

O3—Yb—O4	55.4 (2)	Yb—O6—C9	151.4 (5)
O3—Yb—O5 ¹	84.3 (2)	Yb—N1—C13	122.5 (6)
O3—Yb—O6	82.8 (2)	Yb—N1—C24	119.2 (5)
O3—Yb—N1	129.8 (2)	C13—N1—C24	117.4 (7)
O3—Yb—N2	156.1 (2)	Yb—N2—C22	125.5 (6)
O4—Yb—O5 ¹	139.1 (2)	Yb—N2—C23	118.6 (5)
O4—Yb—O6	82.4 (2)		

Symmetry code: (i) $1 - x, 2 - y, 1 - z$.

H atoms were located by ΔF methods but were not refined. C—H distances were in the range 0.74–1.11 Å.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985) and *DIRDIF* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1303). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 1475–1479

Tricarbonylchromium complexes of four methyl 4,6-*O*-[(η^6 -phenyl)alkylidene]- α -D-glucopyranosides

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Abstract

The crystal structures of the chiral non-racemic η^6 -tricarbonylchromium complexes of three methyl 4,6-*O*-benzylidene- α -D-glucopyranosides, (1)–(3), have been determined, as well as that of the 4,6-*O*-acetal, (4), derived from acetophenone. These compounds are tricarbonyl{(*R*)-methyl 2,3-di-*O*-methyl-4,6-*O*-[(1*S*,3*R*)-(η^6 -3-trimethylsilylphenyl)methylene]- α -D-glucopyranoside}chromium(0), (1), [Cr(C₁₉H₃₀O₆Si)(CO)₃], tricarbonyl{(*R*)-methyl 2,3-di-*O*-methyl-4,6-*O*-[(1*S*,2*R*)-(η^6 -2-trimethylsilylphenyl)methylene]- α -D-glucopyranoside}chromium(0), (2), [Cr(C₁₉H₃₀O₆Si)(CO)₃], tricarbonyl{(*R*)-methyl 2,3-*O*-(1-methylethylidene)-4,6-*O*-[(η^6 -phenyl)methylene]- α -D-glucopyranoside}chromium(0), (3), [Cr(C₁₇H₂₂O₆)(CO)₃], and tricarbonyl{(*S*)-methyl 2,3-di-*O*-methyl-4,6-*O*-[(η^6 -1-phenyl)ethylene]- α -D-glucopyranoside}chromium(0), (4), [Cr(C₁₇H₂₄O₆)(CO)₃].

Comment

In connection with a study into the utilization of (η^6 -arene)Cr(CO)₃ complexes in asymmetric synthesis (Woodgate *et al.*, 1998), we have reported in Rickard *et al.* (1998) the structure of tricarbonyl{(*R*)-methyl 2,3-di-*O*-methyl-4,6-*O*-[(η^6 -phenyl)methylene]- α -D-glucopyranoside}chromium(0), (5), and three of its derivatives, (6)–(8), functionalized in the arene ring by a deprotonation (BuLi)/electrophile quenching sequence. In these derivatives, the newly introduced electrophile (SiMe₃, SME or PPh₂, respectively) occupies an *ortho* aromatic site and in each case the absolute stereochemistry of the η^6 -complexed ring was established as 1*R*,2*S* by single-crystal X-ray determinations.

As well as the *ortho*-SiMe₃ compound, (6) (40%), two other tricarbonylchromium complexes were present in the crude mixture obtained from reactions using Me₃SiCl to quench the intermediate (η^6 -phenyl)lithium anion generated in tetrahydrofuran (THF) (*cf.* Jin *et al.*, 1997). These two complexes have now been isolated and their crystal structures determined by X-ray analyses. Unexpectedly, the major product (48%) proved to be the

meta regioisomer, (1), whose absolute stereochemistry in the arene ring is $1S,3R$. The third product (8%) was the regioisomeric *ortho* complex, (2), the $1S,2R$ diastereoisomer of (6). The crystal structures of (3) and (4) are also presented here.

