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The Crystal Structure of Tetraphenylphosphonium Bis(tetrathiomolybdato)nickelate(II)

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The crystal structure of tetraphenylphosphonium bis(tetrathiomolybdato)nickelate(II), $[P(C_6H_5)_4]_2[Ni(MoS_4)_2]$, has been determined by three-dimensional X-ray methods. The crystals are triclinic with unit cell dimensions $a=12.60(3)$ Å, $b=12.75(3)$ Å, $c=9.41(2)$ Å, $\alpha=113.3(3)°$, $\beta=96.4(3)°$, $\gamma=108.5(3)°$ and space group $P\bar{1}$. The structure was refined by full-matrix least-squares procedures to an R factor of 0.074 using 3867 independent, statistically significant reflections collected on an automatic diffractometer. The nickel atom has planar coordination, and the molybdenum atom has distorted tetrahedral coordination. In the NiS_2Mo ring the Ni – S and the Mo – S distances are all 2.23 Å. Outside the ring the Mo – S distances are 2.15 Å. The NiS_2 and MoS_2 planes are inclined at 169°. The Ni – Mo contact of 2.80 Å is rationalized in terms of the constraint and not in terms of a metal-metal interaction.

Thioanions of the type MS_4^{2-}, M = Mo or W, are known to form complexes, $M'(MS_4)^{2-}$, with ions of the first transition series. The complexes can be isolated in the form of tetraphenylphosphonium salts. For the $Ni(MS_4)_2^{2-}$ complex Müller [1] suggests a planar coordination of the Ni atom and a tetrahedral arrangement for the MS_4 group. Recently [2] the crystal structures of two trinuclear complexes, $\{[(\pi\text{-}C_5H_5)_2M(SCH_3)_2]Ni\}^{2+}$, M = Mo and Nb, have been reported. In the Mo-compound the Ni atom has planar coordination and the Ni – Mo contact is 3.39 Å. However, in the Nb complex the Ni atom has tetrahedral coordination and the Ni – Nb contact is short, 2.78 Å, which was rationalized as metal-metal bonding. An X-ray investigation of the compound, $[P(C_6H_5)_4]_2[Ni(MoS_4)_2]$, was carried out in order to see if the tetrahedral coordination of the Mo atom would cause a metal-metal bonding.

EXPERIMENTAL

Preparation. The compound was prepared by Erik Larsen, Chemistry Department I, University of Copenhagen. In order to obtain crystals sufficiently large for an X-ray investigation, 10^{-4} mol of $[P(C_6H_5)_4]_2MoS_4$ were dissolved in acetonitrile and 5×10^{-5} mol of nickel acetate in acetonitrile were added. The operation was carried out in a glove box under nitrogen. Well developed, red-brownish crystals were formed.

X-Ray technique. A crystal of dimensions 0.07 mm × 0.17 mm × 0.20 mm was used. Space group and preliminary unit cell dimensions were obtained from Weissenberg and precession photographs taken with Cu$K\alpha$- and Mo$K\alpha$-radiation. A set of three-dimensional intensity data was collected by a $\theta-2\theta$ scanning technique on a Picker FACS-1 single crystal X-ray diffractometer. Mo$K\alpha$-radiation was selected using a graphite monochromator. Harmonics were excluded by means of a pulse height discriminator. Reflections within a hemisphere of radius $\sin\theta/\lambda=0.707$ Å^{-1} were measured. 3511 of the 7378 independent reflections showed net intensities less than twice their estimated standard deviation and were designated as "unobserved". They were not included in the refinement of the structure.

Computer programmes. A FORTRAN programme [3] evaluated intensities, calculated standard deviations and Lorentz and polarization corrections. The prepolarization of the incident beam was included. No absorption correction was made ($\mu_{Mo}=12.6$ cm^{-1}). The crystal structure analysis computations were performed on an IBM 370/165 computer using the X-Ray crystallographic programme system of Stewart *et al.*[4] and the drawing programme ORTEP written by Johnson.[5] The atomic scattering factors used were for molybdenum and nickel those computed from relativistic Dirac-Slater wave functions [6] and for sulfur, phosphorus and carbon those computed from numerical Hartree-Fock wave functions.[7]

Table 1a. Atomic coordinates. The estimated standard deviations ($\times 10^4$) are given in parentheses. For phosphorus and carbon isotropic temperature parameters, $U(\times 10^2)$ in Å^2 are given. The estimated standard deviations ($\times 10^3$) are given in parentheses.

