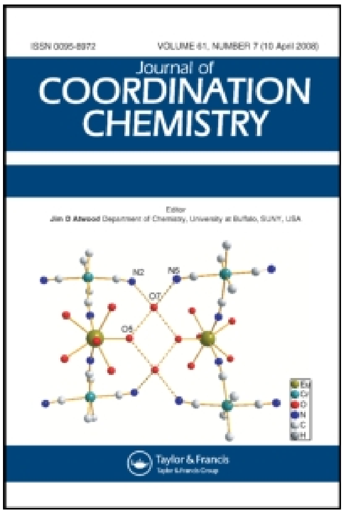

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Nickel(II) complexes with Schiff bases derived from salicylaldehyde or pentanedione and 3-aminopropanethiol

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Nickel(II) complexes with Schiff bases derived from salicylaldehyde or pentanedione and 3-aminopropanethiol

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Template reactions of salicylaldehyde or pentanedione with 3-aminopropanethiol (Hapt) in the presence of Ni(II) ions are described. When salicylaldehyde was used, a dinuclear Ni(II) complex $[Ni(bit')]_2$ (**2**) ($H_2bit' = 2$-(3′-mercaptopropyliminomethyl)phenol) was obtained instead of the reported trinuclear one $[Ni(bit)]_3$ (**1**) ($H_2bit = 2$-(2′-mercaptoethyliminomethyl)-phenol) containing 2-aminoethanethiol (Haet). Starting from pentanedione, the expected dinuclear complex $[Ni(pit')]_2$ ($H_2pit' = 2$-(3′-mercaptopropylimino)pentanol) was not obtained, nor was $[Ni(pit)]_2$ (**3**) ($H_2pit = 2$-(2′-mercaptoethylimino)pentanol). The complex was found to be a trinuclear Ni(II) complex $[Ni\{Ni(apt)_2\}_2]^{2+}$ (**4**), as confirmed by elemental analysis, electronic and NMR spectra. Complexes **1** and **3** were also synthesized and their ^{13}C, ^{1}H–^{1}H and ^{13}C–^{1}H NMR spectra are discussed in detail. The X-ray crystal structure of **2** shows that two Ni(II) ions are connected by the thiolate donor atom from each ligand, resulting in a four-membered ring. Differences in reactivity and properties is due to the presence of an additional methylene group in the aminoalkane arm of the ligand.

Keywords: Template reactions; Aminopropanethiol; Schiff base complexes; Crystal structure; Spectroscopy

1. Introduction

Ni(II) complexes with mixed-ligand environments are of interest because several enzymes contain Ni(II) in the active site with a variety of ligand environments [1, 2]. Nature utilizes metallosulfur clusters to carry out difficult chemistry at ambient temperatures and pressures [3]. Some examples in this regard are the active site of urease which has a dinuclear structure with N and O coordination [4], [NiFe]-hydrogenase

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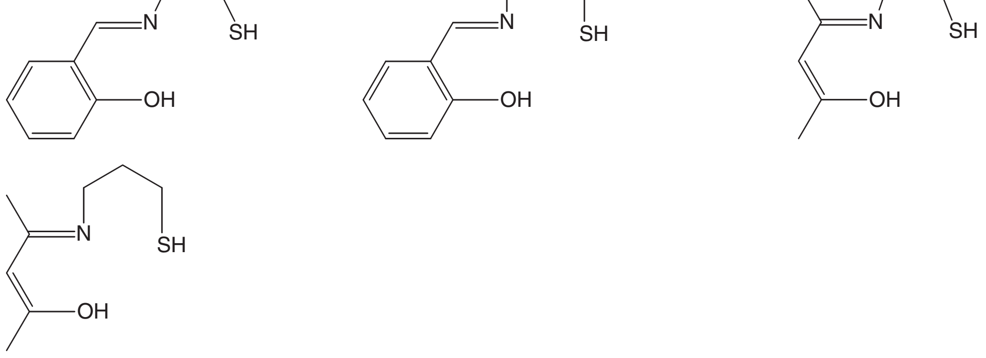
possessing a heterodinuclear structure with double thiolate bridge [5], the enzymes carbon monoxide dehydrogenase (CODH), acetyl-CoA synthase (ACS) and nickel-containing superoxide dismutase with mixed N, O, S environment [6–9]. Structures of several Fe- and [NiFe]-hydrogenases have been discovered [10–13].

