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Structure of Bicyclophtalocyaninatochloroniobium(IV)

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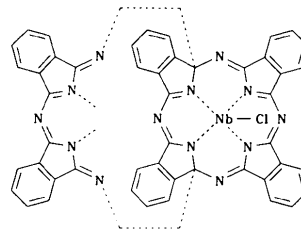
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Abstract. Chloro{12,28-[3-(3-isoindolylimino)-1,1'-isoindolediylidenediamino]niobium(IV), $[\text{Nb}(\text{Cl})(\text{C}_{48}\text{H}_{24}\text{N}_{13})]$, $M_r = 911.17$, monoclinic, $C2/c$, $a = 22.899$ (3), $b = 10.436$ (2), $c = 18.539$ (2) Å, $\beta = 123.09^\circ$, $V = 3711.8$ Å³, $Z = 4$, $D_x = 1.630$ g cm⁻³, $\text{Cu } K\alpha$, $\lambda = 1.54184$ Å, $\mu = 38.4$ cm⁻¹, $F(000) = 1844$, $T = 291$ K. Final R value is 0.033 for 2443 independent reflections with $I \geq 3\sigma(I)$ and 287 refined parameters. The bicyclophtalocyaninato ligand is composed of six isoindole units forming a trigonal prism with its six N donor atoms. The Cl ligand completes the coordination of the Nb atom to a monocapped trigonal prism. The complex has the symmetry C_2 with the Cl, Nb and one of the N atoms of the bicyclophtalocyaninato ligand lying on the twofold axis.

Introduction. Niobium and tantalum show a pronounced tendency towards the coordination number seven. In the case of phthalocyaninato complexes this leads to the formation of compounds like PcMCl_3 ($M = \text{Nb, Ta}$; $\text{H}_2\text{Pc} = \text{phthalocyanine}$) (Gingl & Strähle, 1988) or $[(\text{PcNb})_2\text{O}_2\text{Br}]^+$ (Gingl & Strähle, 1989) with monocapped trigonal prismatic coordination or with a coordination polyhedron characterized as square base-trigonal cap (Muetterties & Wright, 1967).

The preferred coordination number seven presumably also explains the formation of the bicyclophtalocyaninato ligand (see scheme) by template reaction at the Nb atom. $\text{NbCl}(\text{C}_{48}\text{H}_{24}\text{N}_{13})$ is obtained besides tris(2-cyanophenyl)-1,3,5-triazine as a byproduct with the synthesis of PcNbCl_3 from NbOCl_3 and phthalodinitrile. Similar bicyclophtalocyaninato complexes were proposed as precursors for the synthesis of cobalt and copper phthalocyanine (Baumann, Bienert, Rösch,

Vollmann & Wolf, 1956; Perkins & Whelen, 1957; Barnhart & Skiles, 1956).



Experimental. A yellow-green needle of approximate dimensions $0.4 \times 0.1 \times 0.05$ mm was used for the determination of the lattice parameters and the data collection on a single-crystal diffractometer (Enraf-Nonius CAD-4, graphite monochromator, $\text{Cu } K\alpha$ radiation). Accurate values of the lattice constants were obtained from 25 reflections with $11.4 < \theta < 31.8^\circ$. 2831 independent intensity data for $5 \leq \theta \leq 61^\circ$, index range $-25 \leq h \leq 25$, $0 \leq k \leq 11$, $0 \leq l \leq 21$, ω/θ scans; three orientation and three intensity control reflections monitored periodically, no significant variation; intensities were corrected for Lorentz and polarization effects, no absorption correction.

The structure was solved by the Patterson method, which revealed the Nb atom, and subsequent tangent expansion (Sheldrick, 1986). All H atoms were located in a difference electron density map and included in the structure-factor calculation but not refined. Full-matrix least-squares refinement [on F^2 's, unit weights for all 2443 reflections with $I > 3\sigma(I)$] with anisotropic temperature parameters for all non-H atoms converged at $R = 0.033$ ($wR = 0.038$). Maximum shift $\Delta/\sigma = 0.01$, largest peaks in the final difference Fourier map, $+1.5$ and -1.2 e Å⁻³. Atomic scattering factors, f' and f'' from *Internation-*

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Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters U_{eq} (Å²) with e.s.d.'s in parentheses

