1 **Revised Version**

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4 **Complexes Based on Asymmetrically Substituted Pyridine-dithiolene Ligands**

5 **[M(*4*-pedt)₂] (M = Au, Cu, Ni; *4*-pedt = 1-(pyrid-4-yl)-ethylene-1,2-dithiolate): Synthesis,**

6 **Structure and Physical Properties.**

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21

22   **Abstract**

23   The monoanionic Ni, Au and Cu bis(dithiolene) complexes based on the

24   1-(pyridine-4-yl)-ethylene-1,2-dithiolate were prepared and isolated as $[PPh_4]^+$, $[n\text{-}Bu_4N]^+$ and

25    $[Na(18c6)]^+$ salts which were characterised by single-crystal X-ray diffraction, cyclic

26   voltammetry, EPR and magnetic susceptibility measurements. All the complexes adopt a

27   square planar coordination geometry with a trans arrangement of the substituent pyridine

28   rings whose planes are rotated from 13º to 33º relatively to the central MS_4 core. The C-C and

29   C-S bond lengths are consistent with ene-1,2-dithiolate form of the ligand and M^{III} oxidation

30   state. The Ni complexes are paramagnetic with an effective magnetic moment of ~1.7 BM .

31

32   **Introduction**

33   Transition metal bis(dithiolene) complexes have attracted research attention for more than 30

34   years and, due to their rich redox behaviour and favourable solid state interactions in their

35   square-planar geometry, they have been widely used in the preparation of conducting and

36   magnetic materials.[1] These complexes can be seen as inorganic analogues of the

37   corresponding TTF type donors where the transition metal replaces the central C=C bond. The

38   TTF type donors have been at the basis of the large majority of all known molecular

39   conductors and superconductors, and these inorganic analogues offer the additional advantage

40   that depending on the oxidation state and on the transition metal they can be either

41   diamagnetic or paramagnetic with different magnetic moments.

42   Recently there has been an increasing focus of attention on the preparation of donors which,

43   in addition to their electroactive role, can bind directly to transition metals and some TTF

44   derivatives substituted with groups containing N coordinating atoms[2] and their complexes

45   have been recently described.[3] The corresponding inorganic analogues, bis(dithiolene)

46 complexes with ligands bearing nitrogen coordinating groups have been however a lot less

47 explored. Having in mind such type of complexes, we recently focused our interest on

48 bis(dithiolene) complexes based on thio-azo ligands bearing heterocyclic groups and recently

49 described the first neutral Ni bis(dithiolene) complex (formally Ni^{IV}) with alkylpyridyl

50 substituted ligands, Ni(dpesdt)$_2$.[4]

51 Asymmetrically substituted dithiolenes have been significantly less studied in spite of

52 providing also interesting properties[5] namely for magnetic materials[6] and optoelectronics.[7]

53 One example of bis(dithiolene) complexes bearing heterocyclic groups are the M(n-pedt)$_2$

54 complexes (n = 2, 3 or 4), based on the asymmetrically substituted ligand n-pedt = S–

55 C(H)=C(R)–S; R = 4-pyridyl. Ligand 4-pedt was previously presented in a preliminary short

56 report [8]. More recently monoanionic gold bisdithiolene complexes with R = n-pyridyl

57 ligands were also described. [9]

58 In this paper we describe the preparation and characterization of monoanionic [M(4-pedt)$_2$]$^-$

59 complexes of nickel, copper and gold obtained as tetrabutylammonium,

60 tetraphenylphosphonium or sodium 18-crown-6 ether salts.

61

62 **2. Experimental**

63 **2.1. Materials and methods**

64 All manipulations were carried out under anaerobic conditions, unless stated otherwise.

65 Whenever required, the solvents were dried according to the standard literature procedures,[10]

66 freshly distilled, and saturated with nitrogen prior to use. All starting reagents were purchased

67 from commercial sources and used without further purification or synthesised from published

68 methods. The 4-(4-pyridyl)-1,3-dithiol-2-one was synthesised according to literature

69 reports.[8, 11]

70 Elemental analyses of the compounds isolated in theses studies were performed at ITN

71 analytical services using an EA 110 CE Instruments automatic analyzer. Melting points were

72 performed on a Stuart Scientific SMP2.

73

74

75 **2.2. Synthesis**

76 **2.2.1. Tetraphenylphosphonium salt of bis[1-(4-pyridyl)-1,2-ethylenedithiolato]nickel,**

77 **PPh$_4$ [Ni(4-pedt)$_2$] (1):** The 4-(4-pyridyl)-1,3-dithiol-2-one (0.50 g, 2.56 mmol) was added to

78 a sodium methanolate solution (0.147 g; 6.40 mmol; 13 mL) After 45 minutes of stirring,

79 Ni(NO$_3$).6H$_2$O (0.37 g, 1.28 mmol) was added. One hour later the red solution was filtered to

80 an aqueous PPh$_4$Cl solution (0.96 g, 2.56 mmol, 100 mL). A black precipitate appeared

81 immediately from the brown solution. The solid was recovered by filtration, washed with

82 water and recrystallised from acetonitrile to afford black crystals of the nickel salt suitable for

83 X-ray diffraction. 50% yield (0.47 g, 0.64 mmol); m.p. 217-218 ℃. C$_{38}$H$_{30}$NiN$_2$PS$_4$ (Mol.

84 Wt.: 732.59). Elemental Anal. Calc.: C 62.30; H 4.13; N 3.82; S 17.51%. Found: C 62.09;

85 H 4.06; N 3.77; S 17.31%.

86

87 **2.2.2. Tetraphenylphosphonium salt of bis[1-(4-pyridyl)-1,2-ethylenedithiolato]copper**

88 **PPh$_4$ [Cu(4-pedt)$_2$] (2):** The oxo compound (0.10 g; 0.51 mmol) was added to a freshly made

89 sodium methoxide solution (0.023 g; 1.02 mmol, 3 mL) and stirred at room temperature, until

90 total dissolution, followed by drop wise addition of a solution of CuCl$_2$.2H$_2$O (0.043 g;

91 0.25 mmol) in methanol (2 mL). The solution was stirred for one hour and filtered into a

92 PPh$_4$Br methanol solution (0.214 g, 0.51 mmol, 3 mL). No precipitate formation was

93 observed. The reaction vial was opened to the air, a few H$_2$O drops were slowly added until

94　start of incipient precipitation and the mixture was left overnight at 4ºC. The oil that formed

95　was separated from the mixture by centrifugation, dried under vacuum (P_2O_5) and

96　recrystallised from dichloromethane/hexane to be recovered as a microcrystalline precipitate.

97　48% yield (0.089 g, 0.12 mmol); m.p. 162-163 ºC. $C_{38}H_{30}N_2CuS_4$ (Mol. Wt.:737.44).

98　Elemental Anal. Calc.: C, 61.89; H, 4.10; N, 3.80; S, 17.39%. Found: C, 61.72; H, 4.92; N,

99　3.84; S, 18.03%.

100

101　**2.2.3. Tetrabutylammonium salt of bis[1-(4-pyridyl)-1,2-ethylenedithiolato]nickel**

102　**n-Bu$_4$N [Ni(4-pedt)$_2$] (3):** The procedure was similar to the described above. The oxo

103　compound was added (0.10 g; 0.51 mmol) to a freshly made sodium methoxide solution

104　(0.023 g; 1.02 mmol, 3 mL) and stirred at room temperature, until total dissolution, followed

105　by drop wise addition of a solution of $NiCl_2.6H_2O$ (0.061 g; 0.25 mmol) in methanol (2 mL).

106　The red solution was stirred for one hour and then filtered into n-Bu$_4$NBr methanol solution

107　(0.165 g, 0.51 mmol, 3 mL). No precipitate formation was observed. The reaction vial was

108　opened to the air, a few H_2O drops were slowly added until start of incipient precipitation and

109　the mixture was left overnight at 4 ºC. The reddish oil formed was separated from the mixture

110　by centrifugation, dried under vacuum (P_2O_5) and recrystallised from acetone to be recovered

111　as a microcrystalline precipitate. 65% yield (0.105 g, 0.16 mmol); m.p. 133-134 ºC.

112　$C_{30}H_{46}N_3NiS_4$ (Mol. Wt.: 635.66) Elemental Anal. Calc.: C, 56.68; H, 7.29; N, 6.61;

113　S, 20.18%. Found: C, 56.01; H, 7.89; N, 6.12; S, 19.75%.

114

115　**2.2.4.Tetrabutylammonium salt of bis[1-(4-pyridyl)-1,2-ethylenedithiolato]copper,**

116　**n-Bu$_4$N [Cu(4-pedt)$_2$] (4):** Following the same general procedure used for

117　n-Bu$_4$N[Ni(4-pedt)$_2$]. The oxo compound was added (0.10 g; 0.51 mmol) to a freshly made

118　sodium methoxide (0.023 g; 1.02 mmol, 3 mL) stirred until total dissolution, followed by drop

119   wise addition of a solution of $CuCl_2.2H_2O$ (0.043 g; 0.25 mmol) in methanol (2 mL). The

120   solution was stirred for one hour and afterwards filtered onto an *n*-Bu₄NBr methanol solution

121   (0.165 g, 0.51 mmol, 3 mL). No precipitate formation was observed. A few H_2O drops were

122   slowly added until start of incipient precipitation and the mixture was left overnight at 4 ºC.

123   The oil formed was separated from the mixture by centrifugation, dried under vacuum (P_2O_5)

124   and recrystallised from dichloromethane/hexane to be recovered as a microcrystalline

125   precipitate. 41% yield (0.065g, 0.10 mmol); m.p. 160-162 ºC. $C_{30}H_{46}N_3CuS_4$ (Mol. Wt.:

126   640.51) Elemental Anal. Calc.: C, 56.26; H, 7.24; N, 6.56; S, 20.02%. Found: C, 55.83; H,

127   7.01; N, 6.12; S, 19.84%.

128

129   **2.2.5.Tetrabutylammonium   salt   of   bis[1-(4-pyridyl)-1,2-ethylenedithiolato]gold**

130   **n-Bu₄N [Au(*4*-pedt)₂]   (5):**   Following   the   same   general   procedure   used   for

131   *n*-Bu₄N[Ni(*4*-pedt)₂], the oxo compound (0.10 g; 0.51 mmol) was dissolved in a freshly

132   prepared methoxide solution (0.024 mg; 1.02 mmol, 3 mL). The total dissolution of the oxo

133   compound was followed by drop wise addition of a $KAuCl_4.4H_2O$ methanol solution

134   (0.097 g; 0.25 mmol, 2 mL). The brown solution was filtered into an *n*-Bu₄NBr methanol

135   solution (0.165 g, 0.51 mmol, 3 mL). After the addition of a few milliliters of water, the

136   reaction vial was left for several hours at 4 ºC. The brown oil formed was recovered by

137   centrifugation, dried under vacuum (P_2O_5) and recrystallised from dicloromethane/hexane to

138   be recovered as a microcrystalline precipitate. 60% yield (0.115 g, 0.15 mmol); m.p. 127-

139   129 ºC. $C_{30}H_{46}N_3AuS_4$ (Mol. Wt.: 773.93). Elemental Anal. Calc: C, 46.56; H, 5.99; N, 5.43;

140   S, 16.57%. Found: C, 46.21; H, 5.52; N, 5.25; S, 16.39%.

141

142   **2.2.6.Crown   ether   [Na(18c6)]   salt   of   bis[1-(4-pyridyl)-1,2-ethylenedithiolato]nickel**

143   **[Na(18c6)] [Ni(*4*-pedt)₂], (6):** The oxo compound (0.20 g; 1.03 mmol) was added to a freshly

prepared methoxide solution (0.047 g, 2.05 mmol, 5 mL). After stirring until total dissolution, $NiCl_2.6H_2O$ methanol solution (0.122 g; 0.51 mmol, 5 mL) was added. The red solution was stirred for one hour and then filtered into an 18c6 methanol solution (0.271 g, 1.03 mmol, 1 mL). The mixture was left at 4 °C for two weeks. A mixture of amorphous brown and darker polycrystalline precipitate was recovered by vacuum filtration. The mixture was dissolved in dichloromethane and an insoluble precipitate was removed. By slow diffusion of hexane into the dichloromethane solution, it was possible to recover compound **6** as a dark brown polycrystalline material. Yield 0.197 g, 0.29 mmol (58%); m.p. 260-261. $C_{26}H_{34}N_2NaNiO_6S_4$ (Mol.Wt. 680.5)°C. Elemental Anal. . Calc. C 45.89; H 5.04; N 4.12; S 18.85%S. Found: C 45.43; H 5.35; N 4.12; S 18.30%.

2.2.7.Crown ether [Na(18c6)] salt of bis[1-(4-pyridyl)-1,2-ethylenedithiolato] gold [Na(18c6)] [Au(*4*-pedt)$_2$], (7): The oxo compound (0.10 g, 0.51 mmol) was added to a freshly prepared sodium methoxide solution (0.0235 g, 1.02 mmol, 5 ml) and stirred for 45 minutes. The dark red solution was removed from the inert atmosphere and solid $KAuCl_4.4H_2O$ (0.097 g, 0.25 mmol) was added. The mixture was stirred for 2 hours, filtered over Celite to a solution of 18c6 (0.0677 g, 0.25 mmol) in methanol (1 ml) and layered with pentane and left at 4 °C. A few days later, an amorphous brown precipitate was recovered by vacuum filtration. From an attempt to recrystallise from dichloromethane/hexane, an oil was obtained which was dried and characterised. Yield 0.088 g, 0.11 mmol (44%); m.p. 145-146 °C. $C_{26}H_{34}O_6N_2S_4AuNa$ (Mol.Wt. 818.08). Elemental Anal. Calc : C 38.14, H 4.19, N 3.42, S 15.63%. Found: C 38.38, H 4.91, N 3.50, S 15.28%.

168

2.3. Physical characterization

170 Cyclic voltammetry data were obtained using a BAS C3 Cell Stand. The measurements were

171 performed at room temperature in CH_2Cl_2 solutions, containing [n-Bu$_4$] PF$_6$ (0.1M) as

172 supporting electrolyte, with a scan rate of 100 mV/s using platinum wire working and counter

173 electrodes and a Ag/AgCl reference electrode. The [(Me$_5$C$_5$)$_2$Fe]$^+$/[Me$_5$C$_5$)$_2$Fe] ([Fc*]$^+$/[Fc*])

174 couple was used as the internal reference and the potentials of the redox couples observed

175 were referenced to that.

176 Single crystals suitable for X-ray crystallographic analyses were obtained by recrystallisation

177 in acetonitrile, for compound **1**, and by slow diffusion of hexane into a saturated solution of

178 dichloromethane, for compounds **2**, **3**, **5** and **6**. In compound **6** two water molecules were

179 incorporated in the crystal structure to yield compound **6·2H₂O,** due to the presence of air

180 humidity

181 The data for compounds **1, 2, 3, 5** and **6a** were collected on a Bruker AXS APEX CCD area

182 detector X-ray diffractometer equipped with an Oxford Cryosystems low-temperature device

183 at 150 K in the ω and φ scans mode. A semi empirical absorption correction was carried out

184 using SADABS.[12] Data collection, cell refinement and data reduction were done with the

185 SMART and SAINT programs.[13] The structures were solved by direct methods using

186 SIR97[14] and refined by fullmatrix least-squares methods with the SHELXL97[15] program

187 using the winGX software package.[16] Non-hydrogen atoms were refined with anisotropic

188 thermal parameters whereas H-atoms were placed in idealised positions and allowed to refine

189 riding on the parent C atom. In **3** and **5** one of the butyl groups on the cation show disorder

190 that was modelled over two positions with the following occupation factors: 52%:48% and

191 55%:45% respectively. The final difference Fourier map revealed the existence of residual

192 electron densities of: 2.4/-0.89 eA$^{\circ-3}$ for compound **5**, which are located near the Au atom.

193   Molecular graphics were prepared using ORTEP3[17] and Mercury 1.4.2.[18] A summary of the

194   crystal data, structure solution and refinement is listed in Table 1.

195

196

197   Table 1 - Crystallographic data and refinement parameters for complexes $Ph_4P[Ni(4\text{-pedt})_2]$ (**1**), $Ph_4P[Cu(4\text{-pedt})_2]$ (**2**), $n\text{-Bu}_4N[Ni(4\text{-pedt})_2]$ (**3**),

198    $n\text{-Bu}_4N[Au(4\text{-pedt})_2]$ (**5**) and $[Na(18c6)][Ni(4\text{-pedt})_2].2H_2O$ (**6·2H$_2$O**).

Compound	1	2	3	5	6·2H₂O
Formula	$C_{38} H_{30} N_2$ Ni P S_4	$C_{38} H_{30}$ Cu N_2 P S_4	$C_{30} H_{46} N_3$ Ni S_4	$C_{30} H_{46}$ Au $N_3 S_4$	$C_{26} H_{38} N_2$ Na Ni $O_8 S_4$
Formula weight (g mol^{-1})	732.58	737.39	635.65	773.90	712.49
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system, Space group	Monoclinic, $C2/c$	Monoclinic, $C2/c$	Triclinic, P-1	Triclinic, P-1	Monoclinic, $P2_1/n$
a (Å)	26.8750(5)	26.9179(8)	9.0033(2)	8.6211(1)	11.7067(14)
b (Å)	17.3528(3)	17.3541(6)	11.2258(2)	11.1196(2)	9.7243(12)
c (Å)	18.1609(3)	18.1969(5)	16.9070(3)	17.6962(3)	14.3179(18)
α (°)	90	90	107.7870(10)	74.646(1)	90
β (°)	127.5650(10)	127.3820(10)	90.3960(10)	88.829(1)	96.103(2)
γ (°)	90	90	98.3450(10)	80.336(1)	90
V (Å^3), Z	6713.4(2), 8	6754.5(4), 8	1607.48(5), 2	1612.14(4), 2	1620.7(3), 2
ρ_{calc} (Mg/m^3), μ (mm^{-1})	1.450, 0.906	1.450, 0.973	1.313, 0.887	1.594, 4.846	1.468, 0.918
$F(000)$	3032	3040	678	780	750
Crystal size (mm)	0.4 x 0.3 x 0.08	0.30 x 0.20 x 0.16	0.28 x 0.24 x 0.20	0.38 x 0.30 x 0.28	0.20 x 0.12 x 0.10
θ Range (°)	2.83 to 25.03	2.74 to 25.68	3.21 to 25.35	2.64 to 25.68	2.73 to 25.68
Collected hkl	-31≤ h ≤31	-32≤ h ≤32	-10 ≤ h ≤10	-10≤h≤10	-14≤h≤12
	-20≤ k ≤20	-21≤ k ≤21	-13≤ k ≤13	-13≤k≤13	-11≤k≤11
	-21≤ l≤21	-20≤ l≤22	-20 ≤ l≤ 20	-21≤l≤21	-17≤l≤17
Reflections collected	41666	23618	13680	17908	7273
Independent reflections	5910 [R(int) = 0.0424]	6409 [R(int) = 0.0656]	5821 [R(int) = 0.0422]	6122 [R(int) = 0.0306]	3051 [R(int) = 0.0414]
Completeness to θ	25.03 99.7 %	25.68 99.7 %	25.35 98.9 %	25.68 99.7 %	25.68 99.3 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8052 and 0.7133	0.8599 and 0.7590	0.8425 and 0.7893	0.3440 and 0.2603	0.9139 and 0.8378
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5910 / 0 / 418	6409 / 0 / 418	5821 / 6 / 370	6122 / 2 / 370	3051 / 2 / 201
Goodness-of-fit on F^2	1.069	1.049	1.079	1.071	1.035
Final R indices [$I>2\sigma I$)]	$R_1 = 0.0276$, $wR_2 = 0.0711$	$R_1 = 0.0396$, $wR_2 = 0.0868$	$R_1 = 0.0366$, $wR_2 = 0.0899$	$R_1 = 0.0254$, $wR_2 = 0.0590$	$R_1 = 0.0376$, $wR_2 = 0.0791$
R indices (all data)	$R_1 = 0.0341$, w$R_2 = 0.0740$	$R_1 = 0.0644$, $wR_2 = 0.0945$	$R_1 = 0.0482$, $wR_2 = 0.0947$	$R_1 = 0.0401$, $wR_2 = 0.0630$	$R_1 = 0.0659$, $wR_2 = 0.0853$
Larg. diff. peak and hole (e Å^{-3})	0.416 and -0.355	0.422 and -0.473	0.556 and -0.280	2.348 and -0.895	0.392 and -0.502

199

200 EPR spectra were obtained at room temperature on powders using a conventional X-band

201 spectrometer (Bruker ESP 300 E) equipped with a microwave bridge ER041XK, a rectangular

202 cavity operating in T102 mode and a field controller ER 032M system. The modulation

203 amplitude was kept well below the linewidth and the microwave power well below saturation.

