TABLE I

	Esters of								Analyses, %		Activ-
Ro 2-	Alcohol	Acid	Salt	Procedure	Recrystallized from	Yield, %	M.p., °C.	Empirical formula	Calcd.	Found	ity atr. = 1
3631	II	Diphenylacetic		B	Pet. ether	65	85–87	$C_{22}H_{25}O_2N$	C, 78.77 H, 7.51	78.68 7.43	
3631/2	II	Diphenylacetic	H_2SO_4	D	Acetone[a]	90	205–206	$(C_{22}H_{25}O_2N)_2 \cdot H_2SO_4$	C, 68.72 H, 6.82	68.55 6.51	1/10
4201	II	Diphenylacetic	CH_3Br	E	Acetone	80	176–177	$C_{23}H_{28}O_2NBr$	C, 64.18 H, 6.56	64.27 6.61	1/50
3951	III	Diphenylacetic	CH_3Br	E	Isopropanol + acetone + ether	80	165–167	$C_{22}H_{26}O_2NBr$	C, 63.46 H, 6.30	63.04 6.33	1/50
4569	III	Benzilic		C	Acetone + ether + pet. ether	15	156–157	$C_{21}H_{23}O_3N$	C, 74.75 H, 6.87	74.39 6.51	1–2[b]
4570	III	Benzilic	CH_3Br	E	Methanol + acetone + ether	85	231–233	$C_{22}H_{26}O_3NBr$	C, 61.11 H, 6.06	61.10 6.14	1–2
3203	IV	Diphenylacetic	CH_3Br	E	Ethanol + ether + pet. ether	90	212–213	$C_{22}H_{26}O_2NBr$	C, 63.46 H, 6.30	63.31 6.38	1/5
3528	IV	Diphenylacetic	C_2H_5Br	E	Ethanol + ether	90	205–206	$C_{23}H_{28}O_2NBr$	C, 64.18 H, 6.56	63.82 6.43	1/100
5205	IV	Diphenylacetic	$CH_2{=}CHCH_2Br$	E	Acetone[a]	80	149–150	$C_{24}H_{28}O_2NBr$	C, 65.15 H, 6.38	65.05 6.12	1/10
4157	IV	Diphenylacetic	$C_6H_5CH_2Br$	E	Isopropanol	40	171–173	$C_{28}H_{30}O_2NBr$	C, 68.29 H, 6.14	68.70 6.37	1/100
3773	IV	Benzilic	CH_3Br	E	Methanol + acetone + ether	90	240–241	$C_{22}H_{26}O_3NBr$	C, 61.11 H, 6.06	61.25 6.33	1
	IV	Benzilic	CH_3picr.[c]	G	Ethanol		182–183	$C_{28}H_{28}O_{10}N_4$	C, 57.93 H, 4.86	57.77 4.62	
5044	IV	Benzilic	CH_3CS[d]	F	Methanol + acetone + pet. ether	56	221–223	$C_{32}H_{41}O_7NS$	C, 65.84 H, 7.08	65.48 7.04	1
5109	IV	Benzilic	CH_3CS[d]	F	Methanol + acetone + pet. ether	20	209–210	$C_{32}H_{41}O_7NS$	C, 65.84 H, 7.08	65.93 7.29	1
4174	IV	Benzilic	C_2H_5Br	E	Methanol + acetone	90	229–230	$C_{23}H_{28}O_3NBr$	C, 61.88 H, 6.23	61.86 6.19	1
4665	IV	Benzilic	C_3H_7Br	E	Methanol + acetone + ether	90	251–254	$C_{24}H_{30}O_3NBr$	C, 62.60 H, 6.57	62.92 6.51	1
4550	IV	Benzilic	C_4H_9Br	E	Methanol + acetone + ether	80	246–247	$C_{25}H_{32}O_3NBr$	C, 63.29 H, 6.80	63.14 6.60	1
5084	IV	Benzilic	$CH_2{=}CHCH_2Br$	E	Methanol + acetone + pet. ether	80	181–182	$C_{24}H_{28}O_3NBr$	C, 62.88 H, 6.16	62.48 6.23	1
4148	IV	Benzilic	$C_6H_5CH_2Br$	E	Isopropanol[e]	37	223–224	$C_{28}H_{30}O_3NBr$	C, 66.14 H, 5.95	65.85 5.82	1/25
4344	IV	Acetylmandelic	HCl	A	Ethanol + acetone + ether	65	169–178	$C_{17}H_{21}O_4N \cdot HCl$[f]	C, 60.08 H, 6.53	59.90 6.52	1/25

