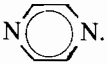
Inorganica Chimica Acta, 15 (1975) L7 - L8

Mixed Valence Properties of μ-Pyrazine-Decacyanodiiron(II, III)

F. FELIX, U. HAUSER, H. SIEGENTHALER, F. WENK, and A. LUDI

Institut für Anorganische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland

Received July 29, 1975

Great similarities have been found in the properties of the complexes $Fe^{II}(CN)_5L^{3-}$ and $Ru^{II}(NH_3)_5L^{2+}$, where L is representing a heterocyclic nitrogen donor.[1] Mixed valence compounds of ruthenium derived from this mononuclear constituent have been extensively studied.[2] This note reports the properties of corresponding complexes $[(CN)_5Fe\text{-pyr-}Fe(CN)_5]^{6-,5-,4-}$ to be denoted as [2,2], [2,3], and [3,3] according to the different combinations of the oxidation states of iron; pyr is pyrazine, .

[2,2] is obtained as a crystalline product by slow evaporation of an equimolar mixture of solutions of $Fe(CN)_5pyr^{3-}$ [1] and $Fe(CN)_5NH_3^{3-}$. An analogous binuclear complex is obtained with 4,4′-bipyridine as a bridging ligand. The $t_{2g} \rightarrow \pi^{\star}$ charge transfer band[1] ($\bar{\nu}$ = 22 kK, ϵ = 5,000) of $Fe(CN)_5pyr^{3-}$ is observed for the binuclear [2,2] at 19.8 kK with ϵ = 12,000. The mixed valence species [2,3] is produced either from [2,2] by oxidation with the appropriate amount of bromine water or electrochemically or by direct combination of equimolar solutions of $Fe(CN)_5NH_3^{2-}$ and $Fe(CN)_5pyr^{3-}$ the formation of the binuclear complex being established by the corresponding Job plot. Its aqueous solution shows the $t_{2g} \rightarrow \pi^{\star}$ transition at 21.8 kK with nearly the same intensity as recorded for $Fe(CN)_5pyr^{3-}$ and a band in the near infrared at 8.5 kK with ϵ = 3,200. This band which is also observed in KBr pellets of solid [2,3] is assigned to the intervalence electron transfer [2,3] → $[3,2]^{\star}$ in analogy to the 7.7 kK band of the corresponding μ-cyano species.[3] This low energy absorption is observed with very small and varying intensities also in solutions of [2,2] indicating partial oxidation. Complete reduction and hence disappearance of the mixed valence transition is achieved by recording the spectra at controlled electrochemical potentials. The results of cyclic voltammograms of the spectroelectrochemical experiments[4] in the potential range +700 to –400 mV *versus* SCE correspond to the two-electron overall process [3,3] + $2e^- \rightleftarrows$ [2,2]. Optical monitoring of this redox reaction shows the mixed valence ion [2,3] to occur as an intermediate at potentials around +200 mV/SCE. The one-electron reactions, [2,2] $- e^- \rightleftarrows$ [2,3], can be repeated for several scanning cycles (–400) to +200 mV) without observing a loss of intensity of the intervalence band whereas the full potential cycle cannot be scanned reversibly due to a decomposition of [3,3].

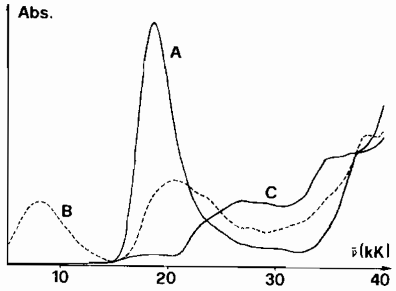


Fig. 1. Absorption spectra of $[(CN)_5Fe\text{-pyr-}Fe(CN)_5]^{n-}$ at different potentials (*versus* SCE). A: –400 mV, [2,2]; B: +200 mV, [2,3]; C: + 700 mV, [3,3].

