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Spectral and Magnetic Properties of the Sodium Salts of 4,4′-Bipyridinebis[pentacyanoferrate(n,n′)]$^{z-}$ (n = II,III; n′ = II,III; z = 6,5,4)

P. A. M. WILLIAMS* and P. J. AYMONINO**

Programma QUINOR, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 y 115, 1900 La Plata, Argentina

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The sodium salts of the complex anions $[(CN)_5Fe(4,4'\text{-bipy})Fe(CN)_5]^{z-}$ with $z = 4$ [1, 2] and 6 [1] have been prepared by Felix and Ludi [1], and their spectroscopic and spectroelectrochemical properties studied in solution together with those of the complex with $z = 5$ [1]. We report now the magnetic and infrared, electronic and Mössbauer spectroscopic properties in the solid state of the pure sodium salts and of a mixture of them containing the anion with $z = 5$. This mixture was obtained by mixing equimolar aqueous solutions of the ferrous and ferric complexes and evaporating the solvent in a Rotavap. Because of the value of the conproportionation constant ($K_c = 4$) [1], the content of the mixture in the mixed valence complex salt should have been equal to the initial concentration of each reactant:

$$[\text{II,II}] + [\text{II,III}] \overset{K_c}{\rightleftharpoons} 2\,[\text{II,III}]$$

The iron content of these salts was determined spectrophotometrically as $[Fe(o\text{-phen})_3]^{2+}$ [3, 4] by first destroying the complexes with $HClO_4$ and H_2SO_4. Water of hydration was determined gravimetrically after drying over P_4O_{10} at 100 °C under reduced pressure. Molar magnetic susceptibilities were measured by the Gouy's method and data were corrected by diamagnetism [5]. IR spectra of Nujol mulls and of aqueous solutions between AgCl plates were recorded with a Perkin Elmer 457 spectrophotometer. Transmission and reflectance UV–Vis spectra of aqueous solutions and of solid samples diluted with MgO, respectively, were obtained with a Shimadzu UV-300 spectrophotometer. Mössbauer spectra were run in a MWE-250 spectrometer calibrated with α–Fe.

Analytical data and molar magnetic susceptibilities for these salts are presented in Table I. As expected for d^6 low spin iron, the totally reduced (II,II) complex is diamagnetic. The other complexes have the paramagnetic susceptibilities expected from the numbers of unpaired electrons.

The infrared spectra for the three substances were obtained in the CN stretching region. In Nujol mulls and in aqueous solutions, bands for $z = 5$ appeared at the same wavenumbers as observed individually for $z = 4$ (2124 cm^{-1}) and $z = 6$ (2046 cm^{-1}, and 2096 cm^{-1}) (see Fig. 1). No additional bands corresponding to an intermediate oxidation state appeared in the spectra. This fact suggests that the specific rate for electron transfer between the two iron nuclei must be smaller than the frequency difference between 2046 and 2124 cm^{-1}, *i.e.*, smaller than 2.2×10^{12} s^{-1} [6]. In fact, the actual value of this constant is 2×10^9 s^{-1} [7], as calculated from the intervalence band [1].

The visible electronic spectra of the three compounds in aqueous solutions were obtained for the sake of comparison with spectra reported previously [1]. Band positions and relative intensities of the bands in the three complexes were found to be the same as in ref. 1, but not the values of the molar absorptivities of the metal-to-ligand charge transfer bands, which agreed with the values reported by Figard *et al.* [2]. Diffuse reflectance spectra of samples mixed with MgO were also obtained. All these data are included in Table II. The blue shifts of the electronic spectra of the solutions in compa-

TABLE I. Analytical Data and Molar Magnetic Susceptibilities

Substance	Water (%)		Iron (%)		$\chi_M \times 10^3$ [a] (mol^{-1})	Spin[b]
	calc.	obs.	calc.	obs.		
$Na_6[Fe_2(CN)_{10}(4,4'\text{-bipy})]\cdot 4H_2O$	9.7	9.4	15.2	14.7	−0.21	
$Na_5[Fe_2(CN)_{10}(4,4'\text{-bipy})]\cdot 8H_2O$[c]	18.3	18.7	14.2	13.9	1.27	0.50
$Na_4[Fe_2(CN)_{10}(4,4'\text{-bipy})]\cdot 7H_2O$	16.9	17.5	15.0	14.5	3.33	0.99

[a] Corrected for diamagnetism. [b] Per nucleus. [c] Results were corrected for the conproportionation constant.

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*Predoctoral fellow of CONICET, Argentina.

**Author to whom correspondence should be addressed. Member of the Carrera del Investigador Científico, CONICET, Argentina.

