

Supporting Information for

*$K_3[Mo_2(SNO_5)_4Cl]_3[Mo_2(SNO_5)_4]$: The First Example of a Heterometallic
Extended Metal Atom Node (HEMAN)*

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Experimental

General

All syntheses were carried out under an inert N₂ atmosphere using standard Schlenk and glovebox techniques unless otherwise specified. Solvents MeCN and THF were dried sequentially over molecular sieves and a Vacuum Atmospheres solvent purification system and degassed prior to use. Pyridine was dried over molecular sieves, distilled from barium oxide under N₂, and stored in an inert atmosphere glovebox prior to use. K₄Mo₂Cl₈ was synthesized from Mo₂(OAc)₄, KCl, and HCl gas.¹ HSNO₅ was synthesized from succinimide and P₄S₁₀.² All other reagents were purchased from Sigma Aldrich and used as received. ¹H, and ¹³C NMR spectra were collected on a Bruker Avance III 500 MHz spectrometer. FTIR (ATR) data were obtained using a Bruker TENSOR 27 spectrometer. Elemental analysis was carried out by Midwest Microlabs in Indianapolis, IN, USA.

Syntheses

tripotassium-tris[(dimolybdenum(tetrakis-monothiosuccinimidato)chloro)]

[dimolybdenum(tetrakis-monothiosuccinimidato)]

(K₃[Mo₂(SNO₅)₄Cl]₃[Mo₂(SNO₅)₄]), (1)

A flask was charged with 104 mg HSNO₅ (0.903 mmol) and 129 mg K₄Mo₂Cl₈ (0.226 mmol). These were suspended in 20 mL MeCN. Then, 250 μL NEt₃ (1.79 mmol) was added via syringe, turning the reaction mixture an orange color. The reaction mixture was heated to 75° C for 16 hours. Over the course of the reaction, the solution gradually became a very dark orange color and deposited crystals on the walls and base of the flask. After cooling to room temperature, the reaction mixture was filtered, washed with 3 x 20 mL MeCN, 3 x 20 mL H₂O, 3 x 20 mL EtOH, and 3 x 20 mL Et₂O. The compound was dried in air. Yield: 35 mg (22 %). X-

ray quality crystals of **1**·10 CH₃CN matching the unit cell of the crystals deposited on the flask were grown from layering the filtrate of the reaction with Et₂O. ¹H NMR (500 MHz, DMSO-d₆) δ 3.55 (m, 32 H), 2.77 (m, 32H). ¹³C (125 MHz, DMSO-d₆) δ 216.53, 189.58, 46.01, 32.54 ppm. IR (ATR, cm⁻¹): 2962 (vw), 2930 (vw), 1731 (m), 1431 (w), 1389 (m), 1230 (s), 1211 (vs), 1125 (w), 995 (vw), 963 (m), 931 (m), 806 (w), 679 (w). Elem. Anal. Calcd. for: C₆₄H₇₈Cl₃K₃Mo₈N₁₆O₂₃S₁₆ (**1**·7H₂O): C, 26.11%; H, 2.67%; N, 7.61%. Found: C, 25.78%; H, 2.22%; N, 7.35%.

pyridinium 4,0-molybdenum(tetrakis-monothiosuccinimidato)chloride
([pyH][4,0-Mo₂(SNO₅)₄Cl]), (2**)**

A flask was charged with 56 mg HSNO₅ (0.49 mmol) and 69 mg K₄Mo₂Cl₈ (0.12 mmol). These were suspended in 15 mL pyridine and heated without stirring at 75° C for 16 hours. Throughout the course of the reaction, X-ray quality crystals of **2**·1.5 py were deposited on the walls and base of the flask. The crystals were collected by filtration, washed with 2 x 20 mL H₂O, 3 x 20 mL EtOH, and dried under vacuum. Yield: 21 mg (23%) ¹H NMR (500 MHz, DMSO-d₆) δ 8.82 ppm (br), 8.34 (br), 7.85 (br), 3.55 (m, 8H) 2.78 (m, 8H). ¹³C (125 MHz, DMSO-d₆) δ 216.54, 189.54, 144.78, 143.60, 126.68, 32.54. IR (ATR, cm⁻¹): 2963 (vw), 1752 (m), 1732 (m), 1524 (vw), 1490 (vw), 1392 (w), 1259 (m), 1229 (m), 1195 (m), 1089 (s), 1019 (s), 963 (m), 940 (m), 866 (m), 799 (vs), 751 9w), 678 (w). Elem. Anal. Calcd for C_{22.65}H_{23.65}ClMo₂N_{5.33}O₄S₄ (**2**·0.33py): C, 34.43%; H, 3.02%; N, 9.45%. Found: C, 34.72%; H, 2.95%; N, 9.03%.

