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A 17 Electron Chromium Complex Having Both Nitrosyl and Unidentate Nitrito Ligands. The Crystal and Molecular Structure of Dinitritonitrosyltripyridinechromium Monopyridine Solvate, $(ONO)_2(NO)(C_5H_5N)_3Cr \cdot C_5H_5N$ [1]

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Irradiation of a solution of $Cr(CO)_6$ *in tetrahydrofuran while purging simultaneously with a stream of nitric oxide gas produces a deep red solution within five minutes. The red solid isolated from the reaction solution eluded purification by standard methods. This solid was dissolved in pyridine and heated to 70 °C. The initial red solution changed to a deep green color from which a green solid was isolated. Extraction of this solid with methylene chloride gave a green solution from which a small amount of a green, solid residue was isolated. This residue crystallized from pyridine solution predominantly as very thin green platelets and several larger red crystals of the title compound, which was identified and characterized structurally by X-ray crystallography. Space group Pnna; Z = 4; unit cell dimensions:* a = *19.148(4) Å,* b = *10.101(2) Å,* c = *12.345(3) Å and V = 2388(1) Å*^{3}*. The molecule is a six-coordinate complex of symmetry* C_2 *having three pyridine ligands in a* meridional *arrangement, with nitrito ligands* trans *to each other and bonded to the Cr atom through only one oxygen atom. The linear nitrosyl ligand is* trans *to one of the pyridine ligands. A crystallographic two-fold axis of rotation passes through the nitrosyl ligand, the Cr atom and the pyridine ligand* trans *to the nitrosyl ligand. The pyridine solvate molecule lies on another crystallographic two-fold axis and appears to be disordered so that the nitrogen atom is scrambled randomly over all six ring atom positions. This is only the second structurally characterized complex with a unidentate, nitrito ligand. It is also of interest as a 17 electron Cr nitrosyl complex, isoelectronic with the* $[Cr(CN)_5NO]^{3-}$ *ion, with which comparison can be made.*

Introduction

The nitrite ion, ONO^-, is a structurally versatile ligand [4]. Probably its best known function is as the unidentate nitro group, in which it is bonded to the metal atom through the nitrogen atom and retains its local C_{2v} symmetry. This arrangement is extremely common and has been documented repeatedly by X-ray crystallography. Two accurately-determined and representative structures are those of $[Co(NH_3)_5NO_2]Br_2$ [5] and $K_2Pb[Cu(NO_2)_6]$ [6]. X-ray crystallographic evidence for other modes of binding of the NO_2^- ion to metal atoms is less voluminous. However, direct evidence demonstrating other modes of coordination has been obtained for: (1) the chelating nitrito ligand as found in $K_3[Hg(NO_2)_4]NO_3$ [7] and $[Cu(NO_2)(bipy)_2]NO_3$ [8], (2) the bridging system, M–N(O)–O–M, as in $[Ni(en)_2NO_2]BF_4$ [9], $[Co(NO)_2(NO_2)]_n$ [10], $[(NH_3)_3Co(\mu\text{-}OH)(\mu\text{-}NO_2)_2Co(NH_3)_3[Cl_3 \cdot H_2O$ [11] and $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}NO_2)Co(NH_3)_4]Cl_4 \cdot 4H_2O$ [12]; (3) the oxygen atom bridging system, M–O(NO)–M, as found in $Co_4(NO)_8(NO_2)_2(N_2O_2)$ [13] and in $[Ni(\beta\text{-picoline})_2(NO_2)_2]_3 \cdot C_6H_6$ [14].

Although complexes having unidentate nitrito ligands are well established on the basis of spectroscopic data, only one X-ray crystallographic structural determination of a complex of this type has been reported, and that in only preliminary form [15]. This lack of structural information may be due to the fact that the nitro isomer is frequently the thermodynamically more stable one and the nitrito isomers are capable of isomerizing to the nitro isomers even in the solid state. Among the best known nitrito complexes are those of the type, $[M(NH_3)_5(ONO)]Cl_2$, where M = Cr(III), Co(III), Rh(III) and Ir(III) [16].

