Anionic Penta-coordinated Complexes of Iron(II) Containing Pyridine-*N*-oxide, γ-Picoline-*N*-oxide, Ascorbic Acid and Pseudohalides

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Abstract

A series of novel complexes of the type $M_2[FeX_4L]$ where $M^+ = K^+$ or Na^+; X = cyanate, thiocyanate or azide; L = pyridine-*N*-oxide, γ-picoline-*N*-oxide or L-ascorbic acid; have been synthesized by the reaction of the metal salt and ligands in the appropriate ratio in mixed solvent (water–ethanol) medium. The complexes were characterized on the basis of their analyses, molar conductance, magnetic susceptibility, infrared, electronic spectral data and molecular weight measurements. The compounds are found to be 1:2 electrolytes and penta-coordinated monomers with presumably square pyramidal geometry.

Introduction

Iron(II) forms a number of complexes mostly in the octahedral and tetrahedral states [1]. However, there exists limited examples of five-coordinated species [2]. The versatility of pyridine-*N*-oxide, substituted pyridine-*N*-oxide and ascorbic acid is well known [2–10]. The ambidentate behaviour of pseudohalides such as cyanate, thiocyanate and the characteristic behaviour of the azide group have also been well studied [11–14]. However, complexes of iron(II) containing pyridine-*N*-oxide and substituted pyridine-*N*-oxide, ascorbic acid and pseudohalides do not appear to have been studied earlier. It was, therefore, thought worthwhile to investigate the reaction of iron(II) with cyanate/thiocyanate/azide ion and pyridine-*N*-oxide/γ-picoline-*N*-oxide/ascorbic acid and stabilize the less common penta-coordination by providing a heteroatom environment around the ferrous ion.

Experimental

Preparation of $K_2[Fe(CNO)_4asa]$, $K_2[Fe(CNO)_4$-$pyNO]$ and $K_2[Fe(CNO)_4\gamma$-$picNO]$

To an aqueous solution of $FeSO_4 \cdot 7H_2O$ (1 mmol), a 6 mmol solution of potassium cyanate was added with stirring. An aqueous solution (1 mmol) of ascorbic acid (asa) or a 1:1 (ethanol + water) solution of pyridine-*N*-oxide (pyNO) and γ-picoline-*N*-oxide (γ-picNO) was added. The resultant solution was stirred vigorously, refluxed for few minutes and cooled. The separated crystals were filtered, washed with ethanol, ether and dried *in vacuo*.

Preparation of $Na_2[Fe(CNS)_4asa]$, $Na_2[Fe(CNS)_4$-$pyNO]$, $Na_2[Fe(CNS)_4\gamma$-$picNO]$, $Na_2[Fe(N_3)_4asa]$, $Na_2[Fe(N_3)_4pyNO]$ and $Na_2[Fe(N_3)_4\gamma$-$picNO]$

A solution of $FeSO_4 \cdot 7H_2O$ in distilled water was treated with an aqueous solution of NaCNS or NaN_3 and an aqueous solution of ascorbic acid (asa)/water alcoholic solution of pyridine-*N*-oxide (pyNO) or γ-picoline-*N*-oxide (γ-picNO) in 1:6:1 ratio, stirred vigorously, refluxed, cooled and extracted from acetone and petroleum ether. The compounds separated were suction filtered, washed with ethanol followed by ether and dried *in vacuo*.

Physical Measurements

All the chemicals used were of Anala-R grade. Iron and sulfur were estimated by standard methods [15]. Carbon and hydrogen analyses were performed by a System Control semiautomatic instrument. The conductance measurements of $\sim 10^{-3}$ M solution in dimethylformamide medium were carried out using a Systronics 303 direct reading conductivity meter with a dip type cell. The magnetic susceptibility measurements were carried out for solid specimens at room temperature (25 ± 1 °C) with a Gouy Balance using $H_g[Co(NCS)_4]$ as calibrant. Diamagnetic corrections were calculated using Pascal's constants [16]. The infrared spectra of the compounds were recorded in the region 4000–400 cm^{-1} using a Perkin-Elmer 337 spectrophotometer as KBr optics. The electronic spectra of the $\sim 10^{-3}$ M solution in dimethylformamide medium were obtained using a Unicam SP-500 spectrophotometer. Molecular weights of the complexes were determined by Rast's method using biphenyl. The relevant analytical, molar conductance and magnetic susceptibility data of the compounds are given in Table 1 and infrared spectral data are recorded in Table 2.

