Pergamon

Tetrahedron: Asymmetry Vol. 6, No. 1, pp. 115-122, 1995

0957-4166/95 $9.50+0.00

0957-4166(94)00366-1

Optically Active Zn^{II} and Pt^{II} Complexes of the 3-Carene Type α-Amino Oxime.

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Abstract:: (*1S,3S,6R*)-3-**N,N**-Dimethylaminocaran-4-one *E*-oxime forms stable 1:1 chelate complexes with $ZnCl_2$ and $PtCl_2$ whose structures are supported by X-ray, ^{1}H, ^{13}C, ^{14}N and ^{195}Pt NMR data. The conformation of the six-membered carbon cycle in the complexes was found to be changed as compared to the starting compound.

Chiral complexes of transition metals are of special interest from the viewpoint of their use in enantioselective organic synthesis. Being the primary source of chirality in the synthesis of a great number of chiral auxiliaries, natural terpenic compounds are not used 'as is' as chiral ligands[1]. At the same time, high optical purity of some easily available terpenes makes them very attractive as starting materials for the synthesis of chiral ligands. Many of the natural terpenes have a carbon-carbon double bond as the only functional group in the molecule and this group is therefore the place of primary chemical modification and introduction of other more polar heteroatomic functions. The most preferable molecules for preparing chiral auxiliaries should be bidentate ligands with cyclic backbone that can form chelates[1].

From this point of view, α-amino oximes derived from natural optically active terpenes[2,3] seem to be possible precursors of functionalized terpenic derivatives. Simple non-cyclic α-amino substituted oximes are known to form complexes with a number of transition metal ions: **Pt**(II)[4] **Ni**(II)[5,6,7], **Co**(III)[8], **Cu**(II)[6,7], **Pd**(II)[7], **Rh**(III)[9,10], and these complexes are rather stable, and their use for extraction of the metal ions from aqueous solutions has been discussed[11]. At the same time, the most stable form of the terpenic α-amino oximes is extremely unfavorable for the formation of mono-nuclear chelates due to the value of dihedral angle **N**(amine)-**C**-**C**-**N**(oxime) of about 120° for the carene and limonene derivatives[3]. Our preliminary experiments have shown that α-amino oximes **1** form stable complexes with different transition metal ions including **Pt**(II), although previous attempts to prepare **Pt**(II) complexes with α-amino oximes having a tertiary amino group

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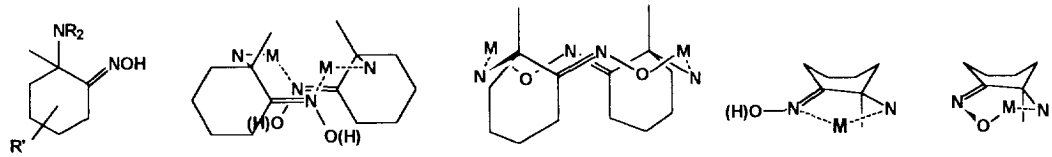
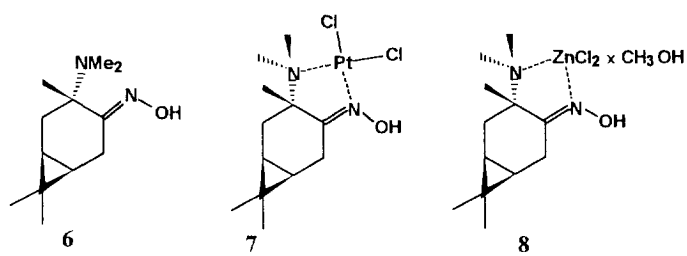
resulted in reduction to platinum metal[4]. Four variants of complex formation have to be considered: (*i*) formation of binuclear complexes **2** (**Me_2 ($LH)_2$** or **Me_2L_2**) of C_2-symmetry with 10-membered ring including two transition metal ions and two molecules of the starting amino oxime (with retention of the carbocyclic moiety conformation, coordination at the amine and oxime nitrogens); (*ii*) formation of binuclear complexes **3** (**Me_2L_2**) of C_2-symmetry with 12-membered cycle (with retention of the carbocyclic moiety conformation, coordination at the amine nitrogen and oxime oxygen); (*iii*) formation of mononuclear complex **4** (**MeLH** or **MeL**) with a changed conformation of the carbocycle (coordination at the amine and oxime nitrogens); (*iv*) formation of mononuclear complexes **5** (**MeL**) with inverted conformation of the carbocycle and inverted configuration of the oxime group. Designing new chiral auxiliaries based on the α-amino oximes and related compounds requires plausible information about the structure of these complexes. To elucidate the nature of the terpenic α-amino oxime complexes, we have chosen, on the one hand, 3-**N**,**N**-dimethylaminocaran-4-one oxime (**6**) as representative of cyclic terpenic α-amino oximes[3] and, on the other hand, **Zn**(II) and **Pt**(II) as representatives of light and heavy *d*-elements whose coordination chemistry varies significantly.