The molecular structure reported here provides the most detailed structural information on an unidentate nitrito ligand. Also, this complex is of interest because of its electronic structure.

Experimental

All reactions and other manipulations were performed under dry, prepurified nitrogen at room temperature unless stated otherwise. Infrared spectra were recorded on a Perkin–Elmer 467 spectrometer and were calibrated with a polystyrene film. Microanalyses were by Midwest Microlab, Ltd., Indianapolis, Indiana.

TABLE I. Atomic Positional and Anisotropic Thermal Parameters for Non-Hydrogen Atoms.[a]

Atom	x	y	z	β_{11} or B_{iso} (Å)^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	–0.0742(1)	1/4	1/4	0.0029(1)	0.0096(3)	0.0079(2)	0	0	–0.0016(3)
O(1)	0.0734(6)	1/4	1/4	0.003(1)	0.015(1)	0.023(2)	0	0	–0.007(1)
O(2)	0.9607(6)	–0.0914(10)	0.3762(9)	0.008(1)	0.021(2)	0.019(1)	0.001(1)	–0.006(1)	–0.000(1)
O(3)	0.9125(4)	0.0793(6)	0.3232(6)	0.004(1)	0.009(1)	0.011(1)	0.002(1)	–0.001(1)	0.001(1)
N(1)	0.0133(6)	1/4	1/4	0.002(1)	0.011(1)	0.012(1)	0	0	–0.004(1)
N(2)	–0.1876(5)	1/4	1/4	0.003(1)	0.008(1)	0.009(1)	0	0	–0.002(1)
N(3)	–0.0826(4)	0.1535(8)	0.1002(7)	0.003(1)	0.010(1)	0.009(1)	–0.000(1)	–0.000(1)	–0.001(1)
N(4)	–0.0290(8)	0.0086(11)	0.3378(9)	0.011(1)	0.009(1)	0.012(1)	–0.001(1)	–0.003(1)	0.002(1)
C(1)	–0.0468(6)	0.1974(10)	0.0140(11)	0.004(1)	0.010(1)	0.011(1)	0.000(1)	0.001(1)	–0.001(1)
C(2)	–0.0498(7)	0.1375(12)	–0.0854(10)	0.005(1)	0.013(2)	0.009(1)	0.001(1)	0.002(1)	–0.002(1)
C(3)	–0.0923(9)	0.0272(13)	–0.0970(11)	0.009(1)	0.013(2)	0.009(1)	0.003(1)	–0.001(1)	–0.003(1)
C(4)	–0.1287(8)	–0.0190(12)	–0.0094(13)	0.007(1)	0.014(2)	0.012(1)	–0.002(1)	0.000(1)	–0.003(1)
C(5)	–0.1222(5)	0.0462(10)	0.0874(9)	0.003(1)	0.010(1)	0.009(1)	0.000(1)	0.000(1)	–0.002(1)
C(6)	0.7752(6)	0.1911(10)	0.3275(9)	0.003(1)	0.011(1)	0.009(1)	0.000(1)	0.001(1)	0.001(1)
C(7)	0.7059(6)	0.1884(10)	0.3312(10)	0.004(1)	0.012(1)	0.011(1)	–0.001(1)	0.002(1)	0.002(1)
C(8)	0.6675(8)	1/4	1/4	0.004(1)	0.011(2)	0.014(2)	0	0	–0.001(2)
N(20)	–0.323(1)	0.485(3)	–0.122(2)	15.3(6)					
N(21)	–0.275(2)	0.390(4)	–0.122(3)	17.9(7)					
N(22)	–0.205(1)	0.395(3)	–0.122(2)	16.2(6)					

[a] Numbers in parentheses are estimated standard deviations in the least significant digits in this and all other tables. The anisotropic temperature parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Preparation of $(ONO)_2(NO)(C_5H_5N)_3Cr(II) \cdot C_5H_5N$

