Electronic Supplementary Information

Metal complexes with two different hydrogen bond donor ligands as anion hosts

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Experimental Section

General: All manipulations were carried out under a nitrogen atmosphere using Schlenk techniques. Compound [Re(OTf)(CO)$_5$][1] was prepared as previously reported. Tetrabutylammonium salts were purchased from Fluka or Aldrich. Deuterated acetonitrile (Cambridge Isotope Laboratories, Inc.) was stored under nitrogen in a Young tube and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 300, DPX-300 or Advance 400 spectrometer. NMR spectra are referred to the internal residual solvent peak for ^{1}H and ^{13}C{^{1}H} NMR. IR solution spectra were obtained in a Perkin-Elmer FT 1720-X spectrometer using 0.2 mm. CaF$_2$ cells. NMR samples were prepared under nitrogen using Kontes manifolds purchased from Aldrich. Oven-dried 5 mm NMR tubes were subjected to several vacuum-nitrogen cycles, filled with the solution of the receptor (prepared separately in a Schlenk tube, typically in a 10^{-2} M concentration in CD$_3$CN) by means of a 1 mL syringe, and stoppered with rubber septa. After the NMR spectrum of the receptor was recorded, the successive aliquots of the tetrabutylammonium salt (typically $4\cdot10^{-2}$ M in CD$_3$CN, separately prepared and kept in a septum-stoppered vial during the titration) were injected through the septum using Hamilton microsyringes (10-100 μL). The volume of each addition was 10 μL before reaching the saturation zone (nearly horizontal line of the titration profile), and 20 or 40 μL afterwards. When the change in δ is small, 20 μL of salt solution were added from the beginning. Data were treated using the WinEQNMR program.[2]

Crystal Structure Determination.

For Compounds 1·ClO$_4$, 2·BAr´$_4$ and 2·ClO$_4$. A crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo Kα X-radiation and a CCD area detector. Data collection was taken only to 2θ= 46 deg, since the intensity of the reflections was very poor from 40 deg upwards. Raw frame data were integrated with the SAINT[3] program. An empirical absorption correction was applied with the program SADABS.[4]

For Compounds 2·NO$_3$ and 2·Br. Data collection was performed at 150(2) K on a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-Kα radiation (λ= 1.5418 Å). Images were collected at a 65 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (4-16 s). Data collection strategy was calculated with the program CrysAlis^{Pro} CCD.[5] Data reduction and cell refinement was performed with the program CrysAlis^{Pro} RED.[5] An empirical absorption correction was applied using the SCALE3 ABSPACK.[5]

Structure solution and refinement (all): Crystal structures were solved by direct methods with SHELXL-97.[6] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. Calculations and drawings were made with SHELXL,PARST[7] and X-Seed[8].

The amino group in the structure of **2·ClO$_4$** adduct (included as Electronic Supplementary Information) exhibited disorder and was resolved in two components of *ca.* 50:50 occupancy. The structure of **2·NO$_3$** contains large voids accessible for solvents, and indeed several peaks can be found in the difference maps. After repeated attempts, only 1/8 of hexane and 1/8 of dichloromethane molecules could be reasonably modelled and refined.

Molecular structure of the [Re(CO)$_3$(Hdmpz)$_2$(2-ampy)]·[ClO$_4$] adduct.

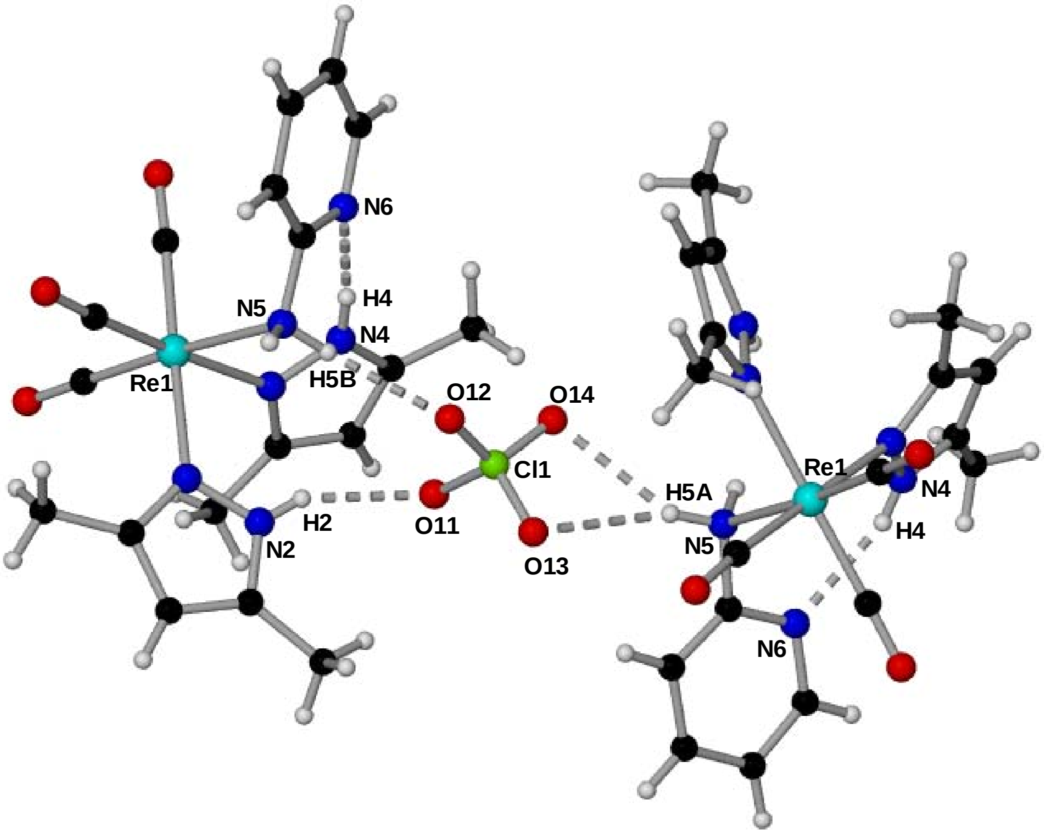


Figure S1. Main hydrogen bonds between perchlorate and the metallic cation in **1**·ClO$_4$ (this figure is a more complete view of Figure 1a).

