O(1)—C(1)	1.269 (6)	C(12)—C(13)	1.378 (9)
O(2)—C(1)	1.270 (6)	C(13)—C(14)	1.365 (9)
O(3)—C(10)	1.263 (6)	C(14)—C(15)	1.39 (1)
O(4)—C(10)	1.239 (6)	C(15)—C(16)	1.376 (9)
O(5)—C(20)	1.234 (7)	N—C(20)	1.303 (7)
C(1)—C(2)	1.482 (6)	N—C(21)	1.432 (7)
C(2)—C(3)	1.371 (7)	N—C(22)	1.469 (8)
C(2)—C(7)	1.365 (8)		
O(6)—U—O(1)	92.7 (2)	O(7)—U—O(1)	87.5 (2)
O(6)—U—O(2)	89.3 (2)	O(7)—U—O(2)	90.3 (2)
O(6)—U—O(3^{i})	90.9 (2)	O(7)—U—O(3^{i})	89.1 (2)
O(6)—U—O(4)	90.2 (2)	O(7)—U—O(4)	90.6 (2)
O(6)—U—O(5)	89.0 (2)	O(7)—U—O(5)	90.3 (2)
O(6)—U—O(7)	179.3 (2)	O(1)—U—O(2)	53.2 (1)
O(2)—U—O(5)	70.8 (1)	O(5)—U—O(3^{i})	78.1 (1)
O(3)—U—O(4^{i})	82.1 (1)	O(4)—U—O(1)	75.9 (1)
O(5)—C(20)—N	124.5 (6)	C(20)—N—C(21)	120.9 (6)
C(20)—N—C(22)	121.9 (6)	C(21)—N—C(22)	117.1 (6)
O(1)—C(1)—O(2)	119.0 (5)	O(1)—C(1)—C(2)	119.8 (5)
O(2)—C(1)—C(2)	121.1 (5)	C(1)—C(2)—C(3)	118.9 (5)
C(1)—C(2)—C(7)	120.3 (5)	C(3)—C(2)—C(7)	120.7 (5)
C(2)—C(3)—C(4)	119.9 (6)	C(3)—C(4)—C(5)	119.3 (6)
C(4)—C(5)—C(6)	120.7 (6)	C(5)—C(6)—C(7)	119.5 (6)
C(2)—C(7)—C(6)	119.9 (6)	O(3)—C(10)—O(4)	122.0 (5)
O(3)—C(10)—C(11)	117.9 (5)	O(4)—C(10)—C(11)	120.1 (5)
C(10)—C(11)—C(12)	120.1 (5)	C(10)—C(11)—C(16)	120.9 (6)
C(12)—C(11)—C(16)	119.0 (6)	C(11)—C(12)—C(13)	121.0 (6)
C(12)—C(13)—C(14)	119.9 (7)	C(13)—C(14)—C(15)	119.4 (7)
C(14)—C(15)—C(16)	120.5 (7)	C(11)—C(16)—C(15)	120.1 (7)

Symmetry code: (i) $-x, -y, -z$.

The compound was prepared by dissolving stoichiometric amounts of solid diaqua(benzoato)chlorodioxouranium(VI) in a dmf solution of β-cyclodextrin. The mixture was stirred at 313 K until a solid non-homogeneous residue was obtained. The residue was dissolved by heating in dmf and the turbid solution was left at room temperature to crystallize.

The structure was solved by the heavy-atom method. The H atoms were located in geometrically calculated positions and allowed to ride on the parent C atoms during the refinements, with a fixed isotropic temperature factor $B = 6$ Å^2. The few residual peaks on the final difference synthesis were close to the U atom. Cell refinement and data collection: Enraf-Nonius CAD-4 software. Data reduction, structure resolution and refinement: *SDP* software (Frenz, 1985). Absorption correction: *DIFABS* (Walker & Stuart, 1983). Molecular graphics: *ORTEP* (Johnson, 1976). All calculations were performed using a MicroVAX II.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares-planes data and r.m.s. amplitudes of thermal vibration have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71236 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1039]

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Structure and Bonding in [$TaCl_4(C_5H_5N)_2$]

GORDON J. MILLER,* JIANHUA LIN AND
VICTOR YOUNG JR

*Ames Laboratory, US Department of Energy and
Department of Chemistry, Iowa State University,
Ames, Iowa 50011, USA*

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Abstract

The title structure, tetrachlorobis(pyridine)tantalum, is characterized by monomeric octahedral complexes, $TaCl_4(py)_2$ (py is pyridine), with the pyridine ligands coordinated in a *trans* configuration. In addition to packing (steric) arguments, an electronic driving force for the observed structure is incorporated, which is evaluated using extended Hückel calculations.

