Synthesis and Crystal Structure of (18-Crown-6)(nitrato)(triphenylphosphine oxide)potassium

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Abstract—A new complex (18-crown-6)(nitrato)(triphenylphosphine oxide)potassium (I) is synthesized, and its crystal structure is studied by X-ray diffraction analysis (space group \( R3m \), \( a = 14.336 \) Å, \( c = 13.776 \) Å, \( Z = 3 \)). The structure is solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation to \( R = 0.034 \) for 1122 independent reflections (CAD4 automated diffractometer, \( \lambda \)Mo\( K_{\alpha} \) radiation). Structure I contains a complex host–guest molecule \([K(\text{An})(18\text{-crown-6})(\text{Ph}_3\text{PO})]\) with crystallographic symmetry \( 3m \) (three planes \( m \) contain three Ph rings of the \( \text{Ph}_3\text{PO} \) ligand and all O atoms of the crown ligand). The coordination polyhedron of the K\(^+\) cation is a distorted hexagonal bipyramid with all the six O atoms of the crown ligand in the base, the O atoms of the \( \text{Ph}_3\text{PO} \) ligand, and one (or two) O atoms of a disordered NO\(_3^-\) ligand in the axial positions.

INTRODUCTION

In this work, we describe the synthesis and results of X-ray diffraction analysis of crystalline (18-crown-6)(nitrato)(triphenylphosphine oxide)potassium complex, \([K(\text{NO}_3)(18\text{-crown-6})(\text{Ph}_3\text{PO})]\) (I). The synthesis and structures of similar complexes with the general formula \([K(\text{An})(18\text{-crown-6})(\text{Ph}_3\text{PO})]\) of the host–guest type [1] were described in [2] (\( \text{An} = \text{I}, \text{Br}, \text{and SCN} \)) and in [3] (\( \text{An} = \text{OCN}, \text{SCN}, \text{and N}_3 \)). X-ray diffraction analysis was carried out for the complexes with \( \text{An} = 1 \) [2] and \( \text{An} = \text{OCN}, \text{SCN}, \text{and N}_3 \) [3]. The crystal structures of these four complexes are isomorphous and highly symmetric (space group \( R3m \)). This work is aimed at searching for new related complexes.

EXPERIMENTAL

Synthesis. Complex I was synthesized as follows. Crystalline 18-crown-6, \( \text{Ph}_3\text{PO} \), and \( \text{KNO}_3 \) taken in a molar ratio of 1 : 1 : 1 were dissolved in an ethanol–water (2 : 1) mixture. The resulting solution was left at room temperature until the solvents evaporated completely and colorless crystals of complex I formed on the flask bottom.

X-ray diffraction analysis. The unit cell parameters and a three-dimensional set of reflection intensities were obtained on an Enraf-Nonius CAD4 X-ray automated diffractometer (Mo\( K_{\alpha} \) radiation, graphite monochromator). The crystals of I are trigonal: empirical formula \( \text{C}_{300}\text{H}_{360}\text{KNO}_{10}\text{P} \), \( M = 643.69 \); \( a = 14.336(2) \), \( c = 13.776(2) \) Å, \( V = 2451.9(6) \) Å\(^3\), \( Z = 3 \), \( \rho_{\text{calc}} = 1.308 \) g/cm\(^3\), \( \mu(\text{Mo}\ K_{\alpha}) = 2.66 \) cm\(^{-1}\), and space group \( R3m \).

Intensities of 1122 reflections were measured in 1/12 of the reciprocal space (0 \( \leq h \leq 18 \), 0 \( \leq k \leq 18 \), 0 \( \leq l \leq 20 \); 2\( \theta \) = 65°) in the \( \omega/2\theta \) scan mode from a single crystal 0.20 \( \times \) 0.20 \( \times \) 1.00 mm in size. A special mode in which the final scan was carried out for all, including very weak, reflections was used to measure intensities. The reflection intensities were corrected for absorption by the semiempirical method [4]. The working set of measured \( F^2(h0l) \) and \( \sigma(F^2) \) values contained 1122 independent reflections.

Structure I was solved by the direct method (SHELXS97) [5] and refined by the full-matrix least-squares method against \( F^2 \) (SHELXL97) [5] in the anisotropic approximation for non-hydrogen atoms. Almost all reflections from the working set (including very weak reflections with \( I < 2\sigma(I) \)), except for several reflections with poorly consistent measured and calculated \( F^2 \) values, were used in the refinement.

At the stage of structure I refinement by the direct method, the NO\(_3^-\) ligand was found to be randomly disordered over the crystallographic position \( 3m \). Two independent O(4) and O(5) positions of three strongly disordered oxygen atoms lie near slightly disordered N atom of the NO\(_3^-\) ligand. The populations of these positions were refined by the introduction of an additional varied parameter [5].

