Two square-pyramidal chromium(V)–nitride complexes: bis(2-methylquinolin-8-olato)nitridochromium(V) and nitridobis(2-sulfidopyridine N-oxide)chromium(V)

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Two new chromium(V)–nitride complexes with a coordination sphere completed by bidentate ligands have been synthesized and structurally characterized. Bis(2-methylquinolin-8-olato)nitridochromium(V), $[Cr(C_{10}H_8NO)_2(N)]$, has the coordination sphere completed by an equatorial N_2O_2 set of ligators. The compound crystallizes with the five-coordinate complexes at sites with twofold rotational symmetry and all Cr—N bond directions aligned with the crystallographic *b* axis. Nitridobis(2-sulfidopyridine N-oxide)chromium(V), $[Cr(C_5H_4N-OS)_2(N)]$, crystallizes with the molecules on general positions and has an equatorial S_2O_2 coordination environment, which is unprecedented among nitride complexes of the first-row transition metals. In both systems, Cr≡N bonds are short at *ca* 1.56 Å.

Comment

The nitride ligand (N^{3-}) is the strongest electron-donating ligand known (Nugent & Mayer, 1988). It also stands out by having a much more developed chemistry of second- and third-row transition metals than of their first-row congeners. The first example of a nitride complex of the first-row transition metals, [Cr(salen)(N)], was therefore prepared as late as 1981 by photolysis of the corresponding Cr^{III}–azide complex (Arshankow & Poznjak, 1981). A few other Cr^V– and Mn^V–nitride complexes have been prepared by this route, *e.g.* $[M(cyclam)(N)(CH_3CN)]^{2+}$ [cyclam is 1,4,7,11-tetraazacyclotetradecane; *M* = Cr (Meyer, Bendix, Bill *et al.*, 1998) and Mn (Meyer, Bendix, Metzler-Nolte *et al.*, 1998)] and [Cr(tacn)(acac)(N)]$^+$ (tacn is 1,4,7-triazacyclononane and acac is acet-

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ylacetonate) (Niemann *et al.*, 1996), but the method fails for systems where the auxiliary ligand sphere is labile. The lack of general methods of synthesis has been the primary obstacle in the development of the nitride chemistry for the first-row transition metals. Recently, we have found (Birk & Bendix, 2003; Bendix, 2003) that N-atom transfer from the easily accessible [Mn(salen)(N)] to $[CrCl_3(THF)_3]$ followed by ligand metathesis is a very general synthetic route to chromium(V)– nitride complexes. By this method, the uncharged complexes $[Cr(quinald)_2(N)]$ (quinald is 2-methylquinolin-8-olate), (I), and $[Cr(tpno)_2(N)]$ (tpno is 2-sulfidopyridine N-oxide), (II), have been prepared.

(I)

(II)
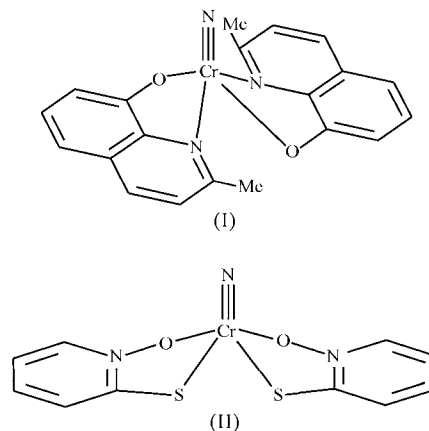
Complexes (I) and (II) are both five-coordinate, with approximately square-pyramidal coordination around the Cr^V atom and with the metal displaced *ca* 0.5 Å out of the plane of the basal ligators towards the nitride ligand (Figs. 1 and 2, and Table 1). Complex (I) crystallizes with the Cr^V≡N bond on a crystallographic twofold axis, making the basal ligators equivalent in pairs. Interestingly, even though complex (II) has the possibility for a molecular mirror plane (Fig. 2), this is not utilized in the crystal packing. The short Cr≡N bonds of 1.5609 (11) and 1.5591 (11) Å in (II) and (I), respectively, are both within the range of those found for other five-coordinate Cr^V–nitride complexes and *ca* 0.05 Å longer than the average Mn^V≡N bond length. In both structures, the nitride ligands
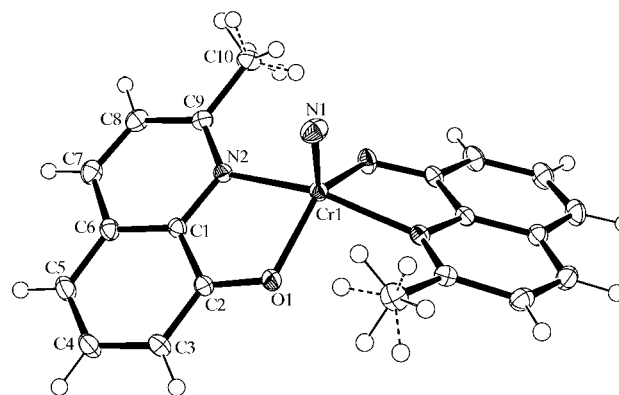