Recently, considerable attention has focussed on the synthesis and structural modelling of Ni(II) complexes with a relevant environment to the above nickel-containing enzymes [14–23]. Most synthetic models contain a mixed-ligand environment. It has also been reported that organic sulfur ligands have great significance because their complexes with molybdenum may serve as models for xanthine oxidase and sulfite oxidase [24–26]. Ni(II) complexes with an S_4-donor environment, incorporating two thiolate sulfur donors and two thioether sulfur donors $[Ni(bsms)_2]$ (Hbsms = 4-mercapto-3,3-dimethyl-1-phenyl-2-thiabutane) and [Ni(xbsms)] (H_2xbsms = α,α'-bis(4-mercapto-3,3-dimethyl-2-thiabutyl)-*o*-xylene), have been reported [27]. These complexes are neutral and can bridge with other metals such as iron. Ni(II) complexes of 1,2-dithiolene ligands have been used intensively studied as materials for molecular magnets, conductors and superconductors [28–32]. Moreover the optical limiting behaviour of nickel-dithiolenes has been investigated [33]. Complexes of copper [34], zinc [35], vanadium [36], cobalt [37] and other metals have also been reported.

Metal complexes of Schiff bases are important because of their antibacterial acivity and antitumor properties [38]. Many Ni(II) Schiff base complexes with N, O and S donor ligands have been synthesized. An example is the Schiff base complex of Ni(II) perchlorate with 2,2′-(ethylenedioxy)dibenzaldehydebis(thiosemicarbazone) (L), $[Ni(L)](ClO_4)_2 \cdot 2(CH_3OH)$ [39]. In the case of mixed-ligand environments the presence of both hard N- and soft S-donors results in interesting stereochemical properties, leading to specific coordination selectivity [40]. One such example is Ni(II) complex obtained by reacting the 3-aminopropyl pendant arm derivative of 1-aza-4,7-dithiacyclononane [41].

In this article syntheses of new ligands formed by condensation of salicylaldehyde or pentanedione with 3-aminopropanethiol (Hapt) are described (figure 1). These ligands could act as tridentates and could coordinate through N, O and S donor atoms.



(H_2bit) (H_2bit′) (H_2pit) (H_2pit′)

Figure 1. Ligands formed by condensation of salicylaldehyde or pentanedione with Hapt.

Studies of reactivity of the Ni(II) complexes of aliphatic thiolates are of particular interest, as they are closely related to the chemical environment observed in certain enzymes. It is reported that they are more reactive than aliphatic thiolates and are useful starting materials for mixed nickel-iron complexes. The advantage of a mixed ligand environment is the better control over the tendency towards polymerization with thiolate ligands in combination with metal ions. This can lead to interesting new mononuclear Ni(II) compounds, which could then function as starting materials for structural models of [NiFe]-hydrogenases [20].

2. Experimental

2.1. *Materials and measurements*

All chemicals used for syntheses were obtained from Wako, TCI or the Kanto Chemical Company. Solvents were used without further purification. Elemental analyses (C, H and N) were performed by the Department of Chemistry in the University of Tsukuba. IR spectra were recorded with a Jasco FT/IR-550 spectrophotometer (KBr discs) in the range 4000–400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM600 spectrometer in $CDCl_3$ using TMS as internal reference or D_2O DSS as internal reference. Magnetic measurements were performed using a Sherwood Scientific MSB-AUTO susceptibility balance. Diamagnetism was taken into account by using Pascal's constants [42]. Electronic spectra were recorded with a Jasco V-560 spectrophotometer. All measurements were carried out at room temperature.

2.2. *Syntheses*

2.2.1. 3-Aminopropanethiol hydrochloride (Hapt · HCl). Hapt · HCl was synthesized stepwise from 3-aminopropanol by following methods described in the literature [43–46].

