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Studies on Potassium Thiocyanatoplatinates II. Crystal Structure of Potassium Hexathiocyanatoplatinate(IV) Dihydrate, $K_2Pt(SCN)_6 \cdot 2H_2O$

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The crystal structure of potassium hexathiocyanatoplatinate(IV) dihydrate, $K_2Pt(SCN)_6 \cdot 2H_2O$, was refined from single-crystal X-ray diffraction data to an *R*-value of 0. 024. $K_2Pt(SCN)_6 \cdot 2H_2O$ crystallizes in the monoclinic space group $P2_1/a$ ($Z = 2$) with the following cell dimensions: $a = 7.303(2)$, $b = 11.143(2)$, $c = 11.338(1)$ Å and $\beta = 99.42(1)°$. The crystal structure consists of layers of close-to-octahedral $[Pt(SCN)_6]^{2-}$ complex anions parallel to the *ab*-plane. Layers are linked by potassium atoms into a three-dimensional network through N–K bonds. whereas no interactions were observed between the complex anions. While the oxygen atoms of the crystal water seem to be coordinated exclusively to the potassium atoms, there exists hydrogen bonding to nitrogen atoms. The nearly linear SCN^- chains have a bent coordination to Pt through the sulfur atoms. The potassium atom is coordinated to three oxygens and six nitrogens in a slightly distorted tricapped trigonal prismatic arrangement. The reasons for the easy elimination of the water molecules and the structural disorder in the anhydrous salt are discussed.

The catalytic activity of platinum and platinum compounds is long established. In addition to the research involved in catalysis, inorganic and organoplatinum compounds have received much attention since Rosenberg *et al.*[1] discovered the antitumor properties of some platinum complexes. Although all the successful drugs, e.g. cis-platin, *cis*-$[Pt(NH_3)_2Cl_2]$, are rather simple complexes, present research is concentrated on more complicated and even exotic compounds.

In spite of the unprecedented boom in research into platinum compounds, structural studies concerning the tetra- or hexathiocyanate complexes of platinum in its most stable oxidation states, i.e. +2 and +4, have been surprisingly few.[2–9] The determination of the crystal structure of $M_2Pt(SCN)_6$, where $M = K^+$, NH_4^+ or Rb^+, has so far been prevented by extensive disorder in the anion and M^+ positions.[4,5,10] Nuclear quadrupole resonance studies with some speculation on the structure of $K_2Pt(SCN)_6$ have also been presented.[11] The thermal decomposition of some transition-metal hexathiocyanatoplatinates have also been reported.[12]

No analysis of the crystal structure of $M_2Pt(SCN)_6 \cdot 2H_2O$ has appeared so far, although the formation of this compound has long been known.[13–16] However, the crystals of $K_2Pt(SCN)_6 \cdot 2H_2O$ have been reported to be monoclinic.[14]

The present paper gives the results of a crystal structure determination for $K_2Pt(SCN)_6 \cdot 2H_2O$. Special attention is paid to finding a plausible explanation of the structural disorder in the anhydrous $K_2Pt(SCN)_6$ as well as of the easy elimination of the water molecules, even at ambient temperature.

Experimental

Sample preparation. Single crystals of $K_2Pt(SCN)_6 \cdot 2H_2O$ were obtained by slow crystallization from an aqueous solution of KSCN with a large excess of H_2PtCl_6 after the rather abrupt precipitation of K_2PtCl_6. The desired product, $K_2Pt(SCN)_6 \cdot 2H_2O$, appeared in the form of regular, dark-red, plate-shaped single crystals. The crystals showed pronounced tendency to twinning and, moreover, decomposed rapidly (within a few hours) in the absence of sufficient water vapor pressure.

Crystallographic measurements. X-Ray diffraction data collection was carried out with a Rikagu AFC5S four-circle single-crystal diffractometer at ambient temperature. The diffractometer was equipped with a graphite monochromator. Because of the evident danger of decomposition of the crystal in the absence of mother

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Table 1. Details of the data collection and structure refinement of $K_2Pt(SCN)_6 \cdot 2H_2O$.

