Preparation, IR and X-Ray Crystal Structure Studies of Tl(I)-2-pyridyl-cyanoxime Complex

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X-Ray, Thallium(I)-2-pyridyl-cyanoxime Complex

The thallium(I)-2-pyridyl-cyanoxime complex was prepared in a 82% yield. An X-ray crystallographic study of C₇H₄N₃OTl (Space group P₂₁/c, a = 4.134(1), b = 8.875(2), c = 22.217(6) °, β = 92.552(2), Z = 4, R = 4.36%, wR = 3.94% for 930 reflections) showed that the complex contains thallium(I) in a trigonal bipyramidal arrangement.

Preparation of C₇H₄N₃OTl

2-Pyridyl-acetonitrile was obtained from Fluka. To a hot (95 °C) aqueous solution of HCONC(CN)C₄H₄N (HPCO) [21] (0.195 g, 1.33 mmol) (50 cm³) small quantities of Tl₂CO₃ were added (0.311 g, 0.63 mmol). The mixture was stirred until the CO₂ gas evolution ceased. When the solution was cooled slowly, a pale-yellow microcrystalline complex was formed. The complex was filtered off and dried in a desiccator over sulphuric acid. Yield: 0.38 g (82%). The complex melts with decomposition at 164 °C. The mother-liquid was kept in the dark for three weeks. During this time red-orange needle-shaped crystals were formed suitable for X-ray single crystal measurements.

For assignments of the vibrational frequencies of the CNO group the ¹⁵N-enriched sodium and thallium(I) derivatives have been prepared. The IR-spectra were recorded on a Carl Zeiss (Jena) UR 20 spectrometer using KBr pellets and Nujol mulls. The representative absorptions of the complexes and of the corresponding sodium salts are presented in Table I.

The TIPCO complex dissolved in water gives an absorption maximum at 24800 cm⁻¹ indicating a thallium coordination to the deprotonated oxime group. The VIS-spectra were recorded on a Spectord UV-VIS M 40 (Carl Zeiss, Jena) spectrometer using 4.78 mmol/l concentration of TIPCO.

C₇H₄N₃OTl
Calcd N 12.09 Tl 58.84%
Found N 12.07 Tl 58.5%

Introduction

The coordination chemistry of cyanoximes of the general formula HONC(CN)−R has been developed during the past decade. In alkaline solutions these ligands are deprotonated to yield yellow colored anions.

HONC(CN)−R + OH" → "ONC(CN)−R + H₂O

(1)

The color originates from the electron transition from the ground state to a low-lying excited state of the nitroso group, comparable to that found in the NO₂⁻ anion [1]. The negative charge in the deprotonated cyanoximes is delocalized. The X-ray single crystal data indicate that the neutral molecules [2] and the corresponding anions have a planar structure both in some of their alkali metal salts and in their 3 d metal complexes [3–6].

Cyanoximes are ambidentate ligands. They form numerous metal complexes demonstrating a variety of bonding modes [6–15].

Several cyanoximes and their metal complexes show biological activity and antimicrobial properties [16–18]. Ligands with heterocyclic substituents are used in analytical chemistry [19, 20].

This paper describes the IR investigations and X-ray single crystal studies of the thallium(I)-2-pyridyl-cyanoxime complex, T[ONC(CN)C₄H₄N].

* Reprint requests to Prof. Dr. H. W. Roesky.

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**Table I.** IR spectral data of C7H4N3OTl and related compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Important bands [cm⁻¹]</th>
<th>(v_{(C=N)})</th>
<th>(v_{(C=O)})</th>
<th>(v_{(C=N)(Py)})</th>
<th>(v_{(C=O)(NO)})</th>
<th>(v_{(C=O)(NO)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaPCO</td>
<td>2208 1595 1285 1180</td>
<td>(1260)*</td>
<td>(1160)*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni[(PCO)₂(H₂O)]</td>
<td>2215 1608 1390 1225</td>
<td>(1370)*</td>
<td>(1205)*</td>
<td>(1370)*</td>
<td>(1205)*</td>
<td></td>
</tr>
<tr>
<td>Ni(PCO)₂</td>
<td>2215 1600 1390 1225</td>
<td>(1370)*</td>
<td>(1205)*</td>
<td>(1370)*</td>
<td>(1205)*</td>
<td></td>
</tr>
<tr>
<td>TlPCO</td>
<td>2210 1590 1170* 1095*</td>
<td>(1155)</td>
<td>(1080)</td>
<td>(1155)</td>
<td>(1080)</td>
<td></td>
</tr>
<tr>
<td>Me₂Sn(PCO)₂</td>
<td>2230 1595 1480 985</td>
<td></td>
<td></td>
<td>(1155)</td>
<td></td>
<td>(1080)</td>
</tr>
</tbody>
</table>

