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Table S1. Rate (k) and equilibrium (K<sub>CBM</sub>) constants for the carbamato formation and equilibrium constant (K<sub>HYD</sub>) for the carbamato hydrolysis at 18 °C in water.

\[
\begin{align*}
\text{CO}_2^{(aq)} + 2 \text{R}_2\text{NH}^{(aq)} & \rightleftharpoons [\text{R}_2\text{NH}_2^+^{(aq)} + [\text{R}_2\text{NCOO}^-]^{(aq)}] \\
[\text{R}_2\text{NCOO}^-]^{(aq)} + \text{H}_2\text{O}^{(l)} & \rightleftharpoons [\text{R}_2\text{NH}_2^+^{(aq)} + \text{HCOO}^-]^{(aq)}
\end{align*}
\]

| Amine   | pK<sub>i</sub> | k (M<sup>-1</sup> min<sup>-1</sup>) | K<sub>CBM</sub> | K<sub>HYD</sub> | Ref. |
|---------|---------------|-------------------------------|----------------|---------------|------|
| NH₃     | 4.76          | 3.8 × 10<sup>4</sup>         | 2.3 × 10<sup>3</sup> | 4.4 × 10<sup>-3</sup> | [1]  |
| **Primary amines** |          |                               |                |               |      |
| NH₂Me   | 3.38          | 8.3 × 10<sup>4</sup>         | 4.0 × 10<sup>6</sup> | 6.0 × 10<sup>-3</sup> | [1]  |
| NH₂Et   | 3.19          | 1.5 × 10<sup>5</sup>         | 2.0 × 10<sup>6</sup> | 1.8 × 10<sup>-2</sup> | [1]  |
| NH₂Pr   | 3.41          | 1.6 × 10<sup>5</sup>         | 1.5 × 10<sup>6</sup> | 1.3 × 10<sup>-2</sup> | [1]  |
| NH₂Pr   | 3.37          | 6.8 × 10<sup>4</sup>         | 3.6 × 10<sup>5</sup> | 6.3 × 10<sup>-2</sup> | [1]  |
| NH₂Bn   | 4.74          | 1.1 × 10<sup>5</sup>         | 8.5 × 10<sup>4</sup> | 1.2 × 10<sup>-2</sup> | [1]  |
| NH₂Ph   | 9.30          | ≈10¹                      | 8.1 × 10<sup>-3</sup> | 3.6               | [1]  |
| NH₃allyl| 4.38          | 1.1 × 10<sup>5</sup>         | 1.6 × 10<sup>5</sup> | 1.5 × 10<sup>-2</sup> | [1]  |
| NH₂Bu   | 3.24          | 2.0 × 10<sup>5</sup>         | 1.1 × 10<sup>6</sup> | 1.6 × 10<sup>-2</sup> | [1]  |
| NH₂Bu   | 3.44          | 7.1 × 10<sup>4</sup>         | 3.8 × 10<sup>6</sup> | 4.9 × 10<sup>-2</sup> | [1]  |
| NH₂Bu   | 3.58          | 1.6 × 10<sup>5</sup>         | 1.3 × 10<sup>6</sup> | 1.0 × 10<sup>-2</sup> | [1]  |
| NH₂Bu   | 3.55          | 1.9 × 10<sup>4</sup>         | 1.1 × 10<sup>6</sup> | 1.0 × 10<sup>-2</sup> | [1]  |
| **Secondary amines** |          |                               |                |               |      |
| NHMe₂   | 3.22          | 6.7 × 10<sup>5</sup>         | 1.6 × 10<sup>6</sup> | 2.2 × 10<sup>-2</sup> | [1]  |
| NHEt₂   | 3.51          | 2.9 × 10<sup>5</sup>         | 7.4 × 10<sup>4</sup> | 2.4 × 10<sup>-1</sup> | [1]  |
| NHPp₂   | 3.09          | 3.0 × 10<sup>5</sup>         | 3.0 × 10<sup>4</sup> | 1.5 × 10<sup>-1</sup> | [1]  |
| NHPp₂   | 3.17          | –                      | None          | –               | [1]  |
| NHBu₂   | 2.54          | 3.1 × 10<sup>5</sup>         | 4.6 × 10<sup>5</sup> | 1.9 × 10<sup>-1</sup> | [1]  |
| NHBu₂   | –             | –                      | None          | –               | [1]  |
| NFBu₂   | 3.41          | 1.3 × 10<sup>5</sup>         | 1.9 × 10<sup>5</sup> | 1.2 × 10<sup>-1</sup> | [1]  |
| Piperidine | 2.95     | 7.8 × 10<sup>4</sup>         | 7.9 × 10<sup>3</sup> | 8.1 × 10<sup>-2</sup> | [1]  |
| 3-MPD   | 3.12          | –                      | 6.9 × 10<sup>6</sup> | 6.2 × 10<sup>-3</sup> | [2]  |
| 4-MPD   | 3.06          | –                      | 5.9 × 10<sup>6</sup> | 8.3 × 10<sup>-3</sup> | [2]  |
| Pyrrolidine | 3.16     | 3.5 × 10<sup>6</sup>         | 1.9 × 10<sup>7</sup> | 2.0 × 10<sup>-3</sup> | [3,4] |
| **Substituted amines** |          |                               |                |               |      |
| MEA     | 4.42          | 8.3 × 10<sup>4</sup>         | 6.0 × 10<sup>4</sup> | 1.9 × 10<sup>-2</sup> | [1]  |
| DEA     | 4.98          | 1.0 × 10<sup>5</sup>         | 2.1 × 10<sup>3</sup> | 1.5 × 10<sup>-1</sup> | [1]  |
| 1-AP<sup>[b]</sup> | 4.75     | 3.2 × 10<sup>5</sup>         | 9.6 × 10<sup>3</sup> | 1.1 × 10<sup>-1</sup> | [3]  |
