Inorganica Chimica Acta, 41 (1980) 151–154
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Crystal and Molecular Structure of [N,N'-ethylenebis(Monothioacetylacetoneiminato)] Zinc(II)

R. CINI, A. CINQUANTINI, P. ORIOLI

Istituto di Chimica Generale, Università di Siena, Siena, Italy

and M. SABAT

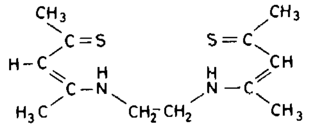
Institute of Chemistry, University of Wrocław, Wrocław, Poland

Received December 18, 1979

The crystal structure of [N,N'-ethylene bis(monothioacetylacetoneiminato)] zinc(II) (Zn(sacacen)) has been determined by X-ray diffraction, and refined to a final R factor of 0.019 over 810 reflections with $I > 2.5\ \sigma(I)$. The compound is monoclinic with the following cell constants: a = *10.988(4),* b = *11.692(2),* c = *12.227(4), Å, β = 116.11(3)°, Z = 4. The structure is formed by discrete molecules in which the zinc atom shows a distorted tetrahedral coordination. The coordination tetrahedron has C_2 crystallographic symmetry. Bond lengths and angles around the zinc atom are: Zn–S = 2.293(1), Zn–N = 2.027(2) Å; N–Zn–S = 96.0(1), S–Zn–S' = 113.6(1), S–Zn–N' = 135.6(1), N–Zn–N' = 83.2(1)°.*

Introduction

N,N'-ethylenebis(monothioacetylacetoneimine)(sacacen) forms with several transition metal ions a series of complexes whose preparation and physicochemical properties have been reported by Cummings *et al.* [1].



Metal complexes with cobalt(II), nickel(II), copper(II), zinc(II), palladium(II) and cadmium(II) have been described. On the basis of molecular weight, magnetic susceptibility and conductivity measurements and pmr, infrared and electronic spectra, all complexes were assigned a square-planar monomeric structure.

It has been also reported that the cobalt(II) complex in the presence of Lewis bases at low temperature binds reversibly with molecular oxygen [2, 3]. A thermodynamic investigation on the oxygenation of Co(sacacen) in nonaqueous solutions has recently appeared [4].

As part of an extensive investigation on the structure of metal complexes which bind molecular oxygen, we have prepared Co(sacacen), Ni(sacacen), Cu(sacacen), Zn(sacacen) and Pd(sacacen). X-ray diagrams of these complexes show the cobalt(II), nickel(II) and palladium(II) compounds to be isomorphous whereas Zn(sacacen) and Cu(sacacen) show different X-ray patterns. It is also evident from the diagrams that Zn(sacacen) and Cu(sacacen) are not isomorphous. These results seem to indicate the existence of different structures in the series of M(sacacen).

An X-ray analysis of [N,N'-tetramethylenebis(monothioacetylacetoneiminato)] zinc(II), which has two additional CH_2 groups in the bridging chain, has shown the zinc atom to have a tetrahedral stereochemistry, although somewhat distorted [5]. However the greater flexibility of this ligand compared with sacacen, does not allow to apply these results to the structure of Zn(sacacen).

We report here the results of a single crystal X-ray analysis on Zn(sacacen).

Experimental

Preparation of the Compounds

Both the ligand and the zinc complex were prepared by the method described in reference [1]. Crystals of Zn(sacacen) suitable for X-ray analysis were obtained from toluene solutions.

Crystal Data

$C_{12}H_{18}N_2S_2Zn$, M = 319.80, monoclinic a = 10.988(4), b = 11.692(2), c = 12.227(4) Å, β = 116.11(3)°, V = 1410.11 Å^3, Z = 4, D_c = 1.507 g cm^{-3}, F(000) = 656. Space group C2/c or Cc from systematic absences. C2/c was initially assumed and confirmed by the successful refinement. Mo-Kα = radiation, λ = 0.7107 Å; μ(MoKα) = 20.17 cm^{-1}.

Intensity Collection

A well-formed monoclinic prism with approximate dimensions 0.22 × 0.22 × 0.47 mm was oriented on a

Philips automatic diffractometer. Accurate cell constants were determined by a least-squares refinement of 25 carefully centered reflections.

Intensity data were collected in the range $4° < 2\theta < 60°$ with the ω–2θ scan technique, at a scan speed of 0.025°/sec and a scan width of 1.00° in ω. Stationary counter, stationary-crystal background counts were taken at each end of the scan range. The intensities of two reflections monitored periodically during data collection did not show any significant variation. 810 reflections with $I > 2.5\ \sigma(I)$ were considered observed and used for the structural determination. Standard deviations on intensities I were calculated according to the expression: $\sigma(I) = [P + 0.25\ (B_1 + B_2)(T_p/T_b)^2 + (0.01\ I)^2]^{1/2}$, where P is the peak count, B_1 and B_2 are the background counts, and T_p and T_b are the count times on the peak and background respectively. Intensities were corrected for Lorentz-polarization effects. Absorption corrections were not applied; a ψ scan on the 0 2 5 reflection showed a maximum deviation of 4% in intensity.