Atom	x	y	z	U
Ni	0.0000(0)	0.0000(0)	0.0000(0)	
Mo	0.1192(1)	0.2588(1)	0.1629(1)	
S1	0.0512(3)	0.1345(2)	−0.1004(3)	
S2	0.0884(2)	0.1220(2)	0.2614(2)	
S3	0.0220(2)	0.3717(2)	0.2446(3)	
S4	0.3007(2)	0.3760(3)	0.2294(5)	
P	0.3344(2)	0.7493(2)	0.1641(2)	2.9(1)
C1	0.2459(6)	0.6127(7)	−0.0220(9)	3.3(1)
C2	0.2780(8)	0.6048(8)	−0.1634(11)	4.5(2)
C3	0.2137(8)	0.4974(8)	−0.3102(11)	4.6(2)
C4	0.1210(8)	0.4033(9)	−0.3117(11)	4.8(2)
C5	0.0893(8)	0.4114(9)	−0.1717(11)	4.9(2)
C6	0.1529(7)	0.5172(8)	−0.0251(10)	4.1(2)
C7	0.2598(6)	0.7693(7)	0.3198(9)	3.2(1)
C8	0.2410(7)	0.6876(8)	0.3881(10)	4.2(2)
C9	0.1887(8)	0.7086(9)	0.5158(11)	4.9(2)
C10	0.1578(8)	0.8092(9)	0.5729(12)	5.1(2)
C11	0.1761(9)	0.8901(10)	0.5058(13)	5.9(2)
C12	0.2271(8)	0.8702(9)	0.3760(11)	4.9(2)
C13	0.3671(6)	0.8836(6)	0.1305(8)	3.0(1)
C14	0.2778(7)	0.8940(7)	0.0403(10)	3.8(2)
C15	0.2994(7)	1.0055(8)	0.0296(11)	4.5(2)
C16	0.4072(8)	1.1038(8)	0.1098(11)	4.7(2)
C17	0.4954(8)	1.0935(8)	0.1956(10)	4.2(2)
C18	0.4766(7)	0.9825(7)	0.2070(9)	3.4(2)
C19	0.4688(7)	0.7396(7)	0.2330(9)	3.6(2)
C20	0.5195(8)	0.7944(9)	0.3979(11)	4.8(2)
C21	0.6276(9)	0.7946(10)	0.4540(13)	5.8(2)
C22	0.6832(10)	0.7432(11)	0.3450(14)	6.4(3)
C23	0.6337(11)	0.6888(12)	0.1802(15)	6.9(3)
C24	0.5240(9)	0.6837(10)	0.1226(13)	5.7(2)

Table 1b. Anisotropic temperature factor parameters, $U_{ij}(\times 10^4)$ in Å^2. The estimated standard deviations ($\times 10^4$) are given in parentheses.
The form of the temperature factor expression is $\exp[-2\pi^2\sum_{ij}h_ih_ja_i^*a_j^*U_{ij}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	381(07)	280(06)	270(06)	144(05)	75(05)	106(05)
Mo	454(04)	360(03)	426(04)	154(03)	120(03)	137(03)
S1	1023(22)	385(11)	341(11)	156(13)	161(12)	194(10)
S2	614(14)	357(10)	296(09)	174(10)	2(09)	117(08)
S3	481(12)	384(11)	672(15)	231(10)	203(11)	214(10)
S4	430(14)	570(16)	1049(25)	122(12)	234(15)	196(16)

CRYSTAL DATA

Crystal system: triclinic
Unit cell: $a = 12.60(3)$ Å, $b = 12.75(3)$ Å, $c = 9.41(2)$ Å,
$\alpha = 113.3(3)°$, $\beta = 96.4(3)°$, $\gamma = 108.5(3)°$.

$d_{obs} = 1.58$ g/cm^3, $d_{calc} = 1.56$ g/cm^3.
One molecule of $[P(C_6H_5)_4]_2[Ni(MoS_4)_2]$ per unit cell.
No piezoelectric effect could be detected.
Possible space groups: $P1$ and $P\bar{1}$.

