of how the electronic structure and bonding interactions in detail vary with ϕ, but clearly, unless such factors permit the syn isomer to adopt a more planar geometry, then the syn form will only be accessible via synthetic routes that lead directly to this configuration and do not permit kinetically facile interconversion. Such routes have not yet been demonstrated.

The situation becomes more acute in the case of the pentamethyl derivatives, as illustrated in Figure 4. The energy minimum for the syn form, at $\phi = 152°$, is conveniently close to 147°. Nevertheless, it is already 0.6 kcal mol^{-1} above that of the minimum in the anti form. Although this energy difference of approximately kT ($kT = 0.59$ kcal mol^{-1} at 298 K) might possibly be overcome by propitious crystal-packing or solvation effects, it could well be enough to greatly favor the anti configuration under conditions that permit interconversion. In light of these results it is understandable that the syn forms of the $[(C_5H_{5-n}Me_n)MoS(\mu\text{-}S)]_2$ complexes have not yet been isolated and characterized structurally.

Conclusion

Interactive molecular graphics can provide a rapid means of probing steric effects in organometallic complexes. Such modeling is thus a valuable complement to the information provided by molecular orbital energy or molecular mechanics calculations. The efficacy of the method has been demonstrated in monitoring intramolecular steric constraints on the conformations of bis(μ-sulfido)bis(sulfidocyclopentadienylmolybdenum) complexes. It has been shown that the intramolecular van der Waals energies of the syn forms of the $[(C_5R_5)MoS(\mu\text{-}S)]_2$ (R = H, Me) dimers are somewhat higher than those of the corresponding anti forms for configurations that have been previously indicated to be electronically the most favorable.

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Low-Temperature Routes to New Structures for Yttrium, Holmium, Erbium, and Thulium Oxychlorides

EDUARDO GARCIA, JOHN D. CORBETT,* JEFF E. FORD, and WILLIAM J. VARY

The pyrohydrolysis of $(NH_4)_3RCl_6$ (R = Y, Dy, Ho, Er, Tm, Yb) has been studied at 270–550 °C. This produces in part the YOF form of YOCl near 500 °C and $R\bar{3}m$ (disordered SmSI + YOF) phases for YOCl, HoOCl, ErOCl, TmOCl and YbOCl at 270–400 °C. Fluxed transformations of the disordered materials yield the new SmSI form of HoOCl (from LiCl–KCl) and YOF-type TmOCl, ErOCl (LiCl–KCl or RCl$_3$), YOCl, and HoOCl (KCl). No new structures are found for Dy and Yb. Reactions with LiCl–KCl or KCl melts also produce R_3O_4Cl phases for R = Y, Yb, Dy, and Ho, the last two being new. The $R\bar{3}m$ oxychlorides of Y, Ho, Er, and Yb are intercalated by sodium in liquid ammonia at room temperature to yield 3R-Na$_x$ROCl. The relationship of these new structure types to the previously known (PbFCl or SmSI) forms of the rare-earth-metal oxychlorides are considered. Different preparative routes are observed to exercise some kinetic control over the structures of the ROCl products even for reactions run at the same temperature. ScOCl has the FeOCl-type layered structure.

Introduction

The majority of the rare-earth-metal oxychlorides, bromides, and iodides exist in the tetragonal PbFCl structure while the heavier chlorides have the rhombohedral (3R) SmSI structure at ambient pressure.[2,3] Erbium at the crossover point is dimorphic, the higher temperature form being the SmSI type. The structure of ScOCl is unknown, but an FeOCl type has been suggested.[2] The situation is summarized as follows:

```
       Sc    Y   La ... Dy  Ho  Er  Tm  Yb  Lu
     FeOCl |←———  PbFCl  ———→|
      (?)                    |←—SmSI——→|
```
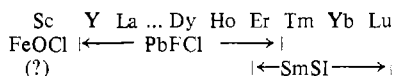
In addition, an obscure work by Ward et al.[4] reported the preparation of a YOCl composition that could be indexed on a large tetragonal cell, although they noted at the same time that the pattern resembled those of the then structurally unknown ErOCl–LuOCl series.

