# Bound and Non-bound Tetracyanoethylene Radical Anion (TCNE<sup>-</sup>) in Copper(I) Triphenylphosphine Complexes. The Crystal Structures of Cu(TCNE)(PPh<sub>3</sub>)<sub>3</sub>, [-(CN)Cu(PPh<sub>3</sub>)<sub>2</sub>(TCNE)Cu(PPh<sub>3</sub>)<sub>2</sub>-]<sub>n</sub> and [(PPh<sub>3</sub>)<sub>3</sub>Cu(CN)Cu(PPh<sub>3</sub>)<sub>3</sub>] [TCNE]

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The reaction of the copper(1) complex  $[Cu(TCNE)]_n$  with triphenylphosphine yields three different modes of incorporation of TCNE<sup>--</sup> into the products  $Cu(TCNE)(PPh_3)_3 1$ ,  $[-(CN)Cu(PPh_3)_2(TCNE)Cu(PPh_3)_2^-]_n 2$  and  $[(PPh_3)_3Cu(CN)Cu(PPh_3)_3]$  [TCNE] 3. In 1, the TCNE<sup>--</sup> is *N*-bound; in 2, *trans-N*-bound TCNE<sup>--</sup> bridges alternate with CN bridges to produce a polymeric structure, and in 3 the TCNE<sup>--</sup> is un-coordinated.

The charge-transfer capabilities of TCNE have made it a natural choice for many conductivity and magnetic studies in which the TCNE<sup>•-</sup> is the anion of mixed salts.<sup>1</sup> As a ligand it has been found as a  $\pi$ -donor<sup>2</sup> as well as *N*-bound TCNE<sup>•.3</sup> Of the latter mode, crystal structures have been reported for Os<sup>4</sup>, V,<sup>5</sup> Mn,<sup>6</sup> Cu<sup>7</sup> and Ir<sup>8</sup> derivatives. As part of our continuing interest in the redox properties of copper, we have investigated the synthesis of copper complexes incorporating TCNE.

Reaction of  $[Cu(TCNE)]_n^9$  with an excess of triphenylphosphine (1:4) in acetonitrile under argon at room temp. affords a green complex Cu(TCNE)(PPh<sub>3</sub>)<sub>3</sub> 1. Using a stoichiometry of 1:2 the reaction leads to a white compound,  $[Cu(TCNE)(PPh_3)_2]$ , which is stable in solution but decomposes in the solid state to a red compound at room temp. within a few hours. When the same reaction takes place in hot acetonitrile, on cooling, red crystals of [-(CN)Cu(PPh\_3)\_2 (TCNE)Cu(PPh\_3)\_2-]<sub>n</sub> 2 form, as a result of partial cleavage of the C-CN bond in TCNE. The scission proceeds much faster in pyridine.<sup>10</sup> With a large excess of PPh<sub>3</sub> (1:6) and longer reaction time [(PPh\_3)\_3Cu(CN)Cu(PPh\_3)\_3] [TCNE] 3 is formed.

The IR spectra of 1, 2, and 3 show bands in the region 2090–2200 cm<sup>-1</sup> that can be assigned to C=N stretching vibrations for TCNE<sup>--</sup> and copper bound cyanide ion. The shifts of vibrational bands to lower frequencies relative to metal-free TCNE<sup>--11</sup> are consistent with TCNE<sup>-12</sup> back-donation of

the electron density from metal to N-bound TCNE<sup>•-</sup> in 1 (2162, 2173 and 2193 cm<sup>-1</sup>) and 2 (2147 and 2190 cm<sup>-1</sup>) and un-coordinated TCNE<sup>•-</sup> in 3 (2140 and 2180 cm<sup>-1</sup>). In addition, the complexes 2 and 3 exhibit bands due to coordinated cyanide ion at 2120 and 2090 cm<sup>-1</sup>, respectively.

The solid state ESR spectra of the TCNE complexes 1, 2, and  $3^{9b}$  are consistent with the presence of the radical anion TCNE<sup>--</sup>.<sup>13</sup> The room temp. magnetic moments of 2 ( $\mu_{eff} =$ 1.74  $\mu_B$ ) and 3 ( $\mu_{eff} = 2.25 \ \mu_B$ ) are in accord with an unpaired electron on TCNE<sup>--</sup>, while that of 1 ( $\mu_{eff} = 1.03 \ \mu_B$ ) is lowered owing to magnetic interactions between pairs of stacked TCNE<sup>--</sup> ligands.

