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A Spectrophotometric Study of the Niobium Catecholato Complexes[1]

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RECEIVED DECEMBER 22, 1958

Using spectrophotometric techniques the products of the reaction of niobium pentoxide and catechol in basic solution have been studied. In 0.01 molar catechol solution the predominant species was found to be $[NbO(cat)]^+$. The formation constant for this species at a *p*H of 10 was determined to be 540. The ammonium salt of the complex was isolated and its formula found to be $(NH_4)_3[NbO(cat)_3]\cdot 2H_2O$. Using the KBr wafer technique the infrared spectrum was determined. In addition to the yellow niobium catecholato complex formed in basic solution, a red colored complex was observed to be produced in concentrated sulfuric acid solutions.

The first niobium–catechol complex was reported in 1932 by Rosenheim and Roehrich[2] who found that freshly precipitated niobium pentoxide could be dissolved in boiling alkaline catechol to form a yellow solution. They reported the isolation of several niobium containing complex salts, among them being $K_2H[NbO(cat)_3]\cdot 2H_2(cat)\cdot 3H_2O$, $(NH_4)_2H[NbO(cat)_3]\cdot {}^1/_2H_2(cat)\cdot 3H_2O$ and $(NH_4)_3[NbO(cat)_3]\cdot 9H_2O$.[3]

Shapiro (1938)[4] and Gillis (1944)[5] described qualitative tests for niobium, utilizing the yellow color developed with catechol in strong sodium acetate solution. In 1946, Karyakin and Telezhnikova reported that the yellow color produced was developed only in alkaline medium.[6]

Tomicek and Jerman, in 1952, outlined a quantitative colorimetric procedure for niobium analysis using the yellow coloration formed with catechol in basic ammonium oxalate solution. These workers reported the extinction maximum for the complex to be around 400–440 mμ.[7]

Because of the scarcity of concrete information concerning the chemical constitution of the yellow niobium–catechol complex in solution, it was the purpose of this investigation to determine the nature of the complex by spectrophotometric analysis, as well as to isolate the complex and elucidate some of its properties. With a logarithmic analysis similar to that used by Kingery and Hume[8] and methods developed by Newman and Hume[9] it was possible to show that a definite complex was present in the range of solution concentrations studied and to calculate a formation constant.

Experimental

Measurements.—Absorption measurements in the visible and ultraviolet regions were made with a Beckman DK-2 Automatic Recording Spectrophotometer. A pair of matched 1 cm. silica cells fitted with 0.9 cm. silica plugs was used for all measurements. A reference blank was used in all cases, and its preparation and composition were identical with the complex solution except that the niobium was missing. The measurements were made at room temperature.

The infrared absorption measurements were made with a Perkin-Elmer Model 21 double beam Infrared Spectrophotometer with NaCl optics. The KBr wafers were formed at 16 tons ram pressure in a Beckman 6223 KBr die.

All *p*H measurements were made with a Beckman Model GS *p*H meter, equipped with a calomel and glass electrode. The instrument was standardized against a special buffer solution supplied by the manufacturer.

Materials.—Catechol (Eastman Practical Grade) was purified by vacuum distillation and then recrystallization from toluene.

Solutions for ultraviolet absorption studies were prepared as follows: 0.025 g. of Nb_2O_5 (Fairmount Chemical Co. Newark, N. J.) was fused in a Vycor crucible with 1–2 g. of $KHSO_4$. After cooling slightly the still warm crucible was added to 200 ml. of hot 2% HCl solution on a hot plate. The precipitated oxide was digested for 30 minutes, then filtered on a büchner funnel using Whatman No. 42 filter paper. The oxide was washed with 200 ml. of hot water, followed by an acetone rinse. Air was pulled through the precipitate until the odor of acetone was no longer detectable. This hydrous oxide then was placed in a 250-ml. round bottom flask containing 150 ml. of 0.01 molar catechol, prepared by dissolving the appropriate amount of solid in stock (100 g./l.) Na_2SO_3 solution. (Note—this stock Na_2SO_3 solution was used in place of water in preparing and/or diluting all solutions.) After 15–20 minutes of gentle refluxing, the Nb_2O_5 dissolved to form a bright yellow solution which, after cooling, was filtered and made up to an exact volume of 250 ml. An aliquot of this solution was analyzed for Nb.