[a] Dissolved in alcohol; solvent removed *in vacuo*. Residual oil crystallized by trituration with acetone. [b] A solution of the base in the calculated amount of dilute hydrochloric acid was used for the pharmacological studies. [c] Picrate. [d] *d*-Camphorsulfonates of optical antipodes. Ro 2-5044 is the dextrorotatory, Ro 2-5109 the levorotatory isomer. [e] Dissolved in methanol; solvent removed *in vacuo*. Residual oil crystallized by trituration with isopropyl alcohol. [f] A direct oxygen determination (Calcd.: O, 18.82. Found: O, 18.75) showed that the compound was the hydrochloride of the acetylmandelic acid ester and not of the mandelic acid ester. The carbon and hydrogen values of these two ester hydrochlorides are very close.

residual thick sirup was dissolved in methanol. To this solution acetone and ether were added, causing the precipitation of crystals (needles, 2 g.) melting around 200°. Further additions of acetone, ether and petroleum ether caused precipitation of more material melting in the same range. These fractions were combined and recrystallized three times from a mixture of methanol, acetone and petroleum ether, giving finally 3.3 g. (56%) of fine needles (Ro 2-5044), having the constant melting point of 221–223° and a constant specific rotation of $[\alpha]^{30}_D$ +30.5 ± 0.5° (*c* 5, in water). This corresponds to a molecular rotation of the *d*-1-methyl-3-benziloyloxyquinuclidinium ion of +128.6 ± 2.9°.

Anal. Calcd. for $C_{32}H_{41}O_7NS$: C, 65.84; H, 7.08. Found: C, 65.48; H, 7.04.

The mother liquors were concentrated and the residues crystallized from a mixture of methanol, acetone and petroleum ether. The lower melting fractions (180–185°) thus obtained were repeatedly recrystallized from the above solvents to yield finally 1.2 g. (20%) of needles having a constant melting point of 209–210° (Ro 2-5109) and giving a distinct mixed melting point depression with the other isomer. The specific optical rotation of this isomer was $[\alpha]^{30}_D$ −13.2 ± 0.5° (*c* 5, in water). The molecular rotation of the *l*-1-methyl-3-benziloyloxyquinuclidinium ion calculated from this value is −125.9 ± 2.4°.

Anal. Calcd. for $C_{32}H_{41}O_7NS$: C, 65.84; H, 7.08. Found: C, 65.93; H, 7.29.

Procedure G. 1-Methyl-3-benziloyloxyquinuclidinium Picrate.—A solution of 0.4 g. of 1-methyl-3-benziloyloxyquinuclidinium bromide (Ro 2-3773) in 10 cc. of water was added to a hot aqueous solution (50 cc.) of 0.4 g. of picric acid. The mixture was cooled and the precipitated oil crystallized.

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Crystal Structures of Rare Earth Oxychlorides

BY D. H. TEMPLETON AND CAROL H. DAUBEN

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Compounds of the rare earth elements show the effects of ionic size on crystal structure with minimum interference from other factors. The ionic radii decrease in a regular way as the atomic number increases, while the configuration of the outer electrons is changed relatively little. Among the compounds which we have studied are the oxychlorides of composition MOCl, where M is a rare earth element. Of these, structures have been reported only for LaOCl,[1] PrOCl[2] and NdOCl[2] which have the PbFCl type[3] structure. Our work was stimulated by a correlation now being made by Koch and Cunningham of the thermodynamic properties of these substances[4,5] with crystal geometry.

Experimental

The oxychlorides of yttrium and all of the rare earth elements except promethium were prepared by Dr. Charles W. Koch and Mr. Richard J. Borg from very pure oxide stocks (similar to those described by Zalkin and Templeton[6]) by reaction with appropriate mixtures of water and hydrogen chloride vapors at elevated temperatures. Powder patterns were taken in cameras of radius 4.5 cm. with CuKα (λ 1.5418 Å.) and CrKα (λ 2.2909 Å.) radiations.

Results

The oxychlorides of the elements lanthanum to holmium have the tetragonal PbFCl type structure. The oxychlorides of thulium, ytterbium and lutetium have another structure which has not been determined. Erbium oxychloride is dimorphic, having been prepared with each of these two structures. The lattice dimensions and unit cell volumes of the tetragonal oxychlorides are listed in Table I, together with previous results. A plot of the unit cell volume as a function of atomic number is a smooth curve except for the usual cusp at gadolinium.

