Synthesis and *X*-Ray Structure of the Tetrameric Molybdenum Complex $[C_{16}H_{13}N_2S_2]^+{}_2[Mo_4Cl_4O_8(OEt)_4]^{2-}$ †

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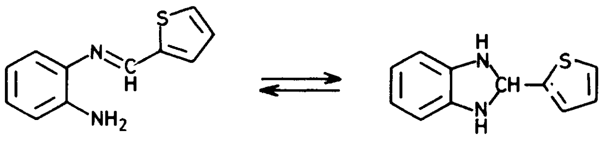
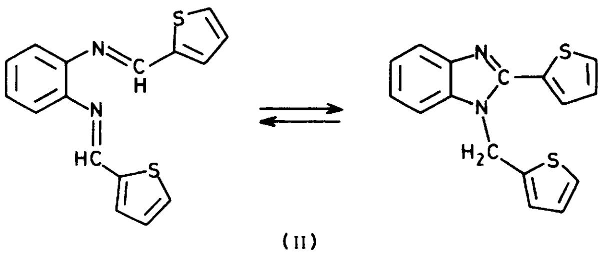
The reactions of $MoCl_5$ with 2-(2′-thienyl)benzimidazole (I) and 2-(2′-thienyl)-1-(2′-thienylmethyl)benzimidazole (II) have been carried out. From the reaction of (I) a molybdenum complex was obtained, which surprisingly was found to contain (II), by *X*-ray diffraction analysis. Crystals of the complex are triclinic, space group $P\bar{1}$, with unit-cell dimensions, a = 10.524(2), b = 14.352(4), c = 10.213(2) Å, α = 95.49(1), β = 100.68(3), γ = 118.79(1)°, Z = 1, and R = 0.076 for 2 129 observed reflections. The structure has been solved by direct methods and refined by least squares. It consists of centrosymmetric tetramers, $[\{MoClO_2(OEt)\}_4]^{2-}$, surrounded by 2-(2′-thienyl)-1-(2′-thienylmethyl)benzimidazolium cations linked to the tetramers through $O \cdots HN^+$ bridges.

In connection with our previous work on the reactivity of molybdenum(V) towards thiol ligands [1] and with our general interest in the biological function of molybdenum, we have investigated the reaction of molybdenum(V) chloride with 2-(2′-thienyl)benzimidazole (I) and 2-(2′-thienyl)-1-(2′-thienylmethyl)benzimidazole (II). Both organic molecules, in the free state, occur in two different forms.



(I)



(II)

While the crystals obtained in the reaction of (II) with $MoCl_5$ were not suitable for an *X*-ray analysis, the compound obtained by a similar reaction using (I) was examined by *X*-ray diffraction. This analysis showed, however, that the organic molecule in the Mo complex was the 2-(2′-thienyl)-1-(2′-thienylmethyl)benzimidazole (II) in the cyclic form. Two independent molybdenum atoms, bonded by oxygen bridges, are present. Crystallographically imposed $\bar{1}$ symmetry causes a tetrameric arrangement. The organic molecule, uncoordinated to metal, is joined to the tetramer through strong hydrogen bonds.

Experimental

Preparation of 2-(2′-*thienyl*)*benzimidazole* (I).—*o*-Phenylenediamine and thiophen-2-carbaldehyde (1 : 1 mol ratio) were refluxed in benzene for *ca.* 1 h; after some hours, from the cooled solution a pale yellow compound was obtained, m.p. 83—84 °C (Found: C, 65.6; H, 5.2; N, 13.7. $C_{11}H_{10}N_2S$ requires C, 65.3; H, 5.0; N, 13.9%); *m*/*e* 92, 119, 169, and 201.

Preparation of 2-(2′-*thienyl*)-1-(2′-*thienylmethyl*)*benzimidazole* (II).—A benzene solution of *o*-phenylenediamine and thiophen-2-carbaldehyde (1 : 2 mol ratio) was refluxed for *ca.* 1 h; on cooling a yellow microcrystalline product was obtained, m.p. 143—144 °C (Found: C, 64.5; H, 4.1; N, 9.7. $C_{16}H_{12}N_2S_2$ requires C, 64.9; H, 4.1; N, 9.5%); *m*/*e* 90, 97, 129, 156, 172, 200, and 296.

