Inorganica Chimica Acta, *201* (1992) 191–196

Ligand behaviour by a bis-pyridazinecarboxamide nickel(II) complex towards nickel(II) β-diketonates. X-ray crystal structure of $[Ni(bpdpn)Ni(hfacac)_2]\cdot CCl_4$ ($H_2bpdpn = N,N'$-bis(3'-pyridazinecarboxamide)-1,3-propane; Hhfacac = hexafluoroacetylacetone)

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(Received March 10, 1992; revised June 2, 1992)

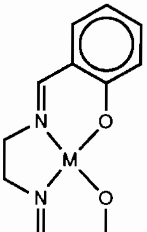
Abstract

The X-ray structure determination is reported for the complex $[Ni(bpdpn)Ni(hfacac)_2]\cdot CCl_4$ ($H_2bpdpn = N,N'$-bis(3'-pyridazinecarboxamide)-1,3-propane, Hhfacac = hexafluoroacetylacetone. The complex is monoclinic, *P2/c*, $a = 22.147(12)$, $b = 10.611(2)$, $c = 32.061(18)$ Å, $\beta = 105.50(3)°$. The deprotonated bis-pyridazinecarboxamide complex Ni(bpdpn) acts as an N,N donor, via the 1-pyridazine nitrogens, to the $Ni(hfacac)_2$ species, resulting in *cis*-N_2O_4 coordination to the β-diketonate species. The magnetic properties of the complex ($\mu_{eff} = 3.22$ BM (304 K), 3.19 BM (89 K)) are consistent with the Ni(bpdpn) entity being diamagnetic, as in the parent complex, and the $Ni(hfacac)_2$ species being paramagnetic. Magnetic and electronic spectral properties indicate that analogous complexes involving the β-diketonate ligands trifluoroacetylacetonate and benzoylacetonate have structures similar to that of $[Ni(bpdpn)Ni(hfacac)_2]\cdot CCl_4$.

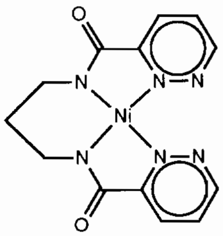
Introduction

There is considerable interest in using metal complexes as ligands in order to produce ligand-bridged complexes [1–4]. A well-known system involves Schiff base complexes such as M(salen) (**I**). Adducts of the type $M(salen)MCl_2\cdot x(H_2O)$, $\{M(salen)\}_2M(ClO_4)_2\cdot x(H_2O)$ and $M(salen)M(hfacac)_2$ (Hhfacac = hexafluoroacetylacetone) have been obtained. The M(salen) and analogous complexes act as O,O-ligands thereby producing oxygen-bridged di- and trinuclear complexes which are often antiferromagnetic [1–4].

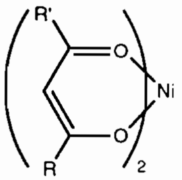
As part of an investigation of 3-substituted pyridazine ligands [5] we have developed a new system in which metal bis-pyridazinecarboxamides such as Ni(bpdpn) (**II**) act as ligands towards metal β-diketonates [6]. We report the X-ray crystal structure of $[Ni(bpdpn)Ni(hfacac)_2]\cdot CCl_4$ ($H_2bpdpn = N,N'$-bis(3'-pyridazinecarboxamide)-1,3-propane; $Ni(hfacac)_2$ = **IIIa**) and the isolation of similar complexes involving the β-diketonates **IIIb** and **IIIc**. Part of this work was reported in a preliminary communication [6]. Pyridazine- and phthalazine-bridged metal complexes are of current interest but previous work has used either the unsubstituted ligands or, much more extensively, a range of disubstituted binucleating ligands [7, 8].



I, M(salen)



II, Ni(bpdpn)



IIIa, $Ni(hfacac)_2$ ($R = R' = CF_3$)
IIIb, $Ni(tfacac)_2$ ($R = CF_3$, $R' = CH_3$)
IIIc, $Ni(bac)_2$ ($R = CH_3$, $R' = Ph$)

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0020-1693/92/$5.00

Experimental

Preparations

H_2bpdpn

1,3-Propanediamine (0.25 g, 3.3 mmol) was added dropwise to a boiling solution of 3-ethylpyridazine-carboxylate [9] (1.0 g, 6.6 mmol) in absolute ethanol (20 ml). The mixture was heated until the volume was reduced to half. Thc product which formed overnight was filtered off, washed with absolute ethanol, and dried in a vacuum desiccator. Yield 0.7 g, 75%; m.p. 208 °C. *Anal.* Found: C, 54.5; H, 5.0; N, 29.2. Calc. for $C_{13}H_{14}N_6O_2$: C, 54.5; H, 4.9; N, 29.4%.