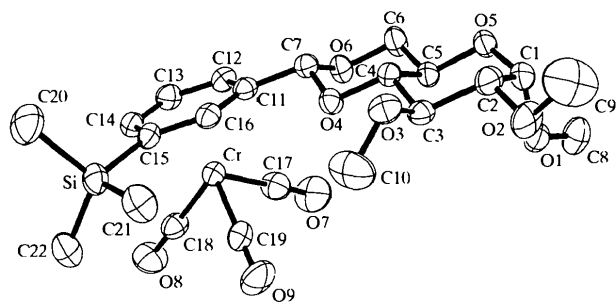
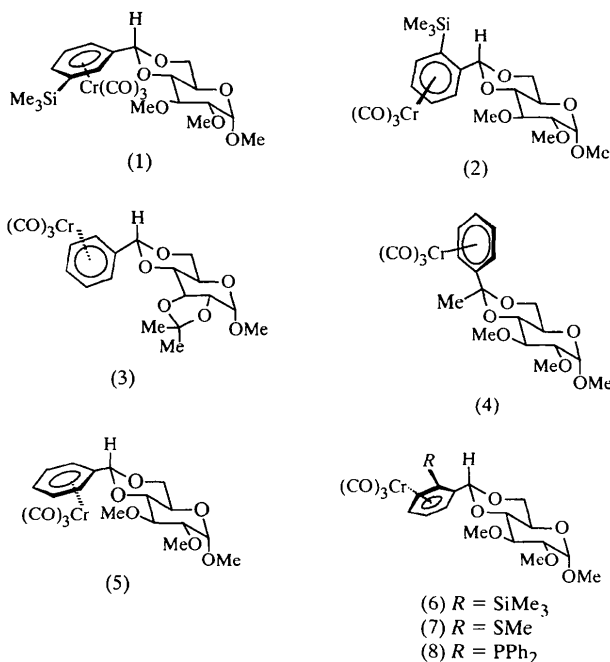


Fig. 1. The structure of (1) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

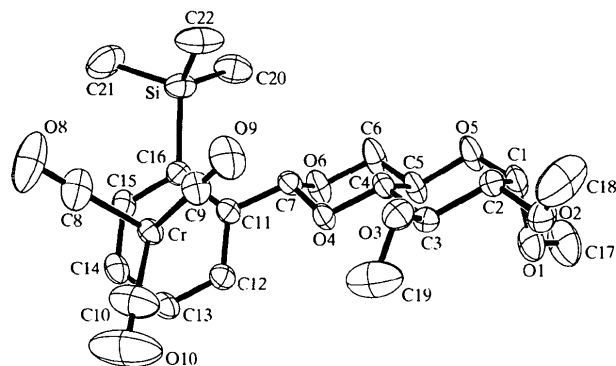


Fig. 2. The structure of (2) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

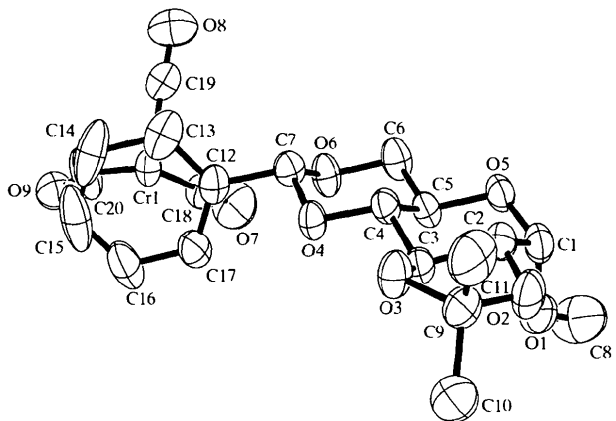


Fig. 3. The structure of (3) showing 50% probability displacement ellipsoids. Only one of the two independent molecules is shown. H atoms have been omitted for clarity.

