## Letters to the editors

Evidence seems conclusive that a 1.6 MeV  $\beta$ -component is absent in the decay of <sup>72</sup>Zn. Although extrapolation from the straight line joining the energy differences between the known Ga and Zn isobars of even mass, as given by WAY and Wood,<sup>(6)</sup> would predict an energy difference of 1.5 MeV between ground states of <sup>72</sup>Zn and <sup>72</sup>Ga, while Cameron's mass formula<sup>(7)</sup> shows a 1.14 MeV mass difference, the observed one is only of about 0.41 MeV.

The assignment of spins is puzzling. Although the low intensity  $\gamma$ -rays observed by HAGEBØ *et al.* were not studied in this work, it is obvious that the main branching in the decay of the even-even nucleus <sup>72</sup>Zn passes through the 0.26 MeV  $\beta$  and the 147 MeV  $\gamma$ -transitions. The log ft value for the  $\beta$ -ray is close to 4.5 which is compatible with an allowed transition and indicates a 1<sup>+</sup> or 0<sup>+</sup> spin for a <sup>72</sup>Ga level at 147 keV. To reach the 3<sup>-</sup> spin of the ground state<sup>(8)</sup> the latter should decay with an M2 or an E3 multipolarity. The theoretical reduced transition probabilities for such a transition are too small to be consistent with the  $\beta$ - $\gamma$  coincidence measurement. Due to this discrepancy, no clear conclusions can be drawn from our work.

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Centre d'Étude de l'Énergie Nucléarie Mol, Belgium

P. Del marmol P. F. Fettweis

<sup>(6)</sup> K. WAY and M. WOOD, Phys. Rev. 94, 119 (1954).

<sup>(7)</sup> A. G. W. CAMERON, AECL report no 433 (1957).

<sup>(8)</sup> Nuclear Data Sheets, National Academy of Science, National Research Council, Washington, D.C. NRC-59-26.

## Potassium pentachlorovanadium (III)

(Received 27 October 1961; in revised form 25 February 1963)

SEVERAL salts of the ion  $[VCL_5H_2O]^{2+}$  were reported in 1904 by STAHLER<sup>(1)</sup>. These were prepared by evaporation of solutions under an HCl atmosphere. He reported that thermal decomposition of these salts led to oxycompounds. The only other work on halide complexes of V(III) that has appeared in the literature is a study of fused salt systems by BECK<sup>(2)</sup> which revealed the existence of KVCl<sub>4</sub>.

We have prepared  $K_2VCl_5$ '4H<sub>2</sub>O by a different route and have dehydrated it to stable  $K_2VCl_5$ . The hydrate was prepared by dissolving VCL<sub>3</sub> in concentrated 11·3 N HCl to give an 0·5 M solution. KCl was then added to give 1·0 M K<sup>+</sup>. Care must be taken to maintain an inert atmosphere (e.g., Ar or N<sub>2</sub>) by using a closed Pyrex<sup>®</sup> vessel equipped with reagent inlet and outlet tubes and a sinteredglass disc for filtration in the absence of air. Hydrogen chloride was bubbled through the solution for 18 hr. During this time the mixture was cooled to  $-30^{\circ}$ C. Green crystals of  $K_2VCl_5$ '4H<sub>2</sub>O separated from solution and were washed with dioxane or CCl<sub>4</sub>. The mother liquor might be more effectively removed with more polar organic solvents if it were not for their destructive effect on K<sub>2</sub>VCl<sub>5</sub>. The tetrahydrate is hygroscopic. When heated in Ar or N<sub>2</sub> to 100-125°C, this tetrahydrate readily loses all of its water to form violet K<sub>2</sub>VCl<sub>5</sub>.

Potassium pentachlorovanadium (III) is a pink hygroscopic crystalline solid. It is thermally stable in air to 270°C and in Ar to 400°C. The decomposition is complex with little VCl<sub>4</sub> being evolved and mixed valence states are found in the residues. A powder pattern was obtained for  $K_2VCl_5$  using filtered Cu radiation and a Straumanis-type X-ray diffraction camera of 57.3 mm radius. The complex pattern obtained probably represents a monoclinic or triclinic structure. A structure similar to that of  $Tl_2AlF_5^3$ , where molecules share an anion to gain octahedral coordination in a chain structure, seems improbable from a comparison of patterns.

<sup>(2)</sup> G. BECK, Z. anorg. allgem. Chem. 174, 31 (1928)

<sup>&</sup>lt;sup>(1)</sup> A. STAHLER, Ber. 37, 4411 (1904).

<sup>(3)</sup> C. BOSSET, ibid. 235, 139-47 (1937).

