The Crystal Structure of β-Dichlorobis[tris-(2-cyanoethyl)phosphine]nickel(II): a Polymer containing Bridging Bidentate Ligand Molecules

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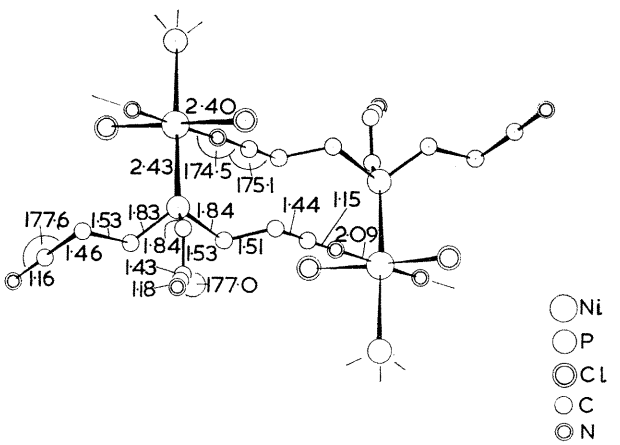
Summary The crystal structure of polymeric β-dichlorobis[tris-(2-cyanoethyl)phosphine]nickel(II) shows that the potentially tetradentate ligand molecules are bidentate and bridge adjacent nickel atoms.

TRIS-(2-CYANOETHYL)PHOSPHINE (cep) has an unusual combination of low steric requirements and very low basicity,[1,2] and can stabilize normal and low oxidation states when acting as a monodentate phosphorus donor, as in $Ni_4(CO)_6$ cep_4,[2] $ReCl_3$ cep,EtOH,[3] and $PtCl_2$ cep_2.[4]

Its versatility as a multidentate donor molecule has recently been demonstrated[4] by the isolation of the complexes $3CoX_2$ cep_2 (X = Cl, Br, or I), in which it is believed to function as a terdentate cyanide-bonded ligand, and the nickel(II) derivatives α- and β-$NiCl_2$ cep_2. Red square-planar α-$NiCl_2$ cep_2, containing monodentate phosphorus-bonded cep molecules, transforms at room-temperature and above to the blue six-co-ordinate β-form. We have now investigated the structure of this latter complex by three-dimensional *X*-ray analysis and confirmed the suggested[4] polymeric structure involving bridging bidentate ligand molecules.

Pale blue plates of β-$NiCl_2$ cep_2 (M = 516·4) are monoclinic, spacegroup $P2_1/n$ with a = 7·684(5), b = 21·060(9), c = 8·285(4) Å, β = 117·20(8)°, U = 1192·5 Å^3, D_m = 1·44 g.cm.$^{-3}$, Z = 2, D_c = 1·438 g.cm.$^{-3}$. Intensities of 2281 independent reflections with $2\theta < 140°$ were recorded with a GE XRD-5 manual diffractometer, using Ni-filtered Cu-K_α radiation and the stationary crystal–stationary counter method. The structure was solved from 2129 non-zero reflexions by conventional Patterson and Fourier methods and refined by full-matrix least-squares (Ni, Cl, P with anisotropic thermal parameters, light atoms isotropic) to the present R of 0·12.



The molecular structure of β-$NiCl_2$ cep_2, *showing the principal bond lengths and angles.*

The two nickel atoms occupy the centres of symmetry 0,0,0 and ½,½,½ in the unit cell. The structure consists of infinite sheets along the *a* axis with the cep ligands acting as bidentate bridges between adjacent nickel atoms, with co-ordination from the phosphorus atom and one of the nitrogen atoms of each ligand molecule. Each cep molecule therefore contains one bonded and two non-bonded cyanoethyl groups (Figure). Estimated standard deviations range from 0·002 (Ni–Cl, P) to 0·015 Å (C–C and C–N) for the distances, and from 0·1 (Cl–Ni–P) to 1·0° (C–C–C and C–C–N) for the angles.

The configuration around each nickel atom is approximately octahedral in the range 88·5—91·5°. The Ni–Cl bond lengths (2·40 Å) are typical of an octahedral nickel(II) species (*cf.* Ni–Cl 2·387 Å in $NiCl_2$ py_4),[5] and the Ni–P bonds (2·43 Å) are appreciably longer than in tetrahedral $NiCl_2(PPh_3)_2$ (2·27 Å)[6] and $Ni_4(CO)_6$ cep_4 (2·16 Å)[2] consistent with the trends expected from stereochemical and oxidation-state differences. The Ni–N bond-lengths of 2·09 Å are close to that expected from comparisons with M–N bond-lengths in the related methyl cyanide derivatives $Cu(NO_3)_2(MeCN)_2$ (1·91 and 1·93 Å),[7] $Cu_2Cl_4(MeCN)_2$ (1·96 Å),[8] and $ZnCl_2(MeCN)_2$ (2·0 Å).[9]

The dimensions of the three cyanoethyl groups of each cep molecule are equivalent to within experimental error, and closely resemble those in $Ni_4(CO)_6$ cep_4.[2] Also, the phosphorus atom and C≡N group in all cyanoethyl chains are approximately *trans*- to one another with respect to rotation about the C–C bonds. Finally, we note a small deviation from linearity in the Ni–N–C–C grouping, the angles at the nitrogen and carbon atoms being 174·1 and 175·1°, respectively, which contrasts with the usual observation that such a group is "linear."[10] However, since some deviation from linearity is observed within the non-bonded cyanoethyl groups (N–C–C = 177·0 and 177·6°) we do not consider this particularly significant.

We thank the S.R.C. for a studentship (to D.F.L.). One of us (M.G.B.D.) gratefully acknowledges the award of an I.C.I. Fellowship.

(*Received, January 29th,* 1969; *Com.* 123.)

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