which were identified by reference to known X-ray diffraction patterns. In cases where a compound of apparently similar nature has been reported, the reference is given. As suggested by Cox and Sharpe,[2] however, some of these may be open to question. Preliminary tests, for example, indicate some differences in color and infrared spectra between the iron(III) complexes prepared from water and from methanol.

A number of metals did not produce fluorometallates. Barium, strontium and calcium precipitated the corresponding metal fluoride. Thallium, selenium, tellurium and antimony bromide solutions gave no precipitate with ammonium fluoride. Mercury(II) appears to form a complex bromide, and lead bromide is too insoluble in methanol. Some metals, such as vanadium, niobium, molybdenum and uranium, produce ammonium oxy- complexes which will be discussed separately.

All complexes give usable X-ray powder patterns, but in some cases only after digestion. Analytical data were also found to improve following digestion either in pure methanol, or in a methanol solution of ammonium fluoride.

Little as yet is known as to the mechanism of the bromination of metal in methanol, or as to the species present in the methanol solutions of the metal bromides. The work of Bradley, Caldwell and Wardlaw[7] with tin(IV) chloride in various alcohols suggests the presence of species such as $SnCl_x(OR)\text{-}ROH$, a suggestion which also appears valid for work we are doing with niobium and vanadium.

DURHAM, N. H.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The *cis–trans* Isomerization of Dihydroxo- and Diaqua-bis-ethylenediamine-cobalt(III) Ions

BY JAMES YING-PEH TONG AND PETER E. YANKWICH

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The rate of isomerization of dihydroxo-bis-ethylenediamine-cobalt(III) ions is independent of hydroxide concentration at hydroxide concentration greater than 0.01 M and increases rapidly as hydroxide concentration becomes less than 10^{-3} M. The total rate constant of isomerization, $(k_c + k_t)$, of the dihydroxo ions in solutions 1 M in ionic strength and 0.01 M or greater in hydroxide concentration has been determined at 35.03° to be 0.155 $(\text{hr.})^{-1}$. The total rate constant of isomerization of the diaqua-bis-ethylenediamine-cobalt(III) ions in 1 M perchloric acid has been determined at 24.84° to be 0.0249 $(\text{hr.})^{-1}$. Since the reaction rates were reported by others to be irreproducible when different preparations were used, synthetic procedures have been modified and the preparations have been tested for kinetically active impurities. The rates have been found to be reproducible when different preparations of purified reactants were used.

Introduction

During a recent study of the alkaline hydrolysis of *cis*-carbonato-bis-ethylenediamine-cobalt(III) ion,[1] we were unable to isolate the intermediate of the hydrolysis reaction. In seeking to elucidate the second step of the alkaline hydrolysis a straight forward approach would be to investigate the reaction between carbonate ion and the dihydroxo-bis-ethylenediamine-cobalt(III) ions. Before such a study is attempted, however, it is necessary to have detailed knowledge of the *cis–trans* isomerization of the dihydroxo ions, possibly the isomerization of the aqua-hydroxo ions, and of the second acid dissociation constants of the diaqua ions.

Bjerrum and Rasmussen[2] determined the first and second acid dissociation constants of the diaqua ions and estimated the half-life of isomerization to be about 25 hours at 25° in a solution 0.5 M in sodium hydroxide and 0.5 M in sodium nitrate. The rate of isomerization of the aqua-hydroxo ions is much higher[3] and has not been measured quantitatively.

In this paper we report quantitative studies on the hydroxide ion dependence of the rates of isomerization of the dihydroxo ions, the rate of isomerization of the diaqua ions, together with modified synthetic procedures and tests of starting materials for kinetically active impurities.

Experimental

Syntheses.—*trans*-Dichloro-bis-ethylenediamine-cobalt (III) chloride was prepared according to reported method,[4] which was modified as follows: (a) the ethylenediamine solution was added to the cobaltous chloride solution under nitrogen atmosphere and with vigorous stirring, (b) the product was thoroughly washed with ice-cold concentrated hydrochloric acid before it was washed with alcohol and ether. (The duration of air oxidation was found to be greatly reduced by the use of an efficient bubbler.) The product was reprecipitated from an aqueous solution by addition of cold concentrated hydrochloric acid and dried at 100°.

trans-Dichloro-bis-ethylenediamine-cobalt(III) perchlorate was precipitated from an ice-cold solution of the *trans*-dichloro chloride with dilute perchloric acid; the precipitate was washed with ice-cold perchloric acid, alcohol and ether.

