Pergamon

0277-5387(94)00340-8

Polyhedron Vol. 14, No. 2, pp. 319-322, 1995
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0277-5387/95 $9.50+0.00

COMMUNICATION

SYNTHESIS OF BIS(*N*-METHYLIMIDAZOL-2-YL)KETONE (BIK) AND CRYSTAL STRUCTURE OF $[Zn(BIK)_2](ClO_4)_2$

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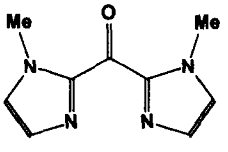
(*Received* 1 *August* 1994; *accepted* 24 *August* 1994)

Abstract—A novel polyimidazole ligand bis(*N*-methylimidazol-2-yl)ketone (BIK) has been synthesized and its first metal complex $[Zn(BIK)_2](ClO_4)_2$ has been structurally established by X-ray crystallography. The zinc atom is coordinated by two chelating BIK ligands in a distorted tetrahedral N_4 environment with Zn—N bonds at 1.997(8) Å and N—Zn—N bond angles at 93.5(5)–137.3(5)°.

In order to provide structural and functional low molecular-weight model complexes for metal enzymes, synthesis of chelating agents comprising imidazole donor groups is highly desirable, since the presence of one or more histidine residues have commonly been observed to participate in the coordination spheres of the active sites of metal enzymes.[1-2] Although a number of chelate ligands have been used as model ligands, the ligating groups are commonly pyridines,[3] pyrazoles,[4] or aliphatic amines.[5] Hitherto only a few polyimidazole ligands have been reported.[6-8] In this paper, we report the synthesis of a diimidazole ligand, bis(*N*-methylimidazol-2-yl)ketone (abbreviated as BIK hereafter) and structural characterization of its first metal complex $[Zn(BIK)_2](ClO_4)_2$ (Scheme 1).



Scheme 1. Structure of BIK ligand.

EXPERIMENTAL

Preparation

Under a nitrogen atmosphere, a 1.3 M solution of *N*-butyllithium in hexane (23 cm^3) was added to 100 cm^3 of anhydrous diethyl ether. Over a 60 min interval, a solution of *N*-methylimidazole (2.54 g, 30 mmol) in anhydrous diethyl ether (20 cm^3) was added dropwise. Then THF (30 cm^3) was added to the mixture with stirring for 20 min. After being cooled to −78°C, methyl chloroformate (14 g) in THF (5 cm^3) was added dropwise via a syringe. When the addition was complete, the resulting mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched by addition of ethanol and the crude product was

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collected after removal of the solvents under reduced pressure. The crude product was purified by flashed chromatography using 10 : 1 and 10 : 2 acetone–ethanol as eluents. The final product was collected as a pale yellow solid (1.4 g, 52%). Found: C, 56.8; H, 5.3; N, 29.5. Calc. for $C_9H_{10}N_4O$: C, 56.8; H, 5.3; N, 29.5%. IR data (cm^{-1}): 3416vs,br, 3093vs, 2793vs, 1672m, 1644m, 1591m, 1539m, 1489m, 1433s, 1314m, 1208m, 1152m, 1103s, 1068s, 1032m, 983m, 934m, 878m, 786m, 723m, 688m, 554m.

A mixture of BIK (0.190 g, 1.0 mmol) and $Zn(ClO_4)_2 \cdot 6H_2O$ (0.186 g, 0.5 mmol) was dissolved in methanol (10 cm^3) at 50°C with stirring. After slow evaporation of the resulting solution at room temperature for a week, pale yellow polyhedral crystals (0.2 g) of $[Zn(BIK)_2](ClO_4)_2$ were obtained. Found: C, 33.7; H, 3.6; N, 17.5. Calc. for $C_{18}H_{20}Cl_2ZnN_8O_{10}$: C, 33.5; H, 3.1; N, 17.4%. IR data (cm^{-1}): 3585m,br, 3567m,br, 3149m, 3128m, 2959w, 2839w, 1644m, 1564w, 1503vs, 1440vs, 1293s, 1243m, 1145vs, 1089vs,br, 1018s, 962m, 913vs, 779s, 751m, 702w, 625s.

