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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

Infrared Absorption Spectra of Inorganic Coördination Complexes. VII. Structural Isomerism of Nitro- and Nitritopentamminecobalt(III) Chlorides[1a,b]

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Infrared spectra of nitropentamminecobalt(III) chloride and nitritopentamminecobalt(III) chloride in the solid state have been measured. Spectral evidence is presented to support the conversion of nitritopentamminecobalt(III) chloride to nitropentamminecobalt(III) chloride. In the spectra of these complexes the deformation vibration frequencies of the NH_3 ligand, degenerate, symmetric and rocking are identified. The remaining absorption bands in the region from 1700 to 650 cm.$^{-1}$ (5.8–15 μ) can be assigned to the nitro and nitrito frequencies. Changes in the spectrum of the nitritopentamminecobalt(III) ion with regard to intensity of certain bands with time are significant. Bands which show such changes in absorption are assigned to those parts of the complex which are responsible for nitrito and nitro vibrations. By comparison of the spectra of the pure nitro and the freshly prepared nitrito isomers, the bands that decrease in intensity can be assigned to the nitrito group, while those new bands that appear and gradually increase in intensity can be assigned to the nitro group.

Introduction

Structural isomerism arises when one or another atom in a coördinating group ligates to the central metal atom of a coördination complex. In the complex ions nitropentamminecobalt(III) and nitritopentamminecobalt(III), the seat of isomerism is the $-NO_2$ ligand which may be present in the coördination sphere in the nitrito form (Co–ONO) or in the more stable nitro form ($Co-NO_2$). Two isomers of nitropentamminecobalt(III) chloride have long been known, an unstable red form which transforms into a yellow-brown form either in solution or in the solid state. On the basis of the colors of these complexes the unstable red form was assigned as the nitrito and the stable yellow-brown form as the nitro isomer. The kinetics of the rearrangement of nitrito complexes to the corresponding nitro compounds have been extensively studied in aqueous solution.[2]

Debye–Scherrer X-ray patterns and ultraviolet spectra[3] of these complexes have been studied by Lecomte and Duval. Infrared spectra of powdered samples of the pentammine compounds have also been determined by Lecomte and Duval[3] who assigned some of the observed bands in the nitro isomer and concluded that the complex exists only in this form.

In this paper are reported infrared spectra of these complexes in the solid state, changes in the infrared spectra associated with the rearrangement of the nitrito complex to the corresponding nitro compound, and assignments of the infrared bands in both the nitro and nitrito isomers in the sodium chloride region.

Experimental

Nitropentamminecobalt(III) chloride and nitritopentamminecobalt(III) chloride were prepared by the method of Walton.[4]

Anal. Calcd. for $[Co(NH_3)_5NO_2]Cl_2$: NH_3, 32.63. Found: NH_3, 32.75. Calcd. for $[Co(NH_3)_5ONO]Cl_2$: NH_3, 32.63. Found: NH_3, 32.80.

Absorption Measurements.—The infrared spectra were obtained by means of a Perkin–Elmer infrared spectrophotometer model 21 using a sodium chloride prism. Spectra of samples, obtained by the potassium bromide disk technique and checked in Nujol mulls, were measured at consecutive time intervals until no further change was observed. Experimental details are the same as reported in a previous communication.[5]

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(1) (a) Paper VI in series, THIS JOURNAL, **77**, 6521 (1955); (b) Presented before the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb., 1955. Supported in part under AEC Contract At(11-1)-38, Radiation Project of the University of Notre Dame; (c) Reverend Thomas J. Lane, C.S.C.

(2) B. Adell, *Svensk Kem. Tid.*, **56**, 318 (1944); **57**, 260 (1945); *Z. anorg. Chem.*, **252**, 272 (1944); **271**, 49 (1952); *Acta. Chem. Scand.*, 1, 624, 659 (1947); **4**, 1 (1950); **5**, 54, 941 (1951); F. Basolo, B. D. Stone, J. G. Bergmann and R. G. Pearson, THIS JOURNAL, **76**, 3079 (1954).

(3) J. Lecomte and Cl. Duval, *Bull. soc. chim.*, **12**, 678 (1945).

(4) H. F. Walton, "Inorganic Preparations," Prentice–Hall, Inc., New York, N. Y., 1948, p. 92.