| 2-AP<sup>[b]</sup> | 4.75     | 6.0 × 10<sup>4</sup>         | 4.0 × 10<sup>3</sup> | 2.5 × 10<sup>-1</sup> | [5]  |
| MPA<sup>[b]</sup> | 4.18     | 5.4 × 10<sup>5</sup>         | 2.5 × 10<sup>3</sup> | 1.5 × 10<sup>-2</sup> | [5]  |
| Compound                     | pK<sub>b</sub> | K<sub>b</sub> Value | pK<sub>b</sub> Value | K<sub>b</sub> Value | Literature References |
|------------------------------|----------------|---------------------|---------------------|---------------------|-----------------------|
| AMP<sup>(b)</sup>            | 4.73           | –                   | None                | –                   | [5]                   |
| 4-PIPDM<sup>(b)</sup>        | 3.71           | 1.3 × 10<sup>6</sup> | 2.7 × 10<sup>3</sup> | 4.1 × 10<sup>-2</sup> | [3,4]                 |
| 4-PIPDE<sup>(b)</sup>        | 3.65           | –                   | 3.0 × 10<sup>5</sup> | 4.2 × 10<sup>-2</sup> | [4]                   |
| Morpholine<sup>(b)</sup>     | 5.78           | 1.6 × 10<sup>5</sup> | 1.4 × 10<sup>3</sup> | 6.8 × 10<sup>-2</sup> | [3,4]                 |
| Thiomorpholine<sup>(b)</sup>| 5.57           | 1.9 × 10<sup>4</sup> | 9.3 × 10<sup>2</sup> | 1.6 × 10<sup>-4</sup> | [3,4]                 |
| Piperazine                   | 4.50           | –                   | 5.5 × 10<sup>4</sup> | 3.2 × 10<sup>-2</sup> | [6]                   |
| 8.67                         | –              | 2.6 × 10<sup>-1</sup> | 4.6 × 10<sup>-2</sup> |                      |                       |
| MPIPZ                        | 4.96           | –                   | 5.1 × 10<sup>3</sup> | 1.2 × 10<sup>-3</sup> | [3]                   |
| 4-AMTHP<sup>(b)</sup>       | 4.37           | 3.6 × 10<sup>5</sup> | 1.9 × 10<sup>3</sup> | 1.3 × 10<sup>-2</sup> | [7]                   |
| Taurine<sup>(b)[c]</sup>    | 5.19           | –                   | 7.1 × 10<sup>3</sup> | 5.1 × 10<sup>-2</sup> | [8]                   |

**Amino acids**

| Compound                     | pK<sub>b</sub> | K<sub>b</sub> Value | pK<sub>b</sub> Value | K<sub>b</sub> Value | Literature References |
|------------------------------|----------------|---------------------|---------------------|---------------------|-----------------------|
| Glycine<sup>(d)</sup>        | 4.49           | 3.2 × 10<sup>5</sup> | 4.4 × 10<sup>4</sup> | 4.2 × 10<sup>-2</sup> | [9]                   |
| Sarcosine<sup>(b)[d]</sup>  | 4.22           | 1.1 × 10<sup>6</sup> | 3.3 × 10<sup>4</sup> | 1.0 × 10<sup>-3</sup> | [10]                  |
| a-Alanine<sup>(d)</sup>      | 4.40           | 6.6 × 10<sup>4</sup> | 1.8 × 10<sup>4</sup> | 1.1 × 10<sup>-1</sup> | [11]                  |
| b-Alanine<sup>(d)</sup>      | 3.86           | 1.1 × 10<sup>6</sup> | 1.9 × 10<sup>5</sup> | 3.1 × 10<sup>-2</sup> | [11]                  |
| Proline<sup>(e)</sup>        | 3.57           | –                   | 5.4 × 10<sup>6</sup> | 2.8 × 10<sup>-3</sup> | [12]                  |
| Lysine<sup>(b)[c]</sup>     | 4.44<sup>(f)</sup> | –                   | 1.7 × 10<sup>6</sup> | 1.2 × 10<sup>-1</sup> | [13]                  |
|                             | 3.24<sup>(g)</sup> | –                   | 6.3 × 10<sup>4</sup> | 5.1 × 10<sup>-1</sup> |                       |

<sup>(a)</sup>pK<sub>b</sub> values are from ref. [1–9,12,13]. For a list of pK<sub>b</sub> see ref. [14,15]. (K<sub>w</sub> = 10<sup>-14.27</sup>); <sup>(b)</sup>Measured at 25°C; <sup>(c)</sup>Potassium salt; <sup>(d)</sup>Sodium Salt; <sup>(e)</sup>Deprotonation of the a-amino group; <sup>(f)</sup>Deprotonation of the amino group on the lateral chain; 3-MPD = 3-methylpiperidine, 4-MPD = 4-methylpiperidine, MEA = monoethanolamine, DEA = diethanolamine, 1-AP = 2-amino-1-propanol, 2-AP = 1-amino-2-propanol, MPA = 3-amino-1-propanol, AMP = 2-amino-2-methyl-1-propanol, 4-PIPDM = 4-piperidine-3-methanol, 4-PIPDE = 4-piperidineethanol, MPIPZ = 1-methylpiperazine, 4-AMTHP = 4-aminomethyltetrahydropyran.