A suspension of 5.0 g (23 mmol) of $Cr(CO)_6$ in 200 ml of freshly distilled tetrahydrofuran was treated with a slow stream (50–60 ml per min) of nitric oxide gas (Matheson, 99% minimum purity) which had been passed through a short trap (10 cm long) held at –78 °C prior to entering the reaction vessel. The nitric oxide was introduced into the reaction solution through a gas-dispersion frit and the unreacted gas exited through a Nujol bubbler. Stirring this solution for several minutes during the nitric oxide purge gave no evidence of reaction. However, irradiation of the reaction solution using a Hanovia Utility UV Quartz Lamp (140 watts) which was placed 7 cm from the reaction flask initiated a reaction and the reaction solution changed to a deep red color after ten min of irradiation. After 28 hr of irradiation with continuous bubbling of nitric oxide, the deep red solution was maintained at –15 °C for 12 hr. The cold solution was filtered to remove unreacted and undissolved $Cr(CO)_6$ and the solvent was stripped under reduced pressure (20 mm, 25 °C). Remaining $Cr(CO)_6$ was removed from the crude red solid by sublimation (0.1 mm, 25 °C), affording 1.25 g of product as a maroon solid. This crude solid could not be purified by normal crystallization or column chromatographic procedures. It was soluble only in polar, donor solvents and it decomposed slowly upon heating between 150°–300 °C. The ir spectrum of a tetrahydrofuran solution of the crude red solid in the 2200–1300 cm^{-1} range showed three bands at 1845 (m), 1720 (s) and 1485 (w) (sh 1455). The ir spectrum of a Fluorolube mull indicated a trace amount of tetrahydrofuran in the solid. The crude solid was dissolved in pyridine to give a red solution which was then heated at 70 °C for 18 hr. During this time the color of the solution changed to a deep green. The reaction solution was filtered and the solvent removed under reduced pressure (20 mm, 70 °C). The crude deep green solid which was isolated was placed in a Soxlet extractor and extracted with methylene chloride. A small amount of a lime colored solid residue was obtained from the extractant after removal of the solvent at reduced pressure (20 mm, 25 °C). This solid residue was dissolved in pyridine and crystallization was induced by a vapor diffusion of trichloroethylene into the pyridine solution at –15 °C affording a mass of very thin lemon colored platelets and about 10 deep red needle-shaped crystals of the title compound which were of suitable size and shape for X-ray crystallography.

Collection of X-ray Data

A red needle crystal measuring approximately 0.27 X 0.21 X 0.15 mm was selected for data collection and was mounted in a glass capillary to protect it from possible air oxidation. Preliminary examina-

TABLE II. Root-mean-square Amplitudes of Thermal Vibration (Å).

Atom	Min	Intermed	Max
Cr	0.208(4)	0.232(3)	0.256(4)
O(1)	0.24(2)	0.24(2)	0.44(2)
O(2)	0.28(1)	0.33(1)	0.46(1)
O(3)	0.18(1)	0.26(1)	0.30(1)
N(1)	0.20(2)	0.22(2)	0.33(2)
N(2)	0.19(2)	0.23(2)	0.28(2)
N(3)	0.22(1)	0.25(1)	0.26(1)
N(4)	0.21(2)	0.30(1)	0.46(2)
C(1)	0.23(2)	0.26(2)	0.31(2)
C(2)	0.22(2)	0.29(2)	0.33(2)
C(3)	0.21(2)	0.28(2)	0.42(2)
C(4)	0.23(2)	0.32(2)	0.36(2)
C(5)	0.21(2)	0.25(2)	0.28(2)
C(6)	0.22(2)	0.23(1)	0.28(1)
C(7)	0.20(2)	0.26(2)	0.32(2)
C(8)	0.24(2)	0.27(2)	0.33(3)

tion on the diffractometer showed orthorhombic symmetry. The systematic absences uniquely defined the space group as Pnna (D_{2h}^6, No. 52). Cell constants at 16 ± 2° obtained from a least-squares refinement of the setting angles for fiteen reflections are: a = 19.148(4), b = 10.101(2), c = 12.345(3) Å. For V = 2388(1) Å^3, mol.wt. = 490.41, and assuming 4 molecules per unit cell, the calculated density is 1.36 cm^{-3}.