Although the absolute configuration is R at both the *meta* site in (1) (Fig. 1) and the *ortho* site in (6), the crystal structures of (1) and (6) [or (2), Fig. 2] show different conformational relationships between the η^6 - $\text{Cr}(\text{CO})_3$ moiety and H7, being *anti* in the former and *syn* in the latter. Therefore, it appears that intramolecular chelation of the silicon electrophile *via* C3—OMe is responsible for the diastereoselection, irrespective of the orientation of the tricarbonylchromium group relative to H7 [cf. Jin *et al.* (1997)].

In order to investigate the structural consequence of incorporating a bulkier protecting group for the $2\alpha,3\beta$ -diol, the η^6 - $\text{Cr}(\text{CO})_3$ complex, (3), was prepared from the 2,3-*O*-isopropylidene-4,6-*O*-benzylidene glucose derivative. The crystal structure (Fig. 3) of the bis-acetal (3) shows that the conformation of the (η^6 -phenyl) $\text{Cr}(\text{CO})_3$ unit is different from that in the 2,3-di-*O*-methyl ether, (5), in which the η^6 - $\text{Cr}(\text{CO})_3$ moiety lies in the concavity defined by the phenyl ring and the glucopyranoside ring. In the bis-acetal (3), however, the steric requirements of the $2\alpha,3\beta$ -isopropylidene ring impose a conformation in which the tricarbonylchromium group is coordinated to the upper face of the phenyl ring. Treatment of (3) with BuLi in THF and then Me_3SiCl gave both of the *ortho*- SiMe_3 diastereoisomers (62% $1R,2S$; 15% $1S,2R$), but none of the *meta* isomer was isolated.

We have also prepared the η^6 - $\text{Cr}(\text{CO})_3$ complex, (4), derived from acetophenone. The crystal structure (Fig. 4) of acetal (4), whose precursor free ligand was prepared under conditions of thermodynamic control, establishes unequivocally that the C7 phenyl group is axial in the more stable epimer; this unexpected configurational preference was deduced previously from ^1H NMR data (Lipták & Fügedi, 1983).

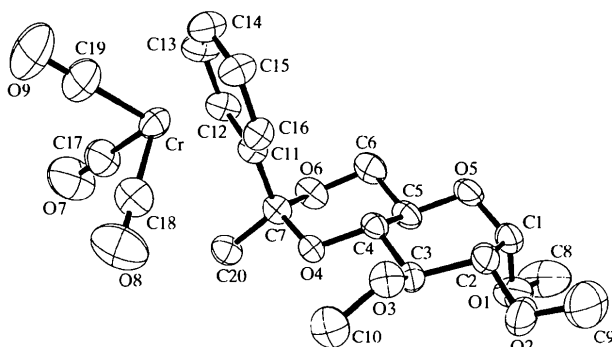


Fig. 4. The structure of (4) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

All molecules show the expected piano-stool arrangement around the Cr atom, with the aromatic ring η^6 -bound. There is some difference in the distance between the aromatic rings and the Cr atom, the distance to the unsubstituted rings being significantly greater. Distances between the Cr atom and the mean plane of the aromatic rings are: 1.703 (1) Å for (1), 1.713 (1) Å for (2), 1.739 (1) and 1.734 (1) Å for the two independent molecules of (3), and 1.725 (1) Å for (4). The Cr—C distances to the carbonyl groups show no such trend and average 1.844 Å.

The six-membered rings all adopt the chair conformation and are *trans* fused. The interatomic distances within these rings are all comparable and show little deviation between molecules. The two independent molecules of (3) are closely similar, except for the rotation about the C7—C12 bond, the torsion angles for the O4—C7—C12—C13 sequence being 113.6 (3) and 95.5 (3)°, respectively, for the two independent molecules.

The absolute configurations were all established according to the method of Flack (1983) and the results all show the correct absolute stereochemistry.

