with C^{14} substitution in the carboxyl group.[17] All parameters were adjusted to maximize the result within the limits of reasonable force constants and other molecular parameters. The resulting 14% effect exceeds all well established observations, consequently there is no reason to question statistical rate theory. There is no difficulty in the selection of other reasonable parameters which yield smaller isotope effects.

The basic formula used by various workers is

$$\frac{k}{k'} = \left(\frac{\mu'}{\mu}\right)^{1/2} \left[1 + \sum_{i=\mathrm{i}}^{3N-6} G(u_{\mathrm{i}})\Delta u_{\mathrm{i}} - \sum_{j=\mathrm{i}}^{3N-7} G(u_{\mathrm{j}}^{\ddagger})\Delta u_{\mathrm{j}}^{\ddagger}\right]$$

where k is a rate constant, μ a reduced mass for the reaction coördinate, the primes indicate the isotopically substituted species, and the G's and u's are the functions defined by Bigeleisen and Mayer.[18] In the earlier calculation of one of us,[16] it was assumed that substitution of C^{14} (or C^{13}) in the carboxyl group which is *not* undergoing reaction would have no effect on the rate. In the formula this arises because, for any vibration in the non-reacting portion of the molecule, there are corresponding $G(u)\Delta u$ terms in the first sum for the initial molecule and in the second sum for the activated complex. If the binding of the non-reacting portion of the molecule is unchanged in the activated complex, then these terms are equal and cancel. Actually, it is quite possible that the binding in these non-reacting portions of the molecule may change. Certain calculations[19] have been published, however, in which mathematical approximations yield spurious effects for isotopic substitution in the non-reacting carboxyl group.

[17] An erroneous statement that this calculation is not applicable to the intramolecular isotope effect is made by Bigeleisen in ref. 3c.

[18] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

[19] Bigeleisen (references cited in 3c) neglects the second sum of $G(u)\Delta u$ (for the activated complex) and thus fails to obtain the cancellation of terms for the stretching vibration of the bond which is not broken.

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Residual Paramagnetism and the Susceptibility of Some Isoelectronic Cobaltammines

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RECEIVED NOVEMBER 5, 1954

The molar magnetic susceptibilities of $[Co(NH_3)_5HCO_2]I_2$ and $[Co(NH_3)_5NO_2]I_2$ were determined by the Gouy method to be $(-72.0 \pm 4.6) \times 10^{-6}$ and $(-45.2 \pm 2.5) \times 10^{-6}$, respectively. "Residual paramagnetism" of Co(III) appears to be $+141 \times 10^{-6}$ and $+165 \times 10^{-6}$, respectively, in contradiction to the prediction of Rosenbohm of $+60 \times 10^{-6}$ for each. Observations of Proctor and Yu on the shift of the nuclear resonance frequency of cobalt in cobalt complexes lead us to suggest the existence of low lying excited electronic levels for these two complexes to account for the observed small diamagnetism.

In the interpretation of the magnetic moments of complex compounds, it is assumed that the several atoms contribute additively to the magnetic susceptibility independent of the nature of the complex. In his extensive investigation of cobalt(III)-ammine complex compounds, Rosenbohm[2] found that a constitutive correction had to be included for Co(III) if conventional diamagnetic increments were to be used for the other atoms. His corrections were $+55 \times 10^{-6}$ for hexammines, $+60 \times 10^{-6}$ for pentammines, and $+73 \times 10^{-6}$ for tetrammines. We question whether such a constant constitutive correction can have validity since it ignores the specific effect of coördinated groups on the electronic distribution in the entire complex. We have therefore measured the magnetic moments of two isoelectronic cobalt(III)-ammines, $[Co(NH_3)_5NO_2]\ I_2$ and $[Co(NH_3)_5HCO_2]I_2$. Since the nitro group and the formato group are similar in structure and isoelectronic, they should contribute approximately equally to the diamagnetism. With the same constitutive correction applied to each complex because they are both pentammines, we are led to expect that the susceptibilities of these two compounds would differ only by the very small difference in the diamagnetism of a nitro group and a formato group.

Experimental

Preparation of Compounds.—Formatopentamminecobalt(III) iodide was made according to the method of Yatsimirski[3] from chloropentamminecobalt(III) chloride, potassium formate and KI. Nitropentamminecobalt(III) iodide was made according to the method described by Walton[4] for the preparation of $[Co(NH_3)_5NO_2]^{++}$ from chloropentamminecobalt(III) chloride, followed by precipitation with a saturated solution of KI. During purification by repeated crystallization, all of the nitrito salt $[Co(NH_3)_5ONO]I_2$ was converted to the more stable nitro salt $[Co(NH_3)_5NO_2]I_2$.