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TABLE 1. Analytical data of the complexes

Compounds (colour)	Molecular weight[a] Found (calc.)	Melting point (°C)	Found (calc.) (%)				μ_{eff} (BM)	Molar conductance (mhos)
			Fe	S	C	H		
$K_2[Fe(CNO)_4asa]$ (dark yellow)	481.6 (477.05)	>250	11.59 (11.68)		24.98 (25.09)	1.48 (1.67)	2.80	171.3
$K_2[Fe(CNO)_4pyNO]$ (dark yellow)	408.7 (397.05)	>250	13.60 (14.06)		26.25 (26.27)	1.20 (1.21)	2.91	130.4
$K_2[Fe(CNO)_4\gamma\text{-picNO}]$ (reddish yellow)	413.7 (401.05)	>250	13.09 (13.92)		28.22 (28.23)	1.59 (1.64)	2.83	130.6
$Na_2[Fe(CNS)_4asa]$ (brown)	517.12 (508.85)	>250	10.82 (10.94)	24.69 (25.08)	23.52 (23.52)	1.54 (1.57)	3.34	119.6
$Na_2[Fe(CNS)_4pyNO]$ (pale yellow)	432.9 (428.85)	>250	12.96 (13.02)	29.77 (29.83)	25.13 (25.17)	1.14 (1.17)	3.61	160.3
$Na_2[Fe(CNS)_4\gamma\text{-pic-NO}]$ (dirty red)	432.1 (432.85)	>250	12.60 (12.90)	28.76 (28.88)	27.03 (27.08)	1.56 (1.58)	3.52	153.7
$Na_2[Fe(N_3)_4asa]$ (dark blue)	449.3 (444.85)	>250	12.43 (12.52)		16.14 (16.15)	1.71 (1.79)	3.01	124.1
$Na_2Fe(N_3)_4pyNO]$ (brown)	365.9 (364.85)	>250	15.26 (15.30)		16.39 (16.44)	1.29 (1.37)	2.90	149.8
$Na_2[Fe(N_3)_4\gamma\text{-pic-NO}]$ (brown)	378.38 (378.85)	>250	14.76 (14.74)		18.96 (19.00)	1.71 (1.85)	2.89	163.2

[a] Calculated for the 2:1 electrolyte.

Results and Discussion

The complexes reported under this investigation were either flaky or macrocrystalline. They were sparingly soluble in most of the organic solvents. The analytical data (Table 1) reveal that the complexes have stoichiometries $M_2[FeX_4L]$, where $M^+ = K^+$ or Na^+; $X^- = CNO^-$, CNS^- or N_3^-; L = pyridine-*N*-oxide, γ-picoline-*N*-oxide or ascorbic acid. The values of Λ_m obtained between 119.6–171.3 ohm^{-1} (Table 1) in dimethylformamide medium indicate that the compounds are 1:2 electrolytes. It has been reported that, for complexes of the type $[Fe(phen)_2X_2]$, where X = Cl, Br, I, OCN, HCOO and CH_3COO, high spin compounds with $\mu_{eff} = 5.0–5.3$ BM are formed and if X = CN, CNO or NO_2, diamagnetic compounds are obtained [17–22]. But, when X = NCS or NCSe there is an unusual change in magnetic moment which varies with temperature. It was suggested that the observed magnetic moment is caused by the presence of spin-state equilibria between the $^5T_2$ and $^1A_1$ ground state [23]. In the present investigation, cyanato and azido complexes exhibit μ_{eff} values ranging between 2.80–3.01 BM as expected for a spin-paired five-coordinate complex with two unpaired electrons. The observed value of magnetic moment for thiocyanato complexes is found between 3.34–3.61 BM, which is higher than the normal value and can be attributed to the partial spin-pairing of electrons due to the presence of the thiocyanate ligand [23]. Similar results (3.55 BM) have also been reported by Karayannis *et al.* [24] for some square planar iron(II) complexes in which the electrons are partially spin-paired [24–26]. The metal isotope technique is used to distinguish a low- and high-spin thiocyanato iron(II) complex [27]. For a high-spin complex ν(Fe–NCS) is observed at 252 cm^{-1} and shifted to higher frequency (528 cm^{-1}) on going to a low-spin complex. The ν(Fe–NCS) band at 515 cm^{-1} for thiocyanato complexes reported under this communication further confirms the pairing of electron spin [27]. The molecular weight measurements of the complexes (Table 1) indicate that they are monomers.

Infrared and Electronic Spectra

The relevant infrared spectral bands together with their assignments are given in Table 2. The cyanato group may coordinate to the metal ion either through oxygen (M–OCN) or nitrogen (M–NCO) or both. Forster and Goodgame obtained ν(C–N) and ν(C–O) bands at 2222 and 1325 cm^{-1}, respectively, for the $[Fe(CNO)_4]^{2-}$ complex [28]. They have also

