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SUPPORTING INFORMATION

Unexpected coupling of Cp and two RNC ligands at a $\{\text{Mo}_2(\mu\text{-SMe})_3\}$ nucleus.
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 Kenneth W. Muir*,

Syntheses and characterization of complexes 1-3
Structural results for complexes 2 and 3

1. Synthesis and characterization of the starting complex 1 :

A solution of $[\text{Mo}_2\text{Cp}_2(\mu\text{-SMe})_3(\text{MeCN})_2](\text{BF}_4)^-$ (0.5g, 0.79 mmol) in dichloro-methane (30 mL) was stirred in the presence of an excess of *t*-BuNC (2.5 equiv : 224 μL) for one hour at room temperature. The solution turned readily from red to orange. The volume was then reduced under vacuum and diethyl ether added to precipitate the complex $[\text{Mo}_2\text{Cp}_2$

$(\mu\text{-SMe})_3(\text{t-BuNC})_2](\text{BF}_4)^-$ (**1**) as an orange solid (0.51g, 90% yield) : ^1H NMR (CDCl_3 , 25°C; δ) 5.27, (s,10H, C_5H_5), 2.43 (s,3H, SCH_3), 2.39 (s,3H, SCH_3), 1.55 (s,18H, CMe_3), 1.36 (s,3H, SCH_3). Anal. Calcd. for $\text{C}_{23}\text{H}_{37}\text{BF}_4\text{Mo}_2\text{N}_2\text{S}_3$: C, 38.5; H, 5.2; N, 3.9. Found : C, 38.3; H, 5.0; N, 3.5.

(1) Barrière, F.; Le Mest, Y.; Pétilion, F.Y.; Pöder-Guillou, S.; Schollhammer, P.; Talarmin, J. *J.Chem.Soc.,Dalton Trans.* 1996,3967.

2. Preparation and characterization of 2 :

A tetrahydrofuran solution (30 mL) of **1** (0.10g, 0.14 mmol) and 4 equivalents (225 μL of a 2.5 M solution of *n*-BuLi in hexane) was stirred overnight at 70°C. After filtration and evaporation of the solvent, the products were extracted with diethyl ether (3 x 10 mL). The diethyl ether was then removed in vacuo from the pooled extracts. Spectroscopic (^1H NMR) analysis of the residue showed that a single species was formed in about 95% yield. Chromatography of the residue on a silica gel column (Elution with $\text{thf-CH}_2\text{Cl}_2$ (1:9)) afforded a pure sample of **2** as an orange powder (0.057g, 71% yield) ; no other species was eluted : ^1H NMR (CDCl_3 , 25°C ; δ) 5.12 (s,5H, C_5H_5), 5.07 (s,5H, C_5H_5), 2.54 (s,3H, SCH_3), 2.48 (s,3H, SCH_3), 1.49 (s,9H, CMe_3), 1.32 (s,3H, SCH_3) ; $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 ,25°C ; δ) 165.6 (CN*t*Bu), 160.9 (CN), 90.2 (C_5H_5), 89.7 (C_5H_5), 57.8 (CMe_3), 29.2 (CMe_3), 24.4 (SCH_3), 23.4 (SCH_3), 10.0 (SCH_3); IR ($\nu(\text{CN})$; *KBr pellet* cm^{-1}) 2134 s, 2075 m; Anal. Calcd. for $\text{C}_{19}\text{H}_{28}\text{Mo}_2\text{S}_3\text{N}_2$, 0.5 CH_2Cl_2 : C,38.1; H,4.8; N,4.5. Found : C,38.3; H,4.8; N,4.3.

3. Synthesis and characterisation of 3 :

A solution of complex **1** (0.1g ; 0.14 mmol) in tetrahydrofuran (30 mL) was stirred in the presence of an excess of NaOH (0.4g; 10 mmol) and 10 equiv of *t*-BuNC (157 μ L; 1.4 mmol) for 14h at 70°C. After filtration and evaporation of the volatiles, the products were extracted with diethyl ether (3 x 10 mL). The diethyl ether was then removed in vacuo from the pooled extracts. Spectroscopic (^1H NMR) analysis of the residue showed that all the starting complex disappeared, and two compounds **2** and **3** were formed in about 30 and 69% yield, respectively. Complexes **2** and **3** were separated by chromatography on a silica gel column. Elution with hexane - CH_2Cl_2 (1 : 1) afforded a red solution of **3**, which was evaporated under vacuum to give **3** as a red solid. Further elution with $\text{thf-CH}_2\text{Cl}_2$ (1 : 9) produced a orange band of **2**. NMR (^1H) spectroscopy indicated that complex **3** exists in solution as two isomers **3a** and **3b** in the ratio 5 : 1 ; these isomers were inseparable by conventional chromatographic techniques and they differ only in the orientations (*syn* or *anti*) of the bridging SMe groups.

Complex **3** was also prepared on stirring at 70°C for 14h a tetrahydrofuran solution of **1** and an excess of either *n*-BuLi (4 equiv) or $(\text{Me}_4\text{N})\text{OH}$ (3 equiv) and 10 equiv of *t*-BuNC. Workup of the product as described above afforded **3** in noticeable yields.

3a : ^1H NMR ($\text{CDCl}_3, 25^\circ\text{C}; \delta$) 6.06 (m, 1H, CH), 5.68 (m, 1H, CH), 5.38 (s, 5H, C_5H_5), 5.12 (m, 1H, CH), 4.78 (m, 1H, CH), 1.75 (s, 3H, SCH₃), 1.57 (s, 3H, SCH₃), 1.44 (s, 3H, SCH₃), 1.37 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.34 (s, 9H, $\text{C}(\text{CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_6, 25^\circ\text{C}; \delta$) 366.9 (Mo $\underline{\text{C}}$ Mo), 149.1 (CN), 106.3, 99.7, 99.5 (C_5H_4), 93.2 (C_5H_5), 91.4, 85.4 (C_3H_4), 63.0 ($\text{C}(\text{CH}_3)_3$), 54.3 ($\text{C}(\text{CH}_3)_3$), 31.8 ($\text{C}(\text{CH}_3)_3$), 29.7 ($\text{C}(\text{CH}_3)_3$), 23.2 (SCH₃), 8.2 (SCH₃), 6.2 (SCH₃).