X-ray Crystallography

Single crystals of **1**·10 CH₃CN and **2**·1.5 py were selected under paratone oil and attached to a MiTeGen MicroMount. They were mounted in a stream of cold N₂ at 100(1) K in a

cold N₂ stream using an Oxford Cryostat and centered in the X-ray beam using a video monitoring system. The crystal evaluation and data collection were performed on a Bruker Quazar APEX-II diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The data were collected using a routine to survey an entire sphere of reciprocal space. The data were integrated using the SAINT routine in APEX-II and corrected for absorption using SADABS.³ The structures were solved *via* direct methods and refined by iterative cycles of least-squares refinement on F^2 followed by difference Fourier synthesis using SHELX2013.⁴ All non-hydrogen atoms were refined anisotropically. The data collection and acquisition parameters for **1**·10 CH₃CN and **2**·1.5 py are included in Table S1.

Electrochemistry

The electrochemical features of **1** were measured by cyclic voltammetry in propylene carbonate at room temperature with 1 mM analyte and 100 mM electrolyte (NEt₄PF₆) using a standard glassy carbon electrode for the working electrode, a platinum wire for the auxiliary electrode, and an Ag/Ag⁺ electrode as the reference electrode. The solution was titrated with a 0.1 M solution of KOTf in propylene carbonate. All electrochemical potentials were internally referenced to the ferrocene/ferrocenium couple. The voltammetry was performed in the range of 750 mV to -850 mV vs. Fc/Fc⁺ at a scan rate of 100 mV s⁻¹.

Crystallographic Details for **1**·10MeCN

Data Collection

An orange crystal with approximate dimensions 0.05 x 0.05 x 0.01 mm³ was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount[®]. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K $_{\alpha}$ ($\lambda = 0.71073 \text{ \AA}$) radiation and the diffractometer to crystal distance of 4.96 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range about ω with the exposure time of 60 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The final cell constants were calculated from a set of 9934 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.70 \AA . A total of 57281 data were harvested by collecting 3 sets of frames with 0.5° scans in ω and ϕ with exposure times of 120 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.^{3b}

Structure Solution and Refinement

The diffraction data were consistent with either of the space groups $P1$ or $P\bar{1}$. The E -statistics strongly suggested a centrosymmetric space group, and the use of $P\bar{1}$ yielded chemically reasonable and computationally stable results of refinement.

A successful solution by the direct methods provided most non-hydrogen atoms from the E -map.^{4a} The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor

calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.^{4b,5}

The asymmetric unit consists of two symmetry independent half molecules of $K_3[Mo_2(SNO_5)_4Cl]_3[Mo_2(SNO_5)_4]$. The $K_3[Mo_2(SNO_5)_4Cl]_3[Mo_2(SNO_5)_4]$ molecules reside on a crystallographic inversion center. Chlorides Cl1 and Cl1A are disordered across the inversion center and have 50% occupancy in the asymmetric unit.

There were several partially occupied solvent molecules of acetonitrile present in the asymmetric unit. A significant amount of time was invested in identifying and refining the disordered molecules. Idealized geometries and thermal parameter restraints were applied to model the molecules but the resulting thermal parameters suggested the molecules were mobile. In addition, the refinement was computationally unstable. The solvent mask option of OLEX2 was used to correct the diffraction data for diffuse scattering effects and to identify the solvate molecules. OLEX2 calculated the upper limit of volume that can be occupied by the solvent to be 1839.5 \AA^3 , or 30.3% of the unit cell volume. The program calculated 461.8 electrons in the unit cell for the diffuse species. This approximately corresponds to 10.5 molecules of acetonitrile in the asymmetric unit (231 electrons). It is very likely that these solvent molecules are disordered over several positions.

The final least-squares refinement of 1151 parameters against 22344 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0675 and 0.1770, respectively. The final difference Fourier map was featureless.