STRUCTURE DETERMINATION

Since there is only one formula unit per cell the Ni atom was chosen to lie in the special position (0,0,0). The coordinates of the Mo atom were readily deduced from a three-dimensional Patterson function. The position of the remaining non-hydrogen atoms were derived from successive Fourier syntheses. Least-squares refinement of coordinates and isotropic temperature factor coefficients gave an R factor of 0.08. Further refinement with anisotropic temperature factor parameters for Mo, Ni, and S lowered the R-value to 0.074 ($R_w = 0.082$).

Table 2a. Some interatomic distances in Å. The estimated standard deviations ($\times 10^3$) are given in parentheses.

Ni – Mo	2.798(08)
Ni – S1	2.228(05)
Ni – S2	2.230(07)
Mo – S1	2.222(06)
Mo – S2	2.232(05)
Mo – S3	2.148(05)
Mo – S4	2.153(06)
P – C1	1.806(08)
P – C7	1.804(09)
P – C13	1.792(10)
P – C19	1.806(10)
Mean P – C	1.802(5)
C1 – C2	1.409(14)
C2 – C3	1.410(11)
C3 – C4	1.378(14)
C4 – C5	1.393(16)
C5 – C6	1.400(11)
C6 – C1	1.384(12)
C7 – C8	1.400(15)
C8 – C9	1.407(15)
C9 – C10	1.380(17)
C10 – C11	1.381(20)
C11 – C12	1.414(17)
C12 – C7	1.397(15)
C13 – C14	1.406(14)
C14 – C15	1.406(16)
C15 – C16	1.389(11)
C16 – C17	1.372(16)
C17 – C18	1.408(15)
C18 – C13	1.404(10)
C19 – C20	1.393(13)
C20 – C21	1.404(17)
C21 – C22	1.376(18)
C22 – C23	1.390(18)
C23 – C24	1.400(19)
C24 – C19	1.399(15)
Mean C – C	1.396(4)

Table 2b. Some interatomic angles (°). The estimated standard deviations ($\times 10$) are given in parentheses.

Ni – S1 – Mo	77.9(2)
Ni – S2 – Mo	77.7(2)
S1 – Ni – S2	101.7(2)
S1 – Mo – S2	101.8(2)
S1 – Mo – S3	111.2(2)
S1 – Mo – S4	111.8(2)
S2 – Mo – S3	110.3(2)
S2 – Mo – S4	111.8(2)
S3 – Mo – S4	109.7(2)
C1 – P – C7	111.7(4)
C1 – P – C13	108.8(4)
C1 – P – C19	110.6(4)
C7 – P – C13	108.0(4)
C7 – P – C19	108.8(4)
C13 – P – C19	108.9(4)
Mean C – P – C	109.5(2)
C6 – C1 – C2	121.2(6)
C1 – C2 – C3	118.9(8)
C2 – C3 – C4	119.3(10)
C3 – C4 – C5	121.6(7)
C4 – C5 – C6	119.6(9)
C5 – C6 – C1	119.3(9)
C12 – C7 – C8	121.0(9)
C7 – C8 – C9	119.0(10)
C8 – C9 – C10	120.0(11)
C9 – C10 – C11	121.1(11)
C10 – C11 – C12	120.1(12)
C11 – C12 – C7	118.6(11)
C18 – C13 – C14	120.4(9)
C13 – C14 – C15	119.0(7)
C14 – C15 – C16	119.8(10)
C15 – C16 – C17	121.4(10)
C16 – C17 – C18	120.0(7)
C17 – C18 – C13	119.3(9)
C24 – C19 – C20	120.7(9)
C19 – C20 – C21	119.7(10)
C20 – C21 – C22	119.3(10)
C21 – C22 – C23	121.4(13)
C22 – C23 – C24	119.8(12)
C23 – C24 – C19	118.9(10)
Mean C – C – C	120.0(4)

Unit weights were used. The weights used in the final least-squares refinement were $w = xy$, where, if $0.33F_{obs} > |F_{calc}|$, then $w = 10^{-9}$, else if $\sin\theta > 0.19$, then $x = 1$, else $x = (\sin\theta)/0.19$ and if $50 > F_{obs}$, then $y = 1$, else $y = 50/F_{obs}$. The resulting agreement factor R was unchanged 0.074 ($R_w = 0.082$).

