

Supporting information

Sb₁₀²⁻ and Sb₂²⁻ Found in [K(18-crown-6)]₆[Sb₁₀] [Sb₄{Mo(CO)₃}₂]·2en: Two Missing

Family Members

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Additional experimental details

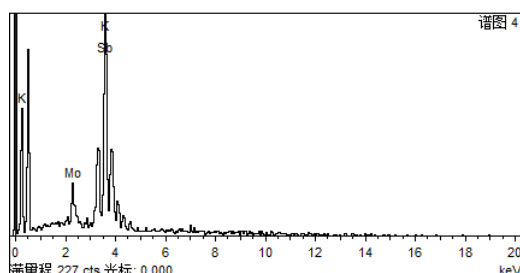
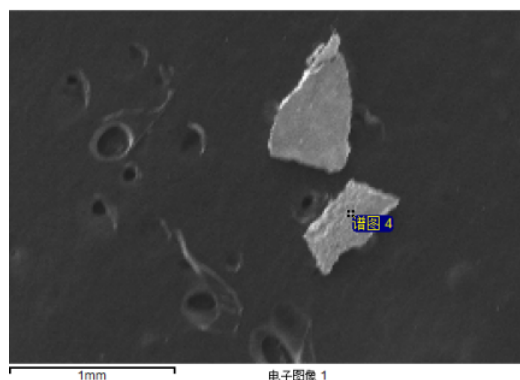
All the reactions and manipulations were performed under argon atmosphere using glove box techniques. Ethylenediamine (Acros, 99%) was distilled over sodium metal and stored in a gastight Schlenk under argon in the glove box. 18-crown-6 (1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane, Alfa-Aesar, 99 %) was dried by refluxing over sodium metal in diethylether and recrystallized from dry n-hexanes. 2, 2, 2-Crypt (4, 7, 13, 16, 21, 24-hexaoxa-1,10-diazabicyclo [8.8.8] hexacosane; 99+%, Acros) was vacuum dried and stored inside an Ar-filled glove box. Toluene was dried with potassium-sodium alloy and stored in an Ar-filled glove box. The elements were initially weighed out in K/Mn/Sb ratio of 1:1:1 mmol and loaded into niobium containers in an argon-filled glove box, the crucibles were then sealed shut by arc welding under argon, then enclosed in evacuated fused silica tubes. The sample was then heated from room temperature to 700°C in 6 hours, held at 700°C for 1 day, subsequently heat to 950°C in 2 hours, held at 950°C, then slowly cooled down to 200°C at a rate of 5°C/h. Finally the sample was cooled to room temperature by switching off the furnace.

Synthesis of [K-(18-crown-6)]₆[Sb₁₀][Sb₄Mo₂(CO)₆]·2en:

the ethylenediamine solution of KMnSb was stirred for 10h, after which (C₇H₈)Mo(CO)₃ was added and stirred for 20min, resulting in a dark red-brown solution which was layered with toluene. Black plate of [K-(18-crown-6)]₆[Sb₁₀][Sb₄Mo₂(CO)₆]·2en(**1**·2en) formed at the bottom of the Schlenk tube after two weeks. The IR spectrum (KBr) of **1** shows the characteristic CO stretching vibrations: 1973 (w, sh), 1888 (m, broad), 1849 cm⁻¹(ms, broad).

Energy Dispersive X-ray (EDX)

Elemental analysis. Microprobe analysis on **1** was performed using a field emission scanning electron microscope (FESEM. JSM6700F) equipped with an energy dispersive X-ray spectroscopy (EDX, Oxford INCA). The energy dispersive spectra (EDS) carried out on surface of the sample proved the presence of K, Mo, Sb with the roughly expected ratio of 3:1:7.



元素	重量	原子
	百分比	百分比
K K	11.14	27.42 3
Mo L	10.89	10.93 1.2
Sb L	77.97	61.65 6.7
总量	100.00	

Electrospray mass spectray

Electrospray mass spectray was recorded from DMF solutions of **1** with nitrogen as sheath gas flow on a Finnigan LCQ- Ion Trap Mass Spectrometer (LCQ DECA-30000 LCQ Deca XP) in negative-ion mode (spray voltage 4.5kV, capillary temperature 275 °C capillary voltage 15V). The samples were made up inside a Ar-filled glovebox and rapidly transferred to the spectrometer in an air-tight syringe by direct infusion with a Harvard syringe pump at 15 mLmin⁻¹.

