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Synthesis and Crystal Structure of the Tetranuclear Organozinc Compound $(C_2H_5)_2Zn_4[N(C_6H_5)COOCH_3]_6 \cdot 2C_6H_6$

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The tetranuclear organozinc compound $(C_2H_5)_2Zn_4[N(C_6H_5)COOCH_3]_6 \cdot 2C_6H_6$ was obtained as a by-product of the reaction of diethylzinc with *N*-phenyl methylcarbamate. A high-yield synthesis was developed, and the various modes of formation were elucidated. The compound was characterized chemically and spectroscopically. Its crystal and molecular structure were determined by a single-crystal x-ray study using three-dimensional x-ray data collected by the ω-scan technique on an Enraf-Nonius CAD4 automated diffractometer. The crystals are triclinic, space group $P\bar{1}$, with one molecular unit and two benzene molecules in a cell with lattice parameters $a = 10.634$ (3) Å, $b = 11.682$ (1) Å, $c = 13.730$ (2) Å, $\alpha = 82.13$ (1)°, $\beta = 82.55$ (2)°, and $\gamma = 78.19$ (2)°. The structure was solved by standard Patterson and Fourier techniques. A block-diagonal least-squares refinement, using anisotropic temperature factors for the nonhydrogen atoms, converged to $R_F = 0.052$ and $R_{wF} = 0.053$ for 6619 independent observed reflections with $I > 2.5\sigma(I)$. The crystal structure contains molecular units $(C_2H_5)_2Zn_4[N(C_6H_5)COOCH_3]_6$ with pairs of benzene molecules in between. The molecular frame consists of a 16-membered ring, $(ZnNCO)_4$, and an eight-membered ring, $(ZnNCO)_2$, sharing two zinc atoms. Two zinc atoms are tetrahedrally surrounded by two oxygen atoms, a carbon atom, and a nitrogen atom, the other two zinc atoms by two oxygen atoms and two nitrogen atoms. The three independent methylcarbamate groups, each with a zinc atom and a phenyl carbon atom bonded to nitrogen, are approximately planar. The Zn–O bond distances range from 1.97 to 2.18 Å. The average Zn–N bond length is 1.971 (13) Å; the Zn–C bond length is 1.963 (5) Å.

Introduction

Trimeric organozinc–nitrogen compounds of the type $[EtZnNRCOR']_3$ (R = Et, Ph; R′ = OMe, NPh_2) are excellent homogeneous catalysts for the trimerization of organic isocyanates.[1] These trimerization reactions are believed to occur via a coordination-template mechanism[2] in which the trimeric organozinc compound complexes with three isocyanate molecules in such a spatial arrangement that trimerization does occur. Since it is obvious that a detailed knowledge of the molecular structure, which cannot be gained from spectroscopic and chemical data alone, is essential for understanding this mechanism, we decided to determine the crystal and molecular structure of EtZnNPhCOOMe, a well-defined, easily crystallizing compound. To this end, the reaction of diethylzinc and *N*-phenyl methylcarbamate was carried out in a way which was known to yield EtZnNPhCOOMe as well-defined crystals.

Surprisingly the structure determination of the crystal selected for x-ray investigation showed that it had the composition $Et_2Zn_4[NPhCOOMe]_6 \cdot 2C_6H_6$. Apparently, a certain small amount of this novel tetranuclear organozinc compound had been formed as a by-product. The present paper reports the modes of formation, the chemical and spectroscopic characterization, and the crystal structure of this compound.

Experimental Section

General Methods. All manipulations were carried out under nitrogen with rigorous exclusion of air and moisture. Diethylzinc was prepared according to Noller[3] and transferred by vacuum distillation from storage vessels into the reaction flasks. *N*-Ethylzinc *N*-phenylmethylcarbamate, EtZnNPhCOOMe, was prepared as described earlier.[4] Molecular weights were determined by ebulliometry in benzene using a Gallenkamp ebulliometer modified for working in a nitrogen atmosphere. NMR spectra were run on Varian XL 100-15 and EM 390 spectrometers using benzene or chloroform as solvents and Me_4Si as internal standard. DTA measurements were performed using samples sealed under nitrogen in glass ampoules.

Preparation of $Et_2Zn_4(NPhCOOMe)_6 \cdot 2C_6H_6$ (A). The title compound, A, was prepared in two different ways.

(a) By Reacting EtZnNPhCOOMe with HNPhCOOMe in a 2:1 Molar Ratio. To a solution of 1.65 g (6.75 mmol) of EtZnNPhCOOMe in 15 mL of benzene, 0.51 g (3.38 mmol) of HNPhCOOMe

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was added as a solution in 5 mL of benzene at 50 °C with stirring. During the addition, a white precipitate formed while gas evolved. This precipitate slowly dissolved again during the next 15 min and a perfectly clear solution resulted. Upon cooling, the product crystallized out in nearly quantitative yield as small block-shaped crystals, which were isolated by washing three times with 10 mL of cold benzene and drying in vacuo.

Anal. Calcd for $C_{64}H_{70}N_6O_{12}Zn_4$ (1376.8): Zn, 18.99; N, 6.10. Found: Zn, 19.01; N, 6.15.

Molecular weight: calculated for $Et_2Zn_4(NPhCOOMe)_6{\cdot}2C_6H_6$ if dissociated completely in two units, 688.4; found 693, 715, and 735 at 1.63, 2.50, and 3.26 wt %, respectively.

(b) By Reacting EtZnNPhCOOMe with $Zn(NPhCOOMe)_2$ in 1:1 Molar Ratio. A total of 1.14 g (4.66 mmol) of EtZnNPhCOOMe, dissolved in 20 mL of benzene, was added to 1.70 g (4.66 mmol) of solid $Zn(NPhCOOMe)_2$. Upon heating to 70 °C with stirring the $Zn(NPhCOOMe)_2$ dissolved completely. The product that crystallized out upon cooling proved to be fully identical with that obtained by route (a).

Crystal Data. Crystal data for $(C_2H_5)_2Zn_4[N(C_6H_5)COOCH_3]_6{\cdot}2C_6H_6$: formula weight 1376.8; triclinic, space group $P\bar{1}$; $Z = 1$; $a = 10.634$ (3) Å, $b = 11.682$ (1) Å, $c = 13.730$ (2) Å, $\alpha = 82.13$ (1)°, $\beta = 82.55$ (2)°, $\gamma = 78.19$ (2)°; Delaunay reduced cell, $a' = 14.096$ Å, $b' = 10.634$ Å, $c' = 13.730$ Å, $\alpha' = 97.45°$, $\beta' = 90.90°$, $\gamma' = 125.79$. The matrix used in the transformation to the Delaunay reduced cell is

$$\begin{pmatrix}a'\\b'\\c'\end{pmatrix}=\begin{pmatrix}\bar{1}10\\100\\00\bar{1}\end{pmatrix}\begin{pmatrix}a\\b\\c\end{pmatrix}$$

ρ(obsd) = 1.40, ρ(calcd) = 1.390 g cm^{-3}; μ(Mo Kα) = 15.5 cm^{-1}; $F(000) = 712$ electrons; $V = 1644.5$ Å^3. Transparent block-shaped crystals were obtained as described above. A suitable specimen was mounted in a Lindemann capillary under nitrogen. Accurate values of the unit cell parameters and the crystal orientation matrix were determined at ambient temperature from a least-squares treatment of the angular settings of 15 reflections, carefully centered on an Enraf-Nonius CAD4 computer-controlled diffractometer using Mo Kα radiation ($\bar{\lambda}$ 0.71069 Å)[5].

