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Synthesis characterisation and stability of mixed aryldichalcogenide bis(diphenylphosphino)ethanenickel(II) complexes. X-ray structure of Ni(dppe)(SeC₆H₄S)

Mary S. Thomas^a, James Darkwa^{a,*}, Emmanuel Y. Osei-Twum^{b,1}, Luis A. Litorja Jr.^b

^aDepartment of Chemistry, University of the North, Private Bag X1106, Sovenga 0727, South Africa ^bResearch Institute, King Fahd University of Petroleum and Minerals, KFUPM Box 1472, Dhahran 31261, Saudi Arabia

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Abstract

Mixed chalcogenide complexes of the type Ni(dppe)(SeC₆H₄S) (dppe=bis(diphenylphosphino)ethane), Ni(dppe)(SC₅H₃NCO₂) and Ni(dppe)(EC₅H₃NE') (E=NH, E'=O; E=E'=NH) have been prepared from the reactions of Ni(dppe)Cl₂ with the appropriate aryldichalcogen or pyridine-based compound, using Et₃N as a base. The relative solution and thermal stabilities of the above compounds, other mixed chalcogen ones, Ni(dppe)(SC₆H₄O), Ni(dppe)(SC₆H₄CO₂) and Ni(dppe)(SC₆H₄NH), and the homoleptic compounds Ni(dppe)(EC₆H₄E') (E=E'=O, E=E'=S; R=H, Me), were established by a combination of electron impact mass spectrometry (EIMS) and fast atom bombardment (FABMS). The most stable ones were the compounds with homoleptic sulfur ligands. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Nickel(II) complexes; Crystal structure; Stability; Mass spectrometry

1. Introduction

Diphosphino organodichalcogenide metal complexes have been investigated for their possible use as anti-cancer agents [1]. Some nickel complexes of this composition are known to catalyse the cyclotrimerisation of dimethylacetylene dicarboxylate [2], as well as to reversibly absorb sulfur dioxide [3]. In solution, some of the diphosphinonickel organodichalcogenide complexes tend to decompose and their stability appears to be dependent on the chalcogen atoms present. The type of chalcogen in the complex could also affect the ability of the compounds to undergo the above two reactions, particularly cyclotrimerisation. The homoleptic complexes oxo $Ni(dppe)(OC_6H_3RO)$ (dppe =bis(diphenylphosphino)ethane, R=H, Me) reported by Bowmaker et al. [4] readily decomposes in solution if they

E-mail address: jdarkwa@uwc.ac.za (J. Darkwa)

are not stored under nitrogen. We have found that Ni(dppe)(SC₆H₄NH) similarly decomposes in solution within 24 h in the presence of air [3]. On the contrary, the homoleptic sulfur and mixed oxo/sulfur compounds are quite stable in solution, even when kept in contact with air. It appears the stability of these phosphino organochal-cogenide complexes is related to how compatible the chalcogen orbitals are with that of the nickel. The sulfur orbitals seem to be quite suitable for interaction with those of the nickel, hence the stability of their compounds.

A measure of the thermal stability of these compounds seem to be reflected in the stability of molecular ions of Ni(dppe)(SC_6H_4S) and Ni(dppe)(SC_6H_3MeS) in the mass spectrometer when the harsh electron impact (EI) ionisation source is used in running their mass spectra [3]. In this project we sought to establish the generality of how the type of chalcogen relates to the stability, solution and thermal, of these compounds. We also wished to establish how the type of mass spectrometric ionisation source could be used as a simple measure of the stability of these compounds. To do this, we carried out the EI and the fast atom bombardment (FAB) mass spectral studies of all new compounds and the previously reported complexes:

^{*}Corresponding author. Present address: Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville 7535, South Africa. Tel.: +27-21-959-3053; fax: +27-21-959-3055.

¹Corresponding author. This author is also a Senior author.



Ni(dppe)(SC₆H₃RS) (R=H (1a), Me (1b) [3], Ni(dppe)(OC₆H₃R'O) (R'=H (2a), Me (2b) [4], Ni(dppe)(SC₆H₄O) (3), Ni(dppe)(SC₆H₄CO₂) (4) and Ni(dppe)(SC₆H₃NH) (5) [2].

