Bis(cyclopentadienyls) with Transition Metal–Mercury Bonds. Part 4.[1] Formation of Niobium–Mercury Bonds and *X*-Ray Crystal Structure of $[Nb(\eta\text{-}C_5H_5)_2\{HgS_2CN(C_2H_5)_2\}_3]$ †

By **René Kergoat, Marek M. Kubicki,** and **Jacques E. Guerchais,*** Laboratoire de Chimie Inorganique Moleculaire, Laboratoire de Recherche, Associé au CNRS No. 322, Faculté des Sciences et Techniques, Université de Bretagne Occidentale, 29283 Brest-Cedex, France
Nicholas C. Norman and **A. Guy Orpen,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

In aromatic solvents (toluene or benzene–toluene) reaction of $[Nb(\eta\text{-}C_5H_5)_2H_3]$, prepared *in situ*, with a variety of mercury(II) salts at room temperature yields complexes with two or three Nb–Hg bonds. The product of the reaction with $[Hg(S_2CNEt_2)_2]$ is $[Nb(\eta\text{-}C_5H_5)_2(HgS_2CNEt_2)_3]$ (1), which has been characterised by single-crystal *X*-ray diffraction. Complex (1) crystallises in the monoclinic space group $P2_1/n$ with a = 12.302(10), b = 18.385(11), c = 16.077(5) Å, β = 108.18(5)°, and Z = 4. The structure has been solved by heavy-atom methods and refined to R 0.072 for 2 876 unique observed diffractometer data $[I > 2\sigma(I)]$. The molecule consists of a rhomboidal tetrametal cluster formally derived from $[Nb(\eta\text{-}C_5H_5)_2H_3]$ by replacement of each hydride ligand by an $Hg(S_2CNEt_2)$ moiety. The dithiocarbamate ligands chelate the mercury atoms asymmetrically with the shorter, stronger Hg–S bond *trans* to the niobium atom and the ligand plane approximately perpendicular to the $NbHg_3$ plane. The Nb–Hg distances are indicative of single bonds (mean 2.790 Å), whilst the Hg–Hg separations average 2.892 Å.

The reaction of HgX_2 (X = Cl, Br, or I) with $[Nb(\eta\text{-}C_5H_5)_2H_3]$ gives $[Nb(\eta\text{-}C_5H_5)_2H(HgX)_2]\cdot xHgX_2$, (2)—(4) ($x$ = 0.5 for X = Cl, x = 1 for X = Br, and x = 0.66 for X = I). Although these adducts do not undergo direct substitution of X by thiolates, the thiolate analogues $[Nb(\eta\text{-}C_5H_5)_2H(HgSR)_2]$ [R = Et (5) or Bu^t (6)] are accessible *via* reaction of the trihydride with $[Hg(SR)_2]$ (R = Et or Bu^t). Products (2)—(6) have been characterised by analytical, ^1H and ^{13}C n.m.r. data.

A NUMBER of bis(cyclopentadienyl), $(cp)_2$, molybdenum complexes containing Mo–Hg bonds have been reported.[1-3] These compounds were prepared by reaction of $[Mo(cp)_2H_2]$ with mercury(II) salts HgX_2 (X = Cl, Br, I, SCN, O_2CMe, or CN) to form adducts $[Mo(cp)_2(HgX)_2]\cdot xHgX_2$ followed by substitution of X by sulphur-containing anionic ligands [$S_2CNEt_2^-$ or SR^- (R = C_2H_5, Pr^i, *etc.*)] forming complexes $[Mo(cp)_2(HgSR)_2]$ and $[Mo(cp)_2(HgS_2CNEt_2)_2]$. This straightforward route to complexes containing transition metal–mercury bonds prompted us to investigate similar reactions with Group 5B metals, using $[Nb(cp)_2H_3]$. The readiness of the Group 5B bis(cyclopentadienyls) to use all three valence orbitals of the ' bent sandwich '[4] in ligand binding raises the possibility of forming planar tetrametallic units. Although tantalum derivatives $[Ta(CO)_6(HgR)]$ containing an Hg–Ta bond have been reported,[5] no complexes containing Nb–Hg bonds are known. This work is a further development of the chemistry of transition metal–mercury–sulphur systems, an area of potential biological significance.

RESULTS AND DISCUSSION

Reaction of $[Nb(cp)_2H_3]$ *with* $[Hg(S_2CNEt_2)_2]$.—Reaction of $[Nb(cp)_2H_3]$ in toluene with $[Hg(S_2CNEt_2)_2]$ in benzene gave a red solution which on solvent evaporation yielded red-brown crystals of $[Nb(cp)_2(HgS_2CNEt_2)_3]$ (1). Complex (1) was characterised by elemental analysis (Table 1), ^1H and ^{13}C n.m.r. spectroscopy (Table 2), and single-crystal *X*-ray structure analysis (Tables 3—6). The molecular structure is illustrated in Figure 1 and the short Hg · · · S contacts between adjacent molecules shown in Figure 2. The derived bond lengths and interbond angles are given in Tables 3 and 4. The crystal structure consists of molecules of (1) linked *via* weak Hg · · · S interactions [Hg(2) · · · S(11') 3.39 Å, where S(11') is related to S(11) by $(-x, -y, -z)$] into dimeric units; there are no other significant short contacts (remaining Hg · · · S > 4.2 Å). Similar intermolecular interactions have been noted for a number of related mercury complexes, *cf.* $[Mo(cp)_2(HgSEt)_2]$[1] Hg · · · S 3.167—3.510 Å and $[\alpha\text{-}Hg(S_2CNEt_2)_2]$[6a] Hg · · · S 3.137 Å. The molecule consists of a rhomboidal metal cluster formally derived from $[Nb(cp)_2H_3]$[7] by replacing the three hydride ligands with HgS_2CNEt_2 moieties. The $NbHg_3$ unit is nearly planar, the angle between the NbHg(1)Hg(2) and NbHg(2)Hg(3) triangles being only 5°. The

