Crystal Structure of *fac*-(1,3-Diphenylpropane-1,3-dionato)tris(isopropoxo)isothiocyanatoniobium(v)

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Crystals of the title compound are triclinic, space group $P\bar{1}$, a = 17.438(7), b = 9.176(3), c = 9.054(3) Å, α = 107.36(5), β = 96.30(5), γ = 82.94(5)°, Z = 2. The structure was solved from diffractometer data by Patterson and Fourier methods, and refined by least-squares calculations to R 0.042 for 1868 independent non-zero reflexions. The complex is monomeric. The six-co-ordinated metal atom is surrounded by the thiocyanate nitrogen atom (Nb–N 2.176 Å), the two oxygen atoms of the dibenzoylmethane (Nb–O 2.087 and 2.083 Å), and the three oxygen atoms of the isopropoxy-groups (Nb–O 1.845, 1.828, and 1.834 Å).

ABOUT fifteen new niobium- and tantalum-(v) alkoxo-isothiocyanato-complexes [1] have been synthesized of formula $[M^V(NCS)_2(OR)_2(dbm)]$ or $[M^V(NCS)(OR)_3$-(dbm)], where $M^V = Nb^V$ or Ta^V, dbm = the ketoenolate ion of the $(PhCO\cdot CH_2\cdot COPh)$ β-diketone, and R = Et in the bis- and Pr in the tris-alkoxo-complexes. In order to resolve the stereochemistry of the metal atom in each case, the X-ray structure of *fac*-(1,3-diphenylpropane-1,3-dionato)tris(isopropoxo)isothiocyanato-niobium(v) $[Nb(NCS)(OPr)_3(dbm)]$ was carried out following that of $[Nb(NCS)_2(OEt)_2(dbm)]$.[2] Crystals were prepared as described previously.[1]

EXPERIMENTAL

Crystal Data.—$C_{25}H_{32}NNbO_5S$, $M = 550.9$, Triclinic, $a = 17.438(7)$, $b = 9.176(3)$, $c = 9.054(3)$ Å, $\alpha = 107.36(5)$, $\beta = 96.30(5)$, $\gamma = 82.94(5)°$, $U = 1\,368.2$ Å^3, $D_m = 1.34$ (by flotation), $Z = 2$, $D_c = 1.338$, $F(000) = 572$. Space group $P\bar{1}$ (C_i^1, No. 2).[3] Ni-filtered Cu-K_α radiation, $\lambda = 1.541\,8$ Å; μ(Cu-K_α) = 47.3 cm^{-1}. Crystal size: $0.075 \times 0.10 \times 0.60$ mm.

Intensities were collected up to $(\sin\theta)/\lambda$ 0.460 Å^{-1} on a CAD 3 Enraf-Nonius diffractometer in the θ—2θ scan mode. The range of each scan consisted of the base width of 0.7° at $2\theta = 0°$ and an increment, $\Delta(2\theta) = 0.3\tan\theta°$, to allow for spectral dispersion; background counts were taken at the extremes of the scan for a time equal to that required for the

scan itself. Standard reflexions remained constant to within $\pm 2\%$ throughout data collection. 1 868 independent reflections having $I \geqslant 3\sigma(I)$, $\sigma(I)$ being based on counting statistics, were corrected for Lorentz and polarization effects and used in the determination and refinement of the structure.

Structure Determination.—All calculations were performed on an IBM 370 168 Computer with ORFLS [4] and N.R.C.[5] programs. The niobium atom was located from a three-dimensional Patterson synthesis. A Fourier map phased on the co-ordinates of this atom enabled location of all non-hydrogen atoms. Scattering factors were those for neutral atoms.[6] Refinement converged to R 0.098 and to 0.056 with anisotropic thermal parameters. All hydrogen atoms were located in a difference synthesis. R was 0.045. During the last cycles of refinement, the weighting scheme used was: $w = (0.303|F_o| + 0.590)^{-1}$ for $|F_o| \leqslant 19.0$ and $w = (0.025|F_o| + 1.585)^{-1}$ for $|F_o| > 19.0$. R converged finally to 0.042, the weighted residual R' being 0.048 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}\}$. Final atom parameters are given in Table 1. Final observed and calculated structure factors, atom thermal parameters, hydrogen atom positional parameters, and details of planes through the molecule are listed in Supplementary Publication No. SUP 21775 (18 pp., 1 microfiche).†

RESULTS AND DISCUSSION

The structure is shown in the Figure with atom numbering system. The interatomic distances and interbond angles are given in Tables 2 and 3.

† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[1] R. Kergoat, M. C. Sénéchal-Tocquer, J. E. Guerchais, and F. Dahan, *Bull. Soc. chim. France*, 1976, 1203.

[2] F. Dahan, R. Kergoat, M. C. Tocquer, and J. E. Guerchais, *Acta Cryst.*, 1976, **B32**, 1038.

[3] 'International Tables for *X*-Ray Crystallography,' vol. I, Kynoch Press, Birmingham, 1952, p. 75.

[4] W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, Oak-Ridge National Laboratory Report, ORNL TM 305, 1962.

[5] F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, N.R.C. Crystallographic Programs for the IBM/360 System, World List of Crystallographic Computer Programs, Oosthoek, Utrecht, 1966, p. 52.

[6] Ref. 3, vol. III, 1962, p. 202.

Among the compounds of niobium- and tantalum-(v) studied with different complexing ligands, some halogeno- or pseudohalogeno-complexes containing neutral organic

Atom	x/a	y/b	z/c
Nb	2 720(0)	7 775(1)	1 913(1)
N	2 102(4)	9 730(9)	1 470(8)
C(S)	1 856(5)	10 759(10)	996(10)
S	1 509(2)	12 163(3)	364(3)
O(1)	3 132(3)	9 278(6)	3 917(5)
O(2)	1 815(3)	7 935(6)	3 321(6)
C(1)	2 839(4)	10 064(8)	5 187(8)
C(2)	1 650(4)	8 765(8)	4 652(8)
C(3)	2 123(4)	9 870(9)	5 587(9)
C(4)	3 342(4)	11 214(8)	6 222(8)
C(5)	4 087(5)	11 202(10)	5 859(10)
C(6)	4 585(6)	12 261(11)	6 790(12)
C(7)	4 309(6)	13 320(11)	8 088(12)
C(8)	3 569(6)	13 361(11)	8 452(11)
C(9)	3 094(5)	12 281(10)	7 531(10)
C(10)	927(4)	8 497(9)	5 200(8)
C(11)	637(5)	9 372(11)	6 558(11)
C(12)	−66(6)	9 080(13)	7 016(11)
C(13)	−428(6)	7 855(14)	6 096(14)
C(14)	−164(6)	6 992(13)	4 737(12)
C(15)	526(5)	7 277(11)	4 269(10)
O(3)	2 085(3)	6 598(6)	293(6)
C(16)	1 435(6)	6 621(17)	−850(12)
C(17)	753(7)	6 205(21)	−375(17)
C(18)	1 688(8)	6 000(20)	−2 376(13)
O(4)	3 201(4)	6 073(7)	2 850(8)
C(19)	3 336(9)	4 972(24)	3 387(26)
C(20)	4 162(10)	4 471(31)	3 565(35)
C(21)	2 832(13)	4 665(26)	4 197(25)
O(5)	3 509(3)	7 958(6)	874(5)
C(22)	3 833(10)	8 655(14)	−50(13)
C(23)	4 018(9)	10 209(15)	798(19)
C(24)	3 813(17)	7 995(22)	−1 563(17)

(bipyridyl [7]) or charged ligands (dithiocarbamates [8] or dithiophosphates [9]) have been reported. Many types of geometries have been found in alkoxo-derivatives according to the nature of the different ligands. Molecular structures have been determined for some of them; the arrangement around the transition-metal corresponds to the pentagonal bipyramid in the case of the dithiocarbamate complexes,[8,10] or to the octahedron with [NbOCl$_2$(OEt)(bipy)].[11]

In the present study, the crystal structure is built up of monomeric [Nb(NCS)(OPr)$_3$(dbm)] molecules. The only intermolecular interactions are van der Waals contacts. The niobium atom is at the centre of a distorted co-ordination octahedron of the nitrogen atom of thiocyanate, the three isopropoxo and the two dbm oxygen atoms.

