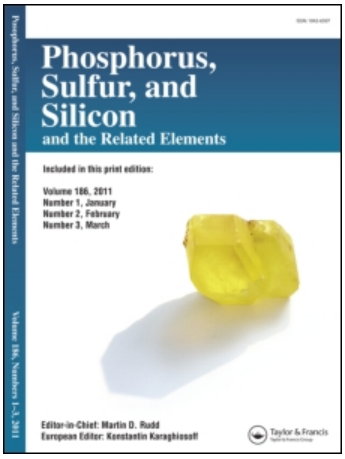


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Metal Complexes of Sulphur-Donor Ligands

C. J. Bowlas[a]; A. E. Underhill[a]; D. Thetford[b]
[a] Department of Chemistry, Institute of Molecular and Biomolecular Electronics, University of Wales, Bangor, Gwynedd, U.K. [b] ICI Specialties, Manchester, UK

To cite this Article Bowlas, C. J. , Underhill, A. E. and Thetford, D.(1992) 'Metal Complexes of Sulphur-Donor Ligands', Phosphorus, Sulfur, and Silicon and the Related Elements, 67: 1, 301 — 304
To link to this Article: DOI: 10.1080/10426509208045851
URL: http://dx.doi.org/10.1080/10426509208045851

Phosphorus, Sulfur, and Silicon, 1992, Vol. 67, pp. 301–304
Reprints available directly from the publisher
Photocopying permitted by license only

METAL COMPLEXES OF SULPHUR-DONOR LIGANDS

C. J. BOWLAS AND A. E. UNDERHILL
Department of Chemistry and Institute of Molecular and Biomolecular Electronics, University of Wales, Bangor, Gwynedd, LL57 2UW, U.K.

D. THETFORD
ICI Specialties, Blackley, Manchester M9 3DA, UK

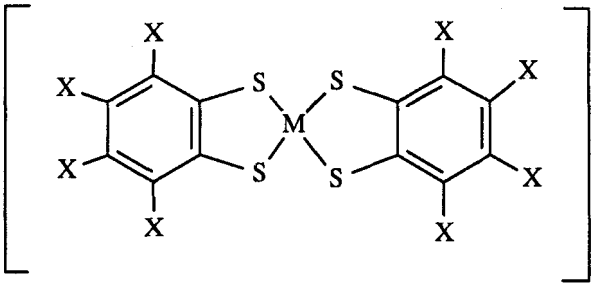
INTRODUCTION

Metal complexes of sulphur-donor ligands have been widely studied, often because of their intense colours and redox properties.[1] More recently they have been shown to exhibit a wide range of structures and properties in the solid state dependent upon the nature and extent of the interactions between the metal complex anions. The metallic and non-linear optical properties of these complexes have recently attracted special attention.[2,3]

Metal dithiolene complexes are highly versatile molecular systems and their properties can be tuned by

(1) changing the nature of the ligand
(2) changing the central metal
(3) changing the counter cation

As part of a series of extensive studies, we have investigated dithiolenes of the type

(TBA) 

where M = Ni, Fe, Pd or Pt and X = Cl or Br.
Complexes of this type where M = Ni and X = Cl, $[Ni(dtcb)_2]^{n-}$, were

first reported and characterised in 1966 by Baker Hawkes et al.[4] The chloro-complex has been shown to display intense absorption in the near-IR region and therefore these compounds have potential applications in the fields of light sensitive glass, security inks and solar switching devices.[5]

We have now carried out further studies on these complexes and have prepared and studied for the first time-complexes where X = Br and M = Ni, $[Ni(dtbb)_2]^{n-}$.

EXPERIMENTAL

Preparation of the Ligand

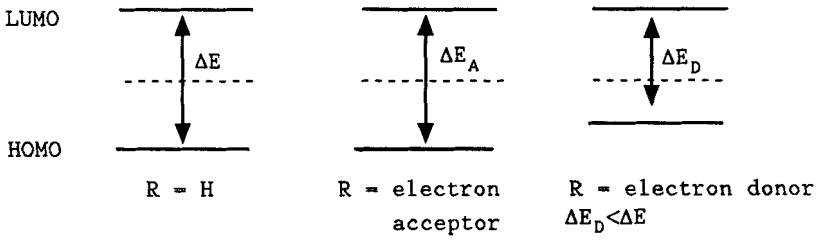
The ligand was prepared as published previously.[4]

Preparation of Metal Complexes

To a dimethylformamide solution containing two equivalents of ligand, one equivalent each of nickel chloride and tetrabutyl ammonium bromide was added. The reaction mixture was stirred under a stream of air for 3 hours, undergoing a colour change from deep red to deep green. The filtered reaction mixture was taken to dryness under reduced pressure, slurried in methanol and then filtered to yield a green microcrystalline powder. Recrystallisation from methylene chloride and methanol gave a green crystalline powder.