TABLE 1

Analytical data

	Analysis (%) [a]			
Complex	C	H	Hg	X
(1) $[Nb(cp)_2(HgS_2CNEt_2)_3]$	23.8	3.3	44.5	3.3
	(23.7)	(3.2)	(47.3)	(3.3)
(2) $[Nb(cp)_2H(HgCl)_2]\cdot 0.5HgCl_2$	14.4	1.3	57.4	12.9
	(14.4)	(1.2)	(60.3)	(12.8)
(3) $[Nb(cp)_2H(HgBr)_2]\cdot HgBr_2$	10.6	1.0	50.1	27.6
	(10.5)	(0.9)	(52.6)	(27.9)
(4) $[Nb(cp)_2H(HgI)_2]\cdot 0.66HgI_2$	9.7	0.9	43.0	
	(10.2)	(0.9)	(45.2)	
(5) $[Nb(cp)_2H(HgSEt)_2]$ [b]	18.5	2.4	54.0	
	(22.5)	(2.8)	(53.7)	
(6) $[Nb(cp)_2H(HgSBu^t)_2]$	26.6	3.6	48.6	
	(26.9)	(3.6)	(49.9)	

[a] Calculated values are given in parentheses. [b] Poor agreement due to sample decomposition.

---

† Bis(cyclopentadienyl)tris[(diethyldithiocarbamato)mercurio]-niobium.

NbHg bond lengths are in the region appropriate for a single bond (mean 2.790 Å), although the central bond Nb–Hg(2) is significantly longer than those to the 'wing tip' mercury atoms [2.808(3) *vs.* 2.785(3), 2.777(3) Å].

TABLE 2

Proton and ^{13}C chemical shifts (relative to $SiMe_4$, p.p.m.)

Complex	Assignment	^1H [a]	^{13}C
(5) [b]	cp	5.14 (s, 10 H)	83.4
	CH_2	3.40 (q, 4 H)	23.1
	CH_3	1.45 (t, 6 H)	19.1
	H	−3.51 (s, 1 H)	
(6) [b]	cp	5.09 (s, 10 H)	83.0
	CH_3	1.58 (s, 18 H)	39.3
	$S-\mathit{C}(CH_3)_3$		128.2
	H	−3.58 (s, 1 H)	
(1) [b]	cp	5.14 (s, 10 H)	83.0
	CH_2	3.85 (q, 6 H)	49.6
	CH_3	1.35 (t, 9 H)	12.2
	$S_2\mathit{C}N$		203.3
(1) [c]	cp	4.43 (s, 10 H)	83.5
	CH_2	3.50 (q, 6 H)	50.2
	CH_3	1.00 (t, 9 H)	13.0
	$S_2\mathit{C}N$		206.0
$[Mo(cp)_2(HgS_2CNEt_2)_2]$ [b,d]	cp	4.80 (s, 10 H)	74.1
	CH_2	3.84 (q, 4 H)	49.9
	CH_3	1.32 (t, 6 H)	12.2
	$S_2\mathit{C}N$		203.1
$[Mo(cp)_2(HgS_2CNEt_2)_2]$ [c]	cp	4.10 (s, 10 H)	74.5
	CH_2	3.61 (q, 4 H)	50.3
	CH_3	1.10 (t, 6 H)	13.0
	$S_2\mathit{C}N$		205.2

[a] q = Quartet. [b] In $CDCl_3$. [c] In C_6D_6. [d] Ref. 3.

These distances are *ca.* 0.1 Å longer than the Mo–Hg bond lengths in $[Mo(cp)_2(HgX)_2]$ [1–3] ($X = S_2CNEt_2$ or SR; Mo–Hg 2.64—2.69 Å). The mercury–mercury distances [2.883(2), 2.901(2) Å] are indicative of a strong interaction between adjacent Hg atoms, *cf.* Hg ··· Hg in metallic mercury 3.00 Å,[8] Hg–Hg in $[Mo(cp)_2(HgX)_2]$ 3.09—3.26 Å,[1–3] $[As(C_6H_5)_4][Fe(CO)_4(HgCl)(HgCl_2)]$ 3.272 Å,[9] and *cis*-$[Fe(CO)_4(HgCl)_2]$ 3.24 Å.[10] These distances are, however, considerably longer than the $Hg^I–Hg^I$ bond in Hg_2Cl_2, 2.50 Å.[11] Whether these short contacts are real 'bonds' or at least partially the consequence of steric compression in the crowded equatorial plane of the bent sandwich is uncertain. The short H ··· H