Comment

Thirty years ago, McCarley and coworkers first reported the synthesis and magnetic susceptibility measurements of $TaCl_4(py)_2$ (McCarley & Boatman, 1963). Their investigations of $TaCl_4(py)_2$ and $TaBr_4(py)_2$ concluded that there is a strong π-bonding component in the Ta–halide interaction, while the weak paramagnetism precluded the existence of Ta_2 dimers, as recognized, for example, in $TaCl_4$ (Schäfer & Kahlenberg, 1960).

During the course of new synthetic approaches towards transition-metal chalcogenide halides in supercritical amines (Miller & Lin, 1992), we have isolated red–brown needles suitable for single-crystal X-ray diffraction, and determined them to be $TaCl_4(py)_2$. We report its crystal structure and discuss the chemical bonding in this communication.

Although the strict crystallographic symmetry of each $TaCl_4(py)_2$ complex is $2/m$ (C_{2h}), the observed geometry is quite close to mmm (D_{2h}). Whereas many Ta and Nb tetrahalide complexes, MX_4L_2, in which L is a two-electron neutral ligand like phosphine and amine, show *cis* conformations (Cotton & Wilkinson, 1988), our determination confirms an earlier

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conjecture based on infra-red spectroscopy (Fowles, Tidmarsh & Walton, 1969).

Contours of the total electronic energy surface are shown in Fig. 2 for the various configurations of *trans*-$TaCl_4(py)_2$, which was calculated using the extended Hückel method (Hoffmann, 1963) [atomic orbital parameters have been deposited as supplementary material; orbital exponents were obtained from standard tables (Clemente & Roetti, 1974), orbital energies for Cl, N, C, H were evaluated from atomic spectral tables (Moore, 1971) and orbital energies for Ta were obtained from earlier investigations on halo–acetylide complexes of Ta (Hoffman, Hoffmann & Fiesel, 1982)]. The various configurations in Fig. 2 are distinguished using the angular variables ϕ and θ, which measure the angular relationship between the two *trans* pyridine ligands as well as the angular difference between a single pyridine and a single Ta—Cl vector. Specifically, ϕ is the dihedral angle between the planes of the two *trans*-coordinated pyridine ligands in the complex, and θ represents the angle between one Ta—Cl bond and one of the pyridine planes. The global energy minimum for these two geometrical parameters is the observed geometry ($\phi = 0$, $\theta = 45°$), and indicates that electronic forces influence the local structure of *trans*-$TaCl_4(py)_2$. Another relative minimum arises for the pyridine ligands mutually perpendicular to each other ($\phi = 90$, $\theta = 45°$). Since total energy maxima occur along the $\theta = 0°$ line, ligand–ligand repulsions between pyridine and chloride also contribute to the ground-state geometry.

The chloride ligands clearly act as π donors to the metal, but pyridine can be either a π donor or π acceptor in transition-metal complexes (Greenwood & Earnshaw, 1984). For example, in titanium–porphyrin complexes, both structural and theoretical investigations suggest that aromatic amines that complete the octahedral coordination at the metal have π-acceptor character (Woo, Hays & Miller, 1992). In this molecule, pyridine is acting as a π donor towards Ta. With these electronic roles of the ligands, can we understand why the *trans* conformation of pyridines is preferred in $TaCl_4(py)_2$?

