groups [O(2)—Me and O(8)—Me, respectively] used to form the link with the next monomer. The greater length of the Na—O(2) [2·371 (6) Å] and Na—O(8) [2·338 (6) Å] bonds compared with the other Na—O distances (see Table 2) reflects the poorer donor properties of methoxy groups *vs* P═O groups. The non-bonding O···O distances (P═O oxygen atoms) vary from 3·127 (7) to 3·239 (6) Å and demonstrate the flexibility of the tripod part of the ligand. This study indicates that *L* ligands alone (*i.e.* not combined with other donor molecules) do not favour the formation of small Na-aggregates, as found in $(NaL_{OEt})_3.2H_2O$. This obviously can be ascribed to the marked tendency of Na ions to have coordination number six or, to a lesser degree, five, a condition which can hardly be satisfied when a triangular array of Na atoms is surrounded only by ligands of the *L* type.

In conclusion the structure described here constitutes the first example in which a ligand of the type $[(\eta^5\text{-}C_5H_5)Co\{P(O)(OR)_2\}_3]^-$ acts as a pentapodal ligand. This property leads to the formation of an organometallic polymer.

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**References**

B. A. Frenz & Associates, Inc. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.
Karle, I. L. (1974). *Biochemistry*, **13**, 2155–2162.
Kläui, W. (1990). *Angew. Chem. Int. Ed. Engl.* **29**, 627–637.
Kläui, W., Lenders, B., Hessner, B. & Evertz, K. (1988). *Organometallics*, **7**, 1357–1363.
Kläui, W., Müller, A., Eberspach, W., Boese, R. & Goldberg, I. (1987). *J. Am. Chem. Soc.* **109**, 164–169.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
Stout, G. H. & Jensen, L. H. (1968). In *X-ray Structure Determination*. New York: Macmillan.

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# Structures of $[Nb_2Cl_6(C_4H_8S)(PEt_3)_2]$, $[Nb_2Cl_6(C_4H_8S)(C_4H_8O)_2]$ and $[Ta_2Cl_6(C_4H_8S)(PMe_3)_2]$

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**Abstract.** Di-$\mu$-chloro-tetrachlorobis(tetrahydrothiophenato)(triethylphosphino)diniobium(III), $[Nb_2Cl_6(C_4H_8S)(PEt_3)_2]$, di-$\mu$-chloro-tetrachlorobis(tetrahydrofuranato)tetrahydrothiophenatodiniobium(III), $[Nb_2Cl_6(C_4H_8S)(C_4H_8O)_2]$ and di-$\mu$-chloro-tetrachlorobistetrahydrothiophenato(trimethylphosphino)ditantalum(III), $[Ta_2Cl_6(C_4H_8S)(PMe_3)_2]$ crystallized in two crystal phases. These molecules are confacial bioctahedra with two bridging Cl atoms and one $C_4H_8S$ molecule. (I) $[Nb_2Cl_6(C_4H_8S)(PEt_3)_2]$, $M_r$ = 723·02, orthorhombic, $P2_12_12_1$, $a$ = 9·512 (2), $b$ = 14·171 (3), $c$ = 21·948 (5) Å, $V$ = 2958 (1) Å$^3$, $Z$ = 4, $D_x$ = 1·623 g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu$ = 14·7 cm$^{-1}$, $F(000)$ = 1456, $T$ = 294 K, $R$ = 0·0471, 2153 unique observed reflections with $I > 3\sigma(I)$. The Nb—Nb distance is 2·718 (1) Å. The Nb—Cl$_{bridge}$ distances range from 2·496 (3) to 2·530 (3) Å and Nb—S distances are 2·456 (3) and 2·461 (3) Å. The range of Nb—Cl$_{terminal}$ distances is 2·392 (4) to 2·406 (3) Å. The Nb—P distances are 2·678 (4) and 2·675 (3) Å. (II) $[Nb_2Cl_6(C_4H_8S)(C_4H_8O)_2]$, $M_r$ = 630·91, monoclinic, $C2/c$, $a$ = 13·367 (4), $b$ = 10·642 (4), $c$ = 15·317 (5) Å, $\beta$ = 93·71°, $V$ = 2174 (1) Å$^3$, $Z$ = 4, $D_x$ = 1·927 g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu$ = 18·5 cm$^{-1}$, $F(000)$ = 1248, $T$ = 294 K, $R$ = 0·0557, 1026 unique observed reflections with $I > 3\sigma(I)$. The Nb—Nb distance is 2·684 (2) Å. The Nb—Cl$_{bridge}$ distances are 2·495 (4) and 2·497 (4) Å and the Nb—S distance is 2·401 (1) Å. The Nb—Cl$_{terminal}$ distances are 2·372 (4) and 2·406 (3) Å. The Nb—O distance is 2·401 (4) Å. (III*a*) $[Ta_2Cl_6(C_4H_8S)(PMe_3)_2]$, $M_r$ = 814·94, triclinic, $P\bar{1}$, $a$ = 10·615 (4), $b$ = 12·189 (2), $c$ = 10·529 (2) Å, $\alpha$ = 102·35 (2), $\beta$ = 117·91 (3), $\gamma$ = 87·86 (2)°, $V$ = 1173 (1) Å$^3$, $Z$ = 2, $D_x$ = 2·307 g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu$ = 101 cm$^{-1}$, $F(000)$ = 760, $T$ = 294 K, $R$ = 0·0692, 3263 unique reflections with $I > 3\sigma(I)$, (III*b*) $[Ta_2Cl_6(C_4H_8S)(PMe_3)_2]$, triclinic, $P\bar{1}$, $a$ = 10·412 (1), $b$ = 10·569 (2), $c$ = 23·763 (6) Å, $\alpha$ = 88·04 (2), $\beta$ = 87·17 (2), $\gamma$ = 64·52 (1)°, $V$ =

