TABLE IV

SUMMARY OF DIFFERENCES IN 2 LOG K_{av} FOR Ni(II), Pb(II) AND Zn(II) WITH A NUMBER OF REAGENTS

Reagent	Metal ions compared and relative stability order	Difference in 2 log K_{av} at 25.0°
6-Mercaptopurine	Pb > Zn	0.5
6-Hydroxypurine	Zn > Pb	0.6[a]
o-Aminobenzenethiol[14]	Pb > Zn	1.3
o-Aminophenol[14]	Zn > Pb	0.7
6-Mercaptopurine	Zn > Ni	1.4
6-Hydroxypurine	Zn ≥ Ni	2.3[a]
o-Aminophenol[14]	Ni ≥ Zn	0.2
Mercaptoacetic acid[16]	Zn > Ni	1.5[b]
β-Mercaptopropionic acid[19]	Zn > Ni	3.2[b]
6-Aminopurine	Zn ≥ Ni	0.4[a]
Ammonia[2]	Zn > Ni	1.2[b,c]

[a] Hydrolysis interferes. [b] In water. [c] At 30° in water.

Pb > Zn > Ni > Co and for 6-hydroxypurine: Cu > Zn, Ni > Pb.

The change in the relative position of lead and zinc in these two compounds is similar to that which was reported by Charles and Freiser with *o*-aminobenzenethiol and *o*-aminophenol,[14] and would seem to reflect a general trend in sulfur-containing reagents.

Concerning the relative positions of zinc and nickel in the 6-mercaptopurine sequence the order may also be attributed to the participation of the sulfur atom in the bonding of the purine–metal complex. Further evidence that zinc(II) forms a stronger complex than nickel(II) when sulfur is involved in the ligand metal bond has been presented by Leussing[18] on the stabilities of mercaptoacetic acid–metal complexes and by Fernando and Freiser[19] on the stabilities of β-mercaptopropionic acid–metal complexes.

Acknowledgment.—The authors gratefully acknowledge the financial assistance of the U. S. Public Health Service.

(18) D. L. Leussing, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1958.

(19) Q. Fernando and H. Freiser, THIS JOURNAL, **80**, 4928 (1958).

PITTSBURGH, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Synthesis and Spectra of Some Chromium(III) Complexes with 2-Methyl-1,2-propanediamine[1a,b]

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Conventional methods for the synthesis of tris-(ethylenediamine)-chromium(III) compounds (and some propylenediamine analogs), when isobutylenediamine (ibn) is used instead of ethylenediamine, generally have been found either to give no reaction or to yield bis-(ibn) complexes. Five new complex compounds have been isolated and characterized by chemical analyses and spectral methods: *trans*-$[Cr(ibn)_2(NCS)_2]SCN$, ox(ibn)Cr-ox-Cr(ibn)ox, $[H_2O(ibn)_2Cr\text{-}O\text{-}Cr(ibn)_2H_2O](SO_4)_2\cdot 7H_2O$, $[(ibn)_2Cr\text{-}(OH)_2\text{-}Cr(ibn)_2](ClO_4)_4$ and $[(ibn)_2Cr\text{-}(OH)_2\text{-}Cr(ibn)_2]Cl_4$. Spectral studies have shown that the latter complex undergoes interesting spectral transformations in aqueous solutions made weakly basic, similar to changes exhibited in the rapid conversion of the acidic rhodo cation to basic rhodo cation and the slower subsequent change to the erythro ion. Evidence was obtained for the existence of the $Cr(ibn)_3^{+3}$ ion. Chromium(III) forms complexes with ibn much less readily than with ethylenediamine or propylenediamine. The tendency of chromium(III) amines to form "ol" or "diol" bridges is greatly accentuated with ibn.

Chromium(III) complexes with ibn are of interest because this unsymmetric, optically inactive 1,2-diamine ligand implies the possible existence of eight diacidobis-(ibn) isomers (2 *trans* and 3 pairs of *d*- and *l*-*cis* isomers), possibly permitting a distinction among different mechanisms of substitution and isomerization reactions of chromium complexes. Apparently no such complexes have been reported in the literature, although compounds of Co(III),[2,3] Ni(II),[4] Cu(II),[4] Pd(II)[5,6] and Pt(II)[6,7] with ibn have been described. From studies[8–11] of some chromium(III) and many cobalt(III) complexes with en, C-substituted en and diamines with three or more methylene groups between the two amine groups, the stability of the complexes with five-membered chelate rings is known[11–13] to be much greater than for complexes with six or more atoms in the ring. Alkyl substitution at the carbon atoms usually affects only slightly the complexing properties of the 1,2-diamines (evidence mainly from cobalt complexes), whereas large effects are sometimes encountered with similar C-substitutions in 1,3-diamines, as for 2,2-dimethyl-1,3-propanediamine (neopentanediamine), a much