Both **Pt**(II) and **Zn**(II) form stable 1:1 complexes **7** and **8** respectively whose IR spectra show absorption of a hydroxyl (3600-3700 cm^{-1}) and no absorption of the **N-O** bond of free oxime group ($\nu_{N\text{-}O}$ 910 cm^{-1} for the starting oxime).



Reaction of amino oxime **6** with **K_2PtCl_4** in the two-phase system (water-chloroform) results in a crystalline complex. This complex is a mono-nuclear chelate of type **4** according to X-ray analysis. Solid state structure of the complex is shown on ***Figure 1***. Data of the NMR ^{1}**H**, ^{13}**C**, ^{14}**N** and ^{195}**Pt** spectra indicate that this complex has the same structure in a solution, and no structure reorganization occurs on dissolving. ^{1}**H** and ^{13}**C** NMR data are collected in the ***Table 1***, ^{14}**N** and ^{195}**Pt** NMR data are given in EXPERIMENTAL.

The chemical shift of ^{195}**Pt** (δ −2182 ppm) is typical for bis-amino complexes of type **$PtCl_2(NH_2R)_2$**[12]. NMR ^{14}**N** shows **Pt** to coordinate both at the amine and oxime nitrogens. The chemical shift of the oxime nitrogen in the starting oxime **6** is −20 ppm (typical range of the oxime nitrogen resonances in a number of simple aliphatic keto oximes is −40÷−60 ppm[13]), while the shift of the oxime nitrogen is −131 ppm in complex **7**. Coordination of **Pt^{II}** at the amine nitrogen does not affect significantly the chemical shift of the nitrogen atom[14], but the change in the spectral line width lends support to the complexation of the amine nitrogen with **Pt^{II}** (δ −350 ppm with $W_{1/2}$ = 4200 Hz for the starting amino oxime **6** and δ −349 ppm with $W_{1/2}$ = 650 Hz for the complex). NMR ^{13}**C** spectrum of **7** exhibits significant change in chemical shifts as compared to the starting

oxime **6** (***Table 1***). Values of the coupling constants $^2J_{C^i\text{-}^{195}Pt}$ and $^3J_{C^i\text{-}^{195}Pt}$ found are in the usual range[15] and clearly show the **N**(amine)-**Pt**-**N**(oxime) coordination and formation of mono-nuclear complex as well. In the case of the bi-nuclear complexe, both C^3 and C^4 atoms should have two sets of constants due to the geminal and vicinal coupling. Unexpectedly, vicinal couplings C^2-C^3-N^2-**Pt** and C^5-C^4-N^1-**Pt** do not correlate with the Karplus type relationship[16].

Table 1. **^{1}H and ^{13}C NMR Data for Compounds 7 and 8[a].**

	7[b]			8[d]	
i	δC^i ($J_{C^i\text{-}^{195}Pt}$, ±0.2Hz)	$\Delta\delta C^{ic}$	δH^i (*J*, Hz)	δC^i	δH^i (*J*, Hz)
1	21.63	+4.9	0.77 *ddd* (8.4, 8.4, 8.4)	20.71[†]	0.58 *ddd* (8.0, 8.0, 8.0)
2	24.43 (13.0)	−7.9	Hα: 2.30 *dd* (17.5, 8.4) Hβ: 1.21 *dd* (17.5, 8.4)	23.79[†]	Hα: 2.27 *dd* (16.7, 8.0) Hβ: 0.77[†] *ddd* (16.7, 8.0)
3	78.16 (26.4)	+19.2	-	65.09	-
4	167.66 (66.3)	+3.8	-	167.29[†]	-
5	19.96 (23.1)	+1.9	Hα: 3.45 *dd* (15.4, 8.0) Hβ: 1.22 *dd* (15.4, 8.0)	17.92	Hα: 3.49[†] *dd* (15.5, 8.0) Hβ: 1.15[†] *dd* (15.5, 8.5)
6	20.62	+0.3	0.98 *ddd* (8.1, 8.1, 8.1)	19.55[†]	0.72[†] *ddd* (8.5, 8.0, 8.0)
7	22.80	+4.4	-	19.97	-
8	27.29	−0.6	1.06 *s**	27.01	0.93*[†] *s*
9	13.80	−0.8	1.04 *s**	13.48	0.92*[†] *s*
10	26.62	+14.3	1.70 *s*, $J_{H^{10}\text{-}^{195}Pt}$ = 4.6 Hz	26.58[†]	1.29[†] *s*
11*	43.97 (<5)		2.74 *s*, $J_{H^{11}\text{-}^{195}Pt}$ = 39.5 Hz	38.19[†]	2.38[†] *s*
12*	50.57 (31.6)		3.00 *s*, $J_{H^{12}\text{-}^{195}Pt}$ = 35.5 Hz	43.71	2.41[†] *s*
=NOH			10.05 *br.s*		11.3[†] *br.s*
CH_3OH				50.29	3.43 *s*

