

## Sodium Diplatinum

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**Abstract.** NaPt<sub>2</sub>,  $M_r = 413.17$ , cubic,  $Fd\bar{3}m$ ,  $a = 7.482(2)$  Å,  $V = 418.8$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 13.1$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 13.4$  cm<sup>-1</sup>,  $F(000) = 1336$ ,  $T = 295$  K. The structure was refined to  $R = 0.034$ ,  $wR = 0.023$  for 132 absorption-corrected observed reflections. NaPt<sub>2</sub> has the cubic MgCu<sub>2</sub> ( $C_{15}$ )-type structure. The Pt–Pt distances (2.645 Å) are significantly shorter than in metallic platinum (2.774 Å).

**Experimental.** During the preparation of alkali-metal-noble-metal alloys difficulties arise from the relatively low boiling points of the alkali metals compared with the high melting temperatures of the noble metals (Loebich & Raub, 1981). As a consequence, most of these alloys are known only in microcrystalline form. The difficulties can be overcome by synthesis in a closed high-pressure system. This has recently been demonstrated in the case of KAu<sub>2</sub> (Range, Rau & Klement, 1988). In a similar way, single crystals of NaPt<sub>2</sub> could now be obtained for the first time. The experiments were carried out in a modified Belt-type high-pressure apparatus (Range & Leeb, 1975) using graphite or pyrophyllite as crucible material and starting with 4:1 mixtures of Na and Pt. Typical reaction conditions were 4.0 GPa, 1650 K, 30 min, annealing at 1050 K under pressure for another 30 min, and subsequent quenching to ambient conditions. The crystals are not very sensitive to air and moisture. A crystal fragment (approximately  $0.03 \times 0.03 \times 0.03$  mm) was used for data collection on an Enraf-Nonius CAD-4 diffractometer (Mo  $K\alpha$ , graphite monochromator). Intensities measured for  $2 \leq \theta \leq 50^\circ$ ;  $\omega$ - $2\theta$  scan technique, scan width ( $0.9 + 0.34 \tan \theta$ )°. Lattice parameters were refined from  $2\theta$  values of 25 reflections in the range  $9.4$ – $39.6^\circ$ . An experimental correction for absorption was applied based on  $\psi$  scans; transmission factors varied between 79 and 99%. Three standard reflections indicated no loss of intensity throughout data collection. Merging of the 2266 collected intensities [ $(\sin \theta)_{\max} / \lambda = 1.078$  Å<sup>-1</sup>;  $-16 \leq h \leq 16$ ,  $-16 \leq k \leq 16$ ,  $-16 \leq l \leq 16$ ] gave 132 unique

Table 1. Atomic coordinates and equivalent isotropic temperature factors (Å<sup>2</sup>)

$$B_{\text{eq}} = \frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Na	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	0.49 (5)
Pt	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0.151 (2)

Origin at centre ( $\bar{3}m$ ).

Table 2. Interatomic distances (Å)

Na–Pt	3.102 (2) (× 12)	Pt–Pt	2.645 (2) (× 6)
–Na	3.240 (2) (× 4)	–Na	3.102 (2) (× 6)

observed reflections ( $R_{\text{int}} = 0.054$ ) which were used for all calculations (program system *SDP*; Enraf–Nonius, 1988).

The structure was solved by routine direct methods. In the least-squares refinement  $|F|$  magnitudes were used to refine occupation factors, anisotropic temperature factors, and an extinction parameter. Convergence was obtained after a few cycles with SOF's for Na and Pt corresponding to the stoichiometry NaPt<sub>2</sub> within two standard deviations. Consequently, the SOF's were fixed again at 100% before performing the final anisotropic refinement. Final  $R = 0.034$ ,  $wR = 0.023$  (including all reflections),  $w^{-1} = \sigma^2(F)$ ,  $(\Delta/\sigma)_{\max} < 0.001$  in final refinement cycle, five parameters,  $S = 0.600$ . Max. features in the final  $\Delta\rho$  map  $+2.5$ ,  $-1.8$  e Å<sup>-3</sup>. Atomic scattering factors and  $f'$ ,  $f''$  values set by *SDP* program. Bond distances and angles were calculated using the program *SADIAN* (Baur & Wenninger, 1969). Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1, derived bond distances in Table 2.† NaPt<sub>2</sub> crystallizes with the cubic MgCu<sub>2</sub> ( $C_{15}$ )-type structure

† Lists of structure factors, anisotropic thermal parameters and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51726 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Friauf, 1927). The Pt–Pt distances (2.645 Å) are significantly shorter than in metallic platinum (2.774 Å).

