

Inorganica Chimica Acta 257 (1997) 49-58

Influence of free and chelating phosphine on the NiS₂P₂ planar chromophore. Synthesis and single crystal structure determination of bis(triphenylphosphine)(*N*,*N*'-iminodiethylenebis(phthalimide)dithiocarbamato)nickel(II) perchlorate, methanol and water solvate and [1,2-bis(diphenylphosphino-*k*.*P*,*P*')ethane]-(*N*,*N*'-iminodiethylenebis(phthalimide)dithiocarbamato)nickel(II) tetraphenylborate water solvate

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Received 26 March 1996; revised 8 July 1996

Abstract

Syntheses and crysta¹ structures of [Ni(padtc)(PPh₃)₂]ClO₄·CH₃OH·H₂O (1) and [Ni(padtc)(dppc)]BPh₄·H₂O (2) (padtc = *NN*⁻ iminodicity]cnebis(phthalimide)dithiocarbamate, dppc = 1.2-bis(diphenylphosphino)ethanc) are reported. Crystal parameters: complex 1, space group *P2*₁/*n*, *a* = 26.388(3), *b* = 12.862(4), *c* = 17.815(2) Å, *B* = 106.03(3)⁶, *V* = 5811.3(2) Å³, Z = 4, *R* = 0.067 for 1150 reflections with *I* > 2*a*(*I*); complex 2, space group *P2*₁/*c*, *a* = 19.722(2), *b* = 34.931(3), *c* = 20.373(3) Å, *B* = 114.54(3)⁶, *V* = 12767.4(4) Å³, *Z* = 4, *R* = 0.067 for 112012 reflections with *I* > 2*a*(*I*). The bulky dithiccarbamate padtc is an umbrella shaped molecule flanking the NiS₂P₂ chromophore. Complex 2 is a molecule with the chelating phosphine dpee. Both the complexes have planar NiS₂P₂ chromophores in keeping with the observed diamagnetism. A relatively short Ni-P distance is observed in the dppe complex 2. The chelating dppe forces the Ni-S distances to be symmetric (2.200(2), 2.204(2) Å) unlike PPh₃ which induces asymmetry (2.227(3), 2.198(2) Å). Shortening of the thioureide C--N bonds (1.307(10) Å in 1, 1.323(7) Å in 2, 1.339(3) Å in free padtc⁻) in the complexes is clear indication of the localisation of the nitrogen electrons between C and N. Thioureide stretching bands in Ni(padtc), [Ni(padtc)(PPh₃)₂]⁺ and [Ni(padtc)(dppc)]⁺ occur at 1494, 1509 and 1512 cm⁻¹, respectively, in keeping with the significant reduction in C-N bond distances.

Keywords: Crystal structures; Nickel complexes; Chromophore complexes; Dithiocarbamate complexes

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]. In solution, the MS_3P_2 chromophore with square pyramidal geometry has also been reported for M = Pd(II), Pt(II). Detailed structural studies on a variety of MS_3P_2 chromophores have also been made [5,6]. Unlike its congeners, Ni(II) is a border line acceptor. Nickel(II) complexes containing NiS₄ chromophores in the planar dithiocarbamates refer to react with soft Lewis bases such as phosphines rather than hard nitrogenous bases such as NH₃ and pyridine, due to the symbiotically induced softness [7,8]. On their reaction with PPh₃ or dppe they form complexes of the chromophore NiS₂P₂ which are diamagnetic in nature [9-11]. Mixed ligand complexes of the type [Ni(S₂CNR₂)XPR₃] have been prepared by the interaction of dithiocarbamate with PR₃ in the presence of NiK₂ [12]. Syntheses and crystal structures of Ni(dtc)Cl(PPh₃)₂[ClO₄,dtc⁻ = [S₂CN(C₂H₃)₂]⁻, [S₂CNH-(C₂H₄OH)]⁻, [S₂CN(C₂H₄OH)₂]⁻, [S₂CN(C₄H₆O]]⁻ and [S₂CN(C₃H₁₀)]⁻ have been reported from our laboratory [13]. Recently a single crystal study of [1,2bis(diphenylphosphino-k.P,P') ethane](4-morpholincar-

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bodithioato)nickel(II)perchlorate dichloromethane solvate showed an interesting thioureide distance [14]. In continuation of our interest on the planar NiS₂P₂ chromophores, the present study was undertaken to understand (i) the influence of increased bulkiness of the dithiocarbamate ligand on the thioureide distance, and (ii) the effect of coordination of free and chelating phosphines on the structure of the chromophore. We report the syntheses and crystal structures of [Ni(padtc)(PPh₃)₂]ClO₄·CH₃OH·H₂O (1) and [Ni-(padtc)(dppe)]BPh₄·H₂O (2) (padtc=(*N*,*N'*-iminodiethylene)bis(pthtalimide)dithiocarbamate) in this paper.

2. Experimental

All the reagents and solvents employed were commercially available high-grade purity materials (E-merck) which were used as such without further purification. Physical measurements: IR spectra were recorded on a JASCO IR-700 spectrophotometer (range 4000-400 cm⁻¹) as KBr pellets; UV-Vis spectra in CHCl₃ were recorded on a JASCO UVIDEC double beam spectrophotometer.

2.1. Bis(N,N'-iminodiethylenebis(phthalimide)dithiocarbamato)nickel(II), Ni(padtc)z

Amine pa [15] (725 mg, 2 mmol) was dissolved in acctonitrile (75 cm³) and carbon disulfide (2 cm³, 40 mmol) was added with continuous stirring under ice cold conditions. To the freshly prepared padtc⁻ solution, an aqueous solution of nickel chloride (240 mg, 1 mmol) was added and stirred

| Laple | el | | | |
|-------|------------|-----|------------|------------|
| Data | collection | and | refinement | parameters |

well. The green precipitate formed was filtered, washed with water and acetonitrile, and finally dried in an oven at 100°C. The complex was insoluble in common organic solvents (yield 70%; decomp. 280°C).

2.2. Bis(triphenylphosphine-k.P,P')(N,N'-iminodiethylenebis(phthalimide)dithiocarbamato)nickel(II)perchlorate, [Ni(padtc)(PPh₁)₂]ClO₄·CH₁OH·H₂O(1)

A mixture of Ni(padtc)₂ (930 mg, 1 mmol), PPh₃ (520 mg, 2 mmol), NiCl₂·6H₂O (120 mg, 0.5 mmol) and NaClO₄ (125 mg, 1 mmol) in methanol-chloroform (75 cm³) was refluxed for about 3 h. Even though the parent complex was insoluble initially, near the boiling point the colour of the suspension changed from green to reddish orange. On concentrating the mother liquor after filtration to 40 cm³ and allowing it to settle for 2 days, a reddish orange compound separated. The compound was filtered and dried over anhydrous calcium chloride. Single crystall satiable for X-ray work were obtained by recrystallisation from chloroform-methanol (yield 60%; m.p. 170°C).

2.3. [1,2-Bis(diphenylphosphino-k.P,P')ethane](N,N'iminodiethylenebis(phthalimide)dithiocarbamato)nickel(II) tetraphenylborate, [Ni(padtc)(dppe)]BPh₄·H₂O (2)

