

**The Crystal and Molecular Structures of  
Bis[bis-( $\pi$ -cyclopentadienyl)niobium(V)-bis- $\mu$ -methanethiolato]nickel(0)  
Tetrafluoroborate Dihydrate and  
Bis[bis-( $\pi$ -cyclopentadienyl)molybdenum(IV)-bis- $\mu$ -methanethiolato]nickel(II)  
Tetrafluoroborate**

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The structures of the title complexes have been determined from linear diffractometer data by X-ray methods. For the Nb complex:  $a = 11.44$ ,  $b = 33.56$ ,  $c = 8.33$  Å,  $\gamma = 92.7^\circ$ , space group  $P2_1/b$ , Mo  $K\alpha$  radiation, 1595 reflexions, final  $R = 0.096$ . For the Mo complex:  $a = 10.15$ ,  $b = 18.82$ ,  $c = 7.85$  Å,  $\beta = 95.0^\circ$ , space group  $P2_1/a$ , Mo  $K\alpha$  radiation, 1839 reflexions, final  $R = 0.072$ . The Nb complex, which is diamagnetic, formally contains Nb(V) and Ni(0). The Ni atom has tetrahedral coordination and the short (2.78 Å) Nb–Ni contact may correspond to a metal–metal bond. In contrast the Mo complex formally contains Mo(IV) and Ni(II); the Ni atom has square-planar coordination and the Mo–Ni contact (3.39 Å) is much longer.

Complexes of the type  $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{SCH}_3)_2$ ,  $\text{M} = \text{Nb}$ ,  $\text{Mo}$  or  $\text{W}$ , react with  $\text{NiCl}_2$  and  $(\text{C}_6\text{H}_5\text{CN})_2\text{Pd}$  (or  $\text{Pt})\text{Cl}_2$  to give trinuclear complexes of the form  $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{SCH}_3)_2\text{M}'(\text{SCH}_3)_2\text{M}(\pi\text{-C}_5\text{H}_5)_2^2 + \text{A}_2^{2-}$ ,  $\text{M} = \text{Nb}$ ,  $\text{Mo}$ ,  $\text{W}$ ;  $\text{M}' = \text{Ni}$ ,  $\text{Pd}$  or  $\text{Pt}$  (Dias & Green, 1969, 1971). The Mo and W complexes were thought to contain  $d^8$  square-planar metal  $\text{M}'$  and, by analogy, the metals  $\text{M}$  would be described as  $d^2$ . In the Nb complexes, however, there are two fewer electrons, formally one less associated with each of the two Nb atoms, although the complex remains diamagnetic. The structures were determined in an attempt to elucidate the chemical and electronic structures of the complexes. A preliminary account of part of this work has appeared (Douglas, Green, Prout & Rees, 1971).

### Experimental

#### Preparation

The compounds were prepared by Douglas & Green (1972).

#### X-ray structure analysis

(i) *Bis[bis-( $\pi$ -cyclopentadienyl)molybdenum(IV)-bis- $\mu$ -methanethiolato]nickel(II) tetrafluoroborate*

$\text{C}_{24}\text{H}_{32}\text{Mo}_2\text{NiS}_4(\text{BF}_4)_2$ ,  $M = 872.9$ , monoclinic,  $a = 10.15$  (1),  $b = 18.82$  (2),  $c = 7.85$  (1) Å,  $\beta = 95.0$  (1)°,  $D_m = 1.916$  g cm<sup>-3</sup> (by flotation),  $Z = 2$ ,  $D_c = 1.917$  g cm<sup>-3</sup>, systematic extinctions:  $h0l$ ,  $h$  odd,  $0k0$ ,  $k$  odd, space group  $P2_1/a$ , ( $C_{2h}^5$ , No. 14, second setting),  $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, z)$ , Mo  $K\alpha$  radiation,  $\lambda = 0.7107$  Å,  $\mu = 17.5$  cm<sup>-1</sup>.

Preliminary cell dimensions and the space group were determined from oscillation and Weissenberg photographs. A single crystal (0.2 × 0.2 × 0.5 mm) was

mounted about  $c$  and the intensities of the reflexions of layers  $hk0$ – $hk8$  were recorded on a Hilger and Watts linear diffractometer with Mo  $K\alpha$  radiation and balanced filters. 1839 independent reflexions with  $I > 3\sigma$  were measured and Lorentz and polarization corrections (but no absorption corrections) were applied.

In space group  $P2_1/a$ , the two cations must lie about the centres of symmetry with the Ni atom at a centre whilst the anions occupy general positions. From the unsharpened Patterson function the positions of the Ni (at  $\frac{1}{2}, 0, 0$  and  $0, \frac{1}{2}, 0$ ) and the Mo were determined. The other non-hydrogen atoms of the cation were obtained from subsequent Fourier syntheses. After the positions of the atoms of the cation had been improved by one cycle of full-matrix least-squares refinement with isotropic temperature factors and unit weights, a possible location of the anion was found from a difference synthesis as a group of diffuse peaks. Least-squares refinement continued with anisotropic temperature factors for the atoms of the cation and isotropic temperature factors for the anion. The refinement converged at  $R = 0.08$ , but the temperature factors of the atoms of the anion were unsatisfactory and its geometry was poor. In another difference synthesis, computed with the F atoms excluded from the phasing, there were, in the neighbourhood of the B atom, five peaks, three large in extent but diffuse in positions appropriate for three F atoms and two smaller, sharper and closer together in the region where the fourth F was expected. Clearly the anion was disordered in a fairly complex manner. It was decided that the anion was best represented by a tetrahedral arrangement of F atoms with anisotropic thermal motion even though this was a gross approximation to the real situation. The refinement then proceeded to the convergence of the well

defined atoms at  $R=0.072$ . Calculations were carried out on the Oxford University ICL 1906A with a program system kindly supplied by Dr G. M. Sheldrick (1972). This program system applies a weighting scheme of the form:  $w = A + |F_o| + B|F_o|^2$ . The constants  $A$  and  $B$  are based on the approximate values suggested by Cruickshank (1961). The atomic scattering factors were from Cromer & Waber (1965).