204 Static magnetic susceptibility measurements in the range 2-300 K were performed using a

205 superconducting longitudinal Faraday system (Oxford Instruments) under a magnetic field of

206 5 T and field gradient of 1 T/m. A polycrystalline sample (~20 mg) was placed inside a

207 previous calibrated thin-wall Teflon bucket. The force was measured with a microbalance

208 (Sartorius S3D-V), applying forward and reverse field gradients. Magnetisation data were

209 corrected for contributions due to the sample holder and core diamagnetism, estimated from

210 tabulated Pascal constants as -385×10^{-6}, -379×10^{-6} and -348×10^{-6} emu/mol for **1, 3** and **6**

211 respectively.

212

213 **3. Results and Discussion**

214 **3.1. Synthesis**

215 The synthesis of the nickel, copper and gold complexes **1** to **7** were performed following

216 standard procedures for this type of dithiolene ligands (Scheme 1). The dithiolate ligand (**L**)

217 was obtained from the corresponding oxo compound by hydrolytic cleavage with sodium

218 methoxide and without intermediate isolation it was reacted with the selected metal salt to

219 give an anionic complex which is precipitated as a salt in the presence of the selected cation.

220 The presence of water was needed to precipitate the dithiolene complex from the solution. In

221 case of **1,** a water solution of the cation was added and the dithiolene complex precipitated

222 immediately as a black precipitate. In the case of compounds **2, 3, 4** and **5** a few drops of

223 water were added at the end of the reaction until the start of incipient precipitation and after

224   keeping the reaction mixture at 4 ºC it was possible to collect the product as fine precipitate

225   which tends to form an oil. Compounds **6** and **7** were obtained without adding water after

226   keeping the solution a few days at 4 ºC until complexes precipitated. These complexes were

227   obtained after recrystallisation from acetonitrile, acetone or dichloromethane/hexane in

228   overall yields between 41 and 65%.

229   Complexes **1-7** were characterised by elemental analyses and cyclic voltammetry studies. The

230   elemental analyses after the recrystallisations are consistent with a 1:1 cation:anion

231   stoichiometry, in agreement with the X-ray crystal structure determination of the diffracting

232   single crystals. While this is expected for M = Au, for Cu and Ni even though starting from a

233    $Ni^{II}Cl_2$ or $Cu^{II}Cl_2$ salt, the dianionic dithiolene complexes could not be obtained, even under

234   nitrogen atmosphere and the monoanionic dithiolene complexes were obtained as evidenced

235   by the X-ray structure determination or by the electronic paramagnetic resonance (EPR)

236   spectroscopy. Whereas complexes **1**, **2**, **3**, **5** and **6·2H₂O** were unambiguously characterised

237   by single X-ray structure determination, compounds **4, 6** and **7** could not be studied by single

238   X-ray diffraction due to their poor crystal quality.
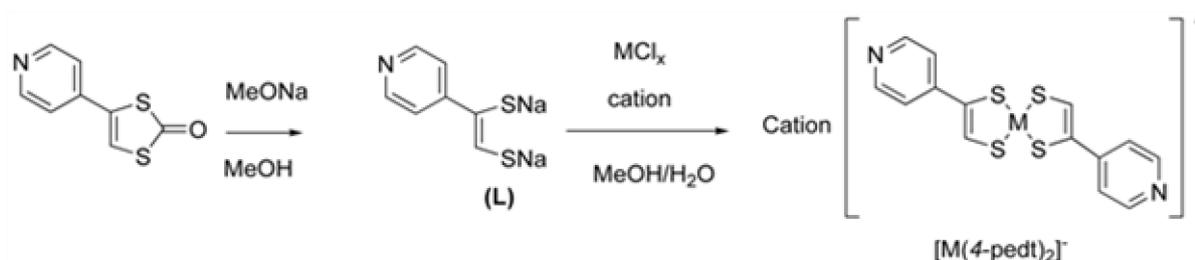
(Ph₄P)[Ni(*4-pedt*)₂] (**1**) η=50%; (Ph₄P)[Cu(*4-pedt*)₂] (**2**) η=48%; (*n*-Bu₄N)[Ni(*4-pedt*)₂] (**3**) η=65%; (*n*-Bu₄N)[Cu(*4-pedt*)₂] (**4**)η=41%;

239   (*n*-Bu₄N)[Au(*4-pedt*)₂] (**5**) η=60%; [Na(18c6)][Ni(*4-pedt*)₂] (**6**) η=58%; [Na(18c6)][Au(*4-pedt*)₂] (**7**) η=44%

240   Scheme 1

241

242

243 **3.2. Crystal Structure**

244 Compounds **1**, **2**, **3, 5** and **6·2H₂O** have been characterised by single crystal X-ray diffraction

245 technique. The ORTEP views of these compounds are shown in Figs. 1-5. Selected bond

246 angles and distances are given in Table 2.
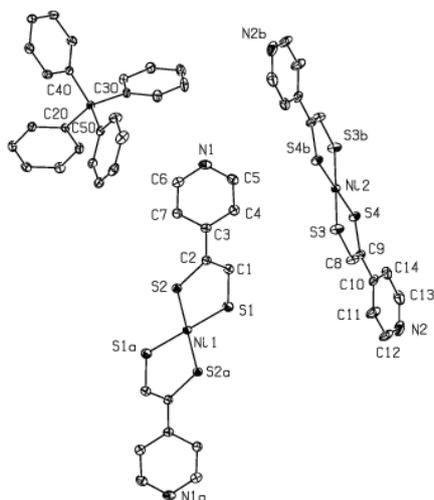
247

248 Figure 1. Ortep views of the cation and the two independent anion units of Ph₄P [Ni(*4*-pedt)₂],

249 (**1**), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30%

250 probability level. H atoms have been omitted for clarity. [Symmetry codes: (a) 2-x, 1-y, 1-z;

251 (b) 1.5-x, 1.5-y, 1-z].
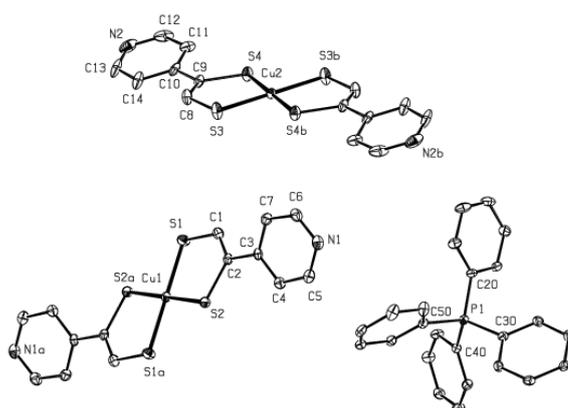
252

253 Figure 2. Ortep views of the cation and the two independent anion units of

254 Ph₄P [Cu(*4*-pedt)₂], (**2**), showing the atomic numbering scheme. Displacement ellipsoids are

255   drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes:

256   (a) 1-x, 1-y, z; (b) 0.5-x, 1.5-y, -z].
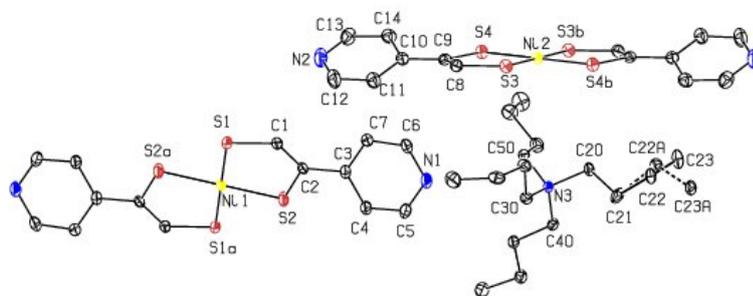
257

258   Figure 3. Ortep views of the cation and the two independent anion units of

259   *n*-Bu$_4$N [Ni(*4*-pedt)$_2$], (**3**), showing the atomic numbering scheme. Displacement ellipsoids

260   are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry

261   codes: (a) -x, -y, -z; (b) 1-x, 1-y, 1-z].
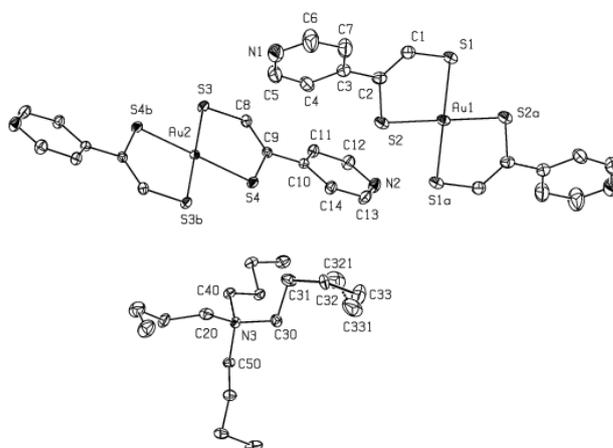
262

263   Figure 4. Ortep views of the cation and the two independent anion units of

264   *n*-Bu$_4$N [Au(*4*-pedt)$_2$], (**5**), showing the atomic numbering scheme. Displacement ellipsoids

265   are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry

266   codes: (a) -x, -y, -z; (b) 1-x, 1-y, 1-z].

267
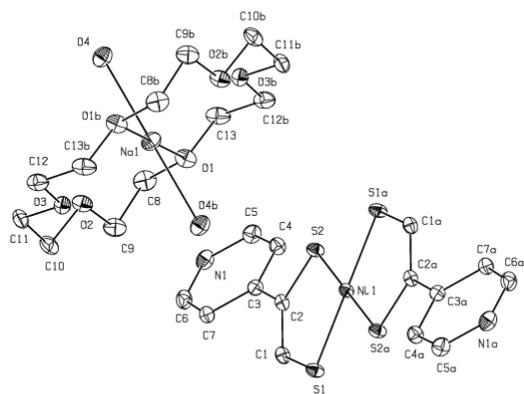
Figure 5. Ortep views of the cation and anion units of [Na(18c6)] [Ni(*4*-pedt)$_2$].2H$_2$O, (**6·2H$_2$O**), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (a) -x, -y, -z; (b) 2-x, 1-y, 1-z].

The monoanionic Ph$_4$P salts **1** and **2** are isostructural and crystallise in the monoclinic system, space group *C2/c*, Z = 8, the asymmetric unit comprising one cation [PPh$_4$]$^+$ located in a general position and two independent half-anions [M(*4*-pedt)$_2$]$^-$; (M = Ni and Cu for compound **1** and **2**, respectively) both with the metals located at an inversion centre. The angle between the two [M(*4*-pedt)$_2$]$^-$ units mean planes is about 49.47º and 49.52º for compound **1** and **2** respectively.

The monoanionic *n*-Bu$_4$N salts **3** and **5** are isostructural and crystallise in the triclinic system, P-1 space group, Z = 2. The asymmetric unit comprising two independent half-anion units; both the metal atoms located at inversion centres and with one cation unit located at a general position. The angle between the anionic units mean planes is about 88.98º and 89.81º for **3** and **5** respectively.

284   The compound **6·2H₂O** crystallises in the monoclinic system, space group $P2_1/n$, $Z = 2$. The

285   asymmetric unit comprises one independent half-anion unit and one independent half-cation

286   unit located at inversion centres.

287   In all complexes, the centrosymmetric anion $[M(4\text{-pedt})_2]^-$ (M = Ni, Cu or Au) adopts a

288   square-planar coordination geometry and a *trans* conformation. The central core of the anions,

289   constituted by the metal atom, the four sulphur atoms and the four carbon atoms, is essentially

290   planar (rms deviation of fitted atoms are 0.0091 Å and 0.0057 Å for compound **1**; 0.0182 and

291   0.0237 Å for compound **2**, 0.0152 Å and 0.0268 Å for compound **3**; 0.0537 Å and 0.0250 Å

292   for compound **5**; 0.0125 Å for compound **6·2H₂O**).

293

294

295   Table 2 - Important bond lengths (in Å) within the metallocycle, the torsion angle ω (in °) between the pyridine group plane and the metallocycle

296   plane and δ-parameter (defined below) for compounds **1, 2, 3, 5** and **6·2H$_2$O**.

297

Compound		1		3		6·2H$_2$O	2		5	
		M = Ni2	M = Ni1	M = Ni1	M = Ni2	M = Ni	M = Cu1	M = Cu2	M = Au2	M = Au1
M-S	(a)	2.1293(5)	2.1507(5)	2.1383(5)	2.1549(6)	2.1375(7)	2.1871(7)	2.1626(7)	2.3078(10)	2.3183(13)
M-S	(a')	2.1474(5)	2.1416(5)	2.1463(6)	2.1478(7)	2.1531(7)	2.1797(8)	2.1812(8)	2.3053(11)	2.3082(11)
S-C	(b)	1.737(2)	1.742(2)	1.739(2)	1.740(3)	1.738(3)	1.771(3)	1.765(3)	1.768(4)	1.771(4)
S-C	(b')	1.715(2)	1.715(2)	1.713(2)	1.715(2)	1.714(3)	1.735(3)	1.740(3)	1.742(4)	1.735(5)
C=C	(c)	1.353(3)	1.351(3)	1.364(3)	1.351(3)	1.354(4)	1.335(4)	1.328(4)	1.345(6)	1.336(6)
C-C	(d)	1.478(3)	1.476(3)	1.474(3)	1.476(3)	1.469(4)	1.481(4)	1.483(4)	1.477(5)	1.476(7)
ω		13.14(6)	28.50(8)	29.51(8)	28.64(7)	33.56(7)	28.92(12)	13.90(8)	21.83(13	33.44(17)
δ		1.26	1.55	1.49	1.44	1.38	2.03	1.42	1.47	2.03

298     $\delta = 100(b-b')/b$

299

300

301   Important bond lengths within the MS_2C_2 metallocycle are collected in Table 2. The average

302   M-S bond lengths are in good agreement with values found in other Ni, Cu and Au

303   monoanionic dithiolate complexes, respectively.[1c),19,20,21] While the central core of the

304   complexes is planar, the two pyridine rings are rotated out of the central core plane with

305   dihedral angles between 13º and 33º depending on the complex, with the majority of them

306   between 21º and 33º, only one of the anionic units in the Ph_4P salts **1** and **2** presents a smaller

307   angle of about 13º. The rotation of the pyridine rings is induced by steric hindrance between

308   hydrogen atoms at the 2-position of the pyridine ring and in the metallocycle carbon but this

309   rotation is also assisted by the interaction with neighbouring molecular units in the solid. The

310   salts **5** and **6·2H₂O** present the higher pyridine rotation values (~33º) and this large value can

311   be ascribed to cation interactions (and also anion interactions in the case of complex **5**) as

312   denoted by several short contacts (see tables SM1-SM2 and figures SM1 SM2).

313   The smaller pyridine rotations of only ~13º, in **1** and **2**, are associated with anionic and

314   cationic interactions, including π-π interactions between the pyridine groups of the

315   [M(*4*-pedt)₂]⁻ units: (see tables SM3-SM4 and figure SM3). The two pyridine rings involved

316   are coplanar with distances close to the sum of the Van der Waals radii, clearly denoting

317   significant π-π interactions (Figure SM3 c) .

318   A feature related to the unsymmetrical nature of the *4*-pedt ligand, is the S-C bond length

319   difference within the metallocycle (Table 2). The shortening of the **b'** bond when compared

320   with the **b** bond can be evaluated in terms of a parameter $\delta = 100(b-b')/b$, as previously done

321   on other unsymmetrical bis-dithiolene complexes as the $[Ni(adt)_2]^-$ (adt = acrylonitrile-1,2-

322   dithiolate) or the $[Ni(tfadt)_2]^-$ (tfadt = 2-(trifluoromethyl)acrylonitrile-1,2-dithiolate) .[6, 22] In

323   our case δ values are between 1.26 and 2.03% in the four structures analysed and it can be

324   attributed to the mesomeric effect of the pyridine group.

325 A long debated aspect of the dithiolene complexes is the so called "non-innocence" of the

326 ligands, which may lead to formal ambiguities in the description of the different oxidation

327 sates of these complexes.[19] In these monoanionic complexes the, ligand may have a

328 significant contribution to the frontier orbitals and can be viewed as being present in one of

329 two extreme forms: the dianionic ene-1,2-dithiolate or the neutral dithioketone.[1a,19] In this

330 particular case of the [M(4-pedt)$_2$]$^-$ dithiolenes where the dithiole ring is not fused to any

331 aromatic ring the lengths of the C–C and C–S bonds provide a direct indication on the nature

332 of a dithiolene ligand. In all complexes studied the C=C (1.32-1.36 Å) and C-S (1.71-1-77 Å)

333 bond lengths were found in the range typical of sp^2 C hybridisation [23] indicative of the ene-

334 1,2-dithiolate form of the dithiolene and M(III) oxidation state.In the solid state, the

335 monoanionic [M(4-pedt)$_2$]$^-$ species with M = Ni, Cu and Au, present different packing

336 patterns and interactions depending on the cation type complexes. The compounds **1** and **2** are

337 isostructural with the previously reported [PPh$_4$]$^+$[Au(4-pedt)$_2$]$^-$.[9] A characteristic of their

338 crystal structure is the occurrence of cation columns along *b+c*, isolated by a alveolar anion

339 arrangement (Figure 6). As **1** and **2** are isostructural, we will only focus our structural analysis

340 on the compound **1**. In the cation column, it is possible to observe cation pairs and the only

341 intra column short contact is H25···C54 (2.785(3) Å) (Figure 7). Such inversion-centred

342 arrangements of PPh$_4$$^+$ cations are a recurrent feature among molecules bearing at least three

343 phenyl rings on the same atoms.[24] In the alveolar anionic arrangement there are no S-S short

344 contacts, but there are several other N···H, S···H, H···H short contacts and π-π interactions

345 (Table SM3). Of particular note are the C52-H52···N2 (3.514(4) Å) and C6-H6···N2

346 (3.537(3) Å) weak hydrogen bonding interactions.