Solutions were then prepared for spectrophotometric scan as follows: using a buret, six 10-ml. portions of the complex solution were measured into small ground glass-stoppered bottles. Varying amounts of the catechol solution and Na_2SO_3 solution were then added in order to bring the catechol concentrations of the respective solutions to 4×10^{-3}, 5×10^{-3}, 6×10^{-3}, 7×10^{-3}, 8×10^{-3} and 9×10^{-3} molar, each containing the same molar concentration of niobium (1.68×10^{-4}). In exactly the same manner, six reference solutions were prepared, differing only from the first in that they contained no niobium.

The absorption curves of these solutions are shown in Fig. 1.

In the niobium catechol solutions the large and fixed concentration of Na_2SO_3 was necessary to maintain the required constant *p*H and ionic strength and also to serve as an antioxidant. Even so, reproducible absorption curves could only be produced by taking into account the age of the catechol solutions. That the spectra of catechol solutions change with time was demonstrated by preparing two solutions of 10^{-4} molar catechol, one in distilled water, the other in the stock Na_2SO_3 solution (*p*H 9.9). These solutions were scanned immediately in the spectrophotometer and then scanned again at 12-hour intervals. The neutral solution showed invariant absorption over a 60-hour period, while the absorbance maximum in the Na_2SO_3 solution not only increased, but shifted toward longer wave lengths. By standardizing the procedure, so that approximately the same length of time elapsed between preparation of solution and absorption measurement, molar extinction coefficients were duplicated within 0.3%.

The Isolation of the Complex.—To a solution of 5 g. of catechol in 50 ml. of concd. NH_4OH contained in a three-neck flask, there was added 2 g. of freshly precipitated,

(1) Based upon Shirley A. Brown's M.S. thesis research. Presented at the Southeastern Regional Meeting of The American Chemical Society, December 11–13, 1958.

(2) A. Rosenheim and E. Roehrich, *Z. anorg. allgem. Chem.*, **204**, 342 (1932).

(3) The symbol (cat) has been employed throughout this paper for the catecholato ligand, $C_6H_4O^{-2}_2$.

(4) M. Ya. Shapiro, *J. Appl. Chem. (U.S.S.R.)*, **11**, 1028 (1938).

(5) J. Gillis, *Mikrochem., Mikrochim. Acta*, **31**, 273 (1944).

(6) Yu. V. Karyakin and P. M. Telezhnikova, *J. Appl. Chem. (U.S.S.R.)*, **19**, 435 (1946).

(7) O. Tomicek and L. Jerman, *Chem. Listy*, **46**, 144 (1952).

(8) W. D. Kingery and D. N. Hume, THIS JOURNAL, **71**, 2393 (1949).

(9) L. Newman and D. N. Hume, *ibid.*, **79**, 4571 (1957).