(ii) *Bis[bis-( $\pi$ -cyclopentadienyl)niobium(V)-bis- $\mu$ -methanethiolato]nickel(0) tetrafluoroborate dihydrate*

$C_{24}H_{32}Nb_2NiS_4(BF_4)_2 \cdot 2H_2O$ ,  $M = 902.8$ , monoclinic,  $a = 11.44$  (1),  $b = 33.56$  (3),  $c = 8.33$  (1) Å,  $\gamma = 92.7$  (1)°,  $D_m = 1.84$  g cm $^{-3}$  (by flotation),  $Z = 4$ ,  $D_c = 1.88$  g cm $^{-1}$ , systematic extinctions  $hk0$ ,  $k$  odd,  $00l$ ,  $l$  odd. Space group  $P2_1/b$ , ( $C_{2h}^5$ , No. 14, first setting), Mo  $K\alpha$  radiation,  $\lambda = 0.7107$  Å,  $\mu = 15.9$  cm $^{-1}$ .

Preliminary cell dimensions and the space group of a dark red-brown crystal,  $0.3 \times 0.1 \times 0.7$  mm, mounted about the unique  $c$  axis were determined from Weissenberg and precession photographs. The cell dimensions were refined and the intensities of 1595 independent reflexions with  $I > 3\sigma$  and tolerably equal backgrounds (layers  $hk0-8$ ) were measured on a Hilger and Watts linear diffractometer with balanced filters. Lorentz and polarization corrections were applied but no absorption corrections were made.

The positions of the metal atoms were determined from an unsharpened Patterson function. A Fourier analysis phased on these atoms gave the positions of the S atoms and C atoms of the cyclopentadienyl rings. All the remaining non-hydrogen atoms except for one water oxygen were located from the subsequent difference syntheses. The trial structure was refined by three cycles of least-squares calculation with isotropic temperature factors, unit weights and a 'large block' approximation to the normal matrix. The remaining

Table 2. *Bis[bis-( $\pi$ -cyclopentadienyl)molybdenum(IV)-bis- $\mu$ -methanethiolato]nickel(II) tetrafluoroborate: interatomic distances (Å) and interbond angles (°)*

Ni—S(1)	2.149 (3)
Ni—S(2)	2.235 (3)
Mo—S(1)	2.491 (3)
Mo—S(2)	2.514 (3)
S(1)—C(1)	1.84 (2)
S(2)—C(2)	1.80 (2)
Mo—C(11)	2.28 (2)
Mo—C(12)	2.27 (2)
Mo—C(13)	2.28 (1)
Mo—C(14)	2.33 (1)
Mo—C(15)	2.35 (1)
C(11)—C(12)	1.40 (2)
C(12)—C(13)	1.40 (3)
C(13)—C(14)	1.41 (3)
C(14)—C(15)	1.39 (3)
C(15)—C(11)	1.39 (3)
Mo—C(21)	2.29 (2)
Mo—C(22)	2.36 (2)
Mo—C(23)	2.36 (2)
Mo—C(24)	2.25 (2)
Mo—C(25)	2.18 (2)
C(21)—C(22)	1.38 (2)
C(22)—C(23)	1.39 (2)
C(23)—C(24)	1.43 (2)
C(24)—C(25)	1.49 (3)
C(25)—C(21)	1.37 (3)
S(1)—Mo—S(2)	70.3 (1)
S(1)—Ni—S(2)	82.2 (1)
C(1)—S(1)—Mo	113.5 (7)
C(1)—S(1)—Ni	114.3 (6)
Mo—S(1)—Ni	93.6 (1)
C(2)—S(2)—Mo	112.2 (5)
C(2)—S(2)—Ni	104.6 (5)
Mo—S(2)—Ni	90.9 (1)
C(11)—C(12)—C(13)	106 (2)
C(12)—C(13)—C(14)	110 (2)
C(13)—C(14)—C(15)	107 (2)
C(14)—C(15)—C(11)	109 (1)
C(15)—C(11)—C(12)	109 (2)
C(21)—C(22)—C(23)	110 (2)
C(22)—C(23)—C(24)	108 (1)

Table 1. *Bis[bis-( $\pi$ -cyclopentadienyl)molybdenum(IV)-bis- $\mu$ -methanethiolato]nickel(II) tetrafluoroborate: final atomic parameters*