Reactions of (I) *and* (II) *with Molybdenum*(V) *Chloride.*—(*a*) $MoCl_5$, dissolved in acetonitrile, was added under nitrogen atmosphere at room temperature to a boiling solution of (II) (2 : 1 mol ratio) in ethanol; from the reaction mixture, after some days, by slow evaporation of the solvent under vacuum, brown-orange crystals were isolated, which were not suitable for an *X*-ray analysis.

(*b*) Reaction of (I), dissolved in boiling ethanol, with $MoCl_5$ in acetonitrile, after some days resulted in the formation of a brown-orange crystalline product. The compound, which is air stable, was examined by *X*-ray diffraction analysis. Analytical and spectroscopic data are in disagreement with the Mo–(I) complex, but are analogous to those found for the complex obtained in the reaction of (II) with $MoCl_5$ (Found: C, 33.7; H, 3.5; N, 4.0. $C_{40}H_{46}Cl_4Mo_4N_4O_{12}S_4$ requires C, 33.6; H, 3.3; N, 3.9%). These results and the successful structural analysis reveal virtually identical structures for the two compounds.

Mass spectra were recorded on a Varian CM-5 spectrometer. The i.r. spectra were obtained on a Perkin-Elmer 457 spectrophotometer in the 4 000—250 cm^{-1} region using KBr discs.

Crystal Data.—$C_{40}H_{46}Cl_4Mo_4N_4O_{12}S_4$, M = 1 428.67, space group $P\bar{1}$, a = 10.524(2), b = 14.352(4), c = 10.213(2)

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† Bis[2-(2′-thienyl)-1-(2′-thienylmethyl)benzimidazolium] 1,2,3,4-tetrachloro-1,2;3,4-di-μ-ethoxo-1,3-diethoxo-1,4;2,3-di-μ-oxo-1,2,4;2,3,4-di-μ_3-oxo-1,2,3,4-tetraoxo-*cyclo*-tetramolybdate(2−) (2*Mo*–*Mo*).

Supplementary data available (No. SUP 23355, 13 pp.): observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Selected i.r. bands (cm^{-1}) of (I), (II), and the Mo complex

(I)	(II)	Mo complex	Assignment
3 450m		3 400m, br	ν(NH)
3 350m		3 250ms	
	3 110m		ν(CH) (aromatic)
	3 095m	3 080m	
3 060w	3 060 (sh)	3 050m	
2 930w	2 940w	2 950mw	ν(CH) (alkyl)
2 860w		2 920w	
		2 700br	
1 610ms	1 615ms	1 625m	ν(CN)
1 595s	1 590mw	1 615 (sh)	
1 560m	1 560m	1 570ms	
1 540 (sh)		1 510m	
1 490ms	1 480m	1 470s	ring
1 460m	1 460vs		
	1 440m	1 440m	
1 430s	1 430vs		
		970s	ν(MoO)
		890m, br	δ(CH) (out-of-plane)
860mw	860m	865w	
835mw	850s	860w	
	840 (sh)	845w	
810m	800m		
		675m	ν(MoOMo)

Å, $\alpha = 95.49(1)$, $\beta = 100.68(3)$, $\gamma = 118.79(1)^\circ$, $U = 1\,297.5$ Å^3, $D_m = 1.80$, $Z = 1$, $D_c = 1.83$ g cm^{-3}, $F(000) = 710$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 13.3 cm^{-1}.

Structure Determination.—A small crystal with dimensions *ca.* 0.14 × 0.32 × 0.03 mm was selected for intensity measurements. Intensity data were collected on a Siemens AED single-crystal computer-controlled diffractometer by the ω/2θ scan technique ($5 < 2\theta < 48^\circ$). Zirconium-filtered molybdenum *X*-radiation was used. A total of 3 936 independent reflections were measured of which only 2 129 [$I > 2\sigma(I)$] were considered to be observed and were used in the subsequent analysis. No absorption correction was made.

The structure was solved by direct methods using the program SHELX.[2] The positions of non-hydrogen atoms were refined by block-matrix least squares using anisotropic temperature factors. The hydrogen atoms of the organic molecule were calculated with standard geometries, but they were not refined. The final *R* value was 0.076 (observed reflections only). The highest residual electron density was 2.3 e Å^{-3} and the deepest pit was −1.7 e Å^{-3}. All the calculations were performed on the C.D.C. Cyber 76 computer of CINECA, Casalecchio, Bologna.

