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Structure of Bis[*N*-(2-pyrrolylmethylene)-*tert*-butylamine]zinc(II), $\text{Zn}(\text{C}_9\text{H}_{13}\text{N}_2)_2$

BY J. A. KANTERS, A. L. SPEK AND R. POSTMA

Structural Chemistry Group, University of Utrecht, Padualaan 8, 3508 TB Utrecht, The Netherlands

AND G. C. VAN STEIN AND G. VAN KOTEN

Laboratory of Inorganic Chemistry, University of Amsterdam, 1018 WV Amsterdam, The Netherlands

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Abstract. $M_r = 363.81$, orthorhombic, *Pbcn*, $a = 17.166$ (5), $b = 7.209$ (5), $c = 15.232$ (3) Å, $V = 1885$ (2) Å³, $Z = 4$, $D_m = 1.25$, $D_x = 1.282$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 13.13$ cm⁻¹, $F(000) = 768$, $T = 294$ K, $R = 0.0398$ for 1591 observed reflections. The Zn atom, which is on a crystallographic twofold axis, is coordinated to four N atoms of the two symmetry-related bidentate pyrrolylmethylene-*tert*-butylamine ligands. These coordinating N atoms form a tetrahedron that is elongated along the bisector of the N–Zn–N ligand angle of the chelating ring.

Introduction. It is well known that Zn^{II} has a catalytic function in substrate reductions by nicotinamide-adenine dinucleotide (NADH) in biological systems and the mechanism of this reduction has been the subject of earlier investigations in polar solvents and often at low pH (Shirai, Chishina & Tanaka, 1975; Branden, Jörnvall, Ekland & Furugren, 1976). From these experiments it has not been possible to decide whether the initial step in the reduction is a proton or an electron transfer.

In order to be able to study substrate reductions in aprotic solvents, it is necessary to have neutral Zn–substrate model compounds available that are soluble in aprotic solvents. The title compound represents such a model and the first aim was to determine accurately its Zn coordination.

Experimental. Synthesized by one of the authors (G. C. van Stein), rod-shaped crystal, $0.58 \times 0.49 \times 0.34$ mm, D_m by flotation, Nonius CAD-4 diffractometer, ω - 2θ scan technique, Zr-filtered Mo *K* α radiation, lattice parameters from ten reflections, one octant of the reflection sphere, 2161 independent intensities measured, h 0–22, k 0–9, l 0–19, $2\theta_{\text{max}} = 55^\circ$, 1591 above $2.5 \sigma(I)$ level; two periodically measured standard reflections showed no significant changes; correction for Lorentz, polarization and absorption (using seven indexed crystal faces, transmission factors 0.591 to 0.640); Patterson and Fourier methods, all H atoms located from difference maps; H atoms, except those of the methyl groups, included in weighted anisotropic full-matrix refinement with constant isotropic thermal parameters equal to those of the carrier atoms, methyl-group H atoms refined in the rigid-rotator model with fixed C–H distances and H–C–H angles, $wR = [\sum w^{1/2}(|F_o| - |F_c|)] / [\sum w^{1/2} F_o] = 0.045$, $w = 1.4515 / [\sigma^2(F_o) + 0.00143 F_o^2]$, $S = 0.70$; refinement of isotropic extinction parameter in the last cycles gave $g = 1.13 \times 10^{-7}$; average and maximum shift/error ratios for non-H parameters were 0.012 and 0.059, respectively, for H parameters 0.018 and 0.034, respectively; final difference map revealed regions of positive and negative densities of about $0.45 \text{ e } \text{Å}^{-3}$ at about 0.8 Å from Zn, the other maxima were below the level of $0.30 \text{ e } \text{Å}^{-3}$; scattering factors from *International Tables for X-ray Crystallography* (1974)

and the anomalous scattering factors from Cromer & Liberman (1970). Calculations performed with the XRAY76 system (Stewart, 1976), the SHELX76 package (Sheldrick, 1976) and the EUCLID package (Spek, 1982) on the Cyber-175 of the University of Utrecht.*

Discussion. Table 1 gives the atomic coordinates and Fig. 1 illustrates the structure and atom numbering.

The zinc atom of the bis-bidentate complex is situated on a crystallographic twofold axis and hence the complex has exact twofold symmetry. Complexes of Co^{II} (Wei, 1972*a*), Ni^{II} (Wei & Einstein, 1972) and two modifications of Cu^{II} (Wei, 1972*b*) with the same ligand have been reported in the literature. Both the Zn and Co

* Lists of structure factors, coordinates of H atoms, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38500 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and thermal parameters ($\text{\AA}^2 \times 10^2$)

Least-squares-derived standard deviations of the least significant figures are given in parentheses.

