pound was determined pycnometrically by water displacement and an average value of 5.78 ± 0.05 g./cc. was obtained.

Chromium was determined by dissolving the sample in boiling, concentrated perchloric acid and titrating the resulting chromium(VI) in potassium iodide solution with sodium thiosulfate. Yttrium was determined as the oxalate. For the sample for which the X-ray data are given in Table I, analysis showed: chromium, 28.75 ± 0.05%; yttrium, 46.1 ± 0.1%. Theoretical percentages for $YCrO_3$ are: chromium, 27.54%; yttrium, 47.06%. If one accepts the formula $YCrO_3$ for the reaction product, the above figures would indicate an excess of about 2.5% Cr_2O_3.

All but two lines of the X-ray powder pattern were indexed on the basis of a monoclinic cell (Table) with dimensions $a = c = 7.61 \pm 0.01$ Å.; $b = 7.54 \pm 0.01$ Å.; $\beta = 92° 56' \pm 6'$. One of the two very weak extra lines matched a medium reflection of the chromic oxide pattern. The remaining chromic oxide lines were effectively covered by the yttrium chromium oxide pattern. Thus a small excess of chromium oxide was indicated by the X-ray evidence and also could be implied from the chemical analysis.

TABLE I

COMPARISON OF OBSERVED AND CALCULATED INTERPLANAR SPACINGS

I	$d_{obs.}$	$d_{calcd.}$	hkl	I	$d_{obsd.}$	$d_{calcd.}$	hkl
vvw	5.59	5.52	$\bar{1}01$	w	1.310	1.310	441
vvw	5.21	5.24	101			1.311	404
w	4.31	4.29	111	w	1.293	1.292	414
m	3.775	3.770	020			1.292	531
		3.801	200	vw	1.273	1.272	351
vw	3.624	(3.62)	Cr_2O_3			1.273	531
s	3.387	3.393	210	w	1.249	1.249	442
		3.377	120			1.248	532
vw	3.054	3.059	121			1.250	610
		3.047	211	w	1.206	1.205	$\bar{6}12$
vw	2.972	2.961	220 β	w+	1.193	1.193	260
s	2.756	2.759	$\bar{2}02$	w	1.183	1.183	540
vvs	2.674	2.677	220			1.182	$\bar{5}61$
s	2.621	2.619	202			1.184	602
m	2.587	2.591	$\bar{2}12$	vw	1.171	1.170	612
w	2.472	2.474	212	vw	1.159	1.159	$\bar{5}24$
vw	2.365	2.368	301			1.159	504
vw	2.312	2.323	$\bar{3}11$	w	1.137	1.137	533
m	2.263	2.259	311			1.139	$\bar{4}52$
		2.266	131	w	1.132	1.132	630
m-	2.223	2.227	$\bar{3}22$	vw	1.117	1.117	542
m	2.152	2.152	222			1.118	$\bar{3}61$
m	2.095	2.097	230			1.118	452
w+	2.049	2.050	$\bar{3}21$	w	1.098	1.098	$\bar{6}32$
w	2.005	2.005	321			1.099	613
		2.007	231	w	1.077	1.076	444
s	1.902	1.901	400			1.077	070
m+	1.883	1.885	040	w	1.070	1.069	$\bar{6}14$
m-	1.858	1.859	$\bar{2}32$	w	1.018	1.018	$\bar{4}62$
m	1.842	1.843	410			1.018	$\bar{4}54$
		1.839	$\bar{3}03$			1.017	$\bar{7}03$
vw	1.815	1.813	232	m-	1.002	1.003	642
		1.812	$\bar{4}11$	m-	0.9936	0.9938	624
vvw	1.737	1.736	$\bar{4}02$			0.9940	722
vvw	1.722	1.723	331				
s	1 690	1.689	240				
		1.692	$\bar{4}12$				
w	1.670	1.672	$\bar{4}21$				
		1.666	402				
w+	1.626	1.627	412				
vvw	1.607	?	?				
vw	1.593	1.594	332				
m+	1.577	1.577	$\bar{4}22$				
m+	1.555	1.557	$\bar{2}42$				
s	1.525	1.524	422				
		1.527	$\bar{4}13$				
m+	1.428	1.429	$\bar{4}32$				
vw	1.404	1.402	250				
vw	1.380	1.380	$\bar{4}04$				
		1.382	423				
w+	1.357	1.357	$\bar{4}14$				
m+	1.339	1.339	440				
vvw	1.325	1.325	$\bar{4}33$				
		1.326	$\bar{4}41$				
		1.324	252				

