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# Preparation and characterization of macrocyclic dinickel complexes coligated by monoalkyl- and dialkylcarbamates

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Dedicated to Professor Dr. Bernhard Lippert with appreciation for his friendship

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## ABSTRACT

The dinuclear nickel(II) complex  $[Ni_2L(CI)]^+(1)$ , where  $(L)^{2-}$  represents a 24-membered binucleating hexamine-dithiophenolate ligand, reacts readily with primary and secondary amines RR'NH in the presence of CO<sub>2</sub> (1 bar) to give dinuclear monoalkyl- and dialkylcarbamate complexes  $[Ni_2L(O_2CNRR')]^+$  (R = H, R' = CH<sub>2</sub>Ph (2), R = H, R' = n-Bu (3), R = H, R' = n-Oct (4), R = H, R' = CH<sub>2</sub>CH<sub>2</sub>OH (5), R = R' = Et (6), and R = R' = CH<sub>2</sub>CH<sub>2</sub>OH (7)). Complexes 2-7 can also be prepared by the reaction of 1 with CO<sub>2</sub>(air)/amine. The carbamate complexes are hydrolyzed in methanolic solution to give the known alkylcarbonate complex  $[Ni_2L(O_2COMe)]^+$  (8). These conversions are less rapid than the transesterification reactions of 8, due to a less electron-demanding carboxyl C(carbamate) atom. All new complexes were either isolated as per-chlorate or tetraphenylborate salts and fully characterized by elemental analysis, UV/Vis, and IR spectros-copy. The structures of 2[BPh<sub>4</sub>] and 7[BPh<sub>4</sub>] have also been determined by X-ray crystallography. They confirm the presence of  $\mu_{1,3}$ -bridging alkylcarbamate units in the products.

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## 1. Introduction

The chemistry of carbamic acid  $H_2NCO_2H$  [1] and its organo derivatives  $R_2NCO_2H$  [2] has been extensively investigated in recent years [3], owing to their relevance in biological systems [4,5], their technological importance [6–8], and their occurrence in interstellar space [9]. Carbamate ligands have also been widely used for the preparation of transition metal complexes [10,11], and some carbamate complexes have found applications as intermediates in organic synthesis [12–16]. We therefore extended our studies to such systems.

In previous papers, we reported a series of coordinatively unsaturated  $[M_2L(L')]^+$  complexes of first row transition metal ions supported by the binucleating hexaaza-dithiophenolate ligand  $L^{2-}$  (Scheme 1). The dinuclear  $[M_2L(L')]^+$  complexes have a rich coordination chemistry since their active coordination site is accessible for a large variety of coligands (L') such as Cl<sup>-</sup> [17], OH<sup>-</sup> [18], NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, N<sub>3</sub><sup>-</sup> [19], BH<sub>4</sub><sup>-</sup> [20], ClO<sub>4</sub><sup>-</sup> [21], and various carboxylates [22–26]. The hydroxo- and boranato-bridged dinickel complexes are unique in the sense that they readily fix carbon dioxide from air in the form of methylcarbonate [Ni<sub>2</sub>L(MeOCO<sub>2</sub>)]<sup>+</sup>

[27-30] or formate complexes  $[Ni_2L(HCO_2)]^+$ , respectively (Scheme 1) [20]. In view of the biological, technological and environmental importance of such reactions, we decided to explore the possibility of fixing CO<sub>2</sub> in the form of carbamate complexes. Our first attempts afforded a series of dinuclear Ni carbamate complexes of the type  $[Ni_2L(O_2CNRR')]^+$ . Their preparation, reactivity, spectroscopic properties and X-ray crystal structures are reported here. To our knowledge, dinuclear nickel amine-thiophenolate coligated by alkyl- or dialkylcarbamates are without precedence in the literature.

#### 2. Experimental

## 2.1. General methods and instrumentation

Complex [Ni<sub>2</sub>L(Cl)][ClO<sub>4</sub>] (**1**[ClO<sub>4</sub>]) was prepared according to the literature procedure [17]. All other compounds were purchased. Melting points were determined with a Waters VG-ZAB-HSQ instrument in open glass capillaries and are uncorrected, infrared spectra were recorded on a Bruker Vector27 FT-IR-spectrometer. Electronic absorption spectra were taken on a JASCO V670 UV/Vis/near spectrometer. Elemental analyses were carried out with a VARIO EL – elemental analyzer.

**CAUTION**! Perchlorate salts are potentially explosive. Only small quantities should be prepared and handled with appropriate care.



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**Scheme 1.** Structures of dinuclear metal complexes  $[M_2L(L')]^{n+}$  supported by the hexaaza-dithiophenolate ligand  $(L)^{2-}(L' = coligand)$  and  $CO_2$  fixation by  $[Ni_2L(OH)]^*$  (Eq. 1) and  $[Ni_2L(BH_4)]^*$  (Eq. 2).