2. Experimental

2.1. Materials and instrumentation

All solvents were analytical grade, but were dried before use. Cyclohexane, hexane and toluene were dried over sodium and dichloromethane over P2O5. The following compounds were used as received from Aldrich: 2-mercapacid, tonicotinic 2-aminonicotinic acid and 2,3diaminopyridine. Thiophenol (Fluka) was also used as received. The complexes $Ni(dppe)(SC_6H_4S),$ $Ni(dppe)(OC_6H_4O),$ Ni(dppe)(SC₆H₃MeS) [3], $Ni(dppe)(OC_6H_3MeO)$ [4], $Ni(dppe)(SC_6H_4O),$ $Ni(dppe)(SC_6H_4CO_2)$, and $Ni(dppe)(SC_6H_4NH)$ [2] were prepared by the literature procedures. The dilithio compound, LiSeC₆H₄SLi, was generated in situ as described

by Rauchfuss et al. [6]. All reactions were performed without exclusion of air, unless otherwise stated.

IR spectra were recorded on a Nicolet 205 FT-IR or a Perkin Elmer Spectrum 1000 FT-IR spectrometers. UV– visible spectra were run on a Varian Cary 1E spectrometer. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Varian Gemini 2000 spectrometer at 200 MHz, 50.28 MHz and 80.95 MHz respectively and referenced to residual CHCl₃ for ¹H (δ 7.26), ¹³C (δ 77.0) and externally to PPh₃ (δ – 5.00) for ³¹P. Mass spectra were recorded on a JEOL JMS-HX100 EBE spectrometer in the Electron Impact (EI) or Fast Atom Bombardment (FAB) mode as described previously [5]. Elemental analyses were performed by the micro analytical laboratory at the University of Cape Town, South Africa as a service.

2.2. Syntheses

2.2.1. $Ni(dppe)(SeC_6H_4S)$ 6

A three necked 500 ml flask, fitted with a pressure equalising dropping funnel and a nitrogen inlet was thoroughly flushed with nitrogen. A solution of thiophenol (0.21 ml, 2.00 mmol) in cyclohexane (20 ml), which had previously been degassed, was slowly added dropwise to a nitrogen saturated solution of N,N,N'N'-tetramethylethylenediamine (TMEDA) (0.8 ml) and n-butyllithium (2.80 ml, 4.00 mmol) in cyclohexane (30 ml) at 0°C. After the addition was complete, the reaction mixture was stirred at 0°C for 30 min and gradually allowed to warm up to room temperature, and stirred for a further 22 h. This was followed by the addition of selenium (0.16 g, 2.00 mmol) and stirred till all the selenium had dissolved, ca. 20 h. A degassed solution of Ni(dppe)Cl₂ (1.06 g, 2.00 mmol) in CH_2Cl_2 (50 ml) was added dropwise via the pressure equalising dropping funnel and stirred for 8 h. Addition of hexane to the resultant solution gave a brown solid, which was recrystallised from CH₂Cl₂/hexane to give Ni(dppe)(SeC₆H₄S). Yield=0.33 g, 25%; melting point= 298-300°C. Anal. Calc. for C₃₂H₂₈PSSeNi·CH₂Cl₂: C, 54.36; H, 4.15; S, 4.40%. Found: C, 54.34; H, 4.19; S, 4.11%. ¹H NMR (CDCl₃): δ 7.78 (m, 8H); 7.48 (m, 12H) (dppe); 7.16 (d, 1H, $J_{\rm HH} = 7.80$ Hz); 6.90 (m, 3H) $(SSeC_6H_4)$; 2.36 (m, 4H) (dppe). ¹³C{¹H} NMR: δ 134.3 (s), 132.5 (s), 132.2 (t, $J_{CP} = 5.38$ Hz), 131.6 (s), 130.9 (s), 130.2 (s), 129.5 (t, $J_{\rm CP}$ = 6.08 Hz), 129.9 (s), 125.4 (s), 26.8 (t, $J_{CP} = 24.78$ Hz). ³¹P{¹H} NMR: δ 59.8 (d, P trans S, $J_{\rm PP}$ = 43.59 Hz); 58.7 (d, P *trans* Se). MS (EI): 644 (M⁺, 45), 430 (10), 398 (100), 370 (32), 353 (78), 289 (70), 262 (82), 185 (63), 183 (89), 108 (20), 77 (10). MS $(FAB+): 644 (M^+, 25). IR (KBr pellet cm^{-1}): 3036w,$ 2882w, 1602m, 1475s, 1433vs, 1406w, 1313w, 1288w, 1195w, 1173m, 1100vs, 1067w, 1026w, 998w, 955m, 875w, 845w, 804w, 755m, 728vs, 692vs, 531vs, 495s, 479m, 430w.