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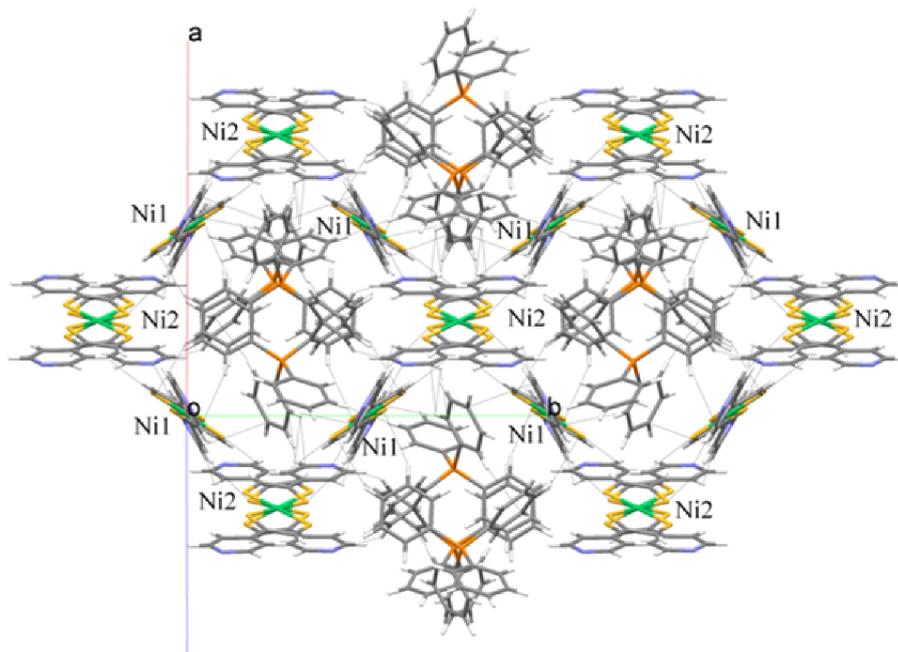
348

349   Figure 6. Crystal structure of **1**, viewed along the cation stacking axis.
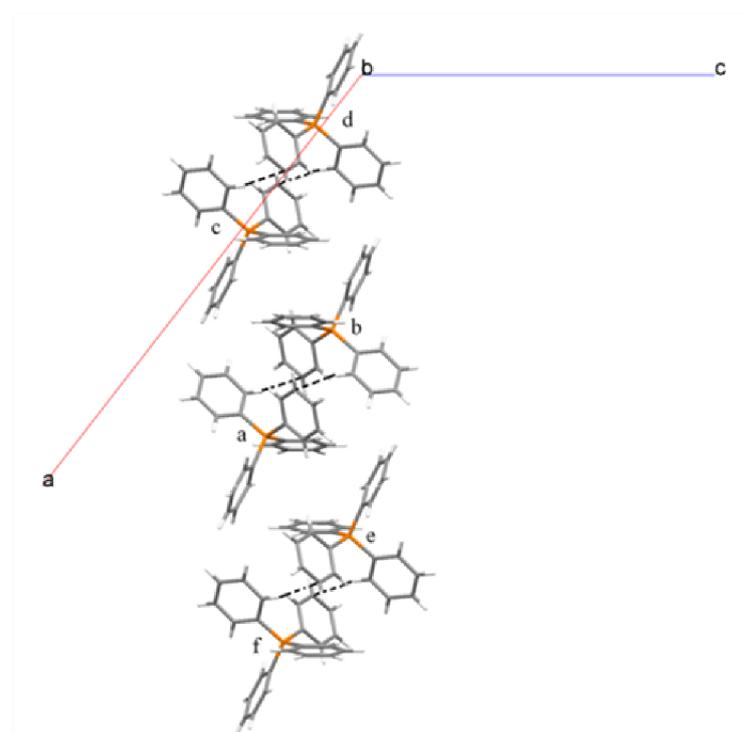
350

351   Figure 7. Chain of $[PPh_4]^+$ cations in compound **1** viewed along *b*. [Symmetry codes: (a) x, y,

352   z; (b) 1.5-x, ½-y, 1-z; (c) -1/2+x, 1/2-y ; -½+z; (d) 1-x, y, 1/2-z ; (e) 2-x, y, 1.5-z ; (f) 1/2+x,

353   1/2-y, 1/2+z].

354

355 The crystal structure of the two tetrabutylammonium salts (**3** and **5**) can be seen as made from

356 parallel mixed chains constituted by pairs of cations alternating with an anion. The parallel

357 chains alternate with sheets of anions (Figure 8). These two compounds have several short

358 intermolecular contacts but none of them corresponds to S-S interactions. (for compound **5**

359 Table SM1).
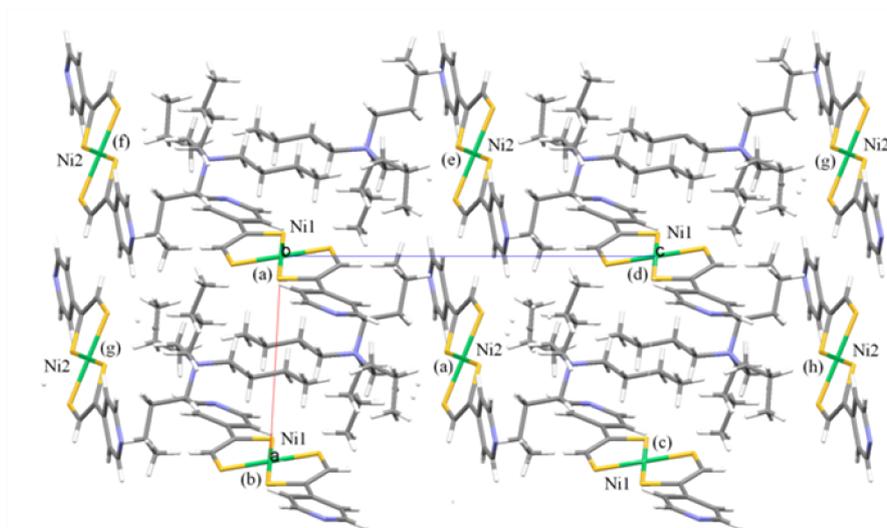
360

361 Figure 8. Crystal structure of **3**, viewed along the *b* axis. [Symmetry codes: (a) x, y, z; (b)

362 1+x, y, z ; (c) 1+x, 1+y, 1+z ; (d) x, 1+y, 1+z ; (e) -1+x, y, z ; (f) -1+x, -1+y, -1+z, (g) x, -1+y,

363 -1+z, (h) x, 1+y, 1+z, (i) -1+x, 1+y, 1+z].

364

365 The crystal structure of compound **6·2H$_2$O** can be described in terms of parallel alternated

366 layers of [Ni(*4*-pedt)$_2$]$^-$ anions and Na(18c6)$^+$ cations. The coordination sphere of the sodium

367 cation is completed by two water molecules, one on each side (Figure 9). The angle between

368 the anionic units mean plan is about 44.53 . Only between anions and cations, there are

369 relevant interactions. Besides several N⋯O, N⋯H, C⋯H, O⋯S, S⋯H short contacts a hydrogen

370 bond N1⋯H4A-O4 (2.916(4) Å) is present, which is the most important, governing the chain-

371 like arrangement anion-cation-anion(…) as depicted in Figure 10.

372
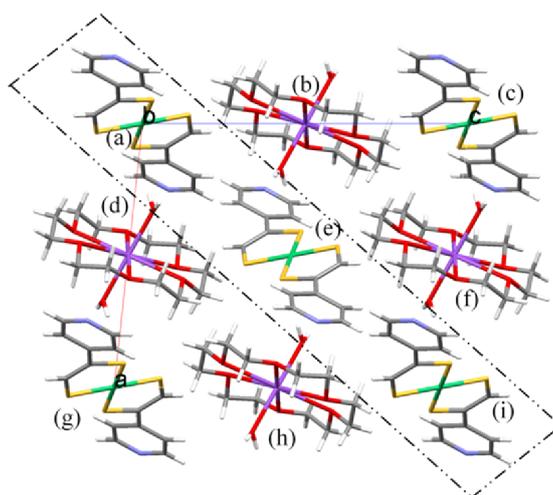
Figure 9. Crystal structure of **6·2H₂O**, viewed along the *b* axis. The dashed box marks a layer

of [Ni(*4*-pedt)₂]⁻ anions. [Symmetry codes: (a) x, y, z; (b) -1+x, y,z, (c) x, y, 1+z, (d) 1.5-x, -

1/2+y, 1/2-z, (e) 1/2-x, 1/2+y, 1/2-z, (f) 1.5-x, -1/2+y, 1.5-z, (g) 1+x, y, z, (h) x, -1+y, z, (i)

1+x, y, 1+z].

377
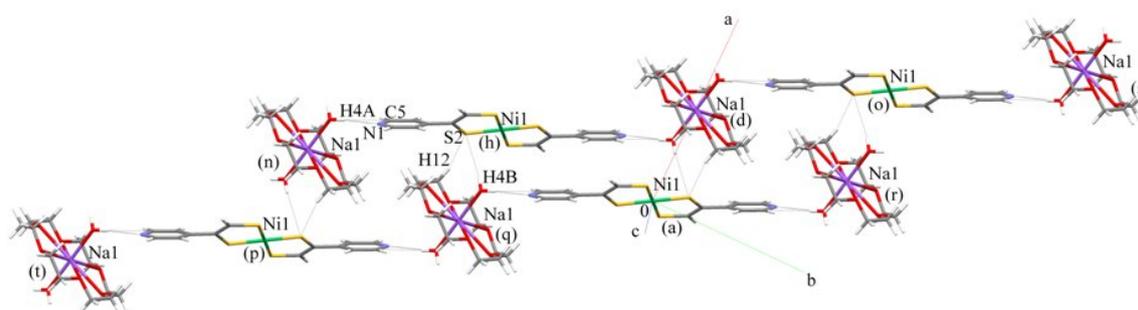
Figure 10. Detail of the mixed layer in **6·2H₂O**, two adjacent mixed chains. [Symmetry codes:

(a) x, y, z; (d) 1.5-x, -1/2+y, 1/2-z, (n) 1/2-x, -2.5+y, 1/2-z, (o) 1+x, 1+y, z, (p) -1+x, -2+y, z,

(q) 1/2-x, -1.5+y, 1/2-z, (r) 1.5-x, 1/2+y, 1/2-z, (s) 2.5-x, 1.5+y, ½-z, (t) -1/2-x, -3.5+y, ½-z].

3.3. Redox behaviour

The redox behaviour of the different complexes was studied by cyclic voltammetry in CH_2Cl_2

solution containing [*n*-Bu₄N] PF₆ (0.1 M) as electrolyte. Each of the compounds **1**, **3** and **6**

385   containing the Ni complex (cyclic voltammogram of compound **6,** Supplementary material,

386   Figure 4 SM) exhibit two quasi reversible redox waves, at circa -0.52 V and 0.30 V vs.

387     $[Fc]^+/[Fc]$ which are ascribed to the couples $[Ni(4\text{-pedt})_2]^{2-}/[Ni(4\text{-pedt})_2]^-$ and $[Ni(4\text{-pedt})_2]^-$

388     $/[Ni(4\text{-pedt})_2]^0$ (Table 3). The $E^{1/2}$ potentials for the Ni complexes in these three compounds

389   are, identical. The variation in the scan rate (from 10 to $200 mVs^{-1}$) monitoring the wave

390   profile, the separation of the peak potentials ($\Delta E > 59 mV$), and the ratio of the cathodic and

391   anodic currents ($-I_p^c/I_p^a \approx 1$) indicate that the processes are quasi reversible. The low values of

392   the first process explain the difficulty in preparing the dianionic complex, which can be

393   spontaneously oxidised by minor amounts of oxygen or other oxidising agents. On the other

394   hand the low value of the second process predicts that the neutral complex can be prepared.

395   However attempts to isolate it were so far not successful.

396   The compounds **2** and **4** containing the Cu complex (cyclic voltammogram of compound **2,**

397   Supplementary material, Figure 5 SM) show also identical cyclic voltammograms with one

398   quasi reversible redox process at ca -0.38 V, ascribed to the couples $[Cu(4\text{-pedt})_2]^{2-}/[Cu(4\text{-}$

399     $pedt)_2]^-$ (Table 3). Scans to higher positive potentials (~0.6V vs. vs. $[Fc]^+/[Fc]$) reveal the

400   existence of an irreversible process which should correspond to the couple $[Cu(4\text{-pedt})_2]^-$

401     $/[Cu(4\text{-pedt})_2]^0$.

402   The compounds **5** and **7** containing the $[Au(4\text{-pedt})_2]^-$ complex (cyclic voltammogram of

403   compound **7,** Supplementary material, Figure 6 SM) both exhibit one oxidation and a

404   reduction process, assigned to the couples $[Au(4\text{-pedt})_2]^-/[Au(4\text{-pedt})_2]^0$ (Table 3). For both

405   gold compounds, the $E^{1/2}$ potentials are very similar. A variation in the scan rate (from 10 to

406     $200 mVs^{-1}$) monitoring the wave profile, the separation of the peak potentials ($\Delta E > 59 mV$), and

407   the ratio of the cathodic and anodic currents ($-I_p^c/I_p^a \neq 1$) indicate that the oxidation is not

408   electrochemically reversible.

409

410   Table 3. Redox potentials (mV, vs. [Fc]$^+$/[Fc]) of **1-6** at room temperature in CH_2Cl_2

411   containing [n-Bu$_4$N] PF$_6$ (0.1 M) with a 100 mVs^{-1} scan rate.

Compound	$[ML_2]^{2-}/[ML_2]^-$	$[ML_2]^-/[ML_2]^0$
[n-Ph$_4$P][Ni(4-pedt)$_2$] (**1**)	-519	297
[n-Ph$_4$P][Cu(4-pedt)$_2$] (**2**)	-374	676
[n-Bu$_4$N][Ni(4-pedt)$_2$] (**3**)	-523	303
[n-Bu$_4$N][Cu(4-pedt)$_2$] (**4**)	-379	771
[n-Bu$_4$N][Au(4-pedt)$_2$] (**5**)		585
[Na(18c6)][Ni(4-pedt)$_2$] (**6**)	-518	298
[Na(18c6)][Au(4-pedt)$_2$] (**7**)		588

412

413   It is known that the nature of the R substituent in the complexes Ni(S$_2$C$_2$R$_2$)$_2$ affects the redox

414   potentials and even a small variation in the electron withdrawing substituent can tune the

415   redox potential.[1a, 25] In this case we observe that the pyridine groups, which are only partially

416   rotated relatively to the central bisdithiolene plane, thus retaining the possibility of interacting

417   via their pi systems, make the *4*-pedt complexes easier to oxidize than phenyl substituted or

418   even unsubstituted edt ligands.[5]

419

420   **3.4. EPR measurements**

421   While the monoanionic Cu and Au complexes are diamagnetic the monoanionic Ni,

422   complexes, as d^7 system in a square planar coordination are expected to be paramagnetic

423   S = 1/2 systems. Indeed the EPR spectra of **1**, **3** and **6**, as powders, show a signal typical of

424   monoanionic Ni dithiolene complexes[1,26,27] with rhombic symmetry, with g$_1$ = 2.1035,

425   g$_2$ = 2.0518, g$_3$ = 2.0128 for the compound **1** and g$_1$ = 2.1153, g$_2$ = 2.0480, g$_3$ = 2.0087 for the

426   compound **6**. In the case of the compound **3** the EPR spectrum denotes the existence of two

427   Ni sites with different g_1 (2.0849 and 2.0834) and g_3 (2.0183 and 2.0113) values but with the

428   same (or very close) g_2 value (2.0701). This should be related with the different

429   crystallographic environments of the two anionic Ni units in the asymmetric unit of the

430   compound **3**. In fact Ni1 unit besides quite asymmetric Ni-S bonds lengths has several short

431   S···H-C contacts with cations which are absent in unit Ni2. In spite of the existence of two

432   different anionic Ni^{III} units in the asymmetric unit of **1,** the two sets of g principal values for

433   this compound are not distinguishable within experimental error in agreement with the fact

434   that the two Ni units present comparable short contacts between the S atoms.

435

436   **3.5. Magnetic susceptibility**

437   The magnetic susceptibility measurements of the compounds **1** and **3** in the range 2-300 K

438   indicate a paramagnetic behaviour with effective magnetic moments essentially temperature

439   independent down to ~15 K with values at room temperature of 1.72 and 1.79 respectively.

440   For compound **6**, the room temperature magnetic moment is 1.67 BM, but it slightly increases

441   upon cooling down to 11 K (1.85 BM), denoting weak ferromagnetic interactions, that are not

442   effective at lower temperature (confirmed by magnetisation vs. magnetic field at 3.1 K – see

443   Supplementary material). These values are consistent with a S = 1/2 state, due to an unpaired

444   electron of a d^7 system in an quadrangular coordinating geometry. The calculated magnetic

445   moment for the three compounds assuming a Curie law for S = ½ and g values g_{av} from EPR

446   is 1.78 BM.

447

448   **Conclusion,**

449   The new paramagnetic complex, $[Ni(4\text{-pedt})_2]^-$, with the dithio-azo *4*-pedt ligand has been

450   synthesised, and isolated as the $[PPh_4]^+$, $[n\text{-Bu}_4N]^+$ and Na^+(18c6) salts, which were

451 characterised by single crystal X-ray diffraction, cyclic voltametry EPR and magnetic

452 susceptibility. These three compounds present three distinct crystal structures and similar

453 magnetic and redox behaviour, characteristic of monoanionic Ni complexes with

454 quadrangular coordinating geometry and exhibit two quasi reversible redox waves, attributed

455 to the $[Ni(4\text{-pedt})_2]^{2-}$ /$[Ni(4\text{-pedt})_2]^-$ and $[Ni(4\text{-pedt})_2]^-$ /$[Ni(4\text{-pedt})_2]^0$ redox processes.

456 Two other complexes with the same dithio-azo ligand have been synthesised, $[Au(4\text{-pedt})_2]^-$

457 and $[Cu(4\text{-pedt})_2]^-$, isolated as the $[n\text{-Bu}_4N]^+$ and $Na^+(18c6)$ salts in case Au and as the

458 $[PPh_4]^+$, $[n\text{-Bu}_4N]^+$ salts in case Cu, all them exhibiting diamagnetic behaviour.

459 The $[n\text{-Bu}_4N]^+$ and $[PPh_4]^+$ salts of Au and Cu complexes are isostrutural with the

460 correspondent Ni ones. Both Ni and Cu complexes present a similar quasi reversible redox

461 process corresponding to the couple $[ML_2]^{2-}/[ML_2]^-$ but they differ in the couple $[ML_2]^-$

462 /$[ML_2]^0$ which is a quasi reversible process for Ni and an irreversible one for Cu. For the Au

463 complexes only the couple $[ML_2]^-/[ML_2]^0$ is observed.