$Ni(bpdpn)\cdot 2H_2O$

A hot solution of nickel(II) acetate tetrahydrate (0.87 g, 0.49 mmol) in water (30 ml) was added to a boiling solution of the ligand H_2bpdpn (1.0 g, 0.49 mmol) in ethanol (70 ml). Triethylamine (0.8 g) in ethanol (10 ml) was added dropwise to the boiling mixture. Heating was continued until the volume was reduced to half. Orange needle-like crystals formed after 2 days. These were washed with water and ethanol, and air-dried. Yield 0.95 g, 72%.

$[Ni(bpdpn)Ni(hfacac)_2]\cdot CCl_4$

A hot solution of $Ni(hfacac)_2\cdot 3H_2O$ [10] (0.70 g, 1.3 mmol) in chloroform (50 ml) was added to a hot solution of $Ni(bpdpn)\cdot 2H_2O$ (0.50 g, 1.3 mmol) in chloroform (80 ml). The mixture was heated until the volume was reduced to half. An equal volume of carbon tetrachloride was added and the mixture was heated for 15 min. Red–brown crystals were collected after 7 days and air-dried. Yield 1.15 g, 90%.

Other complexes

Other Ni–Ni complexes were prepared by methods similar to that for $[Ni(bpdpn)Ni(hfacac)_2]\cdot CCl_4$, using $Ni(tfacac)_2\cdot 3H_2O$ (**IIIb**) and $Ni(bac)_2\cdot H_2O$ (**IIIc**). The complex $[Ni(hfacac)_2(bipy)]$ (bipy = 2,2′-bipyridine) was prepared by the method of Veidis *et al.* [11].

Analyses and physical measurements

These were as previously described [12]. Analytical data for metal complexes are given in Table 1.

X-ray crystal structure determination of $[Ni(bpdpn)Ni(hfacac)_2]\cdot CCl_4$

Intensities were collected at 22 °C for 6759 reflections from a crystal of dimensions 0.17×0.16×0.10 mm with an Enraf-Nonius 4 diffractometer in $\theta/2\theta$ scan mode, using graphite monochromatised molybdenum radiation (λ = 0.7107 Å) and $2\theta_{max}$ of 40°. Data were corrected for absorption using a 12×12×12 Gaussian grid (μ = 13.7 cm^{-1}, A = 0.803–0.877). A total of 3645 reflections with $I>3\sigma(I)$ was deemed to be observed. Crystal data are given in Table 2. The crystal used was carefully selected and was typical of the better crystals.

TABLE 1. Analytical data for metal complexes

Compound	Analyses (%) (Calculated and found)				Colour
	C	H	N	M	
$Ni(bpdpn)\cdot 2H_2O$	41.2	4.2	22.2	15.5	orange
	40.9	4.0	22.0	15.4	
$[Ni(bpdpn)Ni(hfacac)_2]\cdot CCl_4$	29.7	1.5	8.7	12.1	red–brown
	29.8	1.5	8.7	12.3	
$Ni(bpdpn)Ni(tfacac)_2\cdot 2H_2O$	37.1	3.3	11.3	15.8	red–brown
	37.2	3.0	11.3	15.6	
$Ni(bpdpn)Ni(bac)_2\cdot 1.5H_2O$	52.8	4.4	11.2	15.6	red–brown
	52.6	3.9	11.3	15.7	
$[Ni(hfacac)_2(bipy)]$	38.2	1.6	4.5		grey–green
	38.5	1.5	4.8		

TABLE 2. Crystal data for $[Ni(bpdpn)Ni(hfacac)_2]\cdot CCl_4$

Formula	$Ni_2C_{24}H_{14}Cl_4F_{12}N_6O_6$
a (Å)	22.147(12)
b (Å)	10.611(2)
c (Å)	32.061(18)
β (°)	105.50(3)
Z	8
D_c (g cm^{-3})	1.71
Space group	$P2/c$
μMo (cm^{-1})	13.69
V (Å^3)	7260(6)

