COORDINATION COMPLEXES OF BIS(2,2-DIMETHYL-3,5-HEXANE-DIONATO)ZINC WITH ORGANOZINC-OXYGEN AND -NITROGEN COMPOUNDS. CRYSTAL STRUCTURE OF THE COMPLEX FORMED WITH PHENYLZINC PHENOXIDE

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Summary

In benzene solution organozinc-oxygen compounds of the type $(RZnOR')_4$ and bis(2,2-dimethyl-3,5-hexanedionato)zinc $(Zn(pac)_2)$ form complexes of the composition $RZnOR' \cdot Zn(pac)_2$ (R = Et, Ph; R' = Me, Ph), which in boiling benzene exist as dissociating dimers. Interaction of $(EtZnNPh_2)_2$ with $Zn(pac)_2$ affords a crystalline complex $Zn(NPh_2)_2 \cdot Zn(pac)_2$, which is fully dissociated in boiling benzene. The crystal and molecular structure of $[PhZnOPh \cdot Zn(pac)_2]_2$ has been determined. The material crystallizes in the monoclinic space group $P2_1/c$, with two dimeric units in a unit cell with dimensions $a = 12.90(1)$, $b = 11.92(1)$, $c = 23.21(1)$ Å and $\beta = 125.10(5)°$. The structure was solved by direct and Fourier methods and refined by block diagonal least squares to a final R value of 12.9%. The structure contains an eight-membered Zn_4O_4 ring formed by alternating zinc and oxygen atoms. This ring is bridged twice by the oxygen atoms of the two PhZnOPh moieties. The dimeric structure contains four- and six-coordinate zinc atoms and two-, three-, and four-coordinate oxygen atoms.

Introduction

An X-ray study has revealed that solid bis(2,4-pentanedionato)zinc, $Zn(acac)_2$, is associated to trimers via Zn—O coordinate bonds [1] These bonds

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are not very strong as is apparent from the observation that Zn(acac)$_2$ is monomeric in boiling benzene [2] and that mononuclear complexes with well-defined stoechiometry are formed with appropriate ligands such as pyridine [3], 2,2-bipyridyl [2] and TMED [2]. We have previously described novel trinuclear phenylzinc β-diketonate complexes in which a bis(β-diketonato)zinc molecule is coordinated to two phenylzinc β-diketonate molecules [4]. The proposed structure, containing one central six-coordinate and two four-coordinate zinc atoms, has been confirmed by a single crystal X-ray study [5].

Organozinc compounds RZnX are generally associated via intermolecular zinc-heteroatom bonding both in the solid and in solution. The known coordination behaviour of zinc bis(β-diketonates) and of monoorganozinc compounds RZnX [6,7] has led us to investigate the possibility of complex formation between these two types of compounds. The results of this study are presented in this paper which includes the results of a single crystal X-ray study of one of the complexes isolated.

Results

Formation of complexes

Microwave titration [8] of the organozinc-oxygen compounds [EtZnOPh]$_4$ [9], [PhZnOPh]$_4$ [6] and [EtZnOMe]$_4$ [10] with bis(2,2-dimethyl-3,5-hexanedionato)zinc, Zn(pac)$_2$, in benzene solution revealed the formation of complexes of the type RZnOR' Zn(pac)$_2$ When Zn(pac)$_2$ was brought into reaction with these organozinc-oxygen compounds on a preparative scale, in every case the corresponding 1/1 complex RZnOR' Zn(pac)$_2$ was isolated in good yield. Molecular weight determinations in boiling benzene showed all three complexes to be dissociating dimers [RZnOR' Zn(pac)$_2$]$_2$. Only one set of absorptions attributable to 2,2-dimethyl-3,5-hexanedionate groups appeared in the PMR spectra of the pyridine-d_5 solution at ambient temperature. In the IR spectra only absorptions belonging to chelating β-diketonate ligands were present.