On the basis of the values of the unit cell parameters the crystal was found to belong to the triclinic system, $P1$ or $P\bar{1}$. Structure determination excluded $P1$. The standard deviations in the lattice parameters were derived from the comparison of the deviations from integer values of the indices, calculated with the orientational matrix, for the angular settings of the orientation reflections as described by Duisenberg.[6] The calculated density for one molecular unit and two benzene molecules in the unit cell is in agreement with the experimental value obtained by flotation in a mixture of *n*-hexane and carbon tetrachloride.

Collection and Reduction of the Intensity Data. The crystal used for data collection was block-shaped with dimensions 0.5 × 0.4 × 0.4 mm. Intensities for 7959 reflections up to $\theta = 28°$ were collected on the CAD4 diffractometer, equipped with a scintillation counter, in the ω-scan mode using zirconium-filtered Mo Kα radiation. The applied scan angle was $\Delta\omega = 0.52 + 0.92(\tan\theta)°$. The background was measured in an additional scan area of $\Delta\omega/4°$ on both sides of the main scan and with the same scan speed. The intensity of every reflection was measured at the highest possible speed and then, if necessary, at a speed designed to achieve $I_{\min} = 1000$ counts above background. The maximum time of measurement was $t_{\max} = 120$ s. The horizontal and vertical detector aperture were 3 and 4 mm, respectively, and the distance between the crystal and the aperture was 174 mm. An attenuator would have been automatically inserted if a preliminary scan indicated a count rate greater than 50000 counts/s, but it remained unused.[5] The reflections (213) and $(\bar{2}\bar{1}\bar{3})$ were used as standard reflections and their intensities were monitored every 25 reflections.

The net intensity was calculated with

$$I_{\text{net}} = (\text{scale})(S - 2(L + R))/\text{npi}$$

where $(L + R)$ is the total background count, S the scan count, npi the ratio of the maximum possible scan speed to the applied scan speed. The data were scaled with a scale function to take into account short- and long-range fluctuations in the intensity, by interpolation in a polynomial of the third degree through eight neighboring measurement values of each standard reflection, in order to smooth out very short-term fluctuations in the intensity of that standard reflection. There was a linear decay (21%) during the measurement. Fluctuations in the standards were within 2% from the scale function. The standard deviation in the net intensity was calculated with

$$\sigma(I) = \frac{\text{scale}}{\text{npi}}(S + 4(L + R))^{1/2}$$

The intensities of 6619 reflections were above background ($I > 2.5\sigma(I)$); only these reflections were used in the structure determination. The data were corrected for Lorentz and polarization factors (Lp). No correction for absorption was applied. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F)$ by

$$\sigma(F) = [(I + \sigma(I))/Lp]^{1/2} - (I/Lp)^{1/2}$$

Determination and Refinement of the Structure. At the start of the structure determination the unit cell was thought to contain 6 units of EtZnNPhCOOMe (as was calculated from the given structural formula of the main product and the measured density). However, the three-dimensional Patterson map could only be interpreted in terms of a centric configuration of four zinc atoms. The other nonhydrogen atoms were found by subsequent iterative Fourier methods.

The structure was refined by block-diagonal least-squares techniques assuming anisotropic thermal motion for all the nonhydrogen atoms. Twenty-five hydrogen atoms could be located from a difference Fourier synthesis; the other ten positions were calculated. Their temperature factors were related to the anisotropic temperature factors of the carbon atoms, to which they are attached, by

$$U_{\text{carbon}}^{\text{iso}} = {}^{1}/_{3}(U_{11} + U_{22} + U_{33}) \equiv U_{\text{hydrogen}}^{\text{iso}}$$

and were not refined. Unit weights were applied in the preliminary stages of the refinement. The structure refinement then converged to $R_F = 0.052$ and $R_{wF} = 0.049$.[7] Refinement was continued after the introduction of weights on the basis of counting statistics. Weights were calculated with

$$w = (\sigma^2(F_o) + 0.0003F_o^{\,2})^{-1}$$

The function $\sum w(|F_o| - |F_c|)^2$ was not significantly dependent either upon $|F_o|$ or upon $(\sin\theta)/\lambda$, thereby indicating a correctly chosen weighting scheme.

The final R values for 6619 observed reflections are $R_F = 0.052$ and $R_{wF} = 0.053$. A total of 494 parameters including one scale factor were varied. All shifts were less than half their standard deviations when the refinement was stopped. The final positional and thermal parameters of the nonhydrogen atoms are presented in Tables I and II; the corresponding parameters of the hydrogen atoms are given in Table III. The average deviation in an observation of unit weight, defined as $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ where m = number of reflections and n = number of parameters, was 1.45 as compared to the ideal value 1. A final electron density difference Fourier synthesis revealed no significant residual electron density apart from some features less than 0.75 e Å^{-3} around the zinc atoms (with a noise level of 0.25 e Å^{-3}); this may be attributed to the omission of absorption corrections.

Scattering factors for Zn were taken from ref 8; the anomalous part was taken from a compilation by Rietveld.[9] Scattering factors for C, N, and O are those of Cromer and Mann.[10] The values for H are those of Stewart, Davidson, and Simpson.[11] All computer calculations were performed on a CDC CYBER-73 computer at the computer center of the University of Utrecht. Programs used in this structural analysis included the local programs CAD4TAPE (for handling of the diffractometer output, by D Kaas), ORTEP (thermal ellipsoid drawing by C. K. Johnson[12]), and an extended version of the X-RAY SYSTEM (by Stewart et al.[13] and implemented by the Dutch X-RAY SYSTEM group) for most of the other calculations.

Results

Description of the Structure. The crystal structure of the tetranuclear organozinc compound consists of discrete $Et_2Zn_4(NPhCOOMe)_6$ molecular units which are separated by normal van der Waals distances, and pairs of parallel

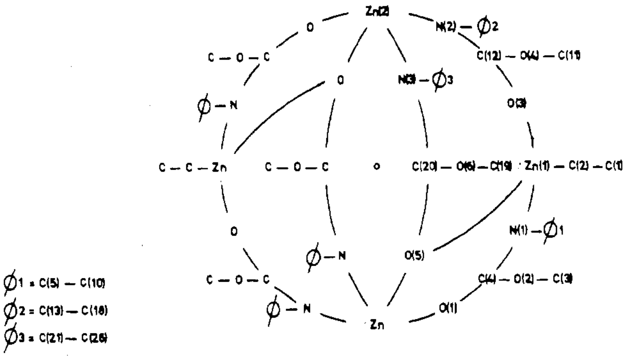


Figure 1. Schematic drawing of the intramolecular bonding in $Et_2Zn_4(NPhCOOMe)_6$.

benzene molecules with a distance between the planes of the benzene rings of 4.213 (7) Å.[14] Figure 1 shows a schematic drawing of the specific bonding in the molecule. A stereoscopic drawing (Figure 2) illustrates the packing of units within the crystal. The adopted numbering scheme along with the thermal vibrational ellipsoids is shown in an ORTEP drawing[12] (Figure 3). Bond distances and bond angles are given in Tables IV and V. No thermal motion corrections to bond lengths were applied.