Crystallography

$C_{18}H_{20}Cl_2ZnN_8O_{10}$, Mol. wt. 644.7, orthorhombic, space group *Fddd* (No. 70), $a = 20.487(5)$, $b = 20.696(6)$, $c = 23.877(7)$ Å, $V = 10124(5)$ Å^3, $Z = 16$, $D_c = 1.692$ Mg m^{-3}, $F(000) = 5248$, Mo-$K\alpha$ ($\lambda = 0.71073$ Å), $\mu = 12.51$ cm^{-1}.

Intensity data (crystal size $0.28 \times 0.40 \times 0.44$ mm^3; $2\theta_{max} = 48°$, 2039 unique data) were collected at 21°C on a Siemens R3m/V diffractometer using the ω-scan (2.9–14.6 deg per min) mode. Data processing, absorption correction (transmission factors 0.607–0.706), structure solution, and full-matrix least-squares refinement were performed with SHELXTL-PC program package.[9] The non-hydrogen atoms were refined anisotropically, except that the two-fold orientationally disordered perchlorate oxygen atoms were subjected to interatomic constraints of $Cl—O = 1.41 \pm 0.01$ Å and $O \cdots O = 2.35 \pm 0.01$ Å, assigned site occupancy factors of 0.5. Hydrogen atoms of the ligands were generated geometrically (C—H = 0.96 Å), assigned isotropic temperature factors and included in the structure-factor calculations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[10] The final R (R_w) value was 0.077 (0.096) for 176 parameters and observed 1200 reflections with $I \geqslant 3\sigma(I)$. The selected bond lengths and bond angles are listed in Table 1. Supplementary materials including non-hydrogen and hydrogen atomic coordinates, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSIONS

The crystal structure of title zinc complex consists of discrete $[Zn(BIK)_2]^{2+}$ cations and perchlorate anions. There are two crystallographically independent but very similar cations in the asymmetric unit. As illustrated in Fig. 1, the zinc atom is coordinated by two chelate BIK ligands in a highly distorted tetrahedral N_4 environment with the Zn—N bond lengths ranging from 1.990(8) to 2.004(8) Å, and the intra ligand and inter ligand N—Zn—N bond angles from 93.5(5) to 137.3(5)°, respectively. The two imidazole moieties of the BIK ligands are not coplanar with the dihedral angles between them being 25 and 37°, respectively for the two independent $[Zn(BIK)_2]^{2+}$ cations, although the pair of imidazole rings are connected by a carbonyl group. So far only two analogous diimidazole ligands have been used in synthesis of model complexes of biological relevance, which are 2,2′-biimidazole[6] and 2,2′-bis(1-methyl-midazolyl) phenylmethoxymethane (BIPhMe).[7] 2,2′-biimidazole molecules can either use one of the imidazole moieties as a bridging imidazolate ligand, or chelate a metal ion to form a five-membered ring with the mean intraligand N—M—N bond angles being about 79.5° for the zinc complexes.[6] The BIPhMe ligand can chelate a zinc ion to form a six-membered chelate ring with the mean intraligand N—Zn—N bond angle at 116.0°. In the present $[Zn(BIK)_2]^{2+}$ cation, the mean Zn—N bond length is comparable to those found for the tetrahedrally coordinated complex $[Zn(BIPhMe)Cl_2]$.[7] In contrast, the mean intraligand N—Zn—N bond angle at 93.5(5)° is significantly smaller than that in the latter complex [116.0(1)°], although the BIPhMe ligand also forms an analogous six-membered chelate ring with the zinc ion. Hence the BIK ligand may be expected to exhibit different coordination behaviour in the formation of metal complexes.

In summary, the synthesis of a new diimidazole ligand and its first zinc complex is reported. We believe that this ligand offers potential for synthesis of model complexes of biological relevance. Further exploration of metal complexes containing the title ligand is in progress.

