($[Co(Hdpa)(dpa)]^+$), 289 ($[Co(Hdpa)(CH_3COO)]^+$). IR (KBr, cm^{-1}): 3428s, 3285w, 3181w, 3066m, 2968m, 1640s, 1582s, 1530s, 1477s, 1437w, 1421w, 1371m, 1269w, 1238s, 1160s, 1057w, 1010s, 907w, 791s, 772s, 674m, 535m, 426m.

Crystals of **3** are purple. Calcd for $C_{24}H_{25}N_6O_2ClNi$ (%): C, 55.12; H, 4.78; N, 16.08. Found (%): C, 55.24; H, 4.85; N, 16.15. MS (ESI, *m*/*z*): 487 ($[Ni(Hdpa)_2(CH_3CH_2CH_2COO)]^+$), 399 ($[Ni(Hdpa)(dpa)]^+$), 316 ($[Ni(Hdpa)(CH_3CH_2CH_2COO)]^+$). IR (KBr, cm^{-1}): 3434s, 3283w, 3179w, 3128w, 3062m, 2965s, 2932w, 1640s, 1583s, 1524s, 1477s, 1434m, 1417m, 1369m, 1315w, 1270w, 1238m, 1158m, 1059w, 1012m, 934w, 907w, 879w, 838w, 785m, 773m, 670w, 646w, 666w, 536w, 433w.

Crystals of **4** are orange. Calcd for $C_{24}H_{25}N_6O_2ClCo$ (%): C, 55.01; H, 4.78; N, 16.05. Found (%): C, 55.11; H, 4.70; N, 15.96. MS (ESI, *m*/*z*): 488 ($[Co(Hdpa)_2(CH_3CH_2CH_2COO)]^+$), 400 ($[Co(Hdpa)(dpa)]^+$), 317 ($[Co(Hdpa)(CH_3CH_2CH_2COO)]^+$). IR(KBr, cm^{-1}): 3447m, 3281w, 3235w, 3177w, 3127w, 3061m, 2960s, 2931w, 2901w, 2871w, 1639s, 1593s, 1581s, 1527s, 1476s, 1433m, 1417m, 1370m, 1314w, 1268w, 1237s, 1170w, 1158m, 1058w, 1008m, 933w, 906w, 880w, 832w, 785m, 775m, 670w, 645w, 605w, 533w, 421w.

Crystals of **6** are orange. Calcd for $C_{27}H_{23}N_6O_2ClCo$ (%): C, 58.12; H, 4.13; N, 15.07. Found (%): C, 58.10; H, 4.16; N, 15.13. MS (ESI, *m*/*z*): 522 ($[Co(Hdpa)_2(C_6H_5COO)]^+$), 400 ($[Co(Hdpa)(dpa)]^+$), 351 ($[Co(Hdpa)(C_6H_5COO)]^+$). IR (KBr, cm^{-1}): 3436s, 3289w, 3241w, 3180w, 3131w, 3064m, 2987s, 2926m, 2855w, 1643s, 1596s, 1583s, 1531s, 1480s, 1419s, 1376m, 1327m, 1267w, 1238s, 1160s, 1056w, 1009s, 907w, 872w, 800s, 774s, 726s, 681w, 645m, 605w, 532m, 425m.

2.2.3. Preparation of $[Ni(Hdpa)_2(C_6H_5COO)]Cl$ (5). A mixture of $NiCl_2 \cdot 6H_2O$ (0.238 g, 1.0 mmol), sodium benzoate (0.144 g, 1.0 mmol), and 2,2′-dipyridylamine (0.342 g, 2.0 mmol) was dissolved in methanol/H_2O (10 mL/10 mL) solution. The resulting mixture was sealed in a 25 mL Teflon-lined autoclave and heated to 150°C for 48 h, then cooled to room temperature. Suitable purple crystals for X-ray crystal structure analysis were obtained. Calcd for $C_{27}H_{23}N_6O_2ClNi$ (%): C, 58.22; H, 4.13; N, 15.09. Found (%): C, 58.14; H, 4.21; N, 15.15. MS(ESI, *m*/*z*): 521 ($[Ni(Hdpa)_2(C_6H_5COO)]^+$), 399 ($[Ni(Hdpa)(dpa)]^+$), 350 ($[Ni(Hdpa)(C_6H_5COO)]^+$). IR (KBr, cm^{-1}): 3436m, 3287w, 3240w, 3179w, 3130w, 3065m, 2985w, 2924m, 2854m, 1643s, 1584s, 1529s, 1479s, 1420s, 1373m, 1326w, 1268w, 1240s, 1160s, 1122w, 1107w, 1057w, 1013s, 907m, 883w, 856 m, 800s, 772s, 727s, 682w, 647m, 605w, 534m, 432m.

