5430 *Inorg. Chem.* **1994,** *33,* 5430−5437

Coordination of Dimethyl(aminomethyl)phosphine Oxide with Zinc(II), Nickel(II), and Palladium(II)

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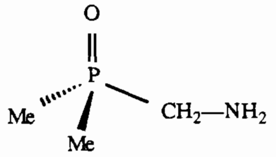
Received February 25, 1994[⊗]

Dimethyl(aminomethyl)phosphine oxide (DMAO) reacts with the zinc halides, giving complexes of different compositions, depending on the reagent ratio, on the halide, and on the order of the addition of the reagents. All three halides give compounds of the composition $ZnX_2(DMAO)$ (X = Cl, Br, I) when a 1:1 reagent ratio is used. An X-ray diffraction study of $ZnBr_2(DMAO)$ shows that this compound is polymeric in the solid state, each zinc ion being coordinated to two bromide ions, the oxygen atom of one DMAO, and the nitrogen atom of another DMAO molecule. The coordination at zinc is distorted tetrahedral. The crystals belong to the space group $P2_1/c$ with $Z = 4$, $a = 8.211(4)$ Å, $b = 12.626(5)$ Å, $c = 9.776(4)$ Å, $\beta = 107.92(4)°$, and $V = 964(1)$ Å^3. The structure was refined to $R = 0.029$ for 1125 reflections. The corresponding chloro and iodo complexes are likely to be isostructural. Acetonitrile solution of the compounds $ZnX_2(DMAO)$ contain mononuclear species which are likely to consist of tetrahedrally coordinated zinc cations bonded to a chelating DMAO molecule and the two anions. Complexes of the compositions $(ZnCl_2)_3(DMAO)_4$ and $ZnX_2(DMAO)_2$ (X = Br, I) are obtained using higher ligand:zinc halide ratios. An X-ray structure determination of the iodo compound shows that the crystal contains polymeric $\{ZnI(DMAO)_2\}^+$ cations and iodide anions. The pseudotetrahedral coordination at zinc is made up of one iodide, the nitrogen atom of a monodentate DMAO, the nitrogen atom of a second DMAO, the latter bridging two zinc ions, and the oxygen atom of a third DMAO molecule, which also bridges two metal ions. The crystals belong to the space group $P2_1/c$ with $Z = 4$, $a = 12.667(1)$ Å, $b = 11.810(2)$ Å, $c = 11.799(1)$ Å, $\beta = 109.91(1)°$, and $V = 1658.7(4)$ Å^3. The structure was refined to $R = 0.028$ for 2604 reflections. Acetonitrile solutions of the compounds $ZnX_2(DMAO)_2$ (X = Br, I) are likely to contain mononuclear four-coordinate species, in which the zinc atoms are bonded to one halide and two DMAO molecules, one of them being monodentate and the other acting as a chelating ligand. The two forms of coordinated DMAO are in rapid equilibrium on the NMR time scale. The preparations of compounds of the compositions $Ni(SCN)_2(DMAO)_2$ and $PdCl_2(DMAO)_2$ are also reported.

Introduction

The synthesis of dimethyl(aminomethyl)phosphine oxide,[1] DMAO (**1**), and its use as a building block for the preparation of polyurethane foams have prompted the investigation of its coordination chemistry. This molecule is a potential bidentate ligand, as phosphine oxides, as well as amines, have good coordinating properties.[2] Ligands of this type are fairly new, and relatively little is known about their coordination chemistry. However, earlier studies described the preparation of a complex formulated as $CuCl_2\{Ph_2P(O)CH_2NH_2{\cdot}HCl\}_2$,[3] and of the related compound $NiCl_2\{Ph_2P(O)CH_2CH_2NH_2{\cdot}HBr\}_2$.[4] More recently, the preparation and characterization of the complexes $CrCl_3(DMAO)_3{\cdot}3H_2O$, $CoX_2(DMAO)_3{\cdot}nH_2O$ (X = Cl, $n = 3$; X = Br, $n = 1$), $NiCl_2(DMAO)_3{\cdot}3H_2O$, and $CuCl_2(DMAO)$,[5] as well



DMAO, 1

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0020-1669/94/1333-5430$04.50/0

Table 1. Preparative Details, Yields, and Melting Points for Zinc, Nickel, and Palladium Complexes of Dimethyl(aminomethyl)phosphine Oxide

no.	compd	prepn procedure[a]	yield, %[b]	solv used for recrystn	mp, °C dec
2	$ZnCl_2(DMAO)$	MeCN or $MeNO_2$, 1:1	92	MeCN or $MeNO_2$	228–228.5
3	$(ZnCl_2)_3(DMAO)_4$	EtOH[c]	96	MeCN, $MeNO_2$ or MeOH	153–154
4	$ZnBr_2(DMAO)$	EtOH, 1:1	97	MeOH or MeCN	243.5–245
5	$ZnBr_2(DMAO)_2$	MeCN, 1:2.2	94	MeCN	136–137
6	$ZnI_2(DMAO)$	EtOH, 1:1	96	MeOH	241–242
7	$ZnI_2(DMAO)_2$	EtOH, 1:2.2	99	EtOH	198–200
8	$Ni(NCS)_2(DMAO)_2$	EtOH, 1:2	89	MeOH	>260
9	$PdCl_2(DMAO)_2$	EtOH, 1:2.2	99	*d*	240–241

[a] Solvent used, reagent ratio. [b] This refers to products before recrystallization. However, analytical data on these samples (see Table 6) show that they are of high purity. [c] This product is obtained irrespective of the reagent ratio used (see Experimental Section). [d] Not recrystallized.

