C22	0.382 (3)	0.652 (4)	0.391 (3)	0.27 (2)
C23	0.608 (3)	0.336 (2)	0.593 (3)	0.163 (12)
C24	0.5243 (17)	0.4139 (12)	0.5576 (11)	0.081 (6)
S1	0.32227 (10)	0.48444 (9)	0.11744 (8)	0.0399 (3)
F1	0.3195 (4)	0.3775 (3)	−0.0037 (3)	0.0906 (17)
F2	0.3594 (4)	0.5691 (4)	0.0110 (3)	0.1014 (17)
F3	0.4919 (3)	0.4434 (4)	0.1082 (3)	0.114 (2)
O2	0.3415 (3)	0.3673 (3)	0.1569 (2)	0.0579 (11)
O3	0.1994 (3)	0.5149 (3)	0.0504 (2)	0.0455 (10)
O4	0.3945 (3)	0.5796 (3)	0.1782 (2)	0.0656 (11)
C20	0.3771 (5)	0.4669 (6)	0.0550 (5)	0.073 (3)

Table 2. *Selected geometric parameters* (Å, °)

Pd—O	2.028 (3)	C16—C18	1.493 (6)
Pd—N1	2.014 (4)	C18—C19	1.492 (8)
Pd—N2	2.100 (3)	O5—C21	1.358 (17)
Pd—C11	2.019 (3)	O5—C24	1.336 (16)
O—C18	1.235 (5)	S1—O2	1.440 (3)
N1—C1	1.345 (6)	S1—O3	1.431 (4)
N1—C5	1.366 (5)	S1—O4	1.429 (3)
N2—C6	1.348 (5)	S1—C20	1.820 (9)
N2—C10	1.347 (6)	F1—C20	1.333 (8)
C5—C6	1.474 (5)	F2—C20	1.340 (8)
C11—C16	1.564 (5)	F3—C20	1.313 (10)
O—Pd—N1	175.41 (14)	C6—N2—C10	118.8 (3)
O—Pd—N2	96.94 (13)	N1—C1—C2	122.7 (3)
O—Pd—C11	84.19 (13)	N1—C5—C4	121.0 (4)
N1—Pd—N2	79.60 (14)	N1—C5—C6	115.5 (3)
N1—Pd—C11	99.45 (15)	N2—C6—C5	115.1 (3)
N2—Pd—C11	176.33 (18)	N2—C6—C7	121.6 (4)
Pd—O—C18	115.7 (3)	N2—C10—C9	122.0 (4)
Pd—N1—C1	125.5 (3)	Pd—C11—C12	111.9 (3)
Pd—N1—C5	115.9 (3)	Pd—C11—C16	108.4 (3)
C1—N1—C5	118.5 (4)	O—C18—C16	120.2 (4)
Pd—N2—C6	113.9 (3)	O—C18—C19	118.9 (4)
Pd—N2—C10	127.2 (3)		

X-ray data were collected for a fragment cut from a large crystal using a scan width $\Delta\omega$ of $(0.99 + 0.35\tan\theta)^\circ$. The transmission range (0.76–1.00) of the absorption correction is comparable with the intensity variations observed in three 360° ψ scans for close-to-axial reflections (0.80–1.00). The diethyl ether molecule was refined with a disorder model. H atoms were refined riding on their carrier atoms with three common isotropic atomic displacement parameters.

Data collection: locally modified CAD-4 (Version 5) software. Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *DIRDIF*92 (Beurskens *et al.*, 1992). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON* (Spek, 1990).

This work was supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1183). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1537–1540

trans-Bis(3-hydroxy-2-phenyl-4*H*-1-benzopyran-4-onato)bis(pyridine)nickel(II)

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(*Received* 20 *September* 1994; *accepted* 17 *January* 1995)

