Pergamon

Polyhedron Vol. 16, No. 23, pp. 3947–3951, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0277–5387/97 $17.00+0.00

PII: S0277–5387(97)00194–0

Synthesis and crystal structure of di [(μ-acetato)(2-acetylpyridine ^{4}N-ethylthiosemicarbazonato)zinc(II)]

Leandro Bresolin,[a] Robert Alan Burrow,[a] Manfredo Hörner,[a] Elena Bermejo[b] and Alfonso Castiñeiras[b]*

[a]Departamento de Química, Universidade Federal de Santa María, Caixa Postal 5001, 97119-900 Santa María-RS, Brazil

[b]Departamento de Química Inorgánica, Universidad de Santiago de Compostela, E-15706 Santiago de Compostela, Spain

(Received 20 March 1997; accepted 13 May 1997)

Abstract—The reaction between zinc(II) acetate and the tridentate ligand 2-acetylpyridine ^{4}N-ethylthio semicarbazone (H4EL) produces a dinuclear complex in which two deprotonated ligands are coordinated to two zinc(II) ions, one penta- and the other hexacoordinate *via* the sulfur thiolato (on deprotonation) atom and the azomethine and pyridine nitrogen atoms. The coordination spheres of the metal atoms being completed by acetate oxygen atoms. One of the acetate ions chelates one zinc atom and bridges between the two *via* a single oxygen, while in the other each oxygen coordinates to a different zinc atom. The results of elemental analysis and IR spectroscopy are included. © 1997 Elsevier Science Ltd

Keywords: zinc(II) complex; 2-acetylpyridine ^{4}N-ethylthiosemicarbazone; X-ray structure.

Thiosemicarbazones have attracted attention on account of both their applications as analytical reagents [1] and their being, in some cases, relatively specific inhibitors of ribonucleotide reductase, which is an important metabolic target for the development of chemotherapeutic agents against cancer [2]. Furthermore, the complexes of thiosemicarbazones with metals possess a wide range of biological activities, including antibacterial, antimalarial, antiviral and antineoplastic effects [3]. Although greatest attention has been attracted by copper(II) derivatives [4], some zinc thiosemicarbazone complexes also have pharmacological activity [5], and it has been suggested that zinc fingers may be a feature of many protein-DNA and protein-RNA interactions.

As part of our on-going study of the synthesis and solid state characterization of thiosemicarbazone–metal complexes, we have prepared a novel pentacoordinate zinc complex derived from zinc(II) acetate by reaction with 2-acetylpyridine ^{4}N-ethylthiosemicarbazone (H4EL). In this paper we describe its synthesis and reports its molecular and crystal structures.

EXPERIMENTAL

Elemental analysis was performed with a Carlo Erba 1108 analyser. The melting point of the new complex was determined with a Büchi apparatus, and its IR spectrum was obtained using KBr pellets on a Bruker IFS28.

4-Ethyl-3-thiosemicarbazide, 2-acetylpyridine and zinc acetate dihyrate were purchased from Aldrich and were used without further purification. 2-Acetylpyridine ^{4}N-ethylthiosemicarbazone (H4EL) was prepared by a published method [6].

Preparation of di(μ-acetato)(2-acetylpyridine ^{4}N*-ethyl thiosemicarbazonato)zinc(II)*

H4EL (67 mg, 0.3 mmol) was dissolved in 25 mL of THF and carefully deprotonated with a small

---

* Author to whom correspondence should be addressed.

amount of metallic sodium powder. This solution was filtered to remove unreacted sodium powder and was then added to a solution of zinc acetate dihydrate (66 mg, 0.3 mmol) in 25 mL of THF. The mixture acquired an intense yellow colour when stirred at room temperature for 1 h. The resulting solution was filtered over dry magnesium sulfate and concentrated to approximately half its volume. Yellow single crystals suitable for X-ray analysis were grown at room temperature by slow diffusion of an acetone/*n*-hexane layer through 5 mL of this concentrate. Yield of crude product: 80%. M.p. 245°C. Anal. found: C, 41.7; H, 4.5; N, 16.2%. $C_{24}H_{32}N_8O_4S_2Zn_2$ requires: C, 41.7; H, 4.7; N, 16.2%.

Crystallographic section

All X-ray data were collected on an Enraf–Nonius CAD-4 diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator at room temperature [7]. The unit cell dimensions were obtained from a least-squares fit to the setting angles of 25 reflections. The data were collected using the ω–2θ scan technique, and were corrected by an empirical method [8] for absorption and for Lorentz and polarization [8] effects. Crystal data and details of data collection are listed in Table 1.

The structure was solved using direct methods [8] and refined on F^2 by full-matrix least-squares techniques with anisotropic displacement factors for all non-hydrogen atoms [8]. The positions of the hydrogen atoms were calculated from the geometry of the molecular skeleton and their thermal displacement parameters were refined isotropically on a groupwise basis. Molecular graphics were obtained using ZORTEP [9].