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2357·6 (9) Å$^3$, $Z = 4$, $D_x = 2{\cdot}296$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 101$ cm$^{-1}$, $F(000) = 1520$, $T = 294$ K, $R = 0{\cdot}0692$, 5549 unique observed reflections with $I > 3\sigma(I)$. For these two crystal phases the average bond distances for Ta—Ta, Ta—S, Ta—$Cl_{bridge}$, Ta—$Cl_{terminal}$ and Ta—P bonds are 2·682 (3), 2·422 (6), 2·502 (13), 2·375 (9) and 2·623 (8) Å, respectively.

**Introduction.** In the early 1970's Mass & McCarley (1973) reported the synthesis and characterization of $M_2X_6(C_4H_8S)_3$, where $M$ = Nb, Ta and $X$ = Cl, Br, I. These complexes became excellent starting materials for the preparation of new $Nb^{III}$ and $Ta^{III}$ compounds. In the past decade a series of ligand-substitution reactions of these dimers with bidentate phosphines has been explored. When two equivalents of bidentate phosphines, such as dmpm (Chakravarty, Cotton, Diebold, Lewis & Roth, 1986), dppm (Cotton & Roth, 1983) or depe (Cotton, Diebold & Roth, 1987) is used, the confacial bioctahedron dimers form edge sharing dimers and the phosphine ligands serve as either bridging or chelating ligands. In the presence of excess dppe the confacial bioctahedral geometry of the $Ta_2X_6(C_4H_8S)_3$ starting material is preserved (Gilletti, Young & Brown, 1989) but the product isolated is tetrameric, $Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}SC_4H_8)(\mu\text{-}Ph_2PCH_2CH_2PPh_2)_2$. The structures of the confacial bioctahedral dimers reported here show that in the case of monodentate ligands the dimers preserve their original geometry.

**Experimental.** (I) $Nb_2Cl_6(C_4H_8S)_3$ (0·66 g, 1 mmol), $PEt_3$ (0·3 ml, 2 mmol), Na/Hg (1 ml, 2 $M$) and 35 ml toluene were stirred in a 100 ml three-neck flask for 2 h. The solution was filtered and layered with 20 ml hexane. Red, rectangular crystals of the product began to grow after one week. Crystal of dimensions 0·40 × 0·30 × 0·20 mm was mounted inside a capillary. Cell constants were derived from least-squares refinement based on 25 reflections having $8 \leq 2\theta \leq 24°$. Intensity data were collected at variable scan speeds (3–30° min$^{-1}$) dependent on a pre-scan count with a skip option, moving-crystal/moving-counter technique, $\omega$–$2\theta$ scans with $4 \leq 2\theta \leq 50°$, using a Nicolet $P3F$ diffractometer. $h = 0 \rightarrow 12$, $k = 0 \rightarrow 17$, $l = -27 \rightarrow 27$. Three standard reflections ($17\bar{2}$, $41\bar{8}$, $\bar{5}21$) revealed no decay of the crystal. Data were corrected for Lorentz and polarization effects. 2864 data collected and averaged to 2153 unique observed reflections with $I > 3\sigma(I)$, $R_{int} = 0{\cdot}025$. Scattering factors were those of *Structure Determination Package* (Frenz, 1985). The Nb, Cl, P and S atoms were located by direct methods, *SHELXS*86 (Sheldrick, 1986) and the C atoms were located and refined by alternating difference Fourier maps with least-squares cycles using *SDP*. The H atoms were not included in the model and all the atoms were refined anisotropically. Final $R = 0{\cdot}0471$ and $wR = 0{\cdot}0594$, where $w = \sigma^2(|F_o|)^{-1}$ and $S = 1{\cdot}463$ for 244 variables. At convergence, $(\Delta/\sigma)_{max} = 0{\cdot}05$, $(\Delta\rho)_{max} = 0{\cdot}96$ and $(\Delta\rho)_{min} = -0{\cdot}58$ e Å$^{-3}$ on final difference Fourier map. Final positional and equivalent isotropic thermal parameters are listed in Table 1.*

