Co-ordination Polymers of Rhodium(1+) with Di-isocyanonaphthalene (1,4 and 1,5) Linkages

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Summary. The template polymerization of tetragonal rhodium(1+) with 1,4- and 1,5-di-isocyanonaphthalenes gives two-dimensional co-ordination polymers with a stacked layers arrangement; the powder *X*-ray diffractometric traces of these polymers are presented and discussed.

THE isomers 1,4- and 1,5-di-isocyanonaphthalene[1] can be regarded as non-chelating bidentate ligands capable of forming stereochemically rigid linkages between metal nuclei with a bridge span of *ca.* 12 Å. Viewing the terminal isocyanide-to-metal bonds as vectors suggests that the terms 'colinear' (1,4) and 'parallel' (1,5) may be used to describe the bridging geometries of these ligands. Compared with the colinear (1,4) ligand, a displacement of 2·42 Å between the parallel vectors in 1,5-di-isocyanonaphthalene requires a slightly longer bridge span (*ca.* 0·2 Å). The co-ordination properties of these bridging ligands were ascertained for a tetragonal rhodium(1+) system.

Di-isocyanonapthalenes (1,4 and 1,5) react with $[Rh(CO)_2Cl]_2$ in CH_2Cl_2 solution to afford quantitative yields of insoluble green polycrystalline polymers which analyse as $[Rh(bridge)_2{}^+Cl^-]_n$. These polymers readily absorb water, and therefore, unless rigorously dried *in vacuo*, are best formulated as $[Rh(bridge)_2{}^+Cl^- \cdot xH_2O]_n$ ($x = 0$–5). A single strong ν(NC) at 2040 ± 5 cm^{-1} in their i.r. spectra may suggest the presence of terminally co-ordinated isocyanides in a symmetric environment.

Two-dimensional models of the $[Rh(bridge)_2]_n$ network which depict the template polymerization of tetragonal Rh^I with 1,4-di-isocyanonaphthalene [Figure (A)] and

TABLE. Powder *X*-ray diffraction angles (θ), interplanary spacings (d), $\sin^2\theta$ ratio (N), and assigned indices for the new polymers (A) and (B).

(A)[c]			(B)[d]			Assigned indices		
$\theta/°$	$d/\text{Å}$	$N_{\text{exp.}}$[a] $[N_{\text{theor.}}]$[b]	$\theta/°$	$d/\text{Å}$	$N_{\text{exp.}}$[a] $[N_{\text{theor.}}]$[b]	h	k	l
3·95	11·18	1 [1]	3·73	11·84	1 [1]	1	0	0
5·80	7·62	2·15[2]	5·50	8·04	2·17[2]	1	1	0
7·75	5·71	3·83[4]	7·55	5·86	4·08[4]	2	0	0
8·70	5·09	4·82[5]	8·45	5·24	5·10[5]	2	1	0
12·10	3·67	9·25[9]	11·35	3·91	9·15[9]	3	0	0
13·10	3·39	(10·82)[e]	13·05	3·41	(12·05)[e]	0	0	1

[a] $N_{\text{exp.}} = \sin^2\theta(hk0)/\sin^2\theta(100)$. [b] $N_{\text{theor.}} = h^2 + k^2$. [c] Space group $P4$; cell dimensions: $a = 11{\cdot}18$, $c = 3{\cdot}39$ Å. [d] Space group $P4$; cell dimensions: $a = 11{\cdot}84$, $c = 3{\cdot}41$ Å. [e] This value does not conform with integral $h^2 + k^2$ terms.

