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Ion–radical Gold–(I) Tetracyanoethylene Complex $[(Ph_3P)_2Au]^+[(NC)_2C{=}C(CN)_2]^{\cdot-}$

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The reaction of $(NC)_2C{=}C(CN)_2$ (TCNE) with $[O(AuPPh_3)_3]^+BF_4^-$ produces the novel ion–radical complex $[(Ph_3P)_2Au]^+[TCNE]^{\cdot-}$ **1**; the X-ray crystal structure, magnetic data and ESR spectra of **1** have been determined.

One-dimensional ion–radical $TCNE^{\cdot-}$ donor–acceptor salts (TCNE = tetracyanoethylene) are of interest owing to their unusual optical, electric [1,2] and magnetic properties.[3] However, only a few metal-containing salts of this type have been structurally characterized.[4–6]

Recently we reported an unusual new conversion of TCNE into the tricyanomethanide anion $[C(CN)_3]^-$. This transformation occurs as a result of $[O(AuPPh_3)_3]^+BF_4^-$ action on TCNE.[7] The reaction proceeds in a complicated manner, the final product being the diamagnetic complex $[(Ph_3P)_2Au]^+[C(CN)_3]^-$.[7] The intermediate product of this reaction, *i.e.*, a novel paramagnetic gold(I) tetracyanoethylene complex $[(Ph_3P)_2Au]^+[TCNE]^{\cdot-}$ **1**, is described here. Complex **1** is a rare example of a gold(I) anion-centred radical complex.

The salt $[O(AuPPh_3)_3]^+BF_4^-$ reacts with three equivalents of TCNE in tetrahydrofuran (THF) at ambient temperature, giving rise to a precipitation of AuCN and a solution; from which yellow crystals were isolated after 26 h; they were analysed as $[(Ph_3P)_2Au]^+[TCNE]^{\cdot-}$ **1** [eqn. (1)].

$$3(NC)_2C{=}C(CN)_2 + [O(AuPPh_3)_3]^+BF_4^- \longrightarrow [(Ph_3P)_2Au]^+[(NC)_2C{=}C(CN)_2]^{\cdot-} \quad (1)$$

1

Compound **1** is soluble in polar solvents and is stable for a few days in air in the solid state; under prolonged contact with aerial oxygen it gradually converts into the diamagnetic complex $[(Ph_3P)_2Au]^+[C(CN)_3]^-$ **2** [eqn. (2)].