#### 2.2. Synthesis of $[Ni_2L(\mu-O_2CNHCH_2Ph)][ClO_4]$ (2[ClO<sub>4</sub>])

A solution of **1**[ClO<sub>4</sub>] (184 mg, 0.200 mmol) and benzylamine (107 mg, 1.00 mmol) in acetonitrile (40 mL) was stirred for 1 day under a CO<sub>2</sub> atmosphere (1 bar). To the resulting pale-green solution was added a solution of  $LiClO_4 \cdot 3H_2O$  (321 mg, 2.00 mmol) in ethanol (20 mL). The solution was quickly concentrated in vacuo to  $\sim$ 20 mL. The resulting green solid was filtered, washed with cold ethanol, and dried in air. The crude product was purified by recrystallization from acetonitrile/ethanol. Yield: 168 mg (81%). M.p.: 326-327 °C (decomp.). IR (KBr): v/cm<sup>-1</sup> 3546 (m, v[NH]), 3456 (m), 2962 (s), 2867 (s), 1597 (s, v<sub>as</sub>[RNHCO<sub>2</sub><sup>-</sup>]), 1459 (s), 1392 (m), 1363 (m), 1342 (m, v<sub>s</sub>[RNHCO<sub>2</sub><sup>-</sup>]), 1306 (m), 1263 (w), 1233 (w), 1202 (w), 1170 (w), 1153 (m), 1094 (vs  $v_3[\mu-ClO_4^{-}]$ ), 1040 (s), 1001 (w), 982 (w), 931 (w), 913 (w), 881 (w), 826 (m), 818 (m), 808 (w), 791 (w), 751 (w), 702 (w), 624 (s,  $v_4[\mu-ClO_4^{-}])$ , 563 (w), 535 (w), 492 (w), 416 (w). UV/Vis (MeCN):  $\lambda_{max}/nm$  ( $\epsilon/$  $M^{-1} cm^{-1}$ ) 270 (17394), 304 (15547), 326 (13044), 658 (42), 1136 (65). Elemental Anal. Calc. for C<sub>46</sub>H<sub>72</sub>ClN<sub>7</sub>Ni<sub>2</sub>O<sub>6</sub>S<sub>2</sub> (1036.08): C, 53.33; H, 7.00; N, 9.46; S, 6.19. Found: C, 53.12; H, 7.22; N, 9.58; S, 6.08%.

## 2.3. Synthesis of $[LNi_2(\mu-O_2CNHCH_2Ph)][BPh_4]$ (2[BPh\_4])

A solution of NaBPh4 (342 mg, 1.00 mmol) in methanol (50 mL) was added to a solution of  $2[ClO_4]$  (104 mg, 0.100 mmol) in methanol (40 mL). The resulting green product was quickly filtered, washed with ethanol and dried in air to give 111 mg (88%) of 2[BPh4] as a green, air-stable, microcrystalline powder. M.p.: 305–306 °C (decomp.). IR (KBr): v/cm<sup>-1</sup> 3546 (w), 3459 (m), 3055 (m), 3031 (m), 2962 (s), 2864 (s), 1598 (s, v<sub>as</sub>[RNHCO<sub>2</sub><sup>-</sup>]), 1479 (s), 1458 (s), 1381 (m), 1362 (m), 1331 (m), 1304 (m), 1263 (m), 1231 (m), 1200 (w), 1168 (w), 1151 (m), 1077 (s), 1066 (s), 1040 (s), 999 (w), 982 (w), 929 (w), 911 (m), 881 (m), 843 (m), 825 (s), 807 (w), 791 (w), 749 (w), 732 (s,  $v[BPh_4^-]$ ), 702 (s,  $v[BPh_4^-]$ ), 629 (m), 611 (s), 582 (w), 562 (w), 534 (w), 469 (w), 415 (w). UV/Vis (MeCN):  $\lambda_{max}/$ nm (ε/M<sup>-1</sup> cm<sup>-1</sup>) 266 (19140), 304 (15208), 327 (13054), 657 (32), 1136 (69). Elemental Anal. Calc. for C<sub>70</sub>H<sub>92</sub>BN<sub>7</sub>Ni<sub>2</sub>O<sub>2</sub>S<sub>2</sub> (1255.85): C, 66.95; H, 7.38; N, 7.81; S, 5.11. Found: C, 66.30; H, 7.60; N, 7.82; S, 5.26%.

#### 2.4. Synthesis of $[Ni_2L(\mu-O_2CNHnC_4H_9)][ClO_4]$ (3[ClO<sub>4</sub>])

This compound was prepared in analogy to **2**[ClO<sub>4</sub>]. Yield: 157 mg (78%). M.p.: >317 °C (decomp.). IR (KBr):  $\nu/cm^{-1}$  3550 (w,  $\nu[NH]$ ), 3459 (m), 2958 (s), 2928 (w), 2899 (w), 2863 (s), 1592 (s,  $\nu_{as}[RNHCO_2^{-}]$ ), 1485 (m), 1462 (s), 1392 (m), 1361 (m), 1349 (w), 1334 (w,  $\nu_{s}[RNHCO_2^{-}]$ ), 1311 (w), 1292 (w), 1263 (m), 1233 (m), 1202 (w), 1170 (m), 1152 (m), 1096 (vs,  $\nu_{3}[ClO_{4}^{-}]$ ), 1040 (s), 1002 (w), 983 (w), 931 (w), 913 (w), 881 (w), 825 (m), 818 (m), 808 (w), 791 (w), 751 (w), 624 (s,  $\nu_{4}[ClO_{4}^{-}]$ ), 563 (w), 541 (w), 535 (w), 492 (w), 416 (w). UV/Vis (MeCN):  $\lambda_{max}/nm$  ( $\epsilon/M^{-1}$  cm<sup>-1</sup>) 656 (46), 1135 (88). Elemental *Anal.* Calc. for C<sub>43</sub>H<sub>74</sub>ClN<sub>7</sub>Ni<sub>2</sub>O<sub>6</sub>S<sub>2</sub> (1002.06): C, 51.54; H, 7.44; N, 9.78; S, 6.40. Found: C, 51.32; H, 7.22; N, 9.82; S, 6.32%.