The molecule is centrosymmetric and can be described in terms of two approximately perpendicular planes (see Table VI) containing an 8- and a 16-membered ring, respectively, sharing two zinc atoms: Zn(2) and Zn(2′). The rings are interlinked by the Zn(1)–O(5) and Zn(1′)–O(5′) bonds; the angle between their least-squares planes is 88°. There are two different kinds of zinc atoms, Zn(1) and Zn(2), both tetrahedrally surrounded by other atoms: Zn(1) by two oxygen atoms, one carbon, and one nitrogen atom (Zn(1)–O(3) = 2.074 (2) Å, Zn(1)–O(5) = 2.180 (2) Å, Zn(1)–C(2) = 1.963(5) Å, Zn(1)–N(1) = 1.993 (2) Å), Zn(2) by two oxygen atoms and two nitrogen atoms (Zn(2)–O(1′) = 1.969 (2) Å, Zn(2)–O(5′) = 2.014(2) Å, Zn(2)–N(2) = 1.947 (2) Å, Zn(2)–N(3) = 1.972 (3) Å). In contrast to the large bond angles N(1)–Zn(1)–C(2) (133.29 (14)°) and N(2)–Zn(2)–N(3) (121.76 (10)°), the O–Zn–O bond angles are almost rectangular (O(3)–Zn(1)–O(5) = 92.08 (8)° and O(1′)–Zn(2)–O(5′) = 93.34 (8)°), which is also observed in $[PhZnOPh{\cdot}Zn(pac)_2]_2$[15] and bis(phenyl(acetylacetonato)-zinc(II))–bis(acetylacetonato)zinc(II).[16]

The atoms N(1), N(2), N(3), C(4), C(12), and C(20) are almost planar trigonal surrounded. The distances N(1)–C(5) (1.437 (4) Å), N(2)–C(13) (1.434 (4) Å), and N(3)–C(21) (1.440 (4) Å) are well in agreement with those in acetanilide, 1.426 (6) Å,[17] but appreciably longer than that in *N*-phenylurethane, 1.405 (6) Å.[18] The N(3)–C(20) distance (1.288 (4) Å) is very short compared to the corresponding distances N(1)–C(4) (1.317 (3) Å) and N(2)–C(12) (1.320

Table I. Final Positional Parameters of the Nonhydrogen Atoms[a]

Atom	*x*	*y*	*z*
Zn(1)	−0.12924 (4)	0.24814 (3)	−0.07482 (2)
Zn(2)	−0.05620 (3)	0.01452 (3)	0.14277 (2)
O(1)	0.0019 (2)	0.0951 (2)	−0.2585 (1)
O(2)	−0.1373 (2)	0.1851 (2)	−0.3653 (1)
O(3)	−0.2424 (2)	0.1401 (2)	0.0120 (1)
O(4)	−0.4125 (2)	0.2088 (2)	0.1180 (2)
O(5)	0.0462 (2)	0.1158 (2)	−0.0584 (1)
O(6)	0.2214 (2)	0.1742 (2)	−0.0206 (2)
N(1)	−0.1728 (2)	0.2310 (2)	−0.2083 (2)
N(2)	−0.2306 (2)	0.0998 (2)	0.1761 (2)
N(3)	0.0894 (2)	0.0968 (2)	0.0998 (2)
C(1)	−0.2140 (8)	0.4530 (7)	0.0406 (7)
C(2)	−0.1058 (5)	0.3830 (4)	−0.0127 (4)
C(3)	−0.0641 (4)	0.1100 (4)	−0.4355 (3)
C(4)	−0.1006 (3)	0.1670 (2)	−0.2742 (2)
C(5)	−0.2921 (3)	0.3050 (3)	−0.2341 (2)
C(6)	−0.3867 (3)	0.2614 (3)	−0.2691 (3)
C(7)	−0.5026 (4)	0.3345 (4)	−0.2894 (3)
C(8)	−0.5248 (4)	0.4496 (4)	−0.2727 (3)
C(9)	−0.4331 (5)	0.4947 (4)	−0.2379 (4)
C(10)	−0.3154 (4)	0.4223 (3)	−0.2187 (3)
C(11)	−0.4850 (4)	0.2560 (5)	0.0355 (3)
C(12)	−0.2919 (3)	0.1496 (3)	0.0989 (2)
C(13)	−0.2874 (3)	0.1148 (3)	0.2752 (2)
C(14)	−0.2953 (3)	0.0165 (3)	0.3419 (2)
C(15)	−0.3441 (4)	0.0282 (4)	0.4395 (3)
C(16)	−0.3831 (4)	0.1369 (4)	0.4704 (3)
C(17)	−0.3747 (4)	0.2330 (4)	0.4064 (3)
C(18)	−0.3262 (4)	0.2232 (3)	0.3085 (3)
C(19)	0.2489 (5)	0.2140 (4)	−0.1237 (3)
C(20)	0.1177 (3)	0.1266 (2)	0.0069 (2)
C(21)	0.1697 (3)	0.1167 (3)	0.1702 (2)
C(22)	0.1223 (5)	0.2008 (5)	0.2325 (4)
C(23)	0.1988 (6)	0.2222 (6)	0.2996 (4)
C(24)	0.3200 (5)	0.1589 (5)	0.3055 (3)
C(25)	0.3648 (4)	0.0742 (4)	0.2462 (3)
C(26)	0.2908 (4)	0.0526 (3)	0.1779 (3)
C(27)	−0.1342 (8)	−0.5619 (5)	0.4061 (6)
C(28)	−0.0884 (7)	−0.4754 (8)	0.3419 (6)
C(29)	−0.1240 (7)	−0.3628 (6)	0.3606 (5)
C(30)	−0.2084 (8)	−0.3388 (5)	0.4419 (5)
C(31)	−0.2508 (7)	−0.4236 (6)	0.5022 (4)
C(32)	−0.2110 (7)	−0.5333 (5)	0.4857 (4)

[a] The estimated standard deviations in the least significant figures are given in parentheses here and in other tables.

