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Tetranuclear Pentaammineruthenium Complexes Bridged by π-Conjugated Tetracyano Ligands Related to TCNE: Syntheses and Spectroscopy of Different Oxidation States[†]

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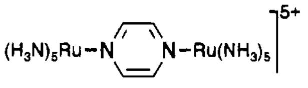
The complexes $\{(\mu_4\text{-TCNX})[\text{Ru(NH}_3)_5]_4\}^{n+}$, TCNX = TCNE (tetracyanoethene), TCNQ (tetracyano-*p*-quinodimethane), TCNP (2,3,5,6-tetracyanopyrazine), and TCNB (1,2,4,5-tetracyanobenzene), were synthesized in the respective (8+) states with PF_6^- (TCNE, TCNQ, TCNP) or CF_3SO_3^- counterions (TCNB). IR, UV/vis/near-IR, and XPS spectroscopies were used to characterize the tetranuclear (8+) ions which exhibit four equivalent nitrile and pentaamminemetal groups and intense long-wavelength optical absorptions. The (8+) ions are easily oxidized to (10+) species and reduced stepwise to (7+) and (6+) ions; EPR, UV/vis/near-IR, and, in part, IR spectroelectrochemical techniques were applied to these oxidation states in the case of the TCNE, TCNQ, and TCNB systems. The complexes may be described as fully delocalized symmetrical tetrametalla π systems $\{(\text{TCNX}^{\delta-})[\text{Ru}^{\text{II}+\delta/4}(\text{NH}_3)_5]_4\}^{n+}$ with partially reduced ligands and fractionally oxidized metal centers. The extent "δ" of metal-to-ligand electron transfer in the ground state is higher for the TCNQ and TCNE complexes than for the tetranuclear TCNP and TCNB compounds.

The coordinatively unsaturated pentaammineruthenium fragment $[\text{Ru(NH}_3)_5]^{n+}$ has played a prominent role in the development of our understanding of thermal and photoinduced electron transfer reactivity. Highlights include ion- or molecule-bridged heterodinuclear complexes $\text{L}_n\text{M}-(\mu\text{-X})-\text{Ru(NH}_3)_5$ as examples for inner-sphere electron transfer processes,[1] the homodinuclear Creutz–Taube ion (**1**), which is now recognized as a delocalized (class III) mixed-valent system,[2] and various ruthenium-modified cytochromes as models for long-range electron transfer in proteins.[3]



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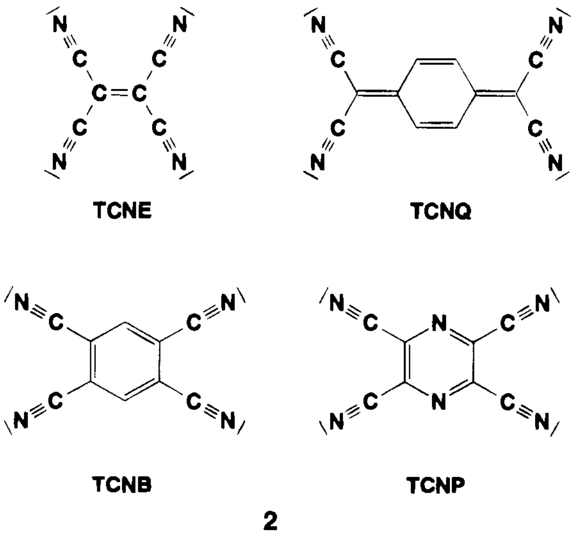
The $[\text{Ru(NH}_3)_5]^{n+}$ complex fragment is distinguished by unusually inert bonds formed from the metal to nitrogen donor ligands in *both* the $n = 2$ and $n = 3$ states, by generally reversible redox processes Ru(II/III) at convenient potentials and with small reorganization energies, and by the hydrophilic nature of the resulting complexes.[4] Furthermore, the $4d^5$ or $4d^6$ ruthenium species are generally assumed to have well-defined electronic structures with low-spin configurations and charge-transfer excited states lying lower than ligand-field excited configurations.[5]



TCNE

TCNQ

TCNB

TCNP

2

Although a vast number of symmetrical dinuclear complexes has been reported in relation to the Creutz–Taube system (**1**) and similar d^5/d^6 mixed-valent dimers,[2,6] there have been few reports of oligomeric analogues of **1**[7] and of complexes in which *four* $\text{Ru(NH}_3)_5$ fragments are coupled by one unsaturated bridging ligand.[8] Considering the preference of pentaammineruthenium to coordinate nitriles, the TCNX ligands TCNE, TCNQ, TCNP, and TCNB (**2**) are obvious candidates for molecular bridges in such complexes. The TCNX molecules are very unusual ligands[9] because of their variable coordination behavior (σ, π), their proven ability to bridge up to four metal

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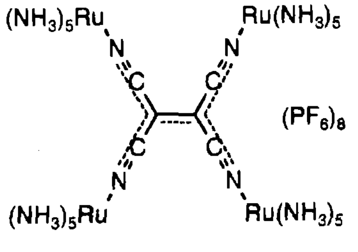
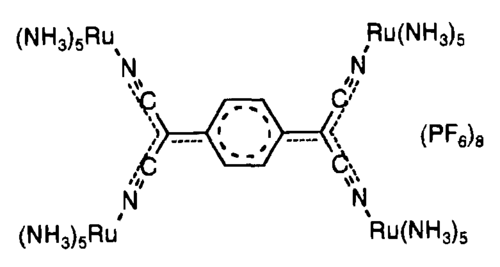
centers,[10,11] their tendency to form aggregates via π/π interaction (stacking), and their noninnocence, i.e. their very facile reduction to anion radicals and further to dianionic forms.[9] Exhaustive coordination of TCNE or TCNQ in complexes has been reported so far only for one ruthenium[8] and two maganese complexes[10] and for a structurally characterized coordination polymer $\{(TCNE)[Rh_2(O_2CCF_3)_4]_2\}_\infty$.[11]

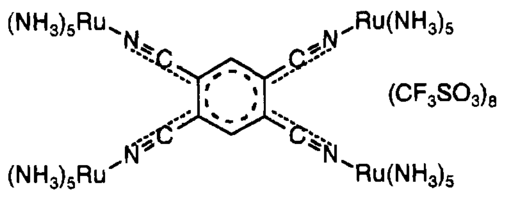
In this paper we describe and discuss the highly unusual electronic structures of tetranuclear complexes "Ru$_4$TCNX^{n+}" (**3**) as evident from cyclic voltammetry, from ^{1}H-NMR, IR, UV/vis/near-IR, and XPS spectroscopy, and from EPR, IR, and UV/vis/near-IR spectroelectrochemistry of the TCNE, TCNQ, and TCNB systems. An earlier report[8a] of the tetranuclear TCNE complex contained implausible spectroscopic results, and we shall demonstrate here that these were apparently based on contaminated material.



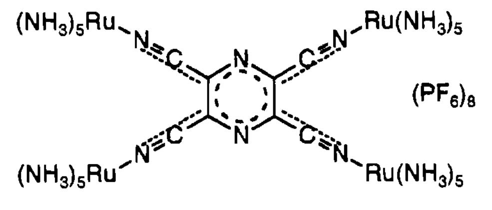
Ru$_4$TCNE



Ru$_4$TCNQ



Ru$_4$TCNB



Ru$_4$TCNP

3

The main question will be that of the proper oxidation state formulation with respect to the bridging ligand (TCNX$^{0/\bullet-/2-}$) and the four metal centers (Ru$^{II/III}$). While the system is thus complicated by the simultaneous presence of one two-step-reducible bridging ligand and four not necessarily equivalent pentaammineruthenium(II or III) fragments, the variation of ligands and the amount of information from various physical methods, including spectroelectrochemistry of several oxidation states, should be sufficient for a meaningful approach to the electronic structure of these unusual compounds.

Experimental Section

Syntheses. Although the tetranuclear complexes are moderately air-stable as solids, their syntheses and handling for spectroscopic purposes require the rigorous exclusion of air. TCNE and TCNQ were used as commercially available, pentaamminechlororuthenium(III) dichloride,[12] pentaammine(trifluoromethanesulfonato)ruthenium(III) trifluoromethanesulfonate,[13] and TCNB[14] were synthesized according to literature methods, and TCNP was donated to us by Professor J. S. Miller (University of Utah).

