Journal of Organometallic Chemistry, 456 (1993) 229–234

JOM 23598

Polyaniline and its derivatives intercalated in the channels of the 3D-[tris(trimethyl)tin hexacyanoferrate]$_\infty$

Safaa Eldin H. Etaiw

Department of Chemistry, Faculty of Science, University of Tanta, Tanta (Egypt)

Amany M.A. Ibrahim

Department of Chemistry, Faculty of Science University of Ain Shams, Cairo (Egypt)

(Received November 30, 1992)

Abstract

The polyaniline and its derivatives have been successfully intercalated within the channels of the 3D-[tris(trimethyl)tin hexacyanoferrate]$_\infty$ to yield novel semiconducting polymeric/CT intercalated complexes. The intercalated complexes are investigated by IR, UV and EPR spectra as well as elemental analysis. The electrical conductivity and the polymerization depend on the nature and number of substituents at the aniline ring as well as on the conditions of the reaction.

1. Introduction

The existence of organometallic 3D-coordination polymers of the type $[(R_3M)_3M_d(CN)_6]_\infty$ where R = alkyl or phenyl, M = Sn, Sb or Pb and M_d = Co or Fe was recently confirmed by the preparation of single crystals of the very insoluble representative $[(Me_3Sn)_3\text{-}Co(CN)_6]_\infty$, followed by a successful X-ray diffraction study [1–3]. More recently, the lead homologue with M_d = Co was successfully subjected to a single-crystal X-ray study [4]. The non-superimposable 3D-networks involve $Me_3M(CN)_2$ units of trigonal bipyramidal $[\cdots CN\text{–}M(Me)_3\text{–}CN \cdots]$ configuration, and remarkably wide parallel channels with a diameter typically of *ca.* 9.5 Å, whose walls are internally coated by constituents of the lipophilic $(Me)_3M$ groups [4]. Thus, the host-attractive properties of these novel organometallic polymers arise from the availability of these large cavities for trapping voluminous organic and organometallic guest cations G^{n+} into the negatively charged host lattice $[(Me_3M)_3M_d^{II}(CN)_6^-]_\infty$ formally accessible by complete reduction of the isostructural M_d^{III} homologue $[(Me_3M)_3M_d^{III}(CN)_6]_\infty$ [5–8].

Now, a stage has been reached at which it is appropriate to design "tailor-made derivatives" for various applications. One of the main potential applications is in the preparation of a new class of semiconducting or metallic intercalative polymers. These 3D-polymeric complexes are insulators at room temperature, but when some heteropolycyclics have been encapsulated within the cavities of the polymeric species, semiconducting or metallic intercalated polymeric complexes should be obtained [9].

The polyheterocyclic compounds have been the subject of intense recent interest [10]. This interest stems from the fact that the oxidized forms of these polymers are electrically conductive. Among such electrically conductive polymers, polyaniline is a particularly attractive material because it has a moderately high conductivity when doped with simple Brönsted acids [11,12] and has good environmental stability [12].

In this study, we report the successful *in situ* intercalation/polymerization of aniline derivatives within the channels of the 3D-[tris(trimethyl tin) hexacyanoferrate]$_\infty$ (**I**), to yield novel polymeric intercalated complexes.

Correspondence to: Professor S.E.H. Etaiw.

0022-328X/93/$6.00

2. Experimental details

2.1. Materials

All reagents used in this study were of a highly pure quality and purchased from either Aldrich or Merck. Most of them were used without further purification. Aniline and its liquid derivatives were doubly distilled under reduced pressure before use.