Our interest in other structural types of YOCl was stimulated by the observation that the oxidative deintercalation of the layered 3R-M^1_xYClO[5] at room temperature led directly to well-crystallized 3R-YOCl in the YOF-type structure,[6] a form hitherto known only for oxyfluorides. This structure in fact is an alternate stacking order of the same slabs or sheets found in the SmSI type. In an attempt to reach this product by a more direct route we discovered that the generation of YOCl by NH_4Cl–Y_2O_3 reactions in air at 300–550 °C, similar to the route used by Ward et al.,[4] also led to the YOF-type structure mixed with the normal PbFCl form. We have subsequently made a more thorough study of this synthesis route to the oxychlorides of yttrium and a number of the heavier lanthanides and have found that a number of new examples of YOF- or SmSI-type structures can be so obtained.

Experimental Section

The R_2O_3 (R = rare-earth element) starting materials were produced at Ames Laboratory and were generally better than 99.95% in the specified metal. KCl was dried at 500 °C while LiCl was slowly sublimed, both under high vacuum. RCl$_3$ compounds of sufficient purity were obtained from the hexahydrates by slow drying under high vacuum. Powder pattern data were secured for samples mounted on cellophane tape by utilizing an Enraf-Nonius Guinier camera with silicon as an internal standard, the 2θ values of the latter being fit to a quadratic in line position. Lattice constants for known structures were calculated by a least-squares fit to indexed 2θ values. Powder patterns were calculated with the program POWD 5.[7] Both the SmSI and YOF structures occur in space group $R\bar{3}m$ with all atoms in special positions 6c (hexagonal cell). The SmSI-type patterns were calculated by using the fractional coordinates reported for YbOCl[8] while those for the YOF form were obtained by adjusting the reported z positional parameters[6] so as to give interatomic distances very similar to those calculated for the SmSI form

(1) Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Materials Sciences Division.
(2) Hulliger, F. *Phys. Chem. Mater. Layered Struct.* **1976,** *5,* 254.
(3) Beck, H. P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976,** *31B,* 1562.
(4) Ward, R.; Orr, W. C.; Katz, L.; Looky, J. T.; Valleta, R. M.; Burgess, T. E. *NYO-6652,* **1956,** 4; *Nucl. Sci. Abstr.* **1961,** *15,* 12903.
(5) Ford, J. E.; Corbett, J. D.; Hwu, S.-J. *Inorg. Chem.* **1983,** *22,* 2789.
(6) Mann, A. W.; Bevan, D. J. N. *Acta Crystallogr., Sect. B* **1970,** *B26,* 2129.

(7) Clark, C. M.; Smith, D. K.; Johnson, G. J. "A Fortran IV Program for Calculating X-Ray Powder Diffraction Patterns—Version V"; Department of Geosciences, The Pennsylvania State University: University Park, PA, 1973.
(8) Brandt, G.; Diehl, R. *Mater. Res. Bull.* **1974,** *9,* 411.

(z(YOF type) = 0.217, 0.133, and 0.389 for Y, O, and Cl, respectively).

The original preparation of a new form of YOCl followed the procedure of Ward et al.,[4] heating Y_2O_3 with excess NH_4Cl in a vertical fused silica tube open at the top, first at 300 °C for 2-3 h and then at 550 °C for 18 h. Recognition of the probable role of $(NH_4)_3YCl_6$[9] as an intermediate led to the use of the more optimal ratios of $NH_4Cl:Y_2O_3$ of >12:1 rather than the earlier (3-5):1. This gave a noticeable increase to ~50% YOF-type material in the final product, the PbFCl form accounting for all of the remaining lines. Thereafter, the usual synthesis reactions consisted of two steps. First, R_2O_3 was intimately ground with 15-20 times as many moles of NH_4Cl and heated in air overnight at 270 °C. Completion of the reaction was indicated by cessation of NH_3 evolution. The second part consisted of heating this product in a fused silica boat for 18-24 h at 270-400 °C either in a short, slightly inclined tube to allow convective flow of air through it or under a slow flow of Ar that had been saturated with water at room temperature. The end of the HCl evolution signaled the completion of the reaction.

