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

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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.

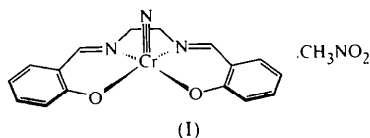
Comment

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



structurally characterized Cr^V-nitrido compound where the isoelectronic oxo analog is known and structurally characterized. Unfortunately, the structure of [Cr(O)(salen)]PF₆·CH₃CN suffers from disorder of the cation (Siddal *et al.*, 1983). The estimated Cr—O distance and chromium out-of-plane displacement are 1.56 (5) and 0.52 (5) Å, respectively. The metal–nitride distance in [Cr(N)(salen)] is 0.04 Å longer compared with the manganese analog (Du Bois *et al.*, 1996), making it likely that the chromium would match or even exceed the manganese–nitrido complex as an N-atom transfer reagent.

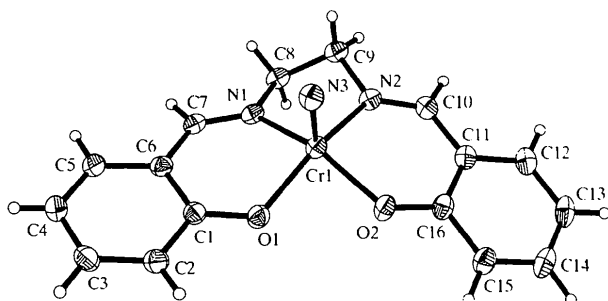


Fig. 1. SHELXTL (Siemens, 1994b) plot showing 35% probability ellipsoids for the non-H atoms of the [Cr(N)(salen)] molecule. H atoms are represented by circles of arbitrary size.

The distances within the salen ligand are as expected and the overall structure of the metal–salen fragment is very close to that found in the analogous manganese complex.

It is clear that despite the facts that chromium in the title compound is only five-coordinate and that some six-coordinate Cr^V-nitrido complexes are known (Niemann *et al.*, 1996), there is no interaction between the co-crystallized nitromethane molecule and the chromium center. This observation is in line with the accepted low-donor ability of nitromethane (Driessen & Groeneveld, 1969).

Experimental

Caution: azides are potentially explosive. Although we have never experienced problems with [Cr(N₃)(salen)]·H₂O, we suggest that the synthesis is carried out by sequential grinding and addition of batches no larger than 0.25 g. Also, sufficient cooling for the mercury lamp to ensure that the reaction mixture is kept below 323 K should be provided. [Cr(N₃)(salen)]·H₂O was prepared according to Ashankow & Poznjak (1981). 1-Butanol (Aldrich) and nitromethane (Fluka)

were purchased and used as received. [Cr(N₃)(salen)]·H₂O (2.0 g), in batches of 0.25 g, was finely ground in an agate mortar and added to 150 ml of 1-butanol in a quartz photolysis apparatus. Between additions, the suspension was photolyzed for 1 h. Upon complete addition of the azide precursor, the reaction mixture was photolyzed for an additional 6 h. The solids were filtered off and washed with diethyl ether. The solid mixture was extracted with nitromethane at room temperature until the extracts were only slightly orange in color. The combined extracts were evaporated to near dryness and 0.66 g (32%) of orange–brown crystals were filtered off and dried. Crystals for diffraction analysis were grown by recrystallization from hot nitromethane. The data crystal was mounted using oil (Paratone-N, Exxon) onto a thin glass fiber with the (011) scattering planes roughly normal to the spindle axis.

Crystal data

[Cr(N)(C₁₆H₁₄N₂O₂)]·
CH₃NO₂
M_r = 393.35
Monoclinic
*P*2₁/*c*
a = 14.8109 (4) Å
b = 9.6159 (3) Å
c = 12.2536 (4) Å
β = 91.705 (1)°
V = 1744.39 (9) Å³
Z = 4
D_x = 1.498 Mg m⁻³
D_m not measured

Mo *K*α radiation
λ = 0.71073 Å
Cell parameters from 6060
reflections
θ = 4–28°
μ = 0.687 mm⁻¹
T = 198 (2) K
Tabular
0.42 × 0.20 × 0.09 mm
Red

Data collection

Siemens Platform CCD
diffractometer
ω scans
Absorption correction:
empirical *via ψ* scans
(Siemens, 1994b)
T_{min} = 0.748, *T_{max}* = 0.897
11 025 measured reflections
4146 independent reflections