2.2. Preparation of the intercalated complexes

A precipitate of the paramagnetic orange polymeric complex **I** (effective magnetic moment *ca.* 2.18 BM) was obtained when aqueous solutions of trimethyltin chloride and $K_3[Fe(CN)_6]$ are mixed in the dark under nitrogen in the molar ratio of 3 : 1. The precipitate was filtered off, washed with water and then CH_2Cl_2, and dried under vacuum at room temperature. The purity and identity of **I** were checked by elemental analysis and IR and UV spectroscopy (Tables 1–3). The reaction of aniline with **I** is spontaneous and gives a black material with a metallic lustre. On the other hand, the aniline derivatives **2–14** react only slowly with **I**, however, on treatment with HCl, a rapid colour change occurs, from dark brown to black (**2** and **3**), from brown to dark brown (**4**), from blue to bluish black (**5**), or from green to greenish brown (**6**). In contrast, the colours of the intercalated complexes **7–14** undergo no change but become more intense with time. Aniline was treated with **I** in the presence of HCl (**1**) and also in its absence (**1***).

In the case of 3-chloroaniline, the reaction at room temperature with the polymeric complex **I** and a few drops of 1 M HCl produces a green colour which turns to dark green after some time and upon further grinding. On the other hand, the reaction of **I** with 3-chloroaniline in the vapour state at 60°C or in the liquid state at 40°C produces only a faint green colour even the reaction time is extended to 3 days. The infrared spectra of the faint green complexes **8** and **9** exhibit bands above and below 2100 cm^{-1}, indicating the presence of $Fe^{II}CN/Fe^{III}CN$ systems, while the electronic spectra show a new broad band at 625 and 650 nm, respectively, due to the intermolecular CT interactions. Thus, the best way to carry out the polymerization involves direct addition of aniline derivatives to **I** at room temperature under nitrogen with grinding or sonication to increase the reaction rate. The IR spectrum of the dark green product **7** exhibits the same bands as poly-3-chloroaniline prepared chemically, and there is no evidence for the anilinium ion or free 3-chloroaniline.

Elemental (including metal) analysis of the intercalated complexes **1–14** indicate that aniline derivatives react with **I** in the molar ratios shown in Table 1. These ratios depend on the nature and position of the substituents in the aniline ring and on the conditions used for the reaction.

2.3. Instruments

The infrared spectra were recorded as KBr discs in the range 4000–200 cm^{-1} using a Perkin-Elmer SP 1430 IR spectrophotometer. The electronic absorption spectra were recorded on a Shimadzu W 250 nm spectrophotometer as Nujol mulls. This technique was used to avoid solvent–solute interactions. The electrical conductivities (σ, Ω^{-1} cm^{-1}) were carried out on a compressed sample using a Super Megohmmeter Model RM 170 (AVo Ltd. Dover, UK). The solid powder

TABLE 1. Colour and elemental analysis data for **I** and its intercalated complexes **1–14**

