Tetrahedron Letters No. 9, pp 715 - 716, 1974. Pergamon Press. Printed in Great Britain.

REACTIONS OF TCNQ WITH PLATINUM DITHIOLATES

E. T. Maas, Jr.
IBM Thomas J. Watson Research Center
Yorktown Heights, New York 10598

(Received in USA 17 October 1973; received in UK for publication 21 January 1974)

Recently attention has been refocused on the compounds formed by the organic acceptor 7,7,8,8-tetracyanoquinodimethan (TCNQ). While TCNQ is not a new species,[1] renewed interest has been shown because of the remarkable electrical transport properties exhibited by compounds of TCNQ with organosulfur donors.[2] Synthetic approaches to TCNQ compounds have usually been limited to: 1) reaction of neutral TCNQ with neutral donors; 2) reaction of various iodides, both organic and inorganic, with neutral TCNQ; and 3) metathetical reactions of LiTCNQ with salts of the desired cation.[3] A study was, therefore, initiated to explore other possible synthetic routes which might be employed to generate TCNQ-containing materials.

The synthetic route described in this report consisted of the reaction of neutral TCNQ with salts of the anionic species commonly referred to as metal dithiolates.[4,5] These metal complexes have received much attention in the past because of their ability to form stable compounds in various formal oxidation states. Recently, Burgess, et al., have interpreted the interaction between selected transition metal dithiolates and various organic acceptors on the basis of equilibria involving discrete donor-acceptor complexes in solution.[6] It was found in many cases that the donor-acceptor complex had dissociated with complete electron transfer resulting in ionic species being present. No attempt was made to characterize solid phases which could be isolated from solution reactions of this type.

Work in this laboratory has centered on the reactions of neutral TCNQ with dithiolates of Pt(II). The dithiolates employed were cis-dicyanoethylene-1,2-dithiolate (or commonly, maleonitriledithiolate = MNT) and toluene-3,4-dithiolate (= TDT). Reactions were carried out at ambient temperatures under anhydrous conditions in high purity acetonitrile. Products were isolated from the reaction mixtures by precipitation and fractional crystallization techniques. The compounds were identified by their characteristic UV-Vis and IR absorption spectra, melting points, X-ray powder diffraction patterns, and, in some cases, by elemental analyses.

Reactions of neutral TCNQ with $[(C_2H_5)_4N]_2Pt(MNT)_2$ in ratios ranging from 1:2 to 2:1 have yielded invariably the complex salt $[(C_2H_5)_4N](TCNQ)_2$. (Salts of the $(TCNQ)_2^-$ ion are referred to as complex salts, while those containing the $TCNQ^-$ ion are referred to as simple salts.) No evidence was found for the incorporation of the platinum dithiolate ion in the solid TCNQ-containing products. The platinum species isolated consisted primarily of $[(C_2H_5)_4N]Pt(MNT)_2$ and some $[(C_2H_5)_4N]_2Pt(MNT)_2$ which remained unreacted when sufficient TCNQ was not present to effect complete conversion to the uninegative Pt-MNT anion.

Similar reactions employing $[(C_2H_5)_4N]_2Pt(TDT)_2$ were found to produce more complex results. Reactions in which the $TCNQ:Pt(TDT)_2^{2-}$ ratio was 1 or less yielded primarily the simple salt $[(C_2H_5)_4N]TCNQ$. When this ratio was increased above one, a mixture of the simple and complex salts was formed. The complex salt became the sole TCNQ-containing product when the ratio of reactants as described above reached two. Again the platinum species in the reactions behaved in an analogous way to those in the MNT system. However, it was noted that the only Pt-containing species obtained from the reaction in which the $TCNQ:Pt(TDT)_2^{2-}$ ratio was 2:1 was an insoluble, presumably polymeric, material. The identity of this material was not definitely determined but no evidence for it containing TCNQ, in any form, was found.

This appears to be the first published report of $[(C_2H_5)_4N]TCNQ$ in the literature; however, the analogous salts of other tetraalkylammonium cations have been reported.[3] $[(C_2H_5)_4N]TCNQ$ is obtained as purple crystals (m.p 161-164°C d.) which are soluble in polar solvents. The infrared and UV-Vis absorption spectra of this salt closely parallel those exhibited by other simple TCNQ salts of onium cations.[3]

The reactions described herein appear to possess the ability to generate both the simple and complex salts of the cation employed. Work is currently in progress to explore further this ability and also to incorporate other interesting cations into TCNQ compounds.

References

1. D. S. Acker and W. R. Hertler, J. Am. Chem. Soc., 84, 3370 (1962).
2. J. Ferraris, D. O. Cowan, V. Walatka, Jr. and J. H. Perlstein, J. Am. Chem. Soc., 95, 948 (1973); L. B. Coleman, A. F. Garito and A. J. Heeger, Solid State Comm., to be published; A. J. Heeger and A. F. Garito, AIP Conf. Proc. (Magnetism and Magnetic Materials), 10, 1476 (1972); J. H. Perlstein, J. P. Ferraris, V. Walatka, Jr., D. O. Cowan and G. A. Candela, ibid., 1494 (1972).
3. L. R. Melby, R. J. Harder, W. R. Hertler, W. Makler, R. E. Benson and W. E. Mochel, J. Am. Chem. Soc., 84, 3374 (1962).
4. J. A. McCleverty, Progr. Inorg. Chem., 10, 49 (1968).
5. G. N. Schrauzer, Accts. Chem. Res., 2, 72 (1969).
6. J. Burgess, K. M. C. Davis, R. D. W. Kemmitt, J. B. Raynor and J. Stocks, Inorg. Chim. Acta, 4, 129 (1970).