General Procedure for the Synthesis of $\{(\mu_4\text{-TCNX})[Ru(NH_3)_5]_4\}(PF_6)_8$. A 1.258 g (4.3 mmol) amount of $[Ru(NH_3)_5Cl]Cl_2$ was dissolved in 25 mL of hot water and reacted at room temperature with amalgamated zinc granules for about 1 h. The brown solution was filtered, and 1 mmol of TCNX in 5 mL of acetone was slowly added to yield a colored solution (green for TCNQ, blue for TCNE and TCNP). After 1 day of stirring at room temperature, the product was precipitated by adding about 5 mL of a saturated aqueous ammonium hexafluorophosphate solution. The precipitate was washed with water (10 mL), 2-propanol (100 mL), and diethyl ether (50 mL). The TCNQ and TCNP complexes were recrystallized at 0 °C from acetone/dichloromethane (2/1). The TCNE complex was dissolved in acetonitrile/water (5/1) which was allowed to slowly evaporate. The precipitating microcrystals were separated from the mother liquor and washed with water. All three complexes were dried for several hours at 30 °C under vacuum to yield dark microcrystals in yields of 73% (TCNE complex), 83% (TCNQ complex), and 22% (TCNP complex).

(**a**) **TCNE Complex.** ^{1}H-NMR (acetone-d_6): δ 2.83 (s, broad, NH_3(eq)), 3.28 (s, broad, NH_3(ax)). Anal. Calcd for $C_6H_{60}F_{48}N_{24}P_8Ru_4$ (M_r 2032.94): C, 3.54; H, 2.89; N, 16.65. Found: C, 3.44; H, 3.19; N, 16.15.

(**b**) **TCNQ Complex.** ^{1}H-NMR (acetone-d_6): δ 2.68 (s, 48H, NH_3(eq)), 3.97 (s, 12H, NH_3(ax)), 7.70 (s, 4H, CH). Anal. Calcd for $C_{12}H_{64}F_{48}N_{24}P_8Ru_4$ (M_r 2109.03): C, 6.83; H, 3.06; N, 15.94. Found: C, 7.01; H, 3.02; N, 15.52.

(**c**) **TCNP Complex.** Anal. Calcd for $C_8H_{60}F_{48}N_{26}P_8Ru_4$ (M_r 2084.98): C, 4.61; H, 2.90; N, 17.47. Anal. Calcd for $C_{10}H_{63}F_{48}N_{27}P_8Ru_4$ (M_r 2126.00): C, 5.65; H, 2.98; N, 17.79 (acetonitrile monosolvate, evidence from weak ν_{CN} bands at 2202 and 2249 cm^{-1}). Found: C, 5.59; H, 3.05; N, 17.39.

Synthesis of $\{(\mu_4\text{-TCNB})[Ru(NH_3)_5]_4\}(CF_3SO_3)_8$. A 1.362 g (2.15 mmol) amount of $[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ was dissolved in 50 mL of acetone and reacted at room temperature with amalgamated zinc granules for about 1 h. The brown solution was filtered, and 89 mg (0.5 mmol) of TCNB in 5 mL of acetone was slowly added to yield a blue-purple solution. After 1 day of stirring at room temperature, the product was precipitated by adding about 1 g of solid tetrabutylammonium trifluoromethanesulfonate. The dark precipitate was washed with 25 mL of dichloromethane and 50 mL of diethyl ether; it was recrystallized at 0 °C from acetone/dichloromethane (2/1) and dried for several hours at 30 °C under vacuum to yield 402 mg (38%) of dark microcrystals. ^{1}H-NMR (acetone-d_6): δ 2.67 (s, broad, NH_3(eq)), 3.58 (s, broad, NH_3(ax)), 8.40 (s, broad). Anal. Calcd for $C_{18}H_{62}F_{24}N_{24}O_{24}Ru_4S_8$ (M_r 2115.72): C, 10.22; H, 2.95; N, 15.89. Found: C, 10.28; H, 2.98; N, 13.65.[17d]

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Table 1. Electrochemical Data[a] for Ligands[b] and Complexes

species	E_{ox2}	E_{ox1}	E_{red1}	E_{red2}	K_c[c]	solvent
TCNE			−0.28	−1.27	6×10^{16}	AN
TCNQ			−0.25	−0.97	2×10^{12}	AN
TCNP			−0.73	−1.96	7×10^{20}	AN
TCNB			−1.06	−2.04	4×10^{16}	AN
Ru_4TCNE^{n+}	+0.79 (95)	+0.37 (80)[d]	−0.75 (125)	−1.11 (140)	1×10^{6}	AN
Ru_4TCNQ^{n+}	+0.64 (110)	+0.19 (60)[d]	−0.59 (105)	−0.84 (80)	2×10^{4}	AN
Ru_4TCNB^{n+}		−0.13 (80)[d]	−0.66 (70)	−1.35 (90)	5×10^{11}	AN
		−0.03 (100)[d]	−0.71 (70)	−1.37 (170)	1.5×10^{11}	DMF

[a] From cyclic voltammetry in 0.1 M Bu_4NPF_6 solution at 100 mV/s. Potentials in V vs $Fc^{0/+}$; peak potential differences for complexes in mV (in parentheses). [b] Reversible (ΔE_{pp} 60−80 mV) one-electron reduction processes. [c] Comproportionation constant for singly reduced species: $\log K_c = (E_{red1} - E_{red2})/0.059$ V. [d] Apparent two-electron oxidation.

Instrumentation. EPR spectra were recorded in the X band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. XPS spectra were recorded on an AEI ES200B spectrometer from films produced by the evaporation of acetone solutions on gold foil. Al $K\alpha_{1,2}$ radiation at 1486.6 eV was used for photoionization; the Au-$4f_{7/2}$ (84.0 eV) or C-1s ionization bands (286.1 eV) served as references. NMR spectra were taken on a Bruker AC 250 spectrometer; infrared spectra were recorded on a Perkin-Elmer 283 or 684 instrument and on a PU 9800 FTIR spectrometer (spectroelectrochemistry). Absorption spectra in the UV/vis/near-IR regions were taken on a Shimadzu UV 160 or a Bruins Instruments Omega 10 spectrometer. Cyclic voltammetry and differential pulse voltammetry were carried out in dry acetonitrile or DMF with 0.1 M Bu_4NPF_6 using a PAR M273 potentiostat and function generator and a three-electrode configuration (glassy carbon working electrode, platinum wire counter electrode, Ag/AgCl as reference). The ferrocene/ferrocenium couple served as internal reference.

Spectroelectrochemical measurements were carried out using an optically transparent thin-layer electrolytic (OTTLE) cell,[15] composed of CaF_2 plates, an Ag reference electrode, and Pt working and counter electrodes. In all experiments described, the spectral features of the initial state could be regenerated, thus confirming the full reversibility.

Hückel MO calculations were performed using the standard procedure[16a] for orbital energies and the McLachlan extension[16b,c] for π-spin density calculations. The parameters used were $h_C = h_{Ru} = 0.0$, $h_{N(CN)} = 1.0$, $h_{N(pz)} = 0.5$; all $k = 1.0$; $\lambda = 1.2$.

Results

Stability and ^{1}H-NMR Spectroscopy. Considering that $[Ru(NH_3)_5]^{2+/3+}$ forms fairly inert bonds to aromatic mono- and dinitriles,[17] it is not surprising that all four π-electron acceptor ligands **2** form tetranuclear complexes **3** upon reaction with 4 equivalents of solvated divalent, i.e. π-electron-rich pentaammineruthenium fragments. However, this reaction requires the total exclusion of air in order to avoid oxidation of the solvate; the air-oxidized material displays a characteristic absorption at about 530 nm, as evident in Figure 3 of ref 8a. As shown below in Figure 4, such features are absent in case of the substances reported here. Purification of the synthetically obtained (8+) forms of the complexes was problematic due to their lability on chromatography columns or microporous glass; furthermore, limited solubility (e.g. of TCNB in aqueous media) sometimes required a change of the solvent and of the counterion. Despite these efforts, the tetranuclear complex of TCNP could not be purified to the same extent as the other three analogues;[17d] not all techniques available have thus been applied to this compound. The limited variability in the solubility of the ionic species was also responsible for the failure to obtain suitable crystals for X-ray structure analysis.

