

Data collection

Siemens R3m/V diffractometer

 $\omega/2\theta$ scans

Absorption correction:

 ψ scans (North *et al.*, 1968) $T_{\min} = 0.731$, $T_{\max} = 0.761$

2902 measured reflections

1451 independent reflections

1034 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.030$ $\theta_{\text{max}} = 27.55^\circ$ $h = 0 \rightarrow 21$ $k = 0 \rightarrow 16$ $l = 0 \rightarrow 15$

(and some Friedel

equivalents)

4 standard reflections

every 400 reflections

intensity decay: <1%

RefinementRefinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.035$ $wR(F^2) = 0.075$ $S = 1.017$

1451 reflections

83 parameters

H-atom parameters

constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0378P)^2$ $+ 0.4082P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.320 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.385 \text{ e } \text{\AA}^{-3}$

Extinction correction:

SHELXTL (Siemens, 1995)

Extinction coefficient:

0.0003 (4)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a'_i a'_j$$

	x	y	z	U_{eq}
Mn1	0	0.08388 (4)	0.13025 (5)	0.0386 (2)
P1	-0.08814 (6)	0	0	0.0385 (3)
C1	0.0815 (2)	0.1395 (2)	0.2153 (2)	0.0532 (7)
O1	0.1337 (2)	0.1722 (2)	0.2672 (2)	0.0794 (7)
C2	0	0.2018 (3)	0.0331 (3)	0.0462 (9)
O2	0	0.2743 (2)	-0.0268 (3)	0.0672 (9)
C3	0	-0.0400 (3)	0.2165 (3)	0.0451 (9)
O3	0	-0.1167 (3)	0.2691 (3)	0.0715 (9)
C4	-0.1628 (2)	-0.0834 (2)	0.0623 (2)	0.0478 (6)
C5	-0.2355 (2)	-0.0481 (2)	0.0364 (2)	0.0540 (7)
C6	-0.3111 (2)	-0.1010 (3)	0.0756 (4)	0.0911 (13)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mn1—C1	1.826 (3)	P1—C4	1.785 (3)
Mn1—C3	1.838 (4)	C4—C5	1.338 (4)
Mn1—C2	1.849 (4)	C5—C5'	1.466 (6)
Mn1—P1	2.3586 (8)	C5—C6	1.507 (4)
P1—Mn1—P1 ⁱⁱ	78.26 (4)	C4—C5—C5'	113.4 (2)
C4—P1—C4'	90.2 (2)	C4—C5—C6	124.5 (3)
Mn1—P1—Mn1 ⁱⁱ	101.75 (4)	C5'—C5—C6	122.0 (2)
C5—C4—P1	111.5 (2)		

Symmetry codes: (i) $x, -y, -z$; (ii) $-x, -y, -z$.

Program(s) used to solve structure: SHELXTL (Siemens, 1995). Program(s) used to refine structure: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1530). Services for accessing these data are described at the back of the journal.

ReferencesAbel, E. W. & Towers, C. (1979). *J. Chem. Soc. Dalton Trans.* pp 814–819.Deeming, A. J., Powell, N. I., Arce, A. J., DeSanctis, Y. & Manzur, J. (1991). *J. Chem. Soc. Dalton Trans.* pp 3381–3386.Flörke, U. & Haupt, H.-J. (1993). *Acta Cryst.* **C49**, 374–376.Flörke, U. & Haupt, H.-J. (1994). *Acta Cryst.* **C50**, 378–380.Flörke, U. & Haupt, H.-J. (1997). *Acta Cryst.* **C53**, 404–406.Holand, S., Charrier, C., Mathey, F., Fischer, J. & Mitschler, A. (1984). *J. Am. Chem. Soc.* **106**, 826–828.Holand, S., Mathey, F. & Fischer, J. (1986). *Polyhedron*, **5**, 1414–1421.Holand, S., Mathey, F., Fischer, J. & Mitschler, A. (1983). *Organometallics*, **2**, 1234–1238.Mathey, F., Fischer, J. & Nelson, J. H. (1983). *Struct. Bonding*, **55**, 153–201.North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.Rosalky, J. M., Metz, B., Mathey, F. & Weiss, R. (1977). *Inorg. Chem.* **16**, 3307–3311.

