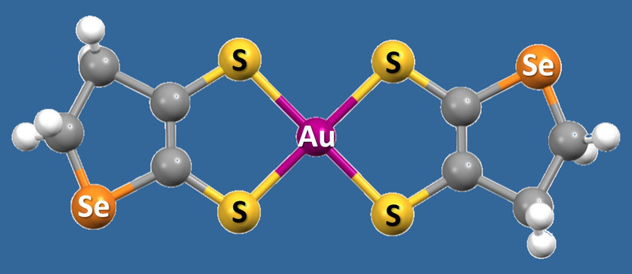
Conducting Neutral Bis(dithiolene) Gold Complex with an Unprecedented Crystal Structure



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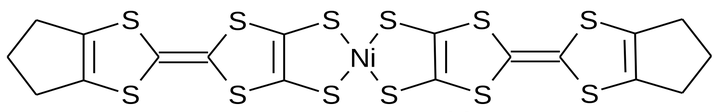
Introduction and Aim

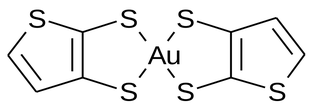
Single Component Molecular Metals (SCMM):

- **Neutral** molecular based materials that display **metallic** behavior!
- **Multifunctional materials** (combining several physical properties).

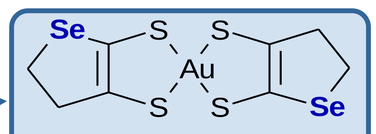
Metallic behaviour → *arises from* → Strong **intermolecular interactions** in solid state → *could be improved by* → **Heavier atoms (selenium)**



[Ni(tmdt)$_2$] [1]



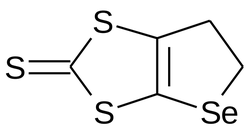
[Au(α-tpdt)$_2$] [2]



[Au(dspdt)$_2$] [3]

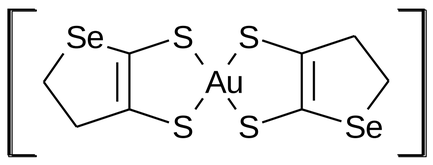
OBJECTIVE: Replacing the S for Se in [Au(α-tpdt)$_2$] and unravel the role of Se in the transport properties.

Synthesis



Proligand [4]

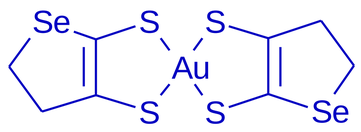
i) MeONa, MeOH
ii) $KAuCl_4$
iii) n-Bu_4NBr



***n*Bu$_4$N[Au(dspdt)$_2$]**

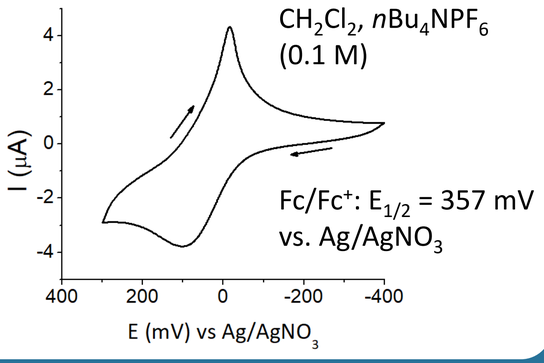
iv) I_2 or electrochemical oxidation

It is possible to oxidize to the neutral species!



[Au(dspdt)$_2$][3]

Cyclic Voltammetry

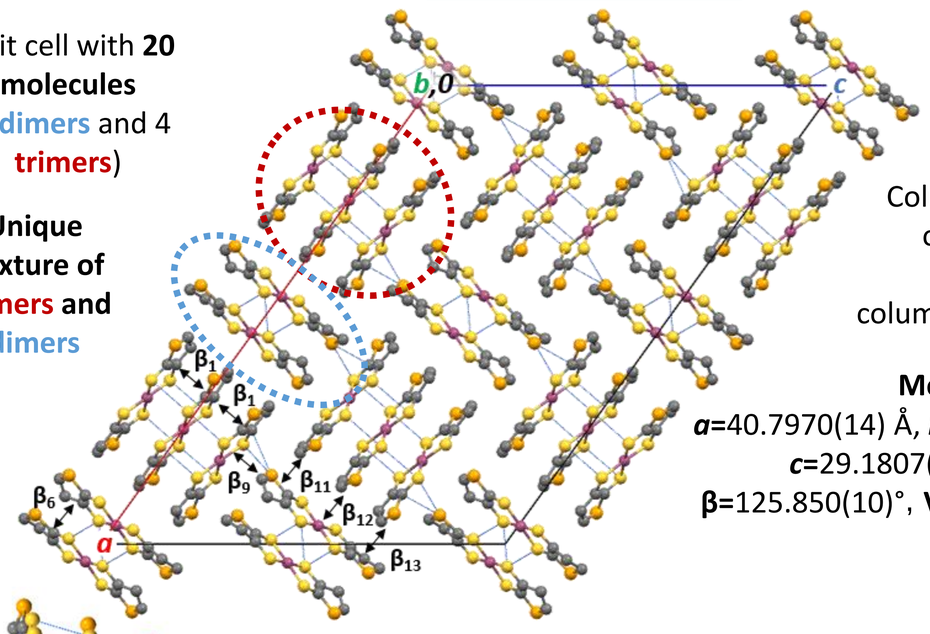


Characterisation of the Neutral [Au(dspdt)$_2$]