2.2.2. $Ni(dppe)(SC_5H_3NCO_2)$ 7

To a solution of Ni(dppe)Cl₂ (1.00 g, 1.89 mmol) and 2-mercaptonicotinic acid (0.29 g, 1.89 mmol) in CH₂Cl₂ (50 ml) was added Et_3N (1 ml). On addition of Et_3N , the mercaptonicotinic acid started to dissolve and the mixture was stirred for 4 h. Hexane was added to the resultant solution to give a dark orange precipitate, which was washed with copious amount of water to remove Et₂NHCl. The product was recrystallised from CH₂Cl₂/hexane, after a CH₂Cl₂ solution was dried over anhydrous Na₂SO₄ overnight, to give analytically pure Ni(dppe)(SC₅H₃NCO₂). Yield=0.92 g, 79%; melting point=254-256°C. Anal. Calc. for $C_{32}H_{27}NO_2P_2SNi$: C, 62.98; H, 4.46; N, 2.30; S, 5.25%. Found: C, 62.71; H, 4.51; N, 2.36; S, 5.14%. ¹H NMR (CDCl₃): δ 8.36 (dd, 1H, $J_{\rm HH} = 7.80$ Hz, $J_{\rm HH} = 2.00$ Hz); 8.25 (dd, 1H, $J_{\rm HH} =$ 4.50 Hz, $J_{\rm HH} = 2.10$ Hz); 6.88 (dd, 1H, $J_{\rm HH} = 7.70$ Hz, $J_{\rm HH} = 4.60$ Hz), (SC₅H₃NCO₂); 2.42 (m, 2H); 2.09 (m, 2H) (dppe). ¹³C{¹H} NMR: δ 150.0 (s), 140.7 (s), 118.6 (s) $(SC_5H_3NCO_2)$; 134.0 (dd $J_{CP} = 24.43$ Hz, $J_{CP'} = 10.31$ Hz); 132.5 (dd, $J_{CP} = 24.40$ Hz, $J_{CP'} = 2.67$ Hz); 129.9 (dd, $J_{\rm CP} = 10.51$ Hz, $J_{\rm CP'} = 6.69$ Hz); 29.5 (dd, $J_{\rm CP} = 35.08$ Hz, $J_{\rm CP'} = 17.93$ Hz); 22.4 (dd, $J_{\rm CP} = 31.68$ Hz, $J_{\rm CP'} = 10.31$ Hz)

(dppe). ³¹P{¹H} NMR: δ 58.0 (d, P *trans* S, J_{PP} =62.86 Hz); 43.5 (d, P *trans* O). MS (FAB+): 609 (M⁺, 100). UV.-vis (CH₂Cl₂): λ_{max} =418 nm. IR (KBr pellet, cm⁻¹): 3043w, 2945w, 1605vs, 1570vs, 1485s, 1436vs, 1387vs, 1346vs, 1184w, 1146s, 1100vs, 1078m, 1028w, 1001m, 867s, 826s, 758vs, 706s, 687s, 531vs, 490s, 476m, 446w, 424w.