(5) J. P. Faust and J. V. Quagliano, THIS JOURNAL, **76**, 5346 (1954).

Results

In Fig. 1 are given the infrared spectra of freshly prepared nitritopentamminecobalt(III) chloride, this isomer aged for five days, and pure nitropentamminecobalt(III) chloride. The spectra of hexamminecobalt(III) chloride and sodium hexanitrocobaltate(III), used to assist in the assignment of NH_3 and NO_2 vibrations, were reported in a previous communication.[5]

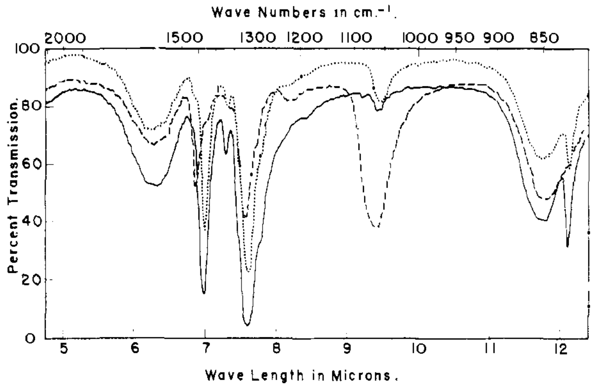

Fig. 1.—Infrared absorption spectra of the complexes: —, nitropentamminecobalt(III) chloride, $[Co(NH_3)_5NO_2]Cl_2$; ----, nitritopentamminecobalt(III) chloride, $[Co(NH_3)_5ONO]Cl_2$, freshly prepared: .... nitritopentamminecobalt(III) chloride, $[Co(NH_3)_5ONO]Cl_2$, aged.

In the 3 μ region peaks are observed for both the nitro and nitrito isomers at 3200 cm.$^{-1}$ and these compare with the peak at 3130 cm.$^{-1}$ of hexamminecobalt(III) chloride, assigned to N–H stretching vibrations. The shift in the N–H stretching frequency in the 3 μ region of NH_3 on coördination is in accord with the results of the extensive studies of ammine complexes reported.[6]

The spectra of both isomers reveal absorption maxima at 1595, about 1315 and 850 cm.$^{-1}$. These are well-defined absorption bands and have contours which correspond to those observed in the spectrum of $[Co(NH_3)_6]Cl_3$.[5] In addition to these characteristic frequencies common to the spectra of metal ammine complexes, the spectrum of the nitrito isomer has two additional peaks, observed at 1460 and 1065 cm.$^{-1}$. On aging, the sample of the nitrito isomer shows a spectrum in which these bands decrease in intensity and simultaneously two new bands appear at 1430 and 825 cm.$^{-1}$ (Fig. 1). These bands which increase in intensity are characteristic of the nitro complex as seen by a comparison of the spectrum of sodium hexanitrocobaltate(III).[5] A gradual change in the shape of the spectrum from the nitrito to the nitro isomer is observed for the unstable nitro complex in Nujol and also when present in a pressed potassium bromide disk. Absorption spectra of nitritopentamminecobalt(III) chloride, ground, and aged in Nujol, were similar to the spectra of samples aged in potassium bromide disks, and no evidence of interaction between the sample and potassium bromide was found.

Discussion

Nakagawa and Mizushima[7] have calculated various deformation vibrations of the CH_3 group in organic molecules. The vibrations of the NH_3 ligand as a whole can be considered quite similar to the CH_3 vibrations and the normal modes of the deformation vibrations of the NH_3 ligand in metal coördination complexes have been calculated and have been shown to be in good agreement with the observed infrared frequencies.[8] By inspection of the spectra of many metal ammine complexes, the three bands observed at about 1600 cm.$^{-1}$, about 1320 cm.$^{-1}$ and about 850 cm.$^{-1}$ have been identified with the degenerate deformation vibration, symmetric deformation vibration and rocking vibration of NH_3 ligands, respectively.

In this study we can easily identify the ligated NH_3 deformation vibrations from the frequency values as well as from the shapes of the corresponding absorption bands. In both the nitro and nitrito isomers the peak observed at 1595 cm.$^{-1}$ (6.3 μ) is assigned to the NH_3 degenerate deformation; the peaks at 1315 cm.$^{-1}$ (7.6 μ) and 1325 cm.$^{-1}$ (7.65 μ) are assigned to the NH_3 symmeteric deformation of the nitro and nitrito isomers, respectively, and the peak at 850 cm.$^{-1}$ (11.8 μ) is assigned to the NH_3 rocking for both complexes.