[a] chemical shifts are given in ppm; numbering scheme is identical with that given on ***Figure 1***; assignments marked with asterisk may have to be reversed; [b] 60 mg/ml in CD_2Cl_2; [c] as compared to the starting amino oxime **6**[3]; [d] 130 mg/ml in $CDCl_3$-CD_2Cl_2 1:1, vol./vol., at −30°C; signals marked with '†' appear at room temperature as broad overlap lines; NMR ^{13}C at −70°C: signals of **C**-2,5,10 atoms become broad again, signal of **C** -3 atom is splitted into four lines at δ 63.91, 64.92, 65.36, 65.67 ppm with relative intensities 1:42:3:2; signal of the oxime carbon is splitted into two lines at δ 155.19 and 167.01 ppm (*ca.* 1:10); NMR ^{1}H at −70°C: hydroxyl protons - broad signals at δ 11.7, 9.9, 7.8, 3.7 ppm (*ca.* 6:1:1:8), CH_3O - δ 3.39 and 3.41 ppm (broad signals, *ca.* 1:1), $(CH_3)_2N$ - δ 2.95, 2.70, 2.39, 2.36 ppm (broad signals, *ca.* 1:1:10:10).

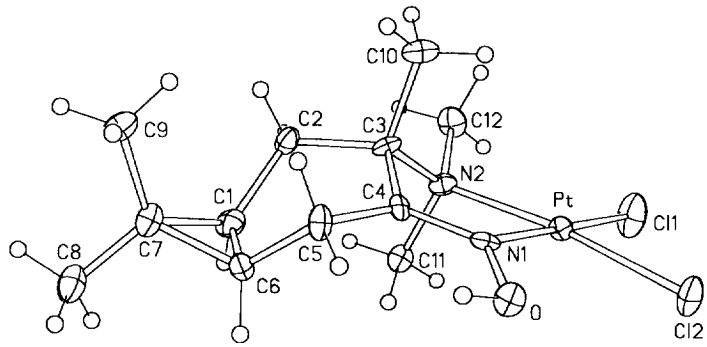
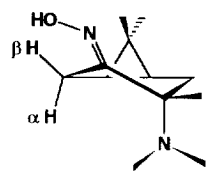


Figure 1.

Molecular structure of compound 7. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) are as follows: Pt-Cl1 2.286(4), Pt-Cl2 2.304(4), Pt-N1 1.973(9), Pt-N2 2.068(9), N1-C4 1.30(1), N1-O 1.38(1). Selected bond angles are as follows: N1-Pt-N2 80.8(3)°, N1-Pt-Cl2 91.0(3)°, N2-Pt-Cl2 170.6(3)°, Cl2-Pt-Cl1 91.9(1)°, Cl1-Pt-N2 96.3(3)°. Fragment N_2PtCl_2 is planar within 0.037 Å. Five-membered cycle has twist conformation, whereas six-membered cycle is twist-boat. (The numbering scheme does not coincide with the numbering of the cyclic systems according to IUPAC).

^{1}**H** NMR spectral data for molecule **7** support the presence of mono-nuclear complex with the same conformation of the six-membered carbon cycle as in the solid state. Experimental and calculated vicinal proton-proton coupling constants for complex **7** tabulated in ***Table 2*** show the complex to have the inverted conformation of the carbon cycle (structure **10**) as compared with the starting compound **6**, whose most stable conformation is represented by structure **9**. One of the $\mathbf{H}^5$ atoms of compound **7** exhibits a large downfield shift (δ 3.45 ppm, ***Table 1***) due to the effect of the oxygen of the oxime group on the $\alpha\mathbf{H}^5$-atom, in contrast to the starting oxime **6** having $\beta\mathbf{H}^5$ downfield proton.



