Electronic Supplementary Material (ESI) for RSC Advances.


# Electronic Supporting Information (ESI)

## Synthesis, structural analysis, solution equilibria and biological activity of rhodium(III) complexes with a quinquedentate polyaminopolycarboxylate

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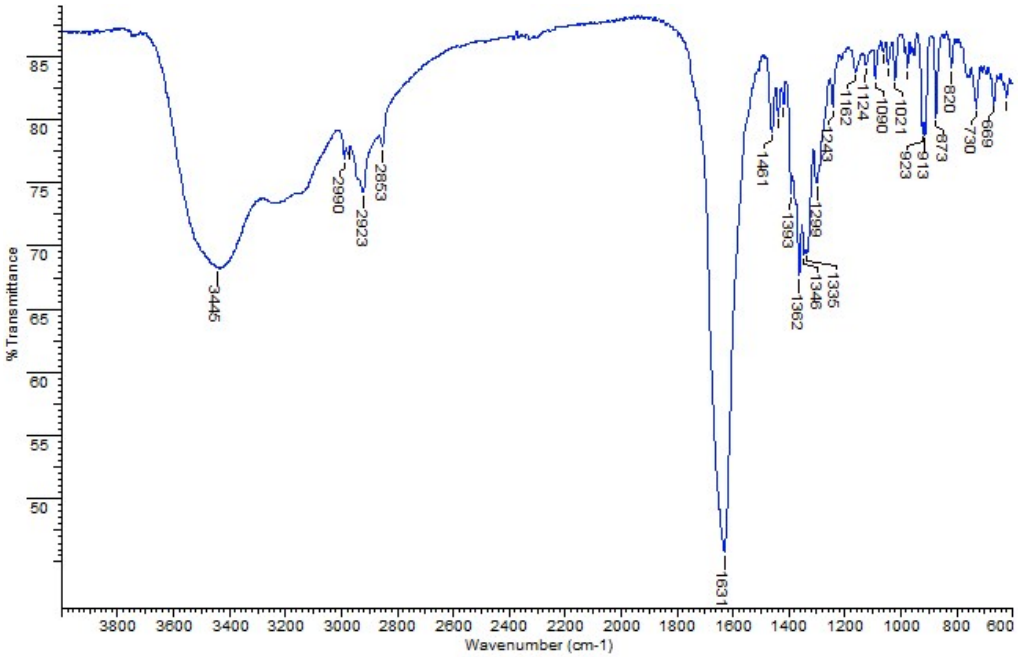