The niobium atom is co-ordinated to thiocyanate by the nitrogen atom, as expected with this metal. The Nb-N bond length (2.176 Å) is longer than in [Nb(NCS)$_2$(OEt)$_2$(dbm)] [2.088 and 2.120 Å (ref. 2)], where the N

[7] C. Djordjevic and V. Katovic, Chem. Comm., 1966, 224.
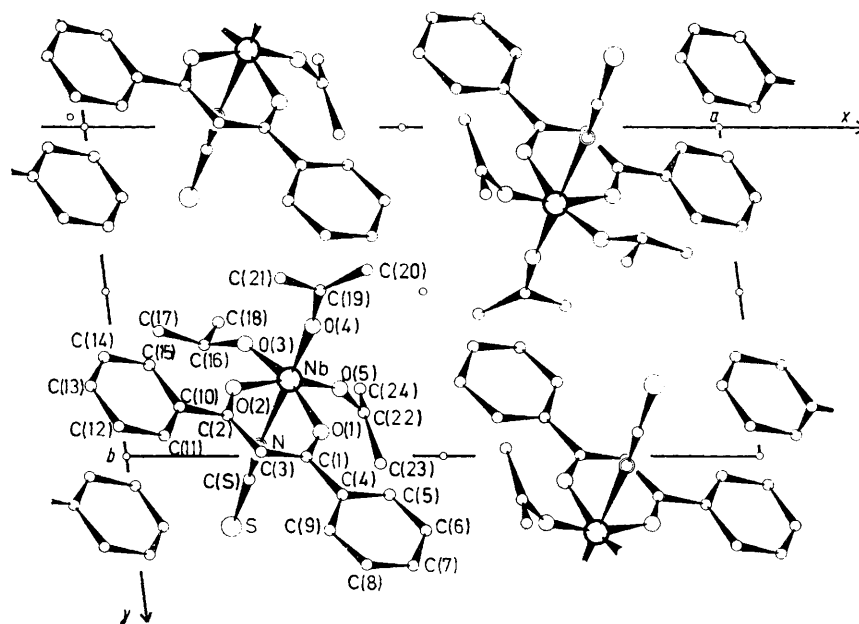[8] D. C. Pantaleo and R. C. Johnson, Inorg. Chem., 1970, 1248.
[9] D. C. Pantaleo and R. C. Johnson, Inorg. Chem., 1971, 1298.
[10] J. C. Dewan, D. L. Kepert, C. L. Raston, D. Taylor, A. H. White, and E. N. Maslen, J.C.S. Dalton, 1973, 2082.

atoms are *trans*. We can compare it with distances for *trans* N atoms in [Ph$_4$As]$_2$[NbO(NCS)$_5$] [2.03 and 2.09, 2.09 and 2.16 Å (ref. 11)], but the Nb-N bond *trans* to the oxo-ligand is longer (2.27 Å). The Nb-N-C angle is 167.2° and N-C-S 179.5°. None of the deviations from linearity in the Nb-N-C-S system is significant.

Nb-O(1)	2.087(5)	Nb-O(4)	1.828(6)
Nb-O(2)	2.083(5)	Nb-O(5)	1.834(5)
Nb-O(3)	1.845(5)	Nb-N	2.176(7)
N-C(S)	1.17(1)	C(S)-S	1.59(1)
O(1)-C(1)	1.28(1)	O(2)-C(2)	1.26(1)
C(1)-C(3)	1.38(1)	C(2)-C(3)	1.40(1)
C(1)-C(4)	1.49(1)	C(2)-C(10)	1.48(1)
C(4)-C(5)	1.37(1)	C(10)-C(11)	1.36(1)
C(5)-C(6)	1.40(1)	C(11)-C(12)	1.41(1)
C(6)-C(7)	1.37(1)	C(12)-C(13)	1.36(2)
C(7)-C(8)	1.36(2)	C(13)-C(14)	1.34(1)
C(8)-C(9)	1.38(1)	C(14)-C(15)	1.40(1)
C(9)-C(4)	1.37(1)	C(15)-C(10)	1.40(1)
O(3)-C(16)	1.45(1)	O(4)-C(19)	1.40(2)
C(16)-C(17)	1.44(2)	C(19)-C(20)	1.46(2)
C(16)-C(18)	1.43(2)	C(19)-C(21)	1.31(3)
O(5)-C(22)	1.39(1)		
C(22)-C(23)	1.46(2)		
C(22)-C(24)	1.32(2)		