A mixture of Ni(padtc)₂ (930 mg, 1 mmol), dppe (400 mg, 1 mmol) and NaBPh₄ (360 mg, 1 mmol) was refluxed in acetonitrile (75 cm³) for about 3 h and the resulting redorange solution was concentrated to \sim 30 cm³ after filtration and allowed to settle for 3 days. The wine red coloured solid

| | 1 | 2 |
|--|---|---|
| Empirical formula | C ₅₈ H ₅₂ ClN ₃ O ₁₀ P ₂ S ₂ Ni | C71H47B1N3O4P3S2Ni |
| M | 1161.3 | 1232.9 |
| Crystal dimensions (mm) | 0.19×0.24×0.32 | $0.17 \times 0.22 \times 0.39$ |
| Crystal system | monoclinic | monoclinic |
| Space group | P2/n | P2,/c |
| a (Å) | 26.388(3) | 19.722(2) |
| ь (Å) | 12.862(4) | 34.931(3) |
| c (Å) | 17.815(2) | -0.373(3) |
| β(°) | 106.03(3) | 114.54(3) |
| V (Å ³) | 5811.3(2) | 12767 4(4) |
| Z | 4 | 8 |
| D _c (g cm ⁻³) | 1.281 | 1.264 |
| F(000) | 2320 | 5072 |
| μ (cm ⁻¹) | 25.234 | 18.976 |
| Scan type | ω-2θ | ω-20 |
| Scan range (°) | 3-70 | 3-70 |
| Index ranges $(\pm h, \pm k, \pm l)$ | -28/0, -14/14, -19/20 | -23/21, $-2/42$, $-1/24$ |
| Reflections collected | 11816 | 25445 |
| Observed reflections, $I > 2\sigma(I)$ | 4150 | 11967 |
| Weighting scheme | $w = 1.226/(\sigma^2 F^2 + 0.03431F^2)$ | $w = 1/[\sigma^2 F^2 + (0.154P)^2 + 6.44P]$ |
| | | $P = (\max(F_{1,2}, 0) + 2F_{2,2})/3$ |
| No. parameters refined | 344 | 2011 |
| Final R, Rw | 0.067, 0.073 | 0.069. 0.188 |

Table 2 Atomic fractional coordinates and U_{eq} (×10⁴ Å²) for [Ni(padtc)-(PPh₃)₂]ClO₄·CH₃OH·H₂O (1)

| Atom | x | у | z | Ueq |
|------------|-----------|--------------|-------------|----------------|
| Nil | 0.4205(1) | 0.4639(1) | 0.1501(1) | 48(5) |
| S1 | 0.3363(1) | 0.4775(2) | 0.0814(1) | 60(9) |
| S2 | 0.4179(1) | 0.3607(2) | 0.0507(1) | 54(8) |
| CI | 0.3509(3) | 0.3843(7) | 0.0219(5) | 51(3) |
| N2 | 0.3169(3) | 0.3363(5) | - 0.0349(4) | 55(3) |
| C3 | 0.2592(4) | 0.3545(9) | ~0.0513(7) | 69(4) |
| C4 | 0.2385(5) | 0.4102(10) | -0.1267(8) | 85(5) |
| N5 | 0.2596(3) | 0.5154(7) | -0.1260(5) | 75(4) |
| C6 | 0.2396(4) | 0.5993(9) | -0.0941(7) | 79(5) |
| C7 | 0.2650(4) | 0.6946(10) | -0.1156(6) | 76(5) |
| C8 | 0.2567(6) | 0.7969(10) | -0.1003(8) | 100(6) |
| C9 | 0.2843(7) | 0.8670(14) | -0.1329(11) | 120(9) |
| C10 | 0.3147(6) | 0.8369(12) | -0.1806(1) | 110(7) |
| C11 | 0.3218(5) | 0.7324(12) | 0.1958(8) | 90(6) |
| C12 | 0.2966(4) | 0.6620(9) | -0.1604(6) | 72(4) |
| C13 | 0.2943(4) | 0.5475(10) | - 0.1675(6) | 77(5) |
| 014 | 0.2068(3) | 0.5910(6) | -0.0586(5) | 102(4) |
| 015 | 0.3173(3) | 0.4881(7) | -0.2013(5) | 103(5) |
| C16 | 0.3338(4) | 0.2584(8) | - 0.0850(6) | 71(4) |
| C17 | 0.3242(5) | 0.1461(9) | - 0.0621(8) | 90(5) |
| N18 | 0.3606(4) | 0.1148(6) | 0.0127(6) | 77(4) |
| C19 | 0.4090(4) | 0.0668(7) | 0.0187(7) | 72(5) |
| C20 | 0.4322(4) | 0.0453(7) | 0.1011(6) | 65(4) |
| C21 | 0.4787(6) | - 0.0030(8) | 0.1360(8) | 86(6) |
| C22 | 0.4948(7) | - 0.0078(10) | 0.2207(9) | 108(7) |
| C23 | 0.4607(9) | 0.0307(12) | 0.2608(9) | 123(9) |
| C24 | 0.4131(8) | 0.0770(12) | 0.2187(10) | 117(9) |
| C25 | 0.4004(5) | 0.0845(8) | 0.1411(7) | 81(5) |
| C26 | 0.3532(5) | 0.1296(8) | 0.0866(8) | 83(5) |
| 027 | 0.4249(3) | 0.0491(5) | -0.0371(5) | 95(4) |
| O28 | 0.3157(3) | 0.1728(7) | 0.0993(5) | 117(5) |
| PI | 0.5063(1) | 0.4431(2) | 0.1982(1) | 48(7) |
| C30 | 0.5304(2) | 0.2617(4) | 0.1331(3) | 61(5) |
| C31 | 0.5499(2) | 0.2014(4) | 0.0822(3) | 67(4) |
| C32 | 0.5758(2) | 0.2488(4) | 0.0327(3) | 67(4) |
| C33 | 0.5822(2) | 0.3565(4) | 0.0342(3) | 65(4) |
| C34 | 0.5627(2) | 0.4168(4) | 0.6851(3) | 54(3) |
| C29 | 0.5368(2) | 0.3694(4) | 0.1346(3) | 44(3) |
| C36 | 0.5782(2) | 0.3569(5) | 0.3311(4) | 74(1) |
| C37 | 0.5907(2) | 0.2969(5) | 0.3989(4) | 103(6) |
| C38 | 0.5508(2) | 0.24/8(5) | 0.4231(4) | 120(7) |
| C39 | 0.4983(2) | 0.2388(3) | 0.3793(4) | 94(5) |
| C40 C25 | 0.4658(2) | 0.3166(3) | 0.3110(4) | 60(4) 61(2) |
| C33 | 0.5256(2) | 0.3079(3) | 0.2674(4) | 52(5) |
| C42 | 0.5195(2) | 0.0340(4) | 0.1439(3) | 70(4) |
| C43 | 0.5409(2) | 0.7555(4) | 0.1436(3) | 70(4) |
| C44 | 0.5812(2) | 0.7070(4) | 0.2079(3) | 69(4) |
| C45 | 0.5782(2) | 0.6024(4) | 0.2720(3) | 61(3) |
| C41 | 0.5702(2) | 0.5690(4) | 0.2079(3) | 47(3) |
| P7 | 0.3377(2) | 0.5611(2) | 0 2440(1) | 55(8) |
| C48 | 0.3474(3) | 0.3907(5) | 0.2716(3) | 75(5) |
| C49 | 0.3179(3) | 0.3348(5) | 0.3118(3) | 103(6) |
| C50 | 0.3088(3) | 0.3761(5) | 0.3792(3) | 139(8) |
| C51 | 0.3292(3) | 0.4734(5) | 0.4065(3) | 121(6) |
| C52 | 0.3587(3) | 0.5293(5) | 0.3663(3) | 89(5) |
| C47 | 0.3679(3) | 0.4879(5) | 0.2988(3) | 62(3) |
| C54 | 0.4699(3) | 0.7276(4) | 0.3160(3) | 73(4) |
| C55 | 0.5121(3) | 0.7698(4) | 9.3733(3) | 84(5) |
| C56 | 0.5405(3) | 0.7079(4) | 0.4349(3) | 91(5) |
| | | | | |

(continued)

Table 2 (continued)

| Atom | x | у | z | U _{eq} |
|------|------------|-------------|-------------|-----------------|
| C57 | 0.5268(3) | 0.6038(4) | 0.4392(3) | 92(6) |
| C58 | 0.4847(3) | 0.5615(4) | 0.3820(3) | 76(4) |
| C53 | 0.4562(3) | 0.6234(4) | 0.3204(3) | 61(3) |
| C60 | 0.3785(2) | 0.7356(5) | 0.1494(4) | 71(4) |
| C61 | 0.3449(2) | 0.8134(5) | 0.1094(4) | 80(5) |
| C62 | 0.2938(2) | 0.8218(5) | 0.1170(4) | 107(6) |
| C63 | 0.2764(2) | 0.7524(5) | 0.1647(4) | 129(7) |
| C64 | 0.3100(2) | 0.6746(5) | 0.2047(4) | 94(5) |
| C59 | 0.3610(2) | 0.6662(5) | 0.1970(4) | 62(4) |
| CI | 0.3364(1) | 1.0473(3) | -0.3818(2) | 112(2) |
| OIP | 0.3087(5) | 0.9800(9) | -0.4386(6) | 200(7) |
| O2P | 0.3881(5) | 1.0551(11) | -0.3735(8) | 216(8) |
| 03P | 0.3271(9) | 1.0421(14) | -0.3131(10) | 329(15) |
| 04P | 0.3199(7) | 1.1453(12) | -0.4101(12) | 373(14) |
| 01W | 0.2500(0) | 0.1715(10) | 0.7500(0) | 131(6) |
| CIM | 0.0498(5) | -0.0060(11) | 0.0269(9) | 86(6) |
| 02M | 0.1067(12) | 0.0810(15) | 0.0762(11) | 238(20) |

which separated from the mother liquor was filtered and dried over anhydrous calcium chloride. Crystals suitable for X-ray structural analysis were obtained by repeated crystallisation from acetonitrile (yield 60%; m.p. 190°C). Both the nickel complexes were found to be diamagnetic.