3294 reflections with
I > 2σ(*I*)
R_{int} = 0.031
θ_{max} = 28.23°
h = -19 → 14
k = -12 → 9
l = -16 → 12
378 standard reflections
frequency: 360 min
intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.042
wR(*F*²) = 0.108
S = 1.116
4141 reflections
303 parameters
All H atoms refined
w = 1/[σ²(*F_o*²) + (0.0377*P*)²
+ 1.3545*P*]
where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = -0.001
Δρ_{max} = 0.500 e Å⁻³
Δρ_{min} = -0.349 e Å⁻³
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cr1—N3	1.559 (2)	Cr1—N2	2.017 (2)
Cr1—O2	1.910 (2)	Cr1—N1	2.019 (2)
Cr1—O1	1.913 (2)		
N3—Cr1—O2	110.03 (9)	O2—Cr1—N2	89.32 (7)
N3—Cr1—O1	105.41 (9)	N3—Cr1—N1	102.74 (9)
O2—Cr1—O1	87.18 (7)	O1—Cr1—N1	88.37 (7)
N3—Cr1—N2	100.64 (9)		

Systematic absences suggested the space group unambiguously. The structure was solved by direct methods (*SHELXS*; Sheldrick, 1990). All atomic parameters were independently refined. The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on F^2 (*SHELXL93*; Sheldrick, 1993). The highest peaks in the final difference Fourier map were in the vicinity of the nitromethane solvate molecule; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution. The nitromethane molecule is disordered. In addition to the crystallographic model presented here, a second structural model was refined with disordered positions for the nitromethane solvate. The following restraints were imposed on the disordered solvate parameters: (i) chemically equivalent bond lengths were restrained to remain equal, with an effective s.u. of 0.01 Å; (ii) anisotropic displacement parameters in bonding directions were restrained to be equal (s.u. 0.01 Å²); (iii) disordered positions closer than 1.2 Å were restrained to have similar displacement parameters (s.u. 0.02 Å²); (iv) disordered methyl H atoms were refined as idealized rotating groups. This model converged with $R1 = 0.039$ [for 3294 data with $I > 2\sigma(I)$] and $wR2 = 0.099$ (for all 4146 data) against 408 parameters with 297 restraints. The five highest peaks in the final difference Fourier map were located between aromatic C atoms; the final map had no other significant features. The [Cr(N)(salen)] host molecule for this alternative refinement was identical (within 1 s.u.) to the first refinement. The N—O bond lengths for the disordered solvate model were closer to expected values; however, the excessive restraints required for convergence undermine confidence in the significance of this improvement.

Data collection: *SMART* (Siemens, 1994a). Cell refinement: *SAINT* (Siemens, 1994a). Data reduction: *SAINT*. Molecular graphics: *SHELXTL* (Siemens, 1994b). Software used to prepare material for publication: *CIFTAB* in *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1529). Services for accessing these data are described at the back of the journal.

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Methyl 5-Deoxy-5-C-[(iododiphenylstannyl)methyl]-2,3-O-isopropylidene- α -D-lyxofuranoside†

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Abstract

A strong intramolecular Sn \cdots O interaction is present in the title molecule, [SnI(C₆H₅)₂(C₁₀H₁₇O₄)], resulting in a distorted trigonal-bipyramidal geometry about the Sn atom.

Comment

A trigonal-bipyramidal arrangement about the Sn atom is present in methyl 5-deoxy-5-C-[(iododiphenylstannyl)methyl]-2,3-O-isopropylidene- α -D-lyxofuranoside, (I), with the non-C atoms, O1 and O3, in axial positions. The distortion from ideal geometry is shown by the angles in Table 1. In particular, the O3—Sn1—C7 angle of 69.6(2)°, which forms the bite angle of the bidentate ligand, is considerably less than 90°. The Sn1—O3 interaction of 2.720(4) Å is longer than the sum of the covalent radii (2.06 Å) but shorter than the sum of the van der Waals radii (3.78 Å) (Bondi, 1964). A five-membered chelate ring is formed by this interaction and Sn—O bond lengths for pentacoordinate C,O-

† Alternative name: (5,6-dideoxy-2,3-O-isopropylidene-1-O-methyl- α -D-lyxofuranosyl-C⁶,O)iododiphenyltin.