THE STRUCTURE OF $Ti(urea)_6(ClO_4)_3$ AT 90 K

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Recently we reported the structure of $Ti(urea)_6(ClO_4)_3$ at room temperature.[1] We found that, as in the triiodide salt,[2,3] the TiO_6 unit in the $Ti(urea)_6^{3+}$ ion had the molecular geometry of a regular octahedron distorted by a "twist" of about 5° about a C_3 axis. The perchlorate ions in the structure presented anomalous features. We proposed a model involving disorder between two perchlorate ions possessing slightly different interatomic angles. We now report the main features of the structure† at 90 K, as part of our program for measuring and interpreting the magnetic susceptibility and absorption spectrum[4] of the compound. As well as providing an account of the change in molecular geometry with temperature, the results support the model for the disorder of the perchlorate ions at room temperature.

As at room temperature, the crystals belong to the space group $R_{\bar{3}c}$. The unit cell dimensions were determined from Weissenberg and oscillation photographs. The c axis, 1·384 nm, is slightly less than the high-temperature value (1·4149 nm), but the a axis, 3·514 nm, is nearly twice as large (1·8132 nm). However, the intensities for odd h or k are very low. The obvious explanation of the a axis doubling is that the disorder in the perchlorate ions is frozen out at low temperature.

X-ray diffraction intensity data were collected at c. 90 K employing the inclined beam oscillation method. A Nonius Weissenberg camera equipped with a nitrogen-flow low-temperature accessory, and modified to prevent frost deposition on the crystal and film and to permit a more reliable measurement of the temperature at the crystal position, was employed. Oscillation was about the c axis. Nickel-filtered Cu K_α radiation was employed, and the crystal was sufficiently small that absorption was not important. The data were indexed, scaled, and corrected by programs lent by Towl and Robertson;[5] 568 reflections were indexed and processed. However, it was not possible to index unambiguously more than a few of the reflections corre-

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[2] Davis, P. H., and Wood, J. S., *Inorg. Chem.*, 1970, **9**, 1111.

[3] Linek, A., Siskova, J., and Jensovsky, L., *Colln Czech. chem. Commun.*, 1966, **31**, 4453.

[4] Dingle, R., *J. chem. Phys.*, 1969, **50**, 545.

[5] Towl, A., and Robertson, G. B., personal communication.

sponding to the a axis doubling and they were scarcely above the background. Consequently the data processed all belonged to h and k even; that is, they belonged to the room-temperature cell.

The data were refined as discussed for the room temperature structure,[1] in the same cell, thus ignoring the a axis doubling. In the following discussion values for the room-temperature parameters are given in brackets after the low temperature values. Isotropic refinement on the same model as the room temperature structure, but neglecting disorder, yielded $R = 0\cdot36$ ($0\cdot20$) with an improbably high value of 17 (14) for the temperature factor of two of the perchlorate oxygen atoms, $O(3)$. Full matrix refinement, permitting anisotropic thermal parameters and employing the model of two separate perchlorate oxygen atoms $O'(3)$ and $O'(4)$ with refined occupancy, in place of $O(3)$, yielded $R = 0\cdot14$ ($0\cdot12$). The occupancy of $O'(3)$ and $O'(4)$ was $0\cdot5$. The thermal parameters did not exceed $9\cdot5\times10^{-3}$ for any atom, and were naturally much reduced from the room temperature values. The parameters for $O'(4)$ were not positive definite, with $\beta_{22} = -7\times10^{-4}$.

As far as the molecular geometry of the $Ti(urea)_6^{3+}$ unit is concerned, the structure is very little altered from room temperature. Those units stack in an hexagonal array of columns down the c axis of the crystal, which is also the C_3 axis of the distorted TiO_6 octahedra. Perchlorate ions fit in interstices between the columns and hydrogen bond to the urea amine residues. The Ti–O bond length is 200 ± 2 pm (204 ± 1 pm). The angle of "twist" of one face of the octahedron relative to the other, about the C_3 axis, is $5\cdot0°$ ($5\cdot0°$). The dihedral angle $\angle C_3$–Ti–O is $55\cdot1°$ ($55\cdot4°$) and is within about $0\cdot5$ estimated standard deviation of the regular octahedral value of $54\cdot8°$.

Within the perchlorate ions the bond lengths show at most slight reduction from the room temperature values and are: Cl–O(2), 139 ± 2 pm (141 ± 1 pm); Cl–O'(3), 153 ± 4 pm (152 ± 3 pm); and Cl–O'(4), 126 ± 3 pm (129 ± 2 pm). The angles within the ion show some differences from the room temperature values:

O(2a)–Cl–O(2b) = 117° (110°)   O(2b)–Cl–O'(3) = 91° (98°)

O(2a)–Cl–O'(3) = 99° (93·5°)   O(2b)–Cl–O'(4) = 126° (122°)

O(2a)–Cl–O'(4) = 114° (116°)   O'(3)–Cl–O'(4) = 97° (112°)

However, in view of the facts that the ions were disordered at the higher temperature, and that the data corresponding to the a axis doubling could not be included at the low temperature, the disagreement is not surprising. It does not alter the argument made earlier[1] that the origin of the alternation in the two perchlorate oxygen atoms concerned is that it enables them to form stronger hydrogen bonds to urea nitrogen atoms than does a regular tetrahedral arrangement. The low temperature data provide support for our model of the origin of the high temperature disorder, but, in the absence of the h and k odd reflections, cannot confirm the details of the alternation of the distorted perchlorate ions between adjacent unit cells which is implicit there.