Results and Discussion

The two-step synthesis reaction appears to involve first the hydrochlorination of R_2O_3 and then the pyrohydrolysis of the intermediate product. Meyer and Ax[9] have clearly shown that the first step of the R_2O_3–NH_4Cl reaction, a historic route to the anhydrous chlorides, involves the formation of a ternary ammonium chlorometalate intermediate, viz.

$$12NH_4Cl + Y_2O_3 \rightarrow 2(NH_4)_3YCl_6 + 3H_2O + 6NH_3$$

which is then thermally decomposed, ultimately to RCl_3. The present work shows that this can be hydrolyzed to oxychlorides, e.g.

$$(NH_4)_3YCl_6 + H_2O \rightarrow YOCl + 3NH_4Cl + 2HCl$$
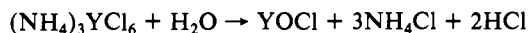
in the neighborhood of 270-500 °C with the production of new low-temperature oxychloride structures for this and some other rare-earth elements. The initial yttrium reactions at 550 °C gave mixtures of well-crystallized PbFCl and YOF forms of YOCl, the relative amount of the former decreasing when the temperature was backed off until at 400 °C the product was only a $R\bar{3}m$-type (YOF + SmSI) material (below). Synthetic results similar to those for YOCl were obtained for ErOCl, but the powder pattern was of poorer quality. For Dy and Ho the decomposition-hydrolysis step was backed off from 400 °C, suitable for single-phase YOCl, to 270-300 °C in an attempt to gain samples free of the PbFCl type, which is normally obtained at higher temperatures for both. Only an $R\bar{3}m$ composite mixed with the PbFCl type was obtained for HoOCl while DyOCl remained in the PbFCl structure. The low-temperature route to TmOCl also gave the $R\bar{3}m$ type, which can be understood as follows.

Both the YOF and SmSI structure types have $R\bar{3}m$ symmetry with tightly bound slabs formed from homoatomic layers sequenced X-R-O-O-R-X in the relative order ABcbCA, that is, with close-packed X and R layers plus O in all of the tetrahedral interstices between pairs of metal atom layers. The difference between the two types is only in the relative sequencing of these slabs, as shown in the (110) sections of the two structures in Figure 1. (The similarly sized O and F in YOF give a rather different proportion to the double layers of nonmetals.[6]) If the slab just described is denoted A according to the relative orientation of the outside members, then SmSI has the relative slab order ABC whereas YOF is sequenced ACB. The ordering of the heavy atoms is the same as found in ZrCl vs. ZrBr[10] or, better, in $ZrClO_{0.43}$ and $ZrBrO_{0.35}$,[11] respectively, where the tetrahedral holes are now only partially occupied by oxygen and significant metal-metal bonding is retained. As with the ZrX alternatives, both structures can be indexed on the same cell with only differences in relative intensities. Table I shows the basis for the assignment of the YOCl phase prepared at 550 °C as the YOF type together with the evidence that this was also one component of a mixture obtained by Ward et al.[4] at 500 °C. Low-angle reflections such as 012, 104, and 015 provide the clearest distinctions. (It should be
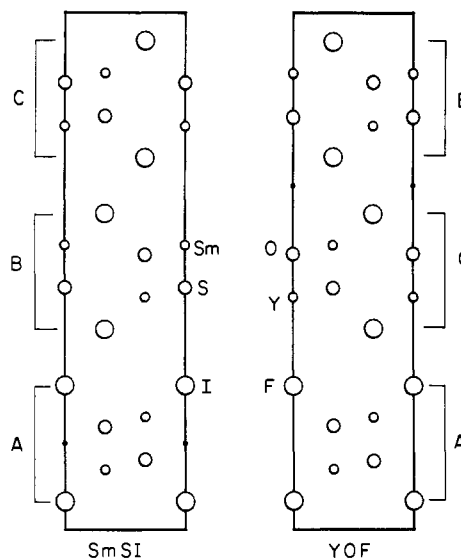

Figure 1. The (110) sections of the SmI-type (left) and YOF-type (right) structures with brackets marked with relative slab orientations: (o) Sm, Y; (O) O; (◯) I, F. The parameters used are those suitable for ROCl. Small dots mark the cell origins.