Structure Solution and Refinement

The structure was solved by the heavy-atom technique with the use of Patterson and Fourier syntheses which gave all the nonhydrogen atom positions. Three cycles of least-squares refinement with isotropic temperature factors, followed by two cycles with anisotropic temperature factors for all the atoms reduced the R factor to 0.055. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = 4F_o^2/\sigma^2(F_o^2)$. A difference Fourier synthesis calculated at this point showed clearly all the hydrogen atoms. These atoms were introduced in the calculation without further refinement of their positions, with a temperature factor U of 0.06 Å^2. Three additional least-squares cycles on nonhydrogen atom parameters gave the final disagreement indices R and R_w of 0.0195 and 0.0218 respectively. R_w is defined as $[\Sigma_w(|F_o| - |F_c|)^2/\Sigma w\ F_o^2]^{1/2}$.

All the calculations were performed with the set of programs SHELX-76 [6] which use the coefficients for analytical approximation to the scattering factors and anomalous dispersion corrections both taken from Int. Tables [7]. The molecular plot was produced by ORTEP [8]. Table I reports the list of the final atomic coordinates and thermal parameters with estimated standard deviations obtained from the least-squares calculations. A list of observed and calculated structure factors is available from the editor.

Description of the Structure

The structure of [N,N′-ethylenebis(monothioacetylacetoneiminato)]zinc(II) consists of discrete molecules, in which the zinc atom shows a distorted tetrahedral stereochemistry. The molecules possess C_2 crystallographic symmetry, the twofold axis passing through the zinc atom. Table II reports bond lengths and angles in the molecule with estimated standard deviations.

The distortion from tetrahedral stereochemistry around the zinc atom in our compound is somewhat larger than in [N,N′-tetramethylenebis(thioacetyl-

TABLE I. Positional Parameters (× 10^4), Thermal Parameters[a] (Å^2 × 10^4), and Estimated Standard Deviations.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	0	1960(0)	2500	474(4)	289(3)	242(3)	0	120(3)	0
S	541(1)	3034(1)	1206(1)	524(5)	431(5)	293(4)	−155(4)	80(3)	26(3)
N	−887(2)	664(2)	1313(2)	463(14)	309(12)	304(13)	−60(11)	165(11)	−42(10)
C(1)	−817(3)	3481(3)	−1205(3)	538(19)	572(21)	360(18)	−32(17)	131(15)	124(15)
C(2)	−701(3)	2644(3)	−218(2)	335(16)	393(15)	280(15)	66(12)	132(12)	28(12)
C(3)	−1517(3)	1716(2)	−543(2)	310(15)	425(17)	244(13)	20(12)	87(11)	−21(11)
C(4)	−1536(3)	716(2)	130(2)	299(14)	386(16)	311(14)	−38(12)	127(11)	−77(12)
C(5)	−2318(3)	−287(3)	−606(3)	567(20)	495(19)	461(18)	−188(16)	187(15)	−162(16)
C(6)	−701(3)	−413(3)	1975(3)	604(20)	313(15)	414(17)	−87(14)	229(15)	−25(13)

Atom[b]	x/a	y/b	z/c	Atom[b]	x/a	y/b	z/c
H(11)	−1582	3235	−1970	H(52)	−2764	−752	−329
H(12)	−956	4273	−988	H(53)	−2986	−6	−1353
H(13)	−56	3478	−1352	H(61)	−1514	−450	2225
H(3)	−2193	1728	−1438	H(62)	−819	−1071	1404
H(51)	−1883	−786	−801				

[a] Anisotropic thermal factors are of the form $\exp[-2\pi^2({}^3\Sigma_{i=1}\ {}^3\Sigma_{j=1}\ h_i h_j a_i^* a_j^* U_{ij})]$. [b] Isotropic thermal factor for hydrogen atoms is U = 0.06 Å^2. Hydrogen atoms are labelled according to the carbon atom to which they are attached.