2.3. *X-ray crystallographic determination*

Crystallographic data were collected on a Bruker Apex DUO diffractometer at 296 K using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The frames were integrated with Bruker SAINT Software package [15] and the data were corrected for absorption using SADABS [16]. The structures were solved by direct methods using SHELXS-97 [17]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares on F^2 using SHELXS-97. Hydrogen atoms were placed in idealized positions except NH of 2,2′-dipyridylamine. Details of crystal data and structure refinements for the six complexes are listed in table 1.

Table 1. Crystallographic data and refinement parameters for **1–6**.

Complex	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{23}H_{25}N_6O_3ClNi$	$C_{23}H_{25}N_6O_3ClCo$	$C_{24}H_{25}N_6O_2ClNi$	$C_{24}H_{25}N_6O_2ClCo$	$C_{27}H_{23}N_6O_2ClNi$	$C_{27}H_{23}N_6O_2ClCo$
Formula weight	527.65	527.87	523.66	523.88	557.67	557.89
Crystal color/shape	Purple/block	Orange/block	Purple/block	Orange/block	Purple/block	Orange/block
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$c2/c$	$c2/c$	$p\bar{1}$	$p\bar{1}$	$c2/c$	$c2/c$
Unit cell dimensions (Å, °)						
a	28.524(4)	28.592(2)	9.7150(19)	9.7613(8)	16.0033(11)	16.135(2)
b	12.6009(17)	12.7108(10)	9.7271(19)	9.7852(8)	15.9348(11)	15.895(2)
c	14.683(2)	14.7422(12)	14.001(3)	13.9968(11)	12.6651(8)	12.7644(16)
α	90	90	106.656(3)	98.704(1)	90	90
β	113.314(3)	113.400(2)	98.378(3)	106.869(2)	125.281(1)	125.997(2)
γ	90	90	99.048(4)	98.813(1)	90	90
Volume (Å^3), Z	4846.5(12), 8	4917.1(7), 8	1226.1(4), 2	1236.90(17), 2	2636.5(3), 4	2648.6(6), 4
Calculated density (g·cm^{-3})	1.446	1.426	1.418	1.407	1.405	1.399
Absorption coefficient (mm^{-1})	0.948	0.843	0.933	0.835	0.873	0.785
$F(000)$	2192	2184	544	542	1152	1148
Reflections collected	17,902	17,860	17,415	17,339	9465	9933
Independent reflections	4392	4460	4411	4432	2354	2391
Crystal size (mm^3)	0.46 × 0.41 × 0.29	0.42 × 0.36 × 0.24	0.30 × 0.25 × 0.20	0.38 × 0.34 × 0.20	0.45 × 0.43 × 0.39	0.42 × 0.37 × 0.26
Goodness-of-fit on F^2	1.081	1.114	1.063	1.112	1.065	1.089
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.034$, $wR_2 = 0.099$	$R_1 = 0.039$, $wR_2 = 0.109$	$R_1 = 0.026$, $wR_2 = 0.081$	$R_1 = 0.024$, $wR_2 = 0.071$	$R_1 = 0.0275$, $wR_2 = 0.0947$	$R_1 = 0.026$, $wR_2 = 0.077$
R indices (all data)	$R_1 = 0.040$, $wR_2 = 0.110$	$R_1 = 0.051$, $wR_2 = 0.124$	$R_1 = 0.031$, $wR_2 = 0.096$	$R_1 = 0.027$, $wR_2 = 0.075$	$R_1 = 0.0401$, $wR_2 = 0.1318$	$R_1 = 0.031$, $wR_2 = 0.080$
Largest difference peak and hole (eÅ^{-3})	0.691 and −0.508	0.796 and −0.565	0.385 and −0.296	0.217 and −0.222	0.682 and −0.733	0.208 and −0.172