Data collection:	
Compound	Potassium hexathiocyanatoplatinate(IV) dihydrate
Formula	$K_2Pt(SCN)_6 \cdot 2H_2O$
Formula weight	657.78
Crystal size/mm^3	$0.10 \times 0.15 \times 0.25$
Scan type	ω–2Θ
Scan speed /° min^{-1} (in ω)	8.0
Crystal system and space group	Monoclinic; $P2_1/a$, C_{2h}^5 (No. 14)[18]
Z	2
Cell constant determination	25 reflections ($48.81 < 2\Theta < 49.77°$)
a/Å	7.303(2)
b/Å	11.143(2)
c/Å	11.338(1)
β/°	99.428(8)
V/Å^3	910.3(3)
D_x/g cm^{-3}	2.400
$F(000)$	620
Radiation, λ/Å	Mo (K_α), 0.71069
Absorption coefficient/cm^{-1}	89.2
2Θ range /°	$6 < 2\Theta < 60$
$[(\sin\Theta)/\lambda)]_{max}$/Å^{-1}	0.70
h, k, l range	10, 16, $\pm$16
No. of reflections collected	2974
No. of unique reflections	2780
R_{int}	0.093
Structure refinement:	
Programs used	TEXSAN[17]
No. of observed reflections	2042 $\{I_{obs} > 3\sigma(I_{obs})\}$
Function minimized	$\Sigma w(\lvert F_{obs}\rvert - \lvert F_{calc}\rvert)^2$
Weighting scheme	$w = 4F_{obs}^2/\sigma^2(F_{obs}^2) = 1/\sigma^2(F_{obs}^2)$
No. of variables	106
Absorption correction	Empirical (ψ-scan data) transmission factor from unity to 0.37
Remaining electron density/Å^{-3}	0.73 (max) and -1.63 (min)
R	0.025
R_w	0.033

liquid, the crystal was glued inside a glass capillary with a diameter of 0.2 mm. The single crystal was not in direct contact with a slight amount of mother liquid present in the capillary. However, the vapor pressure was high enough to prevent the decomposition of the crystal studied.

Three standard reflections were chosen in order to check on the crystal and electronics stability. The intensity of these reflections remained constant throughout the whole measurement. 2780 unique reflections were collected with $\sin\Theta/\lambda < 0.7$ Å^{-1}. The intensities of the reflections were corrected for Lorentz, polarization and absorption (empirical) effects. Additional information on the data collection can be found in Table 1.

The position of the Pt atom was determined by Patterson methods, and those of the K, S, O, N, C and H atoms were found from subsequent Fourier difference electron density calculations with the aid of the TEXSAN crystal structure determination program package.[17] The refinement of the atomic positions based on 2042 reflections with $I_{obs} > 3\sigma(I_{obs})$ yielded the following figures-of-merit: $R = 0.025$, $R_w = 0.033$ and $S = 1.37$. All atoms except hydrogen were refined with anisotropic temperature factors. Further details of the structure refinement are given in Table 1.

Results and discussion

Description of the structure. Some details of the crystal structure of $K_2Pt(SCN)_6 \cdot 2H_2O$ are shown in Table 1. The fractional atomic positions and selected bond distances and angles are compiled in Tables 2 and 3, respectively. The contents of the unit cell illustrated in Fig. 1 show that the centrosymmetric $[Pt(SCN)_6]^{2-}$ anions form layers parallel to the *ab*-crystal plane. Neither a direct Pt–Pt interaction nor any other interaction between the complex anions could be observed. The stacking of $[Pt(SCN)_6]^{2-}$ anions leaves ample space between the layers where the potassium atoms, as well as the water molecules, reside. The main interaction in the bonding of the $[Pt(SCN)_6]^{2-}$ layers into a three-dimensional network are the bonds between N and K atoms.

The Pt^{IV} atom is coordinated to six sulfur atoms of the thiocyanate groups in a slightly distorted octahedral

Table 2. Fractional positional parameters and equivalent temperature factors, B_{eq}, for atoms in $K_2Pt(SCN)_6 \cdot 2H_2O$.

