

LETTERS
TO THE EDITOR

Crystal Structure of *N,N'*-Di-*tert*-Butylurea
as a N,O-Donating Ligand

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Urea and its N-substituted derivatives are usually regarded, proceeding from crystallographic and spectroscopic data for relevant complexes, as O-donating ligands [1]. Such a coordination type was found in a tungsten(VI) complex with *N,N'*-di-*tert*-butylurea (DTBU) [2]. However, deprotonated forms of DTBU can be coordinated in both a N,N- and N,O-bidentate manner to give four-membered chelate and bis(chelate) units (MN₂ and MN₂O₂, respectively), which was confirmed by X-ray diffraction data [3, 4]. The structure of DTBU itself remained unknown.

Single crystals of DTBU as thin colorless needles were obtained in the reaction of this compound with fluosilicic acid in a water-methanol solution. According to the X-ray diffraction data, DTBU crystallizes in a orthorhombic crystal system: $a = 9.4579(14) \text{ \AA}$, $b = 13.823(2) \text{ \AA}$, $c = 17.9603(18) \text{ \AA}$, $V = 2348.1(5) \text{ \AA}^3$, $M = 172.27$, $F(000) = 768$, $\rho(\text{calcd}) = 0.975 \text{ g/cm}^3$, $\mu = 0.064 \text{ mm}^{-1}$, space group $P2_12_12_1$, $Z = 8$. An experimental data array was collected with a Stoe IPDS diffractometer (image plate detector, 180 K, MoK α radiation, $2\theta_{\text{max}} = 51.94^\circ$; $-11 \leq h \leq 11$, $-17 \leq k \leq 17$, $-20 \leq l \leq 22$). The structure was solved by the direct methods followed by Fourier syntheses with fixed hydrogen atoms. Atomic coordinates and thermal parameters were refined for 4596 independent reflections by the least squares method in the anisotropic approximation for all non-hydrogen atoms with the SHELXL97 program [5]. The final residuals are $R = 0.0400$ for $I > 2\sigma(I)$ and $wR_2 = 0.1272$; GOOF (on F_2) = 0.524, $\Delta\rho_{\text{min}} = -0.105$, $\Delta\rho_{\text{max}} = 0.114 \text{ e\AA}^{-3}$.

In a crystal, two independent DTBU molecules are connected by intermolecular H bonds NH...O (N...O 2.888(5)–2.944(5) Å) to form dimers. The C=O bond lengths for two independent DTBU molecules are 1.245(6) and 1.244(6) Å; the C–N bond lengths are 1.363(6) to 1.489(6) Å. The angles NCN are 113.8(5)° and 114.2(5)°; the angles NCO are 122.6(6)° to 123.0(5)°; the CCC angles in *tert*-butyl substituents are close to tetrahedral (107.1(7)°–112.6(8)°). The standard deviations of atoms from the conjugation plane of the amido group for two independent DTBU molecules (A and B) are 0.036 and 0.019 Å, respectively; the dihedral angle A/B is 86.9(1)°. In the structure of DTBU, the thermal vibrations of the *tert*-butyl groups in two independent molecules differ noticeably.

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