

Advances in Preparative Chemistry of Oxides and Fluorides

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A new attempt is made to interpret chemical formulas in the sense of solid state chemistry. Chemical formulas do not reveal the coordination behavior of all particles; therefore, a modified method a la P. Niggli is given to express these terms by formulating "Motifs of Coordination." Furthermore unexpected new results in inorganic solid state chemistry (oxides and fluorides of metals, e.g., $\text{Rb}_8[\text{Zn}_4\text{O}_8]$, BaNiF_6) have been achieved by using new starting materials and new preparative techniques. Numerous examples are given in detail.

The term *advances* can be interpreted in different ways. Here it is restricted mainly to the synthesis of previously unknown compounds. From the abundance of possible examples, those which have been examined by the author's group were chosen. In addition, these as well as other examples cited here illustrate our present view of solid state chemistry and our "philosophy in behind."

I. On the Chemical Language of Formulas

In general, chemical formulas are written following more or less strict conventions, e.g., NaCl or H_2SO_4 , thus provoking one to think conventionally about even unknown compounds, e.g., AuF . To foster new ideas, basically, this needs to be altered (with the exception of textbooks, etc.): The chemical composition of a given compound—known or yet unknown—governs and restricts structural features much more than many chemists may imagine. Whereas in oxides such as Li_2PbO_3 (1) or BaPbO_3 (2), Pb^{IV} shows coordination number (CN) 6, this is not possible in, e.g., Cs_2PbO_3 (3): Cs^+ is too

large to enter octahedral holes of a closest packing of O^{2-} -like Li^+ ; and the ratio $\text{Cs}:\text{Pb} = 2$ is too large to allow the formation of a framework $\text{PbO}_{6/3}$ as in perovskites, e.g., BaPbO_3 . For both reasons, a layer lattice of Pb^{4+} with CN 6 is excluded. Therefore the structural principle according to $[\text{PbO}_{4/2}\text{O}_{1/1}]$ with CN 5 governs a wide range of compounds, from Cs_2PbO_3 and Cs_2PrO_3 (4) to K_2TiO_3 (5) and Cs_2TiS_3 (6). Using Niggli's system of writing chemical formulas of simple compounds (7) such as $\text{SiO}_2 = \text{SiO}_{4/2}$ in an extended manner, one can often foresee whether unusual CNs are to be expected:

"NiO," which perhaps has not previously been obtained as a "pure" material, adopts the NaCl type of structure. Consequently we write, following Niggli, $\text{NiO}_{6/6}$ as well as—and this is a characteristic feature of our variation of Niggli's idea— $\text{OTNi}_{6/6}$. Thus Li_2NiO_2 (9), written as $\text{LiO}_{4/4}(\text{Ni}_{1/2})$ or as $\text{OLi}_{4/4}(\text{Ni}_{1/2})$, immediately leads to the *motif of coordination* $\text{O}:\text{Li}_{4/4}\text{Ni}_{2/4}$, and thence to the corresponding $\text{Ni}:\text{O}_{4/2}$, which easily explains why the motif of the PdCl_2 type of

structure governs the $[\text{NiO}_2]$ part of Li_2NiO_2 . Consequently, we predicted that (then unknown) K_2NiO_2 , once obtained, should structurally follow the motif of coordination $\text{O}:\text{K}_{5/5}(\text{Ni}_{1/2})$, owing to the replacement of Li^+ by the much larger K^+ , with $\text{K}:\text{O}_{5/5}(\text{Ni}_{1/2})$. Here, if the CN of O^{2-} , as in Li_2NiO_2 and NiO , is 6 the motif $\text{Ni}:\text{O}_{2/1}(\text{K}_2)$ is implied. And indeed, K_2NiO_2 , after it was prepared with great difficulty (9), turned out to be a "stuffed derivative" of the XeF_2 type of structure (10, 11) with "isolated" linear groups $\text{O}-\text{Ni}-\text{O}$ characterized by unusually short distances $\text{Ni}-\text{O}$.

This system of writing chemical formulas in all possible ways, e.g., $[\text{PtCl}_6]\text{K}_2 = \text{KCl}(\text{Pt}_{1/2}) = \text{KCl}_{12/4}(\text{Pt}_{1/2}) = \text{ClPt}_{1/6}\text{K}_{4/12}$, leads us to use motifs of coordination, connection, and surrounding, as well as graphs of adjunctions, as a guide and tool for predicting unusual CN's and for describing even complex structures in greater detail than before (12).