TABLE 3

Bond lengths (Å) for (1) [a] with estimated standard deviations in parentheses

Nb–Hg(1)	2.785(3)	S(11)–C(1)	1.74(4)
Nb–Hg(2)	2.808(3)	S(12)–C(1)	1.71(4)
Nb–Hg(3)	2.777(3)	S(21)–C(2)	1.85(5)
Hg(1)–Hg(2)	2.901(2)	S(22)–C(2)	1.64(4)
Hg(2)–Hg(3)	2.883(2)	S(31)–C(3)	1.72(4)
Hg(1)–S(11)	2.513(8)	S(32)–C(3)	1.69(4)
Hg(1)–S(12)	2.919(10)	N(1)–C(1)	1.37(4)
Hg(2)–S(21)	2.526(8)	N(2)–C(2)	1.34(4)
Hg(2)–S(22)	2.825(10)	N(3)–C(3)	1.31(4)
Hg(3)–S(31)	2.516(12)	N(1)–C(11)	1.44(5)
Hg(3)–S(32)	2.75(3)	N(1)–C(13)	1.47(5)
Hg(2)–S(11′)	3.39 [b]	N(2)–C(21)	1.53(6)
Nb–C(41)	2.35(3)	N(2)–C(23)	1.48(5)
Nb–C(42)	2.35(3)	N(3)–C(31)	1.55(6)
Nb–C(43)	2.42(3)	N(3)–C(33)	1.37(8)
Nb–C(44)	2.46(3)	C(11)–C(12)	1.47(5)
Nb–C(45)	2.42(3)	C(13)–C(14)	1.57(5)
Nb–C(51)	2.39(3)	C(21)–C(22)	1.46(5)
Nb–C(52)	2.38(3)	C(23)–C(24)	1.55(5)
Nb–C(53)	2.41(3)	C(31)–C(32)	1.47(6)
Nb–C(54)	2.44(3)	C(33)–C(34)	1.24(8)
Nb–C(55)	2.44(3)		
Nb–cp(4) [c]	2.077		
Nb–cp(5)	2.089		

[a] All cyclopentadienyl C–C and C–H distances were constrained, to 1.42 and 0.96 Å respectively. [b] Intermolecular short contact, see text. [c] cp(4) and cp(5) denote the centroids of the cyclopentadienyl ligands C(41)—C(45) and C(51)—C(55) respectively.

TABLE 4

Interbond angles (°) for (1) [a] with estimated standard deviations in parentheses

Hg(1)–Hg(2)–Hg(3)	116.6(1)
Hg(1)–Hg(2)–Nb	58.4(1)
Hg(3)–Hg(2)–Nb	58.4(1)
Hg(2)–Hg(1)–Nb	59.1(1)
Hg(2)–Hg(3)–Nb	59.5(1)
Hg(2)–Nb–Hg(1)	62.5(1)
Hg(2)–Nb–Hg(3)	62.2(1)
Hg(1)–Nb–Hg(3)	124.4(1)
Hg(1)–Hg(2)–S(21)	121.2(2)
Hg(3)–Hg(2)–S(21)	121.4(2)
Nb–Hg(2)–S(21)	175.4(2)
Hg(1)–Hg(2)–S(22)	107.7(2)
Hg(3)–Hg(2)–S(22)	103.4(2)
Nb–Hg(2)–S(22)	116.6(2)
S(21)–Hg(2)–S(22)	68.1(3)
Hg(2)–Hg(1)–S(11)	128.9(2)
Nb–Hg(1)–S(11)	167.6(2)
Hg(2)–Hg(1)–S(12)	123.8(2)
Nb–Hg(1)–S(12)	118.4(2)
S(11)–Hg(1)–S(12)	66.8(3)
Hg(2)–Hg(3)–S(31)	134.8(3)
Nb–Hg(3)–S(31)	158.0(3)
Hg(2)–Hg(3)–S(32)	110.6(4)
Nb–Hg(3)–S(32)	128.4(4)
S(31)–Hg(3)–S(32)	67.4(5)
Hg(1)–S(11)–C(1)	92.0(10)
Hg(1)–S(12)–C(1)	79.7(12)
Hg(2)–S(21)–C(2)	89.0(11)
Hg(2)–S(22)–C(2)	83.7(13)
Hg(3)–S(31)–C(3)	89.7(12)
Hg(3)–S(32)–C(3)	82.7(14)
C(1)–N(1)–C(11)	122(3)
C(1)–N(1)–C(13)	120(3)
C(11)–N(1)–C(13)	118(3)
C(2)–N(2)–C(21)	117(3)
C(2)–N(2)–C(23)	127(4)
C(21)–N(2)–C(23)	115(3)
C(3)–N(3)–C(31)	121(4)
C(3)–N(3)–C(33)	127(4)
C(31)–N(3)–C(33)	112(4)
S(11)–C(1)–S(12)	121(2)
S(11)–C(1)–N(1)	118(3)
S(12)–C(1)–N(1)	121(3)
S(21)–C(2)–S(22)	119(2)
S(21)–C(2)–N(2)	113(3)
S(22)–C(2)–N(2)	128(4)
S(31)–C(3)–S(32)	118(2)
S(31)–C(3)–N(3)	119(3)
S(32)–C(3)–N(3)	122(3)
N(1)–C(11)–C(12)	118(3)
N(1)–C(13)–C(14)	111(4)
N(2)–C(21)–C(22)	112(3)
N(2)–C(23)–C(24)	108(3)
N(3)–C(31)–C(32)	113(3)
N(3)–C(33)–C(34)	129(6)
cp(4)–Nb–cp(5) [b]	136.0
cp(4)–Nb–Hg(1)	99.5
cp(4)–Nb–Hg(2)	107.1
cp(4)–Nb–Hg(3)	100.4
cp(5)–Nb–Hg(1)	100.7
cp(5)–Nb–Hg(2)	116.9
cp(5)–Nb–Hg(3)	99.6

[a] All cyclopentadienyl C–C–C and C–C–H angles were constrained to D_{5h} symmetry. [b] cp(4) and cp(5) represent the centroids of cyclopentadienyl rings C(41)–C(45) and C(51)–C(55) respectively.