(II) $Nb_2Cl_6(C_4H_8S)_3$ (0·66 g, 1 mmol), benzene (20 ml), $C_4H_8O$ (20 ml) and Na/Hg (0·5 ml, 2$M$) were placed in a 100 ml flask, stirred for 1 h. The red solution was filtered and layered with 20 ml hexane. X-ray-quality crystals of $Nb_2Cl_6(C_4H_8S)(C_4H_8O)_2$ grew after 2 d. A light red, regularly shaped crystal, 0·20 × 0·05 × 0·20 mm, was mounted inside a capillary. Cell constants were derived from least-squares refinement based on 25 reflections having $18 \leq 2\theta \leq 23°$, using a Rigaku AFC5$R$ diffractometer. Intensity data were collected using the $2\theta$–$\omega$ scan technique with $4 \leq 2\theta \leq 50°$, scan speed 8° min$^{-1}$, maximum four scan repetitions. $h = 0 \rightarrow 14$, $k = 0 \rightarrow 11$, $l = -17 \rightarrow 17$. Three standard reflections ($\bar{2}4\bar{4}$, $\bar{2}\bar{2}6$, $\bar{3}3\bar{5}$), measured every 150 reflections, revealed no decay of the crystal. Data were corrected for Lorentz and polarization effects and absorption corrections were made based on $\psi$ scans of six reflections near $\chi = 90°$, using the empirical method of North, Phillips & Matthews (1968); relative $T_{min} = 0{\cdot}8053$, $T_{max} = 1{\cdot}0000$. 1507 data collected and averaged to 1026 unique observed reflections [$I > 3\sigma(I)$], $R_{int} = 0{\cdot}025$. Scattering factors were those of *Structure Determination Package*. The Nb, Cl, S and O atoms were located by direct methods (*SHELXS*86; Sheldrick, 1986) and the C atoms were located and refined by alternating difference Fourier maps with least-squares cycles using *SDP*. The H atoms were not included in the model and all other atoms were refined anisotropically. Final $R = 0{\cdot}0557$ and $wR = 0{\cdot}0709$, where $w = \sigma^2(|F_o|)^{-1}$ and $S = 1{\cdot}402$ for 105 variables. At convergence $(\Delta/\sigma)_{max} = 0{\cdot}01$, $(\Delta\rho)_{max} = 1{\cdot}33$ and $(\Delta\rho)_{min} = -0{\cdot}62$ e Å$^{-3}$ on final difference Fourier map. Final positional and equivalent isotropic thermal parameters are listed in Table 1.

(III) $Ta_2Cl_6(C_4H_8S)(C_4H_8O)_2$ (0·4 g, 0·5 mmol) (Cotton, Diebold & Roth, 1987), Na/Hg (0·6 mmol Na in 0·6 ml Hg) were stirred in a mixture of solvents (15 ml toluene and 1ml $C_4H_8O$) for 10 h. $PMe_3$ (0·25 ml, 2·5 mmol) was added and the solution was stirred for 24 h. The brick-red solution was filtered into a Schlenk tube and layered with hexane (15 ml). After several days green and brown plate-like crystals of the two types of the crystal phases of

* Lists of structure factors, anisotropic thermal parameters and complete intramolecular bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53968 (96 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and equivalent isotropic displacement parameters* (Å$^2$)

