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Note

Synthesis, spectral and single crystal structure determination of [1,3-bis(diphenylphosphino-kP,P')propane(4-morpholinecarbodithioato-S,S') nickel(II) perchlorate and [1,4-bis(diphenylphosphino-kP,P')butane (4-morpholinecarbodithioato-S,S')nickel(II) perchlorate complexes

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Abstract

 $[Ni(mdtc)(1,3-dppp)]ClO_4$ (1), and $[Ni(mdtc)(1,4-dppb))ClO_4$ (2) $[(mdtc^- = 4-morpholinecarbodithioato anion, 1,3-dppp = 1,3-bis(diphenylphosphino)propane, 1,4-dppb = 1,4-bis(diphenylphosphino)butane)] have been prepared from their parent dithiocarbamate. The planar complexes were characterized by electronic and IR spectra. Single crystal X-ray structures of compounds 1 and 2 were determined. Both the complexes have planar NiS₂P₂ chromophores in keeping with the observed diamagnetism. In complexes 1 and 2 the Ni–S and Ni–P distances are symmetric. The thioureide C–N distances of both the complexes show a decreasing trend compared to the C–N distance in the parent Ni(mdtc)₂. The resulting P–Ni–P angles are higher in both the complexes (96.5(1)° in 1, 101.4(8)° in 2) due to puckering of propane and the butyl alkyl chain associated with 1,3-dppp and 1,4-dpppb. © 2001 Elsevier Science B.V. All rights reserved.$

Keywords: Dithiocarbamate; Thioureide; 1,3-Bis(diphenylphosphino)propane; 1,4-Bis(diphenylphosphino)butane; X-ray structures

1. Introduction

Group VIII dithiolates containing planar MS_4 . chromophores show interesting variations in their reactions with Lewis bases [1,2]. Soft Pd(II) and Pt(II) dithiolates preferably interact with soft phosphines to give rise to planar MS_2P_2 chromophores [3,4]. Detailed structural studies on a variety of MS_2P_2 chromophores have also been made [5,6]. Unlike its congeners, Ni(II) is a border line acceptor. Ni(II) complexes of dithiocarbamates are typical planar complexes containing NiS₄ chromophores. The planar dithiocarbamates prefer to react with soft Lewis bases such as phosphines rather than hard nitrogenous bases such as NH₃ and pyridine, due to symbiotically induced softness [7,8]. On reaction with PR₃ or dppe, they form complexes with chromophore NiS_2P_2 which are diamagnetic in nature [9–11]. Mixed complexes of the type [Ni(S₂CNR₂)X(PR₃)] were obtained by reacting NiX₂ with dithiocarbamate and PR₃ [12] Complexes of the type $[Ni(dtc)Cl(PPh_3)]$ and $[Ni(dtc)(PPh_3)_2]ClO_4$ (where $dtc^- = [S_2CN(C_2H_5)_2]^-$, $[S_2CNH(CH_4OH)]^-$, $[S_2CN(C_2H_4OH)_2]^-$, $[S_2CN (C_4H_8O)$]⁻ and $[S_2CN(C_5H_{10}]^-)$ have also been reported from our laboratory [13]. Recently, single crystal structural studies of the following complexes [Ni(dipdtc)(PPh₃)₂]ClO₄, [Ni(dipdtc)(dppe)]ClO₄, [Ni-

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 $(padtc)(PPh_3)_2]ClO_4$, $[Ni(padtc)(dppe)]BPh_4$, $[Ni(mdtc)_2-(dppe)]ClO_4$, $[Ni(pipdtc)(PPh_3)_2]ClO_4$, $Ni(nmedtc)-(PPh_3)_2]ClO_4$, $[Ni(nmedtc)(dppe)]BPh_4$ have been reported from our laboratory [14–18] (where dipdtc⁻ = diisopropyldithiocarbamato anion; padtc⁻ = N,N'-iminodiethylene bisphthalimidedithiocarbamato anion; pipdtc⁻ = piperidinedithiocarbamato anion and nmedtc⁻ = N-methyl, N-ethanoldithiocarbamato anion.