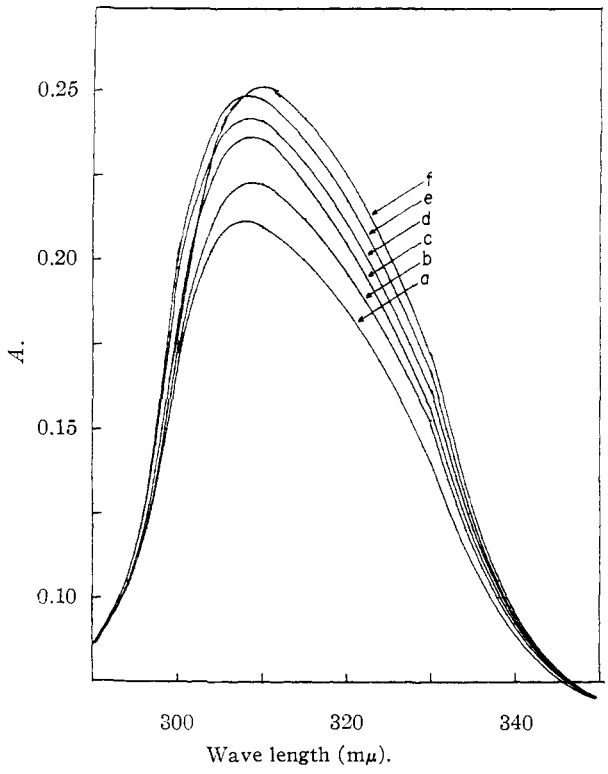

Fig. 1.—Absorption spectra of solutions 1.68×10^{-4} molar in Nb and containing amounts of catechol as follows: (a) 4×10^{-3} molar; (b) 5×10^{-3} molar; (c) 6×10^{-3} molar; (d) 7×10^{-3} molar; (e) 8×10^{-3} molar; (f) 9×10^{-3} molar.

hydrous Nb_2O_5 and 2 g. of $Na_2S_2O_5$ dissolved in 20 ml. of water. N_2 purified O_2 was bubbled through the mixture which was heated for 10–15 minutes, during which time the color deepened from light yellow to a yellow-orange. When the majority of the oxide had dissolved, the heat was removed and a glass tube leading to a small empty flask was inserted in the reaction flask. The N_2 bubbler was replaced by a simple inlet tube and using N_2 pressure, the clear, hot, supernatant liquid was forced into the empty flask. The flask was stoppered quickly and allowed to cool, whereupon the complex crystallized as yellow needles.

After cooling in ice, the complex was filtered quickly with suction, washed once with a small portion of ice water, rinsed several times with anhydrous, peroxide-free, diethyl ether, and stored in a vacuum desiccator containing Drierite. The golden yellow color of the freshly prepared crystals soon changed to a deeper yellow-orange.

Anal. Calcd. for $(NH_4)_3[NbO(cat)_3]\cdot 2H_2O$: C, 41.31; H, 5.35; N, 8.03; Nb, 17.77. Found: C, 40.70; H, 5.36 N, 8.33; Nb, 18.08.

Analytical.—Analysis of niobium-containing catechol solutions was accomplished spectrophotometrically, utilizing the absorption of the Nb–HCl complex at 281 mμ.[10] An aliquot of the solution to be analyzed was placed in a Vycor crucible, and acidified with concd. H_2SO_4. The solution was then evaporated to near dryness. Several more drops of concd. H_2SO_4 were added, along with a few drops of 30% H_2O_2. The crucible then was heated gently until the solution was clear and no carbon remained. If, at this point, the volume was over 1 ml. heating was continued to drive off excess H_2SO_4. When the volume of liquid remaining was very small, the crucible was removed from the heat and rotated slowly, so that the liquid melt would solidify along the side of the crucible. After cooling, the solid melt was dissolved in 100 ml. of concd. HCl. This HCl solution containing the dissolved Nb melt was placed in a ground glass-stoppered cuvette and an identical HCl reference solution was placed in a matched cell. The absorbance was determined at 281 mμ, and from a previously prepared standardization chart, the molar concn. of the Nb was calculated.

The isolated ammonium salt of the complex was analyzed for Nb by placing a weighed sample in a previously weighed crucible. The crucible was heated slowly at first and finally to red heat to drive off all carbon and volatile matter. The residue was weighed as Nb_2O_5.

The carbon, hydrogen and nitrogen analyses were performed by Galbraith Laboratories of Knoxville, Tenn.

(10) J. H. Kanzelmeyer and H. Freund, *Anal. Chem.*, **25**, 1807 (1953).