Siemens (1995). SHELXTL. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

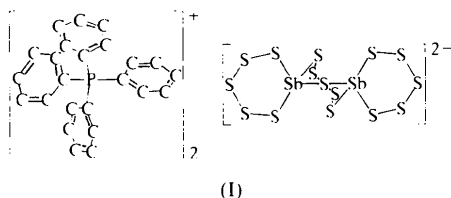
Acta Cryst. (1998). **C54**, 920–923**[Ph₄P]₂[Sb₂S₁₅]**HERME RIJNBERK, CHRISTIAN NÄTHER, MICHAEL SCHUR,
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(Received 22 July 1997; accepted 19 January 1998)

AbstractThe reaction of antimony chloride, sulfur and tetraphenylphosphonium bromide in an aqueous ammonia solution under hydrothermal conditions yields orange crystals of bis(tetraphenylphosphonium) μ -sulfido- μ -tetrasulfido- $S^1:S^4$ -bis[(pentasulfido- S^1,S^5)antimonate], [(C₆H₅)₄P]₂[Sb₂S₁₅]. The structure contains tricyclic molecular Sb₂S₁₅²⁻ anions built up of two distorted ψ -trigonal bipyramidally coordinated antimony centres which are connected by two S_x²⁻ units ($x = 1, 4$) and bound to an additional S₅²⁻ ligand.**Comment**

The structure of the title compound, (I), was determined as part of a project on the synthesis of new chalcogenide compounds using mild solvothermal conditions. Compared to the 'classical' high-temperature route, the low reaction temperatures applied in hydro- or solvothermal synthesis retaining thiometallate or polychalcogenide building blocks enable the construction of molecular or extended structures. Because of the variable coordina-

tion behaviour of antimony, thioantimonates(III) are of particular interest as building units. In our recent work, we have synthesized several new thioantimonate(III) compounds using elemental antimony. Depending on the reaction conditions as well as the nature of the counter-cation, molecular (Bensch & Schur, 1997*a*) or extended structures (Bensch & Schur, 1997*b*, 1998) are observed. The use of antimony chloride in the synthesis leads to crystals of the new molecular thioantimonate $[\text{Ph}_4\text{P}]_2\text{[Sb}_2\text{S}_{15}]$, (I).



The structure of (I) consists of molecular $\text{Sb}_2\text{S}_{15}^{2-}$ anions located around a crystallographic twofold axis as well as tetraphenylphosphonium cations in general positions. In the anion, two symmetry-related antimony centres are connected *via* a tetrasulfido ligand as well as an additional sulfide anion, forming a seven-membered hetero ring. The coordination sphere of each antimony centre is completed by an additional chelating pentasulfido ligand forming a six-membered ring in a chair conformation. In the resulting tricyclic arrangement, the antimony centres act as spiro centres and they are within a strongly distorted ψ -trigonal bipyramidal environment. As expected, the Sb—S distances in the axial positions, 2.6874 (8) and 2.7205 (9) Å, are significantly longer than those in the equatorial positions, 2.5200 (8) and 2.4328 (7) Å. The antimony centre has an additional long intramolecular contact to the opposite S atom of the bridging S_4^{2-} ligand of 3.201 (1) Å, which is significantly shorter than the sum of the van der Waals radii for antimony and sulfur of 3.85 Å. With this secondary bond, the resulting SbS_5 polyhedron can be described as a distorted ψ -octahedron. Such additional long secondary bonds are found in all molecular Sb_2S_x anions (Bensch & Schur, 1997*b*, 1998; Paul *et al.*, 1993) and are also observed in similar tricyclic indium polychalcogenides (Dhingra & Kanatzidis, 1993*a,b*). While the constitution of the $\text{Sb}_2\text{S}_{15}^{2-}$ anion is the same compared to those of pseudo-polymorphic $[\text{Ph}_4\text{P}]_2[\text{Sb}_2\text{S}_{15}]\cdot\text{C}_3\text{N}_2\text{H}_6$ (Bensch & Schur, 1998) and $[\text{Ph}_4\text{P}]_2[\text{Sb}_2\text{S}_{15}]\cdot\text{C}_7\text{H}_8$ (Paul *et al.*, 1993), some conformational differences are observed. The most obvious deviation in the title compound is the decrease of the Sb—S—Sb angle by about 5° to a value of 96.41 (4)°, concomitant with a shortening of the Sb···Sb separation by approximately 0.12 Å. In contrast to the anions of the solvent-containing compounds, that in the title compound exhibits no detectable disorder of the polysulfide ligands. Such disorder, especially the substitution of