Table 2. ^1H and ^{31}P NMR Chemical Shifts (δ, ppm), Coordination Chemical Shifts ($\Delta\delta = \delta_{complex} - \delta_{free\ ligand}$, Hz) for Dimethyl(aminomethyl)phosphine Oxide Complexes with Zinc Halides

	^1H NMR[a]								^{31}P NMR			
	CH_3 (H_a)				CH_2 (H_b)							
no.	δ	$\Delta\delta$	$^2J_{P,H}$	$\Delta^2J_{H,P}$	δ	$\Delta\delta$	$^2J_{P<H}$	$\Delta^2J_{H,P}$	δ[b]	$\Delta\delta$	δ[c]	$\Delta\delta$
1[d]	1.35		12.21		2.85		6.70		40.5		49.7	
2	1.66	0.31	13.81	1.61	3.16	0.31	5.02	1.68	58.2	17.7	50.9	1.2
3	1.61	0.26	13.48	1.27	3.11	0.26	5.47	1.23	54.4	13.9		
4	1.69	0.34	13.98	1.77	3.17	0.32	4.99	1.71	58.9	18.4		
5	1.53	0.18	13.09	0.88	3.02	0.17	5.75	0.95	51.7	11.2	51.2	1.5
6	1.71	0.36	13.96	1.75	3.18	0.33	4.98	1.72	59.7	19.2	51.7	2.0
7	1.60	0.25	13.83	1.62	3.07	0.22	5.46	1.24	52.3	11.2	51.1	1.4

[a] The ^1H NMR spectra were measured at room temperature in CD_3CN; these signals appear as doublets. [b] Measured in CD_3CN. [c] Measured in CD_3OD. [d] NMR data for DMAO·HCl: ^1H NMR $\delta(CH_3) = 1.35$, $\delta(CH_2) = 2.84$; ^{31}P NMR (in CD_3CN) $\delta = 42.7$. NMR data for DMAO·HBr: ^1H NMR $\delta(CD_3) = 1.36$, $\delta(CH_2) = 2.84$; ^{31}P NMR (in CD_3CN) $\delta = 42.8$.

as $PtCl_2(DMAO)_2$, $PtCl_2L(DMAO)$ (L = NH_3, py), and $PdCl_2(DMAO)_2$,[6] were also reported.

This paper describes the preparation and characterization of complexes of the compositions $ZnX_2(DMAO)$ (X = Cl, Br, I), $(ZnCl_2)_3(DMAO)_4$, $ZnY_2(DMAO)_2$ (Y = Br, I), $Ni(SCN)_2(DMAO)_2$, and $PdCl_2(DMAO)_2$. The X-ray crystal structures of $ZnBr_2(DMAO)$ and $ZnI_2(DMAO)_2$ are also reported.

Complexes of the Type $ZnX_2(DMAO)$

Results. Dimethyl(aminomethyl)phosphine oxide (DMAO) reacts with the zinc halides, giving colorless complexes of the composition $ZnX_2(DMAO)$ (X = Cl, Br, and I; **2**, **4**, and **6**, respectively), in high yields, when 1:1 reagent ratios are used. Care must be taken to add DMAO to the zinc salt, as reversing the order of addition of the reagents produces complexes richer in DMAO (see below). The compounds obtained, as well as preparative details and some properties, are given in Table 1. The complexes are soluble in water, but these solutions immediately give silver halide precipitates upon addition of silver nitrate solutions. The complexes are moderately soluble in methanol, ethanol, acetonitrile, and nitromethane but are insoluble in chlorinated hydrocarbon solvents.

Molecular weight determinations in CH_3CN give values in agreement with a mononuclear formulation. However, the corresponding values for $ZnCl_2(DMAO)$ and $ZnI_2(DMAO)$ in CH_3OH are about half those calculated for the corresponding monomeric formulations.

The ^1H and ^{31}P NMR data for these complexes are listed in Table 2. The coordination chemical shifts, $\Delta\delta$ ($\delta_{complex} - \delta_{free\ ligand}$), also given in this table, provide valuable information about the nature of the species present in solution.

The ^{31}P NMR spectra of complexes **2**, **4**, and **6**, in CD_3CN, show that the P—O—groups are coordinated to zinc as the $\Delta\delta$(^{31}P) values of the above compounds are 17.7, 18.4, and 19.2 ppm, respectively. However, ^{31}P NMR measurements in CD_3OD show that, in this solvent, the O-donor of DMAO is unlikely to be coordinated to zinc, as the $\Delta\delta$(^{31}P) values for **2** and **6** are only 1.2 and 2 ppm, respectively.

Coordination chemical shifts ranging from 0.31 to 0.36 ppm are also observed for the CH_3 and CH_2 groups in the ^1H NMR spectra of **2**, **4**, and **6**. Furthermore, the ^{15}N NMR spectra of $Me_2P(O)CH_2{}^{15}NH_2$, DMAO-^{15}N, and $ZnBr_2$(DMAO-^{15}N) in CD_3CN give the values 4.59 and 12.34 ppm, respectively, corresponding to a ^{15}N-coordination chemical shift of *ca.* 8 ppm.

DMAO coordination also causes changes in the values of the $^2J_{P,H}$ coupling constants for the CH_3 and CH_2 groups, the coordination coupling constant, ΔJ ($J_{complex} - J_{free\ ligand}$) ranging from 1.61 to 1.75 Hz.

The infrared spectra of complexes $ZnX_2(DMAO)$ were recorded in KBr pellets, and some significant data are summarized in Table 3. The spectra of the complexes **2**, **4**, and **6**, in the frequency range 4000–300 cm^{-1}, are almost identical. In the solid state, in the P—O stretching region, free DMAO shows a strong band at 1165 cm^{-1} accompanied by a shoulder at 1130 cm^{-1}. For the above complexes, these absorptions are shifted to lower energies by *ca.* 40 cm^{-1}. A change of halide does not result in significant band shifts although the P—O stretch of the chloro complex is sharper than those of the other two complexes.

The infrared spectrum of $ZnBr_2(DMAO)$ (**4**) and that of the corresponding iodide, **6**, were also recorded in CH_3CN solution. As can be seen from the data given in Table 3, in this medium, the P=O stretching frequencies, occurring at 1113 and 1111 cm^{-1}, respectively, differ from those for the free ligand (1730 cm^{-1}); i.e., shifts of *ca.* 60 cm^{-1} are observed. These differences are larger than those (*ca.* 40 cm^{-1}) found in the solid state.

The infrared spectra of complexes **2**, **4**, and **6**, in the region of the N—H stretching vibrations are more complex. The data

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Table 3. Infrared Data (cm^{-1}) for Dimethyl(aminomethyl)phosphine Oxide, Its Complexes with Zinc Halides, and Related Compounds[a]

no.	P—O str	Δ(P—O)[b]	CH_3—P str	N—H str
1	1165 s, 1130 sh		1295 m	3250, 3290, 3350
	(1173)		(1286)	(3156, 3335, 3390)
2	1125 s, 1140 sh	35	1305 m, 1315 sh	3140, 3230, 3280
3	1125 s, 1150 s	35	1300 m, 1315 m	3125, 3175, 3230, 3250, 3280
4	1120 s, 1140 sh	40	1302 s, 1315 m	3140, 3220, 3270
	(1113, 1179)	(60)	(1296)	(3156, 3195, 3269, 3317, 3384)
5	1125 s, 1155 sh	35	1295 s, 1305 m	3050, 3150, 3225, 3260 sh
6	1120 s, 1140 sh	40	1300 s, 1310 m	3120, 3205, 3250
	(1111, 1178)	(62)	(1295)	(3076, 3159, 3268, 3308)
7	1125 s, 1160 s	35	1290 m, 1300 m	3045, 3110, 3165, 3210 sh, 3250 sh
8	1075 sh, 1130 s	45	1295 sh, 1305 m	3180, 3270, 3310
9	1135 s, 1165 s	25	1290 m, 1300 m	3080, 3210

[a] The spectra were recorded in KBr pellets. (Values in parentheses refer to the spectra measured in MeCN solution.) [b] Δ(P—O) gives the shift of the main P—O bands after coordination.