There are five fundamental coordination modes for two pyridine groups around a metal center that would utilize π overlap between the Ta t_{2g} and pyridine p_π and p_σ orbitals: (i) *trans* with coplanar orientations (D_{2h} point symmetry; the observed geometry; $\phi = 0$, $\theta = 45°$ in Fig. 2); (ii) *trans* with the pyridine ligands perpendicular to each other (D_{2d}; $\phi = 45$, $\theta = 45°$ in Fig. 2); (iii) *cis* with coplanar orientations (C_{2v}); (iv) *cis* in which the pyridine planes are perpendicular to each other and give C_{2v} point symmetry; and (v) *cis* with the planes again perpendicular to leave a site symmetry of C_s. Of course, there are an infinite number of *trans* possibilities between (i) and (ii), but these two cases are the limiting geometrical examples. There are also innumerable conformations for the *cis* case, but (iii), (iv) and (v) represent boundary geometries as well. As found in numerous d^2 dioxo complexes (Cotton & Wilkinson, 1988) this d^1 Ta complex achieves the lowest electronic energy in the case of (i). The specific relative orientation of the two pyridine ligands in (i) leads to very weak Ta—N d_π–p_π antibonding interactions, in which the nitrogen p orbital is part of the p_σ orbital manifold of pyridine. We find the following trend in total electronic energy: E(i); 0.00 eV $<$ E(ii); 0.33 eV $<$ E(v); 0.64 eV $\simeq$ E(iv); 0.66 eV $<$ E(iii); 3.23 eV, which are also in agreement with our observed structure.

Fig. 3 illustrates the arrangement of Ta t_{2g} orbitals for the various conformations. The upward shift of the lowest t_{2g} level as we proceed from the lowest energy *trans* to the lowest energy *cis* configuration accounts for color changes observed in other $MX_4(py)_2$ complexes. The energies are labeled using angular overlap model (AOM) parameters (Burdett,

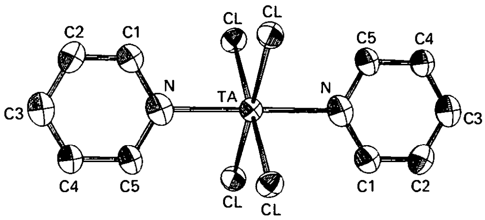

Fig. 1. Molecular structure of *trans*-$TaCl_4(py)_2$.

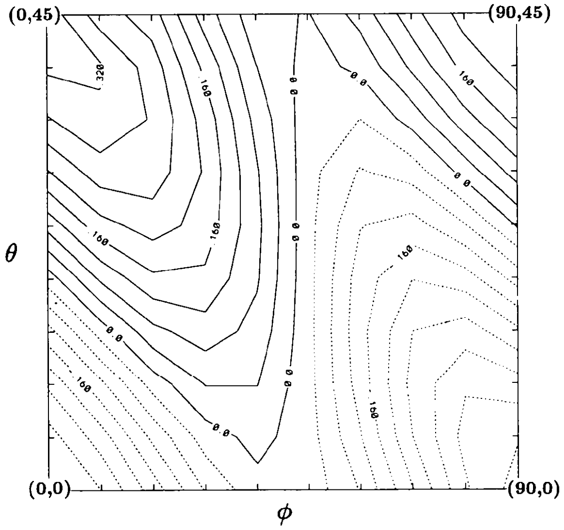

Fig. 2. Contour diagram of the total electronic energy for *trans*-$TaCl_4(py)_2$ as a function of the angular variables (ϕ, θ). Solid lines represent regions near energy minima while dashed lines represent regions near energy maxima. The observed structure ($\phi = 0$, $\theta = 45°$) corresponds to the upper left corner of this figure.

1980), for which we find $e_\pi = 0.53$ eV (Ta—Cl); $e_\pi' = 0.30$ eV (Ta—py p_π); and $e_\pi'' = 0.16$ eV (Ta—py p_σ). The difference between the parameters for chloride and pyridine arises from differences in orbital overlap integrals, while energy differences between pyridine p_π and p_σ orbitals with Ta 5*d* orbitals account for the relationship between the two Ta—py π interactions (pyridine p_π lie closer in energy to Ta 5*d* than the p_σ levels). In addition to Ta–ligand interactions, ligand–ligand repulsions, especially between adjacent pyridine groups, lead to stabilization of the *trans* geometry relative to *cis*.