464 The ability of the pyridine groups of these complexes to coordinate other metals is presently

465 under study and will be reported subsequently.

466

467 **Appendix A. Supplementary material**

468 CCDC 698755, 698756, 698757, 698758 and 698759 contain the supplementary

469 crystallographic data **1**, **2**, **3**, **5** and **6.2H₂O**. These data can be obtained free of charge via

470 http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic

471 Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail:

472 deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the

473 online version.

474

479

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Scheme1
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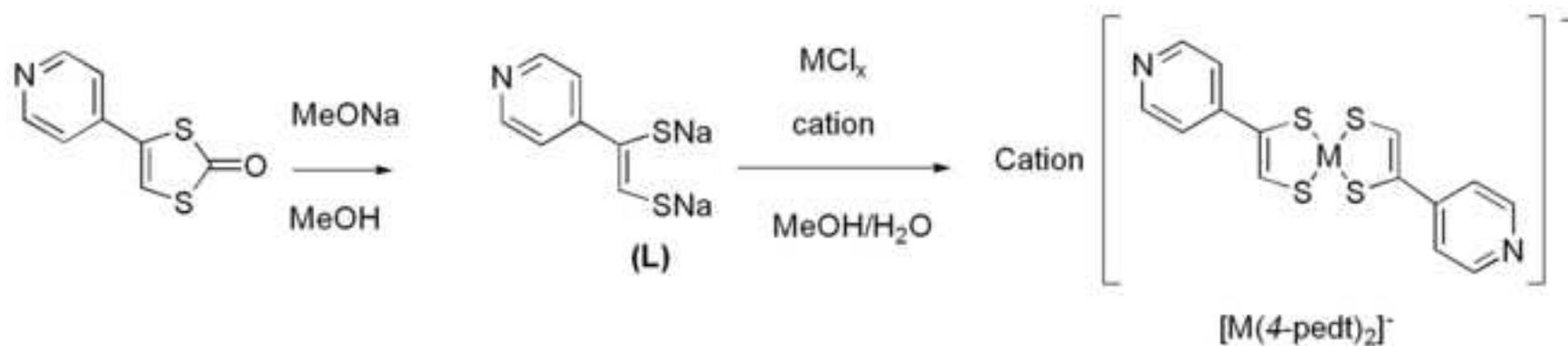
(Ph$_4$P)[Ni(4-pedt)$_2$] (**1**) 50% yield; (Ph$_4$P)[Cu(4-pedt)$_2$] (**2**) 48% yield; (n-Bu$_4$N)[Ni(4-pedt)$_2$] (**3**) 65% yield; (n-Bu$_4$N)[Cu(4-pedt)$_2$] (**4**)41% yield;

(n-Bu$_4$N)[Au(4-pedt)$_2$] (**5**) 60% yield; [Na(18c6)][Ni(4-pedt)$_2$] (**6**) 58% yield; [Na(18c6)][Au(4-pedt)$_2$] (**7**) 44% yield

