Inorganica Chimica Acta
LETTER

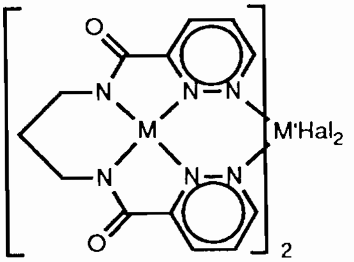
Novel trinuclear pyridazine-bridged metal complexes obtained by using bis-pyridazinecarboxamide metal complexes as ligands

Godfrey C. Chiumia, Md. Abed Ali Miah and David J. Phillips*
School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, NSW 2033 (Australia)

(Received October 10, 1991)

Pyridazine-bridged metal complexes have been extensively studied. Nearly all these investigations have involved the use of binucleating ligands [1, 2]. Established structures involve either polymeric or binuclear arrangements.

We have developed a new approach in which we use metal complexes of quadridentate bis-pyridazinecarboxamides as ligands [3]. We now report that coordination of these metal complexes to metal halides yields the first examples of trinuclear complexes involving pyridazine bridging, as illustrated in I.



I, $[M(bpdpn)]_2M'Hal_2$ (involving N,N-coordination by M(bpdpn) to $M'Hal_2$).

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 trimetallic products obtained by coordinating these M(bpdpn) complexes to metal chlorides.

The deprotonated ligand $bpdpn^{2-}$ appears to act as a distorted square-planar N_4-donor in the parent M(bpdpn) complexes. This is shown by an X-ray structure analysis of $[Cu(bpdpn)H_2O]\cdot H_2O$ which has square-pyramidal N_4O-coordination with an apically coordinated water molecule [4]. Furthermore, the Ni^{II} complex $Ni(bpdpn)\cdot 2H_2O$ is diamagnetic, in keeping with planar N_4-coordination. Also, Stephens and Vagg, 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 [5, 6].

TABLE 1. Magnetic data for parent M(bpdpn) complexes and the resulting trimetallic $\{M(bpdpn)\}_2M'Cl_2$ complexes

Compound[a]	μ_{eff} (BM)[b]		θ (K)[c]
	304 K	89 K	
$Cu(bpdpn)\cdot 2H_2O$[d]	1.95	1.87	−13
$Ni(bpdpn)\cdot 2H_2O$[d]	diamagnetic		
$\{Cu(bpdpn)\}_2CuCl_2$[b]	1.55	1.10	[e]
$\{Cu(bpdpn)\}_2NiCl_2$	3.62[f]	2.48	−210[g]
$\{Ni(bpdpn)\}_2NiCl_2$	3.24	3.08	−10

[a] Satisfactory elemental analyses were obtained for all compounds. [b] The μ_{eff} values in parentheses for $\{Cu(bpdpn)\}_2CuCl_2$ are calculated per mole of Cu^{II}. The remaining data are all calculated per mole of complex. [c] Curie–Weiss law taken as $\chi^{-1}=C(T-\theta)$. [d] Data from ref. 3. [e] Non-linear over the temperature range. [f] Measured at 299 K. [g] Deviated from linearity at lower temperatures.

The magnetic properties (Table 1) of the Cu_3 and Cu_2Ni complexes indicate trinuclear structures, of the type illustrated in I, in which the metal bis-pyridazinecarboxamides act as bidentate N,N-donors, via the 1-pyridazine nitrogens, to the metal chloride entities. Both these complexes are strongly antiferromagnetic. The room temperature μ_{eff} value (per Cu^{II}) of the Cu_3 complex is 1.55 BM; this is below the usual range of *c*. 1.8–2.0 BM for magnetically dilute copper(II). Furthermore the μ_{eff} decreases to 1.10 BM at 89 K. The μ_{eff} value (per mole of complex) of the Cu_2Ni complex is 3.62 BM at room temperature. This is similar to the calculated value of 3.55 BM for a high spin $Cu^{II}{}_2Ni^{II}$ combination in which the constituent metals have typical μ_{eff} values of 1.9 and 3.0 BM. The μ_{eff} value for the Cu_2Ni complex decreases markedly to 2.48 BM at 89 K, yielding a large Weiss θ constant of −210 K.

These magnetic data are good evidence for N,N-coordination by Cu(bpdpn) leading to pyridazine bridging, which commonly produces strong antiferromagnetism [1, 2]. Furthermore, the temperature variations of the magnetic data fit trimer models [7]. The agreement *R* factors ($R=[\Sigma(\chi_{obs}-\chi_{calc})^2/\Sigma(\chi_{obs})^2]^{1/2}$) are 0.014 and 0.007 for the Cu_3 and Cu_2Ni complexes, respectively [7]. In contrast, there is no significant magnetic interaction with the Ni_3 complex, whose magnetism is consistent with the presence of two diamagnetic Ni(bpdpn)

---

*Author to whom correspondence should be addressed.

entities and one paramagnetic nickel(II) chloride species.

The electronic spectra of the deeply coloured parent M(bpdpn)·$2H_2O$ complexes contain intense absorption commencing at *c*. 15 000 cm^{-1} and extending through the higher frequency region. In the trimetallic complexes, this absorption appears to be also present, largely unchanged. In the Ni_3 and Cu_2Ni complexes, structures of type I are expected to produce additional absorption at *c*. 9–10 000 cm^{-1}, associated with the ν_1 ($^3T_{2g} \leftarrow {}^3A_{2g}$) absorption for the nickel(II) chloride entities. In these complexes, there is, in fact, evidence for weak, broad, additional absorption at *c*. 9–10 000 cm^{-1}. With the Cu_3 complex, absorptions from the copper(II) chloride and Cu(bpdpn) species appear to overlap, because there is no significant absorption below *c*. 15 000 cm^{-1}.

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) entities with other metallic species.

References

1 (a) S. K. Mandal, L. K. Thompson, E. J. Gabe, J. Charland and F. L. Lee, *Inorg. Chem., 27* (1988) 855; (b) Tao Wen, L. K. Thompson, F. L. Lee and E. J. Gabe, *Inorg. Chem., 27* (1988) 4190.
2 M. Inoue and M. Kubo, *Coord. Chem. Rev., 21* (1976) 1.
3 M. A. A. Miah and D. J. Phillips, *Inorg. Chim. Acta, 165* (1989) 23.
4 D. C. Craig, M. A. A. Miah and D. J. Phillips, to be published.
5 (a) F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 57* (1982) 43; (b) *88* (1984) 7.
6 F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 90* (1984) 17.
7 E. Sinn and C. M. Harris, *Coord. Chem. Rev., 4* (1969) 391.