The contributions of the hydrogen atoms were neglected. The space group $P\bar{1}$ was assumed in all calculations. The refinement confirms that this choice is correct. The final positional and thermal vibration parameters

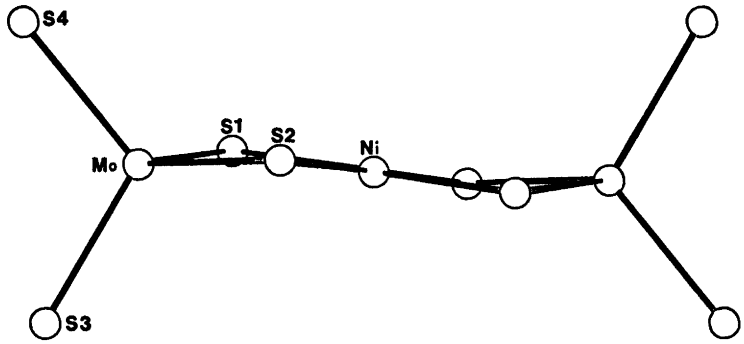

Fig. 1. The $[Ni(MoS_4)_2]^{2-}$ ion.

with their estimated standard deviations are listed in Table 1. Bond distances and angles with their estimated standard deviations are given in Table 2. A list of observed and calculated structure factors may be obtained from the author or the department upon request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystals are built up from isolated anions about symmetry centres and cations in general positions in the cell. In the anion four sulfur atoms form two double bridges between the nickel atom and the two molybdenum atoms (Fig. 1). Each molybdenum atom is coordinated to four sulfur atoms at the corners of a distorted tetrahedron. The NiS_4 group is rigorously planar and the Mo···Ni···Mo system linear owing to the fact that the nickel atom lies at a center of symmetry. The results therefore confirm that the compound has a planar structure around Ni as suggested by Müller.[1] However, the MoS_2NiS_2Mo system is not planar. The molybdenum atoms are displaced 0.26 Å from the NiS_4 plane. The angle between the NiS1S2 plane and the MoS1S2 plane is 169.0° and that between the plane of NiS1Mo and NiS2Mo 171.1°. Within the NiS_2Mo ring there are no significant differences between the Ni–S and Mo–S bonds (Table 2a). The Ni–S distance is that commonly found in other planar NiS_4 complexes.[8] The Mo–S(bridge) distance is somewhat longer and the two Mo–S distances outside the ring are somewhat shorter than 2.18 Å, which is found for the MoS_4^{2-} ion.[9] The coordination polyhedron of the molybdenum is slightly distorted from the tetrahedron because of the small angle in the ring. Therefore all angles involving S1 and S2 are greater than the tetrahedral value while the angle S3–Mo–S4 is equal to it (Table 2b). Neither the two M–S–M angles nor the two S–M–S angles have significantly different values within the fourmembered ring (Table 2b). The obtuse angle at the nickel atom is due to the tetrahedral coordination at the molybdenum atom and to the strain imposed by the planarity of the NiS_4 unit.

The anisotropic mean-square amplitudes of vibration of the two sulfur atoms in the ring are decidedly enlarged in the directions normal to the plane of the ring (Table 1b). Within the ring the Ni-Mo contact is short, 2.798 (0.008) Å. The obtuse angle at the nickel atom makes the dimensions of the NiS_2Mo ring satisfy the Dahl [10] criteria for metal-metal bonding. However, the interaction is perhaps not so substantial as the Ni–Nb bonding in $\{[(\pi\text{-}C_5H_5)_2Nb(SCH_3)_2]_2Ni\}(BF_4)_2.2H_2O$.[2] The two $\{[(\pi\text{-}C_5H_5)_2M(SCH_3)]_2Ni\}^{2+}$-complexes, with M = Mo or Nb are prepared by adding $NiCl_2$ to a solution of $(\pi\text{-}C_5H_5)_2M(SCH_3)_2$. Therefore the compounds would be expected to contain M(IV) and Ni(II). In this case the formal description of the valency state for the Mo-compound will be d^2-d^8-d^2, and for the Nb-compound d^1-d^8-d^1. By transferring one electron from niobium to nickel the situation of fully occupied shells are obtained, d^0-d^{10}-d^0, which is a more favourable state. Since nearly all Ni(0) complexes are tetrahedral molecules, the nickel atom in the above Ni–Nb complex should

Table 3. Least-squares planes for phenyl rings and deviations of the constituent atoms in Å × 10^4. The estimated standard deviations of the atoms from the plane are 0.002 Å for 1, 0.005 Å for 2, 0.009 Å for 3, and 0.013 Å for 4.