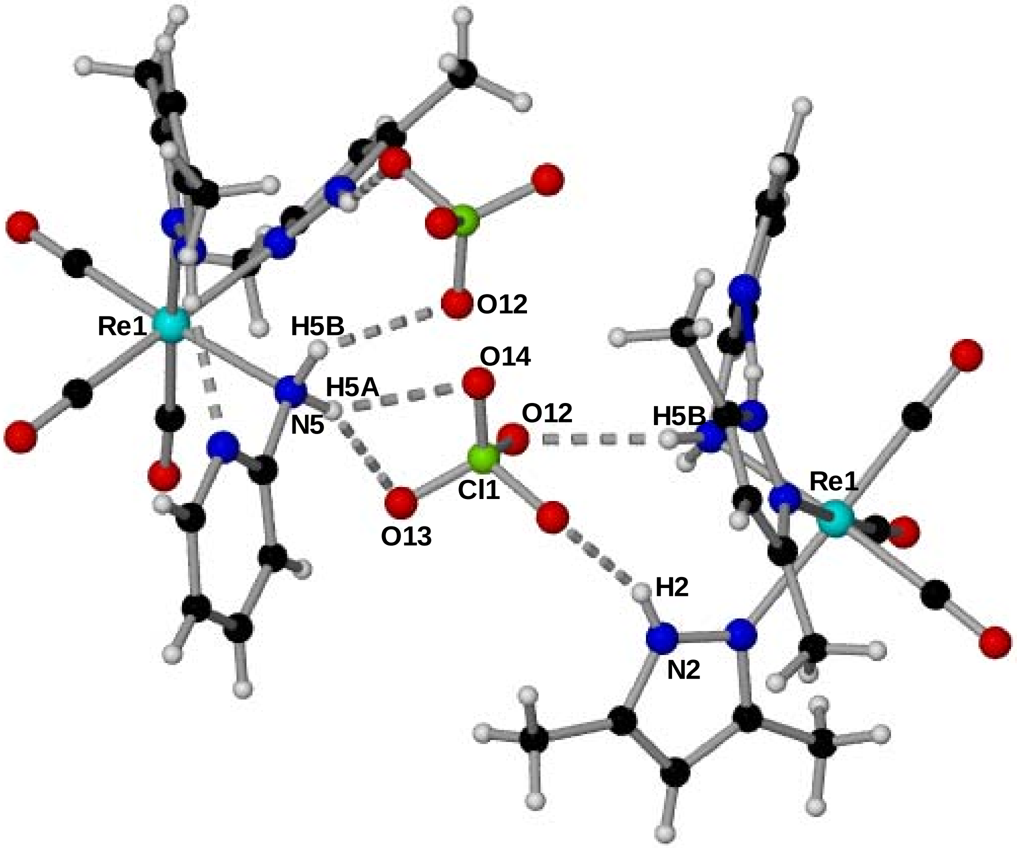


Figure S2. View of [Re(CO)$_3$(Hdmpz)$_2$(2-ampy)]·[ClO$_4$] molecular structure showing that each N-H group of a given NH$_2$ function forms hydrogen bonds with different perchlorate anions.

Table S1. Hydrogen bond lengths (Å) and angles (º) for the **1**·ClO$_4$ adduct.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(11)#1	0.79(6)	2.21(6)	2.932(8)	152(6)
N(4)-H(4)...N(6)	0.79(6)	2.14(6)	2.893(7)	160(6)
N(5)-H(5B)...O(12)#1	0.90	2.32	3.099(8)	144.8
N(5)-H(5A)...O(13)#2	0.90	2.52	3.375(9)	159.0
N(5)-H(5A)...O(14)#2	0.90	2.40	3.197(8)	147.2
N(5)-H(5A)...Cl(1)#2	0.90	2.98	3.880(5)	173.9

