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The Synthesis of 1,1-Dipyrazolylcycloalkane Complexes of Cobalt(II), Nickel(II), Zinc(II) and Mercury(II)

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There is considerable interest in the chemistry of metal complexes formed by poly(pyrazolyl)–Group III anionic ligands [1–4] and by corresponding neutral-alkane [1] and -phosphine [5, 6] ligands. The bidentate dipyrazolylalkanes [1, 7], dipyridyl and *o*-phenanthroline [8, 9] ligands coordinate to metals *via* the common pyridine-type of donor centre. The complexes formed, however, are likely to exhibit significant structural and chemical differences relating to electronic structure, chelate ring size and molecular flexibility or rigidity. A recent publication [10] on chromium(II) complexes of methylenedipyrazoles $(R_2pz)_2CH_2$ prompts us to report our studies of the complexing properties of 1,1-dipyrazolylcycloalkanes. In common with other dipyrazolylmethanes and related systems, these bidentate ligands are capable of forming complexes containing a six-membered $C(N{-}N{-})_2M$ metallocycle. The metallo-ring, however, is fused at a quaternary carbon atom that is common to the cycloalkane ring (Fig. 1). Now the six-atom $[E(N\text{-}N)_2M]$ skeletal arrangements in related systems range from relatively flexible boat conformations to planar or even shallow chair structures [4, 11]. Hence, we anticipate that the ring size of the cycloalkane moiety will dictate the external bond angles about the quaternary carbon centre [12], and thus the 'bite' of the dipyrazolyl ligand. With a view to studying expected structural and/or property modifications, we have prepared a series of 1,1-dipyrazolylcycloalkane (L) complexes of

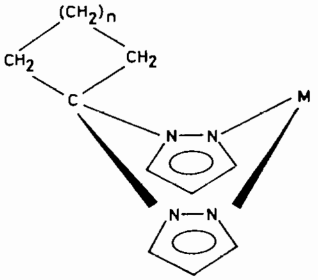

Fig. 1. n = 1, 1,1-dipyrazolylcyclobutane (*but*) complexes; n = 2, 1,1-dipyrazolylcyclopentane (*pent*) complexes; n = 3, 1,1-dipyrazolylcyclohexane (*hex*) complexes. M = Co(II), Ni(II), Zn(II) or Hg(II) with other attached ligands.

TABLE I. Complexes of 1,1-Dipyrazolylalkanes[1,2].

		% Yield	Analytical Data, %					
			Observed			Calculated		
			C	N	H	C	N	H
$CoCl_2$*but*$\cdot H_2O$	Ia	72	35.7	16.7	4.21	35.74	16.67	4.19
$CoCl_2$*pent*$\cdot 0.5(H_2O)$	Ib	59	38.6	16.7	4.24	38.72	16.42	4.40
$CoCl_2$*hex*$\cdot H_2O$	Ic	58	39.0	15.2	4.51	39.58	15.39	4.94
$CoCl_2$*mhex*	Id	80	43.6	15.5	5.00	43.35	15.55	5.04
$NiCl_2$*but*$\cdot H_2O$	IIa	90	36.1	17.0	3.87	35.80	16.72	4.21
$NiCl_2$*pent*	IIb	80	39.5	16.3	4.45	39.81	16.20	4.25
$NiCl_2$*hex*$\cdot H_2O$	IIc	80	39.4	15.3	4.77	39.70	15.42	4.99
$Zn(ClO_4)_2$(*but*)$_2$	IIIa	43	37.4	17.0	4.12	37.48	17.49	3.75
$Zn(ClO_4)_2$*pent*$\cdot 2H_2O$	IIIb	62	26.3	11.6	3.93	26.27	11.15	3.58
$Zn(ClO_4)_2$*hex*$\cdot 2H_2O$	IIIc	74	27.8	11.1	3.75	27.99	10.89	3.89
$HgCl_2$*but*	IVa	33	26.4	12.5	2.74	26.13	12.18	2.63
$HgCl_2$*pent*	IVb	65	27.5	11.9	2.86	27.88	11.83	2.89
$HgCl_2$*hex*	IVc	34	29.6	–	3.31	29.54	11.49	3.31

[1] *but, pent, hex* and *mhex* = 1,1-dipyrazolyl-cyclobutane, -cyclopentane, -cyclohexane and -4-methylcyclohexane, respectively.
[2] The colours were: Ia, purple; Ib, blue; Ic, blue; Id, pale blue; the anhydrous nickel(II) complexes were yellow-brown, while the aquated complexes were green; the complexes of zinc(II) (IIIa–c) and mercury (IVa–c) were white.