**Related literature.** For a tentative phase diagram of the Na–Pt system, based on data given by Loebich & Raub (1981), see Moffatt (1984). The composition of the cubic 1:2 phase was erroneously given as Na<sub>2</sub>Pt in Massalski (1986). The present single-crystal study confirms the MgCu<sub>2</sub>-type structure for NaPt<sub>2</sub>, derived earlier from inconclusive powder diffraction data (Nash, Boyden & Wittig, 1960; Loebich & Raub, 1981).

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## Structure of 2,3,4- $\mu_3$ -Bromo-1,2,3;1,3,4;1,2,4-tri- $\mu_3$ -sulfido-tris[(triphenylphosphine)copper](oxomolybdenum)(3 Cu–Mo)

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**Abstract.** [MoCu<sub>3</sub>Br(O)S<sub>3</sub>{P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}]<sub>3</sub>,  $M_r = 1265$ , triclinic,  $P\bar{1}$ ,  $a = 11.804$  (5),  $b = 13.049$  (4),  $c = 20.406$  (3) Å,  $\alpha = 74.84$  (2),  $\beta = 84.41$  (2),  $\gamma = 63.85$  (3)°,  $V = 2722.7$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.54$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 22.6$  cm<sup>-1</sup>,  $F(000) = 1268$ ,  $T = 296$  K,  $R = 0.064$  for 2890 unique observed reflections with  $I > 3\sigma(I)$ . The Mo atom is tetrahedrally coordinated by three  $\mu_3$ -S atoms and an O atom, and all three Cu atoms are also tetrahedrally coordinated by two  $\mu_3$ -S atoms, a P atom and a Br atom. The bond lengths of Cu– $\mu_3$ -Br (av. 2.791 Å) are much longer than Mo– $\mu_3$ -S (av. 2.256 Å) and Cu– $\mu_3$ -S (av. 2.284 Å), so that the cubane-like core (MoCu<sub>3</sub>-S<sub>3</sub>Br) is distorted. There are three metal–metal bonds with the following bond lengths: Mo–Cu(1) 2.708, Mo–Cu(2) 2.705, Mo–Cu(3) 2.737 Å.

**Experimental.** Crystals of the title compound were prepared by allowing [NMe<sub>4</sub>]<sub>2</sub>[Mo<sub>2</sub>O<sub>2</sub>S(S<sub>2</sub>)<sub>4</sub>].CH<sub>3</sub>CN to react with CuBr and PPh<sub>3</sub> (Wu, Lu, Zhu, Wu & Lu, 1987). Crystal 0.25 × 0.20 × 0.25 mm. Data were collected on a CAD-4  $\kappa$ -geometry diffractometer using Mo  $K\alpha$  radiation.  $\omega/2\theta$  scan, scan speed varied from 3 to 5° min<sup>-1</sup> (in  $\omega$ ), the scan width was 0.60° +

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0.35° tan $\theta$ . Cell constants were obtained by least-squares fit to 25 diffractions' maxima. The intensities were corrected for absorption using empirical scan data (maximum and minimum transmission factors 1.00 and 0.83 respectively) and Lorentz and polarization factors to give a total of 9398 intensities, up to a maximum  $2\theta$  of 50° ( $-14 < h < 14$ ,  $-15 < k < 15$ ,  $0 \leq l < 24$ ). Max.  $(\sin\theta)/\lambda = 0.59$  Å<sup>-1</sup>, 5991 reflections with  $I < 3\sigma(I)$  were considered unobserved. 2890 reflections with  $I > 3\sigma(I)$  and max.  $(\sin\theta)/\lambda = 0.50$  Å<sup>-1</sup> were used

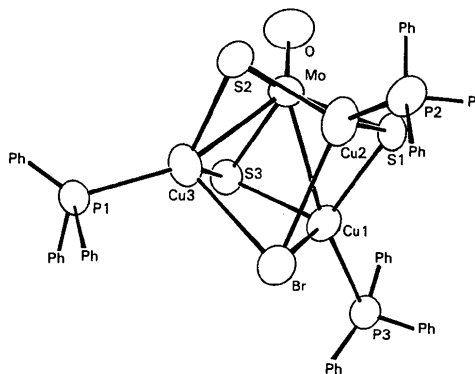


Fig. 1. The configuration of the cluster core of [(MoCu<sub>3</sub>S<sub>3</sub>Br)(O)(PPh<sub>3</sub>)<sub>3</sub>].

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