2.2.3. Ni(dppe)(HNC₅H₃NO)·1/2CH₂Cl₂ 8

Ni(dppe)(HNC₅H₃NO)·1/2CH₂Cl₂ 8 was prepared and isolated a light purple solid via the procedure described for 7, using Ni(dppe)Cl₂ (0.53 g, 1.00 mmol) and 2-aminonicotinic acid (0.11 g, 1.00 mmol). Yield=0.24 g, 43%; melting $point = 229 - 232^{\circ}C.$ Anal. Calc. for C_{31.5}H₂₈ClN₂OP₂Ni: C, 62.26; H, 4.81; N, 4.61%. Found: C, 62.52; H, 5.15; N, 4.67%. ¹H NMR (CDCl₃): δ 7.97 (t, 4H, $J_{\rm HH} = 9.50$ Hz); 7.84 (m, 4H); 7.53(m, 12H) (dppe); 6.75 (s, br, NH); 6.52 (d, 1H, $J_{\rm HH}$ = 7.40 Hz); 6.11 (t, 2H, $J_{\rm HH} = 6.60$ Hz); (HNC₅H₃NO); 2.31 (m, 4H) (dppe). ${}^{3}C{}^{1}H$ NMR: δ 160.4 (s), 133.4 (d $J_{CP} = 10.66$ Hz); 132. (d, $J_{\rm CP} = 21.02$ Hz); 130.1 (dd, $J_{\rm CP} = 23.26$ Hz, $J_{\rm CP'} = 10.69$ Hz) (dppe); 129.3 (s), 128.4 (s), 128.1 (s), 127.1 (s), 118.6(s) (HNC₅H₃NO); 27.4 (dd, J_{CP} =36.25 Hz, $J_{CP'}$ = 13.53 Hz); 24.5 (dd, $J_{CP} = 35.85$ Hz, $J_{CP'} = 11.82$ Hz) (dppe). ³¹P{¹H} NMR: δ 60.1 (d, P *trans* N, $J_{PP} = 72.61$ Hz); 53. 0 (d, P trans O). MS (FAB+): 566 (M⁺, 100). U.V.-vis (CH₂Cl₂): $\lambda_{\text{max}} = 374$ nm. IR (KBr pellet, cm⁻¹): 3395w, 3219w, 3050w, 2910w, 1619s, 1597vs, 1540vs, 1482s, 1433vs, 1351s, 1283vs, 1250s, 1187m, 1100vs, 1067w, 1026m, 999m, 897m, 873s, 859m, 818m, 774m, 744vs, 725vs, 706vs, 689vs, 654m, 624s, 528vs, 492s, 479s, 446w.

2.2.4. $Ni(dppe)(HNC_5H_3NNH) \cdot CH_2Cl_2$ 9

Ni(dppe)(HNC₅H₃NNH)·CH₂Cl₂ 9 was prepared and isolated as described for 7, using Ni(dppe)Cl₂ (0.53 g, 1.00 mmol) and 2,3-diaminopyridine (0.11 g, 1.00 mmol). Yield=0.29 g, 52%. Anal. Calc. for $C_{31}H_{28}ClN_3P_2Ni$: C, 62.26; H, 4.81; N, 4.61%. Found: C, 62.52; H, 5.15; N, 4.67%. ¹H NMR (CDCl₃): δ 7.98 (m, 4H); 7.81 (m, 4H); 7.52 (m, 12H) (dppe); 6.71 (t, 1H, $J_{\rm HH}$ = 5.40 Hz); 6.51 (s, br, NH); 6.24 (d, 1H, $J_{\rm HH}$ = 7.20 Hz); 6.07 (t, 1H, $J_{\rm HH}$ = 6.60 Hz); 3.53 (s, br, 1H) (HNC₅H₃NNH); 2.29 (m, 4H) (dppe). ${}^{31}P{}^{1}H{}$ NMR: δ 63.8 (d, P trans N, $J_{PP} = 57.48$ Hz); 60.5 (d, P trans N). MS (FAB+): 564 (M⁺, 100). U.V.-vis (CH₂Cl₂): $\lambda_{\text{max}} = 398$ nm. IR (KBr pellet, cm⁻¹): 3065w, 2903w, 1603m, 1537s, 1485m, 1433vs, 1381w, 1310s, 1264w, 1187s, 1173w, 1124w, 1100vs, 1075w, 1023w, 998m, 900w, 875m, 821s, 818m, 747w, 728w, 714w, 706w, 692vs, 657w, 643w, 613w, 533vs, 512w, 482s, 442w.

2.3. Crystal structure determination of 6

Single crystals of 6 were obtained from a 2:1 $CH_2Cl_2/$

hexane solution at -15° C. A dark rectangular crystal of size $0.62 \times 0.50 \times 0.30$ mm was mounted in a sealed capillary tube for data collection. All geometric and intensity data were collected on a Siemens SMART diffractometer with a CCD detector. A total of 17 646 reflections (of which 6633 [R(int)=0.0394] were unique) in the range $3.76 < 2\theta < 56.56^{\circ}$ were collected at 296 K with monochromatic MoK α radiation (λ .=0.71073 Å). Absorption correction based on multiple redundant data analysis was applied [7].

Crystal data: $C_{32}H_{28}P_2SSeNi$: monoclinic, $P2_1/c$; a = 11.205(5) Å, b = 20.331(9) Å, c = 13.936(6) Å, $\beta = 113.356(10)^\circ$, V = 2914.5(2) Å³; Z = 4.