RESULTS AND DISCUSSION

Molecular structure of $[Zn(C_{10}H_{13}N_4S)(O_2CCH_3)]_2$

Table 2 lists the principal bond lengths and angles of $[Zn(C_{10}H_{13}N_4S)(O_2CCH_3)]_2$, whose molecular structure is illustrated in Fig. 1 together with the atom-numbering scheme used. The asymmetric unit comprises one molecule of the complex, a dimer in which both zinc atoms are pentacoordinate to three thiosemicarbazone atoms and to an oxygen atom of each of the two acetate groups. The two deprotonated thiosemicarbazone molecules coordinate *via* their thiolato sulfur, azomethine nitrogen and pyridine nitrogen atoms [Zn—S = 2.368(5) and 2.410(6) Å, Zn—N_{azo} = 2.09(2) and 2.13(2) Å, Zn—N_{py} = 2.155(14) and 2.21(2) Å]. Unexpectedly, one of the acetate groups bridges between the two metal atoms *syn–syn* fashion [10] through the O(31)—

Table 1. Crystal data and structure refinement for $[Zn(C_{10}H_{13}N_4S)(O_2CCH_3)]_2$

Compound	$[Zn(C_{10}H_{13}N_4S)(O_2CCH_3)]_2$
Empirical formula	$C_{24}H_{32}N_8O_4S_2Zn_2$
Formula weight	691.44
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system/Space group	Monoclinic/P2$_1$
Unit cell dimensions	$a = 8.443(2)$ Å $\alpha = 90.00(-)°$
	$b = 11.159(2)$ Å $\beta = 96.31(3)°$
	$c = 15.775(3)$ Å $\gamma = 90.00(-)°$
Volume	1477.2(5) Å^3
Z	2
Density (calculated)	1.554 Mg/m^3
Absorption coefficient	1.810 mm^{-1}
F(000)	712
Crystal size/Colour	0.40 × 0.20 × 0.15 mm/yellow
Theta range for data collection	2.43–24.98°
Index ranges	$0 \leqslant h \leqslant 10, 0 \leqslant k \leqslant 13, -18 \leqslant l \leqslant 18$
Reflections collected	2922
Independent reflections	2728 [$R_{int} = 0.0590$]
Reflections observed	1920
Criterion for observation	$I > 2\sigma(I)$
Absorption correction	SHELXA
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2726/1/379
Goodness-of-fit on F^2	1.119
Final *R* indices	$R_1 = 0.0585$, $wR_2 = 0.1498$
Absolute structure parameter	0.10(5)
Extinction coefficient	0.008(2)
Largest diff. peak and hole	0.673 and -0.742 e Å^{-3}

Table 2. Selected bond lengths (Å) and angles (°) for $[\mathrm{Zn(C_{10}H_{13}N_4S)(O_2CCH_3)}]_2$

Zn(1)—O(31)	2.042(13)
Zn(1)—N(12)	2.09(2)
Zn(1)—O(41)	2.150(10)
Zn(1)—N(11)	2.155(14)
Zn(1)—S(1)	2.368(5)
Zn(2)—O(32)	1.963(11)
Zn(2)—O(41)	2.027(11)
Zn(2)—N(22)	2.13(2)
Zn(2)—N(21)	2.21(2)
Zn(2)—S(2)	2.410(6)
O(31)—Zn(1)—N(12)	103.7(5)
O(31)—Zn(1)—O(41)	95.5(4)
N(12)—Zn(1)—O(41)	158.3(5)
O(31)—Zn(1)—N(11)	94.4(5)
N(12)—Zn(1)—N(11)	74.7(6)
O(41)—Zn(1)—N(11)	94.1(5)
O(31)—Zn(1)—S(1)	102.9(4)
N(12)—Zn(1)—S(1)	81.6(4)
O(41)—Zn(1)—S(1)	104.0(3)
N(11)—Zn(1)—S(1)	153.4(4)
O(32)—Zn(2)—O(41)	102.5(5)
O(32)—Zn(2)—N(22)	114.6(5)
O(41)—Zn(2)—N(22)	141.3(5)
O(32)—Zn(2)—N(21)	92.0(6)
O(41)—Zn(2)—N(21)	94.3(6)
N(22)—Zn(2)—N(21)	74.7(6)
O(32)—Zn(2)—S(2)	104.2(4)
O(41)—Zn(2)—S(2)	102.6(3)
N(22)—Zn(2)—S(2)	79.2(5)
N(21)—Zn(2)—S(2)	153.3(4)

C(31)—O(32) unit, with Zn(1)—O(31) and Zn(2)—O(32) distances of 2.042(13) and 1.963(11) Å, respectively, while the other bridges unusually *via* a single oxygen [10], O(41), with Zn(1)—O(41) = 2.150(10) Å and Zn(2)—O(41) = 2.027(11) Å. As a result, there are two distinct $\mathrm{ZnN_2O_2S}$ chromophores in the complex. The Zn(2) polyhedron is a trigonal bipyramid (τ [11] = 0.20) in which N(21) and S(2) are axial and O(32), O(41) and N(22) equatorial; while that of Zn(1) is a square pyramid ($\tau = 0.08$) with O(31) at its apex and N(11), N(12), S(1) and O(41) defining its planar (maximum deviation 0.028 Å), which lies 0.339 Å from the zinc atom. Alternatively, if the Zn(1)—O(42) distance of 2.681(14) Å and the associated O—Zn—X angles are considered indicative of weak bonding (the sum of the van der Waals radii is 2.90 Å) [12], then the second acetate group both chelates and bridges, the geometry around Zn(1) is pseudooctahedral and the new complex constitutes a rare example of a dinuclear zinc(II) species in which the two zinc atoms have different coordination numbers and geometries.