	$x/a$	$y/b$	$z/c$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Mo	0.29324 (9)	0.12425 (5)	0.1407 (1)	0.0310 (5)	0.0259 (4)	0.0434 (7)	0.0006 (4)	0.0068 (4)	0.0040 (3)
Ni	0.5000	0.0000	0.0000	0.0261 (9)	0.0243 (9)	0.0443 (15)	−0.0004 (7)	0.0060 (8)	−0.0031 (7)
S(1)	0.2977 (3)	0.0274 (1)	−0.0749 (5)	0.0276 (13)	0.0301 (13)	0.0572 (23)	−0.0052 (12)	0.0037 (11)	−0.0024 (10)
S(2)	0.5189 (3)	0.1176 (1)	0.0324 (5)	0.0295 (13)	0.0262 (12)	0.0522 (21)	−0.0014 (10)	0.0068 (11)	−0.0053 (9)
C(1)	0.1783 (14)	−0.0444 (8)	−0.045 (4)	0.033 (7)	0.050 (8)	0.141 (21)	−0.033 (10)	0.013 (8)	−0.014 (6)
C(2)	0.5200 (14)	0.1515 (8)	−0.181 (3)	0.051 (7)	0.048 (7)	0.057 (11)	0.009 (6)	0.016 (6)	−0.006 (6)
C(11)	0.2171 (13)	0.1845 (7)	−0.100 (3)	0.045 (7)	0.045 (7)	0.066 (13)	0.012 (6)	0.004 (6)	0.010 (5)
C(12)	0.1080 (14)	0.1562 (8)	−0.025 (3)	0.044 (7)	0.044 (7)	0.092 (16)	−0.004 (7)	0.009 (7)	0.002 (6)
C(13)	0.1051 (16)	0.1905 (10)	0.133 (3)	0.051 (8)	0.077 (11)	0.083 (17)	0.020 (10)	0.014 (8)	0.036 (8)
C(14)	0.2104 (20)	0.2394 (8)	0.156 (3)	0.093 (13)	0.034 (7)	0.096 (19)	−0.021 (8)	−0.013 (11)	0.030 (8)
C(15)	0.2763 (13)	0.2362 (6)	0.008 (2)	0.053 (7)	0.032 (6)	0.047 (11)	0.001 (5)	−0.020 (6)	0.002 (5)
C(21)	0.2125 (18)	0.0638 (9)	0.362 (3)	0.077 (11)	0.062 (10)	0.071 (16)	0.015 (8)	0.032 (10)	−0.013 (8)
C(22)	0.3269 (18)	0.0278 (8)	0.332 (3)	0.086 (11)	0.043 (8)	0.077 (16)	0.030 (8)	0.028 (10)	0.023 (8)
C(23)	0.4357 (14)	0.0721 (8)	0.359 (2)	0.057 (8)	0.063 (8)	0.033 (11)	0.007 (6)	0.001 (6)	0.007 (7)
C(24)	0.3909 (18)	0.1406 (9)	0.407 (3)	0.078 (11)	0.062 (9)	0.043 (13)	0.009 (7)	−0.017 (8)	0.012 (8)
C(25)	0.2449 (22)	0.1329 (11)	0.405 (4)	0.096 (13)	0.075 (12)	0.088 (19)	0.003 (10)	0.044 (12)	0.038 (10)
B(1)	0.3635 (24)	0.3505 (11)	0.552 (3)	0.093 (14)	0.056 (10)	0.061 (17)	−0.002 (9)	0.035 (11)	0.004 (10)
F(1)	0.455 (3)	0.311 (1)	0.498 (7)	0.19 (2)	0.19 (2)	0.62 (8)	−0.21 (4)	0.26 (4)	−0.06 (2)
F(2)	0.295 (6)	0.294 (2)	0.584 (7)	0.45 (6)	0.20 (3)	0.24 (6)	0.06 (3)	0.16 (4)	−0.06 (3)
F(3)	0.244 (2)	0.370 (2)	0.466 (5)	0.10 (1)	0.31 (4)	0.20 (4)	−0.01 (2)	−0.01 (2)	0.05 (2)
F(4)	0.424 (2)	0.405 (1)	0.639 (6)	0.25 (3)	0.13 (1)	0.30 (5)	−0.11 (2)	−0.05 (3)	0.07 (2)

Table 2 (cont.)

C(23)—C(24)—C(25)	104 (1)
C(24)—C(25)—C(21)	108 (1)
C(25)—C(21)—C(22)	109 (2)
B(1)—F(1)	1.30 (3)
B(1)—F(2)	1.30 (4)
B(1)—F(3)	1.38 (3)
B(1)—F(4)	1.35 (3)
F(1)—B(1)—F(2)	90 (3)
F(1)—B(1)—F(3)	128 (3)
F(1)—B(1)—F(4)	108 (2)
F(2)—B(1)—F(3)	81 (3)
F(2)—B(1)—F(4)	138 (4)
F(3)—B(1)—F(4)	113 (2)

water molecule was then located at a suitable peak in a hole in the structure that had been detected by

Watkin's (1972) method. The refinement of the complete structure was first continued with anisotropic temperature factors for the heavy atoms and subsequently for all atoms of the cation. The refinement converged at  $R=0.086$  after five cycles. The weighting scheme used was  $w=1$  if  $|F_o| < 104$ , otherwise  $w=(104/|F_o|)^2$ . Rollett & Ford's Algol system (unpublished work) for the Oxford University KDF9 computer was used for all calculations. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962) corrected for the real part of the anomalous dispersion.

### Results and description of structures

The observed structure amplitudes and structure factors calculated from the final atomic coordinates (listed in Table 1 for the Nb compound and Table 3

Table 3. *Bis[bis-( $\pi$ -cyclopentadienyl)niobium(V)-bis- $\mu$ -methanethiolato]nickel(0) tetrafluoroborate dihydrate: final atomic parameters*

