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

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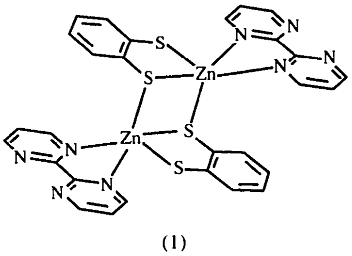
Abstract

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

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is somewhat closer to the former. Thus, although the N(1)—Zn—S(2) angle of 145.4 (2)° is closer to the ideal value for two adjacent equatorial substituents in a trigonal bipyramid than to that for two *trans*-basal substituents in a square pyramid, the Zn–S(1)–S(2)–N(1) unit is far from having the planarity appropriate for consideration as the equatorial component in a trigonal bipyramid. We also note that in the related complex [Zn(BME-DACO)]$_2$ [where BME-DACO is the dianion of *N*,*N*′-bis(mercaptoethyl)-1,5-diazacyclooctane (Tuntulani, Reibenspies, Farmer & Darensbourg, 1992)], the Zn atom is described as having an approximately square-pyramidal coordination geometry, although it is in fact slightly more distorted from the ideal than is the case with (1).

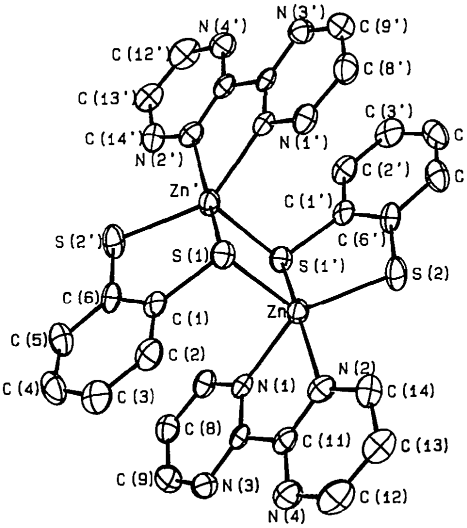

Fig. 1. Perspective view of [Zn(bdt)(bpyrm)]$_2$ showing 50% probability displacement ellipsoids. The primed atoms are related to the unprimed atoms by the center of symmetry. H atoms are omitted for clarity.

A significant feature of (1) is the substantial coplanarity of the phenyl ring of the bdt ligand with one of the bpyrm rings. Both rings are planar with their weighted least-squares planes inclined at a dihedral angle of 14.1 (4)°. This results in a mean interplanar spacing of 3.54 Å and suggests the presence of a significant π-stacking interaction. This interaction would be absent were the bpyrm to function as a bridging ligand and may contribute to the observed mode of association of the two [Zn(bdt)(bpyrm)] moieties. This argument must be viewed with caution since relatively minor changes in the nature of the ligand(s) can lead to quite different results. For example, only mononuclear Pt^{II} (Matsubayashi, Yamaguchi & Tanaka, 1988) and Ni^{III} (Dyachenko *et al.*, 1993) complexes have been obtained with combinations of similar dithiolate and *N*,*N*-heterocyclic ligands. With the exception of [^{n}Bu$_4$P]$_2$[Ni(tdas)$_2$]$_2$ [tdas = 1,2,5-thiadiazole-3,4-dithiolate (Schenk, Hawkins, Wilkes, Underhill, Kobayashi & Kobayashi, 1993)] and an unpublished report of a trinuclear nickel complex (Kovacs, 1994), only Zn^{II} complexes of such mixed-ligand systems seem to form multinuclear species. Since only bis-monothiolate and dithiosquarate complexes, which have been shown to be mononuclear, are luminescent, it appears that the luminescent properties of these complexes are closely associated with the chemical environment within which the whole molecule finds itself and that certain dithiolate ligands tend to form multinuclear systems which do not exhibit emissive behavior. Support for this hypothesis has been obtained from recent results on mixed-ligand Zn^{II} complexes of monothiolate ligands where very subtle changes in ligand structure lead to significant changes in emissive properties (Jordan, Wacholtz & Crosby, 1991). Structural studies of heteroleptic Zn^{II} systems using a wider variety of dithiolate and *N*,*N*-heterocyclic ligands are ongoing.

Experimental

1,2-Benzenedithiol (143.0 mg, 1 mmol) in 25 ml of hot ethanol was added dropwise to a solution of zinc acetate dihydrate (219.5 mg, 1 mmol) in 50 ml of hot ethanol. The white precipitate was dissolved by addition of a small quantity of hot dmf, the solution was brought to reflux and 2,2′-bipyrimidine (79.1 mg, 0.5 mmol) dissolved in 50 ml of hot ethanol was added slowly with stirring. The solution was cooled, allowed to stand for 24 h and the resulting red powder was filtered off and recrystallized from dmf and ethanol. Yield: 75–80%. Analysis: calculated for $C_{28}H_{20}N_8S_4Zn_2$ C 46.22, H 2.77, N 15.40%; found C 46.2, H 3.0, N 15.3%. The crystal sample was obtained by the slow evaporation of a solution of the complex in dmf.

