$\nu_1 + \nu_4$ or $\nu_5 + \nu_3$ at 1108–1138 cm^{-1}, $\nu_2 + \nu_3$ at 1220–1224 cm^{-1}, and $\nu_1 + \nu_3$ at 1370–1396 cm^{-1}.

Notes

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Preparation of an Iron(0) Complex with 2,2'-Bipyridine[1]

BY FRANK S. HALL AND WARREN L. REYNOLDS

The preparation of tris(2,2'-bipyridine)iron(0) has been reported[2] but no quantitative data concerning elemental analyses or physical properties have been published. In this note we report data on Fe, Na, Cl$^-$, C, and N quantitative analyses. Furthermore, it is of interest to inquire as to whether this compound should be regarded as an ionic complex of Fe^{3+} and three bipyridine anions, bipy$^-$, or as a covalent complex with essentially uncharged ligands.
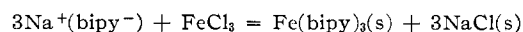
The compound was prepared in anhydrous 1,2-dimethoxyethane[3] (DME) by adding a solution of Na$^+$-(bipy$^-$) in slight excess to solid anhydrous FeCl$_3$ under moisture-free, oxygen-free conditions in an evacuated vessel. The black product precipitate was filtered and washed with pure anhydrous DME in the same vessel.

When chemical analyses of the product were desired, the reaction compartment was opened to the air. The black precipitate formed from the reaction of Na$^+$-(bipy$^-$) and FeCl$_3$ immediately turned red, presumably the result of oxidation to a compound of Fe(bipy)$_3$$^{2+}$ by oxygen and/or water of the air. The red precipitate in the reaction compartment was dissolved in water and transferred to a volumetric flask, and the red solution was brought to volume. The spectrum of the red solution agreed with that of Fe(bipy)$_3$$^{2+}$ formed by standard methods. Chemical analyses for sodium, iron, and chloride ion were performed on aliquots of this solution as described below. In other instances samples of the red precipitate were also submitted to the microanalysis laboratory for carbon and nitrogen analyses so that the C:N ratio could be obtained.

Sodium ion in aqueous solution was determined by the sodium zinc uranyl acetate method. Iron and

chloride ion analyses were performed on the same aliquot of aqueous solution. The iron(II) was oxidized to iron(III) with hydrogen peroxide (the red color of Fe(bipy)$_3$$^{2+}$ was lost), and hydrous ferric oxide was precipitated with ammonia. The filtrate from the filtration and washing of this precipitate was heated to decompose the excess hydrogen peroxide and analyzed for chloride ion by the gravimetric silver chloride method. If the excess hydrogen peroxide was not completely decomposed, oxidation of Ag$^+$ to Ag(II) occurred in the presence of 2,2'-bipyridine, and the silver chloride precipitate was discolored. The hydrous ferric oxide was dissolved in a small amount of 1 M HCl and analyzed for iron by the oxine method or by titration with standard potassium dichromate after reduction with stannous chloride. Sodium, iron, chloride, carbon, and nitrogen analyses gave Na:Cl ratios of 0.98, 0.99, and 0.98 (theoretical 1.00), Na:Fe ratios of 2.94, 2.96, and 2.93 (theoretical 3.00), C:Fe ratios of 29.8, 28.7, and 27.0 (theoretical 30.0), and N:Fe ratios of 6.0, 6.4, and 6.6 (theoretical 6.00). The microanalyses for C and N lacked the high precision of the Na, Cl$^-$, and Fe analyses since the carbon analyses indicated slightly less than three bipyridine groups per Fe atom whereas the nitrogen analyses indicated slightly more than three bipyridine groups per Fe atom.

No soluble chlorides were formed in the reaction between Na$^+$(bipy$^-$) and FeCl$_3$ since no trace of Cl$^-$ passed through the filter out of the reaction compartment. Because the ratio of Na:Cl was 1:1 and the ratio of Na:Fe was 3:1, the reaction

$$3\text{Na}^+(\text{bipy}^-) + \text{FeCl}_3 = \text{Fe(bipy)}_3(s) + 3\text{NaCl}(s)$$

apparently went to completion. Under certain conditions the Na:Cl ratio was 1:1, but the Na:Fe ratio was greater than 3:1, indicating that reduction could be carried beyond iron(0) to form soluble products, perhaps by a reaction such as

$$\text{Na}^+(\text{bipy}^-) + \text{Fe(bipy)}_3(s) \longrightarrow \text{Na}^+[\text{Fe(bipy)}_3{}^-] + \text{bipy}$$
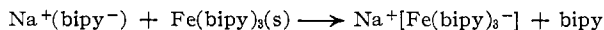
In order to establish that Na$^+$(bipy$^-$) was the only reductant present in the bipyridine solution, the changes in the spectrum of 2,2'-bipyridine in DME were studied as the reduction by sodium progressed. An isosbestic point at 299 mμ was observed in the reduction of the neutral molecule to Na$^+$(bipy$^-$). In the

(1) Abstracted in part from the M.S. thesis of Frank S. Hall, University of Minnesota, 1965.
(2) S. Herzog and H. Präkel, 8th International Conference on Coordination Chemistry, Vienna, Sept 7–11, 1964, p 214.
(3) M. T. Jones and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 4269 (1962).

reduction of $Na^+(bipy^-)$ to $Na^+_2(bipy^{2-})$ three isosbestic points were observed at 487, 608, and 714.5 mμ. Thus, the reduction of the neutral molecule occurred in a stepwise fashion, and no appreciable amounts of $Na^+_2(bipy^{2-})$ and the neutral molecule coexisted in DME as has been implied[2] by the equation written for the reduction of $FeCl_3$ by $Li^+_2(bipy^{2-})$. The molar extinction coefficients of bipyridine for the 282- and 237-mμ absorption peaks were 14.7×10^3 and 11.5×10^3 M^{-1} cm^{-1}, respectively; these are somewhat larger than those reported[4] for other organic solvents. The spectrum of $Na^+(bipy^-)$ has absorption peaks at 560, 530, and 386 mμ; the first two have equal intensities and a molar extinction coefficient of 4300 ± 200, and the latter has a molar extinction coefficient of $18,000 \pm 2000$ M^{-1} cm^{-1}.

