Contribution from the Department of Chemistry, Cleveland State University,
Cleveland, Ohio 44115, and Basic Materials Laboratory, N.A.S.A
Lewis Research Center, Cleveland, Ohio 44135, U.S.A.

The ^{57}Fe Mössbauer Spectrum of Iodopentakis(p-tolylisocyanide)iron(II) Tri-iodide

John W. Schindler, John R. Luoma,* and James P. Cusick

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A cationic coordination complex has been synthesized and isolated as its tri-iodide salt. This salt has been characterized and the ^{57}Fe Mössbauer spectrum has been successfully recorded in spite of the attenuation of the γ-ray beam by the iodine atoms resulting in a reduction of the intensity of the resonant absorption.

Introduction

Berrett and Fitzsimmons[1] synthesized an iron isocyanide coordination complex containing the tri-iodide anion, cyanopentakis(ethylisocyanide)iron(II) tri-iodide. They found this tri-iodide salt of an inorganic complex to be unsuitable for Mössbauer studies because of the severe attenuation of the γ-ray beam by the three iodine atoms. We have synthesized an analogous salt and have obtained its iron Mössbauer spectrum, in spite of the attenuation of the γ-ray beam for four iodine atoms, by utilization of a higher resolution instrument.

Experimental Section

Materials. p-Tolylisocyanide (PTI)was prepared by the method of Appel.[2] Ferrous iodide ($FeI_2 \cdot 4H_2O$) was obtained in reagent grade purity from Alpha Inorganics-Ventron. It was assumed that the iron in the ferrous iodide contained the natural abundance of ^{57}Fe (2.2%).

Synthesis of $[Fe(PTI)_5I]_3$. Iodopentakis (p-tolylisocyanide)iron(II) triiodide, $[Fe(PTI)_5I]I_3$, was isolated as a substantial by-product in the preparation of *cis*–diiodotetrakis(p–tolylisocyanide)iron(II), *cis*–$[Fe(PTI)_4I_2]$, by the method of Malatesta[3]. The complex is reddish-brown and has a melting point of 161.5 - 162.5°C.

Anal.[4a,b] Calcd for $[Fe(CNC_5H_4CH_3)_5I]I_3$: C, 41.81; H, 3.07; N, 6.09; Fe, 4.86; I, 44.17. Found[a]: C, 41.30; H, 2.92; N, 6.35; Fe, 4.82; I, 44.75. Found[b]: C, 41.82; H, 2.97; N, 6.11.

Spectral Measurements. The ultra-violet spectrum was taken on a Cary-15 recording spectrophotometer, using 1 cm quartz cells. The infrared spectrum was recorded on a Beckman IR-20 infrared spectrophotometer in chloform in 0.1 mm KBr cells. A ten-to-one abscissa expansion was done over the CN stretch region. Gaussian line shapes were compared to the observed spectra on a Dupont Instruments 310 Curve Resolver[5]. The N.M.R. spectrum of the complex in $CDCl_3$ was recorded on a Varian T-60 N.M.R. spectrometer.

All instrumental measurements were performed at room temperature.

Mössbauer Spectrometer. The Mössbauer spectrometer used for obtaining the spectrum consisted of a laser interferometer calibrated loud speaker drive system coupled to a Canberra 1024 channel multichannel analyzer interfaced to PDP-11 digital computer. Computations to correct the baseline for experimental geometry and to fit the resonance absorptions with Lorentzian line shapes were performed on an IBM 7094 computer. The γ-ray source for the Mössbauer spectrum was ^{57}Co in palladium foil, and the centre shift was corected[6] to 310 stainless steel. Calibration of this instrument against naural iron foil indicates the accuracy of the velocity scale to be within 0.01 mm/second.

Results and Discussion

The presence of the tri-iodide anion was indicated[1] by an ultra-violet absorption band in the electronic spectrum at 363 nm (27,548 cm^{-1}). Confirmation of the absorption band of the I_3^- anion and of the hypsochromic shift from 370.3 nm (27,000 cm^{-1})[1] to 363 nm in chloroform was obtained by running a U.V. spectrum of a solution of KI + I_2 in chloroform.

The infrared spectrum yields three bands for the

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(1) R.R. Berrett and B.W. Fitzsimmons, *J. Chem. Soc. (A)*, 1967, 525.

(2) R. Appel, R. Kleinstuck and K.D. Ziehn, *Angew. Chem. internat. Edit.*, *83*, 143 (1971).

(3) L. Malatesta, A. Sacco and G. Padoa, *Ann. Chim. (Italy)*, *43*, 617 (1953).

(4) Analyses performed by Alfred Bernhardt Mikroanalytisches laboratorium, 5251 Elbach uber Engelskirchen, Fritz-Pregl-Strasse 14-16, West Germany. a) First analysis b) Check analysis performed on crystals obtained by the same method.

(5) J.W.S. and J.R.L. would like to thank Dr. Ralph Dannley of Case Western Reserve University for the use of this instrument.

(6) A.H. Muir Jr., K.J. Ando and H.M. Coogan, "Mössbauer Effect Data Index 1958-1965", Interscience, New York, 1966.

N≡C stretching frequency, consistent with the three bands ($2A_1+E$) required by group theory[7,8] for a molecule with C_{4v} symmetry. These three bands consists of a medium (A_1) band at 2214 cm^{-1}, a strong (E) band at 2166 cm^{-1} and a weak (A_1) shoulder at 2131 cm^{-1}. Three Gaussian line shapes con formed well to the observed I.R. spectrum.

The N.M.R. spectrum of the complex $CDCl_3$ with TMS yielded a singlet at 2.40 δ for the methyl protons and a complex multiplet centered at 7.41 δ for the aromatic protons.

The 14.4 keV γ-ray background for the Mössbauer spectrum of the polycrystalline sample was approximately 430,000 counts per channel with an average peak resonance of 0.63% and a half-width of 0.12 mm/second. Hypothesizing that *p*-tolylisocyanide will give rise to partial quadrupole splitting (p.q.s.) and partial centre shift (p.c.s.) values similar to the *p*-methoxyphenylisocyanide studied by Bancroft, Mays and Prater[9], we have also calculated the predicted quadrupole splitting (Q.S.) and centre shift (C.S.) by their method for a $FeAB_5$ complex. Compensation for any lattice contribution of the I_3^- anion was neglected. The data are summarized as follows:

	Quadrupole Splitting (mm/sec)	Centre Shift (mm/sec)
Obs.	0.66	+0.04
Calc.	0.80	0.13

Bancroft, *et. al.*, have noted that the worst discrepancies in their method occur with the cationic species, postulating that the assumption, that the contribution from other than nearest neighbors may be neglected, is most likely to break down for ionic compounds, where a significant lattice contribution to the Q.S. from the outer sphere ion may arise.

That this is also the case here is little doubted, but the significance of this measurement is not only that the ^{57}Fe Mössbauer spectrum of this type of coordination complex can be obtained in spite of the attenuation of the γ-ray beam resulting in a reduction in the intensity of the resonance absorption, but also that this type of both inner and outer sphere iodine-containing complex would now be ideal for obtaining the iodine Mössbauer spectrum in an effort to unravel the afore mentioned lattice contribution to the Q.S. from the outer sphere anion.

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(7) F. Bonati and G. Minghetti, *J. Organometal. Chem.*, 22, 195 (1970).
(8) L.E. Orgel, *Inorg. Chem.*, 1962, *1*, 25.
(9) G.M. Bancroft, M.J. Mays and B.E. Prater, *J. Chem. Soc. (A)*, 1970, 956.