**Figure S1.** IR spectrum of [Rh(ed3a)($OH_2$)]·$H_2O$ **(1)** complex.

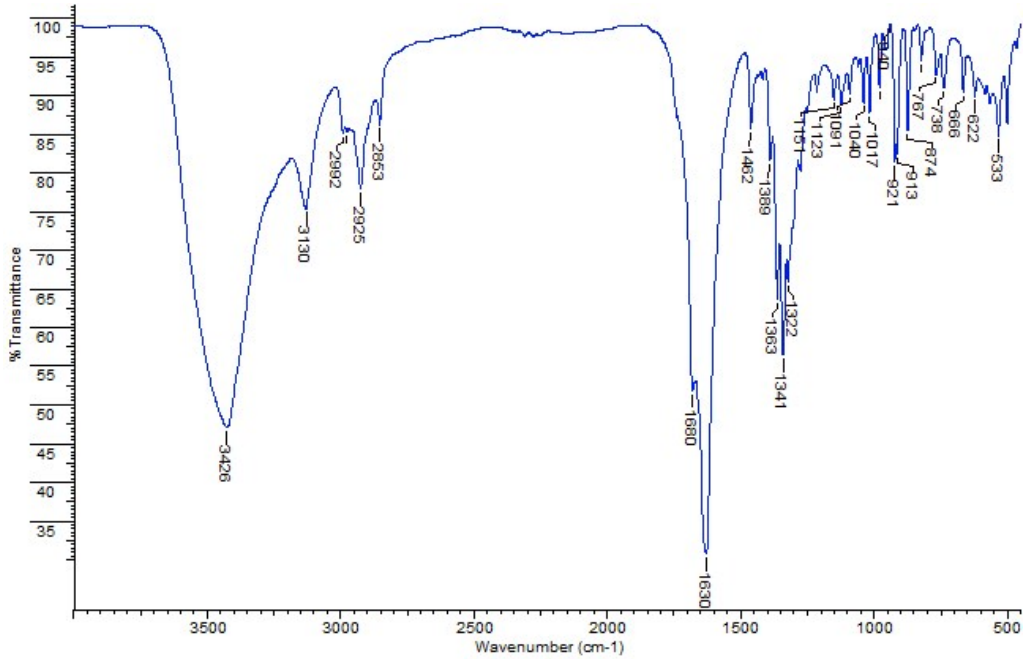


**Figure S2.** IR spectrum of Na[Rh(ed3a)Cl]·$H_2O$ **(2)** complex.

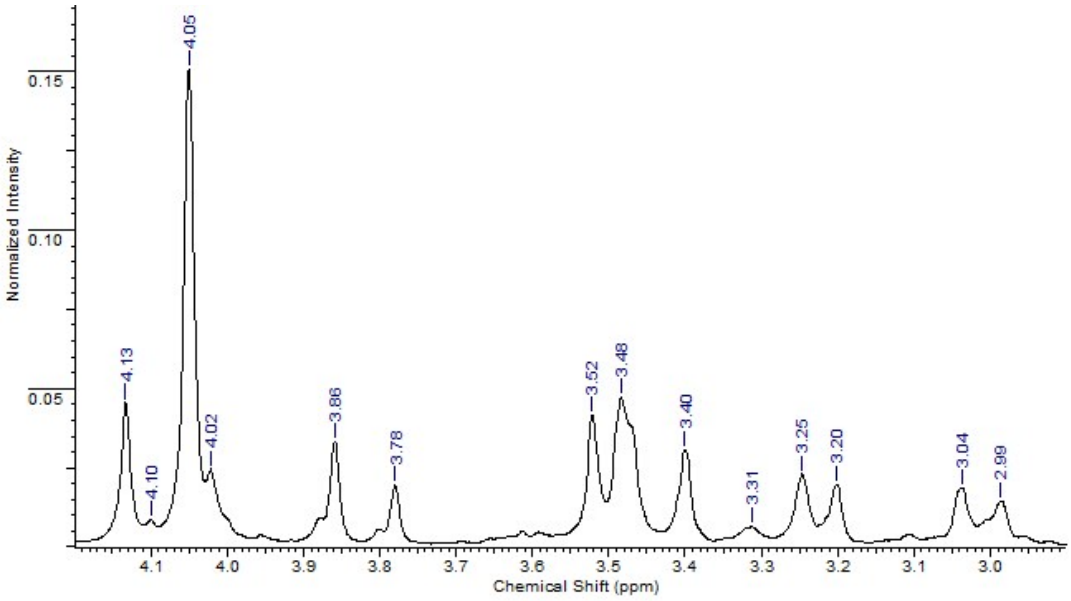


**Figure S3.** $^{1}H$ NMR spectrum of [Rh(ed3a)($OH_2$)]·$H_2O$ **(1)** complex.

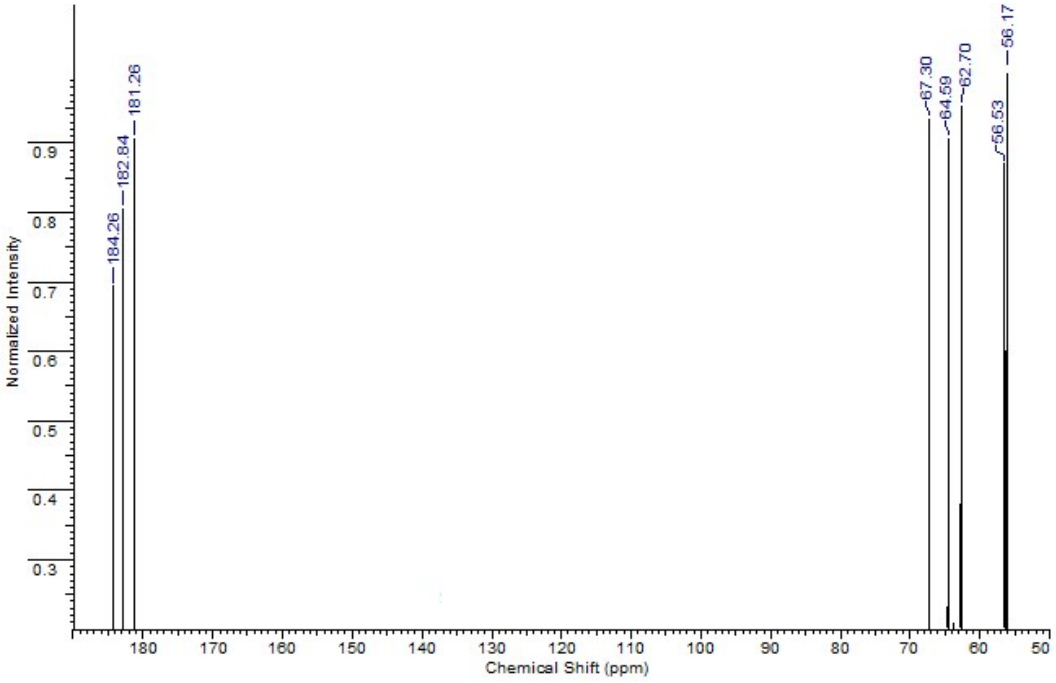


**Figure S4.** $^{13}C$ NMR spectrum of [Rh(ed3a)($OH_2$)]·$H_2O$ **(1)** complex.

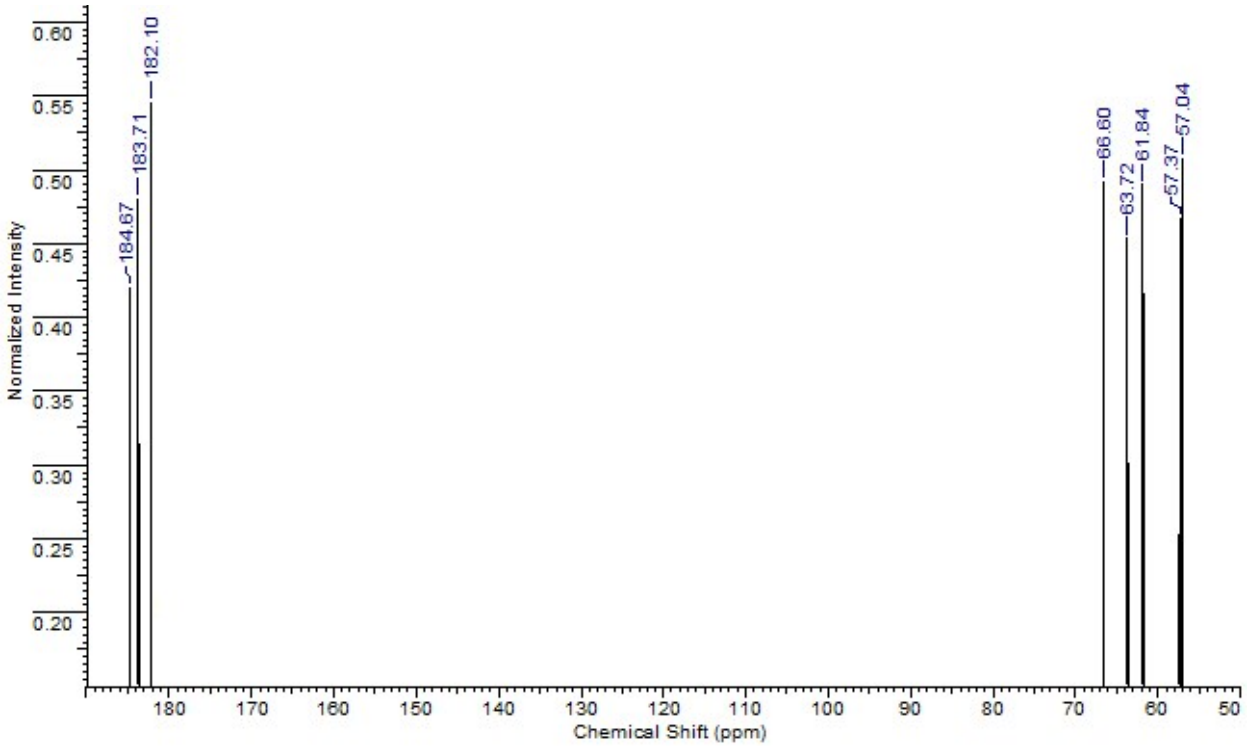


**Figure S5.** $^{13}C$ NMR spectrum of Na[Rh(ed3a)Cl]·$H_2O$ **(2)** complex.

### Further information about Crystal structures

CCDC 1412103 (for **(1)**) and CCDC 1412104 (for **(2)**) contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

#### Crystal data of *cis*-eq-[Rh(ed3a)($OH_2$)]·$H_2O$ (1)

**Table S1.** Atomic coordinates [ · $10^4$] and equivalent isotropic displacement parameters [$Å^2$ · $10^3$] for **(1)**. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| Rh | 8084(1) | 4097(1) | 6292(1) | 7(1) |
| O(1) | 9711(3) | 3950(1) | 9874(2) | 13(1) |
| O(2) | 9555(2) | 3725(1) | 7886(1) | 10(1) |
| O(3) | 11205(3) | 2278(1) | 4930(2) | 20(1) |
| O(4) | 10121(2) | 3574(1) | 5324(2) | 12(1) |
| O(5) | 5014(3) | 3885(1) | 3037(2) | 16(1) |
| O(6) | 6660(2) | 4450(1) | 4683(2) | 11(1) |
| O(7) | 9292(3) | 5298(1) | 6566(2) | 14(1) |
| O(8) | 12184(3) | 5441(1) | 8294(2) | 20(1) |
| N(1) | 5989(3) | 4382(1) | 7350(2) | 10(1) |
| N(2) | 6786(3) | 2971(1) | 5982(2) | 8(1) |
| C(1) | 8870(3) | 4022(2) | 8833(2) | 10(1) |
| C(2) | 6952(4) | 4503(2) | 8606(2) | 12(1) |

| | | | | |
|---|---|---|---|---|
| C(3) | 4535(3) | 3677(2) | 7177(2) | 13(1) |
| C(4) | 5557(4) | 2841(2) | 6987(2) | 12(1) |
| C(5) | 8406(3) | 2351(2) | 5969(2) | 12(1) |
| C(6) | 10036(3) | 2743(2) | 5343(2) | 12(1) |
| C(7) | 5581(3) | 3000(2) | 4757(2) | 11(1) |
| C(8) | 5765(3) | 3831(2) | 4103(2) | 10(1) |

