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Effect of selenium substituents on the formation of mononuclear and dinuclear selenolato nickel(II) complexes. X-ray structure of Ni(dtc)(PPh₃)(SeC₆H₅)⁻¹

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Abstract

Mononuclear and dinuclear nickel complexes, Ni(dtc)(PPh₃)(SeR) (dtc = diethyldithiocarbamate; $R = C_6H_5$, C_6H_4Cl-4) and [Ni(dtc)- $(\mu-SeR')$]₂ ($R' = CH_3$, $CH_2C_6H_5$), were prepared by treatment of Ni(dtc)(PPh₃)Cl with organoselenolate salts. Reactions of Ni(dtc)(PPh₃)(SeR) with one equivalent of sulfur gave the dimeric complexes [Ni(dtc)(μ -SeR)]₂ and SPPh₃. The mononuclear nature of Ni(dtc)(PPh₃)(SeC₆H₅) was established by X-ray crystallography. The complex crystallises in the monoclinic space group $P2_1/n$ with cell dimensions a = 15.047(4), b = 10.286(2), c = 19.475(5) Å, $\beta = 109.84(2)^\circ$, V = 2835(1) Å³ and Z = 4.

Keywords: Crystal structures; Nickel complexes; Organoselenium complexes

1. Introduction

The metalloenzymes that catalyse the reversible two-electron oxidation of dihydrogen, hydrogenases, are known to contain Fe, Ni and S in the most common class [1] and Fe, Ni and Se in another class [2]. Considerable attention has been focused on the synthesis of model compounds of these metalloenzymes in an effort to understand the chemistry involved in the hydrogenases reaction, resulting in the isolation of a number of nickel thiolato complexes. Some of these compounds have high nuclearity as exemplified by $[Ni_3(\mu-S)o-\{SCH_2\}_2C_6H_4)_3]^{2-}$ [3], $Ni_4(\mu-SC_5H_9NMe)_8$ [4] and $Ni_6(SR)_{12}$ (R = (CH₂)₃NMe [5] or (CH₂)₃NHMe₂ [6]).

Formation of mononuclear thiolato complexes of the Group 10 elements appears to be controlled by the sulfur atom. For example monomeric complexes of the type $M(SR)_2L_2$ (M=Ni and Pd) are only known when L is an akyl-substituted monodentate phosphine [7]. In addition to the nature of the phosphine ligand, discrete thiolato complexes are predominant for thiolate ligands containing elec-

tron withdrawing groups that decrease electron density on the S atom. The role electron density plays in complex formation is amply illustrated by our synthesis of [Ni(dtc)- $(\mu$ -SR)]₂ (R = CH₂CH₃, C(CH₃)₃, C₆H₅, C₆H₄CH₃-4) [8] and earlier work by others on [Ni(S₂CSR')(μ -SR')]₂ (R' = CH₂CH₃, CH₂C₆H₅) [9], where high electron density on the sulfur containing ligands lead to dative bond formation with a second nickel atom. Apart from the electron density on the sulfur atom itself, if the organic substituent is electron releasing it increases the electron density on the sulfur and hence the propensity to form multinuclear compounds.

From the above account, it is apparent that the key to synthesising discrete nickel compounds with organochalcogenato ligands could be fine tuning the factors that determine electron density on the chalcogen atom. We report here how the choice of organochalcogenide ligands leads to the formation of mononuclear or dinuclear nickel complexes.

2. Experimental

2.1. Materials and instrumentation

All solvents were of analytical grade and were used without further purification. The selenium compounds were purchased from Aldrich and used as received. Ni(dtc)(PPh₃)Cl was prepared by the literature procedure [10], and reactions

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were performed under a nitrogen atmosphere but worked-up in air.

IR spectra were recorded on a Pye Unicam SP3-300S or a Mattson Polaris FT-IR. ¹H and ¹³C NMR were recorded on a Bruker AC300 MHz, ³¹P NMR on a Jeol FX 90Q and referenced to residual CHCl₃ for ¹H (δ 7.26) and ¹³C (δ 77.0) and to 85% H₃PO₄ for ³¹P. Thermal analyses were performed on a Dupont TA 2000 and elemental analyses by CHN Analysis, Ltd., Leicester, UK.