Acknowledgements—This work is supported by NSFC (Grant No. 29303024) and the National Education Com-

Table 1. Selected bond lengths (Å) and bond angles (°)

Zn(1)—N(1)	2.004(8)	Zn(2)—N(3)	1.990(8)
N(1)—C(1)	1.328(14)	N(1)—C(3)	1.341(12)
N(2)—C(2)	1.359(15)	N(2)—C(3)	1.376(13)
N(2)—C(5)	1.467(15)	O(1)—C(4)	1.224(15)
C(1)—C(2)	1.361(17)	C(3)—C(4)	1.463(11)
N(3)—C(6)	1.368(14)	N(3)—C(8)	1.319(12)
O(2)—C(9)	1.215(17)	N(4)—C(7)	1.354(15)
N(4)—C(8)	1.361(13)	N(4)—C(10)	1.488(16)
C(6)—C(7)	1.371(17)	C(8)—C(9)	1.464(12)
N(1)—Zn(1)—N(1a)	93.5(5)	N(1)—Zn(1)—N(1b)	137.3(5)
N(1a)—Zn(1)—N(1b)	101.7(5)	N(3)—Zn(2)—N(3e)	133.4(5)
N(3)—Zn(2)—N(3d)	104.0(5)	N(3e)—Zn(2)—N(3d)	94.0(5)
Zn(1)—N(1)—C(1)	126.9(7)	Zn(1)—N(1)—C(3)	123.5(7)
Zn(2)—N(3)—C(6)	125.9(7)	Zn(2)—N(3)—C(8)	124.4(7)
C(1)—N(1)—C(3)	106.6(8)	C(2)—N(2)—C(3)	107.1(9)
C(2)—N(2)—C(5)	124.0(10)	C(3)—N(2)—C(5)	128.8(9)
N(1)—C(1)—C(2)	110.9(10)	N(2)—C(2)—C(1)	106.1(10)
N(1)—C(3)—N(2)	109.2(8)	N(1)—C(3)—C(4)	127.6(9)
N(2)—C(3)—C(4)	123.2(8)	O(1)—C(4)—C(3)	120.4(5)
C(3)—C(4)—C(3a)	119.1(11)	C(6)—N(3)—C(8)	108.0(9)
C(7)—N(4)—C(8)	108.9(9)	C(7)—N(4)—C(10)	122.9(10)
C(8)—N(4)—C(10)	128.2(9)	N(3)—C(6)—C(7)	108.4(10)
N(4)—C(7)—C(6)	106.1(10)	N(3)—C(8)—N(4)	108.7(9)
N(3)—C(8)—C(9)	127.3(9)	N(4)—C(8)—C(9)	124.1(8)
O(2)—C(9)—C(8)	119.7(5)	C(8)—C(9)—C(8c)	120.5(11)

Symmetry codes: (a) $0.25-x$, $0.25-y$, z; (b) $0.25-x$, y, $0.25-z$; (c) x, $0.25-y$, $0.25-z$; (d) $1.25-x$, y, $1.25-z$; (e) $1.25-x$, $0.25-y$, z.

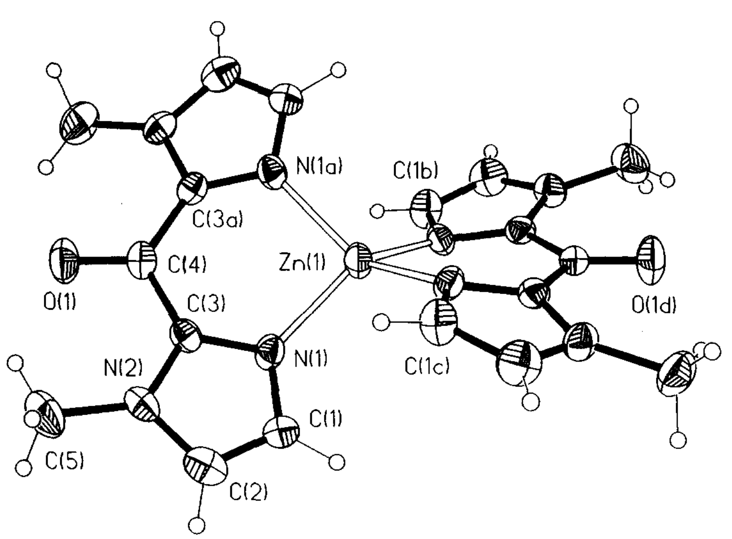

Fig. 1. ORTEP drawing (35% probability) of the cation in $[Zn(BIK)_2](ClO_4)_2$ (1) and atom-numbering scheme.

mission of China with a grant for returned scientists from abroad.

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