Crystal data

$[Zn_2(C_6H_4S_2)_2(C_8H_6N_4)_2]$
$M_r = 727.5$
Monoclinic
$P2_1/n$
$a = 9.349\,(8)$ Å
$b = 13.439\,(8)$ Å
$c = 11.703\,(8)$ Å
$\beta = 108.16\,(3)°$
$V = 1397\,(4)$ Å^3
$Z = 2$
$D_x = 1.729$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.28–14.97°$
$\mu = 2.083$ mm^{-1}
$T = 293$ K
Plate
0.35 × 0.32 × 0.21 mm
Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.5120$, $T_{\max} = 0.9983$
2722 measured reflections
2532 independent reflections

1598 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.03$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 18$
$l = -16 \rightarrow 16$
2 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F
$R = 0.071$
$wR = 0.083$
$S = 2.42$
1598 reflections
190 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 2.43$ e Å^{-3}
$\Delta\rho_{\min} = -1.80$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Zn	0.1186 (1)	0.04566 (8)	−0.06074 (9)	2.17 (2)
S(1)	−0.0034 (3)	0.1214 (2)	0.0734 (2)	2.24 (5)
S(2)	−0.0081 (3)	0.0695 (2)	−0.2618 (2)	2.99 (6)
N(1)	0.3275 (8)	0.0005 (6)	0.0688 (6)	2.1 (2)
N(2)	0.2840 (8)	0.1668 (6)	−0.0585 (7)	2.4 (2)
N(3)	0.5720 (8)	0.0555 (6)	0.1850 (7)	2.5 (2)
N(4)	0.5289 (8)	0.2241 (6)	0.0489 (7)	2.9 (2)
C(1)	0.1370 (9)	0.1076 (7)	0.2165 (7)	2.0 (2)
C(2)	0.248 (1)	0.1823 (7)	0.2502 (8)	2.7 (2)
C(3)	0.361 (1)	0.1774 (8)	0.3586 (9)	3.3 (2)
C(4)	0.367 (1)	0.0980 (8)	0.4343 (9)	3.4 (2)
C(5)	0.260 (1)	0.0241 (7)	0.4028 (8)	3.0 (2)
C(6)	0.141 (1)	0.0283 (6)	0.2926 (8)	2.2 (2)
C(7)	0.347 (1)	−0.0848 (7)	0.1346 (8)	2.5 (2)
C(8)	0.477 (1)	−0.1031 (7)	0.2253 (8)	2.8 (2)
C(9)	0.586 (1)	−0.0309 (8)	0.2466 (9)	3.2 (2)
C(10)	0.4407 (9)	0.0658 (7)	0.0995 (7)	2.0 (2)
C(11)	0.418 (1)	0.1589 (7)	0.0265 (8)	2.1 (2)
C(12)	0.502 (1)	0.3039 (8)	−0.025 (1)	3.6 (3)
C(13)	0.372 (1)	0.3171 (8)	−0.1168 (9)	3.1 (2)
C(14)	0.264 (1)	0.2461 (8)	−0.1305 (8)	2.9 (2)

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

Zn—S(1)	2.433 (3)	Zn—S(2)	2.303 (3)
Zn—S(1^i)	2.475 (3)	Zn—N(1)	2.152 (8)
Zn—N(2)	2.239 (8)	S(1)—C(1)	1.786 (9)
S(2)—C(6^i)	1.767 (9)	N(1)—C(7)	1.36 (1)
N(1)—C(10)	1.34 (1)	N(2)—C(11)	1.34 (1)
N(2)—C(14)	1.34 (1)	N(3)—C(9)	1.35 (1)
N(3)—C(10)	1.33 (1)	N(4)—C(11)	1.32 (1)
N(4)—C(12)	1.35 (1)		
S(1)—Zn—S(2)	113.9 (1)	S(1)—Zn—N(1)	99.7 (2)
S(2)—Zn—N(1)	145.4 (2)	S(1)—Zn—N(2)	98.6 (2)
S(2)—Zn—N(2)	92.5 (2)	N(1)—Zn—N(2)	74.1 (3)
S(1)—Zn—S(1^i)	97.8 (1)	S(1^i)—Zn—S(2)	89.4 (1)
S(1^i)—Zn—N(1)	93.9 (2)	S(1^i)—Zn—N(2)	161.1 (2)
Zn—S(1)—C(1)	101.9 (3)	Zn—S(2)—C(6^i)	102.1 (3)
Zn—N(1)—C(7)	124.8 (6)	Zn—N(1)—C(10)	118.2 (7)
C(7)—N(1)—C(10)	116.3 (8)	Zn—N(2)—C(11)	115.8 (6)
Zn—N(2)—C(14)	127.8 (6)	C(11)—N(2)—C(14)	116.5 (8)
C(9)—N(3)—C(10)	114.0 (8)	C(11)—N(4)—C(12)	114.9 (9)

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

General procedures for crystal orientation, unit-cell determination and refinement, and data collection have been published (Mague & Lloyd, 1988). The heavy-atom positions were obtained from an E map and the remainder of the structure was developed by successive cycles of full-matrix least-squares refinement followed by the calculation of a $\Delta\rho$ map. Following refinement of all non-H atoms with anisotropic displacement parameters, many of the H atoms could be seen in a $\Delta\rho$ map. All H atoms were included as fixed contributors in calculated positions (C—H 0.95 Å), with isotropic displacement parameters 20% larger than those of the attached C atoms, and were updated periodically. The final $\Delta\rho$ map contained some features larger than the peaks attributed to H atoms and which were close to the heavy atoms. These are attributed to a combination of rather poor crystal quality (as evidenced by rather broad diffraction maxima) and an inadequacy in the empirical absorption correction used.