TABLE 5

cp–Nb–cp bending angles, ^1H and ^{13}C chemical shifts of ring carbons and protons in some niobium bis(cyclopentadienides)

Complex	cp–Nb–cp (ω)/°	^1H	^{13}C	Ref.
$[Nb(cp)_2(O{-}O)Cl]$	127.3	*a*		21
$[Nb(cp)_2(S{-}S)(CH_3)]$	128.9	5.57 [b]	105.8	19 [c]
$[\{Nb(cp)_2(SMe)_2\}Ni]^{2+}$	129.7	5.78 [d]		*e*
$[\{Nb(cp)_2Cl\}_2O][BF_4]_2$	129.7			19
$[Nb(cp)_2Cl_2]$	130.3			*f*
$[Nb(cp)_2(SCS)(CH_3)]$	130.9	5.44 [b]	107.0	19 [c]
$[Nb(cp)_2(HgS_2CNEt_2)_3]$	131.5	5.14 [b], 4.43 [g]	83.2(av.)	This work
$[Nb(cp)_2(S{-}S)(CN)]$	132.2	5.98 [h]		*i*
$[Nb(cp)_2(C_2H_4)(C_2H_5)]$	132.4	4.46 [g]	97.6	20
$[Nb(cp)_2H_3]$	141.6	4.80 [j]		7, 23

[a] Insufficiently soluble in current deuteriated solvents. [b] In $CDCl_3$. [c] J. Amaudrut, J. E. Guerchais, and J. Sala-Pala, *J. Organomet. Chem.*, 1978, **157**, C10. [d] In SO_2. [e] K. Prout, S. R. Critchley, and G. V. Rees, *Acta Crystallogr., Sect. B*, 1974, **30**, 2305; W. E. Douglas and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1972, 1796. [f] K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Crystallogr., Sect. B*, 1974, **30**, 2290. [g] In C_6D_6. [h] Solvent not given. [i] R. M. Roder, Ph.D. Thesis, Wisconsin, 1973; *Chem. Abstr.*, 1974, **81**, 307279. [j] In toluene.

TABLE 6

Atomic positional (fractional co-ordinates) parameters for (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Hg(2)	0.137 10(10)	0.127 86(7)	−0.022 21(8)
Hg(1)	0.002 26(11)	0.023 57(6)	−0.147 86(8)
Hg(3)	0.069 82(14)	0.278 29(8)	−0.051 57(10)
Nb	−0.038 7(8)	0.172 25(14)	−0.171 9(2)
S(11)	−0.006 9(9)	−0.112 3(5)	−0.134 3(7)
S(12)	0.086 8(3)	−0.054 6(5)	−0.273 3(6)
S(21)	0.283 0(7)	0.086 8(5)	0.118 6(6)
S(22)	0.361 0(8)	0.126 8(5)	−0.035 0(6)
S(31)	0.089 3(10)	0.388 5(6)	0.044 7(9)
S(32)	0.254(2)	0.363 6(8)	−0.050 3(13)
N(1)	0.045(2)	−0.195 4(14)	−0.253(2)
N(2)	0.498(3)	0.069 7(14)	0.115(2)
N(3)	0.243(3)	0.483 5(14)	0.035(3)
C(1)	0.043(3)	−0.126(2)	−0.224(3)
C(2)	0.395(3)	0.093 4(15)	0.064(3)
C(3)	0.196(3)	0.421(2)	0.006(3)
C(11)	0.020(4)	−0.257(2)	−0.206(3)
C(12)	0.115(3)	−0.290(2)	−0.137(3)
C(13)	0.080(3)	−0.210(2)	−0.331(3)
C(14)	−0.026(4)	−0.215(3)	−0.415(3)
C(21)	0.597(3)	0.075(2)	0.077(3)
C(22)	0.659(3)	0.143(2)	0.101(3)
C(23)	0.529(3)	0.046(2)	0.208(3)
C(24)	0.520(4)	−0.038(2)	0.209(3)
C(31)	0.350(4)	0.510(3)	0.013(3)
C(32)	0.323(4)	0.552(3)	−0.069(3)
C(33)	0.199(6)	0.537(4)	0.074(4)
C(34)	0.222(6)	0.551(4)	0.153(4)
C(41)	−0.059(2)	0.206 1(15)	−0.317(2)
C(42)	0.020(2)	0.255 1(15)	−0.261(2)
C(43)	0.120(2)	0.215 7(15)	−0.217(2)
C(44)	0.104(2)	0.142 3(15)	−0.245(2)
C(45)	−0.007(2)	0.136 4(15)	−0.308(2)
C(51)	−0.241(3)	0.157 9(13)	−0.235 6(14)
C(52)	−0.219(3)	0.231 5(13)	−0.208 8(14)
C(53)	−0.175(3)	0.232 9(13)	−0.116 0(14)
C(54)	−0.170(3)	0.160 1(13)	−0.085 4(14)
C(55)	−0.211(3)	0.113 8(13)	−0.159 3(14)

contacts in $[M(cp)_2H_3]$ ($M = Nb$ or Ta)[7] have been interpreted as the latter. Finally, we note that in the tetra-capped octahedral mercury complex $[Hg_6Rh_4(PMe_3)_{12}]$[12] Hg–Hg separations range from 3.131 to 3.149 Å which interactions are presumably holding the cluster together. The structures of several complexes containing the $Nb(cp)_2$ fragment bound to one other metal atom (*e.g.* Zn,[13] Co,[14] Fe,[15,16] or Mo[17]) have been studied. These niobium–metal bonds are, however, all bridged by ligands [H,[13] CO,[14] H,[15] (σ,π-C_5H_4),[16] and CO[17] respectively]: (1) is, therefore, the first mixed-metal niobium cluster to be structurally characterised, and contains the first unbridged niobium–heterometal bonds thus analysed.