2.2. Reaction of $Ni(dtc)(PPh_3)Cl$ with benzeneselenol: formation of $Ni(dtc)(PPh_3)(SeC_6H_5)$

To a solution of Ni(dtc)(PPh₃)Cl (1.00 g, 2.03 mmol) and $HSeC_6H_5$ (0.31 ml, 2.07 mmol) in toluene (100 ml) was added Et₃N (2 ml). The purple solution immediately turned greenish brown and was stirred for 1 h. The mixture was evaporated to dryness and the resultant residue recrystallised from CH₂Cl₂/hexane to give brown crystals of Ni(dtc)- $(PPh_3)(SeC_6H_5)$ (1.0 g, 79% yield). Anal. Calc. for C₂₉H₃₀NPS₂SeNi: C, 55.70; H, 4.84; N, 2.24. Found: C, 56.29; H, 4.92; N, 2.21%. ¹H NMR, CDCl₃: 7.71 (m, 6H, PPh_3 ; 7.53 (d, $J_{HH} = 6.81$ Hz, 2H, SeC_6H_5); 7.40 (m, 9H, PPh_3 ; 7.02 (m, 3H, SeC_6H_5); 3.46 (q, 4H, dtc); 1.07 (t, 6H, dtc). ${}^{13}C{}^{1}H$ NMR: 140.2s, 137.6s, 134.3 (d, $J_{\rm CP} = 12.28$ Hz), 128.1 (d, $J_{\rm CP} = 9.47$ Hz) (PPh₃); 136.1s, 130.1s, 127.4s, 124.6s (SeC_6H_5); 42.9s, 12.3s (dtc). ${}^{31}P{}^{1}H{}$ NMR: 27.5s (PPh₃). IR (KBr pellet, cm⁻¹): 2982w, 2969w, 2860w, 1571m, 1518s, 1432s, 1356m, 1276s, 1206m, 1151m, 1096s, 1073s, 996m, 911m, 850s, 777m, 743vs, 691vs, 530vs, 508vs, 943vs, 455s, 431m.

2.3. Reaction of Ni(dtc)(PPh₃)Cl with diphenyldiselenide and NaBH₄: formation of Ni(dtc)(PPh₃)(SeC₆H₅)

To a mixture of Ni(dtc)(PPh₃)Cl (1.00 g, 2.03 mmol), diphenyldiselenide (0.32 g, 1.02 mmol) and NaBH₄ (0.10 g, 2.64 mmol) was added degassed MeOH (150 ml). After stirring for 24 h the solvent was removed in vacuo and the brown residue obtained extracted with toluene until the extract was colourless. The toluene solution was evaporated to dryness and the residue recrystallised from CH₂Cl₂/hexane to give Ni(dtc)(PPh₃)(SeC₆H₅) (0.80 g, 63% yield). The analytical data of this product was similar to that from the benzeneselenol reaction.

The reactions of Ni(dtc)(PPh₃)Cl with other diorganodiselenide compounds and NaBH₄ were performed, using 1.0 g of Ni(dtc)(PPh₃)Cl and the appropriate amount of the diorganodiselenide in a 2:1 mole ratio, and worked-up in a similar manner. The analytical data are summarised below for each product.

2.4. $Ni(dtc)(PPh_3)(SeC_6H_4Cl-4)$

Yield 0.67 g, 50%. *Anal*. Calc. for C₂₉H₂₉ClNPS₂SeNi: C, 52.79; H, 4.43; N, 2.12. Found: C, 52.58; H, 4.57; N, 2.44%.

¹H NMR, CDCl₃: 7.75 (m, 6H, PPh₃); 7.40 (m, 9H, PPh₃); 6.94 (br, 4H, SeC₆H₅); 3.57 (q, 4H, dtc); 1.19 (t, 6H, dtc). ¹³C{¹H} NMR: 140.2s, 138.8s, 134.3 (d, J_{CP} =11.24 Hz), 128.1 (d, J_{CP} =9.35 Hz) (PPh₃); 131.5s, 130.2s, 127.4s (SeC₆H₄Cl-4); 43.0s, 12.3s (dtc). ³¹P{¹H} NMR: 27.4s (PPh₃). IR (KBr pellet, cm⁻¹): 2971w, 2969w, 2869w, 1569m, 1522s, 1432s, 1277s, 1205m, 1148m, 1085s, 1008s, 912m, 850s, 818s, 743vs, 629vs, 527vs, 508vs, 491vs.