The monoclinic cell has each of its axes doubled as compared to the fundamental perowskite unit and thus corresponds to eight molecules. Using the density of 5.78 g./cc., the calculated X-ray molecular weight is 190 ± 2 molecular weight units as compared to the formula weight for $YCrO_3$ of 188.9. In itself, this agreement is not conclusive proof for the simple formula, because the molecular weight is not a sensitive test of formula. As examples, $Y_{1.08}Cr_{0.92}O_3$ has a formula weight of 192; $Y_{0.97}Cr_{1.03}O_3$ has a formula weight of 188. When we consider the X-ray and chemical evidence together, however, the simple formula seems well established.

It cannot be stated with certainty that the a and c axes are exactly equal although they are not likely to differ by more than 0.015 Å. If they are exactly equal, then choosing the diagonals of the a,c face as new a and c axes gives a cell for which all the angles are 90°. This cell would imply that the crystal is orthorhombic, rather than monoclinic.

Discussion

The reason for the distortion from cubic symmetry, as indicated by the tolerance factor, is the inadequate size of the yttrium ion. The ratio of yttrium to oxygen univalent radii would indicate a coördination number of eight[3] for yttrium rather than the twelve of the undistorted perowskite structure. The atomic positions have not as yet been determined. However, simply shortening one axis of the cubic cell could reduce the number of nearest neighbors about yttrium from twelve to eight. The attendant adjustment of atomic positions to give the most satisfactory coördination polyhedra could then result in a puckering of the structure as evidenced by the doubled cell.[4]

Acknowledgment.—The authors wish to thank Professors Roland Ward and William C. Orr for helpful discussions. This work was supported in part by the Atomic Energy Commission under Contract No. AT-(30-1)-1154.

(3) Linus Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 382.

(4) H D. Megaw, *Acta Cryst.*, **5**, 739 (1952).

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Some Observations on the 8-Quinolinol and 5,7-Dihalo-8-quinolinol Chelates of Scandium

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RECEIVED JULY 6, 1954

Reaction between scandium ion and 8-quinolinol has been shown[1] to yield the 1 to 4 chelate, $Sc(C_9H_6NO)_3 \cdot C_9H_6NOH$, a compound which is useful for the gravimetric determination of scandium[2] but one which, unlike the comparable thorium and uranium(VI) compounds,[3] cannot be converted to the normal chelate by heating.[1] The absorption spectrum of this compound in toluene amounts to an intense peak at 317 mμ (same wave length as is characteristic of 8-quinolinol) and a much less intense peak at 375 mμ.[4] Absorption spectra data are interpreted in terms of bonding of the extra mole of 8-quinolinol in the solid by lattice forces.[4]

The similarity of the reported absorption spectrum[4] to the spectra of the partially hydrolytically

(1) L. Pokras and P. M. Bernays, THIS JOURNAL, **73**, 7 (1951).

(2) L. Pokras and P. M. Bernays, *Anal. Chem.*, **23**, 757 (1951).

(3) F. J. Frere, THIS JOURNAL, **55**, 4362 (1933).