The structure was determined by phase determination methods (MULTAN 80) [13] and refined using the comprehensive constrained least-squares refinement program RAELS 89 [14]. Restraints to the solution were thought necessary after initial unconstrained refinement gave poor agreement between pseudoequivalent bond lengths and thermal parameters. The structure consists of layers perpendicular to c^* of pseudo $P2/a$ symmetry in which only the two-fold axes are true symmetry elements. A true c-glide operation relates these layers in the true spacegroup $P2/c$. Within a layer, molecules designated A and B are related by a pseudo a-glide $\frac{1}{2}+x$, $1.30-y$, z and a pseudoinversion operator $\frac{1}{2}-x$, $1.30-y$, $\frac{1}{2}-z$ corresponding to the true symmetry operation $-x$, y, $\frac{1}{2}-z$ acting on the pseudo a-glide operation. To understand the effects of the pseudosymmetry it is easiest to use the pseudoinversion operator at $r=\frac{1}{4}$, 0.65, $\frac{1}{4}$.

Ignoring anomalous dispersion effects the structure factor can be written in the form $F(\mathbf{h})=A(\mathbf{h})A'(\mathbf{h})-B(\mathbf{h})B'(\mathbf{h})$ where $A(\mathbf{h})+iB(\mathbf{h})$ is the structure factor of the $P2/a$ layer with respect to an origin at the local pseudoinversion centre and $[A'(\mathbf{h})+iB'(\mathbf{h})]/2=$

exp($2\pi i\mathbf{h}\cdot\mathbf{r}$) is the Fourier transform of the location of the pseudoinversion centre. Consequently should the local pseudoinversion centre impose exact equivalence between molecules A and B in the *P*2/*a* layer then $B(\mathbf{h})$ will be exactly zero. For $B(\mathbf{h})$ to be significant for a particular reflection **h** then $B'(\mathbf{h})$ must be large implying that $A'(\mathbf{h})$ will be small. This implies the refinability of differences across the pseudoinversion centre is very much associated with the weak reflection data. The quality of this data was insufficient to prevent refinement problems and consequently constraint techniques were used. The following model was used.

Anisotropic thermal parameters of atoms pseudosymmetrically related by the *a*-glide were refined under a constraint that imposed the *a*-glide symmetry exactly. H atoms were constrained to occupy sensible geometric positions and were given the same thermal parameters as the atoms to which they were attached. The pseudoequivalent CCl_4 molecules were disordered and were refined as reorientable, relocatable groups with a common refinable tetrahedral geometry (C–Cl 1.692(3)Å). Thermal motion was refined using independent TL parametrisations (6 translation and 6 libration parameters per molecule) common to each disordered pair of CCl_4 with the libration centered on the central C atom of the major component. Occupancies were refined to values of 0.696(6):0.304 for sites A,A′ and 0.812(4):0.188 for sites B,B′.

The C*–CF_3 fragments had disordered F atoms. Two orientations of the F atoms related to each other by a 180° rotation and of occupancies α and $1-\alpha$ were refined for each group. The thermal parameters of each group were refined using TL thermal parameters whose libration was centered on the C* atom. Occupancies of 0.74(1):0.26, 0.97(1):0.03, 0.91(1):0.09, 0.73(1):0.27, were obtained for sites A,A′ for groups centred on C* = C(31), C(32), C(41), C(42) and 0.70(1):0.30, 0.93(1):0.07, 0.78(1):0.21, 0.81(1):0.19 for the corresponding sites B,B′. To allow for variation between C*–CF_3 fragments, the C atoms were independently refined but slack constraints (restraints) were used to impose 3*m* symmetry on each C*–CF_3 fragment by making selected differences in distances and angles approach zero. These extra conditions on the least-squares refinement are included as extra observations.

Slack constraints were also imposed to make differences in bond lengths approach zero for bonds related by the pseudo *a*-glide and to maintain the imposed geometry of the 28 H atoms in the asymmetric unit. In this way 685 variables were used for the blocked least-squares matrix but they represented only 480 independent parameters for the 170 atom sites. Final values of $R(F)=0.067$, $R(F^2)=0.103$, $R_w(F)=0.085$ were obtained for the 3645 reflections with $I>3\sigma(I)$ used in the refinement. Atoms at lesser occupancy sites have been labelled with a prime for the CCl_4 molecule and the F atoms in Table 3.