TABLE 2. Infrared spectral data of complexes

Complexes	Cyanate				Ascorbic acid		Pyridine-*N*-oxide/γ-picoline-*N*-oxide		
	ν_a(NCO)	ν_s(NCO)	δ(NCO)		ν(NCO)	δ(O–H)	ν(N–O)	δ(N–O)	γ(C–H)
$K_2[Fe(CNO)_4asa]$	2105	1355	610, 595		1725	1640			
$K_2[Fe(CNO)_4pyNO]$	2105	1350	600, 590				1180	840	750
$K_2[Fe(CNO)_4\gamma$-pic-NO]	2105	1350	610, 595				1110	840	760
	Thiocyanate								
	ν(C–N)	ν(C–S)	δ(CNS)	ν(Fe–N)					
$Na_2[Fe(CNS)_4asa]$	2040, 2060	840, 755	475	515	1725	1640			
$Na_2[Fe(CNS)_4pyNO]$	2040, 2065	840, 755	470	515			1195	840	755
$Na_2[Fe(CNS)_4\gamma$-pic-NO]	2050, 2065	840, 755	470	515			1120	840	760
	Azide								
	ν_a(NNN)	ν_s(NNN)	δ(NNN)						
$Na_2[Fe(N_3)_4asa]$	2080	1340	610		1715	1640			
$Na_2[Fe(N_3)_4pyNO]$	2090	1340	610				1180	840	760
$Na_2[Fe(N_3)_4\gamma$-pic-NO]	2080	1340	615				1110	840	755

suggested, that for the N-bonded cyanate group, the ν(C–O) appears at ~1300 cm^{-1} and for O-bonded cyanate it occurs at a much lower frequency, below 1200 cm^{-1}. In the present case, the ν(C–N) band was obtained at ~2105 cm^{-1} and the ν(C–O) band at ~1350 cm^{-1} indicating the coordination of the cyanate group through its nitrogen atom. Mitchell and Williams have shown that the (C–N) stretching frequencies are generally lower in isothiocyanate (M–SCN) complexes [29]. The (C–S) stretching frequency at 780–860 cm^{-1} for isothiocyanate and 690–720 cm^{-1} for the thiocyanate group is more useful for distinguishing between these two isomers [30–32]. The thiocyanate group also forms a bridge between two metal atoms. The (C–N) stretching frequency for a bridging group is generally higher than that of a terminal group. In the thiocyanate complexes of iron(II) reported here, the (C–N) stretching frequency was found at ~2040 and 2065 cm^{-1}, and the (C–S) stretching frequency at ~840 and 755 cm^{-1}. Hence, the thiocyanate group is N-bonded to the metal. This is further supported by the appearance of the ν(Fe–NCS) band at ~515 cm^{-1} [27]. The azide group (N_3) can also behave as a terminal or a bridging ligand. Forster and Horrocks have assigned the bands at 2098 and 1342 cm^{-1} to a terminally coordinated azide group [33]. In the present case, the azido bands obtained at 2080 and 1340 cm^{-1} are in agreement with the earlier observation [33] and hence the azido group is terminally bonded. The spectrum of L-ascorbic acid shows two prominent bands at 1775 and 1665 cm^{-1} which have been assigned to ν(CO) and ν(OH) modes, respectively [34]. In the present case, the band at 1775 cm^{-1} appears at 1715 cm^{-1} and the band at 1665 cm^{-1} is found at 1640 cm^{-1}. Absence of bands due to a coordinated hydroxyl group in the complexes suggests that ascorbic acid is in the lactone form, and coordinates through the lactone O-atom as a neutral monodentate ligand [10]. Three fundamental bands at ~1110 and 1195, 840 and ~760 cm^{-1} in the IR spectra of *N*-oxide are assigned to ν(N–O), δ(N–O) and γ(C–H), respectively, indicating that the ligand *N*-oxide coordinates to the metal ion through the oxygen atom [35–39]. The introduction of an electron withdrawing substituent to the pyridine ring of *N*-oxide shifts the ν(N–O) frequency to a higher value [5], whereas, upon complexation it is shifted by 70–30 cm^{-1} to a lower value [27]. In the complexes containing γ-picoline-*N*-oxide, the ν(N–O) was observed at a lower frequency (Table 2) which may partly be due to the introduction of an electron releasing methyl group and partly to complexation.

Low-spin hexa-coordinated complexes show electronic absorption spectral bands at ~18 000 cm^{-1} and between 23 000–37 000 cm^{-1} [40]. Bands were obtained for all complexes in ~10^{-3} M dimethylformamide medium at ~9200 and 5000 cm^{-1}. These bands differ from a low-spin hexa-coordinate complex expected to be formed, if the neutral ligand (say pyNO) is replaced by dimethylformamide (with higher D_q value) and the coordination number is expanded. There is also no appreciable change in colour of the complexes on dissolution. Thus, the possibility of formation of a hexa-coordinated complex is ruled out. Penta-coordinated complexes show trigonal bipyramidal (D_{3h}), square pyramidal (C_{4v}) and a number of intermediate geometries [41]. It has been predicted that, square pyramidal coordination would be favoured by dsp^3 hybridization and the trigonal bipyramidal coordination would be favoured by sp^3d hybridization [42]. The presence of two unpaired electrons ($S = 1$) for the complexes under investigation, suggests that 3d 4s $4p^3$ hybrid orbitals of the metal ion are used for bonding. Also, since the e orbitals of the square pyramidal complex are lower in energy than the e′ orbitals of a trigonal bipyramidal complex, low-spin d^6 ion should favour square pyramidal geometry [43]. In the light of above discussion it is, therefore, suggested that the compounds reported under this communication are low-spin penta-coordinated complexes of iron(II) with a presumably distorted square pyramidal configuration [43].

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