CHEMISTRY LETTERS, pp. 399-402, 1993.

Synthesis and Characterization of Tetra(*tert*-butyl)-2,3-anthracenocyaninatoiron(II) Compounds

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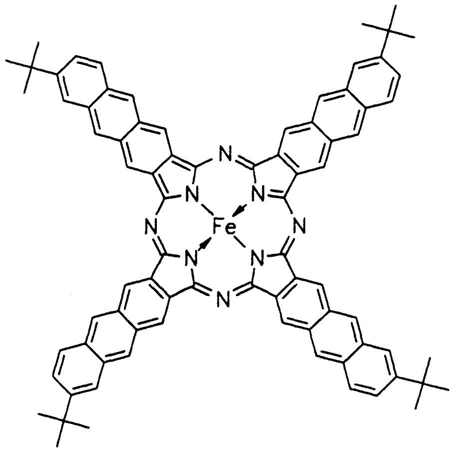
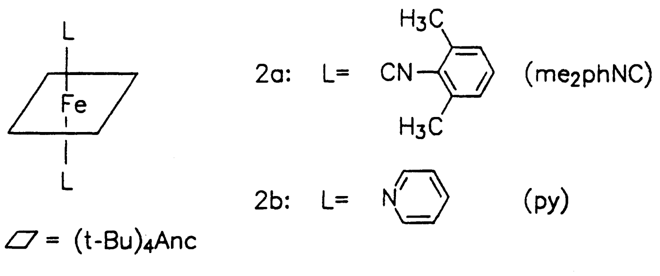
Bis(isocyanide) and bis(pyridine) complexes of tetra(*tert*-butyl)-2,3-anthracenocyaninatoiron(II) were synthesized from 6-*tert*-butyl-2,3-dicyanoanthracene and characterized by UV/Vis, NMR, and Mössbauer spectroscopy. Linear annulation of benzene rings to the phthalocyanine macrocycle produces a bathochromic shift of the Q-band. The first oxidation potential of the 2,3-anthracenocyanine macrocycle determined by cyclic voltammetry is lower than that of 2,3-naphthalocyanine.

Calculations of the electronic properties of annulated phthalocyanines show that linear annulation of benzene rings produces a continuous destabilization of the HOMO level and a narrowing of the HOMO-LUMO energy gap.1) One-dimensional stacks of linearly annulated phthalocyanines are calculated to have lower oxidation potentials and narrower VB-CB energy band gaps than angularly annulated systems.2) These theoretical results are confirmed by our studies on 1,2-naphthalocyanine,3) 9,10-phenanthrenocyanine,4) and 2,3-naphthalocyanine5) and the corresponding bridged stacked systems $[\mathrm{MacML}]_n$. As low gap polymers or even intrinsic conductive compounds may be obtained from systems derived from more extended linearly annulated phthalocyanines we focussed our attention on the synthesis of 2,3-anthracenocyanine.

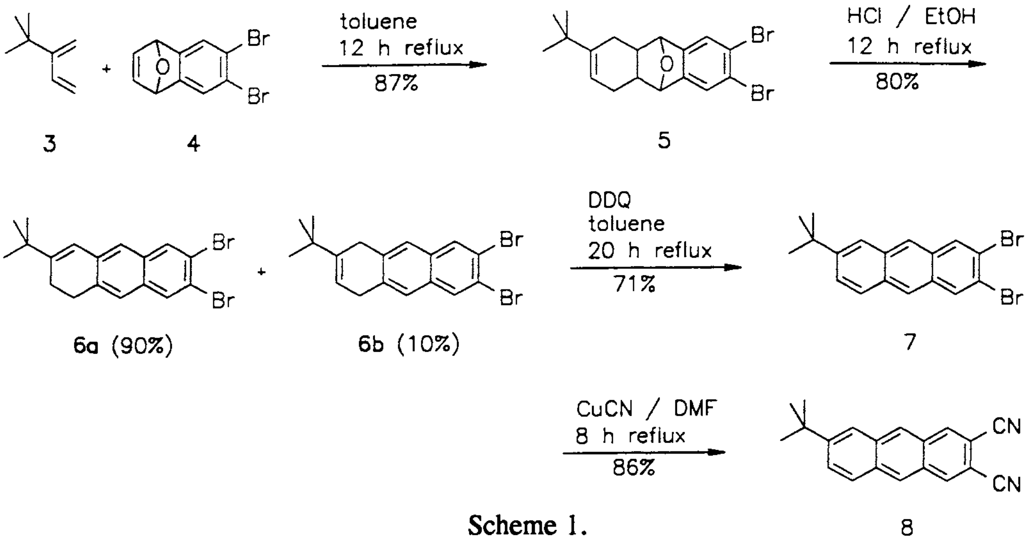
So far, only little is known of unsubstituted6) and octasubstituted6-8) 2,3-anthracenocyanine. Metal free tetra(*tert*-butyl)-2,3-anthracenocyanine and the corresponding cobalt complex have been reported,9) however, no details and no characterization were given. Here, we report the first synthesis of tetra(*tert*-butyl)-2,3-anthracenocyaninato-iron(II) compounds $[(t\text{-Bu})_4\text{-2,3-AncFe}]$.



