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A New Schiff Base Complex: {N-[3-(2-Aminoethylamino)propyl]salicylidene-aminato-O,N,N',N''}bromozinc(II)

VÁCLAV HABER

Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 120 00 Praha 2, Czech Republic

JAN FÁBRY* AND VÁCLAV PETŘÍČEK

Institute of Physics Czech Academy of Sciences, Cukrovarnická 10, 162 00 Praha 6, Czech Republic

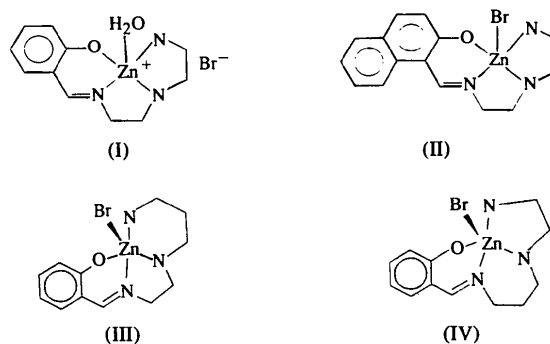
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Abstract

[Zn(satnen)Br], where satnen = H₂N(CH₂)₂NH(CH₂)₃N=CHC₆H₄O⁻, is the first example of a complex containing a tetradentate Schiff base derived from 1,6-diamino-3-azahexane. The Zn atom is bonded to five atoms (Br, O and three N atoms) and its coordination polyhedron can be described either as a distorted trigonal bipyramid (the Br atom being situated in the equatorial plane) or as a distorted tetragonal pyramid (with the Br atom at the apex). The Zn—Br bond is unusually long [2.4812(7) Å]. The bonding distances within the phenyl ring vary between 1.34(2) and 1.42(1) Å. The longer distances involve those C atoms which are connected either to O or to the C(H)=N-fragment. There are two intermolecular N—H...X, X = Br, O, hydrogen bonds; the X = O bond is extremely weak.

Comment

There are two reasons for this study. Firstly, the cation environments in related Zn complexes, *i.e.* in [Zn(saden)H₂O]Br, (I) (Kratochvíl, Ondráček, Novotný & Haber, 1991) and [Zn(naden)Br], (II) (Ondráček, Kratochvíl & Haber, 1994) are highly distorted {saden = N-[2-(2-aminoethylamino)ethyl]-salicylideneaminato-O,N,N',N'' and naden = 1-[2-(2-aminoethylamino)ethylimino]methyl-2-naphtholato-O,N,N',N''}. The distortion is caused at least partly by the short N—N bite distances which manifest themselves by rather acute N—Zn—N' and N'—Zn—N'' angles (79–82°). The longer trimethylene chain between two of the N atoms in the present ligand should partly relieve this strain and so lead to more regular arrangement around the central atom. Secondly, from stability studies of complexes with multidentate ligands, it has been deduced that complexes with adjacent five- and six-membered chelate rings are more stable than those where pairs of either six- or five-membered rings are joined (Hancock, 1992). The present complex can form two isomers, (III) and (IV). From Hancock's conclusions, it can be predicted that (III) would be more stable than (IV). In the solid state the isomeric form proves, rather surprisingly, to be (IV) rather than (II). The structure is depicted in Fig. 1.



All the atoms of the pseudo-aromatic chelate and phenyl rings [O, N(3), C(6)–C(12)] lie approximately in a plane ($\chi^2 = 48.38$). The adjacent six-membered ring [Zn, N(2), C(3), C(4), C(5), N(3)] has a chair conformation. The atoms N(2), C(3), C(5) and N(3) are nearly coplanar ($\chi^2 = 1.11$). The conformation of the five-membered ring is between a half chair and a C(2) envelope: the deviations of C(1) and C(2) from the plane of Zn, N(1) and N(2) are 0.138(7) and $-0.529(8)$ Å, respectively, and the value of the N(1)—C(1)—C(2)—N(2) torsion angle is 53.9(5)°.

When compared with the related naden and saden Zn complexes, the present structure is closer to a trigonal bipyramidal arrangement with N(1) and N(3) in axial positions. In contrast, both N(1) and N(3) are in equatorial positions in (II) (Ondráček, Kratochvíl & Haber, 1994) and (I) (Kratochvíl, Ondráček, Novotný &

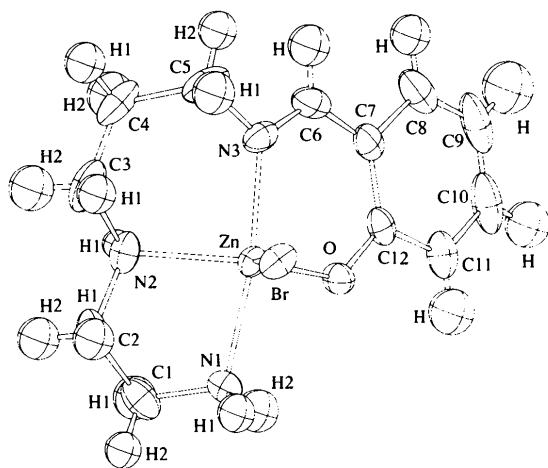


Fig. 1. View of the molecule of $[\text{Zn}(\text{satnen})\text{Br}]$ showing 50% probability ellipsoids.

Haber, 1991). In these complexes the bonds from Zn to axial donor atoms are somewhat longer than those to corresponding atoms in equatorial positions, e.g. in (IV), (II) and (I) the Zn—N(1) bond lengths are, respectively, 2.122 (5), 2.089 (6) and 2.079 (4) Å, and the Zn—N(3) bond lengths are, respectively, 2.082 (6), 2.020 (7) and 2.035 (3) Å. Finally, the value of the N(2)—Zn—N(3) bond angle is much greater in (IV), namely 88.6 (2)° compared with 79.0 (3) and 81.1 (1)° in (II) and (I), respectively, presumably due to the longer trimethylene chain between N(1) and N(2) in satnen.

