Transition Metal Complexes of Derivatized Chiral Dihydro-1,2,4-triazin-6-ones. Part III [1]. X-Ray Crystal Structure Analysis of N,N’-Bis[(1-phenyl-5-isopropyl-4,5-dihydro-6-oxo-1,2,4-triazin-3-yl)ethylidene]-propane-1,3-diamine Nickel(II)

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N,N’-[6-Oxotriazin-3-yl]ethylidene]-1,3-diaminopropane, Nickel Complex

Template reaction of L-3-acetyl-l-phenyl-5-isopropyl-4,5-dihydro-1,2,4-triazin-6-one (\textsuperscript{1b}) with 1,3-diaminopropane and nickel acetate gave the corresponding chiral complex \textsuperscript{4} in high yield. X-ray structure determination showed that the nickel complex is square planar, and the ligand N,N’-bis[(1-phenyl-5-isopropyl-4,5-dihydro-6-oxo-1,2,4-triazin-3-yl)ethylidene]-propane-1,3-diamine is of tetra-aza type where the imine nitrogens and the ring HN(4) nitrogens are the coordinating sites. MS-FAB and NMR spectral data are in agreement with the X-ray structure.

Introduction

Chiral 3-acetyl-4,5-dihydro-1,2,4-triazinones [2] (exemplified by \textsuperscript{1a}) are readily convertible to the respective oximes (\textsuperscript{2}) via the interaction with hydroxylamine (Scheme 1). These oxime derivatives (e.g. \textsuperscript{2a}) proved to be a useful class of bidentate chelating agents, and their derived transition metal complexes are of significant interest for two reasons, namely, the carbon-carbon coupling reaction that took place during the nickel(II) complex formation of \textsuperscript{3} [3] (Scheme 1), and the implication of the chiroptical properties of the resulting complexes as investigated by the CD technique [4]. As we are currently investigating the chelating properties of other derivatized triazinones with some transition metal ions, we have strong evidence that oxime \textsuperscript{2b} (derived from \textsuperscript{1b}, Scheme 1) behaves in an analogous manner to \textsuperscript{2a} towards Ni\textsuperscript{2+} [4].

In an attempt to incorporate the triazinone moiety into a macrocyclic framework by utilizing the template effect [5], we have reacted the C3-acetyl

\begin{center}
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{R} & \textbf{X} & \textbf{1a} & \textbf{1b} & \textbf{2a} & \textbf{2b} \\
\hline
\text{CH}\text{Ph} & \text{O} & \text{Ni(OAc)}\text{2} & \text{EtOH} & \\
\text{CHMe}_{2} & \text{O} & \text{Ni(OAc)}\text{2} & \text{EtOH} & \\
\text{CH}_{2}\text{Ph} & \text{N-OH} & \text{Ni(OAc)}\text{2} & \text{EtOH} & \\
\text{CHMe}_{2} & \text{N-OH} & \text{Ni(OAc)}\text{2} & \text{EtOH} & \\
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\end{tabular}
\end{center}

\textbf{Scheme 1}

\textsuperscript{0932–0776/2000/1100–1074 $06.00$ © 2000 Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com}
compound (lb) with 1,3-diaminopropane in the presence of nickel acetate (Scheme 2). However, we obtained compound 4 in which the carbon-carbon coupling reaction (noted in 3) did not take place, and an open-chain tetradeutate ligand of tetra-aza type (4) was obtained instead.

\[
\text{Scheme 2}
\]

**Results and Discussion**

The required L-3-acetyl-1,2,4-triazinone derivative 1b was prepared in one-pot reaction following reported procedures [2] and was characterized by EI-MS and NMR spectral data. This synthon 1b was utilized to prepare the N,N'-bis-[(1-phenyl-5-isopropyl-4,5-dihydro-6-oxo-1,2,4-triazin-3-yl)ethylidene]-propane-1,3-diamine nickel(II) (4) via direct interaction with 1,3-diaminopropane in the presence of nickel acetate. In this reaction, the so-called template effect operates and the product 4 was obtained in a highly pure state and in high yield. The complex has a time-averaged structure with \( C_2 \) symmetry (i.e., only one set of signals) and that, as expected, the diastereotopic Me groups of a CHMe\(_2\) group give rise to separate signals. This is evidenced from the NMR spectra (see experimental part) which show one set of signals for each type of hydrogen and carbon atoms in both triazinone moieties (rings A and B, Fig. 1). An exception is the two methyl groups of the isopropyl moiety which appear as two sets of signals due to their anisochronous character. This behavior of anisochrony is also observed in compound 1b.

The constitution of 4 was confirmed by X-ray crystal structure determination. The molecular structure of 4 is displayed in Fig. 1. Selected bond lengths and angles are given in Table I. Values of the bond angles around the chelated nickel ion provide further evidence for the nearly square planar geometry of the nickel complex 4. In addition, a solution of 4 in chloroform (10\(^3\) M) is non-conducting indicating that 4 is neutral. Magnetic measurement shows that the complex is also diamagnetic which is indicative of a square planar geometry.

![Fig. 1. ORTEP plot of the molecular structure of 4.](image-url)
### Table I. Selected bond lengths (Å) and angles (°) for 4.