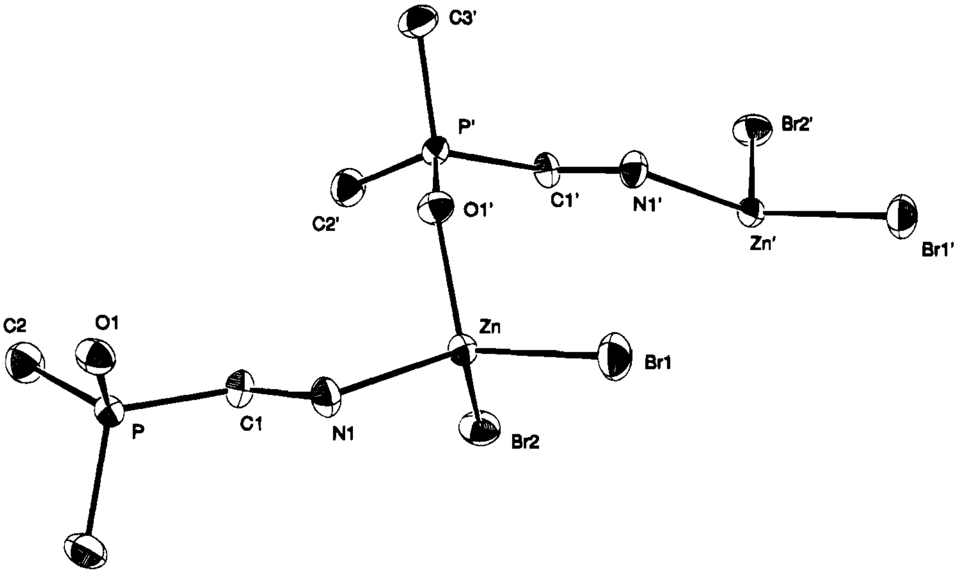

Figure 1. ORTEP view of two monomeric units in $\{ZnBr_2(DMAO)\}_n$ (**4**) (primed atoms are related to those unprimed by the symmetry operation $x, {}^1/_2 - y, z - {}^1/_2$).

recorded in the KBr pellets will be discussed first. All three complexes show three bands in this region (see Table 3), the first between 3120 und 3140 cm^{-1}, the second between 3205 and 3230 cm^{-1}, and the third between 3250 and 3280 cm^{-1}, the lower values for all three bands being found for the iodo complex. As the free DMAO ligand, **1**, in this region, shows three bands at 3250, 3290, and 3350 cm^{-1}, the spectra of the above complexes show the expected shifts to lower energy of the N—H vibrations following coordination.[7]

However, the IR spectra of the above complexes, in this region, when recorded in CH_3CN, show a larger number of bands, 5 for **2** and **4** and 4 for **6**.

X-ray Crystal Structure of $ZnBr_2(DMAO)$], (4). The structure of this complex consists of parallel polymeric chains containing [—Zn(Br_2)—O—PMe_2—C—N—] repeating units. An ORTEP view of two of these units is shown in Figure 1, and a selection of bond distances and angles is given in Table 4.

The coordination at the zinc atom is distorted tetrahedral, the donor atoms being the two bromine atoms, the oxygen atom of one DMAO, and the nitrogen atom of another DMAO.

The Zn—Br distances (2.341(1) and 2.387(1) Å) are typical for tetrahedral complexes of this metal center, as the 22 complexes containing Zn—Br bonds in a tetrahedral environment, found through a literature search,[8] have an average distance of 2.39(±0.06) Å. The presence of Zn—Br bonds of different lengths has also been previously observed, e.g., in the related complex $[CoCl_2(Bz_3PO)_2]$[9] (Co—Cl = 2.255(3) and 2.249(3) Å).

Table 4. Selected Bond Distances (Å) and Angles (deg) in $\{ZnBr_2(DMAO)\}_n$ (**4**)

Zn—Br1	2.341(1)	P—C1	1.817(5)
Zn—Br2	2.387(1)	P—C2	1.765(7)
Zn—O1	1.968(4)	P—C3	1.791(6)
Zn—N1	2.047(4)	C1—N	1.487(7)
P—O1	1.509(4)		
Br1—Zn—Br2	113.53(4)	Br2—Zn—O1	107.8(1)
Br1—Zn—N1	116.7(1)	N1—Zn—O1	102.3(2)
Br1—Zn—O1	106.5(1)	Zn—N1—C1	113.6(3)
Br2—Zn—N1	108.9(1)	Zn—O1—P	134.6(2)

The Br—Zn—Br angle (113.53(4)°) is larger than the tetrahedral value. This is normal for pseudotetrahedral complexes of the type $[MX_2L_2]$, as this angle is 116.6(1)° in $[ZnBr_2(Ph_3PO)_2]$,[10] 114.0(1)° in $[CoCl_2(Ph_3PO)_2]$,[11] and 113.0(1)° in $[CoCl_2(Bz_3PO)_2]$.[9]

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The Zn—N distance in $ZnBr_2(DMAO)$, 2.047(4) Å,[10] is also normal. A literature search[8] for four-coordinate zinc complexes with primary amines gave, for 12 entries, a mean Zn—N distance of 2.032(±0.059) Å.

The Zn—O distance (1.968(4) Å) also falls within the expected range, as indicated by that in $[ZnBr_2(Ph_3PO)_2]$[10] (1.97(1) Å). The former value is also in agreement with the calculated Zn—O distance (*ca.* 1.95 Å) obtained by adding the difference between the ionic radii of four-coordinate Co^{2+} and Zn^{2+} (0.58 and 0.60 Å, respectively)[12] to the average of the Co-O distances in $[CoCl_2(Bz_3PO)_2]$ (1.937(7) and 1.920(6) Å).[9] On the other hand, if one uses the Co—O distances in $[CoCl_2(Ph_3PO)_2]$ (1.977(7) and 2.001(7) Å), one obtains a calculated Zn—O distance of *ca.* 2.01 Å.