Table I. Comparison of Powder Pattern Intensities for Low-Temperature YOCl with Calculations for YOF and SmSI Types

		I_{obsd}		
hkl	I_{calcd} (YOF)	this work	ref 4	I_{calcd} (SmSI)
003	100	S	VS	92
006	15	W	M	13
101	0			18
012	56	M	VS	0
009	9		W	8
104	0	VVW		100
015	70	MS	S	4
107	31	W		1
018	5	W		35
0,0,12	14	MW	M⁻	13
1,0,10	12	VVW	VW	23
0,1,11	20	VVW		0
110	41	S	VS	39
0,0,15	1			0
113	9	VW	W	8
1,0,13	8	W		9
116	6		VVW	5
0,1,14	7			13
021	0			3
202	8	VW	M	0
119	9			9
024	0	W		16
205	13			2
0,0,18	4			4
1,0,16	7	W		6
027	8		M⁻	0
208	1			9
0,1,17	4			3
1,1,12	20	MW	S	19
0,2,10	4			6
2,0,11	7			0

remembered that the intensities are calculated with only good approximations to the real atom positions and that our visually estimated intensities may be affected by some preferred orientation on the mounting tape.)

The gains of a low decomposition temperature for production of $R\bar{3}m$ phases were offset by the appearance of broad bands in all of the powder patterns in the regions that distinguish the YOF-from the SmSI-type structure although the results for YOCl, ErOCl, and TmOCl did pertain to only a single $R\bar{3}m$ "phase". Thus, the otherwise distinctive regions 101-012, 104-015, 018-107, and 1,0,10-0,1,11 banded together while 00l reflections

(9) Meyer, G.; Ax, P. *Mater. Res. Bull.* **1982**, *17*, 247.
(10) Daake, R. L.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 2029.
(11) Seaverson, L. M.; Corbett, J. D. *Inorg. Chem.* **1983**, *22*, 3202.

Table II. Typical Fluxed Transformations of Various ROCl Structures

reacn	init compn	init struct	flux[a]	reacn temp, °C	reacn time, days	product type (other phases)
1	YOCl	R[b]	LiCl-KCl	450	14	R
2	HoOCl	R + PbFCl	LiCl-KCl	450	14	SmSI
3	ErOCl	R	LiCl-KCl	450	14	SmSI
4	YbOCl	R	LiCl-KCl	450	14	SmSI
5	ErOCl	PbFCl	LiCl-KCl	600	0.7	YOF
6	YOCl	R	KCl	850 / 850→700	1 / 1.5	} YOF (30-50%) (Y_2O_3, Y_3O_4Cl)
7	HoOCl	R	KCl	950 / 850→660	2 / 2	} YOF (30%) (Ho_3O_4Cl, Ho_2O_3)
8	HoOCl	R	KCl	800	4	PbFCl (10%) (Ho_2O_3)
9	ErOCl	R	KCl	950 / 950→660	2 / 2	} YOF (10%) (Er_2O_3)
10	ErOCl	PbFCl	KCl	800	0.7	YOF (5%) (Er_2O_3)
11	YOCl	R	YCl_3	910→620	3	PbFCl
12	YOCl	R	YCl_3-KCl[c]	850→490	3	PbFCl
13	ErOCl	R	$ErCl_3$	910→620	3	YOF (80%)[d]
14	TmOCl	R	$TmCl_3$	1000→670	4	SmSI
15	TmOCl	R	$TmCl_3$-KCl[c]	850→490	3	SmSI
16	TmOCl	R	LiCl-KCl	600	1	YOF
17	TmOCl	SmSI	LiCl-KCl	600	1	YOF
18	YOCl	R		900	1	PbFCl

[a] In sealed SiO_2 for LiCl-KCl, Ta for KCl and MCl_3. [b] The disordered SmSI-YOF type, $R\bar{3}m$. [c] ~50:50. [d] Remainder unknown.

remained sharp. This is characteristic of one-dimensional disorder often exhibited by polytypic substances[12] involving translational or rotational disorder of the sheets such that YOF and SmSI forms appear continuously intergrown (grinding ZrCl produces similar effects[10]). Even so, these represent the first indication of a rhombohedral layered structure for YOCl and HoOCl.

Annealing such disordered samples in sealed tantalum containers for 2–7 weeks at up to 750 °C produces no significant changes while temperatures near 900 °C even for short periods did give a sharp YOF-type pattern for YOCl (15–40%) but also substantial conversion to the PbFCl structure and, sometimes, small amounts of Y_3O_4Cl (below) as well. The solution to this proved to be the use of simple salt fluxes that apparently dissolve some of the phases since the treatment gives dramatic improvement in the sharpness of the powder patterns and even the development of visible crystal faces on some samples. Recovery of the sample now follows through solution of the flux in water and drying the product in air at 100–150 °C.