Experimental

The free ligand (*R*)-methyl 2,3-*O*-(1-methylethylidene)-4,6-*O*-[η^6 -(phenyl)methylene]- α -D-glucopyranoside, was prepared from (*R*)-methyl 4,6-*O*-(phenylmethylene)- α -D-glucopyranoside by acetal exchange with 2,2-dimethoxypropane in the presence of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (Kjølberg & Neumann, 1993) in CH_2Cl_2 . (*S*)-Methyl 2,3-di-*O*-methyl-4,6-*O*-[η^6 -(1-phenyl)ethylidene]- α -D-glucopyranoside was prepared from methyl α -D-glucopyranoside by acetal exchange with (1,1-dimethoxyethyl)benzene and pyridinium *p*-toluenesulfonate in CH_2Cl_2 , followed by methylation with $\text{Ag}_2\text{O}/\text{MeI}$ in acetone. Complexes (3) and (4) were formed from the appropriate phenylalkylidene precursor by thermally promoted ligand exchange using $\text{Cr}(\text{CO})_6$ in $\text{Bu}_2\text{O}-\text{THF}$. Complexes (1) and (2) were isolated, together with (6), after treatment of (5) with BuLi in THF at 195 K, addition of chlorotrimethylsilane, and then chromatography on silica gel.

Compound (1)

Crystal data

$[\text{Cr}(\text{C}_{19}\text{H}_{30}\text{O}_6\text{Si})(\text{CO})_3]$

$M_r = 518.55$

Orthorhombic

$P2_12_12_1$

$a = 7.7051(2) \text{ \AA}$

$b = 14.8671(3) \text{ \AA}$

$c = 22.2079(5) \text{ \AA}$

$V = 2543.97(10) \text{ \AA}^3$

$Z = 4$

$D_x = 1.354 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 8192 reflections

$\theta = 2-26^\circ$

$\mu = 0.543 \text{ mm}^{-1}$

$T = 203(2) \text{ K}$

Needle

$0.56 \times 0.09 \times 0.08 \text{ mm}$

Yellow

Data collection

Siemens SMART CCD area-detector diffractometer

ω scans

Absorption correction:

multi-scan (Blessing,

1995)

$T_{\min} = 0.751$, $T_{\max} = 0.958$

14 997 measured reflections

2975 independent reflections

(plus 2162 Friedel-related reflections)

4223 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\max} = 26.4^\circ$

$h = -9 \rightarrow 9$

$k = 0 \rightarrow 18$

$l = 0 \rightarrow 27$

Intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.091$

$S = 1.095$

5137 reflections

304 parameters

H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.0238P)^2$

$+ 1.4132P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.241 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.279 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for

Crystallography (Vol. C)

Absolute structure:

Flack (1983)

Flack parameter = $-0.02(2)$

Compound (2)

Crystal data

$[\text{Cr}(\text{C}_{19}\text{H}_{30}\text{O}_6\text{Si})(\text{CO})_3]$

$M_r = 518.55$

Orthorhombic

$P2_12_12_1$

$a = 11.7885(2) \text{ \AA}$

$b = 14.5002(3) \text{ \AA}$

$c = 15.3639(2) \text{ \AA}$

$V = 2626.24(8) \text{ \AA}^3$

$Z = 4$

$D_x = 1.311 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 8192 reflections

$\theta = 2-26^\circ$

$\mu = 0.526 \text{ mm}^{-1}$

$T = 203(2) \text{ K}$

Irregular fragment

$0.50 \times 0.35 \times 0.28 \text{ mm}$

Yellow

Data collection

Siemens SMART CCD area-detector diffractometer

4858 reflections with

$I > 2\sigma(I)$

ω scans
Absorption correction:
multi-scan (Blessing,
1995)
 $T_{\min} = 0.779$, $T_{\max} = 0.867$
24 839 measured reflections
3030 independent reflections
(plus 2322 Friedel-related
reflections)

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.093$
 $S = 1.026$
5352 reflections
304 parameters
H atoms riding
 $w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.5296P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

