07-Crystallography of Organometallic and Coordination Compounds

Metal alkoxides might represent an alternative, especially as they are generally more attractive for the design of mixed metal species. Barium alkoxides involving fluorinated groups, namely perfluoro-
alkoxyporphyrin OCHF(CH3)2 (ORM) have been obtained either by direct
reaction between the metal and the alcohol or by alcoholysis reactions.
Crystal structure and chemical formula of one of them, crystallized from hexane/alcohol/hydrofluoric acid (THF), have been determined by single crystal X-ray diffraction at 220 K.

Crystal data are as follows: monoclinic symmetry; space group
P21/c; cell parameters a = 22.0 K, b = 24.65(1) A, c = 13.95(1) A,
β = 113.15(3)°; asymmetric unit: one
Ba5(ORA)(ECHFCH3)2(OH)(THF)2 H2O molecule + one not bonded
THF molecule; Z = 4. The molecular structure consists of a classical
paramagnetic cluster of barium atoms, arranged in a square based
pyramid. A µ-π ligand lies at the center of the pyramid squared
basis; 5 µ-OR ligands; 4 µ-OR ligands, THF and 1 H2O ligands are
surrounding the cluster. Thus, each barium atom has 7 to 11
oxygen or fluor atoms as neighbors. Such a high coordination
number for barium atoms explains the relative stability of this alkoxide.

Dimensions are compatible. This would further enhance the
necessary communication for the incommensurate modulation to be observed. Resolution of the struc-
ture options requires an ability to model the anions. The anions
were initially included in the model, as a series of spherically averaged SbCl6, spaced at 1/2c with large UO
thermal parameters. Subsequent to this fractional oriented
anions streaked along c have been used. The progress of
refinement has been monitored by assessing data of
different index condition. Refinement was kept in control
using RALS-89 to refine rigid body thermal parameters and
impose localized symmetry constraints. The anions
appear to have restricted orientation and be clustered
around the same z heights as the cations, 1/2c apart in the
average structure. Refinement is continuing. The observed
incommensurate modulation appears to be the result of the
c axial length being longer than required to have anions
contacting. This allows extra species, presumably
solvent, to be fitted into the channels.

We wish to thank Professor W. Robert Scheidt and Dr.
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providing the data for this problem.

PS-07.05.12 THE MODULATED CRYSTAL STRUCTURE
OF A METALLOPORPHYRIN π-CATION RADICAL.
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The hexachloroantimonic salt of chloronitro tetramethyl
porphyrin radical monocation crystalizes as a modulated
structure with a tetragonal 14/m plane space group;
a: 18.008, b: 2.194, c: 0, β: 90°. A commensurate modulation
exists corresponding to h+k+l = 2n+1 data being weakly
present. The absence condition h+k+l = 2n+1 is maintained
for the l = 0 data. There are also weak satellite reflections
(0.46 c°). A hierarchical approach to structure elucidation
was used, starting with a disordered average structure in
14/m and progressing to structure refinement attempts in
P4/n, and P4/n to try to identify the nature of the modulation.
The cation was located on a 4/m site in 14/m with the
mesityl groups on four separate cations defining a channel
about the c axis which contains the SbCl6 coordination.
These ions appeared streaked along c and individual atoms
are not resolved. Reduction of symmetry to P4/n or P4/n
allows the cation to adopt either a 4 or 4 symmetry
respectively. Pacing requires the SbCl6 to have a 2 axis
between adjacent Cl coincident with a 2 fold crystal
parallel to c. In either space group symmetry creates a
second anion 90° rotated translated along the same axis.
Both of these cannot fit in the axial repeat and one is not
required by chemistry. Ordering to lower the space group
to P 4 causes the h glide absence condition to be violated.
The anions appear to contribute very little to the h+k+l =
2n+1 data. The h+k+l = 2n+1 data has intensity distributed
in h and k rather than l. This appears to correspond to a
related rotation of the mesityl groups which provides a
mechanism for creating the necessary correlation between
columns to see the incommensurate reflections. The c
repeat distance would appear to be determined by contacts
between the mesityl groups of different molecules but
there appears to be a three atom contact between adjacent
chains along c. This is consistent with having an
asymmetric CI3+ ion linking Fe atoms rather than a CI-

PS-07.05.13 STRUCTURAL CHEMISTRY STUDIES ON RARE EARTH
INORGANIC COMPLEXES. By Y. H. Liu, Y. Yin, A. Z. Na, L. M. Li
and S. Q. Xi, Chinagham Institute of Applied Chemistry,
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This report gives a brief account of some of structural
chemistry studies on rare earth inorganic (REA). During the
past years, our research group has succeeded in synthesizing
a series of REA. These compounds respectively belong to
(BrEr2)(La(IO,OCl)Cl)6, Er2(OH)(IO,OCl)Cl, Er2Cl6(OH),
ErCl2(OH)(IO,OCl), ErCl2(OH)(IO,OCl), ErCl2(OH)(IO,OCl),
ErCl2(OH)(IO,OCl), ErCl2(OH)3, ErCl2(OH)3, ErCl4
and ErCl5(OH)Cl, respectively. The chemical structures of these
complexes have been identified by elemental analyses, IR and
mass spectra. Among them, the molecular configuration and
the bond parameters of several typic complexes have been
determined by careful X-ray structural analysis.
The characteristics of the molecular structure of REA have
been summarized. First, the anion groups in REA are
protonated and not coordinated. Second, rare earth atoms
are separated from each other by a distance about 4.5, so that
there are no metal-metal bonds between them. Thirdly, the
coordination number of rare earth metalions is 8-10, their
coordinate configurations forming square antiprism, triplated
trigonal prism and branzed square antiprism respectively.
Finally, these structures can be divided into infinite
three-dimensional network, one-dimensional chain and
bimolecular bridge three classes.

PS-07.05.14 CRYSTAL STRUCTURES OF (AdeH)2SbCl6H2O;
AND (AdeH)3SbCl4H2O (Ade = ADENINE). By Tu Lian-Dong
and Hu Sheng-Zhi, Chemistry Department, Xiamen University,
Xiamen, China.