The dithiocarbamate ligands chelate the mercury atoms asymmetrically, showing one short Hg–S bond [mean 2.518(10) Å] and one weaker interaction [mean Hg–S 2.831(15) Å]. The short Hg–S bonds are *trans* to the niobium atom and the sulphur atoms involved [S(11), S(21), S(31)] lie on the same side of the tetrametal

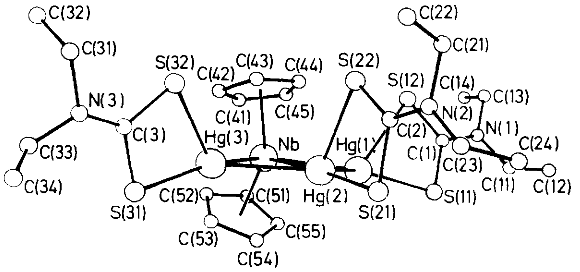


FIGURE 1 Molecular structure of $[Nb(cp)_2(HgS_2CNEt_2)_3]$, (1), showing atom labelling scheme

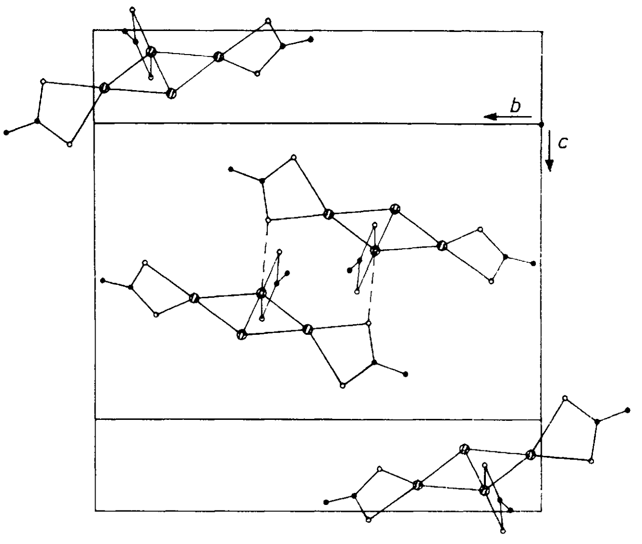
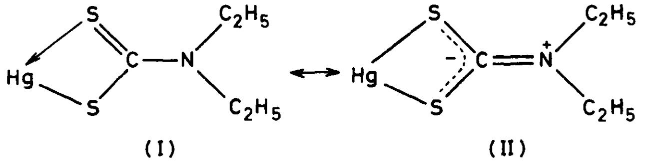


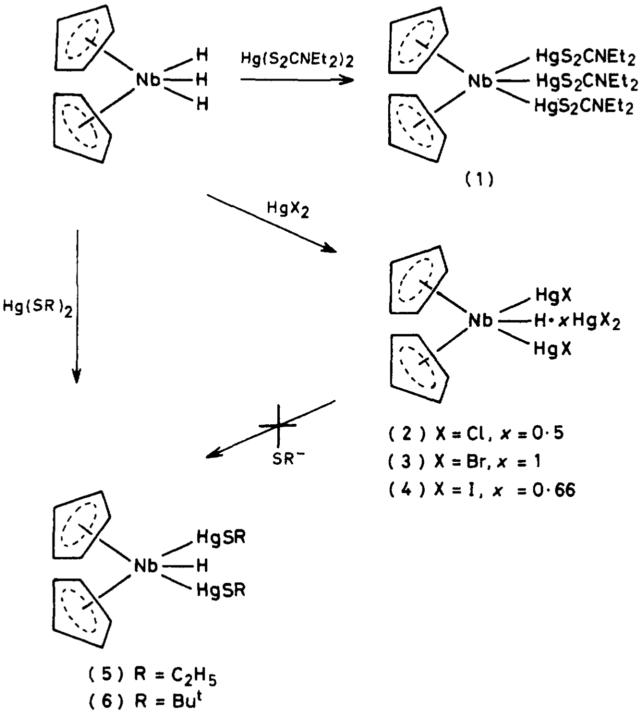
FIGURE 2 Contents of the unit cell of the crystal structure of (1) viewed along *a**; the short intermolecular contact between Hg(2) and S(11) is shown as a dashed line, ethyl and cyclopentadienyl groups are omitted for clarity

plane (0.54, 0.16, and 0.81 Å out of the plane respectively). The weakly bound sulphur atoms are all much further out of the plane and on the opposite side of the $NbHg_3$ plane, see Figure 1 [displacements are 2.21, 2.57, and 2.03 Å for S(12), S(22), and S(32) respectively]. Similarly, asymmetric chelation of mercury by dithiocarbamate ligands has been observed previously, *cf.* β-$[Hg(S_2CNEt_2)_2]$ [6a] Hg–S 2.398(4) and 2.965(4) Å, β-$[Hg(S_2CNPr^i{}_2)_2]$ [18] Hg–S 2.445(4) and 2.645(4) Å, and $[Mo(cp)_2(HgS_2CNEt_2)_2]$ [3] Hg–S 2.50(2) and 2.94(3) Å. There is corresponding, although marginally significant, asymmetry in C–S bond lengths [mean ' short ' C–S 1.69(3) Å, ' long ' C–S 1.77(3) Å] indicating some contribution from canonical form (I). The S_2CNC_2 cores of the dithiocarbamate ligands are planar, indicating that the C–N bond has considerable double-bond character [*i.e.* (II)]. This is confirmed by the short C–N bond lengths [mean 1.34(4) Å], *cf.* 1.33(2) Å in α-$[Hg_2(S_2CNEt_2)_4]$ [6a] and 1.29(2) Å in β-$[Hg(S_2CNEt_2)_2]$.[6a] The i.r. spectrum of (1) shows ν(CN) at 1 485 cm^{-1}, *cf.* 1 482 cm^{-1} in $[Mo(cp)_2(HgS_2CNEt_2)_2]$ and 1 500 cm^{-1} for $[Hg(S_2CNEt_2)_2]$.[6b] The S_2CNEt_2 ligands attached to Hg(1), Hg(2), and Hg(3) are inclined at 68.6, 89.3, and 80.9° to the $NbHg_3$ plane respectively.



