Journal of Organometallic Chemistry, 430 (1992) 87–91
Elsevier Sequoia S.A., Lausanne
JOM 22480

In-situ intercalative oxidation of some pyridine derivatives within the cavity of the three-dimensional polymeric host $[(Me_3Pb)_3Fe(CN)_6]_\infty$

Amany M.A. Ibrahim
Department of Chemistry, Faculty of Science, Ain Shams University, Cairo (Egypt)

Safaa Eldin H. Etaiw and Tarek M. Soliman
Department of Chemistry, Faculty of Science, Tanta University, Tanta (Egypt)

(Received August 12, 1991)

Abstract

Pyridine derivatives acting as guest species can be oxidized by the three-dimensional polymeric host $[(Me_3Pb)_3Fe(CN)_6]_\infty$ forming yellow to brown or red colored CT complexes depending on the degree of charge transfer. The donor molecules can be intercalated within the cavity of the polymeric host in a 1/1 ratio after completion of the reaction. The CT complexes are weak semiconductors under the experimental conditions used.

Introduction

Organotin(IV) and organolead(IV) compounds of the type (R_3MX) (M = Sn or Pb; R = alkyl or aryl; X = halide) can react with hexacyanide *d*-transition metal ions (Fe, Co) to form three-dimensionally linked coordination polymers [1,2] $[R_3M]_nM^d(CN)_{2n}]_\infty$ ($n = 3$). These polymeric complexes are of particular interest since they have Zeolite like structure and form a three-dimensional network in which up to one-third of the $\{M^d-C\equiv N \longrightarrow \overset{|}{M} \longleftarrow N\equiv C\}_\infty$ chains are linear [3]. The large expandable cavities are capable of containing organic groups [3,4]. Nitrogen bases (*e.g.* pyridine) have been intercalated into FeOCl layers [5,6]. Pyridine with FeOCl yields a material exhibiting a good electrical conductivity [7], analyzing as $(pyridine)_{0.33}FeOCl$ [8], in which radical-cation-mediated dimerization of pyridine occurs [9] and in which the pyridine plane is perpendicular (and the C_2-axis parallel) to the layer planes [10]. Furthermore, the superconducting transition temperatures of some transition metal dichalcogenides were found to be

---

Correspondence to: Professor S.E.H. Etaiw, Department of Chemistry, Faculty of Science, Tanta University, Tanta, Egypt.

strongly affected by absorption of pyridine molecules between successive layers [11] (*e.g.* (pyridine)$_{0.5}$TaS$_2$) [12].

In the present study, intercalated charge transfer (CT) complexes, in which pyridine and some pyridine derivatives are present as guest molecules (G) in an $[(Me_3Pb)_3Fe(CN)_6]_\infty$ (I) host matrix, have been prepared and characterized.

Experimental

The compounds Me_3PbCl and $K_3Fe(CN)_6$ in 3/1 molar ratio were dissolved in the minimum amount of water under nitrogen atmosphere in the dark to yield $[(Me_3Pb)_3Fe(CN)_6]_\infty$ (I). The orange precipitate was filtered off and washed with water and then with CH_2Cl_2 and dried under vacuum at room temperature. The purity and identity of the product were checked by elemental analysis, and IR and UV spectroscopy (Tables 1 and 2). Strictly anhydrous conditions were used in preparations of the intercalated CT complexes. The dry freshly prepared I was added to an excess of neat doubly-distilled pyridine derivatives in the dark under nitrogen with continuous grinding or sonication. The colored CT complexes were collected at intervals, washed with ethanol, and dried in vacuum.

The UV spectra were recorded on a Shimadzu 240 W spectrophotometer and the IR spectra on a Perkin–Elmer model 577 spectrophotometer (as KBr discs). The EPR spectra were recorded on a JEOL spectrophotometer model JES-FE2XG. The magnetic susceptibility was determined with a Johnson–Matthey susceptometer devised by D.F. Evans. The electrical conductivity at 300 K was measured with a Super Megohmmeter electrometer model 170, as previously described [13].

