Syntheses and Crystal Structures of Nickel(II) Complexes with Thiolate or/and Phosphine Ligands[†]

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The reactions of Ni²⁺, edt²⁻ and PR₃ (R = Ph or Et) in MeOH gave the complexes [Ni(tpdt)(PPh₃)] 1, [Ni₂(edt)₂(PPh₃)₂] 2, [Ni₂(edt)₂(PEt₃)₂] 3 and [Ni₂(tpdt)₂] 4 (edt = ethane-1,2-dithiolate, tpdt = 3thiapentane-1,5-dithiolate). Complex 3 is orthorhombic and crystallizes in space group *Pbca* with a = 14.086(4), b = 25.569(11), c = 13.768(4) Å, Z = 8, R = 0.060. Complex 4 also crystallizes in the orthorhombic space group *Pbca* with a = 10.935(8), b = 28.826(15), c = 9.437(4) Å, Z = 8, R = 0.047. All the nickel atoms are four-co-ordinated with distorted square-planar geometies of phosphorus and/or sulfur atoms. In the reaction system condensation of edt²⁻ occurs through a C-S bond disruption to form tpdt²⁻, which co-ordinates to the nickel atoms to give complexes 1 and 4.

Phosphine ligands have played a major role in modern coordination chemistry.¹ Phosphine complexes of transition metals have been studied extensively recently, not only due to their variation in geometric and electronic structures and properties, but also because of their application to homogeneous or heterogeneous catalysis.² The mechanism of the hydrodesulfurization process is also of interest to many chemists and transition metals such as cobalt, nickel and niobium play an important role in hydrodesulfurization catalysis. Metal thiolate complexes are known as ubiquitous biological electron-transfer mediators.^{3,4} Yet complexes containing both phosphine and thiolate ligands have received relatively little attention.

In recent years, transition-metal complexes with mixed phosphine and thiolate ligands, such as $[NEt_4][Co(SPh)_3, (PPh_3)], [Co(SPh)_2L][L = Ph_2P(CH_2)_3PPh_2 or Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2], [Co_2(SPh)_4L'][L' = Ph_2PCH_2PPh_2 or Ph_2P(CH_2)_2PPh_2], [Co_3(SC_6H_4S)_3(PBu^*_{3})_3], [Ni(SR)_2-(PBu^*_{3})_2] (R = Ph or C_6H_4Me-p)^{11,12} and [Ni_3\{Ph_2P(CH_2)_3-S\}_4]^{2+13}$ have been prepared. From the reactions of Ni²⁺, ethane-1,2-dithiolate (edt²⁻) and PR₃ (R = Ph or Et) in MeOH we have isolated the complexes [Ni(tpdt)(PPh_3)] 1 (tpdt²⁻ = 3-thiapentane-1,5-dithiolate), [Ni_2(edt)_2(PPh_3)_2] 2, [Ni_2(edt)_2-(PEt_3)_2] 3 and [Ni_2(tpdt)_2] 4, of which the preliminary results of 1 and 2 have been reported.^{14,15} Herein we report their syntheses and the crystal structures of 3 and 4, that of 4 being a redetermination, ¹⁶ together with their reaction mechanism.

Experimental

All operations were carried out under a dinitrogen atmosphere with standard Schlenk techniques unless otherwise indicated. Triethylphosphine was purchased from Aldrich, NiCl₂ and H_2 edt from Merck, and solvents and PPh₃ from Shanghai. The compound Na₂(edt) was prepared from the stoichiometric reaction of H_2 edt with sodium metal in MeOH. All elemental analyses were carried out at this Institute.

Preparation of the Complexes.—[Ni(tpdt)(PPh₃)] 1. Method (a). To a solution of PPh₃ (1.56 g, 6 mmol) in MeOH (35 cm³) was added Na₂(edt) (0.42 g, 3 mmol) in MeOH (3 cm³) and the solution stirred for 20 min. Anhydrous NiCl₂ (0.42 g, 3 mmol) was added to the solution which turned brown gradually. After stirring for 24 h a brown precipitate was formed and the solution was filtered and the filtrate kept in an ice-box for several weeks to yield violet-red crystals of 1 (20%) (Found: C, 55.9; H, 4.8. Calc. for $C_{22}H_{23}NiPS_3$: C, 55.8; H, 4.9%). IR(KBr): 440m, 390m cm⁻¹.