## 2.5. Synthesis of $[Ni_2L(\mu-O_2CNHnC_8H_{17})][ClO_4]$ (4[ClO<sub>4</sub>])

This compound was prepared in analogy to **2**[ClO<sub>4</sub>]. Yield: 165 mg (78%). M.p.: 318 °C (decomp.). IR (KBr):  $\nu/\text{cm}^{-1}$  3538 (m,  $\nu$ [NH]), 2957 (s), 2926 (s), 2858 (s), 1593 (s,  $\nu_{as}[\text{RNHCO}_2^{-}]$ ), 1486 (s), 1460 (s), 1392 (m), 1362 (m), 1347 (w), 1336 (w), 1312 (m), 1293 (w), 1264 (m), 1233 (m), 1203 (w), 1170 (m), 1153 (m), 1095 (vs,  $\nu_3[\text{ClO}_4^{-}]$ ), 1040 (s), 1002 (w), 982 (w), 931 (w), 913 (w), 881 (w), 825 (m), 818 (m), 808 (w), 791 (w), 751 (m), 627 (s,  $\nu_4[\text{ClO}_4^{-}]$ ), 563 (w), 541 (w), 535 (w), 492 (w), 416 (w). UV/ Vis (MeCN):  $\lambda_{max}/\text{nm} (\varepsilon/\text{M}^{-1} \text{ cm}^{-1}) = 656 (45), 1132 (103)$ . Elemental *Anal.* Calc. for C<sub>47</sub>H<sub>82</sub>ClN<sub>7</sub>Ni<sub>2</sub>O<sub>6</sub>S<sub>2</sub> (1058.17): C, 53.35; H, 7.81; N, 9.27; S, 6.06. Found: C, 53.22; H, 7.65; N, 9.30; S, 5.82%.

## 2.6. Synthesis of $[Ni_2L(\mu-O_2CNEt_2)][ClO_4]$ (5[ClO<sub>4</sub>])

A solution of [Ni<sub>2</sub>L(Cl)]ClO<sub>4</sub> (184 mg, 0.200 mmol) and diethylamine (731 mg, 10 mmol) in acetonitrile (40 mL) was stirred under an atmosphere of CO<sub>2</sub> for 2 days, during which time the color of the solution turned from yellow to green. A solution of LiClO<sub>4</sub> · 3H<sub>2</sub>O (320 mg, 2.00 mmol) in ethanol (20 mL) was added, and the clear solution concentrated to ca. 20 mL to produce a green solid that was filtered, washed with cold ethanol and dried in air. Yield: 164 mg (82%). M.p.: 309–310 °C (decomp.). IR (KBr): v/cm<sup>-1</sup> 3430 (br m), 2962 (s), 2926 (w), 2900 (w), 2867 (s), 2805 (w), 1637 (w), 1559 (s, v<sub>as</sub>[R<sub>2</sub>NCO<sub>2</sub><sup>-</sup>]), 1481 (s), 1460 (vs), 1423 (m), 1395 (w), 1374 (vw), 1363 (w), 1309 (s), 1264 (w), 1233 (w), 1202 (w), 1170 (vw), 1152 (m), 1120 (w), 1109 (w), 1081 (vs,  $v_3[ClO_4^{-}])$ , 1040 (m), 1003 (w), 982 (w), 931 (m), 913 (m), 880 (m), 826 (m), 818 (m), 808 (w), 788 (w), 752 (w), 625 (m, v<sub>4</sub>[ClO<sub>4</sub><sup>-</sup>]), 564 (w), 535 (w), 492 (w), 415 (w). UV/Vis (MeCN):  $\lambda_{max}/nm \ (\epsilon/M^{-1} \ cm^{-1}) = 273 \ (20829), \ 305 \ (15337), \ 327 \ (12958),$ 659 (10), 1138 (75). Elemental Anal. Calc. for C<sub>43</sub>H<sub>74</sub>ClN<sub>7</sub>Ni<sub>2</sub>O<sub>6</sub>S<sub>2</sub> (1002.06): C, 51.54; H, 7.44; N, 9.78; S, 6.40. Found: C, 51.39; H, 7.37; N, 9.81; S, 6.22%.

#### 2.7. Synthesis of $[Ni_2L(\mu-O_2CNEt_2)][BPh_4]$ (5[BPh4])

The preparation of this compound was similar to that used for **2**[BPh<sub>4</sub>]. Yield: 111 mg (91%). M.p.: 288–289 °C (decomp.). IR (KBr):  $\nu/\text{cm}^{-1}$  3441 (m), 3059 (m), 3032 (m), 2963 (s), 2866 (s), 1634 (w), 1580 (w), 1555 (s,  $\nu_{as}[R_2\text{NCO}_2^{-1}]$ ), 1481 (s), 1459 (vs), 1421 (s), 1394 (m), 1375 (w), 1362 (m), 1309 (s), 1265 (m), 1232 (m), 1201 (w), 1170 (w), 1152 (m), 1078 (s), 1058 (m), 1041 (m), 1001 (w), 981 (w), 930 (m), 911 (m), 881 (m), 825 (m), 817 (m), 807 (m), 788 (w), 732 (s,  $\nu[\text{BPh}_4^{-1}]$ ), 704 (s,  $\nu[\text{BPh}_4^{-1}]$ ), 629 (m), 612 (m), 563 (w), 534 (w), 468 (w), 415 (w). UV/Vis (MeCN):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}$  cm<sup>-1</sup>) = 304 (14889), 327 (12659), 657 (21), 1137 (69). Elemental *Anal.* Calc. for C<sub>67</sub>H<sub>94</sub>BN<sub>7</sub>Ni<sub>2</sub>O<sub>2</sub>S<sub>2</sub> (1221.84): C, 65.86; H, 7.75; N, 8.02; S, 5.25. Found: C, 65.62; H, 7.74; N, 7.60; S, 5.58%.