In continuation of our interest in planar NiS_2P_2 chromophores, the present study was undertaken to understand the puckering effect of propyl and butyl backbones of 1,3-dppp and 1,4-dppb on NiS_2P_2 chromophores. Synthesis, spectral and single crystal structure determination of [Ni(mdtc)(1,3-dppp)]ClO₄ (1) and Ni(mdtc)(1,4-dppb)]ClO₄ (2) are reported in this paper for the first time.

Table 1

X-ray data collection, solution and refinement details for compounds $1 \mbox{ and } 2$

Compound	1	2
Empirical formula	C ₃₂ H ₃₄ ClNO ₅ P ₂	C ₃₃ H ₃₆ ClNO ₅ P ₂
	S ₂ Ni	S ₂ Ni
M	732.8	746.9
Crystal system	orthorhombic	monoclinic
Space group	P _{nma}	$P2_{1}/c$
a (Å)	21.617(3)	18.636(3)
b (Å)	14.882(3)	21.417(2)
<i>c</i> (Å)	10.611(3)	18.476(4)
α (°)	90	90
β (°)	90	111.35(2)
τ (°)	90	90
U (Å ³)	3413	6868
Ζ	4	8
D_{calc} (g cm ⁻³)	1.4258	1.444
$\mu ({\rm cm}^{-1})$	17.945	8.921
F(000)	3040	3056
λ (Å)	Mo Kα (0.71069)	Mo Ka (0.71069)
θ range (°)	3-30	3–28
Scan type	$w - 2\theta$	$w - 2\theta$
Index range	$0 \le h \le 30$	$-24 \le h \le 23$
	$0 \le k \le 20$	$-14 \le k \le 28$
	$-14 \le l \le 0$	$-24 \le l \le 20$
Reflections collected	5516	17579
Observed reflections		
$[F > 6\sigma(F)]$	2667	16652
Parameters refined	291	1100
Final R, wR		
(observed data)	0.0469; 0.1361	0.0498, 0.1378
Weighting scheme	$w = A / [\sigma^2(F_o)^2 + (BP)^2 + 0.00P$	$w = A / [\sigma^2 (F_o^2) + (BP)^2 + 0.00P]$
	A = 1, B = 0.0421	A = 1, B = 0.0849
	$P = (\max(F_o^2 + 2F_c^2)/3)$	$P = (\max(F_o^2 + 2F_c^2)/3)$
Goodness-of-fit	0.831	0.631

2. Experimental

All the reagents and solvents employed were commercially available high-grade purity materials (E. Merck) used as supplied without further purification.

2.1. Physical measurements

IR spectra were recorded on a JASCO IR-700 spectrophotometer (range $4000-400 \text{ cm}^{-1}$) as KBr pellets. The UV–Vis spectra in CH₂Cl₂ were recorded on a JASCO-UVIDEC 340 double beam spectrophotometer.

2.2. Preparation of the complexes

2.2.1. [1,3-Bis(diphenylphosphino-kP,P')propane]-(4-morpholinecarbodithioato-S,S')nickel(II)perchlorate, [Ni(mdtc)(1,3-dppp)]ClO₄ (1)

A mixture of Ni(mdtc)₂ [19] (382 mg, 1 mmol), 1,3-dppp (414 mg, 1 mmol) NiCl₂· $6H_2O$ (120 mg, 0.5 mmol) and NaClO₄ (125 mg, 1 mmol) in acetonitrile– methanol (1:1, 50 cm³) was refluxed for about 3 h followed by concentration to ca. 25 cm³. The precipitated orange–red compound was filtered and dried over anhydrous calcium chloride. Single crystals suitable for X-ray work were obtained by recrystallization from acetonitrile (yield 70%, m.p. 258°C).