Results and discussion

The complex Ni(bpdpn)·$2H_2O$ is diamagnetic [6] and is expected to involve planar N_4 ligand coordination, as in **II**, similar to that for analogous bis-pyridinecarboxamide complexes [15, 16]. Reaction of Ni(bpdpn)·$2H_2O$ with the β-diketonate Ni(hfacac)$_2$·$3H_2O$ (**IIIa**) in $CHCl_3/CCl_4$ solution yields [Ni(bpdpn)Ni(hfacac)$_2$]·CCl_4. In the X-ray structure of [Ni(bpdpn)Ni(hfacac)$_2$]·CCl_4 there are two independent but almost identical species (A and B), of which only A is discussed in detail. A perspective diagram [17] is given in Fig. 1. Atomic parameters are listed in Table 3, and selected bond lengths and bond angles are given in Table 4. Each Ni(bpdpn) entity (involving Ni(1)) coordinates as a chelating NN-donor, via the 1-pyridazine nitrogens, to a Ni(hfacac)$_2$ moiety (involving Ni(2)). This produces a pyridazine-bridged dinuclear complex with *cis*-N_2O_4 coordination to Ni(2), and with a lattice CCl_4 molecule.

The N_4-coordination to Ni(1) is planar with a slight tetrahedral distortion (deviations ±0.008 Å) from the least-squares plane. This plane (N(1), N(2), N(11), N(21)) involving Ni(1) makes a dihedral angle of 57.0° with the N_2O_2 plane (N(12), N(22), O(31), O(41)) involving Ni(2). As a consequence, the Ni–N_4–Ni bridging arrangement is quite non-planar. The bridging pyridazine nitrogens N(11), N(12), N(21) and N(22) form a good plane (deviations ± 0.009 Å) with which Ni(1) is fairly co-planar (deviation 0.327 Å), but Ni(2) deviates by 1.084 Å from this N_4-plane. This contrasts with the approximately planar M–N_4–M and M–N_2–M arrangements frequently found in bridged complexes with disubstituted pyridazines and phthalazines functioning as binucleating ligands [7, 8].

[Ni(bpdpn)Ni(hfacac)$_2$]·CCl_4 has a μ_{eff} value of 3.22 BM at 304 K almost invariant with temperature (Table 5). This is in keeping with the nickel(II) atoms, in the bis-pyridazinecarboxamide and diketonate entities, being diamagnetic and paramagnetic, respectively.

Reflectance spectra are given in Table 6. The spectrum of [Ni(bpdpn)Ni(hfacac)$_2$]·CCl_4 contains absorption commencing at *c.* 15 000 cm^{-1}, reaching maximum absorbance at *c.* 20 000 cm^{-1}, and extending to higher frequencies. This is typical of diamagnetic nickel(II) [18] and is assigned to the nickel(II) bis-pyridazinecarboxamide entity. Similar absorption is found with the parent complex Ni(bpdpn)·$2H_2O$.

[Ni(bpdpn)Ni(hfacac)$_2$]·CCl_4 contains, in addition, a pronounced absorption band at 10 500 cm^{-1}. The only absorption in this region for the parent

TABLE 3. Atomic parameters for $[Ni(bpdpn)Ni(hfacac)_2] \cdot CCl_4$[a,b]

