his suggestion of an alternative solution to the Patterson map which eventually resulted in the solution of the structure of the trimer and to B. C. Lucas for preliminary work in the area. We also express our appreciation to Professor Arthur Clouse, Indiana University, for supplying the ^{31}P NMR spectrum.

Registry No. $Pt_3(SO_2)_3(PPh_3)_3 \cdot C_7H_8 \cdot SO_2$, 61967-09-7; I, 16009-23-7; $Pt(SO_4)(PPh_3)_2$, 12577-89-8; $Pt(SO_2)_2(PPh_3)_2$, 59187-63-2; $Pt(SO_2)(PPh_3)_3$, 15227-19-7; $Pt(CO)_2(PPh_3)_2$, 15377-00-1.

Supplementary Material Available: Listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and X-Ray Structure Determination of Chromium(I) Nitrosyl Complexes with Macrocyclic Ligands

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Chromium complexes of the macrocyclic ligands *trans*-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenate(2–) ($Me_2[14]tetraenateN_4$) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene ($Me_6[14]4,11\text{-}dieneN_4$) have been prepared. The nitrosyl adducts $Cr(Me_2[14]tetraenatoN_4)(NO)$ (I) and $[Cr(Me_6[14]4,11\text{-}dieneN_4)(NO_2)(NO)]PF_6$ (II) have been obtained by treating the Cr(III) and Cr(II) complexes of $Me_2[14]tetraenateN_4$ and $Me_6[14]4,11\text{-}dieneN_4$, respectively, with alcoholic sodium nitrite. Infrared, conductance, mass spectral, electron spin resonance, and magnetic data indicate that the nitrosyl derivatives I and II contain Cr(I) with a linear M–NO group. Electronic spectra are strongly influenced by the NO group. The crystal and molecular structure of II ($a = 14.844$ (2) Å, $b = 19.586$ (3) Å, $c = 10.213$ (1) Å, $\beta = 127.1$ (9)°, space group $C2/c$, $Z = 4$, $R = 0.061$) confirms the linear M–NO bond. The cation and anion lie on twofold axes. The NO and NO_2 ligands are mutually trans. The hexafluorophosphate is ordered but shows librational motion.

Introduction

Chromium complexes with macrocyclic ligands[1] containing nitrogen donors have received little attention despite the large amount of data compiled for chromium complexes with nitrogen-donor ligands in general. We have now prepared chromium complexes of the macrocyclic ligands *trans*-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene ($Me_2[14]tetraeneN_4$) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene ($Me_6[14]4,11\text{-}dieneN_4$). Stabilization of rare oxidation states[2] by macrocyclic ligands has recently been observed for a variety of transition metals and seemed a definite possibility for chromium. Thus, nitrosyl complexes of Cr(I) are produced when $[Cr(Me_2[14]tetraenatoN_4)(py)_2]PF_6$ or $[Cr(Me_6[14]4,11\text{-}dieneN_4)(py)](PF_6)_2$ reacts with alcoholic sodium nitrite although the starting complexes contain Cr(III) and Cr(II), respectively. Characterization of the nitrosyl complexes by the usual methods reveals that $Cr(Me_2[14]tetraenatoN_4)(NO)$ (I) is remarkably similar to the nitrosyl adducts of chromium porphyrin complexes[3] while $[Cr(Me_6[14]4,11\text{-}dieneN_4)(NO_2)(NO)]PF_6$ (II) is analogous to nitrosyl–amine complexes of chromium.[4] The crystal and molecular structure of II reveals that the nitrosyl ligand is bonded linearly to the chromium and that the macrocycle adopts the typical conformation.

Experimental Section

Physical Measurements. Spectra were obtained using Cary 14R (visible) and Perkin-Elmer 337 and 457 (infrared) spectrophotometers. Magnetic susceptibilities were measured by the Faraday method[5] and corrected using Pascal's constants.[6] Elemental analyses were performed by Galbraith and Schwarzkopf Laboratories. Conductance measurements were made with an Industrial Instruments Model RC 16B conductivity bridge. The mass spectrum was obtained with an AEI MS-9 spectrometer at an ionizing potential of 70 eV. ESR spectra were obtained using a Varian V4500-10A spectrometer with diphenylpicrylhydrazyl (DPPH) as a reference.

Syntheses. All manipulations involving chromium(II) salts and metal complexes were carried out in a Vacuum Atmospheres Dry Lab unless otherwise stated. Reagent grade chemicals were employed in syntheses and physical measurements. Solvents were dried and degassed in the usual manner. Chromium metal (99%, 140 mesh) was purchased from Alfa Inorganics, Beverly, Mass.

