The structure of Pd complexes of 2-(N-methylthiocarbamoyl) amino-4-methyl-thiazole and 2-(N, N-dimethylthiocarbamoyl) amino-4-methylthiazole

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Abstract

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The Structure of Pd Complexes of 2-(N-methylthiocarbamoyl) amino-4-methylthiazole and 2-(N,N-dimethylthiocarbamoyl) amino-4-methylthiazole*

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Reiko Osaka, Yukio Murakami **

(Received September 30, 1977)

Summary

2-(N-methylthiocarbamoyl) amino-4-methylthiazole (1a) forms a complex quickly with Pd²⁺ at room temperature and pH 2, however, it forms both unstable red complex (B) and stable yellow complex (A) depending upon the molar ratio between the ligand (1a) and Pd²⁺. The complex (B) changes to the stable complex (A) instantly when (B) contacts with a base or (1a) is added to a chloroform solution of (B).

On the other hand, 2-(N,N-dimethylthiocarbamoyl) amino-4-methylthiazole (1a) gives only the stable yellow complex (C) under the same condition. The proposed structures for the complex (A), (B) and (C) are reported.

The authors¹ reported the analytical chemistry on 2-(N-alkylthiocarbamoyl) aminothiazole derivatives with 66 metal ions and recently spectroscopic quantitative of Pd²⁺ with 2-(N-methylthiocarbamoyl) amino-4-methylthiazole². Uno et al.³ reported the research on 2-(N-arylthiocarbamoyl) aminothiazole derivatives as organic reagent.

Firstly, the formation of a complex between (1a) and Pd²⁺ will be described. The composition of the chelate at pH 2 through a continuous variation and molar ratio methods indicated that Pd²⁺ : (1a) was 1 : 2 at 283 and 323 nm and 1 : 1 at 377 nm.

To a chloroform solution of (1a) was added a Pd²⁺ solution (adjusted to pH 2 with HCl) and a mixture was shaken for 1 hr. to give the unstable red complex (B) and the stable yellow complex (A) depending on the molar ratio between ligand (1a) and PdCl₂ as shown as Table 1.

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¹ Reported at 96th Ann. Meeting Japan Pharm. Soc., April, (1976)
² Department of Chemistry, Faculty of Science, Tokyo Metropolitan University; Fukasawa, Setagaya-ku, Tokyo 158 Japan.
³) T. Uno, Y. Akihama, Yakugaku Zasshi, 80, 1015 (1960), ibid., 81, 579 (1961)
Mainly (B) was obtained when the molar ratio of ligand (1a) is small. At the ratio of 1 : 2, (A) and (B) were obtained. However, (A) was the main product when the ratio of ligand (1a) is large. These findings were confirmed with TLC (cyclohexane : ethyl acetate=2 : 1).

On the other hand, only the stable yellow complex (C) was obtained at varying molar ratio of 1 : 0.5–6.0 between 2-(N,N-dimethylthiocarbamoyl) amino-4-methylthiazole (1b) and PdCl₂. Both (A) and (C) were stable toward 5N-NaOH, therefore, an excess ligand (1a) or (1b) was removed by washing the reactant with aq. NaOH and then it was purified chromatographically using alumina or silica gel in a column. The yellow complex (A) and (C) showed a negative test for chlorine (Beilstein test). As shown in Fig. 1, the UV absorption curves for (A) and (C) are similar and their $\lambda_{max}$ values are practically identical. Therefore, the similar structure for (A) and (C) was estimated. The unstable red complex (B) gave a positive test for halogen (Beilstein) and its UV curve was markedly different from that of (A) or (C).
Table 1·A Effect of Molar Ratio (PdCl₂ : Ligand) of Reactants

<table>
<thead>
<tr>
<th>PdCl₂ : (la) or (lb)</th>
<th>1 : 0.4</th>
<th>1 : 0.7</th>
<th>1 : 0.8</th>
<th>1 : 0.5</th>
<th>1 : 3</th>
<th>1 : 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>( la )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( lb )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1·B Rf value (TLC) of (la), (lb), (A), (B) and (C)

