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X-Ray Photoelectron Spectra of Copper–Tetracyanoquinodimethane Complexes

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Copper forms[1] two types of complexes with tetracyano-*p*-quinodimethane (TCNQ). Metathesis of cupric sulphate and Li(TCNQ), and related reactions, yield a solid corresponding to the formula Cu(TCNQ)$_2$, whereas the product formed when the parent TCNQ reacts either with metallic copper or certain cuprous salts, has a composition Cu(TCNQ). From their mode of production it seems reasonable to suppose that these complexes contain cupric and cuprous ions, respectively; the formula have been written as Cu^{2+}(TCNQ$^-$)$_2$(A) and Cu$^+$(TCNQ$^-$) (B). Whilst formulation B is consonant with the observed properties of the complex, there are difficulties associated with A. First, no Cu^{2+} signal is detectable in the ESR spectrum of the Cu(TCNQ)$_2$, and, second, static magnetic susceptibility measurements reveal that the so-called cupric compound is apparently diamagnetic.[2] In addition, the IR absorption spectrum of this compound clearly indicates the presence of TCNQ as well as TCNQ$^-$.[2] Hence feasible alternative representations for A are Cu$^+$(TCNQ$^-$)(TCNQ) or (Cu$^+$)$_2$(TCNQ$^-$)$_2$(TCNQ)$_2$, and it has been suggested[1] that the following equilibria might be set up in the solid state:

$$2\mathrm{Cu}^{2+}(\mathrm{TCNQ}^-)_2 \rightleftarrows (\mathrm{Cu}^+)_2(\mathrm{TCNQ}^-)_2(\mathrm{TCNQ})_2$$
$$\rightleftarrows (\mathrm{Cu}^+)_2(\mathrm{TCNQ}^{2-})(\mathrm{TCNQ})_3$$

The X-ray induced photoelectron spectra (ESCA) of the two compounds (hitherto represented as A and B above) have been recorded (on an AEI ES100) under conditions which have been fully descibed[3] for other complexes. The materials were synthesized according to the procedures given in Ref. 1 and the binding energies (Table 1) have been accurately determined using the gold-decoration technique,[4] the subsidiary standard being 84.0 eV for the binding energy of the Au 4f$_{7/2}$ level.[5]

Table 1. Binding energies (eV)

Compounds	Cu 2p$_{1/2}$	Cu 2p$_{3/2}$	Cu 3s	Cu 3p	Cu 3d	N1s
Cu(TCNQ)	951.0	931.2	121.8	74.8	2.2	398.1
Cu(TCNQ)$_2$	950.4	930.4	121.5	74.5	2.1	(398.3)[a]

a) The peak is broad, and the value is approximate. (Precision throughout is ±0.3 eV).

It is to be expected from other works[6] that a chemical shift of about 1.5 eV occurs between copper in +2 and +1 formal oxidation states, yet the metal core level binding energies for the two complexes are almost coincident. Significantly the shapes and half-widths of the Cu 2p and the Cu 3s peaks (Fig. 1) are indistinguishable for the two compounds, and in each case there are no satellites[7] on the higher-binding energy side of the Cu 2p peaks, nor any signs of spin-spin splitting of the Cu 3s levels that is expected for a 3d^9 configuration. These facts prove that the copper ion has, in both cases, the 3d^{10} configuration.

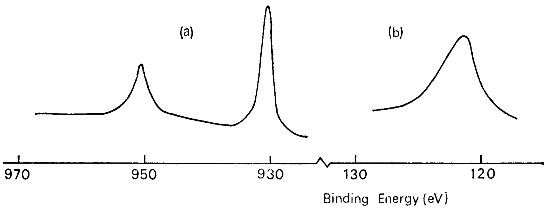

Fig. 1. Copper peaks of Cu(TCNQ)$_2$ (a) Cu 2p (b) Cu 3s.

N1s peaks for the two compounds are, however, revealingly different (Fig. 2). They both exhibit the higher-binding energy satellites, which we have shown elsewhere[3] to be a general feature of TCNQ complexes and which we now know to arise from an intramolecular shake-up (two-electron) mechanism. But of greater significance is the differences in widths of the main peaks. The breadth of the N1s peak in Cu(TCNQ)$_2$ signifies, as does the IR spectra,[2] the presence of two types of nitrogen, namely those due to (TCNQ$^-$) and (TCNQ). Using the N1s peaks observed on TCNQ crystal and K(TCNQ), we synthesized the N1s peak which is expected for the system containing equivalent

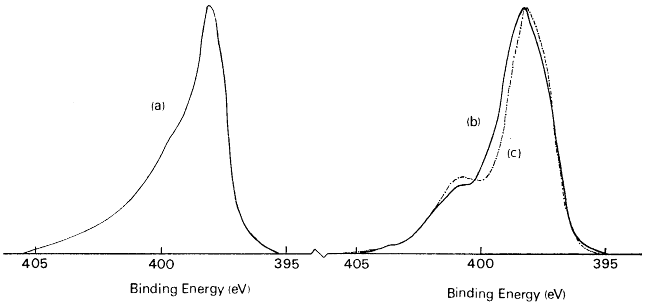

Fig. 2. N1s peaks (a) Cu(TCNQ), (b) Cu(TCNQ)$_2$, (c) Synthesized N1s peak for Cu(TCNQ)$_2$.

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3) I. Ikemoto, J. M. Thomas, and H. Kuroda, *Discuss. Faraday Soc.*, (1972), in press.

4) J. M. Thomas, E. L. Evans, M. Barber, and P. Swift, *Trans. Faraday Soc.*, **67**, 1875 (1971).

5) C. S. Fadley, Ph. D. Thesis (Univ. of California), (1970).

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7) Just as for cuprous compounds free of adsorbed impurities.[8]

8) T. Novakov and R. Prins, *Solid. State Commun*, **9**, 1975 (1971).

9) The observed diamagnetism of this complex seems to be brought from the interaction between (TCNQ$^-$) anion radicals.

amounts of (TCNQ) and (TCNQ$^-$). As shown in Fig. 2, the observed N1s peak of Cu(TCNQ)$_2$ well agrees with the synthesized one. Thus, a possible formulation in place of A is Cu$^+$(TCNQ$^-$)(TCNQ) or (Cu$^+$)$_2$(TCNQ$^-$)$_2$(TCNQ)$_2$.⁹⁾

Cs$_2$(TCNQ)$_3$ as well as (Ph$_3$PMe)(TCNQ)$_2$ is also known to be a 'mixed' complex, frequently formulated as (Cs$^+$)$_2$(TCNQ$^-$)$_2$(TCNQ) and (Ph$_3$PMe)(TCNQ$^-$)-(TCNQ), but its N1s peak shape is distinctly different from that shown here for the mixed cuprous complex. For these two complexes it is not possible to reproduce the N1s peak by a simple superposition of the N1s peaks of TCNQ and K(TCNQ). If there is a significant electron delocalization between (TCNQ$^-$) and (TCNQ), we should naturally expect a disagreement between synthesized and actual spectra. Thus, the good agreement between the observed and synthesized N1s peaks in the case of Cu(TCNQ)$_2$ seems to indicate small electron delocalization between (TCNQ$^-$) and (TCNQ).

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