The structure was solved by the Patterson method for primary atom sites and by difference map for atoms in secondary sites [8]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined without restraints. Full-matrix least squares refinement [9] of 334 parameters on F^2 gave $R_1 = 0.0770$, $wR_2 = 0.2273$, with a weighting scheme of $w^{-1} = \sigma^2 (Fo^2) + (0.100P)^2 + 0.00P$, where $P = (Fo^2 + 2F_c^2)/3$. Goodness-of-Fit=1.591. Max ΔF 2.046 e Å⁻³, min -2.170 e Å⁻³.

3. Results and discussion

3.1. Syntheses and stabilities of complexes

The mixed sulfur–selenium complex was obtained from the reaction of in situ generated $LiSeC_6H_4SLi$ with Ni(dppe)Cl₂ (Eq. (1)).



The complex was isolated as a microcrystalline solid and characterised by a combination of IR, NMR and microanalysis. In addition to peaks of the phosphine, the ¹H NMR spectrum showed a downfield doublet at 7.16 ppm for the proton ortho to the sulfur; while the rest of the protons of the ligand appeared as a multiplet at 6.90 ppm. The ³¹P NMR spectrum is discussed, together with those of the other complexes, later in this report. X-ray diffraction studies confirmed that the SeSC₆H₄ binds to the nickel as a bidentate ligand.

The diselenato analogue was also prepared via the reaction of in situ generated $LiSeC_6H_4SeLi$ with Ni(dppe)Cl₂; but its stability in solution when exposed to

air compared to the mixed sulfur and selenium compound was very low. A similar route was used to prepare the tellurium complex, which had a much lower stability than that of the selenium complex. The selenium and tellurium complexes could be characterised from their ³¹P NMR spectra; which gave singlets at 36.56 and 33.93 ppm respectivley. These peak values are indicative of the effect of the electronegativity of the chalcogen. The relative stabilities of these complexes could be established by leaving solutions of the compounds in CH₂Cl₂. Whereas solutions of **6** could be left in air for more than a day, the diselenato complex rapidly decomposed in air with ¹H NMR signals of the latter disappearing within 24 h.

The stability of these complexes appears to be determined by the compatibility of the metal orbitals with the chalcogen. The more stable compounds, in solution, were the dithiolato, Ni(dppe)(SC₆H₄RS) (R=H, Me) [3] and the mixed oxo-sulfido compounds, Ni(dppe)(SC₆H₄O) and $Ni(dppe)(SC_6H_4CO_2)$ [2]. Synthesis of the dithiolato and the mixed oxo-sulfido compounds could even be performed in the presence of air. When the chalcogens were sulfur and selenium, though the reaction had to be performed in an inert atmosphere, work-up and subsequent storage in air showed that the product was quite stable. On the other hand, solutions of Ni(dppe)(SeC₆H₄Se), and the $Ni(dppe)(SC_6H_4NH)$ previously reported [2] and $Ni(dppe)(OC_6H_3RO)$ (R=H, Me) [4], decomposed when exposed to air. These observations point to a link between the strength of the Ni-chalcogen interactions, with Ni-S being the most stable.

By reacting 2-mercaptonicotinic acid, 2-aminonicotinic acid and 2,3-diaminopyridine respectively with Ni(dppe)Cl₂ in the presence of Et₃N, similar complexes were isolated. Because the pyridine-based ligands were insoluble in toluene, the reactions were carried out in CH₂Cl₂. The ligands were only sparingly soluble in this solvent but the reactions were complete within 24 h. These reactions could also be performed in the presence of air. There was a clear indication of the effect of the nitrogenbased ring on the stability of these compounds. This could be established from the EI and FAB mass spectra; with the FAB spectra showing molecular ions whilst the EI spectra had no molecular ions. Whereas several of the phenylbased ligands showed molecular ions in their EI mass spectra, the complexes with the pyridine-based ligands had no molecular ions. Their molecular ions could only be observed in their FAB spectra. Details of the mass spectral study are discussed latter.