Method (b). To a solution of $Na_2(edt)$ (0.42 g, 3 mmol) in MeOH (3 cm³) and PPh₃ (1.56 g, 6 mmol) in MeCN (40 cm³) was added solid NiCl₂ (0.42 g, 3 mmol). The solution turned blue and then brown. After stirring for 22 h, the dark-brown solution was filtered and the filtrate evaporated in air. After several days brown rectangular crystals of 1 were obtained (30%); IR and X-ray diffraction analyses confirmed that the product was the same as that obtained by method (a).

 $[Ni_2(edt)_2(PPh_3)_2]$ 2. The brown precipitate collected during the preparation of complex 1 in method (a) was dissolved in CH₂Cl₂ (20 cm³) and MeOH (20 cm³) was added. The solution was filtered and the filtrate kept in a refrigerator for several days to give black rhombic crystals of 2 (20%) (Found: C, 58.2; H, 4.1. Calc. for C₄₀H₃₈Ni₂P₂S₄: C, 58.2; H, 4.6%). IR(KBr): 451m, 428m, 392w, 365w, 350vw, 320vw, 245w cm⁻¹.

[Ni₂(edt)₂(PEt₃)₂] **3.** To a solution of PEt₃ (0.88 cm³, 6 mmol) in MeOH (35 cm³) was added Na₂(edt) (0.42 g, 3 mmol) in MeOH (3 cm³) and the mixture stirred for 20 min. The addition of solid NiCl₂·6H₂O (0.71 g, 3 mmol) turned the solution green then quickly brown. The mixture was stirred for 24 h and filtered. The brown-black filtrate was kept at 4 °C for several days to give large quantities of black pyramidal crystals of **3** (62%) (Found: C, 36.0; H, 6.5; Ni, 21.8; P, 10.2; S, 23.5. Calc. for C₁₆H₃₈Ni₂P₂S₄: C, 35.7; H, 7.1; Ni, 21.8; P, 11.9; S, 23.9%). IR(KBr): 420m, 367m, 315w cm⁻¹.

 $[Ni_2(tpdt)_2]$ 4. To a solution of PEt₃ (0.88 cm³, 6 mmol) in MeOH (35 cm³) was added Na₂(edt) (0.42 g, 3 mmol) in MeOH (3 cm³) and the mixture stirred for 20 min. Solid NiCl₂-6H₂O (0.71 g, 3 mmol) was added to the solution which turned green and then quickly brown. The mixture was stirred for 24 h and filtered. The brown-black filtrate was evaporated in air for several days to give black crystals of 4 (12%) (Found: C, 23.0; H, 3.7. Calc. for C₈H₁₆Ni₂S₆: C, 22.8; H, 3.8%). IR(KBr): 386m, 310w cm⁻¹.

X-Ray Crystallography.—A suitable single crystal of complex 3 or 4 was mounted on a glass fibre and data collections were performed at ambient temperature on a Rigaku AFC-5R diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.710$ 73 Å). The crystallographic data and data

[†] Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1994, Issue 1, pp. xxiii-xxviii.

 Table 1
 Summary of crystal data and data collection parameters

3	4
C16H20Ni2P2S4	C.H. Ni2Se
538.11	422.02
14.086(4)	10.935(8)
25.569(11)	28.826(15)
13.768(4)	9.437(4)
90	90
90	90
90	90
4985.71	2974.60
1.441	1.885
$0.5 \times 0.5 \times 0.7$	$0.15 \times 0.25 \times 0.7$
19.783	33.291
0-16	0-13
0-30	0-34
0–16	0-11
2272	1728
4887	3013
3036	2130
217	145
1.19	0.75
0.060	0.047
0.067	0.063
	$\begin{array}{c} \textbf{3} \\ \textbf{C}_{16}\textbf{H}_{38}\textbf{Ni}_2\textbf{P}_2\textbf{S}_4 \\ \textbf{538.11} \\ \textbf{14.086(4)} \\ \textbf{25.569(11)} \\ \textbf{13.768(4)} \\ \textbf{90} \\ \textbf{80} $