	$x/a$	$y/b$	$z/c$	$U_{11}$ or $U_{150}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Nb(1)	0.8314 (2)	0.5852 (1)	-0.1844 (3)	0.025 (1)	0.025 (1)	0.027 (2)	0.000 (2)	-0.002 (2)	0.002 (2)
Nb(2)	0.4344 (2)	0.6425 (1)	0.0983 (3)	0.031 (1)	0.023 (1)	0.031 (2)	-0.013 (2)	0.006 (2)	-0.006 (2)
Ni(1)	0.6321 (3)	0.6130 (1)	-0.0406 (5)	0.028 (1)	0.020 (1)	0.030 (2)	0.001 (2)	0.004 (3)	-0.002 (2)
S(1)	0.8019 (6)	0.6468 (2)	-0.0274 (10)	0.037 (3)	0.030 (3)	0.035 (5)	-0.013 (5)	0.002 (6)	-0.021 (5)
S(2)	0.5155 (5)	0.6505 (2)	-0.1750 (10)	0.037 (3)	0.024 (3)	0.036 (5)	0.000 (5)	-0.011 (6)	-0.003 (5)
S(3)	0.6277 (5)	0.5567 (2)	-0.1728 (10)	0.032 (3)	0.027 (3)	0.029 (5)	-0.017 (5)	-0.008 (5)	-0.006 (5)
S(4)	0.5788 (5)	0.5961 (2)	0.2032 (9)	0.034 (3)	0.031 (3)	0.028 (5)	0.006 (5)	-0.003 (5)	-0.008 (5)
C(21)	1.012 (2)	0.5530 (9)	-0.114 (4)	0.046 (16)	0.047 (15)	0.021 (25)	-0.009 (27)	-0.045 (28)	-0.003 (26)
C(22)	0.977 (2)	0.5734 (10)	0.023 (5)	0.041 (17)	0.077 (20)	0.059 (30)	0.013 (36)	-0.044 (30)	0.048 (30)
C(23)	0.865 (2)	0.5532 (9)	0.075 (4)	0.042 (15)	0.060 (16)	0.034 (24)	0.061 (29)	0.021 (27)	0.045 (26)
C(24)	0.840 (2)	0.5203 (8)	-0.041 (4)	0.061 (16)	0.039 (13)	0.017 (23)	0.072 (25)	-0.012 (26)	-0.046 (23)
C(25)	0.928 (3)	0.5226 (7)	-0.153 (4)	0.084 (19)	0.026 (12)	0.016 (24)	0.015 (25)	-0.003 (28)	0.005 (24)
C(31)	0.872 (3)	0.6399 (10)	-0.381 (4)	0.051 (18)	0.059 (18)	0.051 (32)	-0.008 (34)	-0.016 (32)	-0.003 (30)
C(32)	0.773 (4)	0.6212 (9)	-0.415 (2)	0.042 (16)	0.055 (17)	0.038 (24)	-0.019 (30)	0.009 (27)	0.045 (27)
C(33)	0.789 (2)	0.5793 (9)	-0.457 (5)	0.029 (15)	0.061 (18)	0.078 (32)	0.024 (32)	0.014 (29)	-0.063 (26)
C(34)	0.921 (3)	0.5770 (11)	-0.444 (5)	0.050 (16)	0.090 (22)	0.007 (24)	-0.059 (35)	-0.005 (27)	0.001 (30)
C(35)	0.963 (3)	0.6152 (12)	-0.382 (5)	0.047 (17)	0.100 (25)	0.030 (31)	-0.038 (39)	-0.012 (30)	-0.011 (33)
C(41)	0.557 (3)	0.7010 (7)	0.153 (4)	0.066 (18)	0.038 (13)	0.010 (22)	-0.051 (22)	-0.003 (26)	-0.038 (25)
C(42)	0.452 (2)	0.7133 (9)	0.107 (5)	0.054 (16)	0.011 (11)	0.081 (30)	-0.007 (25)	0.060 (33)	-0.001 (21)
C(43)	0.377 (3)	0.7000 (10)	0.242 (6)	0.088 (24)	0.060 (18)	0.052 (32)	-0.097 (37)	-0.014 (41)	0.031 (33)
C(44)	0.435 (3)	0.6784 (9)	0.354 (6)	0.076 (21)	0.052 (17)	0.054 (39)	-0.056 (35)	0.012 (39)	-0.054 (32)
C(45)	0.547 (3)	0.6793 (9)	0.295 (5)	0.065 (19)	0.048 (17)	0.065 (30)	-0.045 (33)	-0.020 (33)	0.013 (28)
C(51)	0.230 (2)	0.6424 (9)	0.042 (5)	0.046 (16)	0.066 (19)	0.027 (29)	0.021 (31)	-0.007 (27)	-0.025 (28)
C(52)	0.282 (3)	0.6177 (9)	-0.088 (4)	0.074 (19)	0.081 (21)	0.019 (24)	0.019 (25)	0.012 (24)	-0.117 (33)
C(53)	0.325 (2)	0.5851 (7)	-0.000 (4)	0.058 (15)	0.034 (13)	0.024 (22)	-0.010 (22)	0.001 (24)	-0.070 (23)
C(54)	0.295 (2)	0.5862 (8)	0.165 (5)	0.042 (15)	0.043 (15)	0.051 (28)	0.012 (28)	0.036 (29)	-0.018 (24)
C(55)	0.237 (2)	0.6225 (8)	0.198 (5)	0.039 (15)	0.038 (14)	0.065 (28)	-0.040 (30)	0.017 (29)	0.003 (23)
C(1)	0.857 (3)	0.6502 (9)	0.179 (5)	0.050 (17)	0.060 (18)	0.047 (29)	-0.068 (34)	-0.029 (31)	-0.022 (28)
C(2)	0.536 (2)	0.5587 (7)	-0.353 (3)	0.045 (14)	0.032 (12)	0.010 (19)	-0.022 (19)	-0.025 (20)	-0.044 (21)
C(3)	0.580 (3)	0.6974 (8)	-0.232 (5)	0.084 (21)	0.034 (14)	0.040 (28)	0.059 (27)	-0.009 (33)	-0.044 (27)
C(4)	0.531 (3)	0.5413 (9)	0.204 (5)	0.050 (17)	0.057 (17)	0.044 (29)	0.015 (30)	0.001 (29)	-0.033 (27)
B(1)	0.775 (2)	0.4693 (1)	0.444 (4)	0.025 (5)					
F(11)	0.691 (2)	0.4818 (1)	0.543 (3)	0.073 (6)					
F(12)	0.740 (2)	0.4807 (1)	0.285 (5)	0.113 (9)					
F(13)	0.766 (2)	0.4296 (1)	0.434 (3)	0.091 (7)					
F(14)	0.877 (2)	0.4840 (1)	0.468 (4)	0.089 (7)					
B(2)	0.817 (5)	0.2937 (2)	0.368 (10)	0.090 (16)					
F(21)	0.807 (3)	0.3265 (1)	0.451 (6)	0.133 (11)					
F(22)	0.899 (4)	0.2962 (1)	0.265 (8)	0.164 (15)					
F(23)	0.825 (5)	0.2580 (2)	0.427 (12)	0.230 (25)					
F(24)	0.707 (4)	0.2847 (1)	0.300 (8)	0.166 (15)					
O(1)	0.908 (5)	0.2639 (2)	0.787 (11)	0.182 (21)					
O(2)	0.763 (3)	0.2302 (1)	0.035 (7)	0.130 (13)					

Table 4. *Bis[bis-( $\pi$ -cyclopentadienyl)niobium(V)-bis- $\mu$ -methanethiolato]nickel(0) tetrafluoroborate dihydrate: interatomic distances (Å) and interbond angles (°)*