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 -x+1,y-1/2,-z+1/2

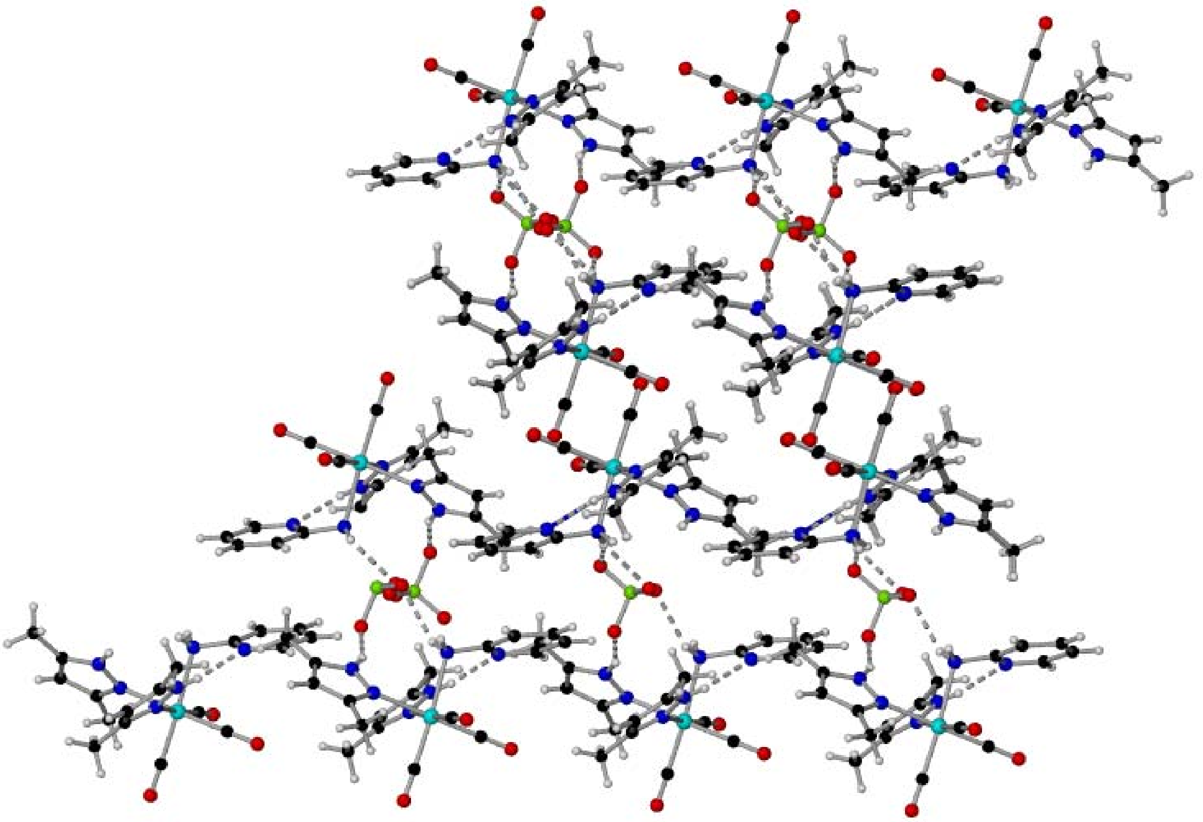


Figure S3. View of the structure of the $[Re(CO)_3(Hdmpz)_2(2\text{-ampy})]\cdot[ClO_4]$ adduct showing the packing of perchlorate anions between chains of cationic rhenium complexes.

Molecular structure of the [Re(CO)$_3$(Hdmpz)$_2$(3-ampy)]·[Br] adduct.

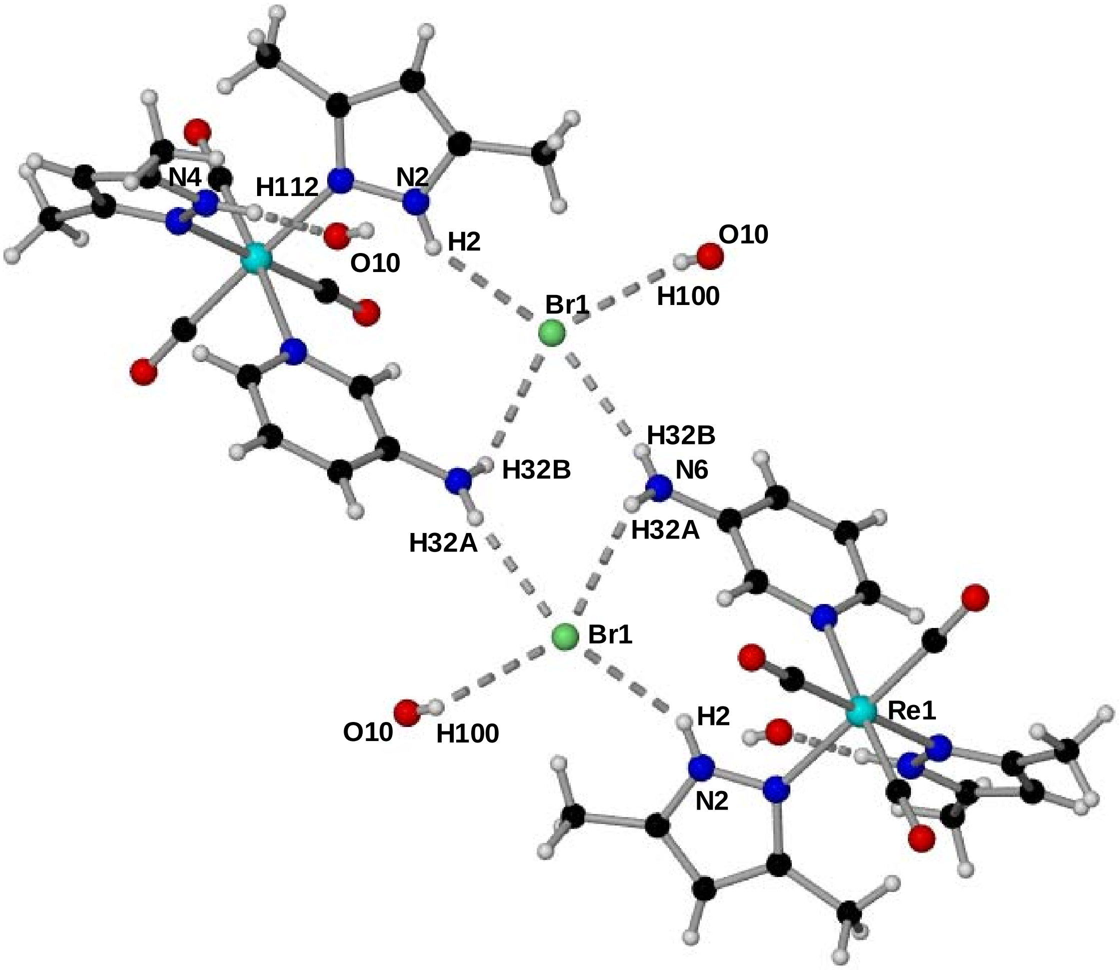


Figure S4. Molecular structure of Re(CO)$_3$(Hdmpz)$_2$(3-ampy)]·[Br] showing the dimeric nature of the adduct, which also contains water molecules.

Table S2. Hydrogen bond lengths (Å) and angles (º) for the **2**·Br adduct.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(10)-H(100)...Br(1)#1	0.58(16)	2.96(16)	3.520(9)	165(22)
N(6)-H(32A)...Br(1)#2	0.86	2.64	3.440(8)	154.9
N(6)-H(32B)...Br(1)#3	0.86	2.87	3.614(10)	145.9
N(4)-H(112)...O(10)	0.87(2)	2.00(4)	2.803(11)	153(7)
N(2)-H(2)...Br(1)#3	0.86	2.79	3.534(8)	146.1

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z+1 #2 x,y,z+1 #3 -x+2,-y+1,-z+1

