ARTICLE

The Amino tetracyanocyclopentadienide system: Light-induced formation of a thermally stable Cyclopentadienyl Radical

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Abstract: Crystals of the Amino tetracyanocyclopentadienyl radical were obtained from the reaction of $CaCl_2$ with $Ag[C_5(CN)_4(NH_2)]$ and recrystallization in MeOH, performed in sunlight. The radical was characterized by X-ray diffraction, EPR and UV Vis spectroscopy as well as by cyclovoltammetry and DFT calculations.

Introduction

More or less stable cyclopentadienyl radicals are known for nearly 100 years.[1] In 1925 the first synthesis of the $[C_5Ph_5]$ radical was reported,[2] which was later characterized by X-ray crystallography,[3] and EPR and UV-Vis-spectroscopy.[4] Closely related $[C_5Ar_5]$ radicals, e.g. **A** (see Chart 1), were described in 2002, and were shown to be thermally stable, but sensitive to O_2 or H_2O.[5] The stability of these radicals was attributed to sterical reasons, and thus it was not so surprising that three other sterically very encumbered radicals, **B**-**D** in Chart 1,[6,7,8] could be isolated and fully characterized. There were also several cyclopentadienyl radicals reported that were not sterically hindered, but contained electron-withdrawing substituents: The intermediate existence of the radicals **E** and **F** was postulated from cyclovoltammetric data of the corresponding anions, but neither the radicals themselves nor any of their decomposition products could be isolated. [9,10] Irradiation of the σ-dimers $[C_5R_5]_2$ (R= Me,[11] COOMe,[12]) within an EPR spectrometer showed the formation of the corresponding radicals **G** and **H**, but these could not be isolated. The pentahalocyclopentadienyl radicals $[C_5X_5]$ (X= F,[13] Cl,[14] and Br [15]) could be isolated in frozen matrices and characterized by EPR spectroscopy, but their inherent instability prevented further characterization. Chart 1 collects the structures of these known cyclopentadienyl radicals.

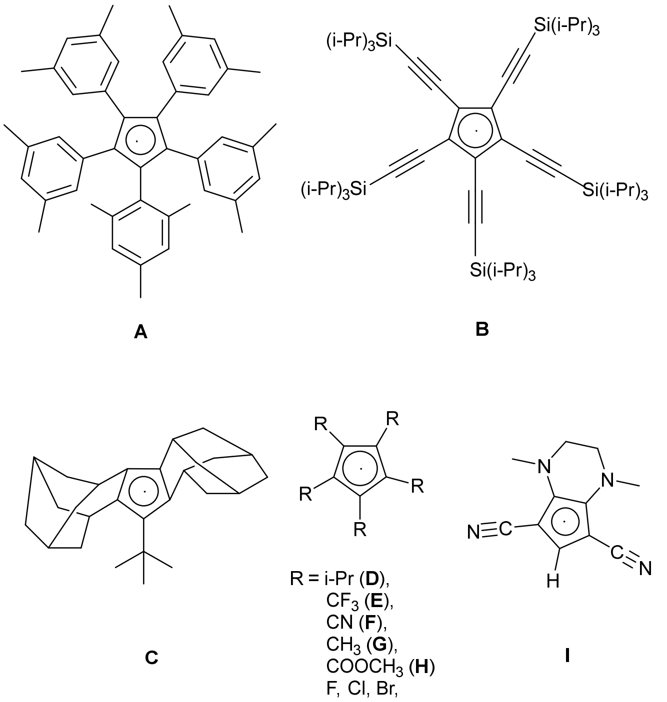

Chart 1: Structures of known cyclopentadienyl radicals, including the presumed intermediate **I**.