Cobalt content was determined by the Volhard method as described by Treadwell and Hall[5] and modified by Streuli.[6] The salts were ignited to oxide and slowly digested in concentrated H_2SO_4. Slow digestion using a barely warm hot plate and infrared heating gave pink $CoSO_4$ after 10–12 hours. A final oven bake for one hour at 450–500° drove off all acid and water. The temperature of the final baking must be regulated carefully to prevent formation of oxide from the sulfate.

Iodine content was determined by the method described by Treadwell and Hall[7] using excess nitrite salt, acid and urea.

Results of the analyses are compared in Table I with theoretical values. The experimental values given are on the basis of four analytical determinations in triplicate on the formato salt and three determinations in triplicate on the nitro salt.

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[1] General Electric Company, Pittsfield, Massachusetts.

[2] E. Rosenbohm, *Z. physik. Chem.*, **93**, 693 (1919).

[3] K. Yatsimirski, *Zhurnal Obshchei Khimii*, **20**, 1408 (1950).

[4] H. Walton, "Inorganic Preparations," Prentice-Hall, New York, N. Y., 1948, p. 92.

[5] F. Treadwell and W. Hall, "Analytical Chemistry," Vol. II, 9th Ed., John Wiley and Sons, New York, N. Y., 1942, p. 603.

[6] C. A. Streuli, Thesis, Cornell University, Ithaca, N. Y., 1950.

[7] Reference 5, Vol. II, 8th Ed., 1935, p. 134.

TABLE I

ANALYTICAL RESULTS FOR COMPLEX COBALT COMPOUNDS

Compound	Co, % Exptl.	Co, % Theor.	I, % Exptl.	I, % Theor.
$[Co(NH_3)_5HCO_2]I_2$	13.43	13.31	57.58	57.30
$[Co(NH_3)_5NO_2]I_2$	13.28	13.27	57.34	57.18

Magnetic Measurements.—Magnetic susceptibilities of the powders were determined by the Gouy method. Samples weighing approximately 10 g. were measured with a semimicro balance sensitive to 0.05 mg. The magnetic field calibration with 30% $NiCl_2$ solution and with proton resonance already has been described by Conroy and Sienko.[8] The difficulty in reproducing sample alignment mentioned in that investigation was decreased by repolishing the pole faces of the electromagnet. In the recalibrated field, the check determination on freshly distilled water gave for the gram susceptibility $(-0.713 \pm 0.009) \times 10^{-6}$ compared to the best literature[9] value of -0.720×10^{-6}.

In order to obviate a correction for oxygen gas, the complex salts were ground up, the sample tube was filled, and the weighings were all performed in a nitrogen atmosphere. All measurements were at 22°. Duplicate determinations at different field strengths ranging from 3000 to 8000 gauss indicated no ferromagnetic impurities.

Results

The magnetic susceptibilities observed are given in Table II. The value quoted for $[Co(NH_3)_5HCO_2]I_2$ is the result of 56 determinations on six samples. The value for $[Co(NH_3)_5NO_2]I_2$ comes from 27 determinations on two samples.

TABLE II

EXPERIMENTAL MAGNETIC SUSCEPTIBILITIES AT 22°

Compound	Molar susceptibility	Probable error
$[Co(NH_3)_5HCO_2]I_2$	-72.0×10^{-6}	$\pm 4.6 \times 10^{-6}$
$[Co(NH_3)_5NO_2]I_2$	-45.2×10^{-6}	$\pm 2.5 \times 10^{-6}$

Discussion

The magnetic moments quoted in Table II indicate a small but real difference between $[Co(NH_3)_5NO_2]I_2$ and $[Co(NH_3)_5HCO_2]I_2$, contrary to the prediction after Rosenbohm. Furthermore, the small magnitude of the magnetic moments indicates that the "residual paramagnetism" or constitutive correction for these cobalt(III) pentammines is much larger than observed by Rosenbohm for other cobalt(III) pentammines. We have considered the possibility that a trace of divalent cobalt impurity accounts for our observations. However, cobalt(II) complexes are easily oxidized and would probably not survive our purification procedure. In addition, the cobalt analysis does not support the presence of such an impurity. To account for the observed difference in molar susceptibility, we would require about 3 mole % of cobalt(II) impurity in the nitro salt. If the impurity were in some such form as $[Co(NH_3)_5H_2O]I_2$ or $[Co(NH_3)_6]I_2$, the cobalt analysis would be higher than theoretical. However, it is actually in the formato salt that the cobalt analysis is higher than theoretical—where the presence of divalent cobalt is not consistent with the larger diamagnetism. To account for the large "residual paramagnetism," we would require approximately 20 mole % of cobalt(II) impurity in both salts. Such a large impurity is inconsistent with our analytical results.