Table S2. Selected X-ray bond distances (Å) and angles (°) in amidinium/guanidinium CO$_2$ adducts.

![Diagram](image)

| Compound | N$^1$-C$^1$ (Å) | C$^1$-O$^1$ (Å) | C$^1$-O$^2$ (Å) | N$^2$-C$^2$ (Å) | C$^2$-N$^2$ (Å) | C$^2$-N$^3$ (Å) | O$^1$-C$^1$-O$^2$ (α) (°) | C$^1$-N$^1$-C$^2$-N$^3$ (β) (°) | Ref. |
|----------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------------------|-----------------------------|------|
| ![Image](image) | 1.480(3)      | 1.257(3)      | 1.229(2)      | 1.369(3)      | 1.332(2)      | 1.338(3)      | 128.6(2)                   | 4.4(2)                      | [16] |
| ![Image](image) | 1.513(3)      | 1.233(3)      | 1.228(3)      | 1.330(3)      | 1.322(3)      | 132.2(2)      | 9.1(2)                     | 132.2(2)                   | [17] |
| ![Image](image) | 1.439(2)      | 1.248(1)      | 1.243(1)      | 1.373(1)      | 1.355(1)      | 1.349(2)      | 130.6(1)                   | 88.9(2)                     | [17] |
| ![Image](image) | 1.432(1)      | 1.251(1)      | 1.243(1)      | 1.368(1)      | 1.338(1)      | 1.392(1)      | 129.09(9)                  | 68.9(1)                     | [17] |
**Table S3.** Selected bond distances (Å) and angles (°) for carbamato ligands in metal complexes (2004-2020).

| Metal center | Carbamate coordination | C-O¹ (Å) | C-O² (Å) | C-N (Å) | O-C-O (°) | Ref. |
|--------------|------------------------|----------|----------|--------|----------|------|
| Al(III)      | B/2                    | 1.284(2) | 1.282(2) | 1.347(2) | 120.0(1) | [18] |
| Al(III)      | B/2                    | 1.300(5) | 1.282(5) | 1.326(5) | 122.3(4) | [19] |
| Al(III)      | B/2                    | 1.280(4) | 1.280(4) | 1.335(4) | 120.4(3) | [20] |
| Bi(III)      | M/1                    | 1.295(5) | 1.250(6) | 1.348(4) | 123.9(4) | [21] |
| Bi(III)      | B/2                    | 1.288(4) | 1.265(4) | 1.360(4) | 122.9(3) |      |
| Bi(III)      | C/2                    | 1.295(4) | 1.274(4) | 1.342(4) | 120.5(3) | [22] |
| Ce(III)      | C/1                    | 1.28(1)  | 1.26(2)  | 1.35(2)  | 120(1)   |      |
|              | B/2                    | 1.28(1)  | 1.26(1)  | 1.34(1)  | 121(1)   |      |
| Ce(III)      | C/2                    | 1.28(1)  | 1.28(1)  | 1.35(1)  | 119(1)   | [23] |
|              | B/3                    | 1.34(1)  | 1.25(1)  | 1.33(1)  | 120.6(9) |      |
|              | B/4                    | 1.311(9) | 1.28(1)  | 1.34(1)  | 119.7(8) |      |
| Ce(IV)       | M/1                    | 1.26(1)  | 1.21(1)  | 1.44(1)  | 128.4(8) |      |
|              | C/2                    | 1.284(9) | 1.23(1)  | 1.39(1)  | 123.5(7) |      |
|              | B/3                    | 1.26(1)  | 1.23(1)  | 1.44(1)  | 128.7(8) |      |
|              | M/1                    | 1.29(3)  | 1.20(3)  | 1.42(2)  | 129.0(2) | [24] |
| Ce(IV)       | B/2                    | 1.293(2) | 1.201(3) | 1.438(3) | 128.3(2) |      |