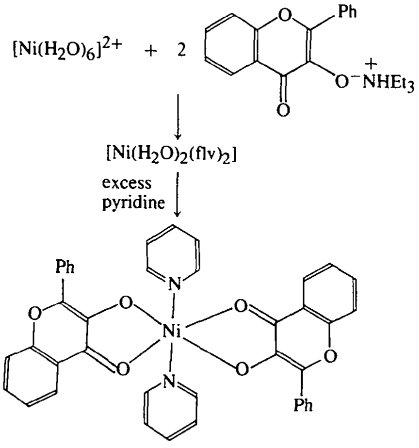
Abstract

3-Hydroxyflavone and bipyridyl ligands coordinate to the Ni^{II} centre in an octahedral arrangement, giving the title complex, $[Ni(C_{15}H_9O_3)_2(C_5H_5N)_2]$. Since the Ni atom lies on a centre of symmetry, all the *trans* O—Ni—O and N—Ni—N bond angles are 180°; those of O—Ni—N are close to 90°. The Ni—O(carbonyl), Ni—O(hydroxy) and Ni—N distances are 2.067 (2), 2.023 (2) and 2.180 (2) Å, respectively. All the C—C bond distances are normal with values between 1.366 (3) and 1.406 (4) Å, except those which are close to the coordinated C—O bonds: C(1)—C(2), C(2)—C(3) and C(9)—C(10) are 1.457 (4), 1.445 (3) and 1.462 (4) Å, respectively. All rings are almost planar, except those involving coordinated O atoms. The dihedral angles between the flavonato planes and the pyridyl ligands are

quite large with values of *ca* 84°. The angles between the planes in the hydroxyflavone ligand are less than 10°.

Comment

The structures of coordinated ligands containing N and O atoms bonded to nickel provide important information on metalloenzyme systems. Complexes of Ni^{II} with ligands such as aminocyclohexanecarboxylate (Haendler, 1993), hexafluoroacetonate (Polam & Porter, 1992), salicyaldehydate (Stewart, Lingafelter & Breazeale, 1961), acetylacetonate and tetramethylethylenediamine (Yamada, Hori & Fukuda, 1993), benzenedicarboxylate and 2,2′-bipyridyl (Poleti, Karanovic & Prelesnik, 1990), glycinate and 2,2′-bipyridyl (Žák, Głowiak, Kameníček & Březina, 1990), carboxylates and silane carboxylate (Morooka *et al.*, 1992) have been reported. Although the structure of flavonol chelated to copper has been reported (Speier, Fiilop & Parkanyi, 1990), little information is available on the analogues of nickel. An ethanolic solution of the triethylammonium salt of the 3-hydroxyflavonato anion reacts with $NiCl_2.6H_2O$ to form $[Ni(H_2O)_2(flv)_2]$, which, on heating with excess pyridine under reflux, produces *trans*-$[Ni(py)_2(flv)_2]$, (I) (flv = 3-hydroxyflavonato and py = pyridine), as shown in the scheme below.



(I)

The crystal structure of (I) is shown in Fig. 1. The Ni atom is octahedrally surrounded by two *trans* py and two chelating flv ligands. All the *trans* O—Ni—O and N—Ni—N bond angles are exactly 180° because the Ni atom lies on a centre of symmetry. The O—Ni—N angles are close to 90° (Table 2). However, the angle subtended by both chelating O atoms at the nickel centre is found to be 81.0 (1)°. This value is consistent with the values reported for other five-membered chelates, such as chelates of Ni^{II} with 1-aminocyclohexanecarboxylato and Cu^I with 3-hydroxyflavonato (Speier *et al.*, 1990) which have values of 81.3 (2) and 79.2 (3)°, respectively. The O(2)—Ni—O(1*a*) inter-flavonato angle [99.0 (1)°] is greater than 90°.

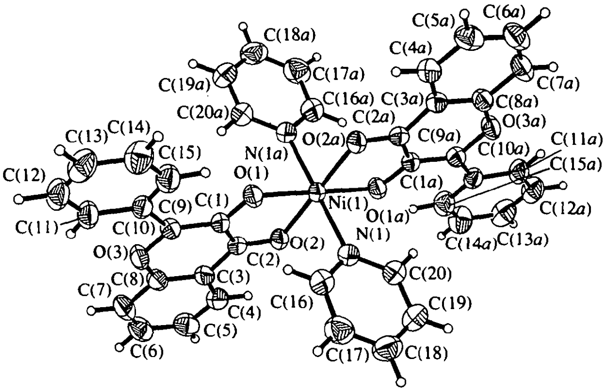


Fig. 1. A view of the title molecule showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

