The Crystal Structure of Cobalt(II) Nicotinate Tetrahydrate: a Non-classical Zwitterion

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Summary The crystal structure of cobalt(II) nicotinate tetrahydrate shows that the carboxylate groups are not co-ordinated and that the molecule is best described as a nonclassical zwitterion.

As an extension of our studies into the electronic and molecular structures of pyridine-carboxylate derivatives of silver(II) and copper(II),[1,2] we have prepared and investigated the related cobalt(II) and nickel(II) complexes.[3] The nickel(II) derivative with picolinic acid (pyridine-2-carboxylic acid) has been shown[4] to have a structure in which the nickel atom is surrounded by an octahedral arrangement of two nitrogen atoms, two chelating oxygens and two aqueous oxygens, the related atoms of the two

picolinic acid molecules being mutually *trans*. We have now carried out a three-dimensional X-ray analysis of cobalt(II) nicotinate tetrahydrate (nicotinic acid = pyridine-3-carboxylic acid) and find this molecule to have a rather unusual structure, in which the carboxylate groups are not co-ordinated.

$(C_6H_4NO_2)_2Co,4H_2O$ crystallizes as pale pink plates in the monoclinic space-group $C2/m$ with $a = 14.133(9)$, $b = 6.882(6)$, $c = 8.486(8)$ Å, $\beta = 118.36(11)°$, $Z = 2$, $U = 726.2$ Å^3, $D_m = 1.70(2)$, $D_c = 1.715$ g./cm.^{3} Intensities of 699 independent reflections with $2\theta \leqslant 50°$ were recorded with a GE XRD-5 manual diffractometer, using Zr-filtered Mo-K_α radiation and the stationary crystal, stationary counter method. The structure was solved

from 679 non-zero reflections by Patterson and Fourier methods and refined by full-matrix least squares (Co, N, C, O anisotropic, H isotropic) to a conventional R factor of 0·046.
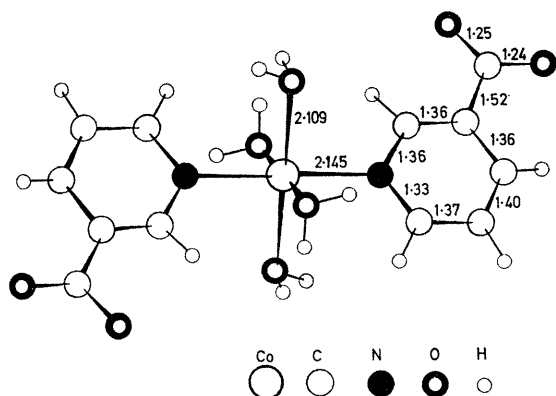

FIGURE. *The molecular structure of cobalt(II) nicotinate tetrahydrate, showing the principal bond lengths.*

The structure consists of discrete molecules of $(C_6H_4NO_2)_2Co$, $4H_2O$ (see Figure). The estimated standard deviations range from 0·004 Å (Co–O, N) to 0·010 Å (C–N, C–O, C–C). The hydrogen positions are reasonable. The molecule has $2/m$ symmetry: the two cobalt atoms in the unit cell occupy special positions (2a) and the atoms of the planar nicotinate positions (4i), while the water molecules are in general positions (8j).

This structure is best described as a nonclassical zwitterion, the charges formally residing on the cobalt and the oxygen atoms of each nicotinate moiety. A further interesting point is the large separation of these charges. The cobalt atom is in a slightly distorted octahedral environment consisting of a planar array of aqueous oxygen atoms and two axial nitrogen atoms. Angles around the cobalt atom range from 89·0 to 91·0°. The Co–N bonds are equivalent to those found in octahedral α-$CoCl_2$,2py (2·14 Å)[5] and the Co–OH_2 bond lengths are shorter than those in $Co(acac)_2$,$2H_2O$ [6] and $[Co(acac)_2$,$H_2O]_2$[7] (2·23 and 2·19 Å, respectively), but are equivalent to those found in $CoCl_2$,$6H_2O$ (2·12 Å).[8,9]

Hydrogen-bonding occurs between adjacent molecules from one of the carboxylate oxygen atoms to two hydrogens from two of the water molecules. Despite this, the two C–O distances are equivalent within experimental error at 1·24 and 1·25 Å.

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