

Crystal structure and thermal stability of potassium tetrathiocyanatoplatinate(II), $K_2Pt(SCN)_4$

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Abstract

The crystal structure of potassium tetrathiocyanatoplatinate(II), $K_2Pt(SCN)_4$, was refined from single crystal X-ray diffraction data to R value of 0.05. $K_2Pt(SCN)_4$ crystallizes in the monoclinic space group $P2_1/c$ ($Z=2$) with the following cell dimensions: $a=4.294(4)$, $b=12.869(8)$, $c=11.055(8)$ Å, and $\beta=98.00(6)^\circ$. The crystal structure consists of layers of planar $[Pt(SCN)_4]^{2-}$ complex anions parallel to the ac plane. Layers are linked by K^+ ions into a three dimensional network through N–K–S bonds. A very weak Pt–S–Pt interaction along the a axis results in $[Pt(SCN)_6]^{4-}$ groups with strong tetragonal distortion. The nearly linear SCN^- chains have a bent coordination to Pt through sulfur atoms. K^+ ions are coordinated to three sulfur and five nitrogen atoms in a strongly distorted bicapped trigonal prism arrangement. Both in air and in inert (argon) atmosphere $K_2Pt(SCN)_4$ is stable up to 200 °C above which it decomposes through complex reactions involving several intermediate phases. The main phases formed are sulfates and oxides in air and sulfides in argon.

Introduction

The catalytic activity of platinum and platinum compounds has been an established fact for a long time. In addition to the research involved in catalysis the inorganic and complex platinum as well as organoplatinum compounds have received much attention since Rosenberg *et al.* [1] discovered in 1969 the antitumor properties of some platinum complexes. Although the first successful drugs, e.g. cis-platin $cis-[Pt(NH_3)_2Cl_2]$, were rather simple complexes, the present research is being concentrated on much more complicated and even exotic compounds. Nowadays complexes like cis-platin are considered only as possible precursors. In the view of the unprecedented boom in the research of platinum compounds the structural studies concerning thiocyanate complexes of platinum in its different stable oxidation states, i.e. +2 and +4, have been, surprisingly enough, relatively few [2–6].

A preliminary but only partly correct analysis of the crystal structure of $K_2Pt(SCN)_4$ has been reported by Zvonkova [2]. The X-ray powder diffraction pat-

tern of the same compound has also been published [3]. The structures of the mixed ligand platinum complexes, *cis*- and *trans*- $Pt(NH_3)_2(SCN)_2$, have been reported [6]. As to Pt^{IV} , the determination of the crystal structure of $M_2Pt(SCN)_6$ where $M=K^+$, NH_4^+ or Rb^+ has been tried [4, 5] but the extensive disorder in anion and M^+ positions has rendered these trials futile. It has, however, been established that Pt^{II} has a tendency toward planar tetracoordinate complexes with Pt–S bonds around 2.3 Å while Pt^{IV} forms octahedrally coordinated complexes with thiocyanate ligands.

The present paper gives the results of the crystal structure determination and the description and interpretation of the thermal decomposition of $K_2Pt(SCN)_4$ in the view of the crystal structure.

Experimental

Sample preparation

The single crystals of $K_2Pt(SCN)_4$ were obtained from an aqueous solution of $K_2Pt(SCN)_6$ which was

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TABLE 1. Details of the data collection and structure refinement