<table>
<thead>
<tr>
<th>solvent</th>
<th>cyclohexane : ethyl acetate</th>
<th>ether : toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 : 1</td>
<td>1 : 1</td>
</tr>
<tr>
<td>plate</td>
<td>Silica gel</td>
<td>Aluminum oxide</td>
</tr>
<tr>
<td>( la )</td>
<td>0.25</td>
<td>0.06</td>
</tr>
<tr>
<td>( A )</td>
<td>0.39</td>
<td>0.36</td>
</tr>
<tr>
<td>( B )</td>
<td>0.31</td>
<td>0.02</td>
</tr>
<tr>
<td>( lb )</td>
<td>0.12</td>
<td>0.07</td>
</tr>
<tr>
<td>( C )</td>
<td>0.48</td>
<td>0.21</td>
</tr>
</tbody>
</table>

The mass spectral data for ligand (la) and (lb) together with the complexes (A), (B) and (C) are shown in Fig. 2. As shown in Chart 1, if the structure of (A) is assumed to have a composition of Pd²⁺ : (la) = 1 : 2 having a molecular formula of C₁₂ H₁₆ N₆ S₄ Pd (MW 478.958), the peaks were observed at m/e 479 for M⁺, m/e 293 for M⁺-(la) and m/e 187 for (la), then the rest of fragmentation pattern corresponds with that of (la). Assuming (C) has a similar structure as (A), the molecular formula should be C₁₄ H₂₀ N₆ S Pd (MW 507.012). The peaks were observed at m/e 507 for M⁺ and m/e 306 for M⁺-(lb) and the rest of the fragmentation pattern corresponds with that of (lb). Although the Rf values were identical and the IR spectral data almost identical for all the samples of the unstable red complex (B) obtained by various absorption materials and eluting solvents during the chromatographic purification step, these decomposition points and the mass spectral data were not identical to each other. The red complex (B) of mp 280° (decomp.) purified through a silica gel column eluting with ether–toluene (1 : 1) mixture showed a small peak of m/e 345 which corresponded with a molecular weight for the structure (B₂) or (B₃) in Chart 2. The analysis for C and Cl did not agree with the corresponding calculated values.
Table 2 shows NMR spectral data of ligand (1a), (1b) and the complexes (A), (B) and (C). (1a) was difficultly soluble in CHCl₃, but (1b) was readily soluble in CHCl₃. The complexes (A), (B) and (C) were difficultly soluble in DMSO-d₆, but soluble in CHCl₃. A chemical shift (CDCl₃, DMSO-d₆) of CH₃ at position 4 of thiazole ring is usually seen at 2.10-2.30 ppm and it shows a doublet (J = 1.0 Hz) by coupling with H at position 5, but varies with a substituent at 3. A chemical shift of methyl at 4 in the complex (A) or (C) shows a high field at around 1.92 ppm. On the other hand, a chemical shift of methyl at 4 in (B) shows a low field shift at 2.59 ppm. Due to the presence of a peak at 2.97 ppm (d, 3H×2, J = 5.0 Hz) and 3.06 ppm (d, 3H, J = 5.0 Hz) for –N–CH₃ in (A) or (B), respectively, it was concluded that –N–CH₃ instead of =N–CH₃ in correct. It was estimated that the L-Pd bond was covalent by replacement instead of coordination, because a N–H signal corresponding to δ 11.40 of ligand (1H, broad) disappeared, although –N–CH₃ appeared at δ 9.06 (1H×2, broad). These findings showed the presence of magnetically equivalent CH₃ groups and supported the proposed structure (A).
Similarly, the proposed structure (C) was supported from the findings that $-\text{N} \left< \text{CH}_3 \right>$ of the two ligands in the complex (C) showed a singlet for $6\text{H}$ at 3.30 ppm ($\text{CDCl}_3$) and 3.31 ppm ($\text{DMSO-d}_6$) and a signal for $\geq \text{N-H}$ disappeared. The unstable complex (B) showed those signals of 1.30-1.50 ppm which did not disappear with $\text{D}_2\text{O}$ addition. These signals varied depending upon the purification methods and under investigation.
As shown below, the ligand (1a) and (1b) have a structure where a thiourea group having three donor sites is connected with a thiazole–ring having two donor sites at position 2.