Compound (3)*Crystal data*

[Cr(C₁₇H₂₂O₆)(CO)₃]
 $M_r = 458.38$
Monoclinic
 $P2_1$
 $a = 7.7593$ (1) Å
 $b = 27.9746$ (3) Å
 $c = 10.2064$ (1) Å
 $\beta = 101.65$ (1)°
 $V = 2169.78$ (4) Å³
 $Z = 4$
 $D_x = 1.403$ Mg m⁻³
 D_m not measured

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
Absorption correction:
multi-scan (Blessing,
1995)
 $T_{\min} = 0.833$, $T_{\max} = 0.889$
13 078 measured reflections
4356 independent reflections
(plus 3055 Friedel-related
reflections)

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.084$
 $S = 1.035$
7411 reflections
546 parameters
H atoms riding

$R_{\text{int}} = 0.057$
 $\theta_{\max} = 26.36^\circ$
 $h = -14 \rightarrow 14$
 $k = 0 \rightarrow 18$
 $l = 0 \rightarrow 19$
Intensity decay: none

$\Delta\rho_{\max} = 0.483$ e Å⁻³
 $\Delta\rho_{\min} = -0.411$ e Å⁻³
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)
Absolute structure:
Flack (1983)
Flack parameter =
-0.016 (17)

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
Cell parameters from 8192
reflections
 $\theta = 2-26^\circ$
 $\mu = 0.574$ mm⁻¹
 $T = 203$ (2) K
Irregular fragment
 $0.33 \times 0.24 \times 0.21$ mm
Yellow

6642 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\max} = 26^\circ$
 $h = -9 \rightarrow 9$
 $k = -34 \rightarrow 30$
 $l = 0 \rightarrow 12$
Intensity decay: none

$(\Delta/\sigma)_{\max} = 0.006$
 $\Delta\rho_{\max} = 0.367$ e Å⁻³
 $\Delta\rho_{\min} = -0.259$ e Å⁻³
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 0.5820P]$
where $P = (F_o^2 + 2F_c^2)/3$

Compound (4)*Crystal data*

[Cr(C₁₇H₂₄O₆)(CO)₃]
 $M_r = 460.39$
Monoclinic
 $P2_1$
 $a = 7.6488$ (1) Å
 $b = 13.3096$ (3) Å
 $c = 11.1206$ (2) Å
 $\beta = 100.08$ (1)°
 $V = 1114.64$ (4) Å³
 $Z = 2$
 $D_x = 1.372$ Mg m⁻³
 D_m not measured

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
Absorption correction:
multi-scan (Blessing,
1995)
 $T_{\min} = 0.756$, $T_{\max} = 0.824$
3930 measured reflections
2294 independent reflections
(plus 1636 Friedel-related
reflections)

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.087$
 $S = 1.059$
3930 reflections
275 parameters
H atoms riding
 $w = 1/[\sigma^2(F_o^2) + (0.0611P)^2 + 0.0283P]$
where $P = (F_o^2 + 2F_c^2)/3$

Absolute structure:
Flack (1983)
Flack parameter = 0.016 (16)

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
Cell parameters from 8192
reflections
 $\theta = 2-26^\circ$
 $\mu = 0.559$ mm⁻¹
 $T = 203$ (2) K
Prism
 $0.53 \times 0.38 \times 0.36$ mm
Yellow

3721 reflections with
 $I > 2\sigma(I)$
 $\theta_{\max} = 26^\circ$
 $h = -9 \rightarrow 9$
 $k = -15 \rightarrow 16$
 $l = 0 \rightarrow 13$
Intensity decay: none

$(\Delta/\sigma)_{\max} = 0.005$
 $\Delta\rho_{\max} = 0.270$ e Å⁻³
 $\Delta\rho_{\min} = -0.340$ e Å⁻³
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)
Absolute structure:
Flack (1983)
Flack parameter = 0.006 (16)

For (3), there are two independent molecules in the unit cell. For all molecules except (1), the carbonyl O atoms show large thermal vibrations, indicative of some disorder in these groups. In one case, O9 in (3), the density could be resolved into two components and this atom has been treated as two half atoms. Some of the C atoms of the methoxy groups similarly have large thermal vibrations, but in no case could these be resolved into two alternative positions. H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds for methyl groups), and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

For all compounds, data collection: *SMART* (Siemens, 1994a); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1994a); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

SHELXTL (Siemens, 1994b); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1240). Services for accessing these data are described at the back of the journal.