Data collection	
Crystal name	potassium tetrathiocyanatoplatinate(II)
Formula	$K_2Pt(SCN)_4$
Formula weight	505.6
Scan type	$2\theta-\omega$
Scan speed ($^{\circ}\text{min}^{-1}$) in 2θ	variable from 0.49 to 29.3
Crystal system and space group	monoclinic $P2_1/c-C_{2h}^5$ (No. 14)
Z	2
Cell constant determination	25 reflections ($20 < 2\theta < 25^{\circ}$)
a (\AA)	4.294(4)
b (\AA)	12.869(8)
c (\AA)	11.055(8)
β ($^{\circ}$)	98.00(6)
V (\AA^3)	604.9(7)
D_x (g cm^{-3})	2.775
Radiation (\AA)	Mo ($K\alpha$) = 0.71069
2θ range ($^{\circ}$)	$0 < 2\theta < 60$
$[(\sin\theta)/\lambda]_{\text{max}}$ (\AA^{-1})	0.70
h, k, l range	$\pm 7, 23, 18$
Number of reflections collected	1921
Structure refinement	
Programs used	XTAL
No. observed reflections	1745 [$F_{\text{obs}} > 3\sigma(F_{\text{obs}})$]
Function minimized	$\sum w(F_{\text{obs}} - F_{\text{calc}})^2$
Weighing scheme	$w = 1/[\sigma^2(F_{\text{obs}})]$
No. variables	70
Absorption correction	empirical (2θ -scan data) transmission factor from unity to 0.24
R	0.050
R_w	0.046

treated with $N_2H_2 \cdot HCl$ in order to reduce the tetravalent platinum to Pt^{II} . A repeated recrystallization yielded $K_2Pt(SCN)_4$ in the form of regular shaped dark red single crystals.

Crystal data

The X-ray diffraction data collection was carried out with a Syntex $P2_1$ four circle single crystal diffractometer at ambient temperature. Two standard reflections were chosen in order to check on the crystal and electronics stability. The intensity of these reflections remained practically constant throughout the whole measurement. A total of 1921 unique reflections was collected with $\sin\theta/\lambda$ less than 0.7 \AA^{-1} . The intensities were corrected for Lorentz, polarization and absorption (empirical) effects. Additional information about the data collection can be found in Table 1.

The position of the Pt atom was determined from a Patterson map and those of the K, S, C, and N atoms were found from subsequent difference electron density calculations with the aid of the XTAL crystal structure determination program [7]. The refinement of the atomic positions was based on 1745 reflections with F_{obs} greater than $3\sigma(F_{\text{obs}})$ and

the reflections were weighed inversely proportional to the estimated variance. All atoms were refined with anisotropic temperature factors. Further details of the structure refinement are given in Table 1.

Thermal analysis

The thermogravimetric (TG and DTG) analyses were carried out with a Perkin-Elmer TGA7 thermogravimetric analyzer of the Perkin-Elmer 7 Series thermal analysis system both in a dynamic air and inert (argon) atmosphere with a heating rate of $2.5^{\circ} \text{min}^{-1}$. The temperature range studied extended to 1160°C . A typical sample weight used was less than 1 mg.

Results and discussion

Description of structure

Details of the determination and refinement of the crystal structure of $K_2Pt(SCN)_4$ can be found in Table 1. The fractional atomic positions are given in Table 2, selected bond distances and angles in Table 3. The contents of the unit cell illustrated in Fig. 1 show that the $[Pt(SCN)_4]^{2-}$ anions form layers

TABLE 2. Fractional positional parameters and equivalent temperature factors U_{eq} for atoms in $K_2Pt(SCN)_4$

Atom	x	y	z	U_{eq}^a
Pt	0.0000(0)	0.0000(0)	0.0000(0)	16.18
S1	0.7868(5)	0.4075(2)	0.1503(2)	25.57
C1	0.9566(19)	0.9242(6)	0.2238(7)	29.14
N1	0.7990(19)	0.9355(7)	0.1290(7)	44.91
S2	0.8573(5)	0.6623(2)	0.0628(2)	31.02
C2	0.7624(19)	0.6540(7)	0.2054(8)	29.23
N2	0.2976(19)	0.1529(7)	0.1974(7)	31.37
K	0.7199(4)	0.1467(2)	0.0301(2)	52.42

^aThe equivalent temperature factor U_{eq} was defined as one third of the trace of the orthogonalized U_{ij} tensor. The U_{eq} values presented above were multiplied by a factor of 10^3 .