The angle between the uncharged donors in **4**, i.e., O—Zn—N (102.35(2)°), is smaller than the tetrahedral value, as has been previously observed in complexes of the type $[MX_2L_2]$. Thus the O—Zn—O angle in $[ZnBr_2(Ph_3PO)_2]$[10] is 100.9(4)° while the O—Co—O angles in $[CoCl_2(Bz_3PO)_2]$[9] and $[CoCl_2(Ph_3PO)_2]$[11] are 104.9(3) and 96.4°, respectively.

Summing up, despite the polymeric nature of the complex, the coordination polyhedron at zinc exhibits no unusual feature.

Discussion. The most striking structural feature of $ZnBr_2(DMAO)$ (**4**) is its polymeric nature in the solid state. However, the preference for the formation of tetrahedral coordination at this metal center and, consequently, of LMX bond angles of *ca.* 109° hinders the formation of a complex containing a chelating DMAO molecule. Furthermore, the lability of this complex in solution, and solubility factors, may also be responsible for the formation of a polymeric compound in the solid state.

This result raises two questions: (1) do the corresponding chloride, $ZnCl_2(DMAO)$ (**2**), and iodide, $ZnI_2(DMAO)$ (**4**), have similar structures in the solid state and (2) what species are formed when **2**, **4**, and **6** are dissolved in CH_3CN? For this purpose it is best to start by discussing the IR spectra as they were recorded both in the solid state and in solution.

As indicated above, the solid state spectra of the three complexes **2**, **4**, and **6** are practically identical in the range 4000—400 cm^{-1}, and thus one can postulate that, in this state, the zinc atoms in **2** and **6** have the same type of coordination polyhedron as in **4**.[13]

The coordination environment at zinc in these complexes in solution is more difficult to establish. However, keeping in mind that at least two of these complexes, **2** and **6** and, presumably, also **4**, are monomeric in acetonitrile solution, one must assume that during the process of dissolution either Zn—O or Zn—N bonds have been broken.

Furthermore, the immediate formation of silver halide from aqueous solutions of complexes **2**, **4**, and **6** shows that, in this medium, also the Zn—X bonds have been solvolyzed. Furthermore, given the low values obtained from the molecular weight determinations of **2**, **4**, and **6** in methanol, partial solvolysis must have occurred also in this solvent. Thus only the data obtained for acetonitrile solutions will be discussed.

The most striking feature of these spectra is their great complexity. Comparison of the P—O stretches for **2**, **4**, and **6**, in CH_3CN solution and in the solid state, indicates that the oxygen atoms remain bonded to zinc in solution. The infrared bands due to the NH_2 groups of the three complexes, in CH_3CN solution, are also quite informative. As can be seen in Figure 2, $ZnBr_2(DMAO)$ in this solvent shows two sets of two bands, the first pair being more intense and appearing at higher energy than the other. This pattern is similar to that observed by Chatt *et al.*[14] in platinum(II) complexes of the type *trans*-$[PtCl_2LL']$ where L is a primary amine. For these compounds the higher energy pair of bands was assigned to the stretching vibrations of the coordinated amine and the lower energy pair of bands to the same amine which, in addition to being coordinated to platinum, is also hydrogen-bonded either to the coordinated halide of another molecule or to a donor solvent. Thus, the spectral pattern and the positions of the band maxima indicate that, in the above zinc—DMAO complexes, also the amine nitrogen remains coordinated in acetonitrile solution.

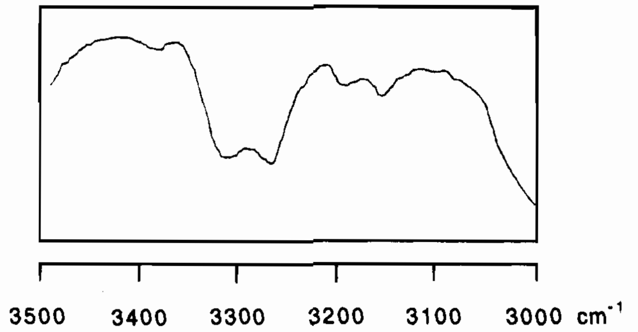

Figure 2. Infrared spectrum of an acetonitrile solution of $ZnBr_2(DMAO)$ (**4**) in the Region 3000—3500 cm^{-1}.

This assignment is confirmed by the ^{15}N NMR of the ^{15}N-enriched ligand, DMAO-^{15}N, and of the complex $[ZnBr_2(DMAO\text{-}^{15}N)]$, recorded in CD_3CN. As mentioned earlier, the free ligand resonance at 4.59 ppm shifts to 12.34 ppm in the spectrum of the above complex. Therefore, these data and the coordination chemical shifts of the ^{31}P and ^{1}H resonances are best interpreted by postulating the formation of an O—Zn—N chelate ring in complexes of this class.

Finally, as molecular weight determinations show that the two halides do not dissociate in CH_3CN, if one assumes that the coordination number of zinc remains 4, as found in the solid state, the structure of complexes of this type in CH_3CN is likely to be pseudotetrahedral with an NOX_2-donor set and chelating DMAO.

Zinc Complexes with Higher Ligand Ratios

Results and Discussion. The reactions of zinc halides with DMAO, in 1:2 ratios, give solids whose compositions vary with the halide. Thus, $ZnCl_2$ gives a product of composition $(ZnCl_2)_3(DMAO)_4$, while the solid obtained using $ZnBr_2$ and ZnI_2 gives microanalytical data fitting the composition $ZnX_2(DMAO)_2$ (X = Br, I). Some preparative details and properties are given in Table 1.

The iodo complex $ZnI_2(DMAO)_2$ will be considered first, as its X-ray crystal structure was determined.

X-ray Crystal Structure of $ZnI_2(DMAO)_2$ (7). The structure of this complex consists of polymeric $\{ZnI(DMAO)_2\}^+$ cations and iodide counterions. An ORTEP view of two monomeric units is given in Figure 3, and a selection of bond distances and angles is given in Table 5. The backbone of the polymeric chains consists of {Zn—O—P—C—N} repeating units. A fragment, consisting of two of them, i.e., —P2—O24—Zn—N21—C21—P2′—O24′—Zn′—N21′—, is shown in Figure 3. The

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(13) A preliminary X-ray crystallographic study of $[ZnCl_2(DMAO)]$ showed that the crystals are monoclinic of space group $P2_1/c$ with cell constants a = 7.975(5) Å, b = 12.312(2) Å, c = 9.615(6) Å, β = 109.12(4)°, and V = 892.0 Å^3. Given these values and those for the corresponding bromo complex, it is likely that the chloro and bromo complexes are isomorphous and isostructural.

