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Pyridazine-bridged Hetero- and Homo-dimetallic Complexes Produced by Using Bis-pyridazinecarboxamide Metal Complexes as Ligands

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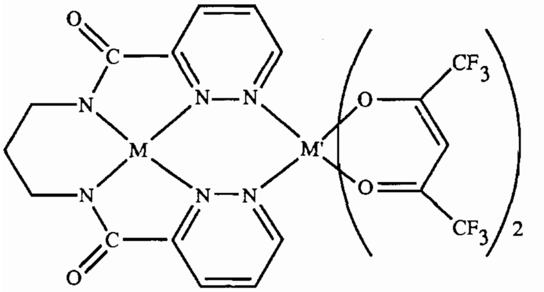
Much work has been carried out on metal complexes with bridging diazine groups involving the N–N fragment. Virtually all of this work has used binucleating ligands based on disubstituted 3,6-pyridazines and 1,4-phthalazines [1, 2]. We report a new approach, based on monosubstituted pyridazines. We find that metal complexes of quadridentate bis-pyridazinecarboxamides can act as NN-donor ligands, coordinating to metal β-diketonates and producing pyridazine-bridged dimetallic complexes, as illustrated in **I**.



I, M(bpdpn)M'(hfacac)$_2$
(involving NN-coordination by M(bpdpn) to M'(hfacac)$_2$)

Examples are shown in Table 1 of parent metal bis-pyridazinecarboxamide complexes, of the type M(bpdpn) (H_2bpdpn = *N*,*N'*-bis(3'-pyridazinecarboxamide)-1,3-propane). Also shown are dimetallic products obtained by coordinating these M(bpdpn) complexes to the metal β-diketonate Ni(hfacac)$_2$ (Hhfacac = hexafluoroacetylacetone).

The deprotonated ligand bpdpn^{2-} appears to act as a distorted square-planar N_4-donor in the parent M(bpdpn) complexes. This is found with [Cu(bpdpn)-H_2O]·H_2O, for which an X-ray structure analysis indicates square-pyramidal N_4O-coordination, with an apically coordinated water molecule [3]. Furthermore, the Ni^{II} complex Ni(bpdpn)·2H_2O is diamagnetic, in keeping with planar N_4-coordination. Also, Stephens, Vagg and coworkers, as part of an extensive series of structure determinations, have shown that the Cu^{II} and Ni^{II} complexes with the corresponding bis-picolinamide ligand involve distorted square-planar N_4-coordination [4, 5].

TABLE 1. Magnetic data for parent M(bpdpn) complexes and the resulting dimetallic M(bpdpn)Ni(hfacac)$_2$ complexes

Compound^a	μ_{eff} (BM)^b		θ (K)^c
	304 K	89 K	
Ni(bpdpn)·2H_2O	diamagnetic		
Cu(bpdpn)·2H_2O	1.95	1.87	−13
Ni(bpdpn)Ni(hfacac)$_2$·CCl_4	3.22	3.19	−3
Cu(bpdpn)Ni(hfacac)$_2$	3.41	2.63	−81^d

^{a}Satisfactory elemental analyses were obtained for all compounds. ^{b}Calculated per mole of complex (including the dimetallic complexes). ^{c}Curie–Weiss law taken as $\chi^{-1} = C(T - \theta)$. ^{d}Deviated from linearity at lower temperatures.

The electronic spectra and magnetic properties (Table 1) of the dimetallic NiNi and CuNi complexes suggest that the metal bis-pyridazinecarboxamide complexes act as bidentate NN-donors, via the 1-pyridazine nitrogens, to the nickel β-diketonate entities, thereby producing *cis*-N_2O_4 coordination to the Ni(hfacac)$_2$ entities, as illustrated in **I**.

The parent M(bpdpn)·2H_2O complexes are deeply coloured and their electronic spectra contain intense absorption commencing at *c.* 15 000 cm^{-1}, and extending through the higher frequency region, but there is no significant absorption below *c.* 15 000 cm^{-1}. In the dimetallic NiNi and CuNi complexes the absorption from the parent M(bpdpn) complexes is present unchanged. However, in these dimetallic complexes there is, in addition, a band at 10 500 cm^{-1}; this band is attributed to the $\nu_1(^3T_{2g} \leftarrow {}^3A_{2g})$ transition of the six-coordinate Ni^{II} β-diketonate entities, and is in the region for NiN_2O_4 species [6]. It is shifted from the 9100 cm^{-1} position in the parent Ni(hfacac)$_2$·3H_2O complex (involving NiO_6 coordination), and this is therefore good evidence for NN-coordination by the M(bpdpn) entities to the Ni(hfacac)$_2$ entity. The region for the higher frequency bands of the Ni^{II} β-diketonate entities is totally obscured by the intense absorption, from the M(bpdpn) entities, mentioned earlier.

The magnetic properties (Table 1) of the CuNi complex are consistent with the presence of high-spin Cu^{II} and Ni^{II}. The room temperature μ_{eff} value of 3.41 BM may be compared with the calculated value of 3.32 BM for a high-spin Cu^{II}Ni^{II} combination in which the constituent metals have the spin-only μ_{eff} values of 1.73 and 2.83 BM respectively. Measurements to liquid nitrogen temperature reveal a large decrease in μ_{eff} and yield a Curie–Weiss θ value of −81 K. This indicates the presence of strong

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antiferromagnetic interaction. This is good evidence for NN-coordination by Cu(bpdpn), as illustrated in **I**, leading to pyridazine-bridging, which commonly produces strong antiferromagnetism [1, 2]. The magnetism of the NiNi complex is consistent with a diamagnetic Ni(bpdpn) entity and a paramagnetic $Ni(hfacac)_2$ species.

X-ray structural studies in this system are underway, and the results will be communicated in due course, together with the results of studies of the interaction of M(bpdpn) complexes with other metallic entities.

References

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