Atomic scattering factors used throughout the calculations were taken from Cromer and Mann [3] for non-hydrogen atoms and from Stewart *et al.*[4] for H atoms. Positional parameters with their estimated standard deviations are given in Table 2 for non-hydrogen atoms and in Table 3 for hydrogen atoms.

Results and Discussion

Chemical Steps.—The transformation of the organic molecule during the course of the reaction (see Experimental section) can be explained by two different chemical steps. First, a hydrolysis process concerning (I), which was probably caused by the presence of ethanol, produced an amount of thiophen-2-carbaldehyde. A subsequent condensation of this last compound with unchanged (I) led to the formation of (II). It has been found already that compounds obtained by condensation of aldehydes or ketones with systems containing NH_2 groups can be easily hydrolysed, particularly in the presence of metal ions such as Co^{II}, Ni^{II}, and Cu^{II}.[5–7]

Infrared Spectra.—The main i.r. bands of (I), (II), and the Mo complex are reported in Table 1. While the i.r. spectrum of (I) is characterized by the presence of two ν(NH) bands in agreement with the hydrogenated form of the *N*-heterocyclic ring, in the spectrum of (II) no bands appear in the 3 500—3 150 cm^{-1} region. The phenyl ring and the thienyl moieties both contribute to the aromatic vibrational absorptions in the spectra of all three compounds. I.r. bands which are assignable without uncertainty to the C–S–C systems are not well identified.

Some considerations emerge from the comparison of the vibrational absorptions of the free molecule (II) with those of the Mo complex, which can be summarized as follows. (*i*) A medium band at 3 250 cm^{-1} appears in the complex spectrum, which suggests the presence of a N–H bond in agreement with a probable protonation of the heterocyclic nitrogen. (*ii*) An increase of the intensity of the stretching bands of the aliphatic C–H bonds is observed in the complex, owing to the ethoxy groups bounded to molybdenum. (*iii*) Two new bands are present at 970 and 675 cm^{-1} which can be attributed to the stretching vibrations of Mo–O and Mo–O–Mo bonds respectively.[8,9] (*iv*) In the region of the C–H out-of-plane deformation vibrations, a new medium band at 890 cm^{-1} appears in addition to the other bands which are also present in the spectrum of free compound (II).[10] (*v*) A precise assignment of ν(Mo–Cl) is not possible owing to the weak resolution in the 400—250 cm^{-1} region.

X-*Ray Structural Studies.*—When the compound was first prepared there was considerable speculation about a possible co-ordination to metal of the organic molecule at least through the nitrogen atoms of the benzimidazole moiety, as already observed in bis[2-(2′-thienyl)-1-(2′-thienylmethyl)]copper(II) nitrate.[11] However, the preferred co-ordination of molybdenum through oxygen atoms, even involving solvent molecules, has given rise to formation of the tetrameric arrangement with oxo-bridges. A projection of the structure on (1 0 0) is shown in Figure 1. It consists of tetrameric groups $[Mo_4Cl_4O_8(OEt)_4]^{2-}$ which lie around the symmetry centres and are surrounded by 2-(2′-thienyl)-1-(2′-thienylmethyl)-benzimidazolium cations linked to the tetramers through O ··· HN$^+$ bridges. The tetramer is shown in Figure 2.

A similar arrangement of molybdenum and oxygen atoms has been previously reported for $[Mo_4Cl_4O_6(OPr)_6]$.[12] These workers prepared this compound by a different method to that used for our title complex, but in both cases the course of the reaction is not clear. It is noteworthy that both compounds have been prepared by treating $MoCl_5$ in propanol and ethanol solutions respectively. The presence of hydroxo-solvents can explain the easy formation of this tetrameric arrangement of oxo- and alkoxy-bridged molybdenum atoms.