3b : ^1H NMR ($\text{CDCl}_3, 25^\circ\text{C}; \delta$) 5.77 (m, 1H, CH), 5.58 (m, 1H, CH), 5.29 (s, 5H, C_5H_5), 4.83 (s, 1H, CH), 4.72 (m, 1H, CH), 1.82 (s, 3H, SCH₃), 1.60 (s, 3H, SCH₃), 1.52 (s, 3H, SCH₃), 1.40 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.38 (s, 9H, $\text{C}(\text{CH}_3)_3$); IR ($\nu(\text{CN})$; KBr pellet cm^{-1}) 1641 m.

3 : Anal. Calcd for $\text{C}_{23}\text{H}_{36}\text{Mo}_2\text{N}_2\text{S}_3$: C, 43.9 ; H, 5.8 ; N, 4.4. Found : C, 43.9; H, 5.9; N, 4.2.

4-Crystallographic characterisation of 2 and 3 :

The crystal structures of **2** (as the monohydrate) and of **3** were determined using data collected with Mo K_{α} radiation on a Nonius KappaCCD diffractometer at 100 K. The procedures and results are summarised in Figures 1 and 2 (see pages 4 & 10) and in the following tables (see pages 4 – 14).

- Table 1.** Crystal data and structure refinement for **2**.
- Table 2.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.
- Table 3.** Bond lengths [\AA] and angles [$^{\circ}$] for **2**.
- Table 4.** Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$
- Table 5.** Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**.
- Table 6.** Analysis of Potential Hydrogen Bonds in **2**
- Table 7.** Crystal data and structure refinement for **3**.
- Table 8.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.
- Table 9.** Bond lengths [\AA] and angles [$^{\circ}$] for **3**.
- Table 10.** Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$
- Table 11.** Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for three.

Table 1. Crystal data and structure refinement for 2.

Identification code	KM3200
Empirical formula	C ₁₉ H ₃₀ Mo ₂ N ₂ O ₅ S ₃
Formula weight	590.51
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2 ₁ /c
Unit cell dimensions	a = 13.5385(5) Å b = 11.2495(4) Å c = 15.5968(6) Å β = 102.796(2)°
Volume	2316.42(15) Å ³
Z	4
Density (calculated)	1.693 Mg/m ³
Absorption coefficient	1.365 mm ⁻¹
F(000)	1192
Crystal size	0.20 x 0.15 x 0.02 mm ³
Theta range for data collection	3.58 to 27.51°
Index ranges	-17 ≤ h ≤ 16, -14 ≤ k ≤ 14, -20 ≤ l ≤ 20
Reflections collected	32515
Independent reflections	5286 [R(int) = 0.0435]
Completeness to theta = 27.51°	99.2 %
Absorption correction	Empirical
Max. and min. transmission	1.030 and 0.970
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5286 / 0 / 258
Goodness-of-fit on F ²	1.106
Final R indices [I > 2σ(I)]	R1 = 0.0387, wR2 = 0.0746
R indices (all data)	R1 = 0.0721, wR2 = 0.0891
Largest diff. peak and hole	0.721 and -0.782 e.Å ⁻³

Figure 1.
Molecular structure of 2
showing 20% ellipsoids and
hydrogen bonding.
Symmetry code:
i. x, 1+y, z
ii. 1-x, 1-y, -z

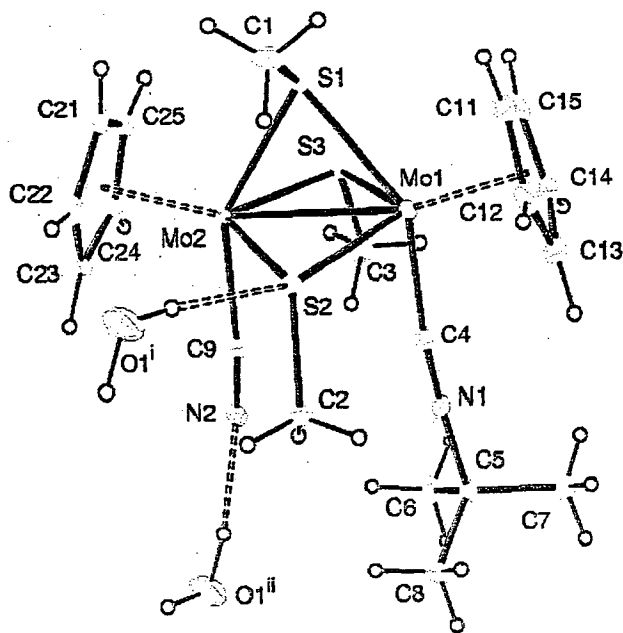


Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 2. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mo(1)	8168(1)	9506(1)	2490(1)	22(1)
Mo(2)	7898(1)	10510(1)	809(1)	22(1)
S(1)	8923(1)	11384(1)	2158(1)	28(1)
S(2)	6698(1)	10701(1)	1778(1)	26(1)
S(3)	9223(1)	9079(1)	1437(1)	26(1)
N(1)	6860(2)	7163(3)	1762(2)	26(1)
N(2)	6510(2)	8304(3)	-194(2)	30(1)
C(1)	8332(3)	12691(4)	2528(3)	42(1)
C(2)	5535(3)	9834(4)	1447(3)	32(1)
C(3)	9028(3)	7573(4)	980(3)	35(1)
C(4)	7301(3)	8027(4)	1971(2)	24(1)
C(5)	6304(3)	6047(4)	1559(3)	27(1)
C(6)	6670(4)	5453(4)	810(3)	42(1)
C(7)	6572(3)	5299(4)	2389(3)	35(1)
C(8)	5177(3)	6335(4)	1304(3)	44(1)
C(9)	6994(3)	9044(4)	202(2)	24(1)
C(11)	8819(4)	10150(5)	3926(3)	44(1)
C(12)	7885(3)	9676(5)	3930(3)	42(1)
C(13)	7916(4)	8461(5)	3705(3)	48(1)
C(14)	8890(4)	8210(5)	3563(3)	50(1)
C(15)	9435(4)	9270(5)	3701(3)	45(1)
C(21)	8297(4)	12335(5)	277(3)	56(2)
C(22)	7270(4)	12156(4)	-95(3)	43(1)
C(23)	7192(3)	11131(4)	-607(3)	33(1)
C(24)	8193(3)	10678(5)	-552(3)	40(1)
C(25)	8853(4)	11431(6)	2(3)	54(2)
O(1)	5091(3)	3062(4)	1260(3)	74(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for 2.

