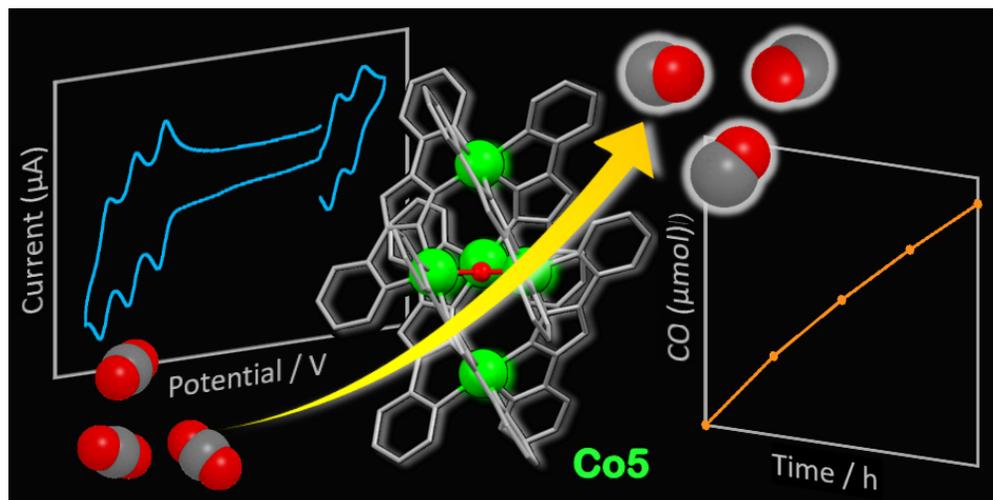


**Effect of metal ion substitution on the catalytic activity of a pentanuclear metal complex**

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## COMMUNICATION

## Effect of metal ion substitution on the catalytic activity of a pentanuclear metal complex

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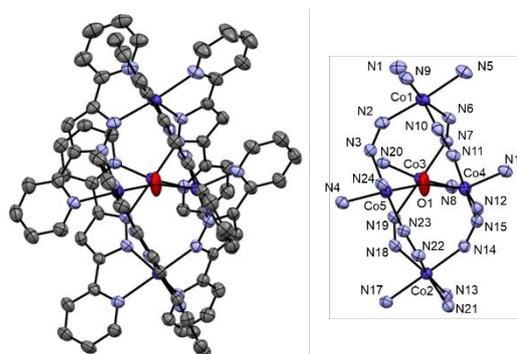
**A pentanuclear cobalt complex that consists of five cobalt ions and six  $\text{bpp}^-$  ligands ( $\text{Co}_5$ ,  $\text{Hbpp} = 3,5\text{-bis}(2\text{-pyridyl})\text{pyrazole}$ ) was synthesized and crystallographically characterized. Electrochemical measurements indicate that  $\text{Co}_5$  has multielectron transfer ability. We also found that  $\text{Co}_5$  reduces  $\text{CO}_2$  to  $\text{CO}$  under photoirradiation in the presence of a photosensitizer.**

Multinuclear metal complexes are attractive materials due to not only their fascinating structure<sup>1-3</sup> but also their unique redox,<sup>4-6</sup> magnetic<sup>7,8</sup> and photochemical<sup>9,10</sup> properties and reactivity,<sup>11-14</sup> which differ from those of mononuclear complexes. Multinuclear structures in metalloenzymes, such as the oxygen evolving complex (OEC),<sup>15,16</sup> nitrogenase<sup>17-19</sup> and CO dehydrogenase,<sup>20,21</sup> work as important catalysts for small-molecule conversion reactions involving multielectron transfer. Therefore, metal complexes with multinuclear structures are expected to be promising candidates for developing efficient artificial catalysts for such reactions. However, a rational strategy to design and construct multinuclear metal complexes that catalyse small-molecule conversion reactions has not been well established.