Conditions and results for these flux processes are summarized in Table II. The LiCl–KCl at flux temperature (450 °C) converts the $R\bar{3}m$ samples of Ho, Er, and Yb oxychlorides to pure SmSI phases, the first representing a new result, while ErOCl in the PbFCl structure is changed to the intermediate (see below) YOF phase and TmOCl in the SmSI form is converted to the YOF structure at 600 °C. The YOCl samples appear to be significantly less soluble, and the gain is small. The similar use of KCl alone with disordered ROCl phases (~10:1) at 800–850 °C for 1–14 days promotes decomposition of some samples to R_2O_3 and R_3O_4Cl (R = Ho, Y), but it also gives 10–50% amounts of the YOF-type phases for Ho, Er, and Y (Table II). A relatively smaller amount of flux and shorter times would probably increase yields appreciably, but pure YOF forms of YOCl and HoOCl may be difficult to obtain by this route. The use of the trichloride itself, which is known to dissolve ROCl and has been used to produce single crystals of YbOCl,[8] gives an 80% yield of ErOCl in the YOF form, the remainder unidentified, while with YOCl this yields only the PbFCl type and with TmOCl, the SmSI type. Powder pattern intensity comparisons with calculated data that confirm the SmSI assignment for HoOCl, ErOCl, TmOCl, and YbOCl and the YOF type for ErOCl and TmOCl are included as supplemental material.

We are unable to account for the fact that Beck[3] obtained the SmSI and not the YOF form of ErOCl on crystallization from $ErCl_3$. However, some of the reported powder pattern intensities

Table III. Formation of Some R_3O_4Cl Phases by LiCl-KCl Reactions

starting material	struct	temp, °C	time, days	% yield M_3O_4Cl (other phases)
YOCl	R^a or PbFCl	600	0.7–1	80–95[b]
DyOCl	PbFCl	650	0.7	100
HoOCl	R	600	0.7	50 (Ho_2O_3)
ErOCl	PbFCl	600	0.7	YOF type only

[a] The disordered $R\bar{3}m$ phase. [b] Remainder unidentified.

appear to be those of a mixture and in places are somewhat inconsistent with either type. Other reports in the literature on ErOCl and TmOCl have generally not recognized the YOF–SmSI alternatives.

Although not the primary purpose of this effort, more R_3O_4Cl phases were discovered in the course of this work beyond those for R = Er, Tm, Yb, and Lu that had been previously obtained by heating the metastable PbFCl types over 600 °C at atmospheric pressure.[13] We observed that this phase could also be obtained for Dy, Ho, and Y from the LiCl–KCl reactions (Table III)[14] but seldom for Er. Good single crystals of the Ho_3O_4Cl phase so obtained were examined by film methods to establish that the short axis of the structure reported by Bärnighausen[15] for Eu_3O_4Br needs to be quadrupled for the holmium oxychloride. Faint lines indicating this need are also seen in the powder patterns of the Dy and Y salts. The phase Y_3O_4Cl turns out to be both the other material in the sample described by Ward et al.[4] and the correct identity of the approximate composition $Y_2O_3\cdot2YOCl$ obtained by Markovskii and co-workers[16] from reaction of a 1:2 Y_2O_3–NH_4Cl mixture in air at 300 °C.

Refined lattice constants for the ROCl and R_3O_4Cl phases are listed in Tables IV and V, respectively. (The quadrupling of the short axis just noted for the latter is not included since the extra lines are all very weak.) The YOCl (YOF) samples obtained directly from R_2O_3–NH_4Cl reactions at 500–550 °C or through deintercalation of K_xYClO yield good patterns and lattice constants that are larger than those of materials obtained with the aid of alkali-metal chloride solvents at higher temperatures. This

(12) Trigunayat, G. C.; Verma, A. R. *Phys. Chem. Mater. Layered Struct.* **1976**, *2*, 318.

(13) Beck, H. P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 1015.

(14) First identified with the aid of powder data provided by H. Beck in a private communication.

(15) Bärnighausen, H.; Beck, H. P.; Grueninger, H. W. *Proc. Rare Earth Res. Conf., 9th* **1971**, 81.

(16) Markovskii, L.; Pesina, E.; Omel'chenko, A.; Kondrashev, D. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1969**, *14*, 7.