Tetraaquochromium(II) chloride, $CrCl_2 \cdot 4H_2O$, was prepared on the bench top under a blanket of nitrogen following the method of Lux and Illman.[7]

Bis(pyridine)chromium(II) chloride, $CrCl_2 \cdot 2py$, was prepared by a method similar to that of Holah and Fackler.[4b]

Tetrakis(pyridine)chromium(II) trifluoromethylsulfonate, $Cr(CF_3SO_3)_2 \cdot 4py$, was prepared by adding dropwise an excess of trifluoromethanesulfonic acid to a slurry of $Cr(OAc)_2$[7] (4.0 g, 11.1 mmol) in acetonitrile (50 mL). The blue solid, which precipitated after reducing the volume of the solution and adding ether, was dissolved in hot ethanol. Pyridine (20 mL) was added slowly. The blue crystalline product formed on cooling to room temperature. It was washed with ethanol and ether, dried under vacuum, and recrystallized from pyridine by addition of ethanol; yield (based on $Cr(OAc)_2$) 81%. Anal. Calcd for $Cr(CF_3SO_3)\cdot4py$: C, 39.65; H, 3.05; N, 8.42. Found: C, 39.37; H, 3.11; N, 8.31.

***trans*-Bis(pyridine)(5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)chromium(III) Hexafluorophosphate, [Cr-(Me_2[14]tetraenatoN_4)(py)$_2$]PF_6.** To a solvent mixture containing acetonitrile (50 mL) and pyridine (10 mL) were added H_2[Me_2-[14]tetraeneN_4](PF_6)$_2$^{8} (5.12 g, 0.01 mol) and $CrCl_2\cdot2py$ (2.81 g, 0.01 mol). Triethylamine (4.04 g, 0.04 mol) was added to the warm solution to aid dissolution. The solution was refluxed for $^1/_2$ h and cooled to room temperature. Filtration, concentrating to ca. 10 mL, and addition of ethanol (40 mL) resulted in the formation of green crystals. These were collected by filtration, washed with ethanol and ether, dried under vacuum, and recrystallized from pyridine by addition of ethanol. Yields ranged from 50 to 60% based on ligand salt.

(5,14-Dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)nitrosylchromium(I), Cr(Me_2[14]tetraenatoN_4)NO. To methanol (50 mL) were added [Cr(Me_2[14]tetraenatoN_4)(py)$_2$]PF_6 (2.0 g, 3.49 mmol) and sodium nitrite (0.5 g, 7.25 mmol). The mixture was refluxed for 1 h, the volume was reduced to dryness, and the resulting solid was extracted with hot benzene. Filtration followed by volume reduction to ca. 10 mL and addition of ethanol (50 mL) to the benzene solution resulted in a green solution which yielded a green solid upon concentrating. The complex was collected by filtration, washed with ethanol and ether, dried under vacuum, and recrystallized from a minimum amount of benzene by addition of ethanol; yield (based on the starting complex) 48%.

Pyridine(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)chromium(II) Hexafluorophosphate, [Cr-(Me_6[14]4,11-dieneN_4)(py)](PF_6)$_2$. To ethanol (50 mL) containing Me_6[14]4,11-diene$N_4\cdot2CF_3SO_3H$^{9} (5.8 g, 10 mmol) and Cr-$(CF_3SO_3)_2\cdot4py$ (6.7 g, 10 mmol) was added excess triethylamine causing the solution to turn brown. The solution was refluxed for a short time and then filtered while hot. NH_4PF_6 (5.0 g, 31 mmol) was added. The solution was again brought to reflux. The brown product which precipitated upon cooling was collected by filtration, washed with ethanol and ether, dried under vacuum, and recrystallized from pyridine by addition of ethanol; yield (based on ligand salt) 83%.

Nitro(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nitrosylchromium(I) Hexafluorophosphate, [Cr(Me_6-[14]4,11-dieneN_4)(NO_2)(NO)]PF_6. To a mixture of acetonitrile (35 mL) and ethanol (15 mL) were added [Cr(Me_6[14]4,11-dieneN_4)(py)](PF_6)$_2$ (1.0 g, 1.43 mmol) and sodium nitrite (0.25 g, 3.62 mmol). The mixture was stirred for 30 min at room temperature and then filtered. Concentrating to ca. 10 mL, addition of ethanol (30 mL), and further reduction in volume produced a green crystalline precipitate. The complex was collected by filtration, washed with ether and ethanol, dried under vacuum, and recrystallized from acetonitrile by addition of ethanol; yield (based on the starting complex) 43%.

Structure Determination and Refinement. Preliminary precession and Weissenberg photographs of a crystal of $CrC_{16}H_{32}N_6O_3PF_6$ (mol wt 553.4), II, showed systematic absences for $h + k$ = odd and $h0l$, l = odd, consistent with space groups Cc ($C_s{}^4$, No. 9) and $C2/c$ ($C_{2h}{}^6$, No. 15).

A platelike crystal (0.1 × 0.1 × 0.05 mm) of II was mounted perpendicular to the short dimension on a Syntex $P\bar{1}$ diffractometer. An orientation matrix and cell constants (a = 14.844 (2), b = 19.586 (3), c = 10.213 (1) Å; β = 127.1 (9)°) were calculated by a least-squares fit of 2θ, ω, ϕ, and χ values for 15 centered reflections. The calculated density (1.55 g/cm^3) for four molecules in a cell of 2368.2 Å^3 agreed well with that observed (1.53 g/cm^3) by flotation.