The reaction of [EtZnNPh$_2$]$_2$ [11] with Zn(pac)$_2$ failed to yield EtZnNPh$_2$ Zn(pac)$_2$, Zn(NPh$_2$)$_2$·Zn(pac)$_2$ being isolated instead. An identical product was isolated from the 1/1 reaction of Zn(NPh$_2$)$_2$ with Zn(pac)$_2$. A molecular weight determination of this complex indicated virtually complete dissociation in boiling benzene.

Molecular structure of [PhZnOPh Zn(pac)$_2$]$_2$

In order to obtain more detailed information about the molecular structure of this type of complex, a single crystal X-ray study of [PhZnOPh Zn(pac)$_2$]$_2$ has been carried out. Two dimer molecules are present in the unit cell. Fig. 1 shows the schematic structure, and Fig. 2 a stereopair drawing Bond distances and bond angles are given in Tables 1 and 2 respectively. The structure contains an eight-membered Zn$_4$O$_4$ ring, formed by Zn(1), O(3), Zn(2'), O(5'), Zn(1'), O(3'), Zn(2) and O(5) The zinc—oxygen bond lengths in this ring vary between 2.03 and 2.08 Å, a normal value for Zn—O coordinate bonds if compared with those reported in the literature, i e. 2.09 Å in [MeZnOMe]$_4$ [12], 2 038 to 2.170 Å in Zn$_7$O$_8$(CH$_3$)$_{14}$ [13], 1.962 Å in Zn(dpm)$_2$ [14] and 2.02 Å in Zn(acac)$_2$ H$_2$O [15]. The ring is bridged twice by the four-coordinate oxygen atoms O(7)
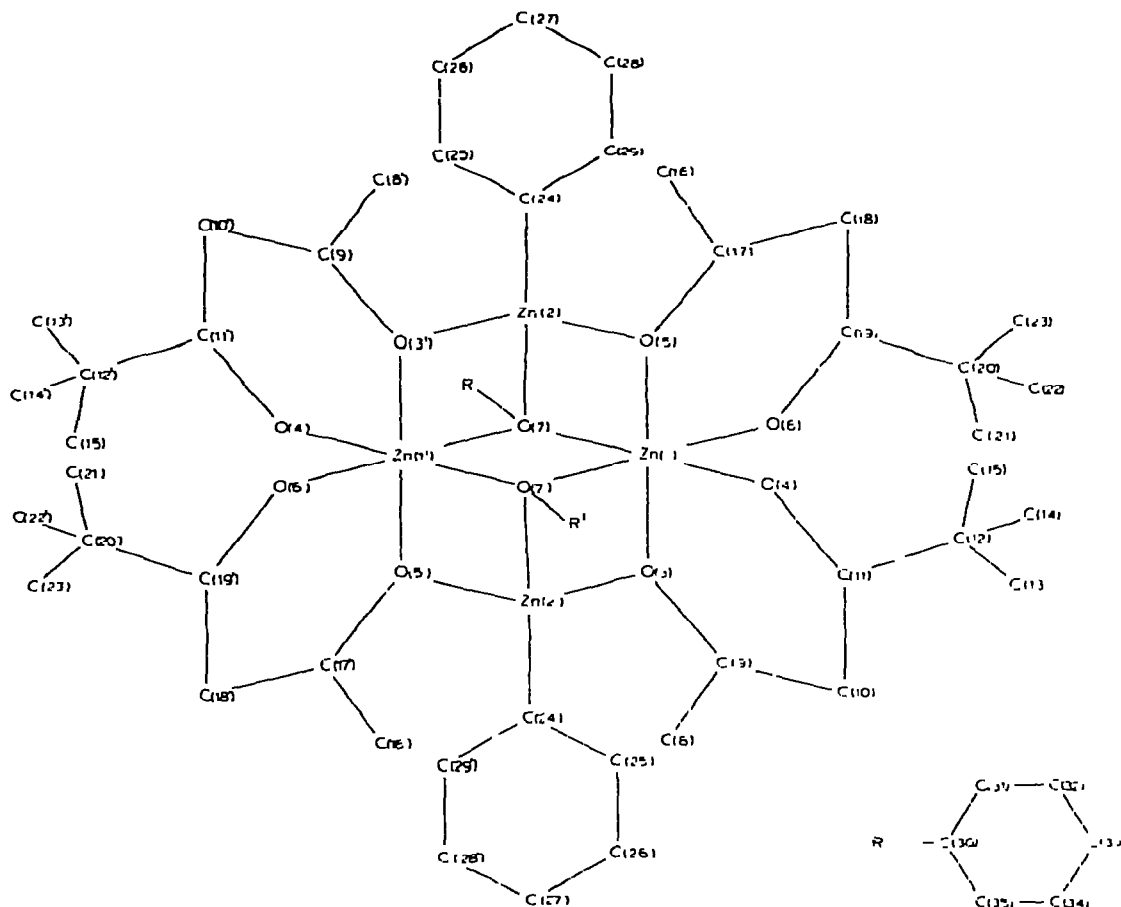
Fig 1 Schematic structure of the [PhZnOPh Zn(pac)₂]₂ complex