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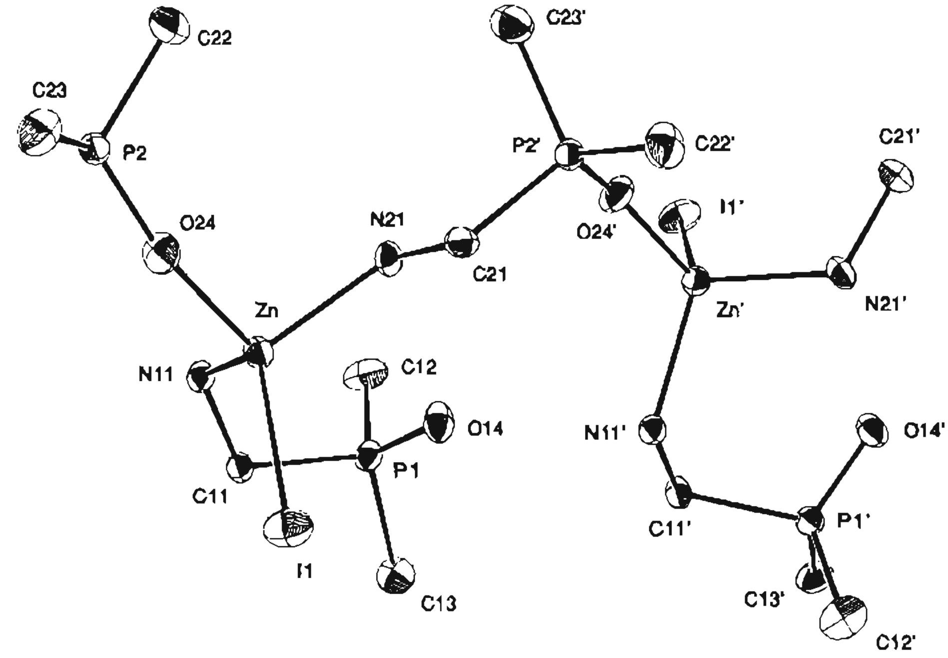


Figure 3. ORTEP view of two monomeric units in $\{ZnI(DMAO)_2^+\}_n$ (7) (primed atoms are related to those unprimed by the symmetry operation x, $^1/_2 - y$, $z - {}^1/_2$).

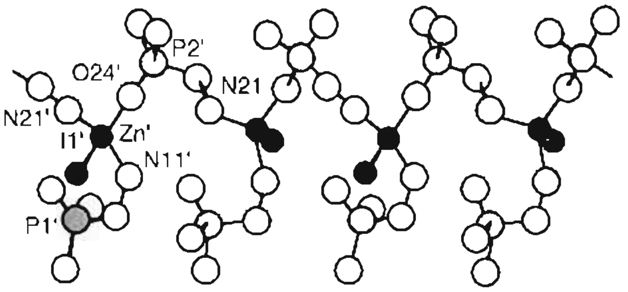


Figure 4. view of part of the polymeric unit $\{ZnI(DMAO)_2^+\}_n$ showing the isotactic arrangement of the monoligated DMAO molecules.

Table 5. Selected Bond Distances (Å) and Angles (deg) in $\{ZnI(DMAO)\}_nI_n$ (7)

Zn—I1	2.516(1)	P1—C12	1.773(5)
Zn—N11	2.049(3)	P1—C13	1.787(4)
Zn—N21	2.039(3)	P2—C22	1.785(4)
Zn—O24	1.950(3)	P2—C23	1.769(4)
P1—O14	1.488(3)	C11—N11	1.483(4)
P2—O24	1.501(3)	C21—N21	1.485(4)
P1—C11	1.811(3)		
I1—Zn—N11	113.80(8)	N21—Zn—O24	101.5(1)
I1—Zn—N21	115.84(9)	N11—Zn—O21	105.7(1)
I1—Zn—O24	109.74(9)	Zn—N—C	115.7(2) (av)
N11—Zn—O24	109.5(1)	Zn—O—P	157.4(2)

pseudotetrahedral coordination at each zinc ion is completed by one iodide ion and the nitrogen atom of a monodentate DMAO molecule, i.e., that containing N11—C11—P1—O14, in Figure 3. Interestingly, the monoligated DMAO molecules are placed along the chain in an isotactic arrangement which is clearly visible in Figure 4.

The bond distances and angles are comparable to those found in the structures of other complexes of the same ligand with two exceptions: (1) the P—O bond in the monodentate ligand, where the oxygen atom is not coordinated to zinc, is shorter than that in the bridging DMAO molecule (1.488(3) and 1.501(3) Å, respectively) and (2) the Zn—O—P angle is much larger (157.4(2)°) than that in the bromo complex 4 (134.6(2)°).

Although the donor set in compound 7 (N_2OI) differs from that in 4 ($NOBr_2$), the patterns of bond angles at zinc in both cases are remarkably similar, the smaller angles in both cases being N—Zn—O (102.3(2) and 101.5(1)°, respectively).

Infrared and NMR Data. The structural data for 7 can be used for the interpretation of the IR and NMR data. The IR spectra of $\{ZnI_2(DMAO)\}_n$, (6) and $\{ZnI(DMAO)_2\}_nI_n$ (7) in the solid state show several differences, the most noticeable of them being the different number of bands. In the region 3700–2700 cm^{-1} the spectrum of the mono-DMAO complex 6 shows two strong bands at 3250 and at 3203 cm^{-1} (presumably the N—H stretches) and three medium bands at 3122, 2980, and 2905 cm^{-1}, the latter two being assigned to C—H vibrations. In the di-DMAO complex, 7, the bands due to the CH vibrations shift to 2960 and 2900 cm^{-1}. Furthermore, the major bands assignable to the NH_2 groups occur at 3182 and 3042 cm^{-1} and are accompanied by two lower intensity bands at 3210 and 3115 cm^{-1}. One also observes a shoulder at 3250 cm^{-1}. Thus, also these spectral data indicate that there are two kinds of coordinated amines, one similar to that in the 1:1 complex and a second more strongly bonded than the first. The dual nature of DMAO coordination is shown also by the P—O stretches: While for the 1:1 complex one observes a broad band at 1126 cm^{-1} and a sharp peak on its high-energy side at 1140 cm^{-1} in RbI, for the 1:2 complex two distinct P—O stretching vibrations at 1125 and 1160 cm^{-1} are observed. It is noteworthy that the higher energy band occurs where the free ligand absorbs, consistent with the presence of an uncoordinated phosphine oxide group.