Carbonato-bis-ethylenediamine-cobalt(III) perchlorate was prepared from freshly precipitated *trans*-dichloro perchlorate by the method of Linhard and Stirn.[5] The preparation was analyzed for cobalt volumetrically,[6] a weighed sample first being converted to cobalt sulfate for this purpose by a rapid method outlined below (Co, exp. 17.44%; theo. 17.41%). The carbonate content was analyzed by treating a known amount of the compound with a slight excess of standard 0.1 M perchloric acid and back titrating the excess acid after the mixture was boiled gently to expel carbon dioxide ($CO_3^{=}$, exp. 17.75%; theor. 17.72%). The perchlorate content was measured by exchanging the perchlorate ions for chloride ions on an Amberlite IR-400 resin column in the chloride form and determining the chloride content of the eluent gravimetrically (Cl, exp. 10.47%; theo. 10.47%).

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(4) Vera Tupizina, Dissertation, Zurich, 1912; J. C. Bailar, Jr., and C. L. Rollinson, *Inorg. Syntheses*, **II**, 222 (1946).

(5) M. Linhard and G. Stirn, *Z. anorg. Chem.*, **268**, 105 (1952).

(6) J. T. Dobbins and J. P. Sanders, *Ind. Eng. Chem., Anal. Ed.*, **6**, 459 (1934).

cis-Diaqua-bis-ethylenediamine-cobalt(III) perchlorate was found to be extremely soluble in water and attempts to separate it from aqueous solution were not successful. *trans*-Diaqua-bis-ethylenediamine-cobalt(III) perchlorate was prepared by acidifying carefully with concentrated perchloric acid the filtrate of a slurry of silver oxide and *trans*-dichloro chloride near ice temperature. It was recrystallized from a filtered aqueous solution near ice temperature by careful addition of perchloric acid. The yield was quite low and the material was hygroscopic. Attempts also were made to synthesize[7] *cis*-diaqua nitrate from the bromide as Bjerrum and Rasmussen have done[2] with bromide prepared in Werner's manner,[8] but this rather round about way was discarded in favor of the method described below.

Diaqua-bis-ethylenediamine-cobalt(III) nitrate was prepared by treating at about 0° *trans*-dichloro chloride, silver oxide (Fisher purified laboratory reagent) and a small amount of water, filtering the mixture at 0°, and precipitating the product by the addition of excess concentrated nitric acid. *A trans*-rich material (tan colored) was separated from a *cis*-rich material (salmon-red colored) by reprecipitation from an aqueous solution with addition of nitric acid. The tan product was precipitated first and separated by filtration; the red product precipitated later. Each product was washed thoroughly with ice-cold alcohol and ether and kept in a vacuum desiccator over magnesium perchlorate at room temperature. Since *trans* nitrate is less soluble than the *cis* nitrate, relatively pure *trans* salt is easier to obtain than pure *cis* salt; however, isomerization seems to take place even in the solid state and *trans* salt does not remain free from *cis*-isomer. The preparations were analyzed for their cationic equivalence by exchanging the cations for hydrogen ions on an Amberlite IR-120 resin column in the hydrogen ion form and titrating the acid in the eluent with standard 0.1 *M* sodium hydroxide potentiometrically (Exp. red 7.39, tan 7.34; theo. 7.48 meq./g.). The preparations were analyzed for cobalt volumetrically (Co, exp. red 14.9%, tan 15.1%; theo. 14.69%). Elemental microanalysis gave the following results: Red: C, 12.0; H, 5.08; N, 23.9%; tan: C, 12.2; H, 5.12; N, 24.3; theo. C, 11.97; H, 5.025; N, 24.44.

Rapid Conversion of Cobalt Complexes to Cobalt Sulfate.—The following reagents (1 to 5 ml. each) were added to a dry sample (0.5 g.) placed in a 600-ml. beaker (covered with a watch glass) separately and carefully in the order given and the mixture was boiled on a hot plate after each addition to expel gaseous product but *not* to dryness: (a) red fuming nitric acid, (b) 20% fuming sulfuric acid, and (c) water. The beaker was removed from heat and the watch glass and the inside wall of the beaker rinsed down carefully with a small amount of water. The contents were then evaporated to dryness in the open beaker. For the more stable compounds, two treatments may be required *before* the solution is evaporated to dryness. The cobalt sulfate thus formed was removed easily by dissolving in hot water.