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TABLE II. Solution (Transmission) and Solid (Diffuse Reflectance) Electronic Spectra

Anion	λ_{max} (nm)		$\log \epsilon^a$		
	Aqueous solution	Solid[b]	This work	Ref. 1	Ref. 2
$[Fe_2(CN)_{10}(4,4'\text{-bipy})]^{6-}$	443	480	3.75	4.11	3.75
$[Fe_2(CN)_{10}(4,4'\text{-bipy})]^{5-}$	432	440	3.54		
$[Fe_2(CN)_{10}(4,4'\text{-bipy})]^{4-}$	425	430	3.32		

[a] Molar absorptivities ($mol^{-1}\ l\ cm^{-1}$) in aqueous solutions. [b] Mixtures with MgO.

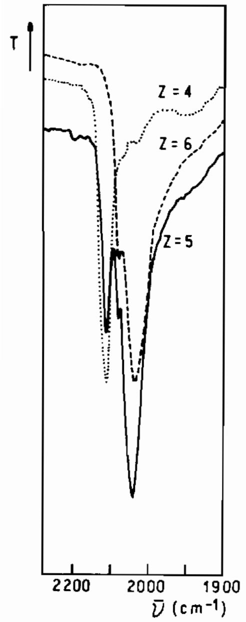

Fig. 1. IR spectra of $[Fe_2(CN)_{10}(4,4'\text{-bipy})]^{z-}$ complexes, with $z = 4$, 5 and 6, in aqueous solutions between AgCl plates.

rison with the solids should be ascribed to solvatochromic effects [8].

Mössbauer data are reported in Table III. The isomeric shift and quadrupole splitting for the totally reduced complex are in good agreement with the values obtained for low–spin Fe(II) complexes $[Fe(CN)_5L]^{3-}$ [9]; e.g., $\delta[Fe(CN)_5(4,4'\text{-bipy})]^{3-} = 0.01$ mm/s (referred to α-iron) and $\Delta[Fe(CN)_5(4,4'\text{-bipy})]^{3-} = 0.93$ mm/s. In the low-spin Fe(III) complexes $[Fe(CN)_5L]^{2-}$, isomeric shifts run from –0.12 to 0.00 mm/s (referred to α–iron) and quadrupole splittings fall in the range of 0.9–2.5 mm/s [9]. The Mössbauer spectra exhibit single doublets for $z = 4$ and $z = 6$, and a superposition of these doublets for $z = 5$. Again, the Mössbauer effect points to a small value for the electron transfer rate constant.

Thus, it is confirmed that there are trapped valence states [10] in the mixed valence compound, as suggested previously [1] by the low value of the delocalization parameter α^2 (0.002) obtained from the intensity of the intervalence band, corresponding to an electron delocalization of only 1%.

TABLE III. Mössbauer Parameters[a]

Substance	Isomeric shift y (mm/s)	Quadrupole splitting Δ (mm/s)
$Na_5[Fe_2(CN)_{10}(4,4'\text{-bipy})]\cdot 8H_2O$	0.00 –0.06	0.87 1.87
$Na_4[Fe_2(CN)_{10}(4,4'\text{-bipy})]\cdot 7H_2O$	–0.095	1.59
$Na_6[Fe_2(CN)_{10}(4,4'\text{-bipy})]\cdot 4H_2O$	0.033	0.84

[a] Referred to α–Fe.

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References

1 F. Felix and A. Ludi, *Inorg. Chem., 17,* 1782 (1978).
2 J. E. Figard, J. V. Paukstelis, E. B. Byrne and J. D. Petersen, *J. Am. Chem. Soc., 99,* 8417 (1977).
3 P. C. Hummel and H. H. Willard, *Ind. Eng. Chem., Anal. Ed., 10,* 3 (1938).
4 J. P. Mehlig and H. R. Hulett, *Ind. Eng. Chem., Anal. Ed., 14,* 869 (1942).
5 D. M. Adams and J. B. Raynor, in 'Advanced Practical Inorganic Chemistry', Wiley, London, 1965, p. 147.
6 H. Taube, *Ann. New York Acad. Sci.,* 481 (1978).
7 C. Creutz, *Prog. Inorg. Chem., 30,* 1 (1983).
8 J. Burgess, J. G. Chambers and R. I. Haines, *Transition Met. Chem., 6,* 145 (1981).
9 C. R. Johnson and R. E. Shepherd, *Inorg. Chem., 22,* 3506 (1983).
10 D. B. Brown and J. T. Wrobleski, in D. B. Brown (ed.), 'Mixed-Valence Compounds', NATO Advanced Study Institutes Series, No. 58, Reidel, Boston, Mass., 1980.