

Azide activation in the coordination sphere of Ru inside the $[PW_{11}O_{39}]^{7-}$ backbone

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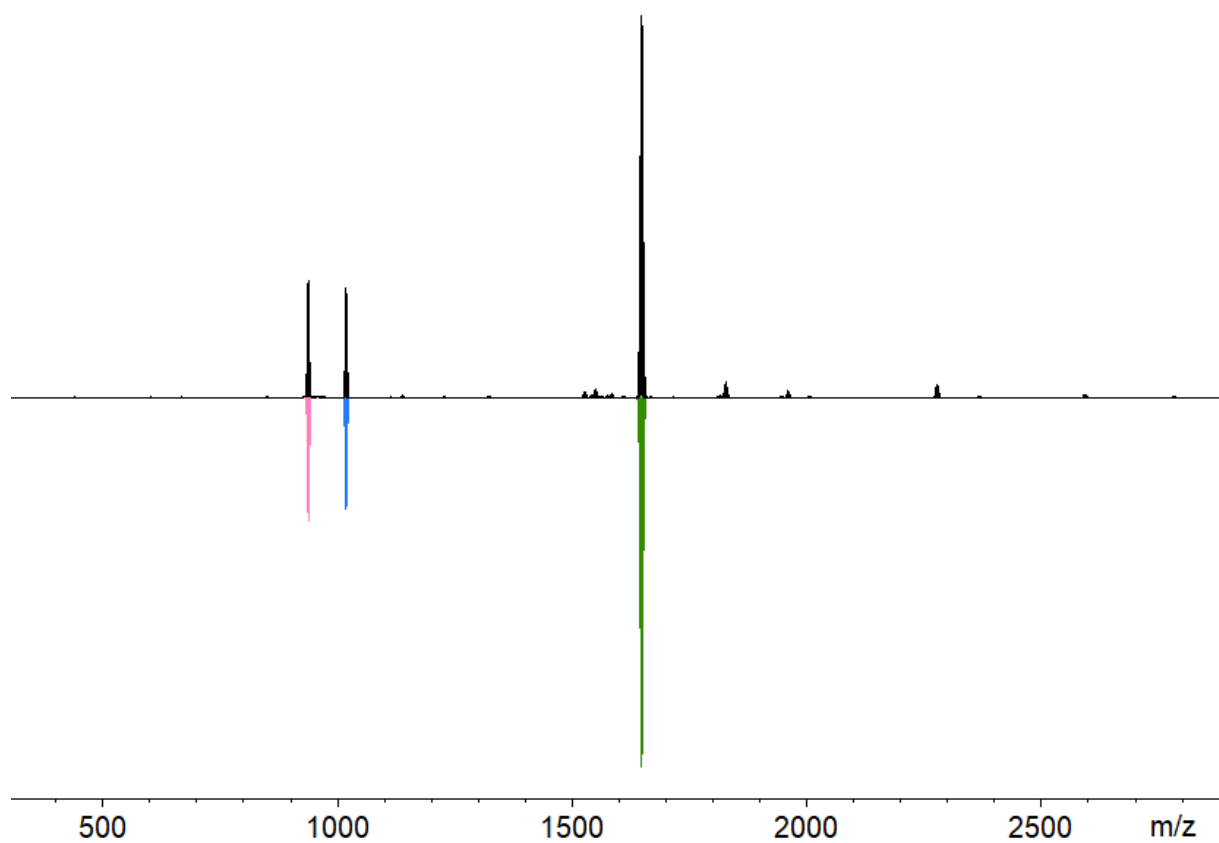


Fig. S1. Full spectrum of Ru-NO (calculated patterns have negative intensities).

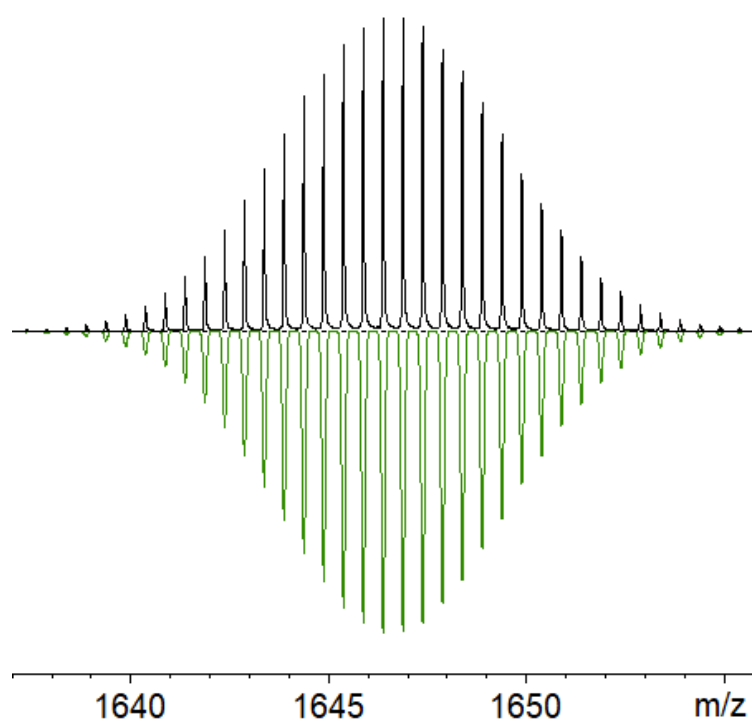


Fig. S2. Zoomed 1637-1661 m/z region of spectrum of Ru-NO (calculated isotopic patterns have negative intensities).

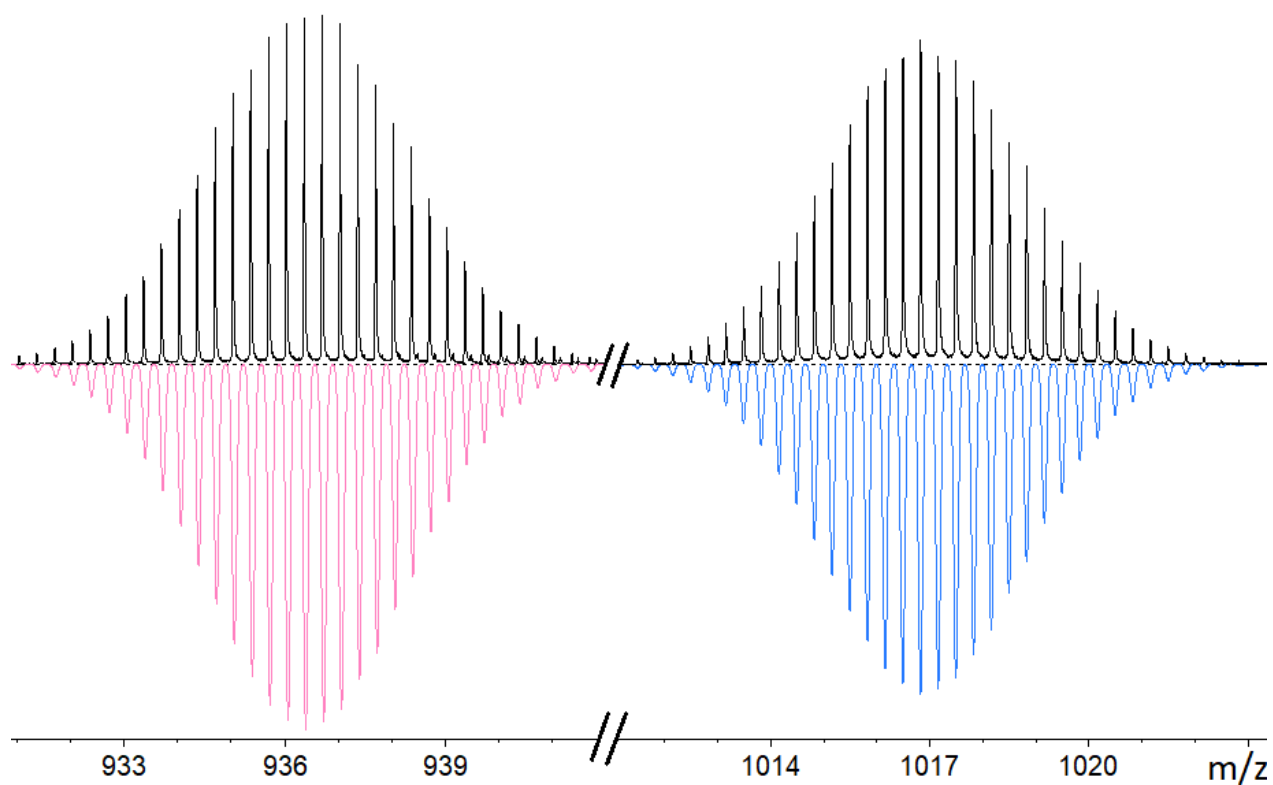


Fig. S3. Zoomed 931-942 m/z and 1011-1023 m/z regions of spectrum of **Ru-NO** (calculated isotopic patterns have negative intensities).