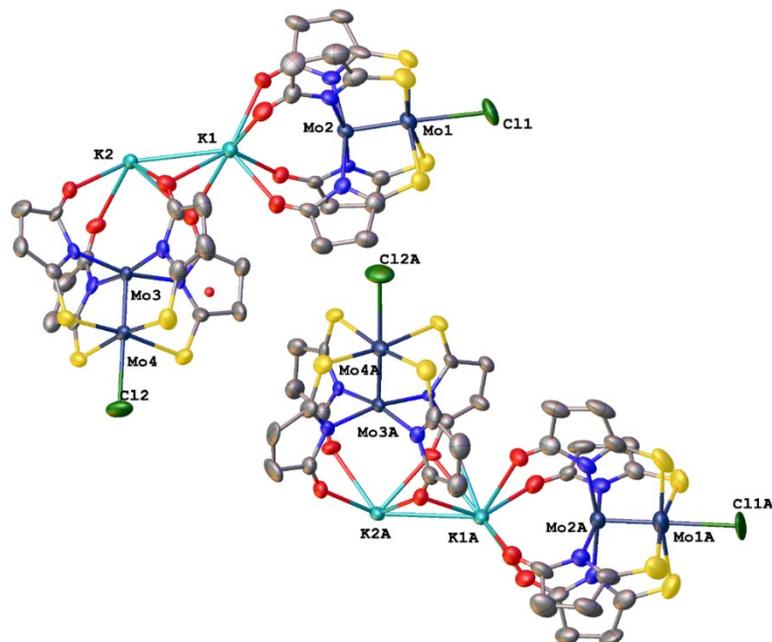


Figure S1. The asymmetric unit of **1**·10MeCN. All atoms are shown as 50% thermal probability ellipsoids. All H atoms are omitted for clarity.

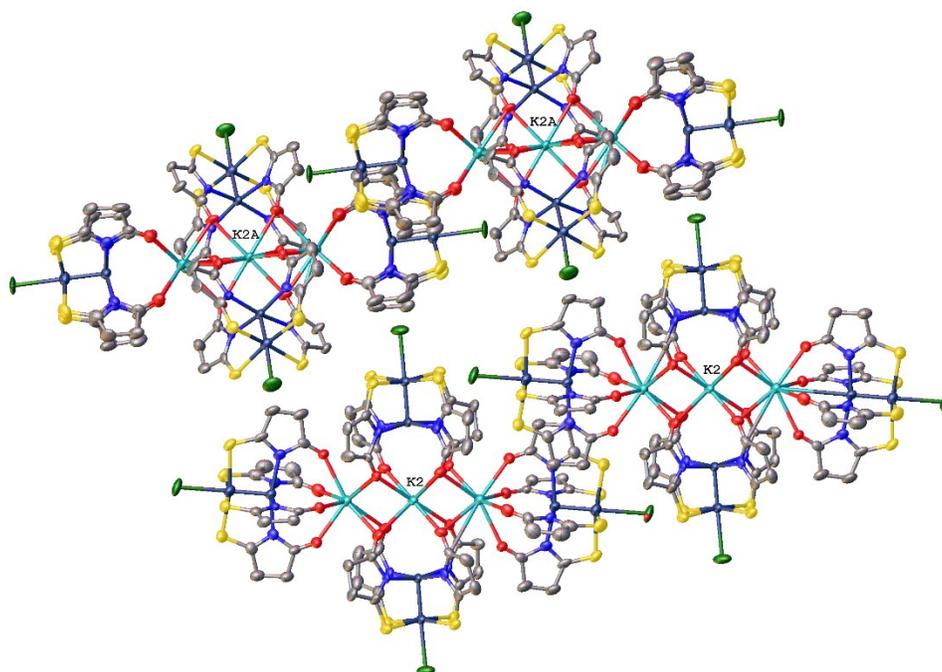


Figure S2. The packing diagram of **1**·10MeCN. All atoms are drawn as 50% thermal probability ellipsoids. All H atoms are omitted for clarity.

Crystallographic Details for 2·1.5py

Data Collection

A red crystal with approximate dimensions 0.056 x 0.094 x 0.098 mm³ was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α ($\lambda = 0.71073 \text{ \AA}$) radiation and the diffractometer to crystal distance of 4.96 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range about ω with the exposure time of 30 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The final cell constants were calculated from a set of 9995 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey reciprocal space to the extent of a full sphere to a resolution of 0.70 Å. A total of 64686 data were harvested by collecting 5 sets of frames with 0.5° scans in ω and ϕ with exposure times of 30 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.^{3b}

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent with the space group $P2_1/c$, which yielded chemically reasonable and computationally stable results of refinement.