No.	Compound	Colour	Elemental analysis Calc. (Found) (%)				
			C	H	N	Fe	Sn
I	$[(Me_3Sn)_3Fe(CN)_6]_\infty$	Orange	25.61(25.80)	3.87(4.90)	11.94(11.10)	7.94(7.86)	50.63(50.10)
1	[Aniline)$_3$ + (**I**)$_2$]$_\infty$	Black	34.19(34.59)	4.48(4.28)	12.46(11.80)	6.62(6.32)	42.24(41.80)
2	[(*o*-Toluidine)$_3$ + (**I**)$_2$]$_\infty$	Black	35.44(35.32)	4.72(4.80)	12.15(12.05)	6.46(6.13)	41.21(40.78)
3	[(*m*-Toluidine)$_3$ + (**I**)$_2$]$_\infty$	Black	35.44(35.58)	4.72(4.87)	12.15(11.89)	6.46(6.57)	41.21(41.86)
4	[(*p*-Toluidine)$_3$ + (**I**)$_2$]$_\infty$	Dark brown	35.44(34.94)	4.72(4.56)	12.15(11.33)	6.46(6.68)	41.21(41.80)
5	[(*p*-Anisidine)$_3$ + (**I**)$_2$]$_\infty$	Bluish black	34.48(34.08)	4.59(4.94)	11.89(10.97)	6.28(6.42)	40.09(40.81)
6	[2,4,6-Trimethylaniline + **I**]$_\infty$	Geenish brown	29.60(29.65)	4.14(4.47)	10.06(10.49)	6.16(6.03)	39.29(38.60)
7	[3-Chloroaniline + **I**]$_\infty$ (RT)	Dark green	30.35(30.47)	4.10(4.36)	11.80(11.01)	6.72(6.61)	42.85(42.02)
8	[(3-Chloroaniline)$_{0.75}$ + **I**] 40°C)	Green	29.31(29.53)	3.97(3.93)	11.83(11.23)	6.98(7.10)	44.56(44.64)
9	[(3-Chloroaniline)$_{0.5}$ + **I**]$_\infty$ 60°C)	Faint green	28.18(28.28)	3.94(3.85)	11.86(11.34)	7.27(7.06)	46.42(45.91)
10	[(4-Chloroaniline)$_{0.9}$ + **I**]$_\infty$	Brown	29.94(29.94)	3.99(4.36)	11.81(11.31)	6.82(6.71)	43.52(42.40)
11	[2,5-Dichloroaniline)$_{0.5}$ + **I**]$_\infty$	Green	27.57(27.96)	3.79(3.85)	11.60(10.82)	7.12(7.10)	45.40(45.23)
12	[2,3,4-Trichloroaniline)$_{0.5}$ + **I**]$_\infty$	Green	26.96(26.92)	3.64(3.28)	11.36(11.69)	6.96(6.72)	44.42(44.00)
13	[2,4,6-Tribromoaniline)$_{0.5}$ + **I**]$_\infty$	Greenish yellow	24.89(24.12)	3.36(3.29)	10.48(10.40)	6.43(6.50)	41.01(40.83)
14	[2,4-Dinitro, 6-chloroaniline)$_{0.75}$ + **I**]$_\infty$	Canary yellow	27.02(27.45)	3.48(3.41)	13.33(13.56)	6.44(6.13)	41.09(40.10)

EPR spectra of the intercalated complexes were recorded on a JEOL spectrophotometer model JES-FE 2XG using dpph as a field marker. Elemental analysis was performed on a Perkin-Elmer 2400 automatic elemental analyzer, and the metal analysis was carried out with a Perkin-Elmer 2380 atomic absorption spectrophotometer.

3. Results and discussion

3.1. *Infrared spectra*

The IR spectra of the polymeric intercalated complexes **1**–**7** and **10** show bands corresponding to the polyaniline derivatives (Table 2). The streching vibrations of the NH bands show a weak broad band in the region 3290–3100 cm^{-1}, while the skeletal vibrations of the phenyl ring appear at around 1590, 1530 and 1460 cm^{-1}. These IR bands are identical with those found in the IR spectra of authentic sample of polyaniline hydrochloride or its derivatives prepared chemically by a published procedure [13], (Fig. 1). There is no evidence of the presence of anilinium ion or free aniline or aniline derivatives.

TABLE 3. Electronic absorption spectra of **I**, **II** and the intercalated complexes **1**–**14**

Compound no.	$1L_a \leftarrow 1A$	$1L_b \leftarrow 1A$	$\pi-\pi^*$ transitions Fe^{II}–CN	$\pi-\pi^*$ transitions Fe^{III}–CN	CT
I	220		300	430	
II	220		320 ^{b}		
1	240	280	380		
2	250	275	325		
3	250	285	330		
4	230	270	320		
5	232	280	320		
6	245	285	340	425wb	
7	240		300	420wb	580
8	240		295	425	650
9	240		300	423	625
10	240		320	420wb	
11	220	245	320	410	680
12	220	243	300	415	660
13	222	246	310	410	685
14	215	250	340	405	435

wb, weak broad band; b, broad.