Table. S1. Peak assignment for ESI-MS spectrum of **Ru-NO**

anion	exp (m/z)	calc (m/z)
$\text{H}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{Ru}(\text{NO})\}]^{4-}$	936.4	936.4
$\text{Bu}_4\text{N}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{Ru}(\text{NO})\}]^{4-}$	1016.8	1016.8
$2\text{Bu}_4\text{N}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{Ru}(\text{NO})\}]^{4-}$	1646.6	1646.6

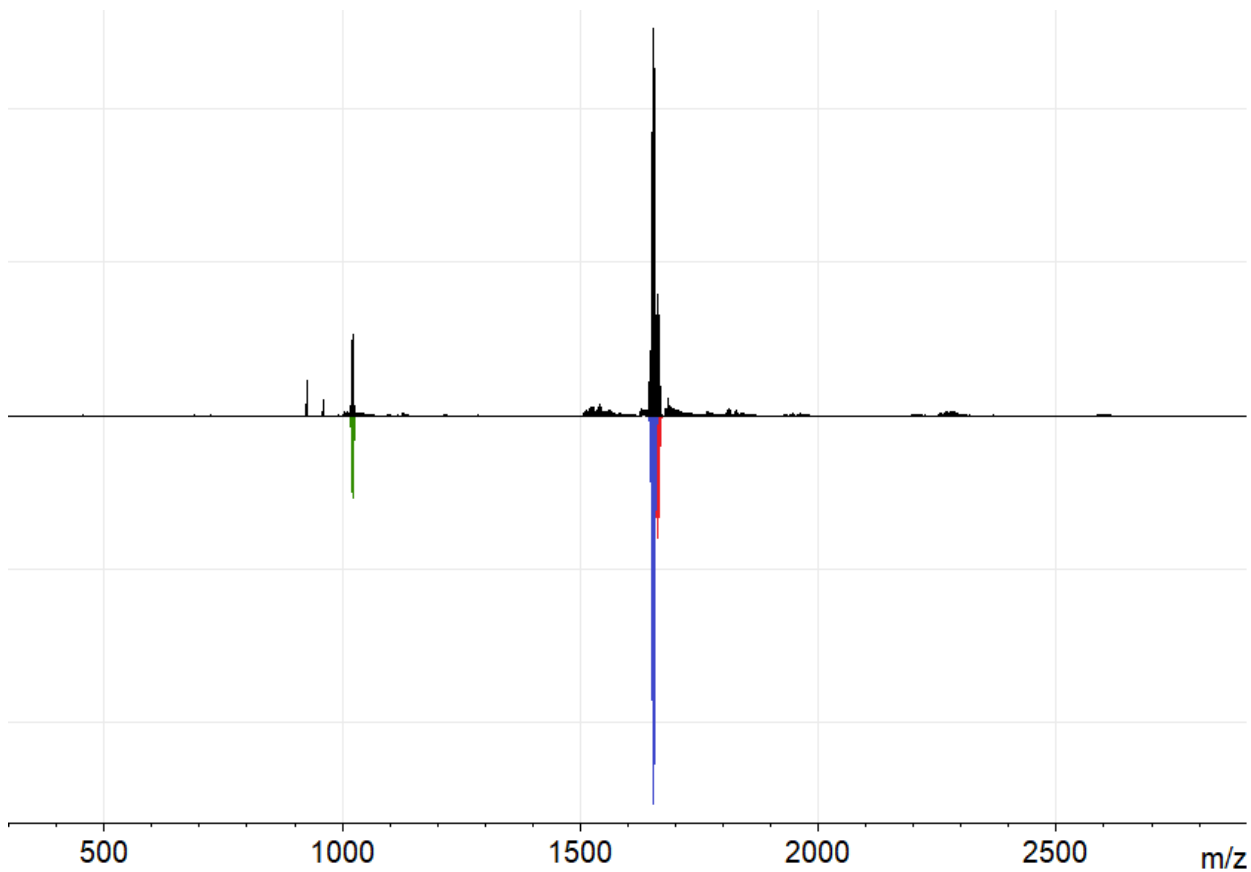


Fig. S4. Full spectrum of Ru-CH₃CN (calculated patterns have negative intensities).

Table. S2. Peak assignment for ESI-MS spectrum of Ru-CH₃CN

anion	exp (m/z)	calc (m/z)
Bu ₄ N ⁺ + [PW ₁₁ O ₃₉ {Ru(CH ₃ CN)}] ⁴⁻	1020.6	1020.6
2Bu ₄ N ⁺ + [PW ₁₁ O ₃₉ {Ru(CH ₃ CN)}] ⁴⁻	1652.1	1652.1
2Bu ₄ N ⁺ + [PW ₁₁ O ₃₉ {Ru(CH ₃ CN)}] ⁴⁻ + H ₂ O	1661.1	1661.1

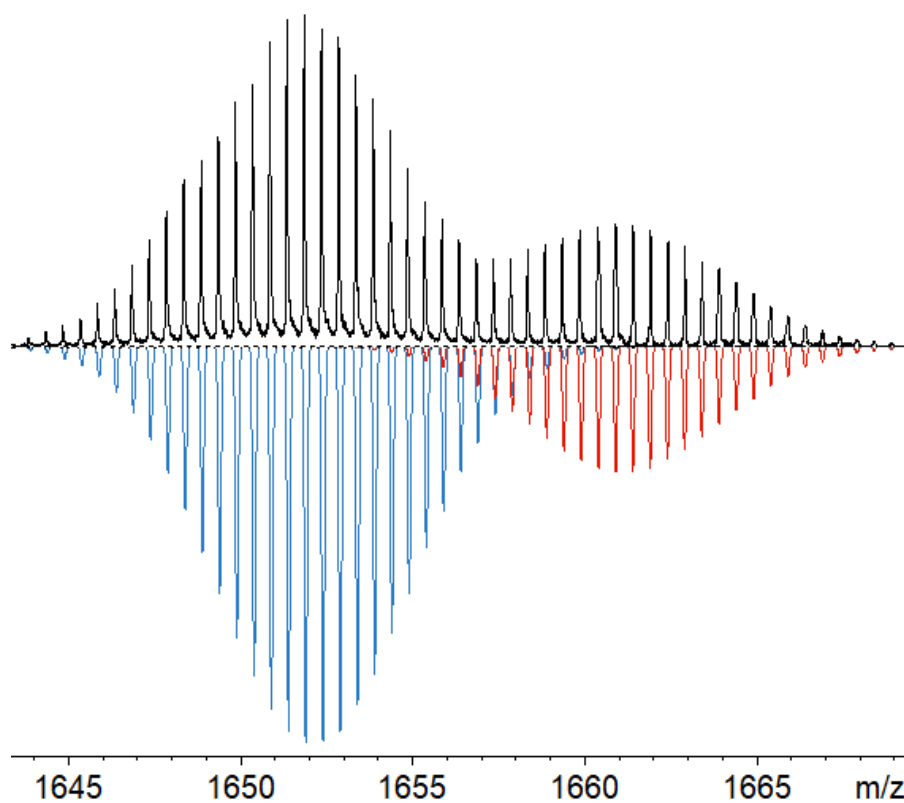


Fig. S5. Zoomed 1643-1670 m/z region of spectrum of Ru-CH₃CN (calculated isotopic patterns have negative intensities).

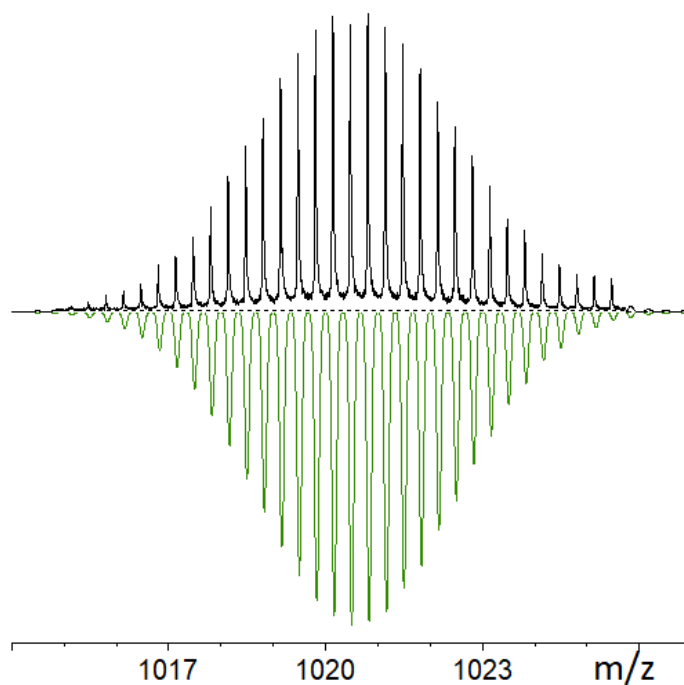


Fig. S6. Zoomed 1014-1027 m/z region of spectrum of Ru-CH₃CN (calculated isotopic patterns have negative intensities).

