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# Synthesis and characterization of cobalt(III) complexes containing 2-pyridinecarboxamide ligands and their application in catalytic oxidation of ethylbenzene with dioxygen†

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**Four novel cobalt(III) complexes were found to have high catalytic activities and excellent selectivities in the oxidation of ethylbenzene to acetophenone using $O_2$ as oxidant without need of solvent.**

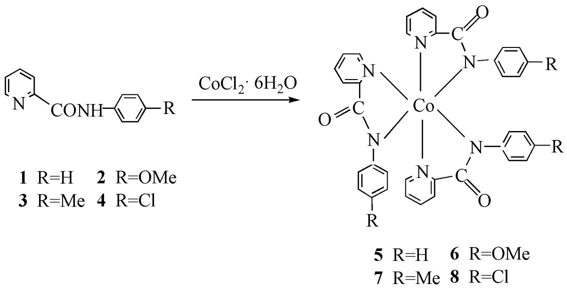
The selective oxidation of organic compounds utilizing dioxygen as a primary oxidant represents an environmentally friendly technology for industrial application.[1] Much effort has been made in the past to activate dioxygen by vast number of biomimetic catalysts or metal complexes for the catalytic oxidation of organic substrates under mild conditions.[2–6] However, the advancement for their industrial application is slow. For example, even though the halogenated porphyrinatoiron(III) complexes greatly increased the catalytic activity in the selective oxidation of alkanes,[7] the practical application of these catalysts is severely limited by the thermal stability of the porphyrins under oxidative conditions.

Recently there has been an increased interest in the development of clean and economical processes for the selective oxidation of ethylbenzene to higher-value added product acetophenone.[8–13] The current industrial production of acetophenone is *via* the oxidation of ethylbenzene with molecular oxygen using cobalt cycloalkanecarboxylate or cobalt acetate as catalyst in acetic acid solvent.[12] This method suffers from its corrosive and environmentally unfriendly nature. Herein, we report for the first time the synthesis of four cobalt pyridinecarboxamide derivatives **5–8** and their remarkable catalytic activities and excellent selectivities in the catalytic dioxygen oxidation of ethylbenzene to acetophenone *without the need of any solvent* and reducing reagent.

Ligands **1–4** were obtained *via* a general procedure[14] from 2-pyridinecarboxylic acid to 2-pyridinecarboxyl chloride[15] followed by the reaction with an appropriate aniline in THF. The oxidation of Co(II) chloride with aerobic oxygen in the presence of ligands **1–4** gave complexes **5–8**.

The longer UV adsorption wavelengths of complexes **5–8** (284–298 nm) than the corresponding free ligands (304–360 nm) were consistent with the presence of the larger conjugation systems in the complexes. For the complexes, the absence of $\nu_{N-H}$ peak in the IR spectra and the disappearance of amido proton peak in the $^1$H NMR spectra indicated that the ligands had lost the amido proton. Besides, free ligands **1–4** exhibited $\nu_{C=O}$ at 1670–1684 cm$^{-1}$ while the $\nu_{C=O}$ of complexes **5–8** were found to shift to 1620–1636 cm$^{-1}$. The lowering of vibration frequency was due to the delocalization of the higher electron density at the deprotonated amide nitrogen.[16] The molecular structures of complexes **6–8** were determined by single crystal X-ray diffraction†‡ and the results were consistent with the corresponding spectroscopic data. It was also found that, for every ligand in the complexes, the pyridine ring and the carbonyl group were on the same plane. The coordinations of these ligands were clearly through the pyridine nitrogen and the negative amido nitrogen ion instead of neutral amide nitrogen or carbonyl oxygen. The deprotonated amido nitrogen was a good σ-donor,[17] which facilitated the aerobic oxidation of Co(II) to Co(III) during the formation of the complex. The three anionic ligands neutralized the trivalent Co$^{3+}$. An ORTEP drawing of complex **6** is shown in Figure 2.

The complexes were found to be highly active and remarkably selective in the oxidation of ethylbenzene to acetophenone using dioxygen as the oxidant, a reaction of high scientific and commercial interest. Typical results of our studies are summarized in Table 1. When the reaction temperature was increased from 120 to 150 °C, the conversion of ethylbenzene increased rapidly from 49.8 to 70.4%. The main product was acetophenone with its selectivity up to 90.2% at 150 °C. Acetophenone productivity was 635 mol per mol catalyst·h, 27 times higher than that of the best system reported previously using Co(OAc)$_2$ combined with pyridine hydrobromide as



