Crystal Structure of bis(isothiocyanato)N,N-bis(2-benzimidazolylmethyl)ethanolaminemanganese(II)

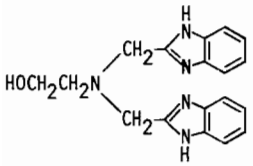
KAZUHIRO TAKAHASHI, YUZO NISHIDA and SIGEO KIDA

Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812, Japan

Received June 10, 1983

In biological systems several enzymes contain manganese ion as a cofactor. However, structural information about the Mn-binding sites is limited [1]). For the Mn-containing superoxide dismutase (Mn-SOD) [2], the coordination of imidazole (histidine residue) has been assumed based on the homology of amino acid sequence for Cu-SOD. Thus studies of Mn-imidazole complexes are desired. However, only a few studies of Mn-imidazole complexes have been reported [3].

In order to study the binding mode between Mn(II) and imidazole nitrogen, we have in this study prepared a Mn(II) complex with N,N-bis(2-benzimidazolylmethyl)ethanolamine, (eta-dbz), and determined its crystal structure by X-ray diffraction.



The title complex, $[Mn(eta\text{–}dbz)(NCS)_2]$, was obtained as well-formed pink prisms from the reaction mixture of $(eta\text{–}dbz\cdot CH_3OH)$ [4] (2 mmol), $Mn(NO_3)_2\cdot 6H_2O$ (2 mmol) and NH_4NCS (5 mmol) in methanol.

Analytical data; Found (Calcd. for $MnC_{20}H_{19}N_7S_2$)%: C 48.83(48.78), H 3.93(3.89), N 19.87(19.91).

The unit cell parameters were determined from 20 reflections, and intensity data were collected by the θ–2θ scan technique ($2.5° < 2\theta < 50°$) on a Rigaku Automatic Four Circle Diffractometer AFC–5 using graphite monochromated Mo Kα radiation, monitoring 3 reflections after every 97 reflections.

Crystal data; space group $P2_12_12_1$ (orthorhombic), a = 18.179(2) Å, b = 13.073(2) Å, c = 9.097(2) Å, V = 2161.9(7) Å^3, Z = 4, Dc = 1.43 g/cm^3, Dm = 1.49 g/cm^3 (by n-C_6H_{12}–BrH_2CCH_2Br flotation), T = 294 K.

The structure solved from Patterson and Differential Fourier methods of the UNICS II [5] using unique 2583 reflections ($Fo > 3\sigma(Fo)$). The structure was refined to $R = \Sigma(Fo\text{-}Fc)/\Sigma Fo = 0.054$ by a block-diagonal least-square method using anisotropic thermal parameters for non-hydrogen atoms.

A perspective drawing and atomic numbering system including selected bond distances and angles are shown in Fig. 1.

Figure 2 shows the projection of the coordination sphere on the N1–N3–NB plane. The coordination

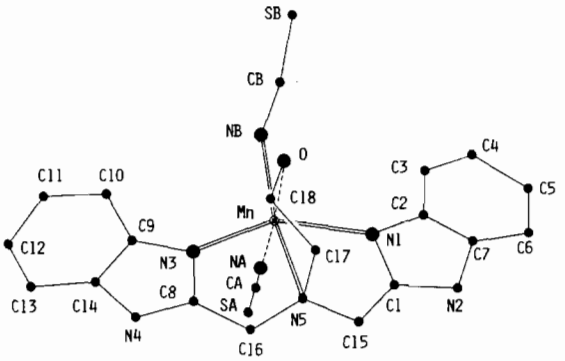


Fig. 1. Perspective drawing of $[Mn(eta\text{–}dbz)(NCS)_2]$. Selected bond distances (Å) are: Mn–N1 2.175(5); Mn–N3 2.183(5); Mn–N5 2.517(5); Mn–NA 2.140(6); Mn–NB 2.107(6); Mn–O 2.400(4), and angles (°) are: N1–Mn–N3 142.8(2); N1–Mn–NB 105.5(2); N3–Mn–NB 110.4(2); NA–Mn–O 177.1(2); N1–Mn–N5 71.6(2); N3–Mn–N5 72.2(2); O–Mn–N5 72.0 (2); NB–Mn–N5 152.1(2); NA–Mn–N5 110.1(2); N1–Mn–O 92.2(2); N3–Mn–O 84.4(2); NB–Mn–O 80.5(2); NA–Mn–N1 90.5(2); NA–Mn–N3 94.2(2); NA–Mn–NB 97.6(2).

