



Synthesis and characterization of novel transition metal complexes with indole acetic acid ligands: Evaluation of their catalytic activity for the oxidation of cyclohexane



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ABSTRACT

Two new transition metal complexes $\text{Co}(\text{IAA})_2(\text{phen})(\text{H}_2\text{O})$ (**1**) and $\text{Ni}(\text{IAA})_2(\text{phen})(\text{H}_2\text{O})$ (**2**) (IAA = indole acetic acid, phen = 1,10-phenanthroline) with IAA and phen as mixed ligands are synthesized and characterized by elemental analysis, IR spectra, UV–Vis spectroscopy and single-crystal X-ray diffraction. The structural analysis shows that the coordination mode of the ligand IAA in complexes **1** and **2** were similar: the former is in a $\mu_1-\eta^1$ linking fashion, while the latter is in a $\mu_1-\eta^1-\eta^1$ linking fashion. In addition, the thermogravimetric analysis of the complexes was investigated in detail. The catalytic activity of the two complexes has been investigated in the oxidation of cyclohexane with the presence of H_2O_2 as primary oxidant under mild conditions, which shows that cobalt complex with IAA ligand exhibited a good catalytic activity with the maximum TON value of 110.

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1. Introduction

Comparing with the heterogeneous catalysts, the transition metal complexes have attracted much attention in various chemical processes for their irreplaceable advantages acting as homogeneous catalysts. However, a huge challenge in heterogeneous reactions is that the intermediates are too active to be captured, which led to a negative effect on understanding the reacting mechanism. Fortunately, homogeneous catalysts can help to stabilize the active intermediates formed during the catalytic cycle.

Research results show that the complexes with different organic ligands exhibited different catalytic activity [1–7]. In general, the organic ligands used in catalysts can be divided into five different types: (i) the schiff based ligands [8–11]. Tümer et al. [9] synthesized Cu(II) and Cr(III) schiff complexes and found that they show good catalytic activities in alkane oxidation using cyclohexane (Cy) or cyclooctane as substrates with 30% H_2O_2 in acetonitrile under mild conditions; (ii) the tripodal scorpionate ligands [12–14]. Pombeiro and co-workers [14] reported that scorpionate iron complexes have highly catalytic activity (TON values up to ca. 385) in the Cy oxidation with H_2O_2 oxidant in MeCN medium; (iii) the pincer chelate ligands [15–17]. Thiel et al. [16] synthesized a series of ruthenium complexes and studied their catalytic activities in the transfer hydrogenation of aryl ketones. The complexes show high

activities with turnover frequency value up to 1200 h^{-1} ; (iv) the triangular amine ligands [18]. Turmanova et al. obtained a series of D32 complexes ($\text{D32} = [\text{DAB-dendr}-(\text{NH}_2)_{32}]$ -poly(propylene imine) dendrimers with 32 primary amino groups) and used them as potential catalysts in the model reaction of cyclohexene oxidation; (v) the carboxylate ligands [19–24]. Rutledge et al. [19] have generated several iron(II) complexes with L-proline ligand and shown their catalytic activities in the alkene dihydroxylation and allylic oxidation using hydrogen peroxide as a oxidant. To improve the catalytic activities of homogeneous catalysts, researchers need to understand the relationship between molecular structure and functional mechanism. Therefore, it is significant to design and synthesize complexes with various ligands, as well as investigate their catalytic activities, particularly to know how to choose better organic ligands to get higher activity.

Indole acetic acid, a kind of biomimetic multifunctional biological substance, is a phytohormone of the auxin series, and has been established as an essential component of associative plant–microbe interactions [25–27]. If such biological substance can be used in catalytic reactions, it will give us a new insight to the application for homogeneous catalysts. To our best knowledge, no reports have been focused on the catalytic performance of the transition metal complexes with indole acetic acid ligands as homogeneous catalysts.

Herein, we designed and synthesized two novel transition metal complexes with indole acetic acid as ligands: $\text{Co}(\text{IAA})_2(\text{phen})(\text{H}_2\text{O})$ (**1**) and $\text{Ni}(\text{IAA})_2(\text{phen})(\text{H}_2\text{O})$ (**2**) (IAA = indole acetic

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acid, phen = 1,10-phenanthroline) and studied their catalytic properties in the H₂O₂ promoted Cy oxidation under mild conditions.

2. Material and methods

2.1. Reagents and instruments

Elemental analyses (C, H and N) were performed on a Perkin Elmer 240C automatic analyzer. IR spectra were recorded on a JASCO FT/IR-480 PLUS Fourier Transform spectrometer (200–4000 cm⁻¹, with pressed KBr pellets). UV–Vis spectra were determined by a JASCO V-570 UV–Vis spectrometer (200–1500 nm, as solids). TG was performed under N₂ atmosphere with a heating rate of 10 °C/min on a Perkin Elmer Diamond TG/DTA. The products of the oxidation were analyzed by a Shimadzu GC-16A series gas chromatograph equipped with a flame ionization detector (FID) and a capillary column (PG2000, column length: 30 m; internal diameter: 0.25 mm). All chemicals used were of analytical grade and without purification. A 30% aqueous solution of hydrogen peroxide was used as primary oxidant in the oxidation reactions.