The Ni—N, Ni—O(1) and Ni—O(2) bond distances are 2.180 (2), 2.023 (2) and 2.067 (2) Å, respectively. The axial Ni—N bond lengths are longer, on average, by 0.136 (4) Å than the Ni—O bond in the equatorial position. The environment of the Ni atom is more ideally octahedral than found in bis(hexafluoroacetylacetonato)bis(triphenylphosphine oxide)nickel(II) (Polam & Porter, 1992). The Ni—O(1) and C(2)—O(2) distances are significantly shorter than Ni—O(2) and C(1)—O(1). This observation signifies that the C(2)—O(2) bond is more ketonic (C=O) in nature while the C(1)—O(1) bond has more single-bond character.

The C—C bond distances in the hydroxyflavonato moiety further emphasize the canonic nature of the pyrone ring. The C(9)—C(1) and C(3)—C(8) bonds of 1.385 (3) and 1.389 (3) Å, respectively, are shorter than C(1)—C(2) which is 1.457 (4) Å in length. The C—C distances in the pyridyl ligands are normal with a mean of 1.376 (6) Å. The N—C distances are slightly shorter than the C—C bond.

The least-square planes are almost coplanar except for plane 1 containing Ni(1)—O(1)—C(1)—C(2)—O(2), which has a mean deviation of 0.027 (16)°. The dihedral angles between the flavonato and pyridyl ligands are quite large with values of *ca* 84°. The flavonato rings are not exactly planar, having dihedral angles ranging between 0.54 (2) and 7.25 (9)°.

Experimental

The green rhombohedral product of the reaction described in the *Comment* was recrystallized from hot acetonitrile. The crystal density D_m was measured by flotation in CCl_4/hexane.

Crystal data

$[Ni(C_{15}H_9O_3)_2(C_5H_5N)_2]$
$M_r = 691.4$

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å

Triclinic
$P\bar{1}$
$a = 8.128\ (3)$ Å
$b = 10.174\ (3)$ Å
$c = 11.191\ (4)$ Å
$\alpha = 115.19\ (3)^\circ$
$\beta = 97.27\ (3)^\circ$
$\gamma = 105.55\ (3)^\circ$
$V = 775.4\ (5)$ Å^3
$Z = 1$
$D_x = 1.480$ Mg m^{-3}
$D_m = 1.470$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 5$–15°
$\mu = 0.681$ mm^{-1}
$T = 298$ K
Rhombohedron
0.48 × 0.44 × 0.16 mm
Green

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: ψ scan
$T_{\min} = 0.571$, $T_{\max} = 0.954$
3748 measured reflections
3504 independent reflections
2976 observed reflections [$F > 4\sigma(F)$]

$R_{\rm int} = 0.0090$
$\theta_{\max} = 27.5^\circ$
$h = 0 \rightarrow 10$
$k = -13 \rightarrow 12$
$l = -14 \rightarrow 14$
2 standard reflections monitored every 200 reflections
intensity decay: insignificant