	x/a	y/b	z/c
Ni(1)A	0.4499(1)	0.5968(1)	0.1770(1)
Ni(2)A	0.5490(1)	0.8324(1)	0.1489(1)
O(1)A	0.2921(4)	0.7146(8)	0.1963(3)
O(2)A	0.5239(4)	0.2601(7)	0.2037(3)
O(31)A	0.5190(4)	0.9863(6)	0.1110(2)
O(32)A	0.6136(3)	0.9433(6)	0.1887(2)
O(41)A	0.6126(3)	0.8039(8)	0.1149(2)
O(42)A	0.4875(3)	0.7223(7)	0.1069(2)
N(12)A	0.4827(3)	0.8657(7)	0.1825(3)
N(11)A	0.4420(4)	0.7754(6)	0.1844(3)
N(1)A	0.3640(3)	0.5962(8)	0.1735(3)
N(22)A	0.5801(3)	0.6766(6)	0.1874(3)
N(21)A	0.5394(3)	0.5833(7)	0.1882(3)
N(2)A	0.4535(4)	0.4236(6)	0.1779(3)
C(14)A	0.4722(5)	0.9814(8)	0.1938(4)
C(13)A	0.4235(6)	1.0152(10)	0.2101(4)
C(12)A	0.3796(5)	0.9266(10)	0.2098(4)
C(11)A	0.3894(4)	0.8043(9)	0.1950(3)
C(O1)A	0.3440(5)	0.6982(10)	0.1887(4)
C(1)A	0.3188(5)	0.4936(11)	0.1599(5)
C(24)A	0.6405(4)	0.6526(10)	0.2020(4)
C(23)A	0.6652(5)	0.5380(10)	0.2174(4)
C(22)A	0.6239(5)	0.4406(11)	0.2169(4)
C(21)A	0.5599(4)	0.4686(9)	0.2007(4)
C(O2)A	0.5089(5)	0.3741(9)	0.1952(4)
C(2)A	0.4016(5)	0.3304(11)	0.1663(5)
C(3)A	0.3438(6)	0.3912(12)	0.1379(5)
C(31)A	0.5519(5)	1.0832(10)	0.1109(4)
C(33)A	0.6089(5)	1.1122(12)	0.1393(4)
C(32)A	0.6338(4)	1.0432(7)	0.1752(3)
C(34)A	0.5225(4)	1.1741(9)	0.0726(4)
F(31)A	0.4653(4)	1.2004(15)	0.0724(5)
F(32)A	0.5228(10)	1.1205(13)	0.0364(3)
F(33)A	0.5547(6)	1.2772(10)	0.0768(5)
C(35)A	0.6935(4)	1.0899(5)	0.2080(3)
F(34)A	0.7338(3)	0.9983(6)	0.2217(2)
F(35)A	0.6813(3)	1.1399(6)	0.2423(2)
F(36)A	0.7227(3)	1.1766(7)	0.1914(2)
C(41)A	0.5986(5)	0.7542(10)	0.0777(3)
C(43)A	0.5446(5)	0.6981(14)	0.0546(4)
C(42)A	0.4952(5)	0.6820(10)	0.0717(3)
C(44)A	0.6520(5)	0.7739(7)	0.0563(2)
F(41)A	0.7060(3)	0.7313(13)	0.0803(3)
F(42)A	0.6605(6)	0.8939(7)	0.0490(4)
F(43)A	0.6417(4)	0.7164(10)	0.0186(2)
C(45)A	0.4393(5)	0.6085(8)	0.0467(3)
F(44)A	0.4393(5)	0.5886(12)	0.0060(2)
F(45)A	0.3860(3)	0.6661(13)	0.0453(5)
F(46)A	0.4355(7)	0.4960(10)	0.0635(3)
Ni(1)B	0.9431(1)	0.7104(1)	0.1797(1)
Ni(2)B	1.0306(1)	0.4713(1)	0.1398(1)
O(1)B	0.7979(4)	0.5933(8)	0.2158(3)
O(2)B	1.0206(4)	1.0446(7)	0.2012(3)
O(31)B	0.9963(4)	0.3135(6)	0.1053(2)
O(32)B	1.1011(3)	0.3644(6)	0.1754(2)
O(41)B	1.0867(3)	0.5056(8)	0.1009(2)
O(42)B	0.9626(3)	0.5790(7)	0.1022(2)
N(12)B	0.9737(4)	0.4392(7)	0.1807(3)
N(11)B	0.9364(4)	0.5313(6)	0.1872(3)
N(1)B	0.8608(3)	0.7120(8)	0.1850(3)
N(22)B	1.0674(4)	0.6284(6)	0.1758(3)
