

20.5 w, 22.65 vw, 24.75 vw, 26.65 vw, 28.25 vw, 30.05 vw, 31.5 vw.

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[1] U. Wannagat, K. Hensen, and F. Vielberg, *Mh. Chem.* 99, 431 (1968).

[2] A. Kaczmarczyk and G. Urry, *J. inorg. nuclear Chem.* 26, 415 (1964); G. Urry, *ibid.* 26, 409 (1964); A. Neumaier, Dissertation, Universität München 1960.

[3] H. Günther and S. Castellano, *Z. Naturforsch.* 23b, 1113 (1968).

[4] H. G. v. Schnering *et al.*, unpublished work.

Application of the Mössbauer Effect to Investigation of the Solid State Reaction of Iron(II) Sulfate with Potassium Cyanide^[1]

By P. Gütlich and K. M. Hasselbach^[*]

The Mössbauer effect^[2] has been used to study the reaction of iron(II) sulfate with potassium cyanide in the solid state as a function of reaction time, temperature, and content of water of crystallization of the iron(II) sulfate.

The reactants were mixed in the molar ratio $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} : \text{KCN} = 1 : 6$ (particle size of both components = 0.2–0.3 mm) and pressed to tablets. The course of the reaction was followed at 5 °C and at 20 °C [Mössbauer spectra measured at –96 °C (temperature of the absorber); radiation source: ⁵⁷Co in platinum (room temperature)].

Depending on the reaction time, the Mössbauer spectra contained up to five, partially overlapping resonance lines. The iron compounds assigned to the experimentally observed data are shown in the Table.

Complex	Chemical isomer shift δ (mm/s)	Quadrupole splitting ΔE_Q (mm/s)
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	$+0.98 \pm 0.02$	3.41 ± 0.02
$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	-0.34 ± 0.02	0
$\text{K}_3[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]$	-0.21 ± 0.02	0.75 ± 0.03

The values of the chemical isomer shifts and quadrupole splittings agree very well with those reported in the literature^[3].

During the reaction the water molecules in the coordination sphere of the magnetically normal ("high spin") complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ are replaced by cyanide ions. Under the experimental conditions used the sole intermediate visible in the Mössbauer spectrum is the magnetically abnormal ("low spin") complex $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$, which is unstable and reacts with further cyanide ions to give the stable complex $[\text{Fe}(\text{CN})_6]^{4-}$.

After suitable standardization of the Mössbauer spectra the three complexes $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Fe}(\text{CN})_6]^{4-}$, and $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ can be determined quantitatively (mean error < $\pm 3\%$) in the presence of each other as a function of various reaction conditions.

Surprisingly, the reaction between $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and KCN in the solid state is relatively fast at 5 °C: the iron(II) sulfate has reacted almost quantitatively after about 30 h. Two partial steps were observed for the consumption of iron(II) sulfate, the rate constants being $k(\text{I})_5 = (3.75 \pm 0.20) \times 10^{-2} \text{ min}^{-1}$ and $k(\text{II})_5 = (1.5 \pm 0.1) \times 10^{-3} \text{ min}^{-1}$. The two steps are ascribed to diffusion of cyanide ions and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ions, respectively, through a zone that is softened by water

liberated on substitution by cyanide ions in the coordination sphere of the iron; the activation energies for the two diffusion steps are $\Delta E_A(\text{I}) = 12.5 \pm 2.0$ and $\Delta E_A(\text{II}) = 17.5 \pm 2.5$ kcal mole⁻¹.

The water content of the iron(II) sulfate plays a very important part in the reaction. This was shown by experiments with $\text{FeSO}_4 \cdot 2.5\text{H}_2\text{O}$ instead of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; in these experiments no change was observed even after 30 days at 5 °C. Use of the Mössbauer effect for the investigation of solid state reactions of the kind described here has the particular advantage that the samples remain in closed containers and can be analyzed without destruction.

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[2] R. L. Mössbauer, *Z. Physik* 151, 124 (1958); *Naturwissenschaften* 45, 538 (1958); *Annu. Rev. nuclear Sci.* 12, 123 (1962).

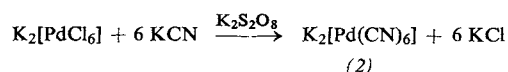
[3] E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem.* 75, 461 (1963); *Angew. Chem. internat. Edit.* 2, 277 (1963).

Potassium Hexacyanopalladate(IV)

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Hexacyanoplatinates(IV) were first described several years ago^[1]. $\text{K}_2[\text{Pt}(\text{CN})_6]$ (1) is formed on reaction of $\text{K}_2[\text{PtI}_6]$ and KCN in the solid state and is very stable. This made it seem possible that hexacyanopalladates(IV) might also exist although Pd^{IV} compounds are in general much less stable than their Pt^{IV} analogs.

An attempted synthesis analogous to that of (1) failed. $\text{K}_2[\text{PdI}_6]$ is unknown; $\text{K}_2[\text{PdCl}_6]$ and $\text{K}_2[\text{PdBr}_6]$ react with KCN in the solid state and in aqueous solution with complete reduction of the Pd^{IV} , partly to tetracyanopalladate(II) and partly to metallic palladium. However, $[\text{Pd}(\text{CN})_6]^{2-}$ can be synthesized in aqueous solution if the reduction is prevented by addition of potassium peroxodisulfate.



On fractional crystallization of the reaction mixture, $\text{K}_2\text{S}_2\text{O}_8$ separates first, then (2), and finally $\text{K}_2[\text{Pd}(\text{CN})_4]$ and K_2SO_4 . The presence of (2) in individual fractions can be determined through the characteristic IR band at 2185 cm^{-1} . The yield averages 19%; use of $\text{K}_2[\text{PdBr}_6]$ as starting material gives lower yields.

Crystals of (2) are colorless, six-sided, domed prisms. The salt is moderately soluble in water, very slightly soluble in ethanol, and insoluble in ether. Above 160 °C it decomposes slowly; it is stable at room temperature to water, dilute acids, concentrated nitric acid, and bromine water. Concentrated sulfuric or hydrochloric acid at room temperature and boiling water decompose it slowly, with reduction to tetracyanopalladate(II) and palladium(II) cyanide. The CN stretching vibration appears in the IR spectrum of (2) at 2185 cm^{-1} , which is appreciably higher than that for $[\text{Pd}(\text{CN})_4]^{2-}$ (2136 cm^{-1}). The relations are similar to those for the corresponding platinum compounds^[2].

Potassium hexacyanopalladate(IV) (2)

A solution of KCN (29.3 g, 0.45 mole) and $\text{K}_2\text{S}_2\text{O}_8$ (12.2 g, 0.045 mole) in water (2.3 l) is added slowly and with stirring to a suspension of K_2PdCl_6 (20.0 g, 0.05 mole) in a solution of $\text{K}_2\text{S}_2\text{O}_8$ (1.35 g, 5 mmoles) in water (250 ml). The prod-