* Frequencies of isotope enriched compounds \([^{15}N-50\% (NO)]\).

Crystallography

Experimental parameters for the title compound are presented in Table II. The crystal was mounted in a glass Lindemann tube. Data were collected on a Siemens-Stoe AED2 diffractometer automated with a computer.

**Table II.** Crystallographic data for C7H4N3OTl.

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C7H4N3OTl</th>
<th>Crystal system</th>
<th>monoclinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>P (_2)/c</td>
<td>Unit cell dimensions</td>
<td>(a = 8.143(1) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b = 8.875(2) \text{ Å})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c = 22.217(6) \text{ Å})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\beta = 92.55(2)°)</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>814.3(3) \text{ Å}³</td>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Formula weight</td>
<td>350.5</td>
<td>Density (calcd)</td>
<td>2.86 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>19.99 mm⁻¹</td>
<td>F(000)</td>
<td>624</td>
</tr>
<tr>
<td>Color; habit</td>
<td>light red needles</td>
<td>Crystal size (mm)</td>
<td>0.3×0.3×1.0</td>
</tr>
<tr>
<td>Diffractometer used</td>
<td>Siemens-Stoe AED2</td>
<td>Radiation</td>
<td>MoK(\alpha) ((\lambda = 0.71069 \text{ Å}))</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293</td>
<td>2(\theta) Range</td>
<td>7.0 to 45.0°</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>2138</td>
<td>Reflections collected</td>
<td>1069 (R_{int} = 5.45%)</td>
</tr>
<tr>
<td>Observed reflections</td>
<td>930 (F &gt; 3.0\sigma(F))</td>
<td>Absorption correction</td>
<td>semiempirical</td>
</tr>
<tr>
<td>Min./max. transmission</td>
<td>0.26/0.53</td>
<td>Weighting scheme</td>
<td>(w = \sigma^2(F) + 0.0002F^2)</td>
</tr>
<tr>
<td>Initial R indices (obs. data)</td>
<td>(R = 4.36%, wR = 3.94%)</td>
<td>Initial R indices (all data)</td>
<td>(R = 4.92%, wR = 4.13%)</td>
</tr>
<tr>
<td>Goodness-of-fit</td>
<td>1.35</td>
<td>Data-to-parameter ratio</td>
<td>8.5:1</td>
</tr>
</tbody>
</table>

Additional X-ray material is available from the Fachinformationszentrum Karlsruhe GmbH, D-W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 56395, the names of the authors and the journal citation. The authors thank Dr. A. A. Kapshuk for discussions.

**Results and Discussion**

**Preparation of C7H4N3OTl**

The thallium(I) complex of \([\text{ONC(CN)C}_5H_4N}\]^– (PCO⁻) was obtained according to eq. (2) or (3).

\[
\begin{align*}
\text{Tl}_2\text{CO}_3 + 2 \text{HPCO} & \rightarrow 2 \text{Tl(POC)} + \text{CO}_2 + \text{H}_2\text{O} \\
\text{Tl}_2\text{CO}_3 + 2 \text{KPCO} & \rightarrow 2 \text{Ti(POC)} + \text{K}_2\text{CO}_3
\end{align*}
\]

Better yields were obtained by reaction (2).