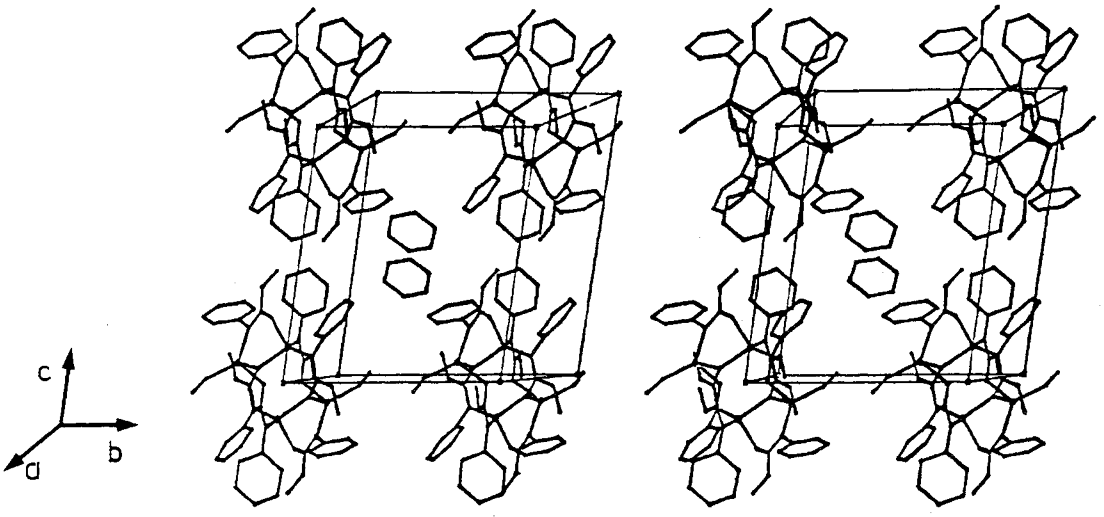


Figure 2. A stereoscopic drawing for $Et_2Zn_4(NPhCOOMe)_6{\cdot}2C_6H_6$. Projection down the a^* axis.

Table II. Final Anisotropic Thermal Parameters of the Nonhydrogen Atoms[a]

Atom	10^2U_{11}	10^2U_{22}	10^2U_{33}	10^2U_{12}	10^2U_{13}	10^2U_{23}
Zn(1)	6.15 (2)	4.25 (2)	3.98 (2)	−0.00 (2)	−1.13 (2)	−0.90 (1)
Zn(2)	3.98 (2)	4.09 (2)	3.76 (2)	−0.08 (1)	−0.83 (1)	−0.58 (1)
O(1)	4.9 (1)	4.7 (1)	3.8 (1)	0.7 (1)	−0.9 (1)	−0.2 (1)
O(2)	6.5 (1)	7.0 (1)	3.4 (1)	1.7 (1)	−1.4 (1)	−1.1 (1)
O(3)	5.8 (1)	6.7 (1)	3.9 (1)	−0.5 (1)	−0.3 (1)	−0.7 (1)
O(4)	4.6 (1)	9.9 (2)	4.5 (1)	1.3 (1)	−0.9 (1)	0.2 (1)
O(5)	5.0 (1)	4.4 (1)	4.2 (1)	−0.3 (1)	−1.6 (1)	−1.0 (1)
O(6)	7.2 (2)	9.3 (2)	4.4 (1)	−3.9 (1)	−1.2 (1)	0.2 (1)
N(1)	5.3 (1)	4.2 (1)	3.4 (1)	0.4 (1)	−0.8 (1)	−0.2 (1)
N(2)	4.1 (1)	5.1 (1)	4.0 (1)	0.3 (1)	−0.5 (1)	−0.4 (1)
N(3)	4.7 (1)	4.7 (1)	3.9 (1)	−1.0 (1)	−1.1 (1)	−0.7 (1)
C(1)	19.2 (7)	17.8 (7)	27.1 (10)	−6.1 (6)	6.5 (7)	−17.7 (7)
C(2)	12.3 (4)	6.2 (2)	10.3 (3)	0.4 (2)	−3.9 (3)	−4.0 (2)
C(3)	7.8 (3)	9.9 (3)	4.7 (2)	1.9 (2)	−1.3 (2)	−2.9 (2)
C(4)	4.8 (2)	4.1 (1)	3.4 (1)	−0.5 (1)	−0.8 (1)	−0.1 (1)
C(5)	5.4 (2)	4.8 (2)	3.4 (1)	0.6 (1)	−0.5 (1)	−0.0 (1)
C(6)	5.5 (2)	6.2 (2)	5.7 (2)	0.2 (2)	−0.9 (2)	−0.1 (2)
C(7)	5.5 (2)	9.8 (3)	6.9 (2)	0.1 (2)	−1.2 (2)	0.2 (2)
C(8)	7.2 (3)	9.4 (3)	8.7 (3)	3.0 (2)	−1.2 (2)	−0.1 (2)
C(9)	10.4 (3)	6.4 (2)	9.9 (3)	3.1 (2)	−2.6 (3)	−1.5 (2)
C(10)	8.2 (3)	5.5 (2)	7.4 (2)	1.4 (2)	−2.6 (2)	−1.2 (2)
C(11)	6.6 (3)	14.0 (4)	6.4 (2)	2.2 (3)	−2.4 (2)	0.5 (2)
C(12)	4.3 (2)	5.2 (2)	4.5 (2)	−0.3 (1)	−0.6 (1)	−0.2 (1)
C(13)	3.5 (1)	5.8 (2)	4.2 (1)	−0.1 (1)	−0.7 (1)	−0.4 (1)
C(14)	6.3 (2)	6.4 (2)	5.2 (2)	−0.3 (2)	0.2 (2)	0.1 (2)
C(15)	7.4 (3)	9.8 (3)	4.8 (2)	−1.2 (2)	−0.2 (2)	0.7 (2)
C(16)	6.9 (3)	12.4 (4)	4.3 (2)	−0.4 (2)	−0.0 (2)	−1.6 (2)
C(17)	8.4 (3)	8.4 (3)	6.7 (2)	−0.0 (2)	−0.4 (2)	−3.1 (2)
C(18)	7.4 (2)	6.3 (2)	5.6 (2)	−0.1 (2)	−0.3 (2)	−1.1 (2)
C(19)	10.6 (3)	11.2 (3)	5.0 (2)	−5.7 (3)	−0.2 (2)	0.3 (2)
C(20)	4.6 (2)	4.3 (1)	4.4 (2)	−0.6 (1)	−1.2 (1)	−0.9 (1)
C(21)	5.7 (2)	6.1 (2)	4.1 (2)	−2.2 (2)	−1.5 (1)	−0.3 (1)
C(22)	9.1 (3)	13.4 (4)	9.5 (3)	0.1 (3)	−3.8 (3)	−6.2 (3)
C(23)	14.2 (5)	17.4 (6)	10.4 (4)	−2.5 (4)	−4.3 (4)	−8.1 (4)
C(24)	13.2 (4)	13.7 (4)	7.4 (3)	−7.2 (4)	−5.5 (3)	0.8 (3)
C(25)	7.6 (3)	10.3 (3)	8.8 (3)	−3.7 (2)	−4.3 (2)	2.4 (2)
C(26)	6.8 (2)	7.1 (2)	6.6 (2)	−1.7 (2)	−2.3 (2)	−0.1 (2)
C(27)	18.8 (7)	9.1 (4)	18.4 (7)	−0.5 (4)	−1.0 (6)	−1.5 (4)
C(28)	13.3 (6)	20.1 (7)	16.1 (7)	−4.0 (5)	1.7 (5)	1.5 (6)
C(29)	20.4 (7)	15.6 (6)	14.8 (5)	−11.9 (5)	−9.2 (5)	7.6 (4)
C(30)	25.7 (9)	9.1 (4)	13.9 (5)	−3.3 (5)	−9.9 (6)	−0.2 (4)
C(31)	18.6 (6)	14.0 (5)	9.0 (4)	−3.5 (5)	−2.7 (4)	−1.1 (3)
C(32)	19.0 (7)	10.7 (4)	11.7 (4)	−6.3 (4)	−4.0 (4)	3.2 (3)

[a] The thermal parameters are in the form $t = \exp[-2\pi^2 \Sigma_i \Sigma_j U_{ij} h_i h_j a_i^* a_j^*]$.

