The present investigation on the behavior of silicon tetrachloride is but one in a series which has for its scope the determination of the reactions also of lead and tin tetrachlorides with amine bodies. Work is also in progress in this laboratory on the conduct of thorium and zirconium tetrachlorides with the same reagents. The results thus obtained will afford a wider study of the fourth group elements, and furnish data for a broader comparison of the reactions of its members.

SOME NEW RUTHENOCYANIDES AND THE DOUBLE FERROCYANIDE OF BARIUM AND POTASSIUM.

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THE resemblance between the double cyanides of iron, ruthenium, and osmium, was first pointed out by Claus,[2] and further developed by Martius,[3] who formed a number of the double osmocyanides. More recently Dufet[4] has described the crystals of potassium ruthenocyanide and osmocyanide and shown their close crystallographic resemblance to the ferrocyanide. The chemistry and the crystallography of the ferrocyanides has been very exhaustively studied by Wyrouboff,[5] and his work affords a valuable starting point for any investigation of the isomorphous ruthenocyanides and osmocyanides.

Since the publication of a recent paper by one of us (Howe)[6] on the ruthenocyanides, several new salts have been prepared, and in all of them the analogy of the ruthenocyanides with the ferrocyanides is complete. The ruthenocyanides are decidedly more soluble than the ferrocyanides and correspondingly more difficult to crystallize. In one salt only have crystals been obtained which were perfect enough to measure.

Strontium Ruthenocyanide, $Sr_2Ru(CN)_6,15H_2O$.—Formed by treating lead ruthenocyanide with dilute sulphuric acid and neutralizing of the hydroruthenocyanic acid formed with strontium

[1] Contributed to the November meeting of the Cincinnati Section of the American Chemical Society, November 16, 1897.

[2] Beiträge zur Chemie der Platinmetalle. pp. 98 and ff.

[3] Ueber die Cyanverbindungen der Platinmetalle. Inaug. Diss., Göttingen, 1860.

[4] *Compt. rend.*, 120, 377.

[5] *Ann. chim. phys.* [4], 16, 280; 21, 271.

[6] This Journal, 18, 981.

hydroxide. The salt obtained by treating "Prussian purple," the ruthenium analogue of Prussian blue, with strontium hydroxide, could not be obtained in a pure condition. Pale straw-colored, elongated plates, probably monoclinic, very soluble in water, and quite efflorescent. By adding alcohol to its hot solution, the salt can be obtained in long, fine needles. It is very difficult to obtain a salt pure enough for analysis, and owing to efflorescence the water determination is low. The corresponding strontium ferrocyanide crystallizes with fifteen molecules of water of crystallization.[1]

ANALYSIS.

I. Crystallized from water. II. Crystallized from dilute alcohol.

	Calculated for		Found.	
	$Sr_2Ru(CN)_6.15H_2O$.	$Sr_2Ru(CN)_6,14H_2O$.	I.	II.
Water	38.41	36.79	36.80	37.12
Ruthenium	14.45	14.83	14.36	....
Strontium	24.94	25.59	25.11	....

Barium Potassium Ruthenocyanide, $K_2BaRu(CN)_6,3H_2O$.—Formed by mixing equivalent solutions of the barium and potassium salts; also, mixed with the barium salt, by treating Prussian purple with barium hydroxide. Crystallizes best from its hot solution in water while evaporating on the water-bath. Pale amber to colorless rhombohedra, hardly distinguishable from the corresponding ferrocyanide, but quite soluble in water. The salt is difficult of analysis, owing to the difficulty of completely decomposing it by heat to obtain the insoluble oxide of ruthenium. Some of the ruthenium invariably went into solution in hydrochloric acid, and from this solution a blue precipitate, insoluble in acids, soon separated, probably $Ru(CN)_2$, but invariably containing both barium and potassium.

ANALYSIS.

	Calculated for	Found.			
	$K_2BaRu(CN)_6,3H_2O$.	I.	II.	III.	IV.
Potassium	14.83	12.98	....	14.51	13.16
Barium	26.07	27.38	25.31	....	25.83
Ruthenium	19.27	18.71	....	....	18.94
Water	10.25	10.19	10.80	10.83	10.99

The water in I was determined by loss, but in the other three analyses by absorption and direct weighing. In these three

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[1] Wyrouboff: *Ann. chim. phys.*, 16, 287.

cases the salt in a closed tube was heated until it began to decompose. It is therefore impossible that the salt can contain five molecules of water, as this would require sixteen per cent.

Wyrouboff[1] describes the barium potassium ferrocyanide as $K_2BaFe(CN)_6,5H_2O$, but crystallographically the two salts resemble each other very closely.

Crystallography of barium potassium ruthenocyanide, $K_2BaRu(CN)_6,3H_2O$. Rhombohedral. $a : c = 1.558$. Angle between basal plane and rhombohedron = 119° 4′. The mean of thirty-nine measurements on eight crystals gave 81° 27′ as the rhombohedral angle. (Calculated = 81° 36′.)

Crystals rhombohedral, with occasional development of basal plane. Rhombohedral faces usually appear pitted, and give a bundle of reflections, making a variation of 50′ in the measured angles; optically negative; double refraction weak. In converging polarized light the cross opens slightly into hyperbolas.

A comparison of the crystallography of the ruthenocyanide with the ferrocyanide as given by Wyrouboff shows their close relationship.