and O(7') of the two PhZnOPh moieties via relatively long zinc-oxygen coordinate bonds (2.17 and 2.19 Å). The Zn—O bond lengths in the β-diketonate rings appear to be independent of the coordination number of the oxygens. For instance the Zn(1)—O(6) bond is nearly equal to the Zn(1)—O(5) bond although
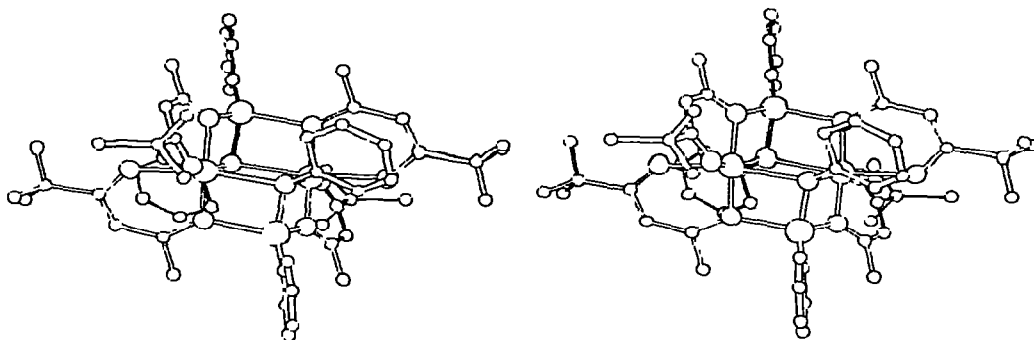

Fig 2 Stereopair drawing of the [PhZnOPh Zn(pac)₂]₂ complex

TABLE 1

BOND DISTANCES (Å) WITH STANDARD DEVIATIONS

Zn(1)—O(3)	2 08(1)	C(12)—C(15)	1 50(5)
Zn(1)—O(4)	2 04(2)	C(16)—C(17)	1 53(3)
Zn(1)—O(5)	2 03(1)	C(17)—C(18)	1 35(3)
Zn(1)—O(6)	2 03(1)	C(18)—C(19)	1 38(3)
Zn(1)—O(7)	2.20(1)	C(19)—C(20)	1 51(3)
Zn(1)—O(7')	2 17(2)	C(20)—C(21)	1 56(4)
Zn(2)—O(5)	2 04(1)	C(20)—C(22)	1 52(6)
Zn(2)—O(7)	2 04(1)	C(20)—C(23)	1 49(4)
Zn(2)—C(24)	1 97(2)	C(24)—C(25)	1 41(3)
Zn(2)—O(3')	2 05(2)	C(24)—C(29)	1 40(3)
O(3)—C(9)	1 31(3)	C(25)—C(26)	1 43(4)
O(4)—C(11)	1 29(3)	C(26)—C(27)	1 44(4)
O(5)—C(17)	1 34(2)	C(27)—C(28)	1 41(4)
O(6)—C(19)	1 30(2)	C(28)—C(29)	1 46(4)
O(7)—C(30)	1 37(2)	C(30)—C(31)	1 38(3)
C(8)—C(9)	1 52(3)	C(30)—C(35)	1 42(3)
C(9)—C(10)	1 34(4)	C(31)—C(32)	1 43(3)
C(10)—C(11)	1 43(3)	C(32)—C(33)	1 38(3)
C(11)—C(12)	1 52(4)	C(33)—C(34)	1 39(3)
C(12)—C(13)	1 53(4)	C(34)—C(35)	1 47(9)
C(12)—C(14)	1 59(5)		