Intensity measurements were made using a variable-speed θ–2θ scan technique. All unique reflections up to a limiting 2θ of 50° were measured. The scan rate was determined from a 2-s intensity measurement of the reflection and varied linearly from 2°/min (<150 counts) to 24°/min (>1500 counts). The intensity, I, was equal to

$$I = (\text{scan rate})(\text{total scan counts} - \text{background counts})$$

Peaks were scanned from 1° below Kα_1 to 1° above Kα_2. Background counts were taken at each end of the range. The estimated standard deviation, $\sigma(I)$, of each reflection is given by

$$\sigma(I) = [\text{total scan counts} + (\text{background counts})^2 + (0.02)^2 I^2]^{1/2}$$

The incident Mo radiation was monochromatized by a low-order reflection (111) of graphite. Four standard reflections were measured after each 96 intensity measurements and showed only minor variations during data collection.

A standardized data set was obtained by scaling the data to the initial value of the sum of the standard reflections. Any duplicate reflections were averaged. Reflections with intensity greater than $3\sigma(I)$ were considered to be observed. Of the 2192 reflections measured, 1853 were considered to have been observed.

Corrections for Lorentz–polarization were of the form $1/Lp = (\sin 2\theta)/(1 + \cos^2 2\theta)$. Scattering factors were from ref 10a for C, N, O, F, and P, from ref 10b for Cr, and from ref 11 for H and are uncorrected for anomalous dispersion. Due to the small crystal size and atomic absorption coefficient (6.55 cm^{-1}), absorption effects were deemed negligible. The natural log of the scale factor and overall temperature factor were estimated from a Wilson plot. Intensity statistics indicated the space group was centric.

The chromium atom position was calculated from a Patterson function. Fourier syntheses in space groups Cc and $C2/c$ phased on the Cr suggested that the centric choice was correct since a peak assignable to the phosphorus could not be found in the acentric map. The successful structure determination carried out in space group $C2/c$ confirmed that choice. Thus, Cr and P are required to lie on twofold axes. Fourier syntheses phased on the Cr, P, and subsequently located atoms revealed the entire macrocyclic complex cation. The fluorine atoms were located in a Fourier synthesis map phased on the cation and phosphorus. R was 0.375 at this point.

Least-squares refinement cycles (4) using individual isotropic thermal parameters reduced R to 0.179. The function minimized was $w^2(k^2|F_o|^2 - |F_c|^2)^2$, where w, the weight, is $\sum_i^N[\sigma(I)_i{}^2(F_o{}^2)_i]^{-1}$, N is the number of measurements of F_o, and k is the scale factor. Conversion to anisotropic thermal parameters followed by least-squares cycles (3) reduced R to 0.099. A difference Fourier synthesis revealed the positions of all 16 hydrogen atoms and indicated that the NO group was indeed linear and not disordered about the twofold axis. The hydrogens were assigned thermal parameters one unit larger than the refined isotropic parameter for the atom to which they were bonded. Least-squares cycles (2) holding the hydrogen parameters constant reduced R to 0.061 and R_w to 0.126. Refinement was terminated since all parameter shifts were less than two estimated standard deviations of the respective parameter. A difference Fourier synthesis calculated at this point showed no peaks assignable to additional atoms or indicative of disordering about the twofold axis. The final data to parameter ratio was 12.2.

Results and Discussion

Synthesis and Characterization of Cr(Me_2[14]-tetraenatoN_4)NO, I, and [Cr(Me_6[14]4,11-dieneN_4)(NO_2)-(NO)]PF_6, II. These complexes were prepared in essentially the same manner (eq 1 and 2). The starting complex [Cr-(Me_2[14]tetraenatoN_4)(py)$_2$]PF_6 was prepared by reaction of $CrCl_2\cdot2py$ and the hexafluorophosphate salt of Me_2[14]-tetraeneN_4 in an acetonitrile–pyridine (5:1) mixture. [Cr-(Me_6[14]4,11-dieneN_4)(py)](PF_6)$_2$ was prepared by reaction of $Cr(CF_3SO_3)_2\cdot4py$ and the trifluoromethylsulfonate salt of Me_6[14]4,11-dieneN_4 in ethanol. A large excess of sodium nitrite was added to the alcoholic solution of the starting complex. Since neither the starting complexes nor the sodium nitrite are very soluble in the alcoholic medium, the solutions were refluxed for a period of time. The neutral complex, I, was extracted with benzene from the residue which remained after evaporating solvent. The cationic complex, II, was isolated as a hexafluorophosphate salt. Satisfactory elemental analyses (Table I) were obtained on recrystallized samples. The same reaction procedure, when used with [Cr(Me_2-[15]tetraenatoN_4)(py)$_2$]PF_6, yielded only the starting complex. It is interesting to note that the neutral complex was prepared from a chromium(III) complex while the cationic complex was prepared from a chromium(II) complex. Wayland et al.^{12}

