The triclinic polymorph of dibromo-[(−)-sparteine-$\kappa^2 N,N'$]zinc(II)

José Luis Alcántara-Flores,[a] Sylvain Bernès,[a]* Yasmi Reyes-Ortega[a] and Rafael Zamorano-Ulloa[b]

[a]Centro de Química, Instituto de Ciencias, Universidad Autónoma de Puebla, AP 1613, 72000 Puebla, Pue., Mexico, and [b]Departamento de Física, Escuela Superior de Física y Matemáticas, IPN, Edif. 9, UP 'ALM', 07738 México, DF, Mexico

Correspondence e-mail: sylvain@eros.pquim.unam.mx

The title compound, [ZnBr$_2$(C$_{15}$H$_{26}$N$_2$)], when synthesized starting from Zn^0, is obtained in two polymorphic forms, one belonging to space group $P2_12_12_1$ and one to $P1$. The present contribution deals with the triclinic phase, which is isostructural with the orthorhombic form but presents a larger metal–metal intermolecular separation; the Zn···Zn distance is 7.4715 (6) Å for the triclinic polymorph as opposed to 6.534 Å for the orthorhombic polymorph.

Comment

The correlation between the tetrahedral coordination of the Cu^{II} ion in type 1 blue copper proteins and some unique spectroscopic features reported for these proteins is a well established fact (Krishnan, 1978; Colman *et al.*, 1978; Solomon *et al.*, 1992; Holland & Tolman, 2000). Some well studied examples are the intense absorption observed in electronic spectra near 600 nm ($\varepsilon \simeq 5000\ M^{-1}\ \text{cm}^{-1}$) and the small Cu hyperfine splitting observed in electron paramagnetic resonance (EPR) spectra ($A_{//} < 70 \times 10^{-4}\ \text{cm}^{-1}$, which is less than half the value observed in common Cu^{II} coordination complexes).

In this context, numerous Cu^{II} complexes containing sparteine as a ligand have been synthesized, with the hope of accurately modeling the spectroscopic and structural features of the catalytic centers of these proteins (Boschmann *et al.*, 1974; Choi *et al.*, 1975; Kim *et al.*, 2001). For the X-ray-characterized complexes, the expected distorted tetrahedral geometry has been observed in most cases, although the spectroscopic characteristics of these complexes did not always fit correctly with those of the proteins (Childers *et al.*, 1975; Lopez *et al.*, 1998; Choi *et al.*, 1995; Lee *et al.*, 2000).

While working with this class of compounds, we prepared by direct synthesis a series of complexes with the general formula $M(\text{SP})X_2$, where SP is the naturally occurring (−)-sparteine ligand, X is Cl or Br, and M is Cu^{II} or Zn^{II}. The Cu^{II} complexes are used for modeling the active site of type 1 blue copper

proteins (structurally and spectroscopically), while the Zn^{II} complexes are used as diluting agents for measuring the hyperfine, and eventually the super-hyperfine, coupling by EPR on powdered samples. To validate the EPR, isostructurality between Cu and Zn complexes has first to be established by X-ray diffraction. In the case of $X = $ Br, both metals yielded two isostructural polymorphic crystalline phases, one in space group $P1$ and one in $P2_12_12_1$, when a direct synthesis was used, *i.e.* using metallic copper or zinc as a starting material (see *Experimental*). The Zn complex described here, (I), corresponds to the triclinic polymorph of Zn(SP)Br$_2$. The orthorhombic phase, which is synthesized using zinc(II) bromide as a starting material, was reported recently by Lee *et al.* (2002).

(I)
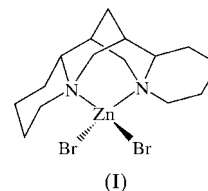
The molecular structure of (I) is, within the experimental s.u. values, identical (Fig. 1) to that of the reported orthorhombic phase. The r.m.s. deviation between the two structures is 0.0362 Å (excluding H atoms). The largest observed deviation for the fit, 0.082 Å, arises for the Br atoms.

In contrast, the symmetry change induces dramatic differences in the packing structures. The orthorhombic phase is stabilized through two intermolecular contacts involving both the Br atoms and the methylene or methine H atoms of SP ligands of symmetry-related molecules, *viz.* Zn—Br1···H15B^i [contact = 2.91 Å and angle = 156°; symmetry code: (i) $\frac{1}{2} - x$, $1 - y$, $-\frac{1}{2} + z$] and Zn—Br2···H7^{ii} [contact = 2.93 Å and angle = 160°; symmetry code: (ii) $\frac{1}{2} - x$, $-y$, $-\frac{1}{2} + z$]. The Br···H separations are then 0.14 and 0.12 Å shorter, respectively, than the van der Waals distances. This arrangement generates layers of connected molecules, with the layers lying normal to the a axis of the orthorhombic cell (Fig. 2).

