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Linkage Isomers of Molybdenum(0) and the Chelate Ligand Pyridine-2-carboxaldehyde-2′-pyridylhydrazone (paphy)

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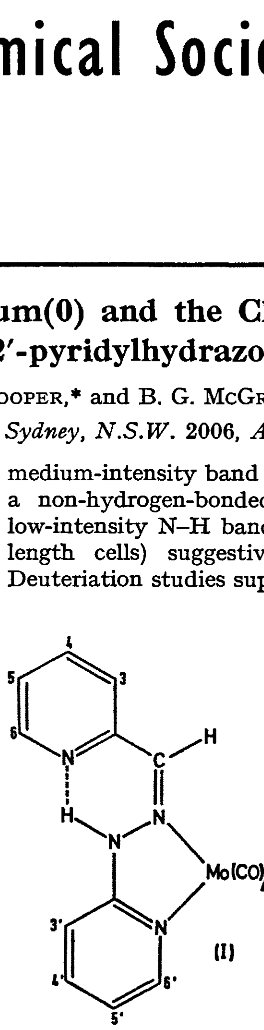
Summary Linkage isomers of a novel type have been prepared with molecular formula $Mo(CO)_4$ paphy, one by the reaction of pyridine-2-carboxaldehyde-2′-pyridylhydrazone (paphy) with the chloropentacarbonylmolybdate(0) anion and the other by direct reaction of paphy with molybdenum hexacarbonyl.

In the course of our studies of metal–nitrogen bonding in complexes of the Group VIA metal carbonyls with pyridine-2-carboxaldehyde-2′-pyridylhydrazone (paphy)†[3,4] and its derivatives,[5] we have isolated linkage isomers of $Mo(CO)_4$-paphy in which different pairs of nitrogen donor atoms in the ligand are co-ordinated to the metal atom.

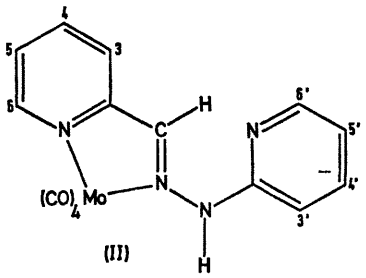
Monodentate ligands known to form isolable linkage isomers (NO_2^-, CN^-, SCN^-, $SeCN^-$, $S_2O_3^{2-}$)[6] do so by changing from one donor element to another; linkage isomerism involving chelating ligands is very uncommon.[7] In the isomers reported here only nitrogen donor atoms are used by the ligand paphy which behaves as a bidentate chelate in each case.

Direct reaction of paphy with molybdenum hexacarbonyl in diglyme at 125° produced an orange-red air-stable diamagnetic crystalline compound (I) with an elemental analysis (C,H,N,Mo) correct for $Mo(CO)_4$paphy. Reaction of the intermediate, tetraethylammonium chloropentacarbonylmolybdate(0) with paphy in diglyme at room temperature gave an orange diamagnetic crystalline compound (II) which also had an elemental analysis correct for $Mo(CO)_4$paphy. In the solid state, (II) is relatively unstable in air (extensive decomposition within one week).

Both (I) and (II) have four i.r. absorption bands in the terminal CO region [$CHCl_3$ solution: (I) 2022(m), 1915(s), 1885(s), and 1836(s) cm^{-1}; (II) 2026(m), 1920(s), 1890(s), and 1840(s) cm^{-1}] characteristic of the *cis*-$Mo(CO)_4L_2$ configuration, but there are important differences in the N–H stretching regions. In carbon disulphide the sharp medium-intensity band of (II) at 3429 cm^{-1} is indicative of a non-hydrogen-bonded amine, while (I) has a broad low-intensity N–H band at 3050—3100 cm^{-1} (5 cm path-length cells) suggestive of strong hydrogen bonding.[8] Deuteriation studies support these assignments.



(I)



(II)

From the ^1H n.m.r. spectra, the deshielded position of the amino-proton resonance in (I) (Table) confirms the presence of strong hydrogen bonding while in (II) the same proton appears not to be hydrogen-bonded. Further support for the structures is found in the resonance frequencies (Table) of the protons 6 and 6′. Protons 6 in (II) and 6′ in (I) are shifted downfield to a similar extent, commensurate with the withdrawal of σ-electron density from the adjacent pyridine nitrogen to the metal.

The coupling of protons 5′ and 6′ in (I) (Table) is considerably greater than $J_{5',6'}$ in the free ligand, which suggests that in (I) these protons are *meta* and *ortho*[9] to a co-ordinated nitrogen atom. A second-order splitting

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† The paphy used in these studies was prepared by the method of Lions and Martin[1] and was therefore in the *anti*-configuration.[2]

pattern of the aldehydic ring in (II) prevents a similar comparison of $J_{5,6}$ values.

TABLE

Compound	N–H proton (δ p.p.m. *ex* Me_4Si)	Shift (δ p.p.m.) relative to position in paphy		$J_{5,6}$	$J_{5',6'}$
		6-H	6′-H		
paphy	10·12	—	—	4·8	4·9
Isomer (I)	15·71	+0·26	+0·41	4·9	5·6
Isomer (II)	9·70	+0·44	+0·24	—	5·1

The higher reaction temperature used to prepare (I) no doubt provides the energy required to isomerize the ligand about the C=N bond. We exclude the possibility that (I) and (II) are polynuclear species on the basis of the elemental analyses, and infrared and n.m.r. evidence.

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