

Table 1* and interatomic distances are given in Table 2. An ORTEP (Johnson, 1976) drawing of the two crystallographically independent anions is shown in Fig. 1.

Related literature. X-ray structures of other *B*-type Anderson-structure heteropolyanions (heteroatom of low oxidation state, protonated polyanion) such as $H_6[X^{n+}Mo_6O_{24}]^{(6-n)-}$ (*X*: heteroatom) have been reported: Cr^{3+} (Perloff, 1970), Cu^{2+} (Ito, Ozeki, Ichida & Sasaki, 1989) and Co^{3+} (Nagano, Lee, Ichida & Sasaki, 1990). *A*-type structures (heteroatom of high oxidation state, nonprotonated polyanion) such as $[X^{n+}Mo_6O_{24}]^{(12-n)-}$ have been

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54000 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

reported: Te^{5+} (Evans, 1974) and I^{7+} (Kondo, Kobayashi & Sasaki, 1980).

We thank the Korea Science and Engineering Foundation for financial support (891-0305-046-1).

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Acta Cryst. (1991). **C47**, 1961–1963

Structure of Carbonyl(2-pyridinethiolato *N*-oxide- κ O, κ S)(triphenylphosphine)rhodium(I)

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(Received 17 December 1990; accepted 22 February 1991)

Abstract. $[Rh(C_5H_4NOS)(CO)\{P(C_6H_5)_3\}]$, $M_r = 519.4$, triclinic, $P\bar{1}$, $a = 9.127$ (1), $b = 9.371$ (1), $c = 14.893$ (1) Å, $\alpha = 85.665$ (6), $\beta = 79.203$ (5), $\gamma = 62.109$ (7)°, $V = 1105.8$ (2) Å³, $Z = 2$, $D_m = 1.53$ (1), $D_x = 1.56$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 9.41$ cm⁻¹, $T = 295$ K, $F(000) = 524$, final $R = 0.0299$ for 5841 observed reflections. The complex has square-planar geometry about the Rh atom. The S atom of the five-membered cyclic thiohydroxamate ring exerts a smaller *trans* influence on the Rh—P bond compared to the six-membered thioacetylacetonate ring in a similar complex [Botha, Basson & Leipoldt (1987). *Inorg. Chim. Acta*, **126**, 25–28]. Bond distances are Rh—O = 2.031 (2), Rh—S = 2.311 (1), Rh—P = 2.278 (1) and Rh—C = 1.800 (3) Å.

Experimental. The title complex was obtained by mixing equimolar amounts of PPh_3 and $[Rh(C_5H_4NOS)(CO)_2]$ in acetone. Suitable yellow needle-like crystals were obtained by slow evapor-

ation of an acetone solution at 263 K. The density was determined by flotation in sodium iodide solution. A crystal of size 0.25 × 0.25 × 0.45 mm was used for data collection on an Enraf-Nonius CAD-4F diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The $\omega/2\theta$ -scan technique was used with variable scan width $\Delta\omega = (0.42 + 0.34\tan\theta)^\circ$, a scan speed maximum of 5.49° min⁻¹ in ω and a maximum scan time of 60 s per reflection. The unit-cell parameters were determined with a least-squares fit of 25 reflections with $23 < \theta < 24^\circ$. The intensity measuring range was $3 < \theta < 30^\circ$. Empirical absorption correction (North, Phillips & Mathews, 1968) was made with minimum correction factor 0.95 and maximum 0.99. The mean intensity of three standard reflections, measured every 3600 s of X-ray exposure, varied from the initial value by -0.7%. All possible reflections with $(\sin\theta)/\lambda < 0.71$ Å⁻¹ in the index ranges $0 < h < 12$, $-13 < k < 13$, $-20 < l < 20$ gave 6226 unique reflections of which 5841 were considered observed with $I >$