2.5. $Ni(dtc)(\mu$ -SeCH₂C₆H₅)]₂·1/2CH₂Cl₂

Yield 0.50 g, 66%. *Anal.* Calc. for $C_{24}H_{35}N_2S_4Se_2Ni_2$: C, 36.94; H, 4.43; N, 3.51. Found: C, 36.96; H, 4.63; N, 3.80%. ¹H NMR, CDCl₃: 7.01 (m, 5H, SeCH₂C₆H₅); 5.35 (s, CH₂Cl₂); 3.57 (q, 4H, dtc); 2.97 (s, 2H, SeCH₂C₆H₅); 1.22 (t, 6H, dtc). ¹³C{¹H} NMR: 139.5s, 129.1s, 128.4s, 126.5s (SeCH₂C₆H₅); 43.8s (dtc); 24.0s (SeCH₂C₆H₅); 12.3s (dtc). IR (KBr pellet, cm⁻¹): 2972w, 2921w, 1518m, 1437s, 1352m, 1276s, 1205m, 1151m, 1076s, 992m, 911m, 850s, 757m, 740m, 696s, 605w, 453w.

2.6. $[Ni(dtc)(\mu-SeCH_3)]_2$

Yield 0.25 g, 41%. *Anal.* Calc. for $C_{12}H_{26}N_2S_4Se_2Ni_2$: C, 23.94; H, 4.35; N. 4.65. Found: C, 24.25; H, 4.36; N, 4.74%. ¹H NMR, CDCl₃: 3.59 (q, 4H, dtc); 1.20 (t, 6H, dtc); 1.10 (s, 3H, SeCH₃). ¹³C{¹H} NMR: 43.8s, 12.4s (dtc); -1.40s (SeCH₃). IR (KBr pellet, cm⁻¹): 2970w, 2916w, 1517vs, 1435s, 1354m, 1278s, 1205m, 1152m, 1077s, 989m, 889m, 847s, 775m, 608w, 543w, 463w.

2.7. Reaction of $Ni(dtc)(PPh_3)(SeR)$ ($R = C_6H_5$, C_6H_4Cl-4) with elemental sulfur: formation of $[Ni(dtc)(\mu-SeR)]_2$

In a typical reaction Ni(dtc)(PPh₃)(SeC₆H₅) (0.25 g, 0.40 mmol) and elemental sulfur (0.013 g, 0.05 mmol) in degassed toluene (30 ml) were stirred at room temperature for 24 h. The brown solution gradually turned green. The mixture was filtered to remove a small amount of a black insoluble solid and about 75 ml of hexane were added to the green filtrate and cooled at -15° C to give a fluffy green solid of [Ni(dtc)(μ -SeC₆H₅)]₂ (0.06 g, 52% yield). ¹H NMR, CDCl₃: 7.80 (s, br); 7.02 (s, br) (SeC₆H₅); 3.55 (br); 1.57 (br) (dtc). ¹³C{¹H} NMR: 137.3s, 128.2s (SeC₆H₅); 43.7s, 12.4s (dtc). IR (KBr pellet, cm⁻¹): 2972w, 2929w, 2869w, 1523vs, 1439vs, 1353s, 1277vs, 1206s, 1154m, 1077m, 992m, 912m, 850m, 780s, 733m, 686m, 490w, 464w.

2.8. $[Ni(dtc)(\mu - SeC_6H_4Cl-4)]_2$

Yield 0.14 g, 77% yield. ¹H NMR, CDCl₃: 7.20 (s, br) (SeC₆H₄Cl-4); 3.44 (br), 1.12 (br) (dtc). ¹³C{¹H} NMR: 136.3s, 127.2s (SeC₆H₄Cl-4); 43.7s, 12.3s (dtc). IR (KBr pellet, cm⁻¹): 2972w, 2928w, 2869w, 1565w, 1516vs, 1439vs, 1353s, 1276vs, 1206s, 1152s, 1077s, 992s, 912s, 850s, 815m, 780m, 736m, 726m, 572w, 491s.

