

Bimetallic metal alkyl systems; synthesis and characterization of the Ni[Salen] · Zn(C₂H₅)₂ adduct

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Abstract

The reaction between Ni[Salen] (Salen = bis(salicylaldehyde)ethylenediiminato) and Zn(C₂H₅)₂ in hydrocarbon solvents yields the Ni[Salen] · Zn(C₂H₅)₂ adduct. An X-ray crystal structure (monoclinic, space group *P*2₁/*c*, *a* 12.835(5), *b* 14.072(11), *c* 13.766(8) Å, β 117.48(5)°, *V* 2206(5) Å³, *Z* = 4) shows that the Zn atom is surprisingly weakly coordinated to the *cis* oxygen atoms of the Salen ligand. The average Zn–O distance is 2.321(6) Å leading to an acute O–Zn–O angle of 63.1(2)°. The C–Zn–C angle of 147.9(4)° is also indicative of a relative weak interaction of the Zn with the Salen oxygen atoms. The Zn atom is displaced 0.78 Å from the least-squares plane of the Ni coordination plane. There were no chemically significant changes in the coordination parameters of Ni[Salen] on adduct formation. Attempts to form adducts with other related systems are discussed.

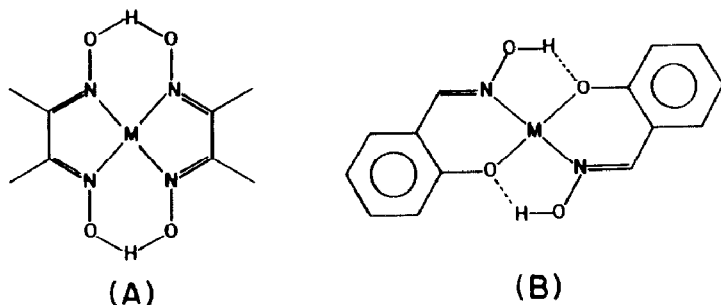
Introduction

The active center of a Ziegler–Natta catalytic system is generated on mixing an alkylaluminum species with a transition metal complex. While the catalysis mechanism is still under investigation, it is believed that an alkyl group is transferred to the transition metal center and that the catalytic site is at the reduced transition metal species. In order for this to occur, some sort of bimetallic species must form, if only transiently.

It has been known for many years that transition metal complexes can behave as neutral ligands and form complexes with both transition and non-transition metal ions [1]. Sinn and co-workers have reported many homonuclear bimetallic complexes which were structurally characterized by spectro and magnetochemical techniques [2]. There are also reports of interactions between Schiff-base transition metal complexes and a variety of neutral molecules such as SnCl₄, AsCl₃, SiCl₄ and Si(CH₃)₂Cl₂, and also transition metal chloride and perchlorate salts [3–7]. In these systems, coordination may or may not lead to configurational changes in the

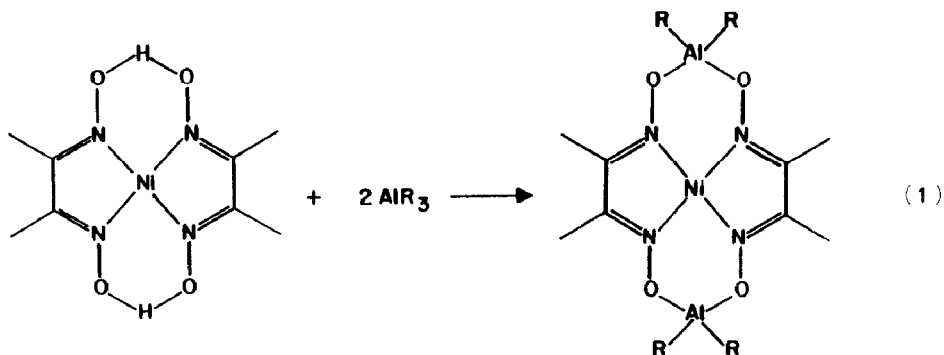
transition metal species. For example, addition of SnCl_4 to square-planar nickel(II) thiocarbonylhydrazones produces an octahedral metal center by the transfer of two chlorine atoms to the nickel [1], but addition of SnCl_4 to cobalt(II) SALEN has no effect on the cobalt coordination geometry [3].