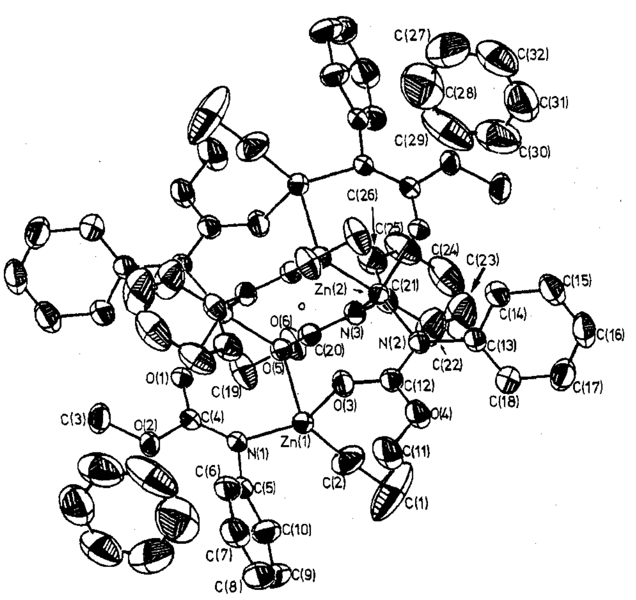


Figure 3. The 40% probability ellipsoids for $Et_2Zn_4(NPhCOOMe)_6 \cdot 2C_6H_6$. The adopted numbering scheme is indicated.

(4) Å) and shorter than usual for an amide group in a planar system (1.32 Å).[19] The O(5)–C(20) bond length (1.283 (4) Å), however, is appreciably longer than the corresponding bond lengths O(1)–C(4) (1.256 (3) Å) and O(3)–C(12) (1.251 (3) Å) and the bond distance C–O(2) (1.206 (6) Å) in ref 18. The C(20)–O(6) distance (1.324 (4) Å) is somewhat shorter than the corresponding distances C(4)–O(2) (1.335 (3) Å) and C(12)–O(4) (1.337 (3) Å) and the bond length C–O(1) (1.344 (6) Å) in ref 18, but this is not significant. The other C–O distances (average 1.437 (2) Å)[14] are in agreement with literature.[20] The average C–C(phenyl), C–H(phenyl), and C–H(methoxy) bond lengths are 1.371 (4), 0.87 (1), and 0.92 (2) Å, respectively.

The three independent methyl carbamate groups, each with a zinc atom and a phenyl carbon atom bonded to nitrogen, are approximately planar. Table VI gives the corresponding least-squares planes. The dihedral angle between the benzene rings and the least-squares planes is 52.8° (plane III, C(5)–C(10)), 58.8° (plane IV, C(13)–C(18)), and 72.2° (plane V, C(21)–C(26)). The configuration of the benzene rings and the methoxy groups about the C(4)–N(1), C(12)–N(2), and C(20)–N(3) bonds is cis, however, twisted by 6.9, 3.9, and 0.5°, respectively, from the exact cis position. This may be explained by the repulsion between the oxygen atom of the methoxy group and carbon atoms of the benzene ring; note in this respect short intramolecular nonbonded distances as O(2)–C(5) (2.625 Å), O(2)–C(6) (2.832 Å), O(4)–C(13) (2.670 Å), O(4)–C(18) (2.918 Å), O(6)–C(21) (2.629 Å), and

Table III. Final Positional and Isotropic Thermal Parameters of the Hydrogen Atoms

Atom	*x*	*y*	*z*	10^2U
H_1(C1)	−0.191 (6)	0.508 (5)	0.069 (4)	18.96
H_2(C1)	−0.274 (6)	0.443 (5)	0.042 (5)	18.96
H_3(C1)	−0.137 (6)	0.375 (5)	0.092 (4)	18.96
H_1(C2)	−0.109 (4)	0.461 (3)	−0.055 (3)	9.39
H_2(C2)	−0.028 (4)	0.367 (3)	0.023 (3)	9.39
H_1(C3)	−0.101 (3)	0.137 (3)	−0.493 (3)	7.59
H_2(C3)	0.017 (3)	0.121 (3)	−0.443 (2)	7.59
H_3(C3)	−0.069 (3)	0.024 (3)	−0.406 (2)	7.59
H(C6)	−0.376 (3)	0.189 (3)	−0.276 (2)	5.80
H(C7)	−0.560 (3)	0.302 (3)	−0.304 (2)	7.51
H(C8)	−0.600 (3)	0.494 (3)	−0.283 (3)	8.33
H(C9)	−0.447 (4)	0.575 (3)	−0.232 (3)	8.88
H(C10)	−0.249 (3)	0.451 (3)	−0.199 (2)	7.05
H_1(C11)	−0.566 (4)	0.293 (3)	0.060 (3)	8.76
H_2(C11)	−0.441 (4)	0.306 (3)	−0.006 (3)	8.76
H_3(C11)	−0.474 (4)	0.206 (3)	−0.007 (3)	8.76
H(C14)	−0.273 (3)	−0.054 (3)	0.319 (2)	5.87
H(C15)	−0.350 (3)	−0.038 (3)	0.481 (2)	7.50
H(C16)	−0.415 (3)	0.139 (3)	0.527 (2)	7.86
H(C17)	−0.389 (3)	0.299 (3)	0.423 (3)	7.99
H(C18)	−0.308 (3)	0.282 (3)	0.267 (2)	6.43
H_1(C19)	0.318 (4)	0.242 (3)	−0.124 (3)	8.98
H_2(C19)	0.279 (4)	0.151 (3)	−0.157 (3)	8.98
H_3(C19)	0.179 (4)	0.277 (3)	−0.135 (3)	8.98
H(C22)	0.037 (4)	0.244 (4)	0.227 (3)	10.47
H(C23)	0.155 (5)	0.264 (4)	0.347 (4)	13.77
H(C24)	0.363 (4)	0.173 (4)	0.346 (3)	11.09
H(C25)	0.447 (4)	0.034 (3)	0.243 (3)	9.07
H(C26)	0.318 (3)	−0.002 (3)	0.142 (2)	6.85
H(C27)	−0.113 (5)	−0.632 (4)	0.390 (4)	15.20
H(C28)	−0.037 (5)	−0.486 (5)	0.302 (4)	16.33
H(C29)	−0.097 (5)	−0.325 (5)	0.330 (4)	15.70
H(C30)	−0.208 (5)	−0.264 (5)	0.438 (4)	15.99
H(C31)	−0.318 (5)	−0.400 (4)	0.552 (3)	13.27
H(C32)	−0.244 (5)	−0.595 (4)	0.526 (4)	13.53

