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Note

Ligand behaviour of a bis-pyridazinecarboxamide nickel(II) complex towards metal 1,1-dithiolates. Formation of pyridazine-bridged complexes $Ni(bpdpn)Ni(R_2dtp)_2$ ($H_2bpdpn = N,N'$-bis(3'-pyridazinecarboxamide)-1,3-propane; $R_2dtp^- =$ dialkyldithiophosphate)

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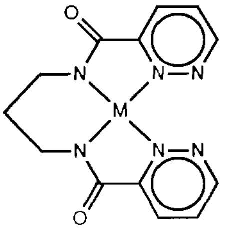
Abstract

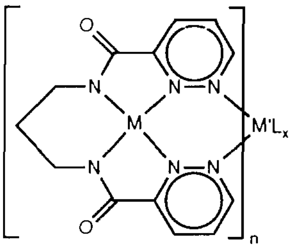
The interaction of the nickel(II) bis-pyridazinecarboxamide complex, $Ni(bpdpn)\cdot 2H_2O$ ($H_2bpdpn = N,N'$-bis(3'-pyridazinecarboxamide)-1,3-propane), with nickel(II) dithiophosphates is described. The resulting dithiophosphate adducts $Ni(bpdpn)Ni(R_2dtp)_2$ ($R_2dtp^- =$ dialkyldithiophosphate, R = Me, Et) are reported. These adducts are paramagnetic, in contrast to the diamagnetism of the parent complexes. Magnetic and spectroscopic data suggest structures involving the coordination of the diamagnetic Ni(bpdpn) entity as an N,N-donor to the $Ni(R_2dtp)_2$ species. This results in *cis*-N_2S_4 coordination to the $Ni(R_2dtp)_2$ species, which, in consequence, are now paramagnetic. The bis-pyridazinecarboxamides, $M(bpdpn)\cdot 2H_2O$ ($M = Ni^{II}$, Cu^{II}), have also been interacted with the diethyldithiocarbamates, $M(Et_2dtc)_2$ (M = Ni, Cu, Zn, Cd), and with the ethylxanthates, $M(Etxan)_2$ (M = Ni, Zn). Also $Cu(pbdpn)\cdot 2H_2O$ has been interacted with $Ni(R_2dtp)_2$. No evidence for adduct formation was observed in these cases, in solution or solid state measurements.

Introduction

There is considerable interest in metal complexes with bridging diazines such as pyridazine and phthalazine [1]. Nearly all this work involves the use of binucleating ligands [2]. We are investigating a new approach in which metal complexes (such as **I**) of bis-pyridazinecarboxamides act as ligands towards other metal systems [3]. We previously described reactions with metal β-diketonates, and with metal salts, which have produced dimeric and trimeric pyridazine-bridged complexes (see **II**) [3].

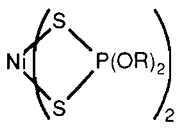


I, M(bpdpn)



II, N,N-coordination of M(bpdpn) to other metal systems

We now report the interaction of metal bis-pyridazinecarboxamides with metal dialkyldithiophosphates, $Ni(R_2dtp)_2$ (**III**), producing pyridazine-bridged NiNi complexes.



III, $Ni(R_2dtp)_2$
IIIa, $Ni(Me_2dtp)_2$ ($R = CH_3$)
IIIb, $Ni(Et_2dtp)_2$ ($R = C_2H_5$)

Experimental

$Ni(bpdpn)Ni(Me_2dtp)_2$

A mixture of $Ni(bpdpn)\cdot 2H_2O$ [3a] (0.20 g, 0.53 mmol) and $Ni(Me_2dtp)_2$ (**IIIa**) [4] (0.20 g, 0.53 mmol) was heated with absolute ethanol (30 ml) until the volume of the resulting solution was reduced to half. The solution was then left for crystallisation in a refrigerator. The dark red product was filtered off, washed with ethanol and dried in a vacuum desiccator over P_2O_5. Yield 0.35 g, 94%. *Anal.* Found: C, 28.8; H, 3.6;

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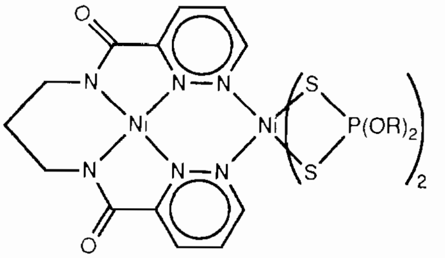
N, 11.7; Ni, 16.6. Calc. for $Ni_2C_{27}H_{24}N_6O_6P_2S_4$: C, 28.5; H, 3.4; N, 11.7; Ni, 16.4%.

Other complexes, analyses and physical measurements

$Ni(bpdpn)Ni(Et_2dtp)_2$ was prepared by a similar method to that given above for $Ni(bpdpn)Ni(Me_2dtp)_2$. *Anal.* Found: C, 32.9; H, 4.4; N, 10.7; Ni, 15.2. Calc. for $Ni_2C_{21}H_{32}N_6O_6P_2S_4$: C, 32.7; H, 4.2; N, 10.9; Ni, 15.2%. Metal 1,1-dithiolates, and their adducts with diimines, were prepared by literature methods [4, 5]. Analyses and physical measurements were as previously described [6].