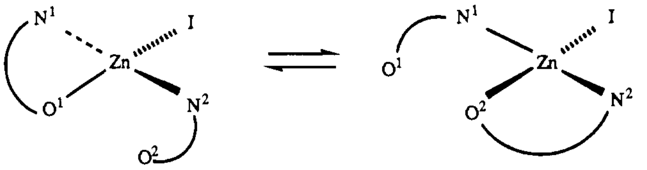
The low solubility of $\{ZnI(DMAO)_2\}_nI_n$ (7) in suitable solvents (e.g., acetonitrile) prevented recording the infrared spectrum in solution; only the molecular weight and the ^1H and ^{31}P NMR spectra in CD_3CN could be measured. The ^{31}P NMR spectral data, recorded in this solvent, show that the coordination environments at the zinc atoms in $ZnI_2(DMAO)_2$ (7) and $ZnI_2(DMAO)$ (6) differ also in solution. Thus their $\delta(^{31}P)$ resonances occur at 52.3 and 59.7 ppm, respectively, the former value being closer to that found for the free ligand (40.5 ppm in CD_3CN). As mentioned earlier, the zinc atom in the mono-DMAO complex 6 in CH_3CN solution has been assigned a pseudotetrahedral structure with an NOI_2 donor set and chelating DMAO. Thus, the $\delta(^{31}P)$ value for the di-DMAO complex 7

Table 6. Analytical Data and Molecular Weights for Complexes of DMAO with Zinc(II), Nickel(II), and Palladium(II)

		anal.,[a] %						mol wt[a]	
no.	compd	C	H	X[b]	N	P	M[c]	in MeOH	in MeCN
2	$ZnCl_2(DMAO)$	14.95	4.13	29.01	5.90	12.99	26.35	118.0	243
		(14.89)	(4.14)	(29.13)	(5.78)	(12.73)	(26.86)	(243.4)	
3	$(ZnCl_2)_3(DMAO)_4$	17.21	4.61	25.78	6.68	14.98	23.09		
		(17.21)	(4.81)	(25.40)	(6.69)	(14.79)	(23.42)		
4	$ZnBr_2(DMAO)$	10.95	3.14	48.37	4.32	9.29	19.38		
		(10.84)	(3.03)	(48.09)	(4.22)	(9.32)	(19.68)		
5	$ZnBr_2(DMAO)_2$	16.97	4.35	35.74	6.63	14.09	14.46		
		(16.40)	(4.59)	(36.37)	(6.37)	(14.09)	(14.88)		
6	$ZnI_2(DMAO)$	8.50	2.34	59.48	3.29	7.42	15.14	190.0	406
		(8.45)	(2.36)	(59.54)	(3.29)	(7.26)	(15.34)	(426.3)	
7	$ZnI_2(DMAO)_2$	13.49	3.80	46.97	5.23	11.43	12.14	163	305
		(13.51)	(3.78)	(47.59)	(5.25)	(11.61)	(12.25)	(533.4)	
8	$Ni(SCN)_2(DMAO)_2$	24.37	5.14		14.63	15.55	15.01		
		(24.69)	(5.18)		(14.40)	(15.09)	(15.09)		
9	$PdCl_2(DMAO)_2$	18.95	5.25	17.95	7.17				
		(18.40)	(5.15)	(18.11)	(7.16)				

[a] Calculated values are given in parentheses. [b] Halogen content. [c] Metal content.

in solution could be indicative of a dynamic equilibrium between a form in which both DMAO molecules are chelated and another in which at least one of these ligands is monodentate and bonded to zinc, as found in the solid state. Taking into account (1) the molecular weight data for **7** in CH_3CN (see Table 6), which are consistent with the presence of two particles in solution, (2) the solid state structure which shows the presence of $\{ZnI(DMAO)_2\}_n^+$ and I^- ions, and (3) the studies of $ZnBr_2(DMAO)$, both in solution and in the solid state, which show the presence of chelated DMAO in solution and bridging DMAO in the solid state, one could postulate that equilibria of the type occur in



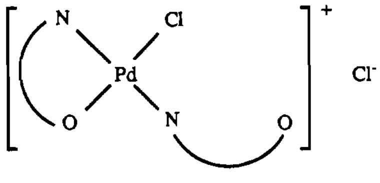
CH_3CN solutions of **7**. The ^1H NMR spectrum of $ZnI_2(DMAO)_2$ also supports this interpretation (see Table 2): both the values of $\delta(H_a)$ (1.60 ppm) and $\delta(H_b)$ (3.07 ppm) move toward the corresponding resonances for the free ligand (1.35 and 2.85 ppm, respectively).

The infrared spectra of the chloro and bromo complexes **3** and **5**, respectively, as found for those of $ZnI_2(DMAO)_2$, (**7**), show more bands than those of the corresponding 1:1 complexes. It can then be presumed that the solid state structures of **3** and **5** are related to that of $ZnI_2(DMAO)_2$.

With regard to the solution data, only ^1H and ^{31}P NMR measurements could be carried out on **3** and **5** because of solubility problems. The NMR data (see Table 2) show that the relationships between the iodo complexes **6** and **7** also exist between (1) $(ZnCl_2)_3(DMAO)_4$ and $ZnCl_2(DMAO)$ and (2) $ZnBr_2(DMAO)_2$ and $ZnBr_2(DMAO)$. Therefore, similar conclusions can be drawn about the structures of **3** and **5** in solution; i.e., both monodentate and chelating DMAO molecules are present and there is fast exchange between two bonding modes on the NMR time scale.