#### 2.8. Synthesis of $[Ni_2L(\mu-O_2CNHCH_2CH_2OH)][ClO_4]$ (6[ClO<sub>4</sub>])

This compound was prepared in analogy to **2**[ClO<sub>4</sub>]. Yield: 171 mg (86%). M.p.: 320–312 °C (decomp.). IR (KBr):  $\nu/$ cm<sup>-1</sup> = 3530 (w,  $\nu$ [NH]), 3389 (s br,  $\nu$ [NH]), 2960 (s), 2868 (s), 1593 (s,  $\nu_{as}$ [RNHCO<sub>2</sub><sup>-</sup>]), 1484 (s), 1461 (w), 1393 (m), 1363 (m), 1315 (m), 1264 (m), 1233 (m), 1202 (w), 1170 (w), 1153 (m), 1099 (vs,  $\nu_3$ [ClO<sub>4</sub><sup>-</sup>]), 1079 (s), 1059 (s), 1041 (s), 1002 (w), 983 (w), 931 (m), 913 (m), 881 (m), 826 (s), 808 (m), 792 (w), 752 (w), 624 (s,  $\nu_4$ [ClO<sub>4</sub><sup>-</sup>]), 564 (w), 537 (w), 494 (w), 416 (w). UV/ Vis (CH<sub>3</sub>CN):  $\lambda_{max}$ /nm ( $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>) 270 (16907), 304 (14975), 326 (12776), 657 (28), 1136 (63). Elemental *Anal.* Calc. for C<sub>41</sub>H<sub>70</sub>ClN<sub>7</sub>Ni<sub>2</sub>O<sub>7</sub>S<sub>2</sub> (990.01): C, 49.74; H, 7.13; N, 9.90; S, 6.48. Found: C, 49.48; H, 7.31; N, 10.12; S, 6.17%.

#### 2.9. Synthesis of $[Ni_2L(\mu-O_2CNHCH_2CH_2OH)][BPh_4]$ (**6** $[BPh_4]$ )

This compound was prepared in a manner identical to that used for **2**[BPh<sub>4</sub>]. Yield: 112 mg (93%). M.p.: 296–297 °C (decomp.). IR (KBr):  $\nu/\text{cm}^{-1}$  3532 (s), 3441 (s), 3054 (m), 3032 (m), 2963 (s), 2868 (s), 2806 (w), 1948 (w), 1817 (w), 1590 (s,  $\nu_{as}[\text{RNHCO}_2^{-}])$ , 1483 (s), 1460 (s), 1427 (m), 1392 (m), 1361 (m), 1316 (m), 1264 (m), 1234 (w), 1201 (w), 1153 (w), 1133 (w), 1111 (w), 1078 (s), 1057 (s), 1041 (s), 1000 (w), 983 (w), 930 (w), 912 (w), 884 (w), 843 (m), 825 (w), 808 (w), 792 (w), 735 (s,  $\nu[\text{BPh}_4^{-}])$ , 656 (w), 630 (m), 613 (m), 562 (w), 535 (w), 493 (w), 470 (w), 415 (w). UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max}/\text{nm}$  ( $\epsilon/\text{M}^{-1}$  cm<sup>-1</sup>) = 266 (21170), 304 (15869), 326 (13530), 657 (35), 1136 (71). Elemental *Anal.* Calc. for C<sub>65</sub>H<sub>90</sub>BN<sub>7</sub>Ni<sub>2</sub>O<sub>3</sub>S<sub>2</sub> (1209.78): C, 64.53; H, 7.50; N, 8.10; S, 5.30. Found: C, 64.43; H, 7.69; N, 7.83; S, 4.82%.

## 2.10. Synthesis of $[Ni_2L(\mu-O_2CN(CH_2CH_2OH)_2)][ClO_4]$ (7[ClO\_4])

This compound was prepared in analogy to **2**[ClO<sub>4</sub>]. Yield: 158 mg (76%). M.p.: 295–296 °C (decomp.). IR (KBr):  $\nu/$  cm<sup>-1</sup> = 3442 (s), 2955 (s), 2869 (s), 2023 (w), 1634 (w), 1564 (s,  $\nu_{as}[R_2NCO_2^{-}])$ , 1461 (s), 1414 (m), 1397 (m), 1363 (m), 1310 (m), 1264 (m), 1233 (m), 1202 (w), 1170 (w), 1153 (m), 1119 (s), 1099 (vs,  $\nu_3[ClO_4^{-}])$ , 1079 (s), 1059 (s), 1041 (s), 1002 (w), 983 (w), 930 (w), 913 (m), 881 (m), 826 (m), 808 (w), 790 (w), 753 (w), 670 (w), 626 (vs,  $\nu_4[ClO_4^{-}])$ , 564 (w), 536 (w), 494 (w), 416 (w). UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max}/m (\epsilon/M^{-1} \text{ cm}^{-1}) = 270$  (16578), 306 (14929), 328 (12721), 660 (31), 1134 (70). Elemental *Anal.* Calc. for C<sub>43</sub>H<sub>74</sub>ClN<sub>7</sub>Ni<sub>2</sub>O<sub>8</sub>S<sub>2</sub> (1034.06): C, 49.94; H, 7.21; N, 9.48; S, 6.20. Found: C, 49.73; H, 7.39; N, 9.68; S, 5.92%.