Radical chemistry in organic synthesis and physical applications has been a growing field of research over the last years. This is particularly due to the rapidly growing field of photoredox catalysis. [16,17] Within this field, two major approaches have developed: 1) Use of metal-based catalysts, either with “noble”[18] or “earth-abundant” metals[19] and 2) use of purely organic compounds, mostly organic dyes.[20] Especially in the latter field, the importance of “push-pull-chromophores” has been stressed.[21] Conceptually related, although not yet tested in the context of photocatalysis, are coordination compounds

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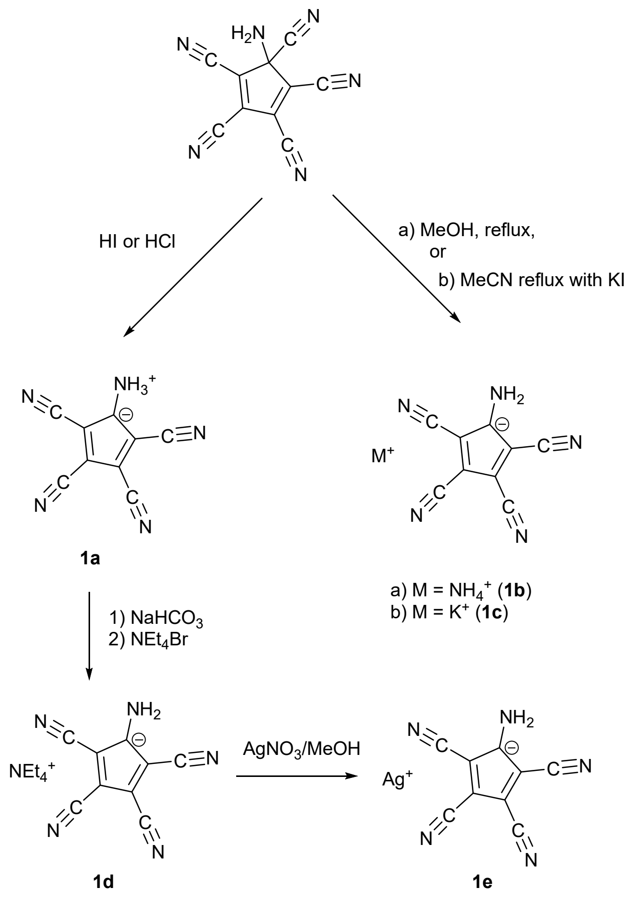
with “non-innocent ligands” [22] and charge-transfer salts of radical cations with polycyano anions.[23]

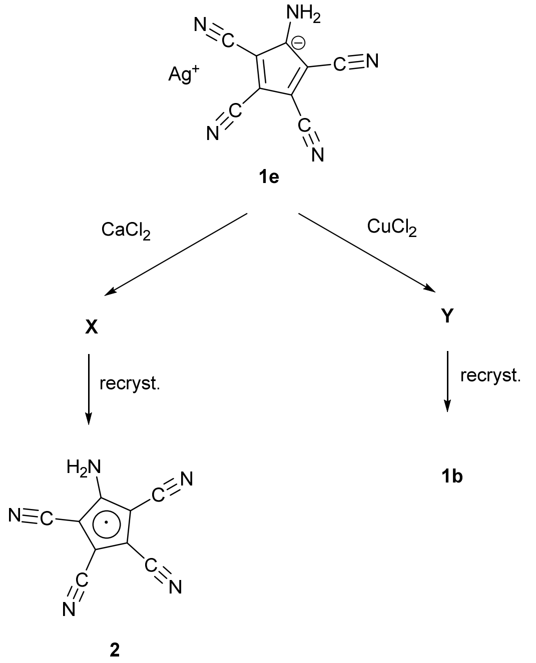
Considering the fact that (un-)substituted cyclopentadienyl systems are arguably the most important ligands in transition-metal organometallics, we reasoned that joining all the above-mentioned concepts by preparing coordination compounds with donor-acceptor-substituted cyclopentadienyl anions or radicals might lead to a new class of photoactive compounds. Possible candidates would be cyclopentadienides with donor groups like OMe or NR_2 and acceptors like COOMe or CN, some of which are known for quite a while (e.g. the potassium salt precursor of radical **I** in Chart 1). [24,25] In the course of our studies on the coordination chemistry of polynitriles we already had looked at the crystal structures of the Na and Mn(II) salts of the $[C_5(CN)_4(NH_2)]$ (“ATCC”) anion.[26] In both structures, the ATCC anion coordinates only via one nitrile function and shows a slight distortion towards an “allyl-ene” form. We decided to have a closer look at the ATCC system.