|              | C/1                    | 1.269(8) | 1.254(7) | 1.357(5) | 118.3(5) |      |
|              | B/2                    | 1.277(4) | 1.271(5) | 1.362(6) | 123.8(4) | [23] |
|              | C/2                    | 1.279(7) | 1.270(4) | 1.346(7) | 119.6(4) |      |
| Cu(II)       | M/1                    | 1.30(3)  | 1.20(3)  | 1.39(3)  | 131(2)   | [25] |
|              | C/2                    | 1.35(2)  | 1.25(2)  | 1.31(2)  | 118(1)   | [26] |
| Cu(II)       | B/2                    | 1.269(6) | 1.259(6) | 1.375(6) | 126.7(4) | [27] |
| Cu(II)       | C/2                    | 1.289(4) | 1.238(4) | 1.375(4) | 123.6(3) |      |
| Cu(II)       | M/1                    | 1.281(3) | 1.236(3) | 1.375(3) | 125.9(2) | [28] |
|              | B/2                    | 1.280(3) | 1.280(3) | 1.367(3) | 125.2(2) |      |
| Element  | Subshell | 1.27(1) | 1.28(1) | 1.34(1) | 119.0(7) |
|----------|----------|---------|---------|---------|-----------|
| Dy(III)  | C/1      | 1.28(1) | 1.28(1) | 1.34(1) | 122.7(7)  |
|          | B/2      | 1.293(9) | 1.25(1) | 1.372(8) | 121.3(6)  |
|          | B/3      | 1.275(8) | 1.27(1) | 1.36(1) | 122.7(7)  |
| Er(III)  | C/1      | 1.295(8) | 1.260(9) | 1.369(9) | 120.5(6)  |
|          | B/2      | 1.272(7) | 1.263(6) | 1.346(8) | 123.3(5)  |
|          | B/3      | 1.305(6) | 1.266(7) | 1.348(6) | 121.0(4)  |
| Er(III)  | D/2      | 1.333(6) | 1.277(6) | 1.315(6) | 115.6(4)  |
| Eu(III)  | C/1      | 1.27(1) | 1.26(1) | 1.37(1) | 120.6(8)  |
|          | B/2      | 1.278(8) | 1.254(6) | 1.336(7) | 123.1(5)  |
|          | B/3      | 1.300(7) | 1.253(6) | 1.340(8) | 122.2(5)  |
| Fe(III)  | B/2      | 1.280(5) | 1.269(5) | 1.346(6) | 125.3(4)  |
| Fe(II)   | M/1      | 1.293(3) | 1.204(3) | 1.401(4) | 128.4(2)  |
| Ga(III)  | B/2      | 1.283(4) | 1.281(5) | 1.345(5) | 122.2(3)  |
|          | C/1      | 1.33(1) | 1.252(8) | 1.39(1) | 117.1(7)  |
|          | B/2      | 1.30(1) | 1.30(1) | 1.37(1) | 122.3(7)  |
| Hf(IV)   | C/1      | 1.32(2) | 1.24(2) | 1.36(2) | 117(1)    |
|          | B/2      | 1.29(1) | 1.26(2) | 1.31(2) | 121(1)    |
| Ir(I)    | M/1      | 1.300(9) | 1.23(1) | 1.36(1) | 125.5(8)  |
| Ir(III)  | M/1      | 1.254(5) | 1.231(7) | 1.391(7) | 124.0(5)  |
| Ir(III)  | M/1      | 1.252(7) | 1.251(6) | 1.401(8) | 124.8(5)  |
| Ir(III)  | M/1      | 1.26(1) | 1.22(1) | 1.395(8) | 124.2(7)  |
| Ir(III)  | M/1      | 1.275(3) | 1.219(2) | 1.474(3) | 128.7(2)  |
| Ir(III)  | C/1      | 1.290(5) | 1.275(5) | 1.334(6) | 117.7(4)  |
| Ir(III)  | D/1      | 1.366(4) | 1.237(4) | 1.327(4) | 120.7     |
| La(III)  | C/1      | 1.25(1) | 1.25(1) | 1.39(1) | 122.0(9)  |
|          | C/2      | 1.29(1) | 1.262(9) | 1.360(9) | 120.5(7)  |
|          | C/3      | 1.28(1) | 1.27(1) | 1.35(1) | 120.1(8)  |
| Li(I)    | B/2      | 1.261(2) | 1.255(2) | 1.401(2) | 124.3(11) |
|          | B/2      | 1.262(4) | 1.254(4) | 1.391(5) | 122.21(3) |
|          | B/3      | 1.285(3) | 1.245(5) | 1.379(4) | 121.53(3) |