Therefore, the whole molecule has five donor sites. The IR and Far–IR spectra on thiourea–metal and thiazole–metal complexes which had been reported elsewhere, will be described first, followed by those of (A), (B) and (C). IR spectra of thiourea (Tu) complexes of Pd, Pt, Zn and Ni reveal that sulfur–metal bands are present in all thiourea complexes studied.\(^4\)\(^5\)

The high frequency N–H bands in the thiourea spectra were not shifted to lower

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Table 2 NMR Spectral Data

Chemical shifts are expressed in δ (ppm) with TMS as internal standard. The coupling constant (J) is expressed in Hz; s, singlet; d, doublet; br, broad.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO-d6</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>CDCl3</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>CDCl3</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
</tbody>
</table>

**Frequency when metal (M)-Tu complexes were formed.** This finding indicates that nitrogen (N)-M bands are not present, but are the bands between sulfur (S) and metal atoms. The formation of S-M bands would give a highly polar structure of the thiourea molecule having greater double bond character of the N-carbon (C) band and a greater single bond character of the C-S bond. The absorption bands (KBr-disk) observed for the M-Tu complexes are assigned as follows5).

changed slightly upon the coordination through S atoms. The conspicuous difference in
the spectrum of Tu and its M-complexes appears in the region at about 1100 cm\textsuperscript{-1}. The
strong absorption of Tu at 1083 cm\textsuperscript{-1} is extremely weakened or disappears on complex
formation. This observation can be explained by the considerable change in the nature of
the N–C bond as well as of the C=S bond on coordination of Tu through the S atom. The
bands observed at about 700 cm\textsuperscript{-1} in the spectra of the complexes correspond to the 730 cm\textsuperscript{-1}
band of Tu. The lowering of frequency can be attributed to the reduced double bond char-
acter of the C=S bond. The C=S stretching coordinate is distributed principally among
three vibrations in Tu, the major proportion at 733 cm\textsuperscript{-1}, and approximately equal propor-
tions at 1414 and at 487 cm\textsuperscript{-1}. The satisfactory assignment of the IR frequencies of
thioacetamide (TAM) and its N-deuterated molecule was reported by Suzuki\textsuperscript{7} with the aid of
a normal coordinate analysis Vrey–Bradley force field. It is of particular interest that the
C=S stretching frequency was assigned around 975 cm\textsuperscript{-1}, as reported by some earlier work-
ers\textsuperscript{8,9,10} instead of a bond near 720 cm\textsuperscript{-1} as favored by the normal coordinate treatment\textsuperscript{7}.

Ray et al.\textsuperscript{11} reinvestigated the normal coordinate of TAM and its seven isotopic
labeled molecules using Vrey–Bradley force constants refined by the least-squares procedure.
The laser Raman spectrum of TAM also has been reported. The agreement between the
observed and calculated frequencies for TAM is excellent. The C=S stretching mode has
been attributed by Suzuki to a band at 720 cm\textsuperscript{-1} which has a major contribution (approx.
60%) from the mode. This assignment was supported by the large red shift of the band by
30–60 cm\textsuperscript{-1}, in M–complexes, where the thiocarbonyl sulfur is the donor\textsuperscript{12,13} and the shift to
675 cm\textsuperscript{-1} on S–methylation\textsuperscript{14} was observed. Thus, the attribution of C=S stretching
vibration to ~ 975 cm\textsuperscript{-1} by Walter et al. is not supported. This band has, however, about
~ 10% C=S stretching mode and shows minor changes on complex formation and
S–methylation. N-Methylthiourea forms a metal–complexes through the sulfur atoms\textsuperscript{15}.