Figure1
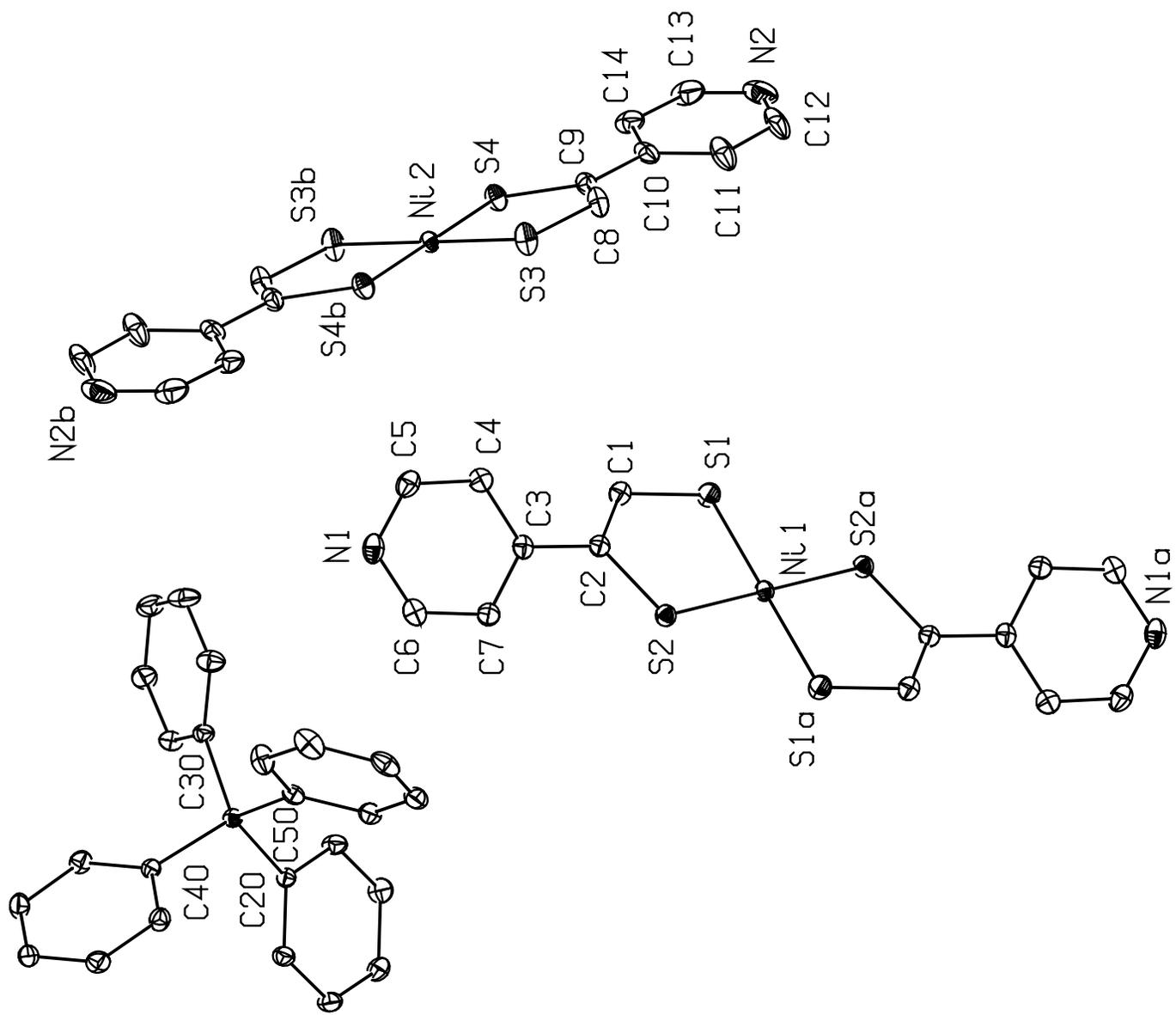
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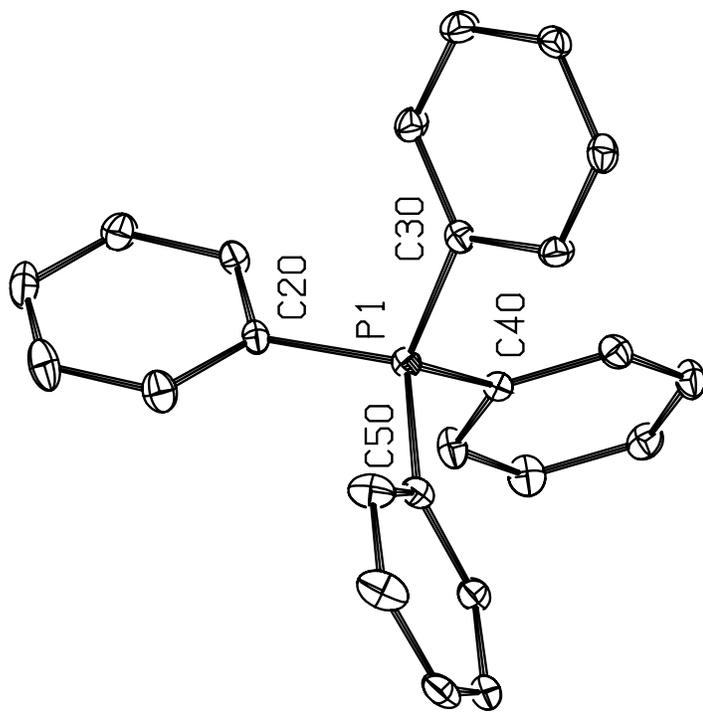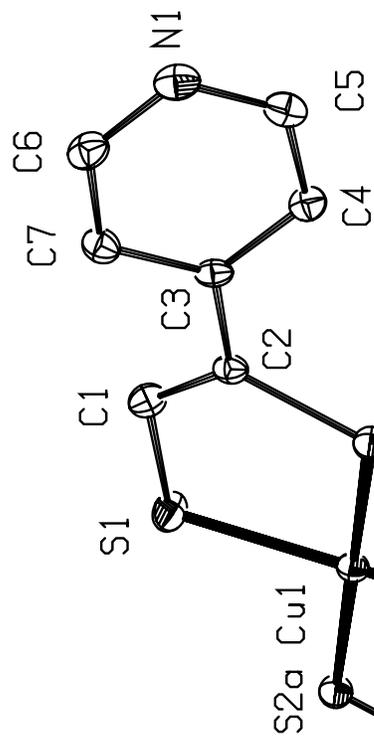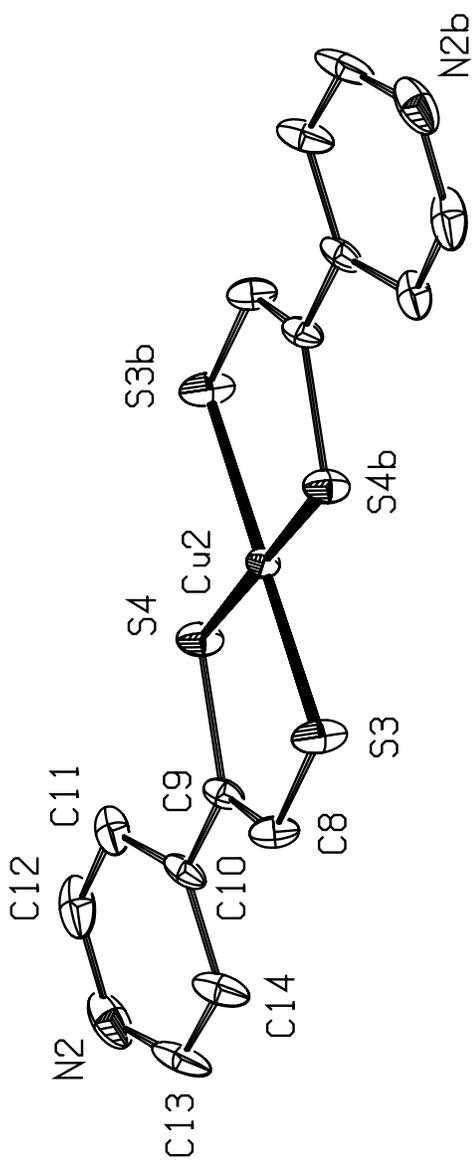
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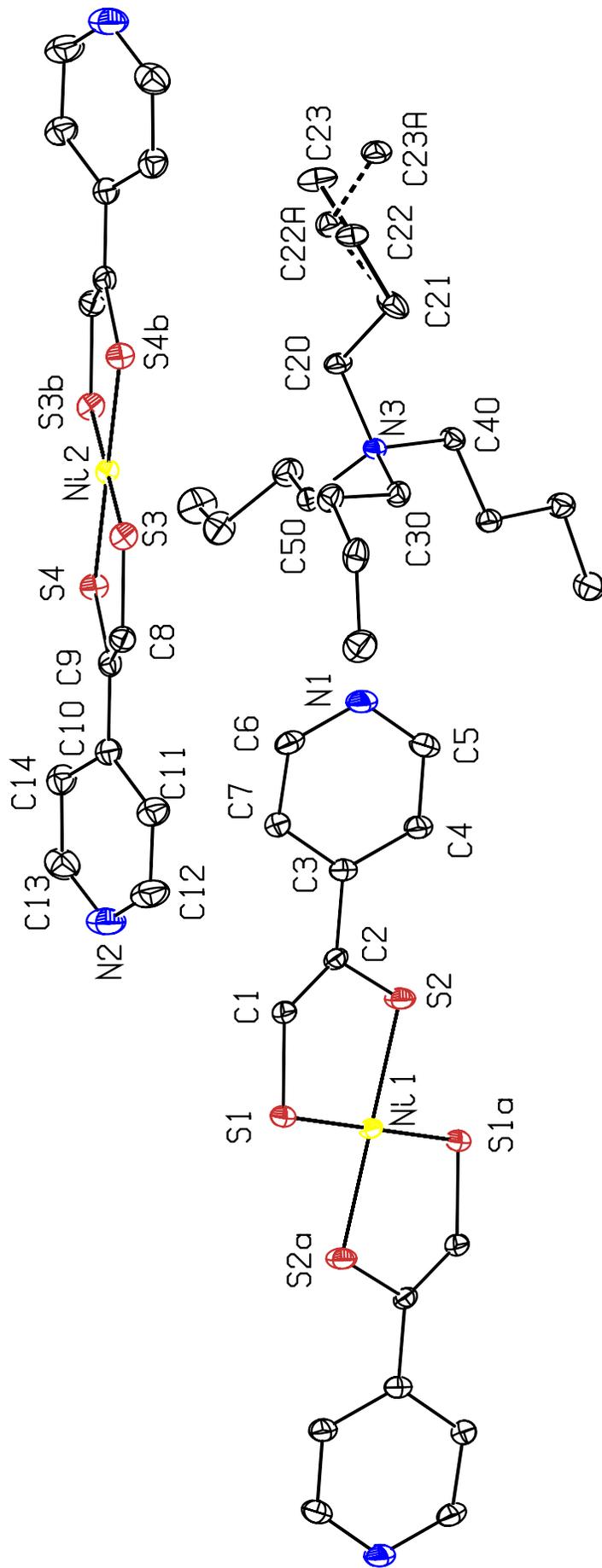
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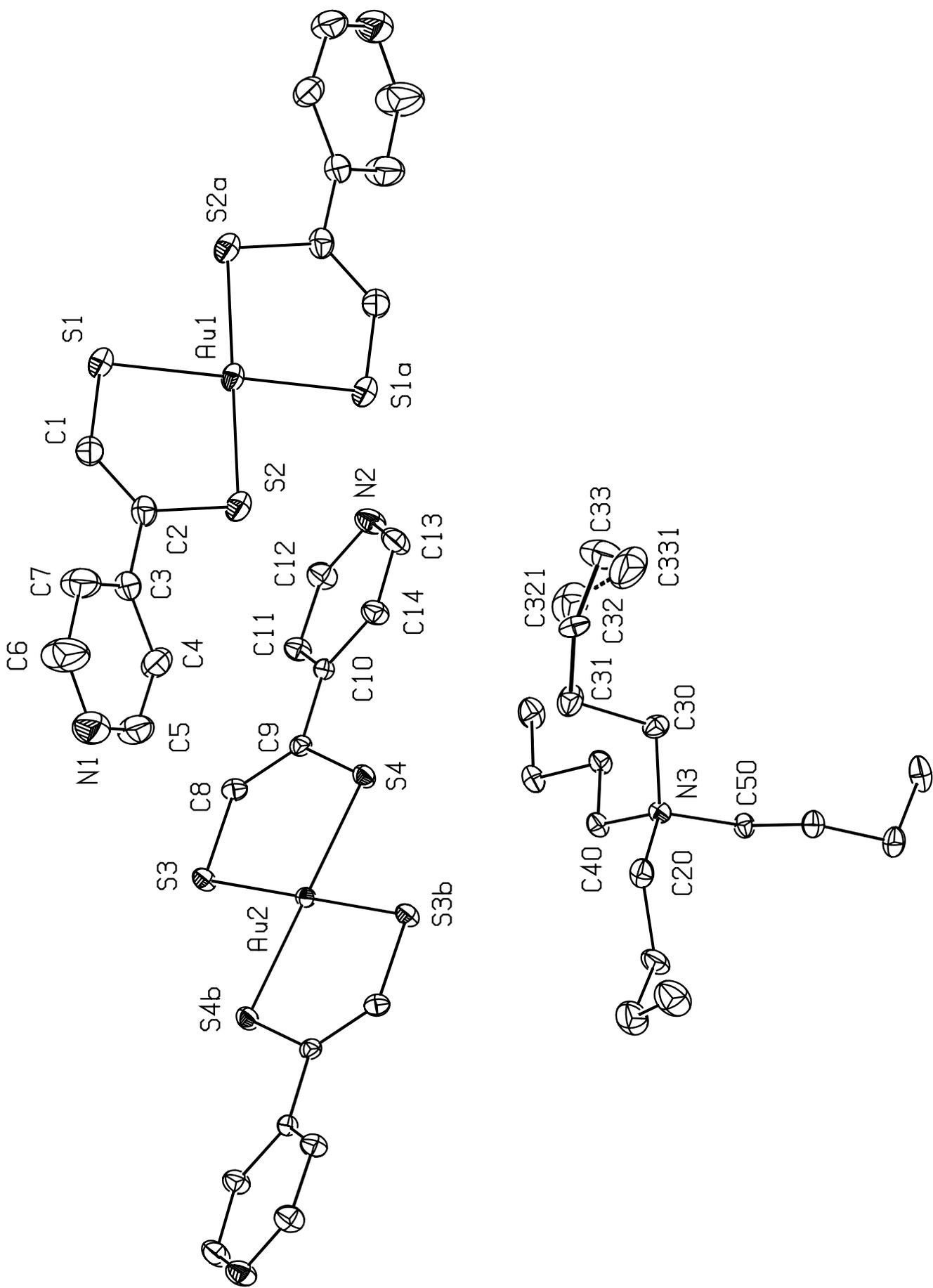
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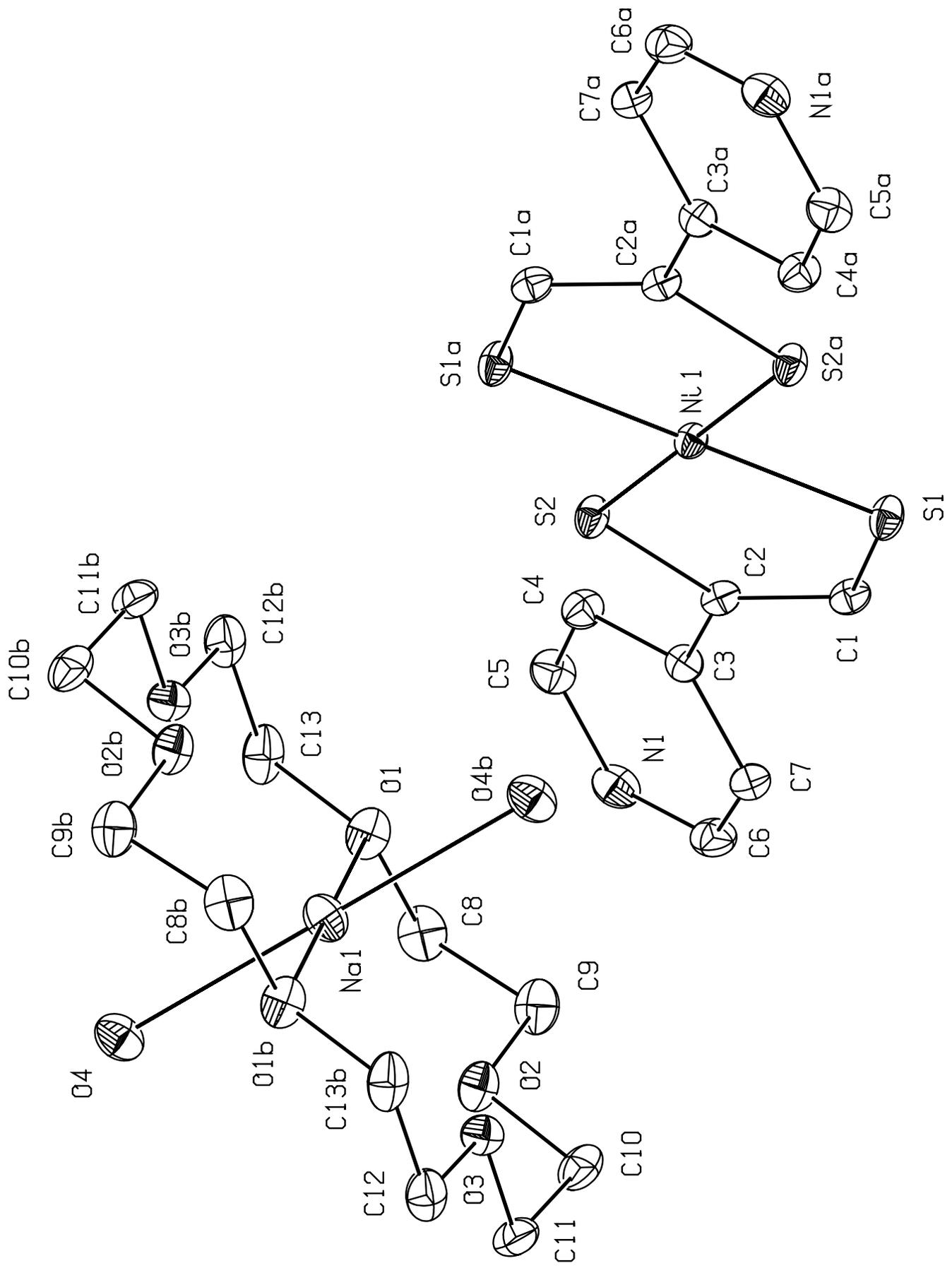
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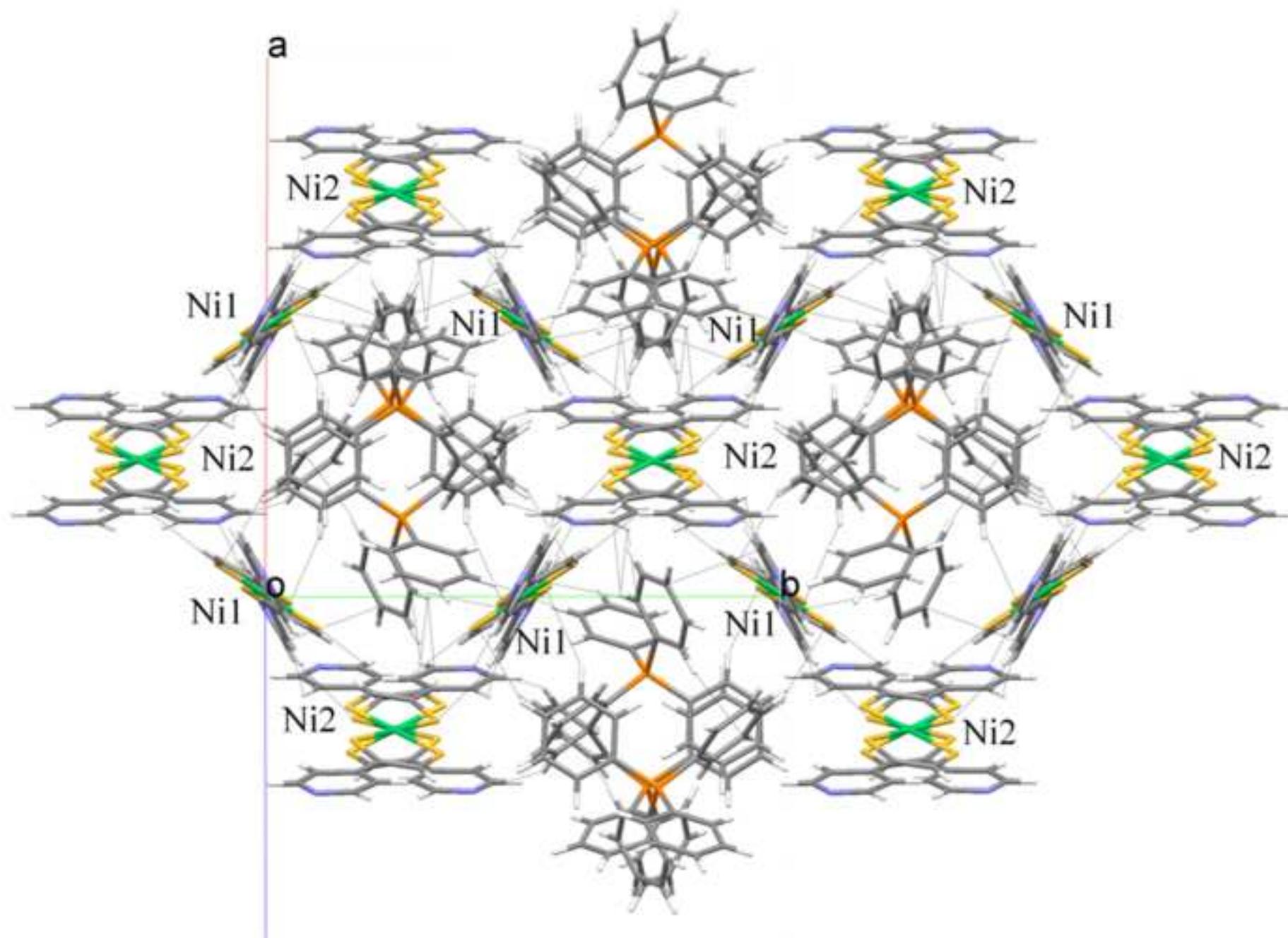
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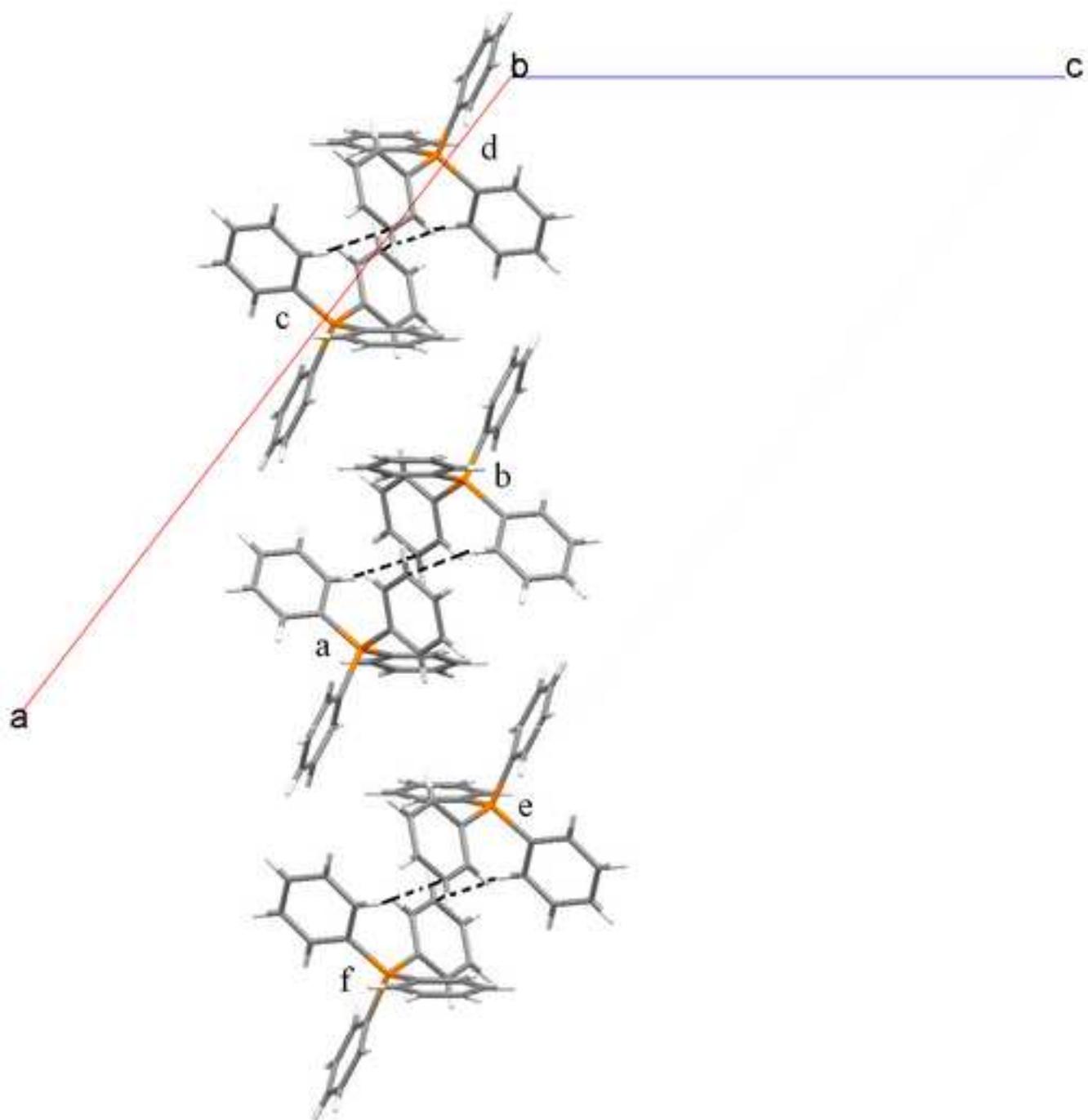
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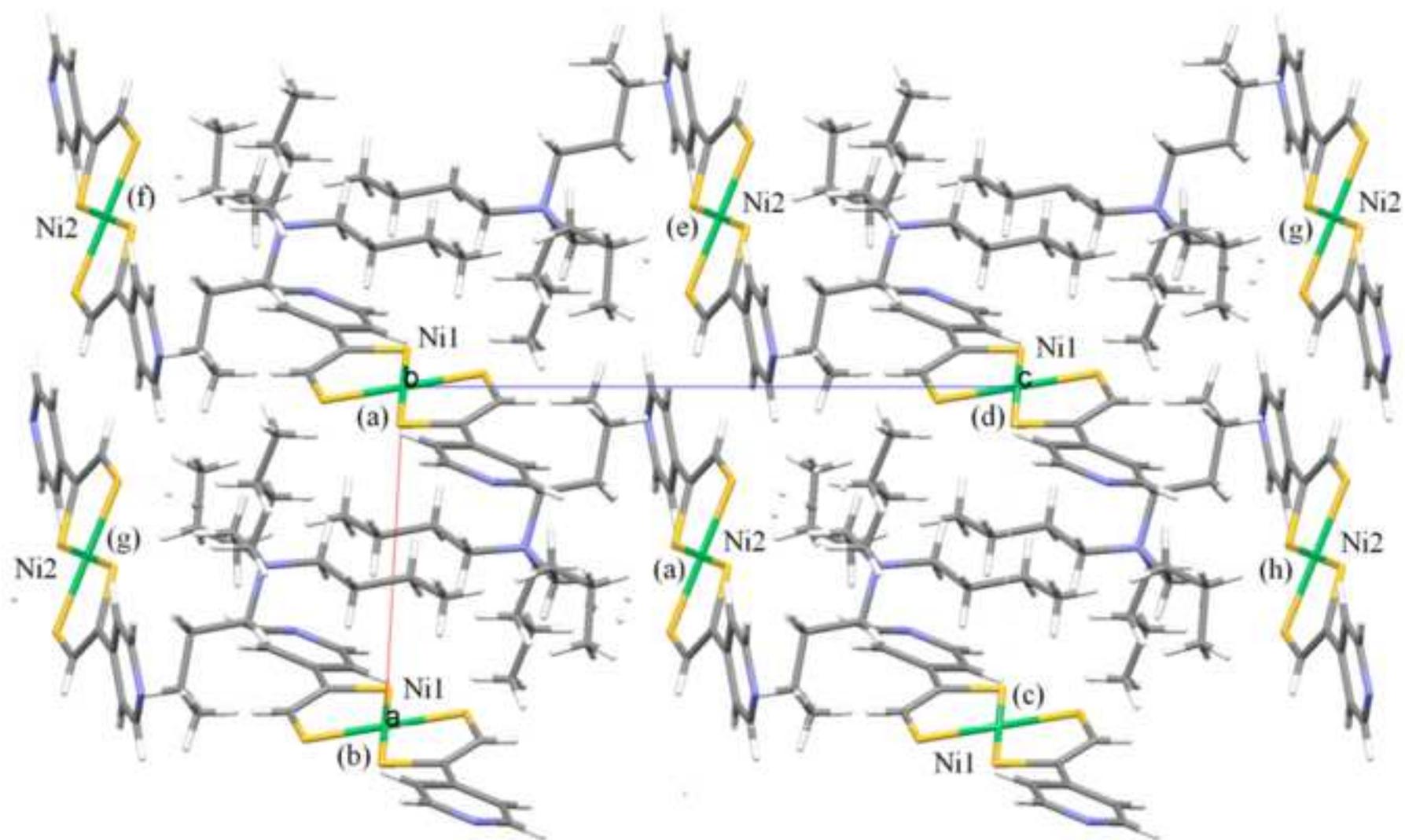
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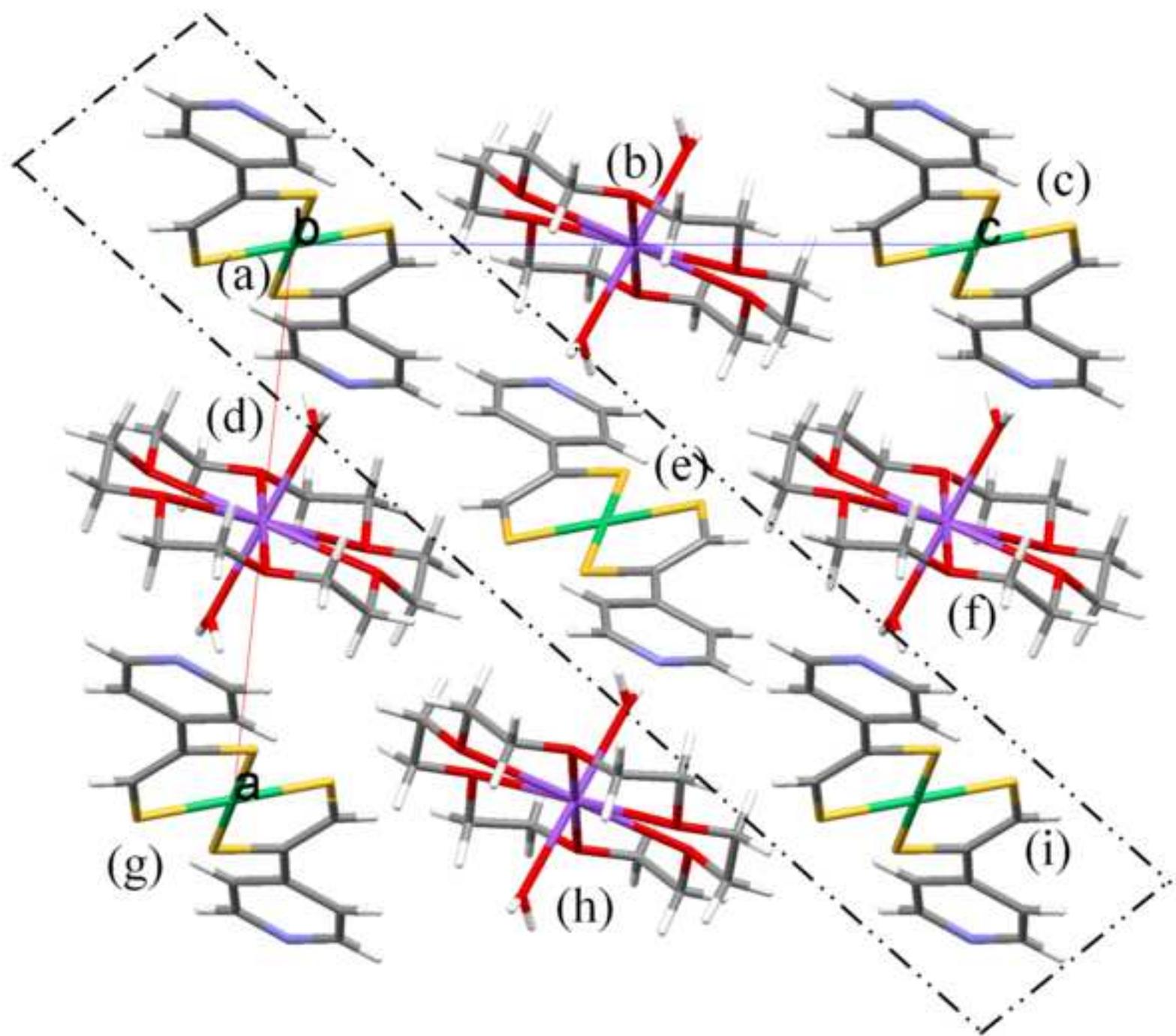
Figure10
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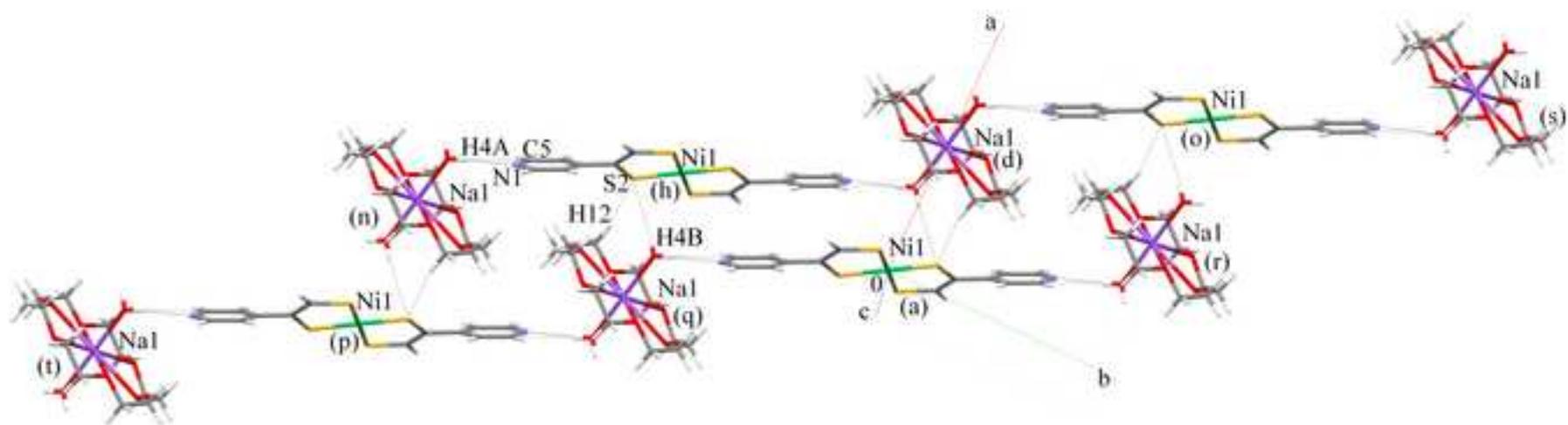
Table1

1   Table 1 - Crystallographic data and refinement parameters for complexes $Ph_4P[Ni(4\text{-pedt})_2]$ (**1**), $Ph_4P[Cu(4\text{-pedt})_2]$ (**2**), $n\text{-Bu}_4N[Ni(4\text{-pedt})_2]$ (**3**),

2     $n\text{-Bu}_4N[Au(4\text{-pedt})_2]$ (**5**) and $[Na(18c6)][Ni(4\text{-pedt})_2].2H_2O$ (**6·2H$_2$O**).