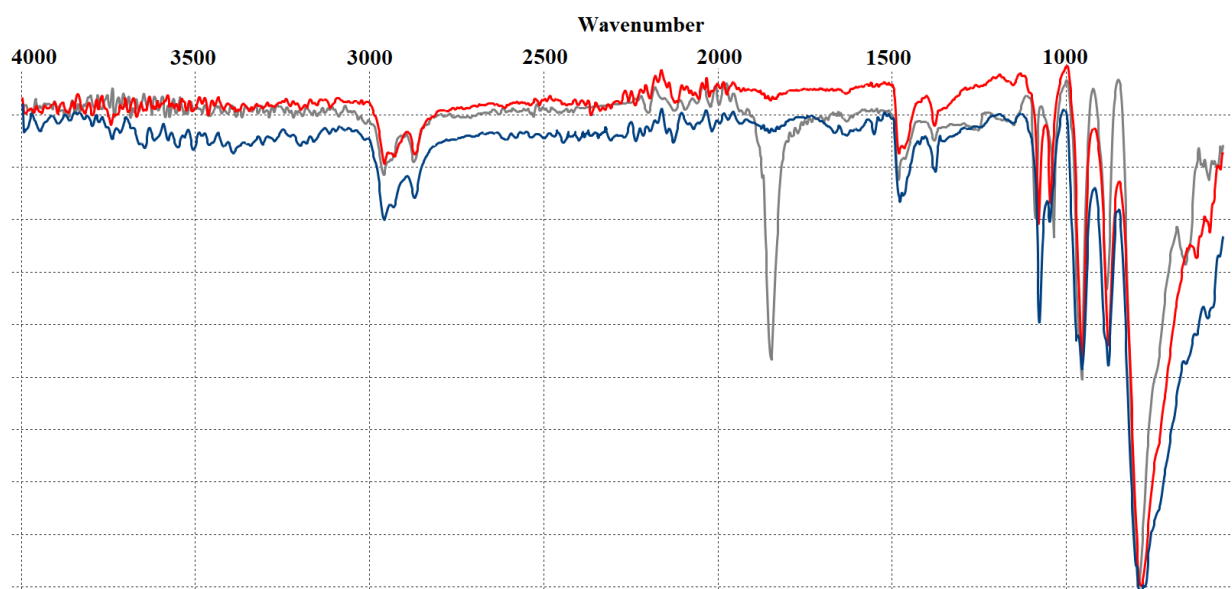


Fig. S7. The FT-IR of Ru-NO (gray), Ru-CH₃CN (red) and Ru-Hc + Ru-N₃ (blue).

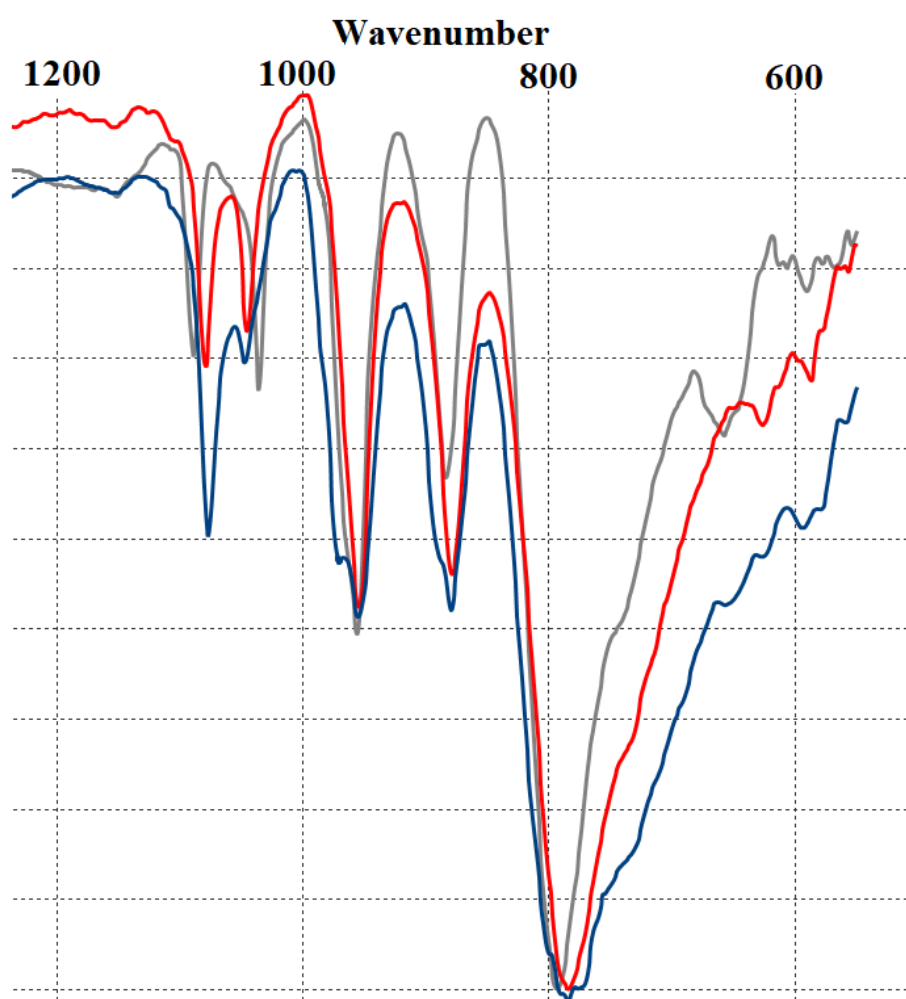


Fig. S8. Zoomed 1200-550 cm⁻¹ region of IR spectra.

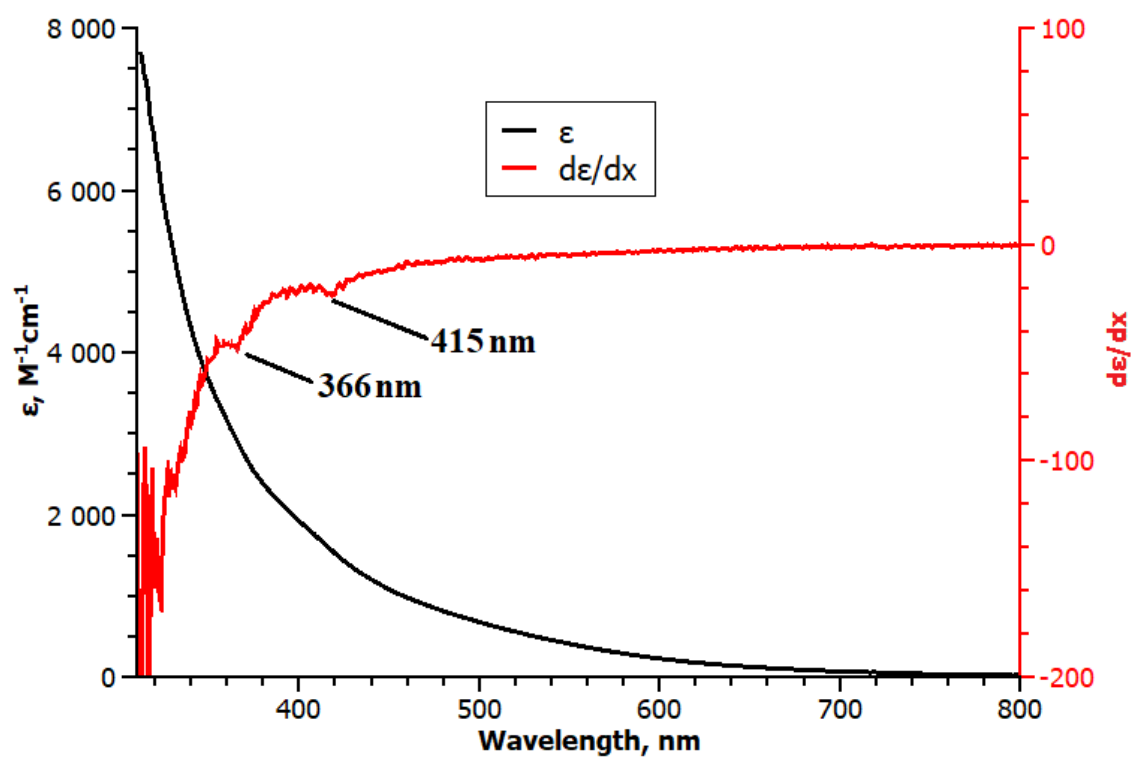


Fig. S9. Spectrum of Ru-Hc + Ru-N₃ (black) and 1st derivative (red).

