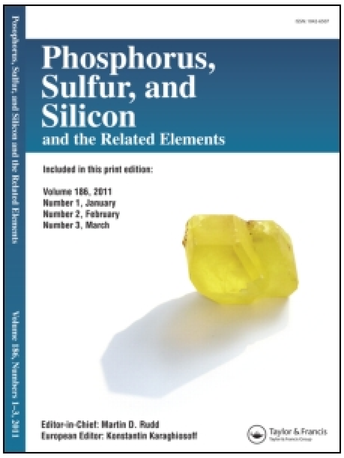

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Characterization of Pentacyano(Phosphine or Phosphite)Ferrates (II) By ^{31}P NMR and Cyclic Voltammetry

H. Inoue[a]; N. Honma[a]; E. Fluck[ab]
[a] Department of Applied Chemistry, Keio University, Yokohama, Japan [b] Gmelin-Institut der Max-Planck-Gesellschaft, Frankfurt am Main 90, Germany

To cite this Article Inoue, H. , Honma, N. and Fluck, E.(1993) 'Characterization of Pentacyano(Phosphine or Phosphite)Ferrates (II) By ^{31}P NMR and Cyclic Voltammetry', Phosphorus, Sulfur, and Silicon and the Related Elements, 77: 1, 77 — 80

To link to this Article: DOI: 10.1080/10426509308045623

URL: http://dx.doi.org/10.1080/10426509308045623

Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, pp. 77–80
Reprints available directly from the publisher
Photocopying permitted by license only

CHARACTERIZATION OF PENTACYANO(PHOSPHINE OR PHOSPHITE)FERRATES(II) BY ^{31}P NMR AND CYCLIC VOLTAMMETRY

HIDENARI INOUE, NAOKO HONMA AND EKKEHARD FLUCK*
Department of Applied Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223 Japan
*Gmelin-Institut der Max-Planck-Gesellschaft, Varrentrappstr. 40/42, D-6000 Frankfurt am Main 90, Germany

Abstract The Fe-P bond in low-spin pentacyanoferrates(II) of the type $Na_3[Fe(CN)_5L]$ (L=phosphine or phosphite) has been characterized by ^{31}P NMR and cyclic voltammetry. The chemical shift in the $^{31}P\{^1H\}$ NMR spectra increases with the redox potential on the cyclic voltammogram. A linear dependence of the chemical shifts on the redox potentials has revealed that the π-back donation from the iron $d\pi$-orbitals to the phosphorus $d\pi$-orbitals plays an important role in the character of the Fe-P bond.

INTRODUCTION

A variety of pentacyanoferrate(II) complexes have received a great deal of attention because they provide an excellent opportunity to study the Fe-P bond in low-spin iron(II) complexes with phosphine or phosphite. The phosphine and phosphite ligands in these monosubstituted octahedral complexes span a considerable range in their bonding capabilities to probe the effect of the substituted ligand on the bonding between the central iron and the cyano ligand. In the previous paper the Fe-P bond in the solid state of pentacyano(phosphine or phosphite)ferrates(II) has been characterized by Mössbauer spectroscopy.[1] A linear correlation between ^{57}Fe Mössbauer isomer shifts and binding energies of core electrons has been also established for a series of model complexes.[2] In spite of considerable interest in spectroscopic characterization of the Fe-P bonds, electrochemical studies and the correlation of electrochemical data with spectroscopic parameters have attracted relatively little attention. In the present work we have prepared a series of structurally closely related complexes of the type $Na_3[Fe(CN)_5L]$ (L = phosphine or phosphite) and characterized the Fe-P bond in the solution of these model complexes by measurements of the ^{31}P

NMR spectra and cyclic voltammograms. In addition, our particular interest is to obtain some insight into the correlation between chemical shifts in ^{31}P NMR and redox potentials in cyclic voltammetry.