Atom	Ring 1	Atom	Ring 2	Atom	Ring 3	Atom	Ring 4
C1	−8	C7	40	C13	91	C19	94
C2	−16	C8	23	C14	−6	C20	71
C3	20	C9	−54	C15	−99	C21	−135
C4	0	C10	24	C16	120	C22	33
C5	−26	C11	38	C17	−33	C23	129
C6	29	C12	−71	C18	−73	C24	−191

have tetrahedral coordination, which the structure determination confirms. In the $\{[(\pi\text{-}C_5H_5)_2Nb(SCH_3)_2]Ni\}^{2+}$ and the $[Ni(MoS_4)_2]^{2-}$ complexes one of the metal ions has a tetrahedral environment. This seems to be enough to make the ring dimensions satisfy the Dahl criteria for metal-metal bonding. The two $[(\pi\text{-}C_5H_5)_2M(SCH_3)_2Ni]^{2+}$-complexes have M−S bond lengths about 2.49 Å while the Mo−S distance in $[Ni(MoS_4)_2]^{2-}$ is only 2.23 Å. In all three compounds the Ni−S bonds are about 2.20 Å. Therefore, the longer Ni−Mo distance in $[(\pi\text{-}C_5H_5)_2Mo(SCH_3)_2Ni]^{2+}$ can be rationalized in terms of small S−M−S angles rather than in terms of an effect from the bond length variation.

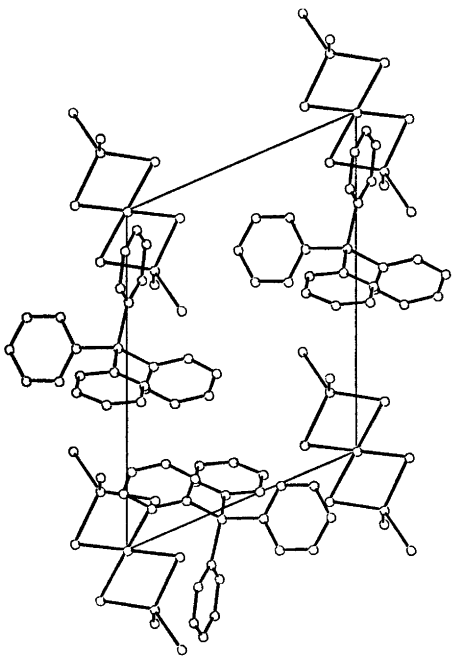

Fig. 2. The projection of the structure viewed perpendicular to the *bc*-plane.

Table 4. The shortest van der Waals distances in Å. The estimated standard deviations (× 10^3) are given in parentheses.

C16−C18 (1−*x*, 2−*y*, −*z*)	3.410(15)
C4−C22 (1−*x*, 1−*y*, −*z*)	3.506(20)
C4−C10 (−*x*, 1−*y*, −*z*)	3.536(15)
S3−C8	3.671(13)
S3−C9	3.711(14)
S3−C5 (−*x*, 1−*y*, −*z*)	3.718(15)
S1−C5	3.743(15)
S3−C10 (−*x*, 1−*y*, 1−*z*)	3.753(14)
S2−C21 (1−*x*, 1−*y*, 1−*z*)	3.784(15)

The bond distances and angles in the tetraphenylphosphonium ion agree with previous studies on structures containing this ion.[11] The angles around the phosphorus atom are close to the tetrahedral value (Table 2b). Average C−C bond lengths are 1.396 Å and average bond angles 120.0°. The least squares planes were calculated for the four rings and, as can be seen from Table 3, all the rings are approximately planar. Plane I (C4−C1−P−C13−C16) and plane II (C10−C7−P−C19−C22) make an angle of 87.1°. The angles between plane I and ring 1 and ring 3 are 45.0 and 41.0° and those between plane II and ring 2 and ring 4 are 56.9 and 20.1°, respectively. Therefore the tetraphenylphosphonium ion does not approximate any symmetrical conformation.

The tetraphenylphosphonium ions are located in the space between the anions (Fig. 2). The cations and the anions are separated by normal van der Waals distances, of which the shortest are shown in Table 4.

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