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
Nb	0.500	0.51697 (4)	0.250	0.0222 (2)
Cl	0.500	0.2754 (1)	0.250	0.0316 (7)
N1	0.5601 (1)	0.6772 (3)	0.2528 (2)	0.025 (2)
N2	0.6082 (1)	0.4842 (3)	0.3671 (2)	0.026 (2)
N3	0.4824 (1)	0.4701 (3)	0.3532 (2)	0.029 (2)
N4	0.500	0.8672 (4)	0.250	0.030 (2)
N5	0.6845 (1)	0.6165 (3)	0.3433 (2)	0.030 (2)
N6	0.5840 (1)	0.3469 (3)	0.4540 (2)	0.031 (2)
N7	0.3696 (1)	0.5675 (3)	0.2997 (2)	0.032 (2)
C1	0.5469 (2)	0.8020 (4)	0.2427 (2)	0.026 (2)
C2	0.5935 (2)	0.8737 (4)	0.2259 (2)	0.028 (2)
C3	0.5909 (2)	0.9989 (4)	0.2003 (2)	0.038 (2)
C4	0.6421 (2)	1.0363 (4)	0.1852 (2)	0.044 (2)
C5	0.6937 (2)	0.9509 (5)	0.1996 (2)	0.046 (3)
C6	0.6959 (2)	0.8258 (4)	0.2249 (2)	0.038 (2)
C7	0.6436 (2)	0.7885 (4)	0.2370 (2)	0.029 (2)
C8	0.6282 (2)	0.6576 (4)	0.2575 (2)	0.030 (2)
C9	0.6733 (2)	0.5365 (4)	0.3860 (2)	0.027 (2)
C10	0.7308 (2)	0.4809 (4)	0.4672 (2)	0.029 (2)
C11	0.8026 (2)	0.4925 (4)	0.5104 (2)	0.037 (2)
C12	0.8425 (2)	0.4221 (5)	0.5854 (3)	0.039 (3)
C13	0.8122 (2)	0.3442 (4)	0.6167 (2)	0.037 (2)
C14	0.7402 (2)	0.3326 (4)	0.5733 (2)	0.035 (2)
C15	0.7007 (2)	0.4013 (4)	0.4978 (2)	0.029 (2)
C16	0.6253 (2)	0.4086 (4)	0.4355 (2)	0.028 (2)
C17	0.5181 (2)	0.3825 (4)	0.4157 (2)	0.029 (2)
C18	0.4758 (2)	0.3322 (4)	0.4479 (2)	0.030 (2)
C19	0.4904 (2)	0.2414 (4)	0.5094 (2)	0.038 (2)
C20	0.4382 (2)	0.2196 (4)	0.5261 (2)	0.041 (2)
C21	0.3761 (2)	0.2881 (4)	0.4828 (2)	0.043 (2)
C22	0.3620 (2)	0.3793 (4)	0.4208 (2)	0.038 (2)
C23	0.4139 (2)	0.3989 (4)	0.4042 (2)	0.032 (2)
C24	0.4173 (2)	0.4883 (4)	0.3452 (2)	0.030 (2)

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

Nb—Cl	2.5214 (8)	N3—C24	1.427 (3)
Nb—N1	2.148 (2)	N4—C1	1.338 (2)
Nb—N2	2.257 (1)	N5—C8	1.462 (3)
Nb—N3	2.215 (2)	N5—C9	1.269 (3)
N1—C1	1.328 (3)	N6—C16	1.336 (3)
N1—C8	1.528 (3)	N6—C17	1.323 (3)
N2—C9	1.441 (2)	N7—C8	1.438 (3)
N2—C16	1.357 (3)	N7—C24	1.258 (3)
N3—C17	1.347 (3)		
Cl—Nb—N1	141.13 (5)	N1—C8—N5	111.6 (2)
Cl—Nb—N2	81.26 (6)	N1—C8—N7'	119.4 (2)
Cl—Nb—N3	77.25 (5)	N1—C8—C7	103.6 (2)
N1—Nb—N1'	77.8 (1)	N5—C8—N7'	104.2 (2)
N1—Nb—N2	75.07 (7)	N5—C8—C7	110.6 (2)
N1—Nb—N3'	77.09 (7)	N7—C8—C7	107.4 (2)
N2—Nb—N3	75.97 (4)		

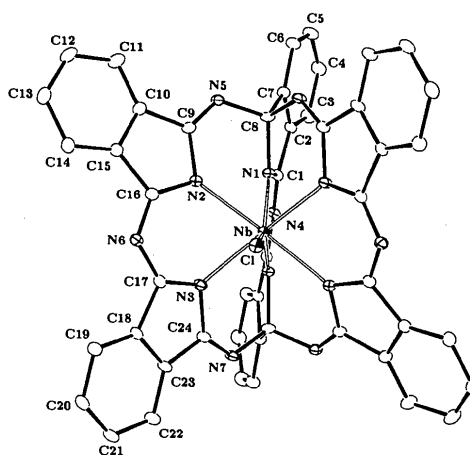


Fig. 1. Structure of bicyclophtalocyaninatochloroniobium (IV).

tional Tables for X-ray Crystallography (1974), all calculations on a Micro VAX II computer using Enraf-Nonius SDP-Plus (Frenz, 1985) and SHELXS86 (Sheldrick, 1986).

Discussion. Table 1* lists fractional atomic coordinates and isotropic thermal parameters of the non-H atoms. Table 2 contains important bond lengths and angles. Fig. 1 shows the structure of the complex and Fig. 2 shows a packing diagram.