The absorption bands in the region from 2000–650 cm.$^{-1}$ remaining to be assigned are associated with vibrations of the NO_2 and ONO ligands, for it has been shown that cobalt–nitrogen stretching frequencies are not expected to appear in this region.[9] On aging the sample of $[Co(NH_3)_5ONO]Cl_2$, the spectra show bands which can be assigned to the nitro ligand; those very strong bands which decrease in intensity can be assigned to the nitrito ligand, arising from rearrangement of the nitrito complex to the corresponding more stable nitro isomer. Those bands at 1430, 1315 and 825 cm.$^{-1}$ which increase in intensity are assigned, from a comparison with the values reported for the hexanitrocobaltate(III) ion, simple nitrites and organonitro compounds,[5] to antisymmetric stretching, symmetric stretching and deformation vibrations, respectively, of the nitro ligand. Similarly, bands of decreasing intensity in the spectra of $[Co(NH_3)_5ONO]Cl_2$ at 1460 and 1065 cm.$^{-1}$ may be assigned to the two ONO stretching vibrations. The 1460 cm.$^{-1}$ band assigned to the CoONO stretching vibration appears at a higher frequency than that assigned to the nitro ligand. Also, in the spectrum of the freshly prepared nitrito isomer, a slight shoulder present at 1430 cm.$^{-1}$ indicates that a trace of the nitro isomer is present in the sample.

On aging the sample of $[Co(NH_3)_5ONO]Cl_2$, the absorption band in the 1450 cm.$^{-1}$ region, which appears to shift to a lower frequency, has been resolved into two sharp bands, one at 1460 cm.$^{-1}$ and the other at 1430 cm.$^{-1}$ (Fig. 1). The band at the higher frequency decreases in intensity on ag-

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(6) G. F. Svatos, C. Curran and J. V. Quagliano, THIS JOURNAL, **77**, 6159 (1955).

(7) I. Nakagawa and S. Mizushima, *Bull. Chem. Soc. Japan*, in press.

(8) S. Mizushima, I. Nakagawa and J. V. Quagliano, *J. Chem. Phys.*, **23**, 1367 (1955).

(9) D. N. Sweeny, I. Nakagawa, S. Mizushima and J. V. Quagliano, THIS JOURNAL, **77**, 889 (1955).

ing and finally disappears completely. The assignment of this band to one of the nitrito stretching frequencies seems reasonable. The band at 1430 cm.$^{-1}$, however, grows in intensity on aging the sample. As described above, this band is identified with the unsymmetrical stretching vibration of the nitro ligand.

In the spectrum of $[Co(NH_3)_5NO_2]Cl_2$, the broad shouldered absorption band with a peak at 1315 cm.$^{-1}$ results from an overlapping of the two peaks previously assigned to the symmetric nitro and the symmetric ammonia vibrations. A comparison of the spectrum of $[Co(NH_3)_5NO_2]Cl_2$ with the superposition of the spectra of $Na_3[CO(NO_2)_6]$ and $[Co(NH_3)_6]Cl_3$ which show absorption bands at 1338 and 1333 cm.$^{-1}$, respectively, makes this evident. Only a single relatively sharp band, however, appears in this region for the freshly prepared nitrito complex. It has been shown that the nitrito isomer on standing several days at room temperature gives rise to an absorption spectrum almost identical with the spectrum of the pure nitro compound. This experimental result can be explained as a change in the coördinating group from (Co–ONO) to (Co–NO_2).

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Infrared Absorption Spectra of Inorganic Coördination Complexes. VIII. Normal Vibrations of Tetracyanoplatinate(II) Ion[1]

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The infrared absorption spectra of potassium tetracyanoplatinate(II) have been recorded over the range from 2 to 40 μ. In addition to the characteristic peak observed at about 2100 cm.$^{-1}$, there were observed several peaks in the low frequency region. The frequency values of these peaks, together with those of the known Raman lines in the same region, can be brought into good agreement with the values of the calculated normal frequencies of the complex cyanide ion. The calculation was made as a nine-body problem on the basis of the Urey–Bradley field.