parallel to the ac crystal plane. The stacking of $[Pt(SCN)_4]^{2-}$ anions is arranged in a way typical of platinum in order to reach an octahedral coordination by contact to two additional sulfur atoms along the a axis (Fig. 2). No direct Pt–Pt interaction can be observed, however. The S1–Pt–S1' (Pt–S1' distance 3.746 Å) linkage is the main interaction in bonding the $[Pt(SCN)_4]^{2-}$ groups within the layer while the adjacent $[Pt(SCN)_4]^{2-}$ layers are bound into a three dimensional network by K^+ ions through N–K–S bonds.

The Pt^{II} atom is coordinated to four sulfur atoms of the thiocyanate groups in a slightly distorted square planar arrangement. The existence of two additional Pt–S' contacts leads to the slight elongation of the planar Pt–S1 bonds and is the main reason for the clear deviation of S1–Pt–S2 angles from 90°.

The thiocyanate groups are close to linear (173.8 and 176.9°) as usual [8]. The weak axial interaction between platinum and S1 atoms seems to distort

the S1–C1–N1 group more (173.8°) than the other SCN group (176.9°). The C–N distances (1.138 and 1.175 Å) correspond to the typical triple $C\equiv N$ bond length (1.16 Å) whereas the S–C distances (1.665 and 1.686 Å) are much shorter than the single S–C bond length (1.73–1.81 Å) [8] indicating at least partial double bond character.

The bonding between a thiocyanate group and a central metal atom can take place either through nitrogen or sulfur. In thiocyanate complexes of lanthanides the coordination through nitrogen gives a nearly linear RE–N–C–S chain [9]. In the case of bonding through sulfur the situation is different [10]. The bonding scheme within the thiocyanate group leaves two possible bonding sites for the terminal sulfur according to a sp^2 hybridization model. The strongly bent Pt–S–C angle (105 to 110°) in the $[Pt(SCN)_4]^{2-}$ group supports this simple model. The effect of the two remote axial sulfurs is rather strong resulting in large Pt–S1–C1 angle distortions from 120°. The bonding scheme between platinum and the two axial sulfurs is more obscure as should be anticipated due to the much greater Pt–S contact distance.

Comparison with the structural data available for other Pt–SCN systems shows that the Pt–S distances obtained in this study are somewhat longer than those given for the mixed ligand complex $Pt(NH_3)_2(SCN)_2$, *i.e.* ≈ 2.32 and 2.27 Å [6], respectively. On the contrary, the Pt–S distances given by Zvonkova [2] for $K_2Pt(SCN)_4$ are much longer, 2.36 and 2.38 Å.

The K^+ ion is eight-coordinated to three sulfur and to five nitrogen atoms in an arrangement which can be described at best as a bicapped trigonal prism – with strong distortions, of course (Fig. 3). The

TABLE 3. Selected bond distances (Å) and angles (°) for $K_2Pt(SCN)_4$

Square planar $[Pt(SCN)_4]^{2-}$					
Pt–S1	2.331(2)	Pt–S2	2.311(2)	S1–Pt–S2	95.8(1)
Pt–S1–C1	104.5(3)	Pt–S2–C2	109.4(3)		
S1–C1	1.665(2)	S2–C2	1.686(2)		
C1–N1	1.175(10)	C2–N2	1.138(12)		
S1–C1–N1	173.8(8)	S2–C2–N2	176.9(8)		
Octahedral $[Pt(SCN)_6]^{4-}$					
Pt–S1'	3.746(3)	S1'–Pt–S1	93.4(1)	S1'–Pt–S2	114.5(1)
Pt–S1'–Pt	86.6(5)	Pt–S1'–C1'	141.4(5)		
Coordination around potassium					
K–N1	2.844(7)	K–N1'	3.081(8)	K–N1''	2.932(8)
K–N2	2.766(8)	K–N2'	2.882(9)		
K–S2	3.304(3)	K–S2'	3.540(3)	K–S1	3.606(3)
Long range contacts (minimum values)					
Pt–Pt	4.294	Pt–K	4.727	K–K	4.233