The actual value of the "residual paramagnetism" is sensitive to the choice of diamagnetic increments for the other portions of the complex compound. We have used for diamagnetic increments the values listed in Table III. Using these values, we calculate for the expected molar susceptibility of $[Co(NH_3)_5NO_2]I_2$ a value of -210×10^{-6} and of $[Co(NH_3)_5HCO_2]I_2$, -213×10^{-6}. To make these additive values agree with the experimental ones, we need a constitutive correction for Co(III) of $+165 \times 10^{-6}$ and $+141 \times 10^{-6}$, respectively, compared to Rosenbohm's prediction of $+60 \times 10^{-6}$.

TABLE III

MOLAR DIAMAGNETIC CORRECTIONS

Group	$\chi \times 10^6$	Source
I^-	-50.6	Brindley and Hoare[10]
NH_3	-17.1	Gray and Farquharson[11]
NO_2^-	-13.1	Trew[12]
HCO_2^-	-16.7	Stoner[13]
Co^{+++}	-10.0	Klemm[14]

It is indeed unfortunate that the idea of a constitutive correction or "residual paramagnetism" has gained such a firm foothold in the interpretation of data on complex compounds. It is true that in the case of organic compounds, the constitutive corrections as developed by Pascal have been amazingly successful in retaining the idea of additivity of diamagnetic increments. But for inorganic complexes, where just the idea of additivity runs counter to the concept of a complex ion as a whole instead of a collection of pieces, the "residual paramagnetism" leads to embarrassingly large values which must be assigned to the central atom.

"Residual paramagnetism" can arise from either (1) quenching of diamagnetism or (2) second-order paramagnetism or both. Quenching of diamagnetism may occur when groups are distorted enough by their neighbors so that the group presents a smaller cross-sectional area to the applied external field. Such distortion of the electronic distribution would have to be enormous to account for our observations. A simple calculation using Slater's one-electron wave functions[15] shows that if only the inner shells of the iodide ions remain active diamagnetically, we already have more diamagnetism than is actually observed.

A more cogent reason for discarding the quenching of diamagnetism as a possible source of the "residual paramagnetism" comes from the recent work of Proctor and Yu[16] on the shift of the nuclear resonance frequency of the cobalt nucleus in various cobalt(III) complexes. For $K_3Co(CN)_6$, $Na_3Co(NO_2)_6$ and $K_3Co(C_2O_4)_3$, resonance is observed at the relative frequencies 1.0000, 1.0074 and 1.0130, respectively, indicating that in the complex the nuclear moment of cobalt is shielded from the external field more fully by the oxalate than by the nitro than by the cyanide groups. This is the or-

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[8] L. E. Conroy and M. J. Sienko, THIS JOURNAL, **74**, 3520 (1952).

[9] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 28.

[10] G. W. Brindley, *Phil. Mag.*, **11**, 786 (1931).

[11] F. W. Gray and J. Farquharson, *ibid.*, **10**, 191 (1930).

[12] V. C. G. Trew, *Trans. Faraday Soc.*, **32**, 1660 (1936).

[13] E. C. Stoner, *Proc. Leeds Phil. Soc.*, **1**, 484 (1929).

[14] W. Klemm, *Z. anorg. allgem. Chem.*, **246**, 347 (1941).

[15] See the excellent review by Myers, *Rev. Mod. Phys.*, **24**, 25 (1952).

[16] W. G. Proctor and F. C. Yu, *Phys. Rev.*, **81**, 20 (1951).

der we would predict since it represents the order of decreasing diamagnetism. In other words, apparently the diamagnetism of the ligands is significantly retained in the complex and is not quenched.

However, as Proctor and Yu suggest, the mere diamagnetic effect is not large enough to explain these large shifts in resonance frequency. Instead, these authors are led to assume "the existence of electronic energy levels very close to that of the ground state" an assumption which is justified by a temperature dependence[16] of the resonant frequency. These low lying electronic energy levels correspond, as Ramsey points out,[17] to those encountered in Van Vleck's second order paramagnetism.

In the case of the pentammine complexes measured in this work, we can therefore account for the high "residual paramagnetism" by assuming low lying excited states. In going from the nitro complex to the formato complex, it will not be surprising to find an appreciable change in magnetic moment since the magnetic susceptibility depends not only on the nature of the excited state but also on its symmetry. The symmetry may be particularly important since the orbital quenching of the moment in the excited state is very sensitive to the electrical symmetry in the complex.