Refinement

Refinement on F
$R = 0.0389$
$wR = 0.0477$
$S = 1.24$
2976 reflections
226 parameters
H atoms fixed; $U_{\rm iso}$ refined
$w = 1/[\sigma^2(F) + 0.0008F^2]$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.68$ e Å^{-3}
$\Delta\rho_{\min} = -0.58$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELXTL/PC* (Sheldrick, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ni(1)	0	0	0	0.033 (1)
N(1)	−0.2421 (2)	−0.0623 (2)	0.0600 (2)	0.039 (1)
O(1)	−0.0319 (2)	−0.2271 (2)	−0.1091 (1)	0.037 (1)
O(2)	−0.1511 (2)	−0.0490 (2)	−0.1870 (1)	0.038 (1)
O(3)	−0.2322 (2)	−0.4893 (2)	−0.4744 (1)	0.040 (1)
C(1)	−0.1141 (3)	−0.2859 (2)	−0.2386 (2)	0.033 (1)
C(2)	−0.1805 (3)	−0.1858 (2)	−0.2771 (2)	0.033 (1)
C(3)	−0.2791 (3)	−0.2494 (2)	−0.4183 (2)	0.035 (1)
C(4)	−0.3530 (3)	−0.1645 (3)	−0.4656 (2)	0.042 (1)
C(5)	−0.4437 (3)	−0.2305 (3)	−0.6007 (2)	0.052 (1)
C(6)	−0.4632 (3)	−0.3829 (3)	−0.6929 (2)	0.054 (1)
C(7)	−0.3926 (3)	−0.4686 (3)	−0.6502 (2)	0.047 (1)
C(8)	−0.3000 (3)	−0.4004 (2)	−0.5117 (2)	0.038 (1)
C(9)	−0.1412 (3)	−0.4342 (2)	−0.3403 (2)	0.035 (1)
C(10)	−0.0857 (3)	−0.5526 (2)	−0.3244 (2)	0.037 (1)
C(11)	−0.1140 (3)	−0.6948 (2)	−0.4401 (2)	0.047 (1)
C(12)	−0.0658 (3)	−0.8080 (3)	−0.4257 (3)	0.055 (1)
C(13)	0.0082 (4)	−0.7863 (3)	−0.2986 (3)	0.059 (1)
C(14)	0.0377 (4)	−0.6473 (3)	−0.1834 (3)	0.059 (1)
C(15)	−0.0078 (3)	−0.5310 (3)	−0.1960 (2)	0.049 (1)
C(16)	−0.3462 (3)	−0.2102 (3)	0.0080 (2)	0.047 (1)
C(17)	−0.5108 (3)	−0.2547 (3)	0.0305 (2)	0.059 (1)
C(18)	−0.5709 (3)	−0.1423 (3)	0.1114 (3)	0.058 (1)
C(19)	−0.4625 (3)	0.0112 (3)	0.1679 (3)	0.058 (1)
C(20)	−0.3025 (3)	0.0458 (3)	0.1398 (2)	0.048 (1)

Table 2. *Selected geometric parameters* (Å, °)