TABLE 2

BOND ANGLES (°) WITH STANDARD DEVIATIONS

O(3)—Zn(1)—O(4)	87 3(6)	O(4)—C(11)—C(12)	113 6(18)
O(3)—Zn(1)—O(5)	170 1(2)	O(5)—C(17)—C(16)	113 7(17)
O(3)—Zn(1)—O(6)	91 5(5)	O(5)—C(17)—C(18)	126 2(17)
O(3)—Zn(1)—O(7)	101 6(5)	O(6)—C(19)—C(18)	123 7(18)
O(3)—Zn(1)—O(7')	78 7(5)	O(6)—C(19)—C(20)	115 1(16)
Zn(1)—O(3)—C(9)	120 7(13)	C(30)—O(7)—Zn(1')	116 8(12)
Zn(1)—O(3)—Zn(2')	100 6(6)	O(7)—C(30)—C(31)	120 2(18)
O(4)—Zn(1)—O(5)	102 5(6)	O(7)—C(30)—C(35)	118 3(16)
O(4)—Zn(1)—O(6)	93 5(6)	C(8)—C(9)—C(10)	117 5(21)
O(4)—Zn(1)—O(7)	89 4(6)	C(9)—C(10)—C(11)	123 6(20)
O(4)—Zn(1)—O(7')	163 1(2)	C(10)—C(11)—C(12)	120 9(20)
Zn(1)—O(4)—C(11)	125 5(12)	C(11)—C(12)—C(13)	112 1(25)
O(5)—Zn(1)—O(6)	88 5(5)	C(11)—C(12)—C(14)	106 9(28)
O(5)—Zn(1)—O(7)	77 5(5)	C(11)—C(12)—C(15)	107 9(24)
O(5)—Zn(1)—O(7')	91 5(6)	C(13)—C(12)—C(14)	98 1(22)
Zn(1)—O(5)—Zn(2)	102 8(6)	C(13)—C(12)—C(15)	115 7(30)
Zn(1)—O(5)—C(17)	135 4(11)	C(14)—C(12)—C(15)	115 7(32)
O(6)—Zn(1)—O(7)	166 8(2)	C(16)—C(17)—C(18)	120 0(17)
O(6)—Zn(1)—O(7')	96 5(5)	C(17)—C(18)—C(19)	127 2(18)
Zn(1)—O(6)—C(19)	128 1(11)	C(18)—C(19)—C(20)	121 1(17)
O(7)—Zn(1)—O(7')	84 3(5)	C(19)—C(20)—C(21)	113 5(20)
Zn(1)—O(7)—Zn(2)	97 2(5)	C(19)—C(20)—C(22)	108 5(22)
Zn(1)—O(7)—C(30)	125 8(11)	C(19)—C(20)—C(23)	111 9(25)
Zn(1)—O(7)—Zn(1')	95 7(5)	C(21)—C(20)—C(22)	108 5(32)
Zn(1)—O(7')—Zn(2')	97 7(6)	C(21)—C(20)—C(23)	103 8(24)
O(5)—Zn(2)—O(7)	81 5(5)	C(22)—C(20)—C(23)	110 7(29)
O(5)—Zn(2)—C(24)	119 3(7)	C(25)—C(24)—C(29)	120 8(19)
O(5)—Zn(2)—O(3')	94 9(6)	C(24)—C(25)—C(26)	124 0(22)
Zn(2)—O(5)—C(17)	131 4(9)	C(24)—C(29)—C(28)	117 8(21)
O(7)—Zn(2)—C(24)	131 0(5)	C(25)—C(26)—C(27)	114 1(23)
O(7)—Zn(2)—O(3')	82 5(5)	C(26)—C(27)—C(28)	123 7(25)
Zn(2)—O(7)—C(30)	117 9(10)	C(27)—C(28)—C(29)	119 6(26)
C(24)—Zn(2)—O(3')	132 6(6)	C(31)—C(30)—C(35)	121 4(17)
Zn(2)—C(24)—C(25)	121 6(16)	C(30)—C(31)—C(32)	121 7(21)
Zn(2)—C(24)—C(29)	117 5(14)	C(30)—C(35)—C(34)	115 0(17)
C(9)—O(3)—Zn(2')	135 5(10)	C(31)—C(32)—C(33)	118 4(20)
O(3)—C(9)—C(8)	114 4(23)	C(32)—C(33)—C(34)	120 3(20)
O(3)—C(9)—C(10)	128 1(16)	C(33)—C(34)—C(35)	122 4(21)
O(4)—C(11)—C(10)	125.4(20)		