The iron(0) compound dissolved sparingly in DME to give a blue-violet solution which had absorption peaks at 525, 502, and 357 mμ; except for the blue shift of approximately 30 mμ, the spectrum of the iron(0) compound in solution closely resembled the Na^+-$(bipy^-)$ spectrum. Shifts of the same order of magnitude have been observed[5] in optical spectra of some negative organic radical ions when they have formed an ion pair with alkali metal ions in solvents such as DME, and since $Na^+(bipy^-)$ has a very small sodium coupling constant[6] and can be regarded as an ion pair rather than as a covalent molecule, the optical evidence indicated that the iron(0) complex in solution contained an iron cation and bipy$^-$ anions. If the iron(0) species in solution was ionic, it did not dissociate appreciably into ions. No esr spectrum of bipy$^-$ was found for the solution. Since the presence of iron (if paramagnetic) could have broadened the esr signal beyond detection, a conductance measurement was made. In a conductance cell with platinum electrodes 1 cm apart the iron(0) solution had a resistance greater than 150,000 ohms, showing that ionic dissociation was negligible. The composition of the iron-(0) species in solution is not precisely known; some dissociation of neutral bipyridine (detected by its intense 283-mμ peak) occurred when the $Fe(bipy)_3$ dissolved. Upon long standing (20 hr) the dissociation was virtually complete.

The solid $Fe(bipy)_3$ was paramagnetic, but attempts to determine its magnetic susceptibility by the Gouy method failed because of traces of metallic iron impurity.

An esr spectrum of $Fe(bipy)_3$ at 9.487×10^9 cps gave an average g value of 2.075 ± 0.003 showing more spin-orbit coupling than could be expected for electrons residing entirely in the bipy$^-$ anions in an ionic complex. The value found for iron(0) is in agreement with the reported[7] values of 2.2125 ± 0.0005 for Ni^{2+}

and 2.1728 ± 0.0005 for Co^+, both d^8 ions. Despite the evidence of the optical spectrum to the contrary, the measured g value for iron(0) indicated that the iron had a d^8 configuration in a covalent complex of Fe-$(bipy)_3$ with neutral ligands.

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The Oxidation of Uranium(IV) Acetate by Silver Acetate in Liquid Ammonia

BY ROBERT J. KLINE AND CARL J. KERSHNER

Silver acetate is a convenient oxidizing agent for use in liquid ammonia. It is readily prepared and purified and produces a heavy metal as a product of the reaction. This can be easily isolated and weighed to give a measure of the reaction.

A green solution of uranium(IV) acetate in liquid ammonia is converted to the yellow of U(VI) in a few hours at room temperature by silver acetate. This reaction is followed by the slow precipitation of a pale yellow substance as the solution color fades. We have examined this reaction in some detail and now report the results of our experiments.

Experimental Section

Materials.—The anhydrous acetates were prepared from hydrated nitrates or chlorides by treatment with acetic anhydride at reflux temperatures. Usually the anhydrous acetates settled out as formed and were purified by recrystallization from glacial acetic acid.

Dioxouranium(VI) acetate was prepared from Baker Analyzed reagent grade dioxouranium(VI) nitrate hexahydrate. *Anal.* Calcd for $UO_2(C_2H_3O_2)_2$: U, 61.32. Found: U, 61.34.

Uranium(IV) acetate was prepared from "specially purified" UCl_4 obtained from the Los Alamos Scientific Laboratories. *Anal.* Calcd for $U(C_2H_3O_2)_4$: U, 50.20. Found: U, 50.14.

Silver acetate was prepared from Baker Analyzed reagent grade silver nitrate. *Anal.* Calcd for $AgC_2H_3O_2$: Ag, 64.62. Found: Ag, 64.56.

Ammonium diuranate was prepared from Baker Analyzed reagent grade dioxouranium(VI) nitrate hexahydrate by precipitation from aqueous solution with dilute ammonium hydroxide. It was purified by dissolution in aqueous sodium carbonate solution, conversion to the nitrate by boiling with nitric acid, and reprecipitation with dilute ammonium hydroxide, filtered, and dried at 110°. *Anal.* Calcd for $(NH_4)_2U_2O_7$: U, 76.3. Found: U, 76.9.

Ammonium dioxotris(acetato)uranate(VI) was obtained by the slow evaporation of a solution of dioxouranium(VI) acetate in saturated aqueous ammonium acetate. The compound was

(4) P. Krumholz, *J. Am. Chem. Soc.*, **73**, 3487 (1951).

(5) K. H. J. Buschow, J. Dieleman, and G. J. Hoitjtink, *J. Chem. Phys.*, **42**, 1993 (1965).

(6) J. dos Santos Veiga, W. L. Reynolds, and J. R. Bolton, *ibid.*, **44**, 2214 (1966).

(7) J. W. Orton, P. Auzins, J. H. E. Griffiths, and J. E. Wertz, *Proc. Phys. Soc.* (London), **78**, 554 (1961).