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| $Nb_2Cl_6$(THT)($PEt_3$)$_2$ | | | | |
| Nb(1) | 0·2203 (1) | 0·54902 (7) | 0·34624 (5) | 3·46 (2) |
| Nb(2) | 0·2119 (1) | 0·50930 (7) | 0·46733 (5) | 3·66 (2) |
| Cl(1) | 0·4191 (3) | 0·6284 (2) | 0·3018 (2) | 4·64 (7) |
| Cl(2) | 0·4044 (4) | 0·5499 (3) | 0·5326 (2) | 5·80 (8) |
| Cl(3) | 0·1633 (5) | 0·3535 (3) | 0·5037 (2) | 6·7 (1) |
| Cl(4) | 0·1802 (4) | 0·4277 (2) | 0·2729 (2) | 5·63 (8) |
| Cl(5) | 0·1997 (3) | 0·6734 (2) | 0·4263 (1) | 4·06 (6) |
| Cl(6) | −0·0043 (3) | 0·5069 (2) | 0·4002 (1) | 4·77 (7) |
| S(1) | 0·3841 (3) | 0·4400 (2) | 0·3966 (2) | 4·16 (6) |
| P(1) | 0·0722 (4) | 0·6641 (3) | 0·2738 (2) | 4·81 (8) |
| P(2) | 0·0399 (3) | 0·5756 (2) | 0·5538 (2) | 4·07 (7) |
| C(1) | 0·579 (1) | 0·4630 (9) | 0·3982 (6) | 4·8 (3) |
| C(2) | 0·396 (2) | 0·3114 (8) | 0·3798 (7) | 5·4 (3) |
| C(3) | 0·547 (2) | 0·298 (1) | 0·3594 (8) | 6·6 (4) |
| C(4) | 0·644 (2) | 0·364 (1) | 0·391 (1) | 8·9 (5) |
| C(11) | 0·126 (2) | 0·795 (1) | 0·2820 (9) | 7·6 (5) |
| C(12) | 0·116 (2) | 0·639 (1) | 0·1910 (6) | 6·1 (4) |
| C(13) | −0·116 (2) | 0·661 (1) | 0·2786 (7) | 7·4 (4) |
| C(14) | 0·066 (2) | 0·844 (1) | 0·3337 (7) | 7·2 (4) |
| C(15) | 0·036 (2) | 0·700 (2) | 0·1441 (7) | 8·6 (5) |
| C(16) | −0·182 (2) | 0·573 (1) | 0·2566 (9) | 7·9 (5) |
| C(21) | 0·087 (1) | 0·533 (1) | 0·6305 (6) | 5·1 (3) |
| C(22) | 0·039 (2) | 0·7073 (9) | 0·5614 (6) | 5·0 (3) |
| C(23) | −0·150 (1) | 0·548 (1) | 0·5446 (7) | 5·5 (3) |
| C(24) | −0·010 (2) | 0·572 (1) | 0·6827 (6) | 6·2 (4) |
| C(25) | 0·174 (2) | 0·749 (1) | 0·5828 (8) | 7·1 (4) |
| C(26) | −0·187 (2) | 0·442 (1) | 0·5523 (8) | 7·1 (4) |
| $Nb_2Cl_6$(THT)(THF)$_2$ | | | | |
| Nb(1) | 0·43450 (9) | 0·2681 (1) | 0·17980 (8) | 2·38 (2) |
| Cl(1) | 0·4105 (3) | 0·3997 (3) | 0·3116 (2) | 3·46 (8) |
| Cl(2) | 0·4762 (3) | 0·1840 (4) | 0·0434 (2) | 4·08 (9) |
| Cl(3) | 0·2709 (3) | 0·1829 (4) | 0·1870 (3) | 3·96 (8) |
| S(1) | 0·500 | 0·0811 (5) | 0·250 | 2·6 (1) |
| O(1) | 0·3651 (8) | 0·4291 (8) | 0·1052 (6) | 3·7 (2) |
| C(1) | 0·296 (1) | 0·411 (1) | 0·031 (1) | 5·2 (4) |
| C(2) | 0·253 (1) | 0·540 (1) | 0·006 (1) | 4·7 (4) |
| C(3) | 0·309 (1) | 0·633 (1) | 0·067 (1) | 5·2 (4) |
| C(4) | 0·394 (2) | 0·562 (1) | 0·115 (1) | 6·0 (5) |
| C(5) | 0·422 (1) | −0·035 (1) | 0·305 (1) | 3·8 (3) |
| C(6) | 0·472 (1) | −0·160 (1) | 0·286 (1) | 7·3 (6) |
| $Ta_2Cl_6$(THT)($PMe_3$)$_2$ | | | | |
| Ta(1) | 0·30958 (7) | 0·25531 (7) | 0·12219 (7) | 2·27 (2) |
| Ta(2) | 0·15317 (7) | 0·26676 (7) | 0·26359 (7) | 2·28 (2) |
| S | 0·4105 (5) | 0·2572 (4) | 0·3823 (5) | 2·4 (1) |
| Cl(1) | 0·1160 (5) | 0·3888 (4) | 0·0892 (5) | 3·2 (1) |
| Cl(2) | 0·0885 (5) | 0·1302 (5) | 0·0236 (5) | 3·1 (1) |
| Cl(3) | 0·4532 (5) | 0·1033 (5) | 0·1085 (6) | 3·9 (1) |
| Cl(4) | 0·4708 (5) | 0·4087 (5) | 0·1757 (5) | 3·7 (1) |
| Cl(5) | 0·1364 (6) | 0·1127 (5) | 0·3645 (6) | 4·1 (1) |
| Cl(6) | 0·1769 (6) | 0·4248 (5) | 0·4521 (6) | 4·1 (1) |
| P(1) | 0·2287 (6) | 0·2281 (6) | −0·1613 (5) | 3·4 (1) |
| P(2) | −0·1221 (5) | 0·2755 (5) | 0·1714 (6) | 3·0 (1) |
| C(1) | 0·548 (2) | 0·369 (2) | 0·533 (2) | 3·4 (5) |
| C(2) | 0·652 (3) | 0·301 (2) | 0·641 (3) | 5·5 (8) |
| C(3) | 0·653 (3) | 0·186 (3) | 0·579 (4) | 8 (1) |
| C(4) | 0·496 (2) | 0·133 (2) | 0·457 (2) | 4·0 (6) |
| C(5) | 0·210 (4) | 0·075 (3) | −0·258 (3) | 8 (1) |
| C(6) | 0·348 (2) | 0·295 (2) | −0·204 (2) | 4·9 (6) |
| C(7) | 0·051 (2) | 0·273 (3) | −0·275 (3) | 5·9 (8) |
| C(8) | −0·240 (2) | 0·164 (2) | 0·018 (2) | 4·4 (6) |
| C(9) | −0·202 (3) | 0·404 (2) | 0·118 (3) | 6·5 (8) |
| C(10) | −0·172 (2) | 0·268 (3) | 0·313 (2) | 4·9 (7) |
| $Ta_2Cl_6$(THT)($PMe_3$)$_2$ | | | | |
| Ta(1*a*) | 0·22545 (8) | 0·64701 (8) | 0·37275 (4) | 2·84 (2) |
| Ta(2*a*) | 0·36053 (8) | 0·81088 (8) | 0·38389 (4) | 2·65 (2) |
| S(*a*) | 0·4822 (5) | 0·5576 (5) | 0·3782 (2) | 3·2 (1) |
| Cl(1*a*) | 0·1745 (5) | 0·8601 (5) | 0·3129 (2) | 3·9 (1) |
| Cl(2*a*) | 0·1412 (5) | 0·8435 (5) | 0·4421 (3) | 3·6 (1) |
| Cl(3*a*) | 0·2224 (6) | 0·4935 (6) | 0·4472 (3) | 4·6 (1) |
| Cl(4*a*) | 0·2715 (6) | 0·5034 (6) | 0·2929 (3) | 5·2 (2) |
| Cl(5*a*) | 0·4880 (6) | 0·8023 (6) | 0·4650 (3) | 4·3 (1) |
| Cl(6*a*) | 0·5172 (6) | 0·8250 (6) | 0·3102 (3) | 4·5 (1) |
| P(1*a*) | −0·0455 (6) | 0·7147 (6) | 0·3597 (3) | 3·8 (1) |
| P(2*a*) | 0·2697 (6) | 1·0819 (5) | 0·3908 (3) | 3·6 (1) |
| C(1*a*) | 0·606 (2) | 0·461 (3) | 0·317 (1) | 5·3 (7) |
| C(2*a*) | 0·709 (4) | 0·326 (3) | 0·344 (1) | 9 (1) |
| C(3*a*) | 0·719 (3) | 0·309 (3) | 0·406 (1) | 9 (1) |

