Synthesis, characterization and structural studies of metal complexes based on dmit, dmt and tbs ligands. Crystal structure of [PPN][Au(dmit)₂].CH₃CN

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Dichalcogenene complexes of the formula [cation][M(dmit)₂]⁻, [cation][M(dmit)₂]⁺ and [cation][M(tbs)₂]⁻ (M = Ni, Cu, Pd, Pt; Au, n = 0-2; dmit = 4,5-dimercapto-1,3-dithiole-2-thione, dmtn = 4,5-dimercapto-1,2-dithiole-3-thione and tbs = thiobenzene-selenolate, cation = trimethyltelluronium, (CH₃)₂Te⁺, bis(triphenylphosphine)iminium, PPN⁺, tetrabutylammonium, Bu₄N⁺, and trimethylammonium, Me₃NH⁺) have been prepared. The spectroscopic and electrochemical behaviour have been studied and compared with the related complexes. Oxidation reactions of these complexes with iodine afforded partially oxidized derivatives which exhibit compressed electrical conductivities of > 10⁻⁶ S cm⁻¹ at room temperature. The [PPN][Au(dmit)₂] complex has been structurally characterized by X-ray crystallography and its structure is compared with the structure of previously reported complexes [(CH₃)₂Te][Au(dmit)₂] and [PPN][Ni(dmit)₂].

Introduction

Currently there is much interest in the study of planar metal complexes of dichalcogenene and mixed chalcogenene ligands because of their metallic and superconducting properties. Several of their charge-transfer salts in this category exhibit superconducting properties. These include (NMMe₄)₀.₅[Ni(dmit)₂]⁻, (NMMe₂Et₂)₀.₅[Pd(dmit)₂]⁻, (NMMe₂Et₂)₀.₅[Pd(dmit)₂]⁻² containing closed-shell cations and (TTF)⁻[Ni(dmit)₂]⁻⁻, α-α'-(TTF)⁻[Pd(dmit)₂]⁻¹, α-(EDT-TTF)[Ni(dmit)₂]⁻¹ containing open-shell cations. Highly conducting Langmuir-Blodgett films based on Au(dmit)₂⁺, and Ni(dmit)²⁻ anions have also been reported. In addition, these metal complexes find applications in non-linear optics and in the preparation of polymeric materials exhibiting photorefractivity.

Recent detailed studies have shown that the change of central metal ions or cations affect their conducting properties. The synthesis and characterization of [M(dmit)₂]⁻ and [M(dmtn)₂]⁻ (M = Au, Cu, Ni, Pd and Pt) complexes with trimethyltelluronium cation and other cations. ESR studies have been carried out extensively to explain their interesting magnetic properties. A single crystal X-ray structure of [PPN][Au(dmit)₂] is described and compared with the reported structures of [(CH₃)₂Te][Au(dmit)₂] and [PPN][Ni(dmit)₂]. Also there is relatively little chemistry reported for the mixed S-Se, S-Te and Se-Te analogues, while much of the recent work has been focussed on the synthesis of metal complexes with dichalcogenenes. Therefore, we have synthesized [M(tbs)₂]⁻⁻ (tbs = thiobenzene-selenolate) complexes with various cations and characterized by spectroscopic and electrochemical techniques in order to compare their properties with their sulphur bdt (benzenedithiolene) and bds (benzenediselenolene) analogues. Our convenient synthetic approach to tbs⁻⁻ has also proved useful for the synthesis of variety of organo-sulphur-selenium heterocycles.

Materials and Methods

Reagents used for the research work were selenium powder (Fluka), tetrabutylammonium bromide (Fluka), NiCl₂ H₂O, ZnCl₂, CuCl₂, PdCl₂, (E. Merck, India), K₂AuCl₄, K₂PtCl₆ (Aldrich), trimethylammonium chloride (Fluka), n-butyl lithium (E. Merck). All solvents were obtained from commercial sources and were purified. In general,
all solvents were distilled prior to use and stored over molecular sieves. All the reactions were carried out under argon with standard Schlenk techniques unless otherwise stated. The dmit ligand was obtained in large quantities as the main product by chemical reduction of carbon disulphide in DMF and was stored as its dibenzoyl salt. Isomerisation of dmit at solution. This was isolated as its zinc salt and all solvents were distilled prior to use and stored over reduction of carbon disulphide in DMF and was converted to the benzoyl ester by reacting with benzyol chloride in acetone. Trimethyltelluronium iodide was prepared by literature method. The trimethyltelluronium cation were prepared following a general procedure and a typical example is given below.

