



HYPOTHESIS Structural differences of the ligand modulate the reactivity of the catalase-like activity of the manganese complexes.

 Py_2N_2

PyN₃

(Pyclen)

 N_4

(Cyclen)

Catalytic Disproportionation of Hydrogen Peroxide by Manganese Complexes of 12-Membered Pyridinophane Macrocycles

David M. Freire, Katherine J. Smith, Kristof Pota, Magy A. Mekhail, Sugam Kharel and Kayla N. Green Green Research Group, Department of Chemistry & Biochemistry, Texas Christian University, Fort Worth, TX, USA

$$H_2O_2$$



Auto Titrator Metrohm 888 PSEQUAD Software

This method is used to determine the optimal pH for maximum concentration of the Mn(II) complex, as well as the thermodynamic stability of the complex formation (log K_{ML}) and the hydroxo complex (log $K_{M(OH)L}$).

Variable I









Glu 148 His 181

^{HO}PyN₃

MeOPyN3

PyN₃

(Pyclen)

pH-Potentiometric Titrations



Unisense O₂ Microsensor

This method is used to obtain the turnover number (TON), the kinetic constant (k) and the activation energy (E_a) for the catalytic production of O₂ from H₂O₂.

TON	log K _{ML}	log К _{м(ОН)L}
11.26(4)	8.34(2)	
24.67(3)	10.11(4)	11.0(5)
28.85(3)	8.26(9)	9.7(2)



The efficiency of the catalyst is determined by the catalytic constant *k*, while robustness is evaluated by the turnover number (TON).



Molecular Oxygen Measurements



Variable II

¹ S ⁻¹)	<i>Ea</i> (kcal mol ⁻¹)	TON	log K _{ML}	log К _{м(ОН)L}	
(1)	4.8(2)	24.67(3)	10.11(4)	11.0(5)	
(1)	4.8(1)	36.89(1)	10.96(4)	10.18(6)	
(1)	4.5(2)	37.31(2)	9.70(9)	9.5(2)	

Conclusions

The results from variable I show that PyN₃ yields the most stable Mn(II) complex and has the right compromise between electron-donor strength and rigidity, which favors the efficiency of the catalyst. On the other hand, Py_2N_2 is more robust (TON) suggesting that secondary amines are susceptible to reactivity with H₂O₂ in presence of manganese. The results from variable II indicate that electron-donating groups in the 4-position of the pyridine increase the overall performance of the Mn complex.

References

Costa, V.; Moradas-Ferreira, P., *Mol. Aspects Med.* **2001**, 22, 217-246.

cience and Engineering Research Cente

Barynin, V. V.; Whittaker, M. M.; Antonyuk, S. V.; Lamzin, V. S.; Harrison, P. M.; Artymiuk, P. J.; Whittaker, J. W., Structure 2001, 9 (8), 725-738. Freire, D. M.; Beeri, D.; Pota, K.; Johnston, H. M.; Palacios, P.; Pierce, B. S.; Sherman, B. D.; Green, K. N., Inorg. Chem. Front. 2020, 7 (7), 1573-1582.