Atom	*x*	*y*	*z*	B_{eq}[a]
Pt	0.0000(0)	0.0000(0)	0.0000(0)	1.423(8)
S1	−0.1257(2)	0.1784(1)	−0.0988(1)	2.37(4)
C1	−0.0619(7)	0.1749(4)	−0.2352(4)	2.3(2)
N1	−0.0303(8)	0.1796(5)	−0.3305(4)	3.6(2)
S2	−0.2448(2)	0.0193(1)	0.1151(1)	2.41(5)
C2	−0.1527(7)	0.0953(5)	0.2402(4)	2.5(2)
N2	−0.1037(8)	0.1439(5)	0.3270(4)	3.6(2)
S3	0.2058(2)	0.1389(1)	0.1129(1)	2.48(5)
C3	0.3316(7)	0.0589(5)	0.2213(4)	2.4(2)
N3	0.4229(9)	0.0101(4)	0.2991(5)	3.8(2)
K	−0.3936(2)	0.1527(1)	−0.5014(1)	2.72(4)
O	−0.7642(6)	0.0876(4)	−0.4913(4)	3.4(2)
H1	−0.8767	0.0915	−0.5486	3.9
H2	−0.7979	0.0741	−0.4174	3.9

[a] The equivalent temperature factor B_{eq} was defined as one third of the trace of the orthogonalized B_{ij} tensor. The B_{eq}-values presented above were multiplied by a factor of 10^2.

arrangement. The thiocyanate groups are, as usual, close to linear [174.2(4), 174.2(7) and 175.6(7)°].[19] The average C–N distance 1.141(7) Å may be compared to the typical triple C≡N bond length (1.16 Å), whereas the average S–C distance 1.688(5) Å is slightly shorter than the single S–C bond length (1.73–1.81 Å),[19] indicating partial double bond character. The slight distortions in the Pt–S bond distances and angles from perfect octahedral symmetry in $[Pt(SCN)_6]^{2-}$, as well as the deviations from linearity in SCN^-, might be caused by the coordination to the K^+ ions and by the rather weak asymmetric hydrogen bonds between some water molecules and the terminal nitrogen atoms.

The bonding between a thiocyanate group and a metal atom can take place through either nitrogen or sulfur. In thiocyanate complexes of lanthanides the coordination through nitrogen gives a nearly linear Pr–N–C–S chain.[20] In the case of bonding through sulfur the situation is different.[21] The bonding scheme within the thiocyanate group leaves two or three possible bonding sites for the terminal sulfur according to the simple sp^2 or sp^3 hybridization models, respectively. The Pt–S–C angles [average value 105.7(2)°] support the sp^3 hybridization model and confirm the presence of a single S–C bond in SCN^-. The Pt–S bond lengths are very uniform, i.e. 2.380(1) and 2.390(1) Å. These values are similar to those obtained for other six-coordinated Pt^{IV} species with sulfur ligands,[22,23] but are clearly longer than those in $K_2Pt(SCN)_4$.[9]

The K^+ ion is nine-coordinated to three oxygen and six nitrogen atoms in an arrangement which is close to a tricapped trigonal prism (Fig. 2). No interaction between potassium and sulfur atoms can be observed. The K–N distances obtained in $K_2Pt(SCN)_6 \cdot 2H_2O$ [from 2.906(5) to 3.210(5) Å] are only slightly longer than those in $KSe(SCN)_3 \cdot \frac{1}{2}H_2O$ (2.792–3.089 Å),[24] KSCN[25] and KN_3 (2.974–2.982 Å)[26] as well as in $K_2Pt(SCN)_4$ (2.766–3.081 Å).[9]

The potassium–oxygen distances are much longer than the value of 2.18 Å obtained, e.g., in KOH.[19] Since the sum of ionic radii for the K^+ and O^{2-} ions, 2.78 Å, is considerably less than all the contact distances between these

Table 3. Selected bond distances (in Å) and angles (in °) for $K_2Pt(SCN)_6 \cdot 2H_2O$.

$[Pt(SCN)_6]^{2-}$ group:					
Pt–S1	2.390(1)	Pt–S2	2.390(1)	Pt–S3	2.380(1)
S1–Pt–S2	85.24(4)	S1–Pt–S3	82.63(5)	S2–Pt–S3	83.64(5)
S1–Pt–S2^{I}	94.76(4)	S1–Pt–S3^{I}	97.37(5)	S2–Pt–S3^{I}	96.36(5)
S1–Pt–S2	94.76(4)	S1–Pt–S3	97.37(5)	S2–1Pt–S3	96.36(5)
Pt–S1–C1	105.6(2)	Pt–S2–C2	105.8(2)	Pt–S3–C3	105.8(2)
S1–C1	1.687(5)	S2–C2	1.694(5)	S3–C3	1.668(6)
C1–N1	1.143(6)	C2–N2	1.128(7)	C3–N3	1.151(7)
S1–C1–N1	174.2(5)	S2–C2–N2	174.2(7)	S3–C3–N3	175.6(7)
Coordination around potassium					
K–N3^{II}	2.906(5)	K–N3^{I}	2.960(6)	K–N1^{III}	2.979(5)
K–N1	3.034(5)	K–N2	3.103(5)	K–N2^{III}	3.210(5)
K–O	2.822(4)	K–O^{IV}	2.922(4)	K–O^{V}	3.041(4)
Long-range contacts (minimum values):					
Pt···Pt^{VI}	6.661(2)	K···K^{V}	3.743(2)		
Bonds and angles involving hydrogen:					
O–H1	0.962	N2···H1	2.077	O···N2^{II}	3.019(7)
O–H2	0.923	N1^{VII}···H2	2.424	O···N1^{VII}	3.051(6)
H1–O–H2	114.7	O1–H1···N2^{II}	166	O1–H2···N1^{VII}	127