Table 1 (*cont.*)

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| C(4*a*) | 0·588 (2) | 0·436 (2) | 0·436 (1) | 4·3 (6) |
| C(5*a*) | −0·128 (2) | 0·622 (2) | 0·405 (1) | 5·6 (6) |
| C(6*a*) | −0·078 (2) | 0·670 (3) | 0·288 (1) | 5·4 (7) |
| C(7*a*) | −0·173 (3) | 0·896 (2) | 0·370 (1) | 6·1 (8) |
| C(8*a*) | 0·185 (3) | 1·154 (2) | 0·460 (1) | 6·0 (7) |
| C(9*a*) | 0·138 (3) | 1·188 (3) | 0·343 (1) | 6·5 (8) |
| C(10*a*) | 0·417 (3) | 1·129 (3) | 0·383 (2) | 7·7 (8) |
| Ta(1*b*) | 0·30619 (8) | 0·85846 (8) | 0·87509 (4) | 2·62 (2) |
| Ta(2*b*) | 0·16867 (8) | 0·69454 (8) | 0·88227 (4) | 2·67 (2) |
| S(*b*) | 0·0495 (5) | 0·9472 (5) | 0·8779 (2) | 3·1 (1) |
| Cl(1*b*) | 0·3736 (5) | 0·6505 (5) | 0·8150 (2) | 3·7 (1) |
| Cl(2*b*) | 0·3699 (5) | 0·6570 (5) | 0·9449 (2) | 3·4 (1) |
| Cl(3*b*) | 0·2880 (6) | 1·0081 (5) | 0·9504 (3) | 4·2 (1) |
| Cl(4*b*) | 0·2844 (6) | 1·0095 (6) | 0·7967 (3) | 4·9 (2) |
| Cl(5*b*) | 0·0208 (6) | 0·6965 (6) | 0·9611 (3) | 4·4 (1) |
| Cl(6*b*) | 0·0340 (6) | 0·6859 (6) | 0·8053 (3) | 4·7 (1) |
| P(1*b*) | 0·5798 (5) | 0·7912 (6) | 0·8650 (3) | 3·7 (1) |
| P(2*b*) | 0·2595 (6) | 0·4214 (5) | 0·8874 (3) | 3·6 (1) |
| C(1*b*) | −0·055 (2) | 1·045 (2) | 0·816 (1) | 4·9 (6) |
| C(2*b*) | −0·154 (3) | 1·189 (3) | 0·845 (1) | 7·5 (9) |
| C(3*b*) | −0·183 (3) | 1·185 (3) | 0·904 (1) | 9 (1) |
| C(4*b*) | −0·073 (2) | 1·063 (2) | 0·934 (1) | 4·3 (6) |
| C(5*b*) | 0·638 (2) | 0·894 (2) | 0·909 (1) | 6·0 (6) |
| C(6*b*) | 0·633 (2) | 0·821 (2) | 0·793 (1) | 4·9 (6) |
| C(7*b*) | 0·699 (2) | 0·615 (3) | 0·879 (1) | 5·9 (8) |
| C(8*b*) | 0·347 (3) | 0·341 (3) | 0·956 (1) | 9·2 (9) |
| C(9*b*) | 0·386 (3) | 0·320 (3) | 0·832 (2) | 7·9 (6) |
| C(10*b*) | 0·109 (3) | 0·369 (2) | 0·883 (1) | 6·8 (8) |