Table I. Analytical Data for the Chromium(I) Nitrosyl Complexes

	% calcd			% found		
Complex	C	H	N	C	H	N
$Cr(Me_2[14]tetraenatoN_4)(NO)$	47.99	6.04	23.32	47.74	6.01	23.38
$[Cr(Me_6[14]4,11\text{-}dieneN_4)(NO_2)(NO)]PF_6$	34.75	5.83	15.19	34.94	5.87	15.28

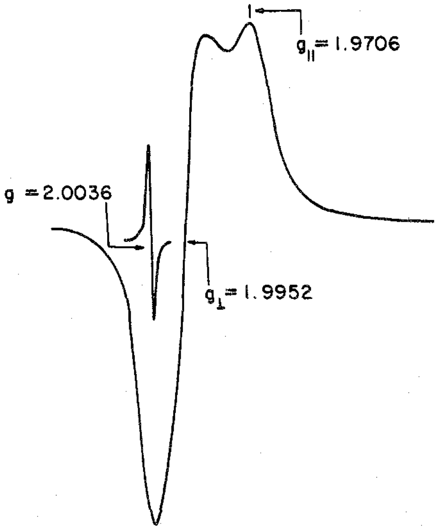
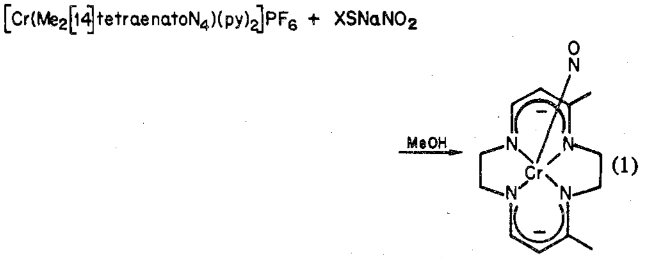
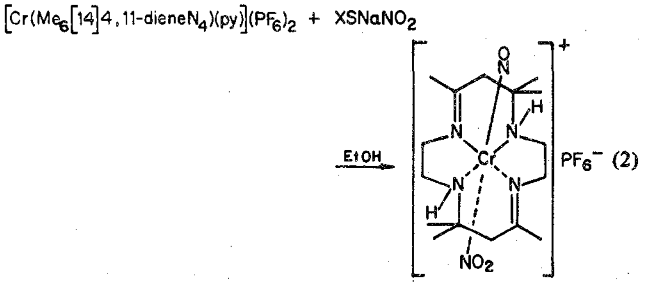


Figure 1. ESR spectrum of $Cr(Me_2[14]tetraenatoN_4)(NO)$.



(1)



(2)

reported the preparation of Cr(TPP)(NO) (TPP = tetraphenylporphyrin) from both $Cr^{II}TPP$ and $Cr^{III}TPP(OMe)$. The preparation of a Cr^I–NO species from a Cr(II) complex can be viewed as simply the transfer of the NO π^* electron to the metal. Using a Cr(III) complex, however, requires a more complicated reaction, whose exact nature has not been determined.

The infrared spectra of the Cr^I–NO complexes indicate the presence of nitrosyl groups, the macrocyclic ligands, and hexafluorophosphate for the cationic complex. The nitrosyl absorptions occur at 1620 and 1640 cm^{-1} for I and II, respectively, indicative of NO^+.[13a] Conductivity data in Table II demonstrate the neutrality of I and the ionic nature of II.[13b] The mass spectrum of the neutral complex gave a parent ion at *m/e* 300, which corresponds to the calculated molecular weight of the complex.

The ESR spectra and magnetic moments of these complexes confirm the monopositive oxidation state of the chromium ion. The magnetic moments of these Cr^I–NO complexes in the solid state (Table II) indicate the presence of one unpaired electron.

Table II. Physical Properties of the Chromium(I) Nitrosyl Complexes

Complex	Color	μ_{eff}, μ_B	Λ,[a] cm^2 Ω^{-1} mol^{-1}
$Cr(Me_2[14]tetraenatoN_4)(NO)$	Green	1.81	<1
$[Cr(Me_6[14]4,11\text{-}dieneN_4)(NO_2)(NO)]PF_6$	Green	1.72	87

[a] Determined using 10^{-3} M CH_3NO_2 solutions at room temperature.

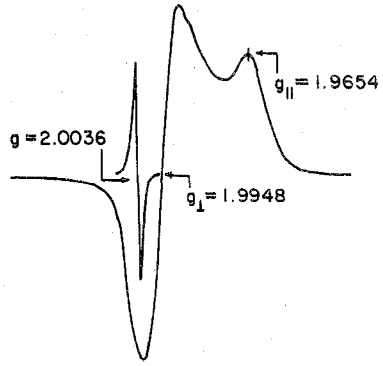


Figure 2. ESR spectrum of $[Cr(Me_6[14]4,11\text{-}dieneN_4)(NO_2)(NO)]PF_6$.