Nb(1)—Ni	2.776 (5)
Nb(2)—Ni	2.765 (5)
Ni—S(1)	2.206 (9)
Ni—S(2)	2.186 (9)
Ni—S(3)	2.186 (9)
Ni—S(4)	2.187 (8)
Nb(1)—S(1)	2.481 (9)
Nb(1)—S(3)	2.480 (8)
Nb(2)—S(2)	2.468 (9)
Nb(2)—S(4)	2.483 (8)
S(1)—C(1)	1.84 (4)
S(2)—C(2)	1.77 (4)
S(3)—C(3)	1.83 (3)
S(4)—C(4)	1.89 (4)
C(21)—C(22)	1.39 (5)
C(22)—C(23)	1.49 (5)
C(23)—C(24)	1.46 (5)
C(24)—C(25)	1.37 (5)
C(25)—C(21)	1.41 (5)
C(21)—Nb(1)	2.45 (4)
C(22)—Nb(1)	2.44 (4)
C(23)—Nb(1)	2.47 (4)
C(24)—Nb(1)	2.49 (3)
C(25)—Nb(1)	2.44 (3)
C(31)—C(32)	1.30 (6)
C(32)—C(33)	1.47 (5)
C(33)—C(34)	1.52 (6)
C(34)—C(35)	1.44 (6)
C(35)—C(31)	1.36 (6)
C(31)—Nb(1)	2.49 (5)
C(32)—Nb(1)	2.38 (4)
C(33)—Nb(1)	2.33 (4)
C(34)—Nb(1)	2.41 (4)
C(35)—Nb(1)	2.41 (5)
C(41)—C(42)	1.34 (5)
C(42)—C(43)	1.47 (6)
C(43)—C(44)	1.37 (7)
C(44)—C(45)	1.38 (6)
C(45)—C(41)	1.39 (5)
C(41)—Nb(2)	2.40 (3)
C(42)—Nb(2)	2.38 (4)
C(43)—Nb(2)	2.39 (5)
C(44)—Nb(2)	2.45 (5)
C(45)—Nb(2)	2.40 (4)
C(51)—C(52)	1.50 (5)
C(52)—C(53)	1.42 (5)
C(53)—C(54)	1.42 (5)
C(54)—C(55)	1.44 (6)
C(55)—C(51)	1.47 (6)
C(51)—Nb(2)	2.40 (4)
C(52)—Nb(2)	2.46 (3)
C(53)—Nb(2)	2.40 (3)
C(54)—Nb(2)	2.48 (4)
C(55)—Nb(2)	2.47 (4)
S(1)—Ni—S(2)	106.0 (3)
S(1)—Ni—S(3)	117.0 (3)
S(1)—Ni—S(4)	108.4 (3)
S(2)—Ni—S(3)	104.5 (3)
S(2)—Ni—S(4)	117.1 (3)
S(3)—Ni—S(4)	104.4 (3)
Nb(1)—Ni—Nb(2)	178.5 (2)
S(1)—Nb(1)—S(3)	98.0 (3)
S(3)—Nb(2)—S(4)	97.8 (3)
Nb(1)—S(1)—Ni	72.3 (3)
C(1)—S(1)—Ni	112 (1)
Nb(1)—S(1)—C(1)	119 (1)
Nb(1)—S(2)—Ni	72.6 (3)
C(2)—S(2)—Ni	114 (1)

Table 4 (cont.)

Nb(1)—S(2)—C(2)	119 (1)
Nb(2)—S(3)—Ni	72.7 (3)
C(3)—S(3)—Ni	112 (1)
Nb(2)—S(3)—C(3)	119 (1)
Nb(2)—S(4)—Ni	72.3 (3)
C(4)—S(4)—Ni	109 (1)
Nb(2)—S(4)—C(4)	116 (1)
C(21)—C(22)—C(23)	106 (3)
C(22)—C(23)—C(24)	106 (3)
C(23)—C(24)—C(25)	107 (3)
C(24)—C(25)—C(21)	111 (3)
C(25)—C(21)—C(22)	110 (3)
C(31)—C(32)—C(33)	112 (4)
C(32)—C(33)—C(34)	102 (3)
C(33)—C(34)—C(35)	106 (3)
C(34)—C(35)—C(31)	108 (4)
C(35)—C(31)—C(32)	112 (4)
C(41)—C(42)—C(43)	102 (3)
C(42)—C(43)—C(44)	113 (4)
C(43)—C(44)—C(45)	103 (4)
C(44)—C(45)—C(41)	111 (4)
C(45)—C(41)—C(42)	111 (3)
C(51)—C(52)—C(53)	102 (3)
C(52)—C(53)—C(54)	113 (3)
C(53)—C(54)—C(55)	109 (3)
C(54)—C(55)—C(51)	104 (3)
C(55)—C(51)—C(52)	111 (3)
B(1)—F(11)	1.34 (4)
B(1)—F(12)	1.45 (5)
B(1)—F(13)	1.33 (5)
B(1)—F(14)	1.26 (5)
F(11)—B(1)—F(12)	106 (3)
F(11)—B(1)—F(13)	109 (3)
F(11)—B(1)—F(14)	116 (3)
F(12)—B(1)—F(13)	101 (3)
F(12)—B(1)—F(14)	108 (3)
F(13)—B(1)—F(14)	115 (3)
B(2)—F(21)	1.31 (10)
B(2)—F(22)	1.27 (11)
B(2)—F(23)	1.30 (13)
B(2)—F(24)	1.39 (10)
F(21)—B(2)—F(22)	113 (7)
F(21)—B(2)—F(23)	126 (8)
F(21)—B(2)—F(24)	107 (7)
F(22)—B(2)—F(23)	103 (8)
F(22)—B(2)—F(24)	113 (7)
F(23)—B(2)—F(24)	93 (7)
F(22)···O(1)	3.07 (9)
F(22)···O(2)	3.27 (9)
F(23)···O(1)	3.14 (14)
F(24)···O(2)	2.95 (9)

for the Mo compound) are available.\* The bond distances and angles with estimated standard deviations are given in Tables 2 and 4. For the Mo complex the full variance-covariance matrix was used in the estimation of the standard deviations but only the leading diagonal terms for the Nb complex.

\* A table of the observed and calculated values has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30480 (26 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

(i) *Bis[bis-( $\pi$ -cyclopentadienyl)molybdenum(IV)-bis- $\mu$ -methanethiolato]nickel(II) tetrafluoroborate*

The crystals are built up from isolated cations about symmetry centres at  $\frac{1}{2}, 0, 0$  and  $0, \frac{1}{2}, 0$  and disordered anions in general positions in the cell.