Mo(1)-C(4)	2.093(4)	S(1)-C(1)	1.828(5)
Mo(1)-C(14)	2.270(4)	S(2)-C(2)	1.825(4)
Mo(1)-C(15)	2.269(4)	S(3)-C(3)	1.835(4)
Mo(1)-C(13)	2.319(4)	N(1)-C(4)	1.150(5)
Mo(1)-C(11)	2.334(4)	N(1)-C(5)	1.461(5)
Mo(1)-C(12)	2.368(4)	N(2)-C(9)	1.151(5)
Mo(1)-S(3)	2.4505(11)	C(5)-C(7)	1.519(6)
Mo(1)-S(1)	2.4511(11)	C(5)-C(6)	1.522(6)
Mo(1)-S(2)	2.4546(10)	C(5)-C(8)	1.524(6)
Mo(1)-Mo(2)	2.8037(5)	C(11)-C(12)	1.374(6)
Mo(2)-C(9)	2.145(4)	C(11)-C(15)	1.389(7)
Mo(2)-C(25)	2.247(5)	C(12)-C(13)	1.414(7)
Mo(2)-C(24)	2.252(4)	C(13)-C(14)	1.413(7)
Mo(2)-C(23)	2.311(4)	C(14)-C(15)	1.395(7)
Mo(2)-C(21)	2.323(5)	C(21)-C(25)	1.388(8)
Mo(2)-C(22)	2.367(4)	C(21)-C(22)	1.398(7)
Mo(2)-S(3)	2.4479(11)	C(22)-C(23)	1.393(6)
Mo(2)-S(1)	2.4549(10)	C(23)-C(24)	1.432(6)
Mo(2)-S(2)	2.4613(11)	C(24)-C(25)	1.385(7)
C(4)-Mo(1)-C(14)	83.51(18)	C(14)-Mo(1)-C(13)	35.85(18)
C(4)-Mo(1)-C(15)	119.00(18)	C(15)-Mo(1)-C(13)	58.76(18)
C(14)-Mo(1)-C(15)	35.79(18)	C(4)-Mo(1)-C(11)	132.69(16)
C(4)-Mo(1)-C(13)	75.00(16)	C(14)-Mo(1)-C(11)	58.86(19)