2.9. Crystal structure determination of $Ni(dtc)(PPh_3)(SeC_6H_5)$

Single crystals of Ni(dtc)(PPh₃)(SeC₆H₅) were obtained by layering a CH₂Cl₂ solution with hexane and cooling the solution at -15° C.

2.9.1. Crystal data

Ni(dtc) (PPh₃) (SeC₆H₅), C₂₉H₃₀NPS₂SeNi, crystal size $0.60 \times 0.42 \times 0.38$ mm, M = 625.32, monoclinic, space group $P2_1/n$, a = 15.047(4), b = 10.286(2), c = 19.475(5) Å, $\beta = 109.84(2)^\circ$, V = 2835(1) Å³, F(000) = 1280, Z = 4, $D_c = 1.46$ g cm⁻³, μ (Mo K α) = 20.6 cm⁻¹.

2.9.2. Data collection and refinement

Reddish-brown crystals were mounted on glass fibre for data collection. All geometric and intensity data were taken from this sample using an automated four-circle Nicolet R3mV diffractometer equipped with Mo K α radiation $(\lambda = 0.71073 \text{ Å})$. The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 31 reflections taken from a rotation photograph and centred by the diffractometer. The ω -2 θ technique was used to measure 5501 reflections (4987 unique) in the range $5 \le 2\theta \le 50^\circ$. Three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarisation effects, and an empirical absorption correction was applied. The 3856 unique data with $I \ge 3.0\sigma(I)$ were used to solve and refine the structure in the monoclinic space group $P2_1/n$.

2.9.3. Structural analyses and refinement

The structure was solved by Patterson methods and developed by using alternating cycles of least-squares refinement and difference-Fourier synthesis. The non-hydrogen atoms were refined anisotropically while hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter (U=0.08 Å²). The final cycle of least-squares refinement included 316 parameters for 3856 variables and did not shift any parameter by more than 0.006 times its standard deviation. The final *R* values were 0.0350 and 0.0370, and the final difference-Fourier was featureless with no peaks greater than 0.35 e Å⁻³. Structure solution used the SHELXTL PLUS program package on a microVax II computer [11]

3. Results and discussion

3.1. Mononuclear nickel(II) complexes

When mixtures of Ni(dtc)(PPh₃)Cl, RSeSeR (R = C_6H_5 and C_6H_4Cl-4) and NaBH₄ in MeOH were stirred overnight at room temperature, moderate yields of brown microcrystalline Ni(dtc)(PPh₃)(SeR) were obtained (Eq. (1)).

$$2Ni(dtc)(PPh_3)Cl + RSeSeR + 2NaBH_4$$

$$\rightarrow 2Ni(dtc)(PPh_3)(SeR) + 2NaCl + B_2H_6 + H_2 \quad (1)$$

The role of NaBH₄ is to generate NaSeR in situ, which subsequently reacts with the nickel starting material to form the products. The phenylselenolato complex, Ni(dtc)-(PPh₃)(SeC₆H₅), could also be prepared by the reaction of Ni(dtc)(PPh₃)Cl and benzeneselenol in the presence of Et₃N (Eq. (2)).

$$Ni(dtc)(PPh_3)Cl+HSeC_6H_5+Et_3N$$

$$\rightarrow$$
Ni(dtc)(PPh₃)(SeC₆H₅)+Et₃NHCl (2)