Given that small-molecule conversion requires transfer of multiple electrons and cleavage/formation of covalent bond(s), catalysts to facilitate these two processes must be developed. Recently, we found that a pentanuclear iron complex composed of five iron ions and six  $\text{bpp}^-$  ligands ( $[\text{Fe}_5\text{O}(\text{bpp})_6]^{3+}$ ,  $\text{Fe}_5$ ,  $\text{Hbpp} = 3,5\text{-bis}(2\text{-pyridyl})\text{pyrazole}$ ) catalyses the conversion of water molecules to dioxygen ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ) with high efficiency.<sup>22</sup> We also demonstrated that multinuclear structure

and coordinatively unsaturated sites are the keys to achieving rapid multielectron transfer and smooth O-O bond formation, respectively. These results imply that the molecular scaffold constructed by five metal ions and six  $\text{bpp}^-$  ligands is an attractive platform to construct catalysts for small-molecule conversion.

Here, we show the synthesis, characterization and catalytic activity of a pentanuclear cobalt complex composed of five cobalt ions and six  $\text{bpp}^-$  ligands ( $\text{Co}_5$ ). Although  $\text{Fe}_5$  exhibited multi-electron oxidation ability, the introduction of cobalt ions into the same molecular scaffold endowed the complex with multi-electron reduction ability. Electrochemical measurements of  $\text{Co}_5$  under a  $\text{CO}_2$  atmosphere indicated the catalytic activity of the complex for  $\text{CO}_2$  reduction. Furthermore, photoirradiation of a solution containing  $\text{Co}_5$  and a photosensitizer under  $\text{CO}_2$  resulted in the formation of  $\text{CO}$ , and the role of  $\text{Co}_5$  as a  $\text{CO}_2$  reduction catalyst was confirmed. Although there exist many examples of mononuclear<sup>23-44</sup> or dinuclear<sup>45,46</sup> metal complexes for  $\text{CO}_2$  reduction, there are a few reports on multinuclear-metal-complex based systems<sup>47,48</sup>. The present study offers a rare example of multinuclear-metal-complex catalyst for  $\text{CO}_2$  reduction.



**Figure 1.** ORTEP drawings of the cationic moiety (left) and core structure (right) of  $\text{Co}_5(\text{BF}_4)_3$ . The atoms are represented by the following colours: Co, blue; O, red; N, purple; C, grey. Hydrogen atoms and crystal solvent molecules are omitted for clarity.

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A pentanuclear cobalt complex (**Co5**) was synthesized by mixing Hbpp ligand and cobalt acetate tetrahydrate (1.2 eq) in methanol at 40 °C in the presence of a base. After the reaction, a few drops of a saturated aqueous solution of NaBF<sub>4</sub> were added to the reaction mixture, and a brown precipitate was collected by filtration to afford the targeted complex in 52% yield (for details of the synthetic procedure, see the electronic supplementary information (ESI)). The complex was characterized by ESI TOF-MS, elemental analysis and single crystal X-ray structural analysis.