**Table S2.** Bond lengths [Å] and angles [°] for **(1)**

| | |
|---|---|
| Rh-O(2) | 2.0183(16) |
| Rh-O(4) | 2.0497(17) |
| Rh-O(6) | 2.0102(16) |
| Rh-O(7) | 2.0723(18) |
| Rh-N(1) | 2.027(2) |
| Rh-N(2) | 1.9964(19) |
| O(1)-C(1) | 1.234(3) |
| O(2)-C(1) | 1.292(3) |
| O(3)-C(6) | 1.221(3) |
| O(4)-C(6) | 1.307(3) |
| O(5)-C(8) | 1.236(3) |
| O(6)-C(8) | 1.284(3) |
| N(1)-C(2) | 1.483(3) |
| N(1)-C(3) | 1.495(3) |
| N(2)-C(4) | 1.498(3) |
| N(2)-C(5) | 1.489(3) |
| N(2)-C(7) | 1.507(3) |
| C(1)-C(2) | 1.525(3) |
| C(3)-C(4) | 1.521(3) |
| C(5)-C(6) | 1.528(3) |
| C(7)-C(8) | 1.507(3) |
| O(2)-Rh-O(4) | 92.01(7) |
| O(2)-Rh-O(7) | 89.03(7) |
| O(2)-Rh-N(1) | 83.06(7) |
| O(4)-Rh-O(7) | 98.62(7) |
| O(6)-Rh-O(2) | 178.62(7) |
| O(6)-Rh-O(4) | 86.64(7) |
| O(6)-Rh-O(7) | 91.45(7) |
| O(6)-Rh-N(1) | 98.21(8) |
| N(1)-Rh-O(4) | 169.01(8) |
| N(1)-Rh-O(7) | 91.14(8) |
| N(2)-Rh-O(2) | 93.66(7) |
| N(2)-Rh-O(4) | 83.09(7) |
| N(2)-Rh-O(6) | 85.90(7) |
| N(2)-Rh-O(7) | 176.77(8) |
| N(2)-Rh-N(1) | 87.42(8) |
| C(1)-O(2)-Rh | 114.23(15) |
| C(6)-O(4)-Rh | 110.92(15) |
| C(8)-O(6)-Rh | 113.08(15) |
| C(2)-N(1)-Rh | 107.39(15) |
| C(2)-N(1)-C(3) | 115.79(19) |
| C(3)-N(1)-Rh | 106.46(14) |
| C(4)-N(2)-Rh | 106.21(14) |
| C(4)-N(2)-C(7) | 111.77(18) |

| | |
|---|---|
| C(5)-N(2)-Rh | 104.81(14) |
| C(5)-N(2)-C(4) | 114.62(18) |
| C(5)-N(2)-C(7) | 110.37(18) |
| C(7)-N(2)-Rh | 108.57(14) |
| O(1)-C(1)-O(2) | 123.3(2) |
| O(1)-C(1)-C(2) | 120.3(2) |
| O(2)-C(1)-C(2) | 116.4(2) |
| N(1)-C(2)-C(1) | 112.15(19) |
| N(1)-C(3)-C(4) | 109.80(19) |
| N(2)-C(4)-C(3) | 107.63(19) |
| N(2)-C(5)-C(6) | 110.07(19) |
| O(3)-C(6)-O(4) | 123.9(2) |
| O(3)-C(6)-C(5) | 119.5(2) |
| O(4)-C(6)-C(5) | 116.5(2) |
| C(8)-C(7)-N(2) | 112.92(19) |
| O(5)-C(8)-O(6) | 123.3(2) |
| O(5)-C(8)-C(7) | 118.0(2) |
| O(6)-C(8)-C(7) | 118.6(2) |

Symmetry transformations used to generate equivalent atoms

**Table S3.** Torsion angles [°] for **(1)**. The torsion angle $w_{ijkl}$ is defined as the angle between the vectors *ji* and *kl* when viewed down *jk* (positive sign indicates clockwise rotation).

| *i-j-k-l* | $w_{ijkl}$ |
|---|---|
| Rh-O(2)-C(1)-O(1) | -170.84(18) |
| Rh-O(2)-C(1)-C(2) | 7.4(3) |
| Rh-O(4)-C(6)-O(3) | -173.08(19) |
| Rh-O(4)-C(6)-C(5) | 4.5(2) |
| Rh-O(6)-C(8)-O(5) | -170.33(19) |
| Rh-O(6)-C(8)-C(7) | 10.8(3) |
| Rh-N(1)-C(2)-C(1) | -25.1(2) |
| Rh-N(1)-C(3)-C(4) | 34.1(2) |
| Rh-N(2)-C(4)-C(3) | 43.3(2) |
| Rh-N(2)-C(5)-C(6) | -38.6(2) |
| Rh-N(2)-C(7)-C(8) | 2.7(2) |
| O(1)-C(1)-C(2)-N(1) | -169.1(2) |
| O(2)-C(1)-C(2)-N(1) | 12.5(3) |
| N(1)-C(3)-C(4)-N(2) | -52.5(2) |
| N(2)-C(5)-C(6)-O(3) | -158.8(2) |
| N(2)-C(5)-C(6)-O(4) | 23.5(3) |
| N(2)-C(7)-C(8)-O(5) | 171.9(2) |
| N(2)-C(7)-C(8)-O(6) | -9.2(3) |
| C(2)-N(1)-C(3)-C(4) | -85.2(2) |
| C(3)-N(1)-C(2)-C(1) | 93.6(2) |
| C(4)-N(2)-C(5)-C(6) | -154.60(19) |
| C(4)-N(2)-C(7)-C(8) | 119.5(2) |
| C(5)-N(2)-C(4)-C(3) | 158.51(19) |
| C(5)-N(2)-C(7)-C(8) | -111.7(2) |
| C(7)-N(2)-C(4)-C(3) | -75.0(2) |
| C(7)-N(2)-C(5)-C(6) | 78.1(2) |

Symmetry transformations used to generate equivalent atoms

## Crystal data of *cis*-eq-[Rh(ed3a)Cl]·$H_2O$ (2)

**Table S4.** Atomic coordinates [ · $10^4$] and equivalent isotropic displacement parameters [$Å^2$ · $10^3$] for **(2)**. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| Rh | 2127(1) | -36(1) | 555(1) | 12(1) |
| Cl | 1769(1) | -913(2) | 1908(1) | 22(1) |
| Na | 4790(2) | -3395(3) | 2181(2) | 30(1) |
| O(1) | 49(3) | -2676(5) | -1909(3) | 28(1) |
| O(2) | 857(2) | -1650(5) | -361(2) | 16(1) |
| O(3) | 4457(3) | -2996(6) | 128(3) | 35(1) |
| O(4) | 3210(2) | -2260(5) | 670(2) | 18(1) |
| O(5) | 3696(2) | 4205(5) | 2413(2) | 23(1) |
| O(6) | 3383(2) | 1646(5) | 1446(2) | 18(1) |
| O(7) | 4359(3) | -1150(6) | 3189(3) | 30(1) |
| N(1) | 2350(3) | 633(6) | -653(3) | 15(1) |
| N(2) | 1247(3) | 2448(6) | 318(3) | 17(1) |
| C(1) | 744(3) | -1694(7) | -1265(4) | 18(1) |
| C(2) | 1539(3) | -504(7) | -1512(3) | 18(1) |
| C(3) | 3502(3) | 0(8) | -421(4) | 20(1) |
| C(4) | 3742(4) | -1903(8) | 148(4) | 23(1) |
| C(5) | 2145(4) | 2757(7) | -804(4) | 18(1) |
| C(6) | 1115(3) | 3197(7) | -663(4) | 21(1) |
| C(7) | 1855(3) | 3757(7) | 1164(4) | 19(1) |
| C(8) | 3058(4) | 3201(7) | 1720(3) | 18(1) |