Simultaneous chelation and bridging by acetate ions has usually been observed in bimetallic compounds such as calcium copper acetate hexahydrate and its isomorph calcium cadmium acetate hexahydrate [13]. Such behaviour has been deemed not to occur in $[\mathrm{HgPCy_3(OAc)_2}]_2$ and $[\mathrm{HgP}(o\text{-}\mathrm{tol})_3\mathrm{(OAc)_2}]_2$ [14] in spite of the relevant secondary Hg—O distances being, as in the new zinc complex, less than the sum of the corresponding van der Waals radii (3.0 Å for Hg—O). However, its occurrence in $[\mathrm{Zn(C_{10}H_{13}N_4S)(OOCCH_3)}]_2$ is supported not only by the Zn—O(42) distance, but also by the similarity of the C(41)—O(42) and C(41)—O(41) distances [1.20(2) and 1.22(2) Å], which both indicate partial double bond character, and by the significant differences between the Zn(1)—4EL and Zn(2)—4EL bond lengths, which strongly suggest that the two zinc atoms have different coordination numbers.

The two zinc atoms, one acetato carbon and the bridging atoms together form a six-membered planar ring (RMS deviation 0.014 Å) in which the Zn· · ·Zn distance of 3.637(2) Å is large enough to rule out any metal–metal bonding. The ring plane virtually contains both acetate groups, and is approximately perpendicular to the planes of the planar thiosemicarbazone chains, with which it forms dihedral angles of 88.9(5)° and 90.0(5)°; the dihedral angle between the two thioseicarbazone chains is 8.8(8)°.

The Zn—S distances are similar to those found in other complexes of zinc(II) with thiosemicarbazones [15], and the Zn—O distances differ little from those of most zinc(II) carboxylate complexes [16], but the Zn—N distances are shorter than usual because of the deprotonation of the ligand [17]. The geometry of the thiosemicarbazone molecules differs from that of the free ligand [18] chiefly as regards the lengths of the C—S and C—$\mathrm{N_{azo}}$ bonds: coordination of the S to the metal atom lengthens the C—S bonds by about 0.7 Å due to the loss of partial π character, while the C—$\mathrm{N_{hyd}}$ bonds are shortened by about 0.3 Å due to the delocalization of charge along the thiosemicarbazone chain as the result of coordination of $\mathrm{N_{azo}}$ and deprotonation of the hydrazinic nitrogen atom.

IR spectrum

Table 3 lists selected bands of the IR spectra of the complex and the free ligand [19]. The chief changes brought about by coordination are loss of the hydrazinic NH stretching mode due to deprotonation [20], the shifting of $\nu(\mathrm{CN_{azo}})$ and ν(NN) to higher wavenumbers due to coordination of the azomethine nitrogen atom, and the shifts in $\nu(\mathrm{CN_{py}})$ and in the in-plane and out-of-plane ring deformation modes due to the coordination of $\mathrm{N_{py}}$. Two strong, broad bands appearing in the spectrum of the complex at 1575 and 1418 $\mathrm{cm^{-1}}$ are attributed to $\nu_{\mathrm{asym}}(\mathrm{COO^-})$ and $\nu_{\mathrm{sym}}(\mathrm{COO^-})$, respectively, but they are not sufficiently resolved as to allow the two different types of acetate to be distinguished. However, the positions of both the $\nu(\mathrm{COO^-})$ bands are consistent with both the C—O bonds of both groups having partial double bond character, as is the difference of 157 $\mathrm{cm^{-1}}$ between

16. H.-B. Bürgi and J. D. Dunitz (eds) *Typical Interatomic Distances in Organic Compounds and Organometallic Compounds and Coordination Complexes of the d- and f-block metals in*: *Structure Correlation*, VCH, Weinheim (1994).
17. Bino, A. and Cohen, N., *Inorg. Chim. Acta*, 1993, **200,** 11.
18. West, D. X., Bain, G. A., Butcher, R. J., Jasinski, J. P., Li, Yu, Pozdniakin, R. Y., Valdés-Martínez, J., Toscano, R. A. and Hernández-Ortega, S., *Polyhedron*, 1996, **15,** 665.
19. West, D. X., Carlson, C. S., Whyte, A. C. and Liberta, A. E., *Trans. Met. Chem.*, 1990, **15,** 43.
20. Iskander, M. F. and El-Sayed, I., *J. Inorg. Nucl. Chem.*, 1971, **33,** 4253.