The composition and symmetry of the complexes with TCNE, TCNQ, and TCNB on the pertinent spectroscopic time scale are evident from ^{1}H-NMR (cf. Experimental Section and ref 8b). All spectra showed the presence of two different kinds of D_2O-exchangeable ammine protons in the appropriate ratio of one (axial) to four (equatorial). While Ru_4TCNQ^{8+} exhibits narrow lines[8b] for (N)H and (C)H protons without any hints of the paramagnetism present,[8b,18] the other two, less paramagnetic complexes[18] feature only broad NMR lines (see Experimental Section). Nevertheless, the number of lines and the integration ratios (for Ru_4TCNQ^{8+}) are as expected for D_{2h}-symmetrical species with full equivalency of all four nitrile-bound pentaammineruthenium groups. For the TCNE and TCNQ complexes, a D_{2d} symmetrical structure with an orthogonal arrangement[19] of negatively charged $C(CN)_2$ groups and/or the *p*-phenylene ring cannot be ruled out, especially if a net two-electron transfer to the ligands were assumed, which would lead to the formation of corresponding C−C single bonds with small barriers to rotation.[9,19,21] However, this torsional degree of freedom is not possible for the TCNP and TCNB complexes, and we shall argue below that all four complexes have a coplanar π-conjugated Ru_4TCNX metalla chromophore.

Electrochemistry. Of the four π-conjugated tetracyano ligands TCNX, the TCNE and TCNQ molecules are reduced most easily, followed by TCNP and then TCNB (Table 1). The potential of the reversible second one-electron reduction does not exactly parallel that of the first reversible electron uptake which leads to quite variable comproportionation constants, K_c, of the anion radical intermediates $TCNX^{\bullet-}$: $TCNQ^{\bullet-}$ has the smallest K_c value whereas $TCNP^{\bullet-}$ displays a particularly large such constant (Table 1).

In their cyclic voltammograms and differential pulse voltammograms,[8b] the isolated (8+) forms of all three tetranuclear complexes studied (Table 1) exhibit two separate

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(18) Room-temperature paramagnetism decreases in the order $Ru_4TCNQ^{8+} > Ru_4TCNB^{8+} > Ru_4TCNE^{8+}$. Analyses of the temperature dependence (2−300 K) and of magnetic coupling will be provided: Waldhör, E.; Moscherosch, M.; Kaim, W.; Jordanov, J. Manuscript in preparation.

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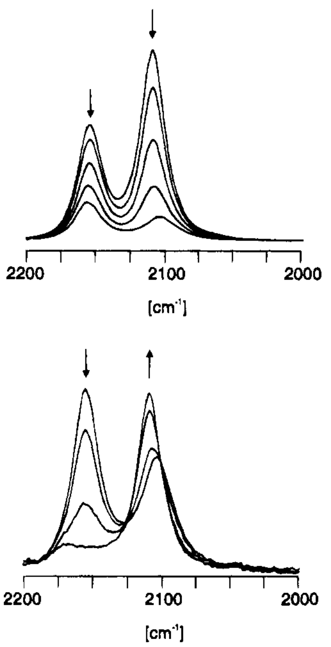


Figure 1. IR spectroelectrochemical changes of the nitrile stretching bands of $Ru_4TCNE^{(8+)\rightarrow(7+)}$ (top) and $Ru_4TCNE^{(7+)\rightarrow(6+)}$ (bottom) in CH_3CN/0.1 M Bu_4NPF_6.

electrochemically reversible or quasi-reversible reduction processes to the (7+) and (6+) states, respectively. The complexes are oxidized to the (10+) forms in what appear to be two-electron steps or two very close one-electron steps.[8b] In the case of TCNE and TCNQ, this is followed by a further, less well defined one-electron oxidation. The electrochemistry of the TCNP complex was not studied in detail because it showed small amounts of disturbing impurities that could not be removed.

The three remaining tetranuclear complexes are much more suitable for spectroelectrochemical studies than the related (cf. below) but dissociatively much more labile tetranuclear complexes $(\mu_4\text{-TCNX})[Mn(CO)_2(C_5Me_5)]_4$, TCNX = TCNE, TCNQ, which show only one reversible reduction wave.[10a] The electrochemical results reported before[8a] for $\{(\mu_4\text{-TCNE})[Ru(NH_3)_5]_4\}(PF_6)_8$, viz., four separate one-electron oxidation waves, could not be reproduced at all.

In comparison to the free ligands, the tetranuclear complexes exhibit first-reduction potentials at values which are *more negative* for the TCNE and TCNQ compounds[10a] but *more positive* for the TCNB analogue (Table 1). The separation between the first- and second-reduction potentials is markedly lowered for the TCNE and TCNQ complexes but less affected for the TCNB derivative. The potential for the two-electron oxidation is lowest for the TCNB complex and highest for the TCNE analogue. Taken together with the most negative first-reduction potential, the (8+) form of the TCNE complex thus exhibits the widest range of existence with about 1.1 V. The relevance of these effects in comparison to those of related dinuclear complexes of π-conjugated dinitriles[17b,c] and tetranuclear manganese complexes[10a] requires an identification of oxidation states of ruthenium and the TCNX ligands as provided by information from spectroscopy.

IR Vibrational Spectroscopy. Symmetry determination and assignments of oxidation states for the polynitrile ligands TCNX are greatly assisted by information from the nitrile stretching bands.[9] Following the detection of at least three reversible electron transfer steps for the TCNE and TCNQ complexes, we could use the technique of IR spectroelectrochemistry (Figure 1), using an OTTLE cell.[15] Table 2 summarizes the data and the relevant reference values for the ligands.

In D_{2h} symmetry, the TCNX ligands and corresponding tetranuclear complexes are expected to show two IR-detectable vibrational bands for the CN stretching (b_{1u}, b_{2u}). In some instances, these two bands may come too close for being resolved; on the other hand, symmetry lowering, e.g. by formation of ion pairs in the reduced state, may increase the number of visible bands between 2000 and 2300 cm^{-1}.[20] In general, the reduction diminishes the π-bond order of the nitrile group which normally[9,21] results in a low-energy shift of the corresponding bands ν_{CN}, an effect which already commences after coordination of π-back-donating metals.[17]

In the (8+) state, the TCNE and TCNQ complexes exhibit two low-energy-shifted ν_{CN} bands with the lower-energy component being more intense; similar observations were made for the tetramanganese complexes $(\mu_4\text{-TCNX})[Mn(CO)_2(C_5Me_5)]_4$, TCNX = TCNE (2160, 2110 cm^{-1}) or TCNX = TCNQ (2170, 2105 cm^{-1}).[10a] The TCNP and TCNB complexes show only broad single features at higher wavenumbers (Table 2). Except for the low-energy component of the TCNQ complex, the shifts $\Delta\nu_{CN}$ between corresponding bands of ligands and the tetranuclear complexes are little changed at about 85 cm^{-1}. On IR spectroelectrochemical reduction of the TCNE and TCNQ systems, the positions of bands remain virtually constant after the first reduction but *increase* on going from the (7+) to the (6+) state. The accompanying intensity variations are shown in Figure 1 by example of the TCNE complex.

The oxidation of the (8+) to the (10+) form resulted in rather weak ν_{CN} bands in the spectroelectrochemical experiment because of the poor solubility of this highly charged state; nevertheless, it could be observed that the bands are shifted to *lower* energies upon oxidation. In all instances, the spectroelectrochemical experiments on the (6+) to (10+) states of the TCNE and TCNQ complexes produced only *two* nitrile stretching bands with separations varying between 35 and 80 cm^{-1}.

EPR Spectroscopy. Assuming a partial electron transfer from the Ru(II) fragments to the TCNX ligands, the EPR data of the *ligand* radical ions can give valuable clues as to the amount of charge being transferred through the nitrile coordination sites. For that purpose, we have obtained a well-resolved EPR spectrum of $TCNP^{\bullet-}$ from the reduction of the parent molecule with thallium metal (Figure 2). Both the *g* factor and the hyperfine coupling parameters lie midway between those of $TCNB^{\bullet-}$ and the pyrazine radical anion (Table 3).

A Hückel MO/McLachlan calculation using established parameters for the heteroatom centers[16] reproduces this result, indicating about the same amount of π-spin density at the pyrazine and nitrile nitrogen centers of $TCNP^{\bullet-}$. In contrast to $TCNB^{\bullet-}$, which has a_u as the singly occupied molecular orbital (SOMO), the TCNP radical anion is calculated with a b_{1u} orbital as the SOMO, thus resembling more pyrazine than tetracyanobenzene in its electronic structure. The nitrile nitrogen coupling constants reflect this situation: the ^{14}N coupling and the spin density at the metal-binding nitrile centers decrease in the order TCNE > TCNB > TCNQ > TCNP.

Despite the radical-generation procedure there is no metal hyperfine coupling from $^{203,205}Tl$ ($I = {}^1/_2$) visible (Figure 2), which suggests a solvent-separated ion pair Tl^+- - -$TCNP^{\bullet-}$, despite the presence of several coordination sites in that radical anion.