In the present complex the two crystallographically independent molybdenum atoms have different environments although both have the same co-ordination. Each molybdenum atom lies at the centre of a distorted octahedron consisting of one terminal chlorine and five oxygen atoms. The Mo–Mo distance of only 2.59 Å, shorter than that (2.669 Å) found in $[Mo_4Cl_4O_6(OPr)_6]$,[12] indicates that the interaction is of such strength as to be considered a metal–metal bond,[13–16] this nevertheless has little effect on the geometries of the co-ordination polyhedra of the molybdenum atoms. The Mo(1) atom is displaced 0.03 Å out of the O(3)-O(5)O(2^{I})O(6) plane and the Mo(2) atom is displaced 0.06 Å out of the O(3)O(4)O(2)O(1) plane, both towards the O(1^{I}) atom. While in this compound four ethoxy groups are co-

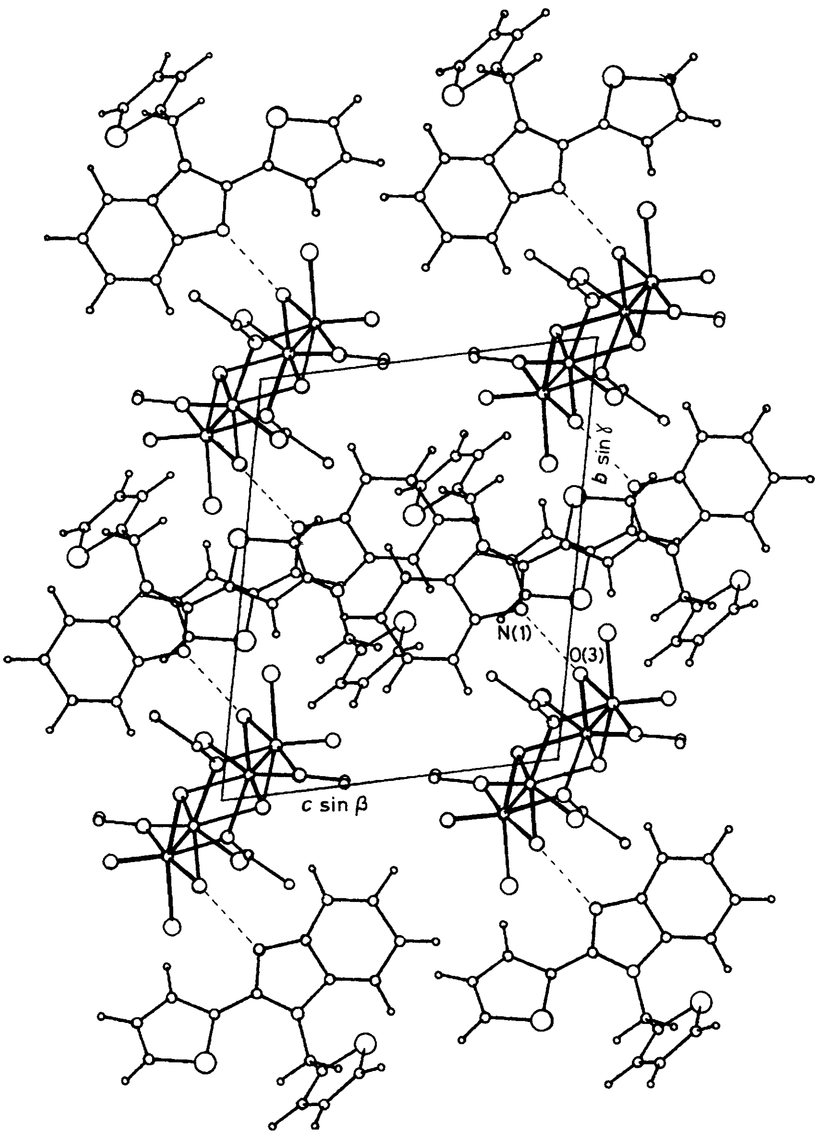

Figure 1. Projection of the structure on the (1 0 0) plane

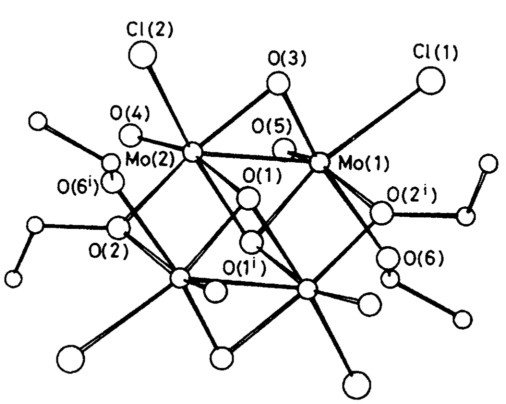

Figure 2. Structure of the tetramer $[Mo_4Cl_4O_8(OEt)_4]^{2-}$

ordinated to metal, in $[Mo_4Cl_4O_6(OPr)_6]$ [12] six propoxide groups are present.