polysulfide ligands of different length, is frequently observed in polysulfide compounds (Banda *et al.*, 1989; Dance, 1997).

The tetraphenylphosphonium cations form pairs with sextuple embracements of the phenyl rings. The intermolecular distance of 6.910 (2) Å between the phosphorus centres in these pairs is less than twice the van der Waals radius of Ph_4P^+ (13.5 Å). Interpenetration of the cations leads to interactions between the three phenyl rings of each cation. These pairs are arranged in honeycomb layers. This specific arrangement of the tetraphenylphosphonium cations is frequently found in polychalcogenide salts as well as other compounds (Dance, 1997; Müller *et al.*, 1984). The anions are stacked along the *c* axis, with a shortest intermolecular S···S distance of 3.833 (2) Å. It has been claimed that supramolecular interactions between the tetraphenylphosphonium cations have a great influence on product formation. Further, it is well documented that different countercations lead to different metal polychalcogenides (Dance, 1997). Therefore, investigations on the influence of different cations on product formation, as well as the dimensionality of compounds obtained in hydrothermal synthesis, are underway.

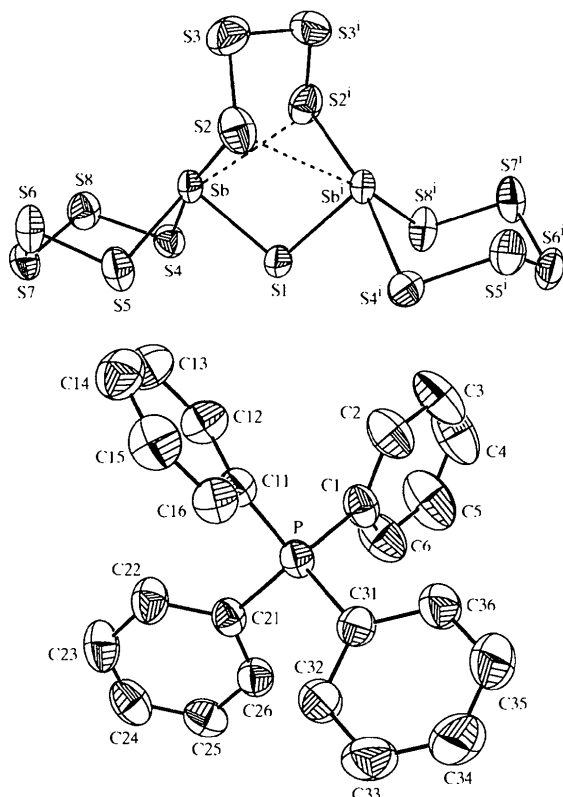


Fig. 1. The crystal structure of $[\text{Ph}_4\text{P}]_2[\text{Sb}_2\text{S}_{15}]$, with labelling and displacement ellipsoids drawn at the 50% probability level [the shortest intramolecular Sb···S distances of 3.201 (1) Å are indicated by dotted lines].

Experimental

Antimony chloride, sulfur and tetraphenylphosphonium bromide (molar ratio 1:9:1) in 5 ml of 2 M ammonia solution were reacted in teflon-lined steel autoclaves at 403 K for 7 d. The product was filtered and washed with deionized water.