4. ³¹P NMR characterization of complexes

The ³¹P NMR spectra of CDCl₃ solutions of all compounds were run at room temperature. All the mixedligand complexes displayed spectra of two doublets, with an AB or AX spin pattern (Table 1); whilst the homochal-

Table 1 ³¹P NMR Spectra of (dppe)Ni aryldiorganochalcogenides

Complex	Chemical Shift (ppm)	$J_{\rm PP}~{ m Hz}$	Δ ppm	Ref.
$Ni(dppe)(SC_6H_4S)$	s, 58.45	_	0	[4]
$Ni(dppe)(SC_6H_3MeS)$	s, 58.62	_	0	[4]
$Ni(dppe)(SC_6H_4O)$	d, 58.88, 47.97	54.95	10.91	[3]
$Ni(dppe)(SC_6H_4Se)$	d, 59.83, 58.72	43.59	1.11	This work
$Ni(dppe)(SeC_6H_4Se)$	s, 36.56	-	0	This work
$Ni(dppe)(TeC_{e}H_{4}Te)$	s, 33.93	_	0	This work
$Ni(dppe)(SC_6H_4CO_2)$	d, 57.19, 41.72	59.90	15.47	[3,10]
$Ni(dppe)(SC_5NH_3CO_2)$	d, 57.98, 43.47	62.86	14.51	This work
$Ni(dppe)(SC_6H_4NH)$	d, 60.44, 59.77	47.56	0.67	[3]
Ni(dppe)(HNC ₅ H ₃ NO)	d, 60.14, 52.94	72.61	7.20	This work
Ni(dppe)(HNC ₅ NH ₃ NH)	d, 63.80, 60.55	57.48	3.25	This work

cogenide complexes of Se and Te gave singlets typical of such compounds [3]. Complexes **7** and **8**, which contain oxygen, gave AX spectra quite similar to those of Ni(dppe)(SC₆H₄O) [2] and Ni(dppe)(SC₆H₄CO₂) [2,10]. The non-oxygen containing complexes, **6** and **9**, had AB spectra also similar to that of Ni(dppe)(SC₆H₄O) [2]. The chemical shifts of the doublets associated with each of the phosphorus atom of the dppe ligand can be linked to the

trans-influence of the chalcogen atom *trans* to the phosphorus. The more polarisable chalcogen has a better *trans*-influence. For example in complex **7**, the chemical shift of the phosphorus *trans* to the S was 58.0 ppm, whilst the phosphorus *trans* to the less polarisable oxygen atom was 43.5 ppm. *Trans*-influence of chalcogens on ³¹P NMR was first observed by Henderson et al. for Pt(dppe)(SC₆H₄CO₂) [10]. Even for the homoleptic com-



Fig. 1. Molecular structure of complex 6.

plex, Ni(dppe{ $S_2C_2(2\text{-pyridine})(H)$ }) [11], the influence of the pyridine nitrogen results in different electronic environment similar to that produced by the polarisability differences described above. This results in two broad singlets (57.4 and 57.2 ppm) for the dppe phosphorus in Ni(dppe{ $S_2C_2(2\text{-pyridine})(H)$ }). It is evident from our results that the *trans*-influence is more pronounced when one of the chalcogens is oxygen and leads to an AX spectrum. It also appears that ³¹P NMR spectroscopy can be used as a measure of the *trans*-influence of atoms. The data in Table 1 seem to indicate that the NH unit, which is isoelectronic with oxygen, has a better *trans*-influence than oxygen.

4.1. Molecular structure of $Ni(dppe)(SeSC_6H_4)$

The coordination geometry about the nickel atom is essentially square planar. The S and Se positions of the mixed dichalcogenide ligand appears to be disordered, thus the exact positions of these atoms could not be established. Fig. 1 gives an ORTEP view of molecule, which clearly depicts the disorder. This resulted in two possible positions and their related bond distances and angles. Table 2 gives selected bond distances and angles of the molecule. The Ni–Se bond distances of 2.256(2) and 2.217(2) Å for the two possible Se sites are only slightly shorter than the bonds in $[Ni(Se_2C_6H_4)_2]^-$ (2.270(5) Å) [12] and Ni(SeP(Ph)_2C_6H_4)_2 (2.280(3) Å) [13]. Other Ni–Se distances with the nickel in a +2 oxidation state show even