$Ta_2Cl_6(C_4H_8S)(PMe_3)_2$ were formed. When the reaction is carried out in $C_4H_8O$, only green crystals are formed, while in toluene only brown crystals are formed. A green crystal of $Ta_2Cl_6(C_4H_8S)(PMe_3)_2$ (III*a*) with the dimensions of 0·35 × 0·25 × 0·05 mm was mounted in a capillary. Cell constants were derived from least-squares refinement based on 25 reflections having $30 \leq 2\theta \leq 40°$ using a Rigaku AFC5*R* diffractometer. Intensity data were collected using the $\omega$–$2\theta$ scan method, fixed scan speed 32° min$^{-1}$, max. repetition scans of four, data collection range $4 \leq 2\theta \leq 55°$. $h = 0 \rightarrow 14$, $k = -16 \rightarrow 16$, $l = -14 \rightarrow 14$. Three standard reflections ($\bar{4}\bar{2}0$, $\bar{5}\bar{2}1$, $\bar{5}21$) revealed 21·3% crystal decay. Data were corrected for decay, Lorentz and polarization effects and absorption corrections were made, based on $\psi$ scans of six reflections near $\chi = 90°$, using the empirical method of North, Phillips & Matthews (1968); relative $T_{min} = 0·2808$, $T_{max} = 1·0000$. 5668 data collected and averaged to 3263 unique observed reflections [$I > 3\sigma(I)$], $R_{int} = 0·041$. Ta, Cl, S and P atoms were located by the Patterson method, *SHELXS*86 (Sheldrick, 1986), and the C atoms were revealed by a combination of difference Fourier synthesis and least-squares refinements. Final $R = 0·0692$ and $wR = 0·0873$, where $w = \sigma^2(|F_o|)^{-1}$ and $S = 1·622$ for 190 variables. At convergence, $(\Delta/\sigma)_{max} = 0·01$, $(\Delta\rho)_{max} = 3·28$ and $(\Delta\rho)_{min} = -1·25$ e Å$^{-3}$ on final difference Fourier map. Final positional and equivalent isotropic thermal parameters are listed in Table 1.

A brown crystal of $Ta_2Cl_6(C_4H_8S)(PMe_3)_2$ (III*b*) with the dimensions of 0·35 × 0·25 × 0·05 mm was mounted in a capillary. Cell constants were derived from least-squares refinement based on 25 reflections having $31 \leq 2\theta \leq 34°$ using an Enraf–Nonius CAD-4 diffractometer. Intensity data were collected using the $\omega$–$2\theta$ scan method, variable scan speed (1·27–5·49° $min^{-1}$ for $\omega$ circle), data collection range $2 \leq 2\theta \leq 46°$, $h = -11 \rightarrow 11$, $k = -11 \rightarrow -11$, $l = 0 \rightarrow 26$. Three standard reflections ($6\bar{1}\bar{9}$, $1\bar{6}9$, $\bar{1}6\bar{9}$), revealed 28·9% crystal decay. Data were corrected for decay, Lorentz and polarization effects and absorption corrections were made, based on $\psi$ scans of seven reflections near $\chi = 90°$, using the empirical method of North, Phillips & Matthews (1968); relative $T_{min} = 0·4923$, $T_{max} = 0·9962$. 6739 data collected and averaged to 5549 unique observed reflections [$I > 3\sigma(I)$], $R_{int} = 0·010$. Ta, Cl, S and P atoms were located by the Patterson method, *SHELXS*86 (Sheldrick, 1986) and the C atoms were revealed by a combination of difference Fourier synthesis and least-squares refinements. Final $R = 0·0692$ and $wR = 0·1088$, where $w = \sigma^2(|F_o|)^{-1}$ and $S = 3·312$ for 190 variables. At convergence, $(\Delta/\sigma)_{max} = 0·075$, $(\Delta\rho)_{max} = 4·65$ and $(\Delta\rho)_{min} = -1·98$ e Å$^{-3}$ on final difference Fourier map. Final positional and equivalent isotropic thermal parameters are listed in Table 1.