O(5) is three-coordinate and O(6) two-coordinate. The lengths of the Zn—O bonds in the eight-membered ring do not differ significantly from those outside the ring

The β-diketonate groups are planar within experimental accuracy but both zinc atoms Zn(1) and Zn(1') are outside these planes. The angle between the plane through Zn(1), O(3), O(4) and the least squares plane determined by O(3), O(4), C(8), C(9), C(10), C(11), C(12) amounts to 23 3° The angle between the planes determined by Zn(1), O(5), O(6) and O(5), O(6), C(16), C(17), C(18), C(19), C(20), respectively, is 3.3°. A similar situation was observed for Zn(acac)₂ H₂O [15] and Zn(benzac)₂ EtOH [16]

Discussion

The formation of coordination complexes between Zn(pac)₂ and the three RZnOR' compounds shows that the β-diketonate oxygens are very powerful electron donors. This is undoubtedly caused by the presence of a neighbouring zinc atom which enhances the electron-density at the oxygens Moreover, in solution monomeric Zn(pac)₂ contains a coordinatively unsaturated zinc atom. In this way, a synergic donor-acceptor behaviour can be expected. The importance of this synergism is revealed by the observation that, although EtZnOMe is generally unreactive towards oxygen-containing ligands [10], it does form a complex with Zn(pac)₂

In solution, the complexes between Zn(pac)₂ and RZnOR' are rather loosely bound since the molecular weight determinations show dissociation. The PMR spectra show only one kind of β-diketonate ligand Similar behaviour in solution is displayed by the trinuclear phenylzinc β-diketonate complexes [4]

The large electron-donating capacity of Zn(pac)₂ is borne out by the crystal structure of [PhZnOPh Zn(pac)₂]₂ in which the zinc—oxygen bond lengths in the Zn(pac)₂ moieties are independent of the coordination number of the oxygen atoms. The high coordination number (four) and the weaker electron-donating power of the phenoxy-group oxygen atoms are in agreement with the relatively great length of their coordinate bonds Electronic influences of the t-butyl and methyl groups of the pac ligands are less important than steric factors, since the oxygens adjacent to the methyl groups, i e. O(5), O(3), O(5') and O(3') form two Zn—O bonds whereas those adjacent to the t-butyl groups form only one. In view of the larger inductive effect of t-butyl groups the opposite would have been expected on electronic grounds. but there may be steric interaction with the phenyl groups bound to zinc

The disproportionation reaction which takes place when Zn(pac)₂ is treated with EtZnNPh₂ may be connected with the fact that the nitrogen atom has only one electron pair available for coordination, which precludes the formation of a complex similar to [RZnOR' Zn(pac)₂]₂. A similar disproportionation was observed by Coates and Ridley [10] in the reaction of MeZnNPh₂ with pyridine.