Table IV. Bond Distances (A) for $Et_2Zn_4(NPhCOOMe)_6 \cdot 2C_6H_6$

Distances from the Zinc Atoms			
Zn(1)-N(1)	1.993 (2)	Zn(2)-N(2)	1.947 (2)
Zn(1)–C(2)	1.963 (5)	Zn(2)-N(3)	1.972 (3)
Zn(1)–O(3)	2.074 (2)	Zn(2)–O(1′)	1.969 (2)
Zn(1)-O(5)	2.180 (2)	Zn(2)–O(5′)	2.014 (2)
Distances within Methylcarbamate Groups			
N(1)-C(4)	1.317 (3)	C(4)–O(2)	1.335 (3)
N(1)-C(5)	1.437 (4)	O(2)–C(3)	1.436 (4)
C(4)–O(1)	1.256 (3)		
N(2)-C(12)	1.320 (4)	C(12)–O(4)	1.337 (3)
N(2)–C(13)	1.434 (4)	O(4)-C(11)	1.436 (5)
C(12)-O(3)	1.251 (3)		
N(3)-C(20)	1.288 (4)	C(20)-O(6)	1.324 (4)
N(3)-C(21)	1.440 (4)	O(6)-C(19)	1.440 (4)
C(20)-O(5)	1.283 (4)		
Distances within Benzene Rings			
C(5)-C(6)	1.379 (5)	C(8)-C(9)	1.363 (7)
C(6)-C(7)	1.385 (5)	C(9)–C(10)	1.393 (6)
C(7)–C(8)	1.363 (7)	C(10)-C(5)	1.383 (5)
C(13)-C(14)	1.376 (4)	C(16)-C(17)	1.338 (6)
C(14)-C(15)	1.388 (5)	C(17)–C(18)	1.387 (5)
C(15)-C(16)	1.361 (6)	C(18)–C(13)	1.371 (5)
C(21)-C(22)	1.366 (6)	C(24)–C(25)	1.339 (7)
C(22)-C(23)	1.384 (9)	C(25)–C(26)	1.379 (7)
C(23)-C(24)	1.355 (8)	C(26)–C(21)	1.360 (5)
C(27)-C(28)	1.371 (11)	C(30)–C(31)	1.316 (9)
C(28)-C(29)	1.342 (11)	C(31)-C(32)	1.306 (9)
C(29)–C(30)	1.361 (10)	C(32)-C(27)	1.316 (9)
Distance within Ethyl Group			
C(1)-C(2)	1.445 (9)		

O(6)–C(26) (3.003 Å). The shortest (nonbonded) Zn–Zn distance is 3.464 Å (Zn(1)–Zn(2′)). Other short intramolecular Zn–Zn distances are Zn(1)–Zn(2) (3.805 Å) and Zn(2)–Zn(2′) (3.988 Å).

Table V. Bond Angles (deg) for $Et_2Zn_4(NPhCOOMe)_6 \cdot 2C_6H_6$

Angles around Zinc Atoms			
N(1)-Zn(1)-C(2)	133.29 (14)	N(2)-Zn(2)-N(3)	121.76 (10)
–O(3)	99.82 (10)	–O(1′)	108.69 (9)
-O(5)	102.93 (8)	-O(5′)	114.29 (10)
C(2)-Zn(1)-O(3)	114.83 (15)	N(3)-Zn(2)-O(1′)	104.60 (9)
-O(5)	105.93 (15)	-O(5′)	109.82 (9)
O(3)-Zn(1)-O(5)	92.08 (8)	O(1′)-Zn(2)–O(5′)	93.34 (8)
Angles within Methylcarbamate Groups			
Zn(1)-N(1)–C(4)	126.8 (2)	O(1)–C(4)-O(2)	118.3 (2)
–C(5)	113.6 (2)	-N(1)	124.9 (3)
C(4)-N(1)–C(5)	119.3 (2)	C(4)-O(2)–C(3)	116.9 (2)
N(1)-C(4)–O(2)	116.7 (2)		
Zn(2)–N(2)-C(12)	114.4 (2)	O(3)–C(12)-O(4)	121.0 (3)
-C(13)	124.0 (2)	-N(2)	122.4 (3)
C(12)-N(2)–C(13)	121.5 (2)	C(12)–O(4)-C(11)	117.8 (3)
N(2)–C(12)-O(4)	116.6 (2)		
Zn(2)-N(3)-C(20)	119.4 (2)	O(5)-C(20)-O(6)	119.5 (2)
–C(21)	120.8 (2)	-N(3)	122.1 (3)
C(20)-N(3)-C(21)	119.7 (3)	C(20)–O(6)-C(19)	118.4 (3)
N(3)–C(20)-O(6)	118.3 (3)		
Angles within Benzene Rings			
N(1)-C(5)-C(6)	122.1 (3)	C(7)-C(8)-C(9)	120.8 (4)
-C(10)	118.9 (3)	C(8)-C(9)-C(10)	119.7 (4)
C(5)-C(6)-C(7)	120.5 (3)	C(9)-C(10)-C(5)	120.2 (4)
C(6)-C(7)-C(8)	119.9 (4)	C(10)-C(5)-C(6)	118.9 (3)
N(2)–C(13)-C(14)	119.0 (3)	C(15)-C(16)-C(17)	119.9 (3)
-C(18)	122.6 (3)	C(16)-C(17)-C(18)	120.7 (4)
C(13)–C(14)-C(15)	120.3 (3)	C(17)-C(18)–C(13)	120.6 (3)
C(14)-C(15)-C(16)	120.2 (3)	C(18)–C(13)-C(14)	118.2 (3)
N(3)–C(21)-C(22)	119.3 (3)	C(23)-C(24)-C(25)	119.3 (5)
-C(26)	121.9 (3)	C(24)-C(25)-C(26)	121.1 (4)
C(21)-C(22)-C(23)	120.0 (4)	C(25)–C(26)–C(21)	120.3 (4)
C(22)-C(23)–C(24)	120.6 (5)	C(26)–C(21)–C(22)	118.8 (4)
C(27)–C(28)-C(29)	119.5 (7)	C(30)–C(31)-C(32)	120.3 (6)
C(28)–C(29)–C(30)	118.0 (6)	C(31)-C(32)-C(27)	121.4 (6)
C(29)-C(30)–C(31)	121.1 (6)	C(32)-C(27)-C(28)	119.4 (6)
Angle within Ethyl Group			
Zn(1)–C(2)-C(1)	120.7 (5)		

There are no abnormal short intermolecular contacts. Two intermolecular contacts are smaller than 3.5 Å: $C(3)_{1(000)}$–$C(3)_{2(00\bar{1})}$ (3.284 Å) and $O(4)_{1(000)}$–$C(25)_{1(\bar{1}00)}$ (3.295 Å). The latter, however, is greater than the sum of the van der Waals radii (3.1 Å). The thermal parameters of the carbon atoms of the ethyl groups and of the nonbonded crystallization benzene molecules are relatively high as is generally observed in structures in which such groups (molecules) are present.