(4) L. Pokras, M. Kilpatrick and P. M. Bernays, *ibid.*, **75**, 1254 (1953).

decomposed 8-quinolinol chelates of thorium[5] and uranium(VI)[6] has prompted a further investigation of the absorption characteristics of solutions of the scandium chelate. Furthermore, the enhanced stabilities of the 5,7-dihalo-8-quinolinol chelates of thorium[7] and uranium(VI)[6] suggested extension of the investigation to the scandium analogs of these compounds.

Experimental

Materials Used.—The source of scandium ion was a sample of the oxalate[8] shown to be spectroscopically free from all impurities except small quantities of calcium. The oxalate was ignited to oxide, and a perchlorate solution containing the equivalent of 0.4578 g. of oxide in 250 ml. was prepared by dissolving in excess 70% perchloric acid, evaporating to remove excess acid, and diluting. The 8-quinolinol and substituted 8-quinolinols used were those previously described.[5-7] The former was used as a solution of 10 g. of reagent in 200 ml. of 2 *N* acetic acid. All halo 8-quinolinols were used as 0.3% solutions in acetone. Chloroform used contained *ca.* 1% ethanol by volume. Other materials were of reagent quality.

Apparatus.—All absorption spectra were measured at *ca.* 25° with a Cary Recording Spectrophotometer, using 5.0 cm. demountable cells with quartz windows. All *p*H measurements were made with a Beckman model G *p*H Meter.

Preparation of Chelates.—The 1 to 4 8-quinolinol chelate was prepared according to the procedure of Pokras and Bernays.[1] In agreement with their work, the normal 1 to 3 compound was not obtained.

With the 5,7-dihalo-8-quinolinols, however, both 1 to 3 and 1 to 4 chelates were obtained, but as is true with both thorium[7] and uranium(VI),[6] the 1 to 3 compounds could not be obtained from the 1 to 4 materials by heating. Rather, separate reactions in the indicated stoichiometries were necessary. All chelates of these types were prepared according to the procedure of Pokras and Bernays[1] with the exceptions that only the calculated quantity of chelating agent was used and that after the addition of the ammonia–ammonium acetate buffer the suspensions were heated on the steam-bath to remove the bulk of the acetone added with the 8-quinolinol type reagent. After cooling, the suspensions were all at *p*H 8.5–9.0. The washed chelates were dried for 2 hours at 100–110° for the 1 to 3 compounds and at 85–90° for the 1 to 4 compounds. All compounds were deep yellow in color and soluble in chloroform, ethanol and benzene. The 1 to 3 compounds were somewhat less soluble than the 1 to 4 compounds.

Anal.[9] Calcd. for $Sc(C_9H_6NO)_3 \cdot C_9H_6NOH$: C, 69.43; H, 4.05; N, 9.00. Found: C, 69.01; H, 4.14; N, 8.85.

Calcd. for $Sc(C_9H_4Cl_2NO)_3$: C, 47.40; H, 1.77; N, 6.14; Cl, 31.20. Found: C, 47.07; H, 2.21; N, 6.02; Cl, 31.57. Calcd. for $Sc(C_9H_4Cl_2NO)_3 \cdot C_9H_4Cl_2NOH$: C, 48.14; H, 1.91; N, 6.24; Cl, 31.60. Found: C, 46.79; H, 2.17; N, 5.91; Cl, 31.34.

Calcd. for $Sc(C_9H_4Br_2NO)_3$: C, 34.10; H, 1.27; N, 4.42; Br, 50.50. Found: C, 34.36; H, 1.89; N, 4.00; Br, 49.26. Calcd. for $Sc(C_9H_4Br_2NO)_3 \cdot C_9H_4Br_2NOH$: C, 34.50; H, 1.36; N, 4.47; Br, 51.00. Found: C, 34.57; H, 1.67; N, 4.37; Br, 50.10.