No intense EPR signals were detected for the even-electron species Ru_4TCNX^{8+} although they are paramagnetic[8b,18] and may show broad ^1H-NMR features. However, one-electron reduction to the odd-electron forms Ru_4TCNX^{7+} (TCNX = TCNE, TCNQ, TCNB) produced EPR signals which could be detected in frozen solution (Table 3). Whereas the TCNE

Table 2. Nitrile Stretching Frequencies ν_{CN} (cm^{-1}) for Ligands[a] and Complexes in Different Oxidation States

	TCNE	TCNQ	TCNP	TCNB
TCNX	2245, 2210[b]	2228[b]	2254, 2248 (sh)[c]	2245 (br)[c]
TCNX$^{\bullet-}$ [b]	2253, 2198, 2178, 2171[f]	2197, 2166		
TCNX^{2-} [b]	2160, 2095	2164, 2096		
Ru$_4$TCNX^{8+} [b]	2163 (s), 2121 (vs)	2153 (s), 2096 (vs)	2159 (br)	2164 (br)
Ru$_4$TCNX^{8+} [d]	2155 (s), 2119 (vs)	2155 (s), 2099 (vs)		
Ru$_4$TCNX^{7+} [d]	2156 (m), 2104 (w)	2154 (m), 2099 (w)		
Ru$_4$TCNX^{6+} [d]	2169 (vw), 2110 (m)	2174 (w), 2132 (w)		
Ru$_4$TCNX^{10+} [d,e]	2138, 2100	2142 (sh), 2066		

[a] Values for TCNE and TCNQ from ref 20. [b] In KBr. [c] In Nujol. [d] From spectroelectrochemistry in acetonitrile/0.1 M Bu$_4$NPF$_6$. [e] Weak bands due to poor solubility. [f] Ion pair with K$^+$.

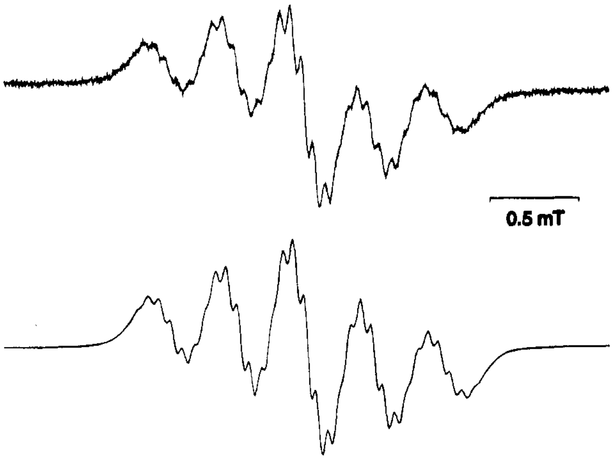


Figure 2. EPR spectrum of TCNP$^{\bullet-}$, generated by reduction of tetracyanopyrazine with thallium in THF solution: (top) experimental spectrum; (bottom) computer-simulated spectrum with 0.070 mT Lorentzian line width.

Table 3. EPR Data[a] for Ligand Radicals and Paramagnetic Complexes

species	$a(^{14}N_{CN})$	$a(^{14}N_{pz})$	$a(^1H)$	$\langle g \rangle$
TCNE$^{\bullet-}$ [b]	0.157			2.0027
TCNQ$^{\bullet-}$ [b]	0.099		0.141	2.0026
TCNP$^{\bullet-}$ [b]	0.062	0.377		2.0032
TCNB$^{\bullet-}$ [c]	0.115		0.111	n.r.
pz$^{\bullet-}$ [b]		0.718	0.264	2.0035

species	g_1	g_2	g_3	$g_3 - g_1$	$\langle g \rangle$[g]
Ru$_4$TCNE^{7+} [d]	2.003	2.003	2.029	0.026	2.012
Ru$_4$TCNQ^{7+} [d]	≈2.019	≈2.019	≈2.019	<0.01	2.019
Ru$_4$TCNB^{7+} [e]	≈2.002	≈2.002	≈2.002	<0.01	2.002
Ru$_2$(pz)$^{5+}$ [f]	1.346	2.489	2.799	1.453	2.298
Ru$_2$(bptz)$^{5+}$ [d,g]	2.019	2.418	2.913	0.884	2.477
Ru$_2$(bptz)$^{3+}$ [d,g]	1.989	2.022	2.022	0.033	2.000

[a] Coupling constants a in mT (1 mT = 10^{-4} G). [b] In THF solution at 293 K. [c] In DMF solution at room temperature.[22] [d] In frozen acetonitrile solution between 3 and 4 K. [e] In frozen DMF solution at 3.4 K. [f] From single-crystal study of **1** at 77 K.[24] [g] Bis(tetraammineruthenium) complexes **8**, from ref 23a. [h] Calculated according to $\langle g \rangle = [(g_1^2 + g_2^2 + g_3^2)/3]^{1/2}$.

compound showed recognizable anisotropic features (Figure 3), the TCNQ and TCNB analogues gave symmetrical broad lines with 5.9 (TCNQ) and 3.0 mT (TCNB) peak-to-peak line widths. Table 3 summarizes the *g* factors and compares them to corresponding values of other ammineruthenium-containing radical complexes[23] or mixed-valent systems.[24]

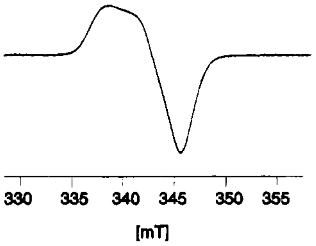
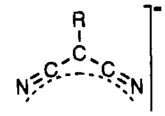


Figure 3. EPR spectrum of a frozen solution of electrolytically generated Ru$_4$TCNE^{7+} in CH$_3$CN/0.1 M Bu$_4$NPF$_6$ at 3.0 K.

UV/Vis/Near-IR Absorption Spectroscopy. All four complex ions Ru$_4$TCNX^{8+} are distinguished by one broad and very intense band in the visible (TCNX = TCNB, TCNP) or near-infrared region (TCNX = TCNE, TCNQ; Figure 4, Table 4). This observation parallels the results obtained for (μ_4-TCNX)[Mn(CO)$_2$(C$_5$Me$_5$)]$_4$, where the corresponding absorption maxima lie at even longer wavelengths (in toluene), viz., at 1104 nm (log ϵ 4.75, $\Delta\nu_{1/2}$ 2285 cm^{-1}; TCNX = TCNE) and at 1418 nm (log ϵ 4.70, $\Delta\delta_{1/2}$ 2460 cm^{-1}; TCNX = TCNQ).[10a] However, intense near-IR bands were also reported for dinuclear mixed-valent complexes (R-MDN)[Ru(NH$_3$)$_5$]$_2$ in which two metal centers are bridged by substituted malonodinitrilato anions, R-MDN$^-$ (**4**).[17c]



R-MDN$^-$

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In aprotic polar solvents, the intense long-wavelength bands of the octacations Ru$_4$TCNX^{8+} display a distinct solvatochromism of the absorption maxima which can be readily correlated ($r \geq 0.998$) with donor numbers, DN,[25] of the solvent (Table 5), suggesting a particular stabilization of the excited states by more "basic" solvents.

UV/vis/near-IR spectroelectrochemistry was performed for the TCNE, TCNQ, and TCNB complexes (cf. Figure 5 and Table 4).

For the TCNE and TCNQ complexes, the reduction (8+) → (7+) and the oxidation (8+) → (10+) (probably two closely overlapping one-electron processes) produce bands at very long wavelengths whereas the (6+) states are characterized by the absence of intense electronic absorptions in the near-infrared region. The (dis)appearance of bands during spectroelectrochemistry is illustrated in Figure 5 for the TCNQ system; Table 4 summarizes all pertinent data. Neither the reported[8a] stepwise one-electron oxidation (8+) → (9+) → (10+) of Ru$_4$TCNE^{n+} nor the implausible insensitivity of the long-wavelength absorp-

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(23) (a) Poppe, J.; Moscherosch, M.; Kaim, W. *Inorg. Chem.* **1993**, *32*, 2640. (b) Poppe, J.; Kaim, W.; Ben Altabef, A.; Katz, N. E. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2105.