Similarly, Voiculescu and co-workers have reported the reactions of organoaluminum compounds with nickel(II), palladium(II), and platinum(II) dimethylglyoximates (A), $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ and salicylaldoximates (B) [8–10]. In these



systems, the alkylaluminum species reacts with the bridging hydroxyl proton, producing ethane and a four-coordinate aluminum-transition metal species. This is shown in eq. 1 for the reaction of $\text{Ni}(\text{dmg})_2$ with triethylaluminum. This reaction is analogous to that of $\text{Ni}(\text{dmg})_2$ with BF_3 . [12] In these systems, there are no changes in the coordination environment about the transition metal centers. Voiculescu and co-workers have also shown that diethylzinc reacts similarly with nickel(II), palladium(II), and copper(II) salicylaldoximes; and diethylzinc moiety replaces the proton at the bridging position [13].

Herein we present an account of the reaction of aluminum and zinc alkyl species with a variety of transition metal Salen complexes. While diethylzinc was the first reported organometallic compound [14], it is still an interesting molecule from a structure and bonding viewpoint. The coordinatively unsaturated dialkylzinc has a linear geometry, and though highly reactive, does not undergo dimerization or oligomerization reactions that characterize its group IIA and IIIA counterparts such as trialkylaluminum and dialkylmagnesium. Relatively little work has been reported on organozinc complexes in recent years and a paucity of data exists on structure and bonding in these complexes as detailed by X-ray crystallographic studies. The



crystal structure of the adduct formed between diethylzinc and nickel(II) Salen* has been determined. This is, to our knowledge, only the second reported example of a complex between an organozinc species and a transition metal chelate compound.

Experimental

Materials. Diethylzinc (1.0 M in hexane) was purchased from the Alfa Chemical Company. All solvents were reagent grade and were dried before use. Benzene and toluene were dried and stored over sodium ribbon; acetonitrile was dried and stored over molecular sieves.

Synthesis. The Salen ligand was synthesized according to published procedures [15] and Ni[Salen] was prepared by stoichiometrically mixing alcoholic solutions of Salen and nickel(II) acetate.

Ni[Salen]Zn · (C₂H₅)₂, C₆H₆. In a typical preparation, 162 mg (0.500 mmol) of Ni[Salen] were suspended in 2.0 ml of benzene in a test tube sealed with a septum cap. The test tube was deaerated with N₂ and 0.50 ml of a 1.0 M solution (0.50 mmol) of Zn(C₂H₅)₂ in hexane was added. A small amount (0.5 ml) of acetonitrile was added to the solution which was then heated to boiling until all the Ni[Salen] had gone into solution. Slow cooling of the reaction mixture yielded red-orange cubic shaped crystals that were extremely air-sensitive.

Ni[Salen] · Zn(C₂H₅)₂, C₇H₈ and Ni[Salen] · Zn(C₂H₅)₂. These complexes were prepared by the above procedure with toluene replacing benzene as the reaction solvent. Two different crystal morphologies were observed and confirmed by single crystal X-ray analysis. One was characterized as the toluene solvate; the other was nonsolvated. The yield of the toluene solvated crystals was greater; the red-orange crystals were tetragonally distorted octahedra. Unsolvated, needle-like crystals were also isolated. As above, the crystals are air-sensitive and decompose rapidly on exposure to the atmosphere.

Physical measurements. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer between 4000 and 500 cm⁻¹ as Nujol mulls on NaCl plates. The ¹H NMR spectra were taken on a 270 MHz Bruker/IBM spectrometer at ambient temperature.

Growth and selection of X-ray crystals. Crystals of all three complexes were grown by slow cooling of their respective reaction mixtures. The solutions were filtered under nitrogen. An appropriate crystal from each was selected, sealed in a glass capillary, and mounted for data collection. For the unsolvated adduct, the crystal dimensions were 0.4 × 0.2 × 0.2 mm³. The dimensions of both the benzene and toluene solvated adducts were approximately 0.3 × 0.3 × 0.3 mm³.