Calcd. for $Sc(C_9H_4ClINO)_3$: C, 33.82; H, 1.26; N, 4.38. Found: C, 32.41; H, 1.61; N, 4.02. Calcd. for $Sc(C_9H_4ClINO)_3 \cdot C_9H_4ClINOH$: C, 34.20; H, 1.36; N, 4.43. Found: C, 34.19; H, 1.70; N, 4.28.

Results and Discussion

Absorption Spectra Studies.—Spectrophotometric data for chloroform solutions of these chelates paralleled closely those obtained for the analogous thorium[5,7] and uranium(VI)[6] compounds except that absorptions were somewhat more intense. Thus, although the unsubstituted 8-quinolinol chelate gave a spectrum characteristic of partially hydrolyzed chelates,[5-7] the addition of halogen atoms gave bathochromic shifts and spectra approaching the normal type.[10,11] However, the addition of even small quantities of water caused the spectra to revert to those of the 8-quinolinol type reagent. As before, differences between the spectra of the 1 to 3 and 1 to 4 chelates are largely differences in absorption intensity. These relationships are shown by the typical data given in Fig. 1. Chloroform solutions of these chelates did not adhere to Beer's law.

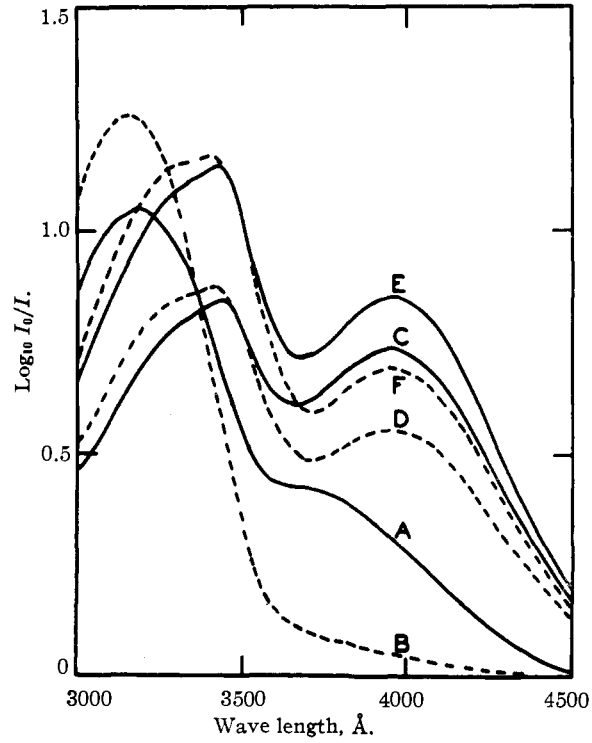

Fig. 1.—Absorption spectra of chloroform solutions of certain chelates: A, $Sc(C_9H_6NO)_3 \cdot C_9H_6NOH$, 1.2 mg. Sc/l.; B, same as A with 1 drop water; C, $Sc(C_9H_4Cl_2NO)_3$, 1.2 mg. Sc/l.; D, same as C with 1 drop water; E, $Sc(C_9H_4Cl_2NO)_3 \cdot C_9H_4Cl_2NOH$, 1.2 mg. Sc/l.; F, same as E with 1 drop water.

As was found with the thorium[5,7] and uranium (VI)[6] systems, hydrolytic decompositions in ethanol solutions are much less striking, although even in this solvent the unsubstituted chelate is still fairly sensitive. These relationships are shown in Fig. 2. Except with the simple 8-quinolinol chelate at 3730 Å., adherence of absolute ethanol solutions of the chelates to Beer's law is good. Data for ethanol solutions are as follows: $Sc(C_9H_6NO)_3 \cdot C_9H_6NOH$: 0.80–1.6 mg. Sc/l., $k_{av.}^{12}$ at 3200 Å. = 149.2, k at 3730 Å. = 117.5–141.3; $Sc(C_9H_4$-