The ¹H NMR spectrum of $Ni(dtc)(PPh_3)(SeC_6H_5)$ showed a triplet and a quartet, respectively, for the CH₃ and CH₂ functionalities of the dtc ligand. In the phenyl region, peaks assignable to both the SeC_6H_5 and PPh₃ ligands were observed. However, in addition to these peaks a triplet and a quartet at 1.20 and 3.56 ppm, respectively, a multiplet at 7.06 ppm together with a doublet at 7.90 ppm were observed as well. These latter sets of peaks were relatively small in intensity and represent a small amount of a second product which could not be separated from the main product, Ni(dtc)- $(PPh_3)(SeC_6H_5)$. The fact that these peaks were found for the products obtained from the two synthetic routes as per Eqs. (1) and (2), discounts the possibility of Et_3NHCl contamination by the latter route. The presence of all three ligands in Ni(dtc)(PPh₃)(SeC₆H₅), identified by IR and ¹H NMR spectra, was confirmed by ¹³C and ³¹P NMR. In contrast, the ¹H NMR of Ni(dtc)(PPh₃)(SeC₆H₄Cl-4) showed only one set of peaks assignable to dtc, PPh₃ and the selenolato ligand. The implications of these spectral differences between $Ni(dtc)(PPh_3)(SeC_6H_5)$ and $Ni(dtc)(PPh_3)$ - (SeC_6H_4Cl-4) will be discussed later.

A structure consistent with the spectroscopic data and the monomer formulation was confirmed by X-ray crystallography. The molecular structure of Ni(dtc)(PPh₃)(SeC₆H₅) is presented in Fig. 1 and some relevant bond distances and angles in Table 1. Atomic coordinates are given in Table 2. The geometry around the nickel atom is distorted square planar. The major deviation from square planar geometry is the S(1)-Ni-S(2) angle of 78.(1)°. The S(1), S(2), P and Se atoms deviate from planar coordination up to 0.055(2) Å. This results in an angle of $4.2(1)^{\circ}$ between the planes defined by the atoms S(1), S(2), Ni and P(1), Se, Ni. The Ni–S bond distances are normal and very similar to the Ni-S distance in Ni(dtc)₂ (2.205(1) Å) [12]. The Ni–Se bond distance of 2.292(1) Å is also comparable to those found for the terminal Ni–Se bonds in $[Ni(\mu-SeC_6H_5)(SeC_6H_5)-$ (MePhen)]₂ (2.340(2) Å) [13] and in $(\eta^5-C_5H_5)$ - $Ni(PPh_3)(SeC_6H_5)$ (2.303(1) Å) [14], but are shorter than the terminal Ni-Se distances in Ni(terpy)(2,3,6- $(CH_3)_3C_6H_2Se_2$ (2.440(3) Å) [15] and Ni(dapa)- $(SeC_6H_5) \cdot CH_3CN$ (dapa = 2,6-bis[1-(phenylimino)ethyl]pyridine) (2.420(1) Å) [15]. However the Ni–P dis-



Fig. 1. Crystal structure of Ni(dtc)(PPh₃)(SeC₆H₅).

Table I	
Selected bond distances and bond	angles for Ni(dtc)(PPh ₃)(SeC ₆ H ₅)

Bond distances (Å)							
Ni(1) - P(1)	2.178(1)	Ni(1)-Se(1)	2.292(1)				
Ni(1)-S(1)	2.208(1)	Ni(1)-S(2)	2.219(1)				
P(1)-C(21)	1.832(4)	P(1)-C(31)	1.817(4)				
P(1)-C(41)	1.820(4)	Se(1)-C(31)	1.922(3)				
S(1)-C(1)	1.720(4)	S(2)-C(1)	1.712(3)				
N(1)-C(1)	1.307(5)	N(1)-C(2)	1.471(5)				
N(1)-C(4)	1.473(5)						
straddle.Bond angles (°)							
P(1)-Ni(1)-Se(1)	91.7(1)	P(1)-Ni(1)-S(1)	171.8(1)				
Se(1)-Ni(1)-S(1)	96.3(1)	P(1)-Ni(1)-S(2)	93.4(1)				
Se(1)-Ni(1)-S(2)	173.9(1)	S(1)-Ni(1)-S(2)	78.7(1)				
Ni(1)-P(1)-C(21)	118.3(1)	Ni(1)-P(1)-C(31)	108.0(1)				
Ni(1)-P(1)-C(41)	116.2(1)	Ni(1)-Se(1)-C(6)	108.4(1)				
Ni(1)-S(1)-C(1)	85.4(1)	Ni(1)-S(2)-C(1)	85.3(1)				
S(1)-C(1)-S(2)	109.8(2)						

tance of 2.178(1) Å varies slightly from that observed in $(\eta^5-C_5H_5)Ni(SeC_6H_5)(PPh_3)$ (2.136(4) Å) [14].