Ni(1)—N(1)	2.180 (2)	Ni(1)—O(1)	2.023 (2)
Ni(1)—O(2)	2.067 (2)	Ni(1)—N(1$^{\rm i}$)	2.180 (2)
Ni(1)—O(1$^{\rm i}$)	2.023 (2)	Ni(1)—O(2$^{\rm i}$)	2.067 (2)
N(1)—C(16)	1.329 (3)	N(1)—C(20)	1.346 (3)
O(1)—C(1)	1.307 (2)	O(2)—C(2)	1.255 (2)
O(3)—C(8)	1.351 (3)	O(3)—C(9)	1.377 (2)
C(1)—C(2)	1.457 (4)	C(1)—C(9)	1.385 (3)
C(2)—C(3)	1.445 (3)	C(3)—C(4)	1.406 (4)
C(3)—C(8)	1.389 (3)	C(4)—C(5)	1.366 (3)
C(5)—C(6)	1.399 (3)	C(6)—C(7)	1.368 (4)
C(7)—C(8)	1.400 (3)	C(9)—C(10)	1.462 (4)
C(10)—C(11)	1.405 (3)	C(10)—C(15)	1.393 (3)
C(11)—C(12)	1.374 (4)	C(12)—C(13)	1.371 (4)
C(13)—C(14)	1.381 (3)	C(14)—C(15)	1.385 (5)
C(16)—C(17)	1.384 (4)	C(17)—C(18)	1.378 (4)
C(18)—C(19)	1.376 (4)	C(19)—C(20)	1.366 (4)
N(1)—Ni(1)—O(1)	90.8 (1)	N(1)—Ni(1)—O(2)	89.8 (1)
O(1)—Ni(1)—O(2)	81.0 (1)	N(1)—Ni(1)—N(1$^{\rm i}$)	180.0 (1)
O(1)—Ni(1)—N(1$^{\rm i}$)	89.2 (1)	O(2)—Ni(1)—N(1$^{\rm i}$)	90.2 (1)
N(1)—Ni(1)—O(1$^{\rm i}$)	89.2 (1)	O(1)—Ni(1)—O(1$^{\rm i}$)	180.0 (1)
O(2)—Ni(1)—O(1$^{\rm i}$)	99.0 (1)	N(1$^{\rm i}$)—Ni(1)—O(1$^{\rm i}$)	90.8 (1)
N(1)—Ni(1)—O(2$^{\rm i}$)	90.2 (1)	O(1)—Ni(1)—O(2$^{\rm i}$)	99.0 (1)
O(2)—Ni(1)—O(2$^{\rm i}$)	180.0 (1)	N(1$^{\rm i}$)—Ni(1)—O(2$^{\rm i}$)	89.8 (1)
O(1$^{\rm i}$)—Ni(1)—O(2$^{\rm i}$)	81.0 (1)	Ni(1)—N(1)—C(16)	121.0 (2)
Ni(1)—N(1)—C(20)	122.0 (1)	C(16)—N(1)—C(20)	116.7 (2)
Ni(1)—O(1)—C(1)	111.8 (1)	Ni(1)—O(2)—C(2)	111.1 (2)
C(8)—O(3)—C(9)	121.0 (1)	O(1)—C(1)—C(2)	116.7 (2)
O(1)—C(1)—C(9)	124.9 (2)	C(2)—C(1)—C(9)	118.4 (2)
O(2)—C(2)—C(1)	119.1 (2)	O(2)—C(2)—C(3)	122.7 (2)
C(1)—C(2)—C(3)	118.2 (2)	C(2)—C(3)—C(4)	122.8 (2)
C(2)—C(3)—C(8)	118.6 (2)	C(4)—C(3)—C(8)	118.6 (2)
C(3)—C(4)—C(5)	120.2 (2)	C(4)—C(5)—C(6)	120.3 (3)
C(5)—C(6)—C(7)	121.0 (2)	C(6)—C(7)—C(8)	118.5 (2)
O(3)—C(8)—C(3)	122.1 (2)	O(3)—C(8)—C(7)	116.4 (2)
C(3)—C(8)—C(7)	121.5 (2)	O(3)—C(9)—C(1)	121.6 (2)
O(3)—C(9)—C(10)	111.0 (1)	C(1)—C(9)—C(10)	127.4 (2)
C(9)—C(10)—C(11)	120.2 (2)	C(9)—C(10)—C(15)	122.0 (2)
C(11)—C(10)—C(15)	117.8 (2)	C(10)—C(11)—C(12)	120.6 (2)
C(11)—C(12)—C(13)	121.1 (2)	C(12)—C(13)—C(14)	119.4 (3)
C(13)—C(14)—C(15)	120.4 (3)	C(10)—C(15)—C(14)	120.8 (2)
N(1)—C(16)—C(17)	123.0 (2)	C(16)—C(17)—C(18)	119.4 (2)
C(17)—C(18)—C(19)	118.0 (3)	C(18)—C(19)—C(20)	119.1 (3)
N(1)—C(20)—C(19)	123.8 (2)		

Symmetry code: (i) $-x, -y, -z$.

The structure was solved by the Patterson method and refined by full-matrix least-squares methods. All riding H atoms were generated geometrically with C—H = 0.96 Å and refined isotropically. *SHELXTL/PC* (Sheldrick, 1990) was used for all calculations.

The authors would like to thank the Malaysian Government and both Universiti Kebangsaan Malaysia and Universiti Sains Malaysia for research grants R & D Nos. 61/89 and 123-3417-2201, respectively.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: LI1124). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1540–1543

A Mixed-Ligand Zinc(II) Complex Containing a Bridging Dithiolate Ligand

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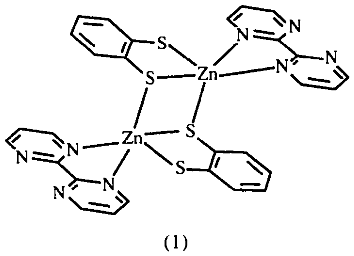
(*Received* 3 *January* 1995; *accepted* 10 *February* 1995)