**Discussion.** The reactions reported here were attempts to use $M_2Cl_6(C_4H_8S)_3$ as starting materials for reducing the metal centers to lower oxidation states. The products isolated, however, were not the reduced species but $M^{III}$ complexes where the terminal $C_4H_8S$ ligands were substituted by $C_4H_8O$, $PMe_3$, and $PEt_3$. Various factors seem to play a role in the reduction of $M_2Cl_6(C_4H_8S)_3$. One point which is certain is that $M_2Cl_6(C_4H_8S)_3$ dimers do not reduce to lower oxidation states in aromatic solvents. Attempts to reduce them in aromatic solvents were the routes taken when $Nb_2Cl_6(C_4H_8S)(PEt_3)_2$ and $Ta_2Cl_6(C_4H_8S)(PMe_3)_2$ were isolated. $Ta_2Cl_6(C_4H_8S)(PMe_3)_2$ was also prepared using other routes. When $C_4H_8O$ is used to reduce $Ta_2Cl_6(C_4H_8S)_3$, green crystals of $Ta_2Cl_6(C_4H_8S)(PMe_3)_2$ are isolated. The reaction of $Ta_2Cl_6(C_4H_8S)_3$ with $PMe_3$ and Na/Hg in a mixture of $C_4H_8O$ and aromatic solvents gives both the green and the brown crystals of $Ta_2Cl_6(C_4H_8S)(PMe_3)_2$. When $Nb_2Cl_6(C_4H_8S)_3$ is reacted in a mixture of $C_4H_8O$/benzene solution, without the presence of phosphines, $Nb_2Cl_6(C_4H_8S)(C_4H_8O)_2$ is crystallized. Although we are certain that aromatic solvents do not form a good medium for the reduction of $M_2X_6(C_4H_8S)_3$, we are unable to understand why in the presence of $C_4H_8O$ these compounds do not reduce further since from similar reactions $[M_2X_6(C_4H_8S)_3]^{2-}$ complexes, possessing triple bonds between the metal atoms, were prepared (Cotton, Diebold & Roth, 1987).

Figs. 1–3 show *ORTEP* (Johnson, 1965) drawings of $Nb_2Cl_6(C_4H_8S)(PEt_3)_2$, $Nb_2Cl_6(C_4H_8S)(C_4H_8O)_2$ and $Ta_2Cl_6(C_4H_8S)(PMe_3)_2$. Owing to the metal–metal interaction, these dimers show a distortion in $M$—($\mu$-Cl)—$M$ and ($\mu$-Cl)—$M$—($\mu$-Cl) angles, from the ideal 70·53 and 90°. The metal–metal distances, ($\mu$-Cl)—$M$—($\mu$-Cl) and $M$—($\mu$-Cl)—$M$ for

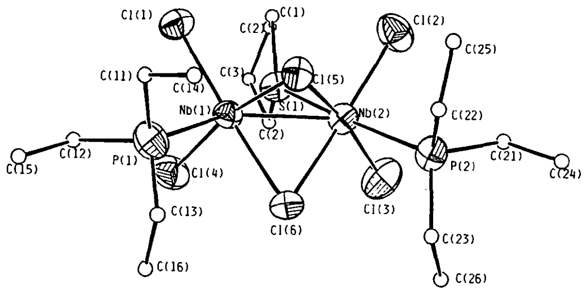


Fig. 1. An *ORTEP* drawing of $Nb_2Cl_6(THT)(PEt_3)_2$ showing the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level. The C atoms are drawn with arbitrary radii.

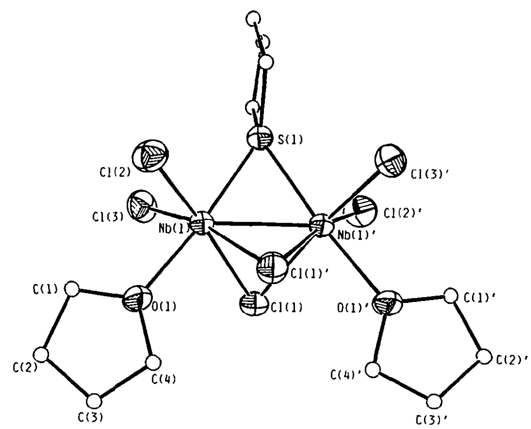


Fig. 2. An *ORTEP* drawing of $Nb_2Cl_6(THT)(THF)_2$ showing the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level. The C atoms are drawn with arbitrary radii.

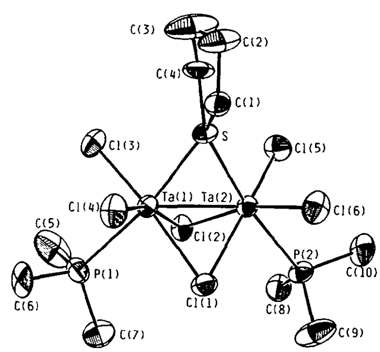


Fig. 3. An *ORTEP* drawing of $Nb_2Cl_6(THT)(PMe_3)_2$ showing the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level.