The IR spectrum of the polymeric complex **I** suffers changes as a result of polymerization of aniline and its derivatives (**1**–**7** and **10**) within its channels. The main changes are the disappearance of the bands at 2144 and 410 cm^{-1} corresponding to stretching vibrations of the Fe^{III}–CN bonds, these being replaced by strong bands at around 2055, 595, 480 and 450 cm^{-1} corresponding to the stretching vibrations of the Fe^{II}–CN bonds. In the case of the polymeric intercalated complexes **6**, **7** and **10**, a weak band appears around 2130 cm^{-1}, in addition to a very weak one at 406 cm^{-1}, due to the stretching vibrations of the Fe^{III}–CN bonds. This indicates the presence of redox reaction in which the aniline monomer or its derivatives, **2**–**5**, are oxidatively polymerized within the channels of the polymeric complex **I** to form stable 3:2 polymeric intercalated complexes, whereas for the polymeric intercalated complexes, **6**, **7** and **10**, the rate of oxidation is slow and the nature of the oxidation products depends on the nature and position of the substituents on the aniline ring and on the conditions used for the reaction. Thus the oxidation reaction is incomplete even

TABLE 2. Infrared spectral data of **I** and its intercalated complexes **1**–**14**

Compound no.	$\nu(NH_2)$	ν(NH)	ν(C–H) aliphatic	$\nu(Fe^{III}$–CN)	$\nu(Fe^{II}$–CN)	ν(C=C) aromatic system	ν(Sn–C)
I			2990, 2905, 780	2144, 410			558
1		3224	2997, 2917, 789		2048, 595, 450	1594, 1529, 1496	553
2		3210	2995, 2910, 790		2055, 596, 448	1590, 1530, 1480	555
3		3200	2997, 2916, 789		2064, 595, 449	1585, 1520, 1460	555
4		3290	2993, 2920, 789		2065, 2031, 596, 455	1582, 1513, 1449	553
5		3222	2999, 2918, 791		2053, 595, 449	1595, 1511, 1463	554
6		3228	2993, 2919, 789	2127W	2055, 597, 455	1580, 1519. 1488	554
7		3249	2997, 2917, 786	2132W	2066, 594, 439	1598, 1519, 1482	552
8	3420		3002, 2920, 790	2147, 411	2075, 599	1624, 1599, 1534, 1481	554
9	3395		3001, 2919, 788	2149, 2133, 411	2070, 597	1622, 1598, 1523, 1482	554
10		3150	2999, 2919, 789	2134W, 406VW	2073, 594, 463	1585, 1533, 1454	554
11	3400		3002, 2920, 790	2141, 2117, 409	2083, 2028, 595VW	1614, 1535, 1519, 1484	555
12	3390		3000, 2920, 791	2146, 410	2083	1614, 1522, 1488	555
13	3360		3003, 2920, 793	2145, 412	2082, 592, 465	1615, 1536, 1490	555
14	3340		2998, 2920, 793	2148, 2114, 411	2087, 595VW	1620, 1588, 1506, 1462	552