Preparation of Solutions.—All chemicals used were of reagent grade. The weights used were calibrated against weights calibrated by the N.B.S. The water used in all experiments was first deionized in a mixed bed ion exchange column and then distilled from a dilute potassium permanganate–sodium hydroxide solution. All glass and quartz vessels were washed promptly after each use with chromic acid–sulfuric acid cleaning solution and drained dry after a final rinse with the specially distilled water.

Sodium perchlorate solution was prepared by neutralizing a sodium hydroxide solution with perchloric acid. The solution was boiled and its *p*H adjusted to about 7 twice. The final solution was filtered hot with a new and cleaned M grade sintered glass filter, and was free from iron. The concentration of sodium perchlorate was determined gravimetrically by evaporating a known volume of solution to dryness and weighing the residue as sodium perchlorate after it was heated to constant weight at 250°.

Carbonate-free standard sodium hydroxide solutions were prepared by diluting pre-standardized commercial reagent grade solution with freshly boiled distilled water. Molar concentrations of all the solutions used were determined at about 25°. The concentrations of solutions at 35° were calculated by multiplying their concentrations at 25° by 0.997 to account for thermal expansion.

Spectrophotometric Equipment and Constant Temperature Baths.—The Beckman quartz spectrophotometer used was converted to the model DU circuit by Mr. V. F. Walters of this Laboratory. The instrument was calibrated with a mercury lamp and the wave length scale found to be within 1 mμ at 579 mμ and within 0.1 mμ at 313 mμ.

Cylindrical spectrophotometric cells with quartz windows were housed in intimate contact with the walls of a hollow brass block thermostated by rapid circulation of water from a constant temperature bath. The temperatures of the baths were determined with a N.B.S. calibrated thermometer to be 24.84 and 35.03° (±0.02°). The cell lengths were found to be 9.985 ± 0.008, 5.018 ± 0.003, 1.993 ± 0.003 and 1.005 ± 0.007 cm., respectively.

The apparent optical densities of a solution containing the cobalt salts and of a similar solution without the cobalt salts (a blank solution) were read using the same cell against air. The difference of the two readings gave the apparent optical density of the cobalt complex ions.

Kinetic Experiments.—A weighed dry sample of the cobalt compound was placed in a 250-ml. erlenmeyer flask with standard 24/40 joint. A solution containing sodium hydroxide (or perchloric acid) with or without sodium perchlorate was placed in a 250-ml. erlenmeyer flask with a long neck bent at 90° and standard 24/40 inner joint. The two flasks were connected without lubricant and partially immersed in the constant temperature bath. At zero time, the flasks were tipped and shaken vigorously to assure thorough mixing.

The reaction was followed spectrophotometrically at 492 mμ (slit width 0.01 mm.) in acidic solutions and at 370 mμ (slit width 0.03 mm.) and 520 mμ (slit width 0.01 mm.) in alkaline solutions. Since the ratio of the molar extinction coefficients, ε, at 492 mμ of the *cis* and *trans* isomers of the diaqua ions is much greater than the ratios at 370 and 520 mμ for the isomers of the dihydroxo ions, it is advantageous to determine the composition of the solution spectrophotometrically in the acidic solutions.[3] With exception of one experiment (Table III, exp. no. 13), all alkaline samples were acidified before spectrophotometric measurements. A measured volume was sampled at 35.0° at given time and delivered into a known volume of perchloric acid and sodium perchlorate mixture at about 20° with vigorous swirling. The final measurements were made at 24.8° within five to ten minutes of the sampling.

The apparent optical densities of the cobalt complex ions, D_t, were measured at given time intervals for one to two half-lives or more of the reaction. Apparent optical densities at "infinite time," D_∞, were measured at a time equivalent to ten half-lives or more. The plots of $\log_e |D_t - D_\infty|$ *vs.* time *t* fitted straight lines within experimental error. Since in each experiment, the hydroxide ion (or the hydrogen ion) concentration remained constant, the linearity indicated that the isomerizations were of first order with respect to the isomer concentrations. The total rate constants, $(k_c + k_t)$, where the subscripts *c* and *t* indicated the reaction from *cis* to *trans* and the reaction from *trans* to *cis*, respectively, were obtained by least squares treatment of equation 1

$$\log_e |D_t - D_\infty| = \log_e |D_0 - D_\infty| - kt \qquad (1)$$

In the present experiments, the optical density at zero time, D_0, was not measured.