	x	y	z	U^*_{eq} or U
Zn	5000	2751 (1)	7500	4.28 (2)
N(1)	6016 (1)	4180 (3)	7230 (1)	4.29 (6)
N(2)	5634 (1)	1534 (3)	8416 (1)	4.31 (6)
C(1)	6182 (2)	5631 (4)	6559 (2)	4.94 (8)
C(2)	6972 (2)	5359 (6)	6133 (3)	8.9 (1)
C(3)	5536 (3)	5546 (5)	5886 (3)	8.2 (1)
C(4)	6164 (2)	7533 (4)	7008 (2)	6.9 (1)
C(5)	6541 (1)	3632 (4)	7766 (2)	4.66 (8)
C(6)	6380 (1)	2242 (4)	8395 (2)	4.59 (8)
C(7)	6834 (2)	1363 (5)	9029 (2)	5.8 (1)
C(8)	6354 (2)	99 (5)	9442 (2)	6.4 (1)
C(9)	5629 (2)	244 (4)	9049 (2)	5.4 (1)
H(5)	6999 (17)	4132 (41)	7764 (17)	4.7
H(7)	7355 (18)	1508 (40)	9147 (19)	5.8
H(8)	6442 (17)	-764 (45)	9900 (19)	6.4
H(9)	5170 (18)	-284 (46)	9156 (22)	5.4

$$* U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

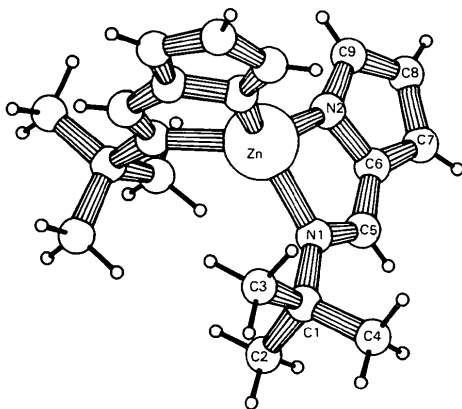


Fig. 1. Molecular configuration and adopted numbering scheme. A crystallographic twofold axis passes through the Zn atom.

complexes crystallize in space group *Pbcn* with almost identical cell dimensions and are essentially isomorphous. The Ni complex, which has disordered *tert*-butyl groups, also crystallizes in *Pbcn* but deviates significantly from isomorphism. The modifications of the Cu complex are triclinic and tetragonal, respectively. The Zn atom is coordinated to four nitrogen atoms which form a distorted tetrahedron. As in the Co complex the tetrahedron is elongated along the direction bisecting the chelating ring, such that the intrachelate N(1)—Zn—N(2) angle is acute [$84.1(1)^\circ$], whereas the three interchelate angles are $120.2(1)$, $123.1(1)$ and $127.3(1)^\circ$, respectively. The Zn—N distances differ appreciably [$2.067(2)$ and $1.975(2)$ Å] and contribute to the distortion of the tetrahedron.

For comparison Table 2 lists various geometries of the metal coordination of the Zn, Co, Ni and Cu complexes.

The bond distances and angles, which are listed in Table 3, compare well with those reported for the Ni and Co complexes. The N—C—C angles in the N(1)—C(1)—(CH₃)₃ fragment vary from $107.3(3)$ to $112.0(3)^\circ$, indicating a tetrahedral configuration of the *tert*-butyl group. The conformation of the *tert*-butyl group relative to the N(1)—C(5) bond deviates about

Table 2. Geometries (\AA , $^\circ$) of the metal coordination in $(\text{C}_9\text{H}_{13}\text{N}_2)_2\text{M}^{\text{II}}$

	Zn	Co	Ni	Cu triclinic	Cu tetragonal
M—N(1)	2.067 (2)	2.066 (8)	2.032 (4)	2.054 (8)	2.044 (14)
M—N(2)	1.975 (2)	1.981 (7)	1.935 (5)	1.939 (8)	1.922 (15)
N(1)—N(2)	2.708 (3)	2.70 (1)	2.65 (1)	2.69 (1)	2.69 (1)
N(1)—M—N(2)	84.1 (1)	83.5 (3)	83.7 (4)	84.7 (4)	85.4 (6)
N(1)—M—N(1')	120.2 (1)	121.8 (4)	116.7 (2)	137.7 (4)	133.4 (9)
N(1)—M—N(2')	123.1 (1)	123.5 (3)	122.1 (2)	109.2 (4)	107.3 (6)
N(2)—M—N(2')	127.3 (1)	126.2 (5)	132.7 (3)	142.1 (5)	148.1 (9)