Results and Discussion



Scheme 1: Synthesis of different salts of the Aminotetracyanocyclopentadienide anion according to *Webster*

Webster had shown in his 1971 patent (see Scheme 1) that the zwitterion $[C_5(CN)_4(NH_3)]$ (**1a**) forms, when the diene $[C_5(CN)_5NH_2]$ was treated either by concentrated HI or HCl. Refluxing the diene in MeOH yielded the salt NH_4^+ $ATCC^-$, (**1b**), while refluxing in MeCN in the presence of KI gave the corresponding potassium salt **1c**. According to this patent, treatment of **1a** with $NaHCO_3$ in water followed by addition of NEt_4Br yielded the tetraethylammonium salt **1d**.[25b] Our synthetic approach to the above-mentioned Na and Mn(II) salts involved the preparation of Ag(ATCC) (**1e**), followed by treatment with NaCl or $MnCl_2$, respectively. When we tried to prepare analogously the corresponding Ca and Cu(II) salts, recrystallization of the obtained products **X** and **Y**, yielded crystals of the neutral radical $[C_5(CN)_4(NH_2)]$ (**2**) or the ammonium salt **1b** (see Scheme 2).



Scheme 2: The reactions of 1e with $CaCl_2$ and CuCl

Figures 1 and 2 show the molecular structures of both compounds.

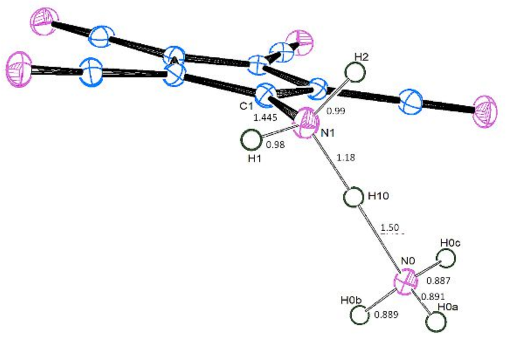


Figure 1: ORTEP-view of **1b**, showing important bond lengths [Å] of the N-H-N bridge. H1, H2 and H10 were localized from difference Fourier syntheses.

The NH_4^+ cation in **1b** might have formed by Cu(II) assisted hydrolysis of a CN bond during recrystallization in MeOH.[25,27] The molecular structure of **1b** shows an asymmetric hydrogen bridge between both ammonium nitrogens. The N1-H10 bond is significantly longer than N1-H1 and N1-H2, but also significantly shorter than the N0-H10 bond (Fig. 1). N1 shows typical tetrahedral angles (99–121°), while in the structure of **2** (Fig. 2) the angles around N1 correspond more to a sp^2 hybridization (angle sum: 355°). This is supported by a significantly shorter ring carbon bond to the amino nitrogen in **2** than in **1b**.