A successful solution by the direct methods provided most non-hydrogen atoms from the E -map.^{4a} The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.^{4b,5}

The asymmetric unit consists of a pyridinium cation, a $[\text{Mo}_2(\text{SNO}_5)_4\text{Cl}]^-$ anion, and two pyridine solvent molecules. The pyridinium cation and pyridine solvent molecule N6 reside on general positions and are both disordered over two positions (major components: 50.3(6)% and 71.0(9)%, respectively). Pyridine solvent molecule N7 is disordered over a crystallographic inversion center (major component: 50%). Bond distance and thermal parameter restraints were used to ensure a chemically reasonable and computationally stable refinement.

The final least-squares refinement of 552 parameters against 7714 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0431 and 0.1057, respectively.

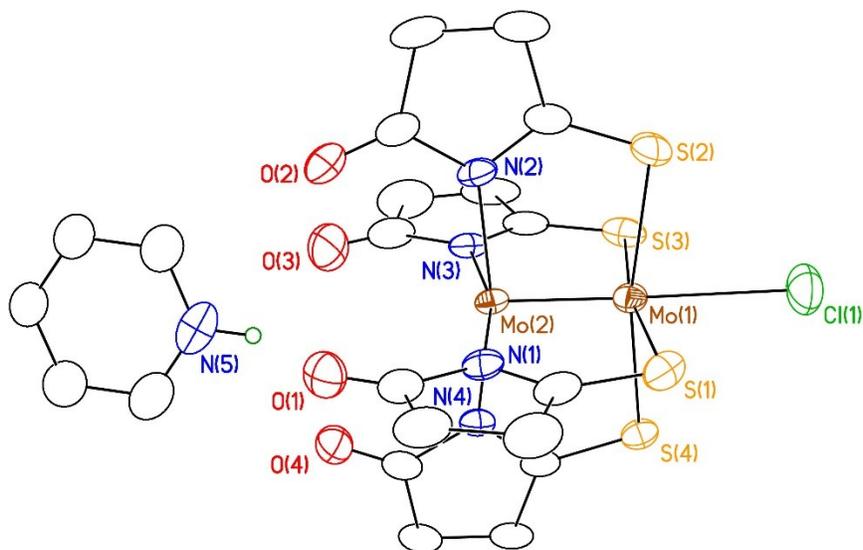


Figure S3. The structure of the 2·1.5py. All atoms are drawn as 50% thermal probability ellipsoids. All H-atoms are omitted for clarity.

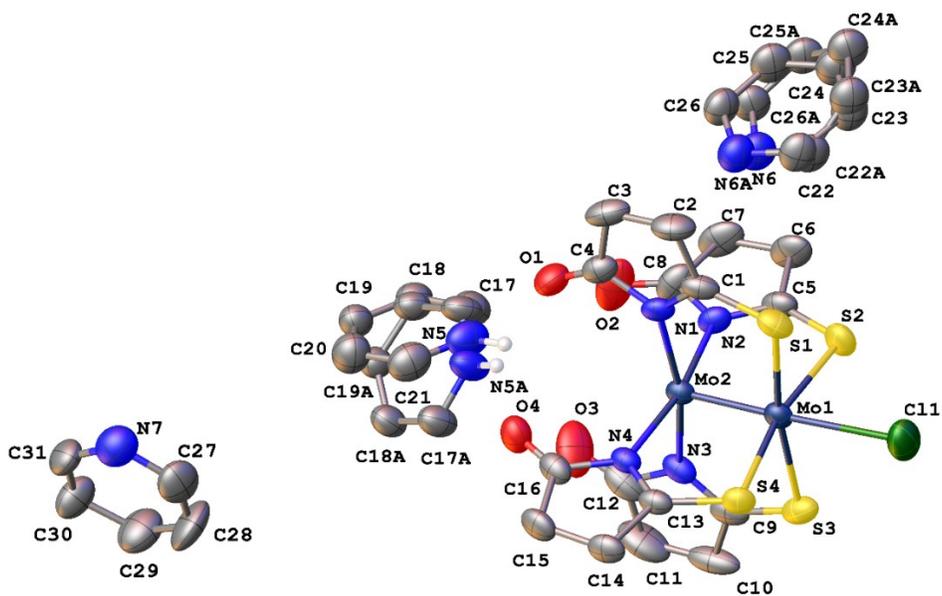


Figure S4. The asymmetric unit of 2·1.5py, including all disordered components. All atoms are drawn as 50% thermal probability ellipsoids. All H atoms, except those on the N of the pyridinium cation, are omitted for clarity.