Figure 1
The molecular structure of (I), including the labelling of the atoms. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

are non-bridging. This fact is evidenced by high ν(Cr—N) stretching frequencies of 1016 and 1007 cm^{-1} for (I) and (II), respectively. In accordance with the low basicity and nucleophilicity normally observed for [Cr≡N]$^{2+}$ and [Mn≡N]$^{2+}$ moieties (Meyer, Bendix, Bill *et al.*, 1998; Meyer, Bendix, Metzler-Nolte *et al.*, 1998).

The vanadyl analogs of both (I) and (II) have been structurally characterized (Shiro & Fernando, 1971; Higes-Rolando *et al.*, 1994, respectively) and are isostructural with their [Cr≡N]$^{2+}$ counterparts. The bond lengths to the auxiliary ligands in the [V^{IV}(O)] complexes are slightly longer than those found in the [Cr^V(N)] systems and the pyramidalization is slightly larger for the vanadyl systems (*cf.* Table 2).

Complexes (I) and (II) differ in the configuration of the bidentate ligands, being *trans* and *cis*, respectively. This difference is common for these ligands and thus unrelated to the metal centre. A rare exception to these preferred configurations is [Co(py)(tpno)$_2$] (py is pyridine), wherein the tpno ligands are in the unusual *trans* configuration (Kang *et al.*, 1993).

The difference in angle between the nitride ligand and equatorial O-atom donors [112.91 (2)°] and N-atom donors [98.828 (18)°] in (I) reflects a significant distortion towards a trigonal-bipyramidal structure (with apical N-atom donors from the bidentate ligands). This contrast to the parent [Cr(quinolin-8-olate)$_2$(N)] complex, which features a regular square-pyramidal coordination of chromium, is caused by the steric demands of the 2-methyl substituents in (I). The packing of the [Cr(quinald)$_2$(N)] molecules is also influenced by the methyl groups, which prevent the π stacking dominating the structure of [Cr(quinolin-8-olate)$_2$(N)]. Nevertheless, a similar overall situation (*cf.* Fig. 3) with aligned (parallel and anti-

parallel) Cr≡N units results also for (I). This packing mode in combination with the electronically isolated molecules (the shortest Cr···Cr distance is 7.519 Å) makes the compound well suited for single-crystal EPR (electron paramagnetic resonance) studies of the bonding anisotropy in the metal–nitride bond (Bendix *et al.*, 2000).

Experimental

For the synthesis of (I), a solution of 8-hydroxyquinaldine (1.559 g, 9.79 mmol, Aldrich 98%) in acetonitrile (6 ml) was added to the solution resulting from an N-atom transfer reaction between [Mn(N)(salen)] (0.810 g, 2.4 mmol) and [CrCl$_3$(THF)$_3$] (0.906 g, 2.416 mmol) in acetonitrile (20 ml), with precipitation commencing immediately. The orange product (0.626 g, 68%) was washed with methanol and recrystallized from boiling toluene (180 ml). Slow evaporation afforded crystals of X-ray quality. For the synthesis of (II), a solution of the sodium salt of 2-mercaptopyridine *N*-oxide hydrate (0.735 g, 4.93 mmol, Aldrich) in methanol (11 ml) was added to the solution resulting from an N-atom transfer reaction between [Mn(N)(salen)] and [CrCl$_3$(THF)$_3$], prepared as described above. The resulting red precipitate (0.490 g, 64%) was collected by filtration and washed with methanol. Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile solution.
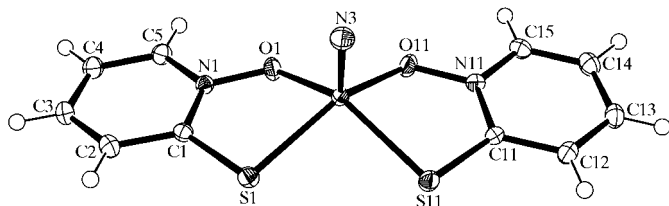