The structural situation of the oxygen atoms in the coordination is quite different; *i.e.* O(1) bridges three molybdenum atoms and two oxide oxygens [O(4) and O(5)] form terminal Mo–O bonds; of the two ethoxy oxygen atoms, O(6) is terminal, while the other [O(2)] bridges two molybdenum atoms. A similar situation has been observed in $[Mo_4Cl_4O_6(OPr)_6]$.[12] The sixth oxygen atom, O(3), which is involved in the O···N contacts with the organic molecule, forms bridges between Mo(1) and Mo(2), the same position being occupied by a propoxide group in $[Mo_4Cl_4O_6(OPr)_6]$.[12]

The Mo–O distances and the O–Mo–O bond angles are given in Table 4. The O(1) atoms show distances from three nearest molybdenum atoms which are not equivalent, one being significantly longer than the other two (1.97, 1.98, and 2.28 Å). The two MoO_2 bridge planes $[Mo(1)O(3)O(1^i)$ and $Mo(2)O(3)O(1^i)]$ intersect each other at angles of 152.0° [155.4° (ref. 16), 156.8° (ref. 12)] and the internal Mo(1)–O(3)–Mo(2) and $Mo(1)–O(1^i)–Mo(2)$ angles are 83.7 and 81.8° respectively {84.6 and 84.9° in $[Mo_4Cl_4O_6(OPr)_6]$ [12]}. The $Mo(1)O(1^i)O(2^i)$ and $Mo(2^i)O(1^i)O(2^i)$ planes form a dihedral angle of 171.7° according to the longer distances Mo–Mo (3.44 Å) and Mo–O (2.12, 2.13, 2.28, and 1.98 Å).

Table 2. Fractional atomic co-ordinates (× 10^4) for non-hydrogen atoms with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	6 473(2)	1 168(1)	−1 492(2)
Mo(2)	4 002(2)	531(1)	−769(2)
Cl(1)	8 776(6)	2 892(4)	−1 122(7)
Cl(2)	3 217(7)	1 492(4)	684(7)
S(1)	6 960(8)	6 239(5)	241(7)
S(2)	6 669(8)	6 272(6)	5 000(7)
N(1)	6 941(20)	3 694(13)	1 553(22)
N(2)	7 947(17)	5 330(12)	2 871(18)
C(1)	7 231(22)	3 586(17)	2 902(23)
C(2)	7 899(24)	4 602(16)	3 751(26)
C(3)	8 314(23)	4 770(17)	5 097(19)
C(4)	8 142(26)	3 908(20)	5 733(22)
C(5)	7 429(30)	2 854(22)	4 816(33)
C(6)	7 022(29)	2 690(18)	3 436(31)
C(7)	7 362(22)	4 743(16)	1 583(24)
C(8)	7 166(21)	5 121(15)	383(23)
C(9)	6 935(30)	4 572(18)	−943(27)
C(10)	6 659(28)	5 094(18)	−1 935(21)
C(11)	6 642(27)	5 981(17)	−1 467(23)
C(12)	8 584(23)	6 502(14)	3 364(19)
C(13)	7 489(20)	6 786(15)	3 758(21)
C(14)	7 087(22)	7 533(14)	3 247(19)
C(15)	6 142(31)	7 598(18)	3 918(33)
C(16)	5 768(25)	6 957(20)	4 891(28)
C(17)	798(23)	−1 366(19)	−889(25)
C(18)	7 626(43)	108(28)	−3 650(33)
C(19)	263(33)	−2 189(24)	−2 243(31)
C(20)	8 960(50)	16(33)	−3 633(43)
O(1)	5 008(14)	273(9)	1 241(14)
O(2)	2 414(15)	−896(9)	−258(15)
O(3)	5 819(14)	1 954(9)	−432(15)
O(4)	2 821(15)	364(11)	−2 275(15)
O(5)	5 805(17)	1 118(11)	−3 164(15)
O(6)	7 618(17)	354(11)	−2 259(15)

Table 3. Calculated fractional co-ordinates (× 10^3) for hydrogen atoms of the organic molecule