IR spectra

IR data were recorded as KBr pellets in Nujol mulls on a Magna 750 FT-IR spectrometer photometer.

DFT theoretical calculations

The density functional theory (DFT) calculations were performed by the means of the GAUSSIAN 03 (Revision D.02) ²³ program package 27 using the B3LYP functional, that is, Beck's hybrid three-parameter exchange functional ²⁴ with the Lee-Yang-Parr correlation functional. ²⁵ the Basis sets were of LANL2DZ quality (LANL2DZ =Los Alamos ECP plus Double Zeta valence) Simultaneous optimizations of the geometric and electronic structure were carried out by using the atomic positions from the single-crystal X-ray analysis. the solvent effects were taken into account by the Polarizable Continuum Model. ²⁶

23 J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O.

Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, revision D.02. Gaussian, Inc., Wallingford CT, 2004.

24 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.

25 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B.*, 1988, **37**, 785-789.

26 (a) M. Cossi, G. Scalmani, N. Rega and V. Barone, *J. Chem. Phys.*, 2002, **117**, 43; (b) V. Barone, M. Cossi and J. Tomasi, *J. Chem. Phys.*, 1997, **107**, 3210-3221.

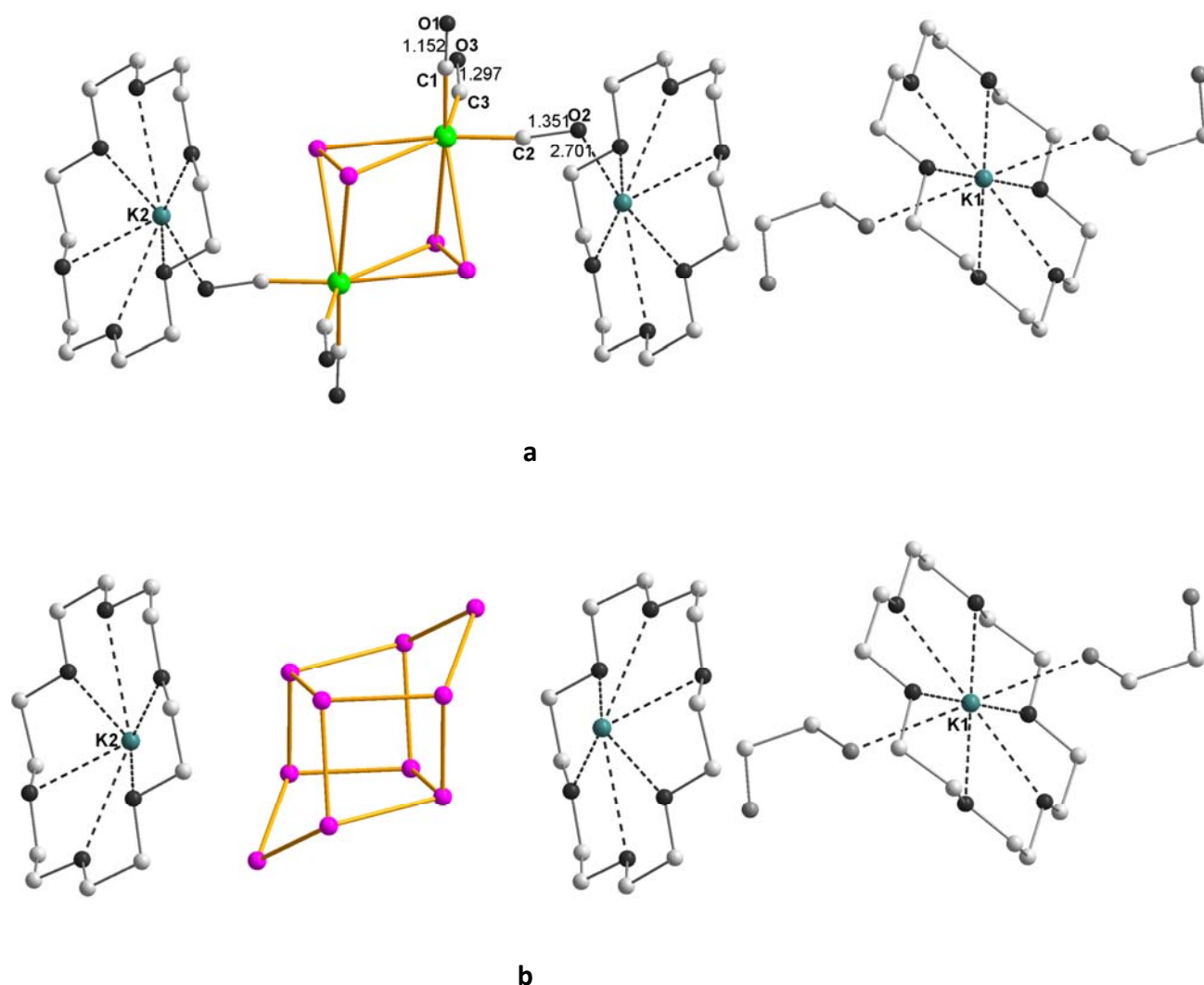


Fig. S1 Interactions between $[\text{Sb}_4\{\text{Mo}(\text{CO})_3\}_2]^{4-}$ (**a**), Sb_{10}^{2-} (**b**), en (right) and $[\text{K}(\text{18-Crown-6})]^+$.