Measurements on the nuclear magnetic resonance of cobalt in these complexes would be of great interest as also would be a study of the temperature dependence of both the magnetic susceptibility and the nuclear resonance shift.

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[17] N. F. Ramsey, *Phys. Rev.*, **86**, 245 (1952).

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Thermodynamic Properties of Sodium Borohydride and Aqueous Borohydride Ion

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RECEIVED NOVEMBER 8, 1954

From isotonic measurements the dissociation pressure of sodium borohydride dihydrate at 25° is 6.23 mm. and the activity of water in its saturated (14.9 molal) aqueous solution is 0.294. From these results the standard free-energy change at 298°K. of the reaction $NaBH_4(s) = Na^+ + BH_4^-$ is -5660 ± 70 cal., leading to a value of $+28.6 \pm 0.1$ kcal. for the standard free energy of formation of BH_4^-(aq.). The standard entropy of the ion is estimated at 25.5 ± 1 e.u. The properties of sodium borohydride are compared to those of the sodium halides and discussed in terms of ionic radius and polarizability. The polarizability of borohydride in its alkali salts is 3.94 Å.^{3}

The increasing use of the alkali borohydrides[1] as reducing agents makes accurate knowledge of their thermodynamic properties desirable. The free energies of solid anhydrous $LiBH_4$ and $NaBH_4$ are known from the thermochemical measurements of Davis, Mason and Stegeman[2] and the heat capacity studies of Johnston and Hallett,[3] but reliable figures for the aqueous borohydride ion have not yet been published. We have measured by a simple isotonic method the dissociation pressure of sodium borohydride dihydrate[1] and the activity of water in its saturated solution at 25°. From these results we have computed the solubility product of the anhydrous salt and thus obtained the standard free energy of the aqueous borohydride ion.

In its physical behavior, borohydride ion resembles the halide ions much as ammonium ion resembles the alkali ions. Its ionic radius[4] of 2.03 Å. lies between those of bromide and iodide ions, but its polarizability (see below) is slightly less than that of bromide. From these facts we are able to estimate the entropy of the aqueous borohydride ion by several independent methods, as well as to discuss the thermodynamic properties of its alkali salts in comparison to those of the halides.

We have also attempted to determine the solubility product of the dihydrate by studying equilibria between an aqueous phase and solid solutions of $NaBH_4{\cdot}2H_2O$ with $NaBr{\cdot}2H_2O$ and $NaI{\cdot}2H_2O$, which form in all proportions. However, the solid solutions displayed sufficient departure from ideal behavior to preclude accurate evaluation of the equilibrium constant, and we merely remark that the results were in rough agreement with that obtained by the direct method.

Experimental

Sodium borohydride (Metal Hydrides, Inc., Beverly, Mass., "Research" grade, *ca.* 90% $NaBH_4$) was recrystallized from Eastman isopropylamine by two methods. Large crystals (5 mm.) of high purity (99.5% $NaBH_4$) were obtained by dissolving the crude salt in the solvent at reflux, cooling and filtering and allowing to stand in a filter flask connected to a Dry Ice–acetone trap. After most of the solvent had passed into the cold trap, crystals were removed with forceps, washed with dry ether and dried under vacuum. Smaller crystals (*ca.* 0.5 mm.) of slightly lower purity (99.0% $NaBH_4$) were obtained in much shorter time by charging the crude salt to the thimble of a Soxhlet extractor, adding about twice the volume of solvent necessary to fill the thimble and start the siphon, and extracting for about 8 hours. The crystals that formed in the flask were removed by filtration and washed and dried as before. The small crystals were used for most of our experiments.

Analyses for borohydride by hydrogen evolution[1] according to the reaction

$$BH_4^- + H^+ + 3H_2O = H_3BO_3 + 4H_2(g)$$

were performed in an all-glass apparatus by slowly dropping 6 *N* HCl into a magnetically stirred solution of the sample in 0.5 *N* NaOH. The water level in the 100-ml. gas buret was periodically adjusted by a levelling bulb, the final adjustment to atmospheric pressure being made a few minutes after hydrogen evolution had ceased. Successive determinations on a given sample usually checked to within 0.5%. Several check analyses were also performed by the acidimetric method,[2] which however tends to give high results.

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[1] H. I. Schlesinger, H. C. Brown and collaborators, THIS JOURNAL, **75**, 186 (1953).

[2] W. D. Davis, L. S. Mason and G. Stegeman, *ibid.*, **71**, 2775 (1949).

[3] H. L. Johnston and N. C. Hallett, *ibid.*, **75**, 1467, 1496 (1953).

[4] S. C. Abrahams and J. Kalnajs, *J. Chem. Phys.*, **22**, 434 (1954).