$(t\text{-Bu})_4$-2,3-AncFe (**1**) (C_{4h} isomer)



Unsubstituted and octaphenyl substituted 2,3-anthracenocyanines synthesized from the corresponding dinitriles proved to be practically insoluble in organic solvents and were hard to purify and to characterize. Therefore, (t-Bu)$_4$-2,3-AncFe (**1**) was prepared starting from 6-*tert*-butyl-2,3-dicyanoanthracene[10] (**8**). The synthesis of **8** was carried out as given in Scheme 1.[11,12]



Scheme 1.

(t-Bu)$_4$-2,3-AncFe (**1**) as a mixture of constitutional isomers was synthesized by refluxing **8** (4 equiv.) and $FeSO_4 \cdot H_2O$ (1 equiv.) in N,N-dimethylaminoethanol under nitrogen for 20 hours. As **1** proved to be very sensitive towards oxidation it was difficult to purify. Hence, crude **1** was coordinated with 2,6-dimethylphenylisocyanide and pyridine to form the bis(isocyanide) complex **2a**[13] and the bis(pyridine) complex **2b**,[14] respectively. The complexes could be purified by chromatography on neutral alumina excluding air. (**2a**: eluent dichloromethane; **2b**: eluent toluene/pyridine (100:1), activity of alumina: IV).

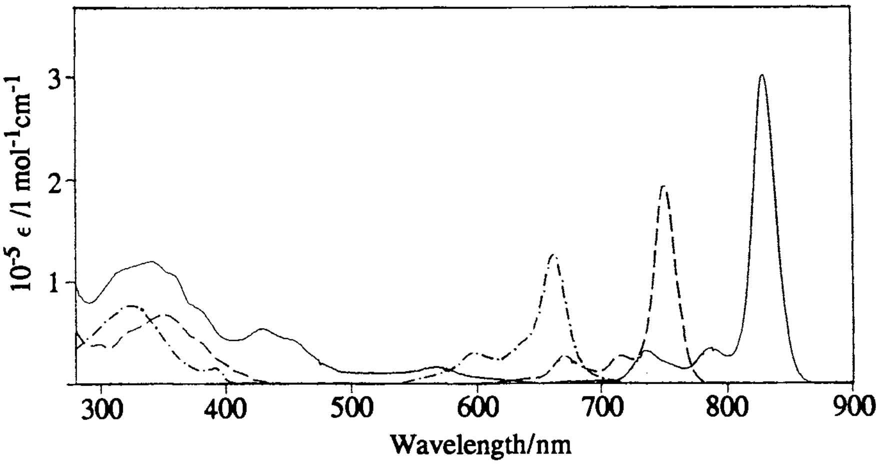


Fig. 1. UV/Vis spectra ($CHCl_3$) of $PcFeL_2$ (-·-), 2,3-$NcFeL_2$ (--) and (t-Bu)$_4$AncFeL_2 (**2a**) (—); L = me_2phNC.