2.4. X-ray crystallography

Details of the crystal data, data collection and refinement parameters for complexes 1 and 2 are summarised in Table 1. The intensity data were collected at ambient temperature on a Siemens AED diffractometer using graphite monochromated Cu K α radiation ($\lambda = 1.5418$ Å). The unit cell parameters were obtained from 48 (0 range: 10.8-17.2°) and 29 (0 range: 11.34-41.2°) well centred reflections for 1 and 2. respectively. Intensity of a standard reflection, recorded for every 100 reflections showed no significant change for both the complexes. The reflections were corrected for Lorentz and polarisation effects. Both the structures were solved by direct methods with the SIR92 [16] program; the refinement procedures were performed by block-matrix using SHELX400 [17] for complex 1 and by full-matrix leastsquares with SHLEX93 [18] for complex 2. All the nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located from ΔF map and refined isotropically. All the calculations were performed on a DELL 486 PC with the CRYSRULER package [19] and PARST program [20]. Atomic coordinates of the non-hydrogen atoms are presented in Tables 2 and 3. Selected bond distances and angles are presented in Tables 4-7.

3. Results and discussion

IR spectra of complexes 1 and 2 show ν C-N bands at 1509 and 1512 cm⁻¹, respectively. The shift in ν C-N values to higher wave number compared to the parent Ni(padtc)₂

| Table 3 |
|---|
| Atomic fractional coordinates ($\times 10^4$) and U_{eq} ($\times 10^4$ Å ²) for[Ni(padtc)(dppe)BPh ₄ ·H ₂ O (2) |
| |

| Atom | Unprimed mo | Unprimed molecule | | | | Primed molecule | | | |
|-----------|-------------|-------------------|------------|-----------------|-----------|-----------------|-----------|------------|--|
| | x | у | z | U _{eq} | x | у | z | Ueq | |
| Nil | 4858(5) | - 4999(2) | 2474(5) | 453(4) | 9347(5) | - 7570(2) | 1563(5) | 461(4) | |
| S1 | 4177(9) | - 5459(4) | - 3189(9) | 564(7) | 9951(9) | - 8060(4) | 2229(9) | 601(7) | |
| S2 | 5448(9) | - 5509(4) | - 1863(9) | 559(6) | 8820(9) | - 8047(4) | 814(9) | 602(6) | |
| P1 | 4301(8) | -4515(4) | - 3155(9) | 501(6) | 8778(9) | -7100(4) | 837(9) | 518(7) | |
| P2 | 5528(8) | -4582(4) | - 1685(8) | 471(6) | 9890(8) | -7142(4) | 2386(9) | 496(6) | |
| Cl | 4591(38) | -4076(17) | - 2596(40) | 561(32) | 8951(40) | - 6666(17) | 1401(38) | 602(33) | |
| C2 | 5405(39) | -4115(17) | - 2139(44) | 592(32) | 9745(41) | -6678(17) | 1920(44) | 629(34) | |
| C3 | 4783(34) | - 5765(15) | - 2546(33) | 465(24) | 9403(35) | -8337(16) | 1500(35) | 512(26) | |
| N4 | 4732(27) | -6145(12) | -2580(27) | 500(21) | 9415(30) | - 8715(13) | (480(30) | 627(25) | |
| C5 | 5279(49) | -6387(21) | -2035(45) | 632(37) | 9957(47) | - 8934(19) | 2095(47) | 744(41) | |
| C6 | 5859(44) | -6544(18) | - 2270(48) | 685(33) | 10622(57) | -9062(22) | 1931(59) | 811(42) | |
| N7 | 6276(31) | - 6245(15) | -2412(32) | 666(27) | 10992(33) | - 8743(15) | 1776(34) | 701(28) | |
| <u>(8</u> | 6069(41) | - 6066(20) | - 3084(47) | 696(36) | 11515(43) | -8503(21) | 2292(52) | 776(40) | |
| ~ | 6632(43) | - 5769(21) | - 2985(47) | 738(38) | 11680(40) | - 8195(20) | 1886(47) | 737(37) | |
| C10 | 6702(59) | - 5511(26) | - 3466(65) | 917(54) | 12142(50) | - 7886(29) | 2132(66) | 977(53) | |
| C10 | 7212(57) | - 5267(20) | - 3776(85) | 1128(60) | 12192(50) | - 7637(37) | 1617(00) | 1202(78) | |
| | 7515(07) | - 3207(30) | - 3220(83) | 120(07) | 11752(64) | - 7705(32) | 990(02) | 1202(78) | |
| C12 | 7814(77) | - 5270(34) | - 2343(93) | 1179(69) | 11/32(04) | - 9015(37) | 649(93) | 1018(55) | |
| | 7773(01) | - 3330(34) | - 2037(83) | 11/6(00) | 11292(32) | - 8013(32) | 046(00) | 1018(33) | |
| C14 | /159(43) | - 3783(22) | | 023(41) | 10234(40) | - 8200(23) | 101(47) | 700(37) | |
| CIS | 6931(44) | -6087(22) | - 1901(33) | 852(39) | 10813(44) | - 8009(22) | 10/1(50) | /01(30) | |
| 016 | 5522(32) | -6151(16) | - 3612(30) | 8/3(28) | 11/62(32) | - 856/(1/) | 2944(33) | 996(30) | |
| 017 | 7241(35) | -6201(18) | - 12//(36) | 1129(34) | 10373(32) | - 8/69(18) | 535(31) | 983(31) | |
| C18 | 4143(40) | - 6339(18) | - 3199(41) | 608(30) | 8892(48) | - 8924(22) | 863(54) | 804(40) | |
| C19 | 3511(42) | - 6481(17) | - 3027(48) | 623(32) | 8259(63) | - 9082(26) | 1006(80) | 1048(58) | |
| N20 | 3140(28) | -6168(13) | - 2827(30) | 571(23) | 7855(41) | - 8790(19) | 1175(46) | 884(37) | |
| C21 | 3347(40) | 6051(19) | -2113(43) | 642(36) | 7330(58) | - 8550(34) | 681(77) | 1115(67) | |
| C22 | 2900(38) | - 5706(18) | -2147(41) | 633(32) | 7136(59) | - 8256(30) | 1068(84) | 1137(65) | |
| C23 | 2875(51) | - 5476(26) | - 1606(57) | 888(44) | 6690(72) | - 7936(45) | 817(120) | 1612(**) | |
| C24 | 2404(62) | - 5165(28) | - 1826(72) | 1010(64) | 6649(125) | - 7694(58) | 1366(187) | 2254(**) | |
| C25 | 1970(65) | - 5086(24) | -2531(76) | 984(60) | 7005(115) | - 7790(50) | 2060(155) | 1845(**) | |
| C26 | 1983(48) | - 5318(22) | - 3074(55) | 821(43) | 7492(82) | - 8090(42) | 2323(103) | 1321(92) | |
| C27 | 2462(37) | - 5631(17) | - 2863(43) | 637(35) | 7540(58) | -8332(26) | 1785(76) | 1031(63) | |
| C28 | 2598(39) | - 5925(18) | - 3328(46) | 654(31) | 8032(58) | - 8661(27) | 1880(67) | 970(52) | |
| 029 | 3805(30) | - 6221(15) | - 1605(29) | 870(28) | 7100(40) | - 8596(25) | 21(51) | 1468(49) | |
| O30 | 2316(29) | - 5973(15) | - 3974(29) | 831(24) | 8502(42) | -8801(20) | 2410(42) | 1164(39) | |
| C31 | 4664(34) | - 4440(17) | - 3828(35) | 571(26) | 9175(34) | -6987(16) | 202(36) | 583(26) | |
| C32 | 5204(52) | -4672(26) | - 3860(50) | 902(48) | 9800(51) | -7173(24) | 233(52) | 879(46) | |
| C33 | 5506(61) | -4596(32) | -4364(62) | 1148(55) | 10127(63) | 7075(29) | - 223(60) | 1081(54) | |
| C34 | 5279(60) | -4284(30) | - 4791(56) | 1023(54) | 9811(74) | -6792(34) | - 721(66) | 1136(64) | |
| C35 | 4752(62) | - 4051(30) | -4761(52) | 976(53) | 9192(58) | -6600(25) | - 764(48) | 912(48) | |
| C36 | 4422(47) | -4121(23) | -4286(44) | 812(37) | 8875(47) | - 6699(21) | - 295(43) | 781(36) | |
| C41 | 3298(34) | -4513(17) | - 3609(34) | 573(24) | 7784(35) | -7133(18) | 292(37) | 620(26) | |
| C42 | 2849(47) | -4286(25) | - 3405(56) | 844(43) | 7261(46) | -6932(26) | 444(58) | 950(44) | |
| C43 | 2079(54) | -4306(33) | - 3761(66) | 1000(55) | 6504(52) | - 6973(34) | -5(69) | 1187(61) | |
| C44 | 1746(47) | - 4551(30) | - 4296(54) | 929(39) | 6273(54) | - 7208(33) | - 595(61) | 1093(47) | |
| C45 | 2173(50) | - 4775(31) | -4528(55) | 898(43) | 6789(56) | - 7404(32) | - 731(55) | 1018(47) | |
| C46 | 2940(40) | -4762(21) | -4186(42) | 706(34) | 7533(47) | -7374(25) | - 310(48) | 854(42) | |
| C51 | 5156(33) | -4508(16) | - 1018(34) | 540(25) | 10871(34) | -7207(17) | 2953(36) | 593(28) | |
| C52 | 4534(40) | - 4709(22) | - 1064(41) | 685(35) | 11073(47) | - 7492(23) | 3490(44) | 758(39) | |
| C53 | 4216(57) | -4636(29) | - 586(54) | 965(49) | 11822(52) | - 7572(29) | 3910(48) | 931(43) | |
| C54 | 4526(60) | -4367(30) | - 58(52) | 979(53) | 12262(53) | -7376(34) | 3806(59) | 1044(54) | |
| C55 | 5156(56) | -4169(27) | 8(49) | 893(48) | 12172(50) | - 7094(36) | 3289(68) | 1048(58) | |
| CS6 | 5479(42) | - 4236(21) | - 470(42) | 702(35) | 11428(43) | - 7014(23) | 2862(48) | 787(30) | |
| C61 | 6525(33) | - 4663(16) | - 1209(34) | 525(28) | 9445(33) | - 7081(16) | 2998(12) | 518(27) | |
| C62 | 6820(45) | - 4811(25) | - 524(45) | 838(38) | 8868(52) | ~ 7307(26) | 2960(51) | 951(47) | |
| C63 | 7586(55) | -4865(31) | - 174(57) | 1046(48) | 8511(60) | - 7253(33) | 3416(50) | 1218(50) | |
| C64 | 8043(45) | - 4783(23) | - 495(56) | 843(40) | 8737(62) | -6963(30) | 3899(54) | 1033(\$4) | |
| C65 | 7746(46) | - 4641(24) | - 1175(59) | 874(45) | 9320(59) | -6737(28) | 3063(40) | 046(40) | |
| -05 | (140(40) | - 4041(24) | - (1/5(59) | 0/4(43) | 7320(37) | -0151(28) | 3903(49) | 940(49) | |