Nickel and Palladium Complexes. Nickel thiocyanate reacts with DMAO, giving a pale blue complex of composition $Ni(SCN)_2(DMAO)_2$. Its color is indicative of high-spin octahedral coordination. Its infrared spectrum (see Table 3) shows that the NH_2 groups are bonded to nickel, as its spectral pattern in the appropriate region is almost identical with that of $ZnBr_2(DMAO)$, where there is X-ray evidence of $Zn—NH_2$ bonding. Furthermore, the nickel complex shows a double band centered at 2100 cm^{-1} (with a splitting of *ca.* 15 cm^{-1}) which is indicative of the presence of S-bonded thiocyanate. The other major feature is the presence of two bands in the P—O region, one at 1130 cm^{-1} with a shoulder on the low-energy side and another at 1075 cm^{-1} with a slight shoulder on the high-energy side. The position of the first band is somewhat lower than those found for the zinc complexes and that of the second is much lower, i.e., 85 cm^{-1}, relative to that for the free ligand. However, low-energy shifts of P—O bands on complex formation of as much as 300 cm^{-1} have been reported.[2] Thus, these bands may be associated with the presence of two DMAO ligands. If one assumes that this complex is mononuclear in the solid state, both the splitting of the $\nu(CN)$ and the presence of two P—O stretching vibrations might indicate that this complex has an octahedral structure with two chelating organic ligands.

Finally, the infrared spectrum of the palladium(II) complex $PdCl_2(DMAO)_2$ in the solid state shows that the amine functions are coordinated to the metal atom and that one of the P—O donor groups is likely to be coordinated and the other free. On the basis of these observations and on the assumption that palladium(II) in this complex shows the usual square planar geometry, one arrives at the unexpected conclusion that this complex could have either the following structure or its isomeric form, in which the N-bonded DMAO is in *trans* position to the O-donor of the chelated DMAO.



Experimental Section

Instrumentation. Proton NMR spectra were recorded on a Bruker WM 250 spectrometer, ^{31}P spectra on a Bruker HX90 spectrometer, and ^{15}N spectra on a Bruker AMX 500. The reference for ^{15}N is liquid NH_3. Melting points were determined on a Büchi SMP 20 apparatus and are uncorrected. Solid state IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer, while the solution spectra were recorded on a Perkin-Elmer 883 spectrometer. Elemental C, H, N, and halogen analyses were performed at the Mikrolabor-ETH Zürich, while the P and metal determinations were carried out by the Analytical Section of the Laboratorium für Anorganische Chemie der ETH Zürich by inductively-coupled plasma emission using the IL Plasma 200 instrument of Allied Analytical Systems, Andover, MA. The Analytical

Table 7. Experimental Data for the X-ray Diffraction Studies of $ZnBr_2(DMAO)$ (**4**) and $ZnI_2(DMAO)_2$ (**7**)

	4	**7**
chem formula	$C_3H_{10}Br_2NOPZn$	$C_6H_{20}I_2N_2O_2P_2Zn$
mol wt	332.28	533.35
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	8.211(4)	12.667(1)
b, Å	12.626(5)	11.810(2)
c, Å	9.776(4)	11.799(1)
β, deg	107.92(4)	109.91(1)
Z	4	4
V, Å^3	964(1)	1658.7(4)
ϱ(calcd), g cm^{-3}	2.738	3.283
μ, cm^{-1}	109.23	82.713
T, °C	23	23
λ, Å (graphite monochromated, Mo Kα)	0.710 69	
transm coeff	0.9996−0.7757	0.9987−0.6406
R_a	0.029	0.028
$R_w{}^b$	0.035	0.040
GOF^c	1.136	1.530

[a] $R = \sum||F_o| - (1/k)|F_c||/\sum|F_o|$. [b] $Rw = |\sum_w(|F_o| - (1/k)|F_c|)^2/\sum_w|F_o|^2]^{1/2}$ where $w = [\sigma^2(F_o)]^{-1}$ and $\sigma(F_o) = [\sigma^2(F_o{}^2) + f^2(F_o{}^2)^2]^{1/2}/2F_o$. [c] $\mathrm{GOF} = [\sum w(|F_o| - (1/k)|F_c|)^2/(n_o - n_v)]^{1/2}$.

Table 8. Final Postional Parameters and Equivalent Isotropic Temperature Factors for **4**

atom	x	y	z	B,^{a} Å^2
Br1	0.73715(9)	0.17718(7)	0.94338(7)	4.23(2)
Br2	0.2598(1)	0.07822(5)	0.77773(7)	3.76(2)
Zn	0.46048(9)	0.17587(6)	0.96379(6)	2.50(1)
P	0.2435(2)	0.1139(1)	1.3432(1)	2.26(3)
O1	0.3838(5)	0.1757(3)	1.4493(4)	2.78(9)
N1	0.4376(6)	0.1307(4)	1.1581(5)	2.8(1)
C1	0.2585(7)	0.1323(5)	1.1631(5)	2.5(1)
C2	0.0355(9)	0.1550(6)	1.3355(7)	3.7(2)
C3	0.2626(9)	−0.0241(5)	1.3874(6)	3.5(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Section also carried out the molecular weight determinations (see Table 6) by vapor pressure osmometry using a Corona 117 instrument of Corona Electric Co. Ltd., Katsuta, Japan.

Starting Materials. The ligand DMAO[1] and the complexes $[PdCl_2(MeCN)_2]$ and $[PdCl_2(PhCN)_2]$[15] were prepared as described in the appropriate references. Nickel thiocyanate was obtained by reacting $NiCl_2$ with KSCN in ethanol as described elsewhere.[16] The other materials were commercial products and were used as obtained.

Syntheses. General Procedure. The appropriate amount of a 0.2 M solution of DMAO was added to the required amount of 0.2 M solution of the metal salt. The solvent and reagent proportions used in each case are given in Table 1. The mixture was stirred at room temperature for *ca.* 5 h. and the solid filtered off, washed with the solvent used, and dried. Elemental analytical data are collected in Table 6. The products thus obtained were recrystallized from the hot solvent given in Table 1. When the order of addition of the reagents was reversed, one obtained complexes richer in DMAO, irrespective of the MX_2:DMAO ratio used. This procedure was used for complexes **1**−**8**, while **3** was prepared as described below.

$[PdCl_2(DMAO)_2]$ (9). A solution of DMAO (0.95 g, 8.9 mmol), in ethanol (15 mL) was added to a stirred suspension of $[PdCl_2(MeCN)_2]$ (1.04 g, 4 mmol). Stirring was continued for *ca.* 40 h, the lemon-yellow solid was filtered off, washed twice with *ca.* 20 mL of EtOH, and dried. The same product was obtained using $[PdCl_2(PhCN)_2]$.

^{15}N-Labeled DMAO was prepared as described by Varbanov *et al.*[2] using, as a starting material, nitrogen-15-enriched (92% atom % ^{15}N) potassium phthalimide from Bio-Rad Laboratories (Richmond, CA).