The data were collected using a Syntex P$\bar{1}$ diffractometer and Mo Kα radiation. The incident beam was monochromatized with a graphite crystal. The operation of the diffractometer has been described previously [17]. Intensity measurements were made at 22° using the θ–2θ scan technique and a scan rate that varied from 2.0 to 24.0°/min depending on the intensity of the reflection. Unique data with 2θ up to 45° were collected with a scan range from 2θ(Mo Kα_1) – 0.8° to 2θ(Mo Kα_2) + 0.8°. Three standard reflections, measured every 100 reflections, showed no significant change in intensity throughout the data collection. The linear absorption coefficient of the compound for Mo Kα radiation is 6.14 cm^{-1}. No absorption correction was applied to the data since the entire range of the percentage transmission was only 85–91%. Lorentz and polarization corrections were made [18]; no extinction correction was deemed necessary. Of the 1830 reflections collected, only the 722 reflections having $F_0^2 > 3\sigma(F_0^2)$ were used in the refinement of the structure. The parameter p used in the calculation of standard deviations was set equal to 0.06 [17].

Solution and Refinement of the Structure [18]

The chromium atom located on the crystallographic two-fold axis was located using a Patterson function. Two cycles of least-squares refinement of its coordinates gave the following agreement factors: $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.42$ and $R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2} = 0.51$, where $|F_0|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and w is the weighting factor given by, $4|F_0|^2/\sigma^2$. Here, σ is the e.s.d. of $|F_0|^2$. Scattering factors were taken from the International Tables [19]. Anomalous dispersion effects were included in calculated structure factors for chromium, using $\Delta f'$ and $\Delta f''$ values given by Cromer and Liberman [20].

A difference Fourier map then revealed the positions of some of the carbon, oxygen and nitrogen atoms. Successive steps of least-squares refinement followed by examination of difference Fourier maps provided the positions of most of the remaining non-hydrogen atoms. Two cycles of isotropic least-squares refinement of the coordinates of 15 of the 19 non-hydrogen atoms lead to agreement indices of R_1 = 0.21 and R_2 = 0.27. During this refinement the nitrosyl ligand and the nitrogen atom and the terminal carbon atom of the pyridine molecule *trans* to the nitrosyl ligand were found to lie on the crystallographic two-fold axis at y = 1/4, z = 1/4.

A difference Fourier map revealed the remaining non-hydrogen atoms. The pyridine molecule of crystallization was located about a second crystallographic two-fold axis. This two-fold axis coincided with the pseudo-six-fold axis of the pyridine molecule.

Several refinement procedures were employed in an attempt to obtain a converged set of positional coordinates for the atoms of the pyridine molecule of crystallization. The best refinement was obtained by locating the positions of the atoms of the ring, which were consistent with a planar, hexagonal ring, directly from the difference Fourier map. These six atoms were weighted as 37/42 of a nitrogen atom, corresponding to a random distribution of the nitrogen and carbon atoms, and then refined isotropically while keeping the other positional coordinates fixed. The positions of the 11 hydrogen atoms were calculated and refinement was resumed with these hydrogen atom positions held fixed with an isotropic temperature parameter of 5.0 Å^2 [21]. Two cycles of anisotropic refinement for the non-hydrogen atoms of the complex and isotropic temperature parameters for the atoms of the pyridine molecule of crystallization converged with no parameter shift exceeding 0.01 times the standard deviation in the parameter, giving final agreement indices of R_1 = 0.059 and R_2 = 0.079. The e.s.d. in an observation of unit weight was 1.77. A table of observed and calculated structure factors is available from the authors on request.