(5) T. Moeller and M. V. Ramaniah, THIS JOURNAL, **75**, 3946 (1953).
(6) T. Moeller and M. V. Ramaniah, *ibid.*, **76**, 5251 (1954).
(7) T. Moeller and M. V. Ramaniah, *ibid.*, **76**, 2022 (1954).
(8) Kindly loaned by Prof. L. L. Quill, Michigan State College.
(9) Although differences in analytical data *alone* are too small to indicate absolutely the formation of both the 1 to 3 and 1 to 4 series, the similarities in absorption spectra differences (Figs. 1 and 2) to those found for the thorium[5,7] and uranium(VI)[6] compounds, where analytical results are more definitive, are sufficient to render the existence of the two series undeniable.
(10) T. Moeller and A. J. Cohen, THIS JOURNAL, **72**, 3546 (1950).
(11) T. Moeller, F. L. Pundsack and A. J. Cohen, *ibid.*, **76**, 2615 (1954).
(12) Specific extinction, k, is given by the relationship $k = (\log_{10} I_0/I)/cl$, l being in cm. and c being expressed as g.Sc/l.

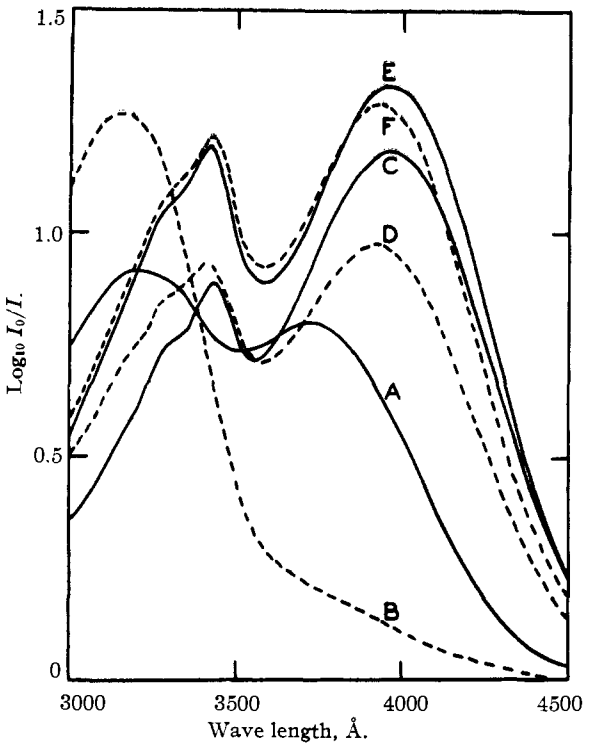

Fig. 2.—Absorption spectra of absolute ethanol solutions of typical chelates: A, $Sc(C_9H_6NO)_3 \cdot C_9H_6NOH$, 1.2 mg. Sc/l.; B, same as A with 10% water by volume; C, $Sc(C_9H_4Cl_2NO)_3$, 1.2 mg. Sc/l.; D, same as C with 20% water by volume; E, $Sc(C_9H_4Cl_2NO)_3 \cdot C_9H_4Cl_2NOH$, 1.2 mg. Sc/l.; F, same as E with 20% water by volume.

$Cl_2NO)_3$: 0.60–1.20 mg. Sc/l., $k_{av.}$ at 3430 Å. = 148.9, $k_{av.}$ at 3970 Å. = 191.3; $Sc(C_9H_4Cl_2NO)_3 \cdot C_9H_4Cl_2NOH$: 0.60–1.20 mg. Sc/l., $k_{av.}$ at 3430 Å. = 201.1, $k_{av.}$ at 3970 Å. = 220.6; $Sc(C_9H_4Br_2)_3 \cdot C_9H_4Br_2NOH$[13]: 0.60–1.20 mg. Sc/l., $k_{av.}$ at 3430 Å. = 217.2, $k_{av.}$ at 3990 Å. = 220.2; $Sc(C_9H_4ClINO)_3$, 0.60–1.20 mg. Sc/l., $k_{av.}$ at 3470 Å. = 160.3, $k_{av.}$ at 4020 Å. = 184.4; $Sc(C_9H_4ClINO)_3 \cdot C_9H_4ClINOH$: 0.50–1.00 mg. Sc./l., $k_{av.}$ at 3470 Å. = 215.3, $k_{av.}$ at 4020 Å. = 210.2.

