The Crystal Structure of Dimeric Dichloro-(2,9-dimethyl-1,10-phenanthroline)nickel(II)

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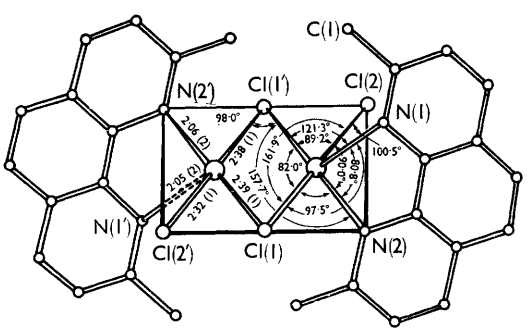
THE series of mono-complexes, $M^{II}Cl_2$ dmp, where M^{II} = Fe^{II}, Co^{II}, β-Ni^{II} and Zn^{II}, and dmp is 2,9-dimethyl-1,10-phenanthroline, has been shown to be isomorphous,[1] with the metal atom having tetrahedral co-ordination.[2] However, the nickel complex exists in two isomeric forms, a purple β-form (μ_{eff} = 3·40 B.M.), and a yellow α-form (3·18 B.M.),[3] which is obtained as a chloroformate. The chloroform is readily driven off by heating. Structural analysis shows the α-compound to be dimeric with an approximately square pyramidal co-ordination for each nickel atom.

Tan coloured, hygroscopic crystals of $[NiCl_2$-dmp$]_2$,$2CHCl_3$ were obtained from chloroform. The crystal used in the determination was mounted in a fine pyrex tube under dry nitrogen: crystal data: $C_{30}H_{26}Cl_{10}N_4Ni_2$; M, 914·6, monoclinic; a = 11·75(1), b = 13·46(2), c = 11·27(2) Å, β = 91·2(1)°; U = 1782 Å^3; D_m = 1·68 (by flotation); Z = 2; D_c 1·70; $F(000)$ = 920; space group, $P2_1/n$ [$\pm(x,y,z;\ \frac{1}{2}=x,\ \frac{1}{2}-y,\ \frac{1}{2}+z)$]; Mo-$K_\alpha$ radiation, Zr-filtered, single-crystal precession photographs. 1450 non-zero reflections were recorded from seven levels (*h*0*l* to *h*4*l* and *hk*0, *hkl*) using multiple exposures for each level.



FIGURE

Atomic co-ordinates for nickel and one chlorine atom were obtained from a three-dimensional Patterson synthesis. The other atoms, except for hydrogen, were located in subsequent Fourier syntheses. Six cycles of full matrix least-squares

refinement, using individual isotropic temperature factors, resulted in a conventional R value of 10·6%.

The dimeric molecule is made up of two monomeric $NiCl_2$ dmp units linked by bridging chlorine atoms. The two halves of the dimer are related by a crystallographically imposed centre of symmetry. The co-ordination around the nickel atom may be approximately described as square-pyramidal (Figure) with the metal displaced 0·4 Å out of the plane defined by Cl(1), Cl(1′), Cl(2), and N(2) in the direction of the apex N(1). There is no interaction between the chloroform and the co-ordination sphere.

An interesting feature of the structure is the large deviation of the N(1)–Ni–Cl(1′) bond angle 121·3° from the expected square pyramidal angle (90°). This distortion is presumably caused by the interaction of the methyl group C(1) with Cl(1′) with a separation of 3·6 Å.

The environment of the nickel atom is intermediate between the regular square pyramidal case[4] and the triangular bypyramidal co-ordination reported for $CuCl_2$ dmp H_2O.[5]

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