Figure 2
The molecular structure of (II), including the labelling of the atoms. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.
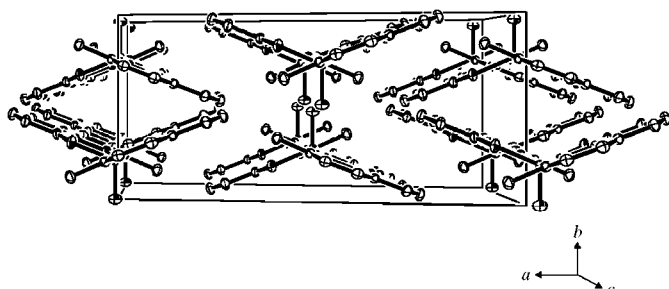

Figure 3
The crystal packing in (I), showing the parallel and antiparallel Cr≡N orientations. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

Compound (I)

Crystal data

[Cr(C$_{10}$H$_8$NO)$_2$(N)]	D_x = 1.516 Mg m^{-3}
M_r = 382.36	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 31 996
a = 16.8980 (14) Å	reflections
b = 7.6853 (7) Å	θ = 2.9–39.9°
c = 13.2955 (12) Å	μ = 0.70 mm^{-1}
β = 103.967 (7)°	T = 122 (1) K
V = 1675.6 (3) Å^3	Prism, orange
Z = 4	0.44 × 0.37 × 0.17 mm

Data collection

Nonius KappaCCD diffractometer	5177 independent reflections
φ and ω scans	4523 reflections with $I > 2\sigma(I)$
Absorption correction: numerical	R_{int} = 0.036
(Gaussian integration; Coppens,	$\theta_{\max}$ = 40.0°
1970)	h = −30 → 30
$T_{\min}$ = 0.813, $T_{\max}$ = 0.918	k = −13 → 13
49 933 measured reflections	l = −24 → 24

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.028	$+ 1.038P]$
$wR(F^2)$ = 0.085	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.14	$(\Delta/\sigma)_{\max} < 0.001$
5177 reflections	$\Delta\rho_{\max}$ = 0.56 e Å^{-3}
120 parameters	$\Delta\rho_{\min}$ = −0.50 e Å^{-3}
H-atom parameters constrained	

Compound (II)

Crystal data

[Cr(C$_5$H$_4$NOS)$_2$(N)]	Mo $K\alpha$ radiation
M_r = 318.31	Cell parameters from 47 810
Orthorhombic, $Pbca$	reflections
a = 11.0511 (12) Å	θ = 2.7–35°
b = 14.1558 (12) Å	μ = 1.30 mm^{-1}
c = 15.2486 (11) Å	T = 122 (1) K
V = 2385.4 (4) Å^3	Block, dark red
Z = 8	0.34 × 0.32 × 0.17 mm
D_x = 1.773 Mg m^{-3}	

Data collection

Nonius KappaCCD diffractometer	5236 independent reflections
φ and ω scans	4479 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (Gaussian integration; Coppens, 1970)	$R_{int} = 0.043$
	$\theta_{max} = 35.0°$
	$h = -17 \rightarrow 17$
$T_{min} = 0.710$, $T_{max} = 0.856$	$k = -22 \rightarrow 22$
85 248 measured reflections	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2 + 2.1443P]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.074$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.07$	$\Delta\rho_{max} = 1.18$ e Å^{-3}
5236 reflections	$\Delta\rho_{min} = -0.43$ e Å^{-3}
163 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °) for nitride complexes (I) and (II).