The UV/Vis spectra (Fig. 1) show the expected bathochromic shift of the Q-band with linear annulation of benzene units. In addition, on going from phthalocyanine to 2,3-anthracenocyanine an increase in the absorption coefficient ϵ is observed. For **2a** the $Q_{0\text{-}0}$ band appears at 829 nm (ϵ/l mol^{-1}cm^{-1} = 3.08 x 10^5) and is even shifted to 851 nm in the corresponding $(ph)_8$-2,3-AncFeL_2 complex.[12c] (For comparison: PcFeL_2, λ_{max} = 658 nm,[15] ϵ/l mol^{-1}cm^{-1} = 1.32 x 10^5;[12c] 2,3-NcFeL_2, λ_{max} = 751 nm, ϵ/l mol^{-1}cm^{-1} = 2.11 x 10^5 ;[12c] L = me_2phNC). Compounds **2a** and **2b** exhibit additional transitions around 440 nm and a very weak absoption near 570 nm. The deep red colour of solutions of the bis(pyridine) complex **2b**, e.g. in toluene, is due to CT-bands around 520 nm while solutions of **2a** are green.

Complexes **2a** and **2b** are diamagnetic and thus can be studied by NMR spectroscopy (spectra were taken in nitrogen saturated solutions with a trace of hydrochinone as antioxidant). Due to the ring current, the signals of the macrocyclic protons are shifted downfield. The methyl resonance of the 2,6-dimethylphenylisocyanide ligand is shifted upfield (**2a**: 0.52 ppm), however, to a lesser extent than in the corresponding 2,3-NcFeL_2 (0.35 ppm) and PcFeL_2 (0.18 ppm)[15] complexes (L = me_2phNC; in $CDCl_3$). This series indicates that the ring current above and near the metal centre decreases with linear annulation of benzene rings.

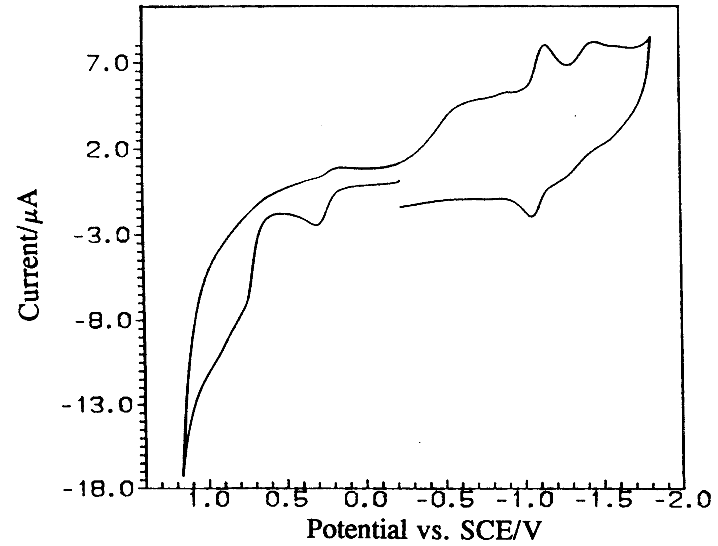


Fig. 2. Cyclic voltammogram of **2b** in pyridine/Bu_4NPF_6. Area of electrode/cm^2 = 0.07; sweep rate/mV s^{-1} = 100.

Figure 2 shows the cyclic voltammogram of **2b** in pyridine solution. There are four redox couples (redox potentials vs. SCE, in parentheses assignments suggested on the basis of spectroeloctrochemical results): - 1,30 V (Mac^{3-}/Mac^{2-}), - 1,10 V (Fe(+I)/Fe(+II)), + 0.26 V (Fe(+III)/Fe(+II)). The second oxidation ascribed to the oxidation of the macrocycle appears as a shoulder (0.75 V) at the solvent limit, yet there is no reductive signal. The same is the case with 2,3-NcFe, but the shoulder lies at 0.9 V.[16] Thus, we conclude that the first oxidation potential of the macrocycle decreases along PcFe, 2,3-NcFe and 2,3-AncFe. There is also a decrease of the oxidation potential of the iron center in the same series (PcFe:[16] 0.69 V, 2,3-NcFe:[16] 0.43 V, **2b**: 0.26 V).