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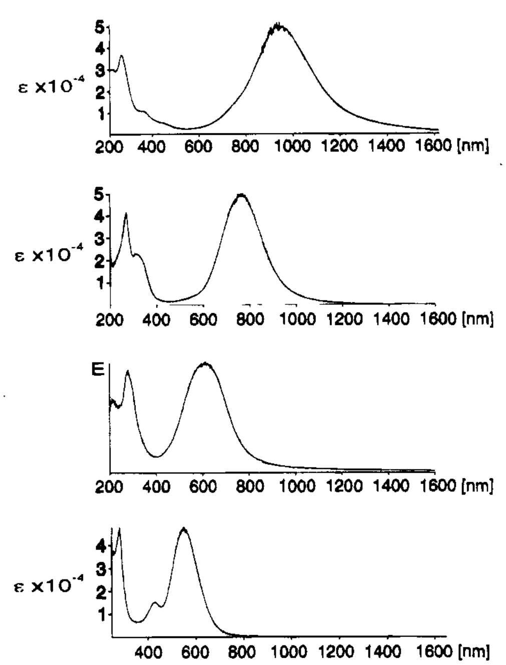


Figure 4. UV/vis/near-IR spectra of Ru_4TCNX^{8+} complexes in acetonitrile (TCNX = TCNQ, TCNE, TCNP, TCNB (from top to bottom)).

Table 4. Absorption Maxima of Tetranuclear Complexes in Different Oxidation States[a]

complex	λ_{max} (log ϵ)[b]
Ru_4TCNE^{10+}	808 (4.43), 485 (sh), 319 (4.32), 267 (4.58)
Ru_4TCNE^{8+}	762 (4.69; $\Delta\nu_{1/2}$ 3480 cm^{-1}),[c] 308 (4.33), 271 (4.62)
Ru_4TCNE^{7+}	907 (4.22), 720 (sh), 435 (3.45), 293 (sh), 258 (4.57)
Ru_4TCNE^{6+}	425 (3.70), 256 (4.58)
Ru_4TCNQ^{10+}	1170 (4.46), 935 (4.35), 454 (3.75), 277 (4.35)
Ru_4TCNQ^{8+}	935 (4.70; $\Delta\nu_{1/2}$ 3260 cm^{-1}),[c] 360 (4.04), 267 (4.55)
Ru_4TCNQ^{7+}	1561 (4.34), 1315 (4.12), 918 (4.23), 460 (4.02), 420 (4.15), 262 (4.60)
Ru_4TCNQ^{6+}	610 (3.84), 350 (4.18), 258 (4.57)
Ru_4TCNP^{8+}	612 ($\Delta\nu_{1/2}$ 6100 cm^{-1}),[c] 277
Ru_4TCNB^{10+}	537 (4.29), 390 (sh), 342 (4.50)
Ru_4TCNB^{8+}	554 (4.68; $\Delta\nu_{1/2}$ 4200 cm^{-1}),[c] 430 (4.18) 625 (4.70; $\Delta\nu_{1/2}$ 4200 cm^{-1}),[c] 485 (4.37); in DMF
Ru_4TCNB^{7+}	574 (4.39), 435 (sh) 672 (4.20), 475 (4.58); in DMF

[a] From spectroscopy or spectroelectrochemistry in acetonitrile (0.1 M Bu_4NPF_6) unless noted otherwise. [b] Wavelengths λ in nm; molar extinction coefficients ϵ in M^{-1} cm^{-1}. [c] $\Delta\nu_{1/2}$: bandwidth at half-height.

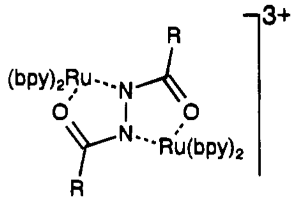
Table 5. Solvatochromism[a] of Long-Wavelength Absorption Bands for Ru_4TCNX^{8+} Tetranuclear Complexes

		TCNX			
	DN[b]	TCNE	TCNQ	TCNP	TCNB
solvent					
DMSO	0.77	12 140	9130	15 150	16 470
DMF	0.69	12 330	9500	15 360	16 640
Me_2CO	0.44	12 940	10 380	16 110	17 510
MeCN	0.36	13 120	10 640	16 340	17 790
correln param[c]					
$-A$		2400	3640	2930	3290
B		13 990	11 970	17 400	18 960

[a] Wavenumbers at the absorption maxima ν_{max} in cm^{-1}. [b] Donor numbers from ref 25. [c] From linear regressions $\nu_{max} = (A \times DN) + B$; correlation coefficients $r \geq 0.998$.

tion band toward such purported stepwise oxidation[8a] could be reproduced. The second reduction of Ru_4TCNB^{8+} proved to be irreversible with respect to spectroelectrochemistry. The two neighboring ionization states (7+) and (10+) showed an intensity decrease and small shifts of the long-wavelength charge transfer band (Table 4) but no new detectable features in the accessible near-IR region (λ < 2500 nm).

X-ray Photoelectron Spectroscopy. The question of (de)-localization in symmetrical mixed-valent complexes, in particular diruthenium species such as the Creutz–Taube ion, has been approched by the XPS technique, which is sensitive toward the oxidation state and involves a very short time scale of experiment at about 10^{-17} s.[26] However, polarizable molecules with weakly coupled metal centers may exhibit two different features corresponding to the Ru(II) and Ru(III) states in spite of an apparent delocalization in the ground state.[26,27] The Creutz–Taube ion (**1**)[26a,b] and other diruthenium complexes (**5**)[27] show this effect; on the other hand, recent reports of system **6**[26c] have clearly shown only one averaged feature for the Ru-3p ionization.



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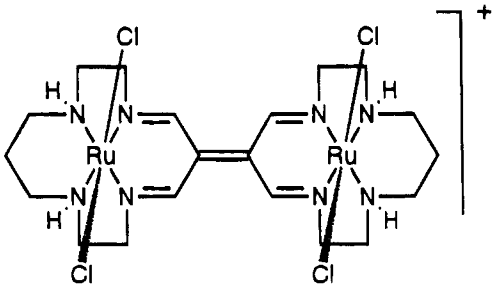

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XPS measurements of the complexes Ru_4TCNX^{8+} in the Ru-3d and N-1s (TCNX = TCNE, TCNQ, TCNB) and Ru-3p regions (TCNX = TCNE) show bands for only one kind of metal center (Figure 6) within the bandwidths at half-height of about 1.7 eV (Ru-$3d_{5/2}$) and 4.0 eV (Ru-$3p_{3/2}$). Together with the recalibrated data for the Creutz–Taube ion, the results are summarized in Table 6.

Discussion

Although nonreduced tetranitrile ligands TCNX and non-oxidized Ru(II) pentaammmine complex fragments were used in the synthesis of the tetranuclear complexes (**3**) in their (8+) forms, it cannot be automatically anticipated that these oxidation states remain unchanged after the 4-fold addition. At least for the highly electron-accepting TCNE and TCNQ systems, a ground state electron transfer according to eq 1 is not unlikely.

$$4[(L)Ru(NH_3)_4]^{2+} + TCNX \xrightarrow{-4L} \{(TCNX^{\delta-})[Ru^{II+\delta/4}(NH_3)_4]_4\}^{8+} \quad (1)$$

The amount δ of total metal-to-ligand electron transfer may vary between 0 and 2. A first indication concerning the differences among complexes **3** comes from the observation

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(26) (a) Citrin, P. H. *J. Am. Chem. Soc.* **1973**, *95*, 6472. (b) Citrin, P. H.; Ginsberg, A. P. *J. Am. Chem. Soc.* **1981**, *103*, 3673. (c) Spreer, L. O.; Alan, C. B.; MacQueen, D. B.; Otvos, J. W.; Calvin, M. *J. Am. Chem. Soc.* **1994**, *116*, 2187.

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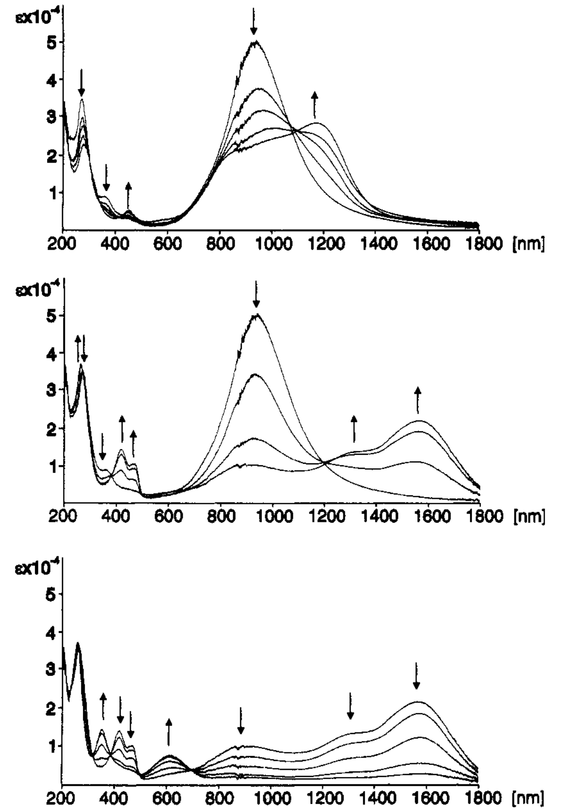


Figure 5. UV/vis/near-IR spectroelectrochemistry of Ru_4TCNQ^{n+}. From top to bottom: (8+) → (10+); (8+) → (7+); (7+) → (6+).