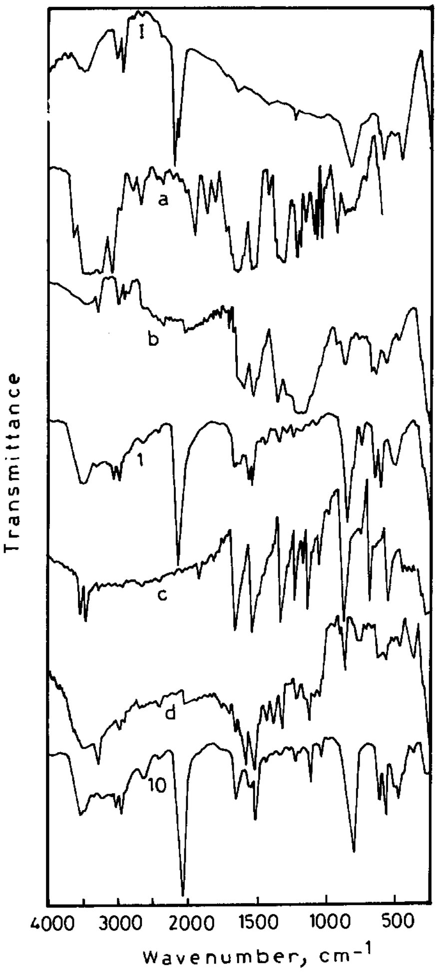

Fig. 1. The infrared spectra of I, 1, 10 and (a) aniline, (b) polyaniline, (c) 4-chloroaniline, (d) poly-4-chloroaniline.

when the reaction is allowed to proceed for a long time until the colour of the product remains unchanged.

The IR spectra also exhibit the bands due to the various modes of vibrations of the trimethyltin group at *ca.* 2997, 2919, 780 and 552 cm^{01} (Table 2), indicating that this group still plays the role of linking the pairs of the iron-bonded cyanide ligands to form the 3D-networks $[\mathrm{Me_3Sn}]_3\mathrm{Fe^{II}(CN)_6^{-}}]_\infty$. On the other hand, the IR spectra of the intercalated complexes **8**, **9**, **11** and **14** exhibit two sharp bands at 3419–3495 cm^{-1} and 3301–3400 cm^{-1} corresponding to $\nu(\mathrm{NH_2})$. Also, the IR spectra of the complexes show the other characteristic bands of the aniline derivatives as well as the bands due to the stretching vibrations of the Fe^{III}–CN bonds at *ca.* 2145 and 410 cm^{-1} and those of the Fe^{II}–CN bonds at 2080, 595 and 450 cm^{-1} (Table 2). In such cases, these aniline derivatives are trapped within the cavity of the polymeric host in the monomeric state and in various stoichiometric ratios (Table 1) depending on the nature and position of the substituents and on the conditions used for the reaction. The aniline derivatives **8**, **9**, **11** and **14** act as donors and the polymer host **I** as an acceptor to form CT intercalated complexes.

3.2. Electronic absorption spectra

Further support for the occurrence of a redox reaction between the polymeric complex **I** and the aniline derivatives **1–7** and **10** is provided by the disappearance of the band at 430 nm corresponding to the electronic transitions of the Fe^{III}–CN system and the appearance of the band around 320 nm of the Fe^{II}–CN system, as well as the bands due to the $^1\mathrm{L_a} \leftarrow 1\mathrm{A}$ and $^1\mathrm{L_b} \leftarrow 1\mathrm{A}$ transitions of the phenyl ring of the aniline derivatives at *ca.* 240 and 280 nm, respectively (Table 3). However, the UV spectra of the polymeric complexes **6**, **7** and **10** also display a weak broad band around 420 nm indicating the presence of the Fe^{III}–CN system. On the other hand, the UV spectra of the intercalated complexes **8**, **9**, **11** and **14** exhibit bands corresponding to the π–π^* transitions of the Fe^{II}–CN/Fe^{III}–CN systems as well as a new broad band in the 625–685 nm region for complexes **8**, **9**, **11** and **13** and 435 nm for **14**. This band corresponds to intermolecular CT transitions from these aniline derivatives to the polymeric complex **I**.

3.3. Electron paramagnetic resonance spectra

The EPR spectrum of the polymeric complex **I** shows various absorptions in the range 1500–3500 G (Fig. 2). The main absorption signals have g values of 1.9784, 2.2003, 2.5005, 2.9164, 3.1470 and 4.5872; these values are similar to those for potassium ferricyanide powder (Table 4 and Fig. 2). The first three values correspond to g_1, g_2 and g_3 previously observed in the EPR spectra of potassium ferricyanide and some iron(III) complexes [14–16]. The g values 2.91 and 3.14 correspond to those observed in the EPR spectra of iron(III) complexes with myoglobin imidazole and myoglobin cyanide [17]. They are attributed to low-spin Fe^{III}, which has a (dE)^5 electronic configuration with one unpaired electron in the dyz orbital, forming a distorted octahedral structure. The weak signal at 4.58 is known to be characteristic of rhombically distorted high-spin iron(III) [18,19], and it can be obtained even from trace amounts of Fe^{III} [20]. On the other hand, a powder sample of $[(\mathrm{Me_3Sn})_4\ \mathrm{Fe(CN)_6}]_\infty$ freshly prepared under nitrogen is EPR inactive.