Results and discussion

The bis-pyridazinecarboxamide complex $Ni(bpdpn)\cdot 2H_2O$ (see **I**, M = Ni) is diamagnetic and appears to involve square planar N_4 coordination by the $bpdpn^{2-}$ ligand [3]. We find that this pyridazinecarboxamide complex reacts with diamagnetic nickel(II) dialkyldithiophosphates, $Ni(R_2dtp)_2$ (**III**), to produce paramagnetic adducts of the type $Ni(bpdpn)Ni(R_2dtp)_2$ (R = Me, Et). The magnetic moments of these complexes are *c.* 3.2 BM per mole of adduct and are largely temperature-invariant (see Table 1). This is consistent with the Ni(bpdpn) entity remaining diamagnetic, as in the parent $Ni(bpdpn)\cdot 2H_2O$ complex, but the nickel(II) dialkyldithiophosphate species becoming paramagnetic. It is proposed that in the adducts the Ni(bpdpn) entity coordinates as an N,N-donor to the nickel(II) dialkyldithiophosphate species, as indicated in **IV**. The change from planar S_4 coordination to six-coordinate N_2S_4 coordination would account for the paramagnetism of the nickel(II) dialkyldithiophosphate species.



IV, proposed structure of $Ni(bpdpn)Ni(R_2dtp)_2$ (involving N,N-coordination of Ni(bpdpn) to $Ni(R_2dtp)_2$)

Similar paramagnetic NiN_2S_4 species are produced by coordination from diimines such as 2,2′-bipyridine to nickel(II) dialkyldithiophosphates [4]. The resulting diimine adducts, $Ni(R_2dtp)_2$(diimine), have absorption bands at *c.* 9000 and *c.* 15 000 cm^{-1}, attributed to the $^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transitions of six-coordinate nickel(II) (see Table 2) [4]. In the pyridazinecarboxamide adducts, $Ni(bpdpn)Ni(R_2dtp)_2$, similar absorptions occur at *c.* 9500 and *c.* 15 000 cm^{-1} (Table 2). The similarity of these absorptions to those in the diimine adducts, $Ni(R_2dtp)_2$(diimine), is good evidence for the formation of N_2S_4 coordination in the pyridazinecarboxamide adducts, $Ni(bpdpn)Ni(R_2dtp)_2$, i.e. the spectra support the structure **IV**.

The spectra of the $Ni(bpdpn)Ni(R_2dtp)_2$ adducts contain strong additional absorption commencing at *c.* 20 000 cm^{-1}, and extending over the higher frequency region. This is probably due, in part, to the Ni(bpdpn) species, since the parent $Ni(bpdpn)\cdot 2H_2O$ complex has similar absorption.

Other studies on metal 1,1-dithiolates

We have carried out considerable work on interactions involving other metal 1,1-dithiolates. The bis-pyridazine-

TABLE 1. Magnetic data

Compound	μ_{eff} (BM)[a,b]		θ (K)[b,c]
	304 K	89 K	
$Ni(bpdpn)Ni(Me_2dtp)_2$	3.20	3.05	−13
$Ni(bpdpn)Ni(Et_2dtp)_2$	3.20	3.10	−7

[a]Calculated per mole of complex [b]Magnetic measurements were made at 304 and 89 K and five intermediate temperatures. [c]Corresponds to θ in $\chi'_M = C(T-\theta)^{-1}$

TABLE 2. Diffuse reflectance spectra

Compound	Absorption maxima[a] ($cm^{-1} \times 10^{-3}$)	Colour
$Ni(bpdpn)\cdot 2H_2O$	*c* 11.0vw, vb, *c.* 20.0sh[b]	orange
$Ni(bpdpn)Ni(Me_2dtp)_2$	9.6, 15.0sh; *c* 20.0sh[b]	dark red
$Ni(bpdpn)Ni(Et_2dtp)_2$	9.5; 15.0sh; *c.* 20.0sh[b]	red
$Ni(Me_2dtp)_2(bipy)$[c]	9.0, 15.1; *c* 22.0sh[b]	green
$Ni(Et_2dtp)_2(bipy)$[c]	9.0, 15.1; *c* 22.0sh[b]	green
$Ni(Et_2dtp)_2(phen)$[d]	9.2, 15.1, *c.* 22.0sh[b]	green

[a]vw, very weak, vb, very broad, sh, shoulder [b]Strong absorption commences here and extends over the higher frequency region [c]bipy = 2,2′-bipyridine [d]phen = 1,10-phenanthroline.

carboxamide complexes M(bpdpn)·$2H_2O$ (M = Ni, Cu) have been interacted with the diethyldithiocarbamates $M(Et_2dtc)_2$ (M = Ni, Cu, Zn, Cd) and with the ethylxanthates $M(Etxan)_2$ (M = Ni, Zn). Also Cu(bpdpn)·$2H_2O$ has been interacted with $Ni(R_2dtp)_2$. The solvents ethanol, acetone and chloroform were used. No evidence for adduct formation was obtained. The X-ray powder patterns of products from these investigations generally corresponded to one or both starting materials. The electronic spectra of solutions containing the reactants in Ni/Ni systems also showed no evidence for adduct formation. In contrast, with the adduct systems $Ni(bpdpn)Ni(R_2dtp)_2$ and $Ni(R_2dtp)_2$(diimine), discussed above, solution studies clearly showed electronic spectral absorptions, at *c.* 9500 and *c.* 15 000 cm^{-1}, indicative of NiN_2S_4 adduct formation.

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