Crystal data

(C₂₄H₂₀P)₂[Sb₂S₁₅]

M_r = 1403.14

Monoclinic

C2/c

a = 18.267 (3) Å

b = 12.122 (2) Å

c = 27.522 (4) Å

β = 108.26 (2)°

V = 5787.4 (16) Å³

Z = 4

D_x = 1.610 Mg m⁻³

D_m not measured

Data collection

Stoe AED-II four-circle diffractometer

ω/θ scans

Absorption correction:

ψ scan (XEMP; Siemens, 1990)

T_{min} = 0.425, *T_{max}* = 0.458

7493 measured reflections

6655 independent reflections

Refinement

Refinement on *F*²

R [*F*² > 2σ(*F*²)] = 0.026

wR (*F*²) = 0.063

S = 1.022

6654 reflections

303 parameters

H atoms: see below

w = 1/[σ²(*F_o*²) + (0.0259*P*)² + 4.0975*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Sb	0.468861 (9)	0.679888 (14)	0.180614 (5)	0.04365 (5)
S1	1/2	0.81365 (8)	1/4	0.0662 (3)
S2	0.59189 (4)	0.55840 (7)	0.23610 (3)	0.0656 (2)
S3	0.52814 (6)	0.41445 (7)	0.22284 (3)	0.0801 (2)
S4	0.34889 (4)	0.81619 (6)	0.14109 (3)	0.0560 (2)
S5	0.32197 (4)	0.75659 (7)	0.06773 (3)	0.0650 (2)
S6	0.40229 (5)	0.82006 (7)	0.03782 (2)	0.0663 (2)
S7	0.50051 (5)	0.72816 (8)	0.06779 (3)	0.0703 (2)
S8	0.55182 (4)	0.78938 (7)	0.14022 (3)	0.0647 (2)
P	0.29348 (3)	0.19976 (5)	0.12954 (2)	0.03780 (13)
C1	0.31953 (13)	0.1813 (2)	0.19766 (8)	0.0461 (5)
C2	0.2768 (2)	0.2332 (3)	0.22415 (10)	0.0655 (8)
C3	0.2950 (2)	0.2162 (4)	0.27658 (11)	0.0837 (11)
C4	0.3537 (2)	0.1481 (4)	0.30082 (12)	0.0925 (13)
C5	0.3952 (2)	0.0953 (4)	0.27491 (12)	0.0951 (13)

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 82 reflections

θ = 15–21°

μ = 1.563 mm⁻¹

T = 293 (2) K

Polyhedron

0.6 × 0.5 × 0.5 mm

Orange

5143 reflections with *I* > 2σ(*I*)

R_{int} = 0.012

θ_{max} = 27.50°

h = -23 → 0

k = -1 → 15

l = -33 → 35

4 standard reflections

frequency: 120 min

intensity decay: negligible

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.465 e Å⁻³

Δρ_{min} = -0.278 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

C6	0.3788 (2)	0.1120 (3)	0.22267 (10)	0.0733 (9)
C11	0.25044 (12)	0.3328 (2)	0.11322 (8)	0.0386 (5)
C12	0.28480 (15)	0.4241 (2)	0.14202 (9)	0.0508 (6)
C13	0.2575 (2)	0.5279 (2)	0.12693 (11)	0.0579 (7)
C14	0.1957 (2)	0.5422 (2)	0.08334 (11)	0.0579 (7)
C15	0.1604 (2)	0.4524 (2)	0.05516 (10)	0.0573 (7)
C16	0.18739 (13)	0.3478 (2)	0.06966 (9)	0.0457 (6)
C21	0.37557 (12)	0.1940 (2)	0.10645 (8)	0.0401 (5)
C22	0.39690 (15)	0.2872 (2)	0.08500 (11)	0.0547 (6)
C23	0.4566 (2)	0.2810 (3)	0.06430 (12)	0.0654 (8)
C24	0.4959 (2)	0.1848 (3)	0.06614 (11)	0.0617 (7)
C25	0.47558 (15)	0.0913 (2)	0.08745 (10)	0.0557 (6)
C26	0.41430 (14)	0.0955 (2)	0.10708 (9)	0.0484 (6)
C31	0.22737 (13)	0.0942 (2)	0.09791 (9)	0.0419 (5)
C32	0.2214 (2)	0.0634 (2)	0.04798 (10)	0.0541 (6)
C33	0.1681 (2)	-0.0150 (3)	0.02348 (12)	0.0667 (8)
C34	0.1216 (2)	-0.0624 (3)	0.04787 (14)	0.0830 (10)
C35	0.1275 (2)	-0.0330 (3)	0.09731 (14)	0.0831 (11)
C36	0.1805 (2)	0.0459 (2)	0.12256 (11)	0.0593 (7)