Abstract

The mixed-ligand Zn^{II} complex bis(μ-1,2-benzenedithiolato)-1κS,1:2$\kappa^2 S'$;2κS,1:2$\kappa^2 S'$-bis[(2,2'-bipyrimidine-$\kappa^2 N^1$,$N^{1'}$)zinc], [$Zn_2(C_6H_4S_2)_2(C_8H_6N_4)_2$], containing benzenedithiolate (bdt) and 2,2'-bipyrimidine (bpyrm) has been synthesized and found to have the dinuclear formulation [Zn(bdt)(bpyrm)]$_2$. The dinuclear complex has crystallographically imposed $\bar{1}$ symmetry with severely distorted square-pyramidal coordination about the metal atoms. One S atom of the bdt ligand bridges the Zn atoms in an asymmetric fashion [Zn—S(1) 2.433 (3), Zn'—S(1) 2.475 (3) Å] while the second S atom is bound in a terminal mode at a shorter distance [Zn—S(2) 2.303 (3) Å]. The formation of a bdt-bridged rather than a bpyrm-bridged species may be favored by a significant π-stacking interaction between the phenyl ring of the bdt ligand and one ring of the bpyrm ligand.

Comment

Highly colored and luminescent complexes result when Zn^{II} is coordinated to an *N*,*N*-heterocycle and either two monothiolate or one dithiolate ligand. This visible transition has been assigned as a ligand-to-ligand charge transfer (LLCT) transition (Koester, 1975; Crosby, Highland & Truesdell, 1985; Truesdell & Crosby, 1985) and is similar to those found in complexes employing either mono- or dithiolate ligands. In some mixed-ligand Zn^{II} complexes containing two substituted monothiolate ligands, two orbitally distinct emissions are observed which exhibit different temperature-dependent behavior (Muresan & Muresan, 1979; Fernandez & Kisch, 1984; Highland & Crosby, 1985; Highland, Brummer & Crosby, 1986; Galin, Razskazovsky & Mel'nikov, 1993; Kutal, 1990). One of these emissions has been assigned as an intraligand $^3\pi$–π^* transition localized on the *N*,*N*-heterocyclic ligand and the other to a primarily LLCT transition. For the more motionally restricted dithiolate complexes known to date, in only one case has more than a single emission been observed (Gronlund, Burt & Wacholtz, 1995). Recent studies have indicated that when the benzenedithiolate (bdt) ligand is used with the planar *N*,*N*-heterocycle 1,10-phenanthroline, unusual multinuclear complexes are obtained (Halvorsen, Wacholtz & Crosby, 1995). Other planar *N*,*N*-heterocycles, such as 2,2'-biquinoline or 4,7-dimethyl-2,3,8,9-dibenzo-11,12-dihydro-1,10-phenanthroline, produce only mononuclear complexes when reacted under varying conditions with bdt as the co-ligand (Wacholtz, 1993). However, with the planar *N*,*N*-heterocycle 2,2'-bipyrimidine (bpyrm), which has two different sites capable of bidentate chelation, a dinuclear species similar to that reported for phenanthroline was observed. We now report that successive additions of 1,2-benzenedithiol and 2,2'-bipyrimidine to zinc(II) acetate in hot ethanol forms dinuclear [Zn(bdt)(bpyrm)]$_2$, (1), in which bdt rather than bpyrm functions as the bridging ligand.



(1)

Complex (1) consists of discrete dinuclear molecules having crystallographically imposed $\bar{1}$ symmetry. There are no unusual intermolecular contacts. A perspective view of (1) is given in Fig. 1, from which it is evident that one of the S atoms of the bdt ligand [S(1)] functions as a bridge between the two Zn atoms. The central Zn_2S_2 moiety contains two distinctly different Zn—S distances, with the bond within the chelate ring [S(1)—Zn' 2.475 (3) Å] being longer than that to the other Zn atom [S(1)—Zn 2.433 (3) Å]. This feature has been noted in other dinuclear Zn^{II} complexes containing bridging dithiolate ligands (Halvorsen, Wacholtz & Crosby, 1995; Tuntulani, Reibenspies, Farmer & Darensbourg, 1992). Both of these Zn—S distances are significantly longer than that involving the non-bridging S atom [Zn—S(2) 2.303 (3) Å], as expected. The coordination about the Zn atom can be described as intermediate between square pyramidal and trigonal bipyramidal but