Details in common: space group *Pbca*; Z = 8; Mo-K α radiation ($\lambda = 0.71073$ Å); graphite monochromator; scan method, θ -2 θ ; 2 θ range 2-50°; unit weighting scheme.

collection parameters are summarized in Table 1. Intensity data were corrected for fluctuations of the monitored reflections, Lorentz-polarization factors, and empirical absorption based psi-scans using DIFABS.¹⁷ The coordinates of the metal atoms were determined by direct methods and the remaining non-hydrogen atoms located from successive Fourier difference syntheses. The structures were refined using full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. All calculations were performed on a VAX 11/785 computer with the SDP program package¹⁸ and the hydrogen atoms were not included in the calculations. Atomic scattering factors were taken from ref. 19.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Syntheses of the Complexes .-- From the reaction system of Ni^{2^+} , edt^{2-} and PR_3 in a 1:1:2 molar ratio in methanol, complexes 1-4 with three different structural types can be isolated. It is interesting that although edt²⁻ was used as the initial reactant, two of the complexes, 1 and 4 possess tpdt²⁻ as a ligand instead of edt²⁻, indicating cleavage of the C-S bond and condensation of two edt²⁻ groups. It has been reported that $[Ni(S_2C_2Ph_2)_2]^{2-}$ can be oxidized by O_2 to $[Ni-(O_2S_2C_2Ph_2)_2]^{2-}$, and the S atom may cleave as SO_2 .²⁰ From the reaction system of Ni²⁺, edt²⁻ and PPh₃ under a N₂ atmosphere, complex 2 was obtained; however, complex 1 can be obtained from the same reaction system in the presence of oxygen because the reaction mixture is left to stand for some time. The yield of 1 increased when the reaction system was opened to the air. It seems that oxygen may also play an important role in the formation of the tpdt²⁻ ligand. When PEt₃ was used instead of PPh_3 we isolated complex 3 under a N_2 atmosphere and 4 in air. These facts show that cleavage of the C-S bond of edt²⁻ and the formation of tpdt²⁻ occurred through the oxidative elimination of a sulfur atom. In related reactions in the absence of PR₃, when the molar ratio of M^{2+} : SR⁻ is 1:2 or that of M^{2+} : SRS²⁻(M = Ni, Pd, *etc.*) is 1:1, insoluble polymers (e.g. $[{M(SR)_2}_n]$ or $[{M(SRS)}_n]$) are given immediately.²¹ Snyder *et al.*²² have studied the formation mechanism of

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 $[Ni_2(edt)_3]^{2-}$, where the species $[Ni(edt)_2]^{2-}$ was believed to be the first intermediate. It is rational that the nickel ions react with edt^{2-} first to form the species $[M(edt)_2]^{2-}$. The presence of phosphine in the reaction system interrupts the polymerization and leads to the formation of different complexes with mixed ligands, depending on the amount of air present in solution.

With these facts the reaction mechanism of these complexes can be deduced and is shown in Scheme 1. The Ni²⁺ ions react first with edt²⁻ to form the intermediate $[Ni(edt)_2]^{2-}$ I from which one Ni–S bond is broken under the attack of PR₃ forming $[Ni(edt)_2(PR_3)]^{2-}$ II which then reacts with solvent or free phosphine by two different routes.

Route a. The other Ni–S bond of the monodentate edt^{2-} is broken and this cleaved edt^{2-} ligand is replaced by a solvent molecule to form a new intermediate, [Ni(edt)(PR₃)(solv)] III. The reaction of free PR₃ with III gives [Ni(edt)(PR₃)₂] IV, or the condensation of two molecules of III yields the dinuclear complexes [Ni₂(edt)₂(PR₃)₂] V (R = Ph 2 or Et 3).