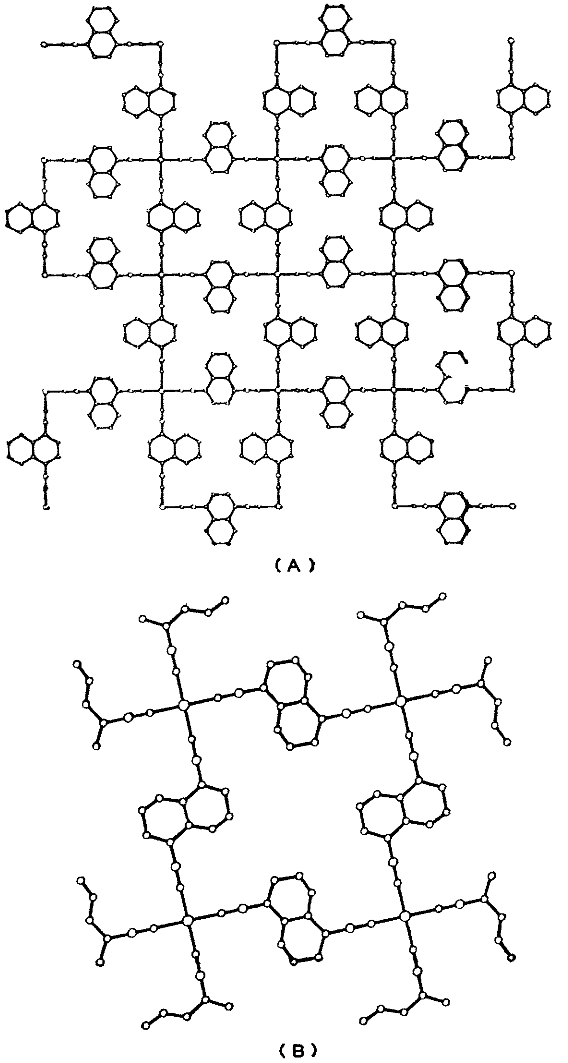

FIGURE. Two-dimensional models of the $[\text{Rh(bridge)}_2]_n$ network in the 1,4- (A) and 1,5- (B) di-isocyanonaphthalene Rh^{I} polymers.

1,5-di-isocyanonaphthalene [Figure (B)] were constructed using idealized bond angles and distances similar to those found in related systems.[2,3] Model calculated cell dimensions are: $a = 11{\cdot}81$ Å for (A)† and $a = 12{\cdot}04$ Å for (B). Based on these models, the shortest interbridging C - - - C distances in (A) (*ca.* 4·6 Å) and (B) (*ca.* 4·3 Å) suggest the absence of steric constraint. In view of the established tendency[2] of the Rh(CNR)_4^+ cation to associate *via* weak $\text{Rh}^{\text{I}}\cdot - - - \text{Rh}^{\text{I}}$ interactions, the three-dimensional model structures of these polymers may be derived by the eclipsed stacking of the two-dimensional models.

The powder *X*-ray diffractometric traces of the new polymers, measured on a Phillips Diffractometer using filtered Cu radiation and a scan speed of 1° (2θ) per min, are especially informative (Table) concerning their structures. Interpretation[4] of the diffraction data in terms of reflections originating from Rh-containing sets of planes appears consistent with the presence of a tetragonal system in these polymers. The most intense reflection in each trace was assigned to the 100 planes, whose spacings [$d(100)$] correspond to the bridge spans. Other *hk*0 reflections were assigned according to a known technique[4] by considering the $N_{\text{exp.}}$ and $N_{\text{theor.}}$ terms (Table). One reflection in each trace, not belonging to the *hk*0 family, was assigned to the 001 planes. This assignment suggests the intermetallic distances [$d(001)$] 3·39 Å in (A) and 3·41 Å in (B), which are compatible with the distances 3·19,[2] 3·21,[3] and 3·25 Å[3] found in related dinuclear complexes of type $[\text{Rh}_2(\text{CNAr})_8]^{2+}$, as well as with distances in the range 3·21—3·36 Å characterized in similar tetragonal polymers of rhodium(1+) with other rigid di-isocyanide linkages.[5]

Compared with the respective model calculated terms, the experimentally determined bridge span in (A) is found to be significantly shorter (*ca.* 0·63 Å), whereas that in (B) is only slightly shorter (*ca.* 0·20 Å). These differences may be attributed, in part, to the non-idealized bond angles expected in the real polymers. The bridge span in (B) has indeed been found to be longer than that in (A), as was anticipated.

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† The cell dimension of (A) is based solely on the rhodium metal array, and does not take into account the presumed benzo ring orientations which require a cell twice its length.

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