Results and discussion

The reactions of $[(Me_3Pb)_3Fe(CN)_6]_\infty$ with an excess of neat pyridine or its derivatives yield charge transfer intercalated complexes analyzing as $[(G)(Me_3Pb)_3Fe(CN)_6]_\infty$. These CT complexes are built up of electron donor and acceptor molecules which can stack independently to form either segregated systems or mixed systems [14]. Pyridine derivatives acting as guest donors are oxidized by the host polymer, which acts as the acceptor, to form yellow to brown or red CT complexes, depending on the degree of charge transfer. The rate of the charge transfer increases with the number of methyl substituents on the pyridine ring. The charge transfer character of the complexes was supported by elemental analysis, UV, IR, EPR spectra and magnetic measurements. The elemental analyses of the

Table 1

Elemental analysis data for I and its CT complexes

Compound	Calc. (found) (%)				
	C	H	N	Pb	Fe
I	18.59 (18.26)	2.81 (3.02)	8.67 (8.34)	64.15 (64.22)	5.76 (5.68)
I (Pyr)	22.91 (21.68)	3.05 (3.02)	9.35 (9.11)	59.33 (60.41)	5.34 (5.59)
I (MePyr)	23.72 (24.19)	3.29 (3.31)	9.22 (8.82)	58.49 (58.31)	5.27 (5.08)
I (2,6-di-MePyr)	24.52 (24.10)	3.44 (3.38)	9.10 (8.74)	57.74 (58.11)	5.20 (5.06)
I (2,4,6-tri-MePyr)	25.33 (25.90)	3.49 (3.22)	8.99 (9.06)	57.05 (56.89)	5.14 (5.09)

Table 2

Properties of I and its CT complexes

Compound	Color	Reaction time (days)	IR (cm^{-1}) [a]			UV-VIS (nm)	$\mu_{\text{eff.}}$ (μ_B)	σ (S cm^{-1}) at 300 K	T (dec.) (°C)
			$Fe^{III}(CN)_6$	$Fe^{II}(CN)_6$	Pb–C				
I	orange	–	2120,2116	–	480	350,410	2.57	2.18×10^{-8}	273
I (Pyr)	yellow	1	2120,2117	2071,2059, 2013,449	494		0.21		
	yellowish brown	3		2071,2059, 2013,448	500	420	diamagnetic	7.2×10^{-8}	300
I (MePyr)	yellow	4	2120,2117	2072,2042, 2027,453	495		0.95		
	yellowish green	5	2120,2116	2072,2048, 2028	494		0.20		
	reddish brown	11	–	2072,2042, 439	497	440	diamagnetic	3.2×10^{-7}	295
I (2,6-di-MePyr)	yellow	2	2120,2116	2042w,2027w	495		0.86		
	brown	5	2116w	2071,2059, 2029,454	494		0.18		
	brown	8	–	2071,2059, 2029,455	494	495	diamagnetic	1.36×10^{-6}	300
I (2,4,6-tri-MePyr)	red	at once	2116vw	2071,2060, 2029,444	495	470	diamagnetic	1.21×10^{-6}	296

[a] w = weak, vw = very weak.

CT complexes present after completion of the reaction indicate that the guest molecules are intercalated within the cavity of the polymeric host in a 1/1 ratio (Table 1). The UV spectra of the solid CT complexes exhibit a new absorption band around 420 or 495 nm corresponding to intermolecular CT transitions (Table 2). The Fe^{III} ions are reduced, partially or completely, to Fe^{II} ions, depending on the time of reaction and on the extent of grinding or sonication, which causes a significant rate enhancement. The IR spectra of the CT complexes show bands at 2120 and 2116 cm^{-1} corresponding to vibrations of the $[Fe^{III}(CN)_6]^{-3}$ system and bands around 2072, 2059, 2013 and 449 cm^{-1} corresponding to vibrations of the $[Fe^{II}(CN)_6]^{-4}$ system (Table 2). This indicates partial reduction of Fe^{III} ions. On the other hand, if the reaction is left long enough to go to completion, the IR bands above 2100 cm^{-1} disappear, indicating complete reduction of Fe^{III} ions. The band at 495 cm^{-1} attributed to vibrations of the Pb–C band shows no significant change on complexation.