Table 2. Selected geometric parameters (Å, °)

Sb—S1	2.4328 (7)	S3—S3'	2.063 (2)
Sb—S8	2.5200 (8)	S4—S5	2.0538 (11)
Sb—S4	2.6874 (8)	S5—S6	2.0441 (12)
Sb—S2	2.7205 (9)	S6—S7	2.0526 (13)
S1—Sb'	2.4328 (7)	S7—S8	2.0570 (11)
S2—S3	2.0659 (13)		
S1—Sb—S8	88.30 (3)	S3—S2—Sb	92.14 (4)
S1—Sb—S4	82.44 (3)	S3'—S3—S2	104.68 (4)
S8—Sb—S4	91.40 (3)	S5—S4—Sb	95.47 (4)
S1—Sb—S2	88.36 (3)	S6—S5—S4	106.41 (5)
S8—Sb—S2	91.58 (3)	S5—S6—S7	106.33 (5)
S4—Sb—S2	170.24 (2)	S6—S7—S8	105.61 (5)
Sb'—S1—Sb	96.41 (4)	S7—S8—Sb	94.76 (4)

Symmetry code: (i) 1 - *x*, *y*, ½ - *z*.

All C, P, S and Sb atoms were refined with anisotropic displacement parameters. The H atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters [*U_{iso}* = 1.2*U_{eq}*(*C_{aromatic}*)] using a riding model with C—H = 0.93 Å.

Data collection: *DIF4* (Stoe & Cie, 1990a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1990b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *SHELXL93*.

This work is supported by the Hermann Willkomm and Hermann Schlosser Foundation as well as the State of Schleswig-Holstein.

Supplementary data for this paper are available from the IUCR electronic archives (Reference: SK1145). Services for accessing these data are described at the back of the journal.

References

- Banda, R. M. H., Dance, I. G., Bailey, T. D., Craig, D. C. & Scudder, M. L. (1989). *Inorg. Chem.* pp. 1862–1871.
- Bensch, W. & Schur, M. (1997a). *Z. Naturforsch. Teil B*, **52**, 405–409.
- Bensch, W. & Schur, M. (1997b). *Z. Kristallogr. New Cryst. Struct.* **212**, 305–307.
- Bensch, W. & Schur, M. (1998). *Z. Anorg. Allg. Chem.* **624**, 310–314.
- Dance, I. G. (1997). *Supramolecular Inorganic Chemistry, in The Crystal as a Supramolecular Entity*, 1st ed., edited by G. R. Desiraju, pp. 137–233. Chichester: Wiley.

- Dhingra, S. S. & Kanatzidis, M. G. (1993a). *Inorg. Chem.* **32**, 1350–1362.
- Dhingra, S. S. & Kanatzidis, M. G. (1993b). *Inorg. Chem.* **32**, 3300–3305.
- Müller, A., Klingelhöfer, P., Eicher, J. & Bohrer, R. (1984). *Z. Kristallogr.* **168**, 121–131.
- Paul, P. P., Rauchfuss, T. B. & Wilson, S. R. (1993). *J. Am. Chem. Soc.* **115**, 3316–3317.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1990). *SHELXTL/PC. Program Package for the Solution, Refinement and Graphical Presentation of Crystal Structures*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Stoe & Cie (1990a). *DIF4. Diffractometer Control Program*. Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1990b). *REDU4. Data Reduction Program*. Version 7.03/DOS. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1998). **C54**, 923–925