**Synthesis of [(CH₃)₃Te]₂[Ni(dmit)]**

The benzyl ester of the ligand dmit (2 mmol) was mixed with sodium methoxide solution (2 ml, 2M) and stirred for 10 min. NiCl₂5H₂O (1 mmol) in methanol (50 ml) was added to this and stirred for another 10 min. To this solution trimethyltelluronium chloride (2 mmol) dissolved in methanol (20 ml) was added and the stirring was continued. After 1 h the black solid, which precipitated out, was filtered, washed with methanol and dried under vacuum. This solid was recrystallized from 1:1 acetone-isopropanol mixture to give crystals of [(CH₃)₃Te][Ni(dmit)] ; yield , 69%. Anal. Found: C, 16.23; H, 1.43; Calcd. for C₁₂H₁₆Te₂NiS₆O: C, 16.09; H, 1.35. IR (KBr pellet) νₛ(C=C) 1380, νₛ(C-S) 940 cm⁻¹. UV/vis λₘₐₓ (nm) 490, 384 and 274.

**Synthesis of [(CH₃)₃Te]₂[Pt(dmit)]**

The benzoyl ester of the ligand (2 mmol) was dissolved in sodium methoxide (7 ml, 2M) to give a red coloured solution. An aqueous solution of potassium tetrachloroplatinate (1 mmol, 20 ml water) was added and stirring continued for half an hour. Trimethyltelluronium chloride (2 mmol) dissolved in methanol (20 ml) was added to the reaction mixture. The black precipitate was collected by filtration after 1 h. The black solid was recrystallized from 1:1 acetone-isopropanol mixture; yield, 71%. Anal. Found: C, 16.08; H, 1.94; Calcd. for C₁₃H₁₈Te₂PtS₁₀: C, 15.44; H, 1.94. IR (KBr pellet) νₛ(C=C) 1430, νₛ(C-S) 1050 and 1030, νₛ(C-S) 910 cm⁻¹. UV/vis λₘₐₓ (nm) 422, 269 and 320.

**Synthesis of [PPN][Au(dmit)]**

The dibenzoil ester of the ligand (2 mmol) was treated with sodium methoxide solution (7 ml, 2M) and stirred for 10 min. CuCl₂ (1 mmol) in methanol (50 ml) was added to this followed by bis(triphenylphosphine)iminium chloride (2 mmol) in methanol (20 ml). The reaction mixture was stirred for 30 min. The dark coloured solid, which precipitated out, was filtered, washed with propanol and dried under vacuum. The product was recrystallized from 1:1 acetone-isopropanol mixture to give crystals of [PPN][Au(dmit)]; yield, 73%. Anal. Found: C, 60.65; H, 3.94; N, 1.73; Calcd. for C₇₆H₄₇P₄N₄CuS₁₀; C, 61.09; H, 3.94; N, 1.83. IR (KBr pellet) νₛ(C=C) 1445, νₛ(C-S) 1060 and 1035, νₛ(C-S) 910 cm⁻¹. UV/vis λₘₐₓ (nm) 456, 385 and 308.

**Synthesis of [PPN][Au(dmit)]**

The [PPN][Au(dmit)] was prepared following the above procedure with methanolic solution of KAuCl₄; yield, 78%. Anal. Found: C, 45.01; H, 3.01; N, 1.61; Calcd. for C₉₃H₄₇P₄N₄AuS₁₀; C, 44.71; H, 2.68; N, 1.24. IR (KBr pellet): νₛ(C=C) 1380, νₛ(C-S) 1060 and 1020, νₛ(C-S) 920 cm⁻¹. UV/vis λₘₐₓ (nm) 465, 350 and 290.

