Supporting Information

$[Ni(dap)_3]_4[As_{10}Cu_2S_{18}]$: a new thioarsenate(II,III) containing the rare $[As_3CuS_6]$ cluster with mixed-valence As^{2+}/As^{3+} ions

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General Remarks

All analytical grade chemicals were obtained commercially and used without further purification. Elemental analyses (C, H, and N) were performed using a PE2400 II elemental analyzer. The UV/Vis spectra were recorded at room temperature using a computer-controlled PE Lambda 900 UV/Vis spectrometer equipped with an integrating sphere in the wavelength range of 250-800 nm. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr disks in the 4000-400 cm^{-1} range. Powder XRD patterns were collected on a D/MAX-3C diffractometer using graphite-mono-chromatized CuKa radiation (λ = 1.5406Å).

Crystal Structure Determination

Single-crystal X-ray diffraction data for **1** were recorded on a Bruker APEX II diffractometer using a ω-scan method with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 296(2) K to a maximum 2θ value (53.0°). The structure of **1** was solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms were refined with anisotropic temperature parameters. The H atoms bonded to C and N atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters, but H atom of C7 atom was not dealt with, due to the disorder of C7 atom. The occupancies of disordered C7/C7' are assigned as 50 and 50 %. Relevant crystal and collection data parameters and refinement results can be found in Table S1. Additional details of crystal data in CIF format can be found in the Supporting Information.

Table S1 Crystallographic data for **1**.

	1
formula	$C_{36}H_{120}As_{10}Cu_2N_{24}Ni_4S_{18}$
Fw	2577.88
crystal system	Monoclinic
space group	C2/c
a, Å	34.03(2)
b, Å	11.901(8)
c, Å	23.495(16)
β, deg	94.843(8)
V, Å^3	9480(11)
Z	4
T, K	296(2)
Calcd density,Mg.m^{-3}	1.805
abs coeff, mm^{-1}	5.121
F(000)	5160
2*θ*(max), deg	53.0
Total reflns collected	29664
Unique reflns	9798
No. of param	433
*R*1[*I*>2σ(*I*)]	0.0378
*wR*2(all data)	0.0896

Table S2. Selected Bond lengths [Å] and angles [deg] for **1**.