In the cation the Ni atoms lie at the symmetry centres. Therefore, the four S atoms necessarily form a planar arrangement and the Mo $\cdots$ Ni $\cdots$ Mo system

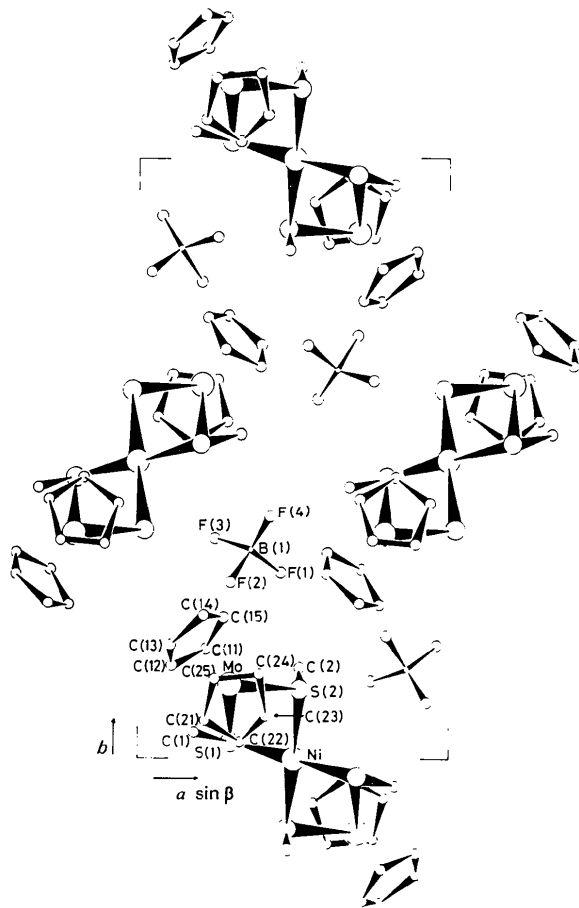


Fig. 1. The crystal structure of bis[bis-( $\pi$ -cyclopentadienyl)molybdenum(IV)-bis- $\mu$ -methanethiolato]nickel(II) tetrafluoroborate projected down the  $c$  axis.

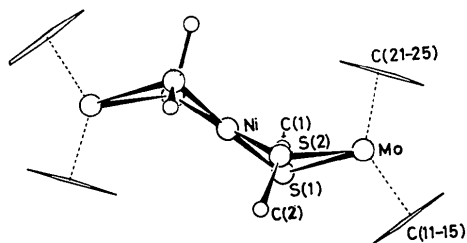


Fig. 2. The bis[bis-( $\pi$ -cyclopentadienyl)molybdenum(IV)-bis- $\mu$ -methanethiolato]nickel(II) cation projected onto the plane containing the normals to the C(21-25) and C(11-15)  $\pi$ -cyclopentadienyl groups at the molybdenum atom.

is necessarily linear but the MoS<sub>2</sub>NiS<sub>2</sub>Mo system is not planar (Fig. 1). The Ni-S bonds [Ni-S(1), 2.149, Ni-S(2), 2.235 Å] differ significantly ( $28\sigma$ ) in length and subtend an angle at the Ni within the four-membered ring of  $82.2^\circ$ . The S atoms of the methanethiol bridges are pyramidal and the methyl groups *trans* with respect to the ring. The Mo atom lies 1.50 Å out of the NiS<sub>4</sub> plane on the same side as C(1) which is 0.71 Å above the plane: C(2) is 1.69 Å below the plane. The angle between the MoS<sub>2</sub> plane and the NiS<sub>4</sub> plane is  $132.7^\circ$  and that between the plane of NiS(1)Mo and NiS(2)Mo  $126.1^\circ$ . Within the four-membered rings the angles at Mo, S(1) and S(2) are  $70.3$ ,  $93.6$  and  $90.9^\circ$  respectively and the Mo-Ni distance 3.39 Å. The MoS<sub>2</sub> plane makes an angle of  $83.6^\circ$  with the plane defined by the Mo atom and the centroids of the  $\pi$ -cyclopentadienyl rings so that S(1) and C(1) twist away from the  $\pi$ -cyclopentadienyl ring containing atoms C(21) to C(25). The geometry of the bis-( $\pi$ -cyclopentadienyl)molybdenum moiety is that commonly found in other bent bis-( $\pi$ -cyclopentadienyl) systems. The  $\pi$ -cyclopentadienyl rings are staggered (Fig. 2) with the Mo atom 1.97 and 1.94 Å along the normals to the rings C(11)-(15) and C(21)-(25) respectively. The ring normals are inclined at an angle of  $128.3^\circ$ . The Mo-C distances are in the range 2.18-2.36 Å with a pattern similar to that found in the amino-acid complexes (Prout, Allison, Delbaere & Gore, 1972) and the C-C distances within the ring are in the range 1.37-1.49 Å and do not vary in any systematic manner.

(ii) *Bis[bis-( $\pi$ -cyclopentadienyl)niobium(V)-bis- $\mu$ -methanethiolato]nickel(0) tetrafluoroborate dihydrate*

The asymmetric unit of the crystal contains one cation, two anions and two water molecules all at general positions in the unit cell (Fig. 3). The two water molecules do not interact with the cation but appear to hydrogen bond to each other, O(1)-O(2)=2.86 Å. There are four short O $\cdots$ F contacts of 2.95, 3.07, 3.14 and 3.27 Å, all to F atoms of the anion at B(2). These contacts are much longer than in well authenticated O-H $\cdots$ F bonds, e.g. 2.68 Å linear in FeSiF<sub>6</sub>·6H<sub>2</sub>O (Hamilton, 1962) and are to the anion with the larger temperature factors for the F atoms. The short contacts are not thought to represent necessarily true O-H $\cdots$ F hydrogen bonds though it is recognized that there will be strong ion-dipole and dipole-dipole interactions between the anions and the water molecules.