II. Use of New Starting Materials

Whereas oxides such as NaLnO_2 (13) and KLnO_2 (14) are more or less easily prepared ($\text{Ln} = \text{La}$ to Lu), oxides RbLnO_2 were obtained at that time with $\text{Ln} = \text{Dy}$ to Lu only (15). All experiments in preparing analogous compounds such as CsNdO_2 failed (16). This striking discrepancy was later solved (18) by using freshly prepared, immensely active samples of Nd_2O_3^* . These were obtained by careful dehydration of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ *in vacuo* in two steps, the first leading to $\text{Nd}(\text{NO}_3)_3$ (free of water), and the second, by thermal decomposition, to Nd_2O_3 at less than 300°C . Thus the formation of NdOOH (a compound which requires higher temperatures to yield inactive samples of Nd_2O_3) was avoided.

Preparing single crystals of ternary oxides with Pb^{2+} -like $\text{K}_2\text{Pb}_2\text{O}_3$ (which, contrary to the literature (18), shows an eight fold but still cubic unit cell), we used underoxidized oxides such as $\text{KO}_{0.45}$ (instead of $\text{KO}_{0.5}$) to

getter the last traces of O_2 (which are always present). After intensive studies of K_4PbO_3 (19) with ClO_3 -like PbO_3 groups, $\text{K}_2\text{Pb}_2\text{O}_3$ and $\text{Rb}_2\text{Pb}_2\text{O}_3$ (20), which are perovskites ($\text{KPbO}_{3/2}$) with one-half of O^{2-} absent, as well as $\text{K}_2[\text{Pb}_2\text{O}_4]$ (20), we repeated experiments started in 1958 to prepare Oxostannates(II) such as K_2SnO_2 and $\text{K}_2\text{Sn}_2\text{O}_3$. Oxostannates(II) have never definitely been prepared before, because of disproportionation of Sn^{II} to Sn^{IV} and metallic Sn. Now using $\text{KO}_{0.45}$ we obtained single crystals of light yellow K_2SnO_2 and deep yellow $\text{K}_2\text{Sn}_2\text{O}_3$ (21) at the first onset. Obviously the disproportionation observed before was induced by the formation of, e.g., K_2SnO_3 formed with traces of O_2 which were not gettered (using K_2O and SnO_2).

III. New Techniques

A serious complication in the synthesis of solid state compounds is the "reaction with the wall." We have used this implication systematically to synthesize new oxides such as K_2NiO_2 , mentioned earlier, as well as others, e.g., Na_4FeO_3 (22), the first oxoferate(II). Surprisingly there are CO_3 -like planar groups $[\text{FeO}_3]$.

Originally we were not able to handle the beautiful colorless transparent single crystals of the Oxoplumbates(II) mentioned above. Because of the layer structure even a gentle touch with a tiny needle of glass leads to multiple splitting, producing many new, much thinner plates of crystals. Last, different electric charges of crystal and the glass needle (produced by intensive friction) enabled us to lift and to transport the mechanically, extremely sensitive, single crystals easily (after several attempts).

Following the ideas of Juza *et al.* (23), we constructed new autoclaves with which one may regularly use fluorine (up to 3000 atm, and $t = 550^\circ\text{C}$) or oxygen (up to 5000 atm and 800°C) to prepare new fluorides or oxides. A long and fruitless search for

BaNiF₆, begun in 1951 (25), was quickly solved. By high-pressure fluorination, we obtained carminered BaNiF₆, which surprisingly showed a new monoclinic form instead of the BaGeF₆-like form we expected. But annealing under pressure (40 000 atm) yielded the expected form immediately. Carminered SrNiF₆ was also obtained, but directly in the expected BaGeF₆ form. New intermediates such as CsRb[NiF₆] or RbK[NiF₆] were prepared in the same way (25). Similarly, Müller (26) obtained single crystals of MnF₄, O₂⁺[MnF₅], and O₂⁺[TiF₅], and O₂⁺[AuF₆] (27); and Jansen, crystals of As₂O₅ (28, 29) and Sb₂O₅ (30) for the first time.