Table IV. Lattice Constants for ROCl Phases

compd	struct type	source	lattice params, Å[a]		V, Å³	lines used
			a	c		
YOCl	YOF	KCl	3.756 (1)	27.726 (6)	338.5 (2)	15
	YOF	LiCl-KCl	3.761 (2)	27.70 (2)	338.9 (5)	16
	YOF	Y₂O₃-NH₄Cl[b]	3.781 (2)	27.93 (1)	345.8	13
	YOF	Y₂O₃-NH₄Cl	3.7895 (5)	28.03 (1)	348.6	11
	YOF	K_xYClO[c]	3.7968 (3)	27.960 (8)	349.1	17
HoOCl	SmSI	LiCl-KCl	3.7681 (5)	27.70 (1)	340.2 (2)	17
	YOF	KCl	3.7677 (4)	27.700 (5)	340.2 (1)	25
ErOCl	SmSI	LiCl-KCl	3.7462 (5)	27.63 (1)	335.4 (1)	13
	YOF	LiCl-KCl	3.7458 (6)	27.73 (1)	336.6 (2)	16
	YOF	Er₂O₃-NH₄Cl	3.766 (1)	27.97 (3)	343.6	
	SmSI[d]	ErCl₃	3.765 (1)	27.92 (2)	342.7	~20
	YOF	ErCl₃	3.767 (1)	27.91 (1)	342.6 (2)	19
TmOCl	SmSI	TmCl₃	3.7425 (4)	27.852 (7)	337.8 (1)	18
	SmSI[d]	TmCl₃	3.743 (2)	27.91 (2)	338.6	~20
	YOF	LiCl-KCl	3.730 (1)	27.74 (1)	333.9 (2)	20
YbOCl	SmSI	LiCl-KCl	3.700 (2)	27.76 (2)	328.6 (4)	15
	SmSI[d]	YbCl₃	3.725 (1)	27.84 (2)	334.5	~20
ScOCl	FeOCl[e]	ScCl₃-Sc₂O₃	a = 3.955 (3), b = 3.465 (1), c = 8.274 (5)			13

[a] Space group $R\bar{3}m$. [b] From ref 4. [c] From deintercalation of K_xYClO.[16] [d] From ref 3. [e] The FeOCl structure is orthorhombic, space group *Pmmn*. Single-crystal photographs are consistent with the lattice parameters deduced from powder patterns and show extinctions consistent with the space group (S.-J. Hwu, private communication).

Table V. Lattice Constants for R_3O_4Cl Phases

R	lattice constants, Å[a]			lines indexed	source
Y	4.057 (1)	11.616 (2)	11.527 (2)	27	b
	4.031 (1)	11.596 (4)	11.586 (3)		c
Dy	4.0648 (5)	11.662 (2)	11.573 (2)	23	b
Ho	4.041 (2)	11.636 (6)	11.557 (5)	13	b
Yb	4.0157 (6)	11.406 (2)	11.316 (1)	30	b
	3.99 (1)	11.44 (2)	11.42 (2)		c

[a] Standard setting, space group *Cmcm*. [b] This work. [c] Reference 13.

difference also pertains to ErOCl, TmOCl, and YbOCl from RCl₃ relative to that from LiCl–KCl where the temperature difference is opposite. The differences in cell volumes are 2–3%. The deviations are the opposite of what would be expected were the alkali-metal chlorides to effect some sort of intercalation. There are no perceivable differences in color between the two types of products. Some degree of nonstoichiometry is possible, but further work on this aspect is not planned at this time.

It does appear possible to intercalate several of the layered ($R\bar{3}m$) compounds through classical liquid-ammonia reactions. Thus YOCl decolorizes a sodium solution in 1 h at room temperature to give a blue-black solid with a c lattice constant that has increased by ~2 Å to 29.85 (5) or 30.07 (1) Å, values that compare well with 29.95 Å obtained for 3R–Na~₀.₁₆YClO containing a YOF-type stacking.[5,17] Similar reactions and products are obtained from NH₃ with Ho, Er, Tm, and Yb ($R\bar{3}m$) oxychlorides (the last is violet colored), but these often give rather broad powder pattern lines and are evidently still somewhat disordered. Annealing these at 200–450 °C to improve their crystallinity usually leads to formation of NaCl and R₂O₃. Attempts to produce intercalated products from the normal (PbFCl) forms of NdOCl or GdOCl via melt reactions with LiCl or KCl plus metal were unsuccessful although the analogous reaction for YOCl, NaCl, and Y does yield the above 3R phase.[17]