The EPR spectra of the polymeric intercalated complexes **1–7** and **10** exhibit one strong symmetrical signal with a g value of *ca.* 2.00 (Table 4 and Figs. 2 and 3). The EPR spectra of complexes **1–5** show no other signals, whereas those of complexes **6**, **7** and **10** show very weak signals at g values corresponding to those of

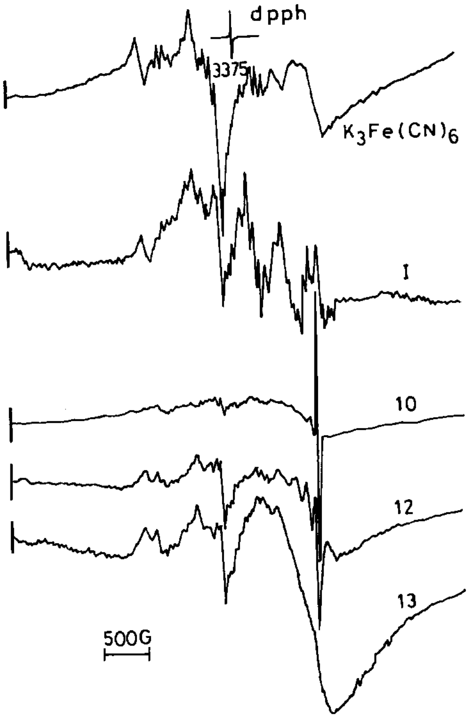

Fig. 2. The EPR spectra of potassium ferricyanide, **I**, **10**, **12** and **13**.

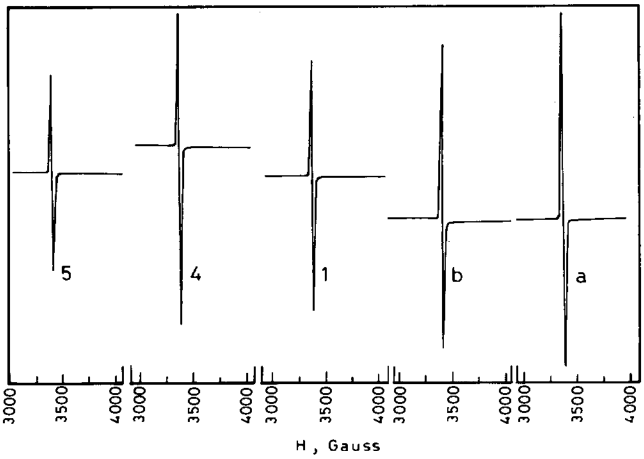

Fig. 3. The EPR spectra of the intercalated complexes **1**, **4** and **5**, and (a) poly-4-chloroaniline, (b) polyaniline.

the polymeric complex **I**. This supports the indication from the IR and UV spectral data that complexes **6**, **7** and **10** contain traces of iron(III). The strong signal is due to the free radical cation of the aniline derivatives and is observed in the EPR spectra of authentic samples of the polyaniline derivatives (Fig. 3). The presence of this strong signal and the disappearance of the signals due to the polymeric complex **I** are good evidence for polymerization of the aniline derivatives **1**–**7** and **10**.