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The solubility of  $K_2VCl_5$  in the common organic solvents, acetone, ether, dioxane, methanol and n-propanol, was moderate and proceeded by decomposition of the complex, giving a solution of VCl<sub>3</sub> and a precipitate of crystalline KCl. Chlorination of  $K_2VCl_5$  by Cl<sub>2</sub> begins at 190°C, yielding VCl<sub>4</sub> vapours and a KCl residue.

The authors are indebted to Mrs. Gloria Faulring for conducting the X-ray examination.

Union Carbide Metals Company

P. H. CRAYTON\* W. A. THOMPSON

\* Present address: The Carborundum Company, Niagara Falls, New York.

## The structure of some new mixed metal oxides containing lithium

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IN THE course of an investigation on the crystal chemistry of compounds with spinel structure we prepared some new mixed metal oxides containing lithium, viz.  $LiMg_{0.5}Ti_{1.5}O_4$ ,  $LiCo_{0.5}Ti_{1.5}O_4$ ,  $LiCo_{0.5}Ti_{1.5}O_4$ ,  $LiCu_{0.6}Ti_{1.5}O_4$  and  $LiZn_{0.5}Ti_{1.5}O_4$ ;  $LiMnTiO_4$  and  $LiGaTiO_4$ ;  $LiCrMnO_4$ ,  $LiRhMnO_4$  and  $Li_{4/3}Mn_{5/3}O_4$ , all with spinel structure and  $LiGaGeO_4$  with phenacite structure.

These compounds were prepared by heating an intimate mixture of high-purity oxides or carbonates for several hours at 950°C in an atmosphere consisting of an 80-20 mixture of oxygen

Formula	Structure	Lattice parameters (Å)	Cation distribution*
LiMg <sub>0.5</sub> Ti <sub>1.5</sub> O <sub>4</sub>	spinel (with superstructure)	a = 8.37	$ \begin{split} &\approx Li_{0.5}Mg_{0.5}[Li_{0.5}Ti_{1.5}] \\ &\approx Li_{0.5}Co_{0.5}[Li_{0.5}Ti_{1.5}] \\ &\approx Li_{0.7}Cu_{0.3}[Li_{0.5}Cu_{0.2}Ti_{1.5}] \\ &\approx Li_{0.5}Zn_{0.5}[Li_{0.5}Ti_{1.5}] \end{split} $
LiCo <sub>0.5</sub> Ti <sub>1.5</sub> O <sub>4</sub>	spinel (with superstructure)	a = 8.36	
LiCu <sub>0.5</sub> Ti <sub>1.5</sub> O <sub>4</sub>	spinel	a = 8.39	
LiCu <sub>0.5</sub> Ti <sub>1.5</sub> O <sub>4</sub>	spinel (with superstructure)	a = 8.37	
LiMnTiO₄	spinel	a = 8.30 $a = 8.28$	Li[Mn <sup>3+</sup> Ti <sup>4+</sup> ]
LiGaTiO₄	spinel		Li <sub>0-3</sub> Ga <sub>0-7</sub> [Li <sub>0-7</sub> Ga <sub>0-3</sub> Ti]
LiGaGeO₄	phenacite	$a = 13.9^{\circ}$ c = 9.29	
LiCrMnO4	spinel	a = 8.19	$\begin{array}{l} Li[Cr^{3+}Mn^{4+}]\\ Li[Rh^{3+}Mn^{4+}]\\ Li[Li_{1/3}Mn^{4+}_{5/3}] \end{array}$
LiRhMnO4	spinel	a = 8.30	
Li4/3Mn5/3O4	spinel	a = 8.19	

TABLE 1.-- NEW MIXED METAL OXIDES CONTAINING LITHIUM

\* octahedral site cations between brackets.

and carbon dioxide. X-ray diagrams were obtained with a Philips X-ray diffractometer using  $CoK\alpha$  or  $CuK\alpha$  radiation. A survey of our results is given in Table 1. The following facts are noteworthy:

(a) The cation distribution of the spinels  $\text{LiMe}_{0.5}^{2+5} \text{Ti}_{1.5}O_4$  was calculated from the intensities of the X-ray reflections starting from the model  $\text{Li}_{0.5+x}\text{Me}_{0.5-x}^{2+}[\text{Li}_{0.5-x}\text{Me}_{x}^{2+}\text{Ti}_{1.5}]O_4$  with ideal oxygen parameter (u = 0.375). For the compounds with Me = Mg, Co and Zn we found 0 < x < 0.1, for the one with Me = Cu  $x \approx 0.2$  (reliability index R about 13 per cent). Besides the spinel reflections we found the same superstructure reflections as have been found for ordered lithium ferrite Fe[Li\_{0.5}Fe\_{1.5}]O\_4^{(1)}. This means that in these titanates we have a 1:3 order of mainly Li<sup>+</sup> and Ti<sup>4+</sup> ions on octahedral sites.

<sup>(1)</sup> P. B. BRAUN, Nature 170, 1123 (1952).