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(1) (a) Abbreviations used: ibn = 2-methyl-1,2-propanediamine (isobutylenediamine); pn = 1,2-propanediamine (propylenediamine); en = ethylenediamine; py = pyridine; ox = oxalato. (b) Work partly supported under Contract AT(11-1)-34, Project 12, between the U. S. Atomic Energy Commission and the University. (c) On leave of absence from the Technical University of Denmark, Copenhagen.

(2) F. Basolo, THIS JOURNAL, **75**, 227 (1953).

(3) R. G. Pearson, C. R. Boston and F. Basolo, *ibid.*, **75**, 3089 (1953).

(4) F. Basolo, Y. T. Chen and R. K. Murmann, *ibid.*, **76**, 956 (1954).

(5) A. G. Lidstone and W. H. Mills, *J. Chem. Soc.*, 1754 (1939).

(6) H. Reihlen and W. Hühn, *Ann.*, **489**, 42 (1931).

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(8) F. Basolo, *Chem. Revs.*, **52**, 459 (1953).

(9) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice–Hall, Inc., New York, N. Y., 1952.

(10) J. C. Bailar, Jr. (editor), "The Chemistry of the Coördination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956.

(11) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

(12) C. L. Rollinson and J. C. Bailar, Jr., THIS JOURNAL, **65**, 250 (1943).

(13) J. C. Bailar, Jr., and J. B. Work, *ibid.*, **68**, 232 (1946).

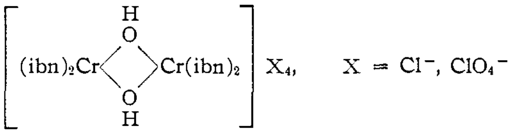
better complexing agent than 1,3-propanediamine (trimethylenediamine).[13] Thus, one might expect by analogy that the 1,2-diamines en, pn and ibn would not differ significantly in their complexing with chromium(III).

We have attempted to prepare certain diacidobis-(ibn)-chromium(III) compounds in connection with kinetic studies of aquation and other reactions of the isomers of a given diacidobis-(ibn) cation. These attempts have revealed interesting differences between ibn on the one hand and en and pn on the other in their complex formation with chromium(III) and have resulted so far in the isolation of five new chromium(III) complex compounds.

Results and Discussion

Thermal decomposition of tris-(en)-chromium (III) compounds, catalyzed by ammonium salts,[14] yields the *cis*- or *trans*-diacidobis-(en) salts depending on the anion present. In order to obtain the tris-(ibn) compounds required for attempts to prepare the diacidobis-(ibn) complexes by the above method, we tried syntheses anlogous to those successful for the tris-(en) complexes (and tris-(pn) complexes in some cases). These methods involve reaction of the anhydrous diamine under suitable conditions with an anhydrous chromium(III) salt such as the sulfate (or dehydrated chrome alum), chloride, tris-(py)-chromium(III) chloride, tris-(en)-chromium(III) chloride and hexamminechromium(III) nitrate. However, treatment of these chromium compounds with excess dried ibn even for several weeks at temperatures up to 110° gave blue-violet bis-(ibn) complexes. Usually only oily products resulted from attempts to isolate compounds from the reaction mixtures.

When anhydrous chromium(III) sulfate or chloride was used, violet solids could be isolated, the analyses and properties of which (see Spectra and Experimental) imply that previously unreported polynuclear complexes with oxo or hydroxo bridges were formed. The crystals obtained from the sulfate can be represented satisfactorily by the formula $[H_2O(ibn)_2Cr{-}O{-}Cr(ibn)_2H_2O](SO_4)_2 \cdot 7H_2O$, and those from the chloride by the formula



$$\left[(ibn)_2Cr\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{\langle\rangle}}Cr(ibn)_2\right]X_4, \quad X = Cl^-, ClO_4^-$$