**Table S5.** Bond lengths [Å] and angles [°] for **(2)**

| | |
|---|---|
| Rh-Cl | 2.3532(12) |
| Rh-O(2) | 2.008(3) |
| Rh-O(4) | 2.074(3) |
| Rh-O(6) | 2.013(3) |
| Rh-N(1) | 2.011(4) |
| Rh-N(2) | 2.031(4) |
| Na-Na#1 | 3.5754(10) |
| Na-Na#2 | 3.5754(10) |
| Na-O(3) | 2.925(5) |
| Na-O(4) | 2.474(3) |
| Na-O(5)#2 | 2.584(4) |
| Na-O(5)#3 | 2.339(4) |
| Na-O(6)#2 | 2.432(3) |
| Na-O(7)#2 | 2.408(5) |
| Na-O(7) | 2.404(5) |
| Na-C(4) | 2.942(6) |
| Na-C(8)#2 | 2.862(5) |
| O(1)-C(1) | 1.221(6) |
| O(2)-C(1) | 1.297(6) |
| O(3)-C(4) | 1.231(6) |
| O(4)-C(4) | 1.287(6) |
| O(5)-Na#1 | 2.584(4) |
| O(5)-Na#4 | 2.339(4) |
| O(5)-C(8) | 1.238(6) |
| O(6)-Na#1 | 2.432(3) |
| O(6)-C(8) | 1.294(6) |

| | |
|---|---|
| O(7)-Na#1 | 2.408(5) |
| O(7)-H(7A) | 0.83(6) |
| O(7)-H(7B) | 0.89(7) |
| N(1)-C(2) | 1.504(6) |
| N(1)-C(3) | 1.495(5) |
| N(1)-C(5) | 1.497(6) |
| N(2)-H(2) | 0.85(5) |
| N(2)-C(6) | 1.495(6) |
| N(2)-C(7) | 1.487(6) |
| C(1)-C(2) | 1.512(6) |
| C(2)-H(2A) | 0.9900 |
| C(2)-H(2B) | 0.9900 |
| C(3)-H(3A) | 0.9900 |
| C(3)-H(3B) | 0.9900 |
| C(3)-C(4) | 1.529(7) |
| C(5)-H(5A) | 0.9900 |
| C(5)-H(5B) | 0.9900 |
| C(5)-C(6) | 1.514(6) |
| C(6)-H(6A) | 0.9900 |
| C(6)-H(6B) | 0.9900 |
| C(7)-H(7C) | 0.9900 |
| C(7)-H(7D) | 0.9900 |
| C(7)-C(8) | 1.514(6) |
| C(8)-Na#1 | 2.862(5) |

| | |
|---|---|
| O(2)-Rh-Cl | 91.11(10) |
| O(2)-Rh-O(4) | 90.05(12) |
| O(2)-Rh-O(6) | 178.33(13) |
| O(2)-Rh-N(1) | 85.55(14) |
| O(2)-Rh-N(2) | 95.39(13) |
| O(4)-Rh-Cl | 97.46(10) |
| O(6)-Rh-Cl | 89.99(10) |
| O(6)-Rh-O(4) | 91.05(12) |
| O(6)-Rh-N(2) | 83.30(14) |
| N(1)-Rh-Cl | 176.63(10) |
| N(1)-Rh-O(4) | 82.97(14) |
| N(1)-Rh-O(6) | 93.34(14) |
| N(1)-Rh-N(2) | 86.90(16) |
| N(2)-Rh-Cl | 93.02(12) |
| N(2)-Rh-O(4) | 168.09(14) |
| Na#1-Na-Na#2 | 151.62(12) |
| O(3)-Na-Na#1 | 97.17(11) |
| O(3)-Na-Na#2 | 107.94(12) |
| O(3)-Na-C(4) | 24.23(12) |
| O(4)-Na-Na#1 | 84.92(10) |
| O(4)-Na-Na#2 | 121.85(11) |
| O(4)-Na-O(3) | 47.33(10) |
| O(4)-Na-O(5)#2 | 105.78(13) |
| O(4)-Na-C(4) | 25.68(12) |
| O(4)-Na-C(8)#2 | 131.33(15) |
| O(5)#3-Na-Na#2 | 46.20(10) |
| O(5)#2-Na-Na#1 | 40.79(9) |
| O(5)#2-Na-Na#2 | 126.53(11) |
| O(5)#3-Na-Na#1 | 133.42(14) |

| | |
|---|---|
| O(5)#2-Na-O(3) | 86.16(12) |
| O(5)#3-Na-O(3) | 113.53(13) |
| O(5)#3-Na-O(4) | 90.95(12) |
| O(5)#3-Na-O(5)#2 | 160.03(10) |
| O(5)#3-Na-O(6)#2 | 110.54(14) |
| O(5)#3-Na-O(7) | 91.92(15) |
| O(5)#3-Na-O(7)#2 | 81.85(14) |
| O(5)#2-Na-C(4) | 88.71(14) |
| O(5)#3-Na-C(4) | 110.57(14) |
| O(5)#3-Na-C(8)#2 | 136.99(15) |
| O(5)#2-Na-C(8)#2 | 25.63(12) |
| O(6)#2-Na-Na#2 | 78.40(11) |
| O(6)#2-Na-Na#1 | 77.08(11) |
| O(6)#2-Na-O(3) | 122.24(13) |
| O(6)#2-Na-O(4) | 158.04(14) |
| O(6)#2-Na-O(5)#2 | 52.27(11) |
| O(6)#2-Na-C(4) | 137.15(15) |
| O(6)#2-Na-C(8)#2 | 26.76(12) |
| O(7)-Na-Na#2 | 120.84(15) |
| O(7)-Na-Na#1 | 42.06(11) |
| O(7)#2-Na-Na#2 | 41.96(11) |
| O(7)#2-Na-Na#1 | 142.61(14) |
| O(7)#2-Na-O(3) | 72.97(14) |
| O(7)-Na-O(3) | 128.99(15) |
| O(7)#2-Na-O(4) | 110.21(15) |
| O(7)-Na-O(4) | 91.56(14) |
| O(7)#2-Na-O(5)#2 | 101.89(14) |
| O(7)-Na-O(5)#2 | 77.06(13) |
| O(7)-Na-O(6)#2 | 83.51(13) |
| O(7)#2-Na-O(6)#2 | 78.42(13) |
| O(7)-Na-O(7)#2 | 157.34(12) |
| O(7)-Na-C(4) | 106.61(15) |
| O(7)#2-Na-C(4) | 95.96(16) |
| O(7)#2-Na-C(8)#2 | 88.79(14) |
| O(7)-Na-C(8)#2 | 80.95(14) |
| C(4)-Na-Na#2 | 124.61(14) |
| C(4)-Na-Na#1 | 83.48(12) |
| C(8)#2-Na-Na#2 | 102.50(12) |
| C(8)#2-Na-Na#1 | 57.79(11) |
| C(8)#2-Na-O(3) | 103.35(14) |
| C(8)#2-Na-C(4) | 112.12(15) |
| C(1)-O(2)-Rh | 114.4(3) |
| C(4)-O(3)-Na | 78.6(3) |
| Rh-O(4)-Na | 127.35(16) |
| C(4)-O(4)-Rh | 110.9(3) |
| C(4)-O(4)-Na | 97.9(3) |
| Na#4-O(5)-Na#1 | 93.01(11) |
| C(8)-O(5)-Na#4 | 121.9(3) |
| C(8)-O(5)-Na#1 | 89.8(3) |
| Rh-O(6)-Na#1 | 143.85(17) |
| C(8)-O(6)-Rh | 113.1(3) |
| C(8)-O(6)-Na#1 | 95.5(3) |
| Na-O(7)-Na#1 | 95.98(14) |
| Na-O(7)-H(7A) | 101(4) |