3.2. Dinuclear nickel(II) complexes

When the reaction in Eq. (1) was performed with diorganodiselenides green dimeric products of general formula $[Ni(dtc)(\mu$ -SeR')]₂ were isolated (Eq. (3)).

 $2Ni(dtc)(PPh_3)Cl + R'SeSeR' + 2NaBH_4$

$$\rightarrow [\operatorname{Ni}(\operatorname{dtc})(\mu-\operatorname{SeR}')]_2 + 2\operatorname{NaCl} + \operatorname{B}_2\operatorname{H}_6 + \operatorname{H}_2 \quad (3)$$

In these reactions PPh_3 was isolated as a by-product, after the main products had been filtered off. The benzyl analogue was isolated as a microcrystalline solid, solvated by CH_2Cl_2 . This was established from the ¹H NMR and elemental anal-

Table 2	
Atomic coordinates ($\times 10$) and equivalent isotropic displacement p	aram-
eters $(\text{\AA} \times 10^3)$	

	x	у	Z	$U_{ m eq}$
Ni(1)	4181(1)	1410(1)	1670(1)	31(1)
P(1)	2926(1)	541(1)	884(1)	31(1)
Se(1)	4531(1)	-473(1)	2338(1)	37(1)
S(1)	5370(1)	2560(1)	2394(1)	44(1)
S(2)	4005(1)	3267(1)	1058(1)	48(1)
N(1)	5171(2)	5038(3)	1920(2)	48(1)
C(1)	4901(2)	3826(2)	1805(2)	38(1)
C(2)	5898(4)	5428(4)	2610(3)	76(2)
C(3)	5487(6)	5877(6)	3165(3)	112(4)
C(4)	4755(3)	6061(4)	1376(3)	57(2)
C(5)	5301(5)	6228(6)	869(3)	92(3)
C(6)	5740(2)	-269(3)	3091(2)	34(1)
C(7)	6508(3)	-944(4)	3043(2)	49(2)
C(8)	7369(3)	-905(5)	3627(3)	69(2)
C(9)	7448(3)	-191(5)	4239(3)	69(2)
C(10)	6688(3)	480(5)	4283(2)	59(2)
C(11)	5836(3)	445(4)	3712(2)	44(1)
C(21)	2489(2)	-993(3)	1128(2)	34(1)
C(22)	2469(3)	-2170(4)	787(2)	44(1)
C(23)	2152(3)	-3277(4)	1045(3)	57(2)
C(24)	1834(3)	-3209(5)	1618(3)	62(2)
C(25)	1816(3)	-2024(5)	1947(2)	60(2)
C(26)	2161(3)	-932(4)	1718(2)	47(1)
C(31)	3162(2)	264(3)	41(2)	33(1)
C(32)	3820(3)	-692(4)	34(2)	45(2)
C(33)	4050(3)	-900(5)	-581(2)	56(2)
C(34)	3662(3)	-134(5)	-1187(2)	56(2)
C(35)	3048(3)	835(5)	-1177(2)	57(2)
C(36)	2796(3)	1048(4)	-565(2)	45(1)
C(41)	1849(2)	1506(3)	642(2)	34(1)
C(42)	1054(3)	1154(4)	57(2)	44(1)
C(43)	217(3)	1835(4)	-96(2)	53(2)
C(44)	160(3)	2857(4)	341(3)	56(2)
C(45)	938(3)	3211(5)	936(2)	57(2)
C(46)	1775(3)	2542(4)	1077(2)	44(1)

Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ii} tensor.

