

## 2.9: Model Chemistry

Some efforts have been reported in the literature to simulate the activity of CA and therefore to obtain further information on the mechanism. The  $pK_a$  of Zn—OH<sub>2</sub> moieties in various complexes has been studied as discussed in Section III.A. The electronic spectra of some cobalt analogues have been found to be similar. One such example is shown in Figure 2.24; the complex  $\text{Co}(\text{TPyMA})\text{OH}_2^{2+}$  (Table 2.3)<sup>10</sup> provides a five-coordinate adduct with a weakly bound axial nitrogen (Figure 2.25A).

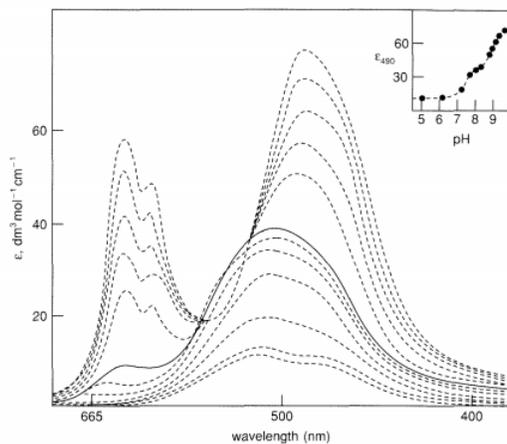


Figure 2.7.<sup>56</sup>

The interconversion between  $\text{Co}(\text{TPyMA})\text{OH}_2^{2+}$  and  $\text{Co}(\text{TPyMA})\text{OH}^+$  was studied by electronic spectroscopy (Figure 2.24). Despite the difference in the number of coordinated nitrogens, the difference between the high- and low-pH forms resembles that of the cobalt enzyme (cf. Figure 2.7).<sup>10</sup>

Table 2.3 shows that only one compound, with zinc(II) as the metal ion, seems to have three nitrogens and a water, whereas all the other models have a higher coordination number<sup>15-17</sup> The simple  $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{OH}]^{2+}$  complex has been shown to accelerate the formation of bicarbonate ( $k = 2 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ ), but, of course, bicarbonate remains coordinated to the metal because of the kinetic inertness of cobalt(III).<sup>102,103</sup> Some relatively ill-defined systems have been reported to have some kind of activity. The ligand shown in Figure 2.25B, with zinc(II) as the metal ion in H<sub>2</sub>O, accelerates the attainment of the equilibrium<sup>104</sup>



with  $k_{\text{obs}} = k_1 + k_{-1} \simeq 10^3 \text{ M}^{-1}\text{s}^{-1}$ . The system in Figure 2.25C, with Zn<sup>2+</sup> and excess imidazole, promotes CO<sub>2</sub> hydration, though not the back reaction.<sup>105</sup> The cobalt(II) analogue shows no activity.<sup>106</sup>

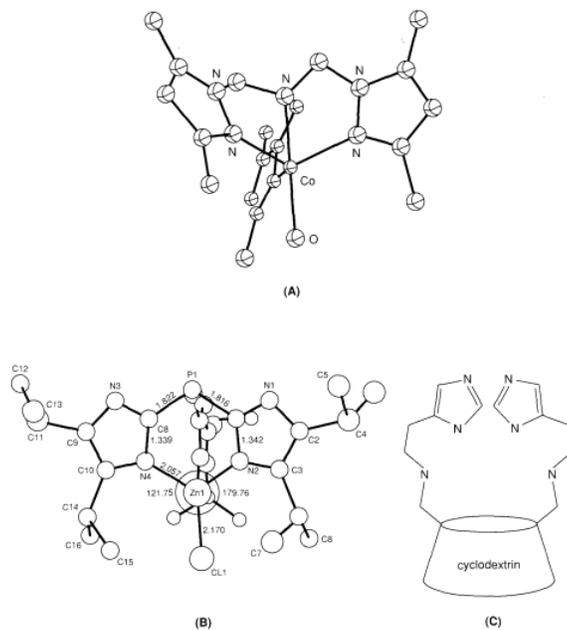


Figure 2.25 - Some multidentate ligands as models of CA: (A) tris-(3,5-dimethyl-1-pyrazolylmethyl) amine<sup>4</sup> (cobalt[II] complex); (B) tris (4,5-diisopropylimidazol-2-yl)phosphine<sup>104</sup> (zinc[II] complex); (C) bis(histamino)  $\beta$ -cyclodextrin.

It can be concluded that the M—OH group can indeed be involved in one step of the enzymatic pathway. The sophistication of the whole enzymatic function has not yet been fully achieved with the present generation of models, even though the functionalization of both hydrophilic and hydrophobic molecules like cyclodextrins (Figure 2.25C) has also been used.<sup>105</sup>

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