If charcoal was used as a catalyst (platinum black was found ineffective) in the synthesis from anhydrous chromium(III) chloride, small amounts of a yellow complex were left after the violet compound formed was extracted with ethanol. Although the yellow complex was produced in very low yields and tended to disappear soon because of hydrolysis, it could be extracted into ice-cold water acidified with hydrochloric acid (color changed fairly rapidly to a red-violet if left alone). Cold dioxane could be added to slow the hydrolysis enough to allow taking the absorption spectrum. The presence of the previously unreported tris-(ibn)-chromium(III) cation was revealed by comparison with the remarkably similar spectra of the tris-(en) and tris-(pn) salts in aqueous solution (Fig. 1). Attempts to precipitate the tris-(ibn) cation were unsuccessful except with potassium hexathiocyanatochromate(III), which gave a chocolate-colored solid, presumably $[Cr(ibn)_3][Cr(SCN)_6]$. Addition of this solid to bismuth(III) nitrate solution precipitated red $Bi[Cr(SCN)_6]$, leaving a yellow solution apparently containing the $Cr(ibn)_3{}^{+3}$ ion (in presence of excess Bi^{+3}). Attempts to concentrate the tris-(ibn) solutions by cation-exchange resins are underway in the hope of ultimately isolating a solid tris-(ibn) compound.

Anhydrous chromium(III) iodide mixed with excess dried ibn gave an immediate red color, turning red-yellow after 10 hr. at 100°. Extraction with acetone, followed by evaporation, left only a red smear. Dissolution in acetone and addition of ether precipitated a yellow solid which formed an oil inside of several minutes on exposure to air.

Tris-(py)-chromium(III) chloride is a convenient starting material for preparing tris-(en)[15] and tris-(pn)[16] compounds, and the tris-(diamines)[17,18] of 1,2-cyclohexanediamine and 1,2-cyclopentanediamine. We found that an excess of ibn reacts with the tris-(py) compound on refluxing, as shown by the formation of red-violet solutions and the odor of py released from the original complex. No crystalline compound could be isolated.

Refluxing excess dried ibn for at least 8 hr. with tris-(en)-chromium(III) chloride or hexamminechromium(III) nitrate gave no evidence of reaction.

In an attempt to adapt the method of Jørgensen,[19] used for preparing hexamminechromium(III) chloride, we treated by this method solutions of chromium(II) chloride (or acetate) with excess ibn. Blue amines were formed, but upon oxidation in the absence of air only violet solutions were obtained.

Anhydrous potassium hexathiocyanatochromate(III) reacts with pn to give the tris-(pn) thiocyanate,[16] whereas with en *trans*-dithiocyanatobis-(en)-chromium(III) thiocyanate results, with only minute amounts of the tris-(en) thiocyanate being formed.[20] With ibn, we were able to get only the analogous dithiocyanatobis-(ibn) compound. This previously unreported complex is presumably one of the two possible *trans* isomers (no evidence was obtained for the presence of more than one of these two isomers) inasmuch as its absorption spectrum strongly resembles those of the homologous *trans* en and pn compounds (Fig. 1); moreover, the aqueous solution of the complex, when treated with chlorine at 0°, exhibited an absorption spectrum similar to that of *trans*-dichlorobis-(en)-chromium(III) cation and the analogous *trans*-pn complex, although isomerization during the chlorination cannot be excluded. The compound isomerizes and hydrolyzes in aqueous solution at separate measurable

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(14) C. L. Rollinson and J. C. Bailar, Jr., "Inorganic Syntheses," Vol. II, W. C. Fernelius, editor, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 200.

(15) P. Pfeiffer, *Z. anorg. Chem.*, **24**, 279 (1900).

(16) P. Pfeiffer and M. Haimann, *Ber.*, **36**, 1063 (1903).

(17) F. M. Jaeger, *Proc. Acad. Sci. Amsterdam*, **40**, 108 (1937).

(18) F. M. Jaeger and L. Bijkerk, *Z. anorg. Chem.*, **233**, 97 (1937).

(19) S. M. Jørgensen, *J. prakt. Chem.*, [2] **30**, 1 (1884).

(20) P. Pfeiffer, *Ber.*, **34**, 4303 (1901).

rates (we are currently studying the kinetics of these reactions), and loss of the third *trans* absorption band with concomitant formation of a typical *cis* spectrum (before aquation has occurred appreciably) is further evidence that the original complex is a *trans* isomer.