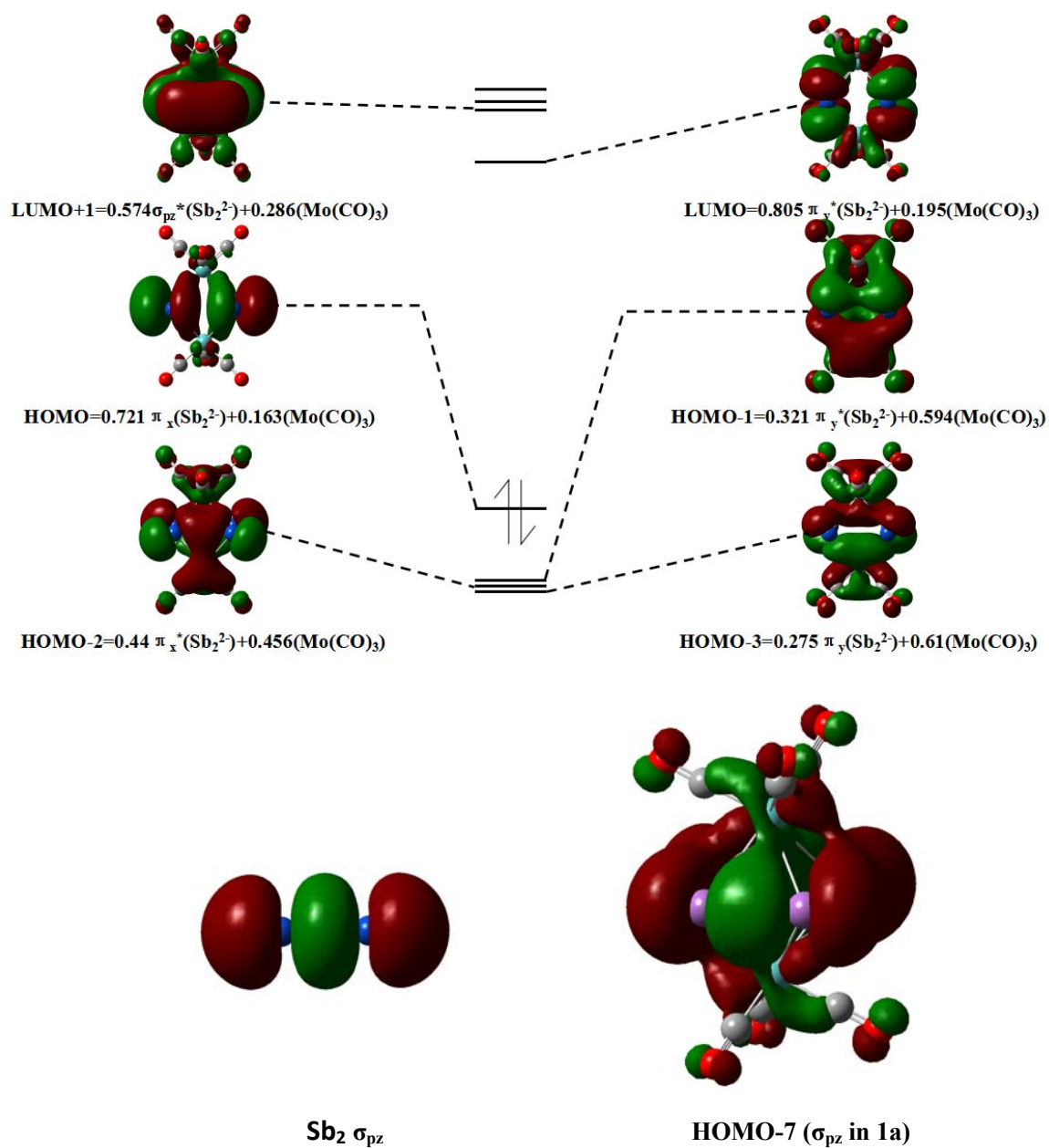


Fig. S2 MO Diagrams of $[\text{Sb}_4\{\text{Mo}(\text{CO})_3\}_2]^{4-}$ showing orbital interactions between Sb_2^{2-} and $\text{Mo}(\text{CO})_3$.