Mode of Formation and Chemical and Spectroscopic Characterization. The title compound, $Et_2Zn_4(NPhCOOMe)_6 \cdot 2C_6H_6$ (A), can be thought to consist of a complex between two molecules of EtZnNPhCOOMe and two molecules of $Zn(NPhCOOMe)_2$. Its formation in the synthesis of EtZnNPhCOOMe, which itself is made by reacting diethylzinc with *N*-phenyl methylcarbamate in 1:1 ratio,[4] can be rationalized by assuming that EtZnNPhCOOMe is slightly disproportionated as follows:

$$2EtZnNPhCOOMe \rightleftarrows Et_2Zn + Zn(NPhCOOMe)_2 \qquad (I)$$

$$2EtZnNPhCOOMe + 2Zn(NPhCOOMe)_2 \xrightarrow{\text{benzene}} Et_2Zn_4(NPhCOOMe)_6 \cdot 2C_6H_6$$

The presence of equilibrium I is corroborated by the observation that a solution of EtZnNPhCOOMe fumes when exposed to traces of air. This phenomenon is typical for solutions containing diethylzinc. Equilibria of this type are quite common for organozinc compounds of the general formula RZnX (R = alkyl or aryl, X = halide, OR, SR, NR_2, etc.). In the cases of phenylzinc β-diketonates[15,21] and phenylzinc chloride[22] these equilibria lead to the exclusive formation of complex associates $R_uZn_vX_w$. A DTA measurement

Table VI. Least-Squares Planes[a]

Atom	Dev from plane, Å	Atom	Dev from plane, Å
	Plane I:[b] 16-Membered Ring		
Zn(1)	1.0929	N(1)	0.0469
Zn(2)	0.3041	N(2)	−0.0600
O(1)	−0.1424	C(4)	−0.2923
O(3)	−0.4406	C(12)	−0.3644
	Plane II:[b] 8-Membered Ring		
Zn(2)	−0.3213	N(3)	0.2106
O(5)	−0.4527	C(20)	0.1120
	Plane III		
Zn(1)	0.1009	C(3)	0.0274
O(1)	−0.0842	C(4)	−0.0347
O(2)	0.1043	C(5)	−0.0661
N(1)	−0.0476		
	Plane IV		
Zn(2)	−0.0238	C(11)	−0.0404
O(3)	0.0301	C(12)	0.0227
O(4)	0.0190	C(13)	0.0134
N(2)	−0.0211		
	Plane V		
Zn(2)	−0.0487	C(19)	−0.0072
O(5)	0.0518	C(20)	−0.0062
O(6)	−0.0497	C(21)	0.0312
N(3)	0.0287		

Equations to Planes

I: $7.563x + 9.590y + 4.132z = 0$

II: $7.585x - 6.243y + 1.370z = 0$

III: $6.605x + 9.602y - 2.280z = 1.599$

IV: $5.701x + 10.928y + 1.963z = 0.142$

V: $-4.200x + 9.489y + 2.140z = 0.728$

[a] The planes are defined in fractional coordinates (x, y, z).
[b] These planes contain the center of symmetry (0, 0, 0).

Table VII. ^1H and ^{13}C NMR Data of $Et_2Zn_4(NPhCOOMe)_6 \cdot 2C_6H_6$ and of $(EtZnNPhCOOMe)_3$

	Chemical shifts in ppm relative to Me_4Si[a]				
	^1H		^{13}C		
Compd	OCH_3	CH_2Zn	OCH_3	CH_2Zn	COOMe
$Et_2Zn_4(NPhCOOMe)_6 \cdot 2C_6H_6$	2.83/ 3.56	0.68	52.86/ 54.29	2.05	160.59/ 163.12
$(EtZnNPhCOOMe)_3$	3.53	0.43	54.90	1.36	163.66

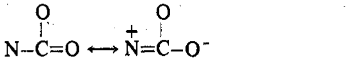
[a] Spectra were recorded in C_6D_6 solution.

of compound A (sealed under nitrogen) showed an endothermic effect at 122 °C, accompanied by liberation of benzene, but the compound did not melt. An exothermic effect was observed at 177 °C, at which temperature the compound melted with decomposition. Molecular weight determinations by ebulliometry in benzene showed that the compound had dissociated completely into two parts. An obvious dissociation path cannot be given, since, although some weak coordinate bonds (Zn(1)–O(5), Zn(1)–O(3), Zn(1′)–O(5′), and Zn(1′)–O(3′), see Figure 1) are present, cleavage of these would still leave the molecule intact.

The ^{13}C NMR spectrum of A, recorded in C_6D_6 at room temperature, showed the presence of only one kind of ethyl group bound to zinc but of two kinds of methylcarbamate groups in roughly 1:2 ratio. This was confirmed by the ^1H NMR spectrum, also in C_6D_6, in which one ethyl group was visible, but two methoxy absorptions with 1:2 intensity ratio. The NMR data are compiled in Table VII together with those of $(EtZnNPhCOOMe)_3$.

Discussion

The O(5)–C(20) distance (1.283 (4) Å) is significantly longer than the C=O distances usually found in carbamates, 1.22 Å.[23] On the other hand, the N(3)–C(20) distance (1.288 (4) Å) is very short compared to that in usual amide groups in planar systems, 1.32 Å.[19] These differences indicate that the contribution of mesomeric form II to the structure of the



$$N{-}\overset{\overset{\displaystyle O}{|}}{C}{=}O \longleftrightarrow \overset{+}{N}{=}\overset{\overset{\displaystyle O}{|}}{C}{-}O^- \qquad \text{(II)}$$

methylcarbamate group has become much more important than in a free carbamate. A necessary condition for this is coplanarity of the methylcarbamate group, which indeed is observed in all three independent groups in the molecule. This delocalization of electrons is the reason that bridging via nitrogen, as observed in organozinc–amines, does not occur here. A bond situation as found here was suggested earlier for analogous organozinc–nitrogen compounds on the basis of IR data.[4,24] The methylcarbamate units in the eight-membered ring contain three-coordinate oxygen atoms and show the most extensive electron delocalization (shortest N—C bonds, longest C=O bonds, see Table IV). The Zn–O coordinate bonds formed by these groups are either quite short (2.014 (2) Å) or appreciably longer (2.180 (2) Å). This contrasts with the Zn–O bonds in some phenylzinc β-diketonates in which four-coordinate oxygens form equally long coordinate bonds to zinc.[15] Figure 4 shows the Newman projections along the C=O bonds to illustrate the directions of the Zn—O coordinate bonds with respect to the planar methylcarbamate groups. In solution, a very different situation exists because complete dissociation occurs. In principle two alternative dissociations may occur, viz., (a) into two identical units $EtZn_2(NPhCOOMe)_3$ or (b) into two different units EtZnNPhCOOMe and $Zn(NPhCOOMe)_2$. It has been found that EtZnNPhCOOMe is a dissociating trimer in solution,[4] so the absence of any concentration dependence of the molecular weight of (A) argues against possibility (b). Also, the NMR spectra of (A) show no absorptions attributable to either EtZnNPhCOOMe or $Zn(NPhCOOMe)_2$. We assume, therefore, that (A) dissociates into two $EtZn_2(NPhCOOMe)_3$ units, when dissolved in benzene.