Compound	1	2	3	5	6·2H$_2$O
Formula	C_{38} H_{30} N_2 Ni P S_4	C_{38} H_{30} Cu N_2 P S_4	C_{30} H_{46} N_3 Ni S_4	C_{30} H_{46} Au N_3 S_4	C_{26} H_{38} N_2 Na Ni O_8 S_4
Formula weight (g mol^{-1})	732.58	737.39	635.65	773.90	712.49
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system, Space group	Monoclinic, $C2/c$	Monoclinic, $C2/c$	Triclinic, P-1	Triclinic, P-1	Monoclinic, $P2_1/n$
a (Å)	26.8750(5)	26.9179(8)	9.0033(2)	8.6211(1)	11.7067(14)
b (Å)	17.3528(3)	17.3541(6)	11.2258(2)	11.1196(2)	9.7243(12)
c (Å)	18.1609(3)	18.1969(5)	16.9070(3)	17.6962(3)	14.3179(18)
α (°)	90	90	107.7870(10)	74.646(1)	90
β (°)	127.5650(10)	127.3820(10)	90.3960(10)	88.829(1)	96.103(2)
γ (°)	90	90	98.3450(10)	80.336(1)	90
V (Å^3), Z	6713.4(2), 8	6754.5(4), 8	1607.48(5), 2	1612.14(4), 2	1620.7(3), 2
ρ_{calc} (Mg/m^3), μ (mm^{-1})	1.450, 0.906	1.450, 0.973	1.313, 0.887	1.594, 4.846	1.468, 0.918
$F(000)$	3032	3040	678	780	750
Crystal size (mm)	0.4 x 0.3 x 0.08	0.30 x 0.20 x 0.16	0.28 x 0.24 x 0.20	0.38 x 0.30 x 0.28	0.20 x 0.12 x 0.10
θ Range (°)	2.83 to 25.03	2.74 to 25.68	3.21 to 25.35	2.64 to 25.68	2.73 to 25.68
Collected hkl	$-31 \le h \le 31$	$-32 \le h \le 32$	$-10 \le h \le 10$	$-10 \le h \le 10$	$-14 \le h \le 12$
	$-20 \le k \le 20$	$-21 \le k \le 21$	$-13 \le k \le 13$	$-13 \le k \le 13$	$-11 \le k \le 11$
	$-21 \le l \le 21$	$-20 \le l \le 22$	$-20 \le l \le 20$	$-21 \le l \le 21$	$-17 \le l \le 17$
Reflections collected	41666	23618	13680	17908	7273
Independent reflections	5910 [R(int) = 0.0424]	6409 [R(int) = 0.0656]	5821 [R(int) = 0.0422]	6122 [R(int) = 0.0306]	3051 [R(int) = 0.0414]
Completeness to θ	25.03 99.7 %	25.68 99.7 %	25.35 98.9 %	25.68 99.7 %	25.68 99.3 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8052 and 0.7133	0.8599 and 0.7590	0.8425 and 0.7893	0.3440 and 0.2603	0.9139 and 0.8378
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5910 / 0 / 418	6409 / 0 / 418	5821 / 6 / 370	6122 / 2 / 370	3051 / 2 / 201
Goodness-of-fit on F^2	1.069	1.049	1.079	1.071	1.035
Final R indices [$I>2\sigma I$)]	$R_1 = 0.0276, wR_2 = 0.0711$	$R_1 = 0.0396, wR_2 = 0.0868$	$R_1 = 0.0366, wR_2 = 0.0899$	$R_1 = 0.0254, wR_2 = 0.0590$	$R_1 = 0.0376, wR_2 = 0.0791$
R indices (all data)	$R_1 = 0.0341, wR_2 = 0.0740$	$R_1 = 0.0644, wR_2 = 0.0945$	$R_1 = 0.0482, wR_2 = 0.0947$	$R_1 = 0.0401, wR_2 = 0.0630$	$R_1 = 0.0659, wR_2 = 0.0853$
Larg. diff. peak and hole (e Å^{-3})	0.416 and -0.355	0.422 and -0.473	0.556 and -0.280	2.348 and -0.895	0.392 and -0.502

3

Table2

1   Table 2 - Important bond lengths (in Å) within the metallocycle, the torsion angle ω (in °) between the pyridine group plane and the metallocycle

2   plane and δ-parameter (defined below) for compounds **1, 2, 3, 5** and **6·2H₂O**.

3

Compound	1		3		6·2H₂O	2		5	
	M = Ni2	M = Ni1	M = Ni1	M = Ni2	M = Ni	M = Cu1	M = Cu2	M = Au2	M = Au1
M-S (a)	2.1293(5)	2.1507(5)	2.1383(5)	2.1549(6)	2.1375(7)	2.1871(7)	2.1626(7)	2.3078(10)	2.3183(13)
M-S (a')	2.1474(5)	2.1416(5)	2.1463(6)	2.1478(7)	2.1531(7)	2.1797(8)	2.1812(8)	2.3053(11)	2.3082(11)
S-C (b)	1.737(2)	1.742(2)	1.739(2)	1.740(3)	1.738(3)	1.771(3)	1.765(3)	1.768(4)	1.771(4)
S-C (b')	1.715(2)	1.715(2)	1.713(2)	1.715(2)	1.714(3)	1.735(3)	1.740(3)	1.742(4)	1.735(5)
C=C (c)	1.353(3)	1.351(3)	1.364(3)	1.351(3)	1.354(4)	1.335(4)	1.328(4)	1.345(6)	1.336(6)
C-C (d)	1.478(3)	1.476(3)	1.474(3)	1.476(3)	1.469(4)	1.481(4)	1.483(4)	1.477(5)	1.476(7)
ω	13.14(6)	28.50(8)	29.51(8)	28.64(7)	33.56(7)	28.92(12)	13.90(8)	21.83(13	33.44(17)
δ	1.26	1.55	1.49	1.44	1.38	2.03	1.42	1.47	2.03

4   δ = 100(b-b')/b

5

Table3

1

2　　Table 3. Redox potentials (mV, vs. $[Fc]^+/[Fc]$) of **1-6** at room temperature in CH_2Cl_2

3　　containing [n-Bu$_4$N] PF$_6$ (0.1 M) with a 100 mVs^{-1} scan rate.

Compound	$[ML_2]^{2-}/[ML_2]^-$	$[ML_2]^-/[ML_2]^0$
[*n*-Ph$_4$P][Ni(*4*-pedt)$_2$] (**1**)	-519	297
[*n*-Ph$_4$P][Cu(*4*-pedt)$_2$] (**2**)	-374	676
[*n*-Bu$_4$N][Ni(*4*-pedt)$_2$] (**3**)	-523	303
[*n*-Bu$_4$N][Cu(*4*-pedt)$_2$] (**4**)	-379	771
[*n*-Bu$_4$N][Au(*4*-pedt)$_2$] (**5**)		585
[Na(18c6)][Ni(*4*-pedt)$_2$] (**6**)	-518	298
[Na(18c6)][Au(*4*-pedt)$_2$] (**7**)		588

4

5

CIF File (Required if manuscript contains crystal structure(s))

