

602. Infrared Spectra of Anhydrous Complex Cyanide Acids.¹

By D. F. EVANS, D. JONES, and G. WILKINSON.

The infrared spectra of the complex cyanide acids $\text{HAu}(\text{CN})_2$, $\text{H}_2\text{Pd}(\text{CN})_4$, $\text{H}_2\text{Pt}(\text{CN})_4$, $\text{H}_3\text{Rh}(\text{CN})_6$, $\text{H}_3\text{Ir}(\text{CN})_6$, $\text{H}_4\text{Fe}(\text{CN})_6$, $\text{H}_4\text{Ru}(\text{CN})_6$, and $\text{H}_4\text{Os}(\text{CN})_6$, and certain of the deuterated acids, have been measured. It is concluded that $\text{H}_4\text{Fe}(\text{CN})_6$, $\text{H}_4\text{Ru}(\text{CN})_6$, and $\text{H}_4\text{Os}(\text{CN})_6$ contain unsymmetrical N-H...N hydrogen bonds, but that symmetrical N-H-N hydrogen bonds are present in the other acids, for which structures are proposed. The preparations of $\text{H}_2\text{Pd}(\text{CN})_4$ and $\text{H}_3\text{Rh}(\text{CN})_6$ are reported.

THE infrared spectra of a number of solid anhydrous protonic acids and deuterio-acids derived from complex transition-metal cyano-ions are collected in the Table and certain of them are shown in Fig. 1. The acids appear to fall into two classes, *viz.*, (a) those in which the number of protons does not equal half the number of cyanide groups, *i.e.*, $\text{H}_4\text{Fe}(\text{CN})_6$, $\text{H}_4\text{Ru}(\text{CN})_6$, and $\text{H}_4\text{Os}(\text{CN})_6$, and (b) those in which the number of protons equals half the number of cyanide groups, *e.g.*, $\text{H}_3\text{Co}(\text{CN})_6$ and $\text{H}_3\text{Ru}(\text{CN})_6$.

Infrared spectra of the acids (in cm^{-1}).

Acid	ν_{CN}	ΔCN^*	M-C stretch or		Others
			M-C≡N bend		
$\text{H}_2\text{Pd}(\text{CN})_4$	2202	59	488		1900—600br,s, max. 820, sh's at 1600w, 1134s, 1010w
$\text{H}_2\text{Pt}(\text{CN})_4$	2203	53	485		1900—600br,s, max. 780, sh's at 1605w, 1136s, 1012w
$\text{H}_3\text{Co}(\text{CN})_6$	2202	59	550		1900—600br,s, max. 720, sh's at 1610w, 1149s, 1075w
$\text{H}_3\text{Rh}(\text{CN})_6$	2208	45	507		1900—600br,s, max. 719, sh's at 1613w, 1176s, 1101w
$\text{H}_3\text{Ir}(\text{CN})_6$	2203	66	510		1900—600br,s, max. 725, sh's at 1623w, 1174s, 1099w
$\text{D}_3\text{Ir}(\text{CN})_6$	2203	66	512		3600—2000br, 1400—400br,s, max. 794, 541sh
$\text{H}_4\text{Fe}(\text{CN})_6$	2106	66	583		3500—2200br, sh's at 3049, 2547, 2200, 1626br,s, 875s
	2086	46			678s, 444m
$\text{H}_4\text{Ru}(\text{CN})_6$	2105	<i>ca.</i> 70	541		3500—2200br,s, sh's at 3050, 2630, 2300, 1590br,s, 877s
	2080	<i>ca.</i> 45			658br, 476br
$\text{H}_4\text{Os}(\text{CN})_6$	2096	51	544		3500—2300br,s, sh's at 3049, 2597, 2250, 1613br,s, 885s
	2070	36			602br,s, 485br,s
$\text{D}_4\text{Fe}(\text{CN})_6$	2092	51	583		2481s, 2290s, 1905w (1600br, H), 1208br,s, 1015w, 640s, 510s, 439m
$\text{D}_4\text{Os}(\text{CN})_6$	2092	47	541		(3021w, 2660w,sh, H), 2469s, 2283, 1916s, (1600br,s, H) 1220br,s, 640s, 495br,s
$\text{HAu}(\text{CN})_2$	2212	71			1400br, 1120br
$\text{DAu}(\text{CN})_2$	2210	69			1020br, 810br

* Difference of ν_{CN} between acid and potassium salt.