RESULTS AND DISCUSSION

In metal dithiolenes there is considerable overlap between the metal d orbitals and the π-system of the ligand to produce a HOMO and LUMO involving extensive delocalisation over the whole metal complex. The properties of the metal complex are determined by the extent of electron occupation of these orbitals and the energy difference between them. The electron occupation of the HOMO and LUMO depends upon the charge on the metal complex, the energy difference between them and the nature of the ligand. Electron withdrawing substituents on the dithiolene ligands stabilise both the HOMO and the LUMO orbitals so that the wavelength is not appreciably shifted.



Electron-donating substituents destabilise the HOMO more than the LUMO and hence there is a shift to longer wavelengths (lower energy). In the series of nickel complexes of dithiolenes, the position of λ_{max} can be shifted from 650 to 1140 nm. The table shows that the position of λ_{max} for the complexes studied here lies in the middle of that range. It is also clear that replacement of the chloro-substituents by bromo-substituents on the benzene ring does not affect the value of λ_{max} and does not have a significant effect on the intensity of the absorption band.

TABLE

	Magnetic Susceptibility	NIR absorption (solution)	
	μ_{eff}(BM)	λ_{max}	ϵ_{max} $mol^{-1}dm^3cm^{-1}$
TBA[Ni(dtcb)$_2$]	1.84	890	1.3×10^4
TBA[Ni(dtbb)$_2$]	1.90	890	1×10^4

Mono-anion metal dithiolenes of the type investigated would be expected to possess one unpaired electron in the LUMO. The magnetic moments (see Table) observed in these complexes are in agreement with the presence of a single unpaired electron. In many mono-anionic nickel dithiolene complexes, the anions associate in the solid state as dimers as a result of the interactions between the unpaired electrons on the individual anions. This leads to a reduction in the magnetic moment of the complex below that expected for one unpaired electron. Often there is a temperature dependent singlet-triplet equilibrium depending upon the interaction energy (J).

Unfortunately, variable temperature magnetic susceptibility results are not available for these two compounds and therefore it is not possible to determine whether the single unpaired electron in these complexes arises from the fact that the molecules are too isolated from one another in the solid state for interactions to occur or whether the anions are present as dimers in the lattice but that the magnetic interaction energy is small compared with thermal energies at room temperature. However, the similarity in the solid state and solution spectra of these complexes suggest that the anions are present as isolated species in the lattice.

Electrocrystallisation of TBA[Ni(dtcb)$_2$] in the presence of TBAClO$_4$ in acetonitrile at a constant current of 1 μA yielded a black microcrystalline solid on the anode of (TBA)$_{0.15}$[Ni(dtcb)$_2$]. A compressed pellet of this compound exhibited a room temperature conductivity of 10^{-3} Scm^{-1} at room temperature. The temperature dependence of the conductivity down to 100K indicated that it was a semiconductor. The value of the conductivity is in agreement with the formation of a partially oxidised metal dithiolene as indicated by the stoichiometry. This suggests that nickel dithiolene mono-anions of this type can interact with one another sufficiently in the solid state to form a conduction pathway. The relatively low value of the room temperature conductivity for a compound of this type, coupled with the semiconductor behaviour suggests that this interaction is not very great and is unlikely to lead to the metallic properties observed for metal complexes with more extended sulphur-donor ligands.

We would like to thank the SERC and ICI for their support.

REFERENCES

1. J. A. McCleverty; Prog. Inorg. Chem., 10, 49(1968).
2. M. M. Ahmed, D. J. Turner, A. E. Underhill, A. Kobayashi, Y. Sasaki and H. Kobayashi; J. Chem. Soc., Dalton Trans., 1759(1984).
3. C. S. Winter, C. A. S. Hill and A. E. Underhill; Appl. Phys. Lett., 58, 107(1991).
4. M. J. Baker-Hawkes, E. Billig and H. B. Gray; J. Am. Chem. Soc., 66(21), 4870-5, (1966).
5. ICI Eur. Pat. Appl. 88304205.3, May 1988.