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Short Communication

A first robust complex of tetradentate TCNQ. Evidence for two weakly coupled diruthenium(II,III) subsystems in symmetrical tetranuclear complexes $\{(\mu_4\text{-TCNX})[\text{Ru(NH}_3)_5]_4\}^{8+}$ (TCNX = TCNE, TCNQ)

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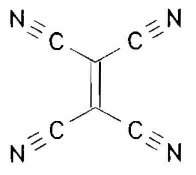
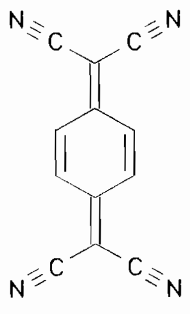
Abstract

The air-stable complexes $\{(\mu_4\text{-TCNX})[\text{Ru(NH}_3)_5]_4\}(\text{PF}_6)_8$ which contain reduced TCNX ligands show spectroscopic equivalence of the four metal coordination sites on the ^{1}H NMR and vibrational time scales and very close lying frontier orbitals (UV–Vis–NIR, electrochemistry). Both the two-electron oxidation behaviour and the magnetic moment of $\mu_{\text{eff}} = 2.7$ suggest a weak interaction between two mixed-valent malonodinitrilato/$(\text{Ru}^{2.5})_2$ subsystems.

Tetranuclear (μ^4) complexes of the small conjugated tetranitrile acceptors TCNE and TCNQ have so far been reported only in the form of $\{(\mu_4\text{-TCNE})[\text{Ru(NH}_3)_5]_4\}(\text{PF}_6)_8$ [1] and $(\mu_4\text{-TCNX})[\text{Mn(CO)}_2(\text{C}_5\text{R}_5)]_4$ (TCNX = TCNE and TCNQ) [2]. Unfortunately, the organometallic manganese complexes display a strong metal-based paramagnetism [2, 3] which precludes meaningful NMR experiments and renders these complexes very (photo)labile, especially in the polar environments necessary for electrochemistry; except for one reversible reduction wave all other redox processes of these organomanganese compounds are irreversible [2].



TCNE



TCNQ

In order to extend the knowledge about the very unusual electronic structure of such polymetalla-π-systems [2] we have prepared the new charged ion $\{(\mu_4\text{-TCNQ})[\text{Ru(NH}_3)_5]_4\}^{8+}$ (**1**) and reinvestigated the previously reported [1] TCNE analogue **2**.

Complex **1** was obtained as the octakis(hexafluorophosphate) salt by reacting an acetone solution of TCNQ with four equivalents of aqueous $[\text{Ru(NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_2$ for 1 day under argon. The completely light- and air-stable dark-green complex was precipitated with a saturated aqueous ammonium hexafluorophosphate solution and recrystallized from acetone/dichloromethane (2/1) in 83% yield. Complex **2** was obtained accordingly. Elemental analysis and a well-resolved ^{1}H NMR spectrum in acetone-d$_6$ (Fig. 1) confirmed the purity and the composition of **1**. (^{1}H NMR of **1** (250 MHz, acetone-d$_6$): δ 2.68 (s, 48H, NH$_3$(eq)), 3.97 (s, 12H, NH$_3$(ax)), 7.70 (s, 4H, CH); NH$_3$ signals exchangable with D$_2$O.) The full equivalence of the TCNQ ring protons and of the axial and equatorial NH$_3$ ligands is supported by the IR vibrational data (IR (KBr pellet). **1**: 3437(br), 3293(s), 3237(s), 3165(s), 2153(s), 2096(vs), 1631(m) cm^{-1}. **2**: 3429(br), 3302(s), 3240(sh), 3177(s), 2163(s), 2121(vs), 1630(m) cm^{-1}) which also indicate high spectroscopic symmetry. The nitrile stretching frequencies at 2153(s) and 2096(vs) cm^{-1} (**1**) and 2163(s) and 2121(vs) cm^{-1} (**2**) in KBr or acetone clearly indicate

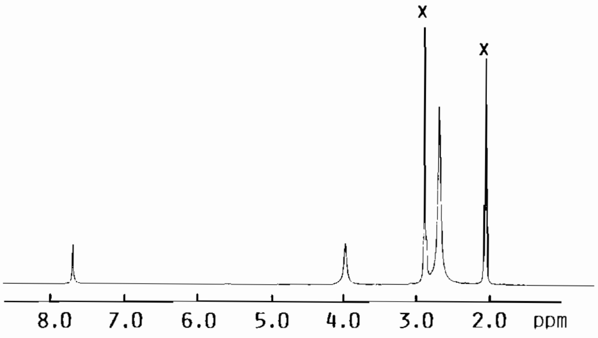


Fig. 1. ^{1}H NMR spectrum of **1** in acetone-d$_6$ (x: H$_2$O and solvent signals).