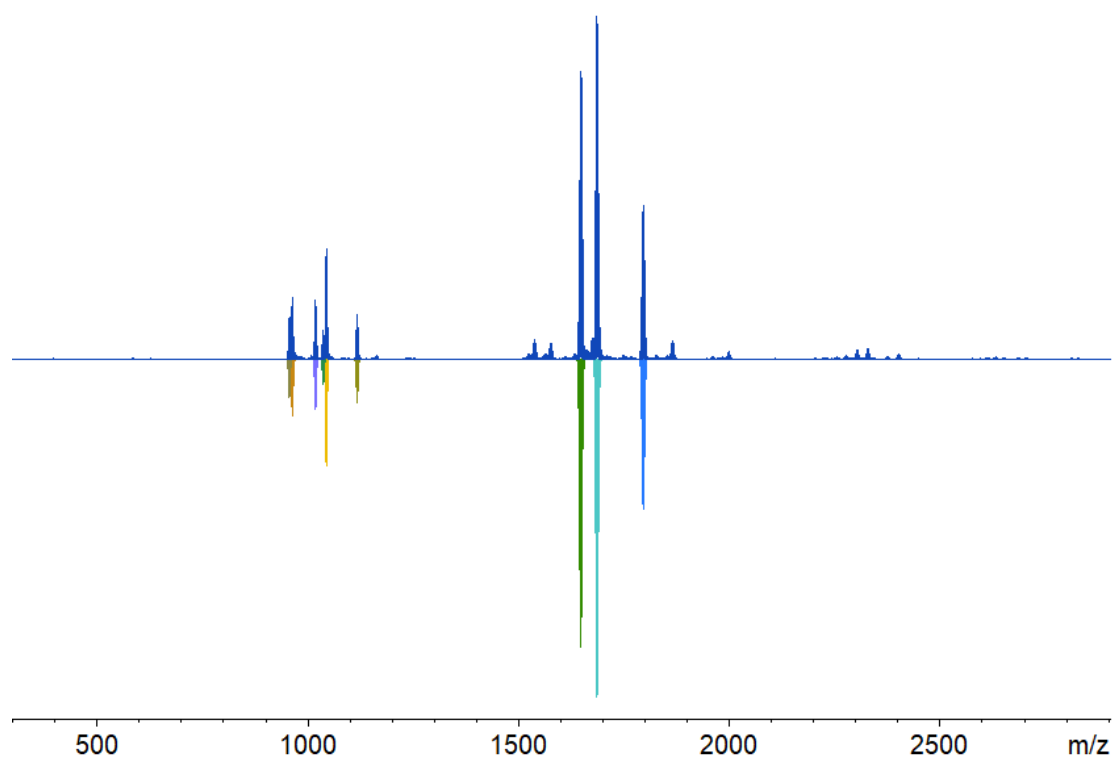


Fig. S10. Full spectrum of Ru-N_3 and $\text{Ru-CH}_3\text{CN}$ (calculated patterns have negative intensities).

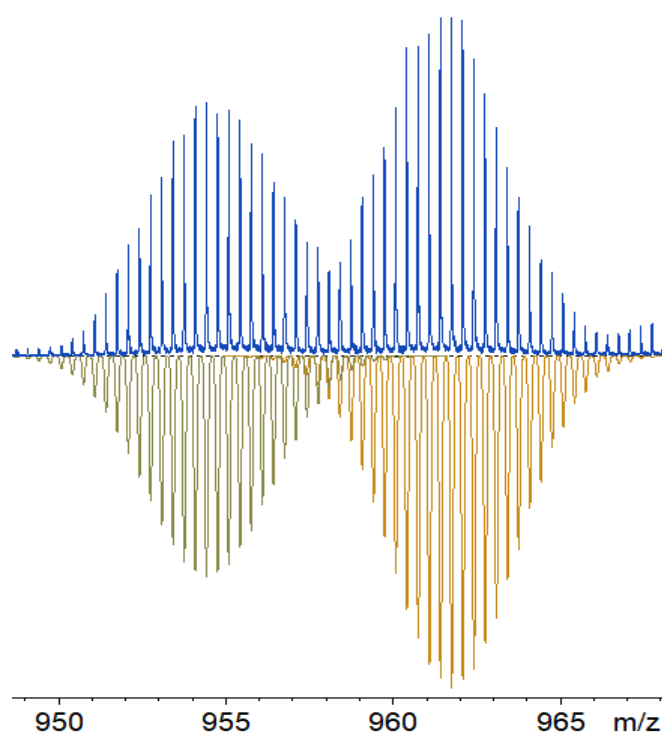


Fig. S11. Zoomed 949-968 m/z region of spectrum of Ru-N_3 and $\text{Ru-CH}_3\text{CN}$ (calculated isotopic patterns have negative intensities).

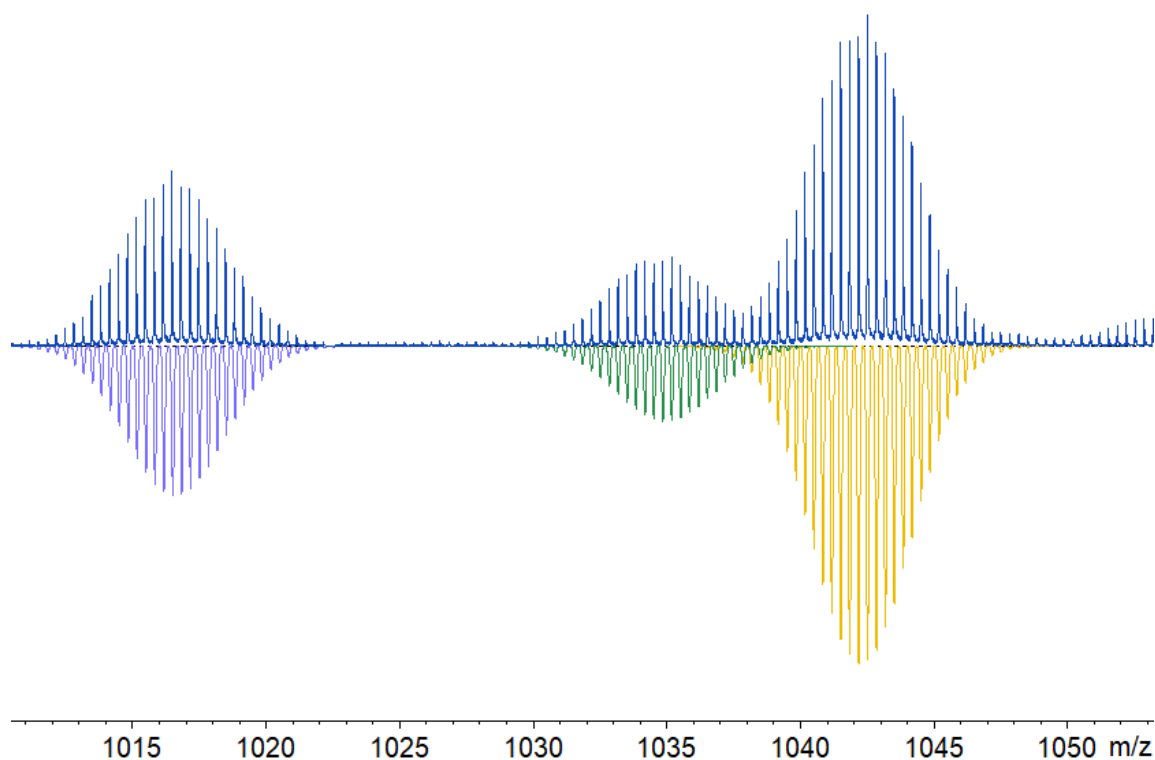


Fig. S12. Zoomed 1011-1053m/z region of spectrum of Ru-N_3 and $\text{Ru-CH}_3\text{CN}$ (calculated isotopic patterns have negative intensities).