ysis. Spectroscopic evidence shows that the only ligands present in these complexes are dtc and SeR'. Based on these data, and supported by elemental analysis, the products of reaction (3) were formulated as $[Ni(dtc)(\mu-SeR')]_2$. Such dimeric compounds are known for $[Ni(S_2CSCH_2C_6H_5)(\mu$ - $SCH_2C_6H_5$]₂ (M = Ni, Pd) [9c], with their structures established by X-ray crystallography. It is conceivable that the intermediate to the dimer is Ni(dtc)(PPh₃)(SeR'), which then loses PPh₃ to give the coordinatively unsaturated 'Ni(dtc)(SeR')', and subsequently dimerising to $[Ni(dtc)(\mu$ -SeR')]₂. Similar observations for the reactions of Ni(dtc)(PPh₃)Cl and alkyl or aryl thiols, leading to the formation of $[Ni(dtc)(\mu-SR)]_2$ (R=CH₂CH₃, C₆H₅ and $C_6H_4CH_3-4$ [8], have been made. In order to investigate that (Ni(dtc)(SeR')) are intermediates to the dimers, $[Ni(dtc)(\mu-SeR')]_2$, we reacted Ni(dtc)(PPh₃(SeR') with elemental sulfur. Treatment of the mononuclear complex, $Ni(dtc)(PPh_3)(SeR')$, with sulfur in 8:1 mole ratio gave the dimers as in Eq. (4).

$$Ni(dtc)(PPh_3)(SeR) + 1/8S_8$$

$$\rightarrow 1/2[\operatorname{Ni}(\operatorname{dtc})(\mu\operatorname{-SeR})]_2 + \operatorname{SPPh}_3$$
 (4)

The olive green solids showed no evidence of PPh₃ in their spectroscopic data as were observed for the SeCH₃ and SeCH₂C₆H₅ analogues. In these two reactions PPh₃ was removed as SPPh₃ and is similar to the observations made for $(\eta^5-C_5H_5)Ni(PPh_3)(SC_6H_5)$ [16] and Ni(dtc)(PPh_3)Cl [17] when reacted with sulfur. It is noteworthy that the ¹H NMR peaks observed for [Ni(dtc)(μ -SeC₆H₅)]₂ are similar to the low intensity peaks found for Ni(dtc)(PPh₃)(SeC₆H₅) (vide supra). This suggests that there is a small amount of [Ni(dtc)(μ -SeC₆H₅)]₂ contamination in the Ni(dtc)-(PPh₃)(SeC₆H₅) isolated; however it is not clear if this is due to an equilibrium between Ni(dtc)(PPh₃)(SeC₆H₅) and [Ni(dtc)(μ -SeC₆H₅)]₂ in solution.

3.3. Thermal gravimetric analysis

Thermolysis of Ni(dtc)(PPh₃)(SeC₆H₅) at a heating rate of 10°C min⁻¹ in a stream of nitrogen, monitored by thermogravimetry, showed no clear cut decomposition pathway. For $Ni(dtc)(PPh_3)(SeC_6H_5)$ the decomposition appeared to be an initial loss of SeC₆H₅. The next two weight changes could not be specifically assigned to any unit of the complex, but similar trends were observed for the thermogram of $Ni(dtc)(PPh_3)(SeC_6H_4Cl-4)$. On the other hand, decomposition of the dimers $[Ni(dtc)(\mu-SeCH_2C_6H_5)]_2$ and $[Ni(dtc)(\mu$ -SeCH₃)]₂ showed loss of dtc. In the case of $[Ni(dtc)(\mu$ -SeCH₃)]₂ the loss of dtc (22.03%) was followed by a combined loss of dtc and SeCH₃ (41.31%). We also observed similar thermograms for $[Ni(dtc)(\mu SeC_6H_5$]₂ and $[Ni(dtc)(\mu - SeC_6H_4Cl-4)]_2$, as were found for the above dimers. This is added evidence to support the dimeric nature of the sulfur reaction products.