C(15)-Mo(1)-C(11)	35.10(17)	C(24)-Mo(2)-S(1)	126.10(13)
C(13)-Mo(1)-C(11)	57.69(17)	C(23)-Mo(2)-S(1)	137.18(11)
C(4)-Mo(1)-C(12)	103.63(17)	C(21)-Mo(2)-S(1)	79.65(12)
C(14)-Mo(1)-C(12)	59.12(18)	C(22)-Mo(2)-S(1)	104.92(12)
C(15)-Mo(1)-C(12)	58.08(17)	S(3)-Mo(2)-S(1)	72.23(4)
C(13)-Mo(1)-C(12)	35.09(17)	C(9)-Mo(2)-S(2)	87.04(11)
C(11)-Mo(1)-C(12)	33.97(16)	C(25)-Mo(2)-S(2)	147.55(18)
C(4)-Mo(1)-S(3)	86.88(11)	C(24)-Mo(2)-S(2)	148.25(12)
C(14)-Mo(1)-S(3)	98.56(13)	C(23)-Mo(2)-S(2)	111.80(11)
C(15)-Mo(1)-S(3)	95.16(13)	C(21)-Mo(2)-S(2)	112.34(17)
C(13)-Mo(1)-S(3)	131.43(15)	C(22)-Mo(2)-S(2)	95.67(13)
C(11)-Mo(1)-S(3)	123.52(13)	S(3)-Mo(2)-S(2)	109.66(4)
C(12)-Mo(1)-S(3)	153.16(12)	S(1)-Mo(2)-S(2)	76.31(3)
C(4)-Mo(1)-S(1)	145.88(11)	C(9)-Mo(2)-Mo(1)	92.66(10)
C(14)-Mo(1)-S(1)	125.29(16)	C(25)-Mo(2)-Mo(1)	137.49(12)
C(15)-Mo(1)-S(1)	90.17(14)	C(24)-Mo(2)-Mo(1)	154.30(12)
C(13)-Mo(1)-S(1)	138.87(12)	C(23)-Mo(2)-Mo(1)	162.97(11)
C(11)-Mo(1)-S(1)	81.30(13)	C(21)-Mo(2)-Mo(1)	134.25(12)
C(12)-Mo(1)-S(1)	107.06(13)	C(22)-Mo(2)-Mo(1)	145.80(12)
S(3)-Mo(1)-S(1)	72.25(4)	S(3)-Mo(2)-Mo(1)	55.13(3)
C(4)-Mo(1)-S(2)	86.06(11)	S(1)-Mo(2)-Mo(1)	55.08(3)
C(14)-Mo(1)-S(2)	149.14(14)	S(2)-Mo(2)-Mo(1)	55.11(2)
C(15)-Mo(1)-S(2)	145.96(14)	C(1)-S(1)-Mo(1)	113.24(16)
C(13)-Mo(1)-S(2)	113.31(14)	C(1)-S(1)-Mo(2)	112.88(15)
C(11)-Mo(1)-S(2)	111.10(14)	Mo(1)-S(1)-Mo(2)	69.71(3)
C(12)-Mo(1)-S(2)	95.68(12)	C(2)-S(2)-Mo(1)	113.42(15)
S(3)-Mo(1)-S(2)	109.80(3)	C(2)-S(2)-Mo(2)	115.13(15)
S(1)-Mo(1)-S(2)	76.51(3)	Mo(1)-S(2)-Mo(2)	69.55(3)
C(4)-Mo(1)-Mo(2)	90.75(10)	C(3)-S(3)-Mo(2)	114.97(13)
C(14)-Mo(1)-Mo(2)	153.35(13)	C(3)-S(3)-Mo(1)	112.69(15)
C(15)-Mo(1)-Mo(2)	138.08(14)	Mo(2)-S(3)-Mo(1)	69.83(3)
C(13)-Mo(1)-Mo(2)	162.98(12)	C(4)-N(1)-C(5)	176.1(4)
C(11)-Mo(1)-Mo(2)	135.73(13)	N(1)-C(4)-Mo(1)	173.5(3)
C(12)-Mo(1)-Mo(2)	147.05(13)	N(1)-C(5)-C(7)	106.1(3)
S(3)-Mo(1)-Mo(2)	55.04(3)	N(1)-C(5)-C(6)	107.7(3)
S(1)-Mo(1)-Mo(2)	55.21(2)	C(7)-C(5)-C(6)	110.7(4)
S(2)-Mo(1)-Mo(2)	55.34(3)	N(1)-C(5)-C(8)	108.2(3)
C(9)-Mo(2)-C(25)	116.75(19)	C(7)-C(5)-C(8)	112.1(4)
C(9)-Mo(2)-C(24)	81.49(16)	C(6)-C(5)-C(8)	111.7(4)
C(25)-Mo(2)-C(24)	35.85(18)	N(2)-C(9)-Mo(2)	173.9(3)
C(9)-Mo(2)-C(23)	74.71(15)	C(12)-C(11)-C(15)	109.2(5)
C(25)-Mo(2)-C(23)	59.53(16)	C(12)-C(11)-Mo(1)	74.4(3)
C(24)-Mo(2)-C(23)	36.55(15)	C(15)-C(11)-Mo(1)	69.9(2)
C(9)-Mo(2)-C(21)	132.63(15)	C(11)-C(12)-C(13)	107.3(5)
C(25)-Mo(2)-C(21)	35.3(2)	C(11)-C(12)-Mo(1)	71.7(3)
C(24)-Mo(2)-C(21)	59.01(19)	C(13)-C(12)-Mo(1)	70.5(2)
C(23)-Mo(2)-C(21)	58.06(15)	C(14)-C(13)-C(12)	108.2(4)
C(9)-Mo(2)-C(22)	104.13(16)	C(14)-C(13)-Mo(1)	70.2(3)
C(25)-Mo(2)-C(22)	58.78(19)	C(12)-C(13)-Mo(1)	74.4(3)
C(24)-Mo(2)-C(22)	59.26(17)	C(15)-C(14)-C(13)	106.6(5)
C(23)-Mo(2)-C(22)	34.62(15)	C(15)-C(14)-Mo(1)	72.0(3)
C(21)-Mo(2)-C(22)	34.66(17)	C(13)-C(14)-Mo(1)	73.9(3)
C(9)-Mo(2)-S(3)	88.11(11)	C(14)-C(15)-C(11)	108.8(5)
C(25)-Mo(2)-S(3)	93.74(15)	C(14)-C(15)-Mo(1)	72.2(2)
C(24)-Mo(2)-S(3)	99.49(12)	C(11)-C(15)-Mo(1)	75.0(3)
C(23)-Mo(2)-S(3)	133.81(12)	C(25)-C(21)-C(22)	108.9(5)
C(21)-Mo(2)-S(3)	121.07(15)	C(25)-C(21)-Mo(2)	69.3(3)
C(22)-Mo(2)-S(3)	152.51(13)	C(22)-C(21)-Mo(2)	74.4(3)
C(9)-Mo(2)-S(1)	147.68(10)	C(23)-C(22)-C(21)	107.4(5)
C(25)-Mo(2)-S(1)	90.53(14)	C(23)-C(22)-Mo(2)	70.5(2)

C(21)-C(22)-Mo(2)	70.9(3)
C(22)-C(23)-C(24)	108.0(4)
C(22)-C(23)-Mo(2)	74.9(2)
C(24)-C(23)-Mo(2)	69.5(2)
C(25)-C(24)-C(23)	106.9(5)
C(25)-C(24)-Mo(2)	71.8(3)
C(23)-C(24)-Mo(2)	73.9(2)
C(24)-C(25)-C(21)	108.8(4)
C(24)-C(25)-Mo(2)	72.3(3)
C(21)-C(25)-Mo(2)	75.3(3)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 2. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
Mo(1)	22(1)	28(1)	16(1)	-1(1)	2(1)	-1(1)
Mo(2)	20(1)	27(1)	18(1)	1(1)	1(1)	-3(1)
S(1)	24(1)	31(1)	25(1)	-3(1)	0(1)	-5(1)
S(2)	22(1)	27(1)	28(1)	-2(1)	5(1)	0(1)
S(3)	20(1)	36(1)	21(1)	-1(1)	3(1)	2(1)
N(1)	31(2)	26(2)	22(2)	3(2)	7(1)	-1(2)
N(2)	30(2)	32(2)	24(2)	-1(2)	0(2)	-2(2)
C(1)	43(3)	38(3)	44(3)	-12(2)	7(2)	-6(2)
C(2)	21(2)	38(3)	36(2)	2(2)	7(2)	-3(2)
C(3)	34(2)	42(3)	29(2)	-3(2)	5(2)	7(2)
C(4)	27(2)	30(2)	17(2)	3(2)	6(2)	3(2)
C(5)	33(2)	24(2)	24(2)	-4(2)	6(2)	-6(2)
C(6)	64(3)	30(3)	29(2)	-1(2)	8(2)	-2(2)
C(7)	41(2)	35(3)	28(2)	2(2)	10(2)	-4(2)
C(8)	34(3)	42(3)	49(3)	-2(2)	-2(2)	-4(2)
C(9)	28(2)	27(2)	16(2)	3(2)	5(2)	2(2)
C(11)	62(3)	49(3)	19(2)	-3(2)	3(2)	-16(3)
C(12)	42(3)	66(4)	21(2)	-3(2)	11(2)	6(3)
C(13)	65(3)	61(4)	16(2)	1(2)	6(2)	-30(3)
C(14)	75(4)	54(4)	20(2)	13(2)	11(2)	26(3)
C(15)	38(3)	69(4)	21(2)	1(2)	-6(2)	4(3)
C(21)	82(4)	35(3)	35(3)	15(2)	-20(3)	-29(3)
C(22)	59(3)	35(3)	33(3)	11(2)	6(2)	8(2)
C(23)	34(2)	39(3)	20(2)	6(2)	-7(2)	-11(2)
C(24)	44(3)	52(3)	25(2)	12(2)	10(2)	7(2)
C(25)	34(3)	76(4)	47(3)	39(3)	-2(2)	-20(3)
O(1)	63(3)	34(2)	102(3)	-5(2)	-32(2)	-2(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 2.