The Improved Synthesis of [Cr(N)(salen)].CH₃NO₂

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(Received 29 October 1997; accepted 13 January 1998)

Abstract

In the title compound, {2,2'-[1,2-ethanediylbis(nitrilomethylidyne)]diphenolato-*O,N,N',O'*}nitridochromium(V) nitromethane solvate, [Cr(N)(C₁₆H₁₄N₂O₂)]·CH₃NO₂, the metal center is five-coordinated. The chromium–nitride bond length is 1.559(2) Å, which is 0.04 Å longer than in the analogous manganese(V) compound. The structure contains a co-crystallized nitromethane molecule. In line with its accepted weak donor properties, this solvent molecule does not interact with the coordinatively unsaturated metal center.

Comment

Nitrido complexes of manganese(V) with auxiliary Schiff base ligands have recently received much attention due of their applicability in N-atom transfer reactions (Du Bois *et al.*, 1997). The reactivity of analogous chromium complexes has not received similar attention

in spite of the fact that they predate the manganese analogs.

[Cr(N)(salen)] {salen is 2,2'-[1,2-ethanediylbis(nitrilomethylidyne)]diphenol} was the very first nitrido complex of a first row transition metal to be prepared (Ashankow & Poznjak, 1981). It has, however, only been characterized by its EPR and IR spectra. The synthetic method employed was to photolyze the chromium(III)–azide complex [Cr(N₃)(salen)].H₂O with light from a high-pressure mercury lamp. The photolysis was carried out on a suspension of the starting material in 1-butanol and the product collected from the solvent by allowing it to evaporate at room temperature. No scale or yield were reported. We find that according to the method described only small amounts of product are obtained due to the limited solubility of the nitrido complex, as well as of the azide precursor, in 1-butanol. By charging the reaction mixture with large amounts of precursor and photolyzing for prolonged periods of time, we can prepare greater amounts of [Cr(N)(salen)], which precipitates and forms a solid mixture with the starting material. Separation of this mixture is not trivial since the similarity of the product and starting material gives them similar solubility properties in almost all common solvents. We have found though that cold nitromethane separates these complexes very efficiently and thus provides a route to the interesting nitrido complex in synthetically useful amounts. It should be remarked further that the analogous manganese complex was reported to be very difficult to purify and crystallize (Du Bois *et al.*, 1996). We found that recrystallization from nitromethane affords efficient purification and yields perfect crystals of mm size of the [Mn(N)(salen)] complex without co-crystallization of the solvent.

The [Cr(N)(salen)] complex is only the fourth Cr^V–nitrido complex to be structurally characterized. It is five-coordinate (Fig. 1) with a Cr–N distance of 1.559(2) Å. This value compares well with distances found in the other three reported Cr^V–nitrido complexes: 1.565(6) Å in nitrido(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(V) (Groves *et al.*, 1983), 1.560(2) Å in nitrido[1,2-bis(2-pyridinecarboxamido)benzene(2-)]chromium(V) (Che *et al.*, 1988) and 1.575(9) Å in six-coordinate nitrido(1,4,7-triazacyclononane)(2,4-pentanedionato)chromium(V) perchlorate (Niemann *et al.*, 1996). The distances are slightly longer than those found in Cr^{VI}–nitrido complexes: 1.544(3) Å in [Cr(N)(N'-Pr₂)₃] (Odom *et al.*, 1995) and 1.538(5) Å in [Cr(N)(OBut)₃] (Chiu *et al.*, 1996). The Cr atom is situated 0.501(1) Å above the mean plane defined by the ligators of the salen ligand. Such a geometry is common for five-coordinate square-pyramidal transition metal complexes. In [Cr(O)Cl₄]⁻, the out-of-plane displacement of the metal atom is 0.561(4) Å (Gahan *et al.*, 1977) and in nitrido(5,10,15,20-tetra-*p*-tolylporphyrinato)chromium(V), it is 0.42 Å (Groves *et al.*, 1982). The title compound, (I), is the first