Results and Discussion

The curves in Fig. 1 show an increase in absorption with increasing catechol concentration. Some irregularities were noted in the region of the peak at 309 mμ, which were felt to be due to minute and uncontrollable differences in catechol concentrations between sample and reference cells, as the latter absorbs strongly in this region. To minimize these effects all calculations were made from absorbance readings at 323 mμ, since here it was reasonable to assume that only the complex species was absorbing.

In Fig. 2 (curve 1) these absorbances were plotted against increasing catechol concentrations,

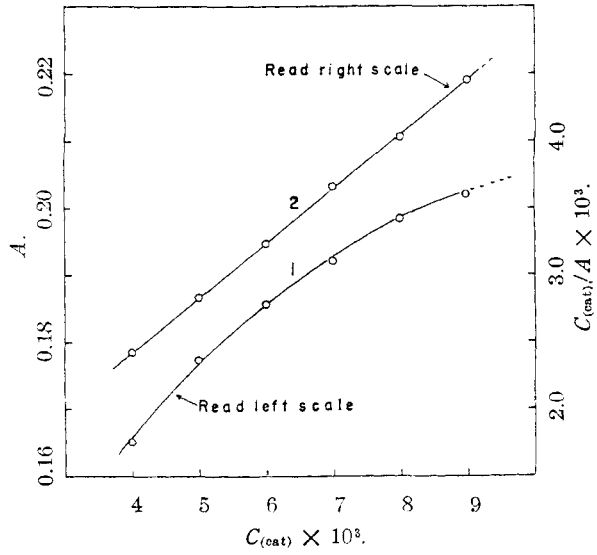

Fig. 2.—Curve 1, absorbance as a function of catechol concentration; curve 2, catechol concentration divided by absorbance as a function of catechol concentration.

where it is obvious that the absorbance has not leveled off and the complex species is still partially ionized. Graphical extrapolation of this curve to a limiting absorbance, A_0, was not feasible; however, an analytical method[11] can be employed successfully for its evaluation. A plot of $C_{(cat)}/A$ *vs.* $C_{(cat)}$ (Fig. 2, curve 2) gives a good straight line. On rearranging the equation of this straight line, it was noted that A equals the reciprocal of the slope of the line when $C_{(cat)}$ approaches infinity. A_0 was computed by this method to be 0.2470, and this value consequently allowed the calculation of the concn. of the complex species, MX_n, and the species with which it was in equilibrium, *i.e.*, X, the catecholate ion, and MX_{n-m}, which was either the hydrated NbO^{+++} ion or a lower complex species.

(11) W. B. Bunger, private communication.

If the formation of this species, MX_n, be represented by the equation

$$MX_{n-m} + mX = MX_n$$

then k_n; the formation constant, is given by

$$k_n = (C_{MX_n})/(C_{MX_{n-m}} \times C_X^m)$$

or the logarithmic form is

$$\log (C_{MX_n}/C_{MX_{n-m}}) = m \log (C_X) + \log (k_n)$$

Thus, a plot of $\log(C_{MX_n}/C_{MX_{m-n}})$ against $\log(C_X)$ should give a straight line with slope "m" and an intercept equal to $\log(k_n)$. This treatment was applied to the data found in these determinations and the results are shown in Fig. 3. This curve is a straight line with a slope of 1.0 and $k_n = 540$.

These results showed only that one ligand group was involved in this step and not necessarily that the complex contained just one catecholate ion per Nb atom. It can be demonstrated that our equation is simply a variation of eq. C13 of Newman and Hume,[9] so two species were present in solution with one absorbing. Further verification of this was obtained when the data were substituted into eq. C12 of Newman and Hume,[9] and a straight line was obtained with a slope of 502 and an intercept of zero. The slope of their eq. C12 equals k_n and agreed reasonably with the previous value, 540, computed from our equation. Under these conditions this latter value was considered more accurate since it was derived using the equilibrium rather than the total catecholate ion concentrations. As evidenced by the intercept of zero, the second species was not absorbing.