**Synthesis of [(CH₃)₃Te]₂[Ni(dmit)]**

[(CH₃)₃Te]₂[Ni(dmit)] (1 mmol) was dissolved in acetone (60 ml) and air was bubbled through the solution for one hour. The volume was then reduced to 30-35 ml by evaporation under reduced pressure. To this solution, was added methanol (30 ml) to give a black precipitate. The precipitate was filtered and washed with methanol. Drying under vacuo for one hour gave crystalline [(CH₃)₃Te][Ni(dmit)]; yield, 71%. Anal. Found: C, 16.91; H, 2.1; Calcd. for
C_{9}H_{17}TeNiS\_2O: C, 17.32; H, 1.45. IR (KBr pellet): \( \nu_{C-(C)} = 1350, \nu_{C-(S)} = 1060 \) and 1040, \( \nu_{C-(S)} = 900 \) cm\(^{-1}\). UV/vis \( \lambda_{\text{max}} \) (nm) 463, 346 and 289.

**Synthesis of [(CH\(_{3}\)HTe)\([\text{Ni(dmit)}]_{2}\)]** 9

The benzoyl ester of the ligand (2 mmol) was reacted with sodium methoxide solution (7 ml, 2M). NiCl\(_{2}\)\(\cdot\)6H\(_{2}\)\(O\) (1 mmol in 20 ml methanol) was added to the above solution. After stirring for 30 min a methanolic solution of trimethyltellurium chloride (2 mmol) was added. The black solid was removed by filtration, washed with methanol and dried under vacuum. The compound was recrystallised from 1:1 acetone-isopropanol mixture; yield, 72%. Anal. Found: C, 11.99; H, 0.56; N, 0.28; Calcd.: C, 14.96; H, 0.38; N, 0.18%.

Complexes 15, 16, 17 and 18 were synthesized following the above procedure with appropriate starting materials.

**[(CH\(_{3}\)HTe)\([\text{Ni(dmit)}]_{2}\)]** 15: yield, 48%. Found: C, 13.36; H, 0.32; Calcd. C, 12.98; H, 0.29%.

**[(CH\(_{3}\)HTe)\([\text{Ni(dmit)}]_{2}\)]** 16: (yield, 51%; Found: C, 13.05; H, 0.62; Calcd. C, 12.93; H, 0.29%.

**[(CH\(_{3}\)HTe)\([\text{Pd(dmit)}]_{2}\)]** 17: yield, 58%. Found: C, 12.80; H, 0.52; Calcd. C, 12.10; H, 0.27%.

**[(CH\(_{3}\)HTe)\([\text{Au(dmit)}]_{2}\)]** 18: yield, 58%. Found: C, 10.38; H, 0.28; Calcd. C, 10.32; H, 0.12%.

**Synthesis of o-thiobenzeneselenolate (tbs\(^{-}\)) ligand 19**

The o-thiobenzeneselenolate (tbs\(^{-}\)) ligand was conveniently prepared from benzenethiol and elemental selenium. Benzenethiol was lithiated with n-butylithium in the presence of TMEDA in hexane. Elemental selenium was added to the dilithiated species to give the ligand as an orange slurry.

**Synthesis of [(CH\(_{3}\)HTe)\([\text{Au(tbs)}]_{2}\)]** 20

A methanolic solution of trimethyltellurium chloride (1 mmol in 30 ml of methanol) was added to a solution of 1-lithioseleno-2-lithiobenzene (1 mmol) dissolved in methanol (10 ml) and stirred for 2 h. A solution of NiCl\(_{2}\)\(\cdot\)6H\(_{2}\)\(O\) (0.5 mmol in methanol 20 ml) was added to the above solution and stirred for additional 1 h. A precipitate which formed was collected by filtration and dried under vacuum; yield, 48%. Anal. Found: C, 29.88; H, 2.88; Calcd. C, 29.75; H, 2.83%. IR (KBr pellet) \( \nu_{\text{cm}^{-1}} \) 3010, 2980, 2960, 1520, 1490, 1380, 1240, 1090, 1040, 760, 690 and 660. UV/vis \( \lambda_{\text{max}} \) (nm) 379, 326 and 250.

Complexes 21-27 were prepared by using the procedure described above.