TABLE I

TETRAGONAL LATTICE PARAMETERS

	a, Å.	c, Å.	Vol. unit cell, Å.³
LaOCl	4.119 ± 0.002	6.883 ± 0.004	116.78
	(4.117)[a]	(6.879)[a]	
	(4.121 ± .003)[b]	(6.885 ± .009)[b]	
CeOCl	4.080 ± .004	6.831 ± .007	113.71
PrOCl	4.051 ± .002	6.810 ± .006	111.76
	(4.053 ± .003)[c]	(6.800 ± .009)[c]	
NdOCl	4.018 ± .002	6.782 ± .004	109.49
	(4.04 ± .03)[c]	(6.77 ± .04)[c]	
SmOCl	3.982 ± .001	6.721 ± .002	106.57
EuOCl	3.965 ± .004	6.695 ± .007	105.25
GdOCl	3.950 ± .002	6.672 ± .004	104.10
TbOCl	3.927 ± .004	6.645 ± .007	102.47
DyOCl	3.911 ± .003	6.620 ± .006	101.26
HoOCl	3.893 ± .003	6.602 ± .004	100.06
ErOCl	3.88 ± .02	6.58 ± .06	99.1
YOCl	3.903 ± .002	6.597 ± .004	100.49
	(3.900 ± .002)[c]	(6.604 ± .004)[c]	

[a] Reference 1. [b] S. Fried, W. Hagemann and W. H. Zachariasen, THIS JOURNAL, 72, 771 (1950). [c] Reference 2.

The PbFCl structure has atoms in the following positions of space group D_{4h}^7 ($P4/nmm$)

$$2\ \mathrm{M\ in\ 2\ (c)}:\ 0,{}^1/_2,u;\ {}^1/_2,0,\bar{u}$$
$$2\ \mathrm{O\ in\ 2\ (a)}:\ 0,0,0;\ {}^1/_2,{}^1/_2,0$$
$$2\ \mathrm{Cl\ in\ 2\ (c)}:\ 0,{}^1/_2,v;\ {}^1/_2,0,\bar{v}$$

Sillén and Nylander[1] have given the parameters as $u = 0.178$ and $v = 0.635$ for LaOCl, while Zachariasen[2] has given them as 0.18 and 0.64, respectively, for NdOCl, PrOCl, PuOCl and YOCl.

Diffraction intensities were calculated for many combinations of values of u and v for both SmOCl and HoOCl. For both compounds the best agreement was found with $u = 0.17$ and $v = 0.63$. The limits of error are estimated as 0.005 and 0.01 for the two parameters. The reflections considered include l values up to 8. The interatomic distances are listed in Table II. The most interesting feature of these distances is that the two types of metal–chlorine distance remain equal (within experimental error) in spite of the very short chlorine–chlorine distance which results. That is, the anion repulsion is much less than one would expect for conventional ionic radii.

TABLE II

INTERATOMIC DISTANCES IN SmOCl AND HoOCl

Atoms	Distance, Å. SmOCl	HoOCl
M–O	2.30	2.25
M–Cl	3.09,[a] 3.11[b]	3.04,[a] 3.05[b]
Cl–O	3.19	3.12
Cl–Cl	3.31	3.24
O–O	2.81	2.75

[a] One neighbor. [b] Four neighbors.

The explanation may lie in a deviation from spherical symmetry of the chloride ion. This equality of metal–chlorine distances also occurs to within experimental error for LaOCl,[1] PrOCl,[2] NdOCl,[2] YOCl[2] and PuOCl,[2] but in these cases the anion–anion distances are not as small because of the greater cation size.

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An Empirical Quantitative Relationship between Structure and Molecular Rotatory Power

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The relationship between optical rotation and structure has been worked out in part by such well-known methods as Hudson's rules of isorotation. However, a generalized treatment either theoretical or empirical, capable of predicting the magnitude of the rotation from the constitution of the active molecule is as yet lacking. The following describes an empirical relationship that enables the rotation of at least the simpler types of optically

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[1] L. G. Sillén and A. L. Nylander, *Svensk. Kem. Tidskr.*, **53**, 367 (1941).

[2] W. H. Zachariasen, *Acta Cryst.*, **2**, 388 (1949).

[3] W. Nieuwenkamp and J. M. Bijvoet, *Z. Krist.*, **81**, 469 (1931).

[4] C. W. Koch, A. Broido and B. B. Cunningham, THIS JOURNAL, **74**, 2349 (1952).

[5] C. W. Koch and B. B. Cunningham, *ibid.*, **75**, 796 (1953).

[6] A. Zalkin and D. H. Templeton, *ibid.*, **75**, 2453 (1953).