Werner[21] prepared *cis*-dichlorobis-(en)-chromium(III) chloride from aqueous en and potassium trioxalatochromate(III) by a series of steps leading through $[Cr(en)_2ox][Cr(en)(ox)_2]$ to $[Cr(en)_2ox]Cl$, from which the desired compound was then made. When we followed this procedure, using ibn instead of en, we isolated in the first step a crystalline compound which we first assumed from its red-violet appearance and method of synthesis to be $[Cr(ibn)_2ox][Cr(ibn)(ox)_2]$. In the subsequent steps no crystalline solid could be isolated, however. Analysis of the red-violet compound gave results in good agreement with the composition ox(ibn)Cr-ox-Cr(ibn)ox. That this previously unreported compound is a non-electrolyte is supported by the fact that none of it is adsorbed from aqueous solution by Dowex 1-X8 anion-exchange resin and only a small amount is adsorbed by Dowex 50-X8 cation-exchange resin under conditions where these two resins adsorb $[Cr(en)_2ox][Cr(en)(ox)_2]$ completely (splitting it 1:1 between the two resins). Absorption spectra are shown in Fig. 3.

In another attempt to prepare diacidobis-(ibn)-chromium(III) complexes directly, we tried a 10% aqueous solution of ibn in place of a solution of en in treating dihydroxodiaquobis-(py)-chromium(III) chloride by the method of Pfeiffer,[22] which has been used successfully for preparing diacidobis-(en) complexes. The strong odor of py produced indicates that ibn can displace py from the complex, but solids could not be isolated from the sirupy violet mixtures obtained with ibn.

It is evident from all of the above that chromium(III) in general forms complexes much less readily with ibn then with en or pn. The apparent difficulty of forming tris-(ibn) compounds appears to be primarily a steric effect of the two methyl groups of ibn which make the introduction of a third ibn ligand on the chromium cation difficult (as is readily seen with Fischer–Hirschfelder molecular models) and not an effect of basicity since the base constants of ibn[23] are only slightly less than those of en[24] and pn.[23] The tendency of chromium(III) amines to form "ol" or "diol" bridges appears to be greatly accentuated with ibn.

Spectra of Luteo and *trans*-Dithiocyanatobis-(diamino) Cations.—Curves A, B, C and D of Fig. 1 show the strong resemblance among the visible absorption spectra of the luteo ions in aqueous solution. Shapes of the spectra and relative positions of the two absorption maxima are the same, the spectra being only somewhat differently placed along the wave length scale. The relative wave lengths of the lower-energy (longer wave length) maximum for the four luteo ions are in agreement with our observation that en and pn, but not ibn, can displace ammonia from hexamminechromium(III) cation. This feature is also displayed by the spectra of the *trans*-dithiocyanatobis-(diamino) cations (curves E, F, G, Fig. 1).