|          | B/4      | 1.273(3) | 1.273(4) | 1.361(5) | 121.0(3)  |
| Li(I)    | B/2      | 1.264(4) | 1.262(4) | 1.338(5) | 123.1(3)  |
|          | B/3      | 1.264(2) | 1.261(3) | 1.355(4) | 120.9(2)  |
|          | B/5      | 1.279(3) | 1.272(3) | 1.342(3) | 120.3(2)  |
| Element | Coordination | Distance 1 | Distance 2 | Distance 3 | Distance 4 |
|---------|--------------|------------|------------|------------|------------|
| Li(I)   | B/3          | 1.30(1)    | 1.26(2)    | 1.33(2)    | 119(1)     |
| Lu(III) | B/2          | 1.30(9)    | 1.24(1)    | 1.34(1)    | 121.6(8)   |
| Mg(II)  | B/2          | 1.26(2)    | 1.25(1)    | 1.36(1)    | 120.4(9)   |
| Mg(II)  | C/3          | 1.30(6)    | 1.29(5)    | 1.32(5)    | 115.3(5)   |
| Mn(II)/Mn(III) | B/2 | 1.261(9)    | 1.25(1)    | 1.348(9)   | 123.7(6)   |
| Nb(V)   | C/1          | 1.306(6)   | 1.295(8)   | 1.323(9)   | 115.3(5)   |
| Nd(III) | C/2          | 1.307(5)   | 1.250(6)   | 1.347(6)   | 119.1(4)   |
| Ni(II)  | M/1          | 1.263(8)   | 1.24(1)    | 1.37(1)    | 127.3(6)   |
| Ni(II)  | M/1          | 1.286(4)   | 1.242(2)   | 1.382(5)   | 125.0(3)   |
| Ni(II)  | M/1          | 1.280(3)   | 1.211(4)   | 1.388(4)   | 126.5(3)   |
| Ni(II)  | M/1          | 1.288(2)   | 1.233(2)   | 1.387(2)   | 126.5(1)   |
| Ni(II)  | M/1          | 1.284(3)   | 1.239(4)   | 1.385(4)   | 124.2(3)   |
| Pd(II)  | M/1          | 1.326(5)   | 1.242(2)   | 1.344(4)   | 125.0(3)   |
| Pt(IV)  | M/1          | 1.326(4)   | 1.235(4)   | 1.354(4)   | 125.1(3)   |
| Pt(IV)  | M/1          | 1.323(3)   | 1.240(2)   | 1.346(3)   | 125.4(2)   |
| Pt(IV)  | M/1          | 1.335(4)   | 1.233(4)   | 1.344(4)   | 125.0(3)   |
| Pt(IV)  | M/1          | 1.325(5)   | 1.219(5)   | 1.354(6)   | 126.1(4)   |
| Pt(IV)  | M/1          | 1.321(3)   | 1.236(3)   | 1.340(3)   | 125.8(2)   |
| Pt(IV)  | M/1          | 1.310(4)   | 1.242(5)   | 1.346(5)   | 124.6(4)   |
| Pt(IV)  | M/1          | 1.327(4)   | 1.249(5)   | 1.336(6)   | 125.0(3)   |
| Re(I)   | M/1          | 1.27(1)    | 1.25(1)    | 1.40(1)    | 125.1(7)   |
| Element | Site | x 1 | y 2 | z 3 | U 4 |
|--------|------|-----|-----|-----|-----|
| Rh(III) | C/1  | 1.281(4) | 1.263(4) | 1.352(4) | 119.6(3) |
| Ru(II)  | C/1  | 1.28(3)  | 1.24(3)  | 1.39(4)  | 123(3)   |
| Ru(II)  | M/1  | 1.301(5) | 1.229(5) | 1.457(6) | 127.3(4) |
| Ru(II)  | M/1  | 1.281(2) | 1.243(2) | 1.390(2) | 126.5(1) |
| Sc(III) | M/1-c| 1.318(5) | 1.209(5) | 1.425(5) | 124.3(4) |
| Sm(III) | C/1  | 1.289(6) | 1.255(7) | 1.364(9) | 120.4(5) |
|         | B/2  | 1.273(4) | 1.270(6) | 1.358(6) | 123.4(4) |
|         | B/3  | 1.304(4) | 1.262(4) | 1.345(6) | 121.6(3) |
| Sn(II)  | M/1  | 1.304(3) | 1.238(3) | 1.366(2) | 121.7(2) |
| Sn(II)  | C/1  | 1.280(3) | 1.272(3) | 1.338(3) | 118.8(2) |
|         | B/2  | 1.295(3) | 1.263(3) | 1.336(3) | 121.8(2) |
| Tb(III) | C/1  | 1.30(2)  | 1.25(2)  | 1.36(3)  | 121.0(2) |