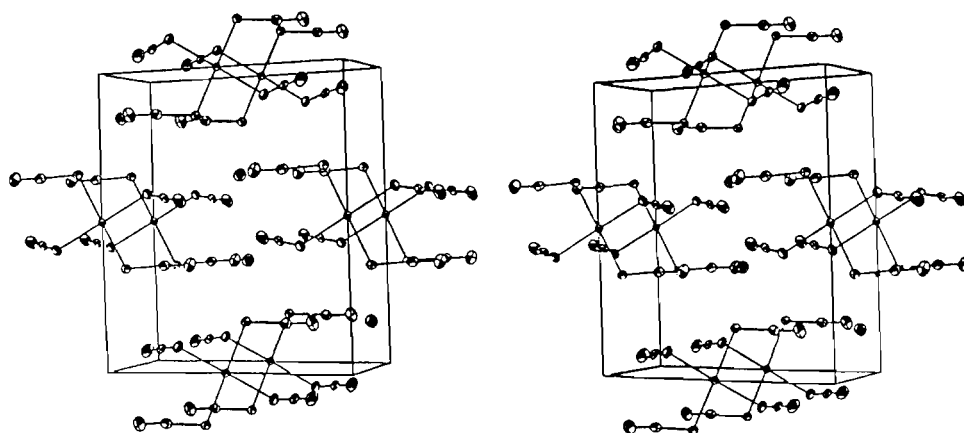


Fig. 1. Stereoscopic ORTEP view of the atoms in the unit cell of $K_2Pt(SCN)_4$. Thermal ellipsoids are drawn at 50% probability. The xy plane of the figure corresponds to the ab plane of the crystal system.

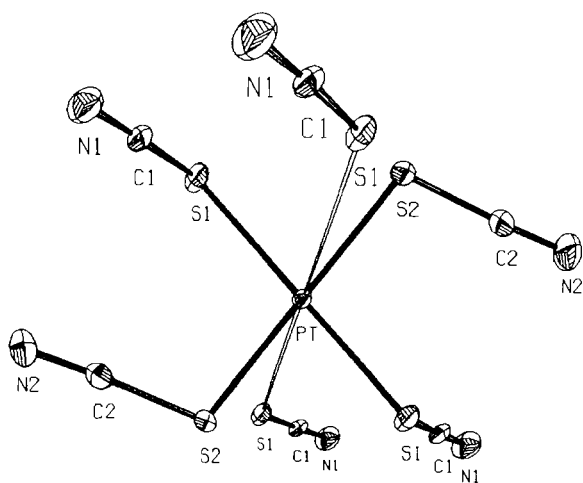


Fig. 2. An ORTEP drawing of the $[Pt(SCN)_6]^{4-}$ group. Thermal ellipsoids are drawn at 65% probability.

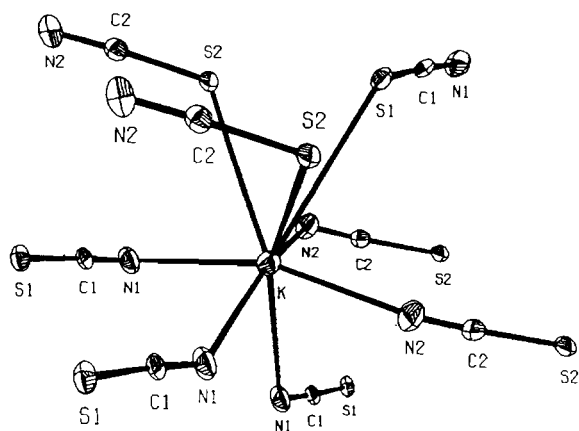


Fig. 3. An ORTEP drawing of the coordination around the K^+ ion. Thermal ellipsoids are drawn at 40% probability.