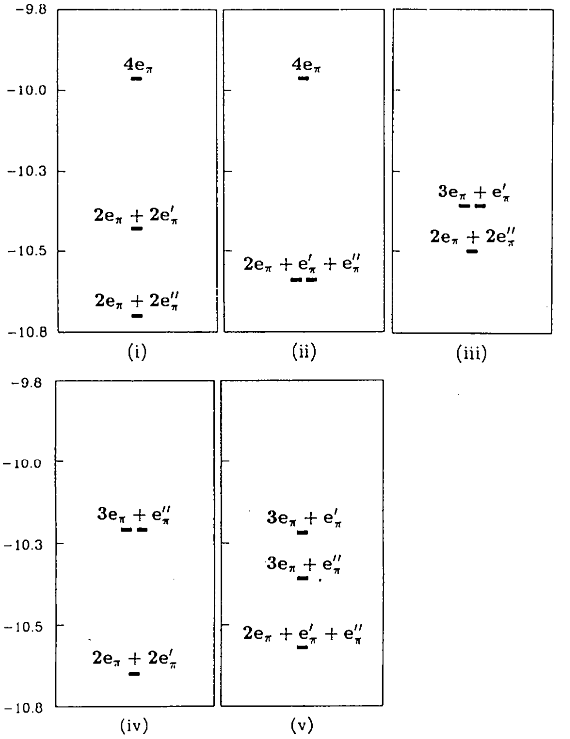

Fig. 3. Calculated molecular orbital energy diagrams showing the Ta t_{2g} levels for the five geometrical isomers, (i)–(v). Values of the energies in terms of AOM parameters are given.

Experimental

Crystal data

$[TaCl_4(C_5H_5N)_2]$
$M_r = 480.96$
Monoclinic
*C*2/*m*
$a = 14.330$ (3) Å
$b = 7.3123$ (6) Å
$c = 7.236$ (1) Å
$\beta = 115.85°$
$V = 682$ (1) Å^3
$Z = 2$
$D_x = 2.34$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 25 reflections
$\theta = 10.1$-$17.4°$
$\mu = 8.81$ mm^{-1}
$T = 295$ K
Needle
0.35 × 0.25 × 0.12 mm
Red-brown
Crystal source: Ta + $TaCl_5$ + Te + pyridine

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.789$, $T_{max} = 0.999$
2128 measured reflections
1068 independent reflections
1062 observed reflections
$[F^2 > 3.0\sigma(F^2)]$

$R_{int} = 0.046$
$\theta_{max} = 25.0°$
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 10$
$l = -10 \rightarrow 10$
3 standard reflections
monitored every 200 reflections
intensity variation: 3.5%

Refinement

Refinement on F^2
Final $R = 0.042$
$wR = 0.059$
$S = 1.05$
1062 reflections
50 parameters
$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{max} = 0.0$
$\Delta\rho_{max} = 5.5$ e Å^{-3}
$\Delta\rho_{min} = -1.9$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

Anisotropically refined atoms are given in the form of the isotropic displacement parameter defined as: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}B_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$, where a^*, b^* and c^* are reciprocal-lattice constants.

	x	y	z	U_{eq}
Ta	0.0	0.0	0.5	0.029 (1)
Cl	0.0683 (1)	0.2288 (2)	0.3617 (3)	0.042 (1)
N	−0.1475 (7)	0.0	0.2139 (12)	0.035 (2)
C(1)	−0.2397 (9)	0.0	0.2186 (16)	0.047 (4)
C(2)	−0.3326 (9)	0.0	0.0434 (19)	0.051 (4)
C(3)	−0.3314 (9)	0.0	−0.1466 (16)	0.044 (3)
C(4)	−0.2367 (10)	0.0	−0.1508 (15)	0.053 (4)
C(5)	−0.1472 (9)	0.0	0.0287 (17)	0.050 (4)

Table 2. *Geometric parameters* (Å, °)

Ta—Cl	2.370 (2)	C(1)—C(2)	1.38 (1)
Ta—N	2.222 (7)	C(2)—C(3)	1.38 (2)
N—C(1)	1.34 (2)	C(3)—C(4)	1.37 (2)
N—C(5)	1.34 (2)	C(4)—C(5)	1.37 (1)
Cl—Ta—Cl	180.0 (1)	N—Ta—N	180.0 (1)
Cl—Ta—Cl	89.8 (1)	C(1)—N—C(5)	117.4 (8)
Cl—Ta—Cl	90.2 (1)	N—C(1)—C(2)	123.0 (12)
Cl—Ta—N	90.4 (2)	C(1)—C(2)—C(3)	119.3 (13)
Cl—Ta—N	89.6 (2)	C(2)—C(3)—C(4)	117.6 (9)
Ta—N—C(1)	121.7 (7)	C(3)—C(4)—C(5)	120.3 (12)
Ta—N—C(5)	120.9 (8)	N—C(5)—C(4)	122.5 (13)