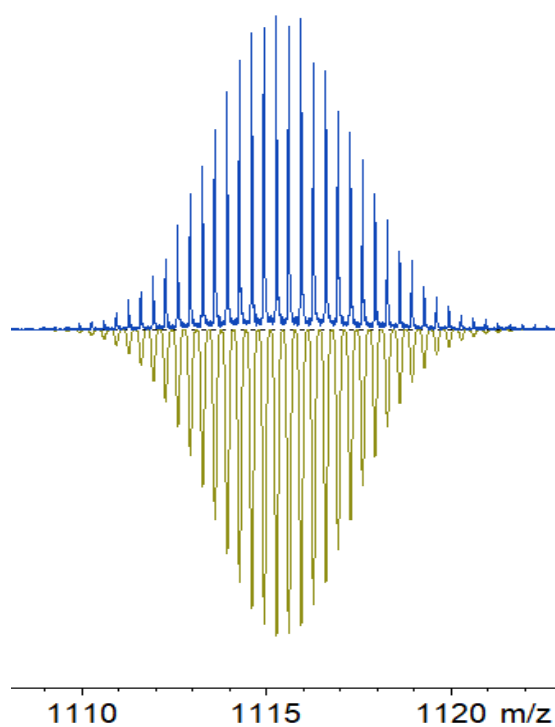


Fig. S13. Zoomed 1108-1123 m/z region of spectrum of Ru-N_3 and $\text{Ru-CH}_3\text{CN}$ (calculated isotopic patterns have negative intensities).

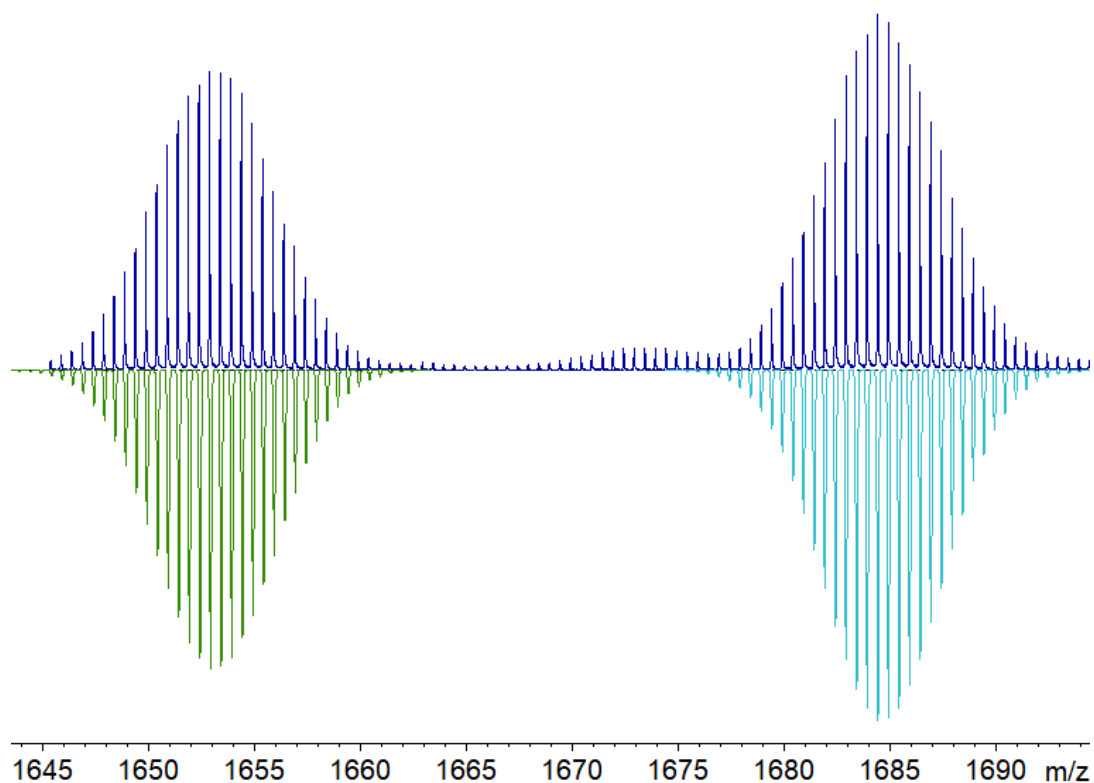


Fig. S14. Zoomed 1644-1695 m/z region of spectrum of Ru-N_3 and $\text{Ru-CH}_3\text{CN}$ (calculated isotopic patterns have negative intensities).

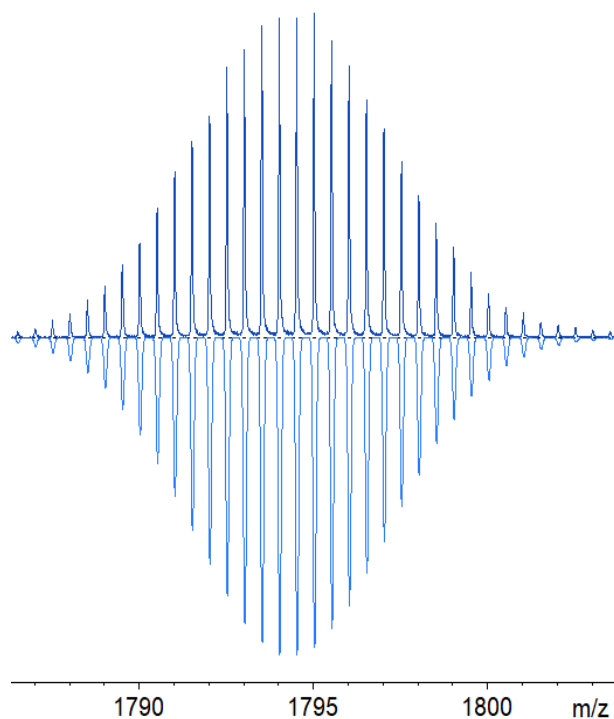


Fig. S15. Zoomed 1786-1804 m/z region of spectrum of Ru-N_3 and $\text{Ru-CH}_3\text{CN}$ (calculated isotopic patterns have negative intensities).

Table. S3. Peak assignment for ESI-MS spectrum of Ru-N₃ and Ru-CH₃CN

anion	exp (m/z)	calc (m/z)
$2\text{H}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_3\}]^{5-} + \text{CH}_3\text{CN}$	954.5	954.5
$\text{Na}^+ + \text{H}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_3\}]^{5-} + \text{CH}_3\text{CN}$	961.8	961.8
$\text{Bu}_4\text{N}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{Ru}(\text{CH}_3\text{CN})\}]^{4-}$	1020.6	1020.6
$\text{Bu}_4\text{N}^+ + \text{H}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_3\}]^{5-} + \text{CH}_3\text{CN}$	1034.9	1034.9
$\text{Bu}_4\text{N}^+ + \text{Na}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_3\}]^{5-} + \text{CH}_3\text{CN}$	1042.3	1042.3
$2\text{Bu}_4\text{N}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_3\}]^{5-} + \text{CH}_3\text{CN}$	1115.4	1115.4
$2\text{Bu}_4\text{N}^+ + \text{H}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_3\}]^{5-}$	1653.1	1653.1
$2\text{Bu}_4\text{N}^+ + \text{Na}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_3\}]^{5-} + \text{CH}_3\text{CN}$	1684.6	1684.6
$3\text{Bu}_4\text{N}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_3\}]^{5-} + \text{CH}_3\text{CN}$	1794.4	1794.4