Single crystal X-ray structural determination, of 1–3 were undertaken.<sup>†</sup> The structure of 1, which crystallizes as an acetonitrile solvate, is depicted in Fig. 1. The complex is monomeric and shows approximate tetrahedral geometry about copper. Copper is bound in an  $\eta^1$  fashion to the TCNE<sup>+-</sup> at a distance of 2.044(2) Å. The angle at the coordinated nitrogen differs from 180° by 22°. Of particular interest is a four-layer stack that is formed by the juxtaposition of an inversion related molecule. Thus, a phenyl ring of one of the triphenylphosphine groups is stacked at a 9.7° tilt 3.443 Å above the plane of the TCNE<sup>+-</sup>. A second, coplanar by



Fig. 1 Structure of Cu(TCNE)(PPh<sub>3</sub>)<sub>3</sub> 1. Bond distances (Å) and angles (°): Cu–P(1), 2.307(1); Cu–P(2), 2.343(1); Cu–P(3), 2.331(1); Cu(1)–N(1), 1.147(4); N(2)–C(5), 1.133(4); N(3)–C(6), 1.134(4); N(4)–C(4), 1.144(4); C(1)–C(2), 1.430(4); C(2)–C(3), 1.397(5); C(3)–C(5), 1.430(4); C(2)–C(6), 1.428(4); C(3)–C(4), 1.439(4); Cu–N(1)–C(1), 158.0(2); N(1)–C(1)–C(2), 176.5(3); C(2)C(6)N(3), 179.2(3); C(3)–C(4)–N(4), 178.2(3)



Fig. 2 The stacking arrangement found in the crystal packing of 1 in a view perpendicular to the least-squares plane of TCNE<sup>--</sup>

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symmetry, TCNE<sup>•-</sup> is stacked 3.149 Å below, followed by another phenyl ring. A view of these four layers is given in Fig. 2. A similar stacking arrangement of phenyl-TCNE<sup>•-</sup> groups occurs in the structure of  $[Os(S_2PMe_2)_2(PPh_3)_3(TCNE)]$ ,<sup>4</sup> in which TCNE<sup>•-</sup> groups are separated by 3.12 Å. Also, a centrosymmetrically related pair of TCNE<sup>•-</sup> moieties is separated by 3.35 Å in the structure of CpMn(CO)<sub>2</sub>(TCNE),<sup>6</sup> and the complex [Cu(pdto)(TCNQ)]<sub>2</sub> (pdto = 1,8-di-2pyridyl-3,6-dithiaoctane) displays a similar stacking of 7,7,8,8tetracyanoquinodimethane radical anions at a separation of 3.12 Å.<sup>14</sup> In 1 the two C(CN)<sub>2</sub> halves of the TCNE<sup>-</sup> are twisted 6.0°, in keeping with TCNE<sup>-</sup>, and not TCNE or TCNE<sup>2-</sup>.<sup>15</sup>

Complex 2 is polymeric with tetrahedral  $Cu(PPh_3)_2$  units bridged by -CN- and N-bound -TCNE- groups. Centres of symmetry at the bridging cyanide groups require that -CN- be disordered with -NC-. The TCNE groups are *trans*-coordinated through the nitrogens. The Cu–N(TCNE<sup>--</sup>) distances are 2.086(4) and 2.014(4) Å, and the angles at nitrogen are 159.6(3) and 166.6(3)°. In contrast to 1, the packing of



**Fig. 3** Structure of  $[-(CN)Cu(PPh_3)_2(TCNE)Cu(PPh_3)_2-]_n 2$ . Bond distances (Å) and angles (°) are Cu(1)-P(1), 2.268(1); Cu(1)-P(2), 2.275(2); Cu(2)-P(3), 2.263(2); Cu(2)-P(4), 2.269(1); C(76)-C(78), 1.418(5); N(1)-C(75), 1.145(6); N(3)-C(79), 1.143(7); N(2)-C(77), 1.147(8); N(4)-C(80), 1.148(6); C(75)-C(76), 1.424(7); C(76)-C(77), 1.414(8); C(78)-C(79), 1.426(8); C(78)-C(80), 1.416(7); C(76)-C(75)-N(1), 178.4(4); C(76)-C(77)-N(2), 178.6(4); C(78)-C(79)-N(3), 178.7(4); C(78)-C(80)-N(4), 178.3(4)



**Fig. 4** Structure of [(PPh<sub>3</sub>)<sub>3</sub>Cu(CN)Cu(PPh<sub>3</sub>)<sub>3</sub>] [TCNE] **3**. Bond distances (Å) and angles (°) are Cu–P(1), 2.349(1); Cu–P(2), 2.368(1); Cu–P(3), 2.342(1); C(56)–C(57), 1.432(4); C(56)–C(68), 1.421(4); C(57)–N(2), 1.134(4); C(58)–N(3), 1.137(4); C(56)–C(57)–N(2), 177.8(4); C(56)–C(58)–N(3), 176.6(4)

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molecules in 2 does not lead to any close stacking interactions. The twist angle for the TCNE<sup>-</sup> is 5.6°.

In complex 3 (Fig. 4) the TCNE<sup> $\cdot-$ </sup> is un-coordinated. The lack of an *N*-terminal coordination to Cu is reflected in the shorter C–N distances, 1.136(4) Å, compared with bonded values of 1.147(4) and 1.146(6)Å in complexes 1 and 2, respectively. In this complex there is full separation of the cation and anion and no dimerisation of the TCNE<sup> $\cdot-$ </sup> groups; inspection of the crystal packing shows the TCNE<sup> $\cdot-$ </sup> buried in a sea of phenyl rings. The geometry of the TCNE<sup> $\cdot-$ </sup> is nearly identical to that found in other salts, for example [Fe-(C<sub>5</sub>Me<sub>4</sub>H)<sub>2</sub><sup> $\cdot+$ </sup>][TCNE<sup> $\cdot-$ </sup>].<sup>16</sup> As was true for 2, the cyanide bridges are at inversion centres in the structure, and the Cu-N, Cu–C distances are averaged. In this structure the TCNE<sup> $\cdot-$ </sup> is also centrosymmetric, and the twist angle is 0°.

