# Metal Complexes as Ligands: Structure and Bonding in New Bis[bis(π-cyclopentadienyl)niobium-bis-μ-methanethiolate]- Complexes of Zerovalent Nickel, Palladium, or Platinum

By W. E. Douglas, M. L. H. Green,* C. K. Prout, and G. V. Rees

(Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR)

Summary The new complexes $[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2$-$M'^{2+}A_2^{2-}$(M' = Ni, Pd, or Pt) are shown by crystal structure determination (M' = Ni) to be tetrahedrally co-ordinated about the metal M'.

THE diamagnetic, d^2 complexes $(\pi\text{-}C_5H_5)_2M(SMe)_2$ (M = Mo or W) readily add to nickel, palladium, or platinum salts forming the complex cations $[(\pi\text{-}C_5H_5)_2M(SR)_2M'(SR)_2M\text{-}(\pi\text{-}C_5H_5)_2]^{2+}$ (M' = Ni, Pd, or Pt) (I) which are also diamagnetic and are thought to contain square-planar, d^8 metal M'.[1]

(I)
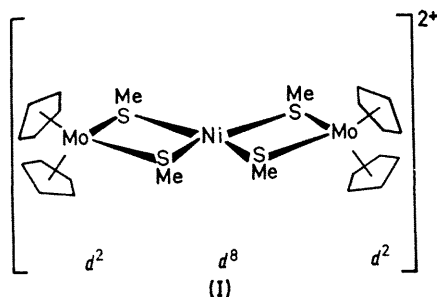
It was, therefore, of interest to study the corresponding d^1 niobium complex $(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ (II). The complex (II) may be made in good yield from the corresponding dichloride and methanethiol in alcoholic base. It is paramagnetic, $\mu_{eff} = 1.71$ B.M., and the e.s.r. spectrum in
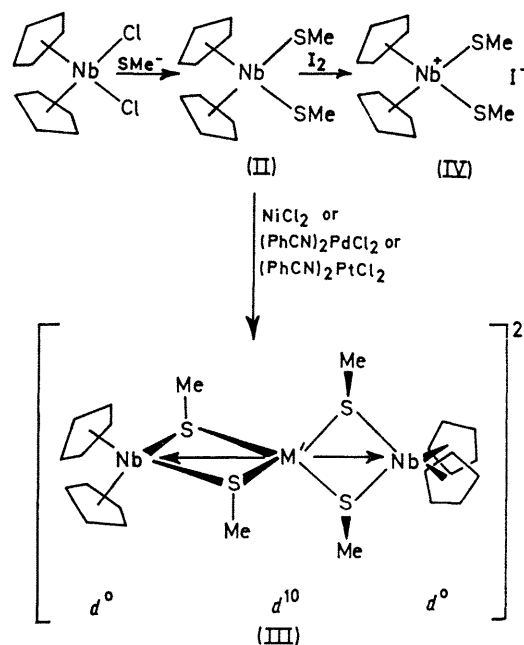
SCHEME

dimethyl sulphoxide shows ten lines ($<g>$ = 1·991, $<a>$ = 25·14).

The complex (II) readily adds to salts of nickel, palladium,

or platinum (see Scheme) giving complexes whose analyses show them to have the stoicheiometry $[(\pi\text{-}C_5H_5)_2Nb(SMe)_2\text{-}M'(MeS)_2Nb(\pi\text{-}C_5H_5)_2]^{2+}[PF_6^-]_2$ (III; M' = Ni, Pd, or Pt). The crystal structure of the tetrafluoroborate salt of the complex (III; M' = Ni) has been determined.

Crystal data: $C_{24}H_{32}Nb_2NiS_4 \cdot (BF_4)_2 \cdot 2H_2O$, $M = 902 \cdot 8$, $a = 11 \cdot 44 \pm 0 \cdot 01$, $b = 33 \cdot 56 \pm 0 \cdot 03$, $c = 8 \cdot 33 \pm 0 \cdot 01$ Å, $\gamma = 92 \cdot 7 \pm 0 \cdot 1°$, $D_m = 1 \cdot 84$, $Z = 4$, $D_c = 1 \cdot 88$. Space group $P2_1/b$ (C_{2h}^5, No. 14) Mo-K_α radiation, $\mu = 15 \cdot 9$ cm^{-1}, linear diffractometer measurement of 3171 independent reflections.

The structure was determined and refined by conventional methods. R is 0·11 with anisotropic temperature factors for the heavy atoms only. The refinement is proceeding.