Collection and reduction of X-ray diffraction data. The diffraction data for all three solvates were obtained on an Enraf-Nonius CAD-4 diffractometer controlled by a Digital PDP 11/34 computer with the use of graphite monochromatized Mo-K_α radiation (λ 0.71073 Å) at room temperature using the θ-2θ scan technique. Unit cell parameters were obtained from the indexing and least-squares refinement of 25 orientation reflections with 2θ limits between 15 and 25°. All three

* Salen = bis(salicylaldehyde)ethylenediiminato.

Table 1

Data collection and refinement parameters for all three solvates

	Ni-Zn ^a unsolv.	Ni-Zn ^a toluene	Ni-Zn ^a benzene
Crystal System:	Triclinic	Monoclinic	Monoclinic
Space Group:	$P\bar{1}$	$C2/c$	$P2_1/c$
a , Å	8.349(4)	13.729(6)	12.835(5)
b , Å	10.300(2)	14.139(4)	14.072(11)
c , Å	11.858(3)	22.996(28)	13.766(8)
α	84.87(2)°	90.0°	90.0°
β	84.84(3)°	92.99(9)°	117.48(5)°
γ	87.72(3)°	90.0°	90.0°
V Å ³	980(2)	4515(9)	2206(5)
Abs. coeff.,	22.34	19.41	19.86
Total data	1977	2296	3071
Data with $I > 2\sigma$	1182	1268	1545
2θ Scan range:	2–40 ^b	2–40 ^b	2–48
R_w :	7.0 ^c	11.2 ^c	6.2
R_σ :	9.7 ^c	12.7 ^c	7.4

^a Ni[Salen]·Zn(C₂H₅)₂. ^b Data collection halted after 75% crystal decomposition. ^c Unacceptable esd's due to crystal decomposition.

compounds diffracted poorly with few observable reflections above 40°. The intensity of three standard reflections were measured after every two hours of X-ray exposure to determine the extent of crystal decomposition.

Ni[Salen]·Zn(C₂H₅)₂, unsolvated. This compound crystallizes in the triclinic crystal system and the space group was determined to be $P\bar{1}$. Apparently, the glass capillary was not air-tight; the diffracted intensities decreased to 75% of their original intensity when the data collection was halted. Visual inspection of the crystal indicated decomposition and no ethane was produced on addition of HCl. The data were corrected for decomposition, Lorentz, and polarization effects, but no correction for absorption was necessary. The details of data collection are summarized in Table 1.

Ni[Salen]·Zn(C₂H₅)₂, toluene. This crystal also underwent extensive loss of intensity (75%) and since the crystal contained a severely disordered toluene molecule (vide-infra), another attempt at data collection on a better sealed crystal seemed pointless. The crystal was monoclinic and the space group was determined from the systematically absent reflections and the distributions of intensities to be $C2/c$. Data were collected in the $+h$, $+k$, $\pm l$ quadrant and were corrected for decomposition, Lorentz, and polarization effects. No correction for absorption was necessary due to the regular shape of the crystal and the low absorption coefficient. See Table 1 for the details of the data collection and refinement.

Ni[Salen]·Zn(C₂H₅)₂, benzene. This crystal did not exhibit any significant intensity deviations for the standard reflections over the duration of data collection. The crystal system is also monoclinic, and the space group determined to be $P2_1/c$. Data were collected in the $+h$, $+k$, $\pm l$ quadrant. The data were corrected for Lorentz and polarization effects, but no absorption correction was necessary in light of the cubic shape of the crystal and the low absorption coefficient. (The details of data collection are presented in Table 1).