The synthesis was designed to produce ternary tantalum telluride chlorides from pyridine solution. Thus, 0.82 g $TaCl_5$ powder (Aesar, 99.99%, resublimed), 0.47 g Ta powder (Aesar, −200 mesh, 99.98%, cleaned in HF/HNO_3 and dried *in vacuo* at 1273 K) and 0.21 g Te powder (Aesar, 99.999%, used as received) were combined in 2.0 g pyridine in an evacuated quartz ampoule. The sealed ampoule was placed in a steel jacket, placed in a tube furnace and heated from room temperature to 523 K in 24 h. After a reaction time of 24 h, the sample was cooled to room temperature over 14 h.

Some red-brown needles were isolated and mounted in evacuated glass capilliaries. After checking for crystal quality with the Weissenberg technique, a crystal suitable for further analysis was selected for data collection at 295 (1) K. Unit-cell parameters were determined from an automatic search routine. Both Lorentz and polarization corrections were applied, as well as correction based on decay in the standard reflections.

The non-centrosymmetric space group *C*2 was the initial choice based upon reflection statistics (*SHELXS*86; Sheldrick, 1985). Nearly all reflections were observed and a crystallographic mirror plane was detected during refinement. The centrosymmetric space group *C*2/*m* is, therefore, the correct space group. The structure consists of mononuclear tantalum complexes surrounded by four Cl atoms [Ta—Cl = 2.370 (2) Å] in an almost square-planar arrangement with two pyridine ligands [Ta—N = 2.222 (7) Å], which reside on the crystallographic mirror plane, completing the coordination octahedron in a *trans* configuration. All H atoms were of the riding-model type with a distance of 0.96 Å and fixed isotropic displacement parameters set equal to that of the adjacent C atoms.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, atomic parameters used in the extended Hückel calculations and crystallographic data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71257 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1043]

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Structure of *trans*-Carbonyl(thiocyanato-*N*)-bis(triethylphosphine)rhodium(I)

Alexander J. Blake,* E. A. V. Ebsworth† and Paul G. Watson

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

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Abstract

The title compound is a four-coordinate Rh^I complex in which the metal is ligated by two mutually *trans* triethylphosphines, a carbonyl and an isothiocyanate group. The molecule lies on a crystallographic twofold axis which passes through the metal, the carbonyl and the isothiocyanate group. Steric factors play a part in determining the coordination mode of the NCS^- ligand: in particular, the bulk of the triethylphosphine ligands disfavours linkage through the larger S atom, whose preference for non-linear coordination would also cause steric problems.

Comment

On the basis of the 'soft' nature of both sulfur and rhodium(I) (Purcell & Kotz, 1977), one would expect that the thiocyanate ligand would be S bonded to the metal centre. However, it has been shown that the mode of binding is very sensitive to steric factors and can indeed be controlled, for example by adjusting the bite angle of a diphosphine chelating a palladium(II) centre (Beran, Mathew, Palenik & Steffen, 1975). Interpretation of the IR spectrum of the title compound (Jennings & Wojcicki, 1967) suggested linkage through the N atom of the NCS^- group (Norbury & Sinha, 1970), a result which we have confirmed. The Rh—CO bond length of 1.775 (6) Å is rather shorter than in most of the related *trans*-$[Rh(CO)X(PR_3)_2]$ (X = Cl, I) complexes (Basson, Leipoldt & Roodt, 1990; Blum, Eisen, Jurgis & Schumann, 1990; Ceriotti, Ciani & Sironi, 1983; Dahan & Choukroun, 1985; Rheingold & Geib, 1987; Monge, Gutierrez-Puebla, Heras & Pinilla, 1983; Heisler, Pickardt & Schumann, 1977). Although the structure of *trans*-$[Rh(CO)Cl(PEt_3)_2]$ has not been reported, these complexes contain phosphines with a range of cone angles (122–182°) which bracket that of PEt_3 (132°) (Tolman, 1977). The

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† Presently Vice-Chancellor, University of Durham, Old Shire Hall, Durham DH1 3HP, England.