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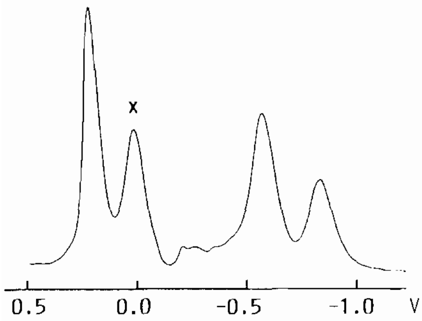
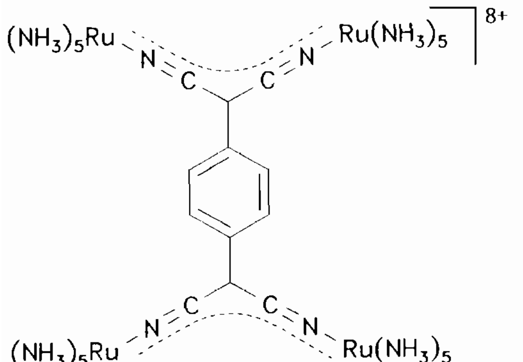


Fig. 2. Differential pulse voltammogram of complex **1** and 1 molar equivalent of ferrocene (x) in CH_3CN/0.1 M Bu_4NPF_6 at 70 mV/s scan rate.



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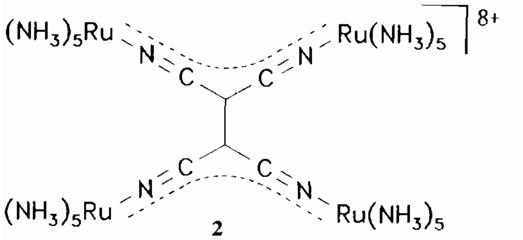

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[4] the reduced nature of the TCNX ligands (oxidation state −II) and hence the partially oxidized, i.e. +II/+III mixed-valent character of the coordinated metals.

Both compounds **1** and **2** show essentially similar electrochemical behaviour (cyclic and differential pulse voltammetry (CH_3CN/0.1 M Bu_4NPF_6, potentials in V versus ferrocene/ferrocenium at 100 mV/s). **1**: oxidation at +0.19 (2e) and +0.64 V (1e), reduction at −0.59 (1e) and −0.84 V (1e). **2**: oxidation at +0.37 (2e) and +0.70 V (1e), reduction at −0.75 (1e) and −1.11 V (1e)) which, for **2**, is very different from the results reported previously [1]*. While two electrochemically reversible one-electron reductions occur at negative potentials versus ferrocene, the oxidation involves a two-electron process for **1** (Fig. 2) and **2**; in contrast, a series of well-separated one-electron processes had been reported for **2** [1]*. Assuming a charge distribution according to the oxidation state formulation (TCNX^{2-})(Ru$^{2.5}$)$_4$, the metal-based two-electron oxidation to (TCNX^{2-})(Ru^{III})$_4$ [5] implies a relatively small interaction between what we interpret as two malonodinitrilato/(Ru$^{2.5}$)$_2$ moieties. Delocalized mixed-valent Ru^{II}Ru^{III} = (Ru$^{2.5}$)$_2$ complexes of malonodinitrile anions were found to be rather stable by Krentzien and Taube [6].

The proximity of HOMO and LUMO, particularly in complex **1**, is not only evident from the small difference of 0.78 V between oxidation and reduction potentials, it is also responsible for the rather broad ($\Delta\nu_{1/2} = 3200$ cm^{-1}) and very intense (ϵ 50 000 M^{-1} cm^{-1}) absorption band in the near-IR region (ν_{max} 10 460 cm^{-1}, E_{max} 1.30 eV). Due to the similarity with optical absorption properties of Ru^{II}Ru^{III} complexes of malonodinitrilato anions [6] we attribute these long-wavelength bands to intervalence transitions (IT) whithin individual RuNCCCNRu moieties.

Additional evidence for the weak coupling of two mixed-valent ($S = 1/2$) dimers comes from magnetic susceptibility measurements of **1** which yield an effective magnetic moment of 2.7 at 298 K, corresponding to two unpaired electrons. Solid **1** shows broad EPR signals with $g_\perp$ 2.53 and $g_\parallel$ 2.03 at 4 K.

Summarizing, the symmetrical complexes **1** and **2** contain apparently two weakly interacting pairs of strongly coupled Ru^{II}Ru^{III} dimers. The weak interaction is attributed to a reduced conjugation within the bridging TCNX ligands, probably caused by non-planarity due to rotation around the carbon–carbon single bonds adjacent to the RuNCCCNRu moieties.

Acknowledgements

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*The UV–Vis spectra of **2** shown in ref. 1 suggest the presence of air-oxidized ruthenium complexes. The absorption at 530 nm [1] is absent when the complex formation is carried out in an argon atmosphere.