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 Woodgate, P. D., Singh, Y. & Rickard, C. E. F. (1998). *J. Organomet. Chem.* **560**, 197–209.

Acta Cryst. (1999). **C55**, 1479–1482

Bis{2-[1-(thiosemicarbazono)ethyl]pyridinium} hexakis(nitrato-*O,O'*)-thorate(IV) tetramethanol solvate

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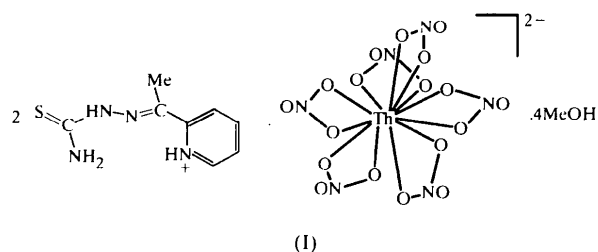
Abstract

Pale yellow crystals of the title compound, (C₈H₁₁N₄S)₂·[Th(NO₃)₆]·4CH₄O, are formed when thorium nitrate and acetylpyridine thiosemicarbazone are refluxed in methanol. Thorium is 12-coordinate. The complex anion possesses inversion symmetry. The almost planar 2-[1-(thiosemicarbazono)ethyl]pyridinium cations show bond lengths which indicate a considerable delocalization of electron density.

Comment

Heterocyclic thiosemicarbazones, as well as their metal complexes, are currently under discussion because of their biological activity (West *et al.*, 1990, and references therein). Although a number of studies dealing with complex-formation properties exists (West *et al.*, 1990, and references therein; Garg *et al.*, 1988, and references therein), comparatively few structural reports have been published (Abram *et al.*, 1998). Studies on reactions of heterocyclic thiosemicarbazones with actinides have not yet been reported. As part of our systematic studies on the complex-formation properties of tri- and pentadentate thiosemicarbazones, we investigated the reaction of 2-acetylpyridine thiosemicarbazone (HAPTSC) with thorium(IV) nitrate.

Heating of Th(NO₃)₄·4H₂O with excess HAPTSC in methanol results in the formation of (H₂ATPSC)₂·[Th(NO₃)₆], which crystallizes upon concentration of the reaction mixture. In this compound, thorium does not form any bonds to the thiosemicarbazone. In the remaining filtrate, however, a thorium thiosemicarbazonato complex of the tentative composition [Th(APTSC)(OH₂)(NO₃)₂][−] could be detected by a fast-atom bombardment (FAB[−]) mass spectrometry peak of reasonable intensity at *m/z* = 583. All attempts to isolate and crystallize this complex have failed up to now. The structure of (H₂APTSC)₂[Th(NO₃)₆]·4MeOH, (I) (Fig. 1), consists of a discrete complex anion and two acetylpyridinium thiosemicarbazone cations. Reasonable hydrogen bonds are only formed between the cations and the cocrystallized solvent, and between the two methanol molecules. Only one very weak hydrogen bond may be attributed between N12 and O33ⁱ of the complex anion [N12—H12 0.82 (5), H12···O33ⁱ 2.32 (5), N12···O33ⁱ 3.095 (4) Å and N12—H12—O33 158 (4)^o; symmetry code: (i) *x*, *y* + 1, *z*] (see Fig. 2).



The metal atom is 12-coordinate with a coordination sphere which can be described as a distorted icosahedron with 12 isosceles and eight equilateral triangles forming the surface of the coordination polyhedron (Fig. 1). The metal is located on a centre of inversion. With this, the structure of the anion comes close to the [Th(NO₃)₆]^{2−} anion (without inversion, but with approximate C₂ symmetry) in tris-2,2'-bipyridinium nitrate hexanitrothorate(IV) (Khan *et al.*, 1984) and in