| | |
|---|---|
| Na#1-O(7)-H(7A) | 113(4) |
| Na-O(7)-H(7B) | 127(4) |
| Na#1-O(7)-H(7B) | 110(4) |
| H(7A)-O(7)-H(7B) | 109(6) |
| C(2)-N(1)-Rh | 108.5(3) |
| C(3)-N(1)-Rh | 105.0(3) |
| C(3)-N(1)-C(2) | 110.0(4) |
| C(3)-N(1)-C(5) | 115.4(4) |
| C(5)-N(1)-Rh | 105.9(3) |
| C(5)-N(1)-C(2) | 111.6(3) |
| Rh-N(2)-H(2) | 112(4) |
| C(6)-N(2)-Rh | 106.4(3) |
| C(6)-N(2)-H(2) | 112(4) |
| C(7)-N(2)-Rh | 107.6(3) |
| C(7)-N(2)-H(2) | 104(4) |
| C(7)-N(2)-C(6) | 114.6(4) |
| O(1)-C(1)-O(2) | 123.1(4) |
| O(1)-C(1)-C(2) | 119.3(4) |
| O(2)-C(1)-C(2) | 117.6(4) |
| N(1)-C(2)-C(1) | 113.8(4) |
| N(1)-C(2)-H(2A) | 108.8 |
| N(1)-C(2)-H(2B) | 108.8 |
| C(1)-C(2)-H(2A) | 108.8 |
| C(1)-C(2)-H(2B) | 108.8 |
| H(2A)-C(2)-H(2B) | 107.7 |
| N(1)-C(3)-H(3A) | 109.8 |
| N(1)-C(3)-H(3B) | 109.8 |
| N(1)-C(3)-C(4) | 109.4(4) |
| H(3A)-C(3)-H(3B) | 108.2 |
| C(4)-C(3)-H(3A) | 109.8 |
| C(4)-C(3)-H(3B) | 109.8 |
| O(3)-C(4)-Na | 77.1(3) |
| O(3)-C(4)-O(4) | 122.3(5) |
| O(3)-C(4)-C(3) | 119.8(5) |
| O(4)-C(4)-Na | 56.4(2) |
| O(4)-C(4)-C(3) | 117.8(4) |
| C(3)-C(4)-Na | 140.7(3) |
| N(1)-C(5)-H(5A) | 110.3 |
| N(1)-C(5)-H(5B) | 110.3 |
| N(1)-C(5)-C(6) | 107.3(4) |
| H(5A)-C(5)-H(5B) | 108.5 |
| C(6)-C(5)-H(5A) | 110.3 |
| C(6)-C(5)-H(5B) | 110.3 |
| N(2)-C(6)-C(5) | 109.6(4) |
| N(2)-C(6)-H(6A) | 109.7 |
| N(2)-C(6)-H(6B) | 109.7 |
| C(5)-C(6)-H(6A) | 109.7 |
| C(5)-C(6)-H(6B) | 109.7 |
| H(6A)-C(6)-H(6B) | 108.2 |
| N(2)-C(7)-H(7C) | 109.1 |
| N(2)-C(7)-H(7D) | 109.1 |
| N(2)-C(7)-C(8) | 112.3(4) |
| H(7C)-C(7)-H(7D) | 107.9 |
| C(8)-C(7)-H(7C) | 109.1 |

| | |
|---|---|
| C(8)-C(7)-H(7D) | 109.1 |
| O(5)-C(8)-Na#1 | 64.5(2) |
| O(5)-C(8)-O(6) | 121.9(4) |
| O(5)-C(8)-C(7) | 120.6(4) |
| O(6)-C(8)-Na#1 | 57.8(2) |
| O(6)-C(8)-C(7) | 117.5(4) |
| C(7)-C(8)-Na#1 | 171.4(3) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+1/2 #2 -x+1,y-1/2,-z+1/2 #3 x,y-1,z #4 x,y+1,z

**Table S6.** Torsion angles [°] for **(2)**. The torsion angle $w_{ijkl}$ is defined as the angle between the vectors *ji* and *kl* when viewed down *jk* (positive sign indicates clockwise rotation).

| *i-j-k-l* | $w_{ijkl}$ |
|---|---|
| Rh-O(2)-C(1)-O(1) | 176.4(4) |
| Rh-O(2)-C(1)-C(2) | -1.9(5) |
| Rh-O(4)-C(4)-Na | 135.1(3) |
| Rh-O(4)-C(4)-O(3) | 177.7(4) |
| Rh-O(4)-C(4)-C(3) | 0.6(5) |
| Rh-O(6)-C(8)-Na#1 | 157.4(3) |
| Rh-O(6)-C(8)-O(5) | 165.4(4) |
| Rh-O(6)-C(8)-C(7) | -14.4(5) |
| Rh-N(1)-C(2)-C(1) | 4.1(4) |
| Rh-N(1)-C(3)-C(4) | 38.7(4) |
| Rh-N(1)-C(5)-C(6) | -44.4(4) |
| Rh-N(2)-C(6)-C(5) | -35.4(4) |
| Rh-N(2)-C(7)-C(8) | 19.8(5) |
| Na-O(3)-C(4)-O(4) | -35.3(4) |
| Na-O(3)-C(4)-C(3) | 141.7(4) |
| Na-O(4)-C(4)-O(3) | 42.6(5) |
| Na-O(4)-C(4)-C(3) | -134.5(4) |
| Na#4-O(5)-C(8)-Na#1 | 93.4(3) |
| Na#1-O(5)-C(8)-O(6) | -7.5(5) |
| Na#4-O(5)-C(8)-O(6) | 85.9(5) |
| Na#4-O(5)-C(8)-C(7) | -94.3(5) |
| Na#1-O(5)-C(8)-C(7) | 172.2(4) |
| Na#1-O(6)-C(8)-O(5) | 8.0(5) |
| Na#1-O(6)-C(8)-C(7) | -171.7(4) |
| O(1)-C(1)-C(2)-N(1) | -179.9(4) |
| O(2)-C(1)-C(2)-N(1) | -1.5(6) |
| N(1)-C(3)-C(4)-Na | -97.1(5) |
| N(1)-C(3)-C(4)-O(3) | 155.6(4) |
| N(1)-C(3)-C(4)-O(4) | -27.2(6) |
| N(1)-C(5)-C(6)-N(2) | 54.2(5) |
| N(2)-C(7)-C(8)-O(5) | 176.0(4) |
| N(2)-C(7)-C(8)-O(6) | -4.2(6) |
| C(2)-N(1)-C(3)-C(4) | -77.9(5) |
| C(2)-N(1)-C(5)-C(6) | 73.4(5) |
| C(3)-N(1)-C(2)-C(1) | 118.4(4) |
| C(3)-N(1)-C(5)-C(6) | -160.1(4) |

| | |
|---|---|
| C(5)-N(1)-C(2)-C(1) | -112.2(4) |
| C(5)-N(1)-C(3)-C(4) | 154.9(4) |
| C(6)-N(2)-C(7)-C(8) | -98.3(5) |
| C(7)-N(2)-C(6)-C(5) | 83.4(5) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+1/2 #2 -x+1,y-1/2,-z+1/2 #3 x,y-1,z
#4 x,y+1,z