Data collection and cell refinement: *CAD-4 Software* (Schagen, Staver, van Meurs & Williams, 1989). Data reduction: *MolEN* (Fair, 1990). Structure solution: *SIR*88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989). Sturcture refinement: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms and least-squares-planes data have been deposited with the IUCr (Reference: BM0001). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Wacholtz, W. F. (1993). Unpublished results.

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[*N*-(3-Aminopropyl)-1,3-propanediamine]diaquasulfatonickel(II) Monohydrate, $[Ni(SO_4)(dpt)(H_2O)_2].H_2O$ [dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$]

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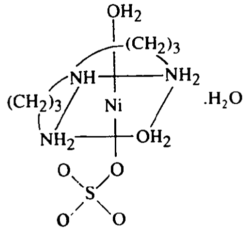
Abstract

The coordination polyhedron about the Ni^{II} atom in $[Ni(SO_4)(dpt)(H_2O)_2].H_2O$, [dpt = *N*-(3-aminopropyl)-1,3-propanediamine] is a distorted octahedron consisting of three N atoms of the dpt ligand coordinating meridionally, one O atom from the monodentate sulfate group and two aqua O atoms. The two six-membered chelate rings are in chair forms. Molecular packing is stabilized by an extensive network of hydrogen bonds involving the triamine N atoms, sulfate O atoms and water molecules.

Comment

Thermally induced solid-state phase transitions in nickel(II)–triamine complexes are documented in the literature (Mukherjee *et al.*, 1994; Koner, Pariya & Ray Chaudhuri, 1993). There has been extensive study (Pariya, Ghosh, Ghosh, Mukherjee, Mukherjee & Ray Chaudhuri, 1995; Ihara, Fukuda & Sone, 1987; Halfpenny, Levason, McAuliffe, Hill & McCullough, 1979) directed towards understanding the role of anions in the metal coordination and conformational changes of the chelate rings of the resulting metal–amine complexes. Pariya, Ghosh & Ray Chaudhuri (1995) have recently reported the synthesis of $Ni(dpt)SO_4.3H_2O$ [dpt = *N*-(3-aminopropyl)-1,3-propanediamine] with a proposed structure of $[Ni(dpt)(H_2O)_3].SO_4$ based on spectral data. An X-ray structure analysis of this complex, (I), was motivated by our continued interest in establishing the coordination geometry around the metal centre and conformation of the chelate rings. An *ORTEP*II (Johnson, 1976) view of the complex with atom-labelling and ring-numbering scheme is shown in Fig. 1.



(I)

The coordination polyhedron around the metal atom is best described as a distorted octahedron with an N_3O_3 chromophore. The three ligand N atoms and one aqua O atom (O6) define the basal plane [Ni distance 0.031 (1) Å] and the remaining two O atoms (one from the sulfate group and the other belonging to the water molecule) are in axial positions. The in-plane distortion is due to the asymmetric nature of the ligand atoms and is reflected by the deviations of the angles formed by the basal plane atoms at the metal centre [83.9 (1)–96.2 (1)°] from 90°. The Ni—N distances, in the range 2.084 (2)–2.099 (3) Å, are consistent with the corresponding values for Ni^{II}–triamine systems with octahedral metal coordination (Table 4). The observed lengthening of Ni—O1 [2.171 (2) Å] compared with Ni—O5 [2.104 (2) Å] and Ni—O6 [2.127 (2) Å] is due to steric constraints introduced by the coordinating bulky SO_4 ligand. An almost ideal chair conformation is displayed by ring *A* with C5 0.716 (4) Å above and Ni 0.655 (1) Å below the least-squares plane through the remaining endocyclic atoms, while ring *B* adopts a significantly distorted chair form with Ni 0.373 (1) Å above and C2 0.753 (4) Å below the plane defined by the other four ring atoms. The dihedral angle between the planar parts of the two chelate rings is 151.9 (2)°. The Cremer & Pople (1975) ring puckering parameters are: q_2 = 0.196 (4), q_3 = −0.513 (3), Q = 0.549 (4) Å, θ = 159.2 (3)°, φ = −20.0 (10)° for ring *A*; q_2 = 0.376 (3), q_3 = −0.407 (3), Q = 0.554 (4) Å, θ = 137.3 (3)°, φ = 21.9 (6)° for ring *B*. There are several intramolecular hydrogen bonds (Table 3) which control the overall

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