(I) (II)

The geometry around niobium is thus closely similar to that observed for the trihydride and for the more accurately characterised tantalum analogue $[Ta(cp)_2H_3]$.[7] The angle (ω) between the cp ring normals at the niobium atom is 131.5°, in the range observed for other ' bent sandwich ' niobium compounds, *cf.* $[Nb(cp)_2(S–S)CH_3]$ 128.9°,[19] $[Nb(cp)_2(C_2H_4)(C_2H_5)]$ 132.4°,[20] and $[Nb(cp)_2(O–O)Cl]$ 127.3°,[21] significantly smaller than in the complexes with less crowding in the equatorial plane of the molecule, *e.g.* $[Nb(cp)_2H_3]$ [7] ω = 141.6 and $[Mo(cp)_2(HgX)_2]$ ω = 138—142° (X = S_2CNEt_2 or SEt).[1,3] The two cp rings are canted by different amounts with respect to the $NbHg_3$ plane, 19.6° [C(41)—C(45)] and 28.9° [C(51)—C(55)]. This difference appears to be intermolecular in origin since the shortest contacts between H(43), H(44), H(45), and S(12), C(22), and S(32) are >3 Å [H(43) · · · S(32) 3.04 Å]. However, there is a contact of 2.72 Å between H(54) and S(11) in an adjacent molecule; this apparently is the cause of the large angle between the tetrametal and C(51)—C(55) cp planes. The cyclopentadienyl rings are staggered, in contrast to the parent trihydride,[7] where they are exactly eclipsed. The intraligand (Hg–Nb–Hg) angles in (1) [58.4(1)°] are somewhat contracted relative to those in $[Nb(cp)_2H_3]$ [63(3)°] and $[Ta(cp)_2H_3]$ [62.9(4)°].[7] These latter values are close to that predicted (64.5°) for ω = 140° on theoretical grounds [4] {ω = 141.6, 139.9, and 131.5° for $[Nb(cp)_2H_3]$, $[Ta(cp)_2H_3]$, and (1) respectively}. In (1), as in the trihydrides, those carbons of the cyclopentadienyl groups furthest from the equatorial ligands are closest to the central Group 5B atom. The ^{13}C chemical shifts for the cp ring carbons are shifted to the highest field yet observed for $Nb(cp)_2$ complexes {83 p.p.m. downfield of $SiMe_4$, *cf.* 109 p.p.m. for $[Nb(cp)_2(S–S)\{SP(S)(OR)_2\}]$ (R = Me, Et, or Pr^i)}.[22]



SCHEME

Reaction of $[Nb(cp)_2H_3]$ *with* HgX_2 (X = Cl, Br, *or* I).—The reaction of $[Nb(cp)_2H_3]$ in toluene with the salts HgX_2 (X = Cl, Br, or I) in benzene gave the insoluble compounds (2)—(4), formulated as adducts of the type $[Nb(cp)_2H(HgX)_2]{\cdot}xHgX_2$, by analogy with the molybdenum and tungsten derivatives $[M(cp)_2(HgX)_2]{\cdot}xHgX_2$ (see Scheme). Very weak and broad i.r. absorption bands in the region 1 700—1 650 cm^{-1} are attributed to ν(Nb–H), *cf.* $[Nb(cp)_2H(CO)]$ [23] 1 695 cm^{-1} and $[Nb(cp)_2H(C_2H_4)]$ [22] 1 735 cm^{-1}. This evidence together with analytical data (Table 1) support the above formulation.

In contrast to the behaviour of the molybdenum analogues, compounds (2)—(4) react with NaSR in benzene leading to the formation of yellow precipitates which are probably hydrolysis products containing Nb=O and/or Nb–O–Nb linkages, and violet or deep red solutions characteristic of niobium(IV) thiolates, with concomitant deposition of metallic mercury. There is no evidence for simple substitution of X^- by SR^- as noted for $[Mo(cp)_2(HgX)_2]{\cdot}xHgX_2$.[1]

Reaction of $[Nb(cp)_2H_3]$ *with* $[Hg(SR)_2]$ (R = Et *or* Bu^t).—In order to attempt the synthesis of mercury thiolate derivatives after the failure of the above route, [Nb(cp)$_2$H$_3$] in toluene was treated with [Hg(SEt)$_2$] and [Hg(SBu^t)$_2$] in benzene. Adducts [Nb(cp)$_2$H(HgSR)$_2$] [(5), R = Et; (6), R = Bu^t] are formed as red crystalline solids (see Scheme). The products were identified on the basis of ^{1}H and ^{13}C n.m.r. and analytical data (Tables 1 and 2). Integration of the proton spectrum showed cp : Et : H (hydride) present in the ratio 2 : 2 : 0.95(10); the hydride chemical shift falls in the same region as the parent trihydride and other Nb(cp)$_2$ monohydride complexes, *cf.* [{Nb(cp)(η-C$_5$H$_4$)H}$_2$] [23] δ −2.07, [Nb(cp)$_2$H(C$_3$H$_6$)] [24] (*exo*) δ −3.04, and [Nb(cp)$_2$H(C$_2$H$_4$)] [23] δ −2.95. These complexes have structures formally derived from the parent trihydride by substitution of the two ' wing tip ' hydride ligands giving time-averaged molecular C_{2v} symmetry as observed in the n.m.r. spectra. That the ' wing tip ' hydrides should have differing reactivity from the central one is not unexpected on the basis of the chemical shifts of these protons in [Nb(cp)$_2$H$_3$] (δ = −2.73 and −3.72 respectively).[23]