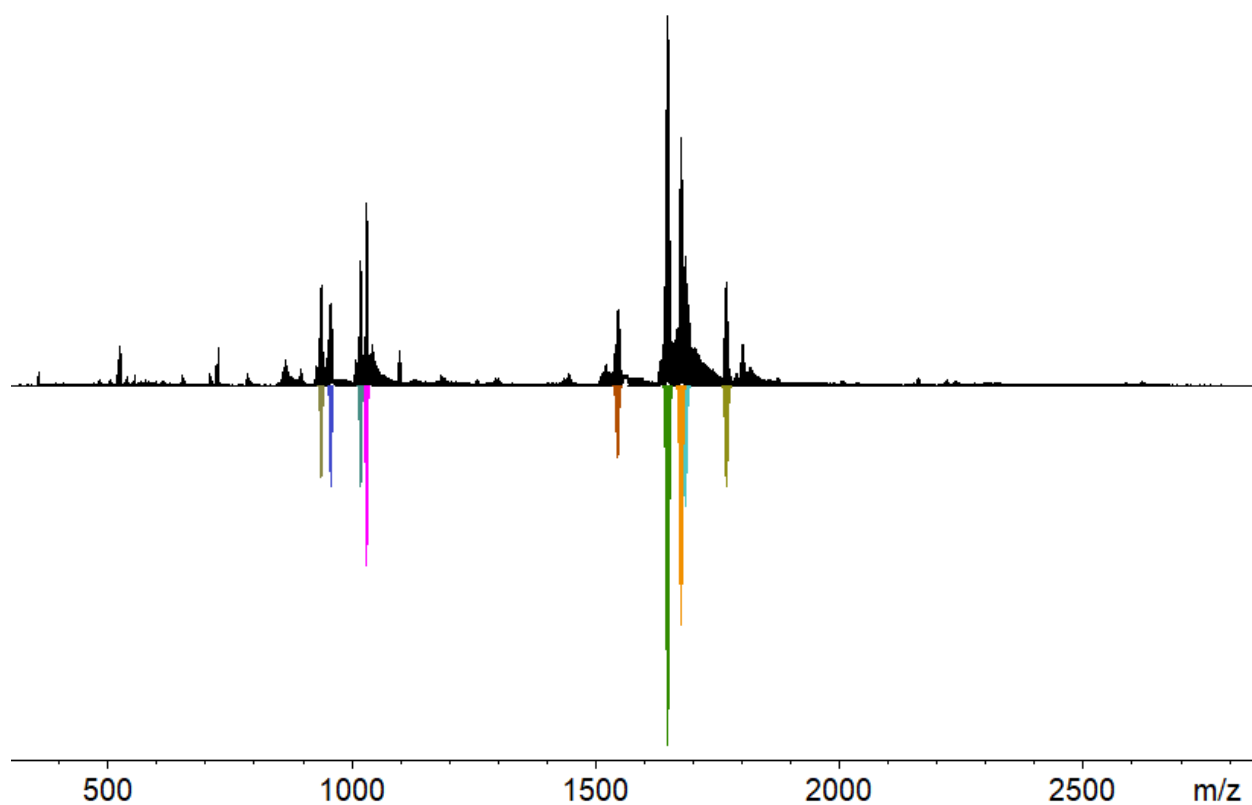


Fig.S16. Full spectrum of Ru-N₃ and Ru-Hc (calculated patterns have negative intensities).

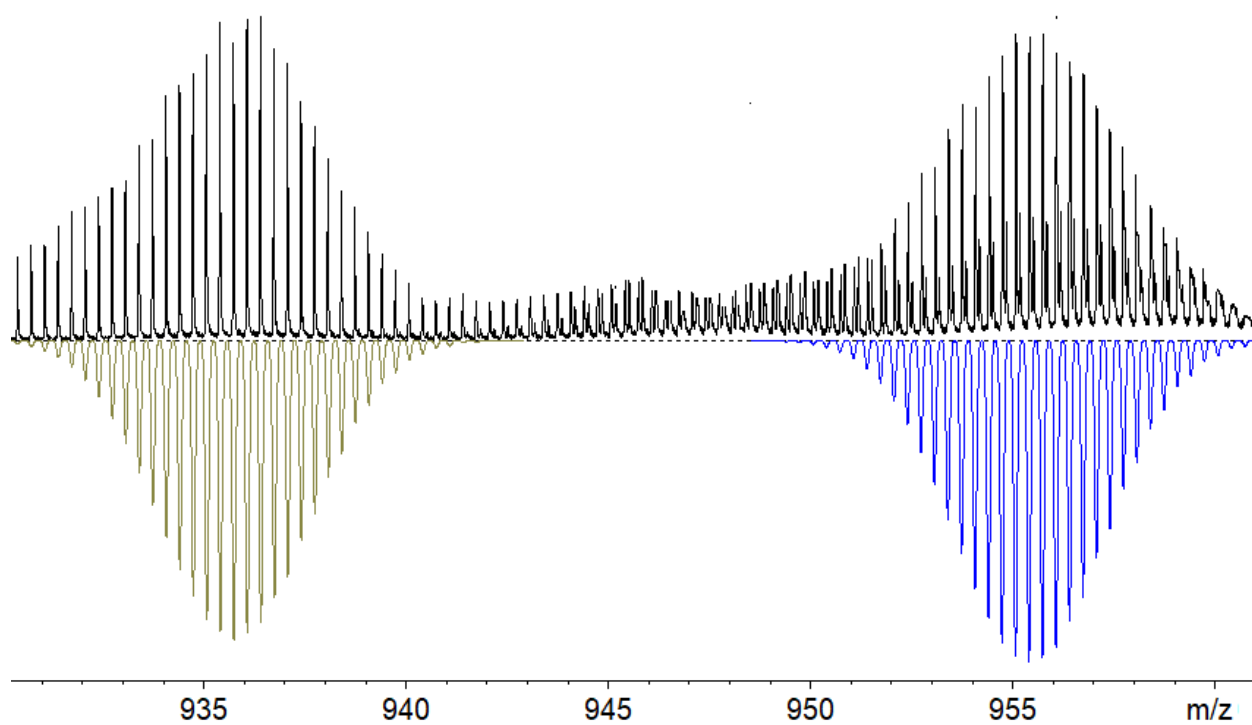


Fig. S17. Zoomed 930-961 m/z region of spectrum of Ru-N₃ and Ru-Hc (calculated isotopic patterns have negative intensities).

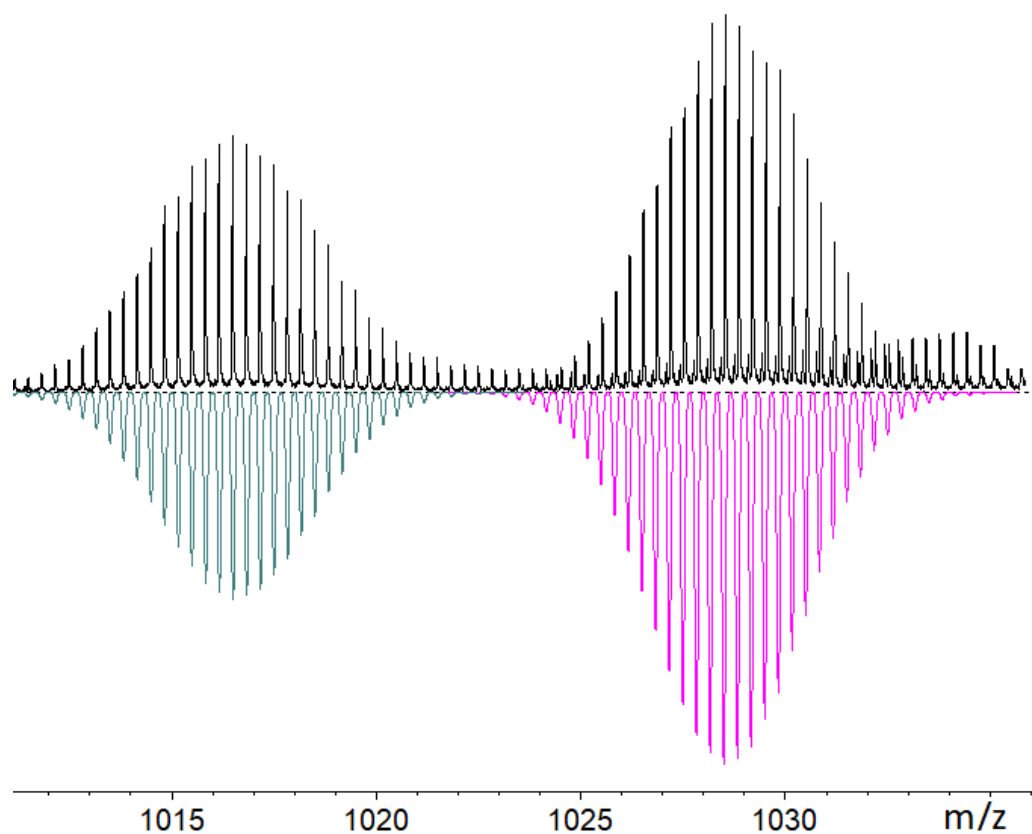


Fig. S18. Zoomed 1011-1036 m/z region of spectrum of Ru-N_3 and Ru-Hc (calculated isotopic patterns have negative intensities).