No systematic trends were found in the data as a function of $\lambda^{-1}\sin\theta$, $|F_0|$, Miller indices or reflec-

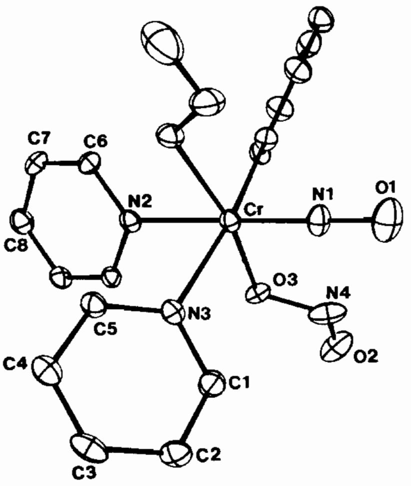

Figure 1. An ORTEP view of $(ONO)_2(NO)(C_5H_5N)_3Cr \cdot C_5H_5N$ showing the atomic numbering scheme. The sizes and shapes of the atoms are determined by their final temperature parameters and their perspective view.

tion number. A final difference Fourier function contained no peaks greater than 0.3 $Å^{-3}$. The atomic coordinates, anisotropic thermal parameters and estimated standard deviations for non-hydrogen atoms are given in Table I. Root-mean-square amplitudes of thermal vibration are given in Table II.

Results

The molecular structure is shown in Figure 1. Tables III and IV list the bond lengths and bond angles, respectively, with their estimated standard deviations. Table V gives the equations for best (least-squares) planes through several sets of atoms, the deviations of individual atoms from these planes and the dihedral angles between pairs of planes. Planes I and III generate two symmetry-related planes by operation of the two-fold axis which passes through the molecule. The dihedral angles between these symmetry-related pairs of planes are 100.9° and 15.9°, respectively. The crystal symmetry also requires that the following two sets of atoms be coplanar; Cr–N(1)–N(2)–N(3)–N(3)′, plane V, and Cr–N(1)–N(2)–O(3)–O(3)′, plane VI. The dihedral angles between plane V and planes I, II and IV are 50.6°, 120.3° and 86.9°, respectively. The dihedral angles between plane VI and planes I, II, IV and V are 93.0°, 30.5°, 2.9° and 89.9°, respectively.

The structure consists of discrete molecules with no abnormal intermolecular contacts. The three pyridine molecules are coordinated to the chromium atom in a *meridional* arrangement. The linear nitrosyl ligand is *trans* to one of the pyridine ligands while the two nitrito ligands are *trans* to each other and *cis* to the nitrosyl ligand. The nitrito groups are bonded to the chromium atom as unidentate, oxygen ligands thus making the stereochemistry of the complex pseudo-octahedral.

TABLE III. Bond Lengths (Å).

Cr–O(3)	1.96(1)
Cr–N(1)	1.68(1)
Cr–N(2)	2.17(1)
Cr–N(3)	2.10(1)
O(1)–N(1)	1.15(1)
O(2)–N(4)	1.13(1)
O(3)–N(4)	1.34(1)
N(2)–C(6)	1.33(1)
N(3)–C(1)	1.34(1)
N(3)–C(5)	1.33(1)
C(1)–C(2)	1.37(1)
C(2)–C(3)	1.39(2)
C(3)–C(4)	1.37(2)
C(4)–C(5)	1.37(1)
C(6)–C(7)	1.33(1)
C(7)–C(8)	1.39(1)
Within the pyridine molecule of crystallization	
N(20)–N(21)	1.33
N(20)–N(22)	1.33
N(21)–N(22)	1.34

Discussion

It is obvious that the chemistry leading to the formation of the title compound is not understood. The origin of the nitrito ligands is not known, although it is possible that nitrogen dioxide was introduced into the reaction solution as an impurity in the nitric oxide gas since only a moderately efficient cold trap was used [22, 23].