2.2.2. $[Ni(bit)]_3$ (1). This complex was synthesized by a method described in the literature [20].

2.2.3. $[Ni(bit')]_2$ (2). To a solution of sodium ethoxide (0.43 g, 6.3 mmol) in 50 cm^3 of ethanol was added Hapt · HCl (0.80 g, 6.3 mmol) and the mixture stirred at room temperature for 20–30 min. NaCl was removed by filtration, and salicylaldehyde (0.77 g, 6.3 mmol) added to the filtrate. The mixture was stirred at room temperature for 1–2 h and an ethanolic solution of $Ni(CH_3COO)_2 \cdot 4H_2O$ (1.56 g, 6.3 mmol) added. The reddish brown solution was stirred for 1 h at room temperature. A reddish brown powder was isolated by filtration and washed with a little ethanol. Yield: 1.17 g, 36%. Dark red crystals suitable for X-ray analysis were grown from a saturated solution in $CHCl_3$ kept in a refrigerator. Anal. Calcd for $C_{20}H_{22}N_2Ni_2O_2S_2 \cdot H_2O$ (%): C, 46.02; H, 4.63; N, 5.36. Found: C, 45.92; H, 4.46; N, 5.23. IR (cm^{-1}): 2927(w), 1609(s), 1536(s), 1468(m), 1448(s), 1400(m), 1330(s), 1257(w), 1209(m), 1148(m), 1128(m), 1077(m), 1039(m), 936(w), 872(w), 825(w), 801(w), 757(s), 619(m), 462(w), 437(m), 415(w), 404(m).

2.2.4. [Ni(pit)]$_2$ (3). This complex was prepared by following a method in the literature [20] with the exception that the complex was also obtained from the filtrate in pure crystalline form.

2.2.5. [Ni{Ni(apt)$_2$}$_2$]Br$_2$(4Br$_2$) (attempt to prepare [Ni(pit′)]$_2$). To a solution of sodium ethoxide (0.43 g, 6.3 mmol) in 20 cm^3 of ethanol was added Hapt · HCl (0.80 g, 6.3 mmol) and the mixture stirred at room temperature for 20–30 min. NaCl was removed by filtration and 2,4-pentanedione (0.63 g, 6.3 mmol) in 20 cm^3 of ethanol was added to the filtrate. The mixture was heated gently for 15 min and an ethanolic solution of $Ni(CH_3COO)_2 \cdot 4H_2O$ (1.56 g, 6.3 mmol) was added. The mixture was refluxed for 1 h, resulting in a dark red solution. Saturated aqueous KBr was added to give the reddish brown complex, which is soluble in water. Yield: 0.93 g, 21%. The complex was not the expected one, [Ni(pit′)]$_2$, and was confirmed as the trinuclear complex of Ni(II) with apt, [Ni{Ni(apt)$_2$}$_2$]Br$_2$ (4Br$_2$). Anal. Calcd for $C_{12}H_{32}Br_2N_4Ni_3S_4$ (%): C, 20.69; H, 4.63; N, 8.04. Found: C, 20.55; H, 4.66; N, 7.60. IR (cm^{-1}): 2949(m), 1595(s), 1512(s), 1414(s), 1359(w), 1252(m), 1199(m), 1109(m), 1057(w), 1016(s), 923(s), 771(m), 657(m), 564(s), 456(w), 447(w), 420(m), 402(m).

2.3. *X-ray crystallography*

Details of the crystal structure determination are listed in table 1. Data were collected and processed using CrystalClear (Rigaku). Intensity data for **2** were collected on a Rigaku Mercury CCD area detector with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71070$ Å) to a maximum 2θ value of 55° at 296 K. The structure was solved by direct methods (SIR97) [47] and expanded using Fourier techniques (DIRDIF99) [48]. Non-hydrogen atoms except for carbon atoms were refined anisotropically; carbon atoms were refined isotropically. Because of the small size of the crystal, the data obtained were not of high quality though the measurements were repeated on three different samples. Hydrogen atoms were not included in the calculations. The structure was refined by full-matrix least-squares techniques. All calculations were performed using the Crystal Structure crystallographic software package [49].