Route b. In the presence of air, $[Ni(edt)_2(PR_3)]^{2^-}$ II may be oxidized to $[Ni(edt)(PR_3)(O_2S_2C_2H_4)]$ VI and leads to the cleavage of a C-S bond where the S atom may cleave as SO₂, similar to that reported in the complex $[Ni(O_2S_2C_2Ph_2)_2]^{2^-.20}$ The remaining carbonium ion intermediate links to the monodentate edt²⁻ ligand with the subsequent formation of tpdt²⁻, which then ligates to the Ni atom to form $[Ni(tpdt)(PR_3)]$ VII (R = Ph 1). In addition when R = Et, the Ni-P bond may be further oxidized by oxygen to cause the

Table 2 Atomic positional parameters of [Ni₂(edt)₂(PEt₃)₂] 3

Atom	x	у	z
Ni(1)	0.153 95(7)	0.156 67(4)	0.508 11(7)
Ni(2)	0.255 22(7)	0.067 14(4)	0.414 66(7)
S(1)	0.111 8(1)	0.075 82(8)	0.475 9(2)
S(2)	0.030 4(2)	0.187 4(1)	0.434 6(2)
S(3)	0.287 9(2)	0.115 88(8)	0.541 7(2)
S(4)	0.396 2(2)	0.078 8(1)	0.356 0(2)
P (1)	0.172 1(2)	0.231 61(9)	0.580 6(2)
P(2)	0.225 7(2)	0.006 1(1)	0.307 7(2)
C(1)	0.021 7(6)	0.083 9(4)	0.378 6(8)
C(2)	-0.041 7(7)	0.129 2(4)	0.408 9(9)
C(3)	0.394 4(6)	0.153 1(4)	0.501 2(8)
C(4)	0.458 9(6)	0.112 7(4)	0.453 1(8)
C(111)	0.275 7(6)	0.237 4(3)	0.662 2(7)
C(112)	0.277 8(8)	0.288 1(4)	0.725 3(7)
C(121)	0.068 2(6)	0.245 1(4)	0.658 9(8)
C(122)	0.051 1(8)	0.201 3(4)	0.732 8(8)
C(131)	0.174 7(7)	0.291 5(3)	0.505 9(7)
C(132)	0.266 9(7)	0.293 8(4)	0.444 3(8)
C(211)	0.325 4(7)	-0.035 2(4)	0.271 2(7)
C(212)	0.372 0(9)	-0.062 5(4)	0.355(1)
C(221)	0.166(1)	0.022 0(5)	0.195 5(8)
C(222)	0.220(1)	0.063 4(5)	0.142(1)
C(231)	0.133 9(8)	-0.043 1(4)	0.367 7(9)
C(232)	0.107(1)	-0.088 7(5)	0.304(1)
Table 3 Sele $(PEt_3)_2$] 3	ected bond lengtl	ns (Å) and angles ($$) for $[Ni_2(edt)_2]$
Ni(1)-Ni(2)	2.988(2)	Ni(2)-S(4)	2.164(3)
Ni(1)-S(1)	2.197(2)	Ni(2) - P(2)	2.186(3)
Ni(1)-S(2)	2.161(3)	S(1) - C(1)	1.86(1)
Ni(1)-S(3)	2.204(2)	S(2) - C(2)	1.84(2)