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
H(3)	877	557	569
H(4)	848	402	681
H(5)	728	218	534
H(6)	659	190	292
H(9)	696	382	−118
H(10)	651	482	−297
H(11)	646	646	−211
H(121)	896	690	255
H(122)	953	678	423
H(14)	747	795	246
H(15)	564	808	370
H(16)	499	688	550

The Mo(2), Mo(2^{i}), O(1), and O(1^{i}) atoms lie in a plane containing the centre of symmetry [Mo(2)–Mo(2^{i}) 3.39 Å]. It is noteworthy that Mo(1) is involved in one triple bridge and Mo(2) in two triple bridges. Both the Mo(2)–O(4) and Mo(1)–O(5) distances (1.70 and 1.70 Å) are in accord with Mo–O terminal bonds found in compounds previously investigated.[12,13–15] The O(5) and O(4) atoms are in eclipsed positions. The Mo–Cl bonds (2.42 and 2.44 Å) are longer than those found in $[Mo_4Cl_4O_6(OPr)_6]$.[12]

The bond lengths and angles of the ethoxy groups (Table 4), one terminal and the other bridging two molybdenum atoms, are not worthy of discussion owing to rather high errors. In fact, the terminal carbon atoms, which also have high thermal parameters, are disordered to some extent.

Table 4. Bond distances (Å) and angles (°) in the tetrameric anion

Mo(1)–Mo(2)	2.587(3)	Mo(1)–O(6)	2.23(2)
Mo(1)–Mo(2^{i})	3.444(3)	Mo(2)–Cl(2)	2.439(8)
Mo(2)–Mo(2^{i})	3.393(3)	Mo(2)–O(1^{i})	1.97(2)
Mo(1)–Cl(1)	2.418(5)	Mo(2)–O(3)	1.95(1)
Mo(1)–O(1^{i})	1.98(1)	Mo(2)–O(4)	1.70(1)
Mo(1)–O(2^{i})	2.13(2)	Mo(2)–O(1)	2.28(1)
Mo(1)–O(3)	1.93(2)	Mo(2)–O(2)	2.12(1)
Mo(1)–O(5)	1.70(2)		
O(1^{i})–Mo(1)–O(2^{i})	74.3(6)	O(1^{i})–Mo(2)–O(4)	104.5(7)
O(1^{i})–Mo(1)–O(6)	86.7(6)	O(1^{i})–Mo(2)–O(3)	93.8(6)
O(2^{i})–Mo(1)–O(6)	74.1(6)	O(3)–Mo(2)–O(4)	107.9(7)
O(1^{i})–Mo(1)–O(5)	102.8(6)	O(1^{i})–Mo(2)–O(1)	74.2(6)
O(2^{i})–Mo(1)–O(5)	159.4(7)	O(3)–Mo(2)–O(1)	88.8(5)
O(5)–Mo(1)–O(6)	85.4(8)	O(4)–Mo(2)–O(1)	163.3(6)
O(2^{i})–Mo(1)–O(3)	93.3(6)	O(1^{i})–Mo(2)–O(2)	87.5(5)
O(1^{i})–Mo(1)–O(3)	94.4(6)	O(3)–Mo(2)–O(2)	156.2(6)
O(3)–Mo(1)–O(5)	107.3(7)	O(4)–Mo(2)–O(2)	94.8(7)
O(3)–Mo(1)–O(6)	166.6(6)	O(1)–Mo(2)–O(2)	68.6(5)
O(1^{i})–Mo(1)–Cl(1)	160.8(5)	O(1^{i})–Mo(2)–Cl(2)	157.8(4)
O(2^{i})–Mo(1)–Cl(1)	86.5(4)	O(3)–Mo(2)–Cl(2)	84.2(4)
O(3)–Mo(1)–Cl(1)	86.3(4)	O(4)–Mo(2)–Cl(2)	97.1(6)
O(5)–Mo(1)–Cl(1)	95.3(5)	O(1)–Mo(2)–Cl(2)	83.6(4)
O(6)–Mo(1)–Cl(1)	88.3(5)	O(2)–Mo(2)–Cl(2)	85.7(5)
Mo(2)–Mo(1)–O(1^{i})	49.0(4)	Mo(1)–Mo(2)–O(1^{i})	49.2(5)
Mo(2)–Mo(1)–O(2^{i})	94.8(4)	Mo(1)–Mo(2)–O(3)	47.7(4)
Mo(2)–Mo(1)–O(3)	48.6(5)	Mo(1)–Mo(2)–O(4)	100.2(5)
Mo(2)–Mo(1)–O(5)	98.3(6)	Mo(1)–Mo(2)–O(1)	91.5(4)
Mo(2)–Mo(1)–O(6)	135.4(4)	Mo(1)–Mo(2)–O(2)	136.4(4)
Mo(2)–Mo(1)–Cl(1)	134.9(2)	Mo(1)–Mo(2)–Cl(2)	131.8(2)
Mo(1)–O(1^{i})–Mo(2)	81.8(5)	Mo(1)–O(3)–Mo(2)	83.7(6)
Mo(1)–O(1^{i})–Mo(2^{i})	107.8(6)	Mo(1)–O(6)–C(18)	126.0(1.9)
Mo(2)–O(1^{i})–Mo(2^{i})	105.8(6)	Mo(2)–O(2)–C(17)	119.6(1.2)
Mo(1)–O(2)–Mo(2^{i})	108.4(7)	Mo(1)–O(2^{i})–C(17)	130.3(1.3)
O(2)–C(17)	1.47(3)	O(2)–C(17)–C(19)	111.4(2.2)
C(17)–C(19)	1.54(4)	O(6)–C(18)–C(20)	107.3(3.5)
O(6)–C(18)	1.43(4)		
C(18)–C(20)	1.47(6)		