Table 1. Crystallographic data for **2**.

Empirical formula	$C_{20}H_{22}N_2Ni_2O_2S_2$	D_{Calcd} (g cm^{-3})	1.648
Formula weight	503.93	μ (cm^{-1})	20.79
Dimensions (mm^3)	$0.18 \times 0.05 \times 0.03$	Total	29 526
Crystal system	orthorhombic	Unique	4742
Space group	$Pca2_1$	R_{int}	0.068
a (Å)	11.3958(8)	Used ($I > 3\sigma(I)$)	1466
b (Å)	20.3091(11)	No. variables	154
c (Å)	8.7736(5)	Final R ($I > 3\sigma(I)$)	0.075
Volume (Å^3)	2030.5(2)	Final Rw	0.098
Z	4	Goodness-of-fit	1.002

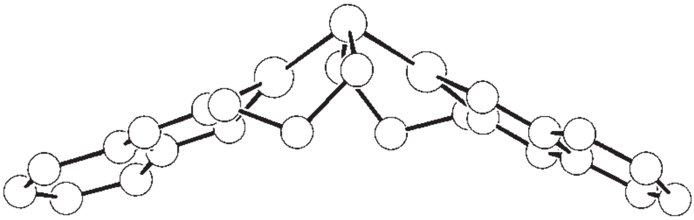
3. Results and discussion

3.1. *Syntheses*

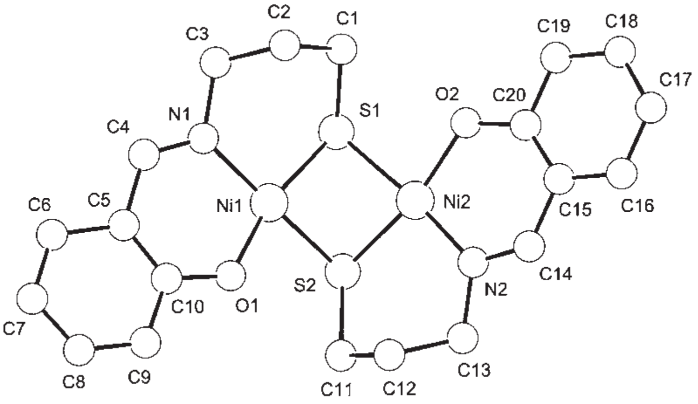
The complexes were synthesized by the template reaction of salicylaldehyde or pentanedione with 3-aminopropanethiol (Hapt) in the presence of Ni(II) ions in alcoholic solution using Schiff base chemistry. Template reaction has advantage that the isolation of the Schiff base ligand with N, O and S donor set is not required and it is obtained as desired in complexes already coordinated to the Ni(II) ion [15, 23]. Complexes **1** and **3** described in this article have also been synthesized before by a template reaction but under slightly different conditions [50] or by the reaction of isolated ligands with Ni(II) ions [51, 52]. Addition of $Ni(CH_3COO)_2 \cdot 4H_2O$ to a mixture of salicylaldehyde and Hapt · HCl in ethanol results in **2**. X-ray analysis showed that a dinuclear complex formed, in contrast with the trinuclear complex in the case of **1** [20]. This shows that the addition of a CH_2 group in the aminoethanethiolate chain affects the resulting complex. On the other hand, similar ligands, for example H^tBuL^1(2-(2-*tert*-butylthiophenyl)benzothiazolidine), gave a mononuclear complex by reacting $[Ni(^tBuL^1)_2]$ with $Ni(CH_3COO)_2 \cdot 4H_2O$ and $[Ni(L^1)]_2$, by the loss of the protecting tertiary butyl group with other Ni(II) salts; while H^tBuL^2(2-(2-*tert*-butylthiophenyl)iminoethylthiol) gave $[Ni(L^2)]_2$ [15]. However, when the reaction was carried out in the presence of acetylacetone following the reaction for the synthesis of **3**, a trinuclear Ni(II) complex with $[Ni(apt)_2]$ terminals, $[Ni\{Ni(apt)_2\}_2]^{2+}$ (**4**), was obtained. This complex was assigned on the basis of elemental analysis, solubility tests, and NMR and IR spectra. The effective magnetic moment μ_{eff} of **2** and **4** showed a low value at room temperature. This is usually observed for low-spin Ni(II) species having square planar geometry. It is thus suggested that the Ni(II) ions adopt square planar geometry in **2** and **4**.