**Table S7.** Hydrogen bonds for **(1)** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(7)-H(7A)...Cl | 0.83(6) | 2.35(7) | 3.171(4) | 173(6) |
| O(7)-H(7B)...O(3)#5 | 0.89(7) | 2.07(7) | 2.912(6) | 157(5) |
| N(2)-H(2)...O(2)#6 | 0.85(5) | 2.05(5) | 2.901(5) | 175(5) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+1/2 #2 -x+1,y-1/2,-z+1/2 #3 x,y-1,z
#4 x,y+1,z #5 x,-y-1/2,z+1/2 #6 -x,-y,-z

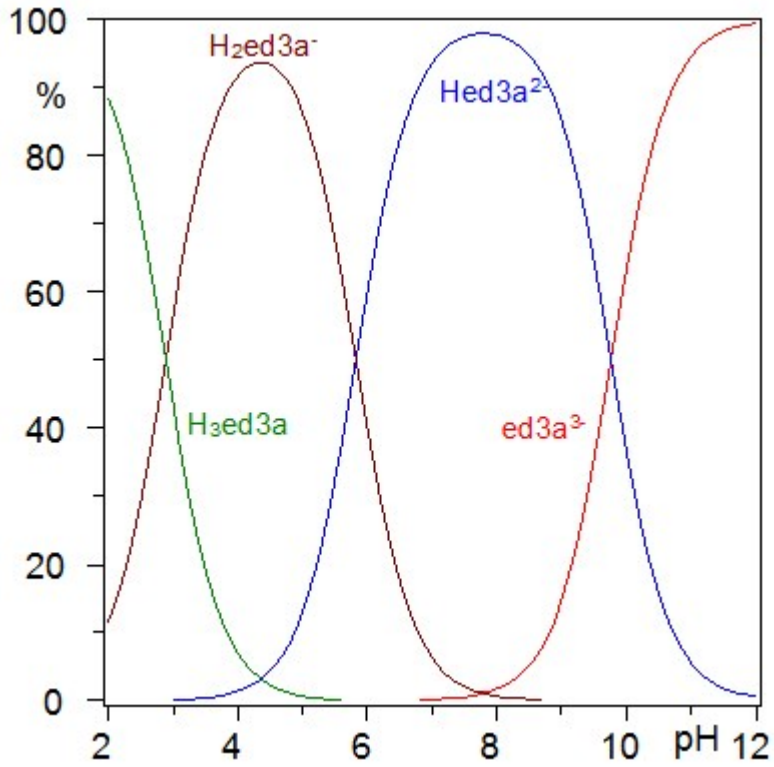


**Figure S6.** Distribution diagram of the ed3a protonated forms. The concentration of ed3a is 2.0 mmol $dm^{-3}$.

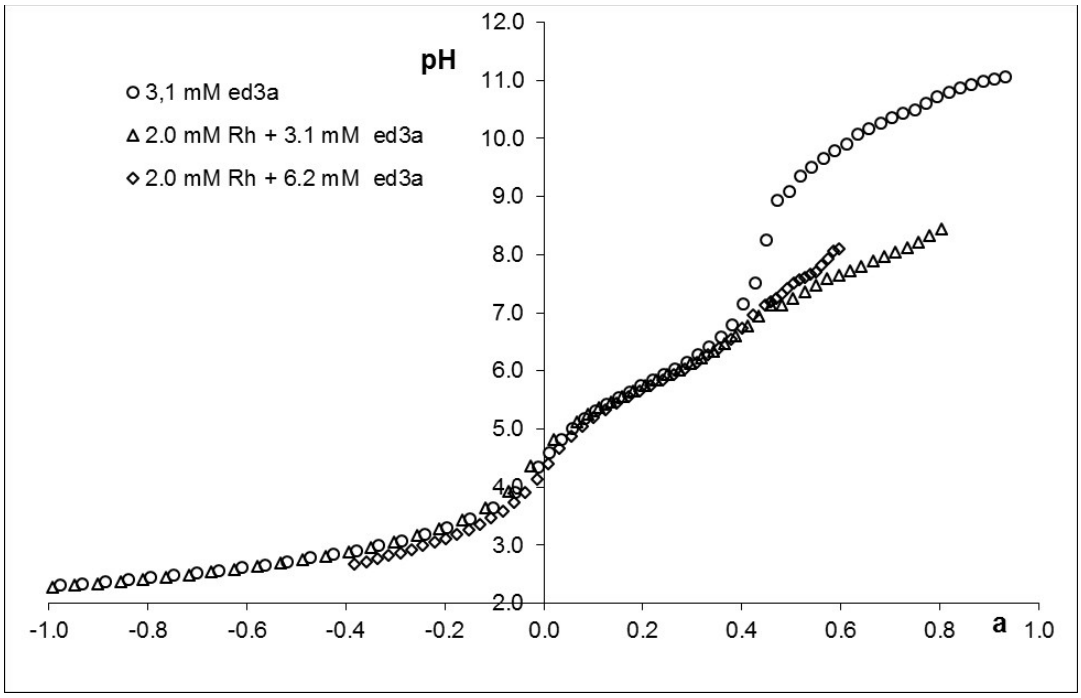


**Figure S7.** Potentiometric titration of $Rh^{3+}$ - ed3a solutions with standard NaOH in 0.1 M NaCl ionic medium at 298 K.