Class (a).—The spectra of these acids are almost identical, and are quite different from those of the others; the spectra of $\text{H}_4\text{Fe}(\text{CN})_6$ and $\text{D}_4\text{Fe}(\text{CN})_6$ (95% deuterated) are curves B and A in Fig. 1. The strong broad absorption in the region 3300—2300 cm^{-1} can be attributed to the stretching modes of hydrogen-bonded N-H bonds. This absorption shows some structure, and in the deuterio-acids three well-defined bands at *ca.* 2480, 2290, and 1905 cm^{-1} are observed, probably due to the presence of hydrogen bonds of different strength, although splitting is often observed in systems where all the hydrogen bonds are equivalent and has been discussed in some detail.²

The bands at *ca.* 1600 and 880 cm^{-1} (which shift appropriately on deuteration, $\nu_{\text{NH}}/\nu_{\text{ND}} = \text{ca. } 1.45$ and *ca.* 1.38, respectively) may both be N-H deformation modes, although it is possible that the 1600 cm^{-1} band is a strongly hydrogen-bonded N-H stretching vibration. The presence of two main cyanide stretching frequencies for these acids, and of asymmetric peaks with low-frequency shoulders for the deuterated acids, is consistent with the presence of unsymmetrical hydrogen bonds.

¹ Preliminary Note, *Nature*, 1963, **199**, 277.² Hadzi, "Hydrogen Bonding," Pergamon Press, New York, 1959.

[1964]

Anhydrous Complex Cyanide Acids.

3165

Class (b).—The spectra of $\text{H}_3\text{Co}(\text{CN})_6$, $\text{H}_3\text{Ru}(\text{CN})_6$, $\text{H}_3\text{Ir}(\text{CN})_6$, $\text{H}_2\text{Pd}(\text{CN})_4$, and $\text{H}_2\text{Pt}(\text{CN})_4$ are exceedingly similar. The main feature is an intense and very broad band centred at about 750 cm^{-1} , with some structure at higher frequencies, which can be assigned to a superposition of hydrogen-bonded N-H stretching and deformation modes (combination bands may also be present). In $\text{D}_3\text{Ir}(\text{CN})_6$ the broad band shifts to lower frequencies.