In the cation, the NiS<sub>4</sub> group has almost exact  $D_{2d}$  symmetry (Fig. 4) and is linked by planar methanethiolato bridges to two ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)Nb moieties so that the Nb-Ni-Nb system is linear and is an approximate  $S_4$  symmetry axis for the cation as a whole including the ( $\pi$ -C<sub>5</sub>H<sub>5</sub>) ligands and thiomethyl groups.

In the  $\pi$ -cyclopentadienyl rings the C-C bonds are in the range 1.30-1.52 Å (mean 1.42 Å) and show no systematic variation. The C atoms are poorly resolved with high temperature factors, a feature not un-

common in  $\pi$ -cyclopentadienyl complexes. The Nb–C distances are in the range 2.33–2.51 Å (mean 2.43 Å), in good agreement with the mean distances in  $(\pi-C_5H_5)_2NbCl_2$  (2.38 Å) and  $[(\pi-C_5H_5)_2NbCl]_2O^{2+}$  (2.40 Å) (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). In both  $(\pi-C_5H_5)_2Nb$  groups the cyclopentadienyl rings are staggered. The perpendicular distances from the Nb atoms to the rings are 2.14 Å [Nb(1)–C(21–25)], 2.08 Å [Nb(1)–C(31–35)], 2.09 Å [Nb(2)–C(41–45)] and 2.10 Å [Nb(2)–C(51–55)]; the 2.10 Å mean is in good agreement with the distances observed in  $(\pi-C_5H_5)_2NbCl_2$  (2.09 Å mean) and  $[(\pi-C_5H_5)_2NbCl]_2O^{2+}$  (2.10 Å mean) (Prout *et al.*, 1974). The perpendiculars to the  $\pi$ -cyclopentadienyl rings at the Nb atoms meet the rings close (0.085 Å mean) to their centroids making angles of 129.4° at Nb(1) and 129.9° at Nb(2) compared with 128.6° observed for the staggered form in  $(\pi-C_5H_5)_2NbCl_2$ .

The point symmetry at the Nb approximates to  $C_{2v}$ . The angles between the ring-centroid–Nb–ring-centroid and S–Nb–S planes are 85.8° for Nb(1) and 85.9° for Nb(2), the deviation from 90° accommodating the steric repulsions of the *trans* methyl groups of the thiolato bridges. The Nb–S distances (2.478 Å mean) are all within 1 e.s.d. of their mean and are consistent with the observed Mo–S distances in  $[(\pi-C_5H_5)_2Mo(\mu-SCH_3)_2]Ni^{2+}$  (2.50 Å) and  $(\pi-C_5H_5)_2Mo(\mu-SCH_3)_2Rh(\pi-C_3H_5)^+$  (2.52 Å) (Prout & Rees, 1974a). However, the S–Nb–S angles (97.9° mean) are greater than those previously found in  $d^1$  complexes (Prout *et al.*, 1974). The S coordination is distorted. The Nb–S–Ni angle (72.5° mean) has the same value (within experimental error) for each S and is grossly less than the expected value (in the range 90–100°) for a thiol bridge. The Nb–S–CH<sub>3</sub> and Ni–S–CH<sub>3</sub> angles (117° mean and 113° mean respectively) are consistent with steric repulsion between the methyl groups and the  $(\pi-C_5H_5)_2Nb$  moiety. The S–Ni–S angles within the NbS<sub>2</sub>Ni rings have expanded from the expected 109 to 117.0° (mean). The NbS<sub>2</sub>Ni rings are almost planar; the angles between the NbS<sub>2</sub> and S<sub>2</sub>Ni planes are 180 and 174° respectively for the Nb(1) and Nb(2) systems. The Nb–Ni distance across the bridge is 2.771 Å (mean). The dimensions of the NbS<sub>2</sub>Ni four-membered bridges are entirely consistent with the Dahl criteria for metal–metal bonding (Dahl, Gil & Feltham, 1969). The coordination at the metal atom is distorted tetrahedral with the point symmetry reduced from  $T_d$  to  $D_{2d}$  by the opening of the internal (with respect to the NiS<sub>2</sub>Nb system) S–Ni–S angle to accommodate the short Nb–Ni contacts; the S(1)–Ni–S(3) and S(2)–Ni–S(4) planes make an angle of 89.3° with each other and the external S–Ni–S angles fall in the range 104.4–108.4°.

### Conclusions

The electronic structure of the Nb complex has been interpreted by Douglas & Green (1972) on the basis

of Green, Green & Prout's (1972) model of the electronic structure of bent bis- $(\pi$ -cyclopentadienyl)–metal systems. It is proposed that the orbitals  $\psi_A$  and  $\psi_C$  (Green, Green & Prout, 1972) are largely involved in the bonding to the ligands and that due to the directional properties of the metal  $d_{z^2}$  orbital the combination  $\psi_B + d_{z^2} + \psi_{B'}$ , where  $\psi_B$  and  $\psi_{B'}$  are associated with Nb(1) and Nb(2) respectively is likely to be a strongly bonding system. Depending whether the energy of  $d_{z^2}$  is higher or lower than  $\psi_B$  and  $\psi_{B'}$ , the