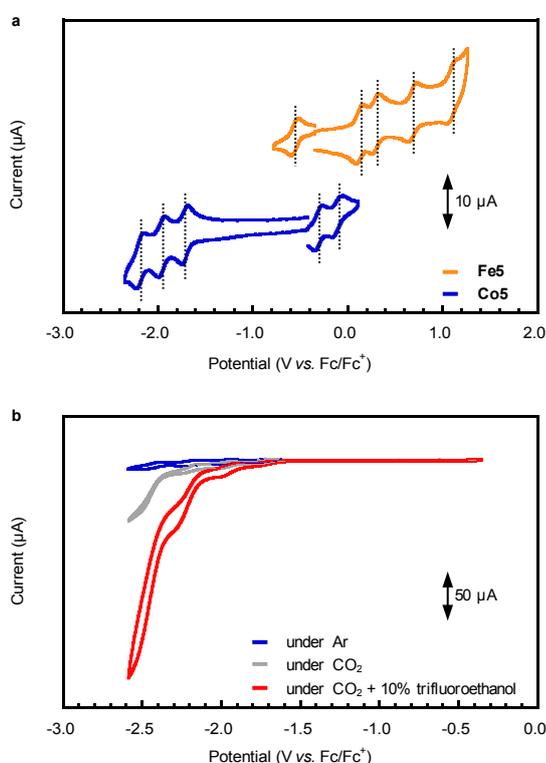
Single crystals of **Co5**(BF<sub>4</sub>)<sub>3</sub> suitable for structural determination were obtained by slow vapour diffusion of diethyl ether into a MeCN solution of **Co5**(BF<sub>4</sub>)<sub>3</sub> at room temperature. Figure 1 shows an ORTEP diagram of **Co5** determined by single-crystal X-ray structural analysis. **Co5** crystallizes in the *P*-1 space group, and the asymmetric unit of the structure contains one **Co5**, three BF<sub>4</sub> anions, one water, one MeCN and two diethyl ether molecules. Therefore, the total charge of **Co5** was determined to be +3. **Co5** exhibits quasi-*D*<sub>3</sub> symmetry and consists of a triangle core wrapped by two [Co( $\mu$ -bpp)<sub>3</sub>] units. The two metal ions at the apical positions (*M*<sub>api</sub>) are hexa-coordinated structures with distorted octahedral geometries, whereas the three metal ions in the triangular core (*M*<sub>core</sub>) exhibit penta-coordinated structures with distorted trigonal bipyramidal geometries. The average bond distance between *M*<sub>api</sub> and the nitrogen atoms of the [M( $\mu$ -bpp)<sub>3</sub>] units of **Co5** is 2.149(5) Å (Table S2), which is the typical value for hexacoordinated Co(II) ions.<sup>49</sup> The average

bond distance between *M*<sub>core</sub> and the oxygen atom of the bridging moiety is 2.009(4) Å, which is larger than that of **Fe5**(BF<sub>4</sub>)<sub>3</sub> (1.961(3) Å). This observation indicates that the bridging ligand at the triangle core of **Co5** is OH<sup>-</sup>, which is different from the core structure of **Fe5**, which has an oxo (O<sup>2-</sup>) bridging moiety. Based on these results, the structure of **Co5** has been determined to be [Co<sup>II</sup><sub>5</sub>OH(bpp)<sub>6</sub>]<sup>3+</sup>.

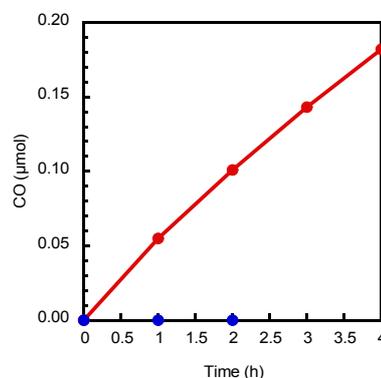
To explore the electron transfer ability of **Co5**, cyclic voltammetry was performed. In a cyclic voltammogram (CV) of **Co5** under an Ar atmosphere (Figure 2a, blue line), the complex displayed two reversible oxidation waves at -0.3 and -0.1 V (vs. ferrocene/ferrocenium (Fc/Fc<sup>+</sup>)) and three reversible reduction waves at -1.7, -2.0, and -2.2 V. The oxidation waves are attributed to the oxidation of cobalt ions (Co<sup>III</sup>/Co<sup>II</sup>) at the apical positions, and the reduction waves are assigned to the reduction of the cobalt ions (Co<sup>II</sup>/Co<sup>I</sup>) at the triangle core. It should be noted that the relevant complex composed of redox inactive metal ions, [Zn<sup>II</sup><sub>5</sub>OH(bpp)<sub>6</sub>]<sup>3+</sup> (**Zn5**), did not show any redox peaks in the potential region of 1.2 - -2.3 V (Figure S2), indicating that ligand-based redox process does not occur both in **Co5** and **Zn5**. This redox behaviour of **Co5** is completely distinct from that of **Fe5**, which shows four reversible oxidation waves and one reversible reduction wave (Figure 2a, orange line), indicating that **Co5** has redox properties suitable for reductive reactions. We also performed the controlled potential electrolysis and confirmed the formation of CO, H<sub>2</sub>, and HCOOH (for details, see the ESI (P.S12-S13)).