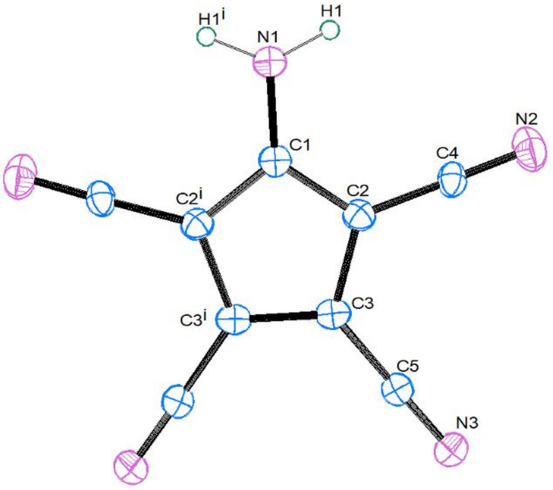


Figure 2: ORTEP view of **2**

Both compounds show the same distortion to an "allyl-ene" system with the amino group bonded to the central allyl carbon (Table S3), as it was observed in the Na and Mn(II) complexes studied by us earlier. When looking at the molecular packing, the presence of large solvent-accessible voids (15% in **1b**, 40% in **2**, see also figures S1 and S2) becomes obvious. In **1b** ATCC anions form one-dimensional chains in *b* direction using H-bridges N1–H1–N3, and these chains are connected to inversion related chains via H-bridges N1–H2–N2 forming thus 12-membered rings. These double-chains are connected in *a* direction via the NH_4 cations using H-bridges N0–H0B–N5 (see Figures S3 and S4). In **2** the ATCC molecules also form one-dimensional chains parallel to *c*, using two H-bridges N1–H11–N3 (see Figure 3).

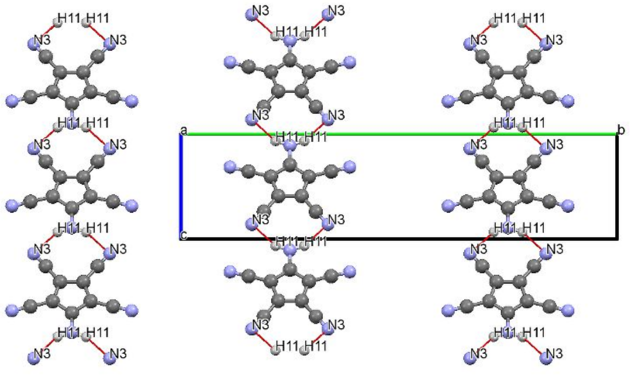


Figure 3: Packing diagram of **2**, including H-bonds, viewed down *a*

However, parallel chains stack in such a manner that the amino nitrogens are 3.345Å above the ring plane of the neighbour chain (see Figures 4 and S5). A similar stacking was also observed in the structure of the NaATCC salt, published earlier[26a] by us (see Figures S6 and S7). The only difference in the stacking is that in **2** the projection of the NH_2 nitrogen on the ring plane nearly coincides with the centroid (distance N–Ct 3.379 Å), while in NaATCC the corresponding projection is closer to the CNH_2 ring carbon (distance N–Ct 3.431 Å vs. a perpendicular distance to the ring plane of 3.342 Å). This arrangement is reminiscent of the π-dimers/ π-stacks observed in chloranil and TCNQ anion radicals.[28]

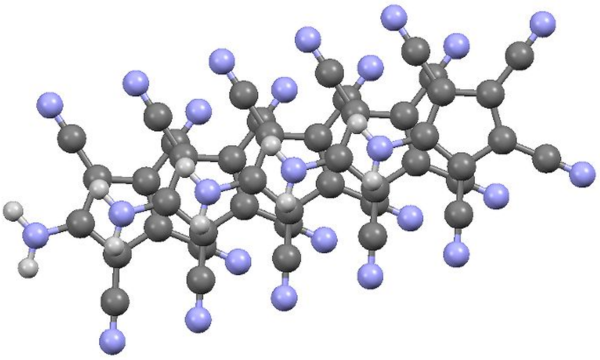


Figure 4: Stacking of the ATCC rings in **2**, viewed perpendicular to the ring planes

ICP/AAS analysis of X shows only trace amounts of Ca^{2+} (0.37%) and no silver; the CHN elemental analysis corresponds to the composition $[C_5(CN)_4(NH_2)(O_2)*3H_2O]$. This is similar to the findings in the sterically encumbered radicals **A** [5] and **D** [6] and shows that the compound is not air-stable. The oxygen does not show up in the crystal structure, however.

We then looked at the mass spectra of **2**. The EI spectrum shows besides the $(M+H)^+$ peak also the $(M+H+O)^+$, $(M+H+CN)^+$, $(M-HCN+O)^+$ and $(M-HCN+O_2)^+$ peaks, while the ESI(+) showed $(M-H+O)^+$ signal as base peak together with the $(M-H+O_2)^+$ peak and some unidentified higher-mass peaks. This is very similar to the mass spectra of **A** and **D**, showing again the oxidative instability of **2**.[5,6]

Next we turned to the (solid-state) EPR spectra of **2** and – for comparison– also of the potassium and silver salts **1c** and **1e** (see Figure 5). The crystals of **2** give EPR Signals at first, but they vanish over the course of hours. Very surprisingly, however, powdered samples of the salts **1c** and **1e**, which had been exposed to sunlight, also showed EPR signals, with slightly lower g values. For comparison, the radicals **A**, **C**, **D** and **G** have g values in the range from 2.0013 to 2.0034.