The IR spectral studies on N, N-dimethylthioformamide (DMeTF) and its M–complexes
indicates that bands at 1560 and 521 cm\textsuperscript{-1} were shifted to higher frequencies; 1580 and 535
cm\textsuperscript{-1}, respectively and the bands at 975 cm\textsuperscript{-1} were shifted slightly lower upon complex
formation. The bands at 1560, 521 and 975 cm\textsuperscript{-1} were assigned to the C=N stretching
coupled with C=S bending and C=S stretching vibrations\textsuperscript{16}. Although a number of IR

\textsuperscript{8} W. Walter and H. P. Kubersky, Ann. Chem., 694, 56 (1966)
\textsuperscript{9} E. Spinner, Spectrochim. Acta, 15, 95 (1959)
\textsuperscript{10} W. Kutzelnigg and R. Mecke, ibid., 17, 530 (1961)
\textsuperscript{15} T. J. Lane and A. Yamaguchi et al., J. Am. Chem. Soc., 81, 3824 (1959)
studies of Tu, TAM and DMeTF complexes have reported as mentioned above, none was extended to the region of M–Ligands vibrations. Adams et al.\textsuperscript{17) reported the results of the Far–IR investigation on some complexes of the types (MTu\textsubscript{6})\textsuperscript{2+}, (M=Pd, Pt) has a low symmetry where weak bands accompany the intense $\nu_{M-S}$: $\nu_{Pd-S}$ appears at 277 (vs) cm\textsuperscript{-1} and is accompanied by two weak bands at lower frequency. The square–planar PdCl\textsubscript{2}–Tu\textsubscript{2} has almost certainly \textit{trans} configuration in that $\nu_{Pd–Cl}$ appears as an intense broad band at ca. 326 cm\textsuperscript{-1} which may be resolved into two contributions. The absorption $\nu_{Pd–S}$ near at 280 cm\textsuperscript{-1} is similarly distorted. The \textit{cis}–PdCl\textsubscript{2}Tu\textsubscript{2} complexes always yield doublet for $\nu_{Pd–Cl}$ clearly separated by at least 10 cm\textsuperscript{-1}.

The M–complexes of thiazole\textsuperscript{18)}, benzothiazole\textsuperscript{191}, and its 2-methyl derivatives have already been reported. Thiazole has both N and S as possible donor sites where the majority of complexes are favored through N-atom. Weaver et al\textsuperscript{201 reported that the synthesis and characterization of complexes having divalent Zn, Pt, Co, Ni and Cu with thiazole and 4- or 2, 4-dialkylthiazoles, accompanying various anions. The nature and position of the substituents showed a profound effect on the stereochemistry of resulting complexes. The zinc chloride, bromide and iodide complexes of 4-methylthiazole (4-Met) and 2, 4-dimethylthiazole (2, 4-DMeT) have a structure ZnX\textsubscript{2}L\textsubscript{2} and were diamagnetic. The similarity in position and splitting of the IR–peaks of the three Pt\textsuperscript{II}–thiazoles as compared to the chloro and bromo derivatives of the analogous pyridine complexes\textsuperscript{21,22,23} leads to an assignments of \textit{cis}–planar geometry and N–coordination for thiazoles. Thiazole complexes resemble pyridine rather the imidazole or amino derivatives. Thus, the maximum ligated Cu–complexes with imidazole, benzimidazole and ammonia are CuCl\textsubscript{2}L\textsubscript{4}, whereas pyridine, thiazole, 4- and 2, 4-dialkylthiazoles and benzothiazole from predominantly CuCl\textsubscript{2}L\textsubscript{2}. This has been explained in terms of the $\sigma$ –donor, $\pi$ –acceptor properties of the ligand maintaining an effective electroneutrality on the central ion. Thiazole being a weaker $\sigma$ –donor and possibly better $\pi$ –acceptor than imidazole will favor structures in which four halides MX\textsubscript{4}L\textsubscript{4} rather than four heterocyclic bases MX\textsubscript{2}L\textsubscript{4} are coordinated. Hughes et al.\textsuperscript{241 are interested in the preparation of model compounds for thiazole– and thiamine–M ion interactions in biological process and have examined the coordination behavior of 4–methylthiazole (4-MeT) with Cu\textsuperscript{II}, Ni\textsuperscript{II}, Cu\textsuperscript{II}, Zn\textsuperscript{II} and Pd\textsuperscript{II} salts. In diamagnetic square planar Pd(4-MeT)\textsubscript{2}Cl\textsubscript{2} the ligand still appears to be N–bonded rather than S–bonded. The Far–IR spectrum indicated a \textit{trans} structure showing one $\nu_{Pd–Cl}$ band: A band at 353 (s) cm\textsuperscript{-1} was assigned to $\nu_{Pd–Cl}$ and a band at 265