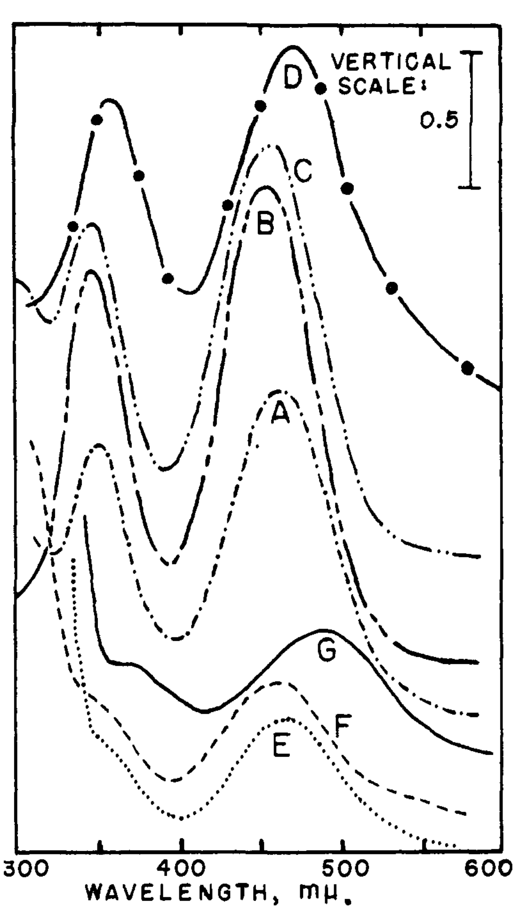

Fig. 1.—Absorption spectra of luteo and *trans*-dithiocyanatobis-(diamino) cations in aqueous solution: A, 0.0311 *f* $[Cr(NH_3)_6](NO_3)_3$, (1.22); B, 0.0251 *f* $[Cr(en)_3]Cl_3$, *p*H ~3, (1.76); C, 0.0187 *f* $[Cr(pn)_3](SCN)_3$, *p*H ~3, (1.50); D, $Cr(ibn)_3^{+3}$ in cold ~1:1 dioxane-water, *p*H ~1, (1.39); E, 0.00700 *f* *trans*-$[Cr(en)_2(NCS)_2]SCN$, (0.50); F, 0.00660 *f* *trans*-$[Cr(pn)_2(NCS)_2]SCN$, (0.48); G, 0.00507 *f* *trans*-$[Cr(ibn)_2(NCS)_2]SCN$, (0.45); numbers inside parentheses give the absorbancy at the long wavelength maximum of each curve.

Spectra of Hydroxo-bridged Cations; Effect of Base.—The hydroxo-bridged complexes of Fig. 2 exhibit certain interesting features. The strong similarity between the absorption spectra (curves D, A) of the $[(en)_2Cr\text{-}(OH)_2\text{-}Cr(en)_2]^{+4}$ and $[(ibn)_2\text{-}Cr\text{-}(OH)_2\text{-}Cr(ibn)_2]^{+4}$ cations in aqueous solution is additional support for the structure assigned to the latter ion. In weakly acid solution these two cations, together with the acidic rhodo complex, $[(NH_3)_5Cr\text{-}OH\text{-}Cr(NH_3)_5]^{+5}$, undergo color changes when the solution is made weakly basic, the color changing at once from red-violet to deep blue and then more slowly returning to nearly the original color. Recently, this change from the blue basic rhodo cation to the erythro product has been shown[25] to be a replacement of one of the ten

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[21] A. Werner, *Ber.*, **44**, 3132 (1911).

[22] P. Pfeiffer, *ibid.*, **40**, 3828 (1907).

[23] F. Basolo, R. K. Murmann and Y. T. Chen, THIS JOURNAL, **75**, 1478 (1953).

[24] J. Bjerrum and P. Andersen *K. Danske Vidensk. Selsk. Math-fys. Medd.*, **22**, No. 7 (1945).

[25] W. K. Wilmarth, H. Graff and S. T. Gustin, THIS JOURNAL, **78**, 2683 (1956).

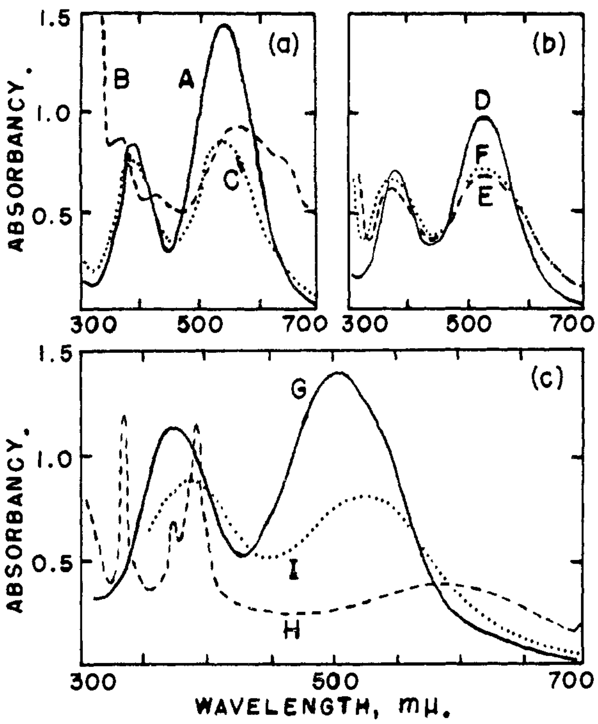

Fig. 2.—Absorption spectra of hydroxo-bridged cations in aqueous solution, showing effect of base (solutions cooled to $\sim$5° before being made basic, then measured at once): (a) [(ibn)$_2$Cr-(OH)$_2$-Cr(ibn)$_2$]Cl$_4$—A, $\sim$0.007 *f* complex in $\sim$0.1 *f* HCl (perchlorate salt gave same spectrum); B, made basic (*p*H $\sim$10); C, 2 hr. later; (b) [(en)$_2$Cr-(OH)$_2$-Cr-(en)$_2$]Cl$_4$—D, 0.027 *f* complex in H$_2$O; E, made basic (*p*H $\sim$10); F, 2 min. later; (c) [(NH$_3$)$_5$Cr-OH-Cr(NH$_3$)$_5$]Cl$_5$—G, $\sim$0.017 *f* complex in $\sim$0.05 *f* HCl; H, made basic (*p*H $\sim$9; a small absorption peak at 700 mμ is only partly shown); I, 2 hr. later.