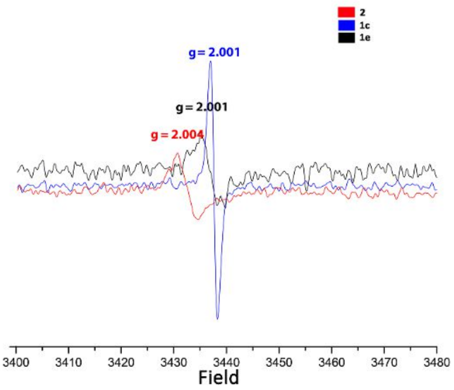


Figure 5: Solid-state EPR spectra of **1c**, **1e** and **2**

As neither Ag^+ nor $[C_5(CN)_4(NH_2)]^-$ have unpaired electrons, the most probable explanation is that the anion acts as a "redox-non-innocent" ligand,[22] i.e. an equilibrium like:

$$Ag^+ + [C_5(CN)_4(NH_2)]^- \leftrightarrow Ag^0 + [C_5(CN)_4(NH_2)]^0$$

might exist. This seems plausible for the Ag^+ compound, however, rather unlikely for the potassium salt.

Table 1: CV data of **1c**, **2, X** and some related compounds

Comp.	E $(Cp^-/Cp°)^a$	E $(Cp°/Cp^+)^a$	Ref.
B		$+0.15^d$	7
C	$-1.78^{d,e}$	$+0.30^d$	8
D	-1.91^c	$+0.58^c$	6b
E	*$+0.38^{c,e}$*	*$+0.52^{c,e}$*	9
F	$1.0^{c,e}$		10
I	*$-0.92^{c,e}$*		29
X	$0.36^{c,g}$	$0.88^{c,g}$	This work
1c	$0.36^{c,g}$	$0.89^{c,g}$	

[a] vs FcH/FcH^+; the data for **D** and **I** were reported rel. to SCE and were corrected by subtraction of 0.38 V; [b] in toluene; [c] in MeCN; [d] in CH_2Cl_2; [e] irreversible; [f] in solid state; [g] anodic peak potential (calc. vs. external Fc/Fc^+)

For further clarification we looked at the electrochemical proper-ties of **1c** and **X** by cyclovoltammetry (Fig. 6, and Fig. S8). Both compounds demonstrate two pairs of peaks at potentials around $E_{1/2}$ of 0.45 V and 0.91 V vs. Ag/0.01M $AgNO_3$, respectively, which could be assigned to Cp^-/Cp^0 redox pair and its subsequent oxidation to the Cp^0/Cp^+ at more positive potentials ac-cording to the literature convention. ~~The detection of the corresponding reduction peaks in the reverse scan and a relatively narrow peak to peak separation (100 mV and 120 mV for the first and the second pairs of peaks, respectively, without any I'R correction) point to the reversible or quasireversible behavior, indicating the high stability of the formed species in the conditions of electrochemical experiment.~~ For comparison, CV data of **B**–**F** and of **I** [24a,29] are collected in Table 1. As can be seen from these data, the alkyl substituted radicals **C** and **D** are formed at very negative potentials and are easily oxidized to the corresponding cations. Both cyano- substituted radicals **F** and **I** apparently are easily oxidized to the cyclopentadienyl cations when formed in the electrochemical experiment from the corresponding anions and do not show up in the cyclovoltammograms. Only the CF_3 substituted radical **E** shows similar electrochemical behaviour to our compounds, although it is more easily oxidized to the cyclopentadienyl cation.