As(1)-S(1)	2.156(2)	Cu(1)-S(6)	2.2121(19)
As(1)-S(3)	2.2700(17)	Cu(1)-S(5)	2.2123(17)
As(1)-S(2)	2.2746(16)	Cu(1)-S(4)	2.2212(18)
As(2)-S(4)	2.1858(19)	Ni(1)-N(9)	2.112(4)
As(2)-S(3)	2.255(2)	Ni(1)-N(7)	2.125(4)
As(2)-As(3)	2.5783(17)	Ni(1)-N(12)	2.127(4)
As(3)-S(5)	2.2062(19)	Ni(1)-N(8)	2.129(4)
As(3)-S(2)	2.256(2)	Ni(1)-N(11)	2.132(4)
As(4)-S(6)	2.1957(18)	Ni(1)-N(10)	2.142(4)
As(4)-S(8)	2.273(2)	Ni(2)-N(4)	2.092(4)
As(4)-S(7)	2.3051(17)	Ni(2)-N(2)	2.112(4)
As(5)-S(9)	2.1668(17)	Ni(2)-N(6)	2.114(4)
As(5)-S(7)	2.2876(17)	Ni(2)-N(1)	2.136(4)
Ni(2)-N(3)	2.146(4)	Ni(2)-N(5)	2.143(4)
S(1)-As(1)-S(3)	101.88(8)	S(6)-As(4)-S(7)	101.71(4)
S(1)-As(1)-S(2)	103.08(7)	S(8)-As(4)-S(7)	101.50(6)
S(3)-As(1)-S(2)	95.13(7)	S(9)-As(5)-S(7)	103.39(7)
S(4)-As(2)-S(3)	106.04(6)	S(9)-As(5)-S(8)#1	99.85(6)
S(4)-As(2)-As(3)	105.18(4)	S(7)-As(5)-S(8)#1	101.62(5)
S(3)-As(2)-As(3)	100.01(5)	S(6)-Cu(1)-S(5)	123.71(6)
S(5)-As(3)-S(2)	104.66(6)	S(6)-Cu(1)-S(4)	123.02(5)
S(5)-As(3)-As(2)	104.21(5)	S(5)-Cu(1)-S(4)	112.77(7)
S(2)-As(3)-As(2)	99.77(4)	N(9)-Ni(1)-N(7)	92.99(16)
S(6)-As(4)-S(8)	95.50(5)	N(9)-Ni(1)-N(12)	93.20(17)
N(4)-Ni(2)-N(6)	91.40(16)	N(7)-Ni(1)-N(12)	171.64(18)
N(2)-Ni(2)-N(6)	94.83(15)	N(9)-Ni(1)-N(8)	93.06(15)
N(4)-Ni(2)-N(1)	172.22(15)	N(7)-Ni(1)-N(8)	81.34(16)
N(2)-Ni(2)-N(1)	80.16(15)	N(12)-Ni(1)-N(8)	92.72(16)
N(6)-Ni(2)-N(1)	95.37(16)	N(9)-Ni(1)-N(11)	171.19(17)
N(4)-Ni(2)-N(5)	92.88(16)	N(7)-Ni(1)-N(11)	93.26(19)
N(2)-Ni(2)-N(5)	170.87(15)	N(12)-Ni(1)-N(11)	81.2(2)
N(6)-Ni(2)-N(5)	81.26(15)	N(8)-Ni(1)-N(11)	94.01(17)
N(1)-Ni(2)-N(5)	91.94(16)	N(9)-Ni(1)-N(10)	81.43(15)
N(4)-Ni(2)-N(3)	80.37(15)	N(7)-Ni(1)-N(10)	91.91(17)
N(2)-Ni(2)-N(3)	93.72(15)	N(12)-Ni(1)-N(10)	94.56(16)
N(6)-Ni(2)-N(3)	168.66(15)	N(8)-Ni(1)-N(10)	171.09(16)
N(1)-Ni(2)-N(3)	93.42(15)	N(11)-Ni(1)-N(10)	92.16(17)
N(5)-Ni(2)-N(3)	91.30(15)	N(4)-Ni(2)-N(2)	95.47(15)

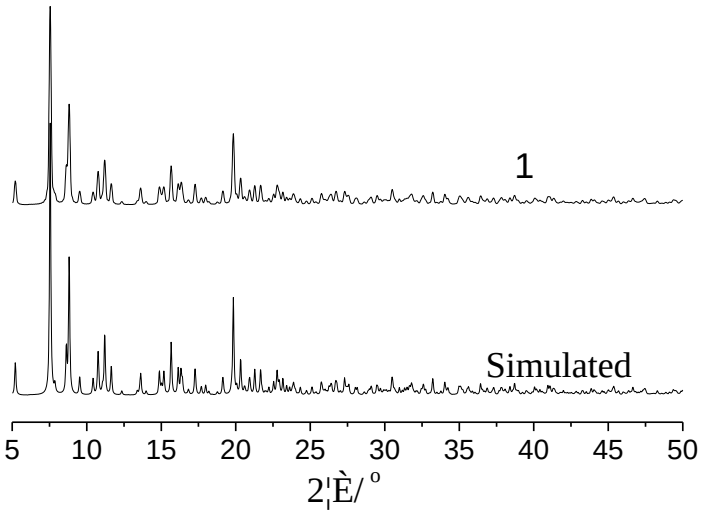

Fig. S1 Simulated and experimental powder XRD patterns of **1**.