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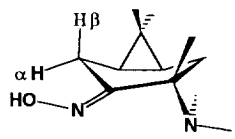

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Reaction of amino oxime **6** with $\mathbf{ZnCl_2}$ in a methanol solution results in 1:1 complex **8** (one molecule of methanol is also incorporated in the structure). NMR spectra of this complex are temperature dependent, spectral lines being too broad at room temperature. At −30°C both ^{1}**H** and ^{13}**C** NMR high resolved spectra were obtained. Comparison of the NMR data for **Zn**-complex **8** (***Table 1***) with those for **Pt**-complex **7** indicates the same type of complexation in both cases[17], complex **8** being less stable one. According to NMR data for complex **8**, at least 4 different structures are in equilibrium, one of the chelate forms being predominant

(*ca.* 90% at –70°C). Four resonances of **C**[3] atom occur in ^{13}**C** NMR spectra within the limited range (δ 63-65 ppm) which can be explain by complexation of the amine nitrogen with **Zn**^{II} in all four forms. At the same time, two resonances of the oxime carbon (δ 155.19 and 167.01 ppm, *ca.* 1:10) establish the presence of the complex-free oxime as well as associated one. The methanol molecule is also involved in the exchange process (the methanol signal in ^{1}**H** NMR spectrum at –70°C is splitted into two lines at 3.39 and 3.41 ppm, ca. 1:1). ***Scheme 1*** shows the most possible exchange processes. The equilibrium drawn may be complicated by (*i*) conformational exchanges in the six-membered carbon cycle of molecules **13** and **14**; (*ii*) formation of 1:2 complexes of the **ZnCl$_2$[N(CH$_3$)$_2$-R]$_2$** type.

Scheme 1.

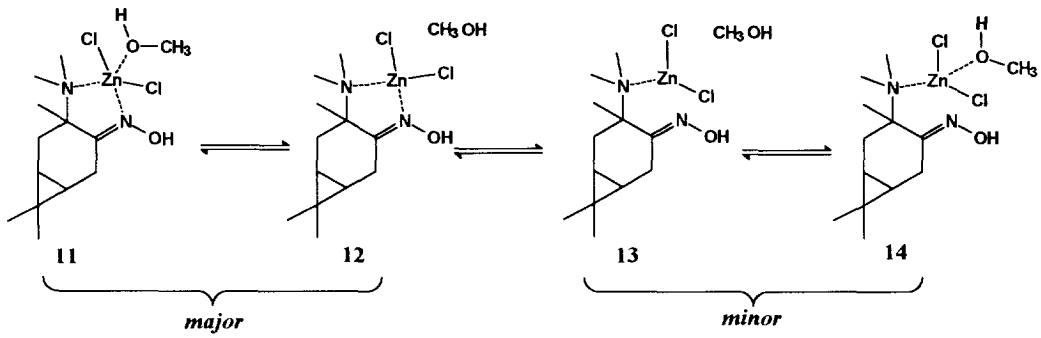

Table 2. **Experimental and Calculated Vicinal Proton-Proton Couplings in the Carbon Frame of Complexes 7 and 8[a].**

	experimental		calculated		experimental
	7	**8**	**10**[b]	**9**[c]	**6**[d]
strain energy (kcal/mol)			53.5	50.1	
$J_{H^1\text{-}\alpha H^2}$	8.4	8.0	9.0	10.5	10.0
$J_{H^1\text{-}\beta H^2}$	8.4	8.0	9.0	6.5	6.0
$J_{H^6\text{-}\alpha H^5}$	8.1	8.0	9.0	10.5	10.0
$J_{H^6\text{-}\beta H^5}$	8.1	8.5	9.0	1.0	0.0

[a] Vicinal couplings $J_{H^i\text{-}H^j}$ (Hz) were calculated for specified geometry obtained by molecular mechanics calculations[18] using MMX-program[19]; [b] geometry of the six-membered ring is very similar for this conformation and **Pt**-complex **7**; optimized orientation of **N,N**-dimethylamino group is as follows: ϕ(**C**2-**C**3-**N**2-**C**11)=–61° and ϕ(**C**2-**C**3-**N**2-**C**12)=66°; [c] optimized orientation of **N,N**-dimethylamino group is as follows: ϕ(**C**2-**C**3-**N**2-**C**11)=55° and ϕ(**C**2-**C**3-**N**2-**C**12)=–179°; [d] the data are taken from ref.[3].