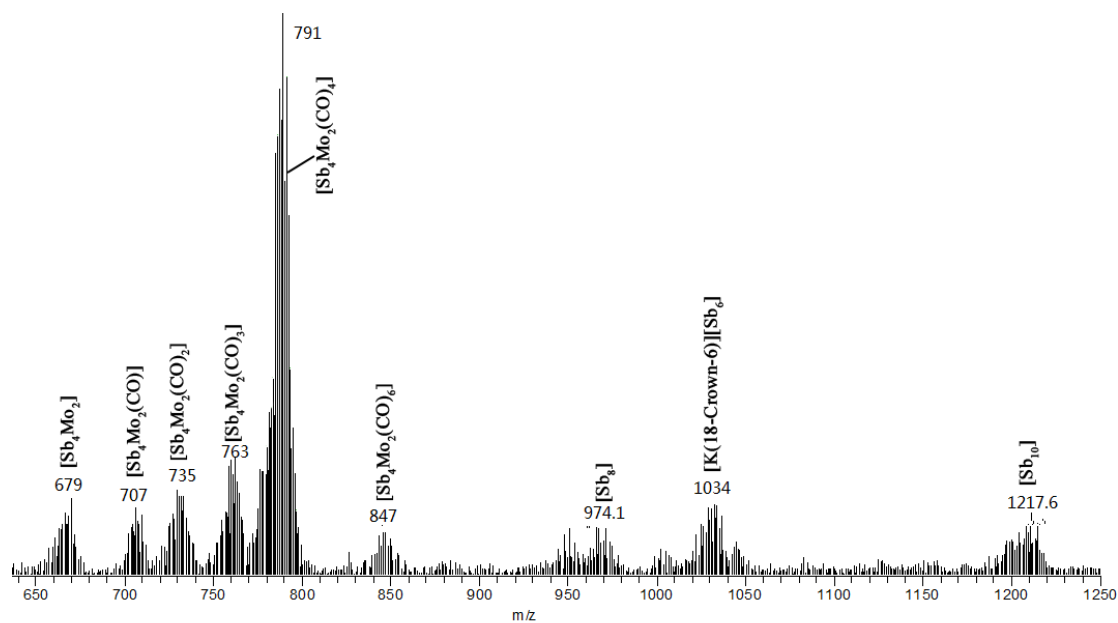


Fig. S3 Electrospray mass spectrum recorded from a DMF solution of **1**. All peaks appear as -1 ion.