N(21)B	1.0303(3)	0.7229(7)	0.1819(3)
N(2)B	0.9469(4)	0.8834(6)	0.1809(3)
C(14)B	0.9670(5)	0.3241(8)	0.1945(4)
C(13)B	0.9230(6)	0.2928(10)	0.2158(4)
C(12)B	0.8816(5)	0.3816(10)	0.2205(4)
C(11)B	0.8904(4)	0.5038(9)	0.2053(3)
C(O1)B	0.8460(5)	0.6102(10)	0.2034(4)
C(1)B	0.8152(5)	0.8150(11)	0.1765(5)
C(24)B	1.1279(4)	0.6518(10)	0.1845(4)
C(23)B	1.1565(5)	0.7645(10)	0.1988(4)
C(22)B	1.1173(5)	0.8627(10)	0.2024(4)
C(21)B	1.0528(4)	0.8369(9)	0.1930(4)
C(O2)B	1.0034(5)	0.9323(9)	0.1922(4)
C(2)B	0.8953(5)	0.9761(10)	0.1753(5)
C(3)B	0.8349(6)	0.9163(12)	0.1514(5)
C(31)B	1.0296(5)	0.2189(10)	0.1027(3)
C(33)B	1.0902(5)	0.1952(12)	0.1265(4)
C(32)B	1.1206(5)	0.2656(8)	0.1608(3)
C(34)B	0.9937(4)	0.1172(9)	0.0703(3)
F(31)B	0.9814(9)	0.1593(11)	0.0308(2)
F(32)B	0.9409(5)	0.0877(13)	0.0785(5)
F(33)B	1.0270(5)	0.0150(9)	0.0728(5)
C(35)B	1.1837(5)	0.2219(6)	0.1905(3)
F(34)B	1.2233(3)	0.3154(7)	0.2003(3)
F(35)B	1.2091(4)	0.1349(8)	0.1718(3)
F(36)B	1.1771(3)	0.1749(7)	0.2267(2)
C(41)B	1.0711(5)	0.5705(10)	0.0669(3)
C(43)B	1.0164(5)	0.6351(14)	0.0512(4)
C(42)B	0.9662(5)	0.6337(10)	0.0681(3)
C(44)B	1.1264(5)	0.5909(8)	0.0472(3)
F(41)B	1.1650(5)	0.4954(14)	0.0550(4)
F(42)B	1.1578(7)	0.6916(14)	0.0633(6)
F(43)B	1.1070(4)	0.6049(16)	0.0052(3)
C(45)B	0.9095(5)	0.7126(8)	0.0488(3)
F(44)B	0.9086(5)	0.8171(8)	0.0707(4)
F(45)B	0.8568(3)	0.6530(9)	0.0473(4)
F(46)B	0.9064(5)	0.7469(12)	0.0088(3)
C(Cl)A	0.2781(3)	0.9873(6)	0.0677(2)
Cl(1)A	0.2563(4)	0.9095(10)	0.1074(3)
Cl(2)A	0.3571(3)	1.0003(11)	0.0811(3)
Cl(3)A	0.2457(5)	1.1328(7)	0.0617(3)
Cl(4)A	0.2534(6)	0.9066(9)	0.0207(3)
C(Cl)B	0.7663(2)	0.3400(4)	0.0802(1)
Cl(1)B	0.7487(3)	0.4260(6)	0.1198(2)
Cl(2)B	0.8449(2)	0.3216(6)	0.0914(2)
Cl(3)B	0.7317(3)	0.1969(5)	0.0773(2)
Cl(4)B	0.7399(3)	0.4154(6)	0.0322(2)
C(Cl)A′	0.2748(7)	0.9690(15)	0.0655(4)
Cl(1)A′	0.2220(9)	0.9863(24)	0.0168(6)
Cl(2)A′	0.2987(11)	0.8171(16)	0.0720(8)
Cl(3)A′	0.2414(12)	1.0093(25)	0.1052(7)
Cl(4)A′	0.3373(8)	1.0633(21)	0.0679(7)
C(Cl)B′	0.7643(7)	0.3541(15)	0.0951(4)
Cl(1)B′	0.7360(12)	0.4171(25)	0.1346(6)
Cl(2)B′	0.7923(12)	0.2079(18)	0.1100(8)
Cl(3)B′	0.7061(8)	0.3453(23)	0.0487(6)
Cl(4)B′	0.8226(9)	0.4461(22)	0.0872(7)
F(31)A′	0.5632(6)	1.1984(17)	0.0513(5)
F(32)A′	0.5058(8)	1.2782(9)	0.0873(4)
F(33)A′	0.4739(7)	1.1215(11)	0.0469(5)
F(34)A′	0.6914(3)	1.2115(4)	0.2153(2)