Table 3. Interatomic distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Zn—N(1)	2.067 (2)	C(5)—C(6)	1.414 (4)
Zn—N(2)	1.975 (2)	C(6)—C(7)	1.393 (4)
N(1)—C(1)	1.490 (3)	C(7)—C(8)	1.380 (5)
N(1)—C(5)	1.279 (3)	C(8)—C(9)	1.385 (5)
N(2)—C(6)	1.379 (3)		
N(2)—C(9)	1.340 (3)	C(5)—H(5)*	0.86 (3)
C(1)—C(2)	1.516 (5)	C(7)—H(7)	0.92 (3)
C(1)—C(3)	1.511 (6)	C(8)—H(8)	0.95 (3)
C(1)—C(4)	1.533 (4)	C(9)—H(9)	0.89 (3)
Zn—N(1)—C(1)	130.4 (2)	C(2)—C(1)—C(3)	111.2 (3)
Zn—N(1)—C(5)	108.3 (2)	C(2)—C(1)—C(4)	109.0 (3)
C(1)—N(1)—C(5)	121.3 (2)	C(3)—C(1)—C(4)	108.9 (3)
Zn—N(2)—C(6)	109.3 (2)	N(1)—C(5)—C(6)	120.9 (2)
Zn—N(2)—C(9)	144.4 (2)	C(5)—C(6)—C(7)	133.1 (2)
C(6)—N(2)—C(9)	106.2 (2)	N(2)—C(6)—C(7)	109.6 (3)
N(1)—C(1)—C(2)	112.0 (3)	N(2)—C(6)—C(5)	117.4 (2)
N(1)—C(1)—C(3)	107.3 (3)	C(6)—C(7)—C(8)	106.4 (3)
N(1)—C(1)—C(4)	108.6 (2)	C(7)—C(8)—C(9)	106.8 (3)
		N(2)—C(9)—C(8)	111.0 (3)

* H atoms of the *tert*-butyl group were refined in the rigid-rotation model with C—H distances and H—C—H angles of 1.08 Å and 109.5° , respectively.

18 (1)° from the ideal staggered conformation, as follows from the three torsion angles C(5)–N(1)–C(1)–C(2) 41.7 (4), C(5)–N(1)–C(1)–C(3) 163.9 (3) and C(5)–N(1)–C(1)–C(4) –78.6 (3)°. For comparison, in the Co complex these angles are 41, 161 and –79° respectively, whereas in the triclinic and tetragonal modifications of the Cu complex the three methyl-group carbon atoms are in near-eclipsed positions.

A striking feature of the structure is the coplanarity of seven out of 11 non-hydrogen atoms of the ligand

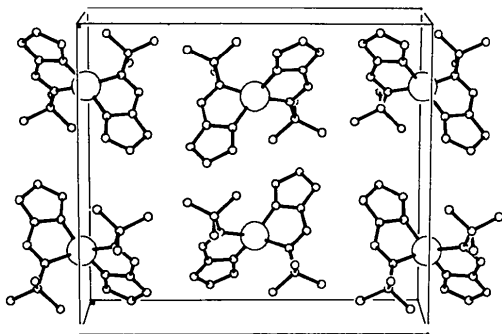


Fig. 2. A view of the unit-cell contents down the *b* axis, with the *a* axis to the right and *c* axis upwards. The origin is in the lower left front corner. H atoms have been omitted.

and the Zn atom.* The two planar fragments, related by the twofold axis, are perpendicular [89.2 (1)°]. The atoms of the pyrrole ring are rigorously coplanar and the same is true for the atoms in the five-ring chelate moiety.*

Fig. 2 gives a view of the cell contents along *b*.

* See deposition footnote.

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Structure du Complexe Dimérique Formé par un Polyéther Macrocyclique Tetrafonctionnel avec l'Ion Potassium, $2C_{24}H_{44}N_4O_{10} \cdot 3KBr \cdot 7H_2O$: un Modèle de Canal Transmembranaire

PAR ANNE-CATHERINE DOCK ET DINO MORAS

Laboratoire de Cristallographie Biologique de l'IBMC, 15 rue René Descartes, 67084 Strasbourg CEDEX, France

ET JEAN-PAUL BEHR ET JEAN-MARIE LEHN

Laboratoire de Chimie Organique Physique, 1 rue Blaise Pascal, 67008 Strasbourg CEDEX, France

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Abstract. $M_r = 1580.4$, triclinic, $P1$, $a = 10.734$ (2), $b = 11.272$ (2), $c = 15.781$ (4) Å, $\alpha = 109.85$ (2), $\beta = 99.35$ (2), $\gamma = 92.18$ (2)°, $V = 1763.1$ Å³, $Z = 1$, $D_x = 1.488$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $F(000) = 824$, room temperature. The structure of the hydrated 3:2 KBr complex of *N,N,N',N'',N''',N''',N''''*-octamethyl-1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxamide (1) was solved by the heavy-atom method and refined to $R = 0.096$ using

6404 significant [$I > 3\sigma(I)$] independent reflections. The molecular packing consists of hydrated polymeric chains formed by the repetition of the dimeric unit $[\{(1), K\}_2 \cdot 3H_2O]^{2+} \cdot [KBr_3 \cdot 4H_2O]^{2-}$ aligned along [110]. It is stabilized by extensive O–H...O and O–H...Br hydrogen bonding through water bridges as well as by K...O ion dipole interactions and Br...CH₃ van der Waals forces. The 18-crown-6 macrocycles are in relaxed conformations with their amide chains extend-