	x	y	z	U(eq)
H(1A)	7615	12565	2437	63
H(1B)	8458	13374	2200	63
H(1C)	8612	12820	3142	63
H(2A)	5648	9187	1079	47
H(2B)	5005	10334	1128	47
H(2C)	5343	9527	1961	47
H(3A)	8316	7434	765	53
H(3B)	9294	7004	1431	53
H(3C)	9370	7492	507	53
H(6A)	6553	5973	309	62
H(6B)	6307	4723	655	62
H(6C)	7382	5287	992	62
H(7A)	7290	5167	2542	52
H(7B)	6227	4549	2289	52
H(7C)	6366	5708	2861	52
H(8A)	4982	6750	1778	65

H(8B)	4797	5610	1187	65
H(8C)	5043	6824	788	65
H(11)	9008	10936	4055	53
H(12)	7334	10079	4056	50
H(13)	7387	7921	3659	57
H(14)	9121	7480	3407	60
H(15)	10102	9372	3651	54
H(21)	8565	12959	647	67
H(22)	6736	12633	-14	51
H(23)	6595	10799	-928	40
H(24)	8367	10007	-834	48
H(25)	9553	11344	163	65
H(1W)	4570(50)	2630(60)	840(40)	110(20)
H(2W)	5520(50)	2510(60)	1460(40)	100(30)

Table 6. Analysis of Potential Hydrogen Bonds in 2
 $d(D...A) < R(D)+R(A)+0.50$, $d(H...A) < R(H)+R(A)-0.12$ Ang., $D-H...A > 100.0$ Deg

Nr	Typ	Res Donor	H...Acceptor [ARU]	D-H	H...A	D...A	D-H...A
1	2	O(1) - H(1W) .. N(2)	[3665.01]	0.98(6)	1.90(7)	2.868(5)	170(6)
2	2	O(1) - H(2W) .. S(2)	[1545.01]	0.86(7)	2.57(7)	3.415(5)	170(6)
3	Intra	1 C(1) - H(1A) .. S(2) []		0.9599	2.5360	3.183(5)	124.78
4	1	C(7) - H(7B) .. O(1) []		0.9602	2.5780	3.448(6)	150.80

[1545.] = x,-1+y,z

[3665.] = 1-x,1-y,-z

Table 7. Crystal data and structure refinement for 3.

Identification code	km3700	
Empirical formula	$C_{23}H_{16}Mo_2N_2S_3$	
Formula weight	628.60	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	$a = 10.16780(1)$ Å	$\beta = 92.535(1)^\circ$
	$b = 20.0542(3)$ Å	
	$c = 12.4313(2)$ Å	
Volume	$2532.35(6)$ Å ³	
Z	4	
Density (calculated)	1.649 Mg/m ³	
Absorption coefficient	1.251 mm ⁻¹	
F(000)	1280	
Crystal size	0.40 x 0.20 x 0.20 mm ³	
Theta range for data collection	3.25 to 30.04°	
Index ranges	$-14 \leq h \leq 14$, $-18 \leq k \leq 28$, $-17 \leq l \leq 17$	
Reflections collected	22281	
Independent reflections	7337 [R(int) = 0.024]	
Completeness to theta = 30.04°	98.9 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7337 / 0 / 279	
Goodness-of-fit on F ²	1.034	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0229, wR2 = 0.0505	
R indices (all data)	R1 = 0.0281, wR2 = 0.0522	
Largest diff. peak and hole	0.78 and -0.59 e.Å ⁻³	

Figure 2. A view of a molecule of 3 showing 20% probability ellipsoids.

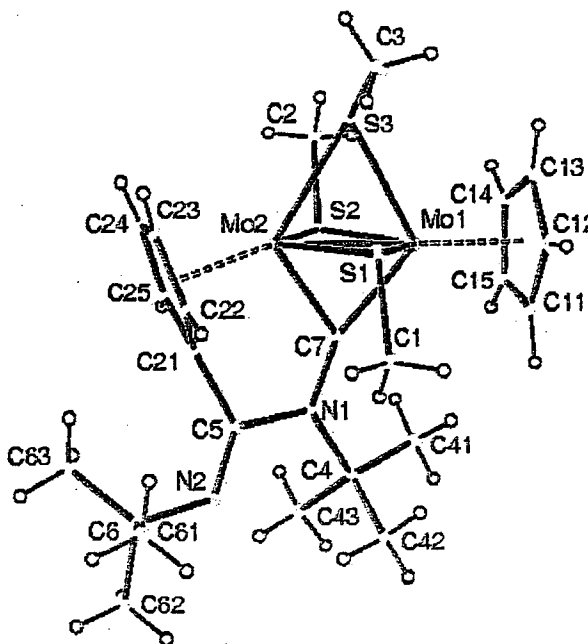


Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^i tensor.