Table 2						
Selected	bond	distances	and	angles	for	6

Bond distances (Å)			
Ni-S(1)	2.263 (6)	Ni-S(2)	2.273 (2)
Ni-Se(1)	2.256 (2)	Ni-Se(2)	2.217 (2)
Ni-P(1)	2.160 (2)	Ni-P (2)	2.173 (2)
S(1) - C(4)	1.861 (8)	S(2)–C(5)	1.939 (7)
Se(1) - C(5)	1.851 (6)	Se(2) - C(4)	1.775 (7)
P(1)–C(91)	1.834 (6)	P(1)-C(101)	1.811 (6)
P(1)-C(11)	1.841 (6)	P(2)–C(71)	1.801 (6)
P(2)–C(81)	1.821 (6)	P(2)–C(12)	1.863 (6)
C(2)–C(3)	1.330 (11)	C(3) - C(4)	1.424 (9)
C(4)-C(5)	1.392 (9)	C(5) - C(6)	1.385 (9)
C(11)-C(12)	1.534 (8)	-	-
Bond distances (°)			
P(1) - Ni(1) - P(2)	86.60 (6)	P(1)-Ni(1)-Se(2)	173.98 (7)
P(2) - Ni(1) - Se(2)	89.48 (8)	P(1) - Ni(1) - S(1)	166.84 (14)
P(2)-Ni(1)-S(1)	88.2 (2)	Se(2) - Ni(1) - S(1)	7.6 (2)
P(1) - Ni(1) - Se(1)	91.85 (6)	P(2)-Ni(1)-Se(1)	174.66 (16)
Se(2) - Ni(1) - Se(1)	92.46 (8)	S(1)-Ni(1)-Se(1)	94.3 (2)
P(1)-Ni(1)-S(2)	90.60 (11)	P(2)-Ni(1)-S(2)	167.53 (11)
Se(2) - Ni(1) - S(2)	94.18 (12)	S(1)-Ni(1)-S(2)	96.9 (2)
Se(1) - Ni(1) - S(2)	7.15 (12)	C(101)–P(1)–C(11)	105.6 (3)
C(101)–P(1)–C(91)	104.1 (13)	C(91) - P(1) - C(11)	102.5 (3)
C(101) - P(1) - Ni(1)	123.2 (2)	C(91) - P(1) - Ni(1)	112.6 (2)
C(11)-P(1)-Ni(1)	106.9 (2)	C(71)-P(2)-Ni(1)	116.8 (2)
C(81)-P(2)-Ni(1)	114.4 (2)	C(12) - P(2) - Ni(4)	109.8 (2)

longer bond distances. such in the as Ni(II)diethyldithiocabarmate phenylselenide complex, $Ni(dtc)(PPh_3)(SeC_6H_5)$ (dtc=diethyldithiocabarmate) (2.317(2) Å) [14] and Ni(η^{5} -C₅H₅)(PPh₃)(SeC₆H₄Cl-4) (2.317(6) Å) [15]. On the other hand, the Ni–S bond distances (2.236(6) Å) and 2.273(2) Å) are longer than similar bonds found in Ni(dppe)(SC₆H₄O) (2.158(1) Å) [2] and Ni(dppe)(SC₆H₄S) (2.145(2) Å) [3].

It is clear from the Ni-chalcogen distances that the disorder affects the Ni-chalcogen interactions. The S–Ni–Se bite angles (92.46(8)°) and 94.3(2)°) though, are quite similar to those found in Ni(dppe)(SC₆H₄O) (94.3(2)°) [2] and Ni(dppe)(SC₆H₄S) (92.4(1)°) [3]. All other bond parameters of **6** are comparable with literature values. The crystal structure thus allows a complete characterisation of the complex and hence a basis for the full interpretation of its mass spectrum.

4.2. Electron impact and fast atom bombardment mass spectrometric study

In a previous study we investigated the effectiveness of electron impact (EI) and fast atom bombardment (FAB) ionisation techniques in characterising nickel-thiolate complexes [5]. None of the complexes in that study showed any molecular ions in the EI spectra, whereas the FAB spectra had the molecular ions of the compounds. In the present study, we investigated the complexes that contained ligands with a combination of oxygen, sulfur, selenium or nitrogen bound to the nickel. Our general observation was that most of the complexes with sulfur as one of the two binding atoms gave molecular ions when either EI or FAB was used. Three of the complexes studied (4, 5 and 7), with sulfur containing ligands, gave no molecular ions in the EI mode. Two of these, 4 and 7, readily lost CO₂ even in the FAB mode (Fig. 2), and could explain why the harsh EI source produced no molecular ions. Complex 5 was found to be unstable in solution [2] and came as no surprise when the EI spectrum had no molecular ion. In addition to complexes 4, 5 and 7, two other complexes (8 and 9) had no molecular ions. However, all complexes had molecular ions when the softer FAB ionisation method was used.