In the case of (I), the only operators available to connect molecules are axis translations. A single short Br···H contact is observed (Table 1), which corresponds to a relatively weak
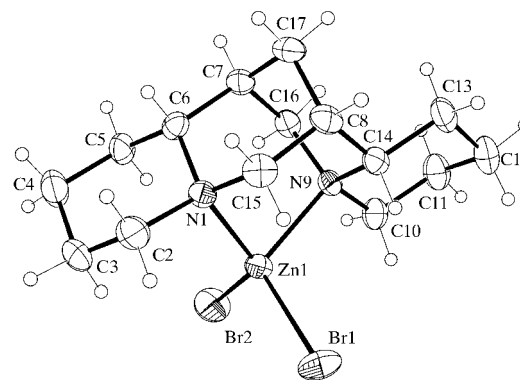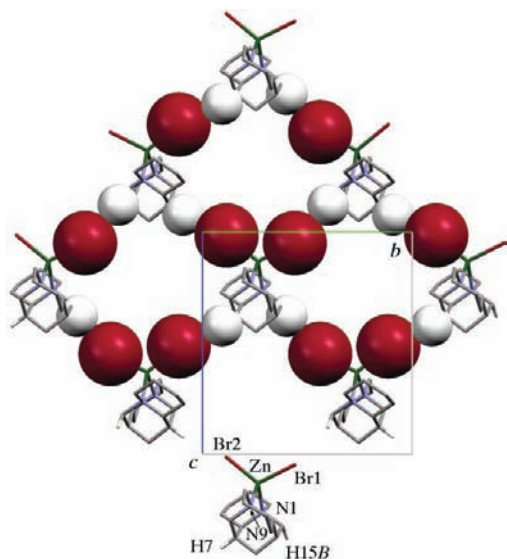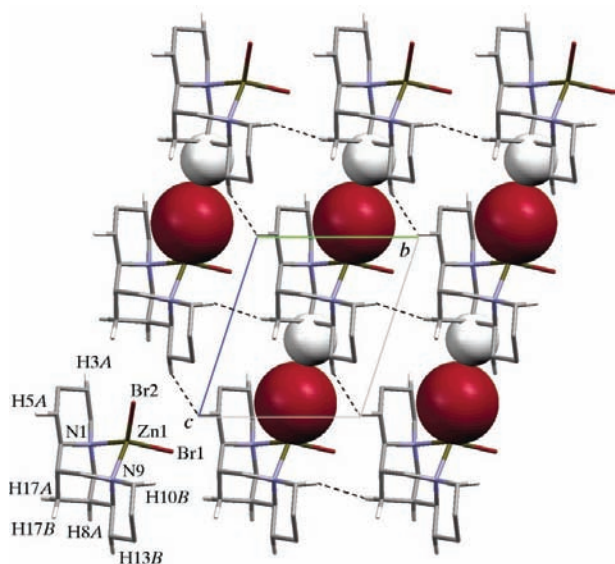

Figure 1
The structure of (I) with displacement ellipsoids at the 40% probability level. The numbering scheme is identical to that adopted by Lee *et al.* (2002) for the orthorhombic phase.

Figure 2
One layer of interconnected $Zn(SP)Br_2$ molecules in the packing structure of the orthorhombic polymorph, viewed down the *a* axis. Nine molecules are represented. The capped sticks representation of the bottom molecule shows the numbering scheme for non-C atoms, and H atoms not involved in the network have been omitted for clarity. For the remaining molecules, atoms Br1, Br2, H7 and H15*B* that connect molecules are represented as van der Waals radii spheres (CCDC, 2002), making obvious the two-dimensional character of the network. For clarity, the labeled molecule is at the equivalent position $(x, -1 + y, 1 + z)$.

interaction, with a difference from the van der Waals distance of 0.06 Å; the resulting network of interconnected molecules is one-dimensional (Fig. 3). Because of these weak contacts, the

Figure 3
The packing structure for (I), viewed down the *a* axis. As in Fig. 2, nine molecules are represented, one of which (bottom left) includes labels for non-C atoms. The retained H atoms are those that give short non-bonding H···H intermolecular contacts. For the remaining molecules, atoms Br2 and H8*A* that connect molecules are represented as van der Waals radii spheres (CCDC, 2002), while dotted lines join H atoms that participate in the H···H contacts network (see Table 1). For clarity, the labeled molecule is at the equivalent position $(x, y, 1 + z)$.

packing index (Spek, 2003) is lowered from 0.683 for the orthorhombic phase to 0.681 for (I). This less efficient packing for (I) is confirmed by an analysis of the intermolecular H···H contacts. The shortest contact observed for the orthorhombic phase is H3*A*···H11*B*[iii] [2.40 Å; symmetry code: (iii) $1 + x, y, z$], *i.e.* a separation equal to the van der Waals distance. However, for (I), the shortest H···H separation is 2.32 Å (Table 1), which corresponds to an actual H···H contact (Fig. 3).

Finally, the metal–metal separations are significantly affected by the symmetry. The observed Zn···Zn[iv] distance is 6.534 Å [symmetry code: (iv) $\frac{1}{2} + x, \frac{1}{2} - y, -z$] in the orthorhombic case, while the Zn···Zn[v] distance is 7.4715 (6) Å [symmetry code: (v) $1 + x, y, z$] for (I). This difference of *ca* 1 Å is unimportant for the Zn^{II}-based compounds but essential for the corresponding Cu^{II}-based compounds that are intended for modeling. Considering that the metal centers should be magnetically isolated in the native proteins, the triclinic phase seems to be a more suitable magnetic model than the orthorhombic one.