Complex (IV) contains an extraordinarily long Zn—Br distance [2.4812 (7) Å]. Among the Zn—Br distances found in the Cambridge Structural Database (Version 5.06 from 1993, 115931 entries; Allen, Kennard & Taylor, 1983) only one is longer: 2.497 (2) Å in $[(\text{C}_8\text{H}_7\text{N}_2)_2\text{NCH}_3\text{ZnBr}_2] \cdot \text{C}_2\text{H}_5\text{OH}$, bis-[(2-benzimidazolyl)methyl]methylaminedibromozinc ethanol solvate (Wirbser & Vahrenkamp, 1992), where Zn is coordinated by three N and two Br atoms in a trigonal bipyramid. The longer Zn—Br bond is formed by an axial Br atom while the significantly shorter one [2.315 (2) Å] is formed by a Br atom in an equatorial position. In (II), the Zn—Br bond length is 2.425 (1) Å.

The Inorganic Crystal Structure Database (Bergerhoff, Hundt, Sievers & Brown, 1983) yielded two reliably determined structures with similar Zn—Br distances: $[\text{Mg}(\text{H}_2\text{O})_6][\text{Zn}_2\text{Br}_6]$ (Duhlev, Faggiani & Brown, 1987b) and $[\text{Zn}(\text{H}_2\text{O})_6][\text{Zn}_2\text{Br}_6]$ (Duhlev, Brown & Faggiani, 1988b); in each of these isostructural compounds there are bridging μ -Zn—Br distances of 2.483 (2) Å.

Zn—Br distances in the $[\text{ZnBr}_4]^-$ anion can vary from 2.378 to 2.438 Å, as was observed in $[\text{Ca}(\text{H}_2\text{O})_5][\text{ZnBr}_4]$, where the distances are affected by hydrogen bonding (Duhlev, Brown & Faggiani, 1988a).

The bond lengths within the phenyl ring show an interesting variation: the distances between C atoms

adjacent either to O or C(6) are significantly longer than those in the C(8)—C(9)—C(10)—C(11) sequence. In Table 3 these distances are compared with those found in the Cambridge Structural Database. It follows from this comparison that the distribution of the observed distances within the benzene ring is not exceptional in the present structure. A correlation was found between the distances $D(2)$ and $D(9)$, and between $D(2)$ and $D(4)$ (*GSTAT*; Allen, Kennard & Taylor, 1983): $D(2) = -0.52 (5) \times D(9) + 2.05 (7)$ and $D(2) = -0.51 (5) \times D(4) + 2.04 (7)$ Å. However, no clear correlation between $D(4)$ and $D(9)$ was found.

It should be noted, however, that the longer axes of the displacement ellipsoids of the ring C atoms (*ORTEPII*; Johnson, 1976) are not perpendicular to the phenyl ring as might be expected, but on the contrary, suggest that the whole molecule undergoes a librational movement about an axis nearly coincident with the Zn—Br bond.

A TLS refinement (Petříček, 1988) in which Zn and Br atoms were treated independently and the rest of the molecule as a rigid body, yielded $R = 0.0518$ (on observed reflections only), $wR = 0.0811$ (on all reflections) and $S = 2.73$ for 87 parameters. The R -factor ratio is $0.0811/0.0777 = 1.0438$; $R(94,3354,0.005) = 1.0363$ (*International Tables for X-ray Crystallography*, 1974; Hamilton, 1965). Thus, the model with the independently moving atoms is to be preferred. The corrections of bonding distances for libration did not exceed 0.01 Å and, therefore, the variation of the bond lengths in Table 3 seems not to be attributable to thermal motion.

Each molecule interacts *via* hydrogen bonds with two others. The H atoms involved are those bonded to N(1), while the acceptor atoms are O and Br [*cf.* $[\text{Mg}(\text{H}_2\text{O})_6]_2[\text{CdBr}_6]$ Duhlev, Faggiani & Brown 1987a) and $[\text{Mg}(\text{H}_2\text{O})_6][\text{Zn}_2\text{Br}_6]$ (Duhlev, Faggiani & Brown, 1987b)]. The hydrogen bond to oxygen is extremely weak. The short O...N(1) intramolecular distance (Table 2) is not a hydrogen bond; the O...H(2N1) distance is too long for it to be so.

Experimental

An equivalent amount of the Schiff base solution, which also contained NaOH, was slowly added to 1.12 g (0.5 mmol) of ZnBr_2 dissolved in methanol. When the resulting solution was allowed to stand in air for several hours, tiny yellowish crystals (up to 0.5 mm) appeared. The yield was 1.1 g (60%). The crystals have a pseudohexagonal habit; the specimen chosen for analysis displayed faces 001 00 $\bar{1}$, 2 $\bar{1}0$, $\bar{2}10$, 210 and $\bar{2}\bar{1}0$. The density D_m was measured by flotation in bromoform/tetrachloromethane.

Prior to the diffractometer experiment, a rather large crystal was aligned along *c* and oscillation, Weissenberg (*hk0* and *hk1*) and precession photographs (*0kl h0l*) were obtained. No unusual features were found on the photographs.

ment: *SDS Program Package* (Petříček & Malý, 1988). Molecular graphics: *ORTEPII* (Johnson, 1976); *PICTUR* (Dušek, 1993).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: MU1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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