2.4. *Catalytic activity of the complexes*

The catalyst (7.5×10^{-2} mmol) was added to a solution of phenyl acetate (1.0 mmol) dissolved in methanol (2.0 mL), then the mixture was stirred at room temperature. Catalytic reaction conversion was monitored by an Agilent 7890A gas chromatograph with a SE-30 capillary column. A solution of the sample (50 µL) from the reaction mixture dissolved in CH_3OH (1 mL) was injected directly into the GC inlet for analysis. Hydrogen (>99.999%) was used as carrier gas at a constant flow of 1.0 mL min^{-1}. The column temperature was maintained at 70°C for 1 min then programmed from 20°C min^{-1} to 300°C. The GC inlet temperature was 250°C and the detector temperature was 260°C. The conversion yield was calculated by area normalization based on phenyl acetate and formation of the phenol.

3. Results and discussion

3.1. *Crystal structures of six complexes*

Six complexes are cation–anion species with similar structures (figure 1), therefore only the structure of **1** is analyzed in detail. Compound **1** consists of $[Ni(Hdpa)_2(CH_3COO)]^+$, a chloride and a methanol (figure 1a). Ni(II) is octahedral with four N donors from two Hdpa and two oxygen atoms from acetate, very different from that of $[Cu(Hdpa)_2(CH_3COO)]^+$ [18]. Pyridine rings of Hdpa form dihedral angles of 29.77(7)° and 21.93(7)°. The cation and anion form hydrogen bonds through N–H···Cl (with D···A of 3.1638(19) Å, Supplementary material), resulting in a 1-D chain (figure 2). The π–π stacking interactions are observed between pyridine rings of Hdpa with a Cg1···Cg1* $(2-x,\ 1-y,\ 1-z)$ separation of 3.9335(15) Å and a Cg2···Cg2* $(2-x, -y,\ 1-z)$ separation of 3.6441(16) Å (where Cg1 and Cg2 are centroids of the N6/C16-C20 and N1/C1-C5 rings) (Supplementary material).

Although these six structures are similar, the bond distances are somewhat different between corresponding Ni and Co complexes (Supplementary material). The aromatic π–π interactions in **2**–**4** are listed in "Supplementary material." There are no π–π interactions in **5** and **6**.

3.2. *Thermal analysis*

Complexes **1** and **2** contain methanol which is from room temperature to 280°C and room temperature to 182°C, respectively. The weight losses are 6.17% and 5.71%, respectively, consistent with calculated values of 6.07% and 6.06%. Decomposition temperatures are 281°C and 182°C for **1** and **2**. Complexes **3**–**6** have no solvent molecules and their decomposition temperatures are 287°C, 217°C, 320°C, and 249°C, respectively. The detailed information is shown in "Supplementary material." The DTA–TG analysis reveals that the decomposition temperatures of Ni complexes are higher than those of corresponding cobalt complexes.