Table 2

Positional parameters for the Ni[Salen]·Zn(C₂H₅)₂ adduct

Atom	x	y	z
Ni	0.01831(9)	-0.0587(1)	-0.11993(9)
Zn	0.2909(1)	-0.1240(1)	-0.03606(9)
O(1)	0.1050(5)	-0.1666(5)	-0.0702(5)
O(2)	0.1611(5)	-0.0002(5)	-0.0509(4)
N(1)	-0.1215(6)	-0.1186(6)	-0.1967(5)
N(2)	-0.0666(6)	0.0527(6)	-0.1588(5)
C(1)	0.0658(7)	-0.2562(7)	-0.0871(6)
C(2)	0.1450(8)	-0.3292(7)	-0.0365(7)
C(3)	0.109(1)	-0.4208(8)	-0.0525(8)
C(4)	-0.0066(9)	-0.4448(8)	-0.1185(8)
C(5)	-0.0845(8)	-0.3744(8)	-0.1697(7)
C(6)	-0.503(7)	-0.2806(7)	-0.1523(6)
C(7)	-0.1350(8)	-0.2097(8)	-0.2047(7)
C(8)	-0.2180(9)	-0.0550(9)	-0.258(1)
C(9)	-0.1927(8)	0.0368(9)	-0.2137(9)
C(10)	-0.0235(8)	0.1373(7)	-0.1321(7)
C(11)	0.0965(8)	0.1604(8)	-0.0736(6)
C(12)	0.1277(9)	0.2574(8)	-0.0528(7)
C(13)	0.240(1)	0.2838(8)	0.0024(9)
C(14)	0.3270(9)	0.2157(9)	0.0396(9)
C(15)	0.3000(8)	0.1224(8)	0.0205(8)
C(16)	0.1852(7)	0.0920(7)	-0.0357(7)
C(1A)	0.4007(8)	-0.1361(8)	0.1209(8)
C(2A)	0.517(1)	-0.163(1)	0.1539(9)
C(3A)	0.263(1)	-0.138(1)	-0.1903(9)
C(4A)	0.336(2)	-0.110(2)	-0.214(1)
C(1S)	0.538(1)	0.4102(9)	0.0246(9)
C(2S)	0.5441(9)	0.453(1)	-0.062(1)
C(3S)	0.5065(9)	0.5462(9)	-0.0840(8)

Solution and refinement of the structures. The structures were solved by direct methods using MULTAN 78 [16]. The initial MULTAN solutions located both metal atoms, the nickel coordination sphere, and a significant portion of the Salen ligand. The ethyl-carbon atoms and any missing ligand carbon atoms were located from successive difference Fourier maps. The structures were refined by successive least-squares and Fourier techniques. Anisotropic thermal parameters were used for all non-hydrogen atoms in the final stages of refinement. Hydrogen atom positions were calculated assuming standard C–H bond distances of 0.95 Å and their isotropic temperature factors were fixed at 5.0. Hydrogen atoms were included in structure factor calculations, but their positions were not refined. While each of the structures was refined essentially to convergence, the limited and poor quality data for the unsolvated and toluene solvated compounds limited the accuracy to less than satisfactory. Thus, atom positions, and bond distances and angles are only reported for the benzene solvated complex. Table 2 lists the positions of the non-hydrogen atoms with their standard deviations for this complex. The final weighted and unweighted R indices are 6.2 and 7.4%, respectively for 1545 reflections with intensities greater than $2\sigma(I)$. A final difference Fourier map was essentially

featureless with no intensities greater than $0.42 e/\text{\AA}^3$. Residual electron density was located about the zinc atom and also in the vicinity of the benzene solvate.

Results and discussion

The $\text{Ni}[\text{Salen}] \cdot \text{Zn}(\text{C}_2\text{H}_5)_2$ adduct is obtained by stoichiometrically mixing a solution of diethylzinc in hexane with a benzene (or toluene)/acetonitrile suspension of nickel Salen. Interaction of the diethylzinc moiety with the nickel complex carries the sparingly soluble nickel Salen species into solution. This is facilitated by slight heating. Bright red crystals were isolated on slow cooling of the reaction mixture and were subjected to an X-ray structure determination.

Description of the structure of $\text{Ni}[\text{Salen}] \cdot \text{Zn}(\text{C}_2\text{H}_5)_2$, C_6H_6 . The crystal structure of the $\text{Ni}[\text{Salen}] \cdot \text{Zn}(\text{C}_2\text{H}_5)_2$ adduct consists of a square-planar nickel Salen moiety coordinated to diethylzinc through interaction with both Salen oxygen atoms. The zinc atom is displaced 0.78 \AA above the plane defined by the nickel coordination sphere. A molecule of benzene solvate is located at a crystallographic inversion center. An ORTEP drawing of the structure with the atom designations is depicted in Fig. 1.