coordination of sulfur and nitrogen atoms to K^+ is rather anisotropic in nature binding the $(Pt(SCN)_4)^{2-}$ anions into a three dimensional network through N–K–S bonds. The shortest K–S distance (3.304 Å) agrees well with those obtained for KSCN and KHS (3.272 and 3.364 Å) [11] but is considerably longer than the K–S distance in K_2S (3.18 Å) [12]. The other two sulfur atoms further apart are, however, clearly within the sum of the van der Waals radii of potassium and sulfur. The K–N distances obtained are very similar to those in $KSe(SCN)_3 \cdot \frac{1}{2}H_2O$ (2.792 to 3.089 Å) [13] as well as in KSCN [11] and KN_3 [14] (2.974 to 2.982 Å). A comparison of the K–S and K–N bond lengths to those obtained by Zvonkova [2] shows that the previous values are partly strongly erroneous probably due to wrong atomic positions.

Thermal decomposition

The thermal decomposition of $K_4Pt(SCN)_4$ offers a rather complicated chain of reactions throughout the whole temperature range accessible to our studies. As could be expected, the atmosphere where the decomposition occurs has a major effect on the decomposition scheme (Fig. 4; Table 4). However, $K_4Pt(SCN)_4$ is thermally stable up to 200 °C both in air and inert atmosphere. In air the first step of decomposition involves a multitude of simultaneous oxidation reactions together with the cleavage of the SCN^- anion; i.e. evolution of N_2 , formation of potassium and platinum sulfides, oxidation of carbon and extra sulfur to corresponding dioxides and finally the oxidation of K_2S to K_2SO_4 . These reactions cannot be resolved due to a high degree of superimposition. In contrast, the following steps of decomposition are rather well isolated and can thus be identified with certainty: first the oxidation of PtS_2 to the corresponding oxide followed by the decomposition of

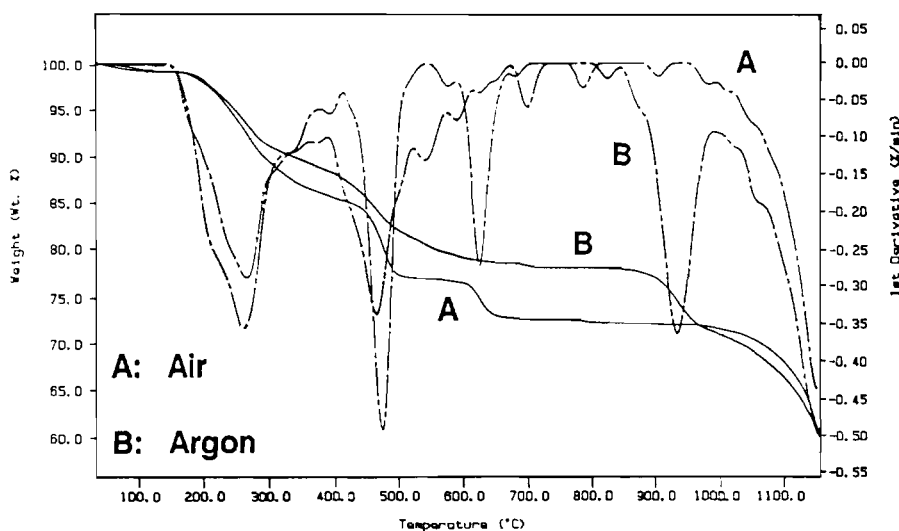


Fig. 4. The TG and DTG curves of the thermal decomposition of $K_2Pt(SCN)_4$ in dynamic air and inert argon atmosphere. The sample weight was less than 1.0 mg and the heating rate was $2.5^\circ \text{ min}^{-1}$.

