The Crystal Structure of $[Ni(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_3]_3,Si_6O_{15},26H_2O$; a New Type of Silicon–Oxygen Double Ring, $Si_6O_{15}{}^{6-}$

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THE crystal structure of $[Ni(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_3],Si_6O_{15}$, $26H_2O$, which is one of the few silicates crystallizing from aqueous solution at room temperature, has been determined. Single crystals were obtained by reaction of an ethylene diamine solution of nickel hydroxide with an ethylenediamine solution of silica.[1,2] The crystals are hexagonal ($P6_3$, a = 17·37 ± 0·01, c = 15·18 ± 0·01 Å, Z = 6). The intensities of 920 non-zero, nonequivalent reflections were measured using a manual diffractometer with Mo-K_α radiation; the crystal was protected against weathering by a shellac film. The structure was determined from the three-dimensional Patterson function with subsequent refinement by three-dimensional electron-density syntheses. Hydrogen positions were not found. After all the other atoms had been found, the structure was refined by least-squares, using all reflections, with Cruickshank and Pilling's[3] weighting scheme. The discrepancy factor (R) was reduced to 0·091 using isotropic temperature factors.

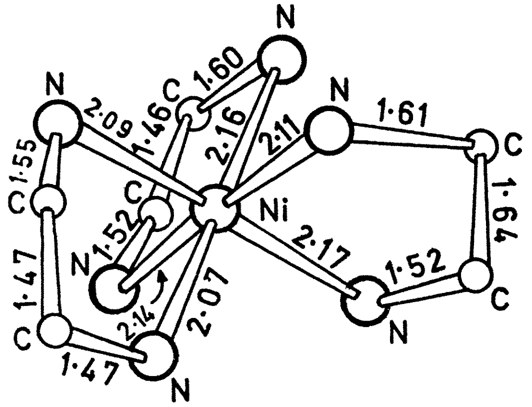

FIGURE 1. *The* L-(Ni en$_3$) *group.*

The main fragments of the structure are the $Ni(en)_3{}^{2+}$ cation and a silicon–oxygen anion of a new type, consisting of a double trigonal ring of composition $Si_6O_{15}{}^{6-}$. These are shown in Figures 1 and 2, respectively. The ring anions are located around the three-fold axes; the bond lengths and angles within them are inside the usual limits.

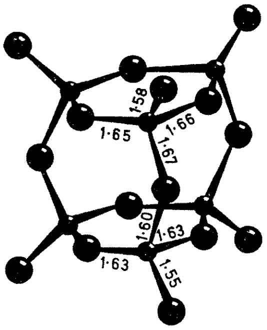

FIGURE 2. *The* Si_6O_{15} *double trigonal ring.*

The $Ni(en)_3{}^{2+}$ complex, though relatively similar to that described in ref. 4,[3] differs due to the absence of a threefold axis. The determination of the absolute configuration, which indicated the L-$[Ni(en)_3{}^{2+}]$ isomer, was made by comparing the intensities of nine pairs of $hk\bar{l}$ and hkl reflections measured using Cu-K_β radiation. A hydrogen-bonding system, formed by the water molecules, links the $Ni(en)_3{}^{2+}$ and $Si_6O_{15}{}^{6-}$ groups.

The structure determination shows that the chemical formula, previously written as $Ni(en)_3,Si_2O_5,8{\cdot}7H_2O$, should be rewritten as $[Ni(en)_3]_3,Si_6O_{15},26H_2O$.

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[3] D. W. J. Cruickshank and D. E. Pilling, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," Pergamon Press, Oxford, 1961, p. 45.

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