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### Experimental

Melting points (uncorrected) were determined using a Gallenkamp melting point apparatus in one-end open glass capillaries. The magnetic moment was measured for a finely ground solid sample of 4 at ambient temperature using a Johnson Matthey Magnetic Susceptibility balance. Optical rotations were measured on a Perkin-Elmer 141 photoelectric spectropolarimeter. NMR spectra were recorded on a Bruker WM-400 spectrometer for solutions in CDCl₃ with TMS as internal reference. Mass spectra (EI) were obtained using a Finnigan MAT TSQ-70 spectrometer at 70 eV; ion source temperature = 200 °C. MS-FAB spectra were obtained with a VG Analytical Ltd. ZAB HS mass spectrometer, equipped with xenon gun operating at 8 keV and 0.8 mA emission using as the sample containing matrix, TG/G, CHCl₃ (thioglycerol/glycerol) or NBA (3-nitrobenzyl alcohol). Elemental analyses were performed at the Laboratories of Quantitative Technologies Inc. (QTI), New Jersey, USA.

L-3-Acetyl-1-phenyl-5-isopropyl-4,5-dihydro-1,2,4-triazin-6-one (1b)

This compound was prepared via direct interaction between 1-chloro-1-phenylhydrazino-2-propanone [6,7] with L-valine methyl ester hydrochloride (Aldrich) in the presence of excess triethylamine according to the general procedure described for the synthesis of analogous chiral triazinones [2]. Yield of pure product = 87%, m.p. = 75–77 °C. - ¹H NMR (400 MHz, CDCl₃); δ = 0.94, 1.01 (2xd, J = 6.8, 7.0 Hz, 6H, CH(CH₃)₂), 2.33 (m, 1H, CH(CH₃)₂), 2.45 (s, 3H, C(OCH₃)), 4.05 (dd, J = 5.3, 3.5 Hz, 1H, H-4'), 7.26 (tt, J = 8.8, 1.3 Hz, 1H, H-4'), 7.40 (dd, J = 8.4, 8.8 Hz, 2H, H-3'/5'), 7.55 (tt, J = 8.4, 1.3 Hz, 2H, H-2'/6'). ¹³C NMR (100 MHz, CDCl₃); δ = 16.6, 18.2 (CH(CH₃)₂), 23.7 (CH₂CO), 32.7 (CH₂CO), 58.9 (C-5), 124.7 (C-2'/6'), 126.9 (C-4'), 128.5 (C-3'/5'), 140.7 (C-3), 141.8 (C-1'), 161.4 (C-6), 192.9 (CH₂C=O). MS (EI, 70 eV); m/z (%) = 259.13047 (M⁺, 63, C₁₄H₁₇N₃O, requires 259.13208), 216(100), 188(57), 174(4), 146(13), 118(5), 104(6), 107(7), 87(10, 100).
N,N'-Bis[(1-phenyl-5-isopropyl-4,5-dihydro-6-oxo-1,2,4-triazin-3-yl)ethylidene]-propane-1,3-diamine nickel(II) (4)

The acetyl compound 1b, (1.56 g, 6 mmol), nickel acetate tetrahydrate (0.75 g, 3 mmol) and absolute ethanol (80 ml) were stirred at rt for few minutes. 1,3-Diaminopropane (0.24 g, 3.25 mmol) in absolute ethanol (20 ml) was then added dropwise over a period of 10 min. The reaction mixture was brought to reflux under constant stirring for 15 h. During the first hour of the reflux time the reaction mixture assumed a blue color, then green during the second and third hours and finally a deep-red color persisted for the rest of the reflux time. The solvent was removed in vacuo and an oily residue was obtained. This was dissolved in 40 ml of dichloromethane and the solution was filtered off. To the filtrate was added 60 ml of hot benzene and the solution was heated for few minutes then set aside overnight. Deep-red crystals were separated. These were filtered off, washed with little benzene and dried in vacuo. Yield = 1.93 g (65%), m.p. > 300 °C. 

The hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 [10]. This resulted in R-values R_1/wR_2 = 0.0757/0.0520 for all data and 0.0640/0.050 for the 2221 observed reflections and 379 variable parameters; GOF = 1.90, residual electron density between 0.47 and -0.37 e/A^3. The hydrogen atoms in the structure were generated except for the methyl groups in which case at least one hydrogen was found on the difference Fourier maps and used to calculate the positions of the others. The hydrogens were included in the calculations, but were not refined.

Acknowledgments
A. S. A. gratefully acknowledges financial support from the Hashemite University, Jordan.

Supplementary materials
Tables of positional parameters, interatomic angles and distances, structural factor amplitudes and thermal parameters and packing diagrams for the structure of compound 4 are available from the Cambridge Crystallographic Data Center under the depository number CCDC 149840.

E-mail: deposit@ccdc.cam.ac.uk
    c) W. Dieckmann, O. Platz, Ber. Dtsch. Chem. Ges. 38, 2986 (1905);
[10] Least squares function minimized: $\Sigma w(\{F_o\} - \{F_c\})^2$, were:
    $w = 1/[\sigma^2(\{F_o\})] = [\sigma^2(\{F_o\}) + p^2F_o^2/4]^{-1}$,
    $\sigma_{\{F_o\}} = \text{e.s.d. based on counting statistics}$, $p = \text{p-factor}$. 