(*continued*)

TABLE 3. (*continued*)

	x/a	y/b	z/c
F(35)A′	0.7439(3)	1.0700(8)	0.1947(2)
F(36)A′	0.7025(3)	1.0333(5)	0.2456(2)
F(41)A′	0.6328(4)	0.8298(10)	0.0184(3)
F(42)A′	0.6783(4)	0.6672(8)	0.0496(3)
F(43)A′	0.6971(4)	0.8446(12)	0.0800(3)
F(44)A′	0.4012(6)	0.5785(16)	0.0705(3)
F(45)A′	0.4545(4)	0.5011(8)	0.0312(4)
F(46)A′	0.4051(5)	0.6711(9)	0.0130(4)
F(31)B′	0.9848(8)	0.0153(8)	0.0906(3)
F(32)B′	1.0253(6)	0.0870(15)	0.0429(4)
F(33)B′	0.9392(5)	0.1596(10)	0.0486(5)
F(34)B′	1.1830(4)	0.1014(5)	0.1989(3)
F(35)B′	1.1973(4)	0.2819(7)	0.2275(2)
F(36)B′	1.2292(3)	0.2419(10)	0.1725(3)
F(41)B′	1.1215(7)	0.6992(10)	0.0273(6)
F(42)B′	1.1288(6)	0.5030(11)	0.0191(4)
F(43)B′	1.1795(4)	0.5897(20)	0.0771(3)
F(44)B′	0.8726(4)	0.6608(10)	0.0138(3)
F(45)B′	0.9244(4)	0.8250(8)	0.0372(4)
F(46)B′	0.8748(4)	0.7311(11)	0.0758(3)

[a]Standard deviations are given in parentheses. [b]Atoms at lesser occupancy sites have been labelled with a prime for the CCl_4 molecule and the fluorine atoms in Table 3.

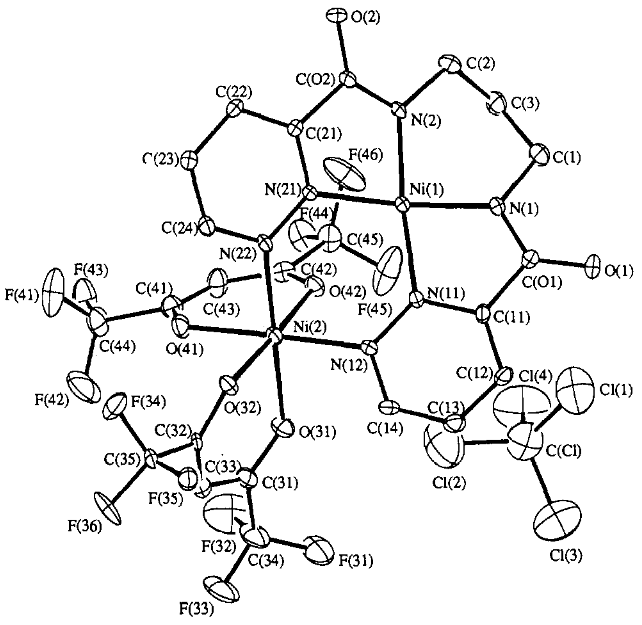

Fig. 1. A perspective drawing of the complex [Ni(bpdpn)-Ni(hfacac)$_2$]·CCl_4.

Ni(bpdpn)·$2H_2O$ complex is some very weak, very broad absorption at *c*. 11 000 cm^{-1}. The pronounced absorption band at 10 500 cm^{-1} in [Ni(bpdpn)Ni-(hfacac)$_2$]·CCl_4 is, therefore, attributed to the ν_1 ($^3T_{2g} \leftarrow {}^3A_{2g}$) transition of the paramagnetic Ni(hfacac)$_2$ species. This band is in the region for an NiN_2O_4 chromophore [18] and this is in keeping with NN-coordination by the Ni(bpdpn) entity to the Ni(hfacac)$_2$ species, as found in the X-ray structure. For example, [Ni(hfacac)$_2$(bipy)] (NiN_2O_4 chromophore, bipy = 2,2′-bipyridine) has ν_1 at 10 200 cm^{-1} whereas Ni(hfacac)$_2$·$3H_2O$ (NiO_6 chromophore) has ν_1 at 9100 cm^{-1} (see Table 6). Dinickel complexes involving other β-diketonates are also reported (Tables 5 and 6). Their

TABLE 4. Selected interatomic distances (Å) and angles (°) for [Ni(bpdpn)Ni(hfacac)$_2$]·CCl_4[a]

