Crystal and Molecular Structure of a Thiolate-Bridged Binuclear Nickel(II) Complex, $[Ni_2\{SCH(CH_2CH_2NH_2)_2\}_2]Br_2$

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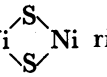
Synopsis. The crystal structure of bis[μ-(1,5-diamino-3-pentanethiolato)-*N,N'*, μ-S]-dinickel(II) bromide was determined by the single-crystal X-ray diffraction method. The complex has a thiolate-bridged binuclear structure, with a dihedral angle 145.2° between the two coodination planes.

Recently, 1,5-diamino-3-pentanol (Hdpl) was synthesized by our group,[1] and shown to form essentially planar binuclear complexes with copper(II) and nickel(II), whose skeletal structure illustrated in Fig. 1 was evidenced by X-ray crystal structure analysis for $Cu_2(dpl)_2Cl_2\cdot 3H_2O$[2] and by diamagnetism for the nickel complex.[1] On the analogy of the above examples, 1,5-diamino-3-pentanethiol (Hdpet) is expected to be a planar binucleating ligand. In fact, the nickel complexes formulated as $Ni_2(dpet)_2X_2$ (X=Br, ClO_4, NO_3, BPh_4) were all diamagnetic implying the planar binuclear structure similar to that shown in Fig. 1.[3] However, in thiolate-bridged binuclear nickel(II) complexes so far known, the two coordination planes are all bent at the S–S bond with dihedral angle of 82.3—110.2° and in our knowledge no planar  ring has ever been reported.[4-7] Thus, we have determined the crystal structure of $Ni_2(dpet)_2Br_2$ by X-ray analysis to see whether the two coordination planes assume a coplanar or bent structure.

Experimental

Reddish brown crystals of $[Ni_2(dpet)_2]Br_2$ were prepared by the method previously reported.[3] A crystal with dimensions of 0.08×0.38×0.54 mm was used for the X-ray analysis. The unit-cell parameters and intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å).

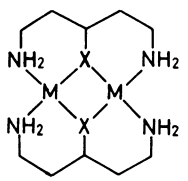


Fig. 1. The binuclear complex cation of dpl or dpet (M=Cu(II) or Ni(II); X=O or S).

Crystal Data: $Ni_2(C_5H_{13}N_2S)_2Br_2$, F.W.=543.65, monoclinic; $P2_1/m$; a=10.072(7), b=18.188(12), and c=5.162(5) Å; β=103.20(7)°; V=920.6(13) Å^3; D_m=1.92, D_c=1.96 g cm^{-3}, Z=2, μ(Mo $K\alpha$)=65.7 cm^{-1}.

The intensity data were collected by the 2θ—ω scan technique with a scan rate of 3° min^{-1}. Three standard reflections were monitored every 50 reflections, and their intensities showed a good stability. A total of 3372 reflections with $2\theta<60°$ were collected. The intensity data were corrected for the Lorentz-polarization effects and for absorption. Independent 1739 reflections with $|F_o|\geq 3\sigma(|F_o|)$ were considered as "observed" and were used for the structure analysis.

The structure was solved by the direct method. Refinement was carried out by the block-diagonal least-squares method. The weighting scheme $w=[\sigma^2_{count}+(0.015|F_o|)^2]^{-1}$ was employed. Hydrogen atoms were inserted in their calculated positions and fixed at the positions. The final discrepancy factors were $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.053$ and $R'=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}=0.052$. Final difference Fourier map was featureless. All the calculations were carried out on the HITAC M-680H computer at the Computer Center of the Institute for Molecular Science by the use of the UNICS-III, *MULTAN* 78, and ORTEP programs.[8] The final positional and thermal parameters with their estimated standard deviations are given in Table 1. The coordinates and isotropic temperature factors of the hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, and the F_o—F_c tables have been deposited as a Document No. 0000 at the Office of the Editor.

Table 1. Fractional Positional Parameters (×10^4) and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2
Br	2514(1)	−294(1)	842(1)	3.4
Ni	3080(1)	1638(1)	6191(1)	2.0
S(1)	1848(2)	2500	7413(4)	2.2
S(2)	4607(2)	2500	7007(4)	2.2
N(1)	1659(6)	889(3)	5490(9)	2.8
N(2)	4388(5)	936(3)	5329(9)	2.7
C(1)	129(9)	2500	5135(18)	2.8
C(2)	−115(7)	1806(4)	3466(13)	3.5
C(3)	185(7)	1099(4)	5028(14)	3.7
C(4)	5230(9)	2500	3938(16)	2.4
C(5)	6008(7)	1797(4)	3788(13)	3.3
C(6)	5119(7)	1131(4)	3199(12)	3.2

Results and Discussion

The crystal structure consists of discrete binuclear cations, $[Ni_2(dpet)_2]^{2+}$, and bromide ions. A perspective view of $[Ni_2(dpet)_2]^{2+}$ is shown in Fig. 2. The cation has a symmetry plane along the S(1)–S(2) bond. As has been anticipated, the complex ion has a thiolate-bridged binuclear structure and each nickel ion is in a square-planar N_2S_2 environment. The Ni–S and Ni–Ni distances are normal as Ni(II)–S(thiolate) and Ni(II)–N(amine) bonds.[4–7,9] Each NiS_2N_2 coordination unit is virtually planar, but the two planes are bent at the S(1)–S(2) bond with a dihedral angle of 145.2°, making a contrast with the binuclear