Introduction

An understanding of the nature of the metal–ligand bonds in complexes is of fundamental significance in the study of coördination compounds. Investigations of the infrared absorption of metal cyanide complexes offer an interesting problem in this field, since these compounds are expected to show relatively simple spectra. Specifically, cyanide frequencies are present at about 2100 cm.$^{-1}$, but no other fundamentals would be expected to appear until the KBr region, where the metal to ligand bond frequencies appear in the vibrational spectra. That such is actually the case may be expected from the Raman studies of Mathieu[3] who calculated only the A_{1g} vibration of the skeleton. Later, this calculation of skeletal motions was improved by Maccoll,[4] using the modified valence–force field but still regarding C≡N as a dynamical unit. However, the nine-body calculation is not very difficult and, as has been shown in previous papers,[5] the Urey–Bradley field is much more suitable to explain the vibrational spectra of such a molecule. Therefore, the normal frequencies were calculated as a nine-body problem using this field, and the computed frequencies have been compared with those obtained in the present investigation, in the region from 5000 to 250 cm.$^{-1}$ (2 to 40 μ).

Experimental

Preparation of Compounds.—Potassium tetracyanoplatinate (II) trihydrate, $K_2Pt(CN)_4 \cdot 3H_2O$, was prepared (a) according to the method of Meillet.[6]

The analysis was carried out on sample dried in an Abderhalden drier at 110° for 3 days. *Anal.* Calcd. for $K_2Pt(CN)_4 \cdot {}^3/_5H_2O$: C, 12.51; N, 14.56. Found: C, 12.46; N, 14.56.

(b) The compound was also prepared according to the method of Claus.[7] This preparation gave a product spectroscopically identical with that of the analyzed sample (a). In the region of the OH stretching frequency some slight differences exist which probably are attributable to different degrees of hydration in the two samples investigated.

Absorption Measurements.—Spectra were obtained by means of a Perkin–Elmer, model 21, infrared spectrophotometer, using CaF_2, NaCl, KBr and CsBr prisms. Preparation of potassium bromide disks was carried out according to the direction of Stimson and O'Donnell.[8] The disks were used for observation in the region of 2 to 24 μ, and the resulting spectra were checked using Nujol mulls of these compounds. In the spectrum of $K_2Pt(CN)_4 \cdot 3H_2O$ obtained by the potassium bromide disk technique a few absorption peaks were observed in the region between 1500 and 600 cm.$^{-1}$ which should not appear according to our calculations. The positions and intensities of these peaks depend upon the previous history of the sample. It has been possible to demonstrate that these absorption peaks are due to the water of crystallization and can be avoided by dehydrating the material at 197° *in vacuo*. Unusual optical behavior of hydrated planar $Pt(CN)_4^=$ complex compounds has been reported.[9,10] Tetrahedral metal cyanide complexes examined in this Laboratory do not show these additional absorption peaks.

Beyond 24 μ the Nujol mull technique was employed; however, KBr disks can be used conveniently up to about 32 μ.

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[1] For paper VII in this series see THIS JOURNAL, **78**, 887 (1956).

[2] (a) Presented in part before the 126th meeting of the American Chemical Society, September, 1954. Supported in part under AEC Contract AT(11-1)-38, Radiation Project of the University of Notre Dame. Abstracted in part from the Ph.D. Thesis of D. M. Sweeny, Notre Dame, 1955. (b) Visiting Professor, from the Faculty of Science, University of Tokyo.

[3] J. Mathieu, *J. chim. phys.*, **36**, 308 (1939).

[4] A. Maccoll, *Proc. Roy. Soc. N.S.W.*, **77**, 130 (1943).

[5] T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949); see also reference 12.

[6] A. Meillet, *J. Pharm. Chim.*, [3] **3**, 444 (1843).

[7] C. Claus, *Ann.*, **107**, 132 (1855).

[8] M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952); see also J. P. Faust and J. V. Quagliano, *ibid.*, **76**, 5346 (1954).

[9] L. A. Levy, *J. Chem. Soc.*, **93**, 1446 (1908).

[10] S. Yamada, *Bull. Chem. Soc. Japan*, **24**, 125 (1951).