EXPERIMENTAL

Phosphine and phosphite ligands were purchased from Strem Chemicals Inc. and sodium amminpentacyanoferrate(II) was obtained from Kanto Chemical Co., Inc. A series of substituted pentacyanoferrates(II) of the type $Na_3[Fe(CN)_5L]$ (L = phosphine or phosphite) were synthesized by a method described in the literature.[1] The complexes obtained were identified by elemental analysis and infrared spectra. The proton-decoupled ^{31}P NMR spectra were taken in the solution of dichloromethane or deuterated chloroform with a Bruker WP-80 instrument at room temperature.[3] The chemical shifts are relative to an external standard of 85 % H_3PO_4. A BAS Model CV-1B control unit was used for cyclic voltammetric measurements. Potassium nitrate was used as a supporting electrolyte. The concentration of KNO_3 in distilled water was 0.5 moldm^{-3} and the concentration of $Na_3[Fe(CN)_5L]$ was about 4×10^{-3} moldm^{-3}. A glassy-carbon working electrode and a platinum counter electrode were used for voltammetric measurements. Potentials were adjusted to the conventional SCE reference.

RESULTS AND DISCUSSION

The $^{31}P\{^1H\}$ NMR spectra of pentacyano(phosphine or phosphite)-ferrates(II) showed only one singlet. The resonance signal of the phosphorus-31 atom shifts downfield upon coordination of the phosphine or phosphite ligand to the central iron atom of the pentacyanoferrates. The chemical shifts observed for $Na_3[Fe(CN)_5L]$ are listed in Table I together with the redox potentials obtained in cyclic voltammetry. The resonance signal of the phosphine complexes appeared at an upfield position compared with that of the phosphite complexes. The chemical shifts of the phosphine and phosphite complexes, δ com., range from 32.5 - 68.9 ppm and 170.7 - 200.6 ppm, respectively. The formation of $Na_3[Fe(CN)_5L]$ complexes from the corresponding free ligands is

TABLE I ^{31}P NMR and cyclic voltammetric data on $Na_3[Fe(CN)_5L]$.

No.	Ligand L	Chemical shift (ppm)^a)		Redox potential (V vs.SCE)		
		δ com.	δ coord.	Ep.c.	Ep.a.	$E_{1/2}$
1	$P(C_2H_5)_3$	48.3	68.0	0.12	0.37	0.25
2	$P(n\text{-}C_4H_9)_3$	32.5	63.2	0.17	0.23	0.20
3	$P[CH(CH_3)_2]_3$	67.2	48.1	0.08	0.33	0.21
4	$P(C_6H_5)_3$	65.0	71.6	0.23	0.49	0.36
5	$P(p\text{-}C_6H_4CH_3)_3$	61.3	69.7	0.30	0.36	0.33
6	$P(p\text{-}C_6H_4OCH_3)_3$	58.2	68.6	0.21	0.46	0.34
7	$P(p\text{-}C_6H_4Cl)_3$	68.9	77.9	0.27	0.53	0.40
8	$P(m\text{-}C_6H_4CH_3)_3$	67.1	72.3	0.19	0.45	0.32
9	$P[N(CH_3)_2]_3$	196.7	74.3	0.40	0.45	0.43
10	$P(C_6H_5)_2(OC_4H_9)$	170.7	59.2	0.28	0.53	0.41
11	$P(C_6H_5)(OC_4H_9)_2$	200.6	42.1	0.37	0.44	0.41
12	$P(OCH_3)_3$	179.3	45.8	0.39	0.66	0.53
13	$P(OC_2H_5)_3$	180.7	48.4	0.31	0.61	0.46
14	$P(O\text{-}n\text{-}C_4H_9)_3$	174.4	35.2	0.29	0.56	0.43
15	$P[OCH(CH_3)_2]_3$	178.8	41.3	0.25	0.51	0.38
16	$P(OCH_2CH_2Cl)_3$	177.1	38.2	0.38	0.65	0.52

a) taken from Ref. 3.

accompanied by a downfield shift of ^{31}P NMR chemical shifts. The so-called coordination shifts, δ coord., range from 35.2 to 77.9 ppm.