The new oxychloride phases fit in very well in terms of their relationships to the other structure types. Beck[13] has demonstrated that an SmSI → PbFCl transition occurs for the ErOCl–LuOCl series under the effect of pressure and has modeled the transition in terms of a series of steps. The common and more compact PbFCl structure for the ROCl phases consists of square nets

(17) Ford, J. E.; Corbett, J. D., to be submitted for publication.

sequenced Cl–R–O–R–Cl... in which one stabilizing factor is the presence of a ninth strong nonmetal interaction for each R across what could otherwise be viewed as a Cl–Cl van der Waals gap. Thus, the compound does not show a characteristic cleavage or intercalation. The transition to SmSI type at ambient pressure for the heavier lanthanides is usually attributed to the smallness of their cations relative to chloride, which would otherwise lead to excess Cl–Cl repulsions and a loss of the ninth neighbor in the PbFCl structure.[2,3] Beck has described the reverse transition under pressure in terms of four steps: (1) a martensitic transition through slab displacements parallel to (001) at the van der Waals gap that converts SmSI to YOF (see Figure 1), this also providing the additional halogen neighbor to R across the gap; (2) compression of the hexagonal double-oxygen layer to a single layer as found in PbFCl; (3) a reorganization of the R and Cl ions relative to oxygen, most likely simultaneously with the second step (Beck referred to the product at this point as the z phase and gave a powder pattern for the presumed z-ErOCl that could be indexed for a large triclinic cell only slightly distorted from trigonal symmetry); (4) A martensitic sliding along [110] that converts the z arrangement to the square layers found in tetragonal PbFCl.

The preparation of the intermediate YOF type of ErOCl and TmOCl for systems where the SmSI and PbFCl structures were already known is as expected. This structure was evidently not seen by Beck, perhaps because the barrier between these under the action of pressure is negligible. Actually, the cell data for ErOCl (but not HoOCl) prepared from alkali-metal halide fluxes (Table IV) suggest the YOF type has a 0.2–0.3% larger volume, making its observation in a pressure experiment unlikely unless appreciable differences in activation energy prevail. The transformation of TmOCl from the SmSI to the YOF form in fluxes under ambient pressure implies that the transition does not require pressure.

One can also in effect gain the YOF form of YOCl as the intercalated 3R-M_xYClO (M = Li–Cs) from high-temperature (>900 °C) reactions. The dependence of the product structure on the nature of the oxide reactant in these instances strongly supports the existence of a direct interconversion between the PbFCl and the YOF types of YOCl. With appropriate amounts of MCl (M = Na–Cs), Y, YCl₃, and Y₂O₃ reactants, one obtains either the 3R-M_xYClO product, which is directly related to YOF by interslab expansion, or a two-slab 2H-M_yYClO structure, which can be derived from the YOF type only through changes in the layering sequence within the slabs, the structure achieved being dependent on the relative amount of MCl used. On the other hand, substitution of YOCl in the normal PbFCl structure for the

YCl_3–Y_2O_3 mixture in the reactants provides *only* the 3R-M_xY-ClO phase,[5,17] clearly via a simple interconversion along the lines suggested by Beck.

The present experiments also show that the polymorphism can be backed off significantly to lighter rare-earth elements by synthesis at lower temperatures, giving HoOCl in both the YOF and SmSI forms and YOCl as the YOF type. The last is not surprising when it is noted that the Y^{3+} and Ho^{3+} crystal radii are virtually identical for a variety of coordination numbers.[18] The cell volume of YOCl is slightly greater than that of HoOCl in the PbFCl form and smaller in the YOF version (Table IV).

The expanded list of polymorphs now known for the heavier lanthanides and yttrium is as follows, where bold-faced type represents the stable forms obtained by more traditional high-temperature methods, and italics, those found in the present work.

Dy	Y	Ho	Er	Tm	Yb	Lu
PbFCl	**PbFCl**	**PbFCl**	**PbFCl**	**PbFCl**	**PbFCl**	**PbFCl**
	YOF	*YOF*	*YOF*	*YOF*		
		SmSI	**SmSI**	**SmSI**	**SmSI**	**SmSI**

The structure of ScOCl was established to be of the FeOCl type (Table IV).