TABLE 4. Electron paramagnetic resonance spectra data of potassium ferricyanide, **I** and its intercalated complexes **1**–**14**

Compound no.	g_1	g_2	g_3	g_4	g_5	g_6
K$_3$[Fe(CN)$_6$]	1.98	2.19	2.49	2.93	3.26	4.58
I	1.97	2.20	2.50	2.91	3.14	4.58
1	2.00					
2	1.99					
3	2.02					
4	1.99					
5	2.00					
6	2.00	2.39 [a]	2.52 [a]	2.91 [a]	3.31 [a]	4.53 [a]
7	2.01	2.10 [a]	2.56 [a]	2.97 [a]	3.23 [a]	4.19 [a]
8	2.00	2.13	2.55	2.95	3.34	4.13
9	2.00	2.11	2.59	2.92	3.21	4.53
10	2.00	2.06 [a]	2.55 [a]	2.99 [a]	3.22 [a]	4.18 [a]
11	2.03	2.19	2.50	2.93	3.23	4.29
12	2.00	2.13	2.49	2.92	3.25	4.55
13	2.00	2.14	2.48	2.91	3.24	4.18
14	2.06	2.24	2.52	2.91	3.22	4.50

[a] Very weak signal.

On the other hand, the EPR spectra of the intermolecular CT complexes **8**, **9**, **11** and **14** exhibit the general features of the EPR spectra of the polymeric complex **I**, indicating depolymerization of these aniline derivatives.

3.4. Electrical conductivity

The addition of aniline and its derivatives to the polymeric host in the presence of 1 M HCl yields semiconducting polymeric intercalated complexes. The conductivity increases as the temperature is increased [21]. The conductivity of **1** is 4.46×10^{-2} Ω-cm^{-1}, which is higher than that (1.51×10^{-4} Ω-cm^{-1}) of a sample of polymeric intercalated complex, **1***, prepared from aniline and the polymeric host without the addition of HCl solution. The protonated form of polyaniline intercalated within the channels of the polymeric host shows a very large increase in conductivity by six orders of magnitude with respect to that for the polymeric host, which is an insulator at room temperature and also by two orders of magnitude with respect to that of the sample prepared in the absence of HCl. The conductivity of the polymeric intercalated complexes **2**–**7** and **10** (Table 5), are lower by two or three orders of magnitude compared with that of **1**, in spite of the fact they behave as semiconductors. This can be attributed to the fact that the primary oxidation products are rather less stable than in the aniline series, being more prone to undergo polymerization, and that the higher quinonoid products are less easily formed. On the other hand, the CT intercalated complexes **8**, **9**, **11** and **14** behave as weak semiconductors or insulators with conductivity values (Table 5) lower

TABLE 5. Conductivity values of **I** and its intercalated complexes **1–14**

Compound no.	σ_{303K} (Ω-cm^{-1})	Compound no.	σ_{303K} (Ω-cm^{-1})
I	4×10^{-8}	**7**	1.79×10^{-5}
1	4.66×10^{-2}	**8**	4.20×10^{-6}
1*	1.51×10^{-4}	**9**	5.62×10^{-6}
2	3×10^{-3}	**10**	3.16×10^{-6}
3	2.82×10^{-4}	**11**	7.08×10^{-7}
4	1.86×10^{-3}	**12**	5.01×10^{-7}
5	6.31×10^{-5}	**13**	1.26×10^{-7}
6	5×10^{-7}	**14**	1.25×10^{-7}

than those for the polymeric intercalated complexes. In general, the conductivity decreases with increase in the number of the substituents on the aniline ring.