(continued)

| Atom | Unprimed m | Unprimed molecule | | | | Primed molecule | | | |
|------|------------|-------------------|------------|-----------------|-----------|-----------------|-----------|-----------------|--|
| | x | y | z | U _{eq} | x | у | z | U _{eq} | |
| C66 | 6991(42) | - 4589(23) | - 1534(47) | 760(38) | 9670(53) | -6798(24) | 3514(48) | 862(46) | |
| BI | 5661(39) | - 2893(19) | -1552(45) | 606(35) | 9900(45) | - 5442(20) | 1985(48) | 679(40) | |
| C71 | 5752(38) | - 2482(17) | -1111(37) | 621(30) | 9878(34) | - 5027(17) | 1580(37) | 634(28) | |
| C72 | 6442(45) | - 2310(20) | - 764(43) | 765(35) | 10293(45) | -4950(22) | 1195(53) | 915(43) | |
| C73 | 6553(62) | - 1976(22) | - 365(47) | 919(43) | 10223(53) | - 4607(28) | 824(61) | 1084(53) | |
| C74 | 5975(68) | - 1799(22) | - 287(48) | 918(52) | 9741(56) | -4333(24) | 834(58) | 1036(49) | |
| C75 | 5285(63) | - 1958(23) | - 633(56) | 945(54) | 9306(56) | -4395(21) | 1212(50) | 908(45) | |
| C76 | 5183(48) | - 2293(20) | - 1030(49) | 841(44) | 9388(42) | - 4740(19) | 1569(42) | 732(35) | |
| C77 | 5758(33) | - 2827(17) | 2305(37) | 608(27) | 9049(42) | - 5626(16) | 1543(52) | 759(38) | |
| C78 | 5823(42) | - 2465(21) | -2571(45) | 717(35) | 8569(56) | - 5749(22) | 1836(79) | 1043(63) | |
| C79 | 5841(45) | - 2400(25) | - 3225(47) | 816(42) | 7875(72) | - 5884(28) | 1467(128) | 1492(**) | |
| C80 | 5779(46) | -2705(26) | - 3682(53) | 862(42) | 7607(70) | - 5904(35) | 725(128) | 1773(++) | |
| C81 | 5725(51) | - 3067(27) | - 3441(52) | 918(46) | 8036(72) | - 5788(28) | 369(85) | 1437(69) | |
| C82 | 5712(46) | - 3120(20) | - 2775(49) | 803(38) | 8740(54) | - 5640(24) | 787(67) | 1118(48) | |
| C83 | 4825(35) | - 3080(16) | - 1772(38) | 609(30) | 10566(39) | -5718(17) | 1947(42) | 680(34) | |
| C84 | 4623(42) | - 3316(20) | - 1324(45) | 712(35) | 11274(47) | - 5717(26) | 2497(55) | 899(44) | |
| C85 | 3912(49) | - 3459(22) | - 1528(56) | 828(43) | 11863(59) | - 5931(36) | 2505(73) | 1166(60) | |
| C86 | 3352(46) | - 3368(23) | -2173(57) | 871(44) | 11731(81) | -6170(33) | 1918(91) | 1249(82) | |
| C87 | 3526(46) | - 3141(25) | - 2643(60) | 906(41) | 11055(76) | -6172(25) | 1342(79) | 1076(64) | |
| C88 | 4233(42) | - 3000(22) | -2431(50) | 818(37) | 10477(52) | - 5951(22) | 1356(51) | 858(43) | |
| C89 | 6312(34) | - 3170(16) | -963(42) | 641(29) | 10056(38) | -5391(17) | 2841(42) | 710(31) | |
| C90 | 6839(43) | - 3386(22) | - 1095(53) | 831(42) | 10083(70) | -5712(23) | 3259(58) | 1223(70) | |
| C91 | 7373(48) | - 3617(27) | - 576(67) | 1009(58) | 10181(73) | 5687(27) | 3990(61) | 1263(78) | |
| C92 | 7405(54) | - 3639(27) | 116(67) | 1066(48) | 10311(50) | - 5341(27) | 4332(56) | 979(44) | |
| C93 | 6919(48) | - 3425(24) | 292(55) | 863(43) | 10299(60) | - 5028(25) | 3928(62) | 1156(55) | |
| C94 | 6386(45) | - 3201(22) | -239(49) | 766(39) | 10198(51) | - 5057(21) | 3215(52) | 923(43) | |
| 01W | 2586(61) | 4347(38) | 4515(46) | 2166(51) | | | | | |