Table 1. Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Rh(1)	1604.0 (2)	1460.6 (2)	3662.7 (1)	42.83 (4)
P(1)	667.7 (7)	2270.4 (7)	2307.5 (4)	38.2 (1)
S(1)	2652.7 (10)	809.1 (9)	5015.9 (5)	62.9 (2)
O(11)	1530 (2)	3620 (2)	3848 (1)	57.2 (4)
N(1)	2188 (3)	3760 (3)	4554 (1)	49.0 (5)
C(31)	770 (3)	4104 (3)	1873 (2)	40.3 (4)
C(21)	-1530 (3)	2748 (3)	2323 (2)	40.1 (4)
C(1)	1781 (4)	-506 (3)	3513 (2)	69 (1)
C(6)	2827 (3)	2525 (3)	5135 (2)	50 (1)
C(32)	1795 (3)	4135 (3)	1067 (2)	49 (1)
O(1)	1958 (4)	-1779 (3)	3411 (2)	114 (1)
C(24)	-4909 (3)	3478 (4)	2458 (2)	62 (1)
C(12)	3477 (3)	-354 (3)	1415 (2)	49 (1)
C(11)	1855 (3)	835 (3)	1355 (2)	41.3 (5)
C(22)	-2177 (3)	1833 (3)	2874 (2)	52 (1)
C(26)	-2585 (3)	4022 (3)	1837 (2)	51 (1)
C(36)	-132 (3)	5494 (3)	2423 (2)	49 (1)
C(16)	1216 (3)	932 (3)	565 (2)	53 (1)
C(15)	2183 (4)	-146 (4)	-158 (2)	63 (1)
C(23)	-3863 (4)	2202 (4)	2934 (2)	64 (1)
C(5)	3621 (4)	2747 (4)	5801 (2)	63 (1)
C(33)	1950 (4)	5528 (4)	820 (2)	65 (1)
C(14)	3785 (4)	-1329 (4)	-88 (2)	59 (1)
C(2)	2173 (4)	5204 (4)	4626 (2)	64 (1)
C(4)	3667 (4)	4181 (5)	5863 (2)	76 (1)
C(34)	1070 (4)	6888 (4)	1367 (2)	73 (1)
C(35)	14 (4)	6883 (3)	2163 (2)	64 (1)
C(13)	4434 (4)	-1433 (3)	688 (2)	55 (1)
C(25)	-4269 (3)	4385 (4)	1906 (2)	60 (1)
C(3)	2904 (4)	5436 (5)	5285 (2)	75 (1)

Vol. III, p. 216). Final $R = 0.0299$, $wR = 0.032$ with unit weights. $(\Delta\rho)_{\text{max}} = 0.34$ and $(\Delta\rho)_{\text{min}} = -0.85 \text{ e \AA}^{-3}$, $(\Delta/\sigma)_{\text{max}} = 0.026$. Final atomic coordinates are given in Table 1, * main geometrical parameters in Table 2 and a perspective view (Johnson, 1976) with atomic labels in Fig. 1.

Related literature. The present structure determination was undertaken to determine the specific isomer formed when only one carbonyl group in complexes of the type $[\text{Rh}(\text{LL}')(\text{CO})_2]$ ($\text{LL}' =$ uninegative bidentate ligands having S, N or O donor atoms) are substituted by triphenylphosphine. The substitution pattern and most of the geometrical parameters compare well with those of $[\text{Rh}(\text{Sacac})(\text{CO})(\text{PPh}_3)]$ and other complexes (Botha, Basson & Leipoldt, 1987), the exception being a significantly shorter Rh—P distance. This is probably due to a weaker π interaction between S and Rh as a result of the smaller bite angle compared to other five- and six-membered (O,O)-, (N,O)- and (S,O)-bonded chelate rings (Graham, Lamprecht, Potgieter, Roodt & Leipoldt, 1990). Bond data for the bidentate ligand can be compared with those of dimethylbis(2-pyridine-thiolato *N*-oxide)tin(IV) (Ng, Wei, Das & Mak, 1987), as well as *N*-methylthiohydroxamate complexes such as $[\text{MoO}_2\{p\text{-CH}_3\text{C}_6\text{H}_4\text{C}(\text{=S})\text{N}(\text{CH}_3)\text{O}\}_2]$ (Cliff, Fallon, Gatehouse, Murray & Newman, 1980) and $[1,1\text{-diphenylhydrazido}(2-)-N^2]\text{bis}(N\text{-methylbenzothiohydroxamato})\text{oxomolybdenum(VI)}$ (Fitzroy, Fallon, Murray, Frederiksen & Tiekink, 1990).