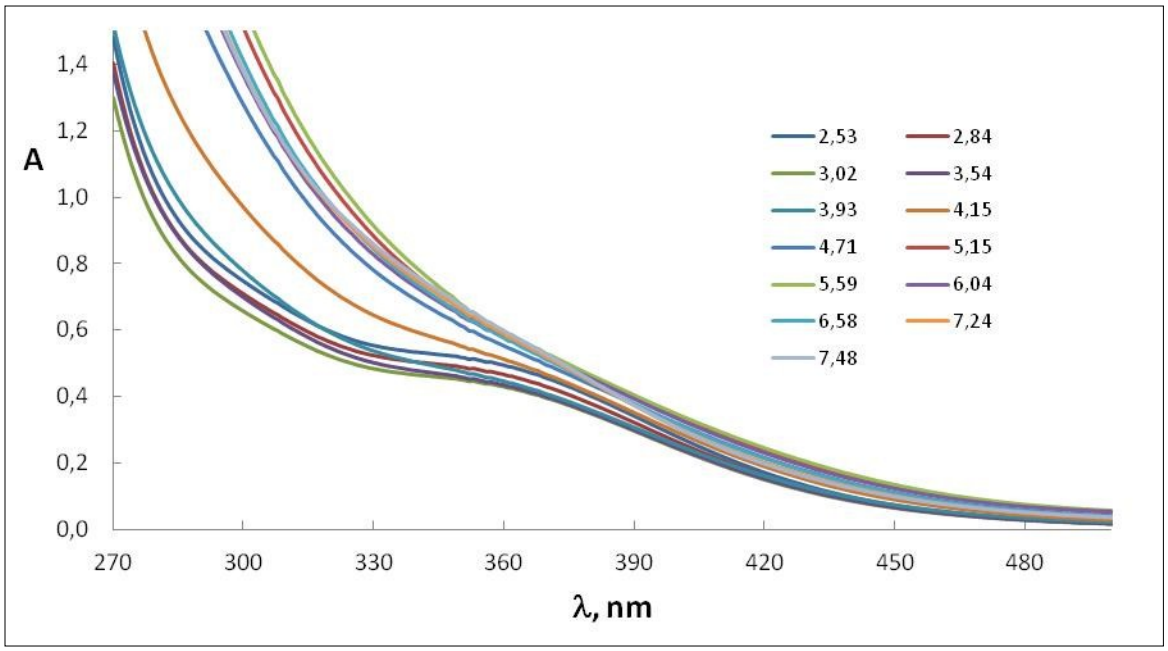


**Figure S8.** UV-Vis spectra of Rh(III) - ed3a solutions at different pH values and ligand (L) to metal (M) concentration ratios: L/M = 1.5.

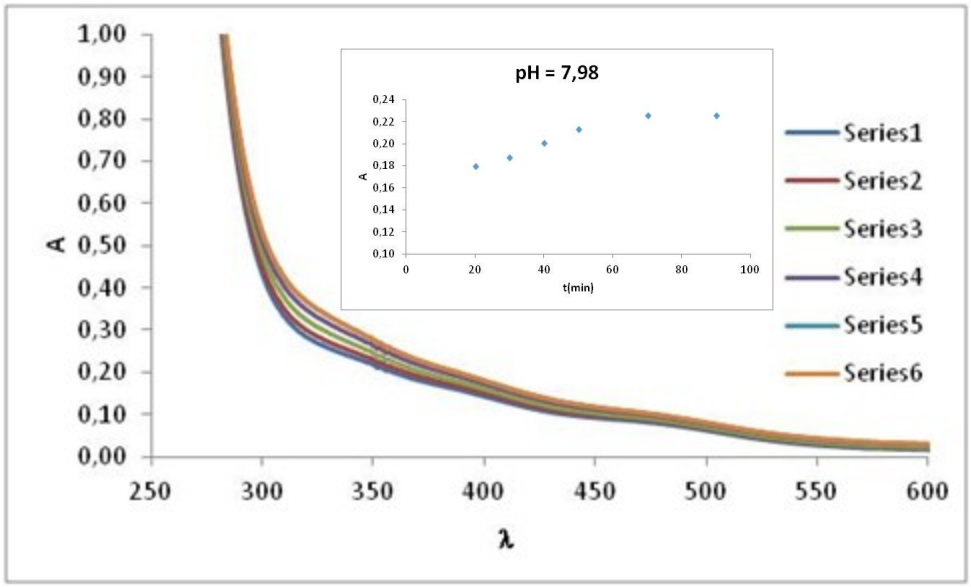


**Figure S9.** UV–Vis spectra recorded at pH = 7.98 a time interval of 20 - 90 min. The insert shows the absorbance (at λ = 372 nm) as a function of times.

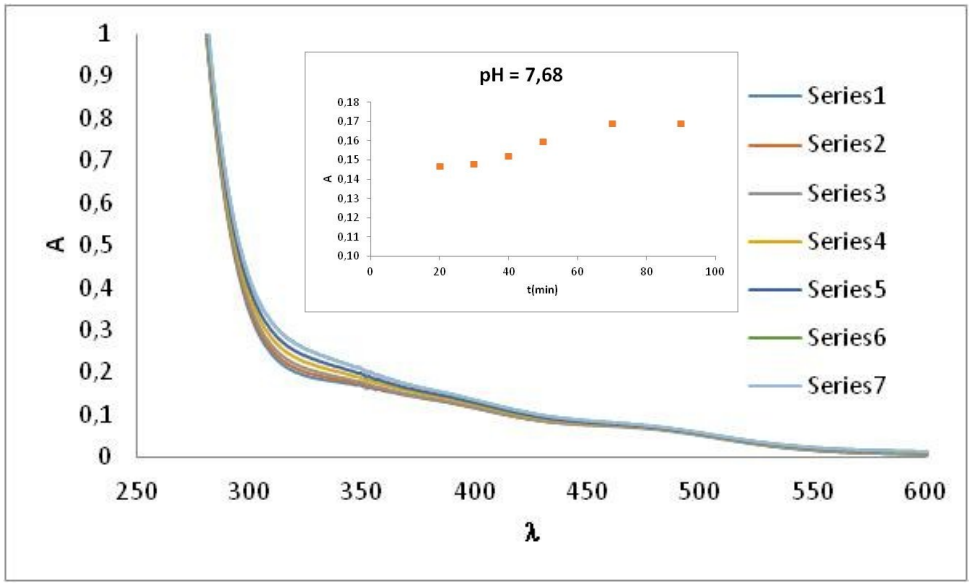


**Figure S10.** UV-Vis spectra recorded at pH = 7.68 a time interval of 20 - 90 min. The insert shows the absorbance (at λ = 372 nm) as a function of times.

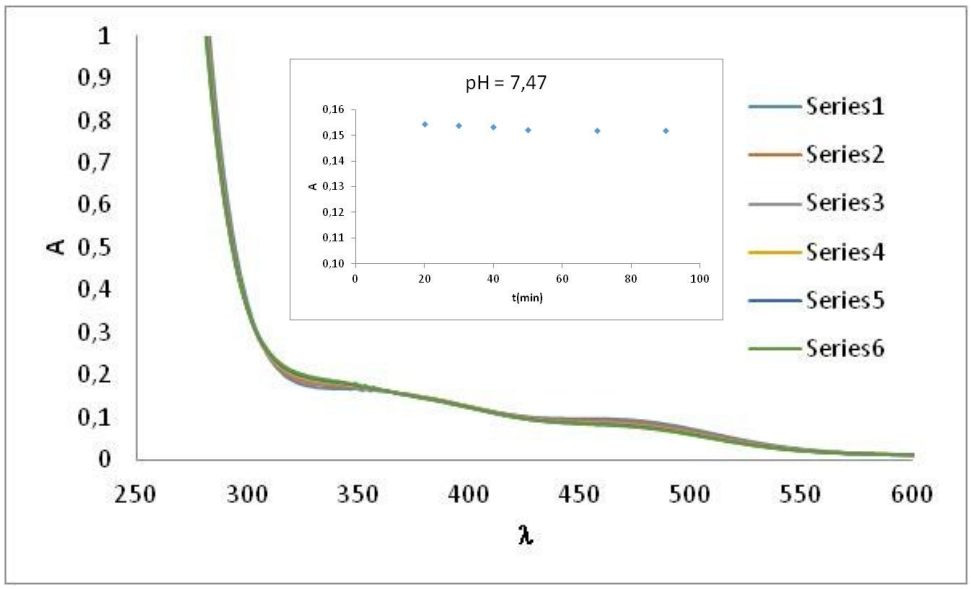


**Figure S11.** UV-Vis spectra recorded at pH = 7.47 a time interval of 20 - 90 min. The insert shows the absorbance (at λ = 372 nm) as a function of times.

