The Structures of Bishistidino-nickel(II), -cobalt(II), and -cadmium(II)

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THE above complexes were prepared from the metal carbonates and either L- or DL-histidine ($C_3H_3N_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$), and crystallised from aqueous solutions.

The racemic nickel compound, $Ni(C_6H_8N_3O_2)_2$, H_2O, is orthorhombic, $Aba2$, with $a = 15{\cdot}18$, $b = 13{\cdot}05$, $c = 7{\cdot}72$ Å, $Z = 4$. Its structure was solved with three-dimensional X-ray intensity data (Cu—K_α radiation), and after least-squares refinement of the parameters, the agreement factor, R, is 0·075. There are equal numbers of molecules of bis-L-histidinonickel and bis-D-histidinonickel. The nickel atoms lie on two-fold axes and are octahedrally co-ordinated by two nitrogens and an oxygen of each histidine group. The bond angles around the nickel atom are all within 10° of the ideal values of 90° and 180°.

Bis-L-histidinocobalt(II), $Co(C_6H_8N_3O_2)_2,H_2O$, is monoclinic, C_2, with $a = 29{\cdot}44$, $b = 8{\cdot}32$, $c = 6{\cdot}35$ Å, $\beta = 90°$, $Z = 4$. Its structure was solved from electron density projections and the parameters are being refined using three-dimensional X-ray intensity data (Mo—K_α radiation). At present $R = 0{\cdot}14$. The configuration of the molecule (which does not lie on a crystallographic two-fold axis) is similar to that in the nickel complex above. The average distances are Co–N(1) 2·14, Co–N(2) 2·17, Co–O(1) 2·13 Å. The conformations of the two histidine groups are slightly different (by up to 10° in dihedral angles) from each other and from that in the nickel complex.

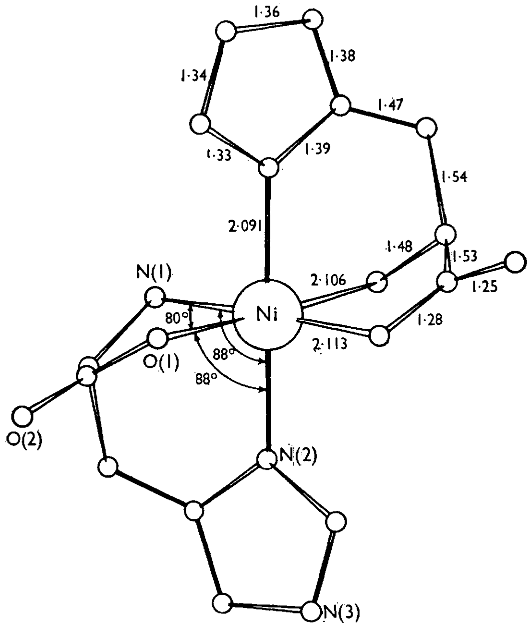
The cell dimensions and (010) electron density projection of bis-L-histidinonickel show that its crystal structure is very like that of bis-L-histidinocobalt. Racemic bis-histidinocobalt crystallises in space group $P2_1/c$, different from both the above structures; it is being studied further.

Bis-L-histidinocadmium is tetragonal, $P4_12_12$, with $a = 7{\cdot}39$, $c = 30{\cdot}5$ Å, and a structure similar to that of the corresponding zinc compound.[1] The (100) electron density projection gave approximate values for all the atomic positional parameters. The metal atoms are on two-fold axes. In the zinc compound the co-ordination group is essentially tetrahedral [to N(1) and N(2) of each histidine] and the carboxyl oxygen atom, O(1) is loosely associated. In the cadmium compound the histidine groups have tilted to allow these six atoms to be at more nearly equal distances from the metal atom.

Cd–N(1) 2·26, Cd–N(2) 2·25, Cd–O(1) 2·49 Å, (e.s.d. ~ 0·05 Å)

Zn–N(1) 2·05, Zn–N(2) 2·04, Zn–O(1) 2·79 Å, (e.s.d. < 0·02 Å)

In no case is the metal atom quite in the plane of the imidazole group co-ordinated to it; the displacements from the imidazole plane range from 0·13 Å in the nickel compound to 1·1 Å in the cadmium compound.



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[1] R. H. Kretsinger, F. A. Cotton, and R. F. Bryan, *Acta Cryst.*, 1963, **16**, 651.