

## Nucleophilic Reactivity of a Copper(II)-Imidazolate Complex

Masaaki Sato, Katsumi Ohmae, Suguru Nagae, and Jun-ichi Nakaya\*

Department of Chemistry, Faculty of Integrated Arts and Sciences, University of Osaka Prefecture, Mozu Umemachi, Sakai, Osaka 591, Japan

Imidazolate co-ordinated to a copper(II) complex with diethylenetriamine had high nucleophilic reactivity in the cleavage of the ester bond of *p*-nitrophenyl benzoate in dimethyl sulphoxide solution.

Imidazole (HIm) and imidazolate (Im) are well known as nucleophiles.<sup>1,2</sup> However, the effect on the reactivity of nucleophiles of complexation with metal ions is not well known. In a cobalt(III) complex ion, co-ordinated imidazolate<sup>3</sup> and thiol<sup>4</sup> are as reactive towards electrophilic substrates as the nonco-ordinated forms are, but no increase in nucleophilicity arising from complexation has been reported previously.

We report here a marked increase in the nucleophilic reactivity of imidazolate when co-ordinated to a copper(II) complex with diethylenetriamine (dien), which served as a tridentate ligand: [Cu(dien)(Im)]ClO<sub>4</sub>, abbreviated as CuIm. This complex has been well characterised; we have reported its structure both as a crystal and in dimethyl sulphoxide (Me<sub>2</sub>SO) solution.<sup>5</sup> Here, to evaluate the reactivity, the reaction rate for cleavage of the ester bond of *p*-nitrophenyl benzoate (PNPB) was examined and compared with the rates for Cu<sup>II</sup>-imidazole complex ([Cu(dien)(ImH)(ClO<sub>4</sub>)<sub>2</sub>], abbreviated as CuImH),<sup>6</sup> HIm, and sodium imidazolate (NaIm).

PNPB itself was stable in Me<sub>2</sub>SO when the solvent had been purified by repeated distillation over calcium hydride. The addition of HIm or CuImH to this solution had no effect. When CuIm or NaIm was added, PNPB decomposed and *p*-nitrophenolate was produced, as seen from the decrease in absorption at 271 nm and the increase at 436 nm, respectively. The formation of an acylated product was detected spectrophotometrically in acetonitrile solution. These results indi-

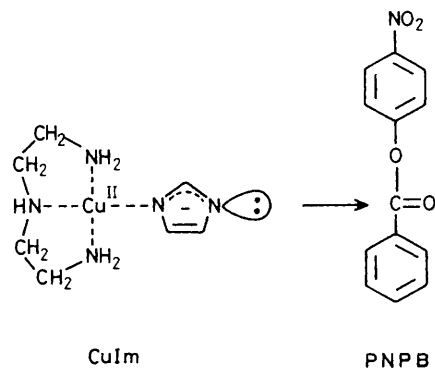
cated that the ester bond of PNPB was cleaved by imidazolates acting as nucleophiles. This reaction followed the second-order rate law; the rate constants are given in Table 1.

With NaIm, the rate constant depended on the nature of the electrolyte in the solution. Since the anion was always perchlorate, we concluded that changes in the rate constant depend on the cation species in the solution. This would mean that the sodium ion of NaIm was displaced by the excess of the

Table 1. Second-order rate constants<sup>a</sup> for the cleavage of the ester bond in PNPB by nucleophiles in Me<sub>2</sub>SO solution containing electrolytes<sup>b</sup> at 25 °C.

Nucleophile	<i>k</i> /dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>			
	None	TEAP <sup>c</sup>	KClO <sub>4</sub>	NaClO <sub>4</sub>
NaIm	— <sup>d</sup>	3.69	0.79	0.38
HIm	0	0	0	0
CuIm	28.47	24.72	25.49	23.45
CuImH	0	0	0	0
CuImEt	0	0	0	0

<sup>a</sup>  $V = k[\text{PNPB}][\text{nucleophile}]$ , <sup>b</sup>  $[\text{electrolyte}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ .  
<sup>c</sup> Tetraethylammonium perchlorate. <sup>d</sup> The reaction was not reproducible.



Scheme 1

cation of the electrolyte, and that the nucleophilic reactivity of the imidazolate changed in consequence. In the three electrolyte systems, the smaller the cation, the smaller the rate constant, probably because the small cation, a hard acid, forms a tight ion pair with imidazolate, a hard base, which reduces the nucleophilicity of the imidazolate. Without an electrolyte, the rate constant was not reproducible, perhaps because of NaIm forming an intermolecular aggregate in the solution.

With CuIm, the rate constants were much larger than with NaIm, and were not affected by the nature of the electrolyte or its absence. The independence of cations was compatible with the fact that imidazolate(1<sup>-</sup>) is bound to the Cu<sup>II</sup> atom (2<sup>+</sup>), with a total charge of +1. When the CuIm was protonated at the imidazolate to become CuImH, the nucleophilic reactivity was zero. The Cu<sup>II</sup>-ethylimidazole complex (CuImEt), which has an ethyl group at the N-1 position of the imidazole ring,<sup>6</sup> was not reactive, either. These results showed that the reactivity of CuIm was derived from nucleophilic attack by the

unshared pair of electrons of the nitrogen atom (N<sub>free</sub>) not co-ordinated to the Cu<sup>II</sup> atom, as shown in Scheme 1.

The co-ordination of the imidazolate to the Cu<sup>II</sup> atom,  $\sigma(\text{Im}) \rightarrow \text{Cu}(d_{x^2-y^2})$ , decreased the electron density of the imidazolate, which would decrease the nucleophilicity. However, there is additional  $p_\pi-d_\pi$  interaction between the N<sub>Cu</sub> and Cu<sup>II</sup> atoms which compensates for the decrease in the electron density,<sup>7</sup> and can affect the unshared pair of electrons of the N<sub>free</sub> nitrogen atom. Therefore, through both  $\sigma$ -bonding and  $p_\pi-d_\pi$  interaction, the nucleophilicity of the imidazolate would be increased. Another possible reason for the high reactivity arises from the effect of the positive charge of the counterion. The imidazolate of the complex is bound to Cu<sup>II</sup> (2<sup>+</sup>), whereas that of sodium imidazolate is bound to Na<sup>+</sup> (1<sup>+</sup>). Thus, the unshared pair of electrons of the N<sub>free</sub> nitrogen atom of the CuIm that make the nucleophilic attack were shielded much less by other cation species in solution than in the NaIm.

In conclusion, CuIm, a new complex-nucleophile, had high nucleophilicity, higher than NaIm and much higher than HIm or CuImH, for the cleavage of the ester bond of PNPB in Me<sub>2</sub>SO solution.

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