(1494 cm⁻¹) is due to the mesomeric drift of electrons from the dithiocarbamate moiety to the metal centre. The vC-S bands appear around 1000 cm⁻¹ without splitting supporting the near isobidentate coordination of the dithiocarbamate moiety [21]. In addition to vC-N and vC-S bands, the spectra showed strong absorption bands at 1100 and 1438 cm⁻¹ due to the presence of ClO₄⁻ and BPh₄⁻ ions, respectively. Electronic spectra of complexes 1 and 2 show three absorption bands at 440, 480 and 495 nm. The 440 nm band is attributed to the charge transfer transitions and the other bands are due to the d-d transitions [13]. Both the complexes are diamagnetic and hence must be in a planar environment with the NiS₂P₂ chromophores which is confirmed by the structural studies presented. The electronic spectra of the two complexes show similarities to the analogous planar, diamagnetic nickel(II) complexes [13].

The molecular structure of complex 1 is shown in Fig. 1. The complex is a discrete $[Ni(padic)(PPh_3)_2]^*$ unit indicating that it is monomeric with no significant intermolecular contacts. Four molecules are present in the unit cell. The molecule is not of perfect square geometry because of the small bite angle (78.5(1)°) associated with the dithiocarbamate ligand. The Ni, S(1), S(2), P(1) and P(2) atoms are coplanar. The planarity of the molecule is in keeping with the observed diamagnetism of the complex. The two Ni–S (2.227(3), 2.198(2) Å) and Ni–P (2.204(3), 2.224(3) Å) bonds are significantly different. Asymmetry in Ni–P bonds is reflected in the Ni–S bond distances. The related C–S bond distances (1.713(9) and 1.726(8) Å) are however symmetric. A similar trend was observed in the [Ni(dedtc)-(PPh₃)₂]⁺ complex [13]. The bond parameters of the dithiocarbamate moiety are normal as observed in the earlier studies.

The phenyl rings show normal bond parameters. Two of the phenyl rings in PPh₃ are pitched to the same extent whereas the third one is almost perpendicular to the Ni-P-C-C plane as a requirement for the packing of the molecules in the unit cell. The oxygen atoms of the ClO₄⁻ ion show large thermal parameters even though there are no short contacts suggesting the presence of disorder. The mean Cl-O distance (1.35(2) Å) is close to the reported value [22]. The O-Cl-O bond angles show large variations indicating distortion from the tetrahedral geometry as observed earlier [14,23]. Similar distortions of the ClO₄ ion in complexes are well known. The solvent molecule CH₃OH in the structure is highly disordered.

Complex 2 is monomeric with eight molecules per unit cell. The molecular structure is given in Fig. 2. The two molecules in the asymmetric unit have different bond parameters, as a packing requirement in the crystal. The fractional coordinates, bond distances and angles are given independently for all the atoms as primed and unprimed atoms in the asymmetric unit. However, comparison of the bond parameters associated with primed atoms holds irue for the

| able 4 | |
|---|---|
| ond distances (Å) for [Ni(padtc)(PPh ₃) ₂]ClO ₄ · CH ₃ OH · H ₂ O (1 |) |

Table 5 Bond angles (°) for [Ni(padtc)(PPh₃)₂]ClO₄·CH₃OH (1)

119.9(6)

120.0(6)

120.7(5)

105.4(11)

110.4(10)

117.1(10)

C62-C63-C64

C60-C59-C64

P2-C59-C60

02P--CI--O4P

OIP-CI-O4P

01P--CI--O2P

120.1(5)

120.1(6)

119.1(4)

100.4(9) 104.8(10)

116.6(9)