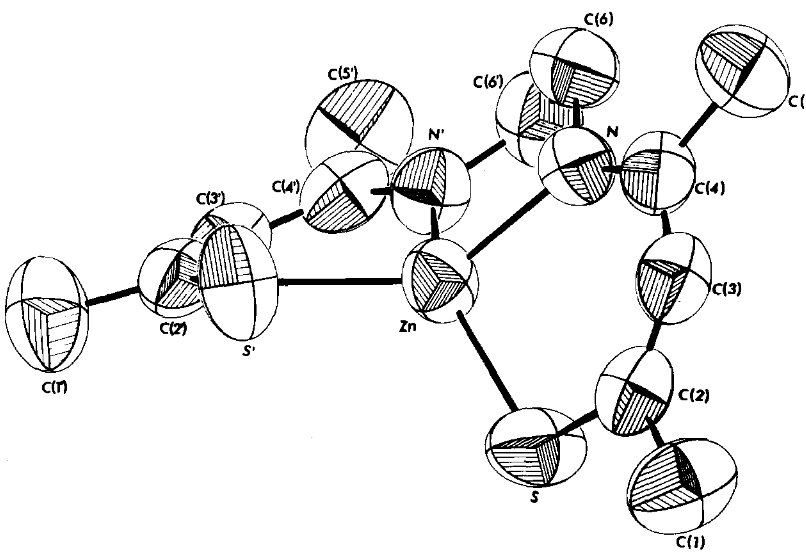


Fig. 1. ORTEP drawing of the molecule, showing the atom labeling. Hydrogen atoms have been omitted (ellipsoids are drawn to 20% probability).

TABLE II. Bond lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses.

a) *Distances*			
Zn–S	2.293(1)	S–C(2)	1.735(3)
Zn–N	2.027(2)	N–C(4)	1.303(3)
		N–C(6)	1.462(4)
C(1)–C(2)	1.516(4)	C(4)–C(5)	1.501(4)
C(2)–C(3)	1.350(4)	C(6)–C(6′)	1.509(6)
C(3)–C(4)	1.435(4)		
b) *Angles*			
N–Zn–S	96.0(1)	C(1)–C(2)–C(3)	118.2(3)
S–Zn–S′	113.6(1)	C(2)–C(3)–C(4)	131.4(3)
S–Zn–N′	135.6(1)	C(3)–C(4)–C(5)	116.3(3)
N–Zn–N′	83.2(1)	C(3)–C(4)–N	122.4(3)
		N–C(4)–C(5)	121.3(3)
		C(4)–N–C(6)	122.0(2)
Zn–S–C(2)	102.8(1)	N–C(6)–C(6′)	108.2(2)
Zn–N–C(4)	128.0(2)		
Zn–N–C(6)	109.9(2)		
S–C(2)–C(1)	112.6(2)		
S–C(2)–C(3)	129.3(2)		

acetoniminato)]zinc(II) which has two additional CH_2 groups in the bridging chain [5]. The angles between the coordination planes defined by the atoms S, Zn, N and S′, Zn, N′ are respectively 55.7° and 84.6°.

The Zn–S and Zn–N distances, as well as bond lengths and angles in the ligand molecule are in agreement with values from similar structures [5].

Table III shows the equations of some interesting least-squares planes and the deviations of the atoms from these planes. It can be seen that the chelate ring is not planar, the largest deviation being –0.617 Å for the zinc atom. The distortion appears very similar in magnitude and direction to what found in [N,N′-tetramethylenebis(thioacetylacetoneiminato)]zinc(II) and therefore it cannot be attributed to the steric constraints of the ethylenediamine bridge [5]. On the other hand the structural determinations of several acetylacetoneiminato metal complexes have shown the chelate ring to be strictly planar in these compounds [9, 10]. It appears therefore that the distortion of the chelate ring is caused by the replacement of the oxygen atom with the sulphur atom, the Zn–S and C–S bond lengths being so much larger than the Zn–O and C–O distances.

An alternative explanation would attribute the distortions to strains caused by the tetrahedral stereochemistry around the zinc atom.

Acknowledgments

We wish to thank the Istituto di Chimica Organica dell'Universitá di Padova for the use of their diffractometer and the CNR for financial support. We are grateful to M. Porcú for technical assistance.

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TABLE III. Equations of Some Significant Least-squares Planes, Deviations of Atoms and Dihedral Angles.

a) Coefficients of the plane equation in the form $Ax + By + Cz = D$, with x, y, z monoclinic fractional coordinates.

Plane	Atoms	A	B	C	D
I	S, C(1), C(2), C(3), C(4), C(5), N	9.7439	−5.2327	−5.9994	−1.9083
II	S, C(1), C(2), C(3)	9.2270	−6.0445	−6.3179	−2.0991
III	N, C(3), C(4), C(5)	10.3181	−3.9364	−5.7407	−1.9333
IV	S, N, Zn	9.0022	−5.4587	−0.7671	−1.2616
V	S′, N′, Zn	9.0022	5.4587	−0.7671	0.8781

b) Atom deviations (Å)

I	S 0.124, C(1) 0.014, C(2) −0.027 C(3) −0.142, C(4) −0.041, C(5) 0.163 N −0.091, C(6) 0.256, Zn −0.617
II	S 0.002, C(1) 0.002, C(2) −0.008 C(3) 0.003, Zn −0.665
III	N 0.003, C(3) 0.003, C(4) −0.008 C(5) 0.002, Zn −0.273

c) Dihedral angles (deg)

I–II 5.6;	I–III 7.6;	II–III 13.2;	IV–V 55.7

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