The crystals contain, in general positions in the unit cell, the cation (see Figure) and tetrafluoroborate anions hydrogen-bonded to the water of crystallisation. In the cation the NiS_4 group has almost exact D_{2d} symmetry and is linked by the thiomethyl bridges to two $(\pi\text{-}C_5H_5)_2Nb$ groups. The four-membered NbS_2Ni rings are very nearly planar: the angle between the S(1)–Nb(1)–S(2) and the S(1)–Ni–S(2) planes and the S(3)–Nb(2)–S(4) and the S(3)–Ni–S(4) planes are 180 and 174° respectively. Within the rings the Nb–Ni contacts are short and the S–Nb–S and S–Ni–S angles are greater (see Table) than the expected values of

TABLE. *Interatomic distances (Å) and angles (°)*

Ni–Nb(1) ..	..	2·77	S(1)–Ni–S(2)	..	117·0
Ni–Nb(2) ..	..	2·77	S(3)–Ni–S(4)	..	117·3
Ni–S(1) ..	..	2·19	S(1)–Nb(1)–S(2)..		98·2
Ni–S(2) ..	..	2·21	S(3)–Nb(2)–S(4)..		98·2
Ni–S(3) ..	..	2·20	Nb(1)–S(1)–Ni ..		72·6
Ni–S(4) ..	..	2·20	Nb(1)–S(2)–Ni ..		72·0
Nb(1)–S(1) ..	..	2·48	Nb(2)–S(3)–Ni ..		72·3
Nb(1)–S(2) ..	..	2·49	Nb(2)–S(4)–Ni ..		72·2
Nb(2)–S(3) ..	..	2·48			
Nb(2)–S(4) ..	..	2·48			

ca. 85 and 109° [the Cl–Nb–Cl angle in $(\pi\text{-}C_5H_5)_2NbCl_2^2$ is 85·5°]. The sulphur co-ordination is pyramidal and the methyl groups are *trans* with respect to the four-membered rings so that the symmetry of the $Ni(SMe)_4$ group is S_4. At Nb(1) and Nb(2), respectively, the planes of the normals to the π-cyclopentadienyl groups make angles of 85·9 and 85·5° with the S–Nb–S planes. These angles are such that S_4 symmetry is preserved about the Nb(1)–Ni–Nb(2) axis Because of the diamagnetism, $\chi_m = -607 \times 10^{-6}$ e.m.u. at 22°, and tetrahedral environment the nickel may be

formally described as zero-valent, d^{10} and the two niobium atoms as pentavalent, d^0. The same description seems appropriate for the other diamagnetic complexes (III; M' = Pd or Pt). The dimensions of the NbS_2Nb rings satisfy the Dahl criteria for metal–metal bonding and suggest that there is substantial niobium–nickel bonding in the complex (III; M' = Ni), especially when these data are compared with the corresponding data for the related complexes $(\pi\text{-}C_5H_5)_2M(SR)_2Mo(CO)_4$, (M = Ti or W)^4. Formally the nickel–niobium bond may be represented as a donor bond from the d^{10} nickel to the 16-electron, d^0 niobium atoms.
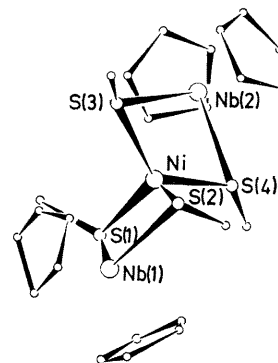

FIGURE. *Projection of molecule along the c-axis.*

It is normally found that saturated sulphur ligands may not stabilise low-valent, electron-rich metal systems as readily as, for example, tertiary phosphine ligands as it is thought that sulphur ligands are not as effective π-acceptor systems as phosphine ligands. The complexes (III) represent the first examples of zero-valent compounds of Ni, Pd, or Pt which might appear to be stabilised by sulphur ligands, and we propose that this arises as a result of an acceptor role for a niobium–nickel bond of essentially σ-symmetry.

Therefore, in the complexes (III) it appears that the system $[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]^+$ is acting as a 2×2-electron σ-donor and a 2-electron σ-*acceptor* ligand: an unusual type of donor–acceptor ligand.

Oxidation of the neutral complex (II) with iodine forms the diamagnetic, d^0 complex cation $[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]^+$ (IV), which may be isolated as iodide or hexafluorophosphate salts.

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[3] L. F. Dahl, E. R. de Gil, and R. D. Feltham, *J. Amer. Chem. Soc.*, 1969, 91, 1653.
[4] T. S. Cameron, C. K. Prout, G. V. Rees, M. L. H. Green, K. K. Joshi, G. R. Davies, B. T. Kilbourn, P. S. Braterman, and V. A. Wilson, *Chem. Comm.*, 1971, 14.