Coordination geometry. Formation of an adduct with diethylzinc has little effect on the coordination environment of the $\text{Ni}[\text{Salen}]$. The bond parameters of the adduct are only slightly perturbed from their 'free' values. [17] These are compared in Table 3 for the nickel coordination sphere. In Table 4, bond angles for both the nickel and the zinc coordination spheres are given. The interaction of the zinc atom with the cis oxygen atoms is surprisingly weak. The average $\text{Zn}-\text{O}$ distance of $2.321(6) \text{ \AA}$ is significantly longer than the sum of the covalent radii (1.97 \AA) and is also long compared to the 2.06 \AA distance reported for $[\text{Zn}(\text{OMe})_2 \cdot (\text{EtZnOMe})_6]$ [18], the 2.078 \AA bond distance of the tetrameric $(\text{CH}_3\text{ZnOCH}_3)_4$ [19], and the 1.94 \AA distance found in the zinc Salen complex. [20] This long $\text{Zn}-\text{O}$ distance leads to an acute $\text{O}-\text{Zn}-\text{O}$ angle of $63.1(2)^\circ$. As a result of the interaction, the $\text{C}-\text{Zn}-\text{C}$ angle is no longer linear, but the angle has closed to $147.9(4)^\circ$. This is much larger than the 109.5° angle expected for a tetrahedral geometry and indicates significant rehybridization of the zinc center. The apparent average $\text{C}-\text{C}$ distance of the zinc

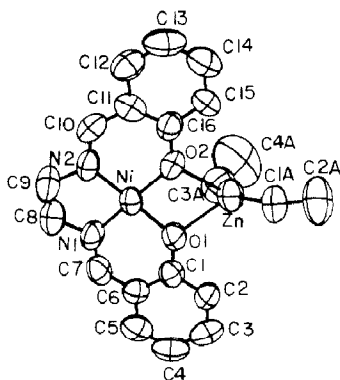


Fig. 1. An ORTEP drawing of the $\text{Ni}[\text{Salen}] \cdot \text{Zn}(\text{C}_2\text{H}_5)_2$ adduct with the atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 3a

Comparison of bond distances for Ni[Salen] and the Ni[Salen]-diethylzinc adduct

Bond	Ni[Salen]	Ni-Zn adduct
Ni-N(1)	1.853(2)	1.816(8)
Ni-N(2)	1.843(2)	1.842(8)
Ni-O(1)	1.858(2)	1.820(6)
Ni-O(2)	1.855(2)	1.825(6)
O(1)-C(1)	1.311(4)	1.34(2)
O(1)-C(2)	1.310(4)	1.33(1)
N(1)-C(7)	1.293(4)	1.29(1)
N(2)-C(10)	1.301(4)	1.29(1)

Table 3b

Comparison of bond angles for Ni[Salen] and the Ni[Salen]-diethylzinc adduct

Angle	Ni[Salen]	Ni-Zn adduct
N(1)-Ni-N(2)	96.3(1)	96.2(4)
O(1)-Ni-O(2)	85.6(1)	83.5(3)
N(1)-Ni-O(1)	94.3(1)	95.8(3)
N(2)-Ni-O(2)	93.9(1)	94.9(3)

ethyl group (1.30 Å) is shorter than the 1.50 Å expected for a carbon-carbon single bond and is artifactual resulting from the large thermal motion of the methyl groups. The average Zn-C bond distance is 1.98 Å. This is shorter than the 2.07 Å reported for $[\text{Zn}(\text{OMe})_2 \cdot (\text{EtZnOMe})_6]$ [18] and slightly longer than the 1.95 Å bond distance in $(\text{CH}_3\text{ZnOCH}_3)_4$ [19] and the 1.94 Å distance reported for dimethylzinc [21].