C61-C62-C63

C63-C64-C59

P2-C59-C64

O3P-CI-O4P

O2P-CI-O3P

OIP-CI-O3P

| Nil-SI | 2.227(3) | Ni1-S2 | 2.198(3) | P1-Ni1-P2 | 99.7(1) | S2-Ni1-P2 | 167.3(1) |
|--------------|----------------------|---------------------------------------|--------------------|----------------|-----------|-------------|-----------|
| NiI-PI | 2.204(3) | Nil-P2 | 2.224(3) | S2-Ni1-P1 | 92.3(1) | S1-Ni1-P2 | 89.9(1) |
| SICI | 1.713(10) | S2-C1 | 1.726(8) | S1-Ni1-P1 | 169.9(1) | S1-Ni1-S2 | 78.5(1) |
| C1-N2 | 1.307(10) | N2-C3 | 1.488(14) | Ni1-S1-C1 | 85.7(3) | Ni1-S2-C1 | 86.3(3) |
| N2-C16 | 1.490(14) | C3C4 | 1.487(17) | S1C1S2 | 109.1(5) | S2-C1-N2 | 125.1(7) |
| C4-N5 | 1.462(17) | N5-C6 | 1.390(15) | S1C1N2 | 125.9(7) | C1-N2-C16 | 121.8(8) |
| N5-C13 | 1.389(15) | C6-C7 | 1.497(17) | C1-N2-C3 | 121.6(8) | C3-N2-C16 | 116.6(8) |
| C6-O14 | 1.209(16) | C/-C8 | 1.3/4(18) | N2-C3-C4 | 110.7(9) | C3-C4-N5 | 113.2(10) |
| C/-Cl2 | 1.370(17) | C10-C9 | 1.364(23) | C4-N5-C13 | 125.2(9) | C4-N5-C6 | 122.4(9) |
| C9-C10 | 1.3/0(28) | C10-C11 | 1.394(22) | C6-N5-C13 | 111.6(9) | N5-C6-014 | 123.6(10) |
| | 1.373(20) | 012-013 | 1.4/6(1/) | N5-C6-C7 | 106.5(9) | C7-C6-O14 | 129.9(10) |
| | 1.232(16) | C10-C17 | 1.341(10) | C6-C7-C12 | 106.6(10) | C6-C7-C8 | 128.8(11) |
| U17-IN18 | 1.406(13) | C10-C20 | 1.390(13) | C8-C7-C12 | 124.4(12) | C7-C8-C9 | 114.2(13) |
| CI0 027 | 1.390(19) | C20-C20 | 1.455(15) | C8C9C10 | 122.7(16) | C9-C10-C11 | 121.6(15) |
| C70-C75 | 1 341(18) | C21-C21 | 1.452(20) | C10-C11-C12 | 116.0(13) | C7-C12-C11 | 121.0(12) |
| C20-C23 | 1 386(29) | C73_C74 | 1405(27) | C11-C12-C13 | 129.1(10) | C7-C12-C13 | 109.7(9) |
| C22-C25 | 1 333(21) | C25-C24 | 1.471(16) | N5-C13-C12 | 105.6(9) | C12-C13-O15 | 130.2(10) |
| C26-028 | 1 209(16) | PL_C79 | 1.876(6) | N5-C13-O15 | 124.2(10) | N2-C16-C17 | 111.9(9) |
| P1 C35 | 1.209(7) | P1_C41 | 1.807(6) | C16C17N18 | 112.5(9) | C17-N18-C26 | 126.3(10) |
| C30_C31 | 1 395(8) | C30-C29 | 1.395(7) | C17-N18-C19 | 123.1(10) | C19-N18-C26 | 110.6(10) |
| C31_C32 | 1 396(8) | C32-C33 | 1 395(7) | N18-C19-O27 | 122.8(10) | N18-C19-C20 | 106.4(9) |
| C33-C34 | 1.395(8) | C34-C29 | 1.396(8) | C20-C19-O27 | 130.8(10) | C19-C20-C25 | 108.3(10) |
| C36-C37 | 1.394(9) | C36-C35 | 1.394(7) | C19-C20-C21 | 128.5(10) | C21-C20-C25 | 123.1(10) |
| C37-C38 | 1.394(9) | C38-C39 | 1.396(7) | C20-C21-C22 | 117.5(12) | C21-C22-C23 | 118.4(15) |
| C39-C40 | 1.395(10) | C40-C35 | 1.397(9) | C22-C23-C24 | 119.2(15) | C23-C24-C25 | 121.1(17) |
| C42-C43 | 1.394(7) | C42-C41 | 1.394(7) | C20-C25-C24 | 120.6(13) | C24-C25-C26 | 129 6(13) |
| C43-C44 | 1.396(7) | C44-C45 | 1.396(7) | C20-C25-C26 | 109 7(10) | N18-C26-C25 | 104 8(10) |
| C45-C46 | 1.395(7) | C46-C41 | 1.396(6) | C25-C26-O28 | 130.2(12) | N18-C26-O28 | 125 1(12) |
| P2C47 | 1.807(8) | P2-C53 | 1.831(6) | Nil-PI-C41 | 109.0(2) | Nil-Pl-C35 | 114.8(2) |
| P2C59 | 1.816(6) | C48-C49 | 1.394(10) | Nil-PI-C29 | 113.8(2) | C35-P1-C41 | 112 5(3) |
| C48-C47 | 1.395(9) | C49-C50 | 1.393(9) | C29-P1-C41 | 104.7(3) | C29-P1-C35 | 101.6(3) |
| C50-C51 | 1.396(9) | C51-C52 | 1.394(10) | C31-C30-C29 | 120 1(5) | C30-C31-C32 | 120 1(5) |
| C52-C47 | 1.396(9) | C54-C55 | 1.396(8) | C31_C32_C33 | 120.0(5) | C32_C13_C34 | 120.1(5) |
| C54-C53 | 1.396(8) | C55-C56 | 1.395(7) | C33_C34_C29 | 120.0(5) | C30_C29_C34 | 120.1(5) |
| C56-C57 | 1.395(8) | C57-C58 | 1.394(8) | P1-C29-C34 | 122 8(4) | PI C20 C20 | 117 2(4) |
| C58-C53 | 1.396(7) | C60-C61 | 1.395(8) | C37_C36_C35 | 120.1(6) | C16 C17 C19 | 120 1(4) |
| C60-C59 | 1.395(10) | C61-C62 | 1.396(8) | C37_C38_C39 | 120.1(6) | C38-C39.C40 | 120.1(0) |
| C62C63 | 1.395(10) | C63-C64 | 1.395(8) | C30-C40 C35 | 120.1(0) | C36 C35 C40 | 119.9(0) |
| C64-C59 | 1.394(8) | CI-OIP | 1.378(11) | PI C25 C40 | 117 2(5) | DI C25 C24 | 120.0(0) |
| CI-O2P | 1.335(14) | CI-O3P | 1.315(20) | C43 C42 C41 | 117.2(3) | CA2 CA2 CAA | 122.8(3) |
| C104P | 1.383(16) | CIM-O2M | 1.884(28) | C43-C44 C45 | 120.1(5) | C42-C43-C44 | 120.0(5) |
| | | · · · · · · · · · · · · · · · · · · · | | C45-C44-C45 | 130.0(5) | C44-C43-C46 | 120.1(5) |
| | | | | DI CAL CAS | 120.0(3) | C42-C41-C40 | 120.0(3) |
| unprimed at | oms also. Therefo | ore, in the following | ng discussion, | Nil P2 C50 | 123.3(4) | F1-C41-C42 | 114.3(4) |
| parameters | associated with p | rimed atoms are o | onsidered for | Nil P2 C47 | 107.4(2) | C52 D2 C50 | 122.9(3) |
| comparison | There is almost | nerfect symmetry | with respect | CAT P2 C50 | 10.8(2) | C33-F2-C39 | 103.3(3) |
| comparison | There is annost | perfect symmetry | with respect | C47-F2-C39 | 100.2(3) | C47-P2-C33 | 103.1(3) |
| to the Ni-S | bond distances (2 | (200(2)) and (2.20) | 4(2) A) Indi- | C49-C40-C4/ | 120.1(3) | CF0 CF1 CT0 | 120.0(6) |
| cating sym | metric bidentate l | bonding to the ni | ckel ion. The | CS1 CS2 CA7 | 120.1(0) | C10-C31-C52 | 120.0(5) |
| related C-S | distances are als | o symmetric such | 1 as 1.726(6) | C31-C32-C47 | 120.1(0) | C48-C47-C52 | 119.9(6) |
| and 1.7246 | 6) Å. The Ni- | P bond distance | s (2.182(2) | CSS CSA CE2 | 120.7(3) | F2-04/-048 | 119.4(4) |
| 2 171(2) Å |) are less asymm | etric compared to | 1 The Ni_P | C55 C56 C57 | 120 1(5) | C54 C57 C59 | 120.1(5) |
| 1: | y we ress asynth | | s at a fine for -F | C\$7 C\$8 C\$2 | 120.1(3) | C54 C52 C58 | 120.1(5) |
| uistance rep | sorted is relatively | snort compared t | o une long NI- | C37-C38-C33 | 120.0(3) | C34-C33-C38 | 120.1(5) |
| P distance | of 2.40 A reported | l earlier [24]. The | e phenyl rings | F2-L33-L38 | 117.8(4) | r2-033-034 | 122.1(4) |
| of the dama | mante auto de auto a | | | C01-C00-C39 | 113'3(2) | 00-001-062 | 120.1(6) |

2.171(2) Å) are less asymmetric compared to 1. The Ni–P distance reported is relatively short compared to the long Ni–P distance of 2.40 Å reported earlier [24]. The phenyl rings of the dppe molecule show normal bond parameters (mean P-C=1.817(8) Å). The other bond parameters of the dithic-carbamate are normal. The bond distances of B–C(Ph) in the BPh₄⁻ ion are in the range 1.650–1.670 Å. The mean B–C distance is 1.657(13) Å and the bond parameters associated with the phenyl rings are normal.

| Table 6 | |
|--|-----------------------------|
| Bond distances (Å) for the two molecules of [Ni(padtc)(dpp | e)]BPh, H ₂ O(2) |