The bicyclophtalocyaninato ligand comprises a phthalocyaninato skeleton of four isoindole units which is bridged by two additional isoindole moieties (see scheme). The six N donor atoms of the whole bicyclophtalocyaninato ligand which are coordinated to the central Nb atom form a trigonal prism. The ligand can also be described as two phthalocyaninato anions having one common half. It

* Lists of the structure factors, H-atom positions, intramolecular bond lengths, bond angles and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52988 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

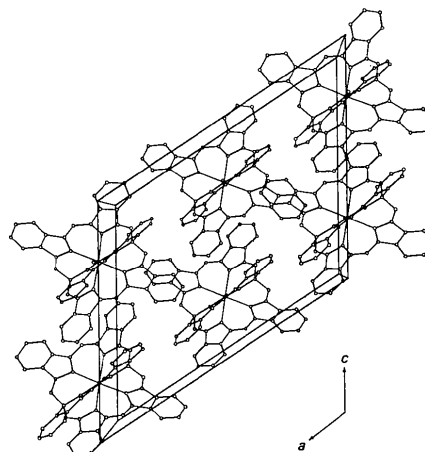


Fig. 2. A perspective drawing of the packing arrangement.

can be assumed that the ligand is less stable than a phthalocyanine anion as the conjugation of the inner 16-membered C—N ring is interrupted at the two

sp^3 -hybridized head atoms C8 and C8' of the ring linkage to a bicyclo system. This is also the main reason for the two connected phthalocyaninato units not being planar. The whole ligand is an anion with three negative charges.

The C—N distances reflect the interruption of the conjugation. The bonds at the head atom C8 average 1.476 Å, and this is close to the expected value for a single bond between sp^3 - and sp^2 -hybridized atoms. They adjoin shorter bonds of about 1.285 Å which represent double bonds. The other C—N distances have intermediate values of 1.323 to 1.441 Å, being typical for a conjugated C—N system.

The coordination of the Nb atom is completed by one chloro ligand to a monocapped trigonal prism. The Cl, Nb and the atom N4 lie on a twofold axis. The complex therefore has the symmetry C_2 .

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Structure of (μ -Acetato- $1\kappa O:2\kappa O'$)-nonacarbonyl- $1\kappa^3 C, 2\kappa^3 C, 3\kappa^3 C$ - μ -hydrido-(triphenylphosphine- $3\kappa P$)-triangulo-triosmium($3Os-Os$) Cyclohexane Solvate

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Abstract. $[\text{Os}_3(\text{C}_2\text{H}_3\text{O}_2)(\text{H})(\text{CO})_9\{\text{P}(\text{C}_6\text{H}_5)_3\}].\text{C}_6\text{H}_{12}$, $M_r = 1229.14$, triclinic, $P\bar{1}$, $a = 13.869$ (3), $b = 14.763$ (4), $c = 10.818$ (4) Å, $\alpha = 109.45$ (4), $\beta = 82.27$ (3), $\gamma = 117.83$ (2)°, $V = 1846.4$ Å³, $Z = 2$, $D_x = 2.210$, $D_m = 2.22$ (7) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 103.8$ cm⁻¹, $F(000) = 1144$, room temperature, $R = 0.038$ for 4841 unique observed reflections [$F > 3\sigma(F)$]. The triangular cluster has the shortest Os—Os edge (2.753 Å) bridged by a bidentate acetate ligand which adopts axial sites. The PPh_3 ligand is in an equatorial site on the Os not involved with the acetate bridge. The hydride ligand was not located directly and is considered to be along the longest Os—Os bond (3.041 Å), *cis* to the phosphine ligand.

Introduction. In the course of characterizing tethered clusters formed by the reaction of $\text{Os}_3\text{H}_2(\text{CO})_{10}$ with a phosphinated silica ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}$) using EXAFS (Cook, 1985) and ³¹P CP-MAS NMR techniques (Alexiev, Clayden, Cook, Dobson, Evans, & Smith, 1986), it became evident that one of the

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isomers of the complex $[\text{Os}_3\text{H}(\text{CO})_9(\text{O}_2\text{CCH}_3)(\text{PPh}_3)]$ exhibited spectroscopic properties which closely matched those of the surface species. Three isomers are formed by the reaction of $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{PPh}_3)]$ with acetic acid, and two of them could be characterized as having hydride and acetate bridges spanning the same Os—Os edge, with one of these metal centres bearing the phosphine substituent. The third isomer, which proved to be the best spectroscopic model for the surface species, evidently had a different ligand disposition and was therefore characterized by X-ray diffraction.

Experimental. The title compound was prepared from the room temperature reaction of $[\text{Os}_3\text{H}_2(\text{CO})_9(\text{PPh}_3)]$ dissolved in the minimum of CH_2Cl_2 with excess acetic acid for 48 h and the products separated by TLC on alumina-coated plates using *n*-hexane/ CH_2Cl_2 (19:1 v/v) as eluant (Alexiev, 1987). Air-stable yellow crystals were obtained from cyclohexane solution and mounted in thin-walled glass capillaries. Preliminary photographic X-ray examination established the crystal system and cell dimensions, and the density was measured by flo-

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