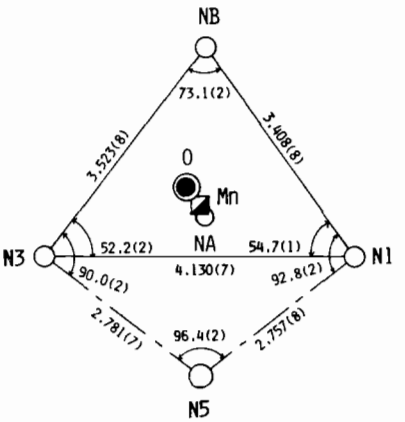


Fig. 2. Projection of the atoms of the coordination sphere on the N1–N3–NB plane and their interatomic distances (Å) and angles (°). Distances (Å) are: O–NB 2.921(8); O–N1 3.300(7); O–N3 3.082(7); O–N5 2.891(7); NA–NB 3.195(8); NA–N1 3.064(8); NA–N3 3.167(8); NA–N5 3.822(8). Best-plane equation of the trigonal plane is: $-0.1585x + 0.8755y - 0.4564z = 0.4664$, and deviations (Å) of some atoms are: Mn 0.14; NA 2.27; N5 –0.89; O –2.24.

0020-1693/83/$3.00

© Elsevier Sequoia/Printed in Switzerland

TABLE I. Average Distance of Metal–Benzimidazolyl Nitrogen Atom of the (eta–dbz) Containing Complexes.

Complex	Distance (Å)	Structure†	Ref.
$[Cu(eta–dbz)Cl]ClO_4 \cdot CH_3OH$	1.96	SP	6-a
$[Cu(eta–dbz)Br]ClO_4 \cdot CH_3OH$	1.96	SP	6-a
$[Zn(eta–dbz)(NCS)_2]$	2.01	Td	6-b
$[Co(eta–dbz)(NCS)_2]$	2.09	Oh	6-b
$[Fe_2(eta–dbz)_2(NO_3)_2](NO_3)_2 \cdot 2DMF$*	2.03	PB	6-c
$[Mn(eta–dbz)(NCS)_2]$	2.18	Oh	this work

† SP; square pyramid, Td; tetrahedron, Oh; octahedron, PB; pentagonal bipyramid. *OH group of (eta–dbz) deprotonates and bridges two Fe(III) ions.

geometry of Mn atom is a distorted octahedron, where the Mn–N5 (2.54 Å) and Mn–O (2.40 Å) distances are considerably longer than the ordinary bond distances of Mn(II) complexes.

Table I shows the average distances between the metal and benzimidazolyl nitrogen atoms for Cu(II), Zn(II), Co(II), Fe(III) and Mn(II) complexes with (eta–dbz). The metal–nitrogen distance of the Mn(II) complex is substantially longer than those of the Cu(II), Zn(II) and Fe(III) complexes, and even a little longer than that of the Co(II) complex whose coordination geometry is a distorted octahedron similar to that of the present Mn(II) complex.

References

1 G. D. Lawrence and D. T. Sawyer, *Coord. Chem. Rev., 27* 173 (1978).
2 C. J. Brock and J. E. Walker, *Biochemistry, 19,* 2873 (1980).
3 V. R. Lehnert and F. Seel, *Z. Anorg. Allg. Chem., 464,* 187 (1980).
4 K. Takahashi, E. Ogawa, N. Oishi, Y. Nishida and S. Kida, *Inorg. Chim. Acta, 66,* 97 (1982).
5 'Universal Crystallographic Computer Program System', ed. by T. Sakurai, The Crystallographic Society of Japan, Tokyo (1967).
6 a) Y. Nishida, K. Takahashi and S. Kida, *Mem. Fac. Sci., Kyushu Univ., ser C. 13(1),* 27 (1981). b), c) to be published.