3.2. *X-ray crystallography*

The structure of **2** is shown in figure 2. Selected bond distances and angles are given in table 2. Complex **2** has a dinuclear structure like **3**, in contrast with complex **1**, which was reported to be trinuclear [20]. Similar to **1** and **3**, each nickel centre adopts square planar geometry and is coordinated by one dianionic tridentate-N,O,S ligand, one arm of which forms a sulfur bridged to the second nickel centre. This result is different to $[Ni(L^1)]_2$ and $[Ni(L^2)]_2$ with NS_2 donor ligands in which the nickel centre has a slightly distorted square planar environment [15]. Ni–S distances can be divided into intramolecular (within each [Ni(pit′)] unit) and intermolecular (between the bridging sulfur with the Ni atoms). Intramolecular distances Ni1–S1 and Ni2–S2 (2.166(6) and 2.173(7) Å) are slightly shorter than those found in **1** (2.194(2)–2.201(2) Å) [20], longer than those in $[Ni(L^1)]_2$ and $[Ni(L^2)]_2$ (average 2.130 Å) [15] and comparable to Ni1–S1 distances in **3** (2.165(5) Å) [20]. The intermolecular distances Ni1–S2 and Ni2–S1 (2.219(8) and 2.230(6) Å) are slightly shorter than in **1** (2.216(2)–2.237(3) Å) and slightly longer that those in **3** (2.211(5) Å) [20], $[Ni(L^1)]_2$ and $[Ni(L^2)]_2$ (average 2.21 Å) [15]. These results show that in the dinuclear complex **2** the first set of distances are shorter than the bridging sulfurs, and this trend is similar to that of **1** which is trinuclear in structure [20], $[Ni(L^1)]_2$ and $[Ni(L^2)]_2$ [15]. It can be inferred that the introduction of an additional CH_2 group in the alkanethiolate arm of the ligand



(top view)



(side view)

Figure 2. Perspective views of **2** with the atom labelling scheme.

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

Ni1–S1	2.166(6)	Ni1–S2	2.219(8)
Ni2–S1	2.230(6)	Ni2–S2	2.173(7)
Ni1–O1	1.86(1)	Ni2–O2	1.87(2)
Ni1–N1	1.90(2)	Ni2–N2	1.86(2)
Ni1···Ni2	2.875(4)		
S1–Ni1–S2	77.2(3)	S1–Ni2–S2	76.8(2)
S1–Ni1–O1	166.2(5)	S2–Ni1–O1	91.6(5)
S1–Ni2–O2	88.7(5)	S2–Ni2–O2	164.8(5)
S1–Ni1–N1	97.9(5)	S2–Ni1–N1	171.3(5)
S1–Ni2–N2	173.5(6)	S2–Ni2–N2	99.4(6)
O1–Ni1–N1	94.2(7)	O2–Ni2–N2	95.5(7)
Ni1–S1–Ni2	81.7(2)	Ni1–S2–Ni2	81.8(3)