**[(CH\(_{3}\)HTe)\([\text{Cu(tbs)}]_{2}\)]** 21: yield, 58%. Found: C, 29.88; H, 2.00; Calcd. for C\(_{25}\)H\(_{17}\)TeCuS\(_{2}\)Se\(_{2}\): C, 29.51; H, 2.81%. IR (KBr pellet) \( \nu_{\text{cm}^{-1}} \) 3020, 2980, 1580, 1550, 1480, 1380, 1310, 1200, 1160, 1090, 1040, 1010, 810, 760, 710, 700 and 660. UV/vis \( \lambda_{\text{max}} \) (nm) 406, 360 and 240.

**[(CH\(_{3}\)HTe)\([\text{Au(tbs)}]_{2}\)]** 22: yield, 61%. Found: C, 24.2; H, 2.28. Calcd. for C\(_{25}\)H\(_{17}\)TeAuS\(_{2}\)Se\(_{2}\): C, 24.22; H, 2.30. IR (KBr pellet) \( \nu_{\text{cm}^{-1}} \) 3020, 2980, 2900, 1660, 1480, 1430, 1380, 1310, 1250, 1180,
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1160, 1090, 1040, 890, 830, 760, and 670. UV/vis
λ_max (nm) 420, 310, and 231.

([Bu4N][Ni(tbsh)]2) 23; yield, 53%. Anal. Found: C, 49.65; H, 7.26; N, 2.03%. Calcd. for C28H42NNiS2Se2:
C, 49.77; H, 6.56; N, 2.07%. IR (KBr pellet) ν(cm⁻¹)
3010, 2970, 2940, 1470, 1410, 1290, 1240,
1165, 1145, 1090, 1040, 955, 760 and 665. UV/vis
λ_max (nm) 377, 323 and 246.

([Bu4N][Cu(tbsh)]2) 24; yield, 55%. Anal. Found: C, 48.86; H, 6.83; N, 2.83%. Calcd. for C28H42NCuS2Se2:
C, 49.44; H, 6.52; N, 2.06%. IR (KBr pellet) ν(cm⁻¹)
3020, 2980, 2940, 1480, 1440, 1325, 1200,
1160, 1085, 1040, 1010, 815, 760, 710, 705 and 665.

([Bu4N][Au(tbsh)]2) 25; yield, 53%. Anal. Found: C, 41.37; H, 5.41; N, 1.72%. Calcd. for C28H42NAuS2Se2:
C, 41.33; H, 5.45; N, 1.72%. IR (KBr pellet) ν(cm⁻¹)
3020, 2980, 2960, 1490, 1440, 1390, 1300, 1250,
1190, 1170, 1100, 1040, 900, 820, 770 and 670.
UV/Vis λ_max (nm) 420, 304 and 258.

([Me3NH][Ni(tbsh)]2) 26; yield, 52%. Anal. Found: C, 36.89; H, 3.70; N, 2.28%. Calcd. for C30H44NNiS2Se2:
C, 36.69; H, 3.70; N, 2.28%. IR (KBr pellet) ν(cm⁻¹)
3010, 2980, 2940, 1480, 1440, 1410, 1290, 1240,
1160, 1140, 1090, 1040, 930, 760 and 660. UV/vis
λ_max (nm) 379, 326 and 250.

([Me3NH][Cu(tbsh)]2) 27; yield, 38%. Anal. Found: C, 28.93; H, 2.89; N, 2.25%. Calcd. for C30H44NCuS2Se2:
C, 28.62; H, 2.88; N, 2.22%. IR (KBr pellet) ν(cm⁻¹)
3020, 2980, 2880, 1710, 1080, 1490, 1420, 1390, 1300, 1240, 1190, 1160, 1090, 1040, 930, 760 and 660. UV/vis
λ_max (nm) 420, 350 and 243.

Physical measurements

Elemental analysis was carried out using a Carlo
Erba 1106 analyzer. Infrared spectra in the range of 4000-6000 cm⁻¹ were recorded on a Perkin-Elmer
grating spectrometer model 681. The solid samples
were examined as KBr pellets. UV-Vis spectra in
acetonitrile solution was recorded with a Schimadzu
UV-260 spectrometer model 273. Measurements were
carried out in acetonitrile containing tetrabutylammonium perchlorate as a supporting
electrolyte, using a conventional cell consisting of
two platinum wires as working and counter electrodes
and an Ag/AgCl electrode as a reference. ESR spectra
were recorded on a Varian E-112 spectrometer.
Electrical conduction measurements were made using a two-probe measurement technique on compressed pellets.