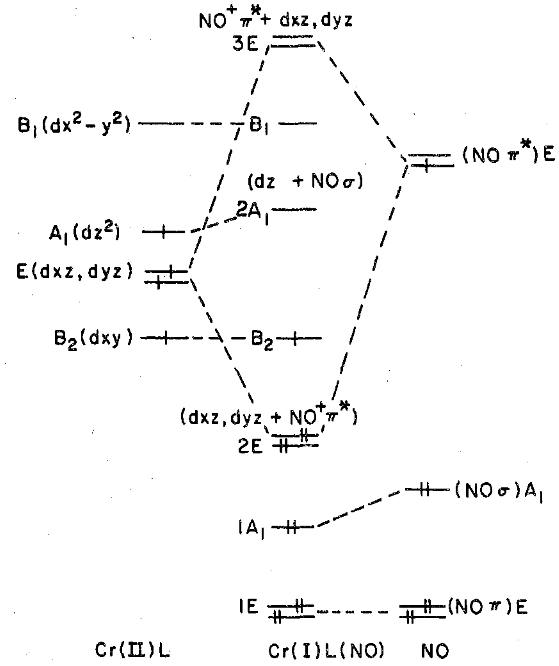


Figure 3. Schematic molecular orbital diagram for the chromium(I) nitrosyl complexes.

Therefore, the d^5 Cr(I) ion must be low spin. The frozen-solution ESR spectra of both complexes (Figures 1 and 2) show axial symmetry with $g_\perp > g_\parallel$. No ^{53}Cr hyperfine or ^{14}N superhyperfine splitting is observed at either liquid nitrogen or room temperature. The low temperature ESR spectra of these complexes are closely similar to the spectra reported for other Cr^I–NO complexes.[12,14] Hyperfine or superhyperfine

Table III. Electronic Spectral Data of the Chromium(I) Nitrosyl Complexes

Complex	$\lambda_{\max}$, μm^{-1} (ϵ)
Cr(Me$_2$[14]tetraenatoN$_4$)(NO)[a]	1.53 (1330), 2.22 sh (2100), 2.60 (7100), 3.26 (16 000)
[Cr(Me$_6$[14]4,11-dieneN$_4$)(NO$_2$)(NO)]PF$_6$[b]	1.54 (45), 2.22 (99), 2.77 (340)

[a] THF solvent. [b] CH$_3$CN solvent.

splitting was usually observed in the room-temperature solution spectra for other complexes.

A schematic MO diagram for the Cr^{I}–NO complexes with macrocyclic ligands appears in Figure 3. The metal d and nitric oxide π^* levels are the principal valence orbitals.[12,15] The Cr^{I}(NO$^+$) units are expected to be linear in order to maximize dπ–π^* bonding; this is consistent with the observed axial **g** tensors for these complexes. In analogy to Cr(TPP)(NO), the odd electron for these macrocyclic ligand complexes is assigned to the d$_{xy}$ molecular orbital since $g_\perp > g_\parallel$.

Electronic spectral data for I and II are presented in Table III. If band intensities are ignored, these spectra are remarkably similar especially in view of the fact that the two complexes have different coordination numbers and very different macrocyclic ligands. This seems to indicate that a molecular orbital scheme such as Figure 3 is applicable to both complexes and that the nitrosyl ligand dominates the electronic configurations of these Cr^{I}–NO complexes. The spectra are closely similar to that of the pentacyanonitrosylchromate(I) anion.[15] The first three bands observed for these complexes may be assigned to the $^2B_2 \rightarrow {}^2A_1$, $^2B_2 \rightarrow {}^2B_1$, and $^2B_2 \rightarrow {}^2E$ transitions, respectively.

Crystal and Molecular Structure of [Cr(Me$_6$[14]4,11-dieneN$_4$)(NO$_2$)(NO)]PF$_6$. Final positional and thermal parameters for nonhydrogen atoms are listed in Table IV; parameters for the hydrogen atoms appear in Table V. Bond distances and angles appear in Table VI. Structure factor tables are available.[16] An ORTEP[17] diagram of the cation is presented in Figure 4.

Twofold axes pass through the chromium and phosphorus atoms resulting in twofold symmetry for both the cationic complex and the hexafluorophosphate anion. The twofold axis passing through O$_2$, N$_4$, Cr, and N$_3$ is readily seen in Figure 4 and relates primed atoms to unprimed atoms of the same designation.

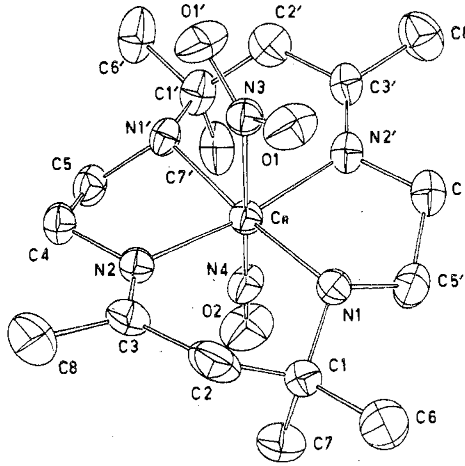


Figure 4. ORTEP[17] diagram of the [Cr(Me$_6$[14]4,11-dieneN$_4$)(NO$_2$)(NO)]$^+$ cation.