Experimental

General methods

All manipulations were carried out under nitrogen with rigorous exclusion

of air and moisture. The organozinc-oxygen and -nitrogen compounds were prepared by published procedures [9,11]. Molecular weights were determined by ebulliometry in benzene. Microwave titrations were carried out in benzene solution, using the apparatus described by Adema and Schrama [8]. NMR spectra were run on Varian HA 100 and T 60 spectrometers using benzene as solvent and TMS as internal reference.

Preparation of bis(2,2-dimethyl-3,5-pentanedionato)zinc, Zn(pac)$_2$

3.7 g (10.6 mmole) of pivaloylacetone was added with stirring to a solution of 1.6 g (13 0 mmole) of diethylzinc in 15 ml of hexane. After 30 min stirring the clear solution was stored overnight at 0° and the colourless precipitate was filtered off After washing with cold (0°) hexane, the product was dried in vacuo Yield 4 1 g, m.p. 153°. (Found. Zn, 18.94. C$_{10}$H$_{26}$O$_3$Zn calcd.· Zn, 18 80%) Mol wt. found: 351 at 2 72 wt %, no concentration dependence, calcd.: 347 8.

Complex of Zn(pac)$_2$ with ethylzinc phenoxide A solution of 0.457 g (1.31 mmole) of Zn(pac)$_2$ was added with stirring to a suspension of 0.246 g (1.31 mmole) of ethylzinc phenoxide in 10 ml of benzene. The suspension cleared during the addition. After removal of the solvent in vacuo, the residue was recrystallized from hexane, washed with hexane and dried in vacuo. Yield 0.5 g, m.p. 154°.(Found: Zn, 24.43. C$_{24}$H$_{36}$O$_5$Zn$_2$ calcd.: Zn, 24.42%.) Mol. wt found. 584 and 663 at 0.60 and 1.26 wt. %, respectively, calcd.: 535.5 for monomeric complex

Complex of Zn(pac)$_2$ with phenylzinc phenoxide This complex was obtained similarly. M.p. 141°. (Found. Zn, 21.18. C$_{28}$H$_{36}$O$_5$Zn$_2$ calcd.: Zn, 21.01%.) Mol. wt. found. 665 and 736 at 0.53 and 1 28 wt. %, respectively, calcd.. 583 5 for monomeric complex.

Complex of Zn(pac)$_2$ with ethylzinc methoxide This complex was prepared similarly. M p. 142°. (Found: Zn, 28 12. C$_{19}$H$_{34}$O$_5$Zn calcd.: Zn, 27 63%.) Mol. wt. found: 531 and 607 at 0 34 and 0.82 wt % , respectively. calcd.· 473 2 for monomeric complex.

Complex of Zn(pac)$_2$ with zinc diphenylamide To a solution of 0.7 g (2 86 mmole) of ethylzinc diphenylamide in 10 ml of benzene, a solution of 0.99 g (2 85 mmole) of Zn(pac)$_2$ was added with stirring. A clear, yellow solution resulted. After 30 min additional stirring the solvent was evaporated in vacuo, leaving a yellow foamy mass. This was crystallized from a 10/1 5 mixture of hexane and benzene, washed with hexane and dried in vacuo Yield 0.8 g; m p. 140°. (Found N, 3.48, Zn, 17 28. C$_{40}$H$_{46}$N$_2$O$_4$Zn$_2$ calcd N, 3.47; Zn, 17 44%.) Mol. wt. found 505 at 1.03 wt. %, no concentration dependence, calcd. 500 0 for complete dissociation into Zn(pac)$_2$ and [Zn(NPh$_2$)$_2$]$_2$

Crystal and molecular structure of the [PhZnOPh Zn(pac)$_2$]$_2$ complex

A crystal with approximate dimensions 0.33 × 0 12 × 0 09 mm was mounted inside a Lindemann capillary. Unit cell parameters were determined by single crystal diffractometry using Cu-K_{α_1} (1.54051 Å) radiation. The crystal was built up from two parts with nearly the same orientation As a consequence, in an ω-scan, the reflections were split up with a maximum of 0.5 degree. Intensity data of 2594 reflections up to $2\theta = 100°$ were collected with a Nonius three circle diffractometer, using nickel filtered Cu-K_α (1.5418 Å) radiation. The intensities of