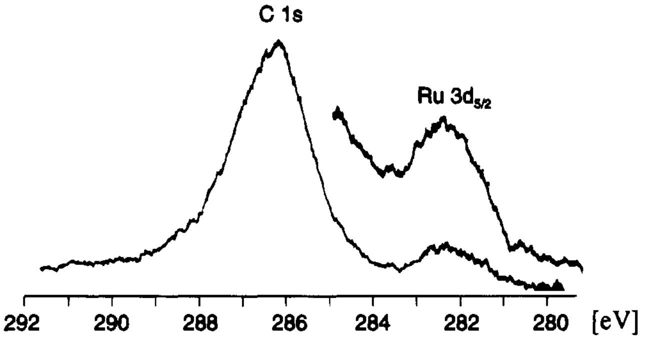


Figure 6. XPS spectrum of Ru_4TCNQ^{8+}. The sample was prepared by evaporation of an acetone solution on gold foil.

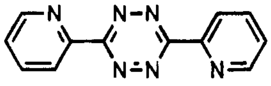
Table 6. XPS Data[a] for Mixed-Valent Pentaammineruthenium Complexes

complex	Ru-$3d_{5/2}$	Ru-$3d_{3/2}$	Ru-$3p_{3/2}$	N-1s
Ru_4TCNE^{8+} [b]	282.2	c	464.7	403.1
Ru_4TCNQ^{8+} [b]	282.5	c	d	402.3
Ru_4TCNB^{8+} [b,e]	282.3	c	d	402.3
$Ru_2(pz)^{5+}$ [f]	281.5 (Ru^{II})	c	463.0 (Ru^{II})	n.r.
	283.8 (Ru^{III})	c	465.8 (Ru^{III})	
$Ru_2(pz)^{5+}$ [g]	281.5 (Ru^{II})	c	463.1 (Ru^{II})	n.r.
	284.1 (Ru^{III})	288.2 (Ru^{III})	466.1 (Ru^{III})	

[a] Binding energy in eV. [b] Counterions as given in the Experimental Section, calibrated against Au-$4f_{7/2}$ (84.0 eV). [c] Obscured by intense C-1s band at 286.1 eV. [d] Not measured. [e] C-1s ionization of $CF_3SO_3^-$ at 293.6 eV. [f] Pentabromide,[26b] recalibrated against C-1s band at 286.1 eV. [g] Pentakis(tosylate),[26a,b] recalibrated against C-1s band at 286.1 eV (284.6 eV in ref 26b).

(Table 1) that the reduction potentials of the complexes with TCNE and TCNQ are more negative than those of the corresponding free ligands whereas the TCNB system displays the "normal" behavior,[28] i.e. a facilitated reduction of the ligand after metal coordination. For the TCNE and TCNQ complexes, one may thus assume that at least 1 electron equiv has been transferred from the metals to the TCNX ligand during coordination.[10a]

The one-electron reduction of complexes Ru_4TCNX^{8+}, TCNX = TCNE, TCNQ, TCNB, to the (7+) forms may then involve either the ligand ($TCNX^{•-} \rightarrow TCNX^{2-}$) or the assembly of the metals ($Ru^{II+(1/4)} \rightarrow Ru^{II}$). In the latter case, the spin would remain on the TCNX radical anion whereas the former alternative implies a tetranuclear mixed-valent complex. EPR spectroscopy should provide an answer to this problem because the contribution from a 4d metal like ruthenium with its high spin–orbit coupling constant to the singly occupied MO should strongly affect the deviation of the *g* factor from the free-electron value *g*(electron) = 2.0023, the *g* anisotropy in the immobilized state, and the relaxation behavior.[29] However, the EPR results for the Ru_4TCNX^{7+} states (Table 3) reveal that the situation may not be as clear-cut as this simple alternative suggests but that the SOMO of the (7+) forms can have a decidedly mixed-metal/TCNX ligand character. The EPR data for Ru_4TCNB^{7+} clearly point to an anion radical complex[29] of ruthenium(II) ammine fragments because similar characteristics, i.e. a small *g* anisotropy with values very close to 2, have been established for paramagnetic ions such as $\{(bptz)][Ru(NH_3)_4]_2\}^{3+}$ (Table 3)[23a] or $[(mpz)Ru(NH_3)_5]^{2+}$, mpz = *N*-methylpyrazinium ($\langle g \rangle$ 2.0021).[23b] In contrast, the nonnegligible deviations of the *g* factors from the free-electron value reveal that the corresponding TCNE and TCNQ complexes species are not simple anion radical complexes like $\{(bptz)[Ru(NH_3)_4]_2\}^{3+}$,[23a] $[(mpz)Ru(NH_3)_5]^{2+}$,[23b] or $(\eta^1\text{-TCNX})Ru_2(CO)_5(\eta^2\text{-L})_2$, L = $(RO)_2PN(Et)P(OR)_2$, with $\langle g \rangle$ 2.002.[30] Nevertheless, the average *g* values and the *g* anisotropy are much too small in comparison with those of true mixed-valent systems (cf. Table 3).[23a,24] It thus seems that at least the SOMOs of Ru_4TCNE^{7+} and Ru_4TCNQ^{7+} are orbitals with fairly equivalent contributions from the TCNX ligand and the transition metal centers, suggesting extensive mixing between π*(TCNX) and 4dπ(Ru) orbitals (cf. Charts 1 and 2).



bptz

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If this description is valid, the frontier MOs of the complexes should be simply calculated using Hückel MO theory,[16a] incorporating the metals as (d)π centers (Charts 1 and 2); such an approach had already been successful in the interpretation of the long-wavelength absorption data for the complexes $(\mu_n\text{-TCNE})[Mn(CO)_2(C_5Me_5)]_n$, $n = 1-4$.[10a] Here we can show that the same approach reproduces the wide variation of long-wavelength absorption maxima of all four Ru_4TCNX^{8+} complexes; Figure 7 shows the corresponding linear correlation between calculated HOMO/LUMO energy differences and the experimental energies at the absorption maxima.

The calculations producing the excellent correlation in Figure 7 give the frontier π-orbital representations as shown for two representative cases in Charts 1 and 2,[10a] confirming the EPR-

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(28) Bruns, W.; Kaim, W.; Ladwig, M.; Olbrich-Deussner, B.; Roth, T.; Schwedereski, B. In *Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds*; Pombeiro, A. J. L., McCleverty, J., Eds.; Kluwer Academic Publishers: Dordrecht, Holland, 1993; p 255.