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[Ph$_4$P]$^+$

[n-Bu$_4$N]$^+$

[M(4-pedt)$_2$]$^-$

M(●)=Ni, Au, Cu

[Na(18c6)]$^+$
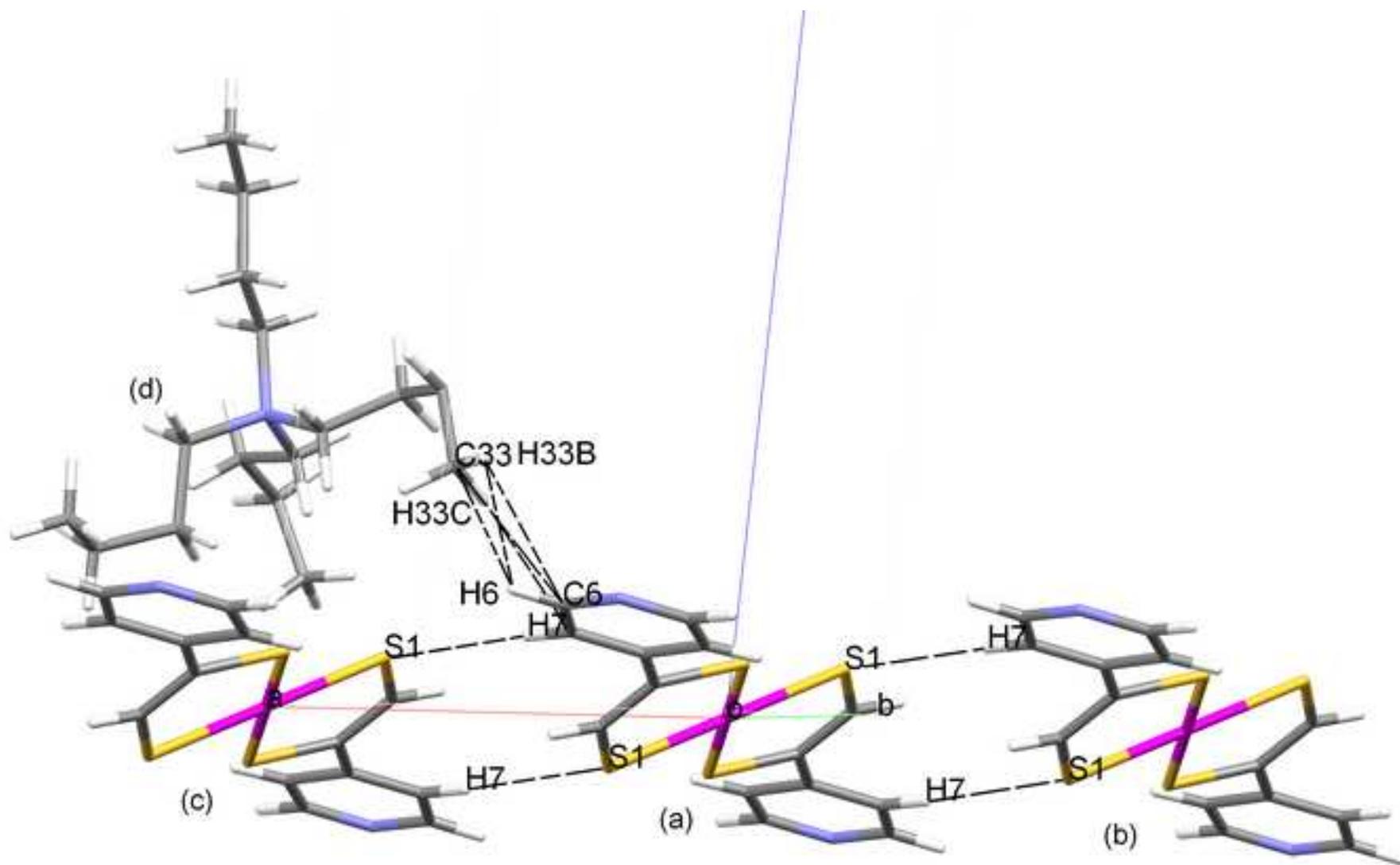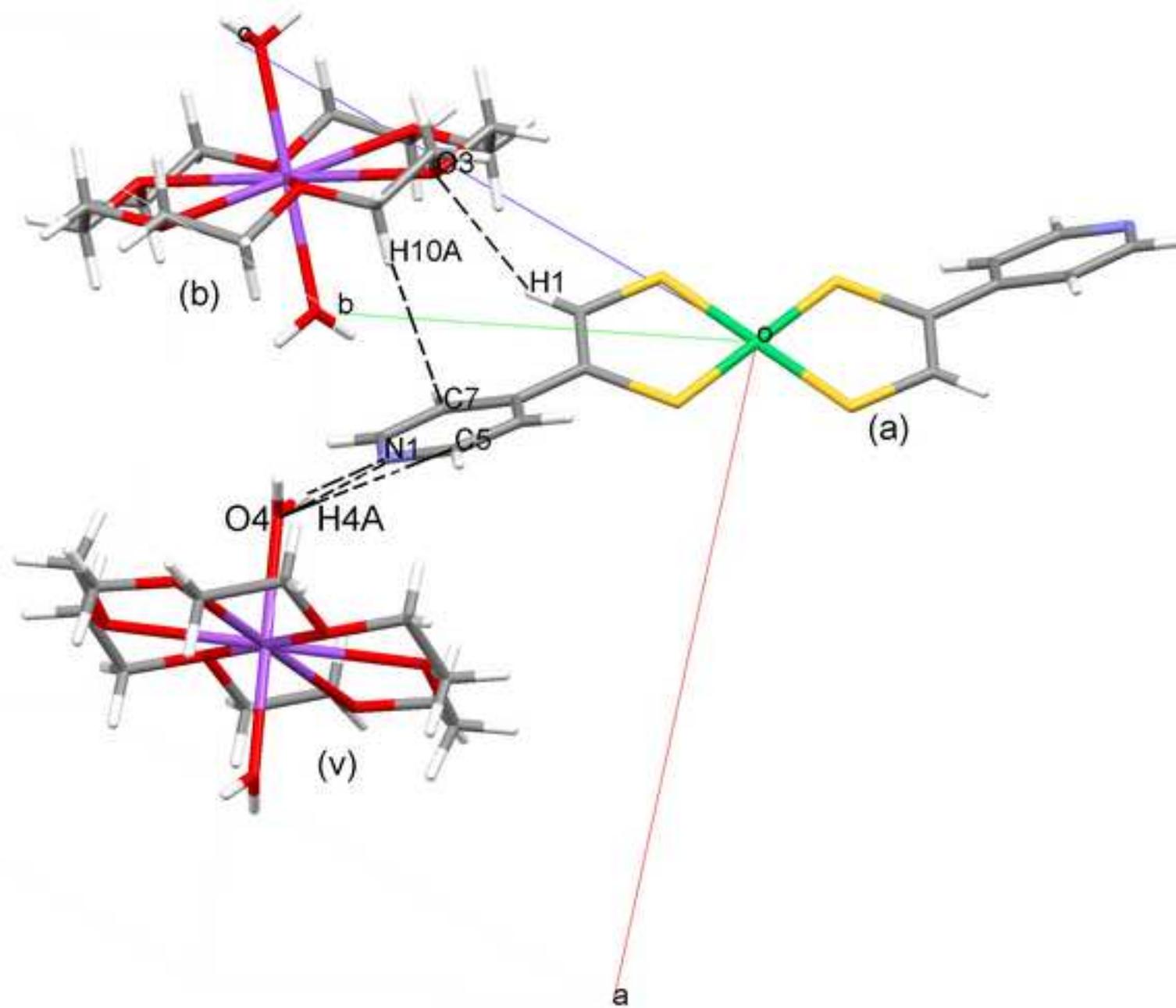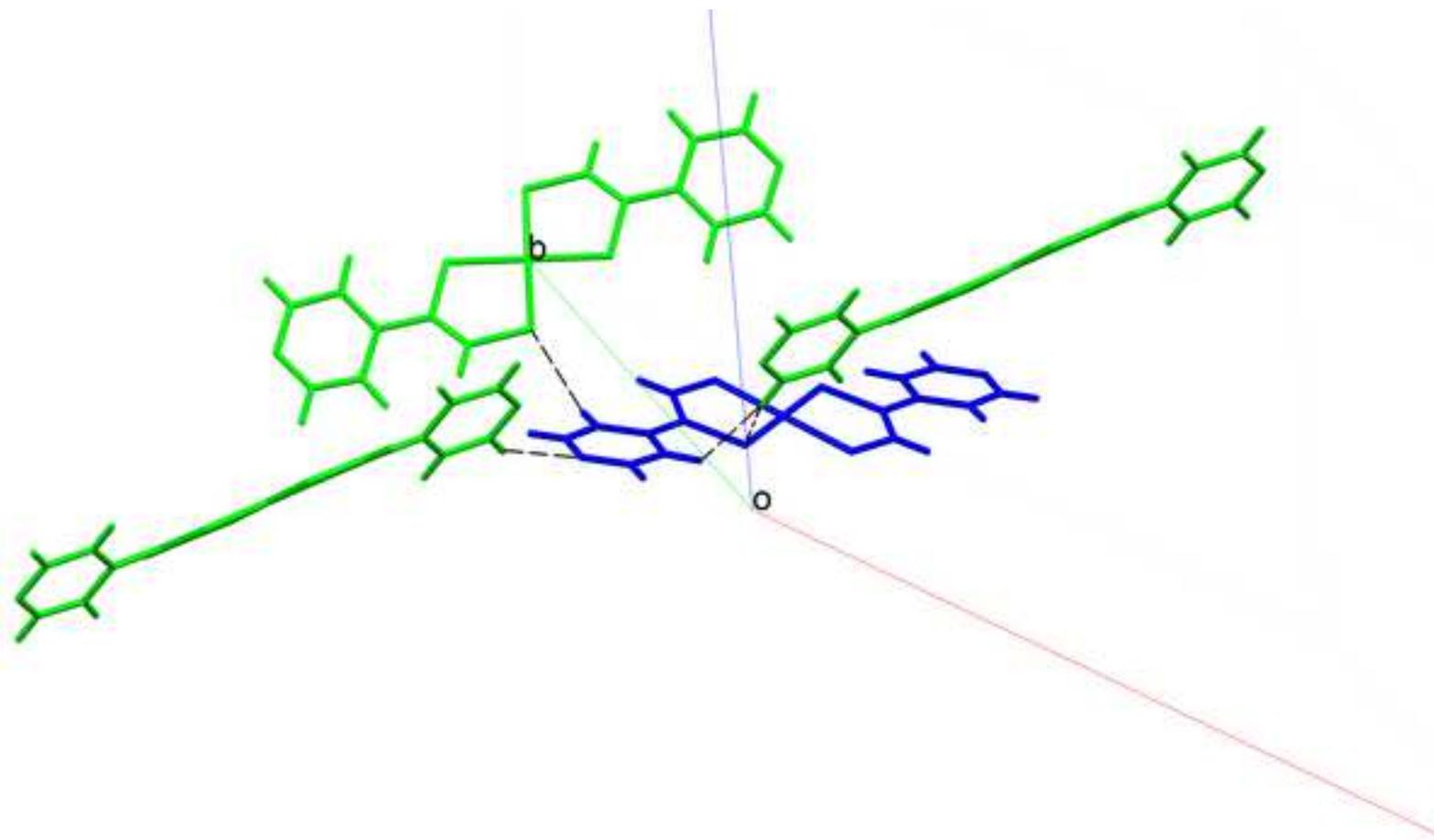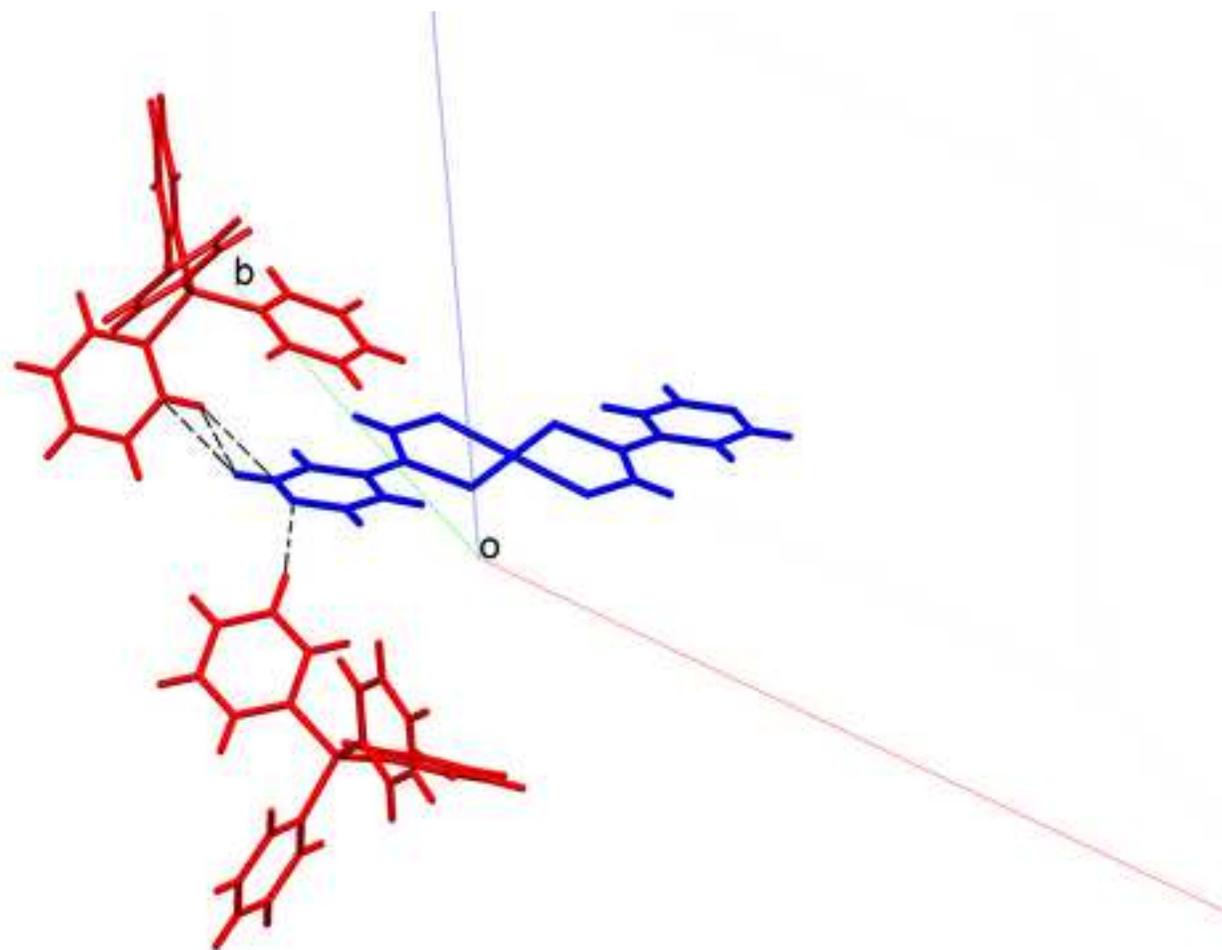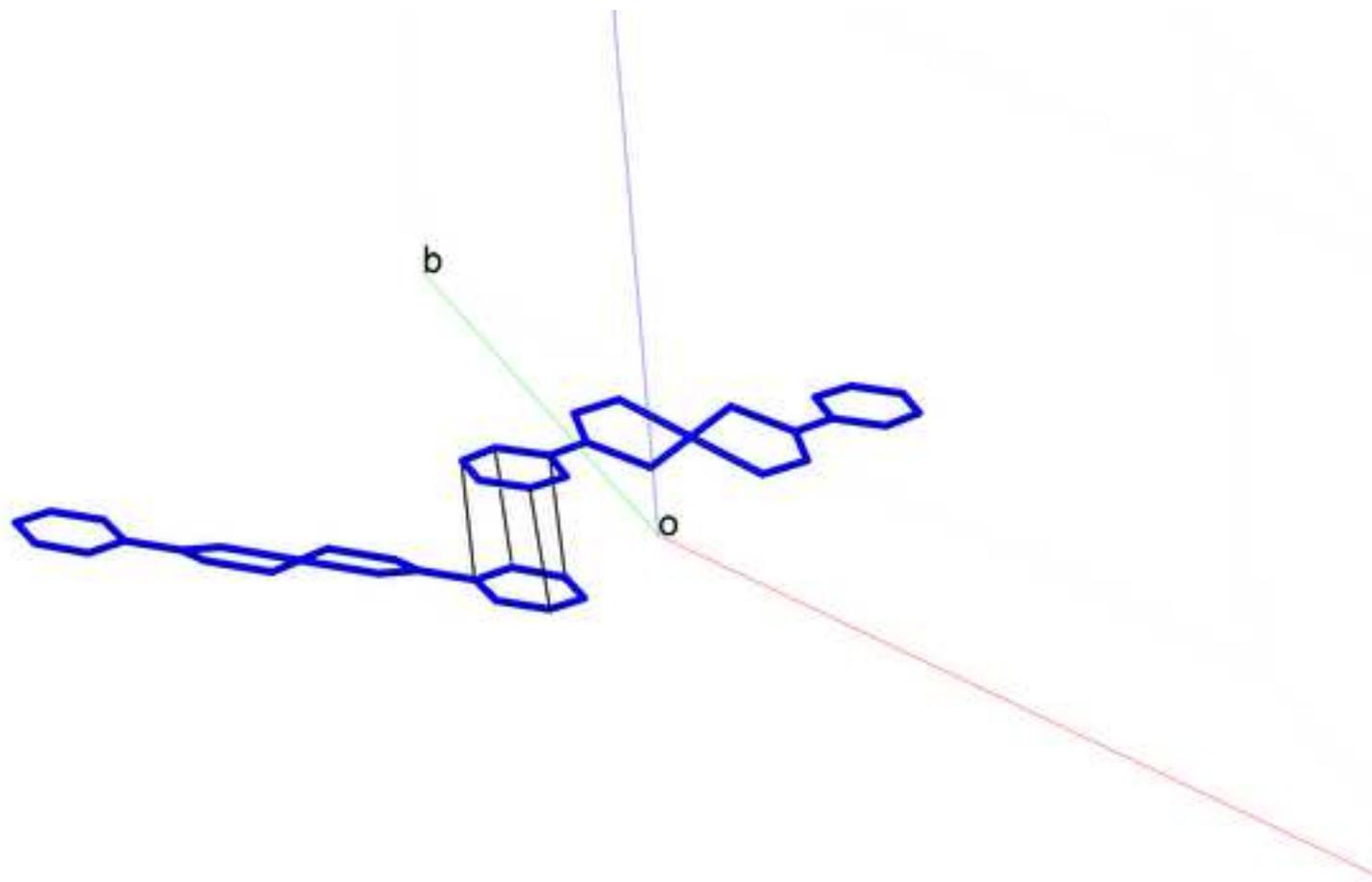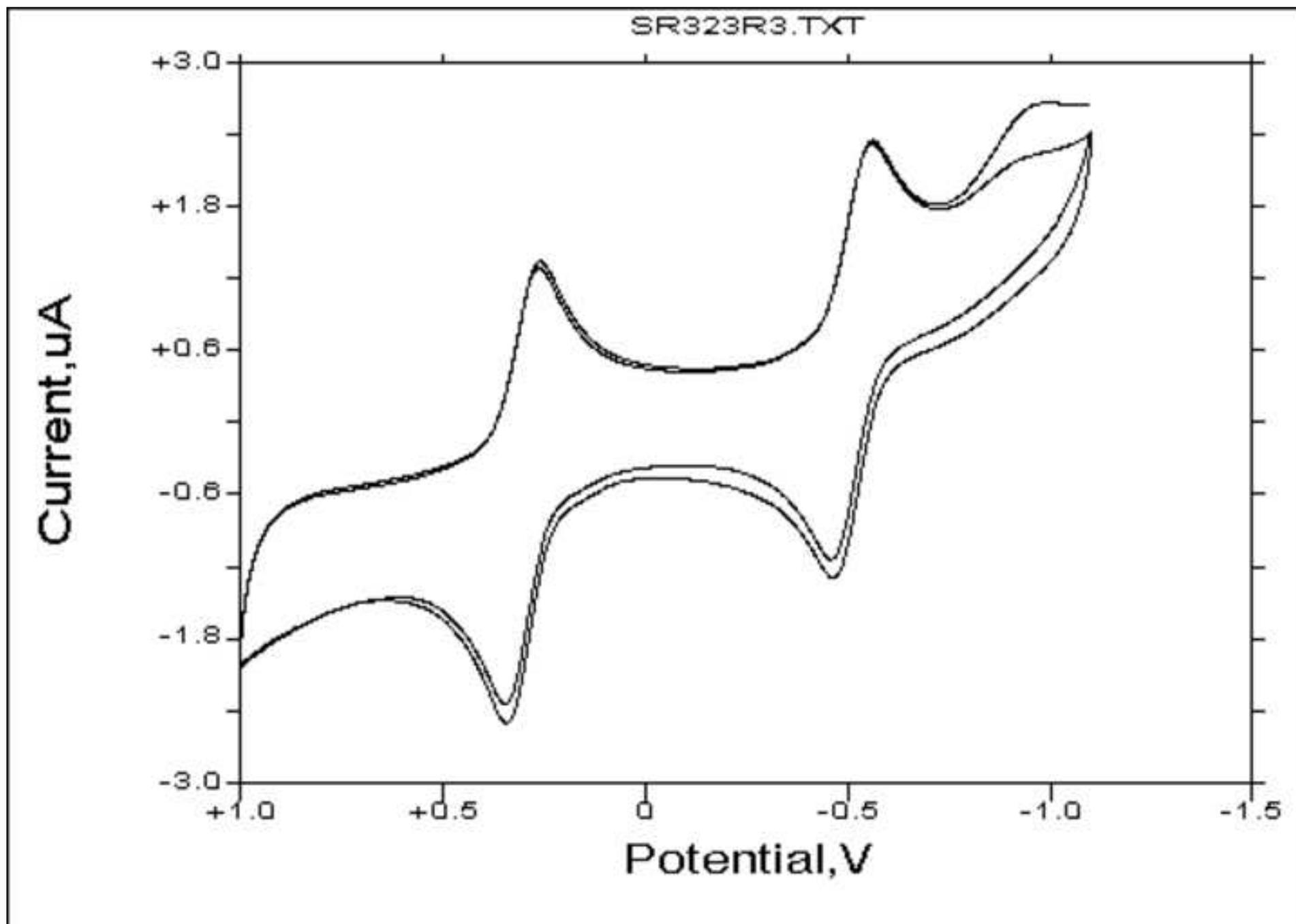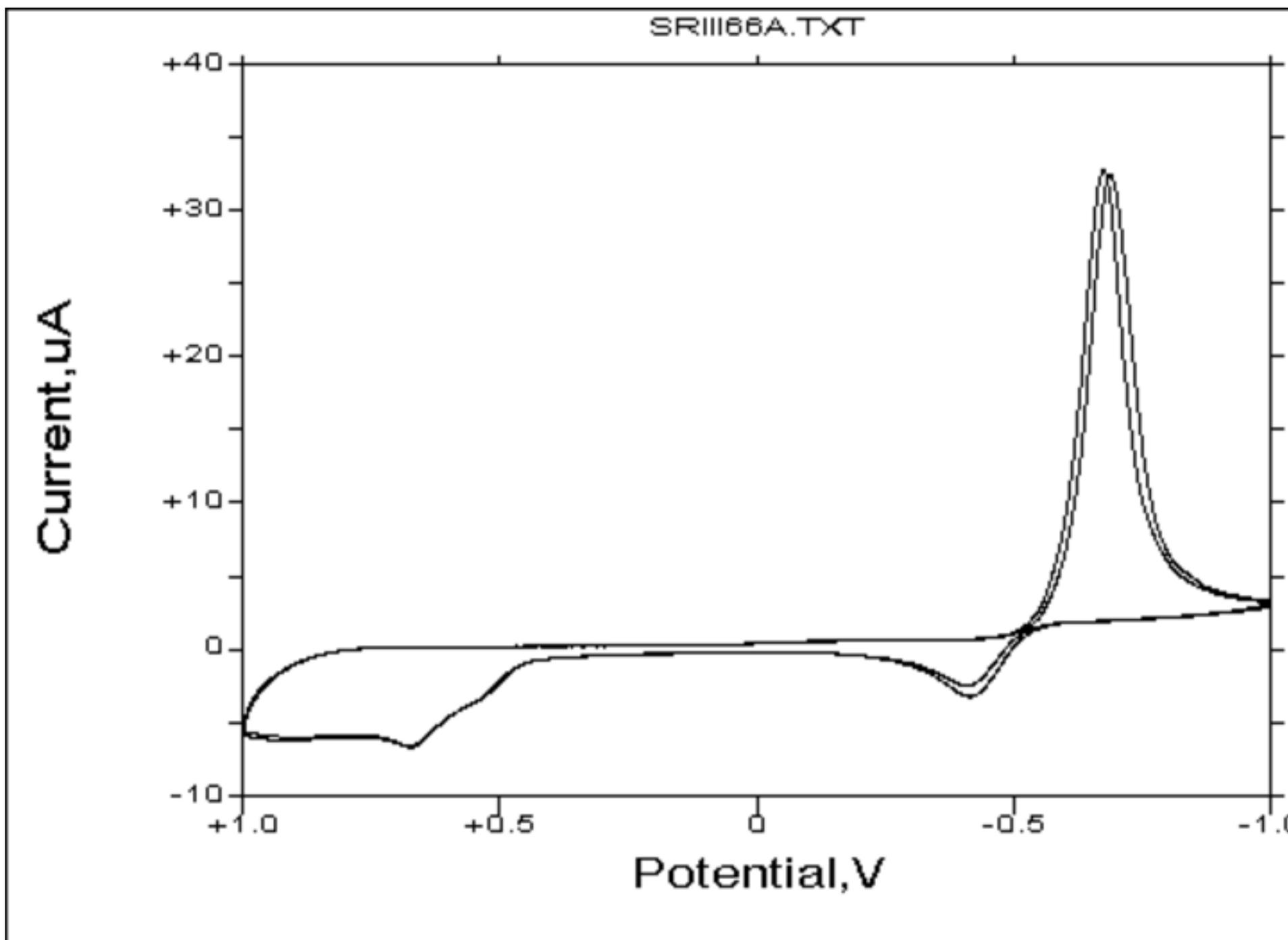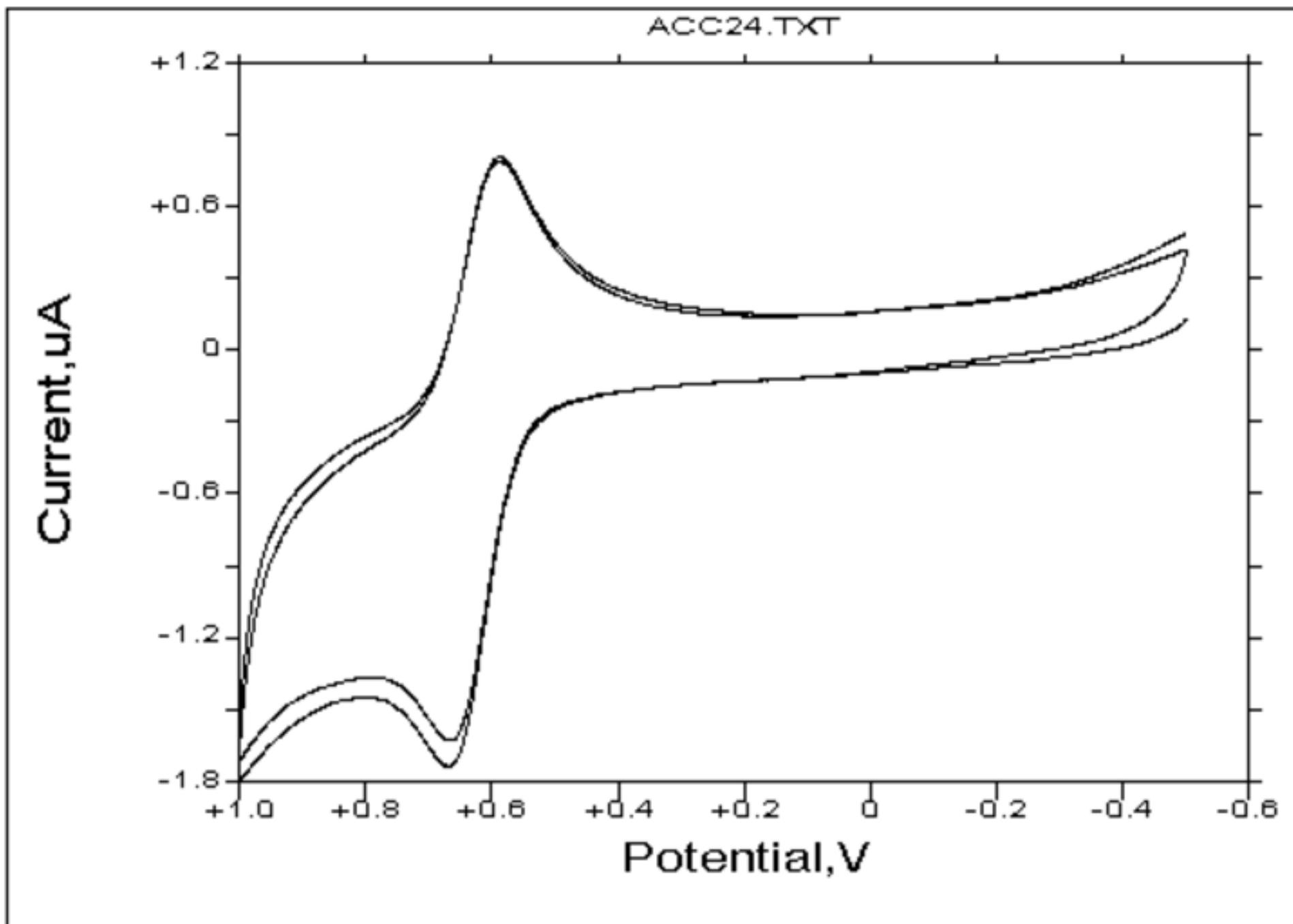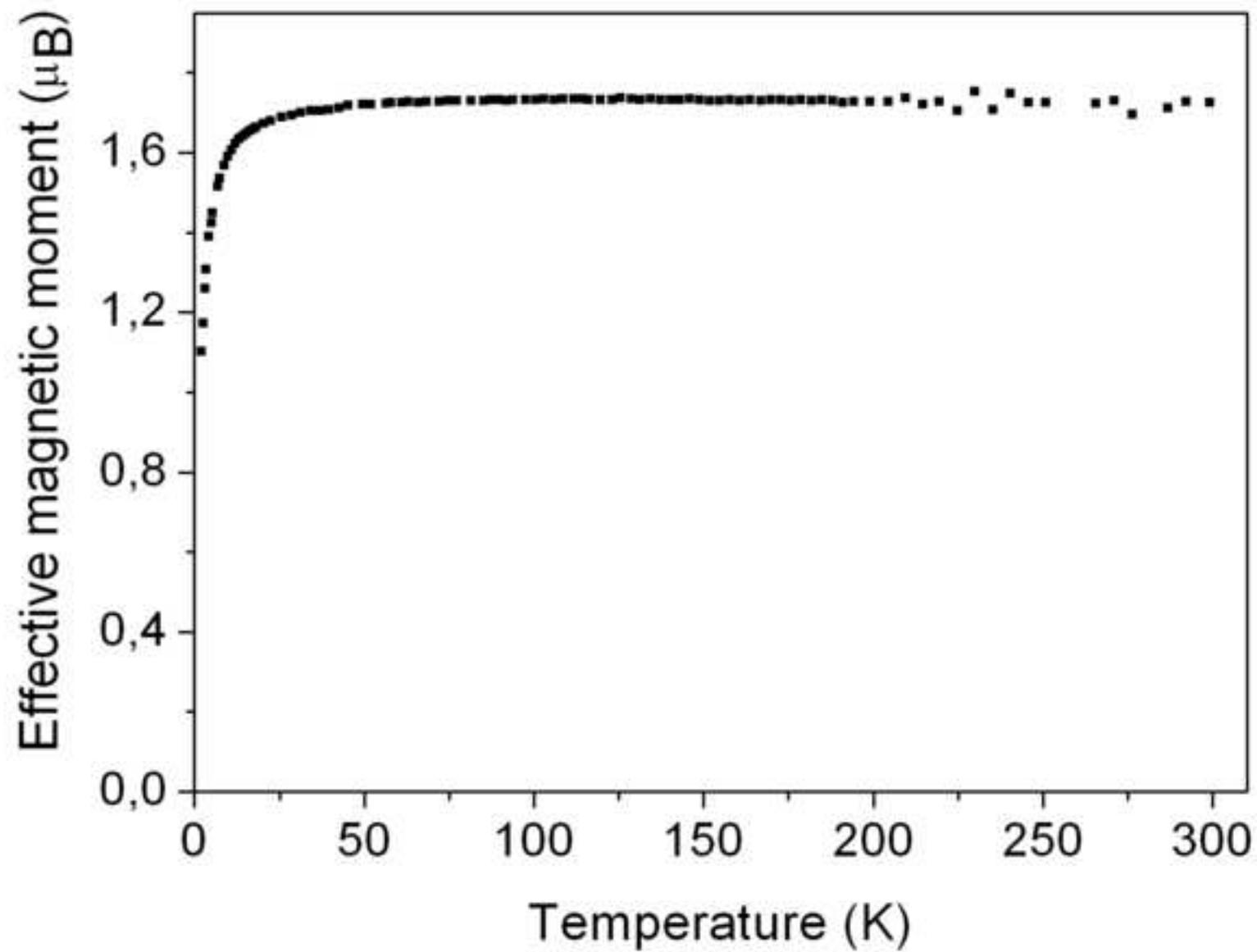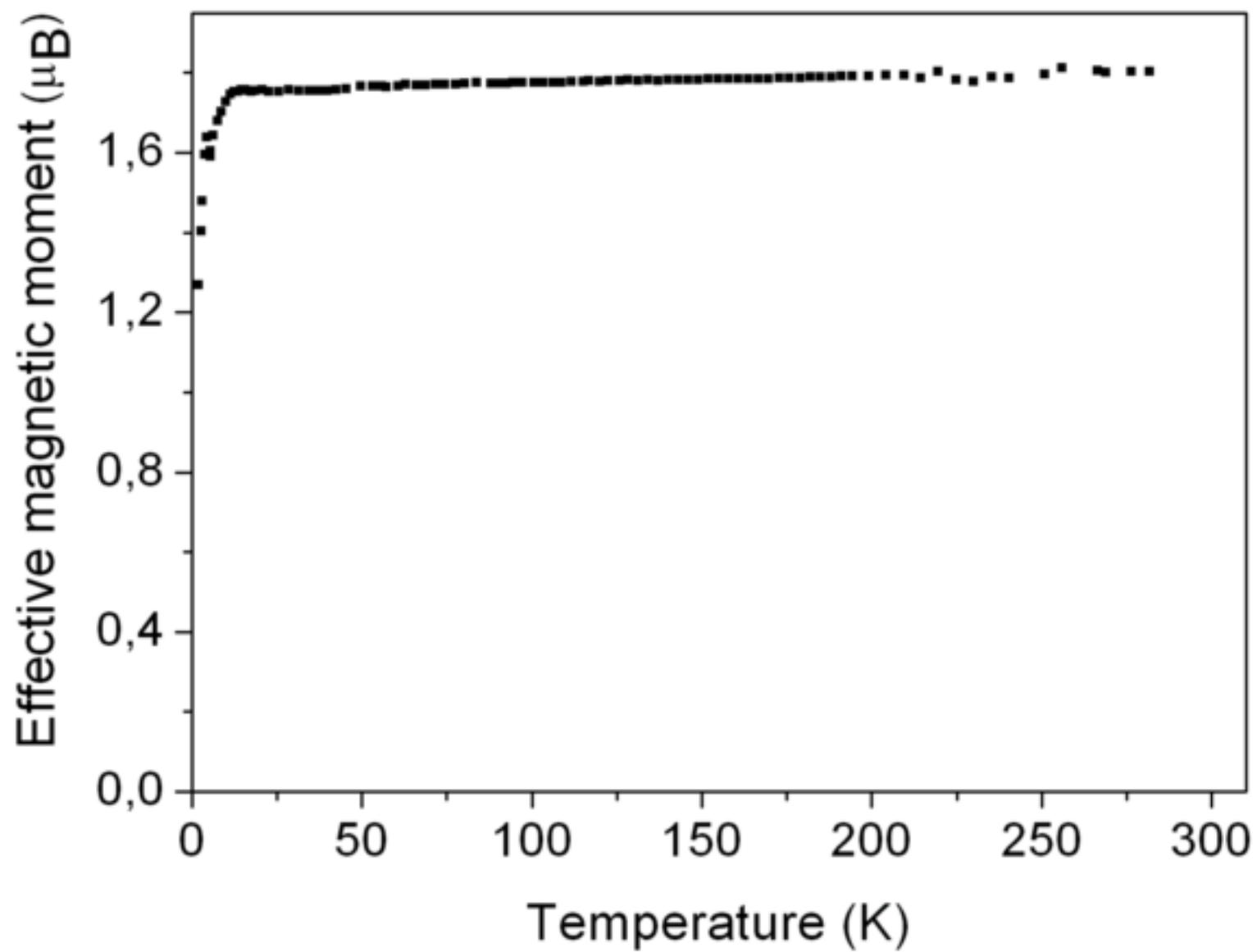