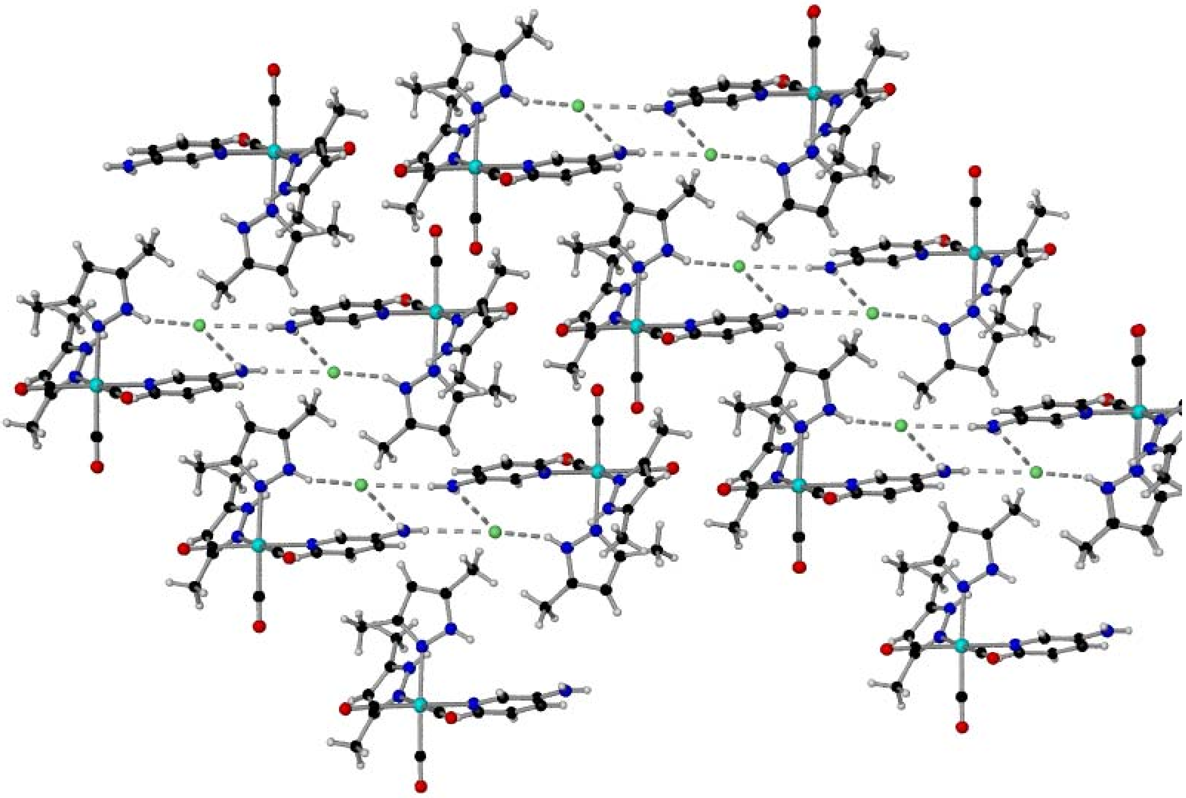


Figure S5. Extended structure of the **2**·Br adduct.

Molecular structure of the [Re(CO)$_3$(Hdmpz)$_2$(3-ampy)]·[NO$_3$] adduct.

The asymmetric unit contains two different rhenium complexes (labelled Re1 and Re2) and two different nitrate anions (the central nitrogen atoms have been labelled N13 and N14). Each nitrate anion interacts through hydrogen bonds with two cationic metallic complexes of the same type, affording two kinds of dimeric adducts (see Figure S6).