Three types of experiments were carried out: (a) *cis-trans* isomerization in 1.00 *M* perchloric acid at 24.84° at various total concentrations of *trans*-rich diaqua nitrate (Table I); (b) *cis-trans* isomerization in alkaline solutions at 35.03° with *trans*-rich as well as *cis*-rich material at various total complex concentrations and hydroxide concentrations at an ionic strength of 1.00 *M* (Table II); (c) *cis-trans* isomerization in alkaline solutions at 35.03° with diaqua perchlorate solutions prepared from carbonato perchlorate at various hydroxide concentrations and ionic strengths (Table III).

Discussion

Bjerrum and Rasmussen[2] reported the half-life for the conversion of *trans*-diaqua ion to the *cis*-diaqua ion, assuming that the reverse reaction is

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[7] The syntheses of the diaqua perchlorate and *cis*-diaqua nitrate (*via* the "brown nitrate" and bromide) were performed by Mr. H. Y. Chen.

[8] A. Werner and G. Jantsch, *Ber.*, **40**, 268 (1907); A. Werner, *ibid.*, **40**, 2119 (1907).

negligible, as

$(NaNO_3)$, M	(HNO_3), M	(Co), M	$t_{1/2}$, hr.
0	0.05	0.00989	15.4
0	.10	.01002	17.0
1.00	.05	.00970	10.6

According to the authors, the experiments were made with their purest preparation of *trans*-diaqua salt and were *reproducible as long as the same preparation was used.* Although our compounds were prepared with great care from recrystallized dichloro chloride, we felt that the question of purity was critical. Three experiments (Table I) were made at 24.84° in 1.00 M perchloric acid with the total complex ion concentration varied over a tenfold range; within experimental error, the rate constant remained constant. This indicates that there are no homogeneous impurities which catalyzed the isomerization by a non-zero order path. In addition, experiment No. 3 was made by diluting ten-fold ten ml. of solution of experiment no. 1 within three minutes after the start of experiment no. 1; the agreement in rate constant within experimental error ruled out the possibility of occurrence of an impurity which was inhomogeneously distributed in the solid state. Experiment no. 2 was made with a different preparation of the complex, but the rate observed agreed with expectation. The average rate constant, $(k_c \pm k_t)$, of isomerization of the diaqua ions is 0.0249 (hr.)$^{-1}$ (probable error $\pm 4.3 \times 10^{-5}$, average residual ± 0.0011). Since the equilibrium in acidic solution greatly favors the *cis*-isomer,[2] $k_t >> k_c$. The half-life of conversion of *trans*-isomer to *cis*-isomer is 27.8 hr. A closer comparison with Bjerrum and Rasmussen's data is limited by differences in media and temperature.

In alkaline solutions at constant ionic strength of 1 M and approximately constant total complex ion concentration of 0.0025 M, the rate of isomerization was independent of hydroxide concentration between 1 and 0.001 M but was several times as great at a hydroxide concentration near 0.001 M. Almost identical experiments were made starting with *cis*-rich material (Table IIa) and starting with *trans*-rich material (Table IIb). Experiments of similar hydroxide concentrations were run simultaneously. Instrumental difficulties during experiments 4, 6, 9 and 10 (which were made simultaneously) were such that the computed rate constants are based on somewhat fewer points than those for the other runs in these tables. The optical densities at infinite time in experiments 9 and 10 were computed from experiments 4 and 6, respectively. The *trans*-rich material seemed to give a slightly higher rate although much of the discrepancy may be due to experimental scattering. The greater difference at 10^{-3} M sodium hydroxide was probably due to the greater sensitivity of the rate to the hydroxide concentration and the larger uncertainty in hydroxide concentration. Since the net hydroxide concentration in all the tables is the difference between added sodium hydroxide concentration and twice the concentration of the complex ions, the lower the net hydroxide concentrations the greater the uncertainties.