Less dramatic conditions are used in the difficult preparation of pure samples of simple compounds such as K₂S, Cs₂S, and Rb₂Se. The well-known synthesis in liquid ammonia yields samples which always show distinct indications of partial ammonolysis. We let the elements react directly in the gas phase in a closed system (31). Starting with these very pure chalcogenides we obtained compounds such as K₆[HgS₄], etc. (32), which had previously been unknown.

The synthesis of well-known compounds such as KOH in the form of samples definitely free of CO₂ and/or H₂O is extremely difficult. We obtained CsOH for the first time, pure and in the form of single crystals, by reacting Cs₂O₂ with H₂, and we proved the purity of our samples by also preparing CsOH from Cs₂O₂, trapped in closed cylinders of Ag, by letting H₂ diffuse through the wall (33).

IV. Some Unexpected Results

I have never been convinced that our early work on Nd^{IV} and Dy^{IV} (34), although confirmed (35) by others, was free of doubt. Now, using high-pressure fluorination, we have finally obtained bright orange fluorescent samples of Cs₂RbNdF₇ and Cs₂RbDyF₇, which according to powder data

are members of the (NH₄)₃ZrF₇ type of structure. BaPrF₆, isotopic with RbPaF₆ (36), and SrPrF₆, LaF₃ type, both colorless, have been obtained for the first time (37).

Surprisingly a reinvestigation of the system Na₂O/NaFeO₂ yielded striking results. We found Na₅[FeO₄] (38) and Na₈[Fe₂O₇] (39) with isolated groups, Na₁₄Fe₆O₁₆ (40) with silicate-like double chains (Zweier-Einfach-Doppelkette; Liebau (41), Na₄[Fe₂O₅] (42) with a layer structure similar to that of Na₄[Si₂O₅] (43), and (always twinned single crystals of) Na₃FeO₃ (45) with a structure still unknown. In all cases Fe³⁺ shows CN 4, which is reminiscent of our cobaltates such as Cs₂[CoO₃] (45) or Li₈[CoO₄]O₂ (46).

In striking contrast to the unexpected similarity between K₆[Fe₂O₆] (47) and K₆[Mn₂O₆] (48), both of which show Al₂Cl₆-like groups [M₂O₆] the expected Jahn-Teller distortion is observed in Na₄Mn₂O₅ (49), which is the first definite example of such NaCl-like oxides with vacancies within the anion part of the lattice. Here Mn³⁺ as well as Na⁺ has tetragonal-pyramidal coordination; Mn³⁺, Jahn-Teller distortion.

We do not know why CsNbO₃ (50) (=Cs₄[Nb₄O₁₂]) shows tetrameric units with CN 5 for Nb⁵⁺ but is, instead, a variant of KIrO₃ (51) with CN 6. Newly obtained RbTaO₃ (52), which, in striking contrast to the literature (53), proved never to have been prepared before in a definite state, is characterized by a complicated layer structure, one-half of Ta having CN 5, and the other CN 6.

There is a close resemblance among new oxogallates such as Na₅[GaO₄] (54), Na₈[Ga₂O₇] (55) and Na₁₄[Ga₆O₁₄] (56). This holds even for Na₅NiO₄ (57), the first Oxoniccolate(III), which in striking contrast to the known examples LiNiO₂ (58) and NaNiO₂ (58) with CN 6, shows tetrahedral "isolated" groups [NiO₄].

Last, $\text{Rb}_8[\text{Zn}_4\text{O}_8]$ (59) and $\text{K}_2[\text{Zn}_6\text{O}_7]$ (60) are the first examples of oxozincates with Zn^{2+} having CN 3.

I would like to conclude with the case of the new fluoride SrRhF_5 (61). The poor quality of the single crystals obtained by annealing forced us to look for possible isotypes. We found BaGaF_5 (62), which was believed to be $\text{Ba}_3\text{Ga}_5\text{F}_{21}$ (63), and elucidated the crystal structure. This is a new, hitherto unknown, type for fluorides $\text{M}^{\text{II}}\text{M}^{\text{III}}\text{F}_5$. Previously formulated (64) $\text{Ba}_3\text{Cr}_5\text{F}_{21}$ is another representative of the new structure, BaCrF_5 .

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