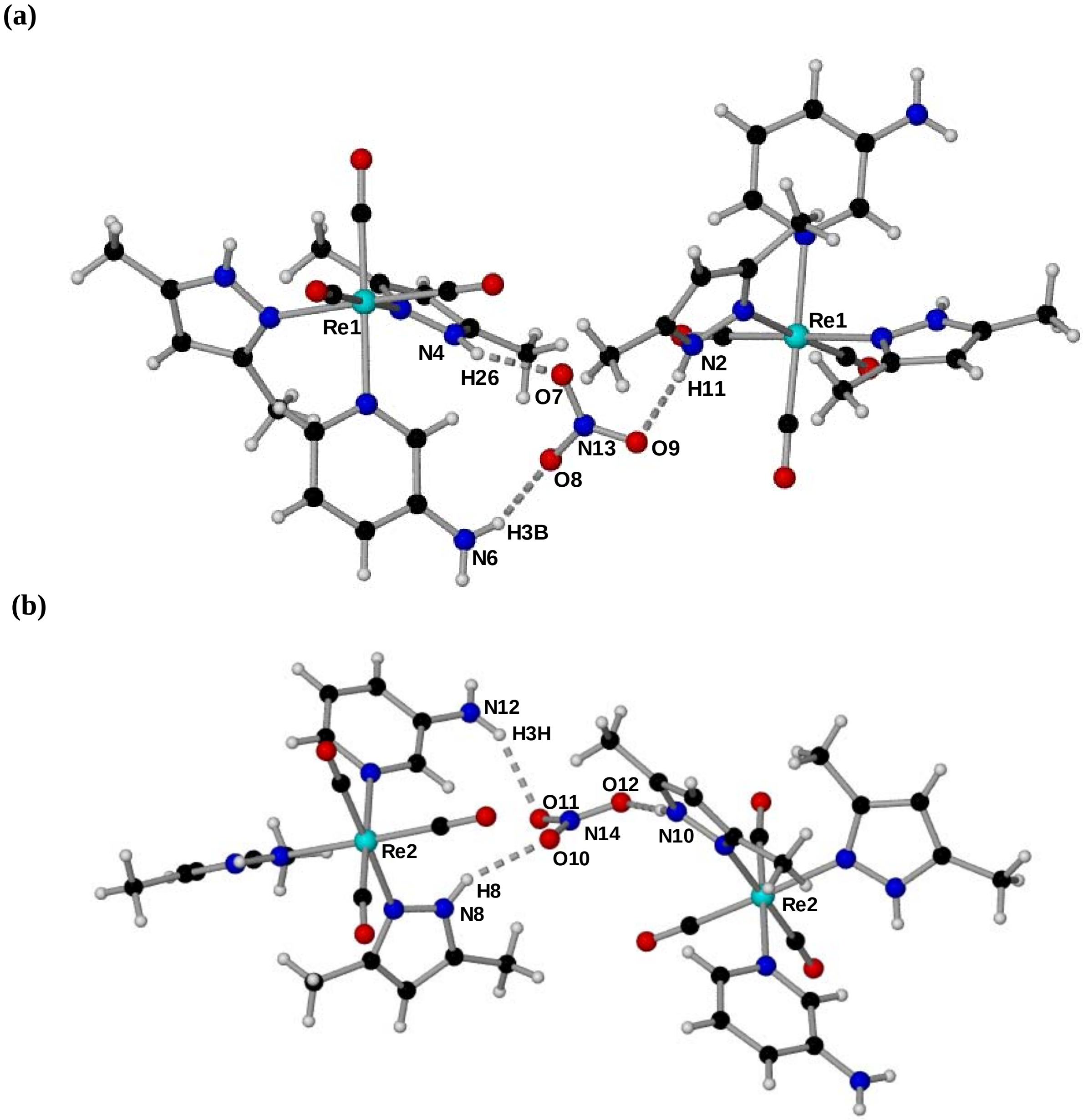


Figure S6. View of the dimers found in the molecular structure of the **2**·NO$_3$ adduct.

Table S3. Hydrogen bond lengths (Å) and angles (º) for the **2**·NO$_3$ adduct.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(12)-H(03H)...O(11)	0.86	2.19	2.98(2)	152.2
N(10)-H(035)...O(12)#2	0.86	1.97	2.832(17)	176.1
N(8)-H(008)...O(10)	0.86	2.18	2.978(13)	153.8
N(6)-H(03B)...O(8)#3	0.86	2.20	3.00(3)	154.0
N(4)-H(026)...O(7)#3	0.86	2.13	2.933(16)	154.8
N(2)-H(011)...O(9)#4	0.86	2.02	2.874(12)	172.7

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 -x+1,y+1/2,-z+3/2 #3 x-1,y-1,z

#4 -x+1,y-1/2,-z+3/2

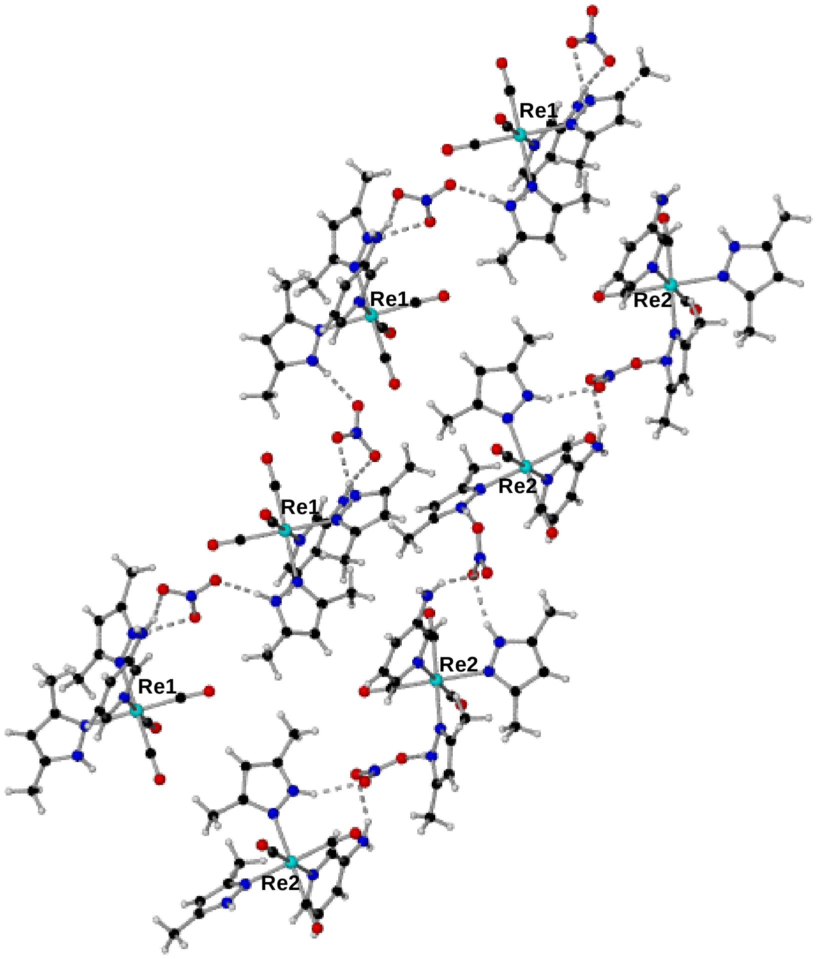


Figure S7. View of the solid state structure of the **2**·NO$_3$ adduct showing the infinite chains formed by alternating cationic complex-anion units. One of chains contains Re1 and nitrate N13, whilst the other contains Re2 and nitrate N14.

Molecular structure of the [Re(CO)$_3$(Hdmpz)$_2$(3-ampy)]·[ClO$_4$] adduct.

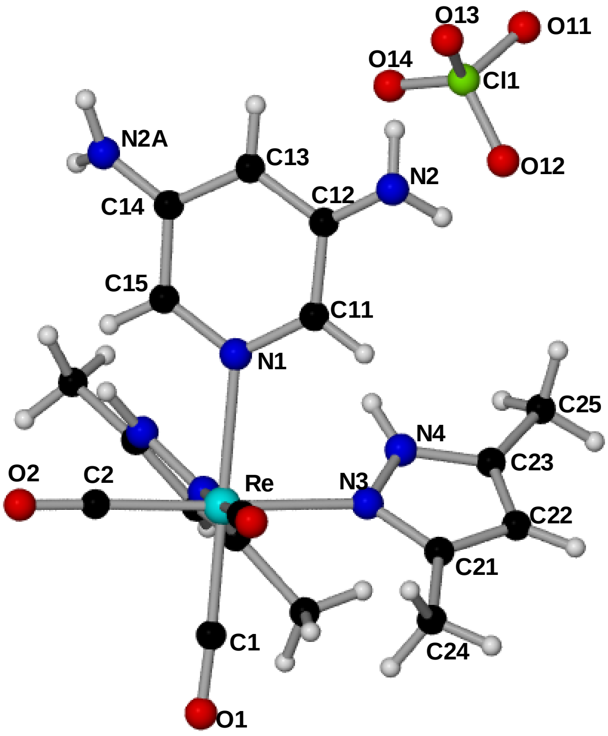


Figure S8. Molecular structure of the **2**·ClO$_4$ adduct showing the disordered NH$_2$ group. Selected crystallographic data for **2**·ClO$_4$: $C_{18}H_{24}ClN_6O_8Re$, M = 674.08, monoclinic, P-1, a = 8.653(3) Å, b = 8.977(4) Å, c = 16.972(7) Å, α = 103.004(7)°, β = 92.846(7)°, γ = 102.560(8)°, 296 K, V = 1247(8) Å^3, Z = 2. 5566 reflections measured, 3535 independent (Rint= 0.0214). R_1 = 0.0326, wR_2 = 0.0892 (all data).