Data collection for X-ray crystallography

A single crystal was mounted on a glass fibre on an
Enraf-Nonius CAD-4 diffractometer, equipped with
graphite monochromated Mo-Kα radiation (λ =
0.71073 Å), ω-2θ scans. The structures were solved
by Patterson method followed by weighted Fourier
synthesis and refined by full-matrix least-square
method. Structure determination package Enraf-
Nonius30 on a VAX 11/750 computer was used for all
calculations and PLUTO drawings31.

X-ray crystal structure determination of

Crystal structure formula C44H33AuN2P2S
M = 1169.33, crystallizes as black plate-like crystals from
acetonitrile by slow evaporation, triclinic space group,
P1, a = 12.3859(10) Å, b = 13.4097(10) Å, c =
15.7789(10) Å, α = 108.269(1)°, β = 97.15(1)°, γ =
99.82(1)°, V = 2407.6(3) Å³, T = 293(2) K, Z = 2,
μ = 3.585 mm⁻¹, 6377 unique reflections collected with
2.08<θ<24.98°, R(int) = 0.0484. Refinement method:
Full-matrix least-squares on F². Final R indices
I>2σ(I): R₁ = 0.0497, wR2 = 0.1170, R (all data): R₁
= 0.0484, wR2 = 0.1169.

Results and Discussion

The synthetic pathways for the compounds in this
study are presented in Scheme 1.

Scheme 1—Synthetic routes for the preparation of the metal complexes

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[Diagram of synthetic routes for the preparation of the metal complexes]

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Synthesis and characterization of [M(dmit)_{2}]^{n-}\text{complexes}

Disodium salt of dmit ligand was treated with metal chlorides (M = Ni, Pd, Pt, Cu, and Au) followed by the addition of a methanolic solution of (CH_{3})_{3}TeCl or PPN'Cl yielded the new metal complexes (1-7). Ni, Pt and Cu complexes form dianionic salts, whereas Au and Pd complexes form monoanionic salts. Complex 8 was prepared from 1 by aerial oxidation of its acetone solution.

X-ray crystal structure of [PPN][Au(dmit)_{2}].MeCN (7)

The molecular structure of [PPN][Au(dmit)_{2}].MeCN (7) was confirmed from its single X-ray crystal structure. The PLUTON view of the molecular structure of complex (7) is shown in Fig. 1. The pertinent bond lengths and bond angles are presented in Table 1. The geometry around the Au is square planar. The complex [PPN][Au(dmit)] crystallizes along with highly disordered solvent molecule in the triclinic space group P1. The packing of the anion in the form of dimers with an interplanar distances of 6.129 Å is very loose as interplanar distance between the two layers is 6.219 Å. The cation PPN' is not linear and exists in a bend configuration with a P-N-P angle of 138.9(5)°.

The packing of the anions in [PPN][Au(dmit)_{2}].MeCN is in the form of dimers with interplanar distances of 6.129 Å whereas in [(CH_{3})_{3}Te][Au(dmit)] \(_{2}\), anions form a layer structure with an interplanar distance of 3.498 Å. The shortest Au-S distance of [(CH_{3})_{3}Te][Au(dmit)] is 2.309 Å but for 7 the shortest Au-S distance is 2.319 Å. The maximum deviation S-Au-S from ideal value is 1.32° for 7 and 1.9° for [(CH_{3})_{3}Te][Au(dmit)] \(_{2}\). The intermolecular S...S distances change significantly with the increase in the size of the cation. The shortest intermolecular S...S contact observed for 7 is 3.3333 Å. In the case of [PCIPh_{3}][Au(S_{2}C_{2}(CF_{3})_{2})] \(_{2}\) [2.288 Å] \(^{32}\), [Au(S_{2}CNBu'_{2})_{2}]_{2}[Au(S_{2}C_{2}(CN)_{2})_{2}] \(_{2}\) [2.309 Å] \(^{33}\), [NBu'_{4}][Au(S_{2}C_{2}H_{2}Me)_{2}] [2.322 Å] \(^{34}\), and [NBu'_{4}][Au(C_{3}S_{5})_{2}] [2.322 Å] \(^{35}\), the S-Au-S angles 91.6(8)° and 88.69(8)° are also close to the values reported for the related complexes. The packing between the two anions is very loose as interplanar distance between the two layers is 6.219 Å. The cation PPN' is not linear and exists in a bend configuration with a P-N-P angle of 138.9(5)°.