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#### Footnote

† Crystal Data for C<sub>62</sub>H<sub>48</sub>CuN<sub>5</sub>P<sub>3</sub> 1, M = 1019.5, monoclinic, a =18.203(3), b = 15.485(3), c = 18.504(3) Å,  $\beta = 94.37(2)^{\circ}, U = 5198(2)$ Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 18 automatically centred reflections,  $\lambda = 0.71073$  Å), space group  $P2_1/n$ (alt.  $P2_1/c$ , no. 14), Z = 4,  $D_c = 1.303$  g cm<sup>-3</sup>, F(000) = 2116. Darkgreen prisms. Crystal dimensions  $0.40 \times 0.45 \times 0.45$  mm;  $\mu$ (Mo-K $\alpha$ ) = 5.58 cm<sup>-1</sup>. For  $C_{79}H_{60}Cu_2N_5P_4$  2, M = 1330.3, triclinic, a 13.258(4), b = 14.242(5), c = 20.152(5) Å,  $\alpha = 75.25(2)$ ,  $\beta = 82.74(2)$ ,  $\gamma = 63.45(2)^\circ$ , U = 3291.6(1) Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 19 automatically centred reflections,  $\lambda =$ 0.71073 Å), space group  $P \bar{1}$ , Z = 2,  $D_c = 1.342$  g cm<sup>-3</sup>, F(000) = 1374. Red plates. Crystal dimensions  $0.075 \times 0.15 \times 0.30$  mm,  $\mu$ (Mo- $K\alpha$  = 7.93 cm<sup>-1</sup>. For C<sub>115</sub>H<sub>90</sub>Cu<sub>2</sub>N<sub>5</sub>P<sub>6</sub> 3, M = 1854, triclinic, a = 12.979(4), b = 14.420(4), c = 14.553(5) Å,  $\alpha = 106.35(2)$ ,  $\beta = 116.19(2)$ ,  $\gamma = 90.62(2)^{\circ}$ , U = 2316.3(10) Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 32 automatically centred reflections,  $\lambda = 071073$  Å), space group  $P\overline{1}$ , Z = 1,  $D_c = 1.330$  g cm<sup>-3</sup> F(000) = 963. Yellow parallelepipeds. Crystal dimensions  $0.24 \times 0.40$  $\times 0.56$  mm,  $\mu$ (Mo-K $\alpha$ ) = 6.17 cm<sup>-1</sup>.

Data were collected at 130 K using graphite-monochromated Mo-K $\alpha$  radiation and  $\omega$  scans on a Syntex P2<sub>1</sub> diffractometer for 1 and 2 and a Siemens R3m/V diffractometer for 3. Compound 1, 20 range, 0– 50°, 9916 reflections measured in the quadrant  $h, k\pm l$ , 9213 unique  $\{R(\text{merge}) = 0.012\}$ , 7112 with  $l > 2\sigma(l)$ , max., min. transmission factors = 0.83, 0.61, no decay. Compound 2, 20 range, 0–50°, 11680 reflections measured in the hemisphere  $h, \pm k\pm l$ , 11657 unique  $\{R(\text{merge}) = 0.044\}$ , 8345 with  $l > 2\sigma(l)$ , max., min. transmission factors = 0.95, 0.93, no decay. Compound 3, 20 range, 0–55°, 10614 unique reflections measured in the hemisphere  $h, \pm k\pm l$ , 8342 with  $I > 2\sigma(I)$ , max., min. transmission factors = 0.88, 0.78, no decay. All structures were solved by direct methods and refined (based on F) using SHELXTL PLUS.<sup>17</sup> All non-hydrogen atoms were refined using anisotropic thermal parameters; hydrogen atoms were included by use of a riding model and fixed isotropic thermal parameters. Compound 1, R = 0.0406,  $R_w = 0.0371$ ,  $w^{-1} = [\sigma^2 (F_0) + 0.0001 F_0^2]$ , 640 parameters, maximum residual electron density 0.69 e Å<sup>-3</sup>. Compound 2, R = 0.0487,  $R_w = 0.0413$ ,  $w^{-1} = [\sigma^2 (F_0) + 0.0001 F_0^2]$ , 801 parameters, maximum residual electron density 0.45 e Å<sup>-3</sup>. Compound 3, R = 0.0438,  $R_w = 0.0452$ ,  $w^{-1} = [\sigma^2 (F_0) + 0.0001 F_0^2]$ , 572 parameters, maximum residual electron density 0.59 e Å<sup>-3</sup>. Atomic positional parameters, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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