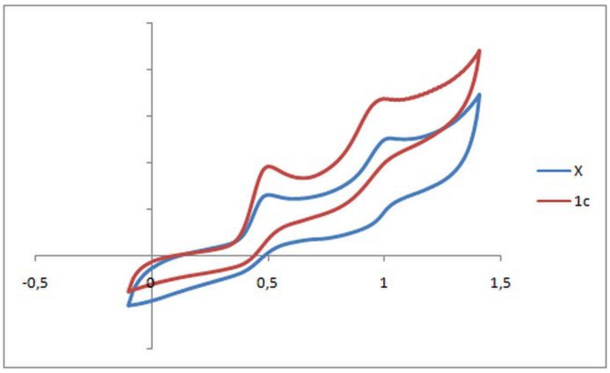


Fig. 6: Cyclovoltammogram of **1c** and **X**. The voltammograms were taken in MeCN on the Pt disk electrode. Ag/0.01 M $AgNO_3$ in MeCN was used as a reference electrode

Next, we had a look at the UV-Vis spectra of **1c**. While in MeOH solution only a broad absorption ranging from 250 to 390 nm could be observed, the reflectance spectrum showed an even broader band ranging nearly over 300 nm, with weak maxima at 220, 277, 386 and 514 nm (Figure 7, "**1c_A**").

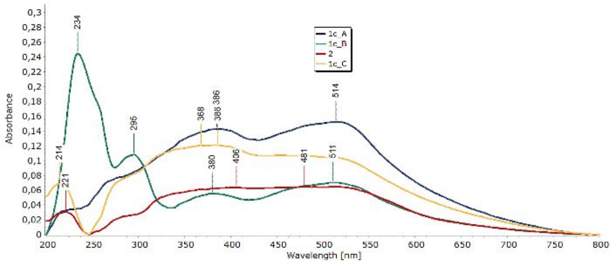


Fig. 7: Reflectance UV-Vis spectra of **1c**, taken in the dark (blue), after 3 h irradiation with an UV lamp operating at 254 nm (green) and after 8h storage in the dark (yellow) and of 2, after storage in the dark (red).

After 3h irradiation at 254 nm, a strong band at 234 nm with a shoulder at 260 nm and a weaker band at 295 nm arise, together with two weak maxima at 380 and 511 nm (Fig. 7, "**1c_B**"). When the sample is stored in the dark for 8 hours, the absorptions at 234 and 295 nm disappear and a spectrum similar to the original one is obtained (Fig. 7, "**1c_C**").

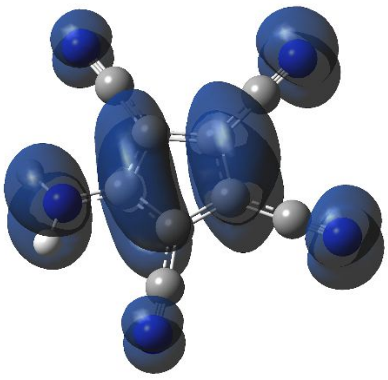


Fig. 8: Spin Density Plot of the Radical **2**

In an effort to find some explanations for the obtained results, we performed DFT calculations on the ATCC anion and radical and the zwitterion **1a**. Based on recent DFT calculations on the $[C_5(CN)_5]$ radical we decided to use the ωB97XD functional with a 6-311++G**basis set for calculations, both for gas and solution phase (PCM model).[30] Figure 8 shows a spin density plot calculated for the radical. Tables 2 and 3 contain the most important results on the energetics of anion and radical.

Table 2: DFT energies of the $[C_5(CN)_4NH_2]$ anion and radical in the gas phase

	Anion	Radical
E_{tot} (gas) [a.u.]	−617.891	−617.738
E_{HOMO} (gas) [a.u.]	−0.168	−0.342
E_{LUMO} (gas) [a.u.]	0.120	−0.047
ΔE (gas) [a.u.]	0.287	0.295
ΔE (gas) [eV]	7.82	8.02
$EA_{adi,g}$ (Radical) [a.u.]	0.153	
$EA_{adi,g}$ (Radical) [eV]	4.149	