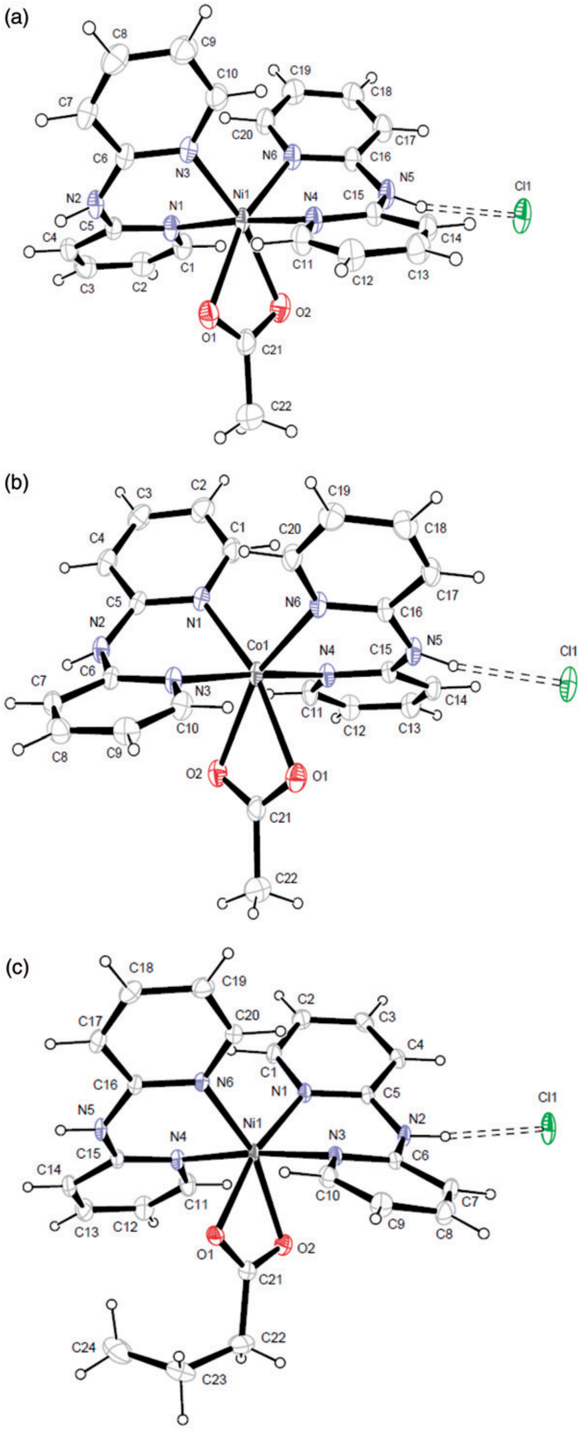


Figure 1. Molecular structures of six complexes with numbering schemes. Thermal ellipsoids are drawn at the 30% probability level.

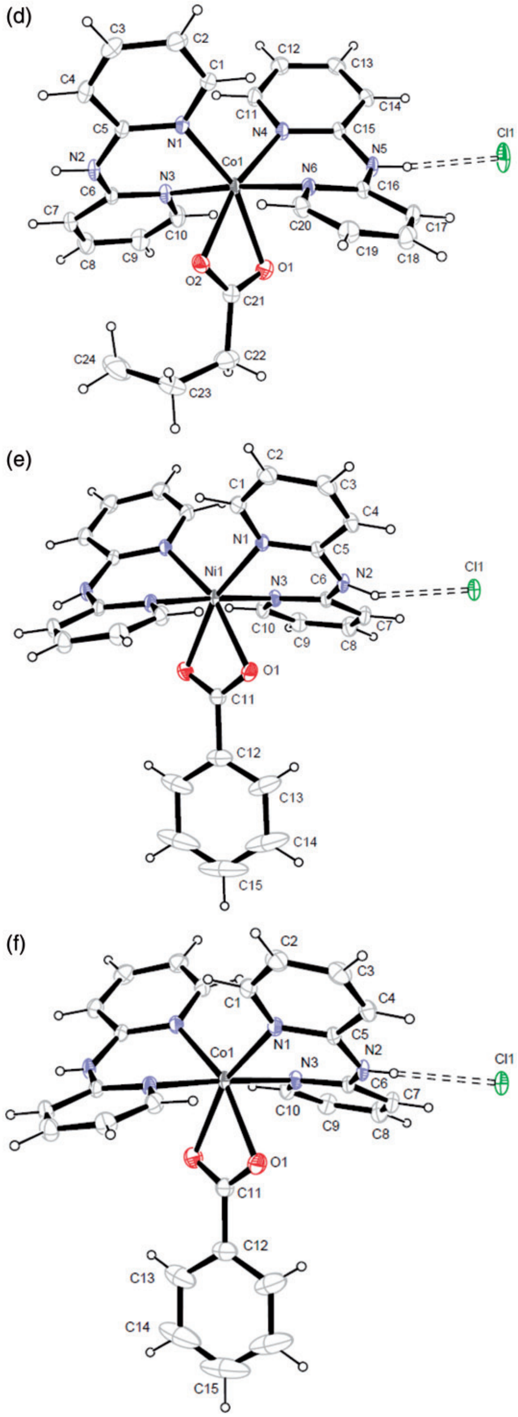


Figure 1. Continued.