Co(II), Ni(II), Zn(II) and Hg(II), and have isolated the types $ML X_2$, ML_2X_2, $MLX_2 \cdot H_2O$ and $MLX_2 \cdot 2H_2O$ (Table I).

The ligands 1,1-dipyrazolyl-cyclobutane (*but*), cyclopentane (*pent*), -cyclohexane (*hex*) and -4-methylcyclohexane (*mhex*) readily coordinate with metal ions in acetone solution. Thus, $HgCl_2$ gives anhydrous derivatives [$HgCl_2L$] (IVa–b), while $CoCl_2$ and $NiCl_2$ tend to give aquated complexed [$MCl_2L \cdot H_2O$] (M = Co, Ia, Ic; M = Ni, IIa, IIc). Under stringently dry conditions, however, the anhydrous complexes [$CoCl_2$(*mhex*)] (Id) and [$NiCl_2$(*pent*)] (IIb) were obtained. Surprisingly, the reactions of equimolar solutions of the aquated zinc(II) ion and *but* gave the anhydrous 2:1 complex [$Zn(ClO_4)_2$(*but*)$_2$] (IIIa). Under similar conditions, the ligands *pent* and *hex* gave di-aquo-1:1 complexes [$Zn(ClO_4)_2L \cdot 2H_2O$] (IIIb, c). Thus, it appears that the larger NN 'bite' in *but* may be more ideal for tetrahedral coordination about Zn^{++} than the corresponding 'bites' in *pent* and *hex*, giving preference to the observed anhydrous 2:1 complex IIIa.

Preliminary ^1H NMR data shows that the pyrazolyl rings are equivalently coordinated in the diamagnetic mercury complexes IVa–c. The cobalt(II) and nickel(II) complexes are high spin (Ia–d, $\mu_{eff} \cong 4.9$ B.M.; IIa–c, $\mu_{eff} \cong 3.3$ B.M.). Details of spectroscopic and structural studies will be reported at a later data.

Experimental

The ligands 1,1-dipyrazolyl-cyclobutane (*but*), -cyclopentane (*pent*), -cyclohexane (*hex*) and -4-methylcyclohexane (*mhex*) were prepared according to published methods [13]. Anhydrous $CrCl_2$ was prepared from the hydrated salt by refluxing in thionyl chloride [14]. Complexes (see Table I) were prepared on a 1 millimolar scale, as follows:

Cobalt(II) complexes: A solution of the appropriate ligand in acetone was added to a stirred, equimolar solution of $CrCl_2$ in acetone. The solution volume was reduced under vacuum, yielding coloured crystals which were filtered off and pumped dry.

Nickel(II) complexes: Equimolar solutions of $NiCl_2 \cdot 6H_2O$ and ligand in acetone were mixed together. The solvent was removed under vaccum, giving a coloured solid which was washed several times with ether and finally dried under vacuum.

Zinc(II) complexes: The method was the same for the cobalt(II) complexes, except that $Zn(ClO_4)_2 \cdot 6H_2O$ was used in place of $CrCl_2$.

Anhydrous complexes: (*a*) of mercury(II). The method was the same as for the cobalt(II) complexes, except that $HgCl_2$ was used in place of $CoCl_2$.

(*b*) [$CoCl_2$(*mhex*)] (Id). The solvent (acetone) was dried before use and the reaction was conducted under dry nitrogen according to the procedure for the cobalt(II) complexes above.

(*c*) [$NiCl_2$(*pent*)] (IIb). A solution of $NiCl_2 \cdot 6H_2O$ in acetone/2,2-dimethoxypropane was heated gently until the colour changed from green to yellow-brown. The solution was cooled, and an equimolar amount of 1,1-dipyrazolylcyclopentane in dry acetone was added. The solution was pumped to dryness, the residue was washed with dry ether, and finally pumped dry under vacuum.

Analyses (C, H and N, see Table I) were performed by the University Analyst, Simon Fraser University.

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