$$\mathbf{1}^{\cdot-} \xrightarrow{[O]} [(Ph_3P)_2Au]^+[C(CN)_3]^- \quad (2)$$

2

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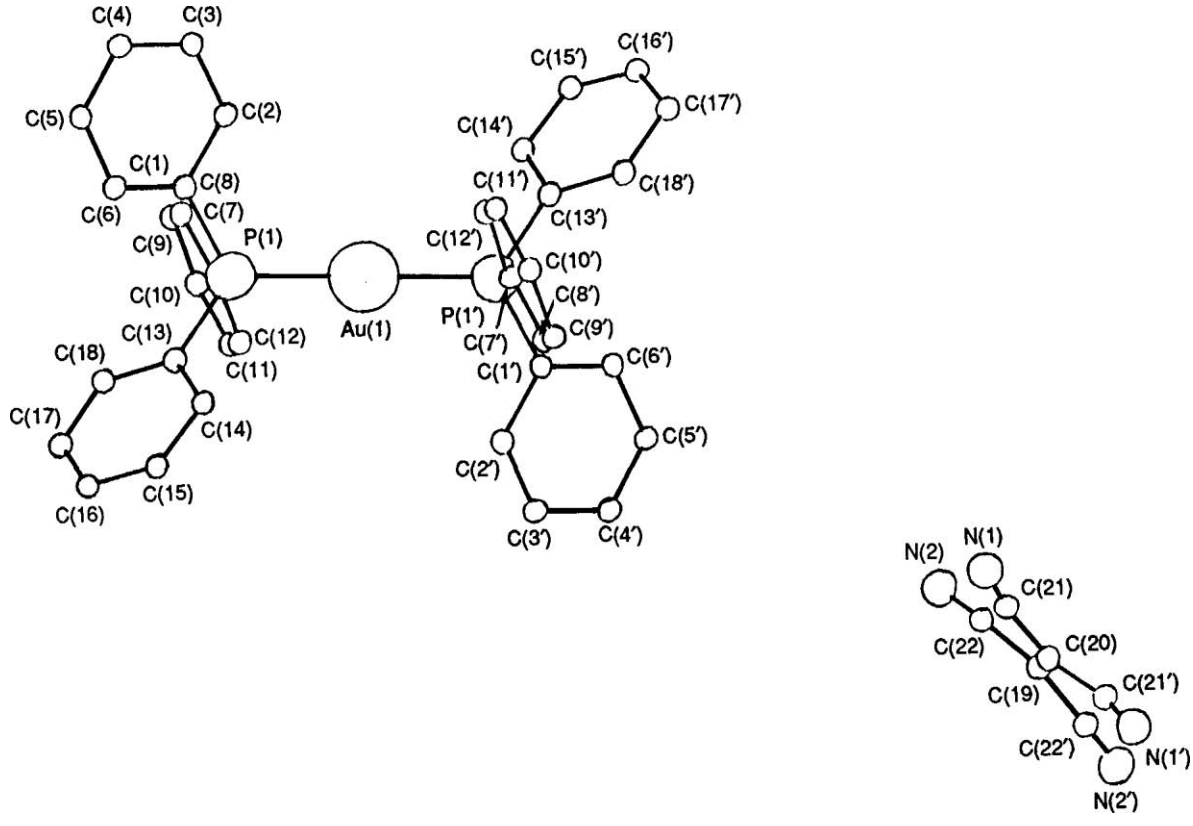

Fig. 1 Structures of the cation and anion of complex **1**

The results of an X-ray structure determination of complex **1** are shown in Fig. 1.† The $[(Ph_3P)_2Au]^+$ cations form a soft cage, with $[TCNE]^{\cdot-}$ radical anions located in the cavities of this frame, and possess quite high mobility.

The Au—P bond length in the linear centrosymmetric cation **1** is equal to 2.314(3) Å and practically coincides with that in $[(Ph_3P)_2Au]^+[C(CN)_3]^-$.[7] This value is within the interval 2.30–2.34 Å,[7] characteristic for Au—P bond lengths in complexes containing the P—Au—P fragment. The radical anion $TCNE^{\cdot-}$ is planar with a second order axis through the C(19) and C(20) atoms. The sums of the angles at these atoms are 361 and 362°, respectively. All the bond lengths in **1** are slightly shortened with respect to those in other $[TCNE]^{\cdot-}$ complexes. Indeed, average bond length values given in the literature for the C—C, C=C and C≡N bonds are 1.45, 1.36 and 1.14 Å,[4–6] while in **1** these bonds are 1.37, 1.26 and 0.98 Å, respectively. However, the geometrical parameters of **1** cannot be resolved accurately due to the considerable thermal motion of the complex as a whole and of its individual fragments. For this reason these values will not be discussed in detail. A large amplitude of atomic thermal motion is in agreement with the absence of short (less than 4 Å) contacts between cations and anions.

ESR spectral data for **1** (in the solid state and in solution) agree with the magnetic susceptibility of a solid sample of **1** and testify to the availability of one unpaired electron located in the TCNE part of the molecule. The ESR spectrum of **1** (THF, 25 °C) reveals 11 lines [9 central more intense ones correspond to four equivalent ^{14}N nuclei ($I = 1$) and two less intense side-lines correspond to ^{13}C satellite signals from ^{13}CN-groups with a hyperfine coupling constant 1.57 (± 0.05) (G = 10^{-4} T). The ESR spectrum of **1** is exactly the same as that of the $TCNE^{\cdot-}$ radical anion in $K^+[TCNE]^{\cdot-}$.[10]

The effective magnetic moments μ_{eff} were calculated for **1** from experimental data on static magnetic susceptibility.[11]‡ The values obtained confirm the availability of one unpaired electron in **1**. On the basis of the temperature dependence of the magnetic susceptibility (Fig. 2), it has been established that even at room temperature the magnetic moment of **1** [μ_{eff} (298 K) = 1.15 μ_B]§ is less than the pure spin magnetic moment for one unpaired electron [μ_{eff} (298 K) = 1.73 μ_B] and decreases with decreasing temperature to 0.5 μ_B below 77 K.