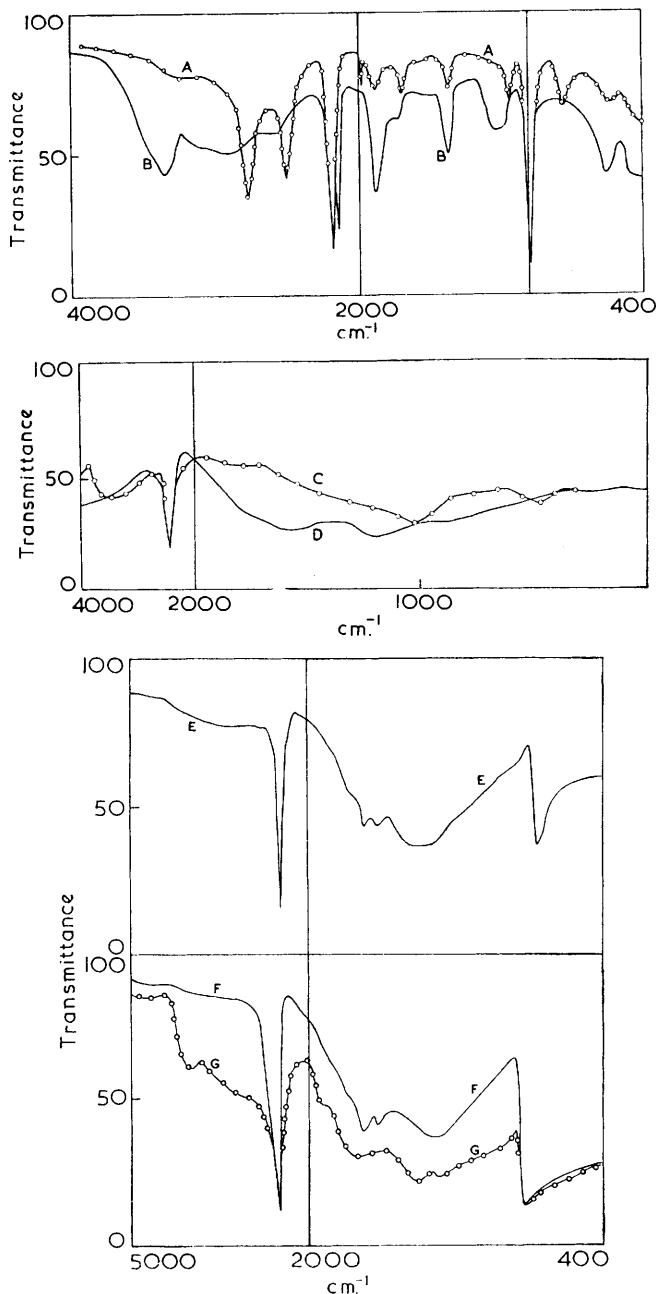


FIG. 1. Infrared spectra. A, $\text{D}_4\text{Fe}(\text{CN})_6$; B, $\text{H}_4\text{Fe}(\text{CN})_6$; C, $\text{DAu}(\text{CN})_2$; D, $\text{HAu}(\text{CN})_2$; E, $\text{H}_2\text{Pt}(\text{CN})_4$; F, $\text{H}_3\text{Ir}(\text{CN})_6$; G, $\text{D}_3\text{Ir}(\text{CN})_6$.

3166 *Evans, Jones, and Wilkinson: Infrared Spectra of*

The structure at *ca.* 1130 cm^{-1} in $\text{H}_3\text{Ir}(\text{CN})_6$ can be correlated with a band at 800 cm^{-1} in $\text{D}_3\text{Ir}(\text{CN})_6$ ($\nu_{\text{NH}}/\nu_{\text{ND}} = 1.417$), and that at 725 cm^{-1} with a band at 541 cm^{-1} in $\text{D}_3\text{Ir}(\text{CN})_6$ ($\nu_{\text{NH}}/\nu_{\text{ND}} = 1.33$). The analogous broad bands in $\text{HAu}(\text{CN})_2$, at 1400 and 1120 cm^{-1} , can be assigned as N-H stretching and deformation modes, respectively; they shift appropriately on deuteration ($\nu_{\text{NH}}/\nu_{\text{ND}} = 1.37$ and 1.38).

The broad absorption bands discussed above are very similar to those found³ in compounds such as potassium hydrogen bisphenylacetate, sodium hydrogen diacetates, and potassium hydrogen maleate, in which there is evidence, based on X-ray or neutron diffraction studies,⁴ that symmetrical hydrogen bonds are present. It seems likely, therefore, that all these cyanide acids contain symmetrical or effectively symmetrical $\text{N} \cdots \text{H} \cdots \text{N}$ hydrogen bonds, *i.e.*, the potential-energy well seen by the proton is similar to that shown in Fig. 2. The potential maximum (if present at all) is probably below the

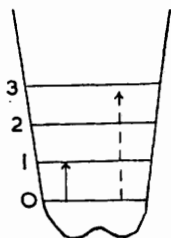


Fig. 2. Potential-energy diagram for proton in symmetrically hydrogen-bonded complex cyanide acids.

ground vibrational level, and the observed stretching mode corresponds to the transition 0—1 which accounts for its very low frequency (cf. ref. 5). The acids $\text{D}_3\text{Ir}(\text{CN})_6$ and $\text{DAu}(\text{CN})_6$ both show a broad and moderately strong band in the 3000 cm^{-1} region. This could be an overtone of the N-D stretching frequency, possibly transition 0—3 in Fig. 2.

The postulate of symmetrical hydrogen bonds is consistent with the observed single cyanide stretching frequencies. These bands, although symmetrical, are broader than those in the corresponding potassium salts, which may be connected with the extreme breadth of the $\text{N} \cdots \text{H} \cdots \text{N}$ absorption. Symmetrical hydrogen bonding also results in reasonable structures for these acids, that is, infinite chains for $\text{HAu}(\text{CN})_2$, infinite sheets for $\text{H}_2\text{Pd}(\text{CN})_4$ and $\text{H}_2\text{Pt}(\text{CN})_4$, and a three-dimensional lattice based on linked octahedra for $\text{H}_3\text{Co}(\text{CN})_6$, $\text{H}_3\text{Rh}(\text{CN})_6$, and $\text{H}_3\text{Ir}(\text{CN})_6$. These structures provide an interpretation of certain features of these acids.⁶ Thus, in the facile formation and decomposition of solid solutions with ether, and addition compounds with alcohol, acetone, etc., by $\text{H}_3\text{Co}(\text{CN})_6$, the organic molecules can be regarded as located in the channels formed by the open structure proposed above. It was found that the infrared spectra of $\text{H}_2\text{Pt}(\text{CN})_4 \cdot 2\text{EtOH}$ and $\text{H}_2\text{Pt}(\text{CN})_4 \cdot \text{EtOH}$ are almost identical with that of $\text{H}_2\text{Pt}(\text{CN})_4$ (with additional frequencies characteristic of ethyl alcohol), indicating that these compounds are adducts and not oxonium salts.