Table 3: DFT energies of the solvated $[C_5(CN)_4NH_2]$ anion and radical

	Anion	Radical
E_{tot} (solv) [a.u.]	-617.960	-617.764
E_{HOMO} (solv) [a.u.]	-0.277	-0.320
E_{LUMO} (solv) [a.u.]	0.002	-0.034
ΔE (solv) [a.u.]	0.279	0.285
ΔE (solv) [eV]	7.60	7.76
$EA_{adi,solv}$ (Radical) [a.u.]	0.196	
$EA_{adi,solv}$ (Radical) [eV]	5.333	

The adiabatic electron affinity can be calculated from the difference of the total energies of radical and anion.[30c,31] The obtained gas-phase value of ca. 4.15 eV is significantly lower than the reported calculated values for $[C_5(CN)_5]$ (5.55±0.03 eV[30c,30a,31]) and $[C_5(CN)_4H]$ (5.00 eV[30c]). Since 4.15 eV corresponds to a wavelength of ca. 299 nm, it appears plausible that the radical **2** can be produced by irradiation of **1c** with UV light of 256 nm. The electron affinity of the radical corresponds to the ionization potential of the anion, and is therefore correlated to the electrochemical oxidation potential of the anion. While exact calculations seem still impossible, most authors agree that a linear relationship of the type

$E_{1/2} = EA - \Delta\Delta G_{solv} - E_{ref}$

holds.[32] There is still some debate on the proper choice for the absolute value for E_{ref},[33] but using E_{ref} = 4.52 eV for SHE in MeCN[34] and 0.624 eV for Fc/Fc^+ vs. SHE,[35] and approximating our calculated EA_{solv} for the difference "EA-ΔΔG" gives a calculated $E_{1/2}$ of 0.186 V vs. ferrocene. If the onset potential of the first anodic wave (0.288 V) is used instead of the anodic peak potential, as suggested by many authors, there is a satisfactory agreement between theory and experiment.

Comparison of the calculated and measured UV-VIS spectra (Figures S12-S14) shows moderate agreement, which is not unexpected considering the measured spectra were solid-state spectra and the calculations were performed on solution species. Similarly, comparison of calculated and observed bond lengths shows poor agreement for **2**, and moderate agreement for **1b** with the calculated geometry for **1a** (Table S3). Again, this is not too surprising, since the solid state crystal structures showed both hydrogen bridging and π-stacking, which do not occur in the gas phase used for the calculations.

Conclusions

Taking all the results together, we believe that the "original" product X of the $CaCl_2$/ AgATCC reaction was the zwitterion **1a**. On exposure to light, this forms the radical **2** presumably with concomitant formation of H_2, similar to the formation of the radi-cals **F** and **G** from irradiation of the corresponding dienes. A DFT calculation on the energy balance of this presumed formation reaction yields a slightly exergonic ΔG_r value (Tables S4 and S5). As a solid, the radical can survive for a certain time. When exposed to air, a dioxygen adduct $\mathbf{2}{*}O_2$ of unknown structure is formed. The fact that the K^+ salt **1c** gives an EPR signal might arise from partial hydrolysis of the ATCC anion (as all the ATCC salts appear to be quite hygroscopic) to give **1a** (which is reported to have a pK_a of 2.0 [25]), which in turn forms the radical **2** on irradiation. Comparison of the crystal structures of **2** and the known NaATCC shows that formation of the radical in the solid state needs only little structural rearrangements.

Experimental

All solvents were of p.a. grade or higher and were used as provided. $(Et_4N)ATCC$ (**1d**) and Ag(ATCC) (**1e**) were prepared according to literature procedures [26a,25b]

5-ammonium-1,2,3,4-tetracyanocyclopentadienide zwitterion (1a)

HCl (conc., 0.5 mL) was added dropwise to a solution of **1e** (164.5 mg, ca. 0.56 mmol,) in MeOH (10 mL) and the mixture was stirred for 1 h at room temperature. The solution was evaporated to a volume of 1 mL and filtered. Addition of CH_2Cl_2 to the yellow filtrate precipitated **1a** as a red powder. Yield: 68 mg (48 %).