is responsible for this difference from **1**, and the presence of oxygen instead of sulfur on the benzene ring and the absence of the phenyl ring cause differences from $[Ni(L^1)]_2$ and $[Ni(L^2)]_2$. The distances between the Ni atoms in **2** (2.875(4) Å) are longer than in **3** (2.726(4) Å) [20], $[Ni(L^1)]_2$ (2.697(2) Å) and $[Ni(L^2)]_2$ (2.814(2) Å) [15]. In the case of **1** the distance between Ni atoms was 3.637(19) Å [20]. The Ni1–S1–S2 angle is 113.2(2)° compared to 107.7(2)° in **3** [20]. Moreover, Ni–O distances in **2** (av. 1.860(1) Å) are longer than those in **1** (av. 1.844(6) Å) and **3** (av. 1.833(12) Å). Ni–N distances in **2** (av. 1.880(2) Å) are slightly longer than those in **1** (av. 1.867(6) Å) and comparable to those in **3** (av. 1.887(13) Å). Ni–S–Ni angles in **2** within the molecules (av. 98.65(5)°) are significantly larger than those in **1** (av. 89.9(2)°) and **3** (av. 90.3(4)°). Ni–S–Ni angles in **2** (av. 81.75(2)°) are smaller than those in **1** (av. 117.4(10)°) and larger than those in **3** (av. 77.01(14)°). S–Ni–S angles in **2** (av. 77.0(2)°) are smaller than those in **1** (av. 86.65(9)°) and **3** (av. 79.22(16)°). Differences in bond distances and angles in **2** and **1** are due to the presence of an additional CH_2 group, resulting in a six-membered ring. Differences from **3** are due to the absence of the aromatic ring as well as CH_2 groups in the carbon chain. It can be simply concluded that the size of the chelate rings affect stereochemical properties.

3.3. *Spectroscopic properties*

Complexes **2** and **4** were characterized spectrochemically by IR and NMR methods, and compared with **1** and **3**. Moreover the electronic spectra of **2** and **4** were measured. Results are explained as follows.

3.3.1. IR spectra. The IR spectrum of **2** showed almost the same pattern as that of **1** [20]. OH and SH stretching vibrations around 3290–3260 and 2900–2600 cm^{-1} were absent, showing that the O and S atoms are involved in coordination to Ni(II). Aromatic C–H stretching, aliphatic stretching and C–H bending vibrations were observed. Moreover, strong C=C and C=N stretching bands around 1600 and 1536 cm^{-1} were observed in **2**, respectively. In the case of **4** the C=C band around 1600 cm^{-1} was absent. This is explained by the formation of a trinuclear Ni(II) complex, $[Ni\{Ni(apt)_2\}_2]^{2+}$, as confirmed by elemental analysis, solubility tests (soluble in polar solvents like H_2O, CH_3OH, C_2H_5OH etc.), electronic and NMR spectra. The C–N stretch was noted in the region 1050–1040 cm^{-1} in **2** but was absent in **4**. Similarly C=N stretching was found at 1536 cm^{-1} in **2**, while it was absent in **4**. The IR therefore shows that **2** contains Schiff base ligands while **4** contains only apt ligands. The reason may be due to a difference in reactivity of apt and aet, while in the case of the Schiff base containing aet a dinuclear Ni(II) Schiff base complex was obtained [20].

3.3.2. NMR spectra. ^1H and ^{13}C NMR spectra of **1–4** were measured to assign the signals accurately (table 3). In **2** the ^1H signal for azomethine, HC=N appeared at 7.69 ppm. This is shifted to lower field compared to related complexes of the bit ligand, for example [B(bit)(bitH)] 8.30 [53], $[Zn(bit)]_2$ 8.32 [35], $[MoO_2(bit)]$ 8.20 [54] and [(SalET)Si(bit)] ($SalETH_2$ = salicylaldehyde-2-hydroxoethylimine) 8.50 [37]. The four aromatic protons were observed between 6.15 and 7.19 ppm in agreement with the chemical shifts of aromatic protons in related complexes [35, 36, 38, 53]. N–CH_2 and S–CH_2 protons were observed as broad signals in the region 1.89–3.36 ppm and showed a lower field shift when compared to the related complexes [35, 36, 38, 52]. The CH_2 protons were observed as somewhat broad signals. ^{13}C NMR spectra of **1** showed 9 signals and that of **2** 10 signals, which were assigned based on two-dimensional (^1H–^{13}C) NMR spectroscopy (table 3). In the case of **2** the signals due to C–O and S–CH_2 shifted to higher field as compared to **1** while signals due to N–CH_2 showed a lower field shift. These differences may arise due to the introduction of an additional

Table 3. NMR spectral data and assignments of signals for **1**–**4** (coupling constants/Hz).