Ni(1)–Ni(2)	2.988(2)	Ni(2)-S(4)	2.164(3)
Ni(1) - S(1)	2.197(2)	Ni(2) - P(2)	2.186(3)
Ni(1) - S(2)	2.161(3)	S(1) - C(1)	1.86(1)
Ni(1)-S(3)	2.204(2)	S(2)-C(2)	1.84(2)
Ni(1) - P(1)	2.175(2)	S(3)-C(3)	1.863(9)
Ni(2) - S(1)	2.200(2)	S(4) - C(4)	1.83(2)
Ni(2)-S(3)	2.196(2)		
Ni(1)-S(1)-Ni(2)	85.62(9)	S(1)-Ni(1)-P(2)	98.95(9)
Ni(1)-S(3)-Ni(2)	85.52(9)	S(3)-Ni(2)-S(4)	91.5(1)
S(1)-Ni(1)-S(2)	91.74(9)	S(3) - Ni(2) - P(2)	169.0(1)
S(1)-Ni(1)-S(3)	80.14(8)	S(4)-Ni(2)-P(2)	91.2(2)
S(1) - Ni(1) - P(1)	162.5(1)	Ni(1)-S(1)-C(1)	103.0(3)
S(2)-Ni(1)-S(3)	163.6(2)	Ni(2)-S(1)-C(1)	111.2(3)
S(2) - Ni(1) - P(1)	89.4(1)	Ni(1)-S(2)-C(2)	103.9(3)
S(3) - Ni(1) - P(1)	102.7(1)	Ni(1)-S(3)-C(3)	112.6(4)
S(1)-Ni(2)-S(3)	80.22(8)	Ni(2)-S(3)-C(3)	102.7(3)
S(1) - Ni(2) - S(4)	166.3(2)	Ni(2)-S(4)-C(4)	103.7(3)

removal of PEt₃ and the formation of the dinickel complex $[Ni_2(tpdt)_2]$ 4, which contains only trisulfur ligands.

In this reaction system, both air and the phosphine played important roles in the process. In the same medium, the reaction of Ni^{2+} and edt^{2-} under N_2 gave rise to $[Ni_2(edt)_3]^{2-}$ or $[Ni_3(edt)_4]^2$ and no cleavage of the C-S bond occurred.^{22,23} The reaction mixture was fully oxidized when the reaction was carried out in air, *i.e.* the PR₃ ligands stabilized the intermediates in our reactions which contained air in the reaction system.

Recently, we used Co⁺ species with a phosphine ligand as initial reactants and obtained a series of Co–S–P complexes, in which the cleaved S atoms from the disruption of the C–S bond of the thiolate ligands were captured by the cluster as inorganic sulfur or Et_2SO_2 .²⁴ It is interesting that Ni²⁺ and Co⁺ are isoelectronic. In the light of these results we propose that in the presence of Ni²⁺ and PR₃, the C–S bond of the edt²⁻ ligand was disrupted by oxidative elimination of a sulfur atom as SO₂, followed by the formation of tpdt²⁻ and complexes 1 or 4.

Structure of $[Ni_2(edt)_2(PEt_3)_2]$ 3.—The atomic coordinates for complex 3 are listed in Table 2 and selected bond lengths and

Table 4	Atomic positional	parameters of [Ni2(tpdt)2] 4
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Atom	x	У	z
Ni(1)	0.322 8(1)	0.158 25(4)	0.542 3(1)
Ni(2)	0.764 0(1)	0.091 60(4)	0.152 9(1)
S(1)	0.241 0(2)	0.088 54(8)	0.576 2(3)
S(2)	0.448 7(2)	0.143 49(8)	0.710 8(3)
S(3)	0.421 3(3)	0.220 26(8)	0.484 2(3)
S(4)	0.185 2(2)	0.161 91(8)	0.374 7(3)
S(5)	0.286 2(2)	0.105 88(8)	0.126 0(3)
S(6)	0.864 2(3)	0.027 24(9)	0.173 2(3)
$\hat{\mathbf{C}}(\mathbf{i})$	0.367(1)	0.443 9(3)	0.166(1)
C(2)	0.486 7(9)	0.417 0(3)	0.159(1)
C(3)	0.085(1)	0.324 1(4)	0.340(1)
C(4)	0.541(1)	0.275 1(4)	0.118(1)
C(5)	0.263(1)	0.693 4(3)	0.215(1)
C(6)	0.160 4(9)	0.666 7(3)	0.138(1)
C(7)	0.070(1)	0.574 5(4)	0.086(1)
C(8)	0.090(1)	0.525 5(4)	0.140(1)