MS: *m/z* (DEI+): 180.9 $[HATCC^+]$. $^{13}C\{1H\}$ NMR (DMSO-d6): δ = 148.04 (C5-NH3), 116.10 (C1-CN), 115.68 (C2-CN), 94.82 (C2), 79.53 (C1). Elemental analysis ($C_9N_5H_3 \cdot H_2O \cdot 1.37$ HCl): calc. C 43.40, N 28.10, H 2.58, found: C 43.32, N 27.81, H 2.59.

Ammonium 5-amino-1,2,3,4-tetracyanocyclopentadienide (1b).

A solution of **1e** (158.7 mg, ca. 0.5 mmol) in MeOH (10 mL) was treated with $CuCl_2$ (33.6 mg, 0.25 mmol). The mixture was stirred for 16 h at room temperature and the formed red solid was isolated by filtration. Extraction with MeCN, evaporation to ca. 1 mL and precipitation with CH_2Cl_2 yielded a red powder. Recrystallization from MeCN/ toluene gave– besides a red powder– colourless crystals of $NH_4(ATCC)$ in small amounts.

A solution of **1e** (164.5 mg, ca. 0.56 mmol) in MeOH (10 mL) was treated with NH_4Cl (26.7 mg, 0.50 mmol) in one portion. The mixture was stirred for 8 h at room temperature. The solution was evaporated to a volume of 1 mL and filtered. Addition of CH_2Cl_2 precipitated **1b** as a red powder. Yield 15 mg (15 %).

MS: *m/z* (FAB-): 180.4 [$ATCC^-$]. Elemental analysis ($C_9N_6H_6 \cdot 0.19\ CH_4O \cdot 0.11\ H_2O$): calc. C 53.54, N 40.75, H 3.40; found C 53.79, N 40.78, H 3.41.

Potassium 5-amino-1,2,3,4-tetracyanocyclopentadienide (1c).

KCl (18.6 mg, 0.25 mmol,) was added to a solution of **1e** (92.2 mg, ca. 0.3 mmol) in MeOH (30 mL). The solution was stirred at RT and under exclusion of light for 16 h. After filtration (to remove AgCl) the solution was evaporated to a volume of 1 mL, filtered again and the product was isolated as a red powder by precipitation with CH_2Cl_2. Yield: 51 mg, 79 %.

MS: *m/z* (MALDI-) = 180.2 [ATCC-]. EA ($K(C_9N_5H_2) \cdot 0.75\ CH_4O \cdot H_2O$): calc. C 44.82, N 26.80, H 2.70, found C 44.99, N 26.90, H 2.45.

5-Amino-1,2,3,4-tetracyanocyclopentadienyl radical (2).

$CaCl_2$ (8.6 mg, 0.08 mmol) was added to a solution of **1e** (57 mg, ca. 0.19 mmol) in MeOH (10 mL) in one portion and the mixture was stirred for 8 h at room temperature. The solution was evaporated to a volume of 1 mL and the formed precipitate was removed by filtration. Addition of CH_2Cl_2 to the yellow filtrate yielded a red powder. Recrystallization from MeOH gave red needles of x-ray quality.

MS: (DEI+): *m/z* = 168.9 [100%, ATCC+O-HCN], 180.9 [15%, $HATCC^+$]; 185.0 [5%, $ATCC+O_2$-HCN]; 196.1 [1%, HATCC+O]; 207.0 [5%, ATCC+HCN]; (ESI+): *m/z* 181.1 [10%, $HATCC^+$]; 195.1 [100%, $C_9N_5OH^+$]; 211.1 [20%, $C_9N_5O_2H^+$]; MS (ESI-): *m/z* 179.0 [100%, $C_9N_5H^-$]; 180.0 [95%, $ATCC^-$]; 181.0 [10%, $HATCC^-$]. ICP-AAS Ag 0.0 %, Ca 0.35 %. Elemental analysis $C_9N_5H_2 \cdot O_2 \cdot 3\ H_2O$): calc. C 40.61, N 26.302, H 3.03, found: C 40.76, N 26.31, H 2.99.

Conflicts of interest

There are no conflicts to declare

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