Table S4. Hydrogen bond lengths (Å) and angles (°) for the **2**·ClO$_4$ adduct.

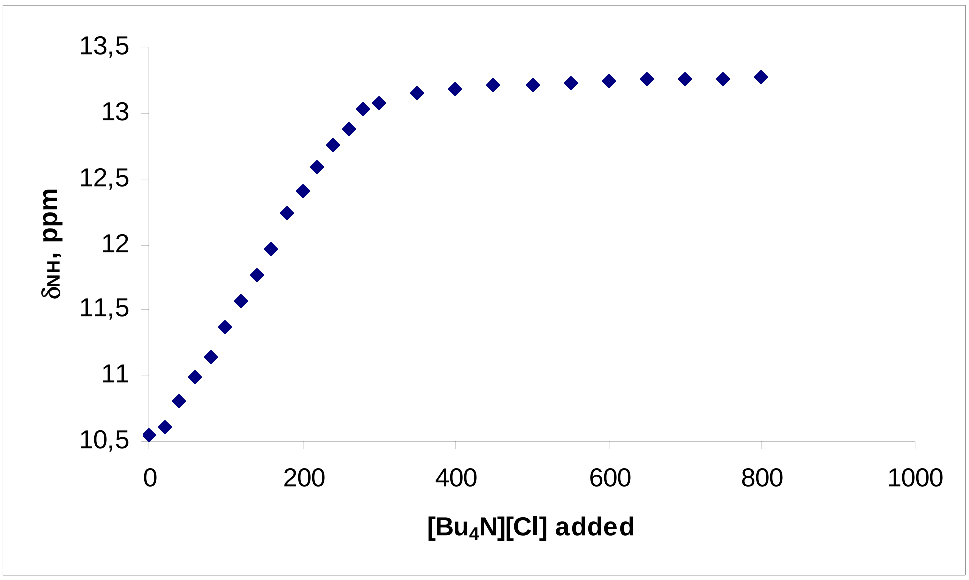
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(90)-H(90B)...N(6)	0.96	2.61	3.296(11)	128.4
N(6)-H(6)...O(12)#1	0.94(8)	2.34(8)	3.103(14)	138(6)
N(4)-H(4)...O(90)	0.86(8)	1.97(8)	2.810(11)	165(8)
N(2A)-H(2A2)...O(11)#1	0.89	2.54	3.38(2)	157.7
N(2A)-H(2A1)...Cl(1)#2	0.89	2.73	3.557(14)	155.3
N(2A)-H(2A1)...O(14)#2	0.89	2.40	3.017(18)	126.9

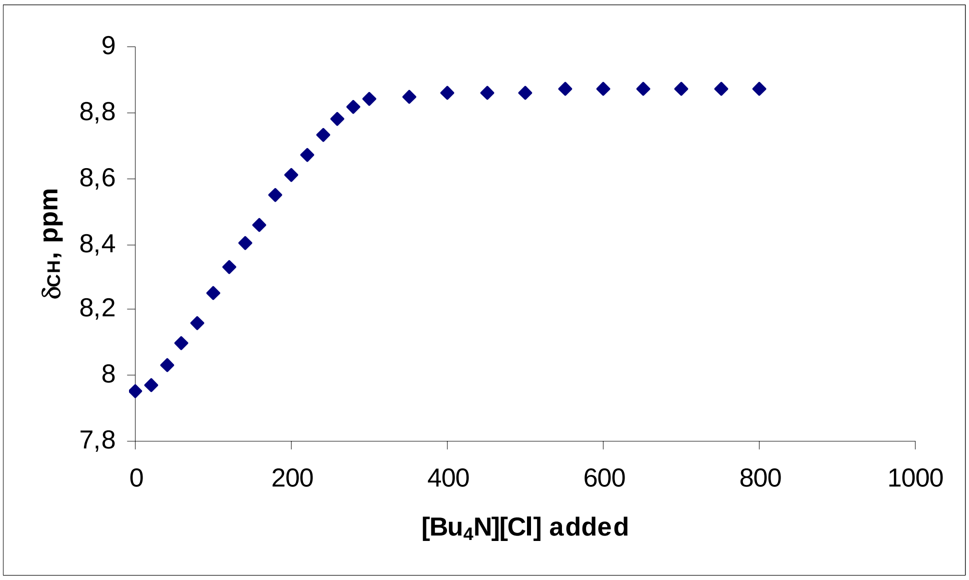
N(2A)-H(2A1)...O(11)#2	0.89	2.35	3.24(2)	173.2
N(2)-H(2B)...O(2)#3	0.89	2.22	3.097(15)	168.5
N(2)-H(2A)...O(14)	0.89	2.39	3.10(2)	136.3