The ^{13}C and ^{1}H chemical shifts for a variety of Nb(cp)$_2$ complexes are presented in Table 5. The correlation between these shifts and the inter-cyclopentadienyl plane angle, ω, derived for [Mo(cp)$_2$X$_2$] complexes [1] does not appear to hold for the niobium analogues. This perhaps indicates that factors other than inter-ring repulsion and the electronegativity of the substituent X determine these shifts.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques and freshly distilled, dried, and degassed benzene and toluene as solvents. Oxygenated or chlorinated solvents prevented formation of well defined products in the case of sulphur-containing ligands. Ethanol could, however, be used for the preparation of the adducts [Nb(cp)$_2$H(HgX)$_2$]·xHgX$_2$ (X = Cl, Br, or I). Infrared spectra of samples were recorded as Nujol mulls on CsI plates or in CsBr pellets in the range 200—4 000 cm^{-1} on Pye–Unicam SP200 and Perkin-Elmer 225 spectrophotometers. Hydrogen-1 and ^{13}C n.m.r. spectra were recorded on a JEOL FX100 spectrometer operating at 99.60 MHz for ^{1}H and 25 MHz for ^{13}C using freshly prepared CDCl$_3$ or C$_6$D$_6$ solutions in tubes sealed under vacuum. Chemical shifts were measured relative to internal SiMe$_4$ or to residual proton signals in the solvents used.

Preparations.—[Nb(cp)$_2$(HgS$_2$CNEt$_2$)$_3$] (1). The compound [Hg(S$_2$CNEt$_2$)$_2$] was prepared as in the literature,[3] and [Nb(cp)$_2$H$_3$] was generated *in situ* from the reaction of [Nb(cp)$_2$Cl$_2$] and NaAlH$_2$(OCH$_2$CH$_2$OCH$_3$)$_2$ in toluene.[25] A solution of [Nb(cp)$_2$H$_3$] {prepared from 1 g of [Nb(cp)$_2$Cl$_2$] and containing *ca.* 0.5 g (2.2 mmol) of the trihydride} was added to a solution of [Hg(S$_2$CNEt$_2$)$_2$] (6.6 mmol) in benzene (40 cm^3). The solution, initially yellow, became red on addition of all the [Nb(cp)$_2$H$_3$]. After evaporation of solvent, red-brown *crystals* were obtained on standing overnight.

[Nb(cp)$_2$H(HgX)$_2$]·xHgX$_2$, (2)—(4). Adducts (2)—(4) were prepared by reaction of [Nb(cp)$_2$H$_3$] [prepared as for (1)] in toluene with the appropriate mercury(II) salt (6.6 mmol), HgX$_2$, dissolved in benzene (10 cm^3). On mixing the solution, a yellow or orange precipitate was formed immediately. After stirring the suspension for *ca.* 5 min, the products (2)—(4) were filtered off and washed with benzene.

[Nb(cp)$_2$H(HgSR)$_2$] [R = Et (5) *or* Bu^t (6)]. Complexes (5) and (6) were prepared as (1) but using the appropriate mercury(II) thiolate salts, [Hg(SR)$_2$] (R = Et or Bu^t), prepared as described in the literature.[26] In these cases, however, prolonged standing of the concentrated solutions gave decomposition to violet, niobium(IV)-containing solutions; crystallisation times were therefore reduced relative to (1).

Molecular-structure Determination of [Nb(cp)$_2$(HgS$_2$CNEt$_2$)$_3$] (1).—The space group and approximate unit-cell dimensions were derived from oscillation and Weissenberg photographs (Cu-K_α radiation). A small single crystal (approximate dimensions 0.6 × 0.2 × 0.2 mm) was mounted under N$_2$ in a glass capillary for low-temperature (230 K) data collection on a Syntex $P2_1$ diffractometer. The cell dimensions were determined by least-squares fits to diffractometer setting angles for 15 strong reflections $20 < 2\theta < 30°$. 3 505 Intensity data were collected in the range $3.0 < 2\theta < 50.0°$ using ω—2θ scans. The scan rate was determined from a 2-s pre-scan of the reflection and varied between 1.50 and 29.3° min^{-1} according to scan count. Reflections with pre-scan count rates below 18 counts s^{-1} were not remeasured.

Two check reflections were measured after every 50 reflections, throughout data collection, and showed an approximate drop in intensity of 50% overall, due to decomposition of the crystal in the X-ray beam. Decay, Lorentz, polarisation, and semi-empirical absorption corrections based on an ellipsoidal model and 379 azimuthal scan data from 10 independent reflections were applied. Transmission factors ranged from 0.107 to 0.056 for the full data set. Merging of equivalent and duplicate reflections gave 2 876 unique intensities with $I > 2\sigma(I)$ which were used in structure determination and refinement.

Crystal data. C$_{25}$H$_{40}$Hg$_3$N$_3$NbS$_6$, M = 1 269.2, Monoclinic, space group $P2_1/n$, a = 12.302(10), b = 18.385(11), c = 16.077(5) Å, β = 108.18(5)°, U = 3 455(4) Å^3, Z = 4, D_c = 2.44 g cm^{-3}, $F(000)$ = 2 351, μ(Mo-K_α) = 139.7 cm^{-1}, λ = 0.710 69 Å, T = 230 K.