2.2.2. [1,4-Bis(diphenylphosphino-kP,P')butane]-(4-morpholinecarbodithioato-S,S')nickel(II)perchlorate, [Ni(mdtc)(1,4-dppb)]ClO₄ (**2**)

A mixture of Ni(mdtc)₂ (382 mg, 1 mmol), 1,4-dppb (428 mg, 1 mmol), NiCl₂· $6H_2O$ (120 mg, 0.5 mmol) and NaClO₄ (125 mg, 1 mmol) in acetonitrile-methanol (2:1, 75 cm³) was refluxed for about 3 h followed by concentration to ca. 25 cm³. A red-orange solution was filtered and left for evaporation. After 2 days, red-orange crystals suitable for X-ray structural analysis were obtained directly (yield 60%, m.p. 250°C).

2.3. X-ray crystallography

Details of the crystal data, data collection and refinement parameters for complexes 1 and 2 are summarized in Table 1. The intensity data were collected at ambient temperature (295 K) on a Philips PW1100 diffractometer (for complex 1) and Siemens AED single crystal diffractometer (for complex 2) with Mo K α radiation ($\lambda = 710$ 690 Å). Structure 1 was solved by direct methods with the SIR92 [20] program and was refined by SHELXL93 [21]. After the isotropic refinement, the data were corrected for absorption using the DIFABS program [22] following the method of Walker and Stuart [23]. For structure 2, one check reflection was measured every 100 reflections without any variation and was 1

Table 2									
Selected	bond	distances	(Å)	and	bond	angles	(°)	for	complex

Ni1-S2	2.214(1)	C18-C19	1.415(9)
Nil-P4	2.180(1)	C19-C20	1.358(10)
S2-C6	1.722(2)	C21-C22	1.389(6)
P4C14	1.826(4)	C20-C21	1.345(8)
P4-C17	1.821(3)	C23-C24	1.373(4)
P4-C23	1.825(3)	C23–C28	1.390(5)
C6-N7	1.305(5)	C24–C25	1.391(6)
N7-C8	1.478(4)	C25-C26	1.349(7)
C8–C9	1.516(6)	C26-C27	1.354(6)
C9–O10	1.419(6)		
S2-Ni1-P4'	170.8(1)	N7-C8-C9	108.6(3)
P4-Ni1-P4'	96.5(1)	C8-C9-O10	110.3(3)
P4-Ni1-S2	92.2(1)	C9-O10-C9'	110.5(2)
S2-Ni1-S2'	79.1(1)	P4-C14-C15	113.2(2)
Ni1-S2-C6	85.2(1)	P4-C23-C28	118.9(2)
Nil-P4-C23	111.2(1)	P4-C23-C24	122.3(2)
Ni1-P4-C17	111.9(1)	C24-C23-C28	118.5(2)
Nil-P4-C14	116.5(1)	C23-C24-C25	120.1(3)
C17-P4-C23	104.6(1)	C24-C25-C26	121.4(3)
C14-P4-C23	105.1(1)	C25-C26-C27	119.2(4)
C14-P4-C17	106.6(1)	C26-C27-C28	121.1(4)
S2-C6-S2	109.8(1)	C23-C28-C27	119.6(3)
S2-C6-N7	125.1(1)	Ni1-S2-C6	85.2(1)
N7-C6-82	125.1(1)	Nil-P4-C14	116.4(1)
C6-N7-C8	123.6(1)	C15-C14-P4	113.3(2)

solved using SIR97 [24], PARST [25] programs, and refined by SHELXL93 [21]. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were fixed isotropically. Selected bond distances and angles are presented in Tables 2 and 3. For complex **2**; two values are (primed, unprimed) are given for each

Table 3

Selected bond distances (Å)	and	bond	angles	(°)	for	complex	2
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bond parameter because the asymmetric unit contains two molecules.

3. Results and discussion

3.1. IR and electronic spectra

IR spectra of complexes 1 and 2 show v(C-N) bands at 1523 and 1527 cm⁻¹, respectively. The shifts in v(C-N) values to higher wave numbers compared with the parent dithiocarbamate (1494 cm⁻¹) are due to the mesomeric drift of electrons from the dithiocarbamate moiety to the metal center. The v(C-S) bands appear at 997 and 992 cm⁻¹ in 1 and 2, respectively without any splitting, supporting the isobidentate coordination of the dithiocarbamate moiety [26]. The electronic absorption bands at 450 and 470 nm for complex 1 and the band at 460 nm for complex 2 are due to d–d transitions [13].