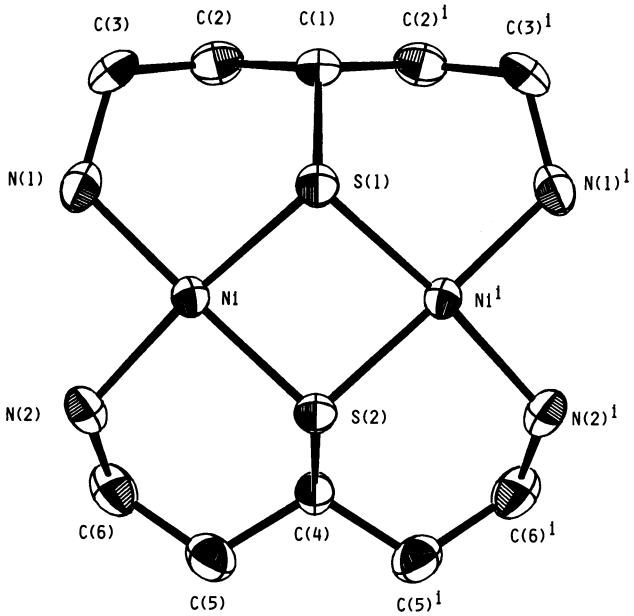


Fig. 2. A perspective view of $[Ni_2(dpet)_2]^{2+}$ ion. Selected bond lengths (l/Å) and angles (ϕ/°) are: Ni–Ni^i 3.134(2), Ni–S(1) 2.180(2), Ni–S(2) 2.169(2), Ni–N(1) 1.950(6), Ni–N(2) 1.958(6); Ni–S(1)–Ni^i 91.9(1), Ni–S(2)–Ni^i 92.5(1), S(1)–Ni–S(2) 81.36(9), S(1)–Ni–N(1) 96.6(2), S(2)–Ni–N(2) 91.8(2), N(1)–Ni–N(2) 90.3(2). Superscript (i) refers to the equivalent position (x, $1/2-y$, z).

metal complexes of dpl.[2] Structural parameters of the present complexes are listed in Table 2 together with those of other thiolate-bridged binuclear nickel(II) complexes.[4–7] As seen in Table 2, the present complex assumes the largest values in the Ni–Ni distance, Ni–S–Ni angle, and the dihedral angle of the two coordination planes, τ. This should be ascribed to the steric requirement of dpet which favors the coplanar structure as supposed from the molecular model study and the planar structure of the analogous complex, $Cu_2(dpl)_2Cl_2 \cdot 3H_2O$. It should be noted here that the dihedral angle, τ, of the present complex is between those of other thiolate-bridged complexes (82.3—110.2°) and 180°. This is understandable as a compromise of the two opposing tendencies, i.e., the steric requirements 1) of the ligand to form a planar structure (τ=180°) and 2) of the thiolate sulfur to form Ni–S bonds with a Ni–S–Ni angle smaller than 90° as observed for several complexes so far reported giving rise to a remarkable bending of the two coordination planes such as τ=82.3—110.2°.

The six-membered chelate ring, Ni–S(1)–C(1)–C(2)–C(3)–N(1), adopts a boat conformation where Ni and C(2) are −0.76 and −0.64 Å from the least-squares plane of the remaining four atoms, whereas the chelate ring, Ni–S(2)–C(4)–C(5)–C(6)–N(2), adopts a chair form where Ni and C(5) are −1.13 and 0.73 Å from the mean plane of the remaining four atoms.

The bromide ions are placed in the vicinity of the amino groups of dpet forming hydrogen bonds (Br···N(1)(x, $y+1$, $z-1$) 3.452(5), Br···N(1)(x, $y+1$, z) 3.474(6) Å).

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Table 2. Comparison of Some Distances (l/Å) and Angles (ϕ/°) in Ni_2S_2 Rings of Thiolate-Bridged Binuclear Ni(II) Complexes

Complex	Ni–Ni	Ni–S	Ni–S–Ni	S–Ni–S	τ[a]	Ref.
$[Ni_2(SC_2H_5)_2(S_2CSC_2H_5)_2]$	2.76	2.179 −2.196	78.3(1) 78.4(1)	81.6(1) 81.1(1)	110.2	6
$[Ni_2(SCH_2CH_2SCH_2CH_2S)_2]$	2.733(5)	2.144 −2.220	76.7(2) 76.8(2)	82.5(2) 82.6(2)	82.3	7
$[Ni_2(C_5H_4NCH_2CH_2NHCH_2CH_2S)_2](ClO_4)_2$	2.739(1)	2.169(1) 2.186(1)	77.94(5)	79.61(6)	110	5
$[Ni_2(dpet)_2]Br_2$	3.134(2)	2.169(2) 2.180(2)	91.9(1) 92.5(1)	81.36(9)	145.2	This study

a) The dihedral angle between the two coordination planes.

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