	x	y	z	$U(\text{eq})$
Mo(1)	2135(1)	2813(1)	7797(1)	9(1)
Mo(2)	-355(1)	2610(1)	7974(1)	8(1)
S(1)	1214(1)	2572(1)	9542(1)	13(1)
S(2)	586(1)	2904(1)	6227(1)	13(1)
S(3)	626(1)	3754(1)	8184(1)	15(1)
N(1)	720(1)	1288(1)	7333(1)	11(1)
N(2)	-778(1)	439(1)	7736(1)	15(1)
C(1)	1571(2)	1719(1)	9955(1)	18(1)
C(2)	354(2)	3749(1)	5679(2)	22(1)
C(3)	790(2)	4094(1)	9547(2)	27(1)
C(4)	1655(2)	797(1)	6840(1)	15(1)
C(5)	-558(2)	1055(1)	7641(1)	11(1)
C(6)	-2043(2)	140(1)	8028(2)	17(1)
C(7)	996(2)	1937(1)	7570(1)	10(1)
C(11)	4268(2)	2409(1)	7920(2)	19(1)
C(12)	4249(2)	2933(1)	8677(1)	20(1)
C(13)	3954(2)	3530(1)	8130(1)	19(1)
C(14)	3781(2)	3385(1)	7012(1)	16(1)
C(15)	3987(2)	2685(1)	6872(1)	16(1)
C(21)	-1443(2)	1629(1)	7855(1)	11(1)
C(22)	-1721(2)	1902(1)	8878(1)	13(1)
C(23)	-2426(2)	2505(1)	8719(1)	15(1)
C(24)	-2613(2)	2606(1)	7585(1)	15(1)
C(25)	-2019(2)	2062(1)	7056(1)	13(1)
C(41)	2780(2)	1177(1)	6351(2)	28(1)
C(42)	2219(2)	319(1)	7703(2)	21(1)
C(43)	925(2)	424(1)	5916(1)	23(1)
C(61)	-2005(2)	69(1)	9258(2)	24(1)
C(62)	-2051(2)	-555(1)	7516(2)	25(1)
C(63)	-3299(2)	504(1)	7631(2)	23(1)

Table 9. Bond lengths [Å] and angles [°] for 3.

Mo(1)-C(7)	2.1169(16)	N(1)-C(7)	1.361(2)
Mo(1)-C(15)	2.2642(16)	N(1)-C(5)	1.448(2)
Mo(1)-C(14)	2.2831(16)	N(1)-C(4)	1.516(2)
Mo(1)-C(11)	2.3138(17)	N(2)-C(5)	1.263(2)
Mo(1)-C(13)	2.3651(17)	N(2)-C(6)	1.479(2)
Mo(1)-C(12)	2.3800(17)	C(4)-C(41)	1.523(3)
Mo(1)-S(1)	2.4482(4)	C(4)-C(42)	1.531(3)
Mo(1)-S(2)	2.4606(4)	C(4)-C(43)	1.534(2)
Mo(1)-S(3)	2.4926(4)	C(5)-C(21)	1.492(2)
Mo(1)-Mo(2)	2.58361(18)	C(6)-C(62)	1.532(3)
Mo(2)-C(7)	2.0061(16)	C(6)-C(61)	1.535(3)
Mo(2)-C(21)	2.2582(16)	C(6)-C(63)	1.533(2)
Mo(2)-C(25)	2.2804(16)	C(11)-C(12)	1.411(3)
Mo(2)-C(22)	2.3124(16)	C(11)-C(15)	1.432(3)
Mo(2)-C(24)	2.3249(16)	C(12)-C(13)	1.403(3)
Mo(2)-C(23)	2.3468(16)	C(13)-C(14)	1.423(2)
Mo(2)-S(1)	2.4650(4)	C(14)-C(15)	1.431(3)
Mo(2)-S(2)	2.4830(4)	C(21)-C(22)	1.424(2)
Mo(2)-S(3)	2.5107(4)	C(21)-C(25)	1.425(2)
S(1)-C(1)	1.8168(19)	C(22)-C(23)	1.415(2)
S(2)-C(2)	1.8378(19)	C(23)-C(24)	1.429(2)
S(3)-C(3)	1.8267(19)	C(24)-C(25)	1.423(2)
C(7)-Mo(1)-C(15)	107.50(6)	C(11)-Mo(1)-S(3)	146.67(5)
C(7)-Mo(1)-C(14)	140.10(6)	C(13)-Mo(1)-S(3)	89.37(5)
C(15)-Mo(1)-C(14)	36.69(6)	C(12)-Mo(1)-S(3)	112.70(5)
C(7)-Mo(1)-C(11)	102.96(7)	S(1)-Mo(1)-S(3)	73.490(15)
C(15)-Mo(1)-C(11)	36.43(6)	S(2)-Mo(1)-S(3)	73.687(15)
C(14)-Mo(1)-C(11)	60.09(7)	C(7)-Mo(1)-Mo(2)	49.31(4)
C(7)-Mo(1)-C(13)	161.33(6)	C(15)-Mo(1)-Mo(2)	149.95(5)
C(15)-Mo(1)-C(13)	59.75(6)	C(14)-Mo(1)-Mo(2)	148.75(5)
C(14)-Mo(1)-C(13)	35.61(6)	C(11)-Mo(1)-Mo(2)	149.18(5)
C(11)-Mo(1)-C(13)	58.52(7)	C(13)-Mo(1)-Mo(2)	147.43(5)
C(7)-Mo(1)-C(12)	128.53(7)	C(12)-Mo(1)-Mo(2)	147.72(4)
C(15)-Mo(1)-C(12)	59.36(6)	S(1)-Mo(1)-Mo(2)	58.592(10)
C(14)-Mo(1)-C(12)	58.79(6)	S(2)-Mo(1)-Mo(2)	58.917(10)
C(11)-Mo(1)-C(12)	34.95(7)	S(3)-Mo(1)-Mo(2)	59.254(11)
C(13)-Mo(1)-C(12)	34.40(7)	C(7)-Mo(2)-C(21)	74.68(6)
C(7)-Mo(1)-S(1)	74.07(4)	C(7)-Mo(2)-C(25)	92.92(6)
C(15)-Mo(1)-S(1)	141.90(5)	C(21)-Mo(2)-C(25)	36.59(6)
C(14)-Mo(1)-S(1)	142.59(5)	C(7)-Mo(2)-C(22)	98.08(6)
C(11)-Mo(1)-S(1)	105.47(5)	C(21)-Mo(2)-C(22)	36.27(6)
C(13)-Mo(1)-S(1)	106.98(4)	C(25)-Mo(2)-C(22)	59.92(6)
C(12)-Mo(1)-S(1)	89.20(4)	C(7)-Mo(2)-C(24)	128.78(6)
C(7)-Mo(1)-S(2)	68.18(4)	C(21)-Mo(2)-C(24)	60.48(6)
C(15)-Mo(1)-S(2)	97.06(5)	C(25)-Mo(2)-C(24)	35.98(6)
C(14)-Mo(1)-S(2)	94.52(5)	C(22)-Mo(2)-C(24)	59.35(6)
C(11)-Mo(1)-S(2)	130.04(5)	C(7)-Mo(2)-C(23)	132.42(6)
C(13)-Mo(1)-S(2)	124.19(5)	C(21)-Mo(2)-C(23)	60.16(6)
C(12)-Mo(1)-S(2)	152.92(5)	C(25)-Mo(2)-C(23)	59.73(6)
S(1)-Mo(1)-S(2)	117.456(14)	C(22)-Mo(2)-C(23)	35.36(6)
C(7)-Mo(1)-S(3)	108.44(4)	C(24)-Mo(2)-C(23)	35.62(6)
C(15)-Mo(1)-S(3)	135.79(5)	C(7)-Mo(2)-S(1)	75.54(4)
C(14)-Mo(1)-S(3)	99.85(5)	C(21)-Mo(2)-S(1)	108.79(4)