References

1 K. Yunlü, N. Höck and R.D. Fischer, *Angew. Chem.*, *97* (1985) 863; *Angew. Chem., Int. Ed. Engl.*, *24* (1985) 879.
2 T.M. Soliman, S.E.H. Etaiw, G. Fendesak and R.D. Fischer, *J. Organomet. Chem.*, *415* (1991) C5.
3 A. Bonardi, C. Carini, C. Pelizzi, G. Pelizzi, G. Predieri, P. Tarasconi, M.A. Zoroddu and K.C. Molloy, *J. Organomet. Chem.*, *401* (1991) 283.
4 U. Behrens, A.K. Brimah, T.M. Soliman, R.D. Fischer, D.C. Apperely, N.A. Davis and R.K. Harris, *Organometallics*, *11* (1992) 1719.
5 P. Brandt, A.K. Brimah and R.D. Fischer, *Angew. Chem.*, *100* (1988) 1578; *Angew. Chem., Int. Ed. Engl.*, *27* (1988) 1521.
6 S. Eller, P. Brandt, A.K. Brimah, P. Schwarz and R.D. Fischer, *Angew. Chem.*, *101* (1989) 1274; *Angew. Chem., Int. Ed. Engl.*, *28* (1989) 1263.
7 S. Eller, M. Adam and R.D. Fischer, *Angew. Chem.*, *102* (1990) 1157; *Angew. Chem. Int., Ed. Engl.*, *29* (1990) 1126.
8 A.M.A. Ibrahim, S.E.H. Etaiw and T.M. Soliman, *J. Organomet. Chem.*, *430* (1992) 87.
9 A.M.A. Ibrahim, T.M. Soliman, S.E.H. Etair and R.D. Fischer, *J. Organomet. Chem.*, in preparation.
10 (a) S.W. Feldberg, *J. Am. Chem. Soc.*, *106* (1984) 4671; (b) G.B. Street, in T.A. Skotheim (ed.), *Handbook of Conducting Polymers*, Marcel Dekker, New York, 1986, Vol. 1; (c) R.J. Waltman and J. Bargon, *Can. J. Chem.*, *64* (1986) 76.
11 (a) R. De Surville, M. Jozefowicz, L.T. Yu, J. Perichon and R. Buvet, *Electrochim. Acta*, *13* (1968) 1451; (b) E.W. Paul, A.T. Ricco and M.S. Wrighton, *J. Phys. Chem.*, *89* (1985) 1441.
12 (a) A.G. MacDiarmid, J.C. Chiang, M. Halpern, W.S. Huang, S.L. Mu, N.L.D. Somasiri, W. Wu and S.I. Yaniger, *Mol. Cryst. Liq. Cryst.*, *121* (1985) 173; (b) L.C. Chiang and A.G. MacDiarmid, *Synth. Met.*, *13* (1986) 193; (c) A.G. MacDiarmid, S.L. Mu, N.L.D. Somarsiri and W. Wu, *Mol Cryst. Liq. Cryst.*, *121* (1985) 187.
13 (a) R. Willstätter and S. Dorogi, *Chem. Ber.*, *42* (1909) 2143; (b) *Chem. Ber.*, *42* (1909) 4118; (c) A.G. Green and A.E. Woodhead, *J. Chem. Soc.*, *97* (1910) 2388; (d) J. Chem. Soc., *101* (1912) 1117.
14 J.M. Baker, B. Bleaney and K.D. Bowers, *Proc. R. Soc.*, *69* (1956) 1205.
15 Y. Nishida, S. Oshio and S. Kida, *Inorg. Chim. Acta*, *23* (1977) 59.
16 P. Beardwood and F.J. Gibson, *J. Chem. Soc., Dalton Trans.*, *4* (1983) 737.
17 H. Hori, *Biochim. Biophys. Acta*, *251* (1971) 227.
18 J. Peisach, W.E. Blumberg, E.T. Lode and M.J. Coon, *J. Biol. Chem.*, *246* (1971) 5877.
19 S.A. Cotton and J.F. Gibson, *J. Chem. Soc. A*, (1971) 803.
20 R. Aasa, S.P.J. Albracht, K.E. Falk, B. Lanne and T. Vanngaed, *Biochim. Biophys. Acta*, *422* (1976) 260.
21 S.E.H. Etaiw and A.M.A. Ibrahim, unpublished.