The coordination of the chromium is octahedral. The four macrocycle nitrogens compose an equatorial plane with nitrosyl and nitro groups in axial positions. The chromium is displaced 0.22 Å out of the equatorial plane toward the NO group (Table VII). Similar distortions have been seen in porphyrin–nitrosyl complexes.[18] The Cr–N(macrocycle) distances of 2.044 (4) and 2.022 (5) Å are similar to the metal–nitrogen distances observed in complexes of nickel(II) and cobalt(III) with analogous ligands.[19] The Cr–N(nitrosyl) bond length of 1.679 (5) Å is within the range of M–NO distances reported previously.[15,20] The Cr–N(nitro) bond length of 2.204 (5) Å is somewhat long compared to those in other nitro complexes.[21] However, the nonbonded contact distances of 2.85 and 2.81 Å between the nitro and macrocyclic nitrogen atoms strongly suggest that closer approach to the metal is hindered if the van der Waals radius of nitrogen is taken as ca. 1.5 Å.[22] The strong bonding of NO$^+$ to Cr(I) distorts the coordination sphere so that the complex resembles a pseudo-square-pyramidal metal with a weak donor in the sixth position. The distortion of the coordination sphere is also apparent in the bond angles. Those angles involving the nitrosyl are 95.9 (1) and 96.6 (1)°, while those involving the nitro group are 83.4 (1) and 84.1 (1)°.

The nitrosyl ligand forms a linear M–NO unit. The N–O distance of 1.193 (6) Å is on the upper limit for N–O bonds[23] in linear nitrosyls and may be due in part to considerable back-bonding by electron-rich Cr(I). The possibility of slight distortion from linearity due to disordering exists, but attempts to elucidate such disorder repeatedly indicated that the nitrosyl is in fact linear.

Table IV. Positional and Thermal Parameters (× 10^4) for Nonhydrogen Atoms[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0000 (0)	1343 (1)	2500 (0)	44 (1)	12 (1)	83 (2)	0 (0)	87 (2)	0 (0)
N1	481 (3)	1235 (2)	4832 (4)	54 (3)	16 (1)	97 (6)	−12 (3)	100 (7)	−12 (4)
N2	1576 (3)	1224 (2)	3154 (4)	52 (3)	15 (1)	113 (6)	−12 (3)	103 (8)	−17 (4)
N3	0000 (0)	218 (2)	2500 (0)	44 (4)	15 (1)	93 (8)	0 (0)	83 (10)	0 (0)
N4	0000 (0)	2200 (2)	2500 (0)	94 (6)	14 (2)	147 (10)	0 (0)	178 (13)	0 (0)
O1	−307 (3)	−106 (1)	1255 (3)	99 (3)	16 (1)	124 (6)	−2 (3)	133 (7)	−16 (3)
O2	0000 (0)	2809 (2)	2500 (0)	176 (8)	14 (1)	262 (12)	0 (0)	296 (17)	0 (0)
C1	1678 (4)	1407 (2)	6229 (5)	60 (4)	27 (1)	102 (7)	−28 (4)	105 (9)	−32 (5)
C2	2460 (4)	986 (2)	6040 (5)	44 (4)	30 (2)	115 (8)	−19 (4)	59 (9)	−2 (6)
C3	2452 (4)	1042 (2)	4553 (6)	51 (4)	17 (1)	131 (8)	−16 (4)	105 (9)	−20 (5)
C4	1555 (4)	1239 (2)	1676 (5)	58 (4)	20 (1)	134 (8)	−10 (3)	136 (10)	−17 (5)
C5	457 (4)	1547 (2)	237 (5)	76 (4)	20 (1)	128 (8)	−1 (4)	156 (10)	3 (5)
C6	1897 (4)	1205 (3)	7837 (6)	72 (5)	61 (3)	100 (8)	−38 (6)	95 (11)	−28 (7)
C7	1909 (5)	2169 (3)	6250 (7)	86 (5)	32 (2)	205 (11)	−51 (5)	190 (13)	−80 (7)
C8	3522 (4)	828 (3)	4845 (6)	50 (4)	34 (2)	164 (10)	4 (4)	92 (11)	−5 (6)
P	5000 (0)	1455 (2)	2500 (0)	50 (2)	67 (1)	128 (4)	0 (0)	103 (4)	0 (0)
F1	4050 (6)	1961 (4)	1883 (7)	288 (8)	194 (5)	342 (13)	327 (11)	374 (18)	100 (13)
F2	5276 (3)	1496 (3)	4235 (5)	108 (4)	136 (3)	172 (7)	−39 (5)	193 (9)	−31 (7)
F3	4077 (3)	929 (4)	1902 (6)	258 (8)	141 (4)	300 (12)	−216 (9)	292 (16)	−98 (10)