| | Unprimed molecule | Primed molecule | | Unprimed molecule | Primed molecule |
|---------|----------------------|--------------------|---------|----------------------|--------------------|
| Nil-Sl | 2.210(2) | 2.200(2) | C34-C35 | 1.340(17) | 1.363(18) |
| Ni1-S2 | 2.208(2) | 2.204(2) | C35-C36 | 1.394(17) | 1.385(16) |
| Nil-PI | 2.174(2) | 2.182(2) | C41-C42 | 1.377(13) | 1.386(13) |
| Nil-P2 | 2.164(2) | 2.171(2) | C41-C46 | 1.393(9) | 1.400(11) |
| \$1-C3 | 1.729(5) | 1.726(6) | C42-C43 | 1.385(13) | 1.398(12) |
| S2-C3 | 1.715(5) | 1.724(6) | C43-C44 | 1.325(15) | 1.367(17) |
| PI-CI | 1.852(7) | 1.845(7) | C44-C45 | 1.370(16) | 1.348(18) |
| PI-C31 | 1.811(8) | 1.815(9) | C45-C46 | 1.379(11) | 1.362(12) |
| P1-C41 | 1.801(6) | 1.811(6) | C51-C52 | 1.382(11) | 1.408(10) |
| P2-C2 | 1.843(7) | 1.838(7) | C51-C56 | 1.400(9) | 1.365(12) |
| P2-C51 | 1.813(8) | 1.809(6) | C52-C53 | 1.383(16) | 1.395(12) |
| P2-C61 | 1.816(6) | 1.812(8) | C53-C54 | 1.366(14) | 1.357(17) |
| C1-C2 | 1.491(9) | 1.482(9) | C54-C55 | 1.379(16) | 1.375(17) |
| C3-N4 | 1.329(7) | 1.323(7) | C55C56 | 1.386(16) | 1.388(11) |
| N4-C5 | 1.453(8) | 1.477(9) | C61-C62 | 1.371(10) | 1.359(12) |
| N4-C18 | 1.477(8) | 1.448(9) | C61-C66 | 1.362(13) | 1.375(10) |
| C5-C6 | 1.515(15) | 1.546(17) | C62-C63 | 1 390(12) | 1.391(19) |
| C6-N7 | 1.430(11) | 1.434(12) | C63-C64 | 1.344(18) | 1.353(15) |
| N7-C8 | 1.402(11) | 1.406(9) | C64-C65 | 1.355(15) | 1.355(16) |
| N7C15 | 1.393(9) | 1.412(12) | C65-C66 | 1.371(11) | 1.372(17) |
| C8-C9 | 1.472(11) | 1.472(13) | B1-C71 | 1.663(10) | 1.658(10) |
| C8-016 | 1.203(8) | 1.229(12) | BI-C77 | 1.641(13) | 1.670(10) |
| C9-C10 | 1,379(16) | 1.367(12) | B1-C83 | 1.653(10) | 1.658(12) |
| C9-C14 | 1.388(11) | 1.385(11) | B1-C89 | 1.654(9) | 1.650(13) |
| C10-C11 | 1.387(16) | 1.392(22) | C71-C72 | 1.383(10) | 1.376(14) |
| C11-C12 | 1.331(20) | 1.388(23) | C71-C76 | 1.370(13) | 1.383(10) |
| C12-C13 | 1.401(23) | 1.365(16) | C72-C/3 | 1.388(11) | 1.393(14) |
| C13-C14 | 1.399(14) | 1.390(16) | C73-C74 | 1.363(18) | 1.356(15) |
| C14-C15 | 1.481(14) | 1.444(11) | C74-C75 | 1.354(15) | 1.387(18) |
| C15-017 | 1.225(12) | 1.214(9) | C75-C76 | 1.388(12) | 1.383(11) |
| C18-C19 | 1.512(13) | 1.499(18) | C77-C78 | 1.401(10) | 1.380(19) |
| C19-N20 | 1.464(10) | 1.421(16) | C77-C82 | 1.379(11) | 1.402(16) |
| N20-C21 | 1.398(10) | 1.387(13) | C78-C79 | 1.365(14) | 1.345(15) |
| N20-C28 | 1.413(8) | 1.405(16) | C79-C80 | 1.388(14) | 1.379(35) |
| C21-C22 | 1.476(10) | 1,440(21) | C80-C81 | 1.376(14) | 1.386(30) |
| C21-O29 | 1.209(8) | 1.238(18) | C81-C82 | 1.381(16) | 1.392(15) |
| C22-C23 | 1.383(14) | 1.381(18) | C83-C84 | 1.402(12) | 1.380(10) |
| C22-C27 | 1.377(10) | 1.368(19) | C83-C88 | 1.394(9) | 1 403(13) |
| C23-C24 | 1.377(14) | 1.432(41) | C84-C85 | 1.379(12) | 1 378(16) |
| C24-C25 | 1.361(18) | 1.333(42) | C85C86 | 1.357(12) | 1.391(22) |
| C25-C26 | 1.378(18) | 1.371(23) | C86-C87 | 1.390(16) | 1.362(18) |
| C26-C27 | 1.393(10) | 1.417(25) | C87-C88 | 1.369(12) | 1.386(18) |
| C27-C28 | 1.493(12) | 1.464(15) | C89C90 | 1.399(12) | 1.395(12) |
| C28-O30 | 1.209(10) | 1.197(12) | C89-C94 | 1.426(14) | 1.359(10) |
| C31-C32 | 1.362(13) | 1.378(12) | C90-C9i | 1.397(12) | 1.423(18) |
| C31-C36 | 1.403(10) | 1.375(9) | C91-C92 | 1.388(20) | 1.366(14) |
| C32-C33 | 1.411(19) | 1.379(19) | C92-C93 | 1.376(17) | 1.361(15) |
| C33-C34 | 1.349(15) | 1.368(15) | C93-C94 | 1.394(11) | 1.385(17) |

In complexes 1 and 2 the Ni–S bond distances are different. Similar differences were found in the Ni(dedtc)ClPPh₃ and [Ni(dedtc)(PPh₃)₂]⁺ (dedtc = diethyldithiocarbamate) complexes reported from our laboratory [13]. The Ni–P distances are also dissimilar in complexes 1 and 2. A comparison of the Ni–P distances in 1 and 2 show1(highly) significant differences, 2.204(3), 2.224(3) and 2.182(2), 2.171(2) Å, respectively. The difference is due to the powerful chelating nature of dppe in complex 2. The chelating nature of dppe forces the corresponding P-Ni-P angle close to 90°, viz. 87.4(1)°, whereas in complex 1 the P-Ni-P angle is 99.7(1)°. Generally, the P-Ni-P angle is greater than 93° for structures incorporating unbridged di- or triphenylphosphine ligands due to steric effects and therefore dppe should be responsible for shortening of the Ni-P bond lengths and reduction of the P-Ni-P angle [14]. The shortening of the Ni-P distance is due to the effective interaction of chelating dppe compared to triphenylphosphine. The N-C-S and C-

| Table 7 | |
|---|---|
| Bond angles (°) for the two molecules of [! | Ni(padtc)(dppe)]BPh ₄ ·H ₂ O(2) |