The pyrohydrolysis of the useful $(NH_4)_3RCl_6$ salts provides a convenient quantitative route to crystalline ROCl phases although these are clearly at the lower limit of coherent crystallinity (to X-rays) for the rhombedral structures of some systems when the pyrohydrolysis is carried out at 400 °C or below. This procedure does prevent the formation of any PbFCl type for YOCl, but a mixture is always obtained of HoOCl. It appears that this route

must exercise some kinetic control over the product since the preparation of disordered ErOCl in this way and its conversion to the SmSI form in LiCl–KCl both take place in the same temperature region where the low-temperature PbFCl modification has been obtained by decomposition of $ErCl_3 \cdot 6H_2O$ in air.[3] We have confirmed the latter result for both YOCl and ErOCl at the same temperature used for the formation of the disordered $R\bar{3}m$ material. It is difficult to imagine a topotactic route for the decomposition of either $(NH_4)_3RCl_6$ or $RCl_3 \cdot 6H_2O$; some nucleation control is likely to be involved. In another contrast, YOCl gives the YOF form (along with Y_3O_4Cl and Y_2O_3) from KCl at 850 °C but the PbFCl type on cooling its solution in YCl_3 from 910 to 620 °C. The decompositions observed in KCl at 800–900 °C and to a lesser degree in LiCl–KCl at ~600 °C doubtlessly are furthered by formation of $M^I_3RCl_6$ and other ternary compounds and could be diminished by the use of relatively less alkali-metal chloride or of a MCl–RCl_3 eutectic solvent. The latter has been briefly explored only for yttrium and thulium. Clearly, these flux processes deserve more attention.

(18) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

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Reactions of Metal Complexes with Carbohydrates: Isolation and Characterization of Novel Nickel(II) Complexes Containing *N*-Glycoside Ligands Derived from Amino Sugars

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Tris(ethylenediamine)nickel(II) ions react with the hydrochloride salts of D-glucosamine, D-galactosamine, or D-mannosamine to give blue-violet, paramagnetic bis(tridentate)nickel(II) complexes in which the tridentate ligand is the *N*-glycoside formed from an amino sugar and a diamine. The nickel(II) complexes have been characterized by elemental analysis, magnetic susceptibility, and electronic, infrared, and circular dichroism spectroscopy. To elucidate the detailed stereochemistry of this system, we have undertaken a crystal and molecular structure determination on the one of the complexes, [Ni(D-*N*-gl-en)$_2$]Br$_2$·4H$_2$O, where D-*N*-gl-en is the tetradentate *N*-glycoside ligand 1-[(2-aminoethyl)amino]-2-amino-1,2-dideoxy-D-glucose. The structure of the complex was determined from the three-dimensional X-ray counter data. The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 16.461$ (2) Å, $b = 23.371$ (3) Å, $c = 15.956$ (3) Å, and $Z = 8$ (two independent molecules per asymmetric unit). The structure was solved by direct methods followed by least-squares and Fourier techniques. Refinement using 4102 reflections with $F_o > 3[\sigma(F_o)]$ gave $R = 0.052$ and $R' = 0.064$. Both structures of the two independent complexes in the asymmetric unit are chemically identical. The two *N*-glycoside ligands complete a distorted-octahedral coordination around the nickel atom in the meridional mode; the complex has approximately C_2 symmetry. Each sugar moiety forms a five-membered chelate ring with the nickel atom in the λ-gauche conformation. The pyranose ring of the sugar is in the usual β-$^4C_1$ form. The relationship between the X-ray crystal structure and the CD spectra of the related metal complexes has been examined.

Amino acids and sugars are important compounds in the building of complex biochemical and biological molecules. These compounds are very interesting in coordination chemistry as ligands and in bioinorganic chemistry in connection with metal-containing enzymes. A great number of transition-metal complexes containing amino acids or their derivatives have been synthesized, isolated, and characterized. In spite of the fact that

it has been well-known that sugars can form complexes with transition metals, the field of sugar–metal complexes is still largely unexplored.

As a significant part of a program of study to elucidate sugar–transition-metal interactions, we have now examined amino sugars. Amino sugars (2-amino-2-deoxyaldoses) are of widespread occurrence in nature. They are combined in many polysaccharides and mucosaccharides of microbiological and animal origin, where they play an important role in physiological processes, and in a number of antibiotics. In spite of the importance of amino sugars

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