\textsuperscript{17) D. Adams et al., J. Chem. Soc., (A) 884 (1967)
19) E. J. Duff and M. N. Hughes et al., ibid. 2354 (1968)
22) D. M. Adams et al., J. Chem. Soc., (A) 734 (1964)
23) G. E. Coates and O. Parkin, ibid., 421 (1963)
Table 3  Infrared Bands ligand (Ia) and chelate (A, B, C) in the 3500
600 cm$^{-1}$ (KBr) and in the 600 - 210 cm$^{-1}$ (Nujol)

<table>
<thead>
<tr>
<th>(Ia) (EtOH)</th>
<th>(A) mp 269* (decomp.)</th>
<th>(B) mp 280* (decomp.)</th>
<th>(C) mp 294* (decomp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mp 253°(EtOH)</td>
<td>3463 (m, br) 3400 (m)</td>
<td>3350 (s) 3320 (s)</td>
<td>3213 (s)</td>
</tr>
<tr>
<td>3170 (s)</td>
<td>3120 (m) 3074 (s)</td>
<td>3100 (m, br)</td>
<td>3100 (m, br) 3110 (w)</td>
</tr>
<tr>
<td>3023 (s, sh)</td>
<td>2950 (s, br) 2925 (m, sh)</td>
<td>2950 (w) 2920 (m)</td>
<td>2950 (m, sh) 2913 (m)</td>
</tr>
<tr>
<td>1589 (vs) 1566 (vs)</td>
<td>1537 (s) 1509 (s)</td>
<td>1540 (vs) 1530 (vs)</td>
<td>1540 (m) 1508 (s)</td>
</tr>
<tr>
<td>1455 (m, br)</td>
<td>1432 (m)</td>
<td>1495 (vs) 1490 (vs)</td>
<td>1450 (vs, sh) 1440 (s) 1439 (w, br)</td>
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<tr>
<td>1390 (s)</td>
<td>1381 (m) 1364 (m)</td>
<td>1390 (s) 1380 (9m)</td>
<td>1391 (vs) 1356 (s)</td>
</tr>
<tr>
<td>1315 (w)</td>
<td>1294 (m)</td>
<td>1320 (m) 1310 (m)</td>
<td>1320 (s) 1300 (m) 1299 (m)</td>
</tr>
<tr>
<td>1292 (m, sh)</td>
<td>1282 (m, sh)</td>
<td>1265 (m, br)</td>
<td>1280 (m) 1260 (w)</td>
</tr>
<tr>
<td>1250 (s, sh)</td>
<td>1240 (s) 1224 (s)</td>
<td>1240 (w)</td>
<td>1198 (w)</td>
</tr>
<tr>
<td>1190 (m)</td>
<td>1175 (m) 1135 (m)</td>
<td>1190 (m)</td>
<td>1175 (m) 1141 (w)</td>
</tr>
</tbody>
</table>