Although the preparation of the title compound was reproducible, the exceedingly low yield and the highly contaminated nature of the product prevented the satisfactory recording of its infrared spectrum. However, the infrared spectra of methylene chloride solutions of mixtures containing both the final red product and the green compound showed a band at 1708 cm^{-1}. The intensity of this band seemed to be proportional to the quantity of the title complex present and is assumed to be the N–O stretching vibration of the linear nitrosyl ligand.

Unfortunately, we are not now in a position to study this chemistry further, and we are therefore terminating our investigation with this report. The identity and structure of the title compound, which will now be discussed in detail, constitute the main positive results.

TABLE IV. Selected Bond Angles (deg.)[a].

O(3)–Cr–O(3)′	165.1(4)	O(2)–N(4)–O(3)	112(1)
O(3)–Cr–N(1)	97.5(2)	C(6)–N(2)–C(6)′	115(1)
O(3)–Cr–N(2)	82 5(2)	C(1)–N(3)–C(5)	118(1)
O(3)–Cr–N(3)	89.3(3)	N(2)–C(6)–C(7)	124(1)
N(1)–Cr–N(3)	94.4(2)	N(3)–C(1)–C(2)	123(1)
N(1)–Cr–N(2)	180.0(0)	N(3)–C(5)–C(4)	123(1)
N(2)–Cr–N(3)	85.6(2)	C(1)–C(2)–C(3)	118(1)
N(3)–Cr–N(3)′	171.2(5)	C(2)–C(3)–C(4)	119(1)
Cr–O(3)–N(4)	115.0(7)	C(3)–C(4)–C(5)	119(1)
Cr–N(1)–O(1)	180.0(0)	C(6)–C(7)–C(8)	120(1)
Cr–N(2)–C(6)	122.3(6)	C(7)–C(8)–C(7)′	116(1)
Cr–N(3)–C(1)	120.5(8)		
Cr–N(3)–C(5)	121.7(8)		
N(21)–N(20)–N(22)″	112		
N(20)–N(21)–N(22)	132		
N(21)–N(22)–N(20)″	116		

[a] The singly primed atoms are generated by the symmetry operation; x, 1/2 – y, 1/2 – z, while the doubly primed atoms are generated by the symmetry operation; 1/2 – x, $\bar{y}$, z in this and all following tables.

The Structure of Cr(ONO)$_2$NOpy$_3$

The geometry of the nitrito ligands, which are crystallographically equivalent, in the chromium complex reported here is similar to that found in the nickel complex, Ni(Me$_2$NCH$_2$CH$_2$NMe$_2$)$_2$(ONO)$_2$ [15], and in methyl nitrite [24]. A comparison of the most relevant geometrical parameters of the nitrito groups in these three molecules is shown in Table VI.

TABLE VI. Dimensions for Several X–O–N–O Compounds.

X–O–N–O	∠XON	∠ONO	d(XO–NO)	d(XON–O)
CH$_3$ONO	109.5[b]	109.5[b]	1.37(2)	1.22(2)
NiL$_2$[a](ONO)$_2$	119.5(8)	115(1)	1.29(2)	1.21(2)
Cr(NO)py$_3$-(ONO)$_2$	115.0(7)	112(1)	1.34(1)	1.13(1)

[a] L = Me$_2$NCH$_2$CH$_2$NMe$_2$. [b] assumed.

The most unique feature of the nitrito ligand in the chromium complex is the very short terminal N(4)–O(2) bond distance of 1.13(1) Å. This bond distance is interpreted best as an N–O bond order of 2.5 as found in gaseous nitric oxide where the equilibrium N–O bond distance is 1.150 Å [25]. In fact, the value of the N(1)–O(1) bond distance of 1.15 Å observed in the nitrosyl ligand of this chromium complex is not significantly different from the terminal N–O distances of the nitrito ligands. This similarity of N–O bond distances adds considerable uncertainty in assigning the infrared band at 1708 cm^{-1} to the nitrosyl ligand stretching vibration. The N–O stretching vibration of *trans*-methyl nitrite occurs at 1678 cm^{-1} [26].