Superscript i indicates atoms at equivalent positions $1 - x, \bar{y}, \bar{z}$.

The organic molecule is illustrated in Figure 1; interatomic distances and angles are reported in Table 5. The benzimidazole group is planar within experimental error. The thienyl group, attached to C(7), is planar but not coplanar and it forms a dihedral angle of 156.4° with the benzimidazole plane. The thienyl group, in a quasi-axial position with respect to the benzimidazole plane, forms a dihedral angle of 116.1° with the latter; the thienyl ring is also planar within experimental error. The thiophenic rings are tilted so that no S ··· S interactions are observed. Packing requirements probably cause a rotation of the thienyl ring, differently from that found in bis[2-(2′-thienyl)-1-(2′-thienylmethyl)]copper(II) nitrate,[11] in which a long S ··· S contact (3.66 Å) is present. The torsion angles N(2)C(12)C(13)S(2) for the two compounds are −59.6° (present work) and −20.2° (ref. 11). Bond distances and angles in the imidazole moiety,[17–19] as well as in thienyl and thienylmethyl groups, are in agreement with literature values.

An interesting feature of the present compound concerns the interaction O(3) ··· N(1) (2.65 Å). The two atoms are closer together than the sum of the van der Waals radii (2.90 Å);[20] this is a good criterion for the existence of a hydrogen bond. This O ··· N contact is among the shortest reported.[20]

The N(1) nitrogen is surrounded by three neighbours, two carbons, C(1) and C(7), and one oxygen, O(3), and it forms a nearly planar triangular arrangement (*sp*^{2} hybrid). The sum of

Table 5. Bond distances (Å) and angles (°) in the organic molecule

C(1)–C(2)	1.38(3)	C(9)–C(10)	1.38(4)
C(2)–C(3)	1.32(3)	C(10)–C(11)	1.33(4)
C(3)–C(4)	1.40(4)	C(11)–S(1)	1.68(2)
C(4)–C(5)	1.45(4)	S(1)–C(8)	1.74(3)
C(5)–C(6)	1.36(4)	N(2)–C(12)	1.47(2)
C(1)–C(6)	1.38(4)	C(12)–C(13)	1.50(4)
C(1)–N(1)	1.40(3)	C(13)–C(14)	1.44(3)
C(2)–N(2)	1.43(3)	C(14)–C(15)	1.34(4)
N(1)–C(7)	1.34(3)	C(15)–C(16)	1.40(4)
N(2)–C(7)	1.34(3)	C(16)–S(2)	1.66(4)
C(7)–C(8)	1.41(3)	S(2)–C(13)	1.69(2)
C(8)–C(9)	1.42(4)		