C(25)-Mo(2)-S(1)	145.10(4)	N(1)-C(7)-Mo(2)	124.15(11)
C(22)-Mo(2)-S(1)	88.74(4)	N(1)-C(7)-Mo(1)	158.29(12)
C(24)-Mo(2)-S(1)	139.72(4)	Mo(2)-C(7)-Mo(1)	77.55(6)
C(23)-Mo(2)-S(1)	104.21(4)	C(12)-C(11)-C(15)	108.14(17)
C(7)-Mo(2)-S(2)	69.27(4)	C(12)-C(11)-Mo(1)	75.09(10)
C(21)-Mo(2)-S(2)	110.88(4)	C(15)-C(11)-Mo(1)	69.90(10)
C(25)-Mo(2)-S(2)	89.03(4)	C(13)-C(12)-C(11)	108.74(16)
C(22)-Mo(2)-S(2)	146.52(4)	C(13)-C(12)-Mo(1)	72.22(10)
C(24)-Mo(2)-S(2)	103.56(4)	C(11)-C(12)-Mo(1)	69.96(10)
C(23)-Mo(2)-S(2)	138.95(5)	C(12)-C(13)-C(14)	108.23(17)
S(1)-Mo(2)-S(2)	115.976(14)	C(12)-C(13)-Mo(1)	73.38(10)
C(7)-Mo(2)-S(3)	111.58(5)	C(14)-C(13)-Mo(1)	69.05(9)
C(21)-Mo(2)-S(3)	173.68(4)	C(13)-C(14)-C(15)	107.88(16)
C(25)-Mo(2)-S(3)	140.85(4)	C(13)-C(14)-Mo(1)	75.34(10)
C(22)-Mo(2)-S(3)	139.03(4)	C(15)-C(14)-Mo(1)	70.94(9)
C(24)-Mo(2)-S(3)	114.15(4)	C(11)-C(15)-C(14)	107.01(16)
C(23)-Mo(2)-S(3)	113.59(4)	C(11)-C(15)-Mo(1)	73.67(10)
S(1)-Mo(2)-S(3)	72.891(15)	C(14)-C(15)-Mo(1)	72.37(9)
S(2)-Mo(2)-S(3)	72.994(14)	C(22)-C(21)-C(25)	107.27(14)
C(7)-Mo(2)-Mo(1)	53.14(5)	C(22)-C(21)-C(5)	126.91(14)
C(21)-Mo(2)-Mo(1)	127.62(4)	C(25)-C(21)-C(5)	125.30(14)
C(25)-Mo(2)-Mo(1)	137.85(4)	C(22)-C(21)-Mo(2)	73.94(9)
C(22)-Mo(2)-Mo(1)	138.57(4)	C(25)-C(21)-Mo(2)	72.55(9)
C(24)-Mo(2)-Mo(1)	160.98(4)	C(5)-C(21)-Mo(2)	112.72(10)
C(23)-Mo(2)-Mo(1)	161.32(4)	C(23)-C(22)-C(21)	108.87(14)
S(1)-Mo(2)-Mo(1)	57.958(10)	C(23)-C(22)-Mo(2)	73.65(9)
S(2)-Mo(2)-Mo(1)	58.069(10)	C(21)-C(22)-Mo(2)	69.79(9)
S(3)-Mo(2)-Mo(1)	58.567(10)	C(22)-C(23)-C(24)	107.64(15)
C(1)-S(1)-Mo(1)	110.91(6)	C(22)-C(23)-Mo(2)	70.99(9)
C(1)-S(1)-Mo(2)	111.54(6)	C(24)-C(23)-Mo(2)	71.35(9)
Mo(1)-S(1)-Mo(2)	63.450(10)	C(25)-C(24)-C(23)	107.84(15)
C(2)-S(2)-Mo(1)	115.45(7)	C(25)-C(24)-Mo(2)	70.31(9)
C(2)-S(2)-Mo(2)	119.63(6)	C(23)-C(24)-Mo(2)	73.02(9)
Mo(1)-S(2)-Mo(2)	63.014(10)	C(24)-C(25)-C(21)	108.35(14)
C(3)-S(3)-Mo(1)	115.49(8)	C(24)-C(25)-Mo(2)	73.72(9)
C(3)-S(3)-Mo(2)	117.22(7)	C(21)-C(25)-Mo(2)	70.86(9)
Mo(1)-S(3)-Mo(2)	62.179(11)		
C(7)-N(1)-C(5)	115.40(13)		
C(7)-N(1)-C(4)	125.54(13)		
C(5)-N(1)-C(4)	118.97(13)		
C(5)-N(2)-C(6)	125.36(15)		
N(1)-C(4)-C(41)	109.40(14)		
N(1)-C(4)-C(42)	110.24(13)		
C(41)-C(4)-C(42)	109.13(16)		
N(1)-C(4)-C(43)	109.11(14)		
C(41)-C(4)-C(43)	106.96(15)		
C(42)-C(4)-C(43)	111.92(15)		
N(2)-C(5)-N(1)	120.28(15)		
N(2)-C(5)-C(21)	128.90(15)		
N(1)-C(5)-C(21)	110.76(13)		
N(2)-C(6)-C(62)	104.80(14)		
N(2)-C(6)-C(61)	107.33(14)		
C(62)-C(6)-C(61)	109.18(16)		
N(2)-C(6)-C(63)	116.74(15)		
C(62)-C(6)-C(63)	108.08(15)		
C(61)-C(6)-C(63)	110.42(16)		