The cyanide stretching frequencies in the acids are greater than those in the corresponding potassium salts, normally by about 60 cm^{-1} (Table). A variety of evidence⁷ indicates that attaching another atom or group to a cyanide group in a complex cyanide increases the cyanide stretching frequency. It is not certain whether this is due to a genuine increase in the force constant of the cyanide group or to vibrational coupling.⁷

EXPERIMENTAL

Analyses for cyanide were by the Microanalytical Laboratory, Imperial College, using the sodium fusion technique.⁸ Infrared spectra were first measured on a Perkin-Elmer Infracord,

³ Speakman and Mills, *J.*, 1961, 1194; Hadzi, *J.*, 1961, 5128, and references therein.

⁴ Peterson and Levy, *J. Chem. Phys.*, 1958, **29**, 948; Bacon and Curry, *Acta Cryst.*, 1960, **13**, 717.

⁵ Snyder and Ibers, *J. Chem. Phys.*, 1962, **36**, 1356.

⁶ For details and references see D. Jones, Ph.D. Thesis, University of London (Imperial College), July 1963.

⁷ Shriver, *J. Amer. Chem. Soc.*, 1963, **85**, 1405, and references therein.

⁸ Lock and Wilkinson, *J.*, 1964, 2281.

since broad bands are most easily observed on the small chart; spectra were subsequently taken on Perkin-Elmer model 21 (CaF₂, NaCl, and KBr optics) and Grubb-Parsons Spectromaster grating instruments. Nujol and Fluorolube mulls were prepared in an atmosphere of dry nitrogen.

Preparations.—The acids were prepared from the potassium salts by the well known hydrochloric acid-ether method which is applicable with certain variations to all the acids, cf. preparation of H₄Fe(CN)₆,⁹ and is illustrated by the procedure given below for H₂Pd(CN)₄. The deuterio-acids D₃Co(CN)₆, D₃Ir(CN)₆, D₄Fe(CN)₆, D₄Os(CN)₆, and DAu(CN)₂ were obtained similarly using concentrated DCl. Repeated exchange of the hydrogen acid with deuterium oxide was adequate in some cases but complete deuteration of H₄Fe(CN)₆ and H₄Os(CN)₆ could not be achieved in this way. The extent of deuteration was checked by examination of the proton magnetic resonance spectra of the acids in deuterium oxide solution; >90% substitution was obtained.

Dihydrogen tetracyanopalladate(II). Concentrated hydrochloric acid (3 ml.) saturated with diethyl ether was added dropwise to a mixture of a saturated aqueous solution of potassium tetracyanopalladate(II) (3 ml.) and ether (3 ml.). Three layers were formed. The oily middle layer was removed and dried *in vacuo* over concentrated sulphuric acid for 24 hr., to leave a white powder. This crude product was dissolved in absolute ethanol, and the solution filtered and evaporated *in vacuo*, to leave the compound [Found: CN, 49.2. C₄H₂N₄Pd requires CN, 49.0%].

Trihydrogen hexacyanorhodate(III). In an analogous manner, from K₃Rh(CN)₆, the acid was obtained as a white powder. The preparation is not reproducible. The acid may be well formed or may be deposited as a viscous sludge (on the sides of the reaction vessel) which may subsequently crystallise; potassium chloride can also be coprecipitated [Found: CN, 60.0. C₆H₃N₆Rh requires CN, 59.57%].

Dihydrogen tetracyanoplatinatate(II) ethanulates. The above procedure gave hydrated H₂Pt(CN)₄ from aqueous solution, and evaporation of an ethanolic solution of this material gave the known red adduct H₂Pt(CN)₄.2EtOH. On drying the latter over concentrated sulphuric acid *in vacuo* for 7 days, the yellow *monoethanolate*, H₂Pt(CN)₄.EtOH was obtained [Found: Pt, 56.4. C₆H₈N₄OPt requires Pt, 56.21%]. The remaining molecule of ethanol was removed *in vacuo* at 100° during 8 hr., to give the yellow anhydrous acid [Found: Pt, 64.4. Calc. for C₄H₂N₄Pt: Pt, 64.8%].

We thank the Ethyl Corporation for a studentship (D. J.), and Johnson, Matthey and Co. Ltd. for the loan of platinum salts.

INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON S.W.7.

[Received, February 19th, 1964.]

⁹ Joannis, *Ann. Chim. Phys.*, 1882, [5] 26, 513; Berzelius, *Schweigger's J.*, 1820, 30, 44.