Crystal Structure

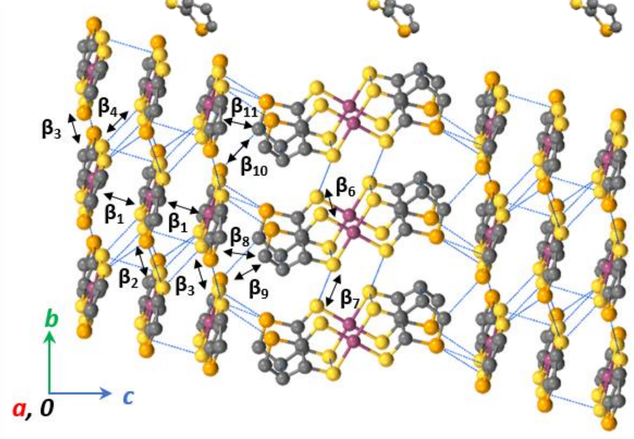
Unit cell with **20 molecules** (4 dimers and 4 trimers)

Unique mixture of trimers and dimers



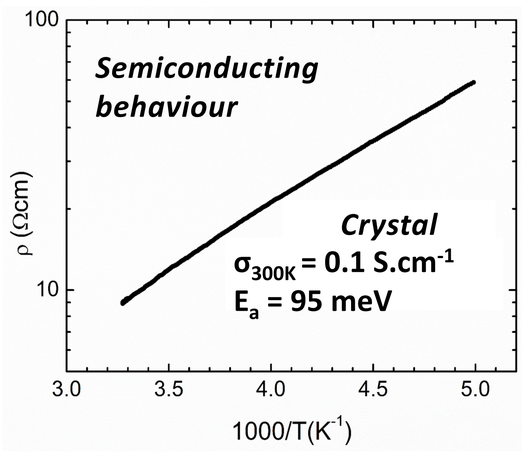
Columns **along b** of side-by-side dimers and columns of trimers.

Monoclinic, *C2/c*
a=40.7970(14) Å, ***b***=6.4600(2) Å, ***c***=29.1807(9) Å, **α=γ**=90°, **β**=125.850(10)°, **V**=6230.9(4) Å^3



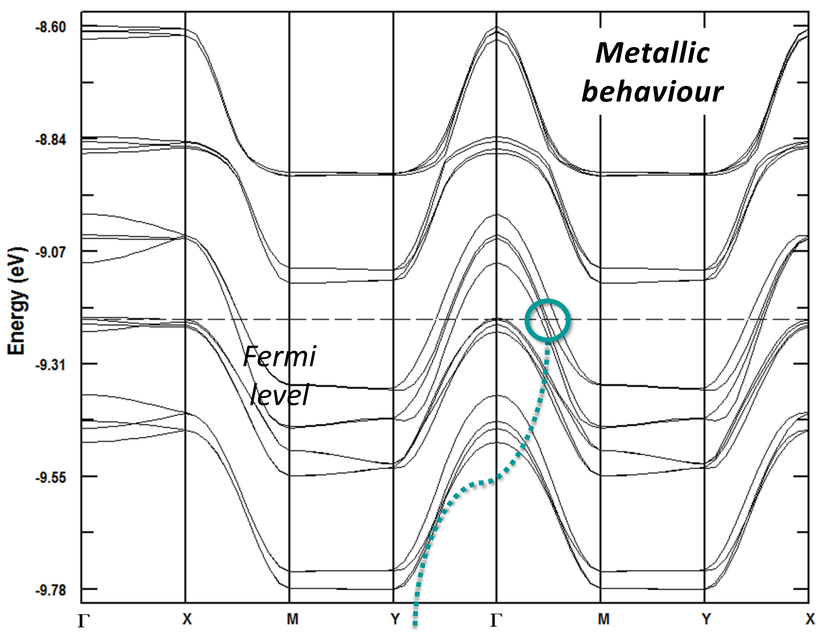
[Au(dspdt)$_2$] is still in the range of **Mott insulator** with unpaired electrons localized in each **trimer**.

Electrical Properties



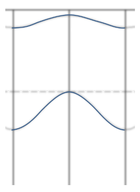
Band Structure

Tight-binding extended Hückel approach

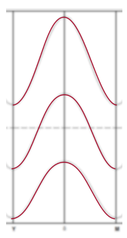


The Fermi level crosses the four central bands

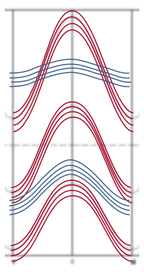
Dimer
2 bands
Semiconductor



Trimer
3 bands
Mott Insulator



4 trimers
4 dimers



Mixture of bands that are **split and partially overlapping** due to intercolumn interactions
↓
Metallic behaviour

Not metallic as predicted by this ***ideal model*** without electron correlation effects

Conclusions

[Au(dspdt)$_2$]...

... **is a conducting** compound based on a single neutral molecule.

... **has a unique crystal structure** composed of dimers and trimers.

... **shows a new conducting mechanism** (interactions between dimers and trimers).

... **is expected** to display metallic behaviour under high pressure.

... **is relevant** because its conduction mechanism may explain the metallic properties observed in similar neutral gold complexes (*e.g.* [Au(α-tpdt)$_2$]).

References

[1] H. Tanaka *et al.*, *Science*, 2001, 291, 285.
[2] D. Belo *et al.*, *Chem. Eur. J.* 2001, 7, 511.
[3] M. F. G. Velho *et al.*, *Dalton Trans.*, 2020, 49, 13737.
[4] T. Jigami *et al.*, *J. Org. Chem.*, 1998, 63, 8865.

Acknowledgements

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