	1[a]	**2**	**3**[a]	**4**
^{1}H NMR				
HC=N	7.70 (1H, s)	7.69 (1H, s)		
Aromatic H	7.21 (1H, dt)	7.19 (1H, dt)		
	(1.7, 1.7)	(7.8, 8.0)		
	7.17 (1H, dd)	7.12 (1H, dd)		
	(1.7, 1.7)	(9.7, 10.0)		
	6.84 (1H, d)	6.72 (1H, d)		
	(8.5)	(12.1)		
	6.58 (1H, dt)	6.55 (1H, dt)		
	(7.7, 6.7)	(9.4, 9.5)		
N–CH$_2$	3.78 (1H, d)	3.36 (1H, br[b])	3.70 (1H, dd)	2.90 (2H, t)
	(5.7)	3.36 (1H, br[b])	(5.3, 5.3)	(7.9)
	3.75 (1H, ddt)	3.16 (1H, br[b])	3.16 (1H, dt)	
	3.75 (1H, ddt)	3.16 (1H, br[b])	(4.7, 4.6)	
S–CH$_2$	2.47 (1H, dt)	2.11 (1H, br[b])	2.41 (1H, dt)	1.98 (2H, t)
	(5.8, 6.2)	2.11 (1H, br[b])	(5.8, 5.8)	(6.7)
	1.70 (1H, dd)	1.89 (1H, br[b])	1.60 (1H, d)	
	(5.2, 4.7)	1.89 (1H, br[b])	(4.1)	
CH$_2$		2.26 (1H, br[b])	2.78 (2H, t)	
			(7.1)	
		1.23 (1H, br[b])		
C=HC–C			4.96 (1H, s)	
CH$_3$			1.92 (3H, s)	
			1.84 (3H, s)	
^{13}C NMR				
C=N	163.70	162.43	175.17	
C=O	160.74	163.88	164.32	
Aromatic C	134.07	133.85		
	133.17	132.99		
	121.09	121.17		
	119.72	118.95		
	115.18	114.81		
N–CH$_2$	68.58	62.08	60.43	42.37
S–CH$_2$	27.54	28.82	28.93	28.63
CH$_2$		19.96		31.97
CH$_3$			24.68	
			21.84	

[a] Only the ^{1}H NMR data have been reported.
[b] Broad signal.

CH$_2$ group in **2** to make a six-membered ring. When compared to the corresponding complex [Zn(bit)]$_2$ the complexes show a lower field shift for C=N (166.6 ppm) and a higher field shift for S–CH$_2$ (22.9 ppm) [35]. The ^{13}C NMR spectrum of **3** showed 7 signals and signals in ^{1}H–^{1}H and ^{1}H–^{13}C NMR spectra showed corresponding coupling. ^{1}H and ^{13}C NMR spectra of **4** showed 3 signals. This indicates the formation of a trinuclear Ni(II) complex with apt ligands instead of the expected Schiff base complex.

3.3.3. Electronic spectra. Electronic for **2** and **4** were compared with those previously reported for **1** and **3**. Complex **2** exhibited absorption bands at 509.4, 391.2, 325.8 and 259.4 nm, showing a shift of all bands lower energy as compared to **1** [20]. Since **2** showed a d–d transition band around 500 nm, it is presumed that the Ni(II) ion in the complex is four-coordinate with square planar geometry in solution, as shown by the X-ray crystal structure determination. In the case of **2**, the apt moiety forms a six-membered ring with Ni(II) ion, unlike the five-membered ring in **1**. The presence of an additional CH_2 group may therefore result in somewhat different spectroscopic properties. Complex **4** showed absorption spectra different from **1**–**3** but similar to a trinuclear Ni(II) complex with apt, $[Ni\{Ni(apt)_2\}_2]^{2+}$ [55]. This shows that the expected Schiff base complex is not formed. Again this can be explained due to a difference of reactivity of apt and aet towards diketone and Ni(II).

Supplementary material

IR spectra of **2** and **4** (figure S1); ^1H–^1H COSY (a) and ^1H–^{13}C HMQC (b) NMR spectra of **2** in $CDCl_3$ (figure S2) are available from the authors upon request.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 287870.

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