$Nb_2Cl_6(C_4H_8S)(PEt_3)_2$, $Nb_2Cl_6(C_4H_8S)(C_4H_8O)_2$ and $Ta_2Cl_6(C_4H_8S)(PMe_3)_2$ are 2·718 (1), 2·684 (2), 2·682 (2) Å, 76·5 (2), 78·0 (1), 76·0 (2), 65·6 (4), 65·1 (1), 64·8 (3)°, respectively.

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### References

CHAKRAVARTY, A. R., COTTON, F. A., DIEBOLD, M. P., LEWIS, D. B. & ROTH, W. J. (1986). *J. Am. Chem. Soc.* **108**, 971–976.
COTTON, F. A., DIEBOLD, M. P. & ROTH, W. J. (1987). *Inorg. Chem.* **26**, 4130–4133.
COTTON, F. A., DIEBOLD, M. P. & ROTH, W. J. (1987). *J. Am. Chem. Soc.* **109**, 5506–5144.
COTTON, F. A. & ROTH, W. J. (1983). *Inorg. Chem.* **22**, 3654–3656.
FRENZ, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*, Version 3.0. Enraf–Nonius, Delft, The Netherlands.
GILLETTI, P. F., YOUNG, V. G. & BROWN, T. M. (1989). *Inorg. Chem.* **28**, 4034–4036.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
MASS, E. T. & MCCARLEY, R. E. (1973). *Inorg. Chem.* **12**, 1096–1101.
NORTH, A. C. T., PHILLIPS, D. C. & MATTHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

*Acta Cryst.* (1991). C**47**, 1621–1624

# Structure of a Monochloro Bridged Polymeric Copper(II)–Di-2-pyridylamine Complex: [Cu(dipyam)Cl($NO_3$)].0·5$H_2O$

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**Abstract.** Di-2-pyridylaminechloronitratocopper(II) hemihydrate, $[CuCl(NO_3)(C_{10}H_9N_3)].0{\cdot}5H_2O$, $M_r$ = 341·21, monoclinic, $P2_1/a$, $a$ = 7·382 (1), $b$ = 21·494 (4), $c$ = 8·032 (1) Å, $\beta$ = 94·26 (1)°, $V$ = 1270·9 Å$^3$, $Z$ = 4, $D_m$ = 1·78, $D_x$ = 1·782 g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7107 Å, $\mu$(Mo $K\alpha$) = 19·47 cm$^{-1}$, $F$(000) = 688. The structure was solved by the heavy-atom method and refined to a final $R$ value of 0·034 for 2736 reflections collected at 294 K. The structure consists of polymeric [Cu(dipyam)Cl($NO_3$)] units bridged by a chloride ion.

**Introduction.** $Cu^{II}$ halides show a wide variety of stereochemical complexity (Smith, 1976; Willett & Geiser, 1984). Observed geometries include four-coordinate, five-coordinate and six-coordinate species. Both the inherent flexibility of the $Cu^{II}$ coordination sphere and the non-stereospecific nature of the rather large spherical halide ion play a crucial role in this respect. Further interest in the crystal chemistry of $Cu^{II}$ halides derives from the bridging ability of the halide ions. The halide ions involved in bridge formation can either form two Cu—$X$ bonds of normal length (a symmetrical bridge) or one normal Cu—$X$ and one long, semi-coordinate Cu···$X$ bond (unsymmetrical bridge). The $Cu^{II}$ ions can be connected by combinations of one, two, or three such bridges.

The di-2-pyridylamine (dipyam) ligand used in this study and similar ligands (rigid or semirigid) are well known for their stabilizing effect of the five-coordinate state of $Cu^{II}$ (Hanson & Hathaway, 1980). However, in complexes containing dipyam, the flexible nature of this ligand results in a greater variety of geometries (Fuller & Jacobson, 1981).

In this paper we report the crystal structure of an unsymmetrically bridged polymeric monochloro-copper complex containing the dipyam ligand.

**Experimental.** The compound was isolated as a by-product in the synthesis of a vitamin $B_6$ complex. Dark green crystals were obtained on slow evaporation of a 2:1:2 mixture of dipyam, pyridoxal hydrochloride and $Cu(NO_3)_2.3H_2O$ in a water/methanol mixture. Density was measured by flotation in a mixture of $CHCl_3$ and $CHBr_3$. A crystal of size 0·28 × 0·21 × 0·12 mm was used in the data collection on a CAD-4 diffractometer. The unit-cell parameters are based on 25 centred reflections within the $\theta$ range 12–18°. Intensity data were collected for 3400 reflections with $\omega/2\theta$ scan, $-9 \le h \le 9$, $0 \le k \le 28$, $0 \le l \le 10$, $(\sin\theta/\lambda)_{max}$ = 0·66 Å$^{-1}$. Variations in three standard reflections (441, 413, 4$\bar{8}\bar{2}$) were less than 8%. The intensities were scaled by the use of these

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