Compound (I)			
Cr1≡N1	1.5591 (11)	N1—Cr1—N2	98.828 (18)
Cr1—O1	1.9082 (6)	N1—Cr1—O2	112.91 (2)
Cr1—N2	2.0827 (6)	O1—Cr1—O1	134.18 (4)
O1—C2	1.3333 (9)	O1—Cr1—N2	91.21 (2)
C1—N2	1.3738 (9)	O1—Cr1—N2	81.92 (2)
N2—C9	1.3327 (10)	N2—Cr1—N2	162.34 (4)
Cr-out-of-plane	0.5312 (5) Å		
Compound (II)			
Cr1≡N3	1.5609 (11)	N3—Cr1—O1	109.24 (5)
Cr1—O1	1.9371 (9)	N3—Cr1—O11	105.79 (5)
Cr1—O11	1.9526 (9)	N3—Cr1—S1	103.02 (5)
Cr1—S1	2.3517 (4)	N3—Cr1—S11	104.57 (5)
Cr1—S11	2.3290 (4)	O1—Cr1—O11	85.22 (4)
O1—N1	1.3515 (12)	S1—Cr1—S11	90.870 (12)
Cr-out-of-plane	0.5724 (4) Å		

Table 2
Comparative geometric parameters (Å, °) for vanadyl complexes.

[V(O)(quinald)₂]^a			
V—O(oxo)	1.600 (8)		
V—O	1.921 (5)	O(oxo)—V—O	116.4 (7)
V—N	2.136 (6)	O(oxo)—V—N	99.5 (5)
[V(O)(tpno)₂]^b			
V—O(oxo)	1.593 (3)		
V—O$_{ave}$	1.956 (3)	O(oxo)—V—O$_{ave}$	108.5 (1)
V—S$_{ave}$	2.373 (2)	O(oxo)—V—S$_{ave}$	106.4 (1)

Notes: (*a*) Shiro & Fernando (1971); (*b*) Higes-Rolando *et al.* (1994).

All H atoms were identified in a difference Fourier map, but were placed in idealized positions (aromatic and methyl C—H = 0.95 and 0.98 Å, respectively). Their isotropic displacement parameters were constrained to $1.2U_{eq}$ of the carrier atom ($1.5U_{eq}$ for methyl groups). Disorder of the methyl group in (I) could be resolved in two well separated conformations with populations 0.633 (18) and 0.367 (18), respectively.

Data collection: *EVALCCD* (Duisenberg *et al.*, 2003) for (I); *COLLECT* (Nonius, 1999) for (II). For both compounds, cell refinement: *COLLECT* (Nonius, 1999); data reduction: *EVALCCD*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG1000). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Arshankow, S. I. & Poznjak, A. L. (1981). *Z. Anorg. Allg. Chem.* **481**, 201–206.
Bendix, J. (2003). *J. Am. Chem. Soc.* **125**, 13348–13349.
Bendix, J., Deeth, R. J., Weyhermüller, T., Bill, E. & Wieghardt, K. (2000). *Inorg. Chem.* **39**, 930–938.
Birk, T. & Bendix, J. (2003). *Inorg. Chem.* **42**, 7608–7615.
Coppens, P. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 255–270. Copenhagen: Munksgaard.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Scheurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
Higes-Rolando, F. J., Perez-Florindo, A., Valenzuela-Calahorro, C., Martin-Ramos, J. D. & Romero-Garzon, J. (1994). *Acta Cryst.* C**50**, 1049–1052.
Kang, B.-S., Xu, Y.-J., Peng, J.-H., Wu, D.-X., Chen, X.-T., Hu, Y.-H., Hong, M.-C. & Lu, J.-X. (1993). *Polyhedron*, **12**, 871–878.
Meyer, K., Bendix, J., Bill, E., Weyhermüller, T. & Wieghardt, K. (1998). *Inorg. Chem.* **37**, 5180–5188.
Meyer, K., Bendix, J., Metzler-Nolte, N., Weyhermüller, T. & Wieghardt, K. (1998). *J. Am. Chem. Soc.* **120**, 7260–7270.
Niemann, A., Bossek, U., Haselhorst, G., Wieghardt, K. & Nuber, B. (1996). *Inorg. Chem.* **35**, 906–915.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Nugent, W. A. & Mayer, J. M. (1988). *Metal–Ligand Multiple Bonds*. New York: John Wiley & Sons.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Shiro, M. & Fernando, Q. (1971). *Anal. Chem.* **43**, 1222–1230.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.