TABLE 1

POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS[a]

	x	y	z	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$2\times10^3\beta_{12}$	$2\times10^4\beta_{23}$	$2\times10^3\beta_{13}$
Zn(1)	0.5591(2)	−0.0111(2)	0.0830(1)	69(1)	38(2)	22(1)	0(1)	1(2)	39(2)
Zn(2)	0.4018(2)	0.4012(2)	−0.0021(1)	75(1)	39(2)	22(1)	20(1)	5(2)	11(3)
O(3)	0.5551(12)	−0.188(9)	0.0710(6)	131(16)	19(10)	46(1)	−18(20)	−12(10)	65(11)
O(4)	0.1693(12)	−0.0316(10)	0.1311(9)	118(15)	83(12)	38(6)	55(21)	17(12)	98(16)
O(5)	0.5761(12)	0.1567(9)	0.0819(6)	111(15)	35(10)	29(1)	30(19)	11(10)	32(11)
O(6)	0.7315(11)	−0.0171(11)	0.1761(6)	85(14)	92(13)	27(1)	20(21)	31(12)	26(13)
O(7)	0.1781(10)	0.0318(9)	−0.0146(6)	91(13)	17(9)	30(1)	11(17)	19(9)	56(13)
C(8)	0.6127(25)	−0.1671(17)	0.1271(12)	232(49)	59(19)	18(10)	54(32)	28(21)	151(35)
C(9)	0.560(21)	−0.2500(11)	0.1216(11)	199(32)	45(15)	16(8)	−8(33)	23(17)	150(29)
C(10)	0.5218(17)	−0.2263(15)	0.1628(10)	101(22)	76(17)	33(8)	15(30)	−24(17)	75(21)
C(11)	0.1701(18)	−0.120(18)	0.162(9)	111(24)	111(23)	18(6)	−53(37)	−14(19)	70(22)
C(12)	0.1189(21)	−0.1021(20)	0.2086(13)	191(35)	186(26)	67(11)	74(19)	52(26)	167(35)
C(13)	0.3442(26)	0.0025(29)	0.1832(16)	177(18)	271(17)	71(11)	215(70)	103(11)	165(41)
C(14)	0.311(17)	−0.1910(28)	0.1826(21)	111(70)	162(36)	143(29)	−1.16(80)	−39(52)	512(85)
C(15)	0.5278(17)	−0.1065(53)	0.2827(17)	232(65)	733(127)	16(17)	184(118)	−11(64)	99(17)
C(16)	0.6666(21)	0.3117(16)	0.1132(11)	119(29)	11(17)	78(12)	1(34)	9(22)	116(33)
C(17)	0.6758(17)	0.2168(16)	0.1312(9)	90(21)	100(20)	26(7)	6(32)	−21(17)	61(20)
C(18)	0.7815(20)	0.1761(16)	0.1906(11)	127(26)	65(17)	27(8)	16(33)	23(18)	60(25)
C(19)	0.8058(16)	0.063(19)	0.2133(10)	51(18)	96(19)	31(7)	10(29)	8(18)	−60(19)
C(20)	0.9247(18)	0.017(19)	0.2816(10)	90(22)	121(21)	25(7)	28(37)	15(20)	−15(20)
C(21)	0.9525(30)	−0.0094(21)	0.2921(21)	229(46)	107(27)	106(20)	9(57)	9(38)	−17(19)
C(22)	0.9107(37)	0.0728(50)	0.1114(17)	271(59)	651(110)	11(11)	515(138)	194(65)	115(60)
C(23)	1.0103(28)	0.0850(37)	0.2989(23)	111(35)	336(65)	127(25)	−130(78)	210(66)	33(18)
C(24)	0.307(17)	0.3195(15)	0.0101(9)	96(21)	62(16)	2(6)	50(29)	4(15)	36(19)
C(25)	0.3235(19)	0.4150(16)	0.0039(11)	116(21)	71(18)	11(8)	−523(31)	−30(19)	84(21)
C(26)	0.265(23)	0.5225(23)	0.0180(12)	110(30)	177(12)	16(9)	17(49)	−19(27)	104(30)
C(27)	0.182(21)	0.1831(22)	0.0365(13)	211(38)	131(28)	15(10)	120(52)	−13(26)	103(34)
C(28)	0.162(21)	0.3687(21)	0.0125(11)	132(31)	192(33)	52(11)	66(51)	−13(30)	106(32)
C(29)	0.226(19)	0.2832(20)	0.0288(11)	104(21)	143(25)	10(8)	81(40)	23(22)	86(25)
C(30)	0.2619(17)	−0.0082(17)	−0.0177(9)	79(21)	104(20)	28(7)	−78(32)	−29(18)	51(20)
C(31)	0.1539(17)	0.0639(20)	−0.0817(11)	63(20)	137(21)	11(9)	80(36)	32(23)	51(23)
C(32)	0.317(22)	0.0149(19)	−0.1029(15)	107(27)	77(23)	90(11)	59(38)	28(27)	81(33)
C(33)	0.0205(20)	−0.0016(19)	−0.0876(13)	111(25)	90(21)	67(12)	30(37)	−1(25)	96(30)
C(34)	0.1278(23)	−0.1593(20)	−0.0112(13)	119(31)	109(21)	51(10)	−58(12)	−12(23)	75(30)
C(35)	0.2566(19)	−0.1203(16)	−0.0189(10)	107(21)	81(19)	3(7)	−51(33)	15(18)	10(23)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{13}hl)]$