According to the theory of Hush[5] the position and intensity of the mixed valence band correspond to an electron delocalization of about 1.5% assuming a Fe–pyr–Fe distance of 8 Å. The calculated[5] half-width of the intervalence band is 4.4 kK in quite good agreement with the observed value of 4.8 kK. The small degree of delocalization, *i.e.* firmly trapped valences, shows [2,3] to belong to class II of mixed valence compounds in the classification of Robin and Day.[6] This conclusion is strongly supported by infrared data. Two distinct CN stretching frequencies at 2060 and 2120 cm^{-1} are observed for [2,3], being diagnostic for cyano complexes of two- and three-valent metal ions, respectively.[7]

Acknowledgment

Financial support by the Swiss National Foundation is gratefully acknowledged.

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Preparation and Doping of $CaLaZrTaO_7$ Pyrochlore

S. LARACH
RCA Laboratories, Princeton, N.J. 08540, U.S.A.

Received July 31, 1975

Belyaev and co-workers[1] recently have described new, complex compounds with pyrochlore structure. Among these materials was $CaLaZrTaO_7$ which has been further investigated in these Laboratories.

The synthesis of $CaLaZrTaO_7$ consisted of two parts, the first being similar to that described by Belyaev. Lanthanum acetate was reacted with tantalum pentoxide at 1250 °C in air, for ten hours, to yield $LaTaO_4$, as established by X-ray analysis. While Belyaev used calcium zirconate prepared from the oxides, we found multi-phase materials to result. Instead, we prepared a calcium carbonate suspension in water, to which was added a solution of zirconium disulfate. This was then reacted with ammonia, digested (hot) for one hour, filtered and dried. This material was fired at 1300 °C in air, for two hours, ground, and refired for two additional hours, to yield $CaZrO_3$, as established by X-ray analysis.

Equimolar proportions of $LaTaO_4$ and $CaZrO_3$ were mixed well, and pressed into pellets, either hot-pressing or cold-pressing techniques being used. For hot-pressing, the materials were heated in vacuum, at 10^4 psi, at a temperature of 1400°–1450 °C, for four hours. The pressed pellets were then re-fired at 1400 °C in air for four hours, to restore the oxygen stoichiometry.

Materials formed by the above method were examined by both powder (film) X-rays and by diffractometry. Materials formed by hot-pressing were pyrochlore with a lattice constant of about 10.625 Å. A weak second phase, of the order of 5%, was sometimes present, and was probably ZrO_2. Belyaev[1] has reported a lattice constant of 10.567 Å for this pyrochlore.

It is of interest that the material formed by cold-pressing contained *two* pyrochlore phases, in addition to ZrO_2. The major pyrochlore phase was the same as the one reported in the hot-pressing case, with a lattice constant of 10.74 Å, and was possibly $LaTaO_4$.

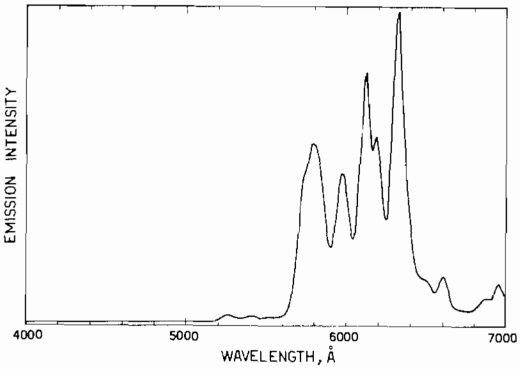

Fig. 1. Spectral distribution of cathodoluminiscence emission from $CaLa_{0.98}Eu_{0.02}ZrTaO_7$.

A luminescent pyrochlore was obtained by doping with europium. Thus, $La_{0.98}Eu_{0.02}TaO_4$ was synthesized, and from this and $CaZrO_2$, $CaLa_{0.98}Eu_{0.02}$-$ZrTaO_7$ was prepared, as described above. Pellets were pressed, using hot pressing, and the resultant materials were examined under cathode-ray excitation. Figure 1 shows the emission spectra obtained for such a material. Activation by other rare-earth ions and by ions of other transition elements also appears feasible.

Acknowledgments

The author is indebted to R. J. Paff for X-ray determinations, to H. I. Moss for pellet-pressing, to J. E. McGowan for synthesis aid, and to J. Gerber for luminescence measurements.

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