| | Unprimed molecule | Primed molecule | | Unprimed molecule | Primed molecule |
|-------------|----------------------|--------------------|-------------|----------------------|--------------------|
| | 86 7(1) | 874(1) | PI_C31_C36 | 1191(5) | 120.2(6) |
| \$2_Ni1_P2 | 962(1) | 174 3(1) | PI-C31-C32 | 120.8(5) | 120.2(0) |
| \$2_Ni1_P1 | 174 9(1) | 97 9(1) | C32-C31-C36 | 120.0(3) | 1194(7) |
| SI_Ni1_P? | 174.3(1) | 95.3(1) | C31-C32-C33 | 1197(8) | 120.2(8) |
| S1_N(1-12 | 979(1) | 1754(1) | C32_C33_C34 | 1197(11) | 1194(11) |
| SI_Ni1_S2 | 79.6(1) | 79.6(1) | C33_C34_C35 | 121.0(10) | 1215(11) |
| Nil_SI_C3 | 84 9(2) | 85.4(2) | C34-C35-C36 | 121.4(9) | 118 8(9) |
| Ni1_\$2_C3 | 85 2(2) | 854(2) | C31-C36-C35 | 118 (8) | 120 7(8) |
| Nil-Pl_C41 | 1191(2) | 119 2(2) | PI_C41_C46 | 1197(5) | 1184(6) |
| NIL PL_C31 | 109.9(2) | 113.2(2) | P1_C41_C42 | 123.6(5) | 123 2(6) |
| Nil_PI_CI | 107 8(2) | 106.7(2) | C42-C41-C46 | 1167(7) | 118 5(7) |
| C31-PI-C41 | 107 8(3) | 104.8(3) | C41-C42-C43 | 121 0(8) | 1195(9) |
| CI_PI_C41 | 107.8(3) | 107.9(3) | C42-C43-C44 | 121.7(10) | 120 9(10) |
| CI_PI_C3I | 103 1(3) | 104.0(3) | C43-C44-C45 | 1191(10) | 118 8(10) |
| Ni1-P2-C61 | 118.9(2) | 112.8(2) | C44-C45-C46 | 120 5(9) | 122 6(10) |
| Nil=P2=C51 | 110 0(2) | 117.4(2) | C41-C46-C45 | 120 9(7) | 1:97(8) |
| Nil_P2_C2 | 108 1 (2) | 106 7(2) | P2-C51-C56 | 120 3(5) | 173 9(5) |
| C51-P2-C61 | 107 9(3) | 105.7(3) | P2-C51-C52 | 120.0(5) | 1178(5) |
| C2_P2_C6I | 107.0(3) | 103.7(3) | C52-C51-C56 | 1196(6) | 118 2 (7) |
| C2-P2-C51 | 103.8(3) | 109.7(3) | C51-C52-C53 | 120.5(7) | 120.3(8) |
| PI-CI-C2 | 106.7(4) | 106.7(4) | C52-C53-C54 | 119.7(10) | 120 2 (9) |
| P2-C2-C1 | 106.0(4) | 106.6(4) | C53-C54-C55 | 120 8(9) | 120.0(10) |
| \$1-C3-\$2 | 110.3(3) | 109 6(3) | C54-C55-C56 | 120 3(8) | 1204(10) |
| \$2-C3-N4 | 125 3(4) | 125.3(5) | C51-C56-C55 | 1191(7) | 121.0(8) |
| SI-C3-N4 | 124.4(4) | 125.1(5) | P2C61C66 | 120.7(5) | 121.0(6) |
| C3-N4-C18 | 121.2(5) | 121.0(5) | P2-C61-C62 | 120.6(6) | 121.8(5) |
| C3-N4-C5 | 121.6(5) | 120.4(5) | C62-C61-C66 | 118.6(7) | 117.2(7) |
| C5-N4-C18 | 117.2(4) | 118.6(5) | C61-C62-C63 | 119.0(8) | 121.8(8) |
| N4-C5-C6 | 112.8(6) | 110.3(6) | C62-C63-C64 | 121.8(9) | 118.8(11) |
| C5-C6-N7 | 111.9(6) | 112.2(6) | C63C64C65 | 118.9(9) | 121.1(10) |
| C6-N7-C15 | 124.8(6) | 123.3(7) | C64-C65-C66 | 120.3(9) | 119.1(9) |
| C6-N7-C8 | 124,4(6) | 125.5(7) | C61-C66-C65 | 121.3(8) | 122.0(8) |
| C8-N7-C15 | 110.8(6) | 110.8(6) | C83-B1-C89 | 110.7(5) | 107.9(6) |
| N7-C8-O16 | 123.5(7) | 122.5(7) | C77-B1-C89 | 113.8(6) | 108.4(6) |
| N7-C8-C9 | 106.5(6) | 106.3(7) | C77-B1-C83 | 107.1(5) | 112.8(5) |
| C9-C8-O16 | 130.0(7) | 131.2(7) | C71-B1-C89 | 103.6(5) | 112.8(5) |
| C8-C9-C14 | 108.2(7) | 107.0(6) | C71-B1-C83 | 111.1(5) | 110.1(5) |
| C8-C9-C10 | 131.0(8) | 129.7(8) | C71-B1C77 | 110.7(5) | 104.9(5) |
| C10-C9-C14 | 120.8(8) | 123.2(8) | B1-C71-C76 | 124.8(6) | 121.0(6) |
| C9-C10-C11 | 118.6(11) | 117.2(11) | B1-C71-C72 | 120.9(6) | 123.7(6) |
| CI0-CI1-C12 | 120.8(11) | 119.7(11) | C72-C71-C76 | 114.2(6) | 115.2(6) |
| C11-C12-C13 | 122.7(13) | 122.8(13) | C71-C72-C73 | 123.2(8) | 121.9(8) |
| C12-C13-C14 | 116.8(12) | 117.7(11) | C72-C73-C74 | 120.9(8) | 120.8(10) |
| C9-C14-C13 | 120.2(9) | 119.4(8) | C73-C74-C75 | 117.3(8) | 119.8(8) |
| CI3-CI4-C15 | 132.0(9) | 130.1(8) | C74-C75-C76 | 121.0(10) | 117.7(9) |
| C9-C14-C15 | 107.8(7) | 110.4(7) | C71-C76-C75 | 123.3(9) | 124.6(8) |
| N7-C15-C14 | 106.6(7) | 105.4(7) | B1-C77-C82 | 123.0(5) | 119.1(7) |
| C14-C15-O17 | 129.6(8) | 131.8(8) | B1-C77-C78 | 123.7(6) | 127.1(9) |
| N7-CI5-O17 | 123.7(7) | 122.8(7) | C78-C?7-C82 | 113.1(6) | 113.6(9) |
| N4-C18-C19 | 112.6(6) | 111.5(8) | C77-C78-C79 | 124.9(7) | 126.1(15) |
| C18-C19-N20 | 112.0(5) | 112.3(8) | C78-C79-C80 | 119.6(8) | 118.0(14) |
| C19-N20-C28 | 124.2(6) | 123.5(9) | C79-C80-C81 | 117.8(8) | 121.3(17) |
| C19-N20-C21 | 122.9(5) | 125.6(10) | C80-C81-C82 | 120.6(8) | 117.3(14) |
| C21-N20-C28 | 112.5(5) | 110.0(8) | C77-C82-C81 | 124.0(6) | 123.6(11) |
| N20-C21-O29 | 122.6(6) | 122.4(10) | B1-C83-C88 | 121.5(6) | 124.0(7) |
| N20-C21-C22 | 106.1(6) | 108.7(11) | B1-C83-C84 | 125.1(6) | 120.9(6) |
| C22-C21-O29 | 131.3(0) | 128.9(11) | C84-C83-C88 | 113.3(6) | 115.1(8) |
| C21-C22-C23 | 130.9(7) | 100.2(10) | | 123.0(7) | 124.8(9) |
| C21-C22-C23 | 130.7(7) | 130.2(13) | L04-L03-L00 | 121.3(8) | 117.4(12) |

(continued)

| | Unprimed molecule | Primed molecule | | Unprimed molecule | Primed molecule |
|-----------------|----------------------|--------------------|-------------|----------------------|--------------------|
| C23-C22-C27 | 121.3(6) | 123.4(12) | C85-C86-C87 | 117.7(9) | 120.8(12) |
| C22-C23-C24 | 116.2(9) | 114.9(19) | C36-C87-C88 | 120.0(9) | 119.9(12) |
| C23-C24-C25 | 123.2(10) | 120.3(19) | C83-C88-C87 | 124.4(8) | 122.0(9) |
| C24-C25-C26 | 120.9(9) | 125.6(23) | b1-C89C94 | 120.7(6) | 126.1(6) |
| C25-C26-C27 | 116.8(8) | 114.4(17) | B1-C89-C90 | 126.2(6) | 120.1(6) |
| C22-C27-C26 | 121.5(7) | 120.9(11) | C90-C89-C94 | 113.1(6) | 113.8(7) |
| C26-C27-C28 | 128.5(7) | 128.2(13) | C89-C90-C91 | 123.6(8) | 122.9(7) |
| C22-C27-C28 | 109.9(6) | 110.7(11) | C90-C91-C92 | 120.2(9) | 120.3(9) |
| N20-C28-C27 | 103.6(6) | 104.3(9) | C91-C92-C93 | 119.6(10) | 116.6(9) |
| C27-C28-O30 | 131.4(6) | 131.6(10) | C92-C93-C94 | 119.0(9) | 122.4(8) |
| N20-C28-O30 | 124.9(6) | 124.1(9) | C89-C94-C93 | 124.5(8) | 123.7(7) |



Fig. 1. Geometry of the {Ni(padcc)(PPh₂)₂} * complex (1) showing the atomic labelling scheme. The hydrogen and solvent molecules were omitted for clarity. The ORTEP diagram is with 30% probability contours for the vibration ellipsoids.

N-C angles of the dithiocarbamate moiety in complexes 1 and 2 are almost identical.

Another important aspect of the comparison is with respect to the thioureide bonds. The thioureide C-N bond distance in padte is 1.359(3) Å [25]. In complex 1 and 2 the thioureide C-N distances are 1.307(10) and 1.323(7) Å, respectively. Significant reduction in the bond distances is a very clear indication of the contribution of the thioureide structure to the molecules. This is inline with the ν C-N absorptions occurring at 1463, 1494, 1509 and 1512 cm⁻¹ for padtc⁻, Ni(padtc)₂, [Ni(padtc)(PPh₃)₂]⁺ and [Ni(padtc)-(dpep)]⁺, respectively.

In conclusion, the following facts are brought out by the present study: planar NiS₂P₂ chromophores depending on the nature of the phosphine induce asymmetry in the *trans* Ni-S distances; chelating dppe forces a symmetrical Ni-S bonding thereby increasing the contribution of the thioureide struc-



Fig. 2. Geometry of the {Ni{padtc}(dppe)}* complex (2) showing the atomic labelling scheme. The hydrogen and solvent molecules were omitted for clarity. The ORTEP diagram is with 30% probability contours for the vibration ellipsoids.

ture. Observed ν C-N values for padtc⁻ and the different complexes also support this fact.

4. Supplementary material

Listing of anisotropic thermal parameters and fractional coordinates of the hydrogen atoms have been deposited with the IUCr. Copies may be obtained through the Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, UK, on request.

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