2310 reflections were above background and treated as observed. The scan angle (1.9°) was selected in such a way that the diffracted intensity of both parts of the crystal was collected Lorentz, and polarization, but no absorption corrections were applied to the data (μ(Cu-K_α) = 23 6 cm^{-1}). The crystal decomposed during the data collection The decay in the intensities of two reference reflections (measured every 50 reflections), was plotted against time This plot was used to rescale the intensities by interpolation The maximum rescaling factor amounts to 1.5.

Crystal data Crystals of [PhZnOPh Zn(pac)$_2$]$_2$ (mol. wt. 1166.0) are monoclinic with a = 12.90(1), b = 11.92(1), c = 23.21(1) Å and β = 125.10(5)°. The volume of the unit cell is 2919 Å^3. The space group is uniquely determined from the extinctions, $0k0$ k = $2n$ + 1, $h0l\cdot l$ = $2n$ + 1, as $P2_1/c$. The calculated density of the crystal is 1 32 g/cm^3 The unit cell contains two dimers (Z = 2).

Structure determination and refinement The crystal structure was solved by direct and Fourier methods. The signs of 373 reflections with E values above 1.42 were determined with the program AUDICE [17] After the structure had been solved, only one sign proved to be incorrect. This solution was the one with the highest figure of merit ($\equiv \Sigma_{H,h}$ sign (E_H) × sign (E_h) × sign (E_{H-h})| $E_H E_h E_{H-h}$|) out of 64 solutions given by the program A Fourier synthesis calculated with these 373 reflections showed the heavy atom positions and the oxygen coordination clearly and in addition part of the rest of the molecule. All atoms were found in a Fourier synthesis calculated from the 12 atomic positions already found The structure was refined by block diagonal least squares to a final R value of 12.9%. The temperature parameters were refined anisotropically. The scattering factors used were those of Cromer et al. [18]. Unit weights were used for all observed reflections Only one reflection was left out, because it apparently suffered from extinction. A final difference map showed no peaks higher than 0.7 e Å^{-3}. The constants applied for the correction for anomalous dispersion of zinc were $\Delta f'$ = −1.73 and $\Delta f''$ = 0 84 Positional and anisotropic thermal parameters are given in Table 3 The thermal parameters of the t-butyl groups are relatively high. The same effect was found by Coetzer and Boeyens [19] in the crystal structure of bis(2,2,6,6-tetramethylheptane-5-thiolo-3-onato)-nickel(II).

Acknowledgements

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