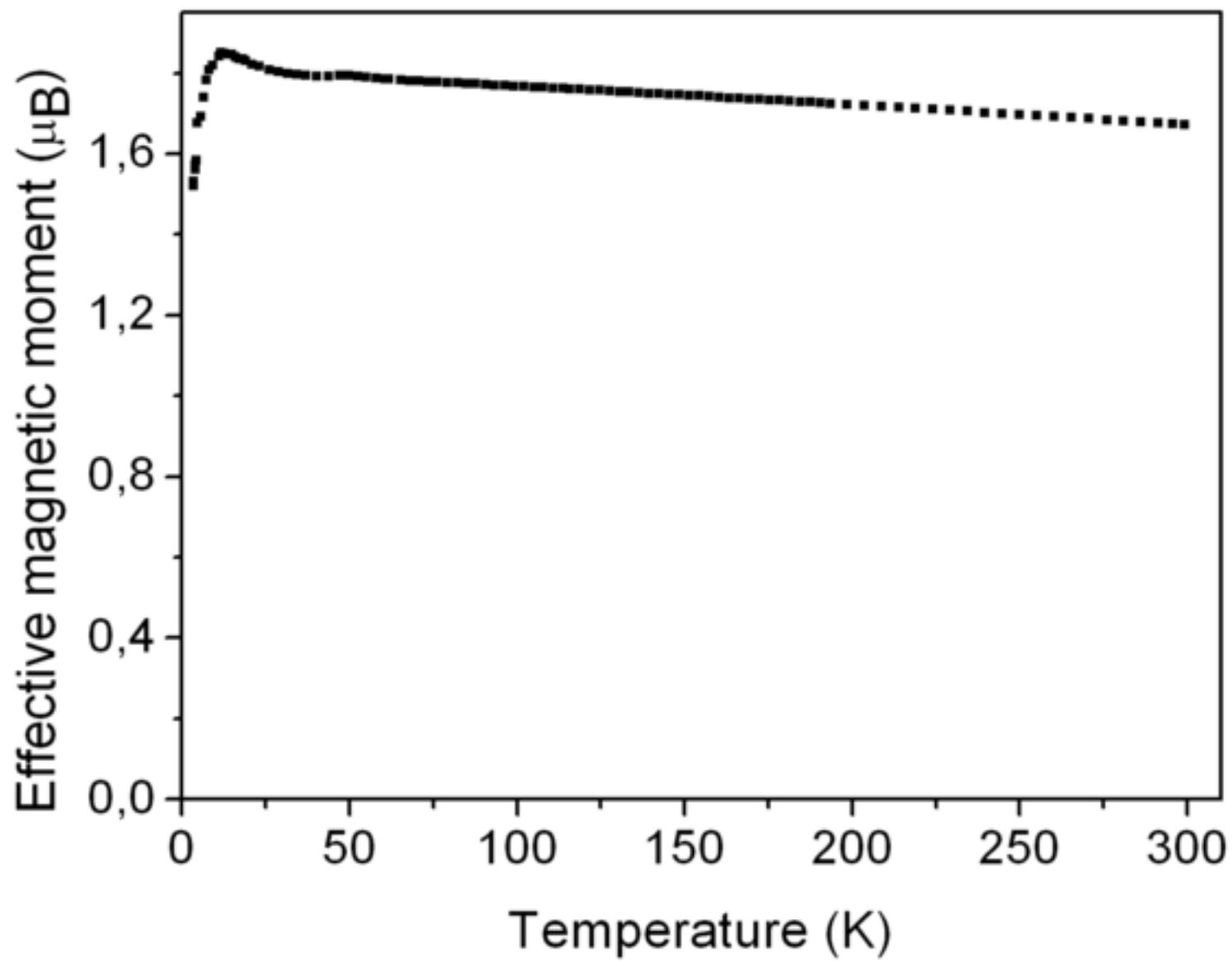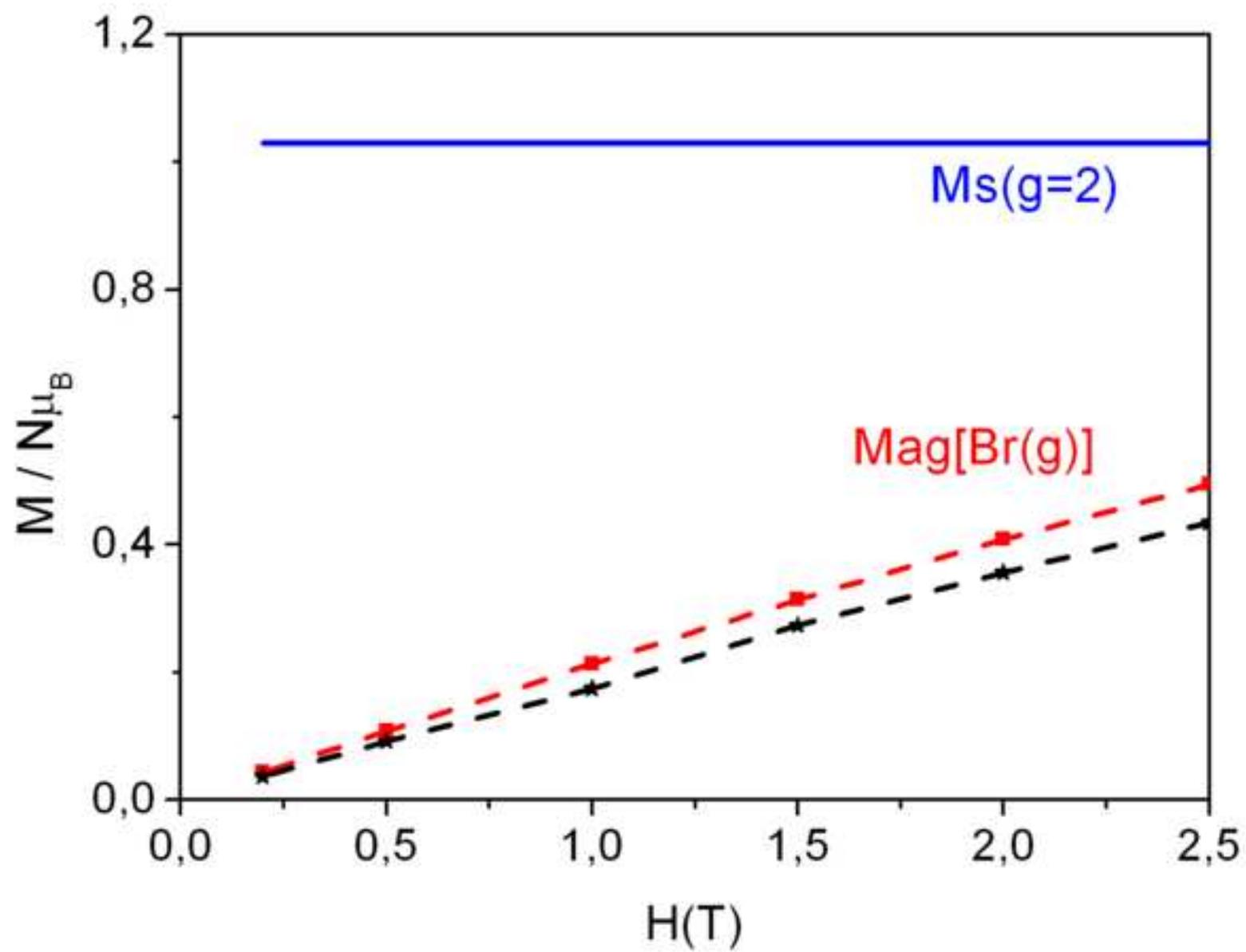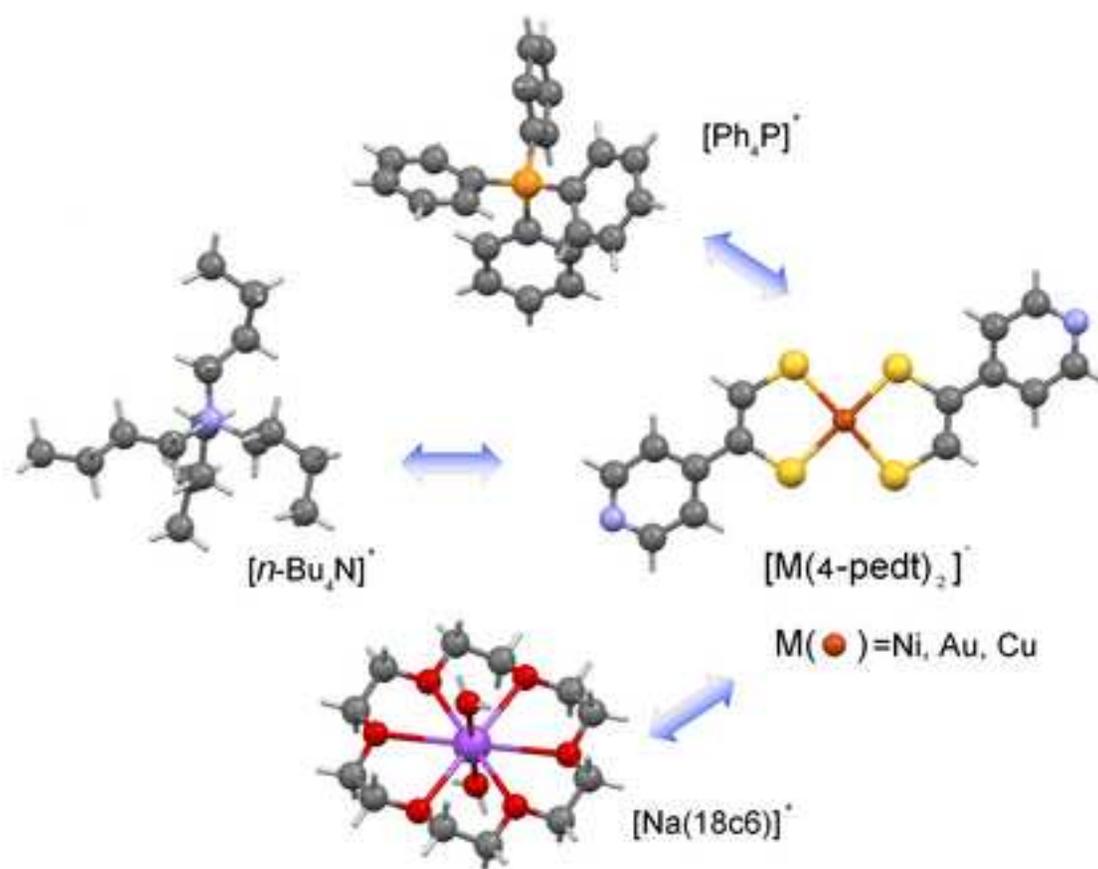
1   **Graphical Abstract**

2

3   The synthesis of M(*4*-pedt)$_2$ complexes of nickel, copper and gold obtained as

4   tetrabutylammonium, tetraphenylphosphonium or sodium 18-crown-6 ether salts are

5   described and these compounds are characterised by single-crystal X-ray diffraction, cyclic

6   voltammetry, EPR and magnetic susceptibility measurements.

7

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