|         | B/2  | 1.27(2)  | 1.26(2)  | 1.38(2)  | 124.0(1) |
| Ti(III) | B/2  | 1.281(4) | 1.268(4) | 1.371(4) | 123.7(3) |
| Ti(IV)  | C/1  | 1.290(5) | 1.277(5) | 1.346(6) | 116.0(4) |
|         | D/1  | 1.340(7) | 1.212(7) | 1.378(9) | 123.4(6) |
|         | M/1-c| 1.308(4) | 1.212(4) | 1.402(5) | 122.9(3) |
| Ti(IV)  | B/2  | 1.295(4) | 1.280(4) | 1.330(6) | 122.6(4) |
| U(IV)   | C/1  | 1.296(5) | 1.268(5) | 1.335(6) | 119.0(3) |
|         | M/1  | 1.287(4) | 1.196(5) | 1.375(6) | 127.0(3) |
| U(IV)   | C/1  | 1.279(7) | 1.258(6) | 1.382(7) | 121.1(5) |
| U(IV)   | M/1-c| 1.317(4) | 1.229(6) | 1.396(6) | 121.8(4) |
| U(IV)   | C/1  | 1.273(7) | 1.263(6) | 1.382(7) | 120.3(5) |
| U(IV)   | D/2  | 1.349(4) | 1.285(5) | 1.304(5) | 115.8(3) |
| U(VI)   | B/2  | 1.33(3)  | 1.25(3)  | 1.43(3)  | 123(2)   |
| W(0)    | D/1-n| 1.283(3) | 1.208(3) | 1.513(3) | 131.0(2) |
| Y(III)  | D/2  | 1.328(8) | 1.292(7) | 1.313(7) | 115.4(5) |
| Yb(III) | C/1  | 1.27(1)  | 1.26(1)  | 1.35(1)  | 119.1(9) |
|         | B/2  | 1.27(1)  | 1.263(9) | 1.356(8) | 123.4(7) |
|         | B/3  | 1.307(7) | 1.243(7) | 1.357(9) | 122.6(6) |
| Yb(III) | D/2  | 1.32(1)  | 1.28(1)  | 1.31(1)  | 115.6(8) |
|         | C/2  | 1.308(6) | 1.240(6) | 1.352(6) | 118.6(5) |
| Zn(II)  | M/1  | 1.276(5) | 1.245(5) | 1.357(6) | 124.8(4) |
| Zn(II)  | B/2  | 1.27(1)  | 1.24(1)  | 1.35(1)  | 125.5(9) |
| Zn(II)  | B/2  | 1.268(3) | 1.265(4) | 1.352(3) | 124.4(4) |
| Element       | Site | Bond Lengths (Å) | Other Angles (°) |
|--------------|------|-----------------|-----------------|
| Zn(II)       | B/3  | 1.299(3) 1.261(3) 1.343(3) 122.0(2) |
| Zn(II)       | B/3  | 1.296(4) 1.273(5) 1.336(5) 122.5(3) [86] |
| Zn(II)       | B/2  | 1.272(2) 1.269(2) 1.355(2) 122.3(2) |
| Zn(II)       | B/2  | 1.272(8) 1.268(7) 1.359(7) 125.9(6) [87] |
| Zn(II)       | M/1  | 1.286(7) 1.225(9) 1.401(8) 124.0(6) [88] |
| Zn(II)       | M/1  | 1.290(3) 1.236(3) 1.379(4) 125.9(2) [89] |
| Zn(II)       | B/2  | 1.276(3) 1.273(3) 1.360(3) 122.7(2) |
| Zn(II)       | B/2  | 126.8(3) 126.8(3) 1.364(5) 125.7(4) [90] |
| Zn(II)       | B/2  | 1.257(6) 1.241(6) 1.353(7) 124.3(5) [91] |
| Zn(II)       | M/1  | 1.287(6) 1.230(7) 1.404(7) 125.0(5) [92] |
| Zn(II)       | B/2  | 1.276(4) 1.264(3) 1.368(3) 123.8(3) |
| Zn(II)       | M/1  | 1.287(4) 1.249(5) 1.380(5) 126.2(3) [93] |
| Zn(II)       | B/2  | 1.269(3) 1.259(4) 1.372(4) 124.9(3) |
| Zn(II)       | B/3  | 1.294(3) 1.253(4) 1.355(4) 123.3(3) |
| Zn(II)       | B/2  | 1.276(5) 1.259(4) 1.371(4) 124.2(3) [94] |
| Zn(II)       | B/2  | 1.271 1.271 1.444 124.4 [95] |
| Zn(II)/Dy(III) | B/2 | 1.30(2) 1.26(2) 1.32(2) 125.0(1) |
| Zn(II)/Tb(III) | B/2 | 1.28(1) 1.27(1) 1.345(9) 125.6(8) [96] |
| Zn(II)/Gd(III) | B/2 | 1.28(1) 1.27(1) 1.34(1) 125.0(1) |
| Zr(IV)       | B/2  | 1.292(5) 1.277(4) 1.332(4) 119.5(3) [97] |
Table S4. NMR and IR data related to the NCO$_2$ moiety in structurally characterized metal carbamato complexes.