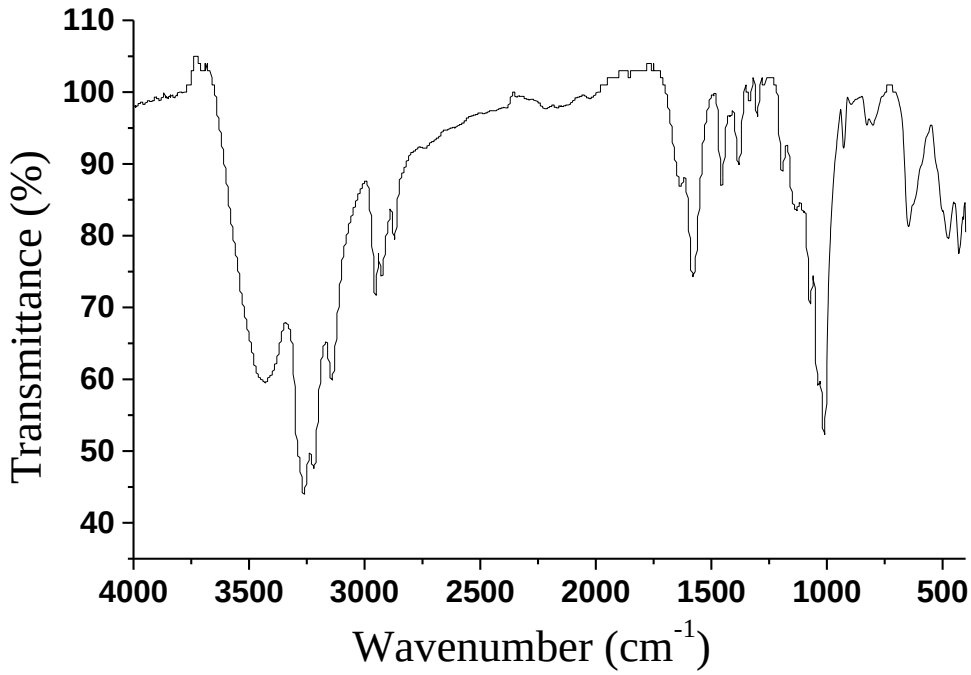

Fig. S2. IR spectrum of **1**.

The appearance of the resonance band centered at 3135–3426 cm^{-1} attributed to the *v*(N-H) vibration of amines confirms the presence of organic ammine groups.

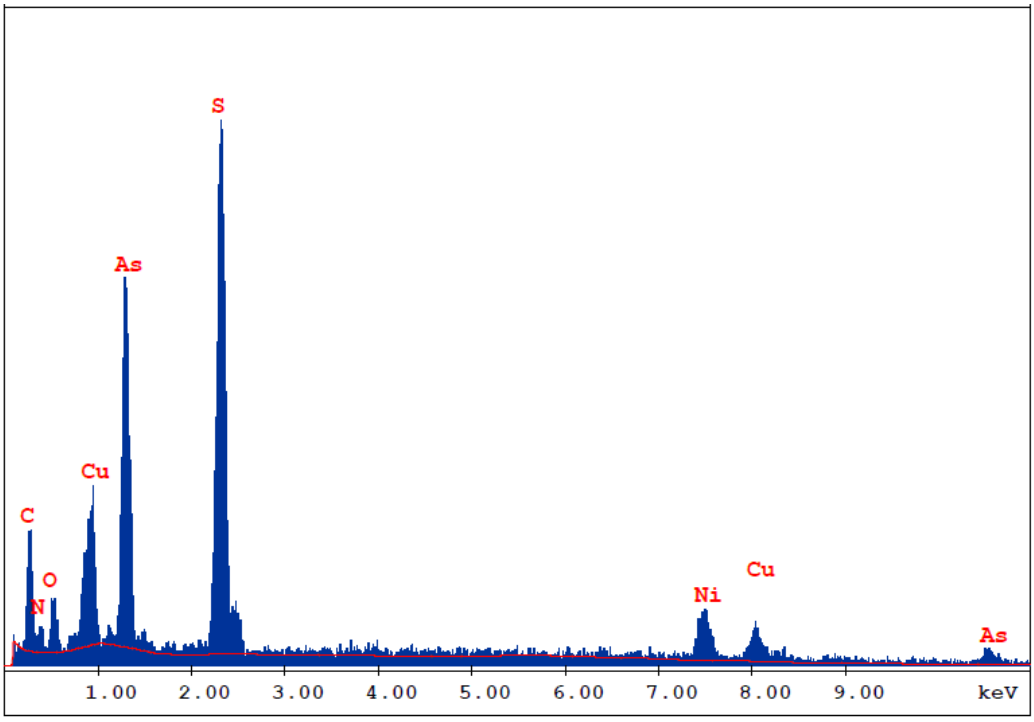

Fig. S3 EDS spectrum of **1**.