Acknowledgment.—Funds received from an E. I. du Pont de Nemours and Company Grant-in-aid for partial support of this investigation are gratefully acknowledged.

(13) $Sc(C_9H_4Br_2NO)_3$ was too difficultly soluble in ethanol to permit study.

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The Interaction of $HgCl_2$ with Sodium Thymonucleate

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RECEIVED MAY 8, 1954

An interesting reaction of sodium thymonucleate (DNA) was investigated by Katz,[1] who found that $HgCl_2$ undergoes a reversible combination with DNA which results in a large increase in the molecular weight as determined by light scattering. Although the identity of the combining species has not been determined, we will tentatively assume for simplicity in this discussion that it is the $HgCl_2$ molecule. Katz further found that the addition of Cl^- or CN^- would completely reverse the complexation leaving free DNA. He interpreted the large increase in the molecular weight that was brought about by the addition of $HgCl_2$, as being the result of partial aggregation. However, he assumed that the $HgCl_2$–DNA complex had the same refractive index increment (dn/dc) as free DNA, while it is probable that the complex has a higher dn/dc value than the free DNA. This would cause his reported molecular weights of the complex to be somewhat too high. With this in mind, partial aggregation need not be postulated.

Further investigation of this reversible complexing reaction has revealed that the ultraviolet absorption spectrum of DNA is substantially altered by the addition of $HgCl_2$. In 0.40 *M* acetate buffer, *p*H 5–6, free DNA has an absorption maximum at 258 mμ. On the addition of $HgCl_2$ (dissolved in the same buffer) the absorption maximum shifts over to 275 mμ. The addition of NaCl to this solution will cause the absorption maximum to again shift back to 258 mμ. This, together with Katz' observations, is strong indication that the DNA–$HgCl_2$ complex is reversed by the addition of NaCl.

On examining the shift of the absorption spectrum more carefully, we find that all curves go through an isosbestic point located at 238.5 mμ (see Fig. 1). Defining r = total moles of added $HgCl_2$/moles P, we find that all curves for which r is less than 0.60 pass through isosbestic points at 238.5 and 262.5 mμ. On increasing the mercury concentration from r = 0.60 to 10, the absorption curves display a new isosbestic point at 274.5 mμ but still pass through the first one at 238.5 mμ.

This behavior suggests in this particular case that the reaction proceeds by at least two steps and that the first reaction is essentially complete before the second reaction begins. If this is the case, the curves in Fig. 1 which pass through the isosbestic points at 238.5 and 262.5 mμ can be considered to result from two components in equilibrium with each other and absorbing ultraviolet light independently.

Choosing two appropriate wave lengths, it is possible to write two simultaneous equations for the total optical density at these wave lengths in terms of the concentration of the free DNA and the concentration of the complex. In this case we have chosen wave lengths of 257.5 and 271.0 mμ because they are near maxima, and yet as far from isosbestic points as possible; the results do not depend on this choice.

$$D_{257.5} = E_{257.5}^{DNA} C^{DNA} + E_{257.5}^{complex} C^{complex}$$

$$D_{271} = E_{271}^{DNA} C^{DNA} + E_{271}^{complex} C^{complex}$$

Employing Chargaff's value of 6650 ± 50 (at 259 mμ in the presence of salt) for the extinction coefficient with respect to phosphorus (E(P)),[2] it is

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(1) S. Katz, THIS JOURNAL, **74**, 2238 (1952).

(2) E. Chargaff and R. Lipshitz, *ibid.*, **75**, 3658 (1953).