| Metal center | Carbamate coordination | $^{13}$C(H) NMR: $\delta$/ppm $^a$ | IR: $\nu$/cm$^{-1}$ $^b$ | Ref. |
|--------------|------------------------|-----------------------------------|-------------------------|------|
| Ag(I)        | C/1                    | 1529, 1478, 1434, 1414, 1368      |                         | [1]  |
| Ag(I)        | B/3                    | 1554, 1520, 1466, 1386            |                         |      |
| Al(III)      | B/2                    | 158.0                             | 1595, 1506              | [19] |
| Au(I)        | M/1                    | 161                               | 1578                    | [98] |
| Au(I)        | M/1                    | 1601, 1580, 1569, 1478, 1468, 1435, 1407, 1371 | [1]  |
| Bi(III)      | B/2, C/2, C/1          | 163.6                             |                         | [22] |
| Ce(III)      | C/1, B/2, C/2, B/3, B/4| 1576, 1558, 1507, 1354, 1260      |                         | [23] |
| Ce(III)      | M/1, C/2, B/3          | 1725, 1683, 1378, 1347, 1286      |                         | [24] |
| Ce(IV)       | M/1                    | 149.9                             | 1732, 1457, 1336        |      |
| Ce(IV)       | C/1, B/2, C/2          | 1562, 1538, 1506, 1350, 1261      |                         | [23] |
| Co(III)      | M/1                    | 165.0                             |                         | [99] |
| Cr(II)       | B/2                    | 1578, 1560, 1510, 1498, 1460, 1433, 1378, 1318 |      |
| Cr(III)      | C/1                    | 1485, 1378, 1337, 1322            |                         | [1]  |
| Cu(II)       | M/1                    | 1570, 1496, 1462, 1452, 1408, 1377, 1311 |      |
| Cu(II)       | B/2                    | 1575, 1550, 1480, 1460, 1420, 1375, 1300 |      |
| Dy(III)      | M/1                    | 1658, 1597, 1554, 1520, 1456, 1390, 1269 | [30] |
| Er(III)      | C/1, B/2, B/3          | 1602, 1540, 1490, 1355            |                         | [31] |
| Eu(III)      | C/1, B/2, B/3          | 1597, 1533, 1488, 1354            |                         |      |
| Er(III)      | D/2                    | 1607, 1580, 1502, 1260            |                         | [32] |
| Fe(II)       | M/1                    | 156                                | 1636, 1304              | [100]|
| Fe(II)       | M/1                    | 162.2                              |                         | [34] |
| Ga(III)      | B/2                    | 165.0                              | 1543, 1452, 1342, 1317  | [35] |
| Ga(III)      | C/1                    | 165.8                              |                         | [36] |
| Ga(III)      | B/2                    | 161.3                              |                         |      |
| Ga(III)      | B/2                    | 165.3                              |                         |      |
| Ga(III)      | C/1                    | 168.2                              |                         |      |
| Element (II) | Charge | Letters | Wavenumbers | References |
|-------------|--------|---------|-------------|------------|
| Gd(III)     | C/1, B/2, B/3 | 1598, 1537, 1485, 1355 | [31] |
| Hf(IV)      | C/1 | 170.2 | | |
| Hf(IV)      | C/1 | 1540, 1510, 1480, 1350 | [1] |
| Hf(IV)      | C/1 | 1540, 1510, 1480, 1350 | | |
| Ho(III)     | C/1, B/2, B/3 | 1601, 1538, 1489, 1354 | [31] |
| Ir(III)     | M/1 | 161.7 | | [40] |
| Ir(I)       | M/1 | 163.2 | | [38] |
| Ir(I)       | M/1 | 159.7 | | |
| Li(I)       | B/2 | 167.2 | | [18] |
| Li(I)       | B/2, B/3, B/5, C/5 | 1594, 1545, 1360, 1265 | [43] |
| Li(I)       | B/3 | 155.1 | 1623, 1261 | |
| Lu(III)     | C/1, B/2, B/3 | 1610, 1530, 1490, 1354 | [31] |
| Mg(II)      | B/2 | 161.5 | | |
| Mg(II)      | B/2, C/3 | 159.8, 159.3 | | [44] |
| Mg(II)      | B/2, C/2, B/3, M/2 | 162.8 | 1611, 1582, 1515, 1283 | [45] |
| Mo(II)      | B/2 | 1510, 1435, 1380, 1315 | | [1] |
| Nb(IV)      | C/1 | 1558, 1505, 1483, 1441, 1377, 1348 | | |
| Nb(V)       | C/1 | 168.1 | 1620, 1576, 1558, 1484, 1433 | [47] |
| Nb(IV)      | C/1, M/1 | 162.3 | | [1] |
| Nd(III)     | C/1, B/2, B/3 | 1593, 1515, 1479, 1354 | [31] |
| Nd(III)     | C/2 | 1616, 1590, 1538, 1445, 1337 | [48] |
| Ni(II)      | M/1 | 161.2 | 1681 | [101] |
| Ni(II)      | B/2 | 1597 | | [49] |
| Ni(II)      | B/2 | 1564 | | |
| Ni(II)      | M/1 | 162.3 | 1629, 1351 | [50] |
| Ni(II)      | M/1 | 160.6 | | [51] |
| Ni(II)      | D/1 | 170.5 | 1617 | [52] |
| Ni(II)      | M/1 | 157.9 | 1667, 1624 | |
| Ni(II)      | M/1 | 159.6 | 1610 | [54] |
| Ni(II)      | M/1 | 162.9 | | [102] |
| Ni(II)      | M/1 | 157.3 | | [55] |
| Ni(II)      | M/1 | 158.3 | | [103] |
| Ni(II)      | M/1 | 159.7 | 1625 | [56] |
| Ni(II)      | C/1 | 160.6 | 1620 | [56] |