The Mössbauer spectra of **2a** and **2b** show one doublet; the values of the isomer shift δ_{Fe} and the quadrupole splitting ΔE_Q are typical for bisaxially coordinated phthalocyaninatoiron(II) compounds[17] (**2a**: δ_{Fe}/mm s^{-1} = 0.20, ΔE_Q/mm s^{-1} = 0.58; **2b**: δ_{Fe}/mm s^{-1} = 0.33, ΔE_Q/mm s^{-1} = 1.88; δ refers to metallic iron, T/K = 82).

Further investigations of substituted and unsubstituted 2,3-anthracenocyanines including complexes with Fe, Ru, Co, Ni, Cu,and polymers of the type $[2,3\text{-AncML}]_n$ are in progress.

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10) **8**: Mp 219 - 220 °C (uncorr.). ^{1}H-NMR ($CDCl_3$) δ: 1.46 (s, 9 H), 7.78 (dd, 1 H, ^4J = 1.9 Hz, ^3J = 9 Hz), 7.98 (d, 1 H, ^4J = 1.9 Hz), 8.05 (d, 1 H, ^3J = 9 Hz), 8.49 (s, broad, 4H). ^{13}C-NMR ($CDCl_3$) δ: 30.81, 35.78, 107.73, 108.00, 116.31, 122.88, 127.93, 128.23, 128.31, 129.04, 129.46, 132.67, 134.30, 137.45, 137.56, 151.55. IR (KBr): ν_{CN}/cm^{-1} = 2226, 2233. MS (EI, 70 eV) m/z (%): 284.1 (M$^+$, 45), 269 (100), 240.9 (40), 227.8 (20), 215.0 (10), 120.5 (15). Anal. Found: C, 84.72; H, 5.85; N, 9.63%. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85%.

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13) **2a**: yield 38% (based on **8**). ^{1}H-NMR ($CDCl_3$) δ: 0.52 (s, 12 H, CH_3; coord. L), 1.57 (s, 36 H, *t*Bu), 6.13 (d, ^3J = 7.7 Hz, 4 H, Ar-*H*; coord. L), 6.40 (t, 2 H, ^3J = 7.7 Hz, Ar-*H*; coord. L), 7.70 (dd, 4 H, ^4J = 1.7 Hz, ^3J = 8.9 Hz), 8.17 (s, broad, 4 H), 8.25 (d, 4 H, ^3J = 8.9 Hz), 9.10 (s, broad, 8 H), 9.95 (s), 9.96 (s) (8 H). IR (KBr): ν_{NC}/cm^{-1} = 2127. MS (FD) m/z: 1193.5 ((*t*-Bu)$_4$AncFe, M$^+$+1). UV/Vis ($CHCl_3$) λ_{max}: 264, 316, 341, 360, 379, 430, 454, 568, 736, 786, 829 nm. Anal. Found: C, 79.61; H, 5.75; N, 9.50%. Calcd for (*t*-Bu)$_4$AncFe(me$_2$phNC)$_2$·2 me$_2$phNC, $C_{116}H_{100}N_{12}Fe$: C, 81.10; H, 5.87; N, 9.78%.

14) **2b**: yield 40% (based on **8**). ^{1}H-NMR (C_5D_5N/C_6D_6) δ: 1.51 (s, 36 H), 7.66 (m, 4 H), 8.13 (m, 8 H), 9.10 (m, 8 H), 10.50 (s, 4 H), 10.55 (s, 4H). MS (FD) m/z: 1192.5 ((*t*-Bu)$_4$AncFe, M$^+$). UV/Vis (pyridine) λ_{max}: 344, 434, 454, 510, 527, 587, 733, 790, 828 nm. Anal. Found: C, 80.26; H, 5.99; N, 9.54%. Calcd for $C_{90}H_{74}N_{10}Fe$: C, 79.98; H, 5.52; N, 10.36%.

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(Received November 16, 1992)