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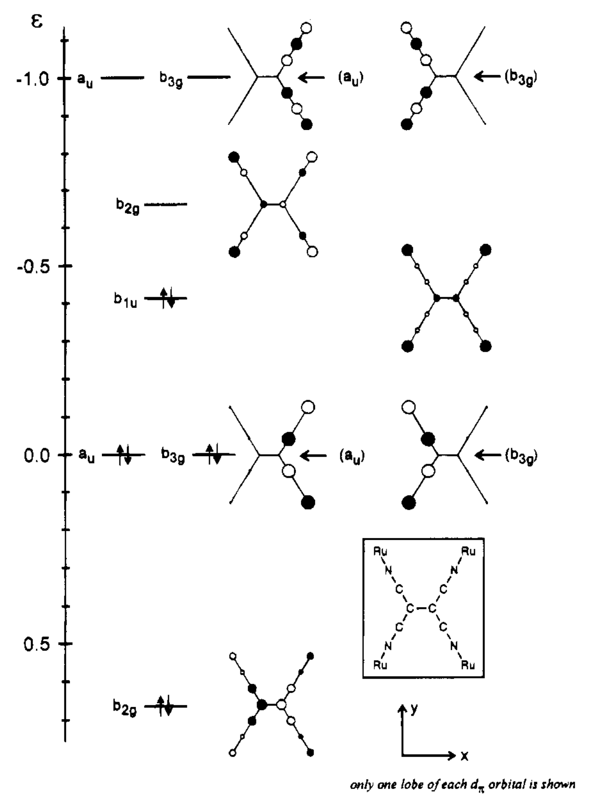
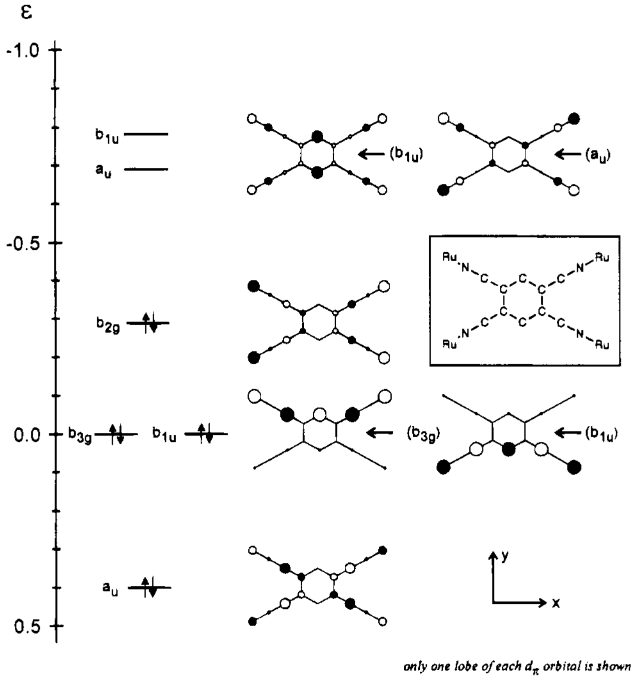
Chart 1



only one lobe of each d_π orbital is shown

Chart 2



only one lobe of each d_π orbital is shown

detectable equivalent contributions from the metal centers and the TCNX ligand π systems to the electronic structure. The frontier orbital situation of Ru_4TCNQ^{8+} is qualitatively comparable to that of Ru_4TCNE^{8+}; on the other hand, the LUMO of Ru_4TCNP^{8+} is of b_{1u} character in contrast to the a_u LUMO in Ru_4TCNB^{8+} (Chart 2). The very intense long-wavelength absorptions may thus be described as resulting from allowed transitions between fully delocalized π-type orbitals. A similar description is now being used to interpret the intense long-wavelength (near-IR) band of the Creutz–Taube ion;[31] however, the bridging ligand does *not* contribute significantly to the SOMO in that kind of mixed-valent species (**1**).[32] Delocalized mixed-valent systems should exhibit little solvatochromism due to the absence of a solvent barrier to intramolecular electron transfer,[2b] however, the high positive charge as obviously present in the Ru_4TCNX^{8+} species gives rise to a negative correlation with the donor number (DN) of the solvent (Table 5), suggesting a special thermodynamic stabilization of the excited states. The strongest solvent dependence occurs for the complex Ru_4TCNQ^{8+} with the largest bridging ligand; the weakest such effect, for the complex of the smallest TCNX ligand, TCNE (Table 5).

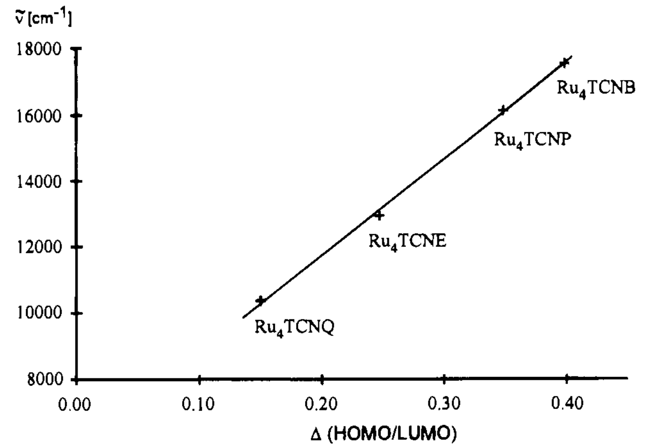


Figure 7. Correlation between HOMO/LUMO differences Δ (in β units) from HMO calculations and absorption maxima of complexes Ru_4TCNX^{8+} in acetone: $\nu = (\Delta \times 29\,105\ \mathrm{cm^{-1}}) + 6045\ \mathrm{cm^{-1}}$; $r = 0.998$.

Differences in the amount δ of metal-to-ligand electron transfer are also obvious from the different stabilities of the (7+) forms with respect to disproportionation. The K_c value of Ru_4TCNB^{7+} is about 10^5 times smaller than that of $TCNB^{\bullet-}$ (Table 1), confirming a still relatively small $\delta < 1$. On the other hand, the tetranuclear complexes with TCNE and TCNQ have a considerably more ($>10^8$ times) diminished K_c of the (7+) forms in relation to the free ligand anions, $TCNX^{\bullet-}$ (Table 1), which suggests a sizable amount of ground state electron transfer $\delta > 1$; similar results concerning K_c were observed for diruthenium complexes of 1,2-diacylhydrazido bridging ligands.[27]

The additional positive charge δ in the product of eq 1 must not necessarily be distributed equally over all four metal centers. In terms of individual integer oxidation states, several combinations can be envisaged for the (8+) form and the neighboring ionization states (Scheme 1).

With respect to symmetry, all available spectroscopies ranging from ^{1}H-NMR (time scale of about 10^{-3} s) via IR vibrational to XPS spectroscopy (time scale of about 10^{-17} s) confirm the equivalence of all four nitrile–pentaammineruthenium moieties in the tetranuclear complexes. Furthermore, the IR spectroelectrochemical studies of the nitrile stretching bands of the (7+), (6+), and (10+) forms of Ru_4TCNX, TCNX = TCNE and TCNQ, show only two such features in each case, supporting the high symmetry also for these oxidation states. From all these results, we conclude that complexes **3**, like the organomanganese analogues described before,[10a] are highly symmetric species under all conditions of measurement.

Extrapolating from the tetranuclear complexes with the very strong acceptor ligands TCNE and TCNQ via the system Ru_4TCNB^{n+} with the comparatively weaker acceptor ligand TCNB, one may arrive at the (dinuclear) complexes {(DCB)-

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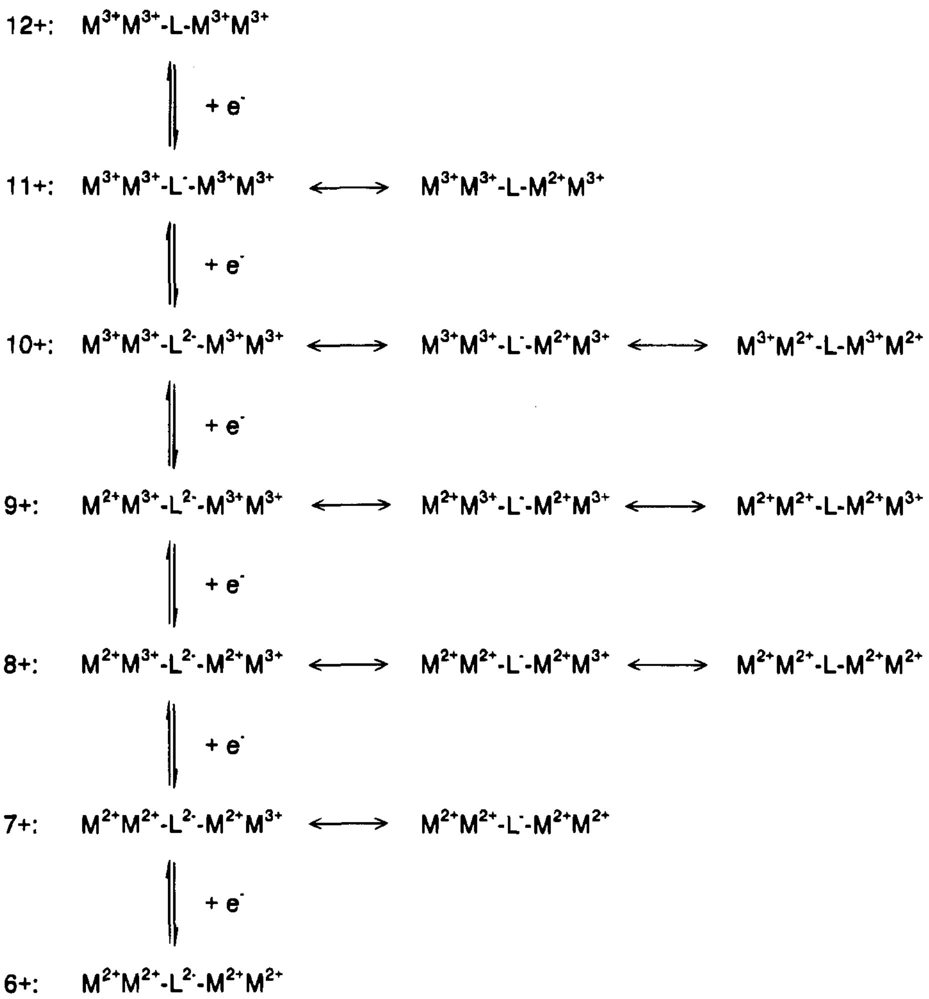
(32) (a) Piepho, S. B. *J. Am. Chem. Soc.* **1990**, *112*, 4197. (b) Kaim, W.; Kasack, V. *Inorg. Chem.* **1990**, *29*, 4696.