Table S1. The X-ray crystallography experimental parameters for structures **1**·10MeCN and **2**·1.5py

Structure	1 · 10 MeCN	2 · 1.5 py
Empirical formula	$\text{K}_3\text{Mo}_8(\text{C}_{64}\text{H}_{64}\text{N}_{16}\text{O}_{16}\text{S}_{16}\text{Cl}_3) \cdot 10(\text{CH}_3\text{CN})$	$[\text{C}_5\text{H}_6\text{N}]^+ [\text{Mo}_2\text{C}_{16}\text{H}_{16}\text{N}_4\text{S}_4\text{O}_4\text{Cl}] \cdot 1.5 (\text{C}_5\text{H}_5\text{N})$
Formula weight	2825.44	882.65
Temperature/K	100.0	100.0
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	16.397(7)	8.762(3)
b/Å	17.295(6)	14.296(5)
c/Å	24.42(1)	26.630(8)
$\alpha/^\circ$	88.31(3)	90
$\beta/^\circ$	79.28(2)	92.43(2)
$\gamma/^\circ$	63.20(2)	90
Volume/Å ³	6061(5)	3333(2)
Z	2	4
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.548	1.759
μ/mm^{-1}	1.298	1.129
F(000)	2784.0	1772.0
Crystal size/mm ³	0.4 × 0.3 × 0.2	0.4 × 0.3 × 0.2
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	2.644 to 50.9	3.062 to 55.202
Index ranges	-19 ≤ h ≤ 19 -20 ≤ k ≤ 20 -29 ≤ l ≤ 29	-11 ≤ h ≤ 11 -18 ≤ k ≤ 18 -34 ≤ l ≤ 34
Reflections collected	57281	64686
Independent reflections	22344 [$R_{\text{int}} = 0.0969$ $R_{\text{sigma}} = 0.1344$]	7714 [$R_{\text{int}} = 0.0526$ $R_{\text{sigma}} = 0.0424$]
Data/restraints/parameters	22344/0/1151	7714/429/552
Goodness-of-fit on F ²	0.931	1.062
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0675 wR2 = 0.1610	R1 = 0.0431 wR2 = 0.0998
Final R indexes [all data]	R1 = 0.1280 wR2 = 0.1770	R1 = 0.0568 wR2 = 0.1061
Largest diff. peak/hole / e Å ⁻³	1.52/-1.32	1.15/-0.49

Table S2. Important bond distances for **2**·1.5 py

	2 ·1.5 py
d(Mo-Mo) (Å)	2.1463(7)
d(Mo-S) (Å)	2.4870[7]
d(Mo-N) (Å)	2.155[2]
d(Mo-Cl) (Å)	2.707(2)

Electrochemistry

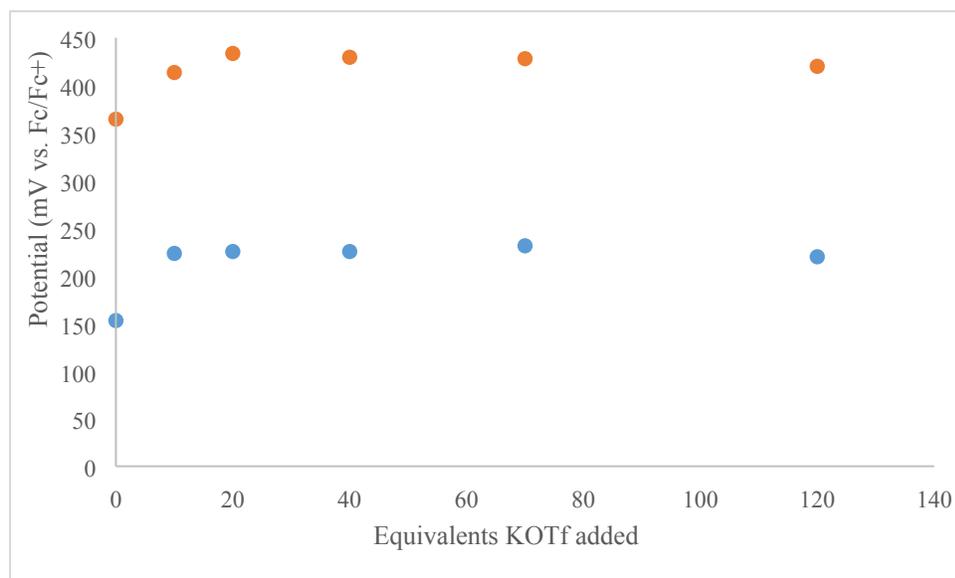


Figure S5. The titration plot of **1** with 0.1 M KOTf. The potential of the first oxidation wave is shown in blue, and the potential of the second oxidation wave is shown in orange.

References

1. J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 7-10.
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