The dithiolato complexes, **1a** and **1b**, were observed to be the most stable with EI ionisation. They gave molecular ions of relative intensities of 60% and 75% respectively. The mixed ligands, sulfur/selenium and sulfur/oxygen, were observed to have molecular ions with 50% intensities. A typical fragmentation pattern for this type compounds is shown by the mixed sulfur/selenium compound (Fig. 3 and Scheme 1). Apart from the molecular ion, there was an ion at m/z = 596, which was assigned to the more stable Ni(dppe)(SC₆H₄S). Since this product was found only in the EI spectrum, it must have resulted from the rearrangement of **6** in the ionisation chamber. Other



Fig. 2. FAB mass spectrum of complex 4.

fragment ions resulting from the molecular ions or the ions therefrom were also observed in the EI spectrum. These have been provisionally assigned ionic structures as: $[(dppe)S]^+ (m/z=430), [dppe]^+ (m/z=398), [(ppe)S]^+ (m/z=353)$ (ppe=phenylphosphinoethane), $[PPh_3]^+ (m/z=262)$ and sequential loss of phenyl groups (Ph₂P m/z=183 and Ph m/z=77). Both the EI and FAB spectra of these complexes show that they are dominated by fragmentation of the dppe ligand.

5. Conclusions

The stability of the bis(diphenylphosphino)nickel(II) complexes described above depend on the nature of the chalcogen. This appears to be determined by the size of the chalcogen atom and hence the atom's effective overlap with the nickel. The small oxygen and the larger selenium and tellurium atoms form less stable complexes compared to the sulfur ones. The stability of mixed oxo/sulfur and



Fig. 3. EI mass spectrum of complex 6.

sulfur/selenium ligand complexes is quite good compared to the homoleptic oxo or selenium analogues.

Mass spectrometry is a simple and quick measure of the stability of these complexes. The more stable ones give molecular ions with the EI ionisation method, whilst the less stable compounds could only give molecular ions with the softer FAB ionisation method.

Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number ccdc 114534.

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References

- P.S. Jarret, O.M.N. Dhudhgail, P.J. Sadler, J. Chem. Soc., Dalton Trans. (1993) 1863.
- [2] M.S. Thomas, J. Darkwa, Polyhedron 17 (1998) 1811.
- [3] J. Darkwa, Inorg. Chim. Acta 257 (1997) 137.
- [4] G.A. Bowmaker, P.W.D. Boyd, G.K. Campbell, Inorg. Chem. 21 (1982) 203.
- [5] J. Darkwa, E.Y. Osei-Twum, L.A. Litorja Jr., Polyhedron 18 (1999) 1115.
- [6] D.M. Giolando, T.B. Rauchfuss, A.L. Rheingold, Inorg. Chem. 26 (1987) 1636.
- [7] G.M. Sheldrick, SADABS, An Empirical Absorption Correction, private communication to subscribers of the Siemens CCD e-mail list.
- [8] G.M. Sheldrick, SHELXS-96, Program for Solving Crystal Structures, Universitat Gottingen, Germany, 1996.
- [9] G.M. Sheldrick, SHELXS-96, Program for the Refinement of Crystal Structures, Universitat Gottingen, Germany, 1996.
- [10] L.J. McCaffery, W. Henderson, B.K. Nicholson, J.E. Mackay, M.B. Dinger, J. Chem. Soc., Dalton Trans. (1997) 2577.
- [11] S.P. Kaiwar, J.K. Hsu, L.M. Liable-Sands, A.L. Rheingold, R.S. Pilato, Inorg. Chem. 36 (1997) 4234.
- [12] D.J. Sandman, G.W. Allen, J.C. Acampora, J.C. Stark, S. Jansen, M.T. Jones, G.J. Ashwell, B.M. Foxman, Inorg. Chem. 26 (1987) 1664.
- [13] R. Curran, J.A. Cunningham, R. Eisenberg, Inorg. Chem. 9 (1970) 2749.
- [14] M. Bonamico, G. Dessey, J. Chem. Soc., Dalton Trans. (1971) 264.
- [15] J. Darkwa, R.M. Moutloali, T. Nyokong, J. Organomet. Chem. 564 (1998) 37.