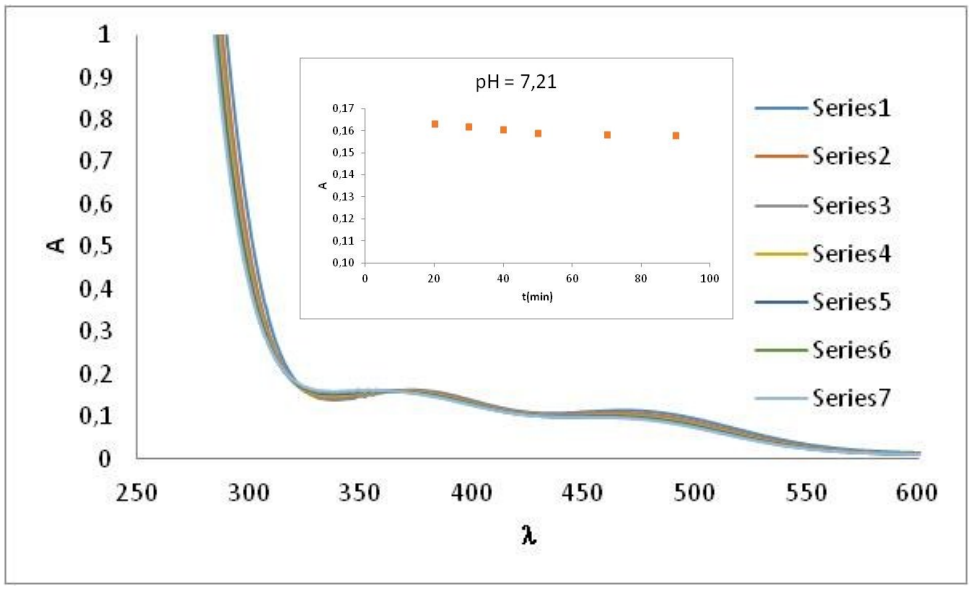


**Figure S12.** UV-Vis spectra recorded at pH = 7.21 a time interval of 20 - 90 min. The insert shows the absorbance (at λ = 372 nm) as a function of times.

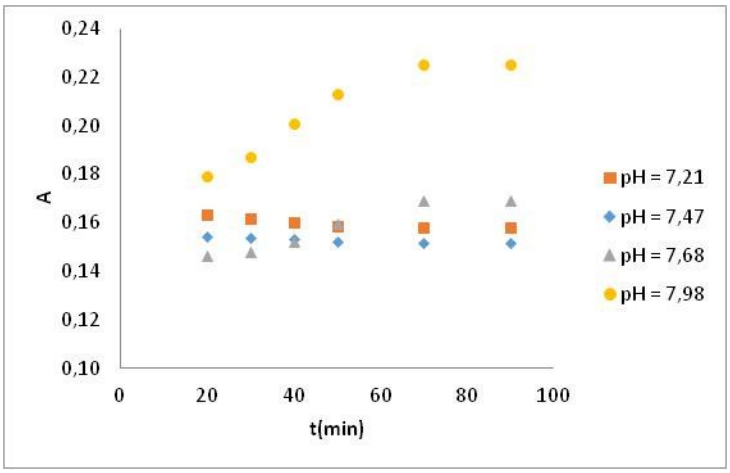


**Figure S13.** The absorbance (at λ = 372 nm) as a function of times at pH = 7 - 8.

**Protonation equilibria of ed3a$^{3-}$**

In order to derive the speciation model for each system the experimental data were plotted as titration parameter a in dependence of pH; the titration parameter a was calculated according to the equation (1):

$$a = \frac{c_{NaOH}V_{NaOH} - V_0 c_{HCl}}{V_0 L} \quad (1)$$

where $V_0$ is the initial volume of the titrated solution and L is the concentration of ed3a$^{3-}$ in the titrated solution. The titration protocol was chosen in such a way that the hydrolysis and complexation reactions would proceed in the conditions as close to true equilibrium as possible. The titrand was added, under energetic stirring of titrated solution. In this way initial formation of insoluble or colloidal rhodium hydroxide, which subsequently, dissolves very slowly, was avoided. The readings of the potential were taken every 2 min until steady values (± 0.1 mV/min) were obtained. Usually stable potential readings were obtained in 3–5 min after addition of the titrant at the beginning of the titration (pH < 4), in 5-10 min at pH 4-6, in 10-15 min at pH 6-7 and in 20–35 min at pH values higher than 7. UV–Vis spectra recorded at pH > 7 a time interval of 20 – 90 min, confirm that the establishment of equilibrium at pH > 7 was necessary to over 30 min (Fig. S9-S13, ESI†). If in the specified time interval no stable potential reading was obtained, the corresponding point was excluded from calculation. The titrations were terminated when drifted potential readings were obtained and turbidity of solutions observed (at pH > 8). Some titrations were carried out in duplicate and some in triplicate. The indication that titrated solution did not become supersaturated, with respect to polymer complexes and insoluble hydroxide, was stable potential readings over prolonged period of time (we arbitrarily chosen to monitor the potential, at the end of titration, for additional 1-2 hr.). The titrations usually lasted longer than 14h. Titration curves of ed3a$^{3-}$ in the presence of $Rh^{3+}$ (Fig. S7, ESI†) are shifted to the right compared to titration curves of ed3a$^{3-}$, indicating complex formation in the system. Since the titration curves of ed3a$^{3-}$ and the $Rh^{3+}$-ed3a$^{3-}$ system coincide at low pH values, this may indicate that complexation reaction does not proceed at pH values lower than ca. 6.

The general three component equilibrium can be written as follows (charges are omitted for simplicity):

$$p\,Rh^{3+} + q\,H + r\,ed3a \rightleftharpoons Rh_pH_q ed3a_r; \quad \beta_{p,q,r} \quad (2)$$

and the corresponding constants are given by:

$$\beta_{p,q,r} = \frac{[\mathrm{Rh}_p\mathrm{H}_q\mathrm{ed3a}_r]}{[\mathrm{Rh}]^p[\mathrm{H}]^q[\mathrm{ed3a}]^r} \quad (3)$$

where ed3a$^{3-}$ is the deprotonated ligand.

In this study, the convention has been adopted where a complex containing a metal ion, M, proton, H and ligand L, takes the general formula MpHqLr, where p, q and r are the stoichiometric indices of the components in the complex. A negative value of q refers to proton removal or hydoxide ion addition during formation of the complex. Three kinds of equilibria were considered in the present study: (a) protonation of ed3a$^{3-}$ anion; (b) hydrolysis of $Rh^{III}$ ion; and (c) general three component equilibria, which include the case q = 0, i.e. the formation of pure binary complexes of $Rh^{III}$. The overall protonation constants of ed3a$^{3-}$ anion were determined in separate experiments. The stability constants of hydrolytic complexes of Rh(II) ion were taken from the IUPAC Stability Constants Database (SC-Database). Thus, for the evaluation of the three component equilibria (c), the binary models (a) and (b) were considered as known. The concentration stability constants of the complexes, $\beta p,q,r$ were calculated with the aid of the suite of computer programs Hyperquad2006.[1]

1. P. Gans, A. Sabatini and A. Vacca, *Talanta,* 1996, **43**, 1739-1753.