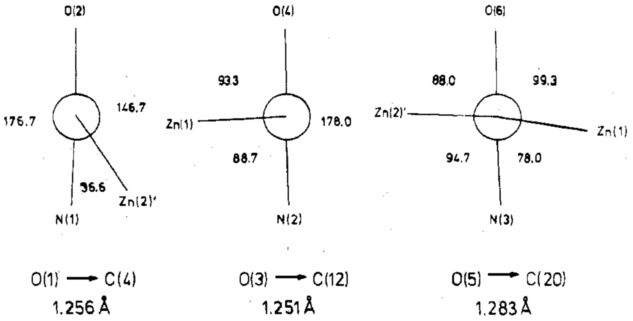


Figure 4. Newman projections along the C=O bonds.

The structure of $Et_2Zn_4(NPhCOOMe)_6 \cdot 2C_6H_6$ well illustrates the complexity of organozinc coordination chemistry. The ubiquitous disproportionation equilibria cause the simultaneous presence of both R_2Zn, RZnX, and ZnX_2 species which, depending on the nature of R, X, and solvent, recombine to give associates of the general formula $R_uZn_vX_w$. The molecular structure in the solid state again may differ from that in solution, as is found in this case.

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Registry No. A, 64938-89-2; EtZnNPhCOOMe, 23151-20-4; HNPhCOOMe, 2603-10-3; $Zn(NPhCOOMe)_2$, 64913-40-2.

Supplementary Material Available: A listing of structure factor amplitudes (40 pages). Ordering information is given on any current masthead page.

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Sulfur Chelates. 32.[1,2] Studies of the Solid-State Molecular Structure and Solution Structures and Dynamics of Bis(phosphine) Adducts of Platinum(II) 1,1-Dithiolates. Molecular Structures of $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$, $Pt(S_2CO)(PPh_3)_2$, and $Pt(S_2CO)(diphos)\cdot{}^1/_4CHCl_3$

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NMR spectra are used to compare the solution structure of $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$ with its solid-state structure. The low-temperature solution structure is different from the structure of the crystalline solid, which is *trans*-PtS_2P_2 in its coordination about the metal. The low-temperature solution structure is that of the cation $[PtS_2CN(i\text{-}Bu)_2(PMe_2Ph)_2]^+$ with a free dithiolate anion. The structure of $Pt(S_2CO)(Ph_3P)_2$ and the diphos analogue show a *cis*-PtS_2P_2 coordination as indicated in spectral studies. They are formed by reacting the platinum(II) xanthate with the phosphine. Phosphine exchange and dithiolate exchange both occur in solutions containing $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$. The dithiolate ligand exchange is solvent dependent. Bimolecular phosphine exchange occurs with a larger rate constant than bimolecular dithiolate exchange and both of these processes appear faster than the bimolecular displacement of phosphine from $[Pt(S_2CNR_2)(PR_3)_2]^+$ by the dithiolate ligand.

Introduction

Our continued interest in the reactions[3,4] of phosphine bases with planar d^8 complexes has led us to reexamine[5] the behavior of bis(1,1-dithiolato)palladium(II) and -platinum(II) complexes in the presence of excess phosphine, using advanced NMR capabilities and single-crystal x-ray crystallography.

Various products are obtained when the ratio of phosphine to bis(1,1-dithiolato)M, M = Ni^{II}, Pd^{II}, or Pt^{II}, exceeds 2:1, depending upon the nature of the dithiolate ligand. Reacting the xanthate and dithiophosphate complexes with excess tertiary phosphine[5] gives the novel complexes $M(PR_3)_2(S_2CO)$ (M = Pd, Pt; R = alkyl or aryl) and $Pd(PR_3)_2[S_2P(O)OEt]$, respectively.

Stephenson and co-workers[10] have suggested a very reasonable mechanism for this reaction (1) involving the formation

$$\begin{gathered} M(S_2COR)_2 + 2L \rightleftharpoons L_2M(S_2COR)^+ + ROCS_2^- \\ ROCS_2^- + L_2M(S_2COR)^+ \rightarrow ROCS_2R + L_2MS_2CO \\ M = Pd^{II}, Pt^{II};\ L = \text{phosphine} \end{gathered} \tag{1}$$

of an ionized dithiolate ligand.

Dithiocarbamate and dithiophosphinate complexes give bis(phosphine) adducts of stoichiometry $Pt(S_2CNR_2)_2(PR_3)_2$[10] and $M(S_2PR_2)_2(PR_3)_2$[7-9,11,12] (M = Pd, Pt; R = alkyl or aryl). Conductivity measurements and NMR studies[9,11,12] suggest that the bis(phosphine) adducts of bis(dithiophosphinato)-palladium(II) and -platinum(II) are ionic. The preliminary report of x-ray structural data of $[Pd(S_2PPh_2)(PEt_3)_2](S_2PPh_2)$ provided by Beevers and Fraser as cited by Alison et al.[9] indicated a structure with four-coordinate palladium in a cis ionic PdS_2P_2 configuration.

A subsequent paper by Alison et al.[10] has proposed that bis(phosphine) adducts of bis(dithiocarbamato)platinum(II) are also ionic compounds of type $[M(PR_3)_2Y]^+Y^-$ [Y being S_2PPh_2, S_2PMe_2, S_2CNR_2; M = Pd, Pt; PR_3 = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3; R = Me, Ph, Et, *i*-Bu (Me = methyl, Et = ethyl, *i*-Bu = isobutyl, Ph = phenyl)]. The ionic formulation is suggested by the presence of IR spectral bands corresponding to those found in $NaS_2CNR_2\cdot3H_2O$ and by the ready synthesis of $[Pt(S_2CNR_2)(PR_3)_2]BPh_4$.

Our studies have shown that the solid-state structures of the dithiocarbamatoplatinum(II) complexes, $Pt(S_2CNR_2)_2(PR_3)_2$, are not cis ionic.[10a] IR studies, colors, and a single-crystal x-ray structure of $Pt[S_2CN(i\text{-}Bu)_2]_2(PMe_2Ph)_2$ (I) verify this conclusion. Thus a difference exists between the solid-state structures of the bis(phosphine) adducts of the dithiophosphinates and the dithiocarbamates.[10a]

Alison and Stephenson[10] reported the ^1H NMR studies of the bis(phosphine) adducts $Pt(S_2CNR_2)_2(PMePh_2)_2$ (R = methyl, ethyl). They found an equilibrium between the mono(phosphine) adduct and bis(phosphine) adduct with the equilibrium lying well to the right of eq 2. They report that

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