Encouraged by the aforementioned results, the electrocatalytic activity of **Co5** for CO<sub>2</sub> reduction was examined. As shown in Figure 2b, the CV of **Co5** measured under CO<sub>2</sub> using anhydrous acetonitrile as a solvent exhibited a large irreversible current at approximately *E*<sub>pc</sub> = -2.2 V. Notably, the intensity of the irreversible current further increased in the presence of trifluoroethanol as a proton source. These results indicate the electrocatalytic activity of the complex for CO<sub>2</sub> reduction.

Subsequently, the catalytic activity of **Co5** for photocatalytic CO<sub>2</sub> reduction was investigated. A photocatalytic CO<sub>2</sub> reduction experiment was conducted in 2 mL of a CO<sub>2</sub>-saturated *N,N*-dimethylacetamide (DMA)/trifluoroethanol (TFE) (17:3, v/v) solution containing **Co5** (30  $\mu$ M) as a catalyst, 1,3-dimethyl-2-



**Figure 2.** Cyclic voltammograms of 0.2 mM solutions of (a) **Co5** (blue line) and **Fe5** (orange line) under Ar and (b) **Co5** under Ar (blue line), CO<sub>2</sub> (grey line) and CO<sub>2</sub> in the presence of 10% trifluoroethanol (red line) in MeCN containing 0.1 M TBAP. The CVs were measured using a GC electrode at a scan rate of (a) 100 or (b) 50 mV s<sup>-1</sup>.



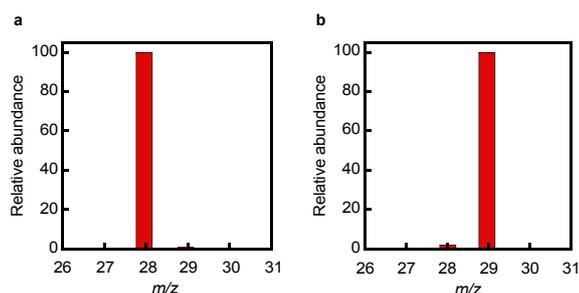
**Figure 3.** Photocatalytic production of CO in the presence of 30  $\mu$ M **Co5** (red line) and in the absence of **Co5** (blue line) in a CO<sub>2</sub>-saturated DMA/TFE (17:3, v/v) solution containing 150  $\mu$ M Ir(ppy)<sub>3</sub> and 0.1 M BIH.

**Table 1.** Control experiments for photocatalytic CO<sub>2</sub> reduction by **Co5** for 2 h. All experiments were carried out at 20 °C.

No.	[Co5] (μM)	[Ir(ppy) <sub>3</sub> ] (μM)	[BIH] (M)	solvent	light (nm)	gas	CO (μmol)	H <sub>2</sub> (μmol)
1	30	150	0.1	DMA/TFE (17:3, v/v)	420	CO <sub>2</sub>	0.10	0.17
2	-	150	0.1	DMA/TFE (17:3, v/v)	420	CO <sub>2</sub>	0	trace
3	30	-	0.1	DMA/TFE (17:3, v/v)	420	CO <sub>2</sub>	0	0
4	30	150	-	DMA/TFE (17:3, v/v)	420	CO <sub>2</sub>	0	0
5	30	150	0.1	DMA/TFE (17:3, v/v)	dark	CO <sub>2</sub>	0	0
6	30	150	0.1	DMA/TFE (17:3, v/v)	420	Ar	0	0.01