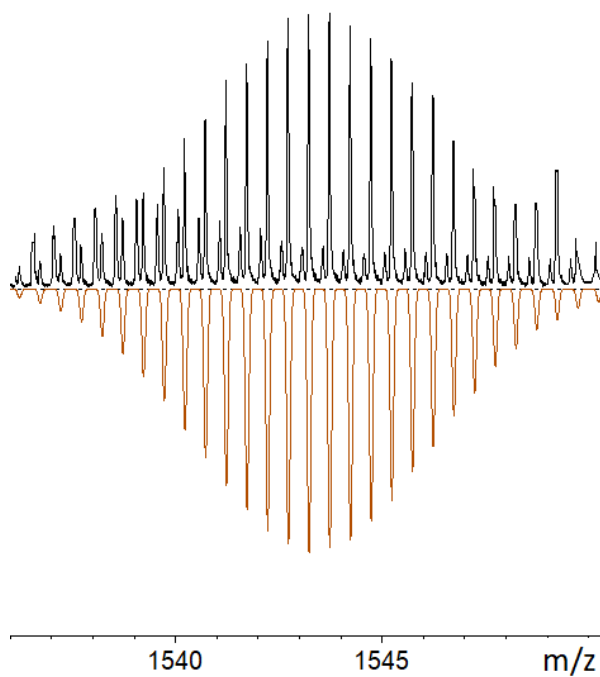


Fig. S19. Zoomed 1536-1550 m/z region of spectrum of Ru-N_3 and Ru-Hc (calculated isotopic patterns have negative intensities).

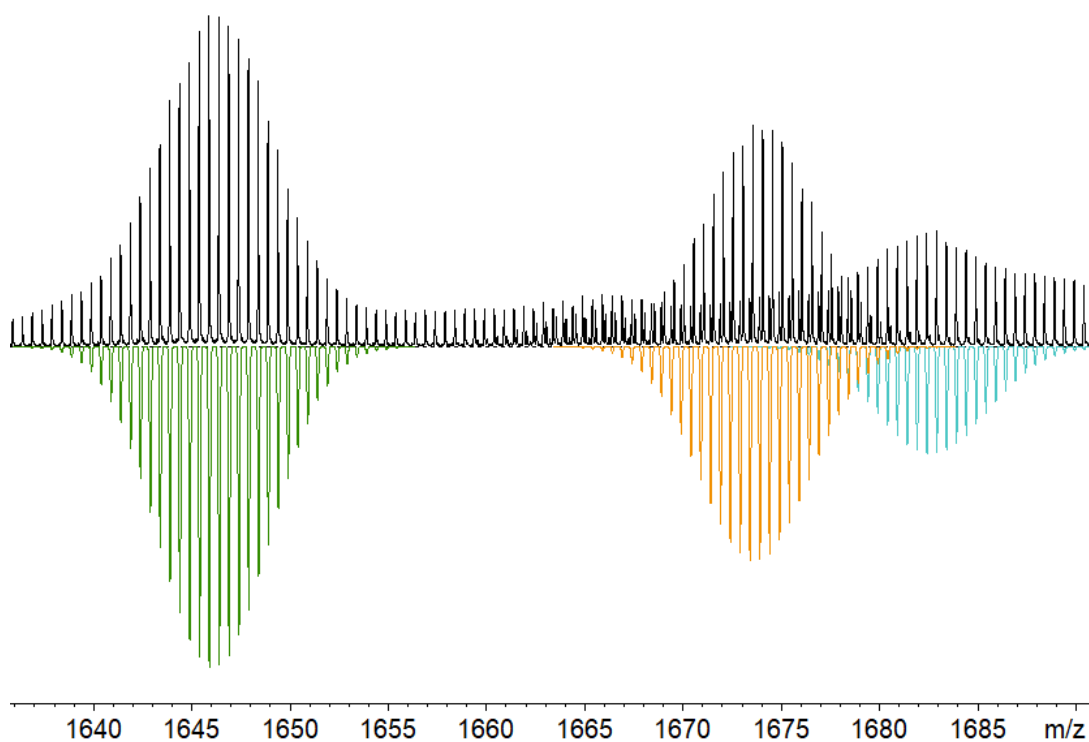


Fig. S20. Zoomed 1636-1691 m/z region of spectrum of Ru-N_3 and Ru-Hc (calculated isotopic patterns have negative intensities).

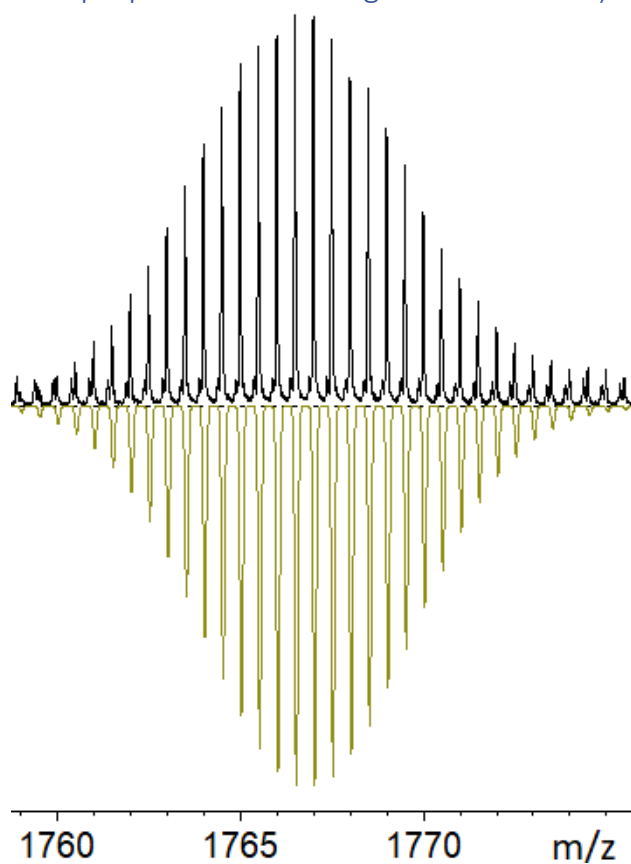


Fig. S21. Zoomed 1759-1776 m/z region of spectrum of Ru-N_3 and Ru-Hc (calculated isotopic patterns have negative intensities).

Table. S4. Peak assignment for ESI-MS spectrum of Ru-N₃ and Ru-Hc

anion	exp (m/z)	calc (m/z)
$2\text{H}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_2\}]^{5-}$	935.8	935.8
$2\text{Na}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_3\}]^{5-}$	955.4	955.4
$\text{Bu}_4\text{N}^+ + \text{H}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_2\}]^{5-}$	1016.6	1016.6
$\text{Bu}_4\text{N}^+ + \text{Na}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_3\}]^{5-}$	1028.6	1028.6
$\text{Bu}_4\text{N}^+ + \text{Na}^+ + \text{H}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_3\}]^{5-}$	1543.4	1543.4
$2\text{Bu}_4\text{N}^+ + \text{H}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_2\}]^{5-}$	1646.1	1646.1
$2\text{Bu}_4\text{N}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{Ru}(\text{Hc})\}]^{4-}$	1673.6	1673.6
$2\text{Bu}_4\text{N}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{Ru}(\text{Hc})\}]^{4-} + \text{H}_2\text{O}$	1682.6	1682.6
$3\text{Bu}_4\text{N}^+ + [\text{PW}_{11}\text{O}_{39}\{\text{RuN}_2\}]^{5-}$	1766.8	1766.8