Table 2. Selected interatomic bond distances (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

Rh(1)—P(1)	2.278 (1)	Rh(1)—S(1)	2.311 (1)
Rh(1)—O(11)	2.031 (2)	Rh(1)—C(1)	1.800 (3)
P(1)—C(31)	1.827 (2)	P(1)—C(21)	1.835 (2)
P(1)—C(11)	1.829 (2)	S(1)—C(6)	1.714 (3)
O(11)—N(1)	1.347 (3)	N(1)—C(6)	1.355 (3)
N(1)—C(2)	1.360 (3)	C(1)—O(1)	1.145 (3)
C(6)—C(5)	1.412 (4)	C(5)—C(4)	1.375 (5)
C(2)—C(3)	1.367 (4)	C(4)—C(3)	1.384 (5)
P(1)—Rh(1)—S(1)	174.7 (1)	P(1)—Rh(1)—O(11)	91.3 (1)
S(1)—Rh(1)—O(11)	83.9 (1)	P(1)—Rh(1)—C(1)	90.7 (1)
S(1)—Rh(1)—C(1)	94.0 (1)	O(11)—Rh(1)—C(1)	177.0 (1)
Rh(1)—P(1)—C(31)	113.3 (1)	Rh(1)—P(1)—C(21)	115.6 (1)
C(31)—P(1)—C(21)	103.8 (1)	Rh(1)—P(1)—C(11)	115.3 (1)
C(31)—P(1)—C(11)	103.0 (1)	C(21)—P(1)—C(11)	104.3 (1)
Rh(1)—S(1)—C(6)	97.7 (1)	Rh(1)—O(11)—N(1)	117.4 (1)
O(11)—N(1)—C(6)	121.4 (2)	O(11)—N(1)—C(2)	115.2 (2)
C(6)—N(1)—C(2)	123.4 (2)	Rh(1)—C(1)—O(1)	177.4 (3)
S(1)—C(6)—N(1)	119.0 (2)	S(1)—C(6)—C(5)	124.3 (2)
N(1)—C(6)—C(5)	116.7 (3)	C(6)—C(5)—C(4)	120.4 (3)
N(1)—C(2)—C(3)	119.8 (3)	C(5)—C(4)—C(3)	120.3 (3)
C(2)—C(3)—C(4)	119.2 (3)		

$3.0\sigma(I)$. No equivalent reflections were measured. The structure was solved by the heavy-atom method using *SHELXS86* (Sheldrick, 1990) and subjected to anisotropic full-matrix least-squares refinement on *F* with 272 positional and thermal parameters using *SHELX76* (Sheldrick, 1976). The H-atom positions were calculated riding on the adjacent C atoms assuming C—H = 1.08 \AA , and refined with an overall isotropic temperature factor. Neutral-atom scattering factors (Cromer & Mann, 1968) and anomalous-dispersion corrections for rhodium were taken from *International Tables for X-ray Crystallography* (1962,

* A least-squares plane and deviations, lists of anisotropic displacement parameters, structure factors, bond distances, angles and atomic parameters including H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54028 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

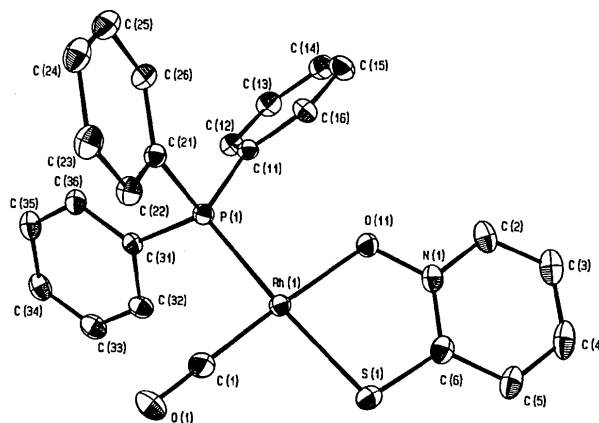


Fig. 1. Perspective view and atomic labelling of the molecule (H atoms omitted for clarity).

The authors gratefully acknowledge financial support from the Foundation for Research and Development and the Central Research Fund of the University of the Orange Free State.

