N-Bonded TCNQ in Stacked Dimeric Systems. Synthesis and Crystal Structure of $[Ru(PPh_3)_2(TCNQ)]_2$ (TCNQ = 7,7,8,8-tetracyanoquinodimethane)

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The reaction of $[Ru(CO)_2(PPh_3)_2(thf)_2](BF_4)_2$ (thf = tetrahydrofuran) with PPh_3 in CH_2Cl_2 and LiTCNQ in methanol leads to the formation of $[Ru(PPh_3)_2(TCNQ)]$; the crystal structure of this compound shows a tetrahedral environment of the ruthenium atom with the TCNQ molecule coordinated *via* N.

In the study of electron transfer processes in inorganic compounds an increasing number of reactions, involving inorganic complexes and donor (D) or acceptor (A) organic molecules, has recently been reported.[1,2] The most interesting properties of the D–A complexes, as electrical and magnetic behaviour, are highly affected by the magnitude of the charge transfer, which is related to the structural disposition of the D and A moieties.

The planar molecule 7,7,8,8-tetracyanoquinodimethane (TCNQ) presents interesting acceptor properties and in recent years several TCNQ–transition metal complexes, $[ML_n](TCNQ)_x$, in which the TCNQ molecules are stacked in different forms, have been published.[1,2] In the case of ruthenium, only arene derivatives or compounds containing macrocyclic groups have been obtained.[3,4]

As part of a project studying the ability of transition metal fragments to introduce structural and electronic modifications in the arrangement of the TCNQ molecules, we are investigating the formation of polynuclear (D–A) systems. In this communication we report the synthesis and structural characterization of an unusual TCNQ–ruthenium(I) compound.

The reaction of $RuCl_2(CO)_2(PPh_3)_2$ with $AgBF_4$ in thf leads to the formation of $[Ru(CO)_2(PPh_3)_2(thf)_2](BF_4)_2$. The reaction of this compound with PPh_3 in CH_2Cl_2 and LiTCNQ in methanol yielded purple crystals of formula $[Ru(PPh_3)_2(TCNQ)]$. In this reaction the reduction of ruthenium(II) to ruthenium(I) is probably caused by the triphenylphosphine. In fact, in the reaction of $[Ru(CO)_2(PPh_3)_2(thf)_2](BF_4)_2$ with PPh_3 in the absence of LiTCNQ a white solid which does not contain carbonyl ligands is formed; the nature of this white solid is under study.

The X-ray crystal structure of $[Ru(PPh_3)_2(TCNQ)]$ is shown in Fig. 1.† The structure of this compound shows the metal in a highly distorted tetrahedral environment, coordinated to two phosphines and two nitrogen atoms of different molecules of TCNQ. All the TCNQ units act as bridges bonding two ruthenium atoms *via* opposite nitrile groups. This structure makes it one of the rare examples to possess direct metal–TCNQ coordination; a similar coordination has been only structurally described for the compounds AgTCNQ,[5] $[Cu(pdto)(TCNQ)]_2$ [pdto = 1,8-bis(2-pyridyl-3,6-dithiaoctane)][6] and Rb^+18-Crown-6 $TCNQ^-$.[7] The disposition of $[Ru(PPh_3)_2(TCNQ)]$ gives rise to dimers

