

X-RAY CRYSTAL STRUCTURE OF [*N,N'*-ETHYLENEBIS(PYRROL-2-YLMETHYLENEAMINATO)]NICKEL(II) COMPLEX

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The 1:1 complex of nickel(II) with *N,N'*-ethylenebis(pyrrol-2-ylmethyleneamine) in benzene-inclusion crystals is a planar complex with a highly strained geometry of coordination, as shown by X-ray structural analysis.

Recently, it has been found by X-ray structural analysis that the 1:1 complex of copper(II) with *N,N'*-ethylenebis(pyrrol-2-ylmethyleneamine), a tetradentate Schiff base of pyrrole-2-carboxyaldehyde, forms such a novel dimer as shown in Fig. 1,<sup>1)</sup> contrary to the general belief that tetradentate Schiff base complexes of pyrrole-2-carboxyaldehyde are all planar.<sup>2,3)</sup> In the above dimer, the tetradentate Schiff base functions as a bis(bidentate) ligand. The reason why this copper(II) complex does not form a planar complex but such a dimer instead may be that the four nitrogen atoms of the ligand are sterically difficult to be accommodated in the positions of square-planar coordination. The above finding awakens another interest in the structures of the other metal complexes with the same ligand, as is often the case with structural studies in coordination chemistry. We report here the X-ray crystal structure of the corresponding nickel(II) complex.

An X-ray analysis of single crystals grown from benzene was undertaken. Crystal data:  $\text{Ni}(\text{C}_{12}\text{H}_{12}\text{N}_4) \cdot 0.5\text{C}_6\text{H}_6$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.809$ ,  $b = 9.847$ ,  $c = 6.892$  Å,  $\alpha = 75.15$ ,  $\beta = 84.57$ ,  $\gamma = 93.81^\circ$ ,  $z = 2$ ,  $V = 702.73$  Å<sup>3</sup>,  $D_c = 1.465$  g cm<sup>-3</sup>. The final *R* factor is 8.1% for 2072 reflections.

[*N,N'*-Ethylenebis(pyrrol-2-ylmethyleneamino)]nickel(II) is a planar complex, in agreement with spectroscopic expectations,<sup>3)</sup> and forms stacks of the molecules with interplanar distances of  $\approx 3.4$  Å in the crystals, as shown in Fig. 2. Its molecular structure is nonsymmetrical, and some bond lengths and angles of the same kinds are considerably different from each other. There are two remarkable structural features in the coordination geometry. One is that both Ni-N(pyrrole) bonds are longer than both

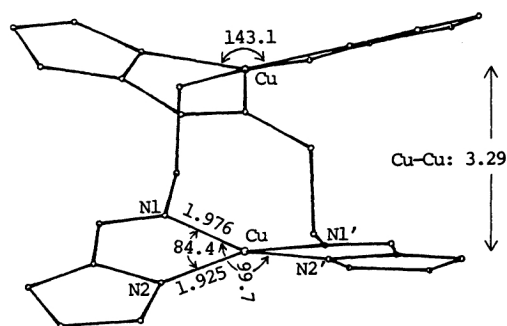


Fig. 1. Dimeric structure of the 1:1 complex of copper(II) with *N,N'*-ethylenebis(pyrrol-2-ylmethyleneamine).<sup>1)</sup>

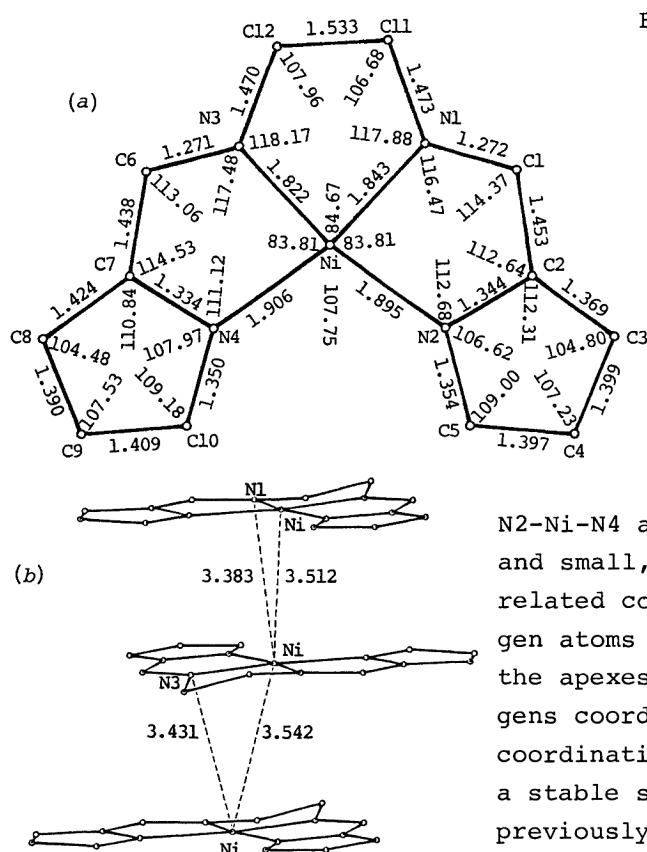


Fig. 2. Structure of  $[N,N'$ -ethylenebis(pyrrol-2-ylmethyleneamino)]nickel(II): (a), viewed along the  $c^*$  axis; (b), viewed approximately along the  $b$  axis. The standard deviations of the bond lengths and angles are about 0.005 Å and 0.05°, respectively.

Ni-N(imine) ones, in contrast with those in strain-free cases of other pyrrole-2-carboxyaldehyde Schiff base complexes.<sup>4,5)</sup> The other is that the

N2-Ni-N4 and N1-Ni-N3 angles are extremely large and small, respectively, compared with those of related complexes. Consequently, the four nitrogen atoms of the present complex are located at the apexes of a trapezoid, and the pyrrole nitrogens coordinate to the nickel atom obliquely; this coordination geometry is remarkably different from a stable square-planar one, as has been predicted previously.<sup>1)</sup> The structural difference thus revealed between the present nickel(II) complex and

the corresponding copper(II) complex is very suggestive in considering the stereochemistry of metal complexes. The crystal field stabilization energy (CFSE) of square-planar ( $D_{4h}$ ) coordination for nickel(II) complexes is twice as large as that for copper(II) complexes.<sup>6)</sup> This suggests that the CFSE of the present nickel(II) complex may be just enough to have a planar coordination geometry with a strained molecular conformation, while the corresponding copper(II) complex has such a less strained dimeric structure as shown in Fig. 1, because its CFSE may not be over the above strain energy.

Details of the structural parameters of these nickel(II) and copper(II) complexes, together with some interesting facts on their crystal structures including solvent molecules, will be reported elsewhere.

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