EXPERIMENTAL

General experimental procedures Removal of all solvents was carried out under reduced pressure and all commercial reagents were used without additional purification. IR spectra were obtained using a ***Specord M-80*** and ***IFS-66*** spectrometers. A ***Polamat A*** polarimeter was used to measure optical rotation at 578 nm. Melting points were obtained using a ***Kofler*** melting point apparatus and are uncorrected. Mass spectra were obtained on a ***LKB-2091*** chromato-mass-spectrometer using the Electron Impact Ionization technique (70eV). NMR spectra were recorded at room temperature (unless otherwise stated) for 5-10% solutions using standard Bruker NMR Software System on a ***Bruker AC 200*** instrument (^{1}**H** 200.13 MHz, ^{13}**C** 50.32 MHz) and a ***Bruker MSL-400*** instrument (^{14}**N** 28.91 MHz, ^{195}**Pt** 86.00 MHz). ^{1}**H** and ^{13}**C** chemical shifts were calculated relative to the solvent signal using as internal standard: $\delta_{\mathbf{H}}$ 7.24 ppm and $\delta_{\mathbf{C}}$ 76.90 ppm for **$CDCl_3$** and $\delta_{\mathbf{H}}$ 5.30 ppm and $\delta_{\mathbf{C}}$ 53.30 ppm for **CD_2Cl_2**. ^{14}**N** chemical shifts were measured relative to the resonance for a 2 M aq. solution of **$NaNO_3$** ($\delta_{\mathbf{N}}$ 0 ppm) using as external standard, ^{195}**Pt** chemical shift was measured relative to the resonance for a 0.3 M solution of **H_2PtCl_6** in water ($\delta_{\mathbf{Pt}}$ 0 ppm) using as external standard.

(1S,3S,6R)-3-**N,N**-Dimethylaminocaran-4-one *E*-oxime (**6**) with $[\alpha]_{578}^{25}$ +105 (*c* 12.1, **$CHCl_3$**) was prepared from (+)-3-carene as described earlier[3]. ^{14}**N** NMR (in **CH_2Cl_2**): δ –20±10 ppm, $W_{1/2}$ 6100 Hz (oxime); δ –350±5 ppm $W_{1/2}$ 4200 Hz (amine).

*[η^2-**N,N'**-{(1S,3S,6R)-3-**N,N**-Dimethylaminocaran-4-one E-oxime}]dichloro platinum* (**7**). A solution of **K_2PtCl_4** (0.20 g, 0.48 mmol) in **H_2O** (5 ml) was added to a solution of oxime **6** (0.10 g, 0.48 mmol) in **$CHCl_3$** (15 ml) and the reaction mixture was shaked for 5 days at room temperature. The organic layer was separated, filtered and diluted with pentane (130 ml) to give greenish-yellow solid that was washed with **Et_2O** (20 ml) and crystallized from a mixture of **Et_2O** and **CH_2Cl_2** to afford the desired complex **7** (0.088 g, 45%). An analytical sample was prepared by crystallization of the product form a mixture of **CH_2Cl_2** and **CH_3CN**. M.p. 250-255°C with decomposition (**CH_2Cl_2-CH_3CN**); found: **C** 30.1, **H** 5.0, **N** 5.6, **Cl** 15.0; calculated for **$C_{12}H_{22}Cl_2N_2OPt$**: **C** 30.26, **H** 4.66, **N** 5.88, **Cl** 14.89; $[\alpha]_{578}^{22}$ –114 (*c* 1.60, **CH_2Cl_2**); IR (1% in **CH_2Cl_2**) cm^{-1}: 3612 (**O-H**), 1047 (**N-O**); IR (0.25% in **KBr**) cm^{-1}: 3215 (**O-H**), 1024 (**N-O**); MS, *m/z* (%): 474 (4.6, **$C_{12}H_{22}Cl_2N_2OPt$**, M^+), 439 (1.7, M^+–**Cl**), 404 (2.0, M^+– **Cl_2**), 193 (7, M^+–**$PtCl_2$**, –**OH**), 149 (40), 134 (100), 119 (23), 107 (20), 106 (24), 91 (13), 79 (12), 77 (14), 65 (9), 56 (13), 45 (37), 44 (75), 38 (57); ^{14}**N** NMR (in **CH_2Cl_2**): δ –131±5 ppm, $W_{1/2}$ 2000 Hz (oxime); δ –349±2 ppm $W_{1/2}$ 650 Hz (amine); ^{195}**Pt** NMR (in **CH_2Cl_2**): δ –2182±2 ppm, $W_{1/2}$ 360 Hz.