Table 5 Selected bond lengths (Å) and angles (°) for $[Ni_2(tpdt)_2]$ 4

Ni(1)-Ni(2)	2.739(2)	S(1)-C(1)	1.87(2)
Ni(1)-S(1)	2.225(3)	S(2) - C(2)	1.857(9)
Ni(1) - S(2)	2.144(3)	S(2)-C(3)	1.83(2)
Ni(1)-S(3)	2.161(2)	S(3) - C(4)	1.83(1)
Ni(1) - S(4)	2.185(2)	S(4) - C(5)	1.85(2)
Ni(2) - S(1)	2.179(3)	S(5)-C(6)	1.85(1)
Ni(2)-S(4)	2.215(3)	S(5) - C(7)	1.85(1)
Ni(2) - S(5)	2.141(3)	S(6)-C(8)	1.84(1)
Ni(2)-S(6)	2.161(3)		. ,
Ni(1)-S(1)-Ni(2)	76.92(9)	S(4)-Ni(2)-S(6)	172.3(1)
Ni(1)-S(4)-Ni(2)	76.99(9)	S(5)-Ni(2)-S(6)	91.2(2)
S(1)-Ni(1)-S(2)	88.5(1)	Ni(1)-S(1)-C(1)	102.7(3)
S(1) - Ni(1) - S(3)	170.5(1)	Ni(1)-S(2)-C(2)	97.8(3)
S(1)-Ni(1)-S(4)	82.5(1)	Ni(1)-S(2)-C(3)	103.3(4)
S(2) - Ni(1) - S(3)	91.8(2)	Ni(1)-S(3)-C(4)	104.1(3)
S(2)-Ni(1)-S(4)	170.9(1)	Ni(1)-S(4)-C(5)	113.8(4)
S(3) - Ni(1) - S(4)	96.9(2)	Ni(2)-S(4)-C(5)	103.7(3)
S(1)-Ni(2)-S(4)	82.9(1)	Ni(2)-S(5)-C(6)	99.0(3)
S(1) - Ni(2) - S(5)	171.2(2)	Ni(2)-S(5)-C(7)	101.7(4)
S(1) - Ni(2) - S(6)	96.4(2)	Ni(2)-S(6)-C(8)	104.3(4)
S(4) - Ni(2) - S(5)	89.0(2)		



Fig. 1 Structure of complex 3 with H atoms omitted

angles in Table 3. The molecular structure (Fig. 1) possesses a non-crystallographic two-fold axis. Each of the nickel atoms is surrounded by one phosphorus and three sulfur atoms in a distorted square-planar arrangement. The dihedral angles of the NiS₂ and NiSP planes fall in the range 159.42–165.03°. Atoms

Ni(1), S(1), S(2), S(3) and P(1) (0.046, -0.312, 0.289, 0.285, -0.262 Å) are vertically displaced from the least-squares plane S(1)S(2)S(3)P(1) and Ni(2), S(1), S(3), S(4) and P(2) (0.008, 0.202, -0.216, 0.196 and -0.183 Å) from the least-squares plane S(1)S(3)S(4)P(2). The two five-membered chelate rings [S(1)S(2)C(1)C(2)Ni(1)] and [S(3)S(4)C(3)C(4)Ni(2)] are nonplanar (the displacements of the C atoms from the NiS₂ planes fall in the range 0.241–0.561 Å). One sulfur atom of each edt²⁻ ligand is shared by a pair of nickel atoms forming a sulfur bridge. All the sulfur atoms in the molecule adopt sp³ configurations inducing non-planarity of the chelate rings and the molecule is bent at the sulfur bridges with the dihedral angle between the S(1)S(2)S(3)P(1) and S(1)S(3)S(4)P planes being 124.22(2)°. The average Ni–S–C angle in a chelate ring



Fig. 2 Structure of complex 4 with H atoms omitted

 $[103.3(3)^{\circ}]$ is less than 109° because of the lone pair electrons of the sulfur atoms. The Ni–Ni distance is 2.988(2) Å, indicating that no direct M–M interaction exists in the molecule. The average Ni–S distances are 2.196(3) Å within the five-membered rings and 2.202(3) Å for the four-membered rings. The average Ni–P bond length of 2.181(3) Å is as expected.