- 38 -
| Frequency (m) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) | Frequency (w) |
|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 1070 (m)     | 1020 (w)     | 1035 (w)     | 1116 (m)     | 982 (m)      | 990 (w)      | 995 (w)      | 995 (w)      | 921 (w)      | 865 (m)      | 865 (m)      | 859 (w)      | 818 (w)      | 770 (w)      | 760 (w)      | 760 (m)      | 748 (m)      | 742 (m, sh)  |
| 710 (w)      | 705 (s)      | 704 (w)      | 670 (w)      | 675 (w, sh)  | 660 (w)      | 665 (w)      | 660 (w)      | 636 (w)      | 618 (w)      | 615 (m)      | 600 (m)      | 605 (w)      | 595 (vs)     | 562 (vs)     | 562 (s)      | 552 (vs)     | 540 (vs)     |
| 460 (w, sh)  | 445 (s)      | 439 (s)      | 410 (w, sh)  | 410 (w, sh)  | 400 (w)      | 380 (w, sh)  | 380 (w, sh)  | 360 (w)      | 360 (w)      | 365 (w)      | 365 (w)      | 365 (w)      | 330 (vs)     | 320 (w, sh)  | 325 (vs)     | 315 (w, sh)  | 280 (m)      |
| 280 (m)      | 265 (m)      | 265 (w)      | 222 (m)      | 225 (w)      | 225 (w)      | 215 (w)      | 215 (w)      | 215 (w)      | 215 (w)      | 215 (w)      | 215 (w)      | 215 (w)      | 215 (w)      | 215 (w)      | 215 (w)      | 215 (w)      | 215 (w)      |

abbreviation vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder
(m) cm$^{-1}$ was assigned to $\nu_{\text{Pd-Cl}}$. If $\text{C}=$S is bonded with Pd in the complex (A) and (B) stretching vibrations for $\text{C}=$S will shift lower and the double bond character of C-N stretching vibration will increase, however, $\nu_{\text{C-N}}$ frequency will not shift higher due to the conjugation with the aromatic thiazole ring as seen in the complex of S-bonded thiourea. As shown in Table 3, the IR spectra of ligand (1a) and (1b) in solid phase shows 3400 (m) cm$^{-1}$ and 3170 (s) cm$^{-1}$ for (1a), 3115 (m) cm$^{-1}$ for (1b) beyond 3100 cm$^{-1}$, while the IR spectra of a dilute solution of both ligand (1a) and (1b) showed a sharp strong band at 3405 cm$^{-1}$ indicating intermolecular hydrogen bonding in solid phase. The spectra (KBr) of the chelates showed strong bands at 3350 cm$^{-1}$ and 3320 cm$^{-1}$ for (A), 3213 cm$^{-1}$ for (B), but no strong absorption beyond 3100 cm$^{-1}$ for (C).

The four very strong absorptions at 1589, 1566, 1537 and 1509 cm$^{-1}$ for ligand (1a) gave a negative shift by deuteration, therefore, they are probably due to $\nu_{\text{C-N}}$ coupled with $\delta_{\text{N-H}}$ vibration mode.

The absorption bands assigned to these modes are 1570 (w, sh), 1560 (m, sh), 1540 (vs) for (A) and 1560 (vs), 1550 (vs) and 1520 (vs) cm$^{-1}$ for (B) showing a negative shift. A strong band near 1450 cm$^{-1}$ in (la), (A) and (B) is assigned to the ring skeletal vibrations. A band at 1380 (m) cm$^{-1}$ in (la) appeared at ca. 1390 (s) cm$^{-1}$ in (A) and (B) and it was assigned to a coupling of $\delta_{\text{C-H}_2}$ and ring skeletal vibrations. The three strong bands at 1250, 1240 and 1220 cm$^{-1}$ for (1a) are the characteristic absorptions of (1a). A band at 1070 (m) cm$^{-1}$ for (1a) was not observed for (A) and (B) and a band at ca. 980 (s) cm$^{-1}$ for (1a) was shifted to ca. 660 (w) cm$^{-1}$ indicating a change in $\text{C}=$S bond. The above NMR, Mass and IR spectral data indicated a presence of a band between Pd and S of the $\text{C}=$S group. In order to identify absorption frequencies of $\nu_{\text{Pd-S}}$ $\nu_{\text{Pd-N}}$ and furthermore $\nu_{\text{Pd-Cl}}$ bond in (B), Far-IR spectra (Nujol) of these compounds were obtained. As described before $\nu_{\text{Pd-S}}$ vibrations for Tu appeared at ca. 280 cm$^{-1}$ and $\nu_{\text{Pd-N}}$ vibration in Th and 4-MeT complexes appeared at ca. 260 cm$^{-1}$

