Journal of The Chemical Society, Chemical Communications

NUMBER 6/1972 22 MARCH

Novel Organometallic Sandwich Complexes Based on Transition-metal Chalcogenides

By B. BACH and J. M. THOMAS*

(*Edward Davies Chemical Laboratories, The University College of Wales, Aberystwyth* SY23 1NE)

Summary Ten new sandwich complexes (intercalates), formed from $NbSe_2$ or TaS_2 and simple nitrogeneous bases, have been prepared and their *X*-ray photoelectron spectra indicate that electrons are transferred from the nitrogen atom to the metallic layers; a simple band model qualitatively accounts for the formation of such compounds.

JUST as graphite accommodates many types of foreign species between the loosely-bonded layer-planes, so also may certain atoms and molecules be intercalated into the van der Waals gap of some transition-metal dichalcogenides. The disulphides of Ti, V, and Cr readily assimilate Na atoms,[1] and alkali-metal atoms may also be incorporated[2] into $NbSe_2$. But of exceptional interest, principally because of their promising superconducting properties, are the recently discovered organometallic intercalates such as TaS_2 (pyridine)$_{0\cdot5}$ and TaS_2(aniline)$_{0\cdot5}$, which Gamble *et al.*[3,4] have shown to be stable, crystalline and ordered.

We report here the isolation of $NbSe_2(L)_{0\cdot5}$ (L = pyridine, piperidine, Et_2NH, Et_3N), $NbSe_2$(ethylenediamine)$_{0\cdot3}$, $TaS_2(L)_{0\cdot5}$ (L = Et_2NH, Et_3N, piperidine), and TaS_2(ethylenediamine)$_{0\cdot2}$.† The compounds, which were relatively unstable in air at room temperature, were formed by exposing, in a sealed vessel for several days, powdered samples of the stoicheiometric dichalcogenides to the vapour of the boiling Lewis base. Weight changes, monitored by a sensitive quartz-helical balance[5] enabled the composition of the sandwich complexes to be estimated. Although it remains to be established whether the whole sequence of first to *n*th stage intercalates can be formed with these layer solids (as with graphite[6]) there is no doubt from our electron microscopic lattice-resolution studies that organic molecules can indeed be inserted between every layer of the parent structure.

X-Ray photoelectron spectroscopic measurements on a

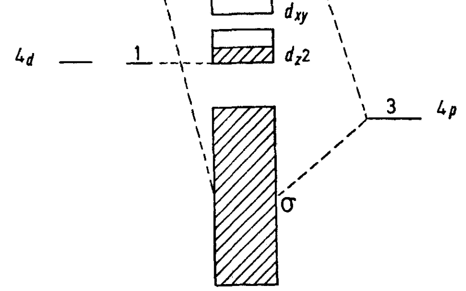

FIGURE. *Schematic illustration of the electronic band structure of* $NbSe_2$.

---

† An error of ±0·1 exists in the organic fraction.

selection of these novel intercalates illumine the nature of the electronic changes involved, but the technique has not yet yielded unequivocal information about the bonding, the instability of the complexes renders determination of absolute binding energies of the core electrons difficult. The N_{1s} peak in all ten intercalates is considerably broader [*e.g.* 3·5 eV fwhm for $NbSe_2(piperidine)_{0\cdot5}$] and frequently has a pronounced shoulder on the high binding-energy side, compared with the narrow peak (1·2 eV fwhm) for the pure nitrogeneous bases. This indicates that electrons are transferred from the nitrogen of the organic molecule to the metallic layer, a fact which is also reflected in the significant widening of the valence band of the $NbSe_2$ upon intercalation of pyridine or aniline (*cf.* analogous studies[7] on graphite intercalates). The broad N_{1s} peak also implies that the organic molecule can be anchored in at least two, and probably many more, configurations between the metallic layers.

A plausible qualitative model, based on early theoretical arguments[8] and recent work[9] on the optical spectra of the layered transition-metal chalcogenides may be formulated for these novel complexes, which are likely to represent a large new class. The band structure of TaS_2 and $NbSe_2$ is illustrated schematically in the Figure. The partly-filled conduction band arises from the overlap of d_{z^2} non-bonding orbitals on the transition-metal atoms; and electrons transferred from the organic molecule may enter this band (leading probably to unequal changes in the binding energy of electrons in the core levels of the metal atom and the chalcogenide atom). This implies that only those metal chalcogenides which have partly-occupied or low lying, empty bands should readily form organometallic and certain other intercalates.

We thank the Science Research Council, the Royal Society, and C.N.R.S. for their support.

(*Received, 7th January* 1972; *Com.* 017.)

---

[1] W. Rudorff, *Chimia (Switz.)*, 1965, **19**, 489.
[2] J. V. Acrivos, W. Y. Liang, J. A. Wilson, and A. D. Yoffe, *J. Phys. Chem.*, 1971, **4**, L18.
[3] F. R. Gamble, F. J. Di Salvo, R. A. Klemm, and J. H. Geballe, *Science*, 1970, **168**, 568.
[4] F. J. Di Salvo, R. Schwall, T. H. Geballe, F. R. Gamble, and J. H. Osiecki, *Phys. Rev. Letters*, 1971, **27**, 310, 314.
[5] J. M. Thomas and B. R. Williams, *Quart. Rev.*, 1965, **19**, 231.
[6] R. C. Croft, *Quart. Rev.*, 1960, **14**, 1.
[7] B. Bach, E. L. Evans, J. M. Thomas, and M. Barber, *Chem. Phys. Letters*, 1971, **10**, 547.
[8] R. Hultgren, *Phys. Rev.*, 1932, **40**, 891.
[9] J. A. Wilson and A. D. Yoffe, *Adv. Phys*, 1969, **18**, 193.