| Pd(II)      | M/1 | 150.6 | | [58] |
| Element  | Form   | Mass | Wavenumbers                     |
|----------|--------|------|---------------------------------|
| Pd(II)   | D/1    | 165.3| 1677                           |
| Pd(II)   | M/1    |      | 1590, 1555, 1475, 1455, 1410, 1375, 1325 |
| Pr(III)  | C/1, B/2, B/3 | 1591 | 1527, 1518, 1353               |
| Pt(II)   | M/1    |      | 1632                           |
| Pt(II)   | M/1    |      | 1586, 1563, 1474, 1458, 1411, 1374, 1326 |
| Pt(IV)   | M/1    | 162.8| 1640, 1629                      |
| Pt(IV)   | M/1    | 163.4| 1629                           |
| Pt(IV)   | M/1    | 163.0| 1628                           |
| Pt(IV)   | M/1    | 160.7| 1654                           |
| Pt(IV)   | M/1    | 165.4|                                |
| Pt(IV)   | M/1    | 164.8|                                |
| Pt(IV)   | M/1    | 163.9|                                |
| Rh(III)  | C/1    |      | 165.1                          |
| Ru(II)   | C/1    |      | 164.0                          |
| Ru(II)   | M/1    | 155  | 1634, 1602                      |
| Ru(II)   | M/1    | 165.03, 163.37 | 1587                  |
| Ru(II)   | C/1    |      | 1505, 1465, 1436, 1380          |
| Sm(III)  | C/1, B/2, B/3 | 1595 | 1531, 1508, 1353               |
| Sn(II)   | M/1    | 161.8| 1595, 1575, 1552, 1524, 1337   |
| Sn(II)   | M/1    | 161.6| 1624, 1554, 1526, 1517, 1238   |
| Sn(II)   | C/1, B/2 | 164.5 | 1539, 1471, 1384, 1259        |
| Ta(V)    | C/1, M/1 | 161.7 |                                |
| Tb(III)  | C/1, B/2 | 1584, 1487, 1374, 1313, 1261   |
| Ti(IV)   | C/1    | 1599, 1512, 1503, 1408, 1266   |
| Ti(IV)   | C/1    | 168.9| 1547, 1501, 1475, 1455, 1346   |
| Ti(IV)   | D/1    | 175.3| 1666, 1514, 1356, 1306         |
| Ti(IV)   | M/1-c  | 152.8| 1657, 1624, 1590, 1558, 1524, 1500, 1407 |
| Ti(IV)   | B/2    | 160.8| 1538, 1473, 1434, 1379, 1299,  |
| Ti(IV)   | C/1    | 169.9|                                |
| Ti(IV)   | C/1    | 169.0|                                |
| Ti(IV)   | C/1    | 170.6| 1550, 1500, 1460, 1320         |
| Ti(IV)   | C/1    | 1597, 1575, 1496s, 1410vs      |
| Element | Form | Position | Wavenumbers        | References |
|---------|------|----------|--------------------|------------|
| U(IV)   | C/1  |          | 1588, 1509, 1456, 1448, 1421 | [76]       |
| U(IV)   | M/1  |          | 1654               | [77]       |
| U(IV)   | C/1  |          | 1492, 1254         | [78]       |
| U(IV)   | M/1-c| -134.2   | 1579, 1648, 1645.  | [79]       |
| U(IV)   | C/1  |          | 2859, 1451, 1378, 1290 | [80]       |
| W(0)    | D/1-n| 159.3    | 1741               | [83]       |
| W(VI)   | M/1  |          | 1636               | [1]        |
| Y(III)  | D/2  |          | 1607, 1585, 1502, 1260 | [32]       |
| Yb(III) | C/1, B/2, B/3 |          | 1604, 1541, 1491, 1355 | [31]       |
| Yb(III) | D/2  |          | 1604, 1584, 1533, 1266 | [32]       |
| Yb(III) | C/2  |          | 1617, 1591, 1538, 1446, 1338 | [48]       |
| Zn(II)  | B/2  |          | 163.9               | 1538, 1402 | [84]       |
| Zn(II)  | B/3  |          | 163.50              |            |            |
| Zn(II)  | B/3  |          | 164.7               |            | [86]       |
| Zn(II)  | B/2  |          | 163.2               |            |            |
| Zn(II)  | B/2  |          | 162.0               |            | [91]       |
| Zn(II)  | M/1  |          | 162 [c]             | 1616, 1596, 1348, 1288 | [92]       |
| Zn(II)  | B/2  |          | 162.5, 163.1        | 1606, 1564 |            | [93]       |
| Zn(II)  | M/1  |          | 161.0               | 1587, 1549 |            |            |
| Zn(II)  | B/2, B/3 |        | 162.8               | 1553, 1485 |            |            |
| Zn(II)  | B/2  |          | 166.0               | 1603, 1592 |            | [94]       |
| Zn(II)  | B/2  |          | 1570, 1510, 1460, 1430, 1380, 1320 | [1]       |
| Zn(II)  | B/2  |          | 1570, 1504, 1430, 1378, 1326 |            |            |
| Zn(II)/Dy(III) | B/2 |          | 1638               |            |            |
| Zn(II)/Tb(III) | B/2 |          | 1642               |            |            | [96]       |
| Zn(II)/Gd(III) | B/2 |          | 1640               |            |            |
| Zr(IV)  | B/2  |          | 162.7               | 1757       |            | [97]       |
| Zr(IV)  | C/1  |          | 170.4               | 1565, 1505, 1450, 1380, 1325 | [1]       |
| Zr(IV)  | C/1  |          | 170.3               | 1535, 1500, 1380, 1360 |            |

[a] Room temperature NMR in CDCl₃ or other solvent; [b] Solid-state IR data; 1800-1300 cm⁻¹ range, weak bands not included. The highest-wavenumber absorption in bold.
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