

ABSTRACT

This dissertation deals with the crystal structure analysis of thiocyanatopentamminecobalt(III) nitrate - $[\text{Co}(\text{NH}_3)_5 \text{NCS}] (\text{NO}_3)_2$ and diffuse scattering of X-rays from crystals of hexamminecobalt(III) nitrate - $[\text{Co}(\text{NH}_3)_6] (\text{NO}_3)_3$.

The preliminary crystallographic examinations of hexamminecobalt(III) nitrate and thiocyanatopentamminecobalt(III) nitrate are described. The lattice parameters and space group symmetry are for (i) thiocyanatopentamminecobalt(III) nitrate, $a = 10.64 \pm 0.04 \text{ \AA}$ and $\text{Fm}\bar{3}\text{m}$, respectively; (ii) hexamminecobalt(III) nitrate, $a = b = 21.66 \pm 0.05 \text{ \AA}$, $c = 33.32 \pm 0.05 \text{ \AA}$ and $\text{P}4_2\text{nm}$.

The determination of the structure of the thiocyanatopentamminecobalt(III) nitrate has been described in both two and three dimensions, and the behaviour of the complex ions is explained. The important findings are: the complex cation $[\text{Co}(\text{NH}_3)_5 \text{NCS}]^{2+}$ is static and disordered along the crystallographic axes displaying on the macroscopic scale perfect octahedral symmetry, and the anion $(\text{NO}_3)^-$ seems to exhibit effective spherical symmetry.

The diffuse scattering of X-rays from crystals of hexamminecobalt(III) nitrate - $[\text{Co}(\text{NH}_3)_6] (\text{NO}_3)_3$ has been studied and the deductions on the behaviour, shape and orientation of the structural units - the cation $[\text{Co}(\text{NH}_3)_6]^{3+}$ and the anion $(\text{NO}_3)^-$ are described.

The important parts of the crystal dynamics of hexamminecobalt(III) nitrate - $[\text{Co}(\text{NH}_3)_6] (\text{NO}_3)_3$, consist of independent rigid body vibrations of important structural units - the sets of ions. Further, the sheet and rod-like diffuse domains suggest that some of the structural units are elongated while others are planar - $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $(\text{NO}_3)^-$ ions respectively.

From the orientations of the diffuse domains it follows that the elongated cations - $[\text{Co}(\text{NH}_3)_6]^{3+}$, have their long axes parallel to the a and b axes of the crystal; while the planar nitrate, anions - $(\text{NO}_3)^-$, are normal to the a b plane and aligned along the diagonal in this plane. The strong elliptic diffuse domains associated with the recls, $\{520\}$, can be thought of as being due to the thermal waves arising out of the atomic vibrations propagated along $\langle 520 \rangle$ directions of the reciprocal lattice.

Finally, the fact that the hexamminecobalt(III) nitrate $[\text{Co}(\text{NH}_3)_6] (\text{NO}_3)_3$ gives diffuse patterns similar to those from the molecular crystals, suggests that probably inter-ionic binding in this case also is quite weak.