TABLE I

Starting material, *trans*-rich nitrate; reaction temperature 24.84°; $(HClO_4) = 1.00$ M

Exp. no.	1	2	3
Total (complex), M	0.01166	0.00517	0.001166
Ionic strength, M	1.07	1.03	1.006
$(k_c + k_t)$,[9] hr.$^{-1}$	0.0265	0.0237	0.0244
ϵ_∞	77.6	81.5	79.4
Probable error[10] $r \times 10^5$	5.9	7.0	2.9

TABLE IIa[11]

Starting material, *cis*-rich nitrate; reaction temperature 35.03°; ionic strength 1.00 M, $(NaNO_3)$ = 2 total (complex)

Exp. no.	4	5	6	7	8
(NaOH), M	0.992	0.947	0.0946	0.00986	0.00102
$(NaClO_4)$, M	0	0	.897	.982	.991
Total (complex), M	0.00240	0.0248	.00257	.00255	.00248
$(k_c + k_t)$, hr.$^{-1}$	.156	.141	.129	.140	.479
ϵ_∞	47.3	44.6	45.8	44.4	45.9
$r \times 10^3$	2.6	0.49	5.2	3.4	23.8

TABLE IIb[11]

Starting material: *trans*-rich nitrate; reaction temperature 35.03°C. Ionic strength 1.00 M $(NaNO_3)$ = 2 total (complex)

Exp. no.	9	10	11	12
(NaOH), M	0.992	0.0946	0.00986	0.00102
$(NaClO_4)$, M	0	.0897	.982	.991
Total (complex), M	0.00237	.00255	.00255	.00248
$(k_c + k_t)$ hr.$^{-1}$	.168	.176	.175	.353
ϵ_∞			44.7	45.9
$r \times 10^3$	3.6	10.5	3.8	20.3

TABLE III

Starting material, *cis*-rich diaqua perchlorate solutions; reaction temperature 35.03°

Exp. no.	13	14	15	16	17
(NaOH), M	0.795	0.747	0.0466	0.00717	0.00142
$(NaClO_4)$, M	.1022	.125	.476	.913	.964
Total (complex), M	.00301	.00374	.0143	.0106	.00968
Ionic strength, M	.900	.876	.537	.930	.975
$(k_c + k_t)$, hr.$^{-1}$	.129 .129	.148	.144	.166	.341
ϵ_∞	73.8 69.5	44.6	43.5	44.6	45.0
Wave length, mμ	370 520	492	492	492	492

In addition, the total complex concentration was varied tenfold between experiments 5 and 6. Although the two experiments differed slightly in hydroxide concentration, since there was probably no hydroxide dependence in this region, the agreement in rate indicated that the *cis*-rich material was free from catalytically active impurities.

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(9) Probable error in $(k_c + k_t)$, r, was calculated with equation 2 based on equations given by Birge[10]

$$r = 0.6745 \left[\frac{n\Sigma v^2/(n-2)}{n\Sigma t^2 - (\Sigma t)^2}\right]^{1/2} \quad (2)$$

where n is the number of observations, t the time, and v the residual

$$v = y_{\text{obsd}} - y_{\text{calcd}} \quad (3)$$

where

$$y = \log_e |D_t - D_\infty| \quad (4)$$

(10) R. T. Birge, *Phys. Rev.*, **40**, 207 (1932).

(11) Sodium nitrate was the product of neutralization of diaqua-bis-ethylenediamine-cobalt(III) nitrate by sodium hydroxide. Since two moles of sodium nitrate was liberated per mole of dihydroxo nitrate formed, $(NaNO_3)$ = 2 total (complex).

The apparent extinction coefficient at infinite time, ϵ_∞, was that of the acidified solution at 25°.

Table III lists some exploratory experiments made with *cis*-rich diaqua perchlorate solution prepared from acid hydrolysis of carbonato-bis-ethylenediamine-cobalt(III) perchlorate. The carbonato perchlorate was prepared with an additional step of purification (precipitation of dichloro perchlorate). In addition it was a much more stable, less hygroscopic, and better defined compound than the diaqua nitrates. The perchlorate is also free from contamination of silver compounds as well as nitrate ions. Direct comparison with other data may not be justified except possibly for experiments 16 and 17 because of the difference in ionic strength. The agreement with other experiments made with different preparations (within the limitation of ionic strength difference) is quite good. The much larger difference in experiment 17 is probably due to uncertainty in hydroxide concentration.