ammonia ligands by a hydroxyl group. For all three binuclear complexes the spectra of the blue "basic" cations are given in Fig. 2 (curves B, E, H), together with spectra of the original ("acidic") and final cations. The change from "acidic" to final cations (curves A, D, G to curves C, F, I, respectively) is characterized in each case by an increase in molar absorbancy index of the shorter wave length peak relative to that of the longer wave length peak; there is also a slight shift in the spectrum toward longer wavelengths except for the ibn complex, for which the shift is negligible apparently because of the weaker complexing of ibn.

The spectral peculiarities exhibited in Fig. 2 during the above reactions in weakly basic solution are interesting. Like the blue basic rhodo ion, the blue species formed immediately from the tetrakis-(ibn)-μ-dihydroxo ion shows a splitting of the absorption bands; according to the crystal-field theory,[26] such splitting implies an increased asymmetry of the complex ion. The splitting shown in Fig. 2 is greatest for the basic rhodo ion (curve H), less for the ibn complex (curve B) and apparently disappeared for the en complex (curve E), behavior related to the increasingly greater rates of the subsequent reactions affecting the blue cations. (To slow the reactions, spectra of the basic solutions of the en complex, and even the ibn complex, were measured at $\sim$5°, although $\sim$25–80% of the blue intermediates were converted before the spectra could be taken.) The splitting can be explained in terms of conversion of a hydroxo-bridge to an oxo bridge, as is already known[25] to occur with the change of the acidic rhodo ion to its basic form, since the oxo oxygen atom will exert a much stronger effect on the 3d electrons of the chromium atom.[27] Since the splitting disappears in the further reaction, the degree of symmetry in the original hydroxo-bridged complexes is presumably regained in the final product, although it is not obvious how this occurs.

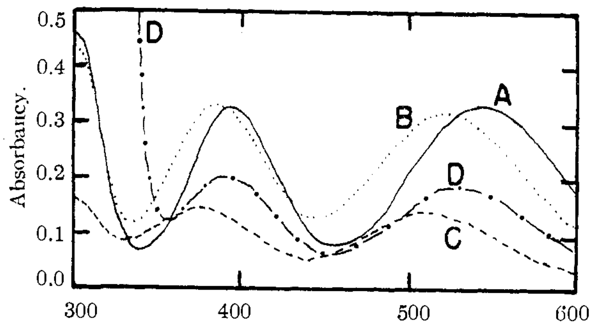

Fig. 3.—Absorption spectra of oxalato complexes in aqueous solution: A, ox(ibn)Cr-ox-Cr(ibn)ox, satd. soln.; B, [Cr(en)$_2$ox][Cr(en)(ox)$_2$], satd. soln.; C, Cr(en)$_2$ox$^+$, eluted from Dowex 50-X8 resin with 6 *f* HCl; D, Cr(en)-(ox)$_2^-$, eluted from Dowex 1-X8 resin with satd. NaNO$_3$.

Spectra of Oxalato Complexes.—Figure 3 gives a comparison between the absorption spectrum of the new compound ox(ibn)Cr-ox-Cr(ibn)ox (curve A) and that of the previously known [Cr(en)$_2$ox][Cr-(en)(ox)$_2$] (curve B) in aqueous solution. The absorption peaks of the former are shifted toward longer wave lengths, in agreement with our finding that ibn is a poorer complexing agent than en. The spectra of the separated Cr(en)$_2$ox$^+$ and Cr-(en)(ox)$_2^-$ ions are also given (curves C, D). No additional peaks were found in the range 600–800 mμ for any of the above species, showing that no significant amount of the original Cr(ox)$_3^{-3}$ was left in the preparations.

Experimental

2-Methyl-1,2-propanediamine.—Several 10-g. lots of this diamine were prepared by reduction of acetone cyanohydrin with lithium aluminum hydride in anhydrous ether.[23,28,29] The yield was only 10–15%. Most of the diamine was donated by Commercial Solvents Corporation, New York. Drying with sodium for two days, and then distillation over sodium, gave the anhydrous diamine. The product was collected at 47–48° (17 mm.); this boiling point is in good agreement with previously reported values.