Scheme 1



$[Ru(NH_3)_5]_2\}^{n+}$ of the three isomeric dicyanobenzenes, DCB.[17b] These latter species have stable (4+) states with MLCT bands between 400 and 460 nm, a very small range of the mixed-valent (5+) species with $K_c < 10^{1.5}$ and weak intervalence bands, and no detectable reduction in the accessible potential range.[17b] In the non-aqueous media used here, the related Ru_4TCNB^{8+} system exhibits a two-electron oxidation wave in a similar potential region, i.e. at about 0 V vs $Fc^{0/+}$ corresponding to about 0.6 V vs NHE.[17b] Further oxidation to the highly charged $[Ru^{III}_4TCNB^0]^{12+}$ form was not observed within the accessible potential window. An intervalence band which could be expected with $\epsilon \approx 100\ M^{-1}\ cm^{-1}$ at about 1000 nm[17b] for the species $[Ru^{III}Ru^{II}_3TCNB^0]^{9+}$ was not detected within the long-wavelength tailing of the broad charge transfer band. In contrast to the situation for dicyanobenzene complexes Ru_2DCB^{4+},[17b] the bridging ligand is much more easily reduced in Ru_4TCNB^{8+}, because of both the higher charge and the lower-lying π^* level of TCNB relative to those of DCBs.

As noted before,[10a] tetranuclear TCNE complexes may be viewed as coupled even-electron dimers of odd-electron dinuclear complexes bridged by malonodinitrilato anions (**4**). Considering the strong metal–metal coupling in such complexes as evident from electrochemistry and spectroscopy,[17c] the apparent strong coupling as observed here among *four* metal centers is not unexpected. The fact that the TCNE complex is hardest to reduce *and* oxidize in the series of Table 1 confirms this strong interaction; the coupling is weaker in the presence of additional π centers as in the analogous TCNQ system. However, the coupling between dinuclear malonodinitrilato-bridged subunits is not strong enough to prevent effective two-electron oxidation behavior of Ru_4TCNE^{8+} and Ru_4TCNQ^{8+}. It is not completely clear at this point whether this effect has an electronic or structural cause; if these are formulated as $TCNE^{2-}$ or $TCNQ^{2-}$ ligands, the low rotational barrier around C–C single bonds thus formed would allow for two weakly coupled malonodinitrilato-bridged mixed-valent moieties and so explain both the two-electron oxidation behavior and the observed paramagnetism. However, detailed magnetic studies of the Ru_4TCNX^{8+} complexes as well as of di- and mononuclear pentaammineruthenium(II) compounds[18] exhibit a pattern similar to that observed for related organometallic Mn(I) complexes,[10b] i.e. a metal-centered paramagnetism based on accessible magnetically excited states (spin-crossover in a d^6 system).[18] Considering the information concerning symmetry and the successful application of Hückel MO theory (Figure 7), we thus conclude that all four Ru_4TCNX^{8+} complexes have an essentially planar arrangement of the TCNX ligand and the four metal centers, the two-electron oxidation being attributed to weak electronic cross-coupling.

The effects observed in the UV/vis/near-IR spectroelectrochemical experiments for the TCNE and TCNQ complexes can be rationalized within the MO scheme (Chart 1). The (8+) forms show intense low-energy ($<14000\ cm^{-1}$) transitions from the HOMO (b_{1u}) to the LUMO (b_{2g}); less intense high-energy transitions ($>22\,000\ cm^{-1}$) are expected from the HOMO to the second lowest unoccupied MO (SLUMO, b_{3g}) and from the second-highest occupied MO (SHOMO, a_u) to the LUMO. After one-electron reduction, the (7+) ions exhibit lower-energy and less-intense transitions $b_{1u} \rightarrow b_{2g}$ and $b_{2g} \rightarrow a_u$, involving the singly occupied MO (SOMO) b_{2g}. At higher energies (20 000–

25 000 cm^{-1}) are transitions which bear some resemblance to those of free radical anions, TCNX$^{\bullet-}$.[21,33] After the second reduction, the resulting (6+) species exhibit no more near-infrared features because both the metal centers and the bridging ligands are fully reduced (Scheme 1), the remaining long-wavelength absorption (>16 000 cm^{-1}) can then be attributed to the b_{2g} (HOMO) → a_u (LUMO) transition. On oxidation to the (10+) state, the now depopulated b_{1u} orbital becomes the LUMO to which near-infrared transitions (<12 500 cm^{-1}) are directed from lower-lying occupied MOs such as b_{3g} or a_u (Chart 1).

Whereas the TCNE and TCNQ complexes exhibit a similar spectroelectrochemical response to oxidation and reduction, the Ru_4TCNB^{8+} complex has a clearly different electronic structure, involving different orbital symmetries (Chart 2). In particular, we could not detect any conspicuous bands in the near-infrared region, either because of low intensities ($a_u \rightarrow b_{1u}$ transition of the (7+) form) or due to very small transition energies.

Spectroelectrochemistry of Ru_4TCNX^{8+}, TCNX = TCNE and TCNQ, with respect to the nitrile stretching frequencies produces initially unexpected results. There is virtually no shift of band positions upon the first reduction, however, the intensity is being reduced. This result suggests unchanged C≡N bond orders and confirms the delocalized nature of the added electron in the (7+) forms as evident also from EPR. Addition of another electron produces a further decrease in band intensity but also a high-energy shift which indicates a strengthening of the CN bonds. The origin of this unusual[9] effect lies in the absence of delocalization between the metals, Ru(II), and the ligands, $TCNX^{2-}$, in this (6+) form; there is only one formulation of oxidation states possible (Scheme 1), including "normal" nitrile/Ru^{II} functions. Conversely, the oxidation of the (8+) ions to the (10+) forms results in an unexpected low-energy shift of the ν_{CN} bands, suggesting a strong nitrile/metal interaction according to several plausible resonance descriptions as summarized in Scheme 1. The seemingly counterintuitive effects of electron transfer on the nitrile stretching bands can therefore be explained by considering the dominant effects from the nitrile-to-metal bonds, thus confirming strong metal/ligand coupling and the formulation of the tetranuclear complexes as tetrametalla π systems (Scheme 1).

The XPS results for the three tetranuclear complexes studied (Table 6) are remarkably similar, showing only one Ru-3d$_{5/2}$ band. The Ru-3d$_{3/2}$ feature is hidden by the intense C-1s ionization band; an additional signal on the high-energy side (which occurs in seemingly "nondelocalized" mixed-valent dimers **1** and **5**[26a,b,33]) is not observed up to 305 eV. A single broad line is also observed for the Ru-3p$_{3/2}$ ionization of Ru_4TCNE^{8+}, similar to the case for the fully valence-averaged compound **6**.[26c]

When one uses a common C-1s ionization maximum at 286.1 eV as reference, the comparison between the systems presented here and the Creutz–Taube ion (which shows apparent "localization" in the XPS experiment[26a,b]) confirms that the metal oxidation state in the tetranuclear compounds lies well between Ru^{II} and Ru^{III}, the valence-averaging being obvious both from Ru-3p and Ru-3d values (Table 6). Other than the Creutz–Taube system, which is assumed to lie close to the border of class III and II mixed-valent behavior,[17,31,32a] the octacations described here are clearly class III species.

In summary, this contribution adds several new features to the otherwise well-established field of ammineruthenium coordination chemistry.[1–5,7,17] We have shown here (i) what to expect when the extent of metal-to-ligand charge transfer in the ground state becomes so extensive that the oxidation state assignments have to be altered or become "fuzzy" and (ii) what effects can arise when four instead of two formally identical metal centers are coupled through symmetrical bridging ligands.

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