N-Nb-O(1)	81.8(2)	N-Nb-O(2)	81.9(2)
N-Nb-O(3)	86.0(2)	N-Nb-O(4)	171.5(3)
N-Nb-O(5)	87.4(2)	O(1)-Nb-O(2)	79.5(2)
O(1)-Nb-O(3)	163.1(2)	O(1)-Nb-O(4)	91.9(2)
O(1)-Nb-O(5)	89.9(2)	O(2)-Nb-O(3)	87.2(2)
O(2)-Nb-O(4)	91.4(2)	O(2)-Nb-O(5)	165.9(2)
O(3)-Nb-O(4)	98.9(3)	O(3)-Nb-O(5)	101.2(2)
O(4)-Nb-O(5)	98.3(3)	Nb-N-C(S)	167.2(7)
N-C(S)-S	179.2(8)	Nb-O(1)-C(1)	134.2(5)
Nb-O(2)-C(2)	136.0(5)	Nb-O(3)-C(16)	148.5(6)
Nb-O(4)-C(19)	159.7(9)	Nb-O(5)-C(22)	153.5(7)
O(1)-C(1)-C(3)	123.8(7)	O(2)-C(2)-C(3)	122.8(7)
O(1)-C(1)-C(4)	114.0(6)	O(2)-C(2)-C(10)	116.2(6)
C(3)-C(1)-C(4)	122.1(7)	C(3)-C(2)-C(10)	120.9(7)
C(1)-C(4)-C(5)	119.1(7)	C(2)-C(10)-C(11)	123.5(7)
C(1)-C(4)-C(9)	122.6(7)	C(2)-C(10)-C(15)	117.7(7)
C(9)-C(4)-C(5)	118.3(8)	C(15)-C(10)-C(11)	118.9(8)
C(4)-C(5)-C(6)	121.4(8)	C(10)-C(11)-C(12)	121.1(9)
C(5)-C(6)-C(7)	118.2(9)	C(11)-C(12)-C(13)	118.1(10)
C(6)-C(7)-C(8)	121.1(10)	C(12)-C(13)-C(14)	122.0(10)
C(7)-C(8)-C(9)	119.5(9)	C(13)-C(14)-C(15)	120.2(10)
C(8)-C(9)-C(4)	121.4(8)	C(14)-C(15)-C(10)	119.5(9)
C(1)-C(3)-C(2)	123.0(7)	O(3)-C(16)-C(17)	110.9(10)
O(3)-C(16)-C(18)	110.0(10)	C(17)-C(16)-C(18)	123.3(11)
O(4)-C(19)-C(20)	111.8(15)	O(4)-C(19)-C(21)	124.9(15)
O(5)-C(22)-C(23)	112.1(11)	C(20)-C(19)-C(21)	121.6(18)
O(5)-C(22)-C(24)	118.8(13)	C(23)-C(22)-C(24)	127.9(13)

The bond distances and angles within the chelating dbm ring are in good agreement with values found in other β-diketone complexes.[2,12,13] The ring is planar, as are the two phenyl rings. The Nb-O(dbm) bond lengths are a little longer (2.087 and 2.083 Å) than in [Nb(NCS)$_2$(OEt)$_2$(dbm)] (2.029 and 2.040 Å),[2] where dbm is *trans* to ethoxo- instead of isopropoxo-ligands.

[11] B. Kamenar and C. K. Prout, J. Chem. Soc. (A), 1970, 2379.
[12] J. Jecny and K. Huml, Acta Cryst., 1974, B30, 1105.
[13] B. Kojic-Prodic, Z. Ruzic-Toros, D. Grdenic, and L. Golic, Acta Cryst., 1974, B30, 300.

Structure viewed along the c axis

The Nb–O(Pr^i) bond lengths (1.845, 1.828, and 1.834 Å) suggest some double-bond character for this linkage. It can be compared to V–O(Pr^i) in [VO(OPr^i)-(oxine)$_2$].[14] This double-bond character is consistent with the very large Nb–O(3)–C(16), Nb–O(4)–C(19), and Nb–O(5)–C(22) bond angles (148.5, 159.7, and 153.5°). σ-Bonding only, with sp^3 hybridization at the oxygen atoms, would be indicated by an angle of 109° or somewhat larger.

The chelated dbm and the two *trans*-isopropoxy-groups are in an equatorial plane. The niobium atom is 0.185 Å from this plane.

[14] W. R. Scheidt, *Inorg. Chem.*, 1973, 1758.