All H atoms were objectively localized in the difference electron density synthesis at the intermediate stage of anisotropic refinement. Then the coordinates
Table 1. Coordinates ($\times 10^4$, $\times 10^3$ for H) and the isotropic thermal parameters $U(\times 10^3)$ of the basis atoms in crystal structure $I^a$

| Atom  | $x$ | $y$ | $z$ | $U$, Å$^2$ | Atom  | $x$ | $y$ | $z$ | $U$, Å$^2$
<table>
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<tr>
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<td>0</td>
<td>5000</td>
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<td>O(4)</td>
<td>-355(5)</td>
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<td>48.5(4)</td>
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<td>-1114.3(7)</td>
<td>4918(2)</td>
<td>46.6(4)</td>
<td>N</td>
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<td>0</td>
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<tr>
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<td>4958(3)</td>
<td>67.8(6)</td>
<td>H(1a)</td>
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<td>2163(3)</td>
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<td>101</td>
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<td>62</td>
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<td>1750(1)</td>
<td>882(3)</td>
<td>83(1)</td>
<td>H(5)</td>
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<td>190</td>
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<td>91</td>
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<td>207(3)</td>
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<td>H(6)</td>
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<td>70.3(8)</td>
<td>H(7)</td>
<td>-54</td>
<td>54</td>
<td>3</td>
<td>84</td>
</tr>
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</table>

*a* The equivalent isotropic thermal parameters $U_{equiv}$ calculated as one third of the trace of the orthogonalized tensor $U_{ij}$ are presented for non-hydrogen atoms. The populations of the positions of the O(4) and O(5) disordered oxygen atoms in the NO$_3$ ligand are equal to 0.50(1).

and isotropic thermal parameters of all H atoms were calculated by the riding model [5] in the procedure of structure I refinement.

The absolute structure parameter was refined for exposed crystal I: $\chi = 0.2(1)$ [6]. In the last cycle of full-matrix refinement, the absolute shifts of all 92 variable parameters were less than 0.001$\sigma$. The final coordinates and thermal parameters of the basis atoms are presented in Table 1.

The final refinement parameters are $R = 0.029$ and $wR_2 = 0.075$ against 1020 reflections with $I \geq 2\sigma(I)$; $R = 0.034$ and $wR_2 = 0.103$ against all reflections; goodness of fit $S$ is 1.07 (for the determination of $wR_2$ and $S$, see [5]). In the final difference Fourier synthesis, $-0.21 < \Delta \rho < 0.19$ eÅ$^{-3}$. The $f^\prime$ curves used and their anomalous dispersion corrections ($f^\prime$ and $f^\prime\prime$) are borrowed from [7].

RESULTS AND DISCUSSION

The crystal structure of the complex molecule $[\text{KNO}_3]\{18\text{-crown-6}\}(\text{PhPO})$ (I) is shown in the figure. The point symmetry of molecule I is $D_{3d}$. The P atom occupies the position 3$m$; the O(3), K$^+$, and N atoms lie in the crystallographic axis 3. Three Ph rings of the Ph$_3$PO ligand, all O atoms of the crown ligand, and disordered O atoms of the NO$_3$ ligand are arranged in the $m$ planes. The bond lengths and the main bond and torsion angles are given in Table 2.

The coordination polyhedron of the K$^+$ cation is a distorted “hexagonal bipyramid” with all the six O atoms of the 18-crown-6 ligand in a base, the O(3) atom of the Ph$_3$PO ligand and one or two (with equal probability of 50%) of the three symmetrically equivalent positions O(4), O(4)$'$, O(4)$''$ of disordered O atoms of the NO$_3$ ligand at the axial vertices. This cation deviates significantly (by 0.299(2) Å) from the mean plane of six O atoms of crown ligand toward NO$_3$ ligand.

In structure I, the average length of six equatorial K–O$_{crown}$ bonds (2.822 Å) is 0.12 Å longer than the K–O(3) axial bond (with the Ph$_3$PO ligand). The average K–O$_{crown}$ distance is somewhat shorter than the sum of the effective ion radius of the K$^+$ cation (1.51 Å for a coordination number of 8 and 1.55 Å for a coordination number of 9) [8] and van der Waals radius of the oxygen atom (1.40–1.52 Å) [9, 10]. The length of another (of one or either two) K–O(4) axial bond (with a disordered NO$_3$ ligand) is much longer (by ~0.23 Å) than K–O(3) and is close to the above-mentioned sum.

The macrocyclic 18-crown-6 ligand has the same point symmetry $C_{3v}$, as molecule I as a whole. However, it also has a pseudoinversion center. Then the approximate symmetry of the 18-crown-6 ligand in I ($D_{3d}$) will be higher than the crystallographic symmetry, being the highest for 18-crown-6 molecules in compounds with this ligand.

In structure I, the 18-crown-6 ligand has its prevailing “crown” conformation corresponding to the approximate symmetry $D_{3d}$. For this conformation, 18 non-hydrogen atoms of a macrocycle (four independent atoms and atoms symmetrically equivalent to them) alternately deviate to different sides from the mean plane. Six O atoms of a macrocycle in I (independent O(1) and O(2)) also deviate alternately to different sides from their mean plane by ±0.187(2) Å. The con-