Table 1—Important bond lengths (Å) and bond angles (°) of [PPN][Au(dmit)_{2}]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(1)-S(1)</td>
<td>2.323(2)</td>
<td>Au(1)-S(5)</td>
<td>2.327(2)</td>
</tr>
<tr>
<td>Au(1)-S(6)</td>
<td>2.320(2)</td>
<td>Au(1)-S(10)</td>
<td>2.319(2)</td>
</tr>
<tr>
<td>P(1)-N(1)</td>
<td>1.576(8)</td>
<td>P(2)-N(1)</td>
<td>1.589(7)</td>
</tr>
<tr>
<td>S(10)-Au(1)-S(6)</td>
<td>91.26(8)</td>
<td>S(10)-Au(1)-S(1)</td>
<td>88.69(8)</td>
</tr>
<tr>
<td>S(6)-Au(1)-S(5)</td>
<td>88.68(8)</td>
<td>S(1)-Au(1)-S(5)</td>
<td>91.38(8)</td>
</tr>
<tr>
<td>S(6)-Au(1)-S(1)</td>
<td>179.44(9)</td>
<td>S(10)-Au(1)-S(5)</td>
<td>178.96(9)</td>
</tr>
<tr>
<td>P(1)-N(1)-P(2)</td>
<td>138.9(5)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of [(CH₃)₂Te][Au(dmit)₂] the shortest S...S contact is 3.217 Å. However, there are no considerable intermolecular S...S contacts in the complex [PPN][Au(dmit)₂]. The cation PPN⁺ in both the complexes [PPN][Au(dmit)₂] and [PPN][Ni(dmit)₂] are not linear and exist in a bent configuration. However, P-N-P bond angle for [PPN][Au(dmit)₂] is much deviated from the nickel complex. The P-N-P bond angle for [PPN][Au(dmit)₂] is 138.9(5)°, whereas for [PPN][Ni(dmit)₂] is 155.2(4)°.

Electronic spectra of dmit complexes were recorded in acetonitrile. M(dmit)₂ complexes generally exhibit three well separated bands in the UV-Vis spectrum, the highest energy and lowest energy bands are due to π-π* transitions of the ligand and the M ← S charge transfer (CT) transitions occur at the center. In case of complex 7, CT transition was accompanied by a shoulder at lower energy due to a second CT transition. For Ni and Au complexes, cyclic voltammograms showed two peaks each vs Ag/AgCl that correspond to the following redox processes.

\[
\begin{align*}
\text{[Ni(dmit)₂]}^{0} + e^{-} & \rightarrow \text{[Ni(dmit)₂]}^{-} & E_{1/2} = 0.25 \text{ V} \\
\text{[Ni(dmit)₂]}^{-} + e^{-} & \rightarrow \text{[Ni(dmit)₂]}^{0} & E_{1/2} = -0.1 \text{ V}
\end{align*}
\]

\[
\begin{align*}
\text{[Au(dmit)₂]}^{0} + 2e^{-} & \rightarrow \text{[Au(dmit)₂]}^{-} & E_{1/2} = 0.28 \text{ V} \\
\text{[Au(dmit)₂]}^{-} + e^{-} & \rightarrow \text{[Au(dmit)₂]}^{0} & E_{1/2} = -0.68 \text{ V}
\end{align*}
\]

In both complexes one peak is reversible and that corresponds to the [M(dmit)⁺]/[M(dmit)⁻] redox couple and second one, quasi-reversible that corresponds to the [M(dmit)²⁺]/[M(dmit)¹⁻] redox couple. The cyclic voltammogram of [PPN][Cu(dmit)₂] consists of two irreversible peaks whereas [(CH₃)₂Te][Pd(dmit)₂] showed only one reversible peak.