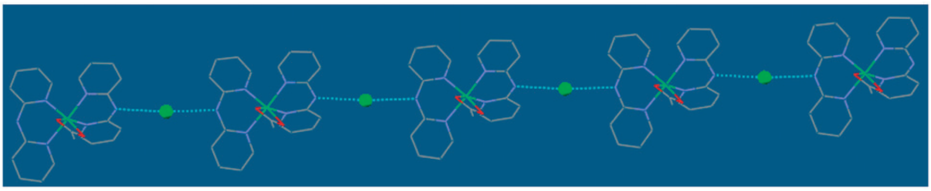


Figure 2. The 1-D hydrogen-bonding chain for **1**.

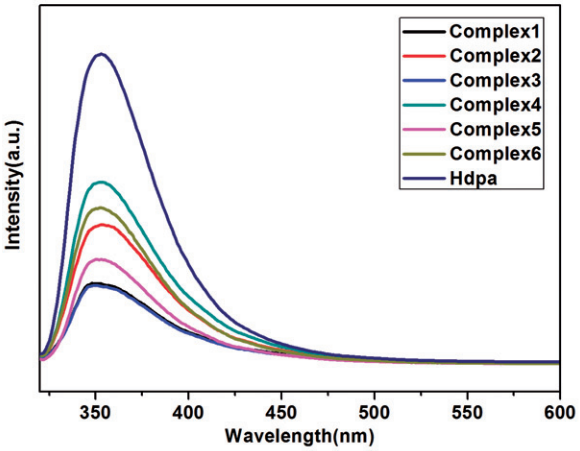


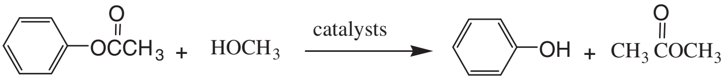
Figure 3. Fluorescence spectra of the six complexes in methanol.

3.3. *UV-Vis spectra*

UV-Vis spectra of the complexes show similar patterns in methanol with concentration of $1.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ and detailed data are listed in "Supplementary material." Three absorptions at about 205, 260, and 314 nm are assigned to the intraligand transitions of Hdpa [19, 20]. Complex **5** has the strongest absorptions, while **6** has relatively weak absorptions, indicating carboxylates with benzene ring and the metal ions are the main factors for absorption strength. Pons and co-workers reported Co(II) and Ni(II) complexes have d–d transitions at 500–700 nm with concentration of $10^{-3}\,\mathrm{mol\,L^{-1}}$ [21, 22]. We performed all complexes at $10^{-3}\,\mathrm{mol\,L^{-1}}$ in methanol (Supplementary material), but no d–d absorption was observed. Lin and Liu point out that the d–d transitions for Co(II) complexes in general are weak and in some cases could not be observed [23].

3.4. *Fluorescence spectra*

Fluorescence spectra were measured in CH_3OH at $1.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ at 298 K ($\lambda_{ex} = 310$ nm). The six complexes together with the ligand have similar fluorescence emissions (figure 3). Emission peaks are at 350 nm for **1**, 353 nm for **2**, 350 nm for **3**, 352 nm for **4**, 351 nm for **5**, and 352 nm for **6**. These emissions are from N-donor



Scheme 1. The transesterification of methanol with phenyl acetate. The products were determined by GC and GC-MS.

Table 2. Effects of metal on transesterification of phenyl acetate with methanol.