Anhydrous Chromium(III) Chloride.—Commercial anhydrous chromium(III) chloride (Fisher Scientific Company, St. Louis, Mo.) was found to contain a reducing impurity

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(26) *E.g.*, W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, **7**, 107 (1956).

(27) S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 735 (1955), have studied spectrophotometrically the hydrolysis of the corresponding [(en)$_2$Co-(OH)$_2$-Co(en)$_2$]$^{+4}$ ion in basic solution; no intermediate spectral peculiarities were reported, although the spectra of the cobalt system otherwise closely resembles the chromium analog.

(28) H. Reihlen, G. Hessling, W. Hühn and E. Weinbrenner, *Ann.*, **493**, 20 (1932).

(29) Z. Welvart, *Compt. rend.*, **238**, 2536 (1954).

which caused the formation of oily products in the reaction with ibn. One liter of 10% aqueous potassium dichromate was added to 100 g. of the impure chloride, several ml. of concd. hydrochloric acid added and the mixture brought to a gentle boil with constant stirring for 10 min. The separated solid was washed by boiling with successive 1-liter portions of distilled water until the wash water gave a negative test for chloride ion. The solid was filtered off and dried at 110°; yield ~100%. The purified product showed no reaction with water or hydrochloric acid even after 3 weeks at 25° or 3 hr. at boiling temperature.

Diaquotetrakis-(ibn)-μ-oxodichromium(III) Sulfate 7-Hydrate.—C.P. hydrated chromium(III) sulfate was finely ground, dehydrated by slowly heating to 100° and keeping it at that temperature for 4 days, then grinding the spongy product. With dried ibn there was no evidence of reaction in 2 hr. at ~25°, but with excess ibn (3 ibn:1 Cr) at 100° the mixture became violet within 1 hr. After 3 hr. the mixture was cooled to ~25° and extracted with 1:1 ether–ethanol to give a violet solution which left an oily residue on evaporation. Acidification of the extract to *p*H ~ 1 with hydrochloric acid and addition of more ether gave a violet solid, which was filtered off, washed with ethanol and ether, then dried over concd. sulfuric acid; yield 5–10% (much unreacted chromium(*III*) sulfate left in reaction mixture).

Anal. Calcd. for $[H_2O(ibn)_2Cr{-}O{-}Cr(ibn)_2H_2O](SO_4)_2 \cdot 7H_2O$: C, 19.40; H, 8.50; ignition residue ($Cr_2O(SO_4)_2$), 31.6. Found: C, 19.39; H, 7.36; ignition residue, 30.22.

The crystals dissolved readily in water. The solution turns from violet to a red-violet on acidification with hydrochloric acid; upon making basic with sodium hydroxide the color returns to violet. slowly becoming green. Prolonged boiling with hydrochloric acid in an attempt to break up the bridge structure gave a green glassy solid which turned deep violet on heating.

Tetrakis-(ibn)-μ-dihydroxodichromium(III) Chloride.—Purified anhydrous chromium(III) chloride showed no evidence of reaction with dried ibn within 2 hr. at ~25°, but at 100° a violet substance formed which was insoluble in the ibn. Reaction seemed to stop in 3–4 hr., apparently because the chromium(III) chloride became coated with product; unreacted chloride was still present after 4 weeks of heating with excess ibn at 110° in a sealed tube. Extraction of the reaction mixture with small amounts of water gave a violet solution from which a violet solid separated on addition of concd. hydrochloric acid. The solid was filtered off, washed with ethanol and ether, then sucked dry; yield usually <5%.

Anal. Calcd. for $[Cr(ibn)_2OH]_2Cl_4 \cdot 4H_2O$: Cr, 14.8; Cl, 20.1; C, 27.3; N, 15.9; H_2O, 10.2. Found: Cr, 14.3; Cl, 21.3; C, 28.8; N, 16.9; H_2O, 13.5. Analysis for H_2O was made by drying the compound at 100 and 144° at 15 mm.; the dried product was analyzed. Calcd. for $[Cr(ibn)_2OH]_2Cl_4$: Cr, 16.4; Cl, 22.5. Found: Cr, 16.3; Cl, 22.4.

The complex is not an aquo complex inasmuch as the easy removal of water from the tetrahydrate and the color do not support such an assumption. All chloride was precipitated immediately on addition of silver nitrate to a weakly acid solution of the compound even at 0°; together with the behavior of the perchlorate salt described below, this shows that all chloride in the compound is anionic rather than ligand chloride.