If another complex species, MX_{n-m}, was present, then another formation constant could be defined as

$$k_{n-m} = (C_{MX_{n-m}})/(C_{MX_{n-m-p}} \times C_X^p)$$

(This is eq. C2 of Newman and Hume[9].) Substitution of our data in eq. C11b of Newman and Hume produced a straight line with the slope, $1/(k_n k_{n-m})$, equal to zero. Such meant that k_{n-m} equaled infinity, which could only be true if the term $C_{MX_{n-m-p}}$ in the above equilibrium equation was also zero.

These arguments would indicate that only the equilibrium as represented by k_n was present and the highest form of the complex present under these concentrations was the $[NbO(cat)]^+$ ion.

The yellow, solid complex isolated from a concentrated ammonium catecholate solution was found to contain three ligands, but no "catechols of crystallization" or as many hydrate waters as reported by Rosenheim and Roehrich.[2] This compound was noted to be very soluble in water, acetone and ethanol; moderately soluble in ethyl acetate; insoluble in diethyl ether, carbon tetrachloride, benzene, nitrobenzene and 1,4-dioxane.

A water solution of this compound scanned as quickly as possible after preparation produced a spectrum similar to that of basic catechol with a broad peak at 290 mμ, but in addition a small shoulder centered at 340 mμ. The absorption curve of a 95% ethanol solution gave a pronounced peak at 340 mμ, then sloped off gradually to the 290–300 mμ region before rising again as the wave length decreased. It must be concluded that the 340 mμ peak was the absorption band of the highest complex, which was stabilized in the 95% ethanol solution, whereas in the water it immediately hydrolyzed to the lower forms and free catecholate ions. Also it was noted that the water solution started to discolor in about one hour while the ethanol solution showed constant absorbance as measured on the spectrophotometer after 36 hours.

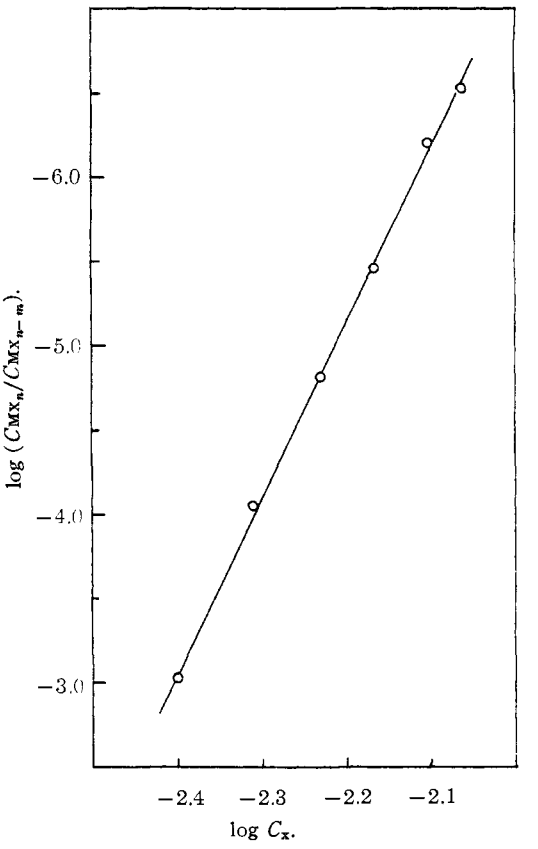

Fig. 3.—Determination of the formation constant, k_n, with two species present and one absorbing.

The infrared spectrum of this solid ammonium oxotricatecholatoniobate(V) dihydrate compound, using the KBr wafer technique, showed a small absorption peak at 10.9 μ which was believed to be due to the NbO bond.[12]

It has been reported[6] previously that the complex only forms in basic solutions. However, in this research it was found that when solid catechol was added to a solution of niobium in 18 molar H_2SO_4, a deep red color developed. This color, which definitely depends upon the Nb concentration, fades slowly on standing and is destroyed by dilution. The nature of this complex was not determined.

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(12) H. A. Szymanski and J. A. Archibald, THIS JOURNAL, **80**, 1811 (1958).