Powder ESR studies were performed at room temperature and 77 K. The dianionic complexes except that of Cu and Au showed an isotropic signal at g = 2.02 due to the presence of free electron located on the thiolate ligand. [(CH₃)₂Te][Pt(dmit)₂] gave an anisotropic signal accompanied by satellites at higher fields due to hyperfine splitting (¹⁹⁵Pt coupling). The principle 'g' values determined for the powder ESR spectrum are found to be \(g_1 = 2.16, g_2 = 2.06, g_3 = 1.89\) with hyperfine coupling constants are \(A_1 = 85\) gauss and \(A_2 = 90\) gauss. The partially oxidized complexes showed stronger ESR signals compared to the monoanionic complexes. The ‘g’ values of both dmt and dmit complexes were around 2.01 – 2.04. The signals were due to the oxidized \(\text{C}_2\text{S}_2\)²⁻ species which occur around 2.01 – 2.04.

**Synthesis and characterization of [M(dmit)₂]⁺⁺ complexes**

Similar reactions of benzoyl ester of dmt with metal chlorides (M = Ni, Pd, Pt, and Cu) in methanol followed by the addition of trimethyltelluronium chloride yielded products 9 to 12. All these chelates were dianionic in nature. Recrystallisation from hot acetone-isopropanol mixture changed the stoichiometry of dianionic salts and only Cu gave a dianionic species after recrystallization. This is probably due to the fact that the dianionic complexes to the monoanionic complexes during recrystallization. Surprisingly, the reaction of salt of dmt with KAuCl₄ gave a neutral species (13).

Electronic spectra of dmt complexes were recorded in acetonitrile. As expected, dmt complexes showed three well separated peaks. While the [Au(dmt)₂]⁻/ [Au(dmt)₂]¹⁻ redox process is observed as essentially a redox wave at -0.64 V vs Ag/AgCl, the [Au(dmt)₂]²⁻/ [Au(dmt)₂]¹⁻ process occurs irreversibly. Both the redox processes of [Au(dmt)₂]⁻ species were observed at lower potential than that of [Au(dmt)₂]¹⁻ species.

Oxidation of monoanionic complexes of dmt and dmt with iodine in acetonitrile gave the partially oxidized salts 14 to 18.

**Synthesis and characterization of [M(tbs)₂]⁺⁺ complexes**

The o-thiobenzeneselenolate (tbs²⁻) ligand (19) is conveniently prepared by ‘one pot’ synthesis by following the procedure reported previously by our group. Although several other methods are available to prepare tbs²⁻ ligand, our method takes the advantage of direct route. The methanolic solution of tbs²⁻ ligand was further reacted with the chlorides of nickel, copper and gold to obtain the corresponding complexes. The complexes 20 to 27 crystallized in good yields as tetrabutylammonium, trimethylammonium and trimethyltelluronium salts.

The complexes exhibit complex electronic spectra which agree reasonably well with those of the corresponding bis(dithiolates) and bis(diselenolates)²³,²⁸. The complexes generally show three
absorption bands in UV spectra. The salient features of the absorption spectrum of \([\text{Me}_3\text{NH}][\text{Ni(tbs)}_2]\) are as follows: The bands observed at 379 nm and 250 nm are due to the intra ligand transitions. The band observed at 326 nm may be due to the LMCT transition. For \([\text{Me}_3\text{Te}][\text{Ni(tbs)}_2]\), the bands were observed at 380, 323 and 248 nm respectively. Au and Cu complexes also showed a similar pattern. For the Au complex, first ligand transition was observed at 420 nm. As observed in the case of dithiolene, most of the monoanionic complexes of tbs do not show appreciable ligand interaction, as judged by the consistency of their electronic spectra in a variety of solvents. The electronic spectra are almost unaltered when solvent is changed from dichloromethane to DMF or DMSO.