Tetrakis-(ibn)-μ-dihydroxochromium(III) Perchlorate.—Making a fairly concentrated aqueous solution of the above tetrachloride 2 *f* in perchloric acid or sodium perchlorate precipitated almost quantitatively a violet solid, with all of the chloride found in the filtrate. Aqueous solutions of the perchlorate and chloride compounds were found to have identical visible absorption spectra. The violet perchlorate was dried at ~25° over magnesium perchlorate in a vacuum desiccator.

Anal. Calcd. for $[Cr(ibn)_2OH]_2(ClO_4)_4$: Cr, 11.7; Cl, 16.0. Found: Cr, 12.1; Cl, 16.1. The ClO_4^- was reduced to Cl^- with Ti^{+3} for the chloride analyses.

***trans*-Dithiocyanatobis-(ibn)-chromium(III) Thiocyanate.**—Finely ground potassium hexathiocyanatochromate(III) 4-hydrate[30] was heated at 110° until the weight loss corresponded to complete dehydration, then heated with dried ibn (5 ibn:1 Cr) at 140° for 8 hr. in a Pyrex system closed to the air by a tube filled with sodium hydroxide pellets (oily products are formed if both reactants are not thoroughly dried). The yellow-brown reaction mixture was extracted with absolute ethanol until the red extracts became practically colorless, leaving an orange-yellow mass. This was dissolved in water at ~60°, filtered rapidly and the filtrate cooled in ice-water, giving a finely crystalline orange-yellow compound which was filtered off, washed with ethanol and dried in air; yield (based on Cr) 50–60%.

Anal. Calcd. for $[Cr(ibn)_2(NCS)_2]SCN$: Cr, 12.9; C, 32.8; N, 24.4; S, 23.9; H, 6.0. Found: Cr, 12.9; C, 32.9; N, 24.4; S, 23.1; H, 6.0.

***trans*-Dithiocyanatobis-(pn)-chromium(III) Thiocyanate.**—This compound was prepared by a method[31] reported to give the *cis* isomer; however, the color and visible absorption spectrum of the complex are very similar to those of the *trans*-en analog. Moreover, treatment of the aqueous solution of the former with chlorine at 0° yielded a solution with an absorption spectrum nearly identical with that of *trans*-dichlorobis-(en)-chromium(III) cation. It appears now that the dithiocyanatobis-(pn) complex is actually the *trans* isomer. The incomplete rotatory-dispersion curves for the *cis*-en and *d*-pn complexes, upon which the assignment[31] of the pn complex as the *cis* isomer was based, apparently were inconclusive.

Dioxalatobis-(ibn)-μ-oxalatodichromium(III).—Potassium trioxalatochromate(III) 3-hydrate (0.2 form. wt.) was dissolved in 200 ml. of water and 0.6 form. wt. ibn added. After 5 min. of boiling, a red-violet solid began to crystallize. The mixture was allowed to cool to room temperature and stand for 2 hr., then filtered and the crystals washed with ice-cold water, then with ethanol and ether; yield (based on Cr) 75–85%.

Anal. Calcd. for ox(ibn)Cr-ox-Cr(ibn)ox: Cr, 19.1; C, 30.9; N, 10.3. Found: Cr, 19.3; C, 31.0; N, 10.3.

Other complex compounds were prepared by standard methods.

Chemical Analyses.—Chromium was determined by a modification of a standard method.[32] Chlorine was determined gravimetrically as silver chloride. Carbon, hydrogen, nitrogen (Dumas), sulfur (oxidized to sulfate by sodium chlorate and determined gravimetrically as barium sulfate) and water were determined by standard micro procedures by Miss Heather King, Departmental Microanalyst.

Spectrophotometry.—Absorption spectra were measured with a Cary Model 11 recording spectrophotometer on fresh solutions (unless otherwise stated) in 10.00-mm. quartz cells at ~25° (unless otherwise indicated). The solvent was used in the reference cell.

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[30] K. G. Poulsen, J. Bjerrum and I. Poulsen, *Acta Chem. Scand.*, **8**, 921 (1954).

[31] T. D. O'Brien, J. P. McReynolds and J. C. Bailar, Jr., THIS JOURNAL, **70**, 749 (1948).

[32] "Scott's Standard Methods of Chemical Analysis," Vol. I, 5th Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1937, p. 301, modified by the use of Ag^+ in place of Mn^{+2} as catalyst in the oxidation to dichromate ion.