The average of the seven rate constants of dihydroxo ion isomerization at hydroxide concentration of 0.01 M or greater is 0.155 (hr.)$^{-1}$ (probable error ± 0.0019, average residual ± 0.016) at 35.03°. Bjerrum and Rasmussen[2] estimated from one experiment (three points) the isomerization rate constant, $(k_c + k_t)$, to be 0.0274 (hr.)$^{-1}$ in a solution 0.5 M in sodium nitrate and 0.5 M in sodium hydroxide at 25°. If the difference between nitrate and perchlorate media is small and if both constants are correct, the reaction would have a very large temperature coefficient, corresponding to $E_{\text{exp}} = 31.5$ kcal.mole^{-1} and $\Delta S^* = +21.4$ e.u.; though the activation energy seems a little high, the entropy of activation is clearly of the proper sign and magnitude. It is interesting to note that our rate in acid solution is lower than theirs and our rate in alkaline solution seemed to be much larger than that to which theirs would extrapolate. It should also be pointed out that in their experiments, the rate in acid solution was measured with *trans* salt and the rate in alkaline solution was measured with *cis* salt. Since they prepared the two salts by two different methods, there was the possibility that the two preparations might have been contaminated in different ways.

Experimentally the criterion of purity (constancy of absorption spectra upon repeated recrystallization) used by Bjerrum and Rasmussen was not sufficient for kinetic studies. The rigorous test of starting material for absence of impurities which catalyze reactions by non-zero order mechanism is the independence of rate on the initial concentration of the starting material. We believe that the syntheses and purifications described above have resulted in relatively catalyst-free compounds.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Structure of Some Aquated Dicyanoammine-nickel(II) Clathrates

BY RUSSELL S. DRAGO, JOON T. KWON AND RONALD D. ARCHER

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On the basis of an X-ray investigation and a reported value for the magnetic moment, a structure was proposed for the dicyanoammine-nickel(II) clathrate of benzene which contained a paramagnetic, square planar, nickel(II) atom. Since planar nickel(II) atoms are usually diamagnetic, it is possible that the benzene, instead of being trapped in the crystal lattice, is interacting with the nickel to produce a paramagnetic tetragonal atom. The magnetic data have been redetermined and the infrared spectra examined to provide additional structural information. The spectra indicate that water is present in these clathrates. The absorption frequencies of benzene and pyrrole attributed to in-plane vibrations are identical in both the clathrate and the pure liquid but those attributed to out-of-plane vibrations are different. A structure containing trapped benzene is proposed which is compatible with the X-ray work and is also compatible with the magnetic moment of 2.1 Bohr magnetons obtained in this study.

Introduction

The preparation of the dicyanoammine-nickel(II) clathrate of benzene was first reported by Hoffman and Kuspert.[1] Subsequently, clathrates of this type containing pyrrole, furane, thiophene, pyridine, phenol and aniline were prepared.[2] A single crystal X-ray investigation was undertaken on the benzene compound[3,4] and the large distance between the carbon atoms of benzene and the atoms of the caging material was interpreted to mean that the organic molecules are not bonded but are simply trapped in the crystal lattice. A structure based on the X-ray findings and a magnetic moment[4,5] of 2.32 Bohr magnetons, was proposed containing nickel atoms in two different modes of combination, one with an octahedral arrangement of the ligands and the other with a planar arrangement. Since the magnetic data were interpreted to indicate that all the nickel atoms are paramagnetic, an attempt was made to rationalize a planar, paramagnetic nickel atom, but the arguments presented are not convincing. The proposed interpretation does not preclude the possibility of weak interaction between an edge of the benzene molecule and the z-axis of the planar nickel atom producing a structure containing only paramagnetic nickel atoms. Infrared and magnetic investigations of some of these clathrates, especially those containing organic molecules which are good elec-

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[1] K. A. Hoffman and F. Kuspert, *Z. anorg. Chem.*, **15**, 204 (1897).

[2] K. A. Hoffman and H. Arnold, *Ber.*, **39**, 339 (1906); K. A. Hoffman and F. Hoechtlen, *ibid.*, **36**, 1149 (1903).

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[4] J. H. Rayner and H. M. Powell, *J. Chem. Soc.*, 319 (1952).

[5] D. Craig, Thesis, University of Sydney, 1942.