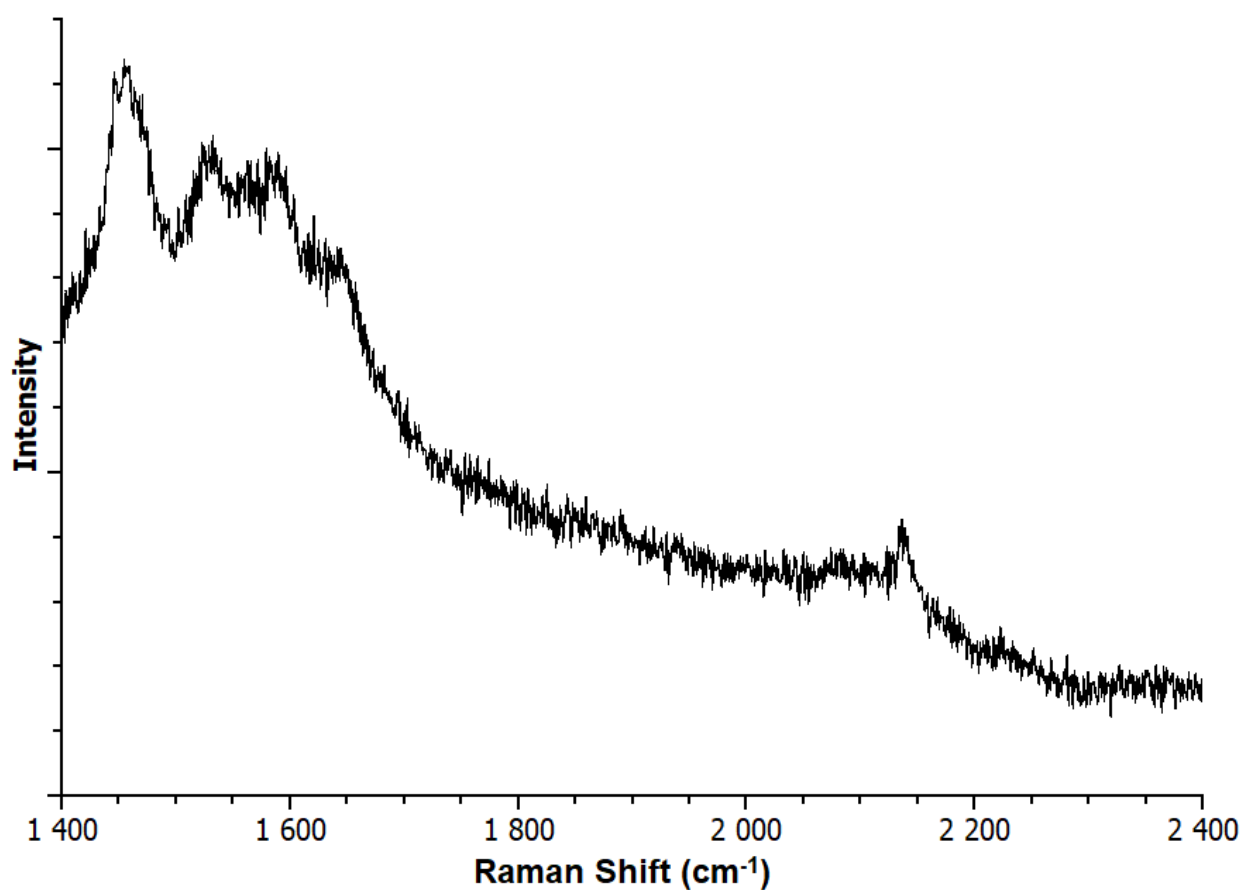


Fig. S22. The Raman spectrum of the solid mixture isolated after the Reaction of Ru-CH₃CN with NaN₃.

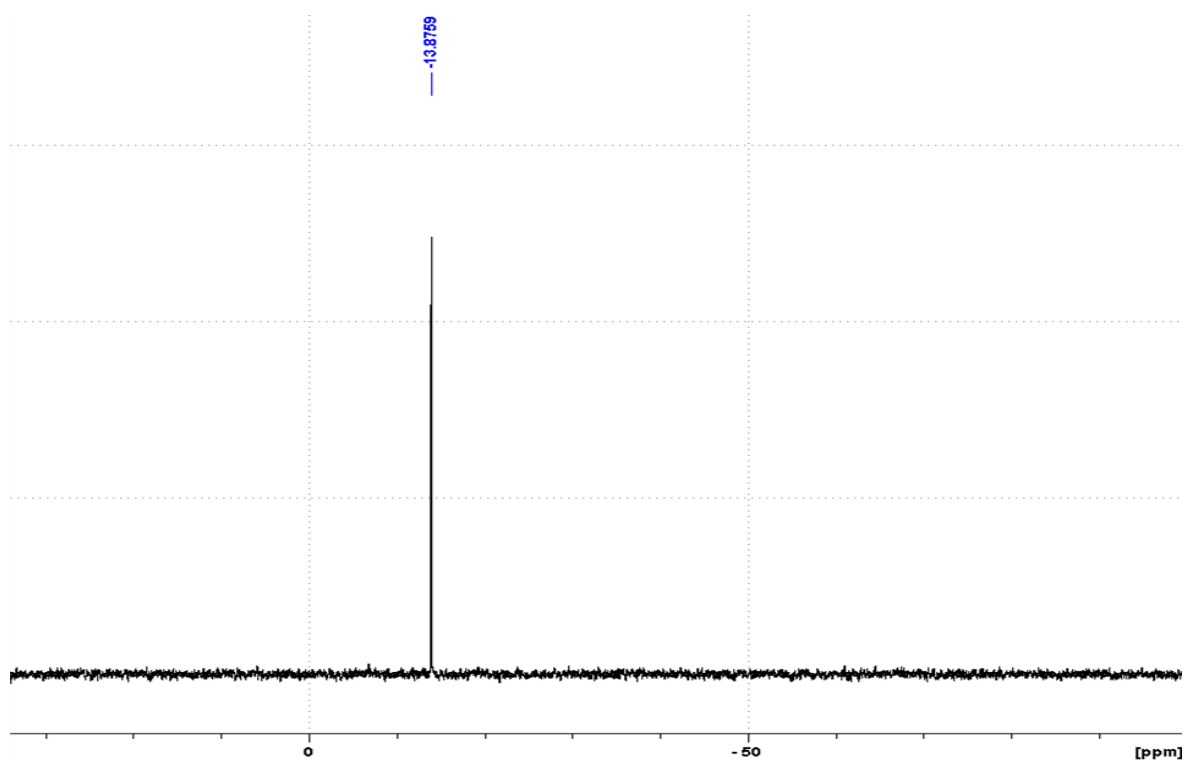


Fig. S23. ^{31}P NMR spectrum of $(\text{Bu}_4\text{N})_3\text{H}[\text{PW}_{11}\text{O}_{39}\{\text{Ru}(\text{NO})\}]$ in the mixture of $\text{CH}_3\text{CN}+\text{CD}_3\text{CN}$ (-13.88 ppm).

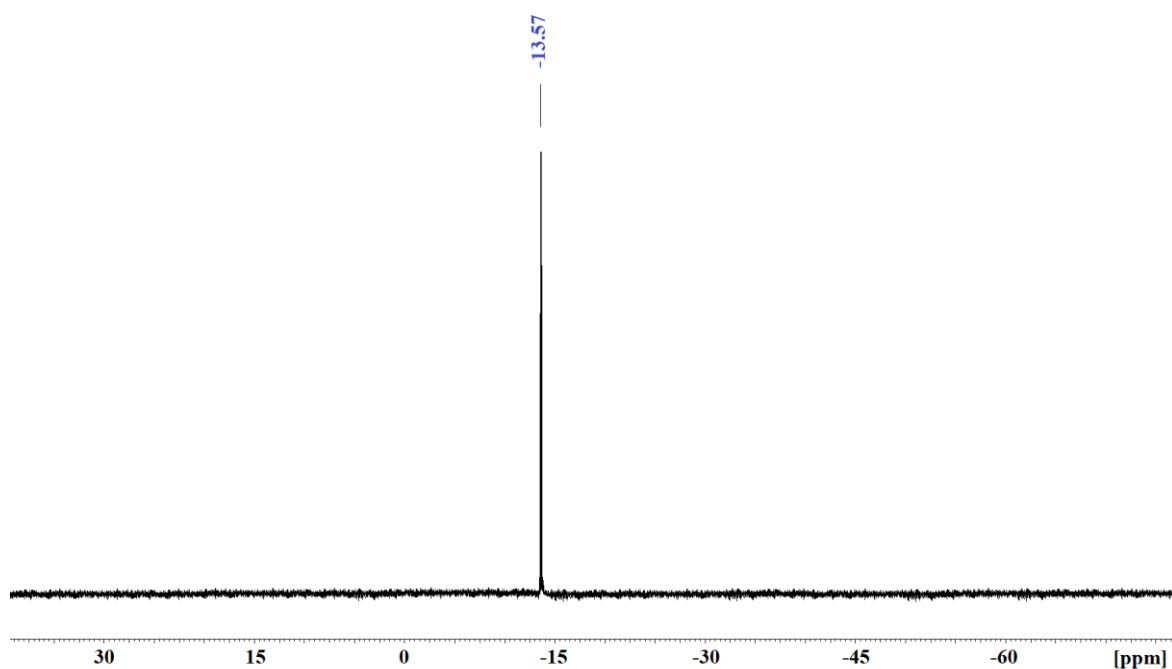


Fig. S24. ^{31}P NMR spectrum of $(\text{Bu}_4\text{N})_4[\text{PW}_{11}\text{O}_{39}\{\text{Ru}(\text{CH}_3\text{CN})\}]$ in the mixture of $\text{CH}_3\text{CN}+\text{CD}_3\text{CN}$ (-13.57 ppm).