phenyl-2,3-dihydro-1H-benzo[d]imidazole<sup>33,39,40</sup> (BIH, 0.1 M) as a sacrificial electron donor (SD) and Ir(ppy)<sub>3</sub><sup>28,30-32,40</sup> (Hppy = 2-phenylpyridine, 150 μM) as a photosensitizer (SD) under visible-light irradiation (blue LED, wavelength λ = 420 nm). As shown in Figure 3, the evolution of CO (0.18 μmol) was observed after 4 h of photoirradiation.

To verify the role of each component in the photoreaction, a series of control experiments were carried out. No CO<sub>2</sub> reduction product was observed when the reaction was performed under argon, in the dark, without **Co5**, without Ir(ppy)<sub>3</sub>, or without BIH (Table 1), showing that all components are required for the catalysis. Isotopic labelling experiments performed under a <sup>13</sup>CO<sub>2</sub> atmosphere also confirmed that the CO originated from CO<sub>2</sub> reduction (Figure 4). The necessity of visible-light and Ir(ppy)<sub>3</sub> indicates that Ir(ppy)<sub>3</sub> functions as the photosensitizer because the complex has a strong absorption band in the visible region (Figure S5), and is frequently used as a photosensitizer in many photocatalytic systems<sup>28,30-32,40</sup>. **Co5** should serve as a catalyst to reduce CO<sub>2</sub> as also evidenced by electrochemical measurements (*vide supra*). The role of BIH should be a sacrificial electron donor as evidenced in previous reports<sup>33,39,40</sup>. We also optimized the reaction conditions, and the maximum turnover reached 58.4 when the **Co5** concentration was decreased to 1 μM (Figure S6). In this optimized condition, the formation of H<sub>2</sub> (TON = 61.8) and formic acid (TON = 55.7) was also detected.



**Figure 4.** Mass spectra of CO generated under (a) <sup>12</sup>CO<sub>2</sub> or (b) <sup>13</sup>CO<sub>2</sub> using a DMA/TFE (17:3, v/v) solution containing 30 μM **Co5**, 150 μM Ir(ppy)<sub>3</sub> and 0.1 M BIH at 20 °C upon irradiation with a blue LED (420 nm) for 2 h

In conclusion, we have investigated the effect of metal ion substitution on the catalytic activity of multinuclear metal complexes. We have developed a novel pentanuclear metal complex that consists of five cobalt ions and six bpp<sup>-</sup> ligands (**Co5**). **Co5** was synthesized by mixing a cobalt source and Hbpp ligand and was crystallographically characterized. Electrochemical measurements revealed that **Co5** exhibits

multielectron reduction ability, making it completely distinct from **Fe5**, which shows multi-electron oxidation ability. Moreover, the cyclic voltammetry of **Co5** under CO<sub>2</sub> indicates the catalytic activity of the complex for CO<sub>2</sub> reduction. Encouraged by these results, we conducted a photochemical reaction under CO<sub>2</sub> in a DMA/TFE solution containing **Co5** (catalyst), Ir(ppy)<sub>3</sub> (photosensitizer) and BIH (sacrificial electron donor) with visible light irradiation. As a result, the photochemical CO<sub>2</sub> reduction proceeded successfully, and CO and HCOOH, which are two-electron reducing products of CO<sub>2</sub>, were generated. The present results demonstrate that the use of multinuclear metal complexes is one of the strategies to develop novel catalysts for multielectron CO<sub>2</sub> reduction. However, at this stage, the catalytic cycle of **Co5** to produce CO and HCOOH remains unclear. Further spectroscopic investigations in conjunction with quantum chemical calculations should lead to the understanding of the catalytic mechanism. Such insight should facilitate the development of a variety of multinuclear-metal-complex-based catalysts for small-molecule conversion.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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