As mentioned above, the zinc is displaced 0.78 Å and is positioned at an angle of 23.2° above the least-squares plane of the nickel coordination sphere. This displace-

Table 4

Selected Ni and Zn coordination sphere bond angles

N(1)-Ni-N(2)	86.2(4)
N(1)-Ni-O(1)	95.8(3)
N(2)-Ni-O(2)	94.9(3)
N(1)-Ni-O(1)	175.9(4)
N(2)-Ni-O(2)	175.4(3)
O(1)-Zn-O(2)	63.1(2)
O(1)-Zn-C(1A)	110.6(4)
O(1)-Zn-C(3A)	95.6(4)
O(2)-Zn-C(1A)	106.2(3)
O(2)-Zn-C(3A)	102.1(4)
Ni-O(1)-Zn	104.9(3)
Ni-O(2)-Zn	102.3(3)
C(1A)-Zn-C(3A)	147.9(4)
Zn-C(1A)-C(2A)	119.6(4)
Zn-C(3A)-C(4A)	118.7(9)

ment is also observed in the unsolvated and toluene-solvated complexes where the zinc is 0.76 and 0.72 Å, respectively, above the plane and suggests that the displacement is not caused by crystal packing forces, but rather is a result of electronic factors. Considering the length of the zinc–oxygen bond and the relatively small size of the diethylzinc moiety, one would not expect steric requirements to contribute significantly to the large out-of-plane distance for the zinc atom. Thus, electronic factors should predominate with the zinc atom coordinated at a position that gives maximum overlap with the lone-pair electrons on the oxygen atom. This suggests that the oxygen electron density is located above the plane of the nickel coordination sphere. Interestingly, the average Ni–O–Zn bond angle is 103.6°, indicative of a tetrahedral arrangement of electron density about the oxygen.

Reactivity studies of dinuclear / metal alkyl systems. The title complex was produced in the course of our investigations of the interaction of metal alkyls with transition metal chelate systems. The complex is stable in the solid state in the absence of air. ^1H NMR spectra of $\text{Ni}(\text{Salen}) \cdot \text{Zn}(\text{C}_2\text{H}_5)_2$ were taken in CDCl_3 and that of $\text{Zn}(\text{C}_2\text{H}_5)_2$ was taken in CD_3CN . The methylene group of $\text{Zn}(\text{C}_2\text{H}_5)_2$ appears as a quartet centered at 0.29 ppm and the methyl group appears as a triplet at 1.32 ppm. On adduct formation with $\text{Ni}(\text{Salen})$, the peaks almost collapse on top of one another. The methylene quartet now appears at 1.17 ppm and the methyl triplet at 1.23 ppm. Apparently, the electronegative oxygen atoms of $\text{Ni}(\text{Salen})$ remove electron density from zinc, reducing the upfield shift of the methylene group. On exposure to air, the crystals decompose rapidly. After ten minutes, the crystals have visibly deteriorated, giving no evidence for the presence of active ethyl groups. A ^1H NMR spectrum of the compound after exposure to air has resonances attributable to alkoxide formation (quartet at 3.75 ppm, triplet at 1.20 ppm). When synthesizing the compound, prolonged heating of the reaction mixture resulted in ligand decomposition, and if air was allowed to diffuse into the system, red-orange prisms of original nickel Salen were isolated.

Addition of two equivalents of diethylzinc to $\text{Ni}(\text{dmg})_2$, dmg = dimethylglyoximate, results in the formation of a bright-red microcrystalline compound that has an active ethyl group. The bridging hydroxyl proton has been replaced with an ethylzinc moiety. Further investigations in this area were not continued in light of Voiculescu's similar studies. [7–10,13].