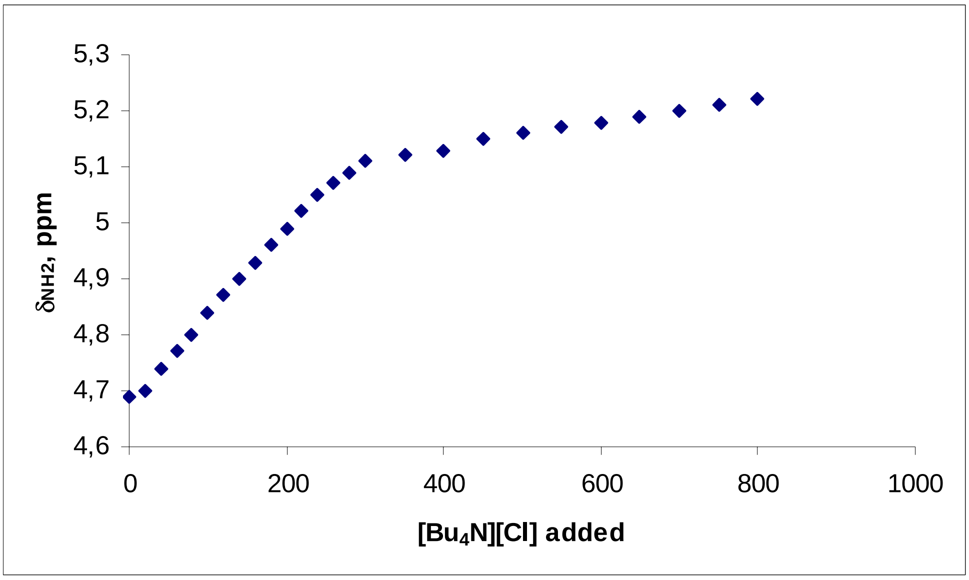
Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+1,-y+1,-z #3 x+1,y,z

^{1}H NMR titration profiles of compound [Re(CO)$_3$(Hdmpz)$_2$(3-ampy)]BAr'$_4$ (2·BAr'$_4$) in CD$_3$CN



