

08.2-53 SYNTHESSES AND CRYSTAL STRUCTURES OF ANILINIUM  $\beta$ -OCTAMOLYBDATEs. By J. M. Gutiérrez-Zorrilla<sup>a</sup>, P. Román<sup>a</sup>, C. Esteban-Calderón<sup>b</sup>, M. Martínez-Ripoll<sup>b</sup> and S. García-Blanco<sup>b</sup>. a) Dept. Química (Inorgánica) Univ. del País Vasco, Aptdo. 644, Bilbao, Spain, b) Dept. Rayos X, Instituto Rocasolano CSIC, Serrano 119, Madrid-6, Spain.

Anilinium  $\beta$ -octamolybdates have been prepared in acidic aqueous solutions (pH=2.5) through:



B = aniline (i), N-methylaniline (ii), N,N-dimethylaniline (iii), N-ethylaniline (iv) and N,N-diethylaniline (v).

Single crystals of all these compounds have been obtained.

Crystal data for (i) are:  $(\text{C}_6\text{H}_5\text{N})_4\text{Mo}_8\text{O}_{26} \cdot \text{H}_2\text{O}$   $a = 10.007(1)$ ,  $b = 8.014(2)$ ,  $c = 14.645(8)$  Å,  $\alpha = 109.81(3)$ ,  $\beta = 108.59(4)$ ,  $\gamma = 85.44(2)^\circ$ ,  $V = 1052.9(6)$  Å<sup>3</sup>,  $Z = 1$ ,  $P1$ ,  $D_0 = 2.49$ ,  $D_x = 2.49 \text{ g cm}^{-3}$ ,  $R = 0.026$ ,  $wR = 0.031$  for 5297 observed reflexions. The structure is built up of  $\beta$ - $(\text{Mo}_8\text{O}_{26})^{4-}$  isolated anions linked to the anilinium cations and water molecules by hydrogen bonds of type N-H...O and O-H...O.

Thermal decomposition of (i) occurs in three steps, the final product being  $\text{MoO}_3$ .

Crystal structures of (ii), (iii), (iv) and (v) are in progress.

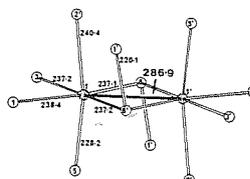
08.2-54 CRYSTAL STRUCTURE OF RUTHENIUM TRIPHOSPHIDE By W.Hönle and H.G. von Schnering, MPI-Fkf, Stuttgart, FRG

In the binary system Ru/P the compounds  $\text{Ru}_2\text{P}$ ,  $\text{RuP}$ ,  $\text{RuP}_2$ , and  $\text{RuP}_3$  are well characterized (B.Aronsson, T.Lundström and S.Rundquist: Borides, Silicides and Phosphides, Methuen, London (1965); W.Jeitschko and D.J.Braun, Acta Crystallogr. B 33,3401(1977)). The preparation of phosphorus rich transition metal phosphides as synthones for ternary superconducting compounds yields from tin melt the new compound  $\text{RuP}_3$ . Crystal structure determination: single crystal, 4-circle diffractometer, 1107 hkl,  $R=3.9\%$ , space group  $P\bar{1}$ ;  $Z=4$ ;  $a=592.5(3)$  pm;  $b=821.3(6)$  pm;  $c=586.6(3)$  pm;  $\alpha=112.35(4)^\circ$ ;  $\beta=107.41(4)^\circ$ ;  $\gamma=98.19(5)^\circ$ .

Atom	x	y	z	U(eq) [pm <sup>2</sup> ]
Ru1	0.06941(9)	0.37246(8)	0.6002(1)	60(6)
Ru2	0.36664(9)	-0.04374(8)	-0.7667(1)	59(5)
P1	0.2179(3)	0.3433(3)	0.0038(4)	82(8)
P2	0.6626(3)	0.2346(3)	0.5558(4)	69(8)
P3	0.0528(3)	0.0594(3)	0.3767(4)	91(9)
P4	0.3168(3)	0.0860(3)	-0.0661(4)	75(8)
P5	0.4703(3)	0.4468(3)	0.6411(4)	81(9)
P6	0.9175(3)	0.3194(3)	0.1478(4)	77(9)

Main structural units are edge sharing  $\text{RuP}_6$  octahedra forming dinuclear  $\text{Ru}_2\text{P}_{10}$  units (Fig.). These units are condensed into chains via trans edges along the c-direction. A second kind of these units connects the chains via adjacent corners. The phosphorus atom network is

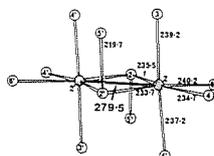
built up of  $[\text{P}_6]^{6-}$  puckered branched chains, containing formally charged P atoms  $\text{P}^{\circ}$  (1,5),  $\text{P}^-$  (3,4), and  $\text{P}^{2-}$  (2,6). Remarkable feature of the structure is the short Ru-Ru bonds (279.5 and 286.9 pm), which are in agreement with the diamagnetism and the semiconducting properties of the compound. The P-P distances are in the range of 218 to 223 pm. For the Ru-P distances cf. the figure.



$\text{RuP}_3$ : building units

Ru atoms dotted, P atoms open circles. The numbers in the circles correspond to the atomic label. The

Ru-Ru bonds are indicated by a bold line.



08.2-55 THE CRYSTAL STRUCTURE OF THE TECHNETIUM POLYARSENIDE  $\text{Tc}_2\text{As}_3$ . By L.H. Dietrich and W. Jeitschko, Anorganisch-Chemisches Institut, Universität Münster, D-4400 Münster, West Germany.

The crystal structure of the new compound  $\text{Tc}_2\text{As}_3$  has been determined from single crystal X ray data. It has triclinic symmetry, space group  $P\bar{1}$ . The lattice constants were refined from Guinier powder data:  $a = 6.575(2)$  Å,  $b = 6.631(2)$  Å,  $c = 8.019(3)$  Å,  $\alpha = 95.70(2)^\circ$ ,  $\beta = 101.99(2)^\circ$ ,  $\gamma = 104.28(2)^\circ$ ,  $V = 327.2$  Å<sup>3</sup> with  $Z = 4$  formula units per cell. The structure was determined by direct and Fourier methods and refined to an R value of 0.051 for 92 variable parameters and 2323 unique structure factors. The Tc atoms are all in distorted octahedral coordination of As atoms with Tc-As distances varying between 2.44 and 2.70 Å. All As atoms have four Tc neighbors. For two of the crystallographically independent As sites these four Tc atoms form a very distorted tetrahedron with bond angles varying between 70 and 138°. The other four As atoms have one additional As neighbor each at distances varying between 2.45 and 2.75 Å. The four Tc neighbors of the As atoms with the short As-As bond of 2.45 Å form the (distorted) square base of a pyramid with the As neighbor at the apex. Thus one may assume that one d state of these pentacoordinated As atoms is participating in the bonding ("sp<sup>3</sup>d hybrid"). If two-electron bonds are assumed for all short near neighbor interactions the Tc atoms obtain approximately d<sup>2</sup> systems. This also depends on how one counts the As-As interactions of 2.65 and 2.75 Å. In addition to the bonding interactions described above, considerable Tc-Tc bonding may be assumed from the way the coordination polyhedra are distorted. Each Tc atom has four Tc neighbors at distances ranging from 2.84 to 3.17 Å. These Tc-Tc bonds may be considered as the reason for the small "tetrahedral" bond angles Tc-As-Tc of down to 70° mentioned above.