#### 2.11. Synthesis of $[Ni_2L(\mu-O_2CN(CH_2CH_2OH)_2)][BPh_4]$ (7[BPh\_4])

This compound was prepared in a manner identical to that used for **2**[BPh<sub>4</sub>]. Yield 116 mg (93%). M.p.: 266–267 °C (decomp.). IR (KBr):  $\nu/\text{cm}^{-1}$  = 3443 (s), 3055 (m), 3035 (m), 2998 (m), 2963 (s), 2868 (s), 2806 (w), 1945 (w), 1633 (w), 1566 (s,  $\nu_{as}[\text{R}_2\text{NCO}_2^{-}]$ ), 1480 (s), 1460 (s), 1420 (m), 1396 (m), 1363 (m), 1309 (m), 1264 (m), 1233 (w), 1201 (m), 1170 (w), 1152 (w), 1077 (s), 1058 (s), 1040 (s), 982 (w), 930 (w), 912 (w), 882 (w), 844 (w), 826 (m), 790 (w), 748 (m), 734 (s,  $\nu[\text{BPh}_4^{-}]$ ), 706 (s,  $\nu[\text{BPh}_4^{-}]$ ), 670 (w), 629 (m), 613 (m), 563 (w), 537 (w), 494 (w), 469 (w), 416 (w). UV/Vis (CH<sub>3</sub>CN):  $\lambda_{max}/\text{nm}$  ( $\epsilon/\text{M}^{-1}$  cm<sup>-1</sup>) 266 (18258), 306 (13948), 328 (11887), 657 (32), 1133 (62). Elemental *Anal.* Calc. for C<sub>67</sub>H<sub>94</sub>BN<sub>7</sub>Ni<sub>2</sub>O<sub>4</sub>S<sub>2</sub> · 2H<sub>2</sub>O (1289.87): C, 62.39; H, 7.66; N, 7.60; S, 4.97. Found: C, 62.16; H, 7.60; N, 7.33; S, 4.62%.

#### 2.12. Reactivity studies

Solubility considerations and the slow rate of the reactions at ambient temperature dictated that all alcoholysis reactions were carried out with the perchlorate complexes in neat methanol at 62 °C. In a typical experiment, a solution of the carbamate complex (ca. 80 mg) in methanol (~100 mL) was refluxed under argon. Samples (ca. 10 mL) of the reaction mixture were removed at regular intervals, taken to dryness, and then analyzed by IR spectroscopy. The relative amounts of precursors and products could be quantified by visual inspection of the intensity of the characteristic stretching frequencies ( $\nu_{as}$ [RR'NCO<sub>2</sub><sup>-</sup>] for **2–7**,  $\nu_{as}$ [CH<sub>3</sub>OCO<sub>2</sub><sup>-</sup>] for **8**).

#### 2.13. Collection and reduction of X-ray data

Single crystals of  $2[BPh_4] \cdot 0.75MeCN \cdot 0.25H_2O$  and  $7[BPh_4] \cdot 0.5MeCN$  were grown by recrystallization from acetonitrile. The data sets were collected at 213(2) K using a STOE IPDS-2T diffractometer and graphite monochromated Mo K $\alpha$  radiation (0.71073 Å). The intensity data were processed with the program STOE X-AREA. Structures were solved by direct methods [31] and refined by full-matrix least-squares on the basis of all data against  $F^2$  using SHELXL-97 [32]. PLATON WAS used to search for higher symmetry [33]. H atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. All non-hydrogen atoms were refined anisotropically. Selected crystallographic data are summarized in Table 1.

In the crystal structure of **2**[BPh<sub>4</sub>]  $\cdot$  0.75MeOH  $\cdot$  0.25H<sub>2</sub>O one solvent site was found to be occupied partially by MeCN and H<sub>2</sub>O solvate molecules. The hydrogen atoms H(7) bonded to the benzylic nitrogen atom N(7) was located unambiguously from final Fourier maps. Water hydrogen atoms were not included in the refinement. In **7**[BPh<sub>4</sub>]<sub>2</sub>  $\cdot$  0.5MeCN two *tert*-butyl groups were found to be rotationally disordered. The disorder was refined with restrained C–C and C $\cdot$  C distances and fixed occupancy factors of 0.50 applying the SADI-instructions implemented in the sHELXL program suite. One of the two hydroxyethyl groups in molecule B was also found to be disordered over two sites with occupancy factors of 0.50 each. Drawings were produced with ORTEP 3 for Windows [34].