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4,6
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1000
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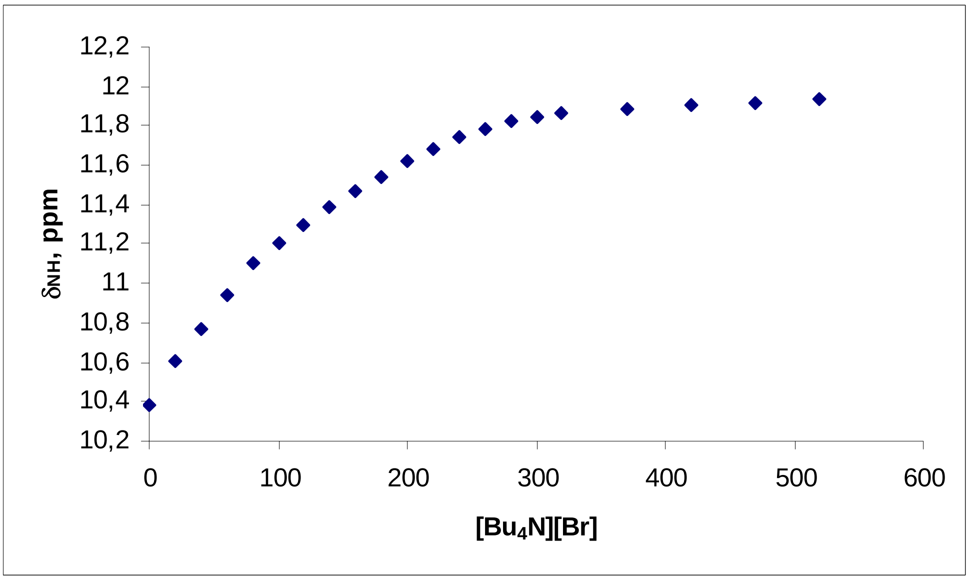
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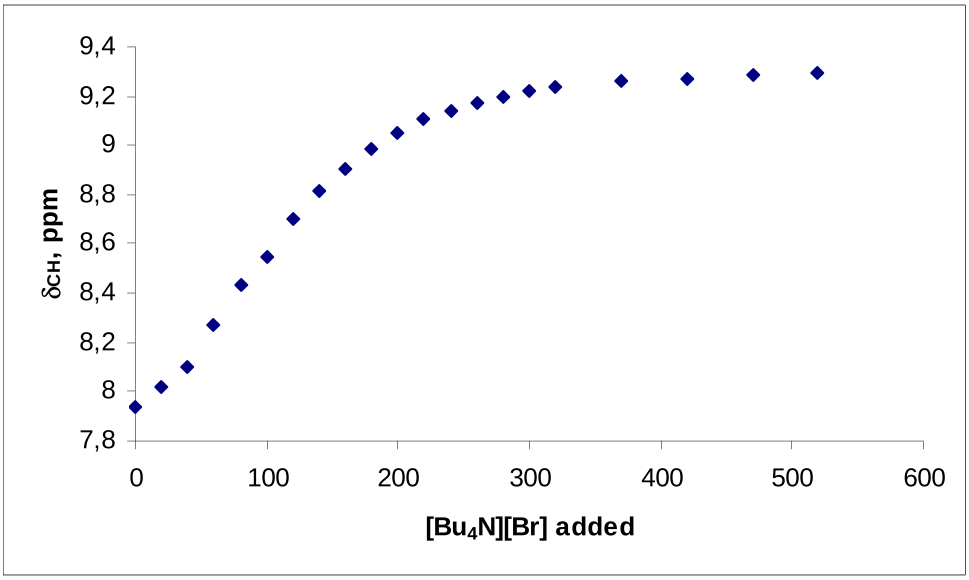
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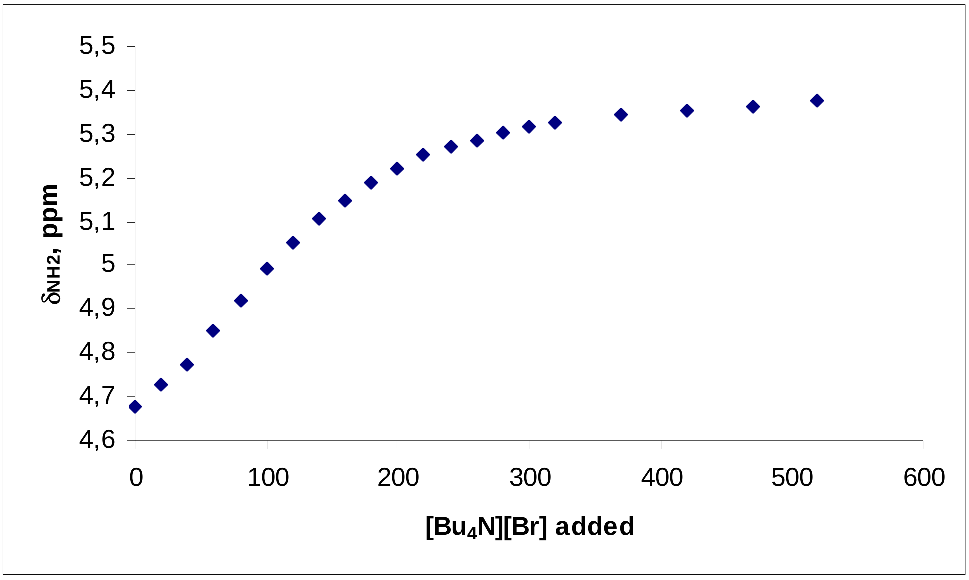
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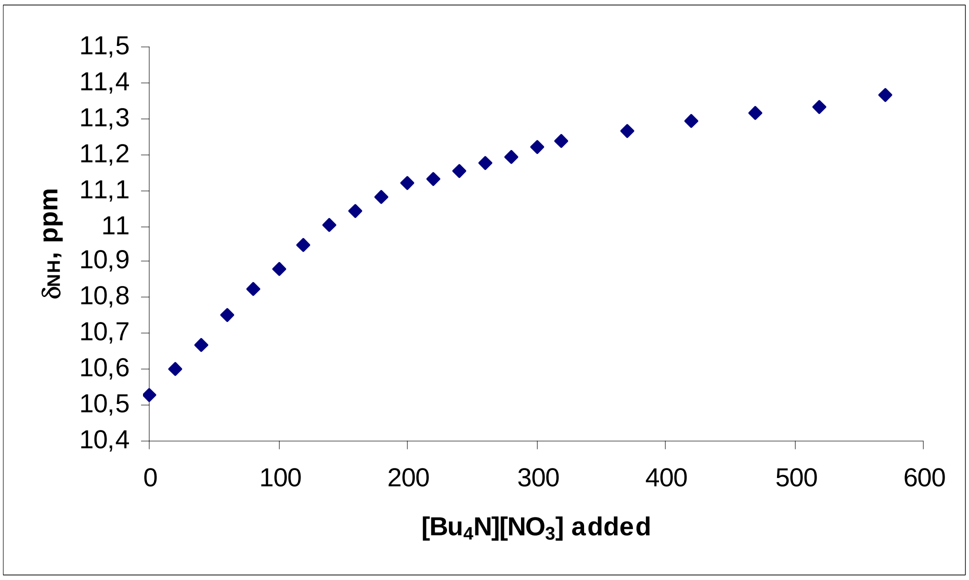
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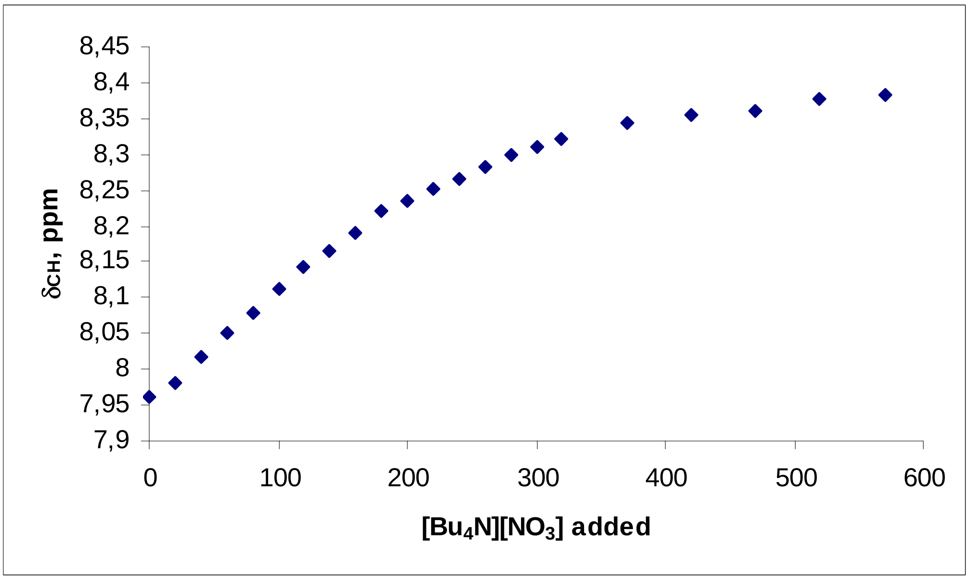
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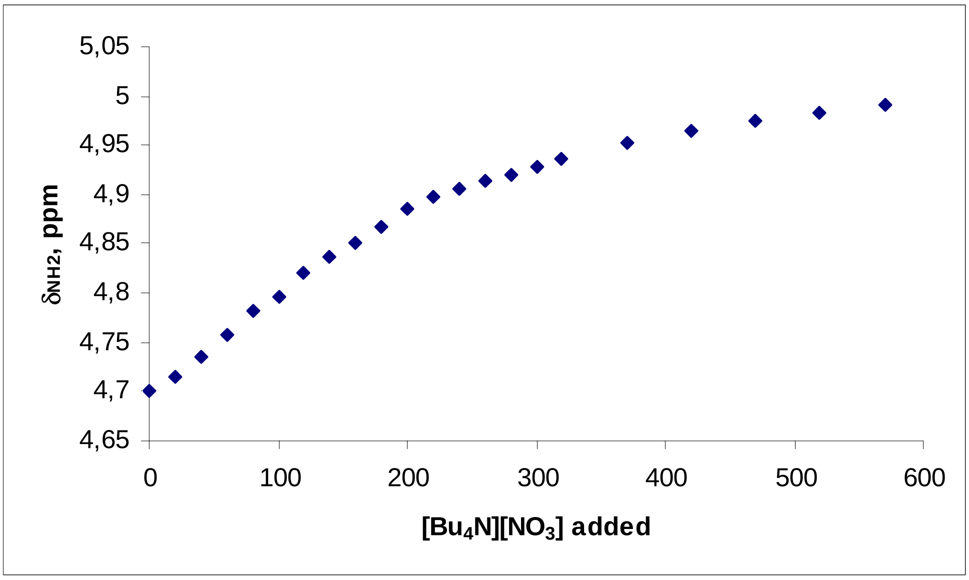

References

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