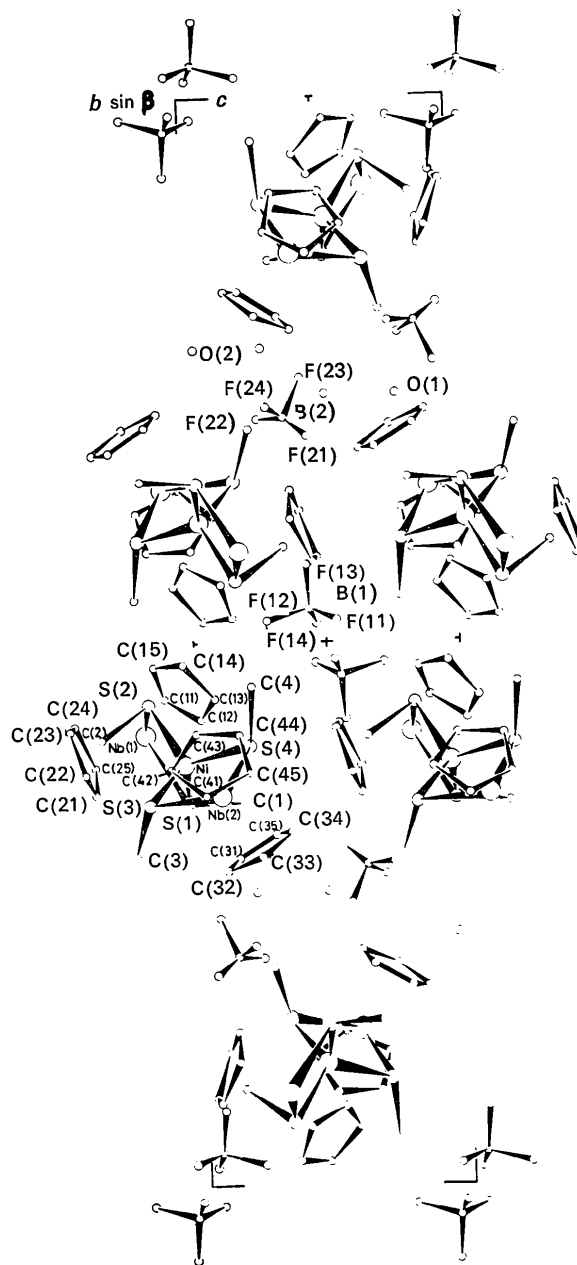


Fig. 3. The crystal structure of bis[bis- $(\pi$ -cyclopentadienyl)–niobium(V)–bis- $\mu$ -methanethiolato]nickel(0) tetrafluoroborate dihydrate projected down the  $a$  axis.

electrons of the bond will be associated largely with the Nb atoms or the Ni atom respectively to give either a  $d^2-d^6-d^2$  system or a  $d^0-d^{10}-d^0$  system. The latter is favoured on general chemical grounds (see Douglas & Green, 1972). The  $d^1-d^8-d^1$  system is rejected because there would be little basis for the short Nb–Ni contact and there would be no explanation for the diamagnetism other than antiferromagnetic coupling.

The interpretation of the stereochemistry of the Mo complex in terms of its electronic structure presents a more difficult problem. This complex has two electrons more than its Nb analogue. The Ni coordination is essentially square planar, a  $d^8$  system with the formal oxidation state +2. The Mo...Ni contact across the methanethiolato bridge is only 3.39 Å, almost the same length as the postulated Ti–Mo bond in  $(\pi-C_5H_5)_2Ti(\mu-SCH_3)_2Mo(CO)_4$ , 3.32 Å (Davies & Kilbourn, 1971) and much shorter than the supposed non-bonded metal–metal contacts in  $(\pi-C_5H_5)_2Mo(\mu-SCH_3)Rh(\pi-C_3H_5)_2^+$ , 3.81 Å, (Prout & Rees, 1974a)  $(\pi-C_5H_5)_2Mo(\mu-S-n-butyl)_2FeCl_2$ , 3.69 Å, (Cameron & Prout, 1972),  $(\pi-C_5H_5)_2W(\mu-SC_6H_5)_2Cr(CO)_4$ , 3.93 Å, (Prout & Rees 1974b). The folding of the bis- $\mu$ -methanethiolato bridge is not an obvious consequence of the bonding requirements of the atoms forming the bridge; models show that planar four-membered rings with the same metal–sulphur bond lengths can have more reasonable bond angles and longer Mo...Ni contacts (e.g. S–Ni–S 90, Ni–S–Mo 96, S–Mo–S 78°,  $d(Ni...Mo)$  3.5 Å). Nor can the fold be thought of in terms of reducing the metal–metal contact without shortening the non-bonding S...S contact because this latter distance would be greater in the planar system. It is believed that the fold of the bridge must be thought of either in terms of the reduction of the repulsive forces between the two bis-( $\pi$ -cyclopentadienyl)molybdenum-bis- $\mu$ -methanethiolato ligands in a manner analogous to the non-coplanar di-(3-methyl-1-phenyl-5-*p*-tolyl-formazyl)nickel(II) (Dale, 1967) or in terms of a bent metal–metal bond as postulated by Dahl & Wei (1963)

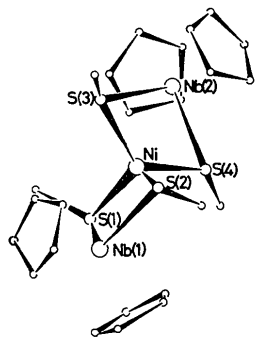


Fig. 4. The bis[bis-( $\pi$ -cyclopentadienyl)niobium(V)-bis- $\mu$ -methanethiolato]nickel(0) cation seen in projection down the crystal  $c$  axis and showing the nickel coordination.

in  $[C_2H_5SFe(CO)_3]_2$ . Models suggest that steric interference between the ligands at the Ni will be in itself insufficient to produce a non-coplanar bridge and could in any case be reduced by increasing the metal–metal contact distance. There is some evidence in fact to suggest that, in related complexes  $(\pi-C_5H_5)_2M(SR)_2M'L_n$ , the fold of the bis- $\mu$ -methanethiolato bridge increases as the possible steric interference between the bridging groups and the ligands  $L_n$  decreases. Thus the angles between the  $MS_2$  and  $S_2M^1$  planes in  $(\pi-C_5H_5)_2Ti(\mu-SCH_3)_2Mo(CO)_4$ ,  $(\pi-C_5H_5)_2W(\mu-SC_6H_5)_2Cr(CO)_4$ ,  $(\pi-C_5H_5)_2Mo(\mu-SCH_3)_2Rh(\pi-C_3H_5)_2$  and  $(\pi-C_5H_5)_2Mo(\mu-Sn-C_4H_9)_2FeCl_2$  are 180, 155, 171, 148°, and whereas in the symmetrical  $(\pi-C_5H_5)(\pi-C_3H_5)MoCl_2$  the bridge is planar. This may point towards a basic non-coplanarity at  $(\mu-SR)_2$  bridges achieved in the absence of steric interference. If in the Mo complex a Mo–Ni bond is formed it presumably involves the donation of the pair of electrons located in  $\psi_A$  (Green, Green & Prout, 1972) to a relatively high-energy orbital of the Ni atom.

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