Table 1			
Crystallographic data for <b>2</b>	BPh₄] · 0.75MeCN ·	0.25H <sub>2</sub> O and 7	BPh <sub>4</sub> ] · 0.5MeCN

Compound	$\textbf{2}[\text{BPh}_4] \cdot 0.75\text{MeCN} \cdot 0.25\text{H}_2\text{O}$	7[BPh4] · 0.5MeCN
Formula	C <sub>71.50</sub> H <sub>94.75</sub> BN <sub>7.75</sub> Ni <sub>2</sub> O <sub>2.25</sub> S <sub>2</sub>	C68H95.50BN7.50Ni2O4S2
M <sub>r</sub> [g/mol]	1291.15	1274.37
Space group	ΡĪ	$P2_1/c$
a (Å)	13.7854(4)	15.563(5)
b (Å)	15.6450(5)	31.695(11)
c (Å)	16.0833(5)	27.595(11)
α (°)	87.920(3)	90.00
β (°)	84.536(2)	105.962(7)
γ (°)	72.500(2)	90.00
V (Å <sup>3</sup> )	3293.05(18)	13087(8)
Ζ	2	8
D <sub>calc.</sub> (g/cm <sup>3</sup> )	1.302	1.294
Crystal size (mm <sup>3</sup> )	$0.20\times0.20\times0.20$	$0.30 \times 0.30 \times 0.10$
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.687	0.693
θ Limits (°)	3.47-28.00	1.00-29.07
Measured reflections	36032	40320
Independent reflections	15865	28420
Observed reflections <sup>a</sup>	13219	4546
Number of parameters	794	1537
$R_1^{\mathbf{b}}(R_1 \text{ all data})$	0.0488 (0.0580)	0.0857 (0.3913)
$wR_2^c$ ( $wR_2$ all data)	0.1463 (0.1529)	0.1706 (0.2642)
Maximum, minimum	0.981/-1.236	0.766/-0.831
peaks (e/Å <sup>3</sup> )		

<sup>a</sup> Observation criterion:  $I \ge 2\sigma(I)$ .

<sup>b</sup>  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$ 

<sup>c</sup>  $wR_2 = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \right\}^{1/2}.$ 

## 3. Results and discussion

#### 3.1. Synthesis and characterization of compounds

Complex [Ni<sub>2</sub>L(Cl)]ClO<sub>4</sub> **1** was found to react smoothly with a variety of amine/CO<sub>2</sub> systems (RNH<sub>2</sub>, R = Bz; *n*-Bu, *n*-Oct; R<sub>2</sub>NH, R = Et; CO<sub>2</sub> (1 bar)) in acetonitrile over reaction times of several hours to give the green cationic carbamate complexes **2–5**. The complexes could be isolated from the reaction mixtures upon addition of an excess of LiClO<sub>4</sub> · 3H<sub>2</sub>O in 70–80% yields (Scheme 2). The same products can also be obtained upon exposure of the reaction solutions to air in similar yields, but these reactions proceed much less rapidly (typically 3–4 days). All carbamate complexes are airstable solids that are readily soluble in a variety of common organic solvents such as dimethylformamide, acetonitrile, and dichloromethane, but insoluble in water. In alcoholic solutions alcoholysis occurs (see below).

Previous work in this laboratory has demonstrated that alcoholic solutions of **1** fix carbon dioxide from air in the form of alkylcarbonate complexes [27,28]. This prompted us to examine reactions of **1** with aminoalcohols/CO<sub>2</sub> and to determine which of the two possible products – alkylcarbonate or alkylcarbamate complex – would form (Scheme 3).

We chose to examine the reactions of **1** with ethanolamine and diethanolamine. Again, under ambient conditions both carbonation reactions ( $CO_2(1 \text{ bar})$  or  $CO_2(\text{air})$ ) proceeded smoothly producing green solutions, from which green crystals of [ $Ni_2L(O_2CNCH_2CH_2OH)$ ]ClO<sub>4</sub> (**6**) and [ $Ni_2L(O_2CN(CH_2CH_2OH)_2)$ ]-ClO<sub>4</sub> (**7**) were obtained in analytically pure form after addition of LiClO<sub>4</sub>, subsequent work-up and recrystallization.

Crystals of the perchlorate salts of **2–7** were not suitable for X-ray crystallographic analysis, therefore selected complexes were transformed into tetraphenylborate salts by salt metathesis reactions with NaBPh<sub>4</sub>. These salts exhibited better crystallinity. It has thus been possible to determine the solid state structures of **2**[BPh<sub>4</sub>] and **7**[BPh<sub>4</sub>] by X-ray crystallography. This confirmed unambiguously the formulation of the products as carbamate complexes as represented in Scheme 2. Thus, carbonation reactions of **1** with amines/CO<sub>2</sub> or aminoalcohols/CO<sub>2</sub> in acetonitrile proceed with strict "carbamate" selectivity.

Finally, we considered it worthwhile to probe whether the carbamate complexes **2–7** would undergo alcoholysis reactions with solvent molecules (Scheme 4) [35]. Indeed when the carbamate complexes are stirred in methanol at ambient temperature a slow conversion to the known methylcarbonate complex **8** takes place (ca. 10% conversion after 1 week by IR spectroscopy). When heated to reflux the reactions complete within a period of 3–5 days. The alkylcarbamate complexes **2–7** differ in this respect from the alkylcarbonate complexes of  $L^{2-}$  such as **8**. These hydrolyse much more



Scheme 2. Synthesis of carbamate complexes 2-7.



Scheme 3. Alkylcarbonate and alkylcarbamate complexes.



Scheme 4. Alcoholysis of alkylcarbamate complexes 2-7.

rapidly (100% conversion at ambient temperature within less than 24 h). This is indicative of extensive electron delocalisation of the nitrogen lone pair into the carboxyl group such that the carbamate is less susceptible for nucleophilic attack by the solvent than the alkycarbonate. It is supported by the crystal structure described below.