Table 9. Final Positional Parameters and Equivalent Isotropic Temperature Factors for **7**

atom	x	y	z	B,^{a} Å^2
I1	0.80512(3)	−0.51937(3)	0.88682(3)	3.542(7)
I2	0.69806(3)	0.04618(3)	0.85783(3)	3.576(7)
Zn	0.74170(4)	−0.31747(4)	0.88666(4)	2.171(9)
P1	0.99076(8)	−0.1965(1)	0.82853(9)	2.16(2)
P2	0.52812(8)	−0.2569(1)	0.98789(9)	2.16(2)
O14	0.8971(2)	−0.2459(3)	0.7270(3)	3.21(7)
O24	0.6185(3)	−0.3103(3)	0.9503(3)	3.28(7)
N11	0.8669(3)	−0.2092(3)	0.9820(3)	2.11(7)
N21	0.6704(3)	−0.2450(3)	0.7211(3)	2.38(7)
C11	0.9794(3)	−0.2309(4)	0.9736(3)	2.27(8)
C12	0.9969(4)	−0.0468(5)	0.8205(5)	4.0(1)
C13	1.1262(4)	−0.2485(5)	0.8387(4)	3.2(1)
C21	0.5903(4)	−0.3175(4)	0.6284(4)	2.53(9)
C22	0.4425(4)	−0.1582(5)	0.8812(4)	3.8(1)
C23	0.4364(4)	−0.3585(5)	1.0140(5)	3.7(1)
H11A	0.998(4)	−0.314(5)	0.984(5)	5(1)*
H11B	1.032(4)	−0.190(4)	1.032(4)	3(1)*
H12A	0.940(5)	−0.021(5)	0.830(6)	6(2)*
H12B	1.044(7)	−0.021(7)	0.852(7)	9(2)*
H12C	1.005(6)	−0.016(5)	0.747(5)	5(1)*
H13B	1.142(4)	−0.229(5)	0.754(4)	3(1)*
H13C	1.125(4)	−0.316(5)	0.839(5)	4(1)*
H13A	1.173(4)	−0.217(5)	0.902(5)	4(1)*
H21A	0.539(6)	−0.376(6)	0.654(6)	8(2)*
H21B	0.644(6)	−0.371(7)	0.614(7)	10(2)*
H22B	0.403(5)	−0.202(6)	0.813(6)	7(2)*
H22A	0.495(5)	−0.094(5)	0.875(6)	6(2)*
H22C	0.390(5)	−0.140(6)	0.912(6)	7(2)*
H23A	0.374(4)	−0.299(4)	1.039(4)	3(1)*
H23C	0.471(5)	−0.400(5)	1.071(5)	5(2)*
H23B	0.401(4)	−0.395(4)	0.950(4)	3(1)*

[a] Starred values are for atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

DMAO·HX (X = Cl or Br) was prepared as follows: To some definite quantitiy of amine was added the equivalent quantity of an aqueous solution of HCl or HBr. After evaporation of the solvent, the residue was washed with absolute ethanol and dried over P_2O_5 in solid paraffin.

$ZnBr_2$(DMAO-^{15}*N*) was prepared using the general procedure described above (see Table 1).

Crystallography

Crystals of $ZnBr_2(DMAO)$ (**4**) suitable for X-ray diffraction were obtained by crystallization from methanol, while those of $ZnI_2(DMAO)_2$, (**7**) were obtained from ethanol. Air-stable crystals of both compounds were mounted on glass fibers, at random orientations, on an Enraf-Nonius CAD4 diffractometer for unit cell and space group determination and for data collection. Unit cell dimensions were obtained by least squares fits of the 2θ values of 25 high-order reflections using the CAD4 centering routines. Selected crystallographic and other relevant data are listed in Table 7 and in supplementary table S1.

Intensities were collected using a variable scan speed to ensure constant statistical precision. Three standard reflections, measured every hour, were used to check the stability of the crystals and of the experimental conditions. The orientations of the crystals were checked by measuring three standards every 300 reflections. Data have been corrected for Lorentz and polarization factors using the data reduction programs of the SDP package.[17] Empirical adsorption corrections were applied by using azimuthal (Ψ) scans of four high-χ angle reflections ($\chi > 87°$, $6.4 < \theta < 12.9°$ for **4** and $\chi > 88°$, $5.7 < \theta < 17.3°$ for **7**). Intensities were considered as observed if $|F_o| > 2.0\sigma|F|$ for **4**, while a 3.0σ cutoff was applied to the data for **7**.

The structures were solved by a combination of Patterson and Fourier methods and refined by full matrix least-squares techniques[17] (the

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(15) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science: London, 1973; p 462.

(16) Schaeffer, W. D.; Rea, A. E. U.S. Pat. 3020123, 1962; Chem Abstr. **1962**, *57*, 1855b.

(17) *Enraf-Nonius Structure Determination Package, SDPD*; Enraf-Nonius: Delft, Holland, 1987.

function minimized being $\Sigma[w(F_o - 1/kF_c)^2]$). No extinction correction was applied. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[18]

For the refinement of the structure of **4**, anisotropic temperature factors were used for all atoms. The contribution of the hydrogen atoms in calculated positions (C—H = 0.95 Å, B(H) = 5.0 Å^2) was taken into account but not refined. Final atomic coordinates and equivalent thermal factors for **4** are given in Table 8.

The refinement of **7** was carried out as above, using anisotropic temperature factors for all atoms except the hydrogens. The latter were refined isotropicallly.

Final atomic coordinates and equivalent thermal factors for **7** are given in Table 9.

Acknowledgment. The authors express their thanks to the Swiss National Science Foundation, the Swiss Federal Bureau of Sciences and Education, and the National Foundation for Scientific Research of Bulgaria for financial support, Dr. L. F. Rhodes for the NMR measurements, and Professor P. S. Pregosin for much valuable discussion.

Supplementary Material Available: Tables giving full experimental data for compounds **4** and **7** (Table S1), anisotropic displacement parameters for **4** (Tables S2), calculated positional parameters for H atoms of **4** (Table S3), an extended list of bond lengths and angles for **4** (Table S4), anisotropic displacement parameters for **7** (Table S5), and an extended list of bond lengths and angles for **7** (Table S6) (15 pages). Ordering information is given on any current masthead page. Tables of final observed and calculated structure factors for **4** and **7** are available from A.A. upon request.

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(18) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.