	Conversion (%)					
Catalyst	2 h	6 h	1d	2d	3d	4d
1	1.84	4.23	7.75	13.72	19.30	24.12
2	14.6	29.2	62.6	78.5	87.6	92.6
3	5.6	10.5	29.8	56.8	61.2	69.5
4	21.6	36.1	71.7	90.7	96.8	98.5
5	1.6	2.5	7.5	12.9	18.5	23.8
6	11.5	26.8	61.1	77.5	85.5	90.5

ligands, ligand-centered π–π^* transition, and electron transfer from ligands to metal. Complex **4** has the strongest emission and emission peaks of cobalt complexes are stronger than those of nickel complexes. The ligand shows stronger absorption than those of complexes, indicating that coordination does not enhance emission.

3.5. *Catalytic activity of the complexes*

Transesterification of methanol with phenyl acetate (scheme 1) catalyzed by **1**–**6** under mild conditions were investigated and the results are listed in table 2. Complexes **1**–**4** are soluble in methanol and these complexes can be employed as homogeneous catalysts, while **5** and **6** were heterogeneous catalysts due to their poor solubility in methanol.

Catalytic data show that the catalytic activities of Ni complexes are lower than those of corresponding Co complexes (table 2), indicating that metal ions have impact on the reaction, which was reported by Kim *et al.* [24]. We also find that carboxylates influence the reaction conversion. The metal butanoate complexes have higher catalytic activities than those of metal acetates or benzoates and **4** is the best catalyst. We further studied the effect of quantity of the catalyst on the reaction for **4**. Reaction rate increased with increase of the amount of **4**. When 3.75×10^{-2} mmol, 7.50×10^{-2} mmol, and 11.25×10^{-2} mmol of **4** were used, the conversion is 29.1%, 36.1%, and 40.3%, respectively, after 6 h; the conversions were all above 95% after 4 days (figure 4).

Previous report [6] showed that $[Zn(Hdpa)(I_2)]$ has lower activity than cation–anion species, such as $[Zn(Hdpa)_2(NO_3)](NO_3)$, but in previous work the neutral catalyst was insoluble in methanol and a heterogeneous catalyst. Our complexes are all cation–anion species. The difference of catalytic activities of **4** and **6** is small, although they are homogeneous and heterogeneous catalysts, respectively. For Ni, the difference of the catalytic activities between **3** and **5** are large. These results further illustrate that the metal ion, carboxylates, and form all influence the reaction.

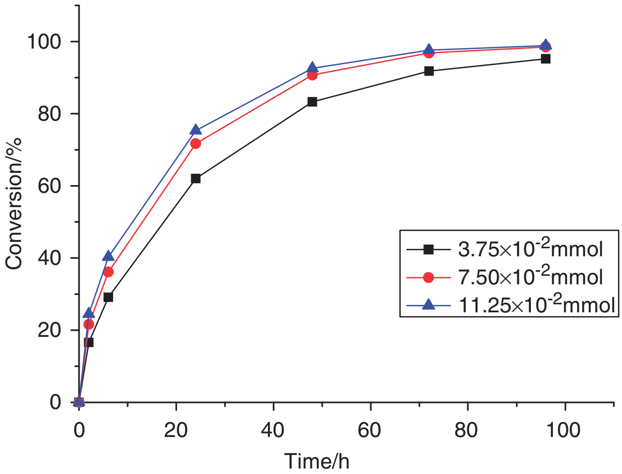


Figure 4. The effect of quantity of **4** on the reaction.

4. Conclusion

Six cation–anion complexes have been synthesized and characterized. Hydrogen bonds (N–H···Cl) extend these complexes into 1-D chains. M–O and M–N bond lengths of Ni complexes are systematically shorter than those of corresponding cobalt complexes. There are π–π interactions between pyridine rings in **1**–**4** while there is no such interaction in **5** and **6**. The complexes were studied as catalysts in transesterification of phenyl acetate with methanol under mild conditions. Complexes **1**–**4** are homogeneous catalysts while **5** and **6** are heterogeneous due to their poor solubility in methanol. Cobalt complexes systematically exhibit higher catalytic activities than corresponding nickel complexes and **4** is the best catalyst. Carboxylates and metal play important roles in the transesterification.

Supplementary material

CCDC 869286-869291 for **1**–**6** contain supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. 21073157).

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