Symmetry codes: $^{I}-x,-y,-z$; $^{II}x-1,y,z-1$; $^{III}x-\frac{1}{2},\frac{1}{2}-y,z$; $^{IV}\frac{1}{2}+x,\frac{1}{2}-y,z$; $^{V}-x-1,-y,-z-1$; $^{VI}\frac{1}{2}-x,\frac{1}{2}+y,-z$; $^{VII}x-1,y,z$.

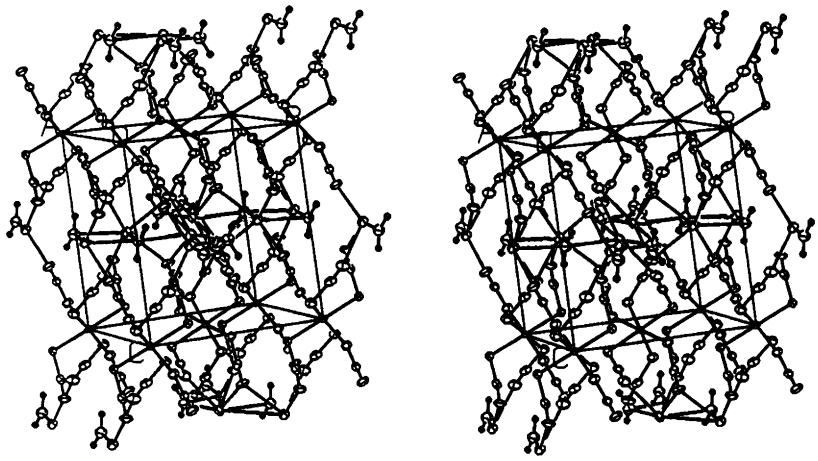

Fig. 1. Stereoscopic ORTEP view of the packing of atoms within the unit cell of $K_2Pt(SCN)_6 \cdot 2H_2O$. Thermal ellipsoids are drawn at 30% probability.

ions in $K_2Pt(SCN)_6 \cdot 2H_2O$ [average value 2.929(4) Å], the K–O bond should be considered as rather weak.

In $K_2Pt(SCN)_6 \cdot 2H_2O$ there exists hydrogen bonding only between the water hydrogens and the nitrogen atoms of the SCN^- chain. Although the minimum N–H distance is only 2.08 Å, the corresponding O–N distance [3.051(6) Å] is longer than the 2.7–2.8 Å usually taken as an indication of strong hydrogen bonding between oxygen and nitrogen. Moreover, there seems to be some competition for the H2 proton from two nearby N atoms. This may have caused the difficulties encountered in the free refinement of the hydrogen positions. The hydrogens thus had to be refined constrained to the positions found from the difference Fourier electron density map.

Comparison with known Pt^{IV}–SCN and Pt^{II}–SCN systems. A comparison with the structural data available from other $[Pt(SCN)_6]^{2-}$ systems with cations having bulky organic ligands[7,8] shows that the Pt–S distances obtained in this study are somewhat longer, probably