**1** R=H **2** R=OMe
**3** R=Me **4** R=Cl

**5** R=H **6** R=OMe
**7** R=Me **8** R=Cl

**Fig. 1** Synthetic route of cobalt(III) complexes.

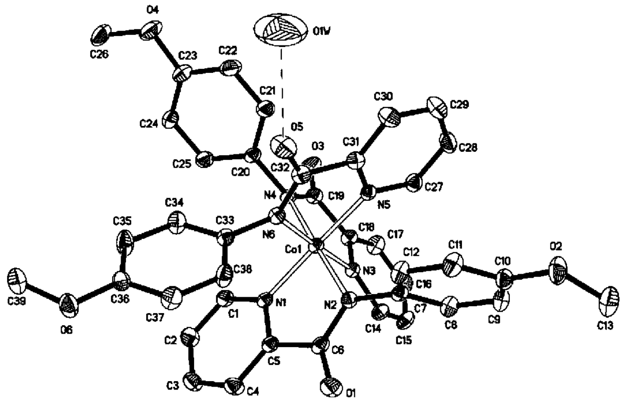


**Fig. 2** Molecular structure of complex **6**.

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† Electronic supplementary information (ESI) available: full experimental and spectroscopic data for all compounds. See http://www.rsc.org/suppdata/cc/b3/b301963b/

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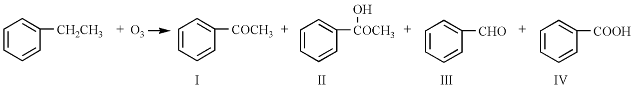
catalysts in acetic acid solvent.[12] Using Co(OAc) as a catalyst under the same conditions as those used in our study, the conversion of ethylbenzene and selectivity of acetophenone were only 40.4 and 80.2%, respectively. These results clearly showed the advantages of the new Co(III) complexes **5–8**. When the reaction temperature was raised to 160 °C, extensive carbonization occurred. For this reason we chose 150 °C as a standard reaction temperature for the rest of our study. On extending the reaction time from 2 to 10 h, both conversion and selectivity of acetophenone increased initially, then the conversion had no obvious change due to the inhibition of the reaction by the products and the selectivity of acetophenone decreased due to the over oxidation to benzoic acid after reaching 90.2% in 4 h. The effect of product inhibition in the catalytic reaction was demonstrated by mixing acetophenone with ethylbenzene (molar ratio 7:3) as starting material and no ethylbenzene conversion was observed under otherwise identical reaction conditions.

On increasing the $O_2$ pressure from 0.8 to 1.8 MPa, the conversion levels increased from 60.0 to 70.7%. Further increase of $O_2$ pressure did not show enhancement in conversion. The effect of pressure on the selectivity for acetophenone was not observed. On increasing the catalyst concentration from 0.5 to 2.0 mmol $L^{-1}$, the ethylbenzene conversion increased from 43.8 to 70.4% with the increase of acetophenone from 83 to 90%. When the catalyst concentration was higher than 2.0 mmol $L^{-1}$, the over oxidation to benzoic acid became more significant and the selectivity to acetophenone decreased. Our further investigation of different substituents on the phenyl ring of the ligands indicated that the conversions of ethylbenzene decreased using complexes **6–8** as catalysts rather than the unsubstituted complex **5**. This may be due to the outer spatial hindrance of octahedral coordination sphere making it somewhat more difficult for the active species to form. On the other hand, the electronic effects of the substituents may increase selectivity to acetophenone. For example, 93.2% selectivity for acetophenone was achieved on 63% conversion using catalyst **6** with methoxyl group on the phenyl ring of ligand **2**.