The nitrito ligands and the chromium atom are nearly coplanar, plane IV, with the nitrogen atoms having the maximum deviation from planarity of 0.035 Å. The nitrosyl ligand and atom N(2) lie exactly in this plane, also. The terminal oxygen atoms of the nitrito ligands are in an "*anti*"

TABLE V. Least-Squares Planes and Dihedral Angles.

Plane	Atoms Defining Plane	Equation of Mean Plane[a]
I	N(3)–C(1)–C(2)–C(3)–C(4)–C(5)	14.767x – 5.922y + 3.063z = –1.8165
II	N(2)–C(6)–C(7)–C(8)–C(7)′–C(6)′	–x + 8.578y + 6.519z = 3.7741
III	Cr–O(3)–N(4)–O(2)	2.645x + 4.363y + 11.002z = 3.6575
IV	Cr–O(3)–N(4)–O(2)–O(3)′–N(4)′–O(2)′	4.224y + 11.214z = 3.8594

Displacement of Atoms from Mean Plane (Å)

Plane I		Plane II		Plane III		Plane IV	
N(3)	–0.005	N(2)	0.000	Cr	–0.012	Cr	0.000
C(1)	–0.001	C(6)	–0.001	O(3)	0.013	O(3)	0.010
C(2)	0.006	C(7)	0.001	N(4)	0.020	N(4)	–0.035
C(3)	–0.005	C(8)	0.000	O(2)	–0.021	O(2)	–0.027
C(4)	–0.001	C(7)′	–0.001			O(3)′	–0.010
C(5)	0.006	C(6)′	0.001			N(4)′	0.035
						O(2)′	0.027

Dihedral Angles between Planes (deg.)

Planes		Planes	
I–II	111.5	II–IV	33.4
I–IV	91 1	III–IV	8.0

[a] Equations have the form Ax + By + Cz = D where x, y, and z are fractional orthorhombic coordinates.

configuration with respect to the chromium atom about the O(3)–N(4) and O(3)′–N(4)′ bonds [15].

The three pyridine ligands have geometries not significantly different from that of free pyridine [27]. The least-squares plane calculated from the positions of the atoms of the N(2)-pyridine ring, plane II, passes directly through the chromium atom and the nitrosyl ligand. This plane intersects the line defined by atoms N(3) and O(3) at a point closer to atom O(3) than to N(3) with a dihedral angle between planes II and IV of 33.4°. The atoms of the N(3) and N(3)′-pyridine rings are practically coplanar, plane I, with the chromium lying 0.007 Å above this plane. Plane I passes between atoms O(3) and N(1), but lies closer to atom O(3). The dihedral angle between planes I and IV is 50.6°.

The Cr–N(2) bond distance of 2.17(1) Å is significantly larger than the Cr–N(3) and Cr–N(3)′ bond distances of 2.096(8) Å. This lengthening may arise from the *trans* effect of the nitrosyl ligand, although the magnitude of this lengthening is slightly larger than would be expected for a linear nitrosyl ligand [28].

The nitrosyl ligand coordinates to the chromium atom in a strictly linear fashion as required by the crystallographically imposed symmetry. The Cr–N(1) bond distance of 1.68(1) Å is not significantly different from the Cr(II)–nitrosyl bond distance of 1.71(1) Å found in the two complexes; $Cr(CN)_5$-$(NO)^{-3}$ [29] and $CrCl(NO)_2(h^5\text{-}C_5H_5)$ [30]. These latter two complexes have Cr–N–O bond angles of 176(1)° and 169(3)°, and N–O bond distances of 1.21(1) Å and 1.14(2) Å, respectively. The N(1)–O(1) bond distance of 1.15(1) Å in the title compound is nearly identical to the value found in a large number of linearly coordinated nitrosyl ligands [28].

The randomly disordered pyridine molecule of crystallization is a planar molecule having a mean C–C bond distance of 1.33 Å and a mean intra-ring bond angle of 120°.

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