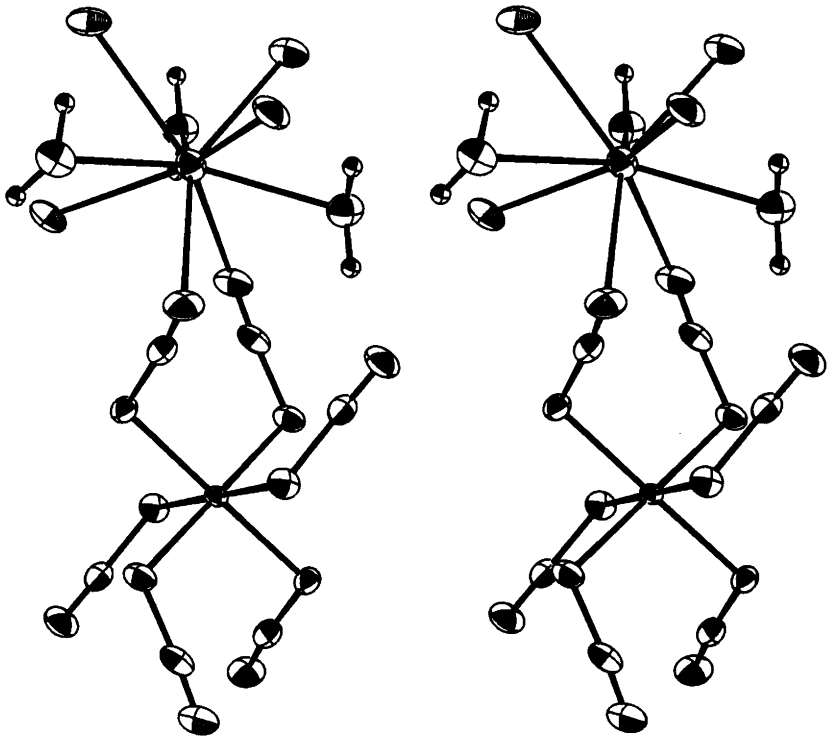

Fig. 2. Stereoscopic ORTEP drawing of the coordination around the potassium (upper part) and platinum (lower part) atoms. Thermal ellipsoids are drawn at 30% probability.

because of the greater space available. In general, the regularity of the bond angles and distances within the $(SCN)^-$ group is remarkably better in the present compound. The comparison is a little difficult owing to the rather inexact results available for the other $[Pt(SCN)_6]^{2-}$ systems. It seems that the $[Pt(SCN)_6]^{2-}$ complex anion is prone to some kind of structural disorder.

The slightly shorter Pt–S distances in $K_2Pt(SCN)_4$ (on average 2.32 Å)[9] probably indicate steric effects of lesser importance due to the square planar coordination. The greater steric effects in $K_2Pt(SCN)_6 \cdot 2H_2O$ are not even partly compensated by the increase in the effective positive charge of the central atom, in agreement with the very slight difference between the ionic radius of $Pt^{(II)}$ and Pt^{IV}, i.e. 0.60 vs. 0.625 Å.[24] The Pt–S–C angles are more distorted in $K_2Pt(SCN)_4$, whereas there are no significant differences in deviations from linearity of the SCN^- chain between the compounds. The differences in the intramolecular C–N and N–S distances are greater in the tetrathiocyanate. This is probably caused by the weak Pt–S contacts formed to achieve an octahedral coordination for Pt^{II}.[9] In contrast to $K_2Pt(SCN)_4$, the coordination around the potassium atom is very regular. In conclusion, the structural distortions within the $[Pt(SCN)_x]^{2-}$ unit as well as around the K^+ ion are much greater in $K_2Pt(SCN)_4$ than in $K_2Pt(SCN)_6 \cdot 2H_2O$.

During the preparation and X-ray diffraction measurements, the $K_2Pt(SCN)_6 \cdot 2H_2O$ crystals were found to be dehydrated very easily, with the subsequent destruction of the sample. The easy elimination of the water molecules most probably results from the cumulative influence of the following two effects: (1) the K–O bonds are weak, with average K–O distances equal to 2.928 Å, and (2) there seem to exist important repulsive forces between the potassium ions as well as between the protons and potassium ions, as indicated by the rather close contacts i.e. K–K = 3.743(2) Å and K–H = 2.907 Å.

The recrystallization of the anhydrous $K_2Pt(SCN)_6$ salt from some nonaqueous organic solvents yields products in which the K^+ and nitrogen positions have been found to be disordered.[4,5,10] In view of the present results, it seems probable that in the dehydrated species, the potassium atom is left with a coordination number that is too low: six as against the usual nine. This in turn leads to an increased attraction toward the nearby nitrogens. Since there seem to be several possibilities to regain a coordination number higher than six, a substantial structural disorder results.

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