The structure was solved by conventional heavy-atom methods (Patterson and difference Fourier). The three mercury atoms were located from the Patterson and all other non-hydrogen atoms from two subsequent Fourier-difference maps.

The structure was refined (full-matrix blocks, blocked-cascade method) with anisotropic thermal parameters for Nb, Hg, S, N, and C(1) C(2), C(3) of the dithiocarbamate groups. All other atoms were refined isotropically, and the carbon atoms of the C$_5$H$_5$ groups constrained to D_{5h} symmetry with C–C 1.420 Å. Hydrogen atoms were not located in difference maps but were included in the final refinement in idealised geometries at 0.96 Å from the relevant carbon atom. In the final cycles of refinement a weighting scheme, $w = [\sigma^2(F_0) + 0.0008\,F_0^2]^{-1}$, was introduced and refinement converged smoothly to give final residuals R = 0.0720, R' = 0.0728. No chemically significant peaks were present in the final difference map. Final atomic co-ordinates are given in Table 6. Complex neutral-atom scattering factors [27] were employed throughout; all calculations were performed using the SHELXTL program package of the NICOLET R3m system. Atomic thermal parameters, details of hydrogen atomic co-ordinates, full bond-length tables, and tables of observed and calculated structure factors have been deposited as Supplementary Publication No. SUP 23228 (27 pp.).*

We thank the S.R.C. for financial support and a research studentship (to N. C. N.).

---

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

[1/1100 *Received*, 13*th July*, 1981]

REFERENCES

[1] Part 3, M. M. Kubicki, R. Kergoat, J. E. Guerchais, I. Bkouche-Waksman, C. Bois, and P. L'Haridon, *J. Organomet. Chem.*, 1981, **219**, 329.

[2] M. M. Kubicki, R. Kergoat, J. E. Guerchais, C. Bois, and P. L'Haridon, *Inorg. Chim. Acta*, 1980, **43**, 17.

[3] M. M. Kubicki, R. Kergoat, J. E. Guerchais, R. Mercier, and J. Douglade, *J. Cryst. Mol. Struct.*, in the press.

[4] J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.

[5] K. A. Keblys and M. Dubeck, *Inorg. Chem.*, 1964, **3**, 1646.

[6] (*a*) H. Iwasaki, *Acta Crystallogr., Sect. B*, 1973, **29**, 2115; (*b*) N. Kobayashi and T. Fujisawa, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2780.

[7] R. D. Wilson, T. F. Koetzle, D. W. Hart, Å. Kvick, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, 1977, **99**, 1775.

[8] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 410.

[9] P. D. Brotherton, D. L. Kepert, A. H. White, and S. B. Wild, *J. Chem. Soc., Dalton Trans.*, 1976, 1870.

[10] C. L. Raston, A. H. White, and S. B. Wild, *Aust. J. Chem.*, 1976, **29**, 1905.

[11] E. Dorm, *Chem. Commun.*, 1971, 466.

[12] R. A. Jones, F. M. Real, G. Wilkinson, A. M. R. Galas, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1981, 126.

[13] M. A. Porai-Koshits, A. S. Antsyshkina, A. A. Pasynskii, G. G. Sadikov, Yu. U. Skripkin, and Y. N. Ostrikova, *Inorg. Chim. Acta*, 1979, **34**, L285.

[14] K. S. Wong, W. R. Scheidt, and J. A. Labinger, *Inorg. Chem.*, 1979, **18**, 1709.

[15] K. S. Wong, W. R. Scheidt, and K. A. Labinger, *Inorg. Chem.*, 1979, **18**, 136.

[16] A. A. Pasynskii, Yu. U. Shripkin, V. T. Kalinnikov, M. A. Porai-Koshits, A. S. Antskyshkina, G. G. Sadikov, and U. N. Ostrikova, *J. Organomet. Chem.*, 1980, **201**, 269.

[17] A. A. Pasynskii, Yu. U. Skripkin, I. L. Evemenbo, V. T. Kalinnikov, G. G. Aleksandrov, V. G. Adrianov, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1979, **165**, 49.

[18] M. Ito and H. Iwasaki, *Acta Crystallogr., Sect. B*, 1979, **35**, 2720.

[19] R. Mercier, J. Douglade, J. Amaudrut, J. Sala-Pala, and J. E. Guerchais, *Acta Crystallogr., Sect. B*, 1980, **36**, 2986.

[20] L. J. Guggenberger, P. Meakin, and F. E. Tebbe, *J. Am. Chem. Soc.*, 1974, **96**, 5420.

[21] I. Bkouche-Waksman, C. Bois, J. Sala-Pala, and J. E. Guerchais, *J. Organomet. Chem.*, 1980, **195**, 307.

[22] B. Viard, J. Sala-Pala, J. Amaudrut, J. E. Guerchais, C. Sanchez, and J. Livage, *Inorg. Chim. Acta*, 1980, **39**, 101.

[23] F. N. Tebbe and G. W. Parshall, *J. Am. Chem. Soc.*, 1971, **93**, 3793.

[24] A. H. Klazinga and J. H. Teuben, *J. Organomet. Chem.*, 1980, **194**, 309.

[25] J. A. Labinger and J. Schwartz, *J. Am. Chem. Soc.*, 1975, **97**, 1596.

[26] W. J. Schlientz and J. K. Ruff, *Inorg. Chem.*, 1972, **11**, 2265.

[27] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.