2.2. Synthesis of complexes

2.2.1. Synthesis of complex (Co(IAA)₂(phen)(H₂O)) (1)

A pink-red transparent solution was got by adding a mixture of IAA (0.09 g, 0.5 mmol) and 1,10-phen (0.05 g, 0.25 mmol) in MeOH (15 mL) to a water solution (7.5 mL) of Co(CH₃COO)₂·4H₂O (0.08 g, 0.3 mmol). Some purple-red crystals suitable for X-ray diffraction analysis were obtained after placing the solution at room temperature for 4 days. Yield (based on Co): 0.12 g, 61.71%. *Anal.* Calc. for C₃₂H₂₆N₄O₅Co: C, 63.48; H, 4.33; N, 9.25. Found: C, 63.32; H, 4.28; N, 9.22%. IR data (KBr, cm⁻¹): 3338, 3105, 3055, 2934, 2906, 1675, 1558, 1456, 1388, 1313, 1276, 1008, 557, 425. UV–Vis (λ_{max}, nm): 216, 260, 334, 412, 536, 1002.

2.2.2. Synthesis of complex (Ni(IAA)₂(phen)(H₂O)) (2)

A mixture of IAA (0.09 g, 0.5 mmol) and 1, 10-phen (0.05 g, 0.25 mmol) in MeOH (15 mL) was added dropwise to a water solution (7.5 mL) of Ni(CH₃COO)₂·4H₂O (0.08 g, 0.3 mmol) with continuous stirring for 3 h to get a low-blue transparent solution. Some green crystals suitable for X-ray diffraction analysis were obtained after placing the solution at room temperature for 5 days. Yield (based on Ni): 0.13 g, 66.8%. *Anal.* Calc. for C₃₂H₂₆N₄O₅Ni: C, 63.50; H, 4.33; N, 9.26. Found: C, 63.45; H, 4.28; N, 9.22%. IR data (KBr, cm⁻¹): 3411, 3253, 3113, 3058, 2957, 2926, 1617, 1556, 1457, 1423, 1353, 1319, 1253, 1009, 642, 425. UV–Vis (λ_{max}, nm): 214, 260, 334, 406, 630, 1056.

2.3. X-ray crystallographic determination

Suitable single crystals of the two complexes were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and a ω scan mode. All the measured independent reflections (*I* > 2σ(*I*)) were used in the structural analysis, and semi-empirical absorption corrections were applied using SADABS [28].

All hydrogen atoms were positioned geometrically and refined using a riding model. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms from coordination water molecules were found in different Fourier map. The crystallographic data and experimental details of the data collection, as well as the structure refinement are given in Table 1. The

Table 1

Crystallographic data and structure refinement for complexes **1** and **2**.

Complexes	1	2
Formula	C ₃₂ H ₂₆ N ₄ O ₅ Co	C ₃₂ H ₂₆ N ₄ O ₅ Ni
<i>M</i> (g mol ⁻¹)	605.50	605.28
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	13.182(3)	13.097(3)
<i>b</i> (Å)	12.875(3)	12.836(3)
<i>c</i> (Å)	16.793(3)	16.875(3)
α (°)	90	90
β (°)	104.26(3)	103.91(3)
γ (°)	90	90
<i>V</i> (Å ³)	2762.3(10)	2753.7(10)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.456	1.460
Crystal size (mm ³)	0.20 × 0.11 × 0.09	0.21 × 0.17 × 0.12
<i>F</i> (000)	1252	1256
μ(Mo Kα) (mm ⁻¹)	0.671	0.755
Reflections collected	26248	26412
Independent reflections (<i>I</i> > 2σ(<i>I</i>))	6288	6264
Parameters	383	391
Δ(ρ) (e Å ⁻³)	0.286 and -0.288	0.335 and -0.299
Goodness-of-fit (GOF)	1.035	1.057
<i>R</i> ₁ ^a	0.0387(0.0570) ^b	0.0466(0.0697) ^b
<i>wR</i> ₂ ^a	0.0850(0.0919) ^b	0.0927(0.1002) ^b

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$; [*F*_o > 4σ(*F*_o)].

^b Based on all data.

drawings were made with Diamond program, and all calculations were performed using SHELX-97 program [29].

2.4. Experimental for catalytic oxidation

The oxidation reactions were carried out under air condition (atmospheric pressure) in a two-necked glass flask, fitted with a water condenser. In a typical experiment, 0.0004 g (6.61 × 10⁻⁷ mol) of the catalyst **1** or **2** was dissolved in 3 mL of desired solvent. Then the required amounts of H₂O₂ and HNO₃ were added in the sequence, followed by 0.85 g (0.01 mol) of Cy. The reaction solution was stirred for 5 h at 40 °C.

For the products analysis, 0.05 g (5.43 × 10⁻⁴ mol) of methylbenzene (internal standard) and 3 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred for 10 min and then a sample (0.2 μL) was taken from the organic phase and analyzed by a GC equipped with a capillary column and a flame ionization detector by the internal standard method. Blank experiments confirm that no cyclohexanol (Cynol) or cyclohexanone (Cyone) are formed in the absence of the metal catalysts under the same conditions.

3. Results and discussion

3.1. Synthesis

The complexes Co(IAA)₂(phen)(H₂O) (**1**) and Ni(IAA)₂(phen)(H₂O) (**2**) were successfully synthesized for the first time by the reacting of Co(Ac)₂·4H₂O or Ni(Ac)₂·4H₂O with IAA and 1,10-phen as mixed ligands in the solution of water–methanol at room temperature. The systematic experiments have been carried out by switching starting materials (Co(Ac)₂·4H₂O, CoCl₂·6H₂O, Ni(Ac)₂·4H₂O and NiCl₂·6H₂O) and solvents (e.g. mixed solution of water–methanol, water–ethanol or water–acetonitrile) to find out the optimum reaction conditions. It was found that: (i) the target products cannot be obtained when CoCl₂·6H₂O or NiCl₂·6H₂O was used as the starting material instead of CoAc₂·4H₂O or NiAc₂·4H₂O; (ii) the addition of water to organic solvent is in favor of being

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