All compounds gave satisfactory elemental analyses and were characterized by IR and UV/Vis spectroscopy, and compounds **2**[BPh<sub>4</sub>] and **7**[BPh<sub>4</sub>] also by X-ray structure analysis. Characterization data for **8** were reported in previous work [27,28]. UV/Vis spectra of **2–7** in acetonitrile are marked by two weak absorption bands above 500 nm typical of octahedral Ni<sup>2+</sup> (d<sup>8</sup>, *S* = 1) ions (Table 2). Values below 500 nm are either associated with  $\pi$ – $\pi$  transitions within the ligand or with RS<sup>–</sup>  $\rightarrow$  Ni<sup>2+</sup> ligand-to-metal charge transfer transitions. The values for the two d–d transitions closely compare with those of the acetato-bridged complex [Ni<sub>2</sub>-L(OAc)]<sup>+</sup> (**9**, [27,28]) as one might expect from the similar N<sub>3</sub>S<sub>2</sub>O coordination environments.

One prominent vibration band is seen in the IR (Table 2), as in other carbamato-bridged complexes [36]. This band is associated with the antisymmetric ( $v_{as}(O_2CNR_2)$ ) stretching modes of the carbamato ligands. The symmetric stretching modes ( $v_s(O_2CNR_2)$ )) could not be located, but are expected to lie in the 1400– 1300 cm<sup>-1</sup> region. Note that the antisymmetric stretching vibration for the monoalkyl carbamate complexes **2–4** and **6** appear at somewhat higher energies than those of the dialkyl carbamate complexes **5** and **7**. The observed values are significantly different

Table 2

Selected spectroscopic data for Ni\_2 carbamate, alkyl carbonate and carboxylate complexes supported by  $(L^{2-})^{a}\,$ 

UV/Vis	$(\lambda_{max}/nm)$	$v_{as}(R-CO_2^-)$	v(NH)	Reference
658	1136	1597	3546	This work
656	1135	1592	3550	This work
656	1132	1593	3538	This work
659	1138	1559	-	This work
657	1136	1593	3530	This work
660	1134	1564	-	This work
650	1108	1635		[27,28]
649	1134	1588		[27,28]
	UV/Vis 658 656 656 659 657 660 650 650 649	UV/Vis (λ <sub>max</sub> /nm) 658 1136 656 1135 656 1132 659 1138 657 1136 660 1134 650 1108 649 1134	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{ c c c c c } UV/Vis(\lambda_{max}/nm) & \nu_{as}(R-CO_2^{-}) & \nu(NH) \\ \hline 658 & 1136 & 1597 & 3546 \\ 656 & 1135 & 1592 & 3550 \\ 656 & 1132 & 1593 & 3538 \\ 659 & 1138 & 1559 & - \\ 657 & 1136 & 1593 & 3530 \\ 660 & 1134 & 1564 & - \\ 650 & 1108 & 1635 & - \\ 649 & 1134 & 1588 & - \\ \hline \end{array}$

<sup>a</sup> Data refer to the perchlorate salts.



**Fig. 1.** Structure of cation **2** in crystals of **2**[BPh<sub>4</sub>] · 0.75MeCN · 0.25H<sub>2</sub>O with thermal ellipsoids drawn at 50% probability. Hydrogen atoms, except H(7), are omitted for reasons of clarity.

from the corresponding antisymmetric ( $\nu_{as}(O_2COR)$ ) stretching mode of the alkylcarbonate complex **8**. For **2–4**, the N–H<sup>amide</sup> stretching vibration appears as a weak sharp band at ca. 3550– 3535 cm<sup>-1</sup>, indicating that the carbamate moiety is not involved in hydrogen bonding interactions. This is confirmed by X-ray crystallography.

The structure of **2**[BPh<sub>4</sub>] confirms the presence of the carbamate complex **2**. Fig. 1 provides an ORTEP representation of the cation **2**, Table 3 lists selected bond lengths and angles. The divalent Ni ions are bridged by the benzylcarbamato ligand in a  $\mu_{1,3}$ -bridging mode, resulting in a Ni $\cdots$ Ni distance of 3.483(1) Å. The carbamate nitrogen is essentially planar, indicative of extensive delocalization of the nitrogen lone pair into the carboxyl group. The C–O bonds are practically identical and the O<sub>2</sub>C–N bond is of length 1.367(3) Å, which is a typical value [2,16]. Note that the O<sub>2</sub>CNH group forms no hydrogen bonds, as already established by IR spectroscopy. This unique situation could arise from the steric protection offered by the supporting ligand (L<sup>2–</sup>). There are no unusual