A terminal trans $\nu_{\text{Pd-Cl}}$ vibrations appeared near 350 cm$^{-1}$ as a singlet and cis $\nu_{\text{Pd-Cl}}$ vibrations as doublet. The bridging Pd-Cl vibration appeared a little lower at ca. 300 cm$^{-1}$.

As shown in Table 3, comparing the 400–200 cm$^{-1}$ region of (1a) with that of (A) and (B), the band at 330 (vs) cm$^{-1}$ in (1a) was not observed for (A) and (B), however, new bands appeared at 295 (w) 265 (m) cm$^{-1}$ in (A) and at 325 (vs), 305 (s), 290 (vs) and 265 (m) cm$^{-1}$ in (B). The new bands at 325 (vs) and 305 (s) cm$^{-1}$ in (B) may be assigned to $\nu_{\text{Pd-Cl}}$ vibrations. In general halogen sensitive bands are fairly readily identified by simple replacement Cl$\rightarrow$Br $\rightarrow$I, therefore, by replacing Cl with Br, the frequencies for the bridging chlorine and the terminal Pd–Cl will be confirmed so that the structure for (B) could be established. The IR spectrum of (1b) and chelate (C) will be discussed fully elsewhere.
Experimental

Typical experimental procedure is illustrated below:

**Synthesis of chelate (A)**

**Method 1.**

The Pd–chelate (A) was prepared by shaking of 1-methylthiocarbamoylamino-4-methylthiazole\(^{25}\) (1a, 0.5g) in a chloroform (115 ml), with aq. solution (65 ml, adjusted the pH to about 2 with HCl) for 1 hr. The molar ratio of ligand (1a) to PdCl\(_2\) was \(8 : 1\). The chloroform layer was separated, washed with 0.1N-NaOH, and H\(_2\)O (200 ml), dried (Na\(_2\)SO\(_4\)), evaporated to dryness, then yellow crystal was obtained. The product was purified through a silica gel column eluting with cyclohexane–ethyl acetate (2 : 1). mp 272° (decomp.) yield 0.14g.

**Method 2.**

The Pd-chelate (A) was prepared by slowly adding a chloroform solution (20 ml) of (O\(_{\equiv}\)C\(\equiv\)N)\(_2\)PdCl\(_2\)\(^{26}\) (1.5g) to a chloroform solution (750 ml) of (1a, 1.5g) and stirred for 40 minutes. The chloroform solution was washed with 0.1N-NaOH, and H\(_2\)O (750 ml), dried (MgSO\(_4\)), and evaporated, to yield crude (A). The product was chromatographed on a silica gel column using ether–toluene (1 : 1) as an eluent. The yellow chelate was obtained and showed a single spot on a silica gel plate (Rf value 0.39). mp 269° (decomp.), yield 1.15g. Anal. Calcd. for (C\(_{12}\)H\(_{16}\)N\(_6\)S\(_4\)Pd, Mol. Wt. 478.958), C, 30.09; H, 3.37; N, 17.55; S, 26.78; Pd, 22.21; Found C, 29.64; H, 3.12; N, 17.26; S, 26.87; Pd, 21.68.