N(1)–C(1)–C(2)	108.5(1.9)	C(8)–C(9)–C(10)	111.9(2.2)
N(1)–C(1)–C(6)	130.8(2.1)	C(9)–C(10)–C(11)	114.8(2.1)
C(2)–C(1)–C(6)	120.6(2.3)	C(10)–C(11)–S(1)	112.2(1.8)
C(1)–C(2)–C(3)	123.1(2.0)	N(2)–C(12)–C(13)	113.8(1.6)
N(2)–C(2)–C(1)	105.8(1.9)	S(2)–C(13)–C(12)	120.2(1.5)
N(2)–C(2)–C(3)	131.1(2.0)	C(12)–C(13)–C(14)	126.9(1.9)
C(2)–C(3)–C(4)	120.4(2.0)	S(2)–C(13)–C(14)	112.8(1.7)
C(3)–C(4)–C(5)	115.1(2.2)	C(13)–C(14)–C(15)	107.8(1.9)
C(4)–C(5)–C(6)	124.2(2.5)	C(14)–C(15)–C(16)	116.9(2.8)
C(1)–C(6)–C(5)	116.6(2.3)	C(15)–C(16)–S(2)	110.5(2.3)
N(1)–C(7)–N(2)	111.1(1.9)	C(1)–N(1)–C(7)	107.3(2.0)
N(2)–C(7)–C(8)	127.0(1.9)	C(2)–N(2)–C(12)	123.5(1.7)
N(1)–C(7)–C(8)	121.9(2.0)	C(7)–N(2)–C(12)	129.2(1.7)
C(7)–C(8)–C(9)	124.9(2.0)	C(2)–N(2)–C(7)	107.2(1.7)
C(7)–C(8)–S(1)	126.4(1.7)	C(8)–S(1)–C(11)	92.7(1.2)
C(9)–C(8)–S(1)	108.4(1.7)	C(16)–S(2)–C(13)	92.1(1.2)

the three co-ordination angles is close to 360° (360.2°) [C(1)N(1)C(7) = 107.3, O(3) · · · N(1)C(1) = 118.5, O(3) · · · N(1)C(7) = 134.4°].

It was not possible to fix the position of the hydrogen atoms by difference-Fourier techniques and consequently establish the presence of OH or NH^+ groups. Unfortunately the low solubility of the complex in common solvents also prevented recording its n.m.r. spectrum. Suspension of the compound in deuteriated dimethyl sulphoxide showed resonances only in the phenyl and ethoxy regions. Despite the precise nature of the complex being difficult to define, the following points are significant. (*a*) The O(1) atom is an oxo and not a hydroxo-ligand. In fact, in the triply bridging hydroxo-groups previously characterised, the oxygen atoms of the OH groups show distances from the three nearest molybdenum which are not equivalent, *one* being significantly shorter than the other two.[21] In the present work, the O(1) atoms, bridging three molybdenum atoms, form *two* distances significantly shorter than the other, as in $[Mo_4Cl_4O_6(OPr)_6]$ [12] in which the bridging atom is an oxo-ligand on the basis of the i.r. spectra. (*b*) The O(3) atom is also an oxo and not a hydroxo-ligand. In fact the Mo(1)–O(3) and Mo(2)–O(3) distances (1.93 and 1.95 Å) are comparable with those found in di-μ-oxo-bis[μ-ethylenediaminetetra-acetato-μ-hydroxo-μ-oxomolybdate-(III,IV)] [14] for the Mo–O–Mo system (1.93 Å); for the Mo–O(H)–Mo bridge the distances are longer (2.08 Å).

The short hydrogen bond, O(3) · · · N(1), with the organic molecule implies therefore that the N(1) atom has been protonated in the course of the reaction. The organic molecule would become the cation while the tetramer acts as the anion. The formula of the present compound can be therefore written as $[C_{16}H_{13}N_2S_2]^+{}_2[Mo_4Cl_4O_8(OEt)_4]^{2-}$, in which two of the Mo atoms show oxidation state +5 and two show oxidation state +6, as previously described in $[Mo_4Cl_4O_6(OPr)_6]$.[12]

Attempts to record the e.p.r. spectrum of a powder sample, with the aim of confirming the oxidation state of the molybdenum atoms, have been unsuccessful, owing to the low amount of the product available; nevertheless, a weak signal was observed in agreement with the presence of paramagnetic species.

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