As observed by Pleschner et al., the cyclic voltammogram of \([\text{Ni(tbs)}_2]^{+}\) complexes showed two peaks. The first one is reversible and corresponds to the \([\text{Ni(tbs)}_2]^+/2[\text{Ni(tbs)}_2]^{-}\) redox couple. The second one is irreversible and corresponds to the \([\text{Ni(tbs)}_2]^+/3[\text{Ni(tbs)}_2]^{-}\) redox couple. For tetrabutylammonium and trimethylammonium salts of \([\text{Ni(tbs)}_2], [\text{Ni(tbs)}_2]^-/2[\text{Ni(tbs)}_2]^{-}\) process is observed at -0.52 V and -0.53 V vs SCE respectively. Cyclic voltammogram of \([\text{Bu}_4\text{Ni}][\text{Cu(tbs)}_2]\) consists of two peaks, both \([\text{Cu(tbs)}_2]^+/2[\text{Cu(tbs)}_2]^{-}\) (0.86 V vs SCE) and \([\text{Cu(tbs)}_2]^+/3[\text{Cu(tbs)}_2]^{-}\) processes were irreversible. In the case of \([\text{Au(tbs)}_2]^{+}\) complex the \([\text{Au(tbs)}_2]^+/2[\text{Au(tbs)}_2]^{-}\) process was irreversible and \([\text{Au(tbs)}_2]^+/3[\text{Au(tbs)}_2]^{-}\) process was quasi-reversible.

Electron Spin Resonance Spectra of \([\text{Me}_3\text{NH}][\text{Ni(tbs)}_2]\) was recorded at 77 K in dimethylformamide-chloroform ‘glass’. Fig. 3 shows three well separated principle \(g\) values: \(g_1 = 2.02, g_2 = 2.07, g_3 = 2.21\) and \(<g> = 2.10\). For \([\text{Ni(bdt)}_2]^{+}\): \(g_1 = 2.02, g_2 = 2.10, g_3 = 2.12\) and \(<g> = 2.08\) and \([\text{Ni(bds)}_2]^{+}\): \(g_1 = 2.07, g_2 = 2.17, g_3 = 2.17\) and \(<g> = 2.14\). The increase in \(g\)-tensor anisotropy by substituting sulphur by selenium, apparently results from the greater spin-orbit coupling of the heavier donor atoms. Hyperfine splitting due to natural abundance of \(^{77}\text{Se}\) (7.5%, \(I = \frac{3}{2}\)) is observed on the high field resonance with a hyperfine coupling constant \(A_1 = 60\) gauss. The low field resonance indicates the possible presence of unresolved \(^{77}\text{Se}\) hyperfine structure. However, since the hyperfine splitting was apparently not observed in the \([\text{Ni(SeC}_2\text{(CF}_3)_2]^{+}\) spectrum, it is possible that both \(\text{cis-}\) and \(\text{trans-}\) isomers of \([\text{Ni(tbs)}_2]^{+}\) exist in the ‘glass’ with only \(g_3\) differing very significantly between the two isomers. The resonance observed at the lowest field may be assigned to the \(\text{cis-}\)isomer, \(g_3\) (cis) = 2.22 (greater the distortions in the molecule, greater will be the anisotropy of the ESR spectrum); \(g_3\) (trans) was found to be 2.21. Ratios of the \(\text{cis-}\) and \(\text{trans-}\)isomers in the mixture were calculated from the intensities of the signals and were found to be 45.83% and 54.17% respectively.

The electrical conductivities of all complexes were measured for a compacted pellet at room temperature. Only partially oxidized complexes showed noticeable room temperature conductivity (Table 2).

**Conclusion**

The synthesis and characterization of several metal complexes with various cations has been reported here and also three of them structurally characterized. The crystallographic studies prove that the change of central metal ions and the size of the cations play a crucial role in determining the crystal structure and
hence the physical properties. For example, the packing of the anions in [PPN][Au(dmit)₂] is in the form of loose dimers with interplanar distances of 6.129 Å whereas in [(CH₃)₂Te][Au(dmit)₂] [34], anions form a layer structure with an interplanar distance of 3.498 Å, where the cations are different. The P-N-P bond angle for [PPN][Au(dmit)₂] is 138.9(5)°, whereas for [PPN][Ni(dmit)₂] is 155.2(4)° where the metal atoms are different. All the monoionic and dianionic complexes were insulators. The partially oxidized complexes, however, showed much higher conductivities. Trimethyltellurium salts of [Au(dmit)₂] and [Ni(dmit)₂] were found to be better conducting than the corresponding PPN analogues. Similarly, dmit complexes showed better conductivity than the corresponding dmt analogues.

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References