BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (9), 2341—2342 (1974)

Mössbauer Spectroscopic Studies of Iron(II) and Iron(III) 1-Nitroso-2-naphtholate Complexes

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(Received May 2, 1974)

Synopsis. The anomalous Mössbauer parameters of iron(II) 1-nitroso-2-naphtholate complex are interpreted by assuming the presence of iron(III) and iron(II) complex species. Partial oxidation of iron(II) by 1-nitroso-2-naphthol is suggested.

Iron 1-nitroso-2-naphtholate complexes known in analytical chemistry are used as the dye "Naphthol Green Y".[1] However, there are not many structural studies on these complexes except for the work by Stukan *et al.*[2] on bis (1-nitroso-2-naphtholato)iron(II) by means of the Mössbauer effect. They reported that bis(1-nitroso-2-naphtholato)iron(II) shows a quadruplet in the Mössbauer spectrum. A component doublet of the spectrum has parameters similar to those for the spectrum of other planar iron complexes, while the quadrupole splitting of the second doublet is similar to that of high-spin iron(II) compounds, although the isomer shift is anomalously more negative than that of the latter. The reason for the appearance of a quadruplet has not so far been clarified.[3] Since no Mössbauer spectroscopic data have been given of tris(1-nitroso-2-naphtholato)iron(III), we examined the Mössbauer spectroscopic character of these complexes.

Dark colored crystallites of tris(1-nitroso-2-naphtholato)iron(III) were prepared from iron(III) trichloride hexahydrate and 1-nitroso-2-naphthol both in ethanol or in acetic acid.[1] The products were identified as $Fe(C_{10}H_6NO_2)_3$ by elemental analysis. The molar magnetic susceptibility observed by the Gouy method was 2.09±0.7 B.M. at room temperature, indicating low-spin ($S=1/2$) iron(III) state. Mössbauer spectra were measured against a $^{57}Co(Pt)$ source moving with constant acceleration at room temperature. A typical Mössbauer spectrum is shown in Fig. 1a. The isomer shift is 0.19 mm/s with respect to metallic iron, the quadrupole splitting being 2.12 mm/s at 78 K. The large quadrupole splitting suggests an octahedral structure with a peripheral configuration.

Optimum conditions for the preparation of a stoichiometric iron(II) 1-nitroso-2-naphtholate complex were studied.[4] An ethanol solution saturated with potassium 1-nitroso-2-naphtholate was prepared by adding a concentrated potassium hydroxide solution to an ethanol solution of 1-nitroso-2-naphthol. The mixture was allowed to stand for one day at room temperature. The resulting blue-green crystallites were filtered and washed with water and ethanol. All the procedures were carried out under nitrogen. Found: Fe, 8.67; C, 55.90; H, 3.53; N, 6.54%. Calcd for $KFe(C_{10}H_6NO_2)_3 2H_2O$: Fe, 8.63; C, 55.65; H, 3.43; N, 6.49%. Magnetic susceptibility measurements indicate that the compound is diamagnetic ($S=0$). A Mössbauer spectrum is shown in Fig. 1b. The isomer shift is 0.22 mm/s and the quadrupole splitting is 0.86 mm/s at 78 K. The fairly large quadrupole splitting suggests an octahedral structure with peripheral configuration as in tris(1-nitroso-2-naphtholato)iron(III).

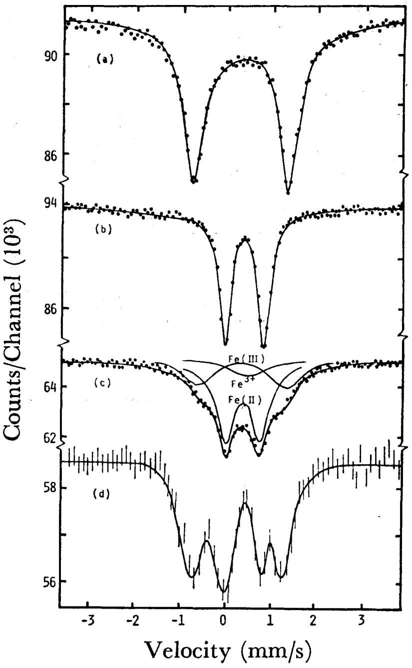

Fig. 1. Mössbauer spectra at 78 K of (a) tris(1-nitroso-2-naphtholato)iron(III), (b) potassium tris(1-nitroso-2-naphtholato)ferrate(II), (c) bis(1-nitroso-2-naphtholato)iron [containing iron(II) and iron(III) species]. (d) Spectrum of bis(1-nitroso-2-naphtholato)iron at 80 K, reproduced from Ref. 4.

The low values of isomer shift found in the tris(1-nitroso-2-naphtholato)iron(III) and potassium tris(1-nitroso-2-naphtholato)ferrate(II) indicate the low-spin iron(III) and iron(II) states, respectively, which are consistent with the magnetic measurements. The results could be ascribed to the back-donation of non-bonding $3d_{t2g}$ electrons of iron to the π^* orbitals of the ligands through nitrogen and oxygen atoms.

Dark green crystallites were obtained by mixing iron(II) dichloride tetrahydrate and 1-nitroso-2-naphthol in a 1 : 2 mole ratio in ethanol under nitrogen. The elemental analysis gives a reproducible result, but always higher iron content as compared with the calculated value for $Fe(C_{10}H_6NO_2)_2H_2O$ and lower

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values for carbon and hydrogen. The apparent molar susceptibility was 3.70 B.M. at room temperature. The Mössbauer spectrum (Fig. 1c) could be decomposed into two doublets and a small singlet assigned to tris(1-nitroso-2-naphtholato)ferrate(II), tris(1-nitroso-2-naphtholato)iron(III), and high-spin iron(III) species, respectively. The results suggest that some iron(II) species are oxidized to iron(III) species probably by 1-nitroso-2-naphthol, as in the reaction of this reagent with cobalt(II) species,5) giving tris(1-nitroso-2-naphtholato)iron(III) and some inorganic iron(III) species. The quadruplet consisting of two doublets seems similar to the spectrum reported by Stukan *et al.* in the values of isomer shift and quadrupole splitting.2) Earlier data on some salicylaldehyde and salicylaldoxime iron(II) chelates2,6) were found by De Vries *et al.* to be erroneous in the interpretation of Mössbauer parameters of what were believed to be pure iron(II) compounds.7) The result on bis(1-nitroso-2-naphtholato)iron may also be interpreted by assuming oxidation of iron(II) species in the preparation of the material, since the obtained potassium tris(1-nitroso-2-naphtholato)ferrate(II) is stable in air at room temperature.

A part of this work was carried out at Ochanomizu University.

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