3.2. Structure analysis

The structure of complex 1, along the numbering scheme is shown in Fig. 1. The crystal contains discrete mononuclear $[Ni(mdtc)(1,3-dppp]^+$ units which have no significant intermolecular contacts. The complex contains planar NiS₂P₂ chromophore in keeping with the observed diamagnetism of the compound. Four formula units are present in the unit cell. The Ni, S and P atoms are coplanar. Ni–S distances are equal; 2.214(1) Å, indicating the symmetric bidentate bonding

	Unprimed	Primed		Unprimed	Primed
Ni1-S2	2.212(1)	2.217(1)	P5C16	1.806(4)	1.808(5)
Ni1-S3	2.216(1)	2.210(1)	P5-C29	1.819(4)	1.831(4)
Nil-P4	2.201(1)	2.202(1)	P5-C35	1.821(5)	1.821(5)
Ni1–P5	2.195(1)	2.193(1)	C6–N7	1.304(4)	1.307(5)
S2-C6	1.708(5)	1.713(5)	N7–C8	1.465(7)	1.479(7)
S3-C6	1.713(5)	1.710(5)	N7-C12	1.480(8)	1.472(7)
P4-C13	1.839(5)	1.838(5)	C8–C9	1.514(9)	1.507(8)
P4-C17	1.806(4)	1.822(5)	C9–O10	1.410(10)	1.422(8)
P4-C23	1.825(5)	1.825(5)			
P4–Ni1–P5	101.5(1)	101.1(1)	C16-P5-C35	104.5(2)	105.2(2)
S3-Ni1-P5	166.7(1)	89.7(1)	C16-P5-C29	103.5(2)	102.7(2)
S3-Ni1-P4	91.1(1)	168.8(1)	S2-C6-S3	109.7(3)	109.2(3)
S2-Ni1-P5	89.0(1)	167.1(1)	S3-C6-N7	125.2(4)	125.5(4)
S2-Ni1-P4	169.5(1)	90.7(1)	S2-C6-N7	125.1(4)	125.3(4)
S2-Ni1-S3	78.3(1)	78.2(1)	C6-N7-C12	123.1(5)	123.2(4)
C13-P4-C23	101.3(2)	101.5(2)	C6-N7-C8	123.4(4)	122.9(4)
C13-P4-C17	106.2(2)	106.9(3)	C8-N7-C12	113.4(4)	113.3(4)
Ni1-P5-C35	112.5(2)	112.3(2)	N7-C8-C9	107.2(5)	108.7(4)
Ni1-P5-C29	110.5(2)	110.3(2)	C9-O10-C11	110.4(6)	109.8(5)
Ni1-P5-C16	119.7(2)	118.7(2)	O10-C11-C12	111.5(7)	111.2(5)
C29-P5-C35	104.7(2)	106.4(2)	N7-C12-C11	107.6(5)	108.3(5)



molecule is planar, in keeping with the observed diamagnetism. The two Ni-S bonds 2.212(1), 2.216(1) Å are not different though the two Ni-P distances 2.201(1), 2.195(1) Å are slightly different. There is a very significant reduction of thioureide C-N bond distance (1.304(4) Å) in [Ni(mdtc)(1,4-dppb)]ClO₄ compared to the distance (1.330(1) Å) in the parent compound [19].

The P-Ni-P angles and Ni-P distances show gradual increase with increase in the back bone length between the two phosphorous atoms. The Ni-P distance reported is relatively a very short distance because of chelation. Lengthening of Ni-P distances, shortening of C-N distance and widening of P-Ni-P bond angle (101.4°) in the present compound are as a result of the presence of flexible alkyl chain connecting the two phosphorous atoms. A similar trend was observed in [Ni(dedtc-)(1,4-dppb)]⁺ complex [28]. The butyl chain lies below the plane of the NiS_2P_2 chromophore with normal P-C and C-C distances.