**Table 1** Results of the oxidation of ethylbenzene to acetophenone



| Entry | Change of reaction condition[a] | Conv[b]% | Sel (%)[c] I | II | III | IV |
|---|---|---|---|---|---|---|
| 1 | 120 °C | 49.8 | 88.0 | 9.3 | 0.5 | 2.2 |
| 2 | 130 °C | 59.0 | 88.4 | 7.5 | 0.5 | 3.6 |
| 3 | 140 °C | 63.8 | 88.5 | 6.7 | 0.6 | 3.9 |
| 4 | 150 °C | 70.4 | 90.2 | 1.6 | 0.7 | 7.0 |
| 5 | 2 h | 66.5 | 87.7 | 4.4 | 0.6 | 7.1 |
| 6 | 4 h | 70.4 | 90.2 | 1.6 | 0.7 | 7.0 |
| 7 | 6 h | 70.5 | 87.7 | 1.2 | 0.4 | 10.4 |
| 8 | 8 h | 70.8 | 86.1 | 1.5 | 0.4 | 11.8 |
| 9 | 10 h | 71.9 | 81.8 | 0.7 | 0.5 | 16.5 |
| 10 | 0.8 MPa | 60.0 | 91.4 | 2.3 | 0.5 | 5.8 |
| 11 | 1.6 MPa | 70.4 | 90.2 | 1.6 | 0.7 | 7.0 |
| 12 | 1.8 MPa | 70.7 | 90.0 | 1.7 | 0.4 | 7.6 |
| 13 | 2.0 MPa | 70.7 | 90.2 | 2.0 | 0.4 | 7.2 |
| 14 | 0.5 mmol/L | 43.8 | 83.0 | 12.2 | 2.6 | 2.1 |
| 15 | 1.0 mmol/L | 45.8 | 85.8 | 10.5 | 1.8 | 1.9 |
| 16 | 2.0 mmol/L | 70.4 | 90.2 | 1.6 | 0.7 | 7.0 |
| 17 | 6.0 mmol/L | 70.3 | 87.5 | 1.3 | 0.3 | 10.6 |
| 18 | 8.0 mmol/L | 70.4 | 87.1 | 1.6 | 0.3 | 10.8 |
| 19 | Catalyst **5** | 70.4 | 90.2 | 1.6 | 0.7 | 7.0 |
| 20 | Catalyst **6** | 63.3 | 93.2 | 3.2 | 0.6 | 3.1 |
| 21 | Catalyst **7** | 64.7 | 91.1 | 1.6 | 0.4 | 6.6 |
| 22 | Catalyst **8** | 64.2 | 83.6 | 2.3 | 0.6 | 12.9 |

[a] For entries 1–18, catalyst **5** was used. Entries 19–22 were the comparison of the effectiveness of the four complexes **5–8**. Standard reaction conditions: ethylbenzene = 8 mol $L^{-1}$, catalyst concentration = 2 mmol $L^{-1}$; $O_2$ pressure = 1.6 MPa; reaction time = 4 h; temperature = 150 °C. [b] Conversion of ethylbenzene. [c] Products were identified by GC (HP 5890 or 4890, column AT-1 30m × 0.25 mm) using authentic samples for comparison.

In summary, we have synthesized and characterized trivalent cobalt complexes containing 2-pyridinecarboxamide ligands and have found them to be highly effective in the catalytic oxidation of ethylbenzene to acetophenone with $O_2$ *in the absence of solvent* and reducing reagent. This economical and environmentally friendly system showed excellent potential for industrial application.

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## Notes and references

‡ *Crystal data*. **6**: $CoC_{39}H_{35}N_6O_7$, M = 785.66, triclinic, $a$ = 10.0802(16), $b$ = 13.104(2), $c$ = 14.813(2) Å, $U$ = 1739.1(5) $Å^3$, $T$ = 294 K, space group $P\bar{1}$, $Z$ = 2, μ(Mo–Kα) = 0.555 $mm^{-1}$, 11760 reflections collected, 7609 independent reflections (*Rint* = 0.0395). The final *R* indices [$I > 2\sigma(I)$]: *R1* = 0.0572, *wR2* = 0.0924, *R* indices (all data): *R1* = 0.1039, *wR2* = 0.1007. **7**: $CoC_{40}H_{39}N_6O_5$, M = 742.7, triclinic, $a$ = 13.756(2), $b$ = 15.878(3), $c$ = 19.388(3) Å, $U$ = 3754.5(10) $Å^3$, $T$ = 294 K, space group $P\bar{1}$, $Z$ = 4, μ(Mo–Kα) = 0.509 $mm^{-1}$, 13115 reflections collected, 13115 independent reflections (*Rint* = 0.0000). The final *R* indices [$I > 2\sigma(I)$]: *R1* = 0.0601, *wR2* = 0.1433, *R* indices (all data): *R1* = 0.1270, *wR2* = 0.1724. Cr. **8**: $C_{36}H_{28}Cl_3CoN_6O_5$, M = 789.92, monoclinic, $a$ = 15.0628(12), $b$ = 14.7653(12), $c$ = 16.8999(14) Å, $U$ = 3693.6(5) $Å^3$, $T$ = 294 K, space group $P2(1)/c$, $Z$ = 4, μ(Mo–Kα) = 0.732 $mm^{-1}$, 8381 reflections collected, 8381 independent reflections (*Rint* = 0.0000). The final *R* indices [$I > 2\sigma(I)$]: *R1* = 0.0512, *wR2* = 0.1306, *R* indices (all data): *R1* = 0.0826, *wR2* = 0.1467. CCDC 189734–189736. See http://www.rsc.org/suppdata/cc/b3/b301963b/ for crystallographic data in .cif or other electronic format.

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