TABLE 4. Thermal decomposition of $K_2Pt(SCN)_4$

Reaction	Weight left (%)		Temperature onset values ($^\circ\text{C}$)	Peak ($^\circ\text{C}$)
	obs.	calc.		
(a) Decomposition scheme in air				
1. $K_2Pt(SCN)_4 + 7O_2 \rightarrow K_2SO_4 \cdot PtS_2 + SO_2 + 2N_2 + 4CO_2$	≈ 85	85.7	200–316	264, 342
2. $K_2SO_4 \cdot PtS_2 + 3O_2 \rightarrow K_2SO_4 \cdot PtO_2 + 2SO_2$	77.9	79.4	457–492	475
3. $K_2SO_4 \cdot PtO_2 \rightarrow K_2SO_4 \cdot Pt + O_2$	73.0	73.0	605–643	623
4. $K_2SO_4 \cdot Pt \rightarrow K_2O \cdot Pt + SO_2 + \frac{1}{2}O_2$	< 60	57.2	990 \rightarrow	> 1150
(b) Decomposition scheme in argon				
1. $K_2Pt(SCN)_4 \rightarrow K_2S \cdot PtS_2 \cdot S \cdot 4C + 2N_2$	≈ 88	89.7	190–292	212, 260
2. $K_2S \cdot PtS_2 \cdot S \cdot 4C \rightarrow K_2S \cdot PtS \cdot 4C + S_2(g)$	76.2	76.2	400–542	466, 571, 697
3. $K_2S \cdot PtS \cdot 4C \rightarrow 2K \cdot PtS \cdot 4C + \frac{1}{2}S_2(g)$	≈ 69	70.0	896–956	930
4. $2K \cdot PtS \cdot 4C \rightarrow PtS \cdot 4C + 2K(g)$	< 60	54.4	980 \rightarrow	> 1150

the latter compound a hundred degrees later. Finally K_2SO_4 decomposes to $K(g)$, a reaction that is perhaps catalysed by metallic Pt.

The decomposition of $K_4Pt(SCN)_4$ in inert argon shows a much simpler behavior including first the cleavage of the SCN^- ligand accompanied by the evolution of N_2 and later $S_2(g)$. The decomposition of K_2S is followed immediately by the sublimation of metallic potassium. As a whole the thermal decomposition of $K_4Pt(SCN)_4$ reveals the importance and stability of the metal–sulfur bonding also in the

case of K^+ where the K–N distances are much shorter than the K–S distances.

References

- 1 B. Rosenberg, L. VanCamp, J. F. Trosko, and V. H. Mansour, *Nature (London)*, 222 (1969) 385.
- 2 Z. V. Zvonkova, *Zh. Fiz. Khim.*, 26 (1952) 1804.
- 3 G. W. Watt and J. A. Cunningham, *J. Electrochem. Soc.*, 110 (1963) 716.

- 4 S. B. Hendricks and H. E. Merwin, *Am. J. Sci.*, 15 (1928) 489.
- 5 Z. V. Zvonkova, *Zh. Fiz. Khim.*, 27 (1963) 100.
- 6 J. J. Blejdelis and G. B. Bokij, *Kristallografiya*, 2 (1957) 281.
- 7 J. M. Stewart and S. R. Hall, *The XTAL System of Crystallographic Programs*, University of Maryland, MD, 1985.
- 8 A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, London, 4th edn., 1975.
- 9 L. Hiltunen, J. Hölsä, W. Streck and B. Jezowska-Trzebiatowska, *J. Less-Common Met.*, 127 (1986) 225.
- 10 S. E. Livingstone, *Q. Rev.*, 19 (1965) 397.
- 11 C. Akers, S. W. Peterson and R. D. Willett, *Acta Crystallogr., Sect. B*, 24 (1968) 1125.
- 12 U. Müller, *Z. Anorg. Allg. Chem.*, 392 (1972) 159.
- 13 S. Hauge and R. A. Henriksen, *Acta Chem. Scand., Ser. A*, 29 (1975) 778.
- 14 C. D. West, *Z. Kristallogr.*, 88 (1934) 97.