Complexes 1 and 2 are symmetric with respect to Ni-S and Ni-P distances. The Ni-S distances of complexes 1 and 2 are normal as found in the parent $Ni(mdtc)_2$ and similar NiS_2P_2 chromophores. Bond parameters in a series of different bisdithiocarbamates and phosphate-substituted planar nickel complexes are given in Table 4.

The P-Ni-P angle and Ni-P distances of complex 2 are significantly higher than those found in complex 1 which are in turn higher than [Ni(mdtc)(1,2,dppe)]⁺ other 1,2-bis(diphenylphosphino)ethane-nickel and chelate. Relative lengthening of Ni-P distances and widening of P-Ni-P bond angles in the present complexes are due to the presence of flexible propyl or butyl alkyl back bones connecting the two phosphorus atoms of complexes 1 and 2, respectively. A similar trend was found in [Ni(dedtc)(1,4-dppb)]⁺ complex [28].

Major structural effect of the butyl back bone (in complex 2) in the place of propyl group (in complex 1) is the widening of P-Ni-P angle and reduction of S-Ni-S angle. There is also significant increase in Ni-P distance in 2. Another important aspect of comparison is with respect to the thioureide bonds. In complexes 1 and 2 the thioureide C-N distances are relatively short compared to long C-N distance reported in the parent $Ni(mdtc)_2$, which is due to the puckering effect of alkyl back bones associated with 1,3-dppp and 1,4-dppb.

4. Supplementary material

Crystallographic deposition of data: The crystallographic data on compounds 1 and 2 are deposited at







to nickel ion. The observed Ni-P distance is relatively short compared to a long Ni-P, 2.40 Å bonded distance reported in the literature [27]. Interestingly, the P-Ni-P angle in the present compound is larger than the angles observed in 1,2-bis(diphenylphosphino)ethane-nickel chelate [16]. In this complex, thioureide C-N bond distance is 1.305(5) Å, which is significantly different from the distance, 1.330(1) Å observed in the parent Ni(mdtc)₂ [19]. The widening of P-Ni-P angle and shortening of C-N distance in the present complex is as a result of the presence of flexible long alkyl chain connecting the two phosphorous atoms [28]. Other bond parameters of the dithiocarbamate moiety are normal. The ClO_4^{-} ion shows large disorder as observed in similar complexes [14-17].

Table 4

1 able 4					
Comparison	of bond	distances	(Å) and	angles	(°) ^a

Complex	Ni–S(1)	Ni–S(2)	Ni–P(1)	Ni–P(2)	C–N	P(1)-Ni-P(2)	S–Ni–S	Reference
Ni(dipdtc) ₂	2.183(3)	2.182(3)			1.307(4)		79.6(1)	[29]
[Ni(dipdtc)(PPh ₃) ₂] ⁺	2.209(3)	2.201(3)	2.215(2)	2.224(3)	1.321(1)	99.4(1)	77.7(1)	[14]
[Ni(dipdtc)(dppe)] ⁺	2.194(2)	2.196(2)	2.165(2)	2.160(2)	1.316(8)	87.3(1)	79.0(1)	[14]
[Ni(dipdtc)(1,3-dppp)] ⁺	2.192(2)	2.209(2)	2.190(2)	2.191(2)	1.314(6)	93.8(1)	78.2(1)	[30]
$[Ni(dedtc)(PPh_3)_2]^+$	2.190(2)	2.239(2)	2.200(2)	2.230(3)	1.307(1)	99.7(1)	78.2(1)	[13]
Ni(mdtc) ₂	2.213(6)	2.212(7)			1.330(1)	~ /	79.16(2)	[19]
[Ni(mdtc)(dppe)] ⁺	2.194(12)	2.213(1)	2.160(1)	2.167(1)	1.351(1)	86.8(4)	79.7(4)	[16]
[Ni(mdtc)(1,3-dppp)] ⁺	2.214(1)	2.214(1)	2.180(1)	2.180(1)	1.305(5)	96.5	79.1	this work
[Ni(mdtc)(1,4-dppb)] ⁺	2.212(1)	2.216(1)	2.201(1)	2.195(1)	1.304(4)	101.4(8)	78.3(7)	this work

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