#### Table 3

Selected bond lengths [Å] in complexes 2, 7, 8 and 9

	2	<b>7</b> <sup>a</sup>	8	9
M(1)-O(1)	1.990(2)	1.990(8) [2.030(8)]	2.021(2)	1.998(2)
M(1) - N(1)	2.287(2)	2.208(9) [2.295(11)]	2.240(3)	2.281(2)
M(1) - N(2)	2.136(2)	2.123(11) [2.162(11)]	2.139(3)	2.152(2)
M(1)-N(3)	2.266(2)	2.330(10) [2.252(11)]	2.278(3)	2.251(2)
M(1) - S(1)	2.4597(6)	2.480(4) [2.444(4)]	2.453(1)	2.4929(9)
M(1)-S(2)	2.4802(6)	2.468(3) [2.474(4)]	2.479(1)	2.448(1)
M(2) - O(2)	2.003(2)	2.014(8) [1.992(8)]	2.003(2)	2.008(2)
M(2) - N(4)	2.335(2)	2.207(10) [2.337(10)]	2.300(3)	2.244(2)
M(2) - N(5)	2.156(2)	2.130(10) [2.136(11)]	2.151(3)	2.158(2)
M(2) - N(6)	2.218(2)	2.327(10) [2.223(10)]	2.227(3)	2.295(2)
M(2) - S(1)	2.4572(6)	2.439(4) [2.464(4)]	2.457(1)	2.493(1)
M(2) - S(2)	2.4681(6)	2.496(4) [2.444(4)]	2.486(1)	2.4500(9)
M–N <sup>b</sup>	2.233(2)	2.221(10) [2.234(10)]	2.223(3)	2.230(2)
M–O <sup>b</sup>	1.997(2)	2.002(8) [2.011(8)]	2.012(2)	2.003(2)
M–S <sup>b</sup>	2.466(6)	2.471(4) [2.457(4)]	2.469(1)	2.471(1)
M···M	3.472(1)	3.453(1) [3.452(1)]	3.491(1)	3.483(1)
C(39)-O(1)	1.264(3)	1.258(14) [1.218(14)]	1.250(4)	1.249(3)
C(39) - O(2)	1.255(3)	1.244(14) [1.267(15)]	1.237(4)	1.252(3)
C(39)–X	1.367(3) <sup>c</sup>	1.430(15) [1.435(15)] <sup>c</sup>	1.361(4) <sup>d</sup>	1.509(4) <sup>e</sup>

<sup>a</sup> There are two crystallographically independent molecules A and B in the asymmetric unit. Values in square-brackets refer to molecule B.

<sup>b</sup> Average values.

<sup>c</sup> X = N.

- <sup>d</sup> X = O.
- <sup>e</sup> X = C.



**Fig. 2.** Structure of one of the two independent cations **7** in crystals of **7**[BPh<sub>4</sub>] - 0.5MeCN with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms, except H(3b) and H(4a), are omitted for reasons of clarity. Only one orientation of the disordered *tert*-butyl group is shown.

features as far as bond lengths and angles around the Ni atoms are concerned. The average Ni–N, Ni–S, and Ni–O distances are 2.233(2), 2.466(6) and 1.997(2) Å, respectively. Similar values were observed in  $[LNi_2(O_2COMe)]^+$  [27,28], and related carboxylatobridged Ni<sub>2</sub> complexes of L<sup>2–</sup> [26] (c.f. Table 3).

Green crystals of **7**[BPh<sub>4</sub>] · 0.5MeCN are monoclinic  $P2_1/c$ . There are two crystallographically independent but chemically almost identical molecules (labelled A and B) in the asymmetric unit. Fig. 2 shows the bis(2-hydroxyethyl)carbamate ligand to be coordinated to the  $[Ni_2L]^{2+}$  unit in a manner identical to the situation found in **2**. Thus, both Ni<sup>II</sup> ions are six-coordinate with three N and two S atoms from L<sup>2–</sup> and one O atom of a  $\mu_{1,3}$ -bridging carbamate group. The carbamate group is again planar, but the C–N distance is by ca. 0.08 Å longer than in **2**. The Ni–O, Ni–S, and Ni–N distances are unexceptional and are very close to the corresponding distances in **2**. The hydroxyethyl units link adjacent complexes via intermolecular hydrogen bonding interactions (d(OH··O) =2.542 and 2.917 Å). Overall, the two structures clearly show that the  $[Ni_2L]^{2+}$  units can expand their binding pockets sufficiently to accommodate  $\mu_{1,3}$ -bridging carbamate ligands.

#### 4. Concluding remarks

A series of novel dinuclear nickel(II) carbamate complexes supported by a hexaamine-dithiophenolate ligand have been synthesized and characterized, namely [Ni<sub>2</sub>L(O<sub>2</sub>CNHBz)]<sup>+</sup> (2), [Ni<sub>2</sub>- $L(O_2CNHn-Bu)]^+$  (**3**),  $[Ni_2L(O_2CNHn-Oct)]^+$  (**4**),  $[Ni_2L(O_2CNEt_2)]^+$ (5),  $[Ni_2L(O_2CNHCH_2CH_2OH)]^+$  (6), and  $[Ni_2L(O_2CN(CH_2CH_2OH)_2]^+$ (7)). The carbonation reactions of 1 with ambidentate aminoalcohols proceed with "carbamate" selectivity. The crystal structures of **2**[BPh<sub>4</sub>] and **7**[BPh<sub>4</sub>] confirm the presence of  $\mu_{1,3}$ -bridging carbamate units showing that the [Ni<sub>2</sub>L]<sup>2+</sup> units can expand their binding pockets sufficiently to accommodate carbamate ligands. All carbamate complexes are hydrolyzed in methanol. These conversions are much slower than the transesterification reaction of the methyl carbonate complex **8**, due to the more extensive electron delocalisation of the nitrogen lone pair into the carboxyl group. Future work is focused on the hydrogenation of the carbamate moiety in the pocket of the complexes.

## 5. Supplementary material

CCDC 668900 and 668901 contain the supplementary crystallographic data for  $2[CIO_4]_2 \cdot 0.75MeCN \cdot 0.25H_2O$  and  $7[BPh_4] \cdot 0.5MeCN$ . These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

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