Barium potassium ferrocyanide.[2]	Barium potassium ruthenocyanide.
Rhombohedral. $a : c = 1.570$.	Rhombohedral. $a : c = 1.558$.
Angle between basal plane and rhombohedron = 118° 53′.	Angle between basal plane and rhombohedron = 119° 4′.
Rhombohedral angle = 98° 48′ (81° 12′).	Rhombohedral angle=81° 36′ (calculated); 81° 27′ (measured).
Optically positive.	Optically negative.

Barium Cesium Ruthenocyanide, $Cs_2BaRu(CN)_6,3H_2O$.—When barium ruthenocyanide is mixed with half the equivalent of cesium sulphate, there separate from the solution, even before it can be filtered from the barium sulphate, unless very dilute, minute, brilliant, yellowish-white to colorless crystals, which under the microscope appear as rhombohedra, with angle of about 83°, and in every way resembling the barium potassium salt, except that the basal plane predominates. They are very insoluble even in hot water, and cannot be recrystallized owing to partial decomposition and precipitation of a blue insoluble

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[1] Wyrouboff: *Ann. chim. phys.*, 21. 279.

[2] Wyrouboff: *loc. cit.*

substance, probably $Ru(CN)_2$. The salt is stable in the air as analyses II and III were made from a salt which had stood exposed in the laboratory for several weeks.

ANALYSIS.

	Calculated for $Cs_2BaRu(CN)_6,3H_2O$.	Found.		
		I.	II.	III.
Cesium	37.18	....	....	36.45
Barium	19.21	19.06	....	18.70
Ruthenium	14.21	....	....	14.33
Water (by loss at 120°)	7.56	7.64	7.31	7.51

The sodium, the magnesium, and the calcium salts have been obtained, but are very difficult to crystallize, owing to their great solubility. The magnesium salt forms very pale green crystals, which are very efflorescent.

The strontium potassium, and the strontium cesium ruthenocyanide have been formed, but not in pure enough condition for analysis. They seem to resemble the barium double salts under the microscope and bear no resemblance to the salt $K_2SrFe(CN)_6$, $3H_2O$, described by Wyrouboff, which crystallizes in prismatic monoclinic crystals. The strontium rubidium ruthenocyanide gives a precipitate on warming its solution, and thus appears to resemble the strontium potassium ferrocyanide which precipitates the anhydrous salt under similar circumstances.

Analysis having shown that the barium potassium ruthenocyanide contains three molecules of water of crystallization, and yet resembles closely the ferrocyanide to which Wyrouboff[1] gives five molecules, a re-examination of the ferrocyanide was made. Bunsen, who first made the salt, gives the formula with three molecules of water, and from analogy to the ruthenocyanide three would be expected. Further, Martius[2] formed the corresponding osmocyanide, to which he gives the formula $K_2BaOs(CN)_6,3H_2O$. His description of the salt would hold equally good for the ruthenocyanide or ferrocyanide, except that it is efflorescent.

A considerable quantity of the ferrocyanide was prepared in this laboratory by Mr. H. W. Drake. The very sparingly soluble barium salt was made by the action of barium chloride on potassium ferrocyanide, and this, mixed with an equivalent

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[1] Wyrouboff: *Loc. cit.*

[2] Martius: Cyanverbindungen, p. 23.

quantity of the potassium salt was dissolved in a large amount of water. On evaporation and cooling the barium potassium salt was deposited in pale straw-colored rhombohedra, often several millimeters across. The salt, contrary to the statement of Wyrouboff, is perfectly stable, and after five months' exposure to the air the crystals are perfectly clear and the surfaces bright. Measurement of the crystal angles, and examination of the optical properties, showed the salt to be identical with that described by Wyrouboff. Analysis showed that the salt has *three* molecules of water of crystallization, and its formula is $K_2BaFe(CN)_6,3H_2O$. The water was determined directly by absorption in a calcium chloride tube, the salt being heated until decomposed.

ANALYSIS.

	Calculated for $K_2BaFe(CN)_6,5H_2O$.	Calculated for $K_2BaFe(CN)_6,3H_2O$.	Found. I.	Found. II.
Water······	17.40	11.38	11.68	11.72
Barium ····	26.55	28.53	28.88	28.61

Barium Cesium Ferrocyanide, $Cs_2BaFe(CN)_6,3H_2O$. This salt, which appears never to have been described, was made for purposes of comparison. It was formed by decomposing barium ferrocyanide with half the equivalent of cesium sulphate in very dilute solution. It crystallizes in very small, slightly yellowish-white rhombohedra, and is very difficultly soluble in water. Its hot solution appears to be stable.

ANALYSIS.

	Calculated for $Cs_2BaFe(CN)_6.3H_2O$.	Found.
Cesium················	39.71	38.03
Barium············· ··	20.53	20.42
Iron···················	8.37	8.53
Water ···· ·· ········	8.07	8.01

Crystallography, rhombohedral. $a:c = 1.515$. Angle between basal plane and rhombohedron = 119° 45′ (calculated). Rhombohedral angle = 82° 30′.

This salt adds confirmatory testimony to the amount of water of crystallization in barium potassium ferrocyanide, and also to the close crystallographical resemblance between the salts of the type $M'BaM'''(CN)_6,3H_2O.(M'=K_2Cs_2\,;\ M'''=Fe,Ru,Os)$.

WASHINGTON AND LEE UNIVERSITY,
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