Structure of $[Ni_2(tpdt)_2]$ 4.—The atomic coordinates for complex 4 are listed in Table 4 and selected bond lengths and angles in Table 5. The structure is the same as that reported in the literature,¹⁶ but the crystallographic data are more accurate. The molecule is dimeric as shown in Fig. 2, each of the Ni atoms being surrounded by four sulfur atoms in an approximately square-planar arrangement. The average Ni–S bond



Fig. 3 Structure of complex 1 with H atoms omitted



Fig. 4 Structure of complex 2 with H atoms omitted

Table 6 Comparison of significant molecular parameters (Å)

Complex	M-M	$M-S_t^a$	$M-S_{t}^{b}$	M–S _b	M–P	Ref.
1		2.174(3)	2.150(2)		2.187(2)	14
2	2.893(2)	2.158(3)		2.200(2)	2.188(2)	15
3	2.988(2)	2.163(3)		2.199(2)	2.181(3)	This work
4	2.739(2)	2.161(3)	2.143(2)	2.220(2)	2.181(3)	This work
$[Ni_2(edt)_3]^{2+}$	2.941(2)	2.187(3)		2.188(2)		22
[Ni ₂ (pdt) ₂ (PPh ₃) ₂]	2.867(2)	2.170(1)		2.205(2)	2.193(2)	26
$[Ni_2(pdt)_2(PEt_3)_2]$	3.025(2)	2.158(3)		2.201(2)	2.184(3)	26

lengths [2.176(3) Å] are much shorter than those in $[Pd_{3}(tpdt)_{3}]$ [2.321(4) Å]²⁵ but similar to those in other Ni–S complexes. The thiolato S–Ni bonds are longer than the thioether S–Ni bond, while the thiolato S–C bonds are comparable to the thioether S–C bonds. The dimer is bent at the sulfur bridges with a dihedral angle of 104.37(4)° between the two NiS₄ planes, the bending of the molecule bringing the two Ni atoms into close proximity with a M–M distance of 2.739(2) Å which is much shorter than those found in $[Pd_3(tpdt)_3][3.52(1) Å]^{25}$ and other Ni–S complexes.

The structures of compounds 1 and 2 are shown for comparison in Figs. 3 and 4; the details have been presented elsewhere.^{14,15}

Comparison of the Structures.-The significant molecular parameters for the present complexes and related ones are listed in Table 6. All the nickel atoms are four-co-ordinated in distorted square-planar geometries. Complexes 2 and 3 can be viewed as two NiS₃P and 4 as two NiS₄ quadrilaterals sharing sides, and the Ni-S and Ni-P distances are almost the same in complexes 2 and 3. The phosphine ligands play important roles in the Ni-Ni distance. The Ni-Ni distance in 2 [2.893(2) Å] is shorter than those in 3 [2.988(2) Å] and $[Ni_2(edt)_3]^{2-}$ [2.941(2) Å]. The phosphine ligand is an electron donor, but the phenyl rings in 2 can be used as an electron bank and the electrons may be fed back to the rings and are more delocalized than those in $[Ni_2(edt)_3]^{2-}$ and 3 hereby inducing the shortest Ni-Ni distance. Because ethyl groups repulse electrons the core of 3 possesses the most electrons compared with $[Ni_2(edt)_3]^{2-}$ and 2 and results in the longest Ni-Ni distance in these complexes. The presence of phosphine ligands also influences the Ni-S bonds, but the effect is not as marked as that for the Ni-Ni distance. The average terminal thiolato S-Ni bond lengths in 1 [2.174(3) Å] and 4 [2.161(3) Å] are longer than the thioether S-Ni bond lengths [2.150(2) and 2.143(3) Å]. The thiolato S-C bond [1.84(1) Å] is longer than the average thioether S-C bond length [1.81(1) Å] in 1, while those in 4 are comparable [1.85(2) vs. 1.85(2) Å]. The difference in characteristics of the bond lengths between 1 and 4 is also due to the influence of PPh₃ in 1 and the difference in their structural configurations.

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