	A	B
Ni(1)–N(1)	1.874(6)	1.876(6)
Ni(1)–N(11)	1.924(6)	1.926(6)
Ni(1)–N(2)	1.839(6)	1.837(6)
Ni(1)–N(21)	1.924(6)	1.919(6)
Ni(2)–O(31)	2.038(6)	2.039(6)
Ni(2)–O(32)	2.020(5)	2.018(5)
Ni(2)–O(41)	2.020(6)	2.015(6)
Ni(2)–O(42)	2.014(5)	2.014(5)
Ni(2)–N(12)	2.069(6)	2.074(6)
Ni(2)–N(22)	2.068(6)	2.067(6)
	A	B
N(1)–Ni(1)–N(11)	83.5(3)	83.6(3)
N(1)–Ni(1)–N(2)	92.1(4)	91.6(4)
N(1)–Ni(1)–N(21)	171.5(4)	171.6(4)
N(11)–Ni(1)–N(2)	170.8(4)	170.9(4)
N(11)–Ni(1)–N(21)	100.0(3)	100.0(3)
N(2)–Ni(1)–N(21)	83.4(3)	83.7(3)
O(31)–Ni(2)–O(32)	88.5(3)	88.0(3)
O(31)–Ni(2)–O(41)	87.8(3)	90.8(3)
O(31)–Ni(2)–O(42)	90.6(3)	91.8(3)
O(31)–Ni(2)–N(12)	90.6(3)	90.4(3)
O(31)–Ni(2)–N(22)	179.7(3)	178.4(3)
O(32)–Ni(2)–O(41)	87.2(3)	86.6(3)
O(32)–Ni(2)–O(42)	176.9(3)	177.3(3)
O(32)–Ni(2)–N(12)	93.0(3)	93.4(3)
O(32)–Ni(2)–N(22)	91.3(3)	90.5(3)
O(41)–Ni(2)–O(42)	89.8(3)	90.7(3)
O(41)–Ni(2)–N(12)	178.3(3)	178.8(3)
O(41)–Ni(2)–N(22)	91.9(3)	89.1(3)
O(42)–Ni(2)–N(12)	90.0(3)	89.3(3)
O(42)–Ni(2)–N(22)	89.6(3)	89.8(3)
N(12)–Ni(2)–N(22)	89.7(3)	89.8(3)

[a]Standard deviations are given in parentheses.

TABLE 5. Magnetic data

Compound	μ_{eff} (BM)[a] 304 K	89 K	θ (K)[b]
[Ni(bpdpn)Ni(hfacac)$_2$]·CCl_4	3.22	3.19	−3
Ni(bpdpn)Ni(tfacac)$_2$·$2H_2O$	3.20	3.15	−4
Ni(bpdpn)Ni(bac)$_2$·$1.5H_2O$	3.22	3.17	−5

[a]Calculated per mole of dinuclear complex. [b]Corresponds to θ in $\chi'_M = C(T-\theta)^{-1}$.

TABLE 6. Diffuse reflectance spectra

Compound	Absorption maxima[a] ($cm^{-1} \times 10^{-3}$)
Ni(bpdpn)·$2H_2O$	*c.* 11.0 vw, vb; *c.* 20.0[b] sh
Ni(hfacac)$_2$·$3H_2O$	9.1; 15.6; *c.* 23.0[b] sh
[Ni(bpdpn)Ni(hfacac)$_2$]·CCl_4	10.5; *c.* 20.0[b] sh
Ni(bpdpn)Ni(tfacac)$_2$·$2H_2O$	10.5; *c.* 20.0[b] sh
Ni(bpdpn)Ni(bac)$_2$·$1.5H_2O$	10.5; *c.* 20.0[b] sh
[Ni(hfacac)$_2$(bipy)]	10.2; 17.0; c. 22.0[b] sh

[a]vw, very weak; vb, very broad; sh, shoulder. [b]Strong absorption extends from here over the higher frequency region.

physical properties and assigned structures are similar to those of [Ni(bpdpn)Ni(hfacac)$_2$]·CCl_4. Further structural studies of the interaction of metal bis-pyridazine-carboxamides with other metal systems are under way, and will be reported in due course.

Supplementary material

All atom and thermal parameters, and all interatomic angles and torsional angles, are available from the authors on request.

Acknowledgements

The award of a maintenance grant (to M.A.A.M.) from the Australian International Development Assistance Bureau is gratefully acknowledged.

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