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Acta Cryst. (1991). **C47**, 1963–1964

Chlorobis(η^5 -cyclopentadienyl)oxoniobium(V)

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(Received 18 December 1990; accepted 18 February 1991)

Abstract. $[\text{Nb}(\text{Cl})(\text{O})(\text{C}_5\text{H}_5)_2]$, $M_r = 274.54$, orthorhombic, $Fdd2$, $a = 14.676$ (4), $b = 44.39$ (1), $c = 6.200$ (1) Å, $V = 4039$ (2) Å³, $Z = 16$, $D_x = 1.806$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 6.87$ cm⁻¹, $F(000) = 2176$, $T = 296$ K, $R_F = 3.09\%$ for 803 observed [$F_o > 6\sigma(F_o)$] reflections and 99 parameters. This Nb^V compound has a typical bent metallocene structure with a centroid–metal–centroid angle of 128.2 (1)°. The Cl–Nb–O angle of 98.4 (2)° is perpendicular to, and bisected by, the centroid–metal–centroid plane. When projected down the centroid–centroid vector, the cyclopentadienyl rings are in a staggered conformation.

Experimental. Pale yellow needles (0.08 × 0.08 × 0.50 mm) prepared by the aerobic oxidation of [$(\eta^5\text{-C}_5\text{H}_5)_2\text{NbH}(\text{tolAs})_2$] in chloroform-*d*. Nicolet R3m diffractometer with graphite monochromator; ω scans; lattice parameters from least-squares fit of 25 reflections ($20 \leq 2\theta \leq 25^\circ$); absorption correction was applied ($\mu = 6.87$ cm⁻¹, thin needle, $T_{\text{max}}/T_{\text{min}} = 1.23$); $2\theta_{\text{max}} = 48^\circ$ ($h = +17$, $k = \pm 51$, $l = +8$); standard reflections 711, 2,16,2, 1,11,3. 1892 reflections collected, 876 unique ($R_{\text{int}} = 2.65\%$), 803 observed with $F_o > 6\sigma(F_o)$, 73 unobserved reflections. Direct-methods (*SOLV*) structure solution; least-squares refinement (on F) on 99 parameters; all non-H atoms anisotropic, H atoms with idealized contributions, cyclopentadienyl rings fixed as rigid planar pentagons (C–C = 1.420 Å), $R_F = 3.09\%$,

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (Å² × 10³)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Nb	7250.9 (4)	580.3 (1)	5000	27.1 (2)
Cl	7011 (2)	1047 (1)	6993 (5)	60 (1)
O	7349 (4)	337 (1)	7180 (10)	44 (2)
C(1)	8916 (4)	501 (2)	5090 (14)	61 (4)
C(2)	8810	818	4899	67 (4)
C(3)	8402	879	2869	69 (4)
C(4)	8256	600	1805	88 (6)
C(5)	8574	366	3178	64 (4)
C(6)	5665 (5)	729 (2)	3941 (21)	111 (8)
C(7)	5617	457	5137	103 (7)
C(8)	6045	227	3905	80 (5)
C(9)	6356	358	1948	69 (5)
C(10)	6121	668	1971	85 (6)

Table 2. Selected bond lengths (Å) and angles (°)

Nb–Cnt(1)	2.171 (6)	Nb–O	1.737 (6)
Nb–Cnt(2)	2.182 (6)	Nb–Cl	2.439 (2)
O–Nb–Cl	98.4 (2)	Cnt(1)–Nb–Cnt(2)	128.2 (1)
O–Nb–Cnt(1)	108.1 (3)	Cl–Nb–Cnt(1)	104.3 (2)
O–Nb–Cnt(2)	108.2 (3)	Cl–Nb–Cnt(2)	105.5 (2)

Cnt(1) = centroid of atoms C(1)–C(5).

Cnt(2) = centroid of atoms C(6)–C(10).

$wR_F = 3.30\%$, $S = 1.170$, $w^{-1} = \sigma(F_o) + gF_o^2$, $g = 0.001$; $(\Delta/\sigma)_{\text{max}} = 0.003$; $\Delta\rho_{\text{max}} = 0.50$, $\Delta\rho_{\text{min}} = -0.59$ e Å⁻³; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149); *SHELXTL* computer program (Sheldrick, 1984).

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