**Molecular structure**

The structure of the TlPCO complex and its stacking order are presented in Fig. 1, the intermolecular contacts are shown in Fig. 2 a and b. The fractional atomic coordinates and selected bond lengths (Å) and angles (°) for TlPCO are listed in Tables III and IV, for which the numbering scheme can be seen in Fig. 3.
The thallium atoms form double chains in direction of the $a$-axis (Figs 1, 2) with a van der Waals distance of 4.13 Å between Tl-atoms and a further distance (longer than van der Waals) of 4.61 Å. The oxygen and nitrogen atoms of the nitroso group of the neighboring ligands are also coordinated to the thallium(I) center (Fig. 2a and b). The non-bonding electron pair of thallium(I) is likely to be located opposite of the N1 atom. N3 shows a Tl–N distance of 3.58 Å (Fig. 1).

The thallium(I) atom is part of a five-membered ring with two strong Tl–N bonds with approximately equal bond distances (2.7 Å, Table IV, Fig. 1). The N(1)T1N(2) bond angle is equal to 60° which is considerably smaller than the angles observed in standard five-membered chelate rings.

The 2-pyridyl-cyanoxime ligand has an essentially planar structure. The angle between the N3C6 plane and the pyridine ring is 4.6°. The displacement of the thallium(I) atom out of the plane is 0.61 Å towards the apical position.

The most important observation in this structure is the pure nitroso form of the cyanoxime anion. It was found that the N2–O1 bond distance (1.228 Å) is characteristic for double bonds [17], while the N2–C6 bond distance (1.407 Å) is close to the values observed for single bonds. Simi-
lar results were obtained for several cyanoximes and also for their salts [3, 4, 23].

**IR spectroscopic studies**

In order to obtain information about the reflectance of the coordination mode of 2-pyridyl-cyanoxime in its IR spectra, further IR studies were undertaken (Table I). The \( \nu_{NO} \) bands in Tl(PCO) as well as in Me\(_2\)Sn(PCO)\(_2\) [24, 25] are shifted to lower wave numbers as compared to the \( \nu_{NO} \) bands in the spectra of Na(PCO), [Ni(PCO)\(_2\)(H\(_2\)O)\(_2\)] or [Ni(PCO)\(_2\)].

It is known that partially filled \( \epsilon_g \) and \( \tau_{2g} \) orbitals of transition metal ions form a “back-bond” type coordination with the N-atom of the nitroso group. Quantum-chemical calculations [26, 27] have shown that the N-atoms of the NO groups in different cyanoxime anions have \( \sigma \)-donor and \( \pi \)-acceptor properties. Accordingly, the complexes with copper(II), nickel(II), palladium(II) or iron(II) metal ions [16, 28] will form bonds with the nitrogen atoms as depicted in Fig. 4a. The electron density on the NO group increases due to this type of bonding, as reflected in \( \nu_{NO} \) vibrations at higher wave numbers.

The coordination mode of Pb(II), Tl(I), Cd(II) and Hg(II) to nitrogen atoms of cyanoxime anion is different. The metal ions having filled orbitals in low-lying states cannot participate in back-bonding. Tl(I) has empty \( p \)-orbitals as well as a filled 6 \( s^2 \) orbital. The possible mode of coordination between these types of metal ions with cyanoximes is shown in Fig. 4b. The \( \sigma \)-donor nitrogen atom donates one electron pair to the \( p_{\sigma}(x,y) \) orbital of Tl(I), which results in a decrease in electron density of the NO group. The \( \nu_{NO} \) band is shifted to lower wave numbers.

| Bond lengths (Å) | Tl(1)–N(1) 2.695(12) | Tl(1)–N(2) 2.704(13) | N(1)–C(5) 1.339(19) | N(1)–C(7) 1.159(20) |
| Bond angles (°) | N(1)–Tl(1)–N(2) 60.2(4) | Tl(1)–N(1)–C(1) 121.1(9) | Tl(1)–N(2)–C(6) 121.2(9) | O(1)–N(1)–C(5) 118.5(12) |

Table IV. Selected bond lengths (Å) and bond angles (°).

Fig. 4. Nature of the chemical bonds between: (a) transition metals, (b) non-transition metals and the nitroso-group.
[3] O. A. Domashevskaya, M. D. Mazus, A. A. Dvor- 


[26] O. A. Domashevskaya, V. D. Khavr'uchenko, and 
[27] R. D. Lampeka, V. S. Kutz, and V. V. Skopenko, 
[28] K. V. Domasevitch, V. V. Skopenko, and N. N. 