[a] Thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table V. Positional Parameters (× 10^4) for Hydrogen Atoms

Atom	Bonded to (dist, Å)	*x*	*y*	*z*
H1	N1 (0.72)	444	869	4877
H2	C6 (0.81)	2557	1200	8612
H3	C6 (0.98)	1745	719	7837
H4	C6 (0.89)	1514	1449	8095
H5	C7 (0.91)	1478	2435	6398
H6	C7 (0.97)	2666	2240	7250
H7	C7 (0.93)	1947	2301	5406
H8	C8 (0.94)	4027	518	5680
H9	C8 (0.88)	3492	681	4010
H10	C8 (0.85)	3972	1165	5250
H11	C2 (0.94)	3162	1148	6968
H12	C2 (0.88)	2343	552	6131
H13	C4 (0.97)	2212	1488	1941
H14	C4 (0.91)	1552	794	1413
H15	C5 (0.87)	426	1466	−629
H16	C5 (0.94)	442	2023	306

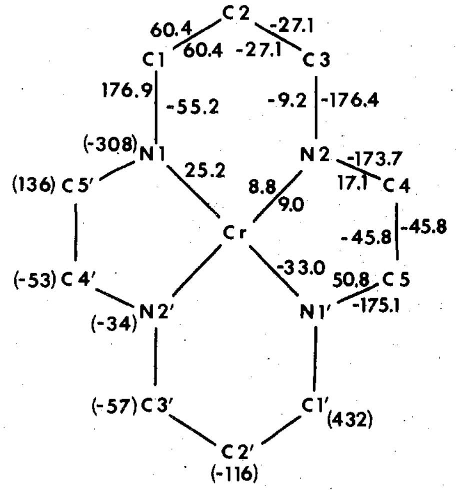


Figure 5. Selected torsion angles and deviations from least-squares plane (in parentheses) for the $[Cr(Me_6[14]4,11\text{-}dieneN_4)(NO_2)(NO)]^+$ cation. Torsion angles are as previously defined.[25] Values outside the macrocycle are torsion angles for the macrocycle backbone; values inside the macrocycle are torsion angles for the chelate rings. Deviations (×10^3) are from the least-squares plane of the macrocycle (plane 4, Table VII).

The nitro group exhibits a N–O bond length of 1.236 (4) Å which is normal for coordinated NO_2^-.[21] The angle O1–N_3–O1′ is also normal at 118.3 (2)°. The orientation of the plane containing O1–N3–O1′ is tilted by 3.8° with respect to the plane containing N1–Cr–N1′ (Table VII). Such alignment of coordinated nitro groups[21b] has been observed before, but no explanation is offered for this phenomenon.

The macrocyclic ligand is best studied by considering both the torsion and bond angles and deviations from planarity. Figure 5 illustrates these features. The torsion angles of the ligand show maximum strain at C4–C5 (−45.8°, strain-free value −60°). All other torsion angles are within 6° of the strain-free value. The bond angles indicate that a large amount of strain occurs at the distal carbon of the six-membered chelate ring (C1–C2–C3 = 127°, strain free value 109.5°). These features are similar to those observed recently in a related Co(III) complex.[19a] A least-squares plane calculation using all atoms in the macrocycle backbone reveals that the greatest deviations occur at C1 (+0.432 Å) and N1 (−0.308 Å). The least-squares plane of atoms involved in the double-bonded system shows small deviations from planarity except for Cr (−0.317 Å).

Table VI

	(A) Bond Distances, Å		
	Coordination Sphere		
Cr–N1	2.044 (4)	Cr–N3	2.204 (5)
Cr–N2	2.022 (5)	Cr–N4	1.679 (5)
	Ligands		
N3–O1	1.236 (4)	C1–C2	1.528 (8)
N4–O2	1.193 (6)	C1–C6	1.522 (7)
N1–C1	1.500 (6)	C1–C7	1.528 (7)
N1–C5′	1.482 (8)	C2–C3	1.516 (7)
N2–C3	1.272 (6)	C3–C8	1.488 (9)
N2–C4	1.492 (6)	C4–C5	1.514 (7)
	PF_6^-		
P–F1	1.516 (9)	P–F3	1.517 (8)
P–F2	1.561 (4)		
	(B) Bond Angles, Deg		
	Involving Cr		
N1–Cr–N2	94.7 (2)	Cr–N1–C1	117.8 (3)
N1–Cr–N3	84.1 (1)	Cr–N1–C5′	104.1 (3)
N1–Cr–N4	95.9 (1)	Cr–N2–C3	126.8 (3)
N1–Cr–N1′	168.2 (2)	Cr–N2–C4	110.5 (3)
N1–Cr–N2′	83.9 (2)	Cr–N3–O1	120.9 (2)
N2–Cr–N3	83.4 (1)	Cr–N4–O2	180.0
N2–Cr–N4	96.6 (1)		
N2–Cr–N2′	166.8 (2)		
N3–Cr–N4	180.0		
	Involving Ligands		
O1–N3–O1′	118.2 (3)	C1–C2–C3	122.7 (4)
C1–N1–C5′	119.5 (4)	N2–C3–C2	122.0 (5)
N1–C1–C2	108.2 (4)	N2–C3–C8	123.3 (5)
N1–C1–C6	109.1 (4)	C2–C3–C8	114.6 (4)
N1–C1–C7	111.1 (4)	C3–N2–C4	121.7 (4)
C2–C1–C6	108.2 (4)	N2–C4–C5	110.1 (4)
C2–C1–C7	110.3 (4)	C4–C5–N1′	108.2 (4)
C6–C1–C7	109.8 (5)		
	Involving PF_6^-		
F1–P–F2	88.8 (4)	F2–P–F3	92.7 (3)
F1–P–F3	83.6 (4)	F2–P–F2′	174.1 (3)
F1–P–F1′	98.3 (4)	F2–P–F3′	91.3 (3)
F1–P–F2′	87.3 (4)	F3–P–F3′	94.6 (4)
F1–P–F3′	178.2 (4)		