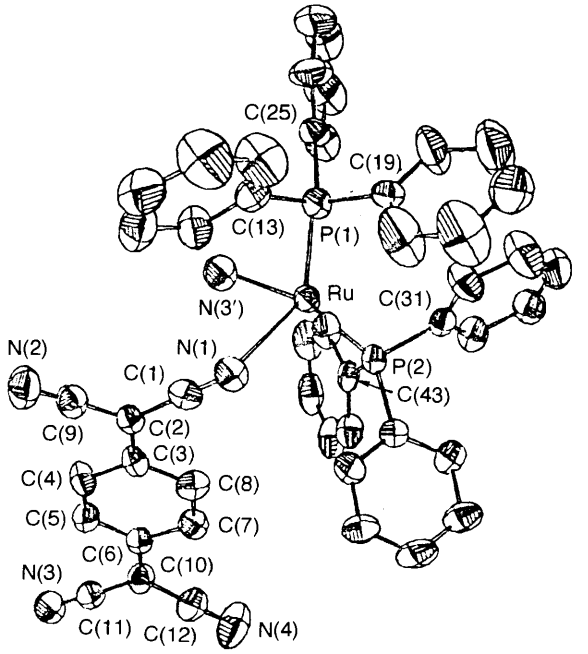

Fig. 1 ORTEP view of $[Ru(PPh_3)_2(TCNQ)]$. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ru–P(1) 2.444(3); Ru–P(2) 2.439(3); Ru–N(1) 2.424(9); Ru–N(3') 2.492(9); N(1)–Ru–N(3') 80.2(2); P(2)–Ru–N(1) 105.0(2); P(1)–Ru–N(1) 112.7(2); P(2)–Ru–N(3') 110.9(2); P(1)–Ru–N(3') 101.7(2); P(1)–Ru–P(2) 133.3(1); Ru–N(1)–C(1) 134.2(8); N(1)–C(1)–C(2) 179.0(1).

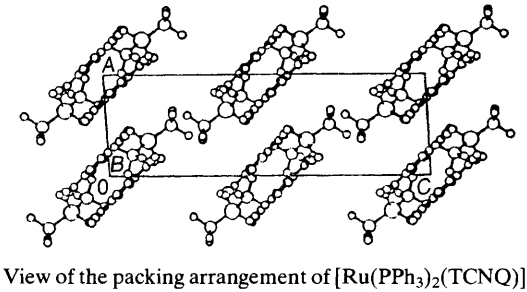

Fig. 2 View of the packing arrangement of $[Ru(PPh_3)_2(TCNQ)]_2$. The hydrogen atoms and the phenyl rings are omitted for clarity.

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† *Crystal data*: A crystal measuring 0.2 × 0.15 × 0.05 mm was mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-monochromated Mo-Kα radiation source (λ = 0.71069 Å) $RuP_2N_4C_{48}H_{32}$, M = 829.8, monoclinic, space group $P21/c$, a = 9.051(8), b = 15.509(3), c = 28.65(1) Å, β = 93.61(6), Z = 4, D_c = 1.37 g cm^{-3}, V = 4014 (4) Å^3. Data were collected in an $\Omega/2\theta$ scan technique from (−12, O, O) to (12, 21, 40) to yield 11645 unique reflections of which 3573 were considered observed having $(I) > 2\sigma(I)$; intensities were corrected for Lorentz and polarization effects. The structure was solved by Patterson and Fourier methods and refined by mixed full-matrix least-squares procedures to give a final R = 5.4% (R_w = 6.2%). Most of the calculations were carried out with X-Ray 80 (J. M. Stewart, F. A. Kundell, J. C. Baldwin, The X-Ray 80 System. Computer Science Center, University of Maryland, College Park, Maryland, 1980).

Atomic coordinates, bond lengths and band angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$[Ru(PPh_3)_2(TCNQ)]_2$. In these units, the TCNQ rings are parallel, though slightly slipped, and almost plane with an average ring–ring distance of 3.29 Å, indicating a short contact between rings like the one existing in the $(TCNQ)_2{}^{2-}$ dimeric anion.[8] The dimers are stacked in the structure with an external bond–external bond overlap between adjacent TCNQ groups. The shortest distance, 3.56 Å [C(2)–C(9′) or C(9)–C(2′)], is coincident with the sum of the van der Waals radii, indicating a very weak or even absence of interaction between adjacent dimers (Fig. 2).

The most characteristic IR bands are consistent with the dimeric TCNQ units observed in the crystal; thus, two bands at 2170 and 2140 cm^{-1} due to ν(CN) are observed. These bands (A_g and B_u modes) indicate the vibronic activation of the A_g modes (unactive in the neutral TCNQ) by intermolecular activation between $TCNQ^-$ radical anions.[9,10] The activation of other A_g modes is also observed at 1570, 1320 and 1168 cm^{-1}. The band observed at 815 cm^{-1} confirms the existence of the negative charge on the TCNQ.[10]

The compound is diamagnetic at room temperature in solid state, but is paramagnetic in solution. The UV–VIS spectrum in DMSO (dimethyl sulphoxide) clearly shows the presence of $TCNQ^-$ in solution. Two-probe conductivity measurements, performed on pressed pellets,[11] indicate that this compound is a weak semiconductor [σ (301 K) = $5.10^{-6}\ \Omega^{-1}\ cm^{-1}$]. The electrical data also show a non-linear electrical behaviour. The magnetic and conductance properties are currently being fully investigated.

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