**Synthesis of chelate (B)**

**Method 1.**

To a chloroform solution (200 ml) of (1a, 0.15g) was added aq. solution (2000 ml, pH about 2) of PdCl\(_2\) (0.3g) and a mixture was shaken for 1 hr to give the unstable complex (B). The molar ratio of ligand (1a) to PdCl\(_2\) was 1 : 2. The chloroform layer was separated, dried (MgSO\(_4\)), and evaporated at low temperature *in vacuo*, to yield red crystal. The red crystal was chromatographed on a silica gel column in the same way as described above, to give 0.1g of (B). mp 280° (decomp.), Anal. Calcd. for (C\(_6\)H\(_8\)N\(_3\)S\(_2\)Pd, Mol. Wt. 345.859) C, 20.84; N, 12.15; S, 18.54; Pd, 30.76; Cl, 15.38, Calcd. for (C\(_6\)H\(_8\)N\(_3\)S\(_2\)PdCl, Mol. Wt. 363.585) C, 19.82; H, 2.22; N, 11.56; S, 17.64; Pd, 29.26; Cl, 19.50, Calcd. for (C\(_6\)H\(_8\)N\(_3\)S\(_2\)PdCl\(_2\), Mol. Wt. 382.132) C, 21.96; H, 2.46; N, 12.81; S, 19.54; Pd, 32.43; Cl, 10.80, Found C, 22.37; H, 2.40; N, 12.14; S, 18.75; Pd, 30.75; Cl, 12.42.

**Method 2.**

The chelate (B) was prepared by mixing (O\(_{\equiv}\)C\(\equiv\)N)\(_2\)PdCl\(_2\) (0.9g) with (1a, 0.3g) in a chloroform solution (200 ml). The chloroform solution was evaporated and the column chromatographic separation of the residue in the same way described above, to give the chelate (B). mp 265° (decomp.), yield 0.88g.

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25) Y. Yamamoto et al., This Annual Report, No 6/7 77 (1961/2), C. A., 60, 514 (1964)
Synthesis of chelate (C)

Method 1,

The Pd chelate (C) was prepared by shaking 1, 1-dimethylthiocarbamoylamino-4-methylthiazole\textsuperscript{27} (1b, 0.8 g) in a chloroform (400 ml) with aq. solution (65 ml, pH about 2) of PdCl\(_2\) (0.8 g) for 1 hr. The molar ratio of ligand (1b) to PdCl\(_2\) was 1 : 1. The chloroform layer was separated, washed with 0.1N-NaOH (250 ml), and water (200 ml), dried (Na\(_2\)SO\(_4\)), evaporated to dryness, then yellow crystal was obtained. The product was purified through a silica gel column eluting with cyclohexane-ethyl acetate (2 : 1). mp 294° (decomp.). Anal. Calcd. for (C\(_{14}\)H\(_{20}\)N\(_6\)S\(_4\)Pd, Mol. Wt. 507.012) C, 33.18; H, 3.98; N, 16.58; S, 25.30, Found C, 33.23; H, 3.43; N, 16.51; S, 25.80.

Synthesis of the 1-methylthiocarbamoylamino-4-methylthiazole-N, N′-d\(_2\)

A ethanol-d\(_1\) (C\(_2\)H\(_5\)OD, 30 ml) solution of 1-methylthiocarbamoylamino-4-methylthiazole \((\text{la}), 0.1 g; \text{mp} 254°, \text{C}_6\text{H}_9\text{N}_3\text{S}_2\) Mol. Wt., 187.287, M\(^+\) 187 (base peak)\) and D\(_2\)O (0.5 ml) was refluxed 8 hr in the presence of triethylamine (60 mg). The solution was evaporated, and the residue was recrystallized from C\(_2\)H\(_5\)OD, affording the (la)-N, N′-d\(_2\) \(\text{mp} 254°, \text{C}_6\text{H}_7\text{N}_3\text{S}_2\text{D}_2\) Mol. Wt., 189.303, M\(^+\) 189 (base peak).

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\(27\) Y. Yamamoto et al., This Annual Report, 12, 116 (1967), C. A., 69, 16654g (1968)