All the pentacyanoferrate(Ⅱ) complexes showed a cyclic voltammogram with a couple of sharp redox peaks. The redox potential $E_1/_2$, which is defined as $E_1/_2$ = (Ep.a. + Ep.c.)/2, ranged from 0.20 - 0.40 V vs. SCE for phosphine complexes and 0.38 - 0.53 V vs. SCE for phosphite complexes. It is noteworthy that the redox potentials of phosphite complexes are high compared with those of phosphine complexes. The redox potential is sensitive to the electron-donating and -accepting property of the phosphine or phosphite ligand, indicating that the oxidation is due to the removal of an electron from an iron-centered molecular orbital. In other words, the redox potentials observed in the cyclic voltammogram are concerned with the electron density on the central iron atom of pentacyano(phosphine or phosphite)ferrates(Ⅱ).

The chemical shifts of the phosphine and phosphite complexes, δ com., are plotted against the redox potentials, $E_1/_2$, in Fig. 1 and 2, respectively. The plot of No. 3 deviates from the regression line probably because this ligand has a large value of Tolman's cone angles in comparison with that of the other phosphorus ligands.[4] A correlation between chemical shifts and redox potentials is poor among the phosphite

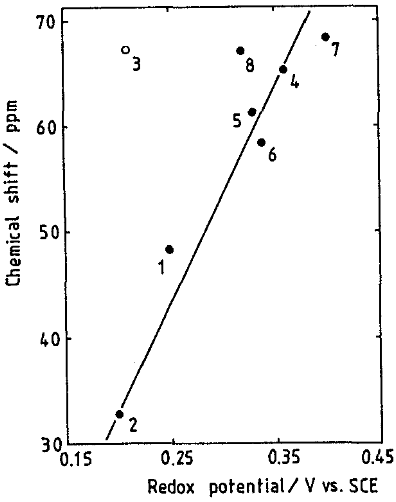

FIGURE 1 Plots of chemical shifts vs. redox potentials in phosphine complexes.

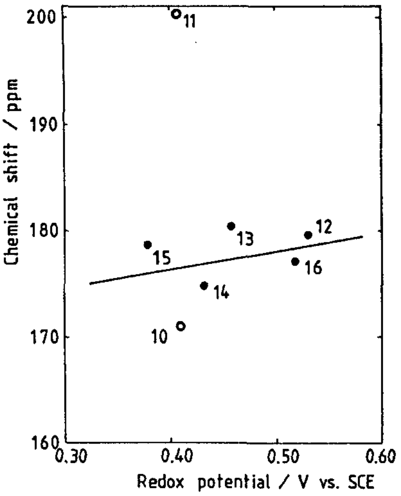

FIGURE 2 Plots of chemical shifts vs. redox potentials in phosphite complexes.

complexes, if the plots of No. 10 and 11 are taken into account. However, there is a good reason to exclude these plots because both are a mixed phosphine or phosphite in which a phosphorus atom is attached by the oxygen and carbon atoms. These deviations of the plots from the regression lines suggest that the ^{31}P NMR chemical shifts are more sensitive to the structural and electronic factors than the electrochemical redox potentials. The plotting of the chemical shifts against the redox potentials has revealed that the chemical shifts measured by ^{31}P NMR spectroscopy increase with the redox potentials determined by cyclic voltammetry. The chemical shift of the phosphorus ligand atom reflects the electron density on the phosphorus atom, while the redox potential is a direct measure of the electron density on the central iron atom. This indicates that the π-back donation from the filled iron dπ-orbitals to the empty phosphorus dπ-orbitals plays an essential role in the character of the Fe-P bond.

REFERENCES

1. H. Inoue, M. Sasagawa, E. Fluck and T. Shirai, Bull. Chem. Soc. Jpn., 56, 3434 (1983).
2. H. Inoue, T. Kobayashi and E. Fluck, Hyp. Int., in press (1992).
3. H. Inoue, M. Sasagawa and E. Fluck, Z. Naturforsch., 40, 22 (1985).
4. C. A. Tolman, J. Am. Chem. Soc., 92, 2956 (1970).