Experimental

Equimolar amounts of zinc (0.123 g), CBr_4 (0.626 g) and (−)-sparteine (0.433 ml) were mixed in dimethyl sulfoxide (5.376 ml). The mixture was heated at 333 K for 30 min and then filtered. The first crop of crystals was collected after 2 d (0.219 g, yield 25.3%, m.p. 566 K). These crystals exhibited a characteristic hexagonal plate habit and were identified as (I). Further crystallization produced small quantities of the orthorhombic polymorph, which can be distinguished from (I) on the basis of its quite isotropic block habit.

Crystal data

$[ZnBr_2(C_{15}H_{26}N_2)]$	$Z = 1$
$M_r = 459.57$	$D_x = 1.766$ Mg m^{-3}
Triclinic, $P1$	Mo $K\alpha$ radiation
$a = 7.4715$ (6) Å	Cell parameters from 84
$b = 7.7082$ (7) Å	reflections
$c = 9.1435$ (6) Å	$\theta = 5.0–13.0°$
$\alpha = 97.429$ (6)°	$\mu = 6.04$ mm^{-1}
$\beta = 112.808$ (5)°	$T = 296$ (1) K
$\gamma = 110.666$ (6)°	Prism, colorless
$V = 432.02$ (7) Å^3	$0.60 \times 0.24 \times 0.16$ mm

Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.048$
$2\theta/\omega$ scans	$\theta_{max} = 30.0°$
Absorption correction: ψ scan	$h = -9 \rightarrow 10$
XSCANS (Siemens, 1996)	$k = -10 \rightarrow 10$
$T_{min} = 0.254$, $T_{max} = 0.381$	$l = -12 \rightarrow 12$
4908 measured reflections	3 standard reflections
4908 independent reflections	every 97 reflections
4244 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$\Delta\rho_{max} = 0.53$ e Å^{-3}
$wR(F^2) = 0.097$	$\Delta\rho_{min} = -0.77$ e Å^{-3}
$S = 1.04$	Extinction correction: *SHELXL*97
4908 reflections	Extinction coefficient: 0.0083 (17)
182 parameters	Absolute structure: Flack (1983);
H-atom parameters constrained	2436 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2$	Flack parameter = −0.016 (13)
$\quad + 0.6283P]$	
$\quad$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected intermolecular contacts (Å).

Br2···H8A^i	2.99	H5A···H13B^{iii}	2.32
H3A···H17B^{ii}	2.32	H10B···H17A^{iv}	2.39

Symmetry codes: (i) $x-1, y, z-1$; (ii) $x, y, z-1$; (iii) $x-1, y-1, z-1$; (iv) $x, 1+y, z$.

H atoms were treated as riding atoms, with C—H distances of 0.97 (CH$_2$) or 0.98 Å (CH).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* and *MERCURY* (CCDC, 2002); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1241). Services for accessing these data are described at the back of the journal.

References

Boschmann, E., Weinstock, L. M. & Carmack, M. (1974). *Inorg. Chem.* **13**, 1297–1300.

CCDC (2002). *MERCURY*. Version 1.1. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England, http://www.ccdc.cam.ac.uk/mercury.

Childers, L. S., Folting, K., Merritt, L. L. Jr & Streib, W. E. (1975). *Acta Cryst.* **B31**, 924–925.

Choi, S.-N., Bereman, R. D. & Wasson, J. R. (1975). *J. Inorg. Nucl. Chem.* **77**, 2087–2090.

Choi, S.-N., Kwon, M. A., Kim, Y., Bereman, R. D., Singh, P., Knight, B. & Seff, K. (1995). *J. Coord. Chem.* **34**, 241–252.

Colman, P. M., Freeman, H. C., Guss, J. M., Murata, M., Norris, V. A., Ramshaw, J. A. M. & Venkatappa, M. P. (1978). *Nature* (London), **272**, 319–324.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Holland, P. L. & Tolman, W. B. (2000). *J. Am. Chem. Soc.* **122**, 6331–6332.

Kim, Y.-J., Kim, S.-O., Kim, Y.-I. & Choi, S.-N. (2001). *Inorg. Chem.* **40**, 4481–4484.

Krishnan, V. G. (1978). *J. Chem. Phys.* **68**, 660–662.

Lee, Y.-M., Chung, G., Kwon, M.-A. & Choi, S.-N. (2000). *Acta Cryst.* C**56**, 67–68.

Lee, Y.-M., Kang, S. K., Kim, Y.-I. & Choi, S.-N. (2002). *Acta Cryst.* C**58**, m453–m454.

Lopez, S., Muravyov, I., Pulley, S. R. & Keller, S. W. (1998). *Acta Cryst.* C**54**, 355–357.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (1998). *SHELXTL-Plus*. Release 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *XSCANS*. Version 2.21. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Solomon, E. I., Baldwin, M. J. & Lowery, M. D. (1992). *Chem. Rev.* **92**, 521–542.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.