This result indicates that magnetic hyper-exchange interactions of an antiferromagnetic type are realised in complex **1**. The experimental curve for the magnetic susceptibility of

† *Crystal data* for **1**: yellow crystals, $C_{42}H_{30}AuN_4P_2$, $M_r = 849.68$, monoclinic, space group $C2/c$, $a = 20.877(3)$, $b = 8.811(1)$, $c = 23.445(4)$ Å, $\beta = 125.09°$, $V = 3529$ Å^3, $Z = 4$, $D_c = 1.59$ g cm^{-3}. The unit cell parameters and intensities of 2271 reflections with $I > \theta(I)$ were measured using an automatic four-circle diffractometer 'SYNTEX P21', λ(Mo-Kα), graphite monochromator, $\theta/2\theta$ scan, $2\theta_{max} \leq 50°$. The structure was solved by heavy atom techniques and refined by least squares techniques isotropically and then anisotropically with X-ray absorption consideration by the DIFABS technique.[9] All H atoms were located by a difference Fourier synthesis and included in the refinement. Final discrepancy factor $R = 0.033$ for 2134 reflections with $F > 5\theta(F)$.

‡ Magnetic susceptibility was measured using the Faraday technique on a unit constructed at the Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR.[11]

§ $\mu_B = 9.27402 \times 10^{-24}$ JT^{-1}.

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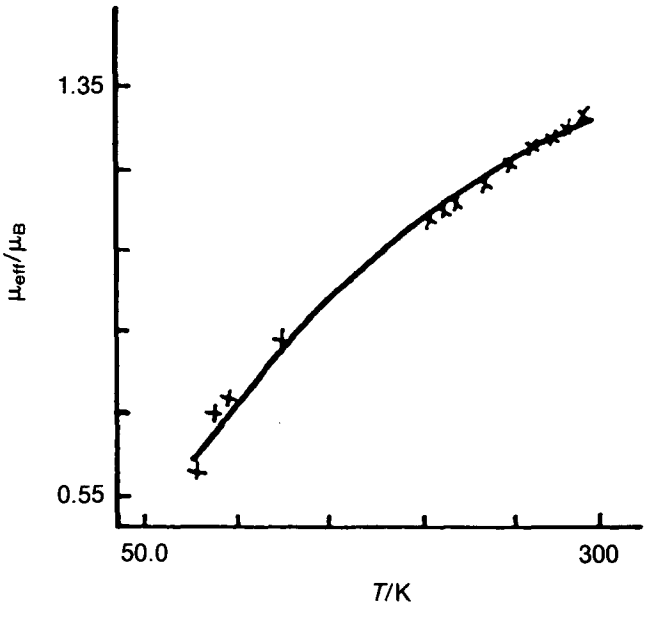

Fig. 2 Dependence of μ_{eff} on T for complex **1**: theoretical curve and experimental data

complex **1** *vs.* T (Fig. 2) is satisfactorily circumscribed in terms of Heisenberg's model for infinite chains of mutually interacting spins having an isotropic spin-Hamiltonian.[11]

Taken together, the magnetic, X-ray and ESR data suggest that complex **1** consists of a diamagnetic cation $[(Ph_3P)_2Au]^+$ and a singly charged anion $(TCNE]^{\cdot-}$ both in the solid state and in solution. These radical anions form infinite chains $—A^{\cdot-}—A^{\cdot-}—A^{\cdot-}—$ ($A^{\cdot-} \equiv [TCNE]^{\cdot-}$) with strong electronic interaction ($J = -103\ cm^{-1}$). The chains are formed as a consequence of the crystal packing in solid **1**, which enables anions to approach closely enough to interaction. The mechanism of the formation of **1** and its transformation into **2** under the action of oxygen is under study.

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