Further support for the occurrence of charge transfer from the guest to the polymeric host comes from magnetic and EPR measurements. The paramagnetism of the polymeric host decreases upon CT complex formation and the product is diamagnetic when reaction is complete (Table 2). The polymeric host exhibits a broad signal with $g = 1.9921$ typical of low-spin octahedrally-surrounded Fe^{III} ions [15]; the signal falls in intensity during the reaction with the guest molecules until it is absent when reaction is complete and only Fe^{II} ions are present.

The CT complexes have higher conductivities than I. However, they are weak semiconductors under our experimental conditions, even though they would be expected to behave as conductors or at least good semiconductors. Syntheses of similar novel CT complexes that may have the hoped-for good electrical conductivities [14] are currently in progress.

Acknowledgments

S.E.H.E. is grateful to the Deutscher Akademischer Austauschdienst (DAAD), Bonn, for a visiting fellowship, T.M.S. to the Egyptian Ministry of Education for a pre-doctoral grant, and A.M.A.I. to Prof. Dr. R.D. Fischer of Hamburg University for laboratory facilities.

References

1 K. Yünlü, N. Höck and R.D. Fischer, Angew. Chem., Int. Ed. Engl., 24 (1985) 879.
2 U. Behrens, A.K. Brimah, T.M. Soliman, R.D. Fischer, D.C. Apperley, N.A. Davies and R.K. Harris, Organometallics, in press.
3 M. Adam, A.K. Brimah, Xing Fu Li and R.D. Fischer, Inorg. Chem., 29 (1990) 1597.
4 P. Brandt, A.K. Brimah and R.D. Fischer, Angew. Chem., Int. Ed. Engl., 27 (1988) 1521.
5 S. Kikkawa, F. Kanamaru and M. Koizumi, Bull. Chem. Soc. Jpn., 52 (1979) 963 and references therein.
6 P. Hagenmuller, J. Portier, B. Barbe and P.Z. Bouclier, Anorg. Allg. Chem., 355 (1967) 209 and references therein.
7 F. Kanamaru, S. Yamanaka, M. Koizumi and S. Nagai, Chem. Lett., (1974) 373.
8 R.H. Herber and Y. Maeda, Inorg. Chem., 20 (1981) 1409.
9 (a) J.F. Lomax, B.N. Diel and T.J. Marks, Mol. Cryst. Liq. Cryst., 121 (1985) 145; (b) A. Salman, H. Eckert and R.H.J. Herber, Chem. Phys., 81 (1984) 5206.

10 (a) C. Reikel, D. Hohlwein and R. Schöllhorn, J. Chem. Soc., Chem. Commun., (1976) 863; (b) Y. Kashihara, A. Nishida, K. Ohshima, J. Harada and H. Yoshioka, J. Phys. Soc. Jpn., 46 (1979) 1393; (c) Y. Kashihara and H. Yoshioka, ibid, 50 (1981) 2084.

11 (a) F.R. Gamble, F.J. Disalvo, R.A. Klemm and T.H. Gaballe, Science, 168 (1970) 568; (b) T.H. Gaballe, Sci. Am., 225 (1971) 22; (c) P.J. Bray and E.G. Sauer, Solid State Commun., 11 (1972) 1239.

12 (a) M.S. Whittingham, Mater. Res. Bull., 13 (1978) 775; (b) R. Ruthardt and A.Z. Weiss, Z. Naturforsch., Teil B, 278 (1972) 1275.

13 S.H. Etaiw, M.M. Ayad and S.S. Assar, Thermochim. Acta, 173 (1990) 1.

14 M. Meneghetti, R. Bozio, C. Bellitto and C. Pecile, J. Chem. Phys., 89 (1988) 2704.

15 Y. Nishida, S. Oshio and S. Kida, Inorg. Chim. Acta, 23 (1977) 59.