It is apparent from the properties of the products isolated that monomer or dimer formation is dependent on the electron density available to the selenium atom and steric effect around the nickel centre. Complexes where the selenium atom is directly attached to aryl groups are monomeric whereas those with alkyl groups are dimers. Mascharak and co-workers have recently shown the importance of steric effect on the aggregation of nickel selenolate complexes, where the less bulky C_6H_5Se forms $[Ni(terpy)(C_6H_5Se)]_2$ but the more bulky $2,4,6-(Me)_{3}C_{6}H_{2}Se$ forms Ni(terpy)((2,4,6-(Me)_{3}C_{6}- $H_2Se)_2$ [13]. On the other hand, decrease in electron density on the nickel could weaken the Ni-PPh₃ interaction in the SeCH₃ and SeCH₂C₆H₅ complexes, since these ligands are electron withdrawing [18]. When PPh₃ was removed from the monomers, increased electron density on the selenium and decreased steric effect led to dimerisation. It is clear that both steric and electronic factors affect the degree of oligomerisation in these complexes. We are currently working on the tellurium analogues of these compounds to establish which of these factors is the dominant one in determining the degree of oligomerisation.

It must be noted that our complexes, which contain dtc and PPh_3 as ancillary ligands, have no biological significance in relation to the chemistry of the hydrogenases enzyme. However, these ancillary ligands to some extent affect the electron density at the nickel centre and hence determine the structure and reactivity of the nickel complexes.

4. Supplementary material

Further crystallographic details can be obtained on request from the Director of the Cambridge Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

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References

- [1] G. Fauque, H.D. Peck, Jr., J.J.G. Moura, B.H. Huynh, Y. Berlier, D.V. Der Vartanian, M. Teixeira, A.E. Pryzybyla, P.A. Lespinat, I. Moura and J. LeGall, *FEMS Microbiol. Rev.*, 55 (1985) 299.
- [2] M. Teixeira, G. Fauque, I. Moura, P.A. Lespinat, Y. Berlier, B. Prickril, H.J. Peck, A.V. Xavier, J. LeGall and J.J. Moura, J. Biochem., 167 (1987) 47.
- [3] W. Tremel, B. Krebs and G. Henkel, Inorg. Chim. Acta, 80 (1983) L31.
- [4] W. Gaete, J. Ros, X. Solans, M. Fon-Altaba and J.L. Brianso, *Inorg. Chem.*, 23 (1984) 39.
- [5] M. Capdevila, P. Gonzalez-Duarte, J. Sola, C. Foces-Foces, F.H. Cano and M. Martinez-Ripoll, *Polyhedron*, 8 (1989) 1253.
- [6] H. Barrea, J. Saudes, M.C. Perucaud and J.L. Brianso, *Polyhedron*, 3 (1984) 969.
- [7] T.B. Rauchfuss, J.S. Shu and D.M. Roundhill, *Inorg. Chem.*, 15 (1976) 2096.
- [8] J. Darkwa, J.M. Frost and L.M. Koczon, Synth. React. Inorg. Met-Org. Chem., 23 (1993) 509.
- [9] (a) A.C. Villa, A.G. Manfredotti, M. Nardelli and C. Pelizzi, J. Chem. Soc., Chem. Commun., (1970) 1322; (b) J.M. Andrews, D. Coucouvanis and J.P. Fackler, Jr., Inorg. Chem., 11 (1972) 493; (c) J.P. Fackler, Jr. and W.J. Zegarski, J. Am. Chem. Soc., 95 (1973) 8566.
- [10] P.L. Maxfield, Inorg. Nucl. Chem. Lett., 6 (1970) 693.

- [11] G.M. Sheldrick, SHELXTL PLUS, an integrated system for refining and display of crystal structures from data, University of Göttingen, Germany, 1986.
- [12] J. Darkwa, unpublished results.
- [13] N. Baidya, B.C. Noll, M.M. Olmstead and P.K. Mascharak, *Inorg. Chem.*, 31 (1992) 2999.
- [14] J. Darkwa, Organometallics, 13 (1994) 4734.

- [15] C.A. Marganian, H. Vazir, N. Baidya, M.M. Olmstead and P.K. Mascharak, J. Am. Chem. Soc., 117 (1995) 1584.
- [16] J. Darkwa, F. Bothata and L.M. Koczon, J. Organomet. Chem., 455 (1993) 235.
- [17] J. Darkwa, W.A.A. Ddamba and L.M. Koczon, Bull. Chem. Soc. Ethiop., 5 (1991) 73.
- [18] M. Sato and T. Yoshida, J. Organomet. Chem., 67 (1974) 395.