Table 10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mo(1)	7(1)	11(1)	11(1)	0(1)	2(1)	-1(1)
Mo(2)	6(1)	8(1)	11(1)	0(1)	1(1)	0(1)
S(1)	11(1)	17(1)	10(1)	-1(1)	1(1)	-2(1)
S(2)	12(1)	17(1)	12(1)	2(1)	1(1)	-1(1)
S(3)	13(1)	10(1)	22(1)	-2(1)	5(1)	-1(1)
N(1)	11(1)	10(1)	14(1)	-1(1)	3(1)	0(1)
N(2)	12(1)	12(1)	20(1)	1(1)	1(1)	-1(1)
C(1)	18(1)	22(1)	15(1)	7(1)	0(1)	3(1)
C(2)	20(1)	24(1)	23(1)	12(1)	2(1)	2(1)
C(3)	31(1)	21(1)	30(1)	-13(1)	13(1)	-9(1)
C(4)	16(1)	13(1)	18(1)	-4(1)	6(1)	2(1)
C(5)	10(1)	13(1)	11(1)	-1(1)	0(1)	-1(1)
C(6)	14(1)	11(1)	26(1)	2(1)	3(1)	-2(1)
C(7)	10(1)	12(1)	9(1)	1(1)	1(1)	1(1)
C(11)	7(1)	23(1)	28(1)	5(1)	3(1)	2(1)
C(12)	7(1)	35(1)	19(1)	2(1)	0(1)	-5(1)
C(13)	11(1)	24(1)	22(1)	-5(1)	3(1)	-7(1)
C(14)	12(1)	20(1)	18(1)	3(1)	4(1)	-4(1)
C(15)	10(1)	20(1)	19(1)	-1(1)	5(1)	-2(1)
C(21)	8(1)	11(1)	14(1)	1(1)	1(1)	-3(1)
C(22)	10(1)	14(1)	14(1)	1(1)	3(1)	-4(1)
C(23)	9(1)	17(1)	20(1)	-3(1)	6(1)	-2(1)
C(24)	9(1)	13(1)	22(1)	2(1)	0(1)	1(1)
C(25)	11(1)	14(1)	15(1)	1(1)	-2(1)	-2(1)
C(41)	27(1)	19(1)	40(1)	-6(1)	23(1)	-1(1)
C(42)	19(1)	19(1)	24(1)	-3(1)	0(1)	8(1)
C(43)	30(1)	21(1)	18(1)	-6(1)	2(1)	4(1)
C(61)	24(1)	22(1)	27(1)	5(1)	5(1)	-6(1)
C(62)	20(1)	15(1)	40(1)	-2(1)	6(1)	-6(1)
C(63)	13(1)	17(1)	38(1)	4(1)	-1(1)	-4(1)

Table 11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for three.

	x	y	z	U(eq)
H(1A)	1572	1437	9330	27
H(1B)	910	1568	10426	27
H(1C)	2418	1702	10325	27
H(2A)	303	4062	6261	33
H(2B)	-447	3765	5241	33
H(2C)	1083	3862	5249	33
H(3A)	637	3747	10059	41
H(3B)	157	4444	9625	41
H(3C)	1661	4270	9672	41
H(11)	4435	1962	8074	23
H(12)	4405	2889	9416	24
H(13)	3885	3949	8444	23
H(14)	3571	3691	6469	20
H(15)	3947	2453	6224	19
H(22)	-1479	1714	9542	15
H(23)	-2714	2785	9256	18
H(24)	-3046	2964	7252	18
H(25)	-2008	1999	6315	16
H(41A)	2428	1514	5872	42
H(41B)	3310	873	5959	42
H(41C)	3313	1383	6915	42
H(42A)	2705	568	8247	32
H(42B)	2794	5	7378	32
H(42C)	1513	84	8023	32
H(43A)	240	156	6199	34
H(43B)	1533	144	5558	34
H(43C)	547	741	5412	34
H(61A)	-1218	-162	9494	36
H(61B)	-2760	-178	9468	36
H(61C)	-2013	503	9582	36
H(62A)	-2070	-512	6746	37
H(62B)	-2816	-794	7725	37
H(62C)	-1273	-792	7757	37
H(63A)	-3394	907	8037	34
H(63B)	-4048	222	7726	34
H(63C)	-3242	611	6882	34