The interaction of triethylaluminum with $\text{Ni}[\text{Salen}]$ was also investigated and the reaction monitored with ^1H NMR. Addition of one equivalent of $\text{Al}(\text{C}_2\text{H}_5)_3$ to an equivalent of $\text{Ni}[\text{Salen}]$ in benzene causes immediate dissolution of $\text{Ni}[\text{Salen}]$ and color change from light red-orange to dark green. The solution is unstable and undergoes rapid ligand decomposition with a concomitant color change to brownish red within ten minutes. Attempts to monitor the reaction with ^1H NMR spectroscopy in benzene were of limited value because the sample becomes paramagnetic. The ethyl region (between 0.0 and 2.0 ppm) undergoes dramatic changes. Initially, the ethyl group appears as a triplet at 1.2 ppm and a quartet at 0.4 ppm. Within minutes, the spectrum becomes very complicated with many new alkyl resonances which are paramagnetically broadened. While solution intermediates could not be identified, the paramagnetism indicates that the nickel coordination environment is no longer square-planar. The difference in behavior for the trialkylaluminum versus dialkylzinc adduct formation with nickel Salen is attributed to the following explanation. When the trialkylaluminum coordinates to the Salen

oxygen atoms, a five-coordinate aluminum center is formed. Transfer of an ethyl group to the nickel atom results in a more stable four-coordinate tetrahedral aluminum environment. With the dialkylzinc adduct, transfer of an ethyl group would produce a highly reactive coordinatively unsaturated three-coordinate zinc species. Thus, the activation energy for transfer for the alkyl group should be high.

Triethylaluminum also reacts with Co[Salen]I producing Co[Salen]C₂H₅ and, presumably, diethylaluminum iodide. As Co[Salen]C₂H₅ has been characterized, investigation of this system was not continued [22].

In a further study, triethylaluminum was added to a benzene suspension of zinc Salen. Heating the complex for 24 h at 75 °C produced no ligand decomposition. Pale yellow needle-like crystals containing an active ethyl group were isolated. The compound was shown to be identical to the aluminum Salen ethyl compound we reported previously [23]. Apparently an ethylaluminum moiety replaced the zinc atom in the Salen ligand. There was no evidence for dialkylzinc adduct formation analogous to the title complex, but this is not unexpected. Dialkylzinc compounds are unstable to thermal degradation at room temperature [24], thus the conditions employing prolonged high temperatures preclude isolation of an adduct complex.

Conclusions

The reaction of diethylzinc with nickel Salen in benzene (or toluene)/acetonitrile solutions produces the adduct Ni[Salen] · Zn(C₂H₅)₂. The compound was isolated as both a benzene and a toluene solvate, as well as an unsolvated complex. Diffraction data were collected for all three crystal morphologies. None of the compounds diffracted very well; all three adduct structures exhibited high degrees of thermal motion which led to relatively high estimated standard deviations for the bond distances and angles. While the thermal motion is high, the size and shape of the thermal ellipsoids are consistent within themselves and are chemically reasonable for librational motion within the plane of the molecule.

Adduct formation has little effect on the nickel Salen moiety; bond parameters are only slightly perturbed. The diethyl coordination geometry of the diethyl zinc species, however, is drastically altered. The zinc is weakly coordinated to both oxygens of the Salen ligand with a O–Zn–O bond angle of ~ 60 ° and is positioned 0.78 Å above the least-squares plane of the nickel coordination sphere. The C–Zn–C bond angle is 147.9(4) °, a significant perturbation from linearity, and the zinc–carbon distance in the adduct is slightly lengthened (0.04 Å) from that of dimethyl zinc. The zinc–carbon bond is somewhat stabilized by adduct formation in that crystals do not fume in air or react violently with water. The complex is still highly reactive; crystals are visibly decomposed after ten minutes exposure to the atmosphere.

The reactivity of triethylaluminum with other transition metal Salen complexes was also investigated and found to be greater than that of diethyl zinc. Instead of a simple Lewis adduct formation, triethyl aluminum appears to transfer an ethyl group to nickel Salen which leads to eventual ligand decomposition. As mentioned, dialkyl zinc systems have been virtually ignored and further investigations into these sorts of systems should be fruitful.

The following material is available: A complete listing of bond distances for Ni[Salen] · Zn(C₂H₅)₂. A complete listing of bond angles for Ni[Salen] · Zn(C₂H₅)₂,

hydrogen atom coordinates for Ni[Salen] · Zn(C₂H₅)₂. Anisotropic thermal parameters for Ni[Salen] · Zn(C₂H₅)₂, and observed and calculated structure factors for Ni[Salen] · (C₂H₅)₂.

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