X-Ray crystallographic experiment. Intensity data for compound 7 were collected at 298(2)°K on a **SYNTEX-$P2_1$** diffractometer using graphite monochromated CuKα radiation (λ = 1.54178 Å). After absorption correction, the structure was solved using SHELX-86, refinement was carried using SHELX-93. The structure of the compounds is shown on ***Figure 1.***

Crystal data and structure refinement for compound **7**:.**$C_{12}H_{22}Cl_{l2}N_2OPt$**; *M* = 476.31; monoclinic; space group $P2_1$; *a* = 7.138(1) Å, *b* = 11.203 (1) Å, *c* = 9.420(1) Å; α = 90°, β = 90.09(1)°, γ = 90°; *U* = 753.3(2) $Å^3$; Z = 2; D_c 2.100 g×cm^{-3}; μ = 20.609 mm^{-1}; *F(000)* = 456. Crystal size 0.80×0.28×0.20 mm^3. Theta range for data collection: from 4.69 to 72.53°. Index ranges: $-8\le h\le 8$, $-4\le k\le 13$, $0\le l\le 11$. Reflections collected: 1572. Independent reflections: 1572 [R(int) = 0.0000]. Absorption correction: analytical on crystal faces followed by DIFABS. Max. and min. transmission: 0.214 and 0.027. Refinment method: full-matrix least-squares on F^2.

Data/restraints/parameters: 1572/0/163. Goodness-of-fit on F^2: 1.114. Final R indices [$I>2\sigma(I)$]: R_1 = 0.0464, wR_2 = 0.1235. R indices (all data): R_1 = 0.0470, wR_2 = 0.1214. Absolute structure parameter: 0.00(3). Extinction coefficient: 0.0057(6). Largest diff. peak and hole: 3.571 and −1.478 e.Å^{-3}.

Atomic coordinates, bond length and angles, and thermal parameters have been deposited in the Cambridge Crystallographic Data Center.

*[η^2-**N,N'**-{(1S,3S,6R)-3-**N,N**-Dimethylaminocaran-4-one E-oxime}]dichloro zinc monomethanol solvate* (**8**). A suspension of **$ZnCl_2$** (0.64 g, 4.7 mmol) and oxime **6** (1.00 g, 4.8 mmol) in **CH_3OH** (6 ml) was stirred at reflux for 5 min, concentrated at reduced pressure to a volume of 2 ml, cooled to 20°C. Dry diethyl ether (15 ml) was added carefully over the concentrated solution baring from the mixing of the layers. The resulting mixture was allowed to stay for 48 h at −10°C, the crystalline presipitate (0.45 g) was dried in vacuo. The mother liquor was evaporated and crystallized again using **CH_3OH** (1 ml) and diethyl ether (15 ml) to give additional portion (0.95 g) of the complex (total yield 1.40 g, 3.7 mmol, 78%). Found: **C** 41.1, **H** 7.4, **N** 7.6, **Cl** 18.9; mol. weight: 391±19 (ebullioscopy in **$CHCl_3$**); calculated for **$C_{12}H_{22}Cl_2N_2OZn \times CH_3OH$**: **C** 41.24, **H** 6.92, **N** 7.40, **Cl** 18.73; 378.64. M.p. 110-115.5°C (**CH_3OH-Et_2O**, 1:4 v/v) $[\alpha]_{578}^{25}$ −100 (*c* 1.78, **$CHCl_3$**) IR (1% in **$CHCl_3$**): 3690 (**O-H**), 3630 (**O-H**), 1670 (**C=N**), 1015 (**N-O**). IR (0.25% in **KBr**): 1010 (**N-O**).

Acknowledgments: The research described in this publication was made possible in part by Grants Nos RCS000 and RAU000 from the International Science Foundation. The authors thank the Novosibirsk Office of the Soros Foundation for computational support of this work.

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(*Received in UK* 8 *August* 1994; *accepted* 10 *October* 1994)