The hexafluorophosphate anion resembles previously determined structures found for this species.[24] Thus, the P–F bond distances range from 1.516 (9) to 1.561 (4) Å. The F–P–F bond angles are in the ranges 83.6 (4)–98.3 (4)° for cis fluorines and 174.1 (3)–178.2 (4)° for trans fluorines.

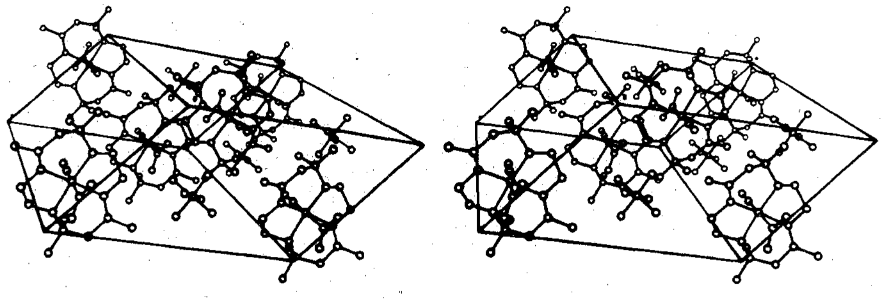


Figure 6. ORTEP[17] stereo packing diagram of the $[Cr(Me_6[14]4,11\text{-}dieneN_4)(NO_2)(NO)]PF_6$ structure.

Table VII. Least-Squares Planes and Deviations[a]

	Plane				
	1 (4 macN's)	2 (N1-Cr-N1′)	3 (NO_2^-)	4 (mac)	5 (dbl bond)
D	2.408 14	− .715 06	−0.874 45	2.915 79	2.908 71
a	−0.000 07	0.934 66	0.955 99	0.212 23	0.226 29
b	1.000 00	0.0	0.0	0.957 36	0.949 49
c	0.000 11	0.355 53	0.293 40	0.196 03	0.217 43
	N1* (11)	Cr* (0)	N3* (0)	N1* (−308)	N2* (15)
	N2* (−11)	N1* (0)	O1* (0)	N2* (−34)	C2* (−20)
	N1′* (11)	N1′* (0)	O1′* (0)	C1* (432)	C3* (26)
	N2′* (−11)			C2* (−116)	C4* (−18)
	Cr (222)			C3* (−57)	C8* (−2)
	N3 (1982)			C4* (−53)	Cr (−317)
	N4 (1901)			C5* (136)	

[a] The number of the plane is given followed by an abbreviation. The equation of the plane is given by $ax + by + cz = D$ (Å), where *D* is the distance from the origin. The designated atoms are followed by their deviations (×10^3 Å) in parentheses. Atoms used in calculating the plane are noted by an asterisk.

Librational motion about the F2–P–F2′ axis shortens the P–F1 and P–F3 distance with respect to the P–F2 distance (1.516 (9) and 1.517 (8) vs. 1.561 (4) Å, respectively) and diminishes the thermal parameters for F2.

The packing diagram (Figure 6) shows the arrangement of the cations and anions along the twofold axes. The only significant intermolecular contact (2.178 (4) Å) is that between O1 of the nitro group and H1 of the saturated nitrogen of the macrocycle.

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Registry No. I, 61966-54-9; II, 62015-61-6; $[Cr(Me_2[14]\text{-}tetraenatoN_4)(py)_2]PF_6$, 61966-56-1; $[Cr(Me_6[14]4,11\text{-}dieneN_4)(py)](PF_6)_2$, 62015-59-2; $Cr(CF_3SO_3)_2\cdot 4py$, 61966-86-7; $CrCl_2\cdot 2py$, 14320-05-9.

Supplementary Material Available: Listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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